# Measuring Molecular Junctions: What Is the Standard?

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The past decade has witnessed a growing body of literature measuring electrical resistance of individual molecules.[1–4] At a base level, this work is driven by the need to miniaturize electronic circuits for smaller and faster computers, sensors, and other instrumentation. Proposals to build electronic devices where a single molecule functions as the active element in the circuit date back at least as far as the molecular rectifier of Aviram and Ratner in 1974.[5] It is in this sense that the term molecular electronics is now commonly used.

**Molecular Electronics.** A molecule represents the smallest unit of matter with well-defined connectivity; thus, molecules are obvious candidates for bottom-up assembly of electronic devices. Perhaps the most intriguing aspect of this idea is that there exists a good understanding of molecules. Chemical synthesis is a massively parallel method to create identical molecules by the mole. Their structures and electronic properties can be tailored and tweaked. We can also characterize them by any manner of spectroscopy and structural probe. Thus, molecules could be ideal building blocks for electronic devices.[6]

However, to make even the simplest molecular electronic device—a molecule connected between two electrodes—presents several practical difficulties (Figure 1). Fabrication is a challenge because of the difference in scale between a molecule, the electrodes, and the small gap between the electrodes. Ironically, making a metal−molecule−metal (M-m-M) junction is not as difficult as verifying that the intended molecule is in the junction, connected and oriented to the electrodes in the intended way. Many clever methods have been employed to create M-m-M junctions.[2,3,7] Examples are mechanical break junctions,[8] crossed wires,[9] mercury junctions,[10] nanopores,[11] electrochemical interfaces,[12,13] and scanning probe microscope (SPM) junctions.[9,14,15] Each technique has its own advantages, for example, the ability to provide images of the contact area, easily cooled to low temperature, or controllable electrode spacing.

Electrical measurement of the junction is straightforward; unfortunately, its interpretation is not straightforward in real laboratory systems where the electrode surface is seldom perfectly controlled. What may not be obvious at the outset is that the electrode−molecule contacts typically present a substantial electronic mismatch because the Fermi level of the metal electrode is not aligned with the HOMO or LUMO of the molecule, but lies between them. As a consequence, measured electrical resistances of M-m-M junctions are typically in the GΩ range, compared to 12.9 kΩ resistance ($G_0 = 2e^2/h$) of a quantum point contact. The molecular bridge also contributes to the measured resistance, but the measurement is a property of the M-m-M junction, not of the molecule itself. A thorough understanding requires separating out each contribution.

The typical approach is to compare measurements of a series of junctions, where the molecules and electrodes are varied systematically. The most frequently measured parameter is the decay constant $\beta$ for

**ABSTRACT** Accurate measurements of electronic properties of molecular junctions are important for both fundamental and practical applications. Often the molecule-electrode contacts are poorly characterized, leading to wide variation in the measured resistance values. A new paper in this issue demonstrates the use of a reference molecule as an internal standard to compensate for the varying conditions of the molecular contact in conductive-tip atomic force microscopy measurements and yields consistent resistances relative to the reference despite variations in absolute resistance.
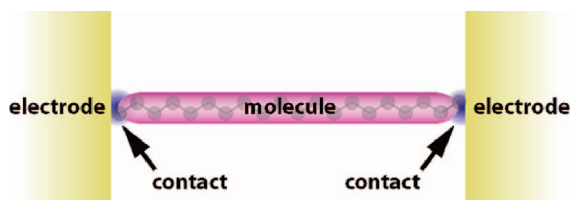
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Figure 1. A simplified schematic demonstrating the most basic molecular electronic device—a molecule connected between two electrodes. The three regions are shown: electrode, molecule, and the molecule−electrode contacts.

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tunneling through the molecular bridge. The junction resistance for a homologous series of molecules of different length, for example, alkanethiols, is measured as a function of alkyl chain length. Provided the molecule−electrode contacts are reproducible, the resistances obey an exponential law where $R = R_0 \exp(\beta l)$. The bridge length is $l$. The contact resistance $R_0$, the resistance of the molecular bridge extrapolated to zero length, contains information about the molecule electrode contact.[16,17]

Accurate experimental measurements of resistance are required to test and to refine theories. This is in turn used to make more accurate predictions of molecular junction properties and to suggest new molecules for experimental study. Many examples of transport measurements through molecules can be found in the literature; however, there is little agreement on the values. This is because the experiments actually measure the resistance of the M-m-M junction. Generally one or both of these metal−molecule contacts is ill defined.

**Internal Reference.** In this issue, Scaini *et al.* use a self-assembled monolayer (SAM) of alkanethiols on the Au(111) surface.[18] The Au substrate acts as one electrode. Be-

cause the SAM is highly ordered, the Au(111)−SAM interface is uniform; hence, the Au substrate−SAM contact is highly reproducible. The other contact is formed by a conductive tip of an atomic force microscope (CT-AFM), which is brought into contact with the top of the SAM, completing the M-m-M junction. The junction resistance is obtained by measuring the current through the junction as a voltage is applied between the probe tip and the substrate. The absolute resistance measured in this way is not reproducible due to a contamination layer on the probe tip. Scaini *et al.* circumvent this problem by use of an internal reference SAM to obtain reproducible relative resistance measurements (Figure 2).

The AFM platform provides several important advantages for going beyond this basic measurement capability. The contact force of the probe tip with the SAM can be precisely controlled. The AFM can image the surface with nanometer resolution so that the structural characteristics of the contact region can be selected to avoid defects and imperfections in the SAM. The ability to image the surface and to position the probe tip precisely is central to the work of Scaini *et al.* To set up the differential measurements, islands of longer or shorter alkanethiol SAM were nanografted into the SAM matrix of a reference alkanethiol.[19] Both images and electrical measurements are performed in the same experiment so that the resistance of *both* the is-

land and the reference SAMs are obtained repeatedly and in rapid succession. This provides nearly simultaneous measurements of the island-reference *relative* resistance and the island-reference *absolute* resistance. The former is the desired measurement, while the latter tracks the condition of the probe-tip. The height difference between the island and the reference SAM is also obtained.

**Up Close and Personal with the Probe Tip.** It is important to emphasize that the requirements for high-resolution imaging using SPM are much less stringent than for electrical measurements. This is because high-resolution imaging only requires a sharp, stable probe tip, either the idealized clean tip or the original tip intentionally or unintentionally modified by a contamination layer, nanoparticle, or a molecule from the sample or elsewhere. On the other hand, electronic measurements require precise knowledge of the molecule−probe tip contact in order to interpret the absolute conductance. In SPM, the probe tip is the least well-characterized part of the instrument. This is because the atomic- and nanometer-scale structure of each probe tip is different and changes during use. This might sound discouraging, but a few molecules jumping on and off between the probe tip and the "clean" surface is not uncommon. Imagine scanning over a carpet of $10^8$ molecules (*e.g.*, the 3 $\mu$m × 3 $\mu$m areas Scaini *et al.* image in their paper); one stray molecule in this area would still produce
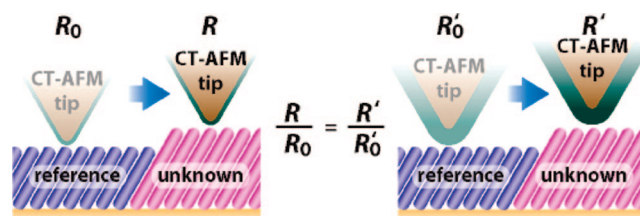


**Figure 2.** Absolute resistance measurements show large variations due to variable "thickness" contamination layers (dark green) on the CT-AFM probe tip. Scaini *et al.* demonstrate that the resistance ratio of the unknown to an internal reference SAM gives reproducible values across many measurements, despite the large observed variations in absolute resistance of the junction across the same measurements.

## CONDUCTIVE PARAFFIN?

The alkanethiol SAMs studied by Scaini *et al*. are essentially monolayers of crystalline paraffin with a thickness determined by the length of the alkyl chain. Conductance of the molecules is measured along their length. How can paraffin be a conductor? Bulk paraffin is a good insulator! The resolution is that these molecules conduct more than vacuum, but much less and differently than metals.

For conventional ohmic conduction (*e.g.,* current flowing in a copper wire), the electrons are in thermal equilibrium at each point along the wire due to collisions with the copper lattice, losing energy to the lattice and heating the wire.

For the M-m-M junction, the mechanism for electron transport is nonresonant coherent tunneling,[11] which only operates over very short distances because of its strong exponential decay with distance. The electrons originate in one electrode, pass through the junction (predominantly) without collision, and ultimately deposit all their energy in the second electrode. The measured conductance is really the probability of an electrode tunneling across the junction, or, put another way, the electronic transparency of the junction. If a junction has multiple layers, the total resistance is approximately the *product* of the tunneling probability of each layer alone.

At first sight, it seems odd that it is easier for an electron to tunnel through an alkyl chain than to tunnel though the equivalent distance in vacuum. This is because the alkyl chain is more polarizable than vacuum, so the barrier to tunneling is lowered. The charge of the electron passing through the molecule can be partially screened by the polarization of the molecule. In contrast, the electron in vacuum is naked. Although the alkyl chain has no delocalized electrons to participate directly in the charge transport, it is more conductive than a vacuum gap of the same length.

Although the details of the mechanism are different from familiar resistors, conductance—the ratio of current to voltage—is still a useful operational concept. For molecules with wide energy gaps and no energy levels near the Fermi level (such as alkanethiols) the tunneling current increases monotonically with applied voltage (nonresonant tunneling). If the molecule has low-lying energy levels, resonant tunneling can be observed, characterized by conductance maxima when the applied voltage aligns a molecular energy level with the energy of the tunneling electrons. This interesting behavior is one basis for the design of molecular switches and memory.[6] A small fraction of electrons traversing the junction do suffer energy loss in the molecule by inelastic processes. This phenomenon is exploited in inelastic tunneling spectroscopy, which gives vibrational information about the molecules in the junction.[25,26] For ordinary transport measurements, inelastic processes are small effects that can be safely ignored.

Returning to bulk paraffin, it is instructive to turn the original question around: why is bulk paraffin an insulator? This is because it has no free carriers and there are no low energy sites to hold an electron were one to tunnel into it. At high voltages, dielectric break down occurs, where the electric fields are sufficient to cause ionization of the paraffin and multiplication of these generated or injected electrons by an avalanche process. However, this is generally a destructive process causing irreversible changes in the material.

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images representative of a clean surface.

An additional molecular layer on the probe tip can have a profound effect on the resistance of the junction, modifying it to an M-m-m′-M junction. Here m′ is the adventitious layer on the tip and m is the molecule of interest. This m-m′ interaction is a bilayer junction, which is interesting in its own right.[20] Scaini *et al*. overcome this difficulty by using a reference molecule as an internal standard. Because m is part of a homologous series, m-m′ is expected to be the same for both the unknown and the reference m. Scaini *et al*. demonstrate this method for alkyl chains from 8 to 18 carbons in length. Although

the absolute resistances measured for the same molecule vary with probe tip and condition, the ratio of the resistance to the internal standard is reproducible.

**Scanning Tunneling Microscopy *vs* Conductive-Tip Atomic Force Microscopy.** The scanning tunneling microscope (STM) is often used to study molecules on surfaces because of its high spatial resolution. The strong exponential decay of electron tunneling with distance largely confines the tunneling current to the atom at the end of the probe tip.[21] The STM also interacts with the sample directly *via* electron tunneling. Feedback control of the tip–sample distance is accomplished using the tunneling current, which

requires a bandwidth of ~1 kHz, practically limiting the tunneling current to >0.1 pA. Constant current (topographic) mode controls the tip–sample distance to maintain a constant tunneling current, convolving the electronic properties of the tunnel junction with the sample topography. When high-resolution images of SAMs are required, the STM operating conditions are set to position the tip so that it is not in contact with the monolayer surface, creating an additional SAM−tip gap, further complicating the issue (Figure 3).[22] The ideal measurement of resistance would be made when the tip is just in contact, but not penetrating the SAM so that the SAM−tip gap goes to zero—a more complex STM experiment.[14]
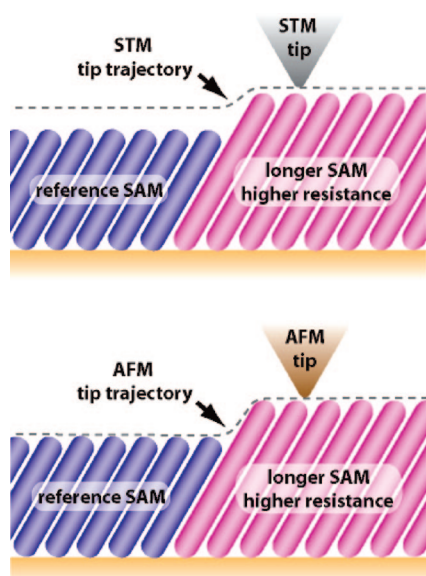
Figure 3. Schematic comparing constant-current STM tip trajectory (top) and AFM constant-contact force tip trajectory (bottom) over a SAM consisting of shorter (lower resistance) and longer (higher resistance) molecules. In constant-current STM topography, the junction resistance is held constant while the SAM—tip distance varies. In CT-AFM, the junction resistance varies while the SAM—tip contact is held constant.

Conductive-tip AFM uses the contact force between a metalized tip and the sample for feedback to maintain a constant tip–sample distance, which is a straightforward way to make comparable SAM—tip

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contacts with SAMs of different length alkyl chains. The electrical measurements are decoupled from the tip–sample distance, permitting smaller tunnel current measurement bandwidths to be used, enabling measurements of tunneling currents 2–3 orders of magnitude lower than typically used for the STM. Consequently, longer and more resistive molecules can be studied. Although current is sensitive to contact force, the force can be made small enough that the probe tip contacts the SAM but does not appreciably distort its structure.

**Conclusion and Outlook.** Although the resistance of molecular junctions can be measured, the values vary widely. In the future, measurements are likely to use internal standards to measure relative transport as demonstrated by Scaini *et al*. One can imagine using a reference molecule with a well-established conductivity and electrode contact behavior in much the same way a reference electrode is used in electrochemistry. This will require establishment and agreement on such a standard as well as definitive measurements of it.

The CT-AFM measurement technique can be expanded to study transport across bilayer junctions, the contact between multiple molecular layers, that is, one molecule on the substrate and the second on the CT-AFM tip.[17,23] Such a configuration is a nanometer-scale version of the electronic tongue,[24] which would reveal chemical information at the molecular scale and form an ultrasensitive chemical detector.

## REFERENCES AND NOTES

1. Metzger, R. M. Electrical Rectification by a Molecule: The Advent of Unimolecular Electronic Devices. *Acc. Chem. Res.* **1999**, *32*, 950–957.
2. Salomon, A.; Cahen, D.; Lindsay, S.; Tomfohr, J.; Engelkes, V. B.; Frisbie, C. D. Comparison of Electronic Transport Measurements on Organic Molecules. *Adv. Mater.* **2003**, *15*, 1881–1890.
3. McCreery, R. L. Molecular Electronic Junctions. *Chem. Mater.* **2004**, *16*, 4477–4496.
4. Lindsay, S. M.; Ratner, M. A. Molecular Transport Junctions: Clearing Mists. *Adv. Mater.* **2007**, *19*, 23–31.
5. Aviram, A.; Ratner, M. A. Molecular Rectifiers. *Chem. Phys. Lett.* **1974**, *29*, 277–283.
6. Reed, M. A.; Tour, J. M. Computing with Molecules. *Sci. Am.* **2000**, *282*, 86–93.
7. Xu, B.; Tao, N. J. Measurement of Single-Molecule Resistance by Repeated Formation of Molecular Junctions. *Science* **2003**, *301*, 1221–1223.
8. Cui, X. D.; Primak, A.; Zarate, X.; Tomfohr, J.; Sankey, O. F.; Moore, A. L.; Moore, T. A.; Gust, D.; Harris, G.; Lindsay, S. M. Reproducible Measurement of Single-Molecule Conductivity. *Science* **2001**, *294*, 571–574.
9. Seferos, D. S.; Blum, A. S.; Kushmerick, J. G.; Bazan, G. C. Single-Molecule Charge-Transport Measurements That Reveal Technique-Dependent Perturbations. *J. Am. Chem. Soc.* **2006**, *128*, 11260–11267.
10. Holmlin, R. E.; Haag, R.; Chabinyc, M. L.; Ismagilov, R. F.; Cohen, A. E.; Terfort, A.; Rampi, M. A.; Whitesides, G. M. Electron Transport through Thin Organic Films in Metal-Insulator-Metal Junctions Based on Self-Assembled Monolayers. *J. Am. Chem. Soc.* **2001**, *123*, 5075–5085.
11. Wang, W.; Lee, T.; Reed, M. A. Mechanism of Electron Conduction in Self-Assembled Alkanethiol Monolayer Devices. *Phys. Rev. B* **2003**, *68*, 035416–035417.
12. Sachs, S. B.; Dudek, S. P.; Hsung, R. P.; Sita, L. R.; Smalley, J. F.; Newton, M. D.; Feldberg, S. W.; Chidsey, C. E. D. Rates of Interfacial Electron Transfer through π-Conjugated Spacers. *J. Am. Chem. Soc.* **1997**, *119*, 10563–10564.
13. Finklea, H. O.; Liu, L.; Ravenscroft, M. S.; Punturi, S. Multiple Electron Tunneling Paths across Self-Assembled Monolayers of Alkanethiols with Attached Ruthenium(II/III) Redox Centers. *J. Phys. Chem.* **1996**, *100*, 18852–18858.
14. Fan, F. R. F.; Yang, J.; Cai, L.; Price, D. W.; Dirk, S. M.; Kosynkin, D. V.; Yao, Y.; Rawlett, A. M.; Tour, J. M.; Bard, A. J. Charge Transport through Self-Assembled Monolayers of Compounds of Interest in Molecular Electronics. *J. Am. Chem. Soc.* **2002**, *124*, 5550–5560.
15. Ishida, T.; Mizutani, W.; Aya, Y.; Ogiso, H.; Sasaki, S.; Tokumoto, H. Electrical Conduction of Conjugated Molecular Sams Studied by Conductive Atomic

Force Microscopy. *J. Phys. Chem. B* **2002**, *106*, 5886–5892.

16. Monnell, J. D.; Stapleton, J. J.; Dirk, S. M.; Reinerth, W. A.; Tour, J. M.; Allara, D. L.; Weiss, P. S. Relative Conductances of Alkaneselenolate and Alkanethiolate Monolayers on Au{111}. *J. Phys. Chem. B* **2005**, *109*, 20343–20349.

17. Wold, D. J.; Frisbie, C. D. Fabrication and Characterization of Metal-Molecule-Metal Junctions by Conducting Probe Atomic Force Microscopy. *J. Am. Chem. Soc.* **2001**, *123*, 5549–5556.

18. Scaini, D.; Castronovo, M.; Casalis, L.; Scoles, G. Electron Transfer Mediating Properties of Hydrocarbons as a Function of Chain Length: A Differential Scanning Conductive Tip Atomic Force Microscopy Investigation. *ACS Nano* **2008**, *2*, 507–515.

19. Liu, G.-y.; Xu, S.; Qian, Y. Nanofabrication of Self-Assembled Monolayers Using Scanning Probe Lithography. *Acc. Chem. Res.* **2000**, *33*, 457–466.

20. Galperin, M.; Nitzan, A.; Sek, S.; Majda, M. Asymmetric Electron Transmission across Asymmetric Alkanethiol Bilayer Junctions. *J. Electroanal. Chem.* **2003**, *550–551*, 337–350.

21. Chen, C. J. *Introduction to Scanning Tunneling Microscopy*, 2nd ed.; Oxford University Press: Oxford, 2007.

22. Bumm, L. A.; Arnold, J. J.; Dunbar, T. D.; Allara, D. L.; Weiss, P. S. Electron Transfer through Organic Molecules. *J. Phys. Chem. B* **1999**, *103*, 8122–8127.

23. John, N. S.; Pati, S. K.; Kulkarni, G. U. Electrical Characteristics of Layered Palladium Alkanethiolates by Conducting Atomic Force Microscopy. *Appl. Phys. Lett.* **2008**, *92*, 013120–013123.

24. Cammann, K.; Ross, B.; Katerkamp, A.; Reinbold, J.; Renneberg, R. Chemical and Biochemical Sensors. *Handbook of Analytical Techniques*; Günzler, H., Williams, A., Eds.; Wiley-VCH: New York; 2001; *2* pp 951−1059.

25. Hansma, P. K. *Tunneling Spectroscopy: Capabilities, Applications, and New Techniques*; Plenum: New York, 1982.

26. Ho, W. Single-Molecule Chemistry. *J. Chem. Phys.* **2002**, *117*, 11033–11061.

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