INTRODUCTION

Many reactions in radiation and photochemistry, physics and biology depend on the transfer of electronic energy. Any advance in the understanding of the energy transfer processes will find immediate application in many areas of research. The process of energy transfer is well observed experimentally by the emission characteristics of the quenching of emission associated with the donor and its replacement by the acceptor (S.A. Azim et al, 2000) .

In any energy transfer process contribute to the donor fluorescence quenching and the acceptor fluorescence enhancement. Basically, quenching reactions are energy transfer processes (Mahmut TOPRAK,2010, Ritty . J. Nedumpara,2008).the following three mechanisms are proposed for energy transfer (R.Ghazy,2003, I. B. Berlin ,1973 ,et al , KA Kozyra, 2002). the subsequent absorption by an acceptor molecule. The second mechanism is Diffusion-controlled collision and energy transfer, which is a non-radiative process occurring during the excitation lifetime of the donor prior to its emission as a photon. This is a solvent viscosity and temperature dependent process, which is effective over intermolecular distances. The other mechanisms is fluorescence Resonant energy transfer (FRET) due to long-range dipole-dipole interaction is in fact a distance dependent interaction between the different electronic excited sates of dye molecules in which excitation energy is transferred from one molecule (donor) to another molecule (acceptor) at the cost of emission from the former molecular system

According to Forster’s theory, the efficiency of FRET depends principally on the following factors: (i) the extent of the overlap between the donor emission and the acceptor absorption, (ii) the orientations of the transition dipoles of the donor and the acceptor, and (iii) the distance between the donor and the acceptor (J.R. Lakowicz . et al,1999, Darakhshan Qaiser et al .2010).

During the past few years, photo-physical properties of laser grade dyes in various solid matrices are attracting great attention because of their numerous optical applications such as guest dopants in organic LEDs, for energy transfer experiments, development of sensors and tuneable solid state dye lasers mixture (G. Hungerford and J.A. Ferreira ,2001, Ritty J Nedumpara ,2004,S. Singh,2003). It is reported in the literature that the type of host determines the characteristic of laser performance (J. Livage .et al,2001, A. Weiss E et al,2003,E Yariv et al,2001).

Incorporating dye laser molecules in solid matrices host eliminates many of the problems, which are faced in liquid dye lasers host (H.R. Aldag, et al,2000, A. Venkateswararao,1999, D. Lo,1998). Attempts have been made to use polymers...
as hosts for organic dyes in order to fabricate solid state dye laser, but these hosts have been shown to be lacking in mechanical, thermal properties and refractive index uniformity (A. Bergmann, et al. 2001). There are many important factors that prove to be preferable for sol–gel technique; such as the technique is low cost and capable of producing uniform glasses of high purity at low processing temperature which allows the inclusion of fluorescent dyes and other optically active molecules, that could not withstand the higher processing temperature of standard glass production; porosity is also controlled in a desired way by using this technique (R. Reisfeld, 1990). Therefore, doping the most photo-stable fluorescent molecules in glass matrices forms an important area of research; it offers an environment to study the photo-physics of dye molecules as well as their interaction with the matrix (B. Dunn and J.I. Zink 1991, S Yang, et al. 2002). Aggregation effects are seen to reduce during gelation process and the photo stability of the dyes is found to enhance when encapsulated in a sol–gel derived matrix (Marina T. et al., 2007).

In this work, the energy transfer from Rh110 dyes laser to Nb dyes laser, in solid state matrices were studied using steady state emission measurements. The effect of donor concentration on energy transfer and its mechanism were studied and discussed. The laser efficiency and the photo stability of the ETDL were also investigated.

**Experimental work:**

**Chemical materials:**

The following materials were used in this study: Rhodamine 110 dye C_{30}H_{38}N_{2}O_{7}Cl, molecular weight 366.80 gm/M and Nile Blue dye laser C_{20}H_{20}N_{2}O_{7}Cl, molecular weight 417.85gm/M, are supplied by Lambda Physik tetraethoxysilane (TEOS), (purity, 98%) as precursors, ethyl alcohol (C_{2}H_{5}OH) for spectroscopy as a solvent, NN dimethylaniline (C_{5}H_{11}NO), (purity, 99%) by GCC (Analytical) as drying control chemical additive (DCCA), deionized water catalysed by hydrochloric acid (HCl, 0.15 M).

**Sample synthesis:**

Using sol-gel method, the xerogel bulk samples were prepared by varying the sol-gel parameters: pH 1, Rmolar ratio (H_{2}O/ Si) is 24.44 and 60°C reaction temperature. Firstly, two solutions were prepared: silicasolution containing 1ml of TEOS and 2ml of pure ethanol were mixed in a suitable mold denoted as sol(I). In another molds, catalyst solution containing deionized water mixed with catalyst, HCl, separately with amount to get deionized water mixed with pure ethanol at volume ratio of 1:4.2, 2.2, 10:2, and was denoted as sol (II). The final solution (II) was slowly added to sol (I) for hydrolysis. The final sol left for 30 min. under magnetic stirrer. After this stage, 0.5 mlof N-N dimethylaniline was added as drying control chemical additives (DCCA). The final sol was poured in a covered glass tube under 60°C. The gelling time for all samples was about 48 hour. After that, the gel samples were aging for 148 hour at 60°C, and then the drying process was achieved by increasing the temperature gradually from 60 to 150°C, in step of 30°C per hour, and kept at 150°C for 60 min. Finally, solid blocks were obtained in the form of cylindrical rods with diameter ~ 0.4cm. The ends of the rods were polished manually and conventional grinding to obtain rods with 2cm in length and reasonably flat surfaces. Figure (1) show photo of some prepared samples as bulk rod shape that appearance with yellow colour and then cascade down to the deep violet colour increasing acceptor concentration.

**RESULT AND DISCUSSION**

The experimental arrangement for fluorescence measurements is shown contains a diode pumped solid state green laser (λ= 531 nm, 60 ns pulse duration, 6 kHz repetition rate, maximum power=50 mw, spectral width1 nm throughout the range (200–1000) nm. and beam diameter 2 mm. The pump beam is line focused on to the sample, along the length, through cylindrical lens of 0.5 meter focal length.

The normalized absorption and fluorescence spectra shapes of such xerogels doped with Rhodamine 110 and Nile blue only shows in Figure (2). The spectral overlapping in the wavelength band ranging from 530 to 630 nm between the
fluorescence band of the Rhodamine 110 dye and the absorption band of the Nile blue dye is suitable for energy transfer from excited Rhodamine 110 donor molecules to Nile blue acceptor molecules. The fluorescence spectra of all the samples are shown in Figures (3), (4) where the fluorescence spectra of dye mixture doped in bulk samples at different concentrations of Nb dye and at 10⁻⁴ and 2 x 10⁻⁴ M of R110 dye respectively. It can be observed from these figures that the fluorescence intensity of Nb increases with increase of its concentration at fixed donor concentration because of reduction of intermolecular distance between the donor and acceptor molecules. It is seen that the wavelength is red shifted with increase in acceptor dye concentration, as with the increase in concentration there is increase in the absorption peak, thereby red shifting the lasing wavelength through self-absorption at shorter wavelengths. Similar explanation is also suggested by (Nhung et al. 2004) in case of other mixtures.

Fig. 2: Absorption spectra of R110 (donor) and fluorescence Spectra of Nb (acceptor doped in silica xerogels.

Fig. 3: Fluorescence spectra of dye mixture in silica xerogels at 10⁻⁴ M R110 and at different concentrations of Nb.

Fig. 4: Fluorescence spectra of dye mixture in silica Xerogels at(2x10⁻⁴ M) R110 and at different concentrations of Nb.

The variation of fluorescence bandwidth at half-maxima (FWHM) of the emission band as a function of acceptor concentration is shown in Figure (5).

Figure (5) implies that the FWHM of acceptor emission decrease with increases the acceptor dye concentration and this due to energy transfer from donor to acceptor. The lowest value of FWHM is found to be 29.3 nm at 2x 10⁻⁴ M of donor (R110) and 5x10⁻⁴ M of acceptor (Nb), while 31nm FWHM is observed for 10⁻⁴ M R110-5x10⁻⁴ M Nb mixture.

The energy transfer rate constant (kET) and the quenching rate constant kSV can be determined from the Stern–Volmer relation, which is formulated as (S. Singh et al 2003, J. Livage, 2001):
\[
\frac{I_D}{I_{DA}} = 1 + K_{ET} \tau_D [A] \qquad (1)
\]

Here \( I_D \) and \( I_{DA} \) represent the fluorescence intensities of donor in the absence and the presence of acceptor, respectively; \([A]\) is the acceptor concentration; and \( \tau_D \) is the fluorescence lifetime of donor in the absence of acceptor. The fluorescence intensities ratio \( I_D / I_{DA} \) increase linearly with the acceptor concentration and thus Stern-Volmer relation of energy transfer is implemented as shown in figure (6). The total rate constant \( K_{ET} \) is the sum of radiative and non radiative transfer rate constants can be calculated from the slope of straight line.

**Fig. 5:** Dependence of fluorescence band width at FWHM versus Nb (acceptor) dye concentration.

**Fig. 6:** \( I_D / I_{DA} \) versus acceptor concentration for the samples of silica Xerogel doped with R110-Nb dye mixture.

The half quenching concentration \([A]^{1/2}\), which is the concentration of the acceptor required to decrease the fluorescence of the donor by one half, can be calculated from this equation (S Yang, et al.,2002, Marina T. Laranjo, et al.,2007):

\[
K_{ET} = \frac{1}{\tau_D[A]^{1/2}} \quad (2)
\]

The fundamental quantity in Forster's theory of resonance energy transfer is \( R_0 \), the critical transfer distance. Forster showed that \( R_0 \) could be calculated from the following equations (T.H. Nhung, et al,2004):

\[
R_0 = \frac{7.35}{\sqrt{[A]^{1/2}}} \quad (3)
\]

It can be also determined the efficiency of energy transfer \( T \) as the following equation: (T.H. Nhung, et al,2004):

\[
T = \frac{I_D}{I_{DA}} \quad (4)
\]

Table (1) involves the experimental results of the spectroscopic parameters which are related to the energy transfer process between two dyes in sol-gel host.

The calculated values of \( K_{ET} \) was found to be in the order of \( 10^{12} \) liter/mol.s, and this indicates that non-radiation resonance energy transfer was the dominant mechanism of energy transfer process for (R110-Nb) dye mixture in silica matrices. Also, the value of \([A]^{1/2}\) increases with increasing the acceptor concentration. This behaviour ascribed to increase the acceptor molecular density that leads to reduce the fluorescence of the donor molecules. On the other side, the critical distance \( R_0 \) decreases with increasing the acceptor concentration and this corresponding with the behavior of the half concentration quenching. Since the range values of \( R_0 \) more than 150 \( \AA \) represent the lower distance required for a radiation energy transfer and less than 6 \( \AA \) for collisional energy transfer(B. B. Raju,1994).Therefore, non-radiative energy transfer may be the dominate mechanism for R110-Nb mixture in silica xerogel matrices according to the range 6 \( \AA < R_0 < 150 \AA \). It can be also observed, from the results listed in table (1), that the energy transfer efficiency increases with the acceptor concentration for each series of donor concentration. The enhancement in efficiency may be due to increase the acceptor concentration and this can be explained as follows;
the donor molecules (R110), at a certain concentration may increase the separation distance between acceptor molecules and thus reducing the acceptor molecules interaction. Therefore, the fluorescence emission of Nb dye will be enhanced and the energy transfer efficiency will increase with increasing the acceptor concentration even at high concentration levels.

Table 1: Some of energy transfer parameters of (R110-Nb) dye mixture doped in silica xerogels at two series of donor concentration and different acceptor concentration.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Donor (R110) concentration</th>
<th>Acceptor (Nb) concentration</th>
<th>$K \times 10^{12}$ liter/mol</th>
<th>$([A])/2\ M$</th>
<th>$R_0 (\AA^0)$</th>
<th>$T%$</th>
</tr>
</thead>
<tbody>
<tr>
<td>RN1</td>
<td>$1 \times 10^{-4}$ M</td>
<td>0.5</td>
<td>1.9142</td>
<td>0.000124</td>
<td>147.24</td>
<td>28</td>
</tr>
<tr>
<td>RN2</td>
<td>$2 \times 10^{-4}$ M</td>
<td>2</td>
<td>0.236</td>
<td>0.0001008</td>
<td>73.28</td>
<td>42</td>
</tr>
<tr>
<td>RN3</td>
<td>$3 \times 10^{-4}$ M</td>
<td>3</td>
<td>0.1894</td>
<td>0.001256</td>
<td>68.10</td>
<td>46</td>
</tr>
<tr>
<td>RN4</td>
<td>$4 \times 10^{-4}$ M</td>
<td>4</td>
<td>0.1666</td>
<td>0.001428</td>
<td>65.26</td>
<td>53</td>
</tr>
<tr>
<td>RN5</td>
<td>$5 \times 10^{-4}$ M</td>
<td>5</td>
<td>0.14920</td>
<td>0.000159</td>
<td>135.55</td>
<td>23</td>
</tr>
<tr>
<td>RN6</td>
<td>$1 \times 10^{-5}$ M</td>
<td>1</td>
<td>0.7687</td>
<td>0.000309</td>
<td>108.63</td>
<td>24</td>
</tr>
<tr>
<td>RN7</td>
<td>$2 \times 10^{-5}$ M</td>
<td>1.5</td>
<td>0.5098</td>
<td>0.000530</td>
<td>90.82</td>
<td>25</td>
</tr>
<tr>
<td>RN8</td>
<td>$3 \times 10^{-5}$ M</td>
<td>2</td>
<td>0.2618</td>
<td>0.000909</td>
<td>75.87</td>
<td>28</td>
</tr>
<tr>
<td>RN9</td>
<td>$4 \times 10^{-5}$ M</td>
<td>3</td>
<td>0.1937</td>
<td>0.001228</td>
<td>68.62</td>
<td>32</td>
</tr>
<tr>
<td>RN10</td>
<td>$5 \times 10^{-6}$ M</td>
<td>4</td>
<td>0.1551</td>
<td>0.001534</td>
<td>63.72</td>
<td>35</td>
</tr>
<tr>
<td>RN11</td>
<td>$6 \times 10^{-6}$ M</td>
<td>5</td>
<td>0.1353</td>
<td>0.001758</td>
<td>60.88</td>
<td>39</td>
</tr>
</tbody>
</table>

Conclusion:

Laser dyes R110-Nb dye mixture was successfully incorporated into inorganic host (silica Xerogel matrix). Two concentrations of R110 dye, which are $1 \times 10^{-4}$ and $2 \times 10^{-4}$ M, were found to be optimum concentrations in which energy transfer quenching process was reduced and thus the fluorescence intensity increased i.e. decreased bandwidth at FWHM. Also, the increasing in energy transfer efficiency gives an indication that the aggregation effect of acceptor molecules and subsequently concentration quenching were reduced. The energy transfer in our recipe was found to be resonance energy transfer because of the large values of constant $K_{ET}$.

RERFRANCES


