Nonlinear absorption and excited state dynamics in Rhodamine B studied using *Z*-scan and degenerate four wave mixing techniques

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Abstract

We report our experimental results of nonlinear absorption and excited state dynamics in Rhodamine B solutions at 532 nm, on resonance of the absorption band and 600 nm at the absorption edge, studied using the standard *Z*-scan and degenerate four wave mixing techniques. We observed saturable absorption at 532 nm and a transition from saturable absorption to reverse saturable absorption at 600 nm with increase in either intensity or concentration. Time-resolved degenerate four wave mixing studies using incoherent light from a broadband dye laser also confirmed the presence of excited state absorption through resonant two-photon absorption. Concentration dependent studies indicate a complex behavior of reverse saturable absorption within saturable absorption. Results are explained using an effective five-level model. The value of two-photon absorption coefficient evaluated using the same model was $\sim 0.58 \times 10^{-8}$ cm/W. © 2002 Elsevier Science B.V. All rights reserved.

1. Introduction

There is considerable interest in understanding the optical nonlinearities of dye solutions for their wide spread of applications ranging from gain media in lasers to all-optical signal processing devices [1–3]. Xanthene family dye molecules are mostly used in dye lasers to generate tunable laser

source, optical shutters [4] and two-photon microscopy [5]. The fluorescence yield and lasing efficiency of these organic dyes has been studied extensively. The basic absorption processes in dyes could be divided into (a) linear absorption (b) saturation of absorption (SA) and (c) reverse saturable absorption (RSA). Saturation of absorption is vital for use of the dyes in mode-locking. The most important application of RSA is for optical limiting devices [6] that protect sensitive optical components, including human eye, from laser-induced damage. Among a variety of materials investigated, the best results were obtained in porphyrins [7], phthalocyanines [8], fullerenes [9]. It is imperative to assess the nonlinear absorption

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and excited state dynamics in such materials owing to their potential applications. Rhodamine B is one of the most commonly used dyes in various spectroscopic studies. Our basic aim in the present study is to examine the nonlinear absorption behavior of Rhodamine B in the visible region since earlier studies were focussed in the 690–1050 nm spectral region [10,11]. The motivation also crops up from the fact that our recent degenerate four wave mixing (DFWM) studies using incoherent light [12] suggested the presence of excited state absorption (ESA) through resonant two-photon absorption (TPA) process. There have been few reports on the nonlinear absorption properties of Rhodamine 6G [13,14] suggesting the presence of TPA or ESA. Furthermore a recent report suggests that a novel Rhodamine B cation fulleride salt shows strong optical limiting [15] at 532 nm and their data suggests that the type of nonlinear absorption in Rhodamine B was saturable and the limiting action was mainly due to the fulleride salt. Here we report our results on the measurement of nonlinear absorption in Rhodamine B at 532 nm and at 600 nm for the first time to our knowledge using the standard Z-scan technique [16]. We also report our results on excited state dynamics obtained using the DFWM technique with incoherent light.

2. Experimental details

The source for all the experiments was a frequency doubled Nd:YAG (6 ns, 10 Hz) laser and a broadband dye laser comprising an oscillator and a single stage amplifier. The laser medium, Rhodamine B in methanol, was transversely pumped by the second harmonic of an Nd:YAG (6 ns, 10 Hz), which delivered a maximum output energy of $\sim$100 mJ at 532 nm. Eight percent of the input power was used to pump the oscillator and the remaining was used for the signal amplification. The oscillator consisted of just a plane mirror and a glass plate ($\sim$8% R) combination with no other dispersive element in the cavity. FWHM (spectral bandwidth) of the output was measured to be $\sim$7 nm. The corresponding coherence time τ_c calculated using the relation $\Delta\tau \cdot \Delta\nu \sim 1$ and also

measured through an autocorrelation technique was $\sim$170 fs [17]. Other essential details of the experimental set up can be found in our previous publications [17–21]. The phase conjugate beam was isolated using a beam splitter and focused on to a fast photodiode. For the open aperture Z-scan experiments the input beam was focused with 80 mm lens and the sample was scanned across the focus using a micrometer translation stage, which was controlled by a computer. The total transmitted light was collected using a large area lens of $f \sim 120$ mm and focused on to a photodiode. Data acquisition consisted of a lock-in amplifier, ADC card, and a PC. Using a knife-edge experiment, the beam waist at focus was estimated to be $\sim$100 μm for the DFWM experiment and $\sim$20 μm for the Z-scan experiment and the corresponding peak intensities were estimated to be $\sim$10^7 W/cm^2 and $\sim$10^8–10^9 W/cm^2, respectively. A variable neutral density filter was used for controlling the intensity of input beam.

3. Results and discussion

Rhodamine B (>99% pure) solutions in the 10^{-3}–10^{-5} M concentration range were made using highly purified spectroscopic grade methanol as the solvent. The linear absorption spectra for different concentrations were obtained using a UV–visible spectrometer and the curves match very well with those reported in literature. Open aperture Z-scans and time-resolved DFWM measurements were performed in 100 and 500 μm cuvettes for 532 and 600 nm excitations, respectively, at different concentrations for various input intensities. One of the two wavelengths chosen for our studies falls on the resonance peak (532 nm) and the other at the absorption edge (600 nm). Fig. 1 shows the nonlinear absorption behavior at 532 nm at different intensities. We observed only saturable absorption behavior for intensities at the focus ranging from 10^8 to $\sim$10^9 W/cm^2. We observed air bubbles at the focal point above 1.4×10^9 W/cm^2 due to thermal energy produced by absorption, thereby reducing the peak of the transmitted intensity. However, at 600 nm excitation, saturable absorption turnover to reverse
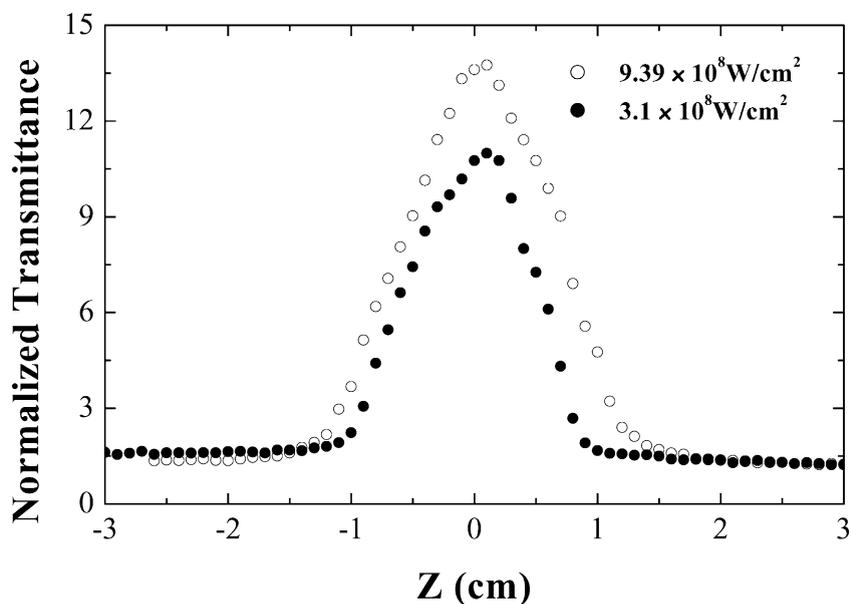
Fig. 1. Open aperture *Z*-scan data of 5.2×10^{-3} M Rhodamine B in methanol at different intensities at 532 nm.

saturable absorption is observed. Fig. 2 shows the open aperture scans at 600 nm for different input intensities and a fixed concentration of 5.2×10^{-3} M. For intensities below 4×10^{8} W/cm^2, a satu-

rable absorption behavior was observed. For increasing intensities ($>1.4 \times 10^{9}$ W/cm^2) the behavior shows a sudden change in its character-istics with a complete switchover from SA to RSA
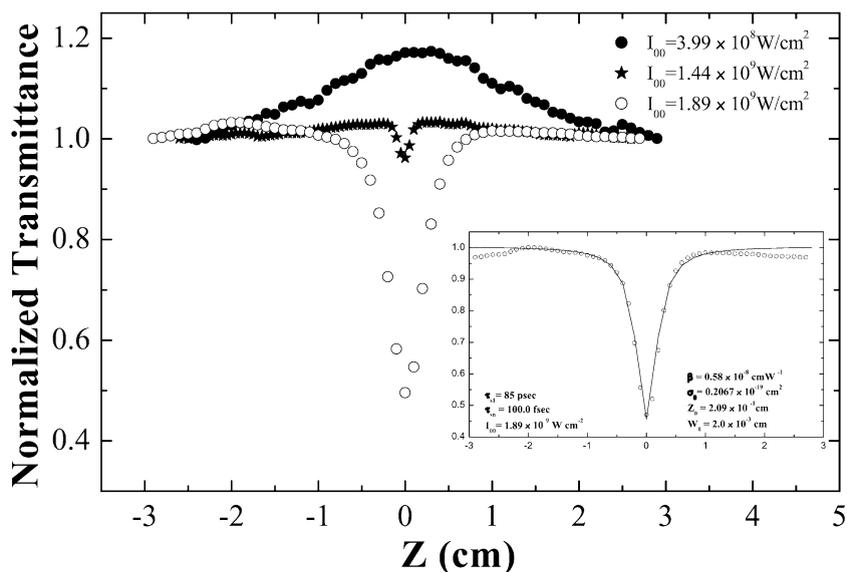

Fig. 2. Open aperture *Z*-scan data of 5.2×10^{-3} M Rhodamine B in methanol at different intensities. Solid line is the theoretical fit using the five-level model in [22].
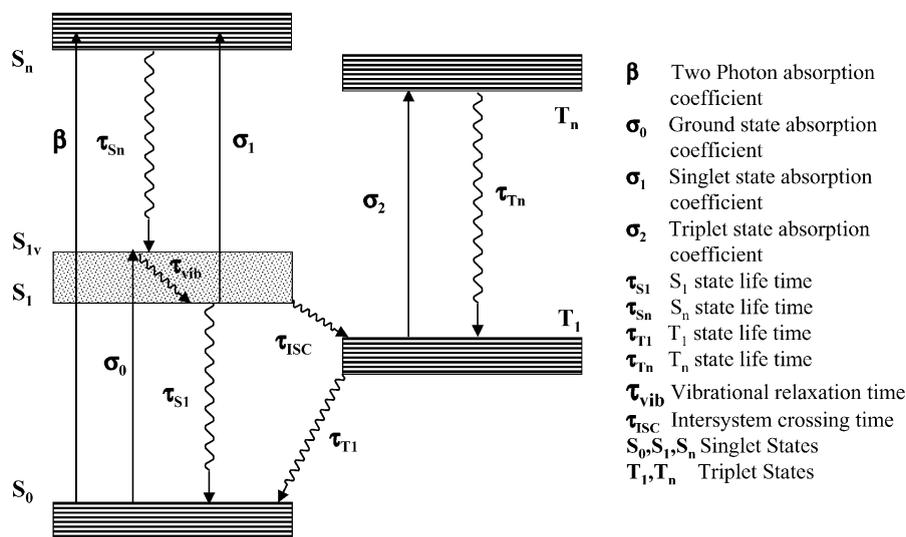
Fig. 3. Energy level diagram of a typical Rhodamine B molecule.

behavior, which could be probably due to either TPA or ESA. At very large intensities ($\sim 1.9 \times 10^9$ W/cm^2) the behavior is completely dominated by RSA. Through a consideration of an effective five-level model [22], shown in Fig. 3 we can clearly understand the different mechanisms responsible for the nonlinear behavior. Depending on the input pulse duration, nonlinear absorption in such materials normally occurs through transitions from (a) $S_0 \rightarrow S_n$ states via instantaneous TPA (b) $S_0 \rightarrow S_1 \rightarrow S_n$ states via a two-step resonant TPA (ESA, if $S_1 \rightarrow S_n$ occurs after vibrational transitions/diffusion within the S_1) or (c) $T_1 \rightarrow T_n$ states via ESA. The intersystem crossing rate ($\tau_{ISC} \sim \mu$s) plays minor role because of the ns/ps life times of the singlet state. For the present studies we, therefore, can neglect the ISC and hence the contribution of the T_1 state. At higher input intensities we expect an enhancement in TPA in agreement with our observation. The theoretical fit shown within the inset of Fig. 2 was obtained by reducing the general five-level model to an effective three-level model including S_0, S_1 and S_n states. In the vicinity of 532 nm, the linear absorption coefficient is very large and strong pumping will lead to saturation rather than RSA [23]. With 600 nm, the excitation is into the lowest of the S_1 energy levels and therefore one expects more of localization of

the energy [24] thereby leading to saturation at lower intensities. Theoretical and numerical calculations for the saturation effects at 532 and 600 nm are being investigated and will be presented in a more comprehensive article at a later stage. That ESA is a fluence dependent process and TPA is intensity dependent process also supports our argument that the valley observed in the Z-scan is predominantly due to resonant TPA. The evaluated TPA coefficient at 600 nm was found to be $\sim 0.58 \times 10^{-8}$ cm/W. We calculated the value of β for two extreme values of singlet state excited state absorption (σ_1). The observed change in transmission and shape of the curves was negligible for $\sigma_1 = 0$ cm^{-2} and 10×10^{-19} cm^{-2} indicating that the predominant mechanism of nonlinear absorption in this case is TPA.

Fig. 4 shows the data obtained at different concentrations for an input intensity of 6.95×10^8 W/cm^2. Most interesting aspect of the data was that for low concentrations we observe saturation of absorption (SA), and with increasing concentration saturation of absorption is followed by RSA. Such kind of behavior has been reported earlier for different molecules including chloro aluminum phthalocyanine (CAP) [25], HITCI [26], polymethine dye [27] and coordination compounds [28]. In the case of CAP and HITCI they argue the
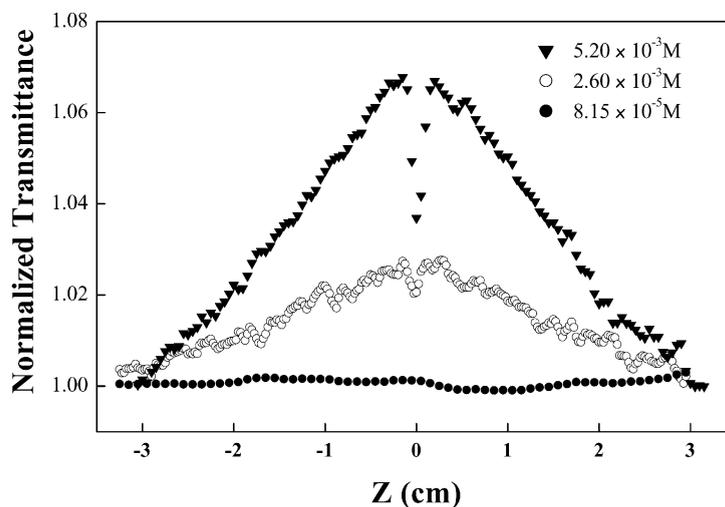
Fig. 4. Open aperture Z-scan data for different concentrations of Rhodamine B at fixed peak intensity of 6.95×10^8 W/cm^2.

presence of such behavior could be due to saturation of the high lying states while for polymethine dye they attribute it to the irreversible damage induced by the input pulses. For ruthenium and osmium complexes of modified terpyridines [28] they observed a super imposed data of TPA, which is due to solvent contribution, and saturation of absorption due to the compounds. The most plausible explanation for the observed behavior in our case is that at higher concentrations these dye molecules tend to form aggregates. The presence of such aggregates can be easily identified through their linear absorption spectrum with new peaks appearing on the S_0–S_1 absorption [29]. This lead to the localization of excited energy in the S_1 states of different aggregates, thereby enhancing the absorption from S_1 to S_n states, which follows the square law for intensity dependence, leading to an enhanced TPA. At lower concentrations monomers are predominant and therefore excitation in the S_1 state diffuses due to dephasing/vibrational relaxation within the S_1 state. However, detailed studies using different input pulse widths are essential in order to completely understand the various mechanisms responsible, studies of which are in progress and will be reported at a later date.

It has been well established that we could achieve ps/fs time resolution in various organic materials by use of DFWM technique with incoherent ns pulses [17–21]. In the present study we measured the phase conjugate signal in Rhodamine B, shown in Fig. 5 for different input intensities as a function of the delay of beam 3 [17]. This kind of two-peak structure has been reported earlier and found to appear due to population in the excited states and short lifetime of the lower excited state S_1 [17]. We observed a second peak (weaker and broader one) only for concentrations of the sample above 10^{-4} M and at input intensities above 800 MW/cm^2. S_n states should be populated in order to observe the second broad peak in the DFWM signal. In the present system this is achieved through resonant TPA, $S_0 \rightarrow S_1 \rightarrow S_n$, which can also be termed as ESA.

At higher concentrations (above 10^{-4} M) we start looking at the excited state absorption from S_1 to S_n. It is well known that formation of aggregates reduces the singlet lifetime. As mentioned earlier the localization of energy in the aggregates also leads to ESA or resonant TPA. We then start observing two-peak structure in the four wave mixing signal. The decay route, then, of the population from S_n states would be into the S_{10} state through the S_{1v} state and finally to the S_0 state. Previous studies [30,31] do indicate the quenching of the S_1 state lifetime at higher concentrations. Smirl et al. [31] reports the excited state lifetime of
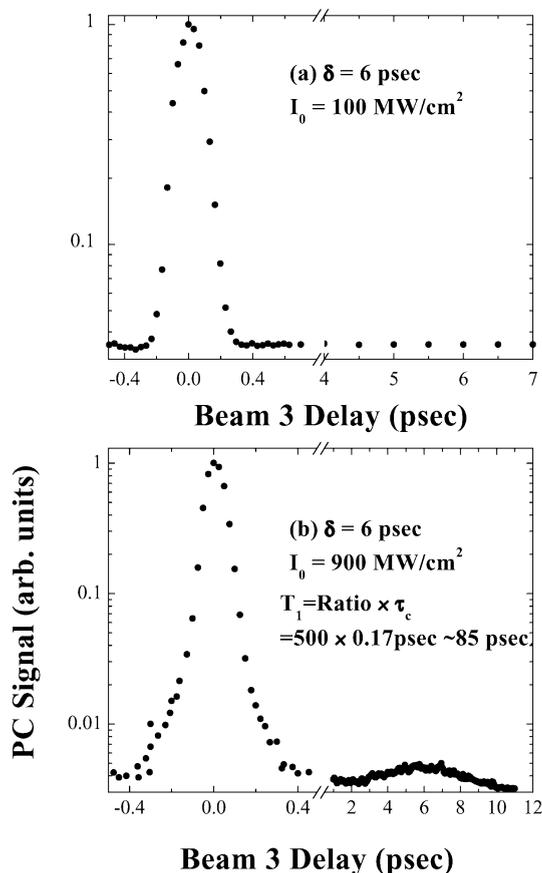
Fig. 5. Phase conjugate signal plotted as a function of delay of beam 3 for a peak intensity of (a) 100 MW/cm^2 and (b) 900 MW/cm^2.

∼95 ps for the Rhodamine B dimer. Even with a concentration of ∼4.6×10^{-4} M the dimeric to monomeric ratio was evaluated to be 0.38 [31]. In our case the value of population relaxation time, T_1, observed and calculated [17] using the ratio of two peaks was ∼85 ps, which is in good agreement with the value reported in the above article. There is less probability of the triplet states being involved in our time-resolved measurements for two reasons: (1) The correlation time $\tau_c \sim 170$ fs is much shorter than $\tau_{ISC} \sim \mu$s, (2) The lifetime of the T_1 state is very long that the ratio of the two peaks has to be very large rendering the second peak well below noise level and unobservable [17], if $T_1 \rightarrow T_n$ absorption is assumed.

4. Conclusions

In summary, our *Z*-scan and time-resolved DFWM studies reveal interesting features in the nonlinear transmittance of the Rhodamine B solution at 600 nm, where switch over from SA behavior to RSA behavior was observed with increase in the intensity or the concentration. We attribute this as due to localization of energy, while resonant TPA takes place. Purely an SA behavior was observed at 532 nm.

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