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EFFECT OF THE EXCITATION DURATION ON THE DECAY BEHAVIOR OF THE TEMPERATURE-INDEPENDENT DELAYED FLUORESCENCE

Shoji TAEN* and Yasuhiko GONDO
Department of Chemistry, Faculty of Science, Kyushu University 33,
Hakozaki, Higashi-ku, Fukuoka 812

Under different excitation durations, the decay law has been studied on the temperature-independent delayed fluorescence in the mixed crystals of benzo[f]quinoline in biphenyl host at 77 K. An extreme reduction of the excitation duration has been found to lead to a decay law of the form, $I_{DF}(t) = I_{DF}(0)/(1 + at)^2$.

Kusumoto et al.$^{1)}$ previously established the existence of the temperature-independent delayed fluorescence (TIDF) in the mixed crystals of benzo[f]quinoline in biphenyl host, besides the usual temperature-dependent delayed fluorescence. The delayed fluorescence (DF) intensity was found to keep constant over a wide range of temperature from 90 K to liquid helium temperature, and the significance of the TIDF was somewhat detailed. However, the nature of the TIDF was not understood. The TIDF was observed to decay nonexponentially in the short time region, whereas exponentially in the long time region. We have studied the TIDF of the same mixed crystals at 77 K, and have found that the TIDF decay behavior depends on the excitation duration. To our knowledge, this is the first report on the effect of the excitation duration on the DF decay behavior.

The chemicals used were obtained from Tokyo Kasei Kogyo Co., Ltd., and were purified as described previously.$^{1)}$ As a delta pulse excitation source, we used a home-made N_2 laser of 8 ns FWHM. As a square wave excitation source, we used a 1-kW super-high-pressure mercury arc lamp, Orc-CH-612, combined with an electromagnetic shutter, Vincent Assoc. 26LOAOX5 and a water filter of 5-cm optical path. The home-made shutter control system incorporates a Toshiba TC4528BP monostable multivibrator. The TIDF decays were displayed on an oscilloscope, Tektronics 475.

Under the square wave excitation of 5 s, the TIDF has been found to decay nonexponentially in the initial time region of 180 ms, giving a half-life of 40 ms. In the case of the N_2 laser excitation, the TIDF decayed faster than in the case of the above square wave excitation. As the duration of the square wave excitation decreased, the TIDF decayed faster, and eventually with a 20-ms duration it decayed essentially in the same manner as that found with the N_2 laser excitation. Consequently, the difference in excitation wavelength between the two light sources is not responsible for the observed different decay behaviors.

If we postulate that two excited triplets annihilate each other to yield one excited singlet, and the other processes can be neglected, the triplet concentration U(t) satisfies the rate equation, $dU/dt = -\gamma U^2$, and the solution is given by $U(t) = U(0)/(1 + at)$, where a is equal to $\gamma U(0)$. Thus, the TIDF intensity, I_{DF}, follows the relation,

$$I_{DF} \propto U(t)^2 \propto 1/(1 + at)^2. \quad (1)$$

As Fig. 1 shows, this relation is realized in the case of the N_2 laser excitation, giving a value of 22 s^{-1} for the parameter a. The FWHM of the N_2 laser pulse is about 8 ns, and is much too short as compared with the triplet-state lifetime. In this context, the N_2 laser pulse can be regarded as a delta pulse. Thus, we can conclude that the decay law of the TIDF is given by relation (1) under delta pulse excitation.

Steudle et al.[2] reported a similar decay law in the CT complex anthracene/s-tetracyanobenzene under flash excitation. However, they never referred to the effect of the excitation duration. Garlick and Wilkins[3] discussed phosphorescence decay laws in inorganic crystals, pointing out that bimolecular theory leads to the same decay law as that reported here; their theory does not incorporate the effect of the excitation duration. We believe that our present finding leads to a significant contribution for elucidation of the nature of the TIDF. In other words, reduction of the excitation duration serves to simplify the observed decay process. In this sense, the N_2 laser excitation will give a powerful tool to elucidate the nature of the TIDF. We are now extending this approach to the usual temperature-dependent DF.

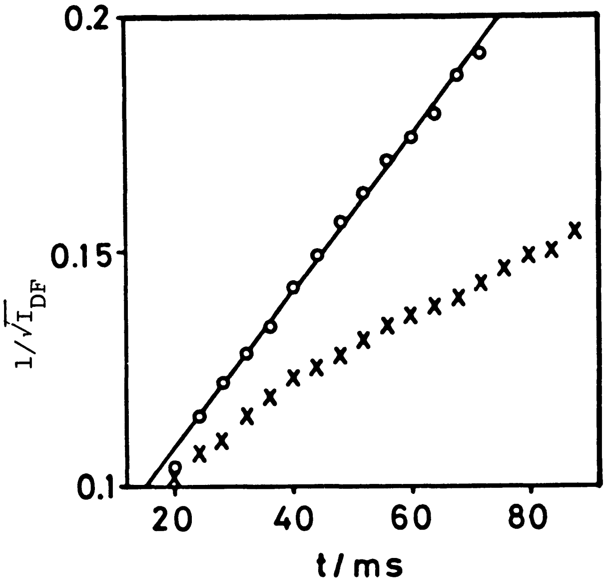

Fig. 1. Plot of $1/\sqrt{I_{DF}}$ vs. t for the mixed crystals of benzo[f]quinoline in biphenyl at 77 K.
Guest concn: 1.0×10^{-2} mol/mol.
x : Square wave excitation for 5 s with a mercury arc lamp.
o : Delta pulse excitation with an N_2 laser.

References

1) Y. Kusumoto, Y. Gondo, and Y. Kanda, Chem. Lett., 1974, 81 ; Bull. Chem. Soc. Jpn., 49, 2706 (1976).
2) W. Steudle, J. Y. von Schütz, and H. Möhwald, Chem. Phys. Lett., 54, 461 (1978).
3) G. F. J. Garlick and M. H. F. Wilkins, Proc. R. Soc. London, Ser. A, 184, 408 (1945).

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