

Effect of the Excitation Source on the Quantum-Yield Measurements of Rhodamine B Laser Dye Studied Using Thermal-Lens Technique

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A dual-beam transient thermal-lens technique was employed for the determination of absolute fluorescence quantum-yield measurements of Rhodamine B laser dye in different solvents. We investigated the effect of excitation on the absolute fluorescence quantum yield of Rhodamine B. 514 nm radiation from an argon ion laser was used as a cw excitation source and 532 nm pulses from a Q-switched Nd:YAG laser were used as a pulsed excitation source. The fluorescence quantum-yield values were found to be strongly influenced by environmental effects as well as the transient nature of the excitation beam. Our results also indicate that parameters, like the concentration of the dye solution, aggregate formation and excited state absorption, affect the absolute values of the fluorescence yield significantly.

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Introduction

Photothermal spectroscopy is a group of highly sensitive methods used to measure the optical absorption and thermal characteristics of a sample.¹⁻³ The basis of photothermal spectroscopy is a photo-induced change in the thermal state of the sample. The advantage of the photothermal technique is that it can be used to investigate the optical properties of materials that are unsuitable with traditional spectrophotometry. In fact, both thermal and fluorescence spectroscopy are complementary: thermal spectroscopy measures the photon energy, which has been converted to heat, while fluorescence spectroscopy observes re-emitted photons. When a medium is illuminated with laser radiation, some of the incident energy is absorbed by the molecules in the ground state, and becoming excited to higher energy states in the process. Following the absorption of a photon, any excess energy of a molecule can be dissipated in many ways. When the decay involves a radiationless process, localized temperature increases are produced, leading to heating of the sample. The thermal fluctuations produced by nonradiative relaxations may be probed optically, since the resulting density change also produces a change in the refractive index. Specifically, the transient refractive index forms an effective lens, which diverges the light as it passes through a sample. This phenomenon is called thermal lensing, and provides a nice example of laser spectroscopy.

The fluorescence quantum yield (Q_f), one of the key photophysical quantities, is a measure of the rate of nonradiative transitions that compete with the emission of light. The

absolute values of Q_f of organic laser dyes are practically important, because they are necessary to calculate thresholds for laser action.⁴ Measurements based on photothermal effects are capable of giving absolute fluorescence yields of highly fluorescent solutions with high accuracy and reproducibility. In order to evaluate the absolute fluorescence efficiency, we must consider both radiative and nonradiative processes taking place in the medium. Because the contribution from nonradiative processes is not directly measurable using the traditional optical detection methods, thermo-optic techniques, such as photoacoustic (PA) and thermal lens (TL) spectroscopic methods, have been adopted for this purpose.^{5,6}

In this present study, the sensitivity and viability of photothermal lensing technique were exploited to determine the absolute fluorescence quantum yield of Rhodamine B (RhB) laser dye. The Q_f values were found to be strongly influenced by different parameters, like environmental effects, concentration of the dye solution and type of excitation (cw or pulsed) source used for the thermal lens measurements.

Experimental

Details of the experimental set up used for the cw thermal lens⁷ and pulsed thermal lens⁸ are given elsewhere. For a transient thermal lens, 532 nm radiation from a frequency-doubled Q-switched Nd:YAG laser (FWHM 9 ns) was used as the pump source to generate a thermal lens in the medium. A 632 nm beam from a 1-mW He-Ne laser source was used to probe the thermal lens effect. The pump and probe beams, focused by separate lenses, passed collinearly through the sample. A filter was placed in the path of the emergent beams, which allowed only the 632 nm wavelength to reach the detector. The thermal lens signal was detected by sampling the intensity of the center portion of the transmitted probe beam by using an optical fiber, where the tip of the fiber served as a finite aperture. The

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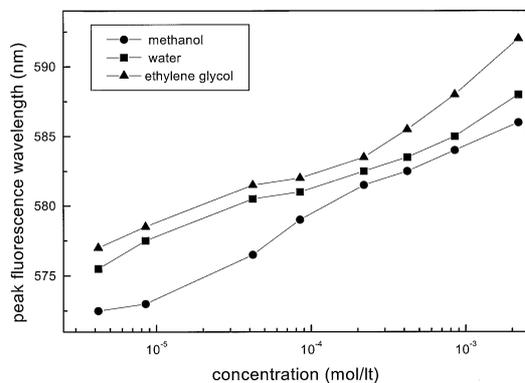


Fig. 1 Variation in the peak fluorescence wavelength with the concentration for RhB laser dye in different solvents under cw argon-ion laser excitation.

pulsed thermal lens signal was detected using a monochromator-photomultiplier tube (PMT) assembly, and was processed with a digital storage oscilloscope. For a cw thermal lens, 514 nm radiation from an argon ion laser was used. The pump beam was chopped at 10 Hz, which allowed lock-in detection of the thermal lens formed in the sample.

For fluorescence studies, the front surface emission was collected and focused by a lens on to an aperture formed by the tip of another optical fiber attached to the entrance slit of a 1-m Spex monochromator, which was coupled to a PMT. The PMT output was fed to a boxcar averager/gated integrator and the averaged output from the boxcar averager (for pulsed excitation) was fed to a chart recorder. For cw laser excitation, a digital lock-in amplifier was used for signal processing. The emission was wavelength scanned in the desired region. The emission showed the characteristic fluorescence spectrum.

Results and Discussion

The absolute fluorescence quantum yield of Rhodamine B was determined using thermal lens method according to the following equation:⁹

$$Q_f = \left(1 - \frac{P_{th}}{P_a}\right) \frac{\lambda_f}{\lambda} \quad (1)$$

where P_{th} is the thermal power degraded into heat, which is directly proportional to the TL signal; P_a is proportional to the TL signal corresponding to the concentration at which the fluorescence intensity is quenched completely, and the ratio of the fluorescence peak wavelength (λ_f) to excitation wavelength (λ) takes account of the Stokes shift.

Fluorescence and thermal lensing studies were carried out for RhB laser dye in different solvents under cw and pulsed laser excitation over a wide concentration range. A concentration dependent change in the fluorescence spectra was observed. The fluorescence spectrum of the highest concentration differed strongly from that recorded at the lowest concentrations. The difference between these is significant in the case of the red shift of the fluorescence and the enhancement of the half width of the fluorescence spectrum with increasing concentration. Figures 1 and 2 represent the peak fluorescence wavelength (pfw) of RhB as a function of the concentration in alcoholic, aqueous and ethylene glycol solutions illuminated using cw and pulsed lasers, respectively. The observed spectral shifts can be

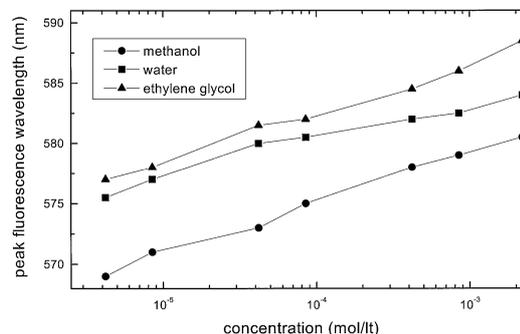


Fig. 2 Change in the peak fluorescence wavelength with the concentration for RhB laser dye in different solvents under Q-switched Nd:YAG laser excitation.

used as a guide to the interaction of the dye with the solvent media.

From Figs. 1 and 2, it can be seen that the fluorescence spectrum of the dye was shifted to smaller energies when the dye concentration was increased. A list of the environmental factors that affect fluorescence phenomena includes interactions with solvents and other dissolved compounds, the temperature, the pH and the concentration of the fluorescence species. Both the absorption and emission spectra as well as the quantum yields of fluorescent molecules are influenced by these parameters. In order to have any effect of aggregates on the fluorescence spectrum, Arbeloa *et al.*¹⁰ carried out these experiments while varying optical path-length of the sample; they found that the fluorescence spectrum of concentrated solutions recorded using very short optical path had the same shape as that observed in dilute solutions. Therefore, aggregate formation at high concentrations had a negligible effect on the observed fluorescence peak shift. The observed peak shift in the fluorescence spectra is a consequence of reabsorption and re-emission.¹¹ Since the emitted wavelength was longer than the absorbed one, reabsorption of fluorescence generated fluorescence emission at redder side. Absorption saturation would lead to a similar red shift, depending on the medium. If the molecules have closely lying levels of different absorption cross section, absorption saturation to each level would lead to a wavelength shift. However, in general, the red shift in dyes is not due to saturation.

It was interesting to compare the pfw shift of dye solutions (in the three solvents studied) under the two different types of excitation *i.e.*, cw and pulsed. The red shift was found to be large if the fluorescence measurements were made with cw excitation compared with pulsed excitation. This can be attributed to the fluorescence reabsorption being more predominant in dye solutions, and hence large Stokes shifts were expected when they were illuminated with cw lasers. With rising pump pulse, intensity of the fluorescence reabsorption was reduced, and the pfw shifted to shorter wavelengths, as is the case with pulsed laser excitation.

Thermal lensing measurements were carried out for RhB solutions with cw and pulsed excitation in different solvents for the determination of Q_f values. The difference in the methods of sample illumination may affect the temporal behavior of thermal lens formation. Indeed, with cw illumination, the measurement was made when the thermal lens was in equilibrium, *i.e.*, when the rate of heat input from the relaxation processes was just balanced by the rate of heat conduction out of the illuminated region; a constant temperature gradient was

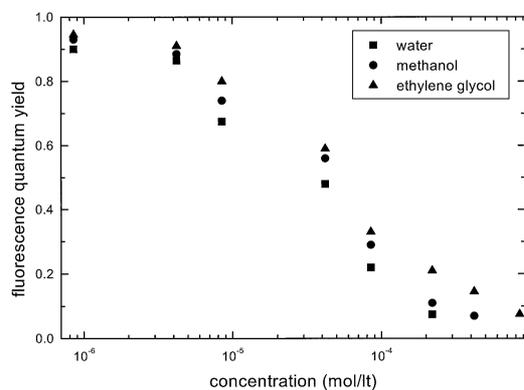


Fig. 3 Variation of Q_f with the concentration of RhB laser dye in different solvents measured using the cw thermal lens method.

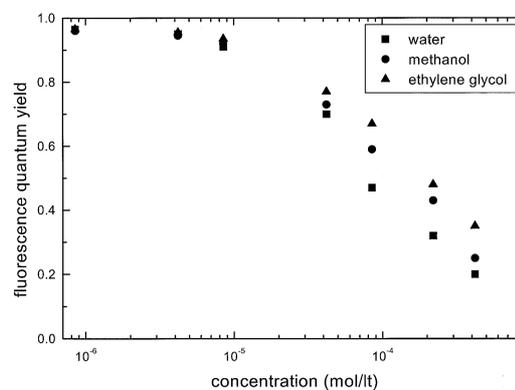


Fig. 4 Variation of Q_f with the concentration of RhB laser dye in different solvents measured using the transient thermal lens method.

achieved, and both the slow and fast decay processes were in equilibrium. On the contrary, with pulsed illumination, the time scales for the various processes were different. A thermal lens from fast relaxation occurred in a short time ($\sim \mu\text{s}$) with respect to subsequent heat conduction, which was of the order of milliseconds. If the slow decaying processes occur on a time scale which is much greater than the acoustic transit time, the relation between the amount of released thermal energy and the magnitude of thermal lens signal may no longer be the same.

The absorption spectra of RhB in methanol, water and ethylene glycol showed that absorption at 632 nm is very small, and hence any perturbation due to the probe beam can be neglected. The dependence of the TL signal on the laser power for RhB in different solvents was studied; the results show that the thermal lens signal intensity varies linearly for the range of cw laser power used for fluorescence quantum yield measurements. With cw excitation, the dependence of the TL signal at powers greater than 20 mW was not studied because aberrational effects began to appear during lensing. In the case of pulsed excitation, at higher laser intensities we observed processes like excited-state absorption along with two-photon absorption.^{8,12} The present thermal lens measurements were performed at low energy levels where the thermal lens signal intensity varied linearly with the laser energy.

Figures 3 and 4 show the variation of Q_f obtained using Eq. (1) for RhB in different solvents as a function of the concentration with cw and pulsed illumination, respectively. It must be noted that the quantum yield of the dye solution decreased at higher concentrations irrespective of the solvent and type of excitation used. The rapid decrease in Q_f at higher concentrations can be attributed mainly to the formation of dimers and higher aggregates which have zero or very small values of Q_f . The strength of the aggregation depends on the structure of the dye, the solvent, the temperature, the pressure and other factors. The decrease in the quantum efficiency at higher concentrations is caused by Foster-type energy transfer to dimers. The equilibrium between monomer and dimer shifts to the side of the latter with increasing concentration. The dimerization of laser dyes like Rhodamine B and Rhodamine 6G is severe enough to prevent laser action unless a deaggregating agent like hexafluoroisopropanol or Ammonyx LO is added to the solution.⁴ In the present case, no such deaggregating agents were added, and hence a significant reduction in Q_f could be expected due to aggregate formation at higher concentrations.

The fluorescence yields reported here demonstrate that it is

generally unjustified to assume that the fluorescence parameters are minimally influenced by the solvent. The absolute yield of RhB measured using this method shows solvent variations of 1 – 15%, especially at higher concentrations, indicating that solvent-solute interactions play a measurable role in modifying the unimolecular decay constants for the excited singlet electronic states. The values of Q_f in aqueous solutions are lower and apparently more concentration dependent than in the corresponding methanolic and ethylene glycol solutions. Two factors are responsible for such a variation in the obtained Q_f values. First, the value of Q_f in aqueous solutions can be expected to be less than that in methanol and ethylene glycol due to a strong quenching effect of water on the fluorescence. Second, as in the case of methanolic and ethylene glycol solutions, the inner filter effect can be expected to result in a decrease of Q_f with increasing concentration.⁴ These two effects would result in a curve for the aqueous Q_f values paralleling those of the methanolic and ethylene glycolic Q_f values. Although it appears to be true in more dilute aqueous solutions, at concentrations above 5×10^{-5} mol/l, there is a more rapid decrease in the value of Q_f , which is due to a considerable formation of dimers in the aqueous solutions. It is interesting to note that the quantum yield of RhB is higher in ethylene glycol than in water or methanol. This suggests that the chromophore is fully rigid in the ground state and loosens up only after excitation, provided the solvent has a low viscosity. In ethylene glycol, the viscosity is sufficiently high to prevent thermal equilibrium from being reached during the radiative lifetime of a few nanoseconds. Hence, the planarity of the ground state is not lost before light emission takes place.⁴

On comparing the values of Q_f obtained with different sources of illumination, the results show that its value does not vary much at low concentrations. With increasing concentration, the absolute value of Q_f decreases more rapidly with cw laser excitation compared to pulsed laser illumination. One of the major mechanisms that may quench the fluorescence emission at these concentrations is relaxation to a triplet state, or intersystem crossing.

It is known that triplet-triplet (T-T) absorption strongly influences the laser action of dyes. It is noteworthy that under the conditions of our experiments with cw excitation of dye solutions the lifetime of the triplet state is much less than the duration of the modulated cw laser excitation. In this case, the concentration of triplet molecules is associated with the concentration of singlet excited molecules (S^*) by the expression¹³ $T = (\tau_T/\tau_S^*)\phi_T S^*$, where τ_T and τ_S^* are the lifetime

of the triplet and singlet excited states, respectively, and ϕ_T is the quantum yield of the intersystem crossing. Hence, a slowly rising pump light pulse would transfer most of the molecules to the triplet state. The intersystem crossing is a dominant mechanism in the cw mode excitation, which effectively reduces the luminescence yield values. On the other hand, the population of the triplet level can be held arbitrarily small if the pumping light intensity rises fast enough, that is, if $t_p \ll 1/k_{st}$, where k_{st} is the $S_1 \rightarrow T_1$ intersystem crossing rate and t_p is the pulse width of the laser. In such laser pumped dye laser systems one may neglect all triplet effects in a first approximation. In the present case, the role of intersystem crossing could be neglected with pulsed laser excitation, since the pulse width of the pump laser (t_p) 9 ns, is such that $t_p \ll 1/k_{st}$, where k_{st} is 10^6 s^{-1} in RhB.¹⁴ This explains the anomaly observed in the variation of Q_f values measured with the different sources of illumination.

The triplet-state absorption is sensitive to the wavelength of excitation. If there is any triplet-state absorption of the excitation laser light, the thermal energy coming out by the relaxation from the higher excited triplet state should also contribute to the thermal lens signal. The triplet states of Rhodamine B have been studied in aqueous and alcohol solutions by means of flash photolysis by Korobov *et al.*¹³ Their studies showed negligible, or no, T-T absorption for the wavelengths 514 nm and 532 nm, whereas the T-T absorption spectra overlaps the singlet fluorescence. Thus the influence of T-T absorption at the pump wavelengths used in our studies could be safely neglected. Moreover, T-T absorption occurs at moderate or high laser intensities.^{5,15} We used low laser powers for measuring the Q_f values. Thus a contribution to the thermal lens signal by relaxation from the excited triplet states is ruled out.

Conclusion

A dual-beam TL technique was successfully employed for determining the absolute value of the fluorescence quantum yield for a wide range of concentrations. For fluorescing materials, like RhB, the TL method is suitable for determining the quantum efficiency, since it requires no standard and is very convenient and useful, especially at higher concentrations, namely near to the fluorescence-quenching regimes. Although it is difficult to ascertain whether photothermal methods are more accurate than fluorescence measurements, the former are less sensitive to experimental errors. While fluorescence generally senses a narrow band of wavelengths, and only a small part of the emitted photons, the photothermal methods are sensitive to the complementary part of the total fluorescence, which means that any change in the emission spectrum arising from the interaction of the emitted photons with the solution are expected not to affect the photothermal signal. However, in strongly absorbing media, there exists an upper limit for the pump beam power, which gives a noise-free TL signal when dual-beam TL technique is employed. This method also requires careful attention to all of the possible photophysical processes associated with the relaxation of the fluorescent

compound.

The fluorescence yields reported here demonstrate that the fluorescence parameters are influenced by the environment of the fluorescing molecule, processes like nonradiative conversion and aggregation of the dye molecule. These are strongly dependent on the excitation source and solvent characteristics, as well as the concentration of the dye solution. Our results indicate that a higher fluorescence yield can be obtained for RhB in ethylene glycol than in methanol or water. This quantum-yield variation with the solvent indicates that solvent-solute interactions play a measurable role in modifying unimolecular decay constants for excited singlet electronic states. The variation in the quantum yield with the concentration of the dye solution showed a decreasing tendency irrespective of the solvent used. At high concentrations, the fluorescence quantum yields became very low, indicating an enhanced non-radiative decay of the excited aggregates. The quantum-yield values were also found to depend on the type of excitation used for the thermal lens formation. With cw excitation, the reduction in the Q_f values is more rapid than with pulsed laser excitation. The presence of inter-system crossing plays a major role in these peculiar phenomena.

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