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Effects of Temperature and Concentration on Spectroscopic Behaviors of Laser Dye

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In this work, the fluorescence spectra of an organic lasing dye were recorded at different temperatures and doping concentrations. Results showed that when the donor concentration fixed and the acceptor concentrations varies for two temperatures (room and low) and for both solvents (ethanol and methanol) used in this work, the peaks of emission of donor and acceptor show a small blue shift. However, this blue shift increases with increasing the acceptor concentrations against donor concentration.

1. Introduction

The properties of transferred waves in the media are determined by the nature of its components. The medium interacts with these waves as a whole when light falls on it, atoms of the medium will be microscopic dipoles which scatter the field of the incident electromagnetic wave [1]. Polarization in the medium, due to the incident electromagnetic radiation, is an indication of the refractive index of this medium. The higher number of dipoles (high polarization) the lower speed of light and the higher refractive index [2]. In materials with high atomic number, the density of electrons is high; therefore they are expected to have a high refractive index considering that the medium is homogeneous [3].

Obstacles arise due to inhomogeneity of the medium. The characteristics of the scattering medium are not the same along the path, especially, if the scatterers are randomly distributed. While the effect of absorption is less complicated than scattering, it varies the amplitude of the incident field, but does not change the propagation direction. Energy transfers from the wave field to the dissipated medium [4].

The basic ideas concerning laser operation deals with mutual interaction of electromagnetic radiation and matter. The electromagnetic wave incident on an atomic or molecular system with energy equals to the amount of the energy difference between two defined states of a specific atomic system may interact with this system [5,6].

Rhodamine B was well known since 1928 it can be used as calibrated wavelength to monochromator [7,8]. Due to these interesting properties, the dyes are often used as probes in studying a variety of physicochemical processes in condensed phase [9].

Lasing compounds are classified, according to their chemical structure and the region that emit in the e. m spectrum, into the following different classes [10]: polymethane dyes: the emission range corresponding to this class is about 700-1000nm, Xanthene dyes: with emission range around 500-700nm, heterocyclic compounds: comparatively, its short emission range lies in the 400-500nm range, and scintillator dyes: their emission is at wavelength <400 nm.

Change of temperature influence the intensity of fluorescence emission. The monomer internal quenching rate parameter (K_{IM}) is found to depend on temperature [11].

$$K_{IM} = K_{IM}^{\circ} + \bar{K}_{IM}e^{-W_{TM}/KT} \qquad (1)$$

with internal quenching rate parameter K_{IM}° which is independent of temperature (T), frequency factor $\bar{K}_{IM}$, activation energy W_{TM} and Boltzmann's constant K. The quantum yield of triplet occupation measurements and its value is unlikely to increase significantly with temperature, because $(S_1 \rightarrow S_0)$ energy gap is large compared with KT [12]. Therefore it is appears that the temperature dependent component of K_{IM} is attributed to intersystem crossing from S_1 to an adjacent triplet state, T_q, sufficiently close in energy to S_1 that the $S_1 \rightarrow T_q$ intersystem crossing rate is influenced by the thermal population of vibrational states of S_1. Accordingly, equation (1) can be written as:

$$K_{IM} = \bar{K}_{TM}e^{-W_{TM}/KT} \qquad (2)$$

At lower temperatures, the spectral widths are usually reduced and the spectra exhibit enhanced vibrational information. The aromatic solution when cooled down to 77 K show that the spectra consist of a number of sharp vibrational bands and split into a series of line wide in favorable cases [13]. Inhomogeneous broadening is observed when the analytic molecules in a liquid solution sample are surrounded by different solvent cages. Each individual molecule will experience a different influence from its immediate surroundings on excited state and ground state of the molecule. If recording a low-temperature fluorescence spectrum of such a solution, each transition will appear as a Gaussian distribution of narrow lines, with a total band width of typically several hundred cm^{-1}. Often matrix inhomogeneity is the major contribution to the overall band width observed in conventional

fluorescence spectroscopy [14]. Consider the vibrational coarse structure of electronic spectra which consist of one or more series of convergent lines. Usually the lines are broad and diffuse. If the resolution is sufficiently good, each line appears as a cluster of many very close lines [15].

2. Experimental Part

The chemicals that have been used in the present work are listed in Table (1).

Laser dye solutions were prepared by dissolving the required amount of the dyes in ethyl alcohol. The weight of the dye (W) was measured using a balance of 10^{-4} g sensitivity (Matter company) and can be calculated using the following equation:

$$W = M_w . V. C / 1000 \qquad (3)$$

where M_w is the molecular weight of the dye (g/mol), V is the volume of the solvent in ml and C is the molar concentration (mol/ltr). A high concentration of 10^{-2} (mol/ltr) of dye solution was firstly prepared and then diluted to 10^{-3}-10^{-6} (mol/ltr) concentrations, respectively.

To dilute the solution, the following equation was used:

$$C_1 V_1 = C_2 V_2 \qquad (4)$$

Here:
C_1 is the high concentration [M], V_1 is the volume before dilution (l), C_2 is the required diluted concentration [M], and V_2 is the total volume after dilution (1).

The basic idea of the cooling system is to improve the coolant temperature and save percentage below zero we used Freon (134a) system as a means of cooling.

UV-visible absorption spectra of the prepared samples were measured in the wavelength range of 200-800nm using METERTECH SP-8001 UV/visible double-beam (Halogen and deuterium lamps) spectrophotometer.

The fluorescence spectra were obtained using F96 which is fluorescence Spectrophotometer unit, Shanghai Lengguang Tech. Co., Ltd. in the emission wavelength range of 180-900nm, with Xenon CW lamp as the excitation source.

Table (1) Specifications of the starting chemical materials

Material	Chemical formula	Color	Purity
Acrivlavina laser dye	$C_{27}H_{25}CIN_6$ (g/mol)	Yellow	Without further purification
Neutral red laser dye	$C_{15}H_{17}CIN_4$ (g/mol)	Red	Without further purification
Ethyl alcohol	C_2H_5OH 46.07 (g/mol)	colorless	99.9%
Methyl alcohol	CH_3OH (g/mol)	colorless	99.9%
Distilled water	H_2O 18 (g/mol)	colorless	-

Another way were used to get the fluorescence spectra is laser induced fluorescence (LIF) of the prepared samples have been recorded through the designed spectrofluormeter using a 405nm diode laser, spectral width of 10nm and beam diameter 2mm. The output signal was detected by a Jarrell Ash monochromator model 82-000, which operates in range from 190 nm to 910 nm with resolution of 0.2Å in the first order. The instrument has 0.5m focal length, with 8 speed electric drive, plane reflection grating of 1180 groove/mm. The detection unit is a photomultiplier PMT (type R666 Hamamatsu) connected to X-Y recorder to record the output signal.

3. Results and Discussion

Figures (1) to (6) show that when the donor concentration fixed and the acceptor concentrations varies for the two temperatures (room and low) and for both solvents (ethanol and methanol), the peaks of emission of donor and acceptor show small shift to short wavelength (blue shift). However, this blue shift increases with increasing the acceptor concentrations against donor concentration. Due to this shift in peak emission wavelength, there is energy absorption due to direct pumping at 455 nm as well as along with indirect pumping from Acr dye molecules as energy transfer process. This is evident from the results that acceptor molecules in dye mixtures were excited by both direct pumping and re-absorption of energy by the excitation transfer from donor molecules that absorbed the pump photons initially. It can be observed from these figures that the fluorescence intensity of acceptor increases with increasing its concentration at fixed donor concentration because of the reduction in intermolecular distance between the donor and acceptor molecules. Also, one can note that the decrease in temperatures leads to increase the emission intensities of acceptor and donor.

These figures also show the fluorescence spectra of Acr and Nut red mixture, which dissolved in methanol and ethanol solvents, at room and low (around -10°C) temperatures. These figures illustrate that the energy transfer clearly occurs with increasing acceptor concentrations with fixed donor concentration, and these behaviors change with changing the donor concentration.

Moreover, at room temperature there are some donor concentrations, such as 10^{-5} M dissolved in ethanol solvent and 10^{-4} M dissolved in methanol, showed weak energy transfer with respect to other concentrations. This behavior can be attributed to the intermolecular quenching. The intermolecular quenching which causes rapid decrease of lifetime with increasing concentration may be explained due to energy transfer to quenching centers. After excitation and within the lifetime of the excited

molecules, diffusion may bring excited state and ground state molecules near together. Besides diffusion an excited molecule may transfer its excitation energy to a nearby unexcited molecule getting itself unexcited. This hopping mechanism may bring after some steps the excitation energy to a reaction center where fast radiation less decay occurs.
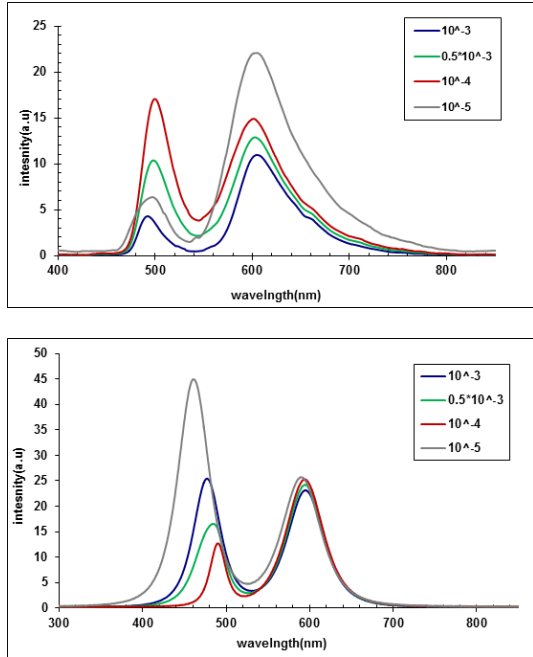
Fig. (1) The fluorescence spectra of lasing compounds mixture for 10^{-3} donor concentration dissolved in ethanol at room temperature (upper) and low temperature (lower)

Furthermore, the decrease in temperatures leads to enhancement in the fluorescence spectra which reduces the relative movement of molecules and, therefore, decreases the rate of collisions of molecules and the internal spacing between them. This means that the intermolecular quenching is reduced to a minimum. Previous studies [16,17] have shown that low temperature leads to high intensity emission spectrum with narrower peak as in these figures.

The solvent, also, has a significant role in the energy transfer, the more polar solvent led to an increase in the transfer of energy. This is caused by the increasing of polarity, which leads to restrict electronic distribution and thus reduce the impact on other molecules and this will reduce the quenching and the clearly appearance of energy transfer.
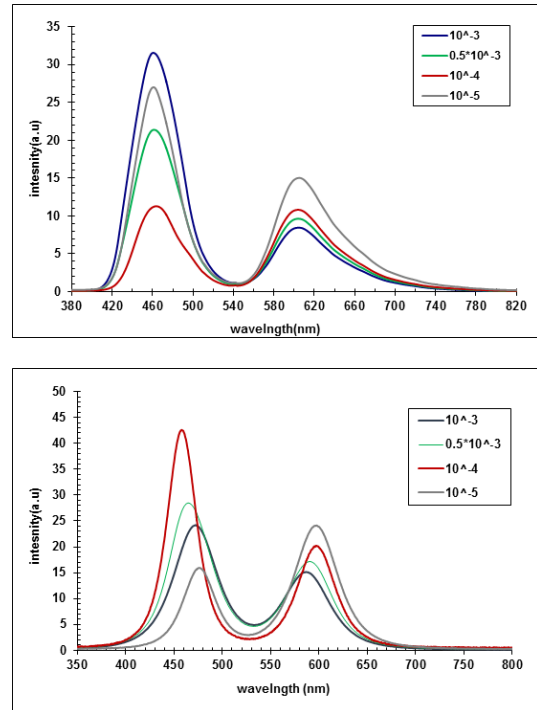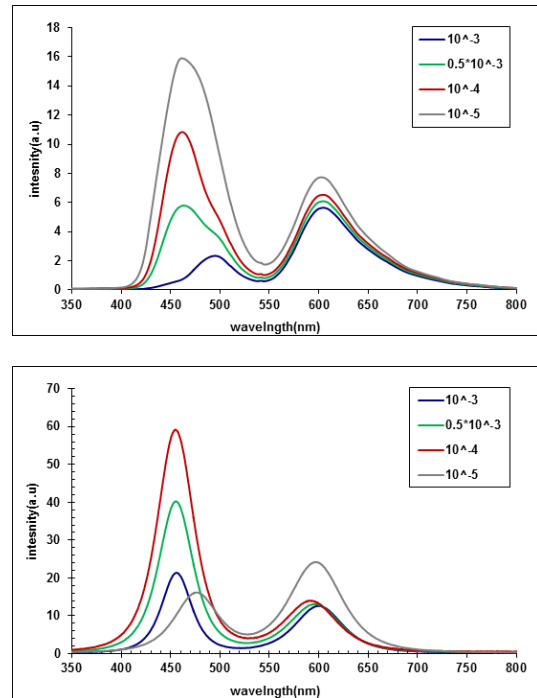
Fig. (2) The fluorescence spectra of lasing compounds mixture for 10^{-4} donor concentration dissolved in ethanol at room temperature (upper) and low temperature (lower)

Fig. (3) The fluorescence spectra of lasing compounds mixture for 10^{-5} donor concentration dissolved in ethanol at room temperature (upper) and low temperature (lower)
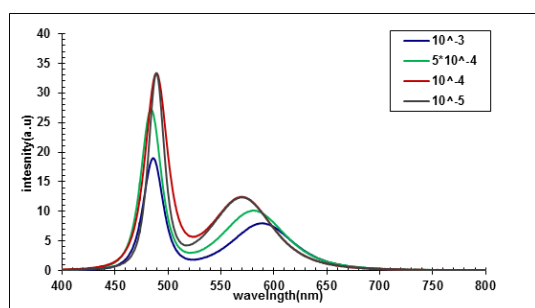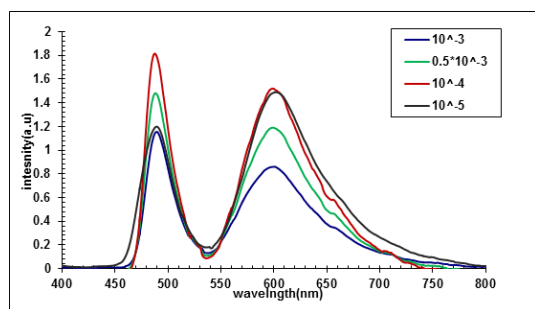
Fig. (4) The fluorescence spectra of lasing compounds mixture for 10^{-3} donor concentration dissolved in methanol at room temperature (upper) and low temperature (lower)
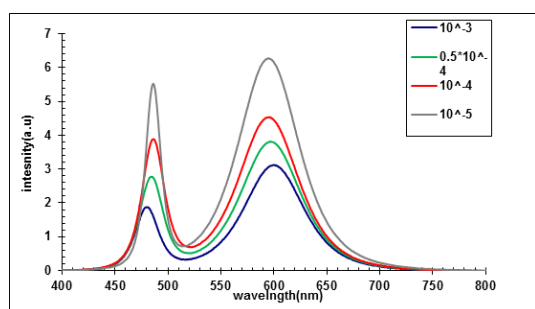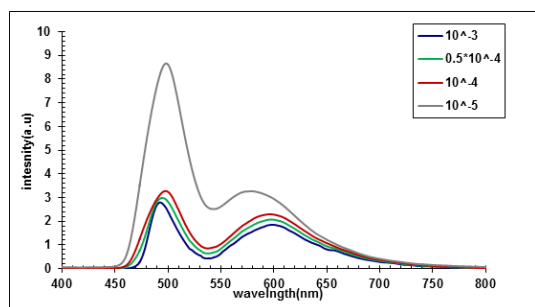

Fig. (5) The fluorescence spectra of lasing compounds mixture for 10^{-4} donor concentration dissolved in methanol at room temperature (upper) and low temperature (lower)

On increasing the temperature, higher vibrational levels of the ground state are populated according to the Boltzmann-distribution and more and more transitions occur from these levels to higher vibrational levels of the first excited electronic state. As a result, the absorption spectrum becomes broader and the superposition of the different levels blurs most of the vibrational fine structure of the band. On the other hand, at lower temperatures, the spectral widths are usually reduced and the spectra

exhibit enhanced vibrational information. Therefore, dye solutions that form a clear organic glass when cooled down to 77 K show spectra comparable to theoretical calculations because of their well-resolved vibrational structure. Further cooling below the glass point, when the free movement of solvent molecules or parts thereof is inhibited, usually brings about no further sharpening of the spectral features [18].
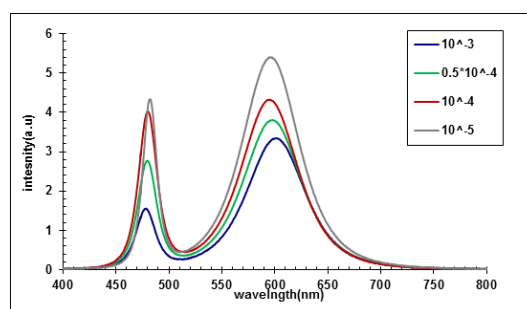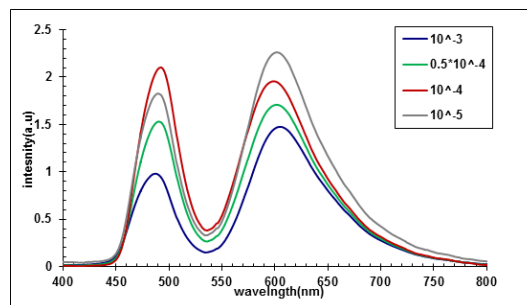

Fig. (6) The fluorescence spectra of lasing compounds mixture for 10^{-5} donor concentration dissolved in methanol at room temperature (upper) and low temperature (lower)

4. Conclusions

According to the results obtained from this work, showed that when the donor concentration fixed and the acceptor concentrations varies for two temperatures (room and low) and for both solvents (ethanol and methanol) used in this work, the peaks of emission of donor and acceptor show a small blue shift. However, this blue shift increases with increasing the acceptor concentrations against donor concentration. On increasing the temperature, the absorption spectrum becomes broader and the superposition of the different levels blurs most of the vibrational fine structure of the band. On the other hand, at lower temperatures, the spectral widths are usually reduced and the spectra exhibit enhanced vibrational information. Therefore, when dye solutions that forming clear organic glass cooled down to 77K, their spectra are comparable to theoretical calculations because of their well-resolved vibrational structure.

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