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Models of Electron Transfer Through Organized Organic Thin Films (OOTFs) Adsorbed on Metal Surfaces

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University of New Mexico Chemistry Department Master's Exam
10 November, 1998

Abstract: *Because of their many useful electrical and mechanical properties, ordered organic monolayer films may be a key material used in future electronics and electrochemical applications. However, the complex relationships among these thin film's structures and bonding, and their electrical and chemical properties remain largely unknown. A discussion of the varied properties of these films and a proposed approach to calculating the electrical conductivities of the these films are provided.*

Introduction

The main focus of this project is the study of the transfer of electrons through organized organic thin films (OOTFs) adsorbed on metal surfaces. The process(es) resulting in electron transfer in OOTFs appear(s) to be very complex. The complexity arises out of the apparent interdependency among the many experimental variables present during formation of alkanethiol films. It is therefore necessary to methodically investigate each variable independently, to learn the true nature of its contribution to the OOTF's electrical properties. This has been accomplished by an extensive review of reported experimental and theoretical works on various alkanethiol SAMs.

Because of the importance of evaluating the literature to develop the insight which will eventually lead to a more complete and fundamental understanding of charge carrier motion through these organized organic thin films, a two-phased project exists. It is best to describe this project as essentially a combination library study and limited research proposal. Consequently, this project conveniently divided into two main areas. Area 1(A1) is the library study and analysis of the reported physical and chemical properties of OOTFs, with an emphasis on how changes among the various properties effect a film's conductivity. Area 2(A2) is the proposed application of theoretical treatments and description of the methodology used to calculate the electrical conductivities of OOTFs. This report provides a comprehensive review of both areas. The reader is encouraged to quickly review area 1 if they are already very familiar with alkanethiol SAMs.

Area 1: Thin Organic Films

Ordered Organic Thin Films (OOTF's), also commonly referred to as Self Assembled Monolayers (SAMs), and both terms are used interchangeably throughout this paper. SAMs have physical properties that are attracting increased amounts of interest by researchers. Among the many possible varieties of SAMs, this is especially true for alkanethiol SAMs absorbed on a gold substrate. The potential suitability of alkanethiol films in the development of electronic devices and their adhesion promotion of a wide range of alkane/ene/yne molecules to a metal surface are two reasons that research groups are increasing their investigation of these films. As there are many varieties of self assembled monolayer film systems, this project will focus primarily on alkane/ene/yne thiol SAMs. Additionally, when the term "alkanethiol" is used without reference to a specific carbon chain, it is meant to describe the complete class of alkane/ene/yne thiol SAMs.

SAM Energetics

During the past decade, many researchers report that alkanethiols are able to spontaneously self assemble and form dense, well oriented layers on solid metallic surfaces[1]. The various interactions involved in the self assembly process are briefly discussed below. For the purpose of this discussion, the energetics of the adsorbing molecule will be divided into three parts: the head group, the alkyl chain, and the end group. First, the head group is covalently bonded (chemisorbed) to the metallic surface, with bonding energies are on the order of 50 kcal/mol[2]. The attraction of the head group to the metallic surface is the strongest interaction, so the molecules attempt to occupy every possible bonding site on the surface. Next, following the bonding of the head group to the metal, there is an increase in the attractive forces among the akyl chains. These attractive forces are the van der Waals (VDW) forces. VDW forces are normally less than 10 kcal/mol, so the chemisorption of the head force is dominant relative to chain's VDW forces. Finally, the interactions resulting from the end group must be considered. These interactions may vary widely depending on end groups. For example, if the end group is a methyl group at the end

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[1] Ulman, A, "Ultrathin Organic Films", Part 3, pg 237, Academic Press, 1991.

[2] Dubois, L ..et al, Proc. Natl. Acad. Sci. USA, 1987, 84, pg 4739.

of an alkyl chain, vibrational studies suggest the energy (kT is less than 1 kcal/mol) at room temperature is sufficient to thermally disorder these groups[3]. Additionally, the trans-gauche isomerization is an endothermic process, while chemisorption & VDW are exothermic.

Chemisorption Bonding Mechanism

The exact mechanism involved in the chemisorption reaction of an alkanethiol with a gold surface is unknown. However, it is known that initially before the alkanethiol bonds to the gold, the alkanethiol molecule has a hydrogen atom attached to the sulfur head group. It is also known that as a result of the sulfur's chemisorption to the gold, the hydrogen atom is removed from the alkanethiol sulfur, and the gold atom becomes (+) charged, while the sulfur atom acquires a (-) charge. Unfortunately, because the reaction's intermediate steps are unknown, it is unclear whether the thiol hydrogen is removed as a H_2O or as a H_2 gas[4]. These two possible reaction mechanisms, are illustrated in Fig 1. Equation 1 in Fig. 1 proposes a reductive elimination of the gold(2) hydride by the oxidative addition of the alkane thiol. Equation 2 in Fig 1. proposes the reaction of the gold(2) hydride with traces of an unknown oxidant species.

Figure 1. Possible reaction mechanisms involved in alkanethiol chemisorption to gold surfaces.

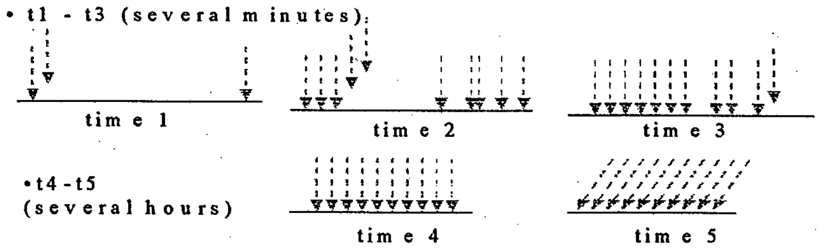
Eqn 1. $RS\text{-}H + (Au^0)n \Longrightarrow RS^{-}\text{--}Au^{+} + 1/2H_2$

Eqn 2. $RS\text{-}H + (Au^0)n + \text{oxidant} \Longrightarrow RS^{-}\text{--}Au^{+} + 1/2H_20$

Kinetics of alkanethiol SAM formation

The formation of an alkanethiol monolayer on gold is believed to be a two step process. Experimental evidence clearly suggests a very rapid step (step 1) that occurs in several minutes, followed by a slower step (step 2), that last for several hours[5]. Additionally it is also reported that the thickness of the film after step 1 (i.e. several minutes) is approximately 90% of the films final thickness, and the tilt angle (theta) of the film reaches its final value after several hours. Another study of alkanethiol kinetics conducted by Bain (ref 5), showed increased rates of formation for longer alkane chains. This relationship is better understood when one recalls the earlier discussion on how the VDW forces relate directly to alkane chain length. These results strongly suggests that step 2 is primarily dominated by VDW interactions from the ordering of the alkanethiol chains. This conclusion is also supported by the times associated with the changes in tilt angle to their final values. For the self assembly process in Fig. 2., step 1 = times 1-3, and step 2 includes times 4-5.

Fig. 2: Self Assembly Process"



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[3] Nuzzo, R. G. et al, J. Chem. Phys, 1990, no 93, pg 767.
[4] Ulman, A, "Ultrathin Organic Films", Part 3, pg 288, Academic Press, 1991.
[5] Bain C.D. et al, J. Am. Chem. Soc., 1989, no 111, pg 235.

SAM Structures

Because a gold (111) surface is different than a gold (100) surface, it is important to consider how these differences affect the bonding and resulting surface geometry of alkanethiol SAMs on gold. The surface structure of gold (111) atoms are known to occur in a hexagonal pattern, while a gold (100) surface usually adopts a reconstructed cubic surface structure[6]. Ignoring the possibility of surface reconstruction, the differences between the 111 and 100 surfaces of gold are illustrated in Fig. 3. The atoms in the 100 surface are spaced so they create a simple cubic 1x1 unit cell, while the atoms in the 111 surface are hexagonal. Also, the density of the 111 surface is higher than the density of the 100 surface, which is expected, since the 111 surface is the closest packed surface. Because of these pronounced differences in the surface of gold 111 and 100, one may suspect there will be similar differences in the resulting alkanethiol monolayers adsorbing to each of these gold surfaces.

Figure 3. Structures of gold (111) and (100) surfaces

gold(111) is hcp has ABABAB structure X = gold atom	gold(100) is cubic, forms 1x1 unit cell
(111)	(100)
X X X X X	X X X X X
X X X X	X X X X X
X X X X X	X X X X X

Compelling experimental data from Low Energy Electron Diffraction and Scanning Tunneling Microscopy suggest there are differences in how an alkanethiol bonds to the two gold surfaces described above[7,8]. In the case of gold 111, it was reported that the alkanethiol sulfur adsorbs in a three-fold hollow site between the gold atoms, resulting in a hexagonal pattern with sulfur-sulfur (S-S) spacing of 4.99 angstroms (Ang.). In contrast, an alkanethiol adlayer on gold 100 results in a base centered square adlayer, with S-S spacing of 4.54 Ang. Additionally, based on the relative low stability of the 4.54 Ang. S-S spacing alkanethiol adlayer, the 100 layer could not be perfectly flat as expected, rather it must be corrugated (this will be further explained in the discussion on surface reconstruction). The resulting structures of an alkanethiol monolayer adsorbed to gold 111 and gold 110 surfaces are further illustrated in Figure 4.

Surface Reconstruction of Gold

In addition the differences between gold 111 and 100 surfaces, it is also believed that these surfaces reconstruct and also exhibit metastable behavior under certain conditions[9,10]. Reconstruction of the gold surface also results in changes in the surface density. Experimental results (ref's 9&10) clearly illustrate the reconstructive behavior of a gold 100 surface under the influence of a negative potential. As a (-).1V potential was applied to the gold 100 surface, the surface developed "waves in the previously flat (1x1) terrace...". At negative .3 to .4V, the gold 100 surface "transformed into corrugated domains", with approximately 20% higher atomic density than the bulk. This potential induced reconstruction was removed if a positive potential was applied to the gold. Similar potential induced surface reconstruction behavior was also discussed for gold 111 surfaces.

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[6] Ross, P.N., D'Agostino, A.T., Electrochemica Acta, vol 37, no 4, 1992, pg 615-23.

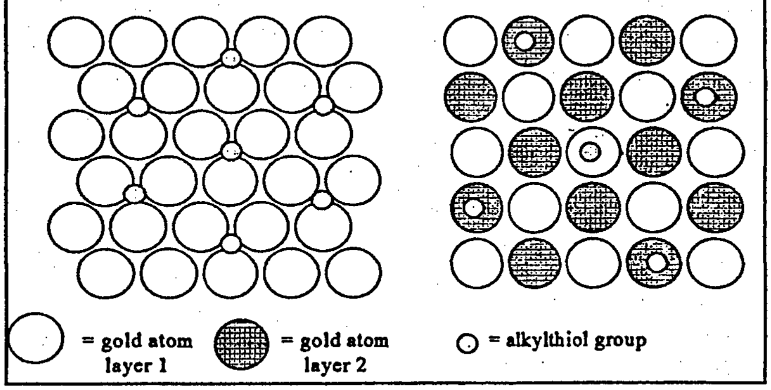
[7] Strong, L., Whitesides, G.M., Langmuir, 1988, no 4, pg 546.

[8] Chidsey, C.E.D., Loiacono, D.N., Langmuir, 1990, no 6, pg 709.

[9] Wendelken, J.F., Zehner, D.M., Surface Science, no 71, 1978, pg 178-84

[10] Xiaoping, G., et al, Phys. Rev. Lett., vol 67, no 5, 29 Jul, 1991, pg 618-621.

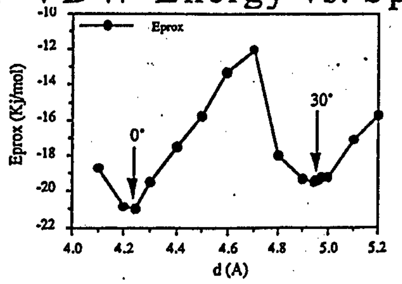
Fig. 4 Gold 111 vs 100 Adlayers



As an aside, since a gold surface is able to reconstruct in response to the application of an electrical potential, one wonders if these geometric changes are influenced by the negative charges of the thiol molecules. If the surface potentials created by molecular dipoles at the gold-sulfur interface did influence the reconstruction of the gold surface, then a more negatively charged sulfur atom would have a greater impact on the rearrangement geometry of the surface.

Recall that in the previous discussion of gold 100 surfaces, in the section titled SAM Structures, the surface structure of the gold 100 surface was also described as corrugated. A closer look at this surface's reported S-S spacing (4.57 Ang.), and the calculated optimal tilt angle as a function of the highest VDW interactions, explains the waves/corrugations in the gold 100 surface. Finally, this analysis is useful for explaining why the measured tilt angle of an alkanethiol film on gold 100 is less than the tilt angle of an alkanethiol on gold 111[11]. Figure 5 is a plot of the calculated optimal VDW interaction energy versus the tilt angle for dodecanethiol ($C_{12}H_{25}SH$). The increasing distance between sulfur atoms is plotted along the horizontal axis, while the decreasing interaction is plotted along the vertical axis. The two minima at approximately 4.25 and 4.96 Ang. illustrate two optimal S-S atomic distances that maximize the VDW forces in this alkanethiol. The minimum at 4.25 Ang. requires a 0 degree tilt angle and the minimum located at 4.95 Ang. requires a 30 degree tilt angle. Based on these best interaction energies illustrated in Fig 5., other similar alkanethiols should have similar S-S spacing consistent with the minima in Fig 5.

Fig 5. VDW Energy vs. Spacing



The best interaction energy (for optimal in-plane tilt) as a function of the spacing (*d*). (From Ulman [87], © 1989, Am. Chem. Soc.)

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[11] Ulman, A, et al..,Langmuir, vol 5, 1989, pg 1147-52.

The maximum value in Fig 5. occurs around S-S spacing of 4.6 to 4.7 Ang., S-S distances where the calculation predicts the weakest VDW forces for our alkanethiol molecule. The greater the reduction in VDW forces, the more unstable the alkanethiol SAM. In the gold 100 case, if the sulfur spacing is 4.57 Ang., and the calculations in Fig 5 are reasonable, then the gold 100 film should be relatively unstable. However, this is not the case. If the gold 100 film is stable, and the data in Fig 4 are accurate, then an explanation for the gold 100 SAM's stability may arise from the corrugated nature of the 100 surface. On such a surface, the height of the surface alternates between adjacent rows of atoms (layers 1&2), and a body centered cubic surface layer is added exactly as shown in Fig 4., with the body center adatom sitting below it nearest neighbors. The key to increased stability in this structure is the alignment of the hydrogen atoms on adjacent alkane chains[12]. By considering the different geometry illustrated in Fig. 4, and the relationship between the spacing, tilt angle, and hydrogen overlap, it is possible to explain the different SAM tilt angles between the gold 111 and 100 surfaces. Future work of this nature could also be used to investigate the reported differences in tilt angles of alkanethiols absorbed on silver surfaces.

Alkanethiol SAM Electrical Conductivity

Because of their widely varied electrical conductivity characteristics, organic films in general are considered ideal for use in electrical devices. However, the underlying reasons for changes in an alkanethiol SAM's electrical properties probably result from a complex interaction among many possible variables. Based on a review of the recent literature, it appears the electrical conductivity of film is determined by the following conditions: the number of carbon atoms in the carbon chain; the intra-chain and inter-chain (carbon-carbon) bonding; how the chain is bonded to the surface; the placement of attached or substituted functional groups; changes in temperature, and solvent effects. Several of these variables were already described in the paper's earlier sections, but their contribution to these variations in an alkanethiol SAMs conductive properties were not addressed. A brief series of examples are given to further illustrate the interdependencies of the conductivity with other film variables.

Example 1: experimentally, it has been shown that an increase in the conductivity of an N-alkanethiol (where N>12) SAM is proportional to the amount of disorder in the alkanethiol film. When the conductive properties of 12-alkanethiol SAMs are compared with silicon dioxide films of similar thickness, under certain conditions the organic films demonstrate improved insulating capabilities. However, if the organic films are disordered the insulating properties are reduced, and the conductivity of the film tends to be much higher[13]. It is not clear from the referenced study how the disorder was introduced into the film (i.e. thermal, mechanical, etc.). Furthermore, whenever an ultra-thin film is disordered, it is also important to determine the increase in conductivity was not caused by the incorporation of defects (holes) in the film.

Example 2: One reported effect of substituting the end group on a thiol surface is to change the tilt angle of the thiol molecules in the film[14]. Used as a rough measure of the relative energy, tilt angle may be used to determine if the structure is in a low or high energy configuration. If a film is not in a low energy configuration, it may be reasonable to expect the film to further relax over time or during annealing.

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[12] Ulman, A, "Ultrathin Organic Films", Part 3, pg pg 315-17, Academic Press, 1991

[13] Boulas.. et al, Phys Rev Lett, 76, no 25, 17 Jun 96, pg 4797.

[14] Tao, Y., Lee, M., Thin Solid Films, 244, 1994, pg 810-14.

Example 3: Halogenation of a thiol SAM changes the dipole moment of the molecule. An unsubstituted alkene thiol has a dipole directed along the axis of the molecule towards the M-S interface. However, a halogenated alkene thiol may have a different dipole moment. For example, for the fluorinated alkane thiol the dipole moment is actually reversed away from the M-S interface and towards the fluorinated end of the molecule. Because the dipole moment is directly related to the surface potential, and thiol tilt angle responds to temperature, changes in temperature may also result in changes in surface potential. Such a pyroelectric effect was reported for the fluorinated alkane thiol on gold mentioned above[15]. It is important to understanding how these halogen substitutions alter the bonding properties of the properties of the films. A greater understanding of this phenomenon may also introduce new data to the ongoing debate over the relationship between temperature and conductivity in SAMs.

Example 4: It is possible to vary the type of metal to systematically investigate how changes in these films properties directly correlate to the resulting changes in the M-S interface. In addition to changes in thiol bond angles, recent experimental evidence also suggests that other electrical properties may be significantly effected just by varying the metal from Au to Ag[16]. Furthermore, the tilt angle of the molecule is reported to decrease when the alkanethiol is bonded to silver. This substitution is expected to directly modify the covalency of the M-S bond. Additionally, electrical conductivity differences arising from the presence of a native oxide on silver (i.e. silver oxide) surfaces must be considered.

From these limited examples, is becomes clear the OOTF's electrical properties depend on many variables. Because the sum of the previous OOTF characterization work does not yet provide the complete picture of how these organic films electrical behaviors change with selected experimental factors, additional experimental studies and a further review of the literature are needed understand the combinations of variables and their individual contributions to conductivity.

3 Types of Electrical Behavior

The previous studies of alkanethiol SAMs absorbed on metal surfaces illustrate a wide range of reported electrical conductivities ranging from insulator to conductor. For the purpose of this discussion, the types of OOTF electrical behaviors are classified according to one of the following conductivity categories: insulators, conductors, and rectifiers. Below, more detailed descriptions of each of the three conductivity categories and representative examples of typical OOTFs for each category are provided.

Because alkanethiol SAMs may be produced with so many different combinations of experimental variables, it may useful to analyze the changes in electrical conductivity as the OOTF's other variables change. For example, the alkanethiol SAMs' electrical conducting and insulating behaviors are reported to depend on variables such as the type of carbon chain comprising the thiol molecule, and the amount of disorder in the film[17]. Additionally, the SAM rectifier properties are suspected to arise out of a combination of the metal-sulfur bonding interactions and the type of carbon chain attached to the sulfur[18]. Table 1 provides a summary of the suspected relationships between reported OOTF electrical properties and other experimental variables. If no experimental data was available for a specific experimental variable listed in table 1, it is represented by a "?".

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[15] Robinson, G.N., et al.., Thin Solid Films, 310, 1997, pg 24-28.
[16] A. Dhirani, et. al., <u>JCP</u> Vol 106(12),3/22/97, pgs 5249-5253.
[17] Boulas, <u>Phy Rev Lett</u>, Vol 76, #25, 6/17/96, pgs 47974800.
[18] A. Dhirani, et. al., <u>JCP</u> Vol 106(12),3/22/97, pgs 5249-5253.

Variables	Insulating OOTF's	Conducting OOTF's	Rectifying OOTF's
conductivity	Low	High	Varied by direction
# of Carbons	More than 12/ < 6	Varies	Varies
unsaturated	No	Yes	Yes
conjugated π bonds	No	Yes	Yes
cross linking	?	?	?
polar head group	No	No	Yes
temperature	?	?	?
order of film	High/Less	Less	High
solvent effect	?	?	?
tilt angle (theta)	?	?	?
Substrate material	?	Au > Ag	Ag > Au

Table 1. Summary of Ordered Organic Thin Film Properties related to conductivity

Insulators. This least conductive class of OOTF's consists of long chain alkanes with representative chain lengths of twelve to eighteen carbon atoms. A typical 2 nm insulating OOTF film has the same conductivity ($\sim 4.6 \times 10^{-15}$ S/cm) as either the bulk (1 um thick) OOTF, bulk polyethylene, and bulk SiO_2[19]. In addition to these excellent bulk insulating characteristics, a few OOTF's are also reported to demonstrate similar insulating properties independent of the film thickness. It is reported that these selected insulating OOTF's demonstrate insulating characteristics in films as thin as 1.9 to 2.6 nm[20].

Conductors. Both OOTF's and many other organic films are capable of acting as conductive layers. Normally a thick organic film may become a conductor if it has been doped with another material. Unfortunately, without the added dopant or if the organic film is too thin, these films are not reliable conductors. This conductivity behavior found in thick organic films is in contrast to the behavior of conductive OOTF's. Typically, conducting OOTF's are formed of shorter carbon chains. In general, decreased chain length in OOTF's results in increased conductive behavior, but there are exceptions.

Rectifiers. This third class of OOTF's exhibit rectifying or asymmetric tunneling behavior at one mono-layer thicknesses. These ordered films are typically terminated with a thiol group and also have a conjugated network of π-bonds along bond axis of the molecule. In principle, other atoms could also be substituted for the thiol group, but no experimental record of this was found. The resulting behavior of this type of OOTF' is a film that acts as a conductor in one direction and a semi-conductor in the other direction, with reported conductive differences sometimes varying by several orders of magnitude.[21]

Area 2: Methodology for Determining Electrical Conductivity

Recall that the continuum dielectric (CD) model calls for the conductivity of a material to decrease with the material's increasing thickness. However, it was recently reported that the conductivity across an alkanethiol SAM was independent of the monolayer's thickness[22]. These reported deviations in the alkanethiol SAM's conductive properties away from what is predicted by a CD model suggest that additional factors must also contribute to conductivity. Because conductivity is essentially the process by which electrons are transported through a material, and very small particles (such as electrons) exhibit quantum behavior, perhaps a quantum mechanical based

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[19] Boulas, et al....

[20] D. Gust, "Molecular Wires and Girders", Nature, Vol 372, 10 November 1994, pgs 133-134.

[21] A. Dhirani, et. al., JCP Vol 106(12),3/22/97, pgs 5249-5253.

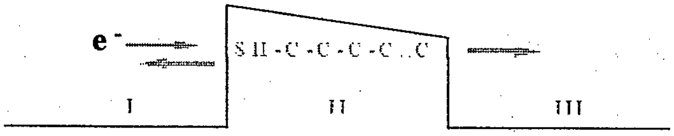
[22] Viullaume, D. et al, Appl. Phys. Lett., vol 69, no 11, 9 Sept, 1996, pg 1646-48.

approximation could be used to better explain the observed conductivities in these films. It is also important to consider the initial energy of the electron relative to the material it is to conduct through. If the electron's energy is lower than the conductor's energy, the electron scatters through the conductor. Conversely, if the electron is initially at an equal or higher energy relative to the conductor, the electron will tunnel through the conductor. Electron tunneling will be assumed.

Electron Tunneling

A simple way to illustrate electron tunneling is to use a one-dimensional (1D) potential barrier model. Figure 6 illustrates the case of electron tunneling through a 1D barrier. As depicted by Fig 6., the tunneling probability results from only the parts of the electron's wavefunction that successfully pass through the barrier. The wavefunction (Psi or Ψ) is divided into 3 areas, Ψ_I left, Ψ_{II} under, and Ψ_{III} to the right of the barrier. Additionally, Ψ_I consists of a forward portion that tunnels into the barrier (Ψ_{If}), and a reverse portion (Ψ_{Ir}) that is reflected backward from the barrier. Only Ψ_{If} and Ψ_{III} contribute to electron tunneling. Therefore, the probability of tunneling can then be expressed as Ψ_{III} / Ψ_{If}. This model will be useful to qualitatively explain many of the alkanethiol's observed conductive properties, but a higher order model could be used more quantitatively to study the conductivity.

Fig 6. 1-D Electron Tunneling



$$\text{Prob}_{\text{Tunnel}} = \text{Psi III/Psi I}_{\text{forward}}$$

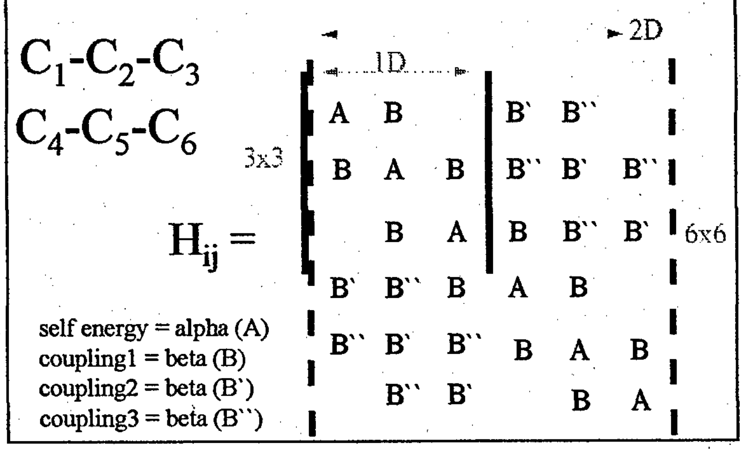
(Prob_T Left to Right)

Hückel Theory

Another way to describe our thin film system is the use of a semi-empirical methodology. If an organic film consists of conjugated hydrocarbons, the delocalized π electron distribution may be approximated using Hückel Molecular Orbital (MO) theory. An assumption of this theory is that the π electrons move in a fixed electrostatic effective potential due to the sigma framework of the molecule. In general, this approach would allow a solution for any N atom conjugated chain by using the resulting secular determinant. The 3x3 matrix illustrated in Fig 7, is the 1D treatment using nearest neighbor interactions (B) of an alkene/yne-thiol. Fortunately, this simple Hückel approach may be extended to more complex (and realistic) systems.

By using Extended Hückel theory it is also possible to study nonconjugated systems and alkanethiols, as well as 2D and 3D systems. This ability to look at more complex systems is possible because the extended model incorporates additional interactions beyond the π interactions used in the simple Hückel model. In other words, the original model could be extended to include the sigma (σ) bonding interactions, other π bonding interactions, and also look at single/multiple row(s) of molecules (2D/3D), where inter-chain interactions are considered. The dashed line matrix shown in Fig 7. illustrates the application of Extended Hückel theory to a 2D alkanethiol system (i.e. 2 parallel carbon chains). From this examples, one should clearly recognize that as the dimensionality and number of possible interactions increases, so does the size of the Hamiltonian matrix.

Fig 7. 1D & 2D Huckel Models



The Beta (β) terms used in Fig 7. represent the interactions discussed above. Note that the 3x3 matrix only contains β's for nearest neighbor interactions for a 3 carbon hydrocarbon chain, while the 6x6 matrix includes an additional β` and β`` interactions. It is important to understand that each type of extra interaction will have its own unique β (i.e. β being nearest neighbor on the same chain versus β` being nearest neighbor inter-chain, and β`` being inter-chain diagonal), and the inclusion of these additional β's into the secular determinant result in different calculated values for the effective Hamilitonian.

The extended model includes the additional interaction terms (β`,β``,etc..). Because the additional interactions are included and not assumed to be zero, the accuracy of this technique should be improved relative to the basic model. Therefore, it is reasonable to expect the extended model will offer the more accurate results. Finally, since the β coupling terms are related to the inter-atomic spacing[23], the better known the structure of the alkanethiol SAM, the better the accuracy of the Hückel calculations. Hence, classical Molecular Dynamics simulations should also be used to calculate the relaxed molecular orientations from which the bond distances and structures are used to estimate β.

Conductivity

This use of Hückel theory to approximate an alkanethiol SAM adsorbed to a metal surface only accounts for the hydrocarbon portion of our system. The metal film, the sulfur atom, and the connections between the ends of the hydrocarbon chain and the metal (or STM tip) must also be considered. Fortunately, a simple relationship (Equation 1) exists between conductivity and all of the components of our system[24].

$$\mathbf{g = 2e^2/\pi\hbar\ \Delta_l\Delta_n|G_{ln}|^2\ \ (Eqn\ 1)}$$

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[23] MD simulation book from Dr. Evans...

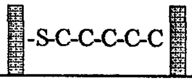
[24] Kemp, M., et al.., J. Phys. Chem., no 100, 1996, pg 8349-55.

Fig. 8 is a useful summary that illustrates how the Green's function relates to conductivity. The Green's function (G_{ln}) is derived from a modified Hamiltonian matrix H_{ij}. The modified Hamilitionian matrix has different ll and nn values, arising from the coupling of the ends of the hydrocarbon chain to the rest of the system. G_{ln} is then obtained by inverting this modified Hamiltonian matrix. The delta (Δ) terms refer to the coupling matrix values between the ends of the alkane thiol and the metal surface (or STM tip). As different alkane/ene/yne molecules and other metals are used, modified β and delta terms must be calculated. In principle, this approach could solve the conductivities of a wide variety of SAM systems. A main challenge of using this approach to determine conductivity is the problem of accurately determining the Δ coupling matrix elements and the β's.

Fig. 8 Conductivity Calculations

- Beta related to atomic spacing(x) by: $B=e^{-ax}$
- H_{ij} directly from tight binding
  - – Eigen energies (Homo-Lumo), Wavefunctions
- Green's Function (G) ~ H^{-1}
- $(g) = \frac{2e^2}{(Pi)(hbar)} (delta_l)(delta_n)|G_{ln}|^2$

Kemp, Molecular Wires:Extended Coupling and Disorder Effects, JPC V100, No 20, 1996



Currently, the method of choice to estimate the Δ terms is based on the Newns-Anderson Chemisorption model[25,26]. This approach's arbitrary nature of the assignment of the coupling element Δ does not provide an understanding of the relationship between the value of the coupling interaction and the actual structure of these interfaces. An alternate method of calculating these coupling interactions is to perform Density Functional Theory (DFT) calculations on our SAM/gold system and use those results to scale the Δ coupling values used in Eqn 1.. This alternate approach, which uses DFT derived Δ values, seems to have the possibility of providing both more accurate and more understandable results when compared against the current computational method.

Summary

Alkane/ene/yne-thiol SAMs exhibit a wide range of electrical conductivity properties. An understanding of the relationship of their physical properties to their conductive properties could open up numerous commercial and scientific applications of these monolayer films. A modified approach to calculating the conductivity of these films is proposed. The proposed determination of the coupling matrix elements, and the use of an extended Hückel model are the key differences between the proposed method and the present computational methods. The results of this project are expected to generate more accurate results for the conductivity calculations and also provide a better qualitative picture of conductivity in SAM films.

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[25] ibid

[26] Kemp, M., et al.., J. Chem. Phys, 101(6), 15 Sept, 1994, pg 5172-78.