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Formation of a Current Through Organic Molecules with Strongly Separated Energy Levels

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A theoretical description of the current formation in a device "source-molecule-drain" (SMD) is carried out for a special type of molecules with strongly separated energy levels. Owing to charge molecule-electrodes hoppings, the vacant molecular levels are populated by the transferred electrons, so that a molecule is kinetically charged. The theoretical explanation of the current-voltage characteristics of a molecule $(Bu_2\ N\ \phi V)_2\ BuPy^+I^-$ *is carried out, and it is shown that the rectification effect appears due to the asymmetric voltage drop across the molecule, as well as asymmetric molecular charging.*

Keywords: electron transfer; kinetic charging; rectification; single molecule

PACS Numbers: 34.70. + e, 72.10.-d, 82.20.Mj

I. INTRODUCTION

It has been noted in the 1980s [1,2], that specific molecular nanostructures are ideal candidates to be utilized in electronics to provide different basic functions such as, e.g., the rectification or electron blockade. The current studies of the charge conductivity of single molecules [3–16] manifest various types of nonlinearity in current-voltage (I–V) characteristics including those with negative differential resistance. Therefore, the problem arises to clarify not only the basic physical principles of charge transmission through molecules but to specify the physical mechanisms responsible for the current formation in each specific case. The important role of molecule-electrode contacts [7,13,17], as well as

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the Coulomb interaction [18], in the formation of the current through a molecule is well established. Moreover, the influence of the electron-phonon coupling on inelastic transfer processes and the phonon-assisted charge transmission becomes understandable [19–24]. But, there exists a huge of problems related to the description of correlation effects that control a single-particle charge transmission through a molecule and, thus, modify the *I–V* characteristics of the molecule. There are two types of correlation effects. The first one is associated with the Coulomb repulsion among the excess electrons/holes trapped by a molecule in the course of the charge transmission through the molecule. The second type refers to kinetic processes responsible for the trapping. It has been shown [23–25] that the Coulomb repulsion forms different transmission channels, while the molecule-electrode and electrode-molecule hoppings determine a probability for extra charges to occupy the molecule. The goal of the present communication is to show the governing role of the inelastic electrode-molecule and molecule-electrode hopping processes in the formation of not only a sequential two-step transmission route but a direct one-step tunneling route. The governing occurs via the kinetic charging of the molecule. Some analytic results are derived for a specific case of the transmission through two frontier molecular orbitals (MOs). It is shown that, at the resonant regime of charge transmission, the kinetic charging becomes essentially important. If the electron hoppings between the molecule and one of the electrodes differ from similar hoppings between the molecule and another electrode, then the kinetic molecular charging becomes asymmetric and depends strongly on the direction of an applied electric field. This results in a specific kinetic rectification effect.

II. MODEL AND BASIC EQUATIONS

To demonstrate the role of kinetic charging in the formation of a current through a molecule, we employ a model where the reference system is associated with two nonmagnetic macroscopic electrodes (source and drain) connected by a molecule (SMD device, Fig. 1a). It is supposed that the energetic structure of each lead is determined by the quasicontinuous band spectrum, while the molecule is characterized by discrete electronic levels. We consider a particular case where the lowest unoccupied molecular orbital (LUMO) is well separated from the set of the rest LUMOs. The same refers to the highest occupied molecular orbital (HOMO) (Fig. 1b). Therefore, in a certain voltage region, one can ignore the participation of the LUMO + 1, LUMO + 2,... and the HOMO − 1, HOMO − 2,... in the formation of the current. [For instance, such a situation occurs for molecule

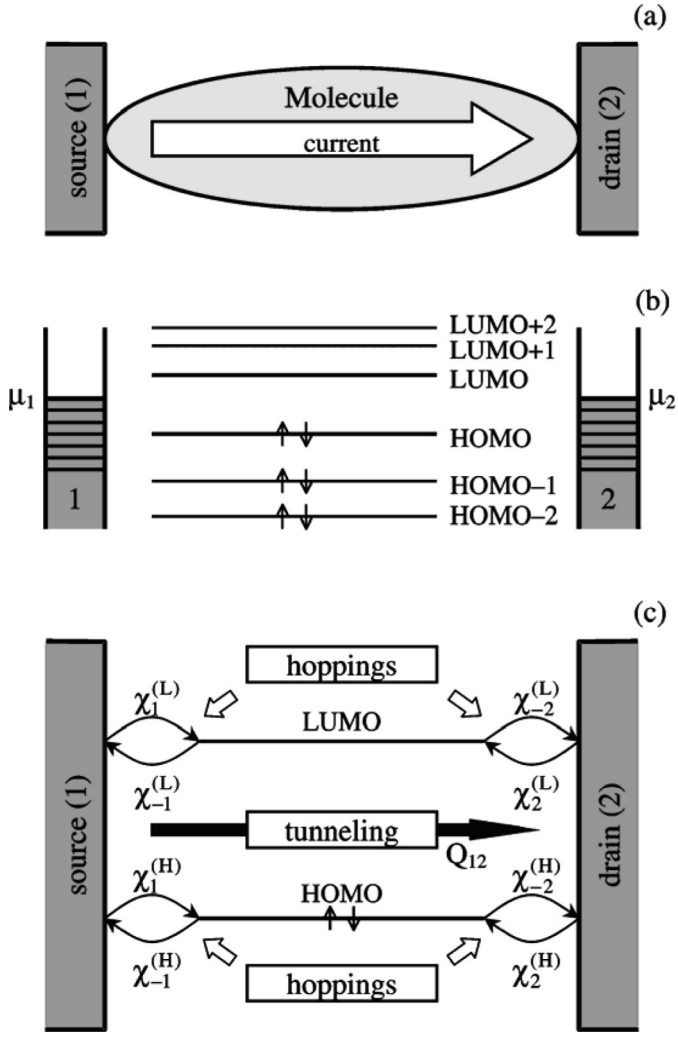

FIGURE 1 Formation of the current through a molecule with two frontier MOs LUMO and HOMO). At the resonant regime of transmission, the electrode-molecule and molecule-electrode hoppings (the respective rates are $\chi_j^{(r)}$ and $\chi_{-j}^{(r)}, j = 1, 2, r = L, H$) lead to the kinetic reduction or kinetic oxidation of the molecule and, thus, to the formation of different transmission channels. Therefore, during the charge transmission along a precise channel, both the sequential (hopping) and tunnel routes are controlled by a charge state of the molecule. Tunneling along all possible channels is denoted through the tunnel flow Q_{12}.

9,10-Bis(2'-para-mercaptophenyl)-ethinyl-antracene in the voltage region [–1V, +1V] [13]]. We also assume the absence of a magnetic field and the zero-spin state for the neutral molecule. A corresponding electronic Hamiltonian for the SMD device can be chosen in the form

$$H_{SMD} = H_{leads} + H_{mol} + V_{leads-mol} \tag{1}$$

where the first term,

$$H_{leads} = \sum_{r=1,2} \sum_{\mathbf{k},\sigma} E_{r\mathbf{k}} a^{+}_{r\mathbf{k}\sigma} a_{r\mathbf{k}\sigma}, \tag{2}$$

refers to the electrodes ($E_{r\mathbf{k}}$ is the energy of an electron with the wave vector $\mathbf{k}$ in the conduction band of the r th electrode; the electron creation operators are denoted as $a^{+}_{r\mathbf{k}\sigma}$, and the annihilation operators as $a_{r\mathbf{k}\sigma}$; the electron spin is fixed by σ). The second term in Eq. (1) is associated with a molecular Hamiltonian written in the Hubbard form,

$$H_{mol} = \sum_{j=L,H} \left[\sum_{\sigma} (\varepsilon_j(V) + U_j c^{+}_{j-\sigma} c_{j-\sigma} + U_{LH} \sum_{j'(\neq j)} \sum_{\sigma'} c^{+}_{j'\sigma'} c_{j'\sigma'}) c^{+}_{j\sigma} c_{j\sigma} \right]. \tag{3}$$

Here, $\varepsilon_j(V)$ is the energy of an electron occupying the j th MO (the respective electron creation and electron annihilation operators are given by $c^{+}_{j\sigma}$ and $c_{j\sigma}$). The Coulomb interaction between two electrons is defined via the repulsion Hubbard parameters U_j (both electrons occupy the LUMO ($j = \mathrm{L}$) or the HOMO ($j = \mathrm{H}$)) and U_{LH} (one electron occupies the LUMO, another the HOMO). The third term in Eq. (1) determines the off-diagonal interaction between the electrodes and the molecule. It reads

$$V_{leads-mol} = \sum_{j=L,H} \sum_{r=1,2} \sum_{\mathbf{k},\sigma} (V_{jr\mathbf{k}} c^{+}_{j\sigma} a_{r\mathbf{k}\sigma} + V^{*}_{jr\mathbf{k}} a^{+}_{r\mathbf{k}\sigma} c_{j\sigma}). \tag{4}$$

Here, the $V_{jr\mathbf{k}}$ defines the transfer coupling between the j th MO (with energy $\varepsilon_j(V)$) and the $r\mathbf{k}$-th band state (with energy $E_{r\mathbf{k}}$). Hamiltonians in the form like Eqs. (1)–(4) were used by various authors to describe the electron transfer through the isolated level of a quantum dot or a molecule (see, e.g., Refs. [26–28]). Since the exchange interaction within the SMD system is assumed to be negligible, a spin state of the system is determined by the spin projection of the electrons involved into a specific transfer process. The model Hamiltonian (1)–(4) allows us to describe the averaged I–V characteristics ignoring a fine phonon structure of the current [29]. It simplifies strongly the analytic description, what is especially important if one studies the problem of dynamic electron-electron correlation in a charge transmitting device.

The main influence of the applied voltage on the charge transfer properties of a molecule occurs via a shift of the molecular energy levels $\varepsilon_j(V)$ [30]. The detailed analysis shows that a linear shift is valid either for a well-localized MO or for a strongly delocalized MO. If, however, the intramolecular distribution of the electronic density is controlled by the applied voltage, then an energy shift becomes nonlinear. For instance, this is happen if the applied voltage is able to transform the localized MOs into the delocalized MOs or vice versa [31]. In what follows, we assume that, in a given voltage region, the energy shift remains linear so that

$$\varepsilon_j(V) = \varepsilon_j(0) + \eta_j eV, \tag{5}$$

where $\varepsilon_j(0)$ is the position of a single-electron level in the absence of the applied voltage, and $V = V_D - V_S$ is the voltage bias between the drain and the source. The quantity η_j denotes the voltage division factor [3,6,10,31].

Following the unified kinetic description of the charge transport in single molecules and molecular wires (see Refs. [23,25] and especially Ref. [24]), one has to derive the time derivative of the total number of electrons present in the source or the drain ($\dot{\mathcal{N}}_1$ and $\dot{\mathcal{N}}_2 = -\dot{\mathcal{N}}_1$, respectively), as well as the time derivative of molecular occupancies $\mathcal{P}(M)$, where the symbol M indicates the precise molecular electronic state. Then the current is calculated by using the expression

$$I = e\dot{\mathcal{N}}_1(t), \tag{6}$$

where the number of electrons in the source,

$$\mathcal{N}_1(t) = \sum_{\mathbf{k}\sigma} P_{1\mathbf{k}\sigma}(t), \tag{7}$$

is defined by the single-electron state population $P_{1\sigma\mathbf{k}\sigma}(t)$. Using the Hamiltonian given by Eqs. (1)–(4), one is able to derive the kinetic equations for single-electron occupancies $P_{1\sigma\mathbf{k}\sigma}(t)$ and, thus, for the quantity $\mathcal{N}_1(t)$. In what follows, we assume that the intra-level Coulomb interaction between the extra electrons exceeds largely the Coulomb interaction between the electrons occupying different frontier Mos, so that $U_L,\ U_H \gg U_{LH}$. This means that two extra (transferred) electrons can occupy the LUMO with a minor probability. Analogously, the removal of two electrons from the HOMO is unlikely. Thus, omitting the kinetic processes that create doubly reduced or doubly oxidized charge molecular states, one derives

$$\dot{\mathcal{N}}_1 = \dot{\mathcal{N}}_1^{(0)} + \dot{\mathcal{N}}_1^{(-)} + \dot{\mathcal{N}}_1^{(+)} + \dot{\mathcal{N}}_1^{(*)}. \tag{8}$$

Here, the symbols (0), (–), and (+) denote, respectively, charge neutral, singly reduced, and singly oxidized states of the molecule. The excited state (*) indicates the electronic configuration of a neutral molecule with singly occupied LUMO and HOMO. Each term on the right-hand side of Eq. (8) includes a contribution from direct and sequential transmission routes, so that

$$\dot{\mathcal{N}}_1^{(j)} = \dot{\mathcal{N}}_{1dir}^{(j)} + \dot{\mathcal{N}}_{1seq}^{(j)}, \quad (j = 0, -, +, *). \tag{9}$$

The precise form of each contribution reads

$$\dot{\mathcal{N}}_{1dir}^{(0)} = -\sum_{\sigma,\sigma'} [Q_{1\sigma\to 2\sigma'}^{(L)}(L0;H2) + Q_{1\sigma\to 2\sigma'}^{(H)}(L0;H2)]\mathcal{P}(L0;H2), \tag{10}$$

$$\begin{aligned}\dot{\mathcal{N}}_{1seq}^{(0)} = &-\sum_{\sigma} [\chi_{1\sigma}^{(L)}\mathcal{P}(L0;H2) - \chi_{-1\sigma}^{(L)}\mathcal{P}(L\sigma;H2)] \\ &-\sum_{\sigma} [\chi_{1\sigma}^{(H)}\mathcal{P}(L0;H-\sigma) - \chi_{-1\sigma}^{(H)}\mathcal{P}(L0;H2)\mathcal{P}(L\sigma;H-\sigma)],\end{aligned} \tag{11}$$

$$\dot{\mathcal{N}}_{1dir}^{(-)} = -\sum_{\sigma_L}\sum_{\sigma,\sigma'} [Q_{1\sigma\to 2\sigma'}^{(L)}(L\sigma_L;H2) + Q_{1\sigma\to 2\sigma'}^{(H)}(L\sigma_L;H2)]\mathcal{P}(L\sigma_L;H2), \tag{12}$$

$$\begin{aligned}\dot{\mathcal{N}}_{1seq}^{(-)} = &-\sum_{\sigma} [\chi_{1\sigma}^{(L)}\mathcal{P}(L0;H2) - \chi_{-1\sigma}^{(L)}\mathcal{P}(L\sigma;H2)] \\ &-\sum_{\sigma_L}\sum_{\sigma} [\chi_{1\sigma}^{(H(L))}(L\sigma_L;H-\sigma) - \chi_{-1\sigma}^{(H(L))}\mathcal{P}(L\sigma_L;H2)],\end{aligned} \tag{13}$$

$$\dot{\mathcal{N}}_{1dir}^{(+)} = -\sum_{\sigma_H}\sum_{\sigma,\sigma'} [Q_{1\sigma\to 2\sigma'}^{(L)}(L0;H\sigma_H) + Q_{1\sigma\to 2\sigma'}^{(H)}(L0;H\sigma_H)]\mathcal{P}(L0;H\sigma_H), \tag{14}$$

$$\begin{aligned}\dot{\mathcal{N}}_{1seq}^{(+)} = &-\sum_{\sigma} [\chi_{1\sigma}^{(H)}\mathcal{P}(L0;H-\sigma) - \chi_{-1\sigma}^{(H)}\mathcal{P}(L0;H2)] \\ &-\sum_{\sigma_H}\sum_{\sigma} [\chi_{1\sigma}^{(L(H))}\mathcal{P}(L0;H\sigma_H) - \chi_{-1\sigma}^{(L(H))}\mathcal{P}(L\sigma;H\sigma_H)],\end{aligned} \tag{15}$$

and

$$\dot{\mathcal{N}}^{(*)}_{1dir} = -\sum_{\sigma_L\sigma_H}\sum_{\sigma,\sigma'}[Q^{(L)}_{1\sigma\to 2\sigma'}(L\sigma_L;H\sigma_H) + Q^{(H)}_{1\sigma\to 2\sigma'}(L\sigma_L;H\sigma_H)]\mathcal{P}(L\sigma_L;H\sigma_H), \tag{16}$$

$$\dot{\mathcal{N}}^{(*)}_{1seq} = -\sum_{\sigma_L}\sum_{\sigma}[\chi^{(H(L))}_{1\sigma}\mathcal{P}(L\sigma_L;H-\sigma) - \chi^{(H(L))}_{-1\sigma}\mathcal{P}(L\sigma_L;H2)] - \sum_{\sigma_H}\sum_{\sigma}[\chi^{(L(H))}_{1\sigma}\mathcal{P}(L0;H\sigma_H) - \chi^{(L(H))}_{-1\sigma}\mathcal{P}(L\sigma;H\sigma_H)]. \tag{17}$$

Symbols "L" and "H" (indicating the tunneling flows $Q^{(L)}_{1\sigma\to 2\sigma'}$ and $Q^{(H)}_{1\sigma\to 2\sigma'}$) characterize the transmission with participation of the LUMO and the HOMO, respectively. Symbols $\nu = L, H, L(H), H(L)$ (refered to the hopping transfer rates) specify the precise transmission channels. Thus, the channel $\nu = L$ indicates the electron transmission through the empty LUMO, whereas the HOMO is doubly occupied by inner electrons. The channel $\nu = H$ is associated with the electron transmission through a singly occupied HOMO while the LUMO is empty. The channel $\nu = L(H)$ supposes the transmission of an electron through the empty LUMO under the condition that the HOMO is occupied by only a single electron. Analogously, the channel $\nu = H(L)$ reflects the electron transmission through a singly occupied HOMO under the condition that the LUMO contains a single extra electron. In Eqs. (10)–(17), the molecular electronic occupancies are defined by the quantities $\mathcal{P}(L0;H2)$ (the LUMO is empty, the HOMO is doubly filled), $\mathcal{P}(L\sigma_L;H2)$ (the LUMO is occupied by a single extra electron with spin projection σ_L, the HOMO is doubly filled), $\mathcal{P}(L0;H\sigma_H)$ (the LUMO is empty, the HOMO contains a single electron with spin projection σ_H), and $\mathcal{P}(L\sigma_L;H\sigma_H)$ (the LUMO and the HOMO are singly populated by the electrons with respective spin projections σ_L and σ_H). Since Hamiltonian (1)–(4) is written in terms of the electron creation and annihilation operators, we describe the transmission of charges through the molecule exclusively as the transfer of electrons, no matter the LUMO or HOMO mediates this transfer. Therefore, the molecular occupancies are associated only with the precise electronic configurations. Figures 2 and 3 illustrate the possible electronic configurations and the respective molecular occupancies that appear during the electron transmission along each indicated channel ν. The occupancies satisfy the normalization condition

$$\mathcal{P}(L0;H2) + \sum_{\sigma}\mathcal{P}(L\sigma;H2) + \sum_{\sigma}\mathcal{P}(L0;H\sigma) + \sum_{\sigma,\sigma'}\mathcal{P}(L\sigma;H\sigma') = 1 \tag{18}$$

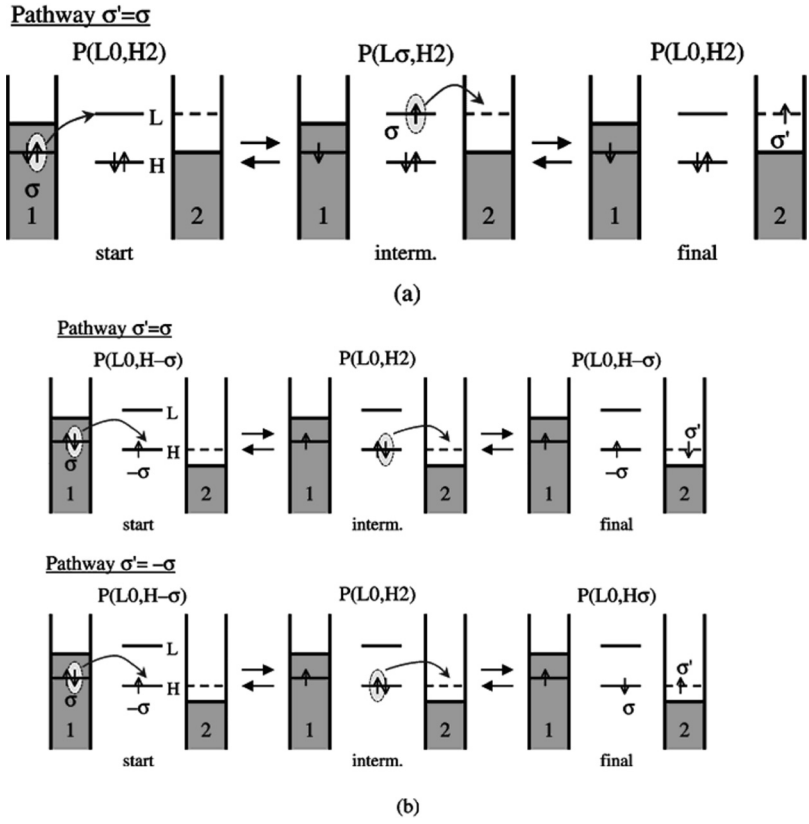

FIGURE 2 Electron transfer along the transmission channels $\nu = L$ (a) and $\nu = H$ (b). Only a single pathway exists for the channel $\nu = L$, while the channel $\nu = H$ includes two electronic pathways associated with the conservation ($\sigma' = \sigma$) and nonconservation ($\sigma' = -\sigma$) of the electron spin projection during both the sequential and tunneling transmissions.

and are governed by the closed set of kinetic equations

$$\dot{\mathcal{P}}(L0;H2) = -\sum_{\sigma}\Big[(\chi^{(L)}_{1\sigma} + \chi^{(L)}_{2\sigma}) + (\chi^{(H)}_{-1\sigma} + \chi^{(H)}_{-2\sigma})\Big]\mathcal{P}(L0;H2) + \sum_{\sigma}\Big[(\chi^{(H)}_{1-\sigma} + \chi^{(H)}_{2-\sigma})\mathcal{P}(L0;H\sigma) + (\chi^{(L)}_{-1\sigma} + \chi^{(L)}_{-2\sigma})\mathcal{P}(L\sigma;H2)\Big],$$

$$\dot{\mathcal{P}}(L\sigma;H2) = -\Big[(\chi^{(L)}_{-1\sigma} + \chi^{(L)}_{-2\sigma}) + \sum_{\sigma'}(\chi^{(H(L))}_{-1\sigma'} + \chi^{(H(L))}_{-2\sigma'})\Big]\mathcal{P}(L\sigma;H2) + (\chi^{(L)}_{1\sigma} + \chi^{(L)}_{2\sigma})\mathcal{P}(L0;H2) + \sum_{\sigma'}(\chi^{(H(L))}_{1-\sigma'} + \chi^{(H(L))}_{2-\sigma'})\mathcal{P}(L\sigma;H\sigma'),$$

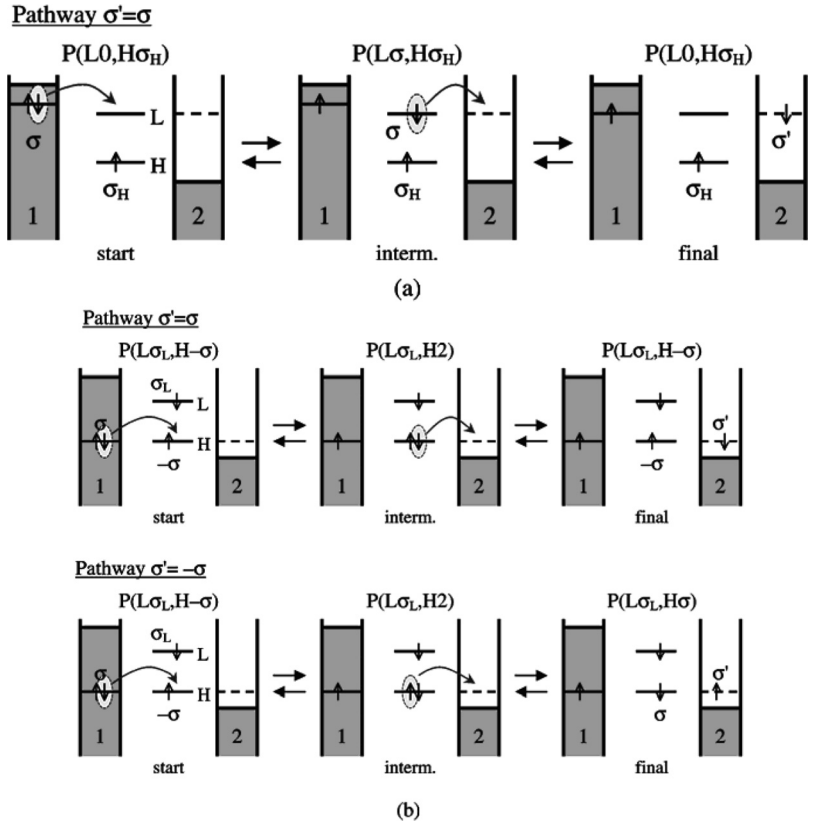

FIGURE 3 Electron transfer along the transmission channels $\nu = L(H)$ (a) and $\nu = H(L)$ (b). Only a single pathway is valid for the channel $\nu = L(H)$, while the channel $\nu = H(L)$ includes two electronic pathways associated with the conservation ($\sigma' = \sigma$) and nonconservation ($\sigma' = -\sigma$) of the electron spin projection during both the sequential and tunneling transmissions.

$$\dot{\mathcal{P}}(L0;H\sigma) = -\Big[(\chi^{(H)}_{1-\sigma} + \chi^{(H)}_{2-\sigma}) + \sum_{\sigma'}(\chi^{(L(H))}_{1\sigma'} + \chi^{(L(H))}_{2\sigma'})\Big]\mathcal{P}(L0;H\sigma)$$
$$+(\chi^{(H)}_{-1-\sigma} + \chi^{(H)}_{-2-\sigma})\mathcal{P}(L0;H2) + \sum_{\sigma'}(\chi^{(L(H))}_{-1\sigma'} + \chi^{(L(H))}_{-2\sigma'})\mathcal{P}(L\sigma';H\sigma),$$
$$\dot{\mathcal{P}}(L\sigma;H\sigma') = -\Big[(\chi^{(L(H))}_{1\sigma} + \chi^{(L(H))}_{-2\sigma}) + (\chi^{(H(L))}_{1-\sigma'} + \chi^{(H(L))}_{2-\sigma'})\Big]\mathcal{P}(L\sigma;H\sigma')$$
$$+(\chi^{(L(H))}_{1\sigma} + \chi^{(L(H))}_{2\sigma})\mathcal{P}(L0;H\sigma') + (\chi^{(H(L))}_{-1-\sigma'} + \chi^{(H(L))}_{-2-\sigma'})\mathcal{P}(L\sigma;H2). \quad (19)$$

In the present article, we consider only stationary *I–V* characteristics of the molecule, and, thus, set (19) is solved under the condition $\dot{\mathcal{P}}(L0;H2)=0$, $\dot{\mathcal{P}}(L\sigma;H2)=0$, $\dot{\mathcal{P}}(L0;H\sigma)=0$, and $\dot{\mathcal{P}}(L\sigma;H\sigma')=0$. In the absence of a magnetic field, the occupancies are independent of the spin projections, so that one can set $\mathcal{P}(L0;H2)\equiv\mathcal{P}_0$, $\mathcal{P}(L\sigma;H2)\equiv\mathcal{P}_L$, $\mathcal{P}(L0;H\sigma)\equiv\mathcal{P}_H$, and $\mathcal{P}(L\sigma;H\sigma')\equiv\mathcal{P}_{LH}$. The same refers to the hopping transfer rates. Noting $\chi^{(\nu)}_{r(-r)\sigma}\equiv\chi^{(\nu)}_{r(-r)}$ and solving set (19), we obtain the analytic expression for stationary molecular occupancies as

$$\begin{aligned}
\mathcal{P}_0 &= \frac{1}{D}\left[(A_{L(H)}+B_{H(L)})A_LB_H+2(A_LB_{H(L)}B_{L(H)}+B_HA_{L(H)}A_{H(L)})\right],\\
\mathcal{P}_L &= \frac{1}{D}\left[2(B_L+A_H)B_{H(L)}B_{L(H)}+(A_{L(H)}+B_{H(L)})B_HB_L\right],\\
\mathcal{P}_H &= \frac{1}{D}\left[2(B_L+A_H)A_{H(L)}A_{L(H)}+(A_{L(H)}+B_{H(L)})A_HA_L\right],\\
\mathcal{P}_{LH} &= \frac{1}{D}\left[2(B_L+A_H)A_{H(L)}B_{L(H)}+A_LA_HB_{L(H)}+B_HB_LA_{H(L)}\right],
\end{aligned}\tag{20}$$

where we have introduced

$$\begin{aligned}
D = {} & (A_{L(H)}+B_{H(L)})(2A_LA_H+2B_HB_L+A_LB_H)\\
& +2A_LB_{L(H)}(B_{H(L)}+2A_H)+2B_HA_{H(L)}(A_{L(H)}+2B_L)\\
& +4(B_L+A_H)(A_{H(L)}A_{L(H)}+B_{H(L)}B_{L(H)}+2B_{L(H)}A_{H(L)})]
\end{aligned}\tag{21}$$

and

$$A_\nu=\chi^{(\nu)}_{-1}+\chi^{(\nu)}_{-2},\ B_\nu=\chi^{(\nu)}_{1}+\chi^{(\nu)}_{2},(\nu=L,H,L(H),H(L)).\tag{22}$$

III. TUNNELING FLOWS AND HOPPING TRANSFER RATES

Substituting expressions (20) into Eqs. (8)–(17) and using definition (6), we can derive the analytic form for the current through a molecule. To do it, we consider, at first, the structure of tunneling flows $Q^{(\nu)}_{1\sigma\to2\sigma'}$. The quantity

$$Q^{(\nu)}_{1\sigma\to2\sigma'}=\frac{2\pi}{\hbar}\sum_{\mathbf{k},\mathbf{q}}|V^{(\nu)}_{2\mathbf{q}\sigma',1\mathbf{k}\sigma}|^2(f_1(E_{1\mathbf{k}}-\mu_1)-f_2(E_{2\mathbf{q}}-\mu_2))\delta(E_{1\mathbf{k}}-E_{2\mathbf{q}})\tag{23}$$

is defined through the Fermi distribution function $f_r(E_{r\mathbf{k}}-\mu_r)=\{\exp[(E_{r\mathbf{k}}-\mu_r)/k_BT]+1\}^{-1}$ for the source ($r=1$) and the drain

($r = 2$), as well as through a distant electrode-electrode coupling

$$V^{(\nu)}_{2\mathbf{q}\sigma',1\mathbf{k}\sigma} = \sum_{i(\nu)} \frac{\langle 2\mathbf{q}\sigma', f(\nu)|V_{leads-mol}|i(\nu)\rangle\langle i(\nu)|V_{leads-mol}|1\mathbf{k}\sigma, s(\nu)\rangle}{E_{tr(\nu)} - E_{i(\nu)} + i\Gamma^{(\nu)}/2} \quad (24)$$

which is responsible for the tunneling electron transmission along the precise channel ν. The distant coupling depends on the starting (s), intermediate (i), and final (f) electronic states of the SMD device. For instance, if the transmission occurs via the channel $\nu = L$ (cf. Fig. 2a), then the mentioned electronic states can be written (in the second quantization representation) as $|1\mathbf{k}\sigma, s(L)\rangle = a^+_{1\mathbf{k}\sigma}c^+_{H+1/2}c^+_{H-1/2}|0\rangle$, $|i(L)\rangle = c^+_{L\sigma}c^+_{H+1/2}c^+_{H-1/2}|0\rangle$, and $|2\mathbf{q}\sigma, f(L)\rangle == a^+_{2\mathbf{q}\sigma}c^+_{H+1/2}c^+_{H-1/2}|0\rangle$ ($|0\rangle$ is the vacuum state for electrons (see more details in Ref. [24]). The corresponding energies are the proper energies of the Hamiltonian $H_0 = H_{leads} + H_{mol}$ [cf. Eqs. (2) and (3)]. Thus, the transmission energy appears as $E_{tr(L)} = E_{1\mathbf{k}} + 2\varepsilon_H(V) + U_H$, while the energy of intermediate state reads $E_{i(L)} = \varepsilon_L(V) + 2U_{LH} + 2\varepsilon_H(V) + U_H$. The broadening parameter $\Gamma^{(L)}$ is defined as the sum

$$\Gamma^{(j)} = \Gamma^{(j)}_1 + \Gamma^{(j)}_2 \quad (25)$$

taken at $j = L$. In Eq. (25),

$$\Gamma^{(j)}_r = 2\pi \sum_{\mathbf{k}} |V_{jr\mathbf{k}}|^2 \delta(E - E_{r\mathbf{k}}), \quad (r = 1, 2, \quad j = L, H) \quad (26)$$

is the partial half-width. [We use the well-known wide-band limit, when the level width (caused by the molecule-electrode interaction (4)) is assumed to be independent of the transmission energy $E = E_{tr}$ [6,13]. In addition, as the LUMO and the HOMO are well separated energetically, each level width is calculated with use of only diagonal self-energies.]

The precise form of the starting, intermediate, and final electronic states of the SMD system allows us to calculate all matrix elements in expression (24). For the channel $\nu = L$, it yields

$$V^{(L)}_{2\mathbf{q}\sigma',1\mathbf{k}\sigma} = \delta_{\sigma,\sigma'} \frac{V^*_{L2\mathbf{q}} V_{L1\mathbf{k}}}{E_{1\mathbf{k}} - (\varepsilon_L(V) + 2U_{LH}) - i\Gamma^{(L)}/2}. \quad (27)$$

Substituting this matrix element in Eq. (23) and taking a linear shift of the MO and Eq. (5) into account, we get (see also Ref. [31])

$$Q^{(L)}_{1\sigma\to 2\sigma'} = \delta_{\sigma,\sigma'} Q^{(L)}_{12}, \quad Q^{(L)}_{12} = \frac{1}{2\pi\hbar} \int_{-|e|V(1-\eta_L)}^{|e|V\eta_L} dx T^{(L)}(x), \quad (28)$$

where

$$T^{(L)}(x) = \frac{\Gamma_1^{(L)}\Gamma_2^{(L)}}{|x - \Delta E^{(L)}(0) - i(\Gamma_1^{(L)} + \Gamma_2^{(L)})/2|^2} \tag{29}$$

is the transmission function for the channel $\nu = L$ with the $\Delta E^{(L)}(0) = (\varepsilon_L(0) + 2U_{LH}) - E_F$ being the unbiased energy gap for the same channel. A similar form for the transmission function exists for other channels. Generally, for any channel, we obtain

$$Q_{12}^{(\nu)} = \pm\frac{1}{\pi\hbar}\frac{\Gamma_1^{(\nu)}\Gamma_2^{(\nu)}}{\Gamma_1^{(\nu)} + \Gamma_2^{(\nu)}}\Phi^{(\nu)}(V). \tag{30}$$

[Signs + and − refer to the electron transmission through the LUMO and the HOMO, respectively.] In Eq. (30), the width parameters are

$$\Gamma_r^{(L(H))} = \Gamma_r^{(L)}, \Gamma_r^{(H(L))} = \Gamma_r^{(H)}, \quad (r = 1, 2). \tag{31}$$

The voltage dependence of the partial flow $Q_{12}^{(\nu)}$ is comprised in the function

$$\Phi^{(\nu)}(V) = \arctan\left(\frac{2\Delta E_2^{(\nu)}(V)}{\Gamma_1^{(\nu)} + \Gamma_2^{(\nu)}}\right) - \arctan\left(\frac{2\Delta E_1^{(\nu)}(V)}{\Gamma_1^{(\nu)} + \Gamma_2^{(\nu)}}\right), \tag{32}$$

through the voltage-dependent gaps $\Delta E_1^{(\nu)}(V)$ and $\Delta E_2^{(\nu)}(V)$. Note that each gap is associated with the own transmission channel. For instance (cf. Fig. 4),

$$\Delta E_1^{(L)}(V) = \Delta E^{(L)}(0) - |e|V\eta_L, \quad \Delta E_2^{(L)}(V) = \Delta E^{(L)}(0) + |e|V(1 - \eta_L), \tag{33}$$

$$\Delta E_1^{(H)}(V) = \Delta E^{(H)}(0) + |e|V\eta_H, \quad \Delta E_2^{(H)}(V) = \Delta E^{(H)}(0) - |e|V(1 - \eta_H). \tag{34}$$

The unbiased gap $\Delta E^{(L)}(0)$ (for the transmission channel $\nu = L$) has been already defined, while a similar gap (for the channel $\nu = H$) reads $\Delta E^{(H)}(0) = E_F - (\varepsilon_H(0) + U_H)$.

The detailed expression for the hopping rates accounting for the electron-vibration interaction can be found in Refs. [23–25]. In the framework of the averaged description under consideration, we

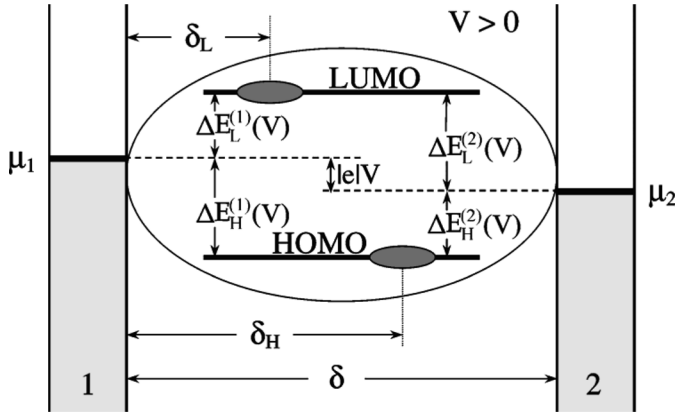

FIGURE 4 Energy gaps associated with the transmission channels $\nu = L$ (the extra electron is transmitted through the LUMO; the HOMO is doubly filled, Fig. 2a) and $\nu = H$ (the extra electron is transmitted through the singly filled HOMO; the LUMO is unfilled, Fig. 2b). The quantities δ_L and δ_H indicate the position of the center of gravity of the electronic density for the LUMO and the HOMO, respectively (the spots show a concentration of the noted density for each frontier MO). The voltage division factors are defined as $\eta_L = \delta_L/\delta$ and $\eta_H = \delta_H/\delta$ [31]. The case is presented when all gaps are positive.

employ the coarse-grained form of the same constants. Adapted to the description of the transmission through only frontier MOs, the transfer rates read

$$\begin{aligned}
\chi_r^{(L,L(H))} &= \frac{1}{\hbar}\Gamma_r^{(L)} n(\Delta E_r^{(L,L(H))}(V)),\\
\chi_{-r}^{(L,L(H))} &= \frac{1}{\hbar}\Gamma_r^{(L)}(1 - n(\Delta E_r^{(L,L(H))}(V))),\\
\chi_r^{(H,H(L))} &= \frac{1}{\hbar}\Gamma_r^{(H)}(1 - n(\Delta E_r^{(H,H(L))}(V))),\\
\chi_{-r}^{(H,H(L))} &= \frac{1}{\hbar}\Gamma_r^{(H)} n(\Delta E_r^{(H,H(L))}(V)),
\end{aligned} \tag{35}$$

where the voltage dependence is concentrated in the distribution function

$$n(\Delta E_r^{(\nu)}(V)) = \frac{1}{\exp[\Delta E_r^{(\nu)}(V)/k_B T] + 1}. \tag{36}$$

IV. RESULTS AND DISCUSSION

The expressions for the tunneling flows as well as for the hopping transfer rates allow us to derive the analytic form of a stationary current. It reads

$$I = I_{dir} + I_{hop}, \tag{37}$$

where

$$I_{dir} = I^{(L)}_{L-B}(\mathcal{P}_0 + 2\mathcal{P}_L) + I^{(H)}_{L-B}(\mathcal{P}_0 + 2\mathcal{P}_H) + 2I^{(L(H))}_{L-B}(\mathcal{P}_H + 2\mathcal{P}_{LH}) + 2I^{(H(L))}_{L-B}(\mathcal{P}_L + 2\mathcal{P}_{LH}) \tag{38}$$

is the direct component of the current associated with a distant one-step electron hopping just between the electrodes. The origin of this hopping is the electrode-electrode electron tunneling with the participation of virtual molecular electronic states. The pure tunneling current along the ν-th transmission channel is described by the Landauer-Büttiker expression

$$I^{(\nu)}_{L-B} = \pm 2I_0 \frac{\Gamma^{(\nu)}_1 \Gamma^{(\nu)}_2}{\Gamma^{(\nu)}_1 + \Gamma^{(\nu)}_2} \Phi^{(\nu)}(V), \tag{39}$$

where we have introduced the current unit $I_0 = (|e|/\pi\hbar) \times 1\text{eV} \approx 80\,\mu\text{A}$. [In Eq. (39), the signs $+$ and $-$ refer to $\nu = L, H(L)$ and $\nu = H, L(H)$, respectively.] Note that, in accordance with Eq. (38), each tunneling transmission channel ν is opened with the corresponding probability $\mathcal{P}_\nu$. Since the latter is defined by the hopping processes in the SMD device, the tunneling is strongly controlled by the sequential transfer processes in the device.

The sequential (hopping) component of the current is given by the expression

$$I_{hop} = 2\pi\hbar I_0[(\chi^{(L)}_1 \mathcal{P}_0 - \chi^{(L)}_{-1}\mathcal{P}_L) + (\chi^{(H)}_1 \mathcal{P}_H - \chi^{(H)}_{-1}\mathcal{P}_0) + 2(\chi^{(L(H))}_1 \mathcal{P}_H - \chi^{(L(H))}_{-1}\mathcal{P}_{LH}) + 2(\chi^{(H(L))}_1 \mathcal{P}_{LH} - \chi^{(H(L))}_{-1}\mathcal{P}_L)]. \tag{40}$$

If the current through a molecule in a given voltage region is associated only with one of the frontier Mos, then each current component is determined by a single term. For instance, if the transmission occurs through the LUMO, then

$$I^{(L)}_{dir} = 2I_0 \frac{\Gamma^{(L)}_1 \Gamma^{(L)}_2}{\Gamma^{(L)}_1 + \Gamma^{(L)}_2} \Phi^{(L)}(V)(\mathcal{P}_0 + 2\mathcal{P}_L). \tag{41}$$

and

$$I_{hop}^{(L)} = 2\pi I_0 \Gamma_1^{(L)} [n(\Delta E_1^{(L)}(V))\mathcal{P}_0 - (1 - n(E_1^{(L)}(V)))\mathcal{P}_L], \qquad (42)$$

where

$$\mathcal{P}_0 = \frac{A_L}{A_L + 2B_L}, \quad \mathcal{P}_L = \frac{B_L}{A_L + 2B_L}, \quad \mathcal{P}_H = \mathcal{P}_{LH} = 0. \qquad (43)$$

Since $\mathcal{P}_0 + 2\mathcal{P}_L = 1$, the direct current through an isolated level is determined by the standard form for a tunnel current. Note, however, that this result is valid at the strong Coulomb repulsion between the extra (transferred) electrons occupying the level in the course of transmission. If it is not the case, then the onsite Coulomb interaction switches on an additional transmission channel for electron tunneling (with the participation of the same isolated molecular level) [23,24]. A model of single level charge transmission is widely used to understand the asymmetry in the *I–V* characteristics of the molecule [13,16,32]. We use a model of single-level transmission to explain the experimental results [16,33] concerning the rectification properties of molecule $\equiv (\mathrm{Bu_2N}\phi\mathrm{V})_2\mathrm{BuPy}^+\mathrm{I}^-$ (cf. the insert in Fig. 5). Consider the *I–V* plot for the first successful cycle of measurements. In the case of the electron transmission through the LUMO, the resonant regimes are switched on at $V = V_1^{(L)}$ and $V = -V_2^{(L)}$, where the resonant voltages $V_r^{(L)}$ are defined by the condition $\Delta E_r^{(L)}(V) = 0$. Therefore, in accordance with Eq. (33), one derives

$$V_1^{(L)} = \frac{\Delta E^{(L)}(0)}{|e|\eta_L}, \quad V_2^{(L)} = \frac{\Delta E^{(L)}(0)}{|e|(1 - \eta_L)}. \qquad (44)$$

Experiments show that (at positive voltages) a sudden rise of the current occurs in the vicinity of 1.8 V. We associate this value with $V_1^{(L)}$. The voltage division factor is estimated with regard for the fact that the central nitrogen atom is positively charged. This means that the electronic density associated with the presence of an extra electron on the LUMO can be concentrated in the vicinity of the central nitrogen atom. Therefore, one can set $\eta_L \approx 0.6$. Using Eq. (44), we can estimate now the unbiased transmission gap, as well as the second resonant voltage. They are $\Delta E^{(L)}(0) \approx 1.01\,\mathrm{eV}$ and $V_2^{(L)} \approx 2.5\,\mathrm{V}$. Figure 5 manifests a rather good agreement between the theory and the experiment. The main discrepancy between the predicted and experimental values occurs in the vicinity of $V \sim V_1^{(L)}$. This indicates that, at $V > 1.5\,\mathrm{V}$, the contribution to the current can come from additional transmission channels. Nevertheless, we see that a single

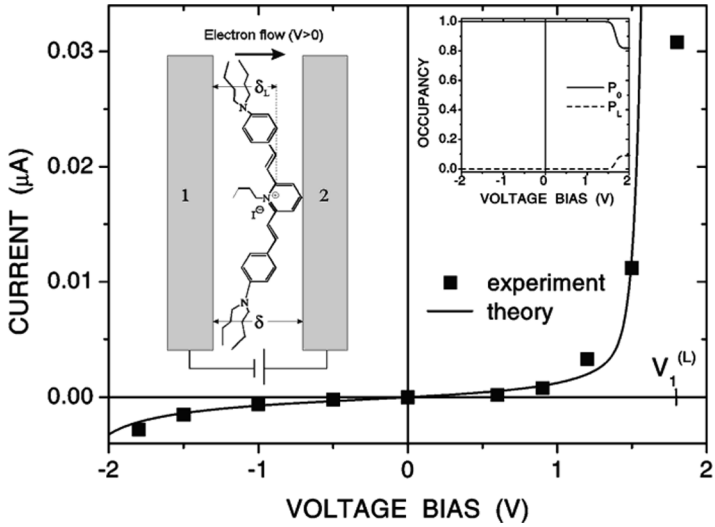

FIGURE 5 *I–V* characteristics of $(Bu_2N\phi V)_2BuPy^+I^-$. The theoretical description on the base of the single-level transmission model. The insert indicates a change of the electron population of the molecule during the charge transmission. The rectification of the current is caused by the asymmetric voltage drop within the molecule ($\eta_L > 1/2$). The calculations are based on Eqs. (41)–(43) and are carried out for the parameter set $\Delta E^{(L)}(0) = 1.01\,\text{eV}$, $\eta_L = 0.6$, $k_BT = 0.025\,\text{eV}$, $\Gamma_1^{(L)} = 0.001\,\text{eV}$, $\Gamma_1^{(R)} = 0.009\,\text{eV}$.

transmission channel associated with the frontier MO gives a dominant contribution to the current.

V. CONCLUSION

The derivation of general expressions for the current mediated by a molecule with two frontier MOs (LUMO and HOMO) is the main result of the present communication. It is shown that the current through the MOs, Eq. (37), contains two components associated with a direct one-step electron transmission from one electrode to another one, as well as with a sequential electron hopping. At the one-step interelectrode charge transmission, the noted molecular levels mediate a tunneling process exhibiting themselves as virtual levels. This means that the intermediate states of the SMD device are not populated by tunneling electrons. At the same time, the charge hopping process (which occurs in parallel with the tunneling) leads to a real population of the MOs. The schemes depicted in Figures 2 and 3 manifest possible starting, intermediate, and final electronic

configurations participating in the charge transfer. Since the character of electron-electron correlations is directly connected with electronic configurations, the contribution of doubly reduced or doubly oxidized molecular states into the common charge transmission becomes negligible at the great onsite Coulomb repulsion between the electrons or the holes. Therefore, in the reference voltage region, only a single extra electron (hole) can occupy the LUMO (HOMO). Thus, from six possible electronic configurations, only four of them, (L0;H2), (Lσ;H2), (L0;Hσ), and (Lσ;Hσ'), are involved in the charge transmission.

Apart pure electron-electron correlations, there exists another type of correlations associated with the kinetic charging of the molecule. It appears at a moderate onsite Coulomb repulsion between the extra (transferred) electrons occupying a single level or/and if at least two MOs are involved into the transmission process. As the kinetic charging determines the weight of transmission channels in the common transfer process, then, due to the normalization condition (18), the enhancement of the transfer along one of the channels leads automatically to a decrease of the charge transmission through the rest channels. Therefore, the control of the tunneling route via the kinetic molecular charging is a specific correlation effect appearing during the charge transmission through the organic molecules with strongly separated molecular levels. This control can be especially significant at the resonant charge transmission if only the hopping processes charge the molecule. A kinetic molecular charging becomes possible if, for a given direction of the current, the efficiency of charge hopping from the donating electrode to the molecule is comparable (or exceeds) the efficiency of charge hopping from the molecule to another electrode. If the noted efficiencies differ significantly, the theory predicts the strong kinetic rectification effect. Thus, diode properties of the molecule are determined not only by the character of the voltage distribution in the SMD device but also by the hopping processes in the device.

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