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Exciton annihilation in molecular crystals at high exciton densities*

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Suna's kinematic equations describing exciton annihilation in aromatic crystals are solved for higher exciton densities n, i.e., where $n \geq \beta/\gamma$, where β is the monomolecular decay rate and γ is the bimolecular annihilation rate constant. It is found that in case of diffusion-limited annihilation, γ is a function of the exciton density n even for n small compared to the lattice site density. In general γ is then a monotonically increasing function of n and these density effects depend on the dimensionality of the exciton motion. For both triplet and singlet excitons, γ is a function of n in one-dimensional and two-dimensional systems only. In the case of singlet excitons, γ depends on n even in three-dimensional systems if reabsorption is a dominant mechanism of exciton motion. Some materials are suggested in which such effects could be experimentally observable.

Mutual annihilation of excitons in organic molecular crystals has been studied by many workers.[1] Suna[2] has presented a system of equations describing exciton annihilation which is valid for the hopping model of exciton motion and which he has solved in the low exciton density limit. In this paper we shall extend the solution of Suna's equations to higher exciton densities.

The kinetics of annihilation of spinless excitions are described in the steady state by

$$0=\alpha-\beta n-\gamma n^2\,, \tag{1}$$

where n is the uniform exciton density, β is the monomolecular decay rate, and γ is the macroscopic annihilation rate. Equation (1) is a generally accepted phenomenological description of annihilation. Suna[2] calculated γ as

$$\gamma=v\sum_{\vec{R}}\lambda(\vec{R})\tilde{\rho}(\vec{R})\,, \tag{2}$$

where $\tilde{\rho}(\vec{R})$ is the annihilation probability per unit time for excitons separated by $\vec{R}$, with $\vec{R}$ the lattice vector and v is the length, surface, or volume per molecule for one-, two-, or three-dimensional systems, respectively. The normalized two-particle distribution function $\tilde{\rho}$ is defined by

$$(nv)^2\tilde{\rho}(\vec{R})=\rho_2(\vec{R}_0,\vec{R}_0+\vec{R})\,, \tag{3}$$

where $\rho_k(\vec{R}_1,\vec{R}_2,\ldots,\vec{R}_k)$, here for $k=2$, is the k-particle distribution function as defined by Suna. $\rho_2(\vec{R}_1,\vec{R}_2)$ represents the probability that there is one exciton at the site $\vec{R}_1$, and one at the site $\vec{R}_2$. For $|\vec{R}|\rightarrow\infty$, $\tilde{\rho}(R)=1$, and $\tilde{\rho}(\vec{R})$ decreases monotonically with decreasing $|\vec{R}|$, because the annihilation causes a depletion of other particles in the vicinity of each particle. Thus each particle is surrounded by a depletion zone which according to Eq. (2) causes γ to be smaller than it would be in the case of a uniform distribution $\tilde{\rho}(\vec{R})=1$. We calculate $\tilde{\rho}$ from[2]

$$\begin{aligned}0={}&2(\beta+\gamma n)+2\sum_{\vec{R}'}\Psi(\vec{R}-\vec{R}')\tilde{\rho}(\vec{R}')\\&-2\tilde{\rho}(\vec{R})\left(\sum_{\vec{R}'}\Psi(\vec{R}')-\Psi(\vec{R})\right)-2\beta\tilde{\rho}(\vec{R})-\lambda(\vec{R})\tilde{\rho}(\vec{R})\\&-nv\sum_{\vec{R}'}[\lambda(\vec{R}'-\vec{R})+\lambda(\vec{R}')]\,\rho_3(\vec{R}_0+\vec{R},\vec{R}_0+\vec{R}',\vec{R}_0)\end{aligned} \tag{4}$$

for $\vec{R}=0$, together with the boundary condition

$$\tilde{\rho}(0)=0\,, \tag{5}$$

which expresses the fact that no two excitons can occupy the same lattice site.

In Eq. (4) the term $2(\beta+\gamma n)=2(1/n)^2\alpha n$ is a source term analogous to α in Eq. (1). Here αn reflects the fact that the pairs are created by a single-particle generation α combined with already existing particles n and $(1/n)^2$ is the normalizing factor. The monomolecular decay term $2\beta\tilde{\rho}(\vec{R})$ is analogous to βn in Eq. (1), and

$$2\sum_{\vec{R}'}\Psi(\vec{R}-\vec{R}')\tilde{\rho}(\vec{R}')-2\tilde{\rho}(\vec{R})\left(\sum_{\vec{R}'}\Psi(\vec{R}')-\Psi(\vec{R})\right)$$

describes the incoherent-particle transport including the exclusion principle $\tilde{\rho}(0)=0$; $\Psi(\vec{R})$ is the jump rate between two lattice sites separated by $\vec{R}$. All these terms contain the factor 2 because Eq. (4) describes pairs of particles; $\lambda(\vec{R})\tilde{\rho}(\vec{R})$ is a sink term which removes pairs with mutual separation $\vec{R}$ at a rate $\lambda(\vec{R})$. Finally, the term

$$nv\sum(\lambda(\vec{R}'-\vec{R})+\lambda(\vec{R}'))\tilde{\rho}_3(\vec{R}_0+\vec{R},\vec{R}_0+\vec{R}',\vec{R}_0)$$

for arbitrary $\vec{R}_0$ is analogous to the term γn^2 of

Eq. (1). It is a higher-order term which is also caused by the annihilation. It contains a three-particle distribution $\tilde{\rho}_3$ defined by

$$(nv)^3\tilde{\rho}_3(\vec{R}_0+\vec{R},\vec{R}_0+\vec{R}',\vec{R}_0)=\rho_3(\vec{R}_0+\vec{R},\vec{R}_0+\vec{R}',\vec{R}_0)\,. \tag{6}$$

The distribution function $\tilde{\rho}_3$ must be calculated from an equation which involves $\tilde{\rho}_4$, etc. Thus Eqs. (1) and (4) are the two lowest equations of an infinite hierarchic system of equations. Finding an exact solution of this system is extremely difficult. Suna has solved the system in the low-density approximation by putting the higher-order terms in all equations equal to zero. In that approximation γ is a constant independent of exciton density n. We shall use an approximation,

$$\tilde{\rho}_3(\vec{R}_1,\vec{R}_2,\vec{R}_3)=\tilde{\rho}(\vec{R}_1-\vec{R}_2)\tilde{\rho}(\vec{R}_2-\vec{R}_3)\tilde{\rho}(\vec{R}_3-\vec{R}_1)\,, \tag{7}$$

which is commonly used in statistical mechanics, e.g., in the theory of liquids.[3] This approximation is good for such three-particle configurations in which not more than two particles (e.g., 1 and 2) are close to each other, and the third one (3) is far away from the pair (1, 2). In the limiting case $|\vec{R}_2-\vec{R}_3|\to\infty$ and $|\vec{R}_1-\vec{R}_3|\to\infty$, the pairs (1, 3) and (2, 3) are not correlated and

$$\tilde{\rho}(\vec{R}_1-\vec{R}_2)=\tilde{\rho}_3(\vec{R}_1,\vec{R}_2,\vec{R}_3)\,, \tag{8}$$

$$\tilde{\rho}(\vec{R}_2-\vec{R}_3)=1\,, \tag{9}$$

$$\tilde{\rho}(R_3-R_1)=1\,. \tag{10}$$

Equations (8)–(10) then agree with Eq. (7).[3(c)] This argument suggests that the approximation Eq. (7) is good only for small particle densities.[3(b),3(c)] However, this approximation has been shown to be "surprisingly successful" as follows directly from computer simulation and indirectly from experiments on fluids.[3(c)] Moreover, we shall solve the annihilation equations for a range of particle densities [see Eq. (16) below] for which the exact validity of Eq. (7) is not critical, and we will show that even in this density range γ may be a function of n.

With the approximation Eq. (7) we obtain from Eq. (4)

$$0=\beta'+\sum_{\vec{R}'}\Psi(\vec{R}-\vec{R}')\tilde{\rho}(\vec{R}')-\tilde{\rho}(\vec{R})\Big(\sum_{\vec{R}'}\Psi(\vec{R}')-\Psi(\vec{R})\Big)-\beta'\tilde{\rho}(\vec{R})-\tfrac{1}{2}\lambda'(\vec{R})\tilde{\rho}(\vec{R})\,, \tag{11}$$

where

$$\beta'=\beta+\gamma n \tag{12}$$

and

$$\lambda'(\vec{R})=\lambda(\vec{R})-2[1-\epsilon(\vec{R})]\gamma n\,, \tag{13}$$

with

$$\epsilon(\vec{R})=\frac{v}{\gamma}\sum_{\vec{R}'}\lambda(\vec{R}')\tilde{\rho}(\vec{R}')\tilde{\rho}(\vec{R}-\vec{R}')\,. \tag{14}$$

Both $\lambda(\vec{R})$ and $1-\epsilon(\vec{R})$ are functions decaying to zero with increasing R, so $\lambda'(R)\to 0$ for $R\to\infty$.

Equation (11) has been solved by Suna in the "smooth approximation,"[2] in which $\tilde{\rho}(\vec{R})$ is nearly constant over those values of $\vec{R}$ for which either $\lambda'(\vec{R})$ or $\Psi(\vec{R})$ are nonzero, and is replaced by the average $\langle\tilde{\rho}\rangle_{\mathrm{av}}$. The smooth approximation is valid if nearest-neighbor jump rates dominate and are nearly isotropic,[2] but this is not a necessary condition. By replacing λ with λ' and β with β' in Suna's solution of Eq. (11), we can calculate γ from the smooth approximation of Eq. (2), which yields

$$\gamma=v\lambda\langle\tilde{\rho}\rangle_{\mathrm{av}}\,, \tag{15}$$

where

$$\lambda=\sum_{\vec{R}}\lambda(\vec{R})\,.$$

Equation (15) is in this case an implicit expression for γ, because $\langle\tilde{\rho}\rangle_{\mathrm{av}}$ on the right-hand side is a function of β' and λ'. The smooth approximation is valid only for

$$\gamma n\ll\lambda \tag{16}$$

because it requires simultaneously a fast decay of $\lambda'(\vec{R})$ and a slow decay of $\tilde{\rho}(\vec{R})$ with increasing R; $\tilde{\rho}(\vec{R})$ causes a slow decay component of $\lambda'(\vec{R})$ because of the approximate relationship

$$\epsilon(\vec{R})\approx\tilde{\rho}(\vec{R})\,. \tag{17}$$

The condition [Eq. (16)] which keeps this slowly decaying component of λ' small is satisfied if the exciton density is much smaller than the density of lattice sites. We shall assume the validity of Eq. (16). The term $2[1-\epsilon(\vec{R})]\gamma n$ can then be neglected, and the quality of the approximation Eq. (7) is not critical.

Thus γ is calculated by only replacing the monomolecular decay rate β by the effective decay rate $\beta+\gamma n$. We obtain according to Suna [Ref. 2, Eqs. (12), (20), (22), and the Green's functions in Table I]

$$\gamma=\frac{\gamma^{\infty}}{1+\gamma^{\infty}/\lambda v}, \tag{18}$$

with

$$\gamma^{\infty}=4[D(\beta+\gamma n)]^{1/2} \tag{19a}$$

for one-dimensional exciton motion,

$$\gamma^{\infty}=-4\pi D/\{\ln[\tfrac{1}{2}(\beta+\gamma n/D)^{1/2}R_a]+0.577\} \tag{19b}$$

for isotropic two-dimensional motion, or

$$\gamma^{\infty} = 8\pi D R_a \tag{19c}$$

for isotropic three-dimensional motion. Here R_a is the average jump distance of the exciton and D is the diffusion coefficient, which is related to $\Psi(\vec{\mathrm{R}})$ by[2]

$$D_{ij} = \tfrac{1}{2} \sum_{\vec{\mathrm{R}}} \Psi(\vec{\mathrm{R}}) R_i R_j \, . \tag{20}$$

In Eqs. (19) it was assumed that

$$\beta + \gamma n \ll D/R_a^2 \, . \tag{21}$$

It is readily seen that in this approximation γ is independent of n only in the three-dimensional case. In general γ is monotonically increasing with increasing n to the upper limit $v\lambda$. This increase is caused by flattening of the pair distribution function owing to larger β'. Owing to the smooth approximation, the results of the discrete lattice model are in this case identical with those of the continuum model[2] if the average jump distance R_a is put equal to the radius of the sphere within which the annihilation takes place.

In case of fast decay $\beta \gtrsim D/R_a^2, \gamma$ is a function of n even for three-dimensional motion. Following the same procedure as in Eqs. (18) and (19), we obtain for isotropic diffusion

$$\gamma^{\infty} = 8\pi D R_a \frac{\Psi}{\beta + \gamma n + \Psi} e^{[(\beta'/D)^{1/2} R_a]} \times \left(1 - \frac{\beta' v}{4\pi D R_a e^{[(\beta'/D)^{1/2} R_a]}}\right) \tag{22}$$

with

$$\Psi = \sum_{\vec{\mathrm{R}}} \Psi(\vec{\mathrm{R}}) \, . \tag{23}$$

If we perform the smooth approximation of Eq. (20), we can replace Ψ in Eq. (22) by

$$\Psi = 6D/R_a^2 \, . \tag{24}$$

For long-range transport $R_a \gg v^{1/3}$ the expression in large parentheses is equal to 1, and with Eqs. (12) and (24) we obtain from Eq. (22)

$$\gamma^{\infty} = 8\pi D R_a \{6D/[6D + R_a^2(\beta + \gamma n)]\} e^{[(\beta + \gamma n/D)^{1/2} R_a]} \, . \tag{25}$$

In this case the smooth approximation is less exact than for short-range transport, and in general Eq. (25) may be just a crude approximation. However, this equation is very instructive at least qualitatively if we compare two cases with the same isotropic three-dimensional diffusion coefficient D, the same annihilation rates $\lambda(R)$, and the same decay rate β, but with different average jump distance R_a. In this comparison the small $R_a \ll (D/\beta + \gamma n)^{1/2}$ must be offset by large jump rates $\Psi(R)$, and large $R_a \ll (D/\beta)^{1/2}$ implies small $\Psi(R)$. According to Eqs. (19c) and (25), only in the latter case is γ a function of n. This difference is clearly not incorporated in the continuum model,[2] and is caused by a different degree of overlap of the exciton path with itself, which is discussed in detail in the random-walk model later in this paper.

The above analysis applies to singlet excitons. For triplet excitons the substitution $\beta \rightarrow \beta + \gamma n$ in Suna's analysis can also be used, because the quenching rate of a triplet pair (1, 2) by a third triplet (3) is independent of the pair spin state of (1, 2) if all spin states of (3) are equally probable. This can be shown easily in the high-magnetic-field representation. In this representation the pure singlet pair state $|S\rangle$ is given by

$$|S\rangle = (1/\sqrt{3})(|0,0\rangle - |+1,-1\rangle - |-1,+1\rangle) \, , \tag{26}$$

where the indices +1, 0, −1 refer to spin quantum numbers of the individual triplets.[4] Therefore, due to spin conservation, only pairs $|0,0\rangle$, $|-1,+1\rangle$, or $|+1,-1\rangle$ can annihilate because they have a nonzero projection onto the $|S\rangle$ state. The annihilation probability is the same for all these pairs.[2,4] If the pair (1, 2) is in one of the states $|0,0\rangle$, $|+1,+1\rangle$, or $|-1,-1\rangle$, it can be quenched by (3) if it is in the state $|0\rangle$, $|-1\rangle$, or $|+1\rangle$, respectively. In all these cases there is only one state of (3) which can quench (1, 2), but it can quench both (1) and (2). On the other hand, in all remaining cases there are always two states of (3) which can quench only one exciton of the pair (1, 2), e.g., if (1, 2) is in the state $|0,+1\rangle$, then $|0\rangle$ is quenched by $|0\rangle$ and $|+1\rangle$ is quenched by $|-1\rangle$. Thus we expect equal average quenching rates of (1, 2) by (3) for all possible states of (1, 2). The assumption of equal population of all single spin levels is satisfactory for magnetic fields ≤10 kG at room temperature.[4]

The increase of the pair decay rate with increasing triplet exciton density causes a broadening of the resonance lines in the magnetic field dependence[2] of delayed fluorescence. The substitution $\beta \rightarrow \beta + \gamma n$ into Suna's expressions[5] for the triplet-triplet annihilation rate is straightforward. Since triplet excitons usually have a long lifetime, Eq. (21) is valid and as with Eqs. (19) we obtain formulas for γ in which density effects are observable only in one- and two-dimensional systems. Examples of such systems are organic polymers,[6] biological membranes,[7] or photosynthetic units.[8] In a quasi-two-dimensional system such as anthracene the three-dimensional equation for pair annihilation can be approximated by a two-dimensional equation in which β is replaced by

$$\beta_{\mathrm{eff}} = \Psi^* + \tfrac{1}{2}\beta + (\Psi\beta + \tfrac{1}{4}\beta^2)^{1/2}\,, \tag{27}$$

where Ψ^* is the out-of-plane hopping rate.[2] In this formally two-dimensional equation β_{eff} is the effective monomolecular decay rate including the possibility that the exciton leaves the plane of this two-dimensional motion. In anthracene[2] $\beta_{\mathrm{eff}} = (2 \pm 1) \times 10^8$ sec^{-1} and obtaining triplet densities such that $\gamma n \approx \beta_{\mathrm{eff}}$ is difficult, so γ is essentially independent of n. However, this applies only to the kinetics of the annihilation, without considering the annihilation products. It is known that the magnetic field modulation of delayed fluorescence is a function of n, because part of the annihilation events leads to a triplet exciton.[9] This dependence has been analyzed elsewhere.[9,10]

For resonant nonradiative diffusion of singlet excitons[11] in aromatic crystals the average hopping rate D/R_a^2 is much larger than β.[12] With $\gamma n \lesssim \beta$, Eq. (21) is satisfied, and from Eqs. (19) it follows that γ is a function of n in one- and two-dimensional systems only. This excludes the aromatic crystals in which the dipole-dipole transfer[11] is dominant, because these crystals generally have at least two nonequivalent molecules per unit cell and the diffusion may be considered nearly three-dimensional. However, in some crystals the diffusion due to reabsorption may be dominant or at least not negligible.[12] The reason for this is that, although the jump rate is relatively small, the jump distance is much larger than in nonradiative transfer. In this case $\beta \approx D/R_a^2$, and according to Eq. (25) γ is a function of n. In the literature experimental data on singlet diffusion in aromatic crystals scatter by more than an order of magnitude, which, we believe, is caused at least in part by the varying roles of reabsorption and surface quenching in different experimental methods. Since the influence of reabsorption in general cannot be excluded even in thin samples because of total reflection at the surface, and since surface effects are not well understood, we would like to propose that detailed measurements be made of the dependence of γ on n in thick samples in order to clarify the ratio between nonradiative and radiative transfer in these systems. In one- and two-dimensional systems the reabsorption is negligible, but according to Eqs. (19a) and (19b) density effects on γ are possible. Again a detailed study of the dependence of γ on n should provide a better understanding of exciton transport. Systems which are worthy of study include the weak charge transfer complexes anthracene (naphthalene) tetracyanobenzene, in which two-dimensional exciton motion has been proposed,[13] and dichloronaphthalene, where again a one-dimensional triplet motion is present.[14]

In view of the similarity between trapping of excitons and annihilation of excitons, which can be seen as mutual trapping, it is expected that similar density effects will occur in trapping. With an increasing density of the traps the exciton lifetime decreases, which flattens the exciton-trap distribution function and increases the trapping rate. This can be illustrated simply in terms of a random-walk model.[15]

It is well known that during random walk a particle can visit the same lattice site more than once and that the probability of this is higher for systems of lower dimensionality.[16] Visiting the same lattice site more than once makes the trapping less efficient. The trapping efficiency is proportional to the ratio

$$\eta = [F(Z)/Z + 1] < 1\,, \tag{28}$$

where Z is the average number of exciton jumps during its lifetime and $F(Z)$ is the average number of sites visited during the exciton lifetime. In general, with smaller Z, that is, with decreasing exciton lifetime, the overlap of the exciton path with itself becomes smaller, which means that η is increasing. For large Z, that is, for long exciton lifetime, η is independent of Z only for three-dimensional motion.[17] For $Z \simeq 1$, which is equivalent to $\beta \approx D/R_a^2$, η is Z dependent even for three-dimensional motion, as can be seen easily by comparing two cases, $Z = 1$ and $Z = 2$. This is essentially the same result as in Eqs. (19) and (25). As in the case of annihilation, measurements of the trapping rate on the trap density in thick doped crystals with bulk excitation would separate the influence of the radiative and nonradiative transfer of excitons. Such a study could be made with the present intense dye lasers on some of the purer aromatic and substituted aromatic hydrocarbons.

In order to plot the density dependence of γ it is convenient to introduce new dimensionless parameters

$$\Gamma_\infty = \gamma_\infty/\lambda v \tag{29}$$

and

$$\Gamma = \gamma/\lambda v\,. \tag{30}$$

The meaning of these parameters is clear if we recall that λv is the annihilation rate for $D \to \infty$ and that γ_∞ is the annihilation rate for $\lambda \to \infty$.[2] With this notation the one-dimensional case is described by

$$\Gamma = \Gamma_\infty/(1 + \Gamma_\infty) \tag{31}$$

and

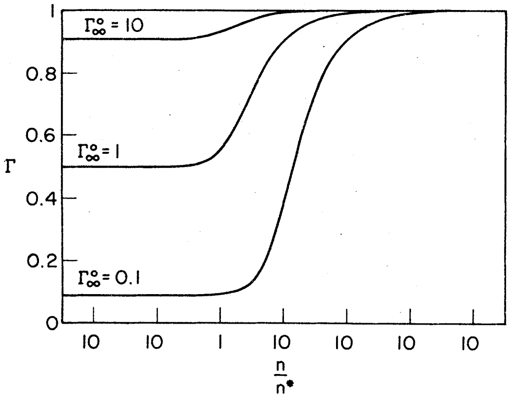

FIG. 1. Dependence of the relative annihilation rate Γ on the relative exciton density n/n^* for one-dimensional diffusion.

$$\Gamma_\infty = \Gamma_\infty^0 (1 + \Gamma n/n^*)^{1/2}\,, \tag{32}$$

where

$$n/n^* = n\lambda v/\beta \tag{33}$$

is the relative exciton density and

$$\Gamma_\infty^0 = \Gamma_\infty\,(n=0)\,. \tag{34}$$

The calculated dependence of Γ on n/n^* is presented in Fig. 1. It is clearly seen from Fig. 1 or Eqs. (31) and (32) that in order to observe the density effect we must be able to obtain exciton densities such that $\Gamma n/n^* \gtrsim 1$. The total change of Γ from $n=0$ to $n \to \infty$ is equal to $1/(1+\Gamma_\infty^0)$. This means that Γ_∞^0 should be small, $\gamma_\infty \lesssim \lambda v$, which is the case for diffusion limited annihilation. In order to obtain the full information from density-dependent experiments in one dimension the exciton density must be varied in a range of at least about five orders of magnitude.

We do not present the plots for Eqs. (19b) and (25); however, these two cases are qualitatively described by Fig. 1. Their main differences are a weaker density dependence of γ_∞ in Eq. (19b) because of the logarithmic function, and a stronger density dependence of γ_∞ in Eq. (25) because of the exponential function. The dependence of the limiting values $\gamma\ (n=0)$ and $\gamma\ (n=\infty)$ on $\gamma_\infty\ (n=0)$, given by Eq. (18), is the same in all cases.

To summarize, in the case of diffusion-limited annihilation of excitons (that is, for $\lambda v \gtrsim \gamma^\infty$), the annihilation rate γ is a monotonically increasing function of the exciton density n. For n much less than lattice site density, γ can be calculated by simply using Suna's results where β is replaced by $\beta + \gamma n$. For n approximately equal to lattice site density, higher-than-second-order correlation of excitons becomes important. The necessary conditions for n dependence of γ are (i) $\gamma n \gtrsim \beta$, and (ii) the dimensionality of the exciton motion is lower than three or the average jump rate of the exciton is comparable to its decay rate. It appears that studies of the dependence of γ on n in materials such as the weak charge transfer complexes anthracene (naphthalene) tetracyanobenzene ($\beta \sim 10^3\ \text{sec}^{-1}$) in which two-dimensional exciton motion has been proposed would be ideal for observing these density effects.

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