Preface

Characterization of photonic materials were carried out using two very interesting techniques, Z-scan and Thermal lens. The z-scan is used for determination of nonlinear optical properties, whereas thermal lens effects was used for determination of fluorescence quantum yield. So the thesis is presented as two sections, one for Z-scan Techniques and the other for Thermal Lens Techniques. It comprises seven chapters.

Chapter 1 - This gives an introduction to nonlinear optics, and some techniques for nonlinear optical material characterization. Among the various nonlinear optical interaction processes, the following processes are discussed in detail. Sum and Difference frequency generation, Optical Parametric Oscillation and Third Order Polarization of which Third harmonic generation (THG) and Intensity dependent Refractive Index (IDRI) are interesting consequences. Other processes described are Self Focusing, Optical bistability, Kerr-lens mode locking (KLM), Self-phase modulation, parametric amplification, and parametric generation, Spontaneous parametric down conversion and Optical rectification. Other important processes that are mentioned are Cross-phase modulation (XPM), Nonlinear Light Scattering- Stimulated Brillouin Scattering and Stimulated Raman Scattering, Optical phase conjugation and Two-photon absorption. It also deals with Nonlinear Optical Materials and some of the Measurement Techniques. Here various methods for nonlinear material characterization are described with special emphasis to z-scan technique. The theoretical details and the methods to analyze and interpret the z-scan transmittance data are discussed in detail. Other methods like degenerate four-wave mixing, nearly degenerate three wave mixing etc are mentioned.

Chapter 2 - In this chapter the experimental results for nonlinear optical absorption in metal phthalocyanines are included. Both open aperture and closed aperture z scan transmittance signals were recorded to study the refractive and absorptive nonlinearities. The samples chosen were metal phthalocyanines viz CoPc, NiPc, ZnPc and CuPc. Dimethyl Formamide (DMF) and Dimethyl Sulphoxide (DMSO) were used as solvents. The laser source was the Q switched Nd:YAG with 10 Hz repetition rate and a pulse width of 8 ns. As the nonlinear sample is scanned along the propagation path of a focused Gaussian
laser beam around its focus, the intensity characteristics of the beam induces a position dependant change of refraction inside the sample. The transmittance of the nonlinear medium through a finite aperture placed in the far field as a function of the sample position is measured. From an open aperture z scan signal, the nonlinear absorption coefficient $\beta$ can be determined and the nonlinear refraction coefficient $\gamma$ can be deduced from the closed aperture data. Optical limiting studies were also performed in ZnPc using the fundamental and second harmonic from the same laser source.

Chapter 3 - Wavelength dependence of saturable and reverse saturable absorption (SA and RSA) of zinc phthalocyanine (ZnPc) was studied using 10 Hz, 8ns pulses from a MOPO in the wavelength range from 520-686 nm, which includes the rising edge of the Q-band in the electronic absorption spectrum. The nonlinear response is wavelength dependent and switching from RSA to SA has been observed as the excitation wavelength changes from the low absorption window region to higher absorption regime near the Q-band. The SA again changes back to RSA when we further move over to the infrared region. Values of the imaginary part of third order susceptibility are calculated for various wavelengths in this range. This study is important in identifying the spectral range over which the nonlinear material acts as RSA based optical limiter. A five level energy model is considered and the resulting rate equations are solved in transient regime and steady state regime to account for the spectral dependence of nonlinear absorption. Following the density matrix formalism, an expression for $\text{Im}(\chi^{(3)})$ in terms of excitation wavelength, the detuning factor, the line shape function etc. was obtained. This can be simulated to see how far it matches with the experimentally obtained results.

Chapter 4 - An introduction to phothermal and photo-pyro techniques is presented in this chapter. The various techniques discussed are photo thermal deflection, thermal lensing, photo acoustic method etc. Special emphasis is given to thermal lensing effects and applications. It also presents the relative advantages and disadvantages of each method.

Chapter 5 - Fluorescence quantum yield (FQY) is the fraction of the molecules that emit a photon after direct excitation by a light source. It provides information on radiationless processes in molecules, and, in the assignment of electronic transitions. The need of a fluorescence standard can be eliminated if we go for photo-thermal method like thermal lens technique. It is a highly sensitive method, which can be used to measure the optical absorption and thermal characteristics of a sample. We use this technique to determine the effect of silver nano particles on the FQY of Rhodamine 6G and also to calculate the
FQY value of a newly synthesized chemical schiff base. We have proved that the presence of Ag sol reduces the quantum yield of Rh6G. A discussion is presented on the possible reasons for this decrease in FQY in terms of formation of charge transfer complexes. Also, we have observed that the presence of silver sol can enhance the thermal lens signal. The fluorescence spectrum of the schiff base obtained from salicylaldehyde and 2-aminophenol is studied using an argon-ion laser as the excitation source and its FQY is determined using a thermal lens method. The quantum-yield values are calculated for various concentrations of the solution in chloroform and also for various excitation wavelengths. The high value of the FQY of this schiff base, will make this sample useful as a fluorescent marker for biological applications. Photo stability and gain studies will assess its suitability as a laser dye.

Chapter 6 - We apply the theory of photo thermal lens formation and also that of pure optical nonlinearity, to account for the phase modulation in a beam as it traverses a nonlinear medium. It is used to simultaneously determine the nonlinear optical refraction and the thermo-optic coefficient. We demonstrate this technique using some metal phthalocyanines dissolved in dimethyl sulphoxide, irradiated by a Q switched Nd:YAG laser with 10 Hz repetition rate and a pulse width of 8 ns. A transient TL signal will be formed in liquid samples, in the nanosecond regime, which we exploit here to simultaneously determine thermo-optic coefficient, dn/dT and the nonlinear optical parameters. we considered the changes in refractive index due to purely optical nonlinearity and also that due to TL formation. This is demonstrated using CoPc and NiPc in DMSO.

Chapter 7 - This chapter summarizes all the experimental results and gives a brief discussion about possible modifications and extensions to the work already done. Some of them are; spectral dependence of nonlinear refraction cross section, time resolved z-scan to clearly understand the nonlinear optical behavior, photo bleaching and gain studies of the schiff base to assess its suitability as a laser dye, and photo pyro technique to calculate the excited state absorption cross section and compare it with the values obtained using z-scan method.

Most of these results are published in peer reviewed journals and also presented in various conferences. The publications are listed at the end of chapter 7.