



Title	Study on triplet-dye molecules under laser excitation using ESR technique
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Furthermore, because the pumping light is single beam, free radicals of the sample solution hardly occur¹ and behavior of triplet molecules can be analyzed more easily using rate equations.

Each dye—rhodamine 6G, rhodamine B, rhodamine S, fluorescein disodium salt, and 2', 7'-dichloro fluorescein—was 5×10^{-3} M in ethanol. The outgassed oxygen-free solution was sealed in each quartz tube and kept at 77 K in a quartz Dewar vessel.¹ In the case of the experiments for temperature dependence, a Varian E-257 variable temperature controller was used. The temperature increase of the sample due to the laser power was measured by the thermocouple. The organic dyes were excited with the unfocused 5145-Å beam of an Ar ion laser.

The observed ESR signals for the dyes are listed in Table I. The triplet lifetimes τ_T , the microwave frequency f , the resonance magnetic field H_{m1n} (H_z), and the relative intensities I_n of H_{m1n} and H_x lines at 77 K are given, whose lines correspond to $\Delta m = \pm 2$ and $\Delta m = 1$ transitions, respectively. The intensities of the latter lines in rhodamine dyes were less than 1/10 of the former and did not depend on the angle between the electric field of the linear polarized light and the dc magnetic field.

The temperature dependence from 77 to 155 K of rhodamine 6G triplet lifetimes was obtained from the decays of H_{m1n} lines for different temperature as shown in Fig. 1. Both the lifetimes and the intensities decreased rapidly at about 130 K. The phase transition of the sample occurred gradually from the rigid solution to the fluid about 150 K.

The saturation curve at 77 K for rhodamine 6G, the triplet concentration being proportional to the intensity of the H_{m1n} line, is shown in Fig. 2. The triplet population at 77 K began to be saturated at a pumping power of about 400 mW. Fluorescent lifetime τ_F measured at 77 K by pulsed N₂ laser excitation was 8.3 ns. From the measurement for optical absorption spectra at 77 K of rhodamine 6G,

¹M. Yamashita and H. Kashiwagi, *J. Chem. Phys.*, vol. 59, p. 2156, 1973.

F.13 Study on Triplet-Dye Molecules under Laser Excitation Using ESR Technique, M. Yamashita and H. Kashiwagi, *Laser Research Section, Radio- & Opto-Electronics Division, Electrotechnical Laboratory, Tanashi, Tokyo, Japan.*

This summary on dye-laser medium discusses temperature dependence of triplet lifetime, triplet concentrations, and inter-system crossing during laser irradiation on the basis of optical saturation. ESR study on the T_1 state during laser excitation has special merits in comparison with the case of mercury arc pumping as follows: because the intensity of the pumping light is very powerful, the triplet population increases remarkably. The conditions enable one to observe optical saturation, weak ESR signals such as $\Delta m = 1$ transitions, and the dependence of the signals on the polarization angle of the pumping light.

TABLE I
ESR DATA FROM RANDOMLY ORIENTED TRIPLET-DYE MOLECULES DURING LASER EXCITATION

Dyes	H_{m1n} line					H_{II}^X line			H_{III}^X line			τ_T (Sec)
	f (GHz)	$H_{m1n,2}$ (G)	$H_{m1n,0}$ (G)	$H_{m1n,1}$ (G)	I_n	f (GHz)	H_{II}^X (G)	ΔH_X (G)	f (GHz)	H_{III}^X (G)	ΔH_X (G)	
Rhodamine 6G	9,240	1600	1609	1617	11	9,232	2716	61	9,235	2868	59	1.2
Rhodamine B	9,241	1597	1605	1614	4	9,239	2700	71	9,230	2876	43	0.8
Rhodamine S	9,238	1598	1607	1615	8	9,240	2715	68	9,230	2865	64	1.1
Fluorescein Disodium Salt	9,238	1583.1	1587.4	1591.2	9	—	—	—	—	—	—	0.2
2', 7'-Dichloro Fluorescein	9,239	1583.4	1588.0	1591.5	11	—	—	—	—	—	—	0.1

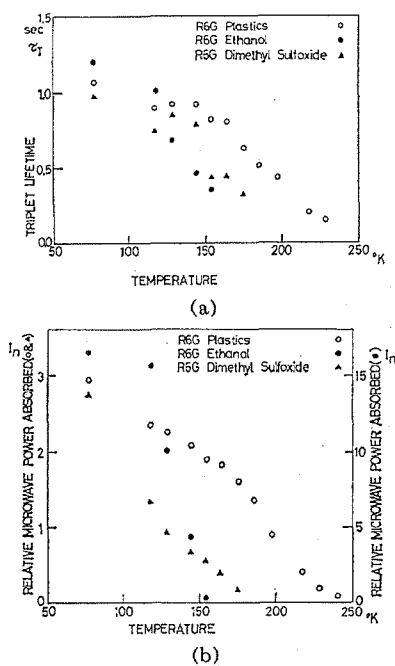


Fig. 1. Temperature dependence of triplet lifetime (a) and relative intensity (b) of H_{min} line of R6G in plastics (4×10^{-4} M), ethanol (5×10^{-3} M), and dimethyl sulfoxide (5×10^{-3} M). Melting points of ethanol and dimethyl sulfoxide are 156 and 281 K, respectively.

it was found that the singlet absorption cross section σ at 5145 Å was 1.5×10^{-16} cm².

Describing the population behavior of dye using a rate-equation analysis under steady-state conditions, we obtain the following equation for triplet concentrations:

$$N_T = \frac{\tau_S \tau_T K_{ST} N \frac{\sigma}{h\nu} I}{1 + \tau_S (\tau_T K_{ST} + 1) \frac{\sigma}{h\nu} I}$$

As a result of computer calculation from this equation with a least squares fit to the measured data in Fig. 2 after substitution of experimentally obtained values, the intersystem crossing rate K_{ST} of rhodamine 6G at 77 K is 0.6×10^5 s⁻¹.

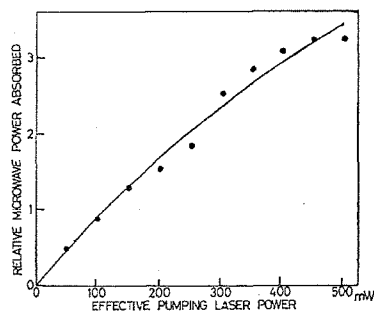


Fig. 2. Dependence of relative intensity of H_{min} line in R6G triplet state on effective pumping laser power (in ethanol solution at 77 K).