Current-Voltage Characteristics of Self-Assembled Monolayers by Scanning Tunneling Microscopy

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This paper presents a comparison of the theoretical and experimental current-voltage (*I-V*) characteristics of a self-assembled monolayer of α,α'-xylyl dithiol molecules on a gold substrate measured with a scanning tunneling microscope probe. Good quantitative agreement is obtained with the tip-molecule distance as the only "fitting parameter." Several other thiol-coupled molecules that we have studied also show similar agreement. The conceptual picture presented in this paper could be useful for the interpretation of *I-V* measurements on molecular monolayers in general. [S0031-9007(97)04094-5]

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Scanning tunneling microscope (STM) images of self-assembled monolayers of different molecules on different substrates (typically gold, [1]) have been reported by many groups. Such images are obtained by recording the *z* coordinate of the tip as it scans the surface at a fixed current [2]. However, there are relatively few reports of current-voltage (*I-V*) characteristics through such molecular monolayers [3–6]. Quantitative comparisons of the theoretical and experimental *I-V* characteristics are limited to the low bias regime (for C_{60} molecules [7]), or to structures with intervening metallic clusters whose *I-V* is limited by the Coulomb blockade due to the cluster [8,9]. This paper presents what is probably the first report describing a quantitative comparison of the theoretical and experimental *I-V* characteristics of individual molecules. Good agreement is obtained with the tip-molecule distance as the only "fitting parameter," providing support for the basic picture for molecular conduction reported last year by a number of groups [10–13]. However, this agreement is obtained only if the potential drop between the molecule and the substrate is taken into account. The conceptual picture presented in this paper could be useful for the interpretation of *I-V* measurements on molecular monolayers in general.

Molecular monolayers generally attach strongly to the gold surface through thiol (—S—) end groups [14,15] giving a strong chemical bond with good orbital overlap. The other contact, typically an STM probe (see Fig. 1), is usually coupled weakly to the molecule. It is commonly assumed that the applied potential eV is dropped entirely between the tip and the molecule, while the molecular potential remains fixed with respect to the substrate [see Fig. 2(b), with $V_{\mathrm{mol}} = 0$]. For a positive substrate voltage (as shown) the molecule conducts strongly as the electrochemical potential in the tip, μ_2, approaches the lowest unoccupied molecular orbital (LUMO); for negative substrate voltage the molecule conducts strongly as μ_2 approaches the highest occupied molecular orbital (HOMO). Based on this picture we should expect the *I-V* characteristics to be strongly asymmetric for all thiol-coupled molecules since the HOMO is a sulfur-based level that couples strongly to the gold while the LUMO is a ring-based level that couples only weakly. The current should thus be much smaller for positive substrate voltage (conduction through the LUMO) than for negative substrate voltage (conduction through the HOMO). However, all the molecules we have studied so far show symmetric *I-V* characteristics (unless the tip is moved very far from the molecule). We see no simple explanation for this observation as long as we assume that the molecular potential remains fixed with respect to the substrate. But, as we will show in this paper, the symmetry of the *I-V* characteristics is explained quite easily once we take the shift in the molecular energy levels under bias into account.

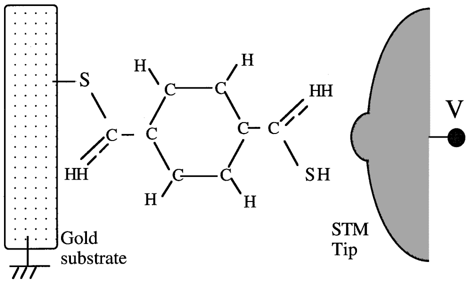

FIG. 1. Self-assembled monolayer of α,α'-xylyl dithiol on a gold substrate (only one molecule of the monolayer is shown for clarity). Also shown schematically is an STM probe used to measure the current-voltage characteristics.

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What is the potential profile?—We assume that the current flows through an individual molecule without any significant lateral conduction through the molecular monolayer. The assumption that the molecular potential is fixed with respect to the substrate is usually justified by arguing that the substrate-molecule resistance R_1 is much smaller than the tip-molecule resistance R_2. Since the current I is the same across either junction, one can write [see Fig. 2(a)]

$$I = \frac{\mu_{\text{mol}} - \mu_1}{R_1} = \frac{\mu_2 - \mu_{\text{mol}}}{R_2} \Rightarrow \frac{\mu_{\text{mol}} - \mu_1}{\mu_2 - \mu_1} = \frac{R_1}{R_1 + R_2} \rightarrow 0$$

as $R_2/R_1 \rightarrow \infty$. However, what this argument proves is that the *electrochemical potential* in the molecule (μ_{mol}) is the same as that of the substrate (μ_1), as shown in Fig. 2(a) [16]. It says nothing about the *electrostatic potential* $\varphi(\mathbf{r})$ which can vary spatially in inhomogeneous conductors even in equilibrium. Such equilibrium variations in $\varphi(\mathbf{r})$ are already included in the calculation of the molecular energy levels. What we need to know is the *change* $\delta\varphi(\mathbf{r})$ in the electrostatic potential under bias which enters the molecular Hamiltonian and affects the molecular energy levels (the electrochemical potential enters only indirectly through charging effects).

To see what $\delta\varphi(\mathbf{r})$ looks like, we first note that inside the substrate or the tip it must be zero, since these regions are charge neutral. If we neglect any charge buildup inside the molecule, $\delta\varphi(\mathbf{r})$ inside the molecule can be obtained by solving the Laplace equation $\nabla^2(\delta\varphi) = 0$. If we view the STM tip and the gold substrate as the two plates of a parallel plate capacitor then the electrostatic potential will vary linearly, as shown in profile C of Fig. 2(a), and the average electrostatic potential in the molecule V_{mol} can be written as $V_{\text{mol}}/V = z_{\text{mol}}/L$, where z_{mol} and L are the distances from the substrate to the center of the molecule and the tip, respectively. To the lowest order of approximation, we can assume that the molecular energy levels simply float up by an amount eV_{mol}. More conveniently, we can take the molecular energy levels as a fixed reference and let the substrate float down by eV_{mol}, as shown in Fig. 2(b):

$$\mu_1 = E_f - \eta eV$$

and

$$\mu_2 = E_f + (1 - \eta)eV \tag{1}$$

(note that $e = -1.6 \times 10^{-19}$ C), where the factor η describes how the electrostatic potential difference V is divided between the two junctions: $\eta \equiv V_{\text{mol}}/V = z_{\text{mol}}/L$. Since the tip has to be within a few angstroms from the end of the molecule in order for the current to be measurable, V_{mol} is approximately half the applied voltage V ($\eta \cong 0.5$).

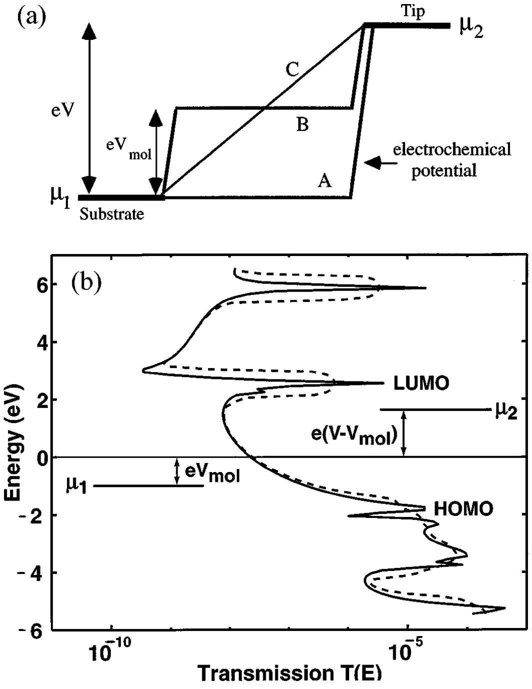

FIG. 2. (a) If we assume that the electrostatic potential varies linearly from the substrate to the tip (C), the average electrostatic potential in the molecule (V_{mol}) will be about half the applied voltage V. The electrochemical potential (A) in the molecule is approximately the same as that of the substrate. (b) Transmission function $T(E)$ through the molecule from the tip to the substrate with (solid) and without (dashed) scattering. Taking the molecular potential as our reference, μ_1 moves down by eV_{mol} while μ_2 moves up by $e(V\text{-}V_{\text{mol}})$ where V_{mol} is the average electrostatic potential in the molecule.

Effect of η on the I-V characteristics.—Figure 2(b) shows the transmission function through the molecule from the tip to the substrate which is calculated using an extended Hückel model for the molecule and taking the metal-molecule bonding into account. It shows peaks at energies corresponding to the molecular energy levels which are broadened further if we include scattering processes in the molecule. The strong asymmetry in the transmission for the levels above and below the gap is evident. Depending on the value of η (that is, V_{mol}), we can obtain very different predictions for the I-V characteristics. If $\eta = 0$, μ_1 is fixed with respect to the molecule. The molecule then conducts strongly when μ_2 coincides with the energy of a molecular orbital, that is, when

$$eV > E_L - E_f \text{ (positive substrate voltage)}$$

or

$$-eV > E_f - E_H \text{ (negative substrate voltage)}.$$

The conductance spectrum shows a gap of $(E_L - E_H)$ equal to the molecular gap. This is the usual case in STM measurements. But consider what happens if η is approximately 0.5 and neither μ_1 nor μ_2 remains fixed with respect to the molecule. The molecule then conducts strongly when either μ_1 or μ_2 coincides with a molecular orbital energy so that the threshold for conduction is given by

$$eV > \min\left(\frac{E_f - E_H}{\eta}, \frac{E_L - E_f}{1-\eta}\right) \quad \text{(positive substrate voltage)} \tag{2a}$$

or

$$-eV > \min\left(\frac{E_f - E_H}{1-\eta}, \frac{E_L - E_f}{\eta}\right) \quad \text{(negative substrate voltage)}, \tag{2b}$$

where min(x,y) denotes the smaller of the quantities x and y.

It is easy to see from Eq. (2) that with $\eta \cong 0.5$ the molecule could conduct through the HOMO *for both bias polarities leading to symmetric I-V characteristics,* if the equilibrium Fermi energy E_f is closer to the HOMO than to the LUMO. This is what we find in all the thiol-coupled molecules when we locate the equilibrium Fermi energy E_f using the relation

$$N = 2(\text{for spin}) \times \sum_i \frac{1}{\pi} \tan^{-1} \frac{\Gamma_i}{\varepsilon_i - E_f}, \tag{3}$$

where Γ_i is the broadening of the energy level located at ε_i and N is the number of electrons in the molecule [17]. The procedure used to calculate Γ_i, ε_i is described below. For α, α'-xylyl dithiol [shown in Fig. 1(a)], we find

$$E_f - E_H = 1.8eV, \qquad E_L - E_f = 2.2eV. \tag{4}$$

From Eqs. (2) and (4) we expect the threshold bias for conduction to be approximately 3.6 V for either bias polarity if we assume $\eta = 0.5$. The calculated *I-V* based on this assumption fits the experimental data quite well, as shown in Fig. 3(a). A calculation with $\eta = 0$, on the other hand, shows hardly any current for positive substrate bias and is clearly in disagreement with experiment.

Theory.—Let us briefly describe the procedure used to calculate the *I-V* shown in Fig. 3. We use the standard expression for the current based on the scattering theory of transport [18]:

$$I = \frac{2e}{h} \int_{-\infty}^{+\infty} dE\, T(E) [f(E - \mu_1) - f(E - \mu_2)]. \tag{5}$$

Here $T(E)$ is the transmission function from the tip to the substrate and $f(E)$ is the Fermi function. The electrochemical potentials μ_1 and μ_2 are obtained from Eq. (1), with the equilibrium Fermi energy E_f located from Eq. (3) as described earlier. We use the extended Hückel method [19] to obtain the Hamiltonian (H) for the isolated molecule and include the effect of the contacts through self-energy functions (Σ) that are calculated taking the proper metal-molecule coupling into account [20]. The eigenenergies of ($H + \Sigma$) are complex: $E_i = \varepsilon_i + i\Gamma_i$. The real part ($\varepsilon_i$) is the energy of a level while the imaginary part (Γ_i) represents its broadening due to the coupling to the metal and describes how effectively the level can empty into the metallic reservoirs. The transmission function $T(E)$ is calculated from H and Σ as described in [12]. It shows peaks at energies corresponding to the molecular energy levels [see Fig. 2(b)]. If we include scattering processes in the molecule through an additional self-energy function [21], the peaks are broadened further, as we would expect. This has no significant effect on the *I-V* characteristics shown in Fig. 3, apart from rounding out the cusps.

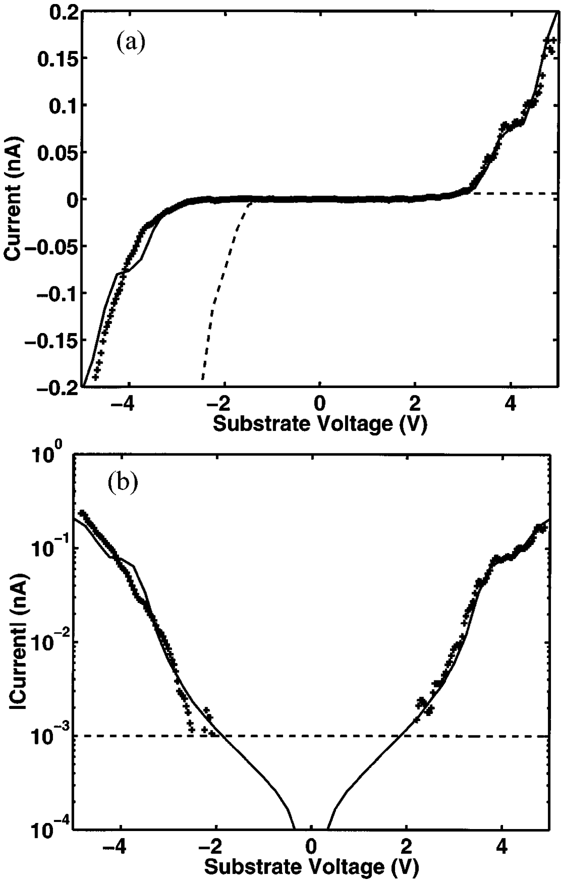

FIG. 3. (a) Current-voltage characteristic for the molecule shown in Fig. 1 plotted on a linear scale: $\eta = 0.5$ (solid), $\eta = 0$ (----), and measured (+). (b) Current-voltage characteristic for the molecule shown in Fig. 1 plotted on a logarithmic scale: $\eta = 0.5$ (solid), and measured (+). Horizontal dash-dotted line represents the noise limit of our preamplifier.

Results—Figure 3(a) shows the experimental *I-V* characteristics measured in ultrahigh vacuum ($\sim 3 \times 10^{-10}$ Torr) with a set current of 0.25 nA at 5 V. The experimental procedure is essentially the same as that described in Ref. [8], except that there is no intervening cluster between the tip and the molecule. There is good agreement between the experiment and the theoretical calculation from Eq. (5) with $\eta = 0.5$. By contrast, with $\eta = 0$ there is hardly any current for positive substrate bias due to the weak coupling to the LUMO, in clear disagreement with experiment. Figure 3(b) shows the

I-V characteristics on a logarithmic scale showing that the agreement (with $\eta = 0.5$) is good over several orders of magnitude of the current. Note that there is no fitting parameter in this calculation apart from the distance from the tip atom to the sulfur atom, which is adjusted to give the same magnitude of the current as the experiment [22].

Discussion and conclusions.—It is evident from Fig. 3 that there is clear disagreement with experiment if we assume that the electrostatic potential follows curve *A* in Fig. 2(a) (the same as the electrochemical potential). We see no simple way to explain the observed characteristics based on profile *A*. But excellent agreement is obtained if we assume that the electrostatic potential follows profile *B* with $V_{\mathrm{mol}} = 0.5$ V (that is, $\eta = 0.5$). The actual electrostatic potential should be calculated from the Poisson equation $\vec{\nabla} \cdot (\varepsilon \vec{\nabla} \delta \varphi) = \delta \rho$, where the change in the charge density $(\delta \rho)$ has to be determined self-consistently [23]. An exchange-correlation potential corresponding to $\delta \rho$ should also be included in the calculation of the molecular energy levels. We find $\delta \rho$ to be negligible for most of the bias range considered here. With $\delta \rho \cong 0$, the potential profile would be linear (profile *C*). However, the agreement with experiment deteriorates significantly if we use profile *C* instead of profile *B*, leading us to believe that the latter is closer to the actual profile. This could be justified by arguing that the molecule has a higher dielectric constant ε compared to the gaps at the ends. The theoretical model presented here should be viewed only as a first step towards a more complete theory that includes other details such as the correct self-consistent potential profile or the structure in the density of states in the contacts. However, we find that the simple model presented here leads to good agreement with experiment not only for α, α'-xylyl dithiol (described in this paper), but also for a number of other thiol-coupled molecules that we have studied. In some cases, an adjustment of the equilibrium Fermi energy E_f leads to better fits with experiment; this can be justified by the fact that E_f is very sensitive to small amounts of broadening and charge transfer. Also, the *I-V* characteristics become asymmetric (like the ones reported in Ref. [4]) when the tip is moved very far from the molecule, but the data can still be described by our model using a suitably modified η.

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[16] In general, a molecule driven far from equilibrium may not have a well-defined electrochemical potential. But if it is strongly coupled to one reservoir (substrate) relative to the other reservoir (tip) as in this case, it remains nearly in equilibrium with the former.

[17] In estimating *N*, we take into account the fact that the molecule has a fractional negative charge (about 0.2 electrons) transferred from the gold contacts. Alternatively, we can include a few gold atoms at each end as part of the molecule. Either approach gives the same result.

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[20] The method used here is essentially the same as that described in Ref. [12], except that the *d* orbitals have been left out completely. A constant density of states is used for the contacts equal to the value at the Fermi energy.

[21] See Ref. [18], Chap. 8, and references therein.

[22] For simplicity, the theoretical model assumes a gold tip bonded to the sulfur atom in the same way as the gold substrate, except that the gold-sulfur distance is longer. In the experiment, Pt/Ir tips were used.

[23] The self-consistent field approach should be adequate, because the strong coupling to the substrate broadens the levels by an amount comparable to the charging energy, which we estimate to be less than 1*eV* from the electron affinity data available for isolated molecules in the gas phase. For weakly coupled molecules, it may be necessary to take single electron charging effects into account.