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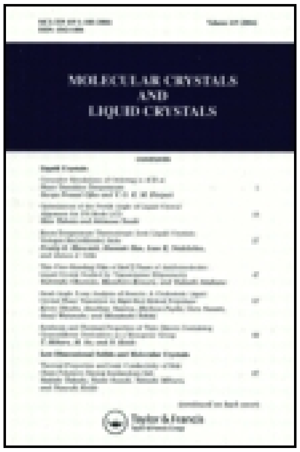

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Phonon Induced Exciton Decay

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Phonon Induced Exciton Decay

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The time dependence of the exciton decay induced by the single vibrational mode was calculated. Neither exponential nor polynomial time decay was found. Three consecutive time intervals appeared. The competing character of the exciton-vibrational and vibration-bath coupling processes is discussed.

Keywords Exciton decay, exciton-vibrational interaction, non-exponential decay, exciton life-time

INTRODUCTION

In some special situations the exciton-vibrational interaction, responsible for the nonradiative exciton decay, may be reduced to the interaction of the exciton with limited number of vibrational modes. This situation is sometimes typical for a localized exciton [1-4]. The exciton energy is transfered to vibrations, and finally to a bath. The bath is represented by fast states (compared to the vibrations) of the surrounding (usually electrons).

THEORY

For the description of the exciton decay a model of the interaction of the exciton and ground states with one vibrational mode is presented. The exciton-vibrational Hamiltonian H_0 can be written as

$$H_0 = \hbar\Omega\left[\beta^+\beta + \frac{(\beta+\beta^+)}{\sqrt{2}}(\Delta(|1\rangle\langle 1| - |2\rangle\langle 2|) + \Delta(|1\rangle\langle 2| + |2\rangle\langle 1|))\right] + \hbar\Omega\varepsilon(|1\rangle\langle 1| - |2\rangle\langle 2|) \qquad (1)$$

Here, vectors $|1\rangle$ and $|2\rangle$ correspond to the excited and ground electronic states, respectively. $2\hbar\Omega\varepsilon$ is the self-trapped exciton energy gap, Ω is the frequency of the vibrational mode, $\hbar\Omega D$ and $\hbar\Omega\Delta$ are the coupling constants of the excited and ground states to the vibrational mode. The coupling constant D corresponds to the distortion of vibrational states with the binding energy equal to $\hbar\Omega D^2/2$ (see Fig. 1.). As a result of the linear coupling, the eigenfrequencies of vibrational modes associated with the ground and excited states are equal. If the term $\hbar\Omega\Delta(|1\rangle\langle 2| + |2\rangle\langle 1|)$ and the dynamics of vibrations are neglected, the potential curves V^1 and V^2 for the excited (self trapped) and ground states, respectively, can be expressed as (Fig. 1)

$$V^{1,2} = \frac{\hbar\Omega}{2}\left(\frac{b+b^+}{\sqrt{2}} \pm D\right)^2 - \frac{\hbar\Omega D^2}{2} \pm \hbar\Omega\varepsilon \quad . \qquad (2)$$

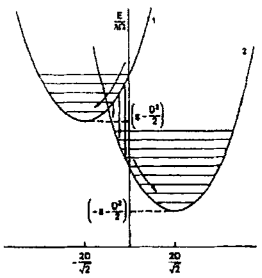

FIGURE 1. Dependence of the potential V^1 (V^2) on vibrational displacement.

For the vibration-bath interactions the generalized Haken-Strobl-Reineker model can be used, because the reservoir is large and fast. Liouville superoperator L^s, describing the influence of the bath on vibrations, can be written in the form (1,2) (vibrational eigenstates are expressed by Greek letters, exciton eigenstates by Latin ones)

$$L^{s}_{m\alpha;n\beta;p\gamma;q\delta} = i\delta_{m;p}\delta_{n;q}\Omega K\,[\,2\delta_{\alpha\beta}\delta_{\gamma\delta}\Big(\ \gamma\delta_{\gamma;\alpha+1} + \alpha\delta_{\gamma;\alpha-1}\exp(\frac{-\hbar\Omega}{kT})$$

$$-\delta_{\gamma\alpha}(\alpha+(\alpha+1)\exp(\frac{-\hbar\Omega}{kT}))\ \Big)$$

$$-(1-\delta_{\alpha\beta})\delta_{\alpha\gamma}\delta_{\beta\delta}(\alpha+\beta+(\alpha+\beta+2)\exp(\frac{-\hbar\Omega}{kT}))\,] \qquad (3)$$

Here, the dynamics of the diagonal and off-diagonal elements (in vibrational indices) is mutualy independent and given by one rate constant K, (It can be related to the vibrational relaxation time, $Kt_{rel} \approx 5$). Diagonal elements correspond to the occupation probability of the vibrational states, while the off-diagonal ones describe the interference of these states. The exciton decay is given by the occupation probability $p(t) \equiv \rho^{red}_{11}(t) \equiv (Tr_{vib}\rho(t))_{11}$. Here, Tr_{vib}... means the trace over the vibrational space. The evolution of the total density matrix operator $\rho(t)$ is given by the relation $\rho(t) = \exp(-iLt)\rho(0)$, where Liouvillian $L = L^{s} + L^{0}$ (L^{0} corresponds to the Hamiltonian H^{0}). The initial density matrix operator (describing the full exciton occupation) is given as

$$\rho(0) = |1\rangle\langle 1| \otimes \exp(-\hbar\Omega b^{+}b / kT) / Tr_{phon}(\exp(-\hbar\Omega b^{+}b / kT)) \qquad (4)$$

RESULTS

The model parameters were taken as follows: $2\varepsilon = 10$, $\hbar\Omega / kT = 10$ (T = 300K, $\hbar\Omega \sim 0.25$ eV, $\hbar\Omega\varepsilon = 2.5$ eV), $\Delta = 0.5, 1, 2, 3$, $D = 0, 1, 2, 3$, $K = 1, 3, 5$.

Dependence of the exciton decay on the parameter *D*

The characteristic dependence $p(t)$ on the parameter D is given in Fig. 2. In general, neither exponential nor power-law decay was observed. For $t < \Omega^{-1}$ a delay in the exciton decay exists, due to the delayed reaction of vibrations to the exciton. For $t <$ 10-20 Ω^{-1}, there is a fast decay corresponding to the thermalization process. In this interval the exciton decay is faster for increasing parameter D, because the more intensive vibration deformation causes the more effective mixing of the excited and ground states. For long time the exciton decay is very weak due to the self-trapping effect.

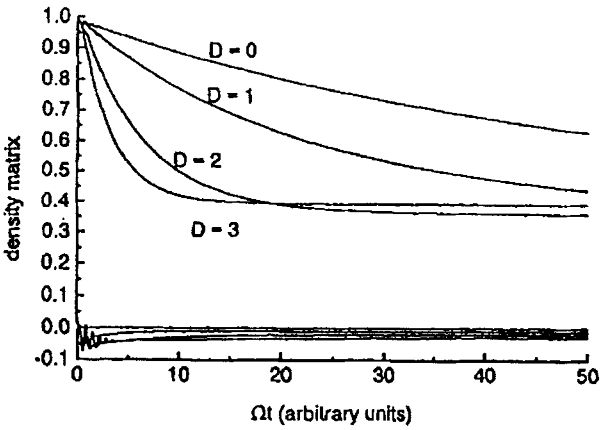

FIGURE 2. Upper curves correspond to $p(t)$, while lower ones to the off- diagonal exciton elements for $K = 1$, $\Delta = 1$.

Dependence of the exciton decay on the parameter Δ

In the middle time interval ($\Omega t \in (1,20)$) a faster exciton decay exists for larger Δ value (even for the same vibrational deformations) (Fig. 3.) In the long time limit the occupation probability is about 50 % due to the strong mutual coupling of the excited and ground states.

Dependence of the exciton decay on the parameter K

With increasing vibrational relaxation rate constant K in the middle time interval the exciton decay is faster. It is associated with the faster relaxation (toward the crossing point) and more efficient mixing of the excited and ground states. In the long time limit a strong vibrational relaxation may cause a strong self-trapping, preventing thus the mixing of the excited and ground states (Fig. 4.).

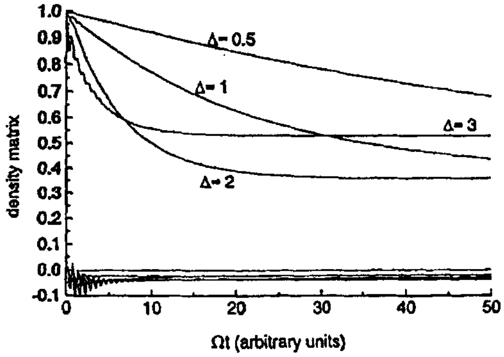

FIGURE 3. Upper curves correspond to $p(t)$, while lower ones to the off-diagonal exciton elements for $K = 1$, $D = 1$.

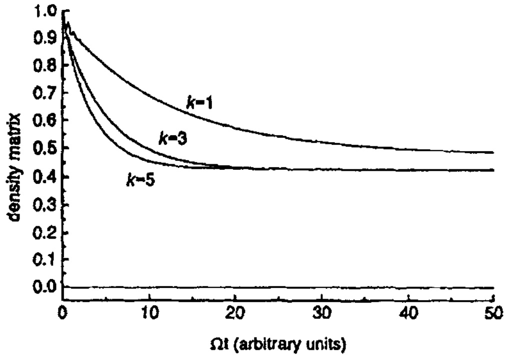

FIGURE 4. Upper curves correspond to $p(t)$, while lower ones to the off-diagonal exciton elements for $\Delta = 2$, $D = 2$.

CONCLUSION

- Neither exponential nor power-law vibration induced exciton decay was observed, but three different time intervals corresponding to various processes were indicated.

- The density matrix evolution strongly depends on competing processes characterized by the interaction parameters D, Δ, and K.

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