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Energy Transfer in Anthracene- and Tetracene-Doped Naphthalene Crystals*

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Energy transfer in thin crystals of anthracene-doped naphthalene and tetracene-doped naphthalene was investigated by monitoring the time evolution of the fluorescence intensities. The observed time dependence of the energy transfer cannot be explained by the theory of exciton diffusion generally invoked to explain energy transfer in molecular crystals. The time dependence is consistent with the predictions of long-range resonance energy transfer, but an anomalously large interaction strength is needed to fit the data. The magnitude of this interaction strength is the same for both types of impurity molecules despite the fact that there is a significant difference in the overlap of their absorption spectra with the host emission spectrum. Similar measurements were made on energy transfer from anthracene molecules to tetracene molecules in a naphthalene host. In this case, the mechanism for energy transfer is expected to be long-range resonance interaction, and it is found that the data can be fitted with the predictions of this theory using the theoretically derived value for the strength of the interaction. Thus the anomalies observed in the single-doped systems are associated only with host-sensitized energy transfer.

I. INTRODUCTION

In a recent series of papers,[1-6] we have reported two important observations in the study of energy transfer in organic molecular crystals. The first of these is that it is theoretically possible to distinguish between different types of energy-transfer mechanisms by investigating the complete time evolution of the fluorescence intensities. The importance of this lies in the fact that the techniques generally employed for studying energy transfer, such as measuring the fluorescent intensities or decay times as a function of impurity concentration, cannot distinguish between different theoretical models of energy transfer. The second observation is that the results we obtained for host-sensitized energy transfer in organic crystals do not agree with the predictions of the theory of exciton diffusion which is generally accepted as the correct model for energy transfer in these systems. In this paper we report on further investigations of energy transfer by monitoring the time evolution of the fluorescence intensities and, specifically, we present results obtained on naphthalene crystals doped with anthracene, tetracene, and doped with both anthracene and tetracene.

Our previous investigations of host-sensitized energy transfer in the systems of tetracene-doped anthracene and anthracene-doped naphthalene showed that a consistent fit of the time-resolved fluorescence intensity data was obtained only if it were assumed that energy transfer takes place through long-range resonant interactions. However, this analysis necessitated the use of an interaction strength much greater than that predicted theoretically. No explanation for this anomaly could be found.

The purpose of this work is to further elucidate the characteristics of energy transfer in organic crystals in an attempt to understand the anomalies reported previously. The specific reason for investigating the time evolution of the fluorescence intensities in a double-doped crystal is to determine if impurity-sensitized energy transfer exhibits the same type of anomaly seen in host-sensitized energy transfer. We find that the results obtained here can be explained by the theory of long-range resonant energy transfer with the theoretically calculated interaction strength. The interest in studying host-sensitized energy transfer for two different impurity molecules in the same host is to determine the effect of different spectral overlaps on the observed anomalies. Here we find that the same anomalously large interaction strength is needed to fit the results for both cases of good and poor spectral overlap.

II. THEORETICAL

The two mechanisms of energy transfer most commonly considered are exciton diffusion[7-9] and long-range resonance.[10,11] The energy-transfer rate in the former theory is independent of time while in the latter theory it depends on $t^{-1/2}$. It is this difference in the time dependence that leads to the different predictions for the time evolution of the fluorescence intensities. The equations governing energy transfer in these two models were discussed previously[3] and here we simply write down the expressions applicable to the results of this work.

The data reported here are analyzed in two ways: by fitting the time evolution of the fluorescence intensities and by measuring the decrease in the fluorescence lifetime of the sensitizer due to the presence of an activator. For the first type of analysis, the following mathematical expressions have been developed to describe the sensitizer and activator fluorescence intensities, with the assumption that energy transfer takes place by long-range resonance interaction with the sensitizer excitation being allowed to diffuse[12,13]:

$$I_S(t)\propto n_S(t)=e^{-\beta_S t}\exp\left[-\gamma(\pi\beta_S t)^{1/2}\left(\frac{1+10.90x\,t^{2/3}+15.74\,x^2t^{4/3}}{1+8.76x\,t^{2/3}}\right)^{3/4}\right], \tag{1}$$

$$I_A(t)\propto n_A(t)=e^{-\beta_A t}\int_0^t\left(\frac{\gamma}{2}(\pi\beta_S)^{1/2}\xi^{-1/2}I_S(\xi)\,e^{\beta_A\xi}\,[P(\xi)/Q(\xi)]^{3/4}\right.$$
$$\left.\times\{1+x\xi^{2/3}[(10.90+31.5x\xi^{2/3})/P(\xi)-8.76/Q(\xi)]\}\right)d\xi\ , \tag{2}$$

where

$$P(t)=1+10.90xt^{2/3}+15.74x^2t^{4/3}\ ,$$

$$Q(t)=1+8.76xt^{2/3}\ .$$

Here $n_S(t)$ and $n_A(t)$ are the concentrations of excited sensitizer and activator states, respectively, β_S and β_A are the reciprocals of the sensitizer and activator decay times, $x=D\beta_S^{-1/3}R_0^{-2}$, and $\gamma=C/C_0=C(\frac{4}{3}\pi R_0^3)$, where D is the diffusion coefficient, C is the activator concentration, C_0 is called the critical concentration, and R_0 is the critical interaction distance. R_0 is defined as the distance over which energy is transferred at which the rate of energy transfer equals the rate of sensitizer deactivation by all other means. Its magnitude is indicative of the strength of the long-range resonant interaction, and can be theoretically derived from the expression

$$R_0=\left(\frac{5.86\times10^{-25}\phi_S}{n^4\bar{\nu}_{SA}{}^4}\int g_S(\bar{\nu})G_A(\bar{\nu})\,d\bar{\nu}\right)^{1/6}, \tag{3}$$

where ϕ_S is the quantum efficiency of the sensitizer, n is the refractive index of the host, $g_S(\bar{\nu})$ and $G_A(\bar{\nu})$ are the spectral distribution functions of the sensitizer emission and activator absorption spectra, respectively, and $\bar{\nu}_{SA}$ is the mean wave number in the region of spectral overlap. If $D=x=0$, the expressions in Eqs. (1) and (2) reduce to those obtained by considering energy transfer by just long-range resonant interaction.

If D is large so that exciton diffusion dominates long-range resonance as the mechanism of energy transfer then the expressions given above are no longer valid, and the fluorescence intensities are, instead, given by

$$I_S(t)\propto n_S(t)=e^{-(\beta_S+k_T)t}\int_0^t G(\xi)\,e^{(\beta_S+k_T)\xi}\,d\xi\ , \tag{4}$$

$$I_A(t)\propto n_A(t)=k_T\,e^{-\beta_A t}\int_0^t n_S(\xi)\,e^{\beta_A\xi}\,d\xi\ , \tag{5}$$

where $G(\xi)$ is the shape of the exciting pulse, and the rate of exciton trapping by an activator molecule is given by

$$k_T=4\pi DRC\ . \tag{6}$$

Here R is taken to be the trapping radius.

If energy transfer is investigated by the more common technique of observing the quenching of the sensitizer fluorescence lifetime, then the trapping rate in exciton diffusion theory can be determined from the equation

$$\tau_S^0/\tau_S=1+\tau_S^0k_T\ , \tag{7}$$

where τ_S^0 and τ_S are the sensitizer decay times in the undoped and doped crystal, respectively. Similarly, the parameter γ and thus R_0 in long-range resonance interaction theory can be determined from sensitizer fluorescence decay time measurements with the equation

$$\tau_S/\tau_S^0=1+\tfrac{1}{2}\pi^{1/2}\gamma\,[\pi^{1/2}\gamma-(\pi\gamma^2+4)^{1/2}]\ . \tag{8}$$

III. EXPERIMENTAL

The samples used in this work were prepared by the method described by Ferguson[14] which consisted of melting small amounts of material between silica disks and then cooling slowly. This technique gave samples about 2 cm in diameter and between 20 and 200 μ thick. Although the crystallinity of these samples was not good, their absorption and emission spectra exhibited the same distinct bands which appear in the spectra of single crystals. The results of previous investigations of the type reported here were found to be independent of crystal quality.[2] The samples investigated included undoped naphthalene, naphthalene containing 3.6×10^{18}- and 4.7×10^{17}-cm^{-3} anthracene, naphthalene containing 2.2×10^{18}- and 1.4×10^{17}-cm^{-3} tetracene, and naphthalene double-doped with 1.08×10^{18}-cm^{-3} anthracene and 1.65×10^{17}-cm^{-3} tetracene and double-doped with 1.2×10^{19}-cm^{-3} anthracene and 6.38×10^{18}-cm^{-3} tetracene.

For the studies of energy transfer from the host crystal to an impurity molecule, the samples were excited with a pulsed x-ray source. This experimental setup has a time resolution of about 3 nsec and was described elsewhere.[3] In order to study impurity-sensitized energy transfer, the anthracene molecules were directly excited by the superradiant light from ZnS pumped by a pulse of electrons. This produced a pulse 50 Å wide, centered at 3450 Å, with a half-width of 2 nsec. This source was also used to determine the intrinsic fluorescence decay time of anthracene in naphthalene. To determine the intrinsic fluorescence decay time of tetracene in naphthalene, superradiant light from ZnSe was used for excitation. This emission is centered at 4870 Å, and has about the same spectral bandwidth and temporal half-width as the ZnS emission.

The continuous fluorescence spectra were obtained using a Bausch and Lomb (BL) 150-W xenon lamp for excitation. The light was passed through a BL high-intensity grating monochromator set to select the desired wavelength for excitation and then focused onto the sample. The fluorescence from the front face of the sample was focused onto the entrance slits of a second high-intensity grating monochromator, detected by a RCA 1-P28A (S-5) photomultiplier tube, amplified, and recorded on a strip chart recorder. The absorption spectra were obtained on a Cary model 14 recording spectrophotometer.

In Figs. 1–3, the results obtained on the time evolution of the fluorescence intensities of the most lightly doped samples of each system are shown. The most important aspect of these data for comparison with theoretical predictions is the time at which the activator fluorescence reaches its maximum intensity t_m. The values obtained for t_m from these three samples are listed in Table I, as are the measured values for the intrinsic fluorescent decay times for the various components of these systems. The data points shown in these figures have an accuracy of about ± 0.03, or less. Similar data were obtained on the heavily doped samples of these systems but are not shown here since the theoretical discrepancies are most apparent in the lightly doped samples.

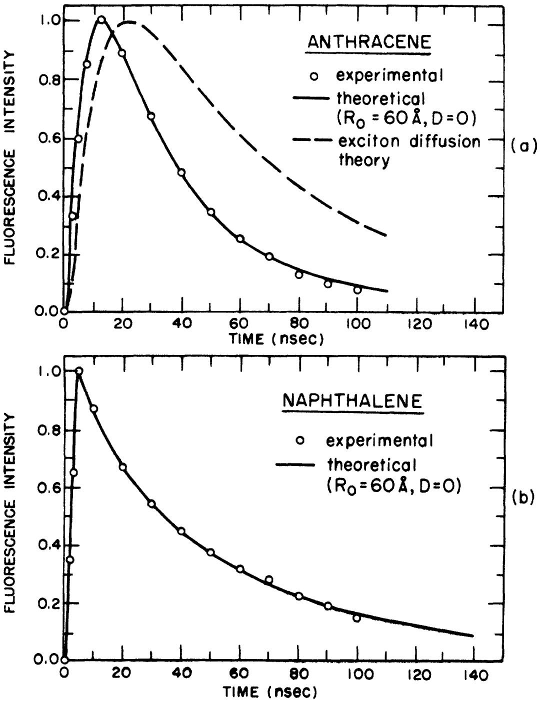

FIG. 1. Time dependence of the fluorescence intensities of naphthalene doped with 4.7×10^{17}-cm^{-3} anthracene after pulsed x-ray excitation (see text for explanation of the theoretical lines).

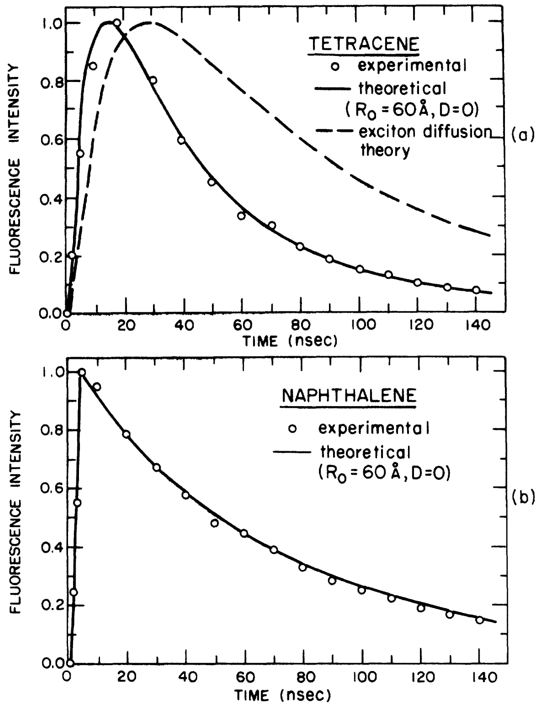

FIG. 2. Time dependence of the fluorescence intensities of naphthalene doped with 1.4×10^{17}-cm^{-3} tetracene after pulsed x-ray excitation (see text for explanation of the theoretical lines).

Figures 4–6 show the relevant fluorescence and absorption spectra for the three systems investigated. The spectral-overlap products are also shown in these figures. The flurorescence curves are normalized in each case, while the values of the molar extinction coefficients for the absorption curves were obtained from Berlman.[15] The resolution of these spectra is ~30 Å and they have been corrected for the photomultiplier-tube response.

IV. DISCUSSION

A. Host-Sensitized Energy Transfer

Numerous investigations have been made of energy transfer in doped napthalene crystals.[16-25] The assumption is generally made in this work that the mechanism of energy transfer is exciton diffusion and the values reported for the energy-transfer parameter k_r range from 3.5×10^2 to 10^5 for various impurity molecules as determined from fluorescence-intensity or lifetime-quenching data and the equations $I_S^0/I_S = \tau_S^0/\tau_S = 1 + k_r C$, where the activator concentration is now expressed in mole ratio. In the following paragraphs we compare the results of these previous investigations with those reported here.

First consider the systems of anthracene-doped naphthalene. If the expression for k_T given in Eq. (6) is used to characterize energy transfer, then the quantity which is actually obtained from experimental data is the product DR. Zima *et al.*[24] and Bowen *et al.*[16] found values of 2.5×10^4 and 5×10^4, respectively, for k_r, and these results give values of 5×10^{-12} and 10^{-11} cm^3 sec^{-1} for DR. A value of $DR = 2\times10^{-12}$ cm^3 sec^{-1} was reported by Hammer and Wolf[25] from similar investigations. If we assume exciton diffusion to be the mechanism for energy transfer and make use of Eqs. (6) and (7), our data give a value of $DR = 2\times10^{-12}$ cm^3 sec^{-1}, which is in agreement with the previously reported results. However, it is important to note that these quenching experiments can also be interpreted in terms of long-range energy-transfer theory and, using Eq. (8), the data are consistent with the predictions of this theory if a value of $R_0 = 57$ Å is used. Thus, this type of analysis by itself cannot distinguish between the two most important types of energy-transfer mechanisms.

A sharp distinction can be seen between the predictions of the two theories with respect to the time evolution of the fluorescence intensities as shown in Fig. 1. Although both theories can be made to give the same good fit to the naphthalene data as shown by the solid line in Fig. 1(b), which is obtained from either Eq. (1) or Eq. (4), the prediction of exciton-diffusion theory for the anthracene curve does not agree with the experimental data. The most important aspect of this discrepancy is in the rise time of the fluorescence which is observed to

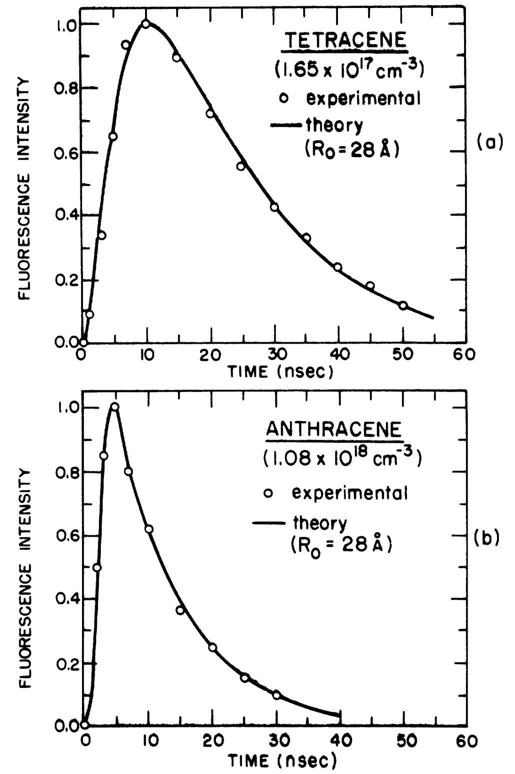

FIG. 3. Time dependence of the fluorescence intensities of 1.08×10^{18} cm^{-3}-antracene and 1.65×10^{17}-cm^{-3} tetracene in naphthalene after excitation with 3450-Å superradiant light (see text for explanation of the theoretical lines).

TABLE I. Summary of measured decay times and theoretical and experimental values for t_m and R_0.

	System			
Parameter	Undoped naphthalene	Naphthalene: anthracene	Naphthalene: tetracene	Naphthalene: anthracene and tetracene
Fluorescence decay time of naphthalene	85 nsec			
Fluorescence decay time of anthracene and tetracene in naphthalene		10 nsec	13 nsec	
Measured t_m for lightly doped samples		12 nsec	18 nsec	8 nsec
Predicted t_m from exciton diffusion		23 nsec	28 nsec	
R_0 needed to fit data		60 Å	60 Å	28 Å
Theoretically predicted R_0		23 Å	12 Å	28 Å

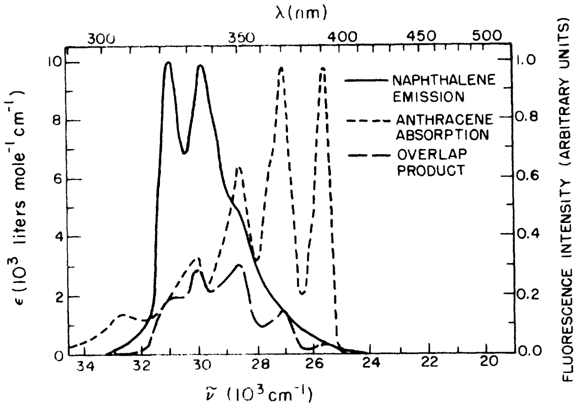

FIG. 4. Fluorescence spectrum of naphthalene, absorption spectrum of anthracene in naphthalene, and their spectral-overlap product.

be 12 nsec and predicted by exciton-diffusion theory to be 23 nsec. It was found that the best fit to the data was obtained using Eqs. (1) and (2) with $R_0 = 60$ Å and $D = 0$ cm^{2}sec^{-1}. With this value for the diffusion coefficient, these equations reduce to those for long-range resonant energy transfer. Note that the value needed for R_0 is essentially the same as that determined from the quenching analysis discussed above. For the heavily doped sample investigated, the predictions of exciton-diffusion theory are much closer to those of long-range energy-transfer theory and therefore come much closer to fitting the observed results. The importance in investigating the heavily doped sample lies in the fact that the theories are much more sensitive to the values of the adjustable parameters for the heavily doped case than for the lightly doped case. This work fixed R_0 at 60 ± 5 Å.

Although the data presented here appear to be qualitatively in agreement with the theory of long-range resonant energy transfer, the quantitative value obtained for R_0 is much greater than that derived from spectral considerations. The spectral-overlap integral is determined from Fig. 4 to be 3.41×10^3 liters mole^{-1}cm^{-1}. Using this value along with $\tilde{\nu}_{SA} = 2.9 \times 10^4$ cm^{-1}, $\phi_S = 0.23$, and $n = 1.4$ in Eq. (3) gives the value $R_0 = 23$ Å, which is consistent with the value of $R_0 = 25$ Å which can be derived from the spectral-overlap data of Zima *et al.*[24] This value is much smaller than the value of ~60 Å needed to fit the fluorescence-quenching and time-evolution data. As shown by Eq. (3), the parameters used in predicting R_0 are taken to the $\frac{1}{6}$ power, so it would take an unreasonably large change in one of these parameters to give the needed value of R_0.

We reported previously on the results of energy-transfer studies in thick crystals of anthracene-doped naphthalene.[3] In that case it was found that the data could be fitted with Eqs. (1) and (2) with the same R_0 of 60 Å that was used here, but with a value of $D = 3 \times 10^{-6}$ cm^{2}sec^{-1}. Later investigations of the effects of sample size on the characteristics of energy transfer in the system of tetracene-doped anthracene indicated that the need for inclusion of a finite value of D in this type of analysis arose from the presence of radiative migration and transfer of energy. The same conclusion appears to be true of the anthracene-doped naphthalene system. For the thick samples investigated previously, the measured value for the decay time of undoped naphthalene was 107 nsec, while a value of 85 nsec was obtained for the thin crystals used in this work. Although according to the results of the detailed investigation made by El Kareh and Wolf[26] this latter value for the naphthalene decay time still indicates that a significant amount of radiative reabsorption is taking place, there appears to have been a sufficient decrease in the amount of reabsorption between thick and thin samples to allow the data obtained on the latter to be fitted with $D = 0$ cm^{2}sec^{-1}.

The results obtained for the tetracene-doped

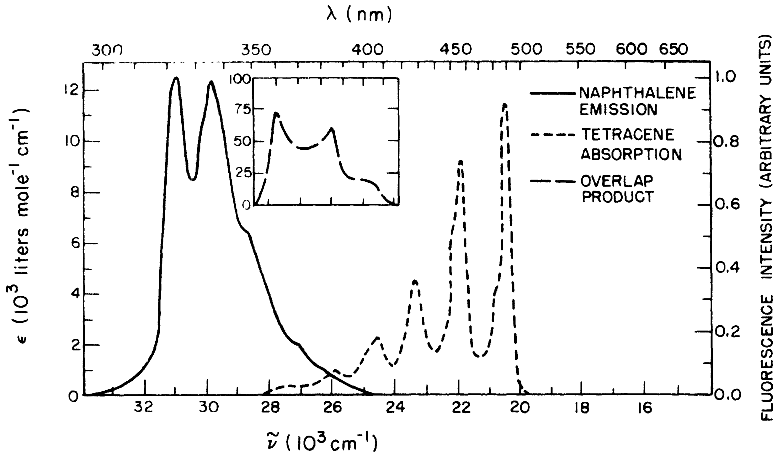

FIG. 5. Fluorescence spectrum of naphthalene, absorption spectrum of tetracene in naphthalene, and their spectral-overlap product.

naphthalene system are similar to those discussed above. As shown in Fig. 2, the same type of discrepancy exists between the predictions of exciton-diffusion theory and the observed-time evolution of the tetracene fluorescence in the lightly doped sample. The difference in theoretically predicted and experimentally observed rise times are listed in Table I. Again it is found that the best fit to the data is obtained from Eqs. (1) and (2) with $R_0 = 60 \pm 5$ Å and $D = 0$ cm^{2}sec^{-1}. The lifetime-quenching data can be fitted using either long-range resonant energy transfer with $R_0 = 53$ Å or exciton-diffusion theory with $DR = 3\times10^{-12}$ cm^{3}sec^{-1}. For this case the spectral overlap is much smaller than that of anthracene-doped naphthalene as seen in Fig. 5. We find the overlap integral to be 55 liters mole^{-1} cm^{-1}; using this along with $\tilde{\nu}_{SA} = 2.7\times10^4$ cm^{-1}, $\phi_S = 0.23$, and $n = 1.4$ in Eq. (3), we get $R_0 = 12$ Å. Again this predicted value is much smaller than the 60-Å value needed to fit the data.

Zima *et al.*[24] found that, for the systems they investigated, the energy-transfer parameter k_r generally increased with an increase in the spectral-overlap integral. They interpreted their results in terms of exciton-diffusion theory and expressed k_T as given in Eq. (6) but multiplied by a probability for energy transfer where this probability was a function of the overlap integral. However, Benz and Wolf[27] found exactly the same values of k_r for anthracene and tetracene in phenanthrene despite the large difference in spectral overlap. The results we report here are consistent with this latter observation, which shows that there is equally efficient energy transfer to anthracene and tetracene in naphthalene.

It is known that β-methyl naphthalene is present as an impurity even in very pure naphthalene crystals. This impurity is an important exciton trap at low temperatures, but is much less important at room temperature where these experiments were conducted. The presence of β-methyl naphthalene cannot be detected by observation of the emission spectrum at room temperature, since its emission spectrum is indistinguishable from that of napthalene. However, if a significant amount of β-methyl naphthalene is present in crystals of anthracene-doped naphthalene, Mansour and Weinreb[28] have shown that the fluorescence decay time of the naphthalene plus β-methyl naphthalene is the same as that of the anthracene. The amount of β-methyl naphthalene present in our samples is not great enough to cause this effect, as can be seen in Figs. 1-3.

Mansour and Weinreb[28] also observed that the fluorescence decay of anthracene in naphthalene is faster than that of the host fluorescence even in lightly doped samples where exciton-diffusion theory predicts that identical decay times should be observed. This is consistent with our results and is what one would expect in the presence of a time-dependent energy-transfer rate. They suggest the possibility of energy transfer by both free and trapped excitons as an explanation for these results. However, we were unable to fit our data with the predictions of such a theory.

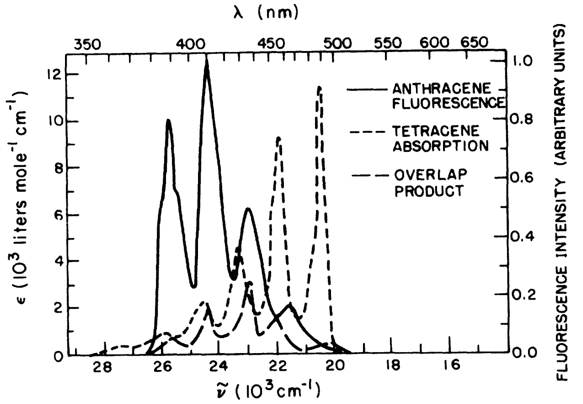

FIG. 6. Fluorescence spectrum of anthracene, absorption spectrum of tetracene in naphthalene, and their spectral-overlap product.

Two other energy-transfer mechanisms were considered in trying to understand the observed discrepancy in the time evolution of the fluorescence intensities. These are energy transfer by virtual excitons and energy transfer by virtual phonons. It has been shown that the first of these mechanisms cannot compete with long-range resonant interaction if allowed dipole-dipole transitions are involved, as is the case for the systems investigated here.[29] Also, the importance of this mechanism is proportional to the energy difference between the excited states of the host and impurity, and it was shown here that the observed anomaly is independent of this energy difference.

The second of these mechanisms has qualitatively the same time dependence as the long-range interaction theory, and thus can be made to fit our data.[30] However, quantitatively the strength of the interaction for this mechanism is porportional to the amount of ionic bonding in the crystal and for molecular crystals this is essentially zero.

B. Impurity-Sensitized Energy Transfer

The data obtained on energy transfer from anthracene to tetracene in a naphthalene host can be fitted by the theory of long-range resonant energy transfer by using Eqs. (1) and (2) with $x = 0$ and a value of 28 Å for R_0. These theoretical predictions are shown in Fig. 3. The lifetime-quenching data are found to be consistent with Eq. (8) if an R_0 of 24 Å is used.

The predicted value for R_0 for this case can be derived from Eq. (3) and the spectra shown in Fig. 6. The spectral-overlap integral is found to be 2.25×10^3 liters mole^{-1} cm^{-1}. Using this value along with $\bar{\nu}_{SA} = 2.3\times10^4$ cm^{-1}, $\phi_S = 0.36$, and $n = 1.4$ gives $R_0 = 28$ Å. Ferguson[14] has also investigated the spectral overlap of anthracene and tetracene in naphthalene. Although he did not give a value for R_0, one can be determined from his data. If Ferguson's Eq. (3) is used, a value of $R_0 = 40$ Å is obtained. However, in deriving his expression for energy-transfer rate, Ferguson sets $n = 1$, and neglects to include a value for ϕ_S. If one uses his data and the correct values for n and ϕ_S, a critical transfer distance of 27 Å is obtained which is consistent with our results. It is important to include both of these factors in considering energy transfer in a crystal, since the former accounts for the change in velocity and density of states of a photon in a crystal, and the latter allows one to use the easily measurable fluorescence lifetime instead of the radiative lifetime in Eqs. (1) and (2).

Thus the results obtained on this system agree with the predictions of long-range resonant energy-transfer theory using the theoretically calculated value of R_0.

V. SUMMARY AND CONCLUSIONS

This paper reports further investigations of energy transfer in molecular crystals by the technique of monitoring the time evolution of the fluorescence intensities. One important result is that no discrepancies were observed between the experimental observations and theoretical predictions for the case of impurity-sensitized energy transfer where it is expected that long-range resonance is the interaction mechanism. This lends credence to the use of this technique in studying energy transfer and shows that the anomaly reported previously is associated specifically with host-sensitized energy transfer.

The second important observation is that this anomaly observed in the time dependence of host-sensitized energy transfer appears to be a property of the host and independent of the type of impurity molecule. It was necessary to use the theory of long-range resonant energy transfer with the same anomalously large value for R_0 to fit the data obtained on both anthracene- and tetracene-doped naphthalene. This is true even though the anthracene absorption spectrum has a much greater overlap with the naphthalene emission spectrum than does that of tetracene. These results are more consistent with a model of energy transfer by exciton trapping than with a model of long-range resonant interaction. However, the migration of excitons is generally thought to be a diffusion process, and this type of motion cannot give rise to the observed time dependence of the energy transfer.

We conclude from the results of this paper, as in previous papers, that the normal mathematical formulation of exciton-diffusion theory cannot explain the time dependence of host-sensitized energy transfer in molecular crystals. The correct model must allow for a decrease in energy-transfer rate with time similar to that contained in the long-range resonant interaction model.

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Effects of X Irradiation on the Ionic Conductivity of Doped SrF_2 Crystals

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The ionic conductivity of SrF_2 doped with various concentrations of Nd^{3+} and Tb^{3+}, as well as of nominally pure SrF_2 crystals, was measured in the extrinsic region. The conductivity was found to increase with the concentration of the dopant, and was attributed mainly to F^- interstitials. The conductivity of the Tb-doped crystals was considerably higher than that of the Nd-doped samples. The difference is attributed to the difference in association between these rare-earth ions and the F^- interstitials. The effect of x irradiation at 80 °K on the extrinsic ionic conductivity was investigated. The x irradiation caused a decrease in the conductivity of the pure and the slightly doped samples, but did not notably influence the conductivity of the heavily doped specimens. The activation energies were not affected by the x irradiation. After annealing to about 600 °K, the original conductivity of all the x-rayed samples was restored. It is assumed that, as a result of the x irradiation at low temperature, F^- interstitial ions transformed to F° atoms. During the heating of the samples, these atoms recombined with electrons trapped at the sites of rare-earth ions and reformed F^- interstitials.

I. INTRODUCTION

The electrical ionic conductivity and its temperature dependence provide a convenient tool for the study of defects in ionic crystals.

It is known that alkaline-earth fluorides, doped with trivalent cations, contain F^- interstitial ions. These interstitials compensate for the excess charge of the trivalent ions, which occupy sites of divalent cations in the lattice.[1,2] The ionic conductivity of the doped crystals in the extrinsic region is due mainly to the motion of these interstitials. Croatto and Bruno[3] measured the ionic conductivity of $SrF_2:LaF_3$, and found an activation energy of 1.06 eV for the F^- interstitials's motion. Barsis and Taylor[4] found an activation energy of 1.0 ± 0.03 eV for the ionic conductivity of pure SrF_2 in the extrinsic region, but they could not determine whether the charge carriers were F^- interstitials or vacancies. The contribution of the cation sublattice to the conductivity was found to be negligible.[5,6]

In the present work the ionic conductivity of SrF_2 single crystals, doped with rare-earth ions of various concentrations, was measured in the extrinsic region and compared with the conductivity of nominally pure SrF_2 crystals. The influence of x irradiation at liquid-nitrogen temperature on the ionic conductivity at higher temperatures was also investigated. The effects of the x irradiation on the conductivity of the various samples enabled us to draw some conclusions concerning the types of defects created by the irradiation.

II. EXPERIMENTAL TECHNIQUE

For our experiments nominally pure SrF_2 crystals and crystals doped with Nd^{3+} (in concentrations of 0.05 and 0.2 at.%) and Tb^{3+} (0.03, 0.1, and 0.3 at.%) were used. These crystals were grown by the crystal-growing laboratory at the Hebrew University of Jerusalem (hereafter referred to as J). Nominally pure SrF_2 crystals were also obtained from Harshaw Company (referred to as H). The specimens were of 1-cm^2 cross section, and about 2 mm thick. The crystals were kept in a vacuum cryostat and were clamped between nickel electrodes.

The electrical circuit consisted of a 300-V dc battery and a Keithley 410 micromicroammeter. The x irradiations were carried out with a tungsten