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Exciton superradiance in molecular crystal slabs

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We investigate the spontaneous emission rate γ of dipolar excitons in molecular crystal slabs of variable thickness, L, ranging from monolayers to bulk crystals. We find a smooth transition between superradiant excitons ($\gamma \propto L$) at thickness small compared to an optical wavelength (λ) and radiatively stable polaritons for thick crystals ($\gamma \propto 1/L$). The maximum cooperativity volume of the molecules in the slab is found to be of the order λ^3.

1. Introduction

Recently there has been much interest in exciton superradiance from molecular and semiconductor systems with confined geometries [1–4]. Exciton superradiance (or "cooperative emission") originates from the fact that in a system small compared to an optical wavelength roughly all oscillator strength of the individual unit cells is collected in one superradiant excited state. Thus, this state has a spontaneous emission rate proportional to the size of the system; all other states have essentially no oscillator strength and are subradiant or dark. On the other hand, it is well known that the enhancement of the emission rate with system size does not continue forever: in infinite bulk crystals, the excitons are coupled to *exactly one* radiation-field mode due to the perfect wave vector selection imposed by the translational symmetry. Thus, no continuum of photon modes is available to cause irreversible exciton decay. Instead, the energy oscillates back and forth between the exciton and the radiation field, and the situation is best described by introducing polaritons: mixed eigenmodes of the polarization and the radiation field [5]. In infinite crystals, polaritons exhibit *no* spontaneous emission. The study of polariton dynamics by nonlinear optical techniques takes an important place within condensed matter research [6]. Obviously, exciton superradiance and the formation of stable polaritons are intimately related: both phenomena are manifestations of excitons coupled to the radiation field, but they represent opposite limits with respect to the size of the excitonic system. In this paper we make a connection between these two regimes by studying the spontaneous emission from excitons in crystal slabs of variable thickness.

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2. Theory and results

We consider a crystal slab of simple cubic structure with lattice constant a that exists of a stack of N parallel infinitely vast monolayers. The lattice sites are occupied by two-level molecules with electronic transition frequency Ω. The molecular transition dipoles μ all have the same orientation, which for simplicity we take to be parallel to the molecular planes. By varying N from 1 to ∞, this model interpolates between a single monolayer and a bulk crystal. We confine ourselves to the study of exciton states that are modulated in the direction perpendicular to the slab (the z-direction) only. In the Heitler–London

approximation [7], these states are governed by the Frenkel exciton Hamiltonian

$$H_{ex} = \hbar\Omega \sum_l B_l^\dagger B_l + \hbar \sum_{l,l'} J_{ll'} B_l^\dagger B_{l'}. \quad (1)$$

Here, $B_l^\dagger(B_l)$ denotes the creation (annihilation) operator for an excitation of the l'th plane ($l = 1, \ldots, N$) that has equal amplitude and phase on all molecules in that plane. Furthermore, the interaction $J_{ll'}$ is the total instantaneous dipole–dipole interaction between an arbitrary molecule in plane l and all molecules in plane l' (the molecular self-interaction is excluded from J_{ll}). The static excitons are the eigenmodes of H_{ex} and have as annihilation operator

$$B_k = \sum_l U_{kl} B_l, \quad (2)$$

where U_{kl} is the unitary transformation that diagonalizes $J_{ll'}$ and the label k takes N discrete values. For dipolar interactions, it is impossible to determine U_{kl} analytically in the case of general N, but for the moment it suffices to keep U_{kl} in its general form.

The radiation field is quantized in an infinite box that is not limited by the finite thickness of the slab. Thus, perfect wave vector selection of the exciton–photon coupling occurs only in the x- and y-direction, and each of the exciton states considered here is coupled to the one-dimensional continuum of photons with wave vectors $(0, 0, q)$. The excitons will decay radiatively by emission into this continuum. We calculated the spontaneous emission rate $\gamma_k(N)$ of the exciton k according to the Fermi golden rule, using the minimal coupling $(\boldsymbol{p} \cdot \boldsymbol{A})$ form for the exciton–photon interaction. The result reads:

$$\gamma_k(N) = \frac{af^2}{8c}\left[|O(k, \tilde{\omega}_k)|^2 + |O(k, -\tilde{\omega}_k)|^2\right], \quad (3)$$

with $f^2 \equiv 8\pi\Omega\mu^2/\hbar a^3$, a measure of the density of oscillator strength in the slab, and $\tilde{\omega}_k \equiv \omega_k/c$, the frequency of the initial exciton divided by the vacuum velocity of light. $O(k, q)$ gives the overlap between the wave functions of the exciton k and the photon with wave vector $(0, 0, q)$:

$$O(k, q) \equiv \sum_l U_{kl} \exp[\mathrm{i}qla]. \quad (4)$$

The two contributions in eq. (3) arise from the two photons with opposite wave vectors, $(0, 0, \pm \tilde{\omega}_k)$, that can conserve energy in the emission process.

We will now apply the general result eq. (3) to specific approximations for the form of the dipolar excitons in the slab. From the extensive literature on lattice dipole sums, it is known that the interaction $J_{ll'}$ drops off very fast with increasing distance between the planes l and l', even though the dipole interaction between individual molecules has an infinite range. In fact, for our specific configuration, $J_{l,l+1} \approx -0.036 J_{ll}$ and $J_{l,l+2}$ is another three orders of magnitude smaller [8]. Therefore, in a simplest approximation we neglect the interactions between different planes and only keep $J_{ll} \equiv J_0$. It is then natural to use the unitary transformation $U_{kl} = \exp(-\mathrm{i}kla)/\sqrt{N}$, with $k = 2\pi m/Na$ $(m = 0, \ldots, N-1)$, which gives wave-like Frenkel excitons with wave number k. The same transformation applies if we impose periodic boundary conditions in the z-direction. $\omega_k = \Omega + J_0$ is now independent of k (no spatial dispersion). The overlap function $O(k, q)$ is easily determined and we eventually find

$$\gamma_k(N) = \frac{af^2}{8Nc}\left[\frac{\sin^2(N\phi^-)}{\sin^2(\phi^-)} + \frac{\sin^2(N\phi^+)}{\sin^2(\phi^+)}\right], \quad (5)$$

with $\phi^\pm \equiv (k \pm \tilde{\omega}_k)a/2$. For the case $N = 1$, eq. (5) gives the decay rate of the monolayer exciton, $\gamma_0 = af^2/4c$, which roughly equals the single-molecule emission rate (Einstein A-coefficient) multiplied by the number of molecules within an area λ^2, with $\lambda \equiv 2\pi c/\omega_k$, the exciton transition wavelength [9]. Thus, for realistic densities, the monolayer exciton is superradiant. Further analysis of eq. (5) reveals that as long as the slab thickness $L \equiv Na$ is small compared to λ, the $k = 0$ exciton is superradiant with decay rate $N\gamma_0$ and all other excitons are relatively dark with emission rates that are orders of magnitude smaller (see fig. 1 for a typical example). In the limiting case where λ/L is taken infinity, $\gamma_k(N) = N\gamma_0\delta_{k,0}$. The superradiant nature of the $k = 0$ state breaks down when L gets in the order of $\lambda/2$, as can be seen from fig. 2. The maximum

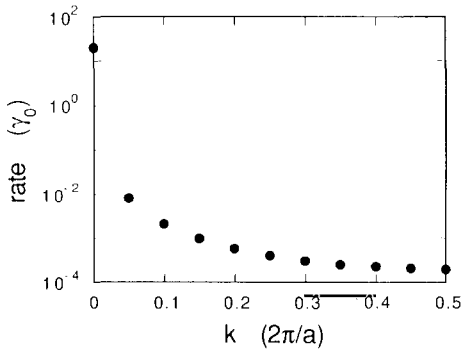

Fig. 1. Radiative decay rate of excitons as a function of wave number in a crystal slab of $N = 20$ monolayers with $\lambda/a = 10^3$ ($L = 0.02\lambda$), according to eq. (5). The decay rates in the second half of the Brillouin zone are obtained by reflection with respect to $k = \pi/a$.

decay rate is reached at $L = 0.37\lambda$ and equals $0.23(\lambda/a)\gamma_0$. The maximum cooperativity volume of the molecules in the slab is thus of the order λ^3. For $L > \lambda/2$, the emission rate shows oscillatory behavior, with an envelope that drops off as $1/L$, so that for $k = 0$ we indeed find a smooth crossover from exciton superradiance in thin slabs to radiative stability in the infinite crystal.

It is interesting to note that for $k \approx \omega_k/c$, eq. (5) predicts an emission rate in thick slabs that is always proportional to L. This implies that superradiance persists up to infinite systems, which contradicts the polariton concept. The reason for this paradox is that the perturbation theory that underlies the Fermi golden rule breaks down at

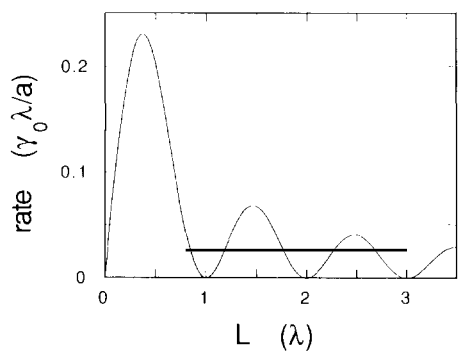

Fig. 2. Radiative decay rate of the $k = 0$ exciton as a function of slab thickness ($L \equiv Na$) according to eq. (5). Note that λ/a typically equals 10^3.

the exciton–photon resonance $k \approx \omega_k/c$. A better theory for this wavenumber region consists in performing perturbation theory with respect to the bulk polaritons; it then appears that at all wave vectors the spontaneous emission rate behaves as $1/L$ for $L \gg \lambda$ [10].

We now briefly turn to the case where the interactions between adjacent planes, $J_{l,l\pm1} \equiv J_1$, are taken into account. The total Hamiltonian is then diagonalized by $U_{pl} = [2/(N+1)]^{1/2} \sin(pla)$, with $p = \pi n/(N+1)a$ $(n = 1, \ldots, N)$, and the exciton frequency is given by $\omega_p = \Omega + J_0 + 2J_1 \cos(pa)$, which does show spatial dispersion. From eq. (3) we find for the decay rate of the exciton p:

$$\gamma_p(N) = \frac{af^2}{8(N+1)c}\left[\frac{\sin(N\Psi^-)}{\sin(\Psi^-)} - (-1)^n \frac{\sin(N\Psi^+)}{\sin(\Psi^+)}\right]^2, \qquad (6)$$

with $\Psi^{\pm} \equiv (p \pm \tilde{\omega}_p)a/2$. If $L \ll \lambda$, this reduces to $2\gamma_0 \operatorname{cotg}^2(pa/2)/(N+1)$ for the odd-n states and to zero for n even. From this it follows that in thin slabs the exciton with wave number $p = \pi/(N+1)a$ $(n = 1)$ is superradiant with decay rate varying between $N\gamma_0$ $(N = 1, 2)$ and $0.81N\gamma_0$ $(1 \ll N \ll \lambda/a)$, and is analogous to the $k = 0$ state above. Again, the superradiant nature of the $n = 1$ state breaks down at $L \approx \lambda/2$, and for $L \gg \lambda$ the decay rate drops off as $1/L$ if p is kept constant (as $1/L^3$ if n is kept constant). The crossover region at $L \approx \lambda/2$ is harder to study in this case, however, as for $n = 1$ the exciton–photon resonance $p = \omega_p/c$ is hit exactly at this thickness.

In summary, we have studied the crossover from exciton superradiance in thin crystal slabs to radiative stability in thick slabs. The present theory is based on the Fermi golden rule for static (instantaneous) excitons coupled to the radiation continuum. In the exciton–photon resonance region, which becomes relevant for $L \gtrsim \lambda$, the radiation field must be treated more explicitly, because there the effect of retardation on the dispersion relation of the crystal's electronic eigenmodes is too strong to treat perturbatively. This

effect can be incorporated by first diagonalizing the subsystem of excitons and photons at a single wave number, resulting in the fully retarded polaritons, and then perturbatively calculating the decay rate of these polaritons in the finite crystal slab caused by the coupling to the continuum of photon modes at other wave numbers [10]. We finally note that the difference between the two exciton models discussed in this paper is analogous to the difference between the cyclic and linear models for one-dimensional aggregates [1].

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