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Estimation of molecular parameters in laser grade dyes: Coumarin 450 and Coumarin 460

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Abstract

Optical gain spectroscopy is exploited to examine photo-physical parameters viz. absorption and emission cross-sections, threshold pump rate, excited to ground state rate constant in two important molecules of Coumarin class of laser grade dyes. The results for the intensity dependent gain coefficient for ethanolic solutions of Coumarin 450 (C-450) and Coumarin 460 (C-460) have been presented in the concentration range from $\sim 1 \times 10^{-5}$ to $\sim 1 \times 10^{-2}$ mol/l under nitrogen laser excitation. The concentration dependent threshold pump rate, small signal gain coefficient and saturation parameter have also been investigated. The results have been explained in terms of variation of fluorescence lifetime with concentration that originates due to excited state absorption.

Keywords: Concentration quenching; Fluorescence lifetime; Small signal gain coefficient; Excited state absorption; Saturation parameter; Threshold pump rate; Optical gain

1. Introduction

In recent years there has been much research interest in the study of various molecular parameters of laser grade dyes known to be coherent source of radiation with a wide tuning range of applications. Coumarins have been found useful as optical brighteners, fluorescence indicators and even as sunburn preventive materials. Due to their analytic and biological uses, the study of Coumarin derivatives has special topical importance. Coumarin molecule as such is non-fluorescent, but it exhibits intense fluorescence on substitution of various functional groups at different positions [1–4]. In general, electron-donating substituents tend to enhance emission intensity while electron-withdrawing substituents tend to diminish it. The intensity of the dye laser beam cannot be increased over a certain range of the pump power and is limited by saturation. This is attributed due to photo-quenching effect as has been reported by various research groups [5,6]. Speiser and coworkers have studied the photo-quenching properties in various dyes and have shown that the effect plays a crucial role in the performance of pulsed laser pumped dye laser systems [7]. However, there are very few experimental studies to explore the phenomenon of excited state absorption associated with photo-quenching for estimating the molecular parameters. The present study focuses on photo-quenching effects in C-450 and C-460 using optical gain measurements. The study of optical gain spectroscopy has been used because of its added advantage over other type of spectroscopy, such as, it is geometry dependent and not directly related to fundamental parameters; it yields unique information about the excited state population density not obtainable by emission or absorption spectroscopy.

2. Experimental details

The dye solutions of different concentrations were pumped by a Molectron (UV-24) pulsed N_2 laser that delivers pulses of 900 kW peak power and 10 ns duration. The rectangular beam

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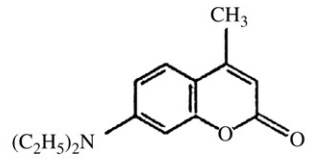
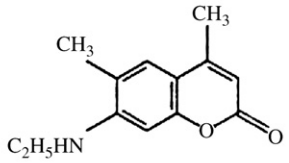


7 Diethyl Amino-4-Methyl coumarin
C 460



7 Ethyl Amino-4,6-dimethyl coumarin
C 450

Fig. 1. Structures of Coumarins.

of cross-section 0.6×3.2 cm^2 at the exit was focused to a line by using a 20 cm focal length cylindrical lens onto a quartz dye cell. The dyes were obtained from M/s Exciton Inc. Ohio, USA and were used as such without further purification. The output from the dye solution was passed through a Jarrel-Ash 0.5 m monochromator to select various wavelengths of interest, and was allowed to fall on the fast photomultiplier tube (Philips XP2020). The pre-amplifier output of photomultiplier (PM) tube after proper amplification was recorded on a 100 MHz oscilloscope. A number of thin glass slides (attenuators) were introduced in between the lens and the dye cell to change the pump intensity. A micrometer arrangement having the least count of 0.005 mm was used with a movable screen to expose the dye solution at different cell lengths. The detailed experimental arrangement has been shown elsewhere [8]. The structure of dyes under investigation is shown in Fig. 1. These Coumarin dyes are polar H-bonding dyes and they undergo dipole–dipole type interaction in polar solvents that lowers the energy levels and, therefore, broadens the spectra [9]. Ethanol being polar solvent is used for all the studies under investigation.

3. Results and discussion

The variation of optical gain with pump intensity at various concentrations of dyes under study has been shown in Figs. 2 and 3. The curves so obtained are almost similar except for little variation in the profiles of maximum and related slope values. The reduction in the optical gain value at higher pump intensities after reaching the maximum can be understood to be due to one of the prominent competitive processes of excited state absorption associated with photo-quenching effect. The intensity dependent fluorescence and hence quantum efficiencies are likely to yield significant information about excited state parameters. The present study provides

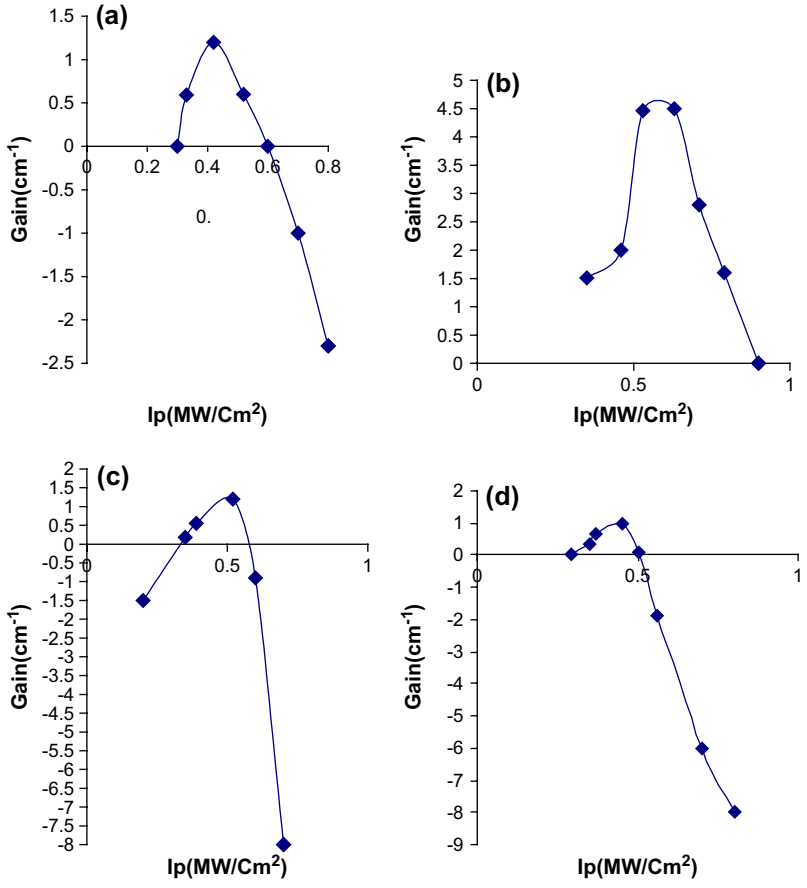


Fig. 2. Gain vs. pump power for C-450 in ethanol: (a) at concentration 1×10^{-2} mol/l; (b) at concentration 5×10^{-3} mol/l; (c) at concentration 1×10^{-3} mol/l; (d) at concentration 1×10^{-4} mol/l [13].

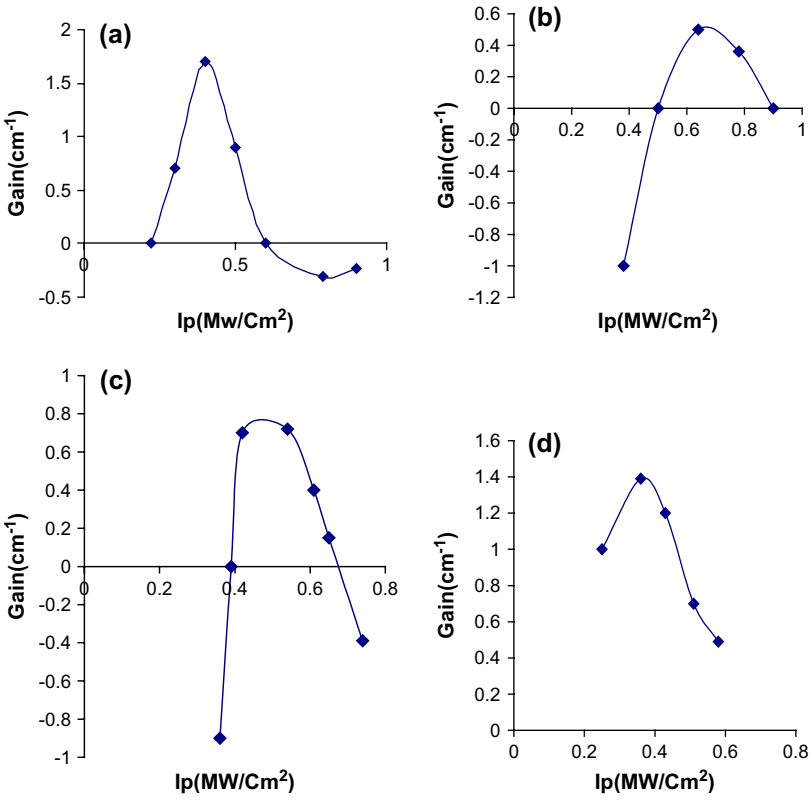


Fig. 3. Gain vs. pump power for C-460 in ethanol: (a) at concentration 1×10^{-4} mol/l, $\lambda = 442$ nm; (b) at concentration 1×10^{-4} mol/l, $\lambda = 448$ nm; (c) at concentration 5×10^{-5} mol/l, $\lambda = 442$ nm; (d) at concentration 1×10^{-5} mol/l, $\lambda = 448$ nm [13].

the estimates of the molecular parameters of excited state of the dye molecules, under intensity dependent gain. These results are in conformity with the conclusion drawn by Spieser [10].

The absorption (α_a) and saturation (γ_s) parameters can be derived through steady state gain equation as has been derived from detailed theoretical considerations already reported in [11]:

$$\alpha_a = \sigma_{01}(l)N \quad (1)$$

$$\gamma_s = N\sigma_{em} \quad (2)$$

where N is the total molecular concentration, $\sigma_{01}(l)$ and σ_{em} are the absorption and emission cross-sections at the laser frequency ν_1 of the state s_1 and s_0, respectively.

The threshold intensity (I_{th}) at a given concentration can be written as follows:

$$I_{th} = \sigma_{01}(l)A_{s1-s0}/\sigma_{01}(p)\sigma_{em} \quad (3)$$

or

$$W_{th} = \sigma_{01}(l)A_{s1-s0}/\sigma_{em} \quad (4)$$

Table 1
Various molecular parameters in C-450 and C-460 in ethanolic solutions

Concentration, mol/l	Wavelength, nm	Small signal gain coefficient (β), cm/MW	Absorption coefficient (α_a), cm^{-1}	Absorption cross-section ($\sigma_{01}(l)$), cm^2	Saturation parameter (γ_s), cm^{-1}	Emission cross-section (σ_{em}), cm^2	A_{s1-s0}, 10^9 s^{-1}	Threshold pump rate (W_{th}), 10^9 s^{-1}	τ, 10^{-9} s
Coumarin 450									
1×10^{-2}	–	1.6	6.5	1.0×10^{-18}	1.30	2.1×19^{-19}	0.49	2.40	2.04
5×10^{-3}	435	6.3	4.4	7.3×10^{-18}	4.49	7.4×10^{-18}	0.50	0.49	2
1×10^{-3}	476	9.1	1.5	2.4×10^{-18}	1.80	2.9×10^{-18}	0.54	0.44	1.85
1×10^{-4}	433	2.8	0.8	1.3×10^{-17}	1.00	1.6×10^{-17}	0.47	0.38	2.12
Coumarin 460									
1×10^{-4}	442	2.03	2.5	4.1×10^{-17}	1.58	2.6×10^{-17}	0.39	0.61	2.56
1×10^{-4}	448	1.61	3.2	5.3×10^{-17}	0.50	0.8×10^{-17}	0.65	4.30	1.53
5×10^{-5}	442	1.75	0.5	8.3×10^{-17}	0.76	1.2×10^{-16}	0.40	0.27	2.5
1×10^{-5}	448	5.0	0.1	1.6×10^{-17}	1.40	2.3×10^{-16}	0.37	0.02	2.7
Coumarin 495[a]									
1×10^{-3}	536	4.8	0.3	0.4×10^{-18}	2.9	4.8×10^{-18}	0.67	0.06	1.4
1×10^{-3}	538	5.4	2.0	3.3×10^{-18}	3.1	5.1×10^{-18}	0.95	0.61	1.05

[a] See Ref. [11].

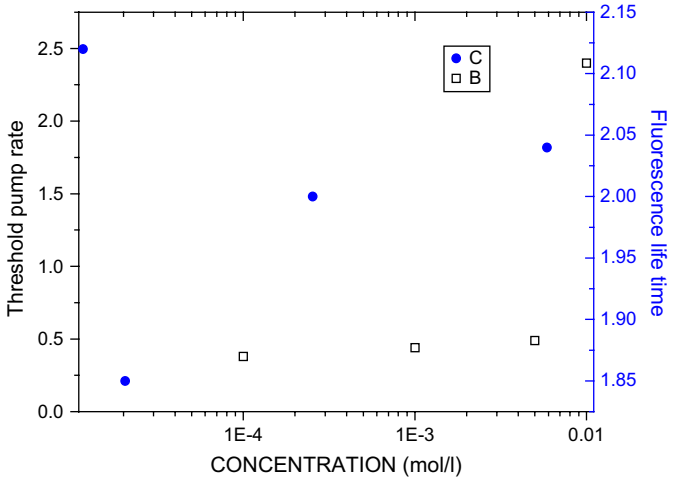


Fig. 4. Concentration dependence of dye C-450 on threshold pump rate (W_{th}) and fluorescence lifetime (τ); □, W_{th} and ●, τ ($1E-x \sim 1\times10^{-x}$, $x=4, 3, 2, 1$).

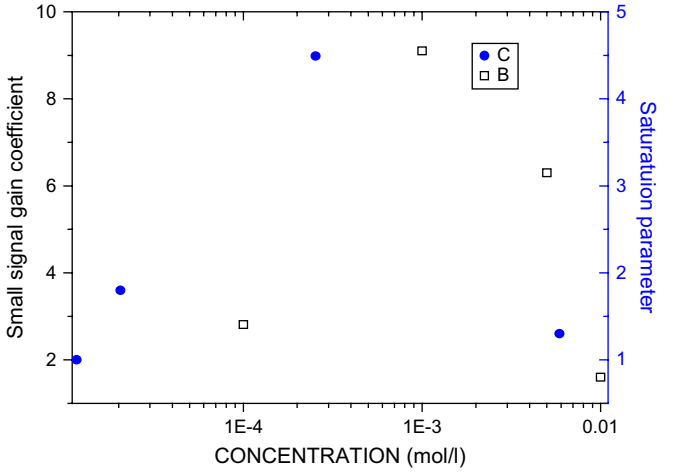


Fig. 6. Concentration dependence of dye C-450 on small signal gain coefficient (β) and saturation parameter (γ_s); □, β and ●, γ_s ($1E-x \sim 1\times10^{-x}$, $x=4, 3, 2, 1$).

where A_{s1-s0} is the excited to ground state rate constant and $\sigma_{01}(p)$ is the absorption cross-section at the pumping frequency ν_p, and W_{th} is threshold pump rate. The molecular parameters calculated for ethanolic solutions of C-450 and C-460, using these equations have been given in Table 1. The value of small signal gain coefficient, β, has been determined from the slope of the straight-line portion of the pump intensity vs. gain curves (Figs. 2 and 3). Saturation and absorption parameters are calculated using Eqs. (1) and (2), respectively. The rate constant for the transition from first excited singlet state to ground state is obtained from Eq. (3).

Fig. 4 depicts the variation of threshold pump rate (W_{th}) and fluorescence lifetime as a function of concentration for C-450. There is a slightly large value of W_{th} at a concentration of $\sim1\times10^{-4}$ mol/l due to trapping of radiation that can be termed as self-absorption–reemission. However, at higher concentrations of $\geq5\times10^{-3}$ mol/l, the increased value of W_{th} may be due to polarization effect and energy deficit in rotation–relaxation of the molecule in solvent environment or may be it could be due to inner filter effect. The effect describes that at low concentration the emission of light is uniform from the front to the back of the sample cuvette and at high concentration more light is emitted from the front than the back. As emitted light only from the middle of the cuvette needs to be detected, the optimum concentration must be chosen so as to assure accurate lifetime measurements. These results are in agreement with the earlier observations made in another Coumarin dye molecule (C-500) by Sanghi and Mohan [12]. The study further shows the decreasing trend of estimated fluorescence lifetime at lower concentration in both the dyes C-450 and C-460 (Figs. 4 and 5). The relevant parameters determining the concentration dependence of the lifetime are radiation trapping, concentration quenching and excimer formation. The behavior of the lifetime at lower concentration is understood to be due to the effect of radiation trapping, that is, self-absorption–reemission that causes the increase in lifetime of the excited state. The important feature of the study, the slight increase in the lifetime values at higher

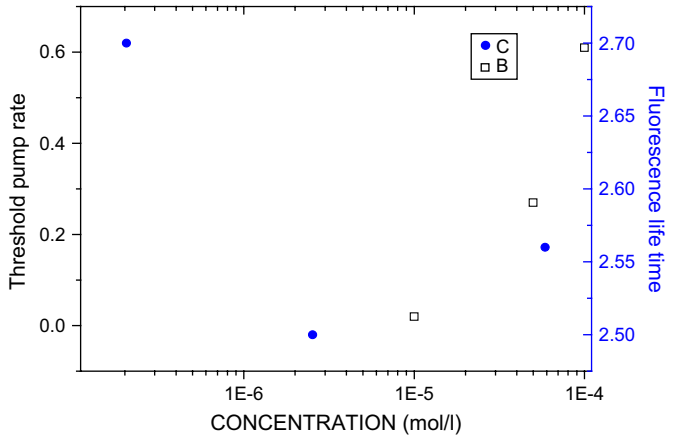


Fig. 5. Concentration dependence of dye C-460 on threshold pump rate (W_{th}) and fluorescence lifetime (τ); □, W_{th} and ●, τ ($1E-x \sim 1\times10^{-x}$, $x=6, 5, 4, 3, 2, 1$).

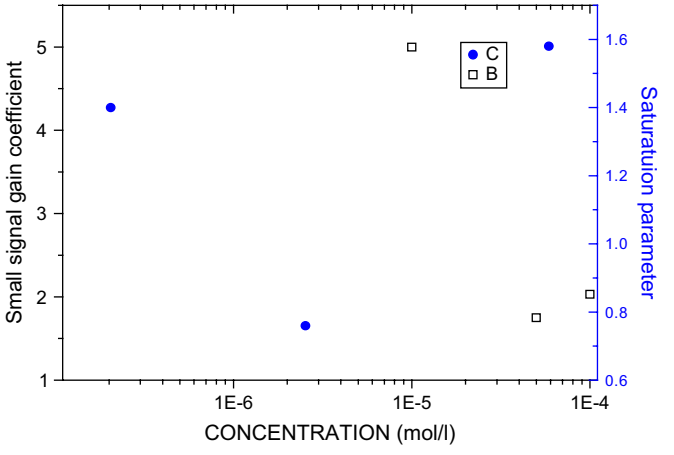


Fig. 7. Concentration dependence of dye C-460 on small signal gain coefficient (β) and saturation parameter (γ_s); □, β and ●, γ_s ($1E-x \sim 1\times10^{-x}$, $x=6, 5, 4, 3, 2, 1$).

concentrations of $\geq 1 \times 10^{-3}$ mol/l, may be attributed due to the excimer formation at higher concentration in which there is an existence of an appreciable fraction of the dye molecules in the excimer state.

The variation of the small signal gain coefficient (β), and saturation parameter (γ_s) with concentration in C-450 has been represented in Fig. 6. A sharp increase in the values of β at concentration $\sim 1 \times 10^{-3}$ mol/l and γ_s at $\sim 5 \times 10^{-3}$ mol/l has been observed and it is again understood on the basis of exciplexes formation in excited states causing the increase in lifetime. At concentration $\sim 1 \times 10^{-4}$ mol/l, the value of β and γ_s decreases probably due to quenching of dye molecules.

The decreasing trend in both β and γ_s at lower concentration of $\sim 5 \times 10^{-5}$ has also been observed in C-460 (Fig. 7) and is again understood to be due to radiation trapping and concentration quenching. The higher value of β and γ_s at higher concentration ($\geq 5 \times 10^{-5}$) is due to aggregate formation in excited states causing the increase in lifetime. This increase in lifetime corresponds to an increase in the small signal gain coefficient and hence the saturation parameter.

4. Conclusion

The present investigation of intensity dependent gain coefficient on dye molecules, C-450 and C-460 provides significant information about the excited state parameters. Excited state absorption associated with photo-quenching plays an important role in the pumping of laser dyes for pulsed laser pumped dye laser systems. These results allow to estimate the various molecular parameters such as absorption and emission cross-sections without exploiting more sophisticated techniques.

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