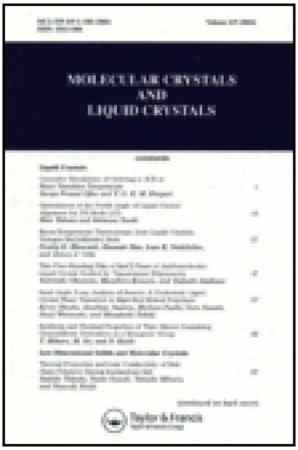

Molecular Crystals and Liquid Crystals

Dependence of Resonant Effects in Excited-State Decay on the form of Inter-State Coupling

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To cite this article: Miroslav Menšík & Karel Král (2008): Dependence of Resonant Effects in Excited-State Decay on the form of Inter-State Coupling, Molecular Crystals and Liquid Crystals, 486:1, 79/[1121]-100/[1142]

To link to this article: http://dx.doi.org/10.1080/15421400801917817

Mol. Cryst. Liq. Cryst., Vol. 486, pp. 79/[1121]–100/[1142], 2008

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400801917817

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Dependence of Resonant Effects in Excited-State Decay on the form of Inter-State Coupling

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Time dependence of excited state decay is studied theoretically. The model system is assumed to consist of two electronic levels coupled to a single vibrational mode and dissipating its energy to a thermal bath. The form of inter-state coupling is assumed to be either a) constant (independent on vibrational coordinate) or b) linear in vibrational coordinate. Generally, the rate of excited state decay resonantly increases when the ratio r of the excitation energy and vibrational quantum takes integer values ($r = 1, 2, 3, \ldots$). The effect is stronger and appears even for $r \geq 2$ when the Huang-Rhys factor is larger and/or the inter-state coupling is explicitly dependent on vibrational coordinate.

Keywords: electron-vibrational interaction; energy transfer; excited state decay; resonance; vertical excitation; vibrational coherence

1. INTRODUCTION

The study of energy transfer and particularly of excited-state decay covers a broad range of physics from, *e.g.*, physics of semiconductors to organic compounds. Although the problem has been intensively studied for several decades it has not been completely solved up to now even in relatively simple systems as, *e.g.*, electronic transitions in organic systems controlled by a single vibrational mode [1]. The situation is not much better understood also in the semiconductor

This work is supported by the grant No. 202/07/0643 of the Czech Science Foundation and grant No. 401770601 of the Grant Agency of the Academy of Sciences of the Czech Republic.

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physics, namely electronic transitions due to the coupling to longitudinal optical (LO-) phonons [2]. Generally, the energy transfer process is different for radiative and non-radiative transitions. The radiative transitions are performed among vibronic eigenstates of the total electronic-vibrational system due to its coupling with photons, which is generally non-zero in the vibronic representation. On the other hand, the pure non-radiative transition cannot appear among the vibronic eigenstates as far as on the basis of basic principles of quantum theory eigenstates cannot be changed during the time evolution. Thus, whenever we speak about non-radiative decay of excited state, this state must not be a true vibronic eigenstate. In what follows, one must exactly define “what state” is then transferred in the energy transfer process. This exact definition means, that the basis of states of the Hilbert space should be defined exactly. We will point out below that exact mathematical definition should be related to a given experiment (or at least to quantum chemical calculation). Usually, two basic approaches in the choice of the electronic basis, namely adiabatic and diabatic ones, are used. The convenience of each choice depends on particular system, but it can be found, in general, that number of coupled diabatic states should be equal to the number of coupled adiabatic ones [3–5]. The adiabatic basis is very close to the true eigenstates if potential energy surfaces (PESs) are well separated. When the adiabatic PESs are close to each other or even they intersect (conical intersection – CI) the non-adiabatic coupling becomes very strong and the diabatic approach seems to be better. The diabatic basis is usually only weakly dependent on vibrational coordinates [6], but such a requirement is so general, that we have too many possibilities to define diabatic states. All of these possible diabatic basis sets are mutually connected by unitary transformations in the Hilbert space of electronic distributions. In what follows, the vibrational dependence of the diabatic inter-state coupling is quite general.

In the following, we will study the energy transfer in the diabatic framework. We will check the time dependences of the diabatic state’s population for two models of the inter-state coupling: a) constant (independent on vibrational coordinates) and b) linear in vibrational coordinate. The article is organized as follows. In the Section 2. models with various form of the inter-state coupling will be discussed and their connection to the concrete experiments and physical phenomena will be discussed. In the Section 3. the model Hamiltonian of two-level electronic system coupled to a single vibrational mode is defined. In the Section 4. the energy damping mechanism is discussed with respect to the choice of diabatic basis. In the Section 5. time dependences of upper diabatic state population will be defined. The decay rates and Rabi oscillations of the occupation probability for both models will be analyzed in the Section 6. The results will be summarized in the Section 7.

2. RELATION OF THE CHOICE OF THE DIABATIC BASIS AND THE FORM OF THE INTER-STATE COUPLING

Before the discussion about various forms of inter-state coupling of diabatic states we mention a little some relations of these states with the adiabatic basis (those obtained by means of quantum chemistry). In the following, the set of vibrational coordinates will be denoted as $\{Q\}$ and the displacement of the i-th vibrational mode is denoted as Q^i. The adiabatic electronic state corresponding to the m-th PES is denoted as $|\varphi_m^{\mathrm{ad}}(Q)\rangle$. The explicit dependence of electronic distribution on vibrational coordinates reflects the fact that during the motion of the wave packet on the given m-th PES the adiabatic electronic state changes. If the energy of the system is restricted to some interval then also the vibrational dynamics can be limited to some interval of vibrational displacements with a probability close to unity. Consequently, we may ask the question, what is the dimension of Hilbert space generated by all adiabatic electronic states in this interval? Let's assume that we travel from a fixed position $\{Q_1\}$ to an arbitrary point $\{Q_2\}$ then we get

$$|\varphi_m^{\mathrm{ad}}(Q_2)\rangle = |\varphi_m^{\mathrm{ad}}(Q_1)\rangle + \int_{Q_1}^{Q_2} \mathrm{d}\vec{Q} \cdot \vec{\nabla}_Q |\varphi_m^{\mathrm{ad}}(Q)\rangle. \tag{1}$$

If during "the travel" the electronic distribution is almost unchanged then the derivative (gradient) of adiabatic states should be also small during the whole trajectory. Namely, we can imagine that during the motion the change of electronic configuration in Eq. (1) represents a rotation of a vector in the Hilbert space. Intuitively, we can see that it is the gradient of the adiabatic electronic states that "creates" dimension of the Hilbert space. When we perform a projection of the "derivative" of the m-th state onto the n-the state we get exactly the non-adiabacity operator defined as follows

$$\tau_{nm}^{i}(Q) = \langle \varphi_n^{\mathrm{ad}}(Q) | \partial_i \varphi_m^{\mathrm{ad}}(Q) \rangle. \tag{2}$$

The non-adiabacity operator is then nothing more then a "measure" of how many of the derivative of electronic state $\varphi_m^{\mathrm{ad}}(Q)$ penetrates into the other PESs ($\varphi_n^{\rm ad}(Q)$). In the same way, the non-adiabacity operator $\tau_{nm}^i(Q)$ couples two electronic adiabatic states $\varphi_n^{ad}(Q)$ and $\varphi_m^{ad}(Q)$. Thus, the dimension of the Hilbert space during "the travel" is equal to the number of non-adiabatically coupled PESs and in the same way to the number of linearly independent diabatic states. For more details we refer the reader to Ref. [3–6].

Let's assume that in the Eq. (1) the final distribution is different form the initial one. Then, the non-adiabatic coupling to at least one another PES during the trajectory should be strong. According to the Hellmann-Feynman theorem

$$\tau_{nm}^i(Q) = \frac{\langle \varphi_n^{\rm ad}(Q)|\partial_i H_e(Q)|\varphi_m^{\rm ad}\rangle}{\varepsilon_m(Q) - \varepsilon_n(Q)}, \tag{3}$$

where $H_e(Q)$ is the electron-vibrational Hamiltonian without nuclear kinetic energy and $\varepsilon_m(Q)$ is the vertical m-thadiabatic energy, we get that in the region of this strong coupling the respective PESs must approach each other. Thus, if the electronic configurations corresponding to various local minima on the PES are different, then the higher adiabatic PESs should be close somewhere in the region of interest and strongly interacting during the wave-packet motion. Such coupling can be thus expected in donor-acceptor systems [7–9], polaron transport in conjugated polymers [10–12] or excimer-charge transfer (CT) states formation [13–15]. Diabatic basis in such systems is commonly defined by the adiabatic electronic configurations, corresponding to different local minima of PES. Unpleasant mathematical objection against such definition of diabatic states follows from the fact, that these states need not be orthogonal. During the othonormalization process any connection to the adiabatic PES is lost. The whole problem of the correct definitions of diabatic states may be solved if the theorem that dimension of diabatic states = dimension of adiabatic states = N is used. Then, e.g., we can choose an arbitrary point $\{Q_0\}$ from the interval of relevant nuclear configuration space and calculate all adiabatic vertical electronic configurations $\{|\varphi_n^{\rm ad}(Q_0)\rangle\}_{\rm n=1,N}$. The vertical diabatic basis is then defined as

$$|\varphi_m\rangle = |\varphi_m^{\rm ad}(Q_0)\rangle \tag{4}$$

The adiabatic Hamiltonian $H_{\rm el}(Q)$ expressed in the "vertical diabatic" basis and expanded to the second-order in vibrational displacements

$Q^i - Q_0^i$ reads as follows

$$\begin{aligned} H_{\mathrm{el}}(Q) = {} & \sum_m |\varphi_m\rangle\langle\varphi_m|\varepsilon_m(Q_0) + \sum_{m,i} |\varphi_m\rangle\langle\varphi_m|D_m^i(Q^i - Q_0^i) \\ & + \sum_{m,i,j} |\varphi_m\rangle\langle\varphi_m|K_m^{i,j}(Q^i - Q_0^i)(Q^j - Q_0^j) \\ & + \sum_{m\neq n,i} |\varphi_m\rangle\langle\varphi_n|\Delta_{mn}^i(Q^i - Q_0^i) \\ & + \sum_{m\neq n,i,j} |\varphi_m\rangle\langle\varphi_n|\Delta_{mn}^{i,j}(Q^i - Q_0^i)(Q^j - Q_0^j). \end{aligned} \tag{5}$$

Here $\varepsilon_m(Q_0)$ are the vertical energies, D_m^i are the on-diagonal linear coupling constants corresponding to m-th electronic state and i-th vibrational mode. Tensors of stiffness constants of respective m-th PES are denoted as $K_m^{i,j}$. We can see that the constant term of the inter-state coupling among vertical diabatic states disappears, while the linear and quadratic terms in the inter-state coupling become dominant and their coupling constants are denoted as Δ_{mn}^i and $\Delta_{mn}^{i,j}$, respectively. Parameters of the Taylor expansion (5) can be obtained from quantum chemistry [16,17]. It can be easily found [17] that the non-adiabacity operator $\tau_{mn}^i(Q)$ and the linear coupling constant Δ_{mn}^i satisfy the following relation

$$\tau_{nm}^i(Q_0) = \frac{\Delta_{nm}^i}{\varepsilon_m(Q_0) - \varepsilon_n(Q_0)} \quad n \neq m, \tag{6}$$

It was shown recently that the vertical coupling model is very good for mapping the vibrational coherence of electronic distribution after excitation [1]. The point Q_0 is arbitrary (the only limitation is that it should be taken from the interval of relevant nuclear configuration space). Usually, for the case of fast excitation, it is taken in the point of PES minimum of the ground state.

From the experimental point of view we cannot measure the non-radiative transitions directly, but we measure them indirectly by various spectroscopic methods including those with time-resolution. The intensity of absorption (emission signal) is directly controlled by the value of transition dipole moments in vibronic representation. In the adiabatic picture we get for the electronic part of transition dipole moment the following expansion

$$\begin{aligned}\langle \varphi_m^{\mathrm{ad}}(Q)|\vec{d}\cdot\vec{e}(Q)|\varphi_n^{\mathrm{ad}}(Q)\rangle &\approx (\vec{d}\cdot\vec{e})_{mn}(Q_0)\\ &+\sum_i Q^i\left\{\frac{\Delta_{nm}^i}{\varepsilon_m(Q_0)-\varepsilon_n(Q_0)}((\vec{e}\cdot\vec{d})_{nn}(Q_0)-(\vec{e}\cdot\vec{d})_{mm}(Q_0))\right.\\ &\quad+\sum_{k(\neq m,n)}\left(\frac{\Delta_{km}^i}{\varepsilon_m(Q_0)-\varepsilon_k(Q_0)}(\vec{e}\cdot\vec{d})_{kn}(Q_0)+\frac{\Delta_{kn}^i}{\varepsilon_n(Q_0)-\varepsilon_k(Q_0)}\right.\\ &\quad\left.\left.\times(\vec{e}\cdot\vec{d})_{mk}(Q_0)\right)\right\}. \quad n\neq m \end{aligned} \tag{7}$$

where $\vec{d}$ is the dipole moment, $\vec{e}$ is the vector of polarization and $(\vec{e}\cdot\vec{d})_{ab}(Q_0)$ are the matrix elements of dipole moments in the vertical diabatic basis. In the Eq. (7) the first term controls the Franck-Condon contribution to the signal, while other terms contribute to the correction of to the vibrational modulation in the case of time-resolved spectrum [18]. Both the Franck-Condon as well as the vibrational terms are controlled by the matrix elements of the type $(\vec{e}\cdot\vec{d})_{ab}(Q_0)$, which decide whether the states $|a\rangle, |b\rangle$ will be active, i.e., bright in the signal. Consequently, those are just bright states, occupation of which is directly measured in the time-resolved signal.

On the other hand, for this purpose, we can define alternative diabatic states as bright and dark states of transition dipole moments [19]. The bright diabatic state $|\psi_1\rangle$ is defined as

$$|\psi_1\rangle=\frac{\sum_{i=1}|\varphi_i\rangle\langle\varphi_i|(\vec{d}\cdot\vec{e})|g\rangle}{\sqrt{\sum_{i=1}|\langle g|(\vec{d}\cdot\vec{e})|\varphi_i\rangle|^2}}, \tag{8}$$

where diabatic state $|g\rangle$ corresponds to the ground adiabatic state at the point Q_0. All diabatic states taken from the excited state manifold, which are orthogonal to the state $|\psi_1\rangle$, are optically dark in the direction of polarization vector $\vec{e}$. Hence, it can be easily checked by simple algebra that the transition from the vertical diabatic basis to that of bright-dark diabatic basis is given by the unitary transformation in the Hilbert space. After that transformation, the inter-state coupling in the bright-dark basis will contain, in general, also constant as well as higher order terms in the vibrational displacement. On the other hand, it was proved in the Ref. [19] that model with just only constant inter-state coupling of bright and dark states [20], cannot be generally accepted for CT-systems, but at least linear terms in the vibrational displacement should be present in the inter-state coupling.

Even more, it was illustrated [1] in the simple model of two-level electronic system coupled to a single vibrational mode, that time dependences corresponding to the constant, linear and quadratic form of inter-state coupling provide very different structure of Rabi oscillation. The difference increased with the Stokes shift (Huang-Rhys factor) of coupled vibrational mode in the excited state. We conjecture that models of time-resolved dynamics, namely definitions of diabatic states, should be taken very carefully and the form of inter-state coupling should be taken properly.

From the numerical point of view the inclusion of all vibrational modes in the numerical simulation is not acceptable so, generally, the concept of separation of vibrational modes into the relevant modes and bath modes is taken into account. The bath modes are usually assumed to provide either weak non-adiabatic coupling or small contribution to the Stokes shift during the electronic transition. Then, if we assume that bath modes are almost in the equilibrium state within a given PES we can easily find that the coherent dynamics of relevant system can be satisfactorily described by the Hamiltonian (5) taking into account just relevant modes and corrected with the additive effective term

$$H_{\mathrm{el}}^{\mathrm{corr}}(Q) = \sum_{m,n} V_{mn}^{\mathrm{Con}}(1 - \delta_{mn})|\varphi_m\rangle\langle\varphi_n|. \tag{9}$$

Here, the effective constant inter-state coupling V_{mn}^{Con} is given by the linear terms of the bath modes approximated by their mean equilibrium values in the respective PESs. Thus, V_{mn}^{Con} can be interpreted as the mean field of the bath modes and it equals to [21]

$$V_{mn}^{\mathrm{Con}} \approx -\sum_{l \in \mathrm{bath}} \Delta_{mn}^{l} \frac{(D_m^l + D_n^l)}{2} \tag{10}$$

we understand that such "mean field" approximation is not correct in the femtosecond time scale but on the picosecond time scale, corresponding to real life-time of excited state, it can be understood as an useful model because bath modes are almost thermalized.

In this section we showed two examples that after the transition from the vertical to the bright-dark diabatic basis or by inclusion of the "mean field approximation" of the bath modes, we get the inter-state coupling of diabatic states to be, at least, a sum of the constant and linear terms in vibrational displacements of relevant modes.

3. DEFINITION OF MODEL HAMILTONIAN: TWO ELECTRONIC LEVELS + SINGLE VIBRATIONAL MODE

Although semiconductor quantum dot (QD) system of GaAs type and organic molecular system are formally different systems it was found recently that they exhibit similar interesting properties in the excited state decay [22]. It was theoretically calculated that the rate of the electronic excited state decay in GaAs quantum-dot exhibits a resonant amplifying for integer values of the ratio of the excitation energy and energy of longitudinal optical (LO) phonons [23]. On the other, it was shown that similar resonant amplifying can be obtained in organic systems modeled by the system consisting of two electronic levels coupled to a single vibrational mode embedded in a heat bath [22]. The similarity of the dexcitation dynamics for these two formally different systems is not so surprising as far as the interaction Hamiltonian of the inter-state coupling for GaAs QD is controlled by the Frölich coupling, which oscillates with the frequency ω of LO-phonons. The non-radiative decay in organic systems is satisfactorily described by the Hamiltonian (5). In the case of a single-mode model the inter-states coupling also oscillates with the frequency ω of the vibrational mode. Thus, oscillating character of the inter-state coupling can add new resonant channels in the deexcitation dynamics.

In the present simulation we study time dynamics of two electronic levels coupled to a single vibrational mode embedded in the dissipative environment. We accept, on the basis of physical discussion in the paragraph above, that the inter-state coupling is a sum of constant, linear and higher-order terms in the vibrational displacement. In the numerical simulation we check separately the models with constant and linear coupling. The model Hamiltonian H is thus written as

$$\begin{aligned} H = |1\rangle\langle 1|\left(\varepsilon + DQ + \hbar\omega\left(\frac{Q^2}{2} + \frac{P^2}{2}\right)\right) + |2\rangle\langle 2|\hbar\omega\left(\frac{Q^2}{2} + \frac{P^2}{2}\right) \\ + W(Q)(|1\rangle\langle 2| + |2\rangle\langle 1|) \end{aligned} \tag{11}$$

where $|1\rangle, |2\rangle$ denote diabatic states, ε is the vertical excitation energy, Q (P) is the vibrational coordinate (momentum), $\hbar\omega$ is the vibrational energy quantum and D is the diagonal coupling constant. The potential of lower state $|2\rangle$ has its minimum at $Q = 0$. The potential of higher diabatic state $|1\rangle$ has its minimum at $Q = -D/\hbar\omega$. The difference between vertical excitation energy and relaxed minimum is $D^2/2\hbar\omega$. For the inter-state coupling $W(Q)$ we assume the following cases: (i) $W(Q) = V$ (constant independent on vibrational coordinate) (ii) $W(Q) = \Delta Q$ (linear in vibrational coordinate).

4. MODEL OF ENERGY DISSIPATION IN THE DIABATIC PICTURE AND CONCEPTS OF BATH MODES

Quantum mechanical systems, as they are defined from basic principles, are fully time-reversible and their time evolution is controlled by the Schrődinger or Liouville equations. The phenomenologically observed time-irreversibility, on the other hand, is contradictory to basic formulation of quantum theory and it is introduced to kinetic equations by hand. It is usually performed on the basis of following assumptions: i) Vibrational modes are separated into relevant and bath modes ii) Master equation for the system consisting of electronic degrees of freedom + relevant modes is derived, while bath modes are projected out iii) Influence of the bath is taken up to the 2nd order in the system-bath coupling iv) Markovian approximation in the memory function is used. Then, the relaxation among eigenlevels of the system is achieved and we get the so-called Redfield approach [24] (without secular approximation). If, additionally, in the relaxation tensor the inter-state coupling is omitted we get the diabatic damping approximation (DDA) [25]. In DDA the relaxation is accomplished among vibrational levels within a given diabatic PESs. The Redfield approach is commonly accepted in the literature as the best among 2nd order theories (within the system-bath coupling). There are but some objections against that. First, the electronic-vibrational Hamiltonian (5) cannot be generally written as a simple sum of system, bath and bilinear system-bath Hamiltonians. This separation is possible just within a given diabatic PES. Namely, it is assumed that initially the system is in the ground PES and under harmonic approximation the vibrational manifold is diagonalized and thermalized by the anharmonic coupling. Then, after excitation, those modes, which will not change their equilibrium positions, will be called bath modes. It is the Duschinsky coupling of modes [26] within a "given diabatic PES" that contributes to the bilinear system-bath coupling. It means that the system-bath coupling is dependent on the choice of diabatic basis itself. Under different choice of diabatic basis we could obtain different scaling of the strength of system-bath coupling. Čápek and Barvík [27] found that if the scaling of the inter-state coupling is comparable to the rate of vibrational relaxation then DDA and Redfield models are undistinguishable in the sense of Davies weak coupling limit [28], i.e., both are exact for times $t \leq \lambda^{-2}$, where λ is the strength of system-bath coupling. For longer times the Redfield approach and DDA may differ [29]. In the following, we will use the DDA approach. In agreement with Ref. [27] we only assume that the matrix elements of the inter-state coupling will not be significantly larger than the rate of vibrational relaxation in the diabatic PESs.

5. TIME DEPENDENCES OF DIABATIC STATES POPULATION

The time evolution of the density matrix $\rho(t)$ of the system (diabatic states + single vibrational mode) is controlled by the Liouville equation

$$\frac{\partial}{\partial t}\rho(t) = -\mathrm{i}\frac{[\mathrm{H}, \rho(t)]}{\hbar} + L^{\mathrm{rel}}\rho(t), \tag{12}$$

where L^{rel} is the relaxation tensor given by the bilinear coupling of the relevant mode to the bath modes. For the relaxation process we assume the DDA [25] and the explicit form of L^{rel} can be found in Ref. 25. For the sake of simplicity we assume that the relaxation in both potentials is similar and it is controlled by just only one parameter k (it corresponds to $\gamma(\omega_m)/(4a_m)$ in Ref. 25). The rate of vibrational relaxation from the level n to the level $n-1$ is proportional to kn. The initial condition corresponds to the fast vertical excitation from the relaxed state of the potential $|2\rangle$ to the state $|1\rangle$. The time evolution of the population $p(t)$ of the state $|1\rangle$ will be calculated, where $p(t)$ is defined as

$$p(t) = \mathrm{Tr}_{\mathrm{bath}}\langle 1|\rho(t)|1\rangle. \tag{13}$$

6. RESULTS OF NUMERICAL SIMULATIONS

In the numerical simulations the vertical excitation energy ε is taken from 25 to 120 meV and vibrational energy $\hbar\omega = 36\,\mathrm{meV}$. These values were also used in Refs. [22–23] for the model GaAs quantum dot and vertical relaxation in the organic system represented by the linear coupling model. We conjecture that such values of vertical excitation energies for organic system can represent the difference between two excited states, when the excited state manifold is satisfactorily described by the system of two diabatic potentials. The on-diagonal coupling constant D is taken from 0 to 11.3 meV. The value of the constant of inter-state coupling $\Delta = 5.6\,\mathrm{meV}$ (linear off-diagonal coupling, i.e., when $W(Q) = \Delta Q$) and $V = 5.6\,\mathrm{meV}(W(Q) = V)$. Such values of parameters of both diabatic potentials correspond to the case of inverted regime and weak inter-state coupling. The rate of vibrational dephasing was taken as $k = 0.03\omega$, $k = 0.05\omega$, $k = 0.1\omega$, $k = 0.2\omega$.

Time dependences of the population $p(t)$ of the upper potential were calculated by the solution of the Eq. (12) and time dependences thus obtained were successfully fitted by the following formula

$$p(t) \approx A_0 + A_1 \exp(-\Gamma_1 t) + A_2 \exp(-\Gamma_2 t)\cos(\Omega_2 t) + A_3 \exp(-\Gamma_3 t)\cos(\Omega_3 t) \tag{14}$$

Parameters of the fit are discussed with respect to the ratio $r = \varepsilon/\hbar\omega$ of the vertical energy to to the vibrational energy quantum.

a) *linear inter-state coupling model*: The dependence of the rate Γ_1 of central decay of the population $p(t)$ on the ratio r is depicted in Figure 1 for the coupling constant $D = 11.3\,\mathrm{meV}$ (the number of vertically excited vibrational levels, so called Huang-Rhys factor, $S = \frac{D^2}{2(\hbar\omega)^2} = \frac{4}{81}$). We can see that strong resonant amplifying appears for integer values of the ratio r. Namely, if the value $r = 1, 2$ the peaks of amplifying are strong. We conclude that maximum intensity of non-radiative energy transfer is for $\varepsilon \approx \hbar\omega$. Below we explain that this condition stems rather from the structure of Franck-Condon factors, the form of inter-state coupling and energy denominators *but not from any resonant "energy conservation law"*. Next, we can see in Figure 1 that for $\varepsilon = \hbar\omega$ the decay rate Γ_1 of the population $p(t)$ is, for a small

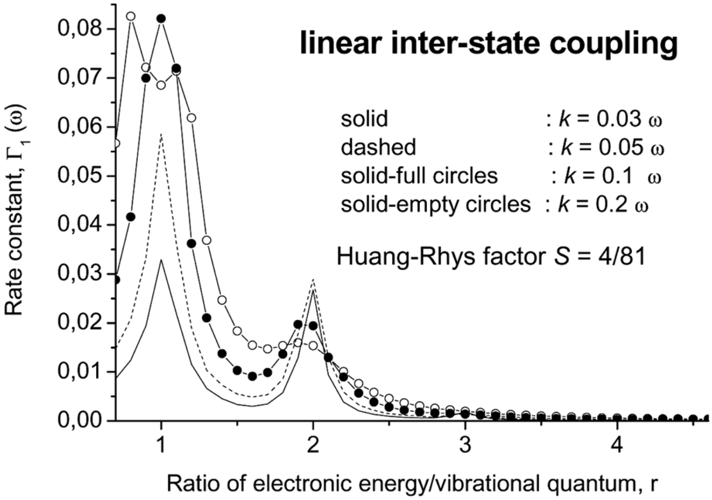

FIGURE 1 Dependence of the rate constant Γ_1 of the excited state decay on the ratio $r = \varepsilon/\hbar\omega$ of the electronic excitation energy ε and vibrational quantum $\hbar\omega$. Various rates of vibrational dephasing k are used, while the value of the Huang-Rhys factor $S = 4/81$. The inter-state coupling is linear with respect to the vibrational coordinate.

rate k of vibrational dephasing, equal to k. Namely, $\Gamma_1 \approx k$. Physically it means, that in the resonant case of linear coupling model, the rate of electronic excited state decay equals to the rate of vibrational decay. This is influenced by the fact, that in the resonant case of linear coupling there is an interplay of the fully coherent exchange between electronic states and vibrational mode and that of vibrational relaxation, which in turn, causes the electronic energy decay. For values $k = 0.2\omega$ the height of the peak is smaller, but broader. It indicates that for higher values of vibrational dephasing the coherent regime becomes gradually smaller. In Figure 2 we demonstrated the dependence of the frequency of Rabi oscillation Ω_3 on the parameter r. We get the following empirical relation $\Omega_3 \approx (r-1)\omega = \varepsilon/\hbar - \omega$. Here, we underline the fact that the Huang-Rhys factor is small because $D \ll \hbar\omega$. So we cannot distinguish numerically, if the relation would have to be $\varepsilon/\hbar - \omega$ or $\varepsilon/\hbar - D^2/(2\hbar^2\omega) - \omega$ as it was observed in Ref. [1] for systems with non-negligible Huang-Rhys factor. The first relation would correspond to the interference of the vertical transition frequency and oscillating field of inter-state coupling, while the second

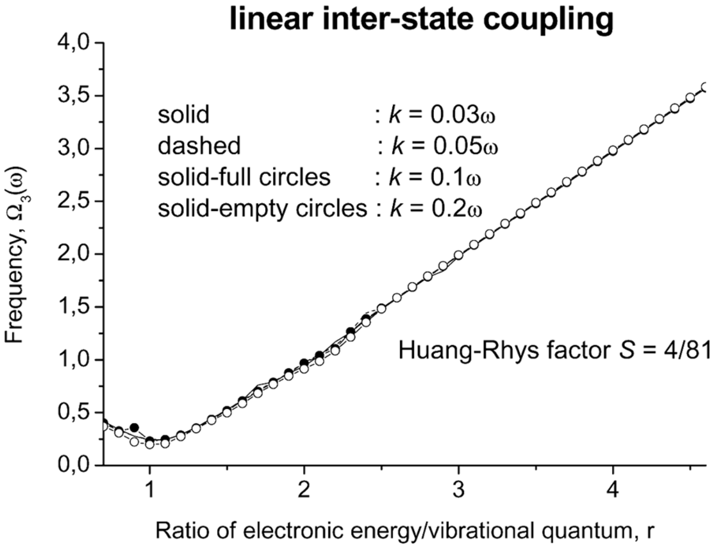

FIGURE 2 Dependence of the frequency Ω_3 of the Rabi oscillation of the excited state population on the ratio $r = \varepsilon/\hbar\omega$ of the electronic excitation energy ε and vibrational quantum $\hbar\omega$. Various rates of vibrational dephasing k are used, while the value of the Huang-Rhys factor $S = 4/81$. The inter-state coupling is linear with respect to the vibrational coordinate.

one to the interference of transition frequency between two relaxed diabatic states and the oscillating field of the inter-state coupling. We conjecture that when the adiabatic approximation can be applied then the Rabi oscillation should rather contain component corresponding to the transition among relaxed (not vertical) levels. In Figure 3 we show the dependence for the frequency Ω_2. For small values of r we cannot exclude deviations from an ideal fit. But for values of r between 2 and 3 we observe linear increase of the Rabi frequency Ω_2. For $r > 3$ Ω_2 takes a constant value $\Omega_2 \approx \omega$. These dependences were the same for all values of the rate of vibrational dephasing k so we conjecture that values of the fit of the coherent oscillations should be correct.

In Figure 4 we show the dependence of the rate constant Γ_1 on the parameter r for $D = 0\,\text{meV}$. We observe that the maximum peak is obtained for $\varepsilon \approx \hbar\omega$. Next, for this point the rate constant Γ_1 also obeys the relation $\Gamma_1 \approx k$. Resonant peaks for higher integer values of the ratio $r = \varepsilon/(\hbar\omega)$ don't exist. We thus conclude that it is the Stokes shift (Huang-Rhys factor) that promotes the formation of the resonant peaks for higher integer values of the parameter r. In Figure 5 we show the relation of the Rabi frequency Ω_2 with respect to the

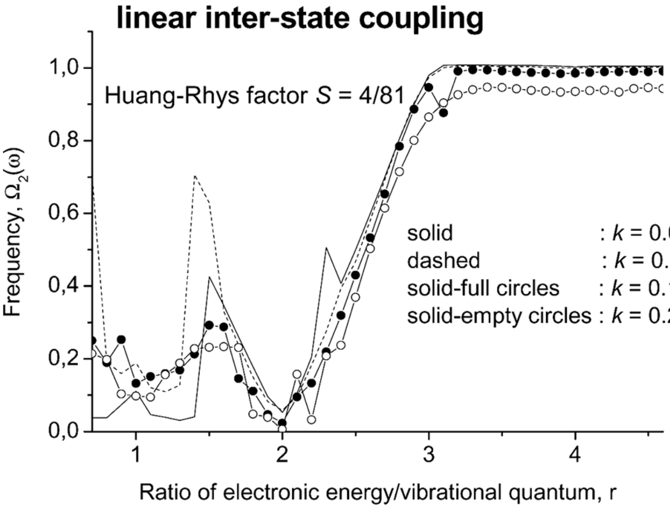

FIGURE 3 Dependence of the frequency Ω_2 of the Rabi oscillation of the excited state population on the ratio $r = \varepsilon/\hbar\omega$ of the electronic excitation energy ε and vibrational quantum $\hbar\omega$. Various rates of vibrational dephasing k are used, while the value of the Huang-Rhys factor $S = 4/81$. The inter-state coupling is linear with respect to the vibrational coordinate.

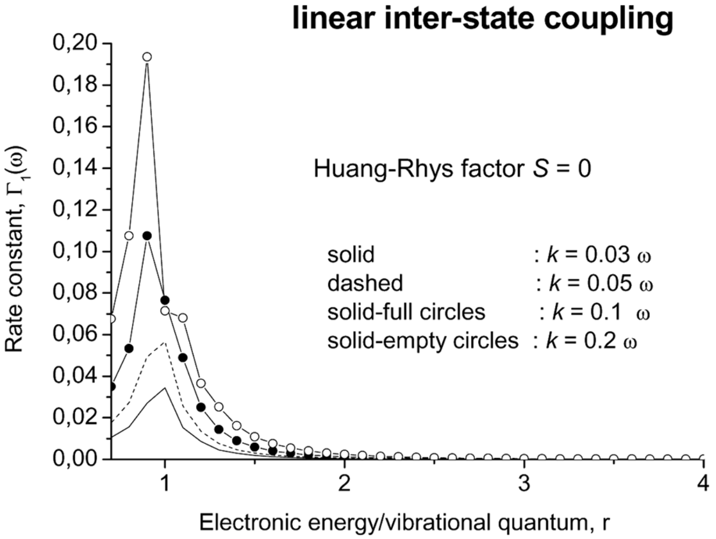

FIGURE 4 Dependence of the rate constant Γ_1 of the excited state decay on the ratio $r = \varepsilon/\hbar\omega$ of the electronic excitation energy ε and vibrational quantum $\hbar\omega$. Various rates of vibrational dephasing k are used, while the value of the Huang-Rhys factor $S = 0$. The inter-state coupling is linear with respect to the vibrational coordinate.

parameter r for $D = 0\,\text{meV}$. For this case the coherent oscillations in the upper potential are strongly suppressed. Consequently, the amplitude of Rabi oscillations are weaker and small deviations, concerning the coherent dynamics, from Eq. (14) are observed. In what follows the fitted curves in Figure 5 are not smooth. Deviations from the smoothness are rather explained to the difficulties of the finding of the global minimum during the fitting procedure than to the real physical behaviour. Potentially, for small values of the Huang-Rhys factor a small correction to the Eq. (14) can be expected as far as the vibrational modulation to the electronic component of the Rabi oscillations is not given by the mean value of the vibrational displacement (which is almost zero) but from its higher-order moments. The dependence of the frequency Ω_3 on r is shown in Figure 6. Here, we can see that up to a certain value of $r > 3$, Ω_3 takes a linear dependence $\Omega_3 \approx \varepsilon/\hbar - \omega$. Then it abruptly jumps onto $\Omega_3 \approx \varepsilon/\hbar + \omega$ dependence. We conclude that it also points out that the oscillatory pattern consisting of just only two harmonic functions is not fully satisfactory when the Huang-Rhys factor is small. Nevertheless, for small values of the Huang-Rhys factor the vibrational modulation is not very important.

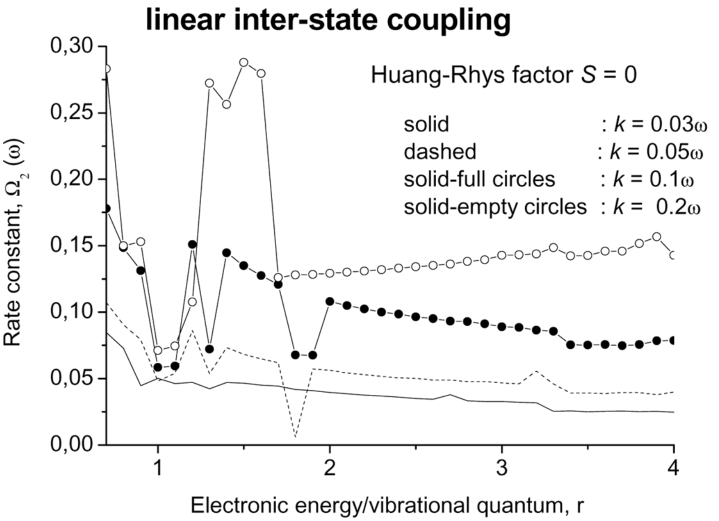

FIGURE 5 Dependence of the frequency Ω_2 of the Rabi oscillation of the excited state population on the ratio $r = \varepsilon/\hbar\omega$ of the electronic excitation energy ε and vibrational quantum $\hbar\omega$. Various rates of vibrational dephasing k are used, while the value of the Huang-Rhys factor $S = 0$. The inter-state coupling is linear with respect to the vibrational coordinate.

b) *constant inter-state coupling model*: Next, we check similar dependences for the constant value of the inter-state coupling $W(\boldsymbol{Q}) = V = 5.6\,\text{meV}$ and for the linear on-diagonal coupling constant $D = 11.3\,\text{meV}$. The rate constant Γ_1 vs. ratio r is shown in Figure 7. For the resonant peaks, we observe, that the intensity of the decay is practically insensitive to the rate of vibrational dephasing. The rate of excited state decay increases with the increasing value of the vibrational dephasing only in the off-resonant region. For the second, the relative contribution of the second resonant peak is significantly smaller compared to the linear coupling model. The coherent structure for the same set of parameters is studied in Figure 8.

Here, we get for the frequency Ω_3 similar dependence as in Figure 2 for the linear coupling model but with the empirical law satisfying the relation $\Omega_3 \approx r\omega = \varepsilon/\hbar$. This corresponds to the energy difference without vibrational exchange. For the frequency Ω_2 we get dependences in Figure 9, which are again very similar to those in Figure 3 for the linear model but the onset of the constant value of Ω_2 is shifted to the values $r = 2$, but not to the value $r = 3$ as it was found for the linear case.

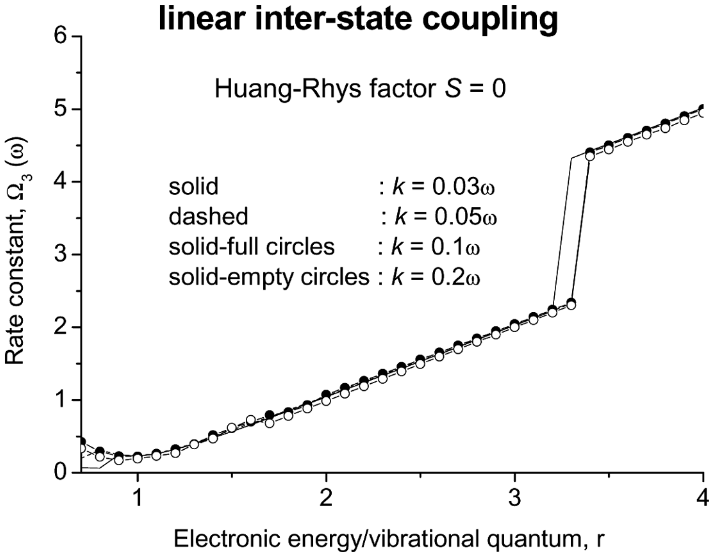

FIGURE 6 Dependence of the frequency Ω_3 of the Rabi oscillation of the excited state population on the ratio $r = \varepsilon/\hbar\omega$ of the electronic excitation energy ε and vibrational quantum $\hbar\omega$. Various rates of vibrational dephasing k are used, while the value of the Huang-Rhys factor $S = 0$. The inter-state coupling is linear with respect to the vibrational coordinate.

Originally, we tried again to check dependences for zero value of the Huang-Rhys factor. For this case we obtained, generally, the values of the excited stated decay so small, which made the fitting procedure very complicated. For this reason we rather checked the dependences for small (but non-zero) values of the Huang-Rhys factor. Namely, we choose $D = 7.2\,\text{meV}$ (Huang-Rhys factor, $S = 1/50$). The dependences of the decay rate are given in the Figure 10. For the higher values of the vibrational dephasing we get also faster decay not only in the resonant interval. In the case of resonace the peaks for stronger vibrational dephasing are smaller and wider. Next, the second resonant peak is smaller than that in Figure 7, promoting thus the idea that it is really the Huang-Rhys factor, which is the key factor in the resonant behaviour. The amplitude of the Rabi oscillations was found to be small and the pronounced vibrational modulation as it was found for the linear coupling model or higher value of the Huang-Rhys factor disappeared. Consequently, we observed a deviation from the fit given by Eq. (14). Instead we found a superposition

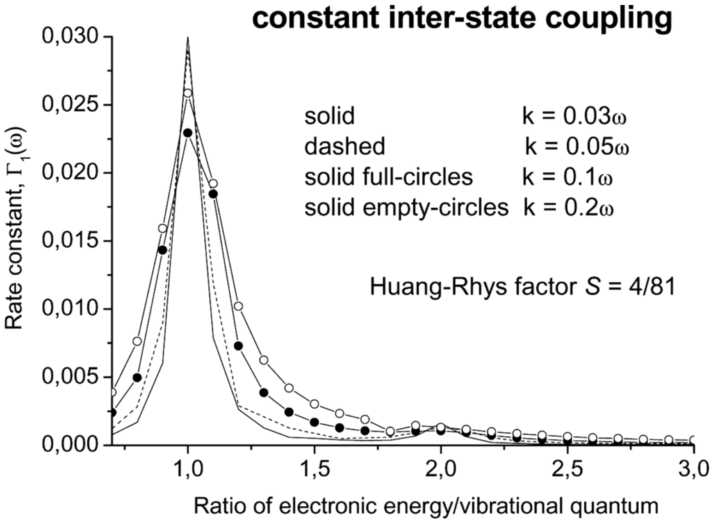

FIGURE 7 Dependence of the rate constant Γ_1 of the excited state decay on the ratio $r = \varepsilon/\hbar\omega$ of the electronic excitation energy ε and vibrational quantum $\hbar\omega$. Various rates of vibrational dephasing k are used, while the value of the Huang-Rhys factor $S = 4/81$. The inter-state coupling is constant with respect to the vibrational coordinate.

of several transition frequencies arising from various linear combinations of $\varepsilon/\hbar$ and ω.

7. DISCUSSION

Direct mathematical derivation of the rate of the excited state decay is very difficult and it would be practically impossible without several simplifying assumptions. It concerns mainly the order of the interaction parameters to which the perturbation calculus should be applied and irreversibility of the excited state decay, which is directly linked to the assumption of the auto-thermalization process in the heat bath.

Here, we just simply estimate it on the basis of a simple Fermi-Golden Rule. First, we assume that the transition appears between vibronic levels of different diabatic potentials. Second, the interaction used will be that of the inter-state coupling. Third, delta-function will be replaced by the Lorentzian line-shape, provided that each M-th vibrational level has a life-time $\sim(k_{\mathrm{M}})^{-1}$ and, finally, all vibronic levels of the excited state will be summed up according to the thermalized initial condition. Then, for the linear inter-state coupling in the

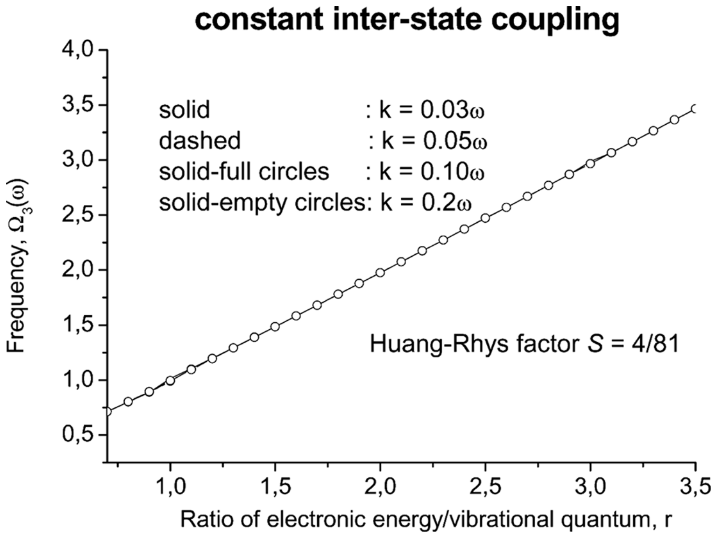

FIGURE 8 Dependence of the frequency Ω_3 of the Rabi oscillation of the excited state population on the ratio $r = \varepsilon/\hbar\omega$ of the electronic excitation energy ε and vibrational quantum $\hbar\omega$. Various rates of vibrational dephasing k are used, while the value of the Huang-Rhys factor $S = 4/81$. The inter-state coupling is constant with respect to the vibrational coordinate.

off-resonant (or near resonant regime) we get the decay rate Γ_1 of the excited state

$$\Gamma_1 \sim \sum_{M,N} \Delta^2 |\langle \chi_M^1 | Q | \chi_N^2 \rangle|^2 \frac{k_M}{(\hbar k_M)^2 + (\varepsilon - \frac{D^2}{2\hbar\omega} + \hbar\omega(M-N))^2} \rho_{MM}, \quad (15)$$

where $|\chi_M^a\rangle$ is the M-th level of a-th potential. It is not difficult to see that the first resonant peak corresponds mainly to the 0–1 transition, which is, due to the linear inter-state coupling, given by the Franck-Condon factor $\langle \chi_0^1 | \chi_0^2 \rangle$!!! In the same way, the second resonant peak is related to the Franck-Condon term $\langle \chi_0^1 | \chi_1^1 \rangle$. Quite generally, *in the linear coupling model*, the intensity of the N-th resonant peak will be proportional to $|\langle \chi_0^1 | \chi_{N-1}^2 \rangle|^2 \approx \frac{S^{N-1}}{(N-1)!} \exp(-S)$. In the exact resonant condition the expression (15) should be corrected by the inclusion of self-energies of vibronic levels. It turns out, by the numerical analysis, that second-order numerator could cancel each other with the self-energy correction in the denominator, leaving thus simply for the first resonant peak

$$\Gamma_1 \sim k, \quad (16)$$

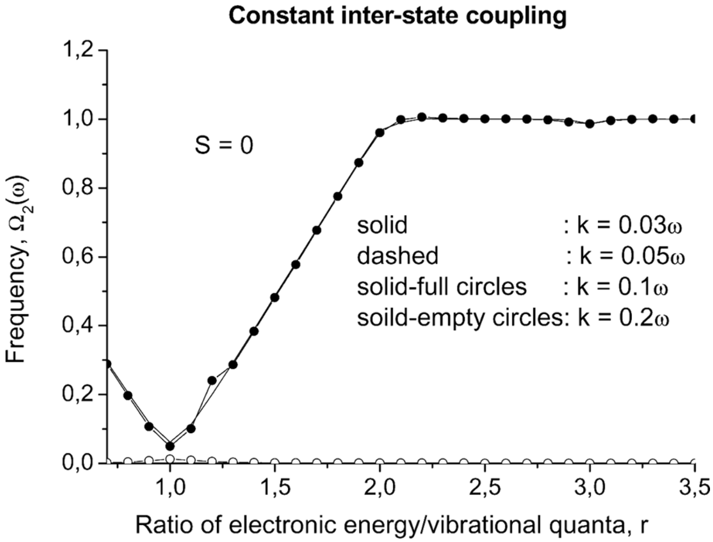

FIGURE 9 Dependence of the frequency Ω_2 of the Rabi oscillation of the excited state population on the ratio $r = \varepsilon/\hbar\omega$ of the electronic excitation energy ε and vibrational quantum $\hbar\omega$ Various rates of vibrational dephasing k are used, while the value of the Huang-Rhys factor $S = 4/81$. The inter-state coupling is constant with respect to the vibrational coordinate.

or in another words, that the excited state decay would exactly match the rate of vibrational decay.

In the case of *constant inter-state coupling* the Fermi Golden Rule adaptation brings out

$$\Gamma_1 \sim \sum_{M,N} V^2 |\langle \chi_M^1 | \chi_N^2 \rangle|^2 \frac{k_M}{(\hbar k_M)^2 + \left(\varepsilon - \frac{D^2}{2\hbar\omega} + \hbar\omega(M-N)\right)^2} \rho_{MM}, \qquad (17)$$

indicating that the N-th resonant peak is formed by the Franck-Condon factors $\langle \chi_0^1 | \chi_N^2 \rangle \sim \frac{S^N}{N!} \exp(-S)$. Consequently, for zero value of the Huang-Rhys factor $S(=D^2/\hbar\omega)$ the resonance disappears. For $S \neq 0$, in the first resonant peak, we again get the relation (16), if the self-energy corrections were taken into account.

The formation of the resonant peaks of the *non-radiative decay in the constant inter-state coupling* can be directly related to the formation of vibrationl side-bands of *luminescence spectra*. Namely, if in the Eq. (17) the coupling constant V were replaced by the electronic transition dipole moment d_{12}, we would immediately get the expression for the spectra of luminescence vibrational side-bands. Thus, the N-th

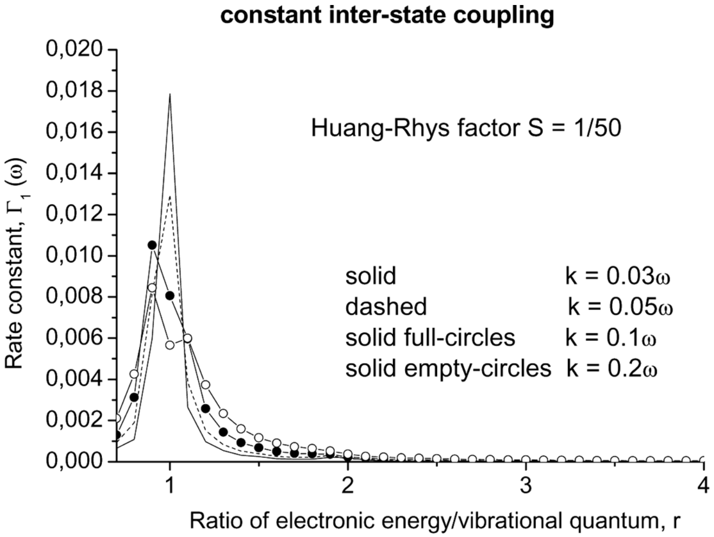

FIGURE 10 Dependence of the rate constant Γ_1 of the excited state decay on the ratio $r = \varepsilon/\hbar\omega$ of the electronic excitation energy ε and vibrational quantum $\hbar\omega$. Various rates of vibrational dephasing k are used, while the value of the Huang-Rhys factor $S = 1/50$. The inter-state coupling is constant with respect to the vibrational coordinate.

resonant peak of non-radiative excited state decay directly maps the N-th vibrational luminescence side-bands.

In this article, the assumptions about the form of the electronic-vibrational interactions were so general that they need not be restricted just to the pure intramolecular transitions or transitions inside the QD systems (if the interaction with LO-phonons were assumed). The same features could be expected for the case of inter-molecular transitions, with possible application to the electron or energy transfer in molecular electronics. Resonant amplification of the current-voltage characteristics with respect to the Huang-Rhys factor were calculated in simple model systems like, *e.g.*, a single oscillator placed between contacts [30].

We expected another investigation in this field, namely, when more complex form of the inter-state coupling may be used, as well as the inclusion of more vibrational modes and electronic states.

8. CONCLUSIONS

- The decay rate of the excited state was calculated for the system of two electronic states and a single vibrational mode embedded in the dissipative environment. Strong resonant amplifying of the decay rate was observed for integer value of the ratio of the electronic excitation energy and vibrational quantum. It was discussed that it is similar to the calculation of resonant amplifying in GaAs quantum dot system.

- The effect significantly increases with the increasing value of the Huang-Rhys factor (Stokes shift) and for the explicit dependence of the inter-state coupling on the vibrational coordinate Q.
- Although the calculations were formally performed for the intra-molecular energy transfer, the results are so general, that they can be applied also for the inter-molecular energy transfer. We conjecture, that the theoretical calculations are related to the field of molecular electronics (FET transistors, quantum dot systems, molecular switches, ...)

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