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Bimolecular Quenching of Triplet Exciton in Crystalline *p*-Dibromobenzene

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The rate constants of the bimolecular quenching (γ), the hopping rate (λ), and the diffusion coefficient (D) of triplet exciton in crystalline *p*-dibromobenzene at temperatures between 160 and 77 K were obtained by analyzing the phosphorescence decay curves at high and low density excitations with the use of an N_2 laser as an exciting pulsed light source. Estimated values of γ, λ, and D at room temperature (300 K) are $(2\pm1)\times10^{-12}$ cm$^3\cdot$s^{-1}, $9\pm4\times10^9$ s^{-1}, and $2\pm1\times10^{-4}$ cm^2 s^{-1}, respectively. The activation energy of the exciton hopping was obtained to be 290 ± 50 cm^{-1}. This implies that the triplet exciton in *p*-dibromobenzene crystal is described in terms of a localized exciton model.

One of the most important properties of excitons is their ability to transport electronic excitation energy without transport of charge. The diffusion constant of a triplet exciton in aromatic crystals has been obtained by several methods: *i.e.* (1) the dependence of an integrated intensity of delayed fluorescence in an aromatic crystal on the spatial distribution of excitons created by spatially inhomogeneous excitation,[1] (2) the absorption spectrum for generation of a triplet exciton by polarized light,[2] (3) surface quenching of a triplet exciton,[3] (4) diffusion of the excitons out of the tracks where they were formed by ionizing radiation,[4] (5) the magnetic field dependence of the effect of triplet excitons on the proton spin-lattice relaxation.[5] In the present paper we determined the diffusion constant of the triplet exciton by observing the phosphorescence decay curve at high and low density excitations using an intense N_2 laser light source in crystalline *p*-dibromobenzene (hereafter abbreviated to DBB). The present method of the determination of exciton migration rate has been applied to the singlet exciton in aromatic crystals[6–8] and the triplet exciton in uranyl salts.[9,10]

Experimental

The determination method of the rate constants of the bimolecular quenching and exciton migration is the same as that described in a previous paper.[8] The excitation pulsed light source is an N_2 laser (Avco Everett Model 950) with the peak power of 48 kW and the pulse width of 10 ns.

DBB was purified by repeated zone meltings. DBB single crystal in a Bridgman tube was cut in a size of $5\times4\times2$ mm^3 ($b\times c\times a$, respectively). Incident laser light was focused on the bc cleavage surface of the crystalline sample. The normal line of the surface and the incident light beam make an angle of about 45° with each other. Cooled nitrogen gas obtained from liquid nitrogen was used to control the tempetarure of the sample crystal between 97 and 160 K.

Results and Discussion

Phosphorescence Decay Curve. The phosphorescence decay curve at low density excitation observed at several temperatures between 77 and 160 K was exponential and was independent of the observing wavelength. This implies that the phosphorescence emission from the crystalline DBB sample used in the present work is not contaminated with the impurity emission. The phosphorescence intensity of DBB deviated from the exponential one at high density excitation at temperature between 77 and 160 K. The phosphorescence decay curves at low and high density excitations at 77 K are shown in Fig. 1. If the faster decay of phosphorescence at high density excitation is due to the biexcitonic quenching, the exciton concentration $n(t)$ at time t after excitation can be given by the following equation:[6,7]

$$1/n(t) = \{1/n(0) + \gamma/\alpha\}\exp(\alpha t) - \gamma/\alpha, \qquad (1)$$

where α and γ are the rate constants of monomolecular and bimolecular anihilation processes, respectively. α is obtained from the decay curve of phosphorescence at low density excitation.

The inverse of the exciton density in an arbitrary unit at high density excitation at 77 K is plotted against $\exp(\alpha t)$, the result being shown in Fig. 2. As is shown in this figure, the existence of a good linear relationship between the two quantities is consistent with the quenching mechanism given by Eq. 1. Therefore the shortening of the phosphorescence decay time observed at high density excitation can be explained in terms of biexcitonic quenching. From the estimation of the initial concentration of the exciton ($n(0)$) and the intercept of the plot of $n(t)^{-1}$ *versus* $\exp(\alpha t)$, γ can be obtained. The initial concentration of the triplet exciton can be

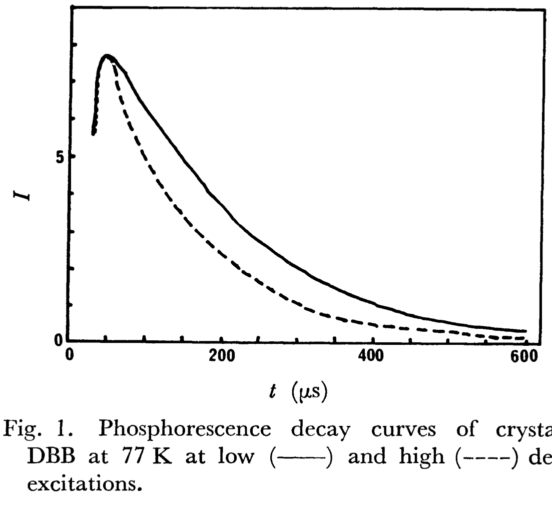

Fig. 1. Phosphorescence decay curves of crystalline DBB at 77 K at low (——) and high (----) density excitations.

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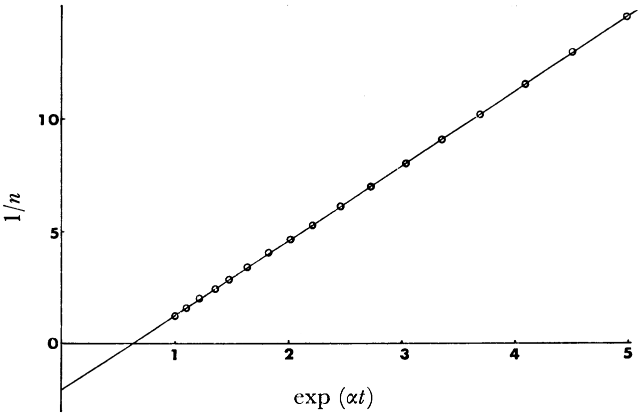

Fig. 2. The plot of $1/n$ *versus* $\exp(\alpha t)$ for the triplet exciton in crystalline DBB at 77 K at high density excitation. n is in an arbitrary unit. The initial concentration, $n(0)$, is estimated to be 1×10^{-3} M ($=6\times10^{17}$ cm^{-3}).

obtained by the $T_1\leftarrow S_0$ absorption cross section of the DBB crystal at the wavelength of the excitation laser pulse.

Estimation of the Initial Concentration of Triplet Exciton. The initial concentration of the triplet exciton, $n(0)$, is estimated by using the following equation:[8)]

$$n(0)=\frac{N_0(1-e^{-1})L}{\Delta S\Delta l}=\frac{0.632N_0L}{\Delta S}\times 2.303\,\varepsilon c$$
$$=\frac{1.455N_0\varepsilon cL}{\Delta S}, \qquad (2)$$

where N_0 and ΔS are the number of photons irradiated and the irradiated area on the sample crystal, respectively. ε and Δl are the molar extinction coefficient and absorption depth of the $T_1\leftarrow S_0$ transition in the DBB crystal at the wavelength of the N_2 laser oscillation, respectively, and L and c are the light transmittance of lenses and dewar and the molar concentration of the DBB crystal, respectively. Crystal data[11)] were used to estimate c to be 9.96 M. From the data on the $T_1\leftarrow S_0$ absorption spectrum of the DBB crystal measured by Castro and Hochstrasser,[12)] molar extinction coefficients parallel to b and c axes at 337.1 nm are estimated to be 5.0 and 7.5 M^{-1} cm^{-1}, respectively. The average of the two values were used for the estimation of $n(0)$ using Eq. 2. By applying these values to Eq. 2, $n(0)$ is estimated to be *ca.* 1×10^{-3} M($=6\times10^{17}$cm^{-3}).

Estimation of γ and Hopping Rate (λ) of Triplet Exciton in DBB Crystal. From the estimated value of $n(0)$ and the intercept of the plot, γ is obtained to be $(4\pm2)\times10^{-14}$ cm^3 s^{-1} at 77 K. The relationship between the biexcitonic quenching rate constant γ and the hopping rate, λ, of the exciton is expressed by the following equation[10)]:

$$\gamma=(2-A)\frac{V_0z_n}{V_{tot}z_u}\frac{\lambda\mu}{\lambda+\mu}. \qquad (3)$$

Here A, z_n, and z_u are the quantum yield of the formation of a triplet exciton from a pair of two nearest neighboring excitons, the number of sites in the nearest neighbor, and the number of molecules in a unit cell of the DBB crystal with volume V_0, respectively, and μ represents the rate of the quenching for a pair of two nearest neighboring excitons.

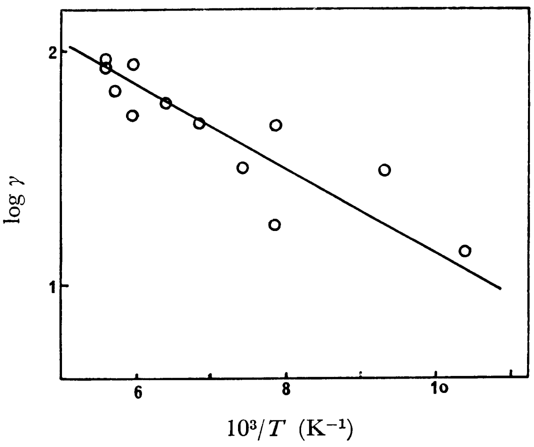

Fig. 3. The logarithmic plot of γ *versus* $1/T$ for the triplet exciton in crystalline DBB.

Now we consider two extreme cases: (1) The rate of bimolecular quenching is determined by that of the transition to the final higher excited state and therefore is thought to be temperature independent. In this case,

$$\gamma=(2-A)\frac{V_0z_n}{z_u}\mu. \qquad (4)$$

(2) The bimolecular quenching rate is determined by the migration rate of the exciton and γ increases or decreases with the increasing temperature dependeng upon the mechanism of exciton migration. With increasing temperature the rate of the exciton migration in the hopping model (Case (b-1): $\lambda=\lambda_h$) increases, while the rate in the coherent model (Case (b-2): $\lambda=\lambda_c$) decreases. In this case,

$$\gamma=(2-A)\frac{V_0z_n}{z_u}\lambda. \qquad (5)$$

The temperature dependence of γ of the triplet exciton in crystalline DBB shows that it can be described in the hopping model (Fig. 3). The activation energy of exciton hopping in DBB is obtained to be 290 ± 50 cm^{-1} from the temperature dependence of γ shown in Fig. 3.

Since it is difficult to determine A experimentally, it is tentatively assumed to be unity. The assumption makes the γ value different by factor of only 2 from that obtained by the assumption of $A=0$. The difference is smaller than the experimental error in the determination of $n(0)$ and hence of γ. The obtained value of γ is listed in Table 1 together with the data of the triplet exciton in crystalline anthracene and pyrene previously reported by Avakian and Merrifield,[13)] and Ern *et al.*,[14)] respectively. The values of γ and D of triplet exciton in crystalline DBB are quite similar to those in crystalline anthracene and pyrene. The similarity in the magnitude of D and hence γ of triplet exciton in anthracene, pyrene, and DBB is in contrast with the difference in the magnitude of γ of singlet exciton in crystalline anthracene ($\gamma=1.25\times10^{13}$ cm^3 s^{-1})[15)] and pyrene ($\gamma=5\times10^{10}$ cm^3 s^{-1}).[16)] This may be interpreted in terms of the expected smaller difference in the ex-

Table 1. The rate of bimolecular quenching, hopping rate and diffusion coefficient of exciton (γ, λ, and D, respectively) in DBB in the comparison with those of anthracene and pyrene

Crystal	DBB		Anthracene[b)]	Pyrene[c)]
Temperature	77 K	300 K	room temperature	room temperature
γ/cm^3 s^{-1}	$(4\pm2)\times10^{-14}$	$(2\pm1)\times10^{-12}$	2×10^{-12}	$(7.5\pm4.0)\times10^{-12}$
λ/s^{-1}	$(2\pm1)\times10^{8}$	$(9\pm4)\times10^{9}$		
D/cm^2 s^{-1}	$(3\pm1.5)\times10^{-5}$	$(2\pm1)\times10^{-4}$	2×10^{-4}	$(8\ \pm4\ )\times10^{-4}$

a) The values of γ, λ, and D at 300 K are estimated by the extrapolation from those values between 77 and 180 K, with use of the activation energy of exciton migration. b) Ref. 15. c) Ref. 16.

change integral than in the electronic coupling among anthracene, pyrene, and DBB.

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