Rotation of $C_{60}$ in a Single-Molecule Contact

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The orientation of individual $C_{60}$ molecules adsorbed on Cu(100) is reversibly switched when the tip of a scanning tunneling microscope is approached to contact the molecule. The probability of switching rises sharply upon displacing the tip beyond a threshold. A mechanical mechanism is suggested to induce the rotation of the molecule.

PACS numbers: 61.48.+c, 68.37.Ef, 73.63.Rt

Using single atoms or molecules as building blocks in electronic circuits currently is of considerable interest. Experimentally, a scanning tunneling microscope has been used to observe hopping of a Xe atom between a Ni surface and the microscope tip. Bistable conformational changes of molecules have also been induced and observed with scanning tunneling microscopy (STM) and other techniques. Recently, the conductance of a molecule has been controlled through the electrostatic field of a nearby adatom. However, the contact regime, where the conductance approaches the conductance quantum, $G_0 = 2e^2/h$ (e: electron charge, h: Planck’s constant) has mostly been explored using mechanically controlled break junctions. A notable exception is the work of Moresco et al., who induced and imaged conformational changes of a porphyrine molecule and recorded conductance data in the tunneling and contact regimes. Overall, detailed experiments which provide information on the geometry of single molecule switches as well as on their conductance are scarce, in contrast to a vast body of theoretical work on molecular conductance.

Here, we report on a controlled rotation of $C_{60}$ on Cu(100) when the molecule is brought into contact with the tip of a scanning tunneling microscope. A sharp threshold of the tip-molecule distance above which switching occurs is observed. It corresponds to junction conductances of $G \approx 0.3 - 0.5 G_0$. The results favor a mechanical switching mechanism.

The experiments were performed using a custom-built scanning tunneling microscope operated at $8 \text{K}$ and in ultrahigh vacuum with a base pressure of $10^{-9} \text{Pa}$. A Cu(100) surface and chemically etched tungsten tips were cleaned by Ar ion bombardment and annealing. Tips were further prepared in vacuo by soft indentations into the copper surface, until intramolecular resolution of $C_{60}$ was achieved (Fig. 1). Given this preparation, 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, the residual gas pressure remaining below $5 \times 10^{-8} \text{Pa}$. Ordering of $C_{60}$ was obtained by subsequent annealing at $500 \text{K}$.

Figure 1 presents constant-current STM images of $C_{60}$ molecules adsorbed on Cu(100). The images were acquired at $1.5 \text{V}$ applied to the sample. At this bias the second-to-lowest unoccupied molecular orbital (LUMO+1) resonance is detected in spectra of the differential conductance (not shown). The pattern therefore reflects the spatial distribution of the density of states of this orbital. The molecules are organized in a hexagonal array and form alternating bright and dim stripes (Fig. 1). The height difference of $0.5 \pm 0.1 \text{Å}$ between the two stripes has been attributed to a missing-row reconstruction of the copper surface following an annealing at $500 \text{K}$. Bright stripes correspond to molecules residing on a single-missing copper row, dim stripes 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). A close-up view is presented in the inset of Fig. 1, where distinct structures can be seen for each orientation. It is well established that images of the unoccupied states of $C_{60}$ reflect the molecular symmetry, in particular, that bright structures at a sample voltage close to the LUMO+1 energy are produced by the pentagon rings. The top-most features of the STM images shown in the inset of Fig. 1 correspond to, from left to right, a hexagon ring (denoted $h$), a hexagon-pentagon bond ($h:p$), an apex atom ($a$), a hexagon-hexagon bond ($h:h$), and a pentagon ring ($p$) to be compared with the sketches in Fig. 1. Molecules with a $h$ and $p$ orientation are adsorbed on double-missing copper rows with a distribution of $31\%$ and $5\%$, respectively. Molecules with $h:p$, $a$ and $h:h$ orientations are adsorbed on single-missing copper rows with a distribution of $56\%$, $4\%$, and $4\%$, respectively.

Having identified the molecular orientations of $C_{60}$ on Cu(100), current versus tip displacement measurements were performed over each orientation. During a current measurement, the STM tip is first placed above the center of a molecule, the feedback loop is then 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 func-
FIG. 1: (Color online) (a) STM image of C$_{60}$ on Cu(100) at $T = 8$ K after annealing at 500 K (sample voltage $V = 1.5$ V, tunneling current $I = 2.5$ nA, size 60 Å × 60 Å). Inset: 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). Image processing using Nanotec WSxM [18].

For currents below $\approx 3 \mu$A the current exhibits an exponential behavior (region I in Fig.2). Within a one-dimensional description of the tunneling barrier where $I \propto \exp(-1.025\sqrt{\Phi\Delta z})$ ($I$: current, $\Delta z$: tip displacement) an apparent barrier height of $\Phi = (10.2 \pm 0.7)$ eV may be extracted. Above $\approx 3 \mu$A a sharp increase of the current up to $\approx 12 \mu$A 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 [19]. Once the bond is established the contact regime is reached (region III). The molecular contact exhibits a conductance of $\approx 0.3$ G$_0$. In the contact region we find a plateau of nearly constant current which starts to rise above a certain tip displacement again. The width and the slope of the plateau as well as the contact conductance depend on the tip shape and on the location where the contact to the molecule was formed.

We observed that approaching the tip by $\approx 1.9$ Å beyond the transition region (II) often causes the molecule to rotate as illustrated by the STM images of Fig.3. The encircled molecule in Fig.3a was contacted by the tip of the microscope. Increasing the tip displacement above a threshold leads to a switch of the adsorption geometry from an $a$ to a $h:p$ configuration (see Fig.3b). Contacting the two $h:p$ molecules encircled in Fig.3b leads to switching of these molecules to $h:h$ and $a$ configurations (see Fig.3c). In some rare cases the molecules rotate in the surface plane, as seen in Figs.3e and 3f. Our observations show that the switching of $a$ and $h:h$ molecules always leads to $h:p$ molecules, while switching of $h:p$ molecules leads to $h:h$ or $a$ species, and no $h$ nor $p$ configurations have been observed. However, contact between the tip and a molecule of the dark row ($h$ or $p$) did not lead to a switching of the molecule adsorption configuration. Modifying the tip apex shape by indentation of the tip into the substrate surface led to the same observations of molecular switching, indicating that this phenomenon is rather tip-independent.

The adsorption configuration of the C$_{60}$ molecule directly determines the current characteristics. While this observation holds for all C$_{60}$ adsorption configurations, we restrict the discussion to the $h:h$ and $h:p$ orientations below. Figure 4 shows averaged conductance curves acquired on a $h:p$ (black curve) and on a $h:h$ (gray curve) molecule. For both measurements the feedback is opened at a current of 1 $\mu$A and a sample voltage of 300 mV. For the used tip the molecules exhibit almost the same contact conductance of $\approx 0.5$ G$_0$. However, for the $h:h$ molecule the contact is established at a smaller tip displacement because of its closer initial tip-molecule dis-
FIG. 3: (Color online) Constant-current STM images ($V = 1.7 \text{ V}, I = 0.1 \text{nA}, 35 \times 20 \text{ Å}$) of the same area of the surface. (a) surface prior to switching experiments; (b)-(f) after contacting the molecules encircled by dashed lines in (a)-(e).

Therefore, each adsorption configuration is recognizable through its conductance curve, provided that the feedback loop parameters are the same for all configurations studied. It is then possible to observe the switching events by measuring subsequent conductance curves on top of the selected molecule, without imaging the molecule. This is illustrated in Fig. 3b. The current curves are assigned to a $h:p$ (black) and a $h:h$ (gray) molecule. The black curve was acquired just before a switching event, while the gray curve was taken directly after. Both curves exhibit fluctuations in the transition region as well as in the contact region when the current starts to rise again. These fluctuations are smoothed in the averaged curves shown in Fig. 3a. Fluctuations in the transition region II have been interpreted in terms of local heating of the molecule [19]. Fluctuations in the contact region III, however, occur at tip displacements around the threshold and rotation is often observed. Therefore, these sudden changes of the current are likely to reflect switching events.

To investigate the probability of switching for different tip displacements we used the fact that the conductance curve is characteristic of the adsorption configuration. For each value of the displacement with same initial conditions 500 conductance measurements were performed and the number of switching events was counted. The switching probability (Fig. 4c) rises sharply above a threshold displacement of $\Delta z \approx -1.9 \text{ Å}$ to $\approx 30\%$ rather independent of the tip displacement. Measurements with larger tip displacements were shown to lead to damage of the tip and of the contacted area.

Below we argue that the molecular rotation is mechanically induced whereas local heating plays a minor role in exciting rotations. An analysis of conductance curves on C$_{60}$ at 300 mV [19] showed that energy dissipation in the tip-molecule junction leads to an effective heating of the junction which could cause rotation of the molecule. However, in the present experiments we varied the total power dissipated by a factor of 40. The switching probability was found to be insensitive to the dissipated power. Although only a small fraction of the total power is dissipated directly at the molecule this finding suggests that thermal excitation alone is not the driving force for switching. Moreover, the tunneling current was not ob-
served to be decisive for inducing rotation. We therefore suggest that mechanical contact with the tip causes C\textsubscript{60} to rotate.

Mechanically induced rotation explains that certain rotation angles are less frequently observed. For instance, switching a C\textsubscript{60} from h:p to h:h or vice versa requires a rotation by 20.6°, while a smaller angle of 11.6° is required for a rotation from h:p to a orientation. The apparent in plane rotation results in a differential adsorption energy. This explains why this specific orientation is rarely observed (see Fig. 1a) indicating a less favorable adsorption energy. For instance, switching a C\textsubscript{60} molecule the apparent in plane rotation results in a differential adsorption energy. This explains why this specific orientation of the h:p molecule is consistent with the observed low frequency of this switching event.

In conclusion, we observed reversible, mechanically controlled switching of the orientation of C\textsubscript{60} in a single-molecule contact. Switching occurs when the tip of the scanning tunneling microscope is approached beyond a well-defined threshold. This threshold is located in the first conductance plateau where G ≈ 0.3 – 0.5 G\textsubscript{0}.

This work was funded by Deutsche Forschungsgemeinschaft through SFB 677.

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