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## Characteristics of two-photon absorption in methanol solutions of Rhodamine 6G using laser induced pulsed photoacoustics

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**Abstract.** Two-photon absorption in methanol solutions of Rhodamine 6G is investigated by photoacoustics using the second harmonic of a pulsed Nd:YAG laser. Competition between one-photon and two-photon processes is observed, depending critically on the sample concentration and input light flux.

### 1. Introduction

Two-photon absorption (TPA) is one of the important non-linear optical processes which becomes relevant in laser dyes at high pump beam intensities. Generally multi-photon excitations lead to population of energy levels to which one-photon transitions are spectroscopically forbidden. TPA processes in dye solutions have been employed for the time duration measurements of picosecond laser pulses by fluorescence trace analysis (Giordmaine *et al* 1967), for the investigation of third harmonic generation process etc. 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. These emissions have been referred to as anti-Stokes fluorescence (ASF), short wavelength luminescence, non-linear fluorescence etc by different authors (Orner and Topp 1975, Catalano and Cingolani 1980, Vabnits *et al* 1986). Different variations of the ASF technique have been applied to study the two-photon characteristics of dye solutions (Hermann and Ducuing 1972b, Rulliere and Kottis 1980, Lin and Topp 1977, Penzkofer and Leupacher 1987). However, in organic dyes the fluorescence quantum yield of ASF is low since higher excited states are depopulated through strong non-radiative coupling to lower levels, thus making the radiative transitions between higher excited singlets and the lower levels very weak. Along with this exists the problem of discrimination of Stokes fluorescence at the detector end, for strongly fluorescing samples. Thus in general, a radiometric estimate of multiphoton processes can lead to highly erroneous results (particularly so in weakly absorbing media) as discussed in an earlier report taking the dye anthracene as a typical example (Hermann and Ducuing 1972b). Further, ASF resulting from different orders of multiphoton excitation (two-photon, three-photon etc) can cover a broad wavelength region extending from the red end of the spectrum to the ultraviolet, thereby limiting the suitability of the ASF

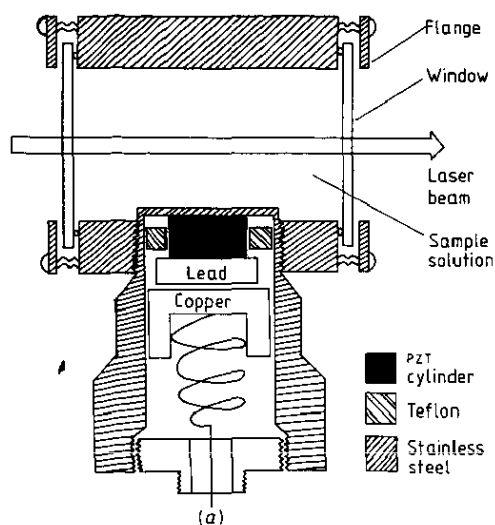
technique, often necessitating sophisticated detection schemes. It is in this context that the applicability of photoacoustic (PA) technique for studying TPA processes becomes significant.

The advantages of employing PA technique for characterizing various molecular processes have been extensively discussed earlier (Siebert *et al* 1980, Patel and Tam 1981, Moll *et al* 1984, Tam 1986). The method relies essentially on the study of acoustic waves generated in the sample due to non-radiative transitions following the absorption of light energy. Measurements of two-photon absorption spectra and cross section carried out by Tam and Patel (1979) in benzene have ensured the indispensability of the PA method in the case of non-fluorescing liquids; however in this report we show that the technique is superior to radiometric methods for fluorescing compounds too. Basically the PA signal amplitude is proportional to the strength of non-radiative transitions occurring in the medium, and in dyes the non-radiative coupling between  $S_n$  ( $n > 1$ ) and  $S_1$  states is very strong giving rise to large PA signals. Furthermore, since PA spectroscopy has been found suitable for weak absorptions (Patel and Tam 1981) as well as for strong absorptions (Sigrist and Chen 1987), studies can be undertaken in a wide range of concentrations of dye solutions. (It is worth mentioning here that the same PA detector can be used with the same sensitivity to monitor different orders of multiphoton excitation.) Recently pulsed sources have been preferred in PA instrumentation since the pulsed photoacoustic (PPA) technique is found to have higher sensitivity, as compared to the CW modulation schemes. The enhanced sensitivity is due to the high peak powers of the pulsed lasers, reaching the MW regime in the present case. Several weak absorptions have thus been detected using this technique. (A detailed description of theoretical and experimental aspects of PPA generation in liquids is given in a number of papers (Patel and Tam 1981, Hutchins 1986, Hutchins and Tam 1986).) In the present communication we report some interesting results obtained from studies of the concentration and pump intensity dependence of TPA in methanol solutions of Rhodamine 6G (R6G) using the PPA technique.

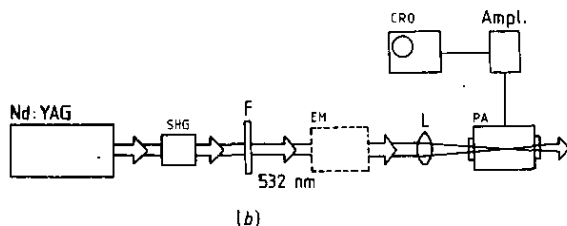
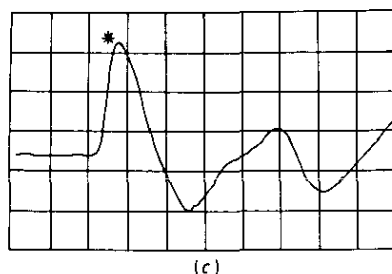
## 2. Experimental set-up

The design of the PA cell and transducer is essentially similar to that described by Patel and Tam (1981) except for some minor changes. The PA cell (figure 1(a)) for holding the dye solutions is made of stainless steel with glass windows for the entry and exit of the laser beam. The transducer that detects the PA signals generated in the sample is a PZT disc of 4 mm thickness and 15 mm diameter, firmly mounted in a stainless steel chamber which is screwed into the PA cell so as to have good contact with the dye solution. A lead disc soldered to a copper disc forms the backing of the PZT, which is spring loaded as shown. Sample contamination by the PZT is avoided in this configuration. Other advantages are: negligible spurious electrical pick-up in hostile environments and the reduction of the ringing effect to a tolerable level. Good acoustic impedance matching between the transducer and the dye solution is also ensured.

The schematic experimental set-up is shown in figure 1(b). The IR eliminated second harmonic output (532 nm) of a Q-switched pulsed Nd:YAG laser (Quanta Ray, DCR-11) was focused by a lens (focal length = 5 cm) into the PA cell containing the sample. The laser was run at a pulse repetition rate of 10 Hz and the pulse duration was about 10 ns. A commercial laser energy meter (Coherent-Lab master) was used



**Figure 1.** (a) The PA cell with transducer chamber screwed in position. (b) Experimental set-up: SHG, second harmonic generator; F, harmonic separator; EM, energy meter; L, lens; PA, photoacoustic cell; ampl., pre-amplifier; CRO, storage oscilloscope. (c) A typical PA signal trace observed on the oscilloscope. The horizontal scale is  $10 \mu\text{s}/\text{division}$  and the vertical scale is  $50 \text{ mV}/\text{division}$ .



to monitor the pump energy. A pulse preamplifier of gain 20 amplified the transducer output and the signal was observed on a Tektronix storage oscilloscope (model 466). In figure 1(c), a typical signal trace is shown. The amplitude of the first pulse in the PA signal trace (marked with an asterisk) was monitored as a function of input pulse energy, with the dye concentration as the changing parameter. Using this experimental set-up a typical solution of R6G in methanol (concentration  $0.069 \text{ mmol l}^{-1}$ ) gave a signal amplitude of  $4.4 \text{ mV}$  for a laser pulse energy of  $6.7 \text{ mJ}$  without the preamplifier. Pulse-to-pulse fluctuations of the signal amplitude were well within 5% of the average value and the reproducibility was high. The absorbance spectra of R6G solutions of various concentrations taken in a  $1 \text{ cm}$  square quartz cuvette were also recorded using a UV-VIS-NIR spectrophotometer (Hitachi model U-3410).

It may be relevant here to note that pulsed photoacoustic generation in liquids is rather a complex phenomenon, which might have its origin from different mechanisms, of which the prominent ones are thermoelastic expansion, vaporization and dielectric breakdown (Hutchins and Tam 1986). The relative probabilities of each of these mechanisms depend on the input laser flux, and it has been shown that the temporal profile of the resulting acoustic pulse differs in each case permitting identification of the particular process. Secondly, the variation of the optical absorptivity of the sample with molecular concentration results in a change of the 'acoustic source' geometry so that the distribution of the acoustic energy in the PA cell can be spherical, cylindrical or planar in different situations. However, in all these cases it is shown that thermoelastic generation will result in the radiation of a dipolar acoustic pulse (Hutchins 1986). For all the samples we studied the PA signal profile was essentially dipolar in nature.

### 3. Results

The important observations resulting from the present studies can be summarized as follows.

(i) Figure 2 depicts the variation of PA signal with concentration. For low laser energies ( $<10$  mJ) the PA signal increases up to a dye concentration of  $\sim 0.12$  mmol  $l^{-1}$ , then decreases up to  $\sim 0.48$  mmol  $l^{-1}$  and then shows a slight but observable increase towards higher concentrations. However, for higher laser energies of 10 mJ and 16 mJ there is a considerable enhancement in PA amplitude at high concentrations. Also, the curve for 16 mJ is of a different pattern, in which the initial increase in PA signal is absent.

(ii) Figure 3 shows the log laser pulse energy ( $\log E_l$ ) plotted against log PA amplitude for different sample concentrations. (The samples have been divided into two groups which will be justified later: one of high concentrations ( $\geq 0.69$  mmol  $l^{-1}$ ) and the other of low concentrations ( $<0.69$  mmol  $l^{-1}$ ). Only three representative samples each are included in the diagrams 3(a) and (b). It may be remembered, however, that this classification is not a rigorous one.) At higher concentrations the log-log plot has two distinct slopes, one with an average value of  $1.1 \pm 0.1$  at lower

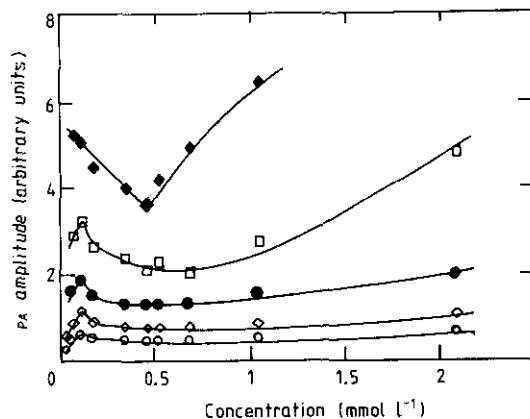


Figure 2. Concentration dependence of photoacoustic signal, measured at various laser pulse energies.  $\circ$ , 2.5 mJ;  $\diamond$ , 4 mJ;  $\bullet$ , 6.3 mJ;  $\square$ , 10 mJ;  $\blacklozenge$ , 16 mJ.

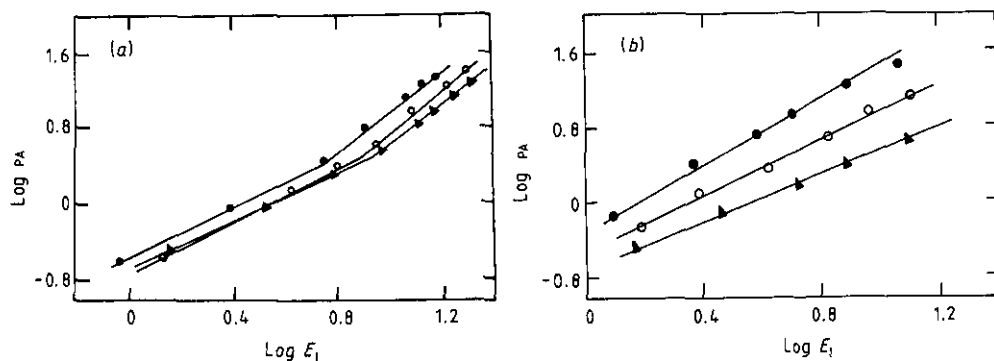


Figure 3. Log laser pulse energy plotted against log PA amplitude. (a) High concentration samples:  $\bullet$ , 2.08 mmol  $l^{-1}$ ;  $\circ$ , 1.04 mmol  $l^{-1}$ ;  $\blacktriangle$ , 0.69 mmol  $l^{-1}$ . (b) Low concentration samples:  $\bullet$ , 0.034 mmol  $l^{-1}$ ;  $\circ$ , 0.069 mmol  $l^{-1}$ ;  $\blacktriangle$ , 0.115 mmol  $l^{-1}$ .

energies and another which is significantly greater than 1, with an average value of  $1.9 \pm 0.1$ , at higher energy values (figure 3(a)). In the low concentration group the behaviour is different, which is obvious from figure 3(b). Here, as concentration increases, the slope changes from  $1.58 \pm 0.1$  to  $1.1 \pm 0.1$ . The calculated slopes for all samples studied are illustrated in figure 4, as a function of concentration.

(iii) Figure 3(a) shows that in the high concentration group there are two distinct regions with different slopes corresponding to lower and higher laser energies. The 'threshold' laser energy required to effect this 'changeover' from lower slope to higher slope region (which in fact shows the transition from a predominantly one-photon absorption (OPA) region to a TPA dominant regime at the molecular level) is found to decrease as concentration increases.

(iv) The absorbance spectra for two dye samples with different dye concentrations (one from the low concentration group and the other from the high concentration group) are shown in figure 5, in which the relative absorbances for the two samples are plotted.

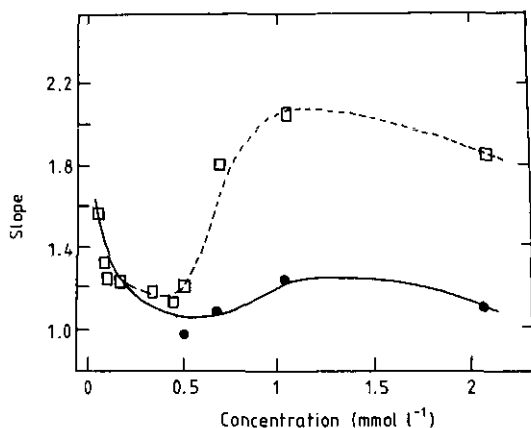


Figure 4. Variation of the slope of log-log plots with respect to the concentration. ●—, laser pulse energy  $< 10$  mJ; —□—, laser pulse energy  $> 10$  mJ.

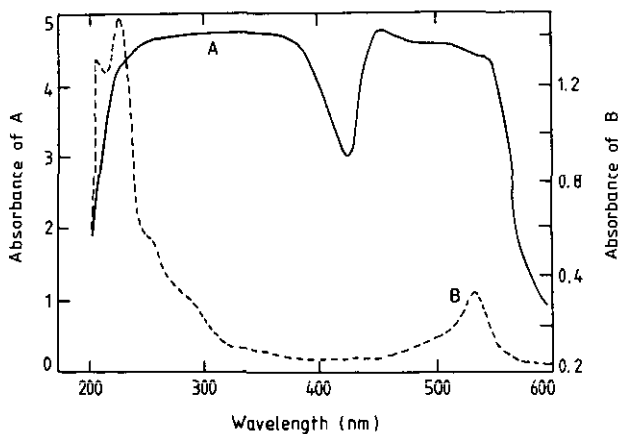


Figure 5. Absorbance spectra for two samples: A,  $2.08 \text{ mmol l}^{-1}$  (high concentration group); B,  $0.069 \text{ mmol l}^{-1}$  (low concentration group).

#### 4. Discussion

The absorption spectrum of R6G in methanol shows maxima at 19 230, 28 571, 36 363 and 41 666  $\text{cm}^{-1}$ , corresponding to the excited singlets  $S_1$ ,  $S_2$ ,  $S_3$  and  $S_4$  respectively. The one-photon excitation with the 532 nm beam raises the R6G molecule to the  $S_1$  state. Excitation to level  $S_3$  is possible either by TPA or two-step excitation. In general under intense pumping, along with TPA and possible multiphoton absorption, excited singlet state absorption (ESA) can also take place in dyes populating higher singlets. But it has been shown that the ESA spectrum of R6G does not significantly overlap its characteristic emission band so that ESA effects will not be prominent with 532 nm excitation (Magde *et al* 1981). (However, when pumped by broad-band sources such as flashlamps, ESA may play a moderate role in populating higher singlets.) Hence the obvious indication is that excitations to the  $S_3$  level by means of 532 nm pumping occur almost completely due to TPA. In any case, excitations to the higher singlet states should lead to the usual non-radiative relaxation  $S_n \rightarrow S_1$  ( $n > 1$ ) giving rise to PA signals. Thus the non-radiative relaxation  $S_3 \rightarrow S_1$  will generate PA signals having a quadratic dependence on laser energy. On the other hand, molecules populating the various vibronic levels of  $S_1$  due to OPA will rapidly de-excite non-radiatively to the lowest vibrational level in the  $S_1$  manifold in accordance with the Franck-Condon principle so as to produce PA signals with a linear dependence on laser energy. Since the excitation energy of R6G from  $S_0$  to  $S_1$  is rather high ( $\sim 19\,000 \text{ cm}^{-1}$ ) non-radiative relaxation of molecules from  $S_1$  to  $S_0$  through internal conversion mechanism cannot be very strong. Also the possibility of intersystem crossing ( $S_3 \rightarrow T_3$ ), which is prevalent in the cw excitation case, is small in pulsed excitation, and such contributions to the PA generation will be negligible (Schafer 1977). This is because the population of the triplet level can be held arbitrarily small if the pulse duration of laser pulse  $t_p$  is smaller than the reciprocal of the intersystem crossing rate  $k_{st}$ . For R6G,  $k_{st} \approx 10^6\text{--}10^7 \text{ s}^{-1}$  and since the laser pulse width is nearly 10 ns in the present experimental set-up ( $t_p \ll 1/k_{st}$ ) PA generation through intersystem crossing can be neglected.

The absorbance spectra (figure 5) show that at relatively low concentrations absorption in the visible region is much lower as compared to that in the ultraviolet. (It might be of interest to note that in R6G: water systems the oscillator strength of UV absorption is slightly lower than that of visible at the same concentration region (Sathy *et al* 1990) which establishes the strong solvent dependence on the spectrum of the dye molecules.) This indicates that in methanol solution, at low concentrations  $S_1$  state of R6G has nearly of the same symmetry ( $A_1$ ) as that of  $S_0$  ( $A_1$ ) while  $S_3$  state will be nearly of  $B_2$  symmetry. Considering the R6G molecule as quasi-symmetric ( $C_{2v}$  group),  $A_1 \rightarrow B_2$  transition moments are weak for two-photon transitions (Hermann and Ducuing 1972a) and this explains the reduced role of TPA at low concentrations as seen from slopes  $< 1.6$ . Indeed due to the lack of perfect symmetry of the molecule the one- and two-photon transitions are always allowed (McClain 1971) whereby there is a competition between OPA and TPA at low concentrations. On the other hand, with increase in concentration the excited state symmetries will be modified by solute-solvent and solute-solute interactions. Even though both UV and visible absorptions are enhanced this symmetry change is more pronounced for  $S_1$ , as seen from the greater increase in  $S_0 \rightarrow S_1$  absorption in comparison to the  $S_0 \rightarrow S_3$  transition (figure 5). This implies that level  $S_1$  will take up more of  $B_2$  symmetry character at high concentrations so as to make  $S_0 \rightarrow S_1$  OPA transition symmetry allowed. Hence as concentration is increased more and more OPA takes place, reducing TPA (figure 4) and the slope comes down

to nearly one. However at higher laser energies a strong enhancement in TPA is observed since the TPA process is more sensitive to variation in laser power as compared to the OPA process.

The peculiar shape of the concentration-PA signal curve (figure 2) is a manifestation of the combined effects of the changes in optical penetration depth and position of the acoustic source in the PA cell with concentration: for a rigorous analysis of this situation the thermal parameters of the solutions also should be taken into consideration.

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