

On the Behavior of the Delayed Luminescence Observed at Temperatures below 4.2 K

By

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The behavior of the delayed luminescence observed at temperatures below 4.2 K has been studied for the mixed crystals of benzo[*f*]quinoline in biphenyl host. Preliminary results obtained with a high guest concentration of 10^{-2} mol/mol are presented in connection with the spin alignment.

1. Introduction

Triplet-triplet annihilation events in the lower temperature region in mixed crystal systems have been the subject of several publications from these laboratories.¹⁻⁸⁾ In these works, the investigations were carried out at temperatures higher than 4.2 K. In order to examine the effects of the spin alignment⁹⁾ on the delayed luminescence (phosphorescence and delayed fluorescence), we have attempted to study the behavior of the delayed luminescence of benzo[*f*]quinoline in biphenyl host below 4.2 K. The results obtained thus far should be regarded as yielding a starting point for future work rather than as composing a report of a completed investigation.

2. Experimental

The chemicals used were obtained from Tokyo Kasei Kogyo Co., Ltd. Biphenyl was recrystallized twice from ethanol, and was further purified by repeated zone refining over 200 passes. Benzo[*f*]quinoline was subjected to the same chemical treatment as described previously,¹⁰⁾ and was finally zone refined with 250 passes. The polycrystalline samples used were prepared from the melts between two fused-silica plates mounted in a copper block holder.^{3,4)}

The temperatures lower than 4.2 K were obtained through reduction of the vapor pressure of the liquid helium in a Dewar cryostat with a vacuum rotary pump ULVAC D-950, and were measured with a calibrated 1/8-W, 51- Ω Allen-Bradley carbon resistor which was attached directly to the silica plate with the GE adhesive of 7031 insulating varnish to ensure good thermal contact. Care was taken to keep the heating of the resistor as minimal as possible, so, for instance, Joule's heat at 1.18 K was smaller than 10^{-6} J.

The other apparatus and techniques were identical to those already described.^{3,4)}

3. Results and Discussion

One of the typical delayed luminescence spectra at 4.2 K is shown in Fig. 1 for the convenience of discussion. We have not observed any appreciable trap-delayed luminescence at the temperature range of 4.2–77 K.^{3,4)} Therefore, the results obtained in this temperature range are all derived from the guest (benzo[*f*]quinoline) in nature.

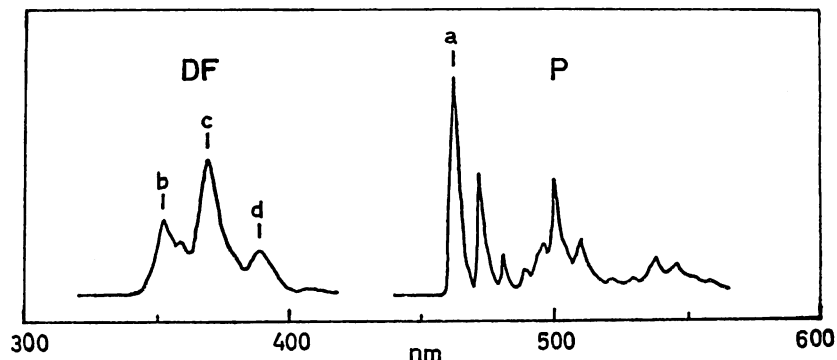


Fig. 1. Delayed fluorescence (DF) and phosphorescence (P) spectra of benzo[*f*]quinoline in biphenyl host at 4.2 K.

Concn.: 1.0×10^{-2} mol/mol. (a) Phosphorescence band at 464 nm, the 0, 0-band; (b), (c), and (d): delayed fluorescence bands at 350, 368, and 389 nm, respectively. Detection sensitivity was raised in the observation of delayed fluorescence.

We examined the temperature dependence in the delayed luminescence at temperatures below 4.2 K in respect of several bands a, b, c, and d shown in Fig. 1. The results obtained with a high guest concentration of 10^{-2} mol/mol are shown in Figs. 2, 3, and 4, and summarized as follows:

- (1) We have observed no trap-delayed luminescence at the temperatures below 4.2 K.
- (2) The delayed fluorescence observed below 4.2 K is but the tail end of the comparatively intense delayed fluorescence whose maximum occurs around 10 K (see Fig. 4 in Ref. 3), in every band shown in Fig. 2.
- (3) The phosphorescence intensity remains constant at temperatures below 4.2 K (Fig. 2) and hence this is also the tail end of that shown in Fig. 4 in Ref. 3.
- (4) Furthermore, at the temperatures below 4.2 K, the decay behavior of the phosphorescence is exponential and independent of temperature (Fig. 3), while the phosphorescence mean lifetimes were found to be 2.07 s and are also very close to the value of the temperature-independent decay observed at temperatures above 4.2 K, *i.e.*, 2.09 s.
- (5) As Fig. 4 shows, the phosphorescence decay is exponential even at 1.18 K.

As can be seen from the above results, we could not observe the spin alignment even at 1.18 K for the benzo[*f*]quinoline-biphenyl mixed crystal system with the concentration

of 1.2×10^{-2} mol/mol. Accordingly, it may be suggested that the benzo[*f*]quinoline-biphenyl system is a system with dominant spin-lattice relaxation. Incidentally, for phenanthrene in a biphenyl or a fluorene crystal, Antheunis¹¹⁾ has observed a spin-lattice relaxation that is of the order of 1000 times faster than the decay from the lowest triplet state to the ground state. In other words, the spin alignment in phenanthrene at 1.2 K could not be observed in biphenyl or fluorene mixed crystal system. It is not clear at present why the relaxation rate in these kinds of the three-ring aromatics doped in biphenyl host crystals is much faster than the decay rate to the ground state.

As the triplet-triplet annihilation events at temperatures where the spin alignment takes place are very interesting subjects in relation to the interaction between triplet sublevels of the guests, a further study on the mixed crystal systems containing the guests where the spin alignment has been observed, *e.g.*, naphthalene, is necessary.

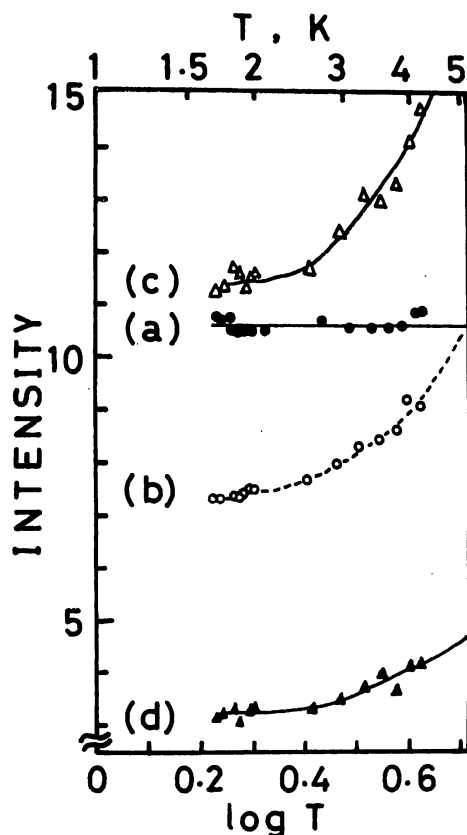


Fig. 2. Temperature dependence of the delayed luminescence of benzo[*f*]quinoline in biphenyl host at temperatures below 4.2 K. Concn.: 1.2×10^{-2} mol/mol.

(a): Phosphorescence intensity observed at the 0, 0-band shown in Fig. 1; (b), (c), and (d): delayed fluorescence intensities observed at the corresponding bands shown in Fig. 1. Magnification of the delayed fluorescence intensity to the phosphorescence intensity: $\times 58$.

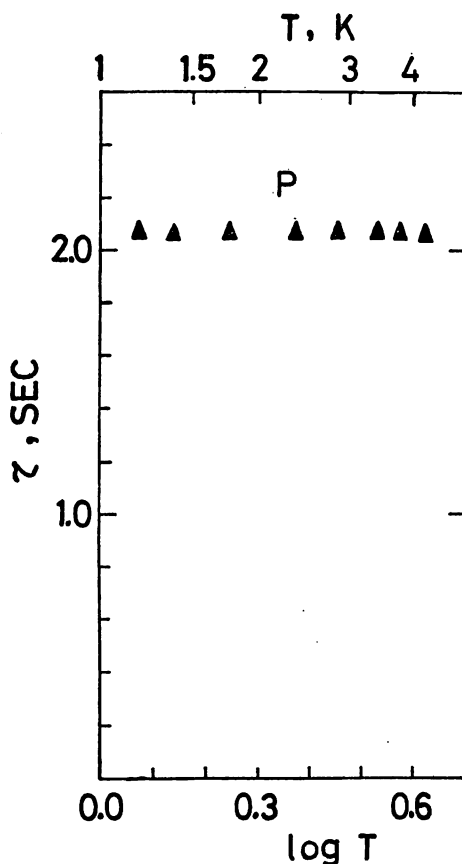


Fig. 3. Temperature dependence of the phosphorescence (P) lifetimes of benzo[*f*]quinoline in biphenyl host at temperatures below 4.2 K. Concn.: 1.2×10^{-2} mol/mol.

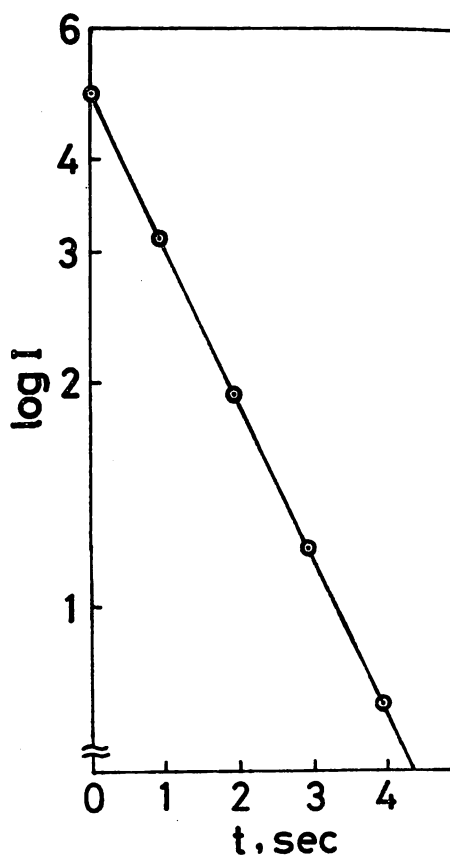


Fig. 4. Phosphorescence decay of benzo[*f*]quinoline in biphenyl host at 1.18 K. Concn.: 1.2×10^{-2} mol/mol.

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