Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

The Bimolecular Annihilation of Excitons and Singlet-Excition Migration in Anthracene Crystals

A. Inoue [a], S. Nagakura [a] & K. Yoshihara [b]

[a] The institute for Solid State Physics, The University of Tokyo, Roppongi, Minato, Tokyo, Japan

[b] The Institute of Physical and Chemical Research, Wako, Saitama, Japan

To cite this article: A. Inoue , S. Nagakura & K. Yoshihara (1974): The Bimolecular Annihilation of Excitons and Singlet-Excition Migration in Anthracene Crystals, Molecular Crystals and Liquid Crystals, 25:3-4, 199-204

To link to this article: http://dx.doi.org/10.1080/15421407408082800

Mol. Cryst. Liq. Cryst., 1974, Vol. 25, pp. 199-204
© Gordon and Breach Science Publishers, Ltd.
Printed in Dordrecht, Holland

The Bimolecular Annihilation of Excitons and Singlet-Excition Migration in Anthracene Crystals

A. INOUE and S. NAGAKURA

The Institute for Solid State Physics,
The University of Tokyo,
Roppongi, Minato, Tokyo, Japan

and

K. YOSHIHARA

The Institute of Physical and Chemical Research,
Wako, Saitama, Japan

(Received February 5, 1973; in final form June 19, 1973)

The mechanism of exciton migration in anthracene crystals was studied by measuring a rate constant, γ, for the bimolecular annihilation of exitons at various temperatures between 5°K and 250°K. Consequently, γ was found to be proportional to $1/\sqrt{T}$. This is in accordance with the band model for the exciton motion. The present method for the study of the singlet-exciton migration, which is free from the trapping effect by impurity-induced lattice defects and from the host-guest interaction effect, is superior to the usual method using host-guest systems.

1. INTRODUCTION

Excitons in molecular crystals can be classified into two groups by their migration modes;[1] the free exciton and the localized exciton. In the case of localized excitons which can be described by the hopping model, their migration requires a thermal activation and the diffusion coefficient increases with the increasing temperature.[2-5] On the other hand, in the case of free excitons which can be described by the band model, their migration is expected to decrease with the increasing temperature, because of the scattering of their coherent motion by phonon.

Agranovich and Konobeev[6] predicted theoretically that the diffusion coefficient of free excitons in molecular crystals is proportional to $1/\sqrt{T}$. Hammer and Wolf[7] studied the temperature dependence of the diffusion coefficient by measuring the sensitized fluorescence of a naphthalene crystal doped with anthracene in the temperature range of 6°K–100°K and obtained a result supporting this theory.

Most of the authors who studied so far the temperature dependence of exciton migration in anthracene crystals measured the sensitized fluorescence of tetracene-doped anthracene crystals and analyzed the results assuming that the excitation transfer is due to the migration of the excitons in the crystals.[8-12] The experimental studies on the exciton migration using the host-guest systems, however, encounter with such difficulties[12] as the localized dispersion effect and trapping effect of guest molecules. These difficulties prohibit us from observing the intrinsic temperature dependence of the exciton migration in anthracene crystals.

Under these circumstances, we undertook to study the exciton migration in pure anthracene crystals by a new method based upon the bimolecular annihilation of excitons which is successfully applied to the study of the localized exciton migration in pure pyrene and perylene crystals.[4]

2. EXPERIMENTAL

High purity anthracene crystals were obtained by the repeated vacuum sublimations and zone refinings of a synthetic material.

The crystal was illuminated on the *ab* plane by 3371 Å pulse radiations from a coaxial nitrogen gas laser,[13,14] the power of which was determined to be 6 kW by a chemical actinometry.[15] The laser beam was focussed on the crystal surface, the spot size being 0.5 mm in diameter. Fluorescence spectra from the samples were measured through a Bausch and Lomb monochromator, a Toshiba UV-39 filter being set in front of its entrance slit to eliminate scattered laser light and a Hamamatsu TV R106 photomultiplier being used as a detector. By the use of neutral density filters, photomultiplier pulse currents were adjusted to be of the order of magnitude of a few mA, far below the saturation current. The decay curves were displayed on a Tektronix 585 oscilloscope and were photographed.

The fluorescence lifetimes of anthracene crystals are shorter than 10 nsec below 90°K. Therefore, a correction must be made for the distortion in the observed time-dependence curve caused by the inability of the measuring circuit to follow a fast change in the fluorescence intensity. An integration circuit for the detecting system including the photomultiplier and the oscilloscope was assumed to consist of a resistor, R, and a capacitor, C. The relation between a corrected time dependence of fluorescence, $f(t)$, and an observed one, $g(t)$, can be given by the following equation from the theory of the four-terminal network.

$$f(t) = g(t) + RC(dg(t)/dt). \qquad (1)$$

The time constant RC was determined in such a way that Eq. (1) is satisfied between a laser pulse signal determined experimentally by a detecting system with a time resolution of 0.5 nsec consisting of a Hamamatsu TV R317 photodiode and a Tektronix 3S1 sampling oscilloscope and that obeserved by the detecting system with the photomultiplier. The corrected fluorescence decay curve, $f(t)$, was obtained below 90°K by the aid of Eq. (1) from $g(t)$ and the RC value thus obtained. The validity of the present method for the correction is described elsewhere.[16]

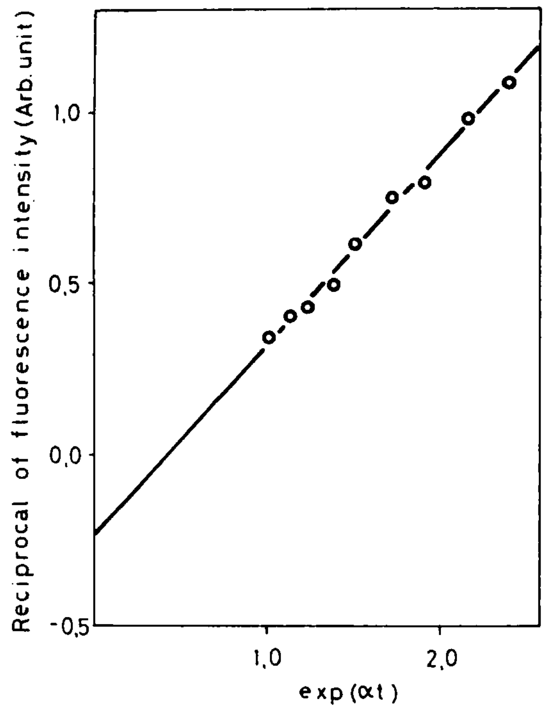

FIGURE 1 A plot of the reciprocal of relative fluorescence intensity *versus* $\exp(\alpha t)$ at 8°K.

3. RESULTS AND DISCUSSION

The time dependence of the concentration, n, of the singlet exciton produced by the high density excitation can be described by the following equation:

$$dn/dt = I(t) - \alpha n - \gamma n^2 . \tag{2}$$

Here, α and γ are the rate constants for the monomolecular and bimolecular exciton annihilation, respectively, and $I(t)$ is the shape of the irradiation pulse. For the determination of the relative value of γ, the origin of time scale, t=0, can be taken at some time immediately after the termination of the irradiation pulse and $I(t)$ can be taken to be equal to zero. Therefore, the integration of Eq. (2) leads to

$$1/n = (1/n_0 + \gamma/\alpha)\exp(\alpha t) - \gamma/\alpha. \tag{3}$$

Here, n_0 is the value of n at t=0. Hence, the linear relation is expected between the reciprocals of the relative fluorescence intensity at time t and exp(αt). This expectation is satisfied, as clearly seen in Figure 1 which shows the result measured at 8°K as an example. The relative value of γ can be 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 temperature dependence of γ was measured between 5°K and 250°K. The plot of log γ *versus* log T shown in Figure 2 brings about a straight line. From its slope, we got the relation $\gamma \propto T^{-p}, p = 0.46 \pm 0.05$.[†]

The biexcitonic annihilation can be interpreted to include two steps; the first step is the encounter of excitons through diffusion process in a crystal and the second step is the energy transfer between the encountered excitons.

Since the second step is calculated to be faster than the first step and is expected to be temperature independent,[17] the rate of singlet-exciton annihilation is determined by the rate of exciton collision. The rate of the encounter of excitons is proportional to the diffusion coefficient of exciton, D, or to the mean velocity of exciton, v, depending on whether the mean free path of exciton, ℓ, is smaller or larger than the collision radius of exciton, R. If $\ell < R$, γ is expressed[6b,18] as

$$\gamma = 8\pi DR \tag{4}$$

[†] The temperature dependence of the absorption intensity of the crystal at 3371 Å was checked by monitoring the laser light intensity transmitted through an evaporated layer of anthracene. No temperature dependence of the absorption intensity was observed. Hence, the temperature dependence of γ is not due to that of n_0.

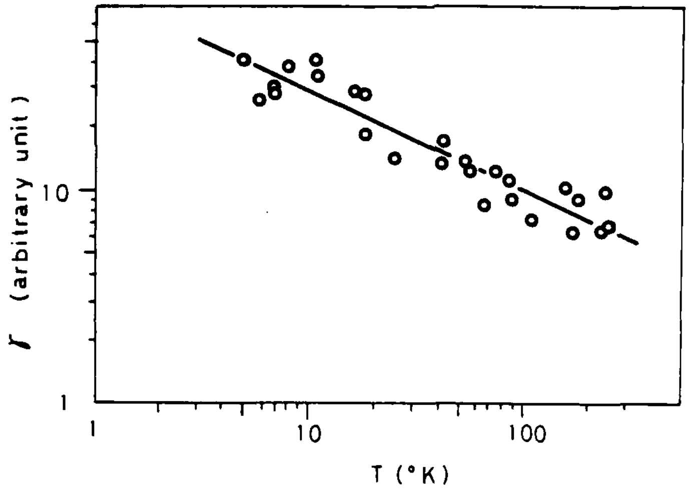

FIGURE 2 A plot of log γ *versus* log T.

while in the case of $\ell > R$

$$\gamma = \sigma v \tag{5}$$

Here, σ is the reaction cross section. In the latter case, however, γ is proportional to $\sqrt{T}$ since v is proportional to $\sqrt{T}$.[6] This contradicts the present experimental result shown in Figure 2.

Assuming the Boltzmann statistics for the wave vector of the exciton, Agranovich and Konobeev[6] presented the relation concerning the exciton scattering by the phonon,

$$D \propto 1/\sqrt{T} \tag{6}$$

for the free exciton moving through a band in the crystal. From Eqs. (4) and (6), γ is expected to be proportional to $1/\sqrt{T}$. The present experimental result satisfies this expectation and supports the band model for the exciton motion in the anthracene crystal.‡

It is clearly shown that the present method, using the rate constant for the biexcitonic annihilation is applicable to the studies on the mechanism of the free exciton motion as well as the localized exciton motion. Furthermore, the

---

‡ Eq. (4) is usually used for the case of hopping model. However, this equation is also valid for free exciton if the collision radius, R, is large compared with the lattice constant of the crystal.[6b] In the present case, R is estimated to be 10~1000 Å by use of the critical radius of exciton collision.[5] Hence, the use of Eq. (4) is not inconsistent with the band model, in the present case.

present method using the pure crystal is superior to the method using host-guest systems in several points described below. The measurements on the pure crystal avoid the effects of specific host-guest interaction, the reabsorption effect of the host fluorescence by guest molecules,[19] the trapping effects of the exciton by the impurity-induced lattice defects at low temperatures, and the disturbance due to the microcrystalline phase of guest molecules in the crystal.[12] Moreover, the present method is expected to be applicable to many other molecular crystals since it is free from the difficulty of choosing guest molecules which have sufficient solubilities in the host material, to which the energy is transferred efficiently from the host molecules, and which have sufficient quantum efficiencies of fluorescence.

Acknowledgement

We are indebted to Dr. T. Okada, The Institute of Physical and Chemical Research, for his technical assistance.

References

1. Davydov, A. S., *Theory of Molecular Excitons*, translated by M. Kasha and M. Oppenheimer Ir., McGraw-Hill Comp., New York, 1962.
2. Trlifaj, M., *Czech. J. Phys.* 6, 533 (1956).
3. (a) Klöpffer, W. and Bauser, H., *Chem. Phys. Letters* 6, 279 (1970).
   (b) Klöpffer, W., Bauser, H., Dolezalek, F., and Naundorf, G., *Molec. Cryst. Liq. Cryst.* 16, 229 (1972).
4. Inoue, A., Yoshihara, K., and Nagakura, S., *Bull. Chem. Soc. Japan* 45, 1973 (1972).
5. Kobayashi, T. and Nagakura, S., *Molec. Phys.* 24, 695 (1972).
6. (a) Agranovich, V. M. and Konobeev, YU. V., *Optics and Spectrosc.* 6, 155 (1959).
   (b) Agranovich, V. M. and Konobeev, YU. V., *Phys. Status Solidi* 27, 435 (1968).
7. Hammer, A. and Wolf, H. C., *Molec. Cryst.* 4, 191 (1968).
8. Lyons, L. E. and White, J. W., *J. Chem. Phys.* 29, 447 (1958).
9. Avakian, P. and Wolf, H. C., *Z. Phys.* 165, 439 (1961).
10. Geschwendtner, K. and Wolf, H. C., *Naturwissenschaften* 48, 42 (1961).
11. Benz, K. W. and Wolf, H. C., *Z. Naturforsch.* 19a, 177 (1964).
12. Wolf, H. C. *Advances Atomic Molec. Phys.*, Vol 3, Academic Press, New York, 1967.
13. Geller, M., Altman, D. E., and DeTemple, T. A., *J. Appl. Phys.* 37, 3639 (1966).
14. Inoue, A., Yoshihara, K., Nagakura, S., Kasuya, T., Minoh, A., Kobayashi, S., and Shimoda, K., *Reports I.P.C.R.* 47, 40 (1971).
15. Hatchard, C. G. and Parker, C. A., *Proc. Roy. Soc.* A235, 518 (1956).
16. Inoue, A., Yoshihara, K., Kasuya, T., and Nagakura, S., *Bull. Chem. Soc. Japan* 45, 720 (1972).
17. Jortner, J., *Phys. Rev. Letters* 20, 244 (1968).
18. Chandrasekhar, S., *Rev. Mod. Phys.* 15, 1 (1943).
19. Kawaoka, K. and Kearns, D. R., *J. Chem. Phys.* 45, 147 (1966).