A MICROSCOPIC THEORY OF NONLINEAR LUMINESCENCE QUENCHING AT HIGH LEVELS OF PUMPING

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A microscopic theory of the exciton annihilation based on the superposition approximation for a three-particle density matrix is proposed. A new effect of the enhancement of luminescence quenching is predicted for excitons with the dispersion law close to one- or two-dimensional.

A decrease in the luminescence quantum yield with increasing external excitation intensity (nonlinear quenching) has been discovered in 1967 [1] and is being intensively studied [2,3]. It is well established that the nonlinear quenching is caused by the exciton annihilation (fusion). The well known equation implying that this reaction proceeds pairwise,

$$\partial C/\partial t = I - \beta C - \gamma C^2, \qquad (1)$$

is commonly used in the phenomenological description of nonlinear quenching. In eq. (1), C is the relative exciton concentration, I is the external excitation intensity relative to the total molecular number in a system, β is the inverse lifetime of an exciton noninteracting with the others, γ is a constant determining the rate of exciton decay due to annihilation. It is worth mentioning that most of the recent experiments can be described by eq. (1) or by an equation analogous to it, but complicated by taking into account the spatial inhomogeneity of pumping. However, there are experimental results [4] showing that at sufficiently high excitation levels this equation fails ‡.

The microscopic approach to describe exciton annihilation was first discussed by Suna [6]. In particular, he has shown that an exact set of exciton density matrix equations in steady-state conditions reduces to eq. (1), if the annihilation term is small compared to the monomolecular decay term

$$\beta \gg \gamma C \qquad (2)$$

Inequality (2) may, in fact, be satisfied, for example, when the magnetic field effect on delayed fluorescence is studied [7]. But in experiments on nonlinear fluorescence quenching it is obviously violated.

A new microscopic theory of exciton annihilation applicable to a much wider concentration region than that implied by (2) is developed in the present paper. Using this theory it is shown that the question concerning the applicability of the phenomenological equation (1) is highly dependent on exciton anisotropy. For excitons with three-dimensional isotropic motion eq. (1) gives qualitatively good results. In the case of one- and two-dimensional excitons the annihilation rate constant has to be replaced by a function $\tilde{\gamma}(I)$. This implies an inclusion into eq. (1) of high concentration effects. Therefore, in crystals with high anisotropy of the dispersion law the dependence of the luminescence quantum yield on excitation intensity is expected to be different from that described by eq. (1).

‡ Eq. (1) is not relevant to describe nonlinear quenching in the case of nearly immovable exciton excitations [5]

We shall discuss the kinetics of nonlinear luminescence quenching for incoherent excitons (exciton motion has a hopping character). As is shown in ref. [8], the coherent exciton motion becomes incoherent after a few scatterings by phonons, impurities, etc. Thus, in studying nonlinear quenching one can assume the excitation motion to be incoherent when the time of coherence destruction in the exciton subsystem is small compared to the exciton annihilation time (the exciton gas is not too dense, the exciton bands are not very wide).

The evolution of a system of incoherent excitons interacting with each other and with an external excitation is completely described by the functions

$$\rho_1(r,t) = \mathrm{Sp}\,\rho(t)\hat{n}_r,$$

$$\rho_2(r,r',t) = \mathrm{Sp}\,\rho(t)\hat{n}_r\hat{n}_{r'}, \quad \ldots, \tag{3}$$

where $\hat{n}_r$ is the operator of the occupancy of an excited state of a molecule at r, $\rho(t)$ is the nonequilibrium density matrix of a crystal. In the spatially homogeneous case the exciton concentration

$$C(t) \equiv \rho_1(r,t).$$

Applying a method analogous to that used in ref. [6] one can show that the functions

$$g_2(r_1 - r_2,t) \equiv \rho_2(r_1,r_2,t)/C^2(t),$$

$$g_3(r_1,r_2,r_3,t) \equiv \rho_3(r_1,r_2,r_3,t)/C^3(t)$$

may be found from the chain of equations

$$\partial C/\partial t = I - \beta C - C^2 \sum_r \omega_r g_2(r,t), \tag{4}$$

$$\partial g_2(r,t)/\partial t = (2I/C)[1 - g_2(r,t)] - (\omega_r - 2W_r)g_2(r,t)$$

$$- 2\sum_{r'} \{W_{r'}[g_2(r,t) - g_2(r',t)]$$

$$+ \tfrac{1}{2}\omega_{r'} C[g_3(r,r+r',r',t) + g_3(-r,r'-r,r',t)$$

$$- 2g_2(r,t)g_2(r',t)]\}. \tag{5}$$

Here W_r is the exciton hopping rate at distance $|r|$, ω_r is the bimolecular annihilation probability for excitons separated by r.

Suna's approach consists in neglecting the contribution of the three-particle distribution function g_3. For terminating the chain of equations we shall apply an approximation analogous to Kirkwood's superposition approximation [9] often used in the theory of dense gases

$$g_3(r_1,r_2,r_3,t)$$

$$= g_2(r_1 - r_2,t)g_2(r_1 - r_3,t)g_2(r_2 - r_3,t). \tag{6}$$

In steady-state conditions, by substituting eq. (6) into eq. (5) we have for the quantities $\nu(r) = 1 - g_2(r)$ $(r \neq 0)$ in the nearest-neighbour approximation

$$\nu(r) = \left[1 + \frac{\alpha - 1}{2(M - \alpha + 1)C}\right]\frac{G_{r0}}{G_{00}}$$

$$+ \frac{-\alpha + 1}{2d}\sum_{s,\Delta}\left[\frac{G_{r0}G_{s0}}{G_{00}} - G_{rs}\right]\nu(s)\nu(s - \Delta), \tag{7}$$

where

$$G_{rr'} = N^{-1}\sum_k \frac{\cos(k\cdot r)\cos(k\cdot r')}{M + \alpha - (M - \alpha + 1)\epsilon(k)},$$

$$\alpha = j/C, \quad M = \beta^{-1}\sum_\Delta W_\Delta,$$

$$\epsilon(k) = (1/2d)\sum_\Delta \cos(k\cdot\Delta),$$

Δ is the vector between nearest neighbour molecules, $2d$ is the number of nearest neighbours in a d-dimensional crystal ($d = 3,2,1$), $j = I/\beta$, N is the total number of molecules.

In this case eq. (4) reduces to

$$C\tilde{\gamma}(J) = \alpha - 1, \tag{8}$$

where the quantity

$$\tilde{\gamma}(J) = \beta^{-1}\sum_\Delta \omega_\Delta [1 - \nu(\Delta)] \tag{9}$$

is the exciton annihilation rate in β units.

Let us consider the case when the monomolecular decay term is negligible compared to the nonlinear decay term, $\alpha \gg 1$. (This is just the opposite condition to that treated by Suna [6].) In addition, the inequality $\alpha \ll M$ must hold;

$$1 \ll \alpha \ll M. \tag{10}$$

Here $M^{1/2}$ is the dimensionless exciton diffusion length. Practically, both sides of eq. (10) may easily be satisfied.

Condition (10) permits us to solve eq. (7) by the iteration procedure. In zeroth approximation we neglect the nonlinear terms of eq. (7). The corrections to the solution defined by

$$(\alpha/M)\sum_r (G_{r0}/G_{00})^3 \approx (\alpha/M)\ln(\alpha/M), \quad d = 3, \qquad \approx (\alpha/M)^{1-1/2d}, \quad d = 2,1 \tag{11}$$

are small and may be neglected. As a result, we get for the annihilation rate

$$\Omega/\tilde{\gamma}(j) = 1 + \Omega/2M, \quad d = 3, \tag{12}$$

$$= 1 + (\Omega/2M)[\ln(4MC/j) - 1], \quad d = 2, \tag{13}$$

$$= 1 + (\Omega/2M)(MC/4j)^{1/2}, \quad d = 1, \tag{14}$$

where $\Omega = \beta^{-1}\Sigma_{\Delta}\omega_{\Delta}$.

In the following we discuss separately the case of a diffusion-controlled annihilation and the case when the opposite situation is realised, i.e. the annihilation process practically does not depend on the exciton motion (kinetic regime).

Note that only for three-dimensional motion is the annihilation controlled by diffusion when $\omega \gg W$ (this is usually implied). But this condition reduces to $\omega \gtrsim W$ in two-, and to $\Omega \gg M^{1/2}$ in one-dimensional cases. The latter may be satisfied even at $\Omega \ll M$ when the exciton diffusion length is sufficiently large. At high concentrations the first two conditions are not much violated, but the third one is to be changed to $\Omega \gg (j/MC)^{1/2}$.

In the case of a diffusion-controlled annihilation the monomolecular decay term is small compared to the annihilation term when

$$C \gg 1/4M^{1/2}, \quad C \gg \ln(4M)/2\pi M, \quad C \gg 1/M,$$

for $d = 1,2,3$, respectively,

As follows from these conditions, for the annihilation effect to be dominant it is necessary to create the densest exciton gas in the case of one-dimensional excitons (at the same values of all the other parameters).

From eqs. (8) and (12)–(14) one can see that the quantum yield dependence on excitation intensity is different for excitons moving in different dimensions. Namely.

$$\Phi(j) = (Mj)^{-1/2}, \quad d = 3, \tag{15}$$

$$\ln[4M\Phi(j)]/\Phi^2(j) = 2\pi Mj, \quad d = 2, \tag{16}$$

$$\Phi(j) = (16M)^{-1/3}j^{-2/3}, \quad d = 1, \tag{17}$$

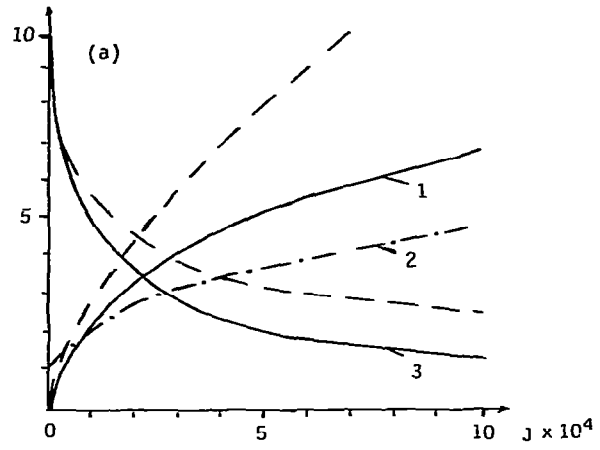
where $\Phi(j) = C/j$.

In the case of a three-dimensional system the quantum yield dependence on intensity coincides with that given by eq. (1) rewritten for steady-state conditions. But for two- and one-dimensional systems there is a qualitative difference between eqs. (16), (17) and the phenomenological dependence.

Eqs. (16) and (17) show that for one- or two-dimensional exciton motion the nonlinear quenching effect is stronger at higher I than at lower I. An effect of this kind has recently been observed in anthracene [4]. To explain it the occurrence of new annihilation centers was supposed. Within our approach eq. (16) may give a quite different explanation of the strengthening of the luminescence quenching at high excitation intensities if two-dimensional exciton motion is relevant to the case In the framework of this hypothesis the effect of an additional quenching may be connected with an increase in the annihilation probability of each exciton as a result of its interaction with many others while it travels. Thus, the annihilation process becomes not a pairwise, but a many-particle reaction at high concentrations

In the kinetic regime of annihilation the peculiarities of exciton motion in different dimensions are no longer important. We have a condition $\Omega C \gg 1$ guaranteeing that the exciton annihilation channel is dominant. The quantum yield then is $\Phi(j) = (\Omega/j)^{1/2}$.

To clarify our results a model calculation of the quantities $\tilde{\gamma}(j)$, $C(j)$ and $\Phi(j)$ was performed. Figs. 1–3 correspond to the one-, two- and three-dimensional cases, respectively. The equality $M = 10^7$, for example, corresponds to a hopping rate of 10^{10} s^{-1} and to a monomolecular decay time of 10^{-3} s which are typical of triplet excitons. For the ratio $\Omega = 10M$ taken the dimensionless annihilation rate $\tilde{\gamma}(0) = \gamma/\beta$ is equal to 1.26×10^4. For this value of $\tilde{\gamma}(0)$ the concentration and quantum yield dependences are represented by the dashed lines, in accordance with Suna's theory. It is



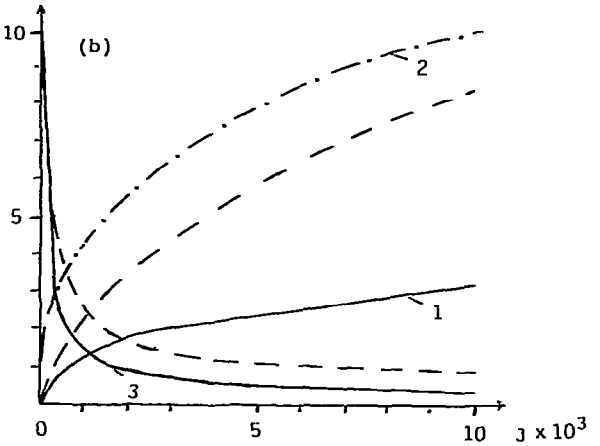


Fig. 1. One-dimensional excitons. $\frac{1}{2}M = 10^7$, $\Omega/M = 10$. (a) Curves 1,2,3 correspond to $5 \times 10^4 C$, $10^{-4}\tilde{\gamma}$, 10Φ, respectively; (b) curves 1,2,3 correspond to $10^4 C$, $10^{-4}\tilde{\gamma}$, 10Φ, respectively. The dashed lines correspond to C and Φ calculated for $\tilde{\gamma}(0) = \gamma\beta^{-1} = 1.26 \times 10^4$.

easily seen that high concentration effects influence appreciably these dependences in the one-dimensional case (solid line, fig. 1)‡. In the three-dimensional case these effects are negligible.

In the one-dimensional case (fig. 1) when α changes

‡ The curves of figs 1–3 were calculated using $\nu(\Delta)$ from eq. (7). Calculations were carried out for $\alpha \ll M$ without using the condition $\alpha \gg 1$.

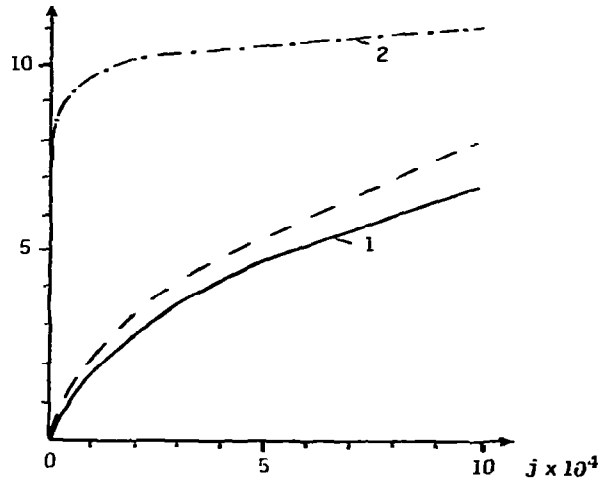


Fig. 2. Two-dimensional excitons. $\frac{1}{4}M = 10^7$, $\Omega/M = 10$. Curves 1,2 correspond to $10^6 C$, $5 \times 10^{-7}\tilde{\gamma}$, respectively. The dashed line corresponds to C calculated for $\tilde{\gamma}(0) = \gamma\beta^{-1} = 1.53 \times 10^7$.

from 1 to 7 the $\tilde{\gamma}(j)$ increases approximately 4 times. When the excitation intensity starting from those values of j where the nonlinear quenching effect is noticeable increases by about two orders of magnitude the quenching is enhanced 3 times (quenching enhancement is proportional to $[\tilde{\gamma}(j)/\tilde{\gamma}(0)]^{1/2}$ for $\alpha \gg 1$).

Our calculation shows that in the case of one-dimensional exciton motion it is necessary to take into ac-

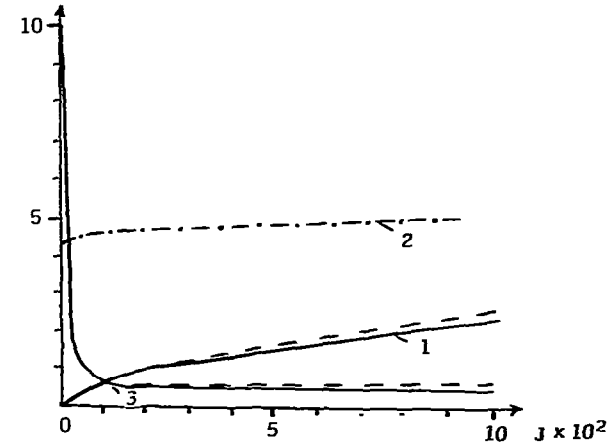


Fig. 3. Three-dimensional excitons. $\frac{1}{6}M = 10^3$, $\Omega/M = 10$. Curves 1,2,3 correspond to $10^3 C$, $2.5 \times 10^{-4}\tilde{\gamma}$, 10Φ, respectively. The dashed lines correspond to C and Φ calculated for $\tilde{\gamma}(0) = \gamma\beta^{-1} = 1.75 \times 10^4$.

count the dependence of the annihilation rate on excitation intensity. This dependence may turn out to be negligible when two-dimensional exciton annihilation takes place. But at sufficiently high concentrations it may also prove to be important.

At the same time, in calculating the annihilation rate constant it is possible to neglect many-particle effects when the annihilation of excitons with three-dimensional isotropic motion is described. Thus, the theory based on eq. (1) is always applicable when $C \ll 1$ only in the case of nearly isotropic three-dimensional exciton motion

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