
PHOTOINDUCED CURRENT THROUGH A SINGLE MOLECULE

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UDC 530.1,537.37, 621.382
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We propose a kinetic model of formation of the photoinduced current through a single organic molecule placed between two metal electrodes. An analytical expression for the combined thermally activated inelastic and distant elastic interelectrode currents with participation of the neutral, charged, and photoexcited states of the molecule is found. The obtained expression is used for the analysis of a behavior of the current and the differential conductivity of the molecule depending on the potential difference applied to the electrodes, as well as on the frequency of the external electromagnetic radiation. We discovered a photostimulated effect of switching between the conducting and low-conducting states of the molecule accompanied by the variation of its conductivity by an order of magnitude.

1. Introduction

The possibility of experimental investigations of conducting properties of separate organic molecules placed between two metal electrodes has opened new prospects for the following minimization of electronic circuit components based on the use of soft-body element basis [1–3]. For today, there have been synthesized a number of molecular compounds with specified characteristics able to play a role of conductors [4], diodes [5, 6], molecular switches [7, 8], transistors [9], and logic and memory units [10, 11]. In this case, the conducting properties of such structures are controlled with the help of both external constant electric fields applied to metal contacts and alternating electromagnetic fields, namely by means of additional irradiation of the “metal–molecule–metal” (MMM) system. This irradiation can result in essential changes of the geometry and electron configuration of a photosensitive compound, which induces, in

turn, variations of the conducting properties of a molecule [12]. Recent experimental investigations of thin layers of protein molecules have demonstrated that the influence of electromagnetic radiation in the optical frequency range can result not only in the improvement of the conductivity of MMM structures but also in the appearance of switching effects between the conducting and nonconducting states of a molecule [13, 14]. Moreover, a number of molecules display pronounced diode properties [15–17], where the density of unidirectional photoinduced current depends on the potential difference applied to the electrodes, which was observed in the course of investigations of derivatives of a cytochrome molecule *c* [17, 18]. When studying the conducting properties of a pair of α -spiral peptides with different directions of the dipole moment simultaneously located on a metal substrate, it was shown that a direction of the photoinduced current could be changed by choosing the wavelength of the external electromagnetic radiation [19]. The generation of the switching effect directly depends on the orientation of the dipole moment of each compound of the pair, which results in the acceleration of the electron transfer in a specified direction. Similar experimental results were obtained studying the photoconducting properties of self-organizing layers of ruthenium-viologen compounds [20].

Theoretical investigations of the photoconductivity of organic molecules are mainly based on the use of two approaches. The first one consists in the application of the method of nonequilibrium Green function (NGF) together with the density-functional method applied to the calculation of the electron structure of a MMM system. The adaptation of the NGF method to the

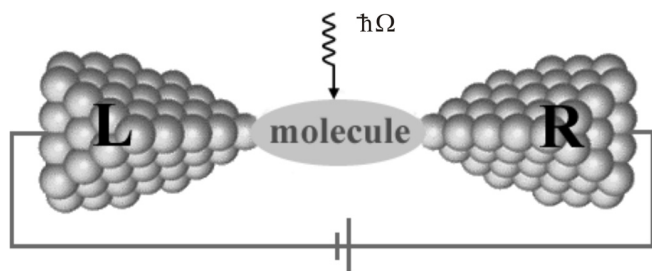


Fig. 1. Molecule placed between two metal electrodes L and R subjected to the potential difference V

calculation of the optical properties of MMM-like structures is presented in [21, 22]. For example, investigating an azobenzene molecule placed between two metal microcontacts by means of the NGF method [23], it was shown that the external photoexcitation allows one to switch between the conducting and nonconducting states of the MMM system. In this case, there can appear two different electron configurations of the molecule, the switching between which is performed by means of a monochromatic electromagnetic wave of a specified frequency. Studies of the photoconductive properties of an anthracene molecule [24] demonstrated that ultraviolet monochromatic light could turn two monomers of the molecule into a dimer. Varying the light frequency, one can realize the inverse process. Calculations have demonstrated that the electroconductivity of a monomer exceeds that of a dimer by several orders of magnitude, which testifies to the practical possibility for the use of an anthracene molecule as a molecular switch.

Another approach to the study of the effect of electromagnetic radiation on the conducting properties of separate molecules consists in the development of quantum-mechanical models that adequately describe photoinduced electron-transport processes in a system. A number of models is based on the application of the Floquet formalism [25, 26] that was earlier used for the description of a behavior of atoms and molecules in strongly oscillating fields and later on was applied (together with many-particle approaches) to the study of electron-transport processes in molecular systems interacting with metal contacts [27, 28].

One more alternative and powerful approach to the description of transport processes in molecular nanostructures controlled by external constant and alternating fields is the method of nonequilibrium density matrix (NDM). This method allowed one to describe the electron-transport processes controlled by external periodic and stochastic fields both in model

systems and in donor-acceptor complexes [29–31]. It was also used for the investigation of the conductivity of separate organic molecules [32, 33] placed between two metal electrodes, as well as for obtaining the expressions for stationary interelectrode currents through molecular wires [34, 35]. The NDM method also served as a basis of the model used to obtain the elastic current through a molecular wire in the case of the external influence of laser radiation on the system [36]. The authors have demonstrated theoretically that the action of a laser pulse can result in the switching between the conducting and nonconducting states of the wire.

In the given work, we apply the NDM method to the study of the formation of the combined thermally activated inelastic and distant elastic photoinduced currents through a separate molecule in the ground, photoexcited, and singly charged states. The main attention will be paid to obtaining the analytical expression for the interelectrode current, as well as to the investigation of the effect of external electromagnetic radiation on the conductivity of the molecule. In particular, we will find the conditions, under which electromagnetic radiation causes the appearance of the effect of switching between the conducting and nonconducting states of the molecule.

2. Effective Hamiltonian of the System

In order to study the mechanisms of formation of a photoinduced current, let us consider a model system consisting of two metal contacts L and R and a molecule placed between them (Fig. 1). Let us assume that the system is exposed to the action of electromagnetic radiation with frequency Ω . The metal electrodes will be considered as macroscopic systems with a quasicontinuous spectrum, whose energies can be disturbed by neither the molecule nor the external radiation.

In the framework of the model, the electron is transmitted between three electron states of the (LMR) (left electrode – molecule – right electrode) system. In the ground state, the transported electron is on one of the electrodes, while the molecule is in the neutral state $|M_0\rangle$. In the $|M^-\rangle$ state, the transported electron is on the molecule, i.e. the molecule is charged and contains one excess electron. The $|M^{-*}\rangle$ state corresponds to the molecule in the photoexcited state, where it goes from the charged one under the action of electromagnetic radiation. In this case, the excess electron appears at a higher molecular orbital.

The Hamiltonian of the LMR system can be presented in the following form:

$$H_{\text{LMR}}(t) = H_{\text{leads}} + H_{\text{mol}} + V_{\text{leads-mol}} + V_{\text{int}}(t), \quad (1)$$

where the first term

$$H_{\text{leads}} = \sum_{r=L,R} \sum_{k,\sigma} E_{rk} |rk\sigma\rangle \langle rk\sigma| \quad (2)$$

represents the Hamiltonian of the electrodes (E_{rk} is the energy of the electron with the wave vector k in the conduction band of the r -th electrode; $|rk\sigma\rangle$ corresponds to the electron state with the spin projection σ).

The second term in formula (1) is the Hamiltonian of the molecule consisting of the purely electron part, the Hamiltonian of the thermostat, and the operator of electron-vibrational interaction of the molecule with its environment, i.e.

$$H_{\text{mol}} = H_{\text{mol}}^{(\text{el})} + H_{\text{vib}} + V_{\text{el-vib}}. \quad (3)$$

The electron part of the Hamiltonian of the molecule reads

$$H_{\text{mol}} = \sum_n E_n(V) |n\rangle \langle n|, \quad (4)$$

where $E_n(V)$ is the electron energy of the molecule in the neutral ($n = M_0$), charged ($n = M^-$), and photoexcited ($n = M^{-*}$) states.

It is worth noting that, in the case of the potential difference V applied to the electrodes, there takes place a shift of the electron energy levels according to the linear law

$$E_{M^-}(V) = E_{M^-}(0) - eV\eta_{M^-},$$

$$E_{M^{-*}}(V) = E_{M^{-*}}(0) - eV\eta_{M^{-*}}, \quad (5)$$

where $E_{M^-(M^{-*})}(0)$ are the electron energies of the molecule undisturbed by the electric field in the charged and photoexcited states, correspondingly, whereas $\eta_{M^-(M^{-*})}$ denote the factors that determine a linear shift of the corresponding electron levels of the molecule under the action of the potential difference V applied to the electrodes.

In the presented model, the electron states of the molecule are related to its vibrational states by means of the electron-vibrational interaction. Restricting ourselves to the standard harmonic approximation, we present the Hamiltonian of the oscillations of nuclei (the Hamiltonian of the thermostat) and the operator of the electron-vibrational interaction in the form

$$H_{\text{vib}} = \sum_{\lambda} \hbar\omega_{\lambda} \left(b_{\lambda}^{\dagger} b_{\lambda} + \frac{1}{2} \right), \quad (6)$$

$$V_{\text{el-vib}} = \sum_{n,\sigma} \sum_{\lambda} \hbar\chi_{n\lambda} (b_{\lambda}^{\dagger} + b_{\lambda}) |n\rangle \langle n|, \quad (7)$$

where ω_{λ} is the frequency of the λ -th normal vibrational mode, b_{λ}^{\dagger} and b_{λ} are the operators of production and destruction of the λ -th vibration, correspondingly, and $\chi_{n\lambda}$ is the constant of the electron-phonon coupling in the n -th electron state of the molecule.

The influence of an external electromagnetic field on the molecule is presented by the last term of Hamiltonian (1). In the dipole approximation, the corresponding interaction operator has form $V_{\text{int}}(t) = -\hat{\mu} \mathbf{E}_0 \cos \Omega t$, where $\hat{\mu}$ stands for the dipole moment operator, while \mathbf{E}_0 is the vector of the field intensity. It is worth noting that the point dimensions of molecules amount to several nanometers, which is much less than the wavelength of electromagnetic radiation in the case where its frequency does not exceed 10^{18} Hz. At such frequencies, the spatial variation of electric and magnetic fields at a distance of the order of molecule dimensions is very weak, which allows one to consider the molecule as a point dipole.

Thus, in the one-dimensional case and the occupation-number representation, the operator of interaction of the field with the molecule with regard for its charged and photoexcited states can be presented in the following way:

$$V_{\text{int}} = \sum_{\sigma} (V_{M^-M^{-*}} \cos \Omega t |M^- \rangle \langle M^{-*}| +$$

$$+ V_{M^{-*}M^-}^* \cos \Omega t |M^{-*} \rangle \langle M^-|). \quad (8)$$

In formula (8), $V_{M^-,M^{-*}} \equiv |\mathbf{E}_0| \langle M^- | \hat{\mu} | M^{-*} \rangle$ is the matrix element of the photoinduced transition between two states of the molecule $|M^- \rangle$ and $|M^{-*} \rangle$.

3. Kinetics of the Current Formation in the LMR System

In our model, each of the states of the LMR system is characterized by the probability of its realization (population), which we denote by $P(M_0, t)$, $P(M^-, t)$, and $P(M^{-*}, t)$. Moreover, the current in the system is formed due to the competition of various electron-transport processes. Such processes run both at the electrode-molecule interface (with direct $\chi_{L(R)n}$ and inverse $\chi_{-L(-R)n}$ ($n = M^-, M^{-*}$) interelectrode transport rates) and inside the molecule between its

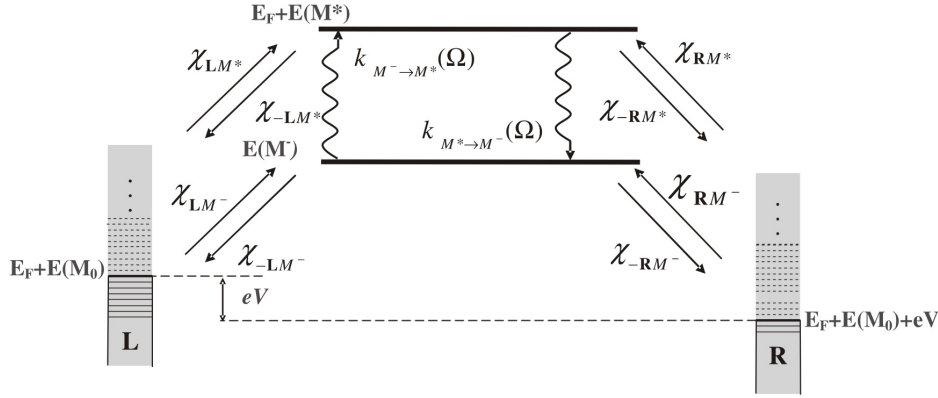


Fig. 2. Kinetic scheme of the formation of a photoinduced current through a molecule placed between two metal electrodes L and R . $E(M_0)$, $E(M^-)$, and $E(M^*)$ are the energies of the molecule in the neutral, charged, and photoexcited states, correspondingly

charged and photoexcited states (with effective direct $k_{M^- \to M^*} = k_{M^- \to M^*}(\Omega)$ and inverse $k_{M^* \to M^-} = k_{M^* \to M^-}(\Omega)$ rates) (Fig. 2). In addition, there takes place the distant tunneling of the electron from one electrode to the other, which results in the formation of the elastic mechanism of charge transfer in the LMR system [32, 33].

In order to derive relations for the nonstationary interelectrode currents, we use the general expressions

$$I_{L \to R}(t) = -e\dot{N}_L(t), \quad I_{R \to L}(t) = e\dot{N}_R(t), \quad (9)$$

where $e > 0$ stands for the absolute value of the electron charge, $\dot{N}_L(t)$ represents the evolution of the number of free electrons with specified spin projection able to pass from the left electrode to the right one through the molecule, whereas $\dot{N}_R(t)$ describes the inverse transmission process: from the right to the left. Each of these quantities is determined in terms of the probabilities $P(n, t)$, ($n = M_0, M^-, M^*$) of realization of the states in the LMR system.

In order to investigate the evolution of the quantum system based on the earlier developed approach [33], one can obtain a closed system of kinetic equations for each population of the states of the LMR system, as well as put down the expression for the evolution of the number of particles $\dot{N}_{L(R)}(t)$ and thus derive the current. In the case where the molecule interacts with the external periodic field with frequency Ω , the system takes the form

$$\dot{P}(M_0, t) = -2(B_{M^-} + B_{M^*})P(M_0, t) + A_{M^-}P(M^-, t) + A_{M^*}P(M^*, t),$$

$$\dot{P}(M^-, t) = -(A_{M^-} + k_{M^- \to M^*}(\Omega))P(M^-, t) +$$

$$+ B_{M^-}P(M_0, t) + k_{M^* \to M^-}(\Omega)P(M^*, t),$$

$$\dot{P}(M^*, t) = -(A_{M^*} + k_{M^* \to M^-}(\Omega))P(M^*, t) +$$

$$+ B_{M^*}P(M_0, t) + k_{M^- \to M^*}(\Omega)P(M^-, t), \quad (10)$$

where $A_n \equiv \chi_{-Ln} + \chi_{-Rn}$, $B_n \equiv \chi_{Ln} + \chi_{Rn}$ ($n = M^-, M^*$) characterize the direct and inverse transitions of the electron between the electrodes and each of the states of the molecule.

In order to solve the system of kinetic equations (10), it is necessary to specify the initial conditions of the system. Let us consider that, before the periodic electromagnetic field was turned on, the system was in the stationary state, so that $P(n, t = 0) = P_n^{(st)}$, where $n = M_0, M^-, M^*$. It is worth noting that $P_n^{(st)} = P_n^{(st)}(V)$ depends on the potential difference V applied to the microelectrodes and can be obtained from the solution of the system of stationary equations at all $\dot{P}(n, t) = 0$. That is why the kinetics of current formation can be studied either under the condition that the potential difference V was already applied to the metal electrodes at the moment of switching on of the external electromagnetic radiation or under the condition $V = 0$. A detailed investigation of the processes of switching on and off of currents through a separate molecule is presented in [37]. We will mainly concentrate on the study of the effect of electromagnetic radiation on the current formation and consider that the potential difference is applied simultaneously with the beginning of the action of the periodic field, so that

the initial conditions can be found from the solution of the system of stationary equations at $V = 0$, i.e. $P(n, t = 0) = P_n^{(st)}(V = 0) \equiv s_n$. Under such initial conditions, the solution of the system of nonstationary kinetic equations (10) takes the form

$$P(n, t) = C_0^{(n)} + \sum_{j=1}^2 C_j^{(n)} \exp[-K_j t], \quad (11)$$

where

$$C_0^{(n)} = F_1^{(n)}(0)/F_2(0),$$

$$C_j^{(n)} = F_1^{(n)} / (-K_j F_2'(p)|_{p=-K_j}), \quad (j = 1, 2), \quad (12)$$

$$K_{1,2} \equiv 1/2 [z_1 \pm \sqrt{z_1^2 - 4z_2}]. \quad (13)$$

Formulas (11) and (12) contain the following notations:

$$\begin{aligned} F_1^{(M_0)}(s) &= s_{M_0} s^2 + [s_{M_0} (A_{M^-} + A_{M^*} + k_{M^- \rightarrow M^*} + \\ &+ k_{M^* \rightarrow M^-}) + s_{M^-} A_{M^-} + s_{M^*} A_{M^*}] s + \\ &+ A_{M^-} A_{M^*} + A_{M^-} k_{M^- \rightarrow M^-} + A_{M^*} k_{M^* \rightarrow M^-}, \\ F_1^{(M^-)}(s) &= s_{M^-} s^2 + [2s_0 B_{M^-} + s_{M^-} (A_{M^*} + 2(B_{M^-} + \\ &+ B_{M^*}) + k_{M^* \rightarrow M^-}(\Omega)) + s_{M^*} k_{M^* \rightarrow M^-}(\Omega)] s + \\ &+ 2(A_{M^*} B_{M^-} + (B_{M^-} + B_{M^*}) k_{M^* \rightarrow M^-}(\Omega)), \\ F_1^{(M^*)}(s) &= s_{M^*} s^2 + [2s_0 B_{M^*} + s_{M^*} (A_{M^-} + \\ &+ 2(B_{M^-} + B_{M^*}) + s_{M^-} k_{M^- \rightarrow M^*}(\Omega) + \\ &+ k_{M^- \rightarrow M^*}(\Omega))] s + 2(A_{M^-} B_{M^*} + \\ &+ (B_{M^-} + B_{M^*}) k_{M^- \rightarrow M^*}(\Omega)), \\ F_2(s) &\equiv s^2 + z_1 s + z_2. \end{aligned} \quad (14)$$

In turn, $z_1 \equiv A_{M^-} + A_{M^*} + 2(B_{M^-} + B_{M^*}) + k_{M^- \rightarrow M^*}(\Omega) + k_{M^* \rightarrow M^-}(\Omega)$ та $z_2 \equiv A_{M^-} A_{M^*} + A_{M^-} k_{M^- \rightarrow M^-} + A_{M^*} k_{M^* \rightarrow M^-} + 2[A_{M^-} B_{M^*} + A_{M^*} B_{M^-} + (B_{M^-} + B_{M^*})(k_{M^- \rightarrow M^*} + k_{M^* \rightarrow M^-})]$.

Formulas (11)–(14) give a possibility to study the time evolution of the population of each state of the LMR system participating in the photoinduced electron-transport process (PETP), as well as allow one to derive an analytical expression for the nonstationary current through a molecule.

4. Photoinduced Current Through the Molecule

Nonstationary case

The problem of determination of the nonstationary interelectrode current substantially differs from the stationary problem which is first of all related to the fact that, during the time preceding the formation of the stationary current, the charge of the molecule can change and, therefore, the number of electrons escaping from one electrode can differ from that coming to the other one [37]. This testifies, in turn, to the necessity of a separate investigation of both the direct $L \rightarrow R$ and inverse $R \rightarrow L$ currents.

In the case of hopping transmission, the direct and inverse interelectrode currents through the molecule can be presented as follows:

$$\begin{aligned} I_{L \rightarrow R}^{\text{hop}}(t) &= I_0 2\pi \hbar [(\chi_{LM^-} + \chi_{LM^*}) P(M_0, t) + \\ &+ 1/2(\chi_{-LM^-} P(M^-, t) - \chi_{-LM^*} P(M^*, t))], \end{aligned} \quad (15)$$

$$\begin{aligned} I_{R \rightarrow L}^{\text{hop}}(t) &= -I_0 2\pi \hbar [(\chi_{RM^-} + \chi_{RM^*}) P(M_0, t) - \\ &- 1/2(\chi_{-RM^-} P(M^-, t) + \chi_{-RM^*} P(M^*, t))]. \end{aligned} \quad (16)$$

In formulas (15), (16), we introduced the quantity $I_0 \equiv |e|/\pi \hbar \approx 77.6 \mu\text{A}$, while the probabilities $P(n, t)$ are determined according to formula (11) together with relations (12)–(14).

In addition to inelastic electron transitions in the LMR system accompanied by the real population of the molecule, there occurs the direct distant tunneling of the electron between the electrodes with participation of the so-called virtual states of the molecule. Such a tunneling makes a contribution to the formation of the interelectrode current and can be determined in the framework of the single approach to the description of kinetic processes in the LMR system developed in [32, 33]. Based on these results, we put down the expressions for the direct and inverse distant elastic components of the current:

$$I_{L \rightarrow R}^{\text{dir}}(t) = I_0 2\pi \hbar \left(\sum_{n=M^-, M^*} Q_{L \rightarrow R}^{(i)} P(n, t) + \right.$$

$$+Q_{L \rightarrow R}^{(0)} P(M_0, t), \quad (17)$$

$$I_{R \rightarrow L}^{\text{dir}}(t) = -I_0 2\pi\hbar \left(\sum_{n=M^-, M^{*-}} Q_{R \rightarrow L}^{(i)} P(n, t) + Q_{R \rightarrow L}^{(0)} P(M_0, t) \right), \quad (18)$$

where $Q_{x \rightarrow y}^{(0)} = Q_{x \rightarrow y}^{(M^-)} + Q_{x \rightarrow y}^{(M^{*-})}$, while $Q_{L \rightarrow R}^{(n)}$ ($Q_{R \rightarrow L}^{(n)}$) represent the elastic electron currents from the left (right) electrode to the right (left) one; moreover, each of them depends on the charge state of the molecule $n = M^-, M^{*-}$. The direct interelectrode electron current is determined by the formula

$$Q_{L \rightarrow R}^{(n)} = \frac{1}{\pi\hbar} \frac{\Gamma_{Ln} \Gamma_{Rn}}{\Gamma_{Ln} + \Gamma_{Rn}} \left(\arctan \frac{2\Delta E_{Rn}(V)}{\Gamma_{Ln} + \Gamma_{Rn}} - \arctan \frac{2\Delta E_{Ln}(V)}{\Gamma_{Ln} + \Gamma_{Rn}} \right). \quad (19)$$

The inverse current $Q_{R \rightarrow L}^{(n)}$ can be obtained from formula (19) substituting the indices L for R and is related to the direct one as $Q_{R \rightarrow L}^{(n)} = -Q_{L \rightarrow R}^{(n)}$. It testifies to the fact that the tunneling electron current is formed in the case of a constant population of the molecule by an excess electron in each of its states participating in the electron-transport process [37]. However, it is worth noting that the tunneling component of the current (17), (18) depends on the charge state of the molecule due to the populations $P(n, t)$ that can be obtained from the solution of the system of kinetic equations (10).

In formula (19), $\Delta E_{Ln}(V)$ and $\Delta E_{Rn}(V)$ represent the energy gaps between the n -th electron level of the molecule and the Fermi level of the corresponding electrode, whereas Γ_{Ln} and Γ_{Rn} determine the broadening of the electron levels of the molecule in its charged $n = M^-$ and photoexcited $n = M^{*-}$ states caused by the presence of metal electrodes and the environment.

Thus, the total direct and inverse interelectrode currents through a molecule placed between two metal electrodes can be presented as the sum of the hopping and elastic components,

$$I_{L \rightarrow R}(t) = I_{L \rightarrow R}^{\text{hop}}(t) + I_{L \rightarrow R}^{\text{dir}}(t), \quad (20)$$

$$I_{R \rightarrow L}(t) = I_{R \rightarrow L}^{\text{hop}}(t) + I_{R \rightarrow L}^{\text{dir}}(t), \quad (21)$$

where the hopping component is calculated with the help of formulas (15), (16), while the elastic tunneling one is determined by (17), (18).

Stationary case

Formulas (20, 21) imply that, in the nonstationary case, $I_{L \rightarrow R}(t) \neq I_{R \rightarrow L}(t)$. The equality of the direct and inverse currents is observed only if the stationary mode is established in the system. In this case, $\dot{N}_{L \rightarrow R} = \dot{N}_{R \rightarrow L} = \text{const}$. It is worth noting that the formation of the stationary current takes place on the time scale $t \sim \tau_{\text{st}} \gg \tau_{\text{ET}}$, where τ_{st} is the characteristic time of reaching the stationary mode, and τ_{ET} is the time of the electron-transport process. Moreover, the approach to the description of kinetic processes in terms of the integral populations of each of the states of the system participating in the ET process supposes that the kinetic processes aimed at the establishment of the stationary mode take place on the time scale much exceeding the time of internal molecular relaxation τ_{rel} . The characteristic time of vibrational relaxation for the majority of molecular structures lies in the range $\tau_{\text{rel}} \sim 10^{-13} - 10^{-11}$ s [38]. That is why, in the framework of our model, we consider that $t \gg \tau_{\text{rel}}$, which in turn allows us to neglect the memory effects related to non-Markov processes in the system. One more approximation used in our model is related to the imposition of a certain constraint on the frequency Ω of the external periodic field acting on the LMR system. The characteristic times of electron-transport processes in the system τ_{ET} are of the order of nanoseconds and higher. That is why, in order to conserve the time linearity of system (10), it is necessary that the time scale of the ET process $t \sim \tau_{\text{ET}} \gg \Omega^{-1}$. In other words, a lot of oscillation periods of the electromagnetic field must pass before the probability of transition of the system from one state to another reaches a significant value [39]. Under such a condition, we can deal with field-average quantities. Taking into account the above-stated considerations, one can put down the system of linear kinetic equations (10) for the investigation of the PETP in the LMR system.

Thus, in the stationary case, the direct and inverse currents coincide. Allowing for the fact that now all $P(n, t) \equiv P_n^{(\text{st})} = \text{const}$ ($n = M_0, M^-, M^{*-}$), one can obtain the following expression for the hopping component of the stationary photoinduced interelectrode current through a molecule placed between two metal electrodes:

$$I_{\text{steady}}^{\text{hop}}(V) = I_0 2\pi\hbar [(\chi_{LM^-} + \chi_{LM^{*-}}) P_{M_0}^{(\text{st})} - 1/2(\chi_{-LM^-} P_{M^-}^{(\text{st})} + \chi_{-LM^{*-}} P_{M^{*-}}^{(\text{st})})], \quad (22)$$

where the quantities

$$P_{M_0}^{(st)} = \frac{1}{D} [A_{M^-} A_{M^{-*}} + A_{M^-} k_{M^{-*} \rightarrow M^-}(\Omega) + A_{M^{-*}} k_{M^- \rightarrow M^{-*}}(\Omega)],$$

$$P_{M^-}^{(st)} = \frac{2}{D} [A_{M^{-*}} B_{M^-} + (B_{M^-} + B_{M^{-*}}) \times k_{M^{-*} \rightarrow M^-}(\Omega)],$$

$$P_{M^{-*}}^{(st)} = \frac{2}{D} [A_{M^-} B_{M^{-*}} + (B_{M^-} + B_{M^{-*}}) \times k_{M^- \rightarrow M^{-*}}(\Omega)] \quad (23)$$

represent the stationary populations of each of the states of the LMR system participating in the ET process and can be obtained from the solution of the system of stationary equations, i.e. from system (10) under the condition that all $\dot{P}(n, t) = 0$. In formula (23), we introduced the quantity $D \equiv A_{M^-} A_{M^{-*}} + A_{M^-} (2 B_{M^{-*}} + k_{M^{-*} \rightarrow M^-}(\Omega)) + A_{M^{-*}} (2 B_{M^-} + k_{M^- \rightarrow M^{-*}}(\Omega)) + 2 (B_{M^-} + B_{M^{-*}}) (k_{M^- \rightarrow M^{-*}}(\Omega) + k_{M^{-*} \rightarrow M^-}(\Omega))$.

The distant elastic component of the current $I_{\text{steady}}^{\text{dir}}(V)$ is determined according to any of formulas (17) or (18) under the condition that all $P(n, t) \equiv P_n^{(st)} = \text{const}$ ($n = M_0, M^-, M^{-*}$), the latter can be found with the help of relation (23). Using new notations, the total current through a molecule is presented as follows:

$$I_{\text{steady}}(V) = I_{\text{steady}}^{\text{hop}}(V) + I_{\text{steady}}^{\text{dir}}(V). \quad (24)$$

5. Transport Rates

In order to investigate the direct (20) and inverse (21) nonstationary currents, as well the effect of electromagnetic radiation on the volt-ampere behavior of the stationary interelectrode current (24), it is necessary to find expressions for the electron transport rates in the LMR system. For the hopping rates of electron transfer between the electrodes and the molecule, we use the expressions obtained in the approximation of a wide metal gap [40]. In our notations, the direct and inverse rates of electron transfer from the left electrode to the molecule have the form

$$\chi_{LM^-} = \frac{1}{\hbar} \Gamma_{LM^-} n_F(\Delta E_{LM^-}),$$

$$\chi_{LM^{-*}} = \frac{1}{\hbar} \Gamma_{LM^{-*}} n_F(\Delta E_{LM^{-*}}),$$

$$\chi_{-LM^-} = \frac{1}{\hbar} \Gamma_{-LM^-} (1 - n_F(\Delta E_{-LM^-})),$$

$$\chi_{-LM^{-*}} = \frac{1}{\hbar} \Gamma_{-LM^{-*}} (1 - n_F(\Delta E_{-LM^{-*}})). \quad (25)$$

Similarly, the rates of electron transfer from the conduction band of the right electrode to the molecule are as follows:

$$\chi_{RM^-} = \frac{1}{\hbar} \Gamma_{RM^-} n_F(\Delta E_{RM^-}),$$

$$\chi_{RM^{-*}} = \frac{1}{\hbar} \Gamma_{RM^{-*}} n_F(\Delta E_{RM^{-*}}),$$

$$\chi_{-RM^-} = \frac{1}{\hbar} \Gamma_{-RM^-} (1 - n_F(\Delta E_{-RM^-})),$$

$$\chi_{-RM^{-*}} = \frac{1}{\hbar} \Gamma_{-RM^{-*}} (1 - n_F(\Delta E_{-RM^{-*}})). \quad (26)$$

In (25, 26), $n_F(\Delta E_{xy}) = [\exp(\Delta E_{xy}/k_B T) + 1]^{-1}$ represents the Fermi distribution function.

The energy gaps between each of the electron levels of the molecule participating in the transmission and the Fermi level of the corresponding electrode are determined with the help of the relations (see Fig. 2 and formula (5))

$$\Delta E_{LM^-(LM^{-*})}(V) \equiv E_{M^-(M^{-*})}(V) - E_F =$$

$$= \Delta E_{LM^-(LM^{-*})}(0) - eV \eta_{M^-(M^{-*})},$$

$$\Delta E_{RM^-(RM^{-*})}(V) \equiv E_{M^-(M^{-*})}(V) - (E_F - eV) =$$

$$= \Delta E_{RM^-(RM^{-*})}(0) - eV (1 - \eta_{M^-(M^{-*})}), \quad (27)$$

where $\Delta E_{LM^-(LM^{-*})}(0) \equiv E_{M^-(M^{-*})}(0) - E_F$ and $\Delta E_{RM^-(RM^{-*})}(0) \equiv E_{M^-(M^{-*})}(0) - E_F$ are the distances between the corresponding electron level of the molecule and the Fermi level E_F of the electrode in the absence of the applied electric field.

For the rates characterizing photoinduced transitions inside the molecule between its charged and photoexcited states, we use the Marcus formulas [41] extended to the case of an external periodic field. The technique used for obtaining the analytical expressions for electron transport rates in the case of an external periodic field acting on the molecule with the help of the NDM method is presented in [30]. Based on these results, one can demonstrate that, in the Bohr approximation at high temperatures, the direct and inverse transfer rates between the charged and photoexcited states of the molecule have the form

$$k_{M^- \rightarrow M^{-*}}(\Omega) = \frac{\pi}{\hbar} \frac{|V_{M^-, M^{-*}}|^2}{\sqrt{4\pi\lambda_r k_B T}} \times \exp\left(-\frac{(\lambda_r + \Delta E_{M^{-*} M^-})^2 + (\hbar\Omega)^2}{4\lambda_r k_B T}\right) \times \cosh\left(\frac{\hbar\Omega(\lambda_r + \Delta E_{M^{-*} M^-})}{2\lambda_r k_B T}\right), \quad (28)$$

$$k_{M^- \rightarrow M^{-*}}(\Omega) = \frac{\pi}{\hbar} \frac{|V_{M^-, M^{-*}}|^2}{\sqrt{4\pi\lambda_r k_B T}} \times \exp\left(-\frac{(\lambda_r - \Delta E_{M^{-*} M^-})^2 + (\hbar\Omega)^2}{4\lambda_r k_B T}\right) \times \cosh\left(\frac{\hbar\Omega(\lambda_r - \Delta E_{M^{-*} M^-})}{2\lambda_r k_B T}\right), \quad (29)$$

where λ_r denotes the reorganization energy, T is the temperature, k_B is the Boltzmann constant, and $\Delta E_{M^{-*} M^-}$ stands for the energy gap between the energies of the molecule in the photoexcited and charged states. Taking formula (5) into account, we obtain

$$\begin{aligned} \Delta E_{M^{-*} M^-} &= E_{M^{-*}}(V) - E_{M^-}(V) = \\ &= \Delta E_{M^{-*} M^-}(0) - eV(\eta_{M^{-*}} - \eta_{M^-}), \end{aligned} \quad (30)$$

where $\Delta E_{M^{-*} M^-}(0)$ is the energy difference of the electron levels of the molecule in the charged and photoexcited states undisturbed by the electric field.

In order to analyze the direct (28) and inverse (29) photoinduced rates, we consider the optical frequency range, in which the electromagnetic wavelength lies in the interval between 400 and 700 nm which corresponds

to the photon energies lying between 1.77 and 3.1 eV. In addition, we consider that the electromagnetic radiation resulting in the transitions of the system from the charged state $|M^- \rangle$ to the photoexcited one $|M^{-*} \rangle$ does not considerably change the center of mass of the electron density at the molecule. In this case, $\eta_{M^-} \approx \eta_{M^{-*}}$. Therefore, the energy difference between the electron energies at the molecule in the $|M^{-*} \rangle$ and $|M^- \rangle$ states practically does not depend on the potential difference V applied to the electrodes ($\Delta E_{M^{-*} M^-} = \Delta E_{M^{-*} M^-}(0)$). However, the energies $E_{M^-}(V)$ and $E_{M^{-*}}(V)$ in formula (5) remain dependent on V . (The case where the transition of the system from the charged state of the molecule to the photoexcited one is accompanied by an essential shift of the position of the electron density at the molecule, i.e. $\eta_{M^-} \neq \eta_{M^{-*}}$ and $\Delta E_{M^{-*} M^-} = \Delta E_{M^{-*} M^-}(V)$, requires special investigation and will be considered in subsequent works).

Let us find the conditions for the maximal influence of electromagnetic radiation on the conducting properties of the molecule. With regard for the structure of the rates (28) and (29) and the fact that $\cosh(x) \approx 1/2 \exp[x]$ at $x \gg 1$ and $\cosh(x) \approx 1/2 \exp[-x]$ at $x \ll 1$, we obtain the approximate expression for the direct rate of transition between the charged and photoexcited states of the molecule:

$$k_{M^- \rightarrow M^{-*}}(\Omega) \approx \frac{\pi}{2\hbar} \frac{|V_{M^- M^{-*}}|^2}{\sqrt{4\pi\lambda_r k_B T}} \times \exp\left(-\frac{(\lambda_r + \Delta E_{M^{-*} M^-} - \hbar\Omega)^2}{4\lambda_r k_B T}\right). \quad (31)$$

From (31), one can see that the rate $k_{M^- \rightarrow M^{-*}}(\Omega)$ reaches its maximum in the region where $\lambda_r + \Delta E_{M^{-*} M^-} \approx \hbar\Omega$. In order to find approximate expressions for the inverse rate of the photoinduced process, let us consider two limit cases: $\lambda_r \ll \Delta E_{M^{-*} M^-}$ and $\lambda_r \gg \Delta E_{M^{-*} M^-}$. In the first case,

$$k_{M^{-*} \rightarrow M^-}(\Omega) \approx \frac{\pi}{2\hbar} \frac{|V_{M^- M^{-*}}|^2}{\sqrt{4\pi\lambda_r k_B T}} \times \exp\left(-\frac{(\Delta E_{M^{-*} M^-} - \hbar\Omega)^2}{4\lambda_r k_B T}\right), \quad (32)$$

and the rate reaches its maximum at $\Delta E_{M^{-*} M^-} \approx \hbar\Omega$. In the second case,

$$k_{M^{-*} \rightarrow M^-}(\Omega) \approx \frac{\pi}{2\hbar} \frac{|V_{M^- M^{-*}}|^2}{\sqrt{4\pi\lambda_r k_B T}}$$

$$\times \exp\left(-\frac{(\lambda_r - \hbar\Omega)^2}{4\lambda_r k_B T}\right), \quad (33)$$

and the rate differs from zero only at $\lambda_r \approx \hbar\Omega$. It is worth noting that, both at $\lambda_r \ll \Delta E_{M^*M^-}$ and at $\lambda_r \gg \Delta E_{M^*M^-}$, the direct and inverse rates coincide, which can be seen from (31)–(33). That is, one can consider that $k_{M^- \rightarrow M^*}(\Omega) \approx k_{M^* \rightarrow M^-}(\Omega) \equiv \chi(\Omega)$. In the case where $\lambda_r \approx \Delta E_{M^*M^-}$, the inverse photoinduced rate decreases with the frequency according to the exponential law $k_{M^* \rightarrow M^-} \sim \exp[-(\hbar\Omega)^2/4\lambda_r k_B T]$ and is practically equal to zero in the optical wavelength range. That is why, for estimations and numerical calculations, we consider the case where $\lambda_r \ll \Delta E_{M^*M^-}$.

6. Stationary Interelectrode Current in the Case of Resonance Transmission

In order to analyze the volt-ampere behavior of the stationary interelectrode current, it is worth noting that, according to the diagram presented in Fig. 2, there exist two types of resonance electron transmission through a molecule. The first one is realized in the case where the electron energy level in the charged state of the molecule coincides with the Fermi level of the right ($V > 0$) or left ($V < 0$) electrode. The second type takes place in the case of the coincidence of the electron energy level in the photoexcited state with the Fermi level of the corresponding electrode. The resonance potential differences can be found with the help of the relations

$$V_{Ln}^{res} = \Delta E_{Ln}(0)/(|e|\eta_j), \quad (n = M^-, M^*), \quad (34)$$

at $V > 0$ and

$$V_{Rn}^{res} = \Delta E_{Rn}(0)/(|e|(1 - \eta_j)), \quad (n = M^-, M^*), \quad (35)$$

at $V < 0$. Let us consider each mode of electron transmission through the molecule and find the approximate expressions for the stationary current.

In the case of pre-resonance transmission, where $0 < |V| < V_{rn}$, ($r = L, R$; $n = M^-, M^*$) and taking into account that the Fermi distribution function $n_F(\varepsilon) \simeq 1$ at $\varepsilon < 0$ and $n_F(\varepsilon) \simeq 0$ at $\varepsilon > 0$, the populations $P_{M_0}^{(st)} \approx 1$, $P_{M^-}^{(st)} \approx 0$, $P_{M^*}^{(st)} \approx 0$. Therefore, $I_{steady}^{hop}(V) \approx 0$ according to formula (22). Thus, in the pre-resonance mode, the current through the molecule is formed only due to the elastic mechanism; moreover, the charged and photoexcited states of the molecule practically play no role in the electron transmission.

At $V_{rM^-} < |V| < V_{rM^*}$, the resonance transmission is realized with participation of the molecular energy

level in the charged state. Moreover, the approximate expressions for the electron populations in the case of a positive potential difference $V > 0$ and a negative one $V < 0$ have the form

$$\begin{aligned} P_{M_0}^{(st)} &\approx \frac{1}{D_L} \left[\frac{\Gamma_{RM^-} (\Gamma_{LM^*} + \Gamma_{RM^*})}{\hbar^2} + \right. \\ &\quad \left. + \frac{\Gamma_{RM^-} + \Gamma_{LM^*} + \Gamma_{RM^*}}{\hbar} \chi(\Omega) \right], \\ P_{M^-}^{(st)} &\approx \frac{2}{D_L} \frac{\Gamma_{LM^-} (\Gamma_{LM^*} + \Gamma_{RM^*})}{\hbar^2} \chi(\Omega), \\ P_{M^*}^{(st)} &\approx \frac{2}{D_L} \frac{\Gamma_{LM^-}}{\hbar} \chi(\Omega) \quad (V \geq 0) \end{aligned} \quad (36)$$

and

$$\begin{aligned} P_{M_0}^{(st)} &\approx \frac{1}{D_R} \left[\frac{\Gamma_{LM^-} \Gamma_{RM^*}}{\hbar^2} + \frac{\Gamma_{LM^-} + \Gamma_{RM^*}}{\hbar} \chi(\Omega) \right], \\ P_{M^-}^{(st)} &\approx \frac{2}{D_R} \left[\frac{\Gamma_{RM^-} \Gamma_{RM^*}}{\hbar^2} + \frac{\Gamma_{RM^-}}{\hbar} \chi(\Omega) \right], \\ P_{M^*}^{(st)} &\approx \frac{2}{D_R} \frac{\Gamma_{RM^-}}{\hbar} \chi(\Omega) \quad (V < 0). \end{aligned} \quad (37)$$

In (36), (37), we introduced the notations

$$\begin{aligned} D_L &\equiv \left[\frac{(\Gamma_{LM^*} + \Gamma_{RM^*})}{\hbar} + \chi(\Omega) \right] \frac{(\Gamma_{RM^-} + 2\Gamma_{LM^-})}{\hbar} + \\ &\quad + \frac{(\Gamma_{RM^-} + 2\Gamma_{LM^-}) \chi(\Omega)}{\hbar} \end{aligned}$$

and

$$\begin{aligned} D_R &\equiv \frac{\Gamma_{LM^-} \Gamma_{RM^*}}{\hbar^2} + \frac{2\Gamma_{RM^-} \Gamma_{RM^*}}{\hbar^2} + \\ &\quad \frac{(\Gamma_{LM^-} + 2\Gamma_{RM^-} + \Gamma_{RM^*}) \chi(\Omega)}{\hbar}. \end{aligned} \quad (38)$$

The hopping component of the stationary interelectrode current in the case of the positive and negative potential differences applied to the electrodes will have, respectively, the form

$$\begin{aligned} I_{steady}^{hop}(V) &\approx I_0 2\pi \left[\Gamma_{LM^-} P_{M_0}^{(st)} - 1/2 \Gamma_{LM^-} \right], \\ I_{steady}^{hop}(V) &\approx -I_0 \pi \left[\Gamma_{LM^-} P_{M^-}^{(st)} + \Gamma_{LM^*} P_{M^*}^{(st)} \right]. \end{aligned} \quad (39)$$

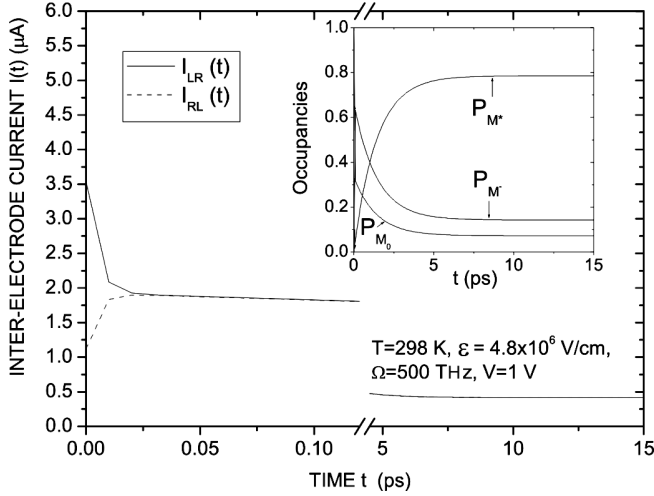


Fig. 3. Establishment of the stationary mode for the direct and inverse interelectrode currents and the populations of each of the states of the LMR system (inset). The calculations were performed based on formulas (20)–(21) and (11) at the following parameters: $\Delta E_{LM^-}(0) = \Delta E_{RM^-}(0) = 0.25$ eV, $\Delta E_{LM^{*-}}(0) = \Delta E_{RM^{*-}}(0) = 1.7$ eV, $\Gamma_{LM^-} = \Gamma_{RM^-} = 0.05$ eV, $\lambda_r = 0.4$ eV, $\Gamma_{LM^{*-}} = \Gamma_{RM^{*-}} = 5 \times 10^{-5}$ eV

In the case of post-resonance transmission where the Fermi level of the right (at $V > 0$) or left (at $V < 0$) electrode reaches the electron energy level of the molecule in the photoexcited state, one can demonstrate that the approximate formulas for the quantities $P_{M_0}^{(st)}$, $P_{M^-}^{(st)}$, and $P_{M^{*-}}^{(st)}$, as well as for the hopping component of the stationary current $I_{steady}^{hop}(V)$, are as follows:

$$P_{M_0}^{(st)} \approx \frac{1}{D_{LL}} \left[\frac{\Gamma_{RM^-} - \Gamma_{RM^{*-}}}{\hbar^2} + \frac{\Gamma_{RM^-} + \Gamma_{RM^{*-}}}{\hbar} \chi(\Omega) \right],$$

$$P_{M^-}^{(st)} \approx \frac{2}{D_{LL}} \left[\frac{\Gamma_{LM^-} - \Gamma_{LM^{*-}}}{\hbar^2} + \frac{\Gamma_{LM^-} + \Gamma_{LM^{*-}}}{\hbar} \chi(\Omega) \right],$$

$$P_{M^{*-}}^{(st)} \approx \frac{2}{D_{LL}} \left[\frac{\Gamma_{RM^-} - \Gamma_{LM^{*-}}}{\hbar^2} + \frac{\Gamma_{LM^-} + \Gamma_{LM^{*-}}}{\hbar} \chi(\Omega) \right],$$

$$(V \geq 0) \quad (40)$$

and

$$P_{M_0}^{(st)} \approx \frac{1}{D_{RR}} \left[\frac{\Gamma_{LM^-} - \Gamma_{LM^{*-}}}{\hbar^2} + \frac{\Gamma_{LM^-} + \Gamma_{RM^{*-}}}{\hbar} \chi(\Omega) \right],$$

$$P_{M^-}^{(st)} \approx \frac{2}{D_{RR}} \left[\frac{\Gamma_{RM^-} - \Gamma_{LM^{*-}}}{\hbar^2} + \frac{\Gamma_{RM^-} + \Gamma_{RM^{*-}}}{\hbar} \chi(\Omega) \right],$$

$$P_{M^{*-}}^{(st)} \approx \frac{2}{D_{RR}} \left[\frac{\Gamma_{LM^-} - \Gamma_{RM^{*-}}}{\hbar^2} + \frac{\Gamma_{RM^-} + \Gamma_{RM^{*-}}}{\hbar} \chi(\Omega) \right]$$

$$(V < 0), \quad (41)$$

where the quantities D_{LL} and D_{RR} are determined with the help of the relations

$$D_{LL} = \Gamma_{RM^-} - \Gamma_{RM^{*-}} / \hbar^2 + 2\Gamma_{RM^-} - \Gamma_{LM^{*-}} / \hbar^2 +$$

$$+ (\Gamma_{RM^-} + 4\Gamma_{LM^-} + 4\Gamma_{LM^{*-}} + \Gamma_{RM^{*-}}) \chi(\Omega) / \hbar +$$

$$+ 2\Gamma_{LM^-} - \Gamma_{RM^{*-}} / \hbar^2,$$

$$D_{RR} = \Gamma_{LM^-} - \Gamma_{LM^{*-}} / \hbar^2 + 2\Gamma_{LM^-} - \Gamma_{RM^{*-}} / \hbar^2 +$$

$$+ (\Gamma_{LM^-} + 4\Gamma_{RM^-} + 4\Gamma_{RM^{*-}} + \Gamma_{LM^{*-}}) \chi(\Omega) / \hbar +$$

$$+ 2\Gamma_{RM^-} - \Gamma_{LM^{*-}} / \hbar^2, \quad (42)$$

Respectively, the approximate expressions for the hopping component of the stationary current, where $|V| > V_{rM^*}$ ($r = L, R$), are as follows:

$$I_{steady}^{hop}(V) \approx I_0 2\pi (\Gamma_{LM^-} + \Gamma_{LM^{*-}}) P_{M_0}^{(st)}, \quad (V \geq 0),$$

$$I_{steady}^{hop}(V) \approx -I_0 \pi (\Gamma_{LM^-} P_{M^-}^{(st)} + \Gamma_{LM^{*-}} P_{M^{*-}}^{(st)}),$$

$$(V < 0). \quad (43)$$

7. Discussion and Basic Results

The analytical expressions for the direct and inverse nonstationary photoinduced currents (20), (21) together with formula (11) for the integral populations of each state of the LMR system participating in the PETP serve as a basis for the investigation of evolution processes in the system. Figure 3 presents the temporal evolution of the direct $I_{L \rightarrow R}(t)$ and inverse $I_{R \rightarrow L}(t)$ interelectrode currents, as well as the electron populations $P(n, t)$ ($n = M_0, M^-, M^{*-}$) of each state of the LMR system taking part in the ET process. One can see that, on the time scale preceding the establishment of the stationary mode in the system, the direct and inverse

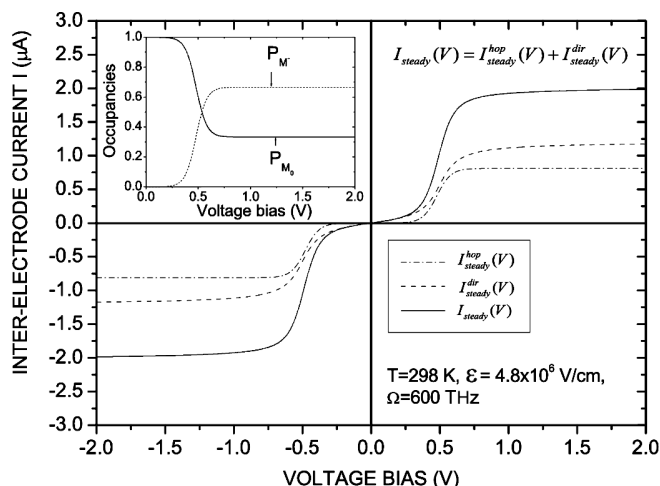


Fig. 4. Volt-ampere characteristic of the current at various frequencies of electromagnetic radiation. In the inset – populations of each of the states of the LMR system participating in the PETP depending on V . The calculations were performed with the use of formulas (23)–(24) at the same parameters as in Fig. 3

currents differ $I_{L \rightarrow R}(t) \neq I_{R \rightarrow L}(t)$. As was mentioned earlier, such a difference in the behavior of the current is, first of all, related to the processes of “detachment” of a part of electrons running from one electrode to the other to charge the molecule.

The establishment of the stationary mode in the system is accompanied by a variation of the integral populations that reach their stationary values (the same way as the current itself) at $t \sim \tau_{st} \gg \tau_{ET}$, (τ_{st} is the characteristic time of reaching the stationary mode).

In what follows, we consider the stationary case and analyze the way, in which the frequency of the external electromagnetic radiations Ω influences the volt-ampere characteristics of the stationary interelectrode current, as well as the conductivity of the molecule.

In the stationary mode, $I_{L \rightarrow R}(t \gg \tau_{ET}) = I_{R \rightarrow L}(t \gg \tau_{ET}) \equiv I_{steady}(V)$, that is why the current can be calculated with the help of formula (24) together with (17) and (22). Figure 4 shows the $I(V)$ characteristic of the current at various frequencies of the external electromagnetic radiation Ω , as well as the behavior of the populations $P(n, t)$ ($n = M_0, M^-, M^{-*}$) depending on V in a wide range of potential differences applied to the electrodes (see the inset). The figure demonstrates the switching effect between the low-conducting and conducting states of the molecule caused by an increase of the frequency of the periodic field. As was already noted, the basic influence of the electromagnetic

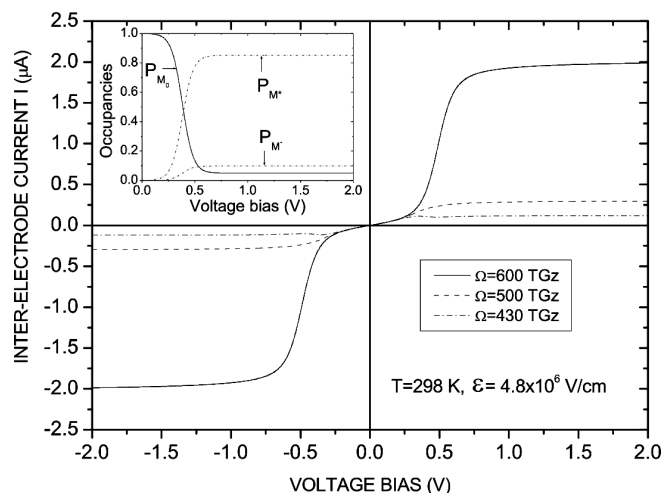


Fig. 5. Hopping component $I_{steady}^{hop}(V)$, distant elastic component $I_{steady}^{dir}(V)$, and total interelectrode current $I_{steady}(V)$ as functions of the potential difference applied to the metal electrodes. In the inset – electron populations $P(n, t)$ ($n = M_0, M^-, M^{-*}$) depending on V . The calculations were performed with the use of formulas (23)–(24) at the same parameters as in Fig. 3

radiation on the current formation in the LMR system is due to photoinduced transitions between the charged and photoexcited states of the molecule controlled by the direct (28) and inverse (29) rates. Such transitions result in a change of the electron population of the molecule and thus can affect its conductivity. According to the approximate formula (32), the inverse (direct) rate at $\lambda_r \ll \Delta E_{M^{-*} M^-}$ will be maximal only if $\Delta E_{M^{-*} M^-} \approx \hbar \Omega$, so that $\chi^{\max} \approx \frac{\pi}{2\hbar} |V_{M^{-*} M^-}|^2 / \sqrt{4\pi \lambda_r k_B T}$. In this case, the population of the photoexcited state of the molecule $P_{M^{-*}}$ is the highest one, which can be seen both from the approximate formulas (40) and (41) and from Fig. 4. Moreover, the current is low, and the molecule is in the low-conducting state. With increasing the field frequency, where $\hbar \Omega > \Delta E_{M^{-*} M^-}$, there takes place an abrupt (exponential) decrease of both the direct $k_{M^- \rightarrow M^{-*}}(\Omega)$ and inverse $k_{M^{-*} \rightarrow M^-}(\Omega)$ rates. In turn, it results in a reduction of the population of the photoexcited electron level of the molecule and, therefore, in an increase of the current. This situation is demonstrated in Fig. 5 (see the inset), where one can also see the volt-ampere behavior of the total current $I_{steady}(V)$, as well as the $I(V)$ dependence of the elastic $I_{steady}^{dir}(V)$ and inelastic $I_{steady}^{hop}(V)$ components of the current. In this case, the electron population of the molecule in the photoexcited state is inessential ($P_{M^{-*}}^{(st)} \approx 0.0015$) and the molecule is in the conducting state.

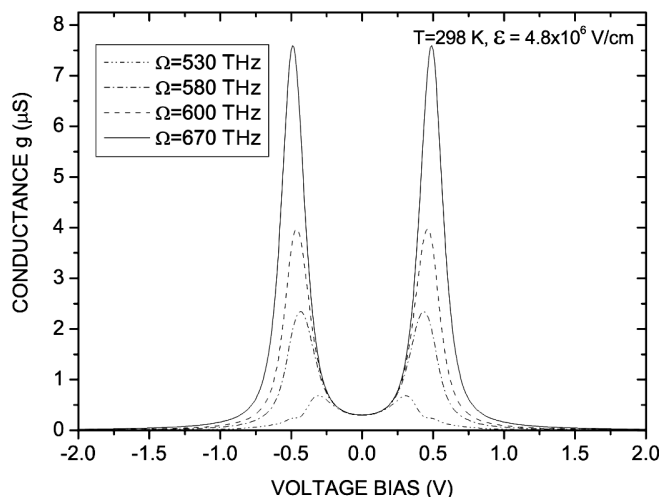


Fig. 6. Differential conductivity of the molecule as a function of the potential difference applied to the electrodes. The calculations were performed at the same parameters as in Fig. 3

Figure 6 shows the differential conductivity $g(V) = dI_{\text{steady}}/dV$ as a function of the potential difference V applied to the electrodes at various frequencies of the electromagnetic radiation. In the figure, one can observe an abrupt rise of the conductivity of the molecule with increasing Ω , which indicates the possibility to use the molecule as a molecular photoswitch.

The calculations have also demonstrated that the further increase of the frequency does not result in the rise of either the current or the differential conductivity testifying to the independence of these quantities on the frequency of the electromagnetic field at $\hbar\Omega \gg \Delta E_{M^*M^-}$. It is caused by the fact that, at high field frequencies, the photoinduced rates rapidly tend to zero due to their structure.

8. Conclusions

The main goal of the work consisted in the investigation of the influence of external electromagnetic radiation on the conducting properties of a separate organic molecule placed between two metal electrodes. For this purpose, we considered a model of the formation of a photoinduced current through the molecule with participation of its neutral, charged, and photoexcited states. Under the condition of fast internal molecular relaxation in the system, we put down the system of linear kinetic equations (10) for the integral populations of each of the states of the LMR system taking part in the electron transmission. Based on the solution of this system (11)–(13), we derived analytical expressions

for the nonstationary direct (20) and inverse (21) photoinduced interelectrode currents, which allowed us to investigate the evolution processes in the LMR system stimulated by the external electromagnetic radiation. On the time scale much exceeding that of electron-transport processes in the system, the current reaches its stationary value. That is why the rest of the work was devoted to the research of the behavior of the stationary interelectrode current (24) depending on the potential difference applied to the metal electrodes. In this case, the main attention was paid to the study of the influence of electromagnetic radiation in the optical wavelength range on the formation of the $I(V)$ characteristics of the current, as well as the search for the conditions, under which such an influence on the conducting properties is the most considerable. It was demonstrated that the external electromagnetic radiation can result in the appearance of the switching effect from the low-conducting state to the conducting one (Fig. 4). It was also shown that the conductivity of the molecule can be changed by an order of magnitude (Fig. 6). The latter fact testifies to the possibility of using the molecule as a molecular switch, whose conducting properties can be controlled due to the irradiation of the molecule by monochromatic light. Such effects were repeatedly observed experimentally [13,14], though the application of our model to the description of photoconducting properties of specific organic molecules requires the additional investigation.

The work was partially supported by the program “Nanostructured systems, nanomaterials, and nanotechnologies” (project No. 3/08-N).

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Received 11.12.08.

Translated from Ukrainian by H.G. Kalyuzhna

ФОТОІНДУКОВАНИЙ СТРУМ ЧЕРЕЗ ПОДИНОКУ
МОЛЕКУЛУ

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Р е з ю м е

Запропоновано кінетичну модель формування фотоіндукованого струму через окрему органічну молекулу, розміщену між двома металевими електродами. Знайдено аналітичний вираз для комбінованого термічно-активованого непружного та дистанційного пружного міжелектродного струмів за участі нейтрального, зарядженого та фотозбудженого станів молекули. На основі одержаного виразу проведено аналіз поведінки струму та диференційної провідності молекули від різниці прикладених до електродів потенціалів, а також від частоти зовнішнього електромагнітного випромінювання. Виявлено фотостимульований ефект переключення між провідним та слабопровідним станами молекули, який супроводжується зміною провідності молекули на порядок величини.