Chapter 7

Conclusions and Future Prospects

7.1 General Conclusions

Nonlinear optical materials use nonlinear dependence of the refractive index on the applied electric field to produce other frequencies. This results in either harmonic generation or frequency shifting. The importance of nonlinear optical materials in lasers and electro-optics became clear in the early days of lasers, since it enabled expansion of their limited spectral regime. Presently, there are a large number of nonlinear optical materials for specific wavelengths, with various damage thresholds, and with various optical characteristics. The unique characteristics of each nonlinear optical material and its various applications are mutually connected.

The nonlinear optical properties of single metal substituted phthalocyanines are investigated using the closed aperture and open aperture z-scan experiments that provide information regarding the refractive and absorptive nonlinearities of the materials. Phthalocyanines find several applications in dyes, photo-conducting materials, cancer therapy etc. The synthesis and applications of Pc materials is a dynamic and multidisciplinary field of research. The materials used for studies in the present thesis are CoPc, NiPc, CuPc and ZnPc. The nonlinear absorption and nonlinear refraction coefficients of all these materials were calculated. The calculated values of nonlinear absorption coefficient for these materials when DMF was used as the solvent, was in the range 5.66 to 6.46 cm/GW at 532 nm, and 3.25 to 7.68 cm/GW at 1064 nm excitation. There was not much change in these values when the solvent was changed to DMSO.
Nonlinear absorption spectrum of ZnPc was extensively studied which resulted in an interesting observation of the nonlinear mechanism changing from RSA to SA when the excitation wavelength changes to the rising edge of Q-band [1]. A 5-level model has been developed using the density matrix formalism to account for the spectral dependence of nonlinear absorption mechanisms. All of these materials are good RSA based optical limiters. The optical limiting studies carried out in ZnPc using the fundamental and second harmonic of the Nd:YAG laser reveal that, the material has a limiting threshold of approximately 2.5 J/cm² at 532 nm and 2.2 J/cm² at 1064 nm excitation, for a concentration of 0.5 mM in DMSO. Moreover, the spectral dependence of nonlinear susceptibility shows that ZnPc can act as an RSA based limiter at wavelengths ranging from 527 to 616 nm and also at 1064 nm. The cross-sections for nonlinear absorption and nonlinear refraction of all these materials were also calculated [2].

Solving the rate equations for a five level system, we can find out the expression for the spectral dependence of nonlinear susceptibility and also the excited state dynamics of the material system [3]. The procedure reveals that triplet to triplet excited state absorption is the reason for RSA behavior of ZnPc.

Fluorescence is a central technology in medicinal testing, drug discovery, biotechnology and imaging. In almost all uses of fluorescence, the fluorophores are in free space condition, in which they radiate energy with minimal interaction with their surroundings. Fluorophore interactions with the local environment affect non radiative decay processes such as quenching, but do not alter the intrinsic rate of radiative decay. Remarkably, proximity of fluorophores to metallic particles can dramatically alter their fluorescent spectral properties in ways that alter the quantum yield and photostability and improve detectability. This aspect was investigated in a commonly used fluorescing material rhodamine 6G in silver nano particle environment. The fluorescence quantum yield was calculated using the thermal lens method. In this study it was observed that rhodamine 6G in liquid form, with silver nanoparticles in its surroundings, has a decreased fluorescence efficiency compared to the case when the nano metals were absent [6]. However since the dye is highly fluorescing on its own, with a quantum yield of more that 95%, this result may not be very surprising. Metal particles usually finds biological applications in enhancing the intrinsic emission of DNA, which exhibits an extremely low quantum yield (\(\sim 10^{-4}\) to \(10^{-5}\)) in solution. The reduction in quantum yield of rhodamine 6G was complimented by the increased thermal lens signals. This study was carried out using the 532 nm CW excitation from a DPSS laser. It was also observed that the presence of silver particles results in an increased thermal lens signal from rhodamine 6G.
The fluorescence quantum yield of a newly synthesized material Hydroxyphenyl imino methyl phenol was also calculated using the same technique [4]. For this study five wavelengths from CW Ar-ion laser was used. This material has remarkable stability such that its fluorescence spectrum did not vary appreciably even after keeping it in dissolved form in chloroform for several days. Its reasonably good fluorescing ability with a quantum yield of nearly 78% is promising and by carrying out photostability and laser emission studies one can verify its suitability as a laser dye.

Thermal nonlinearities are commonly much larger than the electronic nonlinearities of the same material, often by several orders of magnitude. The apertured z-scan data contains both nonlinear absorption and refraction. With the aperture in the far field, the measured values of normalized energy transmission can have two contributions to the nonlinear refraction: one derived from a change in density with heating of the sample, and the other derived from the excited-state contribution to the index. The change in phase $\Delta \phi$ of the electric field through the sample should therefore be suitably modified to take into account of these two influences. Depending on the experimental conditions and the characteristics of the laser pulse, the nature and influence of the thermal effects on the propagating beam will be different. Thermally induced refractive index changes caused by absorption of light in a material have been intensively investigated by various scientists, both experimentally and theoretically for various time scales of the input laser pulses. At these different time scales of the input pulse, the thermal lensing has different manifestations. If the pulse width is longer than a few microseconds, density changes occurring via acoustic propagation may be considered instantaneous for beams having radii of one hundred microns or less (sound velocity $1 \sim 2 \mu m/ns$). Hence, it is the shape of the beam, coupled with thermal diffusion, which dictates the temperature gradient and hence the phase change of the propagating beam in this regime. However, for the single pulses of shorter duration (nanosecond time scale), the refractive index of the medium changes with its the acoustic expansion, generated by local heating (absorptive mode) or by its compression due to the electromagnetic field of the laser beam (electrostrictive mode). Hence, although the refractive index varies linearly with the density, it does not follow the spatial variation of the temperature. If the pulsewidth is in the picosecond regime, the acoustic waves do not have time to propagate, and therefore the density and index cannot change significantly resulting in no lensing effect during the short pulse. However, with high repetition rate pulses there will be the effects of cumulative
thermal lensing. The presence of these two nonlinearities can be made use of in calculating the thermo-optic-coefficient and the nonlinear optical parameters from a single z-scan signal [3,5]. This has been demonstrated using metal phthalocyanines. In the transient regime, one can take into account the refractive index changes due to both purely optical and thermo optic nonlinearity and the phase of the propagating pulse gets affected accordingly. Therefore this method will enable one to find out the nonlinear refractive index and the thermo-optic coefficient simultaneously. Two materials were used for demonstration of this method, CoPc and NiPc dissolved in DMSO. The extracted values of $\gamma$ and $dn/dT$ are in agreement with the values obtained for single metal phthalocyanines and for DMSO respectively.

### 7.2 Future Prospects

There are a lot more aspects of these materials that can further be explored using various techniques. Wavelength dependence of refractive nonlinearities in the same materials can be studied and the theoretical model developed for nonlinear absorption spectrum can be generalized to incorporate both nonlinear refraction and absorption terms as the real and imaginary parts of susceptibility. It is also possible to use a CW laser for the studies of nonlinear properties so that one can adjust the chopping frequency and vary the 'pulse' duration and thus study the nature and dynamics of the thermal nonlinearity. It is also possible to carry out a time resolved z-scan measurement. Extensive investigations can be carried out on the fluorescing ability of the newly synthesized material. It will be interesting to study its amplified spontaneous emission probably by incorporating it into a solid matrix like PMMA.
List of Publications

(References)


APPENDIX : A

SIGNIFICANCE OF TIMESCALES IN NONLINEAR OPTICAL INTERACTIONS.

The origin of optical nonlinearity depends on the relevant time scales of the light interaction with the material. For ultra-fast process in the femtosecond time domain, distortion of the atom’s or molecule’s electron cloud leads to an induced electronic nonlinearity which is weak but very fast. Longer time interactions, for example in the picosecond domain, can lead to coupling with the intrinsic vibrational nuclear motions in a molecule, or can reorient small molecules, leading to a stronger but slower, nonlinear coupling. The vibrational resonant processes, although highly detuned from the very large optical frequency of \( \approx 10^{15} \text{ seconds}^{-1} \) (their resonances lie around \( 10^{13} \text{ seconds}^{-1} \)), can be driven through a three wave interaction involving the original incident optical wave, the above material oscillation and a spontaneously generated scattered optical wave (Stimulated Raman scattering (SRS)). Interaction times of the order of nanoseconds can stimulate hypersonic acoustic waves via a similar three wave interaction called Stimulated Brillouin Scattering (SBS). Even longer interactions can induce thermal coupling which poses a major problem in CW optical devices such as semiconductor lasers, amplifiers and repetitively pumped pulsed systems.

APPENDIX : B

CONSEQUENCES OF INTENSITY DEPENDENT REFRACTIVE INDEX.

There are mainly two consequences of intensity dependent refractive index. One is Optical bistability and the other is Self-focussing/Trapping. A commonly used realization of optical bistability uses a Fabri-Perot resonator, of length \( d \), which contains a medium with intensity dependent refractive index of the form \( n_{tot} = n + n'_2 I \). The intensity \( I \) of the transmitted beam from the Fabri-Perot resonator is given by the Airy-formula,

\[
I_2 = \frac{T_0 I_1}{1 + F \cdot \sin^2(\delta/2)} = T \cdot I_1
\]  

\( I_1 \) is the incoming intensity, \( T \) is the total transmission with \( T_0 = T(\delta = 0) \), \( F \) is a constant connected with finesse, whereas the phase shift for a whole round-trip is

\[
\delta = k_0 n_{tot} 2d = k_0 (n + n'_2 I_i) 2d
\]  

and \( I_i \) is the intensity in the resonator. The output intensity \( I_2 \) can be expressed also with \( I_i \):

\[
I_2 = B \cdot I_i
\]
where $B$ depends on the mirror transmission; thus,

$$T = \frac{I_2}{I_1} = \frac{BI_1}{I_1}$$

The graphical solution for the two sets of equations, for $T = T(I_1)$, Eq. 1 plus Eq. 2 and Eq. 4 yields for small values of $I_1$ only one point of intersection in the curve $T(I_1)$, for larger $I_1$ values three or still more points of intersection. See figure ???. From this result we get $T(I_1)$ and $I_2(I_1)$. Bistability is very important for optical data processing in purely optical logic and computer systems. The switching effect is similar to phase transition. The nonlinear system has positive feedback and can lead to bifurcation and chaos in the output.

Self-focussing is another effect that originates from the nonlinearity of the index of refraction: $n_{tot} = n + \delta n(I)$ Laser light which is propagating in the $z$ direction and which has a Gaussian transverse intensity distribution, experiences the highest refractive index on the axis, where optical path lengths are maximum. Therefore the medium acts as a convex lens. This focussing can compensate the diffraction effects. Depending on the ratio of the light power $P_0$ to some critical power $P_{cr}$, either diffraction or focussing predominates. The limiting case, (neither diffraction nor focussing is called *self-trapping*)

The effect of self-focussing is caused by a single field

$$\hat{E}(x,f) = e(f) \cdot \hat{E}(x,f) \cdot \exp[-jk(f)z], \quad k = k_0n = \left(\frac{\omega}{c}\right)\sqrt{\varepsilon_r}$$

with frequency $f$, but now with a dependence also from the transversal coordinates $x,y$; the polarization unit vector $e$ is directed along the $x$-axis.

**APPENDIX : C**

**PHOTO PYRO TECHNIQUE FOR CALCULATION OF EXCITED STATE ABSORPTION SPECTRUM.**

Pyroelectric technique can be used to detect the temperature change caused as a result of the heat released by various optical processes. Pyroelectricity is the manifestation of a spontaneous temperature dependent electrical polarization. This property results in a temperature dependent potential difference occurring between the two, properly chosen, opposite surfaces of a pyroelectric material [1]. In photo pyroelectric (PPE) technique modulated or pulsed temperature rise in a material is detected by a pyroelectric film sensor attached either at the back of the sample (standard or rear detection scheme with sample being illuminated Figure 1(a) or to its surface (inverse pyroelectric technique with pyroelectric sensor being illuminated Figure 1(b). The heating gives rise to a temperature distribution in the system which depends on the modulation frequency, the geometry and thermal parameters of the assembly. Commonly used PPE sensors are Lithium Tantalite LiTaO$_3$, Lead Zirconium Titanate (PZT)
And Polyvinylidene Flouride (PVDF). The principal advantages of the PPE technique over other photothermal techniques are flat frequency response over a very wide bandwidth, a relatively simple sample cell and the considerable reduction of noise [2].

When a pulsed light source is used, the temperature at a depth ‘x’ and at a time ‘t’ following the surface absorption of an optical pulse is given by

\[
\theta(x, t) = \frac{Q_0}{2\sqrt{\pi \rho c k t}} \exp\left(-\frac{x^2}{4\alpha t}\right)
\]

where \(Q_0\) is the heat source, \(\rho\), \(c\) and \(k\) are the density, specific heat and the thermal conductivity of the sample.

The pyroelectric voltage in time domain is given by

\[
V(t) = e^{t/\tau} \int_0^t dt' e^{t'/\tau} \frac{\rho A}{C_a + C_p} \frac{d}{dt'} \theta_p(t')
\]

where \(\theta_p(t')\) is the spatial average of the temperature in the pyroelectric element. For very short pulses, if the thickness of the sample is considerable, then no heat would reach the pyroelectric sensor. However in these cases, as most of the pyroelectric sensors are piezoelectric, pressure changes caused by the heat release in the sample will result in piezoelectric signals [3]. Hence the signals in these cases should be analyzed as the piezo signals rather than the pyro signals. We tried to measure the excited state absorption cross section, excited state lifetime and triplet state absorption with a pyroelectric setup. As a test sample we used Rhodamine 6G dissolved in water. The excitation source used is a pulsed Nd: YAG laser (9 ns pulses). The pyroelectric sensor used is an electrode coated PVDF film. The pyro signals obtained with 532 nm excitation is shown in figure 2. The PA absorption spectrum recorded using this technique in the same sample at a very high concentration (\(~ 10^{-2}\)molar) is shown in figure 3.
Figure 2: (a) Typical pyro electric signal obtained with Rhodamine 6 G using 532 nm pulsed excitation (b) Enlarged section of one of the peaks in 'a'

Figure 3: photo pyro absorption spectrum of Rh6G at $10^{-2}$ molar concentration in water
References

