

Effect of silver nano particles on the fluorescence quantum yield of Rhodamine 6G determined using dual beam thermal lens method

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Abstract

Nano structured noble metals have very important applications in diverse fields as photovoltaics, catalysis, electronic and magnetic devices, etc. Here, we report the application of dual beam thermal lens technique for the determination of the effect of silver sol on the absolute fluorescence quantum yield (FQY) of the laser dye rhodamine 6G. A 532 nm radiation from a diode pumped solid state laser was used as the excitation source. It has been observed that the presence of silver sol decreases the fluorescence quantum efficiency. This is expected to have a very important consequence in enhancing Raman scattering which is an important spectrochemical tool that provides information on molecular structures. We have also observed that the presence of silver sol can enhance the thermal lens signal which makes the detection of the signal easier at any concentration.

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1. Introduction

Fluorescence quantum yield (FQY) is defined as the fraction of the molecules that emit a photon after direct excitation by a light source [1]. Both from theoretical and practical point of view, fluorescence quantum yield values are important. For example, they provide information on radiationless processes in molecules, and, in the assignment of electronic transitions. It is also of use in assessing the potential of the fluorimetric determination of materials, determining their purity and for judging the suitability of materials as wavelength shifters and laser media. There exist a number of methods for the determination of FQY of a substance. Of these, the most popular one is the comparative method, by using a fluorescence standard. Such methods are based on the fact that if two substances 1 and 2 are studied using the same apparatus, and using the same incident light intensity, the integrated areas under their corrected fluorescence

spectra (S_1 and S_2) are simply related as

$$\frac{S_1}{S_2} = \frac{\phi_2 A_2}{\phi_1 A_1} \quad (1')$$

where ϕ values are quantum yields and A values are absorbances for a specific excitation wavelength. Though this is the most popular method for the determination of fluorescence quantum yield, it requires a series of suitable standard materials if it is to be used over a wide range of wavelengths. There are a number of requirements for a particular standard to be considered ideal. Though most of the criteria can be met by dilute solutions of appropriate compounds, some of the requirements are mutually exclusive.

The need of a fluorescence standard can be eliminated if we go for photothermal method like thermal lens technique. It is a highly sensitive method, which can be used to measure the optical absorption and thermal characteristics of a sample. The advantage of photothermal method is that it can be used to investigate the optical properties of materials that are not possible with traditional spectrophotometry. The thermal and fluorescence spectroscopy which are used here to measure the absolute fluorescence quantum yield are in fact complementary: the former measures the

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photon energy, which is converted into heat, while fluorescence spectroscopy observes re-emitted photons. The thermal fluctuations produced by non-radiative relaxation may be probed optically, since the resulting density changes also produce a change in the refractive index. The transient refractive index forms an effective lens, which diverges the light as it passes through the sample. This phenomenon is called thermal lensing.

FQY is a measure of the rate of non-radiative transitions that compete with the emission of light. Measurements based on photothermal methods are capable of giving absolute values of FQY with high accuracy and reproducibility. The absolute values of FQY of laser dyes are necessary for the calculation of thresholds of laser action. The present paper describes the effect of nano particles on the FQY of a laser dye Rh6G.

Nano particles have a variety of unique spectroscopic, electronic and chemical properties due to their small size and high surface to volume ratios. The coherent oscillation of the free electrons in the conduction band exhibits surface plasmon oscillation and the resulting absorption is called surface plasmon absorption. In the case of noble metal nano particles the surface plasmon absorption band appears in the visible region. Because of this the optical properties of noble metal nano particles have received considerable attention. They are, for example, expected to play very important role in enhancing the Raman scattering and thus to provide important contribution towards sensing and bio-medical applications. It also helps in determining the molecular structure of specific analyte molecules. However, it is inherently a weak effect, often masked by fluorescence. Raman scattering can be enhanced either by resonance or by surface enhancement. In resonance enhancement the laser frequency is tuned to an energy transition of the analyte, in surface enhancement the analyte is adsorbed onto a suitable metal surface. It should also be possible to enhance it, if fluores-

cence could be reduced by some method. The objective of our experiment is to find out the role played by silver sol in the fluorescence efficiency of Rhodamine 6G which is a xanthene dye, having very high quantum yield.

2. Experimental details

2.1. Experimental setup

The dual beam thermal lens setup used for the measurement of thermal lens signal is as shown in Fig. 1. It consists of a diode pumped solid state laser as the heating source and intensity stabilized He–Ne laser as the probe beam. These light beams are made collinear and made to pass through the sample solution by the use of a dichroic mirror and a convex lens. The thermal lens signal is detected by sampling the intensity at the center portion of the probe beam by coupling it to a monochromator–photomultiplier assembly through an optical fibre. The photomultiplier output is further processed using a digital lock-in amplifier (SR850 DSP).

For fluorescence studies the front surface emission is collected in the wavelength region 540–570 nm.

2.2. Preparation of silver sol

Silver sol has been prepared in the laboratory from aqueous solutions of AgNO_3 and NaBH_4 in appropriate concentrations in double distilled water. The steady-state absorption spectrum of sol shows a peak at 410 nm as shown in Fig. 2, which is in agreement with the reported value. The sample solution is prepared by an accurately weighed amount of Rhodamine 6G and dissolving it in double distilled water to obtain samples of various concentrations in the range from 10^{-3} to 10^{-6} M. The absorption spectrum (Fig. 3) was taken using a spectrophotometer (Jasco-V-570).

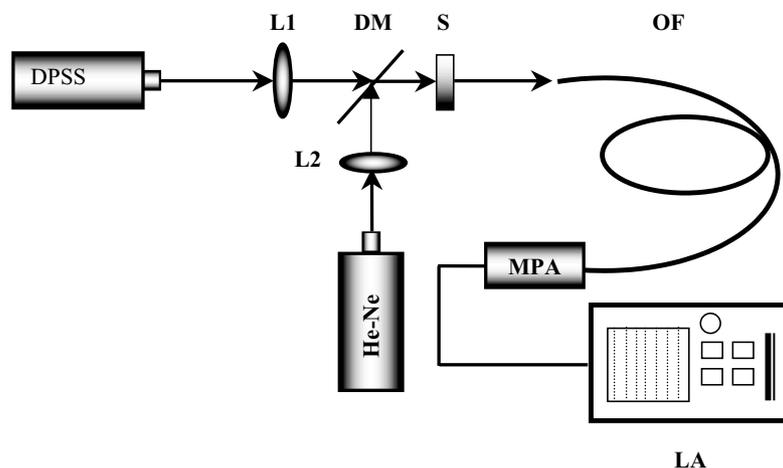


Fig. 1. Schematic diagram of the experimental setup. DPSS: diode pumped solid state laser; L1 and L2: lenses; DM: dichroic mirror; S: sample cell; OF: optical fibre; He–Ne: helium–neon laser; MPA: monochromator–PMT assembly; LA: lock-in amplifier.

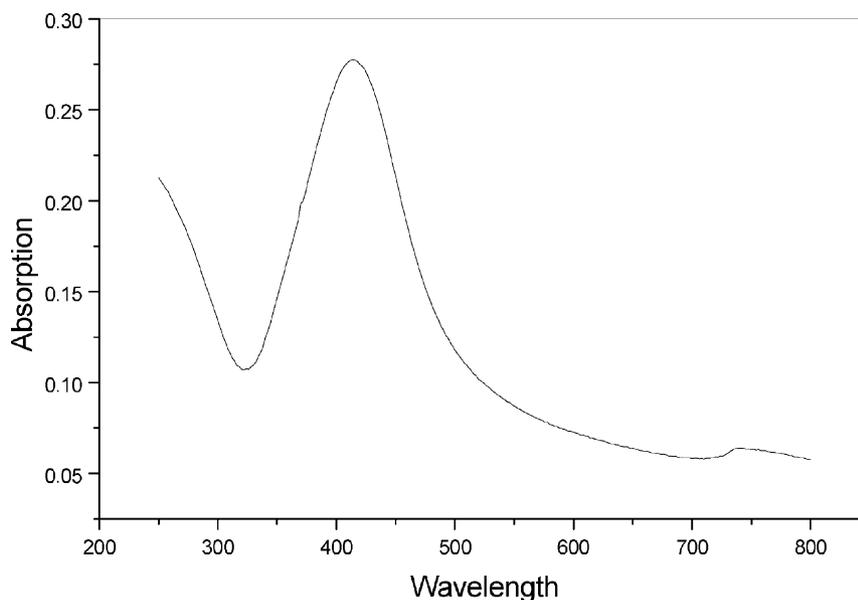


Fig. 2. Absorption spectrum of silver sol.

3. Results and discussion

3.1. Theory

Fluorescence is the emission of photons which results from the transition of the molecule from electronically excited singlet state to the ground state [2]. Such transitions are quantum mechanically allowed and have a typical emissive rate of 10^8 s^{-1} . Fluorescence quenching is the process, which decreases the fluorescence intensity of a given substance. This obviously increases the non-radiative transition and helps in finding out the fluorescence quantum yield values as described below.

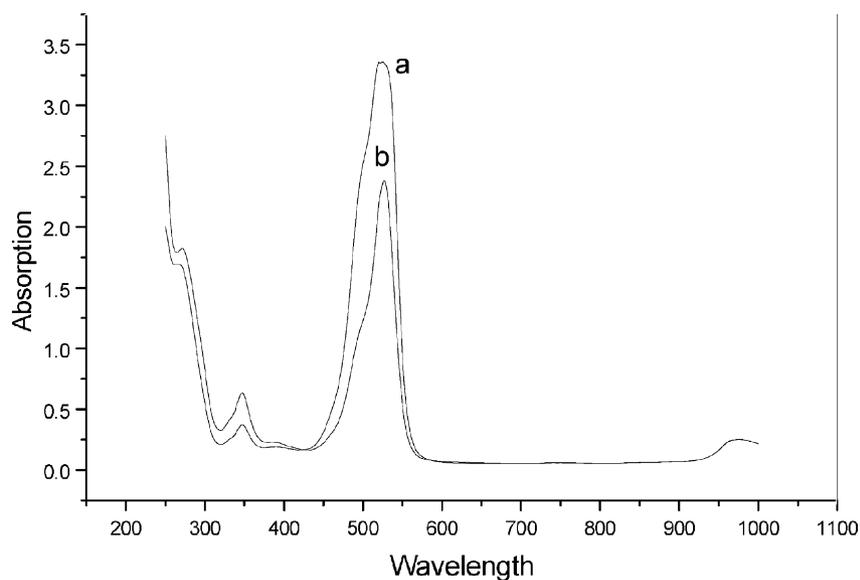
The method is based on the principle of energy conservation. If P_0 is the power of the incident excitation beam and P_t , the power of the transmitted beam, the absorbed power is the sum of the luminescence emission power P_f and the thermal power degraded to heat P_{th} , provided that no photochemical reaction is present.

Hence,

$$P_0 = P_{th} + P_f + P_t \quad (1)$$

so that the transmission ratio is:

$$T = \frac{P_t}{P_0} \quad (2)$$

Fig. 3. Absorption spectrum of the Rhodamine 6G at a concentration of $10^{-4} \text{ mol l}^{-1}$: (a) dye alone; (b) dye with silver sol.

Absorbance is given by:

$$A = 1 - T \quad (3)$$

Thus, the absorbed power is given by:

$$AP_0 = P_{th} + P_f \quad (4)$$

Then,

$$P_f = AP_0 - P_{th} \quad (5)$$

In the case of a completely fluorescence quenched sample, we can consider the entire excitation energy to be converted into non-radiative relaxation process and hence, the fluorescence quantum yield Q_f is given by

$$Q_f = \frac{P_f}{AP_0} \frac{\lambda_f}{\lambda} = \left(1 - \frac{P_{th}}{P_\alpha}\right) \frac{\lambda_f}{\lambda} \quad (6)$$

where

$$P_\alpha = AP_0 \quad (7)$$

and the ratio of the fluorescence wavelength λ_f to the excitation wavelength λ takes account of the Stokes shift. P_{th} is directly proportional to the TL signal η and P_α is proportional to TL signal η_α corresponding to the concentration at which the fluorescence intensity is quenched completely.

Thus, the quantum efficiency can be calculated by equation:

$$Q_f = \frac{\lambda_f}{\lambda} \left(1 - \frac{\eta}{\eta_\alpha}\right) \quad (8)$$

The thermal lens signal η has been measured using the standard technique as described elsewhere [6].

The dye R6G forms aggregates in aqueous solution, which results in reduction of fluorescence with increase in concentration. The concentration at which fluorescence is quenched completely is determined by measuring the fluorescence intensity in a wide range of concentrations.

3.2. The laser excited fluorescence

Fluorescence and thermal lensing studies were carried out for the laser dye Rhodamine 6G dissolved in double distilled water with and without the presence of silver sol, for a wide range of concentrations and also for various values of pump power. The excitation wavelength used was 532 nm. The absorption spectrum of silver sol shows a peak at 410 nm and its absorption at the excitation wavelength is too small to be taken into account.

Fluorescence spectroscopy provides a powerful methodology for investigating the dynamic properties of solutions [2]. Because of Frank–Condon principle absorption spectroscopy can only yield information on the average ground state of the molecules which absorb light. Only solvent molecules that are immediately adjacent to the absorbing species will affect its absorption spectrum. In contrast, fluorescence spectroscopic parameters are sensitive to functions

of all processes which can occur during the excited state lifetime, and these processes can involve other molecules which are over 100 Å away from the fluorophore at the moment of excitation. Although the duration of 10 ns, which is the lifetime of the excited state, may appear to be very brief time span, it is actually long relative to the motions of small molecules in fluid solution. This means that the fluorescence is affected very significantly by the nature of the solvent or, more precisely, by the type of the environment of the fluorophore. Apart from the observation of a concentration dependant red shift of the peak fluorescence emission, our observations show the usual concentration dependant red shift of the fluorescence emission both in the case of dye with and without the presence of silver sol. Such red shift with concentration is more steep in the presence of silver sol (Fig. 4).

This effect can be explained on the basis of solvent relaxation and Stokes shift. It has been observed that the peak fluorescence wavelength increases with concentration of the dye. This implies a loss of energy of the emitted photons or an increase in Stokes shift with concentration. This is due to several dynamic processes which include energy losses due to dissipation of vibrational energy, redistribution of electrons in the surrounding solvent molecules induced by the altered dipole moment of the excited fluorophore, reorientation of the solvent molecules around the excited state dipole, and specific interactions between the fluorophore and the solvent or the solute.

The physical properties of the solvent affect the fluorescence spectra in a number of ways. The solvent can be regarded as a continuum in which the fluorophore is contained. The interaction between the solvent and the fluorophore molecules affect the energy difference between the ground and the excited states. This energy difference in (cm^{-1}) is a property of the refractive index (n) and the dielectric constant (ϵ) of the solvent and is described by Lippert equation [2]

$$\bar{\nu}_a \cong \bar{\nu}_f = \frac{2}{hc} \left(\frac{\epsilon - 1}{2\epsilon + 1} - \frac{n^2 - 1}{2n^2 + 1} \right) \frac{(\mu^* - \mu)^2}{a^3} + \text{const} \quad (9)$$

where h is the Planck's constant, c the speed of light and a the radius of the cavity in which the fluorophore resides. $(\mu^* - \mu)$ is the change in dipole moment.

The increase in peak fluorescence wavelength with concentration of the dye indicates that the ground and the excited states take larger time to get stabilized after the excitation which results in increase in energy difference between them and greater Stokes shift. One of the reasons can be a decrease in refractive index which restricts the movements of electrons within the solvent molecules. Since hydroxyl groups are present in the solvent, there will be second-order effects also, in the above equation, due to induced dipoles. A decrease in ϵ can also make the stabilization time large and thereby increase stokes shift but this energy decrease

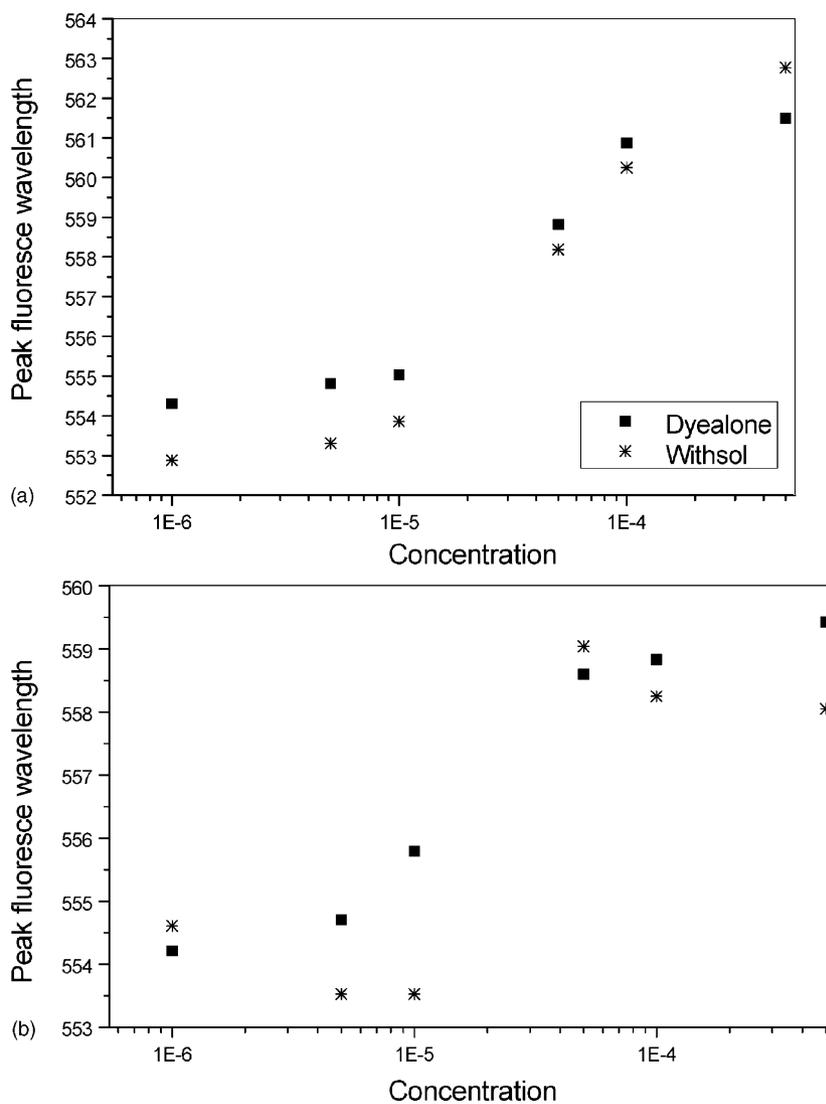


Fig. 4. Variation of peak fluorescence wavelength with concentration at two different pump powers: (a) 14 mW; (b) 28 mW.

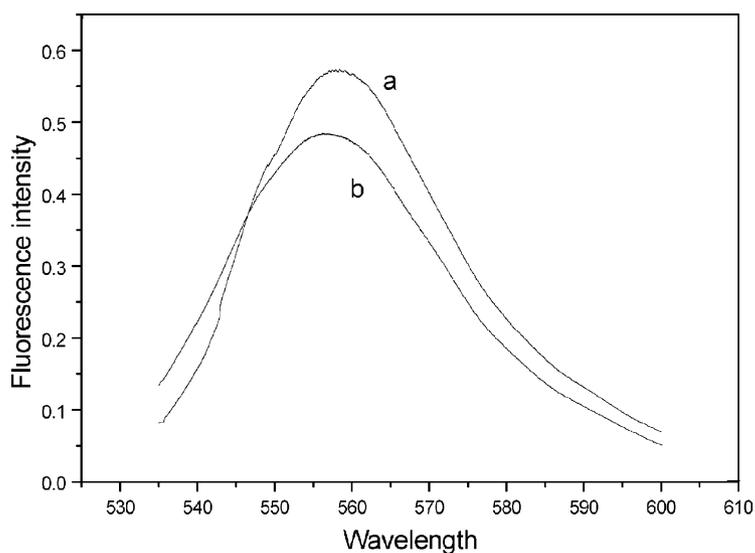


Fig. 5. Fluorescence spectrum of Rhodamine 6G for a concentration of 10^{-4} mol/L: (a) dye alone; (b) dye with silver sol.

of the excited state occurs only after the reorientation of the solvent dipoles. This requires the movement of the entire solvent molecules and not just its electrons. Therefore, in our case where the stabilization of the excited state depends on the ϵ , it can be assumed that as the concentration increases the reorientation of the solvent dipoles becomes slower thereby shifting the excited states to lower energy on the timescales compared to solvent reorientation time.

3.3. The fluorescence quantum yield

The FQY values are calculated using Eq. (8) for various values of dye concentrations. The experiment was done under identical conditions for a wide range of concentrations with and without the presence of silver sol. It is seen that the presence of sol decreases the fluorescence intensity with

accompanying increase in thermal lens signal as seen from Fig. 5. This is one of the main attraction of the present investigation. The addition of the sol enhances the thermal lens signal which makes the detection easier at any concentrations of the sample under study. The FQY variations with concentration are as given in Fig. 6 at two different pump powers of 14 and 28 mW. As is seen from the figure, at higher pump power there is only about 10% reduction in the quantum yield at low concentration in comparison with about 50% reduction at low pump power of 14 mW. At higher concentrations the percentage reductions are almost identical in both cases.

The fluorescence will be affected by the electromagnetic interaction among the optical fields, the fluorophore molecules and the electronic plasma resonance [5]. This plasma resonance can also affect normal Raman scattering

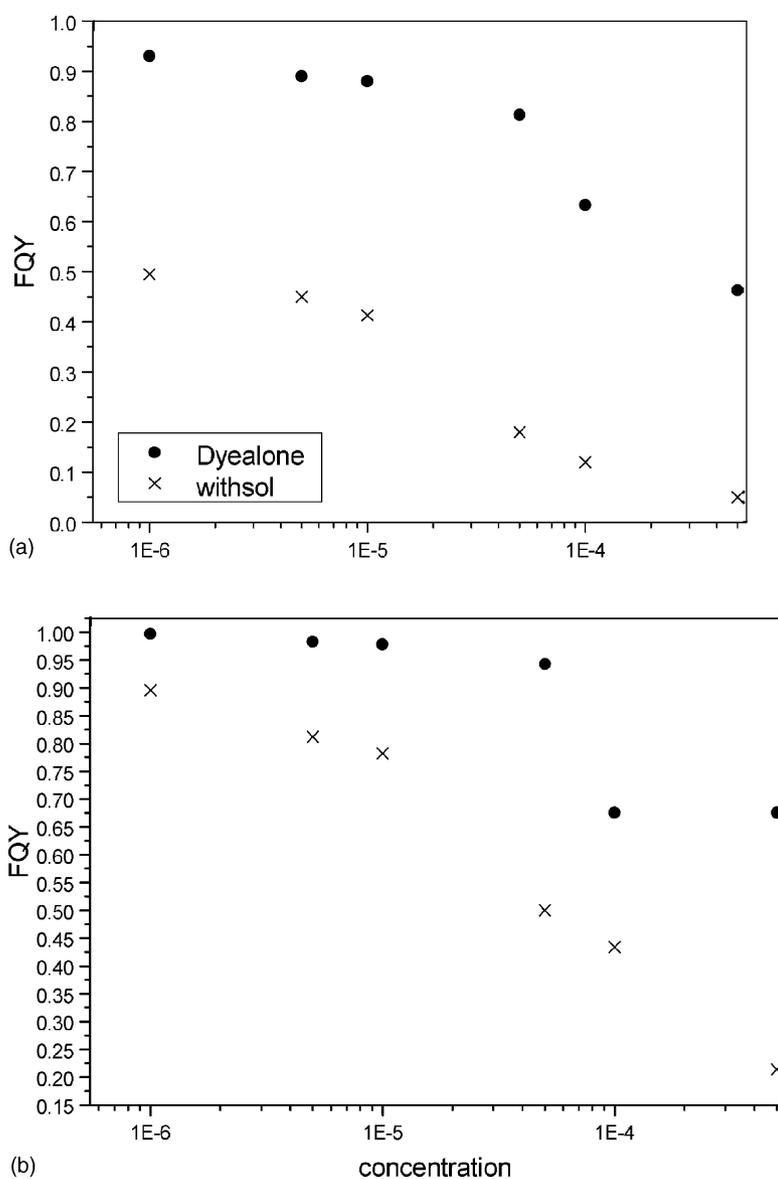


Fig. 6. Variation of FQY with concentration for two different pump powers: (a) 14 mW; (b) 28 mW.

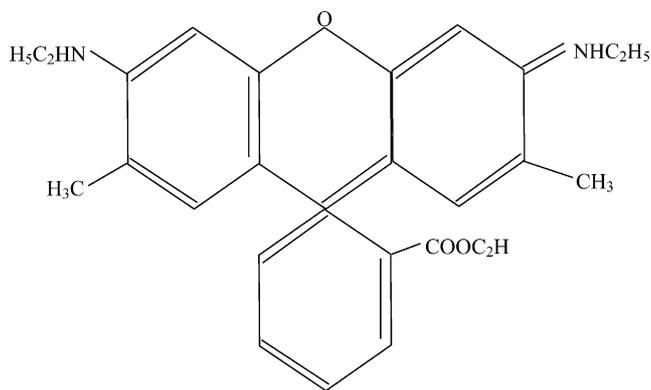


Fig. 7. Molecular structure of Rhodamine 6G.

and resonance Raman scattering in different ways. The silver particles provide an additional decay mechanism, which arises from the possibility of very rapid transfer of the excitation from the dye molecule to the silver particles via the excitation of the plasma resonance. This additional excitation can be either radiative or non-radiative. But since the excitation wavelength that we have used in our experiment (532 nm) is far removed from the plasma resonance wavelength (410 nm) it can be assumed that fluorescence is not much affected by this additional decay mechanism induced by resonance.

3.4. Twisted intramolecular charge transfer (TICT)

Another possible mechanism for the non-radiative decay is the twisted intramolecular charge transfer which accounts for many processes taking place in the fluorophore–solvent environment after the excitation of the dye molecules. Solvent dependence of fluorescence lifetimes of Rh6G has been studied earlier [3] for a number of solvents like H₂O, D₂O, MeOH, EtOH, *i*-PrOH, etc. The dye is proved to be relatively insensitive to the solvent effect, with lifetime restricted in the range from 4.36 to 3.83 ns. This is because the ionization potential of its monoethyl amino group, Fig. 7, is too high to favor TICT state formation. TICT state formation is an important non-radiative decay channel from the planar excited state and therefore, if this channel is absent in Rh6G, in electromagnetically inert environment, its fluorescence quantum yield should be nearly equal to unity. This has been proved to be so in our experiment with FQY \approx 1 with water as the solvent at low concentrations. The fluorescence measurements from the molecules on the silver island film shows a reduction in fluorescence lifetime [5] up to three orders of magnitude which invariably means the appearance of an additional non-radiative decay channel due to the electric field in the vicinity of Ag particles which was otherwise absent.

Therefore, it can be assumed that the presence of silver particles produces a greater optical field for the excited fluorophore and induces the formation of charge transfer complexes. Formation of these resonance hybrids provides a non-radiative decay channel for the excited fluorophore and thereby reduces its fluorescence quantum yield. Moreover, reduction in absorbed light quanta due to scattering by the silver particles also results in reduced fluorescence. Many researchers have already proved that the presence of nano particles like Ag and Au enhance the Raman scattering and resonance Raman scattering [4,7]. As the intensity of the pump laser is increased we do not observe significant reduction in FQY at low dye concentration (Rh6G). This means that the additional de-excitation process in presence of silver sol is intensity dependant. The reason for this behavior is not clear at present. Detailed studies are in progress.

4. Conclusions

In conclusion, we have proved that the presence of Ag sol reduces the quantum yield of Rh6G. Its possible favourable outcome is the enhancement of Raman scattering signal which is inherently weak. A discussion is presented on the possible reasons for this decrease in FQY in terms of the formation of charge transfer complexes. Also, we have observed that the presence of silver sol can enhance the thermal lens signal which makes the detection of signals easier at any concentrations.

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