Anomalous variation of thermal lens signal with concentration from rhodamine B in methanol solution

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Abstract. Thermal lens signals in solutions of rhodamine B laser dye in methanol are measured using the dual beam pump-probe technique. The nature of variations of signal strength with concentration is found to be different for 514 and 488 nm Ar^+ laser excitations. However, both the pump wavelengths produce an oscillatory type variation of thermal lens signal amplitude with the concentration of the dye solution. Probable reasons for this peculiar behaviour (which is absent in the case of fluorescent intensity) are mentioned.

Keywords. Thermal lens; laser dyes.

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1. Introduction

It is well known that the absorption of electromagnetic radiation by atoms or molecules generates thermal energy in the medium due to nonradiative relaxation of excited states. This deexcitation mechanism has provided the physical basis for the development of thermo-optic spectroscopy which includes photoacoustic spectroscopy [1] and photothermal spectroscopy [2]. In the latter, the change in the values of refractive index due to thermo-optic effect generates a virtual optical element (lens, prism etc.) within the sample, thereby changing the propagation properties of a probe beam. Depending on the experimental configuration, different types of optical effects are produced among which one of the, most well known is the thermal lens (TL) phenomenon.

Thermal blooming of laser beam was first observed by Gordon *et al* in 1964 [3]. Absorption of a laser beam followed by nonradiative deexcitation in the sample results in the increase of the temperature of the irradiated region. The temperature distribution of the irradiated region will be the same as the intensity distribution across the beam section which is usually gaussian. Since most liquids have a positive coefficient of thermal expansion, the temperature coefficient of refractive index is negative and consequently thermal lens generated is a divergent one. Another low intensity laser beam can be used to probe the formation of the thermal lens. Thus using a pump-probe method the TL signal can be measured and the data acquired in this manner can throw valuable light regarding the absorption and deexcitation processes taking place in the sample material. In addition to the well-known applications for the estimation of weak optical absorptions [4] the thermal lens technique also allows the measurement of fluorescent quantum yield of dyes [5] and the

determination of the quantum yield of photochemical reaction [6]. In the case of samples showing fluorescence emission, thermo-optic effect is highly sensitive to parameters like concentration, pump power and pump-probe configuration. In this paper we report a peculiar concentration dependence of thermal lens effect in the laser dye rhodamine B.

2. Experimental set-up

The experimental set-up (figure 1) used for the present work is that of the dual beam thermal lens technique similar to the one reported previously by Fang and Swofford [7]. The 514 nm excitation from an argon ion laser (Spectra Physics, Model 171) is used as the pump source to generate the thermal lens in the medium. Radiation of wavelength 632·8 nm from a low power intensity stabilized He-Ne laser source (5 mW, Spectra Physics) is used as the probe beam. Absorption coefficient of rhodamine B at 632·8 nm is very small as compared to that at 514 nm and 488 nm and hence the perturbation of refractive index due to the He-Ne probe beam can be neglected. Pump beam is intensity modulated at 7·5 Hz using a mechanical chopper. Solution of rhodamine B in methanol in a quartz cuvette (1·3 cm × 0·7 cm × 3 cm) is kept in the pump beam path. The probe beam is made to pass collinearly through the sample using a dichroic mirror. Spot sizes of both the probe and pump beams are nearly same and are very small as compared to the optical path length of the cuvette and hence paraxial approximation holds good. A filter is placed in the path of the emergent beams which allows only the 632·8 nm wavelength to reach the detector system.in which the tip of an optical fibre mounted on a XYZ translator serves as the finite aperture. The fibre is coupled to a monochromator-PMT assembly (which also provides further filtering). The signal output from PMT is processed using a lock-in amplifier (Stanford SR 850).

3. Results and discussion

An accurately weighed amount of rhodamine B is dissolved in methanol to get a concentration of $3·45 \times 10^{-3}$ mole/l. From this stock solution, samples with
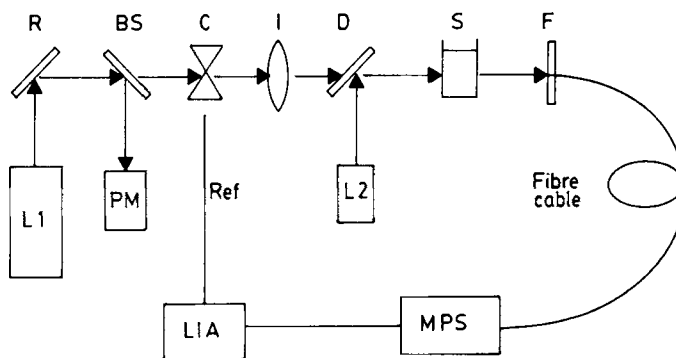

Figure 1. Schematic diagram of the experimental set-up. (L1 – argon ion laser; PM – power meter; C – chopper; 1 – lens; D – dichroic mirror; S – sample cell; L2 – probe laser; F – filter; BS – beam splitter; R – reflector; LIA – lock-in amplifier; MPS – monochromator-PMT assembly).

different concentrations are prepared. Thermal lens signal strength is measured in the dye solutions at various concentrations ranging from 3.45×10^{-3} to 8.7×10^{-6} mole/l. Concentration dependence of thermal lens signal strength is also monitored for different laser powers for 514 and 488 nm excitations from the argon ion laser. Figure 2 shows the variation of thermal lens signal with concentration for different laser powers for 514 nm excitation. This exhibits a type of concentration dependent oscillatory type variation of TL signal strength. With the 514 nm pump wavelength the signal peaks at concentrations of 1.16×10^{-3} and 4.63×10^{-5} mole/l. On decreasing the sample concentration from 1.16×10^{-3} to about 8.7×10^{-6} mole/l the signal intensity generally decreases. At a concentration of 4.63×10^{-5} mole/l the signal has a maximum; but on further decreasing the concentration the signal intensity again drops. The depth of this modulation effect is larger at higher laser powers. Concentration dependence of thermal lens signal for 488 nm excitation at various laser powers is shown in figure 3. For the 488 nm excitation the signal strength is small compared to that of 514 nm exciatation at lower laser powers for all concentrations. As the power is increased the signal strength corresponding to 488 nm increases relative to 514 nm. This is an indication of nonlinear optical absorption [8]. At first the signal strength increases up to a concentration of 8.7×10^{-4} mole/l. The signal intensity slowly decreases in the concentration range 8.7×10^{-4} to 1.16×10^{-3} mole/l. On further increasing the sample concentration, the TL signal begins to increase. It may be noted here that this type of peculiar phenomenon is also observed in the case of photoacoustic signal variations in rhodamine 6G solutions [9]. The dependence of the TL signal strength on concentration at powers above 30 mW has not been studied since aberrational effects begin to appear at these power levels.

Concentration dependence of fluorescence which is measured using·a front surface geometry does not show (figure 4) the behaviour as observed in TL effect. The reason for this peculiar concentration dependent phenomena is not clear
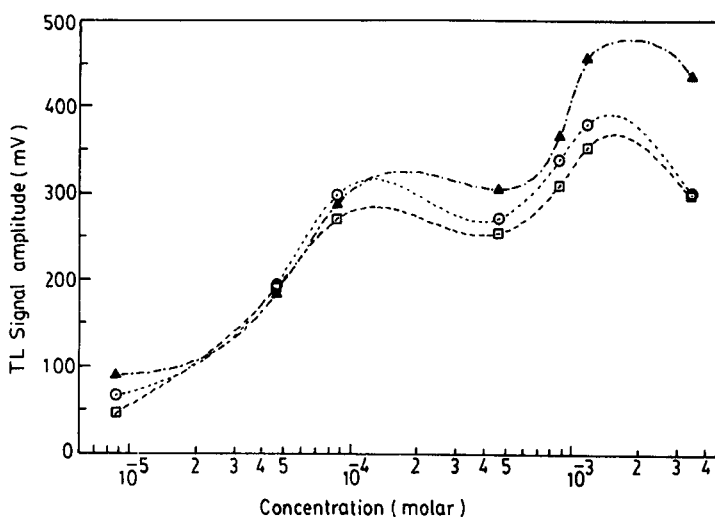
Figure 2. Variation of thermal lens signal strength with concentration at various powers for 514 nm excitation ($\square$ – 15 mW, $\bigcirc$ – 20 mW, $\blacktriangle$ – 25 mW).
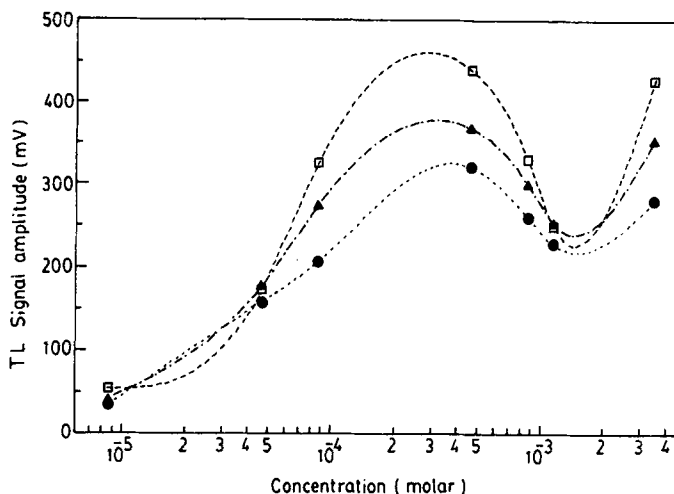
Figure 3. Variation of thermal lens signal strength with concentration at various powers for 488 nm excitation (● – 15 mW, ▲ – 20 mW, □ – 25 mW).
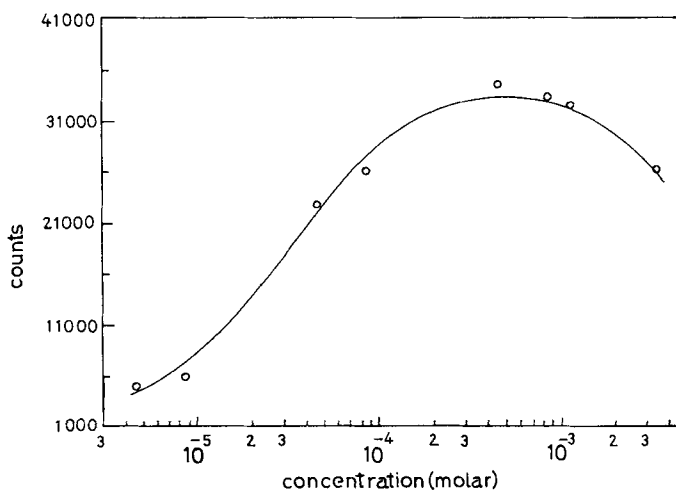
Figure 4. Change in fluorescence intensity with concentration.

at present. It may be attributed to the influence of various complexes formed in the solution at different concentrations and to the probable change in the molecular symmetry of excited states. Usually some deaggregating agents like hexafluoro-isopropanol or ammonyx LO are added into the dye solution to reduce the effect of complex formation [10]. In the present case no such deaggregating agents were added and hence we can expect processes like dimerization at higher concentrations. The role of amplified spontaneous emission which has been found to take place within the dye solution both in the longitudinal and transverse directions of the pump beam also becomes important in this context.

Acknowledgements

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