Nonradiative electron and energy transfer. Explicit estimation of the influence of coherent and dephasing processes in a vibrational bath on electronic dynamics[*]

M. MENŠÍK[1][**], K. L. KRÁL[2]

[1]Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic,
Heyrovský Sq. 2, 162 06 Prague 6, Czech Republic

[2]Institute of Physics, Academy of Sciences of the Czech Republic,
Na Slovance 2, 182 21 Prague 8, Czech Republic

A theoretical model is studied of the coupling of several electronic states to a vibrational manifold. In this approach, the vibrational manifold is divided into two subbaths. The first one, a coherent subbath, interacts coherently with electronic states. The second one, a thermalizing subbath, is responsible for relaxation of vibronic energy. In the first step, the thermalizing subbath is projected out, under the assumption of a standard (Markovian) approximation in the interaction picture and the effective dissipative Liouville equation for a coherent vibronic system (electronic states + coherent bath modes) is thus obtained. Next, "coherent bath modes" are also projected out and irreversible master equations for electronic degrees of freedom are obtained, even without the Markovian approximation. Analytical expressions based on the double projection technique are compared with numerical simulations of a two-level electronic systems interacting with a single vibrational mode embedded in the dissipative environment. We show that the double projection technique can be applied to predict spikes of resonant amplification of electron (vibronic) energy transfer, as well as to analytically test various models of kinetic theories.

Key words: *electron-vibrational interaction; non-adiabatic coupling; resonant energy transfer; vibrational coherence; excited state decay*

1. Introduction

In the standard theoretical studies of the electronic transitions, vibrational degrees of freedom are projected out and obtained kinetic equations are closed with respect to

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the relevant degrees of freedom (e.g., electronic states) [1–4]. The influence of the degrees of freedom projected out (e.g., vibrational modes) on the system of interest (e.g., electrons) is mathematically expressed through effective spectral functions controlling rate constants (memory functions) in kinetic equations. If these spectral functions are exact up to second-order in the system–bath coupling, their analytical forms explicitly consist of a weighted sum of delta functions in the frequency domain. Practically, on the other hand, they are alternatively replaced by phenomenological expressions, like Debye's, Ohmic spectral functions and etc. Physically, it is argued that a vibrational manifold behaves like a heat bath with an implicit auto-thermalization process.

Time-resolved experiments proved, on the other hand, that among vibrational manifolds only a few vibrational modes can retain their coherent character for a longer time, even in the donor-acceptor complexes [5] containing a relatively large number of vibrational modes. Indeed, quantum chemical calculations really proved that often only a few modes have non-zero values of the Huang–Rhys factor or contribute more to the non-adiabatic couplings. Therefore, they keep their coherent character longer than the rest of the modes of a vibrational manifold. Moreover, it was calculated that even in QaAS quantum dot systems, consisting of tens of repeating units, the electronic transfer should by resonantly amplified due to the interaction with longitudinal optical phonons [6]. It seems natural to expect that vibrational modes coupled coherently to electrons should be separated from those that are responsible for the dephasing process due to the anharmonic or Duschinsky couplings.

In the paper, we outline in brief the basics of the so-called double-projection technique where, first, dephasing modes are projected out by means of the standard projection technique and coherent modes are let to develop due to their interactions with electrons and being dephased by the bath of dephasing modes. The obtained kinetic equations for electrons and coherent modes are time irreversible and, in the second step, also coherent modes are projected out. We show that rate constants of electronic transfer thus obtained are directly expressed via parameters of coherent couplings between electrons and vibrational modes (Huang–Rhys factor, non-adiabatic couplings) and relaxation rates of coherent vibrational modes. Consequently, the model thus introduces explicit dependences of the relaxation process, not only with respect to the system–bath coupling but also with respect to the dephasing process in the heat bath. A similar approach may be found, e.g., in Ref. 7. Alternatively, it enables the prediction of critical estimates for various kinetic relaxation theories.

2. The double projection technique

We assume that the systems consisting of electrons and coherent vibrational modes is fully described by the density matrix (statistical) operator $\rho(t)$ that is controlled by the following Liouville equation:

$$\frac{\partial}{\partial t}\rho(t) = -i(L_0 + L^1 + L^{\mathrm{dis}})\rho(t) = -i\frac{\left(H_0 + H^1, \rho(t)\right)}{\hbar} - iL^{\mathrm{dis}}\rho(t) \equiv -i(L_{\mathrm{eff}})\rho(t) \quad (1)$$

Here, $L_0(H_0)$ is the Liouville superoperator (Hamiltonian) of free electrons and vibrations, $L^1(H^1)$ describes their interactions, while L^{dis} controls the impact of the vibrational modes being previously projected out. Formally, we can assume various forms of the dissipative tensors which can be found in the literature (e.g., the Redfield form or diabatic damping approximation (DDA) [8]). The coupling between coherent and dephasing modes may be assumed to be either the Duschinsky coupling or anharmonic coupling, but the Hamiltonian of the system consisting of electrons and coherent vibrational modes is defined as follows

$$H = \sum_j |j\rangle\langle j|(\varepsilon_j + \sum_n \hbar\omega_n\left(\frac{Q_n^2}{2} + \frac{P_n^2}{2}\right) + \sum_n \hbar\omega_n D_n^j Q_n) + \sum_{j,k}|j\rangle\langle k|H_{jk}^1(Q) \quad (2)$$

Here, $|j\rangle$ denotes the j-th electronic diabatic state, with local energy ε_j. $\hbar\omega_n$ is the vibrational energy quantum of the n-th mode, while Q_n and P_n correspond to the normal vibrational coordinates and momenta of the n-th mode, respectively. D_n^j is the diagonal coupling constant of the n-th mode in the j-th PES. Consequently, the corresponding Huang–Rhys factor is $(D_n^j)^2/2$, and the vibrational binding energy of the n-th mode in the j-th PES equals $\hbar\omega_n(D_n^j)/2$. The interstate interaction (between various PESs) $H_{jk}^1(Q)$ is assumed to be a general function of vibrational coordinates. It is straightforward that the vibronic potential of respective PESs in the Hamiltonian (2) are connected by the following unitary transformation

$$S_j \equiv \exp\left(i\sum_n D_j^n P_n\right) \quad (3)$$

corresponding to the shift of equilibrium positions $Q_n \to Q_n + D_n^j$. Now, the Hamiltonian (2) can be rewritten to the form

$$H \equiv H_0 + \sum_{j,k}|j\rangle\langle k|H_{jk}^1(Q) = \sum_j |j\rangle\langle j|S_j(\varepsilon_j^{\mathrm{R}} + H^{\mathrm{v}})S_j^+ + \sum_{j,k}|j\rangle\langle k|H_{jk}^1(Q) \quad (4)$$

where $\varepsilon_j^{\mathrm{R}}$ are "relaxed" electronic energies and the vibrational Hamiltonian

$$H^{\mathrm{v}} = \sum_n \hbar\omega_n\left(\frac{Q_n^2}{2} + \frac{P_n^2}{2}\right) \quad (5)$$

corresponds to the unshifted oscillators.

In the following, we will be interested in the occupation probabilities $p_i(t)$ of the i-th potential energy surfaces (PES). Here, $p_i(t)$ is defined as follows:

$$p_i(t) \equiv \mathrm{Tr}_{\mathrm{vib}} \left(\langle i | \rho(t) | i \rangle \right) \tag{6}$$

where $\mathrm{Tr}_{\mathrm{vib}} \left(\langle i | \rho(t) | i \rangle \right)$ means the trace over the vibrational states of the electronic diagonal elements of the total density matrix $\rho(t)$. Probabilities $p_i(t)$ can also be written in the form

$$p_i(t) = \mathrm{Tr}_{\mathrm{vib}} \left(\langle i | P\rho(t) | i \rangle \right) \tag{7}$$

utilizing the projector P defined as

$$P... = \sum_i |i\rangle\langle i| \otimes S_i \rho_{\mathrm{vib}} S_i^+ \mathrm{Tr}_{\mathrm{vib}} \left(\langle i |...| i \rangle \right) \tag{8}$$

It can be checked by straightforward algebra that the projector P in Eq. (8) also has the following properties

$$P^2 = P \tag{9}$$

$$PL_0 = L_0 P = 0 \tag{10}$$

$$PL^{\mathrm{I}}P = 0 \tag{11}$$

Additionally, we assume that the projector P also satisfies the relation

$$PL^{\mathrm{dis}}P = 0 \tag{12}$$

indicating that during the dissipation process the system thermalizes within a given PES. Now, by also projecting out the coherent modes in Eq. (1) we come to the standard Nakajima–Zwanzig equation to get

$$\frac{\partial}{\partial t} P\rho(t) = -iPL_{\mathrm{eff}} P\rho(t) - \int_0^t d\tau PL_{\mathrm{eff}} \exp\left(-i(1-P)L_{\mathrm{eff}}(t-\tau)\right)(1-P)L_{\mathrm{eff}} P\rho(\tau)$$
$$-iPL_{\mathrm{eff}} \exp\left(-i(1-P)L_{\mathrm{eff}} t\right)(1-P)\rho(0) \tag{13}$$

Equation (13) is quite general, but we can simplify it if we utilize Eqs. (9)–(12).

Also, if for the initial condition term we can assume that $\rho(0) = |1\rangle\langle 1| \otimes \rho_{\mathrm{vib}}$, we get

$$P\rho(0) = \rho(0) \tag{14}$$

Then, Eq. (13) will be simplified to the form

$$\frac{\partial}{\partial t} P\rho(t) = -\int_0^t d\tau P\left(L^{\mathrm{I}} + L^{\mathrm{dis}}\right) \exp\left((-i(1-P)\left(L_0 + L^{\mathrm{I}} + L^{\mathrm{dis}}\right)(t-\tau))\right)(L^{\mathrm{I}} + L^{\mathrm{dis}})P\rho(\tau) \tag{15}$$

The kinetic equation (15), as it stands, is time-irreversible. The relaxation in the memory function is not introduced assumption based on the thermodynamic limit, as it is done in standard approaches but it is based on the influence of dephasing modes (expressed by L^{dis}) which were projected out earlier, i.e., before constructing the master equation (1). The dissipative tensor L^{dis} can be formally taken in the Redfield form [9] but for the internal summation in the tensor we can approximate the vibronic eigenstates by those of non-interacting diabatic PESs (e.g. [8]). The corresponding dissipative tensor will be then denoted as $L^{\text{dis}(0)}$. Alternatively, we can take a perturbative solution of vibronic states to the first order in the interstate coupling $H^{\text{I}}_{jk}(Q)$ and the corresponding first-order correction in the dissipative tensor would be $L^{\text{dis}(1)}$ [10]. Whence, we would get the following equations

$$PL^{\text{dis}(0)} = L^{\text{dis}(0)}P = 0 \tag{16}$$

$$PL^{\text{dis}(1)}P = 0 \tag{17}$$

Equation (15) can be thus rewritten in the form

$$\frac{\partial}{\partial t}P\rho(t) = -\int_0^t d\tau P(L^{\text{I}} + L^{\text{dis}(1)})\exp\left(-i(L_0 + L^{\text{I}} + L^{\text{dis}})(t - \tau)\right)(L^{\text{I}} + L^{\text{dis}(1)})P\rho(\tau) \tag{18}$$

The memory kernel in the last equation is, at least, a second-order one in the interstate coupling. Consequently, if we restrict the kinetic rates just to the second-order in the interstate coupling, we can immediately perform the Markovian approximation because deviations from it would just affect terms of higher order in the expression for the interstate coupling.

An open question here is the convergence of the iteration series in Eq. (18). As will be seen from below, neither the assumption of weak interstate coupling (with respect to the electronic transition energies, i.e., $\left\langle H^{\text{I}}_{jk} \right\rangle << \left| \varepsilon^{\text{R}}_j - \varepsilon^{\text{R}}_k \right|$) nor fast decay of the memory kernel is a sufficient condition for the "second order" approach. According to our numerical simulations introduced below, the interstate coupling must be weak with respect to the vibronic transition energies of the active mode, i.e., the system must be in the "off-resonant limit". The analytical expressions below, exact up to the second order in the interstate coupling equation/expression, will be thus derived on the assumption of the "off-resonant limit".

After making the Markovian approximation, we can perform a formal integration of the memory kernel, thus by considering second-order terms in the interstate coupling equation, we directly get:

$$\frac{\partial}{\partial t}P\rho(t) \approx -P(L^{\text{I}} + L^{\text{dis}(1)})\left(-i(L_0 + L^{\text{dis}(0)})\right)^{-1}$$
$$\left(\exp\left(-i(L_0 + L^{\text{dis}(0)})t\right) - 1\right)(L^{\text{I}} + L^{\text{dis}(1)})P\rho(t) \tag{19}$$

In the next step, we perform the resolvent expansion of the superoperator $(L^0 + L^{\text{dis}(0)})^{-1}$ and in the total expression we only keep first order terms in the expression for the dissipation

$$
\begin{aligned}
\frac{\partial}{\partial t} P\rho(t) \approx &-iPL^I \left(L_0\right)^{-1} \left(\exp\left(-i(L_0 + L^{\text{dis}(0)})t\right) - 1\right) L^I P\rho(t) \\
&+iPL^I L_0^{-1} L^{\text{dis}(0)} L_0^{-1} \left(\exp\left(-i(L_0 + L^{\text{dis}(0)})t\right) - 1\right) L^I P\rho(t) \\
&-iPL^{\text{dis}(1)} L_0^{-1} \left(\exp\left(-i(L_0 + L^{\text{dis}(0)})t\right) - 1\right) L^I P\rho(t) \\
&-iPL^I L_0^{-1} \left(\exp\left(-i(L_0 + L^{\text{dis}(0)})t\right) - 1\right) L^{\text{dis}(1)} P\rho(t)
\end{aligned}
\tag{20}
$$

The master equation (20) contains a contribution from formally different processes. The first term corresponds to gradually decaying coherent Rabi oscillation. The second term is related to the dissipation process controlled due to the DDA [8]. The third and fourth terms correspond to the dissipation process, which incorporates the first order terms of the interstate coupling [10]. If we are finally interested in the decay of the population $p_m(t)$ of the m-th PES we arrive at the equation

$$
\frac{\partial}{\partial t} p_m(t) \approx -\sum_k \left(\left(W_{km}^{\text{Rabi}}\right)(t) + W_{km}^{\text{dis}}(t)\right) p_k(t)
\tag{21}
$$

The rate of the decay of the population $p_m(t)$ is controlled by the rate constant $W_{mm}^{\text{dis}}(t)$, which after time corresponding to the vibrational relaxation in the respective PES can be expressed as

$$
W_{mm}^{\text{dis}} = W_{mm}^{\text{dis}}(t \to \infty) = W_{mm}^{\text{dis}(0)}(t \to \infty) + W_{mm}^{\text{dis}(1)}(t \to \infty)
\tag{22}
$$

with

$$
W_{mm}^{\text{dis}(0)}(t \to \infty) = \text{Tr}_{\text{vib}} \left(\langle m | (L^I [L_0]^{-1} i L^{\text{dis}(0)} \left(L_0\right)^{-1} L^I)(|m\rangle\langle m| \otimes S_m \rho_{\text{vib}} S_m^+ \}) | m \rangle\right)
\tag{23}
$$

$$
\begin{aligned}
W_{mm}^{\text{dis}(1)}(t \to \infty) = &-\text{Tr}_{\text{vib}} \left(\langle m | (i L^{\text{dis}(1)} L_0^{-1} L^I \left(|m\rangle\langle m| \otimes S_m \rho_{\text{vib}} S_m^+\right) | m \rangle\right) \\
&-i\text{Tr}_{\text{vib}} \left(\langle m | (L^I L_0^{-1} L^{\text{dis}(1)} \left(|m\rangle\langle m| \otimes S_m \rho_{\text{vib}} S_m^+\right) | m \rangle\right)
\end{aligned}
\tag{24}
$$

3. Model of two electronic levels coupled to a single vibrational mode

The double-projection technique will be tested on a simple model consisting of coupled two electronic levels with a single vibrational mode. The vibrational mode is also assumed to be embedded in the dephasing bath, so that the system of two electronic levels with a single vibrational mode satisfies Eq. (1). We will solve Eq. (1)

numerically and we get estimates of time dependences of the excited state population $p_1(t)$ by Eq. (6). The dependences of the occupation probabilities are approximated by the following relation

$$p_1(t) \approx A_0 + A_1 \exp(-\Gamma_1 t) + A_2 \exp(-\Gamma_2 t)\cos(\omega_2 t) + A_3 \exp(-\Gamma_3 t)\cos(\omega_3 t) \quad (25)$$

which consists of two decaying Rabi oscillations and a central excited state decay. Formally the Rabi oscillations should include more components but, except for regions having resonant amplification, it can be proved that the approximation with two oscillating components is sufficiently good.
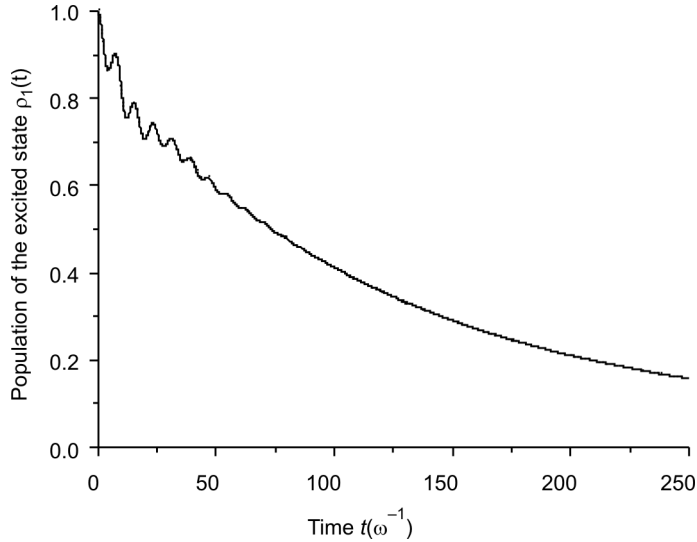

Fig. 1. Time evolution of excited state population $p_1(t)$ for the rate of vibrational relaxation $k = 0.05\omega$ and ratio $r = \varepsilon / \hbar\omega = 1.8$. Calculated values are depicted by the solid curve, while fitted values are depicted by the dotted curve

In Figure 1, the time dependences obtained from the solution to Eqs. (1), (6) cannot be distinguished from those obtained according to Eq. (25). Nevertheless, as we are interested in the decay dynamics, we mainly need to know the parameter Γ_1, i.e., the rate of decay of the excited state. Numerical estimates obtained from data fitting (Eq. (25)) will be compared with the analytically obtained Eq. (23).

The model Hamiltonian of the relevant electronic-vibrational system is defined as

$$
\begin{aligned}
H = |1\rangle\langle 1|\left(\varepsilon + \hbar\omega DQ + \hbar\omega\left(\frac{Q^2}{2} + \frac{P^2}{2}\right)\right) \\
+ |2\rangle\langle 2|\hbar\omega\left(\frac{Q^2}{2} + \frac{P^2}{2}\right) + (|1\rangle\langle 2| + |2\rangle\langle 1|)H_{12}^{\mathrm{I}}(Q)
\end{aligned}
\quad (26)
$$

The parameters of the Hamiltonian (26) have the same meaning as in Eq. (2). For the interstate coupling, we will assume two cases: constant coupling, i.e., $H_{12}^1(Q) = V$ (a) and linear coupling, i.e., $H_{12}^1 = \Delta Q$ (b). The dephasing mechanism in Eq. (1) will be chosen according to the DDA approach of Ref. [8]. For simplicity, we will parametrize it by the rate of vibrational dephasing k (corresponding to $\chi(\omega_m)/(4a_m)$ in Ref. 8).

3.1. Numerical solution

The numerical values will be taken from the model of QD in GaAs as in Ref. 6, where the strong coherent coupling of longitudinal optical phonons in the resonant regions was theoretically predicted. Besides that, these parameters are suitable for the illustration of resonant properties in the weak coupling limit. The limiting value of a small Huang–Rhys factor below is taken for the sake of formal analytic simplicity and also to show that strong resonant amplification of the decay of the excited state is also present for small Huang–Rhys factors. However, it is not too difficult to prove analytically that Eqs. (23), (24) can be used for arbitrary values of Huang–Rhys factors if, in particular, a given dependence of the relaxation tensor and interstate coupling with respect to the vibrational displacement, is used. The last statement can be easily understood if we realize that unitary operators (3), formally appearing in Eqs. (23), (24), shift the equilibrium position $Q_n \to Q_n + D_n^j$ for arbitrary values of the Huang–Rhys factor.

The vibrational energy $\hbar\omega$ will be 36 meV. The electronic separation energy ranges in the interval 25–120 meV. The diagonal coupling constant $\hbar\omega_1 D^1$ ranges from 0 to 11.3 meV. The limiting value 11.3 meV corresponds to the Huang–Rhys factor of 4/81. For the case of constant interstate coupling we set $V = 5.6$ meV, and for the linear model we set $\Delta = 5.6$ meV. We also fixed the room temperature to be $T = 300$ K. The rate of vibrational dephasing k is taken from the weak damping limit up to the limit of the strongly damped oscillator model: $k = 0.03\omega$, $k = 0.05\omega$, $k = 0.1\omega$, $k = 0.2\omega$.

Constant interstate coupling $H_{12}^1 = V$. The numerically calculated dependences of the rate constant Γ_1 on the ratio $r = \varepsilon / \hbar\omega$ of the electronic separation energy ε and vibrational quantum $\hbar\omega$ are shown in Fig. 2. Here we can observe a strong resonant amplification for the resonant condition $\varepsilon = \hbar\omega$ and also weak amplification for the second resonant condition $\varepsilon = 2\hbar\omega$. In this figure, we assumed a very small value for the Huang–Rhys factor $S = 1/50$ (For $S = 0$ we generally get very slow decay, thus we rather took this asymptotically small value of 1/50). The dependences for the increased value of the Huang–Rhys factor $S = 4/81$ are shown in Fig. 3. Again we observe a strong resonant amplification for the first resonant condition $\varepsilon = \hbar\omega$ but also a more pronounced, but still weak, resonant amplification for $\varepsilon = 2\hbar\omega$. In the off-resonant conditions in both figures we observe that the rate Γ_1 linearly increases with the rate of vibrational relaxation k.
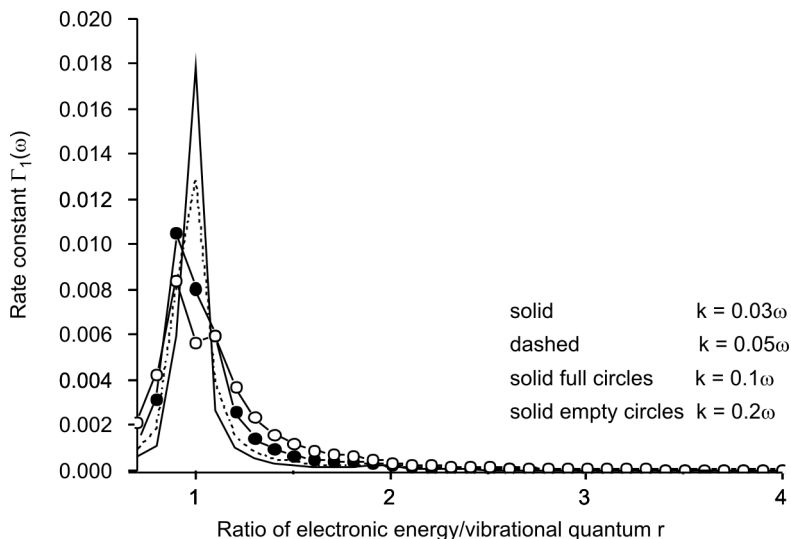
Fig. 2. Dependence of the rate constant Γ_1 of the excited state decay on the ratio $r = \varepsilon/\hbar\omega$ of the electronic excitation energy ε and vibrational quantum $\hbar\omega$. Various rates of vibrational dephasing k are used, while the value of the Huang–Rhys factor $S = 1/50$. The interstate coupling is constant with respect to the vibrational coordinate
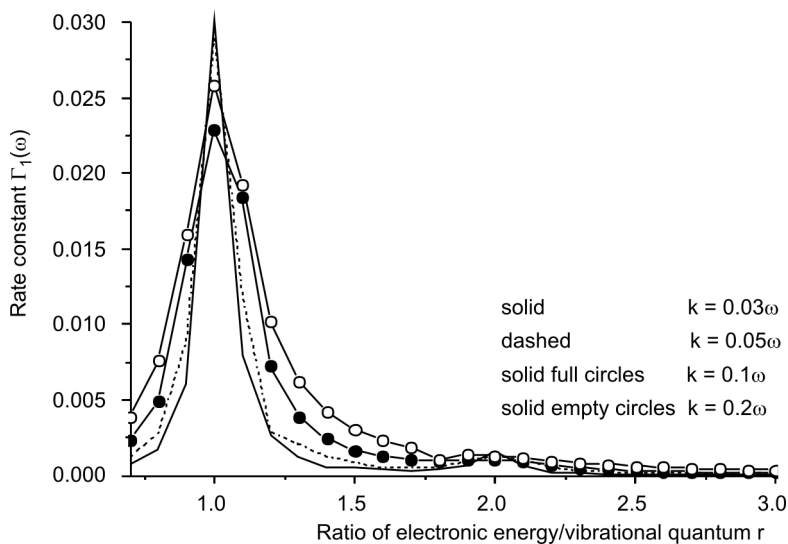

Fig. 3. Dependence of the rate constant Γ_1 of the excited state decay on the ratio $r = \varepsilon/\hbar\omega$ of the electronic excitation energy ε and vibrational quantum $\hbar\omega$. Various rates of vibrational dephasing k are used, while the value of the Huang–Rhys factor $S = 4/81$. The interstate coupling is constant with respect to the vibrational coordinate

Linear interstate coupling $H_{12}^{\mathrm{I}} = \Delta Q$. In the case of interstate coupling, linear with respect to vibrational coordinate, we get even more interesting dependences. In Fig-

ure 4, we also find a strong resonant peak for $\varepsilon = \hbar\omega$ for the Huang–Rhys factor $S = 0$. Besides that we see that in the region of the first resonant pole $\Gamma_1 \approx k$, i.e. the rate of electronic decay equals the rate of vibrational relaxation.
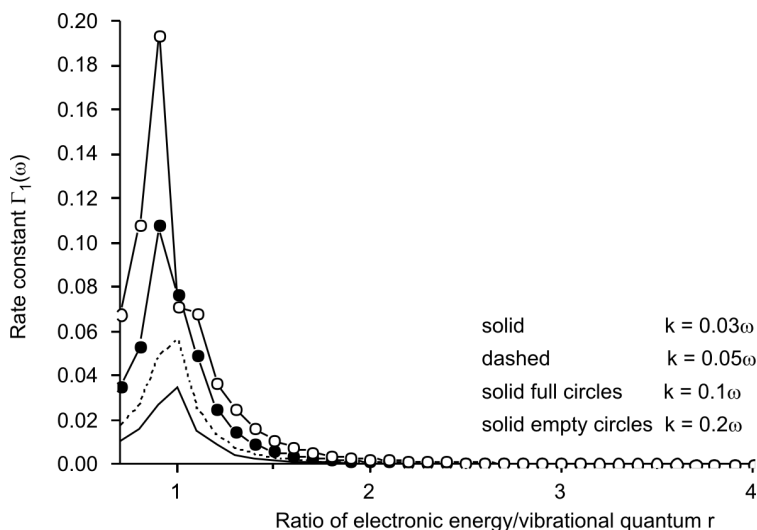
Fig. 4. Dependence of the rate constant Γ_1 of the excited state decay on the ratio $r = \varepsilon/\hbar\omega$ of the electronic excitation energy ε and vibrational quantum $\hbar\omega$. Various rates of vibrational dephasing k are used, while the value of the Huang–Rhys factor $S = 0$. The interstate coupling is linear with respect to the vibrational coordinate
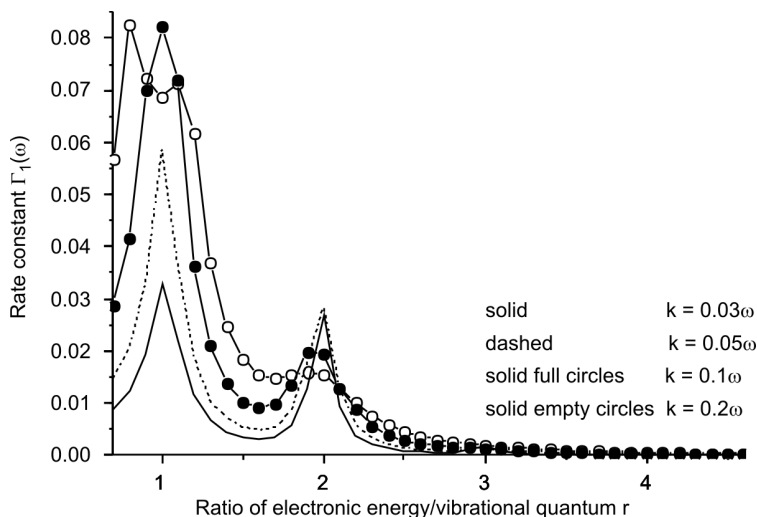
Fig. 5. Dependence of the rate constant Γ_1 of the excited state decay on the ratio $r = \varepsilon/\hbar\omega$ of the electronic excitation energy ε and vibrational quantum $\hbar\omega$. Various rates of vibrational dephasing k are used, while the value of the Huang–Rhys factor $S = 4/81$. The interstate coupling is linear with respect to the vibrational coordinate

If we increase the Huang–Rhys factor S to the value 4/81 (Fig. 5), we again find a strong resonant peak for $\varepsilon = \hbar\omega$ and that at this pole $\Gamma_1 \approx k$ (only for $k = 0.2\omega$ peak is broader due to the overdamped oscillator). Furthermore, we find a very strong resonant peak for $\varepsilon = 2\hbar\omega$.

3.2. Analytical results

In this part, we show results of analytical estimates of the rate of electronic decay Γ_1. It should correspond to the value $W_{mm}^{\mathrm{dis}(0)}$ in Eq. (23). Below we show our results based on the application of the DDA model [8] for the dissipation of the coherent vibrational mode and therefore we utilize Eq. (23). The results taking into account the role of the electronic interstate coupling on the dephasing process in the vibrational manifold will be published elsewhere.

Constant coupling $H_{12}^{\mathrm{I}} = V$. In the analytical calculation, we perform expansion up to the first order in the Huang–Rhys factor $S = D^2/2$. If we insert the constant interstate coupling and the relaxation tensor [8] into Eq. (23), we get after some algebra

$$\Gamma_1 = (VD^1)^2 k \left[\frac{1}{(\omega_{12} - \omega)^2} + \frac{1}{\omega_{12}^2 - \omega^2} \frac{1 + 2n(\omega)}{1 + n(\omega)} + \frac{1}{(\omega_{12} + \omega)^2} \frac{n(\omega)}{(1 + n(\omega))} \right] \quad (27)$$

where $n(\omega) = 1/(e^{\hbar\omega/k_{\mathrm{B}}T} - 1)$ is the Bose-Einstein distribution and $\omega_{12} = \varepsilon/\hbar$ is the transition frequency. Equation (27) confirms our numerical results that in the limit of a small Huang–Rhys factor S there is only one resonant pole at $\varepsilon \approx \hbar\omega$. In the case of strict resonance, Eq. (27) may not be correct because in the case of strong amplification we cannot restrict ourselves just to the second order terms in the interstate coupling. On the other hand, Eq. (27) correctly (in agreement with numerical simulations) predicts the region of the pole $\omega_{12} \sim \omega$ and that it is controlled by the Huang–Rhys factor. For the off-resonant condition, we can expect, on the other hand, a good correspondence at least qualitatively. From Figs. 2 and 3 we directly see the linear increase of Γ_1 with respect to k and $(D^1)^2/2$. Because of the limited scope of this paper, we do not show that in the regions $\hbar\omega_{12} \gg \hbar\omega \gg k_{\mathrm{B}}T$ the dependence $\Gamma_1 \sim 2(VD^1/\omega_{12})^2 k$, stemming directly from Eq. (27), can also be obtained numerically.

Linear coupling $H_{12}^{\mathrm{I}} = \Delta Q$. Limiting again our calculation just to the first order terms in the Huang–Rhys factor $(D^1)^2/2$ we find that we also get a non-zero electronic decay rate $\Gamma_1^{(0)}$ for the zero values of the Huang–Rhys factor. Namely, we obtain

$$\Gamma_1^{(0)} = \frac{2\Delta^2\omega}{\omega_{12}^2 - \omega^2} \frac{k}{1 + n(\omega)} \left[n(\omega) \frac{2\omega}{\omega_{12}^2 - \omega^2} + \frac{1}{\omega_{12} - \omega} \right] \quad (28)$$

that there is just one pole of resonant amplification $\varepsilon = \hbar\omega$ (cf. Fig. 4). The linear increase with the rate of vibrational relaxation k can be also directly checked in Fig. 4, for the off-resonant condition. In the case of resonance, we cannot conclude from Eq. (28) that $\Gamma_1^{(0)} \approx k$, which confirms again that a finite-series perturbation expansion of the interstate coupling is not acceptable, but rather an appropriate self-energy effects in the denominator could be expected. Besides, we see that for zero values of the Huang–Rhys factor only high frequency modes will contribute to the non-radiative decay of the excited state. In agreement with the numerical simulation, we can see that Eq. (28) correctly predicts the region of the resonant pole $\omega_{12} \sim \omega$ and that it is not necessarily controlled by the Huang–Rhys factor.

Keeping just the linear terms in the Huang–Rhys factor for the rate constant $\Gamma_1^{(1)}$ we arrive at the expression

$$
\begin{aligned}
\Gamma_1^{(1)} = \frac{(\Delta D^1)^2}{2} \frac{k}{1+n(\omega)} \Bigg[&\frac{1}{\omega_{12}^2 - \omega^2} + \frac{1}{(\omega_{12}-\omega)^2} + \frac{4}{(\omega_{12}-2\omega)^2} \\
&+ n(\omega)\left(\frac{1}{\omega_{12}^2 - \omega^2} + \frac{3(\omega_{12}^2 + 3\omega^2)}{(\omega_{12}^2 - \omega^2)(\omega_{12}^2 - 9\omega^2)} + \frac{2\omega\omega_{12}}{(\omega_{12}^2 - \omega^2)^2} \right) \\
&+ \left\langle n^2 \right\rangle(\omega)\left(\frac{3}{\omega_{12}^2 - \omega^2} - \frac{3(\omega_{12}^2 + 3\omega^2)}{(\omega_{12}^2 - \omega^2)(\omega_{12}^2 - 9\omega^2)} - \frac{4(\omega_{12}^2 + \omega^2)}{(\omega_{12}^2 - \omega^2)^2} \right) \\
&+ \frac{4(\omega_{12}^2 + 4\omega^2)}{(\omega_{12}^2 - 4\omega^2)^2} + n(\omega)^2 \left(\frac{6(\omega_{12}^2 + 3\omega^2)}{(\omega_{12}^2 - \omega^2)(\omega_{12}^2 - 9\omega^2)} - \frac{2}{\omega_{12}^2 - \omega^2} + \frac{4(\omega_{12}^2 + \omega^2)}{(\omega_{12}^2 - \omega^2)^2} \right) \Bigg]
\end{aligned}
\tag{29}
$$

with the second moment of phonon occupation $\left\langle n^2 \right\rangle(\omega) = \tanh(\hbar\omega/k_B T)n(\omega)$. In comparison with the previous case, we see a richer structure of resonant poles. Here, we recognize also a strong resonant amplification even for $\varepsilon = 2\hbar\omega$, as is also numerically confirmed in Fig. 5. In the case of the first resonance ($\varepsilon = \hbar\omega$), we again cannot confirm the relation $\Gamma_1^{(1)} \approx k$ directly from Eq. (29). On the other hand, we see that if the self-energy of order $(\Delta D^1)^2/2$ were added to the denominator, we would obtain, for the first resonance, the numerically obtained relation $\Gamma_1^{(1)} \approx k$. Again we can observe that analytical formulae can correctly predict the regions of resonant poles and that in the case of linear interstate coupling, the Huang–Rhys factor can also induce the second resonant pole $\varepsilon = 2\hbar\omega$.

Because of the limited scope of this paper, we do not show that in the limit $\hbar\omega_{12} \gg \hbar\omega \gg k_B T$ the analytical formula (29) corresponds fairly well to numerical simulations. Namely, $\Gamma_1 \sim 3(\Delta D^1 / \omega_{12})^2 k$.

4. Conclusion

The vibrational manifold has been separated into two subbaths. The first one, interacting with electronic states via non-adiabatic coupling and the Huang–Rhys factors, was left in the coherent state. The second one, responsible for the dephasing and relaxation of coherent vibrational modes due to the Duschinsky mixing, was projected out. The resulting equations for the system consisting of electrons and coherent vibrational subbath were time irreversible. In the next step, the coherent subbath has also been projected out and finally equations for the occupation probabilities of electronic states were obtained. In the case of weak interstate coupling and in the off-resonant limit, explicit analytical expressions of the electronic decay rates were found. The latter formulae were expressed through the parameters of coherent electronic-vibrational couplings and the relaxation rates of coherent vibrational modes.

The derived analytical formulae were compared with the numerical solutions of the time evolution of a simple two-level electronic system, coupled to a single vibrational mode attached to the thermalizing subbath. We have found that in comparison with numerical simulations analytical expressions correctly predicted the poles of resonant amplification of electronic transfer.

In the case of the off-resonant limit and a weak interstate coupling, the analytical expressions based on the perturbative approach up to the second-order in the interstate coupling corresponded qualitatively to the numerical results. The agreement between the numerical and analytical second order approach was found for transition electronic frequencies. The latter frequencies were larger by an order of magnitude than the vibrational frequency.

We have also shown that the double projection technique provides an analytic expression for the internal relaxation processes in the bath, i.e. the transfer of excess vibrational energy of coherent modes to the dephasing subbath. It will be published elsewhere that we can even predict analytically whether the interstate coupling should be taken into account in the relaxation process in the vibrational manifold. Or, in other words, under which condition the diabatic damping approximation, or its extension to the first order in the interstate coupling or other models like, e.g. the Lindblad model, are correct.

Numerical simulations in the resonant regions proved that in the case of first resonance, the rate of electronic decay equals the dephasing rate of the coupled vibrational mode.

In the near future, we plan to estimate the cooperative and/or competing of more vibrational modes, particularly in the regions of resonant conditions.

An open problem is the analytical estimation of resonant decay rates and also for a stronger interstate coupling. Here, the theory would have to go beyond the standard approach.

The double projection technique presented here can be utilized for arbitrary values of the Huang–Rhys factors, although the analytical formulae presented here, for the sake of simplicity, were shown just up to the first order in the Huang–Rhys factors.

We conjecture that the theoretical background presented in the paper is applicable for systems like quantum dots, molecular transistors, molecular wires and other systems where charge transfer and excited state decay are important. In particular, in the field of molecular transistors, the subject of non-adiabatic couplings have been almost totally neglected. Our simulations showed that under specific conditions of resonant transfer, the non-radiative decay of electronic states can be of the same order as vibrational dephasing. In future, molecular systems embedded between two contacts should take into account the vertical electronic transfer.

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