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Study of the spectral characteristics for the Styryl 9M laser dye

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Abstract : The molecular structure of the Styryl 9M laser dye had been described . Four different concentrations of this dye had been prepared using chloroform solvent .The absorption and fluorescence spectrums of the Styryl 9M laser dye solutions had been taken . The absorption spectral properties as (peak wavelength , peak absorbance and frequency difference at half absorbance maximum) and the fluorescence spectral properties as (peak fluorescence intensity , peak wavelength , full width at half maximum , line width and Stock's shift) had been measured for the prepared solutions . It had been concluded that the dye concentration increasing causes an increasing in the fluorescence photons emitted . The main conclusion is that the highest absorption leads to the fluorescence improvement.
Key words : Styryl 9M laser dye , fluorescence , absorption, properties.

Introduction

The Styryl 9M dye had been used as an active medium for the dye laser and the pulsed operation of the Styryl 9M dye laser had been employed using flash lamp pumping [1]. The picosecond pulses had been obtained from the continuous operation of the Styryl 9 dye laser by a hybrid technique for mode locking [2].

The concept of two dyes (Styryl 9 and Styryl 8) mixing has been successfully applied and operated with LD700 optics ,so the laser action had been occurred at the range of (715-760) nm and (795-845) nm [3].

The sensitivity of the two absorption peaks for the Styryl 9M laser dye to the solvent polarity had been studied and utilized in biological imaging and microscopy [4].

The rapid ,broadband two photon excited fluorescence spectroscopy had been employed for the Styryl 9M laser dye [5]. Two photon action cross-sections of the Styryl 9M laser dye and the number of emitted photons after two photon excitation were measured [6].

The Styryl 9M was used as a laser active medium but in a different way , so it is dissolved in acetone with PMMA polymer at 1:3 mixing ratio , and then put the mixture in a bottom of a little pool to make the nanostructured sample of 100µm thickness. The absorbance and the emission spectrums for these structures were recorded [7].

Styryl 9M is a 2-(6-(4-Dimethylaminophenyl)-2,4-neopentylene-1,3,5-hexatrienyl)-3-methyl-benzothiazolium Perchlorat , and the molecular structure $C_{27}H_{31}N_2O_4SCl$. Styryl 9M had the green , crystalline solid appearance and the absorption maximum (in ethanol) is 585 nm and the molar absorptivity is 5.05×10^4 L $mol^{-1}cm^{-1}$.

The diagram of the molecular structure for the Styryl 9M laser dye had been illustrated in Fig. 1 .

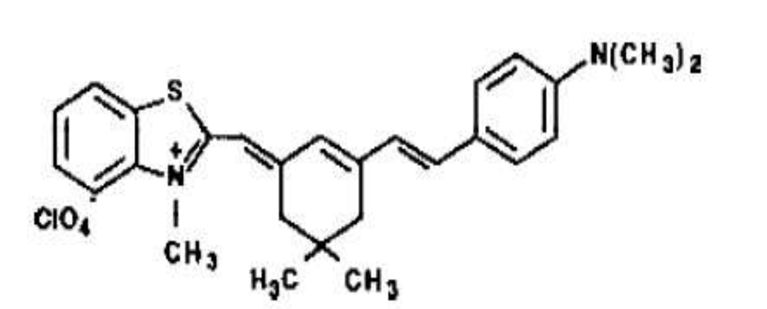

Fig.1The molecular structure of the Styryl 9M laser dye [7-8]

The properties of the laser production for the Styryl 9M laser dye were listed in table (1).

Table 1The lasing characteristics of the Styryl 9M laser dye [8-12]

Pump		*Dye Laser Characteristics*				
Source	*Wavelength [nm]*	*Peak [nm]*	*Range [nm]*	*Effic. [%]*	*Conc. [g/l]*	*Solvent*
XeCl-Excimer	*308*	*840*	*810 - 875*	*9*	*1.10*	*DMSO*
Nitrogen	*337*	*840*	*803 - 875*	*rel.*	*1.03*	*DMSO*
Nd:YAG, 2nd	*532*	*824*	*797 - 851*	*15*	*0.26*	*Pc.*
Cu-vapor	*510*	*815*	*793 - 845*	*14*	*0.67*	*Methanol*
Flashlamp	*-*	*840*	*810 - 860*	*-*	*0.01*	*Pc./Eg.*
CW, Ar^+	*VIS*	*830*	*785 - 900*	*-*	*2.0*	*Pc./Eg.*

1- Theory :

a- Absorption spectral properties

Absorption process can be happened when an incident photon crash the dye molecule in its lower energy state , the dye will be excited due to that the photon is absorbed and its energy is utilized in the dye excitation . This process can be occurred only if the incident photon energy equals to the energy difference between the two states the absorption take place at them .

Absorbance ***A*** can be defined as the logarithmic relative decrease of intensity [13]:

$$A = log_{10}\left(\frac{I_o}{I}\right) \quad .... (1)$$

So the wavelength at the maximum absorbance may be called as ***peak wavelength (nm)*** , while the maximum absorbance can be named as ***peak absorbance (arb.unit)*** and the width of absorption (curve at the half value of maximum absorbance is termed as $(\Delta\nu)_{1/2}$ ***(sec^{-1})*** which is calculated from the absorption spectrum .

b- Fluorescence spectral properties

When an excited dye molecule loss its excitation energy , the dye molecule returns to its energy ground state . This process of the photon emission is called as ***(Fluorescence)*** .

Fluorescence is the result of a three stage process to the fluorescent dye . This process can be shown in the (***Jablonski diagram***) as drawn in fig.2 .

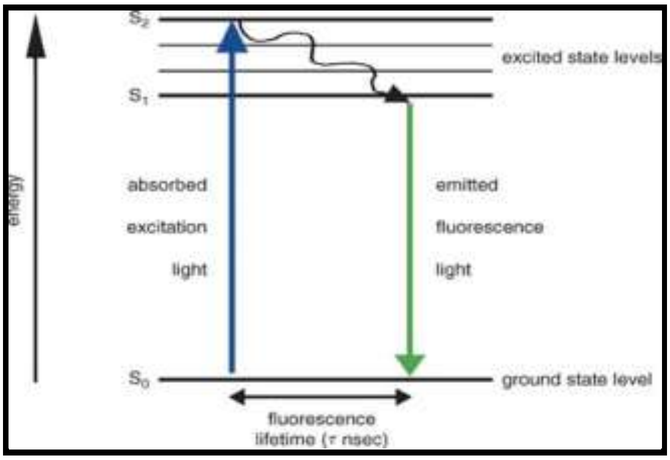

Fig.2 *Jablonski diagram* of three dominant processes for the dye molecule [14]

These processes are: first, ***excitation*** where a photon from an external source , is absorbed by the dye molecule (the photon energy pushes an electron from a ground singlet state to the excited state) . this process is happened within 1 fs. Second ,***Non-radiating transitions*** where several conformational changes had been occurred to the dye molecule within period of electron in the excited states ,as collision. This processes leads to fluorescence energy transfer , collisional quenching ,intersystem crossing and return the molecule to other state not relate with fluorescence emission states[14-16].

From the fluorescence spectrum , the wavelength at the maximum fluorescence intensity is called as ***peak wave length nm*** , while the full width of fluorescence curve at the points of half the fluorescence intensity maximum is named as ***(FWHM full width at half maximum)*** . The difference between the wavelength value of increasing the fluorescence curve approaches to minimum may be named as ***fluorescence line widthnm*** . The ***Stock's shift***is the wavelength difference between the absorption and emission maximum as below [13] :

$$\Delta\lambda_{Stocks} = \lambda_{\max.emission} - \lambda_{max.absorption} \quad \ldots\ldots (2)$$

The principle of Stock's shift is illustrated in fig.3 .

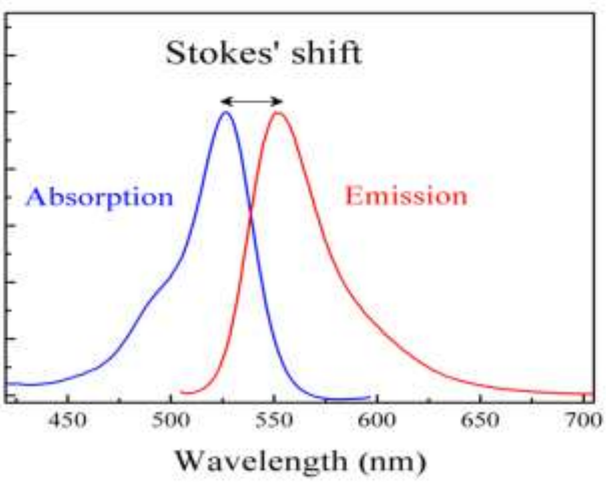

Fig.3 Stock's shift[14-17]

c- Linear optical properties

The linear optical properties related with linear optical response , had been formulated as below :

The absorbance (A) describes the amount of absorbed photons by molecules , can be written as [18]:

$$A = 1 - \log\left(\frac{1}{T}\right) \quad \ldots\ldots\ldots\ldots (3)$$

Where T : is the transmittance of medium which is related with refractive index n as [18]:

$$T = \frac{2n}{n^2+1} \quad \ldots\ldots\ldots\ldots\ldots\ldots (4)$$

The reflectivity (R) explains the reflected photons from a material can be given as a function of (n) as [18]:

$$R = \left[\frac{n-1}{n+1}\right]^2 \quad \ldots\ldots\ldots\ldots\ldots (5)$$

Each of optical properties (A , T and R) depend on the optical density (d) for that medium which can be written as [19]:

$$d = \varepsilon\, C\, \ell \quad \ldots\ldots\ldots\ldots\ldots\ldots (6)$$

Since ε : is the molar extinction coefficient which equals to [19]:

$$\varepsilon = \frac{1}{C\,\ell}\log\left(\frac{P_o}{P}\right) \quad \ldots\ldots\ldots\ldots (7)$$

Where C : is the concentration of medium molecules .

P_o : is the incident power on the random medium .

P_o : is the released power and ℓ : is the penetration length .

2- Experimental part

A four different concentrations of Styryl 9M laser dye (MW= 515.06 g/mol , product of USA , Sigma – Aldrich) had been prepared by weighting (0.001 gm) using digital balance (model- HR-200 , made in Japan) from laser dye . This weight had been dissolved in (10 ml) of chloroform solvent (D- 30926 seelze , Sigma-Aldrich Laborchemikalien Gmbh, Germany)and diluted to obtain (10^{-4} , 10^{-5} and 10^{-6}) mol/l concentrations .To perform a homogeneous solution , A magnetic stirrer (model – HP- 3000 , Lab.companion) had been used .

The absorption spectrum for liquid Styryl 9M samples had been recorded using UV-Vis spectrophotometer (Scinco ,Mega -2100 , made in Korea) and the Fig. (4) shows the absorption spectrum for these samples .

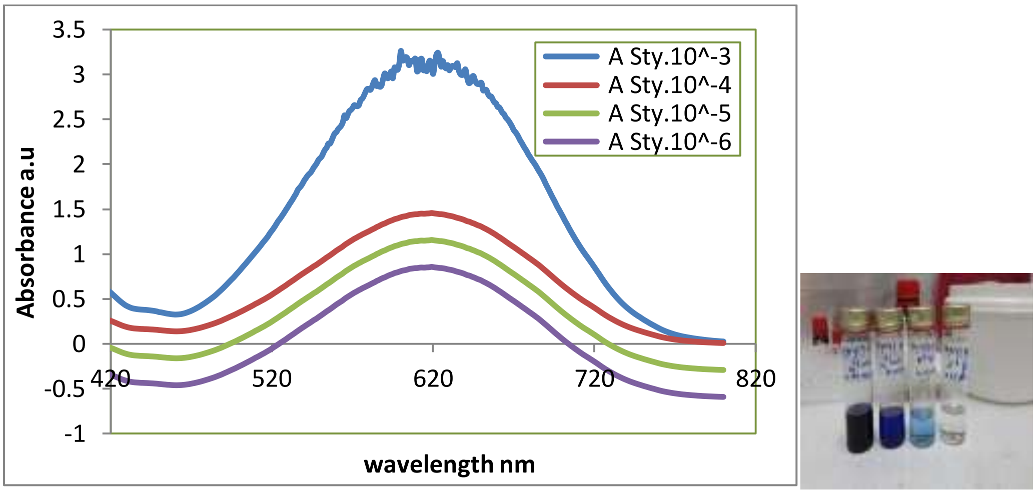

Fig .4 The absorbance spectrum of the solutions of Styryl 9M laser dye in Chloroform And the picture of prepared solutions

The fluorescence spectrum for liquid Styryl 9M samples had been recorded using fluorescence spectrophotometer (model- F96pro , Lengyuang 7ech) and the Fig. (5) shows the fluorescence spectrum for these samples .

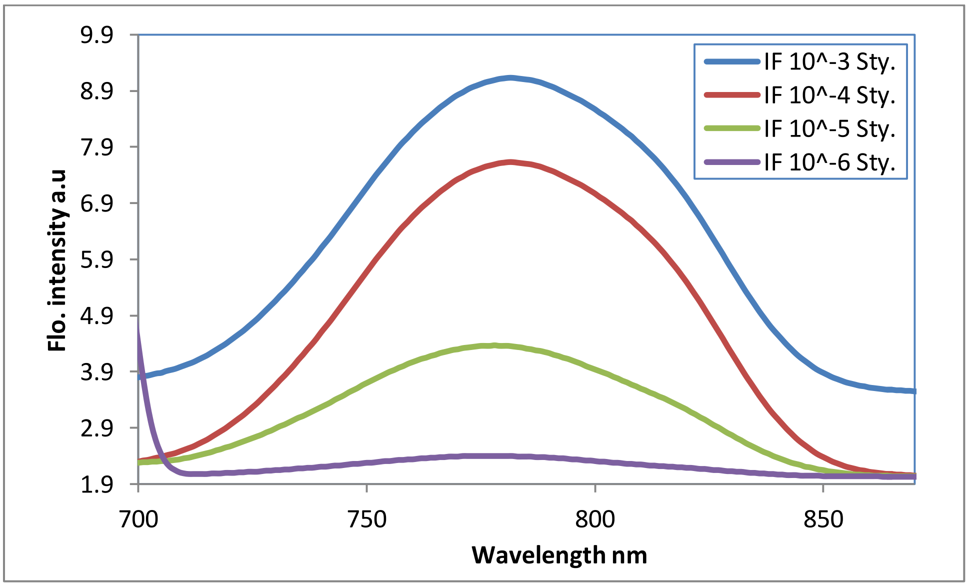

Fig .5 The fluorescence spectrum of the solutions of Styryl 9M laser dye in Chloroform

3- Results :

According to the absorption spectrums shown in Fig.(4), the absorption spectrum characteristics for Styryl 9M laser dye in chloroform solvent at four different concentrations like (Peak wavelength nm , Peak absorbance(arb.unit) and $(\Delta\nu)_{1/2}$ (Sec^{-1}) , had been listed in table (2) .

Table 2 Absorption spectrum characteristics for Styryl 9M laser dye in chloroform solvent at four different concentrations

Concentrations	Peak wavelength nm	Peak absorbance (arb.unit)	$(\Delta\nu)_{1/2}$ Sec^{-1}
10^{-3}Mol/l	615	0.8125	2x10^{+15}
10^{-4}Mol/l	618	0.375	1.9 x10^{+15}
10^{-5}Mol/l	619	0.2875	1.8 x10^{+15}
10^{-6}Mol/l	620	0.22	1.87 x10^{+15}

The Fluorescence spectrum characteristics for Styryl 9M laser dye in chloroform solvent at different concentrations like (Peak wavelength nm , Peak Fluorescence intensity (arb.unit) ,Line width (nm) ,FWHM (nm) and Stock's shift (nm) are calculated as shown in paragraph (2-b and eq. 2) . These Fluorescence spectrum characteristics for Styryl 9M laser dye solutions are illustrated in table (3).

Table 3 Fluorescence spectrum characteristics for Styryl 9M laser dye in chloroform solvent at different concentrations

Con.	Peak wavelength nm	Peak Flo.intensityar b.unit	Line width nm	FWHM nm	Stock's shift nm
10^{-3}Mol/l	777	9.1	200	100	162
10^{-4}Mol/l	781	7.7	170	90	163
10^{-5}Mol/l	783	4.3	160	80	164
10^{-6}Mol/l	785	2.4	140	70	165

The linear optical properties for different Styryl 9M laser dye concentrations in Chloroform solvent as (transmittance T , reflectivity R , absorption coefficient α , refractive index n , molar extinction coefficient ε and the optical density d) had been calculated according to the absorption spectrum characteristics are shown in table (2) by using equations (3-7, respectively) .

These linear optical properties for these solutions are listed in table (4).

Table 4 Linear optical properties for different Styryl 9M laser dye concentrations in Chloroform solvent

Concen.	A	T	R	α	n	ε L mol^{-1} m^{-1}	d
10^{-3}Mol/l	0.8125	0.1539	0.0336	0.5346	12.918	0.8127 x10^{+5}	0.812
10^{-4}Mol/l	0.375	0.4216	0.2034	1.1584	4.5227	3.750 x10^{+5}	0.375
10^{-5}Mol/l	0.287	0.5164	0.1966	1.5136	3.594	28.701 x10^{+5}	0.287
10^{-6}Mol/l	0.22	0.6025	0.1775	1.9745	2.9844	220.042 x10^{+5}	0.220

4- Discussion :

It is clear from the results in table (2) that the maximum absorbance are increased with the increasing of dye molar concentration due to the highest value of dye molecules in the energy ground state which able to absorb adequate incident photons .

The decreasing of wavelength at maximum absorbance with increasing of molar concentration can be attributed to that the high absorption by more dye molecules leads to have more energy , so this decreases the peak wavelength of absorption .

The increasing of $(\Delta\nu)_{1/2}$ with increasing of dye molar concentration can be interpreted by that the more dye molecules in the ground state will be ready to absorb the incident photon .

The results in table (3) shows that the increasing of dye molar concentration increases the maximum of fluorescence intensity because the highest value of excited molecules are fastly decayed to ground state by fluorescence emission process . This is the main reason to decrease the fluorescence wavelength maximum with the increasing of molar concentration because of the participation of the large amount of dye molecules in fluorescence emission with highest molar concentration ,both of fluorescence line width and the full width at half maximum for fluorescence curve , are increased .While the Stock's shift results are decreased with molar concentration increasing which refers to widest intersection region between the absorption and fluorescence spectrums and the highest numbers of the dye molecules are contributed in laser emission .

The results of absorption and fluorescence spectral characteristics in tables (2) and (3) are in good agreement with the published data in ref.[20].

Table (4) shows the linear optical properties for the Styryl 9M laser dye solutions . It is shown from table (4) that the increasing of the dye concentration causes both of an increasing in each of (absorbance refractive index and optical density) and a decreasing in each of (transmittance , reflectance , absorption coefficient and the molar extinction coefficient).

The highest number of dye molecules in the ground state consolidates the optical density for this medium to absorb more incident photons , so less photons can transmits through it , few photons may reflects on it .

The medium of high optical density has high refractive index because of high difference between the optical density values of the dye solution and that of air .

Because of the absorbance increasing at high molar concentration , the loss of excited energy (as non-radiative transitions or collisions with neighboring molecules) are decreased . This leads to less molar extinction coefficient , as shown in the results of ε in table (4).

5- Conclusions

It can be concluded that the Styryl 9M laser dye – Chloroform solution at 10-3 mol/l molar concentration is the best because of it has highest fluorescence characteristics as (the maximum fluorescence intensity , line width and FWHM) . It is important to the laser medium to has more excited molecules incorporate in laser emission process which are clearly appear by the wide intersection region between absorption and fluorescence spectrums . The choosing of the laser medium of high values for each of (optical density and refractive index) and with less values for each coefficients as (molar extinction coefficient and absorption coefficient) , is the more appropriate way to achieve lasing process with high output energy .

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