Preface

Observation of second harmonic generation (SHG) by P A Franken in 1961 marked the birth of nonlinear optics as a new discipline of laser matter interaction. Nonlinear optics is the study of phenomena that result from light induced modifications in the optical properties of the materials. This branch of science explores the coherent coupling of two or more electromagnetic fields in a nonlinear medium to generate new frequencies that are sum or difference of coupling frequencies. Franken attributed the new result to coherent mixing of two optical fields at 694 nm to produce an optical field at 347 nm.

Since then nonlinear optics has been an important area of science and technology. Interest in the study of nonlinear laser matter interactions arises because of two main reasons: (1) it is an effective method of understanding the nonlinear optical (NLO) properties of materials as well as spatial and temporal evolution of the nonlinearity and (2) a number of technological application have been realized and many others have been proposed using NLO effects. In this context investigation of NLO properties of certain important photonic materials was chosen as the topic of research outlined in the proposed thesis. Third order NLO effects are particularly interesting partly because third order effects have greater technological relevance and partly because third order effects are present, in varying degree of strength, in all materials irrespective of symmetry of materials. Organic materials, nanomaterials and photonic band gap materials are among the NLO materials of recent interest. Phthalocyanines (Pcs) and naphthalocyanines (Ncs) are typical organic NLO materials. They form one class of materials investigated here. The other type of material studied in this work is silver nanosol, aqueous solution of silver nanoparticles, which may be considered as a representative of nanomaterials. Origin and dynamics of linear as well as nonlinear optical properties of nanoparticles are completely different from those of organic compounds like Pcs and thus two distinct class of materials have been
investigated. Degenerate four wave mixing and Z-scan were chosen as the experimental techniques for the present investigation. The proposed thesis contains seven chapters. The content of each chapter is described briefly.

**Chapter 1:** In this chapter, the basic concepts and salient features of nonlinear optics are described. Some of the important nonlinear optical effects like optical limiting, optical phase conjugation (OPC) and second harmonic generation (SHG) are mentioned and a few applications of these phenomena in technology are explained. A brief survey of important NLO materials such as organic materials, nanoparticles, nanotubes, quantum wires, quantum dots, photonic band gap (PBG) materials is also given. Emphasis is given to organic materials like PCs and metal nanoparticles, which are the materials of present investigation. The motivation for the present work as well as concise description important results obtained during this work is given at the end.

**Chapter 2:** This chapter contains the relevant theory and experimental details of the degenerate four wave mixing (DFWM) and Z-scan techniques. Back scattering geometry of DFWM was used for the experiments. Variants of Z-scan techniques and other possible configurations of DFWM are mentioned. Specifications of excitation sources and other instruments used for making the measurements are also given.

**Chapter 3:** This chapter contains the results obtained from open aperture Z-scan experiments carried out in solutions of metal substituted phthalocyanines and naphthalocyanines at a fixed wavelength (532nm). Nonlinear absorption coefficient was measured and optical limiting property of these samples was analyzed. All these samples were found to exhibit reverse saturable absorption (RSA) at this wavelength. Samples selected include metal mono phthalocyanines (LaPc, MoOPc) metal subsituted naphthalocyanines (ZnNc, MgNc), metal substituted bis – phthalocyanines \([\text{Eu(Pc)}_2, \text{Sm(Pc)}_2, \text{Nd(Pc)}_2]\) and a bis- naphthalocyanine Eu(Nc)_2. It may be noted that the samples selected cover different structural variants of phthalocyanines.
Besides, metal ions are also different. Among (mono) MPcs, LaPc was found to be better nonlinear absorber. Among bis-Pcs, Eu(Pc)\textsubscript{2} was found to be better nonlinear absorbing material. Pcs in solution form can exhibit negative nonlinear refraction due to thermal lensing effect. Closed aperture measurements were taken in solutions of Pcs and exhibited thermal nonlinearity as expected.

**Chapter 4:** Studies on wavelength dependence of nonlinear absorption in bis-Pcs are too few. In this chapter, a comparative study of wavelength dependence of nonlinear absorption in three bis - Pcs viz. Eu(Pc)\textsubscript{2}, Sm(Pc)\textsubscript{2} and Nd(Pc)\textsubscript{2} in the blue side of their Q-band is given. Objective of the work was to find out the upper wavelength limit for reverse saturable absorption. Such studies help to know whether these samples exhibit optical limiting property over a wide spectral range. Besides, saturation intensity \( I_s \), nonlinear absorption coefficient \( \beta \) and imaginary part of third order susceptibility \( \text{Im}[\chi^{(3)}] \) were measured and resonant enhancement of \( \text{Im}[\chi^{(3)}] \) was also investigated. It was observed that magnitude of resonant enhancement is different in these samples. Nd(Pc)\textsubscript{2} exhibited resonant enhancement of two orders of magnitude but in other two samples, resonant enhancement was not as intense as in the case of Nd(Pc)\textsubscript{2}. While Eu(Pc)\textsubscript{2} and Nd(Pc)\textsubscript{2} exhibited reverse saturable absorption at 604nm, Sm(Pc)\textsubscript{2} exhibited a clear saturable absorption at this wavelength. Since all these samples have similar structures, small but experimentally observable differences between these samples might be arising from slightly varying influence of these metal ions.

**Chapter 5:** This chapter contains the results of degenerate four wave mixing studies carried out in solutions of metal substituted phthalocyanines and naphthalocyanines. Polarizations of interacting beams were so chosen that formation of thermal grating is prevented so that the response we get is entirely electronic. Third order susceptibility \( \chi^{(3)} \), figure of merit of third order nonlinearity \( F = \chi^{(3)}/\alpha \) and isotropically averaged second hyperpolarizability \( \langle \gamma \rangle \) were measured. Samples selected include metal mono
phthalocyanines (LaPc, MoOPc, FePc), metal substituted naphthalocyanines (ZnNc, MgNc, VoONc), metal substituted bis-phthalocyanines [Eu(Pc)₂, Sm(Pc)₂] and a bis-naphthalocyanine Eu(Nc)₂. It may be noted that the samples selected covers different structural variants of Pcs with different levels of π electron conjugation. Moreover metal substituents in these samples also vary. Level of π electron conjugation, nature of metal substituent and dimensionality of the molecules significantly influence the ⟨γ⟩ values. The measurements were carried out with view to exploring the combined influence of these factors on ⟨γ⟩. The results obtained were explained by taking into account the level of π electron conjugation, nature of metal substituent and dimensionality of the samples.

Chapter 6: The results of nonlinear absorption studies in silver nanosol using open aperture Z-scan technique at selected wavelengths near plasmon band are included in this chapter. Nanosol exhibited surface plasmon resonance (SPR) peak around 416nm. An interesting result of this investigation is that this material could act as a reverse saturable absorber and a saturable absorber at the same wavelength, depending entirely on the incident intensity. The results were explained in terms of plausible effects of SPR bleach and photochemical change induced absorption. Besides, closed aperture Z-scan experiments were also performed at 532nm, but result was negative. Divided Z-scan curve did not reveal any sign of positive or negative refraction. Possible reasons for this negative result are also mentioned.

Chapter 7: This chapter contains a brief description of future prospects along with summary and conclusions.

Most of the results included in this thesis have been published / communicated for publication, details of which are given below.
Publications (in journals)


In conference proceedings


ACKNOWLEDGEMENT

I am very thankful to my guide and supervisor, Professor C P Girijavallabhan, for the constant support, suggestions and encouragement that I received from him throughout the period of my Ph. D work. His support and encouragement has been a source of inspiration to me all the time.

I would also like to express my sincere thanks to Professor V P N Nampoori, who always showed deep interest in my work. His comments and suggestions have helped me considerably during the period of research work.

I would like to thank Prof. V M Nandakumaran and Prof. P Radhakrishnan for all the help, they rendered. I am happy to acknowledge CSIR (New Delhi) for Research Fellowship in the form of JRF and SRF. I also thank Mr. Basheer for the help received from him. I am also grateful to the administrative and library staff, for the help I received from them.

Dr. Reji Philip and Dr. Riju C Isac have helped me a lot by giving very good suggestions and also by giving required training, particularly in the initial period of research work. I acknowledge their help with gratitude. Dr. Jayan Thomas and Prof. V Ramakrishnan were kind enough to give me the samples, which made this work possible. I would like to express my gratitude to them.

I would like to express my heart-felt thanks to my all the friends in ISP, Pramod, Binoy, Aneesh, Prasanth, Sajan, Ahammad Teacher, Thomas Lee, Rajesh M, Suresh sir, Jijo, Dilna, Deepthy, Geetha, Pravitha, Santhi, Sister Retty, Rekha Mathew, Rajesh S, Manu, Vinu, Abraham, Unnikrishnan. Without their support and cooperation, this work would not have materialized. Help and advice received from Shelly John is also acknowledged. I would like to thank once again all the persons
who helped me in one way or other for the successful completion of my research work.

I would like to remember with deep sense of gratitude the support received from the parents during the present work

Unnikrishnan K P