Energy transfer studies in binary laser dye Mixtures between Rhodamine 6G and Rhodamine B

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Abstract – In this research we study the energy transfer mechanism in Rhodamine6G as donor, and as Rhodamine B as an acceptors matrix has been studied. The energy transfer process from donor molecules to acceptor molecules in the final samples has been observed spectrally. UV-Vis absorption and fluorescence spectroscopy studies from (400-800) nm for Mixture of (R6G and RB) in Ethanol solvent for different concentration. We notice that the absorption intensity is increased with increasing concentration. We find also that the bandwidth of absorption spectrum is increased when we mix the two dyes together in comparison of each dye alone and these agree with the energy transfer mechanism. To confirm the energy transfer we observed the overlap between the emission spectrum of R6G and excitation spectrum of R8. The results show that the emission properties of acceptor molecules can be enhanced using the dye mixing binary laser dye. The results showed access to a broad spectrum extends from 525nm to 645nm, was obtained on the movement of energy with high efficiency when mixing dyes concentrations (1*10⁻⁵ R6G dye & 1*10⁻⁶ RB dye).

Key wards - Dye laser, Optical properties, Energy transfer.

1 INTRODUCTION

The concept of energy transfer in which electronically excited molecules transfer their energy to neighboring molecules is widely used as an effective tool for the measurement of nanometer scale distances and for the investigations of molecular interactions. It is referred to as a spectroscopic ruler due to its sensitivity over distances of few nanometers [1]. The different mechanisms by which an electronically excited molecule decay to the ground state losing its excitation energy provide lot of information about the structure and dynamics of macromolecules, the interactions of macromolecules with each other, the environmental effects, conformation changes and proximity between molecules. Detection techniques based on energy transfer are very attractive due to their high sensitivity and find wide applications in different fields such as photochemistry, analytical biochemistry, environmental analysis and diagnostics. The energy transfer between donor and acceptor pairs is also found to be very effective in controlling and tuning light emission in laser gain media [2].

The dyes used in lasers contain rather large organic molecules which fluoresce. Organic dye molecules have been widely used in solutions as amplifying media in at unable lasers [3]. Liquid dye has very high gain as laser media. The beam only needs to make a few passes through the liquid to reach full design power. They exhibit a broad gain band width which allows for a broad wavelength tenability and also ultra-shorter pulse generation with passive mode locking [4]. Many efforts are being made in studies aimed to improve dye laser efficiency and to extend their spectral region of operation [5]. Usage could be extended if two or three wavelengths are simultaneously obtained in a broadened region with only one dye system. One of the simplest and most convenient ways to obtain such a laser is to use dye mixtures. Two wavelength laser emissions from two-dye mixture were reported in detail by earlier workers [6]. This type of dye mixture laser is called an energy transfer dye laser (ETDL) [7]. The energy transfer mechanism is used to achieve better performance such as higher lasing efficiency and wide range of oscillation [8].

2 Theory

Detailed theory of energy transfer dye laser is discussed elsewhere [8,9]. The rate constants for the radiativc and nonradiative energy transfer mechanisms are given by Stcrn-Volmer plots given by the equations



where I_{ad} and I_d are the fluorescence intensities of the donor in the absence and presence of acceptor, respectively while \emptyset_{ad} and ϑ_d are corresponding quantum yields. T_{ad} is the fluorescence lifetime of the donor without acceptor and [A] is the acceptor concentration. **K** and **K**_{nr} are total and non-radiativc transfer rate constants respectively. According to the Forster Dexter theory, the critical radius for resonant energy transfer between the donor and acceptor molecules are given by the expression [8,10],

where K^2 is the dipole orientation factor, n is the refractive index of the medium, \mathcal{O}_{od} is the fluorescence quantum yield of the donor in the absence of acceptor and $J(\lambda)$ is the spectral overlap integral given by

where, ϵ_A (λ) is the extinction coefficient of acceptor and $F_D(\lambda)$ is the nuorescence emission intensity of the donor as a function of the total integrated intensity. Evidently, any variation in the values of ϵ_A (λ) and $F_D(\lambda)$ will result in a corresponding change in the energy transfer parameters. However, the fluorescence emission spectrum is independent of excitation wavelength as long as the excitation wavelength is well within the absorption spectrum of the molecule. Hence J(λ) will not have significant dependence on the donor excitation wavelength.

The main mechanisms that have been proposed for energy transfer are [8-12]:

(1) Radiative energy transfer, i.e., the absorption of donor emission by an acceptor molecule. This process can by represented by

Donor emission:	$D^{\bullet} \rightarrow D + h\nu_A$
Acceptor absorption:	$A + h\nu_A \to A^*$

where the asterisk indicates an electronically excited state. In a radiative energy transfer process, the fluorescence lifetime of both the donor and the acceptor dye molecules are kept unchanged.

(2) Diffusion-controlled collision and energy transfer, this process is a nonradiative process and is viscosity dependent.

(3) Resonance energy transfer due to long-range dipole – dipole interaction. All these processes contribute to

the donor fluorescence quenching and enhance the acceptor fluorescence yield. The process of fluorescence quenching is defined as, one that competes with the spontaneous emission process and thereby reduces the lifetime of the excited state of the donor molecule. The process of fluorescence quenching of the donor, *D*, due to the interaction with the acceptor A can be represented by

$$D^* + A \xrightarrow{K_{ET}} D + A^*$$

where K_{RT} is the energy transfer rate constant. Energy transfer reduces the emission intensity from D* and sensitizes emission from A* [12].

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3 EXPERIMENTAL

3.1. MATERIALS AND METHODS

This research was used in each of the following materials;

1.Solvent :

Ethanol has been used as a solvent private analyzes spectral purity with a high (99.99%) of the highest purity available. It was used as a solvent for both Laser dyes, and has solvent at room temperature.

2. Rhodamine 6G :

R6G is a synthetic organic compound available as a dark reddish purple, brown, or red crystalline solid. Belong to xanthene family. The molecular formula (C28H31N2O3Cl), molar mass (479.02 g/mol), solubility in Ethanol at (27 °C) and the structural formula is as shown Figure (1) [13-16].

3. Rhodamine B

RB is a synthetic organic compound available as a dark green crystalline solid. Belong to xanthene family. The molecular formula (C28H31N2O3Cl), molar mass (479.02 g/mol), solubility in Ethanol at (27 °C) and the structural formula is as shown Figure (1) [13-16].



Rhodamine 6G

Rhodamine B

Figure (1): formula the laser dyes.

The solution are prepared of different concentra-

tions and this dissolving from given weight of material to be material to be studied in given volume of solvent used in the preparation of solution and the material is weighted according to the following relation:[12]

Where W the weight of material in (gm), C molar concentration (mol/ l),

M molecular weight (gm/ mol). V the volume of solvent used to dissolve the material in (cm3).

It is diluted concentrations for other concentrations of the dye solution and put the samples in the dark to avoid the optical analysis of the dye laser. The prepared solutions were diluted according to the following equation:[13]

Where M_1 primary concentration, M_2 new concentration, V_1 the volume before dilution, V_2 the volume after dilution.

3.2. UV-VIS ABSORPTION AND FLUORESCENCE SPEC-TRA MEASUREMENT

UV-Vis absorption and fluorescence spectra of the solutions dye laser were recorded data were obtained by a CECIL-CE7200 (England) double beam Spectrophotometer and F96PRO (Chinese) Fluorescence Spectrophotometer respectively; all spectra were measured at room temperature in a quartz cell with (1cm) optical path.

4 RESULTS AND DISCUSSION

Absorption spectra of the RG6 dye dissolved in ethanol for different concentrations (1*10-6, 1*10-5, 1*10-4 and 5*10-4) M with wavelength range (400-800) nm, is as shown Figure (2).Shows absorption spectrum is relatively a broad package extends between (462-564)nm, the bandwidth $\Delta\lambda$ **100 nm**, it has been observed that the absorption spectrum intensity is increased with increasing concentration.



Figure (2): UV-VIS absorption spectrum for R6G at different concentration.

Shown in Figure (3) Absorption spectra of the RB dye dissolved in ethanol for different concentrations (1*10-6, 1*10-5, 1*10-4 and 5*10-4) M with wavelength range (400-800) nm, shows absorption spectrum is relatively a broad package extends between (475-585)nm, the bandwidth $\Delta\lambda$ **110 nm**, it has been observed that the absorption spectrum intensity is increased with increasing concentration.



Figure (3): UV-VIS absorption spectrum for RB at different concentration.

Figure (4) shows the increase absorption spectrum intensity to increase the concentration for both laser dyes, Show that the RB dye increases for intensity of the absorption of the largest comparison with R6G dye. As it shows that the absorption spectrum of shifts about long wavelengths (Infrared wavelengths), an increase of solute concentration for both dyes.



Figure (4): Increase absorbance of the dyes with increasing the concentration of dissolved.

The fluorescence spectra of the RG6 dye dissolved in ethanol for different concentrations (1*10-6, 5*10-6, 1*10-5 and 1*10-4) M with wavelength range (400-800) nm, it can be seen in Figure (5), Compared with the absorption spectrum of the RG6 dye laser described above, it does not identical absorption spectra and fluorescence of the RG6 dye, where displaced fluorescence spectrum about infrared wavelengths (Stokes Shift) because of the energy consumed by the molecule to return to the original position with neighboring molecules are called (Relaxation Energy).



Figure (5): Fluorescence spectra of the R6G dye are different concentrations.

Figure (6) also shows are the fluorescence spectra of the RB dye was different concentrations (1*10-6, 5*10-6, 1*10-5 and 1*10-4) dissolved ethanol at room temperature. It can be seen for both Figure (5), and Figure (6) ware the intensity of fluorescence spectra increases with the concentration of dissolved to that the concentration of the dye up to the value then begins to decrease fluorescence spectrum with the increase in the concentration of dissolved, because extinction of high concentrations, where the solvent at high concentrations tends to the formation of binary molecules of dissolved, as a result of this binary gatherings for the fluorination extinction sometimes.



Figure (6): Fluorescence spectra of the RB dye are different concentrations.

The Figure (7) shows an increase intensity of fluorescence spectra with increasing solute concentration for both laser dyes to a certain extent after decreasing the intensity of spectrum to increase the concentration of dissolved, where we find the intensity shift peak RB dye about quantity peak of the R6G dye as well as its increased intensity of the RB dye in its biggest increase when compared to the R6G dye solute concentration.



Figure (7): Fluorescence spectra of change by increasing the concentration of dissolved for both dyes laser at room temperature.

In order to get energy transfer from the donor molecule to the acceptor molecular, must obtain spectral overlap between fluorescence spectra of the R6G dye donor molecule with the absorption spectra of the RB dye acceptor molecule. The efficiency of energy transfer it depends on the amount of overlap between the spectrums.

Figure (8) shows that the overlap between the spectrums are very good overlap this shows that the trans-

fer of energy between the spectrum with high efficiency.



Figure (8): Overlapping spectrum of fluorescence R6G dye with the absorption spectrum of RB dye.

Figure (9) represents the mechanism of energy transfer from the R6G dye to RB dye, when mixing fixed concentration of R6G dye and changing concentrations of RB dye, as it shows that the fluorescence spectra of dyes are excited wavelength 500nm, we used this wavelength because the RB dye, it has a relatively weak absorption at this wavelength value of as it can be seen decrease the intensity of fluorescence spectrum of the donor dye when increasing the concentration of the dye acceptor, then the increase in the intensity of fluorescence spectrum of the acceptor dye at the increasing concentrations.



Figure (9): Fluorescence spectra of a mixture to fixed concentration of R6G dye and changing concentrations of RB dye.

The Figure (9) shows can be obtained on the intensity of fluorescence spectrum to RB dye is very good, so when energy transfer of irritant dye a wavelength outside the region irritation RB dye. Figure as shows also the fluorescence spectra when mixing concentrations (1*10-5 R6G dye / 1*10-6 RB dye) we see a very wide spectrum extends from 525 nm to 645 nm, this is a very broad spectrum is ideal for the manufacture of lasers for midwife toning on a wide range of wavelengths.

Figure (10) shows the decrease in the intensity of fluorescence spectrum of the R6G dye, increase the intensity of the RB dye when increasing the concentration of the dye acceptor, due to photon fluorescence resulting from the return of the donor molecule to the ground level to detract out of the solution, but re-absorbed by the acceptor molecule to send the status of another photon will be at a wavelength longer than the first photon.



Figure (10): Change the intensity of fluorescence spectrum of the dyes when increasing the concentration of the dye acceptor.

The study energy transfer process when fixed acceptor molecule concentration and increase the concentration donor molecule, it will be the form of fluorescence spectra of the mixture as shown in Figure (11).



Figure (11): Fluorescence spectra of a mixture to fixed concentration of RB dye and changing concentrations of R6G dye.

As seen from the Figure (11) that the intensity of fluorescence spectra of the RB dye irritants be few, when

not in the presence of the donor molecule this then increases the intensity the greater the concentration of the dye donor, in order to provide a larger number of photons with a wavelength within the absorption acceptor molecule, so as to provide the largest number of photons with a wavelength within the absorption acceptor molecule, the convergence of molecules from each other when increasing concentration is this leads to interact more efficiently.

5 CONCLUSION

We concluded from this study, the absorption spectra for both dyes increased with increasing concentrations but this increase is not be the one behavior at high concentrations because of the gatherings molecular. As we can see that the fluorescence spectra also increased with increasing concentrations of dissolved for both dyes but at high concentrations less than the intensity of fluorescence spectrum. Was obtained at the highest intensity of fluorescence spectra at concentration (1*10-5 M) for both dyes. The transfer of energy from the donor R6G dye to the acceptor RB dye when mixing concentrations (1*10-5 R6G dye / 1*10-6 RB dye) more efficiently. Can manufacture new lasers for midwife toning on a wide range of wavelengths.

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