

Photoacoustic detection of two photon absorption in formaldehyde using pulsed dye laser

A V RAVI KUMAR, G PADMAJA, V P N NAMPOORI
and C P G VALLABHAN

Laser Division, Department of Physics, Cochin University of Science and Technology,
Cochin 682022, India

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Abstract. Absorption spectra of formaldehyde molecule in the gas phase have been recorded using photoacoustic (PA) technique with pulsed dye laser at various power levels. The spectral profiles at higher power levels are found to be different from that obtained at lower laser powers. Two photon absorption (TPA) is found to be responsible for the photoacoustic signal at higher laser power while the absorption at lower laser power level is attributed to one photon absorption (OPA) process. Probable assignments for the different transitions are given in this paper.

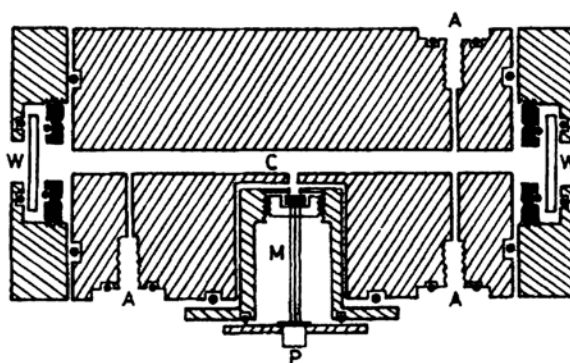
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1. Introduction

Photoacoustic (PA) measurements have now become one of the most effective and versatile techniques to explore phenomena like multiphoton absorption, overtone excitation, internal conversion and inter-system crossing in polyatomic molecules (Patel and Tam 1981). With the ready availability of tunable laser systems, the field has attracted renewed attention. In this communication we report the observation of two photon absorption (TPA) in formaldehyde molecule in the gas phase detected with photoacoustic technique using pulsed dye laser in the visible region.

The photoacoustic cell used in our experiment is shown schematically in figure 1. The cell is a non-resonant one made of aluminium with a cavity diameter of 6 mm and a length of 11 cm. The microphone (Knowles model BT 1759) is placed in a side chamber drilled perpendicular to the direction of propagation of the laser beam. The PA set up is properly shielded from ambient noise and structural vibrations. The cell was first evacuated to rotary vacuum and then formaldehyde vapour at the required pressure was fed into the cavity through a calibrated needle valve and the system was sealed off from the vacuum pump and the gas reservoir. A pulsed dye laser (quanta-ray PDL-2) pumped by the second harmonic of a Q-switched Nd: YAG laser (quanta-ray DCR-11) having a beam divergence < 0.5 mrad was used to excite the PA spectrum in the region 558 nm to 580 nm by focussing the pulsed dye laser output into the PA cell cavity using a quartz lens of focal length 25 cm. The schematic diagram of the experimental set up is shown in figure 2. The laser power was monitored using a



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Figure 1. Schematic diagram of the PA cell: W-quartz windows; C-cell cavity; A-ports for vacuum pump, manometer and gas reservoir; M-microphone chamber; P-3-pin socket for microphone connections.

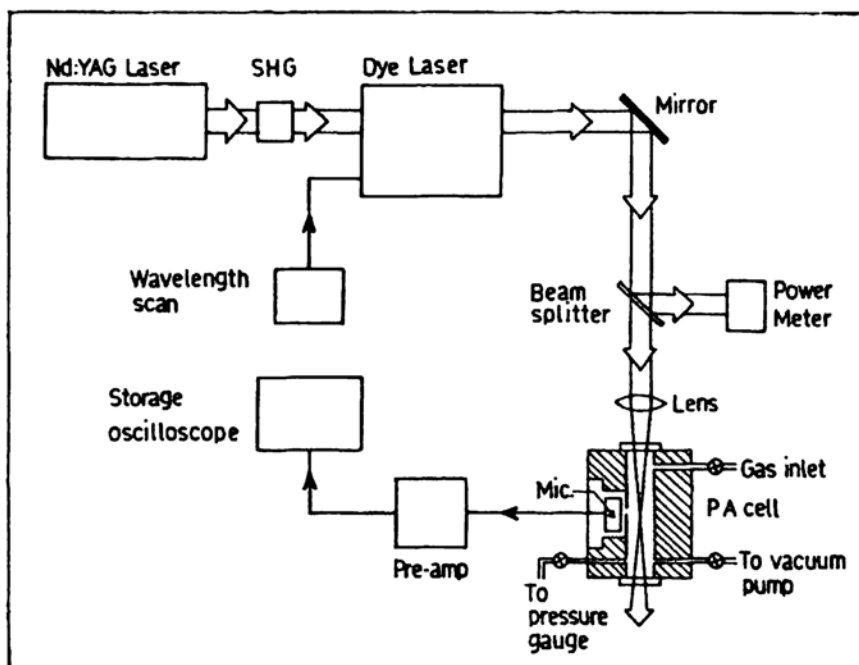


Figure 2. Schematic diagram of the experimental set up.

power meter (Sciencetech model 362). The wavelength of the dye laser was scanned manually over the range 560 nm to 570 nm with a 0.1 nm resolution. The PA signal output was amplified using a low noise broad band pre-amplifier and was displayed on a storage oscilloscope (Tektronix model 466). The PA signal amplitude was measured by taking the height of the first peak in the pattern obtained on the CRO and was averaged over a number of pulses. The result was counterchecked with a box-car averager. The PA signal amplitude was normalised using the readings from the

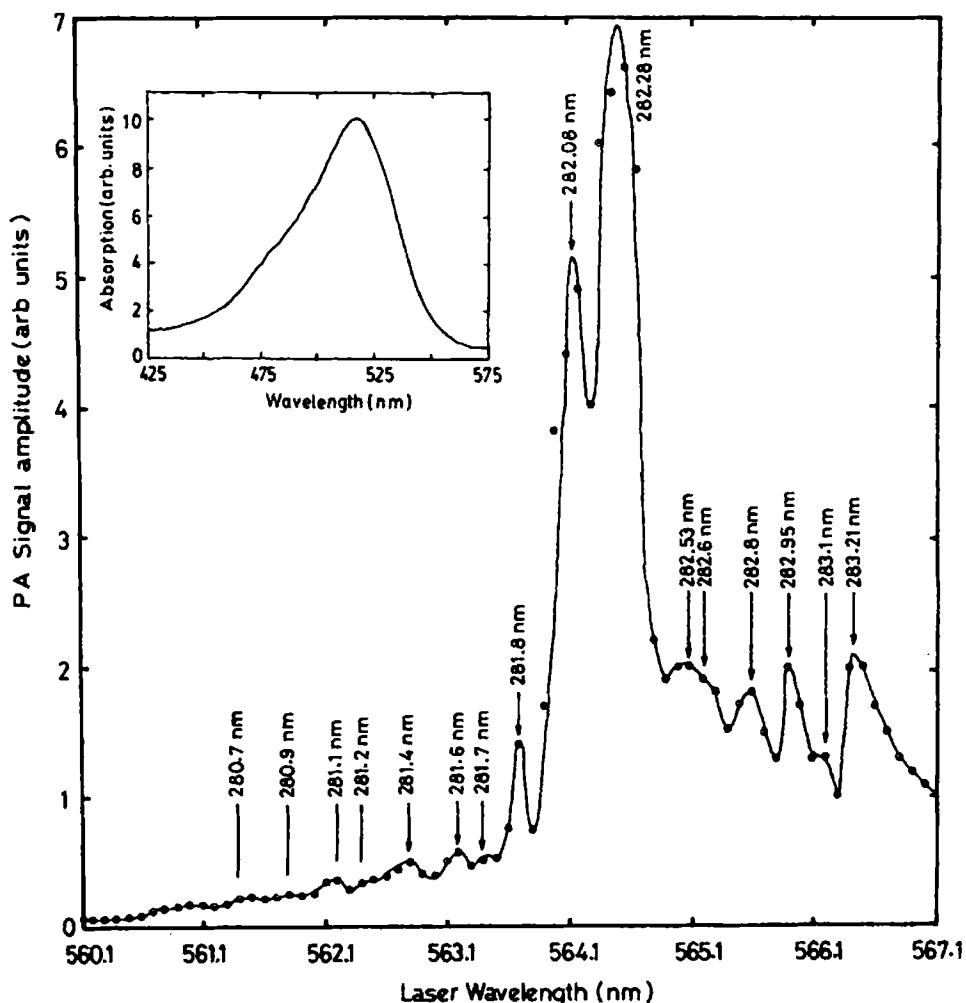


Figure 3. Normalised PA spectrum of formaldehyde vapour obtained with pulsed dye laser at a peak power of 0.6 MW. Inset: The overtone combination band in the visible region in liquid formaldehyde recorded using the UV-VIS-NIR spectrophotometer.

power meter which monitors the dye laser output as a function of wavelength. It has been observed that a continuous gas flow in the PA cell will induce a white noise in the PA signal (Kritchman *et al* 1978) and hence to enhance the SNR, a sealed-off cell was used in our experiment.

Gas phase PA spectrum in formaldehyde obtained with a tunable pulsed laser beam (0.6 MW peak power at 10 Hz repetition rate) shows a prominent peak at 564.5 nm along with a number of weak satellite bands on either side (figure 3). The spectral profiles at lower and higher laser power levels were found to be entirely different and this is illustrated (at a lower resolution of 0.5 nm) in figure 4. Figure 5 shows the log-log plot of the PA signal amplitude vs laser power at 564.5 nm. As seen in the figure, at lower powers, the slope is approximately equal to unity showing one photon absorption (OPA) processes while the slope of value ≈ 2 obtained at higher laser

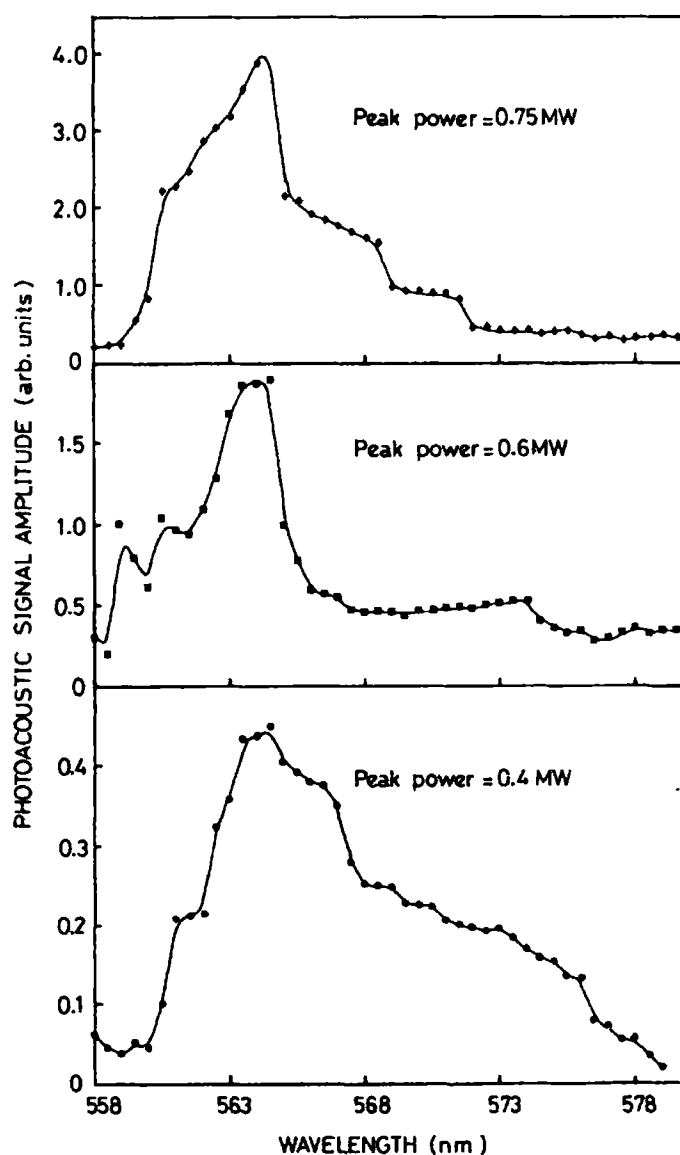


Figure 4. The PA spectral profile of formaldehyde vapour at different laser power levels.

power levels indicate clearly a two photon absorption (TPA) process. The weak bands also have been found to show similar behaviour.

In order to confirm the possibility of existence of OPA, the liquid phase absorption spectrum of formaldehyde was recorded using a UV-VIS-NIR spectrophotometer (Hitachi model U-3410) with considerably increased sensitivity. Spectrum shown as an inset in figure 3, exhibits a weak broad band in the region 425 nm to 575 nm peaking at ≈ 519 nm. This band coincides with the most likely overtone combination $\nu_1^5 \nu_6^3 = 5\nu_1 + 3\nu_6$, where, $\nu_1 = 2766 \text{ cm}^{-1}$ and $\nu_6 = 1251 \text{ cm}^{-1}$ are the two of the six normal mode frequencies of formaldehyde. In the gas phase, generally the peak will

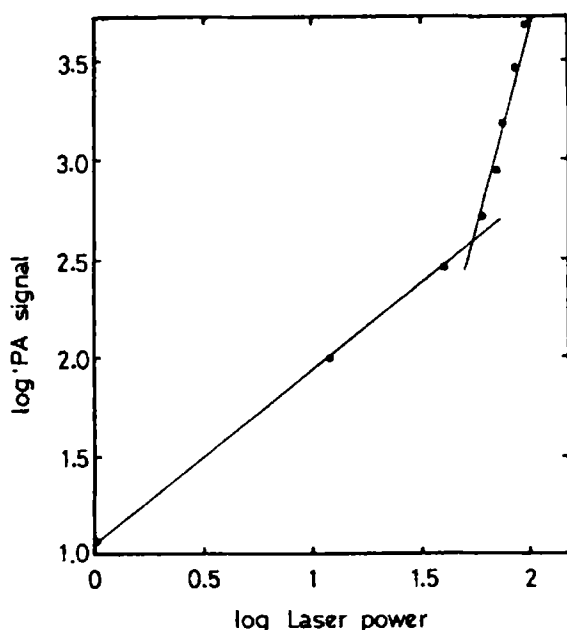


Figure 5. log-log plot of laser power at 564.5 nm vs PA signal amplitude.

shift to longer wavelength side. Also the fine structures will be well resolved in the gas phase.

Formaldehyde molecule does not exhibit any strong absorption in the visible region of the spectrum. Thus the OPA at lower laser power has to be attributed to the excitation of the longer wavelength tail in the overtone combination band. TPA occurring at higher laser power can only be due to the transition between the ground and excited electronic states of formaldehyde.

Formaldehyde contains a carbonyl group with a characteristic weak absorption due to $n \rightarrow \pi^*$ transition ($f = 10^{-4}$ to 10^{-2}) in the UV region (Herzberg 1967). The ground state of formaldehyde has planar configuration with C_{2v} symmetry and is in 1A_1 state. The excited state should be 1A_2 if the molecule is planar in the excited state also. However, the excited state happens to be non planar due to vibronic interaction but does not deviate too much from planarity. This C_s symmetry gives an inversion doubling in the lowest vibrational levels with upper states as $^1A''$. The lower inversion component behaves like A_2 and the upper one like B_2 vibronic level of a planar molecule. Only $^1A_1 \rightarrow B_2$ transition are allowed in OPA. The low oscillator strength of the UV band in OPA spectrum is due to the fact that the upper state is not far from planar structure. In TPA, however, $^1A_1 \rightarrow A_2$ transition can take place. Thus the observed TPA is due to $^1A_1 \rightarrow ^1A''(A_2)$ transition in the region 350 nm to 230 nm. The TPA at ≈ 560 nm is due to one of the members in the 2^*4^1 (Job *et al* 1969) progression ($nv^1 + 1v^1$) with $n = 6$. The satellite bands observed are typical sub band heads in an asymmetric top molecule like formaldehyde.

We have established the occurrence of two photon excitation with pulsed dye laser radiation in the visible region in formaldehyde molecule in gas phase using photoacoustic detection technique. At lower laser power one photon absorption due to overtone combination bands is also observed.

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