Probing the Different Stages in Contacting a Single Molecular Wire

Francesca Moresco,[1] Leo Gross,[1] Micol Alemani,[1] Karl-Heinz Rieder,[1] Hao Tang,[2]
André Gourdon,[2] and Christian Joachim[2]
[1]*Institut für Experimentalphysik, Freie Universität Berlin, Arnimallee 14, D-14195 Berlin, Germany*
[2]*CEMES-CNRS, 29 rue J. Marvig, P.O. Box 4347, F-31055 Toulouse Cedex, France*
(Received 12 March 2003; published 17 July 2003)

A crucial problem in molecular electronics is the control of the electronic contact between a molecule and its electrodes. As a model system, we investigated the contact between the molecular wire group of a $C_{90}H_{98}$ (Lander) molecule and the edge of a Cu(111) monatomic step. The reproducible contact and decontact of the wire was obtained by manipulating the Lander with a low temperature scanning tunneling microscope. The electronic standing wave patterns on the Cu(111) surface serve to monitor the local electronic perturbation caused by the interaction of the wire end with the step edge, giving information on the quality of the contact.

DOI: 10.1103/PhysRevLett.91.036601 PACS numbers: 72.80.Rj, 68.37.Ef, 68.65.La, 85.65.+h

In a molecular device made of a single molecule connected to metallic electrodes, the electronic contact of the molecule with its electrodes plays a fundamental role [1]. Recent investigations have shown that the contact quality depends on many parameters [2,3], which are often difficult to control, and relies on the precise interaction between the molecule end groups and the surface of each electrode [4,5]. The characteristics of a hybrid electronic contact can be unambiguously understood when the edges of the electrodes are atomically ordered, clean, and when the geometry of the molecular unit at the junction is under control at the atomic scale. In this Letter, we report for the first time a detailed investigation, controlled at the atomic scale, of the contact between a molecular wire and a step edge, taken as a model for a metallic electrode.

As a model system for a molecular wire, we use the central group of a $C_{90}H_{98}$ molecule (known as Lander) [6] (Fig. 1). The molecule consists of a long polyaromatic main board (a molecular wire), maintained parallel above the surface by four TBP (di-ter-butyl-phenyl) spacer groups (legs). The legs are bound at very close positions along the molecular wire. This forbids a full rotation of the legs upon adsorption, guarantees a good separation of the wire from the metal surface, and allows the manipulation of the molecules with the low temperature scanning tunneling microscope (LT-STM). Monatomic steps serve as a well-defined contact site for the molecule. As with every noble metal (111) surface, Cu(111) exhibits Shockley-type surface states [7], which lie in the gap of the bulk metal band structure. Surface state electrons are typically scattered by adsorbates or step edges producing standing wave patterns observable by LT-STM [8]. Here, these standing wave patterns are used to monitor the local electronic perturbation caused by the interaction between the molecular wire end and the monatomic step edge.

The experiments are performed in ultrahigh vacuum at a temperature of 8 K using a homebuilt LT-STM [9] capable of atomic and molecular manipulation [10–12]. The molecules are sublimated at 630 K while keeping the substrate below 70 K to avoid post deposit thermal diffusion. The stable and extremely clean monatomic steps (0.21 nm in height) required for the molecule-step edge contact experiments are created by a controlled crash of the tip into the surface, thus forming several hundred nm long glide-plane dislocations with monatomic height. After the step formation, the tip is moved laterally away from the crashing zone to find an atomically clean surface area with the presence of dislocation steps.

Figure 2(A3) shows a typical STM image of a single isolated Lander on a terrace. Its conformation was identified by combining the elastic scattering quantum

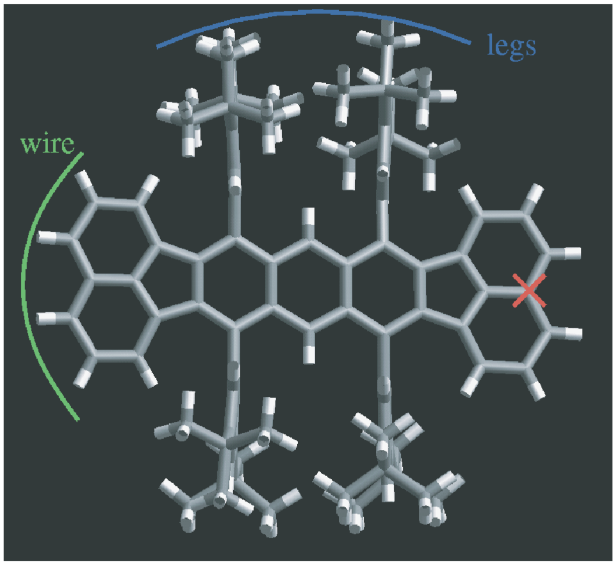

FIG. 1 (color online). Top view of the chemical structure of the manipulated and contacted Lander molecule. The cross indicates the carbon atom selected as a reference for all the z and Δx positions discussed in the text.

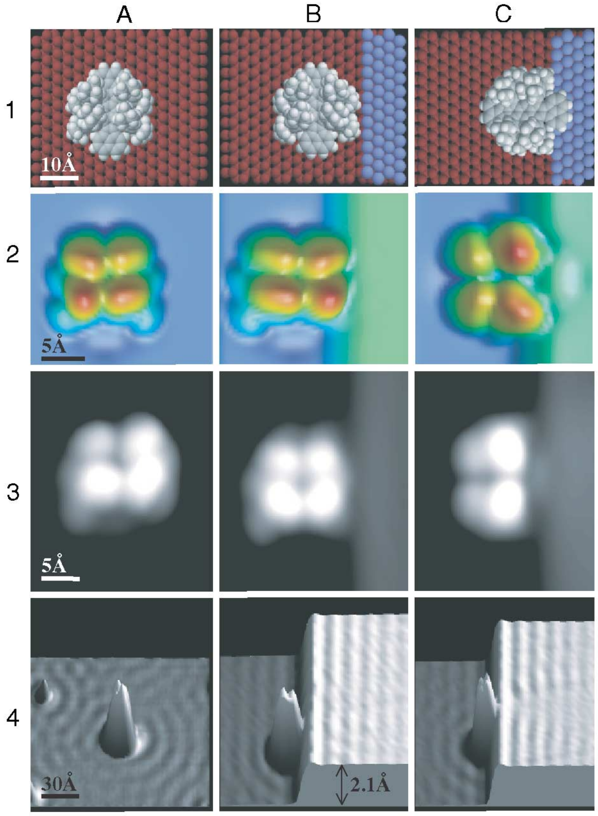

FIG. 2 (color online). Lander molecules on a free Cu(111) surface (column A) and contacted to a (100) step of an edge dislocation. The molecule can be contacted with the molecular board parallel (column B) or orthogonal (column C) to the step. Only in the latter case an influence, due to the molecular board, on the upper terrace becomes visible. In (C2) and (C3), an additional bump corresponding to the contact point of the wire to the step appears and in (C4) a modification of the upper terrace standing wave patterns is visible. Row 1: Sphere models of optimized molecular structures. Row 2: Calculated STM images, corresponding to the models above. Row 3: STM measurements. Black to white distance 3.5 Å, $V = 0.8$ V, $I = 0.2$ nA, $T = 8$ K. Line 4: Pseudo-three-dimensional STM measurements visualizing the standing wave patterns. $V = -0.1$ V, $I = 0.2$ nA, $T = 8$ K.

chemistry (ESQC) image calculation technique with a molecular mechanics optimization of the molecular geometry on the surface, allowing each calculated STM constant current scan to converge towards the experimental one [8]. We find that this molecule is in a parallel-legs conformation [13] [Fig. 2(A1)] and has an average wire height of about 0.36 nm above the surface. We also observe molecules in a cross-legs conformation, similarly as on the Cu(100) [13] and Cu(110) surfaces [14]. A Lander adsorbed on a clean Cu(111) terrace acts as a scattering center for the corresponding 2D electronic states and creates a circular standing wave pattern with a periodicity of about 1.5 nm (measured at a tunneling bias voltage $V_{\mathrm{bias}} = 100$ mV) around each Lander, as presented in Fig. 2(A4).

To bring the molecule in contact with a monatomic step, a chosen Lander that is lying on the lower terrace is laterally manipulated by the STM tip in constant height mode [15]. Knowing the wire orientation relative to the legs, we push the molecule towards the step edge with the central wire either parallel or perpendicular to the step.

When a molecule is pushed to the step with its central wire parallel to it, it reaches the final conformation imaged in Fig. 2(B3). The lower CH_3 groups of the legs close to the step are at a van der Waals distance to the step edge atoms [Fig. 2(B1)] as extracted from the calculated image in Fig. 2(B2). Separated by the legs, the molecular orbitals of the delocalized electrons of the central wire are not interacting with the step edge. After this manipulation, neither the standing wave patterns on the upper terrace [Fig. 2(B4)] nor the effect of the molecule on the standing wave patterns on the lower terrace have changed.

The molecule is now repositioned at the same step with its wire oriented perpendicular to the step edge. A notable modification of the standing wave patterns is observed when the final position of the molecule is reached

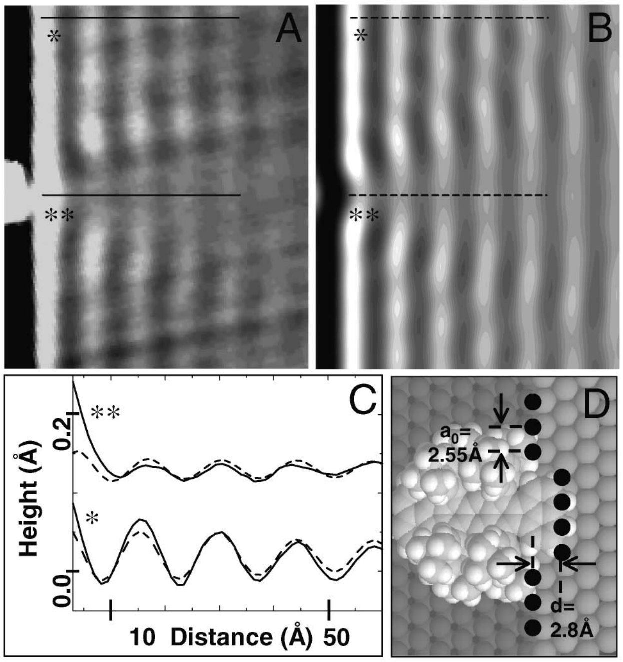

FIG. 3. Electron density patterns in the vicinity of a contacted Lander molecule. (A) Measured image, size (9×11) nm^2. $V = -0.1$ V, $I = 0.2$ nA, $T = 8$ K. (B): Calculated electron density pattern for a scattering geometry as sketched in (D). Image size (9×11) nm^2, height in arbitrary units. (C) Line profiles, taken from the measurement (solid lines) and calculation (dashed lines). The line scans are taken from positions as indicated in (A) and (B). The height scale of the calculation has been adjusted to match the experiment. (D) Model of the geometry of scatterers (black dots) used for the calculation; the model derived by the molecular mechanics calculation is shown faintly as background for comparison.

[Fig. 2(C4)]. The STM-ESQC extraction of the corresponding molecular conformation shows that the terminal naphthalene group of the wire is now on top of the step edge and is electronically coupled with the upper terrace as presented in Fig. 2(C1). As a consequence, this naphthalene end group is now visible in the STM image of the step edge [Fig. 2(C3)]. This new pattern, hereafter called the contact bump, is located just in between the two front legs as confirmed by calculations [Fig. 2(C2)]. At this stage of the contact sequence, the molecule can be decontacted by a reverse manipulation. In this case, the original step edge and molecule STM images are recovered.

Compared to the clean step edge case, the amplitude of the standing wave pattern is reduced at the naphthalene contact location [Fig. 2(C4)]. This effect extends a few 10 nm away from the contact in a characteristic triangular shape. To reproduce the new patterns by calculations, we used the scattering formalism of Heller *et al.* [16]. A simple arrangement of scatterers in the "black dot" limit was used to model the contact: a line of black dots, equally spaced with the nearest neighbor distance of 2.55 Å, representing the step edge and a number of black dots (N), displaced by a distance (d) perpendicular off the line, representing the contact [Fig. 3(D)]. N and d were varied systematically [17] and optimized to obtain best agreement with the experimental data [Fig. 3(A)], leading to $d = 2.8$ Å and $N = 4$. In this case, the calculated pattern [Fig. 3(B)] coincides with the experiment in showing a perturbed region of similar shape descending from the contact point and in this region a decreased wave amplitude and a phase shift [see also line scans in Fig. 3(C)]. In this geometry, size and position of the object formed by the black dots reveal the size and position of the molecular board as in Fig. 2(C1), as determined by molecular mechanics calculations. This indicates that the perturbation of the standing wave patterns on the upper terrace is caused by the naphthalene end group of the molecular wire. Therefore the molecular wire interacts via coupling of the π molecular orbitals of the naphthalene end group with the upper terrace surface states.

The height of the contact bump in the STM images (σ) is related to the electronic interaction between the naphthalene end group and the Cu atoms of the upper terrace, but depends first of all on the geometry of the system. σ varies as a function of both lateral distance Δx between the naphthalene end group and the step edge and vertical distance z between this end and the upper terrace. At the experimental contact position, which corresponds to a distance $\Delta x = +0.48$ nm (see Fig. 4 for the definition of the origin), we deduce by calculations that the legs constrain the naphthalene end to stay $z = 0.35$ nm above the upper terrace. For this geometry, we obtain a calculated value of $\sigma = 13$ pm (in agreement with an experimental value of about 15 pm). This value of σ is very small compared, for example, to the corrugation of 100 pm observed by STM for conjugated molecules chemisorbed on the (111) face of noble metals [18] and is due to the relative large z distance of the naphthalene end group from the upper terrace, imposed by the legs.

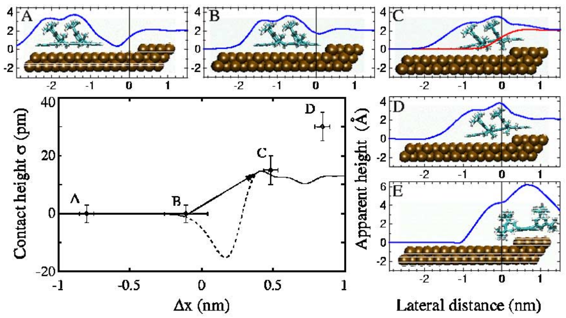

FIG. 4 (color online). Calculated variation of the contact height σ as a function of the lateral position of the molecular wire relative to the step edge for $z = 0.35$ nm relative to the upper terrace. The arrow indicates the experimental jump to contact. The four experimental points are indicated with their error bars. The experimentally identified conformations (A), (B), (C), (D), and (E) are also presented with their corresponding STM experimental scans and the extracted molecular conformations. The origin chosen for the Δx axis is reported. The experimental scan over a free step edge is provided with the conformation (C) for comparison. The top view of the conformation (C) is given in Fig. 2(C2). The large apparent contact bump height in (D) is due to the imaging of the legs CH_3 groups and not to the contact bump itself.

To follow by calculations the different stages of the contact, we have fixed z to the extracted value of 0.35 nm and calculated the variation of σ as a function of Δx in the case of a bare molecular wire, i.e., without considering the legs (Fig. 4, line). We obtain that the most intense contact bump appears at Δx around 0.4 nm, with an average value $\sigma = 13$ pm, in agreement with the results obtained for the complete molecule discussed in the previous paragraph. For larger positive values of Δx, i.e., by moving the molecule towards the step edge, a larger portion of the wire interacts with the upper terrace. On the other hand, when the wire is moved away from the upper terrace, i.e., in the direction of decreasing Δx, a depression in σ appears in the calculated curve around $\Delta x = 0.2$ nm (Fig. 4, dotted line). We attribute this effect to a lowering of the local density of states at the step edge due to the interaction between the naphthalene end group and the step edge. For $\Delta x < -0.2$ nm, the monatomic step edge recovers its original STM shape and the wire is mechanically and electronically decontacted.

To explore the σ curve experimentally, the molecule has to be manipulated step by step toward the step edge. In the conformation A [Fig. 4(A)] the molecule is in a stable position away from the step edge ($\Delta x < -0.2$ nm) with $\sigma = 0$. For $\Delta x > -0.2$ nm, we observe that the molecule is attracted by the step edge towards the mechanical contact conformation B [Fig. 4(B)]. To reach the final electronic contact conformation C [Fig. 4(C)], the molecule is pushed to pass over a small potential barrier for the naphthalene end to reach the upper terrace. The jump to contact occurs for $\Delta x > 0$. As a consequence, the Δx interval of 0.5 nm between B and C is mechanically inaccessible in our case to σ measurements. Occasionally, when pushing again on the molecule, another geometry D [Fig. 4(D)] is observed. Here, the lower CH_3 groups of the front legs are already elevated from the lower terrace. D is a metastable conformation compared to the stable conformation E, where the wire is parallel to the step and located on the upper terrace [Fig. 4(E)]. The conformation E is normally observed when the Lander molecules are evaporated on the substrate maintained at room temperature.

In conclusion, we have shown that the contact between a molecular wire and a step edge (taken as a model for a contact pad edge) can be investigated and controlled at the atomic scale. In the STM image, the quality of this contact is quantitatively determined by measuring the apparent corrugation of the "molecular wire end-edge of the metal" interface. Moreover, the interaction of the terminal part of the wire with the surface states due to the contact notably modifies the electronic standing wave patterns on the upper terrace. The reported characterization of a molecular contact can now to be applied to new molecules, where the molecular wire-pad distance is further reduced, and to atomically ordered metallic contact pads fabricated on the surface of insulators.

The authors gratefully acknowledge partial funding by the European program RTN AMMIST, the IST-FET project BUN, and the Volkswagen foundation project "Single molecule synthesis."

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