Laser induced long-lived emission spectra of laser dyes in rigid glasses at 77 K

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Abstract. Phosphorescence decay of 3-(2'-N-methylbenzimidazolyl)-7-N, N-diethylamino-coumarin; 2,3,5,6-1H, 4H-tetrahydro-8-methylquinolizino-⟨9,9a, 1-gh⟩ coumarin; 2,3,5, 6-1H, 4H-tetrahydro-8-trifluormethylquinolizino-⟨9,9a, 1-gh⟩ coumarin; 9(10H)-acridone; 9-amino-cridine hydrochloride, 1-hydrate and 2-(4-biphenylyl)-5-(4-t-butylphenyl)-1,3, 4-oxadiazole dyes in EPA glass at 77 K have been recorded using N_2 laser. The results were used to determine lifetimes. Emission intensities from the first two dyes have been examined in relation to dye concentration and excitation intensity. The results are discussed.

Keywords. Phosphorescence; delayed fluorescence; triplet-singlet separation; lifetime; triplet-triplet annihilation; biphotonic process; contact complex; spin-orbit interaction.

1. Introduction

The triplet state has a long lifetime and is of considerable importance in photophysical and other energy utilization processes. The triplet (T_1) is commonly populated via the lowest singlet state (S_1) by radiationless intersystem crossing (ISC) process, the direct photoexcitation of triplet state being rare. The deactivation of the triplet state takes place through (i) induced $S_1 \leftsquigarrow T_1$ radiationless transition, (ii) triplet-triplet annihilation (TTA), (iii) radiative $T_1 \rightsquigarrow S_0$ and nonradiative $T_1 \rightsquigarrow S_0$ transitions to ground state and (iv) triplet-triplet absorption. The way the triplet state participates in energy transfer processes is of great significance to lasing processes. Therefore, data about the triplet spectra, the energy levels, the spectral range, decay times and other associated parameters are of importance for a clear understanding of the performance of dye lasers.

Literature survey shows that except for some aromatic compounds and a few laser dyes, triplet state data are not available. Even the existing data on triplets have been derived mostly from $T-T$ absorption either by photolysis or pulsed radiolysis techniques. Most of the laser dyes do not show emission from triplet state at room temperature. Emission from triplets for many dyes have, therefore, not been reported. We have chosen some laser dyes such as 3-(2'-N-methylbenzimidazolyl)-7-N, N-diethyl-aminocoumarin (C 30); 2, 3, 5, 6-1H, 4H-tetrahydro-8-methylquinolizino ⟨9,9a, 1-gh⟩ coumarin(C 102); 2,3,5,6-1H, 4H-tetrahydro-8-trifluormethyl-quinolizino-⟨9, 9a, 1-gh⟩ coumarin (C 540A); 9(10H)-acridone; 9-aminoacridine hydrochloride 1 hydrate

(9AA) and 2-(4-biphenylyl)-5-(4-t-butylphenyl)-1,3,4-oxadiazole (BPBD) for study in a low temperature glass, where triplet and associated   nissions are measurable.

2. Experimental

All the dyes were of spectroscopic grade and were purchased from Eastman Kodak and exciton and solvents from Merck and Fluka. Solutions were prepared in EPA (5:5:2 by volume of ether, isopentane and ethanol at room temperature) and degassed through freezepump thaw cycles. The solutions were placed in a cylindrical quartz cell (1 cm path length) and the cell was quickly immersed in liquid nitrogen-filled quartz Dewar flask with windows snugly fitting the cell. The solutions formed clear rigid glasses. The samples were irradiated by N_2 laser (f.w.h.m. *ca* 5 ns, peak power *ca* 150 kW, repetition rate *ca* 30 Hz) and the spectral emission from the sample cell at right angle to the excitation was monitored using a monochromator, an RCA 931A photomultiplier and an X–Y recorder (Ricken denis, Co., Ltd. Model F-3DG, dynamic response, *ca* 0·01 s/mm). The response time of the system was such that long-lived emissions (phosphorescence and delayed fluorescence) and their decays were detected whereas the normal fluorescence with a lifetime of a few ns did not appear in the recorded spectra.

3. Results and discussion

The dye solutions show no phosphorescence at room temperature, but at 77 K in EPA, they exhibit phosphorescence accompanied by delayed fluorescence. The phosphorescence is detectable only at higher concentrations ($> 1 \times 10^{-4}$ mol dm^{-3}). Figure 1 shows typical (uncorrected) long-lived emission spectra observed from different dyes. Delayed fluorescence (DF) of C 102, 9AA and 9(10H) acridone is very weak compared to phosphorescence and does not change significantly with concentration. In the case of BPBD and C 540A, the DF and phosphorescence are of comparable intensity, but weak. Interestingly, the emissions from C 30 are fairly strong and show marked concentration dependence. Intensity of DF decreases with concentration, suggesting that the emission does not arise from excimers. Except for slight deviation in the beginning, the decay curves are exponential with lifetimes of the order of seconds. Table 1 gives the measured triplet and singlet energies (corresponding to their peaks), the spectral range and decay times.

As can be seen from table 1, with exception of BPBD, the singlet-triplet gap of all dyes is small (7–9 kcal mol^{-1}) and lifetimes are longer than 1 s. These values reflect the (π, π^*) configuration of the triplet states (Becker 1969). Decay emissions from C 102 and C 30 were examined as a function of concentration. The results show that the DF and phosphorescence from C 30 (figure 2) and phosphorescence from C 102 exhibit a concentration dependence. The phosphorescence yield of C 102 increases slightly with concentration in the range 1×10^{-3} to 5×10^{-3} mol dm^{-3} and at the highest possible concentration of 8×10^{-3} mol dm^{-3}, it decreases. According to Zenkovich *et al* (1980), this effect arises as a result of increasing probability of $S_1 \rightsquigarrow T_1$, nonradiative intersystem crossing (ISC) process. The change in ISC probability in the high concentration range is attributed to the enhanced effectiveness of chromophore
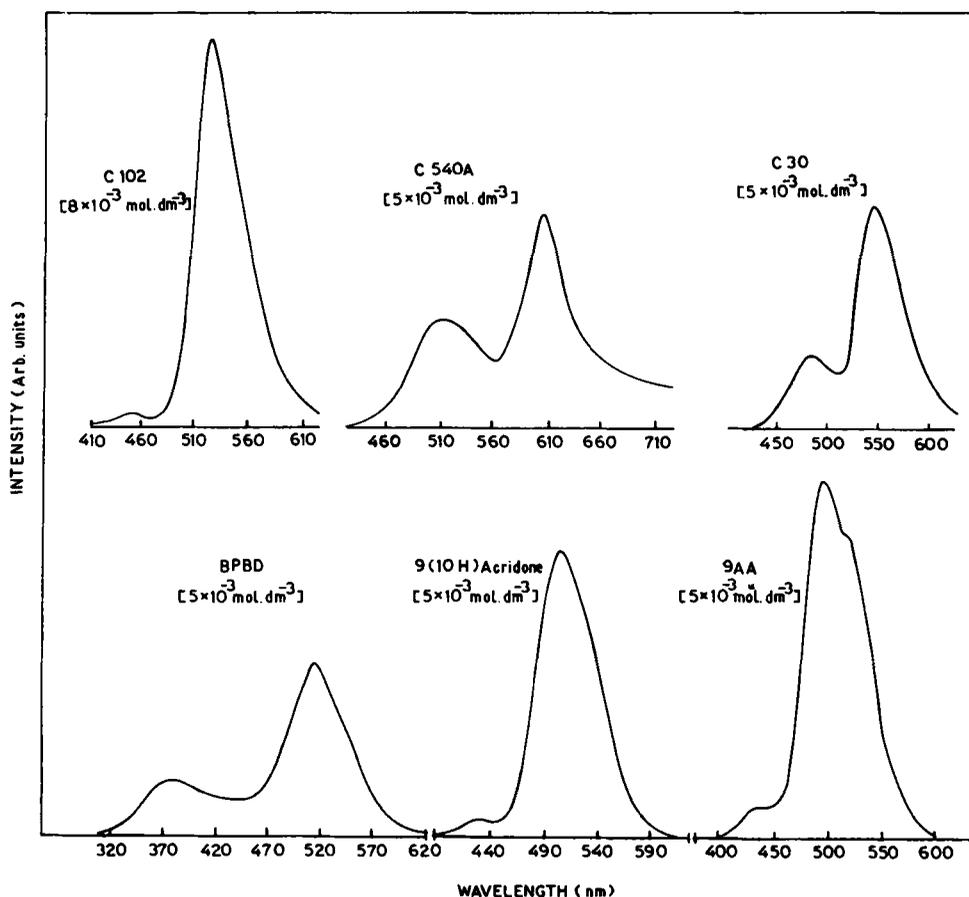
Figure 1. Uncorrected emission spectra of dyes in EPA at 77 K. The shorter wavelength peak corresponds to delayed fluorescence and the longer wavelength peak to phosphorescence.

interactions. Slight reduction in the phosphorescence at the highest concentration may be due to radiative migration (self absorption).

In order to understand the origin of DF, the intensity of DF (I_{DF}) was measured as a function of excitation intensity (I_{ex}) using a set of neutral density filters. The results show that the I_{DF} is proportional to I_{ex}^2, reflecting the biphotonic process for the occurrence of DF. Its emission, measured for three different concentrations, decays with a lifetime which is nearly half the lifetime of the phosphorescence. These findings are consistent with triplet-singlet annihilation (TTA) process:

$$T_1 + T_1 \rightarrow S_1 + S_0$$
$$S_1 \rightarrow S_0 + h\nu. \tag{1}$$

This phenomenon depends on the square of the incident light intensity because the triplet (T_1) arises via the singlet (S_1), and two such events are required to obtain DF of this type. The DF from rigid glasses at 77 K has been observed earlier from some aromatic hydrocarbons (Czarnecki 1961; Muel 1962; Azumi and McGlynn 1963). They

Table 1. Spectral properties of dyes in EPA at 77 K.

Dye molecule	Phosphorescence		E_T (kcal mol^{-1})	E_S (kcal mol^{-1})	$T-S$ Separation (kcal mol^{-1})	τp (s)
	Range (nm)	Peak (nm)				
C 30 (5 × 10^{-3} mol dm^{-3})	525–625	560	51·00	60·85	9·85	2·6
C 102 (8 × 10^{-3} mol dm^{-3})	480–630	524	54·58 (57·7)*	62·00	7·42	3·0
C 540A (5 × 10^{-3} mol dm^{-3})	570–680	610	46·88	54·00	7·12	2·2
9(10H) Acridone (5 × 10^{-3} mol dm^{-3})	430–610	496	57·66	65·45	7·79	3·5
9AA (5 × 10^{-3} mol dm^{-3})	450–600	500	57·20	65·00	7·80	3·6
BPBD (5 × 10^{-3} mol dm^{-3})	460–520	518	55·00	76·00	21·00	2·8

*Measured from absorption spectrum employing the pulsed radiolysis technique by Priyadarsini *et al* (1989)
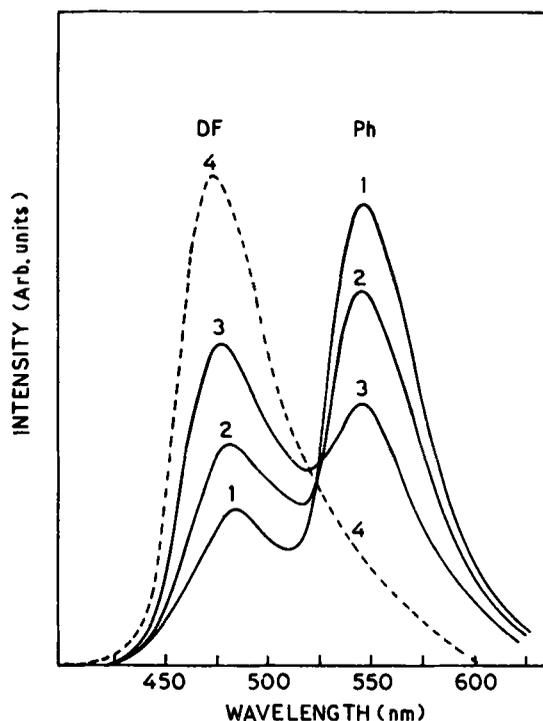

Figure 2. Uncorrected emission spectra of C 30 in EPA (77 K) at various concentrations: Curve (1) 5 × 10^{-3}, (2) 2·5 × 10^{-3}, (3) 1·25 × 10^{-3} and (4) 0·8 × 10^{-3} mol dm^{-3}.

have ascribed this phenomenon to TTA. Lim and co-workers (1962, 1963, 1965) who observed DF from acriflavine in EPA at 77 K, have suggested that the DF originates from the recombination of ions and trapped electrons produced by photoionization

of the dye molecule. Since this process is monophotonic in nature, its occurrence in our study is ruled out. But if we assume that the trapped electrons are produced by photoionization of triplets, the process becomes biphotonic in nature. But the concentration dependence of emission cannot be understood by this process. Various mechanisms have been proposed to account for the process (1) in rigid glasses (Birks 1970), but as yet not much is known about the detailed mechanism.

Unlike other dyes of our study, C 30 displays the following interesting spectral features. An increase in the dye concentration results in the reduction of DF intensity accompanied by the appearance of a new emission (phosphorescence) at longer wavelength, the intensity of which increases with the concentration. This suggests on initial inspection that the new emission may be due to the process:

$$T_1 + S_0 \rightarrow (T_1 S_0) \rightarrow S_0 + S_0 + h\nu. \qquad (2)$$

If the complex $(T_1 S_0)$ is a triplet eximer, it should exhibit its own characteristic spectrum which should be devoid of structure. But our observed emission shows definite structure and no shift is observed in its peak with changing concentration. This observation eliminates the possibility of excimer emission. However, the spectral feature can be explained if we can assume the formation of a contact complex involving two C 30 molecules, one being in the triplet state and other in the singlet state, via the charge transfer interaction. In a contact complex, the triplet state (T_1) molecule is strongly perturbed by the ground state (S_0) molecule leading to the increase in the spin orbit interaction (SOI). The enhancement of SOI is expected to increase the rates of both $T_1 \rightsquigarrow S_0$ non-radiative ISC and $T_1 \rightsquigarrow S_0$ radiative ISC, but the latter process is usually more pronounced, so that the net effect is an increase in phosphorescence yield. The above mentioned process competes efficiently with TTA at higher concentration leading to the reduction in I_{DF}. At lower concentrations, on the other hand, deactivation of the triplet by TTA is more effective. Similar mechanism has been suggested by Ermaganbetov *et al* (1986) for the triplet quenching in xanthene dyes.

Detailed experiments are in progress to quantitatively determine the contributions of mechanisms involved. At the moment the present study provides new data on triplet energies and lifetimes of important laser dyes. Particularly, C 102, 9(10H) acridone and 9AA have high phosphorescence yield and well defined triplet energies and as such may serve as excellent triplet sensitizers for kinetic studies of energy transfer in rigid glasses.

Acknowledgement

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