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STUDIES ON TWO-PHOTON ABSORPTION OF ANILINE USING THERMAL LENS EFFECT

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Two-photon absorption spectrum of aniline is recorded using thermal lens effect with optical parametric oscillator as the pump source. Studies show that the two-photon absorption spectrum observed corresponds to $^1A_1 \rightarrow {}^1B_2$ transition of aniline.

Keywords: Thermal lens; two-photon absorption; aniline, OPO.

1. Introduction

Eversince the discovery of thermal lens effect by Gordon *et al.*[1] this technique of monitoring nonradiative relaxation in excited molecule has been refined by various researches to suite for the study of various phenomena related to light -- matter interactions.[2–11] Most important modification of the thermal lens (TL) technique is the dual beam method developed by Long *et al.*[12] so that one can record the TL spectrum of samples. Detection of TL signal has been improved later on by incorporating optical fibre so as to introduce flexibility in the experimental configuration.[13] One of the important features of TL-based investigations is its effectiveness to study weak optical absorption arising due to weak phenomena like overtone absorption, singlet–triplet absorption, multiphoton absorption etc.

Two-photon absorption (TPA) is one of the important nonlinear optical phenomena which help us in obtaining details about the excited states of molecules which are unobservable in one photon absorption (OPA) process. Usually TPA is studied by monitoring fluorescence emission resulting from radiative relaxations by excited state molecules.[14,15] However, this method cannot be applied for molecules, which are nonfluorescent or those with low fluorescence quantum yield. Studies using the observation of direct optical absorption by molecules are also not a viable

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method since the magnitude of TPA cross-section is very small as compared to that in OPA.[16]

Thermal lensing is a versatile and viable technique for exploring nonlinear processes taking place in organic materials and dyes. When a medium is illuminated with a laser beam, some of the energy is absorbed by the molecules in the ground state and are excited to higher energy states. After the absorption of the photon the excess energy attained by the molecule can be dissipated in many ways. The nonradiative decay process causes the heating of the sample, creating a refractive index gradient in the medium, so that the medium acts as a lens like optical element called the thermal lens. The propagation of the probe beam through the TL will result in either a spreading or a focusing of the beam center, depending upon the temperature coefficient of the thermal expansion of the medium. By measuring the beam centre intensity in the far field, various thermo-optical properties of the materials can be investigated.

TL technique offers substantial advantages over conventional spectral methods with respect to precision, sensitivity and minimum sample required in addition to its noncontact nature. The sensitivity of this technique is suitable to investigate TP spectra of substituted benzene like aniline, toluene etc. Goodman and Rava studied TP spectrum of substituted benzene using multiphoton ionization.[17,18] Bindhu *et al.* demonstrated the TPA studies in fullerenes and organic solvents using photoacoustic effect.[19,20] TL effect to study TP absorption was first used by Twarowoski and Kliger to record the TL spectrum of benzene.[21,22] Thermal lens effect has also been used to detect TPA in laser dyes by monitoring TL signal at a fixed pump beam wavelength.[23] In certain cases TP spectra were recorded using tunable dye lasers having narrow tuning range of about 5 to 20 nm in the visible part of the spectrum. The present paper describes the use of TL effect to record the TP induced thermal lens spectra of aniline using tunable radiation from Optical Parametric Oscillator (OPO) as the excitation source. Optical parametric devices provide wide and continuous wavelength coverage, easy and rapid wavelength tunability, high-energy output and the advantage of being all solid state.

2. Experimental

The experimental setup of dual beam thermal lens technique employed in the present investigation is shown in Fig. 1. In dual beam configuration separate lasers are used for pump and probe beams. This technique is more advantageous since only a single wavelength (probe) is always detected and there needed no correction for the spectral response of the optical elements and detector. Moreover one can record TL spectra only by dual beam setup. The pump beam used for the present study is the radiation from an optical parametric oscillator (Quantaray mopo-700) with tunable output in the range 460–620 nm. Radiation of wavelength 632.8 nm from a low power (1.5 mW) intensity stabilized He-Ne laser source is used as the probe beam. Freshly distilled aniline (Merck) in a quartz cuvette (1 mm) is kept

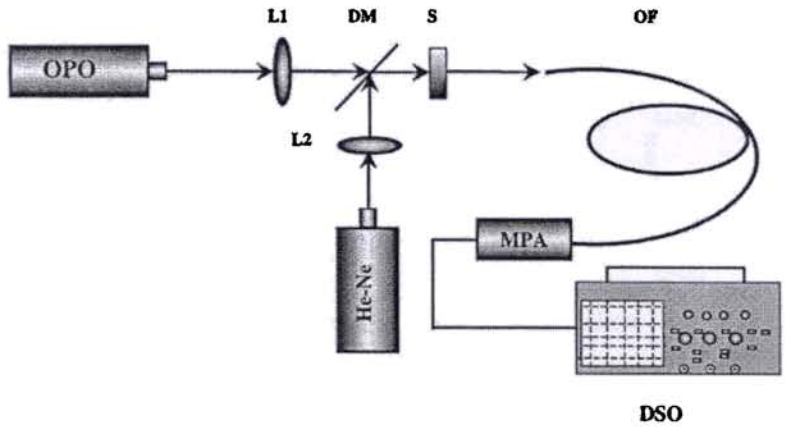

Fig. 1. Schematic diagram of the experimental set up. $\mathbf{L_1}$, $\mathbf{L_2}$ — Lens; **DM** — Dichoric Mirror; **S** — Sample; **OF** — Optic Fibre; **MPA**-Monochromator — PMT assembly; **DSO** — Digital Storage Oscilloscope.

one confocal length past the beam waist. Hu and Whinnery demonstrated that this configuration enhances the thermal lens signal.[2] The probe beam is made to pass collinearly through the sample using a dichroic mirror. An optical fibre mounted on XYZ translator placed at the beam center in the far field serves simultaneously as the finite aperture as well as the detector. The other end of the fibre is coupled to a monochromator-PMT assembly which is set at 632.8 nm. The signal output from PMT is processed using a digital storage oscilloscope (Tektronix, TDS 220). The present work is done at a temperature of 26°C. The absorption spectrum of the sample is recorded using a UV-VIS-IR spectrophotometer (Jasco V-570).

3. Results and Discussion

Absorption spectrum of aniline in the UV-VIS region is given in Fig. 2. The spectrum does not have any peak in the visible region. Two prominent peaks in the UV region at 220 nm and 290 nm correspond to $S_0 \rightarrow S_2$ and $S_0 \rightarrow S_1$ related to $^1A_1 \rightarrow {}^1B_2$ and $^1A_1 \rightarrow {}^1B_1$ transitions respectively. The TL spectrum of aniline is given in Fig. 3. In order to confirm the number of photons involved per absorption, log–log plot of TL signal strength to the pump laser power is made (Fig. 4). It is well known that TL signal $\eta \propto I^n$ where I is the incident photon energy. Log–log plot of η vs. I gives a slope n corresponding to the number of photons taking part in the multiphoton processes. At low pump power the slope of log–log plot is around 1 while at higher laser power the slope is around 2. This means that at lower pump beam power, the phenomena involved is OPA.

Using data from a recent study of overtone absorption of aniline[24,25] it can be found that sixth and seventh overtones of ring CH stretching ($\Delta v = 7, 8$) lie at 531 and 475 nm while $\Delta v = 7$ and $\Delta v = 8$ bands due to NH oscillator lie at 488 and 438 nm. These overtone absorptions overlap with the wavelength region of TL

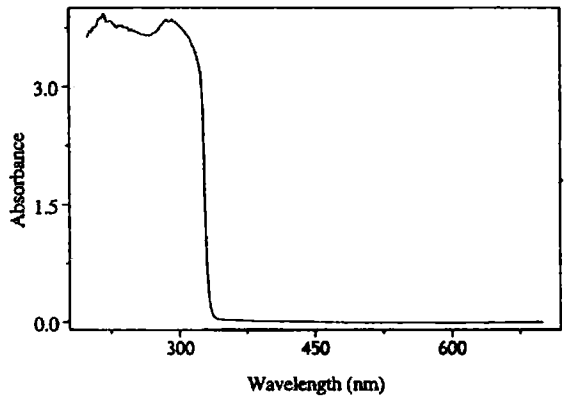

Fig. 2. The absorption spectrum of aniline.

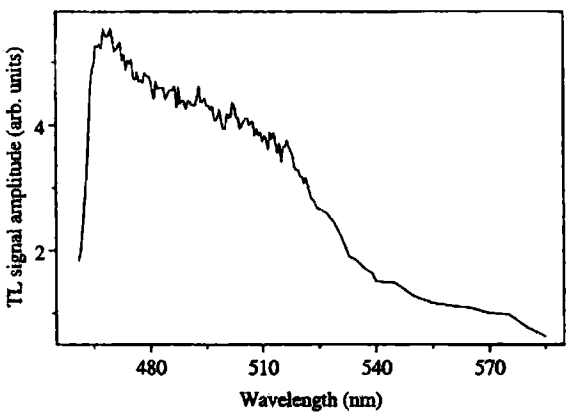

Fig. 3. Thermal lens spectrum of aniline.

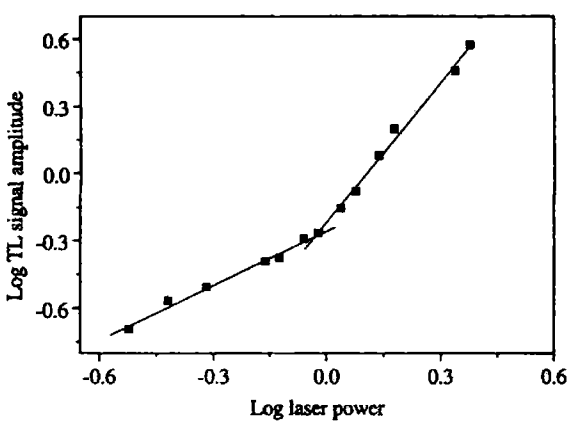

Fig. 4. Log–log plot of thermal lens signal amplitude against laser power.

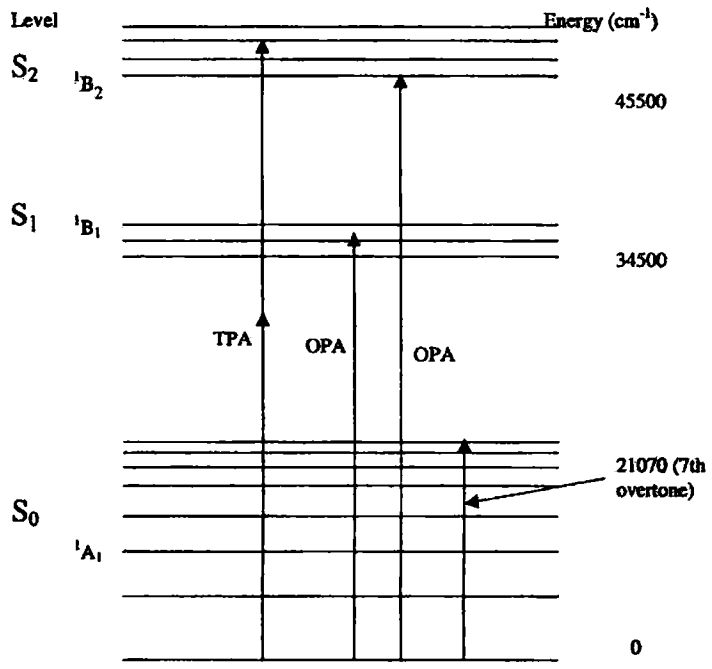

Fig. 5. Schematic energy level diagram showing relevant two-photon and one photon absorptions (TPA, OPA) along with the overtone absorption in the case of Aniline. The level S_2 acquires the symmetry character of S_0 by vibronic coupling so that both OP and TP absorptions are possible.

spectrum recorded in the present experiment. Thus at lower laser power, overtone excitations corresponding to CH and NH oscillators lead to the TL spectrum in the 460–500 nm region.

At higher pump intensity, slope of log–log plot in Fig. 4 is around 2 indicating the existence of two-photon absorption. The TL spectrum shows a sharp peak around 470 nm and prominent shoulder around 490 nm. As mentioned before, the absorption spectrum of aniline in the visible region (Fig. 2) shows two peaks at 200–250 nm and 250–350 nm regions matching to $S_0 \rightarrow S_2$ and $S_0 \rightarrow S_1$ transitions. TP absorptions corresponding to these transitions will be observed at 400–500 nm and 500–700 nm regions. Of these we get TL spectrum only in the 400–500 nm region equivalent to TPA corresponding to $S_0 \rightarrow S_2$ transitions. This means that transition $S_0 \rightarrow S_2$ and $S_0 \rightarrow S_1$ corresponding to $^1A_1 \rightarrow {}^1B_2$ is TPA allowed while $^1A_1 \rightarrow {}^1B_1$ is not. This implies that $^1A_1$ and $^1B_1$ are of opposite symmetries and hence only OPA will be observed matching to $^1A_1 \rightarrow {}^1B_2$ transition. The fact that we get OP and TP absorptions corresponding to $^1A_1 \rightarrow {}^1B_2$ transition implies that $^1B_2$ will also acquire the symmetry of $^1A_1$ state through vibronic coupling.

In conclusion, we have recorded the TL spectrum of aniline in the 460–500 nm region using radiation from an OPO as the excitation beam. Results show that $^1B_2$ acquires same symmetry characteristics of $^1A_1$ through vibronic coupling.