Measurement of Fluorescence Lifetimes of Coumarin Laser Dyes with a Mode-Locked Krypton Ion Laser*

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The fluorescence lifetime of four coumarin laser dyes (C-7, C-30, C-102, and C-120) were measured in three different solvents (methanol, ethanol and water) at dilute and lasing concentrations. The lifetime generally decreases for the more hydrophobic dyes as the solvent polarity increases. There is little change with concentration due to the large Stokes shift.

Molecular parameters for lasing dyes are necessary for both modeling laser efficiency and calculating scale-up parameters. It is known that the fluorescence lifetimes of xanthene dyes (e.g., rhodamine 6G) have a marked dependence on concentration [2]. The small Stokes shift is largely responsible for this concentration dependence. Another major class of laser dyes, the coumarins, exhibit a large Stokes shift [3]. Despite being the important class of blue lasing dyes however, there are little experimental data concerning the fluorescence lifetimes of substituted coumarins [4–6]. Consequently, we have measured the fluorescence lifetime of coumarin 7, coumarin 30, coumarin 102, and coumarin 120 in three common laser solvents (water, methanol, and ethanol) at dilute (10^{-6} M) and lasing (10^{-4} M) concentrations.

The coumarin dyes were obtained from Eastman Kodak and used without further purification. Spectroquality methanol (Burdick and Jackson), 95% ethanol (Gold Shield), and deionized and distilled water were the solvents.

A mode-locked krypton ion laser was used as the excitation source [7]. The near uv line at 413.1 nm was used to excite the coumarin dyes. Typical parameters when mode-locked were 300 mW average power and approximately 60 ps FWHM, corresponding to approximately 60 W peak power. The repetition rate was stepped down to 40 kHz before exciting the sample with a Bragg cell. This acousto-optic device was mounted externally to the laser cavity. The excitation beam was attenuated to approximately 6 W peak power and diffused to minimize stimulated emission and non-linear effects.

The fluorescence was detected with a RCA C 31024 photomultiplier tube biased to decrease the response time [8]. A Schott KV 450 long pass filter was used to eliminate scattering. The signal was processed by a boxcar integrator with a 350 ps sampling head (Princeton Applied Research, 162/163). The overall system response of 1.5 ± 0.2 ns was measured with a Ludox scattering solution. The experimental data in all cases were fitted by a single straight line on a semi-log plot. All fluorescence lifetimes were corrected for the system response using a numerical convolute and compare procedure.

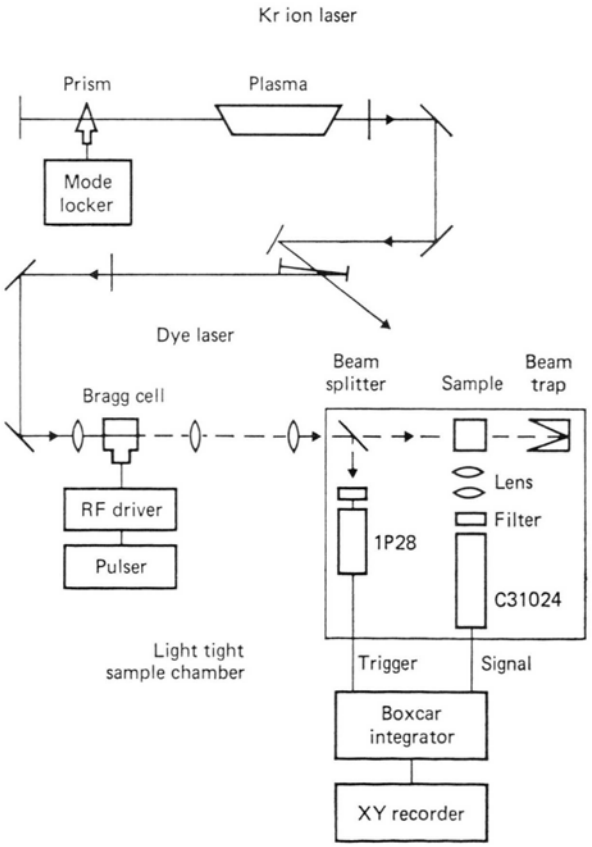

Fig. 1. Schematic of the experimental apparatus for measuring nanosecond fluorescence lifetimes. The excitation source depicted is a mode-locked krypton ion laser synchronously pumping a coumarin dye laser.

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The system was calibrated using solutions of rhodamine 6G in ethanol (10^{-6} M) and riboflavin in water (10^{-5} M). Rhodamine 6G was excited directly with the mode-locked output at 530.9 nm from the krypton ion laser. Riboflavin was excited at 502 nm using the mode-locked output from a synchronously pumped coumarin 30 dye laser [9—11]. Typical output parameters were 40 mW average power and pulsewidths less than 25 ps. Once again, the peak power actually incident on the sample was less than 10 W and the repetition rate was decreased to 40 kHz. Figure 1 is a schematic of the complete experimental apparatus.

Table 1. Fluorescence lifetimes of coumarin laser dyes.

Dye	Solvent	Lifetime (ns)	
		10^{-6} M	10^{-4} M
Coumarin 7	water	2.6	3.0
	methanol	3.4	3.0
	ethanol	3.9	3.9
Coumarin 30	water	1.6	—
	methanol	2.1	1.9
	ethanol	2.7	2.7
Coumarin 102	water	7.4	7.2
	methanol	5.2	4.3
	ethanol	6.5	5.7
Coumarin 120	water	—	6.0
	methanol	—	6.0
	ethanol	—	4.8

The measured lifetimes of 4.8 and 4.4 ns for rhodamine 6G and riboflavin agree well with the literature values [5, 12]. The measured values for the coumarin dyes are summarized in Table 1. All standard deviations are ± 0.2 ns. Signal-to-noise from the dilute coumarin 120 solutions was too poor to obtain good lifetime data. The more concentrated solution of coumarin 30 in water was turbid.

The more hydrophobic coumarins lasing at the longer wavelengths exhibit a smooth increase in lifetime as the solvent becomes less polar and a poorer source of hydrogen bonding (all the coumarins exhibit a large increase in basicity in the excited singlet). The most hydrophilic coumarin, coumarin 120, actually shows a decrease in lifetime as the solvent becomes less polar. For comparison replacing the amino group with a diethyl amino group greatly decreases the lifetime of the excited state [4]. The most rigid dye, coumarin 102, exhibits the longest lifetime.

All the coumarins exhibit a large Stokes shift, attributable to the large increase in dipole moment upon excitation. Thus, there is little change in lifetime upon changing concentration from 10^{-6} to 10^{-4} M.

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