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Abstract. The dual-beam thermal lens technique has been found to be very effective for the measurement of fluorescence quantum yields of dye solutions. The concentration-dependence of the quantum yield of rhodamine B in methanol is studied here using this technique. The observed results are in line with the conclusion that the reduction in the quantum yield in the quenching region is essentially due to the non-radiative relaxation of the absorbed energy. The thermal lens has been found to become abberated above 40 mW of pump laser power. This low value for the upper limit of pump power is due to the fact that the medium is a resonantly absorbing one.

1. Introduction

Knowledge of the fluorescence quantum efficiencies of organic dyes and their concentration-dependence is essential for selecting efficient laser media. Even after making the various corrections for system geometry, re-absorption, polarization and so on, the accuracy of the quantum yield values obtained from photometric measurements is rather poor (Demas and Crosby 1971). In order to evaluate absolute quantum efficiency, we have to consider both the radiative and the non-radiative processes occurring in the medium. Because the contribution from non-radiative processes is not directly measurable using the traditional optical detection methods, thermo-optic techniques have been adopted recently for this purpose (Shen and Snook 1989a, Patel and Tam 1981). Quite recently we measured absolute quantum yields of fluorescence emission from laser dyes using a photo-acoustic technique (Sathy *et al* 1990).

The thermal lens effect (Rasheed *et al* 1987, Bindhu *et al* 1995) is one of the thermo-optical methods usually employed for measurements in the very-low-absorption limit. This effect can be observed using moderate laser intensities in media with absorption coefficients as low as 10^{-7} cm^{-1} (Hue and Whinnery 1973). Formation of a thermal lens or thermal blooming occurs when energy absorbed from a Gaussian beam produces a local heating within the absorbing medium around the beam axis. In such experiments, the sample is exposed to a laser beam, with TEM$_{00}$ mode, which has a Gaussian beam profile and causes excitation of the molecules along the beam path. This excitation may be due to single-photon or multiphoton absorption processes. Thermal relaxation of the excited molecules dissipates heat into the surroundings, thereby creating a temperature distribution which in turn produces a refractive index gradient normal to the beam axis within the medium. This acts as a diverging lens called a thermal lens (TL). Most liquids produce a diverging lens since they have a negative temperature coefficient of refractive index.

In this paper we demonstrate that TL techniques can be very effectively employed to study the optical processes in highly fluorescing materials. For fluorescent materials, the TL effect is sensitive to the fluorescence efficiency which means that any change in the emission characteristics will directly influence the magnitude of the TL signal. The variations in quantum yields of highly fluorescent materials can be effectively studied by this method because of the relatively large changes occurring in the TL signal compared to that in the fluorescence output, especially in the high-concentration limit. Conventional fluorescence quantum yield measurements require the use of accurate luminescence standard samples and comparison of the given samples with a standard one. The TL method offers significant advantages over conventional methods because absolute values of quantum yield can be measured and no standard sample is necessary (Shen and Snook 1989b, Brannon and Magde 1978). However, in a strongly absorbing medium there exists an upper limit for pump
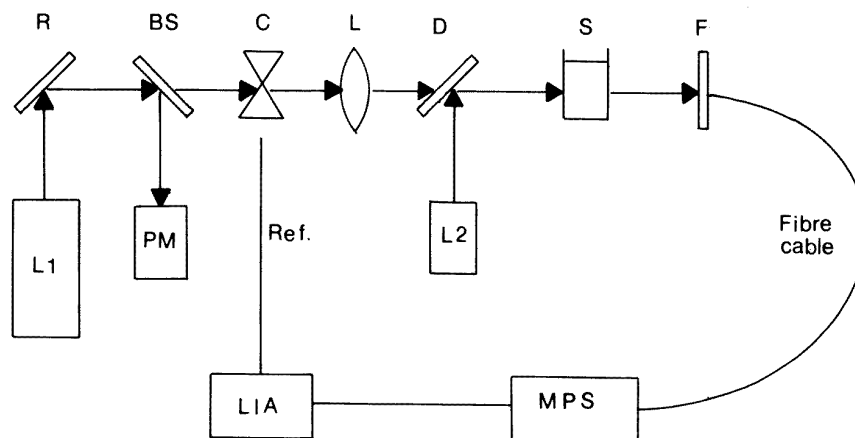
Figure 1. A schematic diagram of the experimental set-up: L1, argon ion laser; PM, power meter; L, lens; D, dichroic mirror; S, sample cell; L2, helium–neon laser; F, filter; BS, beam splitter; R, reflector; LIA, lock-in amplifier; and MPS, monochromator–PMT assembly.

beam power which gives a noise-free TL signal when a dual-beam TL technique is employed. Our results show that, above 40 mW of pump power, the thermal lens becomes abberated due to resonant absorption and appreciable heat generation due to non-radiative transitions.

2. Theory

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, then the absorbed power is the sum of the luminescence emission power I_l and the thermal power degraded to heat I_{th}, provided that no photochemical reaction occurs. Hence

$$I_0 = I_{th} + I_l + I_t \tag{1}$$

so that the transmission ratio is given by

$$T = I_t/I_0 \tag{2}$$

and the absorbance

$$A = 1 - T. \tag{3}$$

Thus the absorbed power is given by

$$AI_0 = I_{th} + I_l. \tag{4}$$

In the case of a totally fluorescence-quenched sample we can consider the entire excitation energy to be converted into non-radiative relaxation processes and hence the fluorecence quantum yield (Q_f) is given by (Brannon and Magde 1978)

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

where $I_\alpha = AI_0$ and the ratio of the fluorescence peak wavelength λ_f to the excitation wavelength λ takes account of the Stokes shift. I_{th} is directly proportional to the TL signal η and I_α is proportional to the

TL signal η_α corresponding to the concentration at which the fluorescence intensity is quenched completely. By knowing λ_f, η and η_α one can directly calculate the quantum efficiency Q_f from

$$Q_f = \frac{\lambda_f}{\lambda}\left(1 - \frac{\eta}{\eta_\alpha}\right).$$

The thermal lens signal η has been measured using the standard technique available in the literature (Hue and Whinnery 1973). The TL signal is taken as the variation of light intensity at the centre of the probe beam (the He–Ne laser beam) arising due to the thermal lensing effect in the medium.

3. Experimental

The experimental set-up (figure 1) for the present dual-beam TL study is almost identical to that reported previously (Fang and Swofford 1983) with minor variations in the detection part. The 514 nm excitation from an argon ion laser (Spectra Physics, Model 171) is used as the pump source to generate the TL in the medium. Radiation of wavelength 632 nm from a low-power intensity-stabilized He–Ne laser source (5 mW, Spectra Physics) is used as the probe beam. The pump beam is intensity-modulated at 7.5 Hz using a mechanical chopper. A solution of rhodamine B in methanol in a quartz cuvette (1.3 cm×0.7 cm×3 cm) is kept in the pump beam's path. The He–Ne laser beam (the probe beam) is made to pass collinearly through the sample with the help of a dichroic mirror. A filter is placed in the path of the emergent beams which allows only the 632 nm wavelength to reach the detector, where the tip of an optical fibre serves as the detector head with a finite aperture. The multimode fibre which also acts as a pin hole is mounted on an $X–Y–Z$ translator. After passing through the fibre the signal enters a monochromator–photomultiplier tube (PMT) assembly (which provides further filtering) and the signal is processed using a digital lock-in amplifier (Stanford SR 850)
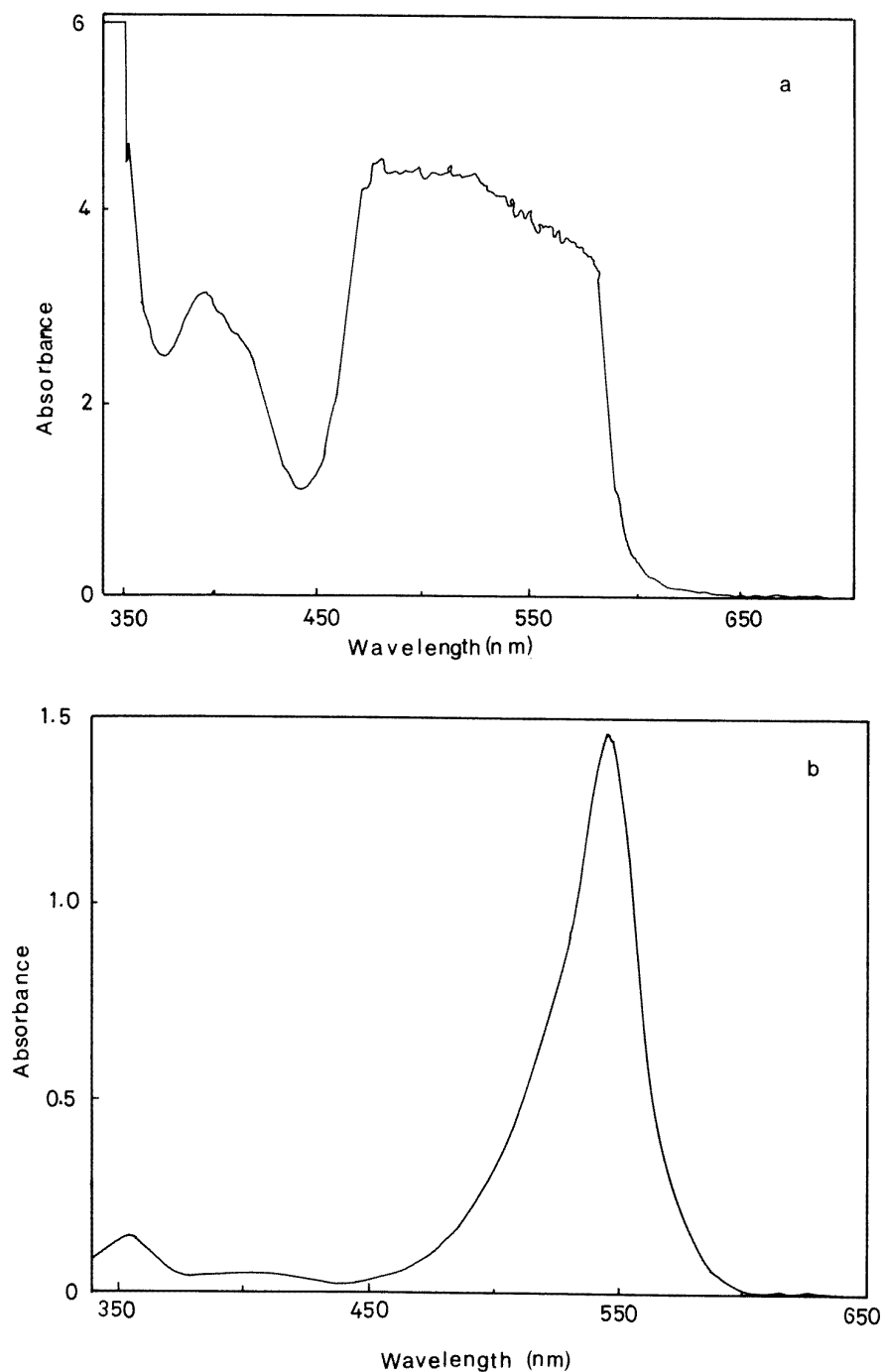
Figure 2. Absorption spectra for rhodamine B in methanol for concentrations (*a*) 8.6×10^{-4} and (*b*) 8.6×10^{-6} mol l^{-1}.

For the fluorescence study, the front surface emission is collected and focused by a lens on to the aperture formed by the tip of another optical fibre attached to the entrance slit of a 1 m Spex monochromator which is coupled to a PMT having an 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). The emission shows the characteristic fluorescence spectrum.

4. Results and discussion

The fluorescence yield and lasing efficiency of a dye medium depend on various parameters like solute–solvent interaction, intersystem crossing, excited state absorption (ESA), two-photon absorption (TPA) and radiative and non-radiative relaxation cross sections. Most of the above-mentioned phenomena depend critically on dye concentration and pump intensity.

The absorption spectrum of methanol shows that it has
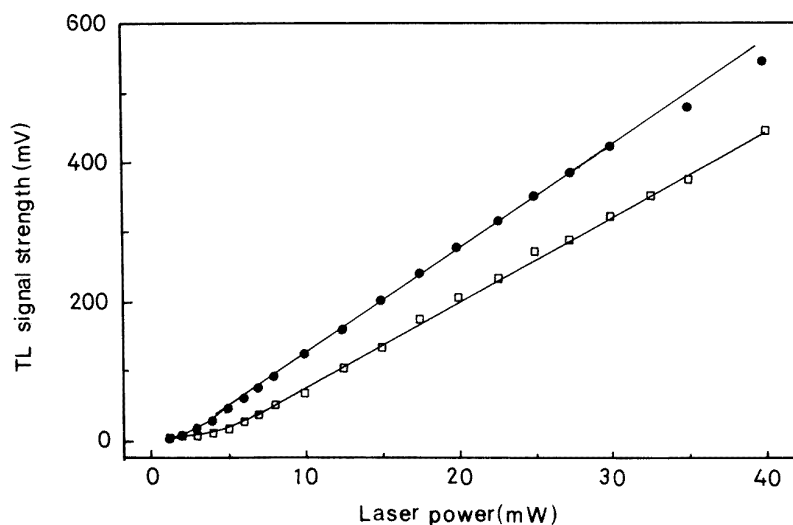
Figure 3. The variation in thermal signal strength with laser power for concentrations ($\bigcirc$) 8.6×10^{-4} and ($\square$) 8.6×10^{-6} mol l^{-1}.
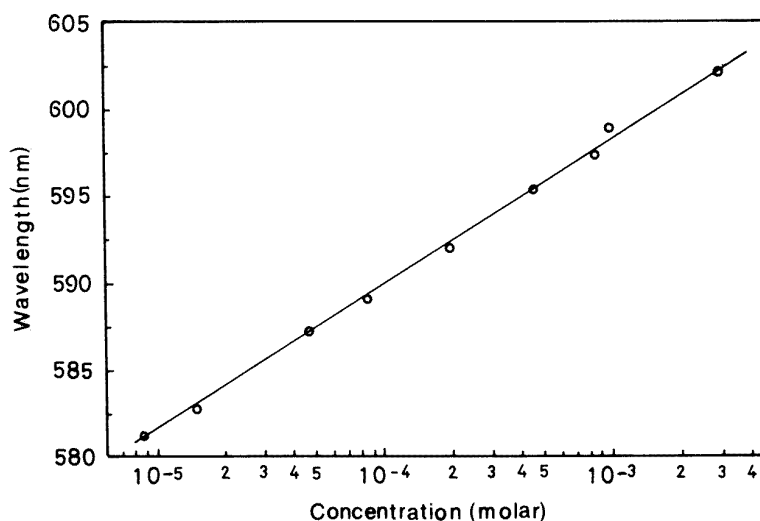

Figure 4. The dependence of peak fluorescence wavelength on concentration.

very low absorption at 514 nm and hence any TL effect due to methanol can be neglected. The absorption spectra of rhodamine B in methanol for concentrations of 8.6×10^{-4} and 8.6×10^{-6} mol l^{-1} are given in figure 2. From these spectra it is clear that absorption at 632 nm is very small and hence any perturbation due to the probe beam can be neglected.

An accurately weighed amount of rhodamine B (Exciton) was dissolved in spectroscopic grade methanol to give a concentration of 3.47×10^{-3} mol l^{-1}. From this stock solution, sample solutions with different concentrations were prepared. The TL signal strength was measured in the dye solution in the concentration range 3.47×10^{-3} to 8.7×10^{-6} mol l^{-1}. The dependence of the TL signal on laser power is given in figure 3, which shows an almost linear relationship. The dependence of the TL signal at powers greater than 40 mW has not been studied since aberrational effects begin to appear at these

power levels. The concentration-dependence of the peak fluorescence wavelength is shown in figure 4, which shows a characteristic Stokes shift, as discussed earlier in the literature (Drexhage 1977).

Figure 5 shows the variation of quantum yield obtained in TL measurements using equation (5) for rhodamine B in methanol as a function of concentration (laser power 30 mW). It clearly reveals a decrease in fluorescence quantum yield Q_f at higher concentrations. This is a direct indication that non-radiative processes become significant at higher concentrations and contribute to enhanced thermal lensing. 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 fluorescence quantum yield. The competition between increasing dimer absorption and decreasing monomer absorption at 514 nm with increasing concentration plays a comaprable (or even greater) role than does direct self-
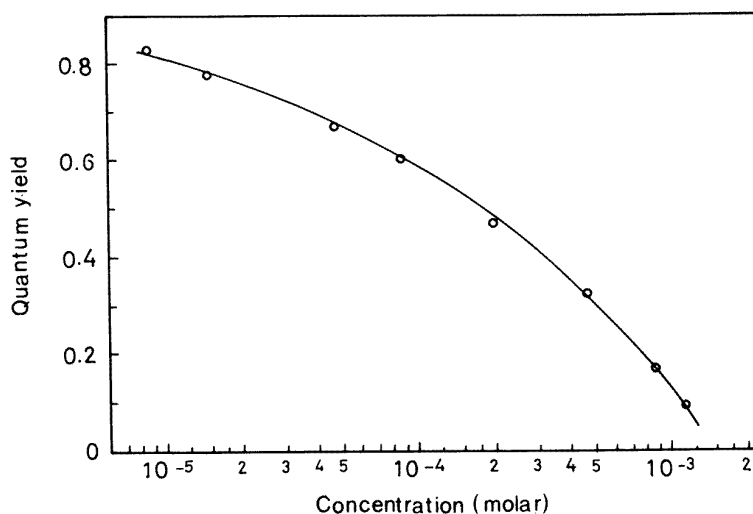
Figure 5. The variation in quantum yield of rhodamine B in methanol with concentration.
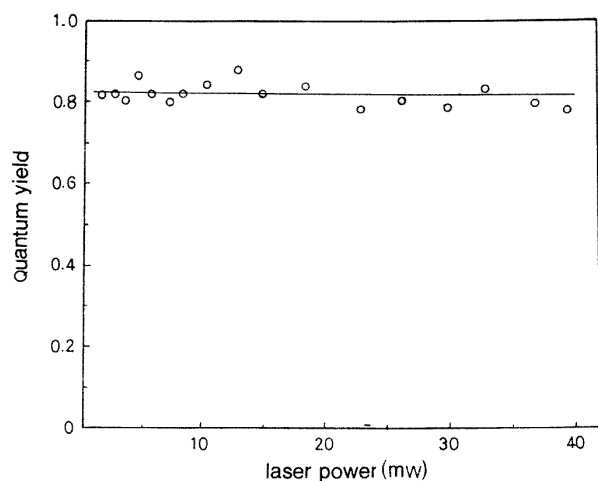
Figure 6. The variation in quantum yield of rhodamine B in methanol with laser power (concentration 8.6×10^{-6} mol l^{-1}).

quenching of fluorescence in the decrease in quantum efficiency. The role of triplet state absorption is also important in this connection (Schafer 1977). Figure 6 shows the variation of Q_f with laser power. From this it can be seenthat Q_f is independent of pump laser power up to 40 mW.

The quantum yield closely depends on the environment of the fluorescing molecule, and on processes like internal non-radiative conversion ($S_1 \rightarrow S_0$), intersystem crossing ($S_1 \rightarrow T_1$), excited singlet state absorption (ESA) and aggregation of dye molecules. These are strongly dependent on excitation source, solvent characteristics and the concentration of the dye solution (Drexhage 1977). It is well known that xanthene dyes like rhodamine B form stable ground state dimers and higher aggregates in aqueous and alcoholic solutions (Lopezarbeloa *et al* 1988, Selanger *et al* 1977, Selwyn and Steinfeld 1972) and the decrease in fluorescence quantum efficiency at higher

concentration is caused by Förster-type energy transfer (electric dipole–electric dipole interaction) to dimers (Penzkofer and Lu 1986, Penzkofer and Leupacher 1987). Such aggregation/complexation effects alter the absorption characteristics of the solution at different concentrations (figures 2(*a*) and (*b*)). The equilibrium between monomers and dimers shifts to the side of the latter with increasing concentration and, at 10^{-3} mol l^{-1} concentration, the dimerization of dyes like rhodamine B and rhodamine 6G is severe enough to prevent laser action (Drexhage 1977) unless de-aggregating agents like hexafluoroisopropanol or ammonyx LO are added to the solution. In the present case no such de-aggregating agents were added and hence a significant reduction in fluorescence quantum yield can be expected due to dimerization at higher concentrations. Our results indeed show such a decrease in quantum yield as the concentration is increased and finally reaches the limit corresponding to fluorescence quenching.

5. Conclusion

A dual-beam thermal lens technique has been found to be useful to study the concentration-dependence of the quantum yield of rhodamine B in methanol. The results clearly show that the quantum yield decreases with increasing concentration within the range 3.47×10^{-4} to 8.7×10^{-6} mol l^{-1}. For fluorescing materials like rhodamine B, the thermal lens method is suitable for quantum efficiency calculation since it requires no standard and is very convenient and useful, especially at higher concentrations, namely near fluorescence quenching.

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