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Time-resolved spectra of coumarin 30-rhodamine 6G dye mixture

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Abstract. The effect of acceptor concentration on the energy transfer from Coumarin 30 (donor) to Rhodamine 6G (acceptor) has been studied. The nature of energy transfer reaction has been studied through lifetime measurements by recording the time-resolved fluorescence decay curves. The energy transfer parameters calculated were used to confirm the occurrence of energy transfer on the basis of the emission-reabsorption effect.

Keywords. Time-resolved spectra; energy transfer; fluorescence; Coumarin-Rhodamine mixture.

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1. Introduction

Excitation transfer in laser dye mixtures has earlier been used to achieve better dye laser performance at the desired wavelengths (Morey 1972; Drake *et al* 1972; Cox and Matise 1980; Berlman *et al* 1973). The mechanism responsible for the intermolecular singlet-singlet electronic energy transfer in dye mixture can be directly determined by lifetime measurements. The studies so far reported in this field have been based on the indirect method of optical gain studies. We have studied the energy transfer mechanism in coumarin 30-rhodamine 6G (C 30-Rh 6G) dye mixture in ethanol by using a laser fluorimeter developed in the laboratory. The dependence of lifetime on dye concentration of the two dye molecules C 30 and Rh 6G in alcoholic solutions of methanol and ethanol, and ethylene glycol has also been studied. An attempt was also made to study the energy transfer mechanism in ethylene glycol, but it was not found to be a good solvent due to the Cage effect (Turro 1967).

The fluorescence lifetime studies in nanosecond range are commonly performed by phase-shift measurements, mode-locked laser systems or single-photon counting technique. Of these methods, the phase-shift measurements provide good speed and accuracy, but offer limited capabilities for the resolution of multiple components. The mode-locked laser systems provide good time resolution in picosecond range, but suffer from poor signal-to-noise ratio. The photon-counting system, on the other hand, operate with excellent signal-to-noise ratio, a wide dynamic range of time, and picosecond lifetime measurement capabilities. A brief account of the single-photon counting system used in the present investigation is shown in figure 1, the details of which have been reported earlier (Bhatti *et al* 1985).

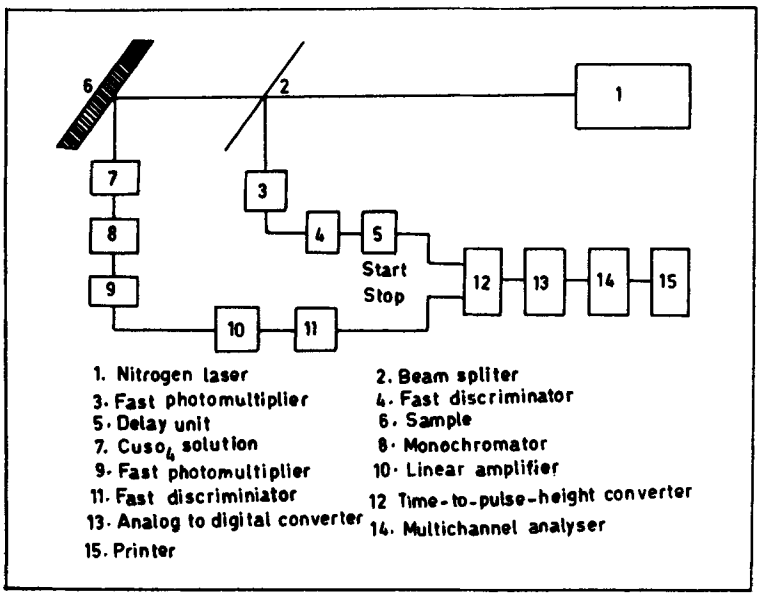

Figure 1. Laser fluorimetric system for subnanosecond life time measurements.

2. Experimental details

The system consists of a pulsed N_2 laser (CEL model NL 103), which delivers pulses of 200 kW peak power and 10 ns duration, and a time-correlated single-photon counting electronics. The output of the N_2-laser is divided into two parts by a beam splitter. One of it is used to excite the sample and the other is used as a reference pulse in the start channel. The fluorescence emission from the sample is directed on to the slit of the monochromator and the signal coming out of it is detected by a fast photomultiplier (Phillips XP 2020). A cuvette of $CuSO_4$ solution inserted between the sample and the monochromator absorbs the scattered and reflected ultraviolet laser radiation. The long optical path of the fluorescent radiation through the glass optics of the monochromator further reduces the presence of the UV radiation, if any. The output signal of the photomultiplier is suitably amplified, discriminated and then delivered to the TPHC as a stop pulse.

The other part of the laser beam divided by the beam splitter is used to illuminate the photocathode of a photomultiplier identical to the one used in the stop channel. The signal from this photomultiplier tube, after discrimination is fed to the start input of the time-to-pulse height converter (TPHC) via a nanosecond delay unit. The TPHC produces an output pulse with a height proportional to the time interval between the start and the subsequent stop pulse. The analog output of the TPHC is converted into digital form by analog-to-digital converter (ADC). The multichannel analyser accumulates the data from ADC and its display on the MCA screen shows a histogram of the accumulated counts (as ordinate) and time (as abscissa), which is equivalent to the fluorescence decay curve. To accurately interpret the decay curve from the data, the time axis of the MCA is calibrated from the shifts produced in the signal peak due to a known delay introduced in the start channel. With the system in the normal mode (TPHC started with reference pulses and stopped with fluorescence

pulses), the limited effects to the data collection rate are the reset time of the TPHC and the conversion time of the electronics consisting of TPHC, ADC and MCA. The interchange of start and stop pulses (reverse mode) as proposed by Hagen *et al* (1970) proved to be advantageous in the present case, as the data accumulation time decreased appreciably. In this mode, the data collection rate is limited only by the percentage of data loss. Also the maximum starting rate is no longer limited by the reset time of the TPHC, ADC and MCA. The possible disadvantage of operation in this mode is the reversal of time scale of MCA. Also some experience of inserting the delay in the stop channel is needed.

In general, the probability of multiphoton events is very low in both these cases (normal as well as reverse modes). This is accomplished by attenuating the light intensity reaching the photomultipliers, so that these events are extremely rare. However, the limited rate of data collection associated with this approach increases the time required to record the spectrum. The precision of measurements in single photon counting technique, on the other hand, is determined by the data collection rate. Therefore, the attenuation had to be optimized in the present case. Further, to reduce the error caused by multiple photon events, the rate of photon being counted should be about 10% of the experimental repetition rate. Under these circumstances the probability of observing two photons in a single experiment is only 5%. Since the N_2-laser has a large photon flux, the data collection rate of 10% could very easily be achieved by reducing the excitation intensity even for samples having considerably low quantum yield.

3. Results and discussion

The results of the lifetime measurements are summarized in figure 2 for pure Rh 6G and in figure 3 for pure C 30 solutions. The behaviour of lifetime at lower concentration is probably due to the effect of radiation trapping, i.e., the self-absorption reemission, which tends to enhance the lifetime. After attaining the maximum, the value of lifetime starts decreasing in all cases because of concentration quenching. In Rh 6G in ethylene glycol and methanolic solutions, the peak position is shifted towards lower concentration side vis-a-vis ethanolic solutions. This can be understood in terms of the solvent effect reported by Masilamani and Sivaram (1982) and Ramakrishnan *et al* (1980). Another interesting feature of these curves is the slight increase in lifetime values at higher concentration of 10^{-2} M using ethylene glycol and methanol. This may be attributed to the formation of excimers at higher concentration. Such an increase in lifetime values at higher concentration has not been reported earlier, perhaps because lifetime studies in dye solutions made so far were primarily dependent on the indirect method of change in optical gain values with concentration. It has been studied by Arbeloa *et al* (1988) that the fluorescence quantum yield of Rh 6G decreases in concentrated ethanolic solutions where aggregates are present. They suggested that the fluorescence yield depends upon the degree of aggregation of molecules in the excited state and the excitation energy migrates between the monomers until it arrives at an aggregate that acts as an energy trap. The formation of non-fluorescent aggregates of Rh 6G has also been expected by Terada and Muto (1986) in their investigation. Thus, the increase in lifetime and the reduction in fluorescence yield at higher concentration can be understood by studying the rate of formation of exciplexs

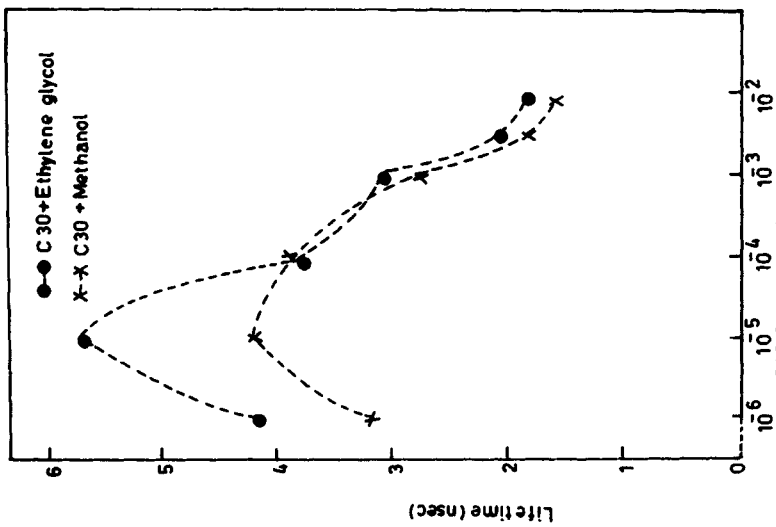

Figure 3. Concentration dependence of fluorescence life time of C 30 in methanol and ethylene glycol.

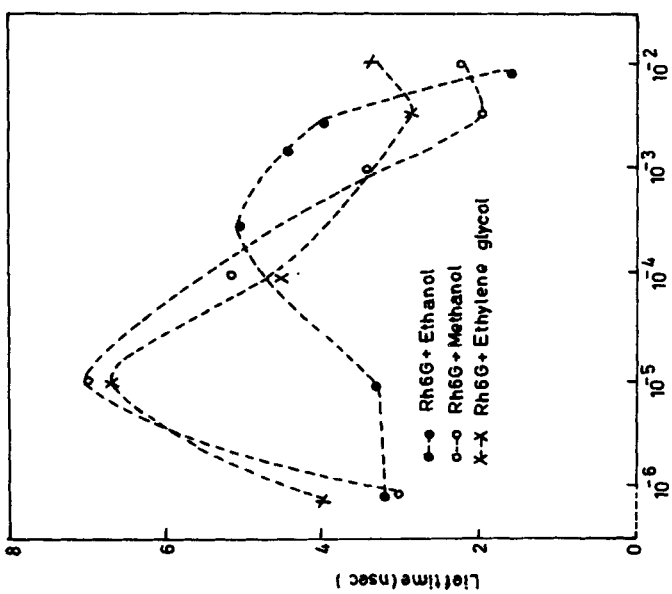

Figure 2. Concentration dependence of fluorescence life time of Rh 6G in ethanol, methanol and ethylene glycol.

as well as extent of monomer-aggregates energy transfer. Another possible explanation for the increase in lifetime values at higher concentration could be due to intersystem crossing, photoquenching (Speiser *et al* 1973; Speiser 1974; Speiser and Bromberg 1975; Speiser and Katraro 1978) or internal conversion. Of these, the first one does not seem to play an important role because it leads to a change in lifetime values by several orders of magnitude. The second one, which is different from bleaching effect as discussed by Speiser *et al* (1973) produces a large reduction in the magnitude of the output signal. The possibility of intersystem crossing as discussed by Atkinson, which becomes important at higher concentration cannot, however, be ruled out as the frequency of the pumping beam is quite high in comparison to that of the fluorescent signal. Atkinson *et al* (1974) have also argued in favour of internal conversion taking place at higher concentration. Urisu and Kajiyama (1976), while studying the dependence of peak gain on the concentration of Rh 6G have also reported an abnormal behaviour when the concentration reaches 10^{-2} M or more, without assigning any reason for it.

The experimentally obtained lifetime values of C 30 as donor (1×10^{-3} M) with varying concentration of Rh 6G as acceptor have been presented in table 1. The study shows significant change from τ_{f0} the measured lifetime of C 30 in the absence of Rh 6G, only when the acceptor concentrations become relatively high. At lower acceptor concentrations ($\sim 10^{-6}$ M), the change from τ_{f0} is very small indicating the dominance of radiative type energy transfer in this mixture (table 1). This result agrees with the prediction that at low acceptor concentration radiative transfer (trivial process) is the main process and the probability of non-radiative transfer (Forster type) is very small.

To evaluate the energy transfer parameters, the measured lifetimes from table 1 were fitted to the Stern–Volmer equation (Turro 1967)

$$1/\tau_f = K_{D\,A}[A] + 1/\tau_{f0} \tag{1}$$

where τ_f is the donor lifetime in the presence of the acceptor, $[A]$ is the acceptor concentration and $K_{D\,A}$ is the excitation transfer rate.

Figure 4 presents a plot of τ_f^{-1} versus Rh 6G concentration. The plot is linear in nature apparently obeying the Stern–Volmer expression for bimolecular quenching. It also gives an evidence of the fact that there is a competition between a bimolecular process of energy transfer and a unimolecular process of fluorescence. The critical

Table 1. Variation in the donor lifetime with the acceptor concentration in ethanolic solutions for fixed donor concentration (1×10^{-3} M).

Acceptor concentration (M)	Donor lifetime (ns)	$1/\tau_f$ ($\times 10^9 s^{-1}$)
0	$6{\cdot}92 \rightarrow \tau_{fo}$	–
1×10^{-6}	$5{\cdot}50 \rightarrow \tau_f$	0·18
5×10^{-6}	$5{\cdot}02 \rightarrow \tau_f$	0·20
1×10^{-5}	$4{\cdot}62 \rightarrow \tau_f$	0·22
5×10^{-5}	$4{\cdot}01 \rightarrow \tau_f$	0·25
1×10^{-4}	$3{\cdot}61 \rightarrow \tau_f$	0·28
3×10^{-4}	$3{\cdot}49 \rightarrow \tau_f$	0·29

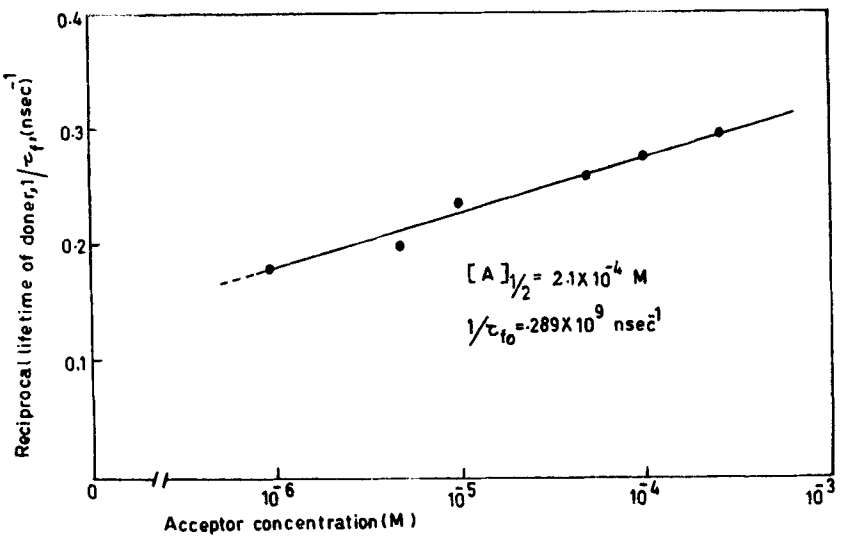

Figure 4. Stern Volmer Plot for C 30–Rh 6G dye mixture in ethanol.

separation, R_0, of donor and acceptor molecules for which the energy transfer from excited donor (D^*) to acceptor (A) and the emission from excited donor are equally probable, can be calculated from the expression

$$R_0 = \{3000/4N[A]_{1/2}\}^{1/3} = 7{\cdot}35/\{[A]_{1/2}\}^{1/3} \tag{2}$$

where $[A]_{1/2}$ is the "half quenching concentration" at which $\tau_f = \frac{1}{2}\tau_{f0}$ and N is the Avogadro's number. Using figure 4 the value of $[A]_{1/2}$ was found to be $2{\cdot}1 \times 10^{-4}$ M. This corresponds to an average of one molecule of the acceptor in a sphere with radius R_0 having excited donor at the centre.

On the basis of the method described above, the values of $K_{D\,A}$ and R_0 were $0{\cdot}68 \times 10^{12}\,S^{-1}$ and 124 Å respectively. The value of $K_{D\,A}$ is much larger than those for collisional transfer. Also the value of R_0 is larger as compared to that of collisional transfer where R_0 values are reported to be in the range 1–10 Å. Similarly it is larger compared to that for resonance transfer where it ranges from 10–90 Å. Thus the present value is typical of the so-called trivial mechanism (emission-reabsorption effect) characterized by critical distance of the order of several angstroms. The results, however, agree with those obtained by Urisu and Kajiyama (1976) using optical gain studies. The results indicate that the energy transfer processes between unlike molecules can be studied by lifetime measurements. However, the reliability of the experimental data, depends largely on the sensitivity and accuracy of the detection system. In the present case, since the accuracy of the laser fluorimeter is in the subnanosecond range and the donor lifetimes are in the nanosecond range, τ_{fo} and $K_{D\,A}$ have been obtained much more accurately.

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