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Studies of nonlinear absorption and aggregation in aqueous solutions of rhodamine 6G using a transient thermal lens technique

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Abstract. 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. The analysis of the observed data showed that the thermal lens method can effectively be utilized to study the nonlinear absorption and aggregation which are taking place in a dye medium.

1. Introduction

Laser dyes like Rhodamine 6G (Rh 6G) are a class of organic molecules which exhibit lasing action under appropriate conditions of excitation. The ultimate utility of these lasers will depend in large measure upon the properties of the dye available. The laser dyes possess a strong absorption generally in the visible and UV regions of the electromagnetic spectrum with fluorescence emission from the first excited singlet state at Stokes-shifted wavelengths [1]. The free-electron model proposed by Kuhn [2, 3] suggests that there is 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 the third-order nonlinear susceptibility, $\chi^{(3)}$, in dyes [4–6]. Since laser dyes are usually pumped at an optical frequency corresponding to or greater than the $S_0 \rightarrow S_1$ transition frequency, then, if any nonlinear processes such as two-photon absorption (TPA) or excited state absorption (ESA) occur at the pump wavelength, in general the dye molecules will be excited to a higher singlet state S_n ($n > 1$). The singlet (S_1) to triplet (T_1) state intersystem crossing will decrease the net available excited singlet state population for stimulated emission, thus affecting the lasing efficiency of dyes. It is well known that nonlinear processes like TPA can occur only in intense laser fields, corresponding to pumping 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

mostly been based on the observation of radiative transitions induced by the same from a higher excited electronic state, usually at a wavelength shorter than the pumping wavelength [7, 8]. The ESA can be observed by resultant quenching of dye fluorescence since this is more sensitive than is the anti-Stokes fluorescence (ASF) technique [9, 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, 12] and photoacoustics [13, 14].

In this paper, the relaxations from the higher excited singlets following TPA or ESA in Rh 6G in water are studied by monitoring the thermal lens signal. Water is one of the common solvents used in dye lasers just because of its unique properties such as nontoxicity and rapid-heat-dissipation capacity. Methods classified as thermal lens (TL) 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. It has been demonstrated that thermal lensing is a versatile and viable technique for investigating the various processes taking place in laser dyes [15–17]. The heat released by the nonradiative relaxation processes generates a volume expansion of the sample and a density change within the excitation region. The refractive index caused by the heat evolution due to the radiationless processes in most cases turns the solution into a divergent lens which defocuses the laser beam. The magnitude S , which is the change in irradiance at the probe-beam intensity relative

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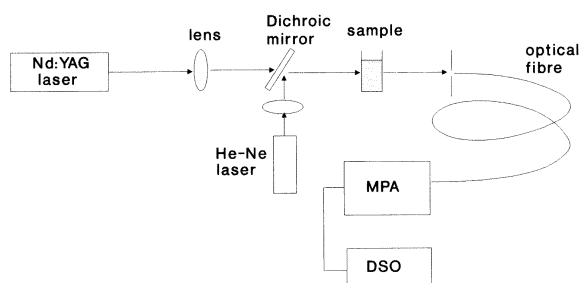


Figure 1. The pulsed thermal lens set-up used in this experiment (MPA, monochromator–PMT assembly; DSO, digital storage oscilloscope).

to its stationary value, is given by [18, 19]

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

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

2. Experimental details

Figure 1 shows the block diagram of the thermal lens spectrophotometer, consisting of a frequency-doubled Q -switched Nd:YAG laser (pulse width 9 ns, maximum energy 110 mJ) as the heating source and an intensity-stabilized He–Ne laser as the probe beam. The sample solution taken in a quartz cuvette having a pathlength of 5 mm is placed into the pump-beam path. The pump and probe beams are focused onto the sample cell and made to pass collinearly through it using suitable convex lenses and by the use of a dichroic mirror.

As the 532 nm radiation passes through the sample-containing cuvette, the molecules absorb some of the incident energy and get excited to higher energy levels. The subsequent de-excitation process can occur radiatively or nonradiatively. It is the nonradiative part that gives rise to thermal lensing. The resulting refractive-index gradient follows the intensity distribution of the exciting pump beam. The position of the cuvette was adjusted to get the maximum value for the TL signal. 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 central portion of the transmitted probe beam was detected by using an optical fibre. The polished tip of a long graded index optical fibre (200 μm core, numerical aperture 0.22) placed 90 cm from the centre of the sample cuvette serves both as an aperture and as a light guide to transfer the probe beam to a monochromator–PMT assembly. Using optical fibres to transmit the laser beams makes the TL technique amenable to remote, *in situ* analysis. It also reduces the influence of mode and pointing variations in the probing laser.

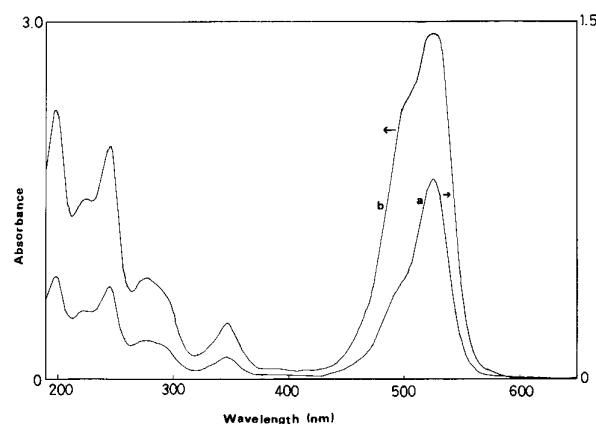


Figure 2. Absorption spectra of rhodamine 6G in water: (a) $2.14 \times 10^{-5} \text{ mol l}^{-1}$ and (b) $8.55 \times 10^{-5} \text{ mol l}^{-1}$.

Here we used a multimode fibre which minimizes alignment procedures and noise problems encountered with single-mode fibres. 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 100 MHz digital averaging oscilloscope (Tektronix TDS 220) 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. In our present experiment, the pulse-repetition rate used was 5 Hz and the time constant for the TL signal is far less than the pulse interval so that the local cumulative heating is insignificant. Also, since our pump laser pulse energy is <100 mJ and the TL signal can be captured using a digital storage oscilloscope even with a single shot, the cumulative bulk heating of the sample can be ignored.

3. Results and discussion

The absorption spectra of Rh 6G in water are recorded with a UV–visible spectrophotometer (Hitachi model 150-20). Typical absorption spectra for these systems are given in figure 2 for various concentrations. The samples were taken in a 5 mm square quartz cuvette. The absorption spectrum of rhodamine 6G in water has maxima at 18 964, 28 889, 36 111 and 40 690 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 the absorption of the probe at 632 nm is negligibly small and hence any perturbations due to the probe beam can be neglected.

The lasing efficiency and fluorescence yield of a dye medium depend on various parameters such as solute–solvent interaction, intersystem crossing, ESA, TPA and radiative and nonradiative relaxation cross sections. Most of the above-mentioned phenomena depend critically on the dye concentration and pump intensity. Transient TL measurements were performed on aqueous solutions of Rh 6G at concentrations ranging from 10^{-3} to $10^{-7} \text{ mol l}^{-1}$ at various input energies. Log–log plots of TL signal amplitude against the laser energy are obtained for each sample. Figure 3 give some such log–log plots. From equation (1), it is clear that the slope will be numerically

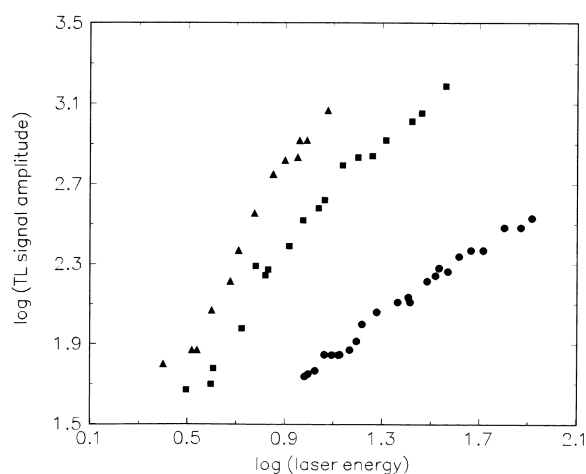


Figure 3. Log–log plots of the thermal lens amplitude versus the incident laser energy for Rh 6G in water: (●), $2.65 \times 10^{-6} \text{ mol l}^{-1}$; (■), $8.55 \times 10^{-5} \text{ mol l}^{-1}$; and (▲), $4.27 \times 10^{-4} \text{ mol l}^{-1}$.

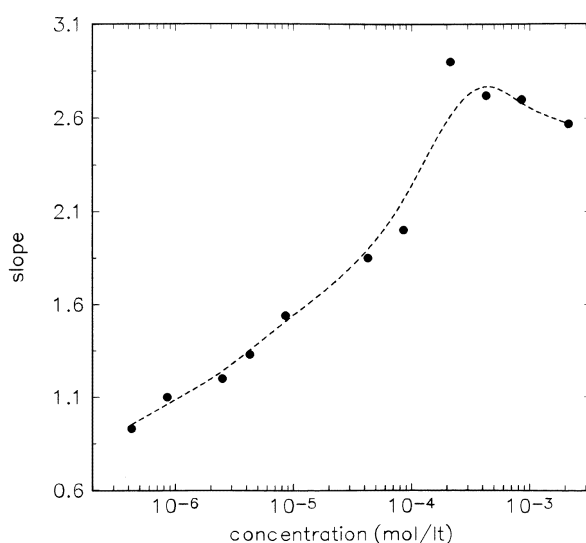


Figure 4. The variation of the slope with the concentration.

equal to the value of m . For solutions of low concentrations the increase in signal intensity is linear. As the concentration of the solution and the incident energy increases, the amount of energy absorbed increases and nonlinear processes begin to occur in the dye solution. A saturation behaviour is observed in the laser energy versus TL signal intensity curve at high irradiance levels, since at high intensities of the incident laser beam, the amount of energy absorbed decreases because the population of the ground state is significantly depleted.

From figure 4 it is clear that the slope, which directly gives the number of photons involved, varies with respect to the concentration. The slope is found to be 0.9 for the lowest concentration studied ($4.5 \times 10^{-7} \text{ mol l}^{-1}$). The slope steadily increases with the concentration and reaches 2.8 at $2 \times 10^{-4} \text{ mol l}^{-1}$, after which it decreases. The curve exhibits three distinct parts with respect to the change in the value of the slope: (i) a low-concentration region (4.5×10^{-7} to $5 \times 10^{-6} \text{ mol l}^{-1}$), with linear variation of the TL signal; (ii) a mid-concentration regime (5×10^{-6} to $8.5 \times 10^{-5} \text{ mol l}^{-1}$)

with quadratic variation of the TL signal (in this region the slope value increases steadily to 2); and (iii) a high-concentration regime ($\geq 10^{-4} \text{ mol l}^{-1}$) for which the slope attains a value of 3 and decreases with any further increase in concentration. These results show that the concentration of the dye molecules has a pronounced effect on the involvement of the various nonlinear processes 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 the S_1 state ($\approx 18\,800 \text{ cm}^{-1}$). Molecules populating the various vibronic levels of the S_1 due to OPA will rapidly de-excite nonradiatively to the lowest vibrational levels in the S_1 manifold in accordance with the Franck–Condon principle, producing TL signals of lesser intensity and with a linear dependence on the laser energy. $S_1 \rightarrow S_0$ internal conversion is negligible for Rh 6G in the monomer form due to its high quantum yield and the comparatively large energy separation between these levels. The possibility of intersystem crossing to the triplet levels can also be ruled out, since the pulse width of the pump laser t_p is about 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 $4.2 \times 10^5 \text{ s}^{-1}$ for Rh 6G [20, 21].

As the concentration increases the slope value becomes 2, which is an indication of the occurrence of various nonlinear absorption processes such as TPA and ESA. There are few reports regarding the occurrence of TPA in Rh 6G laser dye [22–27]. Rulliere and Kottis [22] investigated excited electronic states of Rh 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 the approximate state symmetry. Therefore state symmetries are mixed up in the case of dyes, leading to rather appreciable transition moments for TPA. Sathy *et al* [26, 27] recently obtained similar results using a pulsed photoacoustic technique. The nanosecond laser pulse increases the probability of ESA compared with using picosecond or femtosecond laser sources [22]. Even though a nanosecond laser is used, being of high power output it provides a good power density, sufficient to initiate nonlinear absorption. However, using the present experimental set-up, it is very difficult to distinguish between these two processes (TPA and ESA). The peculiar behaviour of the slope of the curve for the mid-concentration regime can be explained by comparing the cross sections for ground-state absorption, ESA and TPA for Rh 6G at 532 nm. 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 Rh 6G [28]. The reported cross section corresponding for TPA for Rh 6G lies between 10^{-48} and $10^{-50} \text{ cm}^4 \text{ s}$ [21, 29].

In solutions of much higher concentrations we have observed a slope of 2.8 in the log–log plot for Rh 6G. This is an indication of three-photon absorption or three-step processes. Three-step processes like $S_0 \rightarrow S_3 \rightarrow S_n$

are 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 unity [21]. After getting excited to S_3 (by a 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 process 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 Rh 6G molecules go to the S_1 level, whence, by absorbing two more photons simultaneously, the molecules get 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 de-excite from higher S_n levels nonradiatively, giving rise to TL signals of high intensity. Since the three-photon absorption processes are more complex and less studied than other nonlinear phenomena, much more detailed studies on these aspects are needed in order to get a clear picture.

We have also noticed a decrease in the value of the slope of the log–log plot with increasing concentration, especially at higher concentrations. This may be predominantly due to the formation of aggregates in the Rh 6G dye solutions. It is reported that Rh 6G molecules undergo extremely strong aggregation in aqueous solutions at concentrations greater than 10^{-4} mol l^{-1} [30]. At first, the aggregates were considered to be dimers [31, 32]. Then, apart from Rh 6G dimers, trimers [33] also were found in concentrated aqueous solutions. The formation of fluorescent aggregates of higher order than dimers has recently been shown to occur while investigating photophysical properties of aqueous solutions of Rh 6G under high pressure [34].

Considering the equilibrium between rhodamine monomers (m) and rhodamine dimers (d), at concentrations C_m and C_d respectively, the thermal power liberated by the sample solution P_{th} is given by [15]

$$P_{th} = P_0(1 - 10^{-A_t})[A_m/A_t(1 - Q_f\bar{\nu}_f/\nu_a) + A_d/A_t] \quad (2)$$

where A_m , A_d , A_t and Q_f are the monomer, dimer and total absorbances and fluorescence quantum efficiency of the laser dye; P_0 is the incident power and $\bar{\nu}_f$ and ν_a represent the average fluorescence frequency and absorbance frequency respectively. At higher concentrations we do observe a decrease in slope with increasing concentration. In order to check the effect of aggregation on the TL signal, we have plotted the TL signal intensity versus concentration curves.

The TL signal amplitude is greatly affected by the dye concentration. The concentration dependence of the TL signal amplitude is monitored for various laser energies. Figure 5 shows the variation of the TL signal with concentration at various excitation energy levels of the pump beam. The curve exhibits a type of concentration-dependent variation of the TL signal. The TL signal also depends on the dimerization constant, the molar absorptivities and the fluorescence quantum yield of the dye solutions through equation (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

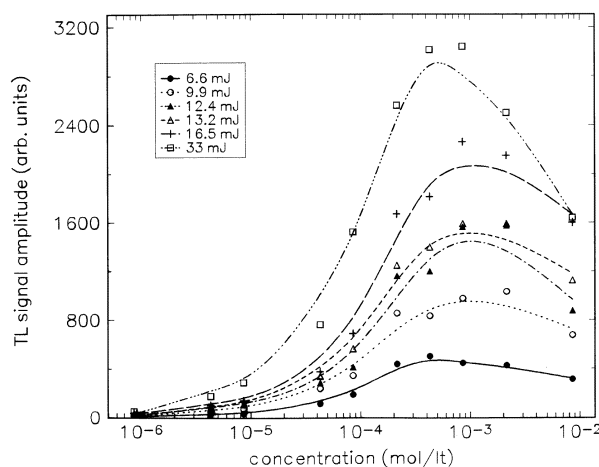


Figure 5. The variation of the thermal lens signal strength as a function of the concentration of Rh 6G in water for various incident laser beam energies.

equation (2) the TL signal is defined by two components: one component corresponding to the energy absorbed by monomers minus the radiated energy and the other component corresponding to all the energy absorbed by the dimers. Dimerization contributes to decreasing the first component (dimers are nonfluorescent which in turn decreases the value of Q_f) and to increasing 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 amounts of energy absorbed by monomers and dimers depend on the dimerization constant and the relative molar absorptivities. In the case of Rh 6G at 525 nm, the molar absorptivity of the dimer is less than half that of the monomer [15, 35]. Therefore, as the concentration increases, the second component in the square brackets of equation (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. The reduction in TL signal intensity at higher concentrations occurs for the following reasons. (i) The emissive Rh 6G monomer can be generated via de-aggregation and energetically it can relax nonradiatively through energy transfer to aggregates. (ii) With increasing concentration, the concentration of dimers 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 enhancement of the 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. Conclusion

The TL technique can be effectively utilized to study various nonlinear processes that are occurring in the Rh 6G laser dye. The ease of the setting up and use of the apparatus make it very attractive for such a task and the

method appears to be complementary to other spectroscopic techniques. The nonlinear properties of the dye molecules vary with concentration. At lower concentrations OPA is prominent. As the concentration increases the occurrence of TPA together with ESA becomes evident, although these two processes are indistinguishable from each other using the present experimental set-up.

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

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