

Coulomb repulsion effect on the tunnel current through the redox molecule in the weak tunneling limit

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Effects are predicted for electron tunneling through a one-level bridged contact immersed in the electrolyte solution at ambient conditions in the case of weak electronic interaction of the bridge molecule with the leads and strong electron-phonon coupling. They are (1) narrow-width ($\sim k_B T$) Coulomb blockade peaks in the current/gate voltage dependence, (2) rectification due to the Coulomb repulsion, and (3) a number of peaks in the differential conductance for the one-level system. Unlike previous work, the number of these peaks can amount to four that is related with oxidized and reduced states of both ionization and affinity levels of the bridge molecule.

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Electron tunneling through the objects of nanoscale or molecular size in solid and liquid junctions continues to attract attention of researchers (see, e.g., review article¹ and references therein). In the theory of these phenomena the interest shifts gradually to the consideration of the systems where the quantum dot or a bridge molecule confined in the tunneling gap interacts strongly with vibrational modes (see Refs. 2 and 3, and a number of recent papers^{4–13}). The physical mechanism of electron transfer in this case have much in common with the so-called redox-mediated electron tunneling in electrochemical systems first considered theoretically in Ref. 14 and further elaborated in a large number of works (e.g., reviewed in Ref. 1). The notion “redox molecule” means that the bridge molecule has two quasistable states with the empty electron level (oxidized state) and occupied one (reduced state). The transitions between these states occur due to thermal fluctuations of the vibrational modes of the polar condensed media. The limit of the weak interaction of the bridge group with the leads (the weak tunneling limit) is one of the important particular cases of the electron tunneling. The electron transfer here is of sequential character with intermediate electron localization at the bridge group due to full relaxation of the vibrational subsystem. The one-electron process was usually considered which corresponds to the spinless model or to the limit of infinitely large Coulomb repulsion U between two electrons occupying the same electron energy level of the bridge group. Even this simple system demonstrates interesting spectroscopic and transistor-like properties with the variation in the gate and bias voltages.¹⁵

The bridge molecules which can accept two or more electrons represent more interesting systems. These may be the molecules with closely located excited one-electron energy levels or the molecules with small or moderate values of the Coulomb repulsion energy U .

A simple and effective method of calculation of the tunnel current in the weak tunneling limit is the use of the rate equations for the populations of the electron states of the system. This method was first applied to the case of one-electron transitions¹⁴ and further elaborated in Refs. 4, 6, 8, and 9. Recently it was extended to many-electron transitions.^{16,17} Calculations of the current/bias voltage de-

pendencies were performed for two-electron transfer through the bridge molecular orbital in the low-temperature limit for the case of the rather weak coupling with phonons and moderate values of the Coulomb repulsion energy.^{16,17} These dependencies demonstrate a steplike structure corresponding to the opening of new channels for the electron transfer with variation in the bias voltage.

The aim of the present paper is to show that, in the case of the weak tunneling limit and the strong interaction of the bridge molecule with the classical vibrational modes considered at the room temperatures ($k_B T \approx 0.025$ eV, where k_B is the Boltzmann constant and T is the temperature), a number of effects take place: (1) the clear-cut Coulomb blockade peaks with the width of the order of $k_B T$ in the tunnel current/gate voltage dependence; (2) a rectification effect in the current/bias voltage curve which depends on the value of the effective Coulomb repulsion energy; (3) in contrast to other works, there are up to four peaks in the differential conductance related with the oxidized and reduced states of both ionization and affinity levels of the bridge molecule.

The Hamiltonian of the system has a standard form:

$$H = H_{el} + \frac{1}{2} \sum_k \hbar \omega_k (p_k^2 + q_k^2), \quad (1)$$

where H_{el} is the effective electronic Hamiltonian:

$$H_{el} = \sum_{m\sigma} \varepsilon_m c_{m\sigma}^+ c_{m\sigma} + \sum_{\sigma} \left[\varepsilon_b(q_k) n_{\sigma} + \frac{1}{2} U n_{\sigma} n_{-\sigma} \right] + \sum_{m\sigma} (V_m c_{\sigma}^+ c_{m\sigma} + V_m^* c_{m\sigma}^+ c_{\sigma}), \quad (2)$$

the subscript m in the right-hand side (rhs) of Eq. (2) runs values k or p , ε_k and ε_p are the electronic energies of the lead quasiparticle states $|k\rangle$ and $|p\rangle$, respectively, σ is the spin projection, and $c_{m\sigma}^+$, $c_{m\sigma}$ are the creation and annihilation operators for these states. $\varepsilon_b(q_k)$ and $n_{\sigma} = c_{\sigma}^+ c_{\sigma}$ are the energy and occupation number operators of the valence orbital $|b\rangle$ of the bridge molecule. The third term in the rhs of Eq. (2) describes the coupling between the electronic states of the leads and the bridge molecule with V_m as the coupling constants. The second term in the rhs of Eq. (1) is the Hamiltonian of the phonon subsystem where p_k and q_k are the dimensionless momenta and coordinates of the solvent modes which will be considered in the classical limit in what

follows. ω_k are the effective frequencies corresponding to the normal modes q_k . Then the electronic energy of the valence orbital has the form

$$\varepsilon_b(q_k) = \varepsilon_b - \sum_k \gamma_k q_k. \quad (3)$$

Here ε_b is the bare “ionization” electronic energy level ε_b of the bridge molecule counted from the Fermi level of the left lead in the case when the electron-phonon interaction is absent and γ_k are the coupling constants describing the interaction of the valence orbital of the bridge molecule with the polarization of the condensed medium.

We consider a weak tunneling limit when Δ , $k_B T_K \ll k_B T \ll \lambda$ so that the rate equation method can be used.⁸ Here $\Delta = \Delta^L + \Delta^R$ is the total coupling strength of the valence level of the redox molecule with the left and right leads while T_K is the Kondo temperature, $\lambda = 0.5 \sum_k \gamma_k^2 / \hbar \omega_k$. The redox molecule can have three charge states: uncharged (0), singly charged (1), and doubly charged (2). The probabilities for these states are denoted as P_0 , $P_1 = P_\sigma + P_{-\sigma}$, and P_2 , where P_σ is the probability for the case when the valence level is occupied by single electron having spin projection σ , $P_\sigma = P_{-\sigma}$, and $P_0 + P_1 + P_2 = 1$. The rate equations have the form

$$dP_0/dt = -2k_{01}P_0 + k_{10}P_1, \quad (4)$$

$$dP_\sigma/dt = k_{01}P_0 - k_{10}P_\sigma - k_{12}P_\sigma + k_{21}P_2, \quad (5)$$

$$dP_2/dt = -2k_{21}P_2 + k_{12}P_1, \quad (6)$$

where $k_{ij} = k_{ij}^L + k_{ij}^R$ are the rate constants for the transitions between the charge states i and j , (i and $j=0, 1, 2$), which are the sum of the contributions from the tunneling to or from the left and right leads. It should be noted that the probability of the simultaneous two-electron transition is negligibly small in the weak tunneling limit because it is proportional to the second order of Δ and, moreover, is characterized by the large value of the Frank-Condon barrier which is four times that for one-electron transfer. Using Eqs. (4)–(6), one obtains for the steady-state probabilities and the tunnel current j

$$P_0 = k_{10}k_{21}/Z, \quad P_1 = 2k_{01}k_{21}/Z, \quad P_2 = k_{01}k_{12}/Z, \quad P_\sigma = P_1/2, \quad (7)$$

$$j = 2e[k_{21}(k_{01}^L k_{10}^R - k_{10}^L k_{01}^R) + k_{01}(k_{12}^L k_{21}^R - k_{21}^L k_{12}^R)]/Z, \quad (8)$$

where $Z = k_{10}k_{21} + k_{01}(k_{12} + 2k_{21})$. If one neglects P_2 (i.e., in the infinite U limit), Eqs. (4)–(8) turn to the corresponding equations of Ref. 6.

The rate constants are calculated using the Fermi golden rule and, for the classical phonon modes, can be written in the form (see, e.g., Ref. 18)

$$k_{ij}^\alpha = k^\alpha \int \frac{d\varepsilon}{2k_B T} f_\alpha(\varepsilon) \exp[-(\lambda - \Delta F_{ji}^\alpha - \varepsilon + \varepsilon_F^\alpha)^2 / 4\lambda k_B T], \quad (9)$$

for $j > i$ and

$$k_{ij}^\alpha = k_{ji}^\alpha \exp(-\Delta F_{ij}^\alpha / k_B T), \quad (10)$$

for $j < i$. Equation (9) represents the multiphonon transition probability for electron transfer from an energy level ε in the metal to the electron energy level of the bridge molecule in the high-temperature limit for the phonons averaged over the electron energy spectrum of the leads. The exponential in the

rhs of Eq. (9) is averaged (over phonon states) Franck-Condon factor in the high-temperature limit. Equation (9) represents an extension of known equations for multiphonon transitions in the bulk of the medium between two localized electron states¹⁹ to the electron transfer between the metal and localized electron state.¹⁸ Here $\alpha=L$ or R , $f_\alpha(\varepsilon)$ are the Fermi functions of the left and right leads having the Fermi energies ε_F^α , the constants k^α are proportional to Δ^α and the detailed balance principle was used in obtaining Eq. (10), $\Delta F_{10}^L = e(\xi\eta + \gamma V) - k_B T \ln(2)$ and $\Delta F_{10}^R = \Delta F_{10}^L - eV$.²⁰ $\eta = \varphi_0 - \varphi$ is the gate voltage, where φ is the potential of the left lead and φ_0 is the equilibrium potential of the left lead for the process of transfer of the first electron (i.e., when $\varphi = \varphi_0$ and $V=0$), the process of the transfer of the first electron to or from the redox molecule is in equilibrium at the left lead so that $2k_{01}^L = k_{10}^L$). The subsequent discussion is limited by the symmetric (with respect to the electron coupling with the leads) tunnel contacts immersed into a polar electrolyte solution or ionic liquid. The presence of the dissolved ions results in screening of the electric potential within the tunnel gap. ξ and γ quantify the effect of the gate voltage and the bias voltage V on the position of the electron energy level of the bridge molecule due to the screening.²⁰ eV is defined as the difference between the electrochemical potentials of the left and right leads. Since the gate voltage was defined with respect to the left lead, the variation in the bias voltage at fixed gate voltage is performed by the variation in the potential of the right lead. This is the reason of possible asymmetry in these systems. $\Delta F_{21}^L = \Delta F_{10}^L - U_{\text{eff}}$ and $\Delta F_{21}^R = \Delta F_{21}^L - eV$ where an effective quantity $U_{\text{eff}} = U - 2\lambda$ appears⁷ because the transfer of the second electron is accompanied by the full relaxation of the vibrational subsystem in the weak tunneling limit. The position of the bare ionization electronic energy level ε_b of the bridge is given now by $\varepsilon_b = -e(\xi\eta + \gamma V) + k_B T \ln(2)$. The position of the “affinity” level is equal to $\varepsilon_b + U_{\text{eff}}$. It should be noted that U_{eff} can be negative (see, e.g., Ref. 21 and references therein). However, only the case $U_{\text{eff}} > 0$ is mainly considered in what follows. It should be emphasized that even for symmetric contacts γ is not necessarily equal to 0.5. For example in the case of the full screening $\gamma=0$. It is clear that for $\gamma < 1/2$ the shift of the position of the electron energy ε_b with respect to the Fermi levels of the left and right leads with the change of the sign of the bias voltage will be different.

The tunnel current can also be calculated using the well-known expression²²

$$j = \frac{2e\Delta^L\Delta^R}{\hbar\Delta} \int_{-\infty}^{\infty} [f_L(\varepsilon) - f_R(\varepsilon)] A(\varepsilon) d\varepsilon, \quad (11)$$

where $A(\varepsilon) = \sum_\sigma A_\sigma(\varepsilon)$, in which $A_\sigma(\varepsilon)$ is the spectral function at the valence level for the electron having spin projection σ . For the spinless model or in the infinite U limit, the spectral function $A(\varepsilon)$ is the linear combination of the spectral functions $A_0(\varepsilon)$ and $A_1(\varepsilon)$ [see Eq. (20) of Ref. 12] in the weak tunneling limit where $A_0(\varepsilon)$ and $A_1(\varepsilon)$ are the spectral functions for the empty or singly occupied bridge molecule, respectively. For finite values of U , two more spectral functions $A_{0a}(\varepsilon)$ and $A_2(\varepsilon)$ should be taken into account. Here $A_{0a}(\varepsilon)$ and $A_2(\varepsilon)$ are the spectral functions of the empty and

occupied levels corresponding to the electron having spin projection σ , in the case when the electron having spin projection $-\sigma$ already occupies the valence level of the redox molecule. In other words, in the case under consideration, the spectral functions $A_0(\varepsilon)$ and $A_1(\varepsilon)$ describe the oxidized and reduced ionization levels, whereas the spectral functions $A_{0a}(\varepsilon)$ and $A_2(\varepsilon)$ describe the oxidized and reduced affinity levels. As a result,

$$A_\sigma(\varepsilon) = P_0 A_0(\varepsilon) + P_\sigma A_1(\varepsilon) + P_{-\sigma} A_{0a}(\varepsilon) + P_2 A_2(\varepsilon). \quad (12)$$

In the weak tunneling limit, the probabilities entering the rhs of Eq. (12) are given by Eq. (7). The spectral functions $A_0(\varepsilon)$, $A_1(\varepsilon)$, $A_{0a}(\varepsilon)$, and $A_2(\varepsilon)$ are independent of Δ , and depend only on the electron-phonon and the electron-electron interactions. The spectral function $A_0(\varepsilon)$ was obtained, e.g., in Ref. 23. Other spectral functions also can be obtained using the method of Ref. 23, which takes into account the electron-phonon interaction leading to their broadening. These functions when normalized to unity are equal to $A_\nu = (4\pi\lambda k_B T)^{-1/2} \exp\{-[\varepsilon - E_\nu(\lambda, \varepsilon_b, U_{\text{eff}})]^2 / 4\lambda k_B T\}$, where $E_0 = \lambda + \varepsilon_b$, $E_1 = -\lambda + \varepsilon_b$, $E_{0a} = \lambda + \varepsilon_b + U_{\text{eff}}$, and $E_2 = -\lambda + \varepsilon_b + U_{\text{eff}}$. The physical meaning of the electron energy levels E_ν is as follows. The positions of the empty ionization and affinity levels are shifted to E_o and E_{0a} due to the electron-phonon interaction. After appropriate thermal fluctuation of the vibrational subsystem accompanied by the thermal fluctuation of the position of the ionization (or affinity) level, the electron is transferred to the ionization level (or affinity level, in the case when the ionization level is filled) followed by the full vibrational relaxation. As a result, the positions of the filled ionization or filled affinity levels are shifted to E_1 or E_2 , respectively.

In the large λ limit ($\lambda \gg |eV|$, $|e\eta|$, $|U_{\text{eff}}|$) and in the case of symmetric coupling ($k^L = k^R = k^0$), a simple expression for the tunnel current can be obtained:

$$j = 2\pi e k^0 2^{1/2} \exp(-\lambda/4k_B T) \times \frac{\text{sh}(eV/4k_B T) \{2 + \exp[(2e\eta_V - U_{\text{eff}})/2k_B T]\}}{8\text{ch}(e\eta_V/2k_B T) + \exp[(3e\eta_V - 2U_{\text{eff}})/2k_B T]}, \quad (13)$$

where $\eta_V = \xi\eta + (\gamma - 1/2)V$ is the effective gate voltage. In this limit $P_0 = 1/Z_p$, $P_1 = \exp(e\eta_V/k_B T)/Z_p$, and $P_2 = 0.25 \exp[(2e\eta_V - U_{\text{eff}})/k_B T]/Z_p$, where $Z_p = 1 + \exp(e\eta_V/k_B T) + 0.25 \exp[(2e\eta_V - U_{\text{eff}})/k_B T]$. In the opposite case, when $|eV| \gg \lambda$, $|e\eta|$, $|U_{\text{eff}}|$, the probabilities goes to $P_0 = P_2 = 1/4$, $P_1 = 1/2$, and the tunnel current tends to $e k^0 (\pi\lambda/k_B T)^{1/2}$.

It can be shown using Eq. (13) that, for $U_{\text{eff}} > 2k_B T \ln(3) \approx 0.055$ eV and at fixed bias voltage, two Coulomb blockade peaks^{7,24} exist in the current/gate voltage curve. They are located at $\eta_V \approx 0$ and $\eta_V \approx U_{\text{eff}}/2 + k_B T \ln(2)$ (see Fig. 1). The minimum of $j(\eta_V)$ curve is at $\eta_V \approx U_{\text{eff}}/2 + k_B T \ln(2)$. At $U_{\text{eff}} < 0.055$ eV both peaks which have approximately the same height merge into one and, at negative values of U_{eff} , lie at $\eta_V \approx U_{\text{eff}}/2 + k_B T \ln(2)$. The $j(\eta_V)$ curve in the region of the left peak coincides with that in the infinite U limit. The Coulomb blockade peaks shown in Fig. 1 are more pronounced than those obtained in Ref. 7 because the width W of these peaks at their half maximums is not

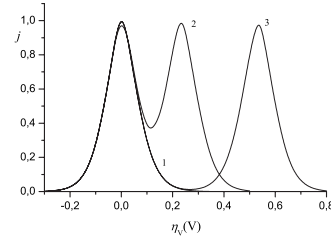


FIG. 1. Dependence of the tunneling current on the effective gate voltage. The current j is normalized to $j_\infty(0)$ where $j_\infty(0)$ is the tunneling current for infinitely large Coulomb repulsion energy at zero value of the effective gate voltage $E_r = 0.5$ eV, $V = 0.1$ V, and $k_B T = 0.025$ eV. 1: $U = \infty$; 2: $U_{\text{eff}} = 0.2$ eV; 3: $U_{\text{eff}} = 0.5$ eV.

equal $\approx U_{\text{eff}}$ (as in Ref. 7) or $\approx \Delta$ (as for the left peak in the strong tunneling limit of the spinless model¹²) but has an order of $k_B T$. More precisely, it follows from Eq. (13) that the width of both peaks is equal to approximately $4k_B T \ln(2 + 3^{1/2}) \approx 0.13$ eV, and is independent of λ and V in the large λ limit. Since $\varepsilon_b = -e\eta_V - eV/2 + k_B T \ln(2)$ in terms of the effective gate voltage, the first and the second Coulomb blockade peaks are located at the values of η_V which correspond to the situations when the average positions of the thermally fluctuating ionization or affinity levels (but not their fixed positions as in the absence of the electron-phonon coupling) hit approximately the center of the energy window (the energy gap between the Fermi levels of the left and right leads).

If $|U_{\text{eff}}|$ and $|eV| \gg k_B T$, $|U_{\text{eff}}| \ll (1 - 2\gamma)|eV|$ then it follows from Eq. (13) that when γ is not equal to $1/2$, $|j(-|V|)|/j(|V|) \approx 2 \exp(U_{\text{eff}}/2k_B T)$. This relationship shows that, at finite U and large λ , the effect of rectification due to the electron-electron interaction takes place (see Fig. 2). When $U_{\text{eff}} < 0$ ($U_{\text{eff}} > 0$), the current is suppressed (enhanced) in the region $V < 0$. If $\gamma = 1/2$, rectification disappears. An important characteristic of the tunnel contact is the differential conductance $g = \partial j / \partial V$ as a function of the bias voltage. When the electron-phonon interaction is absent, the differential conductance can have two peaks at the points $V = \varepsilon_b/e$ and $(\varepsilon_b + U)/e$ in the $T \gg T_K$ regime (see, e.g., Ref. 25). In the case of the strong electron-phonon coupling, we predict a different effect: the differential conductance can have up to four peaks corresponding to the positions E_o , E_1 , E_{0a} , and E_2 of the maxima of the spectral functions A_o , A_1 , A_{0a} , and A_2 , respectively. Indeed, if $eV \gg k_B T$, one can per-

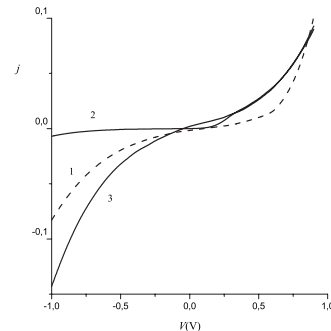


FIG. 2. Dependence of the tunneling current on the bias voltage. The current is normalized to $4ek^0$. $\lambda = 0.5$ eV, $\eta = 0$, $k_B T = 0.025$ eV, and $\gamma = 0.2$. 1: $U = \infty$; 2: $U_{\text{eff}} = -0.2$ eV; 3: $U_{\text{eff}} = 0$.

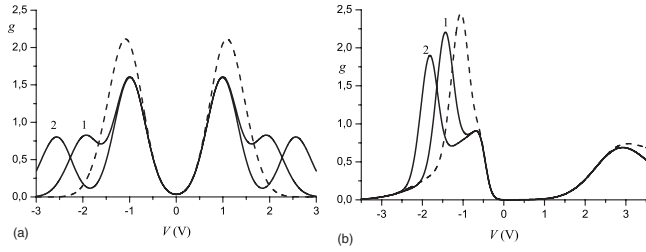


FIG. 3. The differential conductances normalized to $4e^2k^0/(2\lambda)$ as a function of the bias voltage. $\lambda=0.5$ eV and $k_B T=0.025$ eV. Solid lines: $1-U_{\text{eff}}=0.5$ eV; $2-U_{\text{eff}}=0.8$ eV. Dashed lines: $U_{\text{eff}}=0.2$ eV. (a) $\eta=0$, $\gamma=0.5$; (b) $\xi\eta=-0.2$ V, $\gamma=0.2$.

form integration in Eq. (11) from $-eV$ to zero. Furthermore, if one of the probabilities P_ν varies slowly with the variation in the bias voltage, then the corresponding contribution to g is proportional to the corresponding function $A_\nu(-eV)$.

Calculations show that, depending on the values of the parameters of the system, the function $g(V)$ can have from two to four peaks. Figures 3(a) and 3(b) present the curves of the differential conductance for different values of U_{eff} , η , and γ . Figure 3(a) with $\gamma=0.5$ corresponds to the weak screening of the external field by the solution.²⁰ It can be shown that the differential conductance is an even function of the bias voltage in this case. As follows from expressions presented above, $P_0=P_1 \approx 1/2$ and $P_2 \approx 0$ at $\eta=0$, $\gamma=0.5$, $U_{\text{eff}} \gg k_B T$, and small $|V|$. With the increase in $|V|$, P_0 and P_1 vary slowly from $1/2$ to $1/4$ and to $1/2$ again, respectively. Therefore, the differential conductance $g(V)$ has three maxima at $\approx(eV)_1=|(eV)_0|=2\lambda$ and $(eV)_{0a}=-2(\lambda+U_{\text{eff}})$ both for $U_{\text{eff}}=0.5$ and 0.8 eV. However, for $U_{\text{eff}}=0.2$ eV, the maximum at $\approx(eV)_{0a}$ merges with that at $\approx(eV)_0$. In contrast, P_2 varies rapidly with V in the small $|V|$ region so that the position of the right maximum of the $g(V)$ curves for $U_{\text{eff}}=0.5$ and 0.8 eV does not coincide with $(eV)_2=2(\lambda-U_{\text{eff}})$ but is determined by the symmetry property of the function $g(V)$ and equals $\approx|(eV)_{0a}|$.

The case of the intermediate screening ($\gamma=0.2$) is presented in Fig. 3(b) for $\xi\eta=-0.2$. Since here $P_1 \approx P_2 \approx 0$ and $P_0 \approx 1 = \text{const}$ at small $|V|$ in the negative bias region, $g(V)$ has a maximum at $\approx(eV)_0=(\xi\eta-\lambda)/(1-\gamma)$. If P_1 would be constant in the negative bias region, the maximum corresponding to $A_{0a}(\varepsilon)$ might lie at $\approx(eV)_{0a}=-(\lambda+U_{\text{eff}}$

$-\xi\eta)/(1-\gamma)$. For $U_{\text{eff}} \geq 0.5$ and $\gamma=0.2$, one has $|(eV)_{0a}| \geq 1.25$ eV $\gg \lambda \approx 0.5$ eV. In this large bias voltage region $P_1 \approx \text{const}=1/2$ so that a separate maximum at $\approx(eV)_{0a}$ of the $g(V)$ curve really exists for $U_{\text{eff}}=0.5$ and 0.8 eV [see Fig. 3(b)] but it merges again with that at $\approx(eV)_0$ for $U_{\text{eff}}=0.2$ eV.

At $\xi\eta=-0.2$ and $\gamma=0.2$, the probabilities P_1 and P_2 vary rapidly with V in the interval where the maxima at $\approx(eV)_1=(\lambda+\xi\eta)/(1-\gamma)$ and $\approx(eV)_2=(\lambda+\xi\eta-U_{\text{eff}})/(1-\gamma)$, corresponding to $A_1(\varepsilon)$ and $A_2(\varepsilon)$, respectively, may exist. Therefore, the calculated maximum of the $g(V)$ curves related with the reduced ionization level is shifted strongly to right from $(eV)_1$ whereas the maximum related with the spectral function $A_2(\varepsilon)$ disappears at all.

In summary, we have investigated the electric characteristics of the tunnel contact with a redox molecule (which can be in the oxidized and reduced states) in the tunneling gap at room temperature, taking into account the Coulomb interaction between the electrons occupying the same energy level of the bridge molecule and electron-phonon interaction. (1) We have shown that even simple system with one redox level, in the limit of strong electron-phonon interaction, can have two clear-cut Coulomb blockade peaks in the current/gate voltage dependence. Unlike other works, these peaks are rather narrow (the width of the order of $k_B T$) due to the electron-phonon interaction. (2) Another effect related with Coulomb interaction between the electrons is the rectification of the current in the current/bias voltage dependences. This effect in the case of symmetric electron coupling with the leads is related exclusively with the nonsymmetric position of the electron energy level of the bridge molecule at fixed gate voltage due to the screening effect under the variation in the sign of the bias voltage ($\gamma < 1/2$). (3) Unlike the works where the electron-phonon interaction was not taken into account, the conductivity of one-level system as a function of the bias voltage can have up to four peaks related with the oxidized and reduced states of the ionization and affinity levels of the bridge molecule. The mechanism of the transfer of each of two electrons in each two-electron step is related with the fluctuations in the phonon subsystem to the resonance configuration for electron transition followed by full vibrational relaxation.

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