



Interactions between molecular wires and a gold surface

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Abstract

The thiol group attaches strongly to gold surfaces and can thus be used as interconnects of molecular wires in nano electronics. A phenyl molecule attached to gold via a thiol group has been investigated by ab initio Hartree–Fock calculations in order to understand electronic transport through the sulfur–gold bridge. In our analysis of the coupling between gold and the molecule, we found that the electronic system of the gold substrate interacts directly with the conducting states of the molecule and thus forms an ohmic contact to the molecular wire. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

The molecular wire based on conjugated molecules is a fast developing research area in modern electronics [1,2]. The electronic conduction of many different metal/molecule/metal systems has been studied experimentally [3]. Theoretically, the emphasis has been on the molecular wire itself [4] and very little is known about the detailed interaction between the metal contacts and the molecular wire. This interaction can be discussed in terms of chemisorption, in which the molecule forms a chemical bond to the surface, and physisorption in which the molecule interacts much more weakly with the metal contact. The standard approach to chemisorb molecules to a metal contact is to use gold as a contact material and to attach a thiol group to the molecule. The thiol group forms a strong chemical bond to the gold surface. In the case of physisorp-

tion, the molecule is bound to the surface by weak Van der Waals forces. This situation applies for instance to the studies of conductance through C_{60} [4] but also to all cases in which an STM tip is used as one of the leads to contact the molecular wire [4]. Molecular/metal interaction in the case of physisorption is usually described as a weak hopping between neighboring atoms on the metal and the molecule. However, in the case of chemisorption of thiols on gold, the situation becomes much more complex. The symmetry of the gold orbitals forming the bond to sulfur is important as well as the coupling of the sulfur to the rest of the molecular wire.

The purpose of this Letter is to achieve a better understanding of the gold–thiol–molecular wire interaction, in particular to what extent the π electronic wavefunctions of the molecule interact with the sulfur and gold orbitals. The molecule investigated is a phenyl ring with a thiol(-SH) group attached to one of the carbon atoms of the ring. By studying the ground state geometry, the charge transfer and the molecular orbitals of the gold–thiol–

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phenyl system we show possible ways for electronic transport from the gold surface into the molecule.

2. Methodology

The calculations have been performed at the ab initio Hartree–Fock level (HF) [5], using a double-zeta basis set of contracted Gaussian functions including a relativistic effective core potential for gold (LanL2DZ [6–8]).

The (111) gold surface was modeled by a 10-atom cluster. The geometry of the cluster, i.e. the bond lengths and bond angles was fixed to that of a gold lattice (Au–Au bond length is 2.88 Å). It has been shown [9] that an underlying layer of atoms is of great importance for the electronic structure of thioliates on gold. Therefore, the 10-atom cluster consists of a two-layer structure, one upper layer of 7 atoms and one lower layer of 3 atoms. The formation of a chemical bond with the thiol group is a fairly local type of interaction. Thus, even though the gold cluster is very small, we believe that it is large enough to reveal the correct symmetry of the chemical bond and thus to give insight into what type of coupling there is between the π -system of the phenyl molecule and the gold(contact).

The methodology for investigating the electronic properties of the molecule on the gold substrate basically consists of four steps:

1. Geometry optimization of the free molecule (C_6H_5SH).
2. Determination of the equilibrium position of the molecule on the gold surface.
3. Re-optimization of the molecular geometry with the molecule (C_6H_5S) fixed on the position from step 2.
4. Analysis of the molecular orbitals and the corresponding energies for the free molecule and the molecule attached to the gold surface.

For practical reasons it is not possible to allow for a complete geometry relaxation of all the degrees of freedom related to the orientation of the molecule relative to the gold cluster in one single calculation. Since the gold cluster is rather small, there are large

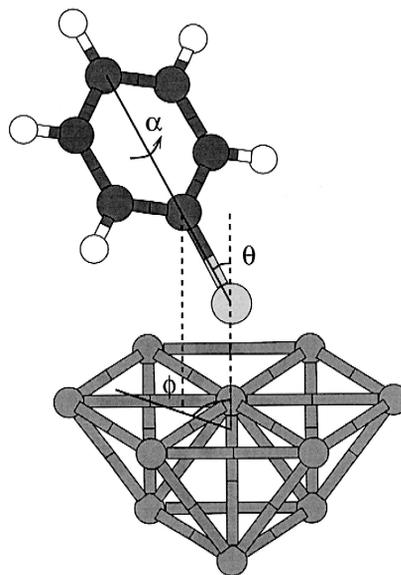


Fig. 1. Sulfur bonded phenyl on a hollow site of the gold cluster.

edge effects that can lead to energy minima that reflect the properties of the cluster rather than of the gold surface. Since we are interested in the properties of the surface, we have to restrict the positioning of the molecule to the interior of the cluster. Fig. 1 shows the total system configuration. The sulfur atom is placed in its predicted equilibrium position [9,10] in the middle of a three atom gold triangle and right above a gold atom in the second layer (see below). The rest of the orientation of the molecule relative to the gold cluster is described in terms of the direction of the S–C bond both relative to the surface normal, angle θ in Fig. 1 and relative to the center of the gold cluster. The latter angle is referred to as the rotation angle, ϕ . Both θ and ϕ have been optimized in this work. Furthermore, we have also optimized the direction of the plane of the phenyl ring. The direction angle, α , is defined as zero when the phenyl plane is perpendicular to the gold (111) surface.

3. Results and discussion

Geometry optimization of the free molecule (C_6H_5SH) results in an S–C distance of 1.83 Å. All

C–C bond lengths are almost identical in the phenyl ring, around 1.39 Å. As an intermediate step we have re-optimized the molecular geometry replacing the hydrogen with a single gold atom. This resulted in a very small change of the S–C bond length to 1.84 Å. The ring structure also remains unchanged with an aromatic structure in which the C–C bond lengths are 1.40 Å. The Au–S bond length is 2.41 Å, which actually is very close to the value we obtain for the 10-atom cluster (see below). Using this geometry we checked first the lateral position of the molecule on the gold surface. Experimentally it is known that the preferred position of the sulfur is in the hollow site, on top of a gold atom in the second layer of the gold substrate [11] (see Fig. 1), it has also been calculated by, e.g., Sellers et al. [9] We have also calculated the total energy of the complex for different positions of the sulfur relative to the surface and observed a clear minimum for the experimentally predicted position. This result indicates that the Au₁₀ cluster is a relevant model at least for the more qualitative features of the gold–thiol interaction. Thus, the type of interactions that determine the position of the thiol-substituted molecule to the surface are independent on the detailed structure of the molecule attached to sulfur.

To obtain the ground state distance between the gold surface and the sulfur atom (placed above a hollow site), we performed a series of total energy calculations, varying this distance between 2.20 and 5.00 Å (see Fig. 2).

When going from small distances to higher (see Curve 1), making use of the density matrix from the *next lower* distance, we see a clear energy minimum for the distance 2.50 Å and a continuous increase in total energy as the distance increases. However, when going from large distances to small (see Curve 2), using the density matrix from the *next higher* distance, for large distances the energy is much lower than the one calculated when going upwards in distances. Obviously, this discrepancy is a computational artifact, i.e. the SCF calculation converges to two different local minima depending on the input density matrix. This has to be due to the fact that there is a substantial energy barrier in redistributing the charge density from that corresponding to the case when a chemical bond is formed (Curve 1) to that of no chemical bond. In order to

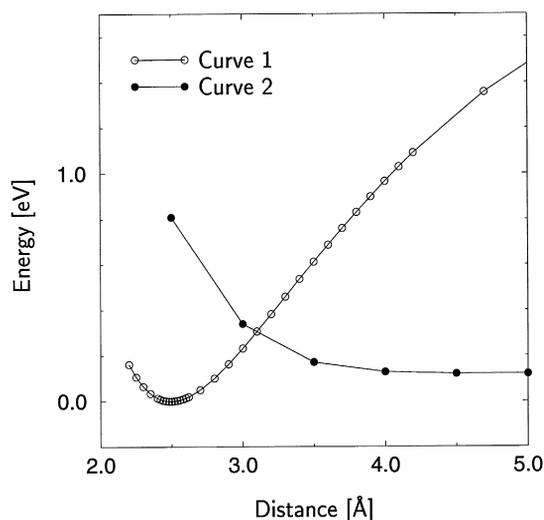


Fig. 2. Total energy of the complex relative to the ground state at different distances between sulfur and the gold surface.

put this in more quantitative terms, in Table 1 are shown the Mulliken charges of the sulfur atom and the S–C bond as well as the Au/S bond order matrix element (related to the bond strength) for different distances between the sulfur atom and the surface. The upper six rows are values from Curve 1 and the two last rows are values from Curve 2.

These values give a clear indication that Curve 2 corresponds to a state for which the molecule and the surface are *not bonded* to each other whereas Curve 1 corresponds to a state for which they *are bonded* to each other.

To get an estimation of the strength of the sulfur/gold ground state bond we consider the difference in total energy between the bonded ground state at 2.50 Å and the sum of the total energies for the gold cluster and the free C₆H₅S molecule (geometry optimized). This energy difference which turns out to be 0.1 eV corresponds to the dissociation energy of the thiol–phenyl system from the gold surface. Due to the computational artifact discussed above, it is difficult to estimate the dissociation barrier, i.e. the barrier when moving the molecule from the ground state at 2.50 Å to infinite separation (see Curve 1). It might be the case that the system remains in its local energy minimum, i.e. the bonded

Table 1

Mulliken charges of the sulfur and S–C bond, bond order matrix element for different sulfur–surface distances. The six upper rows correspond to Curve 1 and the two lowest rows correspond to Curve 2

Distance (Å)	Charge _S	Charge _{S–C}	P _{Au,S}
2.20	–0.120218	–0.31196	0.243263
2.50	–0.171161	–0.41830	0.268583
2.60	–0.187108	–0.44805	0.277842
3.10	–0.243130	–0.55443	0.295237
3.40	–0.270775	–0.60620	0.287846
3.48	–0.272877	–0.61093	0.280174
3.50	+0.162710	+0.04651	0.082116
5.00	+0.092622	–0.03264	0.037194

state, even though the total energy is lower for the non-bonded electronic configuration. However, with thermal fluctuations included we can expect that the energy barrier will be overcome fairly close to the crossing of the two potential curves. A lower limit of the barrier would therefore be approximately 0.3 eV. With this barrier it is likely that the molecule will remain bonded to the gold substrate even in the case of local heating that can be expected when a current is passing through the molecular wire. We also stress that from our calculations, conclusions can only be drawn concerning the dissociation process – not regarding a self-assembling reaction when the approaching molecule is C₆H₅SH and a hydrogen molecule might be created in the surface reaction [9].

Given the position of the sulfur atom in a hollow site, 2.50 Å above the gold surface, we re-optimized the orientation and the structure of the molecule (see Fig. 1. The angle between C–S and the surface normal is $\theta = 37^\circ$. Sellers et al. have calculated this angle to be 0° and 76° corresponding to a sp and sp³ hybridization of sulfur respectively. The rotation angle, defined as 0° when the molecule is directed towards the center atom of the cluster, is $\phi = 50^\circ$ and the tilt angle, defined as 0° when the plane of the phenyl ring is perpendicular to the surface, is $\alpha = 80^\circ$. The overall result is that shown in Fig. 1. It must be stressed however, that the energy surface for changes in all these angles is very flat and that the molecule is likely to rotate quite freely at ambient temperatures.

The energy levels of the molecular orbitals were examined for the thiol–phenyl molecule itself as well as for this system interacting with the gold

cluster (see Fig. 3). The eigenstates of the gold–thiol–phenyl system close to the Fermi level were also analyzed in the simplest possible way, by summing up the squared atomic orbital (LCAO) coefficients on each of the gold, thiol (sulfur) and phenyl subunits, see Table 2. Only the high lying π orbitals of the phenyl system and the gold 5d, 6s and 6p orbitals are involved in these states.

The two pairs of rather isolated highest occupied molecular orbitals (HOMO) and lowest unoccupied molecular orbitals (LUMO) in Au₁₀ shift almost rigidly towards lower energies upon interaction with the thiol–phenyl molecule. Except for HOMO-1, these levels show very weak coupling to the orbitals of the molecule. HOMO-1 has a substantial contribution from sulfur with a small tail into the phenyl

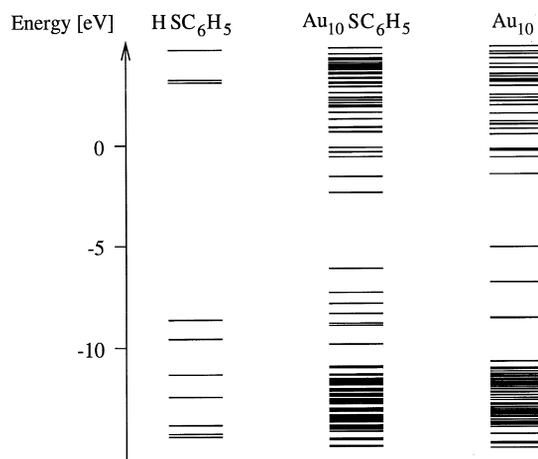


Fig. 3. Energy levels of the isolated molecule the molecule interacting with the gold cluster and the gold cluster alone.

Table 2
Contribution from different orbitals in percent of total molecular orbital, ground state geometry

Orbital	Au ₁₀	S	Phenyl- π
LUMO+2	98.8	0.7	0.5
LUMO+1	97.1	2.2	0.8
LUMO	93.8	3.6	2.5
HOMO	99.4	0.3	0.3
HOMO-1	75.3	17.5	7.2
HOMO-2	43.4	30.3	26.2
HOMO-3	41.1	43.4	15.5
HOMO-4	88.7	6.7	5.1
HOMO-5	9.3	3.0	87.6
HOMO-6	60.1	21.0	18.8
HOMO-7	21.9	23.5	54.5
HOMO-8	76.4	8.5	σ

π -system indicating that this level contributes to the bond between gold and the thiol unit. In the next group of occupied levels, i.e. HOMO-2 to HOMO-5 we find two levels, HOMO-2 and HOMO-3 that show a very strong hybridization between gold, sulfur and the π -system of the phenyl ring. These orbitals could be of great importance for electron transport between the gold surface and the molecular wire since they connect in a coherent way the electronic systems of these units. This situation stands in sharp contrast to the case of tunneling for which there is a barrier for charge injection into the wire. Thus, if connection to both ends of the molecular wire can be made via a thiol bridge, we would expect an ohmic behavior of the current through the wire.

The HOMO-6, which appears in a sub-gap in the occupied part of the spectrum, and the HOMO-7 levels are also very delocalized and couple the extended states of gold to the likewise extended π -states of the phenyl ring. Around 5 eV below the HOMO energy, in HOMO-8, we observe the first contribution from σ a state of the phenyl ring. Also in this state, there is a fairly strong electronic coupling to the orbitals on the thiol group and on the gold cluster.

The hybridization of orbitals located on the gold cluster with orbitals of the thiol unit shows that the gold–sulfur bond has a substantial covalent character. In addition, there is also some ionic contribution to this bond. This is in agreement with studies of SH

and SCH₃ on a hollow site of Au(111) by Sellers et al. By analyzing the Mulliken charges we find that the gold surface has a total deficit of about 0.4 electrons and a corresponding surplus charge on the sulfur atom (−0.2) and on the carbon atom bound to the sulfur (−0.2), see Table 1.

Since the gold cluster is very small, the charge distribution in this cluster is quite different from the image type of charge distribution that is expected for a semi-infinite gold substrate. Thus, the ionic contribution to the gold–sulfur bond is poorly described in the present model and the value of the disassociation energy discussed above is therefore not very precise. The results discussed here should only be considered as an indication that there is a charge transfer at the interface. Very important however, is the observation that the charge transfer is more related to the S–C group than to the molecular wire as a whole. The π -electron system of the molecule would therefore remain essentially ‘undoped’ and we do not expect to observe the formation of defects like polarons or bipolarons on the molecular wire. Another important observation related to the transport from the metal contact into the molecular wire is the dipole layer at the interface that certainly will effect the transport of electrons through the thiol group and into the π system. Thus, in calculations of the conductance, that in most cases are performed using a Hückel type of description of both the wire and the contact, the contact problem probably needs a more careful analysis [12].

In conclusion, the sulfur bridge between a gold contact and an unsaturated molecular wire has been studied using quantum chemical methods. The most important observation is that of molecular orbitals extended from the gold cluster describing the gold contact into the π -system of the molecular wire. This indicates an ohmic type of contact, at least for the short wire that is treated here. For longer wires, this type of state might not be extended all through the system which would lead to a tunneling charge transport process instead. Furthermore, we observe some charge transfer from gold to the S–C group. This charge transfer sets up a dipole layer at the surface. The electrostatic potential associated with this layer is also essential for the charge transport across the interface between the metal contact and the molecular wire.

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