Electronic properties of metal–molecule–metal systems at zero bias: A periodic density functional study

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We have studied the electronic properties of conjugated and saturated dithiol molecules sandwiched between two Au(111) electrodes using first principles density functional calculations with a slab geometry. Relaxation of the molecule/surface adsorption geometry as well as the extended character of the metal electrode states are fully taken into account by our approach. Investigated quantities include the alignment of molecular energy levels with the Fermi energy (E_F) of the metal, the charge transfer and electrostatic potential profile, and the local density of electronic states (LDOS) at E_F. The behavior of the LDOS for benzene–, dibenzene–, and xylyl–dithiol molecules is analyzed and compared with that of alkane–dithiols of various lengths. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1602057]

I. INTRODUCTION

Molecular electronics is a fairly recent research area which proposes to use a few or even a single molecule as the basic units of electronic devices. Compared with the traditional semiconductor technology this new approach would change both the operating principles and the materials used to fabricate the devices. The reason for such a radical change is that molecules are subnanometer scale units which can be made identically, cheaply and easily in industrial quantities. Some prototypes have already been fabricated. For example, the $I-V$ characteristics at room temperature of a benzene-1,4-dithiolate (BDT) molecule sandwiched between two gold (111) surfaces has been measured,[1] molecular electronic devices with a negative differential resistance have been fabricated[2] and memory devices based on organic monolayers have been proven to be able to store data for long times at room temperature.[3]

The molecules studied to date can be divided in two categories. The first category is based on n-alkanethiols $[CH_3(CH_2)_{n-1}SH]$ (Ref. 4) which have large gaps (6 eV or greater) between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) and thus behave as insulators. These molecules have flexible chains that pack well into dense, ordered monolayer films and are useful for forming insulating layers. The second category is based on conjugated molecules which have a smaller (2–4 eV) HOMO–LUMO gap and possess delocalized π-electrons which can contribute to conduction. All these molecules are thiol-terminated, because the sulfur atom binds strongly to the noble metal surfaces used as electrodes.

As experiments have begun to address conductance through such molecular wires successfully, reliable theoretical models are needed. One important theoretical challenge is to accurately describe the electronic coupling between the molecule (a discrete system) and the leads it is attached to (a semi-infinite system). A suitable tool to achieve this goal is density functional theory (DFT), which has been widely employed in the theoretical study of adsorption on metallic surfaces.[5] While much effort has been put in developing theoretical models for the electronic conductance, the modeling of the surface atomic and electronic structure has been typically quite approximate. For instance the surface has been treated with a jellium model[6–8] or with a small cluster of metal atoms attached to the molecule.[9] The purpose of this paper is to investigate the electronic properties of organosulfur monolayers sandwiched between two Au(111) electrodes, using a periodic DFT approach which allows us to realistically describe both the atomic structure and the electronic states of the gold surfaces as well as the properties of strongly adsorbed monolayers. We will focus on the properties of metal–molecule–metal junctions which are relevant to transport under low bias conditions. In particular, we will calculate the local density of states from which properties like the alignment of molecular states with the Fermi energy of the metal electrodes can be quantitatively derived.

II. TECHNICAL DETAILS

Calculations have been carried out using the plane-wave pseudopotential approach within density functional theory in the generalized gradient approximation.[10] To describe the electron-core interaction we used ultrasoft pseudopotentials[11] for Au, C, and H, whereas for S we employed a norm conserving Troullier–Martins[12] pseudopotential. Valence states include $5d$ and $6s$ for Au, $2s$ and $2p$ for C, $3s$, $3p$, and $3d$ for S. All the pseudopotentials have been generated with the Perdew–Wang '91 (PW91) exchange and correlation functional and the one for Au includes scalar relativistic effects. The wave functions are expanded in plane waves with a kinetic energy cutoff of 25 Ry, whereas the cutoff for the augmented electron density is 200 Ry.

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To model the Au(111) surface we use a repeated slab geometry, with slabs of four atomic layers separated by a vacuum at least 8 Å wide. For the self-assembled monolayers of interest the periodicity of the full coverage monolayer is $(\sqrt{3} \times \sqrt{3})R30$ with respect to the (1×1) periodicity of the unreconstructed Au(111) surface. We thus use a supercell which has a $(\sqrt{3} \times \sqrt{3})R30$ unit cell parallel to the surface, corresponding to three Au atoms per layer in the gold slab. The corresponding Brillouin zone has been sampled with 48 k-points, using a $6 \times 6 \times 1$ Monkhorst–Pack grid (6 is for directions parallel to the gold surfaces and 1 for the orthogonal direction). This grid of k-points provides converged values of both the (clean) surface energy and the adsorption energy of a single sulfur atom (see below). In our geometry optimizations, we used the calculated bulk equilibrium lattice constant for gold, which is $a_0 = 7.82$ a.u., to be compared to the experimental value $a_0 = 7.67$ a.u. Optimizations were considered to be converged when each component of the force on each atom was smaller than 0.03 eV Å^{-1}. For the Au(111) surface energy we obtain $\gamma = 758$ erg/cm^2, whereas the experimental values are in the range between 1045 and 1410 erg/cm^2.[13] This underestimate of the surface energy is known to be a frequent shortcoming of DFT–GGA approaches (see e.g., Refs. 14 and 15). Our calculated adsorption energy of a single sulfur atom in a fcc site is $E_{ads} = 3.97$ eV, in agreement with previous theoretical studies.[16]

III. RESULTS

A. Lineup of energy levels, charge transfer and potential profile: The Au(111)–BDT–Au(111) system

Conjugated molecules, like benzene–1,4–dithiolate (HS–C$_6$H$_4$–SH) (BDT), have attracted much interest in the area of molecular electronics because, having delocalized π electrons, they should behave in a way similar to conventional semiconductors. Various electronic devices based on what is believed to be a S–C$_6$H$_4$–S diradical sandwiched between two metallic electrodes have been fabricated.[1] For this radical, the experimental measurements show a nonlinear behavior of the conductance, with a gap of about 0.7 eV, which has been attributed either to a Coulomb blockade effect or to a mismatch between the Fermi level E_F of the metallic electrodes and the closest molecular orbital.[1] For the interpretation of these experimental results the knowledge of the relative position of E_F with respect to the BDT molecular orbitals is essential and this can be readily obtained with our periodic DFT approach. It is also important to understand how the molecular orbitals change upon adsorption and which orbitals are important for the conduction process. Although these and similar questions have been already addressed by previous theoretical studies (see, e.g., Ref. 6), in most cases very simplified models of the metallic surface have been used.

It is widely assumed that, when a thiol molecule R–SH (where R denotes the organic residue) is adsorbed on a gold surface, the H atom of the thiol terminal group desorbs while the sulfur atom of the resulting radical, R–S–, binds strongly to the gold surface[17] (see Fig. 1). Similarly, a dithiol molecule, e.g., BDT, sandwiched between two Au(111) surfaces
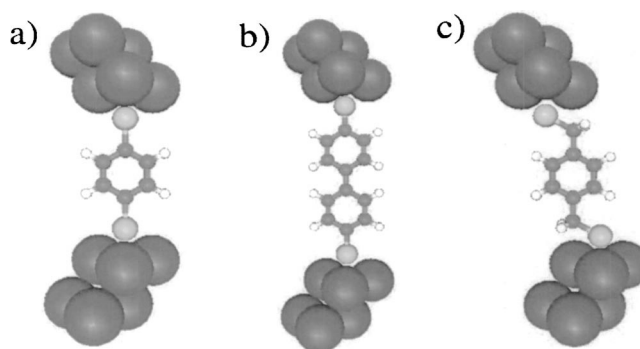

FIG. 1. (a) BDT on Au(111), (b) DBDT on Au(111), (c) XYLYL on Au(111). The atoms in a single supercell are shown.

loses the hydrogens at both thiol terminations and thus becomes, strictly speaking, a diradical. To determine the atomic geometry for such a BDT diradical sandwiched between two Au(111) electrodes, we first optimized the geometry of BDT adsorbed on a single Au(111) surface by relaxing the nuclear coordinates of both the molecule and the surface atoms. As in previous calculations[9] of metal–molecule–metal systems, we have assumed an fcc adsorption site with the molecule perpendicular to the surface, and verified that such a configuration does indeed correspond to a local minimum in the potential energy surface.[18]

Our calculated distance between the sulfur headgroup and the three closest gold atoms is 2.677 Å, while the vertical distance of the sulfur atom from the surface is 2.065 Å. Starting from this adsorption structure, the atomic geometry of BDT sandwiched between the two gold surfaces was obtained by reflecting the atomic positions of the part of the unit cell not containing the vacuum through the plane containing the center of the benzene ring and perpendicular to the molecule's axis. (See Fig. 2.)

In Fig. 3, the density of states (DOS) for the Au(111)–BDT–Au(111) system is compared to that for the clean Au(111) surface and for the isolated BDT diradical. The energy levels of the bare surface and the isolated molecule have
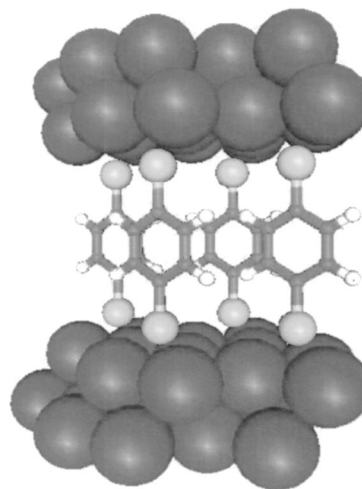

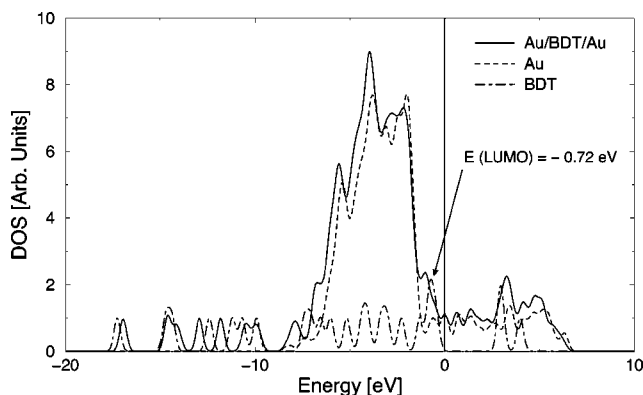FIG. 2. The unit cell of Au(111)–BDT–Au(111) is shown repeated $2 \times 2 \times 1$ times.

FIG. 3. Density of states for the isolated BDT molecule (diradical), the clean Au(111) surface and the Au(111)–BDT–Au(111) system. The arrow indicates the LUMO of the isolated BDT diradical. The reference energy has been taken such that $E_F = 0$.

been aligned by taking the vacuum level as the reference energy. The energy levels of the Au(111)–BDT–Au(111) system and the bare surface have been aligned assuming the same Fermi energy. We notice that the LUMO of the isolated diradical (Fig. 4) lies 0.72 eV below the Fermi energy for the gold surface. When the molecule is adsorbed on the surface, however, the molecular states are modified by the interactions with the metal and with the other molecules in the monolayer, so that somewhat broad bands are formed.[5] To keep track of the molecular LUMO for the metal–molecule–metal system, we analyze the states of the system searching for states with charge distributions similar to those of the isolated LUMO. Within the resulting band of states we select the state with energy close to the average energy of the band. The state found in this way is what we call the ''LUMO'' of the diradical+surface system. For BDT, this LUMO (Fig. 4) is 0.16 eV below E_F, i.e., it has been pushed up in energy with respect to the LUMO in the isolated molecule, even though it is still below the Fermi level. Such a destabilization may be attributed to the electron–electron repulsion in the filled levels.
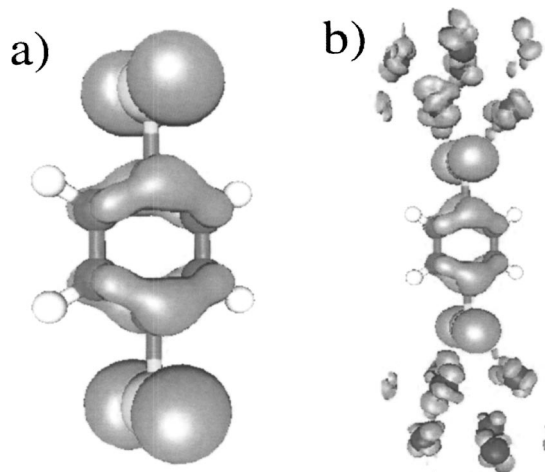

FIG. 4. (a) LUMO of the isolated BDT diradical; (b) molecular LUMO in the Au(111)–BDT–Au(111) system. The latter is delocalized all over the molecule, with a strong contribution coming from the sulfurs.

Given the fact that the (originally empty) molecular LUMO moves below the Fermi level, it is important to study the charge transfer upon adsorption of BDT on Au(111). This has been done by calculating the difference between the charge density of Au(111)–BDT–Au(111) and the sum of the charge densities of the isolated BDT diradical and the bare surface. The results are shown in Fig. 5 (top panel). The main effect of the interaction of gold with the molecule is a redistribution of the charge around the sulfur atom, due to the formation of the chemical bond between sulfur and gold. Some charge moves also inside the carbon ring, giving rise to a repulsive potential in that region, as shown by the potential energy difference in Fig. 5 (bottom panel).

Let us next examine at the projected density of states (PDOS) in Fig. 6. This shows a strong peak right below the Fermi level coming from the sulfur p orbitals, in agreement with the fact that the LUMO has a relevant contribution from p states on the sulfur atoms. However, a population analysis based on the projection of the Kohn–Sham orbitals on atomic orbitals shows that while the total electronic charge in the BDT diradical increases by $0.30e$ upon adsorption, the charge on the sulfur atoms is increased by only $0.03e$, implying a net charge transfer from the gold surface to the carbon ring of the molecule, with only a very small contribution to the sulfurs. This is consistent with the potential energy difference in Fig. 5, which shows no build up of a potential barrier on the sulfur atoms, in contrast to what has been found in previous works.[9] In the sulfur atoms, however, there is an important charge redistribution which involves also the d orbitals of sulfur. In particular, the total charge in the sulfur d orbitals increases from $0.35e$ in the isolated BDT diradical to $1.12e$ in the surface–molecule–surface system. We found this behavior also in the case of alkanethiols adsorbed on a bridge site suggesting that this is a general feature of thiol-terminated molecules due to the hybridization of the sulfur orbitals with the gold atoms of the surface during the formation of the chemical bond.

B. Local density of states

Some insight into the electronic transport properties of molecular devices can be obtained by studying the local density of states (LDOS) of the electrode–molecule–electrode system at zero bias. The expression of the LDOS is

$$\rho(\mathbf{r}, E) = \sum_i |\psi_i(\mathbf{r})|^2 \delta(E_i - E),$$

where ψ_i denote the eigenstates of the system and E_i the corresponding eigenvalues.

Although the LDOS does not fully determine the zero-bias conductivity, regions where the LDOS is depressed are expected to be barriers for electronic flow. Moreover, the spatial decay of the LDOS as a function of molecular length is connected to the decay of the conductance for large gap molecules,[19] as we will see in Sec. III B 2.

1. Conjugated molecules

The LDOS in the in the middle of the carbon ring for Au(111)–BDT–Au(111) as a function of the energy is shown in Fig. 7. We can see that in the energy range close to E_F the
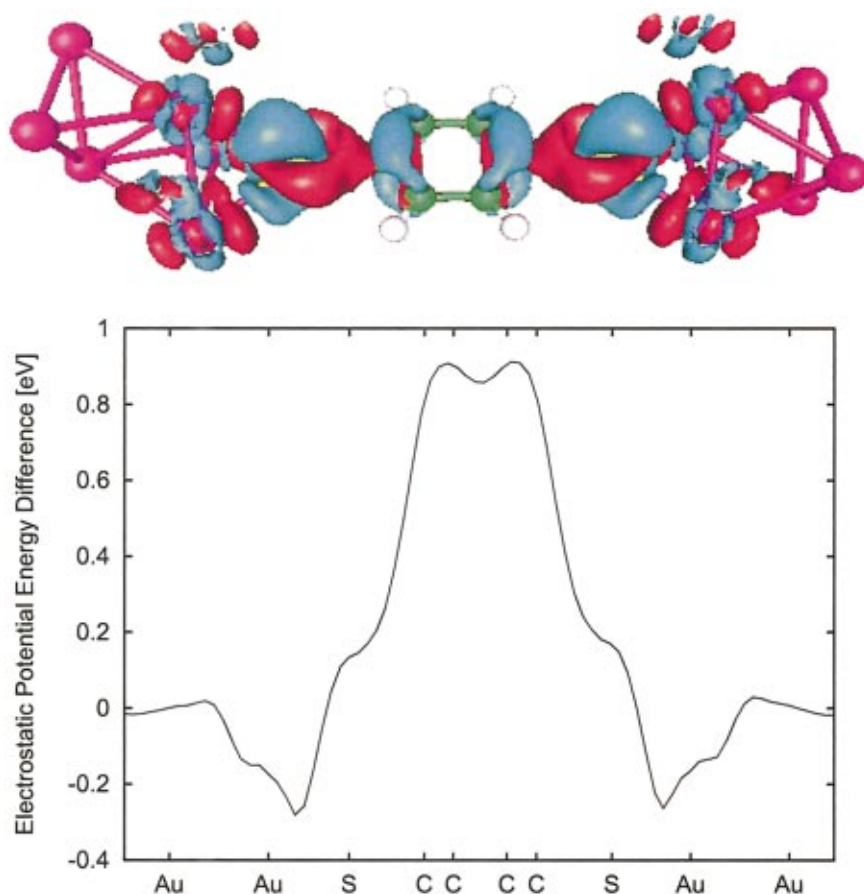
FIG. 5. (Color) Top panel, difference between the charge density of Au(111)–BDT–Au(111) and the sum of the charge densities of the isolated molecule and the clean surface. In blue an isosurface for positive value of the charge density difference, in red an isosurface for a negative value. Notice the similarity between the positive isosurface and the LUMO for the isolated BDT. Bottom panel, electrostatic potential difference between the Au(111)–BDT–Au(111) system and the sum of the electrostatic potential of the isolated molecule and the clean surface. All quantities are averaged in the planes perpendicular to the axis of the system.

LDOS is different from zero. Similarly the LDOS at $E = E_F$ along the molecular axis (see Fig. 8) shows states delocalized throughout the molecule.

To understand the nature of the states at the Fermi energy we studied how the LDOS changes for different types of molecules, by considering the dibenzene-1,8-dithiol (DBDT) molecule, which has two benzene rings (Fig. 1), as well as the α, α' xylyl dithiol molecule (XYLYL), where a CH_2 group is present between the benzene ring and the sul-

fur atoms on each side of the molecule (Fig. 1). The results for both molecules are shown in Figs. 7 and 8, in comparison with the BDT data. We can see that at energies close to E_F the LDOS for DBDT is not significantly different with respect to the BDT case. For the XYLYL molecule, instead, there is a dramatic change in the LDOS, which is strongly reduced near the Fermi energy with respect to the BDT case. Thus we expect that the conductance of the XYLYL molecule should be much lower than the BDT one.[20]
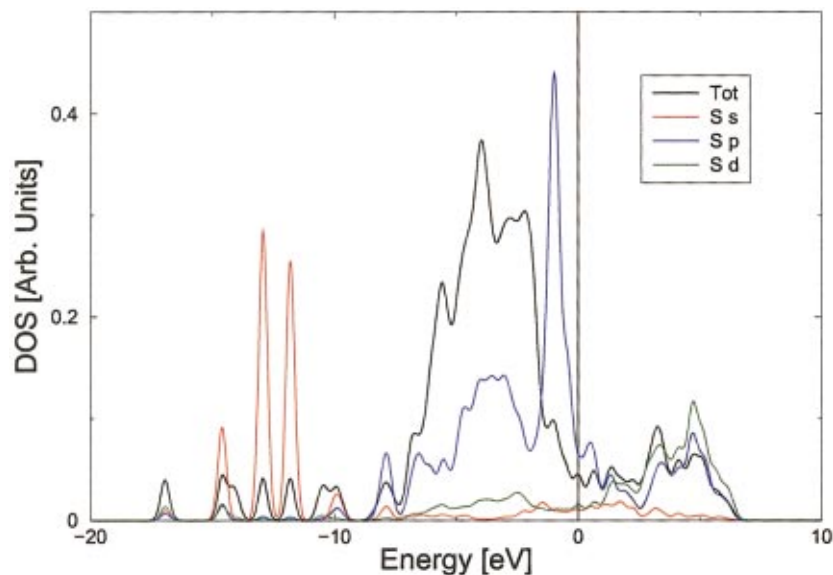

FIG. 6. (Color) Projected density of states for Au(111)–BDT–Au(111). The p orbitals in the sulfur atoms give rise to a peak right below the Fermi level.
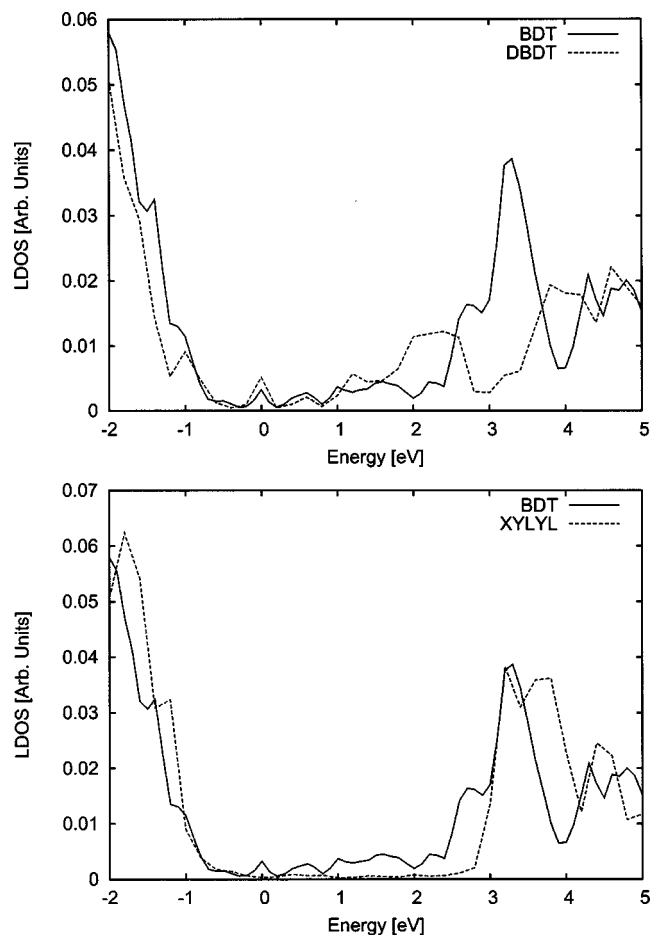
FIG. 7. LDOS in the middle of the benzene ring as a function of the energy. Top panel, BDT vs DBDT. For both molecules, there are states in the middle of the ring in a broad energy region around the Fermi energy ($E_F=0$). Bottom panel, BDT vs XYLYL. For XYLYL, the presence of the CH_2 groups induces a gap of about 3.5 eV.

FIG. 8. LDOS at E_F along the axis of the molecule, averaged over planes perpendicular to the axis. Top panel, BDT vs DBDT. For both molecules, there are states at the Fermi energy delocalized over the benzene ring(s). Bottom panel, BDT vs XYLYL. For XYLYL, the LDOS drops to zero in the region of the ring.

A rationalization of these results can be obtained in the framework of the Newns–Anderson model of adsorption.[5] This model predicts that the atomic state of an adsorbate interacting with a metal surface undergoes a splitting corresponding to a bonding and an antibonding combination with the narrow d-bands, and a broadening due to the interaction with the broad s-band of the metal surface. If we consider as a first step the adsorption of a sulfur atom (the thiol headgroup) on the Au(111) surface, the sulfur p states are split and broadened by the interaction with the d and s bands of gold. These states should then interact with the delocalized π electrons of the benzenelike ring (C_6H_4), so as to give rise to a nonzero LDOS at E_F in the middle of the ring. A necessary condition for such an interaction is that one of the states of the adsorbed sulfur atom and the delocalized states in the C_6H_4 molecule have similar energies. To check this, we calculated the DOS for these two systems (Fig. 9). The adsorption of sulfur (at the fcc site) on Au(111) gives rise to a sharp peak at $E=-0.78$ eV below E_F, corresponding to antibonding Au–S states. This peak is mainly due to the sulfur p orbitals, as shown by Fig. 6. On the other hand, the HOMO and HOMO-1 of the C_6H_4 ring are right below the Fermi level, thus lying close in energy to the sulfur state (see bot-
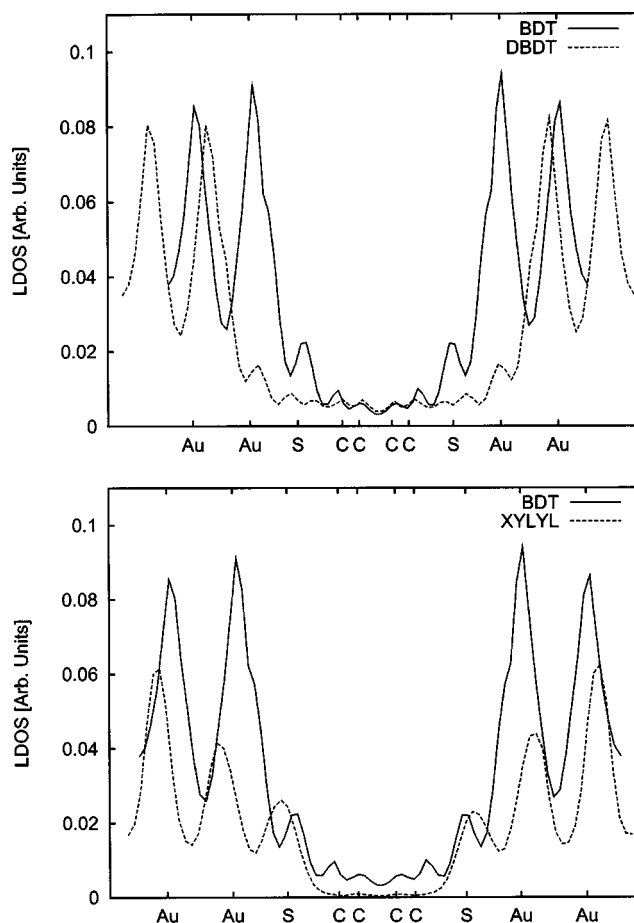
tom panel of Fig. 9). From this analysis we conclude that the interaction of sulfur with the gold surface gives rise to an antibonding state largely localized on the sulfur which lies close in energy to states belonging to the benzene ring. The resulting states are delocalized all over the molecule, as shown by Fig. 4. For the XYLYL molecule, instead, the methylene group has a high HOMO–LUMO gap which suppresses the interaction between the sulfur and the C_6H_4. The delocalization over the molecule is thus lost, and no molecular states are present at E_F.

A similar effect has been found by Lang and Avouris[8] comparing a benzene-1,4-diradical (BDR) with 1,4-dicyanobenzene (DCB): in this case the LDOS at the Fermi level in the carbon ring of DCB is suppressed by the presence of the CN groups at the two ends of the molecule. Calculations on the conductance of these two molecules show that indeed the suppression of the LDOS leads to a much lower conductance in DCB than in BDR.[8]

2. Saturated molecules

Electronic transport through alkanethiol monolayers on Au(111) has been extensively studied. Experiments show that the electronic current flowing across such monolayers decreases exponentially with increasing distance between the
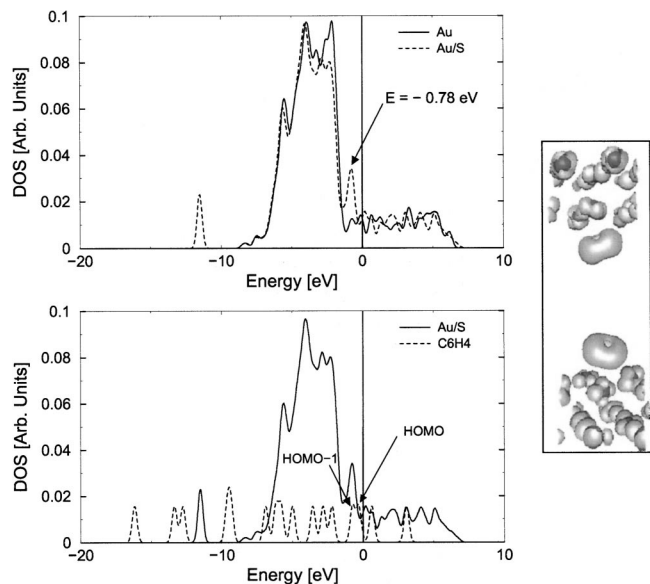
FIG. 9. Left, top panel, DOS for Au(111) and S/Au(111) ($E_F=0$). The adsorption of sulfur on gold gives rise to a peak right below the Fermi energy ($E=-0.78$ eV). Left, bottom panel, DOS for S/Au(111) and C_6H_4. Remark how the peak given by the sulfur lines up with some levels (HOMO and HOMO-1) of the C_6H_4 molecule. Right, shape of the state at $E=-0.78$ eV.

FIG. 10. LDOS at E_F along the axis of the molecule, averaged on planes perpendicular to the axis, and averaged over two CH_2 units. Top panel, log(LDOS) for C4, C8, and C12 with linear fit. Bottom panel, log(LDOS) for C8S2 C12S2, and C8. $E_F=0$. Having one or two chemical bonds per chain does not effect the value of β. The H and F atomic positions refer to the terminal H and F atoms.

electrodes, suggesting a tunneling mechanism for the electronic conduction. The decay constant, that in vacuum is ~ 2.3 Å^{-1}, has a different value that depends on the nature of the molecule filling the gap. For alkanethiols the decay of the current can be described by

$$I=I_0 e^{-\beta_N N},$$

where N is the number of methylene groups in the chain.

Within the simplest model of tunneling through a one-dimensional potential step barrier (of height V_0 and width L), the transmission probability for an incident electron of energy $E=(\hbar^2 k^2/2m)<V_0$ is proportional to $e^{-\beta L}$, with $\beta=2\kappa=2\sqrt{2m(V_0-E)}/\hbar^2$. In the case of tunneling across vacuum, the barrier height is given by the work function of the clean surface, while for a molecule sandwiched between two metal electrodes it can be approximated by the energy difference between E_F and the closest molecular orbital. In this way the barrier height, ϕ_0, becomes $\phi_0=|E_{LUMO}-E_F|$ for tunneling through the LUMO, or $\phi_0=|E_F-E_{HOMO}|$ for tunneling through the HOMO, while the mass m of the electron is replaced by an effective electron mass m^*.

A more accurate estimate of β_N can be obtained using DFT, by monitoring the decay of the LDOS calculated at the Fermi energy along the alkane chain.[19] We performed calculations of the LDOS for alkanethiol chains of different length, C4, C8, and C12, adsorbed on the Au(111) surface. As a first step, we have considered a full monolayer of C4 on Au(111) and optimized the geometry. Previous theoretical studies,[21,22] have indicated that alkanethiols on gold may preferentially adsorb at the bridge site. For C4 we find an adsorption energy of about 2.0 eV, while the tilt angle of the axis of the molecule with respect to the normal to the surface
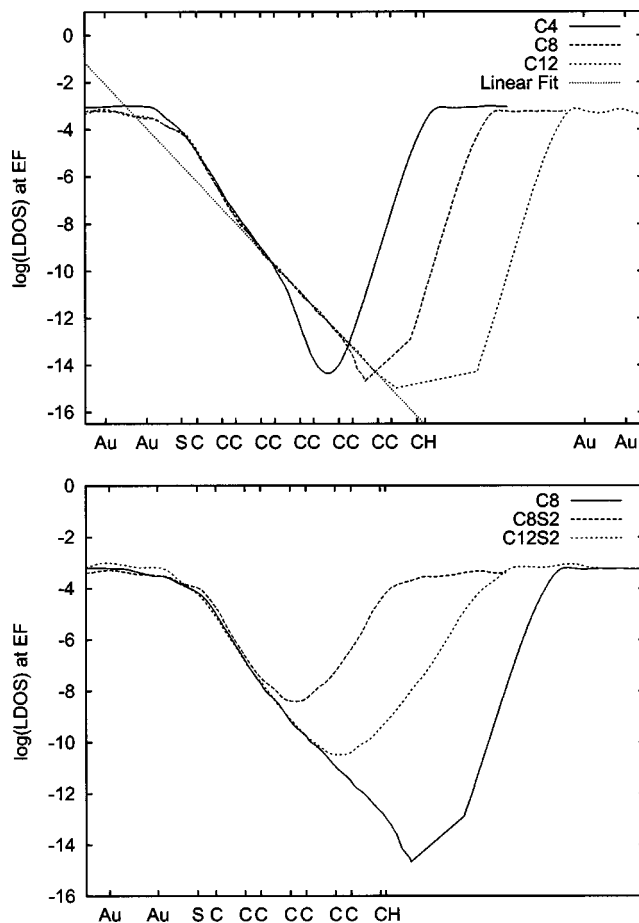
is 23.5°, in fair agreement with the experimental value of $\sim 31°$. The geometries for the other systems (C8, C12) have been obtained from the one of C4, by adding successive CH_2 groups, but without further relaxing the atomic positions.

From the exponential decay of the LDOS at the Fermi energy (Fig. 10) we determine the decay rate $\beta_N=0.95 \pm 0.01$, where the error has been inferred from the difference between the β values obtained from the C8 and the C12 data. This result agrees well with the experimental data $\beta_N \simeq 1$.[23] As a comparison, the computed decay rate of the LDOS in the vacuum for the clean Au(111) surface is 2.27 ± 0.05 Å^{-1}, which gives a value of the energy barrier (in this case coincident with the work function) $\phi_0=4.94 \pm 0.11$ eV. The experimental value for the work function of gold is 5.31 eV,[9] while the value that we determine from the difference between the electrostatic potential in the vacuum and the Fermi energy is 5.27 eV.

An experimental observation, which has to date no clear explanation, is the fact that for dithiol chains with two S–Au contacts, one at each end of the chain, β_N is significantly smaller than in the case with a single contact.[24] The experimental data are $\beta_N \simeq 1$ for the single contact[23] and $\beta_N=0.57 \pm 0.03$ in the double contact case.[24] This indicates that

the effective tunneling barrier ϕ_0 (i.e., the difference between the Fermi energy and the first available channel for conduction) is reduced from about 5 eV for the single contact to about 1.5 eV for two S–Au contacts. To address this problem we computed the LDOS at the Fermi energy for alkanedithiols sandwiched between two Au(111) surfaces. In agreement with recent theoretical work,[19] our calculations do not show any appreciable difference between the one and two contact cases (Fig. 10), with a decay constant which is always of the order of 1.0.

IV. CONCLUSIONS

In this paper we have studied, with a DFT approach, some electronic properties of conjugated and saturated molecules sandwiched between two metal electrodes relevant to electronic transport. We have found that when BDT adsorbs on Au(111) its LUMO falls slightly below the Fermi level of the metal. This gives rise to a charge transfer from the surface to the molecule such that only a charge redistribution takes place on the sulfur atoms while a net charge builds up in the carbon ring. The rearrangement on the sulfurs involves also the d orbitals which get partially filled during the adsorption. This feature is present also in the case of alkanethiols in different adsorption sites.

Studying the LDOS we have found that there are some states available for conduction around the Fermi energy which are delocalized throughout the molecule. These states originate from the coupling between an antibonding sulfur p state (broadened and shifted by the interaction with the surface) and states belonging to the central C_6H_4 group. This has been further confirmed by the study of the effect of the insertion a methyl group between the sulfur and the carbon ring, which decouples the two subsystems and thus suppresses the LDOS at E_F. The picture changes significantly in the case of saturated molecules: here we find a huge HOMO–LUMO gap and no states around E_F and thus the wave function at E_F simply decays exponentially. We have calculated the decay constant which turns out to be in very good agreement with the experimental values available in literature and with previously reported theoretical studies. In contrast to recent experimental reports no appreciable difference in the decay constant for alkane mono- and di-thiols is found.

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