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Vibration-Induced Energy Relaxation in Two-Level System

Miroslav Menšík, Stanislav Nešpůrek*

Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, Heyrovsky Sq. 2, 162 06 Prague 6, Czech Republic
E-mail: mensik@imc.cas.cz

Summary: Energy decay in a general two-level electronic system coupled to a vibrational harmonic mode interacting with a thermal bath is studied theoretically. The model assumes a general form of the off-diagonal elements (in the electronic basis) of the vibrational-electronic interaction. The cases for constant, linear, and quadratic dependence with respect to the vibrational displacement are investigated. For short-time regime, fast oscillations corresponding to a coherent energy exchange between electrons and vibrations appear. Their frequency Ω corresponds to the energy difference ($\hbar\Omega$) between electronic levels. Additionally, for the case of linear or quadratic coupling, the amplitude modulation of the oscillations with the frequency ω equal to that of vibrational motion is found.

Keywords: electron-vibrational interaction; energy transfer; excited state decay

Introduction

The process of energy relaxation in a system consisting of two interacting harmonic-potential energy surfaces (PES) is frequently studied (cf., e.g., [1-6] and references therein). Usually, the coupling between two PESs is assumed to be independent of a vibrational coordinate [1,2], but sometimes a linear [3,4,6] or quadratic dependence [5] is taken into account. In this article we present the studies of all these types of dependences. The Hamiltonian of the electron-vibrational system is taken in the following form (see also Fig. 1)

$$H^{\mathrm{S}} = \hbar\omega[(\varepsilon + DQ + \frac{Q^2}{2} + \frac{P^2}{2})|1\rangle\langle 1| + (-\varepsilon + \frac{Q^2}{2} + \frac{P^2}{2})|2\rangle\langle 2| + W(Q)(|1\rangle\langle 2| + |2\rangle\langle 1|)] \qquad (1)$$

The first (second) round bracket in the Hamiltonian (1) describes PES of, e.g., excited (ground electronic) state (see also Fig. 1). $2\varepsilon\hbar\omega$ is the vertical energy gap. The last bracket denotes the vibration-dependent coupling of both PESs. We assume three cases: (a) $W(Q) = V$ (b) $W(Q) =$

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ΔQ, and (c) $W(Q) = \alpha Q^2$ (where V, Δ and α are interaction constants). Q (P) is a vibrational coordinate (momentum), $\hbar\omega$ is a vibrational energy quantum, and D describes the shift of the position of the minimum of the excited state with respect to the ground state. The electron-vibrational system is also attached to a thermal bath. This interaction is assumed to be linear in the vibrational displacement. Its impact on the system of interest is described by a standard master equation and the resulting tensor L^{REL} of a vibrational relaxation is of zero-th order in the vibration-induced coupling of the respective PES. Its explicit form can be found in, e.g., Ref. [1]. For simplicity, we assume that it is characterized by one rate constant k of the vibrational relaxation. The density matrix operator $\rho^{\mathrm{S}}(t)$ of the relevant system then satisfies the relation

$$\frac{\partial}{\partial t}\rho^{\mathrm{S}}(t) = -\mathrm{i}[H^{\mathrm{S}}, \rho^{\mathrm{S}}(t)]/\hbar + L^{\mathrm{REL}}\rho^{\mathrm{S}}(t) \tag{2}$$

For the initial condition, we assume a fast excitation from the ground to excited state by vertical optical transitions without any change of the vibrational distribution, which is thermalized in the minimum of the ground state (see Fig. 1).

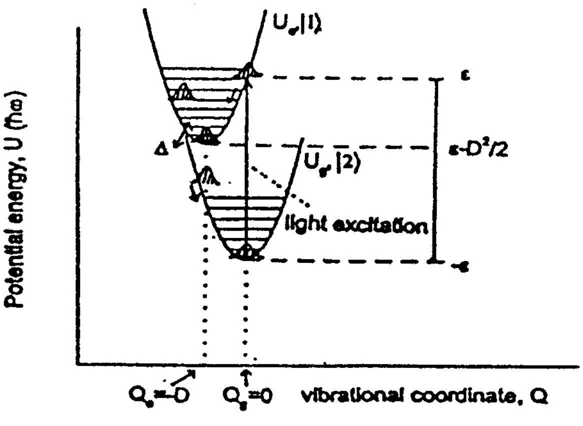

Figure 1. Potential energy surfaces of the excited and ground electronic states. The arrows indicate the process of vibrational relaxation.

The variable of interest, the excited state population $p(t)$, defined as

$$p(t) \equiv \mathrm{Tr}_{\mathrm{vib}}\langle 1|\rho^{\mathrm{S}}(t)|1\rangle \tag{3}$$

is calculated in the time (t) interval ($0.50/\omega$). For the value of parameters introduced below, the edge of the interval is 0.13 ps. Here $\mathrm{Tr}_{\mathrm{vib}}$ means a trace over vibrational mode.

Results

In the numerical simulation, we use the following values of the model parameters: temperature T = 300 K, vibrational energy quantum $\hbar\omega$ = 0.25 eV, vertical excited state energy $2\varepsilon\hbar\omega$ = 2.5 eV, D = 0, 0.5 and 1, rate of the vibrational relaxation $k = 0.3\omega$, 0.1ω and 0.03ω. The interaction energy terms are taken to be comparable with $\hbar\omega$, so V, Δ, and α = 0.5, 1 and 2. The calculated dependences of $p(t)$ for short-time scale are given in Figs. 2 - 4. In general, very fast oscillations of $p(t)$ are superimposed on decay curves. They correspond to a coherent energy exchange between the electronic states and vibrational mode. In Fig. 2 the case of constant interaction is shown. The frequency Ω of these oscillations is associated with the energy difference $\hbar\Omega = 2\varepsilon\hbar\omega$ between the excited and ground electronic states.

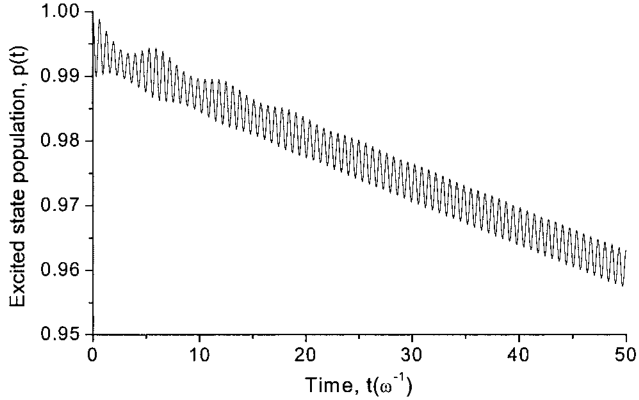

Figure 2. Time dependences of the excited state population for the constant coupling. $V = 0.5$, $k = 0.1\omega$ and $D = 1$.

A slight modulation of the oscillations with the frequency equal to ω were observed. In the case of linear or quadratic dependence (see Figs. 3 and 4), the situation changes.

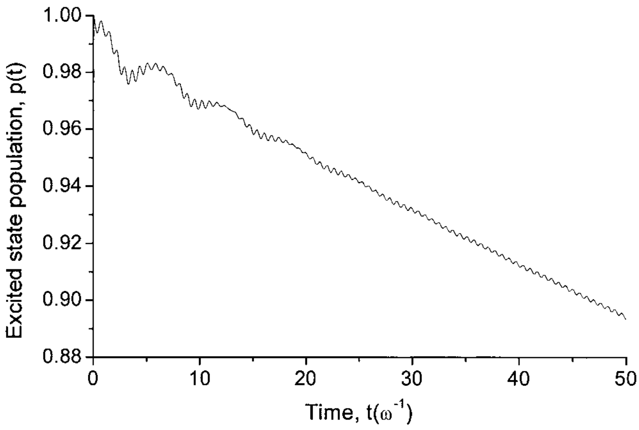

Figure 3. Time dependences of the excited state population for the linear coupling. Δ = 0.5, $k = 0.1\omega$ and $D = 1$.

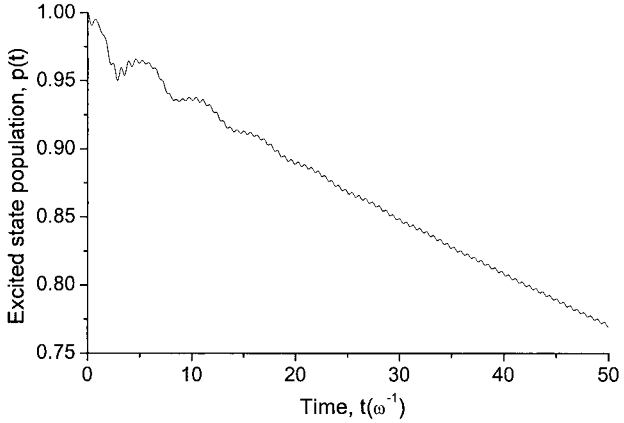

Figure 4. Time dependences of the excited state population for the quadratic coupling. α = 0.5, $k = 0.1\omega$ and $D = 1$.

In general, time duration of the fast oscillations is equal to k^{-1}. The oscillation modulation with the frequency ω is more effective and even dominates if the Stokes shift is larger. As a result, strong oscillations with frequency equal to ω are found. The duration times of these oscillations are equal to k^{-1}. The dependence of the amplitude, frequency, durability of the oscillations and their modulations on the interaction parameters are given in Table 1.

Table 1. Characteristics of coherent oscillations for the constant and linear cases

Frequency Ω	Amplitude A	Modulation frequency φ	Oscillation durability τ^1	Modulation durability τ^2
Constant case: $W(Q) = V$				
$(2\varepsilon(1+\frac{V^2}{\varepsilon^2})-\frac{D^2}{2})\omega$	$\frac{V^2}{2(\varepsilon^2+V^2)}$	ω	$> k^{-1}$	k^{-1}
Linear case: $W(Q) = \Delta Q \sim V_{\mathrm{eff}}$				
$(2\varepsilon(1+\frac{V_{\mathrm{eff}}^2}{\varepsilon^2})-\frac{D^2}{2})\omega-\omega$	$\frac{V_{\mathrm{eff}}^2}{2(\varepsilon^2+V_{\mathrm{eff}}^2)}$	ω	k^{-1}	k^{-1}
Quadratic case: $W(Q) = \alpha Q \sim V_{\mathrm{eff}}$				
$(2\varepsilon(1+\frac{V_{\mathrm{eff}}^2}{\varepsilon^2})-\frac{D^2}{2})\omega$	$\frac{V_{\mathrm{eff}}^2}{2(\varepsilon^2+V_{\mathrm{eff}}^2)}$	ω	$> k^{-1}$	k^{-1}
		2ω (for strong coupling)		

The dependences of the frequencies and amplitudes of coherent oscillations are very similar to that of simple two-level model without inclusion of vibrational states. It is also interesting to see that the frequency of the fast oscillations for the linear case is lower by ω compared to other cases, because the interaction Hamiltonian for linear case causes the vibrational energy exchange $\hbar\omega$. The introduction of the effective value V_{eff} of the interaction for the linear and quadratic case should be understood as a measure of the influence of interaction constants Δ and α on the frequency Ω and amplitude A. For the values of vertical and vibrational energies used above, the period of fast oscillations is about 1.65 fs, while that of the modulation is 16.5 fs. As far as the frequency Ω of fast oscillations equals to the frequency of emitted light (if the radiative processes were taken into account), these oscillations cannot be directly observed optically. On the other hand, the period of the oscillation modulation is, for a real system, at least one order of magnitude slower. Thus, if in the case of a non-radiative excited state decay the ω-dependent modulation exists, then it must be visible in the optical emission decay curves. Such effect does not occur very often in molecular system, because the dynamics of the relevant non-radiative system is only rarely reduced to a single vibrational mode [7]. In the case of several vibrational modes, a destructive interference of vibrational modes will blur the vibrational modulation.

For a long time range, the oscillations disappear and the occupation probability $p(t)$ decays almost exponentially. In Ref. [6] it was shown that in the case of linear dependence of the off-diagonal interaction on the vibrational displacement Q and for small values of the Stokes shift, the rate constant Γ of the occupation probability decay satisfies the following relation

$$\Gamma \sim \Delta^2 k, \tag{4}$$

which reminds of the Fermi golden rule, where the delta function is replaced by the rate constant k of vibrational relaxation. This formula illustrates well the energy decay process. The energy of electronic excitation is transferred coherently to the vibrational mode (this process is represented by the constant Δ of the electron-vibrational interaction) and after that it is dissipated to a bath.

Conclusion

The calculated dependences of the excited state population show that the curve of non-radiative decay contains fast oscillations modulated with the frequency ω, which is associated with a vibrational motion. The modulation is strongly increased in the case of a large Stokes shift and, particularly, if the off-diagonal (in the electronic basis) matrix elements of the electron-vibrational interaction are explicitly dependent on vibrational displacement.

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