

## Investigation of nonlinear absorption and aggregation in aqueous solutions of rhodamine B using thermal lens technique

C V BINDHU, S S HARILAL<sup>1</sup>, V P N NAMPOORI and C P G VALLABHAN<sup>2</sup>

Laser Division, International School of Photonics, Cochin University of Science and Technology, Cochin 682 022, India.

<sup>1</sup> Also at Department of Physics, Sree Narayana College, Cherthala 688 582, India

<sup>2</sup> Email: photonix@md2.vsnl.net.in

MS received 17 October 1998; revised 5 January 1999

**Abstract.** Thermal lensing effect was studied in aqueous solutions of rhodamine B using 532 nm, 9 ns pulses from a Nd:YAG laser. A low intensity He-Ne laser beam was used for probing the thermal lens. Results obtained show that it is appropriate to use this technique for studying nonlinear absorption processes like two photon absorption or excited state absorption and for analyzing dimerization equilibria.

**Keywords.** Thermal lensing; nonlinear absorption; rhodamine B.

**PACS Nos** 42.65; 42.62; 31.70; 42.55

### 1. Introduction

Multiphoton processes which belong to the class of nonlinear optical phenomena have received increasing attention in recent years. This is due to the availability of high power pulsed lasers with which such effects can be induced easily. Multiphoton excitations lead to population of energy levels to which one photon transitions are spectroscopically forbidden. Usually these measurements in absorbing media are carried out by monitoring either the intensity variation in the transmitted beam or anti-Stokes fluorescence emission as a function of pump beam intensity [1]. However the latter technique is not sensitive in cases where the medium has low 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 be detected by monitoring thermal fluctuations produced by non-radiative relaxation processes. These non-radiative relaxations are typically monitored in one or two ways. If the compression-rarefaction pulse produced by the transient temperature pump is measured directly with a pressure transducer such as microphone or PZT, the technique is termed photoacoustics (PA) [2,3].

Alternatively, the temperature/pressure gradient may be probed optically, since the resulting change will also produce a change in refractive index. Since the transient refractive index forms an effective lens, this technique is often called thermal lens (TL) [4,5].

Thermal lens formation results from absorption of the laser light. The absorption produces excited-state molecules which subsequently decay back to ground state. When the decay involves radiationless processes, localized temperature increases in the sample. Since the refractive index depends on temperature, there is a resulting spatial variation of refractive index which is equivalent to the formation of a lens within the medium. In the case of a liquid in a gaussian-shaped beam diverges or blooms. Thermal lens effect has been shown to be a valuable spectroscopic tool. It has been used in the study of weak spectral transitions as well as for quantum yield measurements [6], for the study of thermal properties of various materials [7] and rate and yield of photochemical reaction etc.. Indeed, thermal lens spectroscopy holds great promise in many areas where sensitive spectroscopic probes are needed.

In this paper, the utility of the thermal lens method for studying nonlinear absorption processes and aggregation phenomena which are taking place in aqueous solutions of rhodamine B laser dye is described. Xanthene dyes like rhodamine B show lasing action under appropriate conditions of excitation. As the state  $S_1$  has a radiative lifetime which is longer than the non-radiative relaxation times of the higher excited singlet electronic states, dye molecules in  $S_1$  can undergo absorptive transitions in addition to stimulated emissive transitions in the presence of a pump beam. Since laser dyes are usually pumped at an optical frequency corresponding to or greater than the  $S_0 \rightarrow S_1$  transition frequency the dye molecules may get excited to higher singlet states  $S_n (n > 1)$  via two photon absorption (TPA) or excited state absorption (ESA). The detailed study of these two processes is of great significance because of the widespread use of such dyes in tunable lasers. The highly efficient nonradiative relaxations  $S_n \rightarrow S_1$  release a large amount of thermal energy into the medium and hence such phenomena should be easily detectable by photothermal lensing technique.

The heat released by the nonradiative decay of the dye molecules turns the solution into a divergent lens which defocuses the beam. The TL signal can be expressed as the change of irradiance at the probe beam centre relative to its stationary value [8,9]

$$S = \frac{I(t = 0) - I(t = \infty)}{I(t = 0)} \propto E^m, \quad (1)$$

where  $E$  is the incident laser intensity,  $m$  is the number of photons involved in the generation of the TL signal,  $I(t = 0)$  and  $I(t = \infty)$  are the TL signal amplitude at time  $t = 0$  and  $t = \infty$  respectively. Hence by monitoring the dependence of TL signal amplitude on pump energy, one can identify the occurrence of different processes like one photon absorption ( $m = 1$ ) and multiphoton absorption processes ( $m \geq 2$ ).

## 2. Experimental set-up

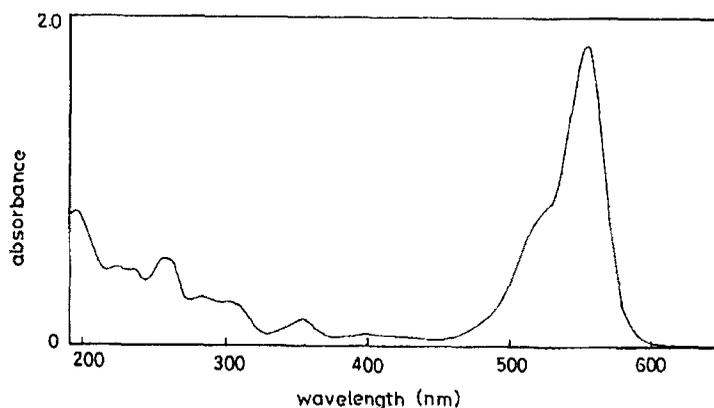
The schematic diagram and details of the experimental set-up is given elsewhere [5]. Briefly, the TL spectrophotometer consists of a pump source which creates the lensing and a probe beam which detects the thermal lens effect. 532 nm pulses from a  $Q$ -switched Nd:YAG laser was used as the heating source. The 632 nm beam from an intensity stabilized He-Ne laser probes the thermal lens formed in the dye solution. The sample solution

taken in a quartz cuvette having pathlength 5 mm was placed in the pump beam path. Both the pump and probe laser beams were focused separately onto the sample cuvette and made to pass collinearly through it using suitable focusing optics and a dichroic mirror. The 532 nm radiation was blocked after the cuvette by a filter.

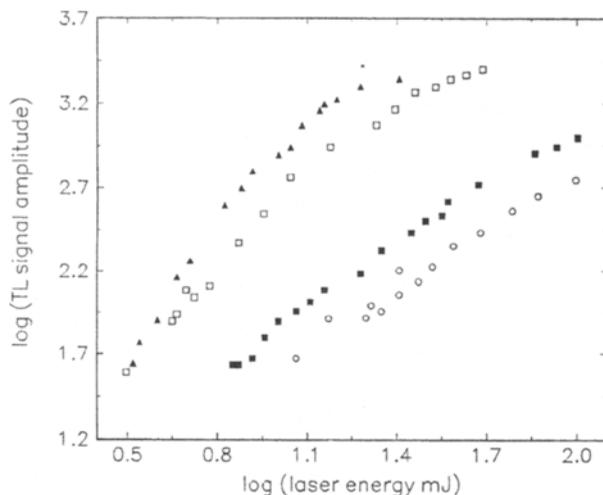
As the 532 nm radiation was passed through the sample containing cuvette, the molecules absorb some of the incident energy and get excited to higher energy levels. The subsequent deexcitation process can occur radiatively or nonradiatively. It is the non-radiative part that gives rise to thermal lens (TL) formation. The resulting refractive index gradient follows the intensity distribution of the exciting pump beam. The TL effect was detected by monitoring the intensity fluctuations in the centre of the probe beam. The TL signal was detected by sampling the intensity of the centre portion of the probe beam through a small aperture. In the present work the intensity of the center portion of the transmitted probe beam was detected by using an optical fiber. The fiber tip serves both as an aperture and as a light guide for the probe beam to the detector consisting of a monochromator-PMT assembly. The monochromator-PMT assembly tuned to the probe beam wavelength (632 nm) provides further filtering of the signal. The signal was recorded using a digital averaging oscilloscope (Tektronix TDS 220) for further processing. The oscilloscope was triggered by a synchronous trigger pulse from the Nd:YAG laser operated at 5 Hz.

### 3. Results and discussion

Rhodamine B (RhB), one of the most widely used dyes, has been found to lase in alcohol, water, ethylene glycol and PMMA. The appearance of RhB in the various media mentioned above has stimulated a further study on spectroscopic and structural properties of this dye in relation to the lasing mechanism. In the present work, TL measurements were performed in aqueous solutions of RhB. TL effect was studied for the concentration range of  $8.55 \times 10^{-7}$  mol/l to  $8.55 \times 10^{-3}$  mol/l and at various incident energy levels. Typical absorption spectrum of



**Figure 1.** Absorption spectrum of rhodamine B in water at a concentration of  $2.14 \times 10^{-5}$  mol/l.



**Figure 2.** Log-log thermal lens amplitude vs incident laser energy for Rh B in water ( $\circ$  -  $8.5 \times 10^{-7}$  mol/l;  $\blacksquare$  -  $4.3 \times 10^{-7}$  mol/l;  $\square$  -  $8.5 \times 10^{-5}$  mol/l;  $\blacktriangle$  -  $8.5 \times 10^{-4}$  mol/l.)

RhB in water recorded with a UV-VIS spectrophotometer (Hitachi model 150-20) is shown in figure 1. From the spectra, it is clear that absorption of the probe wavelength (632 nm) is negligibly small and hence any perturbations due to the probe beam can be neglected.

Log-log plots of TL signal amplitude vs incident laser pulse energy were drawn for each sample. Typical log-log plots are given in figure 2 for different concentrations. From these figures it can be seen that the TL effect increases as incident laser energy increases due to enhanced absorption by dye molecules. At higher illumination the signal tends to saturate due to enhanced depopulation of the ground state. The variation of slope of the log-log plots was studied as a function of concentration of the solution and is given in figure 3. These results show that concentration of the dye molecules has a pronounced effect on the involvement of different nonlinear processes which are taking place in the medium.

At low concentrations, the slope is found to be  $\sim 1$  which indicates one photon absorption (OPA) is prominent. OPA at 532 nm raises the RhB molecules to a vibronic level of  $S_1$  state ( $\sim 18200 \text{ cm}^{-1}$ ). Molecules populating the various vibronic levels of  $S_1$  due to OPA will rapidly deexcite nonradiatively to the lowest vibrational levels in the  $S_1$  manifold in accordance with Franck-Condon principle so as to produce TL signals of lesser intensity and with a linear dependence on laser energy.  $S_1 \rightarrow S_0$  internal conversion is negligible for RhB in the monomer form due to its high quantum yield and comparatively large energy separation between these levels. The possibility for the intersystem crossing to the triplet levels can also be ruled out, since the pulsewidth of the pump laser  $t_p$  is  $\sim 9 \text{ ns}$  in our work such that  $t_p \ll 1/k_{st}$  where  $k_{st}$  is the  $S_1 \rightarrow T_1$  intersystem crossing rate which is  $1.7 \times 10^6 \text{ s}^{-1}$  for RhB [10,11].

As the concentration increases the slope value becomes 2 which is an indication of the occurrence of different nonlinear absorption processes like TPA or ESA. There are few reports regarding the occurrence of TPA in xanthene dyes [12–16]. Rulliere and Kottis [12] investigated excited electronic states of rhodamine 6G solutions by means of two photon spectroscopy. They have explained the existence of TPA via symmetry considerations.

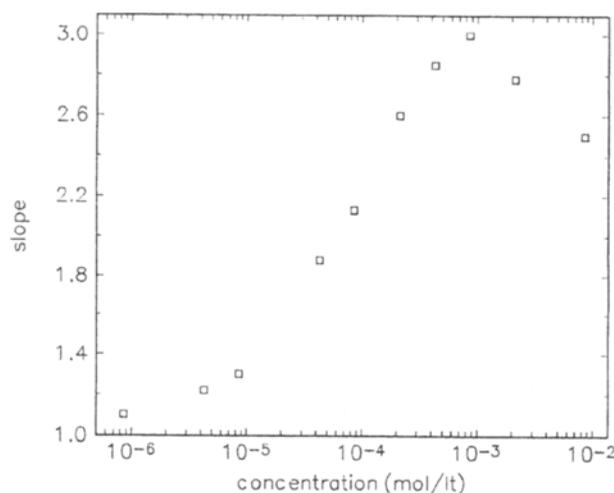


Figure 3. Variation of slope with concentration.

Recently Philip *et al* [16] obtained similar results using pulsed photoacoustic technique. The ns laser pulse increases the possibilities of ESA as compared to a picosecond or femtosecond laser sources [12]. Even though a ns laser is used, being of high power output it provides good power density, sufficient enough to initiate nonlinear absorption. However, using the present experimental set-up, it is very difficult to distinguish between these two processes (TPA and ESA).

In solutions of much higher concentrations we have observed a slope of nearly 3 in the log-log plot for RhB. This is an indication of three photon absorption or a three step processes. Three step processes like  $S_0 \rightarrow S_3 \rightarrow S_n$  is less probable since the lifetime of  $S_3$  is so short that the fraction of the molecules excited to  $S_3$  which decay spontaneously to lower singlets is nearly one. After getting excited to  $S_3$  (by two photon process) the molecules depopulate the  $S_3$  level quickly and efficiently through nonradiative transitions before absorption from  $S_3$  can take place. So this type of three photon processes can safely be neglected. The likely process is that the RhB molecules in the  $S_0$  state may simultaneously absorb three photons and get excited to  $S_n$  levels. Another possible mechanism is the excited two photon absorption from the  $S_1$ . Both the above processes are probable at fairly high concentrations. Subsequent to excitation, the molecules deexcite from higher  $S_n$  levels nonradiatively giving rise to thermal lens signals of high intensity. Since the three photon absorption processes are more complex and less studied compared to other nonlinear phenomena, much more detailed studies on these aspects are needed to get a clear picture.

At much higher concentrations ( $> 2 \times 10^{-4}$  m/l), the slope value shows a decreasing tendency. Aggregation phenomena in the dye solution is expected to play a key role in this peculiar behaviour. It is reported that RhB molecules show extremely strong aggregation in aqueous solutions at concentration greater than  $10^{-4}$  mol/l [17]. Considering the equilibrium between rhodamine monomers (m) and rhodamine dimers (d), at concentrations  $C_m$  and  $C_d$  respectively, and assuming that each component separately obeys Beer's law,

the total absorbance of the solution is given by [18]

$$A_t = A_m + A_d = \frac{l}{2} \left( \epsilon_d C_t + (2\epsilon_m - \epsilon_d) \frac{\sqrt{1 + 8K_d C_t} - 1}{4K_d} \right), \quad (2)$$

where  $l$  is the optical path length,  $\epsilon_m$  and  $\epsilon_d$  the molar absorptivities of monomers and dimers, respectively, at the specified wavelength,  $K_d = C_d/C_m^2$ , the dimerization constant and

$$C_t = C_m + 2C_d \quad (3)$$

the analytical concentration of the dye.

The amount of energy released as light (fluorescence) and as heat (thermal lens) for a solution of monomers and dimers in equilibrium will depend upon the sum of energies absorbed by each component,

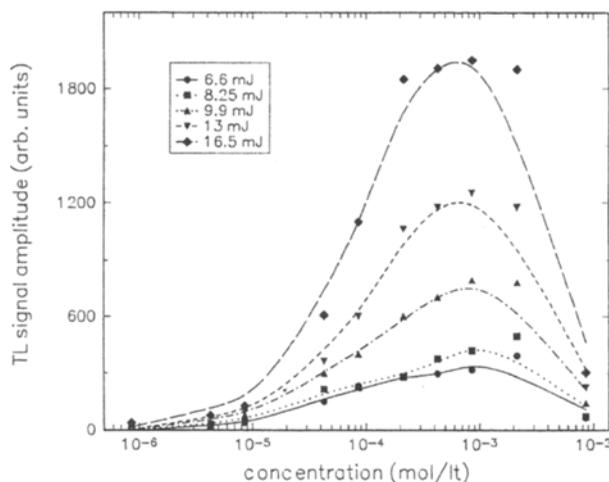
$$P_a = P_{a(m)} + P_{a(d)}. \quad (4)$$

Hence the thermal power liberated by the sample solution  $P_{th}$  is given by [18]

$$P_{th} = P_0(1 - 10^{-A_t})(A_m/A_t(1 - Q_f \bar{\nu}_f/\nu_a) + A_d/A_t) \quad (5)$$

where  $A_m$ ,  $A_d$ ,  $A_t$  and  $Q_f$  are the monomer, dimer, total absorbance and fluorescent quantum efficiency of the laser dye and  $\bar{\nu}_f$  and  $\nu_a$  represent average fluorescence frequency and absorbed frequency respectively. At higher concentrations we do observe a decrease in slope with increase in concentrations. In order to check the effect of aggregation on the TL signal formation, we have studied TL signal intensity vs concentration curves.

It has been observed that TL signal intensity is greatly influenced by the concentration of the dye solution. The variation of the TL signal intensity with concentration is given in figure 4 for different incident energy levels. The TL signal depends on the dimerization constant, the molar absorptivities and the fluorescence quantum yield of the dye solutions through (2). This fact can be inferred from our present experimental observations. For example, the signal intensity goes on increasing up to a particular concentration and then decreases with increasing concentration. According to (2) the TL signal is defined by two components: one component corresponding to the energy absorbed by monomers minus the radiant energy, and the other component corresponding to all the energy absorbed by the dimers. Dimerization contributes to decrease the first component (dimers are nonfluorescent which in turn decreases the value of  $Q_f$ ) and to increase the second component. The ratio  $A_m/A_t$  decreases at the same rate as  $A_d/A_t$  increases, but the variation of  $A_m/A_t$  is weighted by the term  $(1 - Q_f \bar{\nu}_f/\nu_a)$  which is small when the compound is highly fluorescent. The relative amount of energy absorbed by monomers and dimers depends on the dimerization constant and the relative molar absorptivities. Therefore as the concentration increases the second component in the square brackets of (2) for  $P_{th}$  increases faster and the thermal energy corresponding to the loss of two fluorescent monomers is more than compensated by that provided by the formation of one dimer. However, we observed a reduction in TL signal intensity at concentrations greater than  $8.85 \times 10^{-4}$  m/l. This may be due to the following reasons. (1) The emissive RhB monomer can be generated via deaggregation and energetically it can relax nonradiatively through energy transfer to aggregates. (2) With increase in concentration, the concentration of dimer  $C_d$  increases.



**Figure 4.** Variation of thermal lens signal strength as a function of concentration of the Rh B in water for different incident laser energies.

Since a dimer is a combination of two monomers ( $2m \leftrightarrow d$ ), the effective number density of the absorbing molecules becomes less at higher concentration because of the enhanced aggregation phenomena. One may doubt that the decrease in TL signal at higher concentrations may depend upon the cell pathlength due to the nonuniform heating effect. However, we observed similar results when experiments were repeated with a 1 mm cell.

#### 4. Conclusions

The thermal lens technique can be effectively utilized to study different nonlinear processes that are occurring in the RhB laser dye. The ease of the setting up and use of the apparatus are very attractive for such a task and the method appears to be complementary to other spectroscopic techniques. It has been observed that the nonlinear properties of the dye molecules vary with concentration. At lower concentrations one photon absorption is prominent. As the concentration increases occurrence of TPA or ESA is evident, although both the processes are indistinguishable from each other using the present experimental set-up.

It will be very appropriate to use TL spectrometry for analyzing dimerization equilibria because this method is sensitive and should be useful over a wide range of concentrations. The TL method is more efficient to detect dimerization equilibria especially because variation of thermal energy involved in such equilibria is generally more important than the variation of absorbance and fluorescence. We have also noticed a peculiar concentration dependence curve of TL signal amplitude.

#### Acknowledgements

Financial support from Department of Science and Technology (Govt. of India), UGC and CSIR is gratefully acknowledged. The authors are also thankful to Dr. Reji Philip, Tata Institute of Fundamental Research, Mumbai for useful discussions.

## References

- [1] G C Orner and M R Topp, *Chem. Phys. Letts.* **36**, 295 (1975)
- [2] P Sathy, R Philip, V P N Nampoore and C P G Vallabhan, *Opt. Commun.* **74**, 313 (1990)
- [3] C V Bindhu, S S Harilal, R C Issac, V P N Nampoore and C P G Vallabhan, *Pramana – J. Phys.* **44**, 231 (1995)
- [4] J M Harris, *Analytical applications of lasers*, edited by E H Piepmeier (Wiley-Interscience, New York, 1987) Vol. 87
- [5] C V Bindhu, S S Harilal, V P N Nampoore and C P G Vallabhan, *Curr. Sci.* **74**, 764 (1998)
- [6] C V Bindhu, S S Harilal, R C Issac, V P N Nampoore and C P G Vallabhan, *J. Phys.* **D29**, 1074 (1996)
- [7] C V Bindhu, S S Harilal, V P N Nampoore and C P G Vallabhan, *Opt. Engg.* **37**, 2791 (1998)
- [8] A J Twarowski and D S Kliger, *Chem. Phys.* **20**, 259 (1977)
- [9] A J Twarowski and D S Kliger, *Chem. Phys.* **20**, 253 (1977)
- [10] D N Dempster, T Morrow and M F Quinn, *J. Photo. Chem.* **2**, 343 (1974)
- [11] P Sperber and A Penzkofer, *Opt. Quant. Electr.* **18**, 381 (1986)
- [12] C Rulliere and P Kottis, *Chem. Phys. Letts.* **75**, 478 (1980)
- [13] B Focault and J P Hermann, *Opt. Commun.* **15**, 412 (1975)
- [14] H Lin and M Topp, *Chem. Phys. Letts.* **47**, 442 (1977)
- [15] D J Bradley, M H R Hutchinson, H Koetser, T Morrow, G H C New and M S Petty, *Proc. R. Soc. Lond.* **A328**, 97 (1972)
- [16] R Philip, P Sathy, V P N Nampoore and C P G Vallabhan, *J. Phys.* **B25**, 155 (1992)
- [17] F L Arbeloa, P R Ojeda and I L Arbeloa, *J. Chem. Soc. Trans II* **84**, 1903 (1988)
- [18] J Georges. *Spectrochim. Acta* **A51**, 985 (1995)