Spatially Resolved Tunneling along a Molecular Wire

V. J. Langlais,[1] R. R. Schlittler,[1] H. Tang,[2] A. Gourdon,[2] C. Joachim,[2] and J. K. Gimzewski[1,*]

[1]*IBM Research, Zurich Research Laboratory, 8803 Rüschlikon, Switzerland*
[2]*CEMES–CNRS, 29 rue J. Marvig, B.P. 4347, 31055 Toulouse Cedex, France*

We have spatially resolved the electronic penetration of metallic electronic states through a molecular wire connected to an atomically clean contact. The molecular wire, which is 0.3 nm wide and 1.7 nm long, was electronically connected on one side, and a scanning tunneling microscope tip was used as a second movable electronic counterelectrode. The results reveal a clear exponential decay in the transparency (conductance) of the wire with distance from the contacted end. Analysis of the data shows that electrons are transported along the molecular wire by virtual resonance tunneling with an inverse decay length of 4 nm^{-1}, in excellent agreement with theoretical calculations.

The design and synthesis of identical, structurally perfect molecular conductors for tunneling electrons are very appealing for the development of future integrated nanoelectronic devices. Using scanning tunneling microscopy (STM), vertical tunnel junctions and point contacts, comprising a tip-apex molecule-surface geometry, have been used to study the electronic transport through a single molecule [1] and single/double atom wires [2]. Conductance studies using break junctions of gold electrodes coated with benzene-1,4-dithiol have been performed [3]. Recently, electromechanical deformation, induced on STM point contact, of individual C_{60} molecules was used to fabricate an electromechanical amplifier [4]. Single wall and multiwall carbon nanotubes (SWNT [5], MWNT [6]) as well as doped MWNTs [7] have been studied in two-, three-, and four-probe configurations on planar electrodes, and exhibit a large range of metallic to semiconducting electronic characteristics depending on the tube diameter and their wrapping angle in terms of a rolled-up graphene sheet [8].

To date, no experimental data exist on the length dependence of the conductance of a molecular wire, although theoretical calculations have been reported [9]. Such experiments are crucial for the verification of current theories and the establishing of design rules to enable optimization of novel molecular wires.

In this Letter, we report the quantitative determination of the electron transport mechanism along the length of a molecular wire electrically connected to a metallic step at one end. The electronic conductance of the molecule-metal junction was spatially resolved as a function of distance from the step edge and spectroscopic current-voltage (I-V) and current-distance (I-s) measurements were recorded at different points along the wire. Figure 1 shows a schematic view of the experimental principle. By adsorbing a molecular wire onto a metallic step under ultrahigh-vacuum (UHV) conditions, an atomically clean contact between the molecule and the metal is created. This renders spatially resolved measurements along

the length of the molecule experimentally accessible. The molecular wire itself was maintained above the substrate by four spacer units, designed to exhibit low leakage currents to the substrate, as shown in Fig. 1(c). Analogous to a microwave stub, the STM tip can be used as a second, movable counterelectrode to probe the junction conductance in a noninvasive manner.
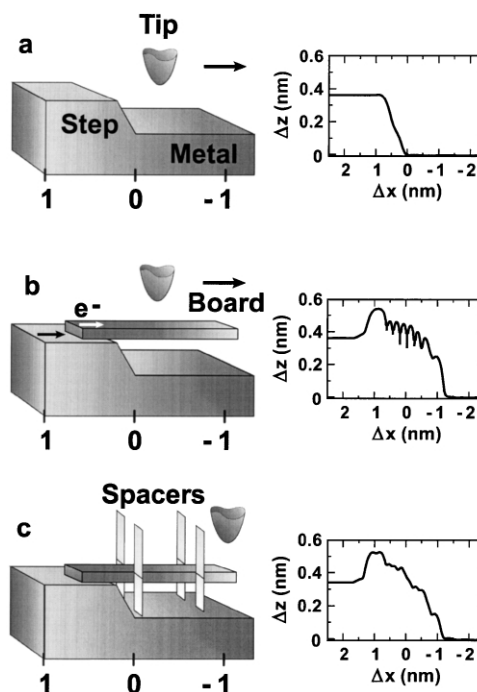

FIG. 1. Schematics of the experimental principle together with theoretically calculated STM profiles. (a) Double atomic steps offer a suitable height to adsorb molecular wires. Calculated STM cross-sectional profile on the double atomic step. (b) Molecular wire electronically coupled to the step. The evanescent wave function from the top terrace leaks into the wire. The profile shows an alternation of nodes and antinodes of the molecular orbitals. (c) The molecular wire is electronically decoupled from the lower terrace by using four spacer units, which modify the fine structure of the profile.

For an applied bias voltage, V_t, within the energy gap defined by the region between the highest-occupied (HOMO) and the lowest-unoccupied molecular orbitals (LUMO), electrons are transported in a virtual resonance tunneling (VRT) regime if the molecule is in intimate contact with the surface. VRT involves nonresonant tunneling through the tails of the HOMO-LUMO manifold close to the Fermi level. The tails result from a broadening of these molecular states owing to electronic coupling with a metallic electrode [1,2,4,9]. The tails of the molecular electronic wave functions at the Fermi level (E_F) exhibit a decay with distance from the metallic contact point. When a molecular wire is not in chemical contact but suspended above the surface by $\approx 0.5-0.7$ nm, the metal-molecule electronic coupling becomes essentially zero, and VRT ceases to be the dominant charge-transfer mechanism. This sensitivity of the coupling with spacing allows individual electronic contact points to be defined by the shape of the molecule. In our experiments, it provides a novel method to obtain quantitative values of the penetration length of the metallic electronic wave function through the molecule from the contact at the step edge [Figs. 1(a) and 1(b)].

The molecular mechanics (MM2, [10]) routine was used to optimize the structural rigidity and conformation. STM elastic scattering quantum chemistry (STM-ESQC, [11]) was used to calculate the STM image and to evaluate the electron transport properties through the wire coupled to the double atomic Cu(100) step acting as an electrical contact. The calculations include electronic coupling with the substrate, as well as the leakage currents through the molecular spacers to the substrate (Fig. 1). A total of 1120 atoms was taken into account in the STM junction: 932 metal atoms (tip apex, surface, and step) plus 188 atoms for the molecule with its spacer legs. The full valence structure of the molecule with 458 molecular orbitals is taken into account in the determination of the tunneling channels [11].

The molecule, synthesized from this computer-optimized design [12], is shown in the inset of Fig. 2. It consists of a central polyaromatic molecular "wire" terminated by a fluoranthene group designed for adsorption on the double atomic copper step. 3,5-di-*tert*-butylphenyl substituents (Tbp) were used as spacers. The experiments were performed under UHV conditions (base pressure $\approx 10^{-11}$ mbar) on atomically clean Cu(100) crystals prepared by sputter-anneal cycles. By using a specific annealing procedure, a high density of multiple steps was engineered [Fig. 2(b)]. Electrochemically etched tungsten tips were heated *in situ* to 1300 K using electron bombardment of the shank, and sputter cleaned using Ne ions before they were used for imaging. Further details of the STM system are described elsewhere [13]. The molecules were deposited by sublimation from a Knudsen cell at a rate of ≈ 0.1 monolayer/min, previously calibrated using an *in situ* quartz crystal microbalance. The
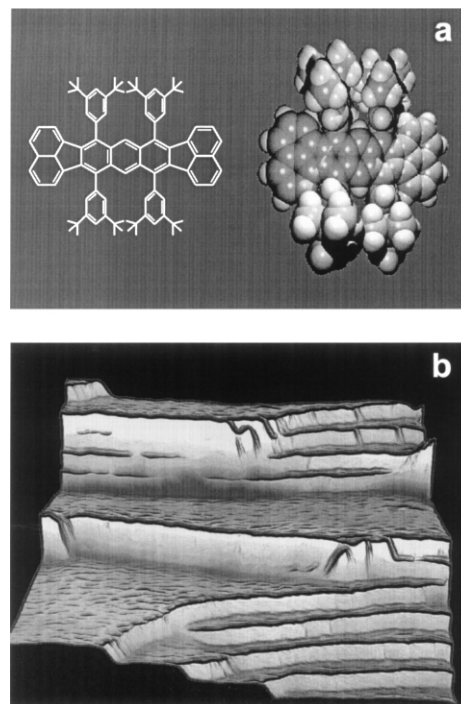

FIG. 2. (a) Space-filling model of the molecular wire used in the experiment. The molecule is 1.7 nm long and 1.4 nm wide with a polyaromatic central wire of 0.3 nm in width. 3,5-di-*tert*-butylphenyl substituents are used as spacers and elevate the molecular wire 0.7 nm above the substrate. (b) 3D pseudoilluminated STM image of single and double atomic steps coexisting on clean Cu(100) ($V_t = 400$ mV, $I_t = 60$ pA).

sample was subsequently annealed at ≈ 500 K to thermally activate molecular diffusion, promoting selective adsorption at atomic steps.

Figure 3(a) shows an STM image obtained at a monolayer coverage on Cu(100). On flat terraces, each molecule displays four lobes corresponding to the four Tbp spacers [14–16]. The spacers, which also elevate the wire above the surface, adapt the orientation of their phenyl rings through steric crowding [14] and simultaneously isolate the molecular wires from each other. At low coverage, the molecules preferentially adsorb onto single and double atomic Cu steps. On monoatomic steps (height ≈ 0.18 nm), the four lobes of the molecular image agree with STM image calculations which show that the main tunneling channels occur through the spacers. Here the molecular axis of the wire also adopts a variety of orientations with respect to the monoatomic step edge.

In contrast, molecular wires adsorbed onto double atomic steps were observed to orient with their long axis preferentially in a close-to-perpendicular direction. Here, the double atomic step height of 0.36 nm ideally matches the height of the molecular wire. The orientation is assigned to an electronic coupling with the molecular wire and a minimization of the free energy through a weak chemisorption with the Cu double step. Figure 3(b)
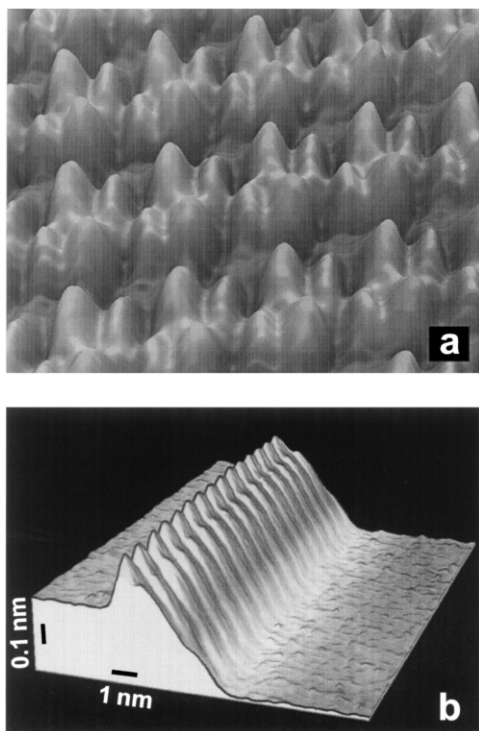
FIG. 3. STM images of (a) a monolayer coverage. Image area: 10 nm $\times$ 10 nm, recorded at a bias voltage $V_t = 370$ mV and tunnel current $I_t = 70$ pA. (b) An array of 15 molecules adsorbed perpendicularly on a double atomic step of Cu(100). The separation between molecules along the step edge is ≈ 2 nm, which results in an insulating lateral distance of ≈ 1.5 nm between the molecular wires.

shows a typical array of molecular wires oriented perpendicularly on a double atomic step. Contrary to our observations of four-lobed structures on single steps or terrace sites, the molecules now appear as a distinctly asymmetric structure with a maximum apparent internal corrugation of 0.6 nm on the molecular wire itself. All of the molecules adsorbed at the double step are also highly similar in form. This change in shape agrees with our theoretical calculations, and the height of the molecular wire at the step edge is a clear signature of electronic coupling between the end of the wire and the step. In this geometry, tunneling from the tip apex occurs through the polyaromatic wire connected to the step edge, which dominates over the weaker tunneling processes through the spacers. Cross sections of the apparent molecular height as a function of the distance from the step taken perpendicular to the double step along the molecular wire axis [Fig. 4(a)] also confirm that adsorption occurs at a double atomic step (height ≈ 0.36 nm). A detailed analysis of these cross sections yields a linear slope of ≈ 0.2 along the molecular wire. The key observation from these profiles is that the apparent height decays approximately linearly as a function of distance from the step. Weaker modulations along the profile are assigned to a combination of a small leakage current flowing through the Tbp substituents and oscilla-

tions along the wire arising from molecular orbital nodes in agreement with the calculated profiles in Fig. 1. The shape of the tip apex used in the calculations was determined from experimental cross sections of clean double atomic steps recorded during the experiment. This profile, similar to Fig. 1(a), assures us that the linear decay observed in the central region of the profile is not influenced by the tip shape, whereas the profiles at the ends of the molecular wire do contain an accountable contribution from the tip shape.

The electrical conductance G_m of a metal-single molecule-metal junction can be defined by three parameters: a contact conductance G_0, an inverse decay length γ,
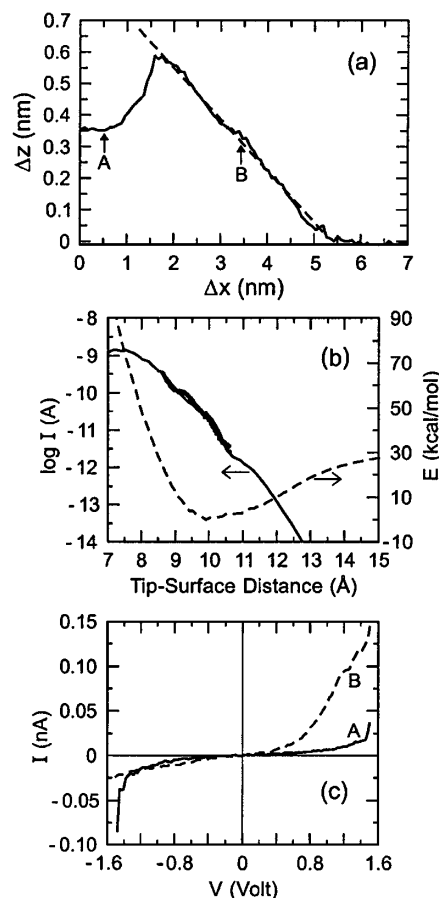

FIG. 4. (a) Cross-sectional profile extracted from Fig. 3(b) along a single molecule. The apparent linear slope was used to extract an experimental inverse decay length $\gamma = 4$ nm^{-1} and a tunneling barrier height $\phi_{mol} = 164$ meV. Cross-sectional profiles taken along other molecular wires exhibit the same values for γ and ϕ_{mol} within an error bar of 5%. ESQC calculations yield a theoretical decay length of 4.3 nm^{-1} and an intramolecular tunneling barrier height of 184 meV [Fig. 1(c)]. (b) Solid line: comparison between experimental and calculated current-distance (I-s) characteristics recorded at point B (a) on the end of the molecular wire (thicker region: experimental data). Dashed line: calculated potential energy of the molecule under compression. Electrical resistance ≈ 80 GΩ. (c) I-V characteristics recorded at points A and B (tunneling conditions: $I = 70$ pA and $V = 0.8$ V).

and the molecular length L [17]. In a VRT regime ($eV_t < E_g$, with E_g the HOMO-LUMO gap of the molecule), the molecular conductance at E_F can be expressed [9] as

$$G_m(E_F) = G_0(E_F)e^{-\gamma L}. \tag{1}$$

This gives an effective horizontal tunnelbarrier $\phi_{mol} = \gamma^2$ from the tip apex to the metallic step edge. To estimate γ from the apparent molecular height profile, we note that the measured tunnel current j as a function of the tip position x is given by

$$j = G_m(x)\exp(-\sqrt{\phi_v}\, z), \tag{2}$$

where x varies between $0 < x < L$, and ϕ_v is the apparent height of the vertical tunnel barrier when the molecule is not compressed by the tip apex [1]. From Eq. (1), $G_m(x) \simeq G_0 \exp(-\gamma x)$, and consequently at constant current $\gamma = (\Delta z/\Delta x)\sqrt{\phi_v}$. From separate I-s measurements on bare regions of the substrate, $\phi_v = 4.1$ eV $\pm 3\%$ was determined. Combined with the experimental value of $\Delta z/\Delta x$ [Fig. 4(a)], $\phi_{mol} = 160$ meV is obtained for tunneling along the molecular wire, in excellent agreement with the theoretical value $\phi_{mol} = 184$ meV.

To confirm the electron transport mechanism through the molecular wire further, the absolute tip apex to surface distance (s) was evaluated by comparing the experimental I-s and the calculated I-s curves on the Cu(100) terrace [point A in Fig. 4(a)]. At point B, tip-molecule contact was determined using the calculated variation of the potential energy under compression in a manner similar to that to determine electrical contact of an STM tip with C_{60} [1] [Fig. 4(b)]. We deduce a contact height of $s = 10.0 \pm 0.2$ Å, which corresponds to a step edge-molecule-tip apex junction with a resistance of ≈ 80 GΩ at 0.8 V applied bias voltage. This value is 4 orders of magnitude lower than the resistance of a lateral step edge-vacuum-tip apex junction [Fig. 1(a)], and clearly shows that, compared to vacuum, the conjugated wire efficiently guides the electronic wave function from the step edge.

Furthermore, at the tunneling conditions of $I = 70$ pA, $V = 0.8$ V (almost the contact height at the end of the molecular wire), the I-V characteristics at points A and B were also measured [Fig. 4(c)] to confirm that the molecular images were recorded in the VRT mode. The spectra show the onset of a molecular state of the wire at $V_t > +0.4$ V from the linear I-V regime at lower voltage, which characterizes the VRT process [9].

The novel design and synthesis of molecular wires adsorbed at double atomic steps enable the use of the STM tip as a type of tunneling potentiometer. We have been able to realize this unique geometry and thereby conduct the first spatially resolved study of the tunnel-transport regime through a single molecule using ultraclean contacts. From cross-sectional profiles of the apparent height of the molecular wire along its length, a quantitative value of the intramolecular tunnel barrier was determined that is in excellent agreement with theory. The similar form of the arrays of molecular wires in STM

also indicates that the self-assembly process at the double atomic steps is highly reproducible. In conjunction with STM experiments, the ability to finely tune molecular structures opens the way to fabricate new forms of molecular wires optimized for electron tunnel transport. In terms of design rules, molecular systems that possess a large G_0 and a small inverse intramolecular decay length γ are good candidates for use as molecular electron waveguides for future molecular electronic devices.

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*To whom correspondence should be addressed.
Email address: gim@zurich.ibm.com

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