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Study of the Fluorescence Energy Transfer in Laser Active Medium Molecules (Acridine Orange and Rhodamine B) Dyes

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Abstract: In this research was the study of the phenomenon of fluorescence energy transfer between two laser dyes. One models have been prepared in this study, the acceptor dye (acridine orange) with the donor dye (rhodamine B). The absorption spectra and the emission spectra of the acridine orange and rhodamine B dyes were studied with different concentrations (1×10^{-3}, 1×10^{-4}, 1×10^{-5}) mL in ethanol solvent. The results of the study showed a significant increase in the intensity of the fluorescence spectra of the mixing samples compared to the dyes individually for all the prepared samples. We note change all the linear optical properties (absorption coefficient, refraction index, quantum yield, lifetime of the energy level of fluorescence) of (acceptor+donor) samples prepared compared to what it was before mixing.

Key words: Dye laser, optical properties, energy transfer, donor-acceptor pair, level of fluorescence, refraction index

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 (Kumar and Unnikrishnan, 2001). 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 (Zalewski and Keller, 1971).

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 (Kailasnath *et al*., 2008). 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 ten-ability and also ultra-shorter pulse generation with passive mode locking (Wang *et al*., 2007). Many efforts are being made in studies aimed to improve dye laser efficiency and to extend their spectral region of operation (Sinha *et al*., 2002). 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 (Ali, 2013). This type of dye mixture laser is called an Energy Transfer Dye Laser (ETDL) (Czimerova and Bujdak, 2013). The energy transfer mechanism is used to achieve better performance such as higher lasing efficiency and wide range of oscillation (Norman and Kellar, 1980).

Principle of Fluorescence Resonance Energy Transfer (FRET): In the process of FRET, initially a donor fluorophore absorbs the energy due to the excitation of incident light and transfer the excitation energy to a nearby chromophore, the acceptor. Energy transfer manifests itself through decrease or quenching of the donor fluorescence and a reduction of excited state lifetime accompanied also by an increase in acceptor

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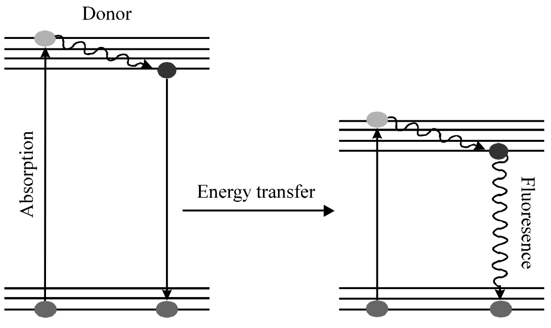

Fig. 1: Jablonski diagram illustrating the FRET process

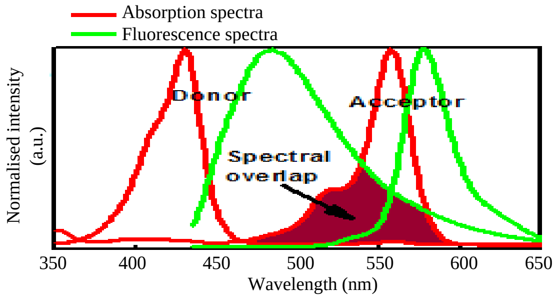

Fig. 2: Absorption and fluorescence spectra of an ideal donor-acceptor pair

fluorescence intensity. Figure 1 is a Jablonski diagram that illustrate the coupled transitions involved between the donor emission and acceptor absorbance in FRET. In presence of suitable acceptor, the donor fluorophore can transfer its excited state energy directly to the acceptor without emitting a photon.

Brown coloured region is the spectral overlap between the fluorescence spectrum of donor and absorption spectrum of acceptor. There are few criteria that must be satisfied in order for FRET to occur. These are:

- The fluorescence emission spectrum of the donor molecule must overlap the absorption or excitation spectrum of the acceptor chromophore (Fig. 2). The degree of overlap is referred to as spectral overlap integral (J)
- The two fluorophore (donor and acceptor) must be in the close proximity to one another (typically 1-10 nm)
- The transition dipole proentations of the donor and acceptor must be approximately parallel to each other
- The fluorescence lifetime of the donor molecule must be of sufficient duration to allow the FRET to occur

MATERIALS AND METHODS

Practical part

The materials used:

- Two dyes laser been selected in accordance with the terms of the mechanics and energy transmission (acridine orange, Rhodamine B)
- Two solvents be suitable for dyes, so, check the mechanics of energy transmission (Ethanol)
- Two devices are used for some measurements (absorption spectrophotometer, fluorescence spectrophotometer)

Preparation of samples: The sample preparation methods of solution (dye+solvent) or from a mixture of two dye preparations with different concentrations and the concentrations usually attend using the equation (Ali and Mahdi, 2012):

$$w = M_W.C.V/1000 \quad (1)$$

Where:

W = Weight of the dissolved dye (g)
M_W = Molecular weight of the dye (g/mol)
V = The Volume of the solvent (mL)
C = The dye Concentration (mol/L)

Used devices: In spectroscopic studies of this kind and when the study of molecular electronic energy levels is used for the following devices: UV-Vis spectrometer and fluorescence spectrometer.

The measurements: Linear optical properties of the dyes the study of the linear optical properties for spectrum prepared dyes (acridine orange and rhodamine B)with different conditions through changed concentration solution and we can also calculate the life time of fluoridation (τ_f) record compound known to his life time as well as the area under the curve as in the following relationship equation which is adopted in the calculations in this research (Al-Khafaji, 1993):

$$\tau F = \frac{a \times \tau fRB}{aRB} \quad (2)$$

As τ_{fRB} represents life time record for a compound which rhodamen B and worth (3.230) ns when the concentration (10^{-4}) M and a_{RB} is the area under the curve fluorescence of rhodamine B and its value (117.6) cm^{-1} a represents the area under the curve required for the compound in this search. It can also be account quantitative output of fluoridation (Φ_F) to find the ratio of the fluorescence spectrum space to the absorption spectrum space, if any (Hercules, 1960):

$$\phi_F = \frac{\int F('v)d'v}{\int \varepsilon('v)d'v} \quad (3)$$

RESULTS AND DISCUSSION

Study the absorption and fluorescence spectra for acridine orange dye and rhodamine B dye in ethanol: It was prepared one concentrations of (10^{-3}, 10^{-4}, 10^{-5}) after dissolves acriden orange dye and rhodamine B dye in a solvent ethanol and then measuring the absorption spectra using (UV-Visible) spectrophotometer) As shown in Fig. 3 and Table 1.

And from the result of absorption spectra obtained spectra transmission and as shown in Fig. 4 and Table 2.

And After obtaining the results of transmission were measured linear absorption coefficients (α_0) and linear refractive index (n_0) for samples prepared after the introduction the result in the computer program as shown in Table 3 and 4.

It was measured fluorescence spectra of samples prepared to dye solution (acriden orange and rhodamine B in ethanol using a fluorescence spectrometer. The results of the measurements as shown in Fig. 5.

Through the results of fluorescence spectra possible account fluorescence lifetime as well as the quantum yield fluorescence, using the relations (2, 3) After calculating the area under the curve of the curved absorption and fluorescence using a computer program (GEUP 6) the results were as shown in Table 5.

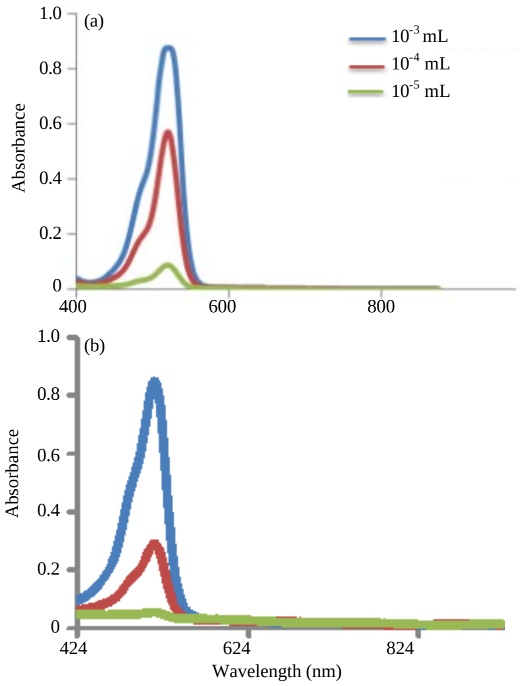

Fig. 3: Absorption spectrum in the region (UV-VIS) for the solution acridine orange dye and rhodamine B dye dissolved in ethanol

Table 1: Absorption spectrum in the region (UV-VIS) for the solution acridine orange dye and rhodamine B dye dissolved in ethanol

C (mL)	λ_{max} (nm)	A
Acriden orange in ethanol		
1×10^{-3}	487	0.835
1×10^{-4}	484	0.275
1×10^{-5}	481	0.056
Rhodamine B in ethanol		
1×10^{-3}	538	0.862
1×10^{-4}	538	0.527
1×10^{-5}	532	0.066

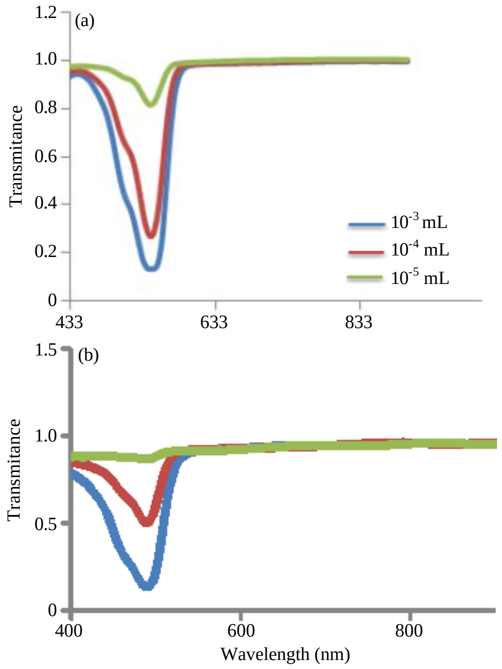

Fig. 4: Spectrum transmission in the region (UV-VIS) for the solution acriden orange dye rhodamine B dye and dissolved in ethanol

Table 2: Transmission spectrum in the region (UV-VIS) for the solution acariden orange dye and rhodamine B dye dissolved in ethanol

C (mL)	λ_{max} (nm)	T
Acriden orange in ethanol		
1×10^{-3}	484	0.159
1×10^{-4}	484	0.530
1×10^{-5}	484	0.875
Rhodamine B in ethanol		
1×10^{-3}	538	0.137
1×10^{-4}	538	0.296
1×10^{-5}	535	0.842

Table 3: Absorption coefficients and refractive index of the dye acriden orange and rhodamine B dye solution dissolved in ethanol

C (mL)	(cm^{-1}) α_o	n_o
Rhodamine B in ethanol		
1×10^{-3}	1.980	2.10
1×10^{-4}	1.290	1.90
1×10^{-5}	0.133	1.30
Acariden orange in ethanol		
1×10^{-3}	0.994	4.50
1×10^{-4}	0.407	1.80
1×10^{-5}	0.035	1.32

Table 4: The florescence intensity the acriden orange dye rhodamine B and solution dissolved in ethanol

C (mL)	λ_{max} (nm)	Relative intensity
Rhodamine B in ethanol		
1×10^{-3}	586	25.65
1×10^{-4}	565	10.67
1×10^{-5}	564	3.51
Acridine orange in ethanol		
1×10^{-3}	527	35.16
1×10^{-4}	517	25.39
1×10^{-5}	504	3.89

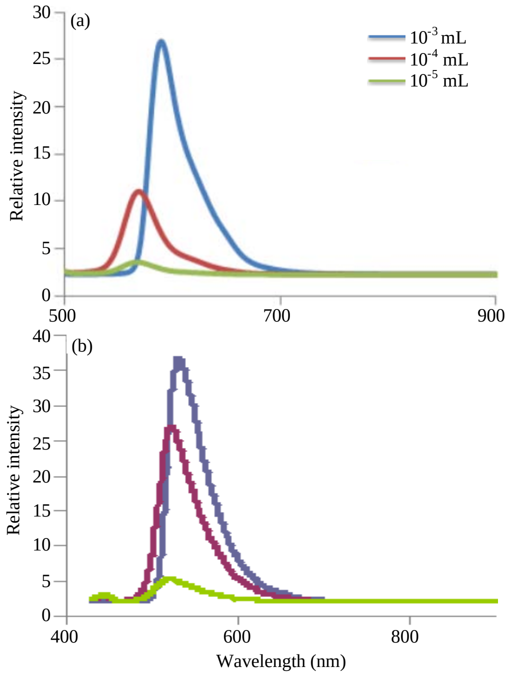

Fig. 5: Spectrum fluorescence acridine orange dye and rhodamine B dye dissolved in ethanol

Study the absorption and fluorescence spectra of mixing acridine orange dye and rhodamine B dye in ethanol: It was prepared one concentration of (10^{-3} ,10^{-4}, 10^{-5}) of mixing acridine orange dye and rhodamine B dye in ethanol then measuring the absorption spectra and as shown in Fig. 5 and 6 and Table 5 and 6. And from the result of absorption spectra obtained spectra transmittance and as shown in Fig. 7 and Table 7.

Table 5: Fluorescence lifetime and the quantum yield fluorescence with different concentrations of the acriden orange dye and rhodamine B dye solution dissolved in ethanol

C (mL)	τ_f (nsec)	ϕ_F
Rhodamine B in ethanol		
1×10^{-3}	4.6×10^{-3}	0.57
1×10^{-4}	3.5×10^{-3}	0.68
1×10^{-5}	2.9×10^{-3}	0.74
Acriden orange in ethanol		
1×10^{-3}	2.19×10^{-3}	0.73
1×10^{-4}	1.87×10^{-3}	0.79
1×10^{-5}	1.61×10^{-3}	0.82

Table 6: Absorption spectrum in the region (UV-VIS) of mixing acridine orange dye and rhodamine B dye in ethanol

C (mL)	λ_{max} (nm)	A
In ethanol		
1×10^{-3}	490	0.921
1×10^{-4}	484	0.143
1×10^{-5}	481	0.033

Table 7: Transmission spectrum in the region (UV-VIS) of mixing acridine orange dye and Rhodamine B dye in ethanol

C (mL)	λ_{max} (nm)	T
In ethanol		
1×10^{-3}	487	0.134
1×10^{-4}	484	0.717
1×10^{-5}	481	0.926

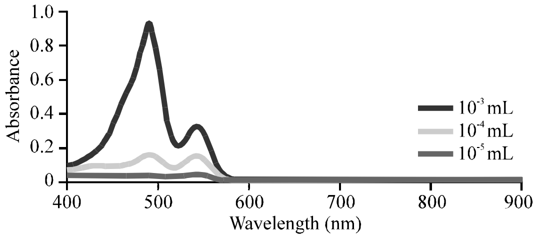

Fig. 6: Absorption spectrum in the region (UV-VIS) of mixing acridine orange dye and rhodamine B dye in ethanol

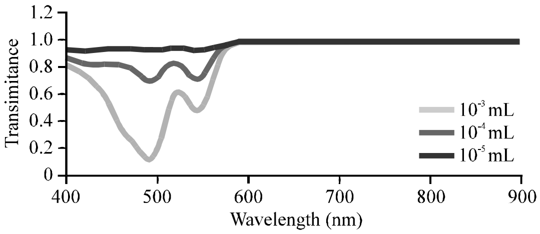

Fig. 7: Spectrum transmission in the region (UV-VIS) of mixing acridine orange dye and rhodamine B dye in ethanol

And after obtaining the results of transmission were measured linear absorption coefficients (α_o) and linear refractive index (n_o) for samples prepared after the introduction the result in the computer program as shown in the Table 8.

Table 8: Absorption coefficients and refractive index of of mixing acridine orange dye and rhodamine B dye in ethanol

C (mL)	(cm^{-1}) α_o	n_o
In ethanol		
1×10^{-3}	1.800	2.1
1×10^{-4}	0.304	1.9
1×10^{-5}	0.070	1.1

Table 9: The fluorescence intensity of mixing acridine orange dye and rhodamine B dye in ethanol

C (mL)	λ_{max} (nm)	Relative intensity
In ethanol		
1×10^{-3}	568	43.41
1×10^{-4}	565	38.42
1×10^{-5}	562	10.29

Table 10: Fluorescence lifetime and the quantum yield fluorescence with different concentrations of mixing acridine orange dye and rhodamine B dye in ethanol

C (mL)	τ_f (nsec)	ϕ_F
In ethanol		
1×10^{-3}	1.5×10^{-3}	0.78
1×10^{-4}	1.2×10^{-3}	0.81
1×10^{-5}	1.02×10^{-3}	0.86

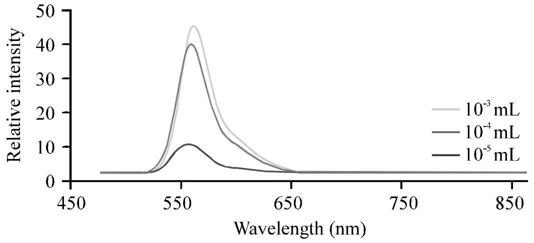

Fig. 8: The fluorescence intensity of mixing acridine orange dye and rhodamine B dye in ethanol

It was measured fluorescence spectra of samples prepared to mixing dye solution (acridine orange+ rhodamine B) using a fluorescence spectrometer. The results of the measurements as shown in Fig. 8 and Table 9.

Through the results of fluorescence spectra possible account fluorescence lifetime as well as the quantum yield fluorescence, using the relations (2, 3) after calculating the area under the curve of the curved absorption and fluorescence using a computer program (GEUP 6). The results were as shown in Table 10.

CONCLUSION

The results of the study showed a significant increase in the intensity of the fluorescence spectra of the mixing samples compared to the dyes individually for all the prepared samples. The most important results obtained were those related to the quantum yield (ϕ_F and the fluorescence lifetime (τ_f) for all mixing samples. The best fluorescence energy transfer was in the second sample of mixing (acridine orange+rodamine B) when using the ethanol solvent and at the concentration of (1×10^{-3}) mL.

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