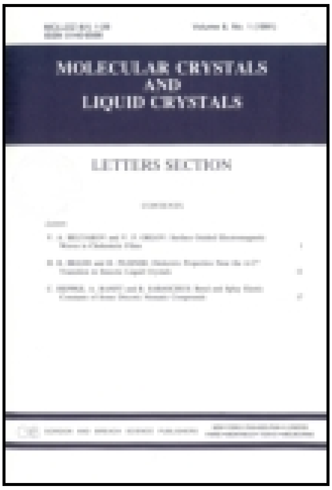

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Conductance Mechanism in a Linear Non-Conjugated Trimethylsilyl-Acetylene Molecule: Tunneling Through Localized States

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The conductance properties of 1,3-(trimethylsilyl)-1-tridecene-6,12-diyne, a non-conjugated trimethylsil-acetylene molecule have been investigated both experimentally and theoretically. Based on scanning tunnelling spectroscopy experiments, a discussion on the mechanisms controlling the charge transfer through this linear molecule is carried out. A specific property of the studied molecule is that it contains localized molecular orbitals. The shifts of the MOs energy levels caused by the applied voltage as well as a distant superexchange coupling between the respective localized MOs are shown to become determining in the formation of a nonlinear hole current through the molecule.

Keywords Charge transport mechanisms; conductance; localized states; STM; monolayer

1. Introduction

Advances in molecular electronics (for an overview see [1–7]) make use of single molecules and molecular wires as building blocks of various electronic devices like rectifiers [4, 8–10], transistors [11–13] and different type of molecular photo devices [14–17]. Therefore, the measurement of conductivity of single molecules is one of the foremost problems at stake in physics of low–dimensional molecular compounds [18]. Most of such measurements has been carried out with thiols chemisorbed on gold: a phenyl dithiol molecule connected to gold electrodes [19, 20], an acetyl protected thiol [21], and an ethynylphenyl based thiol containing a nitro–amine redox center introduced in the central benzene ring [22, 23]. Additionally, one can note the experiments on asymmetric electrical conductivity of molecular monolayers embedded between gold and aluminum electrodes [4, 9]. Experimental

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results fix a strong nonlinear conductance of the molecules depending on numerous factors including the precise symmetry of the molecule, the character of coupling to the leads or the aggregation on the substrate.

Theoretical models [5, 19, 22, 24–29] describing the current–voltage ($I - V$) characteristics of the molecules are mainly based on Landauer–Büttiker approach [35, 36]. Molecule in the device is assumed to be connected to electronic reservoirs where electrons occupy single-electron states of each electrode's conductive band. As to single-electron states of molecule, it is found to be characterized by the lowest unfilled and highest occupied molecular orbitals (LUMOs and HOMOs, respectively). When molecular orbitals (MOs) are not destroyed by the applied electric field, then one can use a rather simple analytic form for the conductance of a symmetric and asymmetric molecules [19, 21, 29].

For the most part the noted results refers to molecules with the extended MOs where the transferred electron is well delocalized over the molecule. In the present paper, we analyze $I - V$ characteristics of the TMSA molecule containing few sites of electron localization for the transferred electron/hole. This means that the MOs participating in an electron transmission through a molecule (the working MOs) exhibit notable asymmetry in distribution of an electron density within the molecule. As a result, an electrostatic shift of molecular energy levels (and, thus, transmission gaps) is determined by specific local voltage division factors.

The paper is organized as follows. In Section II, the experimental results concerning the formation of a molecular monolayer from TMSA molecules is given along with the $I - V$ characteristics of an individual TMSA molecule. Section III is devoted to application of the HOMO–LUMO model for a description of a tunnel current through the molecule. Discussion of the results is given in Section IV. Some concluding remarks are presented in Section V.

2. Experiment

1,3-(trimethylsilyl)-1-tridecene-6,12-diyne (Fig. 1) is an assymetric molecule with localized MO-levels related to triple or double bonds. It belongs to the family of polyunsaturated linear trimethylsilyl-acetylenes (TMSA: –C≡C–Si(CH$_3$)$_3$), that we have discovered as forming self-assembled monolayers (SAMs) by grafting on Au(111) [30, 31]. These TMSA molecules spontaneously adsorb on gold in an upright position, the silicon atom being close to the surface and inducing the creation of a surface Si–Au chemical bond [32, 33]. The high stability of TMSA–based SAMs allows to carry out scanning tunneling microscopy (STM) and scanning tunneling spectroscopy (STS).

The $I - V$ characteristics were obtained by STS on gold substrates coated with a self-assembled monolayer of TMSA (Fig. 2). For deposition on gold, a small quantity of the colorless oil formed by TMSA (≈ 0.05 mg/ml) is mixed in n-tetradecane (99+ purity, Aldrich). A droplet of this solution is then deposited onto the Au(111) substrate, allowing molecules to form a self-assembled monolayer. Reconstructed Au(111) surfaces are prepared from 150 nm thick gold films deposited in ultra high vacuum (5×10^{-8} Pa) onto a freshly cleaved mica surface heated at 600 K followed by a careful annealing in a gas flame (propane-air). Following this treatment, STM images of the gold surface recorded in n-tetradecane reveal atomically flat terraces with the typical $23 \times \sqrt{3}$ "herringbone" reconstruction [34]. STM images with resolution of reconstruction stripes are used to determine the crystallographic orientation of the sample with respect to the scan direction.

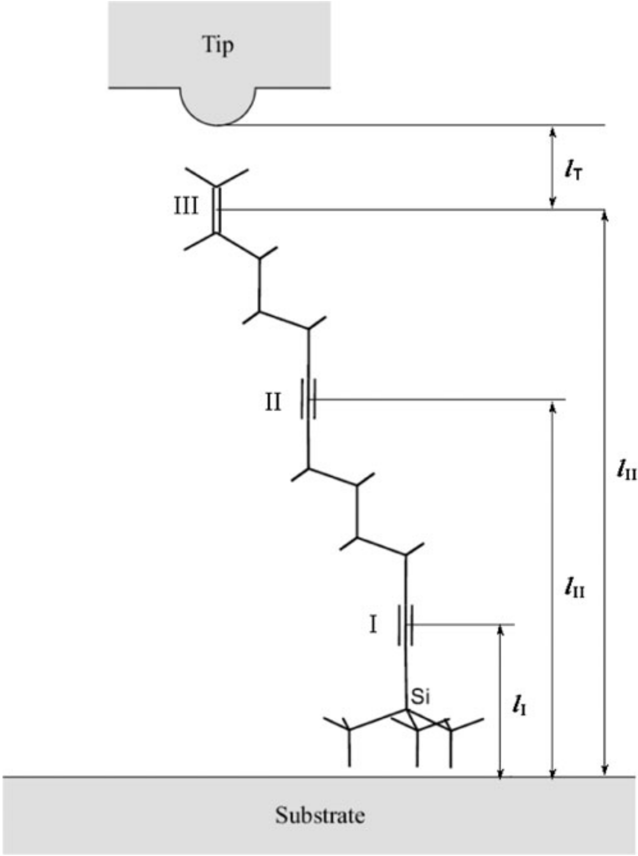


Figure 1. Chemical structure of TMSA and its position with respect to substrate and tip. Distances l_I, l_II and l_III (along the axis perpendicularly to substrate surface) between the sites of electron localization within the molecule are indicated along with distance l_T from a double bond and a tip.

The STM measurements are carried out in a thin layer of solution using a Pico-SPM (Molecular Imaging). The STM tip is a Pt/Ir (80:20) wire sharpened by mechanical cutting. Typical imaging conditions are in the range of (100–300) mV for the substrate bias voltage and (50–500) pA for the tunneling current. STM images recorded in the constant–current mode are obtained with different samples and conditions to test for reproducibility and ensure that the results are free of tip and sample artifacts. Monolayer preparations and imaging are carried out at room temperature.

Scanning tunneling spectra are obtained at a fixed tip sample distance determined by the imaging voltage and the tunneling current used during image recording. Given voltage corresponds to sample voltage. For each recording of a single molecule characteristic, the scan is stopped, after what the feedback loop is switched off in order to apply a voltage ramp in the limits of $-1.9V$ and $+1.9V$. After each acquisition the scan is continued. Scanning tunneling microscopy images are checked to be unchanged after recording of $I - V$ curves. In Fig. 3, the $I - V$ curve represents the average of 50 sweeps recorded on equivalent molecules and going through (0,0) and through the setpoint.

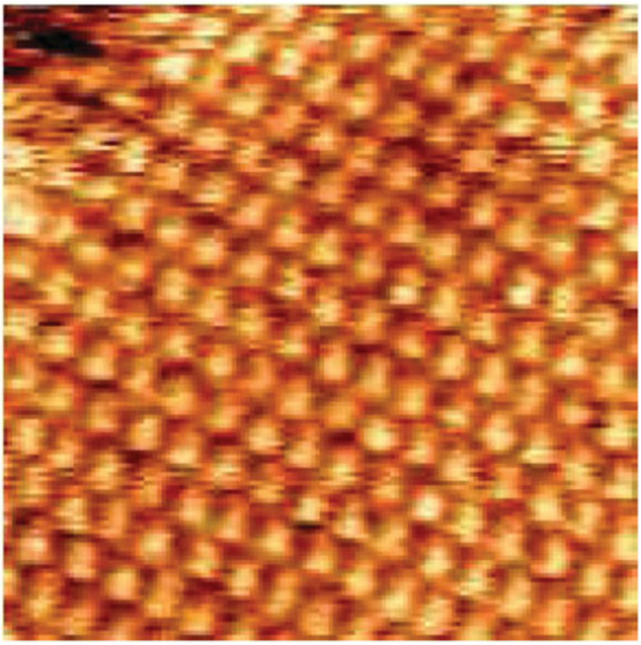


Figure 2. High-resolution STM image ($I_t = 150$ pA; $V_t = 250$ mV; 55×55^2) of a self-assembled monolayer of TMSA on Au(111). It shows a periodic array of bright spots corresponding to individual molecules standing upright on the surface in an hexagonal close-packed arrangement.

3. Theoretical Description

In framework of the Landauer–Büttiker approach [35, 36] the molecule is associated with the scattering centrum so that the transmission of electrons through the molecule appears as elastic or inelastic tunneling. Different applications of Landauer–Büttiker approach for the analysis of the $I - V$ characteristics of molecular junctions one can find, for instance, in refs. [19, 20, 28, 29, 37, 38]. Specific of the TMSA molecule is that its working MOs are strongly localized. Therefore, it is more convenient to employ a description based on the kinetic theory of charge transmission. Last years this theory has been adapted especially for the studies of transient and steady state currents in molecular junctions [39–44].

3.1 Basic Equations

To derive an expression for the current through a TMSA molecule we consider a current formation in the system “lead L-molecule-lead R” (LMR-system) with nonmagnetic leads. In the absence of external magnetic field the Hamiltonian of such system can be written in a standard form

$$H = H_l + H_m + H_{l-m} \tag{1}$$

where the first term,

$$H_l = \sum_{r=L,R} \sum_{\mathrm{k}\sigma} E_{rk} |r\mathrm{k}\sigma\rangle\langle r\mathrm{k}\sigma| \tag{2}$$

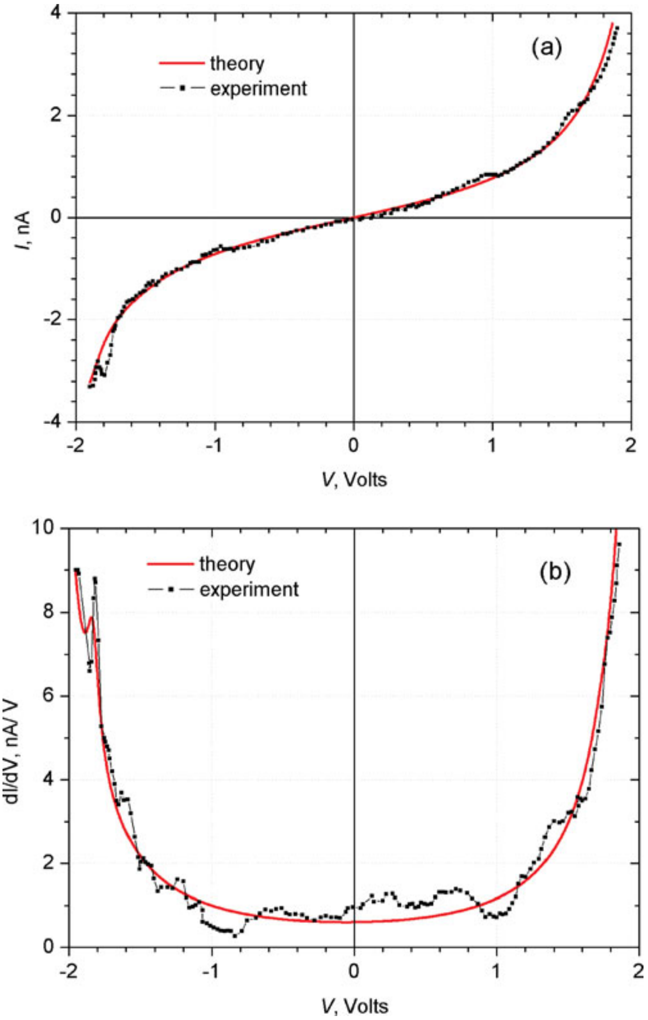


Figure 3. Dependence of tunnel current I (a) and tunnel conductance $g = \mathrm{d}I/\mathrm{d}V$ (b) on voltage bias V. The experimental curve for conductance was subjected to 7-point smoothing. Theoretical curves are calculated with Eqs. (25) and (26) with the parameters from Table 2.

is the Hamiltonian of the leads with E_{rk} being the energy of an electron with wave vector k in the conduction band of the rth lead (respective state is denoted as $|r\mathrm{k}\sigma\rangle$ with σ being the electron spin projection). The second term,

$$H_m = \sum_{N,M} E_{M(N)} |M(N)\rangle\langle M(N)| \tag{3}$$

refers to the molecular Hamiltonian where $E_{M(N)}$ is the energy of molecule in the state $|M(N)\rangle$ (determined in the Fock space). Quantum number M includes, generally, the actual electronic, vibrational, and spin state of the molecule; N is the number of electrons in the molecule. The third term,

$$H_{l-m}=\sum_{r\mathrm{k}\sigma}\sum_{N,MM'}[V_{M'(N+1);r\mathrm{k}\sigma M(N)}|M'(N+1)\rangle\langle M(N)|\langle r\mathrm{k}\sigma|+h.c.] \tag{4}$$

is the Hamiltonian of interaction of the molecule with the leads. Electron hopping between the molecule and the rth electrode is characterized by matrix elements $V_{M'(N+1);r\mathrm{k}\sigma M(N)}$.

In line with the kinetic theory, a tunnel current I through the LMR-system can be calculated with use of expression [39, 41, 42, 44]

$$I=\sum_{N,M}I_{M(N)}P_{M(N)} \tag{5}$$

where

$$I_{M(N)}=|e|\sum_{M'}[Q_{LM(N)\to RM'(N)}-Q_{RM(N)\to LM'(N)}] \tag{6}$$

is the partial tunnel current through the molecule being in the state $M(N)$ with probability $P_{M(N)}$ ($|e|$ is the value of electron charge). Quantity

$$\begin{aligned}Q_{rM(N)\to r'M'(N)}=\frac{2\pi}{\hbar}&\sum_{\mathrm{k}\sigma,}\sum_{\mathrm{k}'\sigma'}f_r(E_{r\mathrm{k}})[1-f_{r'}(E_{r'\mathrm{k}'})]\\&\times|\langle M'(N)r'\mathrm{k}'\sigma'|H_{l-m}\hat{G}(E)H_{l-m}|r\mathrm{k}\sigma M(N)\rangle|^2\\&\times\delta[E_{r\mathrm{k}}+E_{M(N)}-E_{r'\mathrm{k}'}-E_{M'(N)}]\end{aligned} \tag{7}$$

is the transfer rate that characterizes a distant electron transmission between the kσth and the k$'\sigma'$th band states of the rth and the r'th electrodes, respectively. Such transmission appears as a direct single-step elastic (at $M'(N)=M(N)$) or inelastic (at $M'(N)\neq M(N)$) interelectrode electron tunneling. In Eq. (7),

$$\hat{G}(E)=[E-H+\mathrm{i}0^+]^{-1} \tag{8}$$

is the Green's operator defined on the iso-energetic surface $E=E_{r\mathrm{k}}+E_{M(N)}$. Quantity $f_r(E_{r\mathrm{k}})=\{exp[(E_{r\mathrm{k}}-\mu_r)/k_BT]+1\}^{-1}$ is the Fermi–function of the rth electrode with the μ_r being its electrochemical potential; k_B and T are the Boltzmann's constant and temperature, respectively.

When the leads are macroscopic quantum systems, then the influence of the molecular states on the lead's states may be ignored. As a result, Hamiltonian (1) can be transformed into

$$H=H_l+H_m^{(eff)} \tag{9}$$

where

$$H_m^{(eff)}=H_m+\sum_N[\hat{\Sigma}_N^{(L)}(E)+\hat{\Sigma}_N^{(R)}(E)] \tag{10}$$

is the effective molecular Hamiltonian. In Eq. (10), $\hat{\Sigma}_N^{(r)}(\varepsilon)$ is the operator of self-energy defined by its matrix elements

$$\begin{aligned}\sum\nolimits_{M'(N),M(N)}^{(r)}(\varepsilon) &= \langle M'(N)|\hat{\Sigma}_N^{(r)}(\varepsilon)|M(N)\rangle \\ &= \sum_{M''}\sum_{\mathrm{k}\sigma}\left[\frac{V^*_{M''(N+1);r\mathrm{k}\sigma M'(N)}V_{M''(N+1);r\mathrm{k}\sigma M(N)}}{\varepsilon-(E_{M''(N+1)}-E_{r\mathrm{k}\sigma})+\mathrm{i}0^+}\right. \\ &\quad\left.+\frac{V^*_{r\mathrm{k}\sigma M''(N-1);M'(N)}V_{r\mathrm{k}\sigma M''(N-1);M(N)}}{\varepsilon-(E_{r\mathrm{k}\sigma}+E_{M''(N-1)})+\mathrm{i}0^+}\right]. \qquad (11)\end{aligned}$$

Solving the secular equation

$$\mathrm{Det}(H_m^{(eff)}-E\hat{I})=0 \qquad (12)$$

one derives the proper molecular energies $\varepsilon=\varepsilon_{\mu(N)}$ which contain real and imaginary parts, $\varepsilon_{\mu(N)}=E_{\mu(N)}-\mathrm{i}\Gamma_{\mu(N)}/2$. If a molecule-lead interaction is small then the off-diagonal elements $\Sigma^{(r)}_{M'(N),M(N)}(\varepsilon)$ give only a minor contribution in the formation of the proper molecular energy. This means, that in a good approximation, the proper molecular states $|\mu(N)\rangle$ coincide with the molecular states $|M(N)\rangle$ and, thus, the effective molecular Hamiltonian can be written in the following diagonal form

$$H_m^{(eff)}=\sum_{N,M}\varepsilon_{M(N)}|M(N)\rangle\langle M(N)| \qquad (13)$$

where

$$\varepsilon_{M(N)}\approx E_{M(N)}-\mathrm{i}\Gamma_{M(N)}/2. \qquad (14)$$

It is seen that owing to interaction with macroscopic leads, molecular energies $E_{M(N)}$ exhibit the broadening [45] which can be estimated with the expression

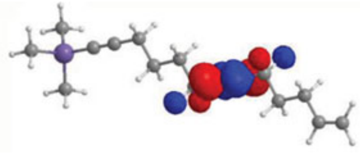
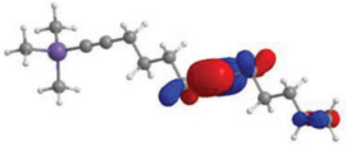
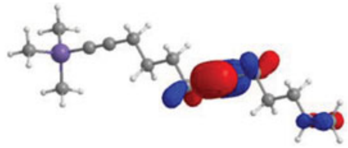
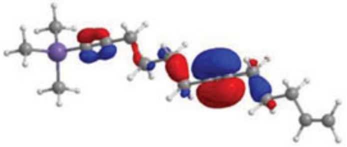
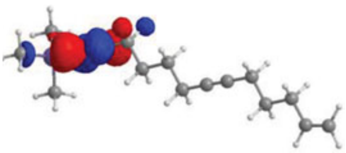
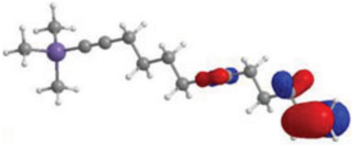
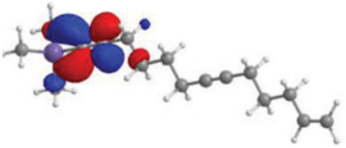
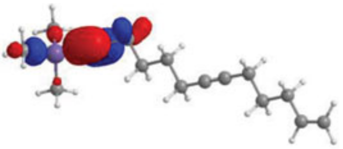
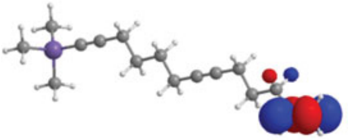
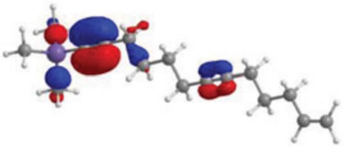
$$\Gamma_{M(N)}=2\mathrm{Im}\sum_{r=L,R}\Sigma^{(r)}_{M(N)M(N)}(E\approx E_{M(N)}). \qquad (15)$$

3.2 Application to the TMSA

To apply the above expressions for a calculation of the tunnel current through the TMSA molecule, let note that in this molecule, all three sites of an electron localization do not contact directly with the substrate and the tip. Therefore, interaction of the localized MOs with the leads do not destroy the MOs. Hence, a calculation of the transfer rate (7) can be performed with use of the diagonal Hamiltonian written in the form (13).

To specify molecular states $|M(N)\rangle$ and respective energies $E_{M(N)}$ related to the TMSA molecule, one has to know its working MOs. The quantum -chemical calculations were applied to the isolated TMSA being in the spinless charge neutral configuration. The geometry optimization and electronic structure calculations were carried out at the density functional theory level with the hybrid B3LYP of three parameter Becke (B3) functional [46] and the Lee–Yang–Parr (LYP) functional [47] which includes both local and non-local correlations and provides generally a good description for the class of molecular systems. The split valence basis set 6–31G(d) was used in all calculations carried by GAUSSIAN’03w

Table 1. Shapes and energies (in eV) of HOMOs and LUMOs wavefunctions calculated at B3LYP/6–31G(d) level

LUMO+4 ($j^* = 5$)	 $\varepsilon_5 = \varepsilon(\pi^*_{2y}) = 1.82$	HOMO ($j = 1$)	 $\varepsilon_1 = \varepsilon(\pi_{2y}) = –6.52$
LUMO+3 ($j^* = 4$)	 $\varepsilon_4 = \varepsilon(\pi^*_{2x}) = 1.66$	HOMO–1 ($j = 2$)	 $\varepsilon_2 = \varepsilon(\pi_{2x}) = –6.59$
LUMO+2 ($j^* = 3$)	 $\varepsilon_3 = \varepsilon(\pi^*_{1y}) = 0.89$	HOMO–2 ($j = 3$)	 $\varepsilon_3 = \varepsilon(\pi) = –6.78$
LUMO+1 ($j^* = 2$)	 $\varepsilon_2 = \varepsilon(\pi^*_{1x}) = 0.82$	HOMO–3 ($j = 4$)	 $\varepsilon_4 = \varepsilon(\pi_{1y}) = –6.81$
LUMO ($j^* = 1$)	 $\varepsilon_1 = \varepsilon(\pi^*) = 0.57$	HOMO–4 ($j = 5$)	 $\varepsilon_5 = \varepsilon(\pi_{1x}) = –6.98$

program suite [48]. Energies of five LUMOs ($j^* = 1(\pi^*), 2(\pi^*_{1x}), 3(\pi^*_{1y}), 4(\pi^*_{2x}), 5(\pi^*_{2y})$) and five HOMOs ($j = 1(\pi_{2y}), 2(\pi_{2x}), 3(\pi), 4(\pi_{1y}), 5(\pi_{1x})$) are represented in Table 1. Just these MOs can be referred to the working MOs. Energies of rest MOs are separated from the noted MOs by more than 1 eV. Since they can give only minor contribution in the charge transmission process, then we take into consideration only the states related to the π–electrons.

As far as the π–bonds are separated by the chains of σ–bonds (associated with the bridging carbon atoms) then one has to expect a linear shift of the MO's energy $\varepsilon_j(V)$ on voltage bias V. Such shift can be characterized by specific local division factor η_j. [For the first time, a similar factor has been introduced for short symmetric molecules embedded between the identical electrodes. A good agreement with experimental data has been achieved at $\eta = 0.5$. It has been shown later [49, 50] that introduction of a division factor

η allows one to describe the rectifying properties even rather complicated asymmetric molecule if only a given molecule contains a single fixed site of localization for the transferred electron/hole.] For the TMSA molecule with three sites of electron localization we introduce three local voltage division factors for the MOs: $\eta(\pi_{1x}) = \eta(\pi_{1y}) = \eta(\pi^*_{1x}) = \eta(\pi^*_{1y}) \equiv \eta_{\mathrm{I}}$, $\eta(\pi_{2x}) = \eta(\pi_{2y}) = \eta(\pi^*_{2x}) = \eta(\pi^*_{2y}) \equiv \eta_{\mathrm{II}}$ and $\eta(\pi) = \eta(\pi^*) \equiv \eta_{\mathrm{III}}$ where

$$\eta_n =\equiv l_n/l, (n = \mathrm{I, II, III}). \tag{16}$$

In Eq. (16), the indexes $n = \mathrm{I}$ and $n = \mathrm{II}$ indicate, respectively, the first and the second triple bonds whereas the $n = \mathrm{III}$ refers to the double bond, Fig. 1. Each length l_n fixes a distance of the corresponding nth bond with respect to the substrate surface; quantity $l = l_{\mathrm{III}} + l_{\mathrm{T}}$ is the distance between the substrate surface and the tip. In line with Fig. 1, the division factors are estimated as $\eta_{\mathrm{I}} \approx 0.20 - 0.25$, $\eta_{\mathrm{II}} \approx 0.50 - 0.55$ and $\eta_{\mathrm{III}} \approx 0.75 - 0.85$. Precise value depends on conformation of the molecule in the monolayer as well as a distance l_T of the tip from the molecule. With introduction of division factors, a voltage dependence of the energy of the $\lambda(= j, j^*)$th MO reads as (the substrate is supposed to be grounded)

$$\varepsilon_\lambda(V) = \varepsilon_\lambda - |e|V\eta_\lambda. \tag{17}$$

In Eq. (17), ε_λ is the MO's energy at zero voltage bias. As to the quantity η_λ, it coincides with one of the division factors defined in the Eq. (16).

For the subsequent analysis, we assume that in the experimentally fixed voltage region [–1.9 V, +1.9 V], formation of the tunnel current is largely achieved by a participation of six molecular states. One of them is the ground state $|0\rangle \equiv |M(N = N_G)\rangle$ corresponding a charge – neutral molecule with energy E_0 (N_G is the number of electrons in the charge - neutral molecule). There are two types of the rest five molecular states. Both are associated with the charged molecule. If a molecule is negatively charged then an extra electron with spin projection σ can occupy one of five j^*th LUMOs. Therefore, we denote respective molecular states as $|j^*\sigma\rangle \equiv |M(N = N_G + 1)\rangle$. Another type of five molecular states refers to positively charged molecule so that molecular states $|j\sigma\rangle \equiv |M(N = N_G - 1)\rangle$ indicate the absence of an electron (presence of the hole) at the jth HOMO. Energies of the negatively and positively charged molecule are denoted through $E^{(-)}_{j^*}$ and $E^{(+)}_j$, respectively. When a molecule is embedded between the leads, its energies are modified. To specify the corresponding additions let note that in the basic expression for the self-energy, Eq. (11), the matrix elements are $V_{M''(N_G+1);r\mathrm{k}\sigma M(N_G)} = \beta_{j^*;r\mathrm{k}}$ and $V_{r\mathrm{k}\sigma M''(N_G-1);M(N_G)} = \beta^*_{j;r\mathrm{k}}$ where $\beta_{\lambda,r\mathrm{k}}$ is the coupling of the $\lambda(= j, j^*)$th MO to the kth band state of the rth electrode. Bearing this fact into consideration and using the Eq. (11) at $N = N_G + 1$ and $N = N_G - 1$, in line with the Eq. (15) one derives $\Gamma_\lambda = \Gamma^{(L)}_\lambda + \Gamma^{(R)}_\lambda$ where quantity

$$\Gamma^{(r)}_\lambda = 2\pi \sum_{\mathrm{k}} |\beta_{\lambda;r\mathrm{k}}|^2 \delta(E - E_{r\mathrm{k}}) \tag{18}$$

is the so called width parameter. It has been earlier shown [28] that if the leads are fabricated from the noble metals (as in our case), then the quantities like $\Gamma^{(r)}_\lambda$ can be chosen as independent of the energy E. As a result, the analysis of $I - V$ characteristics can be performed with the effective molecular Hamiltonian (13) written in the form

$$H^{(eff)}_m = E_0|0\rangle\langle 0| + \sum_{j^*\sigma} \varepsilon^{(-)}_{j^*}|j^*\sigma\rangle\langle j^*\sigma| + \sum_{j\sigma} \varepsilon^{(+)}_j |j\sigma\rangle\langle j\sigma| \tag{19}$$

where $\varepsilon^{(-)}_{j^*} = \varepsilon^{(-)}_{j^*} - (i/2)\Gamma_{j^*}$ and $\varepsilon^{(+)}_j = \varepsilon^{(+)}_j - (i/2)\Gamma_j$.

As in the Landauer–Büttiker approach, we assume that during the tunnel charge transmission, the molecule does not change its ground state $|M(N_G)\rangle \equiv |0\rangle$. This means that in Eq. (5), only the elastic channel $N = N_G$ with $P_{M(N_G)} \equiv P_0 \approx 1$, $P_{M(N_G\,\pm\,1)} \equiv P_{j(j^*)} \approx 0$ is responsible for a current formation. Thus, $I \approx |e|(Q_{L0\to R0} - Q_{R0\to L0})$. Calculation of a distant transfer rates $Q_{L0\to R0}$ and $Q_{R0\to L0}$ (with use of the Eqs. (7), (8) and (19) yields

$$I = \frac{|e|}{\pi\hbar}\left[\sum_{j*}\int_{\Delta E^{(L)}_{-j*}}^{\Delta E^{(R)}_{-j*}} dE T_{j^*}(E) + \sum_{j}\int_{\Delta E^{(R)}_{+j}}^{\Delta E^{(L)}_{+j}} dE T_j(E)\right] \tag{20}$$

where

$$T_{j*}(E) = \frac{\Gamma^{(L)}_{j*}\Gamma^{(R)}_{j*}}{E^2 + (1/4)(\Gamma^{(L)}_{j*} + \Gamma^{(R)}_{j*})^2} \tag{21}$$

and

$$T_j(E) = \frac{\Gamma^{(L)}_{j}\Gamma^{(R)}_{j}}{E^2 + (1/4)(\Gamma^{(L)}_{j} + \Gamma^{(R)}_{j})^2} \tag{22}$$

are the transmission functions. These functions characterize the tunnel electron and the tunnel hole transfer with participation of virtual LUMO– and HOMO–levels, respectively.

Expressions (20)–(22) can be employed for the analysis of $I - V$ characteristics of different types of linear molecules if only the localization of an electron density at their MOs is not destroyed by a voltage bias. For such molecules, a voltage dependence of the current is completely concentrated in the transmission gaps $\Delta E^{(r)}_{-j^*} = E^{(-)}_{j^*} - (E_0 + \mu_r)$ and $\Delta E^{(r)}_{+j} = (E^{(+)}_{j} + \mu_r) - E_0$. Since $E^{(-)}_{j^*} - E_0 \simeq \varepsilon_{j^*}(V)$ and $E^{(+)}_{j} - E_0 \simeq -\varepsilon_j(V)$, then in line with the Eq. (17) one derives

$$\begin{aligned} \Delta E^{(r)}_{-j^*} &= \Delta E_{-j^*} - |e|V\eta_{j^*} + (E_F - \mu_r), \\ \Delta E^{(r)}_{+j} &= \Delta E_{+j} + |e|V\eta_j - (E_F - \mu_r). \end{aligned} \tag{23}$$

Quantities $\Delta E_{-j^*} = \varepsilon_{j^*} - E_F$ and $\Delta E_{+j} = E_F - \varepsilon_j$ refer to the unbiased electron and hole transmission gaps, respectively. Actual voltage shift of transmission gaps follows from the Eq. (23) at $\mu_L = E_F$ and $\mu_R = E_F - |e|V$ (left electrode is grounded).

4. Results and Discussion

To specify the character of the tunnel charge transmission in the TMSA molecule, let note that quantum–chemical methods predict well both a molecular geometry and a charge distribution within a molecule but these methods do not give an exact energy position neither of MO–levels [51] nor of Fermi–level[19]. Therefore, in accordance with quantum-chemical results represented in Table 1 we can only know mutual positions of the MOs levels. Table 1 indicates that energy gap between LUMO– and HOMO–levels of the TMSA molecule exceeds 7 eV. Therefore, in a given voltage region [−1.9 V, +1.9 V] either only LUMO–levels or only HOMO–levels can be, really, responsible for the formation of an interelectrode current. Quantum–chemical calculations give different estimations of Fermi energy E_F of bulk gold from –6 eV up to –10 eV [19, 52] and of gold cluster about –5.2 eV

Table 2. Energy and transport characteristics of TMSA molecule.

MO, j	Energy gap, ΔE_{+j} (in eV)	Local voltage division factor, η_j	Width parameters $\Gamma_j^{(L)}$ (in eV)	Width parameters $\Gamma_j^{(R)}$ (in eV)
1	1.14	0.52	$2.2 \cdot 10^{-3}$	$1.7 \cdot 10^{-3}$
2	1.21	0.52	$2.2 \cdot 10^{-3}$	$1.7 \cdot 10^{-3}$
3	1.40	0.81	3.10^{-6}	$1.1 \cdot 10^{-1}$
4	1.43	0.22	4.10^{-1}	$3.6 \cdot 10^{-6}$
5	1.60	0.22	4.10^{-1}	$3.6 \cdot 10^{-6}$

[53, 54]. This means that in the case of the TMSA, the Fermi–level is expected to be closer to the HOMO level than to the LUMO one. As such the working MOs are associated with five HOMOs so that in the TMSA molecule, a current formation is associated with the hole tunneling. For calculation of the tunnel current one can employ the expression

$$I = \frac{|e|}{\pi\hbar}\sum_{j=1}^{5}\int_{\Delta E_{+j}-|e|V(1-\eta_j)}^{\Delta E_{+j}+|e|V\eta_j} dET_j(E) \tag{24}$$

where transmission function $T_j(E)$ is given by the Eq. (22). Calculation of the integral leads to analytic expressions

$$I = I_0\sum_{j=1}^{5}\frac{\Gamma_j^{(L)}\Gamma_j^{(R)}}{\Gamma_j^{(L)}+\Gamma_j^{(R)}}[\tan^{-1}(\frac{2(\Delta E_{+j}+|e|V\eta_j)}{\Gamma_j^{(L)}+\Gamma_j^{(R)}}) - \\ -\tan^{-1}(\frac{2(\Delta E_{+j}-|e|V(1-\eta_j))}{\Gamma_j^{(L)}+\Gamma_j^{(R)}})] \tag{25}$$

and

$$g = dI/dV = g_0\sum_{j=1}^{5}[\eta_j T_j(\Delta E_{+j}+|e|V\eta_j) + \\ +(1-\eta_j)T_j(\Delta E_{+j}-|e|V(1-\eta_j))]. \tag{26}$$

for the tunnel current and the conductance, respectively. [$I_0 = |e|/\pi\hbar \times 1eV \approx 77.6\ \mu$A is the current unit and $g_0 = e^2/\pi\hbar \approx 7.76 \times 10^{-5}$ Sm is the conductance unit.] Voltage dependence of quantities, $I = I(V)$ and $g = g(V)$ is defined through the local voltage division factors $\eta_1 = \eta_2 = \eta_{\mathrm{I}}$, $\eta_3 = \eta_{\mathrm{III}}$ and $\eta_4 = \eta_5 = \eta_{\mathrm{II}}$ associated with those of the Eq. (16) and the Table 2.

In the following, we employ Eqs.(25) and (26) to analyze the dependence of current and conductance on the applied voltage. Results and comparison with experiment are shown Fig. 3. To provide the description one has to know the width parameters $\Gamma_j^{(L)}$ and $\Gamma_j^{(R)}$, and energy gaps ΔE_{+j}. Parameters $\Gamma_j^{(L)}$ can be estimated with the standard expression [19]

$$\Gamma_j^{(L)} = 2\pi|V_{\mathrm{Au}-j}|^2\rho_{\mathrm{Au}} \tag{27}$$

where ρ_{Au} is the metallic density of states and $V_{\mathrm{Au}-j}$ is the effective matrix element between the jth working MO and the s-state of the surface Au atom. Theory establishes that if two sites of electron localization are connected by the N covalent bonds then a superexchange coupling between the sites decreases proportionally to the factor $(\zeta_{bond})^N$ where parameter $\zeta_{bond} \approx 0.6$ indicates an average drop of a coupling per a single covalent bond [59]. The analysis of $I - V$ characteristics of Au– alkanethiol –Au junctions shows [29] that the drop of the current is proportional to the factor $exp(-\beta N)$ where $\beta \approx 0.95 - 1.0$ is the voltage independent decrease parameter and N is the number of carbon atoms in the alkane chains. One can see that again $\zeta_{bond} = exp(-\beta/2) \approx 0.61$. In our case, a superexchange coupling can be estimated in line with the expression

$$V_{\mathrm{Au}-j} \approx V_{\mathrm{Au-Si}} \times (\zeta_{bond})^{N_j} \tag{28}$$

where $V_{\mathrm{Au-Si}}$ is the Au–Si coupling and N_j is the number of C–C bonds between the Si atom and the triple or double bonds corresponding the localized working jth HOMO. The wave function of the terminal Si atom has a rather good overlap with the s–wave function of the surface Au atom. Therefore, the $V_{\mathrm{Au-Si}}$ can consequently be chosen as an order of value of (1.2–1.8) eV. The quantities $\Gamma_4^{(L)} \simeq \Gamma_5^{(L)}$ are the greatest among the width parameters. This is dictated by the fact that the first triple bond is directly connected with the terminal Si atom (see a distribution of electron density over the molecule, Table 1). Setting $N_4 = N_5 = 1$ and using ρ_{Au} =0.07/eV [19, 60], we obtain $\Gamma_4^{(L)} \simeq \Gamma_5^{(L)}$ = (0.3–0.5) eV from Eq. (27). Note that similar value for the width parameters is often used for calculation of the current in different types of molecular junctions (see, for instance, the examples in refs. [43, 55, 56]).

Using the Eqs. (27) and (28) one arrives to expression

$$\Gamma_j^{(L)} = \Gamma_{4(5)}^{(L)} \times (\zeta_{bond})^{2N_{j-I}} \tag{29}$$

allowing one to estimate rest parameters via fixation of the number $N_{j-\mathrm{I}}$ of C–C bonds connecting the first triple bond with the second triple bond or the double bond. In the case of HOMO ($j = 1$) and HOMO–1 ($j = 2$), five covalent C–C bonds connect the first and the second triple bonds so that $N_{1-\mathrm{I}} = N_{2-\mathrm{I}} = 5$. It gives $\Gamma_1^{(L)} \simeq \Gamma_2^{(L)} = (1.7\text{–}2.9)\cdot 10^{-3}$eV. In the case of HOMO–2 ($j = 3$), the first triple bond is connected with the double bond by eleven C–C bonds. Setting $N_{3-\mathrm{I}} = 11$ one derives $\Gamma_3^{(L)} = (3.4\text{–}5.7)\cdot 10^{-6}$ eV.

Estimating the width parameters $\Gamma_j^{(R)}$ is a much more difficult problem because of the absence of a direct contact between TMSA and the tip, and because of the presence of a nonuniform electric field in between the molecule and the tip. It is only possible to state that $\Gamma_3^{(R)} < \Gamma_{4(5)}^{(L)}$. For further we set $\Gamma_3^{(R)} \approx 0.1$ eV. To estimate rest width parameters associated with interaction of the molecule with the right lead, we use the expression

$$\Gamma_j^{(R)} = \Gamma_3^{(R)} \times (\zeta_{bond})^{2N_{j-\mathrm{III}}} \tag{30}$$

where $N_{j-\mathrm{III}}$ is the number of C–C bonds between the double bond (the third site of electron localization in the TMSA) and the bonds corresponding the jth MOs. Taking the $N_{1-\mathrm{III}} = N_{2-\mathrm{III}} = 4$ and $N_{4-\mathrm{III}} = N_{5-\mathrm{III}} = 10$ one obtains $\Gamma_1^{(R)} \simeq \Gamma_2^{(R)} = 1.7\cdot 10^{-3}$eV and $\Gamma_4^{(R)} \simeq \Gamma_5^{(R)} = 3.6\cdot 10^{-6}$eV, respectively. The above-mentioned values are only rough estimations of the width parameters. The actual values of $\Gamma_j^{(L)}$ and $\Gamma_j^{(R)}$ can be bigger or smaller but they do not differ by more than one order of magnitude from the tentative width parameters.

To estimate the unbiased transmission gaps $\Delta E_{+j} \approx E_F - \varepsilon_j$, let remind that quantum–chemical methods do not give an exact energy position of MO–levels and Fermi–level. Nevertheless, these methods allow one to know mutual positions of the MOs levels. To this end, we use the following relation between the gaps

$$\Delta E_{+j'} = \Delta E_{+j} + \varepsilon_j - \varepsilon_{j'}. \qquad (31)$$

Setting in this relation one of the gap as a semi-phenomenological parameter, we can estimate all working transmission gaps [61] (cf. Table 2).

Above estimations allow us to specify the parameters in the Eqs.(25) and (26). Fig. 3 manifests a quite good correspondence of theory to experimental results on interelectrode current $I = I(V)$ and conductance $g = g(V)$. Table 2 accumulates the parameters which are used to obtain theoretical curves in Fig. 3. [In the calculations, we use the mean of each division factor.]

5. Conclusion

We describe a conductivity of a linear molecule where LUMO– and HOMO–levels correspond to the localized π^*– and π–electrons and where the triple and double bonds are well separated by covalent carbon-carbon bonds. Quantum–mechanical calculations show that the main contribution in formation of charge transmission through the TMSA molecule belongs to the HOMO, HOMO–1, . . . , and HOMO–4. Therefore, a current formation can be interpreted as a hole tunneling with participation of the noted five HOMOs. These HOMOs can be referred to the working MOs of the TMSA. The carbon atoms form superexchange couplings between the π–electrons located mainly at the triple and double bonds. However, in the TMSA molecule, superexchange couplings are too weak to form the extended π–MOs. Therefore, the conductivity in TMSA molecule is mainly determined by its localized MO's levels broadened by an interaction with the substrate and the tip. It is important to note that the shift of the MO–levels caused by the applied voltage, is determined by three strongly determined voltage division factors, Eq. (16). The latter are completely associated with the position of triple and double bonds with respect to the substrate surface. The biased shifts of the localized MO–levels as well as a long–range coupling between the localized MOs distinguishes the conductivity of a polyunsaturated but non-conjugated TMSA molecule as compared to the molecules having the extended MOs. [In the molecules having the extended MOs, the only division factor is usually used to characterize level shifts (see, as an example, ref. [19]).] Weak interaction between the sites of electron localization allow us to reduce complicated theoretical expressions to simple analytical form for the current, Eq. (25) and the conductance, Eq. (26). Both forms contain identical set of parameters. The advantage of the theory is that despite a charge transmission through each jth MO–level is characterized by four parameters (among them the division factor η_j, the transmission gap ΔE_{+j}, and the width parameters $\Gamma_j^{(L)}$ and $\Gamma_j^{(R)}$) so that twenty parameters describe the transmission through five working MOs, only three semi–phenomenological parameters (ΔE_{+1}, $\Gamma_{4(5)}^{(L)}$ and $\Gamma_3^{(R)}$) can be chosen as independent fitting parameters. This is explained by the fact that along with general formulae describing the dependence of tunnel current and conductance on a voltage bias, we use additional analytic expressions allowing us to estimate the theoretical parameters. For instance, the fixation of the TMSA in the layer deposed on the substrate, determines the position of the triple and double bonds with respect to the substrate surface and, thus, the division factors become specified (via the relation (16)). The number of covalent bonds connecting the triple and double bonds allows us to estimate the width parameters formed owing to the superexchange couplings between the π–MOs (cf. Eqs. (29) and (30)). As to the transmission gaps, they are estimated with use of relation Eq. (31) and the data of quantum-chemical calculations represented in Table 1.

Semi-phenomenological approach employed in the present paper, can be useful for the analysis of $I-V$ characteristics and the conductance of various linear molecules containing the localized π–bonds.

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