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Multiphoton Absorption studies in aqueous solutions of rhodamine 6G laser dye using transient thermal lens technique

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Dual beam transient thermal lens studies were carried out in aqueous solutions of rhodamine 6G 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 as well as excited state 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

Laser dyes like Rhodamine 6G (Rh 6G) are a class of organic molecules which show lasing action under appropriate conditions of excitation. Dye lasers are among the most useful types of lasers because of their easy tunability, wavelength coverage and simplicity. The ultimate utility of these lasers will depend in large measure upon the properties of the dye available. The free electron model proposed by Kuhn [1] suggests broad delocalization of the π electrons over the molecular chains, leading to large optical nonlinearities in dye molecules. This prediction has been verified by various reports testifying to the large values of third order nonlinear susceptibility, $\chi^{(3)}$ in dyes [2, 3]. 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 processes like two photon absorption (TPA) or ESA 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 TPA can occur only at intense laser fields, corresponding to pump intensities of the order of 10^8 W cm⁻² or higher. The detailed study of these two processes (ESA and TPA) 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 [4]. However in organic dyes the fluorescence quantum yield of antistokes fluorescence (ASF) is low since higher excited states are depopulated through strong nonradiative coupling to lower levels. Also these radiative relaxation processes are not very sensitive especially at higher concentrations. The ESA can be observed by resultant quenching of dye fluorescence since this is more sensitive than the ASF technique [5, 6]. 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 [7] or photoacoustics [8].

In this paper, the relaxations from the higher excited singlets following TPA or ESA in Rh 6G in water *viz.* studied by monitoring the photothermal lensing technique is reported.

Methods classified as thermal lens spectroscopy are based upon a thermal change in the optical properties of a sample on the absorption of laser energy which leads to a temperature rise in the sample and

consequently to the formation of an inhomogeneous spatial profile of the refractive index. The heat released by the nonradiative relaxation processes generates a volume expansion in the sample and a density change within the excitation region. The refractive index caused by the heat evolution due to the radiationless processes, turns in most cases the solution into a divergent lens which defocuses the laser beam. The magnitude S which is the change of irradiance at the probe beam intensity relative to its stationary value, is given by [9, 10]

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

where E is the incident laser intensity, m is the number of photons involved in the generation of the thermal lens signal, $I(t=0)$ and $I(t=\infty)$ are the thermal lens signal strength at time $t=0$ and $t=\infty$ respectively. 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 ($m=1$) and multiphoton absorption processes ($m \geq 2$).

2 Experimental

Details of the experimental setup is given elsewhere [22]. The thermal lens spectrophotometer, consisting of a frequency doubled Q-switched Nd:YAG laser (pulse width 9 ns) 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 was placed in the pump beam path. The pump and probe beams were 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 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 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 (100 MHz, Tektronix TDS 220) which provides a complete time domain representation of the signal. The

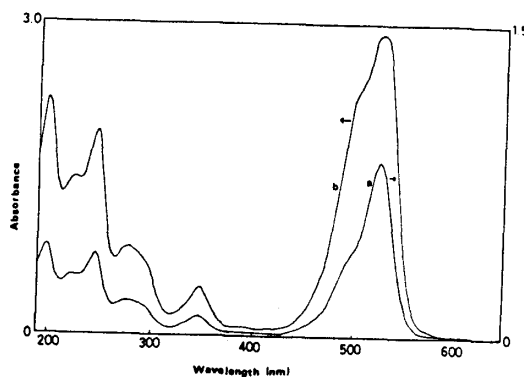


Figure 1: Absorption Spectra of rhodamine 6G in water (a - 2.14×10^{-5} mol/l and b - 8.55×10^{-5} mol/l)

oscilloscope was triggered by a synchronous trigger pulse from the Nd:YAG laser operated at 5 Hz.

3 Results and discussion

The lasing efficiency and fluorescence yield of a dye medium depend on various parameters like solute-solvent interaction, intersystem crossing, ESA, TPA and radiative and nonradiative relaxation cross sections. Most of the above mentioned phenomena depend critically on dye concentration and pump intensity. The absorption spectra of Rh 6G in water are recorded with a UV-VIS spectrophotometer (Hitachi model 150-20). Typical absorption spectra for these systems are given in fig. 1 for different concentrations. The sample was taken in a 0.5 cm square quartz cuvette. The absorption spectrum of Rh 6G in water shows maxima at 18964, 28889, 36111 and 40690 cm^{-1} corresponding to the excited singlets S_1, S_2, S_3 and S_4 respectively. From the absorption studies it is clear that absorption of the probe at 632 nm probe laser wavelength is negligibly small and hence any perturbations due to the probe beam can be safely neglected. Transient thermal lens measurements were made from aqueous solutions of Rh 6G for different concentrations ranging from 10^{-3} to 10^{-7} mol/l at various input energies. Log-log plots of thermal lens signal against laser energy are obtained for each sample. Fig. 2 give some of the

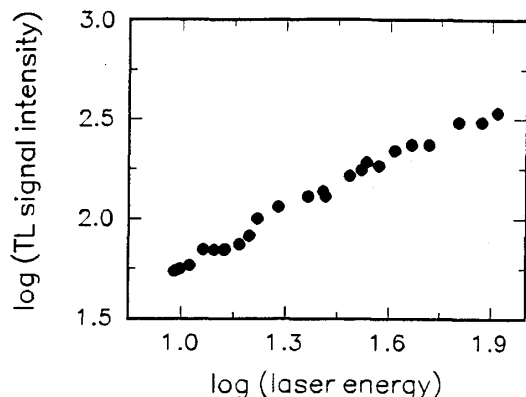


Figure 2: Typical Log-log plots of thermal lens amplitude vs incident laser energy for Rh 6G in water at a concentration of 2.65×10^{-6} mol/lit

log-log plots of thermal lens signal strength as a function of laser energy. From eqn. 1, it is clear that the slope will be numerically equal to the value of m . For solutions of low concentrations the increase in signal intensity is linear irrespective of the solvent used. As the concentration increases the signal intensity also increases. As the concentration of the solution and incident energy increases, the amount of energy absorbed increases and nonlinear processes begins to appear in the dye solution particularly for higher concentrated solutions. A saturation behaviour is observed in the laser energy vs TL signal intensity curve in our results at high irradiance levels. At very higher radiation intensities of incident laser, the amount of energy absorbed decrease, because of the population of the ground state is significantly depleted. Fig. 3 represents the variation of the slope with concentration for these samples.

From fig. 3 it is clear that the slope which directly gives the number of photons involved, varies with respect to concentration and solvent used. The slope is found to be 0.9 for the lowest concentration studied (4.5×10^{-7} mol/lit). The slope steadily increases with concentration and reaches 2.8 at 2×10^{-4} mol/lit after which it decreases. The curve in fig. 3 exhibits three distinct parts with respect to the change in the value of slope: (a) low concentration region (4.5×10^{-7} to 5×10^{-6} mol/lit), with linear variation of TL signal; (b) mid concen-

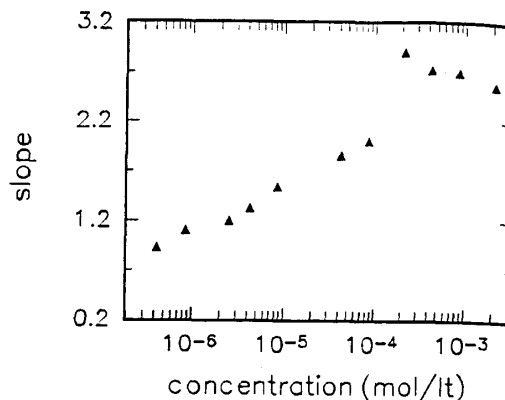


Figure 3: Variation of slope with concentration

tration regime (5×10^{-6} to 8.5×10^{-5} mol/lit) with quadratic variation of TL signal. In this region the slope value increases steadily with concentration and reached at 2; (c) high concentration regime ($\geq 10^{-4}$ mol/lit) where the slope attains a value of ~ 3 and its value decreases with further increase in concentration. These results show that concentration of the dye molecules in different environment has a pronounced effect on the involvement of different process which are taking place in the medium.

In solutions of low concentration one photon absorption (OPA) is prominent. OPA at 532 nm raises the Rh 6G molecules to a vibronic level of S_1 state (~ 18800 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 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 ~ 9 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 $4.2 \times 10^5 \text{ s}^{-1}$ in Rh 6G [12].

As the concentration increases the slope value becomes 2 which is an indication of the occurrence of

TPA. Under intense pumping excitation of Rh 6G molecules to higher excited levels ($S_0 \rightarrow S_3$) 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 $S_n \rightarrow S_1$ nonradiative coupling. These signals should have a quadratic dependence on laser energy. Along with TPA, ESA can also occur populating the higher excited singlets.

There are few reports regarding the occurrence of TPA in Rh 6G laser dye [12, 13, 14]. 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. 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. Therefore state symmetries are mixed up in the case of dyes, leading to rather comparable transition moments for TPA. Recently Sathy et al obtained similar results using pulsed photoacoustic technique [14]. 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. The peculiar behaviour of the slope of the curve at mid concentration regime can be explained by comparing the cross sections for ground state absorption, excited state absorption and two photon absorption for rhodamine 6G at 532 nm [15]. The absorption cross section ($\sigma_{S_0 \rightarrow S_1}(\omega_p) = 3.8 \times 10^{-16} \text{cm}^{-2}$) and emission cross section ($\sigma_{S_1 \rightarrow S_0}(\omega_l) = 1.2 \times 10^{-16} \text{cm}^{-2}$) are nearly equal and the cross section corresponding to ESA ($\sigma_{S_1 \rightarrow S_3}(\omega_p) = 4 \times 10^{-17} \text{cm}^{-2}$) is smaller by an order of magnitude for rhodamine 6G. The reported cross section corresponding for TPA for Rh 6G lies between 10^{-48} and $10^{-50} \text{cm}^4 \text{sec}$ [16].

In solutions of much higher concentrations we have observed a slope of $\simeq 2.8$ in the log-log plot for Rh 6G. 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 Rh 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 RG 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.

We have also noticed that a decrease in the value of slope in the log-log plot with increase in concentration especially at higher concentrations. This may be predominantly due to the formation of aggregates in the Rh6G laser dye solutions. Usually xanthene dyes like Rh6G forms stable ground state dimers and higher aggregates at concentrations greater than 10^{-4}mol/l . One of the most extensively studied compounds from among xanthene dyes is Rh6G, which shows extremely strong aggregation in aqueous solutions [17]. At first, the aggregates were assigned to the dimers. Then, apart from Rh6G dimers, trimers [18] also were found in concentrated aqueous solutions.

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 [19]

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

where l is the optical path length, ϵ_m and ϵ_d the mo-

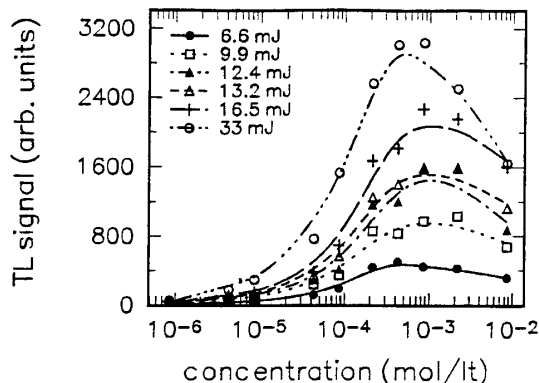


Figure 4: Variation of thermal lens signal strength as a function of concentration of the aqueous solutions of Rh 6G for different incident laser energies

lar absorptivities of monomers and dimers, respectively, at the specified wavelength, $K_d = C_d/C_m^2$, the dimerization constant and $C_t = C_m + 2C_d$ 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, $P_a = P_{a(m)} + P_{a(d)}$. Hence the thermal power liberated by the sample solution P_{th} is given by [19]

$$P_{th} = P_0(1 - 10^{-A_t})[A_m/A_t(1 - Q_{f(m)}\bar{\nu}_f/\nu_a) + A_d/A_t] \quad (3)$$

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 ν_f and ν_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 thermal lens signal formation, we have charted thermal lens signal intensity vs concentration curves. It can be noted that there occurs a decrease in thermal lens signal intensity with increasing concentration in the higher concentration regions irrespective of the solvents used.

The TL signal intensity is greatly affected by the dye concentration. Concentration dependence of TL signal strength is monitored for different laser energies. Fig. 4 shows the variation of the TL signal with

concentration at different excitation energy levels of the pump beam for different solvents. The curve exhibits a type of concentration dependent variation of TL signal. As is clear from the figure, the signal intensity goes on increasing with concentration for low power levels. At lower concentrations the TL effect is small. As excitation energy increases the power absorbed by the dye molecules also increases which in turn causes an enhancement in the TL signal. At higher irradiation intensities of incident radiation, TL signal rises up to a particular concentration beyond which it begins to decrease. The signal peaks at a concentration of 4×10^{-4} mole/l irrespective of the solvent medium. It may be noted here that the photothermal signal amplitude is highly solvent dependent.

The TL signal also depends on the dimerization constant, the molar absorptivities and the fluorescence quantum yield of the dye solutions through eqn. (3). 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 eqn. (3) 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 in eqn. (3) (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 $(1 - \phi_{f(m)}\bar{\nu}_f/\nu_a)$ in eqn. (3) 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. In the case of Rh6G at 525 nm, the molar absorptivity of the dimer is more than two times lower than that of the monomer [19, 20]. Therefore as the concentration increases the second component in the square brackets of eqn. (3) 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. The reduction in thermal lens signal

intensity at higher concentrations is due to following reasons. (1) The emissive Rh6G 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. 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.

4 Conclusion

The thermal lens technique can be effectively utilized to distinguish between different nonlinear processes that are occurring in the Rh 6G 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 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 along with ESA 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. It will be very appropriate to use thermal lens spectrometry for analyzing dimerization equilibria because this method is sensitive and should be useful over a wide range of concentrations. The thermal lens 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.

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