Study on the determination of molecular distance in organic dye mixtures using dual beam thermal lens technique

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Abstract

A sensitive method based on the principle of photothermal phenomena to study the energy transfer processes in organic dye mixtures is presented. A dual beam thermal lens method can be very effectively used as an alternate technique to determine the molecular distance between donor and acceptor in fluorescein–rhodamine B mixture using optical parametric oscillator.
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1. Introduction

The energy transfer has become an important phenomenon owing to the numerous applications in biochemical research and radiation Physics. The mechanism of energy transfer in laser dye mixtures is also used to improve the efficiency and to broaden its spectral range of dye lasers [1–4]. When a molecule is excited to higher energy levels, energy transfer (ET) is one of the different ways to divest itself of its excess energy. ET between similar molecules in liquid solutions results in the depolarization and self-quenching of the fluorescence of such solutions. Between unlike molecules, the corresponding transfer process results in the quenching of the fluorescence of one species and the sensitization of the fluorescence of the other. The main mechanisms involved in the electronic energy transfer in molecular systems are of (a) radiative and (b) nonradiative types. In radiative transfer, the emission of a quantum of light by one molecule (donor) is followed by the absorption of the emitted photon by a second molecule (acceptor). Nonradiative transfer involves the simultaneous de-excitation of the donor and the excitation of the acceptor, a one step process and is mainly due

to Coulombic or exchange interaction. Coulombic resonance energy transfer occurs via the electromagnetic field. ET does not require physical contact of the interacting partners, and it is dependent on the inverse sixth power of the intermolecular separation [5]. The probability of such transfer is large if the emission spectrum of the donor overlaps with the absorption spectrum of the acceptor partially. The exchange interaction is a collisional transfer, that requires close approach of the donor and acceptor and which is of the order of collisional diameters [6,7] (5–10 Å).

Fluorescence energy transfer is a technique now widely applied to probe biological and other complex systems for the determination of fluorophore separation and structure [8]. In this technique donor molecules are excited in the presence of acceptor molecules and the luminescence yield of donor and or acceptor are measured as a function of concentration. Hence, this method cannot be applied to nonfluorescent samples. However, photothermal methods measure the photon energy which has been converted into heat while fluorescence observes the re-emitted photons and hence both thermal and fluorescence spectroscopy are complementary to each other.

Except the work of Georges and Rai [9,10] not many results have been reported in which energy transfer phenomenon is monitored using nonradiative measurement techniques. Among the photothermal techniques thermal lensing is a versatile and viable technique which can be

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used to study the energy transfer mechanisms in organic dye mixtures [11]. One of the important features of this technique is that it is a highly sensitive method for measuring the absorbance of light in a multitude of samples based on physical changes that occur in the sample during irradiation.

In the present paper, we demonstrate the use of the thermal lens (TL) technique to determine the distance between the donor and the acceptor in fluorescein (donor)–rhodamine B (acceptor) mixtures. When a medium is illuminated with a Gaussian laser beam, some of the energy absorbed by the molecules in the ground state is excited to higher energy states. After 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, creates 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 sample. The TL effect has been exploited for a number of measurements such as determination of absorptivities as low as $10^{-7}\,cm^{-1}$, evaluation of triplet quantum yield in solid and liquid phases, thermal diffusivity of various solvents, study of the multiphoton processes, calorimetric trace analysis, realization of optical logic gates and to identify an intermediate vibronic level from which nonradiative de-excitation is predominant [12–18]. The TL technique offers substantial advantages over conventional spectral methods with respect to precision, sensitivity, and minimum sample required in addition to its noncontact nature.

pump and probe beams. This technique is more advantageous since only a single wavelength (probe) is always detected and are needed no correction for the spectral response of the optical elements and detector. The excitation radiation employed in the present investigation is 470 nm radiation from an Optical Parametric Oscillator (Quantaray mopo-700). 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. Samples in a quartz cuvette (1 mm) are kept one confocal length past the beam waist. 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 donor and acceptor in ethanol are recorded with a UV–vis–IR spectrophotometer (Jasco V-570). For the fluorescence study, the front surface emission is collected and focused by a lens to the entrance slit of a 1 m Spex monochromator, which is coupled to a PMT having an S20 cathode. The PMT output is fed to a lock-in amplifier .The emission wavelength is scanned in the specified region (400–650 nm).

An accurately weighed amount of rhodamine B is dissolved in spectroscopic grade ethanol to give a concentration of 1.79 mmol$\,l^{-1}$. From this stock solution, sample solutions with different concentrations ranging from 1.79 to 0.0798 mmol$\,l^{-1}$ are prepared. Donor having a concentration of 0.24 mmol$\,l^{-1}$ is mixed with the different concentrations of rhodamine B.

2. Experimental

The experimental setup of the dual beam thermal lens technique employed in the present investigation is shown in Fig. 1. In the dual beam configuration separate lasers are used for

3. Results and discussion

Forster developed a quantitative expression for the rate of electronic energy transfer due to dipole–dipole interaction
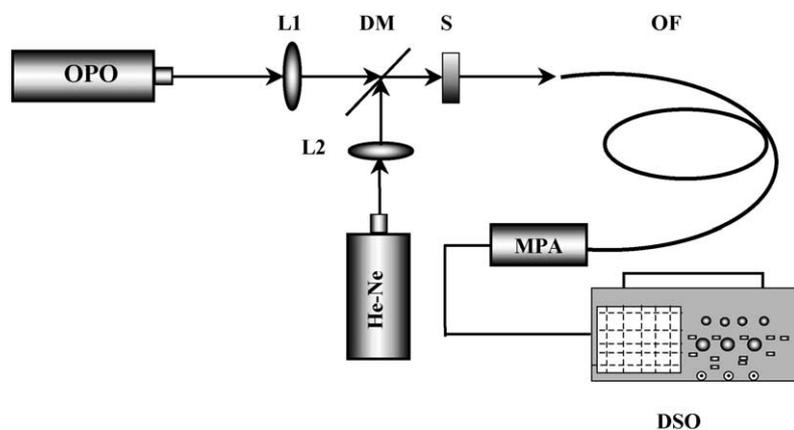

Fig. 1. Schematic diagram of the experimental set up. L_1, L_2: lens; DM: dichoric mirror; S: sample; OF: optic fibre, MPA: monochromator–PMT assembly; DSO: digital storage oscilloscope.

as [5]

$$K = \frac{9000 \ln 10 k^2}{128\pi^6 NR^6 \tau} \int\limits_0^\infty F_D(\nu)\varepsilon_A(\nu)\frac{d\nu}{\nu^4} \qquad (1)$$

The spectral overlap integral is given as [5]

$$J = \int\limits_0^\infty F_D(\nu)\varepsilon_A(\nu)\,d\nu \qquad (2)$$

in which $F_D(\nu)$ is the spectral distribution of the donor emission, $\varepsilon_A(\nu)$ is the spectral distribution of the acceptor absorption, ν is the wave number of the excitation radiation, N is Avogadro's number, τ is the intrinsic or radiative lifetime of the excited sensitizer, n is the refractive index of the solvent, k^2 is the orientation factor and R is the mutual distance between both molecules. Since transfer rates depend on the distance between the molecules, a useful relation between the radius of the quenching sphere R and the concentration of the acceptor is given by

$$R(\text{Å}) = \frac{7.35}{(c_0)^{1/3}} \qquad (3)$$

The Stern–Volmer equation [19], modified by Inokutti and Hiryama [20] can be written as

$$\frac{\phi}{\phi_0} = \left(1 + \frac{c}{c_0}\right)^{-1} \qquad (4)$$

This equation can be rewritten as

$$\frac{\eta_L^o}{\eta_L^A} = 1 - \frac{c}{c_0} \qquad (5)$$

where η_L^o is the thermal lens signal measured for donor alone, η_L^A is the TL signal in the presence of acceptor and c_0 is an arbitrary reference concentration. In order to calculate the distance between the molecules in the mixture, the ratio of the TL signal of the donor alone at a concentration of 0.24 mmol l^{-1} to the TL signal of the mixture with acceptor concentration ranging from 1.79 to 0.0798 mmol l^{-1} are investigated.

Fig. 2 gives the absorption spectrum of fluorescein at a concentration of 0.24 mmol l^{-1}. The absorption spectrum shows a twin peak since fluorescein can exist in different ionic forms. The monoanion and dianion absorbs at 454 and 490 nm, respectively [21]. The emission spectrum of fluorescein and absorption spectrum of rhodamine B in ethanol is shown in Fig. 3. Considerable overlap between emission of donor and absorption of acceptor is evident. When fluorescein is excited with blue light (470 nm), it will normally give off green light. However, if fluorescein is in close proximity to rhodamine B, it will transfer its total energy to the rhodamine B in a radiationless transfer. Now rhodamine B will give off red fluorescence. The contribution to acceptor fluorescence due to direct excitation is very small as can be seen from Fig. 3. Florescence spectra of fluorescein (concentration 2.4×10^{-4} mol l^{-1}) in presence of various concentrations of
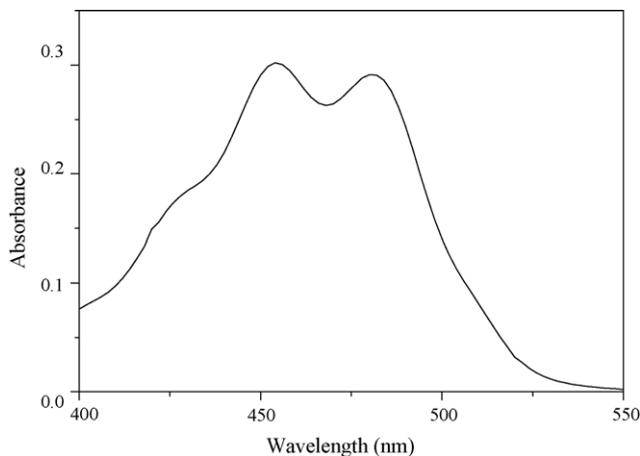

Fig. 2. Absorption spectrum of fluorescein.

rhodamine B (concentration varying from 7.98×10^{-5} to 1.79×10^{-3} mol l^{-1}) are shown in Fig. 4. The successive quenching of fluorescein emission accompanied by enhancement in the intensity of rhodamine B fluorescence is due to energy transfer from fluorescein to rhodamine B. The observed red shift in the acceptor fluorescence with increasing acceptor concentration may be due to Stoke's shift and radiative migration among acceptors [22].

At low acceptor concentration (below 4.49×10^{-4} mol l^{-1}) due to fast donor–donor transport/translational diffusion, donor fluorescence decay is exponential. And thus the higher calculated value of R may be due to the influence of diffusion on direct energy transfer [23,24]. Decay of fluorescein (concentration 2.4×10^{-4} mol l^{-1}) in presence of acceptor concentration higher than 4.49×10^{-4} mol l^{-1} deviates from exponential behavior (Forster kinetics). When the distance between the molecule is, $R = 57$ Å, long-range dipole–dipole interaction is the dominating mechanism and at this acceptor concentration (1.79 mmol l^{-1}) the fluorescence of the donor is completely quenched. Various
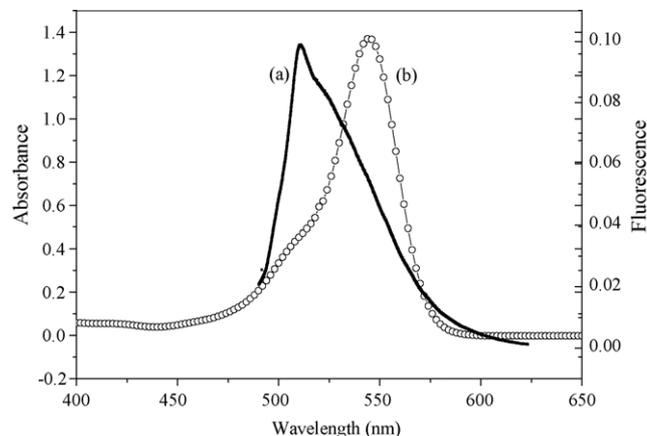

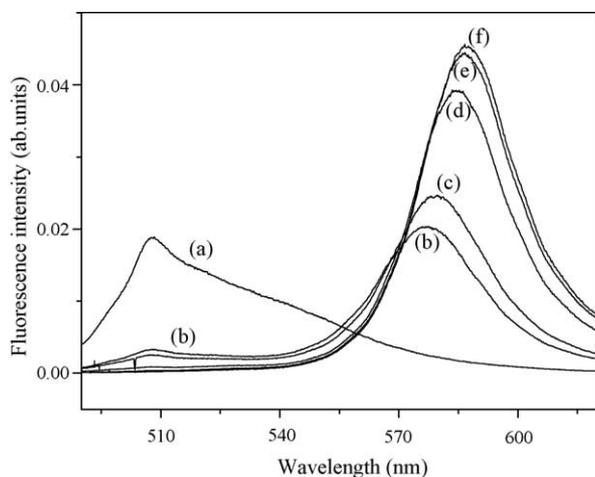Fig. 3. Emission spectrum of fluorescein (a) and absorption spectrum of rhodamine B (b).

Fig. 4. Variation of fluorescence intensities of fluorescein–rhodamine B system in ethanol. Fluorescein concentration is fixed at 2.4×10^{-4} mol l^{-1} (a) and rhodamine B concentrations in mmol l^{-1} are (b) 0.0798 (c) 0.120 (d) 0.449 (e) 1.20 (f) 1.79.

Table 1
Observed values of reduced concentrations and distances between the molecules at different acceptor concentrations

Acceptor concentration (mol l^{-1})	TL-ratio	Reduced concentration c_0 (mmol l^{-1})	R (Å)
7.98×10^{-5}	0.504	0.161	135
1.20×10^{-4}	0.435	0.218	123
4.49×10^{-4}	0.206	0.565	89
1.20×10^{-3}	0.172	1.446	65
1.79×10^{-3}	0.153	2.119	57

observed energy transfer parameters, reduced concentration and distance between the molecules for each acceptor concentration are given in Table 1.

4. Conclusion

The thermal lens technique has been successfully employed for the determination of the distance between the donor and acceptor in dye mixtures at different acceptor concentrations. The energy transfer by exchange interaction has been neglected because (a) the concentration of donor and acceptor was taken less than 2×10^{-3} mol l^{-1} and hence collisional encounter due to short range would be very rare (b) no new fluorescence peaks were detected in the mixture to indicate any fluorescence exciplex formation. In the concentration range we used the quantum efficiency of radiationless

transfer from donor to acceptor is insensitive to both Forster and Stern–Volmer kinetics.

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