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P Sathy, Reji Philip, V. P. N. Nampoori, C. P. G. Vallabhan

Institutions: Cochin University of Science and Technology

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Fluorescence quantum yield of rhodamine 6G using pulsed photoacoustic technique

P SATHY, REJI PHILIP, V P N NAMPOORI and C P G VALLABHAN

Laser Division, Department of Physics, Cochin University of Science and Technology, Cochin 682 022, India

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Abstract. Experimental method for measuring photoacoustic(PA) signals generated by a pulsed laser beam in liquids is described. The pulsed PA technique is found to be a convenient and accurate method for determination of quantum yield in fluorescent dye solutions. Concentration dependence of quantum yield of rhodamine 6G in water is studied using the above method. The results indicate that the quantum yield decreases with increase in concentration in the quenching region in agreement with the existing reports based on radiometric measurements.

Keywords. Rhodamine 6G; pulsed photoacoustics; fluorescence; quantum yield.

PACS Nos 33-50; 33-10

The knowledge of fluorescence quantum efficiency of organic dyes is important in selecting efficient dye laser media. Even after the various corrections for system geometry, re-absorption, polarization etc., the accuracy of the quantum yield values obtained from photometric measurements is rather poor (Demas and Gosby 1971). In order to evaluate the absolute quantum efficiency we have to consider both the radiative and non-radiative relaxation processes taking place in the medium. As the contribution due to non-radiative processes is not directly measurable using the traditional optical detection methods, photoacoustic(PA) and thermal lens techniques have been adopted recently for this purpose. The viability of the PA method as a complement to fluorescence spectroscopy, and its relative advantages have been extensively described earlier (Rosencwaig 1978; David Cahen *et al* 1980; Patel and Tam 1981).

For fluorescent materials photoacoustic detection is sensitive to the total fluorescence, which means that any change in the emission characteristics will influence the PA signal. The variations in quantum yield of highly fluorescent materials can be effectively studied by this method because of the relatively large changes occurring in PA signal compared to that in fluorescence output (David Cahen *et al* 1980).

Of the several configurations possible for PA instrumentation, pulsed PA is the most sensitive, as the high peak power delivered by a pulsed laser source can generate acoustic signals of considerable magnitudes (Patel and Tam 1979). In this paper we report the results obtained from the measurements of fluorescence efficiency of the laser dye rhodamine 6G using pulsed PA technique together with fluorescence measurements.

In the case of fluorescent samples with quantum yield ϕ_F , PA signal $P(\lambda)$ can be

written as (Malkin and Cahen 1979),

$$P(\lambda) = \alpha(\lambda)[1 - (\phi_F/\lambda_F)\lambda]. \quad (1)$$

where λ and λ_F are the excitation wavelength and the fluorescence peak wavelength respectively. α is the fraction of light absorbed in that part of the sample that participates in the generation of the PA signal. In the case of a totally fluorescence quenched sample we can consider the entire excitation energy to be converted to non-radiative relaxation processes and hence

$$P(\lambda) = P_a(\lambda) \equiv \alpha(\lambda), \quad \text{and} \\ \frac{P}{P_a} = 1 - (\phi_F/\lambda_F)\lambda \quad (2)$$

If λ_F is known, ϕ_F can be obtained directly (Razumova and Starobogatov 1977; Auzel *et al* 1979) using the equation

$$\phi_F = \frac{\lambda_F}{\lambda} \left[1 - \frac{P}{P_a} \right]. \quad (3)$$

Schematic experimental set up is shown in figure 1. The IR eliminated second harmonic output (532 nm) of a frequency doubled Q-switched pulsed Nd:YAG laser (quanta-ray-DCR-11) acts as the exciting light source. To prepare the samples, commercial laser grade Rh6G (exciton) was dissolved in triply distilled water without further purification. A small fraction of the beam reaches a reference photodiode PD (10 ns risetime) from a beam splitter BS1 and the major part is again split into two beams of equal strengths by a second beam splitter BS2. One part is allowed to pass through the PA cell containing the sample solution of Rh6G. A PZT transducer is screwed onto the PA cell. The design and fabrication of the PA cell and the transducer are based on earlier works (Patel and Tam 1981; Reji Philip *et al* 1988). Figure 2(a) shows the geometry of the PZT transducer. A PZT disc of 4 mm thick and 15 mm diameter is firmly mounted in a stainless steel casing, whose front diaphragm (1 mm thick) is polished on both sides. A lead disc soldered to a copper disc forms the

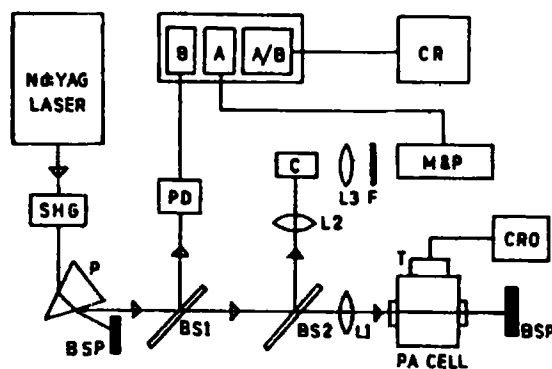


Figure 1. Experimental set-up for the determination of fluorescence quantum yield of liquids. SHG-Second harmonic generator, P-Prism, BSP-Beam stop, CR-Chart recorder, C-Cuvette, M & P-Monochromator and PMT, T-PZT Transducer.

backing plate of the PZT, which is spring loaded to the diaphragm as shown. This design has the advantages of high sensitivity, minimal ringing effect, excellent rejection of spurious electrical pick up and effective isolation of piezoelectric transducer from corrosive and contaminating liquid samples. Figure 2(b) shows the PA cell with the transducer screwed into it. The cell was made of stainless steel with an inner diameter of 2 cm with suitable glass windows for the entry of the laser beam. The PA signal generated in the liquid sample is detected by the transducer, which is fed to a storage oscilloscope (Tektronix, model 466). The transient PA pulses are successively monitored on the oscilloscope and the average amplitude is noted. Unlike the experimental set up of Lahmann and Ludewig (Lahmann *et al* 1977) we have used a nonresonant PA cell in conjunction with a pulsed laser source of high peak power. Hence the acoustic attenuation effects will be negligible here, and we do not expect any appreciable variation in system sensitivity with changes in concentration of the sample solution, that demands a correction for the observed values.

The other part of the laser beam from BS2 is focussed (by the cylindrical lens L2) on to a cuvette that contains the solution of same concentration as the sample taken in the PA cell, and the fluorescence emission is focussed by the convex lens L3 onto the entrance slit of a 0.5 m Jarrell-Ash monochromator. A filter *F* checks the entry of the scattered laser radiation into the monochromator. The emission is wavelength scanned in the region 530–630 nm and the optical intensity is detected by a photomultiplier tube [EMI(9684)]. The signal from the photomultiplier tube is suitably gated, and normalized to the laser power by employing the gated integrators A and B (both EG & G model 163) along with the A/B option of the boxcar averager (EG & G 162). The output is fed to a chart recorder.

Amplitudes of PA signal and fluorescence emission are plotted against concentration in the range of 10^{-6} mol/l to 10^{-4} mol/l in figure 3. The fluorescence emission has the characteristic peak near 560 nm and any specific dependence of the peak wavelength on concentration was not observed within the range studied. As seen from the figure, PA signal varies linearly in the low concentration region.

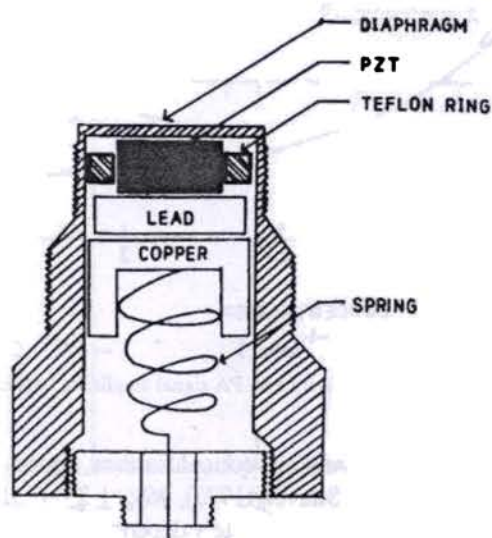


Figure 2a. The PZT transducer.

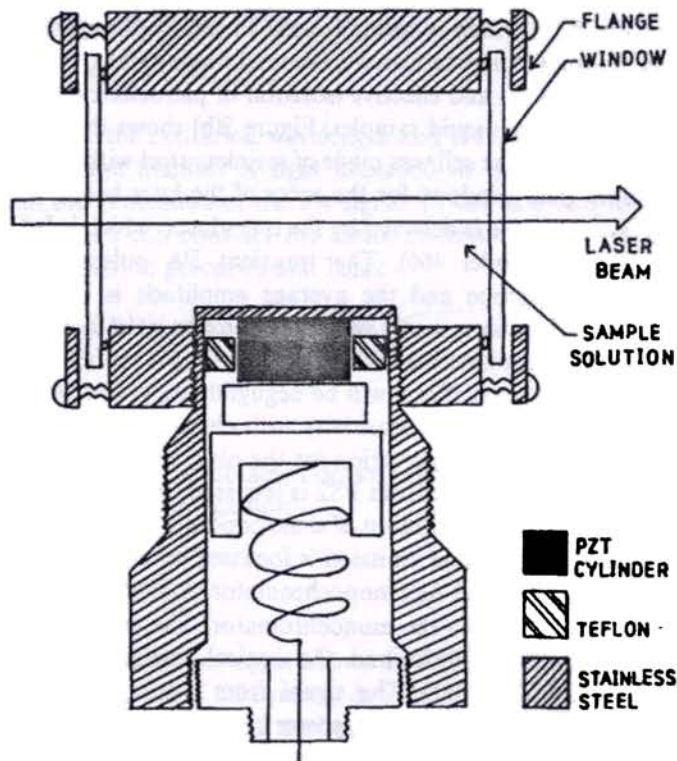


Figure 2b. The PA cell with transducer screwed in position.

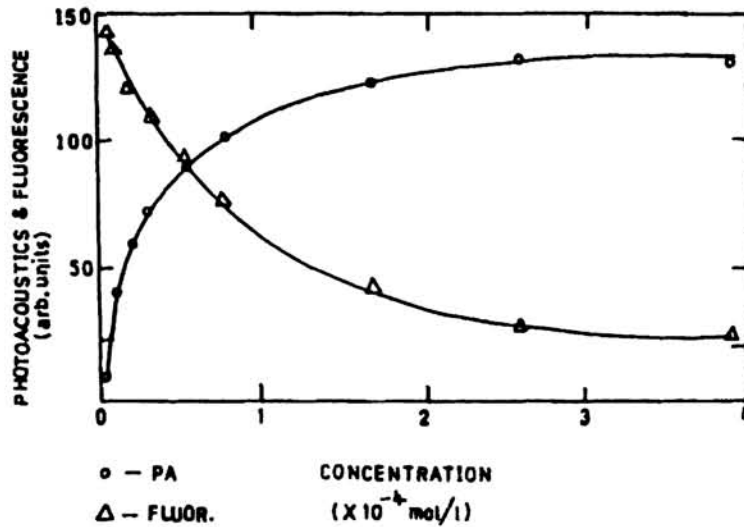


Figure 3. Variation of fluorescence intensity and PA signal amplitude with concentration.

The earlier estimates have shown that for selected concentrations, aqueous solutions of Rh6G has a quantum efficiency of 92% (Snively 1973), $96\% \pm 2\%$ (Lahmann and Ludwig 1977) etc. However, the quantum yield intimately depends on the environment of the fluorescing molecule, and the processes like internal non-radiative conversion

($S_1 \rightarrow S_0$), intersystem crossing ($S_1 \rightarrow T_1$), excited singlet state absorption (ESSA) and aggregation of dye molecules are strongly dependent on the solvent characteristics as well as on concentration (Drexhage 1973). The role of the excitation source also is important in this respect, as many of the above phenomena become significant in the medium when the input energy exceeds certain critical value. It has been known that Rh6G forms stable ground state dimers and higher aggregates in aqueous solution, and the decrease of Rh6G fluorescence quantum efficiency at higher concentrations is caused by Förster-type energy transfer (electric dipole-electric dipole interaction) to dimers (Penzkofer and Leupacher 1987). The equilibrium between monomers and dimers shifts to the side of the latter with increasing concentration and at 10^{-4} M concentration, the dimerization of dyes like RhB and Rh6G is severe enough to prevent laser action (Drexhage 1973) unless a deaggregating agent 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. Our studies in the 10^{-4} M concentration region are generally in agreement with these earlier observations. However, we have used a pulsed laser source of high peak power for excitation of the medium in contrast with the Tungsten lamp used by Penzkofer and Leupacher (1987) and hence many of the above nonlinear processes are likely to occur here. Therefore slight departures of our results from the numerical values of previous workers are to be expected. This was actually observed, and the quantum yield was found to decrease rapidly as the concentration was increased. From figure 3 it is seen that at the highest concentration used here PA signal shows a saturation behaviour. Correspondingly, the fluorescence emission is very weak. PA signal corresponding to this concentration gives the value of $P(\alpha)$. The calculated value of the quantum yield at the lowest concentration studied (3.2×10^{-6} M) is 0.90 ± 0.02 , and the yield decreases rapidly at higher concentration region. Figure 4 is the plot of variation of ϕ_F with concentration. Apart from a small variation, the quantum yield is almost independent of concentration in the 10^{-6} M region, and the rapid decrease in ϕ_F at higher concentrations can be attributed mainly to the formation of dimers and higher aggregates which have zero or small fluorescence quantum yield. Also, collisional

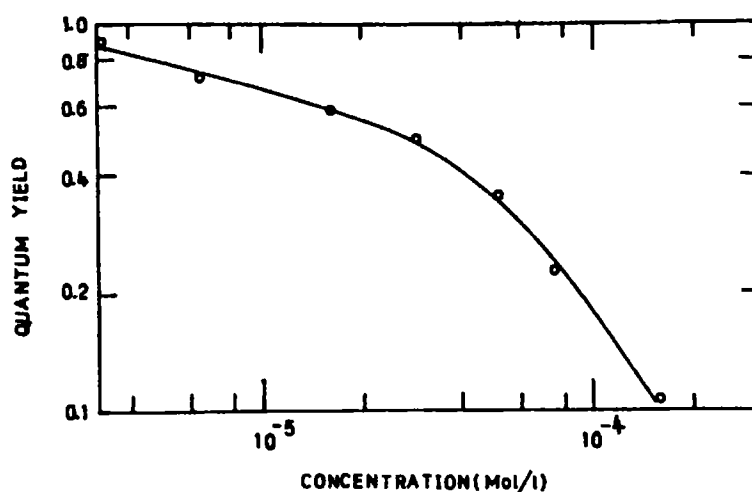


Figure 4. Variation of quantum yield of Rh6G in water with concentration.

quenching, occurrence of two-photon and two-step excitations in the samples when irradiated with a high power laser source (Sathy *et al* 1990) and the influence of other processes mentioned earlier can contribute to the reduction in yield.

The study of concentration dependence of the quantum yield of Rh6G solution in water using the PA technique confirms that the quantum yield decreases with increase in concentration. The simplicity of instrumentation, ease of measurement and the unambiguous nature of results clearly establish the above method as an accurate technique for the estimation of fluorescence quantum yields. For fluorescing materials like Rh6G the measurement of the quantum yield by PA technique is very convenient and useful especially in the higher concentrations, i.e. near fluorescence quenching. For example, the fluorescence quantum yield of laser dyes in various solvents at various concentrations can be measured to analyze the effect of solvent quenching and concentration quenching on the fluorescence properties of the medium.

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