Influence of the medium on the fluorescence of copper vapor laser pumped rhodamine 6G dye: dynamic case

Nidhi Sharma,[a] **N. Singh,**[b] **H. S. Vora,**[b] and **Sneh Lata Goyal**[a]

[a]*Department of Applied Physics, Guru Jambheshwar University, Hisar−125001, Haryana, India*
[b]*Raja Ramanna Centre for Advanced Technology, Indore–452013, M P, India*
nidhi_sharma2004@rediffmail.com

Abstract: In this paper, observed fluorescence characteristics of rhodamine 6G in ethylene glycol solvent, under copper vapor laser (CVL) excitation, are presented. The study is conducted in dynamic conditions as a function of the Reynolds numbers of the fluid flow.

The introduction, experimental details, and static results of this study are given in [1]. In this second part, the dye solution was flowed through the dye cell. A sufficient velocity of the dye solution is required to minimize the thermal effects encountered by high repetition rate of copper vapor laser pump beam. An important parameter characterizing a fluid flow dynamics is the Reynolds number (R), which is given by [2]

$$R = (u_{av}D_H)/v \tag{1}$$

where u_{av} is the average flow velocity, D_H is the hydraulic diameter and v is the kinematic viscosity of the fluid. The hydraulic diameter is given by

$$D_H = 2ah/(a+h) \tag{2}$$

where a, h are the width and the length of the dye cell respectively. The hydraulic diameter is also known as the characteristics length, L. This quantity characterizes the dimension of the flow as a whole, and arises from the boundary conditions of the fluid dynamics problem. For the dye cell used in our experiment, the estimated R in the pump region are in the $90.6 < R < 1630.8$ range. Since $R < 2000$, the flow in all these cases is laminar [3, 4].

The fluorescence spectra have been observed at adjusted flow rates from 1 to 18 liters per minute (l/min.). Fig.1 shows the typical fluorescence spectrum pattern at different R. The fluorescence spectrum labeled a, b, c, d and e are at 0 ($R = 0.0$), 1 ($R = 90.6$), 3 ($R = 271.8$), 8 ($R = 724.8$), and 18 ($R = 1630.8$) l/min., respectively. Both the fluorescence width and peak wavelength changes with flow of the dye solution. Fig.2 shows the variation of fluorescence bandwidth as function of R. The FWHM of the fluorescence spectra initially shows a sharp
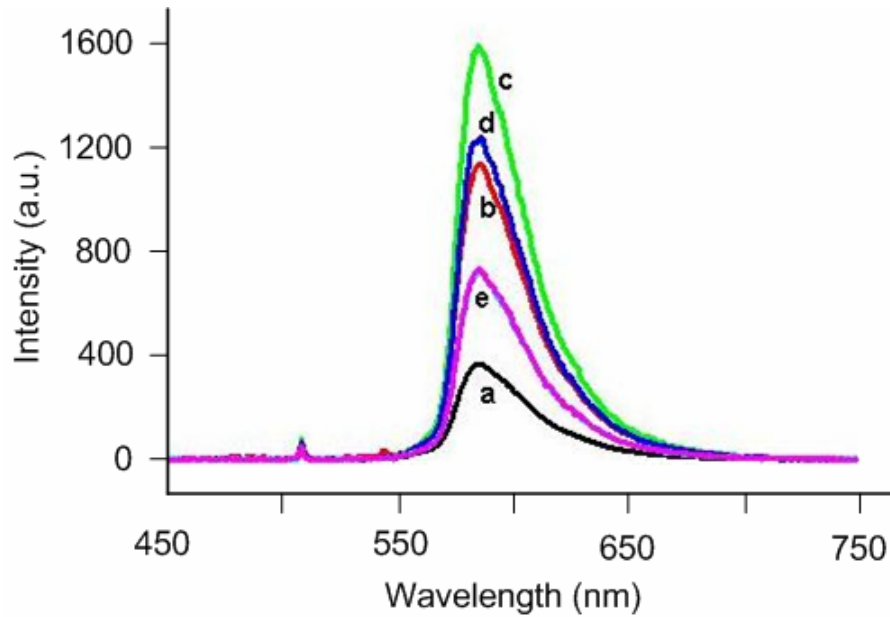
Fig. 1. The typical fluorescence spectrum pattern at different Reynolds numbers. Here a = 0, b = 1, c = 3, d = 8, and a =18 l/min.

decreases with increasing R. However, after $R = 996.6$, its change is small. The fluorescence width is always smaller than that in the static case. Thus, the flow of the dye solution significantly affects the emission width of rhodamine 6G dye. Fig.3 shows the variation of peak wavelength as function of R. The peak wavelength changes significantly with increasing R. It decreases sharply from the stationary case to $R = 150$, shows a V-shape in the range of $200 < R < 400$, a sharp increase up to 700, and decreases slowly after that. Fig.4 shows the variation of peak intensity with R. When the solution is stationary, the peak intensity is small. As the flow increases, the intensity increased to a maximum value and then decreases. However, after $R = 825.4$ the intensity become almost constant up to $R = 1630.8$.
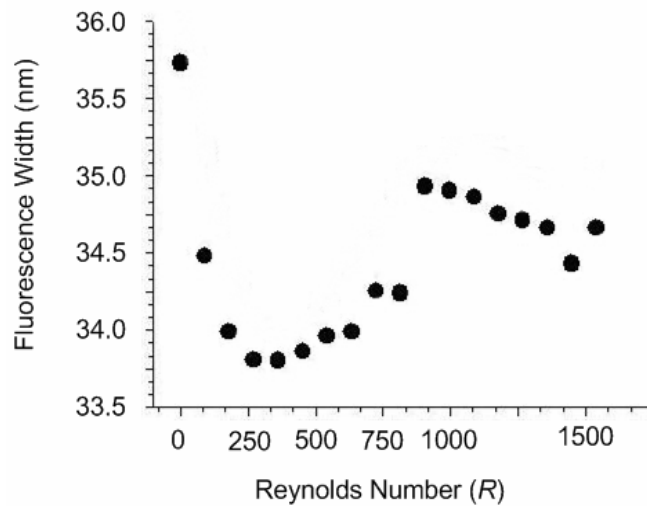

Fig. 2. The variation of fluorescence bandwidth as a function of the Reynolds number.
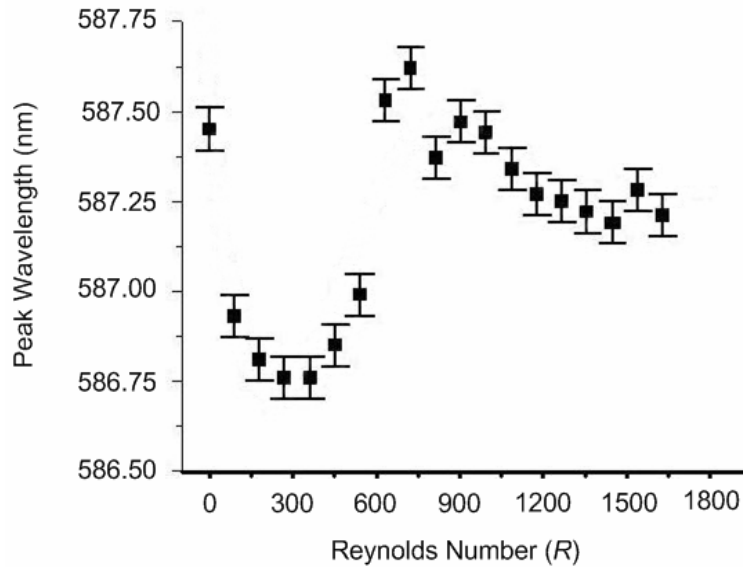
Fig. 3. The variation of emission peak wavelength as a function of the Reynolds number.

Ahmed *et al.* [5] have observed the effect of multiple light scattering and self absorption on the fluorescence and excitation spectra of dyes in random media created by adding TiO_2 particles the solution. They observed that the presence of random scattering in the luminescent bodies affects the spectrum of the fluorescent radiation observed at the surface of these bodies. The primary effects observed were red shifts in the emission spectra with respect to the intrinsic fluorescence emission. However, in our case, there were no external agencies added to the solution and only physical conditions of the medium were altered.

As the temperature of the medium increases, the number of molecules available in the higher rotational-vibrational levels of the ground state increases. The thermal excitations also increase
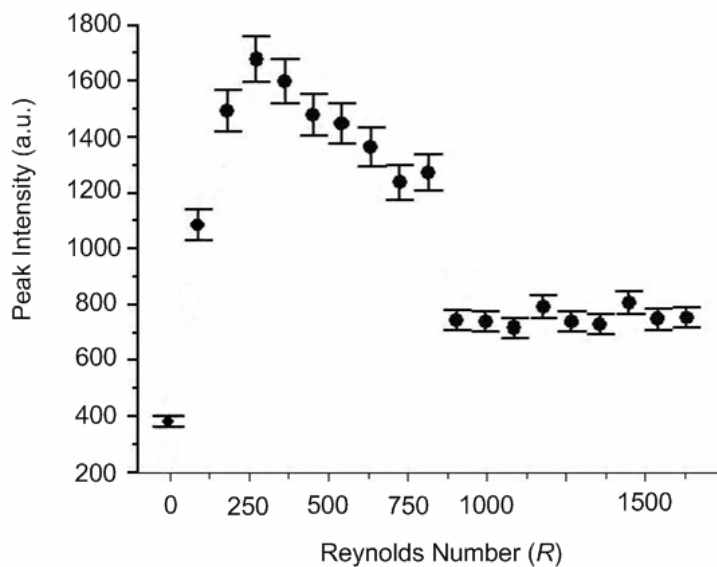

Fig. 4. The variation of intensity, at the peak wavelength, with Reynolds Number.

the rate of nonradiative transition routed in different ways [6-8]. This results in termination of the transition at higher sub-levels of ground state and hence changes the emission wavelength and its FWHM. The nonradiative transitions enhance the heating effect in the medium and reduce the quantum yields. This is reflected in the decrease observed in the peak intensity (as shown in Fig. 4). Absorption of the pump light in the dye cell causes a thermal heating resulting in fluctuations in density and hence perturbations in the refractive index of the solution, leading to refractive index gradients. This leads to a scattering of the light passing through it, which increases further, with temperature of the dye solution. Therefore, increased scattering and non-radiative processes are responsible for the decrease in intensity of the peak wavelength with temperature in a stationary solution.

   Since the pump beam is absorbed in the dye medium following the exponential absorption law, the maximum absorption predominantly lies close to the pump beam entrance window. This leads to a refractive index gradient in the dye solution. When the dye solution is flowed through the dye cell, the temperature dependent refractive index gradient is minimized, which in turn reduces the degree of scattering and non-radiative transitions. By virtue of this, the peak wavelength and fluorescence FWHM decreases and continues toward a lower value where flow velocity is sufficiently enough to remove the maximum amount of heat from the pump region. At the same time, the intensity of the observed fluorescence increases and continues to towards a maximum value.

   As the Reynolds number, $R = (uL)/v$ (given here in an equivalent form) is further increased, e.g. by increasing the velocity of the flow, the motion becomes unstable even within laminar region of flow. When the velocity fluctuations u_l occurs in a region of size l of the basic laminar flow the amount of energy per unit mass per unit time which goes over from the initial flow to the fluctuational motion [9] is

$$k = u_l^3/l \tag{3}$$

 If (u_l/l) is the local velocity gradient of fluctuation, then the energy dissipated as heat per unit mass of the fluid per unit time is of the order of [9]

$$\varepsilon = (vu_l^2)/l^2 \tag{4}$$

The ratio

$$k/\varepsilon = (u_l^3/l)/(vu_l^2/l^2) = lu_l/v = R_l \tag{5}$$

is the "inner" Reynolds number corresponding to the fluctuations of size l. As the number R is increased, the laminar motion loses stability and velocity fluctuations u_l occur with geometrical dimensions l. As R is increased further, the "first order" velocity fluctuations that arise lose stability themselves and can transfer energy to new "second order" fluctuations [9]. As the number R is increased further, the "second order" fluctuations become unstable, and so on. In this way, the energy received from larger perturbations is transfered to smaller and smaller perturbations [9]. In the smallest velocity perturbations with sizes l_0, this is converted into heat [9]. The rate of dissipation of energy into heat is determined by the local velocity gradients in

these smallest perturbations [9] of the order

$$\varepsilon = (v u_0^2)/l_0^2 \tag{6}$$

The quantity l_0 can be expressed in terms of dimension of the largest eddies L, which are comparable with the dimension of the flow [9]

$$l_0 = L R^{-3/4} \tag{7}$$

and

$$u_0 = u_L R^{-1/4} \tag{8}$$

Thus, the larger R of the flow as a whole (so called bulk flow), the smaller the size of the velocity inhomogeneities that can arises.

It is known that large size characteristics length fluctuations provide small deflection to the incident radiation and small size gives large scattering. As the velocity gets higher and higher, both solute and solvent have higher kinetic energy, which perturbs the state and rate of the non-radiative processes and the rotational–vibrational sublevels interactions. By virtue of this, the peak wavelength and its FWHM change. The local velocity gradients increase with an increase in the flow velocities across the pump region near the solid-liquid surface. This results in increased scattering of the emitted photons in the medium and hence a decrease in observed intensity outside the medium. The decreasing characteristics size of the chaotic and irregular flow motion is responsible for decreasing the peak intensity in the $271.8 < R < 906$ range. After this, the number length scale is so small that it cannot produce further changes.

In conclusion, the fluorescence width, peak wavelength and peak emission intensity of rhodamine 6G dye changes with the physical conditions associated with the active dye molecules. The temperature dependent refractive index of the medium, due to absorption of the pump beam and flow induced the refractive index non-uniformities due to the local velocity gradients created within the boundary layers affects the spectrum of the fluorescent organic dyes. The inertial and viscous forces present within a luminescent medium affect the luminescence observed outside the medium. The characteristics length developed in the flow also play a dominant role on the light passing through it, apart from the other factors.

References

1. N. Sharma, N. Singh, H. S. Vora, and S. L. Goyal, *Opt. J.* **1**, 13 (2007).
2. M. Amit, G. Bialolenker, D. Levron and Z. Burshtein, *J. Appl. Phys.* **63**, 1293 (1988).
3. G. T. Davies, *Turbulent Phenomena* (Academic, New York, 1972) Chapter 1.
4. J. P. Holman, *Heat Transfer* (McGraw Hill, London, 1976)
5. S. A. Ahmed, Z–W. Zang, K. M. Yoo, M. A. Ali, and R. R. Alfano, *Appl. Opt.* **33**, 2746 (1994).
6. Y. Maruyama, M. Kato and T. Arisawa, *Opt. Eng.* **35**, 1084 (1996).
7. P. R. Hammond, *J. Chem. Phys.* **70**, 3884 (1979).
8. I. L. Gandel'man, M. V. Melishchuk, and E. A Tikhonov, *Sov. J. Quantum Electron.* **13**, 817 (1983).
9. V. I. Tatarski, *Wave Propagation in a Turbulent Medium* (McGraw Hill, New York, 1961).