

# Reabsorption Effect and Fluorescence Decay Times in Naphthalene Crystals

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## Abstract

The reabsorption effect and the kinetics of the fluorescence in the naphthalene crystals were investigated by mean of the nanosecond light pulse method from 80 K to 280 K. The increase of the reabsorption with increasing the temperature was interpreted as being due to the hot-band transition. The temperature dependence of the intrinsic decay times could be explained in term of the vibronically allowed electric dipole transition.

## 1. Introduction

In organic crystals, the fluorescence decay times are influenced by the reabsorption of the fluorescence, defects and impurities. Reabsorption, due to the overlap of the absorption and fluorescence spectra, depends on crystal-size, the range of the overlapping and the exciting wavelength. Therefore, it is difficult to obtain the intrinsic fluorescence decay times. EL-Karech and Wolf measured the apparent decay times of naphthalene crystals with different thickness, and obtained the intrinsic decay times by extrapolating to the thickness of zero[1]. They analyzed the temperature dependence of the decay times, assuming that the exciton were distributed on two Davydov bands in thermal equilibrium.

In the present work, the fluorescence decay times in naphthalene crystals having 5-50  $\mu\text{m}$  diameters were measured. From the analysis, a new absorption band induced by the thermal energy was found and the mechanism of the temperature dependence of the intrinsic decay times was clarified.

## 2. Experimental Method

Naphthalene of scintillation grade was obtained from Wako Chemical Co. and purified by zone-refining for 100 passes. Microcrystals of various size were obtained by grinding of the crystals and which were then classified into different sizes. These crystals were annealed for 50 minutes at 50°C. By annealing, the defects disappeared and transparent crystals were obtained.

Measurements were made of the fluorescence decay times of the crystals by the pulse method. The crystals were excited by the radiation of 310 nm light from a pulsed discharge

lamp through Hitachi 139 monochromator. The half-width of light pulse was about 10 nsec.

### 3. Results and Discussion

The fluorescence spectra of naphthalene crystals of 10  $\mu\text{m}$  and 1 mm in the mean diameter are shown in fig.1. The high energy part of the fluorescence spectra in fig.1 are eliminated by the reabsorption of the emission. Such size-effects of the reabsorption occur in the fluorescence decay times. Fig.2 shows the temperature dependence of the apparent fluorescence decay times of crystals (5 and 50  $\mu\text{m}$  in the mean diameter). The emission decays with a single exponential from 80K to 280K. The dependence of the decay times between the two sizes was similar. Fig.3 shows the relation between decay times and crystal-sizes at different temperature. Above 40  $\mu\text{m}$  diameter, the decay times became constant.

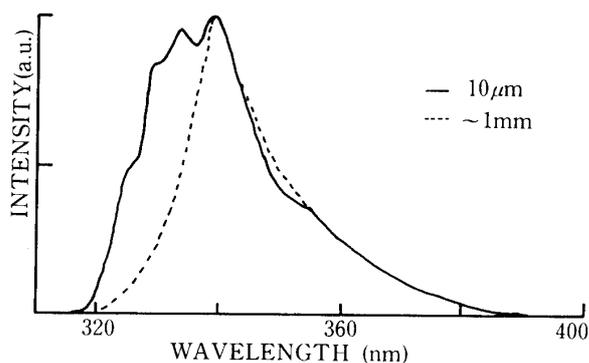


Fig.1 The fluorescence spectra of the naphthalene crystals of 10  $\mu\text{m}$  (—) and 1 mm (---) at room temperature.

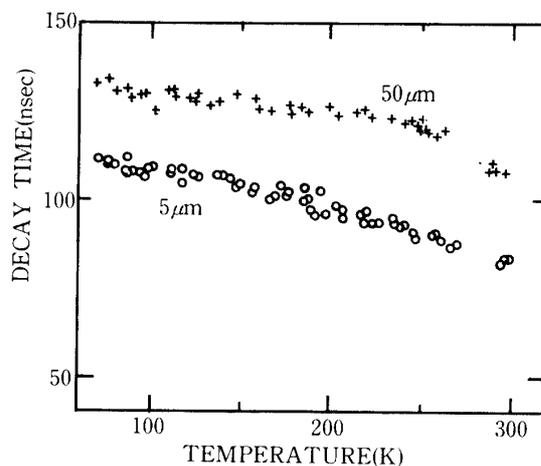


Fig.2 The temperature dependence of the fluorescence decay times. (5  $\mu\text{m}$  (○) and 50  $\mu\text{m}$  (+) in the diameter).

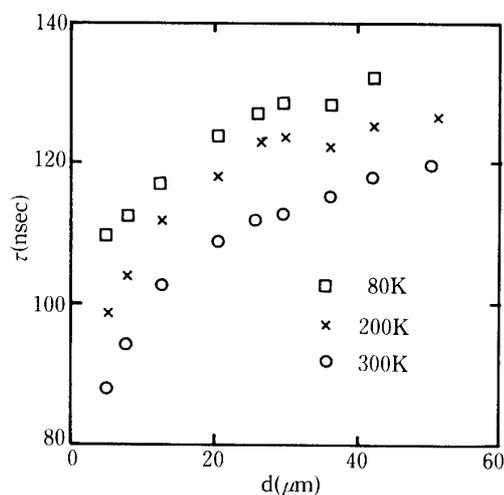


Fig.3 The relation between the decay times and the crystal-size at different temperature.

In naphthalene crystals, the emission spectrum overlaps with the absorption spectrum. In such a case, the apparent decay time  $\tau$  and the quantum yield  $\eta$  are written as follows [2];

$$\tau = \frac{\tau_0}{1 - a\eta} \quad (1)$$

where  $\tau_0$  is the intrinsic decay time and  $a$  the rate of the reabsorption. The parameter  $a$  depends on the overlap between the absorption spectrum  $k(\nu)$  and the normalized fluorescence spectrum  $F(\nu)$  and the crystal thickness  $d$ ;

$$a = \int F(\nu) \cdot (1 - k(\nu)) \cdot d \, d\nu \quad (2)$$

In equation 2,  $k(\nu)$  is replaced by the mean absorption coefficient  $\bar{k}$  of the overlap region between the absorption and emission spectra. When the value of  $d$  is small, the equation 2 is written as follows;

$$a = \bar{k} \cdot d \quad (3)$$

The values of  $\tau_0$  were obtained from equation 1 and 3 as follows.

- (1) the tentative value of  $\tau_0$  was obtained by extrapolating to zero size in figure 3 at each temperature.
- (2) At each size and each temperature, the value of  $a$  was obtained by substituting the tentative value for the intrinsic decay time  $\tau_0$  in equation 1.
- (3) When the values of  $a$  and  $d$  obtained in the process 2 do not satisfy the equation 3, the tentative values of  $\tau_0$  were corrected. The value of  $\eta$  was taken from ref.3.

Fig.4 shows the relation between  $a$  and  $d$  below 25  $\mu\text{m}$  diameter at different temperature. The values of  $a$  seem to be proportional to the crystal-size  $d$  below 20  $\mu\text{m}$ . The mean absorption coefficient  $\bar{k}$  (the slope of the line in fig.4) became larger with increasing temperature. Fig.5 shows the temperature dependence of  $\bar{k}$ . the values of  $\bar{k}$  were about 115  $\text{cm}^{-1}$  at 100 K and 320  $\text{cm}^{-1}$  at 280 K. These values are reasonable because the values of the absorption coefficient in the region of the overlap between the absorption and emission spectra are 0–1000  $\text{cm}^{-1}$ [4].

The temperature dependence of  $\bar{k}$  was analyzed in the equation

$$\bar{k} = k_0 + P \cdot \exp(-\Delta E/kT) \quad (4)$$

where  $k_0$  is the mean absorption coefficient which is temperature independent,  $p$  the constant and  $\Delta E$  the activation energy. In fig.5, the solid curve is calculated by the equation (6). Then, the value of  $k_0$  is 115  $\text{cm}^{-1}$ ,  $p$   $2 \times 10^3 \text{ cm}^{-1}$  and  $\Delta E$  0.058 eV(464  $\text{cm}^{-1}$ ). The temperature dependence of  $\bar{k}$  seems to indicate that the new absorption band was induced by the thermal energy in the lower energy region of the 0–0 transition energy. The activation

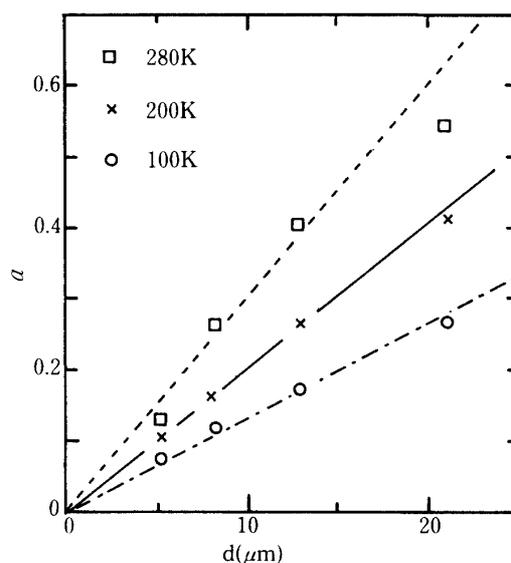


Fig.4 The relation between the mean crystal diameter and the rate of the reabsorption.

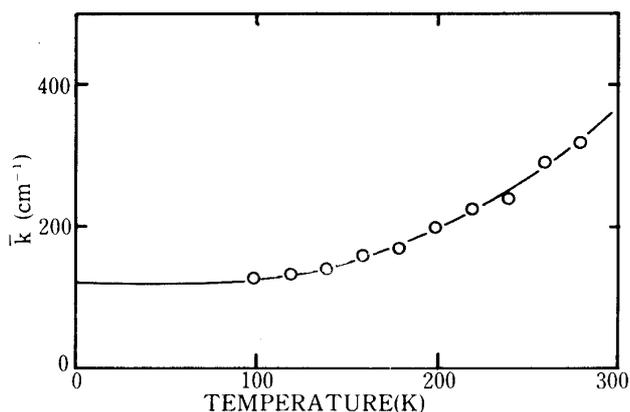


Fig.5 The temperature dependence of the mean absorption coefficients  $\bar{k}$ . The solid line was obtained by eq.4.

energy 0.058 eV is approximately equal to one of the molecular vibration energy ( $502 \text{ cm}^{-1}$ ) [5]. Therefore, the new absorption band is probably due to the transition from the hot level in the ground state. As this new band absorbs the emission of naphthalene, the fluorescence spectrum of naphthalene crystal changes with increasing temperature of the crystals.

The fluorescence spectrum of naphthalene crystals consists of two series; M series are observed in a crystal and a solution, and K series are intense in a crystal. M series predominant over K series at the fluorescence intensity in the crystals [5]. The 0-0 transition of M series is forbidden. However, the forbidden transition become allowed by the coupling with

the molecular vibration. In such a case, Liehr and Ballhause gave the probability  $1/\tau_r$  of the radiative transition [6];

$$1/\tau_r = \alpha \cdot \coth \frac{h\nu}{2kT} \quad (5)$$

where  $\alpha$  is the parameter,  $\nu$  the frequency of molecular vibration coupling with the 0–0 transition band. As the  $\tau_r$  is given by  $\tau_0/\eta$ , the  $\tau_r$  was analyzed in term of the equation 5 as shown in figure 6. Then, the following values were obtained ;

$$\alpha = 6.8 \times 10^6 \text{ sec}^{-1}$$

$$h\nu = 480 \text{ cm}^{-1}$$

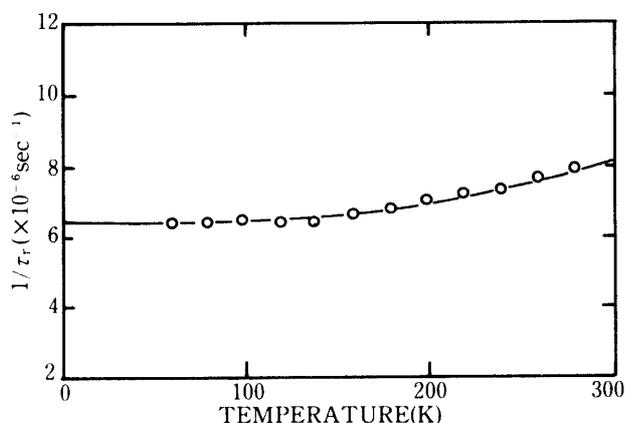


Fig.6 The temperature dependence of the radiative transition probabilities  $1/\tau_r$ .

The value of  $h\nu$  is approximately equal to one of molecular vibration energy  $502 \text{ cm}^{-1}$  mentioned above [5]. Therefore, the temperature dependence of the intrinsic decay times of naphthalene crystals could be elucidated by the vibronically allowed electric dipole transition.

#### References

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