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Nonlinear Properties of an Inter-Electrode Current Through a Short Molecular Wire

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The formation of current through a *short* molecular wire is determined not only by jumps of separate transferring electrons between the sites of electron localization within the wire, but the effect of Coulomb repulsion of the electrons must be accounted for as well. This repulsion blocks the appearance of an additional transferring electron in the wire if the wire already contains the transferring electron at an arbitrary wire unit. The Coulomb inhibition effect results in a strong nonlinearity of both, the inelastic inter-electrode current-voltage characteristics and current-temperature characteristics. Among the characteristic novel features are the saturation of the current at high voltage bias and its suppression at both, low and high temperatures.

Keywords: molecular wire; inter-electrode current; Coulomb inhibition

INTRODUCTION

There are a number of synthesised macromolecular nanostructures like metallomacrociclic assembles[1], metal containing fullerene structures [2], conductive polymers [3], rigid oligoporphyrins [4], to name only a few,

where electron transfer (ET) proceeds as an inelastic electron hopping localization within the specific structure units of a molecular nanostructure. When such a molecular nanostructure is embedded between two microelectrodes we deal with a so-termed molecular wire. In recent years, the main focus has centred around the behaviour of the elastic tunnel current mediated by a molecular wire [5-9]. At the same time, inelastic tunnel current has previously been studied in the simplest model of a molecular wire[10,11]; namely when inelastic ET involves the terminal units only while all inter wire sites play solely a virtual bridging role for a superexchange mechanism. Thus, nonlinear effects caused by Coulomb repulsion between the transferring electrons have previously not been taken into consideration.

The objective of the present work is to clarify the basic properties of an inelastic inter-electrode current formed by electron hopping across the wire units. The hopping mechanism assumes a fast relaxation process within each wire unit. When the molecular wire is rather *short* in length, a strong Coulomb repulsion appears between the transferring electrons captured by the wire units. Here, the role of such a repulsion along with the character of inter-site and site-electrode transfer quantum rates is studied in the context of nonlinear properties for the emerging current.

THEORETICAL MODEL

Let a voltage V be applied between the left (L) and the right (R) electrodes connected by a regular molecular wire of N identical units, Fig. 1.

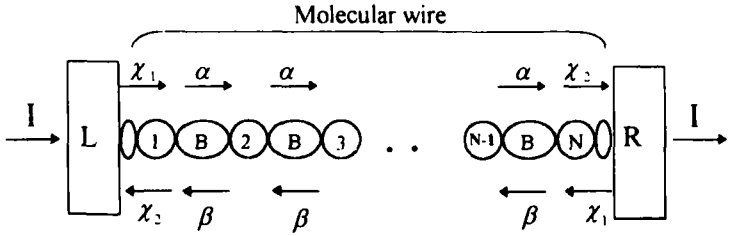

FIGURE 1 Scheme of kinetic processes in molecular wire of N units.

The units are separated by spacers/bridges (B): this implies that the site-site couplings are far too small to keep the coherency in the course of inter-electrode ET. Therefore, the relaxation process within each wire unit with forward (α) and backward (β) site-site quantum transfer rates. Correspondingly, the hopping between terminal wire units and adjacent leads is characterised by the site-electrode (χ_1) and the electrode-site (χ_2) transfer rate. The form of all these rates can be obtained within the framework of a Golden rule calculation. Generally, one has to solve a set of quantum kinetic equations for the wire occupancies which has a complicated structure due to a Coulomb repulsion of the electrons in the course of their transfer across a molecular wire.

In the present paper, a model of strong Coulomb repulsion is considered which assumes that the molecular wire is closed for the ET if the wire already contains the transferring electron [12]. Such a situation can be realised with a short molecular wire (not more than 40-50 Å in length). In the framework of model, the number of possible wire states involved in the ET, becomes drastically reduced. Only those states with zero and single transferring electron per wire are the working wire states. Let W_0 and W_n, (n = 1,2,...N), denote the weights of corresponding working states. As far as only a single transferring electron can occupy the wire in the course of ET, it is useful to introduce the average site occupancy P_n which characterises the chance for the transferring electron to be captured by the n-wire unit. In terms of these average site occupancies the weight for the empty wire state is of the form $W_0 = \prod_{n=1}^{N}(1-P_n) \equiv \prod_{n=1}^{N}(1+U_n)^{-1}$ whereas the weight of wire state with the transferring electron captured by the n-unit reads instead $W_n = P_n\prod_{j\neq n}^{N}(1-P_j) = W_0U_n$. The weights specify the probabilities $P_0 = W_0/(W_0+\sum_{j=1}^{N}W_j)$ and $P_n = W_n/(W_0+\sum_{j=1}^{N}W_j)$ to find the *wire* with no transferring electron and with single captured electron, respectively; thus, the average number of captured electrons is

$$\bar{n} = \sum_{n=1}^{N} P_n = \frac{\sum_{n=1}^{N} U_n}{1+\sum_{n=1}^{N} U_n}. \qquad (1)$$

The current itself is given by $I = -2e\dot{N}_L = 2e\dot{N}_R$ (the factor 2 appears due to two equivalent spin projections of an electron). In accord with the scheme of Fig. 1, the time derivation of number of electrons related to the L-th electrode is $\dot{N}_L = -\chi_1 W_0 + \chi_2 W_1$. This equation has to be completed by the set of equations for W_0 and all W_n. These quantities follow from the set of nonlinear kinetic equations for the site occupancies P_n. We have derived those nonlinear equations from a quantum master equation for the corresponding many-particle system. Simultaneously, we specified all transfer rates χ_1, χ_2, α, and β. Below, we restrict ourselves by the analysis of steady state ET only. In this case, set of nonlinear kinetic equations for P_n reduces to the set of *linear* equations for the auxiliary quantities U_n; it thus can be solved in the form

$$U_n = kf_N^{(n)}, \quad f_N^{(n)} = \frac{1-\gamma^{N-1}+2\zeta\gamma^{N-n}(1-\gamma)}{1-\gamma^{N-1}+\zeta(1+\gamma^{N-1})(1-\gamma)} . \qquad (2)$$

In Eq. (2), the quantities $\kappa \equiv \chi_1/\chi_2$, $\gamma \equiv \beta/\alpha$, and $\zeta \equiv \alpha/\chi_2$ characterise the ratio of transfer rates while the function $f_N^{(n)}$ specifies the transfer properties of the wire. It follows from the solution of the set of nonlinear equations that the current can be represented in form $I = 2eW_0\chi_1(1-f_N^{(1)})$ where W_0 can be looked upon as a transmission factor.

To analyze the properties of the resulting inter-electrode current we note that the terminal units of the wire are supposed to be positioned not very far from the corresponding electrode surfaces, cf. Fig.1. This means that the transfer rates χ_1 and χ_2 are practically voltage-independent quantities. We can introduce therefore a characteristic voltage independent parameter $I_0 \equiv 2e\chi_2$. To estimate the order of magnitude for I_0 one notes that site-electrode transfer rate χ_2 determines the width Γ of the localized electronic level coupled to the leads [13], i.e. with the value being of the order of $(10^{-2} - 10^{2})$ cm^{-1}, depending on distance from the lead surface; e.g. at $\chi_2 = \Gamma/\hbar = 1cm^{-1} \approx 3\cdot 10^{10}$ sec^{-1}, we obtain that $I_0 \approx 10^{-8} A$. As far as the width Γ possesses only a minor dependence on temperature, we find that parameter I_0 presents a tem-perature insensitive value as well. Bearing this fact in mind we shall analyse just a relative current,

$$i \equiv I/I_0 = kW_0(1 - f_N^{(1)}). \qquad (3)$$

RESULTS AND DISCUSSION

Below, we discuss the results of our model for the case $\zeta << 1$. This situation corresponds to a slow site-site hopping in comparison with the site-electrode hopping. The case occurs when the site-site distance exceeds the site-electrode distance, cf. Fig.1. At $\zeta << 1$, we have $f_N^{(n)} \approx 1$ and $1 - f_N^{(1)} \approx \zeta(1-\gamma)$, yielding

$$i \equiv I/I_0 = \zeta \exp(-d)(1-\gamma)(1+\exp(-d))^{-N} \qquad (4)$$

where $k \equiv \exp(-d)$ and $d \equiv \Delta E_0/k_B T$. Here, $\Delta E_0 = E_0 - E_F$ is the energy difference between the position of the transferring electron being captured by a wire unit, and the position of an electron on the Fermi-surface of the electrode [11,12]; T denotes the temperature and k_B is the Boltzmann constant.

In accord with the form (4), the complete voltage dependence of nonlinear ET is dictated by the ratio $\gamma = \exp[-(E_n - E_{n+1})/k_B T]$, where $E_n - E_{n+1} = eV/(N-1)$ reflects the voltage drop caused by the site-site energy bias for two neighbouring wire units. Because the ratio $\gamma = \exp[-V/V_0(N-1)]$ vanishes at $V \gg V_0 \equiv k_B T/e$, the current then reaches its saturation value which is a function of the temperature T and the number N of wire units. E.g. if we take $I_0 \approx 10^{-8}$ A/sec according to the preceding discussion, then for a wire of 6 units one obtains $I_{satur} \approx 3.5$ pA. At a small voltage bias, $V << V_0$, the current rises with the voltage in accord with Ohm's law, $I = GV$, where G is the conductance. Analytically, this result follows from Eq. (3) if one takes into consideration the relation that $1 - \gamma \approx V/V_0(N-1)$.

Next, let the voltage be a fixed value. Upon introducing parameter $a = \Delta E_0/k_B T_0$ and the dimensionless temperature $\Theta = T/T_0$ where $T_0 \equiv eV/k_B$, we can recast Eq. (3) as follows

$$i \equiv I/I_0 = \zeta e^{-\frac{a}{\Theta}}(1 - e^{-\frac{a}{\Theta(N-1)}})(1 + e^{-\frac{a}{\Theta}})^{-N} \quad . \qquad (5)$$

This form depicts clearly that the inter-electrode current vanishes in the two limiting cases of low and high temperatures, see Fig. 2. In order to

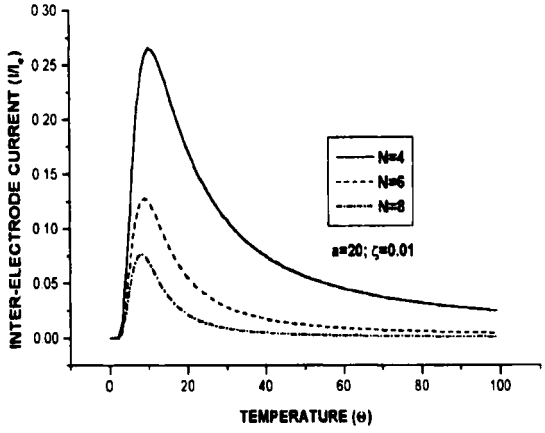

FIGURE 2 Inter-electrode current *vs* temperature ($I_e \equiv I_0 \cdot 10^{-4}$).

comprehend its temperature dependence, we note that at low temperature ($\Theta \ll 1$) the result (5) reduces to a simple law $I \approx \zeta \exp(-a/\Theta)$. The factor $\exp(-a/\Theta)$ determines the efficiency of a thermal process which delivers the electrons from the Fermi surface of electrode into the molecular wire. When Θ is very low, essentially no electrons can get onto the wire, yielding $I = 0$. With increasing temperature, the thermal process starts to deliver electrons to the wire; the wire captures these electrons, and hence the average number of captured electrons, $\bar{n}$, increases as well, but consistently does not exceed one, see in Fig. 3.

This rise of current is accompanied by an increase of $\bar{n}$. It can also be deduced from the analytic form

$$\bar{n} = Ne^{-\frac{a}{\Theta}}\left(1 + Ne^{-\frac{a}{\Theta}}\right)^{-1} \tag{6}$$

which follows from Eq. (1) at $\zeta \ll 1$. The saturation of $\bar{n}$ occurs around a temperature $T \approx (10 - 20)T_0$. In this very same temperature regime the current reaches its maximal value. The following decrease of the current with increasing rise of temperature, results from the enhanced role of backward ET. At $T \gg T_0$ we have $\alpha \approx \beta$ and thus the forward and backward ET fluxes become compensated.

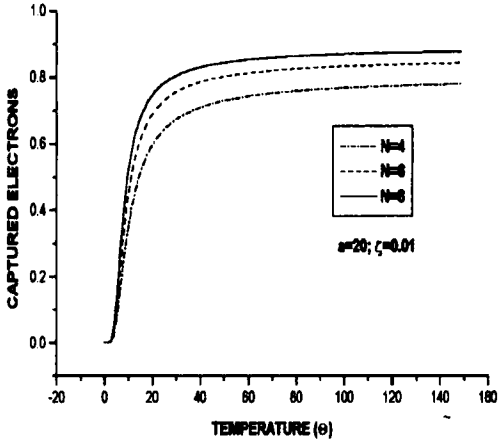

FIGURE 3 Average number of captured electrons *vs* temperature.

CONCLUSION

A kinetic model for a nonlinear electron transfer process has been presented with this work. The model is based on Coulomb repulsion of transfering electrons captured by the structural units of a molecular wire. The important case of a short wire with strong Coulomb repulsion is considered: then, the wire is assumed to be closed for the transfer if even a single transferring electron has been already captured by the wire in the course of ET. In this case, only a limited number of wire states participates in the formation of an inter-electrode electron current. The current is thus determined by virtue of a competition between various

transfer quantum rates and the mechanism of strong Coulomb repulsion. Our novel approach may as well be applied to studies of transfer processes in polymer and biopolymer structures and in ion channels.

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