PHYSICAL REVIEW B **86**, 075456 (2012)

Variable-temperature study of the transport through a single octanethiol molecule

René Heimbuch,[1] Hairong Wu,[1,2] Avijit Kumar,[1] Bene Poelsema,[1] Peter Schön,[2] G. Julius Vancso,[2] and Harold J. W. Zandvliet[1]
[1]*Physics of Interfaces and Nanomaterials, MESA+ Institute for Nanotechnology, University of Twente, P.O. Box 217,*
7500 AE Enschede, The Netherlands
[2]*Materials Science and Technology of Polymers, MESA+ Institute for Nanotechnology, University of Twente, P.O. Box 217,*
7500 AE Enschede, The Netherlands

(Received 2 April 2012; revised manuscript received 2 August 2012; published 24 August 2012)

Working on a true molecular level is essential for advances in the field of molecular electronics. Techniques have to be perfected and new approaches have to be developed in order to characterize the properties of a single molecule. In this work we report temperature-dependent transport studies of a single octanethiol molecule trapped between the apex of a scanning tunneling microscope tip and a substrate. At each temperature the molecule is brought into contact by decreasing the gap between tip and substrate in a controlled way. At a positive sample bias the molecule jumps into contact upon approaching the substrate by 0.16 ± 0.01 nm with respect to a fixed reference point defined by a sample bias of $+1.5$ V and a tunneling current of 0.5 nA. The conductance of octanethiol is temperature independent, demonstrating that either tunneling or ballistic transport is the main transport mechanism.

DOI: 10.1103/PhysRevB.86.075456 PACS number(s): 73.63.Rt, 74.25.F−, 85.65.+h

The field of molecular electronics, emerging from the potential use of single molecules as elementary building blocks for functional devices, has attracted much attention over the last few decades.[1] A prerequisite for the advancement of this research field is the ability to measure the properties of an individual molecule. From an application point of view the conductance of a molecule is by far the most important property. But how can we measure the conductance of a single molecule? This, at first glance, very simple and elementary question turns out to be tough to answer properly. Contacting a single molecule is a very delicate process that requires great care and ultimate precision. Although several successful and elegant approaches to contact a single molecule have recently been put forward,[2–21] there is still a need to come up with alternative and more flexible routes to contact a single molecule.

In order to obtain a better understanding of the charge transport through a single molecule, it is of key importance to perform transport experiments in which the length and the temperature of the molecules are varied in a controlled way. Lafferentz *et al.* demonstrated conductance measurements while changing the length of a single polyfluorene molecule.[13] The molecule was continuously pulled up from a Au(111) surface using the tip of a scanning tunneling microscope (STM).

A rather straightforward method to contact a single molecule is to trap it between a substrate and the apex of the STM tip. Once contacted, the conductance of the molecule can easily be measured. However, this method does not allow for a measurement of the temperature dependence of the conductance of the molecule because even the slightest change in temperature will lead to a change of the substrate-tip separation and thus to a compressed, stretched, or detached state of the molecule. This is presumably the main reason why there are only a few examples in literature where single molecule conductance has been measured as a function of temperature. An exception is a recent study by Sedghi *et al.* where the temperature dependence of the conductance of short chains of porphyrin molecules was measured in a temperature range from 300 to 375 K.[15]

Using STM to create a well-defined substrate-molecule-tip junction that can actively be opened and closed in an accurate and controlled way will diminish the problem of a thermally induced varying substrate-tip separation. Recently, we put forward a method that relies on a combination of current-voltage (*I*-*V*) and current-distance (*I*-*Z*) spectroscopy to open and close an electrode-molecule-electrode junction in a well-defined way.[17] Using this recipe we are able to trap a single octanethiol between two electrodes at a temperature of 77 K, one electrode being the tungsten tip of the STM and the other an atomic platinum chain on a Ge(001) substrate. The controllability of this junction, i.e., the ability to manage the cessation and initiation of contact with high accuracy, allows for a feedback mechanism that can be sustained over a wide temperature range. This approach differs significantly from methods that use static contacts for the molecule, e.g., break junction methods.[4,5,22] In our work, at every measurement the contact was freshly established, and after the *I*-*Z*/*I*-*V* traces were recorded the contact was broken again, so that the junction could rearrange itself to its reference point. Therefore, the junction itself remained uniform, i.e., in particular the electrode-electrode separation, throughout the whole experiment.

There are several possible molecular transport mechanisms, e.g., thermionic emission, hopping, Fowler-Nordheim tunneling, and direct tunneling. Thermionic emission and hopping are temperature dependent, whereas tunneling is temperature independent. Direct tunneling usually occurs at biases smaller than the work function, while Fowler-Nordheim tunneling takes place at biases that exceed the work function. In addition, Fowler-Nordheim tunneling in the STM setup will lead to field emission resonances, also referred to as Gundlach oscillations, which show up as well-defined oscillations in *I*-*V* and *I*-*Z* traces.[23]

In this work we present an approach to measure the conductance of a single octanethiol molecule as a function of temperature in a well-defined and accurate way. The transport measurements reveal that the conductance of an octanethiol molecule is temperature independent, indicating that the transport mechanism through the octanthiol molecule is direct tunneling.

All experiments are performed in an ultrahigh-vacuum low-temperature scanning tunneling microscope (UHV LT-STM). The molecules where deposited on Pt/Ge(001) substrates that have been cleaned and prepared in ultrahigh vacuum. Flat, *n*-type Ge(001) substrates (4×10 mm^2), were cleaned using 500 eV Argon ion bombardment followed by annealing at 1100 K until atomically clean and flat (001) surfaces were obtained. Well-ordered arrays of atomic Pt chains were produced by deposition of half a monolayer of Pt onto the substrate and annealing at 1100 K.[24,25] Subsequently, octanethiol molecules (98.5% pure, purchased from Sigma-Aldrich) were introduced into the chamber for 20–60 sec at a pressure of 2.5×10^{-7} Torr via a leak valve that allows the sample to be exposed to a precise dose of molecules. The atomic Pt chains are very helpful in locating and immobilizing the molecules on the substrate for the attachment process.[12] The sample was then transferred to the LT-STM, cooled down to 77 K, and subsequently imaged.

In Fig. 1 scanning tunneling microscopy images of Pt modified Ge(001), before and after the exposure to 10 Langmuir (L) of octanethiol, are depicted. The vast majority of octanethiol molecules prefer to adsorb on the self-organizing atomic chains. We subsequently pick up a single octanethiol molecule by placing the tip over the molecule, opening the feedback loop and bringing the electrochemically etched tungsten STM tip several angstrom closer to the surface than the normal tunneling distance. Since the success rate of this pick up experiment is not very high we often had to repeat this procedure before a single molecule was picked up from an atomic Pt chain. After every attempt we recorded *I-V* and *I-Z* spectra to affirm if we had indeed an octanethiol molecule dangling at the apex of the STM tip.[17] In Fig. 2 an illustration of an octanethiol molecule attached to the apex of the STM tip is shown. A successful attachment of an octanethiol molecule to the STM tip can be proven either via an *I-Z* measurement [see Fig. 3(a)] or an *I-V* measurement. In case of attachment, the *I-V* curves change from a symmetric shape to a rectifying behavior (see Ref. 17). Once the molecule is attached to the tip, the configuration is very stable and remains unchanged over a large number of experiments. Figure 3(a) shows two different *I-Z* curves recorded at a bias voltage of 1.5 V and a setpoint current of 0.5 nA. The dashed line shows the response of a tunneling junction in case no molecule is attached to either substrate or STM tip. The solid line displays the *I-Z* response of a molecule trapped within the STM junction. After a small, but well-defined, tip displacement, the current suddenly jumps to a much larger value. At this point the molecule bridges the gap between substrate and STM tip. The attachment process is judged successful when the characteristic jump into contact can be reproduced on random locations of the substrate (e.g., positions where no molecule could previously be found). Furthermore, contact of the molecule never occurs at negative bias voltage.[17] Therefore, when changing the polarity

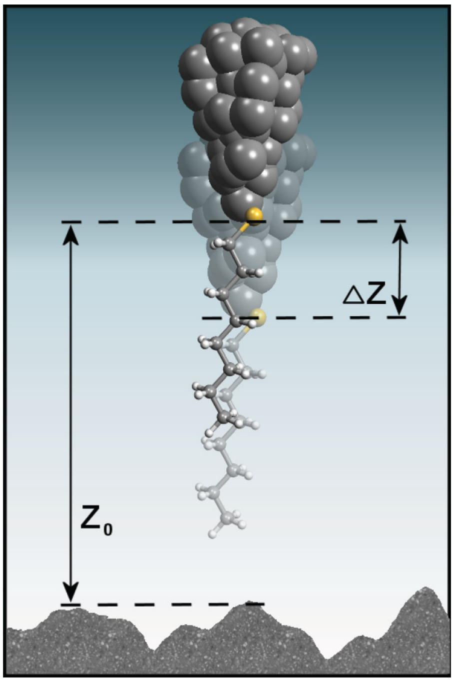

FIG. 2. (Color online) Illustration of an octanethiol molecule attached to the apex of an STM tip with an initial separation Z_0 to the surface. The tip displacement, ΔZ, is the distance the tip moves closer to the surface during an *I-Z* measurement. For the sake of simplicity we assume that only the sulfur atom of the octanethiol molecule binds to the apex of the scanning tunneling microscope.

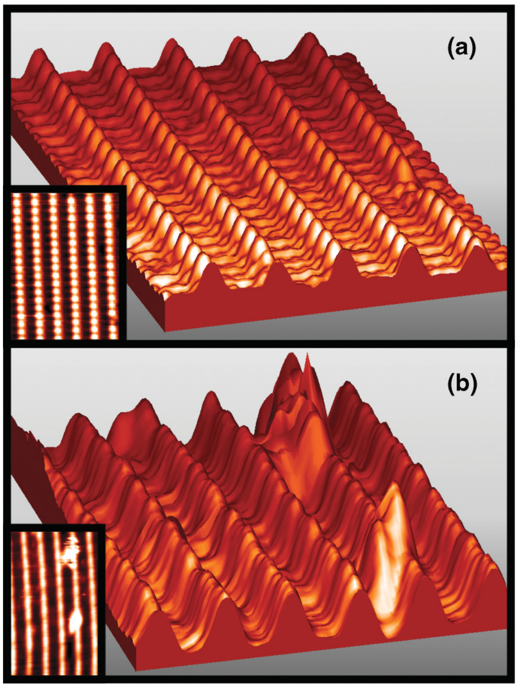

FIG. 1. (Color online) (a) Scanning tunneling microscopy image (8×8 nm) of a Pt modified Ge(001) substrate with a 2D image of the same location in the inset. (b) Scanning tunneling microscopy image (8×8 nm) of the same surface as in (a) after the exposure to 10 Langmuir of octanethiols with a 2D image of the same location in the inset.

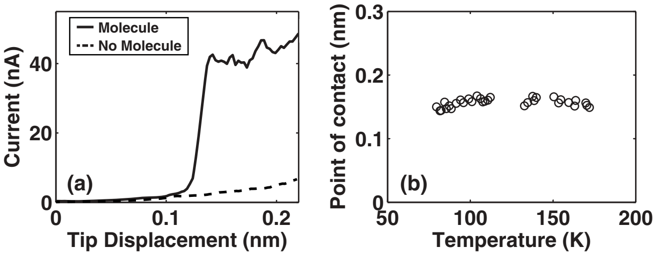

FIG. 3. (a) Example of an *I-Z* curve without (dashed line) and with (solid line) an octanethiol molecule attached to the STM tip. Both traces where recorded at 77 K, at a fixed setpoint (tunnel current 0.5 nA and sample bias +1.5 V). (b) Tip displacement at which the molecule jumps into contact vs temperature. The displacement (point of contact) is measured with respect to the setpoint values (tunnel current 0.5 nA and sample bias +1.5 V).

no jump should appear and the current-distance curve follows an exponential behavior (as seen by the dashed line in Fig. 3).

With the molecule attached to the tip of the STM, we constantly scanned the surface for many hours. We did not refill the cryostat with liquid nitrogen (LN_2) and after some time the LN_2 was fully evaporated, causing the STM to slowly heat up. The temperature was carefully monitored during the experiment. Every few degrees (typically 1–2 K) we measured a series of *I-Z* curves. All the traces were recorded at a positive bias voltage of +1.5 V and a setpoint current of 0.5 nA to ensure that the molecule made contact upon approaching the substrate. Within one *I-Z* measurement the feedback loop was switched off and the current was recorded as the STM tip moved a total of 0.4 nm towards the surface. After every *I-Z* measurement the feedback loop was switched back on again to allow the tip to move back to its initial position, thus breaking the contact again. At this point the junction returns to the original configuration defined by its setpoint value, i.e., a tunnel current of 0.5 nA and a sample bias of 1.5 V, after every single measurement and thereby providing us with a well-defined and fixed reference point. We measured a series of *I-Z* traces for temperatures ranging from 77 to 172 K. Beyond 180 K the thermal drift of the instrument started to affect the measurements and therefore we were unable to achieve accurate and well reproducible experimental data.

We have corrected all the *I-Z* measurements to compensate for the temperature-dependent response of the piezo crystals by applying a factor of the expansion coefficient. This changes the distance value to the actual value that the tip has moved at the specific temperature of the measurement. The measurements are very comparable to the results obtained at 77 K in a previous experiment, where we studied the switching behavior of a single octanethiol molecule.[17] First, the jump into contact occurs at the same tip-substrate separation (after approaching the substrate by $\Delta Z = 0.15$–0.17 nm with respect to our fixed and well-defined setpoint, i.e., $I = 0.5$ nA and $V = +1.5$ V). The variation in ΔZ is comparable to the measurements that were recorded at 77 K. Second, the current value that is reached after the molecules makes contact is the same as previously recorded at 77 K, i.e., ≈ 45 nA. Since we never detected a second jump in the *I-Z* traces, we have to conclude that only a single molecule is trapped between tip and substrate.

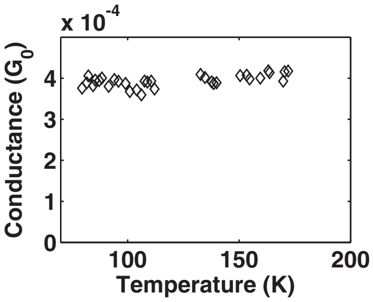

FIG. 4. Conductance of an electrode single octanethiol molecule-electrode junction vs temperature. $G_0 = 2e^2/h$ is the conductance quantum.

Figure 3(b) shows a plot of the tip displacement values at which the molecule jumps into contact versus the temperature. One can easily see that within the recorded temperature window the point of contact remains amazingly constant. The mechanism for the molecule to jump into contact is thus temperature independent. This definitely supports the idea that the cause for the jump into contact is the electric field applied between STM tip and substrate, as has been put forward previously.[17]

The conductance of the molecule has been determined at a sample bias of +1.5 V, i.e., well below the reported tunneling barrier of an octanethiol molecule (see Fig. 4).[26] Throughout the experiment the conductance through the molecule remains constant at a value of 30 nS, a value that is consistent with reports from literature.[26] In theory, the transport mechanisms that are temperature independent are ballistic transport and quantum-mechanical tunneling. In principle there are two tunneling processes: direct tunneling or Fowler-Nordheim tunneling.[27,28] Fowler-Nordheim tunneling only occurs at high voltages, i.e., voltages larger than the work function ($V > \Phi/e$). Since the voltages applied in our experiments are significantly smaller than the 4 eV barrier (assuming that the Fermi edge lies somewhere in the middle of the 8–9 eV gap between highest occupied and lowest unoccupied molecular orbitals of the octanethiol molecule[29]), we have to exclude Fowler-Nordheim tunneling. The conductance of a tunnel barrier decreases exponentially with the width (L) of the barrier, i.e., $G \propto e^{-\beta L}$. The total conductance of the substrate-molecule-tip junction can be written as

$$G_{\text{total}} = \frac{2e^2}{h} T_{\text{total}}, \qquad (1)$$

where T_{total} is the total transmission coefficient of the substrate-molecule-tip junction. If we assume that the conductance of the octanethiol molecule is much smaller than the contact conductance we find that the conductance of a single octanethiol molecule is ≈ 30 nS, which agrees well with large area junctions data.[29] However, hybridization of the electronic states of the molecule and the electrodes will also affect the transport mechanism. Since our experiments reveal a single molecule conductance, that is about a factor of 3 larger than obtained previously by a method where the sulfur atom of the octanethiol binds to the substrate rather than to the tip, we propose that in our experiments not one but two carbon atoms of the tail of the octanethiol molecule are involved in bonding with substrate. The latter conclusion is supported by the observation that we have to move the tip 0.16 ± 0.01 nm, which compares favorably with the projected C-C bond distance (0.155 nm), closer to the substrate as compared to the experiments reported in Ref. 17.

In summary, we have shown how a substrate-octanethiol-STM tip junction can be used to study the conductance of a single octanethiol molecule. In a well-defined manner we were able to extract the transport properties of this molecule as a function of temperature. By making use of the ability of the junction to be controlled by the applied electric field, we were able to set a contact, well defined in respect to the reference point for each measurement. The immense advantage of this method is that we can very accurately adjust the gap between the two electrodes, which is an absolute prerequisite for precise single molecule transport measurements. The conductance of an octanethiol molecule is temperature independent, demonstrating that the main transport mechanism is dominated by either direct quantum-mechanical tunneling or ballistic transport. The amount of control over a single molecule junction we have demonstrated here will open yet another door into the understanding and realization of molecular electronics.

ACKNOWLEDGMENTS

We would like to thank the Stichting voor Fundamenteel Onderzoek der Materie (Grant No. FOM, 10ODE01), the Nederlandse Organisatie voor Wetenschappelijk onderzoek (Grant No. NWO/CW ECHO.08.F2.008), and the Strategic Research Orientation "Enabling Technologies" of the MESA+ Institute for Nanotechnology for financial support.

---

[1] A. Aviram and M. A. Ratner, Chem. Phys. Lett. **29**, 277 (1974).

[2] C. Joachim, J. K. Gimzewski, R. R. Schlittler, and C. Chavy, Phys. Rev. Lett. **74**, 2102 (1995).

[3] M. A. Reed, C. Zhou, C. J. Muller, T. P. Burgin, and J. M. Tour, Science **278**, 252 (1997).

[4] R. H. M. Smit, Y. Noat, C. Untiedt, N. D. Lang, M. C. Van Hemert, and J. M. Van Ruitenbeek, Nature (London) **419**, 906 (2002).

[5] J. Reichert, R. Ochs, D. Beckmann, H. B. Weber, M. Mayor, and H. V. Löhneysen, Phys. Rev. Lett. **88**, 176804 (2002).

[6] W. Haiss, H. van Zalinge, S. J. Higgins, D. Bethell, H. Höbenreich, D. J. Schiffrin, and R. J. Nichols, J. Am. Chem. Soc. **125**, 15294 (2003).

[7] S. Stojkovic, C. Joachim, L. Grill, and F. Moresco, Chem. Phys. Lett. **408**, 134 (2005).

[8] F. Moresco, Phys. Rep. **399**, 175 (2004).

[9] N. Néel, J. Kröger, L. Limot, T. Frederiksen, M. Brandbyge, and R. Berndt, Phys. Rev. Lett. **98**, 065502 (2007).

[10] R. Temirov, A. Lassise, F. B. Anders, and F. S. Tautz, Nanotechnology **19**(6), 065401 (2008).

[11] A. F. Takács, F. Witt, S. Schmaus, T. Balashov, M. Bowen, E. Beaurepaire, and W. Wulfhekel, Phys. Rev. B **78**, 233404 (2008).

[12] D. Kockmann, B. Poelsema, and H. J. W. Zandvliet, Nano Lett. **9**, 1147 (2009).

[13] L. Lafferentz, F. Ample, H. Yu, S. Hecht, C. Joachim, and L. Grill, Science **323**, 1193 (2009).

[14] S. Guo, J. Hihath, I. Díez-Pérez, and N. Tao, J. Am. Chem. Soc. **133**, 19189 (2011).

[15] G. Sedghi, V. M. García-Suárez, L. J. Esdaile, H. L. Anderson, C. J. Lambert, S. Martín, D. Bethell, S. J. Higgins, M. Elliott, N. Bennett, J. E. MacDonald, and R. J. Nichols, Nature Nanotechnology **6**, 517 (2011).

[16] S. Chang, J. He, P. Zhang, B. Gyarfas, and S. Lindsay, J. Am. Chem. Soc. **133**, 14267 (2011).

[17] A. Kumar, R. Heimbuch, B. Poelsema, and H. J. W. Zandvliet, J. Phys.: Condens. Matter **24**, 082201 (2012).

[18] C. Li, I. Pobelov, T. Wandlowski, A. Bagrets, A. Arnold, and F. Evers, J. Am. Chem. Soc. **130**, 318 (2008).

[19] C. Li, A. Mishchenko, I. Pobelov, and T. Wandlowski, Chimia **64**, 383 (2010).

[20] G. Schull, T. Frederiksen, M. Brandbyge, and R. Berndt, Phys. Rev. Lett. **103**, 206803 (2009).

[21] G. Schull, T. Frederiksen, A. Arnau, D. Sánchez-Portal, and R. Berndt, Nature Nanotechnology **6**, 23 (2011).

[22] J. M. Van Ruitenbeek, A. Alvarez, I. Piñeyro, C. Grahmann, P. Joyez, M. H. Devoret, D. Esteve, and C. Urbina, Rev. Sci. Instrum. **67**, 108 (1996).

[23] K. Gundlach, Solid-State Electron. **9**, 949 (1966).

[24] O. Gurlu, O. A. Adam, H. J. Zandvliet, and B. Poelsema, Appl. Phys. Lett. **83**, 4610 (2003).

[25] N. Oncel, A. Van Houselt, J. Huijben, A.-S. Hallbäck, O. Gurlu, H. J. W. Zandvliet, and B. Poelsema, Phys. Rev. Lett. **95**, 116801 (2005).

[26] H. B. Akkerman and B. De Boer, J. Phys.: Condens. Matter **20**, (2008).

[27] S. Karthäuser, J. Phys.: Condens. Matter **23**, 013001 (2011).

[28] S. J. Van der Molen and P. Liljeroth, J. Phys.: Condens. Matter **22**, 133001 (2010).

[29] W. Wang, T. Lee, and M. Reed, Proc. IEEE **93**, 1815 (2005).