

## PULSED PHOTOACOUSTIC DETERMINATION OF ABSOLUTE FLUORESCENT QUANTUM YIELD OF THE LASER DYE RHODAMINE B

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Pulsed photoacoustic technique which is found to be a very convenient and accurate method, is used for the determination of absolute fluorescence quantum yield of laser dye rhodamine B. Concentration and power dependence of quantum yield of rhodamine B in methanol for excitation at 532 nm is reported here. Results show that a rapid decrease in quantum yield as the concentration is increased and finally it reaches the limit corresponding to fluorescence quenching.

### 1. Introduction

Fluorescence quantum yield, defined as the fraction of those initially excited molecules which returns directly to the ground state by a radiative transition, is an important quantity in the context of radiation processes in molecules. The fluorescence quantum yield is one of the important parameters in determining the lasing characteristics of the active medium of a laser and for calculating thresholds for laser action. In conventional luminescence yield measurements, the luminescence intensity of the material under study is compared with a standard substance with known quantum yield.<sup>1</sup> In this kind of measurements it is necessary to introduce corrections for system geometry, re-absorption, polarization etc. Even after making the various corrections the accuracy of the quantum yield values is rather poor. In order to evaluate absolute quantum efficiency, we have to consider both the radiative and nonradiative processes taking place in the medium. As the contribution from nonradiative processes is not directly measurable using the traditional optical detection methods, thermo-optic techniques such as photoacoustic<sup>2-4</sup> and thermal lensing<sup>5,6</sup> have been adopted widely for this purpose in recent times.

The advantages of using photoacoustic (PA) technique for characterizing various molecular processes have been extensively discussed by various workers.<sup>7-9</sup> The

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PA effect is essentially an energy — conversion process. On irradiation with a pulsed laser beam, a part of the absorbed energy is converted into translational energy of the molecules by nonradiative relaxation processes. This deexcitation channel finally results in the production of an acoustic wave. The amplitude of the acoustic signal obviously depends on the amount of energy absorbed.<sup>10</sup> Of the several configurations of PA measurements pulsed PA is the most sensitive as the high power delivered by a pulsed laser can generate acoustic signals of considerable magnitudes. Because of its high sensitivity, pulsed PA is ideally suited for probing the nonradiative relaxations and this technique has recently been used to study two photon absorption processes in certain laser dyes<sup>11</sup> as well as in organic vapours.<sup>12</sup>

It may be recalled that for fluorescent materials, PA detection is sensitive to the total fluorescence emission. Any change in the emission characteristics will affect the PA signal.<sup>13</sup> PA detection is very effective if small variations in quantum yield of highly fluorescent materials are to be studied because the change in PA signal will be relatively much larger than that occurring in the fluorescence emissions. This paper presents the results of measurements of absolute fluorescence quantum yield of the laser dye rhodamine B using pulsed PA experimental set up.

## 2. Theoretical

The method is based on the principle of energy conservation. If  $I_0$  is the power of the incident excitation beam and  $I_t$  is the power of the transmitted beam, the absorbed power is the sum of the luminescence emission power  $I_l$  and the thermal power degraded to heat  $I_{th}$ , provided that any photo chemical reaction is absent. Hence,

$$I_0 = I_{th} + I_l + I_t \quad (1)$$

so that the transmission ratio is given by

$$T = \frac{I_t}{I_0} \quad (2)$$

and absorbance

$$A = 1 - T \quad (3)$$

Thus the absorbed power is given by

$$AI_0 = I_{th} + I_l \quad (4)$$

In the case of a totally fluorescence quenched sample we can consider entire excitation energy to be converted into heat by nonradiative relaxation process and hence the fluorescence quantum yield ( $Q_f$ ) is given by<sup>13,14</sup>

$$Q_f = \frac{I_l}{AI_0} \frac{\lambda_f}{\lambda} = \left[ 1 - \frac{I_{th}}{I_\alpha} \right] \frac{\lambda_f}{\lambda} \quad (5)$$

where  $I_\alpha = AI_0$  and the ratio of the fluorescence peak wavelength  $\lambda_f$  to excitation wavelength  $\lambda$  takes account of the stokes shift.  $I_{th}$  is directly proportional to the PA

signal  $P_{th}$  and  $J_a$  is proportional to PA signal  $P_a$  corresponding to the concentration at which the fluorescence intensity is quenched completely. By knowing  $\lambda_f$ ,  $P$  and  $P_a$  one can directly calculate the quantum efficiency  $Q_f$  from equation

$$Q_f = \frac{\lambda_f}{\lambda} \left( 1 - \frac{P}{P_a} \right). \quad (6)$$

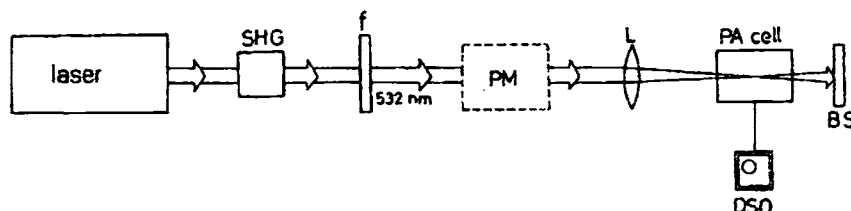


Fig. 1. Schematic diagram of the experimental set up: SHG, second-harmonic generator; f, dichroic filter; PM, laser energy/power meter; L, convex lens; DSO, digital storage oscilloscope; and BS, beam stopper.

### 3. Experimental Set Up

The schematic experimental set up is shown in Fig. 1. Except for minor variations the design of the PA cell is similar to that described by Patel and Tam.<sup>4</sup> PA cell is made of stainless steel and it is provided with glass windows for the entry and exit of the laser beam. The acoustic transducer that detects the laser induced PA signals consists of a lead-zirconate-titanate (PZT) disc of 4 mm thickness and 15 mm diameter, firmly mounted in a stainless steel chamber which is screwed onto the PA cell.<sup>8</sup> The purpose of mounting the PZT disc inside the stainless steel casing is to minimize external electrical pick up and to prevent sample contamination by PZT (and vice versa). The diaphragm of the transducer chamber has a thickness of 0.5 mm and it is finely polished. A lead disc followed by a copper disc forms the backing of the PZT, which is spring loaded within the chamber. Spurious electrical pick-up is negligible, and signal ringing is reduced to a tolerable level.

The second harmonic output beam (532 nm) from a (Q-switched Nd:YAG laser is focused by a convex lens (focal length 5 cm) into the PA cell containing the sample at room temperature (23°C). The lens position is adjusted so that the beam focus is at the center of the cell. A dichroic filter oriented at 45° to the beam axis separates the fundamental frequency component (1064 nm) from the second harmonic. The laser pulse width (FWHM) is  $\approx 8$  ns and the pulse repetition frequency is 10 Hz. The incident power is monitored by a laser power meter (Scientech model 362) and the transducer output is observed on a 200 MHz digital storage oscilloscope (Iwatsu model DS 8621). The averaged amplitude of the first pulse in the PA signal trace is monitored as a function of laser power.

For the fluorescence study, the front surface emission is collected and focused by a lens on to the aperture formed by the tip of an optical fiber attached to the entrance slit of a 1 meter Spex monochromator which is coupled to a PMT having S20 cathode. The PMT output is fed to a photon counter (SR 400) which is coupled to a PC/AT for data processing. The emission is wavelength scanned in the desired region (540–670 nm) and it shows the characteristic fluorescence spectrum of rhodamine B. The dependence of fluorescence peak wavelength on concentration is given elsewhere and this shows characteristic Stoke's shift.<sup>15</sup>

#### 4. Results and Discussion

An accurately weighed amount of rhodamine B (Exciton) is dissolved in spectroscopic grade methanol to give concentration of  $3.47 \times 10^{-3}$  moles/lit. From this stock solution, sample solutions with different concentration were prepared. The PA signal strength from the dye solution was measured in the concentration range of  $3.47 \times 10^{-3}$  to  $1 \times 10^{-5}$  moles/lit. Absorption spectrum of methanol shows that it has very low absorption at 532 nm and hence any PA effect due to methanol is neglected. The quantum yield closely depends on the environment of the fluorescing molecule and the processes like internal nonradiative conversion ( $S_1 \rightarrow S_0$ ), intersystem crossing ( $S_1 \rightarrow T_1$ ), excited singlet state absorption (ESA), two photon absorption, aggregation of dye molecules, radiative and nonradiative relaxation cross section etc. Most of the above mentioned phenomena depend eventually on dye concentration and pump intensity. Role of the excitation source is also important in this context as many of the above mentioned phenomena become significant in the medium when the input energy exceeds certain critical value. The intersystem crossing rate depends on the rise time of the pump pulse. Slowly varying pump light pulse would transfer most of the molecules to the triplet state and deplete the ground state population correspondingly. To a first approximation intersystem crossing to the triplet levels can be ruled out, since the pulse width  $t_p$  of the pump laser in our case is only about 8 ns such that  $t_p \ll 1/k_{st}$ , where  $k_{st}$  is the  $S_1 \rightarrow T_1$  intersystem crossing rate which is of the order of  $10^6 - 10^7 \text{ s}^{-1}$  in rhodamine B laser dye.<sup>16</sup>

We have measured the PA signals produced from sample solutions of rhodamine B in methanol at different concentrations (ranging from  $3.47 \times 10^{-3}$  to  $1 \times 10^{-5} \text{ mol l}^{-1}$ ) for various input energies (0–75 mJ). The variation of PA signal amplitude with incident laser energies for different concentrations of dye solution is given in Fig. 2. It is found that the signal increases with incident energy for all concentrations, showing a linear dependence on pump intensity.

The quantum yield ( $Q_f$ ) measurements are carried out using Eq. (6) for different concentrations (in the range  $3.47 \times 10^{-3} \text{ mole/lit} - 1 \times 10^{-5} \text{ mole/lit}$ ) and pump energies (up to 75 mJ). Figure 3 shows the variation of  $Q_f$  as a function of concentration (laser energy 50 mJ). The plot clearly reveals a decrease in fluorescence quantum yield  $Q_f$  at higher concentrations. The calculated value of  $Q_f$  at the lowest

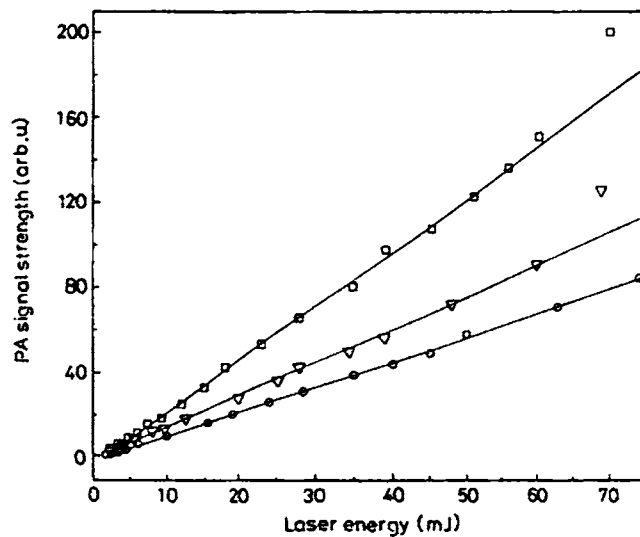


Fig. 2. The variation of PA signal strength with laser energy for different concentrations ( $\square$  —  $3.47 \times 10^{-3}$  moles/lit,  $\nabla$  —  $8.7 \times 10^{-4}$  moles/lit and  $\circ$  —  $8.7 \times 10^{-5}$  moles/lit).

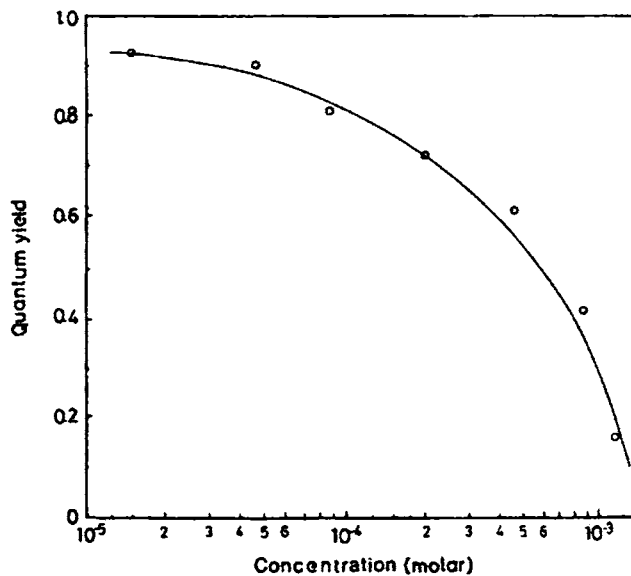


Fig. 3. Variation of quantum yield of rhodamine B in methanol with concentration.

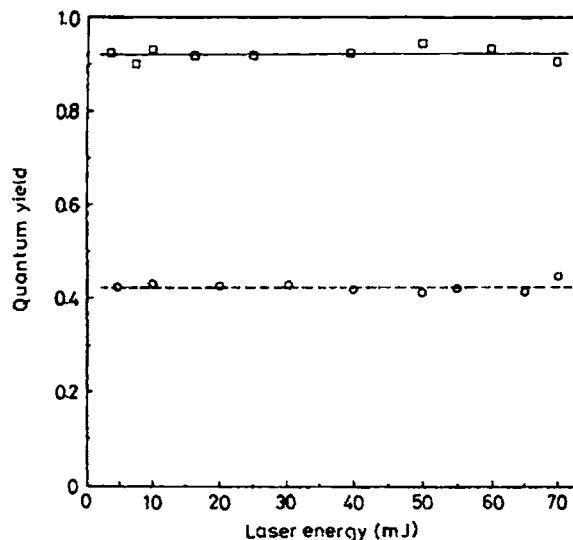


Fig. 4. Variation of quantum yield of rhodamine B in methanol with laser energy for different concentrations (□ —  $1 \times 10^{-5}$  moles/l and o —  $8.7 \times 10^{-4}$  moles/l).

concentration studied is  $0.92 \pm 0.02$  and the yield decreases sharply with increasing concentration. This is a direct indication that nonradiative processes become significant at higher concentrations and contributes to enhanced PA signals. It is found that the calculated fluorescence yield from PA measurements is slightly higher compared to the  $Q_f$  values obtained using cw dual beam thermal lens calorimetry at 514 nm  $Ar^+$  excitation.<sup>15</sup> This is due to the fact that with cw excitation source, intersystem crossing rate to the triplet states becomes more prominent which in turn decreases the  $Q_f$  to a great extent.

It is well known that xanthene dyes like rhodamine B form unstable ground state dimers and higher aggregates in alcoholic solutions.<sup>17-19</sup> The rapid decrease in  $Q_f$  at higher concentrations is mainly due to the formation of dimers and higher aggregates which have very small fluorescence quantum yield. The decrease in fluorescence quantum efficiency at higher concentrations is caused by Förster-type excitation energy migration transfer from monomers (electric dipole-electric dipole interaction) to weakly fluorescing dimers.<sup>20</sup>

In rhodamine B methanol solutions, ground state dimer formation is unstable and closely spaced pairs dominate the fluorescence behavior at higher concentrations. Within the life time of the excited monomer, an excited monomer and a ground state monomer come so near together that they interact mutually and form an excited quenching center. The strong radiationless deactivation of excitation in these quenching centers reduces the fluorescence emissions.<sup>21,22</sup> Such aggregation/complexing effects alter the absorption characteristics of the solution at differ-

ent concentrations. The fluorescence can be quenched by dimers only while monomer molecules and statistical traps can fluoresce with respective quantum yields in which the total quantum yield is directly related to the total concentration of the molecules in the solution. The equilibrium between monomers and dimers shifts to the side of the latter with increasing concentration and at  $10^{-3}$  M concentration, the dimerization of dyes like rhodamine B and rhodamine 6G is severe enough to prevent laser action<sup>23</sup> unless deaggregating agents like hexafluoroisopropanol or ammonyx LO is added to the solution. In the present case no such deaggregating agents were added and hence a significant reduction in fluorescence quantum yield can be expected due to dimerization at higher concentration. Our results indeed show such a decrease in quantum yield as the concentration is increased and finally it reaches the limit corresponding to fluorescence quenching.

The variation of  $Q_f$  with laser energy for rhodamine B in methanol is given in Fig. 4, which shows that  $Q_f$  is independent of the pump energy in the range of present studies.

#### 4. Conclusion

Fluorescence quantum yield measurements of rhodamine B solutions have been carried out using pulsed PA technique with 532 nm excitation from a Q-switched Nd:YAG laser. PA method proves to be a viable and versatile tool for quantum yield measurements. The PA technique is highly sensitive since any change in the PA signal will be relatively much larger than fluorescence.

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#### References

1. J. N. Demas and G. A. Crosby, *J. Phys. Chem.* **75**, 991 (1971).
2. G. A. West, J. J. Barrett, D. R. Siebert, and K. V. Reddy, *Rev. Sci. Instrum.* **54**, 797 (1983).
3. C. K. N. Patel and A. C. Tam, *Rev. Mod. Phys.* **53**, 517 (1981).
4. S. S. Harilal, R. C. Issac, C. V. Bindhu, V. P. N. Nampoore, and C. P. G. Vallabhan, *Mod. Phys. Letts.* **9**, 871 (1995).
5. H. L. Fang and R. L. Swofford, *Ultra Sensitive Laser Spectroscopy* (Academic, London, 1983), p. 175.
6. N. J. Dovichi and J. M. Harris, *Anal. Chem.* **53**, 106 (1981).
7. A. C. Tam and C. K. N. Patel, *Nature* **280**, 304 (1979).
8. P. Sathy, R. Philip, V. P. N. Nampoore and C. P. G. Vallabhan, *J. Phys. D: Appl. Phys.* **27**, 2019 (1994).
9. C. V. Bindhu, S. S. Harilal, R. C. Issac, G. K. Varier, V. P. N. Nampoore, and C. P. G. Vallabhan, *Pramana — J. Phys.* **45**, 231 (1995).

10. A. Rosenwaig, *Photoacoustics and Photoacoustic Spectroscopy* (Wiley, New York, 1980), p. 158.
11. R. Philip, P. Sathy, V. P. N. Nampoori, and C. P. G. Vallabhan, *J. Phys. B: Atm. Mol. Opt. Phys.* **25**, 155 (1991).
12. A. V. R. Kumar, G. Padmaja, V. P. N. Nampoori, and C. P. G. Vallabhan, *Photoacoustic and Photothermal Phenomena II*, ed. J. C. Murphy (Springer-Verlag, Heidelberg, 1990), p. 360.
13. D. Cahen, H. Garty, and R. S. Becker, *J. Phys. Chem.* **B4**, 3384 (1980).
14. M. J. Adams, J. G. Highfield, and G. F. Kirkbright, *Anal. Chem.* **49**, 1850 (1977).
15. C. V. Bindhu, S. S. Harilal, R. C. Issac, V. P. N. Nampoori and C. P. G. Vallabhan, *J. Phys. D — Appl. Phys.* **29**, 1074 (1996).
16. F. P. Schäfer, *Dye Lasers*, ed. F. P. Schäfer (Springer-Verlag, Berlin, 1977), p. 34.
17. F. Lopezarbeloa, P. Ruizojeda, and I. Lopezarbeloa, *Chem. Phys. Letts.* **148**, 253 (1988).
18. K. A. Selanger, J. Falnes, and T. Sikkeland, *J. Phys. Chem.* **81**, 1960 (1977).
19. J. E. Selwyn and J. I. Steinfeld, *J. Phys. Chem.* **76**, 762 (1972).
20. A. Penzkofer and W. Leupacher, *J. Lumin.* **37**, 61 (1987).
21. A. Penzkofer and Y. Lu, *Chem. Phys.* **103**, 399 (1986).
22. K. Sienicki, *Chem. Phys.* **146**, 79 (1990).
23. K. H. Drexhage, *Dye Lasers*, ed. F. P. Schäfer (Springer-Verlag, Berlin, 1977), p. 159.