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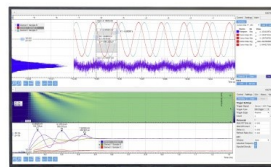
Gate-tunable electroluminescence in Aviram–Ratner-type molecules: Kinetic description

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ABSTRACT

A theoretical study of the mechanisms of electroluminescence (EL) generation in photoactive molecules with donor and acceptor centers linked by saturated σ-bonds (molecules of the Aviram–Ratner-type) is presented. The approach is based on the kinetics of single-electron transitions between many-body molecular states. This study shows that the EL polarity arises due to asymmetric coupling of molecular orbitals of the photochromic part of the molecule to the electrodes. The gate voltage controls the power of the EL through the occupancy of the excited singlet state. The shifting of the orbital energies forms a resonant or a non-resonant path for the transmission of electrons through the molecule. The action of the gate voltage is reflected in specific critical voltages. An analytical dependence of the critical voltages on the energies of molecular states involved in the formation of EL, as well as on the gate voltage, was derived for both positive and negative polarities. Conditions under which the gate voltage lowers the absolute value of the bias voltage that is responsible for the activation of the resonance mechanism of EL formation were also established. This is an important factor in control of EL in molecular junctions.

I. INTRODUCTION

Clarification of the mechanisms of electron transport formation and control in nanoscale inorganic, organic, and biological structures[1–4] is one of the priority tasks of modern molecular electronics, molecular optoelectronics, and molecular spintronics.[5–22] In molecular junctions "source (electrode 1)–molecule–drain (electrode 2)"(1M2), the transmission of electrons is carried out along complex routes, which in extreme cases are reduced to sequential and interelectrode one-step electron hoppings (including superexchange coherent jumps mediated by the structural units of the molecular wires[23–27]). The effectiveness of transport routes depends on a large number of factors. Among those, the main ones are the couplings of molecular orbitals (MOs) to the conducting states of the electrodes and the position of the MO levels relative to the Fermi levels of the electrodes.

Molecular optoelectronics aims at using photoactive molecules as elements of nanoscale devices, where the energy of light quanta is converted into electron current or the energy of moving electrons is used to generate light quanta. To this end, a large number of studies to reveal the nature of optoelectronic processes in 1M2 systems have been performed (see, for example, papers on the formation of light-induced conductivity (experiment[28–31] and theory[12,32–37]) and electrically driven for photon generation (experiment[38–44] and theory[32,34,44–47]).

It is well established that electron tunneling through a nanoscale molecular junction can lead to the formation of plasmons. The frequencies of plasmons depend on the volume and

configuration of the cavity in which the molecular junction is located. If the frequency of the dipole plasmon mode coincides with the frequency of the optical transition in the fluorophore-containing molecule, the intensity of EL of the emitter molecule can increase significantly.[38,40,43,48–50] The studies of EL of the molecules in which electronic states are formed from *delocalized* MOs provided an opportunity to use current theoretical models to explain the conductive and electron-optical processes in 1M2 systems. As an example, note the recent papers[37] and Ref. [47], where theoretical description based on the use of many-body molecular states was utilized to analyze EL in a phthalocyanine molecule and polythiophene chain molecule, respectively.

At the same time, the 1M2 junctions, where the molecular states involved in conductivity and optical transitions are formed from strictly *localized* fluorophore MOs, exist. This type of molecules were proposed for use as molecular rectifiers by Aviram and Ratner in their famous work.[5] Aviram–Ratner (AR)-type molecules contain donor (D) and acceptor (A) groups linked by saturated σ-bonds. This stabilizes the localization of the transported electron at the centers D and A, thereby improving the rectification properties of D−σ−A molecules. The strong rectification properties of AR-type molecules have been demonstrated by Metzger in numerous experiments.[51] The theory of electron transfer through localized frontier MOs explains the strong bipolarity of the current–voltage (IV) characteristics of the D−σ−A molecules by the difference in the energy gaps between the levels of the mentioned MOs and Fermi levels of the electrodes, as well as the difference between the coupling of the sites D and A to the corresponding electrodes.[52,53] It should be noted here that, despite the fact that the IV characteristics of many D−σ−A molecules have been investigated in sufficient detail, to the authors' knowledge, the features of the optoelectronic properties of this type of molecules have not yet been studied. Meanwhile, since these molecules have a pronounced asymmetry in the distribution of electron density over the frontier MOs, one should expect a notable bipolarity of both photoconductivity and EL. This argues for the need of a detailed study of the optoelectronic properties of D−σ−A molecules.

In this paper, we study the physics of EL formation in molecules of AR (D−σ−A)-type under conditions when light quanta are generated by the bias voltage, in the presence of a gate voltage. An important result of this study is that the gate voltage can tune the position of the molecular levels to ensure the formation of EL at a lower bias voltage. This opens up a new way to control the generation of photons in single-molecular optoelectronic devices.

II. BASIC EQUATIONS

It was found that EL in molecular junctions can only be observed if the chromophore group (fluorophore) of the molecule is isolated from the electrodes so that non-radiative processes caused by the interaction of the fluorophore with electrodes cannot quench EL. For isolation, oxide films[28,38,48,49] and monolayer-thick salt islands[37,43] are used. In the phenomenological description, these isolating structures (spacers) are modeled by the tunneling barriers. The same refers to the chains with saturated bonds, which connect the chromophore structure of the molecule with the electrodes.[44] Taking into account the isolation of the fluorophore by spacers 1 and
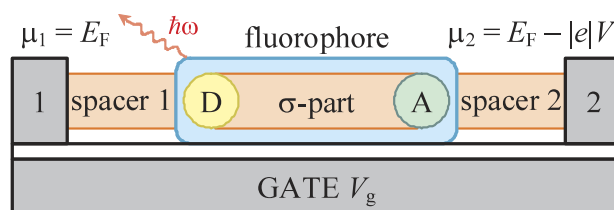

FIG. 1. A molecule of the Aviram–Ratner-type in the "electrode 1–molecule–electrode 2" junction (1M2 system). Spacers 1 and 2 separate the photoactive region of the molecule, D−σ−A, from the electrodes. The gate voltage V_g equally shifts the energy levels of the molecule, while the bias voltage V creates a gradient of the electric field between the grounded electrode 1 and electrode 2; this gradient is used to excite the molecule.

2 (see Fig. 1), we suggest that the interaction of the fluorophore with the electrodes does not lead to a notable change in the frequencies of optical transitions in the fluorophore.

Despite the fact that EL is caused by interelectrode transfer of single electrons, the transfer process itself occurs in a multi-electron system. To take this fact into account, a many-body approach is used to describe electron transfer. An example is the description of transient[12,35,54] and stationary[44] photocurrents in a molecular photodiode, as well as stationary EL in photoactive molecular junctions.[37,43,46,47] Here, we use the approach in Ref. [55], in which the occupation number representation allows one to simultaneously obtain kinetic equations for multi-electron molecular occupancies (the probabilities of populating molecular states), as well as expressions for the electron current[12,35] and EL power.[46,47]

A. Hamiltonian of the "1M2 + photon field" system

We will consider the formation of EL under conditions where the interactions of the fluorophore with the electrodes and the photon field have little effect on the electronic terms of the fluorophore. Therefore, the main part of interactions within the system "1M2 + photon field" are concentrated in the Hamiltonian

$$H_0 = H_{el} + H_f + H_m. \tag{1}$$

In it,

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

$$H_f = \sum_{\mathbf{q}\xi} \hbar\omega_q \left(b_{\mathbf{q}\xi}^+ b_{\mathbf{q}\xi} + 1/2 \right), \tag{3}$$

and

$$H_m = \sum_{M(N)} E_{M(N)} |M(N)\rangle\langle M(N)| \tag{4}$$

are the Hamiltonians of the electrodes, the photon field, and the molecule, respectively. The creation (annihilation) Fermi operators $a_{r\mathbf{k}\sigma}^+ (a_{r\mathbf{k}\sigma})$ and Bose operators $b_{\mathbf{q}\xi}^+ (b_{\mathbf{q}\xi})$ act on the corresponding one-particle states $|N_{r\mathbf{k}\sigma}\rangle$ and $|n_{\mathbf{q}\xi}\rangle$. We consider non-magnetic electrodes in the absence of a magnetic field. Therefore, the electron energy in the conduction band of the rth electrode, $E_{r\mathbf{k}}$, does not depend on the projection of the electron spin. Photons are considered as free particles whose energy, $\hbar\omega_q = \hbar cq$, linearly

depends on the modulus $q = |\mathbf{q}|$ of the photon wavevector $\mathbf{q}$ (c is the speed of light). In the occupation number representation, the eigenstates of the Hamiltonian (1) appear as[47,55,56] $|a\rangle = |M(N)\rangle \times \prod_{r\mathbf{k}\sigma} |N_{r\mathbf{k}\sigma}\rangle \times \prod_{\mathbf{q}\xi} |n_{\mathbf{q}\xi}\rangle$, where $N_{r\mathbf{k}\sigma} = 0, 1$ is the occupation number for an electron with wavevector $\mathbf{k}$ and spin projection $\sigma = \pm 1/2(\uparrow, \downarrow)$ in the conduction band of the $r(= 1, 2)$th electrode; $n_{\mathbf{q}\xi} = 0, 1, 2, \ldots$ is the occupation number for the photon with wavevector $\mathbf{q}$ and polarization ξ. Energy of the $|a\rangle$th state is given by the expression $E_a = E_{M(N)} + \sum_{r\mathbf{k}\sigma} E_{r\mathbf{k}} N_{r\mathbf{k}\sigma} + \sum_{\mathbf{q}\xi} \hbar \omega_q (n_{\mathbf{q}\xi} + 1/2)$, which is the eigenvalue of the Hamiltonian (1).

Transitions in the 1M2 system occur under the influence of the interactions of the molecule with the electrodes and the photon field. The first interaction can be represented in the form[12,55]

$$V_{m-e} = \sum_{N,MM'} \sum_{r\mathbf{k}\sigma} \left[V_{M'(N+1);r\mathbf{k}\sigma M(N)} |M'\rangle\langle M| a_{r\mathbf{k}\sigma} \right.$$
$$\left. + V_{r\mathbf{k}\sigma M(N);M'(N+1)} a^+_{r\mathbf{k}\sigma} |M\rangle\langle M'| \right], \quad (5)$$

where the matrix element

$$V_{M'(N+1);r\mathbf{k}\sigma M(N)} = \sum_\lambda \beta_{\lambda,r\mathbf{k}} \langle M'(N+1)| c^+_{\lambda\sigma} |M(N)\rangle \quad (6)$$

characterizes the process of molecular recharging, $|1_{r\mathbf{k}\sigma}\rangle |M(N)\rangle \to |0_{r\mathbf{k}\sigma}\rangle |M'(N+1)\rangle$, caused by the arrival of an electron from the $\mathbf{k}\sigma$th occupied band state of the rth electrode. The reverse process, $|0_{r\mathbf{k}\sigma}\rangle |M(N)\rangle \to |1_{r\mathbf{k}\sigma}\rangle |M'(N-1)\rangle$, is characterized by the matrix element $V_{r\mathbf{k}\sigma M'(N-1);M(N)} = V^*_{M(N);r\mathbf{k}\sigma M'(N-1)}$, where $\mathbf{k}\sigma$ should now belong to the empty state of the conduction band. In the formula (6), $\beta_{\lambda,r\mathbf{k}}$ is the spin-independent coupling between the λth MO and the $r\mathbf{k}$th state; $c^+_{\lambda\sigma}(c_{\lambda\sigma})$ is the electron creation (annihilation) operator with the spin projection σ onto the λth MO (Table I). As in Ref. 44, we assume that in the multi-electron system λ, there is a Kohn–Sham MO.

The second type of interaction connects optical transitions in a molecule with a photon field. In the dipole approximation, this interaction reads

$$V_{m-f} = i \sum_{N,MM'} G_{MM'} (|M\rangle\langle M'| - |M'\rangle\langle M|), \quad (7)$$

TABLE I. List of main variables utilized in this paper.

Symbol	Meaning
μ_1, μ_2	Chemical potentials, Eq. (31)
$V(V_g)$	Bias (gate) voltage
$\eta_L(\eta_H)$	Voltage division factor, Fig. 4
$\Delta E^{(r)}_{M(N)M'(N\pm1)}$	Basic transmission gap, Eq. (16), Fig. 2
$\Delta E^{(r)}_{\pm j}$	Transmission gap in the five-state model, Eq. (44)
ϵ_λ	Energy of λth MO, Eq. (32)
$\Gamma^{(r)}_\lambda$	Width parameter for λth MO, Eq. (42)
E_j, E_α	Energies of molecular states; Eqs. (29) and (30)
$\Gamma_j(\Gamma_\alpha)$	Molecular width parameters, Figs. 5 and 7
$\epsilon_L(\epsilon_H)$	Offset of the unbiased LUMO(HOMO) level, Eq. (54)
$V^{(r)}_{\alpha j}$	Critical voltage, Eq. (53)

where quantity $G_{MM'} = (1/c)\omega_{MM'} \mathbf{A} \mathbf{d}_{MM'}$ characterizes the coupling between the molecule and the field. In it, $\mathbf{d}_{MM'}$ and $\omega_{MM'} = (1/\hbar)(E_{M(N)} - E_{M'(N)})$ are, respectively, the dipole moment and frequency of the intramolecular optical transition $|M(N)\rangle \to |M'(N)\rangle$ at the fixed number of electrons N. The vector potential of the electromagnetic field, $\mathbf{A} = \sum_{\mathbf{q}\xi} A_q \mathbf{e}_{\mathbf{q}\xi} (b_{\mathbf{q}\xi} + b^+_{\mathbf{q}\xi})$, is given in the Coulomb gauge and in the Heisenberg representation;[57] $A_q = c(2\pi\hbar/V_0\omega_q)^{1/2}$ is the amplitude of the vector potential (V_0 is the volume of the cavity in which the photon field is formed).

The current passing through the 1M2 system is a non-equilibrium transport process, where a molecule mediates an electron transmission from one electrode to another. If the transmission is carried out with the participation of a fluorophore molecule, the electron current can spend part of its energy on the formation of EL. To describe the current and EL, it is convenient to use the non-equilibrium density matrix method.[58] In this method, the temporal behavior of the physical value O is determined by the density matrix of the system $\rho(t)$ through the relation $O(t) = tr(\rho(t)\hat{O})$, where $\hat{O}$ is the operator of the O (in the Heisenberg representation). The $\rho(t)$ evolves in time t in accordance with the Liouville equation $\dot{\rho}(t) = (i/\hbar)[H, \rho(t)] - \hat{D}\rho(t)$, where H is the Hamiltonian of the open system and $\hat{D}$ is the relaxation superoperator characterizing dissipative processes in the system. In our case, the open system is the "1M2 + photon field" system. It is assumed that the characteristic transition times in the 1M2 junction, τ_{tr}, far exceed the characteristic times τ_{rel} of relaxation processes, which are responsible for establishing the equilibrium distribution both between vibrational levels in molecular terms and band levels in electrodes. (It is these fast intramolecular and intrametal transitions that are represented in the $\hat{D}$.) For this reason, it becomes possible to describe the kinetic phenomena in the "1M2 + photon field" system using the equilibrium Boltzmann and Fermi distribution functions. The many-body states $|a\rangle$ include the states of quasicontinuous and continuous energy spectra associated, respectively, with conduction bands and the photon field. This gives a reason to use the delta functions $\delta(E_a - E_{a'})$ instead of Lorentzians $(\kappa_{aa'}/2\pi)[(E_a - E_{a'})^2 + \kappa^2_{aa'}/4]^{-1}$.[59] Thus, on a time scale of the order $\Delta t \sim \tau_{tr} \gg \tau_{rel}$, transitions between states $|a\rangle$ and $|a'\rangle$ can be characterized by rates,

$$\mathcal{K}_{a \to a'} = (2\pi/\hbar)|T_{a'a}|^2 \delta(E_a - E_{a'}). \quad (8)$$

Expression (8) coincides exactly with the probability of a transition in a unit time of a quantum system under the action of the operator $\hat{T} = H' + H'G(E)H'$ for a transition on the energy shell $E = E_a = E_b$.[60,61] Here, H' is the Hamiltonian responsible for direct $a \rightleftharpoons b$ transitions, and $G(E) = [E - H + i0^+]^{-1}$ is the Green operator in which H is the total Hamiltonian of the system. Rates $\mathcal{K}_{a \to a'}$ specify the *Pauli master equation* for the probabilities $P(a; t) = \langle a|\rho(t)|a\rangle$ to find a many-body system in the ath quantum state,

$$\dot{P}(a; t) = \sum_{a'} [\mathcal{K}_{a \to a'} P(a; t) - \mathcal{K}_{a' \to a} P(a'; t)]. \quad (9)$$

To get kinetic equations for the occupancies of molecular states, $P(M(N), t)$, put $\hat{O} = |M(N)\rangle\langle M(N)|$ and, thus, $P(M(N), t) = tr'(\rho(t)|M(N)\rangle\langle M(N)|) = \sum_{a'} P(a, t)$ [the summation is taken over all quantum numbers of the 1M2 system excluding the $M(N)$]. Using

this definition, we arrive at the following Pauli balance-like equations for molecular occupancies (cf. Appendix),

$$\dot{P}(M(N);t) = - \sum_{M'(N')} [\mathcal{K}_{M(N)\to M'(N')} P(M(N);t)$$
$$- \mathcal{K}_{M'(N')\to M(N)} P(M'(N');t)]. \quad (10)$$

The transition rates are given by the expression

$$\mathcal{K}_{M(N)\to M'(N')} = K^{(charging)}_{M(N)\to M'(N')} + K^{(intramol)}_{M(N)\to M'(N')}, \quad (11)$$

where the first component on the right-hand side characterizes the transitions accompanied by the recharging of the molecule. Other component,

$$K^{(intramol)}_{M(N)\to M'(N')} = K^{(f)}_{M(N)\to M'(N)} + K^{(nrad)}_{M(N)\to M'(N)}, \quad (12)$$

includes the transition rates, which do not change the charge state of the molecule.

1. Molecule charging rates

Molecule recharging is due to the interaction of the molecule with the electrodes. Expressions for the corresponding rates are presented in many papers.[12,37,44,55] They can be represented as

$$K^{(charging)}_{M(N)\to M'(N')} = \sum_{r} \chi^{(r)}_{M(N)\to M'(N')}, \quad (13)$$

where rate

$$\chi^{(r)}_{M(N)\to M'(N')} = (1/\hbar)\Gamma^{(r)}_{M(N)\to M'(N')}$$
$$\times [f_r(E)\delta_{N',N+1} + (1 - f_r(E))\delta_{N',N-1}] \quad (14)$$

characterizes the hopping of an electron between the molecule and the rth electrode. In Eq. (14), $f_r(E) = \{\exp[(E - \mu_r)/k_BT] + 1\}^{-1}$ is the Fermi distribution function (μ_r is the chemical potential of the rth electrode and T and k_B are the absolute temperature and Boltzmann constant, respectively). The maximal value of the hopping rate is determined by the quantity

$$\Gamma^{(r)}_{M(N)\to M'(N')} = 2\pi \sum_{\mathbf{k}\sigma} \left[|V_{M'(N+1);r\mathbf{k}\sigma M(N)}|^2 \delta_{N',N+1} \right.$$
$$\left. + |V_{r\mathbf{k}\sigma M'(N-1);M(N)}|^2 \delta_{N',N-1} \right] \delta(E_{r\mathbf{k}} - E), \quad (15)$$

which in accordance with the definition of matrix elements $V_{M'(N+1);r\mathbf{k}\sigma M(N)}$ and $V_{r\mathbf{k}\sigma M'(N-1);M(N)}$ depends on how the recharge energies of the molecule, $E = E_{M'(N+1)} - E_{M(N)}$ (if $N' = N + 1$) and $E = E_{M(N)} - E_{M'(N-1)}$ (if $N' = N - 1$), are located with respect to the chemical potential of the rth electrode (Fig. 2). This means that rates (14) are controlled by the magnitude and sign of the transmission gaps,[35,47]

$$\Delta E^{(r)}_{M(N)M'(N+1)} = (E_{M'(N+1)} - E_{M(N)}) - \mu_r,$$
$$\Delta E^{(r)}_{M(N)M'(N-1)} = \mu_r - (E_{M(N)} - E_{M'(N-1)}). \quad (16)$$

If the gaps are positive, then it is more favorable for the molecule to be in a state with a given number of electrons N than in states
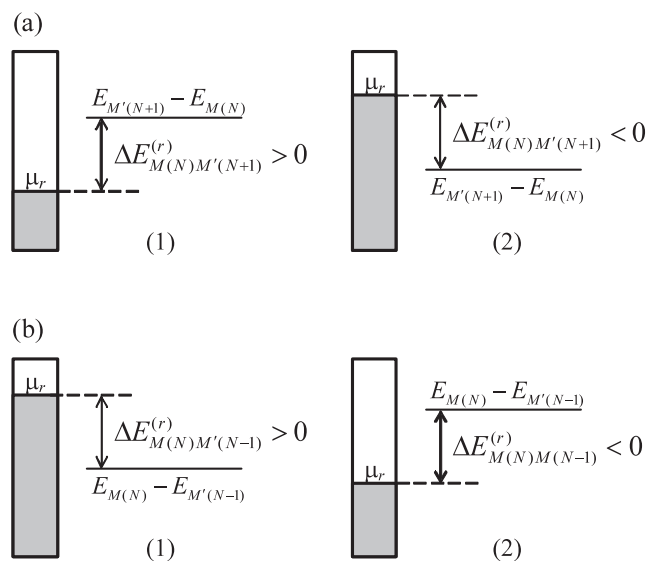

FIG. 2. Signs of main transmission gaps, Eq. (16), are determined by the energy distance between the chemical potential of the rth electrode, μ_r, and the energy difference between negatively charged, $|M(N' = N + 1)\rangle$, and neutral, $|M(N)\rangle$, molecular states (a), and also between neutral, $|M(N)\rangle$, and positively charged, $|M(N' = N - 1)\rangle$, states (b).

with a reduced ($N' = N - 1$) or increased ($N' = N + 1$) number of electrons.

2. Intramolecular transition rates

Intramolecular transitions, $M(N) \to M'(N)$, at which the number of electrons does not change, can occur both with emission or absorption of quanta of the electromagnetic field and non-radiation. In the presence of a photon field, transitions are initiated by interaction (7). When considering the spontaneous emission of a molecule, it is assumed that the photon field has a continuous energy spectrum in the vicinity of the frequency $\omega_q = \omega_{MM'} > 0$. Therefore, the rate of the spontaneous radiation can be written as

$$K^{(f)}_{M(N)\to M'(N)} = \sum_{\mathbf{q}\xi} K_{\mathbf{q}\xi}(M(N) \to M'(N)), \quad (17)$$

where

$$K_{\mathbf{q}\xi}(M(N) \to M'(N)) = \frac{2\pi}{\hbar^2} |\mathbf{E}_{\mathbf{q}\xi}\mathbf{d}_{MM'}|^2 \delta(\omega_{MM'} - \omega_q) \quad (18)$$

is the contribution to the transition rate associated with a single photon mode $\mathbf{q}\xi$ under condition $\mathbf{q}^2 = (\omega_{MM'}/c)^2$. In Eq. (18), $\mathbf{E}_{\mathbf{q}\xi} = (i/c)\omega_q A_q \mathbf{e}_{\mathbf{q}\xi}$ is the electric component of the photon field. As for the rate of non-radiative transitions,

$$K^{(nrad)}_{M(N)\to M'(N)} = K^{(i)}_{M(N)\to M'(N)} + K^{(ine)}_{M(N)\to M'(N)}, \quad (19)$$

and the contribution to it is provided by the intramolecular conversion [component $K^{(i)}_{M(N)\to M'(N)}$], as well as the inelastic electron tunneling due to the interaction (5). The rate of inelastic tunneling,

$$K_{M(N) \to M'(N)}^{(ine)} = \sum_{r,r'} K_{rM(N) \to r'M'(N)}, \tag{20}$$

is determined by the components [cf. Eq. (A4)],

$$
\begin{aligned}
& K_{rM(N) \to r'M'(N)} \\
& = \frac{1}{\pi\hbar} \Theta\left(\mu_r + E_{M(N)} - \mu_{r'} - E_{M'(N)}\right) \\
& \times \sum_{\tilde{M}} \left\{ \frac{\Gamma_{M(N) \to \tilde{M}(N+1)}^{(r)} \Gamma_{\tilde{M}(N+1) \to M'(N)}^{(r')}}{\Gamma_{\tilde{M}(N+1)}} \right. \\
& \times \left[\arctan \frac{2\Delta E_{\tilde{M}(N+1)M'(N)}^{(r')}}{\Gamma_{\tilde{M}(N+1)}} - \arctan \frac{2\Delta E_{\tilde{M}(N+1)M(N)}^{(r)}}{\Gamma_{\tilde{M}(N+1)}} \right] \\
& + \frac{\Gamma_{M(N) \to \tilde{M}(N-1)}^{(r')} \Gamma_{\tilde{M}(N-1) \to M'(N)}^{(r)}}{\Gamma_{\tilde{M}(N-1)}} \\
& \times \left. \left[\arctan \frac{2\Delta E_{\tilde{M}(N-1)M'(N)}^{(r)}}{\Gamma_{\tilde{M}(N-1)}} - \arctan \frac{2\Delta E_{\tilde{M}(N-1)M(N)}^{(r')}}{\Gamma_{\tilde{M}(N-1)}} \right] \right\}. \tag{21}
\end{aligned}
$$

These rates characterize the process at which electrons occupying the single-particle states $\mathbf{k}\sigma$ of the conduction band of the rth electrode are transferred to the empty single-particle states $\mathbf{k}'\sigma'$ of the conduction band of the r'th electrode. The quantity $\Gamma_{\tilde{M}(\tilde{N})}$ plays a role of broadening of the molecular level $E_{\tilde{M}(\tilde{N})}$ caused by the interaction with the electrodes. It can be evaluated based on expressions

$$\Gamma_{M(N)} = \sum_r \sum_{M'(N')} \Gamma_{M(N) \to M'(N')}^{(r)} \Theta\left(\Delta E_{M(N)M'(N')}^{(r)}\right) \tag{22}$$

and (15). A fundamentally important conclusion follows from Eq. (22): the broadening of the molecular level with energy $E_{M(N)}$ substantially depends on the sign of the transmission gaps (7) and, as a result, is controlled by an electric field (see details in Sec. III).

B. Electron current

To obtain the expression for the electron current outgoing from the rth electrode, $I_r(t) = e\dot{N}_r(t)$, we note that the number of electrons leaving the electrode per unit time can be found by using the definition $\dot{N}_r(t) = \sum_{\mathbf{k}\sigma} \dot{P}(1_{r\mathbf{k}\sigma}, t)$, where $P(1_{r\mathbf{k}\sigma}, t)$ is the probability of population of the $|N_{r\mathbf{k}\sigma}\rangle$th conductive state at $N_{r\mathbf{k}\sigma} = 1$. To find the $P(N_{r\mathbf{k}\sigma}, t)$, we put $\hat{O} = |N_{r\mathbf{k}\sigma}\rangle\langle N_{r\mathbf{k}\sigma}|$ and, thus, $P(r\mathbf{k}\sigma, t) = tr(N_{r\mathbf{k}\sigma}\rho(t)|N_{r\mathbf{k}\sigma}\rangle\langle N_{r\mathbf{k}\sigma}|) = \sum_a N_{r\mathbf{k}\sigma}\langle a|\rho(t)|a\rangle = \sum_a N_{r\mathbf{k}\sigma}P(a, t)$. Therefore, the electron current is found from the expression

$$I_r(t) = e \sum_{r\mathbf{k}\sigma} \sum_{a,a'} N_{r\mathbf{k}\sigma}[\mathcal{K}_{a \to a'}P_a(t) - \mathcal{K}_{a' \to a}P_{a'}(t)]. \tag{23}$$

This yields

$$I_r(t) = e \sum_N \sum_M [\Pi_r^{(0)}(M;N) + \Pi_r^{(1)}(M;N)]P_{M(N)}(t). \tag{24}$$

Here,

$$\Pi_r^{(0)} = \sum_{M'} [K_{rM(N) \to r'M'(N)} - K_{r'M'(N) \to rM'(N)}] \tag{25}$$

and

$$\Pi_r^{(1)} = \sum_{M'} [\chi_{M(N) \to M'(N+1)}^{(r)} - \chi_{M(N) \to M'(N-1)}^{(r)}] \tag{26}$$

are the partial electron flows caused by electron transfer along routes in which the molecule does not change its charge and changes its charge by one unit, respectively. It is important that the formation of current $I_r(t)$ and populations $P(M(N); t)$ is carried out by the same kinetic processes and, therefore, is characterized by the same transition rates.

C. Molecular radiation power

In classical electrodynamics, the radiation power of a system having an induced dipole moment $\mathbf{D}$ is determined by the expression $\mathcal{P}(t) = -\mathbf{D}\dot{\mathbf{E}}(t)$, where $\dot{\mathbf{E}}$ is the time derivative of the electric component of the electromagnetic field. Therefore, in the quantum case, setting $\hat{O} = -\mathbf{d}\dot{\mathbf{E}}$, we obtain

$$\mathcal{P}(t) = -tr(\rho(t)\mathbf{d}\dot{\mathbf{E}}). \tag{27}$$

Here, $\mathbf{d}$ is the operator of the dipole moment of the molecule, and $\dot{\mathbf{E}} = (i/\hbar c)[\mathbf{A}, H_f]$ is the time derivative of the operator of the electric component of the photon field. The rate of the intramolecular $M(N) \to M'(N)$ transition, accompanied by the emission of a single photon with a frequency of $\omega_q = \omega_{MM'}$, is determined by Eqs. (17) and (18). When a cavity creates an average number of photons $n_{\mathbf{q}\xi}$ of the mode $\mathbf{q}\xi$, then the molecule emits and absorbs the $\mathbf{q}\xi$-photon with probabilities that are proportional to the factors $(n_{\mathbf{q}\xi} + 1)P(M(N), t)$ and $n_{\mathbf{q}\xi}P(M'(N), t)$, respectively. Expanding the expression (27) with use of the method described in Ref. 47, we get [cf. Eq. (A2)]

$$
\begin{aligned}
\mathcal{P}(t) = \mathcal{P}(\omega_{MM'}; t) = \sum_{\mathbf{q}\xi} \hbar\omega_q K_{\mathbf{q}\xi}(M(N) \to M'(N)) \\
\times [(n_{\mathbf{q}\xi} + 1)P(M(N), t) - n_{\mathbf{q}\xi}P(M'(N), t)]. \tag{28}
\end{aligned}
$$

This expression can be used to estimate the radiation power of a molecule occurring in a photon field. The spontaneous emission occurs in the absence of photon generation in the cavity, i.e., for $n_{\mathbf{q}\xi} = 0$.

III. FIVE-STATE MODEL OF THE FLUOROPHORE

To apply the above expressions to the description of EL, it is necessary to specify the molecular states $|M(N)\rangle$. In a condensed medium, the formation of luminescence of a molecule occurs mainly with the participation of the ground singlet, excited singlet, and excited triplet states. Since the chromophore part of the molecule in the optoelectronic 1M2 junction is well isolated from the electrodes by using spacers, the three molecular states mentioned above retain their participation in the formation of EL. At the same time, the interaction (5) leads to the recharging of the molecule so that the charged molecular states are also involved in the formation of EL. To find the actual molecular states, $|M(N)\rangle$, and the corresponding energies, $E_{M(N)}$, methods of quantum mechanics of molecules are used (see the examples in Refs. 37 and 44). However, the basic features of EL formation can be elucidated by setting states and

energies within the framework of widely used physical models. We will employ the model where photoactive molecular states correspond to those electronic configurations of a molecule that arise when electrons occupy the HOMO and LUMO. For Aviram–Ratner photochromic molecules, the formation of these MOs is shown in Fig. 3.

The symbol $M = M(N)$ includes electronic $[m(N)]$ and vibrational ($v_m = 0, 1, 2, \ldots$) quantum numbers of a molecule with N electrons, i.e., $|M(N)\rangle \simeq |m(N)\rangle|v_m\rangle$. Below, we will define N as the number of electrons of a molecule in charge-neutral states. Since the interaction (5) is responsible for one-electron charge exchange, we will additionally take into account the states of the molecule with the number of electrons $N + 1$ and $N - 1$. Let $s_Z = 0, \pm 1$ be the spin projection of the molecule in the excited triplet state, and $\sigma = \uparrow\downarrow$ is the projection of the spin of an electron located on the HOMO (LUMO). Then, denoting through $|m(N)\rangle = |S_0\rangle, |S\rangle, |T, s_z\rangle, |m(N-1)\rangle = |+, \sigma\rangle$, and $|m(N+1)\rangle = |-, \sigma\rangle$, respectively, for the neutral and charged molecular states, in the second quantization representation, we have the following expressions: $|S_0\rangle \equiv |0\rangle = |c_{H\uparrow}^+ c_{H\downarrow}^+\rangle$, $|S\rangle = (1/\sqrt{2})|(c_{H\uparrow}^+ c_{L\downarrow}^+ - c_{H\downarrow}^+ c_{L\uparrow}^+)\rangle$, $|T, 0\rangle = 1/\sqrt{2}|(c_{H\uparrow}^+ c_{L\downarrow}^+ + c_{H\downarrow}^+ c_{L\uparrow}^+)\rangle$, $|m_T, +1(-1)\rangle = |c_{H\uparrow(\downarrow)}^+ c_{L\uparrow(\downarrow)}^+\rangle$, $|+, \sigma\rangle = |c_{H\sigma}^+\rangle$, and $|-, \sigma\rangle = |c_{H\uparrow}^+ c_{H\downarrow}^+ c_{L\sigma}^+\rangle$. The corresponding energies of neutral (E_j, $j = 0, S, T$) and singly charged (E_α, $\alpha = \pm$) molecular states are

$$E_0 = 2\varepsilon_H,$$
$$E_S = \varepsilon_H + \varepsilon_L + U_{HL} + (3/2)J_{HL}, \quad (29)$$
$$E_T = \varepsilon_H + \varepsilon_L + U_{HL} - (1/2)J_{HL}$$

and

$$E_+ = \varepsilon_H,$$
$$E_- = 2\varepsilon_H + \varepsilon_L + 2U_{HL}. \quad (30)$$

In Eqs. (29) and (30), quantity ε_λ is the orbital energy for Kohn–Sham orbitals, $\lambda = H(\text{HOMO}), L(\text{LUMO})$. This energy shows a shift due to a bias voltage V and a gate voltage V_g. If the electrode 1 is grounded and, thus, the chemical potentials of the electrodes are
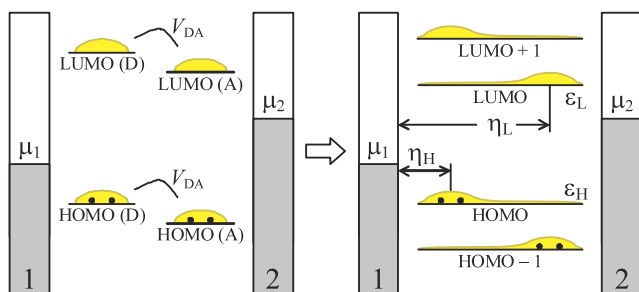

FIG. 3. Scheme of the formation of the HOMO and LUMO in Aviram–Ratner-type molecules. Interaction V_{DA} between the donor (D) and acceptor (A) photoactive units leads to partial delocalization of the localized orbitals of the D and A units, forming LUMO, LUMO + 1, HOMO, and HOMO −1. The values of η_L and η_H characterize the distance from the "centers of gravity" of electron densities at the LUMO and HOMO. The orbital energies of the latter are denoted by ε_L and ε_H, respectively.

$$\mu_r = E_F - |e|V\delta_{r,2} \quad (31)$$

(E_F is the energy of the Fermi level), then

$$\varepsilon_\lambda = \varepsilon_\lambda^{(0)} - |e|V_g - |e|\eta_\lambda V \quad (32)$$

[$\varepsilon_\lambda^{(0)}$ is the unbiased orbital energy]. Parameter $\eta_\lambda(<1)$ fixes the location of the "center of gravity" of the electronic density on the HOMO (LUMO) relative to electrode 1 (cf. Fig. 3). In molecular energies, quantities U_{HL} and J_{HL} are the parameters of the Coulomb and exchange interaction of the electrons occupying the HOMO and LUMO. Note that the energies E_T and E_α correspond to molecular states that are triple and double degenerate according to the spin projection, respectively.

Calculating basic quantities (15) and (16) with the use of all five molecular states $|M_j\rangle$ and $|M_\alpha\rangle$ as well as corresponding energies E_j and E_α allows us to derive analytic expressions for above molecular charging and molecular transition rates and, thus, to specify the kinetic equations, current, and molecular radiation power. In this paper, we restrict ourselves to the analysis of the physical mechanisms of the formation of only spontaneous EL in AR-type molecules.

A. Power of EL at spontaneous emission

The purely spontaneous transition $M(N) \to M'(N)$ leads to the generation of a single photon emitted by an excited molecule. In the case under consideration, $M(N) = m_S, v_S$ and $M'(N) = m_0, v_0$. Putting $n_{\mathbf{q}\xi} = 0$ in Eq. (28) and using Eq. (18), for the power of spontaneous emission at the $m_S v_S \to m_0 v_0$ transition, we get the following expression:

$$\mathcal{P}(\omega_{S v_S, 0 v_0}; t) = \frac{4 d_s^2}{3 c^3} \langle v_0 | v_S \rangle^2 \omega_{S v_S, 0 v_0}^4 P(m_S, v_S; t). \quad (33)$$

Here, d_s is the value of the dipole moment of the pure electronic transition, $\langle v_0 | v_S \rangle$ is the overlap integral for the vibration functions of the excited singlet and the ground singlet molecular terms, and $\omega_{s v_s, 0 v_0} = (1/\hbar)(E_{S v_S} - E_{0 v_0})$ is the frequency of the optical electron–vibration transition. At times $t \gg \tau_{rel}$ under consideration, between the populations of the vibrational levels of the term m, there is a relation $P(m, v_m; t)/P(m, v_m'; t) = \exp[-\hbar\omega_m(v_m - v_m')/k_B T]$. Therefore,

$$P(m, v_m; t) = W(v_m) P(m; t), \quad (34)$$

where $W(v_m) = \exp\left[-\frac{\hbar\omega_m v_m}{k_B T}\right] / \sum_{v_m} \exp\left[-\frac{\hbar\omega_m v_m}{k_B T}\right]$ is the probability of occupancy of the v_mth vibration level and $P(m; t) = \sum_{v_m} P(m, v_m; t)$ is the integral occupancy of the mth molecular term. Given the equality (34), from Eq. (33), we obtain the following expression for the radiation power at the frequency $\omega = \omega_{S v_S, 0 v_0}$:

$$\mathcal{P}(\omega_{S v_S, 0 v_0}; t) = \hbar\omega_{S v_S, 0 v_0} K_{rad}(\omega_{S v_S, 0 v_0}) P(S; t). \quad (35)$$

Here,

$$K_{rad}(\omega_{Sv_S,0v_0}) = \frac{4d_s^2}{3c^3\hbar}\omega_{Sv_S,0v_0}^3 W(v_S)\langle v_0|v_S\rangle^2 \qquad (36)$$

is the rate of the spontaneous $Sv_S \to 0v_0$ transition. The integral rate of the radiation transition $M_S \to M_0$ is the sum of the partial rates,

$$k_{rad} = \sum_{v_S,v_0} K_{rad}(\omega_{Sv_S,0v_0}). \qquad (37)$$

B. Master equations for integral occupancies of molecular terms

As follows from expression (35), the power of spontaneous radiation is controlled by the population of the excited singlet state/term of the molecule. The temporal behavior of $P(S;t)$ and the occupancies of other molecular states are determined by the set of kinetic equations (10). Due to the relationship between partial and integral occupancies, Eq. (34), the set (10) is reduced to equations for integral occupancies $P(m;t)$. For states degenerated from the projections of spins, an additional summation is introduced so that the integral occupancies of the triplet and charged states/terms are defined as $P(T;t) = \sum_{s_Z}\sum_{v_T}P(Ts_Z,v_T;t)$ and $P(\pm;t) = \sum_\sigma\sum_{v_\pm}P(\pm\sigma,v_\pm;t)$, respectively. Given these definitions, we obtain from the basic Eq. (10) the following set of kinetic equations ($j, j' = 0, S, T; \alpha = +, -$):

$$\dot{P}(j;t) = -\left[\left(\sum_\alpha q_{j\to\alpha} + \sum_{j'} q_{j\to j'}\right)P(j;t)\right.$$
$$\left. - \left(\sum_\alpha q_{\alpha\to j}P(\alpha;t) + \sum_{j'} q_{j'\to j}P(j';t)\right)\right],$$

$$\dot{P}(\alpha;t) = -\sum_j [q_{\alpha\to j}P(\alpha;t) - q_{j\to\alpha}P(j;t)], \qquad (38)$$

where molecular occupancies satisfy the normalization condition,

$$\sum_j P(j;t) + \sum_\alpha P(\alpha;t) = 1. \qquad (39)$$

Figure 4 shows the scheme of transitions between the five states involved in the formation of EL in a 1M2 junction. The transition rates are determined by the expressions

$$q_{\alpha j} = \left(\delta_{j,0} + (1/2)\delta_{j,S} + (3/2)\delta_{j,T}\right)\left(K_{\alpha j}^{(1)} + K_{\alpha j}^{(2)}\right),$$
$$q_{j\alpha} = \left(2\delta_{j,0} + \delta_{j,S} + \delta_{j,T}\right)\left(K_{j\alpha}^{(1)} + K_{j\alpha}^{(2)}\right). \qquad (40)$$

The kinetic equations (38) and the corresponding transition rates (40) follow from the master Eq. (10) if relations of the type $\sum_\sigma\sum_{vv'}\chi_{S,v\to+,\sigma,v'}^{(r)}P(S,v;t) = (1/2)K_{S+}^{(r)}P(S;t) \equiv q_{S+}P(S;t)$ are used. Here, $K_{S+}^{(r)} = (\Gamma_L^{(r)}/\hbar)\sum_{vv'}W(v)\langle v'|v\rangle^2[1 - f_r(E_{S,v} - E_{+,v'})]$ is the charging rate characterizing the transition between the electron-vibrational states belonging to the M_Sth and M_+th molecular terms. Below, to discuss the physics of EL formation, we will choose a simpler form for the rates by setting $\langle v'|v\rangle = \delta_{v',v}$. This allows
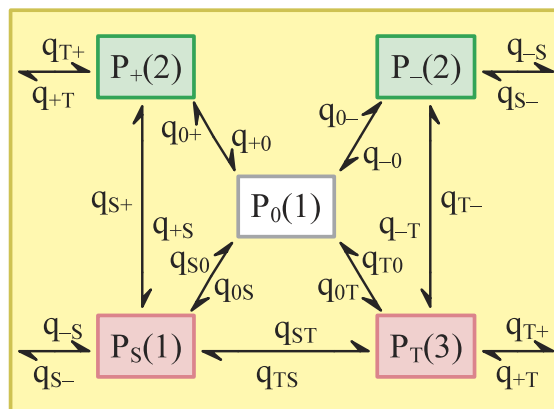

FIG. 4. Scheme of one-electron kinetic transitions between many-body states of a fluorophore in the model of five active molecular states, the integral occupancies of which are denoted by P_j ($j = 0, S, T$) and P_α ($\alpha = \pm$). The degeneracy of states according to spin projections is indicated in brackets.

us to write the elementary rates of the molecule recharge in the forms

$$K_{j\alpha}^{(r)} = \frac{1}{\hbar}\Gamma_\lambda^{(r)} N(\Delta E_{\alpha j}^{(r)})(\delta_{j,S(T)}(\delta_{\alpha,+}\delta_{\lambda,L} + \delta_{\alpha,-}\delta_{\lambda,H}),$$
$$K_{0\alpha}^{(r)} = \frac{1}{\hbar}\Gamma_\lambda^{(r)} N(\Delta E_{\alpha 0}^{(r)})(\delta_{\alpha,+}\delta_{\lambda,H} + \delta_{\alpha,-}\delta_{\lambda,L}), \qquad (41)$$

and $K_{\alpha j}^{(r)} = \exp[\Delta E_{\alpha j}^{(r)}/k_B T]K_{j\alpha}^{(r)}$. Here,

$$\Gamma_\lambda^{(r)} = 2\pi\sum_{\mathbf{k}}|\beta_{\lambda,r\mathbf{k}}|^2\delta(E_{r\mathbf{k}} - \varepsilon_\lambda) \qquad (42)$$

is the width parameter characterizing the broadening of the level of the λth MO. It is the parameters $\Gamma_\lambda^{(r)}$ that characterize the kinetics of electron transfer between the HOMO(LUMO) and the electrodes, Fig. 5. Function

$$N(\Delta E_{\alpha j}^{(r)}) = \{\exp[\Delta E_{\alpha j}^{(r)}/k_B T] + 1\}^{-1} \qquad (43)$$

controls the on/off resonance transmission of an electron between the electrode and the molecule through a change in the sign of the transmission gaps,

$$\Delta E_{+j}^{(r)} = (E_+ + \mu_r) - E_j,$$
$$\Delta E_{-j}^{(r)} = E_- - (E_j + \mu_r). \qquad (44)$$

In a similar way, using formulas (19) and (21) and the approach derived in Refs. 35 and 47, we obtain

$$q_{j\to j'} = K_{j\to j'}^{(i)} + K_{j\to j'}^{(ine)}. \qquad (45)$$

The rate $K_{j\to j'}^{(i)}$ is determined by the interterm non-radiative transitions. The component
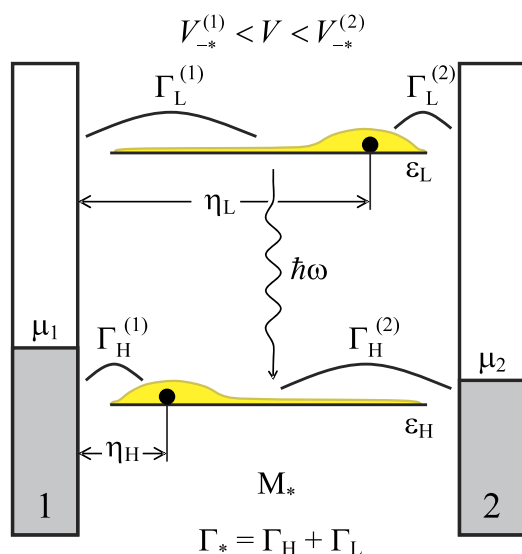
FIG. 5. The asymmetric coupling of the LUMO and HOMO to electrodes 1 and 2 is manifested in the relations $\Gamma_L^{(1)} \ll \Gamma_L^{(2)}$ and $\Gamma_H^{(1)} \gg \Gamma_H^{(2)}$ between the parameters $\Gamma_\lambda^{(r)}$, Eq. (42), which characterize the widths of the orbital energy levels ε_λ if the latter take a virtual part in electron transmission. The broadening of the molecular energy level is expressed through $\Gamma_\lambda^{(r)}$ in accordance with formula (49). The electronic configuration for the virtual excited state of the molecule is shown, which corresponds to a certain arrangement of the LUMO and HOMO relative to chemical potential electrodes. The corresponding broadening of the molecular energy $E_* = E_S \simeq E_T$ is characterized by the value $\Gamma_*/2$ with $\Gamma_\lambda = \Gamma_\lambda^{(1)} + \Gamma_\lambda^{(2)}$.

$$K_{j \to j'}^{(ine)} = \frac{1}{2\pi\hbar} \sum_{rr'(=1,2)} \Theta(E_j + \mu_r - E_{j'} - \mu_{r'})$$
$$\times \left[\frac{\Gamma_L^{(r)} \Gamma_L^{(r')}}{\Gamma_+} \left(\varphi_{+j'}^{(r)} - \varphi_{+j}^{(r')} \right) + \frac{\Gamma_H^{(r)} \Gamma_H^{(r')}}{\Gamma_-} \left(\varphi_{-j'}^{(r')} - \varphi_{-j}^{(r)} \right) \right] \tag{46}$$

determines the rate of $j(= S) \to j'(= T)$ or $j(= T) \to j'(= S)$ transitions, whereas quantity

$$K_{j \to j'}^{(ine)} = \frac{1}{\pi\hbar} \sum_{rr'(=1,2)} \Theta(E_j + \mu_r - E_{j'} - \mu_{r'})$$
$$+ \left[\delta_{j,0} \delta_{j',S(T)} \Gamma_L^{(r)} \Gamma_H^{(r')} + \delta_{j,S(T)} \delta_{j',0} \Gamma_H^{(r)} \Gamma_L^{(r')} \right]$$
$$\times \left[\frac{1}{\Gamma_+} \left(\varphi_{+j'}^{(r)} - \varphi_{+j}^{(r')} \right) + \frac{1}{\Gamma_-} \left(\varphi_{-j'}^{(r')} - \varphi_{-j}^{(r)} \right) \right] \right\} \tag{47}$$

characterizes the rate of $M_0 \rightleftharpoons M_{S(T)}$ transitions. Intramolecular transition rates [(46) and (47)] appear due to an inelastic interelectrode electron tunneling. This is reflected in the quantity

$$\varphi_{\alpha j}^{(r)} = \arctan\left(2\Delta E_{\alpha j}^{(r)}/\Gamma_\alpha\right), \tag{48}$$

which includes the transmission gap $\Delta E_{\alpha j}^{(r)}$ and the broadening of the energy level E_α of a charged molecule,

$$\Gamma_\alpha = \sum_r \left\{ \left[\Gamma_H^{(r)} \delta_{\alpha,+} + \Gamma_L^{(r)} \delta_{\alpha,-} \right] \Theta(\Delta E_{\alpha 0}^{(r)}) \right.$$
$$\left. + \left[\Gamma_L^{(r)} \delta_{\alpha,+} + \Gamma_H^{(r)} \delta_{\alpha,-} \right] \sum_j \left(\frac{1}{2}\delta_{j,S} + \frac{3}{2}\delta_{j,T} \right) \Theta(\Delta E_{\alpha j}^{(r)}) \right\}. \tag{49}$$

IV. RESULTS AND DISCUSSION

In accordance with the expressions (35) and (36), the power of the spontaneous emission is proportional to the occupancy $P(S; t)$ of the excited singlet state of the molecule. This reflects the fact of kinetic control of the radiation efficiency. Here, we consider the steady state transmission regime that occurs when $t \gg \tau_{tr}$. During this regime, the integral occupancies of molecular terms cease to depend on time. We denote the corresponding occupancies as P_j ($j = 0, S, T$) and P_α ($\alpha = +, -$). Equations (35) and (36) show that the power of a stationary EL at the frequency $\omega = \omega_{Sv,0v'}$ can be represented as

$$\mathcal{P} = \mathcal{P}_{rad}(\omega) P_S, \tag{50}$$

where $\mathcal{P}_{rad}(\omega) = \sum_{v,v'} \hbar\omega_{Sv,0v'} K_{rad}(\omega_{Sv,0v'})$ is the theoretically possible maximal integral power of the photon emission at the $M_S \to M_0$ transition. In the simplest case, when $\langle v'|v \rangle \approx \delta_{v',v}$, it reduces to

$$\mathcal{P}_{rad}(\omega) = \frac{4d_s^2}{3c^3} \omega^4. \tag{51}$$

The value of $\mathcal{P}_{rad}(\omega)$ reflects the efficiency of the intramolecular transition, while the effect of electrodes on the EL power is concentrated in the P_S. Below, the main attention is paid to elucidating the control mechanisms of radiation power through the population of the singlet state $|S\rangle$. The value of P_S, like other occupancies, is determined from the set of kinetic equations under conditions $\dot{P}(j; t) = 0$ and $\dot{P}(\alpha; t) = 0$.

The necessary condition for the appearance of EL is the inequality,

$$|eV| \geq (E_S - E_0)/\hbar. \tag{52}$$

However, if the regime of resonant transmission of electrons across the molecule is not fulfilled, then the radiation intensity is too low to observe EL. As already noted above and in Refs. 46 and 47, for the appearance of resonant transmission, it is necessary that the basic transmission gaps (16) had negative values. The same refers to the gaps (44) appearing in the model of five active molecular states. In addition, for asymmetric molecules, which include AR-type molecules, the relation between the parameters $\Gamma_\lambda^{(r)}$ plays a decisive role in the appearance of the EL polarity.[47] Finally, the non-radiative quenching of EL due to inelastic tunneling is of great importance. The effectiveness of this quenching is determined both by the values $\Delta E_{\alpha j}$ and $\Gamma_\lambda^{(r)}$, and by the broadenings Γ_+ and Γ_- of virtual levels of the charged molecule.

A. Critical voltages

The condition $\Delta E_{\alpha j}^{(r)} = 0$, in which the transmission gap changes its sign, determines the specific critical voltage $V_{\alpha j}^{(r)}$ at which

a resonant electron transfer occurs between the rth electrode and the molecule. Using definitions (44) and formulas (29)–(32), we can write analytic expressions for all quantities $V_{\alpha j}^{(r)}$. The photoactive AR-type molecules probably belong to the molecules with a small exchange interaction between groups D and A. This is due to the weak overlap of the HOMO and LUMO wave functions localized far from each other (cf. Fig. 5). So, $J_{HL} \simeq 0$, and therefore, $E_S \simeq E_T \equiv E_*$. Given this circumstance, we obtain the following expressions for critical voltages $[V_{\alpha S}^{(r)} \simeq V_{\alpha T}^{(r)} \equiv V_{\alpha *}^{(r)}]$:

$$V_{+*}^{(r)} = \frac{2(\epsilon_L/|e| - V_g)}{(2\eta_L - 1) - (-1)^r},$$

$$V_{-*}^{(r)} = \frac{2[(\epsilon_H + U_c)/|e| - V_g]}{(2\eta_H - 1) - (-1)^r},$$

$$V_{-0}^{(r)} = \frac{2[(\epsilon_L + U_c)/|e| - V_g]}{(2\eta_L - 1) - (-1)^r}, \quad (53)$$

$$V_{+0}^{(r)} = \frac{2(\epsilon_H/|e| - V_g)}{(2\eta_H - 1) - (-1)^r}.$$

[We use the Coulomb parameter U_c instead of U_{LH}, assuming that the interaction of the electron occupying the LUMO occurs not only with the electron/electrons filling the HOMO but also with other charges of the molecule.] In Eq. (53), the values ϵ_L and ϵ_H are the offsets of the LUMO and HOMO levels from the unbiased Fermi level. In the simplest model, they are

$$\epsilon_L = \tilde{\epsilon}_L^{(0)} + U_{HL} - E_F(> 0),$$

$$\epsilon_H = \epsilon_H^{(0)} - E_F(< 0). \quad (54)$$

In this paper, ϵ_L and ϵ_H are considered only as parameters determining the LUMO–HOMO gap,

$$\Delta E_{LH} = \epsilon_L - \epsilon_H. \quad (55)$$

This gap corresponds to the energy $E_S - E_0 = \hbar\omega_{S0}$ of a vertical $M_S \to M_0$ transition within the molecule with a negligible exchange interaction.

Physically, in the vicinity of $V = V_{\alpha j}^{(r)}$, the regime of electron transmission through the molecule is rearranged, since it becomes energetically more profitable for the molecule to change its electronic configuration. As Fig. 6 shows, the values of $V_{\alpha j}^{(r)}$ are well manifested at those values of V near which at least one of the molecular states is well populated. It is noteworthy that, at a given asymmetry of the 1M2 system and chosen parameters, the appearance of excited singlet and triplet states occurs due to transitions from a positively charged state, while a negatively charged state is practically not realized.

B. Asymmetry in kinetics

Due to the lack of experimental data concerning the optoelectronic properties of 1M2 junctions with AR-type molecules, the parameters of the theory are considered as phenomenological quantities. Therefore, graphs (6) and (8)–(10) demonstrate only
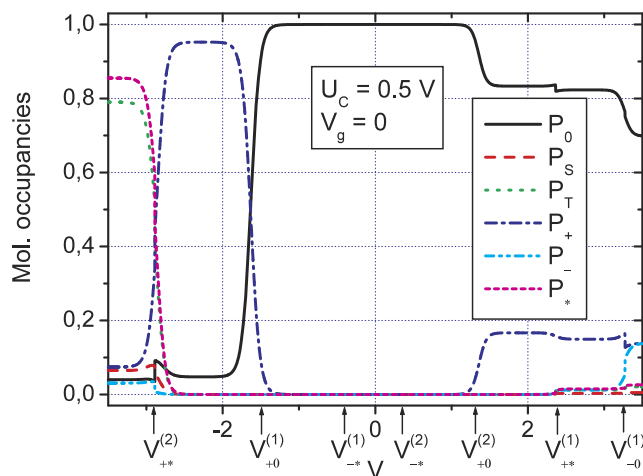

FIG. 6. Dependence of occupancies of states of AR-type molecules on bias voltage V in the absence of gate voltage ($V_g = 0$). The critical voltages, Eq. (53), indicate those values of $V = V_{\alpha j}^{(r)}$ in the vicinity of which there is an abrupt change in the populations P_+, P_-, P_0, and $P_* = P_S + P_T$. No changes are observed at $V_{-*}^{(1)} \leq V \leq V_{-*}^{(2)}$ since in this voltage range, the populations P_- and P_* are negligible. The magnitude of the exchange interaction is small ($J_{HL} \approx 0$), and therefore, changes in the values of P_S and P_T, as well as their total occupancy P_*, occur at the same value of V. Parameters used in calculations: $\Gamma_L^{(2)} = \Gamma_H^{(1)} \equiv \Gamma = 10^{-5}$ eV; $\Gamma_H^{(1)} = \Gamma_L^{(2)} \equiv \Gamma' = 10^{-6}$ eV; $\epsilon_L = 1.3$ eV, $\epsilon_H = -0.7$ eV; $\eta_L = 0.55$, $\eta_H = 0.45$; $K_{ST}^{(i)} = K_{TS}^{(i)} = 3 \times 10^6$ s^{-1}, $K_{T0}^{(i)} = 3 \times 10^3$ s^{-1}, $K_{S0}^{(i)} = k_{rad} = 3 \times 10^9$ s^{-1}, $K_{0S}^{(i)} = K_{0T}^{(i)} = 0$; and $T = 100$ K.

the qualitative behavior of the populations of the molecular states involved in the kinetics of EL formation.

The asymmetry of the kinetics of electron transfer between the molecule and each of the electrodes is notably manifested in the formation of those electronic configurations in the molecule for which the HOMO and LUMO levels are in resonance with the filled or free levels of the conduction bands of the electrodes. For definiteness, we are discussing a situation where

$$\Gamma_H^{(1)} = \Gamma_L^{(2)} \equiv \Gamma,$$

$$\Gamma_H^{(2)} = \Gamma_L^{(1)} \equiv \Gamma'(\ll \Gamma). \quad (56)$$

In accordance with the inequalities (56) (see also Fig. 5), we can say that among the four possible electronic configurations shown in Fig. 7(a), in the range $V_{+*}^{(2)} < V < V_{+0}^{(1)}$, the configuration with a positively charged molecule will be the most stable. However, if $V < V_{+*}^{(2)}$, Fig. 7(b), then the electronic configuration with an excited molecule becomes the most stable. In this case, the resonance mechanism of EL formation is turned on.

Thus, based only on the knowledge of the signs of transmission gaps and the relations between the parameters $\Gamma_\lambda^{(r)}$, it is possible to predict which molecular state can be realized in a specific voltage interval. In particular, if the electrode 1 is grounded and the inequality (56) holds, then the excited state $|S\rangle$, responsible for the appearance of EL, has the extreme population at $V < V_{+*}^{(2)}$. On the
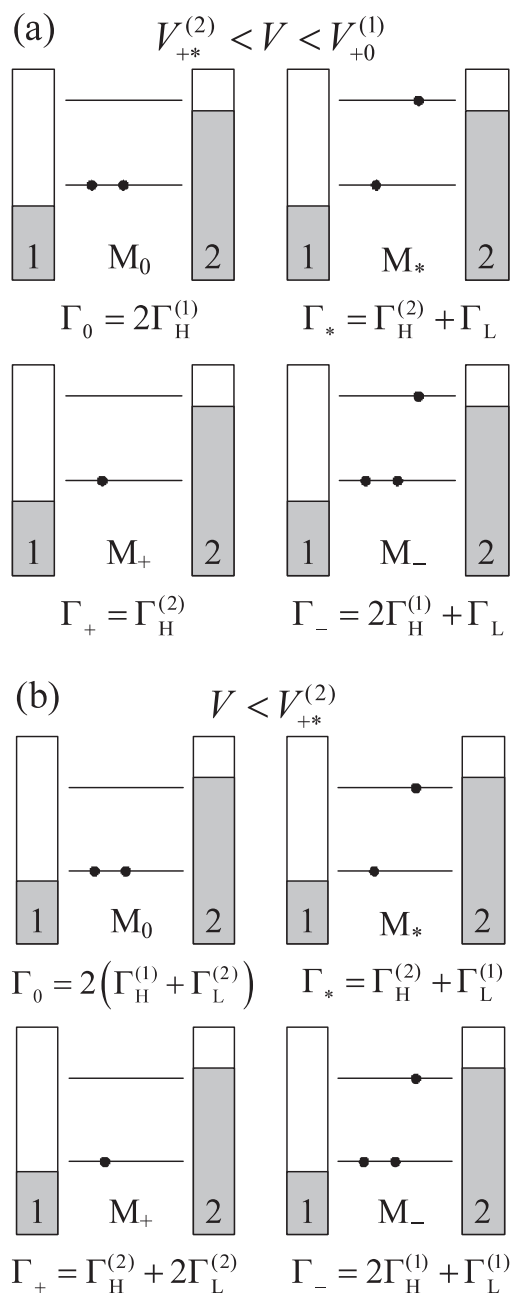
FIG. 7. Electronic configurations of a fluorophore molecule under conditions when the energy of the LUMO level exceeds the chemical potentials of both electrodes (a) or only one of the electrodes (b). Stable electron configurations correspond to a positively charged molecule, M_+, and an excited uncharged molecule, M_* [(a) and (b), respectively]. The broadening of molecular levels is shown when the corresponding molecular states participate virtually in the transfer of electrons through the molecule, $\Gamma_L = \Gamma_L^{(1)} + \Gamma_L^{(2)}$.

contrary, EL is practically not realized with positive polarity. We also note the minor occupancy of the state of a negatively charged molecule with both positive and negative polarities. This fact indicates that, in the voltage region under consideration, the Coulomb

interaction, characterized by the parameter U_c, has an insignificant effect on the population of molecular states. The calculations show a similar dependence of P_j and P_α on V, and there is a complete coincidence of the bias voltage at which an abrupt change in the populations occurs. This is clearly seen when comparing the behavior of the occupancies in Figs. 6 and 8, as well as critical voltages given in Table II.

Let us pay attention to another important result, which is due to the formation of broadening of the energy levels of virtual molecular states involved in a nonelastic electron transmission with the rates (47). We consider a situation when electrodes are fabricated from noble metals having wide conduction bands. Therefore, as is assumed in many works, the orbital broadening parameters $\Gamma_\lambda^{(r)}$, Eq. (42), can be considered as independent of V, V_g, and E. At the same time, the broadenings Γ_α, Eq. (49), of the molecular levels significantly depend on where the value of V is relative to $V_{\alpha j}^{(r)}$ (compare the widths of the molecular levels in Fig. 7).

C. Gate-tunable EL

We consider an example of photoactive asymmetric 1M2 junction where at $V_g = 0$ and chosen magnitude of parameters, the states of a negatively charged molecule have a minor effect on electron transmission, Fig. 9(b). However, the gate voltage is able to change the magnitude of stationary occupancies at a fixed bias voltage. This is clearly seen from the analysis of all panels represented in Fig. 9. For example, a large magnitude of the occupancy P_- appears at positive V_g even at small negative V. It is very important that the gate-tunable shift in the molecular energies can reduce the absolute value of critical voltage $V_{+*}^{(2)}$, at which the formation of the excited
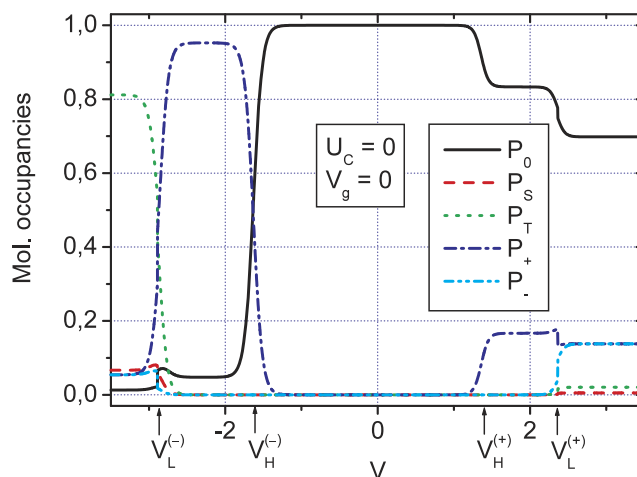

FIG. 8. Dependence of molecular occupancies on the bias voltage V for the same magnitudes of the parameters as those in Fig. 6, with the exception of U_c and V_g. Comparison with Fig. 6 shows that with the same offsets ϵ_L and ϵ_H, Eq. (54), the following coincidence of critical voltages takes place: $V_{+*}^{(2)} = V_L^{(-)}$, $V_{+0}^{(1)} = V_H^{(-)}$, $V_{+0}^{(2)} = V_H^{(+)}$, and $V_{+*}^{(1)} = V_L^{(+)}$. This means that in the region under consideration V, the Coulomb interaction associated with the parameter U_c has an insignificant effect on the dependence of molecular occupancies on a bias voltage. Parameters of calculations are the same as those in Fig. 6, except U_c and V_g.

TABLE II. Numerical values (in eV) of critical voltages (C.V.) at zero gate voltage and $\epsilon_L = 1.3$ eV, $\epsilon_H = -0.7$ eV, Eq. (54).

C.V.	$U_c = 0.5$	$U_c = 0$	C.V.
$V^{(2)}_{-0}$	−4.00		
$V^{(2)}_{+*}$	−2.89	−2.89	$V^{(-)}_L$
$V^{(1)}_{+0}$	−1.56	−1.56	$V^{(-)}_H$
$V^{(1)}_{-*}$	−0.44		
$V^{(2)}_{-*}$	0.36		
$V^{(2)}_{+0}$	1.27	1.27	$V^{(+)}_H$
$V^{(1)}_{+*}$	2.36	2.36	$V^{(+)}_L$
$V^{(1)}_{-0}$	3.27		

singlet molecular state starts. The occupancies are connected by normalization condition (39), and therefore, an increase/decrease in the occupancy of one state is reflected on the occupancies of other states. The walls separate domains with different numerical values of one and the same value of P_j or P_α. At the same time, the lines $V = V^{(r)}_{j\alpha}$ along the walls divide the concrete pair of occupancies P_j and P_α.

A comparison of Figs. 9(b)–9(d) shows that, for $V_g \neq 0$, there are ranges of V and V_g values in which both positively and negatively charged molecules can participate in the formation of excited singlet and triplet states and, thus, in the appearance of EL. Moreover, at $V_g \neq 0$, the formation of an excited singlet state can occur at lower absolute values of the bias voltage V. This is due to the fact that the gate voltage shifting the orbital energies ε_λ, Eq. (32), relative to the position of chemical potentials μ_r, Eq. (31), adjusts the molecular levels so that the corresponding transmission gaps (53) change their sign from positive to negative at lower absolute values of V.

As follows from the comparison of Figs. 6 and 8, as well as the data in Table II, in the absence of a gate voltage, the appearance of an excited state of the molecule and, thus, the generation of EL occurs at $V \geq V^{(+)}_L$ and $V \leq V^{(-)}_L$. The gate voltage leads to a shift of critical potentials to a higher or a lower side. Our theory shows that there are certain values of $V^{(+)}_g$ and $V^{(-)}_g$, when EL generation begins to occur at lower absolute values of V, i.e., at $V \leq V^*_+$ (positive polarity) and $V \geq V^*_-$ (negative polarity). The gate voltages $V^{(\alpha)}_g$ are found from the condition $V^{(\alpha)}_H = V^{(\alpha)}_L$, where $V^{(+)}_H = V^{(2)}_{+0}$, $V^{(+)}_L = V^{(1)}_{+*}$, $V^{(-)}_H = V^{(1)}_{+0}$, and $V^{(-)}_L = V^{(2)}_{+*}$. According to (53), this yields
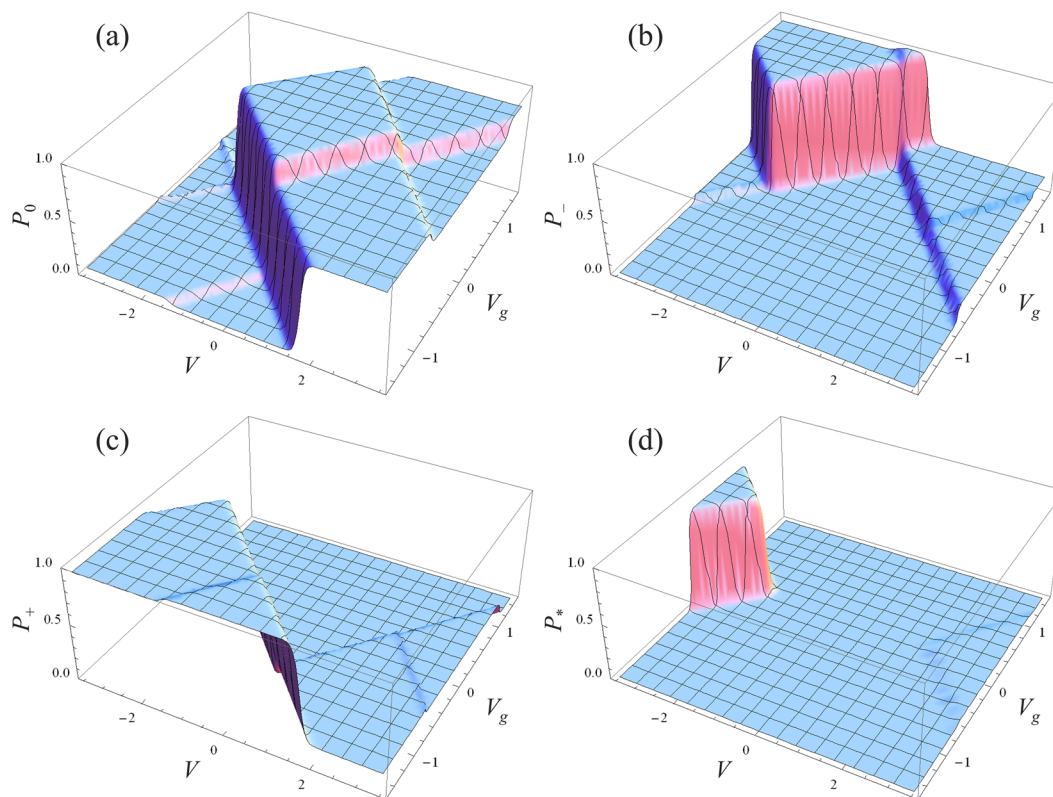
FIG. 9. The behavior of stationary molecular occupancies P_0, P_-, P_+, and $P_* = P_S + P_T$ under the influence of the bias and the gate voltages [(a)–(d), respectively]. The walls separating the populations follow the lines $V = V^{(r)}_{\alpha j}$. Parameters of calculations are the same as those in Fig. 6, with the exception $U_c = 0$.

$$V_g^{(+)} = \frac{\epsilon_L(1 - \eta_H) + \epsilon_H \eta_L}{|e|(1 + \eta_L - \eta_H)},$$

$$V_g^{(-)} = \frac{\epsilon_L \eta_H + \epsilon_H(1 - \eta_L)}{|e|(1 + \eta_H - \eta_L)}. \tag{57}$$

$V_g^{(+)}$ is positive if $(1 - \eta_H)/\eta_L > |\epsilon_H|/\epsilon_L$, and $V_g^{(-)}$ is negative if $\eta_H/(1 - \eta_L) < |\epsilon_H|/\epsilon_L$. With the same arrangement of the "centers of gravity" of the electron densities relative to electrode 1 (cf. Fig. 5), i.e., at $\eta_L = \eta_H \equiv \eta$, we get $V_g^{(+)} > 0$ if $\epsilon_L/\Delta E_{LH} > \eta$ and $V_g^{(-)} < 0$ if $|\epsilon_H|/\Delta E_{LH} > \eta$, where ΔE_{LH} is the LUMO–HOMO gap, Eq. (55). As an example, consider a particular case when $\eta_H = 1 - \eta_L$. Then, $V_g^{(-)} = V_g^{(+)} = (\epsilon_L + \epsilon_H)/2|e|$. With the parameters that we use, this yields $V_g^{(-)} = V_g^{(+)} = 0.30$ V, and accordingly, $V_+^* = 1.82$ V and $V_-^* = -2.22$ V. Figure 10 shows that it is precisely at these lowest (in absolute values) bias voltages that spontaneous light emission can appear in the 1M2 system under consideration.

The rates of non-radiative $M_S \rightarrow M_0$ and $M_T \rightarrow M_0$ transitions caused by the interaction of a molecule with electrodes are equal. In the regions $V \geq V_{-0}^{(1)}$ and $V < V_{-0}^{(2)}$, where EL is acceptable, Eq. (47), and the inequality $\Gamma \gg \Gamma'$, Eq. (56), yield $K_{S\rightarrow0}^{(ine)} = K_{T\rightarrow0}^{(ine)} \equiv k_{nrad}$. The rate k_{nrad} is $2\Gamma/\hbar$ and $(\Gamma')^2/\Gamma\hbar$ with positive and negative polarities, respectively. Despite the identity of non-radiative rates $K_{S\rightarrow0}^{(ine)}$ and $K_{T\rightarrow0}^{(ine)}$, the stationary occupancy of the triplet state P_T is much higher than the stationary occupancy of the singlet state P_S. This is explained by the fact that the rate of the radiative transition $K_{S\rightarrow0}^{(rad)}$ = k_{rad}, Eq. (36), strongly exceeds the rate $K_{T\rightarrow0}^{(rad)}$ of magnetic dipole transition. Thus, the triplet state is kinetically enriched in the process of EL formation. This important circumstance should be taken into account when analyzing experimental data on EL in 1M2 junctions even with a weak exchange interaction between the donor and acceptor centers of a photoactive molecule.
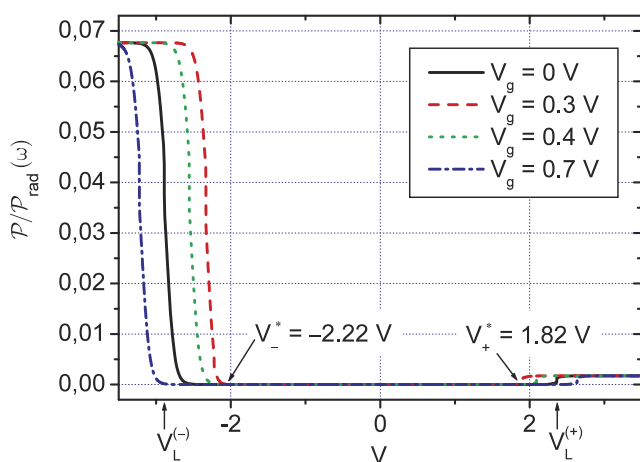

FIG. 10. The dependence of the spontaneous emission power of a molecule in the photoactive molecular junction 1M2, Eq. (50), for various magnitudes of the gate voltage. By changing V_g, suppression or stepwise rise of EL is achieved at a fixed value of V. The voltages V_-^* and V_+^* correspond to the lowest in the absolute values of V at which EL begins to appear [compare with Fig. 9(d)]. Parameters of calculations are the same as those in Fig. 6, with the exception of V_g.

The role of the gate tuning is clearly seen from a comparison of the electronic configurations presented in Fig. 7. In the bias voltage region $V_{+*}^{(2)} < V < V_{+0}^{(1)}$, the LUMO level is above the Fermi level of electrode 2 [Fig. 7(a)]. The gate voltage shifts the LUMO and HOMO levels down so that, at a certain value of V_g, the LUMO level becomes lower than the Fermi level of electrode 2 and, thus, is able to receive an electron from this electrode. If, in this case, the HOMO level remains in energy higher than the Fermi level of electrode 1, then due to inequality (56), the electronic configuration with an excited molecule becomes more stable among other configurations. Thus, the gate voltage contributes to the resonant inclusion of EL. This is a new important mechanism for the tuning and control of EL.

V. CONCLUSION

This work is devoted to elucidating the role of the bias voltage and the gate voltage in the formation and regulation of EL in asymmetric molecules of the Aviram–Ratner (AR)-type, where the D and A centers are linked by saturated σ-bonds.[5] D–σ–A molecules have good rectification properties.[51] At the same time, no studies of the optoelectronic properties of AR-type molecules have been published. Our theoretical results show that the asymmetry of the 1M2 system, where the AR molecule acts as a fluorophore, leads to a number of EL features. In order to study the physics of EL formation, in Sec. III, the kinetic approach developed for studying electron transport processes in many-body systems (Sec. II) is adapted to study electron transmission in a 1M2 system. To obtain analytical expressions for the transition rates that determine the kinetics of EL formation, we used a fluorophore model with five active states (the ground and two excited states of a neutral molecule, as well as states of a positively and a negatively charged molecule[35,37,44,46]). Such an analytical treatment model can serve as an important step in understanding the physical processes in the devices based on individual organic molecules.

The results that are important for understanding the processes of formation and control of EL include the following. We showed how kinetic processes in the 1M2 system regulate ET (electron transfer) power through occupation of the singlet state. The transmission of an electron through the molecule, on one hand, leads to an increase in the occupation of the singlet (and triplet) state and, on the other hand, generates non-radiative quenching processes. In addition, the spontaneous emission process itself contributes to a decrease in the occupation of the singlet state. The kinetic equations (38) presented here allow us to take into account these and other processes through the corresponding rates and, thereby, to describe the dependence of the EL power on the magnitude and polarity of the bias potentials as well as gate potential (see P_S behavior in Figs. 6 and 8–10).

If the $|\mu_1 - \mu_2|$ energy is enough to excite the molecule, but there is no resonant transfer of electrons between the molecule and the electrodes, the gate voltage is able to shift the orbital energy in such a way that the resonance regime of electron transmission becomes possible. This regime is the basis for the occurrence of EL. We have shown how, even under conditions of resonant electron transmission, an asymmetric coupling of molecular orbitals to electrodes leads to a pronounced EL polarity. Thus, the property of the gate voltage to tune the electron transfer regime in the

photoactive molecular junction can be used to trigger EL or to cancel EL, which is an important physical controlling factor. This is a quite new result that reveals the physics of optoelectronic processes in photoactive molecules, especially in asymmetric AR-type molecules.

APPENDIX: TRANSITION RATES

To get analytical expressions for the rates that determine the kinetic equations (10), we will follow the approach used in the papers[12,35,47,56]. It is assumed that, as in mesoscopy, the electron-transport process in the 1M2 junction does not notably change the electron distribution in the conduction bands of the electrodes. Therefore, on the right-hand side of Eq. (9), which is valid for $t \gg \tau_{rel}$, the occupancy $P(a; t)$ of the many-body state $|a\rangle$ contains the product of time-independent one-particle occupancies $P(n_{\mathbf{q}\xi}; t \gg \tau_{rel}) \equiv P(n_{\mathbf{q}\xi})$ and $P(N_{r\mathbf{k}\sigma}; t \gg \tau_{rel}) \equiv P(N_{r\mathbf{k}\sigma})$. The latter coincide with the Fermi distribution functions, i.e., $P(1_{r\mathbf{k}\sigma}) \simeq f_r(E_{r\mathbf{k}})$ and $P(0_{r\mathbf{k}\sigma}) \simeq 1 - f_r(E_{r\mathbf{k}})$. Molecular occupancies and one-particle occupancies satisfy the normalization conditions $\sum_{M(N)} P(M(N); t) = 1$, $\sum_{n_s=0}^{\infty} P(n_s) = 1$ ($s \equiv \mathbf{q}\xi$), and $\sum_{N_\nu=0,1} P(N_\nu) = 1$ ($\nu \equiv r\mathbf{k}\sigma$), respectively. Using the definition $P(M(N), t) = \sum_{\mathcal{N},n} P(a, t)$, where $\mathcal{N} = \{N_{r\mathbf{k}\sigma}\}$ and $n = \{n_{\mathbf{q}\xi}\}$ are complete sets of the corresponding quantum numbers, we obtain from the system of Eq. (9) a system of Eq. (10), where

$$
\begin{aligned}
\mathcal{K}_{M(N)\to M'(N')} = \frac{2\pi}{\hbar} \sum_{\mathcal{N}',n'} \sum_{\mathcal{N},n} \prod_s P(n_s) \prod_\nu P(N_\nu) \\
\times \left| \langle M'(N'); \mathcal{N}', n' | \hat{T} | M(N); \mathcal{N}, n \rangle \right|^2 \delta \\
\times \left[E_{M(N)} - E_{M'(N')} + \sum_\nu E_\nu (N_\nu - N'_\nu) \right. \\
\left. + \sum_s \hbar\omega_q (n_s - n'_s) \right].
\end{aligned}
\tag{A1}
$$

In the 1M2 system under consideration, the operator for transitions on the energy shell $E = E_{M(N)} + \sum_\nu E_\nu N_\nu + \sum_s \hbar\omega_s n_s = E_{M'(N')} + \sum_\nu E_\nu N'_\nu + \sum_s \hbar\omega_s n'_s$ appears as $\hat{T} = H' + H'G(E)H'$, where $G(E) = [E - (H_0 + H') + i0^+]^{-1}$ is the Green operator [H_0 is the Hamiltonian (1) and $H' = V_{m-e} + V_{m-f}$]. The $\hat{T}$ operator is convenient for getting the transition rates with the desired precision. Since the interactions V_{m-e} and V_{m-f} are perturbations, we consider the contribution to the kinetics of the main types of transition rates caused by these perturbations.

In the Born approximation, for which $|\langle a'|\hat{T}|a\rangle|^2 \approx |\langle a'|H'|a\rangle|^2$, the expression for molecular charging rates follows from Eq. (A1) if in the H' only the interaction V_{m-e}, Eq. (5), is used. The fact is also taken into consideration that the number of photons of each mode

$s = \mathbf{q}\xi$ does not change, i.e., $n'_s = n_s$. Similarly, to get an expression for the radiation rate, it suffices to use the interaction V_{m-f}, Eq. (7), and take into account the fact that in the Born approximation, the electrons belonging to the electrodes do not participate in the radiation $M(N) \to M'(N)$ transition, i.e., $N'_\nu = N_\nu$ for any $\nu = r\mathbf{k}\sigma$. As a result, we obtain from Eq. (A1) the following expression for the rate of light emission:

$$
K_{M(N)\to M'(N)}^{(emission)} = \sum_s (1 + \bar{n}_s) K_s(M(N) \to M'(N)),
\tag{A2}
$$

where $\bar{n}_s = \sum_{n_s=0}^{\infty} n_s P(n_s)$ is the average number of photons of the mode $s = \mathbf{q}\xi$. In the case of spontaneous emission, when $\bar{n}_s = 0$, we obtain Eq. (17).

Interaction V_{m-e} can lead to a photonless intramolecular $M(N) \to M'(N)$ transition. The corresponding rate is obtained from Eq. (A1) if for $V_{m-f} = 0$ the term $H'G(E)H'$ is used in the $\hat{T}$ operator. This leads to Eq. (20), where

$$
\begin{aligned}
K_{rM\to r'M'} = \frac{2\pi}{\hbar} \sum_{\mathbf{k}\sigma} \sum_{\mathbf{k}'\sigma'} f_r(E_{r\mathbf{k}}) \left[1 - f_{r'}(E_{r'\mathbf{k}'}) \right] \\
\times \left| \langle 0_{r\mathbf{k}\sigma}, M'1_{r'\mathbf{k}'\sigma'} | V_{m-e} G(\epsilon) V_{m-e} | 1_{r\mathbf{k}\sigma}, M0_{r'\mathbf{k}'\sigma'} \rangle \right|^2 \\
\times \delta [E_{r\mathbf{k}} + E_{M(N)} - E_{r'\mathbf{k}'} - E_{M'(N)}].
\end{aligned}
\tag{A3}
$$

Here, $G(\epsilon) = [\epsilon - (H_e + H_m^{(eff)})]^{-1}$ is the Green operator with $\epsilon = E_{r\mathbf{k}} + E_{M(N)} = E_{r'\mathbf{k}'} + E_{M'(N)}$ and $H_m^{(eff)} = H_m + \hat{\Sigma}$. As the V_{e-m} is considered as the perturbation, then only diagonal elements of the self-energy operator, $\Sigma_{MM} = \langle M(N)|\hat{\Sigma}|M(N)\rangle$, give the main contribution in the effective Hamiltonian of the molecule. Thus, one can put $H_m^{(eff)} \approx \sum_{M(N)} (E_{M(N)} - (i/2)\Gamma_{M(N)}) |M(N)\rangle\langle M(N)|$, where the broadening $\Gamma_{M(N)}/2 = \text{Im}\Sigma_{MM}$ is defined through Eqs. (15) and (22). With the introduction of the values $\Gamma_{M(N)}$ and $\Gamma_{M(N)\to M'(N\pm1)}^{(r)}$, the expression (A3) can be rewritten in the form

$$
\begin{aligned}
\mathcal{K}_{rM(N)\to r'M'(N)} \\
= \frac{1}{2\pi\hbar} \int_{-\infty}^{+\infty} dE f_r(E - X_{MM'}^{(-)}) \left[1 - f_{r'}(E + X_{MM'}^{(-)}) \right] \\
\times \sum_{\bar{M}} \left[\frac{\Gamma_{M(N)\to\bar{M}(N+1)}^{(r)} \Gamma_{\bar{M}(N+1)\to M'(N)}^{(r')}}{(E + X_{MM'}^{(+)} - E_{\bar{M}(N+1)})^2 + (\Gamma_{\bar{M}}(N+1)/2)^2} \right. \\
\left. + \frac{\Gamma_{M(N)\to\bar{M}(N-1)}^{(r')} \Gamma_{\bar{M}(N-1)\to M'(N)}^{(r)}}{(E - X_{MM'}^{(+)} + E_{\bar{M}(N-1)})^2 + (\Gamma_{\bar{M}(N-1)}/2)^2} \right],
\end{aligned}
\tag{A4}
$$

where $X_{MM'}^{(\pm)} \equiv [E_{M(N)} \pm E_{M'(N)}]/2$. Note now that a notable difference between the Fermi function $f_r(\epsilon)$ and the Heaviside step function $\Theta(\mu_r - \epsilon)$ takes place only in the vicinity of $\epsilon = \mu_r$ of width $k_B T$. Following the results of Ref. 62, we can infer that if the offset $|\mu_r - \epsilon|$ exceeds $k_B T$ by more than one order of magnitude, then to calculate the integral, replacing $f_r(\epsilon)$ with $\Theta(\mu_r - \epsilon)$ is reasonable. Taking this into account, we will replace the integration interval $[-\infty, +\infty]$ by $[\mu_r + X_{MM'}^{(-)}, \mu_{r'} - X_{MM'}^{(-)}]$. In the wide-band limit, which is often used for the estimations, quantities Γ are independent of the integration variable E. This allows us to calculate the integral and get the expression (21), which works well if $|\Delta E_{M(N)M(N\pm1)}^{(r)}|/k_B T > 5$.

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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