OBSERVATION OF TWO-PHOTON ABSORPTION IN RHODAMINE 6G
USING PHOTOACOUSTIC TECHNIQUE

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Two-photon absorption in Rhodamine 6G using the second harmonic of a pulsed Q-switched Nd:YAG laser has been studied by photoacoustic technique. It is observed that there is a competition between one-photon and two-photon absorption processes. At lower concentration the two-photon process is predominant over the one-photon process.

1. Introduction

Rhodamine 6G is one of the members in the family of xanthene dyes which has been extensively studied in relation to its lasing properties. Fluorescence yield and hence the lasing efficiency of a dye medium depends on various parameters like solute–solvent interaction, intersystem crossing, excited state absorption, two-photon absorption (TPA), radiative and non-radiative relaxation cross sections etc. Most of the above mentioned phenomena depend on the dye concentration and pump intensity. Of all the processes listed, two-photon absorption (TPA) is an important one which will help in a deeper understanding of the nature of energy levels, and various aspects of interstate coupling and molecular relaxation.

Usually two methods are used to study TPA. The first is based on the direct measurement of the light absorbed due to TP absorption in the same way as one-photon absorption (OPA) spectra are obtained [1,2]. In the second method fluorescence emission is monitored as a function of excitation intensity and wavelength [3-5]. Both of the above techniques monitor radiative relaxation processes which are not very sensitive especially at higher concentrations. In dyes, non-radiative relaxations are very much predominant since radiative coupling from S_n ($n>1$) states to lower levels is very small as compared to non-radiative coupling. Therefore TPA can be better studied by analysing the non-radiative processes

which can be stimulated and measured directly by photoacoustic technique [6]. Photoacoustic (PA) technique can supplement fluorescence spectroscopy to evaluate various excitation and de-excitation mechanisms in the molecular regime. This method can be used especially in cases where the conventional transmission or reflectance measurements are difficult.

Of several configurations of PA techniques [7] it has been demonstrated [8] that pulsed PA technique is very sensitive, as the pulsed lasers can transfer megawatts of power into the medium. Pulsed PA technique has been used for diverse applications ranging from the detection of weak optical absorptions to the measurement of ultrasonic velocity in condensed matter [9].

In the present paper we report the study of TPA in a Rh6G solution of various concentrations using pulsed PA technique.

2. Experimental set-up

The crucial element in the experimental system is the transducer which detects the pulsed laser induced PA signals. This follows the design described by Patel and Tam [6]. The transducer consisting of a PZT disc 4 mm thick and 15 mm in diameter is firmly mounted in a stainless steel casing with a front diaphragm of the same material having a thickness of 1 mm. The sample cell for dye solution is made

313

of stainless steel with proper windows. The design of the transducer is such as to minimize error factors in measurement like spurious electrical pickup, ringing effect etc. Further, good acoustic impedance matching between the transducer and the dye solution also is achieved.

A schematic experimental setup is shown in fig. 1. The second harmonic (532 nm) output of a frequency doubled Q-switched pulsed Nd:YAG laser (Spectra Physics model DCR 11) was used as the exciting radiation source for producing the acoustic signal in the sample. For a definite concentration of the sample, for various laser powers the amplitude of the acoustic signal was monitored by a gated integrator (EG&G model 163). The laser power was monitored by a fast photodiode (Hewlett Packard), the output of which was given to another identical gated integrator. Both these outputs were then fed to a boxcar averager (EG&G model 162), and the normalized PA amplitude versus the laser power was obtained. The experiment was repeated for various

concentrations of the sample. The absorption spectra of the Rhodamine 6G solution of various concentrations also were recorded using a UV-VIS-NIR spectrophotometer (Hitachi model U-3410).

3. Results and discussion

The samples taken can be broadly classified into a set of lower concentrations and a set of higher concentrations. This classification is based on the observation that the PA signal amplitude depends on the laser power in distinct manners, in either group A general observation for the group of low concentration samples is that the log–log plots of photoacoustic signal against laser energy are straight lines having slopes greater than unity (fig. 2). On the other hand in the group of higher concentrations (fig. 3), the slopes are in the order of one and greater than one at the lower and higher laser energies respectively, for each sample. Analysis of the curves (fig
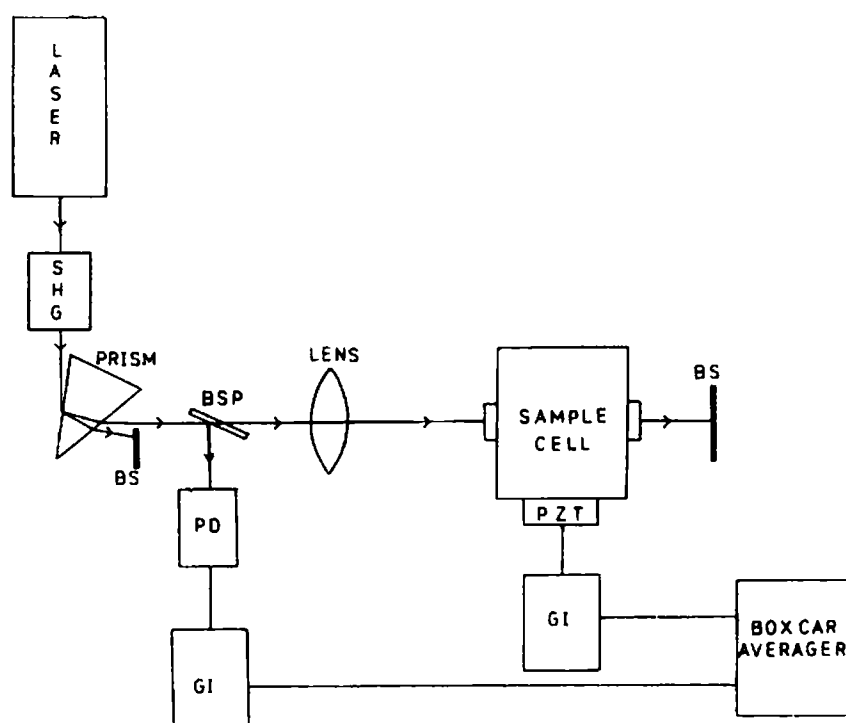

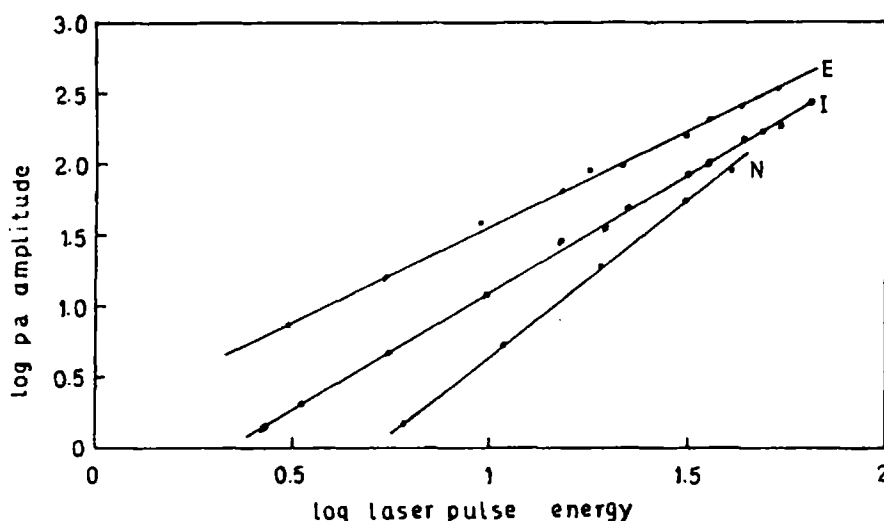Fig. 1. Experimental set-up. BS – beam stop, BSP – beam splitter. GI – gated integrator, PD – photodiode.

314

Fig. 2. Log-log plot of photacoustic signal amplitude against laser pulse energy for the group of low concentration samples, in the order $E>I>N$. $E=4.434\times10^{-4}$ moles/litre, $I=2.137\times10^{-4}$ moles/litre, $N=0.555\times10^{-4}$ moles/litre.

2) drawn for the group of low concentrations reveals that the slope of the log–log plot decreases from 2.37 to 1.3 as concentration is increased. In the group of higher concentrations while lower slope is almost one, the higher slope is evidently greater than one, and the threshold of this change in slope varies inversely with concentration.

OPA in Rhodamine 6G is due to the strong absorption at 532.8 nm, corresponding to excitation from S_0 to one of the vibronic levels of S_1 at 18769 cm^{-1}. In the log–log plot this corresponds to a slope of one. A slope of the order of two can be either due to TPA ($S_0\rightarrow S_3$) or two-step absorption process ($S_0\rightarrow S_1\rightarrow S_3$), S_3 lying at 37000 cm^{-1}. At low concentrations the predominance of TP process is revealed from the curves in fig. 2. At higher concentrations the higher vibrational levels of the lowest singlet state S_0 get populated building increased chances for one photon excitation in addition to TPA, and this competition brings about reduction in the slope of log–log plot from a value of two. This is clear from fig. 3.

Fig. 4 shows absorption spectra of Rh6G at two concentrations of which one is high (1.78×10^{-4} moles/litre) and the other is low (0.807×10^{-4} moles/litre). From the spectra it can be seen that absorption $S_0\rightarrow S_1$ has a very high oscillator strength as compared to uv absorption. The S_0 state of Rho-

damine 6G belongs to A_1 symmetry while S_1 belongs to B_2 symmetry. S_n ($n>1$) states have more of A_1 character. Hence in one photon process $S_0(A_1)\rightarrow S_1(B_2)$ is strongly allowed while the absorption $S_0\rightarrow S_3$ is very weak. Reverse is the case for TPA process. At low concentrations TPA process is more favoured and is revealed by the value of slope ≈2 (fig. 2). Even though a two-step process is also a probable mechanism, polarization studies by Lin and Topp [10] and Rulliere and Kottis [5] favour TPA process in xanthene dyes. As the concentration is increased the OPA process in uv region gets enhanced due to various types of complex formations and other interactions as revealed in the absorption spectra. This implies that S_3 at higher concentrations takes up more of B_2 character so that $S_0\rightarrow S_3$ is allowed strongly in OPA. This means that S_1 and S_3 both have similar symmetry states so that $S_1\rightarrow S_3$ excitation by OP process decreases and hence contributions due to two step excitation ($S_0\rightarrow S_1\rightarrow S_3$) as well as TPA process ($S_0\rightarrow S_3$) get decreased. The decrease in the slope with increase in sample concentration can be thus explained.

Variation of the slope of log–log plot of PA signal against laser energy with concentration (for the set of low concentrations) is shown in fig. 5. It is seen that as the concentration is decreased, the slope is increased from 1.3 at higher concentration to 2.37 at
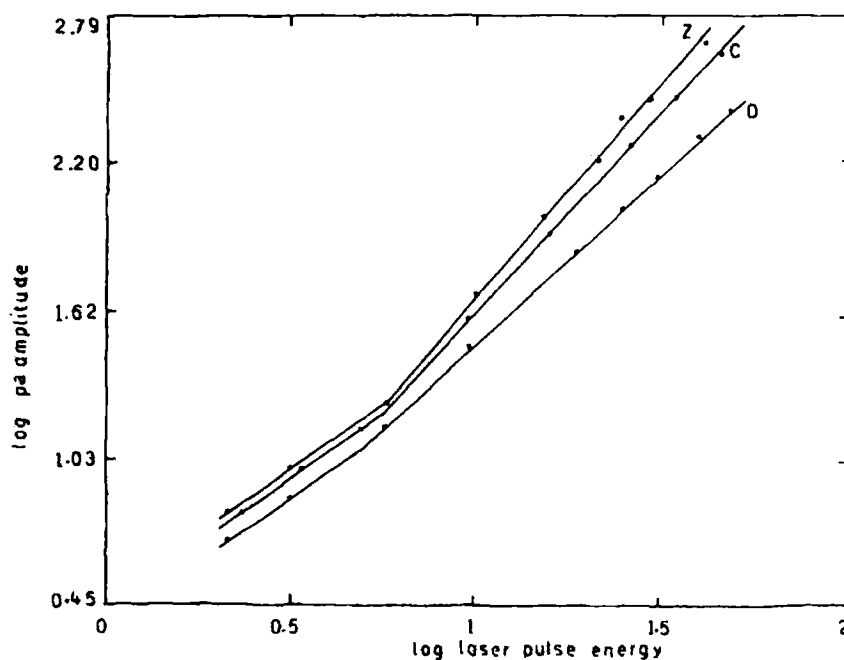
315

Fig. 3. Log–log plot of photoacoustic signal amplitude against laser pulse energy for the group of high concentration samples, in the order $Z > C > D$. $Z = 12.95 \times 10^{-4}$ moles/litre, $C = 6.91 \times 10^{-4}$ moles/litre, $D = 5.32 \times 10^{-4}$ moles/litre.
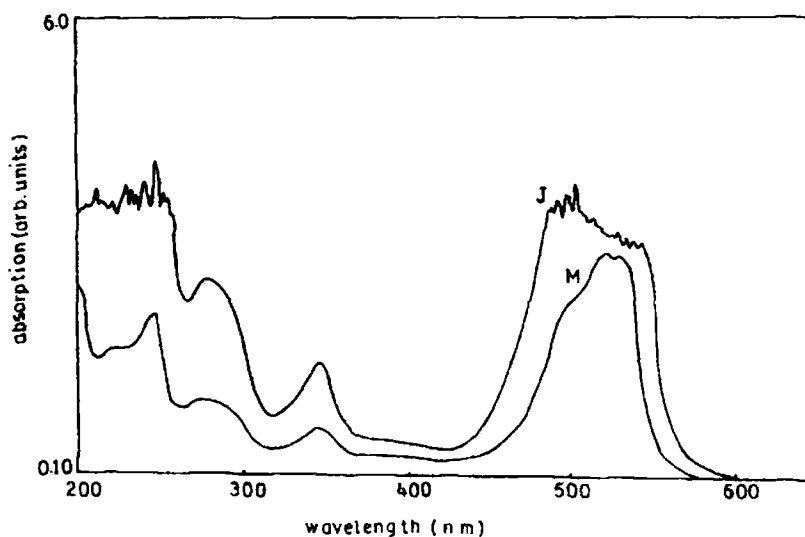

Fig. 4. Absorption spectra of Rhodamine 6G in water at two different concentrations, $M = 0.807 \times 10^{-4}$ moles/litre, $J = 1.78 \times 10^{-4}$ moles/litre.

lower concentration. This tendency is an obvious indication towards the probability of multiphoton processes in the samples of very low concentrations. At

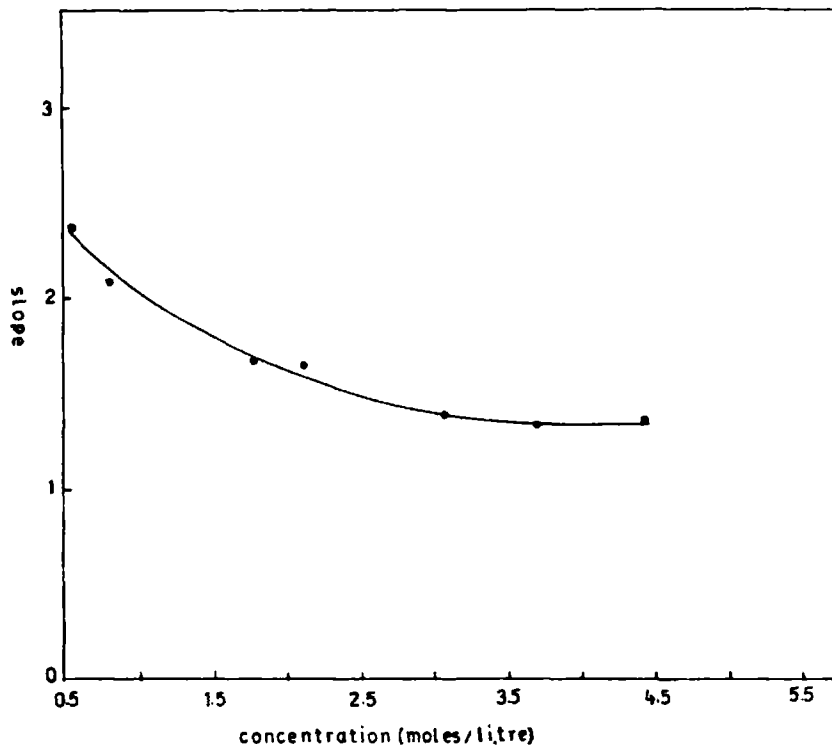higher concentration OPA process predominates over TPA phenomena.

316

Fig. 5. Variation of the slope of log–log plot of PA signal against laser pulse energy with concentration (for the set of low concentration samples).

4. Conclusion

TPA in Rhodamine 6G solution has been studied using pulsed photoacoustic technique. It is observed that there is competition between OPA and TPA and at higher laser power TPA is predominant. At higher concentrations TPA process is found to decrease due to excited state taking up opposite parity state (B_2) as compared to that of the ground state (A_1).

Acknowledgment

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317