

Thermal and Sample-Size Effects on the Fluorescence Lifetime and Energy Transfer in Tetracene-Doped Anthracene[†]

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(Received 30 April 1970)

The fluorescence decay time of anthracene crystals was studied for crystals of various sizes at numerous temperatures between 4.2 and 300 °K. The decrease in the lifetime observed between 300 and ~140 °K is attributed to changes in the amount of reabsorption, while the decrease observed between ~75 and 25 °K is consistent with fluorescence emission from two types of levels with different intrinsic lifetimes whose populations are in thermal equilibrium. The time evolution of the anthracene and tetracene fluorescence intensities was also investigated for samples of various sizes and at numerous temperatures. The results cannot be explained by exciton diffusion theory and are consistent with the predictions of long-range-interaction theory only if an anomalously large value is assumed for the strength of the interaction. This discrepancy is not yet understood, but it is shown that it is not due to the effects of reabsorption.

I. INTRODUCTION

Energy transfer in tetracene-doped anthracene and similar systems has been studied extensively by measuring relative fluorescence intensities or decay times.¹ We recently demonstrated the importance of studying the complete time evolution of the fluorescence intensities in investigating energy transfer.²⁻⁴ This technique elucidates the time dependence of the processes involved and can thus be used to distinguish between different types of energy-transfer mechanisms having different time dependences.

Energy transfer in tetracene-doped anthracene is usually attributed to the diffusion of singlet excitons. However, the predictions of exciton diffusion theory do not agree with our observations of the time dependence of the fluorescence intensities as reported previously. These results also disagree with the predictions of the theory of long-range resonant energy transfer, and the best fit to the data was obtained using a combined theory of diffusion plus long-range interaction. This theory required an anomalously large interaction strength and small value of diffusion coefficient in order to fit the data. No explanation was found for these anomalies, but it was shown that they were independent of both the method of crystal growth and the method of excitation and that they also occur in the system of anthracene-doped naphthalene.

In this paper we report the results of an investigation of the energy transfer made at numerous temperatures between 4.2 and 300 °K and on crystals of various sizes. The purpose of this extension of our previous work is to determine whether or not radiative reabsorption is the cause of the

observed discrepancies and to ascertain whether or not these discrepancies exist at very low temperatures where excitons are thought to be trapped and energy transfer should take place by long-range interaction. The results show that these discrepancies are not due to reabsorption, and they do occur even at low temperatures.

In order to carry out the investigation described above it was first necessary to measure the temperature dependence of the fluorescence decay time of undoped anthracene under the same experimental conditions. We also report these results here since results of similar measurements appearing in the literature disagree with one another. We attribute the change in lifetime observed at high temperatures to reabsorption effects and that observed at low temperatures to the existence of two fluorescing levels with different intrinsic lifetimes.

II. THEORETICAL

A. Theories of Energy Transfer

Two basic theories of electronic energy transfer in solids with no accompanying charge migration have been developed. These are exciton diffusion⁵⁻⁷ and long-range resonant interaction.^{8,9} Although the physical interaction by which the energy is transferred is the same for both mechanisms (electromagnetic multipole-multipole resonance), they differ in that the former is a multi-step process while the latter is a single-step process. Thus, in the exciton diffusion model the distribution of sensitizers and activators remains random in time and the energy-transfer rate is constant. In the long-range-interaction model, the energy-transfer rate is a function of the sep-

aration between sensitizer and activator, and therefore excited sensitizers located close to activators transfer their energy and decrease in number more rapidly than those located at greater distances from activators. Thus, in this model the random distribution of sensitizers and activators present at zero time becomes less random with time as fewer excited sensitizers are located near activators. The efficiency of energy transfer decreases with time in this case.

Since fluorescence intensities are proportional to excited-state populations, the time dependence of the sensitizer and activator intensities can be derived from simple rate equations¹⁰:

$$\dot{n}_A(t) = G(t) - \beta_A n_A(t) - k n_A(t), \quad (1)$$

$$\dot{n}_T(t) = k n_A(t) - \beta_T n_T(t). \quad (2)$$

Here n_A and n_T are the excited-state populations of sensitizers (anthracene) and activators (tetracene), respectively; $G(t)$ is the rate of generation of sensitizer singlet excitons, assumed to be proportional to the instantaneous intensity of the excitation pulse; β_A and β_T are the reciprocals of the decay times of the anthracene excitons τ_A and the excited tetracene molecules τ_T , respectively, including both radiative and nonradiative processes but in the absence of energy transfer; and k is the energy-transfer probability per unit time.

For exciton diffusion theory $k = 4\pi DRN_T$ where D is the diffusion coefficient; R is the interaction distance; and N_T is the concentration of activators.^{11, 12} The solutions of Eqs. (1) and (2) are then given by

$$n_A(t) = \exp[-(\beta_A + k)t] \int_0^t G(\xi) \exp[(\beta_A + k)\xi] d\xi, \quad (3)$$

$$n_T(t) = k \exp(-\beta_T t) \int_0^t n_A(\xi) \exp(\beta_T \xi) d\xi. \quad (4)$$

For long-range resonant energy transfer by dipole-dipole interaction, k is expressed as

$$k = P_{AT} = (1/\tau_A^0) (R_0/R_{AT})^6, \quad (5)$$

where

$$R_0 = \left(\frac{3f^T \Phi}{4(2\pi n)^4 \bar{\nu}_{AT}^4} \frac{e^2}{mc^2} \int g_A(\bar{\nu}) g_T(\bar{\nu}) d\bar{\nu} \right)^{1/6}. \quad (6)$$

Here $g_A(\bar{\nu})$ and $g_T(\bar{\nu})$ are the spectral distribution functions of the anthracene emission and tetracene absorption spectra, respectively; $\bar{\nu}_{AT}$ is the mean wave number in the region of spectral overlap; R_{AT} is the distance between sensitizer and activator molecules; f^T is the oscillator strength of the transition in the activator; and Φ is a molecular-orientation factor. The "critical concentration" is defined by $C_0 = (\frac{4}{3}\pi R_0^3)^{-1}$, where R_0 is the distance between sensitizer and activator sites at which the energy-transfer probability is equal to

the probability for deexcitation in the absence of energy transfer. For δ -function excitation the solutions to Eqs. (1) and (2) are then given by^{8, 2}

$$n_A(t) = n_A(0) \exp[-\beta_A t - \gamma(\pi\beta_A t)^{1/2}], \quad (7)$$

$$n_T(t) = \gamma\beta_A^{1/2} e^{-\beta_T t} \int_0^t e^{\xi\beta_T} n_A(\xi) \xi^{-1/2} d\xi, \quad (8)$$

where $\gamma = N_T/C_0$.

B. Effects of Temperature Variation

The theoretical predictions of Eqs. (3), (4), (7), and (8) are all affected by changes in $\beta_A = \tau_A^{-1}$. There are two important mechanisms which may cause changes in τ_A with changes in temperature. The first is simply a change in the fluorescing state. If two fluorescence states with different intrinsic lifetimes exist and are coupled by radiationless transitions, then the observed lifetime will be a weighted combination of these intrinsic lifetimes and will vary with temperature as the populations of the two states change. This situation can be described by rate equations similar to Eqs. (1) and (2), where k now represents the transition rate for the radiationless processes connecting the two states and terms must be added for processes going in the opposite direction. These rate equations can then be solved to give the observed fluorescence lifetime. If the populations are in thermal equilibrium the lifetime is given by

$$\tau_A = \frac{1 + G \exp(-\Delta E/kT)}{\tau_L^{-1} + \tau_U^{-1} G \exp(-\Delta E/kT)}, \quad (9)$$

where τ_L and τ_U are the intrinsic lifetimes of the two states, ΔE is their energy difference, and G is the ratio of the degeneracies of the two states.

The second mechanism which may cause a change in τ_A with temperature is reabsorption. The theories of reabsorption have not been developed to the extent that they can be incorporated into the energy-transfer theories except by using the lifetime lengthened by reabsorption in equations such as (3), (4), (7), and (8).^{13, 14} The amount of lifetime lengthening can be predicted from the amount of overlap of the absorption and emission spectra.¹⁴ This overlap can change with temperature.

In exciton diffusion theory, D may also be a function of temperature. This functional dependence is complicated and not well understood, and very little work has been done to determine it experimentally. However, it has been suggested that the temperature dependence may be exponential for localized excitons,⁷ while for free excitons $D \propto T^{-1/2}$ at high temperatures and $D \propto T^{-1}$ at low temperatures.¹⁵

In the long-range-interaction theory, R_0 may also be a function of temperature. This is due to

the possible temperature variation in the overlap integral.

III. EXPERIMENTAL

A. Samples and Apparatus

The temperature dependence of the time evolution of the fluorescence intensity was studied in two undoped anthracene crystals obtained from the Harshaw Chemical Company and in three vapor-grown single crystals containing 1-, 12-, and 83-ppm tetracene molecules, respectively. The sample dimensions were approximately $5 \times 10 \times 3$ mm. Similar measurements were made on several undoped samples with thicknesses between 50 and 500 μ and on a sample containing 1-ppm tetracene which was 267 μ thick.

The samples were mounted in a Janis liquid-helium cryostat capable of varying the temperature continuously from below 4 $^{\circ}$ K to above room temperature. The temperature was controlled automatically to within a few tenths of a degree and measured with germanium or platinum sensors. The excitation was provided by a 600-keV x-ray source having a total pulse duration of about 6 nsec and a pulse width at half-maximum of about 3 nsec. The fluorescence emission from the samples was transported through a shielded light pipe to an ITTT F4030(S-11) photomultiplier tube having a 2-nsec rise time. The signal was displayed and photographed on a Tektronix 454 oscilloscope with a 2.4-nsec rise time. The anthracene and tetracene fluorescences were separately isolated with the appropriate filters.

B. Results

Figure 1 shows the results obtained from the measurements of the anthracene fluorescence decay time τ_A , for the thick samples between 4.2 and 300 $^{\circ}$ K, the data for the two undoped samples having been averaged to give the points shown in the figure. The points for all the samples represent an average of three decay pictures and the accuracy is approximately ± 1 nsec. The 4-nsec decay time measured at 300 $^{\circ}$ K for the 83-ppm sample is about the limit of the measuring ability of the apparatus, and no change in τ_A could be detected at lower temperatures. For the other samples there appear to be four distinct regions having different types of variation of τ_A with temperature. From 300 to 140 $^{\circ}$ K a decrease in τ_A occurs. Between 140 and 75 $^{\circ}$ K, the lifetime is approximately constant. Another decrease in τ_A occurs between 75 and 25 $^{\circ}$ K and at lower temperatures no variation in the decay time was observed.

Figure 2 shows the dependence of the fluorescence decay time of undoped anthracene on crystal thickness. At 300 $^{\circ}$ K τ_A decreases significant-

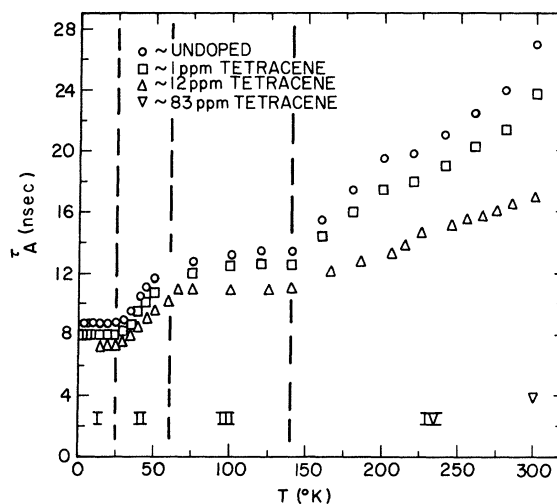


FIG. 1. Temperature dependence of the anthracene fluorescence lifetime of x-ray-excited thick crystals.

ly with a decrease in crystal thickness and extrapolates to ~ 11 nsec for zero thickness. The data taken at 100 and 4.2 $^{\circ}$ K have only a slight dependence on crystal thickness and extrapolate to values of ~ 10.4 and ~ 6.5 nsec, respectively, for zero thickness.

The time evolution of the anthracene and tetracene fluorescence intensities for the 267- μ -thick 1-ppm sample is shown in Figs. 3-5 for 300, 100, and 4.2 $^{\circ}$ K, respectively. Each datum point is the average from three pictures and the spread in data is ± 0.03 or less.

IV. DISCUSSION

A. Undoped Anthracene

The variation of τ_A with temperature shown in Fig. 1 for the undoped samples is essentially the same as that reported earlier by Liebson and co-workers.¹⁶ Similar results have been obtained using surface (uv) excitation; however, the values of the observed lifetimes are less, presumably because of less reabsorption.¹⁷

The decrease in τ_A with decreasing temperature in region IV of Fig. 1 is accompanied by an increase in fluorescence intensity. This is consistent with previous observations although the magnitude of the effect varies in reports by different investigators.^{16, 18} The simultaneous decrease in lifetime and increase in fluorescence intensity has been attributed to a change in the amount of reabsorption. However, various attempts to correct for the effects of reabsorption have led to completely different results. Logan *et al.*¹⁷ used theoretical correction formulas¹⁴ and continuous-fluorescence spectral data to account for reab-

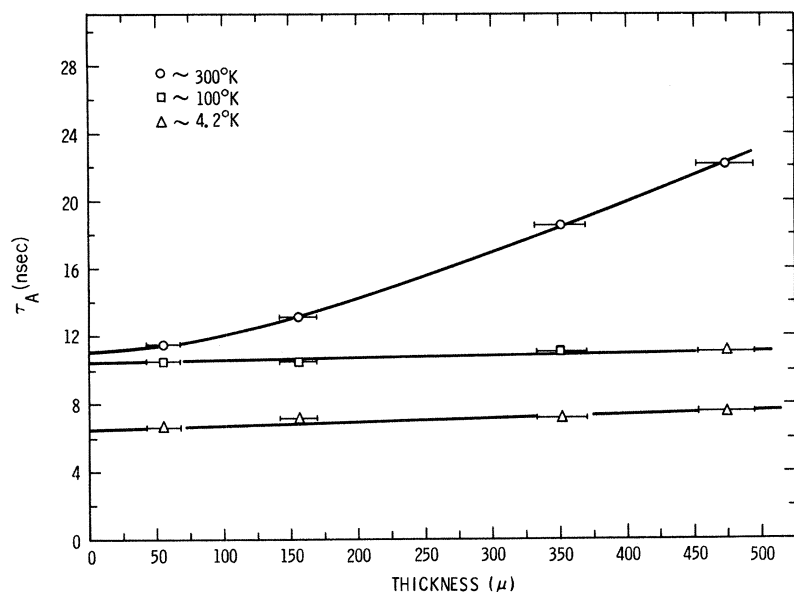


FIG. 2. Variation of anthracene fluorescence lifetime with crystal thickness.

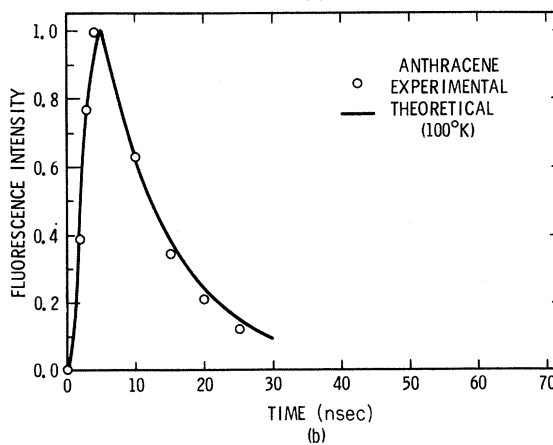
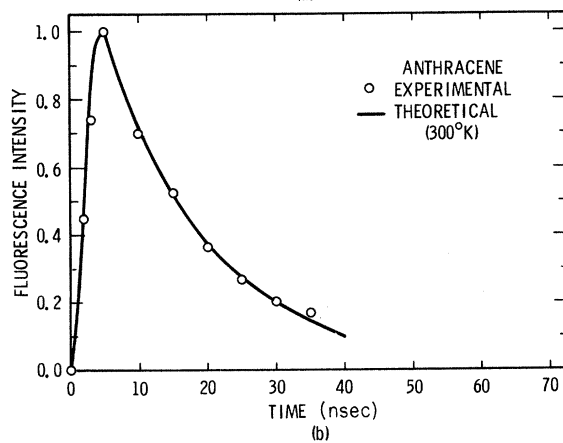
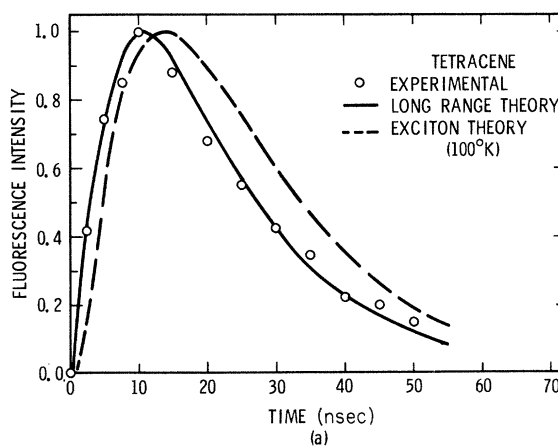
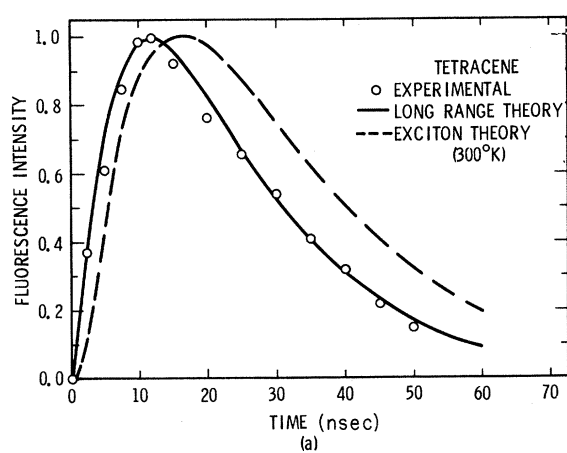


FIG. 3. Time dependence of the fluorescence intensities in anthracene crystals 267μ thick doped with 1-ppm tetracene at 300°K .

FIG. 4. Time dependence of the fluorescence intensities in anthracene crystals 267μ thick doped with 1-ppm tetracene at 100°K .

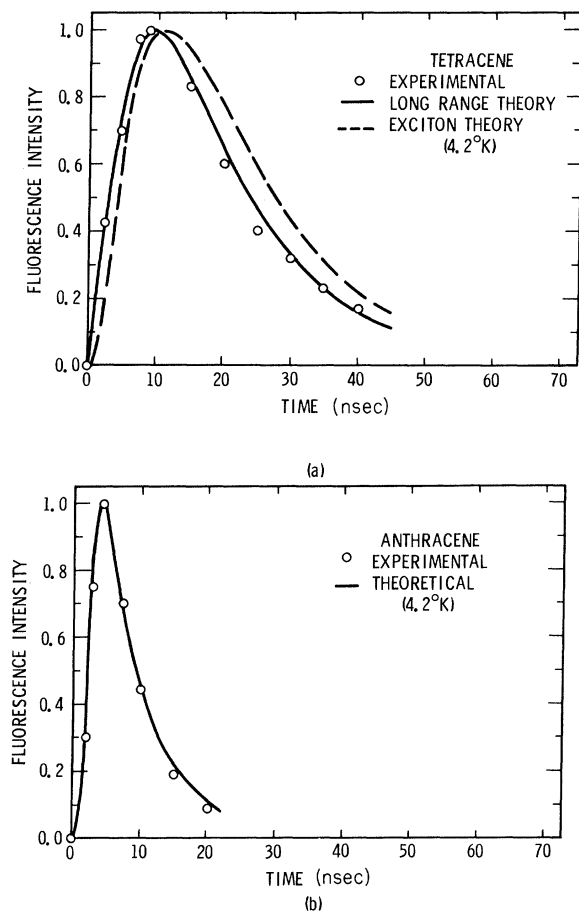


FIG. 5. Time dependence of the fluorescence intensities in anthracene crystals 267μ thick doped with 1-ppm tetracene at 4.2°K .

sorption effects and concluded that in the absence of reabsorption τ_A is essentially independent of temperature. Their corrected values for τ_A lie between about 5 and 6 nsec, which is much less than the value of ~ 10 nsec that Birks¹⁴ concludes is the fluorescence decay time at room temperature with no reabsorption. Tomura *et al.*¹⁹ measured τ_A as a function of crystal size and extrapolated to zero size to eliminate reabsorption effects. This procedure led to a value of $\tau_A = 10$ nsec at room temperature and a decrease to about 6 nsec at 100°K . They attribute this temperature dependence to the presence of two Davydov states with different decay times whose populations are in thermal equilibrium. However, we have been unable to fit their data with the theoretical predictions based on such a model.

We attempted to account for reabsorption effects by measuring τ_A as a function of crystal

thickness and extrapolating to zero size as shown in Fig. 2. Our data show that τ_A extrapolates to values of ~ 11 and ~ 10.5 nsec at 300 and 100°K , respectively. These values are consistent with that predicted by Birks,¹⁴ and the difference between the two values is probably due to errors in the extrapolation procedure. No change in intensity was observed between 300 and 100°K for the $56\text{-}\mu$ -thick sample. The results are consistent with attributing the temperature dependence of the fluorescence intensity and lifetime in region IV of Fig. 1 to a change in the amount of reabsorption.

The decrease in τ_A between ~ 75 and $\sim 25^\circ\text{K}$ (region II in Fig. 1) also appears in previously published data^{16, 17} but no explanation has been suggested. This decrease in fluorescence lifetime also occurs in thin samples as seen in Fig. 2 where the 4.2°K data for τ_A extrapolate to a value of ~ 6.5 nsec at zero thickness. In both thick and thin crystals a slight increase in the fluorescence intensity is observed as temperature is lowered in this region.

Wolf and co-workers²⁰⁻²² studied the fluorescence intensities and energy transfer at these temperatures and conclude that excitons are being trapped in perturbed states ("x-traps") having a fluorescence spectrum with the same vibronic structure but shifted to lower energies by an amount ΔE . Our lifetime data can also be interpreted in terms of a two-state model. If it is assumed that the populations of perturbed and unperturbed states are in thermal equilibrium, then the observed fluorescence decay time can be expressed as a weighted combination of the intrinsic decay times of the two types of states as given by Eq. (9) where G is the ratio of unperturbed states to perturbed states.

Figure 6 shows the results of fitting Eq. (9) to the low-temperature lifetime data for the $56\text{-}\mu$ -thick sample. ΔE was taken from Avakian and Wolf²⁰ to be 250 cm^{-1} , 6.6 nsec was used for τ_L , and 10.5 nsec was used for τ_U . The best fit to our data is then obtained for a perturbed-state concentration of ~ 180 ppm. From intensity data Benz and Wolf²¹ determined a trap concentration of ~ 40 ppm for their anthracene samples while Propstl and Wolf²² found a trap concentration of ~ 100 ppm for their naphthalene samples.

It should also be noted that measurements by Helfrich and Lipsett²³ indicate the presence of exciton traps distributed exponentially in energy below the free-exciton band. Even in extremely pure crystals they find trap concentrations on the order of several ppm and feel that these are due to structural imperfections instead of chemical impurities.

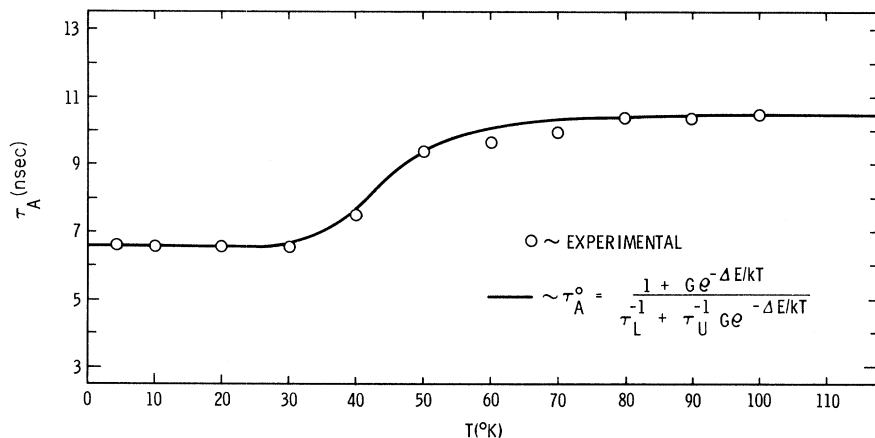


FIG. 6. Variation of anthracene fluorescence lifetime in a $56\text{-}\mu$ -thick crystal at low temperatures.

B. Tetracene-Doped Anthracene

The temperature variation of the anthracene fluorescence is similar to that in the undoped samples. The amount of decrease in τ_A with temperature in region IV of Fig. 1 appears to be less in the doped samples. This decrease is again accompanied by a significant increase in the anthracene-fluorescence intensity while a smaller increase in tetracene-fluorescence intensity was observed. In the thin ($267\text{-}\mu$) 1-ppm sample both the anthracene and tetracene fluorescence intensities were constant in this region. For both the thin- and thick-doped samples in region II of Fig. 1 only a slight increase in the anthracene fluorescence intensity is observed, while a more distinct increase in the tetracene fluorescence is seen.

The energy-transfer probability per unit time can be expressed as

$$P_{AT}(\text{sec}^{-1}) = \tau_{AT}^{-1} = \tau_A^{-1} - (\tau_A^0)^{-1}, \quad (10)$$

where τ_A and τ_A^0 are the anthracene decay times in doped and undoped samples, respectively. Figure 7 shows the temperature dependence of P_{AT} . For the thick samples P_{AT} is essentially constant above 75°K and increases between 75 and 25°K . The data obtained at three temperatures for the thin 1-ppm sample are also shown and the temperature dependence implied by the four regions of Fig. 1 indicated by a dashed line. This sample shows a slight increase in P_{AT} with decreasing temperature in region IV and another increase in region II. This latter increase is on the same order as that observed in the thick samples. It is interesting to note that if P_{AT} is expressed in terms of a diffusion coefficient, then the high-temperature increase observed in the thin sample implies an increase in D proportional to $T^{-1/2}$. This would be predicted if the predominant exciton scattering mechanism were by phonons.¹⁵ However,

the small magnitude of the increase coupled with accuracy of the data make any serious interpretation of this type unwarranted.

Our data differ from those of Tomura *et al.*,¹⁹ who report a sharp decrease in P_{AT} for the sample at high temperatures and a slight decrease in the low-temperature region. Avakian and Wolf²⁰ observed a decrease in tetracene-fluorescence intensity at low temperatures while Lacey *et al.*²⁴ found that chemically pure (zoned-refined) crystals showed an increase in energy transfer in this temperature region.

As was done in previous room-temperature measurements, an attempt was made to elucidate the time dependence of the energy-transfer mechanisms by studying the time evolution of the anthracene and tetracene fluorescence intensities.

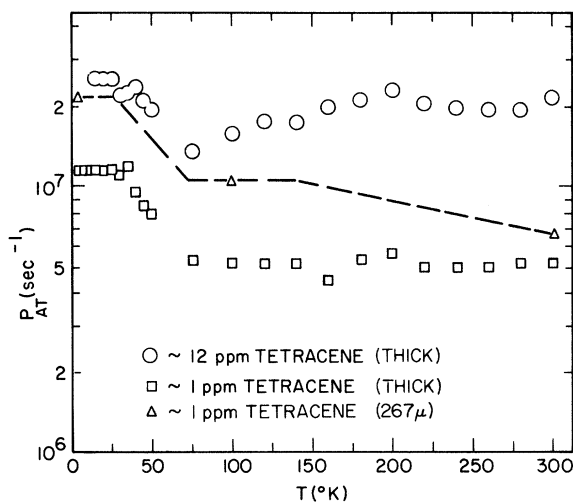


FIG. 7. Temperature dependence of the energy-transfer rate in tetracene-doped anthracene.

To obtain the predicted curves of the theories discussed in Sec. III, Eqs. (3), (4), and (8) can be numerically integrated using the measured values of β_A and β_T and treating k or γ as adjustable parameters. In Eq. (3) the experimentally determined pulse shape is used for $G(\xi)$. In order to compare the predictions of Eq. (7) with experimental results, the exciting pulse was treated as a series of equally spaced δ functions with magnitudes proportional to the height of the pulse at the time of the function. Each δ function produces a curve having the shape of Eq. (7) with different $n_s(0)$, and the sum of these curves is compared with experimental results.

Using the above procedure, the theories discussed in Sec. III give the same best fit to the measured time evolution of the anthracene intensity as shown by the solid lines in Figs. 3(b), 4(b), and 5(b) for the thin 1-ppm sample. This is also true for all the thick samples with various concentrations of tetracene. The dashed lines in Figs. 3(a), 4(a), and 5(a) represent the predictions of exciton diffusion theory given by Eq. (4) for the thin 1-ppm sample at three temperatures. They disagree with the experimental data, especially with respect to the rise time of the tetracene fluorescence. This is also true for the thick lightly doped samples at these temperatures. For the heavily doped samples, the predictions of the two theories for the tetracene fluorescence are indistinguishable.

For the thin sample where reabsorption effects are negligible, the predictions of long-range-interaction theory given by Eq. (8) can be made to agree with the tetracene fluorescence intensity at all temperatures, as indicated by the solid lines in Figs. 3(a), 4(a), and 5(a). However, to achieve this fit it is necessary to use an R_0 on the order of 100 Å, which is much greater than the value of 30 Å estimated from spectral considerations. This is true at all temperatures. For the thick samples it is necessary to use a combined theory of energy transfer by long-range interaction and exciton diffusion to obtain a good fit to the data at room temperature and at 100 °K.^{4, 25, 26} The phenomenological fitting parameters required by this theory are again an R_0 on the order of 100 Å and a diffusion coefficient more than two orders of magnitude smaller than the value generally reported for D . At temperatures below 25 °K for the thick samples, the best fit to the data is given by long-range-interaction theory with an $R_0 \approx 100$ Å.

It is possible that the need for including a small amount of diffusion in obtaining a theoretical fit to the thick-crystal data is due to the effect of reabsorption of tending to randomize the distribution of excited sensitizers. However, it is ex-

tremely difficult to describe this type of effect mathematically, and none of the existing theories of reabsorption have been developed to the extent that they can be compared with this type of datum.¹³

It is generally thought that at temperatures ≤ 25 °K singlet excitons in anthracene are trapped and, thus, long-range interaction should be the dominant energy-transfer mechanism at these temperatures. However, as pointed out previously, it is still necessary to employ an anomalously large value of R_0 to fit theory and experiments even at these temperatures.

Assuming that an R_0 parameter can be used to characterize energy transfer, in this case it appears that R_0 is independent of temperature. It is difficult to say whether or not this is to be expected, since any temperature dependence of R_0 should be contained in the spectral overlap integral. Both the anthracene emission and tetracene absorption spectra will sharpen as temperature is lowered, and the anthracene spectrum also shifts position and undergoes a rearrangement of intensity distribution within each emission band and among the bands.¹⁸ A careful spectral analysis would be necessary at each temperature to determine any predicted change in R_0 .

V. SUMMARY AND CONCLUSIONS

This paper extends our previous investigations of energy transfer in tetracene-doped anthracene to low temperatures and to crystals of small size. The results indicate that the current theories of energy transfer are not adequate for explaining phenomena occurring in short times. They also show that radiative energy migration and reabsorption are not responsible for the observed anomalies in the time dependence of the energy transfer.

The variation of the anthracene fluorescence decay time with temperature above 140 °K is shown to depend on crystal thickness and thus can be attributed to reabsorption. This is consistent with the theory of Birks¹⁴ but disagrees with the temperature dependence of the results of Tomura *et al.*¹⁹ and with the magnitude of the decay time reported by Logan *et al.*¹⁷ The latter data may be affected by surface quenching. The decrease in anthracene decay time below ~ 75 °K is shown to be consistent with a model of two types of fluorescing levels with different intrinsic lifetimes whose populations are in thermal equilibrium. This is consistent with the exciton-trapping model developed to explain relative intensity measurements.²⁰⁻²²

Our data show an increase in energy transfer from anthracene to tetracene below ~ 75 °K. Both

increases and decreases in energy transfer in this temperature region have been reported previously by other investigators.^{20, 24} Thus, this effect appears to vary from sample to sample and may be related to the number of crystal imperfections in the sample and to whether these are structural imperfections acting as trapping sites or chemical imperfections acting as quenching centers.

It was found that exciton diffusion theory cannot predict the correct time dependence for the energy transfer, especially with respect to the rise time of the tetracene-fluorescence intensity in the lightly doped samples. This is true for both thick and thin samples at all temperatures. For thin samples it was possible to fit the time evolution of the fluorescence intensities with the predictions of long-range-energy-transfer theory only if an anomalously large value was used for the magnitude of the interaction. This is true even at low temperatures, where long-range interaction is ex-

pected to be the dominant mechanism of energy transfer.

In conclusion, the anomalies in the time dependence of the energy transfer in this type of system reported previously for thick crystals at room temperature are not resolved by studying thin crystals or by working at low temperatures. In order to explain the data a theory must be developed in which the energy-transfer rate depends on time in such a way that energy transfer is more efficient at short times than at long times.

ACKNOWLEDGMENTS

The author wishes to acknowledge the benefit of many helpful discussions on this work with R. G. Kepler and gratefully acknowledges the technical assistance of P. M. Beeson. He is also grateful to A. C. Saxman for a critical reading of the manuscript.

[†]Work supported by the U. S. Atomic Energy Commission.

¹See the recent review article by H. C. Wolf, in *Advances in Atomic and Molecular Physics*, Vol. 3, edited by D. R. Bates and I. Estermann (Academic, New York, 1967), p. 119, and references therein.

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