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Electron transport through a metal-molecule-metal junction

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Molecules of bisthiolterthiophene have been adsorbed on the two facing gold electrodes of a mechanically controllable break junction in order to form metal-molecule(s)-metal junctions. Current-voltage (I-V) characteristics have been recorded at room temperature. Zero bias conductances were measured in the 10-100 nS range and different kinds of non-linear I-V curves with step-like features were reproducibly obtained. Switching between different kinds of I-V curves could be induced by varying the distance between the two metallic electrodes. The experimental results are discussed within the framework of tunneling transport models explicitly taking into account the discrete nature of the electronic spectrum of the molecule.

I. INTRODUCTION

Molecular electronics, understood as ‘making an information processing device with a single molecule’ requires synthesizing molecules with electronics functionalities and connecting them together and to external electrodes. In the seventies, A. Aviram and M. A. Ratner [1], and F. L. Carter [2] proposed challenging design of molecules analogous to diodes or triodes. Since then, molecules of these types have been synthesized, and some connection techniques have been developed. State of the art is the connection of a few molecules, and even of a single one, to conducting electrodes. This was first achieved using a Scanning Tunneling Microscope by positioning a metallic tip above molecules deposited on a conducting substrate [3]. Electronic properties of various molecules [4–16], and eventually single C_{60} ones [17,18] have been investigated in this way. The conclusion reached from these experiments is that a molecule can have a non-zero conductance determined by its molecular orbital structure [18–20]. Using a STM to contact a molecule however suffers from intrinsic limitations, such as the asymmetry of the junctions and, at least at room temperature, the lack of the mechanical stability necessary to maintain a stable chemical bond between the molecule and the tip. These limitations, together with the improvement of lithographic techniques, have prompted the emergence of complementary techniques. In the last three years, two alternative techniques have been proposed for contacting a molecule to metallic electrodes. The first one consists in fabricating a series of metallic electrodes, to which the molecule is contacted, at the surface of a substrate. This technique, so far restricted to molecules longer than at least 5 nm [21], has been used, in particular, to investigate carbon nanotubes [22,23]. The second one is to use a mechanically controllable break (MCB) junction [24,25]. It consists in breaking a small metallic wire, introducing molecules with end-groups reactive to this metal into the gap,

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and adjusting the gap between the two facing electrodes to a distance comparable to the length of the molecule in order to contact it. This technique combines the advantages of the previous ones: it allows to connect a short molecule between similar electrodes while maintaining a very high stability (down to 0.2 pm/hour for nanofabricated **MCB** junctions) [26]. As demonstrated recently by Reed et al [24], it opens up the possibility to measure electrical transport through a very few molecules chemically bound to two electrodes, and possibly through a single one -the actual number being however very difficult to know .

In the present paper, we describe the use of gold **MCB** junctions to investigate the electronic transport properties through bisthiolterthiophene 2,5"-bis(acetylthio)-5,2'5',2"-terthienyl (**T3**) molecules. We show (i) that different types of reproducible I-V characteristics can be obtained and (ii) that varying the distance between the two electrodes induces a switch between different I-V curves. Finally, we discuss the interpretation of the experimental results within the framework of two different models which both explicitly include the discrete nature of the electronic levels of the molecule: (i) a coherent model which treats the molecule as a scattering impurity between two metallic wires, and (ii) a sequential tunneling model, in which the molecule is assumed to be weakly coupled through tunnel junctions to each metallic electrode.

II. EXPERIMENTAL TECHNIQUES AND RESULTS

A. Sample fabrication

The aim of the experiment is sketched on Fig.1. The conjugated molecule **T3**, to be connected to the electrodes of the **MCB** junction, was synthesized from terthiophene. A thiolate function was substituted at both ends of the molecule for its ability to strongly react with gold surfaces [27]. The thiolate functions were protected by thioester formation with acetic anhydride in order to avoid successive oxidative oligomerization that would generate polydisulfides [28] in solution; the protecting acetate groups were removed just before immersion of the gold electrodes into the **T3** solution (Fig2).

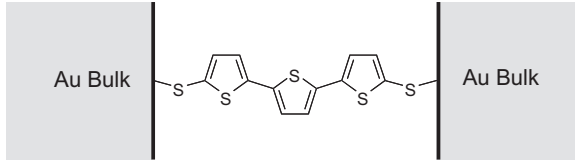


FIG. 1. Ideal Sample. A conjugated molecule is chemisorbed onto the gold electrodes via the thiolate terminal groups.

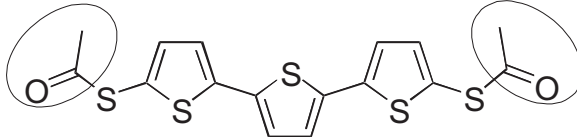


FIG. 2. Representation of the **T3** molecule. Acetyl protecting groups are visible (circled) at each end. They were removed prior to the assembly process.

Suspended metallic microbridges were fabricated as described in Ref. [26]. First, an insulating layer of polyimide PI 2610 from Dupont de Nemours was spun on a polished phosphor-bronze substrate. Using standard e-beam lithography techniques, a metallic nanostructure with the appropriate shape was then deposited on a 4 mm × 20 mm chip. In our case, the metallic layer consisted in a 100 nm thick gold layer, with an underneath 0.2 nm thick titanium adhesion layer and a 5 nm thick aluminum protection layer on top. Finally, isotropic reactive ion etching of the PI layer produced a metallic bridge suspended between anchoring pads (Fig.3). The suspended length was of the order of 3 μm, and the central constriction was less than 100 nm wide.

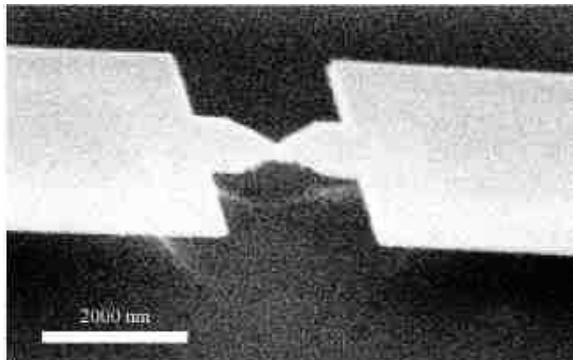


FIG. 3. Scanning electron microscope picture of a suspended junction before breaking.

The chip was then mounted in a three point bending configuration. The chip, resting on two countersupports, was bent by pushing on its center with a driving rod, actuated through a coarse adjustment screw, until the bridge breaks, as indicated by infinite electrical resistance. The

molecules were then self-assembled onto the freshly broken gold electrodes by immersion of the suspended junction in a droplet of a 5×10^{-4} M solution of **T3** in trichloro-1,1,1-ethane. The droplet was supplied by a Hamilton syringe mounted 0.5 mm above the junction. In order to improve the self-assembly process of the molecules, the acetyl protecting group of the dithiol was hydrolyzed in situ by adding 0.1 % of dimethylaminoethanol 1 min before the experiment. The gold electrodes were kept in solution for 1 min, then the solvent was evaporated. After that, Argon was continuously flushed through the shielded sealed box containing the set-up. These conditions were chosen so as to hinder the formation of di- or polydi-sulfides. In a final step, the bridge gap was reduced using a piezoelectric fine adjustment of the driving rod until a non zero conduction was detected (Fig. 4).

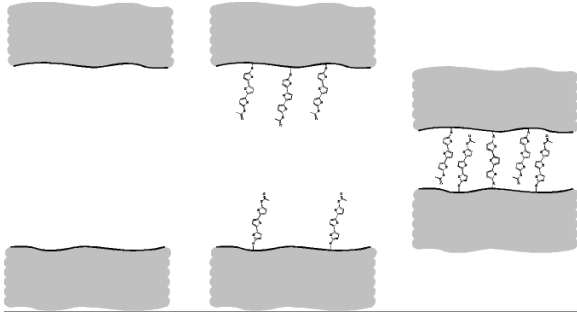


FIG. 4. Actual experiment: the top and bottom gold electrodes are first separated by breaking the junction (left), **T3** molecules are adsorbed onto them (middle) and the electrodes are brought closer to allow I-V measurements (right) on a single or a small number of molecules.

B. Experimental setup

All electrical connections were filtered with low-pass RC filters. The junction was voltage biased, and the current was measured using an I/V converter. Typically, 512 points were collected for each I-V curve by sweeping the voltage from -2 V to 2 V in 0.2 to 20 seconds.

C. Control experiments and Calibration

As a control experiment, we first recorded the I-V characteristics of a metal-air-metal junction. I-V characteristics are linear, and the variations of the conductance with the piezoelectric actuator elongation are shown in Fig.5. Assuming elastic deformation of the substrate and a barrier height of 1 eV for a gold-air-gold tunnel junction

[29], the observed exponential dependence [30] provides a calibration of the displacement ratio r between the piezo elongation and the inter-electrode spacing. The obtained value $r = 3.3 \times 10^{-5}$ is consistent with the geometrical estimate [26,31] $r = 6tu/L^2 = 3.75 \times 10^{-5}$, where $t = 0.3$ mm is the substrate thickness, $u = 3 \mu\text{m}$ is the distance between the anchoring points, and $L = 1.2$ cm is the distance between the two countersupports.

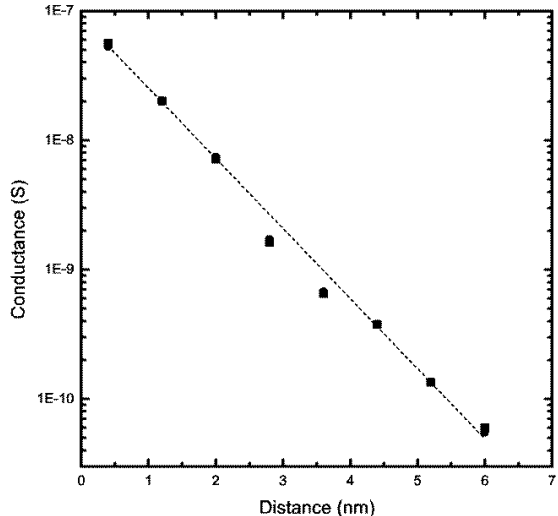


FIG. 5. Conductance of a metal-air-metal junction as a function of the variation of the inter-electrode spacing (dots). The origin of the horizontal axis is arbitrary. The dashed line correspond to the WKB exponential variation assuming a barrier height of 1 eV(see text).

I-V characteristics of a metal-air-metal junction after 1 min immersion in the pure solvent were also measured. I-V curves were featureless and exhibited a linear behaviour at low bias.

D. Measurements of Au-T3-Au junctions

During a typical experiment on Au-**T3**-Au junctions, stability periods with a duration 1-20 min alternate with instability periods generally lasting a few minutes. This behavior was always observed on the four samples that have been measured. A series of I-V characteristics, recorded subsequently, are shown in Fig.6. Although different I-V characteristics could be observed, the reproducible ones are of one of the two types of I-Vs shown in Fig.7. Asymmetric I-Vs of type (a) are more often observed and more stable than symmetric ones of type (b).

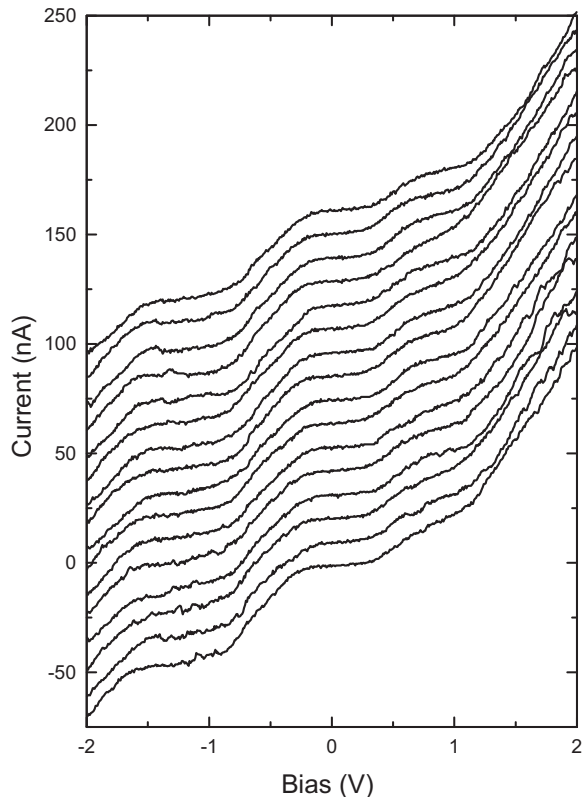


FIG. 6. Consecutive single sweep I-V curves recorded at room temperature for a gold-**T3**-gold junction. Curves are shifted vertically for clarity.

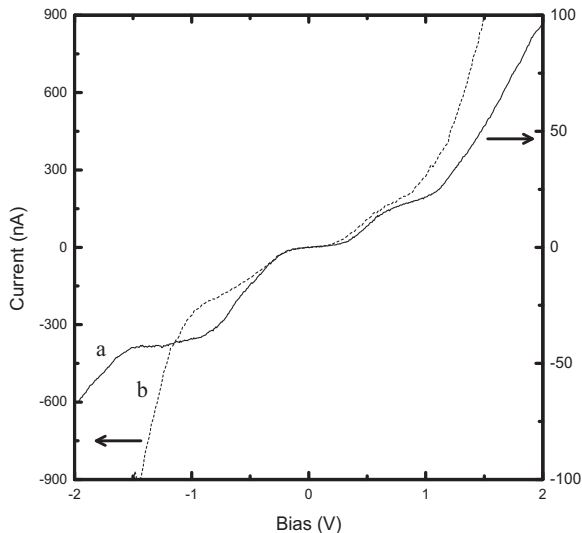


FIG. 7. Typical (a) asymmetric (solid line) and (b) symmetric (dashed line) I-V curves recorded at room temperature for gold-**T3**-gold junctions. Both curves were obtained by averaging over 5 voltage sweeps.

Fig.8 shows typical asymmetric curves.

The measured zero bias conductance of type (a) junctions is of the order of 10 nS. The asymmetric

I-V characteristic is non-linear with step-like features, and the current increases linearly at large voltage.

The measured zero bias conductance of type (b) junctions is larger, about 80 nS. The symmetric I-V characteristic is also non-linear with smaller step-like features. At $V \geq 1$ V, the current rises faster than linearly with V .

Fig.8 shows a mechanically induced transition between different I-V curves. A series of reproducible type (a') I-Vs was first recorded. The inter-electrode spacing was then reduced by 0.04 nm approximately, and a series of type (a'') I-Vs were then recorded. It should be noted that upon reduction of the gap size, the zero bias conductance first *decreased* from 13 nS to 6 nS.

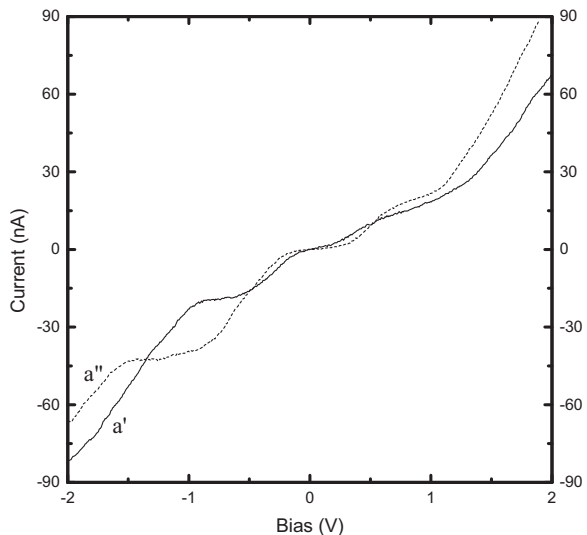


FIG. 8. I-V curves recorded (a') before (solid line) and (a'') after (dashed line) reduction of the inter-electrode spacing by ca 0.4nm. Both I-V curves were obtained by averaging over 5 voltage sweeps.

III. DISCUSSION

Before discussing transport models, we first present the electronic properties of the isolated **T3** molecule and their modification upon adsorption onto the electrodes.

A. Electronic properties of a **T3** molecule

Fig. 9 (triangles) shows the electronic spectrum of an isolated deprotected **T3** molecule calculated using a standard extended Hückel technique, starting from a forced planar geometry optimized at the AM1 level [32]. Although properties of the **T3** molecule adsorbed onto gold are not known,

except for the adsorption of **T3** in a matrix of dodecanethiol [33], other rigid rods α,ω -dithiols have been shown to form assemblies onto gold, in which one thiol group binds to the surface while the other thiol group projects upward at the outer surface of the self-assembled monolayer [28]. Furthermore, organised self-assembled monolayers of bis-(2,2':5',2''-terthien-5-yl)disulfide have been described [34]. From these studies, it seems plausible that the **T3** molecule, once deprotected, reacts onto the gold electrodes with (i) the formation of a Au-S bond and (ii) the terthiophene moiety pointing upward rather than laying on the surface of the electrode. One key question concerns the position of the Fermi level of the electrodes relatively to the molecular electronic levels. The latter are expected to shift so that the Fermi level of gold falls in the HOMO-LUMO gap, its position being determined by the amount of charge displaced on the molecule. It has been shown that the formation of the Au-S bond involves a formal negative charge transfer, δ^- from the metal to the molecule. The values of δ^- ranges from 0.2 to 0.6 electron for thiolate adsorption on gold [15,16,35] [36]. Using the method described in reference [37], we found a position of the Fermi Level of -10.5 ± 0.06 eV in the energy scale used for the molecule. The HOMO is thus closer to the Fermi level than the LUMO, with $E_F - E_{HOMO} = 0.2 \pm 0.06$ eV [38]. However, given the approximations made in the calculation and the uncertainty about the exact amount of charge transferred, it seems reasonable to keep this difference as an adjustable parameter within the [0 - 0.7eV] range, i.e. Fermi Level between HOMO and midgap.

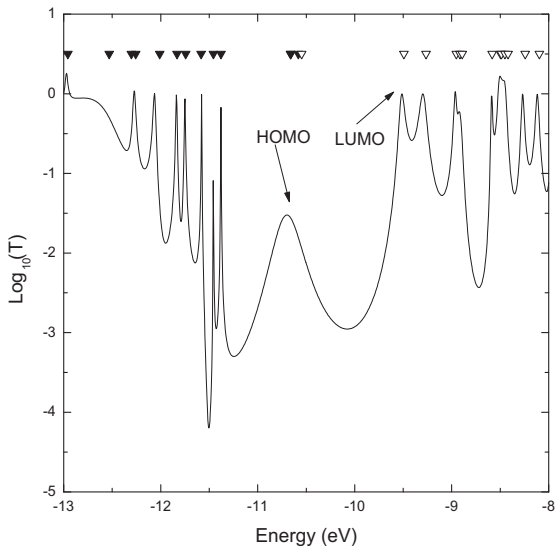


FIG. 9. Transmission function of the **T3** molecule calculated by the **ESQC** technique. The triangles represent the energy level positions of the isolated molecule (filled occupied MO's and open unoccupied MO's of the deprotected **T3** diradical). HOMO and LUMO refer to the gap of **T3** adsorbed on the two electrodes. The energy scale reference is arbitrary.

B. Linear regime

At low bias ($V \leq 0.1V$), the I-V characteristics are linear. The measured zero bias conductance are respectively 80nS, 6nS and 13nS for the curves in Fig.8 and Fig.7.

We first calculated the transport properties of the gold-molecule-gold junction by the Electron Scattering Quantum Chemistry (**ESQC**) technique [19,39,40]. This technique has proven to quantitatively account for the low bias conductance of single adsorbed molecules as probed by STM [17]. It treats the molecule as a defect which breaks the translational invariance of the metal, and therefore scatters incident electrons. The **ESQC** technique ignores both the electron-electron and electron-phonon interactions and neglects charging effects. It assumes that the scattering is elastic because for molecule of small length, the tunneling time is shorter than the intramolecular relaxation times. An extended Hückel model is used to build up the matrix representation of the multichannel scattering Hamiltonian taking into account the complete chemical description of the electrodes and of the molecule. The calculated multichannel transmission coefficient $T(E)$ of an electron at a given energy E is shown in Fig. 9. The linear conductance G of the metal-molecule-metal junction is then determined using the Landauer formula [41],

$$G = \frac{2e^2}{h} T(E_F)$$

where E_f is the Fermi level of the electrodes.

The prediction for G thus depends on the estimated position of the electronic spectrum relatively to the Fermi energy E_F , on the exact conformation of the molecule in the junction and of the coupling of the molecule to the electrodes. The strength of coupling is determined by the length of the Au-S bonds. The S atoms were assumed to be adsorbed in a hollow site of the gold surface. A bond length of 1.905 Å was used in the present calculation [35]. This is the shortest distance, we found in the literature. It thus provides an upper bound for the coupling strength. Assuming a symmetric coupling at both ends of the molecule,

the calculated conductances for $E_F - E_{HOMO} = 0.6(\text{midgap}), 0.2$ and 0 eV are 87, 585, 2306 nS, respectively. Although the order of magnitude of these values is comparable with the measured one $G \simeq 80$ nS for type (b) junctions [42], the discrepancy indicates that the coupling of the molecule to the electrodes is smaller than estimated. This finding can be compared with the results published recently by Emberly and Kirczenow [43]. In that paper, it is shown that the experimental conductance of gold-benzene di-thiol-gold junctions, reported in ref. [24] can be accounted for by a transport model based on the Landauer formalism provided that artificially large bond lengths (i.e. small couplings) are used. In our case the discrepancy between theory and experience seems less important but could also be reduced using longer Au-S bonds: for example $G_0=87\text{nS}$ at midgap for Au-S=1.905Å reduces to $G_0=20\text{nS}$ at midgap for Au-S=3Å.

C. Non linear regime

We now discuss the step-like features found in the I-V characteristics at large bias voltage and their possible interpretations.

At first, we can rule out the simplified Coulomb blockade model put forward by Reed et al to account for their experimental observations in a similar experiment with benzene dithiolate [24]. Indeed, this model, which considers the molecule as a usual metallic island forming a small capacitor with each electrode, predicts a series of steps which are not observed.

Consequently, we attribute the steps to the discreteness of the molecular levels [44]. We present and discuss below two models which both involve the discrete electronic levels of the molecule explicitly. The first one is a coherent tunneling model derived from the **ESQC** technique, whereas the second is a sequential tunneling model. Basically, they differ by the fact that the electron resides (sequential tunneling) or not (coherent tunneling) on the molecule during the transfer.

Given the symmetry of the molecule, symmetric I-V characteristics are expected in the case of symmetric couplings. Thus type (b) characteristics only will be analyzed below.

1. Coherent tunneling model

The coherent tunneling model is based on an extension of the **ESQC** technique outlined above. It supposes that the coupling to the electrodes is strong, in other terms that the tunneling time of

an electron through the molecule is much smaller than the intramolecular vibronic relaxation time: i.e. the molecule is not charged by the tunneling process, the electron having no time to be completely delocalized in the molecule after the initial tunneling step at the metal -molecule electronic contact. The current is calculated using [45]:

$$I(V) = \frac{e^2}{\pi\hbar} \int_{-\infty}^{+\infty} T(E, V) (f(E - \mu_1) - f(E - \mu_2)) dE \quad (1)$$

in which the effect of the bias voltage V on the $T(E)$ spectrum is included; $\mu_{1,2}$ is the chemical potential of the electrode 1,2, and $f(\epsilon)$ denotes the Fermi function at the temperature of the experiment. In the case of a symmetric junction, the voltage at the molecule lies halfway between the electrode voltages. In order to calculate the current, we make the crude approximation that $T(E, V) \simeq T(E - eV/2, 0)$ where $T(E, 0)$ is the spectrum of Fig. 9. Equation 1 then predicts the I-V characteristic shown in Fig. 10.

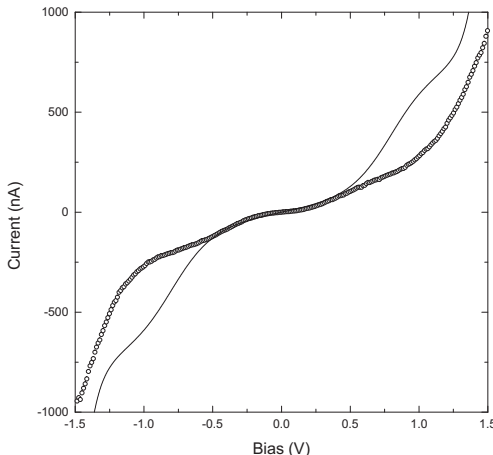


FIG. 10. Experimental symmetric I-V curve (diamonds). I-V curve (solid line) calculated with the coherent model. The calculation (see text) has been done using: $E_F - E_{Homo}=0.4\text{eV}$.

For both polarities, the first resonances occur through the HOMO and the HOMO-1 levels. This results from the assumption that the equilibrium Fermi level is closer to the HOMO than to the LUMO [15]. In this model, the shape and height of the steps is only due to the broadening of the molecular levels by the coupling with the electrodes. In particular, the height of a step in the I-V curve is directly proportional to the area of the corresponding peak in the $T(E, V)$ spectrum.

The experimental curve is well reproduced for the $[-0.5V, 0.5V]$ range. Outside of this range, the calculated current is higher than the experimental one. It should be noted that the only adjustable parameter used in the calculation is the position of the Fermi level. Here we have taken $E_F - E_{HOMO} = 0.4$ eV. In this calculation, the magnitude of the current depends on the following points: i) the overlap between the orbitals of the outer Au atoms and of the sulfur atoms; ii) the localisation of the molecular orbital and its symmetry, iii) perfect symmetry between the two contacts [46]. The applied voltage is expected, especially at high bias, to affect points ii) and iii), both of which should tend to decrease the calculated current and thus reduce the discrepancy.

2. Sequential tunneling model

In this model, the molecule is treated as a quantum dot with discrete energy levels weakly coupled to both electrodes through tunnel junctions. It considers the tunneling of an electron through the metal-molecule-metal junction as a sequential process [47], the molecule being successively charged and discharged. At first sight, the existence of tunnel barriers at both ends of the molecule can be questioned since the sulfur species chemically adsorbed on the electrodes do contribute to the HOMO and LUMO, both orbitals being delocalised over the entire molecule. However, the existence of barriers to the injection of carriers at metal-oligothiophene junction have been reported in the literature [48]. Furthermore, the possible existence of a barrier to injection at a gold -thioacetylbiphenyl interface has also been recently put forward by Zhou et al [49] to interpret experimental data of conduction in a metal/self-assembled monolayer/metal heterostructure.

Electron tunneling rates through both metal-molecule junctions are obtained from a Golden rule calculation. The current is calculated by solving a master equation connecting the different charge states of the molecule (see Appendix A).

To calculate the I-V characteristics, we have taken the apparent position of the molecular levels given by the $T(E)$ spectrum of Fig. 9 in order to account for the shift of the level upon adsorption of the molecule onto the electrodes. For the sake of simplicity, we adjusted the experimental curve considering only two levels (HOMO and LUMO) because the charging of the molecule will most likely involve these two levels. The best adjustment of the experimental data is obtained assuming the HOMO to be located at the equilibrium

Fermi level [50]. For this calculation, a charging energy of $E_c=0.19$ eV was used, which is comparable to values reported for C_{60} molecules by Porath et al [47]. This is about one order of magnitude smaller than the calculated charging energy for an isolated molecule but a strong reduction of the charging energy is expected for molecules adsorbed onto metallic electrodes.

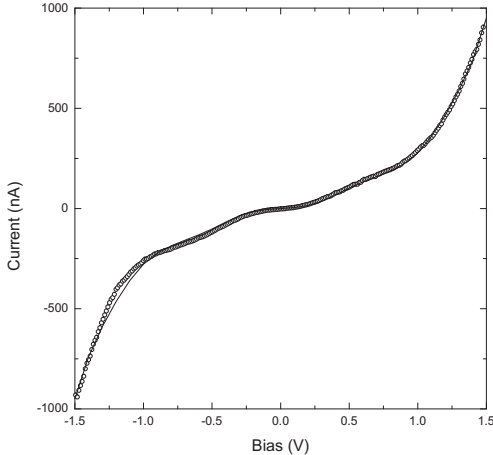


FIG. 11. Experimental symmetric I-V curve (diamonds). I-V curve (solid line) calculated within the framework of the sequential model. The calculation (see text) has been done using: $E_F = E_{Homo}$, $\phi = 0.47$ eV and $d = 0.53$ nm .

As can be seen in Fig. 11, a good qualitative description of the experimental data can be obtained once the tunneling barrier parameters are adjusted to fit the magnitude of the current step. A prefactor is included to account for the barrier suppression at high bias [51] (See Appendix A). The phenomenological parameters (accounting for the barrier height and width respectively) used to fit the data are $\phi = 0.47$ eV and $d = 5.3$ Å. This approximation is a very crude way to account for the contact barriers at both ends of the molecule. However, though the value for the barrier width is large, the orders of magnitude for ϕ and d are not unrealistic.

A more microscopic approach for the transparencies of the barriers would be to use the extended Huckel calculation to compute the overlap of the molecular orbitals (involved in the change of the total number of electrons in the molecule) with the Au leads and then estimate the rates from the broadening of these levels upon coupling. In the present case, the levels involved in the transport are the HOMOs levels. We have calculated the broadening of these levels using the ESQC technique assuming a Au-S distance of 1.905 Å and

considering each molecular orbital separately to avoid any interference effect between orbitals (such an interference effect takes place, for example, between the HOMO and HOMO-1 orbitals in the $T(E)$ spectrum in Fig. 9 and explains the non unity value of the corresponding peak). We found a width at half maximum of 0.4eV corresponding to a transfer rate of about $3 \cdot 10^{14}$ Hz. This is too high when compared to the experimental rates of the order of 10^{12} Hz. To get the right order of magnitude artificially large Au-S distances have to be used (typically 6 Å). This shows that the calculation of the coupling strength based on the extended Hückel model likely leads to an overestimated value as already pointed out in the linear regime subsection above. At present, this microscopic approach unfortunately cannot be used to estimate the barrier suppression at high bias, because the extended Hückel calculation do not take into account the modification of the orbitals under bias.

3. Discussion

To summarize, both the coherent model at low bias and the sequential model at large bias give qualitative fits of the experimental I-V curves. This provides support to the hypothesis that the step like features in the I-V curve indeed originate in the discreteness of the molecular levels. However a quantitative fit of the data has not been achieved. This may be explained as follows. First, the effect of the applied bias on the relative position of the resonances in the $T(E)$ spectrum is neglected, since we consider that the bias effect is to shift $T(E)$ as a whole. Although the electric fields involved in the experiments are always lower than 1×10^9 V/m, the position of the levels is expected to be modified [52]. Preliminary calculation using the DFT formalism have shown that the HOMO-LUMO gap of the bisthiol-bisthiophene molecule is indeed reduced under an electric field [53], and this effect is expected to take place also with **T3**. Another effect of the field is to modify the coupling between the molecule and the electrodes. This should show up in the $T(E, V)$ spectrum as a modification of the width of the peaks and consequently in the I(V) as a modification of the height of the steps.

Second, in the calculation, the molecule is assumed to be in the vacuum. In reality, given the experimental conditions, the molecule can be assumed to be surrounded by Argon and probably a few solvent molecules. We have not taken this environment into account in our calculations. Smoothing of the theoretical I-Vs of both models is ex-

pected due to this polarizable surrounding.

Additional experimental results and theoretical calculations are clearly needed to help deciding between sequential and coherent tunneling or a combination of both. This includes : (i) measurements in a better controlled environment (UHV), and at low temperature to determine the origin of the broadening of the steps in the I-V curve, (ii) calculation of the potential profile along the molecule in order to determine whether tunneling barriers are present at the end of the molecule or not and (iii) estimation of the tunneling times involved in the processes. Furthermore, it should be noted that two proposed model indeed correspond to extreme cases. In the coherent one, the charging effect is neglected, whereas in the sequential one, the quantum coherence is neglected. In our qualitative fits, it turns out that the order of magnitude of the molecular level broadening (coherent model) and charging energy(sequential model) are comparable. Thus a proper model will very likely have to take into account both coherent and sequential transport.

Compared to the symmetric case, the interpretation of the asymmetric I(V) curves of Fig. 7 (curve a) and Fig 8 is more complicated because we can no longer assume that the coupling to the electrodes is symmetric at both ends of the molecule. First, these data likely correspond to the case where at least one end of the molecule is less coupled to the electrode than in the case of the symmetric curve since i) the zero bias conductance is smaller than in the symmetric case and ii) the high bias behaviour of the current is linear-like rather than exponential-like. Second, the effect of mechanically pushing on the molecule(s) induces a change between two different stable curves. Such an effect has been used recently at low bias to realise an electromechanical amplifier based on a C60 molecule [54]. In the present case, two explanations of the observations can be put forward: either the coupling of the molecule to the electrodes is changed by the mechanical action, or a change in the conformation of the molecule was induced.

IV. CONCLUSION

In this paper, we have investigated the transport properties of molecules of 2,5''-bis(acetylthio)-5,2',5',2''-terthienyl self-assembled in the adjustable gap of a metallic break junction. We have observed that the I-V characteristics recorded at room temperature are not always symmetric with respect to the polarity of the applied bias and show two different regimes: a linear regime at low bias

$V < 0.1$ V and a highly non-linear regime with step-like features at higher voltage. The order of magnitude of the measured zero bias conductance is comparable to the theoretical calculation made with the **ESQC** technique assuming a single molecule in the gap of the break junction. This indicates that these experiments likely involve a very few molecules. We have obtained qualitative fits of the symmetric I-V curves using two different models of transport, a coherent one for the low bias range and a sequential one for the high bias range, both of which explicitly involve the electronic structure of the molecule. Finally, we have shown that the mechanical action of decreasing the gap size by 0.04 nm induces a strong modification of the I-V curves.

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APPENDIX A: THE SEQUENTIAL MODEL

1. Description of the system

We consider a molecule weakly coupled via tunnel barriers to two electrons reservoirs (Fig.12). We assume that the transfer of an electron through the metal-molecule-metal junction occurs through subsequent tunneling events at both ends of the molecule

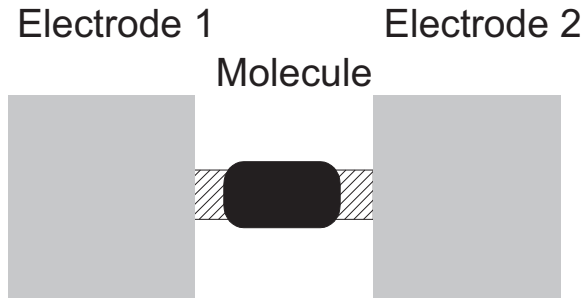


FIG. 12. Scheme of the metal-molecule-metal junction, consisting of a molecule weakly coupled to electrodes via tunnel barriers (hatched)

The reservoirs are described by a continuum of states (temperature T and Fermi energy E_F , occupation according to the Fermi-Dirac statistics $f(E - E_F) = (1 + \exp((E - E_F)/kT))^{-1}$). Under bias V the electrochemical potentials of the electrodes are given by

$$\begin{cases} \mu_2 = E_F + (1 - \eta) eV \\ \mu_1 = E_F - \eta eV \end{cases} \quad (\text{A1})$$

where η is a parameter used to describe the strength of coupling at both ends of the molecule. In the case of the symmetric coupling, we have $\eta=1/2$.

The molecule is accounted for by a set of K discrete molecular orbitals. The i^{th} state of the molecule is described by its energy E_i and the vector $(\lambda_1^i, \lambda_2^i, \dots, \lambda_K^i)$ where λ_k^i is the occupation number of the k^{th} molecular orbital of energy ε_k . The corresponding total number of electrons in the molecule is $n_i = \sum_{k=1}^K \lambda_k^i$. The energy of the i^{th} state is

$$E_i = \sum_{k=1}^K \lambda_k^i \varepsilon_k + E_C (n_i - n_g)^2 \quad (\text{A2})$$

where E_C is the Coulomb energy and n_g is the ground state number of electrons in the molecule plus the offset charge.

2. Calculation of the transfer rates

The rate of transfer of electrons through the tunnel barriers are calculated by application of the Fermi golden rule assuming that the tunneling processes are elastic.

The rate $\Gamma_{i,j}^{k+}$ for the process connecting the i^{th} state and j^{th} state through the transfer of one electron from electrode k onto the molecule is given by.

$$\Gamma_{i,j}^{k+} = \frac{2\pi}{\hbar} |T_{i,j}|^2 \rho_k f(E_j - E_i)$$

where T_{ij} is the tunnel matrix element coupling the states i and j , and ρ_k is the density of states of the electrode k, assumed constant around the Fermi level.

We define in the same way $\Gamma_{i,j}^{k-}$ connecting the states i and j by transferring one electron from the molecule onto electrode k.

$$\Gamma_{i,j}^{k-} = \frac{2\pi}{\hbar} |T_{i,j}|^2 \rho_k (1 - f(E_i - E_j))$$

Assuming that the tunneling barriers have a height ϕ and a width d , we apply a WKB type approximation for the tunneling matrix element

$$|T_{i,j}(V_b)|^2 \propto \exp(-2 \frac{\sqrt{2m(\phi - eV_b)}}{\hbar} d)$$

where V_b is the voltage drop across a tunnel junction.

3. Calculation of the current

The matrix $\underline{\Gamma}$ connecting the different states of the molecule is [55]

$$\underline{\Gamma} = \underline{\Gamma}^{1+} + \underline{\Gamma}^{1-} + \underline{\Gamma}^{2+} + \underline{\Gamma}^{2-} \quad (\text{A3})$$

We introduce the vector \underline{P} , which i^{th} component is the probability of having the molecule in state i . The evolution of the system is then described by

$$\frac{d}{dt} P_i = \sum_j (\Gamma_{ji} P_j - \Gamma_{ij} P_i) \quad (\text{A4})$$

defining \underline{M} by $M_{ij} = \Gamma_{ji}$ $i \neq j$ and $M_{ii} = -\sum_j \Gamma_{ij}$ equation A4 becomes,

$$\frac{d}{dt} \underline{P} = \underline{M} \underline{P}$$

We look for a stationary solution $\hat{\underline{P}}$ assuming that a permanent regime rapidly sets in

$$\hat{\underline{P}} = \ker \underline{M}$$

The current is finally obtained by calculating the net number of electrons transferred from right to left through either junction:

$$I = e \sum_{i,j} \hat{P}_j (\Gamma_{ji}^{1-} - \Gamma_{ji}^{1+}) = -e \sum_{i,j} \hat{P}_j (\Gamma_{ji}^{2-} - \Gamma_{ji}^{2+}) \quad (\text{A5})$$

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