Chapter 4

Lander/Cu(211) – Selective Adsorption and Surface Restructuring

In the first part of this work, the adsorption of single Lander (SL) molecules on Cu(211) has been studied for different adsorption temperatures. The sample temperatures during preparation were chosen between 330 K and 70 K, to investigate the adsorption of the molecules with and without surface diffusion after evaporation. Different adsorption geometries and interesting effects like selective adsorption and adsorbate induced restructuring are observed. STM measurements will be compared with ESQC calculated images to determine the exact molecular adsorption conformations.[98]

The stepped Cu(211) surface (see section 3.2.2) has been chosen as substrate in order to study the effect of a nano-structured surface on the adsorption and lateral manipulation of Lander molecules (section 3.3.1). The distance between two intrinsic steps on the Cu(211) surface is 6.26 Å, which is approximately one third of the length of a Lander molecule. Thus, it can be expected that the adsorption is influenced by the corrugation of the substrate, showing interesting new properties with respect to the adsorption on flat surfaces. Furthermore, the lateral manipulation of molecules on a stepped surface can be expected to be strongly anisotropic, i.e. one would expect a larger diffusion barrier in the direction perpendicular to the intrinsic steps, than parallel to the steps. Such properties of the stepped

Cu(211) surface can therefore be used to increase the control of STM induced lateral manipulation of large organic molecules.

Concerning the construction of atomically defined structures from large molecules with the STM, a structured surface as template is useful to confine some degrees of freedom, which can not be controlled otherwise. In the case of Lander on Cu(211) it will be shown that the adsorption position perpendicular to the direction of manipulation and the molecular orientation are maintained during the manipulation. The intrinsic steps act like a rail, guiding the molecular movement and thereby increasing the precision and reproducibility of STM induced lateral manipulations.[98]

4.1 Preparation at Low Sample Temperature

By depositing the molecules at low sample temperature, the molecular surface diffusion is frozen in and the molecules are found at their initial adsorption site after evaporation. A typical measurement performed after preparation at a temperature of 80 K is shown in Fig. 4.1. Each Lander molecule appears as expected as four bright protrusions of a height of (4.0 ± 0.5) Å (see section 3.3.1), which are belonging to the four spacer legs of the molecules. The equally spaced lines in the $[01\bar{1}]$ direction, visible in the image, correspond to the intrinsic step edges of the Cu(211) surface, i.e. their distance is 6.26 Å. Many smaller adsorbates, probably molecular fragments, can be seen in the STM images. Such adsorbates are sometimes picked up by the tip, causing scanning stripes in the fast scanning direction (the horizontal line in Fig. 4.1). This contamination is due to the increased sticking coefficient during preparations at low sample temperature.

In case of a preparation temperature of 80 K or lower, the molecules are found separated from each other on the free Cu(211) terraces. Differences in terms of arrangement, relative height, and orientation of the four protrusions are observed for different molecules. These differences are explained by adsorption in different molecular conformations.
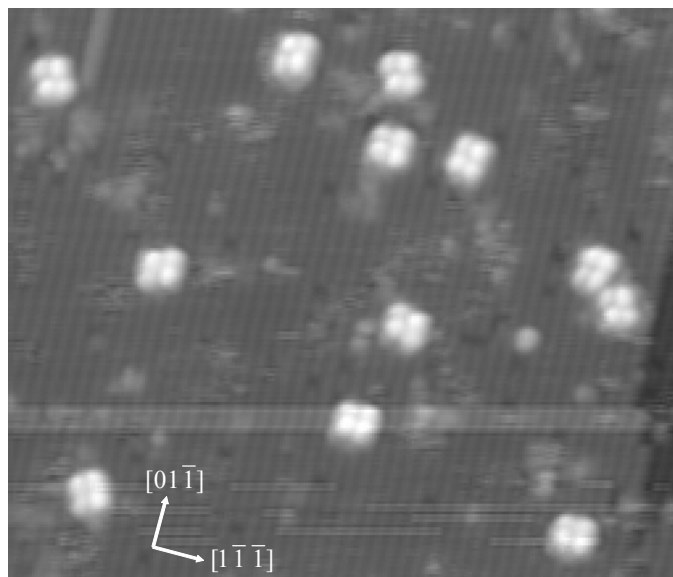
Fig. 4.1. STM measurement of Lander molecules on Cu(211), T_{evap} = 80 K, image size 18×20 nm², U = 0.8 V, I = 0.2 nA, T = 8 K. Molecules appear as four bright lobes, the intrinsic steps of the Cu(211) surface can be seen, running in $[01\bar{1}]$ direction.
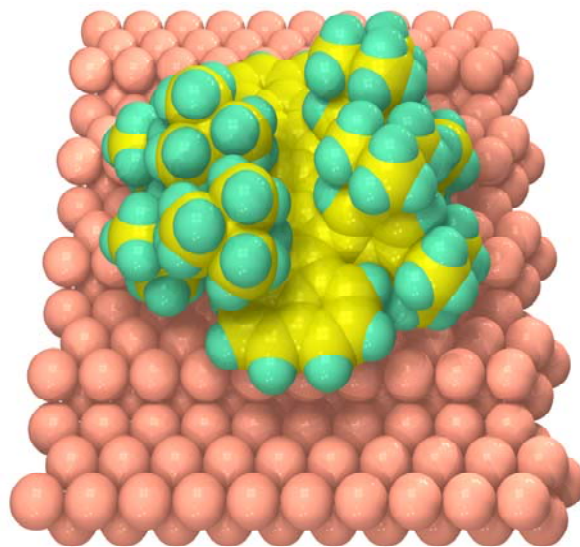

Fig. 4.2. Model of a Lander molecule adsorbed on Cu(211). In this case the crossed legs, orthogonal board, i.e. C_O, conformation is shown.

To correlate the appearance of the molecules in STM images to specific adsorption conformations, STM measurements of single molecules are compared with ESQC calculations (see section 2.5). As first step of the calculations, the energetically preferred adsorption conformations are determined using molecular mechanics (MM) optimizations. A sphere model, showing a Lander adsorbed on Cu(211) as calculated by MM, is shown in Fig. 4.2.

Four energetically close conformations, which differ in the internal conformation (tilt of TBP spacer legs) and in orientation of the board are found. Models displaying the result of the MM calculations for all four conformations are shown in panels A and B of Fig. 4.3. The corresponding modelled STM images obtained by the ESQC method, are reported in Fig. 4.3 panel C. In STM measurements (Fig. 4.3 panel D) all four predicted conformations can be distinguished and identified by comparison with the calculated images. About 95% of the molecules are found in one of these four conformations (and 5% in another, fifth conformation).

The same internal conformations, i.e. crossed legs (C) and symmetric legs (S), as observed on other Cu surfaces[93, 95, 96] (described in section 3.3.1) are found on Cu(211). In accordance to the observations on the other Cu surfaces, the crossed legs conformation appears dominantly, by a ratio of 5:1 on Cu(211), indicating a slightly lower total energy.

Due to the intrinsic steps of the Cu(211) substrate, the molecules show characteristic orientations with respect to the substrate. Two molecular orientations are predicted to be energetically stable. In combination with the two internal conformations (crossed legs: C, parallel legs: S) they give rise to the overall four observed conformations: The molecules are rotated either with the board parallel to the intrinsic steps (C_P and S_P: Row 1 and 2 in Fig. 4.3) or orthogonal to the steps (C_O and S_O: Row 3 and 4 in Fig. 4.3). Experimental results confirm that almost all molecules are either in parallel (50 %) or in orthogonal (45 %) orientation. Only 5 % of the molecules are found in an additional orientation, which has not been predicted by the calculations, with the board tilted by approximately 45° with respect to the $[01\bar{1}]$ direction.
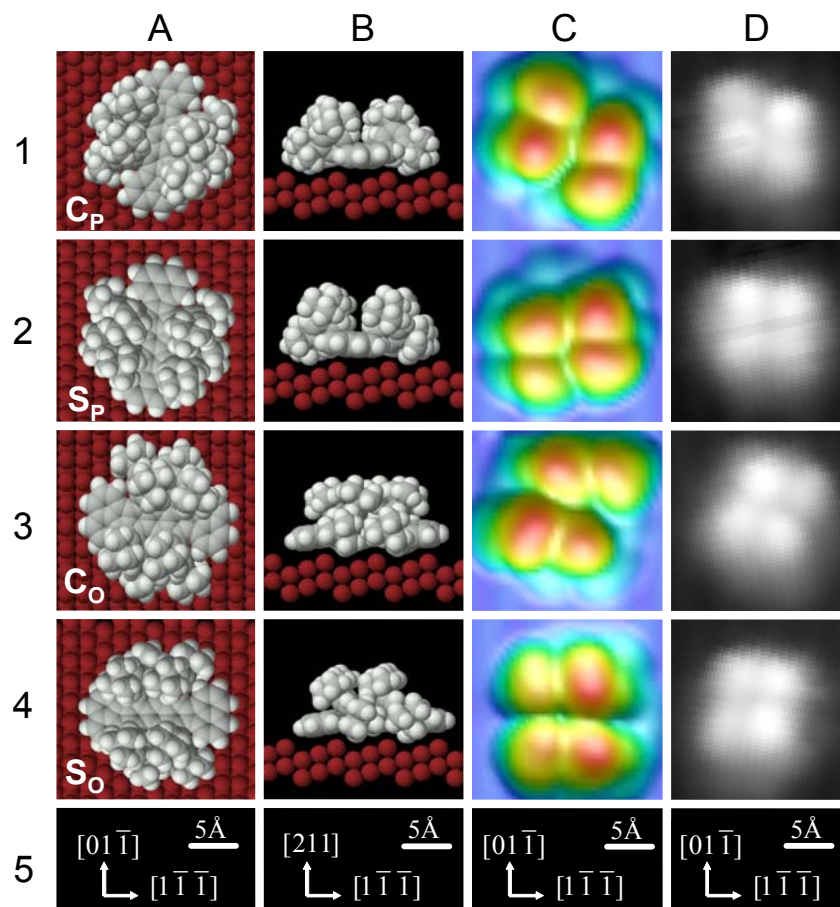
Fig. 4.3. Adsorption conformations for Lander on Cu(211) at low temperature. Models of molecular mechanics (MM) optimization (panel A from top, panel B from side). Calculated STM images using ESQC (panel C) and STM measurements (panel D) for all four predicted conformations (row 1-4) i.e. C_P (crossed legs, parallel orientation), S_P (symmetric legs, parallel orientation), C_O (crossed legs, orthogonal orientation), and S_O (symmetric legs, orthogonal orientation). In row 5 the orientation and scale for each panel is indicated.

From comparison with the calculated images the detailed intramolecular contrast can be understood as being due to the deformations of the σ-bonds of the molecular legs. STM images always reveal one bright and one less bright bump on each side of the molecular board. Due to the rotation of the σ-bonds the top CH_3 group of the brighter leg is positioned above the bottom CH_3 group of the other leg, thus opening an additional tunnelling channel through both legs. Therefore the legs of a molecule are imaged with a different apparent height, though their geometrical height is equal.

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The weak elevation surrounding the molecules, visible in both experimental and calculated images, is in part due to imaging the lower CH_3 groups at the bottom of the legs, which become visible due to the bending of the σ-bonds. The apparent shape of the molecules is characteristic for STM images and has also been reported with almost identical details on Cu(110)[95, 96], Cu(100)[93], and Cu(111) (section 5.1).
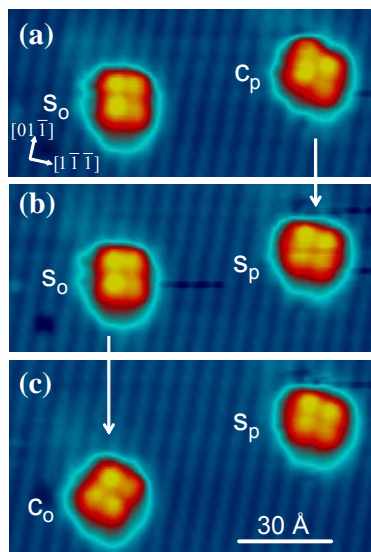

Fig. 4.4. STM images (U = 0.8 V, I = 0.2 nA) of Lander molecules on the defect free Cu(211) surface. The molecules have been switched into different conformations between the images by means of STM manipulation (manipulation parameters: U = 50 mV, I = 10^{-7} A).

By means of lateral STM induced manipulation it is possible to switch the molecular conformation between parallel legs and crossed legs, as it is shown in Fig. 4.4. To switch the conformation of molecules, the tip is moved across a molecule with a decreased tunnelling resistance of about 0.5 MΩ. The switching occurs randomly between the previously described conformations and not every manipulation attempt results in a change of conformation. Such conformational changes have also been reported on Cu(100) by Kuntze et al.[93]

4.2 Preparation at High Sample Temperature

After evaporation at higher sample temperatures (160 K to 330 K) the Lander molecules are always found at defect sites, usually at step edges, indicating that surface diffusion is not hindered.
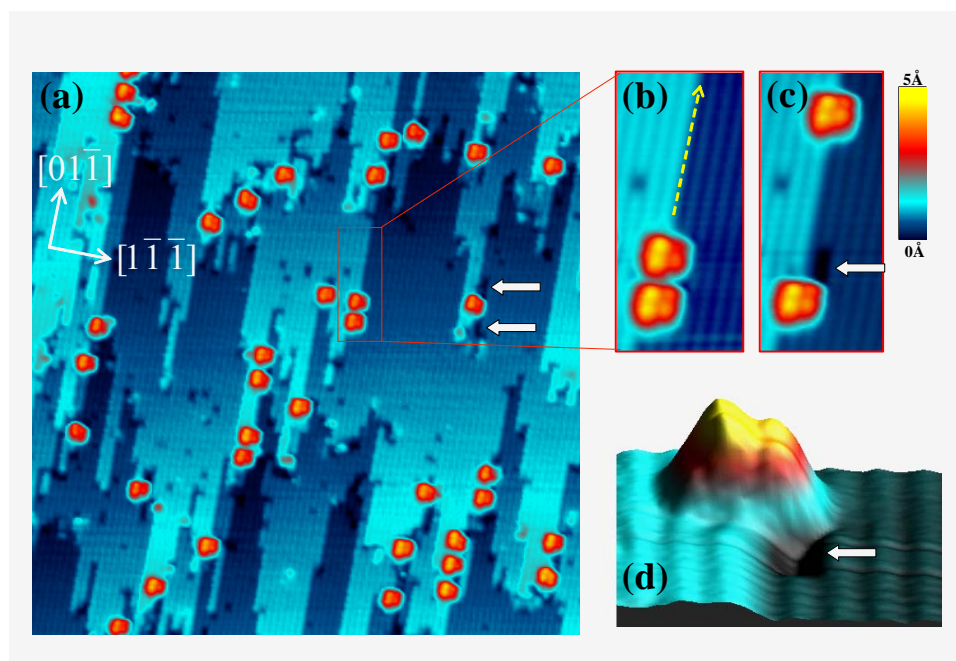

Fig. 4.5. STM-measurements (U = 0.8 V, I = 0.2 nA) of Lander on Cu(211) prepared at 330 K. (a) Overview (image size: 35×30 nm²). Note that all Lander molecules are exclusively adsorbed at (311) steps. The rectangle indicates the picture frame of (b) and (c). Between (b) and (c) (image size: 3.5×9 nm²) one molecule has been moved along the step edge by STM manipulation, revealing the underlying restructuring of the substrate step. (d) Pseudo 3-dimensional representation of an STM measurement of a single Lander molecule at a step edge. Restructured areas are indicated by white arrows.

A typical overview scan after preparation at 330 K is shown in Fig. 4.5(a). The molecules adsorb selectively at the $[01\bar{1}]$ directed terrace steps, furthermore exclusively at (311) steps, i.e. at steps leading downward with respect to the $[1\bar{1}\bar{1}]$ direction, and never at (111) steps. The board of the molecule is always aligned parallel to the step edge, whereas the internal conformation can again differ between crossed legs and parallel legs conformations. The covered (311)

steps are restructured in the presence of Lander molecules. When the molecules are moved away from their adsorption site (Fig. 4.5 (b)) by lateral manipulation, ditches on the lower side of the step edge become visible (Fig. 4.5 (c)). These ditches are rarely observed for clean Cu(211) surfaces and their number increases as the deposited amount of Lander molecules increases, pointing to a surface restructuring induced by the Lander molecules. The observation of restructured steps extending over the molecules as in Fig. 4.6, visible without prior manipulation of the Landers, rules out the possibility of the restructuring being created by the STM manipulation.
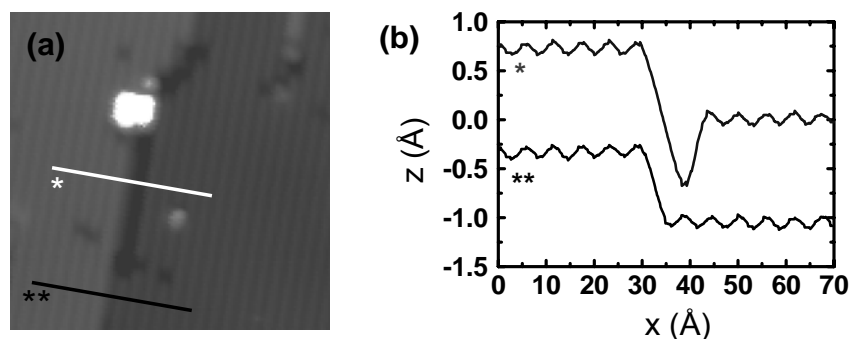

Fig. 4.6. (a) STM-measurement (U = 0.8 V, I = 0.2 nA, image size 14×14 nm²) the restructuring of the step edge is extended several nm away from the adsorption position of the molecule. (b) Line scans across the step edge with restructuring (top) and without restructuring (virgin step edge) (bottom).

From STM measurements with atomic resolution, I have deduced a model of the restructured surface (Fig. 4.7 (a) and (b)): In front of a (311) step a close-packed row of adatoms is missing creating a (311) and a (111) micro facet. Thus, the already existing (311) facet of the (311) step is extended to a width of three unit cells (3 × 4.23 Å = 12.7 Å), matching the width of a Lander molecule (15 Å). The molecule is located on the (311) facet and oriented parallel to the close-packed rows.

Model

STM

(a1)

(c1)

(a2)

6.26 Å

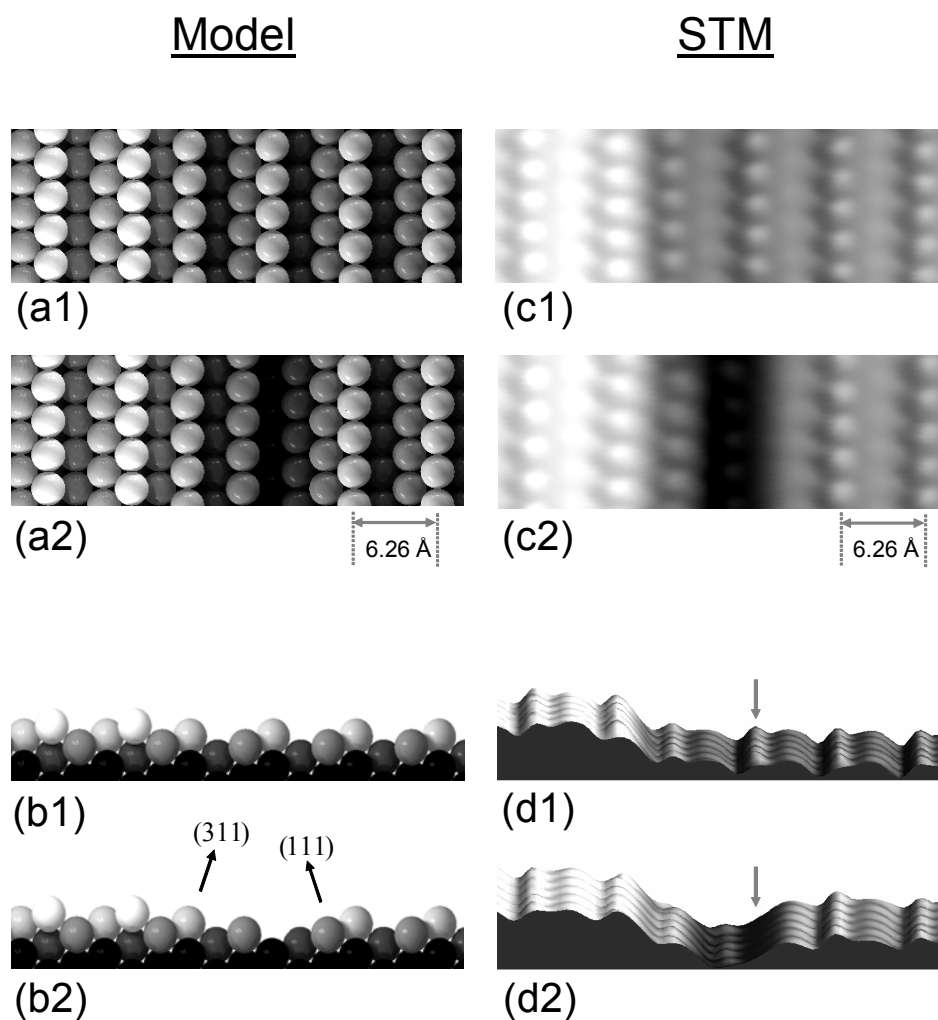(c2)

6.26 Å

(b1)

(311) (111)

(b2)

(d1)

(d2)

Fig. 4.7. Sphere models and STM measurements of a virgin (indexed by 1) and a restructured (indexed by 2) Cu(211) surface with a (311) step. (a), (b) Sphere models in top and side view, respectively. (c) High resolution STM measurements (size: 3.2 × 1.2 nm²; U = 0.2 V, I = 10 nA. The restructured step edge shown in (c2) was covered by a Lander molecule, which has been picked up with the tip before this measurement. The topography of the STM images differs from the models because of tip effects. (d) pseudo 3-dimensional STM images. The arrow in (d1) indicates the position of the row that is missing in case of the restructuring (d2).
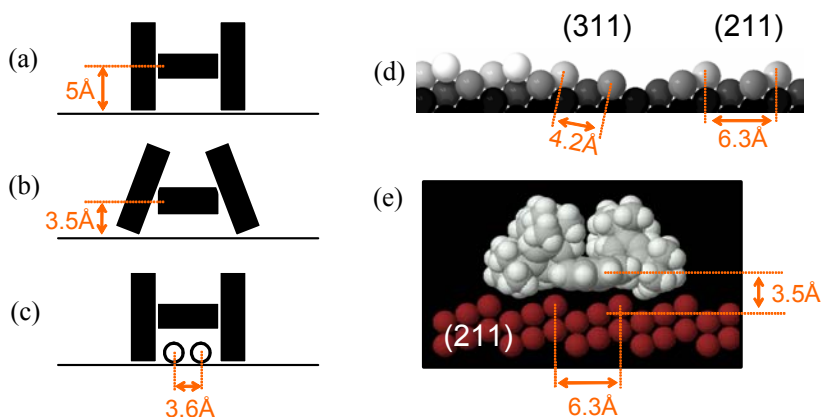
Fig. 4.8. Qualitative models to illustrate the reason for the selective adsorption. (a) Idealistic case, the board should be elevated 5 Å, if the spacer legs would be perpendicular to the board. (b) Real case, attractive van-der-Waals forces lower the position of the molecular board and induce strain in the legs σ bonds. (c) Energetically preferred nano-structured surface, schematic model of the restructuring as observed on Cu(110)[95]. (d) Model of the restructured (311) step of the Cu(211) surface. (e) Model of the calculated adsorption of a Lander on the (211) surface.

The driving force of the restructuring and selective adsorption can be seen in the attractive van der Waals forces between molecule and surface. On a flat terrace the aromatic molecular board is attracted towards the surface resulting in a deformation of the spacer legs σ-bonds and energy is accumulated in the strain of the molecule. Hence, a restructuring of the surface, in which the molecular board is supported by a nano-structured surface, allows van der Waals bonding towards the molecular board with less strain of the molecule and therefore is energetically favourable. A similar effect has been observed for the Lander induced restructuring on Cu(110), where the molecular board is supported by a 3.6 Å spaced double row of close-packed adatoms.[95] The situation on Cu(211) is comparable: While the spacing of the Cu(211) intrinsic steps (6.3 Å) is to large to allow much strain relief and the (111) step is an atomically smooth facet, the (311) facet exhibits close-packed rows with a spacing of 4.2 Å, thus providing a preferred adsorption geometry with a double row of step atoms supporting the Lander molecular board. A similar faceting of the Cu(211) surface into (111) and (311) facets, also with selective growth on the (311) facets, has been reported before for NaCl on Cu(211) by Fölsch et al.[119]

As stated before, the restructuring sometimes extends beyond the adsorption position of the Lander molecules (Fig. 4.6). This may be explained by the diffusion of the Lander along step edges, leading to uncovered restructured areas along the movement path of the molecule. Finding restructured areas in the vicinity of molecules without a molecule on top indicates a small energy difference between virgin and restructured surface.
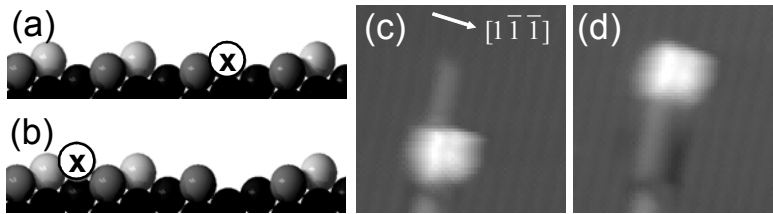

Fig. 4.9. Restructuring on the plane terrace. (a) Model of a perfect (211) terrace. When the indicated atoms are changed the structure of the restructured (311) step (b) is formed, without the presence of a terrace step. Such a situation was also observed in the experiment. The molecule was removed from its initial adsorption site (c) to reveal the missing row restructuring (d).

An estimation of the formation energy of the restructured surface can be made by comparing the situation in Fig. 4.9 (a) and (b), where the restructuring is formed without the presence of a step edge. The total number of atoms is the same for both, the virgin (211) surface and the restructured surface. In such cases the energy difference can be calculated roughly using the effective medium theory[120, 121], taking into account pair-interaction up to the next-nearest-neighbour and nearest-neighbour three-body-interaction. The energy difference can be estimated using the formula given in[121]:

$$E(N_1, N_2) \cong V_2(12 - N_1) + \frac{1}{2}V_3(12 - N_1)^2 + V_2^{'}(6 - N_2). \qquad (4\text{-}1)$$

The coordination numbers are N_1 (nearest-neighbour, 12 in bulk) and N_2 (next-nearest-neighbour, 6 in bulk) and the energies are $V_2 = 109$ meV, $V_3 = 2.3$ meV,

and $V_2' = 24.6$ meV.[121] In the case of the restructuring on Cu(211), as depicted in Fig. 4.9, the calculated energy difference for the first atom that changes from virgin ($N_1=7$, $N_2=3$) to restructured surface ($N_1=5$, $N_2=3$) is 0.25 eV. The coordination numbers of the second and following atoms that move from kink sites of the former virgin to the restructured site do not change ($N_1=6$, $N_2=3$). Therefore the calculated energy to form the restructuring is 0.25 eV, independent of the length of the restructured row. This value is only one third of the energy difference calculated for the Lander induced restructuring on a Cu(110) terrace, i.e. 0.75 eV.[95] An experimental confirmation of these different energies can be seen in the sample temperature needed to form the restructuring, i.e. about 470 K in case of Cu(110), while 160 K is sufficient in the case of Cu(211). Moreover, in the case of Cu(110) additional energy contributions of 0.04 eV per Cu dimer added to the restructured row are estimated.[95] For this reason the restructuring forms only under the Lander molecules and never extends beyond the molecule in the case of Cu(110), i.e. the restructuring has a fixed length of (8±1) atoms. On Cu(211) where only the first atom positional change costs energy, the restructuring is often extended several nm beyond the adsorption site of the Lander molecule (Fig. 4.6).

The molecular adsorption site influences the deformation of the molecule and therefore also the appearance of Lander molecules in STM topographs, which is investigated next. The apparent heights and distances of the legs are measured for molecules at different adsorption sites. Molecules that are adsorbed on a flat terrace, at a restructured step, and at a not-restructured (virgin) step are compared. The distance of the legs across the board as well as the apparent leg heights are determined for a large number of measurements (20-80 for each value in Table 4.1). Only molecules in the symmetrical legs conformation are taken into account, in order to exclude contributions to the legs height difference Δh from an asymmetrical tilting of the legs. Typical line scans are displayed in Fig. 4.10 and the mean values are given in Table 4.1.
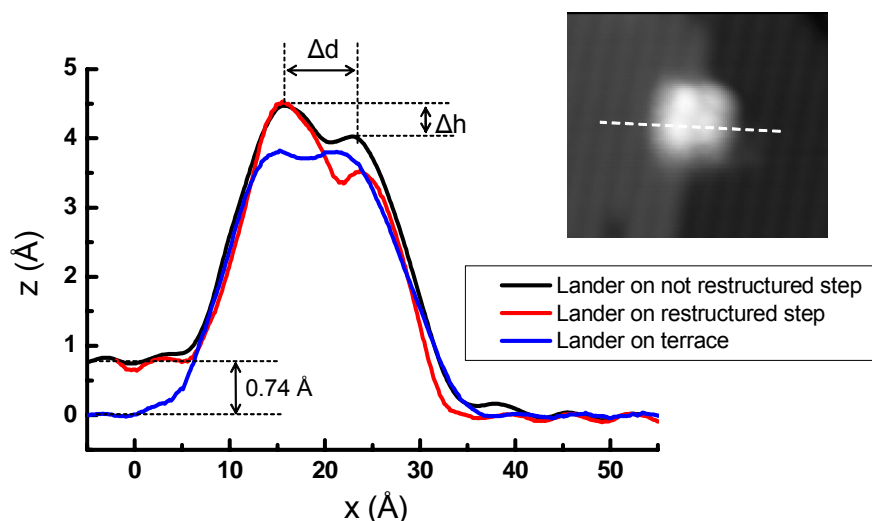
Fig. 4.10. Line scans across Lander molecules (as indicated in the inset) at three different adsorption sites. The terrace step height of 0.74 Å is indicated. Average values for Δd and Δh are given in

	Lander on terrace	Lander on restructured step	Lander on not-restructured step
Upper Legs height h_{up} (measured with respect to lower terrace)	3.9 ± 0.2	4.6 ± 0.2	4.5 ± 0.3
Lower legs height h_{low} (measured with respect to lower terrace)	3.9 ± 0.2	3.5 ± 0.2	4.0 ± 0.3
Δh (h_{up} - h_{low})	-	1.1 ± 0.3	0.5 ± 0.4
Δd (distance of bumps)	7.1 ± 0.2	7.6 ± 0.5	7.4 ± 0.8

Table 4.1. Averaged bump heights and distances for different molecular adsorption sites. All values in Å. The values of the first two columns are averaged over approx. 50 independent measurements. Adsorption on the terrace is achieved by low temperature deposition (T < 80 K), while adsorption on the restructured step is achieved by high temperature deposition (T > 160 K). For the last column only about 20 measurements with sufficient resolution were available, the corresponding adsorption site on a not-restructured step has to be archived via STM manipulation.

The measured height of the legs on the flat terrace is (3.9 ± 0.2) Å and in both cases of adsorption on steps the upper leg is imaged with this height corresponding to the upper terrace (i.e. 3.9 Å + 0.74 Å = 4.6 Å). In case of the restructured step, the leg to the lower side of the step is significantly lowered, not only with respect to the not-restructured step, but also with respect to the adsorption site on a flat terrace. This is due to the described interface restructuring, since the missing row is located at the adsorption site of the lower leg. The height difference of $\Delta h = (1.1 \pm 0.3)$ Å is in good agreement with the 10° slope of the (311) facet, which would lead to an expected Δh of 1.2 Å.

I have compared the distances of the legs (Δd) in order to observe the expected relaxation in the bonding angle Φ of the legs σ-bonds, which should result in an increased leg to leg distance across the board, as observed for Landers on Cu(110)[93]. (In this case, Δd increases by 1.7 Å on the restructured adsorption site with respect to adsorption on the terrace). The increase in Δd due to the restructuring is less in case of the Cu(211) crystal face, i.e. (0.5 ± 0.6) Å. (The large error is due to the molecular tilt with respect to the surface plane). Correspondingly, the height of the structure supporting the Lander molecule is smaller in the case of Cu(211) compared to Cu(110).

To conclude the comparison of the restructurings found on Cu(211) and Cu(110), it can be stated that the driving force for the restructuring in both cases is similar, i.e. strain relief in the molecular σ-bonds and increased overlap between the π-orbitals of the molecular board with the surface. However, in the case of the restructuring on Cu(211) the energy gain due to adsorption at the restructured site is smaller compared to Cu(110), but also the energy needed to form the restructuring is only about one third in the case of Cu(211) compared to Cu(110).

4.3 Formation of Molecular Chains

It is possible to manipulate Lander molecules along the step edges, both at natural steps and at restructured steps. The manipulations in this case are all performed in constant height mode, resulting in pushing of the molecules. Thus, the tip does not enter the region between the molecules when they are brought close to each other. The manipulation signal in these cases is a regular saw-tooth with the periodicity of the substrate.[122] The manipulation of Lander molecules is described in detail later in this work, exemplarily on the Cu(111) surface in section 5.2.
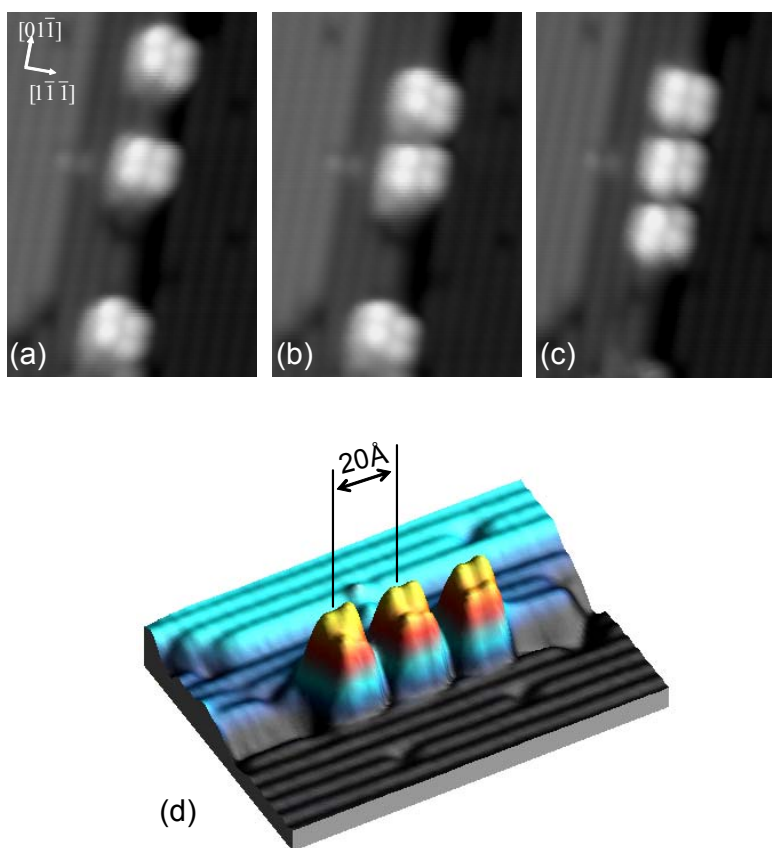

Fig. 4.11. STM measurements of Lander molecules at a restructured step edge (image size: 7 × 11 nm²; U = 0.8 V, I = 0.2 nA). Between (a), (b), and (c) STM lateral manipulation in the constant current mode have been performed to form a chain of molecules. The molecules are always oriented with their boards in $[01\bar{1}]$ direction. (d) Pseudo 3-dimensional representation of (c). 20 Å is the minimal centre to centre distance that could be achieved by STM manipulation for two neighbouring molecules.

In the case of lateral manipulation along the step edges, the molecules always remain in the conformation described above, e.g. with the board at the step edge and oriented parallel to the step. Therefore the step edge acts as a rail on which the Lander molecules are kept oriented and positioned along a straight line. This guidance guarantees atomic precision in orientation and position (perpendicular to the direction of manipulation) during an STM manipulation of a molecule.

In the series of images shown in Fig. 4.11, STM manipulation along a restructured step edge is used to align three Lander molecules. The distance of the molecules in Fig. 4.11(c) is 20 Å (measured from centre to centre), matching the van-der-Waals bonding distance. This is the closest distance that can be achieved by lateral manipulation. If a molecule is tentatively pushed closer to the next, both molecules move simultaneously, keeping a distance of at least 20 Å. Fig. 4.11(d) shows a pseudo 3D representation of an image of the three molecules which are aligned by means of STM induced manipulation.

4.4 Conclusions

The adsorption of Lander molecules, model systems for single molecular wires, on the Cu(211) surface has been investigated in dependence of temperature: For the low temperature range (up to 80 K) the exact adsorption geometry on the defect free Cu(211) surface is determined with very good agreement between experiment and theory employing the MM+ESQC method for different molecular conformations. It shows the possibility of STM to distinguish accurately even between small changes in the orientation and internal conformation of the organic molecules. The good agreement between experimental STM images and calculated ones using MM+ESQC allows to deduce the exact molecular geometries of the different conformations as were found by MM calculations. For this reason the orientation and internal conformation of a single Lander molecule can be unambiguously determined by STM measurements. This is an important result in view of the following chapter, where the exact determination of the molecular orientation will be necessary.

After preparation above 160 K, the Landers adsorb selectively at (311) steps, which are restructured in the presence of the Lander molecules. The reasons for the restructuring have been discussed and compared to the adsorbate induced restructuring that is observed on Cu(110). The reason for the restructuring is found in the strain relief of the molecular σ-bonds and in an increased overlap between the π-orbitals of the molecular board with the surface.

In the case of Lander on the stepped Cu(211) substrate, I have shown that the selectively decorated (311) step edges can be used as atomically precise guidance to form molecular chains, suggesting how selective adsorption and surface restructuring processes can be combined with LT-STM manipulation to form atomically defined nano-structures from large organic molecules. The precise alignment of Lander molecules is an important step towards the STM induced reaction between single molecular wires, in order to form elongated wires or networks. In ongoing research different chemical reactive terminations of molecules are tested for their ability to be connected by STM induced chemical reactions.