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# TWO AND THREE PHOTON ABSORPTION IN RHODAMINE 6G METHANOL SOLUTIONS USING PULSED THERMAL LENS TECHNIQUE

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Dual beam transient thermal lens studies were carried out in rhodamine 6G methanol solutions using 532 nm pulses from a frequency doubled Nd:YAG laser. Analysis of thermal lens signal shows the existence of different nonlinear processes like two photon absorption and three photon absorption phenomena along with one photon absorption. Concentration of the dye in the solution has been found to influence the occurrence of the different processes in a significant way.

## 1. Introduction

There has been considerable interest in understanding the optical nonlinearities of dye solutions. The free-electron model proposed by Kuhn[1] suggests broad delocalization of $\pi$-electrons over the molecular chain, leading to large optical nonlinearities in dye molecules. This model assume that the $\pi$-electrons can move freely along the chromophore group. This prediction has been verified by various reports testifying to the large values of third order nonlinear susceptibility, $\chi^{(3)}$ in dyes.[2–4] The strength and nature of the induced nonlinearity can be described in terms of nonlinear susceptibility or equivalently in terms of the changes in the absorption coefficient and refractive index of the medium. Depending upon the excitation frequency in relation to the absorption line centre, the amplitude and phase contributions to a nonlinear process vary significantly.

Since laser dyes are usually pumped at an optical frequency corresponding to or greater than the $S_0 \rightarrow S_1$ transition frequency and if nonlinear processes like two photon absorption (TPA) or three photon absorption occur at the pump wavelength, in general the dye molecules will be excited to a higher singlet state $S_n (n > 1)$. It is well known that the nonlinear processes like two photon absorption (TPA) can

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occur only at intense laser fields, corresponding to pump intensities of the order of $10^8$ $\mathrm{Wcm}^{-2}$ or higher.[5–7] The detailed study of multiphoton absorption processes is of great significance because of the widespread use of such dyes in tunable lasers.

The study of TPA and higher order multiphoton excitations has been mostly based on the observation of radiative transitions induced by the same from a higher excited electronic state usually at a shorter wavelength than the pump wavelength.[8,9] But these radiative relaxation processes are not very sensitive especially at higher concentrations. In organic dyes anti-Stokes fluorescence (ASF) from higher excited singlets is extremely weak since these short lived states primarily relax nonradiatively to the $S_1$ state, prior to $S_1 \rightarrow S_0$ fluorescence.[10] However, since the highly efficient nonradiative relaxations $S_n \rightarrow S_1$ release a large amount of thermal energy into the medium, such phenomena should be easily detectable by photothermal techniques like thermal lensing[11] or photoacoustics.[12,13] In this paper we show that the relaxation from the higher excited singlets following multiphoton absorption in rhodamine 6G laser dye in methanol can be conveniently studied using thermal lens technique.

In a typical thermal lens (TL) experiment, a Gaussian laser beam is passed through the sample. By absorbing some of the incident energy, the molecules get excited to higher energy levels. Nonradiative de-excitation of these excited molecules generates a temperature rise in the sample and consequently to the formation of an inhomogeneous spatial profile of the refractive index which acts as an optical lens. Since most liquids expand on heating, temperature coefficient of refractive index, dn/dT, is negative and hence the lens formed is a divergent one. A second low power laser beam is used to probe the formation/deformation of the thermal lens. The pump and the probe beams are combined collinearly, propagating in the same region in the sample. The probe beam is then isolated from the pump beam using optical filters. The TL signal strength is monitored as the intensity change in the centre of the probe beam. Thermal lens method can be effectively utilized for the determination of absolute quantum yield,[14] thermal diffusivity,[15] absorbance of materials[16] and reaction kinetics studies[17] apart from the nonlinear studies like TPA or multiphoton absorption phenomena.[18,19]

In thermal lens spectrometry the signal intensity is proportional to the power of the heating laser source.[18] Then

$$S \propto E^n , \tag{1}$$

where $S$ is the thermal lens signal intensity, $E$, pump laser energy and $n$, number of photons involved in the absorption process. Hence by monitoring the dependence of thermal lens signal amplitude on pump energy, one can identify the occurrence of different processes like one photon absorption ($n = 1$) and multiphoton absorption processes ($n \geq 2$).

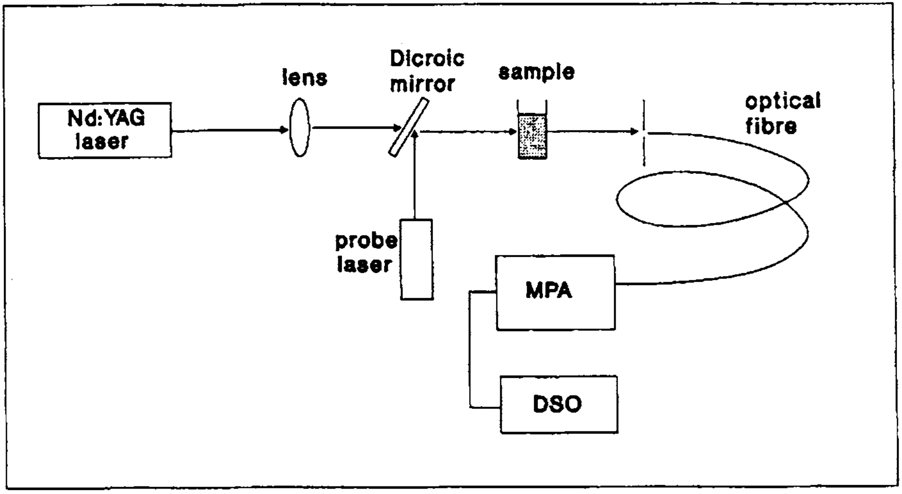

Fig. 1. The pulsed thermal lens set up used in this experiment (MPA — monochromator — PMT assembly, DSO — digital storage oscilloscope).

## 2. Experimental

Figure 1 shows the block diagram of the thermal lens spectrophotometer, consisting of a frequency doubled Q-switched Nd:YAG laser as the heating source and an intensity stabilized He–Ne laser as the probe beam. The sample solution taken in a quartz cuvette having pathlength 5 mm is placed in the pump beam path. The pump and probe beams are focussed onto the sample cell and made to pass collinearly through it using suitable convex lenses and by the use of a dichroic mirror. The excitation beam was blocked after the sample cuvette by a filter. The polished tip of a 10 m long graded index optical fiber (200 $\mu$m core, NA 0.22) placed at 90 cm away from the centre of the sample cuvette serves both as an aperture and as a light guide for the probe beam to a monochromator — PMT assembly. The monochromator — PMT assembly tuned to the probe beam wavelength (632.8 nm) provides further filtering of the signal. The TL signal was recorded using a digital averaging oscilloscope which provides a complete time domain representation of the signal. The oscilloscope was triggered by a synchronous trigger pulse from the Nd:YAG laser operated at 5 Hz. The collinearity of the two beams was verified by using Z-scan technique.

## 3. Results and Discussion

The absorption spectra for rhodamine 6G methanol solutions at low and high concentrations are given in Fig. 2. The spectra for different concentrations in the same solvent show variations. Only the absorption spectra taken for low concentration is relevant, since a signal saturation is observed at high concentrations. The

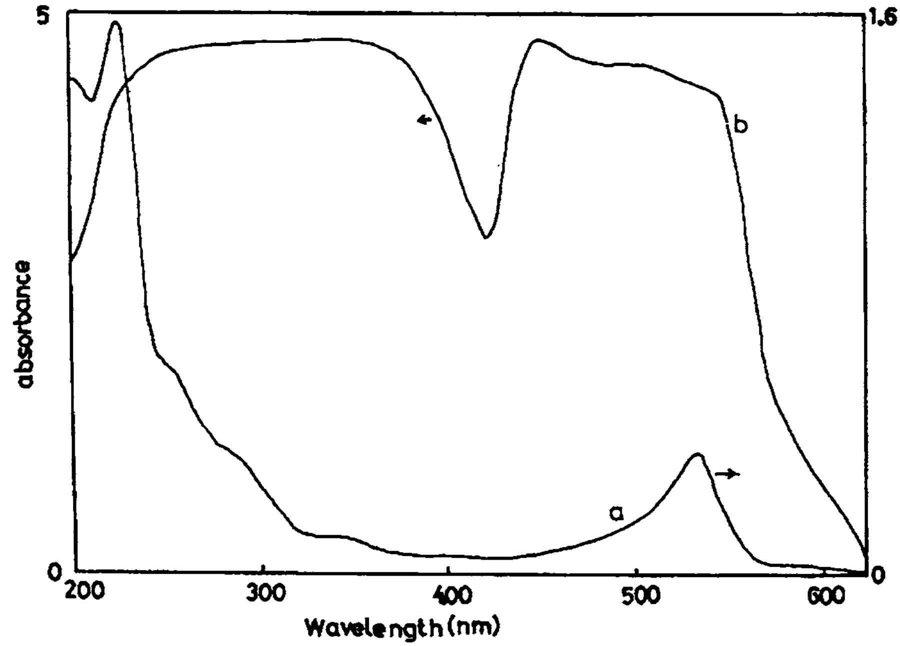

**Fig. 2.** Absorption spectra of rhodamine 6G in methanol (a — $6.9 \times 10^{-5}$ mol/lt and b — $2.13 \times 10^{-3}$ mol/lt).

samples were taken in a 1 cm square quartz cuvette. The absorption spectrum of Rhodamine 6G in methanol shows maxima at 18875, 29000, 37000 and 41670 $cm^{-1}$ corresponding to the excited singlets $S_1$, $S_2$, $S_3$ and $S_4$ respectively. From these spectra it is clear that absorption at 632 nm (probe laser wavelength) is negligibly small and hence any perturbations due to the probe beam can be safely neglected.

The lasing efficiency and fluorescence yield of a dye medium depend on various parameters like solute–solvent interaction, intersystem crossing, excited state absorption (ESA), TPA and radiative and nonradiative relaxation cross sections. Most of the above mentioned phenomena depend critically on dye concentration and pump intensity. Transient thermal lens measurements were made from sample solutions of rhodamine 6G in methanol at varying concentrations ranging from $10^{-3}$ to $10^{-7}$ mol/lt at various input energies. Log–log plots of thermal lens signal against laser energy are obtained for each sample. Figure 3 gives some of the log–log plots of thermal lens signal strength as a function of laser energy in methanol at different concentrations.

Figure 4 represents the variation of the slope with concentration for these samples. From this figure it is clear that the slope, which directly gives the number of photons involved, varies with respect to concentration. The slope is found to be 0.8 for the lowest concentration studied ($4.5 \times 10^{-7}$ mol/lt). The slope steadily increases with concentration and reaches 3 at $8 \times 10^{-5}$ mol/lt after which it

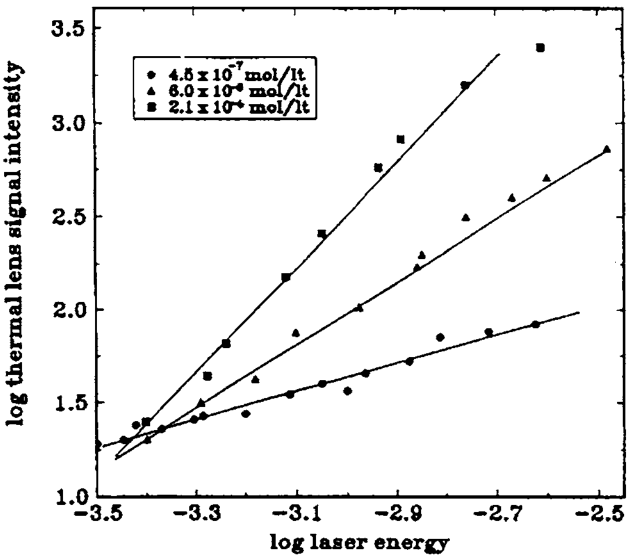

Fig. 3. Log thermal lens amplitude vs log laser energy for rhodamine 6G methanol solutions at different concentrations.

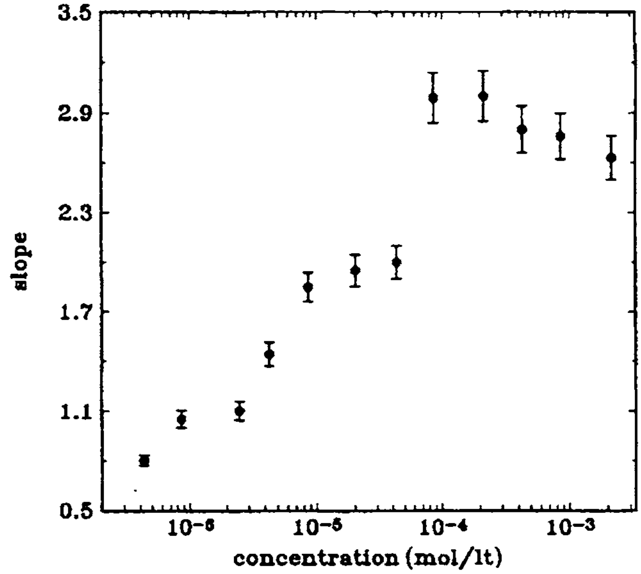

**Fig. 4.** Variation of slope with concentration.

decreases. Figure 4 gives the direct indication of the many photon process involved in the generation of thermal lens signal. The curve exhibits three distinct parts with respect to the change in the value of slope.

In solutions of low concentration one photon absorption (OPA) is prominent. The slope varies from 0.8 to 1.45. OPA at 532 nm raises the rhodamine 6G molecules to a vibronic level of $S_1$ state ($\sim$ 18800 $\text{cm}^{-1}$). 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. $S_1 \to S_0$ internal conversion is negligible for rhodamine 6G 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. The pulse width of the pump laser $t_p$ is $\sim$ 9 ns in our work such that $t_p \ll 1/k_{st}$ where $k_{st}$ is the $S_1 \to T_1$ intersystem crossing rate which is $4.2 \times 10^5\ \text{s}^{-1}$ in rhodamine 6G.[20,21]

The slope goes on increasing with respect to concentration and reaches a value of 2 at $5 \times 10^{-5}$ mol/lt which is an indication of the occurrence of TPA. Under intense pumping excitation of rhodamine 6G molecules to higher excited levels ($S_0 \to S_3$) can take place by means of absorption of two 532 nm photons simultaneously. Subsequent to TPA excitation in the dye, TL signals are generated due to the strong $S_n \to S_1$ nonradiative coupling. These signals should have a quadratic dependence on laser energy. Rulliere and Kottis[22] investigated excited electronic states of rhodamine 6G solutions by means of two photon Spectroscopy. They have explained the existence of TPA via symmetry considerations. TPA can be understood in terms of symmetry allowed transitions; indeed due to the lack of symmetry of the molecule, the one and two photon transitions are always allowed, only the relative magnitude of the two transition moments varies with approximate state symmetry. Recently Sathy *et al.* obtained similar results using pulsed photoacoustic technique.[5,6] Along with TPA, excited state absorption (ESA) can also occur populating the higher excited singlets. The ns laser pulse increases the possibilities of ESA as compared to a ps or fs laser sources.[22] Even though a ns laser is used, being of high power output it provides good power density, sufficient enough to initiate nonlinear absorption.

In solutions of much higher concentrations we have observed a slope of $\sim$ 3 in the log–log plot for rhodamine 6G. Three step processes like $S_0 \to S_3 \to S_n$ 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.[3] 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 rhodamine 6G molecules in the $S_0$ state may simultaneously absorb three photons and get excited to $S_n$ levels. Another possible mechanism is that by OPA the rhodamine 6G molecules go to the $S_1$ level from where by absorbing two more photons simultaneously the molecules gets excited to the $S_n$ levels (excited two photon absorption). 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.

## 4. Conclusion

The thermal lens technique can be effectively utilized to distinguish between different nonlinear processes that are occurring in the rhodamine 6G laser dye. The basic principle of thermal lens technique is similar to the two photon excitation technique, it merely takes advantage of radiationless decay processes following excitation rather than emission processes. 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 way of doing it. The nonlinear properties of the dye molecules vary with concentration. At lower concentrations OPA is prominent. As the concentration increases occurrence of TPA is evident. At higher concentrations three photon processes begin to appear. The decrease in slope at higher concentrations is expected to be due to the aggregate formation.

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