

Statistical Approach to Investigating Transport through Single Molecules

Emanuel Lörtscher,¹ Heiko B. Weber,² and Heike Riel¹

¹IBM Research GmbH, 8803 Rüschlikon, Switzerland

²University of Erlangen, 91058 Erlangen, Germany

(Received 24 May 2006; published 27 April 2007)

We present a statistical approach that combines comprehensive current-voltage data acquisition during the controlled manipulation of a molecular junction with subsequent statistical analysis. Thereby the most probable transport characteristics can be determined. The excellent sensitivity of this impartial approach to even subnanometer-long molecules is illustrated by benzene-1,4-dithiol and 4,4''-bis(acetylthiol)-2,2',5',2''-tetramethyl-[1,1';4',1''] terphenyl results.

DOI: 10.1103/PhysRevLett.98.176807

PACS numbers: 73.23.-b, 73.63.Rt, 81.07.Nb, 85.65.+h

The fundamental understanding of charge transport through single molecules is a key issue in molecular electronics [1–3]. A number of techniques to contact small ensembles of molecules have been developed [4–8]. In all measurements, contact effects have to be considered as electronic processes are influenced by the microscopic details of the molecule-metal contacts. It is therefore important to investigate transport properties of a molecular junction during formation and breaking. Here, we present a statistical approach using the mechanically controllable break-junction (MCBJ) method [9,10] to monitor transport properties during repeated formation and breaking of a single-molecule junction.

Our MCBJ system is mounted on a cryostat and operated under ultrahigh-vacuum conditions. A gold bridge of length s on a flexible substrate of thickness t (see [11] for details) is mounted in a bending mechanism (distance between the supports: L). A force applied on the back side of the substrate introduces extension which stretches and finally breaks the constriction, creating two separated electrodes. The ratio r between pushing rod translation Δh and electrode separation Δd is $r = \Delta d/\Delta h = (6ts)/L^2$, in our geometry $\approx 2 \times 10^{-5}$. Backbending of the substrate allows the electrodes to be approached with subatomic resolution. Microscopic changes of the tips during breaking prevent an absolute distance calibration. Instead, a relative distance calibration can be performed by analyzing the dependence of the tunneling current I on d : $I(d) \propto \exp(-\sqrt{8m_e\Phi_{\text{Au}}}d/\hbar)$, with m_e the electron mass, and Φ_{Au} the work function of gold. Breaking creates two atomically sharp electrode tips indicated by the observation of conductance quantization. The molecules possess two thiol linkers in order to become immobilized on the metal surface by establishing a covalent S-Au bond. A droplet of solution is deposited onto the chip and the solvent immediately evaporates [11]. To prevent clustering, the concentration is very low ($\approx 10^{-4}$ mol l⁻¹) and the linker groups are protected by acetyl groups which are released *in situ* when establishing contact to the gold surface. Since the gap distance is set to be larger than the

length of the molecules, they can bond to one electrode only. During closing of the junction molecules can bridge the gap between the electrodes by establishing the second chemical bond to the counterelectrode, thus forming a molecular junction.

Figure 1 shows the resistance R of a molecular junction when approaching the electrodes stepwise under a constant bias. Initially, the junction is open and molecules are attached to only one electrode without bridging the gap, indicated by Teraohm ($\text{T}\Omega$) resistance [Fig. 1(a)]. When decreasing the electrode distance, a sudden drop in R of at least 3 orders of magnitude is observed. During further closing, R is almost constant over a wide range [Fig. 1(b)]. In this intermediate regime, R is about 1 M Ω –100 M Ω . If the junction is closed further, R drops again over 2 orders of magnitude and a value of the inverse of the conductance quantum $R_0 = 1/G_0 = \hbar/4\pi e^2 = 12.9$ k Ω is measured [Fig. 1(c)], indicating a closed metal-metal point contact.

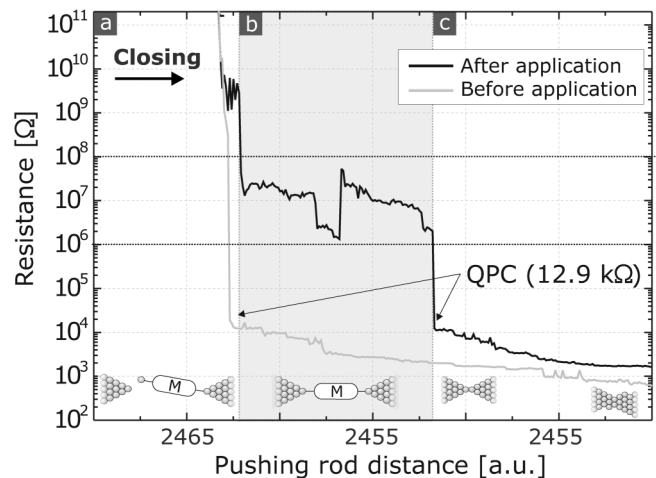


FIG. 1. Closing of a molecular junction (2 mV applied): (a) Open junction with $R > 1 \text{ T}\Omega$, (b) formation of metal-molecule-metal junction, and (c) closed metal-metal point contact (QPC) with $R < 12.9 \text{ k}\Omega$. The gray curve shows the closing behavior without molecules.

A subsequent opening cycle exhibits a similar behavior, again with the appearance of an intermediate regime between the fully open ($R > 1 \text{ T}\Omega$) and the fully closed junction ($R \leq R_0$). The appearance of such an intermediate regime in the closing and the opening direction strongly differs from the tunneling characteristic between the electrodes in absence of molecules (dashed line in Fig. 1, recorded prior to the application of molecules). Therefore, we attribute this regime to the formation of a molecular junction in which at least one molecule bridges the gap between the electrodes. The comparison of similar molecules indicated that very few, ideally individual, molecules are contacted [7].

Instead of applying constant voltage to determine the conductance of a molecule [5,8], we are interested in studying the transport properties over a voltage range in which we can probe the first molecular orbitals (typically 0.5–3.0 V). Therefore, we continuously acquire current-voltage curves (I - V) during stepwise closing and opening, corresponding to different microscopic configurations of the molecular junction. Starting from an open junction with molecules attached to only one electrode [Fig. 2(a)], a current in the sub-picoampere (pA) range is measured. When decreasing the distance between the electrodes, an abrupt jump to stable and reproducible I - V curves is observed. Now, the current flow is in the nanoampere (nA) range and the I - V curves exhibit a nonlinear behavior [Fig. 2(b)], which shows the characteristic signature of the particular metal-molecule-metal system under investigation. During further closing, the I - V characteristics are maintained over a range that is in good agreement with the length of the intermediate regime observed during closing or opening under a constant bias [Fig. 1(b)]. Beyond this region, a sudden jump to much higher currents in the microampere (μA) range occurs where the I - V characteristics are linear, indicating a closed metal-metal junction [Fig. 2(c)]. At this stage, the direction of electrode motion is reversed and a subsequent opening cycle is performed accordingly. This closing-opening procedure is repeated

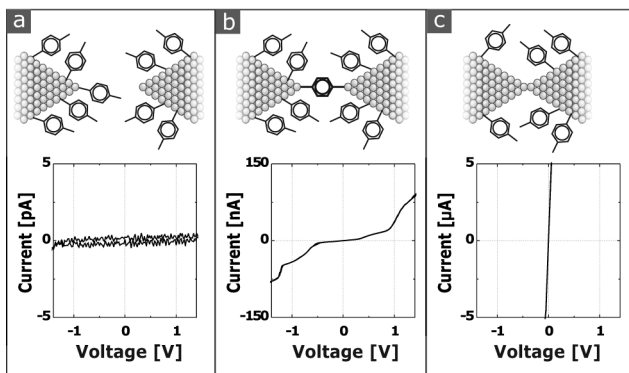


FIG. 2. Schematics of the junction with corresponding I - V curves (experimental data): (a) Open junction with molecules attached so far to one electrode only, (b) metal-molecule-metal junction, and (c) a closed metal-metal contact.

several dozen times. Owing to the above-mentioned ductility induced drifts in the electrodes, we control the junction via the resistance measured rather than via Δh . This automated measurement procedure provides objectivity to the investigations, and the entirety of all data represents a reliable basis for statistical analysis. To determine, for example, the number of molecules captured in the junction, conductance histograms at any arbitrary voltage can be extracted from huge data sets. Thereby, the most probable I - V characteristics in the ensemble of all measured curves can be identified.

As an illustrative example for our approach, Fig. 3(a) shows an extensive data set of 1500 I - V curves acquired at 300 K using 4,4''-bis(acetylthiol)-2,2',5',2''-tetramethyl-[1,1';4',1''] terphenyl [TPDT; see inset of Fig. 3(a)]. The data set contains 25 opening and closing cycles. Linear characteristics representing metal-metal contacts are excluded. Figure 3(a) shows three distinct sets of I - V curves: S1, S2, and S3. The transport properties are not influenced by the measurement protocol, e.g., different reversal criteria for the electrode movement. The current histograms extracted at ± 0.4 V [Fig. 3(b)] indicate that the majority of I - V curves is located in set S1. Figure 3(c) shows a subset of S1 in which the electrode distance was varied in increments of 7.5 pm. The current depends exponentially on the distance between the electrodes indicating tunneling. By contrast, the sets S2 and S3 can be attributed to a metal-molecule-metal junction [Fig. 3(a)]. Within these sets, a few special I - V curves can be found that exhibit stochastic switching [12] between the two traces shown in Fig. 3(d). Using our approach, we are able to monitor the entire spectrum of I - V curves during the formation and breaking of a molecular junction and to determine objectively the most probable transport characteristics. The stochastic fluctuations in the molecule-metal contact do not relax over time but disappear at lower temperatures as it can be seen in results on the benzene-1,4-dithiol (BDT). This prototypical molecule is of fundamental interest as it is one of the simplest molecules consisting of a conjugated system that is strongly coupled via two tunneling barriers to metallic leads. The pioneering experimental work was conducted by Reed *et al.* [13], using the MCBJ technique with a manually notched wire covered by a self-assembled monolayer of BDT molecules. This work triggered many theoretical investigations [14–16]. Depending on the various approximations and models, the calculated conductances often differ from the experimental data [8,13,17]. In our measurement, the Au-BDT-Au system is cooled down to low temperatures after having reached the intermediate regime of the closing trace at room temperature. This procedure causes the electrodes to be withdrawn due to thermal expansion $\Delta d \approx (5\text{--}10) \text{ nm}$ for $\Delta T = 250 \text{ K}$, resulting in a breaking of the molecular junction. Now, starting again with an open junction, I - V curves are acquired using the statistical approach. Figure 4(a) shows a set of I - V raw data curves for BDT taken at 250 K representing several dozens of curves acquired at each electrode

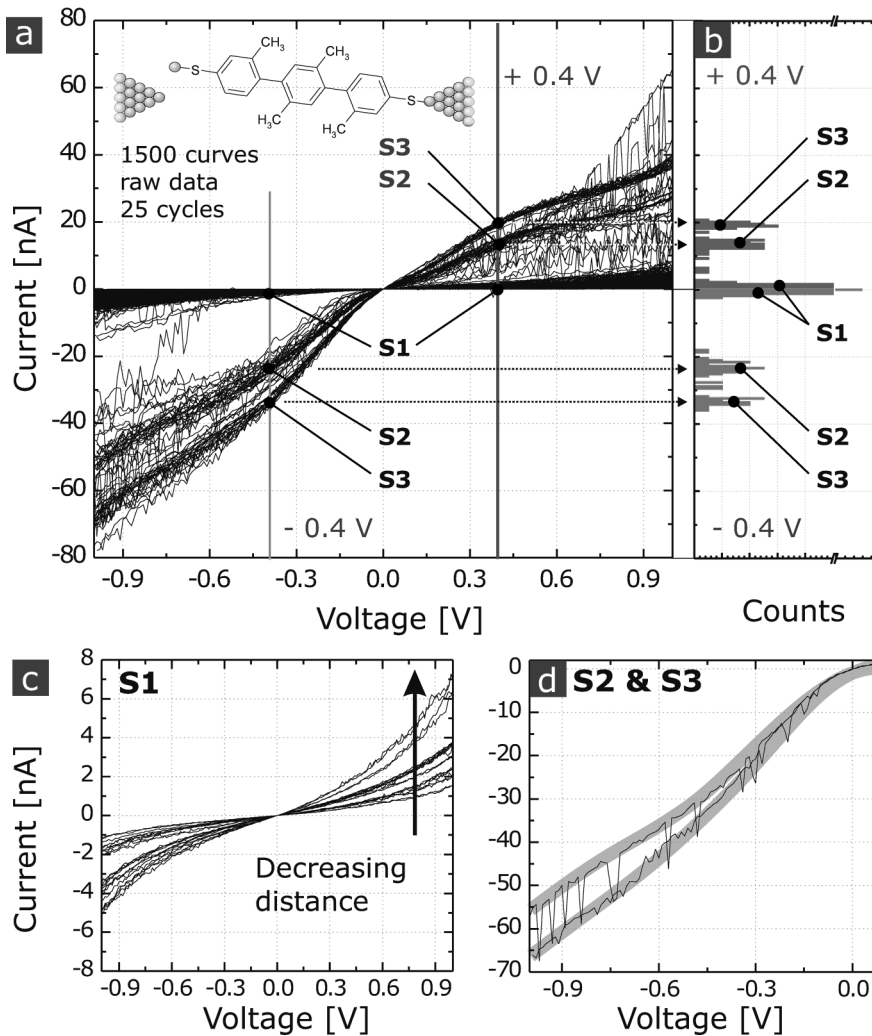


FIG. 3. (a) 1500 I - V curves acquired at 300 K for TPDT (see inset for molecular structure). (b) Current spectrum extracted at ± 0.4 V. (c) I - V curves for various distances indicate tunneling (in set S1). (d) Selected I - V curves revealing stochastic switching between the distinct traces of S2 and S3 (represented by the broad gray stripes).

position. The slight asymmetries of the raw data disappear when plotting all curves measured in the regime of cumulative occurrence and creating their envelope (gray area). Between 100 and 250 K, the molecular junction can be opened and reformed for many cycles. In contrast, at 50 K [Fig. 4(b)], data acquisition is only possible for a few cycles at each position because the junction becomes unstable. For both data sets, two peaks in the plot of the differential conductance (G_{Diff}) vs voltage are present. At 250 K, they are located at approximately -0.5 V and $+0.4$ V, defining a conductance gap $2 \Delta_{\text{cond}}$ of 0.9 V. At 50 K [Fig. 4(b)], $2 \Delta_{\text{cond}}$ is on the order of 0.6 V. Such a significant shift of 300 mV for $\Delta T = 200$ K cannot solely be explained by freeze-out of vibrational modes. Instead a different charge transfer from the metal to the molecule resulting in an altered charging energy can shift the resonant molecular energy levels and thus the conductance gap. Furthermore, different atomistic configurations of the molecule-metal contact at various temperatures can also lead to such an effect. In Fig. 4(b), the current signal above $+0.6$ V and below -0.6 V reveals significantly more noise, which is inherent to the metal-BDT-metal system. This is found to be very similar to the data presented in [15]

for $V = \pm 3.0$ V. At 300 K, in contrast to [13], we were not able to establish a metal-BDT-metal junction prior to a metal-metal contact when performing I - V curves, even for samples that formed molecular junctions at lower temperatures. This could be due to the mentioned ductile response to deformation of the gold electrodes, which is more pronounced at higher temperatures and exceeds obviously a critical value for the subnanometer-long BDT (S-S distance: 0.627 nm) under such high electric fields of about 1.4×10^9 V/m. Though on the first sight, our findings look similar to [13], several strong differences should be stressed: First, the voltage scale is substantially reduced, with a conductance gap of 0.3 V (1.4 V in [13]), and a stability region limited to ± 1.2 V (± 5 V in [13]). No further steps were observed within the voltage window available. The conductance values beyond the first current step, although recorded at different temperatures, are rather similar, 70 nS compared to 45 nS [13]. Compared to theoretical results [14–16] both experimental values are 2 to 3 orders of magnitude lower. However, the overall shape of the I - V characteristics reveals a pronounced conductance gap and fluctuations for a certain threshold voltage [16] similar to the experimental results.

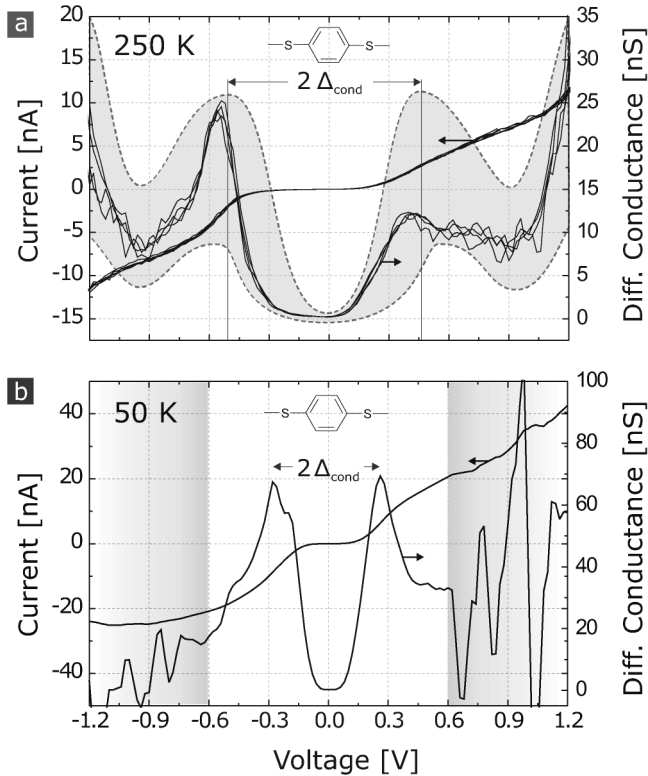


FIG. 4. I - V and G_{Diff} - V characteristics of BDT measured at (a) 250 K and (b) 50 K. The gray area in (a) shows the envelope of all curves measured.

For much smaller voltages, resistance histograms can be acquired even at 300 K. Figure 5 shows histograms (100 opening and closing cycles) measured at a voltage of 5 mV in the absence of molecules and in the presence of BDT molecules. For creating histograms, all the curves measured during opening and closing cycles were taken into

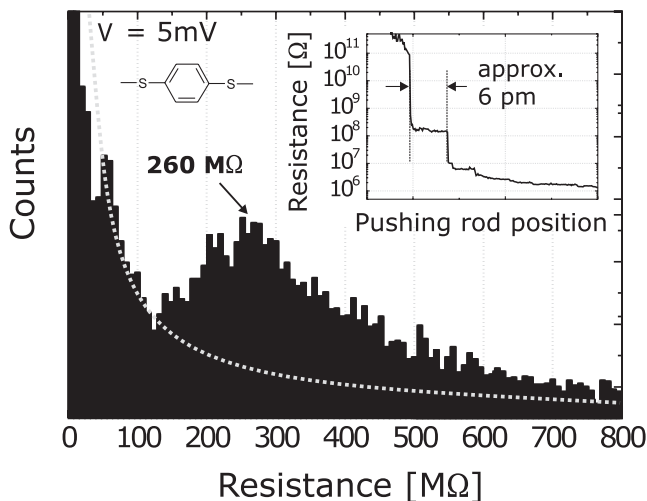


FIG. 5. Resistance histograms taken at 300 K for 100 closing and opening cycles in the absence of molecules (gray dashed line), and in the presence of BDT molecules.

account and no artificial selection of curves exhibiting plateau formation was made. A peak in the resistance spectrum around 260 M Ω appears when BDT molecules are captured in the junction. The peak is broad because of variations in the microscopic details of the molecular junction due to repeated opening and closing.

In summary, we have presented a novel statistical approach for the investigation of charge transport through single-molecule junctions during repeated formation and breaking. The approach monitors the full spectrum of transport properties of different microscopic configurations. The entirety of the data acquired is used for subsequent statistical analysis which therefore introduces impartiality to the measurement. Thereby the most probable characteristics and the variations can be determined. The excellent sensitivity to even subnanometer-long molecules is demonstrated by measurements of charge transport through a single benzene-1,4-dithiol molecule.

We are grateful to W. Riess, S. Karg, and P. Seidler for discussions and acknowledge the technical support of M. Tschudy, D. Secker, M. Bergler, and C. Rettner. We thank M. Mayor and his group for providing the molecules.

- [1] M. A. Ratner and A. Aviram, *Chem. Phys. Lett.* **29**, 277 (1974).
- [2] M. Ratner, *Mater. Today* **5**, 20 (2002).
- [3] *Molecular Electronics: Commercial Insights, Chemistry, Devices, Architecture and Programming*, edited by N.J. Teaneck (World Scientific, Singapore, 2003).
- [4] J. Chen, M. A. Reed, A. M. Rawlett, and J. M. Tour, *Science* **286**, 1550 (1999).
- [5] R. Smit, Y. Noat, C. Untiedt, N. Lang, M. van Hemert, and J. van Ruitenbeek, *Nature (London)* **419**, 906 (2002).
- [6] J. G. Kushmerick, D. B. Holt, J. C. Yang, J. Naciri, M. H. Moore, and R. Shashidhar, *Phys. Rev. Lett.* **89**, 086802 (2002).
- [7] J. Reichert, H. B. Weber, M. Mayor, and H. v. Löhneysen, *Appl. Phys. Lett.* **82**, 4137 (2003).
- [8] X. Xiao, B. Xu, and N. Tao, *Nano Lett.* **4**, 267 (2004).
- [9] C. J. Muller, J. M. van Ruitenbeek, and L. J. deJongh, *Physica (Amsterdam)* **C191**, 485 (1992).
- [10] J. Moreland and J. W. Elkin, *J. Appl. Phys.* **58**, 3888 (1985).
- [11] E. Lörtscher, J. W. Ciszek, J. M. Tour, and H. Riel, *Small* **2**, 973 (2006).
- [12] G. Ramachandran, T. Hopson, A. Rawlett, L. Nagahara, A. Primak, and S. Lindsay, *Science* **300**, 1413 (2003).
- [13] M. Reed, C. Zhou, C. Muller, T. Burgin, and J. Tour, *Science* **278**, 252 (1997).
- [14] S. Yaliraki, A. Roitberg, C. Gonzalez, V. Mujica, and M. Ratner, *J. Chem. Phys.* **111**, 6997 (1999).
- [15] H. Gronbeck, A. Curioni, and W. Andreoni, *J. Am. Chem. Soc.* **122**, 3839 (2000).
- [16] K. Stokbro, J. Taylor, M. Brandbyge, J. Mozos, and P. Ordejón, *Comput. Mater. Sci.* **27**, 151 (2003).
- [17] L. Venkataraman, J. Klare, I. Tam, C. Nuckolls, M. Hybertsen, and M. Steigerwald, *Nano Lett.* **6**, 458 (2006).