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Photoacoustic observation of excited singlet state absorption in the laser dye Rhodamine 6G

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Abstract. $S_1 \rightarrow S_3$ excited singlet state absorption and two-photon absorption in Rhodamine 6G at the pump wavelengths of 532 and 1064 nm respectively are investigated. The advantages of employing the pulsed photoacoustic technique for conveniently observing excited singlet state absorption are discussed. It is shown that, since photoacoustics and fluorescence are complementary phenomena, analysis using both techniques will yield a better understanding of optical processes in molecules like Rhodamine 6G.

1. Introduction

Laser dyes, which form the active media of several kinds of dye lasers, are compounds having a strong absorption generally in the visible and UV regions of the spectrum, with fluorescence emission from the first excited singlet state at Stokes-shifted wavelengths. The different processes occurring in a typical dye molecule subsequent to optical absorption are shown in figure 1. The free-electron model proposed by Kuhn (1958) suggests broad delocalization of the π electrons over the molecular chain, 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 dye (Hermann 1974, Hermann and Ducuing 1974, Leupacher and Penzkofer 1985). An interesting consequence is that, in a typical dye laser system, several nonlinear effects including two-photon absorption (TPA) can occur in the pumped region of the dye solution since the pump intensities are normally of the order of 10^8 W cm^{-2} or higher. Another possibility is that of excited singlet state absorption (ESA) from the lasing level (namely, the S_1 state), which reduces the effective stimulated emission cross section of laser dyes significantly in some cases (Wieder 1972, Sahar *et al* 1976). An example is the laser dye Rhodamine 6G, in which an ESA maximum at 440 nm and submaxima at 400, 530 and 565 nm have been identified (Sahar and Treves 1977, Falkenstein *et al* 1978, Magde *et al* 1981). Since laser dyes are usually pumped at an optical frequency corresponding to or greater than the $S_0 \rightarrow S_1$ transition frequency, if TPA and/or ESA occur at the pump wavelength then the molecule will be raised to a higher excited singlet state,

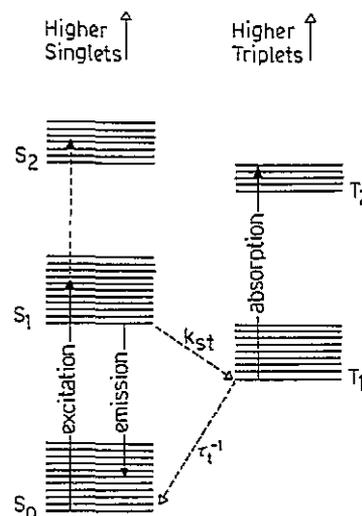


Figure 1. The different optical processes in a typical dye molecule. $S_0 \rightarrow S_1$ excitation, $S_1 \rightarrow S_2$ excited state absorption, $T_1 \rightarrow T_2$ triplet absorption and $S_1 \rightarrow S_0$ fluorescence emission are shown. k_{st} and τ_1^{-1} are the rate constants for $S_1 \rightarrow T_1$ intersystem crossing and $T_1 \rightarrow S_0$ phosphorescence respectively.

S_n ($n > 1$) in general.

The identification and study of TPA in various compounds has been mostly based on observation of radiative transitions induced from an excited electronic state, usually at a shorter wavelength than the pump wavelength (called anti-Stokes fluorescence, or ASF) (Ormer and Topp 1975, Aristov and Shevandin 1978). In organic dyes ASF from higher excited singlets is extremely weak since these short-lived states primarily relax non-radiatively to the S_1 state, prior to $S_1 \rightarrow S_0$ fluorescence. The ESA, on the other hand,

is usually observed by resultant quenching of dye fluorescence since this is more sensitive than the ASF technique. However, since the highly efficient non-radiative relaxations $S_n \rightarrow S_1$ release a large amount of thermal energy into the medium, these phenomena should be detectable by photothermal techniques such as thermal lensing or photoacoustics. In this paper we show that relaxation from higher excited singlets following TPA or ESA in suitable organic media can be conveniently studied by monitoring the thermal effect due to non-radiative relaxation rather than ASF or fluorescence quenching. Pulsed photoacoustics is ideally suited for probing non-radiative relaxations since it is highly sensitive (Tam 1986) and the need for a probe laser beam can be obviated.

The pulsed photoacoustic (PA) signal generated in an absorbing liquid due to one-photon absorption (OPA) at frequency ν is given by (Rosencwaig 1980)

$$q(\nu) = AI(\nu)\eta(\nu) \quad (1)$$

where $I(\nu)$ is the absorbed energy in the laser pulse and $\eta(\nu)$ is the quantum yield of the non-radiative transition. The constant A is a function of the cell geometry, acoustic transducer properties and ultrasonic attenuation of the solution.

If the laser intensity is sufficiently high, multi-photon and/or multi-step absorptions to various levels m can also occur, and the PA signal is then given by

$$q(\nu) = \sum_{m=1}^n A[I(\nu)]^m \eta(\nu_m) \quad (2)$$

where $\eta(\nu_m)$ now represents the quantum efficiency for downward non-radiative transitions from an excited energy level. From equation (2) it is clear that, if PA signals are generated in a sample due to two-photon absorption or two-step excitation ($m = 2$) and subsequent non-radiative relaxation, then these signals will have a quadratic dependence on the pump energy. Hence, by monitoring the dependence of PA signal amplitude on pump energy, one can identify the occurrence of such processes, if any, in the sample.

In this paper we report the observation of excited singlet state absorption in the laser dye Rhodamine 6G by a pulsed photoacoustic technique. Pump pulses are obtained from a frequency-doubled Nd:YAG laser at 532 nm, which is the typical pump wavelength for the Rhodamine 6G dye laser. Ethylene glycol is chosen as the solvent that is usually preferred in dye jets (often mixed with methanol or ethanol) for jitter-free operation.

2. Experimental

The schematic experimental set-up is shown in figure 2(a). Except for minor variations, the design of the PA cell that contains the sample is similar to that of the liquid PA cell described by Patel and Tam (1981). The PA cell is made of stainless steel with glass windows

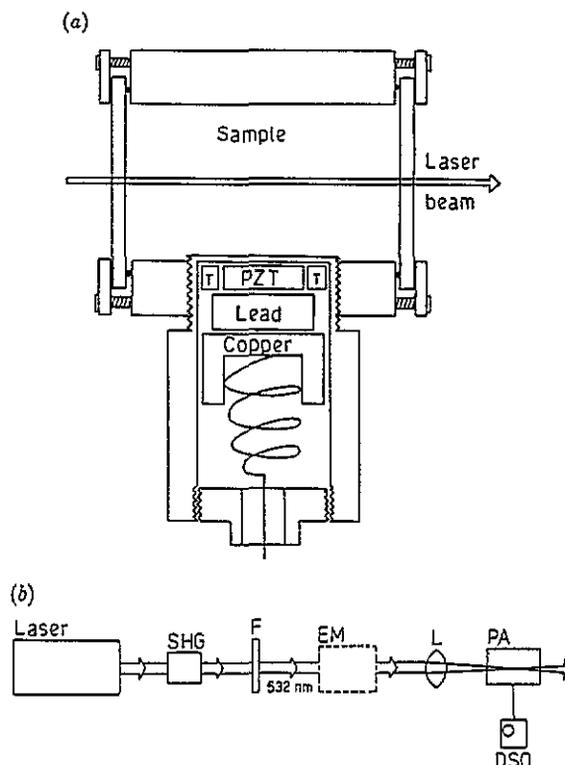


Figure 2. (a) Schematic experimental set-up: SHG, second-harmonic generator; F, dichroic filter; EM, laser energy meter; L, convex lens; PA, photoacoustic cell; and DSO, digital storage oscilloscope. (b) The photoacoustic cell and the transducer chamber: PZT, lead zirconate titanate disc; and T, Teflon ring.

for entry and exit of the laser beam. The acoustic transducer that detects the laser-induced PA signals is a lead zirconate titanate (PZT) disc of 4 mm thickness and 15 mm diameter, firmly mounted in a stainless steel chamber, which is screwed into the PA cell (figure 2(b)). The front diaphragm of the chamber of thickness 0.5 mm is finely polished. A lead disc followed by a copper disc forms the backing of the PZT, which is spring-loaded as shown. In this configuration sample contamination by the PZT is avoided while good acoustic impedance matching between the transducer and the dye solution is ensured. Spurious electrical pick-up is negligible, and signal ringing is reduced to a tolerable level.

The second-harmonic output beam (at 532 nm) from a Q -switched pulsed Nd:YAG laser (Quanta-Ray, DCR-11) is focused by a convex lens (focal length 5 cm) into the PA cell containing the sample. The lens position is adjusted so that the beam focus is at the cell centre. A dichroic filter oriented at 45° to the beam axis separates the fundamental frequency component (1064 nm) from the second harmonic. The laser pulse width (FWHM) is about 10 ns and the pulse repetition frequency is 14 Hz. The pump pulse energy is monitored by a laser power/energy meter (Scientech 362) and the transducer output is observed on a digital storage oscilloscope. The averaged amplitude of the first pulse in the PA signal trace is monitored as a function of pump pulse energy, with dye concentration as the changing parameter.

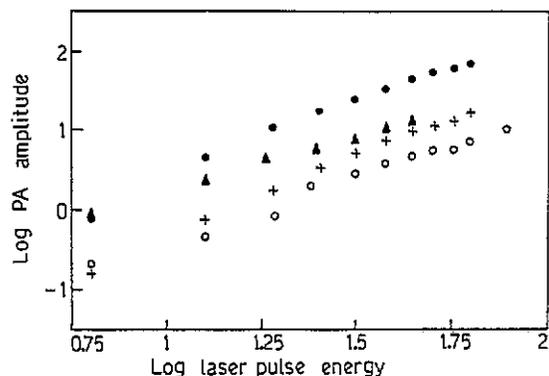


Figure 3. Log-log plots of photoacoustic signal against pump laser energy for some representative samples. \blacktriangle : 1.8×10^{-6} , \bullet : 1.1×10^{-5} , $+$: 7.1×10^{-5} , \circ : 5.3×10^{-4} mol l $^{-1}$.

3. Results and discussion

One-photon absorption at 532 nm raises the Rhodamine 6G molecule to a vibronic level of the S_1 state (about 18 000 cm^{-1}). Excitation to level S_3 (about 37 000 cm^{-1}) can take place by $S_0 \rightarrow S_3$ two-photon absorption and $S_1 \rightarrow S_3$ excited singlet state absorption. However, it is important to note that the TPA cross section at this wavelength will be typically much smaller than the ESA cross section in Rhodamine 6G (Sahar and Treves 1977, Hermann and Ducuing 1972). $S_1 \rightarrow S_0$ internal conversion is negligible for Rhodamine 6G in the monomer form due to its high quantum yield and the comparatively large energy separation of about 18 000 cm^{-1} . To a first approximation intersystem crossing to the triplet levels can also be ruled out, since the pulse width (t) of the pump laser pulse is only about 10 ns in our case, such that $t \ll 1/k_{st}$ where k_{st} is the $S_1 \rightarrow T_1$ intersystem crossing rate, which is of the order of 10^6 – 10^7 s^{-1} in Rhodamine 6G (Schafer 1977). Thus, non-radiative relaxations in the dye are limited to the $S_3 \rightarrow S_1$ transition and thermalization in the S_1 and S_0 states. The PA signals, having a quadratic dependence on pump energy, are generated due to the strong $S_3 \rightarrow S_1$ non-radiative relaxation. On the other hand, molecules populating the various vibronic levels of S_1 due to OPA will rapidly thermalize in the S_1 manifold (and later in S_1 after fluorescence), producing PA signals with a linear dependence on pump energy.

We have measured the PA signals produced from sample solutions of Rhodamine 6G in ethylene glycol at different concentrations (ranging from 10^{-3} – 10^{-6} mol l $^{-1}$) and various input laser energies (6–50 mJ). The log-log plots of PA signal against laser energy are plotted for each sample (figure 3) and the slopes of the plots are calculated. From equation (2) it is clear that this slope will be numerically equal to the value of m . The slope for the lowest concentration studied (1.8×10^{-6} mol l $^{-1}$) is found to be 1.5. The slope steadily increases with concentration and reaches 2 at 7×10^{-5} mol l $^{-1}$, above which the slope is found to decrease, reaching a value of 1.3 at 7.1×10^{-4} mol l $^{-1}$. Figure 4 shows the variation of the slope with concentration.

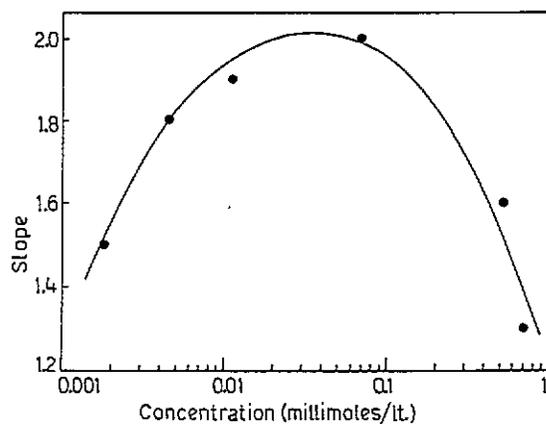


Figure 4. The slope of the log-log plots as a function of sample concentration at 532 nm pumping.

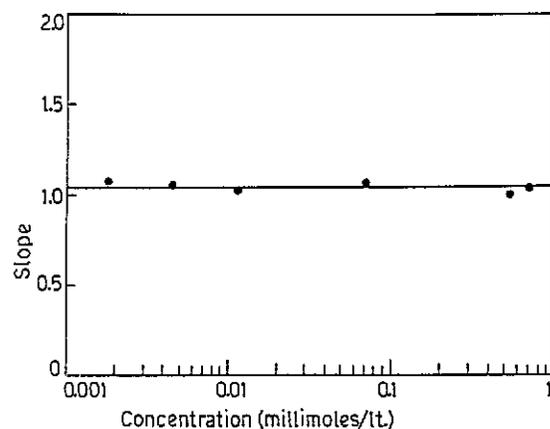


Figure 5. The slope of the log-log plots as a function of sample concentration at 1064 nm pumping.

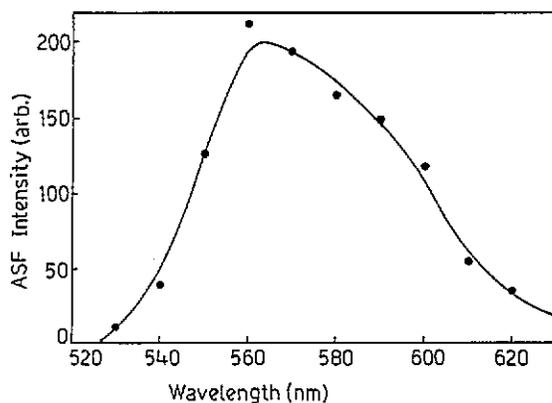


Figure 6. The measured anti-Stokes fluorescence spectrum of Rhodamine 6G at 1064 nm pumping.

This peculiar behaviour of the slope curve can be explained by comparing the cross sections for ground state absorption, excited state absorption and stimulated emission for Rhodamine 6G, given in table 1 (Duarte and Hillman 1990). Whereas the absorption and emission cross sections are nearly equal, the ESA cross section is smaller by an order of magnitude. Since the TPA cross section will be much smaller, its effects on the PA measurements can be neglected. In the case of low-concentration samples, population inversion is easily achieved along the beam path even at low pump

Table 1. Cross sections for Rhodamine 6G ($\lambda_p = 530$ nm, $\lambda_l = 580$ nm).

Ground state pump's	
absorption cross section	$\sigma_{S_0 \rightarrow S_1}(\omega_p) = 3.8 \times 10^{-16}$ cm ²
Excited state laser's	
emission cross section	$\sigma_{S_1 \rightarrow S_0}(\omega_l) = 1.2 \times 10^{-16}$ cm ²
Excited state pump's	
absorption cross section	$\sigma_{S_1 \rightarrow S_3}(\omega_p) = 4 \times 10^{-17}$ cm ²

energies, and stimulated emission effectively competes with ESA, bringing down the slope well below 2. However, as the concentration increases and absorption length (reciprocal absorption coefficient) becomes less than the sample length in the PA cell, population inversion may not occur in several regions of the illuminated solution away from the front surface, such that substantial ESA takes place rather than stimulated emission. Since for monomeric Rhodamine 6G in solution $\eta(\nu_m)$ approaches unity for $S_3 \rightarrow S_1$ transition whereas it is negligible for $S_1 \rightarrow S_0$ transition, increased ESA results in a slope increase towards 2. At still higher concentrations, dimers and higher aggregates are formed in the solution, which absorb the pump radiation to reach the S_1 level but relax non-radiatively to the ground state (Selwyn and Steinfeld 1972). These non-fluorescing aggregates usually reduce the fluorescence quantum yield of the dye considerably, to the extent of stopping laser action altogether in some cases. We have also observed the usual concentration-quenching of fluorescence intensity at high concentrations. Further, pump intensity as experienced by the molecules will be lower here since the absorption length becomes very small. The combined effect of aggregate formation and high absorption in effect enhances one-photon-induced PA signal generation, which is revealed from the slope tending towards unity.

Photoacoustic technique may not always be an effective way to study nonlinear optical effects like TPA and ESA. For example, we measured the PA signals induced by 1064 nm radiation from the Nd:YAG laser in the same samples described above. Here the observed signals are very strong, suggesting that they primarily result from overtone absorption and subsequent vibrational relaxation taking place in the solvent molecules, which is a strong one-photon non-radiative process. $S_0 \rightarrow S_1$ TPA is of course possible at 1064 nm pumping in Rhodamine 6G (Hermann and Ducuing 1972, Penzkofer and Leupacher 1987) but since

its cross section is very small (about 10^{-49} cm⁴ s) and the subsequent relaxation of S_1 is strongly radiative, PA signal generation through this two-photon channel will be much weaker. Hence one can expect the slope to be nearly unity for all samples, and we have observed the same from the corresponding log-log plots (figure 5). However, the two-photon-induced $S_1 \rightarrow S_0$ ASF in this case is sufficiently strong to be detected by a sensitive monochromator-PMT combination. After replacing the PA cell by a quartz cuvette containing the sample and removing the focusing lens and dichroic filter we measured the ASF spectrum, which is shown in figure 6. This result exemplifies the complementarity of PA and fluorescence techniques in those studies where relaxations of different energy levels of the same molecule are to be simultaneously investigated.

Acknowledgments

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