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

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Version of record first published: 28 Mar 2007.

To cite this article: T. Kobayashi & S. Nagakura (1974): Reabsorption and High Density Excitation Effects on the Time-Resolved Fluorescence Spectra of Anthracene Crystal, Molecular Crystals and Liquid Crystals, 26:1-2, 33-43

To link to this article: http://dx.doi.org/10.1080/15421407408084821

Mol. Cryst. Liq. Cryst., 1974, Vol. 26, pp. 33-43

Printed in Dordrecht, Holland

Reabsorption and High Density Excitation Effects on the Time-Resolved Fluorescence Spectra of Anthracene Crystal

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(*Received February 12, 1973*)

The spectral dependence of fluorescence lifetime and the time-resolved fluorescence spectra at high and low density excitations were measured for pure anthracene crystals. A nitrogen gas laser was used as excitation source. The fluorescence lifetime with low density excitation was found to be shorter in the shorter wavelength region than in the longer wavelength region and to be longer over whole wavelength region for the thick crystal than for the thin crystals or powders. This can be explained by the reabsorption effect. Furthermore, a fluorescence intensity increment due to high density excitation was found to be more predominant in the shorter wavelength region than in the longer wavelength region. This high density excitation effect is discussed in terms of decreasing reabsorption caused by the ground state depletion.

INTRODUCTION

The fluorescence decay time of anthracene crystal has hitherto been measured by many authors.[1-7] The values observed diverge in the wide range from 3.1 ns

to 250 ns.[1,2] This discrepancy may mainly be due to two effects; the reabsorption effect and the impurity effect. When reabsorption is not negligible, the observed decay time depends upon the size and form of the sample crystal and other experimental conditions. Impurities also influence the dacay time of the anthracene fluorescence, since the migration rate of singlet exciton in the crystal is rather fast and the energy transfer from host anthracene molecules to guest impurity molecules is efficient.

The anthracene crystals used at the early stage of the studies were much less pure than those now available.[3-6] Furthermore, corrections for the reabsorption have scarcely been made or have been made rather inadequately. Munro *et al.*[7] studied the reabsorption effect on the fluorescence lifetime of crystalline anthracene, but these authors only measured the integrated fluorescence decay rate, and did not measure the lifetime dependence on the emission wavelength.

With high density excitation and the subsequent large exciton densities, fluorescence decay processes and spectra may be expected to change by exciton-exciton interactions. The bimolecular quenching process of fluorescence due to the interaction between excited species under high density excitation has been observed for organic molecular crystals[8-11] and also for solutions containing excited aromatic molecules[12] excimers,[13,14] or exciplexes.[14,15]

Recently, Yoshihara, Inoue, and one of the present authors (S.N.)[16] observed that the fluorescence spectrum of the 1,2,4,5-tetracyanobenzene-naphthalene charge-transfer complex crystal was broadened under the high density excitation, and this phenomenon was interpreted in terms of a dipole-dipole interaction between charge-transfer excitons. The effect of high density excitation on the fluorescence spectra was also studied for the crystals of fluoranthene and 1,2,4,5-tetracyanobenzene-durene charge-transfer complex. The spectral change observed for the former was explained by the temperature elevation at high density excitation.[11]

Generally speaking, the spectral changes observed with high density excitation may also be due to effects other than the above-mentioned exciton-exciton interaction and temperature elevation. In the present paper, we report the results of a study of the spectral change due to the reabsorption effect at the low density and high density excitations for anthracene, in which we have measured time-resolved fluorescence spectra and spectral dependence of the lifetime following excitation by a nitrogen gas laser. The spectral change at the high density excitation can be explained by considering the reabsorption decrease due to the depletion of ground state molecules, in addition to exciton-exciton interactions and induced emission.

EXPERIMENTAL

A pulsed nitrogen gas laser (AVCO-EVERETT model 1000) was used as the excitation source for the measurements of the lifetimes and fluorescence spectra. The exciting light pulse at 3371 Å is of ca. 10 ns duration, ca. 1 mJ total energy, and ca. 100 kW peak intensity. The laser beam is principally composed of the two parallel beams and thus the intensity distribution of its cross section (3 mm x 40 mm) is not homogeneous.[17] However, this did not seriously interfere with the measurements of the decay times and fluorescence spectra because the laser beam was focused on an area about 1 mm x 8 mm. The intensity of the laser beam was attenuated by neutral density filters (aluminum evaporated quartz plates). The emission from a sample crystal was also reduced by a neutral density filter made from copper mesh. The fluorescence was detected at the direction perpendicular to the excitation laser beam.

The fluorescence decay times were measured with a system consisting of a grating monochromator (Shimadzu Bausch and Lomb 1200 grooves/mm), a photomultiplier, and an oscilloscope (HITACHI model V 1000). The details of the system was described previously.[11,12,14] Experimental error in the decay time measurements is less than 1 ns.

The time-resolved fluorescence spectra (hereafter abbreviated to TRFS) and the integrated fluorescence spectra (hereafter abbreviated to IFS) over the time interval much longer than the duration time (10 ns) were measured by a Spex model 1704 grating monochromator attached with an EMI 6256S photomultiplier. The signal from the photomultiplier was detected through a boxar integrator (PAR model 160) with an aperture time of 10 ns through an RG 58 A/U coaxial cable. The cable is terminated by 50Ω and 100 kΩ impedances for the measurements of TRFS and IFS, respectively. The time constant of the detection system for the latter case is ~10 μs which is long enough to integrate the fluorescence spectra.

Steady state fluorescence spectra excited by a 100 kW high pressure mercury lamp were measured by a JASCO CT-50 grating monochromator with and RCA 1P28 or HTV R106 photomultiplier.

Ultra-pure crystals of synthesized anthracene were kindly supplied by Professor Iwashima and Professor Inokuchi.[18]

RESULTS AND DISCUSSION

Spectral dependence of the fluorescence lifetime of the anthracene crystal

The IFS at room temperature (295°K) of anthracene crystal with the size of ca. 1.5 x 4 x 5 mm^3 and of a powder anthracene sample are shown in Figure 1, the

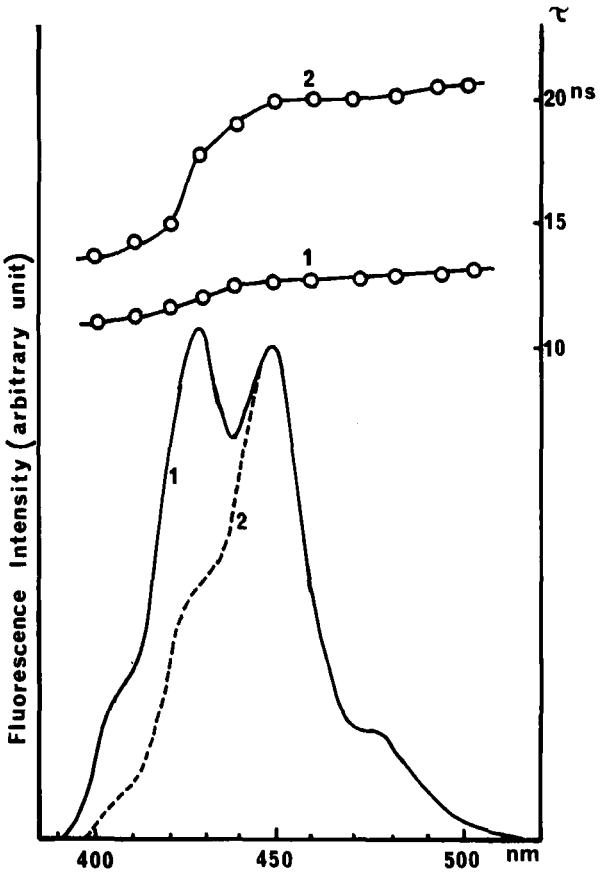

FIGURE 1 IFS and spectral dependence of fluorescence lifetime observed for anthracene at 295°K: curve 1, for the powder sample; curve 2, for the thick crystal.

intensities being normalized with regard to the peak intensity at 447 nm. The vibrational bands at 405, 424, 447, and 474 nm are hereafter referred to as A,B,C, and D bands, respectively. The patterns of fluorescence spectra observed with the two samples are completely coincident with each other at the wavelength region longer than 447 nm, while in the shorter wavelength region the fluorescence intensity of the thick crystal is much weaker than that of the powder sample.

The fluorescence lifetimes were measured at every ten nanometers from 400 to 550 nm for the two samples, the result being shown in Figure 1. The lifetime of the thick crystal ranges from 20.6 ns at 500 nm to 13.7 ns at 400 nm, while that of the powder sample has the values between 13.1 ns (at 500 nm) and

10.9 ns (at 400 nm). From the results we see the general tendencies that shorter lifetimes were obtained in the shorter wavelength region for both samples and that the thick crystal shows the longer fluorescence lifetime in all the observed wavelength region than the powder sample.

In order to clarify the cause of the above-mentioned spectral dependence of the fluorescence lifetime of anthracene, the TRFS were observed for the thick crystal, the result being shown in Figure 2. In this figure the emission intensities are normalized with regard to the peak intensity of band C, and the origin of the time scale is taken at the time of the highest fluorescence intensity. As is clearly seen from Figures 1 and 2, the positions of the vibrational bands of TRFS of the thick crystal agree well with those of IFS and also with those of IFS of the thin crystal.

In order to investigate further the cause for the difference in the relative intensity at shorter wavelength region among TRFS at different times after excitation as shown in Figure 2, the spectral dependence of $\log(I_2(\lambda)/I_1(\lambda))$ was obtained. Here, $I_1(\lambda)$ and $I_2(\lambda)$ are the intensities at a wavelength λ of the TRFS whose aperture time is centered at 20 ns and 0 ns after the time of the highest

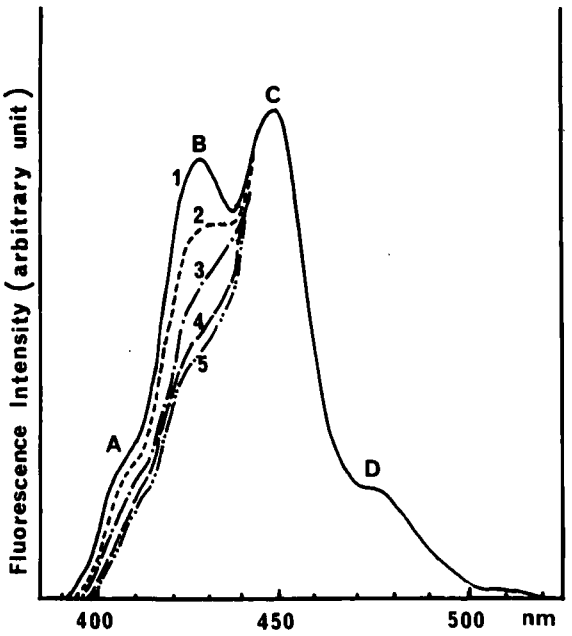

FIGURE 2 TRFS and IFS of a thick anthracene crystal at 295°K. Curves, 1, 2, 3, and 4 are TRFS measured 0, 5, 10, and 20 ns after the highest intensity time, respectively, and curve 5 is IFS.

fluorescence intensity. The result is shown in Figure 3. The curves of $\log(I_2(\lambda)/I_1(\lambda))$ agree well with the absorption spectrum of the evaporated thin film of anthracene. This fact shows that the long-lifetime emission suffers from the reabsorption effect more seriously than the short-lifetime emission† and that the spectral dependence of the lifetime is mainly caused by this effect.

According to the theory of reabsorption, the fluorescence lifetime increases and the quantum yield decreases by the reabsorption and reemission effects. A fluorescence intensity, $L(\nu)$, at wave number ν and a fluorescence lifetime, τ, may be given by the following equations,[5,19]

$$L(\nu)/L_0(\nu) = (1 - r(\nu))/(1 - QR) \quad (1)$$

$$\tau/\tau_0 = 1/(1 - QR) \quad (2)$$

Here $r(\nu)$, Q, and R are the probability of the reabsorption of photon at a wave number ν, the fluorescence quantum yield, and the efficiency of the reabsorption for the total emitted photons, respectively, and $L_0(\nu)$ and τ_0 indicate the fluorescence intensity and liftime without the reabsortion effect, respectively.‡ The above equations can explain the facts that the fluorescence intensity reduces and the duration time increases by the reabsorption effect. In order to explain the spectral dependence of the fluorescence lifetime observed in the present study, however, we must consider further details of the reabsorption mechanism which is disregarded in the derivation of Eqs. (1) and (2). These equations are based upon several assumptions for the sake of simplicity. One of these assumptions is that the reabsorption probability is independent from the origin and emitting direction of a fluorescence photon. This assumption is valid only when the primary fluorescence originates at the central part of a uniform spherical crystal. In the case of excitation near the surface of a thick crystal, the reabsorption probability depends on whether the photon is emitted towards the surface or away from it. Initially there is a higher density of emitting sites near the crystal surface, but with increasing time this density becomes more even throughout the crystal. For this reason, the probability that the reemitted light at the shorter wavelength region can escape from the crystal also decreases with the increasing time. Hence, the fluorescence intensity decreases more rapidly with time in the

† The classification of the fluorescene into long- and short-lifetime components is of course somewhat practical and not essential, because the times of reabsorptions and reemissions may be distributed from zero to infinity and also because the fluorescence duration times of the components may have the values between the intrinsic lifetime of anthracene molecule (~5 ns[1,2]) to infinity.

‡ The fluorescence lifetime of anthracene crystal with the least reabsorption effect is found to have the value near the intrinsic lifetime of excited anthracene "molecule". Therefore τ_0 may be considered to be the intrinsic fluorescence lifetime of anthracene molecule.

shorter wavelength region than in the longer wavelength region, and the fluorescence lifetime is shorter in the shorter wavelength region than in the longer wavelength region.

Figure 2 shows that the fluorescence spectra observed immediately after the irradiation are only slightly affected by reabsorption, while at the later times, reabsorption becomes considerably predominant. This may also be explained by the fact that the excitons produced near the crystal surface migrate toward the inner part where the reabsorption probability is greater than in the crystal surface.

The effect of the excitation intensity on the emission of the anthracene crystal

The TRFS and IFS of pure anthracene crystal at low and high density excitations are shown in Figure 4. The fluorescence spectra are normalized with respect to the peak intensity of band C. As is shown in this figure, the relative intensity of fluorescence in the shorter wavelength region to that in the longer wavelength region is higher for the high density excitation than for the low density excitation both in the TRFS and IFS, while the peak positions of the

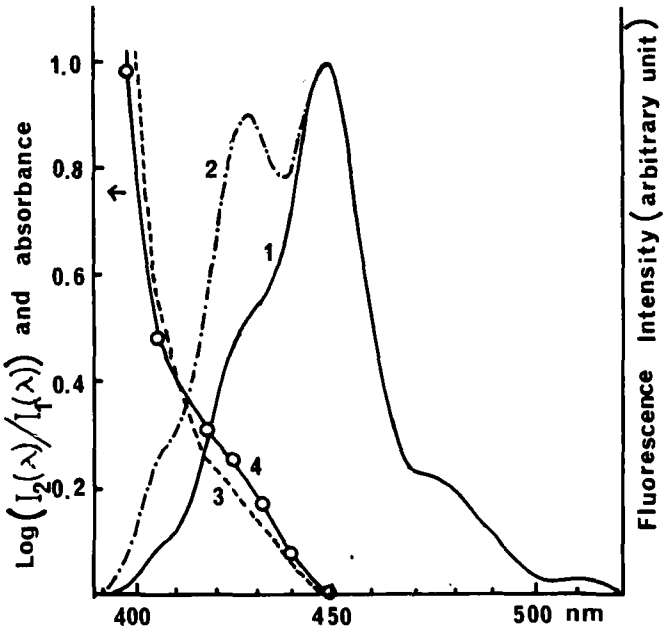

FIGURE 3 $I_1(\lambda)$, $I_2(\lambda)$, and log $[I_2(\lambda)/I_1(\lambda)]$ obtained for a thick anthracene crystal. Curves 1, 2, and 3 indicate $I_1(\lambda)$, $I_2(\lambda)$, and $\log(I_2/I_1)$, respectively, and curve 4 the absorption spectra of evaporated thin film of anthracene on a quartz plate.

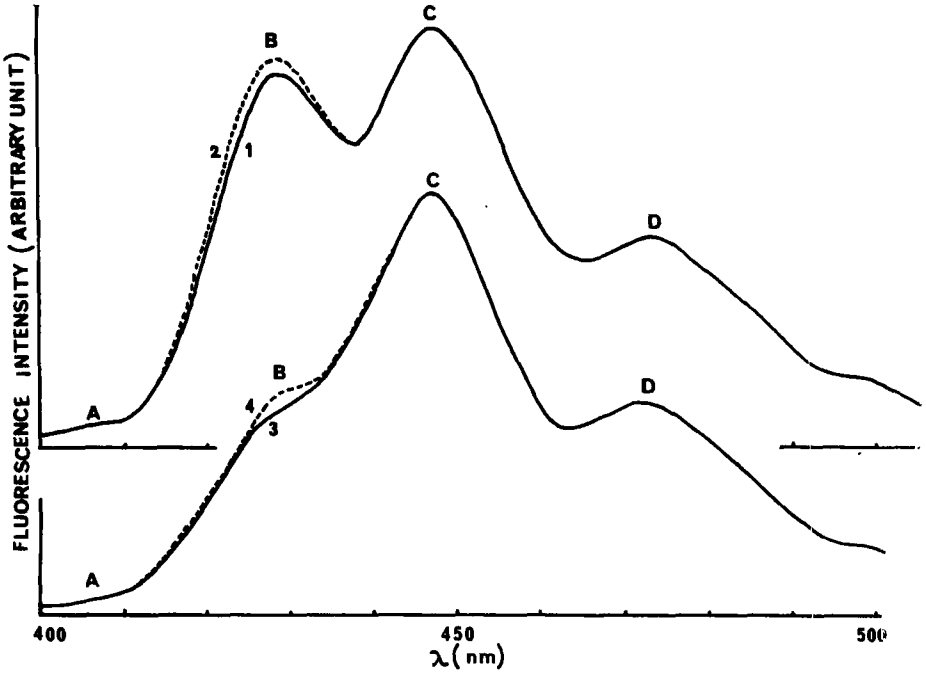

FIGURE 4 IFS and TRFS of thick anthracene crystal at low and high density excitations.
Curve 1. TRFS at low density excitation at the time of the highest fluorescence intensity ($I_S = 3.9$ kW).
Curve 2. TRFS at high density excitation at the time of the highest fluorescence intensity ($I_S = 105$ kW).
Curve 3. IFS at low density excitation ($I_S = 3.9$kW).
Curve 4. IFS at high density excitation ($I_S = 105$ kW).

vibrational bands are independent of the irradiation light intensity within the range of experimental errors.

In Figure 5, the intensity ratio between bands B and C, I_B/I_C, is plotted against the intensity of the excitation light pulse, I_S. The I_B/I_C value increases by about 4.6 and 1.9% for the TRFS and IFS, respectively, when the excitation light source increases by about 25 times.

Neither color change nor decomposition of the crystal was found after the exposure of about 2×10^4 laser shots. Furthermore, the repetitive low density excitations before and after the high density excitation at the same spot of the crystal gave the almost same results. Therefore, the increment in I_B/I_C caused by the high density excitation is not mainly due to any irreversible chemical reaction. †

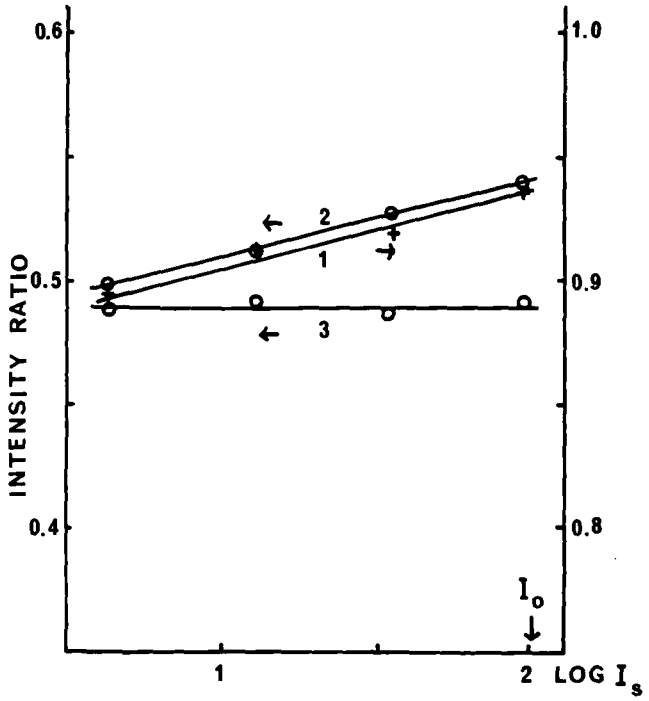

FIGURE 5 The I_S dependence of the relative intensity of vibrational bands in the fluorescence spectrum measured with a thick anthracene crystal at 295°K. Curves 1, 2, and 3 are for I_B/I_C in TRFS, I_B/I_C in IFS, and I_D/I_C in IFS, respectively. I_S is the peak intensity of the laser light in the unit of kW. I_0 is the highest laser intensity (105 kW on 0.08 cm^2).

There are four tentative interpretations for this phenomenon; (a) the spectrum is affected by the exciton-exciton interaction in anthracene crystal at high density excitation. (b) The effect of the reabsorption becomes less prominent because of the ground state depletion of anthracene molecules under the high density excitation. (c) The induced emission appears at high density excitation. (d) The emission spectrum is affected by the reabsorption effect caused by transitions from the lowest excited singlet state to higher excited singlet states of anthracene.

Among the above-mentioned possibilities, (d) can immediately be excluded since there is no $S_n \leftarrow S_1$ absorption of anthracene molecule in the region under consideration, judging from the data in solution.[20,21]

† Many repetitions of the high and low density excitations at the same spot caused a very slight change in the fluorescence spectrum of the anthracene crystal. This paper is concerned with only the data obtained before the samples showed the change.

We now consider the increase in the intensity of band B in terms of the depletion of molecules in their ground state. The intensity ratio of this band to band C in the case of no reabsorption, $(I_B/I_C)_0$, was estimated to be about 2.0 from the fluorescence spectrum of anthracene in dilute solution. The ratio at low density excitation for the thick crystal, $(I_B/I_C)_L$, was found to be 0.48. The relation between these two quantities is given by the following equation,

$$(I_B/I_C)_L = (I_B/I_C)_0 10^{-\Delta\epsilon c\bar{\ell}} \tag{3}$$

Here $\Delta\epsilon$, c, and $\bar{\ell}$ are, respectively, the difference in the peak molar extinction coefficients between bands B and C, the molar concentration of anthracene in the pure crystal, and the average distance between the point of the emission in crystal and the point of the surface of the crystal from where the detected photon leaves. With these $(I_B/I_C)_0$ and $(I_B/I_C)_L$ values, $\Delta\epsilon c\bar{\ell}$ was 0.62. Since $c = 7.06$ M, $\Delta\epsilon\bar{\ell}$ was ca. 0.09 M^{-1}.

The intensity ratio at high density excitation $(I_B/I_C)_H$, is given by the following equation on the assumption that the decrease in I_B/I_C is caused by the ground state depletion

$$(I_B/I_C)_H = (I_B/I_C)_0 10^{-\Delta\epsilon c'\bar{\ell}}, \tag{4}$$

where c' is the molar concentration of the anthracene molecule in the ground state at high density excitation. The difference Δc between c and c' shows the degree of the ground state depletion. From Eqs. (3) and (4), the following relation was obtained.

$$[(I_B/I_C)_H/(I_B/I_C)_L] = 10^{+\Delta\epsilon\Delta c\bar{\ell}} \tag{5}$$

The exciton density is the function of the penetration depth from the crystal surface. Here we consider the average density in the excited region with the volume $\Delta V = \Delta S\Delta\ell$, where ΔS and $\Delta\ell$ are the irradiated area on the crystalline surface by focused laser light, and the average penetration depth which is given by the inverse of $2.303\,\epsilon_{3371}\,c$, ϵ_{3371} being the molar extinction coefficient of the sample at the wavelength of the excitation light pulse (3371 Å). The exciton density on the irradiated surface is 0.6321^{-1} times the average value. The average exciton density is then given by the following equation;

$$n_0 = LS\frac{I_0(1-2.718^{-1})}{\Delta S\Delta\ell} = LSI_0\frac{0.6321\,\epsilon_{3371}c}{\Delta S}$$

where L, S, and I_0 are the factor of loss of laser pulse intensity caused by the reflection on the surface of a lens and a sample tube and by the absorption by them, the factor of saturation, and the number of phontons per pulse, respectively. I_0 and ΔS are obtained experimentally to be 8.8×10^{14} photons/pulse and 0.08 cm^2, respectively. ϵ_{3371} was taken to be 2750 M^{-1} cm^{-1},[22] S

was obtained experimentally by plotting emission intensities versus the laser pulse intensities changed by the neutral density filters. By abdopting these values in Eq. (6) n_0 was obtained to be 1.5% of the ground state anthracene molecules.

Singlet excitons of anthracene migrate rapidly and some of them may diffuse out from the pulse irradiated volume of anthracene crystal. Therefore the estimated value, 1.5%, is the upper limit for the initial exciton density in anthracene crystal. By inserting $\Delta c/c = 0.015$ into Eq. (5), $[(I_B/I_C)_H/(I_B/I_C)_L]$ was found to be 1.022. This gives the upper limit of the effect of the ground state deplection upon the I_B/I_C value. Since the observed $[(I_B/I_C)_H/(I_B/I_C)_L]$ value is 1.046, only about 50% of the observed value is explained in terms of the effect of the ground state depletion. Therefore the increase in the fluorescence intensity in the shorter wavelength region is caused by the combination of ground state depletion together with some other effect such as the exciton-exciton interaction and/or the appearance of the induced emission of anthracene crystal at high density excitation.

Acknowledgement

The authors should like to express their sincere gratitudes to Professor H. Inokuchi and Professor S. Iwashima for their kindness in providing them with pure anthracene crystal.

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