

LASER INDUCED THERMAL LENS EFFECT IN RHODAMINE B — SIGNATURE OF RESONANT TWO PHOTON ABSORPTION

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Measurement of thermal lensing signal as a function of laser power made in Rhodamine B solutions in methanol give clear evidence of two photon absorption process within certain concentration ranges when 488 nm Ar⁺ laser beam is used as the pump source. Only one photon process is found to occur when 514 nm and 476 nm beams are used as the pump.

1. Introduction

The thermal lens (TL) spectroscopy is one of the high sensitive absorbance methods based on the measurement of the temperature rise following the conversion of the absorbed optical radiation into heat through non-radiative relaxation processes.¹ Absorption of a laser beam generates thermal energy in the medium through non-radiative de-excitation resulting 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 cross-section which is usually Gaussian. Since most liquids have a positive coefficient of thermal expansion, 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. The thermal lens generated by the refractive index gradient is detected by its effect on the intensity at the centre of the probe laser measured through a pinhole aperture with a photodiode and the data acquired in this manner can throw valuable light regarding the absorption and de-excitation processes taking place in the sample material. The effect can be observed at moderate laser intensities with absorption coefficient as low as 10^{-7} cm^{-1} . In addition to the well known applications for the estimation of weak optical absorptions, the thermal lens

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technique also allows the measurement of radiative as well as non-radiative quantum yield of dyes, the reaction kinematics of various photochemical reactions etc.

Two-photon absorption is one of the nonlinear absorption processes which affects the lasing efficiency of laser dyes.² Usually these measurements in absorbing media are carried out by monitoring either the intensity variation in the transmitted beam^{3,4} or that anti-stokes fluorescence emission as a function of pump beam intensity.^{5,6} However the latter technique is not sensitive in cases where the medium has low fluorescence quantum yield while the former cannot be applied in samples where fractional variation of transmitted beam intensity due to resonant two photon process is very small. Very weak optical absorption processes can also be monitored using non-radiative relaxation processes in the medium using thermo-optic techniques like photoacoustic effect,⁷ thermal lens effect⁸ etc. It has been shown that photoacoustic technique is very effective to study two photon absorption in laser dyes and in certain organic liquids.^{9,10} The method of employing thermo-optic effect becomes very useful in the high concentration limit of dye solutions where fluorescence quantum yield is extremely small and thermo-optic effect is much more pronounced.¹¹

The present paper deals with the use of dual beam thermal lens effect in detecting resonant two photon absorption in one of the important laser dyes viz., Rhodamine B.

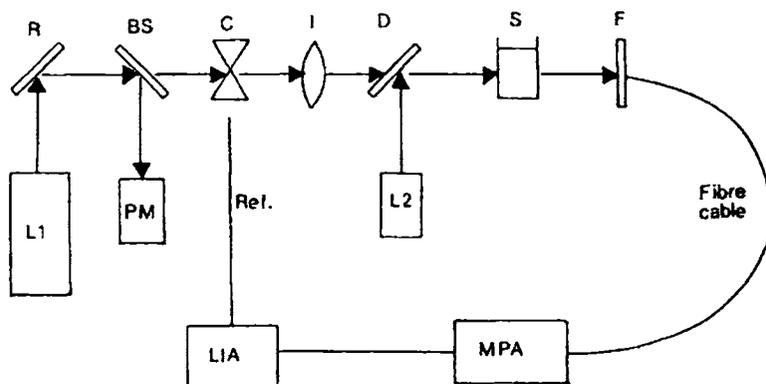


Fig. 1. Schematic diagram of the experimental set up. (L1 — pump laser, L2 — probe laser; R — reflector; BS — beam splitter; C — chopper; l — lens; D — dichroic mirror; S — sample cell; F — filter; LIA — lock-in amplifier; MPS — monochromator — PMT assembly.

2. Experimental Set-Up

The schematic diagram of the experimental set up, which essentially is a dual beam TL configuration^{12,13} is shown in Fig. 1. Argon ion laser (Spectra Physics model 171) is used as the pump source to generate the TL in the medium 632.8 nm beam from a low power stabilized He-Ne laser source (5 mW, Spectra Physics)

is used as the probe beam. Pump beams intensity is modulated at 7.5 Hz using a mechanical chopper so as to facilitate signal detection using lock-in amplifier. Solutions of Rhodamine B (Exciton) in methanol (spectroscopic grade) taken in a quartz cuvette (1.3 cm × 0.7 cm × 3 cm) is kept in the path such that the probe and the pump beams overlap collinearly within the sample. The sample cell which is placed one confocal length past the focus of a long focal length lens. Hu and Whinnery demonstrated that this configuration allows the thermal lens to exhibit the maximum defocusing effect on the laser beam. The optical filter placed in the path of the emergent beam allows He-Ne laser beam to reach the detector head. The tip of an optical fibre (which provides a finite aperture) coupled to Monochromator-Photomultiplier Tube (PMT) assembly acts as the aperture head. The output signal from the PMT is processed using a digital lock-in amplifier (Stanford SR 850).

Formation of the TL (which in this case is a diverging lens) in the dye solution causes the probe beam to diverge so that the intensity at the fibre tip is reduced. The decrease in light intensity (measured as a voltage output from PMT) with respect to that in the absence of pump beam is taken as the TL signal strength. Experiments were carried out using 514 nm, 488 nm and 476 nm lines from the Ar⁺ laser at various dye concentrations.

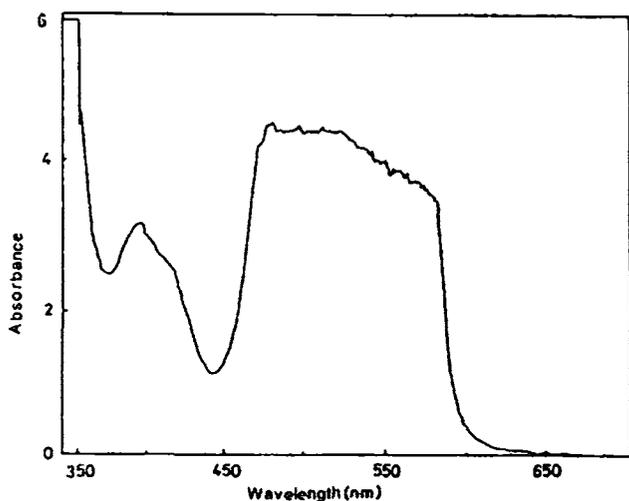
3. Results and Discussion

An accurately weighed amount of Rhodamine B is dissolved in methanol to get a concentration of 3.5×10^{-3} mole/l. From this stock solution, samples with different concentrations are prepared. TL signal strength were measured in the dye solution at various concentrations ranging from 3.47×10^{-3} to 8.7×10^{-6} moles/l. Figure 2 gives the absorption spectrum of Rhodamine B in methanol in the visible and ultra violet range for concentrations of 8.6×10^{-4} moles/l and 8.6×10^{-6} moles/l respectively. Absorption spectrum of methanol shows that it has very low absorption at these Ar ion laser excitation wavelengths and hence any thermal lens effect due to methanol is neglected. The absorption at 633 nm due to the probe beam is very small and hence any perturbation due to the probe beam can be neglected.

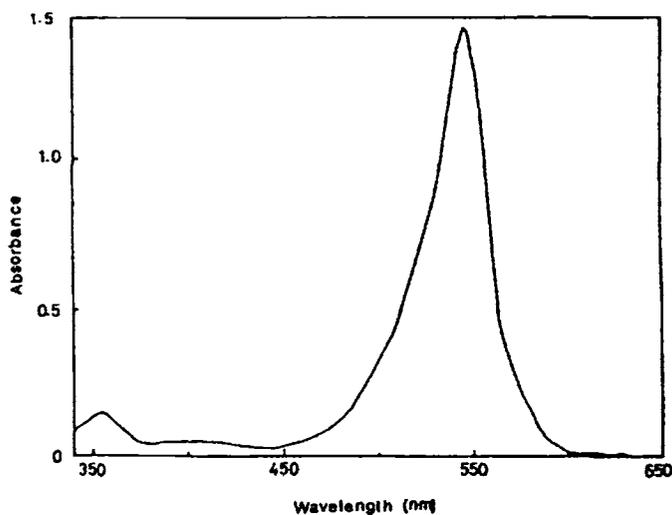
If there is any multi-photon and/or multi-step absorptions to various levels m , then in analogous to photoacoustic effect,¹⁴ the TL signal strength $T(\nu)$ can be written as

$$T(\nu) = AI^n(\nu)\eta(\nu) \quad (1)$$

where $I(\nu)$ is the intensity of the pump beam, $\eta(\nu)$ is the quantum yield of the non-radiative transition and A is the constant which depends on the cell geometry, detector characteristics etc. It is assumed that the constant A does not depend on the dye concentration significantly. If the thermal lens generated in the sample due to two photon absorption or two step excitation ($m = 2$) and subsequent non-radiative relaxation, then the signal will have quadratic dependence on pump intensity. Hence by monitoring the dependence of thermal lens signal amplitude on pump power, one can identify the occurrence of different processes.



(a)



(b)

Fig. 2. Absorption spectra for Rhodamine B in methanol for concentration (a) 8.6×10^{-4} moles/lit and (b) 8.6×10^{-6} moles/lit.

We have measured thermal lens signal produced from sample solutions of Rhodamine B in methanol at different concentrations and various input laser powers (5–40 mW). The dependence of thermal lens signal at powers greater than 40 mW has not been studied since aberrational effects begin to appear at these power

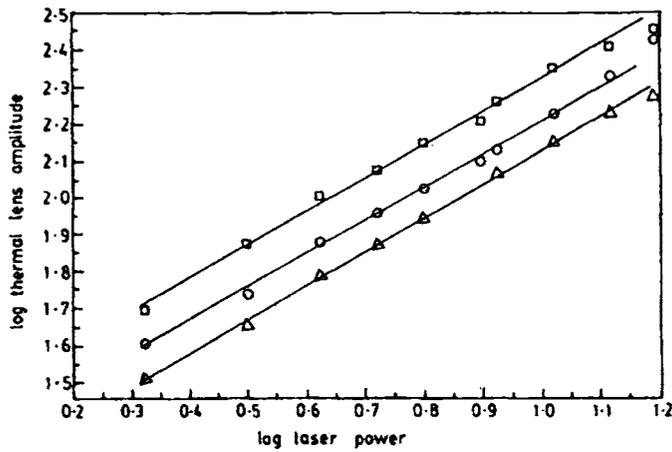


Fig. 3. Log-log plot of thermal lens signal amplitude against laser power for 514 nm. (\square — 3.48×10^{-3} moles/lit, \circ — 8.69×10^{-4} moles/lit, Δ — 8.69×10^{-5} moles/lit).

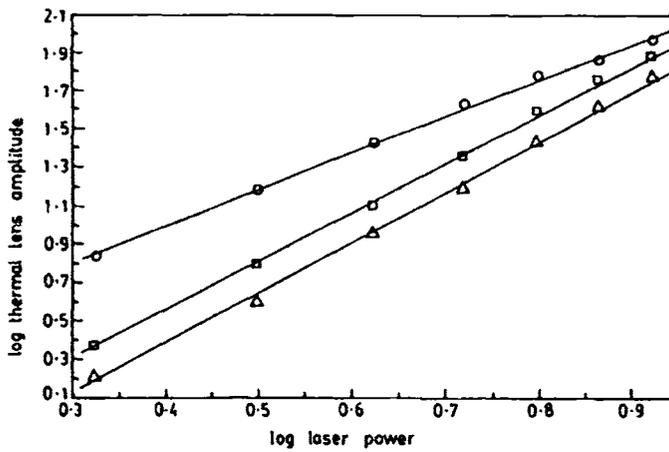


Fig. 4. Log-log plot of thermal lens signal amplitude against laser power for 488 nm. (\circ — 4.63×10^{-5} moles/lit, \square — 8.69×10^{-4} moles/lit, Δ — 8.69×10^{-5} moles/lit).

levels. Log-log plot of thermal lens signal against laser power are plotted for each sample for 514 nm, 488 nm and 476 nm. Figures 3 and 4 give some of the typical log-log plots of thermal lens signal strength as a function of laser power in the case of Rhodamine B solution. As is clear from the figures, slopes of the log-log plots in the case of 514 nm pump excitation are $\approx 1 \pm 0.1$ for all concentrations of dye

solutions. However, in the case of 488 nm excitation, the plots give slopes $\simeq 1$ at low concentrations ($< 4.6 \times 10^{-5}$ molar/lit) while it is $\simeq 2 \pm 0.2$ for concentration above 9×10^{-5} molar/lit. Figure 5 represents variation of slope as a function of concentration in the cases of excitations at wavelengths 514 and 488 nm.

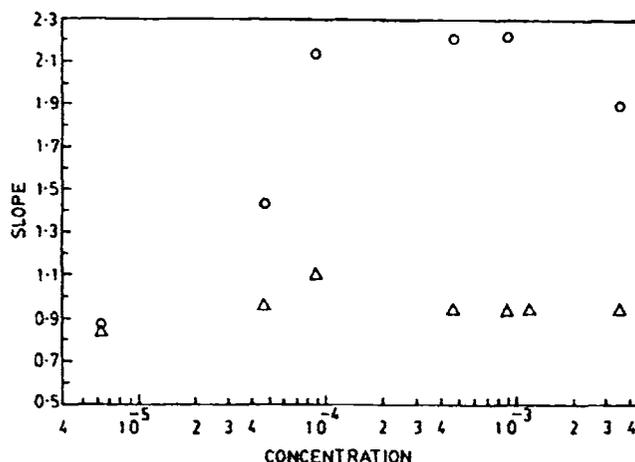


Fig. 5. Variation of the slope of TL signal against laser power with concentration (o — 488 nm, Δ — 514 nm).

The only explanation which one can be provided for the observation of slope 2 is the occurrence of two-photon (TP) process. The absorption spectrum indicates large one photon absorption (OPA) in the visible region (corresponding to $S_0 \rightarrow S_1$ transition) as compared to those in the UV region ($S_0 \rightarrow S_n$). This suggests the possibility that S_0 and S_n states have approximately same symmetry properties. Use of 488 nm and 514 nm radiations excite vibronic levels of different overall symmetries (vibrational + electronic) so that 488 nm excitation favors TPA while 514 nm favors OPA. Many photon process in nonlinear media are usually observed using the radiation from pulsed laser.^{15,16} There are only a few reports regarding the observation of multiphoton absorption using cw laser excitation.^{17,18} Biraben *et al.*¹⁸ observed resonance two photon transitions in Na using cw excitation source. It is known that multiphoton transition probabilities are enhanced under resonant conditions and can be observed under moderate incident intensity. Our results show that 488 nm radiation excites two photon process in Rhodamine B solution through resonance enhancement. The fact that 488 nm excitation shows resonant two TP processes above certain concentration level implies certain concentration dependent symmetry perturbation of the corresponding vibrational level. Concentration dependent symmetry perturbation have been observed in other systems also. Studies using 476 nm also gives OPA similar to the results obtained using 514 nm excitation.

In conclusion, strong thermal lens signals have been obtained from Rhodamine B laser dye solutions in methanol using Ar⁺ laser lines as pump source. Thermal lens effect has been found to depend very much on the concentrations of the dye solutions as well as the wavelength of the pump beam. We have shown that there is a wavelength of the pump beam. We have shown that there is a wavelength selective TPA at 488 nm excitation of Rhodamine B solution in methanol while only OPA process is detected using 514 nm and 476 nm as pump beams.

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