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Triplet Exciton Phosphorescence in Crystalline Anthracene*

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Long-lived triplet excitons in anthracene crystals were detected by simultaneous observation of both their weak red phosphorescence and the delayed blue fluorescence which results from exciton-exciton interaction. Absorption and emission spectra at room temperature show that the interacting excitons are free, i.e., they correspond to the electronic excitation levels of the pure crystal. Decay curves obey the anticipated bimolecular-interaction kinetic equations. The triplet radiative lifetime is about 60 sec. In contrast to the results at room temperature, the low-temperature behavior is dominated by exciton-tapping effects. The interaction between free and shallowly trapped excitons is much more efficient in yielding delayed blue fluorescence than is the free-free interaction which is dominant at room temperature.

INTRODUCTION

THE problem of exciton transport has been reviewed by Knox.[1] Triplet excitons in organic molecular crystals from a convenient system for the study of exciton motion. In crystalline anthracene triplet excitons corresponding in energy to red quanta have lifetimes (nonradiative) of the order of 10^{-2} sec. Bimolecular interaction of these excitons yields delayed blue fluorescence[2–6] (see Fig. 1). This exciton-exciton interaction upgrades energy in a manner analogous to two-photon absorption. Diffusion coefficients in the range 10^{-4}–10^{-2} cm^2 sec^{-1} have been measured at room temperature.[7,8]

Three alternative mechanisms have been proposed to describe exciton motion and interaction: (1) hopping over nearest-neighbor sites; (2) long-range resonance transfer; and (3) narrow-band transport. As described by Jortner *et al.*,[6] quantum-mechanical hopping between nearest-neighbor sites does not require thermal activation. One would not expect a strong temperature dependence in this model. Robinson and co-workers[9] have found that a model of long-range resonance transfer describes excitation transfer between organic molecules in solid rare-gas crystals. Similar experiments have been reported by Kellogg.[10] This model seems applicable only to excitons localized at dilute defect sites. Excitons moving in a narrow band, analogous to the motion of electrons and holes, would have a temperature-independent average velocity at temperatures such that kT is much greater than the bandwidth. A condition for applicability of the band model is that the exciton mean free path be greater than the lattice spacing.

Several experiments measuring the delayed blue fluorescence have been performed in attempts to distinguish between the alternative transport mechanisms. Temperature-dependent measurements have been reported by Singh and Lipsett,[11] Singh *et al.*,[5] Kepler,[12] McMahon and Kestigian,[13] and Hoesterey.[14] Such experiments are awkward in the sense that the mobile triplet excitons are not detected directly. Thus inferences must be drawn concerning their concentration. The situation is further complicated by exciton-trapping effects at low temperatures.

With the direct detection[15,16] of triplet excitons by

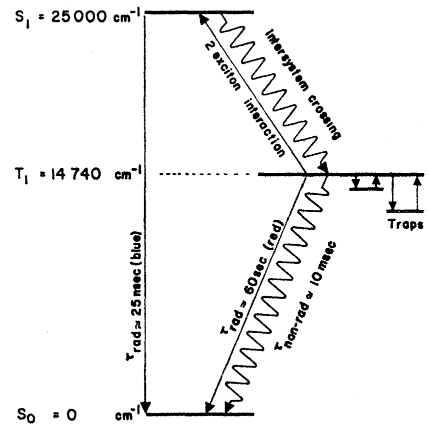

FIG. 1. Anthracene energy-level diagram. For simplicity transitions from triplet-trapping levels to singlet levels are not shown.

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* This work was supported by the U. S. Atomic Energy Commission.

[1] R. S. Knox, *Theory of Excitons* (Academic Press Inc., New York, 1963), p. 184.

[2] C. Kittel, *Introduction to Solid State Physics* (John Wiley & Sons, Inc., New York, 1966), 3rd ed., p. 546.

[3] R. G. Kepler, J. C. Caris, P. Avakian, and E. Abramson, Phys. Rev. Letters **10**, 400 (1963).

[4] J. L. Hall, D. A. Jennings, and R. M. McClintock, Phys. Rev. Letters **11**, 364 (1963).

[5] S. Singh, W. J. Jones, W. Siebrand, B. P. Stoicheff, and W. G. Schneider, J. Chem. Phys. **42**, 330 (1965).

[6] J. Jortner, S. A. Rice, J. L. Katz, and S. Choi, J. Chem. Phys. **42**, 309 (1965).

[7] R. G. Kepler and A. C. Switendick, Phys. Rev. Letters **15**, 56 (1965).

[8] D. F. Williams, J. Adolph, and W. G. Schneider, J. Chem. Phys. **45**, 575 (1966); D. F. Williams and J. Adolph, *ibid.* **46**, 4252 (1967).

[9] H. Sternlicht, G. C. Nieman, and G. W. Robinson, J. Chem. Phys. **38**, 1326 (1963).

[10] R. E. Kellogg, J. Chem. Phys. **41**, 3046 (1964).

[11] S. Singh and F. R. Lipsett, J. Chem. Phys. **41**, 1163 (1964).

[12] R. G. Kepler, Bull. Am. Phys. Soc. **11**, 269 (1966).

[13] D. H. McMahon and M. Kestigian, J. Chem. Phys. **46**, 137 (1967).

[14] D. C. Hoesterey, Bull. Am. Phys. Soc. **12**, 401 (1967).

[15] G. C. Smith, Bull. Am. Phys. Soc. **11**, 777 (1966).

[16] D. F. Williams and W. G. Schneider, J. Chem. Phys. **45**, 4756 (1966).

means of their phosphorescence it became possible to monitor their concentration and lifetime directly. Their interaction can be determined simultaneously by the usual measurement of delayed blue fluorescence. The present temperature-dependent experiments of this kind were begun in an attempt to distinguish among the alternative exciton-transport models.

EXPERIMENTAL ARRANGEMENT

In the present experiments triplets were populated in two ways (Fig. 2):

(1) directly with red light from a xenon lamp;

(2) by two-photon absorption of Q-switched ruby laser light yielding singlets, followed by intersystem crossing to triplets.

In the first method, the source and detector were made to view the crystal alternately by means of a rotating drum phosphorscope. With laser excitation, extreme precautions were necessary to prevent the detecting photomultiplier from being exposed to light from the laser rod or flash lamps. This was accomplished by means of two photographic shutters, one in front of the laser and the second in front of the photomultiplier. They were electrically operated so that the first was closed before the second was opened. The detector was not active until about 10 msec after the laser excitation pulse.

The detection of weak-red and near-infrared phosphorescence required the use of cooled photomultipliers (EMI 9558, S-20 and RCA 7102, S-1). The 7102 was cooled in a specially constructed, horizontal liquid-nitrogen cryostat. Precautions such as shielded coaxial anode lead were taken to reduce dark current to about 2×10^{-13} A with 1160 V applied to the tube. Weak blue light was detected using a cooled EMI 6256S photomultiplier. An oscilloscope with photographic recording was used in the laser experiments. For the chopped-light experiments the time average current was measured with a Keithley 417 Picoammeter and recorded on a strip chart. Decay characteristics were obtained at low chopping rates as in the laser experiments or utilizing an NS-544, Digital Memory Oscilloscope and point plot X-Y recorder. Bausch and Lomb high-intensity grating monochromators (modified to allow motor-driven scan) were used for measurements of emission spectra. The absolute spectral sensitivity of the monochromator grating detector was determined by calibration against an Eppley thermopile. High-resolution measurements of the triplet absorption were made on a 1-m Czerny-Turner scanning spectrometer with resolution and absolute calibration better than 3 Å.

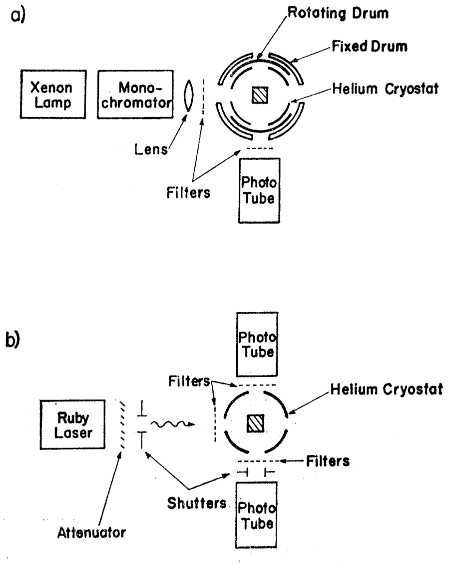

FIG. 2. Experimental arrangements: (a) chopped light with dc xenon lamp excitation; (b) q-switched laser experiment. The upper phototube monitored the prompt fluoresence.

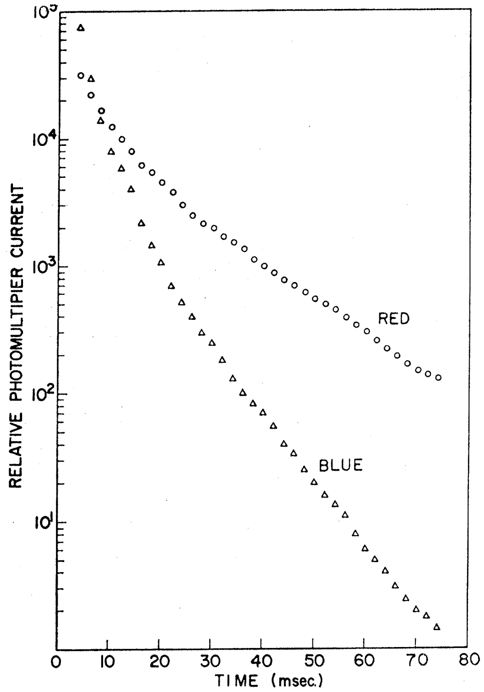

FIG. 3. Red and blue decay curves with ruby laser excitation of Harshaw anthracene at room temperature. The absolute red intensity is actually much weaker than the blue. It is shifted about three orders of magnitude to allow plotting on the same figure.

A variety of anthracene crystals were studied, some grown by various techniques in this laboratory, others obtained from the Harshaw Chemical Co. The experimental methods were useful, however, only for crystals exhibiting relatively long triplet lifetimes, i.e., many milliseconds. All crystals exhibited internal fracturing after temperature cycling but this did not alter their response more than might be due to the increased

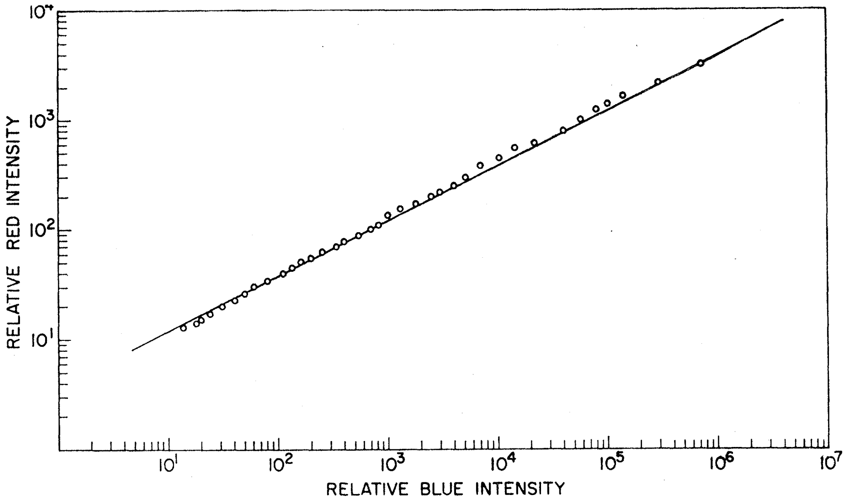

FIG. 4. Log-log plot of red versus blue intensity. Same data as Fig. 3. The line is drawn with slope $\frac{1}{2}$.

internal light scattering. In the laser experiments, the beam was attenuated to avoid crystal damage.

ROOM-TEMPERATURE KINETICS

Following laser excitation delayed blue decay curves similar to those previously measured[3–5] were observed. The superexponential portion at early times is the result of triplet-triplet annihilation at high densities while the exponential decay is the result of nonradiative loss of triplets. Figure 3 shows that a simultaneous red phosphorescence emission exists which decayed one-half as fast. This is to be expected assuming that the bimolecular model applied. The total rate of blue emission is

$$B_T = \tfrac{1}{2}\gamma n_t^2 V, \tag{1}$$

where γ is the bimolecular-interaction constant, n_t is the triplet concentration, and V is the excited volume. For simplicity, the excitation is assumed homogeneous and triplet-triplet interactions are assumed to yield blue quanta instantaneously.

The rate of red emission is given by

$$R_T = \tau_{\text{rad}}^{-1} n_t V, \tag{2}$$

where τ_{rad} is the triplet radiative lifetime. Thus,

$$B_T = (\gamma/2V)\tau_{\text{rad}}^2 R_T^2. \tag{3}$$

In the exponential portion of the decay,

$$R_T = Ce^{-t/\tau}, \tag{4}$$

where τ is the nonradiative (observed) lifetime, so that

$$B_T = (\gamma/2V)\tau_{\text{rad}}^2 C^2 e^{-2t/\tau}. \tag{5}$$

Thus, the measured exponential blue decay is twice as fast as the red. The quadratic relation of Eq. (3) does not depend on time; thus, it is applicable at all points on the decay curves. The data of Fig. 3 are replotted in Fig. 4 as log R_T versus log B_T to demonstrate the validity of the square law relationship, Eq. (3), in both the exponential and bimolecular portions of the decay curves.

Equation (3) shows that a plot of $B_T^{1/2}$ versus R_T is linear with slope,

$$(\gamma/2V)^{1/2}\tau_{\text{rad}},$$

i.e., the slope is proportional to the radiative lifetime. Such a plot is shown in Fig. 5. Using an estimate of excited volume, $\gamma = 2.5.10^{-11}$ cm^3/sec, and measured absolute total red and blue emission rates, R_T and B_T, a radiative lifetime is calculated to be

$$\tau_{\text{rad}} \approx 60 \text{ sec},$$

with an uncertainty factor of about 2. An estimate of triplet radiative lifetime of about 20 sec has been obtained[17] by integration of the triplet absorption

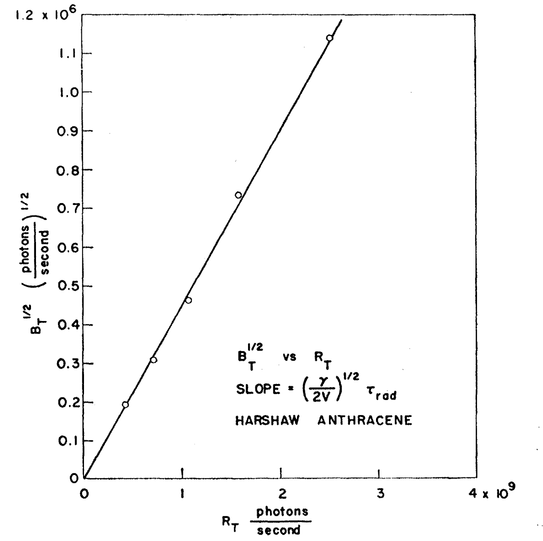

FIG. 5. Square root of total blue emission rate versus total red emission rate. Absolute values are corrected for detector spectral response. Harshaw anthracene at room temperature.

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[17] R. E. Kellogg and N. Convers Wyeth, J. Chem. Phys. 45, 3156 (1966).

spectrum. Typical triplet radiative lifetimes in other aromatic hydrocarbons are about 30 sec.[18] As expected, this is indeed much longer than the nonradiative lifetime τ of about 10^{-2} sec.[19]

PHOSPHORESCENCE SPECTRA

Although the red phosphorescence emission spectrum can be measured with laser excitation, it is more convenient to use chopped light. Figure 6(a) shows the phosphorescence spectrum at 300°K.[20] The phosphorescence spectrum strongly resembles that measured by Lewis and Kasha[21] in solid solution. At room temperature, there is evidence of the tail of the delayed blue emission in the phosphorescence spectrum. Figure 6(c) shows a portion of the triplet absorption spectrum measured at low temperature. The technique was that of detecting a broad band of red phosphorescence while scanning the exciting wavelength. The phosphoroscope allowed detection only of energy stored in the crystal. This technique has two advantages over the indirect method of Avakain *et al.*[22] First, the detected signal is linearly related to the triplet absorption coefficient. Second, it can be employed over a wider range of temperature since it does not depend on triplet-triplet interaction which becomes very improbable at certain temperatures. When folded about the zero-zero line at 14 740 cm^{-1} there is approximate mirror symmetry of the vibrational lines. At 300°K there was no measurable shift of the zero-zero line between absorption and emission (less than 30Å possible error). This is taken as evidence that pure-crystal electron states, i.e., free excitons are involved at room temperature.

There is a surprising range of values in the literature for the absolute energy of the 0-0 transition. Because of the weak interaction of the molecular triplet state with its environment, one expects only small variations of energy among measurements in solid solutions, in plastics, and in crystalline anthracene. Temperature also should be relatively unimportant. Literature values range from 14 700 cm^{-1} (Lewis and Kasha[21]) to 14 927 cm^{-1} (Padye *et al.*[23]). In order to try to resolve this uncertainty in absolute energy, higher-resolution measurements of the 0-0 line were made using the indirect absorption method[22] with crystalline anthracene at room temperature. Measured with 3-Å resolution, the line was found to be asymmetrical toward lower energy with a width of about 140 cm^{-1}. The peak position was at 14 740 cm^{-1} with an absolute error of ± 10 cm^{-1} as determined by calibration with a neon spectral lamp with the spectrometer and recording instruments operating as in the measurement of the absorption peak. This value is relevant to calculations such as those of Kellogg[24] dealing with the position of the second-excited triplet state.

When cooled to about 20°K the phosphorescence spectrum differs from that observed at room tempera-

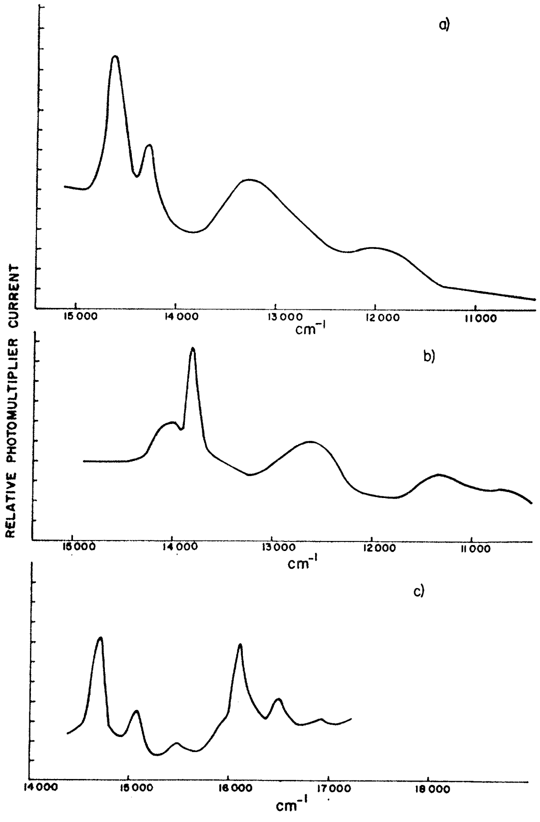

FIG. 6. (a) Room-temperature triplet phosphorescence spectrum. (b) Triplet phosphorescence at 18°K. (c) Phosphorescence excitation spectrum at 33°K. Note that the phosphorescence energy scales are reflected about the 0-0 line. Resolution was 50 Å with no correction applied for small spectral variations of detector sensitivity and excitation intensity.

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[18] R. E. Kellogg and R. G. Bennett, J. Chem. Phys. 41, 3042 (1964).

[19] These phosphorescence results are relevant to the conjecture [H. Y. Sun, J. Jortner, and S. A. Rice, J. Chem. Phys. 44, 2539 (1966)] that the lifetime of the triplet state in a glass is enhanced by the difficulty of removing vibrational energy from the "hot" molecule. Since this difficulty presumably does not occur in crystalline anthracene, one might expect the phosphorescence quantum yield to be larger in the glass. The present experiment gives a quantum yield of a few times 10^{-4} in agreement with that found in solution [G. Porter and F. Wilkinson, Proc. Roy. Soc. (London) **A264**, 1 (1961)]. Thus the conjecture is not supported by the present result. The apparent absence (Ref. 23) of phosphorescence emission at energies greater than that of the 0-0 transition in the glass is a more cogent objection to the conjecture. In fact triplet lifetimes in large pure anthracene crystals are similar to those observed in a glass suggesting that there is no direct "medium effect." In footnote 9 of the conjecture, the sentence appears: "Pure crystals of benzene, naphthalene, and anthracene do not phosphoresce." The present work shows this statement to be incorrect in the case of anthracene.

[20] Results kindly made available by D. F. Williams (unpublished) show a very similar room-temperature phosphorescence spectrum.

[21] G. N. Lewis and M. Kasha, J. Am. Chem. Soc. **66**, 2100 (1944).

[22] P. Avakian, E. Abramson, R. G. Kepler, and J. C. Caris, J. Chem. Phys. **39**, 1127 (1963).

[23] M. R. Padhye, S. P. McGlynn, and M. Kasha, J. Chem. Phys. 24, 588 (1956).

[24] R. E. Kellogg, J. Chem. Phys. 44, 411 (1966).

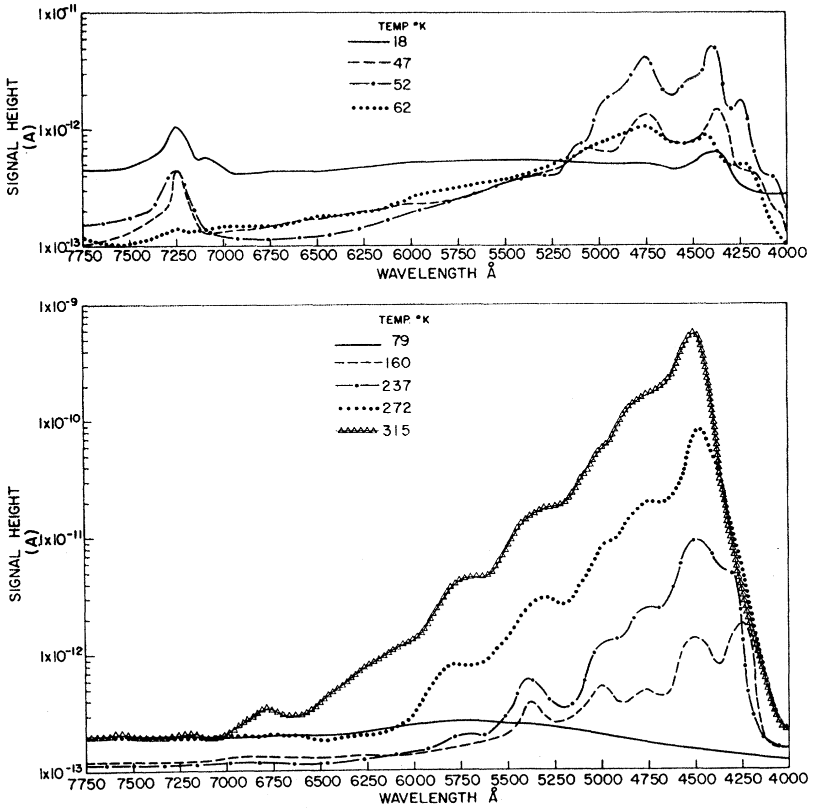

FIG. 7. Visible delayed emission spectra at selected temperatures. The temperatures shown are divided into two ranges for clarity. Chopped, weakly absorbed, blue light excitation was used.

ture. Figure 6(b) shows that the 0-0 line at 14 740 cm^{-1} is absent and that the most prominent line now appears at about 13 860 cm^{-1}, corresponding to a shift of 880 cm^{-1}. This shift is consistent with a model of triplet exciton trapping. The progressive changes in delayed visible emission spectra are shown in Fig. 7 with temperature as a parameter. Weakly absorbed blue light was used to create triplets by intersystem crossing. It is apparent that the delayed blue emission spectrum is also shifted at low temperatures. This might be expected if the interaction of a free triplet with a trapped triplet results in a singlet state which fluoresces at the same defect site. The loss of short-wavelength blue emission near room temperature is probably due to the change of self-absorption with the shift of crystal absorption to longer wavelengths.[25]

TEMPERATURE DEPENDENCE

The red and blue emissions were examined as functions of temperature using filters passing broad spectral ranges. Figure 8 shows the result for chopped-light experiments with red excitation. The results for a Harshaw crystal are taken as typical. The blue maximum at about 50°K corresponds to an inflection point in the red phosphorescence intensity. The results correspond to the experiment of Singh and Lipsett[11] except that a phosphoroscope is used in the present experiment so that one detects only the delayed component.

The chopped-light experiments reported here are similar to those of McMahon and Kestigian[13] with the exception of different ranges of temperature. At room temperature, the crystals used in the present measurements exhibited much longer lifetimes than those observed in that work. As suggested,[13] this discrepancy is probably due to the presence of deep traps which are not important in the present experiments.

Similar experiments with laser excitation are shown in Fig. 9. The values shown are the red and blue intensities 15 msec after laser excitation. Thus decay-time variations have much greater influence than in chopped-light experiments. The similar absolute high-temperature red intensities in three different crystals are indicative of absorption and phosphorescence processes which are not influenced by variable impurity concentrations. This experiment is similar to that reported by Singh *et al.*[5] for high-intensity excitation, with the addition of simultaneous direct monitoring of the triplet concentration by means of their phosphorescence. This can be distinguished from the tail of the blue emission only at times many milliseconds after the laser excitation; and then it is extremely weak. This may account for their lack of success in attempts to observe phosphorescence.

While there is substantial variation from crystal to

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[25] I. Nakada, J. Phys. Soc. Japan **20**, 346 (1965).

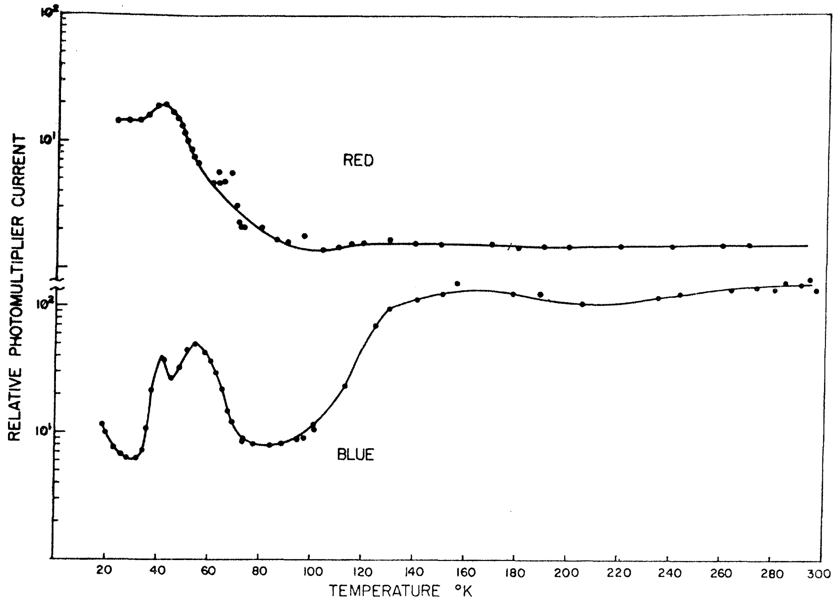

Fig. 8. Temperature dependence of delayed red and blue emission in chopped-light experiments with a Harshaw crystal. The crystal was excited with red light at 6250 Å. The output red light filter was a Corning 2-64. The blue output, actually much stronger, was passed through 5 cm of $CuSO_4$ solution.

crystal in the temperature dependence of delayed blue fluorescence, the red phosphorescence generally increases monotonically toward lower temperatures with inflection points corresponding to maxima in blue emission. In these laser experiments the prompt blue fluorescence was monitored with an FW-114 photodiode. The peak intensity was independent of temperature. At low temperatures, the prompt blue pulse closely resembled the laser excitation pulse. Near room temperature an additional exponential tail appeared which had a decay time of about 30 nsec. The 15-msec data were normalized to compensate for laser intensity fluctuations according to the peak prompt blue fluorescence intensity. The normalization is linear for phosphorescence and quadratic for delayed blue luminescence. Since triplets are populated by intersystem crossing from singlets, the longer singlet decay time at high temperature may result in more triplets. This effect may be responsible for the increases in red intensity observed near room temperature in the experiments in which triplets are populated via singlet states. It is interesting to note that the *integrated* prompt blue fluorescence increases with increasing temperature. The observed behavior is not consistent with the fluorescence reabsorption explanation for the longer decay time.[26]

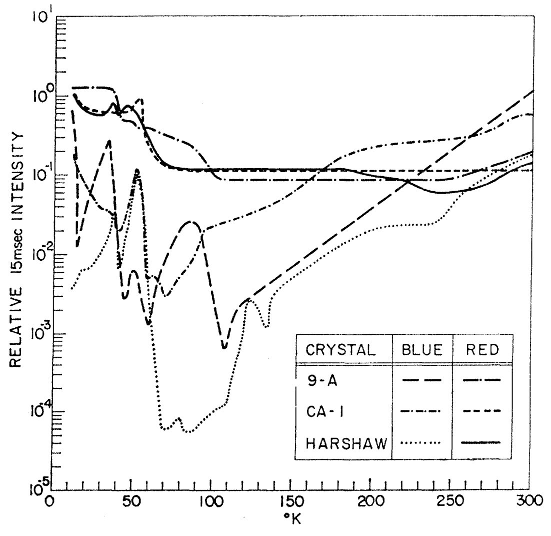

Fig. 9. Temperature dependence of delayed emission rates 15 msec after laser excitation. The red emission is shifted upward about three orders of magnitude to allow convenient presentation. The data are corrected for laser intensity fluctuations according to the peak prompt blue fluorescence intensity.

The blue intensity maximum at 50°K is associated with a maximum in decay time. This is consistent with the much larger red and blue intensity variations in the laser experiments which sample the emission rate 15 msec after excitation. In contrast, the chopped-light experiments integrate all emission delayed more than a fraction of a millisecond. The latter experiment approaches a steady-state measurement.

IMPURITY EFFECTS AT ROOM TEMPERATURE

A variety of nominally pure crystals of similar size were stimulated by a laser pulse and the blue and red emissions measured in the 10–40-msec time range. A log-log plot, Fig. 10, shows that the delayed blue intensity varied over several orders of magnitude for a given red emission rate. According to the model, all of these lines should be superimposed. Since they are not, three alternative explanations are possible: (1) the triplet concentration or radiative lifetime changes; (2) the bimolecular interaction coefficient γ is not constant;

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[26] J. B. Birks, Proc. Phys. Soc. (London) 79, 494 (1962).

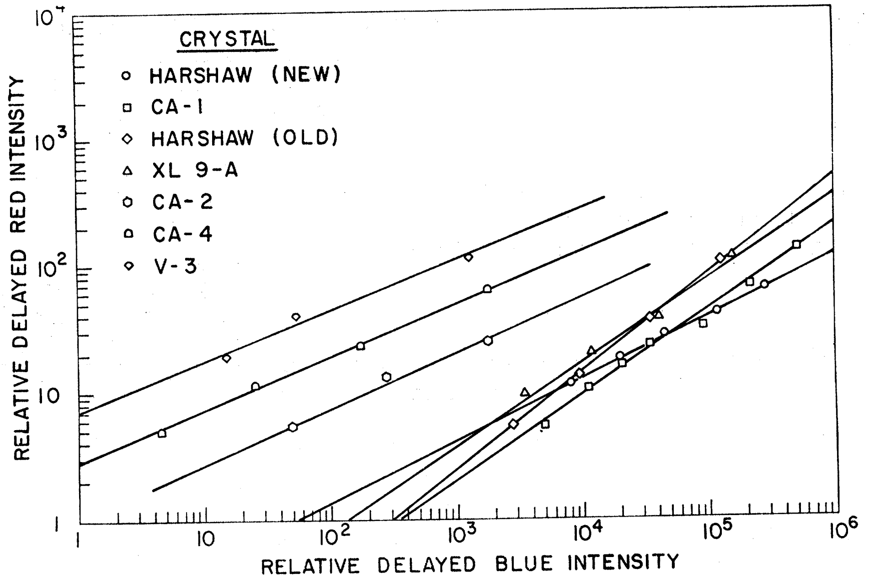

FIG. 10. Log-log red versus blue intensity for various crystals following laser excitation at room temperature.

or (3) the model is not general enough. Since the absolute rates of red phosphorescence are similar, it is probable that the first alternative is not a suitable explanation. The second alternative might imply a reduction of triplet macroscopic mobility due to an effect such as multiple trapping. The third alternative might, for example, require modification of the theory to include free-trapped interaction. It is apparent that a given rate of delayed blue emission does not directly specify a total triplet concentration.

In a particularly striking case (not shown) a crystal doped with $\frac{1}{4}$-ppm tetracene exhibited a delayed blue intensity weaker by a factor of about 10^6 while the red emission was comparable to that of undoped crystals. The simplest interpretation is that triplet energy is localized, or trapped, preventing bimolecular interaction but not greatly changing the radiative and nonradiative lifetimes.

DISCUSSION

The room-temperature results confirm that triplet excitons are the source of delayed blue fluorescence. It is particularly significant that there is no measurable shift of the 0-0 line from absorption to emission showing that the triplet electronic level of the "pure" crystal is responsible, and not some form of trapped-exciton resonance interaction.

The temperature-dependent results are consistent with the assumption that the population of triplet states is nearly temperature-independent in all methods of excitation. The red-in-blue-out data of Fig. 8 are most likely to be uninfluenced by crystal defects due to the direct population of the triplet state. A model such as that of Siebrand,[27] i.e., invoking the possibility of temperature-dependent trapping and interaction of free and trapped excitons, can be made to yield a very similar result. Consider the model as shown in Fig. 1, in which E_0 is the free triplet energy, 14 740 cm^{-1}, E_1, E_2, etc. are trap depths such that phosphorescence from trap i is emitted at energy E_0-E_i. The probability (per second) for capture of a free exciton in traps at the ith level is P_i. This formulation ignores details of trap concentration and cross section. The probability of thermal emptying to the free state is $Ae^{-E_i/kT}$, where A is an "attempt frequency" of the order of 10^{13} sec^{-1}. Assuming no saturation effects, i.e., weak excitation or large trap concentrations, the rates of change of triplet concentrations are

$$dn_0/dt=\alpha I+\sum n_iAe^{-E_i/kT}-(\beta_0+\sum P_i)n_0, \quad (6)$$

$$dn_i/dt=P_in_0-n_iAe^{-E_i/kT}-\beta_in_i, \quad (7)$$

where αI is the excitation rate and β_i^{-1} is the nonradiative lifetime of the ith triplet level. Bimolecular interaction terms are assumed small and the radiative decay is negligible. All summations are assumed to be over $i>0$.

In steady state, this yields

$$n_0=\frac{\alpha I}{\beta_0}\left[1+\sum\frac{\beta_i}{\beta_0}\frac{P_i}{\beta_i+Ae^{-E_i/kT}}\right]^{-1}, \quad (8)$$

and

$$n_i=\frac{p_in_0}{\beta_i+Ae^{-E_i/kT}}. \quad (9)$$

Assuming that the radiative transition probability is independent of trapping, the rate of red emission is [see Eq. (2)]

$$R_T=\tau_{\mathrm{rad}}^{-1}V(n_0+\sum n_i). \quad (10)$$

Siebrand[27] showed that maxima in delayed blue emission occur only if the lifetime $\beta_i^{-1}>2\beta_0^{-1}$. In

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[27] W. Siebrand, J. Chem. Phys. 42, 3951 (1965).

actual fact, he found it necessary to use ratios of 5–6 in order to fit the data of Singh and Lipsett.[11] In the present measurements these triplet lifetimes were actually measured and the ratios are never substantially larger than 2. It is, however, still possible to construct pronounced maxima if one assumes that the interaction of trapped and free triplets may be more likely to yield a delayed blue quantum than is the free-free interaction. The total rate of blue emission is then

$$B_T=\tfrac{1}{2}\gamma V n_0(n_0+\sum G_i n_i)\,. \tag{11}$$

Consider the special case of two trapping levels with $E_i\approx 880$ cm^{-1} and $E_2\approx 2020$ cm^{-1} corresponding to the two prominent low-temperature phosphorescence peaks in Fig. 6. Decay-time data yield $\beta_0=\beta_2\approx 100$ sec^{-1} and $\beta_1\approx 50$ sec^{-1}. Assume the remaining parameters to be $A=10^{13}$ sec^{-1}, $P_1=10^4$ sec^{-1}, $P_2=10^3$ sec^{-1}, $G_1=15$, $G_2=1$. Trial and error shows that this set of values yields the best agreement with the delayed blue measured with chopped red excitation. Factors proportional to the red and blue emission rates are computed with normalization according to the generation rate αI. These functions are shown in Fig. 11. It is apparent that the trapping model with measured optical trap depths can yield the measured temperatures of delayed blue maxima and corresponding inflection points of red intensity shown in Figs. 8 and 9.

The calculated increase of red intensity at low temperature is not as large as that measured experimentally. Since similar increases are measured for both laser and chopped-light experiments, where different mechanisms of triplet population are operative, the discrepancy is probably not due to an increased population at low temperature. The shallowly trapped triplets probably have a larger radiative transition probability.

The maximum at about 50°K occurs because the product of free-triplet concentration and shallowly trapped triplet concentration is a maximum. At lower temperatures there are no thermally released free triplets. At temperatures much higher than 50°K there are no triplets remaining in the traps with an optical depth of 880 cm^{-1}. At higher temperatures the trapped triplets are quickly exhausted and captured by the deeper traps, which are less efficient in yielding delayed blue.

The consideration of only the two most prominent trap depths in the low-temperature phosphorescence spectrum is an oversimplification. The inclusion of the subsidiary maximum at 7100 Å in Fig. 7 would lead to the subsidiary maximum at about 38°K in Fig. 8. Since the 7100 Å maximum disappears from the phosphorescence spectrum above 38°K, one is inclined to infer that the structure in the spectrum is due to various trapping levels rather than molecular vibrations as seems to be the case at room temperature. If this inference is correct, the continuum of phosphorescence emission into the near infrared in Fig. 6 implies the monotonic increase of delayed blue above 120°K. This is consistent with Siebrand's prediction[27] of a distribution of deep trapping levels. The absence of pronounced structure in the red phosphorescence spectrum at intermediate temperatures might also be considered as evidence for a continuum of trapping levels.

It should be noted that the steady-state solution is not totally equivalent to the chopped-light experiments. In particular, the two-trap model assumes population only into the free-triplet state. In contrast, in the experiment with the phosphoroscope, the triplets have time to be trapped before the detector views the crystal so that the only free triplets available are those thermally excited from traps. This discrepancy is responsible for the constant blue intensity below 40°K in Fig. 11 while Fig. 8 shows a larger actual decrease. The question of the time-dependent solutions to the trapping model will be treated in another paper.

A few remarks are in order concerning the uniqueness of the assumed parameters. The value of A is chosen to approximate a phonon frequency or a frequency of molecular vibration. The results are quite insensitive to choice of A. P_1 and P_2 must be greater than the β values to account for processes limited by trapping rather than by nonradiative decay, i.e., for the traps to have any influence. Preliminary results from experiments utilizing strobe lamp excitation confirm the approximate value of P_1. P_1 must be greater than P_2 in order to yield a pronounced blue maximum. G_1 and G_2 determine the relative values of delayed blue intensity at the 50°K maximum, at the minimum at about 90°K, and in the high-temperature range above 140°K. A G_2 value of 1 implies an n_0n_2 interaction as strong as the n_0^2 interaction. A G_1 value greater than 1 is necessary to secure a maximum. This is shown by the dotted line in Fig. 11. Variation of G_1 by a factor of 2 to 3 is easily possible.

Since $\beta_0=\beta_2$, as an experimental fact, and $G_2=1$ yields a satisfactory fit to the temperature dependence, the deep trap ($E_2\approx 2020$ cm^{-1}) seems to resemble the free exciton much more closely than does the shallow trap. It may, therefore, be more intrinsic, e.g., characteristic of a mechanical, rather than chemical, lattice defect. There are some indications of intrinsic lattice defect formation in crystals such as anthracene.[28,29] It is also possible that it is evidence of self-trapping.

Alternative models involving a temperature-dependent mobility or velocity might yield blue maxima, in analogy to work with photoconductivity in inorganics,[30] but they cannot account for the measured decay-time variations. Above 140°K the data of Fig. 8 imply a nearly constant exciton interaction.

A free-trapped interaction 15 times more efficient

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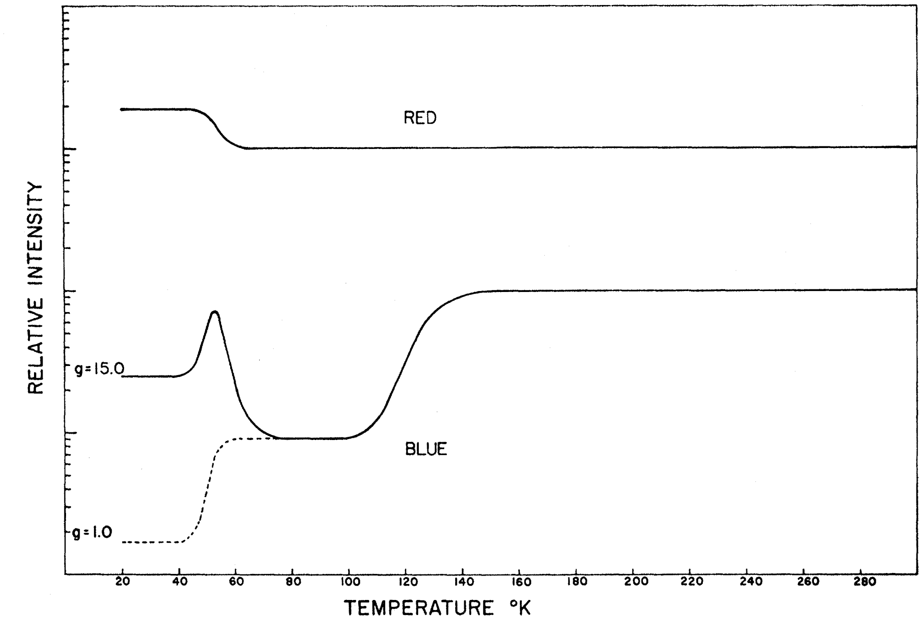

FIG. 11. Steady-state calculated red and blue temperature dependence. The parameters are: $E_1=880$ cm^{-1}, $E_2=2020$ cm^{-1}, $A=10^{13}$, $P_1=10^4$, $P_2=10^3$, $\beta_0=\beta_2=100$, $\beta_1=50$, $G_1=15$, and $G_2=1$. The dotted curve shows the absence of a maximum for $G_1=1.0$.

than a free-free interaction has implications for the hopping model.[6] Instead of thinking of $G_1=15$ as an "enhancement factor" for free-trapped interaction, the argument may be reversed to say that less than one in 15 collisions between free excitons results in mutual annihilation. This factor is in addition to the statistical factor,[6] such as $\frac{1}{9}$, required by spin conservation. In the hopping model the bimolecular-interaction coefficient γ is proportional to the diffusion coefficient. Given an absolute experimental determination of γ, the value of the diffusion coefficient D implied becomes 15 times greater than that found assuming every collision to result in annihilation. The time per hop τ_h must then be smaller corresponding to the relation $D=a^2/2\tau_h$.

The trapping model of Siebrand[27] used in this paper implicitly assumes a temperature-independent γ. Above about 140°K this seems clearly to be the case. At lower temperatures, there is no evidence of a large change. Such behavior would be expected for exciton motion in a narrow band of width W at least for temperatures such that $kT>W$.

For the purposes of visualization, microscopic exciton motion seems to have photonlike character with a group velocity drastically reduced by resonance interaction with the crystal. Elastic scattering leads to macroscopic diffusion of exciton energy.

SUMMARY

These experiments have shown that free-triplet excitons are the mobile states responsible for long-range energy transport. In anthracene crystals their radiative lifetime is about 60 sec. Trapping effects dominate the temperature dependence of delayed blue fluorescence even in nominally pure crystals. Trapped excitons show phosphorescence at low temperatures which is shifted to lower energies corresponding to the thermal depths of the traps. Maxima in delayed blue intensity as a function of temperature can be described in terms of a free-trapped exciton interaction which is many times more likely to yield delayed blue fluorescence than is the free-free bimolecular interaction which is dominant at room temperature. The preference for exciton-exciton interaction at particular defect sites has implications for inhomogeneous systems; the upgrading of mobile excitons to quanta of higher energy probably occurs at specific sites.

There is no evidence for a direct resonance type trapped-trapped exciton interaction. There is no indication of any strong temperature dependence of the free-exciton interaction. Under certain conditions, however, multiple trapping must occur yielding a trap-modulated exciton motion analogous to that observed for carriers.[31] Neglect of this effect could allow a misleading interpretation of other measurements. Because of the long triplet exciton lifetime, in which it can sample a very large number of lattice sites, the relative crystal purity required to observe an "intrinsic" temperature dependence exceeds that possible with present crystal-preparation methods.

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