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
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Based on the nonequilibrium density matrix theory we put forward a unified description of the transient and the steady state current formation through a molecular junction. It is demonstrated that the current follows the time evolution of the populations of those molecular charged states which participate in the inter-electrode charge transmission. As an example, the formation of switch-on/switch-off currents is analyzed for a junction where the molecule has two active terminal sites. It is shown that just after a sudden voltage switch-on or switch-off, the resulting transient currents can significantly exceed their steady state value. This feature is caused by molecular charging or discharging processes, which are fast compared to those processes responsible for establishing the steady state current in the junction. The largest transient currents appear if the coupling of the molecule to the adjacent electrodes is asymmetric, or if the applied voltage causes a transformation of extended molecular states into localized ones. © *2011 American Institute of Physics*. [doi:10.1063/1.3582927]

I. INTRODUCTION

Based on intensive experimental and theoretical work carried out during the last 15 years, pivotal progress could be achieved in understanding the physical mechanisms of charge transmission through a single molecular attached to nanoelectrodes. It was possible to clarify the influence of structure and energetics on the formation of the elastic as well as inelastic component of the current.[1–9] Less emphasis, particularly from the experimental viewpoint, has been devoted to the case where an *ac* voltage has been applied to the junction. This is of particular interest when trying to control a biased current with fast switches. Besides, the creation of molecular photo devices such as photodiodes, photoresistors, photoamplifiers etc., is flourishing, see, for instance, Refs. (10–20 and 21–27).

While most of the results mainly concern steady state current–voltage (I–V)-characteristics of molecular junctions it represents an important issue to uncover the junction behavior associated with its nonstationary charge transmission. Now, the temporal behavior of the current corresponds to different types of processes including the dissipation of current fluctuations, the formation of the stationary regime in the junctions, the time-dependent response of the current to the action of applied *dc*- and *ac*- fields, etc. In what follows, we study the formation of these transient switch-on and switch-off currents as they appear after the sudden alteration of the bias voltage in the left electrode, molecule, right electrode (L–M–R) system. Preliminary theoretical results concerning such emerging transient currents have been recently described for stylistic setups in Refs. 28 and 29 where it could be demonstrated that the switch-on and switch-off currents are associated with molecular charging and molecular discharging processes, respectively. In particular, for the case of strongly

asymmetric molecule-lead couplings these currents can, in fact, significantly exceed their steady state values. This in turn might affect the overall structural stability of such L–M–R setups.

The objective of the present study is to examine the formation of transient switch-on and switch-off currents in a molecular junction where electron transmission through the molecule covers more than a single molecular orbital. This allows one not only to generalize the results obtained in the framework of the simplest model with only a single frontier MO,[28,29] but aids to understand the physics of such transient processes for physically more realistic L–M–R systems.

II. BASIC EQUATIONS

We start with the standard form of Hamiltonian for the L–M–R molecular wire system,

$$H(t) = H_0(t) + H' \qquad (1)$$

where

$$H_0(t) = H_{\text{electrode}} + H_{\text{mol}}(t) \qquad (2)$$

is the main part of the entire system with

$$H_{\text{electrode}} = \sum_{r=L,R} \sum_{\mathbf{k}\sigma} E_{r\mathbf{k}\sigma} \, a_{r\mathbf{k}\sigma}^+ a_{r\mathbf{k}\sigma} \qquad (3)$$

being the electronic Hamiltonian of the macroscopic electrodes. In Eq. (3), $E_{r\mathbf{k}\sigma}$ is the energy of an electron with spin projection σ occupying the $\mathbf{k}$th single-electron state in the conducting band of the rth electrode ($a_{r\mathbf{k}\sigma}^+$ and $a_{r\mathbf{k}\sigma}$ are the respective electron creation and annihilation operators[30]). The Hamiltonian

$$H_{\text{mol}}(t) = \sum_{M(N)} E(M(N); V(t))|M(N)\rangle\langle M(N)| \qquad (4)$$

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refers to the molecule embedded between the electrodes. The energy $E(M(N); V(t))$ of the $|M(N)\rangle$th molecular state is a function of the voltage $V(t)$ applied to the device and, thus, the dependence of the energy on the voltage is completely determined by the behavior of the voltage function $V = V(t)$. Here, the quantum number M covers those of the electronic, vibrational, and spin states of the molecule. The number of electrons in the molecule is denoted by N. The orthonormality condition $\langle M(N)|M'(N')\rangle = \delta_{MM'}\delta_{NN'}$ is valid in the Fock-space where the state $|M(N)\rangle$ can be written, for instance, in the occupation number representation, for more details see Ref. 31. The second term in Eq. (1) is the off-diagonal interaction responsible for electron hopping between the molecule and the left (L) electrode or the right (R) electrode. Its specific form reads

$$H' = \sum_{r=L,R} \sum_{\mathbf{k}\sigma} \sum_{M(N)} \sum_{M'(N+1)} [V_{M'(N+1);r\mathbf{k}\sigma M(N)}$$
$$\times |M'(N+1)\rangle\langle M(N)| a_{r\mathbf{k}\sigma} + h.c.]. \quad (5)$$

In Eq. (5), the matrix element $V_{M'(N+1);r\mathbf{k}\sigma M(N)} = \langle M'(N+1)|H'|r\mathbf{k}\sigma M(N)\rangle$ characterizes the electron hopping where an electron is annihilated in the $\mathbf{k}\sigma$th state of the rth conduction band and appears in the molecule. As a result, the molecule accepts an additional electron and changes its state $|M(N)\rangle$ to $|M'(N+1)\rangle$. The reverse hopping is characterized by the matrix element $V_{r\mathbf{k}\sigma M(N);M'(N+1)} = V^*_{M'(N+1),r\mathbf{k}\sigma M(N)}$.

A. Master equation for molecular state populations

It is well-known that the formation of a steady state current through a molecule is mainly determined by the charge hopping processes between the electrodes and the molecule.[31–34] Just these inelastic processes vary the state populations $P(M(N); t)$ of the molecule and thus become responsible for the formation of transient switch-on/off currents in the junctions. To derive the kinetic equations describing the evolution of the state populations $P(M(N); t)$ we use the nonequilibrium density matrix approach[35–37] and take into account the fact that the Hamiltonian (1) is a time-dependent operator. In line with the approach presented in Refs. 31 and 33 one arrives at the following generalized master equation

$$\dot{P}(M(N); t) = -\int_0^t d\tau$$
$$\times \sum_{M'(N')} \{\mathcal{G}[M(N) \to M'(N'); t, \tau] P(M(N); t-\tau)$$
$$- \mathcal{G}[M'(N') \to M(N); t, \tau] P(M'(N'); t-\tau)\}. \quad (6)$$

Here, the transition properties of the molecule are characterized by the quantities

$$\mathcal{G}[M(N) \to M'(N'); t, \tau]$$
$$= \frac{1}{\hbar^2} \sum_{L,R} \sum_{L',R'} W_L(t-\tau) W_R(t-\tau)$$
$$\times \langle LM(N)R|[H', U(t,\tau)[H', \hat{\Pi}']U^+(t,\tau)]|LM(N)R\rangle. \quad (7)$$

In the states $|LM(N)R\rangle$ and $|L'M'(N')R'\rangle$ the symbols L and R indicate the sets of occupation numbers so that $L(R) \equiv \{N_{L(R)\mathbf{k}_1\sigma_1}, N_{L(R)\mathbf{k}_2\sigma_2}, \ldots\}$ and $L'(R') \equiv \{N'_{L(R)\mathbf{k}_1\sigma_1}, N'_{L(R)\mathbf{k}_2\sigma_2}, \ldots\}$. Thus, in Eq. (7) the summation is over $N_{L\mathbf{k}_j\sigma_j}, N_{R\mathbf{k}_j\sigma_j}, N'_{L\mathbf{k}_j\sigma_j}, N'_{R\mathbf{k}_j\sigma_j} = 0, 1$. The quantity $W_r(t-\tau) = \prod_j P(N_{r\mathbf{k}_j\sigma_j}; t-\tau)$ represents the total probability for the electrons to occupy the single-electron states of the rth electrode. The separate electron probability to populate the band state $r\mathbf{k}\sigma$ is defined by the function $P(1_{r\mathbf{k}\sigma}; t-\tau)$ while $P(0_{r\mathbf{k}\sigma}; t-\tau)$ is the probability to find the same state without an electron.[38] In Eq. (7), we have introduced the time-evolution operator

$$U(t, \tau) = \hat{P}\exp\left\{-\frac{i}{\hbar}\int_{t-\tau}^t d\tau' [H_0(\tau') + (1-\hat{T}_d)H']\right\}, \quad (8)$$

where $\hat{P}$ is Dyson's chronological operator, $\hat{\Pi}' \equiv \hat{\Pi}_{L'M'(N')R'} = |L'M'(N')R'\rangle\langle L'M'(N')R'|$ is the projection operator, and $\hat{T}_d$ denotes the projection operator onto the diagonal part of an operator.

The quantities $\mathcal{G}(M(N) \to M'(N'); t, \tau)$ characterize the transitions between the molecular states $|M(N)\rangle$ and $|M'(N')\rangle$. Since these quantities include an external field in a nonlinear manner, the set of kinetic equations (6) allows one to describe different regimes of processes which are determined by the concrete form of the applied stochastic, regular or pulsed *ac*-fields.

B. Kinetic equations for molecular state populations

In this study, we consider the temporal behavior of the current caused by de facto sudden changes of the applied voltage $V = V_{\text{bias}}(t)$ from its initial value V_i to its final value V_f. This causes to change the molecular energies $E(M(N); V_{\text{bias}}(t))$ from $E(M(N); V_i)$ to the $E(M(N); V_f)$. Let τ_{bias} and τ_{st} be the characteristic time of the voltage change and of the formation of a stationary current at a fixed bias voltage, respectively. Then, for the presumed fast alteration of the $V_{\text{bias}}(t)$, the inequality

$$\tau_{\text{bias}} \ll \tau_{\text{st}} \quad (9)$$

must be obeyed. Therefore, if one describes an evolution process on the time scale $\Delta t \sim \tau_{\text{st}}$, it becomes possible to omit the dependence of the voltage bias on t setting $V_{\text{bias}}(t) = V_f$ in the expressions (7) and (8).

The validity of inequality (9) supposes a weak coupling of the molecule to the electrodes so that the states of the molecule are not changed (except the appearance of small broadening of molecular energy levels). Besides, the coupling does not modify relaxation transitions within the molecule. Let us estimate, for instance, the characteristic time τ_{st} for a stationary current of the order 1 nA. For such current, the molecule transmits about 10^9 electrons per second. Therefore, the mean time for the appearance of an extra (transferred) electron at the molecule is about 10^{-9} s. Just this value can be associated with the τ_{st}. [An analytic expression for τ_{st} valid for a two-site L–M–R device, follows from Eqs. (69)–(71); see also Eq. (73).] The given estimate shows that inequality

(9) is satisfied for $\tau_{\text{bias}} \ll 10^{-9}$ s and, thus, is in correspondence with the sudden switch approximation.

Inequality (9) allows to substitute the time dependent probabilities $P(1_{r\mathbf{k}\sigma}; t - \tau)$ and $P(0_{r\mathbf{k}\sigma}; t - \tau)$ by respective steady state probabilities $f_r(E_{r\mathbf{k}\sigma})$ and $1 - f_r(E_{r\mathbf{k}\sigma})$ where

$$f_r(E_{r\mathbf{k}\sigma}) = \{\exp\left[(E_{r\mathbf{k}\sigma}) - \mu_r\right] + 1\}^{-1}, \quad (10)$$

denotes the Fermi-function with $\mu_r = \mu_r(V)$ being the chemical potential of the rth electrode. The condition (9) also allows one to ignore the delay processes caused by the alteration of $V = V_{\text{bias}}(t)$. This reduces the set of equations (6) to the set of coarse-grained balancelike equations

$$\dot{P}(M(N); t) = - \sum_{M'(N')} \left\{ \mathcal{K}[M(N) \to M'(N')] \, P(M(N); t) \right.$$
$$\left. - \mathcal{K}[M'(N') \to M(N)] \, P(M'(N'); t) \right\}, \quad (11)$$

where the quantities

$$\mathcal{K}[M(N) \to M'(N')]$$
$$= \sum_{L,R} \sum_{L',R'} W_L \, W_R \mathcal{K}[LM(N)R \to L'M'(N')R']. \quad (12)$$

determine the transfer rates describing the intra-molecular transitions within the molecule induced via its coupling to the electrodes. In Eq. (12),

$$W_r = \prod_l P(N_{r\mathbf{k}_l\sigma_l}), \quad (13)$$

denotes the equilibrium distribution for the electrons belonging to the rth electrode. The partial transfer rates

$$\mathcal{K}[LM(N)R \to L'M'(N')R']$$
$$= \frac{2\pi}{\hbar} \, |\langle L'M'(N')R'|\hat{T}|LM(N)R\rangle|^2$$
$$\times \delta[E_L + E_R + E_{M(N)} - E_{L'} - E_{R'} - E_{M'(N')}], \quad (14)$$

characterize the transitions in the entire L–M–R system with $E_{M(N)} \equiv E(M(N), V)$ being the molecular energies at a given bias voltage V. The energies of the electrons at the rth electrode,

$$E_r = \sum_{r\mathbf{k}\sigma} E_{r\mathbf{k}\sigma} N_{r\mathbf{k}\sigma} = E_{r\mathbf{k}_1\sigma_1} N_{r\mathbf{k}_1\sigma_1} + E_{r\mathbf{k}_2\sigma_2} N_{r\mathbf{k}_2\sigma_2} + \dots$$
$$(15)$$

and

$$E_{r'} = \sum_{r\mathbf{k}\sigma} E_{r\mathbf{k}\sigma} N'_{r\mathbf{k}\sigma} = E_{r\mathbf{k}_1\sigma_1} N'_{r\mathbf{k}_1\sigma_1} + E_{r\mathbf{k}_2\sigma_2} N'_{r\mathbf{k}_2\sigma_2} + \dots,$$
$$(16)$$

are defined by the set of single-electron occupation numbers $\{N_{r\mathbf{k}_1\sigma_1}, N_{r\mathbf{k}_2\sigma_2}, \dots\}$ and $\{N'_{r\mathbf{k}_1\sigma_1}, N'_{r\mathbf{k}_2\sigma_2}, \dots\}$, respectively. The matrix elements $\langle L'R'M'(N')|\hat{T}|LRM(N)\rangle$ are calculated using the operator

$$\hat{T} = H' + H'\hat{G}(E)H' \quad (17)$$

for a transition on the energy shell.[30,31] Here, the Green's operator

$$\hat{G}(E) = \frac{1}{H_0 + H' + i0^+} \quad (18)$$

is calculated with the Hamiltonian H_0 [Eq. (2)]. Due to the condition [Eq. (9)] the molecular energies $E(M(N); V)$ are taken at a fixed bias voltage $V = V_{\text{bias}}$.

Because the off-diagonal interaction H' [Eq. (5)] is responsible for a single-electron transfer between an electrode and the molecule, this interaction only leads to a single-electron reduction or a single-electron oxidation of the molecule. The transfer rates characterizing these recharging processes read

$$\mathcal{K}[M(N) \to M'(N \pm 1)] = \sum_{r=L,R} \chi^{(r)}_{M(N) \to M'(N\pm1)}, \quad (19)$$

where

$$\chi^{(r)}_{M(N) \to M'(N+1)} = \frac{2\pi}{\hbar} \sum_{\mathbf{k}\sigma} |V_{M'(N+1); r\mathbf{k}\sigma M(N)}|^2 f_r(E_{r\mathbf{k}\sigma})$$
$$\times \delta[E_{r\mathbf{k}\sigma} + E_{M(N)} - E_{M'(N+1)}] \quad (20)$$

and

$$\chi^{(r)}_{M(N) \to M'(N-1)} = \frac{2\pi}{\hbar} \sum_{\mathbf{k}\sigma} |V_{r\mathbf{k}\sigma M'(N-1); M(N)}|^2 [1 - f_r(E_{r\mathbf{k}\sigma})]$$
$$\times \delta[E_{r\mathbf{k}\sigma} + E_{M'(N-1)} - E_{M(N)}], \quad (21)$$

are the forward (electrode $r \to$ molecule) and backward (molecule $\to$ electrode r) rate constants, respectively. The remaining reduction–oxidation rate constants, $\chi^{(r)}_{M'(N-1) \to M(N)}$ and $\chi^{(r)}_{M'(N+1) \to M(N)}$, are defined in a similar way. The above given transfer rates are derived in the framework of the Born approximation with respect to the transfer operator H'. More involved transfer processes are originated by the operator $H'\hat{G}(E)H'$ [second term in the right hand side of Eq. (17)]. The explicit form for these rates are given in Appendix A.

C. Sequential and distant current components

The current through the rth electrode,

$$I_r(t) = e \, (\delta_{r,L} - \delta_{r,R}) \, \dot{N}_r(t), \quad (22)$$

($e = -|e| < 0$ is the electron charge), is defined by the the number of electrons per time leaving the rth electrode, $N_r(t) = \sum_{r\mathbf{k}\sigma} N_{r\mathbf{k}\sigma} P(N_{r\mathbf{k}\sigma}; t) = \sum_{r\mathbf{k}\sigma} P(1_{r\mathbf{k}\sigma}; t)$, i.e., by the single-electron populations $P(1_{r\mathbf{k}\sigma}; t) = 1 - P(0_{r\mathbf{k}\sigma}; t)$. Using the density matrix method adapted for description of transfer processes in the L–M–R system[31,33] and bearing in mind the condition (9), one can see that these populations obey the kinetic equations

$$\dot{P}(1_{r\mathbf{k}\sigma}; t) = - \sum_{M M'} \sum_{\{N_{r'\mathbf{k}'\sigma'}\}} \sum_{\{N'_{r'\mathbf{k}'\sigma'}\}} \prod_j P(N_{r'\mathbf{k}'_j\sigma'_j})$$
$$\times \left\{ \mathcal{K}[1_{r\mathbf{k}\sigma} M(N)\{N_{r'\mathbf{k}'\sigma'}\} \to 0_{r\mathbf{k}\sigma} M'(N')\{N'_{r'\mathbf{k}'\sigma'}\}] \right.$$
$$\times P(M(N); t) \, f_r(E_{r\mathbf{k}\sigma}) - \mathcal{K}[0_{r\mathbf{k}\sigma} M'(N')\{N'_{r'\mathbf{k}'\sigma'}\}$$
$$\left. \to 1_{r\mathbf{k}\sigma} M(N)\{N_{r'\mathbf{k}'\sigma'}\}] P(M'(N'); t) [1 - f_r(E_{r\mathbf{k}\sigma})] \right\}.$$
$$(23)$$

In this context, the fact has been used that for macroscopic electrodes, one can set $P(1_{r\mathbf{k}\sigma}; t) \simeq f_r(E_{r\mathbf{k}\sigma})$ and $P(0_{r\mathbf{k}\sigma}; t) \simeq 1 - f_r(E_{r\mathbf{k}\sigma})$ on the right side of Eq. (23).[39]

In Eq. (23), the transfer rates are calculated in line with Eq. (14), using the operator (17). Therefore, the kinetic equation (23) includes transfer processes related to the sequential and the distant electron transitions. These processes result in a formation of stationary populations of molecular states and, thus, in a steady state current I_{steady}. During the formation of a stationary regime of charge transmission, however, the number of electrons per time leaving the left electrode ($\dot{N}_L(t)$) does not coincide with the number of electrons per time arriving at the right electrode ($-\dot{N}_R(t)$). Accordingly, the currents through the left and the right electrodes may deviate from each other. The reason for this is the kinetic recharging of the molecule.

Using the definition (22) and the kinetic equations (23) one obtains the following expression for the current through the rth electrode

$$I_r(t) = I_{\text{seq}}^{(r)}(t) + I_{\text{dir}}^{(r)}(t). \tag{24}$$

The current is composed of two contributions. The first one,

$$I_{\text{seq}}^{(r)}(t) = |e|(\delta_{r,L} - \delta_{r,R}) \sum_{MM'} \left[\chi_{M(N)\to M'(N+1)}^{(r)} P(M(N); t) \right.$$
$$\left. - \chi_{M'(N+1)\to M(N)}^{(r)} P(M'(N+1); t) \right], \tag{25}$$

is defined by the hopping of electrons between the molecule and the electrodes. Since the hopping is caused by the operator H', the expression (25) contains the transfer rates given by Eqs. (20) and (21). The second contribution, i.e.,

$$I_{\text{dir}}^{(r)}(t) = |e|(\delta_{r,L} - \delta_{r,R})(1 - \delta_{r,r'})$$
$$\times \sum_{MM'} [Q_{rM(N)\to r'M'(N)} - Q_{r'M(N)\to rM'(N)}]$$
$$\times P(M(N); t) \tag{26}$$

is associated with the difference of the direct inelastic one-step tunneling charge flow between the rth and the r'th electrode. Each of the $r \to r'$ tunnel charge flow

$$Q_{rM(N)\to r'M'(N)}$$
$$= \frac{2\pi}{\hbar} \sum_{\mathbf{k}\sigma} \sum_{\mathbf{k}'\sigma'} f_r(E_{r\mathbf{k}\sigma})[1 - f_{r'}(E_{r'\mathbf{k}'\sigma'})]$$
$$\times \left| \sum_{\tilde{M}} \left[\frac{V_{r'\mathbf{k}'\sigma'\tilde{M}(N-1);M(N)} V_{M'(N);r\mathbf{k}\sigma \tilde{M}(N-1)}}{\mathcal{E}(M(N)) - E_{r'\mathbf{k}'\sigma'} - \mathcal{E}(\tilde{M}(N-1))} \right. \right.$$
$$\left. \left. + \frac{V_{r'\mathbf{k}'\sigma'M'(N);\tilde{M}(N+1)} V_{\tilde{M}(N+1);r\mathbf{k}\sigma M(N)}}{\mathcal{E}(M(N)) + E_{r\mathbf{k}\sigma} - \mathcal{E}(\tilde{M}(N+1))} \right] \right|^2$$
$$\times \delta[E_{M'(N)} + E_{r'\mathbf{k}'\sigma'} - E_{M(N)} - E_{r\mathbf{k}\sigma}], \tag{27}$$

is determined by the operator $H'G(E)H'$. Therefore, in the denominators of Eq. (27), the molecular energies $\mathcal{E}(M(N))$ [Eq. (A1)] include the self-energies caused by the couplings of the molecule to the electrodes. Elastic tunneling charge flow occurs for those transmission channels for which $M'(N) = M(N)$.

III. TWO-SITE L–M–R SYSTEM

The expressions (24)–(27) form the basis for the subsequent analysis of the various regimes of current evolution

initiated by the fast alteration of the applied voltage. In all cases the sequential as well as the tunneling route of charge transmission are controlled by the population of charged molecular states via the respective probabilities $P(M(N); t)$. Thus, the current evolution including the relaxation to the steady state regime follows the behavior of the $P(M(N); t)$. Their time dependence is described by the set of kinetic equations (11) with rate constants given by the expressions (19) and (A5)–(A7). To arrive at a detailed understanding of the formation of transient switch-on and switch-off currents in the junctions we consider a well-established model valid for a non-magnetic L–M–R device where the molecule is characterized by the terminal sites 1 and 2.

A. Energetics of the charged two-site molecule

To specify the shift of the molecular energies $E_{M(N)} = E(M(N); V)$ due to the voltage $V = V_{\text{bias}}$ we assume that in the absence of magnetic interactions each molecular state can be represented by its charge ν and the set of vibrational sub-states $v_\nu \equiv \{v_\nu^{(s)}\}$ (s indicates the vibrational mode) so that $|M(N_G + \nu)\rangle = |\nu; v_\nu\rangle$. In the framework of the Born–Oppenheimer ansatz, electronic and vibrational molecular states are separated and, thus, $|\nu; v_\nu\rangle \simeq |\nu\rangle|v_\nu\rangle$. Therefore, we may write $E(M(N_G + \nu); V) \simeq \epsilon_\nu(V) + \epsilon_\nu^{(\text{vibr})}(v_\nu)$ where the voltage dependence of the molecular energy is located on its electronic part $\epsilon_\nu(V)$ while the vibrational part of the energy, $\epsilon_0^{(\text{vibr})}(v_\nu)$, is independent of V.

The shift of the electronic energies $\epsilon_\nu(V)$ against the voltage bias $V = V_{\text{bias}}$ is defined by a charge distribution within the molecule. As a rule, if the molecule has a zero spin in its ground state $|M(N_G)\rangle$, all N_G electrons of the molecule fill completely the HOMO, HOMO-1, HOMO-2,... while the LUMO, LUMO+1, LUMO+2,... remain empty. It means that the total molecular charge ν is assumed to be zero. For the sake of convenience, we suppose that the terminal molecular sites 1 and 2 carry the fixed charges $Z_1 e$ and $Z_2 e$, respectively; for a neutral molecule, $Z_2 = -Z_1$. This allows one to represent the electronic energy in the ground state as

$$\epsilon_0(V) = \epsilon_0 + e[Z_1\eta_1 + Z_2(1 - \eta_2)] V, \tag{28}$$

while the left electrode is maintained at zero voltage. Here, ϵ_0 is the unbiased energy part and η_j is the voltage division factor for the jth site.

1. Energies of a singly charged molecule

Accepting an extra electron the molecule becomes singly charged ($\nu = 1$). Let the localized LUMO $|j\rangle$ which belongs to site $j(= 1, 2)$ be well separated from the remaining LUMO's of the same site. Then, the electronic energies of the localized states are

$$\epsilon_1^{(1)}(V) = \epsilon_1^{(1)} + e[(Z_1 + 1)\eta_1 + Z_2(1 - \eta_2)] V,$$
$$\epsilon_1^{(2)}(V) = \epsilon_1^{(2)} + e[Z_1\eta_1 + (Z_2 + 1)(1 - \eta_2)] V, \tag{29}$$

with $\epsilon_1^{(1)}$ and $\epsilon_1^{(2)}$ being the unbiased parts of site 1 and 2, respectively. To specify the states and energies of the charged molecule we employ Hückel's approach. Accordingly, the
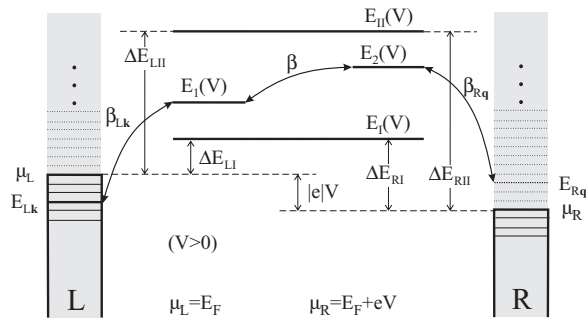
FIG. 1. Energy scheme of the left electrode–molecule–right electrode device with a singly charged molecule. The coupling between the sites (parameter β) and the couplings between the molecule and the electrodes (parameters $\beta_{L\mathbf{k}}$ and $\beta_{R\mathbf{q}}$) translates the site energies [Eq. (29)] into the energies of extended molecular states [Eq. (31)]. $E_1(V)$ and $E_2(V)$ are the electron affinities [Eq. (34)] $\Delta E_{L\alpha}$ and $\Delta E_{R\alpha}$ are the transmission gaps [Eq. (64)].

electronic states of molecule $|I\rangle$ and $|II\rangle$ form a superposition of its localized electronic states $|1\rangle$ and $|2\rangle$.[40] In our case, such a state is formed in the presence of both intersite interaction (the coupling parameter is β) and of the interaction of the terminal sites of the molecule with the adjacent electrodes (the coupling parameters are $\beta_{L\mathbf{k}}$ and $\beta_{R\mathbf{q}}$), cf. Fig. 1. With these interactions, the energies [Eq. (29)] are transformed into the following more complex form:[41,42]

$$\mathcal{E}_\alpha(V) = E_\alpha(V) - i\Gamma_\alpha(V)/2 , \tag{30}$$

where

$$E_\alpha(V) = (1/2)\left[E_1^{(1)}(V) + E_1^{(2)}(V) + (-1)^\alpha \rho(V)\cos\psi(V)\right] \tag{31}$$

is the energy of the $\alpha(= I, II)$th extended singly charged molecular state and

$$\Gamma_\alpha(V) = (\Gamma_L + \Gamma_R)/2 + (-1)^\alpha \rho(V)\sin\psi(V) \tag{32}$$

is the parameter determining the broadening of the αth molecular level. The quantities

$$\rho(V) = 4\sqrt{[\Delta E^2(V) + 4\beta^2 - \Delta\gamma^2]^2 + 4\Delta E^2(V)\Delta\gamma^2} ,$$

$$\text{tg } 2\psi(V) = \frac{2\Delta E(V)\Delta\gamma}{\Delta E^2(V) + 4\beta^2 - \Delta\gamma^2}, \tag{33}$$

specify the dependence of the energy $E_\alpha(V)$ and the width parameter $\Gamma_\alpha(V)$ on the applied voltage. For the sake of convenience, we measure electronic energies from the energy of the molecular ground state, so that the energy

$$E_1^{(j)}(V) = \epsilon_1^{(j)}(V) - \epsilon_0(V), \quad (j = 1, 2), \tag{34}$$

is treated as the single-electron affinity for the jth terminal site whereas

$$\Delta E(V) = E_1^{(2)}(V) - E_1^{(1)}(V) \tag{35}$$

has to be referred to the difference between the site affinities. In Eq. (33), the quantity

$$\Delta\gamma = (\Gamma_R - \Gamma_L)/2 \tag{36}$$

is expressed via the contact width parameters Γ_L and Γ_R. Moreover, we employ the well known wide-band

approximation[1] which allows to omit the real part of the self-energy (A2) and to ignore the energy dependence of the width E.[43]

2. Energy of a double-charged molecule

In the case of a doubly reduced molecule, one needs to take into consideration also the Coulomb interaction between the two extra electrons placed either at the same molecular site or at different sites. As a rule, Coulomb electron–electron repulsion within the site strongly exceeds the repulsion between electrons occupying different sites. Bearing in mind this fact, we take into consideration only those doubly charged molecular states $|M(N_G + 2)\rangle$ where the transferred electrons occupy different terminal sites. Therefore, the electronic energy of the doubly charged molecule assumes the form

$$\mathcal{E}_2(V) \simeq E_2(V) - i\Gamma_2/2 , \quad (\Gamma_2 = \Gamma_L + \Gamma_R), \tag{37}$$

where we have introduced the two-electron affinity [compare this expression with the single-electron affinity, Eq. (34)]

$$E_2(V) = \epsilon_2(V) - \epsilon_0(V). \tag{38}$$

The term

$$\epsilon_2(V) = \epsilon_2 + e[(Z_1 + 1)\eta_1 + (Z_2 + 1)(1 - \eta_2)] V \tag{39}$$

contains an unbiased part $\epsilon_2 = \epsilon_1^{(1)} + \epsilon_2^{(1)} + U$ with the parameter U characterizing the repulsion between the extra electrons located at sites 1 and 2.

Adding to the electronic energies $E_\nu(V)$ the vibrational energies $\epsilon_\nu^{(\text{vibr})}(v_\nu)$ one obtains in the case of a two-site molecule with a single LUMO per site the energy:

$$\mathcal{E}(M(N)) = \delta_{N,N_G} E(v_0) + \delta_{N,N_G+1}\left[E(v_\alpha) - i\Gamma_\alpha/2\right]$$
$$+ \delta_{N,N_G+2}\left[E(v_2) - i\Gamma_2/2\right] \tag{40}$$

where, within in the harmonic approximation,

$$E(v_\nu) = E_\nu(V) + \sum_s \hbar\omega_\nu^{(s)} v_\nu^{(s)} \tag{41}$$

is the electron-vibrational energy of the molecule being in the $\nu(= 0, 1(\alpha), 2)$th charged state (energies of zero-point vibrations, $(\hbar/2)\sum_s \omega_\nu^{(s)}$, are included in the $E_\nu(V)$). In Eq. (41), $\omega_\nu^{(s)}$ is the frequency of the sth vibrational mode.

B. Electron hopping processes

Denoting the molecular electron-vibrational states by $M(N_G) \equiv v_0$, $M(N_G + 1) \equiv v_I, v_{II}$, and $M(N_G + 2) \equiv v_2$ one can calculate the transfer rates $\mathcal{K}(v_\nu \to v_{\nu'}) = \sum_{r=L,R} \chi^{(r)}(v_\nu \to v_{\nu'})$ responsible for molecular charging/discharging. To solve the set of balance-like equations (11) for the populations $P(v_\nu; t)$ one has to know the characteristic time τ_{vib} necessary to form a Boltzmann distribution among vibrational sub-states belonging to each electronic level ν. The situation is strongly simplified in the case of fast vibrational relaxation. In this important case, the essential inequality,

$$\tau_{\text{vib}} \ll \tau_{\text{st}} , \tag{42}$$

is obeyed, so that the ratio $P(v_\nu; t)/P(v'_\nu; t)$ $= \prod_s \exp[-\hbar\omega_\nu^{(s)}(v_\nu^{(s)} - v_\nu'^{(s)})/k_BT]$ is well fulfilled on the time scale $\Delta t \gg \tau_{vib}$. This leads to the relation that

$$P(v_\nu; t) = W(v_\nu) P(\nu; t), \tag{43}$$

which indicates that the electron-vibrational populations of the νth electronic level can be expressed by the integral population

$$P(\nu; t) = \sum_{v_\nu} P(v_\nu; t) \tag{44}$$

as well as by the equilibrium vibrational distribution function $W(v_\nu) = \prod_s W(v_\nu^{(s)})$ where

$$W\left(v_\nu^{(s)}\right) = \frac{\exp\left(-\hbar\omega_\nu^{(s)} v_\nu^{(s)}/k_BT\right)}{\sum_{v_\nu^{(s)}} \exp\left(-\hbar\omega_\nu^{(s)} v_\nu^{(s)}/k_BT\right)} \tag{45}$$

is the probability for the sth vibrational sub-state to be populated during the charge transmission through a molecule. Note that the integral populations satisfy the normalization condition

$$P(0; t) + 2\sum_{\alpha=I,II} P(\alpha; t) + 4P(2; t) = 1, \tag{46}$$

where the factors 2 and 4 reflect a spin degeneracy of the electronic states associated with respective singly and doubly charged molecule.

Since inequalities (9) and (42) are valid, one can describe the various processes in the L–M–R device in using the coarse-grained kinetic equations, which only determine the integral molecular level populations [Eq. (44)]. These equations follow from the set (11) if one utilizes the relation (43) and the normalization condition $\sum_{v_\nu} W(v_\nu) = 1$. The equations take the form ($\alpha' \neq \alpha$)

$$\dot{P}(0; t) = -\left[2\sum_{\alpha=I,II} K_{0\to\alpha} + 4K_{0\to2}\right] P(0; t)$$
$$+ 2\sum_{\alpha=I,II} K_{\alpha\to0} P(\alpha; t) + 4K_{2\to0} P(2; t),$$

$$\dot{P}(\alpha; t) = -[K_{\alpha\to0} + 2K_{\alpha\to2} + K_{\alpha\to\alpha'}] P(\alpha; t)$$
$$+ K_{0\to\alpha} P(0; t) + 2K_{2\to\alpha'} P(2; t) + K_{\alpha'\to\alpha} P(\alpha'; t),$$

$$\dot{P}(2; t) = -\left[\sum_{\alpha=I,II} K_{2\to\alpha} + K_{2\to0}\right] P(2; t)$$
$$+ \sum_{\alpha=\pm} K_{\alpha\to2} P(\alpha; t) + K_{0\to2} P(2; t). \tag{47}$$

In Eq. (47), the recharging transfer rates

$$K_{\nu\to\nu'} = \sum_{r=L,R} \chi_{\nu\to\nu'}^{(r)} \tag{48}$$

are defined through the sum of contact rate constants (cf. Fig. 2)

$$\chi_{\nu\to\nu'}^{(r)} = \sum_{v_\nu v_{\nu'}} W(v_\nu)\chi^{(r)}(v_\nu \to v_{\nu'}). \tag{49}$$

The concrete form for the $\chi_{\nu\to\nu'}^{(r)}$ follows from Eqs. (20) and (21) (for $\nu' = \nu \pm 1$) as well as from Eqs. (A5)–(A7) (for ν'
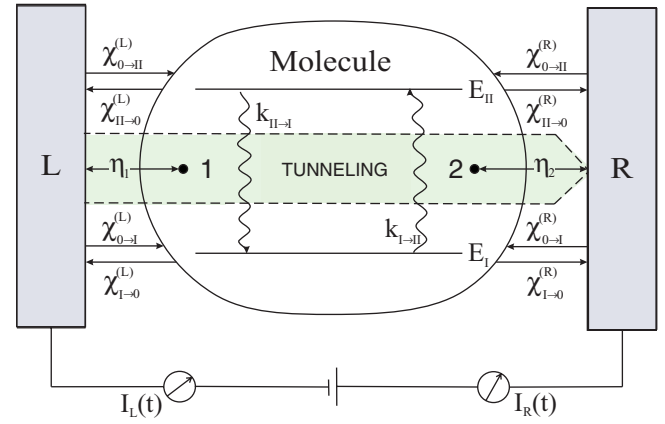

FIG. 2. Scheme of single-electron kinetic processes in the L–M–R device including a two-site molecule (voltage division factors η_1 and η_2 fix the relative distances from the sites to the adjacent electrodes). The scheme is valid at a strong Coulomb repulsion between the transferred electrons. Molecular charging occurs due to an electron hopping between the molecule and the electrodes (respective contact transfer rates are $\chi_{0\to\alpha}^{(L(R))}$ and $\chi_{0\to\alpha}^{(L(R))}$), ($\alpha = I, II$). The direct one-step electrode–electrode transmission is associated with a tunneling process mediated by the molecule being in the uncharged and singly charged states.

$= \nu$ and $\nu' = \nu \pm 2$, respectively). Thus, if $\nu' = \nu + 1$, then

$$\chi_{\nu\to\nu'}^{(r)} = (\Gamma_r/\hbar) \sum_{v_\nu v_{\nu'}} W(v_\nu) N[\Delta E^{(r)}(v_{\nu'}, v_\nu)][\delta_{r,L}\xi^2\delta_{\alpha,I}$$
$$+ (1 - \xi^2)\delta_{\alpha,II} + \delta_{r,R}(1 - \xi^2)\delta_{\alpha,I} + \xi^2\delta_{\alpha,II})] \tag{50}$$

and

$$\chi_{\nu'\to\nu}^{(r)} = \exp\left[\Delta E_{\nu'\nu}^{(r)}/k_BT\right] \chi_{\nu\to\nu'}^{(r)}. \tag{51}$$

In Eq. (50),

$$\Delta E^{(r)}(v_{\nu'}, v_\nu) = \Delta E_{\nu'\nu}^{(r)} + \hbar\sum_s \left[\omega_{\nu'}^{(s)} v_{\nu'}^{(s)} - \omega_\nu^{(s)} v_\nu^{(s)}\right] \tag{52}$$

denotes the energy gap between the electron-vibrational states $v_{\nu'}$ and v_ν belonging to the electron levels ν' and ν. It is just this energy gap which enters the distribution function

$$N[\Delta E^{(r)}(v_{\nu'}, v_\nu)] = \frac{1}{e^{\Delta E^{(r)}(v_{\nu'}, v_\nu)/k_BT} + 1} \tag{53}$$

while the pure electronic transmission gap

$$\Delta E_{\nu'\nu}^{(r)} = E_{\nu'} - (E_\nu + \mu_r), \tag{54}$$

specifies the relation (51) between the backward and forward contact transfer rates. Note that in Eqs. (50)–(54), one has to set $\nu' = \alpha$ (if $\nu = 0$) and $\nu' = 2$ (if $\nu = \alpha$). In Eq. (50), the parameter

$$\xi = \frac{2\beta}{[(\Delta E - \rho\cos\psi)^2 + (\Delta\gamma - \rho\sin\psi)^2 + 4\beta^2]^{1/2}}, \tag{55}$$

specifies the delocalization of an extra electron over the molecule coupled to the electrodes. The dependence of this parameter on the voltage bias V appears in the quantities

$\Delta E = \Delta E(V)$, $\rho = \rho(V)$, and $\psi = \psi(V)$, cf. respective definitions (33)–(36).

Before proceeding further, let us note that the current evolution in a molecular device is controlled by an evolution of the molecular state populations $P(\nu; t)$ [cf. the basic expressions (25) and (26)]. In turn, the populations evolve in correspondence with the kinetic equations (47). However, one has to remark that any transient behavior of the populations depends strongly on the initial state of the L–M–R system (via the initial molecular populations $P(\nu; 0)$). Here, we consider the formation of transient currents subject to the condition that the populations $P(\nu; 0)$ have been already formed before a sudden alteration of the voltage appears (from $V = V_i$ to $V = V_f$). It means that the $P(\nu; 0)$ are found from the solution of the kinetic equations (47) at the stationary condition $\dot{P}(\nu; t) = 0$ and with transfer rates taken at $V = V_i$. Concerning the evolution of the transient molecular populations $P(\nu; t)$ the latter are formed at $V = V_f$. Therefore, the $P(\nu; t)$ are found from a solution of the kinetic equations (47) with transfer rates taken at $V = V_f$ (but with initial populations $P(\nu; 0)$ found at $V = V_i$).

C. Sequential and distant current components

Upon the introduction of the contact rate constants $\chi^{(r)}_{\nu \to \nu'}$, the sequential (hopping) current component [Eq. (25)] takes the form

$$I^{(r)}_{\text{seq}}(t) = I_0 \, 2\pi\hbar (\delta_{r,L} - \delta_{r,R}) \Big[\sum_\alpha \big(\chi^{(r)}_{0 \to \alpha} $$
$$+ 2\chi^{(r)}_{0 \to 2} \big) P(0; t) + 2 \sum_\alpha \chi^{(r)}_{\alpha \to 2} P(\alpha; t) $$
$$- \sum_\alpha \chi^{(r)}_{\alpha \to 0} P(\alpha; t) - 2 \sum_\alpha \big(\chi^{(r)}_{2 \to \alpha} + \chi^{(r)}_{2 \to 0} \big) P(2; t) \Big], $$

$$(56)$$

where $I_0 = |e|/\pi\hbar (\times 1\text{eV}) \approx 77.6 \ \mu$A is the current unit. While the unit I_0 is measured in microampere the quantities such as $\hbar\chi^{(r)}_{\nu' \to \nu}$ and Γ_r are taken in electron volt. And, the direct current component results are taken as the sum of the tunnel currents $I^{(\nu)}_{\text{tun}}$ weighted by the probabilities of realizing a particular molecular charging state $\nu(= 0, 1, 2)$, yielding

$$I_{\text{dir}}(t) = I^{(L)}_{\text{dir}}(t) = I^{(R)}_{\text{dir}}(t) $$
$$= I^{(0)}_{\text{tun}} P(0; t) + 2 \sum_\alpha I^{(\alpha)}_{\text{tun}} P(\alpha; t) + 2 I^{(2)}_{\text{tun}} P(2; t). $$

$$(57)$$

Here, the tunnel current of the νth channel is given by the expression

$$I^{(\nu)}_{\text{tun}} = (1 - e^{-|\mu_L - \mu_R|/k_B T}) I_0 (\Gamma_L \Gamma_R \beta^2/\rho^2) $$
$$\times \sum_{\nu_\nu} W(\nu_\nu) \int_{\mu_R + E(\nu'_\nu)}^{\mu_L + E(\nu_\nu)} dE \, \Lambda^{(\nu)}(\nu_\nu \nu'_\nu; E), $$

$$(58)$$

where the factors

$$\Lambda^{(0)}(\nu_0 \nu'_0; E) = \Big| \sum_\alpha \sum_{\nu_\alpha} \frac{(-1)^\alpha \langle \nu'_0 | \nu_\alpha \rangle \langle \nu_\alpha | \nu_0 \rangle}{E - E(\nu_\alpha) + i\Gamma_\alpha/2} \Big|^2, \quad (59)$$

$$\Lambda^{(\alpha)}(\nu_\alpha \nu'_\alpha; E) $$
$$= \Big| \sum_{\nu_2} \frac{\langle \nu'_\alpha | \nu_2 \rangle \langle \nu_2 | \nu_\alpha \rangle}{E - E(\nu_2) + i(\Gamma_2 - \Gamma_\alpha)/2} $$
$$+ \sum_{\nu_0} \frac{\langle \nu'_\alpha | \nu_0 \rangle \langle \nu_0 | \nu_\alpha \rangle}{E(\nu_\alpha) + E(\nu'_\alpha) - E(\nu_0) - i\Gamma_\alpha/2 - E} \Big|^2, $$

$$(60)$$

and

$$\Lambda^{(2)}(\nu_0 \nu'_0; E) $$
$$= \Big| \sum_\alpha \sum_{\nu_\alpha} \frac{(-1)^\alpha \langle \nu'_2 | \nu_\alpha \rangle \langle \nu_\alpha | \nu_2 \rangle}{E(\nu_2) + E(\nu'_2) - E(\nu_\alpha) - i(\Gamma_2 - \Gamma_\alpha)/2 - E} \Big|^2 $$

$$(61)$$

define the character of the direct (distant) inelastic tunneling transmission between the electrodes along the νth channel.

IV. RESULTS AND DISCUSSION

Equations (58)–(61) for the current components and the kinetic equations (47) with respective transfer rates [Eqs. (48)–(51)] allow one to analyze different regimes of electron transmission through the molecular junction. And, they offer an understanding of the mechanism responsible for the formation of transient and steady state currents. Note that the evolution of the sequential and the direct current component is completely determined by the variation of the molecular state populations. Note also that during the transient process the sequential current components do not agree with their absolute values for the left and the right electrodes. Such an agreement only occurs for the direct current components. Therefore, independent of the details of current formation, the following relations are valid $I^{(R)}_{\text{seq}}(t) \neq I^{(L)}_{\text{seq}}(t)$ and $I^{(R)}_{\text{dir}}(t) = I^{(L)}_{\text{dir}}(t)$. Consequently, the temporal behavior of the total transient currents $I_R(t)$ and $I_L(t)$ markedly differ. The currents become only identical in the case of steady state transmission, i.e., at $t \gg \tau_{st}$ when

$$I_{\text{steady}} = I_L(t \gg \tau_{\text{st}}) = I_R(t \gg \tau_{\text{st}}). \quad (62)$$

Next, in order to clarify the physics of transient processes and the formation of a steady state current, we restrict ourselves to the analysis of smooth current–voltage ($I - V$) characteristics ignoring the vibrational structure of the molecule. Contributions of vibrational degrees of freedom to the $I - V$ characteristics become obvious if one uses the methods of inelastic electron tunneling spectroscopy.[6,44–46] We also consider the current evolution at those voltages where the effects of Coulomb repulsion between the transferred electrons are unimportant so that only a single-electron occupation of the molecule by extra (transferred) electrons becomes responsible for the transmission process. The noted simplification offers a suitable analytic expressions for the current. Thus, the sequential contribution to the current through the rth electrode

can then be represented as

$$I_{seq}^{(r)}(t) = I_0 \, 2\pi \, (\delta_{r,L} - \delta_{r,R}) \, \Gamma_r \{\xi^2 \, [N(\Delta E_{r\alpha}) \, P(0;t)$$
$$- (1 - N(\Delta Er\alpha)) \, P(\alpha;t)] + (1 - \xi^2) \, [N(\Delta E_{r\alpha'})$$
$$\times P(0;t) - (1 - N(\Delta E_{r\alpha'})) \, P(\alpha';t)]\}, \qquad (63)$$

where one has to set $\alpha = I(II), \alpha' = II(I)$ if $r = L(R)$. In Eq. (63) the parameter ξ is defined by Eq. (55) whereas the distribution function follows from Eq. (53) by substituting the electron-vibrational energy gap $\Delta E^{(r)}(v_{v'}, v_v)$ by the pure electronic transmission gap, cf. Fig. 1,

$$\Delta E_{\alpha 0}^{(r)} \equiv \Delta E_{r\alpha} = E_\alpha(V) - \mu_r. \qquad (64)$$

The energies $\mu_L = E_F$ and $\mu_R = E_F + eV$ denote the chemical potentials for identical electrodes, E_F is the Fermi energy and the $E_\alpha(V)$ is the single-electron affinity defined by Eq. (31) [the site affinities $E_1^{(j)}(V)$ are defined in Eq. (34)].

Considering the direct current contribution, it can be readily seen that it is related to the transmission channels $v = 0$ and $v = \alpha = I, II$ so that Eq. (57) reduces to

$$I_{dir}(t) \simeq I_{tun}^{(0)} \, P(0;t) + 2 \, I_{tun}^{(I)} P(I;t) + 2 I_{tun}^{(II)} P(II;t). \qquad (65)$$

Respective tunneling currents are calculated in line with the expression

$$I_{tun}^{(v)} = (1 - e^{-|eV|/k_B T}) \, I_0 \, \Gamma_L \Gamma_R \beta^2 \, \mathcal{R}_v, \qquad (66)$$

where

$$\mathcal{R}_0 = \int_{\mu_r}^{\mu_L} \frac{dE}{[(E - E_I)^2 + \Gamma_I^2/4][(E - E_{II})^2 + \Gamma_{II}^2/4]} \qquad (67)$$

and

$$\mathcal{R}_\alpha = \frac{1}{\rho^2} \int_{\mu_R}^{\mu_L} \frac{dE}{(E - E_\alpha)^2 + \Gamma_\alpha^2/4}, \quad (\alpha = I, II). \qquad (68)$$

In these equations the molecular energies $E_\alpha = E_\alpha(V)$ and their widths $\Gamma_\alpha/2 = \Gamma_\alpha(V)/2$ are given by Eqs. (31) and (33), respectively.

A small population of the state with two extra electrons in the molecule (i.e., $P(2;t) \simeq 0$) is achieved if $\exp[-\Delta E_{2\alpha}^{(r)}/k_B T] \ll 1$, where $\Delta E_{2\alpha}^{(r)} = E_2(V) - (E_\alpha(V) + \mu_r)$ is the electronic transmission gap between the doubly and the singly charged states of the molecule. We assume that in the voltage region under consideration the noted small population is realized. Therefore, setting $P(2;t) \simeq 0$ one ends up with the following solution of the set (47):

$$P(v;t) = P_v + C_v^{(1)} e^{-K_1 t} + C_v^{(2)} e^{-K_2 t}, \quad (v = 0, I, II). \qquad (69)$$

Here, the overall transfer rates K_1 and K_2 describe the formation of steady state molecular populations $P_v = P(v;t \gg \tau_{st}^{(j)})$ with the characteristic times $\tau_{st}^{(j)} = K_j^{-1}$, $(j = 1, 2)$. The related rates read

$$K_j = (1/2) \, [a_1 + a_2 - (-1)^j \sqrt{(a_1 - a_2)^2 + 4b_1 b_2}], \qquad (70)$$

where the quantities

$$a_1 = 2K_{I \to 0} + 2K_{0 \to I} + K_{I \to II}, \quad b_1 = K_{II \to I} - 2K_{0 \to I},$$
$$a_2 = 2K_{II \to 0} + 2K_{0 \to II} + K_{II \to I}, \quad b_2 = K_{I \to II} - 2K_{0 \to II} \qquad (71)$$

are expressed by the state-to-state transfer rates $K_{v \to v'}$. The same rates determine the steady state molecular populations P_v as well as the pre-exponential factors $C_v^{(1)}$ and $C_v^{(2)}$. Concrete formulas for these quantities can be found in the Appendices B and C.

The above given expressions for the current components and the molecular populations allow one to analyze different regimes of charge transmission in the two-site L–M–R device at a sudden alteration of the applied voltage. One of the important regimes is realized at a negligible population of the upper molecular state, $P(II;t) \simeq 0$. For this regime, the transmission pathway initially involves the lowest charged state of the molecule so that the time dependence of the populations takes the form

$$P(v;t) \simeq P_v + (P(v;0) - P_v) \, e^{-K_{st} t}, \quad (v = 0, I), \qquad (72)$$

where

$$K_{st} \simeq \chi_{LI}[1 + N(\Delta E_{LI})] + \chi_{RI}[1 + N(\Delta E_{RI})] \qquad (73)$$

is the overall transfer rate that determines the characteristic time $\tau_{st} = K_{st}^{-1}$ to reach stationary charge transmission. The quantity K_{st} is expressed via the contact rate constants

$$\chi_{LI} = \Gamma_L \xi^2/\hbar, \quad \chi_{RI} = \Gamma_R (1 - \xi^2)/\hbar. \qquad (74)$$

These rate constants also define the kinetics of the formation of the sequential current components. Thus, the steady-state sequential current component reads

$$I_{steady}^{(seq)} \simeq I_0 \, 2\pi\hbar \frac{\chi_{LI} \chi_{RI}}{K_{st}} [N(\Delta E_{LI}) - N(\Delta E_{RI})]. \qquad (75)$$

We also quote the expressions for the maximal and minimal values of the sequential current components formed just after the sudden increase of the voltage. They follow as

$$I_{seq}^{(L)max} \simeq I_0 \frac{2\pi\hbar \chi_{LI}}{1 + N(\Delta E_I)} [N(\Delta E_{LI}) - N(\Delta E_I)] \qquad (76)$$

and

$$I_{seq}^{(R)min} \simeq I_0 \frac{2\pi\hbar \chi_{RI}}{1 + N(\Delta E_I)} [N(\Delta E_I) - N(\Delta E_{RI})], \qquad (77)$$

respectively. In Eqs. (76) and (77), the quantity $\Delta E_I = \Delta E_{LI} = \Delta E_{RI}$ denotes the unbiased transmission gap.

Equations (75)–(77) offer an analysis of the transient switch-on processes independent of the width parameters Γ_L and Γ_R, the delocalization parameter ξ, and the transmission gaps ΔE_{LI} and ΔE_{RI}.

A. Switch-on currents

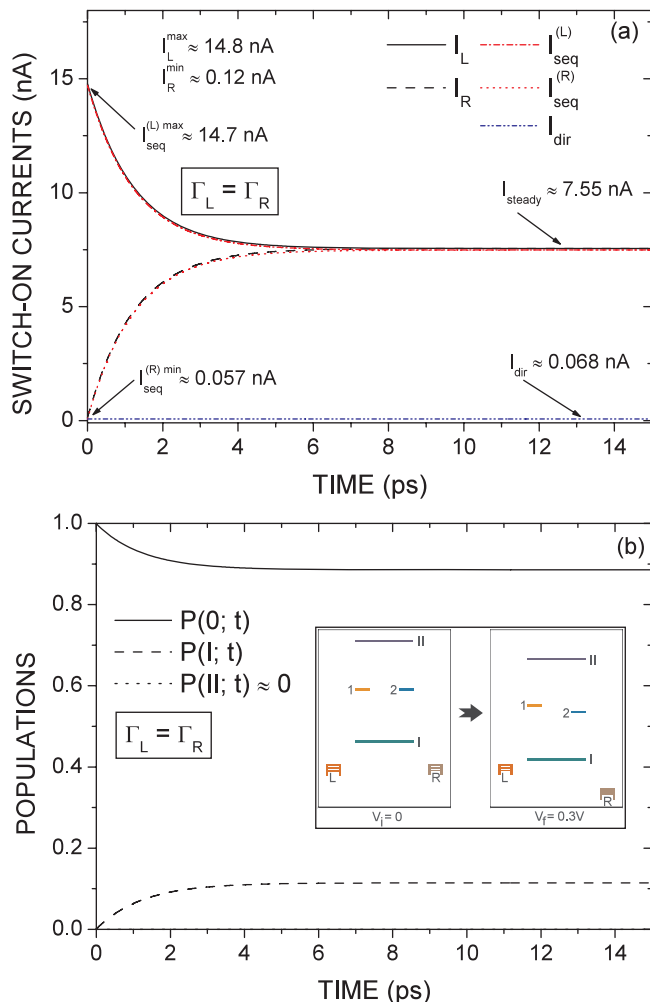Figures (3)–(8) display the evolution of transient switch-on currents,

FIG. 3. Off-resonant switch-on currents in a molecular junction with identical couplings of the molecular terminal sites to the respective electrodes (a) and time-evolution of the molecular populations (b). Note the negligible contribution from the direct (tunnel) current component to the total current. The switch-on currents display a symmetric movement to I_{steady}. [Here and in the following figures, the inserts in panels (b) show the position of the molecular levels (related to the extended MOs, I, and II, and the local MOs 1 and 2) with respect to the Fermi-levels of the electrodes L and R.] The calculations are based on Eqs. (24), (63), (65), and (69) with $\Delta E_1(0) = \Delta E_2(0) = 0.6$ eV, $\eta_1 = \eta_2 = 0.4$, $\beta = 0.4$ eV, $V_i = 0$, $V_f = 0.3$ V, $\Gamma_L = \Gamma_R = 5 \times 10^{-4}$ eV.
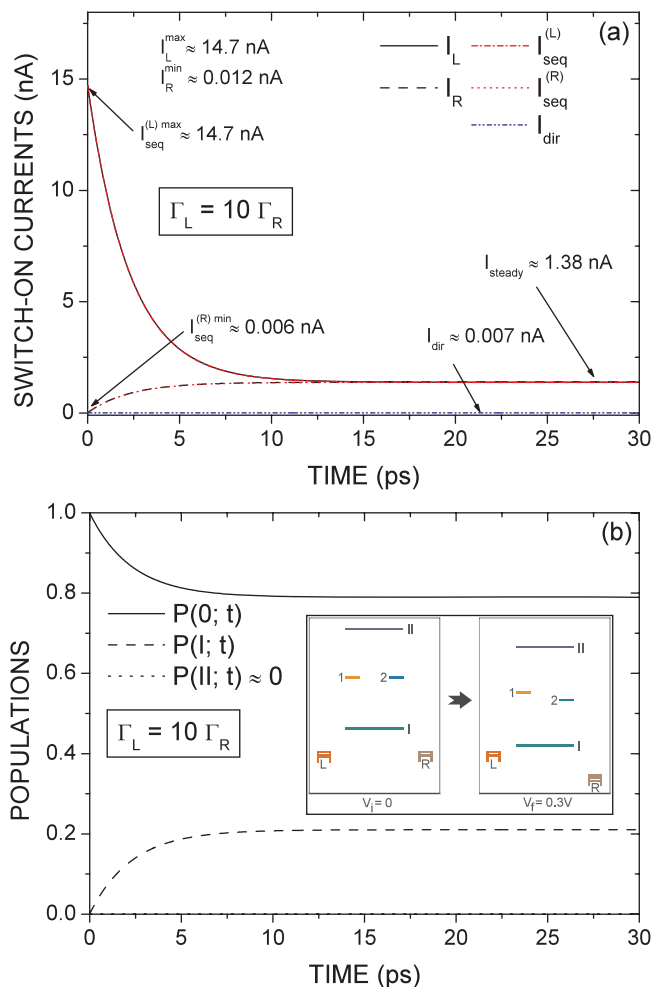
FIG. 4. Off-resonant switch-on currents in a molecular junction different couplings of the molecular terminal sites to the respective electrodes (a) and time dependence of the molecular level populations (b). Note the negligible contribution from the direct (tunnel) current component to the total current. Switch-on currents show a nonsymmetric evolution to I_{steady}. The switch-on current through the left contact, I_L^{max}, exceeds noticeably I_{steady}. The calculations are based on Eqs. (24), (63), (65), and (69). The parameters are the same as in Fig. 3 except $\Gamma_R = 5 \times 10^{-5}$ eV.

formed just after a sudden change of the applied voltage from $V = V_i(= 0)$ to $V = V_f(> 0)$, at room temperature and at identical terminal sites with symmetric ($\Gamma_L = \Gamma_R$) and asymmetric ($\Gamma_L = 10\Gamma_R$) couplings of the molecule to the electrodes, respectively. All calculations are performed with unbiased site gaps $\Delta E_1(0) = \Delta E_2(0)$, where $\Delta E_j(0) \equiv E_1^{(j)}(0) - E_F$ ($E_1^{(j)}(0)$ is the unbiased electron affinity [Eq. (34)] for the jth terminal site).

1. Off-resonant transmission regime, Figs. (3) and (4)

This regime occurs if the shift of the molecular energy levels I and II caused by the applied voltage $V = V_f$ is not large. Then, even the lowest level I remains at a position above the Fermi levels of the electrodes (cf. the insets in Figs. 3(b) and 4(b)). During the off-resonant regime, all transmission

gaps $\Delta E_{r\alpha}$, Eq. (64) are positive. Therefore, the population of the charged molecular states $|I\rangle$ and $|II\rangle$ increases only slightly (cf. Figs. 3(b) and 4(b)) and, therefore, the transmission channels are mainly related to the molecule being in its ground state and particularly in the state I. Following from this the analysis of the evolution behavior of the transient currents can be performed with the use of the simple expressions (75)–(77). At the given set of parameters, the direct current component is rather small whereas thermal activation leads to a much more efficient charge transmission along the sequential routes (Figs. 3(a) and 4(a)). In the case of a symmetric contact of the molecule to the electrodes ($\Gamma_L = \Gamma_R$), the evolution of the currents $I_L(t) \simeq I_{seq}^{(L)}(t)$ and $I_R(t) \simeq I_{seq}^{(R)}(t)$ display a symmetric behavior while relaxing towards the steady state current I_{steady}. Note that the steady state current differs marginally from the maximal switch-on current $I_L^{max} \simeq I_{seq}^{(L)}(0)$ and minimal switch-on current $I_R^{min} \simeq I_{seq}^{(R)}(0)$.
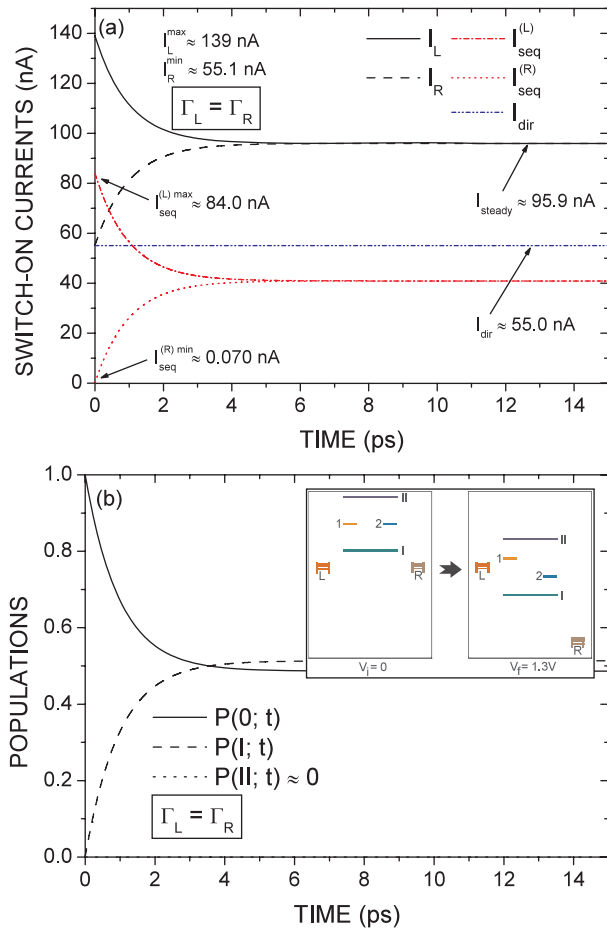
FIG. 5. Formation of switch-on currents in the molecular junction at resonant charge transmission with the participation of the lowest molecular level of a singly charged molecule (a) and time–dependence of the molecular level populations (b). Identical couplings of the molecular terminal sites to the respective electrodes has been assumed. A noticeable contribution of the direct (tunnel) current component to the total current can be seen. The switch-on currents display a symmetric evolution to I_{steady}. The calculations are based on Eqs. (24), (63), (65), and (69). The parameters are the same as in Fig. 3, except $V_f = 1.3$ V.
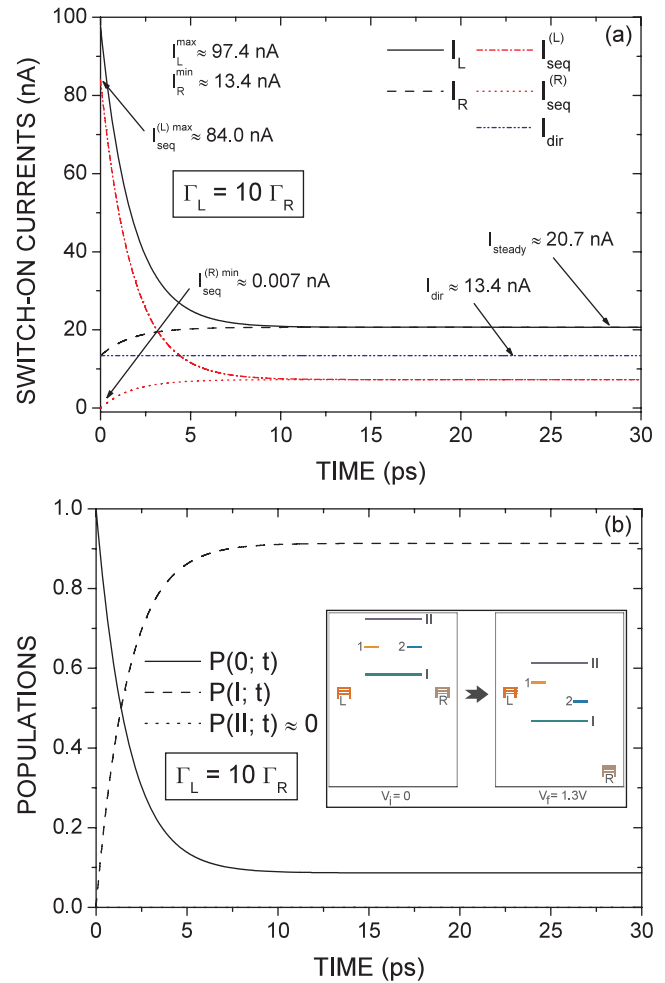

FIG. 6. Formation of switch-on currents in the molecular junction at a resonant charge transmission with the participation of the lowest level of the singly charged molecule (a) and time dependence of the molecular level populations (b). Different couplings of the molecular terminal sites to the respective electrodes have been assumed. In comparison to the symmetric case the suppression of the direct (tunnel) current component to the total current becomes obvious. The switch-on currents demonstrate a nonsymmetric movement to I_{steady}. The initial switch-on current through the left contact exceeds noticeably the steady state current. The calculations are based on Eqs. (24), (63), (65), and (69). The parameters are the same as those for Fig. 4 except $V_f = 1.3$ V.

Figure 3(a) depicts that $I_L^{\max} - I_{\text{steady}} \simeq I_{\text{steady}}$ and, $I_{\text{steady}} - I_R^{\min} \simeq I_{\text{steady}}$, $I_R^{\max} \simeq I_{\text{seq}}^{(R)}(t \gg \tau_{st}) \simeq I_{\text{steady}}$.

The behavior of the currents changes drastically in the presence of asymmetric contacts of the molecule to the electrodes [here, at $\Gamma_L = 10\Gamma_R$, cf. Fig. 4(a)]. In this case we find $I_L^{\max} \gg I_{\text{steady}}$ and $I_R^{\max} \simeq I_{\text{steady}}$. The appearance of a large switch-on current $I_L^{\max}$ compared to I_{steady} is originated by the efficient injection of an extra electron from the left electrode and a much less efficient transfer of an extra electron from the molecule to the right electrode. These results are easily explained by Eqs. (75)–(77) if one notices the fact that in the off-resonant voltage region all distribution functions satisfy the condition $N(\Delta E_{r\alpha}) \ll 1$. Besides, at a given applied voltage, the inequality $N(\Delta E_{LI}) \gg N(\Delta E_I) \gg N(\Delta E_{RI})$ is valid with high accuracy so that the ratio of the currents, $\zeta = I_L^{\max}/I_{\text{steady}}$, can be estimated as $\zeta \simeq 1 + (\chi_{LI}/\chi_{RI})$. In the case of strong delocalization of an extra electron across the molecular sites 1 and 2 (when $\Delta E(V)^2 \ll 4\beta^2$ and, thus, $\xi^2 \simeq 1/2$), it yields $\zeta \simeq 1 + (\Gamma_L/\Gamma_R)$. Therefore, at $V = V_f = 0.3$ V one obtains $\zeta \simeq 2$ (at symmetric

electrodes-molecule contacts) and $\zeta \simeq (\Gamma_L/\Gamma_R) \gg 1$ (at asymmetric contacts). Thus, at strongly different couplings of the terminal molecular sites to the adjacent electrodes, the maximal value of the switch-on current $I_L^{\max}$ can significantly exceed the steady state current I_{steady}. The ratio ζ can become large if the state I is associated with the presence of an extra electron mainly at the site 1 (so that $\xi^2 \sim 1$). Such a case can be realized at a weak inter-site coupling β, i.e., at a negligible electron delocalization.

2. Resonant transmission through a single molecular level, Figs. 5 and 6

Electron transmission occurs subject to the condition that only the lowest molecular level I is positioned below the Fermi-level of the left electrode, thus $\Delta E_{LI} \geq 0$, whereas
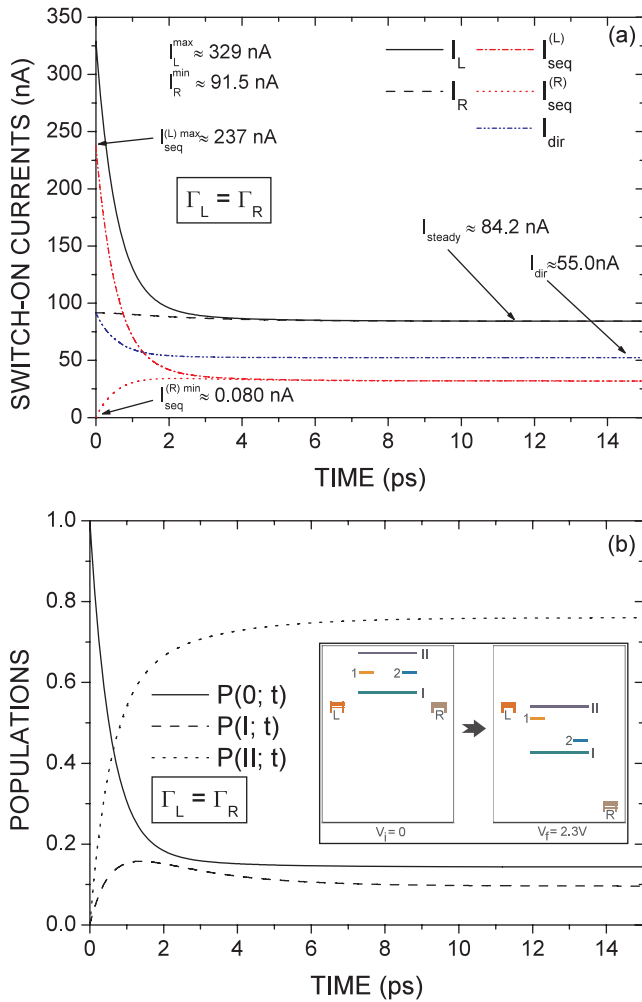
FIG. 7. Formation of switch-on currents in the molecular junction at resonant charge transmission with the participation of both molecular levels of the singly charged molecule (a) and time dependence of the molecular level populations (b). Identical couplings of the molecular terminal sites to the respective electrodes have been assumed. A small contribution of the direct (tunnel) current component to the total current can be seen. The switch-on currents demonstrate a symmetric motion to I_{steady}. The calculations are based on the Eqs. (24), (63), (65), and (69). The parameters are the same as in Fig. 3 except $V_f = 2.3$ V.
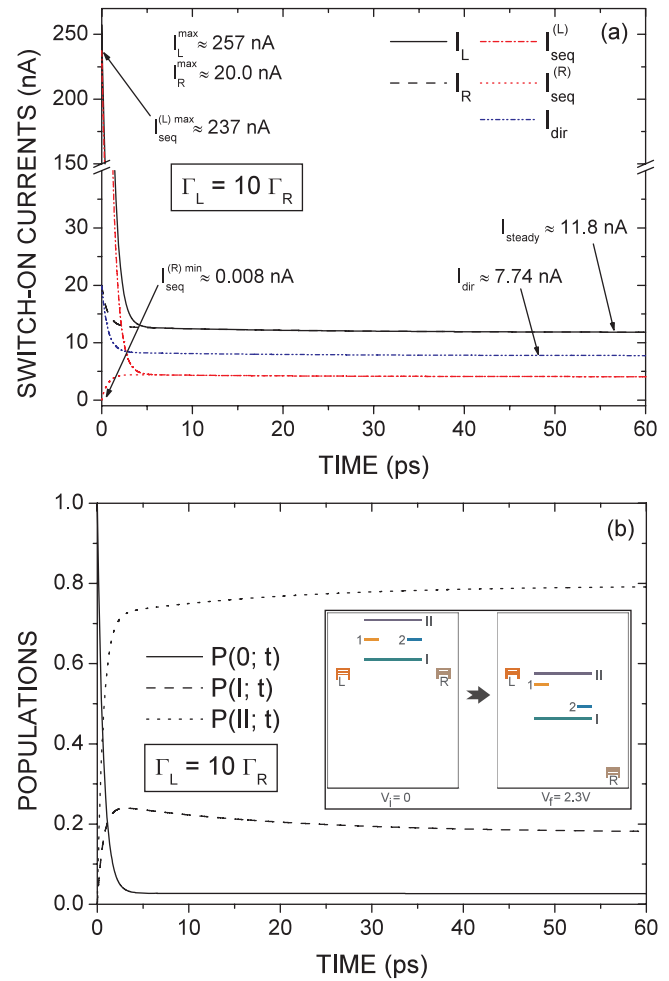

FIG. 8. Formation of switch-on currents in the molecular junction at a resonant charge transmission with the participation of both molecular levels of the singly charged molecule (a) and time dependence of the molecular level populations (b). Different couplings of the molecular terminal sites to the respective electrodes have been assumed. In comparison to the symmetric case, one notices the reduction of the direct (tunnel) current component. The switch-on currents demonstrate a strongly asymmetric motion to I_{steady}. The initial value of the switch-on current through the left contact, I_L^{max}, exceeds significantly the steady state current. This can be explained by the transformation of the extended molecular states into localized ones. The calculations are based on Eqs. (24), (63), (65), and (69). The parameters are the same as in Fig. 4 except $V_f = 2.3$ V.

$\Delta E_{LII} > 0$, $\Delta E_{RI} > 0$, $\Delta E_{RII} > 0$ (see the insets in Figs. 5(b) and 6(b). Since the tunneling route of transmission includes resonances with one of the molecular levels, the contribution of the direct component $I_{dir}(t)$ to the total currents $I_L(t)$ and $I_R(t)$ becomes comparable to the contribution of the sequential components $I_{seq}^{(L)}(t)$ and $I_{seq}^{(R)}(t)$ (Fig. 5). However, the direct component does not exhibit any noticeable time dependence. This observation can be explained by the fact that the molecular level II is positioned above the Fermi-levels of both electrodes and does not participate in the resonant transmission. Therefore, the main contribution in the integral [Eq. (67)] is related to the region around $E \simeq E_I$. Since at a given $V = V_f$ one derives $\cos \psi(V) \simeq 1$, $E_I - E_{II} \simeq \rho(V)$, then $\mathcal{R}_0 \simeq \mathcal{R}_I$. This reduces Eq. (57) to the form $I_{dir} \simeq I_{tun}^{(0)}[P(0;t) + 2P(I;t)]$. As a result, owing to the conditions (46) and $P(II;t) \simeq 0$, the direct current is a time-independent quantity, $I_{dir} \simeq I_{tun}^{(0)}$. In the case of symmetric

contacts of the molecule to the electrodes, the deviation of the extremal values of the switch-on currents from their common steady state current is not large ($I_L^{max} - I_{steady} \simeq I_{steady} - I_R^{min}$). This can be explained by the fact that at a given voltage bias (at which $\Delta E(V)^2 \sim 4\beta^2$), the delocalization of the transferred electron across the two terminal sites remains rather perfect. Therefore, a large switch-on current is only possible at different couplings of the terminal sites to the respective electrodes. This conclusion is well corroborated by the results depicted in Fig. 6(a).

3. Double-resonant transmission, Figs. 7 and 8

This behavior occurs if both molecular levels, I and II, are positioned below the Fermi-level of the left electrode.
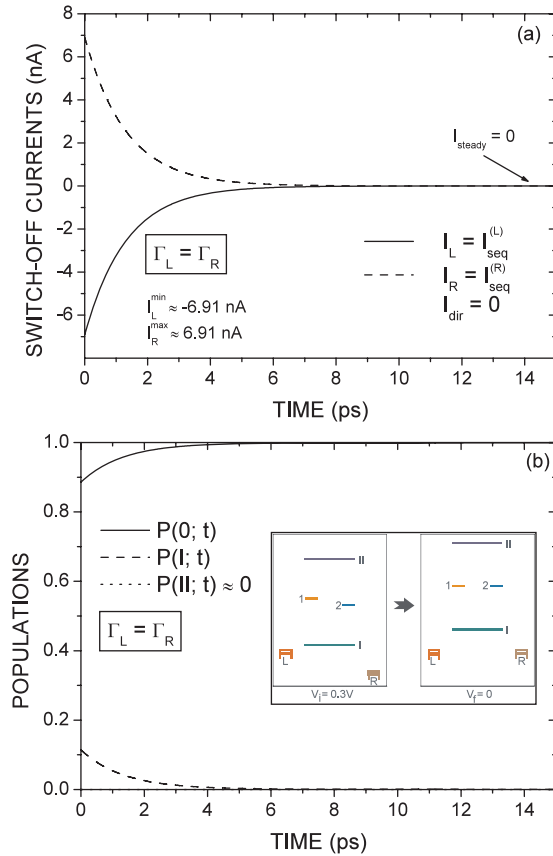
FIG. 9. Formation of switch-off currents in the molecular junction at a small population of the charged molecular states (a) and the time dependence of molecular populations formed at $V_i = 0.3$ V (b). An identical coupling of the molecular terminal sites to the respective electrodes results in a symmetric evolution of the switch-off currents to $I_{\text{steady}} = 0$. The calculations are based on Eqs. (24), (63), (65), and (69). The parameters are the same as in Fig. 3 except $V_i = 0.3$ V, $V_f = 0$.
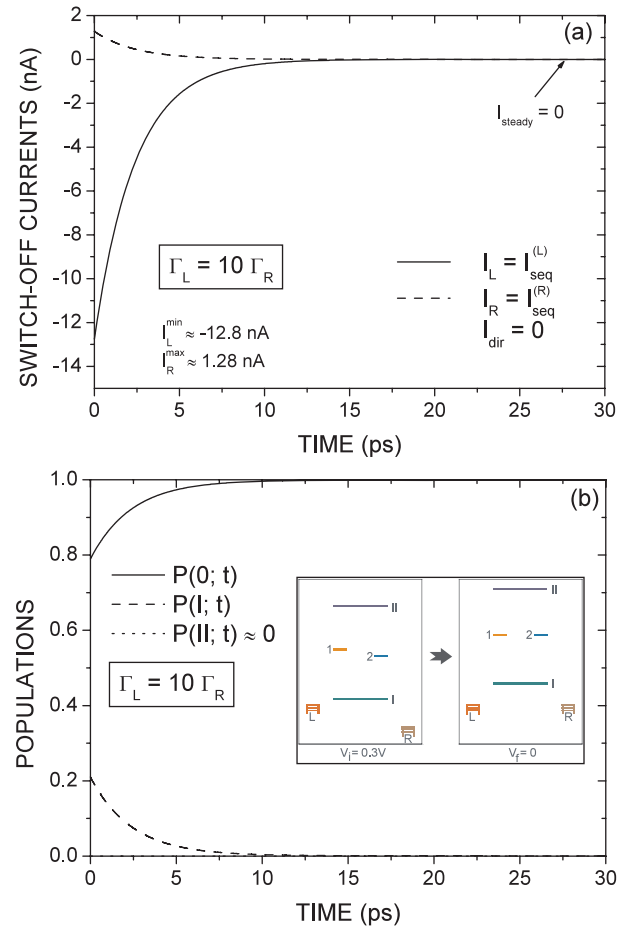

FIG. 10. Formation of switch-off currents in the molecular junction at a small population of the charged molecular states (a) and the time dependence of molecular populations formed at $V_i = 0.3$ V (b). Nonsymmetric couplings of the molecular terminal sites to the respective electrodes give rise to a non-symmetric evolution of the switch-off currents towards $I_{\text{steady}} = 0$. The calculations are based on Eqs. (24), (63), (65), and (69). The parameters are the same as in Fig. 9 except $\Gamma_L = 10\Gamma_R$.

Therefore, $\Delta E_{LI} < 0$, $\Delta E_{LII} < 0$, $\Delta E_{RI} > 0$, $\Delta E_{RII} > 0$, see the insets in Figs. 7(b) and 8(b). Due to a resonant transmission with the participation of both levels, a direct component of the current displays a temporal behavior similar to that of the hopping components (see Figs. 7(a) and 8(a)). Such a behavior can be explained by the fact that now all molecular probabilities including the $P(II; t)$, change their magnitude. The main reason is that at $V = V_f = 2.3$ V, the difference $\Delta E(V)$ between the site energies becomes too large so that $\Delta E(V)^2 \gg 4\beta^2$ and, thus, the extended molecular states $|I\rangle$ and $|II\rangle$ are in fact transformed into the localized states $|2\rangle$ and $|1\rangle$, respectively. As a result, the coupling of electrode L to the lowest level I becomes small (the mixture parameter (55) fulfills the condition $\xi^2 \ll 1$) whereas the coupling of the same level to the electrode R is large. Therefore, an extra electron hops from level I into the right electrode with a rate which strongly exceeds the rate of electron exit from the left electrode. A different situation appears in relation to level II. According to the fast transition of an extra electron from the left electrode to the state $|II\rangle \simeq |1\rangle$ and a slow exit of this electron into the right electrode, a large starting switch-on current I_L^{max} (compared to the steady state current I_{steady}) is formed. This appears even at an identical coupling of terminal sites to the adjacent electrodes (see Fig. 7(a)). A much larger

deviation of I_L^{max} from I_{steady} can be observed at an asymmetric coupling of the terminal sites to the electrodes, Fig. 8(a).

B. Switch-off currents

After switching on the voltage, the L–M–R system evolves to its stationary state at which the currents $I_L(t)$ and $I_R(t)$ become time independent and coincide with the steady state current $I_L(t \gg \tau_{\text{st}}) = I_R(t \gg \tau_{\text{st}}) = I_{\text{steady}}$ ($\neq 0$) (see Figs. 3(a)–8(a)). Simultaneously, the molecule is charged in such a way that the populations $P(I; t \gg \tau_{\text{st}})$ and $P(II; t \gg \tau_{\text{st}})$ of the charged states exceed the initial populations formed at $V = 0$ (cf. Figs. 3(b)–8(b)). Molecular charging is especially pronounced in the resonant regime of transmission (cf. Figs. (5)–(8)).

Let us focus next on the switch-off currents. These are formed just after the sudden change of the applied voltage from $V = V_i (\neq 0)$ to $V = V_f (= 0)$. In Figs. (9)–(11), the results are presented for $V_i > 0$. After switching-off the voltage, the L–M–R system evolves to its ground charge state where a current is absent so that $I_L(t \gg \tau_{\text{st}}) = I_R(t \gg \tau_{\text{st}})$
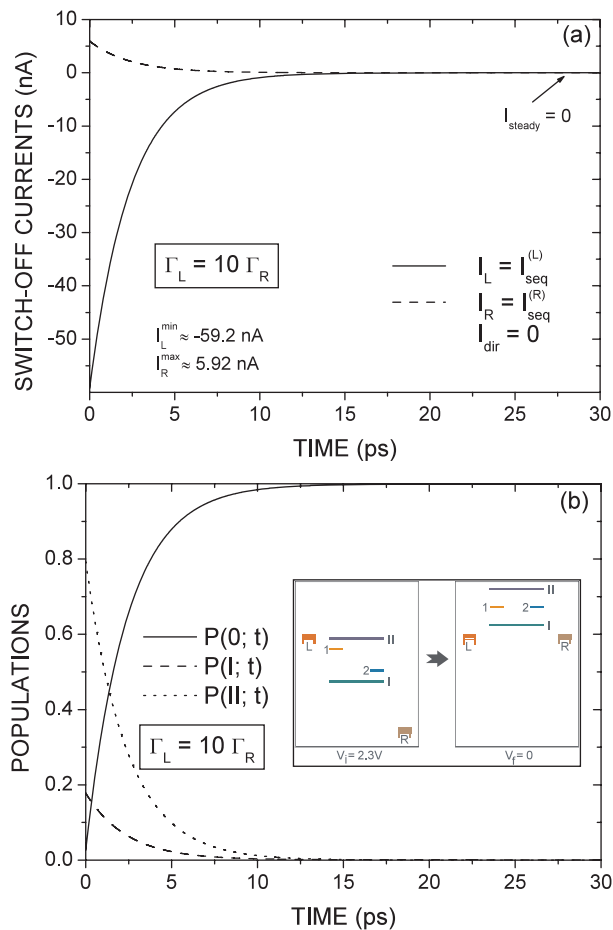
FIG. 11. Formation of switch-off currents in the molecular junction at a small population of the charged molecular states (a) and the time dependence of molecular populations formed at $V_i = 2.3$ V(b). Nonsymmetric couplings of the molecular terminal sites to the respective electrodes yield a nonsymmetric evolution of the switch-off currents towards $I_{steady} = 0$. The calculations are based on Eqs. (24), (63), (65), and (69). The parameters are the same as in Fig. 10 except that $V_i = 2.3$ V.
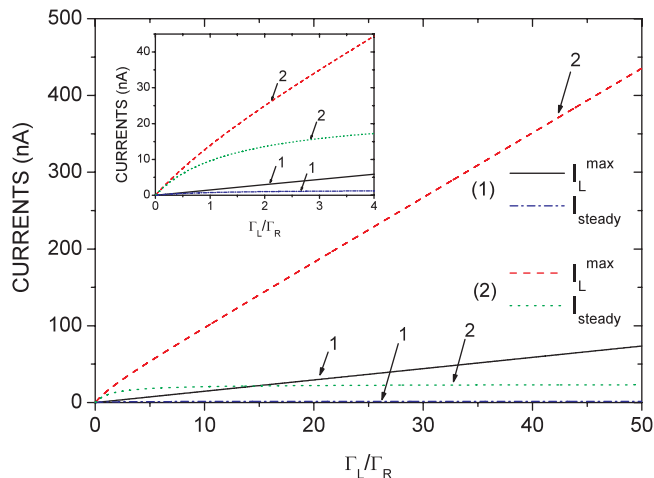

FIG. 12. Enhancement of the switch-on current as a function of the molecule-electrode coupling asymmetry. If $(\Gamma_L / \Gamma_R) > 1$ the asymmetry does not affect the steady-state current. The numbers 1 and 2 indicate the curves calculated at $V = 0.3$ V and $V = 1.3$ V, respectively. The calculations are based on Eqs. (24), (63), (65), and (69). The parameters are the same as in Fig. 3 except $\Gamma_R = 5 \times 10^{-5}$ eV.

$= I_{steady} = 0$. The evolution is accompanied by discharging of the molecule. In contrast to the switch-on process, which occurs at $V_f \neq 0$, the switch-off charge transmission takes place at $V_f = 0$. Therefore, any contribution of a direct component to the total switch-off current is absent. Besides, the currents $I_L(t)$ and $I_R(t)$ have opposite signs. The maximal value of the switch-off current strongly depends on the initial populations $P(I; 0)$ and $P(II; 0)$ which are identical to the steady state probabilities P_I and P_{II}, attained before switching-off the voltage. If the probabilities $P(v; 0)$ have been realized during off-resonant charge transmission, then $P(I; 0)$ and $P(II; 0)$, become small. Figures 9(b) and 10(b) depict the small magnitude of the noted initial populations created at $V_i = 0.3$ V and the respective switch-off currents. In the case of symmetric couplings of the terminal groups to the electrodes, the time-dependence of the switch-off currents completely coincides so that $|I_L^{min}| = I_R^{max}$ (cf. Fig. 9(a)) while at an asymmetric coupling the relation $|I_L^{min}| = 10 I_R^{max}$ is observed in complete correspondence to the ratio Γ_L / Γ_R (cf. Fig. 10(a)). There is no basic difference with respect to the time-dependence

of switch-off currents if the initial populations $P(I; 0)$ and $P(II; 0)$ have been formed during a resonant charge transmission (cf. Fig. 11(a) with Fig. 10(a)). The only distinction concerns the switch-off current $|I_L^{min}|$, presented in Fig. 11(a), which significantly exceeds the corresponding current value depicted in Fig. 10(a).

At the end of this section we underline that appearance of a large difference between the transient currents and the steady-state current is originated by the asymmetric charge kinetics in the L–M–R junction. In the case of the switch-on process the asymmetry appears if the rate of charge injection from the left electrode to the molecule exceeds the rate of moving an electron from the molecule into the right electrode. This asymmetry of rates is caused by nonidentical couplings of the molecule to the electrodes. Figure 12 illustrates this statement at the off-resonant and the single-level resonant regime of charge transmission (when $N(\Delta E_{LI}) \ll 1$ and $N(\Delta E_{LI}) \simeq 1$, respectively). In Fig. 12, respective curves are labeled by 1 and 2. It is seen that for both regimes, a maximal value of the switch-on current, I_L^{max}, increases linearly against the ratio (Γ_L / Γ_R) of the width parameters. In contrast, the steady-state current I_{steady} increases if only $\Gamma_L \leq \Gamma_R$ (see the inset in Fig. 12). I_{steady} is not changed for $\Gamma_L / \Gamma_R > 1$. This effect can be explained in using the expressions (75)–(77) valid at $P(II; t) \simeq 0$. Actually, in line with Eqs. (75) and (76) the current I_L^{max} is proportional to the $\chi_{LI} N(\Delta E_{LI})$ and, thus, $I_L^{max} \sim \Gamma_L$. At the same time, I_{steady} is proportional to the $[\chi_{LI} \chi_{RI} / (\chi_{LI} + \chi_{RI})] N(\Delta E_{LI})$. Therefore, one can see that $I_L^{max} \sim \Gamma_L$ whereas $I_{steady} (\sim \Gamma_R)$ is not changed in the region where $(\Gamma_L / \Gamma_R) > 1$. This behavior corresponds to a situation where the inter-electrode steady-state charge flow is limited by the slowest kinetic process (here, by the hopping transition of an electron from the molecular level I to the right electrode).

V. CONCLUSION

A unified description of current evolution in a molecular junctions towards a steady state has been offered. The description allows to analyze the direct (tunneling) as well as the sequential (hopping) electron transmission, using a particular set of parameters (level broadening, energy gaps, and inter-site couplings). Charging and discharging of the molecule mainly determine the efficiency of electron transmission along the channels associated with the charged states of the molecule. An important finding is that the currents through the left and the right contacts ($I_L(t)$ and $I_R(t)$, respectively) differ from each other before a common steady state current I_{steady} is formed. Depending on the couplings of the molecule to the electrodes, the difference can become rather large. As an example, the evolution of switch-on/-off currents has been analyzed in the framework of an inter-electrode molecular wire system which contains a molecule with two active terminal sites. This setup allows one to clarify the effect of contacts on the current formation as well as the influence of inter-site couplings. The latter determine the extent of delocalization of an extra (transferred) electron over the molecule. If the delocalization is large, the electron density is concentrated at the terminal sites with nearly equal weights (the delocalization parameter ξ, Eq. (55) is about $1/\sqrt{2}$). As a result, the evolution of the switch-on currents $I_L(t)$ and $I_R(t)$ is rather symmetric (cf. Figs. 3(a) and 5(a)).

Features of asymmetry can be induced in two different ways. First, asymmetry is realized when the couplings of the terminal sites to the respective electrodes differ from each other (cf. Figs. 3(a) and 5(a) with the corresponding Figs. 4(a) and 6(a)). And second, current asymmetry can occur if well-localized MOs are formed, either by a given molecular structure or by the applied voltage. The latter possibility is demonstrated in Fig. 7(a), where the asymmetry appears as a result of the transformation of the extended MOs into localized ones. This regime emerges when the delocalization parameter ξ starts to fulfill the relation $\xi^2 \ll 1$. After a change of the MOs, the transferred electron is located either at the left or the right terminal site. Thus, a voltage division asymmetry in the couplings of the molecular levels to the electrodes is intrinsically introduced. As a result, an asymmetric evolution of the switch-on currents $I_L(t)$ and $I_R(t)$ appears even for identical couplings of the terminal sites to the electrodes (cf. Figs. 5(a) and 7(a)). The asymmetry leads to a considerable difference between the maximum value $I_L^{\max} = I_L(0)$ of the switch-on current $I_L(t)$ and the steady state current I_{steady}. Differences between $I_L^{\max}$ and I_{steady} are strongly amplified if an asymmetric coupling is already present(cf. Figs. 8 and 12). In this case, the tunneling route of electron transmission initiates a small contribution to the total current so that the asymmetric behavior of the switch-on current is completely caused by the sequential route.

The basic difference between the behavior of the switch-off and switch-on currents is caused by the fact that after switching-off the source-drain voltage, the electron transmission occurs in the absence of a voltage bias. Therefore, the direct current component disappears. This in turn results in an extension of the terminal MOs of the charged molecule across the whole molecule. Moreover, the asymmetric behavior of the switch-off currents is solely determined by the asymmetry with respect to the couplings of terminal sites to the adjacent electrodes (see Figs. 9–10). Note that a similar effect exists even if the charge transmission occurs with the participation of the frontier orbital only.[28,29] In this way the appearance of large transient switch-on/off currents in the molecular junctions with nonidentical couplings of the molecule to the electrodes can be realized. The effect becomes more pronounced for molecules with sustainable localized molecular orbitals. Generally, the formation of large switch-on (switch-off) currents in molecular junctions originates from fast charging (discharging) of the molecule as compared to a slower formation of the steady state current.

Such effects caused by the appearance of significant switch-on/off currents may play a guiding role in devising realistic molecular devices. Large currents can cause large heating in the contact region, resulting in a destabilization of the molecule-lead contacts up to their full destruction. In addition, conformational transitions of the molecule can be induced as well as the formation of uncontrollable large electric and magnetic fields.

The detection of transient currents represents a particular experimental challenge. This is mainly due to the fact that in the transmission process only a single or, may be, two extra electrons can enter the molecule resulting in very small currents. To measure temporal changes of such currents is extremely difficult. Alternatively, one may also take into consideration the fact that an extra electron is able to modify the spectral or magnetic properties of the molecule and, thus, spectroscopic or EPR methods can be used to identify those striking signatures of transient charge transfer processes in the L–M–R device.

APPENDIX A: TRANSFER RATES BEYOND THE BORN APPROXIMATION

The operator $H'\hat{G}(E)H'$ (second term on the right-hand side of Eq. (17)) gives rise to transitions where the molecule does not alter its charging state ($N' = N$) or changes its charge by that of two electrons ($N' = N \pm 2$). The derivation of respective transfer rates is based on the Eqs. (12)–(16). To calculate the necessary matrix elements $\langle L'M(N')R'|H'\hat{G}(E)H'|LM(N)R \rangle$ we note that the Green's operator (18) is specified by the entire Hamiltonian $H = H_0 + H'$. At the macroscopic electrodes, this Hamiltonian can be reduced to a diagonal form [31,33] so that $H = H_{\text{electrode}} + H_{\text{mol}}^{(\text{eff})}$ where $H_{\text{mol}}^{(\text{eff})} = \sum_{M(N)} \mathcal{E}(M(N))|M(N)\rangle\langle M(N)|$ is the modified molecular Hamiltonian. Here, the molecular energies

$$\mathcal{E}(M(N)) \simeq E_{M(N)} + \Sigma_{MM}^{(L)}(\mathcal{E}) + \Sigma_{MM}^{(R)}(\mathcal{E}) \qquad (A1)$$

contain self-energies $(r = L, R)$

$$\Sigma_{MM}^{(r)}(\mathcal{E}) \simeq \sum_{\mathbf{k}\sigma} \sum_{M'} \frac{|V_{M(N);r\mathbf{k}\sigma M'(N-1)}|^2}{\mathcal{E} - (E_{r\mathbf{k}\sigma} + E_{M'(N-1)}) + i0^+} \quad (A2)$$

caused by the interaction of the molecule with the electrodes. The imaginary part of the self-energy

$$\Gamma_{M(N)}^{(r)}(\mathcal{E}) \simeq 2\pi \sum_{\mathbf{k}\sigma} |V_{M(N);r\mathbf{k}\sigma M'(N-1)}|^2$$
$$\times \delta[\mathcal{E} - (E_{r\mathbf{k}\sigma} + E_{M'(N-1)})], \quad (A3)$$

fixes the molecular level-broadening (width) parameters.[47] With the introduction of the molecular energies (A1) the general form of the desirable matrix elements is

$$\langle L'M(N')R'|H'\hat{G}(E)H'|LM(N)R\rangle = \sum_{\tilde{L}\tilde{M}(\tilde{N})\tilde{R}}$$
$$\times \frac{\langle L'M(N')R'|H'|\tilde{L}\tilde{M}(\tilde{N})\tilde{R}\rangle\langle|\tilde{L}\tilde{M}(\tilde{N})\tilde{R}|H'|LM(N)R\rangle}{E - E_{\tilde{L}} - \mathcal{E}_{\tilde{M}(\tilde{N})} - E_{\tilde{R}}} .$$
$$(A4)$$

This matrix element characterizes transitions on the energy shell $E = E_L + E_{M(N)} + E_R = E_{L'} + E(M'(N')) + E_{R'}$ (cf. definitions (15) and (16) for the energies E_r and $E_{r'}$, respectively).

Setting $N' = N, N \pm 2$ we achieve respective transfer rates. The transfer rate retaining the charge state of the molecule reads

$$\chi_{M(N)\to M'(N)}^{(r)}$$
$$= \frac{2\pi}{\hbar} \sum_{\mathbf{k}\sigma} \sum_{\mathbf{k}'\sigma'} (1 - \delta_{r\mathbf{k}\sigma, r'\mathbf{k}'\sigma'}) f_r(E_{r\mathbf{k}\sigma}) [1 - f_{r'}(E_{r'\mathbf{k}'\sigma'})]$$
$$\times \left| \sum_{\tilde{M}} \left[\frac{V_{M'(N);r'\mathbf{k}'\sigma'\tilde{M}(N-1)} V_{r\mathbf{k}\sigma\tilde{M}(N-1);M(N)}}{\mathcal{E}(M(N)) - E_{r'\mathbf{k}'\sigma'} - \mathcal{E}(\tilde{M}(N-1))} \right.\right.$$
$$\left.\left. + \frac{V_{r'\mathbf{k}'\sigma'M'(N);\tilde{M}(N+1)} V_{\tilde{M}(N+1);r\mathbf{k}\sigma M(N)}}{E_{r\mathbf{k}\sigma} + \mathcal{E}(M(N)) - \mathcal{E}(\tilde{M}(N+1))} \right] \right|^2$$
$$\times \delta[E_{r\mathbf{k}\sigma} + E_{M(N)} - E_{r'\mathbf{k}'\sigma'} - E_{M'(N)}]$$
$$+ \frac{2\pi}{\hbar} \sum_{\mathbf{k}\sigma} \left[[1 - f_r(E_{r\mathbf{k}\sigma})] \right.$$
$$\times \left| \sum_{\tilde{M}} \frac{V_{M'(N);r\mathbf{k}\sigma\tilde{M}(N-1)} V_{r\mathbf{k}\sigma\tilde{M}(N-1);M(N)}}{\mathcal{E}(M(N)) - E_{r\mathbf{k}\sigma} - \mathcal{E}(\tilde{M}(N-1))} \right|^2$$
$$+ f_r(E_{r\mathbf{k}\sigma}) \left| \sum_{\tilde{M}} \frac{V_{r\mathbf{k}\sigma M'(N);\tilde{M}(N+1)} V_{\tilde{M}(N+1);r\mathbf{k}\sigma M(N)}}{E_{r\mathbf{k}\sigma} + \mathcal{E}(M(N)) - \mathcal{E}(\tilde{M}(N+1))} \right|^2 \right]$$
$$\times \delta[E_{M(N)} - E_{M'(N)}]. \quad (A5)$$

The transfer rates describing double molecular oxidation and double reduction (caused by the electrodes) take the form

$$\chi_{M(N)\to M'(N-2)}^{(r)}$$
$$= \frac{2\pi}{\hbar} \sum_{\mathbf{k}\sigma} \sum_{\mathbf{k}'\sigma'} (1 - \delta_{r\mathbf{k}\sigma, r'\mathbf{k}'\sigma'}) [1 - f_r(E_{r\mathbf{k}\sigma})]$$
$$\times [1 - f_{r'}(E_{r'\mathbf{k}'\sigma'})]$$

$$\times \left| \sum_{\tilde{M}} \frac{V_{r'\mathbf{k}'\sigma'M'(N-2);\tilde{M}(N-1)} V_{r\mathbf{k}\sigma\tilde{M}(N-1);M(N)}}{\mathcal{E}(M(N)) - E_{r\mathbf{k}\sigma} - \mathcal{E}(\tilde{M}(N-1))} \right|^2$$
$$\times \delta[E_{r\mathbf{k}\sigma} + E_{r'\mathbf{k}'\sigma'} + E_{M'(N-2)} - E_{M(N)}] \quad (A6)$$

and

$$\chi_{M(N)\to M'(N+2)}^{(r)}$$
$$= \frac{2\pi}{\hbar} \sum_{\mathbf{k}\sigma} \sum_{\mathbf{k}'\sigma'} (1 - \delta_{r\mathbf{k}\sigma, r'\mathbf{k}'\sigma'}) f_r(E_{r\mathbf{k}\sigma}) f_{r'}(E_{r'\mathbf{k}'\sigma'})$$
$$\times \left| \sum_{\tilde{M}} \frac{V_{M'(N+2);r'\mathbf{k}'\sigma'\tilde{M}(N+1)} V_{\tilde{M}(N+1);r\mathbf{k}\sigma M(N)}}{E_{r\mathbf{k}\sigma} + \mathcal{E}(M(N)) - \mathcal{E}(\tilde{M}(N+1))} \right|^2$$
$$\times \delta[E_{r\mathbf{k}\sigma} + E_{r'\mathbf{k}'\sigma'} + E_{M(N)} - E_{M'(N+2)}], \quad (A7)$$

respectively.

APPENDIX B: STEADY STATE MOLECULAR POPULATIONS

In Eq. (69), steady state populations P_ν are found from the kinetic equations (47) at $V = V_f$. Setting $\dot{P}(\nu; t) = 0$ one obtains

$$P_0 = \frac{1}{\Delta} (K_{I\to0}K_{II\to0} + K_{I\to0}K_{II\to I} + K_{II\to0}K_{I\to II}).$$
$$(B1)$$

$$P_I = \frac{1}{\Delta} [K_{0\to I}K_{II\to0} + (K_{0\to I} + K_{0\to II})K_{II\to I}],$$

$$P_{II} = \frac{1}{\Delta} [K_{0\to II}K_{I\to0} + (K_{0\to I} + K_{0\to II})K_{I\to II}],$$
$$(B2)$$

where

$$\Delta = K_{I\to0}K_{II\to0} + 2(K_{0\to I} + K_{0\to II})(K_{I\to II} + K_{II\to I})$$
$$+ K_{II\to0}(2K_{0\to I} + K_{I\to II}) + K_{I\to0}(2K_{0\to II} + K_{II\to I}),$$
$$(B3)$$

APPENDIX C: PRE-EXPONENTIAL FACTORS

In Eq. (69), the concrete form of the pre-exponential factors is given by

$$C_0^{(1)} = \frac{1}{K_1(K_1 - K_2)} \{P(0;0)[(K_{I\to0} + K_{I\to II} - K_1)$$
$$\times (K_{II\to0} + K_{II\to I} - K_1) - K_{I\to II}K_{II\to I}]$$
$$+ P(I;0)[K_{I\to0}(K_{II\to0} + K_{II\to I} - K_1)$$
$$+ K_{I\to II}K_{II\to0}] + P(II;0)[K_{II\to0}(K_{I\to0} + K_{I\to II}$$
$$- K_1) + K_{II\to I}K_{I\to0}]\},$$
$$(C1)$$

$$C_I^{(1)} = \frac{1}{K_1(K_1 - K_2)} \{P(0;0)[2K_{0\to I}(K_{II\to0} + K_{II\to I} - K_1)$$
$$+ 2K_{I\to II}K_{II\to I}] + P(I;0)[(2K_{I\to0} + 2K_{II\to0} - K_1)$$

$$\times (K_{II \to 0} + K_{II \to I} - K_1) - 2K_{0 \to II} K_{II \to 0}]$$
$$+ P(II;0)[K_{II \to I}(2K_{I \to 0} + 2K_{II \to 0} - K_1)$$
$$+ 2K_{I \to 0} K_{II \to 0}]\}, \tag{C2}$$

and

$$C_{II}^{(1)} = \frac{1}{K_1(K_1 - K_2)} \{P(0;0)[2K_{II \to 0}(K_{I \to 0} + K_{I \to II}$$
$$- K_1) + 2K_{I \to II} K_{I \to 0}] + P(I;0)[K_{I \to II}(2K_{I \to 0}$$
$$+ 2K_{II \to 0} - K_1) + 2K_{I \to 0} K_{II \to 0}]$$
$$+ P(II;0)[(2K_{I \to 0} + 2K_{II \to 0} - K_1)(K_{I \to 0}$$
$$+ K_{I \to II} - K_1) - 2K_{0 \to I} K_{I \to 0}]\}. \tag{C3}$$

The factors are expressed not only by state-to-state transfer rates at $V = V_f$, but also by the initial molecular populations $P(\nu;0)$ formed at $V = V_i$. Therefore, the quantities P_ν and $P(\nu;0)$ are calculated with the same expressions (B1)–(B3) but at $V = V_f$ and $V = V_i$, respectively. The form of the $C_\nu^{(2)}$ follows from Eqs. (C1)–(C3) if one substitutes $K_1(K_2)$ by $K_2(K_1)$.

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