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Formation of the current through a molecule with two terminal groups is studied on the assumption that these groups exhibit themselves as donor and acceptor sites with respect to the electrodes. It is shown that the hopping and tunnel charge transfer mechanisms are generally responsible for the current formation, but the efficiency of a tunnel charge transmission is controlled by a hopping one via a molecular charging. An analytic expression for the current is derived, and the experimental data are explained. It is shown that, in the pre-resonant voltage region, even the simplest single-level version of the theory can describe the experiment with a rather good accuracy.

Keywords: interelectrode current; kinetic equations; molecular charging

PACS: 05.20.Dd 05.60. + w

I. INTRODUCTION

At present, two theoretical approaches are largely employed to describe the current-voltage (I–V) characteristics of single molecules and molecular wires. One of them is based on the nonequilibrium Green's function formalism [1–6], another uses the nonequilibrium density matrix method [7–9]. But, independently of a precise theoretical method, one has to have the appropriated physical model which allows one to understand the experimental results. One of such models

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supposes that the terminal groups of a single molecule or molecular wire exhibit themselves as an intermediate donor (D) unit and an intermediate acceptor (A) unit. Originally, the D-A model of charge transmission through a molecule has been proposed by Aviram and Ratner [10] to understand the rectification properties of organic molecules. Later on, a similar model has been used by Metzger *et al.* [11–13] to explain the current asymmetry in organic molecules containing the D and A centers. A theoretical description of the electron transmission through the system "D-bridge-A" embedded between the metallic electrodes can be found in Refs. [14–16], where the hopping mechanism of charge transfer has been considered. However, it is well known that, apart from the hopping transfer, a molecular structure can mediate the tunnel transmission as well. A goal of the present work is to describe the charge transmission through a linear molecule with a certain number of sites of electron localization, taking into account both the hopping and tunnel routes. To this end, we use the density matrix method allowing us to provide a unified description of the elastic and inelastic charge transfer processes in single molecules [8,9,17,18]. We derive an analytic expression for the current through a molecule with two terminal units. It is assumed that the internal molecular units exhibit themselves as a bridging system responsible for the formation of both superexchange and sequential (hopping) routes during the charge transmission from one terminal unit to another one.

II. MODEL AND THEORY

Let a linear molecule with N regularly positioned interior sites and two terminal sites be embedded between metallic electrodes (see Fig. 1). The energy structure of such a molecule is presented in Figure 2. We restrict ourselves by consideration of the nonadiabatic electron transfer (ET) under conditions when the interior sites play the role of a bridging structure. This means that the energy levels of the lowest unoccupied molecular orbitals (LUMOs) of these units are separated by large energy gaps from similar levels belonging to the terminal units. Therefore, the interior LUMOs are not practically occupied during a charge transmission. In contrast, the LUMOs belonging to the terminal units can be occupied by the transferred electrons. Thus, the terminal units exhibit themselves as the donor (D) and the acceptor (A) with respect to the electrodes. Similar model has been already employed to describe an inelastic (hopping) mechanism of current formation [14,15]. The main result is that the D and A centers are coupled by a superexchange interaction caused by interior bridging units. As to the model under consideration, it is assumed that each

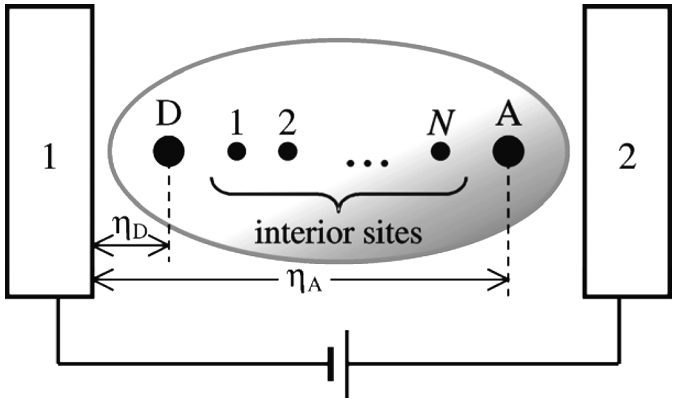

FIGURE 1 Molecule with N interior and two terminal units (D and A) is embedded between the electrodes. η_D and η_A are the normalized distances of the center of gravity for the electronic densities localized within the respective terminal units.

terminal unit is coupled to the electrodes either directly (contact with an adjacent electrode) or through the bridging structure (contact with a distant electrode). In addition, both the terminal sites along with bridging sites form direct electrode-electrode couplings responsible for a tunnel route, where the LUMOs and HOMOs exhibit themselves as virtual states. [In Fig. 2b, the D-A superexchange couplings are denoted via $V_{DA}^{(L)}$ and $V_{DA}^{(H)}$, respectively.] Thus, the current through a molecule is associated with the electrode-molecule charge hopping as well as with the direct tunneling. We consider a case where two frontier molecular orbitals (MOs) participate in the current formation. One orbital (HOMO) belongs to the D unit, and another one (LUMO) is referred to the A unit (Aviram-Ratner model [10]). Such a case is realized for slightly polarized molecules [11–13].

The current is calculated on the base of the general expression

$$I = e\dot{N}_1(t), \tag{1}$$

where $e<0$ denotes the electron charge and $\dot{N}_1(t) = -\dot{N}_2(t)$ is the time-derivative of the number of electrons present at the left (right) electrode. Following the approach developed in Ref. [9], we get the equation for $\dot{N}_1(t)$, as well for molecular occupancies *P(M)*. In the case of the transmission through frontier MOs, only three molecular charge states mediate the transfer process. These states are M_0 (molecule is in the ground (charge neutral) state), M^- (molecule is singly reduced), and M^+ (molecule is singly oxidized). [Here, we ignore the role of

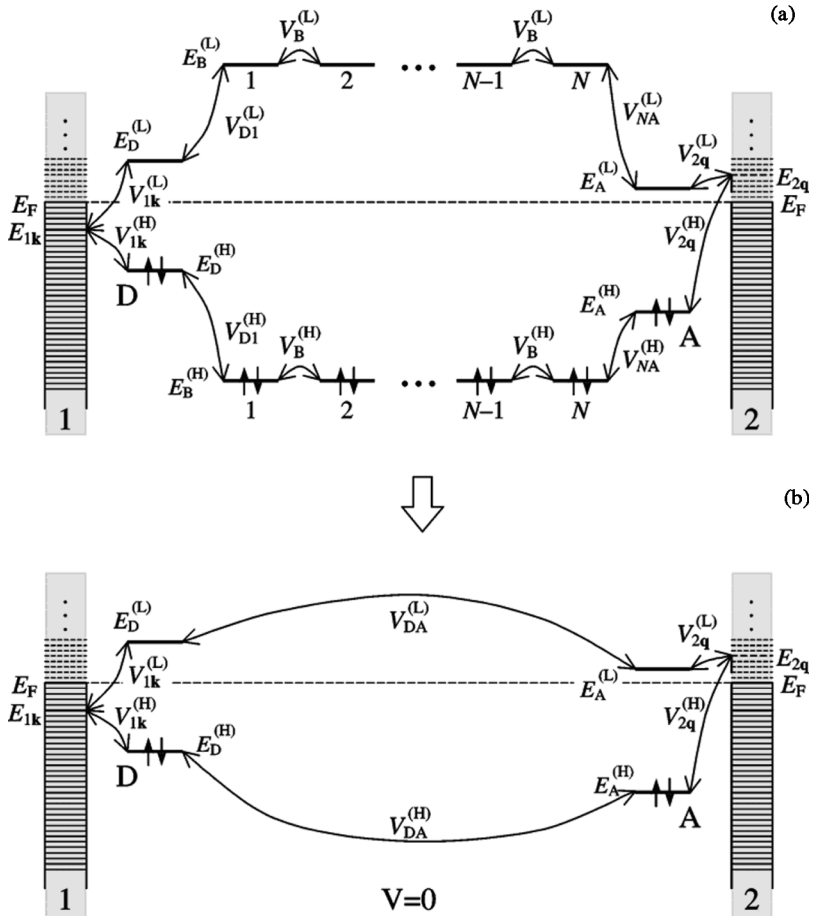

FIGURE 2 Energy scheme of a linear molecule with N interior and two terminal sites. Only the levels corresponding the frontier MOs (LUMO and HOMO) are presented along with respective intersite couplings $V_r^{(j)}(j = L, H,$ $r = D1,\ B,\ NA)$ as well as with the electrode-molecule couplings $V_{1\mathbf{k}}^{(j)}$ and $V_{2\mathbf{q}}^{(j)}$ (a). Due to a negligible population of the interior LUMOs and due to a deep energy position of the interior HOMOs, two distant superexchange couplings, $V_{DA}^{(L)}$ and $V_{DA}^{(L)}$, are formed between the terminal sites. This allows us to describe a transfer process in the framework of simplified scheme (b).

excited molecular states in the transmission process.] The derivation of the evolution equation for the $\dot{N}_1(t)$ yields $\dot{N}_1(t) = \dot{N}_{1tun}(t) + \dot{N}_{1hop}(t)$. The first term

$$\dot{N}_{1tun}(t) = -2[Q_{12}^{(L)}(P(M_0) + 2P(M^-)) + Q_{12}^{(H)}(P(M_0) + 2P(M^+))] \quad (2)$$

is associated with a tunnel electron transmission, whereas the second term

$$\dot{N}_{1hop}(t) = -2[\chi_1^{(L)}P(M_0) + \chi_1^{(H)}P(M^+) - \chi_{-1}^{(L)}P(M^-) - \chi_{-1}^{(H)}P(M_0)] \quad (3)$$

reflects a hopping route for the transferred electrons. In Eq. (2), the quantities $Q_{12}^{(L)}$ and $Q_{12}^{(H)}$ denote the net electron flows through the LUMO and the HOMO. [Transmission along the channels associated with a charge-neutral but excited molecular state is ignored.] The derivation of the analytic form for the net flows can be found in Refs. [9,17]. In the case under consideration, this form reads

$$Q_{12}^{(v)} = \pm\frac{1}{\pi\hbar}\frac{\Gamma_1^{(v)}\Gamma_2^{(v)}}{\Gamma_1^{(v)} + \Gamma_2^{(v)}}\Phi^{(v)}(V), \quad (4)$$

where the signs + and − refer to the channels attributed to the LUMO and the HOMO, respectively. The voltage dependence of each flow is concentrated in the function

$$\Phi^{(v)}(V) = \arctan\left(\frac{2\Delta E_2^{(v)}(V)}{\Gamma_1^{(v)} + \Gamma_2^{(v)}}\right) - \arctan\left(\frac{2\Delta E_1^{(v)}(V)}{\Gamma_1^{(v)} + \Gamma_2^{(v)}}\right), \quad (5)$$

through the voltage dependent gaps $\Delta E_1^{(v)}(V)$ and $\Delta E_2^{(v)}(V)$. [Generally, the width parameters $\Gamma_1^{(v)}$ and $\Gamma_2^{(v)}$ are also voltage dependent functions. But, the main voltage behavior of the flow is controlled by the level shifts. Therefore, we consider the effects resulted only from an alteration of the gaps.]

The transmission gaps are defined as $\Delta E_r^{(L)} = E(M^-) - (E(M_0) + \mu_r)$ and $\Delta E_r^{(H)} = (E(M^+) + \mu_r) - E(M_0)$, where $E(M_0), E(M^-)$, and $E(M^+)$ are the electronic energies of the molecule. In the model under consideration, the LUMO and the HOMO are attributed to the A- and D-sites, respectively (cf. Fig. 2). We can introduce, thus, the voltage division factors $\eta_L = \eta_A$ and $\eta_H = \eta_D$ (cf. Fig. 1) characterizing, respectively, the LUMO-level shift and the HOMO-level shift. This yields

$$\Delta E_r^{(j)}(V) = \Delta E^{(j)}(0) + eV\eta_j - \mu_r, \quad (j = L, H; r = 1, 2). \quad (6)$$

In Eq. (6), $\Delta E^{(L)}(0) > 0$ is the unbiased gap between the LUMO-level and the Fermi-level of the electrode, while the gap $\Delta E^{(H)}(0) > 0$ characterizes the energy difference between the Fermi-level and the HOMO-level.

Form (4) for the net flow has been derived in the wide-band approximation which is quite appropriate for the analysis of current-voltage characteristics. In the same approximation, the hopping rates appear

as (cf. also Refs. [8,9])

$$\chi_r^{(L)} = \frac{1}{\hbar}\Gamma_r^{(L)} n(\Delta E_r^{(L)}(V)), \quad \chi_{-r}^{(L)} = \frac{1}{\hbar}\Gamma_r^{(L)}(1 - n(\Delta E_r^{(L)}(V))),$$
$$\chi_r^{(H)} = \frac{1}{\hbar}\Gamma_r^{(H)}(1 - n(\Delta E_r^{(H)}(V))), \quad \chi_{-r}^{(H)} = \frac{1}{\hbar}\Gamma_r^{(H)} n(\Delta E_r^{(H)}(V)), \qquad (7)$$

where the voltage dependence is concentrated in the distribution function

$$n(\Delta E_r^{(v)}(V)) = \frac{1}{\exp[\Delta E_r^{(v)}(V)/k_B T] + 1}. \qquad (8)$$

In line with Eqs. (2) and (3), each transmission channel is switched on with a definite probability associated with the molecular occupancies $P(M)$ ($M = M_0$, M^-, M^+). Using the approach developed in Refs. [9,19], we obtain the following system of kinetic equations for the desirable molecular occupancies

$$\dot{P}(M_0) = -2(B_L + A_H)P(M_0) + 2B_H P(M^+) + 2A_L P(M^-),$$
$$\dot{P}(M^-) = -A_L P(M^-) + B_L P(M_0),$$
$$\dot{P}(M^+) = -B_H P(M^+) + A_H P(M_0), \qquad (9)$$

where

$$A_L = \sum_{r=1,2} \Gamma_r^{(L)}(1 - n(\Delta E_r^{(L)}(V))), \quad B_L = \sum_{r=1,2} \Gamma_r^{(L)} n(\Delta E_r^{(L)}(V)),$$
$$A_H = \sum_{r=1,2} \Gamma_r^{(H)} n(\Delta E_r^{(H)}(V)), \quad B_H = \sum_{r=1,2} \Gamma_r^{(H)}(1 - n(\Delta E_r^{(H)}(V))). \qquad (10)$$

III. RESULTS AND DISCUSSION

The above-derived expressions for the flows and the hopping rates allow us to present the inter-electrode current in the following analytic form:

$$I = I_{dir} + I_{hop},$$
$$I_{dir} = 2I_0 \frac{\Gamma_1^{(L)}\Gamma_2^{(L)}}{\Gamma_1^{(L)} + \Gamma_2^{(L)}} \Phi^{(L)}(V)(P(M_0) + 2P(M^-))$$
$$- 2I_0 \frac{\Gamma_1^{(H)}\Gamma_2^{(H)}}{\Gamma_1^{(H)} + \Gamma_2^{(H)}} \Phi^{(H)}(V)(P(M_0) + 2P(M^+)),$$
$$I_{hop} = 2\pi I_0 \Gamma_1^{(L)}[n(\Delta E_1^{(L)}(V))P(M_0) - (1 - n(\Delta E_1^{(L)}(V)))P(M^-)]$$
$$- 2\pi I_0 \Gamma_1^{(H)}[n(\Delta E_1^{(H)}(V))P(M_0) - (1 - n(\Delta E_1^{(H)}(V)))P(M^+)]. \qquad (11)$$

[In Eq. (11), $I_0 = |e|/\pi\hbar \times 1eV \approx 80\,\mu\text{A}$ is the current unit.]

We restrict our consideration by the stationary case where the molecular occupancies become time independent. Therefore, setting $\dot{P}(M_0) = \dot{P}(M^-) = \dot{P}(M^+) = 0$ and solving system (9) with the use of the normalization condition $P(M_0) + 2P(M^-) + 2P(M^+) = 1$, we derive

$$P(M_0) = A_L B_H / D, \quad P(M^-) = B_L B_H / D, \quad P(M^+) = A_L A_H / D,$$
$$D = 2A_L A_H + B_L B_H + A_L B_H. \tag{12}$$

The current components I_{dir} and I_{hop} are associated with the tunnel and sequential (hopping) routes. Each route includes two electronic pathways referred to the frontier MOs. Despite the fact that the real transmission is related to an electron transfer, the pathway through the HOMO appears as a transmission of the positive charge (hole). [Note the sign – before the corresponding partial term.] It follows from the form of the I_{dir} that a tunnel current component is controlled by a sequential transmission process via the alteration of molecular occupancies $P(M_0), P(M^-)$, and $P(M^+)$. The occupancies are defined by Eq. (12) depending, thus, on the width parameters $\Gamma_r^{(j)}$ and the transmission gaps $\Delta E_r^{(j)}(V), (j = L,\ H;\ r = 1, 2)$. In fact, the hopping charge transfer process governs the tunneling process charging and recharging the molecule during a charge hopping. Such a kinetic control can be especially significant at the resonant transmission of electrons/holes. Figure 3 shows the sequential and tunnel charge routes with the participation of frontier MOs belonging to the D-site and the A-site. The case of positive voltages is presented. At $V > 0$, only two resonant regimes for a charge transmission are switched on, at $V = V_1^{(L)}$ and at $V = V_2^{(H)}$. The resonant voltages $V_r^{(j)}$ are defined from the condition $\Delta E_r^{(j)}(V) = 0$ so that, in line with Eq. (6), we get

$$V_1^{(L)} = \Delta E^{(L)}(0)/|e|\eta_L, \qquad V_2^{(H)} = \Delta E^{(H)}(0)/|e|(1 - \eta_H). \tag{13}$$

Analogously, at $V < 0$, the resonant voltages appear as

$$V_2^{(L)} = \Delta E^{(L)}(0)/|e|(1 - \eta_L), \qquad V_1^{(H)} = \Delta E^{(H)}(0)/|e|\eta_H. \tag{14}$$

In Figure 3, the case $V > 0$ is presented where a resonant charge transmission through the LUMO occurs earlier than a similar transmission through the HOMO. Before the first resonance is switched on, the occupancy of the LUMO (and thus, the A-site) by an extra (transferred) electron is minor. This means that the hopping current component I_{hop} is negligible so that the total current is associated only with the current component I_{dir}. The latter is formed owing to a tunnel pre-resonant transmission through the LUMO and the HOMO. It is illustrated by scheme (b) of Figure 3 where only a tunnel pathway between the

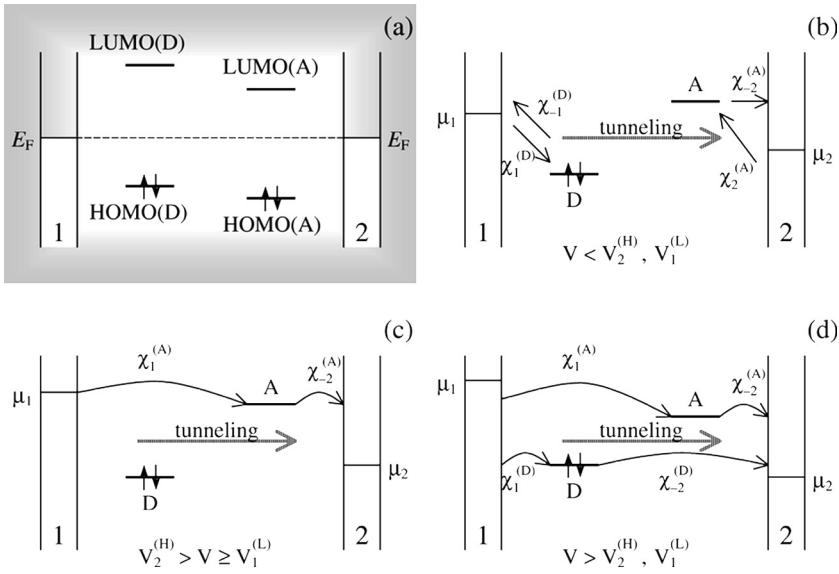

FIGURE 3 Tunnel and sequential routes in the molecule with two terminal sites D and A (a). The LUMO of the A-site and the HOMO of the D-site (Aviram-Ratner model [10]) participate in the tunnel and hopping transmission processes as the frontier MOs (b, c, d). The case of positive V is shown.

electrodes (the arrow) exists. [Hopping process does not connect the electrodes and thus does not support an interelectrode charge transfer.] Note that, in the pre-resonant voltage region, the occupancies are $P(M_0) \approx 1$, $P(M^-) \approx 0$, $P(M^+) \approx 0$. The resonant transmission starts at $V = V_1^{(L)}$. It switches on an electron hopping from electrode 1 to the A-site (transfer rate $\chi_1^{(A)}$). Now the A-site becomes really populated by the transferred electron, which then hops to electrode 2 (transfer rate $\chi_{-2}^{(A)}$). Such a sequential process forms the current component I_{hop} and, simultaneously, charges the molecule. The tunnel current component I_{dir} is formed due to a resonant electronic transmission through the LUMO as well as a pre-resonant hole transmission through the HOMO. In voltage region $V_2^{(H)} > V > V_1^{(L)}$ (scheme (c) of Fig. 3), both tunnel and hopping current components associated with the LUMO pathway achieve their saturated values, while the hopping through the HOMO remains ineffective (despite a tunneling with the participation of the HOMO increases). In the intermediate voltage region $V_2^{(H)} > V > V_1^{(L)}$, due to a kinetic charging of the molecule, one derives $P(M_0) < 1$, $P(M^-) > 0, P(M^+) \approx 0$. Switching on the second resonant transmission process is associated with the HOMO pathway at $V = V_2^{(H)}$. When

$V \geq V_2^{(H)}$, one of the electrons occupying the HOMO (i.e. the D-site) hops (transfer rate $\chi_{-2}^{(D)}$) to electrode 2 or, what is the same, the hole hops from electrode 2 to the HOMO. Afterward an electron from electrode 1 hops (transfer rate $\chi_1^{(D)}$) at the singly occupied HOMO or, what is the same, the hole hops from the HOMO to electrode 1 (cf. scheme (d) of Fig. 3). When $V \geq V_2^{(H)}$, both the hopping and tunnel components of the current associated with the HOMO pathway achieve their saturated values. Since $V_2^{(H)} > V_1^{(L)}$, a total current becomes also completely saturated in the voltage region $V \geq V_2^{(H)}$. This is due to the fact that both frontier MOs are completely involved into a transmission process. Note that, in this case, a charge state of the molecule is defined by the nonzero occupancies $P(M_0), P(M^-)$, and $P(M^+)$.

As a rule, the unbiased transmission gaps $\Delta E^{(L)}(0)$ and $\Delta E^{(H)}(0)$ differ from each other. Therefore, in a certain voltage region, only a single frontier MO can give a dominant contribution to the current formation. As an example, let us consider the current-voltage

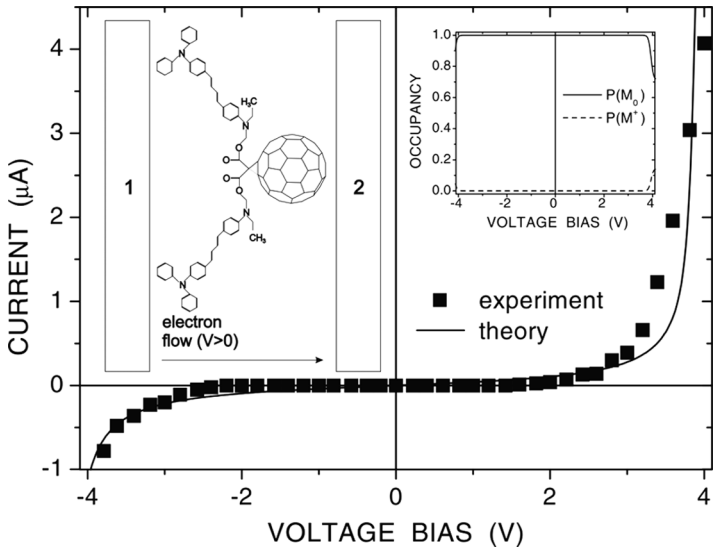

FIGURE 4 Current voltage characteristics of the monolayer of molecules $[(\phi_3\mathrm{N})-(\mathrm{CH})_4-\phi-\mathrm{N}(\mathrm{C_2H_5})\mathrm{CH_2O}-\mathrm{C(O)}]_2\mathrm{C}-\mathrm{C60}$ (insert). Experimental data are presented in the averaged form to show the smoothed behavior of the current. [The smoothing of the original data presented in Fig. 12.19a of Ref. [21].] The theoretical curve is calculated with the use of Eq. (11), where only a single pathway (along the HOMO) is taken into account. The fitting parameters are $\Delta E^{(H)}(0) = 2.05$ eV, $\eta_H = 0.48, \Gamma_1^{(H)} = 0.02$ eV, $\Gamma_2^{(H)} = 0.1$ eV.

characteristics of a rather complicated molecule $[(\phi_3\mathrm{N})-(\mathrm{CH})_4-\phi-\mathrm{N}(\mathrm{C_2H_5})\mathrm{CH_2O}-\mathrm{C(O)}]_2\mathrm{C}-\mathrm{C60}$ (Fig. 4). A monolayer of these molecules demonstrates the rectification properties in the vicinity $|V| > 4\ V$ [20, 21]. To understand the current behavior, let us note that the donor groups of the molecule are associated with two tails attached (with the participation of COO^- groups) to the fullerene. It is supposed below that the HOMO-level of the donor groups of each molecule is closer to the Fermi-level of the gold electrodes as compared with the LUMO-level of the acceptor groups. Therefore, the current is mainly determined by the transmission of charges just through the HOMO (second terms in expression (11) for I_{dir} and I_{hop}). Since the contact of the fullerene with electrode 1 is more strong in comparison to the contact of the tails with electrode 2, we can assume the validity of the inequality $\Gamma_1^{(H)} \ll \Gamma_2^{(H)}$. Figure 4 shows that the transmission through a single level gives a quite good correspondence between the theory and the experiment. The discrepancy appears only at voltages $|V| > 4\,\mathrm{V}$, when additional MOs are involved in the transmission process. [The description of the current behavior at large applied voltages is a subject of special studies].

IV. CONCLUSION

In the present paper, the Aviram-Ratner model is employed to understand the formation of the current through a molecule with two frontier MOs belonging to the terminal groups. These groups exhibit themselves as the donor and acceptor units with respect to the adjacent electrodes. In contrast with the earlier proposed scheme of description based on recharging the terminal molecular groups during the charge hopping between the molecular groups and the electrodes [10,21], we take into consideration a tunnel transmission route controlled by the molecular charging and recharging. It switches on a resonant tunneling not only between the terminal site and the adjacent electrode but between the same terminal site and a distant electrode. Thus, in line with the schemes in Figure 2, we get two resonances at positive voltages $V = V_1^{(L)}$ and $V = V_2^{(H)}$, Eq. (13), and two resonances at negative voltages $V = -V_2^{(L)}$ and $V = -V_1^{(H)}$, Eq. (14). At the same time, the above-mentioned scheme of a pure hopping description of the transmission does not suppose the resonances at $V = V_1^{(L)}$ and $V = V_2^{(H)}$. This fact can lead to strong rectification properties of the molecule if only the HOMO-level of the D-site and the LUMO-level of the A-site (cf. scheme (a) in Fig. 2) are responsible for the current formation. However, our studies show that the manner in which a

charge transmission forms an interelectrode current strongly depends not only on the precise position of molecular levels but the efficiency of both hopping and tunnel routes.

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