

## Photoacoustic spectra of some laser dyes

R S RAM and OM PRAKASH

Division of Standards, National Physical Laboratory, New Delhi 110012, India

MS received 8 July 1987; revised 11 November 1987

**Abstract.** Photoacoustic spectra of rhodamine 110, rhodamine 6 G, rhodamine B, rhodamine 101 and coumarin 102 laser dyes have been recorded at room temperature of 25° C in the spectral range of 350–750 nm. These samples were taken in powder as well as in solution forms. For this purpose the closed and the open photoacoustic cells have been used. It is hoped the present study would be useful for characterization of these dyes.

**Keywords.** Photoacoustic spectroscopy; absorption spectrum; laser dyes.

PACS No. 78-40

### 1. Introduction

The continuous absorption and high rigidity of dye molecules make them suitable for use as an active medium (Schafer 1973) in dye lasers. In order to characterize the dyes, it is desirable to know their absorption features. Rohatgi and Singhal (1966) recorded the absorption spectra of rhodamine B in H<sub>2</sub>O at 22° C. Solwyn and Steinfeld (1972) studied the aqueous solutions of rhodamine B and rhodamine 6 G. The absorption spectra of coumarin-102, rhodamine 110 and rhodamine 6 G were also reported by Drexhage (1972, 1973). As in the above cases, when absorption studies are conducted to characterize laser dyes by conventional techniques, they create difficulties due to excessive light scattering and/or opacity of the sample and considerable sample preparation problems. They are not therefore useful over a wide wavelength range. For this purpose one can employ the method of photoacoustic spectroscopy, (PAS) (Pao 1977; Rosencwaig 1980; Helander 1983) which is free from the above difficulties. Photoacoustic (PA) spectra of dye solutions of melachite green in ethanol and PA spectra of mixed solutions of melachite green and rhodamine 6 G were recorded and compared with their calculated PA spectra (Schneider and Moller 1983) and found to be in good agreement. The PA spectra of a few dye solutions were recorded by Helander (1983) using an open PA cell. The conventional absorption and PA spectra of a few dyes have also been compared earlier (Rosencwaig 1980). In the present study the photoacoustic spectroscopic technique has been used to record the spectra of rhodamine 110, rhodamine 6 G, rhodamine B, rhodamine 101 and coumarin 102 in powder as well as in solution form.

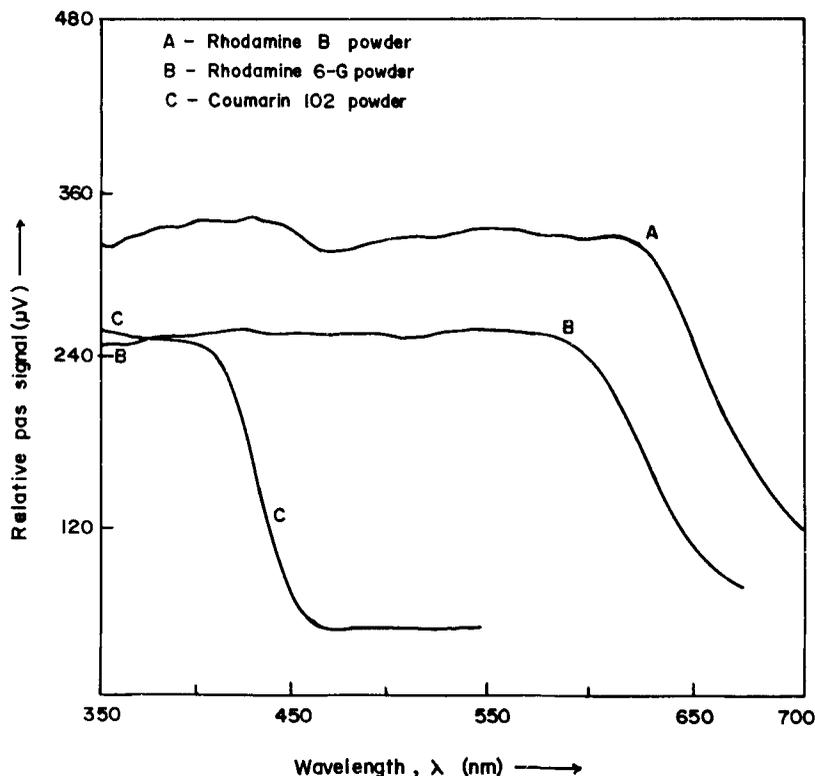
## 2. Experimental

### 2.1 Closed PAS cell

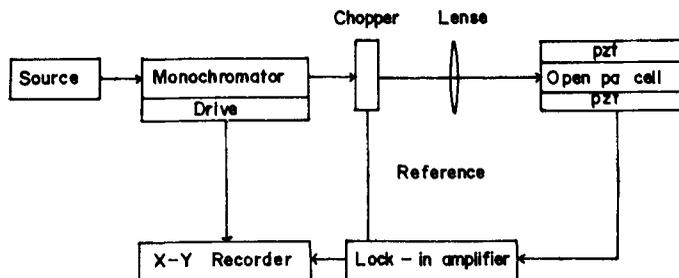
Normalized PA spectra of rhodamine 110, rhodamine 6 G, rhodamine B, rhodamine 101 and coumarin 102 laser dyes have been recorded in powder form using a closed PA cell and a microphone as a detector on a double beam PA spectrophotometer (Bhide *et al* 1983). The samples were obtained from M/s Exciton Chemical Company, Ohio, USA. The microphone detection system was sensitive and suitable for powder samples. The typical PA spectra of some of these dyes are shown in figure 1. The spectra of all the dyes except that of coumarin 102 are presented in the spectral range from 350 to 700 nm. In the case of coumarin 102, a spectral range of 350–550 nm was covered. The light was chopped at a frequency of 35 Hz. The time constant for lock-in-amplifiers was set at 3 sec with a scan speed of monochromator at 50 nm/min.

### 2.2 Open PAS cell

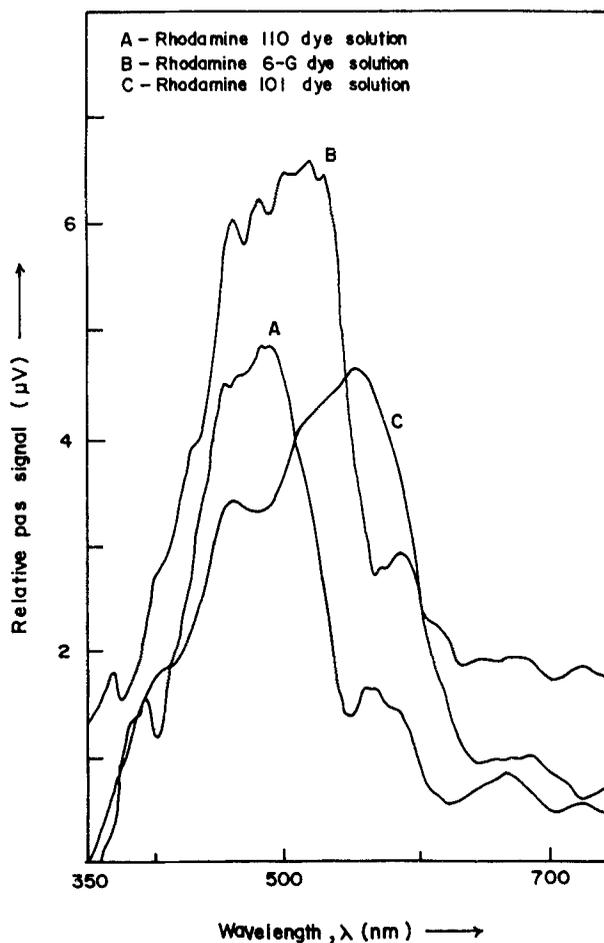
The PA spectra of these dyes were also recorded in solution prepared for use in our dye lasers, on the above mentioned PA spectrophotometer with some modification. Here



**Figure 1.** Photoacoustic spectra of powders of rhodamine B, rhodamine 6 G and coumarin 102 laser dyes.



**Figure 2.** Block diagram of a single beam photoacoustic spectrophotometer incorporating an open photoacoustic cell.



**Figure 3.** Photoacoustic spectra of solutions of rhodamine 110, rhodamine 6G and rhodamine 101 laser dyes in ethylene glycol.

the closed PA cell was replaced by an open PA cell (Helander 1983) where PZT-5 sensors were used in place of the microphone. The block diagram of this spectrophotometer is shown in figure 2. The radiation from the monochromator was chopped at a frequency of 12 Hz and focussed into the sample solution using suitable quartz

optics. Thus, the unnormalized spectrum of the sample solution was recorded in single beam mode. As the PZT is less sensitive and the signal strength generated in liquid sample was relatively less, all the radiation had to be allowed from the monochromator into the sample cell to get an appreciable signal strength. A time constant for lock-in-amplifier was set at 10 sec with a scan speed of monochromator to 20 nm/min. Typical spectra of some of the solutions of rhodamine 110, rhodamine 6 G and rhodamine 101 laser dyes in ethylene glycol thus recorded in the spectral range from 350–750 nm are shown in figure 3. The generation of PA signal in an open PA cell has been described (Helander 1983; Sigrist 1986; Tam and Patel 1980) in the literature. The theoretical analysis of the amplitude and phase of the photoacoustic signal has been carried out by Teng and Royce (1980) based on one-dimensional model. The advantage of open PA cell is that it is free from all external acoustical noise. However the spectra recorded in closed as well as open PA cell are identical. But with closed cell with vapour of the liquid is likely to damage the diaphragm of the microphone on prolonged use. Though the PA spectrum of rhodamine 6 G solution was reported earlier (Schneider and Moller 1983) the PA spectra of solutions of rhodamine B, rhodamine 110, rhodamine 101 and coumarin 102 laser dyes and PA spectra of their powder including that of rhodamine 6 G have been recorded for the first time.

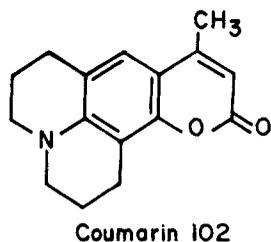
### 3. Results and discussion

Figure 1 shows that the absorption in powder rhodamine B increases rapidly below 700 nm, attains a maximum value around 613 nm and, except for some variation, gets saturated and extends upto 350 nm. In rhodamine 6 G, the absorption increases below 675 nm and after attaining a maximum value around 575 nm gets saturated attending up to 350 nm. In the case of coumarin 102 the absorption rapidly rises below 470 nm, reaches a maximum value at 400 nm and then gets saturated extending up to 350 nm. All these spectra were recorded under similar experimental conditions. The saturation effect (Fuchsman and Silversmith 1979) in the PA spectra of a dye sample is due to its high absorbance towards radiation. However saturation can be avoided effectively by grinding the sample with alumina or by dissolving the sample in a suitable solvent.

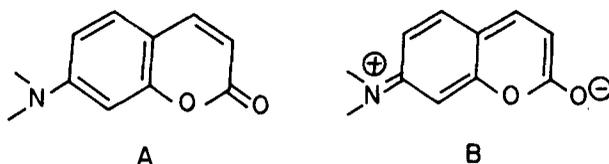
PA spectra of rhodamine 110, rhodamine 6 G and rhodamine 101, solutions in ethylene glycol (figure 3) reveal that absorption in rhodamine 110 rapidly rises below 600 nm attains a maximum value around 475 nm and then rapidly decreases up to 360 nm. Similarly in the case of rhodamine 6 G and rhodamine 101, the absorption increases below 650 nm, attains a maximum at about 510 nm and 550 nm respectively and then decreases up to 350 nm in both cases. These spectra were also recorded under similar experimental conditions for comparative study. The values of  $\lambda_{\max}$  thus recorded are comparable to the reported values (Kodak 1982; Exciton 1982) and are given in table 1. The slight difference is due to the solution of the dyes in different solvents in both cases.

It is thus evident that for powder samples, absorption rises in the visible region and after attaining a certain maximum value becomes nearly constant due to the saturation effect extending into the ultraviolet region. But on dissolving them in suitable solvents (ethylene glycol in the present case), their absorption is confined and shifted to a





**Figure 7.** Structural formula of coumarin 102.



**Figure 8.** Mesomeric structures of coumarin 102. **a.** Structure A, **b.** Structure B.

The other group of laser dyes is coumarin with a substitution (Schafer 1973) of an amino or hydroxyl group in the 7th position for example coumarin 102 (figure 7). The chromophore of such compounds can be derived by the mesomeric forms A and B, (figure 8a, b). The absorption maximum for this dye is at 390 nm and shifts to longer wavelengths with increasing polarity of the solvent (Schafer 1973) with respect to the dye.

The absorption spectrum of a dye in solution is blurred and continuous and confined to a certain wavelength region. The absorption of a dye in solution is effected by: (i) the number of atoms in a dye molecule; (ii) vibrations of the dye molecule at the fundamental frequencies and their overtones and (iii) the state of coupling of vibrations of the dye molecule with its electronic transitions. The electronic transitions of the molecule create a change in electron density which results in a change of bond length of the molecule broadening the individual lines (Schafer 1973).

#### 4. Conclusion

The laser dyes are used in solution form and by knowing the absorption features of a dye without any additive and its solution in a suitable solvent one can ascertain the spectral range of utility of the laser dye. Further when a dye molecule is in excited states  $S_1$  or  $T_1$ , it gives a well-defined spectra (Schafer 1973) which is difficult to be measured by conventional techniques. However the PAS method can easily measure the excited state  $S_1$  or  $T_1$  absorption spectrum and life-times of a dye in solution (Yee and Kliger 1983). PAS can be used to record the absorption spectra of dyes over a wide spectral range from ultraviolet to near infrared region.

#### Acknowledgements

The authors thank Dr. P Helander and his guide Prof. I Lundstrom of the Laboratory of Applied Physics, Department of Physics and Measurement Technology, IFM

Linköping Institute of Technology, Sweden, for supply of an open photoacoustic cell to study the liquids, and a copy of the PhD Thesis of Dr. P Helander. The authors are also grateful to Dr. S P Varma for useful suggestions and constant encouragement.

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