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FORMATION OF ELECTROLUMINESCENCE IN AN ELECTRODE–MOLECULE–ELECTRODE SYSTEM

The kinetics of electroluminescence formation in an electrode–molecule–electrode system has been considered in the framework of the HOMO–LUMO model. The appearance of electroluminescence in a charge-neutral molecule is shown to be driven by the hopping and tunneling mechanisms of electron transfer between the electrodes. The corresponding electron transmission is found to occur with the participation of both real and virtual states of the charged molecule. Conditions for the electron transmission through the molecule to occur by the hopping and tunneling mechanisms in the resonant regime are determined. In this case, the molecular electrofluorescence and molecular phosphorescence, as well as the current through the molecule, achieve their maximum values.

Keywords: electron transport, molecular electroluminescence, separate molecule.

1. Introduction

The scanning tunnel microscope (STM) allows the electroluminescence to be observed in various systems, e.g., metal surfaces, metal particles, semiconductor heterostructures, quantum dots, and so forth, as well as in self-assembling molecular monolayers. As for separate molecules, their luminescence was revealed for the first time in 1988, while studying the electron density in molecules adsorbed on a substrate [1, 2].

During the last decade, the optical properties of molecules, which are located on a metal substrate, were mainly studied in connection with their further application in optoelectronics. However, the emission associated with the excitation of surface plasmons in the regions between an STM tip and the metal substrate [3, 4] becomes a significant obstacle in studying the molecular electroluminescence. The direct observation of the electroluminescence from molecules turned out possible only provided that the molecule is isolated from the metal substrate either by means of thin dielectric films [5–8] or by using a few molecular monolayers [9–13]. We would like to mention also the experiments dealing with the luminescence of single molecules [5, 14] attached to an ultra-thin layer of aluminum oxide grown up on a NiAl substrate. The obtained plots describing the radiation intensity distribution over the photon energy differ considerably from one another depending on the type of an applied tip. However, the curves obtained by subtracting plasmon modes from experimental curves were found to be considerably similar [5], which testifies that the intramolecular luminescence does not depend on the type of an STM tip.

The results obtained in the course of the experiments with molecular layers [9, 15, 16] showed that the intramolecular luminescence does not depend on the voltage polarity, provided that the applied voltage biases are identical. This fact testifies that the molecular levels are not coupled with the substrate, but are shifted under the action of the applied voltage bias. It was also demonstrated that the molecular electron structure and the resonance of the molecular levels with the Fermi levels in the substrate and a tip are the key factors for the molecular lumi-

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nescence to take place. Moreover, the luminescence was observed only if the voltage bias exceeds the energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). The further experiments with other materials used as insulating layers and surface molecular layers [10, 17–20] brought about similar results. In addition, the asymmetry of molecular fluorescence and phosphorescence with respect to the applied voltage polarity, which was detected in works [6, 7, 21] for C_{60} and C_{70} molecular crystals, was associated with the asymmetry of HOMO and LUMO levels with respect to the Fermi energies in an STM tip and the substrate [22], as well as with different tip–molecule and molecule–substrate energy barriers [6, 23].

According to the aforesaid, we may assert that the energy arrangement of HOMO and LUMO levels in relation to the Fermi levels in the electrodes plays an important role in the formation of the electroluminescence phenomenon. However, the mechanisms engaged, when the current through a single molecule forces this molecule to emit photons, remains poorly investigated theoretically. This work aims at elucidating how the transmission gaps in the system electrode 1–molecule–electrode 2 (1M2) affect the formation of fluorescence and phosphorescence by the molecule and how this phenomenon depends on the applied voltage bias. For this purpose, we consider the kinetics of current formation in the 1M2 system in the framework of the HOMO–LUMO model.

2. Basic equations

Following works [24–28], let us consider a model of 1M2 system consisting of a molecule coupled with two non-magnetic electrodes. The Hamiltonian of the system in the standard form looks like

$$H = H_{\mathrm{el}} + H_{\mathrm{mol}} + H_{\mathrm{em}}. \tag{1}$$

The first term,

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

is the Hamiltonian of electrodes. Here, $E_{r\mathbf{k}}$ is the energy of an electron in the conduction band of the r-th electrode and characterized by the wave vector $\mathbf{k}$ (for non-magnetic electrodes and in the absence of a magnetic field, this energy does not depend on the projection of the electron spin σ). The quantities $a^{+}_{r\mathbf{k}\sigma}$ and $a_{r\mathbf{k}\sigma}$ are the operators of creation and annihilation, respectively, of an electron in the one-electron state $r\mathbf{k}\sigma$. The second term in Eq. (1),

$$H_{\mathrm{mol}} = \sum_{\lambda} \Bigg[\sum_{\sigma} \left(\varepsilon_{\lambda\sigma} + U_{\lambda} c^{+}_{\lambda\, -\sigma} c_{\lambda\, -\sigma} \right) c^{+}_{\lambda\sigma} c_{\lambda\sigma} + + \frac{1}{2} \sum_{\lambda' \neq \lambda} \left(\sum_{\sigma\sigma'} U_{\lambda\lambda'} c^{+}_{\lambda\sigma} c_{\lambda\sigma} c^{+}_{\lambda'\sigma'} c_{\lambda'\sigma'} - J_{\lambda\lambda'} \hat{s}_{\lambda} \hat{s}_{\lambda'} \right) \Bigg], \tag{3}$$

is the Hamiltonian of the molecule. Here, $\varepsilon_{\lambda\sigma}$ is the energy of the electron that occupies the λ-th molecular orbital (MO) with the spin projection σ; the parameters U_{λ} and $U_{\lambda\lambda'}$ determine the Coulomb interaction between electrons on the same MO and on different MOs, respectively; the parameter $J_{\lambda\lambda'}$ characterizes the exchange interaction between electrons on different MOs; the operators of creation and annihilation of an electron on the λ-th orbital and with the spin projection σ are designated as $c^{+}_{\lambda\sigma}$ and $c_{\lambda\sigma}$, respectively; and $\hat{s}_{\lambda}$ is the spin operator for the electron that occupies the λ-th MO. The third term in Eq. (1),

$$H_{\mathrm{em}} = \sum_{\lambda} \sum_{r\mathbf{k}\sigma} \left(\beta_{\lambda,r\mathbf{k}} c^{+}_{\lambda\sigma} a_{r\mathbf{k}\sigma} + \beta^{*}_{\lambda,r\mathbf{k}} a^{+}_{r\mathbf{k}\sigma} c_{\lambda\sigma} \right), \tag{4}$$

describes the interaction between the molecule and the electrodes. Here, $\beta_{\lambda,r\mathbf{k}}$ are matrix elements that characterize the interaction between the one-electron states of the molecule and the r-th electrode.

The transmission of electrons in the 1M2 system forms a current consisting of the hopping and tunneling components,

$$I^{(r)}(t) = I^{(r)}_{\mathrm{seq}}(t) + I_{\mathrm{dir}}(t). \tag{5}$$

The hopping component $I^{(r)}_{\mathrm{seq}}(t)$ is generated by the sequential transfer of an electron from the r-th electrode to the molecule and, afterward, from the molecule to the other electrode. The tunneling current component $I_{\mathrm{dir}}(t)$ is a result of the direct distance transfer of an electron between the electrodes. The MOs participate in this transfer virtually, i.e. the electron is not captured by the molecule. As a result, even under non-stationary conditions, the numbers of tunneling electrons that leave one of the electrodes and enter the other precisely equal each other, i.e. $I_{\mathrm{dir}}(t) \equiv I^{(1)}_{\mathrm{dir}}(t) \equiv -I^{(2)}_{\mathrm{dir}}(t)$.

In this work, the case of a weak interaction between the molecule and electrons is considered. Therefore, the individual properties of the molecule remain invariant, and Hamiltonian (3) can be expressed in the form [25, 26]

$$H_{\text{mol}} = \sum_{M,\,N} E_{M(N)} \,|M(N)\rangle\, \langle M(N)|, \tag{6}$$

where $|M(N)\rangle$ and $E_{M(N)}$ are the eigenstates and the characteristic energies, respectively, of the molecule (N is the number of electrons in the molecule). Let $N = N_{\text{G}}$ be the number of electrons in a non-charged (neutral) molecule, which can be in the ground state ($M(N_{\text{G}}) = M_0$) or in the excited singlet or triplet one ($M^*(N_{\text{G}}) = M_{\text{S}}, M_{\text{T}}$). We also adopt that the Coulomb repulsion in the doubly charged molecule is so large that, besides the neutrally charged states indicated above, only the states of singly charged molecule ($M(N_{\text{G}} - 1) = M_+, M(N_{\text{G}} + 1) = M_-$) can participate in the electron transfer through the molecule in a wide interval of the applied voltage bias. In the framework of this model, the hopping component of the current through the r-th electrode is written down as follows:

$$I_{\text{seq}}^{(r)}(t) = |e|\,(-1)^{r+1} \sum_{NMM'} \Big[K^{(r)}_{M(N)\to M'(N+1)} - - K^{(r)}_{M(N)\to M'(N-1)}\Big] P(M(N),t). \tag{7}$$

where $|e|$ is the elementary charge. In expression (7), the electron jumps between the r-th electrode and the molecule are characterized by the rates $K^{(r)}_{M(N)\to M'(N\pm1)}$, in which $N = N_{\text{G}}$. The current component

$$I_{\text{dir}}(t) = |e| \sum_{NMM'} \Big[K^{(12)}_{M(N)\to M'(N)} - - K^{(21)}_{M(N)\to M'(N)}\Big] P(M(N),t) \tag{8}$$

corresponds to the direct distance transfer of electrons between the electrodes and takes into account the contributions made by the elastic ($M'(N) = = M(N)$) and inelastic ($M'(N) \neq M(N)$) electron tunneling from electrode r to electrode r'. The corresponding tunneling rates are designated as $K^{(rr')}_{M(N)\to M'(N)}$, where $N = N_G, N_G \pm 1$.

The both current components are the sums of partial contributions. The weights of the latter are determined by the probabilities $P(M(N);t)$ to find the molecule at the time moment t in one of the above-indicated neutral (M_0, M_{S}, M_{T}) or charged (M_+, M_-) states. The evolution of the molecular population probabilities is described by the system of kinetic equations,

$$\dot{P}(M(N);t) = -\sum_{N',M'} \Big[K_{M(N)\to M'(N')} P(M(N),t) - - K_{M'(N')\to M(N)} P(M'(N'),t)\Big], \tag{9}$$

which should be solved with regard for the normalization condition

$$\sum_{N,M} P(M(N),t) = 1. \tag{10}$$

In Eqs. (9), the rate constants

$$K_{M(N)\to M'(N)} = \sum_{rr'} [(1 - \delta_{M'M}) + + (1 - \delta_{r'r})\delta_{M'M}] K^{(rr')}_{M(N)\to M'(N)}$$

and

$$K_{M(N)\to M'(N\pm1)} = \sum_{r} K^{(r)}_{M(N)\to M'(N\pm1)}$$

can be calculated with the help of expressions presented in works [24–26].

3. HOMO–LUMO Model

The further specification of the theory is made for organic molecules, which are luminescent owing to the electron transition from the half-filled LUMO onto the half-filled HOMO. We suppose that both the LUMO and the HOMO belong to the photochromic group of the molecule, which is connected to the electrodes by means of saturated bonds. Those bonds play the role of tunnel barriers (spacers), so that the interaction between the photochromic group and the electrodes is supposed to be weak. Therefore, the account for the quantities $\beta_{H,r\mathbf{k}}$ and $\beta_{L,r\mathbf{k}}$ in Hamiltonian (4), which describe the interaction of the HOMO and LUMO with the band states in the r-th electrode (see Fig. 1), can result in only an insignificant broadening of energy levels (see expression (15)). In the framework of the HOMO–LUMO model, the excited singlet, $M_{\rm S}$, and triplet, $M_{\rm T}$, states are formed by two unpaired electrons located on the HOMO and LUMO. In this case, the triplet state $M_{\rm T} = M_{\rm Tm}$ is associated with three spin projections, $m = 0$ and ± 1. Similarly, the charged states of the molecule are characterized by the spin projections of the unpaired electron that occupies the corresponding MO. In our case, $M(N_{\rm G}+1) = M_{-}(\sigma_{\rm L})$ and $M(N_{\rm G}-1) = M_{+}(\sigma_{\rm H})$, where $\sigma_{\rm L} = \pm 1/2$ and $\sigma_{\rm H} = \pm 1/2$ are the spin projections of unpaired electrons on the LUMO and HOMO, respectively.

In the absence of a magnetic field, the excited triplet state of the molecule is triply degenerate, and each state of the charged molecule is doubly degenerate. Taking into account the degeneration of molecular states, it is convenient to introduce the quantities $P(0;t)$, $P({\rm S};t)$, $P({\rm T};t) = \sum_{\rm m=0,\pm1} P({\rm Tm};t)$, $P(-;t) = \sum_{\sigma_{\rm L}} P(M_{-}(\sigma_{\rm L});t)$, and $P(+;t) = \sum_{\sigma_{\rm H}} P(M_{+}(\sigma_{\rm H});t)$, which determine the total probability for the molecule to be found in the indicated states with the energies E_0, $E_{\rm S}$, $E_{\rm T}$, E_{-}, and E_{+}, respectively. In what follows, we will consider that the energy E_{+} is high and, consequently, the probability $P(+;t)$ for the molecule to be formed in a positively charged state is low. From Eqs. (9), supposing that $P(+;t) \simeq 0$, we obtain the following system of kinetic equations:

$$\begin{aligned}
\dot{P}(0,t) &= -\left(K_{0\rm S} + 3K_{0\rm T} + 2K_{0-}+\right) P(0,t) + \\
&+ K_{\rm S0}P({\rm S},t) + K_{\rm T0}P({\rm T},t) + K_{-0}P(-,t), \\
\dot{P}({\rm S},t) &= -\left(K_{\rm S0} + 3K_{\rm ST} + K_{\rm S-}\right) P({\rm S},t) + \\
&+ K_{0\rm S}P(0,t) + K_{\rm TS}P({\rm T},t) + \frac{1}{2}K_{-\rm S}P(-,t), \\
\dot{P}({\rm T},t) &= -\left(K_{\rm T0} + K_{\rm TS} + K_{\rm T-}\right) P({\rm T},t) + \\
&+ 3K_{0\rm T}P(0,t) + 3K_{\rm ST}P({\rm S},t) + \frac{3}{2}K_{-\rm T}P(-,t), \\
\dot{P}(-,t) &= -\left(K_{-0} + \frac{1}{2}K_{-\rm S} + \frac{3}{2}K_{-\rm T}\right) P(-,t) + \\
&+ 2K_{0-}P(0,t) + K_{\rm S-}P({\rm S},t) + K_{\rm T-}P({\rm T},t).
\end{aligned} \qquad (11)$$

The system must be solved with regard for the normalization condition,

$$P(0,t) + P({\rm S},t) + P({\rm T},t) + P(-,t) = 1. \qquad (12)$$

The coefficients 2, 3, 1/2, and 3/2 in Eqs. (11) account for the degeneration of states, between which

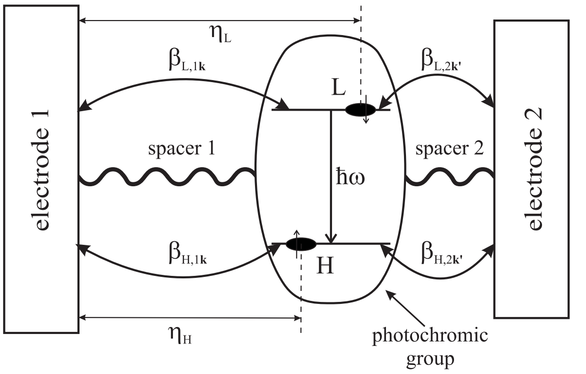

Fig. 1. A photochromic molecular group separated from the electrode surfaces by spacers. The parameters $\eta_{\rm H}$ and $\eta_{\rm L}$ characterize the position of maxima for the electron densities localized on HOMO (H) and LUMO (L). Interaction of HOMO and LUMO with the band states in the electrodes is governed by the parameters $\beta_{\rm H,1\mathbf{k}(2\mathbf{k}')}$ and $\beta_{\rm L,1\mathbf{k}(2\mathbf{k}')}$, respectively

the electron transitions take place. The quantities $K_{j\,-}$ and $K_{-\,j}$ $(j = 0,{\rm S},{\rm T})$ are the rates of one-electron recharge of the molecule. The transitions $M_0 \rightleftarrows M_{\rm S(T)}$ and $M_{\rm S(T)} \rightleftarrows M_0$ between the neutrally charged states of the molecule are described by the rates $K_{0\rm S(T)} = k^{\rm (f)}_{\rm S(T)} + Q_{0\rm S(T)}$ and $K_{\rm S(T)0} = k^{\rm (d)}_{\rm S(T)} + Q_{\rm S(T)0}$, where $k^{\rm (f)}_{\rm S(T)}$ and $k^{\rm (d)}_{\rm S(T)}$ stand for the rates of molecule excitation and luminescence, respectively, owing to the interaction of the molecule with an external electromagnetic field (while considering the electroluminescence formed in the absence of a molecular excitation by the external field, we must put $k^{\rm (f)}_{\rm S(T)} = 0$). The rates $Q_{\rm S(T)0}$ and $Q_{0\rm S(T)}$ characterize radiationless transitions between the same ground and excited states of the molecule. Those rates arise owing to the interaction between the molecule and the electrodes. The radiationless transitions S $\rightleftarrows$ T in the molecule are characterized by the rates $K_{\rm ST} = k^{(i)}_{\rm ST} + Q_{\rm ST}$ and $K_{\rm TS} = k^{(i)}_{\rm TS} + Q_{\rm TS}$, which are governed by both intramolecular interactions (the components $k^{(i)}_{\rm ST}$ and $k^{(i)}_{\rm TS}$) and the interaction between the molecule and the electrodes (the components $Q_{\rm ST}$ and $Q_{\rm TS}$). The diagram of kinetic processes described by the system of equations (11) is depicted in Fig. 2.

Using general expressions for the hopping and direct distance transition rates in the 1M2 system [25, 26] and applying the widely known wide-band approximation for the electrodes [29], we obtain the following expressions for the rates of one-electron

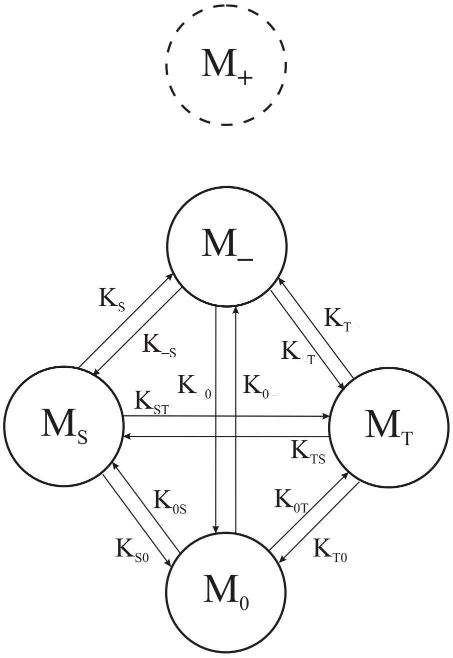

Fig. 2. Kinetic diagram of transitions in the 1M2 system. The weakly populated state M_+ corresponding to a positively charged molecule is excluded from consideration

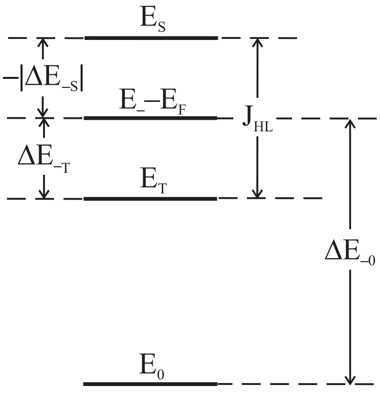

Fig. 3. Transmission gaps in the 1M2 system (the highly located molecular state M_+ is not taken into account)

recharge of the molecule:

$$
\begin{aligned}
K_{-\,j} &= \sum_r K_{-\,j}^{(r)},\\
K_{j\,-} &= \sum_r K_{j\,-}^{(r)}, \quad (j = \mathrm{S}, \mathrm{T}).
\end{aligned}
\tag{13}
$$

In turn, those rates are expressed in terms of the electron hopping rates between the molecule and the r-th electrode as follows:

$$
\begin{aligned}
K_{-\,j}^{(r)} &= \frac{1}{\hbar}\,\Gamma_{\mathrm{H}}^{(r)}\left(1 - n(\Delta E_{-\,j}^{(r)})\right),\\
K_{-\,0}^{(r)} &= \frac{1}{\hbar}\,\Gamma_{\mathrm{L}}^{(r)}\left(1 - n(\Delta E_{-\,0}^{(r)})\right),\\
K_{j\,-}^{(r)} &= \frac{1}{\hbar}\,\Gamma_{\mathrm{H}}^{(r)} n(\Delta E_{-\,j}^{(r)}),\\
K_{0\,-}^{(r)} &= \frac{1}{\hbar}\,\Gamma_{\mathrm{L}}^{(r)} n(\Delta E_{-\,j}^{(r)}).
\end{aligned}
\tag{14}
$$

Here, the parameters

$$
\Gamma_{\lambda}^{(r)} = 2\pi \sum_{\mathbf{k}} |\beta_{\lambda, r\mathbf{k}}|^2\, \delta(E - E_{r\mathbf{k}}) \quad (\lambda = \mathrm{H}, \mathrm{L})
\tag{15}
$$

characterize the broadening of molecular energy levels owing to the interaction between the λ-th MO and conduction electrons in the r-th electrode, and the distribution

$$
n(\Delta E_j^{(r)}) = \left(e^{\Delta E_j^{(r)}/k_{\mathrm{B}}T} + 1\right)^{-1}
\tag{16}
$$

determines the dependence of the hopping rates on the temperature T. The transmission gaps

$$
\begin{aligned}
\Delta E_{-\,j}^{(1)} &= \Delta E_{-\,j} - \eta_{\mathrm{H}}\,|e|\,V, \quad (j = \mathrm{S}, \mathrm{T}),\\
\Delta E_{-\,j}^{(2)} &= \Delta E_{-\,j} + (1 - \eta_{\mathrm{H}})\,|e|\,V,\\
\Delta E_{-\,0}^{(1)} &= \Delta E_{-\,0} - \eta_{\mathrm{L}}\,|e|\,V,\\
\Delta E_{-\,0}^{(2)} &= \Delta E_{-\,0} + (1 - \eta_{\mathrm{L}})\,|e|\,V
\end{aligned}
\tag{17}
$$

are equal to the energy differences between the states of the 1M2 system with a negatively charged molecule and a neutral one. At $V = 0$, those gaps are determined by the quantities ΔE_{-0} and ΔE_{-j} (see Fig. 3). The growth or reduction of the gaps under the influence of the applied voltage bias depends on the arrangement of the photochromic group with respect to the electrodes and on the electron density distribution in the molecule. In the framework of a phenomenological approach, the dependence of gaps (17) on V is governed by the so-called "voltage division factors" [27,29]. In our case, these are the dimensionless parameters η_{H} and η_{L} related to HOMO and LUMO, respectively (Fig. 1).

The level width parameters (15) and the transmission gaps depending on the voltage bias (see

Eqs. (17)) are responsible for the rates of intramolecular transitions. Using the approach expounded in works [25, 28], we obtain the following formulas for those rates:

$$Q_{j0} = \sum_r Q_{j0}^{(r)}\,, \quad Q_{0j} = \sum_r Q_{0j}^{(r)}\,, \quad (j = \mathrm{S}, \mathrm{T}), \tag{18}$$

and

$$Q_{\mathrm{ST}} = \sum_{rr'} Q_{\mathrm{ST}}^{(rr')}\,, \quad Q_{\mathrm{TS}} = \sum_{rr'} Q_{\mathrm{TS}}^{(rr')}, \tag{19}$$

where

$$Q_{j\,0}^{(1)} = \frac{1}{\pi\hbar}\Gamma_{\mathrm{H}}^{(1)}\Gamma_{\mathrm{L}}^{(2)}\left[\frac{1}{\Gamma_-}\left(\varphi_{-0}^{(2)} - \varphi_{-j}^{(1)}\right)\right] \times$$

$$\times\,\theta(\Delta E_{-0}^{(1)} - \Delta E_{-j}^{(2)}),$$

$$Q_{j\,0}^{(2)} = \frac{1}{\pi\hbar}\Gamma_{\mathrm{H}}^{(2)}\Gamma_{\mathrm{L}}^{(1)}\left[\frac{1}{\Gamma_-}\left(\varphi_{-0}^{(1)} - \varphi_{-j}^{(2)}\right)\right] \times$$

$$\times\,\theta(\Delta E_{-0}^{(2)} - \Delta E_{-j}^{(1)}),$$

$$Q_{0\,j}^{(1)} = \frac{1}{\pi\hbar}\Gamma_{\mathrm{L}}^{(1)}\Gamma_{\mathrm{H}}^{(2)}\left[\frac{1}{\Gamma_-}\left(\varphi_{-\,j}^{(2)} - \varphi_{-0}^{(1)}\right)\right] \times$$

$$\times\,\theta(\Delta E_{-\,j}^{(1)} - \Delta E_{-\,0}^{(2)}),$$

$$Q_{0\,j}^{(2)} = \frac{1}{\pi\hbar}\Gamma_{\mathrm{L}}^{(2)}\Gamma_{\mathrm{H}}^{(1)}\left[\frac{1}{\Gamma_-}\left(\varphi_{-\,j}^{(1)} - \varphi_{-0}^{(2)}\right)\right] \times$$

$$\times\theta(\Delta E_{-\,j}^{(2)} - \Delta E_{-\,0}^{(1)})\,, \tag{20}$$

and

$$Q_{jj'}^{(rr')} = \frac{1}{2\pi\hbar}\left[\frac{\Gamma_{\mathrm{H}}^{(r)}\Gamma_{\mathrm{H}}^{(r')}}{\Gamma_-}\left(\varphi_{-j'}^{(r')} - \varphi_{-j}^{(r)}\right)\right] \times$$

$$\times\,\theta(\Delta E_{-j'}^{(r')} - \Delta E_{-j}^{(r)}). \tag{21}$$

In expressions (20) and (21), $\theta(x)$ is the theta-function. We also introduced the notations $\varphi_{-\,j}^{(r)} = \arctan(2\Delta E_{-\,j}^{(r)}/\Gamma_-)$ and $\Gamma_- = \sum_r(\Gamma_{\mathrm{L}}^{(r)} + 2\Gamma_{\mathrm{H}}^{(r)})$.

Since the probability $P(+;t)$ to find the molecule in the positively charged state is negligibly low, the hopping component (7) of the current looks like

$$I_{\mathrm{seq}}^{(r)}(t) = 2\pi\hbar\, I_0\,(\delta_{r,1} - \delta_{r,2})\left\{K_{0-}^{(r)}P(0;t) + \right.$$

$$+\,\frac{1}{2}K_{\mathrm{S}-}^{(r)}P(\mathrm{S};t) + \frac{1}{2}K_{\mathrm{T}-}^{(r)}P(\mathrm{T};t) -$$

$$\left. -\left(\frac{1}{2}K_{-0}^{(r)} + \frac{1}{4}K_{-\mathrm{S}}^{(r)} + \frac{3}{4}K_{-\mathrm{T}}^{(r)}\right)P(-;t)\right\}, \tag{22}$$

where the hopping rates $K_{-j}^{(r)}$ and $K_{j-}^{(r)}$ are determined by Eqs. (14). In Eq. (22), the current unit $I_0 = (|e|\pi/\hbar) \times 1$ eV ≈ 77.6 μA was introduced. This means that, in calculations, the magnitudes of width parameters (15) and transmission gaps (18) must be taken in electronvolts. In contrast to the hopping component of the current, the tunneling one (Eq. (8)) contains two terms,

$$I_{\mathrm{dir}}(t) = I_{\mathrm{dir}}^{(\mathrm{ela})}(t) + I_{\mathrm{dir}}^{(\mathrm{ine})}(t)\,. \tag{23}$$

The first term,

$$I_{\mathrm{dir}}^{(\mathrm{ela})}(t) = \pi\hbar\, I_0\,[Q_{00}P(0;t) + Q_{\mathrm{SS}}P(\mathrm{S};t) +$$

$$+\,3Q_{\mathrm{TT}}P(\mathrm{T};0) + Q_{--}P(-;0)] \tag{24}$$

arises owing to the elastic electron tunneling, during which the electron state of the molecule is not changed. This process is characterized by the rates

$$Q_{00} = \frac{2}{\pi\hbar}\frac{\Gamma_{\mathrm{L}}^{(1)}\Gamma_{\mathrm{L}}^{(2)}}{\Gamma_-}\left(\varphi_{-\,0}^{(2)} - \varphi_{-\,0}^{(1)}\right),$$

$$Q_{\mathrm{SS}} = \frac{1}{2\pi\hbar}\frac{\Gamma_{\mathrm{H}}^{(1)}\Gamma_{\mathrm{H}}^{(2)}}{\Gamma_-}\left(\varphi_{-\,\mathrm{S}}^{(2)} - \varphi_{-\,\mathrm{S}}^{(1)}\right),$$

$$Q_{\mathrm{TT}} = \frac{1}{2\pi\hbar}\frac{\Gamma_{\mathrm{H}}^{(1)}\Gamma_{\mathrm{H}}^{(2)}}{\Gamma_-}\left(\varphi_{-\,\mathrm{T}}^{(2)} - \varphi_{-\,\mathrm{T}}^{(1)}\right),$$

$$Q_{--} = \frac{1}{2\pi\hbar}\frac{\Gamma_{\mathrm{L}}^{(1)}\Gamma_{\mathrm{L}}^{(2)}}{\Gamma_0}\left(\bar{\varphi}_{-\,0}^{(2)} - \bar{\varphi}_{-\,0}^{(1)}\right) +$$

$$+\,\frac{\Gamma_{\mathrm{H}}^{(1)}\Gamma_{\mathrm{H}}^{(2)}}{\Gamma_*}\left[\left(\bar{\varphi}_{-\,\mathrm{S}}^{(2)} - \bar{\varphi}_{-\,\mathrm{S}}^{(1)}\right) + 3\left(\bar{\varphi}_{-\,\mathrm{T}}^{(2)} - \bar{\varphi}_{-\,\mathrm{T}}^{(1)}\right)\right], \tag{25}$$

where $\bar{\varphi}_{-\,j}^{(r)} = \arctan\left(2\Delta E_{-\,j}^{(r)}/\Gamma_j\right)$ with $j = 0$, S, and T; $\Gamma_0 = \sum_r 2\left(\Gamma_{\mathrm{H}}^{(r)} + \Gamma_{\mathrm{L}}^{(r)}\right)$; and $\Gamma_* = \Gamma_{\mathrm{S}} = \Gamma_{\mathrm{T}} = \sum_r\left(\Gamma_{\mathrm{H}}^{(r)} + \Gamma_{\mathrm{L}}^{(r)}\right)$. The second term in Eq. (23) reads

$$I_{\mathrm{dir}}^{(\mathrm{ine})}(t) = \pi\hbar\, I_0\left[(R_{0\mathrm{S}} + 3R_{0\mathrm{T}})P(0;t) + \right.$$

$$\left. +\,(R_{\mathrm{S}0} + 3R_{\mathrm{ST}})P(\mathrm{S};t) + (R_{\mathrm{T}0} + R_{\mathrm{TS}})P(\mathrm{T};t)\right], \tag{26}$$

where $R_{0\mathrm{S(T)}} = Q_{0\mathrm{S(T)}}^{(12)} - Q_{0\mathrm{S(T)}}^{(21)}$, $R_{\mathrm{S(T)}0} = Q_{\mathrm{S(T)}0}^{(12)} - Q_{\mathrm{S(T)}0}^{(21)}$, $R_{\mathrm{ST}} = Q_{\mathrm{ST}}^{(12)} - Q_{\mathrm{ST}}^{(21)}$, and $R_{\mathrm{TS}} = Q_{\mathrm{TS}}^{(12)} - Q_{\mathrm{TS}}^{(21)}$. This term corresponds to the process of inelastic electron tunneling, which is accompanied by the intramolecular transitions $M_{\mathrm{S(T)}} \rightleftarrows M_0$ and $M_{\mathrm{S}} \rightleftarrows M_{\mathrm{T}}$. In Fig. 4, the inelastic and elastic tunnel transitions of an electron from electrode 1 to electrode 2 are represented by arrows.

4. Discussion of Results

In this work, we study the dependence of the stationary molecular electroluminescence on the voltage bias V applied to the electrodes. This luminescence is formed at $t \gg \tau_{st}$, where τ_{st} is a characteristic settling time for the stationary values of molecular population probabilities $P_j \equiv P(j; t \gg \tau_{st})$. The electroluminescence intensity is governed by the singlet–singlet (fluorescence) and triplet–singlet (phosphorescence) light-emission channels and, therefore, consists of two components, $\mathcal{J} = \mathcal{J}_{\rm flu} + \mathcal{J}_{\rm pho}$. Each of them is proportional to the probability to find a molecule in the given excited state, i.e. $\mathcal{J}_{\rm flu} = \mathcal{J}_{\rm flu}^{(0)} P_{\rm S}$ and $\mathcal{J}_{\rm pho} = \mathcal{J}_{\rm pho}^{(0)} P_{\rm T}$. Here, the intensities $\mathcal{J}_{\rm flu}^{(0)}$ and $\mathcal{J}_{\rm pho}^{(0)}$ are determined by the probabilities of the singlet–singlet and singlet–triplet intramolecular transitions, respectively. Provided a weak coupling between the photochromic group of the molecule and the electrodes, those probabilities can be regarded as independent of the applied voltage bias V. Therefore, the dependences of intensities $\mathcal{J}_{\rm flu}$ and $\mathcal{J}_{\rm pho}$ on V are completely contained in the molecular population probabilities $P_{\rm S}$ and $P_{\rm T}$. Bearing this circumstance in mind, in order to understand the physics of the electroluminescence formation, it is enough to consider the dependences of its normalized intensities

$$\zeta_{\rm flu} = \mathcal{J}_{\rm flu}/\mathcal{J}_{\rm flu}^{(0)} = P_{\rm S} \tag{27}$$

and

$$\zeta_{\rm pho} = \mathcal{J}_{\rm pho}/\mathcal{J}_{\rm pho}^{(0)} = P_{\rm T}. \tag{28}$$

on V. The corresponding probabilities $P_{\rm S}$ and $P_{\rm T}$ (as well as the probability P_-) are determined by solving the system of equations (11), provided that $\dot{P}(j;t) = 0$.

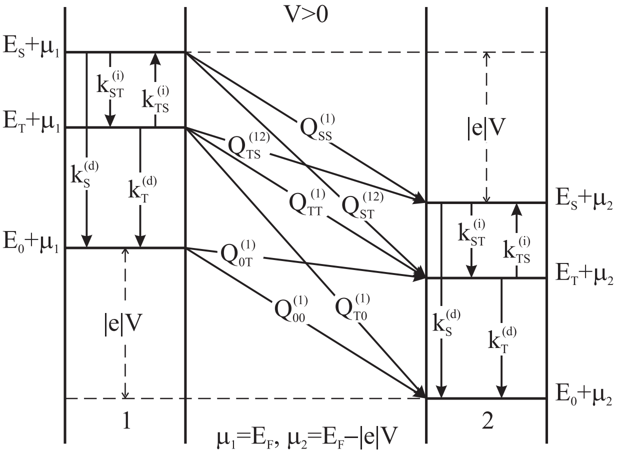

Fig. 4. Transitions between the states of an uncharged molecule, being in contact with the electrodes. The rates $k_{\rm ST}^{\rm (i)}$, $k_{\rm TS}^{\rm (i)}$, $k_{\rm S}^{\rm (d)}$, and $k_{\rm T}^{\rm (d)}$ are related to intramolecular interactions, whereas the rates $Q_{\rm 0S}^{(1)}$, $Q_{\rm 0T}^{(1)}$, $Q_{\rm ST}^{(12)}$, and $Q_{\rm TS}^{(12)}$ characterize the molecular transitions accompanied by the inelastic electron tunneling from electrode 1 to electrode 2. The rates of elastic electron tunneling, $Q_{jj}^{(1)}$ ($j = 0, {\rm S}, {\rm T}$), induce no intramolecular transitions, but can excite plasmons with frequencies $\omega \le |e|V/\hbar$ in electrode 2

In the framework of the HOMO–LUMO model, both the sequential (hopping) and direct (tunneling) transmissions of electrons are driven by physical quantities of two types. The first group includes parameters describing the broadening of molecular energy levels. They reflect the relation between the molecule and the electrodes and, hence, determine, to a great extent, the current magnitude in the 1M2 system. The available results of measurements demonstrate that the typical current in a molecular diode (an asymmetric 1M2 system) does not exceed 1 nA. At larger currents, the contact section is heated up, which makes the molecule fixation between the electrodes uncontrollable. For estimations, we selected the values of width parameters such that they did not exceed 10^{-6} eV by the order of magnitude. The corresponding maximum current through the molecule was of the order of 0.1 nA. The physical quantities of the second important type comprise the transmission gaps (17). The gap signs determine the resonant or nonresonant mode of electron transmission. The researches carried out in this work showed that the current in the 1M2 system and the accompanying electroluminescence became appreciable, when the signs of the gaps $\Delta E_{-0}^{(1)}$ and $\Delta E_{-0}^{(2)}$ are negative. For the sake of definiteness, we will confine the consideration to the case $V > 0$. The analysis for $V < 0$ can be carried out analogously.

According to expressions (17), the dependences of gaps on V is regulated by the factors $\eta_{\rm H}$ and $\eta_{\rm L}$. The results obtained in those cases are depicted in Figs. 5 and 6. Figure 5 illustrates the case where the photochromic group is located asymmetrically between the electrodes (in the case concerned, closer to electrode 2), and the distributions of the electron density on the HOMO and LUMO correspond to a strong electron delocalization on each MO. In

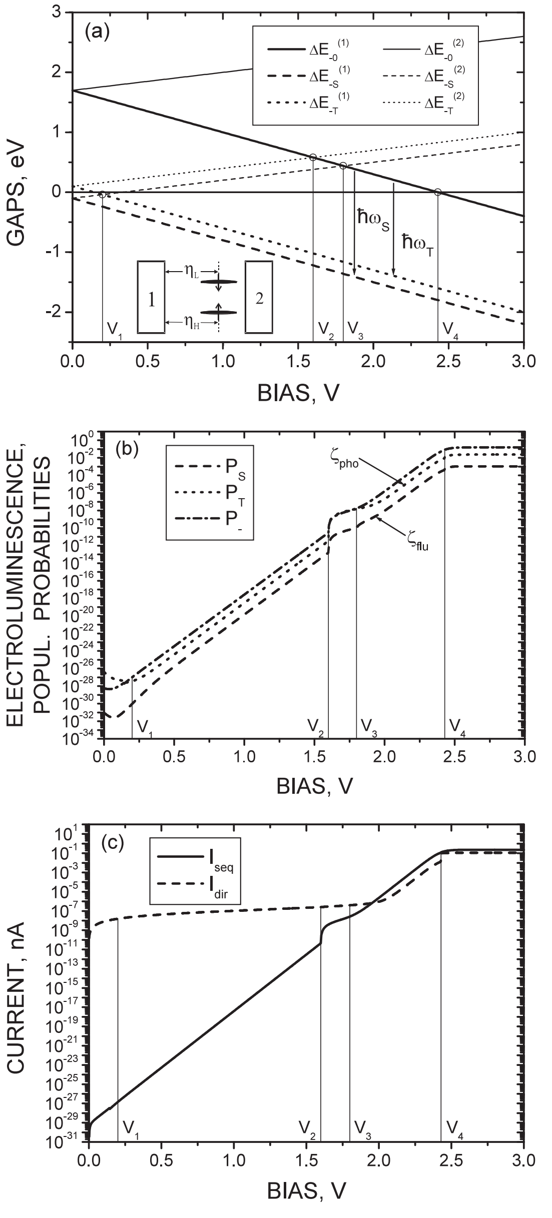

Fig. 5. Dependences of transmission gaps (*a*), molecular state population probabilities (*b*), and current (*c*) on the voltage bias V applied to the electrodes. The electron densities on HOMO and LUMO are delocalized ($\eta_{\mathrm{L}} \approx \eta_{\mathrm{H}} = 0.7$). The fluorescence, ω_{S}, and phosphorescence, ω_{T}, frequencies are independent of V (*a*). At $V = V_4$, the nonresonant transmission mode is switched over to the resonant one. The calculations were carried out for $\hbar\omega_{\mathrm{S}} = 1.8$ eV (red light), $\Delta E_{-0} = 1.7$ eV, $\Delta E_{-\mathrm{S}} = -0.1$ eV, $\Delta E_{-\mathrm{T}} = 0.1$ eV, $J_{\mathrm{HL}} = 0.2$ eV, $\Gamma_{\mathrm{H}}^{(1)} = \Gamma_{\mathrm{L}}^{(1)} = 5 \times 10^{-7}$ eV, $\Gamma_{\mathrm{H}}^{(2)} = \Gamma_{\mathrm{L}}^{(2)} = 5 \times 10^{-6}$ eV, $k_{\mathrm{S}}^{(d)} = 10^{10}$ s^{-1}, $k_{\mathrm{ST}}^{(i)} = 10^{7}$ s^{-1}, $k_{\mathrm{TS}}^{(i)} = \exp\left(-J_{\mathrm{HL}}/k_{\mathrm{B}}T\right) k_{\mathrm{ST}}^{(i)} \approx 5 \times 10^{3}$ s^{-1}, and $T = 300$ K

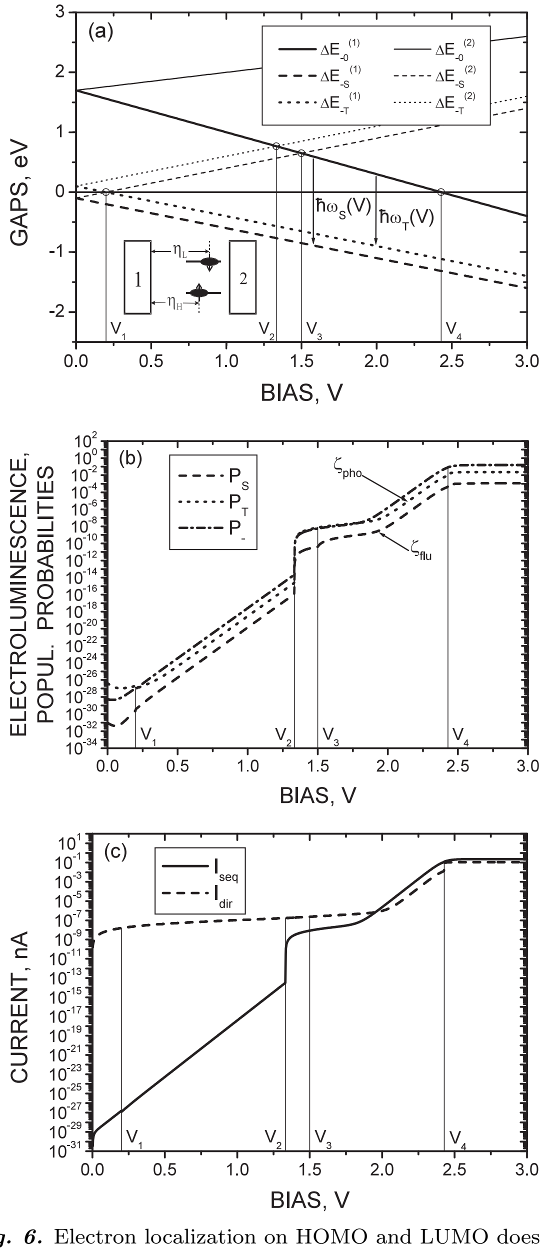

Fig. 6. Electron localization on HOMO and LUMO does not affect the character of electron transmission: analogously to Fig. 5, the behavior of the electroluminescence intensity and the current imitates that of molecular population probabilities. The basic difference consists in that the fluorescence and phosphorescence frequencies depend now on V (*a*). The calculations parameters are the same as in Fig. 5, but $\eta_{\mathrm{L}} = 0.7$, $\eta_{\mathrm{H}} = 0.5$, $\Gamma_{\mathrm{H}}^{(1)} = \Gamma_{\mathrm{H}}^{(2)} = 10^{-6}$ eV, $\Gamma_{\mathrm{L}}^{(1)} = 5 \times 10^{-7}$ eV, and $\Gamma_{\mathrm{L}}^{(2)} = 5 \times 10^{-6}$ eV

this case, the values of factors η_{H} and η_{L} are identical. From Fig. 5, *a*, one can see that the gap signs can change as the voltage bias V increases. This circumstance gives rise to a situation where the switching between the transmission modes, from the nonresonant to resonant one and *vice versa*, becomes possible for a specific transition. The characteristic value of voltage bias $V = V_j^{(r)}$, at which the switching occurs, is determined by the condition $\Delta E^{(r)}_{-j} = 0$. In particular, at $V = V_{\mathrm{S}}^{(2)} = |\Delta E_{-\mathrm{S}}|/|e|(1-\eta_{\mathrm{H}})$, the gap $\Delta E^{(2)}_{-S}$ changes its sign from negative to positive. Whereas, at $V = V_{\mathrm{T}}^{(1)} = \Delta E_{-\mathrm{T}}/|e|\eta_{\mathrm{H}}$, the gap $\Delta E^{(1)}_{-T}$ changes its sign from positive to negative. The values of $V_{\mathrm{S}}^{(2)}$ and $V_{\mathrm{T}}^{(1)}$ are in a vicinity of $V = V_1$, which is determined by the condition $\Delta E^{(2)}_{-S} = \Delta E^{(1)}_{-T}$. It is easy to see that $V_1 = J_{\mathrm{HL}}/|e|$, where $J_{\mathrm{HL}} = E_{\mathrm{S}} - E_{\mathrm{T}}$ is the exchange interaction between unpaired electrons located on the HOMO and LUMO. In Fig. 5, we also marked the voltage biases $V = V_2$ and $V = V_3$, at which the equalities $\Delta E^{(1)}_{-0} = \Delta E^{(2)}_{-\mathrm{T}}$ and $\Delta E^{(1)}_{-0} = \Delta E^{(2)}_{-\mathrm{S}}$, respectively, hold true. A special attention should be paid to the value $V = V_4 \equiv V_0^{(1)} = \Delta E_{-0}|/|e|\eta_{\mathrm{L}}$, at which the transmission mode switching takes place. At $V < V_4$, the hopping transition $M_0 \to M_-$ (giving rise to the molecule charging) runs in the nonresonant mode, whereas the same transition at $V > V_4$ uses the resonant way.

In order to understand the transformation of one transmission mode into the other, let us discuss the electron jump from electrode 1 to the molecule, when the latter is in the excited state M_{T}. The jump occurs if the basic condition of *hopping electron transmission,* $E_{\mathrm{T}} + E_{1\mathbf{k}} = E_-$, is obeyed. Concerning the transmission mode itself, it is determined by distribution (16). For electrons located above the Fermi level (i.e. at $E_{1\mathbf{k}} > \mu_1$), the basic condition of transmission looks like $E_- - E_{\mathrm{T}} > \mu_1$, which gives rise to the inequality $\Delta E^{(1)}_{-\mathrm{T}} > 0$. Hence, it follows from expressions (14) and (16) that, if $V < V_{\mathrm{T}}^{(1)}$, the electron hopping rate exponentially falls down as the gap increases: $K^{(1)}_{\mathrm{T}-} \approx (1/\hbar)\Gamma^{(1)}_{\mathrm{H}} \exp\left(-\Delta E^{(1)}_{-\mathrm{T}}/k_{\mathrm{B}}T\right)$. This fact testifies to the nonresonant mode of hopping transmission. Therefore, electron jumps occur only provided the temperature activation of conduction electrons. For electrons located below the Fermi level (i.e. at $E_{1\mathbf{k}} < \mu_1$), the basic equation of hopping transmission is satisfied if $\Delta E^{(1)}_{-\mathrm{T}} < 0$, i.e. at $V > V_{\mathrm{T}}^{(1)}$. In this case, the electron hopping rate $K^{(1)}_{\mathrm{T}-} \approx (1/\hbar)\Gamma^{(1)}_{\mathrm{H}}$ becomes maximal and independent of the gap magnitude and, hence, of the temperature and the voltage bias. Therefore, the mode of resonant hopping transmission is established.

In the case of *direct distance electron transmission,* when the electron tunneling between the electrodes is accompanied by the transition $M_j \to M_{j'}$ in the neutrally charged molecule, the conditions for the resonant and nonresonant tunneling remain the same as for the hopping transmission. However, the nonresonant mode is possible now even without the temperature activation of electrons. The explanation consists in that the negatively charged state M_- of the molecule participates in the electron tunneling in a virtual manner; that is why the energy of this state is not included into the basic condition of distance transmission, $E_j + E_{1\mathbf{k}} = E_{j'} + E_{2\mathbf{k}'}$. For instance, let us consider the V-dependence of the rate $Q^{(1)}_{\mathrm{T}0}$. This parameter characterizes the efficiency of direct inelastic distance tunneling of the electron from electrode 1 to electrode 2 (see Fig. 4), which is accompanied by the degradation of the triplet molecular excitation. The process concerned is governed by the interaction of the molecule with the electrodes. According to expression (20), the transmission mode is determined by the factor $\varphi^{(2)}_{-0} - \varphi^{(1)}_{-\mathrm{T}}$. At $V > 0$, the gap $\Delta E^{(1)}_{-\mathrm{T}}$ is always positive. Therefore, considering the smallness of the width parameters $\Gamma^{(r)}_{\mathrm{H}}$ and $\Gamma^{(r)}_{\mathrm{L}}$, we obtain (see also works [27, 28])

$$\varphi^{(2)}_{-0}-\varphi^{(1)}_{-\mathrm{T}}\approx\frac{\pi}{2}\left[1-\frac{\Delta E^{(1)}_{-\mathrm{T}}}{|\Delta E^{(1)}_{-\mathrm{T}}|}+\frac{\Gamma_-}{\pi}\left(\frac{1}{\Delta E^{(1)}_{-\mathrm{T}}}-\frac{1}{\Delta E^{(2)}_{-0}}\right)\right].$$

At $\Delta E^{(1)}_{-\mathrm{T}} > 0$ (i.e. at $V < V_{\mathrm{T}}^{(1)}$) with regard for $1/\Delta E^{(2)}_{-0} \ll 1/\Delta E^{(1)}_{-\mathrm{T}}$, we obtain the following expression for the rate of $M_{\mathrm{T}} \to M_0$ transition: $Q^{(1)}_{\mathrm{T}0} \approx (1/4\hbar)\left(\Gamma^{(1)}_{\mathrm{H}}\Gamma^{(2)}_{\mathrm{L}}/\Delta E^{(1)}_{-\mathrm{T}}\right)$. At the same time, if $\Delta E^{(1)}_{-\mathrm{T}} < 0$, we obtain $Q^{(1)}_{\mathrm{T}0} \approx (1/2\hbar)\left(\Gamma^{(1)}_{\mathrm{H}}\Gamma^{(2)}_{\mathrm{L}}/\Gamma_-\right)$. It is evident that, owing to the strong inequality $\Gamma_-/\left|\Delta E^{(1)}_{-\mathrm{T}}\right| \ll 1$, the change of the $\Delta E^{(1)}_{-\mathrm{T}}$ gap sign from positive to negative results in a drastic growth of the inelastic tunneling rate. Since this rate ceases to depend on the magnitude of transmission gap $\Delta E^{(1)}_{-\mathrm{T}}$, the inelastic electron tunneling and the degradation of triplet excitation run in the resonant mode.

The characteristic values of voltage bias $V = V_n$, $(n = 1, ..., 4)$, which were indicated above, reveal themselves directly in the populations of molecular states. As a result, the jumps are observed both in the molecular electroluminescence intensity (Fig. 5, *b*) and in the current through the molecule (Fig. 5, *c*). At the zero voltage bias between the electrodes ($V = 0$), the current strictly equals zero. The populations of the singlet and triplet excited states of the molecule, even if the latter is in the charged state, are scanty (the temperature-induced populations of levels with the energies E_S, E_T, and E_- are negligibly low). Accordingly, the temperature-activated luminescence is also scanty. If the voltage bias is switched on, the magnitudes of transmission gaps start to change. In particular, at $V > V_1$, the energy of the 1M2 system with the negatively charged molecule becomes lower than the energy of the same system but with the molecule in the excited state, M_S or M_T. As the voltage bias grows up to $V = V_4$, the electron transmission runs in the nonresonant mode, when the condition $E_- > E_0 + \mu_1$ is satisfied. Although the population probabilities P_-, P_S, and P_T become higher, nevertheless, in spite of the jumps observed at $V = V_2$ and $V = V_3$, they remain so insignificant that the electroluminescence and the current are still too low (see Figs. 5, *b* and *c*). The transmission mode changes at $V = V_4$, when the main transmission gap $\Delta E^{(1)}_{-0}$ changes its sign (see Fig. 5, *a*). At $V > V_4$, the inequality $E_0 + \mu_1 > E_-$ is satisfied. Since $\Delta E^{(1)}_{-0} < 0$ now, the electron jumps from electrode 1 to the molecule without activation, i.e. in the resonant manner. As a result, the probabilities P_-, P_S, and P_T achieve their threshold values (Fig. 5, *b*). Those values correspond to certain values of luminescence intensity and current (Figs. 5, *b* and *c*), which can be measured experimentally. For instance, in works [30, 31], an intensity of photons of about 10^4 photon/s was registered at a tunnel current of 1 nA, which coincides with the estimations of the quantum efficiency of an order of 10^{-4} photon/electron [32, 33].

By comparing the results presented in Figs. 5 and 6, we may assert that, at the fixed values of width parameters $\Gamma^{(r)}_\lambda$ and initial transmission gaps ΔE_{-j}, the luminescence intensity and the current depend on the voltage bias V in a similar manner. The both quantities imitate the behavior of the probabilities P_-, P_S, and P_T, undergoing appreciable changes in a vicinity of the characteristic voltage biases $V = V_n$, $(n = 1, ..., 4)$ (see Table). However, there is a substantial difference associated with the fluorescence and phosphorescence frequencies – $\omega_\mathrm{S} = (E_\mathrm{S} - E_0)/\hbar$ and $\omega_\mathrm{T} = (E_\mathrm{T} - E_0)/\hbar$, respectively. In the case of strong electron delocalization on HOMO and LUMO, those frequencies do not depend on the voltage bias V (Fig. 5, *a*). But the V-dependence of the frequencies arises when the factors η_H and η_L, which govern the magnitudes of transmission gaps, do not coincide (see Figs. 1 and 6, *a*). As follows from Fig. 6, *a*, the frequencies ω_S and ω_T decrease, as the voltage bias V grows. The reason for this phenomenon consists in the different shifts of electron energy levels for HOMO and LUMO. Analytically, this is a consequence of the expression

$$\hbar\omega_{\mathrm{S(T)}}(V) = \hbar\omega_{\mathrm{S(T)}} - |e|V|(\eta_\mathrm{L} - \eta_\mathrm{H}). \tag{29}$$

Note that expression (29) is satisfied at both the nonresonant and resonant transmission modes. At the same time, the luminescence intensity and the current become independent of V only if the transmission mode is resonant. This can be seen if one compares panels *a* in Figs. 5 and 6 with panels *b* and *c* in the corresponding figures.

As follows from Figs. 5, *b* and 6, *b*, the ratio between the normalized intensities does not depend on V. This circumstance is associated with the fact that, under stationary conditions, $\zeta_\mathrm{pho}/\zeta_\mathrm{flo} = P_\mathrm{T}/P_\mathrm{S} = \exp(J_\mathrm{HL}/k_\mathrm{B}T)$; therefore, if the temperature is fixed, the indicated relation is completely determined by the magnitude of exchange splitting J_HL between the excited singlet and triplet states. The results de-

Characteristic voltage biases

Voltage division factors	Biases (in Volts)			
	V_1	V_2	V_3	V_4
$\eta_H = 0.7$, $\eta_L = 0.7$	0.2	1.6	1.8	2.43
$\eta_H = 0.5$, $\eta_L = 0.5$	0.2	1.6	1.8	3.4
$\eta_H = 0.5$, $\eta_L = 0.7$	0.2	1.33	1.5	2.43

picted in Figs. 5 and 6 were calculated for $J_{\mathrm{HL}} = 0.2$ eV. This value is in agreement with the magnitudes of exchange splitting between excited singlet and triplet states in organic molecules. The corresponding splitting for those molecules can amount to a few tenths of electronvolts [34].

The exchange splitting is also governs the ratio between the phosphorescence and fluorescence intensities; this fact follows from the expression

$$\xi = \mathcal{J}_{\mathrm{pho}}/\mathcal{J}_{\mathrm{flu}} = \xi^{(0)} \exp\left(J_{\mathrm{HL}}/k_{\mathrm{B}}T\right), \tag{30}$$

where $\xi^{(0)} = \mathcal{J}^{(0)}_{\mathrm{pho}}/\mathcal{J}^{(0)}_{\mathrm{flu}}$. Fluorescence and phosphorescence are associated with the corresponding dipole and magneto-dipole transitions in the molecule. Therefore, as a rule, $\xi^{(0)} \sim 10^{-4} \div 10^{-6}$. Hence, for the fixed values of $\xi^{(0)}$ and temperature T, the contribution to the total luminescence intensity $\mathcal{J} = \mathcal{J}_{\mathrm{flu}} + \mathcal{J}_{\mathrm{pho}}$ depends substantially on the exchange splitting of the singlet and triplet levels. In particular, for $\xi^{(0)} = 10^{-5}$ and $J_{\mathrm{HL}} = 0.2$ eV, we obtain $\xi \approx 3 \times 10^{-2}$, which testifies to an appreciable excess of the fluorescence intensity over the phosphorescence one. However, already at $J_{\mathrm{HL}} = 0.4$ eV and the same room temperature of 300 K, we have $\xi \approx 9 \times 10^{2}$. Hence, under those conditions, the main contribution to electroluminescence is made by phosphorescence.

5. Conclusions

In this work, with the use of the HOMO–LUMO models for the electron states in a photochromic molecule, the physics of electroluminescence formation in the 1M2 system has been studied. Fluorescence and phosphorescence were demonstrated to arise owing to the kinetic processes of two types. One of them is described as the electron jumps from one of the electrodes onto the molecule that is in the ground state. As a result, the molecule becomes charged following the scheme $M_0 \to M_-$. Then, the charged molecule gives an electron to the other electrode, but remains in the excited state. This process corresponds to the molecule discharge following the scheme $M_- \to M_{\mathrm{S(T)}}$. Being in the excited state, the molecule can be luminescent with the frequency $\omega_{\mathrm{S(T)}} = (E_{\mathrm{S(T)}} - E_0)/\hbar$. Hence, the directed transitions with populating the transient state M_-, i.e. $M_0 \to M_- \to M_{\mathrm{S(T)}} \to M_0$, take place in the molecule. The kinetic process of the second type is described as a direct distance jump of the electron from one electrode to the other, with the molecule being simultaneously excited, by following the scheme $M_0 \to M_{\mathrm{S(T)}}$. In this process, the transient state M_- of the molecule is not populated with the transported electron, but participates in the excitation and the electron transport in a virtual manner. The distance jump is based on the inelastic electron tunneling. In this case, for the molecule to be excited, the energy $|e|V$ must exceed the difference $E_{\mathrm{S(T)}} - E_0$. The process of molecular electroluminescence is the most effective at the resonant mode of electron transmission, when the electron jumps from the electrode onto the molecule without activation, and the tunneling rate does not depend on the transmission gap magnitude. We have demonstrated that the luminescence frequencies ω_{S} and ω_{T} can depend on the applied voltage bias V even in the resonant transmission mode, when the luminescence intensity does not depend any more on V. Expectedly, the effect can be observed in 1M2 systems with photochromic molecules, the electron density distribution in which are considerably different for HOMO and LUMO; molecules with localized MOs are an example.

The main attention was focused on the analysis of those electron states in the1M2 system that are responsible for the electroluminescence formation mechanism. Therefore, only the integral electroluminescence yield was evaluated. In order to elucidate a detailed structure of the radiation spectrum and the temperature dependence of the electroluminescence intensity, the influence of electron–vibration interactions relating to the molecule itself and to the region of its contact with the electrodes must be taken into account. For this purpose, one has to know detailed experimental data on electroluminescence spectra. As far as we know, such detailed experimental data have been absent till now. At the same time, we note that phonons reveal themselves in the current-voltage characteristics of organic molecules as steps [24, 35, 36]. A similar structure should be expected for electroluminescence spectra as well.

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ФОРМУВАННЯ ЕЛЕКТРОЛЮМІНЕСЦЕНЦІЇ В СИСТЕМІ ЕЛЕКТРОД–МОЛЕКУЛА–ЕЛЕКТРОД

Резюме

У межах HOMO–LUMO моделі розглянуто кінетику формування електролюмінесценції в системі "електрод 1–молекула–електрод 2". Показано, що виникнення електролюмінесценції в зарядово нейтральній молекулі зумовлено стрибковим та тунельним механізмами переносу електрона між електродами. Відповідна електронна трансмісія відбувається за участю як реальних, так і віртуальних станів зарядженої молекули. Знайдено умови, за яких стрибковий та тунельний транспорт електронів через молекулу відбуваються в резонансному режимі. У такому режимі електрофлуоресценція та електрофосфоресценція молекули, а також струм через молекулу досягають своїх найбільших значень.