CHAPTER 4

EXPERIMENTAL TECHNIQUES

The search for materials with large optical nonlinearities with fast response time has led to the investigation of nonlinear optical organic materials. Organic materials with large third order nonlinearities are promising candidates for various photonic applications such as optical switching, optical rectification and optical limiting. From the view point of applications to optical devices, organic materials have several distinguishing features: processability, cost effectiveness and ease of forming large area films. Liquid solutions of laser dyes also serve as versatile sources of coherent tunable radiation with many applications in different fields. The nonlinear optical properties of an organic material can severely affect the temporal and spatial behavior of a light beam propagating through that medium. A variety of physical mechanisms can result in independent contributions to the refractive index. In liquids of isotropic molecules, the nonlinearity may arise from molecular redistribution or by electronic polarizability caused by a distortion of electronic clouds, or by resonance effects such as saturation absorption or two-photon absorption. A large contribution to the nonlinear refractive index can also occur due to thermal effects. Organic nonlinear optical materials are thought to play a key role in the future of nonlinear optics. A greater understanding of the photophysical properties of the dye molecules is essential to understand the nonlinear optical properties of dye molecules to a better extent. Therefore, a study of the spectral characteristics of the laser dyes becomes essential. This chapter explains the details of spectrophotometer and spectrofluorometer used for recording absorption and
fluorescence spectra, pico second time correlated single photon counting technique for lifetime measurements and the experimental set-up and the lasers used for measuring the nonlinear refractive index of dyes in liquid and solid medium.

4.1 SPECTROPHOTOMETER

The basic block diagram of spectrophotometer (SL 159 UV-VIS spectrophotometer) is shown in Figure 4.1 (SL159 UV-VIS spectrophotometer). This consists of a light source (Deuterium (D₂) and Tungsten (W) halogen lamps), monochromator (Czerny-Turner type with 1200 lines/mm holographic grating), detector (wide range Photo diode), and computer. The light from the halogen lamp is passed through the monochromator to get the required wavelength. This is allowed to pass through the sample. The amount of light that is transmitted depends on the absorption of the solution. The transmitted light is allowed to fall on a detector, which is a measure of the transmittance, and from this value the instrument directly gives the value of absorption.

![Figure 4.1 Block diagram of spectrophotometer](image)

4.1.1 Absorption Spectra

The absorption spectra of the dyes in liquid medium are recorded using the Perkin-Elmer Lambda spectrophotometer. The concentration of the dye in liquid are kept at 0.01 mM. The spectral parameters of the dyes are calculated as follows:
The bandwidth ($\Delta \nu_{1/2}$ in cm$^{-1}$) of the absorption spectra is calculated by measuring the full width at half maximum of absorbance.

The molar extinction coefficient $\varepsilon(\lambda)$ (in M$^{-1}$ cm$^{-1}$) at the peak wavelength of the absorption spectra is calculated using the relation,

$$\varepsilon(\lambda) = \frac{OD}{LC}, \text{ in L mol}^{-1} \text{ cm}^{-1}$$

(4.1)

where $OD$ is the absorbance at the peak wavelength of the absorption spectra, $L$ is the path length of the dye solution medium (in cm) and $C$ is the molar concentration of dye (in moles/liter).

The oscillator strength ($f$) was calculated by using the relation,

$$f = 4.33 \times 10^{-33} \varepsilon(\lambda) (\Delta \nu_{1/2}) \text{ in L/mol cm}^2.$$  

(4.2)

4.2 SPECTROFLUOROMETER

To obtain the fluorescence or excitation spectrum of the liquid sample, this is a vital instrument. This instrument is interfaced with a computer, so that a small program can be written and the required excitation wavelength, emission scan range, scan speed etc., can be fed to the instrument through the computer. We can get the fluorescence spectrum excitation spectrum either on the CRT or on a dot matrix printer. The basic block diagram of spectrofluorometer is shown in Figure 4.2. Spectrofluorometer consists of a Xenon lamp which excites the sample. The fluorescence is collected at right angles to the direction of excitation. The Xenon lamp emits light in the entire spectrum including UV, visible and IR. Therefore, using monochromator, we have to select a particular wavelength out of this band to
excite the sample, which is controlled by stepper motor. Similarly, the fluorescence of the sample is also broad band and this is also passed through the monochromator to get a single spectrum. The output fluorescence is directed by a photo detector and this signal is amplified (variable gain amplifier) so that the output relative intensity can be calibrated to a fixed value. F-4500 FL Spectrophotometer is used to record the fluorescence spectra of the dye solutions.

Figure 4.2 Block diagram of spectrofluorometer

4.2.1 Fluorescence Spectra

The fluorescence spectra of the dyes in liquid medium are recorded at low concentration of the dye (0.01 mM) and these spectra are corrected using quinine sulphate is 0.1N H$_2$SO$_4$ and fluorescein in 0.1N NaOH. The fluorescence spectral bandwidth (FWHM) is calculated by measuring the full width at half maximum of fluorescence intensity.

In order to understand the solute-media (solvent/polymer) interactions, stokes shift is calculated from the absorption and fluorescence
spectra. The Stoke’s shift \((\nu_a - \nu_f)\) of the absorption and fluorescence maxima of dyes in different media is calculated using the relation,

\[
\nu_a - \nu_f = \frac{1}{\lambda_a} \cdot \frac{1}{\lambda_f} \text{ in cm}^{-1}.
\]  

(4.3)

4.2.2 Fluorescence Quantum Yield

The fluorescence quantum yield of the dyes is one of the most important parameters in determining the lasing characteristics of the active medium of a dye laser. The fluorescence quantum yield is to quantify the efficiency of the emission process.

Fluorescence quantum yield of dyes in liquid media is experimentally determined by comparison of dye emission with that of a dye of known quantum yield.

The quantum yields are calculated using the expression (Demas and Crosby 1971),

\[
\phi_f = \left( \frac{A_{\text{sam}}}{A_{\text{ref}}} \right) \times \left( \frac{a_{\text{ref}}}{a_{\text{sam}}} \right) \times \left( \frac{n_{\text{sam}}}{n_{\text{ref}}} \right)^2 \phi'_f,
\]  

(4.4)

where, \(A_{\text{sam}}\) and \(A_{\text{ref}}\) are the areas under the corrected fluorescence spectrum, \(a_{\text{sam}}\) and \(a_{\text{ref}}\) are the absorbances at the exciting wavelength 500 nm, \(n_{\text{sam}}\) and \(n_{\text{ref}}\) are the refractive indices of the respective solvent and reference, respectively. Rhodamine B (Rh B) in ethanol is taken as the fluorescence standard, for quantum yield determination of dyes which had absorption in the region 500 nm – 560 nm. \(\phi'_f\) is the quantum yield of Rh B is taken to be 0.50 (Kartstens et al 1980 and Casey et al 1988). The fluorescence spectra is corrected using quinine sulphate is 0.1N H\(_2\)SO\(_4\) and fluorescence is
0.1N NaOH (Govindanunny and Sivaram 1980). Care is taken to record all the spectra under identical conditions. Very optically dilute solution of the reference and sample are taken so as to avoid re-absorption (Morris et al. 1976, Hamel and Hirayama 1983, Kubin and Flecher 1982). Cresyl violet in methanol (Dougloous Madge et al. 1979) is taken as the fluorescence standard for the dyes with absorption in the range 590 nm – 640 nm. The fluorescence quantum yield of Cresyl violet is taken to be 0.54.

4.3 FLUORESCENCE LIFETIME

4.3.1 Introduction

Picosecond time correlated single photon counting technique is used for determining the fluorescence lifetime of dye molecules in liquid and in solid medium. Fluorescence lifetime is the decay time of the molecule and it can be defined in the time domain in terms of the rate of depopulation of the first excited singlet states following δ-function (i.e., impulse) optical excitation from the ground state. As the excited state population is proportional to the fluorescence quantum intensity, the fluorescence lifetime can be determine experimentally by measuring the time taken for the fluorescence intensity to fall to 1/e of its initial value following δ-function excitation. This observation forms the basis of time correlated single-photon counting technique whereby the quantum nature of the light enable the time distribution of individual photon within the decay profile to be recorded. There are two methods for measuring fluorescence lifetimes. They are pulse fluorometry, which relates to measurements performed in the time domain phase and modulation fluorometry relating to the frequency domain. The basic principle of pulse fluorometry is that the sample is excited by a fast pulse of light from a spark source or laser and the time dependence of the fluorometry decay is then recorded. Phase and modulation fluorescence
incorporates a modulated excitation source such that the finite fluorescence lifetime of the sample causes the fluorescence emission waveform to be phase shifted and of different amplitude with respect to the excitation waveform. Traditional phase fluorometers using sinusoidally modular excitation operated at few frequencies restricts applications to simple fluorescence decay kinetics that is one or two exponential. The use of pulse excitation with mode-locked laser has overcome this limitation by making a wider range of frequencies, and hence a better description of the frequency response of sample and apparatus are readily available.

4.3.2 The Time Correlated Single Photon Counting Technique

The time-correlated single photon counting fluorometer consists of a pulse light source, usually a flash lamp or mode locked laser, which generates multi photon excitation pulses, which stimulates absorption in an assembly of sample molecules. At low levels of excitation power, each sample molecule absorbs one photon at the most, on a time scale which is instantaneous. The subsequent de-excitation of these molecules through the emission of fluorescence photon occurs with a distribution of the time delays which is normally exponential. The single photon timing technique records this distribution by measuring the time delays of the individual fluorescence photons with respect to the excitation pulse. When the excitation occurs, a synchronization pulse or ‘start’ timing pulse trigger the charging of a capacitor in the TAC (Time-to-Amplitude converter). The voltage on the capacitor increases linearly until either a preselected time range is reached or a ‘stop’ timing pulse is detected. The latter is initiated by detection of a fluorescence photon and the ‘start-stop’ time interval generates a proportional voltage across the capacitor. This voltage pulse is stored according to amplitude using an analog-to-digital converter within a multichannel analyzer (MCA). On repeating the ‘start-stop’ cycle many times, a histogram
representative of the fluorescence decay is acquired in the MCA memory. The data parameter can then be extracted using numerical and statistical procedures. Photomultipliers are the most widely used single-photon timing devices, and in order to minimize the registering of noise pulses and to ensure that the timing definition of the ‘start’ and ‘stop’ pulses is largely independent of the signal pulse height, discriminators are used. The shape provides the time definition for the pulses in the start and stop channel. The aim of decay time experiment is to study decay kinetics. This is an indirect process: The measurement system yields fluorescence decay curves, consisting of intensity values at some hundreds or thousands of consecutive short-time periods (channels) after the time of pulsed excitation. The parameters describing the kinetics are then obtained by reducing these data using statistical methods of data analysis (Lakowicz 1991).

4.3.3 Experimental Set-up

The fluorescence lifetime measurements are performed using a light emitting diode (LED) and single photon counting set-up. The LED (Spectra Physics) emitting light at 450 nm with pulse width of 1.4 ns is used to excite the sample. The emission monochromator is in Seya-Namioka configuration with 10 cm focal length and f/3 aperture. The wavelength selection in the monochromator is achieved either manually or automatically via the PC. The emission is detected at right angles to the excitation beam using a Hamamatsu 323P MCP photomultiplier. The emission is collected at magic angle polarization (54.7°) to avoid bias due to polarization effects for all viewing angles. The instrument response time is approximately 50 ps.

The single photon counting (SPC) measurements relies on the concept that the probability distribution for the emission single photon after an excitation event yields the actual intensity against time distribution of all
the photons emitted as a result of excitation. The characteristic feature of the single photon counting technique is that ‘one’ photon is detected for each exciting event. A schematic representation of picosecond time correlated single photon counting set-up is shown in Figure 4.3. A part of incident Picosecond pulse train from FHG is focused on a picosecond photo diode (PD). The photodiode signal is fed into constant fraction discriminator (CFD, ORTEC) and in turn generates the precise timing pulse. The output of CFD normally serves as the start pulse of the time-to-amplitude converters (TAC). However, the present experiments are carried out in “reverse” mode in order to minimize data collection time. The photodiode signal is used as stop signal for the time to amplitude converter. When the first fluorescent photon detected by the MCP photomultiplier generates pulse, the pulse is fed in to constant fraction discriminator (CFD). This serves as a start signal for TAC. The MCP photomultiplier output is directly read on α rate meter (RM). The time difference between the start and stop pulse is due to the time taken by the excited state to relax and emit a photon. The TAC converts this time difference to voltage, which is then fed into the computer via a multichannel analyzer (MCA) card (Using Data station software by Oxford Corporation, UK). Summing over many pulses the MCA builds up a probability histogram of counts versus time channels.

The fluorescence decay measured is further analyzed using IBH (DASS–6) software library, which includes an iterative shift of the fitted function as part of chi-squared goodness of the fit criterion. The single exponential decay function is fitted according to the relation

\[ I(t) = A \exp(-t/\tau) \]  

(4.5)
The bi-exponential decay is fitted according to the relation

\[ I(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2) \]  

(4.6)

where \( A_1 \) and \( A_2 \) are the pre-exponential factors and \( \tau_1 \) and \( \tau_2 \) are the pre-exponential factors and \( \tau_1 \) and \( \tau_2 \) are the fluorescence lifetime.

**Figure 4.3** Experimental setup of time correlated single photon counting technique

**4.4 INTRODUCTION TO NONLINEAR OPTICS**

The field of Nonlinear Optics today has grown into a vast enterprise with a considerable potential for technological applications. The nonlinear optical (NLO) materials needed for optimized components, however, have not yet been realized. New nonlinear optical materials and devices are in various stages of development. The Z-scan technique, based on the principle of spatial beam distortion arising from an optically induced nonlinear refractive index offers experimental simplicity as well as sensitivity. Information about the basic nonlinear characteristics of the materials, namely the sign and magnitude of the nonlinear refraction and the coefficient of absorption are
deduced from the dependence of the far field on-axis irradiance versus the position of the sample relative to the focal plane. In cases where nonlinear refraction is accompanied by nonlinear absorption, it is possible to separately evaluate the nonlinear refraction as well as the nonlinear absorption, by performing two Z-scans, one with and the other without an aperture. The transmittance of the closed is affected by both nonlinear refraction and absorption. The peak-to-valley normalized transmittance for the closed aperture z-scan data after dividing it by the corresponding open aperture z-scan data (to account for the nonlinear absorption in the medium), gives the contribution of pure refractive nonlinearity.

4.4.1 Z-Scan Technique for Determining the Nonlinear Refractive Index

4.4.1.1 Principle of Z-scan technique

The basic idea behind the Z-scan technique is self-focusing. Using a Gaussian laser beam, the transmittance of a nonlinear medium through a finite aperture placed in the far field as a function of the sample position (Z) with respect to the focal plane can be measured. The principle is to move the sample along the optical axis in the vicinity of the laser beam focused on an external lens. For each position of the sample around the focus, the induced lens inside the sample possesses different focal lengths. This focal length depends on the incident Gaussian shape. The experiment consists of the measurement of the irradiance through a small aperture in a far field for each position versus the focus position. The sign of \( n_2 \) determines the vergence of the lens, positive or negative. When the sample has negative refraction, it can be regarded as a concave lens near the focal position. As the sample position becomes close from the negative position of z to the focal position, the sample shifts the focal position to the positive z-direction. Therefore the beam at the aperture plane is suppressed and the intensity of the detectable beam becomes
larger than the intensity without the sample at the negative side. As the sample position becomes close from the positive position of $z$ to the focal position, the sample spreads the beam at the aperture plane and detectable intensity is larger at the positive side. Any nonlinear absorption present in the sample can be found in a measurement where the aperture is removed (open aperture $Z$-scan) and is replaced by a lens to collect the entire transmitted laser beam.

A pre-focal transmittance maximum (peak) followed by a post-focal minimum (valley) determines the refractive nonlinearity is negative. On the other hand, for positive refractive nonlinearity, there will be a valley followed by a peak (Figure 4.4). An extremely useful feature of this technique is that the sign of the nonlinear index is immediately known from the $Z$-scan traces.

![Figure 4.4](image)

**Figure 4.4** Characteristic curves depicting both positive and negative nonlinear refraction as measured by $Z$-scan
For the present study the Z-scan technique is performed on the dyes/films in order to determine third-order optical nonlinearities using the theory proposed by Sheik-Bahae et al (1990).

4.4.1.2 Theory

In general, for cubic nonlinearity, the index of refraction $n$ is expressed in terms of $n_2$ (esu or m$^2$/W).

$$n = n_0 + \frac{n_2}{2} |E|^2 = n_0 + n_2 I \quad (4.7)$$

where $n_0$ is the linear refractive index, $E$ is the peak electric field (cgs) and $I$ is the incident light intensity (MKS) within the sample. The relation between esu and m$^2$/W is given by

$$n_2 \text{ (esu)} = \left( \frac{cn_0}{40\pi} \right) n_2 \left( \frac{m^2}{W} \right) \quad (4.8)$$

where $c$ (m/s) is the velocity of light in vacuum.

Assuming a TEM$_{00}$ Gaussian beam of waist radius $\omega_0$ traveling in the +Z direction, the magnitude of the electric field $E$ can be written as,

$$|E(r, Z, t)| = |E_0(t)| \frac{\omega_0}{\omega(Z)} \exp \left( \frac{-r^2}{\omega^2(Z)} \right) \quad (4.9)$$

where $\omega^2(Z) = \omega_0^2 \left( 1 + Z^2 / Z_0^2 \right)$ is the beam radius at $Z$, $Z_0 = k\omega_0^2/2$ is the diffraction length of the beam, $k = 2\pi/\lambda$ is the wave vector and $\lambda$ is the
wavelength of light. \( E_0 \) denotes the radiation electric field at the focus and contains the temporal envelope of the laser beam.

If the sample length is small enough such that changes in the beam diameter within the sample due to either diffraction or nonlinear refraction can be neglected, the medium is regarded as thin. In this case, the amplitude and nonlinear phase change \( \Delta \phi \) of the electric field within the sample is expressed by

\[
\frac{d\Delta \phi}{dz} = (2\pi / \lambda )\Delta n \tag{4.10a}
\]

and

\[
\frac{d|E|}{dz} = -(\alpha / 2)|E| \tag{4.10b}
\]

where \( \alpha \) is the linear absorption coefficient and \( z \) is the depth within the sample. Equations (4.10a) and (4.10b) are solved to give the phase shift \( \Delta \phi \) at the exit surface of the sample, which simply follows the radial variation of the incident irradiance at a given position of the sample \( Z \).

\[
\Delta \phi(r, Z, t) = \frac{\Delta \Phi_0}{1 + Z^2 / Z_0^2} \exp \left( \frac{-2r^2}{\omega^2(Z)} \right) \tag{4.11}
\]

The on-axis phase shift at the focus is defined as

\[
\Delta \Phi_0(t) = k \Delta n_0(t) L_{\text{eff}} \tag{4.12}
\]

where \( L_{\text{eff}} = (1 - e^{-\alpha L}) / \alpha \), with \( L \) the sample length and \( \alpha \) is the linear absorption coefficient. Here \( \Delta n_0 = n_2 I_0(t) \) with \( I_0(t) \) being the on-axis
irradiance at focus (i.e. $Z = 0$). One can ignore the Fresnel reflection losses such that $I_0(t)$ is the irradiance within the sample.

The electric field at the surface of the sample now contains the nonlinear phase distortion.

$$E'(r, Z, t) = E(r, Z, t) \exp(-\alpha L/2) \exp\left(i\Delta\varphi(r, Z, t)\right)$$ (4.13)

By virtue of Huygens’s principle, the far field pattern of the beam at the aperture plane can be obtained through Henkel transformation of $E'$.

Having calculated the electric field at the aperture, one can obtain the normalized instantaneous $Z$–scan power transmittance as,

$$T(z, t) = \frac{\int_0^r |E_a(\Delta\Phi_0, r, Z, t)|^2 r dr}{S \int_0^\infty |E_a(0, r, Z, t)|^2 r dr}$$ (4.14)

where $r_a$ is the aperture radius and $S$ is the aperture transmittance in the linear regime.

The measurable quantity $\Delta T_{p-v}$ can be defined as the difference between the normalized peak and valley transmittances, $T_p - T_v$. The variation of this quantity as a function of $|\Delta\Phi_0|$ is given by (Xia et al 1994).

$$\Delta T_{p-v} = 0.406(1-S)^{0.25} |\Delta\Phi_0|$$ (4.15)

where $S$ is the aperture linear transmittance (0.4), $\Delta\Phi_0$ is the on-axis phase shift.
The on-axis phase shift is related to the third order nonlinear refractive index by,

$$|\Delta\phi_0| = k n_2 L_{\text{eff}} I_0$$  \hspace{1cm} (4.16)$$

where \( k = 2\pi/\lambda \), \( L_{\text{eff}} = [1-\exp(-\alpha L)]/\alpha \) is the effective thickness of the sample, \( \alpha \) is the linear absorption coefficient, \( L \) is the thickness of the sample, \( I_0 \) is the on-axis irradiance at focus and \( n_2 \) is the third order nonlinear refractive index.

The nonlinear absorption coefficient \( \beta \) can be estimated from the open aperture \( Z \)-scan data. The normalized transmittance for the open aperture condition (Sheik-Bahae et al 1990) is given by,

$$T(z,S=1) = \sum_{m=0}^{\infty} \frac{\left[-q_o(z)\right]^m}{(m+1)^{3/2}}$$  \hspace{1cm} (4.17)$$

for \( q_o(0) < 1 \), where \( q_o(z) = \beta I_0 L_{\text{eff}}/(1+ z^2/z_R^2) \), \( z_R = k \omega_o^2/2 \) is the diffraction length of the beam and \( \omega_o \) is the beam waist radius at the focal point and \( k = 2\pi/\lambda \) is the wave vector.

The experimental measurements of \( n_2 \) and \( \beta \) allow one to determine the real and imaginary parts of the third-order nonlinear optical susceptibility \( \chi^{(3)} \) according to the following relations (Cassano et al 2001),

$$\text{Re}\chi^{(3)} \text{ (esu)} = 10^{-4} \frac{\varepsilon_0 c}{n_o^2} n_2^2 (\text{cm}^2/\text{W}) / \pi$$  \hspace{1cm} (4.18)$$

$$\text{Im}\chi^{(3)} \text{ (esu)} = 10^{-2} \frac{\varepsilon_0 c}{n_o^2} n_2^2 \lambda \beta (\text{cm/W}) / 4\pi^2$$  \hspace{1cm} (4.19)$$
where $\varepsilon_0$ is the vacuum permittivity, and $c$ is the light velocity in vacuum, $n_0$ is the linear refractive index of the material and $\lambda$ is the laser wavelength. The absolute value of $\chi^{(3)}$ was calculated from the equation, $|\chi^{(3)}| = \sqrt{\text{Re}(\chi^{(3)})^2 + \text{Im}(\chi^{(3)})^2}$.

### 4.4.1.3 Experimental set-up

The transmittance of the sample through the aperture is monitored in the far field as a function of the position $Z$, of the nonlinear sample in the vicinity of the linear optics focal position. The required scan range in an experiment depends on the beam parameters and the sample thickness $L$. A critical parameter is the diffraction length, $Z_0$, of the focused beam defined as $\frac{\pi w_0^2}{\lambda}$ for a Gaussian beam where $w_0$ is the focal spot size (half-width at the $1/e^2$ maximum in the irradiance). For “thin” samples (i.e. $L \leq Z_0$), although all the information is theoretically contained within a scan range of $\pm Z_0$, it is preferable to scan the sample for $\approx \pm 5Z_0$ or more. This requirement, simplifies data interpretation when the sample’s surface roughness or optical beam imperfections introduce background “noise” into the measurement system. In many practical cases where considerable laser power fluctuations may occur during the scan, a reference detector can be used to monitor and normalize the transmittance. To eliminate the possible noise due to spatial beam fluctuations, this reference arm can be further modified to include a lens and an aperture identical to those in the nonlinear arm. The position of the aperture is rather arbitrary as long as its distance from the focus, $d \gg Z_0$. Typical values range from $20Z_0$ to $100Z_0$. The size of the aperture is signified by its transmittance, $S$, in the linear regime, i.e. when the sample has been placed far away from the focus. In most reported experiments, $0.1 < S < 0.5$ has been used for determining nonlinear refraction.
In the Figure 4.5, describing the Z-scan, a purely refractive nonlinearity was considered assuming that no absorptive nonlinearities (such as multiphoton or saturation of absorption) are present. Qualitatively, multiphoton absorption suppresses the peak and enhances the valley, while saturation produces the opposite effect. The sensitivity to nonlinear refraction is entirely due to the aperture, and removal of the aperture completely eliminates the effect. However, in this case, the Z-scan will still be sensitive to nonlinear absorption. Nonlinear absorption coefficients can be extracted from such “open” aperture experiments. S=1 case corresponds to collecting all the transmitted light and therefore is insensitive to any nonlinear beam distortion due to nonlinear refraction. Such a scheme, referred to as an “open aperture” Z-scan, is suited for measuring nonlinear absorption (β) in the sample.

One of the attractive features of the Z-scan technique is the ease and simplicity by which the nonlinear optical coefficients can be determined with a high degree of accuracy. Accurate determinations of the nonlinear coefficients such as $n_2$ or β depends on the laser source is characterized in
terms of its temporal and spatial profiles, power or energy content and stability.

Once a specific type of nonlinearity is assumed (e.g. an ultra fast $\chi^{(3)}$ response), a Z-scan can be rigorously modeled for any beam shape and sample thickness by solving the appropriate Maxwell’s equations. However, a number of valid assumptions and approximations will lead to simple analytical expressions, making data analysis easy yet precise. Aside from the usual SVEA (slowly varying envelope approximation), a major simplification results when we assume that the nonlinear sample is “thin” so that neither diffraction nor nonlinear refraction cause any change of beam profile within the nonlinear sample. This implies that $L<<Z_0$ and $L<<Z_0/\Delta\Phi_0$ respectively where $\Delta\Phi_0$ is the maximum nonlinearity-induced phase distortion. The latter requirement assures “external self-action” and simply states that the effective focal length of the induced nonlinear lens in the sample should be much smaller then the sample thickness itself. In most experiments using the Z-scan technique we find that this second criterion is automatically met since $\Delta\Phi_0$ is small.

In the present study, the Z-scan technique is used to evaluate the nonlinear refractive index $n_2$, nonlinear absorption coefficient $\beta$ and third-order nonlinear optical susceptibility $\chi^{(3)}$ of the chosen organic dyes.

Z-scan measurements are carried out using a 532nm diode-pumped Nd: YAG laser beam (Coherent Compass™ 215M-50) and He-Ne laser of wavelength 633nm (research Electro Optics 30995) depending on the absorption wavelength of the organic dye used.