Exciton-Exciton Interaction and Exciton Migration in Anthracene, Pyrene, and Perylene Crystals

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The bimolecular annihilation of singlet excitons in pyrene, perylene, and anthracene crystals was studied by the aid of a nitrogen gas laser. The rate constant, γ, for bimolecular annihilation was estimated at 293°K to be 9×10^{-15} and 8×10^{-14} cm^3 sec^{-1} for pyrene and perylene, respectively. The temperature dependence of γ was measured with the result that it increases with the increasing temperature for the pyrene and perylene crystals, while it is almost independent of temperature for anthracene between 77°K and 293°K. The difference in the temperature dependence of γ was attributed to the difference in the mechanism of the exciton migration of the crystals. The method developed by the present authors for studying the exciton migration based on the exciton bimolecular annihilation was compared with that obtained previously by the use of mixed crystals.

In the last decade, a number of studies have been made of the singlet-exciton migration in aromatic hydrocarbon crystals;[1–5] most of them have been concerned with the fluorescence from host or guest molecules in mixed crystals. However, in the study of the exciton migration, it is desirable to use pure crystals to avoid specific host-guest interaction, the reflection of excitons by guest molecules, and the reabsorption of host fluorescence by guest molecules.[5] The exciton-exciton collision annihilation first sutdied by Bergman, Levine, and Jortner[6] may be useful for this purpose. They studied this phenomenon by observing the radiative decay of the fluorescence from a densely-excited anthracene crystal. Bimolecular collision annihilation was also observed for the pyrene crystal.[7]

The mechanism of the bimolecular exciton annihilation involves the exciton-transfer process followed by a collision ionization of an exciton pair through the autoionization level.[8] Since the former process may be rate-determining,[9,10] the exciton transfer in molecular crystals may be studied by measuring the rate constant, γ, for the bimolecular annihilation. In the present work, the γ value was estimated by measuring the fluorescence decay of densely-excited pyrene and perylene crystals. Furthermore, its temperature dependence was studied for anthracene, pyrene, and perylene crystals in order to clarify the mechanism of the exciton migration.

Experimental

Pyrene and anthracene were purified by vacuum sublimation and zone refining. Pure perylene was obtained by recrystallization of the synthetic material from a toluene solution.[11] Single crystals and polycrystalline samples of these materials were used for the experiment. The samples were excited by pulse radiations with half-widths of about 4 nsec at 3371 Å from a coaxial nitrogen laser.[12,13] The laser power of ~20 kW was measured by the chemical actinometry[14] in each experiment, in order to evaluate the exciton density. The laser beam was focused on a spot about 0.8 mm of diameter on the crystal surface. Filters were used in order to attenuate the intensity of the laser beam. The fluorescence from the samples was passed through a Bausch and Lomb monochromator and was detected by an RCA 1P28 photomultiplier, a Toshiba UV-39 filter being set in front of the entrance slit of the monochromator to eliminate the scattered laser light. By the use of neutral density filters, the photomultiplier pulse current was adjusted to be of the order of magnitude of a few mA, far below its saturation current. The decay curves were displayed on a Tektronix 585 oscilloscope and were photographed. The bimolecular rate constant was estimated by the least-squares method.

Results and Discussion

Estimation of γ Values. Some typical oscilloscope tracings of the fluorescence decays at the low- and high-density excitations are shown in Fig. 1, taking the perylene at 293°K as an example. Semilogarithmic plots of the decay curves are shown in Fig. 2. The decay curve deviates pronouncedly from an exponential decay at the high-density excitation, while it is regarded as exponential at the low-density excitation. The results can be interpreted in terms of the exciton-exciton annihilation. When the bimolecular annihilation of excitons takes place, the singlet-exciton density, n, after the termination of the laser may be represented by Eq. (1):

$$\mathrm{d}n/\mathrm{d}t = -\alpha n - \gamma n^2 \qquad (1)$$

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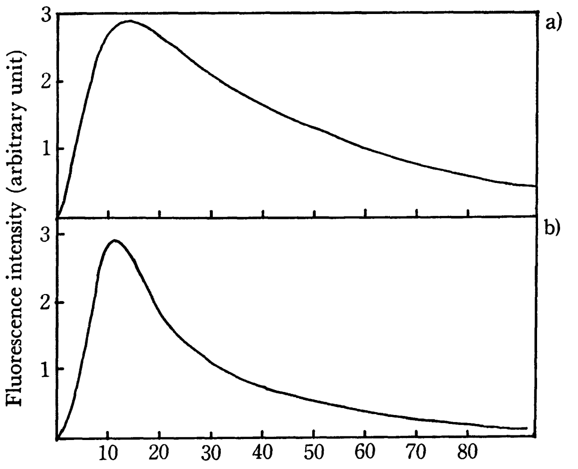

Fig. 1. The fluorescence decay of singlet excitons of perylene crystal at low (a) and high (b) density excitations at 293°K.

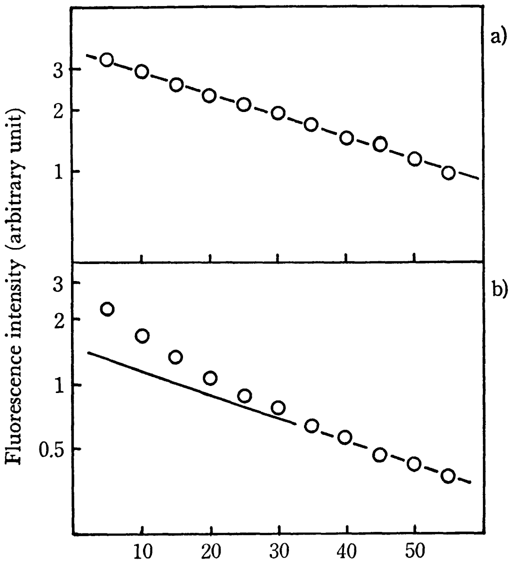

Fig. 2. Semilogarithmic plots of perylene fluorescence intensity *versus* time at low (a) and high (b) exciton density at 293°K.

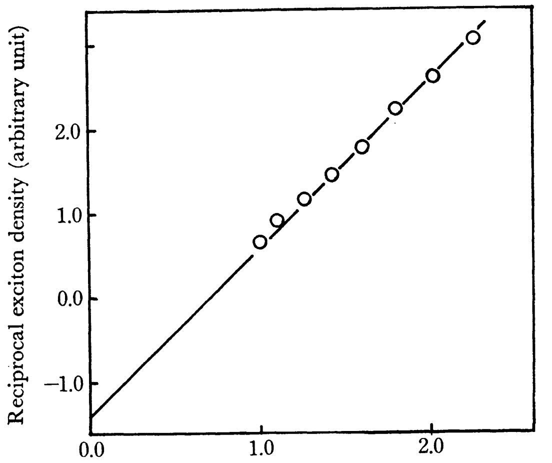

Fig. 3. A plot of the reciprocal exciton density *versus* exp(αt) of perylene crystal at 293°K.

Integration of Eq. (1) gives the following equation:

$$1/n = (1/n_0+\gamma/\alpha)\exp(\alpha t) - \gamma/\alpha \tag{2}$$

where n_0 is the initial exciton density. A linear relationship is expected to be satisfied between $1/n$ and $\exp(\alpha t)$. This relationship was found to be satisfied for the perylene and pyrene crystals at 293°K. The result for the perylene crystal taken as an example is shown in Fig. 3. The γ value was obtained from γ/α corresponding to the intercept of the straight line with the ordinate and from the monomolecular decay constant, α, obtained by the low-density excitation.

The initial exciton densities, n_0's, were estimated for the pyrene and perylene crystals on the following three assumptions. (1) Since the life-times of singlet excitons in the crystal are much longer than the pulse duration of the nitrogen laser, the time dependence of the excitation pulse may be represented by a delta function. (2) The crystals absorb the laser-pulse photons following the Lambert-Beer law. The initial exciton density (cm^{-3}) can be written:

$$n_0 = (N_0/S)(1-1/10^{\varepsilon cl})/l \tag{3}$$

Here, N_0, S, and ε are the number of photons in a laser pulse, the area of the crystal surface illuminated by the laser beam, and the molar extinction coefficient of the crystal, respectively. Furthermore, c is the molar concentration of the crystal, as determined from the crystal data.[15] By determining the penetration depth, l, in such a way that $10^{\varepsilon cl}$ equals e, the mean exciton density in a volume of Sl was calculated. (3) Since the unpolarized laser beam was irradiated perpendicular to the *ab* plane of the perylene single crystal, the molar extinction coefficient was estimated by averaging the polarized values in this plane observed by Hochstrasser.[16] For pyrene, the molar extinction coefficient of the solution[17] was used, since the fluorescence decay was observed for a multicrystalline sample. In the case of anthracene, the exciton may not stay within the irradiated volume during the measurement time, since its migration rate is considered to be very fast. This makes it difficult to determine the accurate value of n_0 and prevents us from determining the γ value for anthracene.

The γ values at 293°K were estimated to be 9×10^{-15} and $8\times10^{-14}\,\mathrm{cm^3sec^{-1}}$ for the pyrene and perylene crystals, respectively.

Mechanism of Exciton Transfer. It is a central question whether the band model or the hopping model is applicable to the energy transfer in molecular crystals. The applicability of these two models is dependent upon the strength of the molecular interaction in the crystals.[18] Under the framework of the band model, the efficiency of energy transfer may be expected to decrease with the increasing temperature since the phonon scatters the coherent diffusion of the

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[15] For perylene crystal; D. M. Donaldson, J. M. Robertson, and J.G. White, *Proc. Roy. Soc., Ser. A*, **220**, 311 (1953). For pyrene crystal; J. M. Robertson and J. G. White, *J. Chem. Soc.*, **1947**, 358.

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exciton and limits the mean free path of the exciton.[19] This has actually been found by Hammer and Wolf[20] for naphthalene in the temperature range from 100°K to 6°K. In careful experiments adopting the host-guest systems, no indication of a thermally activated energy transfer process was found in such monomeric molecular crystals as anthracene and naphthalene.[3]

The magnitude of the molecular interaction in the crystal is related with that of the jump time. The time for pyrene was determined to be 2×10^{-11} sec at room temperature from an impurity-quenching experiment.[4] This value is larger by two orders of magnitude than that of anthracene (2×10^{-13} sec) which was obtained from the Davydov-splitting or impurity-quenching experiment.[3] This means that the exciton diffusion is slower by two orders of magnitude for pyrene than for anthracene.

When the free path approaches the distance between neighboring molecules, the hopping model may be a good approximation for the energy transfer. In such dimeric crystals as pyrene and perylene, the lowest excited singlet state is an excited dimer state.[21] Since the electronic interaction between an excited dimer and a ground state dimer is weak,[22] the hopping model may be applicable to this case. Hence, the transfer of the dimer exciton will be assisted by the thermal activation through the lattice phonon.

We measured the temperature dependence of γ; the results are shown in Figs. 4 and 5, which give the plots of log γ *versus* $1/T$ for the pyrene and perylene crystals, respectively. From the slopes of the straight lines, we determined the apparent activation energies to be 330 and 290 cm^{-1} for the pyrene and perylene crystals, respectively.

These results are consistent with the recent studies by Klöpffer and Bauser.[4] They measured the fluorescence spectra of the mixed crystal of 10^{-3} mol/mol coronene in pyrene and observed structured coronene fluorescence spectra at 298°K, while at 77°K the only broad fluorescence spectrum of pyrene was observed. This result shows that the energy transfer in the pyrene crystal is completely frozen-in at low temperature.

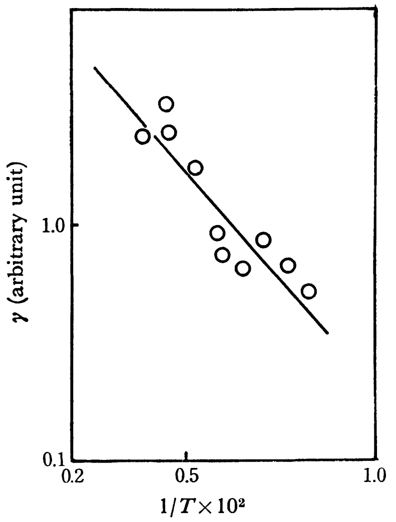

Fig. 4. A plot of log γ *versus* $1/T$ of pyrene multicrystalline sample.

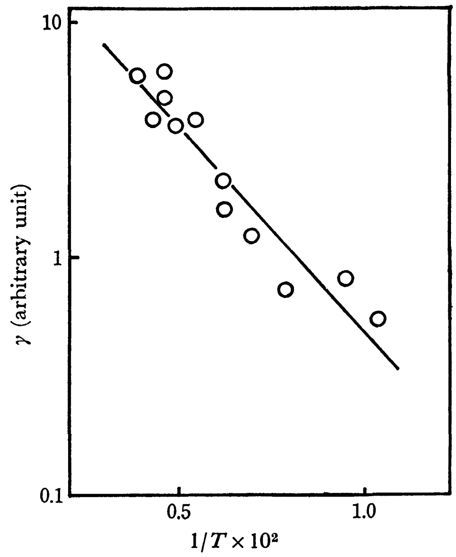

Fig. 5. A plot of log γ *versus* $1/T$ of perylene single crystal.

The anthracene crystal takes the monomeric structure and no excited dimer is formed in the crystal. The electronic interaction between the excited singlet state and the ground state is very strong. The energy transfer is accomplished by the diffusion of monomer excitons due to the dipole-dipole and exchange interactions, and it requires no thermal activation energy. The band model may be applicable to this case. As is seen in Fig. 6, the γ value is almost independent of temperature in the range of 77—293°K. This result is also consistent with the study of energy transfer in a mixed crystal done by Geschwendtner and Wolf.[2] The fluorescence intensity of the guest tetracene molecule in the host anthracene crystal was temperature-independent between 45—80°K, indicating a small coupling of phonon for the energy-transfer process in the anthracene crystal.

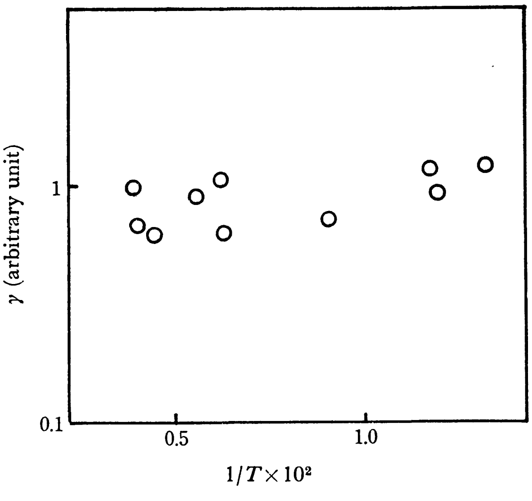

Fig. 6. A plot of log γ *versus* $1/T$ of anthracene single crystal.

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The present study of the exciton interaction based on the exciton-transfer process gives the results consistent with those obtained by previous studies using guest molecules in host crystals. In our opinion, however, the present method may be superior to the host-guest systems since it deals with pure crystals. This avoids specific host-guest interactions, the reflection of the excitons by guest molecules, and the reabsorption of the host fluorescence by guest molecules.[5] It is also in favor of the present method that there is no difficulty in choosing the proper guest substances; therefore, we can remove the limitation that the energy-transfer experiment have been made for only a few molecular crystals.

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