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Rotation of C_{60} in a single-molecule contact

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The tip of a low-temperature scanning tunneling microscope is moved vertically into contact with single C_{60} molecules on Cu(100), while monitoring the current. Three of five observed molecular orientations on the copper surface display rotations of their adsorption configuration when approaching the tip beyond a threshold value. Possible mechanisms for the tip-induced rotation are discussed.

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Nanoscale systems have attracted increasing attention for applications in molecular electronics,[1] where molecules are expected to be the building blocks of electronic circuits. The scanning tunneling microscope is one of the most promising techniques for creating prototype molecular structures and testing their properties. Small objects can be changed in the tunneling regime through voltage pulsing of the microscope tip or tip-assisted lateral manipulation,[2] so as to mimic electronic effects potentially relevant for a nanoscale circuit, such as switching. The rolling of a single C_{60} molecule on a silicon surface by subsequent bond breaking between the molecule and the surface, for instance, demonstrated the control of a complex sequence of coupled rotational and translational dynamics.[3] Bistable conformational changes of molecules have been reported from several systems.[4–9] Recently, the conductance of a molecule adsorbed on a H-terminated Si(100) surface has also been controlled through the electrostatic field of a nearby atom.[10]

Quite surprisingly, the manipulation through controlled contact with the tip of a scanning tunneling microscope has only been explored on some rare occasions. Contrary to previous studies described above, during contact manipulation, the tip vertically approaches a molecule until the conductance approaches the conductance quantum $G_0=2e^2/h$ (where e is the electron charge and h is Planck's constant). Heating and/or mechanical forces acting between the tip and the molecule may then produce conformational changes.[11] A molecular junction—the molecule being sandwiched between the tip and the metal substrate—is also formed in this way, with knowledge of molecular identity and location.[12,13] Studying the conformational changes induced in the molecule therefore also provides information on the stability of the molecular junction. Concerning this last point, there is a strong demand for experimental studies in view of the vast body of theoretical work on molecular conductance—see, for instance, Refs. 14 and 15 and references therein.

Here, we investigate the prototypical molecular contact between a metal tip and single C_{60} molecules adsorbed on a Cu(100) surface. Low-temperature scanning tunneling microscopy (STM) offers the important feature that molecular orientations prior to contact can conveniently be distinguished since no thermally excited molecular rotation is present. Upon contact, a threshold for the tip excursion is evidenced beyond which changes can be induced in the molecular orientation as revealed by images acquired after contact. The results favor a mechanical effect as the driving force for the tip-induced rotation.

The experiments were performed using a custom-built STM operated at 8 K and in an ultrahigh vacuum with a base pressure of 10^{-9} Pa. A Cu(100) surface and chemically etched tungsten tips were cleaned by argon ion bombardment and annealing. Tips were further prepared *in vacuo* by soft indentations into the copper surface until an intramolecular resolution of C_{60} was achieved (Fig. 1). Given this preparation, the tips were most likely covered with substrate material. The C_{60} molecules were deposited onto the clean surface at room temperature from a heated tantalum crucible, with the residual gas pressure remaining below 5×10^{-8} Pa. Ordered domains of C_{60} were obtained by subsequent annealing at 500 K.

Figure 1(a) presents the constant-current STM images of C_{60} molecules adsorbed on Cu(100). The images were acquired with 1.5 V applied to the sample. At this voltage, the second-to-lowest unoccupied molecular orbital (LUMO+1) resonance is detected in spectra of the differential conductance (not shown). The molecules are organized in a nearly hexagonal array and form alternating bright and dim stripes [Fig. 1(a)]. The height difference of 0.5 ± 0.1 Å between the two stripes has been attributed to a missing-row reconstruction of the copper surface, subsequent to the annealing at 500 K.[16] Bright stripes correspond to molecules residing on a single-missing copper row, while dim stripes correspond to molecules residing on a double-missing copper row. An inspection of 700 molecules acquired with different tips shows that C_{60} adopts five molecular orientations on the surface. Three additional orientations are identified with respect to the previous study on Cu(100).[16] A close-up view is presented in Fig. 1(a) where distinct structures can be seen for each orientation. Images of unoccupied states of C_{60} reflect the molecular symmetry:[17,18] in particular, bright structures at a sample voltage close to the LUMO+1 energy are produced by the pentagon rings.[19–21] The topmost features of the STM images shown in the lower part of Fig. 1(a) correspond then to, from left to right, a hexagon ring (denoted h), a hexagon-pentagon bond ($h{:}p$), a hexagon-hexagon bond ($h{:}h$), an apex atom (a), and a pentagon ring (p) to be compared with the sketches in Fig. 1(b). Molecules with h and p orientations are adsorbed on double-missing copper rows with distributions of 31% and 5%, respectively. Molecules with $h{:}p$, a, and $h{:}h$ orientations are adsorbed on single-missing copper rows with distributions of 56%, 4%, and 4%, respectively.

Current versus tip displacement measurements were performed over each orientation. During this measurement, the

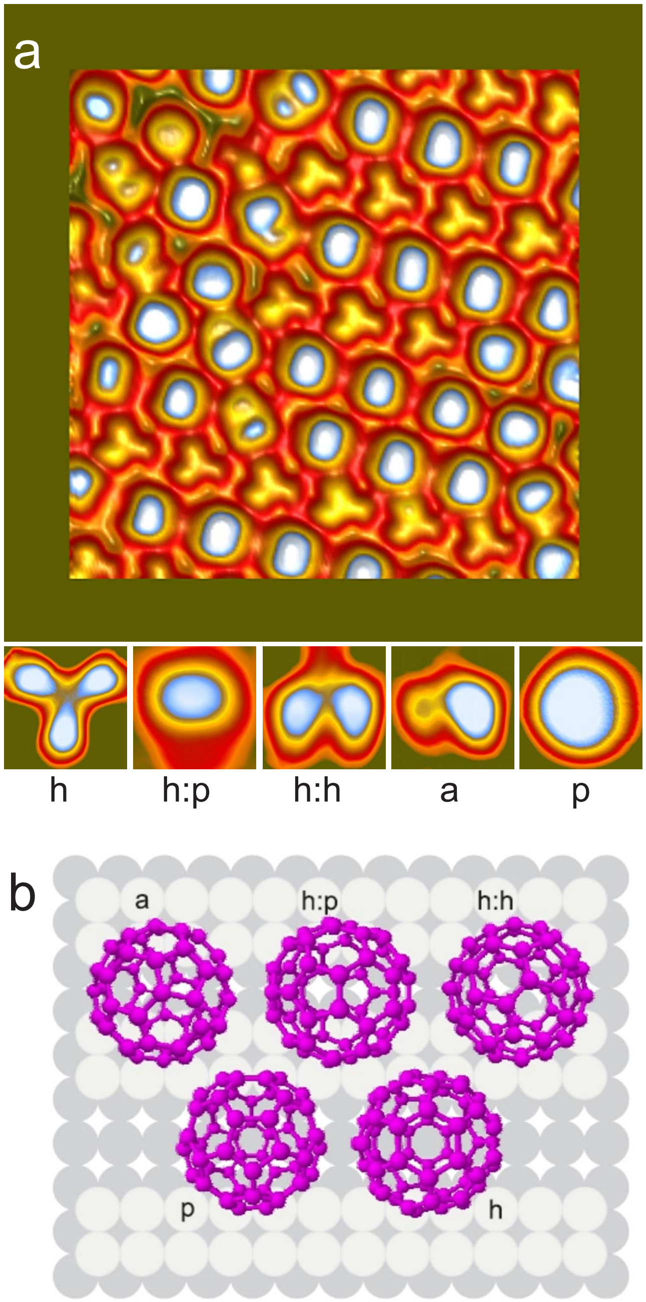

FIG. 1. (Color online) (a) Top: pseudo-three-dimensional image of C_{60} on Cu(100) at 8 K after annealing at 500 K (sample voltage $V=1.5$ V, tunneling current $I=2.5$ nA, and size 58×58 Å^2). Bottom: close-up view of the five adsorption configurations. (b) Sketches of different C_{60} orientations on reconstructed Cu(100). First (second) layer of substrate is depicted as bright (dark) circles.

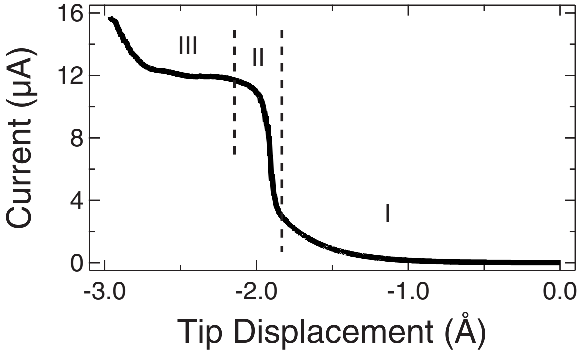

FIG. 2. Current versus tip displacement for C_{60} with $h{:}p$ orientation. The current curve spans (I) the tunneling, (II) the transition, and (III) the contact regimes. Zero-displacement corresponds to feedback loop parameters of 500 mV and 3 nA.

STM tip is first placed above the center of a molecule, the feedback loop is opened, and the tip is approached toward the molecule at a given sample voltage simultaneously recording the current. Figure 2 shows a typical current curve as a function of tip displacement. For currents below 3 μA, the current exhibits an exponential behavior (region I in Fig. 2). Within a one-dimensional description of the tunneling barrier where $I\propto\exp(-1.025\sqrt{\Phi}\Delta z)$ (with I the current and Δz the tip displacement), an apparent barrier height of $\Phi=10.2\pm0.7$ eV may be extracted. Above 3 μA, a sharp increase in the current up to 12 μA is observed (region II), signaling the formation of a bond between a carbon atom of C_{60} and a copper atom at the tip apex.[12] Once the bond is established, the contact regime is reached (region III) and the conductance is typically a fraction of G_0. In the contact region after a nearly constant plateau, the current starts to rise again. The width and the slope of the plateau depend on the tip shape and on the location where the contact to the molecule is formed.

We observed that displacing the tip beyond a threshold excursion can cause the molecule to rotate. The threshold is located at displacements in region III where the current starts to increase again. Rotations of the molecule are illustrated by the STM images of Fig. 3. In the starting image [Fig. 3(a)], molecules in the top and bottom rows are in the $h{:}p$ configuration, and in the middle row, a molecule in the a configuration is flanked by two molecules with p orientation. After a tip contact with the central molecule [Fig. 3(b)]—where the contact is indicated by a multi—the adsorption geometry of the molecule changes from a to $h{:}p$. The neighboring molecules are not affected. Contacting the $h{:}p$ molecules in the

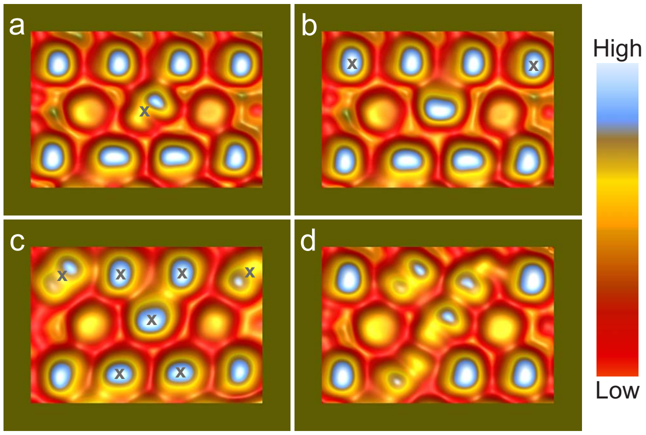

FIG. 3. (Color online) Pseudo-three-dimensional images ($V=1.7$ V, $I=0.1$ nA, and 33×23 Å^2) of a same area of the surface. (a) Surface prior to contact experiments. (b)–(d) After contacting the molecules (marked by multi).

top corners one-by-one changes their configuration to h:h (left corner of Fig. 3(c)] and to a (right). A new tip contact with these two molecules [Fig. 3(d)] changes them back to their original h:p orientation. Finally, a tip contact with the h:p molecule in the center and with four h:p neighboring molecules [Fig. 3(d)] changes their orientation to h:h or a. In some rare cases, the molecules rotate in the surface plane by 90°, as seen for the third molecule in the bottom row of Fig. 3(d). Tip contact with the h:p configuration always leads to a and h:h configurations and vice versa. No changes in the adsorption geometry were observed for h and p molecules (dark row) for the tip excursions investigated. Modifying the tip apex by indentations in the copper surface led to the same observations, which indicates that this phenomenon is tip independent or that our *in vacuo* tip preparation results in similar tip apices.

The adsorption configuration of the C_{60} molecule, i.e., its orientation on Cu(100), can also be monitored directly from current versus tip displacement measurements. While this observation holds for all C_{60} adsorption configurations, below we discuss the h:h and h:p orientations. Figure 4(a) shows the averaged current curves acquired on an h:p (black curve) molecule and on an h:h (gray curve) molecule. For both measurements, the feedback loop is opened at a bias voltage of 300 mV and a current of 1 μA. We arbitrarily choose $\Delta z=0$ for these settings. Both molecules present approximately the same conductance of $0.5G_0$ at contact. However, since the contact with the h:h molecule is established at a smaller tip excursion compared to h:p, both orientations are recognizable through their current curves. It is then possible to observe the changes in the adsorption geometry by monitoring the current on top of a given molecule, without imaging the molecule. This is illustrated in Fig. 4(b) where curves are assigned to h:p (black) and h:h (gray) molecules. The black curve was acquired just before a change in the molecular orientation, while the gray curve was taken directly after a change. To determine the probability for a rotation to occur with tip displacement, the tip was displaced 500 times to a given excursion and, concomitantly, changes in the current were monitored. The probability [Fig. 4(c)] rises sharply to a nearly constant value of 30% above a threshold displacement of $\Delta z=-1.9$ Å. Measurements with tip displacements <-2.3 Å were shown to lead to the damage of the tip and of the contacted area.

To explore whether hysteresislike effects may be observable, in Fig. 5, we present a current curve comprising a full cycle for the tip displacement—the feedback loop is opened at a bias voltage of 300 mV and a current of 1 μA, and $\Delta z=0$ is fixed to these feedback loop settings, as indicated in Figs. 4(a) and 4(b). The approach is performed over a molecule of h:h orientation (gray) but, upon retraction, this orientation has changed to h:p (black), as revealed by STM images (not shown). The rotation from h:h to h:p most probably occurred at displacements exceeding ≈ -2.1 Å since both current curves coincide for displacements <-2.1 Å (see square in Fig. 5). Upon tip retraction, current curves deviate from each other for displacements >-2.1 Å. At zero displacement, the current through the h:p molecule is slightly higher than that through the h:h molecule (see inset of Fig. 5). With $I_{h:p}=1.5$ μA, $I_{h:h}=1.0$ μA, and an apparent barrier height of $\Phi \approx 10$ eV (see above and Ref. 13), we find a corresponding height difference of ≈ 0.15 Å, which is close to the height difference inferred from the cross-sectional profiles in constant-current STM images acquired at 300 mV; i.e., at that voltage, the current traces in Fig. 5 were acquired. We notice that the displacement of ≈ -0.23 Å at which both current curves intersect (see circle in the inset of Fig. 5) likewise reflects the difference in the apparent height of the molecules.

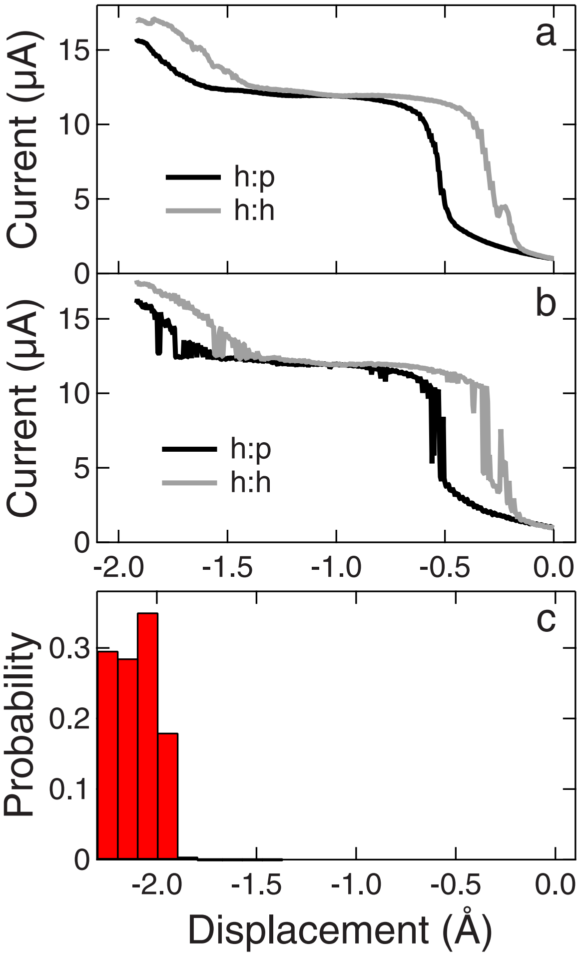

FIG. 4. (Color online) (a) Averaged current versus tip displacement curves acquired on top of h:p (black curve) and h:h (gray curve) configurations. For both curves, the feedback loop is opened at 300 mV and 1 μA. (b) Single current versus displacement curve of h:p molecule (black) together with single current curve characteristic of the h:h configuration (gray). (c) Probability of a change in orientation as a function of tip displacement. Feedback loop opened at 300 mV and 1 μA.

Based on the collected data, some plausible assumptions may be made regarding the mechanism behind the tip-induced rotation of C_{60}—a detailed numerical analysis is beyond the scope of this paper. The first aspect to consider is the heating of the molecular junction. An analysis of data recorded at 300 mV showed that energy dissipation in the tip-molecule junction leads to an effective heating of the junction, from 8 to 400 K.[12] This could cause a rotation of the molecule. However, the energy dissipation translates into an increased current fluctuation in region II [see Fig. 4(b)]—

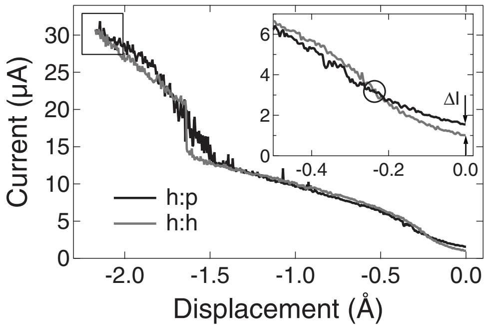

FIG. 5. Current curves acquired during tip approach (gray) and tip retraction from a C_{60} molecule. During the tip displacement the molecule changed from $h:h$ to $h:p$, most probably at a tip displacement exceeding −2.1 Å where current curves coincide (square). Feedback loop settings prior to data acquisition: 1 μA and 300 mV. Inset: close-up view of current traces close to zero tip displacement, showing a current difference of $\Delta I \approx 0.5$ μA which is related to a different apparent height of the molecules.

the fluctuations are smoothed in the averaged curves shown in Figs. 3 and 4(a). If the heat dissipation were causing the rotation, rotations would already occur before contact. This is in contrast to the observation of a threshold for the tip displacement [Fig. 4(c)]. In the experiments, the total power dissipated at the junction was varied by a factor of 40. The rotation probability was found to be insensitive to this variation which is additional indication that thermal excitation alone is not the driving force for the rotation. We therefore suggest that the mechanical contact with the tip is the main cause for C_{60} to rotate.

The current curves presented in Fig. 4(a) show, after a relatively flat plateau, a sustained rise of the current. In this region, in particular, for displacements larger than the threshold displacement, the slope strongly depends on the tip shape as well as on the position of the contact over the molecule. For all measurements, this continuous rise was observed to lead to a discontinuous jump of the current (Fig. 5)—on the 100 μs time scale of data acquisition. This jump is attributed to a modified geometry of the contact atomic structure.[12,22] It is reasonable to assume that during the rise of the current preceding the rearrangement of the contact atomic structure, the molecule adsorption geometry is already slightly modified, as suggested by the approach and retraction curves of Fig. 5. Once the tip is retracted, the molecule returns to one of its possible stable configurations. A rotation is observed when this final configuration differs from the initial one prior to tip contact.

This scenario implies that rotations preferably occur between specific pairs of orientations. For instance, a rotation of C_{60} from $h:p$ to $h:h$ or vice versa requires an angle of 20.6°, while a smaller angle of 11.6° is required for a rotation from $h:p$ to a orientation. These angles are considerably smaller than the rotation angle of 37.4° to change an h molecule to a p molecule and vice versa. The apparent rotation by 90° in the surface plane [Figs. 3(e) and 3(f)] can also be achieved by out-of-plane rotations of 19.2° and 36.0° for the $h:p$ and $h:h$ orientations, respectively. The large angle needed for the apparent in-plane rotation of the $h:h$ molecule is consistent with the observed low frequency of this rotation. In the case of the $h:p$ molecule, the apparent in-plane rotation results in a different adsorption geometry on the copper surface, now with the carbon–carbon bond between the hexagon and the pentagon of the molecule parallel to the copper missing row. This specific orientation of the $h:p$ molecule is rarely observed [see Fig. 1(a)], indicating a less favorable adsorption energy. This explains why this specific event is rare despite the relatively small angle needed to induce an apparent in-plane rotation of 90°.

In conclusion, we observed changes in the orientation of C_{60} during tip-molecule contact, resulting in a rotation of C_{60} on the Cu(100) surface once the tip is retracted. Since the rotation occurs only beyond a well-defined tip excursion, the origin of this effect is likely mechanical. We hope that these results will prompt theoretical investigations into a model system which is numerically amenable.

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