

## Negative differential resistance in the scanning-tunneling spectroscopy of organic molecules

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In the interpretation of scanning-tunneling spectroscopy data on molecular nanostructures the tunneling conductance is often assumed to be proportional to the local density of states of the molecule. This precludes the possibility of observing negative differential resistance (NDR). We report here the observation of NDR in the current-voltage ( $I$ - $V$ ) characteristics of a self-assembled monolayer of 4-*p*-terphenylthiol molecules on the Au(111) surface measured using a platinum tip. We argue that the NDR arises from narrow features in the local density of states of the tip apex atom and show that depending on the electrostatic potential profile across the system, NDR could be observed in one or both bias directions. [S0163-1829(99)50712-1]

Electron transport through molecular nanostructures has been widely studied in recent years, using the scanning-tunneling microscope (STM) or the mechanically controllable break junction.<sup>1,2</sup> The tunneling conductance  $dI/dV$  is commonly assumed to reflect the local density of states (LDOS) of the molecule:<sup>3</sup>  $dI/dV \sim \rho(E = E_F + eV)$ ,  $E_F$  being the equilibrium Fermi energy. A more accurate description, as proposed in Ref. 1, is to take a weighted average of the density of states:

$$dI/dV \sim \eta \rho(E = \mu_1) + (1 - \eta) \rho(E = \mu_2), \quad (1)$$

where  $\mu_1$  and  $\mu_2$  are the electrochemical potentials of the two contacts, the factor  $\eta$  describes the voltage division across the molecule:  $\mu_1 = E_F - \eta eV$  and  $\mu_2 = E_F + (1 - \eta)eV$ . Based on this viewpoint, NDR, i.e., a negative slope in the  $I$ - $V$  curve, cannot occur since the density of states is non-negative. Experimentally, however, NDR is often observed for monolayers of long molecules self-assembled on the Au(111) surface (Fig. 1 and Fig. 2).

A possible scenario that can lead to NDR at the atomic level was studied theoretically by Lang<sup>4</sup> and experimentally by Avouris and co-workers.<sup>5</sup> The essential argument is that if there is a weak link between two parts of the conducting system, each of which has relatively narrow features in the density of states in the energy range of interest, NDR is likely to occur. This is readily understood from the transfer Hamiltonian point of view,<sup>6</sup> which relates the current to the product of the density of states  $\rho_L$  and  $\rho_R$  on the two sides of the weak link. As the bias is changed, the current can decrease if two narrow features in  $\rho_L$  and  $\rho_R$  move away from alignment. For the structure we studied (Fig. 2), the weak link is the STM tip-molecule junction. If the tip has a featureless density of states, as is implicitly assumed in the derivation of Eq. (1), we would not expect this scenario to apply. However, narrow features in the density of states can develop in a realistic tip. This has been widely recognized in

the STM study of surfaces<sup>6</sup> and has been used to explain the NDR in the  $I$ - $V$  characteristics of boron-exposed silicon surfaces.<sup>5</sup> More recently, Yeyati *et al.*<sup>7</sup> have studied the electronic structure of a sharp gold tip in the context of conductance quantization in the atomic-size gold contacts and shown that narrow resonant states can develop at the tip apex atom if the tip geometry is sufficiently sharp.

In this paper we present an explanation of the occurrence of NDR which takes into account (1) the electronic structure of the sharp platinum tip (used in our STM measurement<sup>8</sup>) and (2) the electrostatic potential profile across the tip/molecule system. Using a tip model similar to Yeyati *et al.*,<sup>7</sup> we find narrow features in the LDOS of the tip apex atom below the equilibrium Fermi energy  $E_F$  [Fig. 3(a)]. Since the LDOS of the molecule also exhibits sharp features, we expect NDR to occur under applied bias. However, since the narrow features in the LDOS of the tip apex atom are

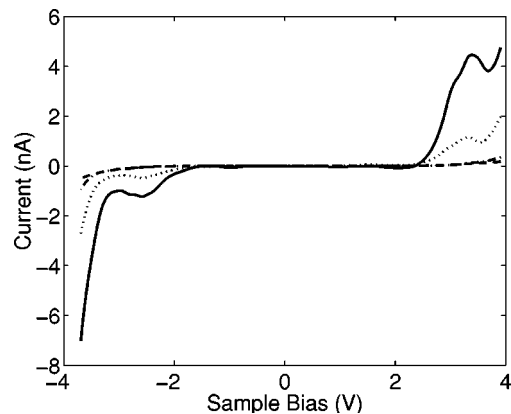


FIG. 1. Experimental  $I$ - $V$  characteristics of the molecule shown in Fig. 2(a) as a function of the molecule-tip distance. A negative differential resistance is observed for small tip/SAM separation. The set point voltage is  $-5$  V; the set point currents range between 3.05 nA and 30.5 nA.

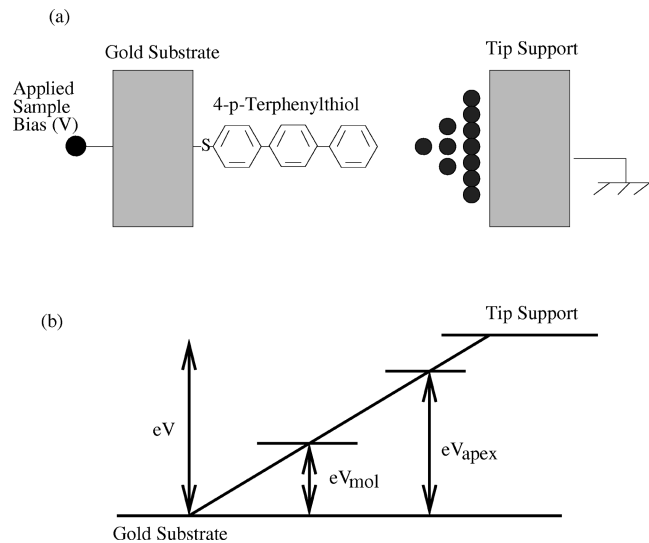


FIG. 2. (a) SAM of 4-*p*-terphenylthiol on the Au(111) surface (only one molecule is shown here for clarity), also shown is the STM tip. (b) Electrostatic potential profile from the gold substrate to the tip support under applied bias (here we only show the case of positive sample bias).

below  $E_F$ , NDR will occur only at positive sample bias if the electrostatic potential of the tip apex atom is the same as that of the tip support. But NDR can occur in both bias directions if a significant amount of the voltage is dropped

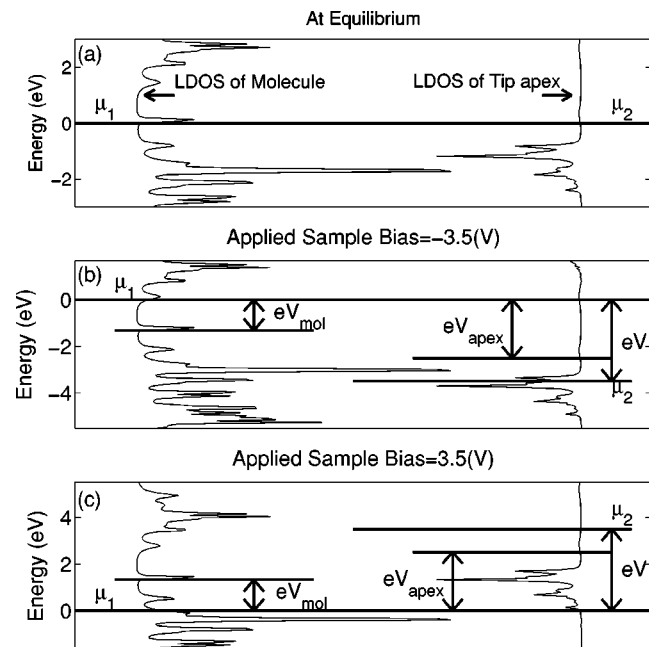


FIG. 3. Illustration of how the narrow features in the LDOS of the molecule and the tip apex atom sweep past each other under applied bias. The electrochemical potential of the gold substrate  $\mu_1$  is taken as energy reference. (The LDOS curves have been horizontally offset for clarity.) Parameters used are the same as those used for the  $I$ - $V$  calculation in Fig. 4(a). (a) At equilibrium,  $\mu_1 = \mu_2 = E_F$ ; (b) at negative sample bias, the LDOS curves of the molecule and the tip apex atom float down relative to the gold substrate; (c) at positive sample bias, the LDOS curves of the molecule and the tip apex atom float up relative to the gold substrate. NDR always occurs before the sample bias reaches  $\pm 3.5$ (V).

between the tip apex atom and the tip support. We argue that for a very sharp tip geometry, this is likely to be true when the tip is close to the molecule. Since the tip is composed of a small cluster of platinum atoms, the screening length in this region can be much larger than that in the bulk and also larger than the cluster size, making it possible to maintain an electrostatic potential drop between the tip apex and the tip support under applied bias. Experimentally, NDR is observed in both bias directions when the tip is very close to the molecule, in agreement with this theoretical scenario.

Our model is illustrated in Fig. 2(a). The self-assembled monolayer (SAM) of 4-*p*-terphenylthiol molecules are synthesized using standard procedure.  $I$ - $V$  data presented in this paper represents the average of 25-50 consecutive  $I(V)$  sweeps taken at a fixed position on the sample.<sup>9</sup> The SAM's attach strongly to the Au(111) surface through the sulfur end atom forming a strong chemical bond with good orbital overlap.<sup>10</sup> The STM tip usually couples weakly to the molecule, corresponding to the physisorption situation. As in our previous studies,<sup>1</sup> we will use the extended Hückel theory (EHT) to describe the whole molecule-STM system (recent justification for using EHT in the STM study of metal surfaces can be found in Ref. 11), taking into account the  $5d6s6p$  orbitals of platinum and gold.

Similar to Yeyati *et al.*,<sup>7</sup> we model the tip geometry as a small cluster of 11 Pt atoms stacked on the (111) surface of the semi-infinite support.<sup>12</sup> The tip is composed of a monoatomic apex, a second layer with three nearest-neighbor atoms and a third layer with seven nearest-neighbor atoms [we have also included 14 Pt atoms on the surface of the tip support and 6 Au atoms on the Au(111) surface in the calculation of  $I$ - $V$  curves]. The on-site energies for the orbitals of the three layers of tip atoms are modified self-consistently by adjusting the occupation number of each orbital to that of the neutral atom until local charge neutrality is achieved on each atomic site, as described in Refs. 7, 11, and 18.

We calculate the current using the standard expression:<sup>13</sup>

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

$$\approx \frac{2e}{h} \int_{\mu_1}^{\mu_2} dE T(E, V), \quad (2)$$

where  $f(E)$  is the Fermi distribution,  $\mu_1, \mu_2$  are the electrochemical potential of the gold substrate and the tip support, respectively, with  $\mu_2 = \mu_1 + eV$ .<sup>14</sup> The transmission  $T(E, V)$  can be calculated using the scattering theory of transport, as we shall describe shortly, but we can get more insight if we use the transfer Hamiltonian formalism<sup>6</sup> to relate the transmission to the local density of states on either side of the STM tip-molecule junction:

$$T(E, V) = 4\pi^2 |M_{LR}|^2 \rho_L(E - eV_L) \rho_R(E - eV_R), \quad (3)$$

where  $M_{LR}$  is the coupling matrix element and  $V_L$  and  $V_R$  are the electrostatic potentials of the molecule and the tip apex atom, respectively.

The LDOS of both the molecule and the tip apex atom show narrow features [Fig. 3(a)], which are calculated from the Green's function of the molecule/tip system using:<sup>15</sup>

$$\rho_{molecule(tip)} = -\frac{1}{\pi} \text{Tr}\{\text{Im}(GS)_{molecule(tip)}\}, \quad (4)$$

where  $G(E)$  is defined by  $G(E)(ES-H)=(ES-H)G(E)=I$ , and  $S$  is the overlap matrix. The narrow features in the LDOS of the tip apex atom can be understood qualitatively from the fact that platinum is a third row transition metal, whose LDOS around the equilibrium Fermi energy  $E_F$  is mostly due to the contribution of the  $5d$  orbitals, located slightly below  $E_F$ . For the given sharp tip geometry, the coupling of the tip apex atom to its local environment is weak, so that the levels remain fairly sharp.

*What is the electrostatic potential profile?* Applying an external bias changes the relative electrochemical potential of the gold substrate and the tip support, which are assumed to act as infinite electron reservoirs. The electrostatic potential  $\varphi(r)$  also changes, whose value is determined by the Poisson equation  $\nabla^2 \delta\varphi(r) = e\delta n(r)$ . Only the change in the electrostatic potential  $\delta\varphi(r)$  needs to be calculated (which in turn modifies the molecular Hamiltonian) since its equilibrium value has been included in the equilibrium Hamiltonian. The change in the electrostatic potential of each electrode follows that of the electrochemical potential and provides the boundary condition for the Poisson equation. It is important to note that the three layers of tip atoms should be treated on an equal footing with the molecule when evaluating the electrostatic potential change, i.e., the whole molecule/tip system is viewed as an ‘‘extended molecule’’ sandwiched between the two electrodes. In the tip region, the electrochemical and the electrostatic potential can be different from those inside the tip support and from each other.<sup>16</sup>

In general, an external electric field will cause charge redistribution in the molecule/tip system, which in turn modifies the applied field until self-consistency is achieved. As a first approximation, we will neglect such charge redistribution within the molecule/tip system, and assume that the gold substrate and the tip support act as two infinite parallel plates of a capacitor. The electrostatic potential then varies linearly, as shown in Fig. 2(b). For simplicity, we assume that the energy levels of the molecule simply float up by an amount  $V_{mol}$  which is taken as a fitting parameter.<sup>17</sup> The origin of NDR can now be understood by examining how the narrow features in the LDOS of the molecule and the tip apex atom sweep past each other under applied bias (Fig. 3). As evident from Fig. 3, NDR will occur in both bias directions if we assume a significant voltage drop between the tip apex and the tip support, i.e.,  $eV_{apex} < eV$ .

It can be seen from Fig. 4(a) that this approach predicts the  $I$ - $V$  characteristics quite well with four fitting parameters, namely the tip-molecule distance, the equilibrium Fermi energy  $E_F$ , the constant coupling matrix element  $M_{LR}$ , and the electrostatic potential change of the molecule. We also calculated the transmission function using the scattering theory of transport (see page 148 in Ref. 13):

$$T(E, V) = \text{Tr}\{\Gamma_L(E)G^R(E, V)\Gamma_R(E - eV)G^A(E, V)\} \quad (5)$$

which takes arbitrary sample/electrode coupling into account. A better fit to the experiment can be achieved by taking charging effects within the molecule into account. In tight-binding theory, this can be done assuming  $V_{mol} = V_0 + U\delta n_{mol}/e$ , where  $V_0$  is the average electrostatic potential

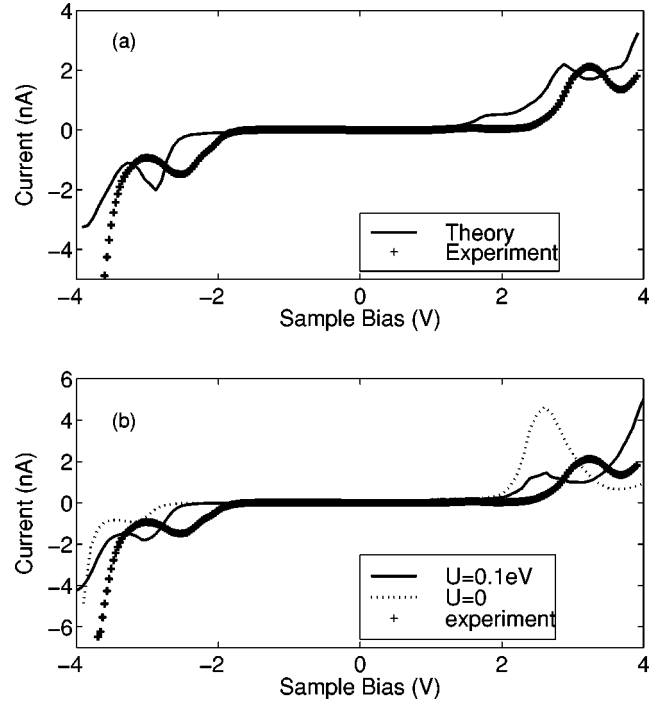


FIG. 4. (a)  $I$ - $V$  characteristics calculated using the transfer Hamiltonian theory for tip-molecule distance = 3.50 Å. Parameters used are  $|M_{LR}|^2 = 8.2 \times 10^{-8}$  (eV)<sup>2</sup>,  $E_F = -11.05$  (eV), and  $V_{mol} = 0.4$  V. (b)  $I$ - $V$  characteristics calculated using the scattering theory for tip-molecule distance = 3.50 Å,  $E_F = -11.15$  (eV).

change of the molecule without charge buildup and  $\delta n_{mol}$  is the excess number of electrons in the molecule induced by the applied bias. Since the molecule is strongly coupled to the gold substrate, we can assume that it is in equilibrium with the gold substrate and obtain  $\delta n_{mol}$  and  $V_{mol}$  from the following self-consistent equation:

$$\begin{aligned} \delta n_{mol} &= \int_{-\infty}^{\mu_1} \rho_{mol}(E - eV_{mol}) dE - \int_{-\infty}^{\mu_1} \rho_{mol}(E) dE \\ &= \int_{\mu_1}^{\mu_1 - eV_0 - U\delta n_{mol}} \rho_{mol}(E) dE. \end{aligned} \quad (6)$$

The charging energy for an isolated molecule,  $U_0$ , can be estimated from the energy gap  $E_g$  in the molecular optical spectra, the electron affinity  $A$ , and the ionization potential  $I$  of the molecule:  $U_0 = (I - A - E_g)/2 \sim 0.75$  eV, using  $I - A \sim 4$  eV and  $E_g \sim 2.5$  eV.<sup>19</sup> In the present configuration, we expect that the charging energy can be reduced significantly due to the presence of the semi-infinite substrate.<sup>18</sup> In fact we find that the best fit to the experiment is obtained with  $U = 0.1$  eV [Fig. 4(b)].

In conclusion, we have presented a simple explanation for the NDR observed in the STM  $I$ - $V$  characteristics of a self-assembled monolayer of 4-*p*-terphenylthiol molecules in terms of the electronic structure of the sharp platinum tip. The major approximation in our theory is the use of the extended Hückel theory and a simplified treatment of the electrostatic potential variation. A central factor in understanding the NDR is the narrow features in the LDOS of the tip apex atom which has been noted by other authors in different contexts. However, this alone is not enough to ex-

plain the occurrence of NDR in both bias directions. NDR for negative sample bias can be understood only if we allow for an electrostatic potential drop between the tip apex and the tip support. This is possible for very sharp tip geometries, where the screening length is large. But if the tip is relatively flat, the potential drop between the tip apex atom and the tip support will be reduced. Indeed, experimentally for some of our tips we do observe NDR for positive sample bias only. However, even with these tips, we often observe NDR in both bias directions when we move the tip closer to the molecule, indicating a significant increase in the potential drop between the tip apex and the tip support. It is not clear to us why the potential drop should increase significantly, since the distance range by which the tips move is relatively small.

We believe that a more complete theory is needed that evaluates both the electron density distribution and the potential variation self-consistently for the entire electrode/sample system, along the lines described by Lang.<sup>20</sup> This is currently under investigation. Our main purpose here is to show that the electrostatic potential profiles play a crucial role in determining the shape of the  $I$ - $V$  characteristics of molecular nanostructures—a role that has not been adequately recognized.

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