Chapter 1

Introduction

A coloured substance having affinity to the substrate to which it is applied is called dye. In India and Middle East dyeing has been carried out for over 5000 years as per archaeological evidence. The main sources of dye were animal, vegetable or mineral. By far the greatest source of dyes has been from the plant kingdom, notably roots, berries, bark, leaves and wood, but only a few have ever been used on a commercial scale. The first human-made (synthetic) organic dye, mauveine, was discovered by William Henry Perkin in 1856. Many thousands of synthetic dyes have since been prepared. Nowadays these are used as colourant for cotton, leather, wool, silk, nylon, and paper etc.

The dyes, which are used as active medium for laser generation, are called laser dyes. The lasing range covered by different dyes is from 0.3 to 1.3 $\mu$m. The dye lasers were first discovered by Sorokin and his colleagues [1, 2].

1.1 Classes of Laser Dyes

Laser dyes can be classified into various groups, such as, xanthenes, polymethines, oxazines, coumarins, anthracenes, acridines, azines and phthalozianins, depending on their structure. Since we have studied few dyes of xanthene and coumarin groups only, therefore, these two groups of dye are discussed below.

1.1.1 Rhodamine and Other Xanthenes

The xanthene system is probably the most well known fluorescent dye class and it includes such familiar dyes as the rhodamines and fluorescein. The basic xanthene nucleus is shown in figure 1.1, where $R_1$ is usually a substituted phenyl group and $R_2$ and $R_3$ are, generally, the methyl or ethyl groups. The most important xanthenes are the rhodamines.
The rhodamine is a family of related fluorescent dyes. Examples of rhodamine dyes are rhodamine 6G (Rh6G) and rhodamine B (RhB). The visible absorption band of xanthene corresponds to charge redistribution between two amino groups shown in figure 1.1. It can be appreciated that due to the symmetrical π electron system there can be no static dipole moment parallel to the x-axis in either the ground or excited state. The main absorption band of rhodamine corresponds to a transition moment parallel to the x-axis of the dye (left to right side of the page) and gives absorption between 450 nm and 600 nm. Transition parallel to y-axis (bottom to up side of the page) usually gives absorption in the ultra-violet, although inserting strong electron acceptors or donators in to a pendent phenyl group can push this absorption band into the visible. The most efficient lasing wavelength for the dye is frequently at much longer wavelength than the fluorescence maximum and so the two should not be confused. The stokes shifts for rhodamines are usually around 20-30 nm and the quoted lasing wavelengths do not correspond to the expected fluorescence maxima. RhB, for example, absorbs at 554 nm in acidic ethanol, has a fluorescence maximum at 580 nm, and shows highest lasing efficiency at 627 nm in the same solvent [3]. Fluorescence efficiencies for the rhodamines are generally high, for example Rh6G and RhB both have quantum yields close to unity [4].

It is a general belief that electrostatic interaction exists between the rhodamine dye molecules in solution to form aggregates such as dimer which is in turn affected by several factors such as concentration, temperature and solvent nature [5, 6]. The aggregative properties of rhodamine dyes in isotropic solvent have been studied. There are studies which discuss the aggregation of rhodamine 6G and rhodamine B in ordered nematic solvent using polarized spectroscopy [7]. The anisotropic solvent affects the self association and solvation of rhodamine dyes. The molecular interaction between rhodamine 6G liquid crystal molecules has been found to be stronger than with the ordinary solvents. Solvent effect on two photon absorption and fluorescence of rhodamine dyes has
been studied using conventional open aperture Z scan experiments [8, 9] and two photon fluorescence studies [10, 11].

1.1.1 Rhodamine 6G

The structure of rhodamine 6G is shown in figure 1.2. The chemical formula and name of rhodamine 6G are C_{28}H_{31}N_{2}O_{3}Cl and xanthylum,9-[2-(ethoxycarbonyl) phenyl]-3,6-bis-(ethylamino)-2,7-dimethyl-chloride, respectively. Rhodamine 6G is an excellent laser and forensic light source dye. It can be dissolved in water or organic solvents or it can be introduced into magnetic powder to form a fluorescent magnetic powder. It is the dye of many latent print examiners. Rhodamine 6G usually comes in three different forms. First is the Rhodamine 6G chloride which is a bronze/red powder with the chemical formula C_{27}H_{29}ClN_{2}O_{3}. It is highly soluble but this formulation is very corrosive to all metals except stainless steel. Other formulation are less soluble, but also less corrosive. Rhodamine 6G perchlorate, C_{27}H_{29}ClN_{2}O_{7}, comes in the form of red crystals where as rhodamine 6G tetrafluoroborate, C_{27}H_{29}BF_{4}N_{2}O_{3}, appears as maroon crystals.

As a tracer dye Rh6G is used within water to determine the rate and direction of flow and transport. Rhodamine dyes fluoresce and can thus be detected with fluorometers. Rhodamine dyes are used extensively in biotechnology applications such as fluorescence microscopy. It is pumped by the 2nd harmonic (532 nm) from an Nd:YAG or nitrogen laser. The dye has a remarkably high photostability, high quantum yield (0.95) [12], low cost, and its lasing range has close proximity to its absorption maximum (approximately 530 nm). The lasing range of the dye is 555 to 585 nm with a maximum at 566 nm. The Rh6G has been utilized as a probe molecule for high sensitive detections, such as single molecule detection using surface enhancement resonance Raman scattering [12-19]. It has also been used for non-linear vibrational detection using hyper Raman scattering.
Nanometer scale detection has also been done by Rh6G using near field Raman spectroscopy [21-23].

### 1.1.1.2 Rhodamine B

The structure of rhodamine B, which is also known as rhodamine 610, is shown in figure 1.3. The chemical name and formula for RhB are 9-(2-carboxyphenyl)-6-diethylamino-3-xanthenylidene-diethylammonium chloride and $C_{28}H_{31}ClN_2O_3$, respectively. It is highly soluble in water. Rhodamine B is tunable around 610 nm when used as a laser dye. Its luminescence quantum yield is 0.65 in basic ethanol [12] and 0.68 in 94% ethanol [24]. The fluorescence yield is found to be temperature dependent [25]. It is usually available in the form of green crystals or reddish-violet powder. It shows stability under normal conditions of use and storage.

### 1.1.1.3 Rhodamine 575

It is also a member of rhodamine family of dyes and has structure similar to other rhodamine dyes except different peripheral substitutions as shown in figure 1.4. Its name and formula are 2-[6-(ethylamino)-3-(ethylimino)-2,7-dimethyl-3H-xanthen-9-yl]-benzoic acid and $C_{26}H_{27}N_2O_7Cl$, respectively. It is available in the form of red crystalline powder. Fluorescence and absorption wavelengths for rhodamine 575 are 555 nm and 518 nm, respectively.

### 1.1.2 Coumarins

Coumarin is a chemical compound that has a vanilla like flavor and found in many plants, notably in high concentration in the tonka bean, woodruff, and bison grass. The name
comes from a French word, coumarou, for the tonka beans. Coumarin is a oxygen heterocycle. Coumarin can occur either free or combined with the sugar glucose (coumarin glycoside). These dyes are used widely as anticoagulants and also as gain medium in some tunable dye lasers in ultra-violet and blue region of visible light. The absorption maxima of these dyes lie in ultra-violet region, where as emission maximum lies in ultra-violet or blue region. Chemical name and formula of coumarin are 1,2-benzopyrone-2H-1-benzopyran-2-one and C₉H₆O₂, respectively. Structure of coumarin dye is shown in figure 1.5. Coumarin has blood-thinning, anti-fungicidal and anti-tumor activities. It is helpful in increasing blood flow in the veins and decreasing capillary permeability. High dose of coumarin for a long time can be toxic.

Coumarins are well known laser dyes [26-28] and are useful probes in variety of chemical and physiochemical studies [29-34]. Coumarin doped di-(N-carbazole) biphenyl thin films have been found to have possible applications as organic semiconductors and optical memory materials [35]. Some of the coumarin derivatives also have biological and medicinal applications [36-38].
1.1.2.1 Coumarin 500

Structure of coumarin 500 dye is shown in figure 1.6. Its chemical name and formula are 7-(ethylamino)-4-(trifluoromethyl)-2H-1-benzopyran-2-one and C\textsubscript{12}H\textsubscript{10}F\textsubscript{3}NO\textsubscript{2}, respectively. It comes in the form of yellow needles. Its absorption and emission wavelengths are 392 and 495 nm, respectively.

1.1.2.2 Coumarin 522B

Its chemical formula is C\textsubscript{12}H\textsubscript{6}F\textsubscript{3}NO\textsubscript{2}. It is available in the form of yellow crystals. Structure of this dye is shown in figure 1.7. Its absorption and emission wavelengths are 412 and 515 nm, respectively.

1.1.2.3 Coumarin 540

Its chemical name and formula are 3-(2-benzothiazolyl)-7-(diethylamino)-2H-1-benzopyran-2-one and C\textsubscript{20}H\textsubscript{18}N\textsubscript{2}O\textsubscript{2}S, respectively. This dye is available in the form of orange crys-
Figure 1.8: Structure of coumarin 540.

tals. Its absorption and emission wavelengths are 460 and 505 nm, respectively. Structure of this dye is shown in figure 1.8.

1.2 Spectroscopic Techniques

Dyes mentioned in the previous section have been studied by various spectroscopic techniques, as described below.

1.2.1 Electronic Absorption and Emission Spectroscopy

The ultraviolet-visible (UV-Vis) radiation causes electronic transitions within a molecule, promoting bonding and nonbonding electrons to higher less stable antibonding orbitals. Therefore, electronic absorption (or UV-Vis absorption) spectra of molecules provides information about the electron density and changes in it due to the interaction with other molecules. Identical information is provided by the electronic emission (fluorescence) spectroscopy.

1.2.1.1 Absorption and Emission spectra

The Absorption and Emission spectra of a common laser dye are shown in figure 1.9. The emission band appears to be the mirror image of absorption band and is lower in frequency. Both the spectra are broadened which may be due to the overlapping of energy levels or some broadening mechanism. This is the characteristic of large organic molecules in liquid state and can be represented by an energy level diagram as shown in figure 1.10.

Two types of states, the singlet (\(S_1, S_2\) etc.) and triplet states (\(T_1, T_2\) etc.) as designated by net electronic spin, are shown in the figure. The probability of singlet state to triplet
Figure 1.9: Typical absorption and emission spectra of a laser dye.

Figure 1.10: Typical singlet and triplet energy levels of a laser dye.

state transition is very low because an electron spin flip is required for this. The large organic dye molecules give rise to broad overlapping energy levels and spectra due to the presence of many internal degree of freedom. The energy transfer within a band is faster than the spontaneous decay rates for interband transitions.

For lasing action the dye molecules are excited by pumping from lower vibronic level of ground state $S_0$ to one of the upper vibronic levels of excited state $S_1$. A rapid relaxation occurs to the lower vibronic level of $S_0$ state. The laser action occurs between this level and one of the upper vibronic levels of $S_0$ from which it returns by non radiative decay to the lowest level.
The presence of triplet state causes a problem which limits the laser action. The ground state molecules are not excited to triplet state by pump as these transitions are forbidden. But a molecule in $S_1$ can decay to state $T_1$ (inter state crossing) which is due to collisions. If the life time of state $T_1$ is greater than the time required for intersystem crossing, the molecules will accumulate in state $T_1$. The transition $T_1 \rightarrow T_2$ is allowed and the wavelength corresponding to this absorption is almost equal to that corresponding to fluorescence transition $S_1 \rightarrow S_0$. Therefore, the inter system crossing will reduce the number of molecules available in upper state for laser action and the gain is reduced. However, the addition of oxygen to the solution works for the quenching of triplet state which reduces the life time of $T_1$ state.

Optical properties and chemical behavior of coumarin 500 under the influence of atmospheric positive electric pulsed corona discharges have been examined by Keskin et al [39]. Change in some optical parameters has been observed by them when the dye is irradiated with ultraviolet-visible radiation and corona discharge. A decrease in optical density on the absorption spectrum is found along with formation of photo-products due to the removal of chromaticity.

The effect of solvent polarity on the photophysical properties of coumarin 6 dye has been investigated by Satpati et al [40]. The dye shows different behavior in different solvents. In case of non polar solvents the dye shows unusual deviations in comparison to the linear correlations with the solvent polarity observed in other solvents. These deviations are explained on the basis of different conformations adopted for the dye at its 7-N-(ethyl)$_2$ group in non polar and other solvents.

A comparative study of fluorescence of coumarin derivatives has been made using different solvents of varying properties [41]. Solvent effect on absorption and fluorescence spectra of coumarin dyes has also been studied by Manne kutla et al [42]. This particular study reports effects of general solvents, alcohols and binary mixtures at 298 K. Appearance of bathochromic shift in absorbance and fluorescence spectra with increasing solvent polarity indicated the involvement of $\pi - \pi^*$ transitions. The determined dipole moments of excited state were more than their ground state counterparts in all the solvents.

The last decade has seen a major growth of interest in fluorescent dyes for specialized applications, ranging from lasers to biological labels, pH indicators, sensor, non-linear optical material and sensitization of solar cells [43-47]. In fact, it is the great sensitivity of fluorescence towards instrumental detection that has made fluorescent dyes so important in so many areas of detection and analysis. This increased interest in the study of fluorescent dyes can be attributed to two main factors:

(a) The availability of inexpensive diode lasers that provide convenient monochromatic
(b) The fact that the longer emission wavelength of dyes like rhodamine (Rh) minimizes interference from background emission, as such unwanted fluorescence invariably occurs at short wavelengths.

Several structural factors contribute to the phenomenon of fluorescence in the dye. These factors are generally, influenced by the environment of the dye such as solvent, pH, host material in which dye is dispersed and of course water impurities in the sample. Even the subtlest structural change can result in unpredictable changes in fluorescence efficiency and fluorescence quantum yield [48]. A dye is most likely to exhibit fluorescence if its molecular structure has all the following characteristics; high structure rigidity, high planarity of the σ electron system, an absence of groups which cause steric crowding, no nitro groups, no azo groups, no high atomic number halogens except chlorine, no chelating metal atom, and no pendant phenyl groups, especially on nitrogen and oxygen atoms. The introduction of low atomic weight halogens (usually fluorine) into the chromophore gives an acceptable increase in photo stability without loss of fluorescence, so enabling their continued use in many of the more demanding applications.

In theory an ideal fluorescent dye should be nonplanar and of low symmetry in the ground state and become more planar, rigid and of higher symmetry in the singlet state [48]. The Stokes shift is related to the phenomena of fluorescence. The Stokes shift can be related to the geometry change on excitation and can be predicated using molecular orbital calculations [49]. In such calculations the Stokes shift is related to the width of the absorption band - the broader the band the larger the Stokes shift although the relationship is largely empirical.

The fluorescence of laser dyes is also affected by the presence of other particles. Recently, fluorescence modulation of acridine and coumarin dyes by silver nano particles has been studied by Sobatini and co-workers [50]. The presence of silver particles affects the photophysical properties of coumarin dyes in 2-propanol. It is suggested that the fluorescence quenching occurs as a result of the binding of the dyes onto the surface of Ag nanoparticles, providing a fast and efficient path to excited state non-radiative deactivation. Study of fluorescence decays of amino-coumarin dyes in polymer hosts like polymethylmethacrylate, polystyrene and ethylene-butane rubber and also in ethyl acetate and toluene has also been reported [51]. The study concludes that many of the dye-solvent and dye-polymer combinations show single exponential decays with life time from 2.3 ns to 3.9 ns. The dyes in ethylene butane rubber show small deviation from single exponential decay.
The orientation and aggregation behavior of rhodamine dye in insoluble film at air-water interface under compression has already been studied [52]. The absorption and fluorescence spectra of the rhodamine dye are affected significantly by compression at interface. The observed changes arise due to the formation of aggregated species and subsequently their structural rearrangement on the water surface during compression. The spectroscopic behavior of the monolayer is associated with its rheological properties and the transition from disordered monomers to dimers, from dimers to aggregates and from aggregates to two dimensional arrays. The studies of second harmonic generation explain that the rhodamine molecules in the expanded film region are oriented with their $C_2$ axis which is tilted away from the surface normal at angle $\theta$ within the range of 31-39°. According to preferable intermolecular interaction with the water sub-phase and surrounding molecules the rotational distribution around the $C_2$ axis is assumed to be 45-60°. The angle distribution becomes slightly narrower due to the increase of molecular ordering because of two dimensional external pressure. The second harmonic generation intensity increases sharply along with the production of phase shift when compression is increased. This is due to the formation of blue shifted aggregates with their electronic transition in resonance with the incident laser frequency.

Transient absorption spectrum of coumarin 153 in acetonitrile and methanol has been reported with 40 fs time resolution by Kovalenko et al [53]. It has been observed that an excited-state absorption band $S_1 \rightarrow S_n$, with a peak at 428 nm, leads to a terminal state which is iso-energetic with the terminal state for a strong ground-state absorption band $S_0 \rightarrow S_m$ at 220 nm. The excited-state absorption experiences only a small shift towards the shorter wavelength with time. The stimulated emission revealed two transient isosbestic points. These observations have been discussed based on two different models. The first model explains the evolution of the stimulated emission band due to solvation dynamics. The second model assumes that the terminal states $S_m$ and $S_n$ are vibronically coupled in such a way that the coupled vibronic manifold is optically accessible both from $S_0$ and $S_1$.

Lewis and Maroncelli [54] measured the absorption and emission transition moments, fluorescence life times and quantum yields of the coumarin 153 in different solvents. Measured values of absorption and emission transition moments were independent of the solvents, however absorption and emission wavelengths were found to be dependent on the solvents.
1.2.2 Vibrational Spectroscopy

In molecular system, there are many vibrational/rotational levels that can accommodate the electron. Therefore, electronic spectroscopic data do not provide information about the vibrational energy levels of the molecule. Study of vibrational spectroscopy provides rich and unique information about the bonding arrangement in a molecule in liquid or vapour state. Frequency of a vibrational band depends on the force constant and the mass, whereas intensity depends on the extent of overlapping of the vibrational wave functions of two different levels involved in a vibrational transition. Width of the observed band provides information about the decay and de-phasing processes.

Vibrations of a molecule can be probed by either Raman scattering technique or infrared (IR) absorption spectroscopy, which are complimentary to each other. IR spectroscopy involves measuring of the direct absorption of photons with the appropriate energy to excite molecular bond vibrations, whereas, Raman spectroscopy measures the excitation of vibrations in an indirect manner. These techniques are complementary because some vibrational transitions that are, generally, observed in IR spectroscopy are not observed in Raman spectroscopy, and vice versa.

Infrared spectroscopy is a helpful tool to identify compounds or investigate sample composition when combined with other spectroscopic techniques. The IR spectrum can be broadly divided into three regions; the near-, mid- and far- infrared, named for their relation to the visible spectrum. The far-infrared, approximately 400-10 cm\(^{-1}\) (1000-30 \(\mu\)m), lying adjacent to the microwave region, has low energy and may be used for rotational spectroscopy. The mid-infrared, approximately 4000-400 cm\(^{-1}\) (30-1.4 \(\mu\)m) may be used to study the fundamental vibrations and associated rotational-vibrational structure. The higher energy near-IR radiations between 14000-4000 cm\(^{-1}\) (1.4-0.8 \(\mu\)m) can excite overtone or harmonic vibrations.

Infrared spectroscopy utilizes the fact that molecules have specific frequencies at which they rotate or vibrate corresponding to discrete energy levels. These resonant frequencies are dependent upon:

i. The shape of the molecular potential energy surfaces

ii. The masses of the atoms and,

iii. The associated vibronic coupling.

Infrared spectroscopy is a very useful tool in the industry as well as in research field. It is used for measurement, quality control and dynamic measurement. Now the quality of tea leaves can be assessed using IR spectroscopy [55]. IR spectroscopy has also been utilized in microelectronics successfully [56].
The instruments used are now small, and can be carried easily, even for use in field trials. Some instruments are capable so much that they can automatically detect what substance is being measured from a store of thousands of reference spectra held in storage. This technique works very well exclusively on samples with covalent bonds. Simple spectra with high level of purity can be obtained from samples with few IR active modes. More complex molecular structures lead to more absorption bands and more complex spectra. The technique has been used for the characterization of very complex mixtures. IR spectroscopy can be also be used to identify chemicals from spills, paints, polymers, coatings, drugs, and contaminants. It is perhaps the most powerful tool for identifying types of chemical bonds (functional groups). The wavelength of light absorbed is characteristic of the chemical bond. By analysing the infrared absorption spectrum, one can determine the chemical bonds in a molecule. IR spectra of pure compounds are so unique that they are like a molecular “fingerprint”. For identification of less common materials FTIR is combined with nuclear magnetic resonance, X-ray diffraction and/or other techniques. As absorption strength is proportional to concentration, FTIR can be used for some quantitative analyses.

The Raman scattering under resonance condition has been utilized extensively in the study of vibrations of some bio molecules. However, owing to strong fluorescence of Rh6G, it is extremely difficult to obtain a good quality Raman spectrum even under resonance condition. Hence, molecules like Rh6G have been studied by the surface enhanced Raman scattering (SERS) technique in which intensities are up by 6 orders of magnitude [57, 58]. On the other hand, IR absorption data are sparsely available on Rh6G because of the fact that its IR spectrum is crowded with the large number of vibrational bands as the molecule does not possess any symmetry. Therefore, it is not an easy task to decipher information from IR spectra of macromolecule like Rh6G. Irrespective of these difficulties/shortcomings; IR spectroscopy can still be used in the study of interaction of Rh6G and other dyes with other organic molecules, since this technique is quite useful in arriving at the structure and bonding arrangements in these complexes. In certain situations, IR spectroscopy alone may provide sufficient amount of data for the study of interactions between molecules. However, very strong absorption in the IR region does not allow one to obtain precise information from standard transmission spectra recorded on dispersive IR spectrophotometer. In these cases, Fourier transform infrared (FTIR) spectroscopy provides spectra of suitable quality due to high transmission of the energy, high resolution and the possibility of improvement of the signal to noise ratio by accumulation of interferograms. The tip enhanced near field Raman and IR absorption bands of Rh6G have been reported and also been assigned using density functional theory [59]. The different bands are assigned by using Raman and IR intensities and also the frequencies of
the vibrational modes. The spectral changes in resonance Raman and surface enhanced resonance Raman scattering (SERRS) of Rh6G are predicted by the vibrational and electronic transition calculations using DFT technique. However, IR spectroscopy cannot be applied to the dyes doped in solid matrix. For this purpose, Raman spectroscopy under resonance condition can be applied to suppress the Raman scattering from the solid host and to enhance the Raman signal from the dispersed dye [60].

### 1.3 Photophysics of Laser dyes

Photophysical properties of laser dyes like absorptivity, fluorescence yield, Stokes shift and triplet formation have high influence on lasing characteristics of dye laser. Laser dyes are characterized by large absorptivities which can be measured by their molar extinction coefficients, $\varepsilon$ (measured in litre/mole cm$^{-1}$ or M$^{-1}$cm$^{-1}$). Due to this feature, high optical densities are associated with moderate concentrations of dye. The degree of rearrangement of electron density in a dye molecule due to the absorption of photons is related to the transition dipole moment or oscillation strength ($f$) for the electronic transition. The oscillator strength is related to a first approximation using classical theory to the extinction coefficient ($\varepsilon$) as [61]

$$f = 4.3 \times 10^{-9} \int \varepsilon \, d\nu = 4.3 \times 10^{-9} \varepsilon_{\text{max}} \Delta\nu_{1/2}$$  \hspace{1cm} (1.1)

where $\nu$ is the energy (in wavenumbers). The rate constant for fluorescence emission is related to $f$ as

$$k_f = \nu_{\text{max}}^2 f$$  \hspace{1cm} (1.2)

Where $\nu_{\text{max}}$ is the energy corresponding to the maximum wavelength of absorption. The probabilities of spontaneous emission and stimulated emission are related to the size of transition moment and oscillator strength. For organic dyes dissolved in liquid the most concerned electronic energy levels are the ground state $S_0$ and the first electronic excited state $S_1$ as shown in figure1.11. The absorption of light promotes an electron in bonding orbital to an antibonding (virtual) orbital of the molecule. The dye laser can be viewed as a four level system in which the most probable excitations populate upper vibrational levels in $S_1$, which is followed by a vibrational relaxation to the zeroth level in $S_1$. Now the emission occurs to repopulate an upper vibrational level of ground state $S_0$. The most common laser dyes are not optimally designed for laser action with respect to the shaping of absorption - emission bands of organic dyes [62, 63]. The bands are broadened...
because of vibrational relaxation. The strength of emission and absorption is associated with 0-0 transitions for which the probability of stimulated emission is low. The absorption and emission spectra for rhodamine B are shown in figure 1.12. The process of dye fluorescence ($k_f$) must compete with non-radiative decay of excited species by internal conversion to the ground state $k_d$. The inter system crossing process helps in the forma-
tion of dye triplet. For emission the quantum efficiency, $\varphi_f$, is given by

$$\varphi_f = \frac{k_f}{k_f + k_{isc} + k_d} \quad (1.3)$$

where $k_{isc}$ is the rate of intersystem crossing.

For inter system crossing laser dyes show low quantum yields. Typically measured fluorescence yield $\varphi_f$ range from 0.6 to 1.0.

### 1.4 Solvent Effect on Dye Parameters

The performance of laser dyes in terms of alteration of fluorescence yield, life time and wavelength can be affected by the selection of solvent. This was observed by Drexhage that dyes perform better when rigidly fixed in planar geometries [4, 64]. The effects of some selected solvents on the fluorescence yield and life time parameters for coumarin dye have also been reported [65-67]. Solvent effects are important in determining the photophysical properties of dye molecule in solution. The fluorescence life time of rhodamine B in a series of normal alcohols had been measured as a function of temperature [68]. The non radiative rate constants were calculated from the fluorescence life times and quantum yields. Activation energies were obtained from the Arrhenius plots of non radiative rate constant. It was found that the variation of the non radiative rate constant with the solvent polarity and temperature was consistent with a photophysical mechanism that involves equilibrium between the planar and twisted configuration of the diethylamino groups on xanthene ring of rhodamine B and internal conversion from the twisted configuration. The activation energy was found to be equal to the free energy difference between the twisted and planar configurations. The dependence of the free energy difference and the rate constant for internal conversion from the twisted configuration on the solvent polarity determines the variation of non-radiative rate constant with solvent.

### 1.5 Dye Aggregation

Potential driving forces for aggregation make the solvent molecules free from the solvation spheres which surrounds individual dye structure. Ojeda et al studied the aggregation of rhodamine 6G in ethanol [69]. The formation of dimer results in subtle shifts in absorption due to exciton interaction. In dimers or higher aggregates the fluorescence is almost suppressed. This change is connected to the reduced lifetime of aggregated forms of organic dyes. For instance rhodamine B monomer and dimer in water display excited state
lifetimes of 1.6 ns and 100 ps [70], respectively. These values point towards a high rate of non radiative decay for the dye dimer. The aggregation of rhodamine 6G in the nematic liquid crystal was studied using polarized spectroscopy [7]. The study also provided the information about the voltage dependence of Rh6G electronic spectra and contrast ratio of the dye dissolved in nematic host. The results of the study showed the appearance of red shift for Rh6G in liquid crystalline solvents indicating strong molecular interactions between the liquid crystal molecules and the dye molecule. The interaction was found to be greater than that observed for the ordinary solvents like acetone and ethanol. Further, the aggregation of the dye depends on the electric field strength also. The increasing of the dimer formation is most evident at the voltages higher than 20 volts.

### 1.6 Chemical Properties

Organic dyes are stable under irradiance due to which these have been applied in the area of the dyeing of fabrics, colour photography and photoconductivity [71, 72]. Photochemical changes in different organic dyes have been reviewed by Chibisov and Korobov [73]. Laser dyes have been investigated under following two points.

**(a)** Reports of characteristics of dye solutions under actual or simulated lasing conditions.

**(b)** Studies for identification of mechanism of photochemical degradation.

Dye photobleaching for rhodamine and other laser dyes was demonstrated by Weber group [74-76] which included the effects of oxygen on irradiated solutions and the addition of detergent additives. Early studies and subsequent reports reveal the bleaching of the primary absorption bands of the dyes. There is loss of lasing chromophore, which is accompanied by some increase in the absorption at shorter wavelength of dye or photoproduct. In dye lasers at high pump energies the photolysis occurs with multiple photon events which are uncommon to dye photochemistry under normal irradiation conditions. Upper state population through sequential two photon excitation can be categorized as;

1. Triplet → Triplet absorption:

\[ S_0 \rightarrow S_1 \rightarrow T_1 \rightarrow T_n \]

2. Excitation to higher excited singlet states [77]

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Photoquenching (reversible loss of fluorescent $S_1$ species) and irreversible dye losses due to the intervention of upper singlet levels have been characterized by second mechanism [78]. The first mechanism is of low probability due to low inter-system crossing yields but triplets are long lived. The singlet mechanism plays a role at high pump powers where $S_1$ species will have a considerable absorption cross section. When the dye is in excited states, photochemical products such as radicals can build in concentration. A classification of multiple photon phenomena, in which absorption by long lived photo-products leads to secondary chemical reactions, has been provided [79].

1.7 Aims and Objectives

The aim of this study is to investigate the effect of environment on the laser dyes in different liquid and solid media. It is also well known that the tunable range of a dye laser depends on the solvent to some extent, due to the change in fluorescence spectrum of dye. This indicates that some type of interaction takes place between laser dye and solvent. Moreover, water impurities enter the dye solution with the passage of time. It is also known that the Rh6G dye in water forms dimer, which reduces the fluorescence quantum yield of the dye, thus affecting the output power of a Rh6G dye laser. Therefore, it is equally important to study the effect of water impurities on the structure of a given dye. Similarly, fluorescence yield of dyes, particularly Rh6G, depends on the presence of oxygen in the solution. Moreover, Rh6G embedded in the solid matrix interacts with the host material, which causes the change in the electronic absorption, emission and vibrational properties of the dye [60, 80, 81]. Therefore, we have studied the effects of different environment on the structure of laser dyes of xanthene and coumarin family by utilizing various electronic and vibrational spectroscopic techniques. The effects in terms of changes in bonding structure and interaction with the media was investigated due to their importance in sensing, biological labeling and laser emission properties of the dyes.
Bibliography


