CHAPTER 4

EXPERIMENTAL TECHNIQUES

4.1 INTRODUCTION

This chapter describes the experimental set up for closed Z-scan presented by Sheik – Bahae for determining the nonlinear refractive index of the materials medium. Also, the details regarding the picosecond single photon counting technique for measuring the fluorescence lifetime, the spectrophotometer and spectrofluorometer for studying the spectral characteristics is also described.

4.2 Z-SCAN TECHNIQUE FOR DETERMINING THE NONLINEAR REFRACTIVE INDEX

4.2.1 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. Let us consider a sample of negative nonlinear refractive index and thickness smaller than the diffraction length of the focused beam (a thin medium). When the sample is far away from the focus (negative Z direction) the beam irradiance is low. This means that the nonlinear refraction is negligible and hence the transmittance remains relatively constant. As the sample is moved towards the focus, the beam irradiance increases which leads to self-lensing in the sample. This is because, near the focus, the sample diverges the beam and hence after the focus, the
beam converges leading to increased beam irradiance. But when the sample is at the focus, \((Z = 0)\) the self-defocusing increases the beam divergence, leading to beam broadening at the aperture, and thus a decrease in transmittance. This suggests that there is a null as the sample crosses the focal planes. This is analogous to placing a thin lens at or near the focus, resulting in a minimal change of the far field pattern of the beam. The Z-scan is completed as the sample is moved away from the focus (positive \(Z\)) such that the transmittance becomes linear since the irradiance is again low.

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. An extremely useful feature of this technique is that the sign of the nonlinear refractive index is immediately known from the Z-scan traces.

The sensitivity to nonlinear refraction is entirely due to the aperture and removal of the aperture completely eliminates the effect. For the present study the Z-scan is performed with aperture in order to determine nonlinear refraction.

4.2.2 Theory

The index of refraction \(n\) is expressed in terms of nonlinear refractive index \(n_2\) (esu) or \(\gamma\) \((m^2/W)\) through

\[
n = n_0 + \frac{n_2}{2} |E|^2 = n_0 + \gamma I,
\]

(4.1)

where \(n_0\) is the linear index of refraction, \(E\) is the peak electric field (cgs), and \(I\) denote the irradiance (MKS) of the laser beam within the sample. Assuming
a \text{TEM}_{\omega_0} \) Gaussian beam of beam waist radius \( \omega_0 \) travelling in the +Z direction, then \( E \) can be written as,

\[
E(z,r,t) = E_0(t) \frac{\omega_o}{\omega(Z)} \exp(-\frac{r^2}{\omega^2(Z)}) \cdot \exp(-\frac{i k r^2}{2 R(Z)}) e^{i\phi(Z,t)},
\]

(4.2)

where \( \omega^2(Z) = \omega_0^2 (1+Z^2/Z_0^2) \) is the beam radius, \( R(Z) = Z(1+Z_0^2/Z^2) \) is the radius of the curvature of the wave front at \( Z \), \( Z_0 = k \omega_o^2/2 \) is the diffraction length of the beam, \( k = 2\pi/\lambda \) is the wave vector and \( \lambda \) is the laser wavelength, all in free space. \( E_0(t) \) denotes the radiation electric field at the focus and contains the temporal envelope of the laser pulse. The \( e^{-i\phi(Z,t)} \) term contains all the radially uniform phase variations. As the radial phase variation of \( \Delta\phi(r) \) is required, the slowly varying envelope approximation (SVEA) applies, and all other phase changes that are uniform in \( r \) are ignored.

If the sample length (\( L \)) is small enough 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 which case the self-refraction process is referred to as “external self-action” (Weaire .D et al, 1974). For linear diffraction this implies that \( L \ll Z_0 \), while for nonlinear refraction, \( L \ll Z_0/\Delta\phi(0) \). Since, \( \Delta\phi \) is small, the second criterion is automatically met. Additionally, the first criterion for linear diffraction is more restrictive, and it is sufficient to replace it with \( L < Z_0 \). This assumption simplifies the problem, and the amplitude \( \sqrt{I} \) and phase \( \phi \) of the electric field as a function of \( z' \) are governed in the SVEA by a pair of simple equations:
\[
\frac{d\Delta \varphi}{dZ} = \Delta n(I) k,
\] (4.3)

and
\[
\frac{dI}{dZ'} = - \alpha(I) I,
\] (4.4)

where \( Z' \) is the propagation depth in the sample and \( \alpha(I) \), in general, includes linear and nonlinear absorption terms.

Phase shift \( \Delta \varphi \) at the exit surface of the sample,
\[
\Delta \varphi(Z,r,t) = \Delta \varphi_0(Z,t) \exp \left( \frac{-2r^2}{\omega^2(Z)} \right),
\] (4.5)

with
\[
\Delta \varphi_0(Z,t) = \frac{\Delta \varphi_0(t)}{1 + Z^2 / Z_0^2}.
\] (4.6)

\( \Delta \varphi_0(t) \), the on-axis phase shift at the focus, is defined as
\[
\Delta \varphi_0(Z,t) = \Delta n_0(t) L_{\text{eff}},
\] (4.7)

where \( L_{\text{eff}} = (1 - e^{-\alpha L}) / \alpha \), (4.8)

with \( L \) the sample length and \( \alpha \) the linear absorption coefficient. Here
\[
\Delta n_0 = \gamma I_0(t)
\] (4.9)

with \( I_0(t) \) being the on-axis irradiance at focus (\( Z = 0 \)). Fresnel reflection losses are neglected such that \( I_0(t) \) is the irradiance within the sample.
The complex electric field exiting the sample \( E_e \) contains the nonlinear phase distortion

\[
E_e (r,Z,t) = E(Z,r,t) e^{-\alpha L} e^{i\Delta \phi(Z,r,t)}. \quad (4.10)
\]

Here,

\[
e^{i\Delta \phi(Z,r,t)} = \sum_{m=0}^{\infty} \frac{[i\Delta \phi_0(Z,t)]^m}{m!} e^{-2mr^2/\omega^2(Z)}. \quad (4.11)
\]

The measurable quantity \( \Delta T_{p-v} \) is the difference between the normalized peak and valley transmittance: \( T_p - T_v \). The quantity \( \Delta T_{p-v} \) varies as a function of \( |\Delta \phi_0| \) and is independent of laser wavelength, geometry of the experimental set-up and the sign of nonlinearity. For small aperture \((s = 0)\) and for small phase distortion \( \Delta T_{p-v} \) is found to be linearly dependent on \( |\Delta \phi_0| \)

\[
\Delta T_{p-v} = |\Delta \phi_0| \times 0.406. \quad (4.12)
\]

Sheik-Bahae et al (1990) has shown that this relation is accurate to within 0.5% for \( |\Delta \phi_0| \leq \pi \). For large apertures, the following relationship can be used to include such variations within an ± 2% accuracy:

\[
\Delta T_{p-v} \approx 0.406 (1-s)^{0.25}|\Delta \phi_0|,
\]

for \( |\Delta \phi_0| \leq \pi \). \quad (4.13)

The above equation can be readily used to estimate nonlinear refractive index \((n_2)\) with a good accuracy after the Z-scan is performed.
4.2.3 Experimental set-up

The experimental set-up for closed Z- scan is shown in Figure 4.1. The set-up has a Helium neon (He-Ne) laser (\(\lambda = 632.8\text{nm}, 10\text{mW}\)) as the light source, a positive lens of focal length \(f = 4\text{cm}\), a sample of thickness 1mm, and an aperture in the far field followed by PMT(RCA 931) connected to an oscilloscope serving as detector. The sample is moved along the beam direction using a motorized stage.

Assume, for instance, a material with negative refractive index and a thickness smaller than the diffraction length of the focused beam (a thin medium). This can be regarded as a thin lens of variable focal length. Starting the scan from a distance far away from the focus (negative Z), the beam irradiance is low and negligible nonlinear refraction occurs; hence the transmittance \((D_2|D_1)\) remains relatively constant, where \(D_1\) and \(D_2\) are detectors. As the sample is brought closer to focus, the beam irradiance increases, leading to self-lensing in the sample. A negative self-lensing prior to focus will tend to collimate the beam, causing a beam narrowing at the aperture which results in an increase in the measured transmittance. As the scan in Z continues and the sample passes the focal plane to the light (positive Z), the same self-defocusing increases the beam divergence, leading to beam broadening at the aperture, and thus a decrease in transmittance: This suggests that there is a null as the sample crosses the focal plane. This is analogous to placing a thin lens at or near the focus, resulting in a minimal change of the far-field pattern of the beam. The Z-scan is completed as the sample is moved away from the focus (positive Z) such that the transmittance becomes linear since the irradiance is again low. Induced beam broadening and narrowing of this type have been previously observed and explained during nonlinear refraction measurements of some semi-conductor (Hill et al, 1982, Boggess et al, 1984).
Figure 4.1 The closed Z-scan set up

(D1, D2 detectors, BS beam splitter, L convex lens, S sample)
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 $\delta$-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 determined experimentally by measuring the time taken for the fluorescence intensity to fall to $1/e$ of its initial value following $\delta$-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 pico second laser and single photon counting set-up. A Diode pumped Millena cw laser (Spectra Physics) 532 nm is used to pump the Ti-sapphire rod in Tsunnami picosecond mode locked laser system (Spectra Physics model No. 4960 M3S). The Ti-Sapphire rods is oriented at Brewster angle to the laser beam. The wavelength tuning range is 720-850 nm. i.e., standard Pico configuration. The pulse repetition rate is 82 MHz and FWHM is less than 2 ps. Scanning auto correlator (Model 409-08, Spectra Physics) is used to check the shape and duration of the pulse from the Tsunnami. The pulse is displayed on an oscilloscope for real time viewing. The laser pulse is next focused to the pulse picker (Model 3980, Spectra Physics). It selects the pulse from 82 MHz train at a maximum pulse selection rate of 4 MHz. The output from the pulse picker is frequency doubled flexible Harmonic generator (FHG-23, Spectra Physics). The frequency double 375 nm output 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 4.2. A part of incident Pico second pulse train from FHG is focused on a picosecond photo diode (PD). The photodiode signal is fed into constant fraction discriminator (CFD, ORTEC) and inturn 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 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

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

(4.14)
Figure 4.2 Experimental setup of Time Correlated Single Photon Counting Technique
The bi-exponential decay is fitted according to the relation

\[ I(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2) \]  \hspace{1cm} (4.15)

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

4.4 SPECTROPHOTOMETER

The basic block diagram of spectrophotometer (SL 159 UV – VIS spectrophotometer) is shown in Figure 4.3 (SL159 UV-VIS spectrophotometer). This consists of a light source (Deuterium (D\(_2\)) 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.

4.4.1 Absorption Spectra

The absorption spectra of the dyes in liquid and solid medium were recorded using the Hitachi U2000 model spectrophotometer. The concentration of the dye in liquid and solid medium is kept at 0.05 mM. The spectral parameter of the dyes were calculated as follows:

The bandwidth \( (\Delta \nu_{1/2} \text{ in cm}^{-1}) \) of the absorption spectra was calculated by measuring the full width at half maximum of absorbance.
The molar extinction coefficient $\varepsilon(\lambda)$ (in $\text{M}^{-1}\text{cm}^{-1}$) at the peak wavelength of the absorption spectra was calculated using the relation,

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

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,

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

4.5 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 4.4. 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
Figure 4.3  Block diagram of spectrophotometer

Figure 4.4  Block diagram of spectrofluorometer
value. Hitachi F2000 spectrofluorometer was used to record the fluorescence spectra of the dye solutions. Fluorescence spectra of the solid samples were obtained by using rectangular shaped polymer rods directly.

4.5.1 Fluorescence spectra

The fluorescence spectra of the dyes in liquid and in solid medium were recorded at low concentration of the dye (0.05 mM) and these spectra were corrected using quinine sulphate is 0.1N H$_2$SO$_4$ and fluorescein in 0.1N NaOH. The fluorescence spectral bandwidth (FWHM) was 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,

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

4.6 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 solid and 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 (Demos and Crosby 1971),

$$\varphi_f = \left( \frac{A_{\text{sam}}}{A_{\text{ref}}} \right) \times \left( \frac{a_{\text{sam}}}{a_{\text{ref}}} \right) \times \left( \frac{n_{\text{sam}}}{n_{\text{ref}}} \right) \varphi_f^\prime, \quad (4.19)$$

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 500nm, $n_{\text{sam}}$ and $n_{\text{ref}}$ are the refractive indices of the respective solvent and reference, respectively. Rhodamine 6G (R 6G) in ethanol is used as the reference for quantum yield determination. The absorbance of R 6G in ethanol at 500 nm is 0.66. $\varphi_f^\prime$ is the quantum yield of R 6G (0.95). The fluorescence spectra is corrected using quinine sulphate is 0.1N H$_2$SO$_4$ and fluorescence is 0.1N NaOH (Govindanuny 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).

### 4.6.1 Radiative and Non-radiative rate constants

The radiative ($K_r$) and Non-radiative ($K_{nr}$) decay rate constants are calculated from the fluorescence quantum yield ($\varphi_f$) and life time ($\tau_f$) using the relation,

$$K_r = \frac{\varphi_f}{\tau_f} \quad (4.20a)$$

and

$$K_{nr} = \frac{(1-\varphi_f)}{\tau_f}. \quad (4.20b)$$