

Conductance of Molecular Wires: Influence of Molecule–Electrode Binding

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Abstract: We report on the effect of modifying the molecule–electrode binding interface of an α,α' -xylyl-dithiol molecular wire. We find that except for the length of the surface bond, the conductance is not affected by variations of the surface geometry. We also compare the conductance of different terminal atom–electrode metal combinations and find that the conductance is substantially larger when the wire is terminated by selenium rather than sulfur or oxygen. We also find that gold makes a better electrode than silver.

1. Introduction

Synthetic advances based on molecular self-assembly¹ and measurement techniques including scanning probe spectroscopy,² break junction,³ and other specialized techniques⁴ have permitted the preparation and measurement of currents in single molecular strands or molecular wires. In these structures (typical examples include aromatic dithiols,³ carbon spheres⁵ or nanotubes,⁶ or alkene thiols⁷), the conductance is measured directly.

The task of molecular wire theory is to understand the factors that influence the flow of current through a single molecule connecting two electrodes and subsequently to make predictions for suitable molecule–electrode systems. When the molecule couples to each electrode through a single orbital, the theory predicts that in the linear regime⁸

$$g = g_c \Delta_L \Delta_R G^2 \quad (1)$$

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where g is the conductance, g_c is the quantum of conductance, Δ_L and Δ_R measure the strength of the coupling between the molecule and the left and right electrodes and the Green's function matrix element, G , depends on the structure of the molecule. The separation of the conductance into two parts, one that depends on the interface and one that depends largely on the molecule, is a central feature of this theory.⁸ The result is obtained from a scattering approach used by several groups^{9–12} and the Newns–Anderson¹³ chemisorption description of the coupling of the molecule with the electrodes.

Theoretical work has so far focused on understanding the molecular contribution, G .^{9–11} Different from the case of atomic wires,^{14,15} previous work has concentrated on finding criteria for selecting molecular wires (usually based on electron delocalization in one direction) and on assessing the impact of geometric,¹⁶ energetic, and structural¹⁷ or thermal effects,¹⁸ on the conductance.

Less attention has been paid to the molecule–electrode interface. Recent work by Emberly and Kirzenow shows that the surface bonding can be strong enough to distort the electronic structure of the molecule.⁹ Work by Joachim's group shows

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that changing the contact geometry can substantially affect the conductance.¹¹ Extension of the formalism to two-dimensional electrodes shows a definite effect of electrode dimensionality.¹⁹ These results suggest that along with changing the molecule, transport control might also be achieved by modifications at the interface.

Experimentally, the geometry of the molecule–electrode interface is poorly understood. A major experimental concern has been the “alignment” of the molecule to the electrode. In either the break junction or the scanning tunneling microscope (STM) setup, neither the terminal atom–metal bond length nor the angle between the molecule and the metal plane is likely to be optimal. Additionally, it is not clear where the terminal atom sits on the surface, whether at the hollow site or on top of a surface atom. As Joachim’s group observed,¹¹ and as calculations on model systems demonstrated,¹⁹ the conductance can be sensitive to the contact geometry. In view of this, one should question the accuracy of theoretical conductance calculations if they are based on ideal geometries. It is possible to make predictions, however, if we turn the problem around. Starting with a geometry, we can compute the conductance and then repeat the calculation with a slightly different geometry. Using this procedure, we can assess whether a given geometrical factor is crucial.

The majority of systems studied so far use thiol-terminated molecules, because of sulfur’s ability to bond to gold surfaces.^{20–22} There is substantial interest in other terminal group/electrode metal combinations.¹ A priori, it is difficult to assess which will be the optimal combination of electrode–molecule–electrode junctions for conductance.

In this article, we address these issues focusing on the experimentally relevant molecule α,α' -xylyl-dithiol (XDT). Of prime concern is the clear necessity to perform realistic calculations. In section 2, we present the essential theoretical details. In section 3, we address three experimentally relevant aspects of the interface problem and their effect on the conductance: (i) variations in the surface geometry, (ii) the chemical nature of the terminal atom, (iii) and change of the electrode metal. We will show that, other than the distance between the electrode and the terminal atom, the conductance is relatively insensitive to geometrical surface variations. Furthermore, we will show that, for this molecule, selenium is a better terminal atom than sulfur or oxygen, with a factor of 25 increase in conductance upon Se substitution for S. Finally, we find that gold is better than silver by a factor of 5. These results are analyzed and discussed in section 4.

2. Theory

2.1. Extensions. To address the effects of geometry, terminal atom, and electrode metal, we need to extend the formalism leading to eq 1. Similar extensions have been used by Joachim’s group, Emberly and Kirczenow, and the Purdue group.^{9–11}

We consider a semi-infinite right electrode R, a semi-infinite left electrode L, and a molecule M sandwiched between. The Hamiltonian matrix element between two orbitals i and j is H_{ij} . The overlap between the orbitals is S_{ij} .

We define $M = ES - H$, where E is the Fermi energy. Using multiple-channel scattering theory,²³ and making the assumption

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that no matrix elements connect the two electrodes, we find that the zero voltage conductance is

$$g = g_c \text{Tr}(\Gamma \Delta_L \Gamma^+ \Delta_R) \quad (2)$$

Here, Γ , M , Δ , and Σ are matrices. The Green’s function, Γ , is defined by

$$\Gamma(M - \Sigma_L - \Sigma_R) = 1 \quad (3)$$

where M is restricted to the molecular subspace. M is calculated at the Fermi level. The self-energy matrix, Σ_L , is defined by

$$\Sigma_L = M_{ML} M_{LL}^{-1} M_{LM} \quad (4)$$

where M and L refer to the molecule and to the left electrode, respectively. A similar expression follows for Σ_R . Finally,

$$\Delta_L = -\frac{1}{\pi} \text{Im}(\Sigma_L) \quad (5)$$

This generalizes the previous conductance formula of eq 1 in three essential ways. First, it allows for multiple orbital interaction between the molecule and the electrode. Second, it supports nonorthogonal orbitals on the molecule. Finally, it handles an arbitrary number of nonorthogonal orbitals per site in the electrodes.

Equations 2, 3, and 5 are straightforward to compute. The calculation of the self-energy matrixes is fairly involved. The essential difficulty lies in the fact that the self-energy can have an imaginary part only in the continuum limit, and solving for a continuum is only possible in very few cases (like the Newns–Anderson problem discussed in refs 8 and 19). A method has to be devised that applies to cases of arbitrary complexity.

We solve this problem as follows. We make the assumptions that the molecule only interacts with the atoms on the first electrode plane and that, within the electrode, only the nearest planes interact. Given these assumptions, we can show that the Σ matrixes only depend on the Green’s function matrix elements at the surface. Next, we derive a self-consistent equation for Γ after observing that adding a plane to a semi-infinite solid reproduces the same semi-infinite solid. Defining labels 1 and 2 to refer to the first and second plane, we finally find that the surface Green’s function obeys

$$\Gamma_{11}(M_{11} - M_{12}\Gamma_{11}M_{21}) = 1 \quad (6)$$

We note that self-consistency alone is enough to produce a complex self-energy matrix, as can be verified by applying eq 6 to the simple Newns–Anderson model.

Equation 6 is nontrivial to solve because the surface has infinite extent. Taking advantage of the 2D translational symmetry in the plane, the equation can be mapped and solved for in reciprocal space.

2.2. Parameters and Geometry. The optimization of the molecular geometry is performed by placing each metal atom in a trigonal metal cage (extended molecule). There are many reasons to include the metal atoms at this level. One is to take into account the different nature of the local environment around the atomic contact. Second, from this extended molecule we can extract information about the molecule–interface complex, such as the self-energy and the amount of electronic charge transfer.

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The molecular Hamiltonian and overlap matrix are calculated at the extended-Hückel level (see for example refs 24 and 25). This method has the advantage of intuitive clarity, and from chemisorption studies of small clusters and other metal systems, it is known to be at least qualitatively correct. In view of the nature of the method, we must emphasize that the most important conclusions of our calculations are trends rather than absolute numbers. Nevertheless, the extended Hückel molecular description has been successful in describing experimental results in both conductance calculations^{9–11,18} as well as the related problem of STM imaging.^{26,27} Additionally, preliminary calculations with the simplified model of ref 8 has given results very close to reported experimental values:²⁸ for the system of ref 7 the calculated resistance was 9.2 M Ω to the experimental 6–9 M Ω , and for the system of ref 5 the resistance was 116.6 M Ω from theory and 54.8 \pm 13 M Ω from the experiment.

For the bare molecule, we use the standard parametrization of the ZINDO package. For gold and silver, we use the parameters of ref 29. The reason for this choice is that the orbital exponent parameters are adjusted so as to make the density of states of a cluster (s,p,d basis set) similar to that of the bulk. The experimental valence state ionization potential values (VSIP) are taken from ref 30. Thus, there are 6 valence electrons on each chalcogen atom and 11 on each of the noble metal atoms.

The starting point geometry at the molecule–electrode interface is either taken from ab initio results (sulfur on gold and silver³¹) or inferred from chemisorption studies (oxygen and selenium on gold³²).

The Hamiltonian and overlap matrix in the electrodes are computed using a standard parametrization for bulk elemental solids.³³

3. Results

We choose α,α' -xylyl-dithiol (XDT) as the core molecule for our study. The conductance of this molecule has been extensively studied, both experimentally²¹ and theoretically.¹⁰

The sulfur atom is placed on the hollow site of a Au(111) surface, equidistant from three gold atoms at 2.4 Å. Ab initio geometry optimization of thiols on gold and silver shows that this is the preferred geometry for this surface.³¹ There is also ample experimental evidence supporting this.³⁴ We refer to this as the optimal configuration throughout the paper.

The conductance spectrum is shown in Figure 1. The spectrum consists of a series of valleys and peaks. From a transport perspective, the most important peaks are the valence peak, at –11 eV, and the conduction peak, at –7 eV. In the gap between the valence and conduction peaks, the conductance decreases by up to 4 orders of magnitude.

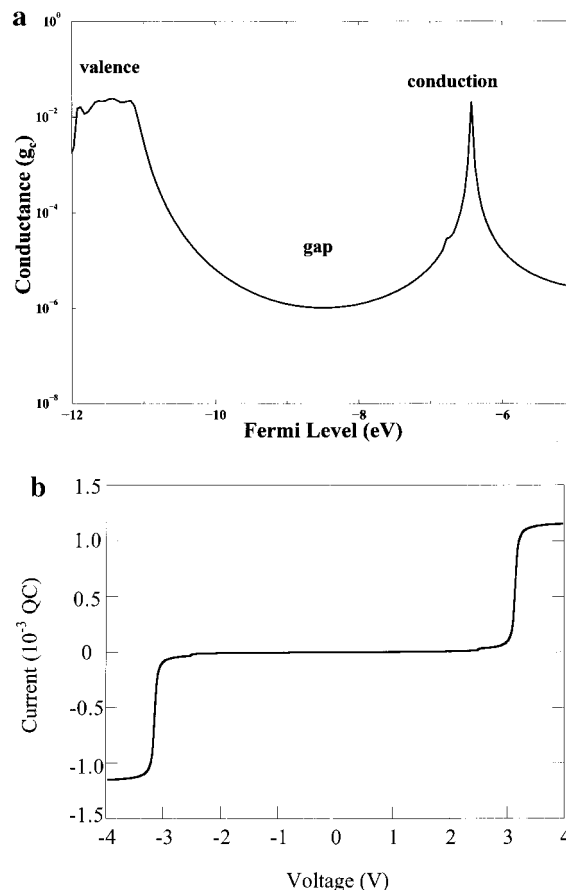


Figure 1. (a) Conductance spectrum of α,α' -xylyl-dithiol on Au(111). The interface geometry is variationally optimal. The spectrum has three parts: the valence peak near –11 eV, the conduction peak near –7 eV, and the gap between. The computed conductance decreases by 4 orders of magnitude in the gap. (b) Corresponding current–voltage characteristic. The current, given in units of the quantum of current, is given by⁴⁸

$$I = \int_0^{-eV} dE f_D(E) (1 - f_A(E + eV)) g(E)/e$$

where the Fermi level of the donor defines the zero of energy. Here, $V = 0$ corresponds to $E_F = -8$ eV. The conductance $g(E)$ is obtained at zero voltage. It is this function that is used to obtain the current at different voltages corresponding to the conductance computed at different Fermi energies, that is, the current is the sum of all of the conductances from the states between the two Fermi levels. The results therefore are only valid for low voltage. The I – V has to be symmetric as expected from the system we are describing.⁴⁹

The conduction peak corresponds to the benzene LUMO. Because of the energy mismatch, the LUMO mixes very weakly with the sulfur atoms.

The valence peak is more complex. Unlike the LUMO, the benzene HOMO is quasi-degenerate with the six sulfur p orbitals. Consequently, the valence peak is made of eight levels, four of which are purely made of sulfur p orbitals. The other four involve a mixture of benzene HOMO and sulfur p.

These results are similar to those reported in the literature.¹⁰ We find a smaller conductance at the valley minimum and only one broad valence peak, instead of two resolved peaks, as predicted by the Purdue group. These differences arise, we think, because of the different bond length choice (see Figures 2 and 6).

3.1. Surface Geometry Effects: XDT on Au(111). 3.1.1. Bond Length Variation. We assume that initially the molecule is bonded optimally at both the base and tip electrodes, that is,

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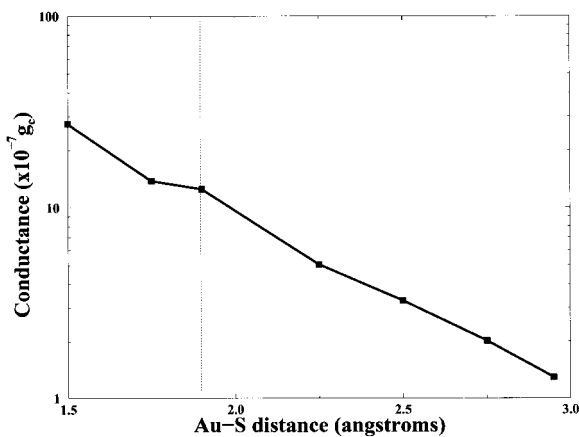


Figure 2. Effect of stretching/shortening the Au–S bond length. The x -axis shows the perpendicular distance from the terminal sulfur to the gold plane, rather than the actual Au–S bond length. Optimal bonding is shown by the dashed line. As expected, the conductance decreases exponentially when the bond is stretched.

the perpendicular distance of the S to the surface of a triangle of gold atoms is 1.905 Å, and the S is sitting on top of the hollow site so that it is equidistant from each gold atom. Then, we move the tip toward and away from the molecule. This mimics a typical STM experiment. It also mimics the stretching and shortening of the Au–S bond, as is believed to happen in a break junction.³ We change the perpendicular distance of the S to the gold surface, while the S remains equidistant from each gold atom.

For practical purposes, we locate the Fermi energy at 3 eV above the HOMO level. We justify this choice in section 4. The effect on the conductance is shown in Figure 2. We find that the conductance decreases exponentially with tip–sulfur distance, at a rate of 1 decade per Å.

This result was expected. Typically, the STM current on a clean surface decreases exponentially with increasing STM gap, at a rate of about 1 decade per Å.^{5,35}

3.1.2. Tip Angle Variation. We initially assume optimal bonding at the base and tip electrodes. In this case the normal to the gold plane and the line through the C–S bond coincide. Keeping the Au–S bond length constant, we then consider the effect of tilting the tip plane with respect to the molecular axis. The S is still equidistant from the three gold atoms, but the C–S bond forms an angle with the normal to the original plane. This corresponds, for example, to an STM experiment performed with a slanted tip or to bonding with the side of the tip.

The effect on the conductance is shown in Figure 3. We find that the conductance is almost independent of tilt angle.

The absence of directionality is reasonable. The metal surface presents the terminal sulfur with a smooth electronic distribution. Because of the equivalence of the three sulfur p orbitals, the surface bonding lacks directionality. The result is also consistent with the conclusions reached in ref 31, where it was attributed to rehybridization of the Au orbitals, and to the high degree of π character of the molecular orbitals.

From an experimental point of view, this is a welcome result. It shows that fluctuations of the surface bond angle do not affect the value of the measured conductance.

3.1.3. Terminal Sulfur Location. Ab initio calculations³¹ show that there are two energetically favorable configurations for a sulfur atom on a Au(111) surface: at the hollow site of a gold triangle and on top of a gold atom. Because of the small

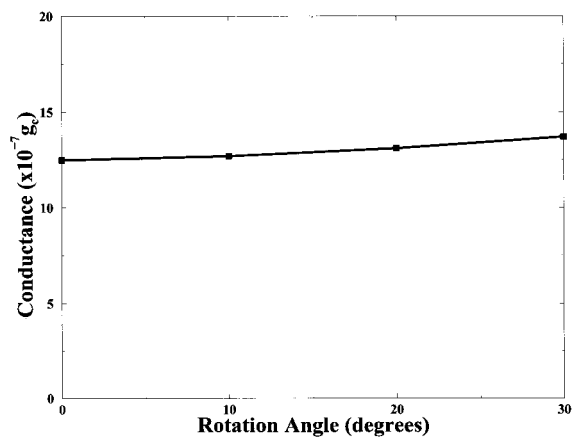


Figure 3. Effect of tilting the gold plane around the optimal configuration. The conductance is not affected by the angle.

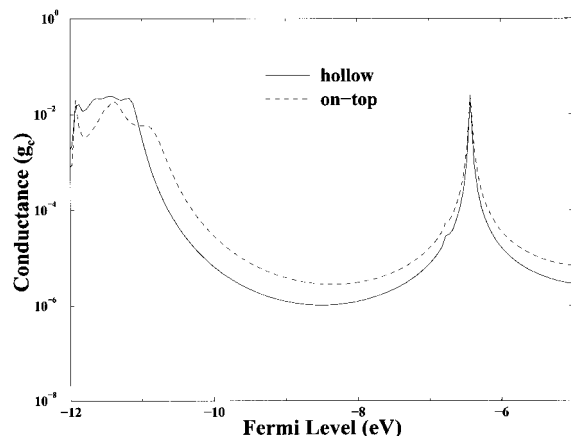


Figure 4. Comparison of hollow and on-top spectra. In the gap, the on-top conductance increases slightly. The conduction peak is not affected by the change in configuration, and the valence peak shifts slightly.

energy difference between these configurations, both are expected to be important under experimental conditions.

Two very different behaviors can arise due to this freedom. If the conductances of the two configurations are very different, the conductance will flicker in time-dependent fashion each time the sulfur jumps from one configuration to the other. If, on the other hand, the two conductances are similar, motion of the sulfur will have no measurable effect. It is therefore important to compare the conductances in the hollow and in the on-top configurations.

Figure 4 shows the effect of moving the tip sulfur between the two positions (optimal bonding is assumed at the base electrode). We find that the conductance spectrum is not affected by the change. The only observable effect we find is a small increase of the conductance in the HOMO–LUMO gap. However, this effect is small and might even be an artifact of the model.

In view of this, we predict that the conductance will not flicker in time. Also, and important from an experimental perspective, we conclude that the precise configuration assumed by the system does not affect significantly the value of the measured conductance.

3.2. Effect of Terminal Atom: O, Se on Au(111). At present, most experimental systems use thiol-terminated molecules because of sulfur's ability to make a strong bond with a gold surface. Sulfur's strong bonding to gold suggests that other chalcogens, i.e., oxygen and selenium, might be good substitu-

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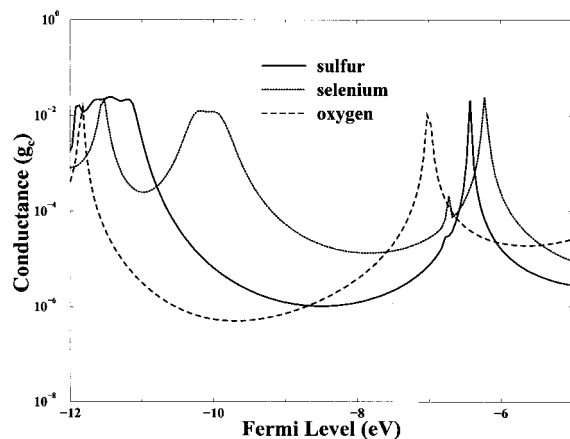


Figure 5. Effect of changing the terminal atom. In going from oxygen to sulfur to selenium, (i) the conductance in the gap increases, (ii) the gap decreases, and (iii) the conduction and the valence peak shift up. Selenium is by far the best terminal atom, conducting 25 times better than sulfur in the gap.

uents. Chemisorption studies of these three atoms on other (111) surfaces strongly suggest they will also bind to Au(111).³² STM characterization of benzeneselenol monolayers on Au(111) also supports this conjecture.³⁶

Figure 5 compares the conductance spectra of the molecule when it is terminated by oxygen, sulfur, and selenium. In all three cases, the electrode surface is Au(111), and the terminal atom sits at the hollow site. Two trends can be recognized from the spectra: (i) Going down the periodic table, the conductance at the spectrum minimum increases (1 to 3 to 75 from O to S to Se). Selenium provides, by far, the largest conductance for this junction. (ii) Going down the periodic table, both the HOMO and the LUMO shift up in energy. These results will be discussed in section 4; they suggest that selenium makes a better contact than oxygen and sulfur. In view of the factor of 25 enhancement, we think this conclusion is robust against Hamiltonian parametrization and believe it should be tested experimentally.

3.3. Effect of Electrode Metal: XDT on Ag(111). Sulfur's good bonding to gold suggests we also analyze the effect of replacing gold with silver. Chemisorption studies show that the bonding of sulfur on silver is stronger. From eq 1, the conductance on silver may be larger.

In Figure 6, we compare the conductance spectra of XDT when the electrodes are made of gold and silver. We find that within the gap, the silver conductance is smaller than that of gold by about a factor of 5. We find no change in the position of the conductance maxima, except for the better resolution of the Ag-valence peak levels. Because of the factor of 5 reduction that we find, we think this conclusion is robust against Hamiltonian parametrization. An explanation for this trend will be given in the Discussion.

4. Discussion

4.1. On the Bonding between Terminal Atom and Interface. How can we know a priori which terminal atom is best for a particular metallic electrode? It is clear that a strong chemical bond is essential, but not determinative. We have compared three atoms of the same group of the periodic table (O, S, Se) as terminal atoms of the same molecule attached to two noble metals (Ag, Au). All of these systems are isoelec-

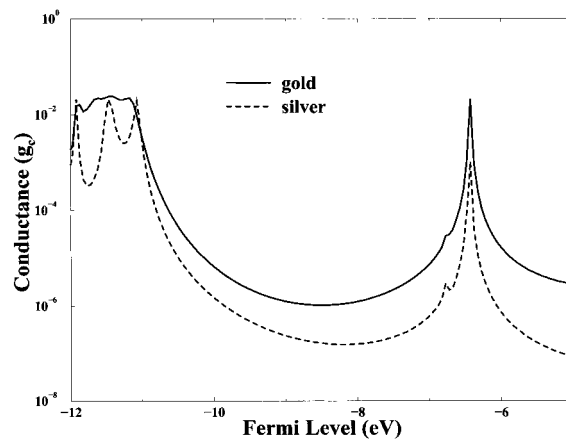


Figure 6. Effect of changing the electrode metal. The conductance in the gap increases. The conduction band peak is not affected by the change. The position of the valence band peak does not change, but the levels that comprise it are better resolved for silver.

tronic; the number of valence orbitals³⁷ does not enter. From experimental studies, we know that thiols bond more strongly to Ag(111) than to Au(111). However, this occurs concomitantly with a weakening of the adjacent C–S bond. The energy of the bond between the organic thiolate and the gold substrate is approximately 40–45 kcal/mol.³⁴

An experiment that provides comparative information is surface Raman scattering of alkanethiols adsorbed on Au and Ag.³⁸ The frequencies of both $\nu(\text{C–S})$ bands are lower on Ag surfaces than on Au, suggesting a stronger bond between S and Ag. Another experiment that investigates the adsorption of ethanethiol on Au(110) and Ag(110) uses temperature-programmed reaction spectroscopy.³⁹ An increase in strength of the S–Ag bond compared to the S–Au is observed. Simultaneously, a weakening of the C–S bond from the stronger M–S bond is inferred from decomposition studies of the adsorbed species at high temperatures. Namely, it is easier to cleave the C–S thiolate bond on silver than it is on gold. This is also consistent with the relative enthalpies of formation of the sulfides $\Delta H_f(\text{Au}_2\text{S}) = +29$ kJ/mol vs $\Delta H_f(\text{Ag}_2\text{S}) = -32$ kJ/mol.³⁹ Similar conclusions are obtained from photoemission spectroscopy of hexadecanethiol monolayers self-assembled on Ag(111) and Au(111).⁴⁰

For selenols on metal substrates, the experimental work is more limited. In benzeneselenol monolayers, the selenium Au(111) bond is stronger than the corresponding thiophenols.³⁶ On the contrary, docosanethiol chemisorbs more strongly to Au(111) than the docosaneselenol monolayers.⁴¹

The implication for molecular wire conductance is that the strength of the bond at the interface should be strong, but not so strong that it weakens the bonding between the terminal atom and the rest of the molecule. (Formally, the stronger chemisorption will increase Δ , but weaker intramolecular binding will decrease G). As will also become apparent below, the whole molecular orbital needs to be considered. Due to this interplay, it is difficult at this stage to identify simple general design rules.

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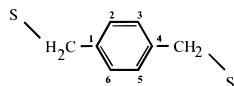


Figure 7. Sketch of α,α' -xylyl-dithiol, showing the locations of C1 to C6.

4.2. Terminal Atom. To understand the effect of terminal atom, we need to return to the conductance spectrum shown in Figure 1. Three elements of the spectrum are relevant to the discussion: the valence peak at -11 eV, the conduction peak at -7 eV, and the gap between.

The valence peak has a complex structure. The sulfur p orbitals lie at -12 eV, and are nearly degenerate with the benzene HOMO. Consequently, the valence peak is made of eight energy levels. The levels are not resolved because of the broadening caused by the electrodes. Four of the levels are entirely located on sulfur. The other four levels consist of a mixture of sulfur p's and benzene HOMO.

Going to oxygen has the following effect. The oxygen p orbitals lie near -16 eV too deep to mix with the HOMO. Consequently, the valence peak of the oxygen spectrum is entirely due to benzene.

For selenium, the p's lie at -10 eV, above the benzene HOMO. Because of the energy mismatch, benzene and selenium weakly mix. Consequently, the valence peak is almost entirely due to selenium. The Au/Se example is an unusual situation in which the valence peak position is not necessarily determined by the molecule.

The conduction peak is simpler to understand. It consists of two levels, almost entirely localized on the benzene ring. These levels correspond to the two degenerate benzene LUMO levels. They do not mix with the sulfur p orbitals because of the 4 eV energy mismatch and because the methylenes that separate the terminal p's from the benzene act effectively as a tunneling barrier.

The small interaction with the terminal p's breaks the degeneracy. The two LUMO levels have different structures. The first one, called *I*, has weight on C2, C3, C5, and C6 (see Figure 7). The other, *E*, has weight on C1 and C4. Both *I* and *E* have π character. Because *I* has no weight at C1 and C4, it is largely independent of substitutions performed outside the ring. For that reason, *I* remains unchanged when sulfur is replaced with oxygen or selenium. The other level, *E*, has weight at C1 and C4, and consequently, its energy depends on the terminal atom.

We can understand why *E* moves up in energy as we go down the periodic table. Modeling the terminal-LUMO-terminal complex as a three-site system, with the last two sites degenerate, a simple calculation shows that, as the terminal energy increases, the energy of the highest eigenstate moves up. Going from oxygen to sulfur to selenium, the energy of the p orbitals increases. Consequently, the LUMO energy increases. We expect that this molecular orbital is more important for conduction than the one with nodes at para position. Indeed, it has been recently found⁴² for poly(*p*-phenylene vinylene) that, when the molecular orbital has nodes at the C1 and C4 positions, there is negligible delocalization of charges among rings, that is, the charges are localized on the benzene ring. When, on the other hand, there is substantial charge on the carbons at C1 and C4, the charge can delocalize on neighboring atoms or even over the whole chain.

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Finally, since the terminal p orbital energy increases as we go down the periodic table, the gap between valence and conduction peaks decreases from O to S to Se. The reduction in gap is the main reason that the selenium system is more conductive than that with sulfur or oxygen.

4.3. Electrode Metal. A similar explanation helps clarify the reason gold conducts better. Figure 6 shows that the positions of the valence and conduction peaks are the same for the two materials. While the gold valence peak is smooth, for silver the peak splits into three resolved components. This is a consequence of sulfur's weaker coupling to the π system when the electrode is silver. The weaker coupling also means that being narrower, the levels do not extend as deeply in the gap. Consequently, the conductance of silver at midgap is smaller.

4.4. On the Position of the Fermi Level. The absolute positions of either the isolated metal Fermi level or the gas-phase molecular levels are relatively straightforward to obtain. On the other hand, finding the relative position of the Fermi level to the HOMO, after contact is established, is more difficult. From a predictive standpoint, this difficulty is disastrous. In every study reported so far (see for instance Figures 1, 4–6, and refs 8–11), the conductance in the HOMO-LUMO gap was found to be extremely sensitive to the Fermi level position (a change of 0.1 eV is enough to change the conductance by a factor of 5). For the purpose of making quantitative predictions, a method for finding the Fermi level position is needed. This point is also discussed in ref 10a.

Experimental access to this information is essential. Photoemission spectroscopy (PS),⁴³ widely used to extract information about metallic surfaces on which foreign atoms and small molecules or polymers are chemisorbed or physisorbed, can be combined with work function measurements to determine the position of the Fermi level with respect to the molecular HOMO, after adsorption of the molecule on the surface.^{44–47} Two very different types of behaviors have been observed. When the chemisorption is accompanied by substantial charge transfer and creation of a dipole layer, the molecular levels are tied to the metal Fermi level. This is the case of both C_{60} ⁴⁶ and 8-hydroxyquinoline aluminum (Alq),⁴⁷ (2.25 eV for C_{60} on Ag, Au, Mg, Cr; 1.7 eV for Alq on Au, Mg). In the opposite case of negligible charge transfer, i.e., alkanes and other wide-gap molecules, the work function changes, but the HOMO remains unchanged.⁴⁴ Here, the HOMO is tied to the vacuum.

The molecule we study in this article, α,α' -xylyl-dithiol, is closer to the first case than to the second. This justifies the assumption of constant HOMO-Fermi level spacing when studying the Au-S bond length and tilt angle dependences. However, we have found no experimental report giving the exact location of the Fermi level. For that reason, only the trends we see, rather than the exact values for the conductance, should be considered.

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(49) The calculated conductance of Figure 1a will be broadened by inelastic scattering,^{10a} and by disorder effects on the wire.^{17a} The correct calculation of the *I*-*V* curve requires^{4d,8b,10a} replacing $g(E)$ by $g(E,V)$ and knowledge of the self-consistent electrostatic potential at all points.

The absence of this information also makes a comparison with the experimentally reported values of the resistance of this type of molecule^{3,7} difficult. Our numbers in the valley of the conductance spectrum on all figures are too low compared to experiment, but a small adjustment in the position of the Fermi level can account for this. It will also make the conductance of these junctions more comparable to an electrical wire.

Summary

We have considered three aspects of the molecule–electrode interface and their effects on the conductance g : geometry variations, chemical nature of terminal atom, and different metals for the electrode. All of our calculations are performed with the same molecular backbone, α,α' -xylyl.

We find that with one exception, varying the surface geometry does not affect the conductance in a significant way. Our findings agree with previous studies on model systems.¹⁹ The

only factor that alters the conductance substantially is the distance between the electrode and the terminal atom.

We find a strong dependence of the conductance on the chemical nature of the terminal atom. The conductance in the gap increases from 1 to 3 to 75, for O to S to Se, respectively. Se is by far the best terminal atom for the molecule we consider.

Finally, we find that changing the electrode metal affects the conductance. In particular, Au(111) conducts 5 times better than Ag(111).

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