Chapter 4

Manipulation of Lander molecules on Cu(211)

This chapter reports on the manipulation of Lander molecules on the stepped (211) surface of copper. The Lander was specially designed in order to study the electronic properties of single molecular wires on metallic surfaces by STM [82]. It is composed of a central planar polyaromatic board, that constitutes the wire, and four spacer groups attached to the wire by means of insulating $\sigma$-bonds. Such spacer groups serve to separate the board from the metal surface thus preserving its electronic integrity and allowing its manipulation.

This molecule has been intensively studied in our group [57, 83–87]. In particular, an atomically well defined contact between a metal electrode and the molecular wire has been firstly established [85]. Moreover, scattering of surface state electrons of Cu(111) have been used to probe the interaction between the molecular wire and a metal electrode.

In this work, I have investigated in detail the manipulation mechanism of a Lander molecule on Cu(211).

Low-temperature STM is a unique tool for studying the properties of atoms and single molecules adsorbed on a surface and for manipulating them with atomic scale precision [12, 14, 18, 56]. By recording the STM signal during the manipulation (see section 2.5.1) the motion of atoms or small molecules on a surface can be investigated in detail. Furthermore, detailed information on the motion of large molecules (molecular flexure and reorientation of the internal conformation) can be extracted by studying the manipulation signal [55]. Molecular deformations are induced by the interaction with the tip apex and depend on the surface atomic corrugation, which is the energy landscape within which the molecule moves. Considering such an influence of the surface geometry, the Cu(211) surface has been chosen in this study because of its anisotropy, which help to
increase the control in the manipulation of adsorbed molecules.

4.1 The Cu(211) surface

A copper crystal has a face centered cubic (fcc) structure with a lattice constant of \( a = 3.61 \) Å. The Cu(211) surface consists of \( (111) \) facets separated by \( (100) \) steps running in the \([0\bar{1}1]\) direction (Fig. 4.1). The distance between atoms along the \([0\bar{1}1]\) direction is 2.55 Å, while the intrinsic steps are separated in the \([1\bar{1}1]\) direction by 6.26 Å. These intrinsic steps constitute ideal rails for moving a molecule along a fixed direction. The Cu(211) surface was prepared by several cycles of sputtering with 1.3 keV Ne ions followed by annealing at 770 K.

![Figure 4.1: Sphere model of the stepped Cu(211) surface. (a) Side view and (b) front view. The distance between two adjacent surface steps is indicated in (a), while the lattice parameter is shown in (b).](image)

4.2 Lander molecule

The Lander molecule \( (C_{90}H_{98}) \) was synthesised by A. Gourdon and collaborators at the Nanoscience Group, CEMES-CNRS, in Toulouse (France) [82]. It consists (see Fig. 4.2) of a central polyaromatic conducting board (about 17 Å long and 6 Å wide) composed of a \( \pi \)-system terminated by two fuoranthene groups, and four spacer groups which are 3,5-di-tert-butyl-phenyl (TBP) groups. These spacer groups have little electronic coupling with the main board (they are attached to the board with \( \sigma \)-bonds) and with the surface. They are used to elevate the central board from the surface, reducing the electronic coupling with the surface and helping in the manipulation of the molecule. In the gas phase, the
4.3. Adsorption

A small amount of molecules, between $10^{-2}$ and $10^{-3}$ monolayer (ML), have been adsorbed on Cu(211) by evaporation from a Knudsen cell at 630 K. The process has been monitored by a home built quartz microbalance that has been calibrated using STM images. During the deposition of the molecules, the temperature of the substrate ($T_{\text{substrate}}$) was chosen between 70 and 330 K. At $T_{\text{substrate}} < 80$ K, the molecules are found to be isolated on the Cu(211) terraces, while at $T_{\text{substrate}} > 120$ K the molecules diffuse towards step edges [84]. The STM images were recorded in constant current mode at a sample voltage between +1 and -1 V and at a tunneling current between 0.1 and 1 nA. No sig-
Figure 4.3: Overview STM image of Lander molecules adsorbed on Cu(211) after preparation at $T_{\text{substrate}}$ = 80 K. The parallel underlying stripes visible in the STM image are the intrinsic steps of Cu(211). STM parameters: $U = -1$ V, $I = 0.2$ nA, $T = 7$ K; Image dimensions = $(300 \times 180)$ Å$^2$.

Significant change in the image of the Lander molecule have been observed by varying the sample voltage.

Fig. 4.3 shows an overview STM image of Lander molecules adsorbed on Cu(211) after preparation at $T_{\text{substrate}}$ = 80 K. The parallel underlying stripes visible in the image are the intrinsic steps of the Cu(211) surface. Each molecule appears as four lobes with an apparent height of $(4.0 \pm 0.5)$ Å. The molecules show different conformations, as they have either a rectangular shape or a rhomboidal one and present different orientations with respect to the substrate directions.

It is known from previous investigations [84, 85, 90–92] and from elastic scattering quantum chemistry (ESQC) calculations (see Section 4.6), that the four lobes visible in the STM images correspond to the TPB groups of the molecule, while the orientation of the Lander board is always parallel to the pair of intensity maxima with the shorter distance. However, the central board is not visible in the STM images because it is kept too far away from the surface by the legs (its molecular orbitals are not strongly enough electronically coupled to the surface) to induce an observable contribution to the STM contrast compared to the legs corrugation. In the gas phase the legs of the molecule stay perpendicular to the molecular board, as shown in Fig. 4.4(a). Upon adsorption, the central board of the molecule is attracted to the surface by van der Waals forces. Due
4.3. Adsorption

**Figure 4.4:** Molecular conformations. (a) Scheme of the molecule in the gas phase: the spacer legs are perpendicular to the molecular board. (b) Scheme of the molecule upon adsorption (side view). The legs rotate around the $\sigma$-bond forming an angle $\theta$ with the normal of the molecular board. (c) Scheme of the molecule upon adsorption (front view). The legs bend around the $\sigma$-bond forming an angle $\Phi$ with the direction perpendicular to the molecular board. (d) Scheme of the possible legs conformations upon adsorption: Parallel legs conformation (top), crossed legs conformation (bottom). (e) STM image showing two molecules. The left molecule is in the symmetric legs conformation, while the right molecule is in the crossed legs conformation. STM parameters: $I = 0.3$ nA; $U = -1$ V; $T = 7$ K. Image dimensions: $(100 \times 60)$ Å$^2$

to this attractive interaction, the legs rotate around the $\sigma$-bonds with the central board (as shown in Fig. 4.4(b)) and are bend from the direction perpendicular to the board as indicated in 4.4(c). Two legs on the same side of the molecular board are always rotated in the same direction because of steric hindrance, but legs on opposite sides can be rotated either in the same direction or in opposite directions. The first conformation is called *parallel legs* while the second one is called *crossed legs* conformation (Fig. 4.4(c)). The molecules in the first conformation are imaged by STM by a rectangular shape, while the molecules in the latter conformation show a rhombic shape.
Figure 4.5: Models (in a front view) of the calculated adsorption geometry of the Lander molecule on Cu(211) when the molecular board is parallel to the intrinsic steps of the surface (a) and perpendicular to them (b).

Figure 4.6: Comparison between experimental and calculated STM images of Lander molecule on Cu(211) for all its adsorption conformations. (a) Scheme of the four conformations (as found in a molecular mechanics calculation). (b) STM images calculated with ESQC method for each conformation of a Lander on Cu(211). (c) Corresponding STM experimental images for each conformation. STM parameters: I = 0.3 nA; U = −0.9 V. Image dimensions = (30×30) Å².
In Fig. 4.4(d) it is possible to see two molecules, one in the crossed legs conformation (top molecule) and one in the parallel legs conformation (bottom molecule). The crossed leg conformation appears dominantly on Cu(211) by a ratio of 5:1, indicating a lower total energy [84]. In addition to the legs conformations existing also on other copper surfaces, the Lander molecule presents two more stable conformations on Cu(211) depending on the parallel or orthogonal orientation of its central board with respect to the intrinsic steps of the Cu(211) surface [84]. In Fig. 4.5 the models calculated with MM by C. Joachim and collaborators (CEMES-CNRS, in Toulouse) of the adsorption geometry for the two molecular board orientations is shown.

The two molecular board orientations in combination with the two internal conformations give rise to four possible molecular conformations upon adsorption. The four conformations of the Lander on Cu(211) are schematically summarized in Fig. 4.6(a). In Fig. 4.6(b) and Fig. 4.6(c) the calculated STM images with ESQC method by C. Joachim and collaborators and the experimental measurements corresponding to those conformations are reported. The agreement between calculated and measured images is very good. Notice that in each conformation two legs appear brighter. This is due a combination of tunneling channels through the upper part of one leg and the lower part of the leg on the same side of the molecular board.

When the temperature of the substrate during the molecular deposition ($T_{\text{substrate}}$) is larger than 120 K, Lander molecules are found at step edges (see Fig. 4.7(a)). This indicates that the molecules diffuse at these preparation temperatures. In this case, the board of the molecules is oriented parallel to the step edge, while two legs are adsorbed on the upper terrace of the step and two on the lower (see Fig. 4.7(c-d)). The legs conformation can be either the parallel or the crossed one. Furthermore, as shown in better detail in [84], the Lander induces a reconstruction of the step upon adsorption.

In order to perform manipulation experiments with isolated molecules on terraces, I have chosen to deposit the molecules at low $T_{\text{substrate}}$. 
4.4 Constant height manipulation on Cu(211)

It has been shown [54] that a successful manipulation of large organic molecules can be better achieved by using the manipulation in constant height.

To manipulate a Lander between two assigned points A and B in a constant height mode (see Fig. 4.8(a)), the tip is first moved from A to B and back in constant current mode in order to determine the inclination of the surface. Then, the tip is positioned on the initial point A and the tip to surface distance Z (defined by the center-to-center distance between the surface and the tip apex end atom) is decreased of a chosen quantity DZ (in a typical range between 2 Å and 5 Å). In the following the tip is moved in constant
4.4. Constant height manipulation on Cu(211)

Figure 4.8: (a) Scheme of the manipulation in constant height. During the manipulation the tip height is reduced by a quantity $DZ$ with respect to the initial tunneling parameters. The value $Z$ is the tip height during the path in constant height (considering the center of the tip apex end atom and the copper atom of the surface under tip). (b) Scheme of the signals recorded during the manipulation in constant height: While the tip is moved in constant height the tunneling current flowing in the STM junction is recorded. The current shows pronounced dips, that are due to the molecule “jumping” from one adsorption site to the next.

height mode from point A to B with the feedback loop switched off. The experimental calibration of the Z distances is obtained by measuring the electrical point contact position between the tip apex end and the surface, before any series of manipulations. In this manipulation mode, the interaction between the tip and the molecule is always kept strong and instabilities in the vertical position of the tip (that can occur in the constant current manipulation mode, described in Sec. 2.5.1) are avoided. During a manipulation sequence, the STM tunneling current $I(X)$ is recorded as a function of the tip apex displacement $X$ between A and B (see Fig. 4.8(b)). The experimental $I(X)$ curve contains detailed information about the motion of the molecule on the surface during the manipulation process. At the end of the manipulation process, the tunneling parameters are restored and the tip returns to the initial position A in constant current mode. The applied voltage during the manipulation varies between 30 and 50 mV. Small voltage values are applied during the manipulation in order to avoid electric field effects or vibrational excitations through tunneling of electrons. An etched W wire is used as STM tip, but since the tip was formed by controlled contact with the Cu surface, the tip apex is expected to be covered by copper atoms.
Figure 4.9: Formation of a molecular chain by means of STM manipulation. (a) STM image before the manipulation. (b) STM image recorded after 27 manipulations. STM parameters: \( U = -1 \, \text{V}, \, I = 0.2 \, \text{nA}, \, T = 7 \, \text{K} \); Image dimensions = (300 × 180) Å\(^2\). During the manipulations: \( Z = 5.2 \, \text{Å}, \, U = 0.05 \, \text{V} \).

Following this manipulation procedure, Lander molecules can be moved in a controlled way on Cu(211) [86]. In Fig. 4.9 the manipulation is used to assemble molecules along a straight line with equal spacings. Fig. 4.9(a) shows the image before the manipulation. The STM image in Fig. 4.9(b) has been recorded after 27 manipulation attempts.

The manipulation process was investigated in dependence on the direction of the manipulation relative to the surface: either parallel to the intrinsic Cu(211) steps or perpendicular to them, i.e. in the [01\overline{1}] direction or in the [1\overline{1}1] respectively.
4.4. Constant height manipulation on Cu(211)

Figure 4.10: Manipulation experiment: The arrows indicate the motion of the tip during a manipulation. In each image the conformation of the molecule and its orientation are shown by a scheme. (a) Lander before the manipulation in the symmetric legs conformation. (b) Lander after a first manipulation in the crossed legs conformation. (c) Lander in the crossed legs conformation after a second manipulation. (d) After the third manipulation, the Lander is still in the crossed legs conformation, but with the orientation of the legs inverted with respect to the image in (c). STM parameters: $U = -0.9 \text{ V}$, $I = 0.2 \text{ nA}$, $T = 7 \text{ K}$; During the manipulation in (a) and (b) $Z = 5.6 \text{ Å}$, $U = 0.03 \text{ V}$, in (c) $Z = 5.1 \text{ Å}$, $U = 0.03 \text{ V}$.

An example of a manipulation experiment is shown in Fig. 4.10, where three subsequent manipulations have been performed. The motion of the tip during the process is indicated by arrows. The manipulation path of the tip is chosen in order to push the legs of the molecule. In the figures 4.10(a) and (b) the manipulation is performed in the direction parallel to the intrinsic surface steps, while in Fig. 4.10(c) in the direction perpendicular to the steps. In each image the legs conformation and molecular orientation are shown by a scheme. During a manipulation, the Lander molecule can change its legs conformation (Fig. 4.10(a)-(b) and (c)-(d)). Notice that after the manipulation in Fig. 4.10(c)-(d) the molecule is found shifted in the direction parallel to copper rows even though the manipulation is performed in the direction perpendicular to them. In general, during the manipulation the molecule can change its molecular board orientation, being found after
the manipulation rotated by 90°. Usually the molecule is found after the manipulation in one of the four stable adsorption geometries, which are shown in Fig. 4.6. In the present investigation, 304 manipulations attempts have been performed following the described procedure. The results are shown in Tab. 4.1. The molecules were manipulated 219 times along an intrinsic Cu(211) step. 67% of those manipulations were successful, while in the remaining cases the molecule was either destroyed (4%), jumped to the tip (5%), or did not move at all (23%). In very few cases (1%) when the molecule was manipulated along the intrinsic surface steps it moved in other directions.

Manipulations perpendicular to an intrinsic Cu(211) step have been done 85 times. 37% of those manipulations were successful, in 2% of the cases the molecule was destroyed, in 8% of the cases jumped to the tip, and in 36% of the attempts did not move at all.

In 52% of the manipulations parallel to the step edges, the molecule has changed its conformation or is found rotated (16%) after the manipulation. In the case of manipulation perpendicular to the step edges a conformational change is observed in 60% of the cases, while the rotation of the molecular board in 26% of the manipulation attempts. From this statistical analysis it appears clear that the manipulation parallel to the intrinsic steps is easier and more successful than perpendicular to them. The reason is that on Cu(211) the diffusion barrier is much higher perpendicular to the intrinsic steps than parallel to them. Sometimes (17%), even if the aim is to manipulate perpendicular to the steps, the Lander

<table>
<thead>
<tr>
<th>Manipulation direction</th>
<th>Parallel to the [01\overline{1}]</th>
<th>Perpendicular to the [01\overline{1}]</th>
</tr>
</thead>
<tbody>
<tr>
<td>N of manipulations</td>
<td>219</td>
<td>85</td>
</tr>
<tr>
<td>Success (%)</td>
<td>67</td>
<td>37</td>
</tr>
<tr>
<td>No motion (%)</td>
<td>23</td>
<td>36</td>
</tr>
<tr>
<td>Motion in an other direction (%)</td>
<td>1</td>
<td>17</td>
</tr>
<tr>
<td>Molecule destroyed (%)</td>
<td>4</td>
<td>2</td>
</tr>
<tr>
<td>Molecule on the tip (%)</td>
<td>5</td>
<td>8</td>
</tr>
<tr>
<td>Conformational change (%)</td>
<td>52</td>
<td>60</td>
</tr>
<tr>
<td>Orientation change (%)</td>
<td>16</td>
<td>26</td>
</tr>
</tbody>
</table>

Table 4.1: Statistics of the manipulation experiments.
molecule moves parallel to the steps (as it happens in Fig. 4.10(c)-(d)), showing how favorable and easier this type of motion is. Moreover, the orientation of the molecular board for parallel manipulation changes less frequently than in the case of a manipulation perpendicular to the intrinsic steps, confirming the rail role of the top surface Cu atomic rows. A similar behavior has been observed [84] when Lander molecules, adsorbed on step edges (both natural and reconstructed), have been manipulated along the step edge: the step edges act as a guidance for the manipulation and the molecules always remained in the same adsorption geometry, as described in Section 4.3: two legs on the upper terrace and two legs on the lower, with the central board parallel to the step edge. It is important to note that not every attempt to manipulate the Lander molecule was successful (Tab. 4.1). Therefore, a statistical analysis of the manipulation is crucial in order to gain control of the manipulation process.

4.5 Manipulation signal

4.5.1 Manipulation parallel to the Cu(211) steps

Figure 4.11: Experimental constant height manipulation of a Lander molecule in the [01\overline{1}] direction, parallel to the intrinsic steps of the Cu(211). (a) Lander on a terrace before the manipulation in the crossed legs conformation; the black arrow indicates the exact path performed by the tip during the process. (b) Lander after the manipulation. (c) Current signal recorded during the process. STM parameters: (a), (b): $U = 0.9$ V, $I = 0.2$ nA, $T = 7$ K; (c): $Z = 5.6$ Å, $U = 0.03$ V.

Fig. 4.11 shows a lateral manipulation of a Lander molecule in the [01\overline{1}] direction, parallel to the intrinsic steps of Cu(211). It is performed by pushing a single rear leg with
the tip. The STM images of the Lander molecule before and after the manipulation are presented in Fig. 4.11(a) and 4.11(b), the I(X) signal recorded during this manipulation is shown in Fig. 4.11(c). In Fig. 4.11(a), the arrow indicates the exact path followed by the tip apex during the manipulation. In the experiment, the tip-surface distance $Z$ was 5.6 Å and a voltage of $V = 30$ mV was applied. After the manipulation, the Lander molecule is still in its crossed legs conformation, with the board parallel to the intrinsic steps of the Cu(211), but the orientation of the legs pair is inverted. In fact the molecule in Fig. 4.11(b) is the mirror image of the molecule in Fig. 4.11(a).

Typically, in the case of manipulation parallel to the copper rows, the current curves are composed of periodic and regular peaks, similarly to the case shown in Fig. 4.11(c). Here, the periodicity 2.6 Å matches the Cu(211) lattice constant of 2.55 Å very well. This means that during the manipulation the molecule jumps from one adsorption site to the next. The STM tip, moving in constant height, experiences a periodic increase and decrease of the current flowing. As can be seen from the current signal (Fig. 4.11(c)), the manipulation happens in the *pushing* mode, which is described in Section 2.5.1. This kind of manipulation takes place through repulsive forces between the tip and the molecule. As typical for the pushing mode, in the initial part of the curve in Fig.4.11(c) the current increases as the tip moves in the direction of the molecule until the molecule experiences a threshold repulsive force. The current signal shows a sudden drop as the molecule jumps away from the tip. As the tip approaches laterally the new position of the molecule, the signal increases until the molecule jumps again. This cycle is then repeated. At the beginning of the manipulation sequence an initial weaker peak can be observed (Fig. 4.11(c)). This feature is typical for the manipulation of a Lander molecule and is always present in the manipulation curves. It can also be noted that in the continuous regime no internal characteristic structure is present in a given I(X) peak. A fine structure would result from internal movements of the molecule, as it was observed for example in the case of Cu-tetra-3,5 di-ter-butyl-phenyl porphyrin (TBPP) molecule manipulated on Cu(100) [20].

To interpret the I(X) experimental signal in detail, C. Joachim and his collaborators at the Nanoscience Group, CEMES-CNRS, in Toulouse (France) have performed theoretical calculations of the manipulation I(X) signal [86] (for a complete description of the calculation method see Ref. [95]). Molecular mechanics (MM) calculations are used
4.5. Manipulation signal

to optimize the molecular conformations, while the tunneling current during the lateral
motion of the tip in constant height is calculated with the ESQC method described in
Section 2.4. At each 0.05 Å interval of the tip apex motion (the experimental points have
a resolution of 0.04 Å), the Lander conformation and its position on the Cu(211) surface
are optimized by molecular mechanics calculations and the ESQC constant height tunnel-
ing current is calculated. The tip is modeled by a copper apex with a [110] orientation,
exhibiting four (111) facets.

In Fig.4.12(c) the calculated signal during the manipulation parallel to the intrinsic
steps of Cu(211) is shown. The typical experimental I(X) signal for manipulation parallel
to the intrinsic surface steps is well reproduced by the calculation for Z=5.7 Å (notice
that in the experiments Z varies between 5.9 Å and 4.2 Å). Even the initial weaker peak
observed in the experimental I(X) is present in the calculations.

In order to identify which parts of the molecule contribute to the current signal and
which are the tunneling channels involved in the process, the full manipulation signal I(X)
has been decomposed. To achieve this, the molecular mechanics and the deformations
of the complete Lander molecule have been used and the contributions of the different
molecular orbitals have been analyzed. The different I(X) contributions can be identified
as shown in Fig. 4.12(b) for the board (I_b(X)) and in Fig. 4.12(d) for the pushed leg (I_l(X)).
The conformational changes of the corresponding parts of the Lander are also extracted
from the molecular mechanics calculation: in Fig. 4.12(a) the variation of the distance z
between the rear end of the board and the Cu(211) surface is presented and in Fig. 4.12(e)
the rotation angle θ of the pushed leg is shown.

Comparing the I(X) current intensity in figures 4.12(c), 4.12(b) and 4.12(d), one de-
duces that the main contribution to the calculated I(X) signal comes from the molecular
board. The reason of that can be understood by considering the whole manipulation mech-
anism. When the tip apex approaches the Lander by a rear leg in constant height mode,
three characteristic situations can be highlighted:

\textbf{i}: X \leq 8 Å. During the lateral tip-approach, the board rear is lifted from z=3.35 Å
to z=3.91 Å by attractive van der Waals interactions until the electronic point contact
between the board and the tip occurs at X\approx 8 Å: the tunnel current through the board is
still very low.
Figure 4.12: Calculated manipulation signal of the Lander molecule at constant height mode on Cu(211) for \( Z = 5.7 \, \text{Å} \). (a) Distance variation \( z \) between the rear part of the Lander board and the surface during the manipulation sequence. (b) Contribution to \( I_b(X) \) signal coming from the molecular board. (c) \( I(X) \) calculated for the complete Lander molecule. (d) \( I_l(X) \) contribution coming from the pushed leg. Notice the different scaling of the y-axis, with respect to (b) and (c). Notice further that the three other legs contribute very little to the tunneling current. (e) Angular variation \( (\theta) \) of the pushed leg during a manipulation sequence.
ii: The transitory regime ($8 < X \leq 13 \, \text{Å}$). The board is forced to be close to the surface ($z=3.21 \, \text{Å}$). This creates the initial current peak at $X=9.5 \, \text{Å}$ in Fig.4.11(c). In the meantime, the current contribution from the leg $I_l(X)$ does not vary a lot. The most significant current originating from the leg in this regime is between $X=10 \, \text{Å}$ and $X=13 \, \text{Å}$, when the tip is electronically contacting the pushed leg. After this short sequence, the tip apex pushes on the leg and $\theta$ increases (see Fig.4.11(e)). As a result, the board is lifted up again from the surface from $3.2 \, \text{Å}$ to $3.9 \, \text{Å}$. This does not result in a decrease of $I_b(X)$ through the board since now the tip apex is also in close proximity with it.

iii: Permanent manipulation regime ($X \geq 13 \, \text{Å}$). The legs adopt an orientation ($\theta \approx 40.5^0$) compatible with a specific value of $z$ (around $3.8 \, \text{Å}$). The steric crowding, that is the repulsive interaction between hydrogen atoms of the legs and of the board, maintains a minimum in $z$ that corresponds to a minimum in $\theta$. At this stage, the tip is forcing the molecule to jump from stable adsorption site to the next one. The rear end of the board is regularly oscillating in $z$ by $0.1 \, \text{Å}$, providing the observed experimental $I_b(X)$ signal oscillating between 9 and 14 nA. The complete $I(X)$ signal is the superposition of the board and leg contributions.

From this calculations, it is possible to conclude that the main contribution to the $I(X)$ signal comes from the board. This effect can be explained due to the peculiar topography of the Cu(211) surface, where the [011] rows work as rails for the manipulation of the molecule. When the board of the Lander is oriented in the direction of such rails, a row of Cu atoms is always located between the legs just under the board (see Fig. 4.5). The legs of the molecule maintain the board separated from the surface and prevent a large electronic interaction between the molecular orbitals of the board and the atomic orbitals of the rows. However, any variation of the board-surface distance $z$ will nevertheless induce a variation of this interaction and thus a variation of the tunneling current. A tunneling path through the Lander board will therefore be created. As indicated in Fig.4.12(a), pushing on a rear leg provides enough deformation to the board to induce a variation of $z$ sufficient to make the tunneling current through the board larger than the tunnel current through the leg. Moreover, while each maximum of the complete $I(X)$ curve in Fig.4.12(c) is in phase with a minimum of $z$, $I(X)$ is out of phase with the $\theta$ variations.
Figure 4.13: Manipulation perpendicularly to the intrinsic steps of the surface. (a) Lander before the manipulation in the crossed legs conformation. (b) Lander after the manipulation in the symmetric legs conformation. (c) Current signal recorded during the process. STM parameters: (a), (b): $U = -1 \text{ V}$, $I = 0.2 \text{ nA}$, $T = 7 \text{ K}$; (c): $Z = 5.1 \text{ Å}$, $U = 0.05 \text{ V}$.

4.5.2 Manipulation perpendicular to the Cu(211) steps

In Fig. 4.13 an example of manipulation perpendicular to the step edges is shown. The manipulation was performed by moving the tip along the [111] direction on the legs of the molecule at a tip-surface distance $Z = 5.1 \text{ Å}$ and applying a voltage $V = 50 \text{ mV}$. During the process, the molecule changes its legs conformation. Before the manipulation (Fig. 4.13(a)) it is in the crossed legs conformation while after the manipulation (Fig. 4.13(b)), it is in the parallel legs conformation. The recorded manipulation signal $I(X)$ in Fig. 4.13(c) does not exhibit any periodicity and the peaks are irregular in intensity, length and shape.

By considering all the manipulation curves measured in the [111] direction, one finds no reproducible behavior in the current. It is impossible to isolate a typical representative experimental curve to compare with calculated $I(X)$ signals, as in the case of manipulation parallel to the intrinsic steps. It is therefore not possible in this case to determine the detailed internal deformation of the molecule on the surface by comparing the experimental with the calculated curves. The diffusion barrier is much higher perpendicular to the surface rails (intrinsic steps) than parallel to them. Thus, during the manipulation perpendicular to the steps, the tip has to provide a higher force to move the molecule. Probably, before the molecule moves, some energy is accumulated within the molecule, which is
afterward relaxed in a statistical way (the molecule deformations are uncontrolled).

4.6 Conclusion

In this chapter, the manipulation in constant height mode of single Lander molecules on Cu(211) has been studied. From a statistical analysis of the experiment, it turns out that the steps of Cu(211) act as rails for manipulating the Lander avoiding movements of the molecules in other directions and keeping fixed the orientation of the molecules.

By recording the tunneling current signal $I(X)$ during the manipulation and by comparing it with calculations, one can conclude that $I(X)$ provides information on the mechanical motions of molecular parts that are not directly in interaction with the tip apex during the manipulation sequence. This is due to the fact that the intramolecular deformation induced by the manipulation can open a tunneling path through the molecular board, even if the tip apex pushes and is in close contact with a leg of the molecule. Moreover, it is possible to conclude that a regular $I(X)$ signal is not always obtained during a successful manipulation. It requires a specific optimization of the surface and of the molecule to be manipulated, as can be seen in the comparison of manipulation along and perpendicular to the Cu(211) intrinsic steps. The manipulation can be achieved in both cases, but a regular current signal is obtained only in the manipulation along the steps. Along the $[01\bar{1}]$ direction, a periodic signal can be observed, since the molecule is guided by the surface rails (intrinsic steps) and moves regularly hoping from one stable adsorption site to the next. Perpendicular to that, the relatively large steps act as a barrier for the manipulation and the hopping over those steps occurs in a more or less random way.