
RECTIFICATION PROPERTIES OF A MOLECULAR WIRE CAUSED BY ITS TERMINAL GROUPS

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The current-voltage characteristics of a molecular wire are analyzed for a particular scheme of its energy levels. It is assumed that the levels of the lowest unoccupied molecular orbitals (LUMO) of internal wire units are energetically positioned much higher than the Fermi levels of metal electrodes and the LUMO levels of the terminal groups. The latter act as the specific intermediate donor and acceptor centers and control the current formation via the combined superexchange and sequential hopping mechanism of electron transfer. It is shown the blocking of the interelectrode current at a large voltage bias is caused by the strong electron-phonon interaction. Additionally, the rectification effect of a wire is obtained in the case of a nonvanishing donor-acceptor driving force, provided the superexchange mechanism dominates the current formation.

1. Introduction

In recent years, the great progress in molecular electronics has been made due to the development of new methods of study of the conduction of separate molecules [1–4]. In particular, the mechanisms of elastic tunneling, which are based on the use of the Büttiker–Landauer formula [5, 6] widely applied in mesoscopy for the description of the scattering phenomena in semiconductors and quantum dots, were clarified. It is worth noting that this method was developed in the early works [7–10] and applied to the analysis of the current-voltage characteristics of individual molecules. Then it was extended by other authors while studying the currents along molecular wires [11]. It was established that the main role in the conduction of a molecule is related to the electronic structure of a molecule, a type of the coupling of a molecule with metal contacts, and the position of the Fermi level of the metal of electrodes relative to the levels of highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO) of a molecule. The interaction of surface atoms of the electrode metal leads to a change of the HOMO and LUMO levels of a molecule and to the appearance of the imaginary addition in the spectrum of a molecule, which indicates the significance of metal contacts in a molecular device [12–14]. The presence of a strong

influence of metal contacts on the conduction properties of organic molecules was also demonstrated due to the application of powerful quantum-chemical methods of the *ab initio* type [15, 16]. These calculations are based on the density functional method which was firstly applied to the description of the conduction of carbon chains [17, 18] and then of molecules together with the use of model Hamiltonians [19] and the method of nonequilibrium Green's function [11, 20–22]. The quantum-chemical calculations allow one to calculate the electron spectrum, the distribution of charges, and the density of states of a single molecule and molecular complexes which are composed from the molecule itself and several layers of atoms of the electrode metal. The results of calculations indicate the strong modification of the electron spectrum of a molecule caused by the presence of metal contacts. The method of combination of quantum-chemical calculations with the elasticity-based model of electron transport based on the use of the Büttiker–Landauer formula is one of the powerful methods of study of the conduction properties of organic molecules. This method was used in the description of experimental data on the conduction of short molecules, in particular, in the study of currents through molecules of xylyl dithion and phenyl dithiol [24]. However, its application to more complicated molecules reveals the disagreement of the results of theoretical calculations and experimental data on the current and the conduction by several orders, which requires to introduce a certain scaling [23]. This fact emphasizes the complicated nature of the mechanism which defines the conduction of organic molecules, by indicating the necessity of the additional account of other factors which influence the formation of the interelectrode current, in particular, the profile of electrostatic potential along a molecule [18, 25–27] and inelastic effects caused by the presence of the environment of a molecular system.

The elastic model of scattering can serve the basis for the description of the current-voltage characteristics of currents through short molecular structures at low temperatures. Just under such a condition, the effect

of relaxation effects caused by the presence of the nuclear vibration degrees of freedom of a molecule is slight. But, at finite temperatures, in particular, at room one, the breaking of coherency occurs during the electron transport, which leads to the appearance of the inelastic mechanism of charge transfer. A certain progress in the study of the inelastic tunneling was made due to the extension of the Büttiker—Landauer theory to the case of inelastic processes. We mention work [28], where the influence of the elastic and inelastic interelectrode tunnelings on the current-voltage characteristics of a two-center molecule was taken into account, and work [29] presenting the multichannel scattering technique applied to the analysis of transport properties of molecular wires. The authors of work [28] developed the procedure of calculations of the transmission coefficient which enters the Büttiker—Landauer formula with regard for inelastic effects accompanied by the creation or destruction of phonons in the process of interelectrode tunneling. The calculated interelectrode current through a two-center molecule revealed a complicated combination of the contributions of the long-range elastic and inelastic mechanisms. Moreover, it was shown that the role of elastic effects decreases with increase in the electric field.

Another powerful method of study of the effect of relaxation factors on the current-voltage characteristics of the current is the method of the nonequilibrium density matrix which was rather successfully used in the study of the effects of charge transfer in donor-acceptor systems and then was applied to the investigation of the conduction of individual molecules [1, 30, 38, 39]. Intense relaxation processes in molecular systems can lead to the localization of an electron on a molecule, which allows one to consider the electron transport in the form of quantum hops of the electron along a molecular wire. At great applied electric fields, the important role is played by the Coulomb repulsion between transferred electrons which is especially significant in short molecular wires. The electron-electron correlation can serve one of the reasons inducing the blocking of the interelectrode current and thus the appearance of negative differential resistance (NDR) [40–42]. Just this mechanism was taken as a basic one in the interpretation of the recently obtained experimental current-voltage characteristics of currents through nanopores [43].

The present work is devoted to the clarification of the influence of terminal groups of a molecular wire on the current-voltage characteristics of the interelectrode current along a molecular wire, in which the terminal groups play the role of a donor and an acceptor of an

electron. The study of the conduction of such systems was performed earlier in [44], where the connection between the differential resistance and the long-range superexchange rate of electron transfer between the donor and acceptor redox-centers was established in the framework of an elasticity-based model. In work [45], the main attention was concentrated at studying the effect of the donor-acceptor interaction on the current-voltage characteristics of the current. Here, we will use our model of formation of the combined thermally activated inelastic and elastic interelectrode current along a molecular wire of this type. The essence of the model is presented in works [31, 32]. As distinct from work [31], where the analysis of the effect of dynamic and relaxation factors on the dependence of the interelectrode current on the length of a molecular wire was performed, we will analyze the current-voltage $I(V)$ characteristics of the current and the differential conduction $g \equiv \frac{dI}{dV}$ and will show how the energy properties of the terminal groups of a wire and their geometric arrangement relative to microelectrodes can influence the rectification properties of a molecular wire.

2. Model and Theory

In order to study the effect of the terminal groups of a wire on the current-voltage characteristics of the interelectrode current, we consider the model of formation of the combined thermally activated inelastic and long-range elastic interelectrode currents along a molecular wire, in which the terminal groups play the role of a donor and an acceptor of an electron [31]. For this purpose, we consider a molecular chain of length L which includes $N + 2$ centers of electron localization which are positioned between two metal microelectrodes **L** and **R**, Fig. 1, *a*. We denote the distances between the terminal groups of a wire and the surface of microelectrodes by, respectively, l_L and l_R and the distance between neighboring centers of a molecular wire by l . Due to the influence of the polarization effects caused by metal microelectrodes, there occurs a decrease of the LUMO levels of the terminal groups 0 and $N + 1$ of a wire relative to LUMO levels of the rest of centers $n = 1, 2, \dots, N$. This leads to the appearance of the specific superexchange interaction between the 0 and $(N + 1)$ centers.

We assume that a rapid relaxation exists in the system in the scope of each of the centers of electron localization in a wire, and it occurs much faster than the electron transfer ET process, i.e. $\tau_{tr} \gg \tau_{rel}$, where τ_{tr} and τ_{rel} are, respectively, the durations of the ET process and

the relaxation. This condition allows one to consider the ET process in the form of quantum hops of an electron in the wire between the centers of electron localization. Under the action of the difference of potentials V applied to the microelectrodes, an electron which comes from the metal surface on the terminal groups of the wire with effective direct χ_L (χ_R) and reverse χ_{-L} (χ_{-R}) rates can move along the wire via the sequential hopping mechanism with effective direct $\alpha_{0(N)}$, α and reverse $\beta_{0(N)}$, β rates or can distantly tunnel between the terminal groups of the wire with rates k_1 and k_2 .

In order to find the general formula for the interelectrode current, we will use an equation of the type

$$I = -e\dot{N}_L(t) \quad (1)$$

where e is the the electron charge, and $\dot{N}_L = -\dot{N}_R$ is the time variation of the number of free electrons with a given spin projection which can be expressed in terms of the integral populations of the centers of the wire. To determine \dot{N}_L , we use a system of linear kinetic equations for the integral populations of each of the centers of the wire. The relevant system of kinetic equations was obtained in work [31] within the spin-boson model under the condition of a strong relaxation in the scope of each of the centers of electron localization in the form

$$\begin{aligned} \dot{N}_L &= -\chi_L + \Gamma_L P_0, \\ \dot{P}_0 &= -(\Gamma_{-L} + \alpha_0 + k_1)P_0 + \chi_L + \beta_0 P_1 + k_2 P_{N+1}, \\ \dot{P}_1 &= -(\alpha + \beta_0)P_1 + \alpha_0 P_0 + \beta P_2, \\ \dot{P}_n &= -(\alpha + \beta)P_n + \alpha P_{n-1} + \beta P_{n+1}, \quad (n = 2, \dots, N-1), \\ \dot{P}_N &= -(\alpha_N + \beta)P_N + \alpha P_{N-1} + \beta_N P_{N+1}, \\ \dot{P}_{N+1} &= -(\Gamma_R + \beta_N + k_2)P_{N+1} + \chi_R + \alpha_N P_N + k_1 P_0, \\ \dot{N}_R &= -\chi_R + \Gamma_R P_{N+1}, \end{aligned} \quad (2)$$

where the index m can take only the values $2, 3, \dots, N-1$.

We note that the linearity of the given system of kinetic equations is conserved only if the population of the centers of the regular part of the wire ($n = 1, 2, \dots, N$) is small during the whole ET process. Such a situation is typical of the systems, in which the LUMO levels of the centers of a regular chain are positioned much higher than the LUMO levels of the terminal groups of the wire.

The rate constants which enter the system of equations (5) describe the one-electron transitions

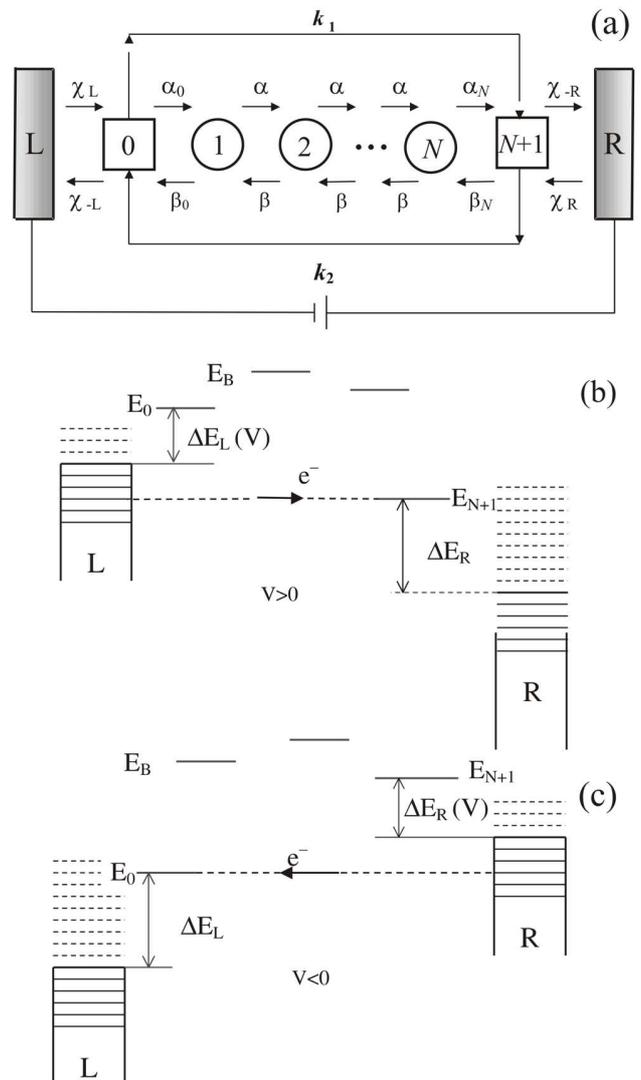


Fig. 1. Kinetic scheme of the formation of the interelectrode current along a molecular wire with $N + 2$ centers of electron localization (a). The energy position of the LUMO levels of a molecular wire for positive $V > 0$ (b) and negative $V < 0$ (c) difference of potentials applied to microelectrodes

between the neighboring centers of electron localization and can be determined in the Born approximation. A specific formula for the rates will be given in what follows. The quantities

$$\Gamma_{L(R)} \equiv \chi_{L(R)} + \chi_{-L(-R)} \quad (3)$$

define the broadening of the electron levels of the terminal groups of the wire caused by their interaction with levels of the conduction band of the metal of the

left and right microelectrodes and with the vibrational degrees of freedom of the thermostat.

We restrict ourselves by the stationary case where all the integral populations of the centers of the wire are constant, i.e. $\dot{P}_m = 0$, ($m = 0, 1, \dots, N, N + 1$) and $\dot{N}_L = -\dot{N}_R = \text{const}$. In this case, the system of equations (2) is reduced to the system of linear algebraic equations

$$\sum_{m=0}^{N+1} A_{nm} P_m = C_n, \quad (n = 0, 1, \dots, N + 1). \quad (4)$$

Here, A_{mn} is the basic matrix of system (2), and $C_n = \chi_L \delta_{n0} + \chi_R \delta_{nN+1}$. System (4) allows us to obtain the analytic expression for each of the quantities P_m for any number N of the centers of electron localization in the wire. Therefore, the stationary interelectrode current looks as

$$I = e \frac{\chi_L \Gamma_R R_{N+1} - \chi_R \Gamma_L R_0}{\Gamma_L R_0 + \Gamma_R R_{N+1}}, \quad (5)$$

where the constants R_0 and R_{N+1} are expressed in terms of the rates of one-electron transfer as follows:

$$\begin{aligned} R_0 = & (\chi_L + \chi_R) \{ k_2 [(\alpha \alpha_N + \beta \beta_0 + \alpha_N \beta_0) D(N-2) - \\ & - (\alpha_N + \beta_0) \alpha \beta D(N-3)] + \beta_0 \beta_N \beta^{N-1} \} + \\ & + \chi_L \Gamma_R [(\alpha \alpha_N + \beta \beta_0 + \alpha_N \beta_0) D(N-2) - \\ & - (\alpha_N + \beta_0) \alpha \beta D(N-3)], \end{aligned} \quad (6)$$

and

$$\begin{aligned} R_{N+1} = & (\chi_L + \chi_R) \{ k_1 [(\alpha \alpha_N + \beta \beta_0 + \alpha_N \beta_0) D(N-2) - \\ & - (\alpha_N + \beta_0) \alpha \beta D(N-3)] + \alpha_0 \alpha_N \alpha^{N-1} \} + \\ & + \chi_R \Gamma_L [(\alpha \alpha_N + \beta \beta_0 + \alpha_N \beta_0) D(N-2) - \\ & - (\alpha_N + \beta_0) \alpha \beta D(N-3)]. \end{aligned} \quad (7)$$

In formulas (6, 7),

$$D(M) \equiv (\alpha \beta)^{M/2} \frac{\sinh \Lambda (M+1)}{\sinh \Lambda}, \quad (e^\Lambda = \sqrt{\alpha/\beta}). \quad (8)$$

3. Analytic Formula for the Stationary Interelectrode Current

To calculate the $I - V$ characteristics of a molecular wire, it is necessary to obtain the formulas for the rate constants of electron transfer which enter formulas (5–8). For this purpose, we will determine the energy position of an electron in the wire under the action of the

difference of potentials applied to the microelectrodes V . Considering the case of the nonadiabatic electron transfer, we assume that the electron interaction between the neighboring centers of electron localization $V_{10}, V_{n,n+1} \equiv V_B$ ($n = 1, 2, \dots, N$) and V_{NN+1} is small and does not lead to the formation of extended LUMO states of the molecular wire. The energy of an electron localized at the n -th center of the molecular chain E_m is composed from the nonperturbed energy of LUMO, which is denoted as E_m^0 , and the addition caused by an external electric field ΔE_m , i.e. $E_m = E_m^0 + \Delta E_m$. In the case of a regular molecular wire, we have the following formulas for the energies of electron localization in the wire:

$$\begin{aligned} E_0 &= E_0^0 - eV \eta_L, \\ E_n &= E_n^0 - eV (\eta_L + n \eta_M), \quad (n = 1, 2, \dots, N), \\ E_{N+1} &= E_{N+1}^0 - eV (1 - \eta_R). \end{aligned} \quad (9)$$

Here, we used the notations $\eta_L \equiv l_L/L$, $\eta_R \equiv l_R/L$ and $\eta_M \equiv l/L$ which are named the “voltage division factor”. The parameters η_L and η_R define the potential drop between the terminal groups of the wire and the corresponding metal microelectrodes **L** and **R**, and the parameter η characterizes the potential drop between the neighboring centers of electron localization of the wire. The energy positions of the electron levels for positive $V > 0$ and negative applied difference of potentials $V < 0$ are shown in Fig. 1, *b* and 1, *c*, respectively.

In the general case, the rate of one-electron transfer between two centers of electron localization m and n is given by the relation

$$k_{mn} = \frac{2\pi}{\hbar} |V_{mn}|^2 (FC)_{mn}, \quad (10)$$

where $(FC)_{mn}$ is named the Franck–Condon factor for the $m \rightarrow n$ transition [33, 34]. To determine its specific form, we use the Song–Marcus model [35, 36] which involves the strong interaction of the electron transition $m \rightarrow n$ and a single reaction coordinate with the frequency ω_{mn} , whereas the interaction with the environment (thermostat) is characterized by the rearrangement energy λ_{mn} . Under such conditions, one can derive the well-known Jortner formula [37] for the Franck–Condon factor: $(FC)_{mn} = (1/\hbar \omega_{mn}) \Phi_{mn}$, where

$$\Phi_{mn} = \exp \left[-S_{mn} \coth \frac{\hbar \omega_{mn}}{k_B T} \right] \left(\frac{1 + n(\omega_{mn})}{n(\omega_{mn})} \right)^{\nu_{mn}/2} \times$$

$$\times I_{|\nu_{mn}|} \left(2S_{mn} [n(\omega_{mn})(1 + n(\omega_{mn}))]^{1/2} \right). \quad (11)$$

This formula includes the modified Bessel function I_ν and the Fermi distribution function $n(\omega) = [1 + \exp(\hbar\omega_0/k_B T)]^{-1}$. We also introduced the following notations: $S_{mn} \equiv \lambda_{mn}/\hbar\omega_{mn}$, $\nu_{mn} \equiv (E_m - E_n)/\hbar\omega_{mn}$. We now can determine all the direct rates of electron transfer (ET):

$$\beta_0 = \frac{2\pi}{\hbar} \frac{|V_1|^2}{\omega_{10}} \Phi_{10}, \quad (12)$$

$$\alpha_N = \frac{2\pi}{\hbar} \frac{|V_N|^2}{\omega_{NN+1}} \Phi_{NN+1}, \quad (13)$$

$$\alpha = \frac{2\pi}{\hbar} \frac{|V_B|^2}{\omega_{mm+1}} \Phi_{mm+1}, \quad (14)$$

$$k_1 = \frac{2\pi}{\hbar} \frac{|V_{0N+1}|^2}{\omega_{0N+1}} \Phi_{0N+1}. \quad (15)$$

The reverse rates of ET can be expressed through the direct ones with the help of the relations

$$\alpha_0 = \beta_0 \exp[-\Delta E_1/k_B T],$$

$$\beta_N = \alpha_N \exp[-\Delta E_N/k_B T],$$

$$\beta = \alpha \exp[-eV\eta/k_B T], \quad (n = 1, \dots, N-1),$$

$$k_2 = k_1 \exp[-(E_0 - E_{N+1})/k_B T], \quad (16)$$

where the corresponding energy gaps have the following form:

$$\Delta E_1 = E_1 - E_0 = \Delta E_1^0 - eV\eta_M,$$

$$\Delta E_m = E_m - E_{m+1} = eV\eta_M, \quad (n = 1, \dots, N),$$

$$\Delta E = E_0 - E_{N+1} = \Delta E^0 + eV(1 - \eta_L - \eta_R). \quad (17)$$

Here, $\Delta E_1^0 \equiv E_1^0 - E_0^0$ is the difference of energies between the LUMO levels of the 1-st and 0-th centers of a molecular wire which are not perturbed by the electric field, and $\Delta E^0 \equiv E_0^0 - E_{N+1}^0$ defines the difference of energies for the LUMO of the terminal groups of the wire in the case where $V = 0$.

In formula (15), the quantity $|V_{0N+1}|^2$ is the squared matrix element of the superexchange interaction between the 0-th and $N+1$ -th centers of a molecular wire, whose formula is well-known from the theory of donor-acceptor transfer [38, 39]. In our notation, it takes the following form:

$$|V_{0N+1}|^2 \equiv |V_{0N+1}(V)|^2 = \frac{|V_{01} V_B^{N-1} V_{NN+1}|^2}{\prod_{m=1}^N \Delta E_{m0} \Delta E_{mN+1}}. \quad (18)$$

We note that the matrix element of the superexchange interaction is a function of the difference of applied potentials V . This function enters the formulas for the energy gaps $\Delta E_{m0} \equiv E_m - E_0$ and $\Delta E_{mN+1} \equiv E_m - E_{N+1}$, where the energies E_0 , E_m ($m = 1, 2, \dots, N$) and E_{N+1} are determined with the use of Eq. (9).

In order to obtain the analytic formula for the squared matrix element of the superexchange interaction $|V_{0N+1}(V)|^2$, we consider the products $\prod_{m=1}^N \Delta E_{m0}$ and $\prod_{m=1}^N \Delta E_{mN+1}$. With regard for definition (9) of the energies, we can represent the formulas for the energy gaps ΔE_{m0} and ΔE_{mN+1} in the form

$$\Delta E_{m0} = E_m - E_0 = \Delta E_1^0 - eV\eta_M m,$$

$$\Delta E_{mN+1} = E_m - E_{N+1} = \Delta E_N^0 - eV\eta_M(N-m+1). \quad (19)$$

Then we can write

$$\prod_{m=1}^N \Delta E_{m0} = (\Delta E_1^0)^N \exp \left\{ \sum_{m=1}^N \ln \left[1 - \frac{eV\eta_M}{\Delta E_1^0} m \right] \right\},$$

$$\prod_{m=1}^N \Delta E_{mN+1} = (\Delta E_N^0)^N \exp \left\{ \sum_{m=1}^N \ln \left[1 - \frac{eV\eta_M}{\Delta E_N^0} \times \right. \right.$$

$$\left. \left. \times (N-m+1) \right] \right\}. \quad (20)$$

If the conditions $|eV\eta_M| \ll \Delta E_1^0$ and $|eV\eta_M(N-m+1)| \ll \Delta E_N^0$ (they hold at small values of the applied potential difference V) are satisfied, we can expand $\ln[1-x_1]$ and $\ln[1-x_2]$ in the small quantities $x_1 \equiv eV\eta_M m/\Delta E_1^0$ and $x_2 \equiv eV\eta_M(N-m+1)/\Delta E_N^0$. Taking only the first term of the expansion into account, we get

$$\prod_{m=1}^N \Delta E_{m0} = (\Delta E_1^0)^N e^{\phi_0(V)},$$

$$\prod_{m=1}^N \Delta E_{mN+1} = (\Delta E_N^0)^N e^{\phi_N(V)}, \quad (21)$$

where the functions $\phi_0(V)$ and $\phi_N(V)$ are

$$\phi_0(V) = - \sum_{m=1}^N \frac{eV\eta_M}{\Delta E_1^0} m = - \frac{eV\eta_M}{2\Delta E_1^0} N(N+1),$$

$$\phi_N(V) = \sum_{m=1}^N \frac{eV\eta_M}{\Delta E_N^0} (N-m+1) = \frac{eV\eta_M}{2\Delta E_N^0} N(N+1). \quad (22)$$

Thus, we arrive at the formula for the squared matrix element of the superexchange interaction

$$|V_{0N+1}(V)|^2 = |V_{0N+1}(0)|^2 e^{\phi_0(V) + \phi_N(V)}, \quad (23)$$

where

$$|V_{0N+1}(0)|^2 \equiv \frac{|V_{01}V_{NN+1}|^2}{\Delta E_1^0 \Delta E_N^0} \left(\frac{V_B}{\sqrt{\Delta E_1^0 \Delta E_N^0}} \right)^{2(N-1)}. \quad (24)$$

is the squared matrix element of the superexchange interaction between the terminal groups of a molecular wire in the case where the applied electric field is zero.

We chose the direct and reverse rates which describe hops of the electron between terminal groups of the wire and microelectrodes in the following form [40, 41]:

$$\chi_{-L(-R)} = \chi_0 [1 - n_F(\Delta E_{L(R)})] \Phi_0^{(L(R))}, \quad (25)$$

$$\chi_{L(R)} = \chi_{-L(R)} \exp[-\Delta E_L(R)/k_B T]. \quad (26)$$

Here, $n_F(\Delta E_L(R)) = [\exp(\Delta E_{L(R)}/k_B T + 1)]^{-1}$ is the Fermi distribution function with the introduced energy gaps which are determined with the help of the relations

$$\begin{aligned} \Delta E_L &= E_0 - E_F = \Delta E_L^0 - eV\eta_L, \\ \Delta E_R &= E_{N+1} - (E_F - eV) = \Delta E_R^0 + eV\eta_R, \end{aligned} \quad (27)$$

respectively, for the left and right microelectrodes, and E_F is the Fermi energy of the microelectrode metal. The functions $\Phi_0^{(L(R))}$ are set by the following formulas:

$$\begin{aligned} \Phi_0^{(L)} &= e^{-S_0 \coth(\hbar\omega_0/k_B T)} I_0 \left(2S_0 [n(\omega_0)(1 + n(\omega_0))]^{1/2} \right), \\ \Phi_0^{(R)} &= e^{-S_{N+1} \coth(\hbar\omega_{N+1}/k_B T)} \times \\ &\times I_0 \left(2S_{N+1} [n(\omega_{N+1})(1 + n(\omega_{N+1}))]^{1/2} \right). \end{aligned} \quad (28)$$

The quantities S_0 and S_{N+1} are related to the rearrangement energies and the frequencies referred to the terminal groups of the wire as follows: $S_{0(N+1)} \equiv \lambda_{0(N+1)}/\hbar\omega_{0(N+1)}$. In formula (25), the parameter χ_0 presents the energy broadening of a one-electron level which is caused by the interaction with one of the metal microelectrodes in the case of the absence of the electron-phonon interaction.

Taking (16) and (26) into account, we can get

$$\begin{aligned} \chi_{-L}\chi_R\beta_0\beta_N\beta^{N-1} &= \chi_{-R}\chi_L\alpha_0\alpha_N \exp(-eV/k_B T), \\ \chi_R\chi_{-L}k_2 &= \chi_{-R}\chi_Lk_1 \exp(-eV/k_B T). \end{aligned} \quad (29)$$

The above-written relations for the rates of ET allow us to reduce the formula for the stationary interelectrode current (5) to a more compact form. We will consider separately the cases of positive and negative differences of applied potentials. If $V > 0$, we get, in view of (29),

$$I^{(+)}(V) = e \left[1 - \exp(-eV/k_B T) \right] \frac{\chi_L}{\Gamma_L} \frac{F_1^+}{F_2^+}, \quad (30)$$

where

$$F_1^+ = k_1 \left(\frac{1 - \gamma_+^{N-1}}{1 - \gamma_+} + \frac{\alpha}{\beta_0} + \frac{\alpha}{\alpha_N} \gamma_+^{N-1} \right) + \frac{\alpha_0}{\beta_0} \alpha, \quad (31)$$

and

$$\begin{aligned} F_2^+ &= \left(1 + \frac{k_1}{\Gamma_L} + \frac{k_2}{\Gamma_R} \right) \left(\frac{1 - \gamma_+^{N-1}}{1 - \gamma_+} + \frac{\alpha}{\beta_0} + \frac{\alpha}{\alpha_N} \gamma_+^{N-1} \right) + \\ &+ \frac{\alpha\alpha_0}{\beta_0\Gamma_L} + \frac{\alpha\beta_N}{\Gamma_R\alpha_N} \gamma_+^{N-1}. \end{aligned} \quad (32)$$

Analogously, for $V < 0$, we get

$$I^{(-)}(V) = -e \left[1 - \exp(-|eV|/k_B T) \right] \frac{\chi_R}{\Gamma_R} \frac{F_1^-}{F_2^-}, \quad (33)$$

where

$$F_1^- = k_2 \left(\frac{1 - \gamma_-^{N-1}}{1 - \gamma_-} + \frac{\beta}{\alpha_N} + \frac{\beta}{\beta_0} \gamma_-^{N-1} \right) + \frac{\beta_N}{\alpha_N} \beta, \quad (34)$$

and

$$\begin{aligned} F_2^- &= \left(1 + \frac{k_1}{\Gamma_L} + \frac{k_2}{\Gamma_R} \right) \left(\frac{1 - \gamma_-^{N-1}}{1 - \gamma_-} + \frac{\beta}{\alpha_N} + \frac{\beta}{\beta_0} \gamma_-^{N-1} \right) + \\ &+ \frac{\beta_N\beta}{\alpha_N\Gamma_R} + \frac{\beta\alpha_0}{\Gamma_L\beta_0} \gamma_-^{N-1}. \end{aligned} \quad (35)$$

In formulas (31)-(32) and (34)-(35), we introduced the parameters

$$\begin{aligned} \gamma_+ &\equiv \beta/\alpha = \exp(-eV\eta_M/k_B T), \\ \gamma_- &\equiv \alpha/\beta = \exp(-|eV|\eta_M/k_B T) \end{aligned} \quad (36)$$

which characterize the interrelation between the reverse and direct rates of ET in the scope of the regular part of the wire for $V > 0$ and $V < 0$, respectively. Combining (30) and (33), we can write the formula for the stationary interelectrode current in the form

$$I = \theta(V)I^{(+)}(V) + (1 - \theta(V))I^{(-)}(V), \quad (37)$$

where $\theta(V)$ is the theta function. Formula (37) is the final expression for the stationary combined thermally activated inelastic and long-range elastic interelectrode current which is valid for both positive and negative potential differences V .

4. Simplified Formula for the Current

The expression for the stationary interelectrode current (37) is a complicated combination of both contributions from the thermally activated inelastic mechanism which is characterized by the rates $\alpha_{0(N)}, \alpha, \beta_{0(N)}$, and β and the long-range superexchange mechanism which is described with the help of the direct k_1 and reverse k_2 rates of ET between the terminal groups of the wire. Such a combination is a result of the rather complicated dependence of the current on the difference of potentials applied to microelectrodes V . However, if the inequalities

$$k_1, \alpha_0 \ll \Gamma_L, \quad k_2, \beta_N \ll \Gamma_R, \quad (38)$$

which correspond to faster hops of the electron from the terminal groups of the wire on the electrodes as compared with the hops into the wire, are satisfied, then the interelectrode current (37) can be easily presented in the form of the sum of both contributions as

$$I = I_{\text{sup}}(V) + I_{\text{seq}}(V). \quad (39)$$

The superexchange component of the current is set by the relation

$$I_{\text{sup}}(V) = e \left[1 - \exp(-|eV|/k_B T) \right] \left[\theta(V) \chi_L / \Gamma_L k_1 - (1 - \theta(V)) \chi_R / \Gamma_R k_2 \right] \quad (40)$$

which shows that the superexchange contribution is concentrated in the rates k_1 (for $V > 0$) and k_2 (for $V < 0$). These rates describe the long-range electron transfer between the terminal groups of the molecular wire. Respectively, the hopping component of the current is defined as

$$I_{\text{seq}}(V) = e \left[1 - \exp(-|eV|/k_B T) \right] \left[\theta(V) \frac{\chi_L}{\Gamma_L} \frac{\alpha_0 \alpha_N}{\beta_0 + \alpha_N} \times \left[1 + \xi_+ \frac{1 - \gamma_+^{N-1}}{1 - \gamma_+} \right]^{-1} + (\theta(V) - 1) \frac{\chi_R}{\Gamma_R} \frac{\beta_0 \beta_N}{\beta_0 + \alpha_N} \times \left[1 + \xi_- \frac{1 - \gamma_-^{N-1}}{1 - \gamma_-} \right]^{-1} \right], \quad (41)$$

where we introduced the parameters

$$\xi_+ = \frac{1 - (\alpha/\alpha_N)(1 - \gamma)}{(\alpha/\beta_0) + (\alpha/\alpha_N)}, \quad \xi_- = \frac{1 - (\beta/\beta_0)(1 - \gamma_-)}{(\beta/\alpha_N) + (\beta/\beta_0)}. \quad (42)$$

The hopping component of the current depends on the quantities γ_+ and γ_- and the rates which correspond to the thermally activated hopping mechanism of electron transfer. The latter enter the quantities ξ_+ and ξ_- . Formulas (40)–(42) allow us to analyze the contribution of each of the mechanisms to the general dependence of the interelectrode current on the potential difference.

5. Discussion and Main Results

The analytic formula obtained by us for the combined thermally activated inelastic and long-range elastic stationary interelectrode current, Eq. (37) and its approximate variant, which is the sum of the superexchange and hopping components (37), can serve as a basis for studying the influence of dynamic and relaxation factors on the current-voltage characteristics of the current through a molecular wire, where the terminal groups play the role of a donor and an acceptor for an electron. In addition, we will study the dependence of the differential conduction $g(V)$ on the difference of applied potentials V which is connected with the current by the relation

$$g(V) = \frac{dI(V)}{dV}. \quad (43)$$

In Fig. 2,*a* and Fig. 2,*b*, we demonstrate the agreement between the full and approximate (39) formulas describing the dependences of the current-voltage characteristic of the current and the differential conduction through a symmetric molecular wire on the difference of potentials applied to the microelectrodes.

The performed analysis of the $I - V$ characteristics showed that, for the short molecular chains, in which the LUMO levels of the regular part of a wire are much higher than the LUMO levels of the terminal groups (this corresponds to great energy gaps ΔE_0^0 and ΔE_{N+1}^0), the elasticity-based mechanism of $I_{\text{sup}}(V)$ dominates as compared with the sequential one of $I_{\text{seq}}(V)$ (see the insert in Fig. 2,*a*).

In the case of a molecular wire with the energy asymmetry conditioned by a nonzero value of the driving reaction force ΔE^0 , we observe the asymmetric current-voltage behavior of the current (see Fig. 3,*a*) and the conduction (Fig. 3,*b*). Thus, a molecular wire reveals the rectification properties which become stronger with increase in ΔE^0 . The rectification properties of a molecular wire are conditioned by the asymmetry of the matrix element of the superexchange interaction (23). We note that if $\Delta E^0 = 0$, then $\Delta E_1^0 = \Delta E_N^0$, and, for small V , we can consider that $|V_{0N+1}(V)|^2 \approx |V_{0N+1}(0)|^2$. As a result, we observe the symmetric behavior of the current (Fig. 3,*a*). But if $\Delta E^0 \neq 0$, for example if $\Delta E_1^0 < \Delta E_N^0$, we are faced with the asymmetry of the $I(V)$ characteristic of the current caused by the exponential growth of $|V_{0N+1}(V)|^2 \approx \exp(\phi_0(V) + \phi_N(V))$ for $V < 0$ [see (23)].

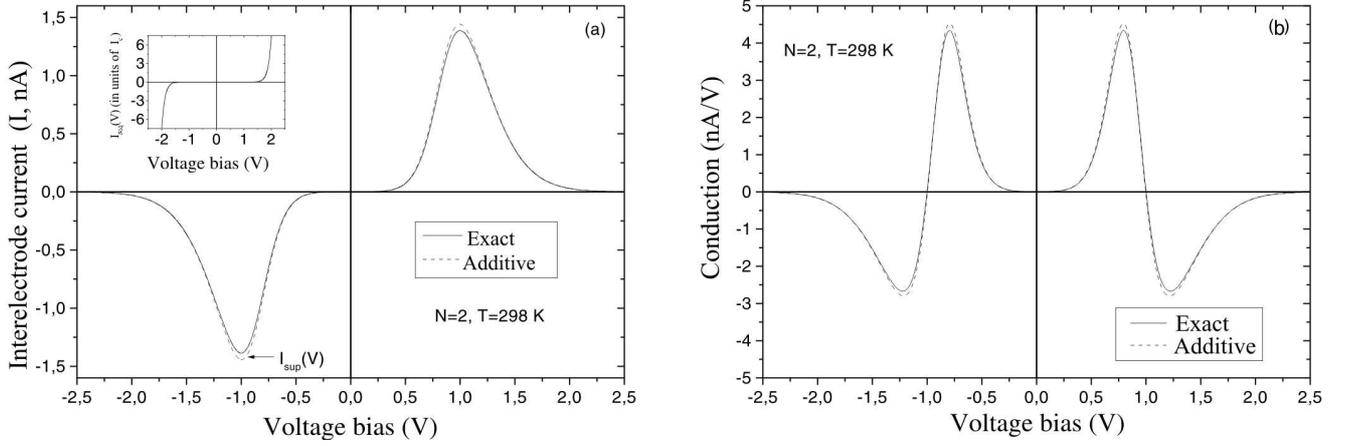


Fig. 2. Current-voltage characteristic (a) and differential conduction of a wire (b) in a wide range of voltages. The agreement between the full (37) and approximate (39) descriptions of the dependence of the interelectrode current on the potential difference V (a) is seen. The insert shows the sequential component of the current $I_{\text{seq}}(V)$ (in units of I_e). The calculations were carried out with the parameters: $\Delta E_L^0 = \Delta E_R^0 = 0.25$ eV, $\Delta E_1^0 = \Delta E_1^0 = 1.15$ eV, $V_{10} = V_{NN+1} = 0.09$ eV, $V_B = 0.1$ eV, $\lambda_{10} = \lambda_{NN+1} = 1$ eV, $\lambda_B = 1.4$ eV, $\lambda_{0N+1} = 0.4$ eV, $\omega_{01} = \omega_B = \omega_{NN+1} = \omega_{0N+1} = 500$ cm^{-1} , $\omega_0 = \omega_{N+1} = 800$ cm^{-1} , $\chi_0 = 10^{14}$, $\eta_L = \eta_R = 0.25$, and $\eta_M = 0.16$

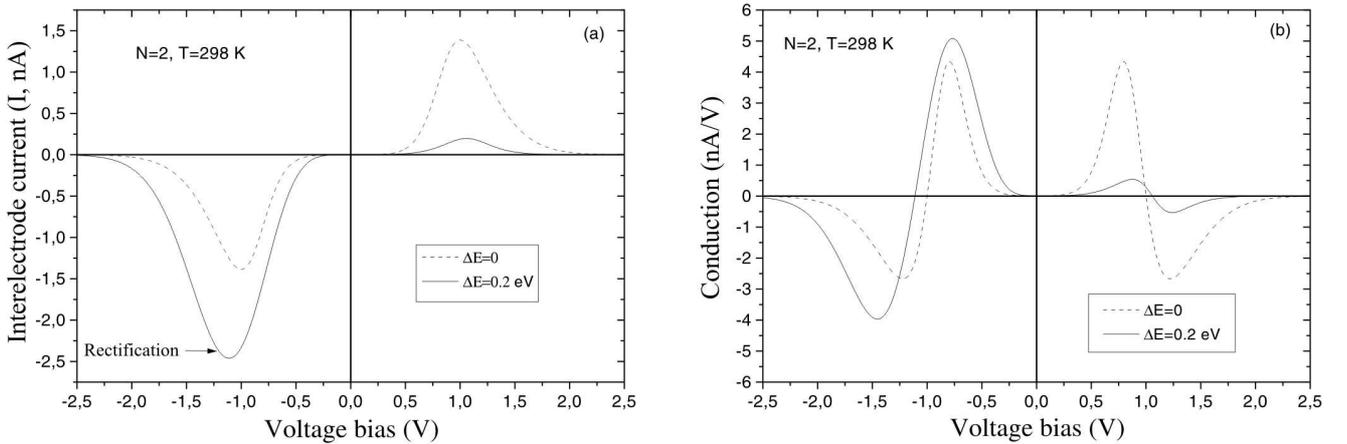


Fig. 3. Rectification properties of the interelectrode current conditioned by the energy asymmetry of a molecular wire (a) and the asymmetric current-voltage behavior of the differential conduction (b). The calculations were carried out with the same parameters as in Fig. 2

To analyze the dependence of the current on the potential difference, we consider the case where the vibrational energy of centers $\hbar\omega_{0N+1}$ strongly exceeds the average thermal energy $k_B T$ so that $n(\omega_{0N+1}) \ll 1$. In this case, the Bessel function which determines the Franck–Condon factor of the rates k_1 and k_2 is a small value. Therefore, $I_\nu(z) \approx \frac{z}{2} / \Gamma(\nu + 1)$ [46], where $\Gamma(x)$ is the gamma-function. Taking this asymptotics into account, we can write

$$k_1 \approx \frac{2\pi}{\hbar^2 \omega_{0N+1}} |V_{0N+1}(V)| e^{-S_{0N+1}} S_{0N+1}^{\nu_+} / \Gamma(\nu_+ + 1),$$

$$k_2 \approx \frac{2\pi}{\hbar^2 \omega_{0N+1}} |V_{0N+1}(V)| e^{-S_{0N+1}} S_{0N+1}^{\nu_-} / \Gamma(\nu_- + 1), \quad (44)$$

where

$$\nu_+ \equiv \nu_{0N+1} = \frac{1}{\hbar\omega_{0N+1}} (\Delta E^0 + |eV|(1 - \eta_L - \eta_R)),$$

$$\nu_- \equiv \nu_{N+10} = \frac{1}{\hbar\omega_{0N+1}} (-\Delta E^0 + |eV|(1 - \eta_L - \eta_R)). \quad (45)$$

With increase in V , the energy levels of LUMO of a wire decrease, which corresponds to the growth of the interelectrode current. At some value of $V = V_{\text{res}}$ where the energy level E_0 of the electron captured by the extreme left center becomes lower than the Fermi energy level E_F of the corresponding microelectrode (in the case where $V > 0$), the so-called resonance mode is switched on. In the analogous situation for $V < 0$, let the level E_{N+1} become equal to the Fermi energy level of the right microelectrode. In this case, the interelectrode current reaches the maximum value. For $V \gg V_{\text{res}}$, $\nu_{\pm} \gg 1$, and thus we can approximately consider that $\Gamma(\nu_{\pm} + 1) \approx \sqrt{2\pi/\nu_{\pm}} \nu_{\pm}^{\nu_{\pm}} \exp(-\nu_{\pm})$. This indicates the sharp drop of the rates k_1 and k_2 and, as a result, the blocking of the interelectrode current. The quantities ν_{\pm} are responsible for the number of phonons which are captured during the hop of an electron between the terminal groups of a wire. Therefore, the greater the number of vibrational quanta captured during the (ET) process, the less the efficiency of the electron transfer. At great values of the difference of applied potentials, i.e. if $V \gg 1$, ν_{\pm} are also great. In this case, the direct superexchange rate k_1 for $V > 0$ and, analogously, the reverse rate k_2 for $V < 0$ become small. Moreover, the superexchange component of the current $I_{\text{sup}}(V)$ decreases, and, as a result, the interelectrode current becomes blocked for great V .

One more factor, in addition to the energy one, which affects the rectification properties of a molecular wire is a geometric position of terminal groups of a wire relative to microelectrodes. In many experiments on the study of the conduction of organic molecules, in particular, with the help of scanning tunneling microscopy, one of the ends of a molecule which is positioned on a metal substrate is fixed, whereas the other end is free. With the help of a scanning needle, one can vary the distance between it and the free end of a molecule and thus can control the potential drop between the metal microelectrode and the end center of the wire [47]. In our model, such a control can be realized with the help of the parameters η_L and η_R . In this case, the parameter η_R can be fixed, and η_L can be variable, and one can obtain the effect of rectification of the current even if the driving reaction force ΔE^0 is zero. In Fig. 4, we show how a geometric asymmetry leads to the rectification properties of a molecular wire which become stronger with increase in the potential drop at the left end of a wire.

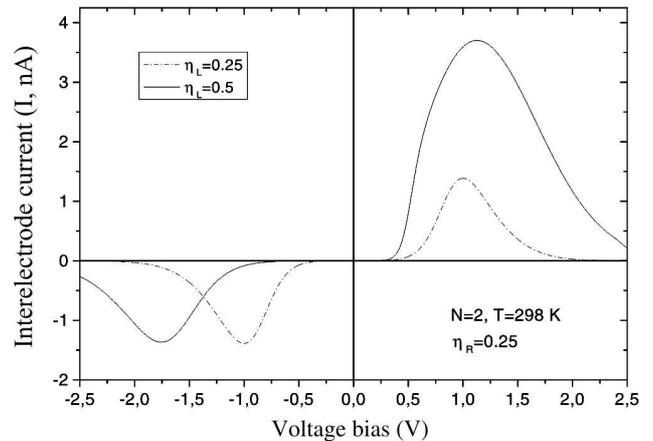


Fig. 4. Rectification properties of the interelectrode current caused by the geometric asymmetry of a molecular wire. The calculations were carried out with the same parameters as in Fig. 2

6. Conclusion

Our goal was to study the role of the terminal groups of a molecular wire in the formation of a combined thermally activated inelastic and long-range elastic interelectrode current along a molecular wire, in which the terminal groups play the role of a donor and an acceptor of the electron. The main attention was paid to the analysis of the influence of the energetic and geometric characteristics of a molecular wire on the current-voltage characteristics of the current. While analyzing the $I-V$ characteristics of a wire, we used the analytic formula for the stationary interelectrode current (37) which is a complicated combination of the contributions of both the long-range superexchange mechanism and the sequential hopping one. However, for short molecular chains the superexchange mechanism turns out to be dominant relative to the hopping one (Fig. 2, a). Therefore, we can consider that $I \approx I_{\text{sup}}(V)$. The contribution of the sequential component is slight and can play a certain role only for long molecular chains. We have revealed the nonlinear behavior of the current $I = I(V)$ which can be symmetric for the identical positions of the LUMO levels of the terminal groups of a wire (Fig. 2, a) with the zero driving reaction force ΔE^0 and asymmetric with clearly manifested rectification properties (Fig. 3, a). Just the asymmetry (relative to V) of the squared matrix element of the superexchange interaction between the terminal groups of a wire $|V_{0N+1}(V)|^2$ can serve as the basic factor which influences the rectification properties of a molecular wire.

In addition, we have shown that, under great electric fields, there occurs the blocking of the interelectrode current, which is caused by the effect of the relaxation factors due to the presence of the thermal environment. Namely the strong electron-phonon interaction can lead to a sharp decrease in the interelectrode current when it reaches some peak value I_{peak} . This happens after the switch-on of the resonance mode when the LUMO levels of the terminal groups of a wire fall below the Fermi level of the electrode metal. For a symmetric molecular wire, $I_{\text{peak}} \approx 1.35$ nA, and the resonance value of the potential difference $V_{\text{res}} \approx 1$ V. Just for such a potential difference, the differential conduction becomes zero (Fig. 2, b). For $V > V_{\text{res}}$, the region of negative differential conduction ($g(V) < 0$) arises. We note that similar $I-V$ characteristics were observed experimentally in the study of the conduction of nanopores [43, 48]. However, the application of the presented theory to the description of experimental data will require the additional analysis.

The rectification of the interelectrode current can occur also in the case of the geometric asymmetry of a molecular wire, in particular for different values of the potential drops between the electrodes and the terminal groups of a wire, which is controlled by the factors η_L and η_R (see Fig. 4). When η_L increases and η_R is fixed, the peak value of the current increases for $V > 0$, whereas it is practically constant for $V < 0$.

In conclusion, we emphasize that the energy position of the terminal groups of a wire relative to each other and their geometric disposition near the microelectrodes are defining factors which influence the rectification properties of the interelectrode current, by indicating two possible mechanisms of control over the current: the geometric and energetic ones. At the same time, the phenomenon of the blocking of the interelectrode current (and, as a result, the appearance of negative differential conduction) is related to the relaxation processes which are running in the system.

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ВИПРЯМНІ ВЛАСТИВОСТІ МОЛЕКУЛЯРНОГО ПРОВОДУ, ЗУМОВЛЕНІ ЙОГО КРАЙОВИМИ ГРУПАМИ

Я.Р. Зелінський, Е.Г. Петров

Резюме

Проаналізовано вольт-амперні характеристики молекулярного проводу, в якому рівні найнижчих незаповнених молекулярних орбіталей (ННМО) внутрішньої частини проводу лежать значно вище як за рівень Фермі металевих електродів, так і за рівні ННМО кінцевих груп. Останні відіграють роль донорного та акцепторного центрів і забезпечують дію комбінованого дистанційного суперобмінного і послідовного стрибкового механізмів електронного переносу. Показано, що при великих значеннях прикладеної до мікроелектродів різниці потенціалів відбувається блокування міжелектродного струму, зумовлене сильною електрон-фононою взаємодією. Додатково виявлено ефект випрямлення струму у випадку молекулярного проводу із ненульовим значенням керуючої донорно-акцепторної сили реакції, коли суперобмінний механізм є домінуючим у формуванні струму.