Conformations of a molecular wire adsorbed on a metal surface

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The conformation changes of a molecular wire induced upon adsorption on a Cu(001) surface are investigated by low-temperature scanning tunneling microscopy. Measured images are compared with calculations using the elastic-scattering quantum chemistry technique, allowing the extraction of molecular adsorption geometries on terraces and at steps. The molecular bonds prove to be very flexible, resulting in different conformations upon adsorption compared to the molecular gas-phase structure.

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The demand for smaller and smaller devices in microelectronics will ultimately lead to the synthesis of circuits at the molecular scale. One possible approach to implement such circuits is the use of hybrid molecular or monomolecular devices.[1] Using single molecules as functional units (e.g., diodes) connected to metallic contacts in hybrid molecular devices has already been proposed 20 years ago.[2] Since then, molecules have been found useful as wires,[3–5] switches,[6,7] even diodes or transistors.[8–10]

An inherent problem of all devices where a molecule is to be interfaced to a surface is if and how its functionality will be affected by the substrate. Largish molecules can promote local restructuring[11] or extended faceting of the substrate.[12] Even anticipating the structure of an adsorbed molecule from its gas-phase or crystalline conformation is far from trivial, since different substrates may favor different conformations, as demonstrated for CuTBPP (Cu-tetra-3,5 *di-tert-butyl-phenyl porphyrin*).[13] As we will show below, even on the very same substrate the adsorption of a given molecule can lead to a variety of conformations. Attaching molecules to atomic steps, e.g., to establish electronic contact between the molecule and the step, introduces additional degrees of freedom which affect the structure of the molecule.

For our study, we choose a synthetic molecule we call Lander consisting of a polyaromatic board lifted above the surface by four DTP (*di-tert-butyl-phenyl*)-substituents (Fig. 1). The molecule was suggested as a short (1.7 nm long) and efficient wire for tunneling electrons.[3]

Experiments were performed in an ultrahigh vacuum chamber (base pressure in the low 10^{-10} mbar range and below 10^{-11} mbar for the preparation and scanning tunneling microscope (STM) chamber, respectively), equipped with a home-built low-temperature STM.[14] An atomically clean Cu(001) surface was prepared by standard procedures, i.e., repeated cycles of sputter cleaning (1-keV Ne ions) at room temperature followed by subsequent annealing to approximately 700 K for 15 min. The molecules were sublimated from a Knudsen cell at an evaporation rate of less than 0.15 monolayers (ML's)/min, as monitored by a quartz crystal microbalance. The sample was held at room temperature during deposition and was transferred to the STM and cooled down to 4.6 K prior to imaging. Electrochemically etched tungsten tips were prepared *in situ* by electron bombardement and Ne^+ sputtering before insertion in the STM.[15]

For extracting the details of molecular conformations and bonding geometries, measured STM images and cross sections were compared with calculated ones. For the calculations, the elastic-scattering quantum chemistry (ESQC) routines[16] were used along with molecular mechanics optimization of the Lander physisorption on the Cu(001) terraces and step edges. Our ESQC routine is based on the calculation of the full scattering matrix of the tunnel junction of the STM.[17]

Figure 2(a) shows an STM image of Lander molecules adsorbed on Cu(001). The Lander decorates atomic steps and adsorbs on terraces as isolated units and aggregates of a few (typically 2–4) molecules. At low coverages (approximately 0.1 ML) the molecules adsorb exclusively at step edges, indicating sufficiently high diffusion rates on Cu(001) at room temperature to promote migration to step and kink sites. We note that contrary to Ref. 3, no annealing after molecular deposition was used. In earlier experiments with Cu-TBPP equipped with the same DTP substituents as molecular legs, no molecular diffusion on Cu(001) was observed at room temperature.[19] This indicates a lower diffusion barrier for the

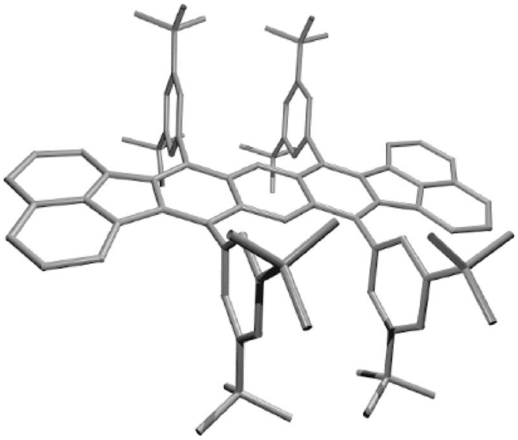

FIG. 1. Three-dimensional model of the lander molecule in its gas phase conformation [cf. also Fig. 2(c)]. The four DTP legs are oriented perpendicularly to the central molecular wire. The hydrogen atoms are not shown for reasons of clarity.

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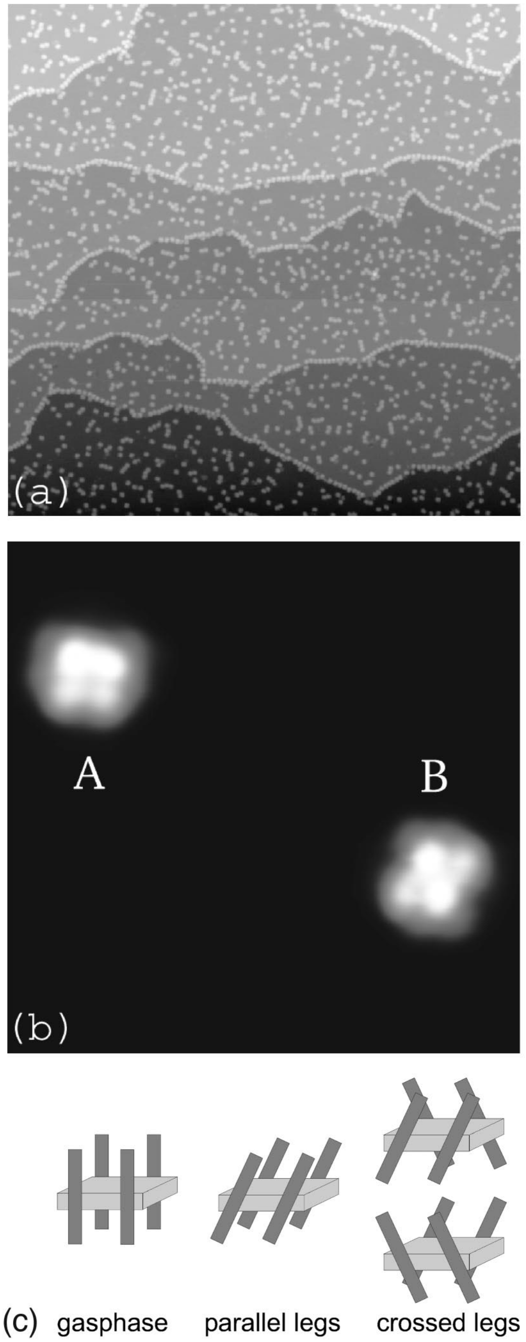

FIG. 2. (a) Lander molecules adsorbed on Cu(001). The steps are completely decorated and excess molecules are adsorbed on the terraces. Image size $(200\ \mathrm{nm})^2$, $I=100$ pA, $U=1010$ mV. (b) Two isolated molecules in different conformations. Image size $(9\ \mathrm{nm})^2$, $I=50$ pA, $U=2000$ mV, $T=4.6$ K. (c) Illustration of the schematic conformations. The molecule is symbolized as a board with four legs (the DTP groups) attached.

Lander molecule on Cu(001) compared to Cu-TBPP on this surface. We attribute this difference to a better adaptability of the Cu-TBPP legs to the surface atomic corrugation. Due to steric hindrance, the Lander legs do not have the possibility of a large rotation around their σ-bond attachment to the board in comparison with Cu-TBPP. At the low temperatures used for imaging (4.6 and 50 K) in our experiments, molecular diffusion is completely suppressed.

The molecules appear as four bright lobes in STM images, as reported previously in Ref. 3 and for Cu-TBPP.[13,19] According to ESQC calculations, the tunneling occurs primarily via the DTP substituents, while the central molecular wire contributes very little to the tunneling current at high junction resistances of typically 10 GΩ in our experiments.

Owing to this intramolecular contrast, three molecular conformations have been identified on flat terraces from high-resolution STM images, two of which are presented in Fig. 2(b). The schematic drawings in Fig. 2(c) illustrate the main differences between the two conformations. Due to the symmetry of the σ bond between the DTP substituents and the central wire, the spacer legs can rotate around the bond axis. In the gas phase, the DTP groups are perpendicular to the central molecular board, as was found also for Cu-TBPP.[13,19] For adsorbed molecules, this minimum-energy conformation is altered by molecule-substrate interactions, forcing the bond rotation angles to change. Due to steric hindrance, the legs positioned on the same side of the central molecular wire always rotate in the same direction, resulting in two qualitatively different conformations: (i) The DTP legs on both sides of the central wire rotate in the same direction. We call this conformation the parallel-legs conformation. It leads to an overall square shape of the molecule in STM images. (ii) the DTP legs on both sides rotate in different directions. This is called the crossed-legs conformation. It leads to rhombic shaped molecules as imaged by STM. The third conformation is a mirror symmetric enantiomer of the latter (we note that the molecule is not chiral in the gas phase, chirality is only induced upon adsorption).

According to molecular mechanics calculations the crossed-legs conformation is lower in energy by 2 kcal/mol (87 meV/molecule) in agreement with the experimentally observed ratio of parallel-legs molecules to the far more abundant crossed-legs molecules at low temperature (ratios of 1:50 and less are typically observed). Reducing the STM junction resistance while scanning over a single Lander can result in a change from the parallel to the crossed-legs conformation and vice versa, confirming that the energy difference between these two conformations is small.

To extract the detailed molecular conformation of the Lander, calculated images of the different conformations are compared with the corresponding experimental images. If only rotation of the DTP groups around the σ bond is allowed in the calculations, only a poor agreement between experimental and calculated images is achieved. By considerable bending of the DTP legs towards the central board, accompanied by a substantial lowering of the board from 0.7 to 0.37 nm above the surface, the agreement with experimental images and cross sections is improved condiderably (Fig. 3).

This deformation of the leg upon adsorption is governed by the van der Waals attraction of the central board towards the surface. This attraction forces the board to approach the surface and constrains the legs to be twisted. There are two major twisting directions per leg: a rotation around the σ bond and a bending of this bond. A full 90° rotation of each

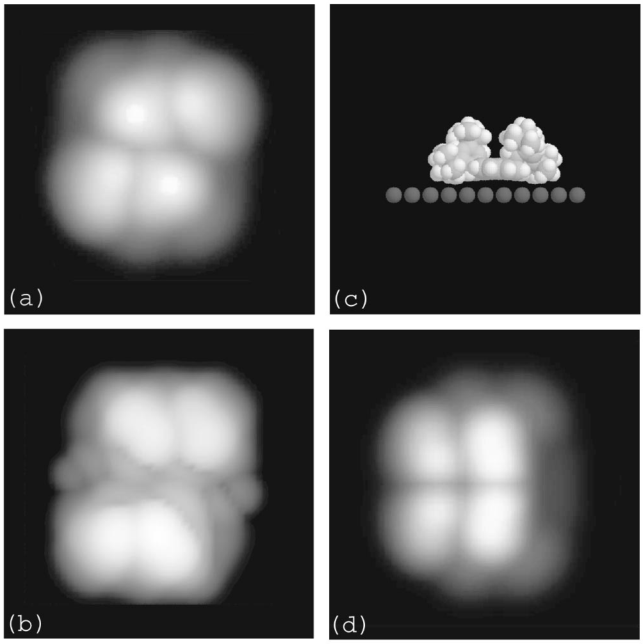

FIG. 3. Simulated STM images for different conformations. The central molecular board is oriented along the image horizontal, size of all images is (3.3 nm)^2. (a) After optimizing the geometry for the crossed-legs conformation [cf. Fig. 2(b), molecule "B," and (c)] taking into account the experimental data. The central molecular wire is lifted 0.37 nm above the surface by the DTP legs. (b) Same conformation before optimizing, height of the central wire is 0.7 nm. (c) Ball model of the optimized conformation in (a). Note the inward bending of the DTP legs towards the molecular board. (d) Image of the parallel legs conformation after optimization [cf. Fig. 2(b), molecule "A," and (c)].

leg is forbidden by the steric hindrance of the two legs on the same side of the board. As a consequence, the constraint is shared between the bending of the σ bond and a rotation around each bond.

The detailed intramolecular contrast also stems from the leg rotations. STM images always reveal one bright and one less bright bump on each side of the molecule, which is explained as follows: Upon rotation, the top CH_3 group of one leg is located above the bottom CH_3 group of the second leg on the same side of the molecular board [cf. schematic drawings in Fig. 2(c)]. Hence, if the tip is positioned above this top CH_3 group, the tunneling path towards the metal encompasses two such groups, which reduces the tunneling resistance and makes the tip retract, i.e., the leg appears higher. For the other leg the tunnel current flows via the molecular orbitals of the top CH_3 groups directly towards the surface, resulting in a high resistance and a shallow appearance of this leg.

The weak elevation surrounding molecules both in experimental and calculated images is in part due to molecular features (imaging of the CH_3 groups at the bottom of the legs), but as well induced by the lateral extension of the tunneling tip. When the atom at the apex has already passed the molecule and the tip starts approaching the surface, the extended facets at the sides of the apex contribute to the tunnel current giving rise to these features. This is not to be confused with a double-tip artifact. In experimental images, the tip-size effects and the molecular fine structure are indistinguishable and cannot be deconvoluted.

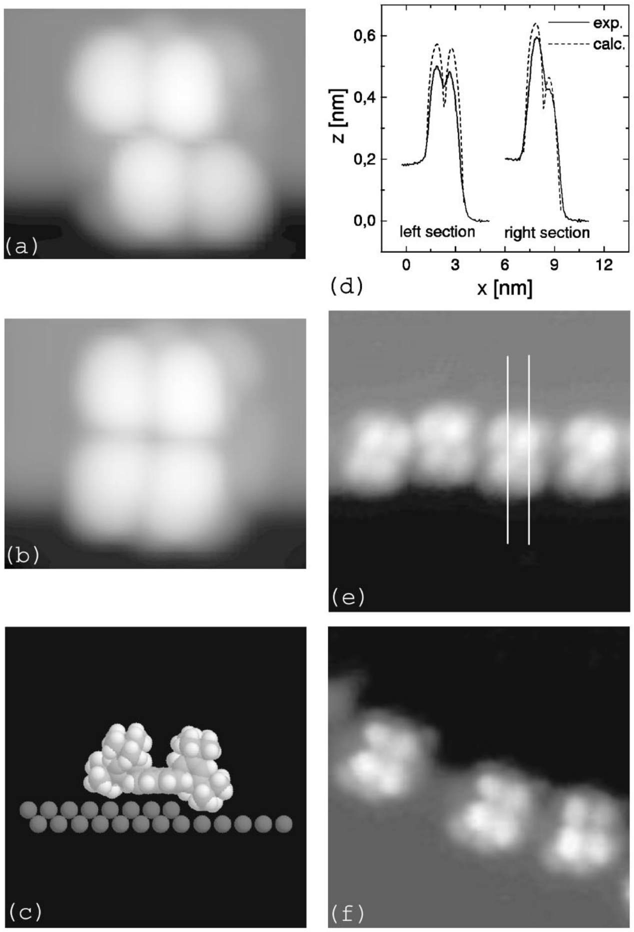

FIG. 4. Molecules adsorbed at monoatomic steps. (a) Calculated image with the molecule in the lowest energy conformation [crossed legs, central molecular board oriented parallel to the step with two DTP substituents resting on the upper terrace, cf. (c)]. (b) Calculated image with the molecule in the parallel-legs conformation. Orientation and leg placement as in (a). (c) Ball-model used for calculating (a). The molecule is viewed from the front with its board parallel to the step. (d) Comparison between experimental and calculated sections across the molecule shown in (a) and (e). Sections on the right are displaced for clarity. (e) Experimental image of a few molecules in the conformation shown in (a). Due to the flexibility of the bonds, the respective bond rotation angles of the molecules may differ sligthly, depending on the exact orientation with respect to the step. The lines indicate the direction of the sections in (d). Image size (8 nm)^2, $I = 100$ pA, $U = 2000$ mV, $T = 4.6$ K. (f) STM image of three molecules in the conformation shown in (b). Image size (6.7 nm)^2, $I = 100$ pA, $U = 1000$ mV, $T = 4.6$ K.

After the extraction of the conformations of the Landers adsorbed on a terrace, it is of special interest to know how the molecule adsorbs at the edge of a step, since it was designed for establishing an electronic contact between the end of the central molecular wire and the edge of a step stabilized at the substrate surface. In contrast to Ref. 3, we focus on single instead of double steps, since the former are the naturally occurring step type on clean Cu(001) surfaces.[20] While for double steps on Cu(001) the molecule was proposed to adsorb on the lower terrace with the central board perpendicular to the step, at single steps on the same surface we find a completely different adsorption geometry. From comparison of ESQC-calculated STM images with experimental data of the Lander adsorbed on step edges, we conclude that the molecule adsorbs with the central board parallel to the step. Two legs remain on the upper terrace and the two other legs adsorb on the lower terrace (Fig. 4).

As judged from a comparision of cross sectional profiles [Fig. 4(d)], the qualitative agreement is good, but small height differences between experimental and simulated scans still remain. This could eventually be further optimized by using a more realistic tip and fine tuning of bond angles. However, since the molecule's flexibility leads to a scatter in the experimental data of approximately ±0.2 Å, indicating a variety of slightly different adsorption geometries, a further refinement does not appear to be useful.

Qualitatively, due to the flexibility of the bonds between the legs and the wire, two conformations can also be distinguished for the adsorption geometry along the step edge, a parallel and a crossed-legs conformation. For the crossed one, molecular mechanics indicates a slightly lower van der Waals total energy of -89.5 kcal/mol (-3.883 eV/molecule) compared to -89.3 kcal/mol (-3.874 eV/molecule) for a parallel-legs conformation. Judging from the small amount of parallel-legs molecules observed experimentally along the step, this small energy difference of only 9 meV per molecule is sufficient at low temperature to trigger an almost exclusive adsorption in the crossed-legs conformation. Other adsorption geometries are not observed, in agreement with their comparatively high total energies. For example, the conformation with the central board perpendicular to the step edge and two legs resting on the upper terrace is next lowest in energy, but already differs by more than 20 kcal/mol from the parallel-board conformations.

In conclusion, we have investigated conformational changes induced upon adsorption of a synthetic molecule on Cu(001). The molecule was designed as a central molecular board lifted above the substrate by four DTP substituents and should act as a molecular wire when contacted to an atomic step. Comparison of experimental and calculated STM images allows the extraction of the detailed conformations for molecules adsorbed on terraces and at single atomic steps. It turns out that the DTP legs are rotated and significantly deformed due to the interaction of the molecule's central molecular wire with the surface. This results in a lowering of the central board to only 0.37 nm above the surface, compared to 0.7 nm for the unperturbed molecule. As a consequence, at monoatomic steps, this molecule is stabilized with the wire parallel to the edge, preventing good electronic contact between the wire's end groups and the step. Implementing more rigid legs could be a way to favor adsorption with the molecule oriented perpendicular to atomic steps.

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[15] During image acquisition, the tips were formed by field emission and controlled tip-sample contacts with the tip positioned over bare terraces to avoid contamination with molecular fragments. Owing to this tip sharpening procedure, we assume that the tip apex is comprised of Cu atoms. This was taken into account in the calculations, cf. Ref. 17.

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[17] The description of this junction encompasses the surface, the adsorbate, the tip apex, and both the bulk material supporting the tip apex and the surface. The tip apex was described by five layers of Cu atoms ordered in a pyramidal shape with (111) facets. The Lander is described taking into account all its valence molecular orbitals. For every tip apex position, 695 molecular orbitals are used to describe the electronic properties of the STM junction containing the Lander. All the electronic interactions inside this junction are calculated using a semiempirical extended Hückel approximation with a double zeta basis set to properly reproduce the tip apex wave function in space away from the outermost tip atom. The molecular mechanics routine used to optimize the Lander geometry in the tunnel junction is a standard MM2 force field (Ref. 18) routine with generalized potential for surface metal atoms.

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