Development of temporal spectroscopic properties for Xerogel matrices doped with Rhodamine 6G dye

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Abstract: The solid host of a laser dye modifies its spectroscopic properties with respect to its liquid host. During the Sol-Gel process the dye molecules suffer from changing their environment. Two parameters affect this matter, the change in the concentration due to the evaporation of the solvent (drying) and the caging of dye molecules inside the pores or attachment to the silica network. Rhodamine 6G absorption and fluorescence spectra with different concentrations, during Sol-Gel time processing, have been studied. Both, absorption and fluorescence spectra of the dye in the solid host, for different concentrations, show a blue-shift relative to its liquid phase.
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1 Introduction

For a normal coloured dye, it is the absorption of the dye that is of interest, while for a laser dye the fluorescence spectrum is of more importance. Some of the most important laser dyes are the substituted tricyclic ring structures, such as Rhodamine 6G (from Xanthene's family), which has conjugated bonds (successive single and double bonds) associated with the organic dye's typical absorbance in the visible region of the electromagnetic spectrum [1]. Solid-state dye lasers, consisting of an organic dye dissolved in a solid matrix, have been the subject of much interest since their demonstration nearly four decades ago [2].

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The emitted energy will be less than the absorbed energy if the molecule relaxes non-radiatively to a long-lived excited state. As a result, the wavelength of the fluorescence peak will be longer than the wavelength of maximum absorption [3]. The excited molecules may lose energy in the form of heat through a non-radiative process to reach a lower vibrational level of the excited state. A non-radiative loss of energy that occurs following the absorption and subsequent fluorescence processes causes the emitted photon to be of a lower frequency than that of the absorbed photon and produces a red shift between the absorption and fluorescence spectra. Solid hosts containing laser dyes hold much promise as the gain media for visible, tunable solid-state lasers [4]. The lack of photostability in a fluorescent dye represents a permanent decline in the fluorescence output upon optical pumping, typically reflecting the chemical modification of the molecule [5].

An improvement in photostability can be achieved by caging or isolating the dye molecule, which reduces the interactions with other species (e.g. oxygen or other dye molecules, etc) [5–8]. Caging a laser dye within a silica matrix has shown improved photostability with respect to solvent hosts [5, 9, 10]. Silylated dyes are organic molecules that have been chemically altered to provide alkoxysilane functionality [11]. This allows the dye molecule to participate in the hydrolysis and condensation reactions during Sol-Gel processing of the host and allows the active molecule to bond covalently to the host matrix. Covalent dye attachment will inherently prevent the dye from having translational motion within the pores of the silica matrix. This should decrease the number of dynamic interactions producing photodegradation. Also, covalently bonding the dye as opposed to simple dissolution of the dye within the matrix increases the probability that the dye will be completely caged by the silica matrix, reducing the extent to which impurities or nonbonded dyes will migrate to and interact with the caged molecules. The increased probability of caging stems from the fact that the dye already has a portion of itself protected by the alkoxysilane group, and the silane is very likely to interact with the silica matrix to create a more complete cage [11]. The application of pressure on the optical properties of Sol-Gel products were studied by Costa et. al [12].

2 Experimental method

2.1 Chemical material

The following materials were used: tetraethylorthosilicate (TEOS) (purity 95 %) was supplied by Ibn Sina state Co. and then redistilled twice in our laboratory; Ethanol (purity 99.9 %) was supplied by Gainland Chemical Company, U.K.; doubly deionized water supplied by Al Mansor Co.; Rhodamine 6G dye laser, molecular weight 591.06 gm/M, was supplied by Lambda Physik, Lc (6400).

2.2 Sample preparation

Firstly the dye solution was prepared by dissolving Rhodamine 6G in Ethanol at a concentration of 5×10^{-3}M. Then 4.5 ml of deionized H_2O (acidified to 0.15 M HCl, pH =1) was added to the dye solution at H_2O : dye solution molar ratios of 1.5:1. The product solution was then added to 2.8-ml Ethanol. The solutions were refluxed for one hour and the final solution denoted as sol (A). Separately, 1-ml of TEOS, and 2-ml of Ethanol were mixed in a glass beaker at a TEOS: H_2O molar ratio of 1:4.5. Because water and alkoxides are immiscible, a mutual solvent such as ethanol is, therefore, utilized. The solution was then mixed for a few minutes allowing the TEOS to prehydrolyze. The product solution was denoted as sol (B). Sol (A) was then mixed with sol (B) for a few minutes and then poured into a beaker. After aging for 72 h, the final solutions were poured in ten glass tubes of 0.3 mm in diameter and 80 mm in length. Each tube contained 0.8 ml of the final solution. These tubes were left to dry in an oven at 40 °C. All the above steps were repeated with several solutions (1×10^{-3}, 5×10^{-4}, 1×10^{-4} and 5×10^{-5}M).

2.3 Measuring instruments

The fluorescence layout applied in this study is shown in Fig. 1. Laser-induced fluorescence of the dyes was recorded through a spectrophotometer using a diode-pumped solid state green laser of wavelength 531.5nm, continuous wave (CW) with an output power of 10 mW with a line width < 0.1 nm and a 2mm beam diameter. This laser has a suitable wavelength that lies within the peak absorption band of the dye used in this work.
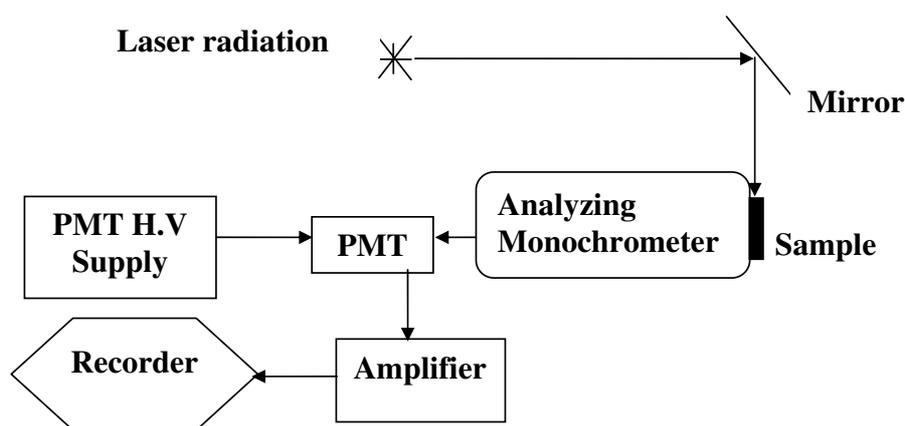

Fig. 1 Schematic diagram of the fluorescence spectrum measuring equipments.

The dye emission was detected with a Jarrell ash monochrometer model 82-000. This unit is an Ebert scanning spectrometer, 0.5 meter focal length, with eight speed electric drives and plane reflection grating of 1180 groove / mm. The detection unit is a photomultiplier PMT (type S666 Hamamatsu) which was connected to an X-Y/t recorder (Siemens) to record the output signal via an amplifier.

Centra-5 UV-VIS spectrometer supplied by GBC Scientific Equipment Pty Ltd. (Australia) was used in this experiment for absorption measurements.

3 Results and discussion

The interaction with the adjacent molecule (or molecules) may perturb the energy levels of the excited aromatic hydrocarbon molecule, and modify its photophysical properties and behavior. This phenomenon occurs in concentrated or aggregated systems. In this work the dye solutions were prepared at fixed concentrations, and then added to the silica solution to prepare Xerogels by the Sol-Gel technique. The final solution, before drying, had a lower concentration than the initial dye solution. At a low concentration solution the dye molecules become more relaxed with relatively large intermolecular distances. These conditions will, therefore, reduce perturbation processes affecting the dye molecules that modify their energy levels. Hence, changing the concentration and other environmental conditions, such as solvent-solute interaction, will change the perturbation effects causing a corresponding absorption (or emission) spectral shift. During the drying time, the concentration increases, resulting in a corresponding increase of the absorption spectral shift with the increase in drying times.
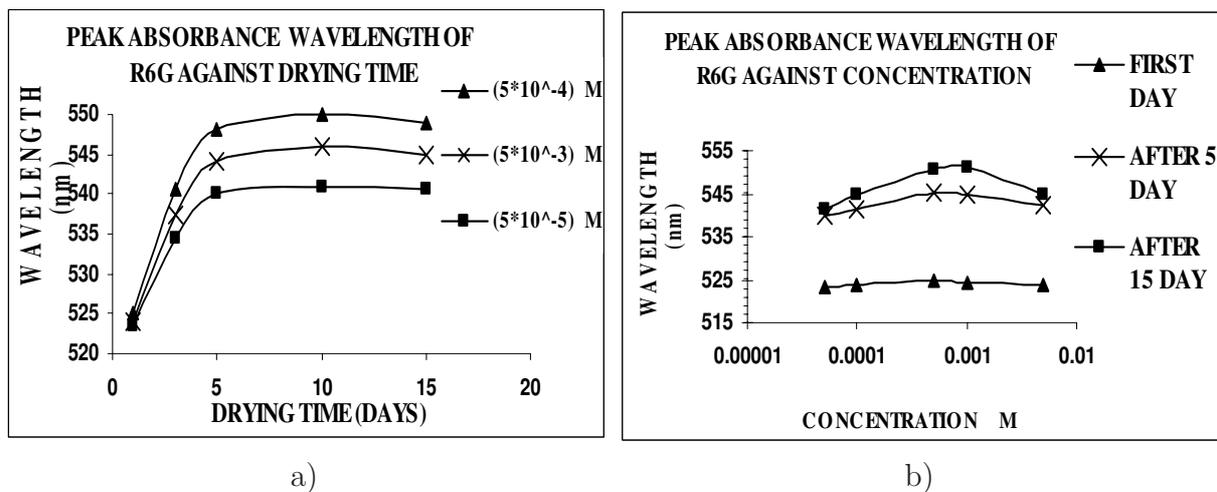

Fig. 2 The peak absorbance wavelength in Sol-Gel solution of Rhodamine 6G (a) against drying time with various concentrations, and (b) against concentration with various drying times.

Fig. 2a shows the variation of the peak absorption wavelength λ_{Amax} with drying time for given initial dye concentrations. These curves show that the (red) shift of the peak increases as the drying time increases. However, most of the shift occurs in the first 5 days. Fig. 2b shows the dependence of λ_{Amax} on the concentration [M] for a given drying time. These curves show that the shift ($\Delta\lambda$) increases as the concentration increases, reaching a maximum value at about (1×10^{-3} M) and then decreases. This may be attributed to temporal development of the host environment. At the lower concentration (5×10^{-5} M), the change in the concentration during the drying process until the final

drying time, doesn't interrupt the bimolecular processes dramatically. Similarly, at the higher concentrations the influence was clear.
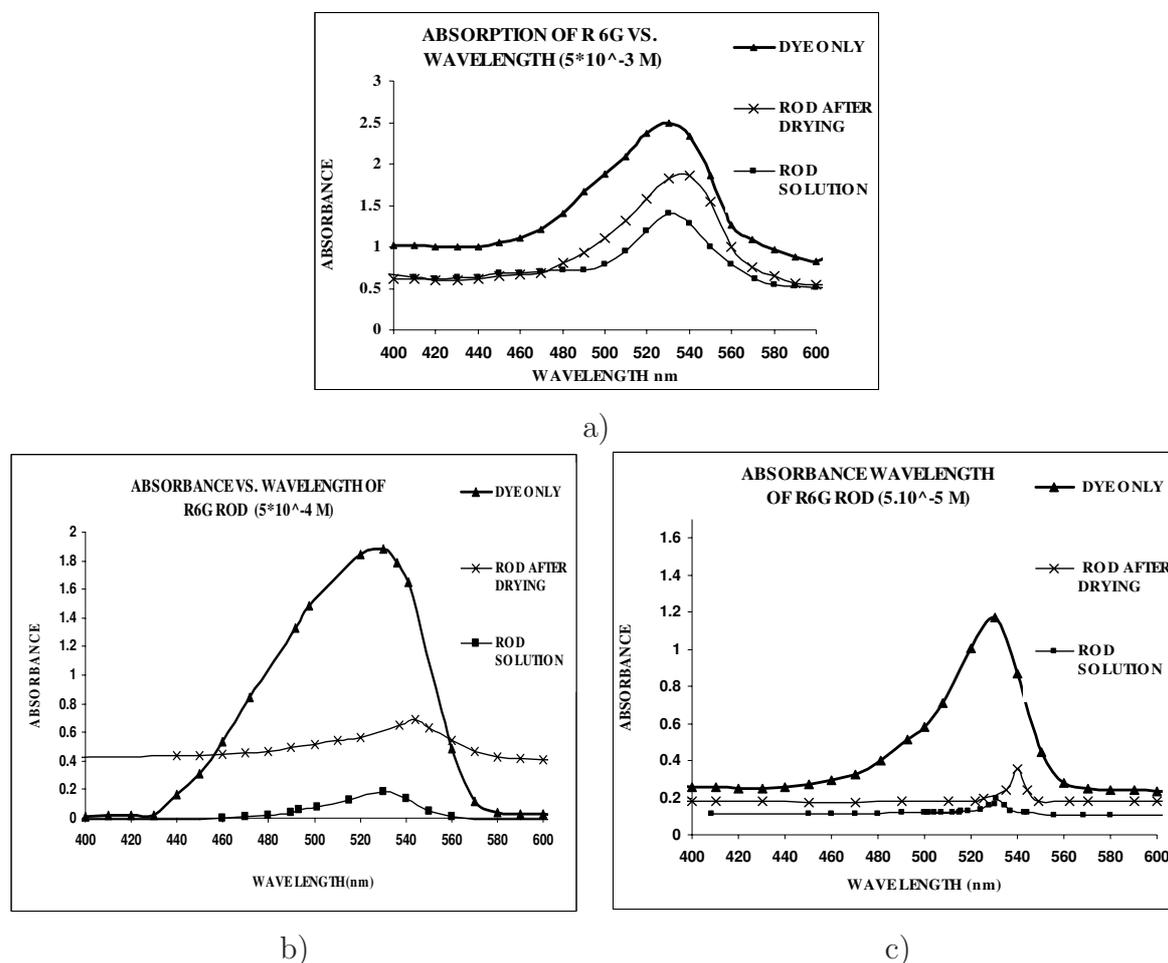

a)

b)

c)

Fig. 3 The absorbance versus wavelength of R 6G dye and rod solutions, for initial concentrations, (a) 5×10^{-3} M, (b) 5×10^{-4} M, (c) 5×10^{-5} M.

Figs. 3a, b, c show the absorption spectra (absorbance vs. wavelength) of Rhodamine 6G: dye solution in ethanol (D-S), Sol-Gel rod, in Sol-Gel solution (S-G-R), and solid solution rod after drying (S-S-R), for fixed initial concentrations (5×10^{-5} to 5×10^{-3}M).

These figures show that the peak wavelength λ_{Amax} is shifted towards longer wavelengths going from D-S→ S-G-R → S-S-R.

From the Beer-Lambert law [3], we have:

$$I = I_o 10^{-\epsilon[M]d} \tag{1}$$

where I is the intensity of the transmitted light beam, I_o is the intensity of the incident beam, ϵ is the decadic molar extinction coefficient, [M] is the molar concentration and d is the sample thickness. According to Eq. (1) the absorbed intensity ($I_a = I_o - I$) of the light by the sample, and also the absorbance A ($= \log I_o /I$) are expected to increase with an increase in the concentration (in the absence of any bimolecular effects).
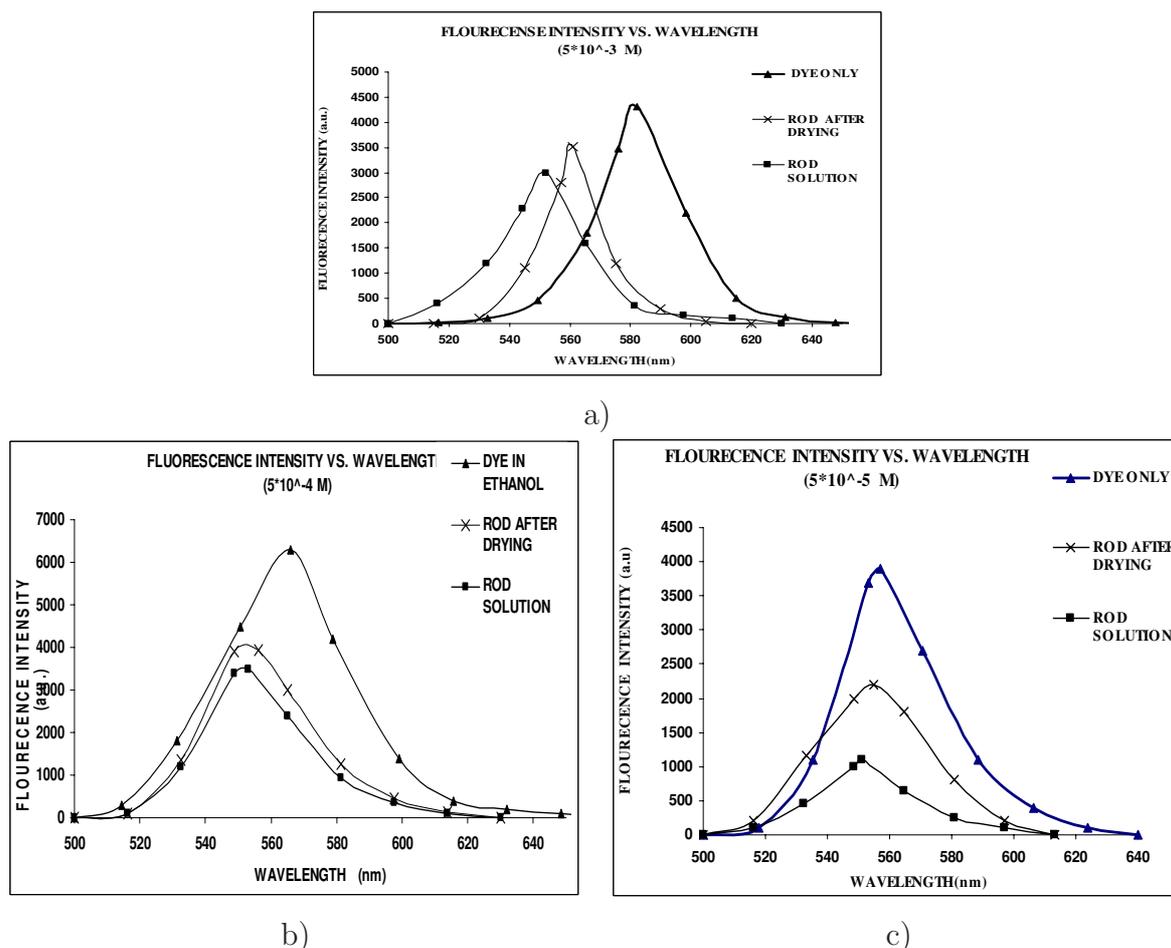
a)

b)

c)

Fig. 4 The fluorescence intensity versus wavelength of R 6G dye and rod solutions, for initial concentrations, (a) 5×10^{-3} M, (b) 5×10^{-4} M, (c) 5×10^{-5} M.

One can see from Figs. 3a, b, and c that the absorbance decreases going from D-S $\rightarrow$ S-S-R $\rightarrow$ S-G-R. This means that the actual concentration decreases in the same direction, and this is in agreement with the previously mentioned conclusion about the change of concentration of these solvents. When a solid host is used the dye molecules are caged inside the pores of the host. Also, some of the dye molecules are incorporated within the Xerogel network. This leads to more isolation of the dye molecules and hence less perturbation and gives lower red-shifts than one would expect.

In Figs. 4a, b and c the fluorescence spectra are illustrated for Rhodamine 6G: dye solution, rod solution and dry rod solution, for fixed initial concentrations (5×10^{-5} to 5×10^{-3}M). It is clear from Fig. 4a of the highest concentration (5×10^{-3} M) that the peak wavelength of the fluorescence spectra is shifted towards shorter wavelengths (blue-shift) going from D-S $\rightarrow$ S-S-R $\rightarrow$ S-G-R, i.e. in the direction of the decreasing actual concentration. Other lower concentrations show less distinctive shifting.

It can also be seen from Figs. 4a, b, and c that the fluorescence intensity decreases going from D-S $\rightarrow$ S-S-R $\rightarrow$ S-G-R. This can be attributed to a decrease in the actual concentration and hence a corresponding decrease of the absorbed intensity, I_a, (as mentioned

earlier) in the same direction. This will cause a corresponding decrease of the fluorescence intensity, I_F, which is proportional to I_a ($I_{F=}q_F\ I_a$, where q_F is the fluorescence quantum efficiency).

Fig. 5 demonstrates the variation of the peak fluorescence wavelength, λ_{Fmax}, with the drying time (τ_d), for Rhodamine 6G of 5×10^{-3} M concentration. The figure shows that the shift towards longer wavelengths increases monotonically with an increase in drying time. This may be attributed mainly to the continuous increase in the concentration as τ_d increases.

Several bimolecular processes in liquid state commonly compete with the fluorescence emission, such as collisional impurity quenching, concentration quenching and self-absorption. The first two processes are diffusion-controlled and their second order rate parameters increase with concentration (of quencher or the fluorescent dye) and decrease with viscosity of the solution [3]. As the Sol-Gel process goes on, the first two quenching processes are reduced. On the other hand an increase in the concentration during the drying process will increase the fluorescence emission and self-absorption. Also, the increase in concentration may cause dimer and aggregates formation. The fluorescence intensity increases with increasing the concentration, reaching a maximum value at an initial concentration of 5×10^{-4} M, then decreases as can be deduced from figures (4a, b, c). Hence, besides the perturbations mentioned earlier, these bimolecular processes may modify the fluorescence emission and cause the observed spectral shift.
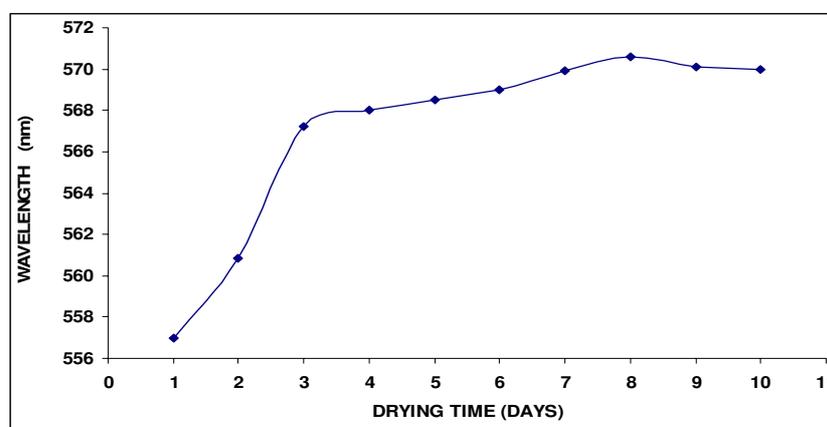

Fig. 5 Peak fluorescence wavelength against drying time for R6G dye of concentration 5×10^{-3} M.

4   Conclusions

An increase in the concentration during the drying of laser dye solutions in the Sol-Gel processes must be taken into account when one chooses the starting concentration of the laser dye. Solid Xerogel matrices doped with the Rhodamine dye increase the ability of preparation of high-concentration samples and minimize the interactions with the adjacent dye molecules.

Acknowledgment

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