

Models of electron transport through organic molecular monolayers self-assembled on nanoscale metallic contacts

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We propose a model of electrical conduction through self-assembled monolayers (SAM's) of organic molecules that bridge the gap between a pair of nanoscale metallic contacts. In this model each molecule bonds chemically to only one of the contacts. For dense SAM's the dominant electric current path is through two overlapping molecules each bonded to a different metal contact whereas for dilute SAM's the current flows through a single molecule. The model accounts quantitatively for the experimental data of M. A. Reed *et al.* [Science **278**, 252 (1997)] on gold break junctions containing benzene-dithiol (BDT) SAM's, including the magnitude of the measured differential conductance. It also accounts for the striking differences between the data on the Au/BDT system and the recent measurements of J. Reichert *et al.* [cond-mat/0106219, 2001 (unpublished)] on a somewhat different system, namely, the strong asymmetry of the current-voltage characteristic and the larger size of the differential conductance found in latter experiments. We also present calculations of electron transport through dense and dilute SAM's of $\text{SC}_6\text{H}_4\text{S-CH}_3$ molecules. Experiments on these systems should test the validity of the proposed model.

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I. INTRODUCTION

During the past few years there have been several remarkable experiments measuring electrical conduction through small organic molecules connecting nanoscale metallic contacts.^{1–6} The experiments showed that these novel molecular wire systems have a variety of interesting transport properties such as rectification,³ negative differential resistance,⁷ and switching behavior⁴ to name just a few. There has also been theoretical work providing insights into the measured phenomena.^{2,8–15}

Some of these molecular wire experiments involved the measurement of the electrical conductance of self-assembled molecular monolayers (SAM's) bridging a mechanically controlled metal break junction.^{1,6} A break junction is made by spanning two metallic contacts by a metallic nanowire, which is then stretched and broken using piezos. This yields two atomically sharp metallic nanocontacts. In the experiments^{1,6} the break junction was exposed to a solution of the organic molecule of interest. The molecules, which were functionalized at both ends with a chemical group that binds with the metal, self-assembled onto both of the metallic tips. The solution was then evaporated, leaving behind two metal tips coated with organic molecules. The tips were then brought together, a bias voltage was applied between them and the resulting electric current that flowed from tip to tip through the SAM's was measured.

In the first experiment of this type 1,4 benzene-dithiol (BDT) molecules formed the self-assembled monolayers on the tips of a gold break junction.¹ The break junction was exposed to a solution of BDT for a long period of time, resulting in high coverage SAM's on both gold tips. Measurements on this system at room temperature displayed an apparently insulating region for bias values between approximately -0.7 and 0.7 volts, nearly symmetric differential

conductance in the range from -4 to $+4$ volts and some asymmetry at higher bias. The measured conductance was much lower than the quantum $2e^2/h$ that sets the conductance scale for single-channel metallic nanowires; the first conductance plateau occurred at a resistance of $22\text{ M}\Omega$. More recently, experiments have been performed with similar but somewhat larger molecules, with SAM's of much lower coverage on the gold tips.⁶ These systems displayed quite different properties than in the first experiment: The differential conductance was sometimes asymmetric and the current could only be measured to approximately 1 volt before breakdown occurred. The measured current was also larger than in the first experiment, a resistance of $1\text{ M}\Omega$ being measured at a bias of 1 V . The reasons for these differences are not fully understood, however it has been suggested⁶ that the conductance asymmetry observed in the latter experiments⁶ may be due to the molecule being more strongly coupled electrically to one metal tip than to the other.

There have been several theoretical studies of the BDT/gold break-junction system and they have yielded qualitatively similar results.^{11,13–15} All of these studies considered a single molecule bridging the two gold contacts with a chemical bond formed between each gold tip and the molecule. They all found a region of lower differential conductance at low bias due to the Fermi level of the gold contacts falling within the HOMO-LUMO gap of the molecule, and strong increases in the differential conductance at higher biases due to the onset of transport through resonant states of the molecule hybridized with the metal tips. The calculated conductance curves were symmetric in the bias voltage since the molecule was assumed to be bonded symmetrically to the two gold contacts. These features of the calculated conductance resemble the experimental data qualitatively and the increases in the calculated conductance occur at values of the bias voltage similar to those in the experiment. However the

magnitudes of the calculated electric currents and differential conductances^{11,13–15} exceeded the experimentally measured values¹ by factors ranging from approximately 20 to several hundred, depending on the specifics of the molecular wire geometry being modeled.

In this article, we explore an alternate explanation of the first experiment¹ and find that it is able to account for the observed data. The first puzzle that it addresses is why the observed conductance is so low, even though it has been demonstrated theoretically^{11,13–15} that the system has the potential to exhibit much higher conductances. A second question that it addresses is why the observed current-voltage characteristic of the system changes little when the break junction with the SAM's is pulled apart and brought back together many times at room temperature,¹ even though within the framework of the previous theoretical models this process would require the breaking of chemical bonds and the attendant local disruption and possible rearrangement of the SAM's and/or gold atoms involved in the bonding. A third question that it addresses is why one experiment¹ displays a symmetric differential conductance curve while the other⁶ is occasionally asymmetric. It also accounts for the magnitude of the measured conductance being considerably larger in the second experiment⁶ than in the first.¹

In the model that we propose here, each molecule is chemically bonded to only one contact. In the first experiment¹ where the SAM coverage is high, we suggest that the current is carried not through one single molecule, but through (at least) an overlapping pair of molecules, with one molecule bonded to each tip. It has been previously shown theoretically, that having neighboring molecules through which the current can flow can have important consequences.⁹ Here we consider the effects that overlapping BDT molecules may have in the break-junction measurement.

In the present model the low observed conductance in the first experiment¹ is a consequence of the weak electrical coupling between the two overlapping molecules: Although each molecule may have strong electrical coupling to the lead to which it is attached, the rate limiting step is the transmission of electrons between the two molecules. This is akin to electrical conduction in graphite, which consists of stacked graphene layers: The in-plane conductivity is metallic, while the conductivity perpendicular to the planes is lower by two or more orders of magnitude.¹⁶ In the present model because no chemical bonds are formed between the overlapping molecules or between the two leads, the SAM's are easily pulled apart with no requirement for bond breaking and the process is reversible. Regarding the observed symmetric behavior of the differential conductance,¹ we argue that this symmetry arises from the system having the ability to sample all possible energetically favorable configurations of the overlapping molecules. Hence even though a given configuration of the two molecules may be asymmetric, because of thermal fluctuations the mirror configuration will also be sampled. Hence the average over the transport properties of all configurations yields a symmetric result, the small residual asymmetry of the current voltage characteristic in the first experiment¹ being due to differences between the atomic

structures of the two tips. For experiments where the SAM coverage is low, asymmetric coupling can occur between the two metallic contacts.⁶ This has been shown to lead to asymmetric differential conductance.¹⁷ The break down at relatively low bias in the second experiment occurs because the gold tips form a short, since they are not stabilized by a dense SAM.⁶

Finally an experiment comes readily to mind that would test the above explanation: Instead of using a molecule that has thiols on both ends, consider a molecule that is capped on one end by a group such as CH_3 that is known not to form a chemical bond to gold¹⁸ so that a single molecule *cannot* bond to *both* metal tips. We show below that if the tips are coated with dense SAM's of such molecules then behavior very similar to that observed in the BDT break junction system¹ should occur because the current would be carried through a pair of overlapping molecules rather than through a single molecule. However, for low density SAM's where the occurrence of an overlapping pair of molecules at the tips is unlikely, asymmetric differential conductance should be observed. Our calculations for the CH_3 -capped BDT system also indicate that if the current flows from contact to contact through a *single* molecule quite high electron transmission probabilities can be obtained even if only one end of the molecule bonds chemically to a metal contact. This offers a possible explanation as to why the conductance observed in the second experiment⁶ was larger than in the first.¹⁷

In Sec. II we briefly discuss the possible configurations of the BDT–gold break-junction system that have been proposed previously together with our proposal of overlapping BDT molecules bonded to the opposing metal tips, in relation to what is known experimentally and theoretically about the structure and energetics of SAM's of similar molecules on gold surfaces. In Sec. III we summarize the method that we use to calculate the electron transport properties of the systems in Sec. II, and then present the results of our calculations. We also present our results for a system that can be used for an experimental test of our suggestion that the current flows through overlapping molecules in the BDT–gold break-junction system. Our conclusions are given in Sec. IV.

II. STRUCTURAL AND ENERGETIC CONSIDERATIONS

Figures 1(a) and 1(b) show a single 1,4 benzene-dithiol (BDT) molecule bridging a pair of gold nano-contacts. The two configurations shown are representative of those that have been studied theoretically to date.^{11,13–15} In Fig. 1(a) the sulfur end groups bind over a hollow site on the gold tips [in this case a fourfold site on (100) gold tips]. In this configuration there is strong chemical and electrical coupling between the gold s and d valence orbitals with the π and σ states on the molecule. In Fig. 1(b), the sulfur atoms chemically bind over a single gold atom on each tip. In this case, the valence s orbital on the gold atom is only electrically coupled to the σ states on the molecule because of symmetry, while the d and p orbitals on the gold atom have electrical coupling to both π and σ states on the molecule. There is no overwhelming evidence in the literature for either configuration (a) or (b). A self-consistent study of SCH_3 on gold

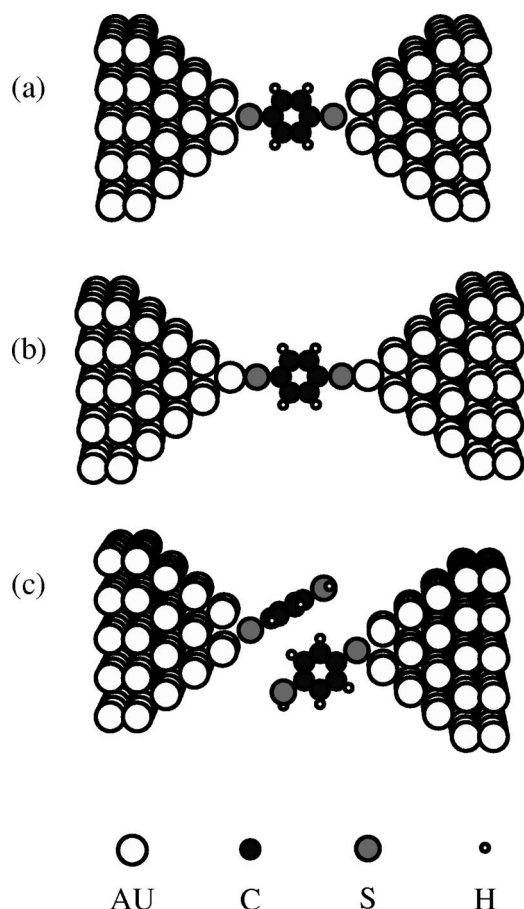


FIG. 1. Schematic of the molecular wire configurations considered. In all cases, the gold clusters shown correspond to (100) gold tips. The molecule depicted is 1,4 benzene-dithiol(ate) (BDT). (a) Hollow site binding of the end sulfur atoms to the gold tips. (b) On-site binding of the end sulfur atoms to the gold tips. (c) Overlapping BDT molecules with rings oriented roughly perpendicularly to each other, with hollow site binding to the gold tips.

showed that it is energetically favorable for the sulfur to sit over hollow sites on the gold surface.¹⁹ Experimental work on SAM's made of thiol-containing molecules seem to give evidence of both configurations.^{20,21} SAM's where the sulfurs bind over hollow sites tend to have the molecules oriented perpendicular to the surface, while those where bonding occurs on top of a Au atom or on a bridge site tend to have the molecules tilted with respect to the surface normal.²² In the next section, transport results will be presented for these two configurations showing that neither of them adequately explains the experimental findings.

Instead of the above configurations that involve only a single molecule in an essential way, we propose that the current may flow through overlapping molecules as is illustrated in Fig. 1(c). For the experiment where the break junction was exposed to a solution of BDT for a long period of time,¹ it is reasonable to assume that most of the possible binding sites on each gold surface would be occupied. Hence when the SAM-coated tips are brought together it seems unlikely that a single molecule would be able to form chemical bonds to *both* contacts. Instead, we suggest that opposing

molecules on each tip overlap as is shown in the figure. The ends of the molecules that do not bond chemically to a gold surface remain as thiols (SH).

Since two molecules are involved it is necessary to consider the orientation of each molecule with respect to the other: Because the experiment was done at room temperature¹ it is reasonable to assume each molecule to be subject to vibrational and rotational excitations. With two neighboring molecules, steric constraints also should play a role. Although, undoubtedly, both molecules rotate and vibrate with respect to each other we argue that on average the faces of the two benzene rings should be oriented perpendicularly to each other because of electrostatic effects. The rings of carbons in similar molecules have been shown to have negative charge on their sides, whereas the hydrogens all have positive charge.²² Thus a favorable configuration of two rings which minimizes the electrostatic energy should be one in which they are oriented perpendicularly to each other; this has been found to give rise to herring-bone patterns in molecular dynamics simulations of SAM's of benzene-thiol and similar molecules on gold.²² Figure 1(c) shows a possible configuration, where each molecule on the tip is bonded over a hollow site and the molecules orient themselves to avoid steric clashes and minimize the electrostatic forces between them. In this configuration there is strong chemical and electrical coupling between a given molecule and the gold lead to which it is attached, but weak electrical coupling between the overlapping molecules.

III. ELECTRON TRANSPORT CALCULATIONS

Before presenting the results of our transport calculations for the above systems, we comment briefly on the theoretical method that we use.¹¹ In the literature a variety of techniques have been used to evaluate the transport properties of molecular wire systems. Most calculate the current using the Landauer approach which relates the electric current to single-electron scattering.^{23,24} Where they differ is in how they solve the scattering problem. Here, methods range from semiempirical tight-binding approaches^{2,8,11,12} to self-consistent techniques with varying degrees of sophistication,^{10,14,25–28} and more recently full many-body treatment.²⁹ Depending on the system being studied, the approaches yield qualitatively and often quantitatively similar results.^{10,30}

In this study our principal objective is to compare the currents and conductances calculated for quite different models that involve large numbers of atoms, and to include the effects of disorder. The calculated currents and conductances differ from model to model by orders of magnitude. Because of this a semiempirical tight-binding approach to the solution of the scattering problem is sufficiently accurate for the present purpose while being well suited to treating the large numbers of atoms involved. (However later in this section we also discuss qualitatively some of the effects that should be expected from self-consistent corrections to the scattering potential.) In order to make a proper comparison between the predictions of the different models possible we present our results for the new model introduced in this article together

with the results of new calculations for the systems shown in Figs. 1(a) and 1(b) for the same values of the model parameters.

In our calculations we solve Schrödinger's equation $H(\{q\}, V)|\Psi^\alpha\rangle = E|\Psi^\alpha\rangle$ for the single particle scattering state $|\Psi^\alpha\rangle$ for all propagating modes $\{\alpha\}$ with energy E in both the left and right leads. We use an extended Hückel Hamiltonian H , which implicitly depends on the charge distribution $\{q\}$ and explicitly depends on the voltage bias V applied between the leads. The boundary conditions imposed on a given scattering state are the following: In the source lead the wave function is an initial propagating mode plus a sum over reflected propagating and evanescent modes; on the molecule the wave function is a linear combination of atomic orbitals; in the drain the wave function is a sum over transmitted propagating and evanescent modes. From the calculated scattering states we evaluate the transmission probability $T(E)$ for an electron to scatter at energy E from one lead to the other via the molecular junction. The current is then calculated via the Landauer expression^{23,24}

$$I(V) = \frac{2e^2}{h} \int dE T(E) [F(\mu_s, T) - F(\mu_d, T)], \quad (1)$$

where $F(\mu, T)$ is the equilibrium Fermi distribution with $\mu_{s/d} = E_F \pm eV/2$ the source/drain electrochemical potentials, E_F the common Fermi energy, and T is the temperature. The differential conductance is calculated by taking the derivative of the current with respect to bias voltage, dI/dV .

The transmission probability and differential conductance were calculated for each of the systems depicted in Fig. 1, Sec. II. We simulate the junction region using gold clusters to which we attach the BDT molecule(s). Each (100) gold cluster consists of a 4×4 , 3×3 , and 2×2 layer of atoms, forming a 29 atom cluster which forms each tip of the metal break junction. [In the case of on-site binding, an extra gold atom is placed on top of the 2×2 layer as shown in Fig. 1(b).] The full s , p , d set of gold valence orbitals is used to model these clusters except where it is explicitly stated otherwise. The BDT molecule consists of a benzene ring with the 1 and 4 hydrogens replaced with sulfur atoms. For the case where we consider overlapping BDT molecules, one end remains a thiol, which has a hydrogen bonded to the sulfur as shown in Fig. 1(c). The sulfur atoms that bond to the gold are positioned 2 Å from the ends of the gold clusters. We use the standard extended Hückel parameters³¹ to represent the valence orbitals of each atom in the system, and evaluate the necessary site energies, hopping energies and overlaps that make up the Hamiltonian and overlap matrices that go into the solution of Schrödinger's equation. We attach to this molecular junction, semi-infinite 5×5 simple cubic multimode leads to act as source and drain. Each atom in the lead is simulated using just a single goldlike s orbital. We include disorder by randomly displacing each atom in the gold clusters by a distance consistent with the Debye-waller factor for gold. For the BDT molecule, we consider random displacements of each atom in the plane of the ring. We do this to approximate the vibrational disorder that will be present in the above systems at room temperature. For the

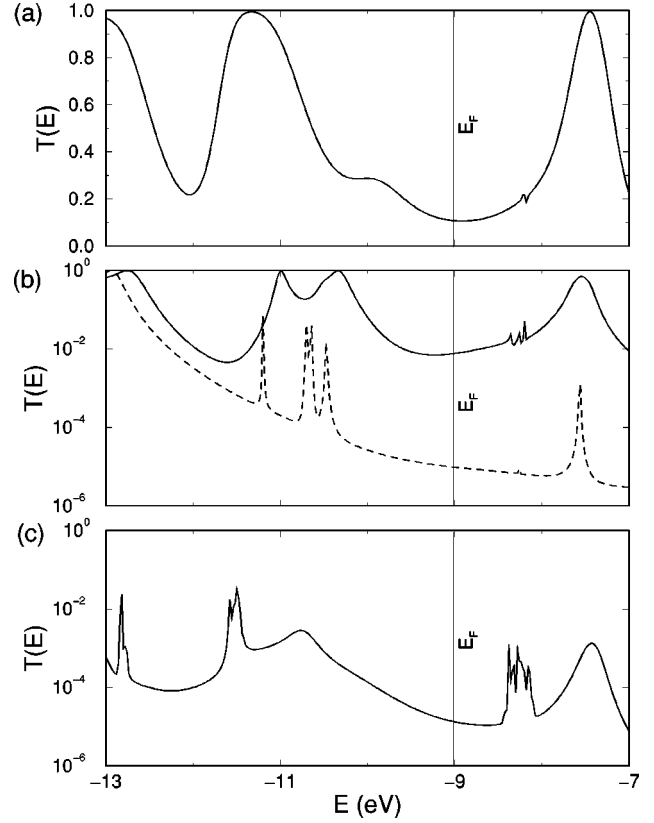


FIG. 2. Calculated average transmission probability at zero applied bias over 20 different atomic configurations for (a) the system shown in Fig. 1(a), (b) Fig. 1(b), and (c) Fig. 1(c).

overlapping ring system, we consider one molecule to assume a random tilt angle (between 20 and 40°) with respect to the normal from the gold surface and then orient the second BDT molecule so that its ring is oriented perpendicular to the first, allowing for 20° fluctuations. We impose steric constraints by demanding that the atoms between the two BDT molecules be at distances ≥ 3 Å. The transmission probabilities shown below are the average of transmission probabilities over 20 atomic configurations for each system shown in Sec. II.

In Figs. 2(a) and 2(b), the average transmission probability is shown as a function of incident electron energy for the two cases where a single molecule bridges the break junction. The case of binding over a hollow site is shown in Fig. 2(a). There are several broad resonances where strong transmission occurs. These resonances are due to highly hybridized molecule/gold states, with the resonances below -10 eV being due to the molecular HOMO states and those above -9 eV arising from the LUMO states. The weak resonance at -8.2 eV is due to the LUMO π^* state which is localized on the benzene ring. Similar behavior can be seen for the solid line in Fig. 2(b) which corresponds to the on-site binding configuration. The resonances occur at slightly different incident energies due to the different hybridization which arises from the different coupling of the molecule to the metal contacts. The multiple resonances near -8.2 eV are due to the single LUMO state. Because coupling to it is weak, the effects of disorder are most clearly

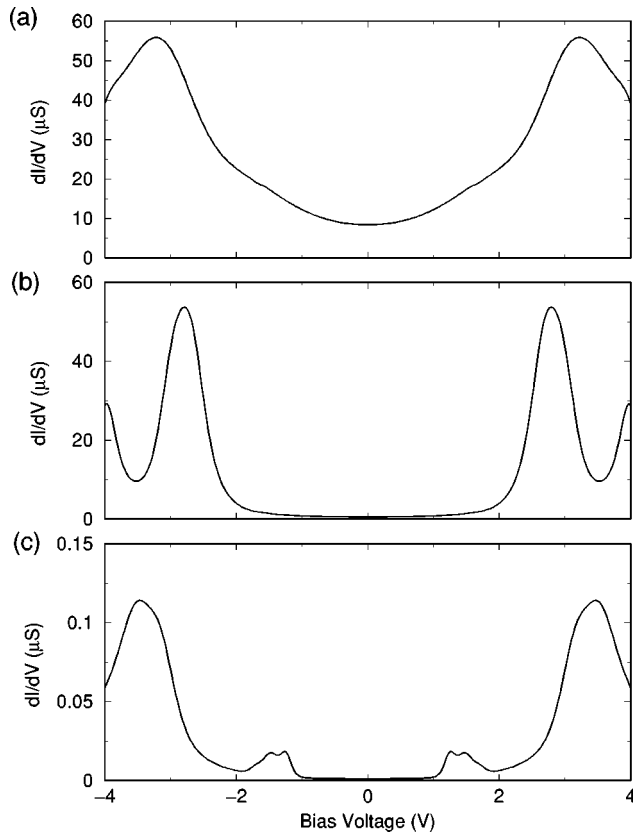


FIG. 3. Calculated differential conductance at room temperature assuming a Fermi energy of -9 eV for each configuration (a), (b), and (c) shown in Fig. 1.

seen, as the energy level shifts due to vibrational effects. Of note is the dashed curve in Fig. 2(b). This corresponds to a calculation where only gold valence s orbitals are used. In this case, the π states of the HOMO and LUMO are much more weakly coupled to the gold because of the orthogonality between the s orbital and the π orbitals. The magnitude of the transmission is down significantly. However, the solid curve, which corresponds to using all the valence orbitals of gold, reveals that there is in fact strong electrical coupling even in the situation where the sulfurs bind directly over a single gold atom. The HOMO states couple to the valence d orbitals of gold while the LUMO states couple to the p orbitals as well. Hence, extended Hückel theory predicts the electrical coupling to be strong for both hollow site and on-site binding situations.

Because of the strong electrical coupling, the calculated conductance of the molecular junction for the above two configurations is much higher than that found experimentally.¹ This is shown in Figs. 3(a) and 3(b), in which we present the calculated differential conductance for the two cases. The Fermi energy was chosen to be -9 eV, which is consistent for the parameters used for gold in the above simulations. The peaks in the differential conductance can be attributed to conduction through the hybridized LUMO and HOMO states. Quantitatively, the conductances in Figs. 3(a) and 3(b) are 2–3 orders of magnitude greater than those found experimentally.

Figure 2(c) shows the average transmission probability for the configurations of two overlapping molecules that are described in Sec. II. Because of the weak electrical coupling between the two BDT molecules, the overall magnitude is down by 2–3 orders from Figs. 2(a) and 2(b).³² With the weaker coupling, the molecular resonances are sharper as the broadening due to hybridization is reduced. The additional resonances at the LUMO are now due not only to vibrational disorder but also to the fact that the wave function overlap between the two molecules results in a splitting of the almost degenerate LUMO levels. In the limit of averaging over an infinite number of configurations these peaks would smear into one broad peak. Figure 3(c) shows the calculated differential conductance at room temperature for the case of overlapping molecules. The first rise in conductance is due to resonant transmission between the LUMO of the molecules. The second rise can be attributed to transmission between the next LUMO state and also the HOMO state. The qualitative and quantitative agreement with the experimental data¹ is quite striking: Not only do the features in the calculated differential conductance curve appear at same values of the bias as in the experimental data, but also the magnitude of the calculated conductance is close to that which was observed in the experiment.

We now address briefly the effects that the changes in the self-consistent potential that result from the bias applied between the contacts should have on the transport results, as the above differential conductance plots were calculated from the transmission probabilities evaluated at zero bias. As a test of the sensitivity of our results to such corrections we calculated the transmission probabilities at several applied voltage biases for all the above systems making plausible assumptions regarding the form of the self-consistent potential profile across the molecule. For cases (a) and (b) which had only a single molecule bridging the junction, it was assumed that the voltage drops only at the metal contacts (an assumption that is supported qualitatively by the results of self-consistent calculations for some strongly coupled molecular wire systems^{26–28}) and determined that the resonances do not shift appreciably. For the case of overlapping molecules, we assumed that 75% of the voltage drops between the two molecules while the other 25% drops at the metal contacts (this is a simple assumption which may or may not reflect the true potential profile of the system). We found that the resonances do shift somewhat and that the transmission probability is asymmetric as a function of voltage for a given configuration of the two overlapping molecules. This might lead one to conclude that the conductance properties then must also be asymmetric as a function of voltage, which would be in disagreement with what was found experimentally.¹ However, because all possible orientations of the two molecules are being sampled in the course of a measurement, for each orientation of the two molecules, the mirror image of that orientation will also occur. For example, given configuration A of the overlapping molecules, and configuration B being its mirror image, we found the following relations between transmission probabilities: $T_A(E, V) \neq T_A(E, -V)$, but $T_A(E, V) = T_B(E, -V)$. The total transmission at nonzero bias in this system will be an aver-

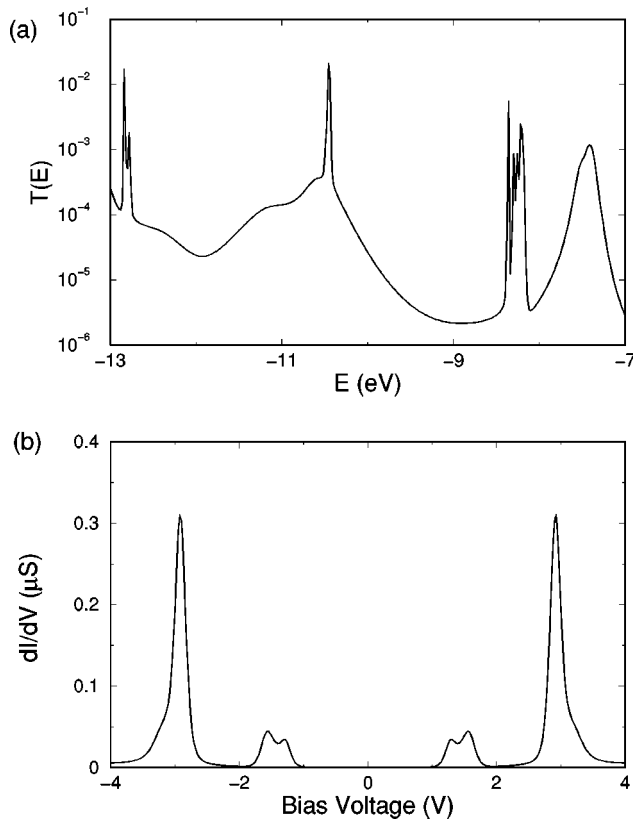


FIG. 4. Transport properties of two overlapping BDT molecules, each capped with a single methyl (CH_3) group on one end. (a) Average transmission probability over 20 different atomic configurations. (b) Calculated differential conductance at room temperature assuming a Fermi energy of -9 eV.

age over configurations A and their mirror images B, yielding $T(E, V) = 1/2 \langle T_A(E, V) + T_B(E, V) \rangle = 1/2 \langle T_A(E, V) + T_A(E, -V) \rangle$ which is symmetric as a function of voltage. Hence, the situation where the current would be carried by overlapping molecules does yield symmetric differential conductance characteristics consistent with what was found experimentally. It is also important to note that the orders of magnitude of the differential conductances calculated for the model configurations (a), (b), and (c) did not change overall when these changes were made in our model potential profiles, further supporting the validity of our conclusions.

The present interpretation of the results of the BDT/Au break junction experiment¹ may be tested experimentally by carrying out measurements on a system in which the SAM's consist of molecules such that only one end of the molecule may bond chemically to a gold contact. In an experiment where SAM's of high coverage are allowed to form on both contacts, we predict that similar behavior to that observed in the BDT/Au break junction experiment¹ should be seen, namely, very weak conductance and symmetric dI/dV as a function of applied bias. If the current is actually being carried via a single molecule, then we would expect asymmetric conductance due to the asymmetric coupling of the single molecule to the metal contacts.

We have modeled the transport properties of two overlapping SAM's made of $\text{SC}_6\text{H}_4\text{S-CH}_3$ molecules. This molecule

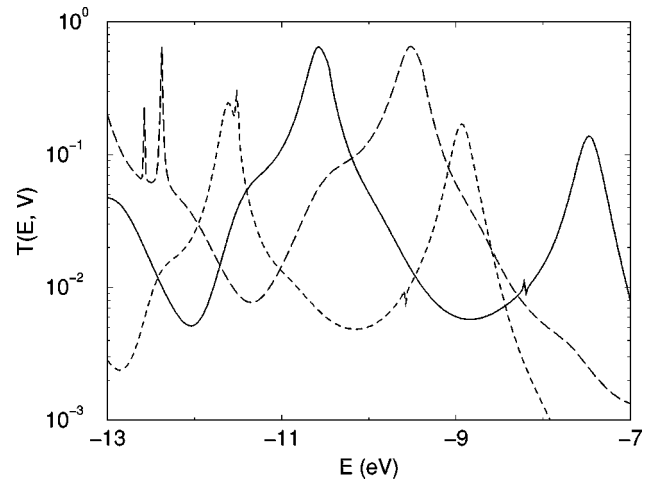


FIG. 5. Transmission probability as a function of incident electron energy for several applied biases for a single BDT molecule capped with a single methyl (CH_3) group on one end in a gold break junction. (Solid line: 0 V; short-dash line: -2 V; long-dash line: 2 V.)

is the same as a BDT molecule except that one of the sulfurs is capped by a methyl group. The methyl group should not form a chemical bond with the gold surface. Hence the molecule will only bond chemically to the gold via the sulfur at the end of the molecule not capped with the methyl group. When the break junction is brought together, the molecules on the gold tips should overlap but not be able to form a chemical bond to a second gold tip. Thus the possibility of a single molecule bonding symmetrically to the two gold tips is ruled out in this experiment and for dense SAM's the dominant path for electron transport will be from one molecule to the other. Figure 4(a) shows the average transmission probability for this system. The magnitude is similar to that of Fig. 2(c). The differences between the transmission probability of BDT and that of BDT capped with a methyl group is due to the slightly different orbitals that arise by capping with the CH_3 . The calculated differential conductance is shown in Fig. 4(b). Again it displays features similar to those for the overlapping BDT molecules. The first rise in conductance is again due to resonant transport through the LUMO's of the two molecules. This is followed by a sharp rise in conductance corresponding to the strong resonance with the HOMO near 3 volts. Hence we predict that capped BDT molecules should yield similar transport characteristics to those of BDT when the two dense SAM's overlap.

Finally we argue that for a measurement where the SAM density is low, and only a single molecule of the CH_3 -capped BDT bridges the gap, asymmetric differential conductance should result. Because of the weak coupling at one contact, the system is asymmetric and the transport characteristics at negative bias will be different from those at positive bias. To verify this we have calculated the transmission probability for this system at an applied bias of -2 V, 0 V and $+2$ V which is shown in Fig. 5. A simple potential profile was assumed—the potential drops linearly across the weak contact. (We base this assumption on self-consistent calculations which have shown that in systems that have a weak contact,

the potential drops roughly linearly across the gap.²⁸) It can be seen that the transmission probability for the case where the applied bias is -2 V (short-dash) is different from the $+2$ V (long-dash) situation. Because of this asymmetry, the differential conductance will not be symmetric between negative and positive bias. Although a simple potential profile was assumed, we believe that qualitatively similar results would also be obtained if the potential were calculated self-consistently. Hence, a single BDT-CH₃ molecule in a break-junction should display asymmetric transport characteristics as a function of applied bias. We predict that qualitatively similar behavior should be seen for benzene-thiol SAM's as well.

It should also be noted that the strengths of the transmission resonances in Fig. 5 are considerably larger than those in Fig. 4(a). This implies that the magnitude of the conductance of a break junction bridged by a single BDT-CH₃ molecule can be larger overall than the conductance of an overlapping pair in a junction with dense SAM's, even though the methyl group does not bond chemically to the gold. (Here we have assumed that the gold surface is clean with no adsorbate between it and the methyl group.) Within our model this result is consistent with the observation that the measured resistance (1 M ohm at a 1 V bias) of the junction bridged by a single molecule in the second experiment⁶ is much smaller than the resistance measured in the first experiment.¹

IV. CONCLUSIONS

In conclusion, we have proposed a model of electrical conduction through self-assembled molecular monolayers

that bridge mechanically controlled metal break junctions. In this model each molecule bonds chemically to only one of the contacts. For dense SAM's the dominant electric current path is through two overlapping molecules each of them bonded to a different metal electrode whereas for dilute SAM's the current flows through a single molecule. The model accounts quantitatively for the experimental findings of Reed *et al.*¹ on electron transport through gold break junctions containing benzene-dithiol SAM's, including the magnitude of the measured differential conductance that was not explained satisfactorily in previous theoretical work. The model also accounts qualitatively for the striking differences between the experimental results of Reed *et al.*¹ and the more recent measurements of Reichert *et al.*⁶ on a somewhat different system, namely the asymmetry of the current-voltage characteristics and the much larger size of the differential conductance found in latter experiments. We have also presented calculations of electron transport through break junctions containing both dense and dilute SAM's of SC₆H₄S-CH₃ molecules. Experiments on these systems should provide a convincing test of the validity of the present model.

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- ¹M.A. Reed, C. Zhou, C.J. Muller, T.P. Burgin, and J.M. Tour, *Science* **278**, 252 (1997).
- ²S. Datta, W. Tian, S. Hong, R. Reifenberger, J.I. Henderson, and C.P. Kubiak, *Phys. Rev. Lett.* **79**, 2530 (1997).
- ³R.M. Metzger, B. Chen, and M.P. Cava, *Thin Solid Films* **327/329**, 326 (1998).
- ⁴C.P. Collier, G. Mattersteig, E.W. Wong, Y. Luo, K. Beverly, J. Sampaio, F.M. Raymo, J.F. Stoddart, and J.R. Heath, *Science* **289**, 1172 (2000).
- ⁵J.K. Gimzewski and C. Joachim, *Science* **283**, 1683 (1999).
- ⁶J. Reichert, R. Ochs, D. Beckman, H.B. Weber, M. Mayor, and H.v. Löhneysen, cond-mat/0106219, 2001 (unpublished).
- ⁷J. Chen, M.A. Reed, A.M. Rawlett, and J.M. Tour, *Science* **286**, 1550 (1999).
- ⁸M. Magoga and C. Joachim, *Phys. Rev. B* **56**, 4722 (1997).
- ⁹S.N. Yaliraki and M.A. Ratner, *J. Chem. Phys.* **109**, 5036 (1998).
- ¹⁰N.D. Lang and P. Avouris, *Phys. Rev. Lett.* **81**, 3515 (1998).
- ¹¹E. Emberly and G. Kirczenow, *Phys. Rev. B* **58**, 10 911 (1998).
- ¹²S.N. Yaliraki, M. Kemp, and M.A. Ratner, *J. Am. Chem. Soc.* **121**, 3428 (1999).
- ¹³L.E. Hall, J.R. Reimers, N.S. Hush, and K. Silverbrook, *J. Chem. Phys.* **112**, 1510 (2000).
- ¹⁴M. Di Ventra, S.T. Pantelides, and N.D. Lang, *Phys. Rev. Lett.* **84**, 979 (2000).
- ¹⁵Extended Hückel calculations of transport through BDT/Au systems have also been reported by S. Datta and collaborators (unpublished).
- ¹⁶See C. Uher, R.L. Hockey, and E. Ben-Jacob, *Phys. Rev. B* **35**, 4483 (1987) and references therein.
- ¹⁷C. Zhou, M.R. Deshpande, and M.A. Reed, *Appl. Phys. Lett.* **71**, 611 (1997).
- ¹⁸We are grateful to Ross Hill for bringing this system to our attention.
- ¹⁹H. Sellers, A. Ulman, Y. Schnidman, and J.E. Eilers, *J. Am. Chem. Soc.* **115**, 9389 (1993).
- ²⁰L. Wan, M. Terashima, H. Noda, and M. Osawa, *J. Phys. Chem. B* **104**, 3563 (2000).
- ²¹K. Bandopadhyay and K. Vijayamohanan, *Langmuir* **14**, 6924 (1998).
- ²²H.H. Jung, Y.D. Won, S. Shin, and K. Kim, *Langmuir* **15**, 1147 (1999).
- ²³R. Landauer, *IBM J. Res. Dev.* **1**, 223 (1957); *Phys. Lett.* **85A**, 91 (1981).
- ²⁴For a comprehensive review of Landauer-Büttiker theory, see S. Datta, *Electronic Transport in Mesoscopic Systems* (Cambridge University Press, Cambridge, England, 1995).
- ²⁵J. Taylor, H. Guo, and J. Wang, *Phys. Rev. B* **63**, 121104 (2001).
- ²⁶V. Mujica, A.E. Roitberg, and M. Ratner, *J. Chem. Phys.* **112**, 6834 (2000).

- ²⁷E. Emberly and G. Kirczenow, Phys. Rev. B **62**, 10 451 (2000).
²⁸E. Emberly and G. Kirczenow (unpublished).
²⁹M. Hettler and H. Schöller (unpublished).
³⁰E. Emberly and G. Kirczenow, Phys. Rev. B **60**, 6028 (1999).
³¹S. P. McGlynn, L. G. Vanquickenborne, M. Kinoshita, and D. G. Carrol, *Introduction to Applied Quantum Chemistry* (Holt,

Reinhart and Winston, New York, 1972), Chap. 3.

- ³²We found that the transmission probability was larger for the energetically unfavorable configuration where the two molecules are aligned parallel compared to the more favorable perpendicular alignment.