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Control of the Current through a Molecule: The Role of Conformation Transitions

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A model of conformation control of the current through a molecule embedded between the electrodes is proposed, and the analytic expressions for the hopping and the tunnel current components are derived for the case of two charged molecular conformations. It is shown that if one of the conformations provides the best molecule-electrode contact, and if the energy position of this conformation is higher of that for another contact conformation, then the contact conformation at the resonant regime of charge transmission governs the current formation only at slow conformation transitions.

Keywords: current-voltage characteristics; electron transmission; molecular conformations

I. INTRODUCTION

Experimental studies of conductivity of single molecules suggest that, for a given molecule, the type of molecule-electrode contacts is the most substantial factor controlling the current behavior (see, for instance, [1–5]). It has been shown that the chemical contacts provide a much more strong current through a molecule and molecular wires as compared with the physical contacts (mainly of van der Waals type). The reason is that the chemical bonds guarantee the best overlap of electron wave functions among structure groups forming an "electrode 1-molecule-electrode 2" (1M2) device. But, despite the overlap of molecular orbitals (MOs) forming σ-bonds is much more greater than that

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for π-bonds, the electron transmission along the π-bonds is much more effective. This conclusion follows from the fact that the energy of an electron (hole) occupying the empty (filled) π-MO is positioned noticeably closer to the electrode's Fermi-level. The analysis of molecular current-voltage (*I-V*) characteristics shows that the formation of a current in a 1M2-device is associated with two principally different routes. One of them supposes a single-step inter-electrode tunnel electron (hole) transfer with virtual occupation of the molecule by the transferred charges. The second route is associated with charge hopping between the molecule and the adjacent electrodes. This leads to a real occupation of empty (filled) MOs by the transferred electrons (holes) and, thus, to a molecular charging. Recent investigations show a serious influence of molecular charging on the formation of not only the inelastic hopping current component but the tunnel current component as well [6–8].

In the present communication, we show that a molecular charging can be responsible for a control over the current formation via transitions between the charged molecular conformations.

II. MODEL AND BASIC EXPRESSIONS FOR CURRENT COMPONENTS

To clarify a role of molecular conformations in the current formation, let us consider a model where the molecule embedded between two electrodes has a single conformation in its neutral (ground) charge state (denoted by symbol 0) and two conformations in the singly charged state (these charged conformations are denoted by symbols a and b). A single-charged molecular state is assumed to be formed in the course of electron hopping transfer with participation of the only active (frontier) MO. [Coulomb repulsion among extra (transferred) electrons occupying the molecule is assumed to be too large to provide the presence of more than one extra electron at the molecule.] In the kinetic approach for the description of charge transfer in a 1M2-device [7,8], the charge hopping processes are characterized by the forward (electrode–molecule) contact rates χ_{1j} and χ_{2j}, as well as by the backward (molecule–electrode) contact rates χ_{-1j} and χ_{-2j}, where the symbol $j(=a,b)$ indicates the charged conformations of the molecule. Intramolecular rate constants characterizing the transitions between the conformations are denoted as K_{ab} and K_{ba}. The complete scheme of kinetic processes is depicted in Figure 1. Owing to the noted transfer processes, the molecule can be in one of three states (0, a, and b) with the respective probabilities $P(0,t)$), $P(a,t) = \sum_{\sigma=\pm1/2} P(a\sigma,t)$, and $P_b(t) = \sum_{\sigma=\pm1/2} P(b\sigma,t)$. These probabilities satisfy a simple

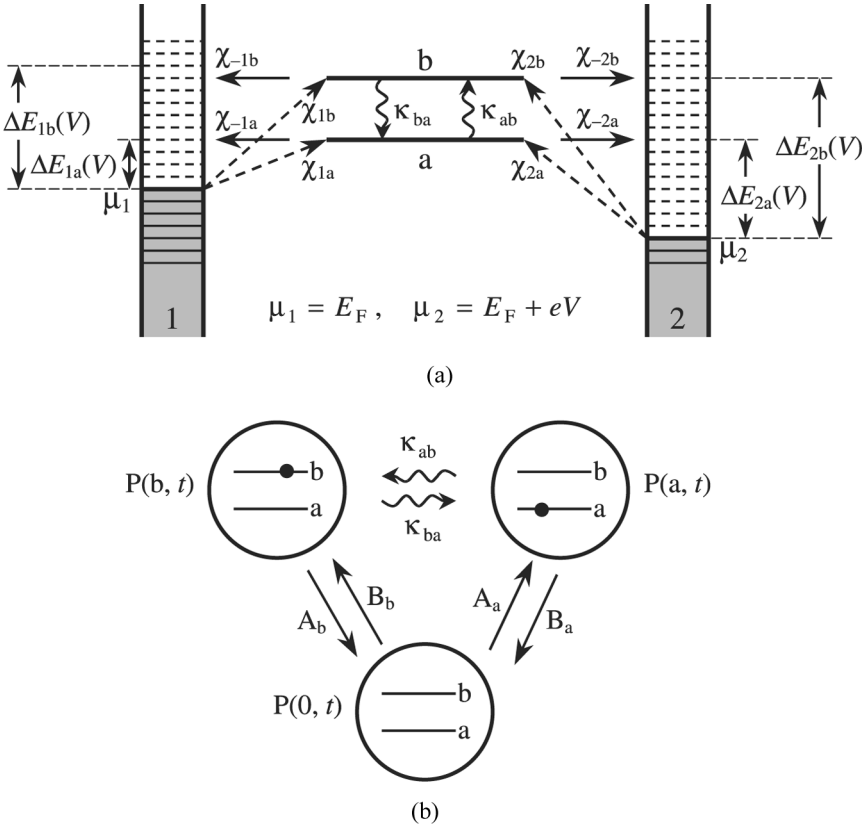


FIGURE 1 Scheme of charge hopping processes in the "electrode-molecule-electrode" device (a), as well as the respective kinetic transitions (b). Rate constants χ_{rj} and χ_{-rj} characterize the forward (electrode-molecule) and backward (molecule-electrode) electron hopping processes, while the rates κ_{ab} and κ_{ba} characterize inter-conformation transitions between the conformations a and b of a singly charged molecule. Transfer rates A_j and B_j, Eq. (2), are responsible for discharging and charging the molecule, respectively.

normalization condition $P(0,t)+P(a,t)+P(b,t)=1$ and evolve in line with the following closed system of kinetic equations:

$$\dot{P}(0,t) = -2\sum_{j=a,b} B_j P(0,t) + \sum_{j=a,b} A_j P(j,t),$$

$$\dot{P}(j,t) = -(A_j + \mathrm{K}_{jj'})P(j,t) + 2B_j P(0,t) + \mathrm{K}_{j'j}P(j',t), (j' \neq j), \quad (1)$$

where

$$A_j = \chi_{1j} + \chi_{2j},\ B_j = \chi_{-1j} + \chi_{-2j}, (j = a, b), \tag{2}$$

are the transfer rates responsible for a molecular charging.

In the most cases, the contacts are fabricated from noble metals having wide conduction bands. This fact allows us to utilize the so-called wide-band approximation [1,2,9,10]. For the contact rates, it yields [6,7]

$$\chi_{rj} = (\Gamma_{rj}/\hbar)F_{rj}, \chi_{-rj} = \chi_{rj}e^{\Delta E_{rj}(V)/k_BT}, (r = 1, 2; j = a, b), \tag{3}$$

where Γ_{rj} is the width parameter, and

$$F_{rj} = \sum_{v_j v_0} W(v_j)\langle v_j|v_0\rangle^2 n(\Delta E_{rj}(v_j, v_0; V)) \tag{4}$$

is a factor associated with the electron-vibration interaction within the molecule. This factor includes the distribution function $W(v) = \exp[-\hbar\omega(v + 1/2))/k_BT]/\sum_v \exp[-\hbar\omega(v + 1/2)/k_BT]$ with $\omega = \omega_j$ being the frequency of the respective vibrational mode, k_B is the Boltzmann's constant, T is the absolute temperature. The quantity $\langle v_j|v_0\rangle$ is the overlap integral between the vibrational functions related to different electronic terms (one term belongs to the j th conformation of the charged molecule, another term relates to a neutral molecule). The quantity

$$n(\Delta E_{rj}(v_j, v_0; V)) = \left[\exp \Delta E_{rj}(v_j, v_0; V)/k_BT) + 1\right]^{-1} \tag{5}$$

is a Fermi-like distribution function associated with the electron-vibrational transfer gap

$$\Delta E_{rj}(v_j, v_0; V) = \Delta E_{rj}(V) + \hbar\omega_j(v_j + 1/2) - \hbar\omega_0(v_0 + 1/2). \tag{6}$$

Here, we have also introduced a pure electronic transfer gap

$$\Delta E_{rj}(V) = E_j(V) - (\mu_r + E_0)\ , \tag{7}$$

where $E_j(V) = E_j(0) + e\eta_j V$ is the electronic energy for a charged molecule (η_j is the voltage division factor for the j th conformation), E_0 is the electronic energy for an uncharged molecule, and μ_r is the chemical potential for the r th electrode. In what follows, we set $\mu_1 = E_F$ and $\mu_2 = E_F + eV$ (the 1st electrode is assumed to be grounded).

Generally, before a steady state current is established in the 1M2-device (with the characteristic time τ_{ET}), the transient currents through the first and the second electrodes do not coincide, i.e., $I_1(t) \neq I_2(t)$. The coincidence occurs only at $t > \tau_{ET}$. In line with the

kinetic approach, we derive the following expression for the transient current through the r th electrode:

$$I_r(t) = I_r^{(hop)}(t) + I_r^{(dir)}(t), (r = 1, 2). \tag{8}$$

The component

$$I_r^{(hop)}(t) = (-1)^{r+1} \sum_{j=a,b} [I_{0\to j}^{(r,hop)} P(0,t) - (1/2) I_{j\to 0}^{(r,hop)} P(j,t)] \tag{9}$$

includes the mechanism of current formation due to the hopping electron motion along the sequential route. The molecular occupancies $P_0(t)$ and $P_j(t)$ give the probabilities to involve a specific electron route in the formation of the current. This refers not only to the hopping (sequential) route but for the tunnel route as well (see below). In the case of a single frontier MO under consideration, the forward ($0 \longrightarrow j$) and the backward ($j \longrightarrow 0$) contact currents are exclusively defined by the contact rates so that ($I_0 \equiv |e|/\pi\hbar \approx 77.6 \mu$A)

$$I_{0\to j}^{(r,hop)} = 2\pi\hbar I_0 \chi_{rj}, I_{j\to 0}^{(r,hop)} = 2\pi\hbar I_0 \chi_{-rj}. \tag{10}$$

In contrast, the component

$$I_{dir}(t) \equiv I_1^{(dir)}(t) = I_2^{(dir)}(t) = \sum_{j=a,b} \left[I_{0(j)}^{(tun)} P(0,t) + I_{j(0)}^{(tun)} P(j,t) \right] \tag{11}$$

is formed owing to the transfer processes associated with distant electron jumps from one electrode to another one. These distant jumps are achieved owing to the superexchange electron coupling between the electrodes at which the transferred electron is virtually captured by the molecule. When the tunneling occurs with participation of a neutral molecule, then a virtual intermediate state of the 1M2-device includes the j th charged molecular conformation state, and thus

$$\begin{aligned} I_{0(j)}^{(tun)} =& 2I_0 \Gamma_{1j} \Gamma_{2j} \int_{-\infty}^{+\infty} dE \int_{-\infty}^{+\infty} dE' \\ & \times \sum_{v_0 v_0'} \left| \sum_{v_j} \frac{\langle v_0' | v_j \rangle \langle v_j | v_0 \rangle}{(E + E_0 + \hbar\omega_0(v_0 + 1/2)) - (E_j(V) + \hbar\omega_j(v_j + 1/2)) + i(\Gamma_{1j}) + \Gamma_{2j})/2} \right|^2 \\ & \times \left[W(v_0) f_1(E)(1 - f_2(E')) - W(v_0')(1 - f_1(E)) f_2(E') \right] \\ & \times \delta(E - E' + \hbar\omega_0(v_0 - v_0')). \end{aligned} \tag{12}$$

[$f_r(E)$ and $\delta(\varepsilon)$ are the Fermi distribution function and the δ-function, respectively.] If the molecule is already charged, then the formation of the superexchange interelectrode coupling occurs with participation of a virtual state corresponding to the charge neutral molecular state 0. Consequently,

$$
\begin{aligned}
I_{0(j)}^{(tun)} =& 2I_0\Gamma_{1j}\Gamma_{2j}\int_{-\infty}^{+\infty}dE\int_{-\infty}^{+\infty}dE' \\
&\times\sum_{v_j v_j'}\left|\sum_{v_0}\frac{\langle v_j'|v_0\rangle\langle v_0|v_j\rangle}{(E_j(V)+\hbar\omega_j(v_j+1/2))}\right|^2 \\
&\qquad -(E'+E_0+\hbar\omega_0(v_0+1/2))-i(\Gamma_{1j}+\Gamma_{2j})/2 \\
&\times\left[W(v_j)f_1(E)(1-f_2(E'))-W(v_j')(1-f_1(E))f_2(E')\right] \\
&\times\delta(E-E'+\hbar\omega_j(v_j-v_j')).
\end{aligned}
\tag{13}
$$

The above expressions for the current components allow us to analyze the formation of the current at different regimes of electron transfer through the conformationally flexible molecule. It is important to note that the evolution of the current to its steady state value is completely defined by the evolution of the probabilities $P(\nu,t)$. In line with the solution to system (1), the probabilities (molecular occupancies) evolve as

$$
P(\nu,t)=P_{st}(\nu)+C_{\nu 1}e^{-t/\tau_{ET}^{(1)}}+C_{\nu 2}e^{-t/\tau_{ET}^{(2)}},\qquad(\nu=0,a,b).
\tag{14}
$$

Here, the stationary probabilities read

$$
\begin{aligned}
P_{st}(0)&=\frac{1}{D}(A_aA_b+A_a\mathrm{K}_{ba}+A_b\mathrm{K}_{ab}),\\
P_{st}(a)&=\frac{1}{D}[A_bB_a+(B_a+B_b)\mathrm{K}_{ba}],\\
P_{st}(b)&=\frac{1}{D}(A_aB_b+(B_a+B_b)\mathrm{K}_{ab}),
\end{aligned}
\tag{15}
$$

where $D\equiv A_aA_b+A_a(2B_b+\mathrm{K}_{bq})+A_b(2B_a+\mathrm{K}_{qb})+2(B_a+B_b)(\mathrm{K}_{ab}+\mathrm{K}_{ba})$. The characteristic times $\tau_{ET}^{(1)}=K_1^{-1}$ and $\tau_{ET}^{(2)}=K_1^{-2}$ that specify the adaptation of molecular occupancies to their stationary values are determined through the overall transfer rates ($s=1,2$)

$$
K_s=\frac{1}{2}[\alpha_1+\alpha_2-(-1)^s\sqrt{(\alpha_1-\alpha_2)^2+4\beta_1\beta_2}],
\tag{16}
$$

where $\alpha_1\equiv A_a+2B_a+\mathrm{K}_{ab},\alpha_2\equiv A_b+2B_b+\mathrm{K}_{ba},\beta_1\equiv 2B_a-\mathrm{K}_{ba}$, and $\beta_2\equiv 2B_b-\mathrm{K}_{ab}$.

III. RESULTS AND DISCUSSION

In the present communication, we discuss only the stationary regime of the current formation. This means that the above expressions for the probabilities (molecular occupancies) are estimated at $t > \tau_{ET}^{(1,2)}$ where $P(\nu, t > \tau_{ET}^{(1,2)}) = P_{st}(\nu)$ [cf. Eq. (14)]. During the steady regime of charge transfer, the number of outgoing electrons (leaving the 1st electrode at $V > 0$) is exactly coincide with the number of incoming electrons (arriving at the 2nd electrode at $V > 0$). Therefore, $I_1(t > \tau_{ET}) = I_2(t > \tau_{ET}) \equiv I$. The total steady state current

$$I = I_{hop} + I_{dir} \tag{17}$$

contains the hopping and the direct (tunnel) components. The hopping current component can be found from expression (9) if one sets $r = 1$ or $r = 2$. This yields

$$I_{hop} = \sum_{j=a,b} [I_{0 \longrightarrow j}^{(1,hop)} P_{st}(0) - (1/2) I_{j \longrightarrow 0}^{(1,hop)} P_{st}(j)]. \tag{18}$$

Analogously, the form of the direct current component follows from Eq. (11) so that

$$I_{dir} = \sum_{j=a,b} [I_{0(j)}^{(tun)} P_{st}(0) + I_{j(0)}^{(tun)} P_{st}(j)]. \tag{19}$$

To have a more clear analytic results, we restrict ourself by a coarse-grained description, by ignoring, thus, a fine vibrational structure of $I - V$ curves. (The details concerning the fine vibrational structure can be found in Refs. [6,7,11–13]) In the framework of the coarse-grained description, one has to set $\langle v_0 | v_j \rangle \approx \delta_{v_0, v_j}$. This reduces the contact rate constants, Eq. (3), to a much simpler form

$$\chi_{rj} = (\Gamma_{rj}/\hbar) n(\Delta E_{rj}(V)), \chi_{-rj} = (\Gamma_{rj}/\hbar)[1 - n(\Delta E_{rj}(V))]. \tag{20}$$

As to the tunnel currents, Eqs. (12) and (13), they do not differ from each other and appear in the following well-known Landauer–Büttiker form:

$$I_{L-B}^{(j)} \equiv I_{0(j)}^{(tun)} = I_{j(0)}^{(tun)} = 2I_0 \frac{\Gamma_{1j}\Gamma_{2j}}{\Gamma_{1j} + \Gamma_{2j}} \left[arctg\left(\frac{2\Delta E_{2j}(V)}{\Gamma_{1j} + \Gamma_{2j}} \right) - arctg\left(\frac{2\Delta E_{1j}(V)}{\Gamma_{1j} + \Gamma_{2j}} \right) \right]. \tag{21}$$

Note that the pure electronic transfer gaps $\Delta E_{1j}(V)$ and $\Delta E_{2j}(V)$ (cf. Fig. 1) are identical for both the hopping and tunneling electron

routes. When the gap $\Delta E_{rj}(V)$ becomes negative, the resonant regime of charge transfer is opened for the pathway associated with the r th molecular conformation. The opening of the resonant transfer occurs at $V \geq V_{1j}$ (at $V > 0$) and $V \leq -V_{2j}$ (at $V < 0$). The form of each resonant voltage V_{rj} is derived from the condition $\Delta E_{rj}(V) = 0$. It yields $[\Delta E_j(0) = E_j(0) - (E_0 + E_F)]$

$$V_{1j} = \Delta E_j(0)/|e|\eta_j,\ V_{2j} = -\Delta E_j(0)/|e|(1-\eta_j). \tag{22}$$

For the sake of definiteness, we set $\Delta E_b(0) > \Delta E_a(0)$ below so that $V_{1b} > V_{1a} > 0$ and $V_{2b} < V_{2a} < 0$. To consider the off-resonant, single-resonant, and double-resonant regimes of charge transfer in the 1M2-device, we note that, for a number of organic molecules, the ratio of rate constants characterizing the conformation transitions within the molecule satisfies the condition $\mathrm{K}_{ab}/\mathrm{K}_{ba} = \exp[-(E_b(V) - E_a(V))/k_BT] = 1$ irrespective of the applied voltage V. Thus, one can set $\mathrm{K}_{ab} = 0$ and $\mathrm{K}_{ba} \equiv \mathrm{K} \neq 0$. The current-voltage characteristics of the molecule with a single frontier MO and with two conformations (for a charged molecule) are depicted at Figures 2 and 3. Now we discuss the current formation during three above-noted transfer regimes.

(A). Off-Resonant Transfer Regime

This regime exists in the voltage region $0 < V < V_{1a}$ $(0 > V > V_{2a})$, where each transfer gap $\Delta E_{rj}(V)$ remains positive. Therefore, at low and room temperatures, one can set $n(\Delta E_{rj}(V)); 0$. This yields $\chi_{rj} \approx 0$, $\chi_{-rj} = (\Gamma_{rj}/\hbar)$. The evolution of initial molecular occupancies, $P(\nu, 0)$, $(\nu = 0, a, b)$, to their steady state values, $P_{st}(\nu) \equiv P(\nu, t > \tau_{ET}^{(1)}, \tau_{ET}^{(2)})$, is described by Eq. (14) with the characteristic times $\tau_{ET}^{(1)} = \hbar/(\Gamma_{1a} + \Gamma_{1b})$ and $\tau_{ET}^{(2)} = \hbar/(\Gamma_{2a} + \Gamma_{2b} + \hbar\mathrm{K})$. But, due to the activation character of the hopping process, a difference between the initial and the steady state occupancies remains minor so that $P_{st}(0) \approx P(0,0) \approx 1$, $P_{st}(j) \approx P(j,0) \approx 0$. This is a reason why the hopping component of the current is too small. It is clearly seen from Figures 2 and 3 at $|V| < |V_{ra}|$.

(B). Single-Resonant Transfer Regime

When the applied voltage is in the region $V_{1a} \leq V < V_{1b}$ $(V_{2a} \geqslant V > V_{2b})$, the gap $\Delta E_{1a}(V)(\Delta E_{2a}(V))$ becomes negative, while the gap $\Delta E_{1b}(V)$ $(\Delta E_{2b}(V))$ remains positive. Therefore, with a high accuracy, one can set $n(\Delta E_{1a}(V)) \approx 1$, $n(\Delta E_{1b}(V)) \approx 0$, $n(\Delta E_{2a}(V)) \approx 0$, $n(\Delta E_{2b}(V)) \approx 0$ (at $V > 0$) and $n(\Delta E_{1a}(V)) \approx 0$,

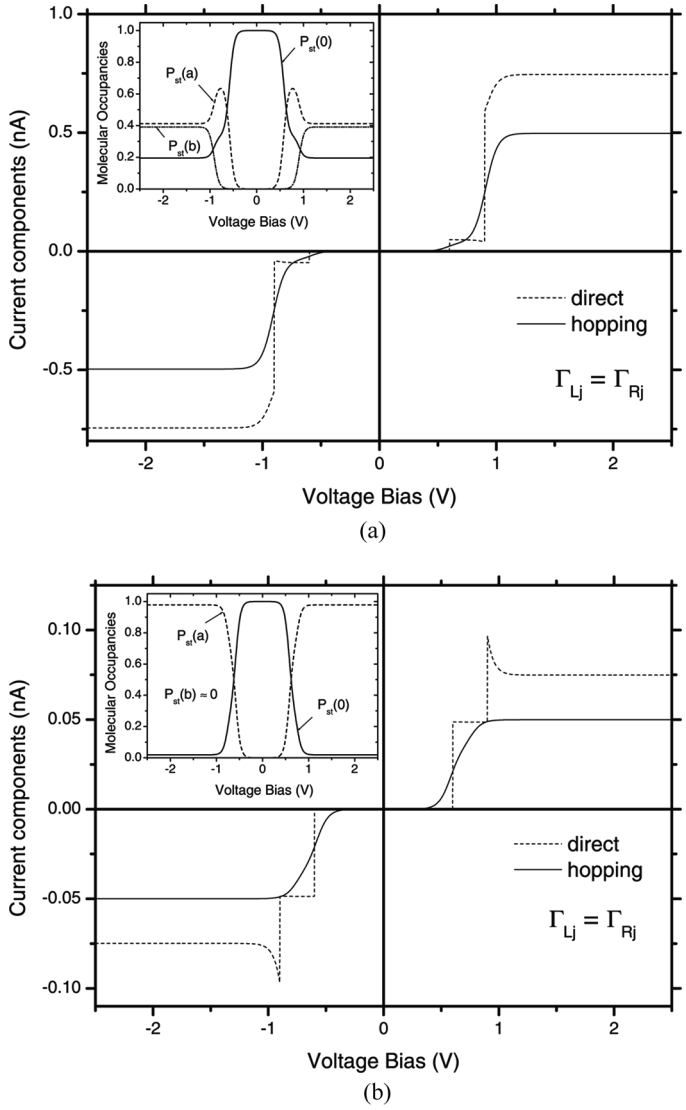
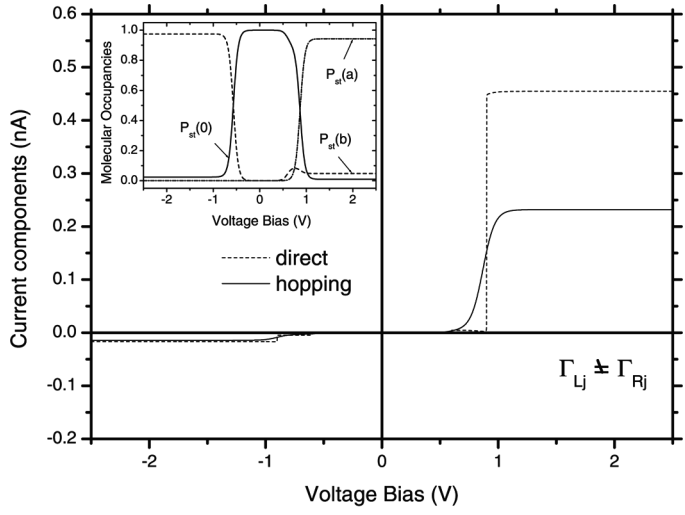
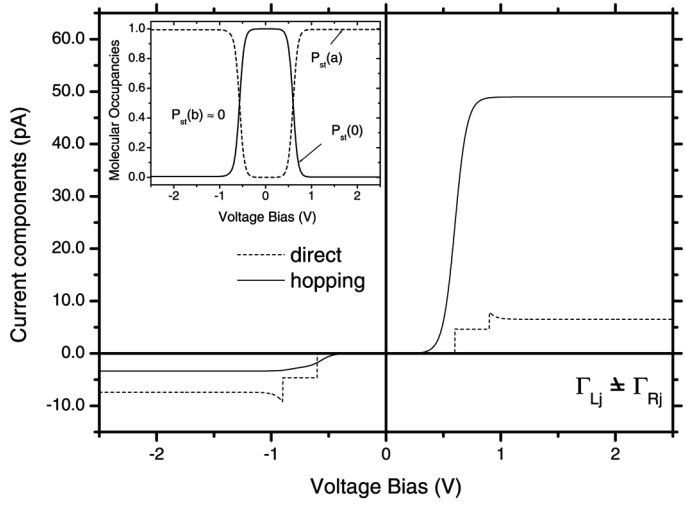


FIGURE 2 Current-voltage characteristics of a molecule with two charged conformations at slow (a) and fast (b) inter-conformation transitions. Symmetric coupling of the molecule to electrodes 1 and 2. Diode properties are absent, $-I(-V) = I(V)$. The calculations are performed at $\Gamma_{1a} = \Gamma_{2a} = 2 \cdot 10^{-7}$ eV, $\Gamma_{1b} = \Gamma_{2b} = 5 \cdot 10^{-6}$ eV, $\Delta E_a(0) = 0.30$ eV, $\Delta E_b(0) = 0.45$ eV, $\eta_a = \eta_b = 0.5$; $\kappa_{ab} \approx 0$, $\hbar\kappa_{ba} \equiv \hbar\kappa = 10^{-8}$ eV (panel a), $\hbar\kappa_{ba} \equiv \hbar\kappa = 10^{-4}$ eV (panel b).



(a)



(b)

FIGURE 3 Diode properties of a molecule with two charged conformations at slow (a) and fast (b) inter-conformation transitions, $-I(-V) \neq I(V)$. Asymmetric coupling of the molecule to the electrodes 1 and 2. The calculations at $\Gamma_{1a} = 10^{-8}\,\text{eV}$, $\Gamma_{2a} = 2\cdot10^{-7}\,\text{eV}$, $\Gamma_{1b} = 5\cdot10^{-5}\,\text{eV}$, $\Gamma_{2b} = \cdot10^{-6}\,\text{eV}$, $\Delta E_a(0) = 0.30\,\text{eV}$, $\Delta E_b(0) = 0.45\,\text{eV}$, $\eta_a = \eta_b = 0.5$; $\kappa_{ab} \approx 0$, $\hbar\kappa_{ba} \equiv \hbar\kappa = 10^{-8}\,\text{eV}$ (panel a), $\hbar\kappa_{ba} \equiv \hbar\kappa = 10^{-4}\,\text{eV}$ (panel b).

$n(\Delta E_{1b}(V)) \approx 0$, $n(\Delta E_{2a}(V)) \approx 1$, $n(\Delta E_{2b}(V)) \approx 0$ (at $V < 0$). Now the electron hopping from electrode 1 to the molecule (at $V > 0$) or from electrode 2 to the molecule (at $V < 0$) does not require a temperature activation so that one can say about the resonant electron hopping to the molecule. Due to the resonant hopping, the molecule occurs in the a th charged conformation. Adaptation of the occupancies to their steady state values is carried out with the characteristic times $\tau_{ET}^{(1)} = \hbar/(2\Gamma_{ra} + \Gamma_{r'b})$ and $\tau_{ET}^{(2)} = \hbar/(\Gamma_{2a} + \Gamma_{2b} + \hbar\kappa)$, while

$$P_{st}(0) \approx \frac{\Gamma_{r'a}}{2\Gamma_{ra} + \Gamma_{r'a}},\ P_{st}(a) \approx \frac{2\Gamma_{ra}}{2\Gamma_{r'a} + \Gamma_{ra}},\ P_{st}(b) \approx 0. \tag{23}$$

[One has to set $r = 1, r' = 2$ at $V > 0$ and $r = 2,\ r' = 1$ at $V < 0$.]

During the single-resonant transmission regime, the hopping current component reads

$$I_{hop}; \pi I_0 \Gamma_{1a} \times \begin{cases} 2P_{st}(0) & \text{if} \quad V > 0 \\ -P_{st}(a) & \text{if} \quad V < 0. \end{cases} \tag{24}$$

As to the direct (tunnel) component, the latter is defined by the expression

$$I_{dir}; I_{L-B}^{(a)} + I_{L-B}^{(b)} P_{st}(0). \tag{25}$$

[It has been taken the fact into account that, during the single-resonant transmission regime, the normalization condition reads $P_{st}(0) + P_{st}(a) \approx 1$.] In Eq. (25), only the first term reflects the resonant character of transmission via the creation of the a th molecular conformation. The contribution of the second term to the direct current component is governed by the weight of the ground (charge neutral) molecular state.

(C). Double-Resonant Transmission Regime

This regime works if only $V \geqslant V_{1b}$ or $V \leq V_{2b}$. Setting $n(\Delta E_{1j}(V)) \approx 1, n(\Delta E_{2j}(V)) \approx 0$ (at $V > 0$) and $n(\Delta E_{1j}(V)) \approx 0$, $n(\Delta E_{2j}(V)) \approx 1$ (at $V < 0$), we obtain

$$\begin{aligned} P_{st}(0) &\approx \frac{1}{D}\Gamma_{r'a}(\Gamma_{r'b} + \hbar\kappa), \\ P_{st}(a) &\approx \frac{2}{D}[\Gamma_{ra}\Gamma_{r'b} + \hbar\kappa(\Gamma_{ra} + \Gamma_{rb})], \\ P_{st}(b) &\approx \frac{2}{D}\Gamma_{rb}\Gamma_{r'a}, \\ D &= \Gamma_{r'a}\Gamma_{r'b} + \Gamma_{r'a}(2\Gamma_{rb} + \hbar\kappa) + 2\Gamma_{ra}\Gamma_{r'b} + 2\hbar\kappa(\Gamma_{ra} + \Gamma_{rb}). \end{aligned} \tag{26}$$

The adaptation of initial occupancies to the steady-state occupancies is characterized by the overall transfer rates (16), where $\alpha_1 = (2\Gamma_{ra} + \Gamma_{r'a})/\hbar$, $\alpha_2 = (2\Gamma_{rb} + \Gamma_{r'b})/\hbar + \kappa$, $\beta_1 = 2\Gamma_{ra}/\hbar - \kappa$, $\beta_2 = 2\Gamma_{rb}/\hbar$. [Here and in Eq. (26), one has to set $r = 1, r' = 2$ if $V > 0$; $r = 2, r' = 1$ if $V < 0$.] The hopping and direct current components are given by the analytic expressions

$$I_{hop} \approx \pi I_0 \times \begin{cases} 2(\Gamma_{1a} + \Gamma_{1b})P_{st}(0) & \text{if } v > 0 \\ -(\Gamma_{1a}P_{st}(a) + \Gamma_{1b}P_{st}(b)) & \text{if } V < 0, \end{cases} \tag{27}$$

and

$$I_{dir} \approx I^{(a)}_{L-B}[P_{st}(0) + P_{st}(a)] + I^{(b)}_{L-B}[P_{st}(0) + P_{st}(b)], \tag{28}$$

respectively. One can see that, during the double-resonant regime of transmission, both the hopping and direct current components are formed with participation of two charged molecular conformations, a and b. Therefore, the $I - V$ characteristics of the molecule becomes

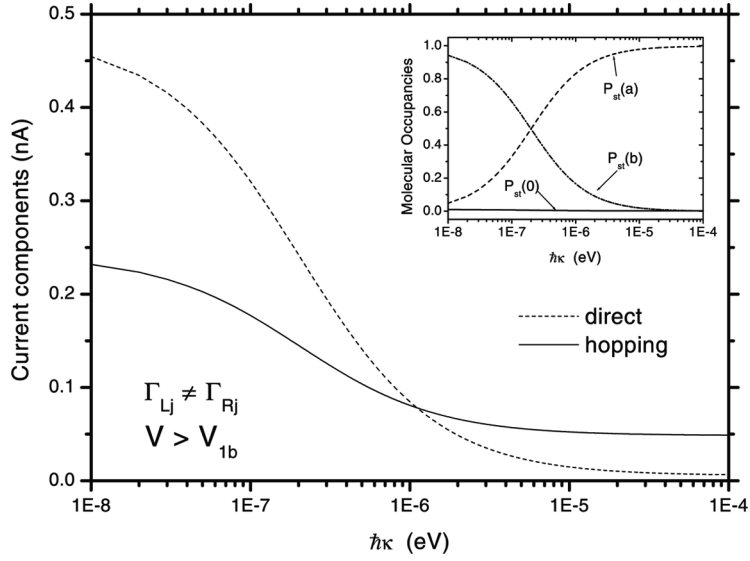


FIGURE 4 Dependence of the current through a molecule with two charged conformations on the efficiency of inter-conformation transitions. The molecule in the charged conformation b is assumed to be more strongly coupled to the electrodes, and the transferred electron in this conformation has a higher energy in comparison to that for the conformation a. The calculations with the parameters as those for Figure 3.

dependent not only on the transmission gaps and the character of electrode-molecule couplings (via the width parameters Γ_{rj}) but also on the efficiency of inter-conformation transitions (via the transfer rate κ), cf. Figure 4.

IV. CONCLUSION

It follows from the results of the present communication that, under the conditions when a flexible molecule participates in the formation of an inter-electrode current, the character of the current formation depends strongly on the efficiency of conformation transitions within the charged molecule. Thus, if the contact of the molecule to the electrodes is strong in the b th and weak in the a th charged molecular conformations, the hopping and direct (tunnel) components becomes large (small) at the slow (fast) inter-conformation transfer rate κ. It is well seen from comparison of Figures 2a,b which present the $I-V$ characteristics of the molecule with identical coupling to the adjacent electrodes. The effect is strongly manifested in the case of asymmetric coupling to the electrodes, cf. Figures 3a,b. Figure 4 indicates that the effect of the conformation control over the charge transmission is more significant for a direct (tunnel) component of the current. The comparison of the insets to Figures 3a,b shows that such a difference is associated with the probability $P(b,t)$ which has a nonzero value at slow inter-conformation transitions in the case of double-resonant regime of the transmission.

The results of the present work make it possible to conclude that the activation of one or other conformation either by the charge transfer through the molecule or via the light illumination of the molecule can be one of the effective mechanisms of the current control in the "electrode—molecule–electrode" device.

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