1

PROPERTIES OF ORGANIC DYES

1.1 INTRODUCTION

The most important characteristic of organic dyes, used as laser active material, is its tunability. Its qualities of continuous tunability, efficient narrow band operation, wide spectral range and simplicity have made it an indispensable tool for research in the optical investigation of matter. Since the discovery of the dye laser by Scrokin et al.\(^1\) in 1966, this field has progressed rapidly into an advanced technology.

Organic dyes, according to commonly accepted terminology, are a class of colored substances which are useful for their ability to impart color to other substances. Presently, the definition is broadened to include organic compounds which have a strong absorption band somewhere from the ultraviolet to the near infrared. Organic compounds with this property contain an extended system of conjugated bonds. These multiple bonds not only have a profound effect on chemical reactivity, but also influence the spectroscopic properties. Organic compounds without double or triple bonds usually absorb at wavelengths below 160 nm, corresponding to a photon energy of 180 Kcal/mole. This energy is higher than the dissociation energy of most chemical bonds, therefore photochemical decomposition is likely to occur, so such compounds are not suitable as active media in lasers. In unsaturated compounds, all bonds are formed by \(\sigma\) electrons; these are characterised by the rotational symmetry of their wave function with respect to their bond direction. Double and triple bonds also contain a \(\sigma\) - bond, but in addition use \(\pi\) electrons
for bonding. The π electrons are characterised by a wave function having a node at the nucleus and rotational symmetry along a line through the nuclear and normal to the plane subtended by the orbitals of the three σ electrons of the carbon or heteroatom. A π bond is formed by the lateral overlap of the π-electron orbitals, which is maximal when the symmetry axes of the orbitals are parallel. Hence, in this position, bond energy is highest and the energy of the molecule is minimal, thus giving a planar molecular skeleton of high rigidity. The basic mechanism responsible for light absorption by compounds containing conjugated double bonds is the same, in whatever part of the spectrum these compounds have their longest wavelength absorption band, whether near-infrared, visible or near-ultraviolet.

The broad tuning range made available by using different dyes as active media enables one to cover almost the entire visible range. Coumarin dyes emit in the blue-green region and xanthene dyes emit in the yellow-red region. Figure 1.1 illustrates the tuning range of various dye molecules.

\[ \text{Figure 1.1 Tuning Range of Various Classes of Organic Dyes} \]

1.2 ENERGY LEVELS OF A TYPICAL DYE MOLECULE

The dye molecule has two groups of states, the singlet states \((S_0, S_1, S_2 \ldots)\) and the triplet states \((T_1, T_2 \ldots)\). The singlet states occur when the
total spin of the excited electron; in each molecule is equal to zero. The triplet states occur when the total spin is one. Singlet-triplet and triplet-singlet transitions are far less likely than transitions between two singlets or between two triplet states. A simplified energy level diagram showing the important transitions is shown in Figure 1.2. The dye laser is pumped by the absorption of photons, which excite the molecules from the ground state $S_0$ to the first excited state $S_1$. There is a very rapid decay by a non-radiative process to the lowest energy states of $S_1$. The laser transition occurs between a state near the bottom of $S_1$ and an intermediate state $S_0$. Since there are many vibrational rotational sublevels within $S_0$ and $S_1$, the resulting emission line is very broad. The triplet states $T_1$ and $T_2$ are not involved directly in the laser action, but they have a pronounced effect in hindering the efficiency of laser action.

Figure 1.2  Schematic diagram of the energy levels of a typical dye molecule
1.3 **ABSORPTION AND EMISSION SPECTRUM**

The long wavelength absorption band of dyes is attributed to the transition from the electronic ground state $S_0$ to the first excited singlet state $S_1$. The transition moment for this process is typically very large, thus giving rise to an absorption band with an oscillator strength of the order of unity. The reverse process $S_1 \rightarrow S_0$ is responsible for the spontaneous emission known as fluorescence and for the stimulated emission in dye lasers. Because of the large transition moment, the rate of spontaneous emission is rather high (radiative life time is of the order of nano seconds) and the gain of the dye laser may exceed that of a solid state laser by several orders of magnitude. When the dye laser is pumped, the dye molecules are excited typically to some higher level in the singlet manifold, from which they relax within pico seconds to the lowest vibronic level of $S_1$ i.e the upper lasing level. For optimum lasing efficiency, it would be desirable for the dye molecules to remain in this level until they are subjected to the stimulated emission. However, there are many non-radiative processes that can compete effectively with the light emission and thus reduce the fluorescence efficiency to a degree that depends in a complicated fashion on the molecular structure of the dye. In the ideal laser dye, these processes should be negligible so that the quantum yield of fluorescence has the highest possible value. An efficient laser dye in its first excited singlet state also should have negligible absorption at the wavelength of the pump lights and of the laser emission as well.

When a dye is excited by an external source of short wavelength light, it emits radiations at longer wavelengths. The energy difference between the absorbed and emitted photon is accounted by a non-radiative transition in the dye, in the form of heat. The absorption and emission spectrum of a typical laser dye (Rh 6G) is shown in Figure 1.3. The fluorescence curve extending much of the yellow and red portions of the spectrum is shifted to longer
wavelengths compared to that of the absorption curve in the green and yellow. The dye fluorescence covers an extremely broad band of visible frequencies which can be explained by its energy level scheme.

Figure 1.3  Absorption and Emission Spectrum of a typical laser dye (Rh 6G)

1.4 PUMPING OF DYE LASERS

All dye lasers are optically pumped. The pumping requirement is that the pump light source must have an output near the peak of the absorption band of the dye. By the nature of the dye, the laser output occurs at wavelengths longer than that of the excitation source. For a dye fluorescing in the deep blue, a pump source with ultra violet output is required. Flash lamp comparable in rise-time and intensity to giant pulse ruby lasers are developed for pumping dye lasers. It is also possible to pump dyes using Nitrogen laser or Argon ion laser as sources. Because of the extremely high small signal gain of most laser dyes, only a small amount of active medium is needed. However, the intense absorption and subsequent heating of the small volume of the dye and the rapid build up of the triplet state population necessitates a continuous and rapid change of the pumped volume. Failure to do so produces a heated dye that
decomposes, resulting in increased absorption losses for the systems. The spectral width of the dye laser output depends mainly on the passive band width of the resonator and the number of light passes taking place in the resonator. The band width is determined by the angular dispersion of the wavelength selection and the divergence of the dye laser beam incident on it. For wavelength selection, tuning elements such as gratings and prisms are used. For narrower line widths and single mode operation, interferometric devices, usually FP etalons are used in conjunction with the above tuning elements both for CW and pulsed dye lasers.

1.5 INTERACTION OF LASER RADIATIONS WITH ORGANIC DYES

The interaction of laser radiations with organic dyes and the subsequent photophysical processes taking place are discussed with the help of the general energy level scheme of a dye molecule. The schematic diagram of the general energy levels of a typical dye molecule in solution is given in Figure 1.2. A manifold of singlet electronic states $S_0, \ldots, S_n$ and triplet $T_1, \ldots, T_n$ exist, of which the important states required for the description of the interaction of radiation with dyes are shown. Each electronic state has a number of vibrational levels superimposed on it. For dye molecules, the average separation between the vibrational levels is generally in the 1200-1600 cm$^{-1}$ range. In addition, each vibronic level is characterised by closely spaced rotational levels superimposed on it. These rotational levels are broadened by frequent collisions with solvent molecules and form a near continuum between each vibrational level. This gives rise to the characteristic broad, absorption and emission bands in the electronic spectra of dye molecules in solution. If the ground state $S_0$ of the molecule is in thermal equilibrium with its surroundings, then at room temperature ($kT \sim 200$ cm$^{-1}$) most of the molecules are in the lowest vibrational level of $S_0$. Thus, in the absorption process, the molecule is
raised from the lowest vibrational level of S₀ to various rotational vibrational levels of the excited singlet states S₁ . . . Sₙ.

In Figure 1.2, the straight vertical arrows denote the optical absorption and radiative emission processes. The radiative emission of the singlet state S₁ is called fluorescence and that of the triplet state T₁, phosphorescence. The horizontal arrows designate the non-radiative transition processes of internal conversion (IC) and intersystem crossing (ISC). The wavy arrows indicate the vibrational relaxation processes.

Depending on the wavelength of excitation, the molecule may be excited to the first excited singlet state S₁ or higher excited singlet states Sₙ (n > 1). Deexcitation of an excited dye molecule takes place through fluorescence emission or through various non-radiative processes. The relative probabilities of these different modes of deexcitation are governed by the structure of the dye and the properties of the solvent used. Fluorescence is found to occur in almost all dyes from the lowest vibronic level of S₁. This indicates that for most dyes, the fluorescence process is independent of the initial electronic state Sₙ or the initial vibronic level of S₁ to which the molecule may be excited. This is due to the fact that a rapid non-radiative transition (internal conversion) occurs between Sₙ and S₁ usually in times of the order of 10⁻¹¹ - 10⁻¹² s. Vibrational relaxation in the S₁ state also occurs in times of the order of pico seconds. These times are very short in comparison to the life time of the S₁ state which is of the order of nanoseconds. Therefore, the fluorescence quantum efficiency, the fluorescence spectrum and the fluorescence life time of the most dye molecules are independent of the wavelength of excitation. The excitation process S₀ → Sₙ (n > 1) is undesirable for a dye laser as compared to the excitation to S₁ state, because of the large amount of energy that would be dissipated as heat in the subsequent Sₙ → S₁ relaxation. Fluorescence (and hence stimulated emission) takes place from the lowest vibronic level of S₁ to
various vibrational-rotational levels of $S_0$. Fast vibrational relaxation brings the molecule back to the lowest vibronic level of $S_0$. The other important processes are (1) inter-system crossing $S_1 \rightarrow T_1$ and subsequent $T_1 \rightarrow T_n$ absorption at pump or laser wavelengths (2) the excited state absorption from $S_1$ to $S_n$ which may also occur at the pump or laser wavelength. Both these processes have a profound influence on the performance of the dye laser.

1.6 EFFECT OF TRIPLET STATE

In the case of flash lamp on CW laser pumped dye lasers, triplet states become important because of the long rise time or duration of the pump light pulse. The triplet state has a very long lifetime compared to the singlet state. It is observed that there is a maximum in the excited singlet state population density $n_1$ which is reached while the pump light intensity is still rising. This maximum is higher for a faster rise of the pump light and also for a higher quantum yield of fluorescence. Despite the continuing rise of the pump light intensity, $n_1$ falls to a low value after passing the maximum since the ground state becomes depleted and virtually all of the molecules accumulate in the triplet state. Thus a dye laser may be pumped above threshold by a fast-rising light source. Also, the molecules accumulated in the triplet state gives rise to triplet-triplet absorption spectra which very often extend into the region of the fluorescence emission. The triplet population density can be reduced to a sufficiently low level by reducing the lifetime of the triplet state. This is achieved by adding to the dye solution suitable molecules that enhance the intersystem crossing rate from the triplet to the ground state. Unsaturated hydrocarbons are used as triplet quencher. Here, the energy transfer occurs in such a way that energy as well as spin is exchanged between the dye and the acceptor molecule. In a dye molecule, where the $\pi$ electron of the chromophore can make a loop when oscillating between the end groups, the triplet yield will be higher than in a related compound where this loop is blocked.
The oscillating electrons create an orbital magnetic moment which couples with the spin of the electrons. This increased spin-orbit coupling thus enhances the rate of intersystem crossing, thus giving rise to a higher triplet yield.\textsuperscript{10} Triplet and singlet energy levels, their spin states and intersystem crossing are shown in the Figure 1.4. The internal conversion and loss of vibrational energy are shown as wavy lines.

![Figure 1.4](image)

1.7 NON-RADIATIVE PROCESSES

There are many non-radiative processes that can compete effectively with the light emission and thus reduce the fluorescence efficiency to a degree that depends in a complicated fashion on the molecular structure of the dye. These non-radiative processes can be grouped into those that cause a direct
relaxation to the ground state $S_0$ (internal conversion) and those that are responsible for intersystem crossing to the triplet manifold. Because of the relatively long lifetime of the triplet molecules (micro seconds), the dye accumulates during the pumping process in the triplet state $T_1$ which often has considerable absorption for the laser light. Thus not only are some of the dye molecules taken away from the lasing process, but owing to the triplet-triplet absorption, they cause an additional loss in the laser. The non-radiative decay to the ground state is comparatively less harmful for laser action. Also an efficient laser dye in its first excited singlet state should have negligible absorption at the wavelength of the pump light and of the laser emission as well. Otherwise, losses would occur, as in triplet-triplet absorption, because the decay to the first excited singlet or triplet level is non-radiative.

The laser dye should have an absorption spectrum which matches the spectral distribution of the pump source. Since a substantial part of the light energy emitted by flash lamps is in the ultra violet region, only dyes with moderate to strong absorption throughout this region can take full advantage of the pump light. If, on the other hand, the pump source is a laser with monochromatic emission, the dye should have a strong absorption at this wavelength. Although, in principle, a small absorption coefficient can be compensated for with a higher concentration. This is often not desirable because it also increases the absorption at the lasing wavelength, thus enhancing the cavity losses. In order to achieve a broad tuning range, these dyes are required that have an unusually wide fluorescence band; or mixtures of dyes that absorb at the same wavelength but fluoresce with different stokes shifts. Fluorescent dyes that react in the excited state to form a fluorescent product that is unstable in the ground state can be considered ideal for this purpose. Here, the concentrations may be adjusted so that the gain in the regions of fluorescence of the original dye and its reaction product are approximately equal. Following the emission of light, the reaction product
dissociates immediately and no additional absorption interfering with the lasing process encountered, such as is likely to be the case in a mixed solution of several dyes.

Inevitably during the lasing process a certain amount of thermal energy is released giving rise to temperature gradients in the solution that may cause optical inhomogeneities. Water and heavy water are the best media in this respect. Therefore the ideal laser dye should be soluble in water and still maintain its lasing properties.

1.8 INTERNAL CONVERSION

The non-radiative decay of the lowest excited singlet state $S_1$ directly to the ground state $S_0$ is mostly responsible for the loss of fluorescence efficiency in organic dyes. Depending on the molecular structure of the dye and the properties of the solvent, the rate of relaxation can vary by many orders of magnitude. Since there are several different structural features that contribute to the non-radiative decay $S_1 \rightarrow S_0$, the relation between the molecular structure and fluorescence efficiency can be puzzling. In general, the structural mobility increases the rate of internal conversion and a dye with a high rigidity will have high fluorescence.

1.9 STABILITY OF DYES-TEMPERATURE DEPENDENCE

The thermal and photochemical stability of dyes is of very importance for laser applications. These properties, however, vary so widely with the chemical structure that practically no general valid rules can be formulated. Thermal stability is closely related to the long wavelength limit of absorption. A dye absorbing in the near infrared has a low lying excited singlet state and even slightly lower than that, a meta stable triplet state. The triplet state has two unpaired electrons and thus, chemically speaking, biradical character. There is a good reason to assume that most of the dye molecules that reach this highly
reactive state by thermal excitation will react with the solvent molecules, dissolved oxygen, impurities or other dye molecules to yield decomposition products. The decomposition would be of pseudo-first order with a reaction constant

\[ k_1 = A \exp\left(-\frac{E_A}{RT}\right) \]

where \( A \) is the Arrhenius constant and has most often a value of \( 10^{12} \, \text{s}^{-1} \) for reactions of this type \( (10^{10} - 10^{14} \, \text{s}^{-1}) \).

\( E_A \) is the activation energy

\( R \) is the gas constant and

\( T \) is the absolute temperature.

The half-life of such a dye in solution is

\[ t_{1/2} = \ln 2/k_1. \]

Assuming a minimum practical lifetime as one day, the above relations yield an activation energy of 24 KCal/mole corresponding to a wavelength of 1.2 \( \mu \text{m} \). If \( A = 10^{10} \, \text{s}^{-1} \) this shifts the wavelength to 1.7 \( \mu \text{m} \). If we assume that a year is the minimum useful half life of the dye (and \( A = 10^{12} \, \text{s}^{-1} \)) we get a wavelength of 1.0 \( \mu \text{m} \).

1.10 WAVELENGTH LIMITS

Obviously, it becomes more and more difficult to find stable dyes having the maximum of their long wavelength band of absorption in the infra red beyond 1.0 \( \mu \text{m} \) and there is a little hope of ever-preparing a dye absorbing beyond 1.7 \( \mu \text{m} \) that will be stable in solution at room temperature. Thus dye laser operation at room temperature in the infra red will be restricted to wavelengths not extending far beyond 1.0 \( \mu \text{m} \). The short wavelength limit of dye laser operation is given by the absorption of dyes containing only two conjugated double bonds and having their long wavelength absorption band at
wave lengths of about 220 nm. Since the fluorescence and hence the laser emission is always red shifted, dye lasers can hardly be expected to operate at wavelengths below about 250 nm. At this wavelength, however, photochemical decomposition already competes effectively with radiative deactivation of the molecule, since the energy of the absorbed quantum is higher than the energy of any bond in the molecule. The temperature dependence of the dye laser wavelength is that the laser emission is shifted towards shorter wavelengths with decreasing temperature.

1.11 ENVIRONMENTAL EFFECTS

The surroundings of the dye molecules affect the rates of non-radiative as well as radiative processes to a considerable degree.

1.11.1 Influence of solvent

The acidity of the solvent relative to the dye influences the dye laser emission. Many dyes show fluorescence as cations, neutral molecules and anions. Correspondingly, the dye laser emission of such molecules usually changes with the pH of the solution, since, generally the different ionization states of the molecule fluoresce at different wavelengths. An important subdivision of these dyes is that of molecules whose acidity in the excited state is considerably different from that in the ground state due to the changes of the π electron distribution with excitation. Donor-acceptor charge transfer complex formation between a dye and ε solvent molecule can occur in the ground state as well as in the excited state. The complex is stable only in the excited state and cannot be detected in the absorption spectrum. The rate of complex formation is limited by the diffusion of the two constituents. It is thus proportional to the product of the concentrations and strongly depend upon the
viscosity of the solution. If the excited complex \((A^- D^+)\) is non-fluorescing, the addition of \(D\) to \(A\) results merely in quenching of fluorescence of \(A\). This is generally believed to be a possible mechanism of the so-called dynamic quenching of fluorescence. On the other hand, if the excited complex is fluorescent, a new fluorescence band appears, while the original fluorescence disappears with increasing concentration of \(D\), which might be one of the constituents of a solvent mixture. A methanol solution of a pyrylium dye in a flash lamp pumped laser showed a significant lowering of the threshold and displacement of laser wavelength by 10 nm to the red on addition of a small quantity of dimethyl aniline as a result of the formation of a charge-transfer complex in the excited state. The wavelength coverage of laser pumped dye-laser is determined on the short wavelength side by the shortest available pump laser wavelengths of sufficiently high peak power; on the long wavelength side it is given by the stability of the dyes used. The shortest wavelength of a dye laser reported is 336-360 nm for p-terphenyl in cyclohexane or ethanol pumped by a Nitrogen laser. The near infrared is well covered by nineteen different cyanines and mixtures; 710-1000 nm at powers higher than 1 mw. Pumping a solution of polymethine dye, by a neodymium glass laser yielded a dye laser emission at 1176 nm. At any wavelength between these extreme there are several dyes available that are suitable for laser pumped dye lasers.

1.1.2 Aggregation of dye molecules

Organic dyes in polar solutions have a tendency to form dimers and higher aggregates. The dimers usually have a strong absorption band at shorter wavelengths than the monomers and often an additional weaker band at the
long wavelength side of the monomer band.\textsuperscript{16,17} The equilibrium between monomers and dimers shifts to the side of the latter with increasing dye concentration.\textsuperscript{18} Not only part of the pump light is absorbed by the non-fluorescent dimers, but the dimers also increase the cavity losses owing to the long-wavelength absorption band which is in the same region as the fluorescence of the monomers. An attractive dispersion force between the highly polarizable dye chromophores plays an important role for the aggregation of organic dyes. Also the high dielectric constant of the solution reduces the Coulomb repulsion between the charged molecules leading to the aggregate formation.\textsuperscript{18}

1.11.3 \textit{Excited state reactions}

There is usually a strong interaction between excited molecules of organic dyes and those in the ground state in organic solvents. The fluorescence at higher concentrations is strongly quenched owing to collisions of the excited dye molecules with those in the ground state. Although the fluorescence of the majority of organic compounds is quenched at high concentrations, for some of the dyes, a new band appears when the concentration is increased.\textsuperscript{18-21} This new band is due to dimers that exist only in the excited state (excimers).

Following the emission of a photon, they immediately dissociate into ground state monomers. An excited molecule may also react with a molecule of a different species (of the solvent or other dye molecules in a mixture of dyes) to form an excited complex (exciplex) which on radiative de-excitation decomposes immediately into the components.\textsuperscript{22} Since the ground state of excimers and exciplexes is unstable, these species are ideal lasing compounds, provided the fluorescence efficiency is high and no disturbing triplet effect
Because some compounds become more basic or acidic on optical excitation, they may pick up a proton from the solution or lose one to the solution (protolysis)\(^1\)\(^8\). If the new forms are fluorescent, they have the same advantage as exciplexes.\(^{24}\)

1.11.4 fluorescence quenching by energy transfer

Another mechanism by which excited states, singlet as well as triplet, are quenched externally can operate if the quenching molecule has a level of energy equal to or lower than that of the state to be quenched. Under favourable conditions such energy transfer can occur over distances up to about 10 nm. In liquid solutions, where the molecules can approach each other very closely, energy transfer process are very efficient, provided the diffusion time is shorter than the life time of the excited state. The low-lying excited singlet states and the paramagnetic properties of oxygen are utilised for the quenching of triplet states of the dyes.\(^{25,26}\) Several other compounds have been reported to quench triplets of laser dyes.\(^{27}\) Energy transfer dye lasers are utilised for covering a wide wavelength range of tuning without changing the dye.\(^{28-32}\) Here one of the dyes is excited and the energy is transferred effectively from one to the other and so on. The energy transfer mechanisms involved may be radiative or non-radiative. In radiative type energy transfer, the donor dye emits a photon and it is absorbed by the acceptor. The non-radiative energy transfer can be diffusion controlled or due to long range dipole-dipole interaction.

1.12 hydrogen vibrations

In certain dyes, even if their chromophore is fully rigid and planar, can occur another type of internal conversion. It is independent of temperature and solvent viscosity. It involves the conversion of the lowest vibronic level of the excited state \(S_1\) to a higher vibronic level of the ground state \(S_0\), which then
rapidly relaxes to the lowest vibronic level of $S_0$. The probability for this process is inversely proportional to the change in vibronic quantum number during the conversion. Because of the comparatively small mass of the hydrogen atom, the quantum of hydrogen stretching vibrations have the highest energies in organic dyes and thus hydrogen vibrations are very likely to contribute to the mechanism. It can be expected that only those hydrogen atoms that are directly attached to the chromophore of the dye will influence the non-radiative process $S_1 \rightarrow S_0$. Further more, this mechanism should become increasingly effective with decreasing energy difference between $S_1$ and $S_0$. On the other hand, a replacement of hydrogen by deuterium should reduce the rate of non-radiative decay by this mechanism and thus increase the fluorescence efficiency (Cresyl Violet). This mechanism can be expected to seriously reduce the fluorescence efficiency of infrared dyes.

1.13 OTHER INTRAMOLECULAR QUENCHING PROCESSES

In addition to the mechanism of internal conversion discussed, there are several other intramolecular processes that may cause quenching of fluorescence. For instance, if a part of the dye molecule is strongly electron-donating or withdrawing a reversible charge transfer may occur between this group and the excited chromophore resulting in the loss of electronic excitation. A substituent with a low-lying singlet or triplet state may quench the fluorescence via energy transfer. It is possible that under certain circumstances, the intersystem crossing process $S_1 \rightarrow T_1$ effectively drains the state $S_1$ before the emission of fluorescence.

Excitation with tunable dye laser leads to photo ionization\textsuperscript{19} of neutral atom and molecules. A photon first excites a certain state of the discrete energy spectrum and a second photon then ionizes the excited atoms or molecule. This two step ionization can be highly selective. Pulsed tunable dye lasers of kW power lead to photo detachment of electrons from negative ions.
At laser intensities, quenching of fluorescence results due to bleaching effects and simultaneous multiphoton absorption\(^2\) With an intense pump pulse, transitions to vibronic levels deplete the ground state and reduce the absorption of the sample. This is called bleaching.\(^2\) For life times comparable to or shorter than the pump pulse duration, the excited state lifetime may be inferred from transmission measurements of the pump pulse. The faster the molecules return to the ground state, the more it will be to bleach the dyes. The depopulation of the \(S_1\) state may also be probed by time delayed excited state absorption measurements. If the relaxation time \(\tau_F\) is comparable to or shorter than the pump pulse duration \(\Delta t\) (i.e. \(\tau_F \leq \Delta t\)), the transmission of the pump pulse at a fixed peak intensity depends on the ratio \(\Delta t/\tau_F\) which indicates how often the molecules return to the ground state within the excitation pulse duration. Using pico-second pump pulses the technique is applicable to dyes with pico second recovery times. Such dyes are frequently used as saturable absorbers.

The intensity dependent bleaching of the pump pulse is used to determine the \(S_1\)-state lifetime and the study of triplet states. The molecular size and the solvent viscosity influence the bleaching. The phenomenon of photo bleaching is observed at low laser intensities.

In a two-photon absorption process, two photons are simultaneously absorbed. Being a higher order process, its absorption cross-section is many orders of magnitude smaller than that of a single photon absorption. Even so, two-photon absorption is readily observable with lasers and has become a valuable spectroscopic technique.

The high light intensities available from lasers have opened the way to various new non-linear spectroscopic techniques involving changes of level populations, refractive indices, susceptibilities etc. When molecules are irradiated with monochromatic light, some of the scattered light is shifted from the frequency of the incident light by resonant frequencies of the scatterer. This
inelastic scattering is known as Raman scattering and has become a useful tool for the study of molecular vibration frequencies. The advent of various fixed-frequency lasers has revolutionized the instrumentation of this analytic technique and has stimulated intensive research efforts, in particular, the study of Raman scatterings from lattice vibrations, spin waves or electronic excitation in solids.

Of the different photophysical processes taking place in the interaction of radiation with dyes, photoquenching due to the excited state absorption is very important. This effect occurs when molecules in their excited state again absorb a photon. This photon, in general, through a radiationless process is converted into heat and therefore doesn’t contribute to the yield. The different types of interactions are important in determining the proper pumping conditions and designing laser pumped dye lasers.

1.14 TWISTED INTRAMOLECULAR CHARGE TRANSFER (TICT)

Many organic dye molecules possessing non-rigid structure undergo spontaneous intramolecular rotational relaxation processes in the excited state leading to an energy – minimum far away from the initial geometry which is called adiabatic photoreaction as it occurs entirely in the excited state. In these compounds, two aromatic moieties are linked by a single bond, and excited state rotational relaxation occurs towards a twisted conformation coupled with intramolecular electron transfer. Photophysical properties of many coumarin derivatives have been explained in terms of the formation and stabilization of TICT state. In favourable cases the product of an adiabatic photoreaction is emissive, and thus its properties can be studied conveniently by time-resolved or time-integrated fluorescence spectroscopy. From the kinetic measurements, informations can be drawn as to the medium influence on the reaction rate. Thus, these dyes with a large amplitude motion leading to an
emissive photochemical product are well suited to act as fluorescence probe of the microenvironment.\textsuperscript{45} Even in case where the TICT product is non emissive, the primary excited state is quenched by the photoreactions and its kinetics can still be followed by observing the precursor fluorescence. The product emission is usually strongly red shifted with respect to the emission of the precursor. Therefore, absorption and emission hardly overlap, and reabsorption processes are minimised.

Grabowski's model of TICT formation is shown in Figure 1.5 which illustrates an adiabatic photo reaction leading from an excited precursor with near-planar conformation and strong but incomplete charge transfer (locally excited ‘LE’) to an excited product with twisted conformation and virtually complete charge separation (TICT state). The species with optical gain at short wavelength, for which there exists a corresponding fluorescence band is called the Normal Form (NF). The species producing ASE at longer wavelength is identified with the TICT conformation.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{Grabowski_model.png}
\caption{Grabowski’s model of TICT formation}
\end{figure}

The energy of the TICT states is governed by the electron donor and electron acceptor properties of the subsystems. A convenient measure of these quantities are the ionization potential (IP) and the electron affinity (EA), or oxidation and reduction potentials. Hence the TICT energy can be represented as

\[ E (TICT) = IP (donor) - EA (acceptor) + C + \Delta E_{solv} \]
C and $\Delta E_{\text{solv}}$ are correction factors regarding the Coulombic stabilization by the radical anion or cation attraction in the TICT state and describing the solvent stabilization energy.\textsuperscript{46} The reason for an energy minimum in $S_1$ and a maximum in $S_0$ for the TICT energy is the interaction of the ground with the excited state.\textsuperscript{47}

Although for every twisted bichromophoric system, several TICT states exist corresponding to transitions from different donor to different acceptor orbitals, TICT formation occurs spontaneously only if it is exothermic in $S_1$ i. e. if the energy of the lowest TICT state is below that of the planar LE state, i. e. if the inequality $E(\text{TICT}) < E(\text{LE})$ holds. Usually, $E(\text{LE})$ depends much more weakly on IP and EA than $E(\text{TICT})$ such that by changing IP and/or EA of one or the other subsystems, the driving force for TICT formation can be tuned, and TICT formation can be switched on and off.

The most important properties of TICT states are as follows:

* Normally, the energy minimum of the TICT state occurs for the perpendicular conformation, such that the $\pi$ systems of donor and acceptor are perpendicular and decoupled from each other.

* Because of this decoupling, the fluorescence from TICT states is ‘forbidden’ i. e. weak unless other effects like vibronic coupling with allowed states counteract (which is often the case).

* Triplet and singlet TICT states are expected to be nearly degenerate.

* TICT formation kinetics can be governed by tuning the TICT energy by rigidization of the twisting moieties or ortho-alkyl substitution or incorporation in a rigid matrix (glass or polymer).\textsuperscript{44, 48, 49}

The dominant stabilization of the twisted intramolecular charge transfer state is due to a short range specific interaction with a polar solvent molecule.
A secondary solvent effect arises from a further stabilization of the complex by long range polarization interactions with solvent molecules and makes the electron transfer step energetically favourable. The observation of two bands in the gain spectra (simultaneous dual band superradiance) of some non-rigid dyes in polar solvents is of great interest. The anomalous long wavelength peak formation is attributed to TICT state formation in the excited state. The dominant stabilization of the TICT state is due to the long range specific polarization interaction with polar solvent molecules. The non-radiative decay path ICT → TICT transition is found to be dependent on the dye structure and substituent pattern. It is observed that only dyes having a non-rigid structure exhibit the TICT state in their excited state.

In the work presented here, the effect of Excited State Absorption (ESA) at the laser intensities in transversely pumped, pulsed dye laser amplifier (PDLA) is theoretically examined. It is observed that ESA along with ground state absorption introduces a non-linear loss term in the amplifier equation. The results are interpreted in relation to previous experiments on fluorescence quenching of 7D4MC and Rh 6G dye molecules. The experimental findings reported by Arun Gaur et al. are theoretically reanalysed in terms of the gain factor, threshold pump intensity and efficiency using the coupled differential equations for ground and excited state population given by Speiser et al. The pump power vs gain yields various molecular parameters for CV and FDS molecules. The study reveals the rigid and non-rigid behaviour of CV and FDS dye systems respectively. FDS shows TICT due to its non-rigid structure.

The excitation energy transfer process in two pairs of binary dye systems (1) SF : RhB and (2) SF : CV in ethanol excited by Argon ion laser have been analysed. By the use of the dye mixture, the range of tunability and efficiency are found to be increased. The shift in peak emission wavelengths of
the donor and acceptor is explained. Optical parameters of energy transfer like rate of energy transfer, critical transfer radius, fluorescence line widths, emission cross-sections and gain have been determined. It was established that the dominant mechanism in energy transfer in the binary dye mixture is radiative. A similar experiment is done with a ternary dye mixture system consisting of SF:RhB:CV in ethanol. The tunability range is found to be increased by energy transfer (490 nm to 650 nm). Different optical parameters of energy transfer have been found and the dominant mechanism in the energy transfer is found to be radiative. The ternary dye mixture system, the emission of which is peaked about the green, yellow and orange wavelengths, can be used effectively in the multi wavelength lidar systems for optical investigations.
REFERENCES