Comparison between *s*- and *d*-electron mediated transport in a photoswitching dithienylethene molecule using *ab initio* transport methods

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The influence of the electrode's Fermi surface on the transport properties of a photoswitching molecule is investigated with state-of-the-art *ab initio* transport methods. We report results for the conducting properties of the two forms of dithienylethene attached either to Ag or to nonmagnetic Ni leads. The I - V curves of the Ag/dithienylethene/Ag device are found to be very similar to those reported previously for Au. In contrast, when Ni is used as the electrode material the zero-bias transmission coefficient is profoundly different as a result of the role played by the Ni *d* bands in the bonding between the molecule and the electrodes. Intriguingly, despite these differences the overall conducting properties depend little on the electrode material. We thus conclude that electron transport in dithienylethene is, for the cases studied, mainly governed by the intrinsic electronic structure of the molecule.

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I. INTRODUCTION

One interesting class of molecules for use in the field of molecular electronics^{1–7} is that of photoswitching complexes, whose geometry undergoes reversible changes between different states when acted upon by light. In particular, molecules that switch between states with different conducting properties are appealing candidates for use in organic optoelectronics. Recently we presented a theoretical investigation, based on a combination of density-functional theory (DFT) and the nonequilibrium Green's function (NEGF) method, of the energetics and the transport properties of one of these systems, namely a dithienylethene (DTE) molecule attached to gold electrodes.⁸ In general we found a large difference in the low-bias conductance between the DTE closed and open form, which could be attributed to the intrinsic electronic structure of the molecule. By defining

$$\mathcal{R} = I_{\text{closed}}/I_{\text{open}} \quad (1)$$

as the ratio between the currents in the closed and open configuration, we found $\mathcal{R} \sim 20$ at low bias. At higher bias the ratio is still larger than unity, although the magnitude is reduced. Such a bias dependence of the conduction, and hence of $\mathcal{R}$, was found to be due to molecular-orbital re-hybridization in an electric field.

Here the transport properties of the same molecule are investigated for two different electrode materials, namely Ag and Ni. The purpose of our study is to obtain a quantitative description of the transport characteristics of DTE attached to Ag leads, and to achieve a qualitative understanding of the influence of electrode *d* electrons on the transport. To this goal nonmagnetic Ni is considered. Therefore our results for Ni should not be interpreted as descriptive of real Ni electrodes, but merely as a tool for understanding the role played by a

d-electron metal on the transport. Spin-polarized calculations for Ni leads will be the subject of a future investigation.

In general we find that the low-bias conductances of the two accessible DTE geometries differ by a factor ~ 35 for Ag/DTE/Ag and by ~ 40 for Ni/DTE/Ni, suggesting that molecular optoelectronic switches with a large on/off ratio can be constructed with DTE and different electrodes' metals. Away from the low-bias regime a detailed analysis of the transmission coefficients as a function of the applied voltage helps in understanding the current-voltage (I - V) characteristics. In the case of Ag, these are largely determined by electric-field driven molecular-orbital rehybridization, similarly to what was previously found for Au.⁸ In contrast, orbital rehybridization is less pronounced when Ni electrodes are employed. However, the transmission coefficient still changes under applied voltage, but this time the changes are mainly due to a shifting in energy of the corresponding molecular levels. In particular, we show that the transport characteristics can differ substantially depending on the properties of the lead materials, and that a self-consistent approach is necessary at finite bias to reveal the differences.

Photoswitching DTE derivatives change their conformation in solution from a closed to an open structure under visible light (400–700 nm) and reverse under UV conditions (<400 nm); see Fig. 1. Several studies, both experimental^{9–14} and theoretical,^{13–18} on the switching reaction and transport properties of DTE derivatives attached to gold contacts have recently appeared.^{19–27} For instance, using break-junction experiments, Dulic *et al.* found that the conductance of the closed molecule is three orders of magnitude larger than that of the open one. Other experimental works have reported smaller ratios between the current for the closed and open conformations, namely $\mathcal{R} \sim 25$,¹⁰ $\mathcal{R} \sim 16$,¹¹ and $\mathcal{R} \sim 131$,¹⁴ depending on the precise experimental setup. These latter experiments are in

FIG. 1. (Color online) The two geometrical configurations of the DTE molecule investigated in this work. The closed form of the molecule is shown in the top panel and the open form in the one below. Color code: light gray small balls (light blue) H; dark gray (red) C; light gray large balls (light gray) S.

good agreement with our theoretical result of $\mathcal{R} \sim 20$ in the low-bias regime.⁸

II. COMPUTATIONAL METHODS

We have performed electronic structure and geometry optimization calculations with the DFT code SIESTA.²² SIESTA utilizes norm-conserving, nonlocal Troullier-Martins pseudopotentials²³ for the core electrons, together with an efficient numerical atomic orbital basis set²⁴ for the valence ones. The exchange and correlation energy functional is approximated with the Perdew-Burke-Ernzerhof²⁵ form of the generalized gradient approximation. Electronic transport calculations are carried out with the SMEAGOL code,^{26–28} which interfaces the NEGF scheme for transport^{26–30} with the DFT numerical implementation contained in SIESTA.

In a transport calculation the system is divided into three parts: a left-hand side lead, a scattering region, and a right-hand side lead. The scattering region is defined as the region of space where scattering takes place, i.e., where the electrostatic potential deviates from that of the electrodes. This typically contains the molecule of interest and a number of atomic layers of the leads large enough for the electron screening to be effective. SMEAGOL then calculates the scattering region Green's function

$$G(E, V) = [E + i0^+ - H(V) - \Sigma_L(E, V) - \Sigma_R(E, V)]^{-1}, \quad (2)$$

which enters into a self-consistent procedure leading to the nonequilibrium charge density and the electrostatic potential drop.^{26–28} The electrostatic problem is solved by setting the potential to the left- and the right-hand sides to match those of the bulk electrodes plus a shift induced by the applied bias. The total Hartree potential can be separated into a periodic part and a slope (in practice a sawlike potential). The periodic part is solved in the usual way by using fast Fourier transforms (FFTs), whereas the slope is added afterward.³¹

In Eq. (2), $H(V)$ is the Hamiltonian of the scattering region (a functional of the charge density), V is the applied

FIG. 2. (Color online) Geometry of the closed form of the molecule inserted between two Ag leads.

potential, E is the energy, and Σ_α ($\alpha = L, R$) are the energy- and bias-dependent self-energies of the electrodes.²⁸ These latter describe the interaction of the scattering region with the electrodes and establish the appropriate boundary conditions to the problem. Once the self-consistent procedure is converged the transmission function can be evaluated from a Landauer-Büttiker-like formula as

$$T(E, V) = \text{Tr}[\Gamma_L(E, V)G(E, V)\Gamma_R(E, V)G^\dagger(E, V)], \quad (3)$$

where $\Gamma_\alpha(E, V) = i(\Sigma_\alpha - \Sigma_\alpha^\dagger)$ is the coupling matrix for lead α . The transmission function of Eq. (3) can be integrated over the bias window to yield the current $I(V)$,

$$I(V) = \frac{2e}{h} \int_{-\infty}^{\infty} T(E, V)[f(E - \mu_L) - f(E - \mu_R)]dE, \quad (4)$$

where $f(E - \mu_\alpha)$ is the Fermi function calculated at $E - \mu_\alpha$ with μ_α being the chemical potential of the α th lead.

Our calculations then proceed as follows. First, the equilibrium structures of the two molecular configurations in vacuum are found by coordinates optimization. The forces are optimized to below 0.002 eV/Å. The molecule is subsequently inserted into the scattering region, which consists of five layers of the lead metal on each side of the molecule. These are oriented along the fcc [100] direction; they have a cross section of 3×3 atoms and a lattice constant equal to the experimental one for the bulk. We chose to anchor the molecule to the leads at the hollow site of the (100) surface, since this is the energetically preferred site;¹⁷ see Fig. 2. The distance between the lead's surface and the S end atom—the anchoring distance d —was set to 1.9 Å for both lead materials in order to facilitate a more direct comparison between the results for Ag and Ni leads, as well as with the results obtained previously for Au.⁸ The true (optimized) anchoring distances are also calculated for the closed molecule by relaxation, and have been found to be $d = 1.93$ Å for the Ag leads and $d = 1.41$ Å for the Ni leads. Since the true anchoring distance for Ni leads differs significantly from the chosen distance of $d = 1.9$ Å we perform conductance calculations with both distances for comparison. As far as the open molecule is concerned, we have found in our previous study that the relaxed anchoring distance is somewhat smaller than that for the closed molecule, but that this small difference has little effect on the transport characteristics.

We use a double- ζ plus polarization orbital basis set for all the atoms in the molecule. In contrast, the atoms in the leads are treated respectively at the single- ζ (d orbitals) and double- ζ plus polarization (s orbitals) level.

FIG. 3. (Color online) Lead's surface DOS projected over s and d orbitals of Au, Ag, and Ni.

III. RESULTS AND DISCUSSIONS

Here we present the I - V characteristics, calculated either self-consistently or from the zero-bias transmission, the transmission coefficients at finite bias, and the projected density of states (PDOS) for the molecular levels relevant for the conduction for both the closed and open forms of DTE attached to either Ag or Ni. First we briefly discuss the different properties of the electrode materials considered (Ag, Ni, and, for comparison, also Au). In Fig. 3 the PDOS for the leads' surfaces is shown. The most relevant feature is the presence, in the case of Ni, of a dominant contribution to the DOS at the Fermi level E_F , originating from electrons with d character. These are likely to affect the electron transport since they can provide a bonding character to DTE different than that of Ag and Au, for which only s electrons contribute to the Fermi surface. Also important for the transport are the energies of the DTE molecular levels. These are shown in Fig. 4 for both the closed and the open configuration and they will be discussed in more detail together with the description of the transmission coefficients.

FIG. 4. (Color online) Density of states for the two conformations of the DTE molecule in vacuum.

FIG. 5. (Color online) Self-consistent I - V characteristics for the closed and open molecules sandwiched between two Ag electrodes. Also shown in the inset is the ratio between the current for the closed and the open molecule with the large anchoring distance.

A. Ag electrodes

The I - V characteristics for the Ag/DTE/Ag device are presented in Fig. 5. For small bias voltage we observe a large $\mathcal{R} \sim 35$, which decreases to ~ 5 at 1 V and then stays around the same value for increasing bias. The overall I - V characteristic is quite similar to the one obtained for the Au/DTE/Au device.⁸ In Fig. 6 the I - V characteristic for the same molecular junction but calculated non-self-consistently (i.e., by integrating over the bias window the zero-bias transmission coefficient) is presented as a reference. The results in Figs. 6 and 5 show a similar behavior at the onset of the applied bias and a similar decrease in $\mathcal{R}$ up to about 1 V. However, for larger bias we observe a qualitative difference between the two cases, since for the non-self-consistent calculation $\mathcal{R}$ drops below 1 at about 1.3 V, when the current through the open molecule becomes larger than that for the closed one.

This difference suggests a strong dependence of the transmission coefficient $T(E)$ on V . By looking at the I - V

FIG. 6. (Color online) Non-self-consistent I - V characteristics for the closed and open molecules sandwiched between two Ag electrodes. This is obtained by integrating the zero-bias transmission function over the bias window. The inset shows the ratio between the calculated current for the closed and open molecules.

FIG. 7. (Color online) Transmission coefficient as a function of energy for the closed molecule at different bias voltages. The vertical lines denotes the bias window.

curves for the closed and open molecules in Figs. 5 and 6 one can infer that the dependence of $T(E)$ over bias is more significant for the open molecule since the difference between the self-consistent and the non-self-consistent solution is more pronounced. Our analysis of $T(E, V)$, presented in Fig. 7, reveals that this is indeed the case. First, we observe a close resemblance of the transmission coefficient at zero bias with the DOS of the isolated molecule (see the upper panel of Fig. 4). In fact, if the DOS of the isolated closed molecule is shifted by 0.6 eV to higher energies, it will almost perfectly overlap with the peaks in the zero-bias transmission coefficient (note that for the isolated molecule the position of E_F is undefined within the HOMO-LUMO gap). The peak just below the Fermi level, corresponding to the DTE highest occupied molecular orbital (HOMO), is the only one contributing to the current at small bias. When the bias is increased such a peak is slowly pushed down in energy due to the molecule charge depletion. However, the shift is slower than the movement of the lower bound of the bias window (the lower of the two chemical potentials in the electrodes), so that eventually the entire peak contributes to the current (see Fig. 5). At $V = 2$ V also the transmission peak at around 1.2 eV, corresponding to the lowest unoccupied molecular orbital (LUMO), begins to contribute to the current. This gives rise to the upturn in the I - V curve for voltages above 2.5 V. Importantly, the overall change of the transmission with bias for the closed molecule is rather small.

The transmission coefficient for the open molecule is presented in Fig. 8. Just as for the closed one we find a one-to-one correspondence between the transmission peaks at $V = 0$ and those in the molecule DOS (lower panel of Fig. 4). The broad peak in the zero-bias transmission coefficient below E_F is composed of the molecular HOMO and the two states just below it (respectively, the HOMO-1 and HOMO-2). The peak at around 2.1 eV corresponds to the molecular LUMO. For small bias we expect little current, since $T(E_F)$ is tiny. As the bias is increased one could expect a large current as the broad peak below E_F enters the bias window. This is what we observe in the non-self-consistent result of Fig. 6. However, the self-consistent calculations gives a rather different picture.

FIG. 8. (Color online) Transmission coefficient as a function of energy for the open molecule at different bias voltages. The vertical lines denote the bias window.

In fact, the rightmost and leftmost parts of the transmission peak both disappear completely as V is ramped up. As a result only the tail of the peak can enter the bias window and the current remains small. At voltages above 2 V only the central part of the initially broad peak below E_F is still visible in $T(E, V)$. We then conclude that the transmission coefficient for the open DTE shows a very strong bias dependence, with a suppression of transmission peaks for increasing bias. This is at the origin of the differences between the self-consistent and the non-self-consistent I - V .

This behavior is analogous to what was previously found for Au electrodes.⁸ In that case the suppression of some peaks in the transmission coefficients was demonstrated to be related to the polarization of the electronic states across the molecular bridge induced by the external electric field. The polarization gives rise to uneven electronic coupling of the molecule to the right-hand and the left-hand electrode and hence a suppression of the corresponding transmission (see Ref. 32 for an extensive discussion of such a mechanism).

In order to explain the origin of the transmission peak suppression we now perform a detailed analysis of the electronic states of DTE in the junctions at finite bias. Our quantitative tool is the PDOS associated to specific atoms of the molecule, in particular that of the carbon atoms indicated as C_1 , C_2 , C_3 , and C_4 in Fig. 1. These are atoms symmetric with respect to the molecule mirror plane (dividing the molecule into a left and a right half) and the redistribution of their charge density will help us in understanding the effects of the voltage over the molecular levels. Such an analysis is carried out for the closed isomer in Fig. 9 where the PDOS as a function of E and for different V is presented. We observe that the zero-bias peaks in the transmission coefficient correspond to electronic states that are spread evenly over the four C atoms (the PDOS is essentially the same for the four representative C's), i.e., over the length of the molecule. The situation does not change at moderate biases as the relative contributions of the pairs C_1 - C_4 and C_2 - C_3 is similar. This means that the molecular levels are equally coupled to the two leads resulting in a large transmission. As the bias approaches 1.5–2.0 V,

FIG. 9. (Color online) Projected density of states for four C atoms of the closed isomer at different applied bias. The atom labels C_1 , C_2 , C_3 and C_4 are defined in figure 1.

the PDOS displays an uneven charge redistribution, typical of orbital rehybridization, so that the relevant molecular orbitals are now more localized on one side of DTE. However, the effect is still too weak to suppress significantly the peaks in the transmission coefficient.

For the open molecule the PDOS shows a different behavior (see Fig. 10). At zero bias the atoms contained in the pairs C_1 - C_4 and C_2 - C_3 contribute evenly to the PDOS. However, already at 0.5 V the PDOS indicates a polarization of the electronic states. Especially for the C_1 - C_4 pair the peaks at around -0.5 eV and -1.3 eV receive a completely different contribution from the two atoms. This coincides with a decrease in intensity of the corresponding peaks in $T(E, V)$. As the bias is increased this charge redistribution is magnified, indicating electron polarization of the corresponding molecular states. For the peak around -0.8 eV (which is shifted down to -1.2 eV at 2.0 V) the polarization is not as strong. In fact, even at 2.0 V such a state receives even contributions from the C_2 - C_3 pair, and so the corresponding transmission peak preserves its intensity.

We thus conclude that the observed suppression of the peaks in the transmission coefficient for the open molecule is due to

FIG. 10. (Color online) Projected density of states for four C atoms of the open isomer at different applied bias. The atom labels C_1 , C_2 , C_3 , and C_4 are defined in Fig. 1.

the DTE molecular orbitals' polarization and rehybridization at applied bias. Such a polarization causes an uneven coupling of the electronic states to the leads, and hence a reduction in the transmission coefficient. This mechanism was previously reported for the same molecule attached to Au.⁸ The main difference between Au and Ag is that such an effect appears stronger in Ag. We attribute this difference to the different alignment of the *d* levels with respect to E_F in Au and Ag. In Au the 5*d* states are 2 eV below E_F , while in Ag this distance is increased to 3 eV.

B. Ni electrodes

After having examined electron transport in devices where the electrodes have a Fermi surface dominated by states with mainly *s* character (Au or Ag) we now turn our attention to electrodes characterized by a strong *d*-orbital component in their DOS at the Fermi level. This is the case for Ni, which we discuss next. The calculated I - V curves are presented in Fig. 11 for both the molecule configurations and the two different anchoring distances between the molecule and the electrodes. When the anchoring distance is $d = 1.9$ Å we note that there is a large $\mathcal{R}$ ratio at the onset of the applied bias, reaching up to a value of around 40. This ratio increases steadily to over 50 for voltages just above 1 V, as the result of an increase in the current for the closed configuration is not compensated by an increase of that of the open one. For voltages above 1 V also the current for the open structure starts to grow and consequently $\mathcal{R}$ is reduced. This is particularly pronounced for $V > 2$ V where $\mathcal{R}$ saturates at about 5.

In general our results for the Ni/DTE/Ni devices appear rather similar to those for Ag/DTE/Ag. The main differences are purely quantitative, namely that the current for the closed molecule and Ni leads is larger than that calculated for Ag over the entire bias range (~ 30 μ A at 1.5 V for Ni compared to ~ 20 μ A for Ag). Also the current for the open molecule is smaller for Ni than for Ag over the entire bias range (0.7 μ A at 1.5 V for Ni compared to ~ 5 μ A for Ag). When the molecule-electrodes distance is reduced we observe no significant changes to such a picture, as one can see by looking

FIG. 11. (Color online) Self-consistent I - V characteristics for the closed and open molecules sandwiched between two Ni electrodes. The inset shows the ratio between the calculated current for the closed and open molecule.

FIG. 12. (Color online) Non-self-consistent I - V characteristics for the closed and open molecules sandwiched between two Ni electrodes. This is obtained by integrating the zero-bias transmission function over the bias window. The inset shows the ratio between the calculated current for the closed and open molecule.

at the results for a bond distance of $d = 1.4$ Å, also shown in Fig. 11. The main feature is a systematic increase of the current for the closed configuration and a small decrease of that for the open one. This difference results in a larger R ratio as shown in the inset. However, the shape of the I - V curve remains largely unaffected by the bond distance. We can then conclude that changing the anchoring distance in the case of Ni electrodes does not have any profound effect on the junction transport properties.

As for the case of Ag electrodes also for Ni we compare the self-consistent I - V curves with those obtained by simply integrating the zero-bias transmission coefficient (see Fig. 12). Surprisingly in this case there is little difference between the self-consistent and the non-self-consistent results, in stark contrast with what was shown before for Ag and Au.⁸ Guided by the results of the previous section one may then expect that for Ni electrodes the transmission coefficients do not depend significantly on the applied bias for either the closed configuration or for the open one. Such a conjecture is put to the test in Figs. 13 and 14, where we present $T(E, V)$, respectively, for the closed and open configuration, both calculated for a junction with an anchoring distance of $d = 1.9$ Å.

Let us start our analysis from the closed configuration of DTE. The most distinguishable feature of $T(E, V)$ in the case of Ni electrodes is the broad zero-bias peak at around E_F . This has a width of approximately 1 eV to compare with only 0.2 eV for the case when the Ag electrodes are used (see Fig. 7). Such a peak originates from the coupling of the molecule HOMO with the d bands of the electrodes. The Ni d states have a total bandwidth of about 5 eV with their band center approximately located at the position of the DTE HOMO. The electronic coupling between the molecule and the electrodes is then strong and the transmission peak broad. Note also that such a peak presents some fine structure, which is due to the relatively localized nature of the Ni d states resulting in rather flat bands or, equivalently, sharp peaks in the DOS. For energies 1 eV above E_F there is no more d character in the Ni DOS. The zero-bias transmission coefficient here is therefore

FIG. 13. (Color online) Transmission coefficient as a function of energy for the closed molecule sandwiched between two Ni electrodes at different voltages. The vertical lines denote the bias window.

similar to that of Ag, since only s states in the electrodes couple to the molecule.

As the bias increases the main peak at E_F splits and gets progressively suppressed. Such a behavior originates from the shift in energy of the Ni d -band edges of the two electrodes, i.e., from the fact that the energy position of the d bands of the electrodes approximately coincide with that of their relative chemical potentials. This is a feature typical of transition metals and it is the dominant mechanism leading to the voltage dependence of the tunneling magnetoresistance in Fe/MgO/Fe tunnel junctions.^{33,34} One can clearly appreciate the splitting of the main peak at 2 V, where now two broad peaks in $T(E, V)$ appear respectively at -1 eV and 1 eV (the peak at 1 eV overlaps to some degree with the s -related peak originally placed at 1.2 eV at zero bias). We then conclude that the transmission coefficient of the closed molecule attached to Ni leads exhibits a significant bias dependence. Incidentally, this does not lead to a large difference between the self-consistently and the non-self-consistently calculated I - V curves simply because

FIG. 14. (Color online) Transmission coefficient as a function of energy for the open molecule sandwiched between two Ni electrodes at different voltages. The vertical lines denotes the bias window.

the integrated transmission coefficient under the bias window at finite bias coincidentally roughly equals the zero-bias transmission coefficient integrated over the same bias window.

We next move to discussing $T(E, V)$ for the open molecule, which is presented in Fig. 14. In this case the difference between Ni and Ag electrodes is quite significant. In particular, the broad zero-bias peak just below E_F present in the case of Ag leads is completely suppressed for Ni and replaced by two much narrower peaks respectively at -1.3 eV and -2.0 eV below E_F . These correspond to the open molecule HOMO-1 (-1.4 eV below E_F) and HOMO-2 (-1.8 eV below E_F) (see Fig. 4). As a result the transmission coefficient around the Fermi level remains very small. The application of a moderate external bias does not contribute much to enhancing the transmission, since there is no significant movement of the transmission peaks and the bias window is not large enough to comprise any of the HOMO or LUMO states. This explains the very small current observed in Fig. 11 for the open molecule. As the bias reaches 2.0 V the tail of the peak around -1.3 eV starts to contribute to the current and gives rise to the current increase for $V > 2.0$ V. Since there is no substantial drift of any of the transmission peaks with bias, the non-self-consistent I - V (Fig. 12) is a good approximation of the self-consistent one (Fig. 11).

In summary, the calculated transmission coefficients for devices made with Ni electrodes evolve with bias almost in the opposite way of those devices constructed with Ag electrodes. Thus while for the Ag/DTE/Ag junction we have reported a strong bias dependence of $T(E, V)$ for the open molecule and little to no bias-dependent features for the closed one, the situation is reversed when Ni is used. In this case $T(E, V)$ changes significantly with bias for the closed molecule but very little for the open one. As in the case of Ag, we now rationalize the bias dependence of the transmission coefficient by presenting the PDOS as a function of bias for four selected C atoms at either side of the molecule (these are the same C_1 , C_2 , C_3 , and C_4 discussed before). Our results for the closed molecule are presented in Fig. 15. Clearly, at zero bias the PDOS of the pairs C_1 - C_4 and C_2 - C_3 are rather similar and

FIG. 15. (Color online) Projected density of states for four C atoms of the closed isomer at different applied bias. The atom labels S_1 , S_2 , C_1 , C_2 , C_3 , and C_4 are defined in Fig. 1. The vertical lines define the bias window.

FIG. 16. (Color online) Projected density of states for four C atoms of the open isomer at different applied bias. The atom labels S_1 , S_2 , C_1 , C_2 , C_3 , and C_4 are defined in Fig. 1. The vertical lines define the bias window.

remain so at all the applied voltages. The only effect of the external potential is a split and a rigid shift of the main HOMO peak with respect to the electrode Fermi level. As discussed previously this corresponds to the movement with bias of the Ni d -band edge, to which the HOMO is strongly electronically coupled.

The PDOS for the open molecule is shown next in Fig. 16. Also in this case the atomic contributions within the C_1 - C_4 and C_2 - C_3 pairs are very similar at zero-bias. However, as an external voltage is applied we observe a redistribution of the PDOS within the atoms forming the pairs, in particular for C_1 - C_4 . This indicates a polarization of the relevant molecular orbitals and the development of asymmetric electronic coupling to the electrodes. As such the transmission coefficient is reduced, as one can see by following the change in amplitude with bias of the transmission peak at -1.3 eV below E_F (see Fig. 14). The PDOS analysis also reveals the reason why the transmission coefficient is so close to zero for energies down to -1.0 eV below E_F . In fact, in that spectral region the PDOS for the C_2 - C_3 pair is tiny, so that there is no molecular state with significant wave-function amplitude over the C_2 and C_3 atoms. Therefore the only channel for electron transfer at these energies is tunneling, and the current is small.

FIG. 17. (Color online) PDOS for one Ag lead surface atom and the S_1 atom at $V = 0$ V. The atom label S_1 is defined in Fig. 1.

FIG. 18. (Color online) PDOS for one Ni lead surface atom and the S_1 atom at $V = 0$ V. The PDOS for the Ni 3d states have been scaled by a factor 0.1 for visibility. The atom label S_1 is defined in Fig. 1.

In order to further compare the results for Ag and Ni electrodes we now analyze the electronic coupling between the leads and the molecule. In Figs. 17 and 18 we present the PDOS for one of the lead atoms bonded to the molecule and the S atom of the anchoring thiol group for both the open and the closed molecule, and either Ag or Ni leads (the atomic labels have been defined in Fig. 1).

In the case of Ag leads (see Fig. 17) the PDOS for the S_1 atom follows closely the carbon PDOS presented in Figs. 9 and 10. In particular, it is dominated by the S 3p shell. In contrast, the PDOS for the Ag lead atom shows no significant features, with a slightly smaller contribution originating from the 4d shell compared to those of the 5s and 5p ones. When Ni electrodes are used the situation changes drastically (see Fig. 18). Now the PDOS for the S_1 atom (still mostly dominated by the 3p orbitals) is strongly influenced by the presence of the Ni 3d bands at the Fermi level. This indicates *p-d* hybridization at the interface.

In summary, while for Ag the S atoms participate to molecular states extending over the entire molecule, for Ni the S atoms hybridize with Ni bands of dominantly *d* character. In Ag the free electronlike *s* electrons dominate at E_F . This is a band with a large dispersion and little features so that the molecular levels of the free molecules are not significantly distorted but only broadened. In the case of Ni, the Fermi surface is predominantly *d* in character. This is a band rather localized in energy with orbitals tightly confined in space. Its electronic coupling with the molecule is both rather strong and sensitively dependent on the structure of the local electrostatic potential. Strong hybridization with these relatively localized states causes a significant realignment of the molecular states with the Fermi level, a fine structure in $T(E)$, and a dynamical dependence on the external voltage.

IV. CONCLUSIONS

We have performed fully self-consistent finite bias transport calculations for both the closed and open form of a

dithienylethene molecule attached to either Ag or nonmagnetic Ni electrodes. We have found a high $\mathcal{R}$ ratio between the currents of the closed and the open molecule at small bias ($\mathcal{R} = 35$ for Ag and $\mathcal{R} = 40$ for Ni), which generally persists up to higher voltages. For instance, $\mathcal{R} = 5$ for Ag at $V > 1$ V, while $\mathcal{R} = 20$ even for $V = 2$ V for Ni. The difference in the zero-bias conductance between the closed and the open form of the molecule is attributed to that the molecular levels align differently with respect to the lead Fermi level for the two cases. However, when an external voltage is applied also molecular-orbital re-hybridization contributes to determine the I - V curve. Interestingly, although the transmission coefficient as a function of energy and bias changes significantly as the electrodes material is changed, the resulting I - V curves for Ag and Ni are qualitatively similar.

In the case of Ag electrodes the open form of the molecule presents significant orbital rehybridization as the bias is increased. This results in the suppression of the transmission over a broad spectral range and consequently in a small electron current. The same feature is absent for the closed molecule and this gives rise to the large $\mathcal{R}$ observed. As such the behavior of Ag as electrode material for dithienylethene is similar to the one previously reported for Au.⁸

When the electrodes are made of Ni the situation is different from that of Ag and Au. In general the coupling of the molecule with the electrodes is strong and dominated by the *p-d* hybridization between the S 3p and the Ni 3d shells. At zero bias the transmission coefficient at E_F for the closed molecule is larger than that of the same molecule and Ag leads. In contrast, the Fermi level is placed in the middle of the HOMO-LUMO gap of the open molecule and the current remains small up to about 2 V. When an external voltage is applied, the various molecular levels shift in energy together with the electrode *d* bands, in a similar fashion to what happens in Fe/MgO/Fe tunnel junctions.

In conclusion, we do not observe a marked difference between the I - V curves of devices made with either Ag or nonmagnetic Ni leads, indicating that the gross features of the electron transport in dithienylethene depend on the intrinsic properties of the molecule itself for the cases studied here. As such, although the coupling between the molecule and the electrodes is different for Ag and Ni the calculated I - V curves are qualitatively similar. Our conclusions are in agreement with earlier calculations of transport in carbon nanotubes attached to metallic leads.^{35,36}

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