CHAPTER 1

INTRODUCTION

1.1 INTRODUCTION

One of the most successful laser sources known today are dye lasers due to their significant contribution to science and technology. Such versatility arises from the wide choice of molecular dyes available coupled with the large variety of excitation sources (lasers and flash lamps). The main features of dye lasers are their tunability and narrow bandwidth operation over a range of wavelength from about 300-1900 nm using a suitable dye–solvent combination. Dye lasers have broadband fluorescence typically of the order of 40 nm and under suitable conditions the gain can be made to exist almost over the entire range. And hence, the dye lasers are very good broadband oscillators. The dye laser medium consists of an organic dye, usually dissolved in a liquid organic solvent and can be pumped in CW mode as well as pulsed mode, and can produce ultra short time duration pulses of femto second. A dye laser can be used as a primary laser in specific applications or it can be used as a frequency converter to convert coherent radiation produced by one laser device into laser radiation at a more useful wavelength (Durate and Hillman 1990).

As a large volume of toxic and flammable organic solvents, are required in dye lasers, introduced the added problems of solvent evaporation and flow fluctuations, thereby limiting the use of dye lasers in some technical applications. Hence, solid matrices containing laser dyes have been developed in recent years in order to develop practical solid state dye lasers. The broad
band tunability in the visible region of liquid dye lasers are retained in solid host media with an advantage of clean and inexpensive active elements that readily exchanged to access different spectral regions with different dyes. This property encourages one to fabricate conventional optical elements (lenses, prisms, deflecting plates etc.) for many laser applications and specific elements of laser optical systems (active elements with lasing eyes, passive Q-switches, spatially inhomogeneous bleachable filters etc.). These systems improve system performance considerably by providing simplicity in handling, reliability and operation over wide temperature ranges for long time etc. (Dyumaev et al 1992). The compact solid-state dispersive dye laser oscillator provides a series and inexpensive alternative for spectroscopy and other analytical applications (Durate 1994, 1995). The implementation of new ways for incorporating the organic molecules into the solid matrix have agitated confusion in the solid state dye laser field and as a result significant advances have been made in the development of practical tunable solid state dye lasers. The main deficiency of this approach maintains to be the low laser damage threshold of the material, low conversion efficiency and the thermal and photodegradation of the dye that is still much ahead than that of the same dye in liquid medium. Any further improvements in solid state dye laser require greater understanding of the photophysical properties of the dye molecules in polymer matrices. Therefore to understand the behavior of these dyes in solid matrix, a study of the photophysics of laser dyes becomes essential. This chapter presents a review of the photo physical studies made by various authors on solid state dye laser.

1.2 SOLID STATE DYE LASER: A REVIEW

Soffer and McFarland (1967) demonstrated efficient spectral narrowing and tunability over a wide spectral range, in solid and liquid organic dye lasers using diffraction gratings as cavity reflectors. This seems to
be the first report in solid state dye laser. Peterson and Snavely (1968) obtained laser action from Rhodamine 6G (R6G) and Rhodamine B in polymethyl methacrylate (PMMA). The results obtained by these authors were not much encouraging initially, with low lasing efficiency and fast photo-degradation of the dye. As a result not many studies were carried out on solid state dye lasers. Kusakawa and Takahashi (1968) studied the temperature dependence of laser induced damage in polymethylmethacrylate with Q-switched ruby laser. They explained the cause of this damage in a plastic is due to the fact that photon energy is more absorbed by the particle of dye and is converted more to heat than the consumption in thermal relaxation.

Kusakawa et al (1969) reported that the amorphous transparent dielectrics such as organic high polymers have no definite threshold value of laser induced damage because such materials have no definite band structure. They studied the laser-induced damage in polyalkyl methacrylates.

Kaminow et al (1972) studied the photobleaching of organic laser dyes in solid matrices and reported that the bleaching rate is linearly proportional to the intensity of incident radiation, indicating a one-photon process. As per them, bleaching occurs while the molecule is either in the first excited singlet or lowest triplet state and is probably due to excited state reactions with impurities or with the host itself. Reich and Neumann (1974) studied the photobleaching of R6G in polyacrylonitrile matrix a function of temperature by exciting the dyes with Argon-ion laser of wavelength 514.5 nm. The increase of microscopic rigidity of the “polymer cage” around the dye molecule at low temperature was attributed to the temperature dependence of photobleaching number in PMMA. Wang and Gampel (1976) obtained a conversion of 47% from R6G doped PMMA mounted in a rotating assembly when pumped by second harmonic of Q-switched Nd: YAG laser. Connell and Saito (1983) reviewed the study on single and multiple-shot laser
damage to plastics, high power laser studies of dye impregnated plastics and the progress in understanding the physics of the photobleaching process.

Gramov et al (1985) obtained efficient laser generation from Xanthene dyes impregnated into modified polymethyl methacrylates. Introducing a suitable low molecular additive increases the conversion efficiency and resistance to dye photobleaching.

Since then a number of solid host materials have been introduced and in most cases the laser dyes have been developed in solid host. The host materials were silica gel, xerogel or polymers. Reisfeld et al (1989) obtained laser action at 580 nm from perylene dye BASF 241 doped in the combination of sol-gel with organic polymer pumped by a second harmonic Nd: YAG laser and obtained a slope efficiency of 3.5%. Salin et al (1989) obtained a conversion efficiency of 20% from sulfurhodamine 640-doped silica gel pumped by frequency doubled Nd: YAG laser.


Altman et al (1991) studied the lasing properties of R6G and Rhodamine B doped ORMOSIL and obtained a conversion efficiency of 39% and the lifetime exceeding 50,000 pulses with a 500 µJ pump source. In 1992 Lo et al studied the fluorescence and lasing properties of coumarin doped silica samples prepared by sol-gel process and obtained the conversion efficiency of 36%.
Larrue et al (1994) studied optical gain characteristics of R6G perchlorate doped ORMOSIL modified with Tetraethylene glycol and obtained the efficiency as high as 35% with the lasing threshold less than 90 µJ when pumped with frequency doubled Q-switched Nd: YAG laser.

In 1995, Lam et al obtained narrow line width blue laser from silica slabs doped with coumarin 460 and conversion efficiency of 5.5%. Ye et al (1996) studied the lasing and fluorescence properties of two laser dyes (Exallite 377 and LD 390) in the silica matrices prepared by sol-gel method.

These reports confirm that polymers are most suitable host media for incorporating laser dyes. An important advantage of transparent polymers compared with inorganic glasses and crystals is that they exhibit superior optical homogeneity, which is essential for narrow line width oscillators. Though there are different polymers (polymethyl methacrylate, polycarbonate, polystyrene, polyhydroxyethyl methacrylate etc) used as a host material for dye laser applications, the most often used polymeric material is polymethyl methacrylate (PMMA) because of its best optical transparency and its laser damage resistance. Connell and Saito (1983) rank it first among other polymers. This property facilitates one to fabricate conventional optical elements for various laser applications such as optical fiber amplifier. Akhiro et al (1995) synthesized a Graded – Index Polymer Optical Fiber Amplifier (GIPOFA) for high power amplification of the tunable wavelength in the visible region.

In, modern years, significant advances has been made in the field of dye doped polymer lasers with laser damage threshold comparable to or even higher than that of inorganic glasses and crystals. The laser damage resistance was increased by doping PMMA with low molecular additives. Dyumaev et al (1992) presented the results of the investigation of modified polymethyl methacrylate doped with xanthene-series dyes, phthalocyanine, and chelates.
A high laser-damage resistance was attained when the concentration of the additive was 20%. They used ethanol, ethylene glycol ether, ether, polyether, carbonate ether and glycol ether as modifiers. Amat-Guerri et al (1993) investigated the lasing properties of R6G dissolved in poly(2-hydroxyethyl methacrylate) known as P(HEMA) matrix. They obtained a conversion efficiency of 2.2% after adding ethylene glycol dimethacrylate (DEGMA) with P(HEMA) and obtained the lifetime of about 600 pulses.

In order to increase the photostability and conversion efficiency of the dye doped polymer laser, covalent bonding of the dye molecule to the polymeric chain is essential. The modification of the rigidity of the polymeric material by controlled cross linking with a bifunctional monomer improved certain degrees of the photostability and the energy conversion efficiency. Copolymerization with appropriate monomers increased the photostability with lasing efficiencies similar to those found in liquid medium.

Costela et al (1995) obtained the best photostability (≈10,000 pulses) and highest lasing efficiency (~21.5%) when R6G was doped in P(HEMA:MMA)1:1 copolymer. The lasing efficiency similar to that found for R6G in ethanol. Costela et al (1996) obtained lasing efficiency from modified R6G molecules copolymerized with methacrylic monomer and found that lifetime (measured as an 80% efficiency drop) in excess of 20,000 shots with nitrogen laser excitation with a repetition rate of 2Hz. Costela et al (1997) increased the photostability of the dye doped polymer by doping R6G with two covalently bonded 1,8 Naphthalimide groups dissolved in 1:1 MMA:PMMA copolymer. However, the conversion efficiency of dye doped polymer was decreased due to the incorporation of imidazonaphthalimide group.

Ramalingam et al (1998) studied the laser characteristics of R6G doped PMMA rods modified with ethyl alcohol (EtOH) under nitrogen laser
excitation. They reported the conversion efficiency of the polymer rods under 2\textsuperscript{nd} harmonic Nd:YAG laser to be 18\% and for the liquid R6G solution of the same concentration under same conditions to be 25\%. They also studied the photobleaching by measuring the number of pumping pulses after which the output decreased by 20\% of the initial value.

Somasundaram et al (1999) studied the laser characteristics of R6G doped PMMA rods, modified with EtOH under nitrogen laser and second harmonic Nd:YAG laser excitation. R6G dye doped polymer exhibited a less bleaching rate under nitrogen laser excitation than when excited with 2\textsuperscript{nd} harmonic of Q-switched Nd: YAG laser. They concluded that the photobleaching depends on the power and pulse width of the excited laser source. They also found that the dye doped polymer rod when rotated uniformly about its cylindrical axis, under nitrogen laser excitation, decreases the laser intensity to 5\% of its initial value after 20,000 pulses, which when excited under a fixed position reduces the bleaching rate. It led to the conclusion that if the exposed region is continuously changed photobleaching rate can be very much minimized.

Somasundaram et al (2000a) studied the laser characteristics of coumarin 1 doped PMMA rods modified with EtOH under nitrogen laser excitation. They observed that the gain of dye in solid environment was less than that in the liquid environment. And also noted that the photobleaching rate was faster when the rod was in a fixed position . Somasundaram et al (2000) studied the laser characteristics of Coumarin 490-doped polymethyl methacrylate rods modified with EtOH under nitrogen laser and 3\textsuperscript{rd} harmonic Nd: YAG laser excitation. They reported that gain of the dye in the solid medium is less than that of the liquid medium and also laser damage is less when rotating the rod which excited.
Vijila et al (2001) studied in detail the influence of medium on the photophysical properties of a fluorinated coumarin (coumarin 485). They observed that the gain of coumarin 485 on modified PMMA increases with increase in dielectric constant of the medium while in the liquid medium, the reverse effect. Also found that the gain coefficient of coumarin 485 in a solid shows 90% reduction when compared to the liquid medium. They noted the photobleaching effect decreases with the increase in dielectric constant of the medium. This confirms that the fluorine-substituted coumarin molecules get distorted in the highly polar environment and it can be reduced by modifying the medium with less polar solvents.

1.3 SCOPE AND IMPORTANCE OF THE PRESENT RESEARCH WORK

Review of literature shows that most of the work done with solid state dye lasers are on its spectral and the laser characteristics (photobleaching rate, conversion efficiency etc.). These studies show that the Amplified spontaneous emission intensity decreases when the dye doped rods is continuously exposed to nitrogen laser radiation. This decrease in intensity may be due to change in refractive index, which results in a lensing effect on the optical beam above certain power threshold values. This leads is non-linear refraction. In order to understand the interaction of light of high intensity with matter, resulting a considerable alteration of the properties of matter itself, the study of Nonlinear optics is essential. Physics would be dull if all the physical phenomena around us were linear. When light interacts with the matter the refractive index and hence the speed of light in an optical medium change with light intensity, light can alter its frequency as it passes through a nonlinear optical medium and even the principle of superposition is violated.
In order to study the non-linearity in dye doped polymers, the thin polymer films of thickness 1mm are prepared. Materials exhibiting nonlinear optical behavior have attracted intense interest in the recent years because of their applicability in a variety of optical devices. Devices based on these materials exploit various types of nonlinear behavior, including scattering two-photon absorption, self-focusing and self defocusing. With the rapid development of optical communication, people have the higher demand for the photoelectron device and light storage medium. Not only the rapid response but also the larger third-order nonlinear susceptibility for materials is needed.

Sheik-Bahae et al (1989) presented a simple yet highly sensitive single-beam experimental technique for the determination of both sign and magnitude of non-linear refractive index (n_2). They demonstrated this method on 1mm thick CS_2 cell and 2.5mm thick BaF_2 crystal using 300 ns pulses from a single-longitudinal-mode TEA CO_2 laser and frequency- doubled Nd:YAG laser respectively. They concluded that the simplicity and sensitivity of the technique makes it attractive as a screening test to give the sign, magnitude, and order of nonlinear response of new nonlinear optical materials. Sheik-Bahae et al (1990) reported a sensitive single-beam technique for measuring both the nonlinear refractive index and nonlinear absorption coefficient in a detail and demonstration its applicability to variety of materials. They obtained nonlinear refraction in a number of materials such as CS_2 and transparent dielectrics at wavelength of 532 nm, 10.6 μm and 1.06 μm. In cases where nonlinear refraction is accompanied by nonlinear absorption, they have evaluated the nonlinear refraction as well as nonlinear absorption by performing a second z-scan with aperture removal. They demonstrated this method for ZnSe at 532 nm where two-photon absorption was observed and absorption coefficient was found as 5.8 cm/GW, which is in good agreement with previously measured value of 5.5 cm/GW.

Yin et al (2000) reported a simplified Z-scan technique based on a study on the symmetry features of a typical Z-scan curve. The contributions from two-photon absorption (TPA) and nonlinear refraction (NLR) were separated easily from a closed-aperture Z-scan curve using this method on ZnSe, CdS and ZnTe semiconductors with 120-fs laser pulses. They used this method to determine TPA coefficient independently of the uncertainty of focus, from which they calculated the focus of the laser accurately. Minjoung Kyoung et al (2000) studied the nonlinear optical properties of Au:TiO₂ composites, using Z-scan technique. The sample exhibited a self-defocusing. They obtained the sign and magnitude of χ(3) by shifting data to the theory.

Brzozowski et al (2001) reported the third-order non-linearity of azobenzenes and related performance parameters using Z-scan and degenerate four wave mixing (DFWM). They found sign and magnitude of kerr coefficient n₂ as well as two-photon absorption by closed and open Z-scan methods. They noted that DFWM allows easier analysis of the temporal characteristics of the non-linear mechanism than Z-scan but does not reveal the sign of the non-linearity.

Xiaodong Liu et al (2001) studied the features of the closed aperture (CA) Z-scan transmittance curves in detail when the third-order non-linear refraction and absorption, both of which can be independently positive
or negative, are simultaneously present. They found that, whether the peak-valley or valley-peak structure exist or not depends on the ratio of the imaginary part $\chi_I^{(3)}$ to the real part $\chi_R^{(3)}$ of the third order nonlinear susceptibility $\chi^3$ which are caused by nonlinear refraction and absorption respectively.

Nalda de et al (2002) measured the nonlinear refractive index and absorption coefficient of the Cu:Al$_2$O$_3$ films on glass substrates by Z-scan technique. Venugopal Rao et al (2002) reported the experimental results of the nonlinear absorption and excited static dynamics in Rhodamine B in methanol at 532 nm, and 600 nm, using the standard Z-scan and degenerate four wave mixing techniques. They observed saturable absorption at 532 nm and a transition from saturable absorption to reverse saturable absorption at 600 nm with increase in either intensity or concentration.

Umakanta Tripathy et al (2002) studied optical non-linearity of 5,5’-dichloro-11-diphenyl-amino-3,3’-diethyl-10,2-ethylinethiatricarbocyanine perchlorate (IR140) in dimethyl sulphoxide using a single beam transmission technique. They found nonlinear parameters using Z-scan technique.

Liu Zhi-Bo et al (2003) analyzed the influence of nonlinear absorption on the determination of nonlinear refraction by Z-scan. They carried out experiments on CS$_2$ solution of C$_{60}$ derivative. Ji et al (2003) investigated the linear and nonlinear optical properties of a new amphiphilic conjugated polymer, hydroxylated pyridyl para-phenylene (Py-PhPPP), both in CH$_2$Cl$_2$ solution and coated on quartz substrate. They used Z-scan technique with nanosecond laser pulses of wavelength ranging from 430 to 600 nm, and observed a large nonlinear absorption and refraction and determined in the same terms of the effective third-order nonlinear-optical susceptibilities.
Ruilong Zong et al (2004) deduced the sign and magnitude of the three-order nonlinear refraction and absorption of optically transparent Hg nanorods/ anodic alumina membrane (AAM) composite film from the two transmittance curves (Z-scan) measured with or without a finite aperture in the far field, and they found that the technique offers simplicity as well as high sensitivity.

Thomas Olivier et al (2004) presented the results of Z-scan studies carried out on fused silica at 1064 nm and 532 nm with two different nanosecond pulse duration. They obtained higher value of the non-linear refractive index than in the femtosecond regime and showed that these values depend on pulse duration, which indicates the contribution of nanosecond mechanisms like electrostriction.

Del Nero et al (2005) described experimental and theoretical studies of the third-order nonlinear optical coefficients of methyl orange solutions under different PH conditions. They obtained the experimental data using the Z-scan technique for the third-order nonlinear optical properties of this compound which allowed them to determine the nonlinear refractive index and nonlinear absorption coefficient under picosecond excitation in the visible spectral region.

Review of literature shows that there have been much less work carried on the study of nonlinearities of dyes in solid medium. Further studies on the optical non-linear characteristics of solid medium will lead to synthesis and fabrication of new elements, which have potential applications in optical limiting, bistability and optical storage devices. Dyes chosen for our studies are cresyl violet, crystal violet, malachite green, methyl orange, acridine orange, LD473, night blue, victoria blue, congo red and methylene blue. In order to get a deeper insight into the understanding of dyes, a study on its spectral characteristics become important. Hence, we have chosen these dyes
exhibiting nonlinearity, from the different dye families. Due to the high laser damage resistance and optical homogeneity of PMMA, it ranks first as a host material. In order to attain high laser damage resistance, PMMA is modified with solvents. The solvent chosen for modifying PMMA is moderately polar, non-protic solvent (n-Butyl acetate). The study of the nonlinearity of these dyes in solid and in liquid are carried out using Z-scan method proposed by Sheik-Bahae et al (1990) and the result are intercompared. Material characterization of the synthesized dye doped polymer rod is studied by Thermogravimetric analysis (TGA), Fourier Transform Infra-Red spectroscopic analysis (FTIR) and Microhardness testing using Vicker’s microhardness tester. The results are compared with the PMMA rod.

Further steady state fluorescence and absorption measurements have been made to provide additional data for understanding the spectral behavior of dyes in solid medium. The spectral parameters such as molecular absorption coefficients, oscillator strength, bandwidth, fluorescence bandwidth and Stoke’s shift of dyes are calculated from absorption and fluorescence spectra. The fluorescence quantum yields of the dyes in solid and liquid medium are experimentally determined. The fluorescence lifetime of the dyes in solid and liquid medium is experimentally determined using time correlated single photon counting technique. The radiative and non-radiative decay constants are also calculated.

In order to understand the lasing characteristics of these dyes, the general properties of laser dyes becomes important. Hence the general properties of laser dye, energy level diagram and solvent effects are presented in the following sections.
1.4 GENERAL PROPERTIES OF ORGANIC DYES

Organic dyes are unsaturated hydrocarbons containing conjugated double bonds and have a high absorption in the ultra-violet and visible part of the spectrum. In the dye molecule, bonds are formed by $\sigma$ electrons and $\pi$ electrons. The $\sigma$ electrons are characterized by the rotational symmetric of their wave function with respect to the bond direction. i.e., the line connecting the two nuclei that are linked by the bond. The $\pi$ electrons are characterized by a wave function having a node at the nucleus & rotational symmetry along a line through the nucleus and normal to the plane subtended by the orbital of the 3 $\sigma$ electrons of the carbon or hetero atom. A $\pi$ bond is formed by the lateral overlap of the $\pi$ electron orbitals which is maximal when the symmetry axes of the orbitals are parallel.

The various possible electronic transitions of the dyes are $\pi-\pi^*$, $\sigma-\sigma^*$ and n-$\pi^*$. Of these transitions, $\sigma-\sigma^*$ transitions occur in the wavelength region of about 200nm or less, the dye molecule tends to disassociate the photochemically when excited to energies corresponding to this wavelength region. The n-$\pi^*$transition occurs in the near UV or visible region. But this transition is very weak. The $\pi-\pi^*$ transition also occurs in the near UV or visible or in the near IR region and this transition is strong. Dyes generally have a strong absorption and emission transitions in the near UV or visible or in the IR region. This makes $\pi-\pi^*$ transition of the molecule more probable in laser processes.

1.4.1 Energy levels and transition in organic dye molecules

A dye molecule contains a large number of atoms and will have a number of possible energy states due to electronic, vibration and rotational motions. Therefore, the complete energy level diagram will be complicated. The electronic transitions of large complex molecules can be represented by
Jablonski diagram as shown in Figure 1.1, which gives the configuration of the state in terms of one coordinate only.

The energy levels of the organic molecules are named as single when the total spin becomes zero and an triplet states when the total spin is unity. In general, dye molecules have pairs of electrons in the ground state.

Figure 1.1  Energy level diagram of a dye molecule
and the total spin is zero. And due to this, there exists only singlet ground states \( (S_0) \). When the molecule is excited, one of the electrons in the \( \pi \) electrons cloud goes to the higher electronic state. In the excited state, the electrons may have its spin either parallel or anti-parallel to the ground state. Due to this both the singlet and triplet states exist in the excited states are designated as \( S_1, S_2, \ldots, S_n \) and \( T_1, T_2, \ldots, T_n \) respectively. The triplet state is lower in energy than the corresponding singlet state (Parker 1968). Each electronic state has many vibrational and rotational states, which are represented by horizontal lines in each electronic state.

Electronic transition between the singlet- singlet or triplet-triplet states are allowed, but between singlet and triplet are forbidden. The energy gap between \( S_1\) and \( S_2 \) or \( S_2\) and \( S_3 \) or \( T_1\) and \( T_2 \) excited states is less. As a result, vibrational levels of one state \( (S_1) \) overlap with those of the other \( (S_2) \). This leads to a strong non-radiative decay to lower states by vibrational relaxation, when the molecules are excited to higher energy states such as \( S_2, S_3 \) etc. This takes place in time duration of the order in pico seconds. The non-radiative process between the singlet-singlet or triplet-triplet states is termed as internal conversion.

For a dye molecule, the energy gap between \( S_1 \) and \( S_2 \) will be high compared to those between other higher states and internal conversion in weak. A radiative transition occurs between them. This emission is termed as fluorescence. The transition from singlet to triplet or vice-versa is termed as intersystem crossing. Some of the molecules in \( S_1 \) may decay non-radiatively to the triplet state \( T_1 \). This tripping of spin of the molecules in the excited states due to the perturbation arising out of spin- orbit coupling which increases with the number of atoms in the molecule and also with the atomic number of the atoms constituting the molecule. The radiative transition between \( T_1 \) and \( S_0 \) states is termed as phosphorescence, which is forbidden.
and weak. Hence $T_1$ is usually a metastable state. The lifetime of the triplet state $T_1$ is in the range of milli seconds to seconds depending upon the environment of the molecule. However, in liquid media, the molecule in $T_1$ decays to $S_0$ non-radiatively in 100 ns due to collisions with solvent molecules at room temperature.

The absorption and emission spectra of dyes are broad bands. The broad band characteristics are due to the vibrational structure and the change in the inter nuclear distances on excitation. The minima of $S_1$ and $S_2$ states have different configuration coordinates. This causes the emission peak to be shifted to the longer wavelength side of the absorption peak. This shift is called the Stoke’s shift. A number of factors can influence the absorption & emission processes between $S_0$ and $S_1$ states by causing changes in the magnitude of the various competing processes (Parker 1968, Birks 1970, Mataga and Kuboto 1970, Becker 1969, Schafter 1975).

1.5 SOLVENT EFFECTS ON ENERGY OF ELECTRONIC STATES

The nature and the energy of the electronically excited states of a dye molecule determine the photo-physical & photochemical properties of a dye molecule. The effect of solvent media on the energies of electronic states of solute molecule, i.e., an electrostatic interaction between solute & solvent particles, known as “solvation”, is of considerable importance in photo-physics and photo-chemistry.

When a dye is dissolved in a solvent, the solvent molecules arrange themselves around the dye molecule in such a way as to minimize the energy of the system. The dye molecule undergoes interactions with these solvent molecules and attains thermal equilibrium.
The interaction between the dye molecule and the solvent molecule can be broadly divided into two types. They are the long-range and short-range (specific) interactions.

### 1.5.1 Long-Range Interactions

The long-range interaction between the dye molecule & the solvent molecule arises due to electrostatic forces between them. This interaction varies inversely with the square of the distance. This can be further subdivided as follows:

1. (i) between polar dye and polar solvent (dipole-dipole interactions),

2. (ii) between polar dye and non-polar solvent (dipole-induced dipole interaction),

3. (iii) between non-polar dye and polar solvent (induced dipole-dipole interaction),

4. (iv) between non-polar dye and non-polar solvent (induced dipole-induced dipole interaction).

Each interaction leads to a stabilization of the energy of the excited state, which results in a red shift in the absorption and fluorescence spectra, depending upon the strength of the interaction, in varying proportions. It is observed that when the polarity of the solvent increases, the absorption and fluorescence spectra show a red shift. This is due to the stabilization of the molecule in energy due to the reaction field of the surrounding solvent molecular acting on it. The reaction field arises from the orientation and inductive polarization of the solvent molecule owing to the solute dipole. Each electronic state has a well-defined charge distribution, dipole moment,
molecular configuration etc. Due to this, the strength of the long-range interaction will vary from state to state.

A Dye molecule excitation results in a recorded electron distribution. The process is instantaneous (< 10\(^{-15}\) sec) and the solvent molecules in the cage reorient themselves to conform to the new electronic distribution of the excited molecule. Solvent cage rearrangement or relaxation takes place in times of the order of 10\(^{-11}\) s, which is rapid compared to the lifetime of the lowest excited singlet state (around 10\(^{-9}\) – 10\(^{-8}\) sec). Consequently fluorescence originates from the excited solute molecules in a thermal equilibrium state and shows a red shift. This state is lower than the lowest vibrational state of \(S_1\).

The shift is the absorption and fluorescence spectra due to the long-range interactions between the solute and solvent molecule can be related to solvent polarity parameter.

\[
\Delta f = \frac{\epsilon - 1}{2\epsilon + 1} - \frac{n^2 - 1}{2n^2 + 1} \tag{1.1}
\]

which depends on the dielectric constant \(\epsilon\) and refractive index \(n\) of the solvent.

1.5.2 Specific interactions

The specific interaction arises from the overlap of electron densities of the interacting molecules. This interaction gives rise to new molecular species which may be formed in ground state or in the excited state. This interaction may be between one or two molecules of the same type or of different type. Since these interactions are stronger than the long-range interaction, the electronic spectra exhibit considerable shift in wavelength (Mataga and Kuboto 1970, Becker 1969)
Some examples of short-range interactions:

(a) An aggregation in ground state (dimmers) or in the excited state (excimers) or in both.

(b) A complex formation between different molecules in the ground.

(c) A complex formation between different molecules in the excited state (exciplex formation).

(d) An acid-base interaction in the ground state or in the excited state.

1.6 NONLINEAR OPTICS

1.6.1 The concept of Nonlinearity in Optics

The birth of nonlinear optics occurred at the same time as that of laser, in early 1960’s. Nonlinearity is a property of the medium through which light travels rather than a property of the light itself.

Nonlinear optics deals with interaction of light of high intensity with matter, resulting a considerable alteration of the properties of matter itself.

When light beam propagates through a medium, the oscillating electromagnetic field induces an electric polarization on all the electrons comprising the medium. Since the inner electrons of the atom are tightly bound to the nuclei, the major polarizing effect is exerted on the outer electrons. With ordinary light sources the radiation fields are much smaller than the fields that bind the electrons to the atoms. Hence, the radiation acts as small perturbation. This produces a polarization that is proportional to the electric field of the light wave. However, when the radiation field is
comparable with the atomic fields, \(10^8 \, \text{V/cm}\) the relationship between the polarization and the field is no longer a linear one.

### 1.6.2 Nonlinear Optical Phenomena

The requisite light field required to exhibit the non-linearity are obtainable with lasers. The relation between the polarization \(P\) and the electric field \(E\) is a linear one when \(E\) is small, but becomes comparable with the interatomic fields.

The nonlinear polarization can be written in a power series expansion as

\[
P = \varepsilon_0 \left\{ \chi^{(1)} E + \chi^{(2)} E^2 + \chi^{(3)} E^3 + \ldots \right\}
\]  

(1.2)

Where \(E\) is the total electric field which is made up of a number of different frequencies, polarizations, \(k\) vectors etc and \(\chi^{(n)}\) is the \(n^{th}\) order susceptibility. This expansion is often written as a sum of two terms

\[
P = P^L + P^{NL}
\]

(1.3)

Where linear polarization is

\[
P^L = \varepsilon_0 \chi E
\]

(1.4)

and nonlinear polarization is

\[
P^{NL} = \varepsilon_0 \chi^{(2)} E^2 + \varepsilon_0 \chi^{(3)} E^3 + \ldots
\]

(1.5)

Linear terms:

The linear optical susceptibility \(\chi^{(1)}\) governs the linear optical properties of a medium such as index of refraction, absorption, gain, birefringence etc. The index of refraction contains the essential information
about the macroscopic properties of the medium, is usually denoted by a single number and is sufficient for describing the linear optical properties. These properties constitute the subject of Classical objects.

Second Order Terms:

Second order effects are primarily parametric in nature, i.e., the interaction of light waves with matter do not involve transfer of energy to or from the medium. These include:

- Second Harmonic Generation (SHG),
- Optical Rectification,
- Parametric mixing,
- Pockel’s Effect.

Because of symmetry restriction, the even order susceptibilities vanish in materials with inversion symmetry. As a result, these effects are commonly observed only in crystals that lack inversion symmetry.

Third Order Terms:

The $\chi^{(3)}$ effects take place in all materials irrespective of their symmetry. Third order parametric processes are also used for frequency conversion. Third order processes can be observed with electric dipole interactions in materials that have center of symmetry, such as gases, liquids and some solids, since in these materials they are the lowest order non-zero nonlinearities allowed by electric dipole transitions. Included among these are
Third Harmonic Generation (THG)
Non-degenerate Four-Wave Mixing
Stimulated Raman Scattering (SRS)
Stimulated Brillouin Scattering (SBS)
Degenerative Four Wave Mixing (DFWM)
Two-Photon Absorption (TPA)
Self-focusing

SBS, SRS, DFWM are the most widely used third order technique for generating phase conjugate beams for various applications as well as for characterizing the nonlinear optical behavior of different media.

1.6.3 Significance of Nonlinear Optical (NLO) Phenomena

The scope of nonlinear optics includes all phenomena in which the optical parameters of materials are changed with irradiation of light, resulting from the contributions of higher order susceptibility. The impact of NLO on Science and Technology has been two fold. First it has enhanced our understanding of fundamental light-matter interactions. Second it has been a driving force in rejuvenation of optical technology for several areas of science and technology especially in the areas of communication, control and computing. Some of the important applications of NLO phenomena are parametric mixing which is used for developing tunable solid state lasers, optical bistability to develop photonic switching and optical limiting for radiation protection. The bottleneck in present day photonics technology is in developing ideal materials in which all these can be realized effectively.

Nonlinear Optical effects (direct or indirect) may be used to make all optical switches. A switch is a device that establishes and releases
connections among transmission paths in a communication or signal processing system. The electronic switches are used to switch electrical signals.

Optical storage of data has been one of the brightest spots in technology for the past decade. This is because optical memories store huge amount of data and the time taken to read these memories is of the order of speed of light. The main feature of holographic memories is that they are associative in nature, the reading time is less and the information can be accessed by non-mechanical means.