

## Photoacoustic studies on excitation transfer in Rh6G and RhB dye mixture

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**Abstract.** The photoacoustic spectra of Rhodamine 6G (Rh6G), Rhodamine B (RhB) dyes and their mixtures were recorded at different concentrations. It is observed that in the mixture the photoacoustic signal increases due to excitation transfer from Rh6G to RhB in the wavelength region 480–530 nm. The excitation transfer rate estimated from these data show that resonance is dominant rather than the collisional transfer process.

**Keywords.** Photoacoustic spectroscopy; excitation transfer; Rhodamine 6G; Rhodamine B; dyes.

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### 1. Introduction

Photoacoustic detection is widely used in spectroscopy, especially in cases where conventional transmission and reflectance techniques are not applicable (Rosencwaig 1978). In this technique one measures that part of the absorbed radiation by the sample which is converted into heat *via* nonradiative relaxations. The data can be used to study fluorescent materials, where it can complement the information obtained from fluorescence spectroscopy. The excitation transfer processes have been studied in organic dyes using optical techniques by measuring the fluorescence quantum efficiency and the life time of donor in the presence and absence of acceptor molecules (Peterson and Snavely 1968; Dienes and Madden 1973; Lin and Dienes 1973; Burlamacchi *et al* 1975; Lamola 1969). In the present work we report on the photoacoustic measurements in mixtures of Rhodamine B (RhB) and Rhodamine 6G (Rh6G) dye solutions which provide data on nonradiative relaxations in these systems (Rai 1983).

### 2. Experimental

The organic dyes Rh6G and RhB (Merck Germany) were used without any further purification. Mixtures of the two dye solutions were made from equal volumes of each dye solution either of the same or different molar concentration. The solutions of the dyes were prepared in doubly-distilled ethanol.

A single beam photoacoustic spectrometer was used (Rai *et al* 1982) for recording the photoacoustic spectra. The light source was a Phillips 600 W tungsten halogen lamp. The light from lamp is condensed on the entrance slit of the monochromator (CEL HM 104, 0.25 m grating) using two planoconvex lenses. A variable speed chopper (EG and G PARC model 125 A) was used for chopping the incident light at a chopping frequency of

22.5 Hz. The liquid samples were kept in cylindrical stainless steel cuvette of the photoacoustic cell which was fitted with an electret microphone. The photoacoustic signal and the reference signal from the chopper were fed into a lock-in amplifier and the phase angle was kept unchanged during the measurements.

To remove the effect of power dependence of light source on PAS signal at all wavelengths the photoacoustic signal from the sample at each wavelength was divided by the corresponding photoacoustic signal obtained using carbon black as sample.

### 3. Results and discussion

#### 3.1 Photoacoustic spectra of Rh6G and RhB

The photoacoustic spectra of solutions of RhB and Rh6G in ethanol at different concentrations are shown in figures 1A, and 1B respectively, and are in good agreement with their optical spectra reported earlier (Selwyn and Steinfield 1972). The peak at 550 nm in RhB and that at 530 nm in Rh6G corresponds to the  $S_1 \leftarrow S_0$  transitions in the two molecules, and it is found that for the same concentration and similar experimental conditions RhB gives a higher PAS signal than Rh6G. This is to be expected as nonradiative de-excitation is complementary to radiative de-excitation (fluorescence) and fluorescence efficiency in RhB is 40% at 25°C whereas it is 95% for Rh6G (Prasad *et al* 1978). In Rh6G no PAS spectrum below  $10^{-3}$  M/l was got probably due to high fluorescence and low nonradiative efficiencies at lower concentrations.

#### 3.2 Photoacoustic spectra of mixtures of Rh6G and RhB

The photoacoustic spectra of mixed solutions of Rh6G and RhB are shown in figures 2A, 2B and 2C. Equal volumes of RhB and Rh6G solutions were mixed to prepare 8

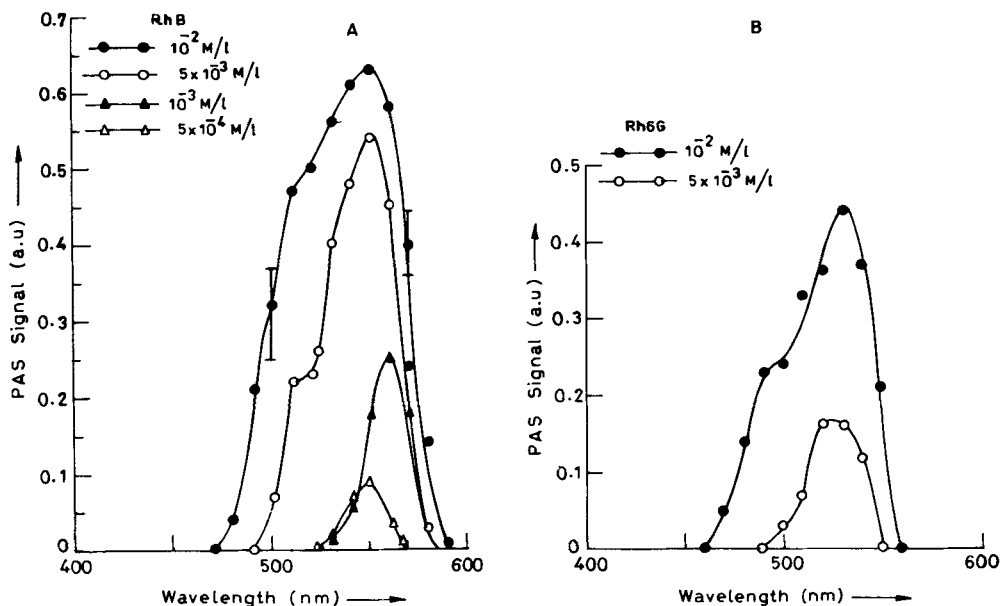


Figure 1. Photoacoustic spectrum of Rhodamine B and Rhodamine 6G.

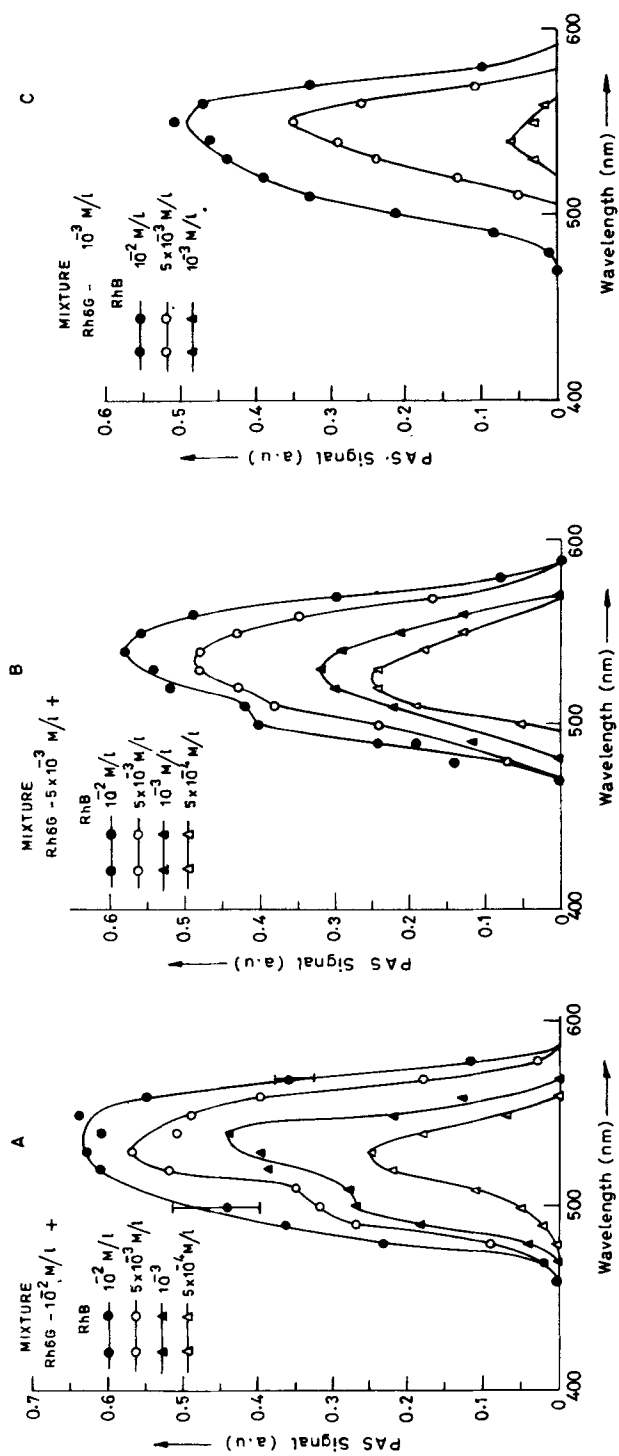


Figure 2. Photoacoustic spectrum of mixture of Rhodamine 6G and Rhodamine B.

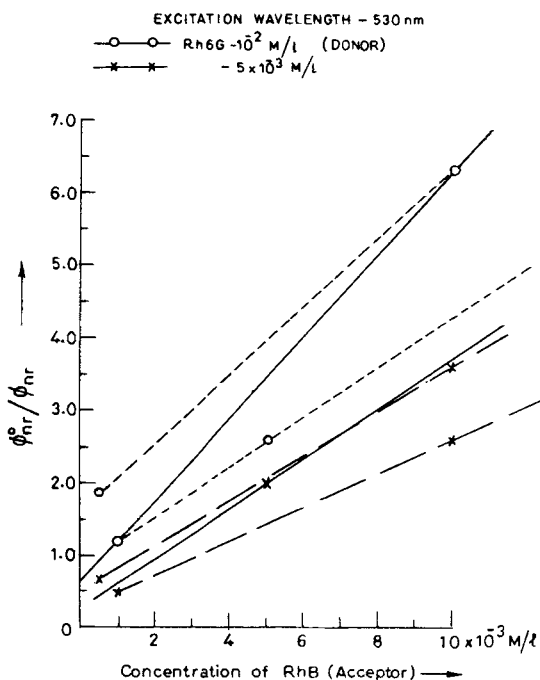
different mixtures. The significant observation in a PA spectra of the mixtures is an increase in the signal strength at lower wavelengths (from 480 nm to 540 nm) when compared to the PA spectra of RhB and Rh6G of corresponding concentrations. In our opinion the enhancement results from the fact that a small fraction of Rh6G molecules relaxing by emission of fluorescence, lead to excitation of some RhB molecules by absorption of this radiation and a large fraction of them relaxing nonradiatively. Another observation is a blue shift of the peak in the photoacoustic spectra of the mixtures with lower concentrations of RhB. This results from the dominant effect of Rh6G which has a large absorption cross-section at lower wavelengths.

### 3.3 Evaluation of rate constant

The variation of the ratio of the PA signal of pure donor (Rh6G) to the PA signal of the donor in the presence of the acceptor dye (RhB),  $\phi_{nr}^0/\phi_{nr}$  is plotted with the acceptor (RhB) concentration (figure 3). It appears to follow the Stern Volmer relation modified for nonradiative transition

$$\phi_{nr}^0/\phi_{nr} = 1 + K\tau[A]$$

where  $\phi_{nr}^0$  is the photoacoustic signal of Rh6G (donor) in the absence of acceptor (RhB),  $\phi_{nr}$  is the photoacoustic signal in the presence of acceptor (RhB),  $K$  is the rate constant for the excitation transfer,  $\tau$  is the life-time of the Rh6G molecules and  $[A]$  is the acceptor (RhB) concentration. Such curves are plotted for two different donor (Rh6G)



**Figure 3.** Variation of relative PAS signal of Rh6G(donor) in the absence and presence of RhB (acceptor) with concentration of RhB (acceptor).

concentrations of  $10^{-2}$  M/l and  $5 \times 10^{-3}$  M/l for an excitation wavelength of 530 nm with the concentration of the acceptor dye (RhB) varied from  $10^{-2}$  M/l to  $5 \times 10^{-4}$  M/l. To get  $\phi_{nr}$  we obtained the difference signal from the mixtures of Rh6G and RhB by subtracting the signals of pure RhB of appropriate concentrations. The signal amplitude at 530 nm in the difference spectrum for each mixture provides the  $\phi_{nr}$  for the corresponding mixture. The slope of the curve in figure 3 gives the  $K\tau$  value. The life-times for Rh6G at concentrations of  $10^{-2}$  M/l and  $5 \times 10^{-3}$  M/l is 2.4 n sec and 2.7 n sec respectively (Lin and Dienes 1973). Using these life-time values we find  $K$  as  $2.4 \times 10^{11}$  and  $1.23 \times 10^{11}$  litre mol $^{-1}$  sec $^{-1}$  respectively. The dotted lines in figure 3 show the possible variation in the slope of  $\phi_{nr}^0/\phi_{nr}$  vs RhB concentration for Rh6G concentration of  $10^{-2}$  M/l and  $5 \times 10^{-3}$  M/l and it gives the variation in the value of  $K$   $\pm 0.28 \times 10^{11}$  litre mol $^{-1}$  sec $^{-1}$  and  $\pm 0.12 \times 10^{11}$  litre mol $^{-1}$  sec $^{-1}$  respectively. It is to be noted that the value of excitation transfer rate obtained here is typical of resonance transfer (Lin and Dienes 1973; Wilkinson 1967; Bennet and Elkellong 1968). This is to be compared with the values of the collisional transfer rate of  $10^9$ – $10^{10}$  litre mol $^{-1}$  sec $^{-1}$  observed experimentally as well as calculated from the Debye equation (Debye 1942). Our results thus show that resonance energy transfer is 10 times faster than collisional transfer.

#### 4. Conclusion

We conclude that although the radiative and collisional processes contribute to the energy transfer in the Rh6G–RhB dye mixture the resonance transfer due to long range dipole–dipole interaction is the dominant mechanism of the efficient excitation transfer.

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