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Pulsed photoacoustic technique to study nonlinear processes in liquids: Results in toluene

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Abstract. Pulsed photoacoustic measurements have been carried out in toluene at 532 nm wavelength using a Q-switched frequency doubled Nd:YAG laser. The variation of photoacoustic signal amplitude with incident laser power indicates that at lower laser powers one photon absorption takes place at this wavelength while a clear two photon absorption occurs in this liquid at higher laser powers. The studies made here demonstrate that pulsed photoacoustic technique is simple and effective for the investigation of multiphoton processes in liquids.

Keywords. Photoacoustics; multiphoton phenomena.

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1. Introduction

The advantages of employing photoacoustic (PA) technique for characterizing various molecular processes have been extensively discussed earlier [1, 2]. The method relies essentially on the study of acoustic waves generated in the sample due to nonradiative transitions following the absorption of light energy. Even though PA approach has become an accepted method to study thermal and optical properties of materials during the last two decades, not much work has been reported in utilizing this effect to investigate multiphoton processes, especially in organic molecules, where efficient nonradiative relaxations $S_n \rightarrow S_1$ release a significant amount of thermal energy into the medium.

The identification and analysis of multiphoton absorption (MPA) in nonlinear optical media have been mostly based either on the observation of radiative transitions [3–5] or on the variation in the transmitted beam intensity [6, 7]. However, the latter technique is not very sensitive in all cases especially where variation in transmitted intensity due to MPA is small, while the former is useful only in samples having large fluorescence quantum yield. Measurements of thermo-optic effect is an alternate method to identify MPA in nonlinear media where probability of nonradiative relaxation of excited molecules is large. PA effect is one such thermo-optic phenomenon which can provide useful information regarding the multiphoton processes [8].

Of the several configurations of PA measurements it has been demonstrated that pulsed PA technique [9, 10] is very effective to detect such optical phenomena since one can have sufficient photon density to induce nonlinear effects in the medium and

the pulsed PA technique has higher sensitivity as compared to the continuous wave modulation schemes. Because of its high sensitivity, pulsed PA is ideally suited for probing the nonradiative relaxations [11] and the technique has recently been used to study two photon absorption (TPA) process in certain laser dyes [12] as well as in organic vapours [13]. Since organic liquids like toluene are extensively used for various technical applications such as solvents for laser dyes, fullerenes etc., the nonlinear properties of these solvents become a subject of great importance. Considerable interest exists in the study of multiphoton processes in these molecules as it throws much light on the nature of energy levels and other aspects like inter-state coupling and molecular relaxations. Even though TPA in toluene has been reported earlier by several authors, in this communication we demonstrate pulsed PA as an effective and versatile technique to study MPA in liquids.

The pulsed PA signal $q(v)$ generated in an absorbing liquid at incident laser frequency v is given by [14]

$$q(v) = AI(v)^n \eta(v) \tag{1}$$

where $I(v)$ is the incident laser power, $\eta(v)$ is the quantum yield of the nonradiative transition and n is the number of photons absorbed. The constant A is a function of the cell geometry, acoustic transducer properties and the ultrasonic attenuation in the solution. Equation (1) shows that by monitoring the dependence of PA signal amplitude as a function of laser power, one can identify the occurrence of multiphoton processes if any, in the sample.

2. Experimental set up

The schematic experimental set up is shown in figure 1. The PA cell is made of stainless steel with glass windows for the 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 onto the PA cell. The purpose of mounting the PZT cylinder inside the stainless steel casing is to minimize external electrical pick up and to prevent sample contamination by PZT (and vice versa). The diaphragm of the chamber has a thickness of 0·5 mm and it is finely polished. A lead disk followed by a copper disk forms the backing of the PZT which is spring loaded within the chamber. Details of the cell fabrication is given by Sathy *et al* [15].

The second harmonic output beam (532 nm) from a Q-switched pulsed Nd:YAG laser (Quanta-Ray, DCR-11) is focussed using a convex lens (focal length 5 cm) into the PA cell containing spectroscopic grade toluene. The lens position is adjusted so that the beam focus is at the centre of cell which is at a perpendicular distance of

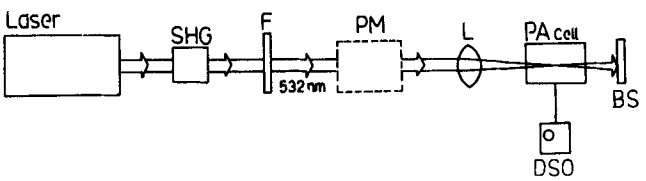

Figure 1. Schematic diagram of the experimental set up. SHG, second harmonic generator; F, harmonic separator; PM, power meter; L, lens; BS, beam stopper; DSO, digital storage oscilloscope.

1·53 cm from the transducer. The spot size at the focal point is measured as 200 μm in diameter. A dichroic filter oriented at 45° to the beam axis separates the fundamental radiation (1064 nm) from the second harmonic. The laser pulse width (FWHM) is $\simeq$ 10 ns and the pulse repetition frequency is 16 Hz. The incident power is monitored using a laser power meter (Scientech model 362) and the transducer output is measured from a digital storage oscilloscope (Iwatsu model DS 8621). The averaged amplitude of the first pulse in the PA signal trace is monitored as a function of the input laser power.

3. Results and discussion

Figure 2 shows the oscilloscope trace of the PA signal produced in toluene. The acoustic signal exhibits a delay of 12 μs with respect to the pump pulse which corresponds to the propagation time of the acoustic signal from the focal region to the piezoelectric detector. This time interval corresponds to the velocity of 1275 m/s which is comparable with the reported value (1300 m/s) of ultrasonic velocity [16] in toluene. From (1) it is clear that TPA process requires a slope two for the log–log plot of PA signal strength against laser power. Figure 3 shows such a plot obtained in the present case. As is clear from figure 3, the slope of log–log plot is nearly unity at low laser power region whereas the slope changes to $\simeq$ 2 at higher laser powers. This shows that at lower laser powers, the optical absorption phenomenon is essentially mediated by one photon process (OPA) while at higher laser powers TPA is favoured.

One photon process in toluene can be explained on the basis of overtone excitation of toluene molecule. CH stretching vibration in toluene has a fundamental frequency (ω_e) at 3100 cm^{-1} with anharmonicity parameter ($\omega_e x_e$) 65 cm^{-1}. The sixth overtone corresponding to $\Delta v = 7$ in toluene lies at 529 nm which is very near to the pump wavelength 532 nm. Thus at lower laser power, excitation of 6th overtone of CH vibration in toluene takes place through OPA resulting into a PA signal which varies linearly with incident laser power.

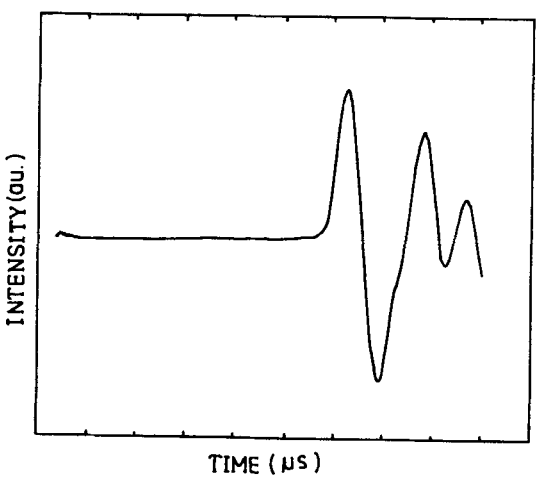

Figure 2. A typical PA signal trace observed on the oscilloscope. The horizontal scale is 2 μs/div.

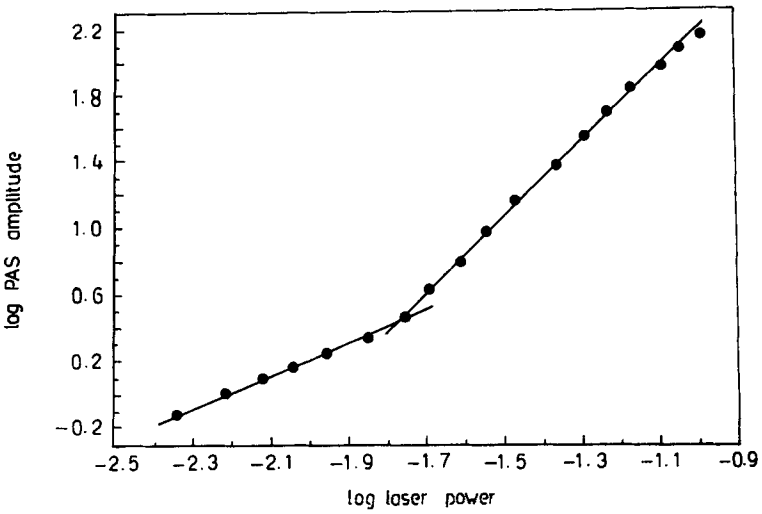

Figure 3. Log laser power plotted against log PA amplitude.

Electronic spectrum of toluene shows a sharp UV band at 274 nm corresponding to $^1A_{1g} - {}^1B_{2u}$ transition which nearly coincides with two photon energy at 532 nm radiation [17]. At higher laser powers, toluene molecules are excited to $^1B_{2u}$ state through TPA. The nonradiative relaxation which follows this process produces the PA signal with characteristic slope two in the log–log plot.

In conclusion we have demonstrated the effectiveness and utility of pulsed PA technique for the study of nonlinear optical processes in liquid medium like toluene. The nature of variation of PA signal amplitude with laser power clearly confirms the occurrence of TPA in toluene at 532 nm. The technique used here is quite suited for experimental investigation of multiphoton processes in liquid media and holds great promise for such studies in many similar organic liquids.

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