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# Molecular Diode at Fast Switching on (off) Regime

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*It is shown that after a sudden change of the voltage bias in device "electrode–molecule–electrode", only the hopping current components are able to achieve a great value as compared to the steady current. The effect becomes especially noticeable at asymmetric coupling of the molecule to each electrode. At such asymmetry, the molecule exhibits itself as a molecular diode which is kinetically recharged during the transfer of electrons through a molecule. Just a specific kinetic molecular charging (at switching on the voltage) and discharging (at switching off the voltage) become responsible for a formation of switch-on and switch-off currents.*

**Keywords:** charge transmission; kinetic equations; molecular charging; molecular discharging; tunneling

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## I. INTRODUCTION

Molecular diode is the simplest basic element which performs a transformation of electric signals in molecular circuits. The first model of molecular diode has been proposed by Aviram and Ratner in the 70th [1]. But, the experimental verification of diode properties has been only obtained in last ten years [2–5]. It has shown that noticeable rectification behavior of organic molecules appears at strongly asymmetric profile of electric potential along the molecule [6,7]. At the same time, a rectification behavior of single molecules is also caused by a specific molecular charging which is happen at inelastic electron

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transmission through a molecule [8,9]. The charging factor becomes especially significant at resonant electron/hole transmission. Note, that the reliable experimental results on molecular conductivity have been only obtained when a stationary regime of charge transmission is supported. However, an important information on mechanisms of chasrge transmission through single molecules and nanomolecular systems one can obtain studying the current evolution to a steady state just after alteration of the inter-electrode voltage. In the present communication, we study the physics of current evolution in a molecular diode at fast alteration of applied voltage.



## II. BASIC EXPRESSIONS FOR A CURRENT EVOLUTION

To understand the physics of current evolution in a molecular device from its initial value (formed just after a voltage alteration) to its steady value (formed at $t \gg \tau_{st}$ where $\tau_{st}$ is the characteristic time of establishment of a stationary charge transmission in the device), we model a molecular diode as the system "electrode L–molecule–electrode R" (LMR-system) where only a single electronic level related to the lowest unoccupied molecular orbital (LUMO), dominates in formation of the current through a molecule. It is supposed that this level is well separated energetically from the rest empty and filled levels (cf. Fig. 1). Similar single-level models are often used to clarify the physics of charge transmission through organic molecules [8–15].

In this communication, we assume a strong Coulomb repulsion between two extra electrons occupying the molecule. Therefore, in the voltage region under consideration only neutral ($M_0$) and singly ($M_1$) charged states of the molecule participate in formation of the current. Probability for realization of the noted states is defined through respective charge molecular occupancies $W(M_0,t)$ and $W(M_1,t)$. Evolution of the occupancies is determined by hopping transmission of electrons from the electrodes to the molecular level. [In Fig. 2, respective contact rate constants are denoted via $\chi_r$ and $\chi_{-r}$, $(r = L,R)$.] General form of kinetic equations for charge molecular occupancies have been derived in Ref. [9]. For our case of charge neutral and singly charged molecular states they read

$$\begin{aligned} \dot{W}(M_0,t) &= -2k_f W(M_0,t) + k_b W(M_1,t), \\ \dot{W}(M_1,t) &= -k_b W(M_1,t) + 2k_f W(0,t) \end{aligned} \tag{1}$$

where

$$k_f = \chi_L + \chi_R, \quad k_b = \chi_{-L} + \chi_{-R}. \tag{2}$$

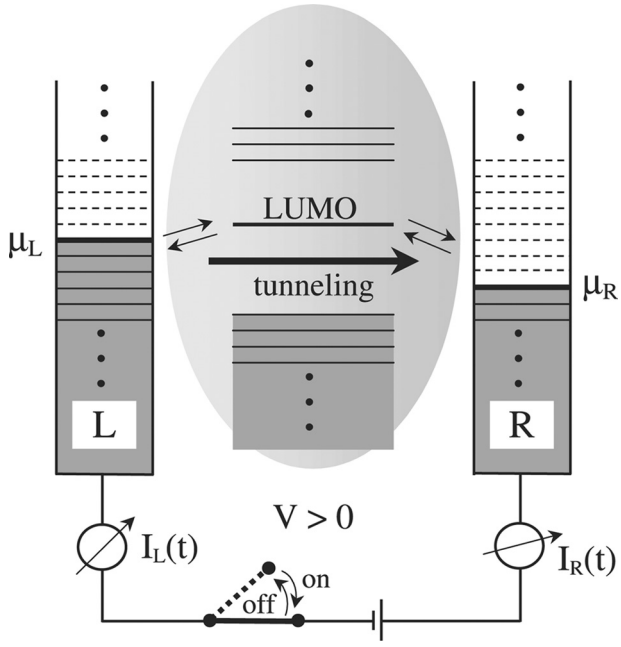



**FIGURE 1** LMR-system as a molecular diode with the only frontier molecular orbital. Current formation occurs through real and virtual population of the LUMO by the transferred electrons. Before a steady current is established in LMR-system, the currents $I_L(t)$ and $I_R(t)$ through the electrodes remain unequal.

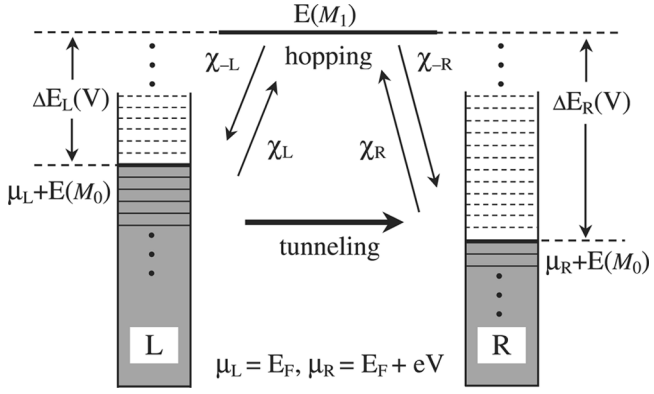



**FIGURE 2** Charge hopping transmission in molecular diode with active LUMO. Electrode-molecule and molecule-electrode rate constants are denoted via $\chi_{L(R)}$ and $\chi_{-L(-R)}$, respectively. Resonant regime is opened when one of transmission gaps, $\Delta E_L(V)$ or $\Delta E_R(V)$, vanishes.

are the charge transfer rates. Molecular occupancies satisfy the normalization condition

$$W(M_0,t) + W(M_1,t) = 1. \tag{3}$$

The form of kinetic Eq. (1) is valid if only rate constants $\chi_\nu = \chi_\nu(V), \chi_{-\nu} = \chi_{-\nu}(V)$ and, thus, transfer rates $k_f = k_f(V)$, $k_b = k_b(V)$ are time-independent quantities. If the applied voltage is time-dependent, i.e., $V = V(t)$, then, generally, one have to employ much more complicated non-Marcovian form of kinetic equations. Below we consider only the fast voltage alteration. At such switching on (off) regime, the kinetic equations, Eq. (1) are quite suitable for description of current evolution. Kinetic theory shows that a current through each separate electrode $r$ contains direct and hopping components so that $I_r(t) = I_r^{(dir)}(t) + I_r^{(hop)}(t)$. Direct component is given by expression $I_r^{(dir)}(t) = I^{(tun)}[W(M_0,t) + W(M_1,t)]$ which is identical for $r = L$ and $r = R$. Such identity is explained by the fact that a direct current is formed by the tunneling electrons which do not really populate the molecule. In line with normalization condition (3), a direct current is time-independent quantity which is determined by a standard Landauer expression [6]

$$I^{(tun)} = I_0 \int_{-\infty}^{+\infty} dE \frac{[f_L(E) - f_R(E)]\Gamma_L(E)\Gamma_R(E)}{[E - (E(M_1) - E(M_0)]^2 + [\Gamma_L(E) + \Gamma_R(E)]^2/4} \tag{4}$$

where $f_R(E) = \{\exp[(E - \mu_r)/k_BT]\}^{-1}$ is the Fermi distribution function of the $r$ th electrode ($\mu_r$ is the chemical potential, $k_B$ is the Boltzmann's constant, $T$ is the absolute temperature). Width parameters $\Gamma_L(E)$ and $\Gamma_R(E)$ reflect interaction of the molecule with respective electrodes. Introduction of the current unit $I_0 = 2|e|/h \approx 77.6$ μA supposes that all energy quantities including the width parameters, have to be taken in electron-volts. [It is important to note that if more than one extra electron can occupy the molecule, then a direct current component becomes dependent on charged state of the molecule (via molecular occupancies). Formation of such direct current includes more than one tunnel route. But that more complicated case is beyond our consideration.]

Sequential (hopping) charge transmission includes a real population of molecular level by the transferred electron. This leads to a difference between the hopping currents related to each electrode. Following the kinetic approach to description of charge transfer processes in LMR-system one derives ($h$ is the Planck's constant)

$$I_L^{(hop)}(t) = I_0 h[\chi_L W(M_0,t) - \chi_{-L} W(M_1,t)],$$
$$I_R^{(hop)}(t) = -I_0 h[\chi_R W(M_0,t) - \chi_{-R} W(M_1,t)]. \quad (5)$$

It is clear seen that an evolution of each hopping current is governed by relaxation of charge molecular occupancies to their steady values $W_{st}(M_\nu;V) \equiv W(M_\nu, t \gg \tau_{st}), (\nu = 0,1)$, formed at given fixed voltage $V$. Solving the set (1) at stationary condition $\dot{W}(M_\nu,t) = 0$, with taken into account the normalization condition (3) one derives

$$W_{st}(M_0;V) = \frac{k_b(V)}{2k_f(V) + k_b(V)}, W_{st}(M_1;V) = \frac{2k_f(V)}{2k_f(V) + k_b(V)}. \quad (6)$$

Let $\tau_{alt}$ be the characteristic time of fast voltage alteration from $V = V_1$ to $V = V_2$. Fast alteration means that $\tau_{st} \gg \tau_{alt}$. Therefore, if one describes evolution of the occupancies at $t \gg \tau_{alt}$, then solution of the set (1) is performed at initial condition $W(M_\nu, t = 0) \simeq W(M_\nu, t \ll \tau_{alt}) \equiv W_{st}(M_\nu;V_1)$ whereas the occupancies theirselve evolve at $V = V_2$. Thus, the solution to set (1) reads

$$W(M_\nu,t) = W_{st}(M_\nu;V_2) + [W_{st}(M_\nu;V_1) - W_{st}(M_\nu;V_2)]e^{-t/\tau_{st}} \quad (7)$$

where quantities $W_{st}(M_\nu;V)$ are given by Eq. (6). In fact, the Eq. (7) describes a relaxation of molecular occupancies in LMR-system from their steady values existed at $V = V_1$ (i.e., before a voltage alteration) to the occupancies formed at new voltage $V = V_2$. This relaxation occurs with the characteristic time

$$\tau_{st} = \tau_{st}(V_2) = [2k_f(V_2) + k_b(V_2)]^{-1} \quad (8)$$

## III. RESULTS AND DISCUSSION

On the base of derived analytic expressions one can conclude that evolution of the current through the $r$th electrode is defined by a sum of tunnel and hopping components,

$$I_r(t) = I^{(tun)} + I_r^{(hop)}(t), \quad (r = L,R). \quad (9)$$

To specify a tunnel component we use a well known wide-band approximation [6]. In line with this approximations, the width

parameters $\Gamma_L$ and $\Gamma_R$ are energy independent values. This allows us to reduce Eq. (4) to a much more simple form $I_L^{(dir)}(t) = I_R^{(dir)}(t) \equiv I_{dir}(t) = I^{(tun)}$ where

$$I^{(tun)} = 2I_0 \frac{\Gamma_L \Gamma_R}{\Gamma_L + \Gamma_R} \left[ \arctan\left( \frac{2\Delta E_R(V_2)}{\Gamma_L + \Gamma_R} \right) - \arctan\left( \frac{2\Delta E_L(V_2)}{\Gamma_L + \Gamma_R} \right) \right]. \quad (10)$$

[In Eq. (10) we have introduced the transmission gaps $\Delta E_L(V) = E(M_1) - (E(M_0) + \mu_L)$ and $\Delta E_R(V) = E(M_1) - (E(M_0) + \mu_R)$ (cf. Fig. 2).] Whereas the tunnel current component, Eq. (10) is a time-independent value, the hopping components, Eq. (5) are also time-dependent quantities. To analyze evolution of these current components one has to specify the form of contact rate constants that characterize a relaxation of occupancies. For the sake of definiteness, we consider the case of small nuclear displacement. Respective contact rate constants are obtained in the form [8,9]

$$\begin{aligned} \chi_r(V) &\simeq \frac{1}{\hbar} \Gamma_r n(\Delta E_r(V)), \\ \chi_{-r}(V) &\simeq \frac{1}{\hbar} \Gamma_r [1 - n(\Delta E_r(V))] \end{aligned} \quad (11)$$

with

$$n(\Delta E_r(V)) = \frac{1}{\exp[\Delta E_r(V)/k_B T] + 1} \quad (12)$$

being the electronic distribution function with a voltage controlled transmission gap. [Note that the gaps for both tunnel and hopping charge transmission are identical.] When an extra electron occupies the MO then an energy shift of molecular level is defined by voltage division factor $\eta$ [6]. We consider a situation when the left electrode is held at zero voltage so that $\mu_L = E_F$, $\mu_R = E_F + eV$ where $E_F$ is the Fermi energy for both (identical) electrodes. In this case, one derives $E(M_1) - E(M_0) = \Delta E(0) + e\eta V$ and thus

$$\begin{aligned} \Delta E_L(V) &= \Delta E(0) + \eta eV, \\ \Delta E_R(V) &= \Delta E(0) - (1 - \eta) eV. \end{aligned} \quad (13)$$

Here, $\Delta E(0)$ is the unbiased transmission gap.

To have at hand a more suitable expression for the hopping current components we substitute the rate constants, Eq. (11) and the occupancies, Eq. (7) into the Eq. (5). It yields

$$I_r^{(hop)}(t) = I_{st}^{(hop)}(V_2) + [I_r^{(hop)}(0) - I_{st}^{(hop)}(V_2)]e^{-t/\tau_{st}(V_2)} \tag{14}$$

where the characteristic time

$$\tau_{st}(V_2) = \frac{\hbar}{\Gamma_L[1 + n(\Delta E_L(V_2))] + \Gamma_R[1 + n(\Delta E_R(V_2))]} \tag{15}$$

is associated with adaptation of the hopping current components to their common steady value

$$I_{st}^{(hop)}(V_2) \equiv I_L^{(hop)}(t \gg \tau_{st}(V_2)) = I_R^{(hop)}(t \gg \tau_{st}(V_2))$$
$$= I_0 \frac{2\pi\Gamma_L\Gamma_R}{\sum\limits_{r=L,R} \Gamma_r[1 + n(\Delta E_r(V_2))]}[n(\Delta E_L(V_2) - n(\Delta E_R(V_2)]. \tag{16}$$

The adaptation starts from initial currents

$$I_L^{(hop)}(0) \equiv I_L^{(hop)}(t \ll \tau_{alt}) = I_0 \frac{2\pi\Gamma_L}{\sum\limits_{r=L,R} \Gamma_r[1 + n(\Delta E_r(V_2))]}$$
$$\times \sum_{r=L,R} \Gamma_r[n(\Delta E_L(V_2)) - n(\Delta E_r(V_1))] \tag{17}$$

and

$$I_R^{(hop)}(0) \equiv I_R^{(hop)}(t \ll \tau_{alt}) = -I_0 \frac{2\pi\Gamma_R}{\sum\limits_{r=L,R} \Gamma_r[1 + n(\Delta E_r(V_2))]}$$
$$\times \sum_{r=L,R} \Gamma_r[n(\Delta E_R(V_2)) - n(\Delta E_r(V_1))] \tag{18}$$

that are formed just after a sudden alteration of the applied voltage from $V = V_1$ to $V = V_2$. Therefore, we attribute quantities $I_L^{(hop)}(0)$ and $I_R^{(hop)}(0)$ to the switch-on currents (if $V_1 = 0, V_2 = V$) or to the switch-off currents (if $V_1 = V, V_2 = 0$).

Current evolution depends strongly on the transmission gaps, Eq. (13). When the gap $\Delta E_r(V)$ is positive then an electron tunneling occurs in off-resonant regime and thus a tunnel current is not large. As to the hopping current components, they vanish at zero temperature

(since a charge hopping process requires a temperature activation). Situation changes principally if $\Delta E_r(V) \leq 0$. Now a molecular level becomes resonant to one of the filled electrode's level. It forms a tunnel and a hopping resonant charge transmission in LMR-system. Now, an electron hopping does not require more a temperature activation. Condition $\Delta E_r(V) = 0$ determines those resonant voltages $V = V_r^{(res)}$ that open a resonant regime of current formation. It is not difficult to see that a resonant regime with the left (right) electrode is happen only at positive (negative) voltages when $V \geq V_L^{(res)} (V \leq V_R^{(res)})$ where

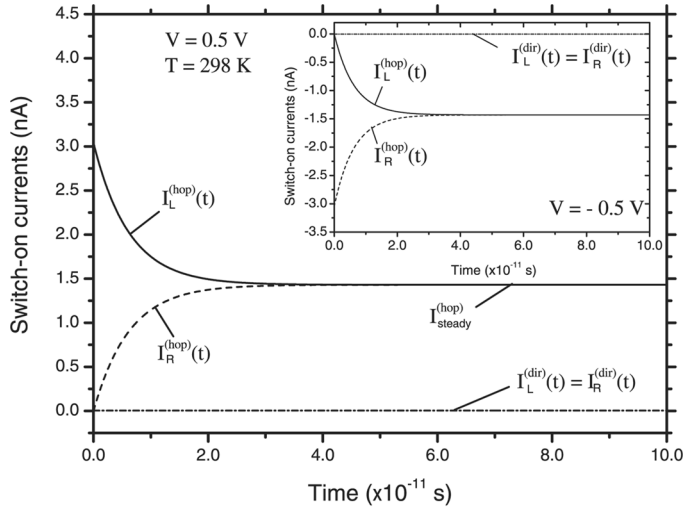
$$V_L^{(res)} = \frac{\Delta E(0)}{|e|\eta} > 0, \quad V_R^{(res)} = -\frac{\Delta E(0)}{|e|(1-\eta)} < 0. \tag{19}$$

Therefore, two voltage intervals are important for the analysis, $0 < V < V_L^{(res)}$ and $V \geq V_L^{(res)} (at\ V > 0)$ as well as $0 > V > V_R^{(res)}$ and $V \leq V_R^{(res)} (at\ V < 0)$.

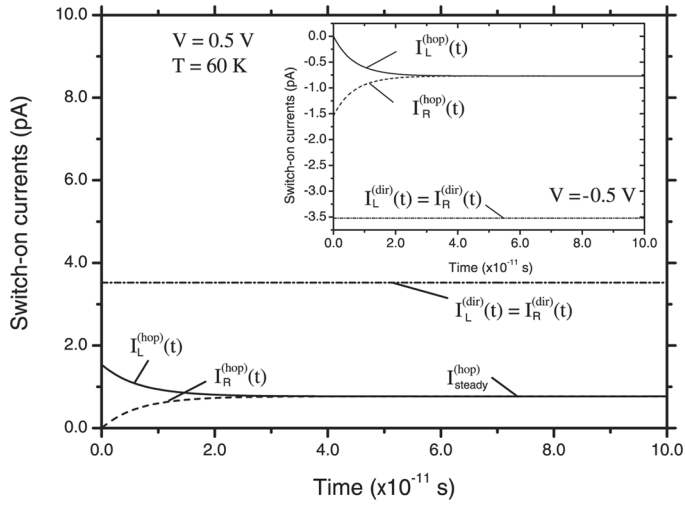
## III.1 Switch-on Currents

For description of current evolution at a sudden switching on the voltage, one has to set $V_1 = 0$ and $V_2 \neq 0$. The switching on effect becomes especially clear if a voltage jump exceeds 0.1 V. Figures 3 and 4 illustrate a current evolution at off-resonant and resonant charge transmission, respectively. We have to pay attention on three principal peculiarities. The first one reflects the fact that a direct (tunnel) current component does not depend on time being equal to its steady value. In off-resonant voltage region $0 < V < V_L^{(res)}$ (or $0 > V > V_R^{(res)}$) where $V = V_2$, a tunnel current component at does or does not exceed the hopping current components. At the fixed transmission gaps, Eq. (13) this is defined by a concrete temperature (cf. Figs. 3a and 3b). The second peculiarity concerns a large difference between absolute value of the switching on currents $I_L^{(hop)}(0)$ and $I_R^{(hop)}(0)$ both at off-resonant and resonant regimes of charge transmission. This fact is easy explained on the base of simplified analytic expressions for the currents. Actually, at voltage alteration of $|V_2 - V_1| = |V| > 0.1$ V, one can set $n(\Delta E_L(V)) \gg n(\Delta E(0)) \gg n(\Delta E_R(V))$ (if $V > 0$) and $n(\Delta E_R(V)) \gg n(\Delta E(0)) \gg n(\Delta E_L(V))$ (if $V < 0$). It allows us to rewrite Eq. (16) in much more simple form

$$I_{st}^{(hop)} \simeq sign(V) I_0 \frac{2\pi \Gamma_L \Gamma_R n(\Delta E_r(V))}{\Gamma_r [1 + n(\Delta E_r(V))] + \Gamma_{r'}} \tag{20}$$




(a)




(b)

**FIGURE 3** Current evolution in LMR-system during the off-resonant transmission at room (a) and low (b) temperature. The evolution starts just after an instantaneous rise of the applied voltage from $V = 0$ to $V \neq 0$. Hopping and direct (tunnel) electron transmission occurs through the LUMO. The switch-on hopping current and the steady hopping current drop strongly at low temperature. Direct (tunnel) current $I_L^{(dir)}(t) = I_R^{(dir)}(t) = I^{(tun)}$ is time and temperature independent value. The case of symmetric coupling of the molecule to the electrodes is presented. No large difference between the switch-on hopping current and the steady state hopping current. The calculations are based on Eqs. (10) and (14) at $\Delta E(0) = 0.3$ eV, $\Gamma_L = \Gamma_R = 5 \cdot 10^{-5}$ eV; $V = \pm 0.5$ V; $\eta = 0.5$.

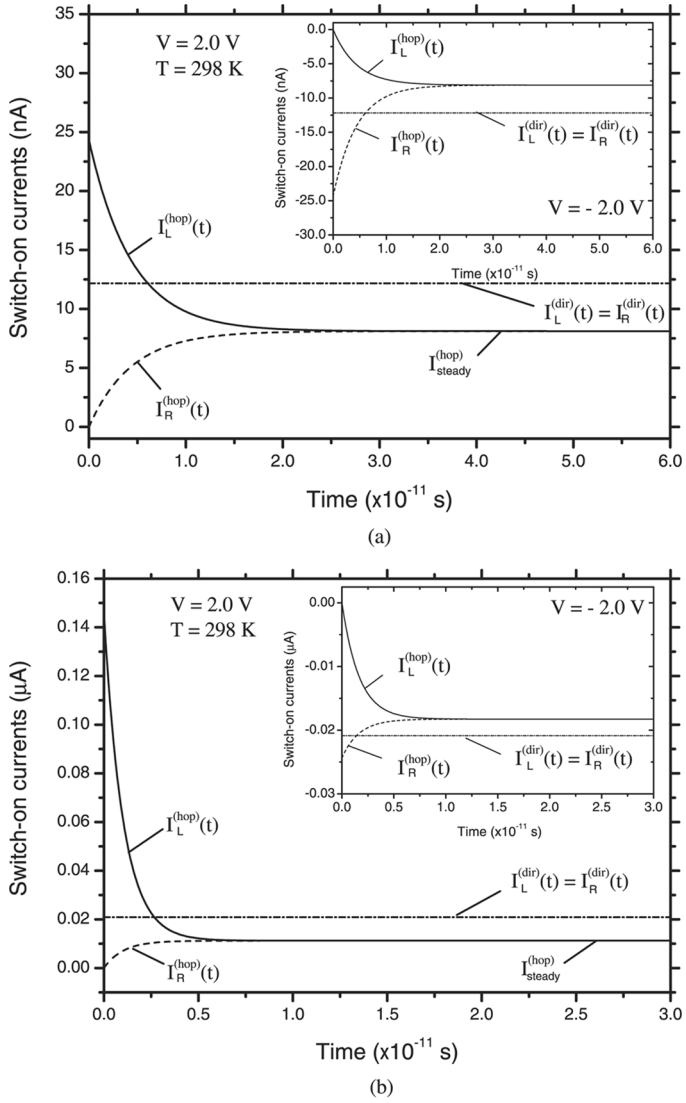



**FIGURE 4** Evolution of current components in LMR-system just after an instantaneous rise of the applied voltage from $V = 0$ to $V \neq 0$. Resonant regime of transmission through the LUMO is shown for the case of symmetric (a) and asymmetric (b) coupling of the molecule to the electrodes. At asymmetric coupling, a maximal value of the switch-on hopping current differs strongly on the steady current. Direct (tunnel) current $I_L^{(dir)}(t) = I_R^{(dir)}(t) = I^{(tun)}$ is time and temperature independent value. The calculations are based on Eqs. (10) and (14) at $\Delta E(0) = 0.3$ eV, $\Gamma_L = \Gamma_R = 5 \cdot 10^{-5}$ eV (a), $\Gamma_L = 3 \cdot 10^{-3}$ eV, $\Gamma_R = 5 \cdot 10^{-5}$ eV (b); $V = \pm 2$V, $T = 298$ K; $\eta = 0.5$.

where one has to set $r = L, r' = R$ (at $V = V_2 > 0$) and $r = R, r' = L$ (at $V = V_2 < 0$). Analogously, setting $V_1 = 0, V_2 = V$ we derive from Eq. (17) and (18) the following expression for switch-on currents,

$$I_L^{(hop)}(0) \simeq I_0 2\pi\Gamma_L n(\Delta E_L(V)),$$
$$I_R^{(hop)}(0) \simeq I_0 2\pi\Gamma_R n(\Delta E(0)),\ (V > 0) \tag{21}$$

and

$$I_L^{(hop)}(0) \simeq\ -I_0 2\pi\Gamma_L n(\Delta E(0)),$$
$$I_R^{(hop)}(0) \simeq -I_0 2\pi\Gamma_R n(\Delta E_R(V)),\ (V < 0). \tag{22}$$

It is not difficult to see that quantity

$$\zeta_{L/R}^{(on)} = \frac{I_L^{(hop)}(0)}{I_R^{(hop)}(0)} = \frac{\Gamma_L}{\Gamma_R} \times \begin{cases} n(\Delta E_L(V))/n(\Delta E(0)) & \text{if } V > 0 \\ n(\Delta E(0))/n(\Delta E_R(V)) & \text{if } V < 0 \end{cases} \tag{23}$$

varies in wide region dependently on a precise magnitude of the applied voltage as well as the width parameters. Quantity $\zeta_{L/R}^{(on)} = \zeta_{L/R}^{(on)}(V)$ can be large (at $V > 0$) or small (at $V < 0$) both at symmetric and nonsymmetric coupling of the molecule to the electrodes (i.e., at $\Gamma_L = \Gamma_R$ and $\Gamma_L \neq \Gamma_R$, respectively). The third peculiarity refers to a ratio between the switch-on currents and the steady current. Let, for instance, an applied voltage be positive and $\Gamma_L \geq \Gamma_R$. In this case, the ratio of a maximal switch-on current to a steady hopping current reads

$$\zeta^{(on)} = \frac{I_L^{(hop)}(0)}{I_{st}^{(hop)}} = 1 + \frac{\Gamma_L}{\Gamma_R}[1 + n(\Delta E_L(V))]. \tag{24}$$

In contrast with quantity $\zeta_{L/R}^{(on)}$ (which is large even at $\Gamma_L = \Gamma_R$) the ratio (24) depends strongly on relation between the width parameters. If $\Gamma_L = \Gamma_R$ then the $\zeta^{(on)}$ is equal to 2 and 3 (at off-resonant and resonant transmission regimes, respectively). But, the ratio becomes large at $\Gamma_L/\Gamma_R \gg 1$. Thus, the quantity like $\zeta^{(on)}$ can be employed as the characteristic of switching on effect in a molecular diode. It is important to stress that the effect appears only at asymmetric coupling of the molecule to the electrodes (compare Figs. 4a and 4b). Note also, that a tunnel current component as well as a steady hopping current component alternate insignificantly even though one of the width parameters (the $\Gamma_L$ in our case) increases strongly. At the same time, the condition $\Gamma_r/\Gamma_{r'} \gg 1, (r' \neq r)$, leads to large switching on effect at $V > 0, r = L, r' = R$ or $V < 0, r = R, r' = L$.

## III. 2 Switch-Off Currents

Let a voltage bias drop suddenly from $V_1 = V$ to $V_2 = 0$ so that the establishment of steady current in LMR-system is achieved at identical chemical potentials of the electrodes, i.e., at $\mu_L = \mu_R = E_F$. Due to such regime of transmission a common current, Eq. (9) does not contain a distant (tunnel) current component. As to the hopping current components $I_L^{(hop)}(t)$ and $I_R^{(hop)}(t)$, they evolve to a common value $I_{st}^{(hop)} = I_{st}^{(hop)}(V_2) = 0$. Figure 5 manifests a current behavior at symmetric (panel a) and asymmetric (panel b) coupling of the molecule to the electrodes. At symmetric coupling, an absolute value of switching off current $I_L^{(hop)}(0)$ coincides with the $I_R^{(hop)}(0)$ whereas at strong asymmetric coupling there is a dramatic difference between the noted currents. One can also indicate a switch-off effect which lies in the fact that one of the switch-off currents (the $I_L^{(hop)}(0)$ in our case) exceeds strongly a steady current $I_{st}^{(hop)} = I_{st}^{(hop)}(V_1)$ formed at $V_1 = V$. [Comparison of Fig. 4b and Fig. 5b shows that $I_{st}^{(hop)}(V = 2\text{V}) \approx 10\text{n}A$ and $I_L^{(hop)}(0) \approx -70\,\text{n}A$.] All noted peculiarities can be explained on the base of analytic expressions

$$I_L^{(hop)}(0) \simeq -I_0 2\pi\Gamma_L \Phi_{LR}(V),$$
$$I_R^{(hop)}(0) \simeq I_0 2\pi\Gamma_R \Phi_{LR}(V),\ (V > 0), \tag{25}$$

and

$$I_L^{(hop)}(0) \simeq -I_0 2\pi\Gamma_L \Phi_{RL}(V),$$
$$I_R^{(hop)}(0) \simeq I_0 2\pi\Gamma_R \Phi_{RL}(V),\ (V > 0), \tag{26}$$

[Eqs. (25) and (26) follow from respective Eqs. (17) and (18) at $V_1 = V, V_2 = 0$ and $|V_1 - V_2| > 0.1$ V.] In Eqs. (25) and (26), we have introduced the factor

$$\Phi_{LR}(V) = \frac{\Gamma_L n(\Delta E_L(V)) - \Gamma_R n(\Delta E(0))}{\Gamma_L[1 + n(\Delta E_L(V))] + \Gamma_R}. \tag{27}$$

Expressions (25)–(27) show that quantity

$$\zeta_{L/R}^{(off)} = \left|\frac{I_L^{(hop)}(0)}{I_R^{(hop)}(0)}\right| = \frac{\Gamma_L}{\Gamma_R}. \tag{28}$$

varies in wide region dependently on a precise magnitude of the applied voltage as well as the width parameters. Quantity $\zeta_{L/R}^{(off)}$ becomes large at strong coupling asymmetry (i.e., at $\Gamma_L \gg \Gamma_R$) independently on the voltage polarity. Note that a ratio of maximal

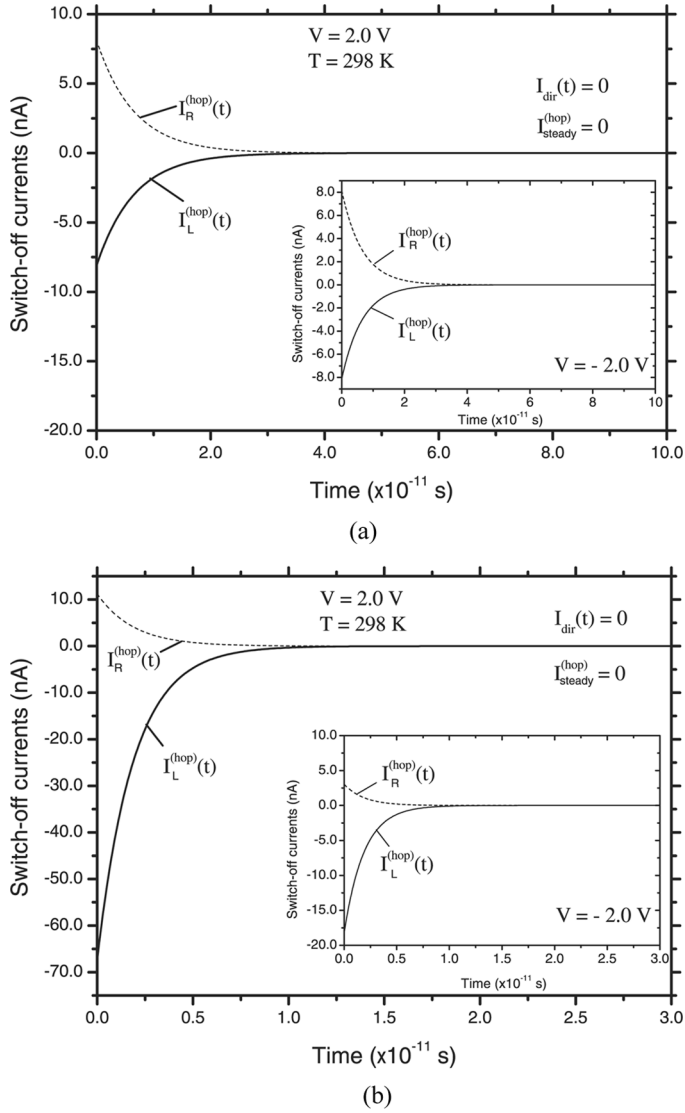



**FIGURE 5** Evolution of current components in LMR-system just after an instantaneous drop of the applied voltage from $V \neq 0$ to $V = 0$. Resonant regime of transmission through the LUMO is shown for the case of symmetric (a) and asymmetric (b) coupling of the molecule to the electrodes. At asymmetric coupling, a maximal value of the switch-off hopping current differs strongly on the steady current formed at $V = \pm 2$ V. Direct (tunnel) current $I_L^{(dir)}(t) = I_R^{(dir)}(t) = I^{(tun)}$ is completely absent. The calculations are based on Eqs. (10) and (14) at $\Delta E(0) = 0.3$ eV, $\Gamma_L = \Gamma_R = 5 \cdot 10^{-5}$ eV (a), $\Gamma_L = 3 \cdot 10^{-3}$ eV, $\Gamma_R = 5 \cdot 10^{-5}$ eV (b); $T = 298$ K; $\eta = 0.5$.

switch-off current (the $|I_L^{(hop)}(0)|$ in a given case) to steady current $I_{st}^{(hop)} = I_{st}^{(hop)}(V_1 = V)$ is also determined through Eq. (28) and can be large. At last, one has to pay attention that independently on the sign of starting steady current $I_{st}^{(hop)}(V_1 = V)$ the current $I_L^{(hop)}(t)$ is negative while the current $I_R^{(hop)}(t)$ is positive. This fact indicates that switch-off currents $I_L^{(hop)}(0)$ and $I_R^{(hop)}(0)$ reflect a starting kinetics of molecular discharge. [If LMR-system exhibits itself as a molecular diode, one of the switching currents exceeds strongly the second one, cf. Fig. 5b.]

## IV. CONCLUSIONS

Based on the simplest model of system "electrode L-molecule-electrode R" (LMR) we show analytically that at a sudden alteration of applied voltage from $V_1$ to $V_2$, the currents $I_L^{(hop)}(t)$ and $I_R^{(hop)}(t)$ through respective electrodes (cf. Fig. 1) do not coincide for as long as the charge transmission process in a molecular diode remains transient. Steady current $I_{st}^{(hop)}$ is formed only at $t \gg \tau_{st}$ where quantity $\tau_{st}$ is the time that characterizes the establishment of stationary electron transmission in LMR-system. At symmetric coupling of the molecule to the electrodes, the switch-on (-off) currents $I_L^{(hop)}(0)$ and $I_R^{(hop)}(0)$ appearing just after a sudden voltage alteration from $V_1 = 0$ to $V_2 = V \neq 0$ (or from $V_1 = V \neq 0$ to $V_2 = 0$), do not strongly differ from steady current $I_{st}^{(hop)}$ formed at $V \neq 0$. But, if the noted coupling is strongly asymmetric, then diode properties of the molecule embedded between the electrodes, become significant so that one of the switch-on or switch-off currents ($I_L^{(hop)}(0)$ or $I_R^{(hop)}(0)$) exceeds noticeably the $I_{st}^{(hop)}$ (cf. Eqs. (24) and (28) at $\Gamma_L \gg \Gamma_R$ as well as Fig. 4b and Fig. 5b). This effect may be very important in molecular electronics where single molecules are assumed to use as basic functional elements. It follows from the results presented in a given communication, that it is desirable, where possible, to avoid the use strongly asymmetric contacts of molecular diode with the leads.

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