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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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Keywords: Thermal lens; Energy transfer; Organic dyes

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.

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 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 1^{-1} are prepared. Donor having a concentration of 0.24 mmol l^{-1} is mixed with the different concentrations of rhodamine B.

3. Results and discussion

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

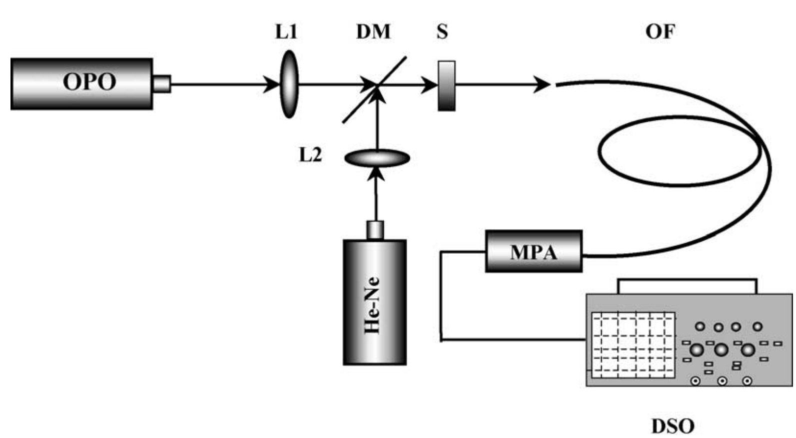

Fig. 1. Schematic diagram of the experimental set up. L_1, L_2: lens; DM: dichoric mirror; S: sample; OF: optic fibre, MPA: monochromator–PMT assembly; DSO: digital storage oscilloscope.

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