

## Low-temperature conductance measurements on single molecules

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An experimental protocol which allows to perform conductance spectroscopy on organic molecules at low temperatures ( $T \approx 30$  K) has been developed. This extends the method of mechanically controlled break junctions which has recently demonstrated to be suitable to contact single molecules at room temperature. The conductance data obtained at low  $T$  with a conjugated sample molecule show a highly improved data quality with a higher stability, narrower linewidth, and substantially reduced noise. Thus, the comparability of experimental data with other measurements as well as with theoretical simulations is considerably improved. © 2003 American Institute of Physics. [DOI: 10.1063/1.1574844]

Molecular electronics employing single molecules as active functional units is a promising technological concept of fast-growing interest. With molecule-based systems it may, for example, be possible to achieve higher storage densities in conjunction with a simplified production technology.<sup>1</sup> Our research is dedicated to understand the fundamental processes of electron conduction through individual molecules. This is a crucial requirement for the purposeful design of molecules for electronic functionalities. Here we present a method to perform low-temperature conductance measurements ( $T \approx 30$  K) of single-molecule contacts with the mechanically controlled break-junction (MCB) technique. While only few such measurements exist at RT,<sup>2-5</sup> low- $T$  measurements are desirable for several reasons: First, the physics is then considerably simpler (e.g., no vibrations). Further, at low  $T$  it should be possible to reduce atomic-scale rearrangements on the electrode surface which strongly affect the measurements at RT.<sup>6</sup> Another complementary method has also been used for single-molecule contacts at low  $T$ .<sup>7</sup> In contrast to the MCB technique discussed here, this electromigration method allows for a field-effect transistor setup, but does not provide well-controlled distance control between the contacts.

Earlier experiments have demonstrated that the conductance of single-molecule junctions can be determined at RT by means of MCBs,<sup>4</sup> which provide a tunable-distance electrode pair. It consists of a metallic wire structured on a flexible substrate with a narrow bridge-like constriction,<sup>8,9</sup> serving as a predetermined fracture point. If the substrate is bent, the bridge on top stretches, until it finally tears apart, yielding a nanoscopic pair of electrodes facing each other. Due to the ultralow transmission ratio between the inflection of the substrate and the expansion at the surface the electrode distance is controllable with subangstrom resolution and possesses a high mechanical stability. However, cooling down a given contact is barely possible because of the different ther-

mal expansion coefficients of the materials used which result in a badly controlled drift of the electrode spacing ( $\approx 1$  nm in our experiments upon cooling from RT to 30 K). An electronic adjustment (feedback control) of the electrode gap during cooling would require the knowledge of the absolute distance during this process which is not easily accessible experimentally. The molecules investigated in this experiment are rigid rod-like organic molecules with a length of approximately 2 nm (Fig. 1). The molecules possess a  $\pi$ -electron system between the acetyl-protected sulfur functional groups at their ends, which are designed to split off when the molecules bind covalently to the gold electrode surface. This procedure, however, is expected to work only at RT, because at low  $T$  there is not enough energy available for the deprotection reaction. Hence, we have to find an experimental protocol which yields low- $T$  contacts, but avoids temperature sweeps of a given junction as well as surface reactions at low  $T$ .

This protocol starts with the procedure for RT measurements.<sup>4</sup> When applying a solution of acetate-protected thiol-functionalized molecules (Fig. 1) on a freshly opened pair of electrodes, a molecular layer on the gold surface is formed. The molecules split off their acetate protection group upon contact and bind covalently with one end to the gold surface.<sup>10,11</sup> At this point, the other side of the molecule remains protected. Due to the short application times ( $\approx 60$  s) we do not expect a cohesive monolayer in our experiments.<sup>10</sup> The high surface mobility of the polarizable molecules allows to draw them into the contact region be-

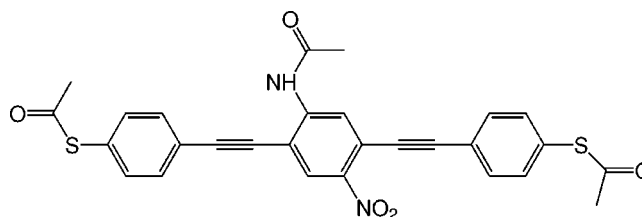


FIG. 1. 2,5-di[2'-(para-acetylmercaptophenyl)ethynyl]-4-nitro-acetylaniline, with acetyl-protected terminal thiol groups for immobilization on the gold surfaces of the MCB.

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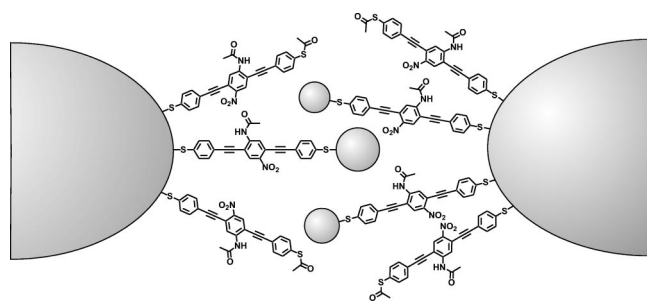


FIG. 2. Scenario between the MCB after closing and reopening at RT. Upon contact with the opposite electrode, the protection groups of the formerly bridging molecules have partly been replaced by clusters of a few Au atoms.

tween the electrodes by means of a dc electric field which is provided by a finite bias voltage. Hence, we decrease the electrode distance while  $U=1-1.5$  V is applied and we monitor the current until the first molecule touches the opposite electrode, splits off its protection group and binds covalently to the counter electrode. At this moment a sharp increase in current is recorded. Often, a molecular junction is now established which allows to record stable current-voltage characteristics ( $IV$ s) in a voltage window of  $(-1.2, 1.2$  V) for the given molecules. More details about the RT measurements can be found in Ref. 4. It is expected that all bonds in the molecule are more stable than a Au-Au bond, an assumption which has been confirmed by molecular dynamics simulations.<sup>12</sup> There, it has been shown that when a thiol-ended molecule is pulled off the gold surface, the molecule rather picks one or more Au atoms out of the surface than breaking the Au-S bond. Consequently, the protocol is based on the idea of terminating the molecules in the junction with a Au atom (or possibly a few Au atoms) by closing and reopening the junction (see Fig. 2). Then, the junction can be cooled down while it is open and reestablished at low  $T$  without involving any further organic chemical reactions (the formation of a Au-Au bond is considered to have a negligible activation barrier).

The experiment was made in an UHV-compatible chamber. The break-junction setup was mounted on a continuous-gas-flow cryostat inset which allows to cool down the sample to  $\approx 30$  K  $\pm$  10 K (The large error bar is due to insufficient thermal equilibrium in our setup where rather quick measurements are required. We did not perform *in situ* thermometry on the chip, the difference between the sample's temperature and that of the thermometer was determined in a separate calibration experiment.). After applying the molecules from solution the junction was established in vacuum at RT until a resistance of the order of 10 k $\Omega$  was observed. This corresponds to numerous molecules which close the gap. Then the usual procedure was pursued until a single-molecule signature was found. After that the junction was reopened and then cooled down to 30 K within  $\approx 15$  min. It is crucial to pump the chamber thoroughly to the best available base pressure (in our case  $3 \times 10^{-8}$  mbar) prior to cooling down. Otherwise, adsorbates will condense on the electrode surface and will prevent the reestablishment of a molecular junction at low  $T$ . In addition to turbomolecular pumps and ion getter pumps, we further used a cup-like shield at cryogenic temperatures to provide a cold trap close to the electrode pair. At  $T \approx 30$  K, the junction was re-

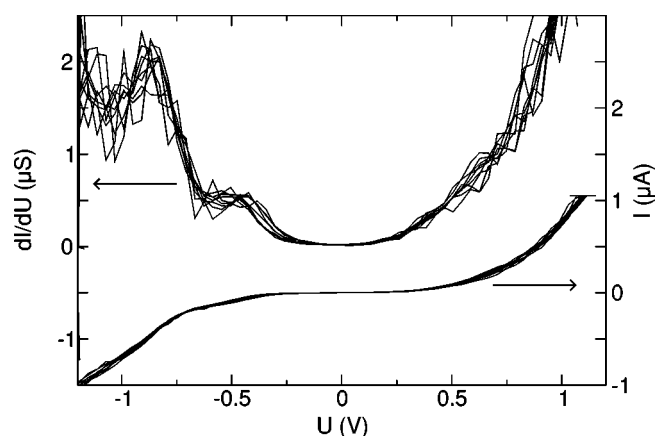


FIG. 3. Current-voltage raw data of a molecular junction at room temperature. When the junction is closed, a sudden transition to a stable state is observed. Then the voltage was ramped several times up and down and the current (lower lines) was measured. The upper lines represent the numerically differentiated data  $dI/dU$  (after Ref. 4).

proached. Similarly to RT, first a tunnel current and then a sudden increase of the current was observed. At this stage, stable  $IV$ s could be recorded which will be discussed later. For comparison, we first show previously published data from RT measurements: Figure 3 shows nine  $IV$ s as well as the differential conductance  $dI/dV$  of the molecule in a stable configuration. Rounded step-like features are visible in the  $IV$  (red lines) which appear as broadened peaks in  $dI/dV$  (blue lines). The peak structure can qualitatively be explained within a coherent transport scenario.<sup>6,13</sup> As soon as a molecular orbital gets in resonance with the Fermi level of one of the electrodes, transport through this molecular orbital may be enabled resulting in a step-like increase of the current. After observing a stable spectrum for several minutes as shown in Fig. 3, the  $IV$  often spontaneously changes into characteristics which may be also reproducible for several minutes. This jump-like switching is attributed to microscopic atomic or molecular rearrangements in the junction which are typical for a single-molecule junction. Note also the considerable noise in the data which is not created by the measurement electronics but by the molecular junction itself, as verified in control experiments.

Low- $T$  data taken at  $T=30$  K are shown in Fig. 4(a). The low-bias region displays a strongly suppressed conductance ( $\leq 1$  nS). The linewidth of the peaks in  $dI/dV$  is much smaller compared to RT measurements [of the order of 250 meV (full width at half maximum) at RT, 30 meV at 30 K] and the overall data quality has substantially improved (less noise). Due to the narrower linewidth smaller peaks which cannot be seen at RT appear. For example, the peak at  $U = -0.53$  V has a substantially reduced counterpart at opposite bias ( $U=0.38$  V), which is not visible in the RT data.

The data observed for this spatially asymmetric molecule are always asymmetric with respect to voltage inversion, as discussed in detail in Ref. 4. This indicates that only very few molecules (most likely a single one) contribute to the conductance, because a large number of molecules, randomly oriented, would result in symmetric  $IV$ s. The conductance pattern at Fig. 4(b) was obtained only minutes after the pattern in Fig. 4(a), after opening and closing the junction. The two spectra appear roughly as mirror images of each other.

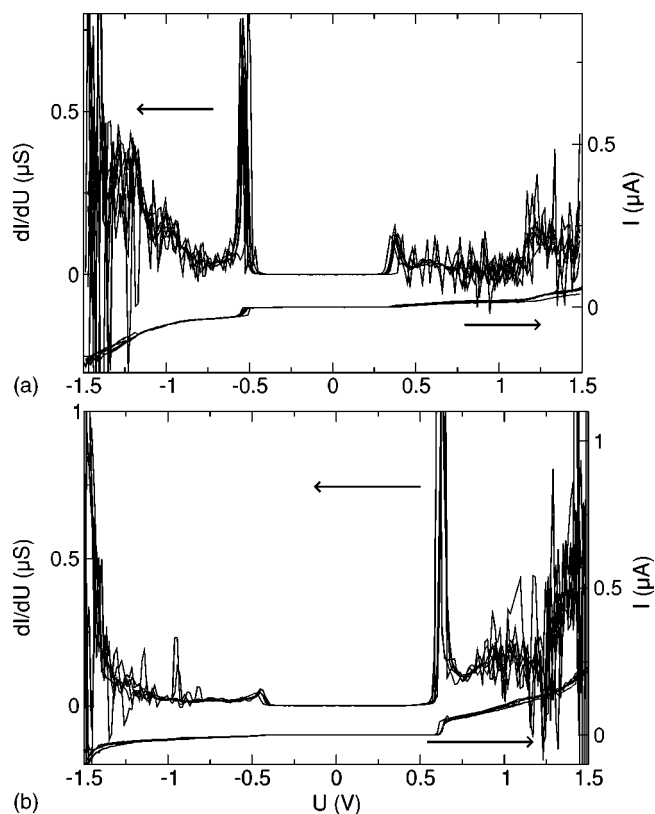


FIG. 4. (a), (b) Current–voltage raw data (lower lines) and the differential conductance  $dU/dI$  (upper lines) as a function of the applied bias voltage  $U$  at 30 K for several subsequent sweeps. First (a) was recorded. Then the junction was opened and closed again, resulting in the different configuration (b).

other with respect to voltage inversion. Apparently, another oppositely oriented molecule has replaced the one shown in Fig. 4(a). While the absolute value of the current, taken at  $U = 1$  V, varies for different junctions from 0.1 to 1  $\mu\text{A}$  at RT, the current in the present junction is  $I \approx 60$ –100 nA for the two junctions shown here. Whether this reduction stems from different microscopic arrangements, from reduced molecular motion or from suppressed thermal activation cannot be deduced from the data. We do not see signs that adsorbates influence the measurements (e.g., Ohmic behavior at low voltages) as was observed in previous experiments with insufficient vacuum. Another improvement of the low- $T$

measurements is the smaller range of different  $IV$ s. For the RT measurements a rather broad range of sample-to-sample fluctuations was attributed to different microscopic realizations.<sup>4,14</sup> In particular microscopically different thiol-gold junctions were found to strongly affect the energetic level as well as the charge distribution of the highest occupied molecular orbital. The difference of the bonding energies of these different realizations are, however, only small<sup>6</sup> and thus no configuration is clearly statistically preferred. The smaller number of variations in the recorded low- $T$  spectra might indicate that here energetically favorable configurations occur more frequently. The presented method improves the investigation of single-molecule junctions, contributing to both, the comparability with theory as well as with other experiments. Finally, genuine low- $T$  experiments, for example with superconducting electrodes are now possible.

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