

Transition from Direct Tunneling to Field Emission in Metal-Molecule-Metal Junctions

Jeremy M. Beebe,¹ BongSoo Kim,² J. W. Gadzuk,¹ C. Daniel Frisbie,^{3,*} and James G. Kushmerick^{1,†}

¹National Institute of Standards and Technology, Gaithersburg, Maryland 20899, USA

²Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455, USA

³Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, Minnesota 55455, USA

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Current-voltage measurements of metal-molecule-metal junctions formed from π -conjugated thiols exhibit an inflection point on a plot of $\ln(I/V^2)$ vs $1/V$, consistent with a change in transport mechanism from direct tunneling to field emission. The transition voltage was found to scale linearly with the offset in energy between the Au Fermi level and the highest occupied molecular orbital as determined by ultraviolet photoelectron spectroscopy. Asymmetric voltage drops at the two metal-molecule interfaces cause the transition voltage to be dependent on bias polarity.

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The overarching goal of molecular electronics is the design and implementation of nanoscale circuit elements based on the nonlinear current-voltage characteristics of molecules. A number of intriguing current-voltage characteristics have been observed for two-terminal metal-molecule-metal junctions, including negative differential resistance [1,2] and molecular switching [3–5]. Each of these behaviors could potentially prove useful for a range of electronics applications. The ability to rationally design molecular electronic components hinges on a fundamental understanding of the charge transport mechanism in such junctions [6]. To that end, Wang *et al.* have clearly demonstrated that for the case of alkyl-based junctions the charge transport mechanism is direct tunneling over a ± 1 V range [7]. Direct tunneling refers to nonresonant tunneling that occurs when the applied bias is less than the barrier height. The dominance of direct tunneling in alkyl systems is not surprising, due to their large (~ 8 eV) highest occupied molecular orbital–lowest unoccupied molecular orbital (HOMO-LUMO) gaps. In these junctions, a transition to hopping or diffusive transport is difficult, because field-induced breakdown occurs prior to reaching the bias necessary to bring about the change in mechanism [8,9]. In contrast to the alkyl case, the mechanism of charge transport in junctions containing π -conjugated molecules is still under debate. In particular, Selzer *et al.* have demonstrated that the local environment and the means in which molecules are contacted can determine whether tunneling or a thermally activated process dominates charge transport for an oligo(phenyleneethynylene) derivative [10]. In a more general sense, the decreased HOMO-LUMO gap of the conjugated species increases the likelihood of accessing different transport mechanisms, such as resonant tunneling or electron hopping, prior to device breakdown. In this Letter, we provide evidence for a mechanistic transition from direct tunneling to field emission [11] at moderate bias (≤ 1 V) for a number of π -conjugated thiols. This change in mechanism can be described by the transition from a trapezoidal to a

triangular tunneling barrier. By combining the transport results with photoelectron spectroscopy experiments, we are able to correlate the voltage at which the mechanistic transition occurs with the energy level alignment for a given molecular junction.

As mentioned above, direct tunneling is the dominant charge transport mechanism in junctions incorporating alkanes [7] and π -conjugated [10] monolayers. The simplest way to model the current-voltage behavior of a molecular junction is as an arbitrary tunnel barrier within the Simmons approximation [12]:

$$I = \frac{qA}{4\pi^2\hbar d^2} \left\{ \left(\phi - \frac{qV}{2} \right) \exp\left(-\frac{2d\sqrt{2m_e}}{\hbar} \sqrt{\phi - \frac{qV}{2}} \right) - \left(\phi + \frac{qV}{2} \right) \exp\left(-\frac{2d\sqrt{2m_e}}{\hbar} \sqrt{\phi + \frac{qV}{2}} \right) \right\}, \quad (1)$$

where A is the junction area, d is the barrier width, m_e is the electron effective mass, ϕ is the barrier height, and q is the electronic charge. In molecular junctions, the barrier width corresponds to the molecular length, and the barrier height can be approximated by the energy offset between the electrode Fermi level and the nearest molecular orbital. Equation (1) describes a trapezoidal barrier when the applied bias is less than the barrier height. In the zero-bias limit, the barrier is rectangular, and Eq. (1) reduces to

$$I \propto V \exp\left(-\frac{2d\sqrt{2m_e\phi}}{\hbar} \right). \quad (2)$$

At the opposite limit, when the applied bias exceeds the barrier height, the barrier transitions from trapezoidal to triangular, and the current-voltage dependence can be described as follows:

$$I \propto V^2 \exp\left(-\frac{4d\sqrt{2m_e\phi^3}}{3\hbar qV} \right). \quad (3)$$

Tunneling in the high-voltage regime is synonymous with

tunneling through a triangular barrier and with the terms field emission and Fowler-Nordheim tunneling [13]. To extract meaningful information from the high-voltage regime, it is useful to linearize Eq. (3):

$$\ln\left(\frac{I}{V^2}\right) \propto -\frac{4d\sqrt{2m_e\phi^3}}{3\hbar q}\left(\frac{1}{V}\right). \quad (4)$$

From Eq. (4), it is obvious that a plot of $\ln(I/V^2)$ against $1/V$ will yield a line, the slope of which will depend on the barrier height. Because field emission experiments generally involve barriers with both substantial width and height, no measurable current flows prior to the onset of field emission. Therefore, a transition from direct tunneling to field emission will only be seen for the case of a small barrier height and width, such as is found in metal-molecule-metal junctions. To experimentally examine the transition from direct tunneling to field emission requires recasting Eq. (2) in terms of the variables $\ln(I/V^2)$ and $1/V$ so it can be directly compared to Eq. (4). The resulting equation is as follows:

$$\ln\left(\frac{I}{V^2}\right) \propto \ln\left(\frac{1}{V}\right) - \frac{2d\sqrt{2m_e\phi}}{\hbar}. \quad (5)$$

From Eq. (5), a plot of $\ln(I/V^2)$ against $1/V$ will exhibit a logarithmic growth in the low-bias regime. When the applied bias is near the barrier height, the mechanisms compete, causing a transition from logarithmic growth to linear decay. This transition corresponds to the voltage required to change the shape of the barrier from trapezoidal to triangular. We choose to refer to this special value of applied bias as the transition voltage, or V_{trans} . It should be noted that measurement of V_{trans} provides a means of experimentally estimating the height of the original rectangular barrier. Because the Simmons equation as outlined in Eq. (1) does not explicitly account for voltage drops at the contacts or the image potential of the tunneling electron, V_{trans} remains an estimate, and not an exact measure of the barrier height.

To examine the current-voltage behavior of molecular junctions, two platforms were employed: conducting probe-atomic force microscopy (CP-AFM) [8,14–16] and crossed-wire tunnel junctions [17,18] (Fig. 1). In both techniques, molecules are self-assembled onto one electrode using thiol-Au chemistry. The second electrode is then placed into soft mechanical contact with the molecular layer, thereby avoiding the damage that can be induced by evaporated top contacts [19,20]. In both platforms, a bias (± 1.0 V) is swept at the top electrode, the bottom electrode is held at ground, and the current through the junction is measured. Reported values are the averages of 20–100 I - V traces per self-assembled monolayer. In this Letter, we focus on a collection of π -conjugated molecules terminated in thiol linkers (Fig. 1). The method of assembly, monolayer characterization, and low-bias current-voltage behavior of these molecules has been previously

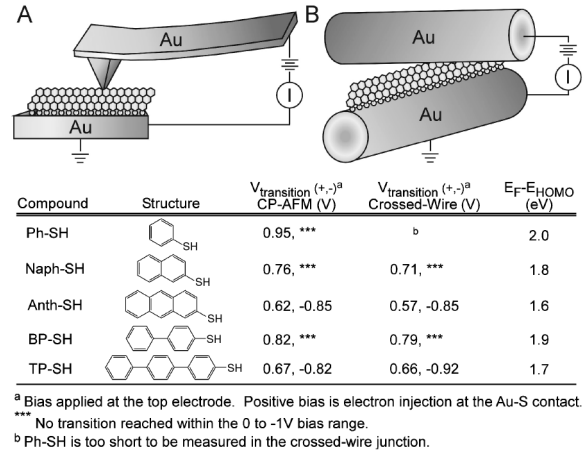


FIG. 1. Schematic representation of (a) CP-AFM and (b) crossed-wire molecular junctions. The table included within the figure shows our adopted nomenclature as well as the structures, transition voltages, and energy level offsets for each of the molecules used in this study. Positive bias corresponds to electron (hole) injection at the Au-S (Au-phenyl) interface.

reported [21]. All molecules studied are known to form monolayers of similar surface coverage on Au surfaces.

Figure 2 shows the average of 100 I - V traces for a Au-anthracenethiol-Au junction collected using CP-AFM, plotted on the axes specified by Eq. (4). The inset displays the same data plotted on standard current-voltage axes. Though a systematic study of the temperature dependence of the current-voltage data is necessary to unambiguously assign a charge transport mechanism, it is likely that the mechanism is direct tunneling at low bias. This assertion is supported by the conclusions of Selzer *et al.* regarding π -conjugated monolayers [10], the sigmoidal shape of

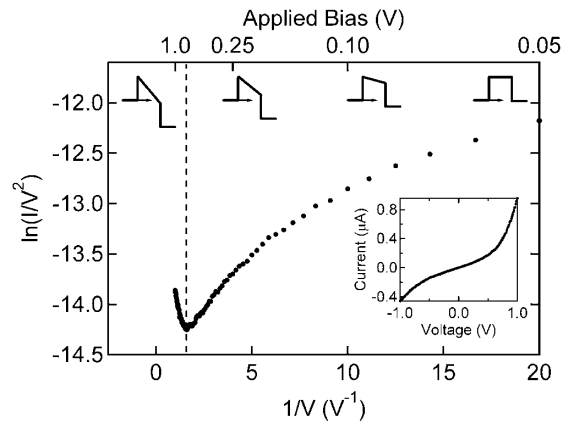


FIG. 2. Solid circles represent the average of 100 I - V curves for a Au-anthracenethiol-Au junction measured by CP-AFM. The dashed line corresponds to the voltage at which the tunneling barrier transitions from trapezoidal to triangular (V_{trans}). Also shown are representations of the barrier shape at various values of applied bias. The inset shows current-voltage data on standard axes.

the I - V curve shown in Fig. 2, and the previously observed exponential dependence of resistance on molecular length [21]. The dashed line in Fig. 2 denotes the voltage required for transition from direct tunneling to field emission (V_{trans}) for anthracenethiol. The shape of the curve in the two bias regions matches the shape predicted by Eqs. (4) and (5) (linear decrease at high bias and logarithmic growth at low bias). There is no evidence of negative differential resistance at any point in the curve, suggesting that the mechanistic transition is not one of nonresonant to resonant tunneling. Each molecule employed in this study exhibited a data curve qualitatively similar to that shown for anthracenethiol. Measurements on alkanethiol junctions (not shown) do not exhibit a V_{trans} inflection point over the same ± 1 V range, consistent with the conclusions of Wang *et al.* [7] that direct tunneling is the charge transport mechanism in such junctions. Transition voltages for each of the π -conjugated molecules are compiled in Fig. 1. Note the excellent agreement of V_{trans} measured in the CP-AFM and crossed-wire geometries.

Figure 3 shows linear scaling of V_{trans} with the difference in energy between the Au Fermi level and molecular HOMO. In this graph, the x coordinates were determined from ultraviolet photoelectron spectroscopy (UPS) [21]. The linear scaling matches the behavior expected if the barrier height was set by the E_F - E_{HOMO} offset and demonstrates that V_{trans} corresponds to a *molecular signature*. Although linear scaling is observed between V_{trans} and the E_F - E_{HOMO} offset, there is a significant discrepancy between the barrier heights predicted by these two methods. The effective barrier lowering observed in the charge transport measurements can be attributed to a number of factors. Primarily, we are modeling the tunnel barrier as a simple geometric shape (rectangular, trapezoidal, triangular), and are not taking into account the image potential, which would effectively reduce the area of the potential barrier by rounding off the corners and reducing the thickness [12]. Proper modeling of these systems should use a molecularly derived potential barrier [22]. Another reason

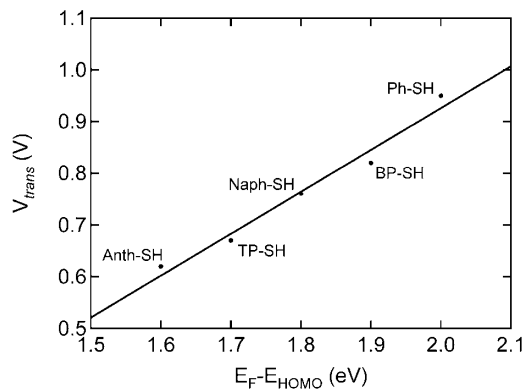


FIG. 3. V_{trans} (CP-AFM) versus E_F - E_{HOMO} energy difference (UPS).

for the difference between the value of V_{trans} and E_F - E_{HOMO} is that the position of the HOMO level was determined from the peak maxima in the UPS [21]. The onset of the UPS peak would yield a better match with V_{trans} ; however, the difficulty in unambiguously assigning this value precludes its use.

It is important to note that there is a strong dependence of V_{trans} on bias polarity (Fig. 1). In all cases, V_{trans} is lower when a positive bias is applied to the Au-phenyl interface. We attribute this directly to the asymmetry in the two metal-molecule contacts. We have previously shown how such contact asymmetries can lead to rectification in molecular junctions due to unequal voltage drops at the two interfaces [17,23]. Similarly, we have demonstrated that symmetric dithiols exhibit lower contact resistance (less voltage drop) than asymmetric monothiols [24]. Figure 4 shows schematically how V_{trans} is affected by asymmetric voltage drops at the two metal-molecule interfaces. The energy diagrams are drawn to correspond to the specific (hypothetical) case of a drop of 50% of the applied bias at the left contact, and 50% across the molecule, with no voltage drop at the right contact. In Figs. 4(b) and 4(c), the magnitude of the applied bias is constant, but the polarity is opposite. In Fig. 4(b), enough bias is applied to cause a transition from a trapezoidal barrier to a triangular barrier. From the diagram in Fig. 4(c), it is obvious that the barrier has not yet become triangular. The monothiol molecules used in this study lead to an inherent asymmetric voltage drop at the two metal-molecule contacts. Reexamination of the data in Ref. [18] shows that symmetric dithiols with phenylene-vinylene and phenylene-ethynylene backbones exhibit identical values of V_{trans} for both bias polarities. This confirms that the observed polarity dependence of V_{trans} is a direct consequence of the asymmetric metal-molecule contacts.

A final point is that the barrier shape transition model holds for different test platforms. As shown in Fig. 1, the transition voltage as measured by CP-AFM agrees well with that measured by crossed-wire junctions for a given

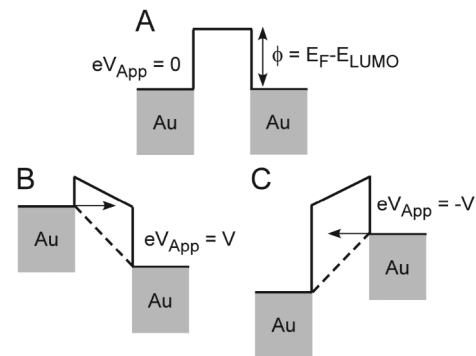


FIG. 4. Effect of asymmetric voltage drops on V_{trans} . Note that the figure is drawn for LUMO-mediated electron tunneling, but the model also applies for HOMO-mediated hole tunneling. See text for full description.

molecule. We determine the standard deviation of the transition voltage to be 0.07 V. Therefore, the slight differences between V_{trans} measured by CP-AFM and by crossed-wire junctions are within the measurement uncertainty. This cross-platform agreement highlights the fact that the observed behavior depends on the identity of the molecule in the junction, and not on the manner in which the junction was fabricated. The junction area, electrode roughness, and applied load are different for the two platforms, yet both techniques measure the same value of V_{trans} for a given molecule. In a field where measurement of the same molecule in different device platforms often yields widely varying data, this result supports not only the validity of the model, but also the quality of data obtained from both test structures.

In summary, we have demonstrated that Au-molecule-Au junctions formed from π -conjugated thiols exhibit current-voltage behavior consistent with a transition from a trapezoidal barrier to a triangular barrier at moderate bias. The voltage required to bring about this transition was found to depend linearly on the energy offset between the junction Fermi level and molecular HOMO as measured by UPS. The linear dependence of V_{trans} on the HOMO position demonstrates that this measurement provides an alternative method to determine the apparent height of the tunneling barrier in molecular junctions. The observed shift in V_{trans} with bias polarity demonstrates the importance of interfacial voltage drops in determining the current-voltage behavior of molecular devices. We are currently examining the effect of varying the metal at either contact, as changing the metal will change the alignment of the molecular HOMO relative to the junction Fermi level [25]. Preliminary results show V_{trans} to be temperature dependent, and we are currently exploring the implications of this temperature dependence on the proposed mechanism. Further, we are developing a more detailed numerical treatment of the observed tunneling barrier transition in order to directly incorporate the effects of voltage drops at the metal-molecule interfaces.

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*Electronic address: frisbie@cems.umn.edu

†Electronic address: james.kushmerick@nist.gov

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