**IV** characteristics of molecular wires in the presence of intramolecular vibrational energy redistribution

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**Abstract**

Various interaction mechanisms may contribute to the current–voltage (**IV**) characteristics of a single molecule embedded between two nano-electrodes. Here, we focus on a microscopic modeling of intramolecular vibrational energy redistribution (IVR) and its influence on the formation of a stationary current. The computations are based on a generalized master equation approach, restricted to weak molecule–lead coupling as well as weak IVR-coupling of a primary reaction coordinate to a thermal bath of secondary coordinates. The pronounced dependence of the **IV** characteristics on the properties of the reaction coordinate such as its reorganization energy upon charging of the molecule is demonstrated. Furthermore, the shortcomings of a relaxation time model of IVR are underlined.

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**1. Introduction**

Although discussed for more than three decades the vision of molecular electronics never lost its attraction. Nowadays individual molecules can be contacted and current–voltage (**IV**) characteristics as well as the related transport noise can be measured (for a recent overview see, e.g., [1–4]). While in the early 1990s theoretical activities have been focused on the pure electronic properties of such nano-devices it has soon been realized that the molecular vibrational degrees of freedom (DOF) cannot be ignored [2]. The participation of molecular vibrations turns charge transmission into an inelastic transport process and it is responsible for electronic energy dissipation, thus controlling the degree of heat accumulation. To account for vibrations in the course of charge transmission different approaches have been suggested. They are based on the use of rate and density matrix equations [5–8] or on the scattering formalism reformulated to include vibrational DOF either in a wavefunction description [9,10] or in the framework of non-equilibrium Green’s functions [11].

A first attempt to include non-equilibrium vibrations has been undertaken in [12]. It was followed by several theories which are strongly influenced by the treatment of transport properties of mesoscopic solid state structures in particular semiconductor quantum dots [13–16]. For example, in Ref. [16] the non-equilibrium behavior of molecular vibrations in the course of charge transmission was considered on the basis of a simple relaxation time model of vibrational energy dissipation. It is the aim of the present Letter to go beyond this description and to scrutinize different microscopic models of intramolecular vibrational energy redistribution (IVR).

IVR represents the fundamental process in which energy deposited in a particular vibrational coordinate is transferred into all other coordinates of a polyatomic system (cf., e.g., [17–19]). After photoexcitation, electron transfer, and even electron transmission through a molecule embedded between nano-electrodes, selected vibrational coordinates may become excited (in the following called reaction coordinates). For the case of external voltage induced charge transmission this has been demonstrated, for example, in Ref. [20] for single copper phthalocyanine molecules. Here, signatures have been found of the participation of a distinct vibration either of the inner ring of the
phthalocyanine macrocycle or related to out-of-plane displacements of particular atomic groups.

If IVR is assumed to be fast compared to the charge transmission the molecular vibrational DOF can be characterized by an equilibrium distribution with a temperature $T$ fixed by the environment (case of \textit{instantaneous} IVR). If the time scales are comparable one may expect the formation of a non-equilibrium vibrational distribution, i.e. an increase of the level of vibrational excitation when the current is passing through the system. In the following, we will investigate how the properties of the used IVR model are reflected in the $IV$ characteristics. To this end we will focus on a generic model where a single reaction coordinate is coupled in a specific way to secondary (reservoir) coordinates. The reaction coordinate participates in the charge transmission process since its equilibrium position changes upon charging of the molecule, i.e. the respective potential energy surface (PES) is different for the neutral molecule and the molecule with a single excess electron taken.

The Letter is organized as follows: after introducing the respective Hamiltonian for the system left electrode–molecule–right electrode (LMR system) in Section 2, the derivation of generalized master equations for the populations of the different molecular electron-vibrational states is briefly sketched in Section 3. Concentrating on the case of weak molecule–lead coupling numerical results highlighting the influence of different IVR mechanisms on the $IV$ characteristics are discussed in Section 4. A summary is given in the final Section 5.

2. Model for the molecule–lead system

In the following, we will introduce a rather general model [21] which should facilitate the consideration of a variety of even complex situations. The initial application in Section 4 will focus, however, on simple cases which may serve for future reference. Let us consider a molecular system characterized by different adiabatic electronic states, $\phi_a$, describing the neutral as well as the charged system, that is its different redox states [22]. A specific realization of these states may incorporate the effects of an applied voltage $V$ and of the electrode’s polarization, i.e. it can be assumed without restriction that these states have been determined in a self-consistent quantum chemical calculation. The number of excess electrons (holes) is specified by $N (N = \ldots, -1, 0, 1, \ldots)$. To each of these states belongs a manifold of vibrational states, $\omega_{nm}$, resulting in an electron-vibrational spectrum $\hbar \omega_{nm} = \hbar \omega_a + \hbar \omega_{nm}$ with electronic energy $\hbar \omega_a$ (minimum of the related PES plus vibrational zero-point energy) and vibrational energy $\hbar \omega_{nm}$ (starting at zero, see also Fig. 1). These adiabatic molecular states are coupled via transfer integrals to the leads which will be labeled by $X (= L, R)$. Transfer integrals of the type $V_X(a(N+1), b(N), \Omega)$ describe the capture of an excess electron with energy $\hbar \Omega$ from lead $X$, thereby moving the molecule from an $N$-fold to an $N+1$-fold charged state. The reverse process is characterized by $V_X(a(N-1), b(N), \Omega)$. The description of the leads assumes continuous electronic energies based on the introduction of the respective density of states $\mathcal{N}_X(\Omega)$.

Next we assume that only a subset of the vibrational DOF is involved in the charging and discharging processes (the reaction coordinates) which are denoted as $q = \{ q \}$. Although a more general description is possible, for the present purpose it is sufficient to restrict the model to harmonic normal mode vibrations. In fact the vibrational states introduced above (cf. Fig. 1) shall belong to the reaction coordinate. All remaining DOF, $Z = \{ Z \}$, shall also be harmonic with frequencies $\omega_z$. If the molecule–lead system is studied in the liquid phase the number of these coordinates becomes large otherwise it may be rather restricted. Nevertheless, we suppose that they form a thermal environment with a continuous density of states. Notice, that such a system–bath like separation is well known from the theory of donor–acceptor electron transfer [19,23]. In this context usually different models are discussed: in the most simple case the coupling between both subsets of DOF is of the bilinear type, $\sim q_i Z_j$, i.e. the reaction coordinates couple linearly to all bath coordinates. A more general type of interaction Hamiltonian may include nonlinearities in the reaction coordinate as well as in the bath coordinates.

In the following, we will consider models where the system–bath coupling is linear with respect to the $Z_i$. Furthermore, we neglect a possible coupling among the electronic states. For this model the following matrix elements of the system–bath coupling potential can be introduced using the reaction coordinate wavefunctions:

\begin{equation}
V(a\mu, a\nu; Z) = \sum_{i} m_i(a\mu, a\nu)Z_i.
\end{equation}

Here, the matrix elements $m_i(a\mu, a\nu)$ define the strength of transitions among the reaction coordinate’s states. In the usual treatment of system–bath coupling [19] the bath coordinates enter via their thermal equilibrium correlation.
functions as well as associated spectral densities (they will be specified in the following section). To conclude we emphasize that the restriction to a coupling linear in the bath coordinates is motivated by the desire to keep the model simple. Higher-order contributions could easily be incorporated with the main effect of different temperature dependences of the relaxation rates [19].

3. Master equations, current formula, and rate expressions

There exist different approaches to compute the IV characteristics of single molecules. Here, we focus on the derivation of general master equations for the electron-vibrational state populations \( P_{\mu l}(t) \), which can easily be used to calculate the stationary current \( I \) at an applied voltage \( V \) (cf., e.g., [7,15]). This has the advantage that one avoids the calculation of off-diagonal density matrix elements which are not needed for the stationary current [14].

The general strategy of this approach has been detailed previously (see, for example, [6,19,24]). It is based on a projection superoperator extracting the populations, \( P_{\mu l}(t) \), of interest. In the present situation one has to include the many-electron statistical operators \( \hat{W}_l \) and \( \hat{W}_R \) describing the stationary non-equilibrium state of the left and the right lead at the applied voltage, respectively [7,8,14]. Moreover, the thermal equilibrium statistical operator \( \hat{R}_{\text{vib}} \) of the bath DOF enters. The projection superoperator then takes the form \( \mathcal{P} \ldots = \sum_{\mu l} \hat{W}_{\mu l} \text{tr} \{ \hat{\Pi}_{\mu l} \ldots \} \), where \( \hat{\Pi}_{\mu l} \) projects onto the electron-vibrational state with quantum numbers \( \mu l \). The overall statistical operator reads \( \hat{\Pi}_{\mu l} = \hat{W}_l \hat{W}_R \hat{R}_{\text{vib}} \hat{\Pi}_{\mu l} \). Finally, the trace is defined with respect to all molecular states including those of the thermal bath vibrations and of the electronic states of both leads. The form of \( \hat{\Pi}_{\mu l} \) indicates that the approach will be based on expansions with respect to the molecule–lead coupling and with respect to system–bath IVR coupling. In contrast, the electron-vibrational coupling for the reaction coordinate is treated non-perturbatively.

After application of the projection operator to the total non-equilibrium statistical operator, \( \mathcal{P} \hat{W}(t) \), it is a standard procedure to obtain the Nakajima–Zwanzig identity for this projected quantity and to arrive at the generalized master equation \( \frac{\partial P_{\mu l}(t)}{\partial t} = \sum_{\mu l} \int d\tau K_{\mu l}(\tau) P_{\mu l}(t - \tau) \) (see, e.g., Ref. [19]). The central advantage of this approach lies in the fact that the memory kernel, \( K_{\mu l}(\tau) \), can be formulated using different types of couplings without being restricted to a low-order perturbation expansion. Instead, partial summations are possible (for more details, see Refs. [7,25]). In order to compute the stationary current we have to solve the generalized master equation in the limit \( t \to \infty \) resulting in \( 0 = \sum_{\mu l} K_{\mu l}(\omega = 0) P_{\mu l}(t \to \infty) \). The expression includes the zero-frequency component of the Fourier-transformed kernel \( K_{\mu l}(\omega) \) which has the form \( K_{\mu l}(\omega) = -i \text{tr} \{ \hat{\Pi}_{\mu l} \hat{G}(\omega) \hat{\Pi}_{\mu l} \hat{W}_{\mu l} \} \) (2) with \( \hat{G} \) denoting the Green’s superoperator defined by the complete Liouvillian \( \mathcal{L} \) [26]. Although the whole treatment does not include the separation of \( \mathcal{L} \) into a zero-order part \( \mathcal{L}_0 \) and the perturbation \( \mathcal{P} \), the form of \( \mathcal{P} \), i.e. the separation of the equilibrium statistical operator \( \hat{W}_{\mu l} \), suggests the concrete form of \( \mathcal{P} \) as mentioned above.

The stationary current is obtained by calculating the number of electrons moving, for example, through the left lead [7,15]. Since we focus on the case of weak molecule–lead coupling the direct lead–lead charge transmission can be ignored and we have

\[
I \equiv I_L = 2|e| \sum_{\mu l} \sum_{k(N) = b(N+1)} k_{\text{mol-lead}}^{(\text{mol-lead})} P_{\mu l}(t \to \infty) - 2|e| \sum_{\mu l} \sum_{k(N) = b(N-1)} k_{\text{mol-lead}}^{(\text{mol-lead})} P_{\mu l}(t \to \infty).
\]

The populations follow from a solution of the generalized master equations and the \( k_{\text{mol-lead}}^{(\text{mol-lead})} \) denote transfer rates due to the coupling between the molecule and the left lead, only.

In the following, we will concentrate on rates \( k_{\text{mol-lead}}^{(\text{mol-lead})} \) being of second-order with respect to the molecule–lead coupling and rates \( k_{\text{IVR}} \) being of second-order with respect to the chosen IVR coupling mechanism. Mixed types of processes do not appear at this level of approximation. The calculation of the respective rates is straightforward. Here, we only quote the results (for details, see [25]). The molecule–lead coupling rates are also known from the literature (cf. Ref. [14,16]) and read (note \( \varepsilon(\mu l, bv) = (\varepsilon(\mu l) - \varepsilon(bv)) \))

\[
k_{\text{mol-lead}}^{(\text{mol-lead})} = \frac{4\pi}{\hbar^2} \left| \langle \varepsilon(\mu l) | \varepsilon(bv) \rangle \right|^2 \times \sum_{X} \mathcal{N}(\varepsilon(\mu l, bv)) |V_X(a, b, \varepsilon(\mu l, bv))|^2 \times [1 - f_2(\varepsilon(\mu l, bv) - \mu_X)].
\]

Here, the charging of the molecule in state \( \phi_0 \) corresponds to the presence of \( N - 1 \) excess electrons. The rate describes single electron outflow. If \( \phi_0 \) refers to \( N + 1 \) excess electrons and if the \( \varepsilon(\mu l, bv) \) are replaced by their negative values as well as \( 1 - f_2 \) by \( f_2 \) the resulting rate describes single electron injection. Each rate is proportional to the vibrational wavefunction overlap expression (Franck-Condon factor) and contains the Fermi functions at the respective chemical potential \( \mu_X \). According to our second-order calculations the bath coordinates do not enter the rate expressions, Eq. (4). If the latter are thermally averaged over the initial vibrational states and are summed up with respect to the final vibrational states, standard rates of molecule–lead charge transfer in the weak-coupling limit are obtained [7].

In the limit of weak system–bath coupling the second-order form of Eq. (2) with respect to \( V(\mu l, av, Z) \), Eq. (1), can be used to compute the respective relaxation rates \( k_{\text{IVR}}^{(\text{IVR})} \) entering the generalized master equations. Noting
that the bath harmonic potentials have been assumed to be a set of independent harmonic oscillators one obtains the following expression (whose general structure is well known [19]):

$$k_{a(N)\mu\rightarrow a(N)\nu} = |m(\mu, \nu, a)|^2 \left[ \left( 1 + n(\mu, \nu, a) \right) J_a(\mu, \nu, a) + n(\mu, \nu, a) J_a(\mu, \nu, a) \right].$$  \hspace{1cm} (5)

The derivation makes the additional assumption that the separation $m_a(\mu, \nu, a) = k_{a(N)} \times m(\mu, \nu, a)$ in Eq. (1) is valid. Further we have introduced the spectral densities $J_a(\omega) = 2\pi \sum_k k_{a(N)} \delta(\omega - \omega_k)$, where the $\omega_k$ are transition frequencies between the molecular electron-vibrational levels and $n$ denotes the Bose–Einstein distribution function.

The rate expressions introduced so far are rather general. The $k_{a(N)\mu\rightarrow a(N)\nu}$ may account for a specific density of states of the leads and for an energy dependence of the transfer integrals, whereas $k_{a(N)}$ may include very different IVR mechanisms according to the actual coupling model. Moreover, all expressions are valid for an arbitrary charging state of the molecule.

4. Numerical results for transitions between neutral and singly charged molecular states

The following discussion will be restricted to current formation through the molecule limited to its neutral, i.e. $N = 0$-state and its singly charged (reduced) state $N = 1$ (denoted as $\phi_0$ and $\phi_1$, respectively, excited electronic states of the molecule are neglected). The effect of current rectification is also outside the scope of the present discussion, and we assume symmetric contacts. Moreover, the so-called broad-band approximation is introduced replacing $\mathcal{N}_X(\Omega)$ and $V_X(\alpha, \beta, \Omega)$ by mean, i.e. frequency-independent values $\bar{\mathcal{N}}$ and $\bar{V}$ which are further specified to transitions between the neutral and singly charged molecule. Finally, for the purpose of investigating the principal effects of IVR, it is sufficient to work within the approximation of a symmetrically applied voltage (the molecular levels are shifted by the applied voltage like the energy of a point charge positioned in the center between both leads), i.e. we set $\mu_L = \mu_0 + e|V|/2$ and $\mu_R = \mu_0 - e|V|/2$ ($\mu_0$ is the chemical potential of the leads at $V = 0$).

Once the rates of IVR have been specified, the stationary solution of the generalized master equation can be determined. We note that in the limit $t \rightarrow \infty$ the solution of the generalized master equation coincides with that of the ordinary master equations (without memory) using as rate constants the Fourier-transformed memory kernels at zero-frequency. Therefore, ordinary master equations are solved numerically for large $t$. Then, the obtained values of electron-vibrational level populations $P_{\mu\mu}$ ($a = 0, 1$) are used to calculate the stationary current according to Eq. (3). Besides the individual $P_{\mu\mu}$ below, we will also discuss the overall population of the neutral state $P_0 = \sum_{\mu} P_{\mu\mu}$ and of the singly charged state $P_1 = \sum_{\mu} P_{\mu1}$.

Two limits are of interest: the case of a unique IVR rate characterized by a single relaxation time and the case of instantaneous IVR. In the former case one has to replace $k_{a(N)\mu\rightarrow a(N)\nu}$ by $f_{th}(\hbar \omega_{a\nu}/\tau_{IVR})$, where $f_{th}$ denotes the thermal distribution with respect to the reaction coordinate states and $\tau_{IVR}$ is the unique vibrational life-time. This results in the well-known relaxation time approximation: $(\partial P_{\mu\nu}/\partial t)_{IVR} = -1/\tau_{IVR} \times (P_{\mu\nu} - f_{th}(\hbar \omega_{a\nu}) \sum_{\nu} P_{\nu\nu})$. The second limiting case of instantaneous IVR assumes fast vibrational relaxation on the time-scale of charge transmission and is introduced by setting $P_{\mu\nu}(t) = f_{th}(\hbar \omega_{a\nu}) P_{\mu\nu}(t)$, i.e. the vibrational equilibrium distributions and the electronic populations are separated. Accordingly related rate equations are obtained for the overall electronic state populations $P_{\mu\nu}(t)$.

Let us specify the model parameters used in the subsequent computations. We will exclusively concentrate on the low temperature case with $k_B T = 1$ meV. For the contacts we take the values $\bar{\mathcal{N}}/\hbar = 10$ eV and $\bar{V} = 10$ meV. This yields a level broadening [7], $\Gamma = \pi \bar{\mathcal{N}} \bar{V}/\hbar^2$, of about 3 meV and a stationary current below 100 pA (a current between 0.1 and 0.2 nA has been reported, for example, in Ref. [20]). Both numbers indicate that we indeed work in the limit of weak molecule–lead coupling. The electronic reference energy of our considerations is the energy needed to singly charge the molecule in relation to the Fermi energy. We set $\hbar \epsilon_{10} - \mu_0 = 100$ meV resulting in $IV$ characteristics with finite values of the current just at finite values of the applied voltage. The reaction coordinate is considered in harmonic approximation with vibrational energy $\hbar \omega_{a\nu} = 50$ meV (representing an average of what has been reported in Ref. [20]). A further important parameter of the description is the relative displacement between the PES which belongs to the neutral molecule and the one referring to the molecule with a single excess electron attached. Within the harmonic description and by changing from $q$ to the dimensionless coordinate $Q$ (given as the sum of the harmonic oscillator annihilation and creation operators) the neutral molecule PES is written here as $U_Q(Q) = \hbar \omega_{a\nu} (Q + 2 g_0)^2/4$. In the singly charged case we have the same PES but with $g_0$ replaced by $g_1$. (The dimensionless coupling constants $g_0$ and $g_1$ determine the actual shift with respect to the origin according to $-2g_0$ and $-2g_1$, respectively.) Thus $\Delta g = g_1 - g_0$ is a measure of the nuclear rearrangement upon charging of the molecule. The quantity $E_1 = \hbar \omega_{a\nu} \Delta g^2$ is known as the reorganization energy. We will consider $\Delta g = 1$ and 3 resulting in $E_2 = 50$ and 450 meV, respectively.

For the following discussion, we apply the general current formula, Eq. (3), to the present model. Let us separate the stationary distributions $P_{\mu\mu}$ into the overall electronic state population $P_0$ and the (normalized) non-equilibrium vibrational distribution $f_{\mu\nu} = P_{\mu\mu}/P_\nu$. Concentrating on the case $\nu > 0$ it follows that:

$$I \propto P_0 \sum_{\mu \rho} f_{\mu\mu} \langle \psi_{\mu\nu} | \tilde{\mathcal{L}}_{\nu} | \psi_{\mu\nu} \rangle^2 f_{\nu}(\hbar \omega_{a\nu} (\nu - \mu) - \Delta E_1),$$

where the factor two from spin degeneracy is neglected (spinless model) and we introduce $\Delta E_1 = \nu |V/2 + \mu_0 - \hbar \epsilon_{10}|$. 

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A finite current appears if $\Delta E_L > \hbar \omega_{\text{vib}} (v - \mu)$ with the first contribution occurring for $\Delta E_L > 0$ (at $v = \mu$).

Considering a bilinear coupling between a single harmonic reaction coordinate $q$ and a thermal reservoir of secondary coordinates $Z_q$ the matrix element in the mode-coupling potential Eq. (1) entering the rate formula, Eq. (5) are specified to the simple expression $m(\alpha \mu, \alpha v) = \langle \xi_{\alpha \mu} \rangle \langle \xi_{\alpha v} \rangle \ (a = 0, 1)$. As a result the rate of IVR takes the form $k_{\alpha \mu \alpha v}^{\text{IVR}} = \delta_{\gamma \mu, 0} (\mu + 1) n(\omega_{\text{vib}}) J_{\alpha}(\omega_{\text{vib}}) + \delta_{\gamma \mu, 0} \beta (1 + n(\omega_{\text{vib}})) J_{\alpha}(\omega_{\text{vib}})$. The two values, $J_{\alpha}(\omega_{\text{vib}})$ and $J_{\gamma}(\omega_{\text{vib}})$, of the spectral densities represent parameters of the theory regulating the strength of IVR. Moreover, they determine the life-time $\tau_{\alpha \mu}$ of the first excited vibrational state due to spontaneous transition to the ground state according to $1/J_{\alpha}$. For the used values of $h J_{\alpha}$ varying between 0.01 and 10 meV the life-time covers the range between 65 ps and 65 fs.

Fig. 2 displays the IV characteristics for a rather modest reorganization energy of 50 meV and for different strengths of IVR, together with the curve for instantaneous IVR. Let us start with the case of instantaneous IVR, where for the chosen low temperature ($k_B T = 1$ meV) the distributions $f_{\alpha \mu}$ are reduced to $\delta_{\alpha \mu, 0}$. The current starts to flow (for $V > 0$) if $\Delta E_L$ becomes larger than zero. The channel for the transition of the neutral molecule (being in its vibrational ground state) into the vibrational ground state of the charged molecular state is open. For small reorganization energies $\langle \xi_{00} \rangle$ represents the largest overlap integral (only somewhat below 1), and this channel dominates the IV characteristics (cf. Eq. (6) and Fig. 2). Increasing $V$ further the second channel opens if $\Delta E_L > \hbar \omega_{\text{vib}}$, and so on. Overall the IV characteristics reflects the distribution of Franck–Condon factors $|\langle \xi_{00} \rangle|$. Changing to finite vibrational relaxation times the full distribution of the vibrational levels of the neutral state, $f_{00 \mu}$, contributes a finite current appears for all terms with $\mu = v$ in the estimate of the current presented in Eq. (6). For the parameters of Fig. 2 there is no change for the first channel. But increasing $V$ the following channels contribute less effective due to the small Franck–Condon factor. This observation is in line with the behavior of the stationary populations $P_{\alpha \mu}$ shown in Fig. 3 versus applied voltage. Increasing $V$ increases the population of higher vibrational levels until the lowest 4 levels in this example are almost equally populated. At larger $V$ ($V > 0.6$ V in the present model) various channels are opened for charge injection and the resulting redistribution due to IVR causes this rather homogeneous population in the stationary regime. We also stress that the same IV characteristics are obtained for a somewhat increased molecule–lead coupling if at the same time the strength of IVR is also increased (increasing the molecule–lead coupling by a certain factor via an increase of the broadening $\Gamma$ requires a similar increase of the IVR rate via an increase of the spectral densities $J_{\alpha}$). Therefore, changing to a current of above 500 pA.

**Fig. 2.** IV characteristics for a bilinear coupling model of IVR at $k_B T = 1$ meV and for $E = 50$ meV ($\Delta E_L = 1$). Full line: $h J_0 = h J_1 = 0.01$ meV, dashed line: $h J_0 = h J_1 = 0.1$ meV, dashed-dotted line: $h J_0 = h J_1 = 1$ meV, dotted line: instantaneous IVR (nearly equivalent to the case with $h J_0 = h J_1 = 10$ meV, other parameters see text).

**Fig. 3.** Stationary electron-vibrational state populations $P_{0 \mu}$ (a) and $P_{1 \mu}$ (b) versus applied voltage (parameters correspond to those used in Fig. 2, case $h J_0 = h J_1 = 0.1$ meV). Full line: $\mu = 0$, dashed line: $\mu = 1$, dashed-dotted line: $\mu = 2$, dotted line: $\mu = 3$. The upper dotted curves in (a,b) correspond to the overall population ($P_0$ and $P_1$).
the IV curves of Fig. 2 (below that of instantaneous IVR) would correspond to $J_{\alpha}^{\ast}$ values between 0.1 and 10 meV (vibrational life-times of 6.5 ps down to 65 fs). Apparently, the behavior displayed in Fig. 2 should be also observable at somewhat higher values of the current (as long as it is guaranteed that one remains in the limit of weak molecule–lead coupling and of singly charged molecular states).

While a finite relaxation time leads to a decrease of the current independent of $V$ if the reorganization energy is small, in the case of a larger reorganization energy as displayed in Fig. 4 finite relaxation time results in an increase of the current for voltages below 1 V. In this voltage region $f_{0\mu}$ already becomes finite for excited vibrational levels thus leading to a larger resulting current than in the case of instantaneous IVR where $f_{0\mu}=\delta_{\mu,0}$. We also underline that the relaxation time model leads to a deviation from the used microscopic model if larger reorganization energies are considered (cf. Fig. 4b) The IV characteristics for electronic state dependent IVR is given in Fig. 4 as well.

Comparing the overall populations $P_0$ and $P_1$ drawn in Fig. 3 (small reorganization energy) with those for larger reorganization energy (not shown) the behavior versus voltage is not so different. In particular, in the limit of a large applied voltage one obtains $P_0 \approx P_1 \approx 0.5$ (the population of the electronic two-level system becomes well balanced). The molecule attached to the two electrodes appears in a mixed state of the neutral molecule and the charged molecule with nearly equal probability.

The non-equilibrium character of the open molecular state is also underlined in Fig. 5 displaying the mean number of vibrational quanta excited in the molecule at a finite voltage. As it has to be expected this number becomes particularly large for weak IVR. In the opposite case vibrational excitation of the active mode is redistributed among other modes resulting in an overall vibrational heating of the molecule.

5. Conclusion

The present Letter discusses in detail the influence of the concrete mechanism of intramolecular vibrational energy redistribution (IVR) on the current–voltage (IV) characteristics of a single molecule embedded between two nanoelectrodes. These studies have been motivated by previous predictions that a vibrational heating upon charge transmission through a single molecule may represent a crucial mechanisms influencing the current formation and even destroying the molecular system by bond-breaking and dissociation [2]. Our computations have been based on a generalized master equation approach but were restricted to a weak molecule–lead coupling as well as a weak IVR coupling mechanism. We also stress again that the used single reaction coordinate model does not represent an oversimplification.
but agrees with respective experimental data [20]. The obtained $IV$ characteristics should in principle allow for rather clear conclusions on the type of IVR operating in a given molecular system (for example by detecting the slope of the current versus the applied voltage). Shortcomings of a relaxation time model of IVR have also been demonstrated.

Moreover, our calculations demonstrate the misleading nature of the following argument: to get the characteristic time for the transmission of a single electron through a molecule attached to two leads one may divide the elementary charge by the actual value of the current ($\tau_{ct} = e/I$). This yields about 1 ns for a typical current of 100 pA in our calculations. So, one expects an effect of non-equilibrium vibrations only for rather long vibrational relaxation times much larger than 10 ps. However, it could be demonstrated here that the $IV$ characteristics deviates from the case of instantaneous relaxation even if the characteristic time of vibrational relaxation is around 1 ps or less. Thus, in any realistic situations one has to use the complete electron-vibrational distribution function when calculating $IV$ characteristics.

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References

[26] The Green’s superoperator $\hat{G}$ is given as $(\alpha - \hat{G} + i\tau)^{-1}$ where the Liouvillian follows as $\hat{L}_0 + (1 - \hat{G})\tau$. While the zero-order part remains unaffected the coupling part is modified by the presence of the projection superoperator. For the particular consequences we refer to [19,25].