

Studies of Ultrafast Excited State Dynamics in Corroles, Naphthosapphyrins, Phthalocyanines and Porphyrins

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**Doctor of Philosophy
in Physics**

by

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November 2015.

DECLARATION

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*For my Amma, Achan,
Kunjechi & Vellechi..*

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CHAPTER 1

Introduction

ABSTRACT

This chapter presents the background and the motivation for various studies performed in this thesis. It provides the significance and principles of techniques used to investigate the various spectroscopic processes of organic molecules and their interaction with ultrashort laser pulses. Different spectroscopic techniques are employed to detect or measure and understand these processes. The relevance of ultrafast spectroscopic studies for understanding high energy materials is highlighted. The significance and characteristics of ultrashort pulses are also explained in detail. A summary of thesis outline is provided at the end of the chapter.

1.1 Motivation and Introduction

With advances in the development of ultrashort [picosecond (ps) and femtosecond (fs)] pulsed lasers in the last two decades, a new area of research has evolved which enabled the observation of real time molecular and atomic processes such as chemical bond breaking, bond formation, atomic motions in chemical reactions, charge transfer processes, chemical decomposition, inter-atomic electron motion etc. [1,2]. Usually this time window encompasses picosecond (10^{-12} s) to attosecond (10^{-18} s, as) time scales which are commonly considered as ‘ultrafast’ timescales. Several state-of-the-art spectroscopic techniques have been developed to monitor the spectral and temporal dynamics in ultrafast time domain. In order to measure such fast molecular processes, we need a system whose temporal resolution is in the time scale less than the phenomenon of interest to be investigated. In other words in order to measure an ultrafast event, we need a tool which has superior resolution than that of the event. Except the Streak camera, there are no electronic devices which can provide desired temporal resolution. Moreover, Streak camera can only resolve events slower than 10^{-12} s [41]. Therefore, measurement techniques in which the response of the detector is irrelevant have been developed over the last two decades. In this context, pump-probe spectroscopy has been the popular choice in which the temporal resolution depends on the duration of pump and probe pulses [3-9]. In a typical pump-probe technique, a short (in time) pump pulse excites the sample molecules of our interest and induces a change in its optical properties via various ultrafast processes. After a definite time delay, another pulse called probe arrives at the sample. The whole idea of pump-probe spectroscopy is to investigate this probe pulse after its interaction with the excited sample molecule. By monitoring finite number of measurements of probe at various time delays, one can map the time dependence of the excited molecular processes [10]. Femtosecond time-resolved spectroscopy became first real time measurement of time required to break the bonds in molecular photo fragmentation [11]. In 1985, Knox et al. [12] generated 8 fs laser pulses whereas the current shortest pulses reported by Zhao et al. [13] are ~ 67 attoseconds long. They have recently developed attosecond transient absorption spectroscopy to study inter-atomic electron dynamics [14]. The evolution of time-resolved spectroscopies over the years is summarized in

figure.1.1. Contemporary research has invested heavily in the field of ultrafast laser spectroscopy to understand the ultrafast photo-physics of molecules via time-resolved spectroscopy, terahertz time domain spectroscopy, two dimensional infrared spectroscopy etc.[15-17]. Besides high temporal resolution, the ultrashort laser pulses possess high peak intensities by which a number of nonlinear optical (NLO) processes can be invoked when they interact with matter. These include multi-photon absorption, saturable absorption, Kerr lens mode locking etc. and can contribute in the photo physics of various novel organic molecules.

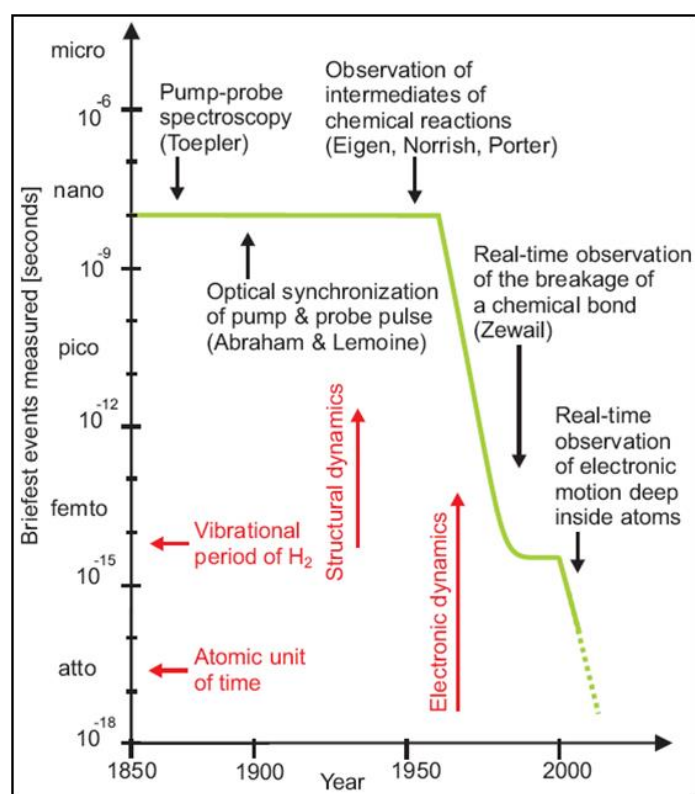


Figure 1.1 The evolution of ultrashort pulse capability for real time observation of ultrafast processes (adapted from reference [18])

Energetic molecules release huge amount of energy when they are detonated and this energy can be used for both military and civilian applications. The detonation of these molecules can be achieved with the help of sparks, shock, lasers and arcs. The ultimate aim of researchers all over the world is to develop novel energetic materials with higher energy released at short time scales, superior stability, long shelf-life while producing environmentally safe by-products and being cost effective at the same time. Understanding the processes after detonation of energetic molecules is extremely challenging and several attempts

have been made in the past few years. Though the propagation of shock and temperature occur on much slower time scales (micro to milliseconds), the chemical evolution and decomposition process take place on a faster scale (sub-nanosecond). Ultrafast kinetics plays inevitable part in deciding the specificity of energetic molecules under a mechanical perturbation. The mechanisms in the detonation and dynamics of decomposition of these sensitive materials should be clearly understood to explore the possibilities of designing superior materials. It has earlier been suggested that the molecular excited states play critical role in the detonation of energetic molecules [19]. Rajchenbach et al. investigated several energetic molecules and found that the population from the Franck-Condon states transferred to lowest vibrational states in the excited state within 1-10 ps through non-radiative transitions. This excited state played a crucial role on the explosive capability of molecule. It was also observed that higher the number of nitro groups in the molecule, faster was the population transfer due to charge localization on the electron withdrawing nitro group. The non-radiative channel increases the local heating creating a temperature gradient. This accelerates the decomposition reactions which involve breakage of particular chemical bonds and release of energy and, as a consequence, the temperature increases [19].

Theoretical studies on the time dependence of volume, stress, temperature and electronic density of states in Hydrazoic Acid (HN_3) under detonation demonstrated that the peak chemical reactions occurred in the 2-10 ps time scales. They observed that band gap of the material decreased upon shock compression and states were observed within the gap during the region of peak chemical reactions in these time scales [20]. The decomposition of electronically excited energetic molecules including Furazan, Imidazole, 1,1 –diamino-2,2-dinitroethene (FOX-7), dimethyl nitramine (DMNA), 1,3,5-trinitroperhydro-1,3,5-triazine (RDX), 1,3,5,7-tetranitro-1,2,5,7-tetraazacyclooctane (HMX), Nitromethane (NM) were studied by Bernstein et al. using nanosecond (ns) energy resolved and fs time resolved techniques [21-26]. The relaxation of excited electronic states was followed by the crossing of multidimensional electronic potential energy surfaces (PESs). This crossing is known as conical intersections (CI). The electronically excited states transfer energy to the vibrational levels of ground electronic state while relaxing through internal conversion (IC) and CI. In case of DMNA the

molecule was excited at 271 nm and probed at 405.6 nm. The singlet excited state S_1 lifetime was determined to be 50 fs and the PES crossing between S_1 and singlet ground state S_0 caused the ultrafast decay along the reaction co-ordinate which involved out-of-plane bending mode of DMNA NO_2 group. Some of the lifetime data obtained from femtosecond pump-probe techniques for various energetic molecules are summarized in table 1.1. The relaxation of S_1 lifetime of 2,2',4,4',6,6'-hexanitrostilbene (HNS) was followed by intersystem crossing from S_1 to T_1 [27].

Compound name	Relaxation time scale
1,3,3-trinitroazetidine (TNAZ)	<50 fs [28]
HMX & RDX	<180 fs [29]
Dicyclopentadiene (DCPD)	240 fs [30]
2,2',4,4',6,6'-hexanitrostilbene	6 ps (S_1 lifetime) [27]
Nitromethane	36 fs [31]
DMNA	50 fs [32]

Table 1.1 Lifetime data obtained from femtosecond pump-probe techniques for commonly used energetic molecules in defence applications.

Dlott et al. studied vibrational energy dynamics of liquid nitromethane by exciting the symmetric or asymmetric CH- or CD- vibration modes [33]. The vibrationally hot molecules dissipate energy to colder bath of phonons. This process is known as vibrational cooling (VC). These hotter phonons can excite the vibrationally colder molecule. This energy transfer is termed as ‘multi phonon up-pumping’. Recently, Chu et al. have studied the ultrafast dynamic response of 2, 2',4,4',6,6'-hexanitrostilbene (HNS) in solution by time-resolved coherent anti Stokes Raman (CARS) technique in which high frequency vibrational modes could be excited and temporal dynamics is observed. They observed the relaxation of excited vibrational mode ν_s (NO_2) at 1385 cm^{-1} was $\sim 0.38\text{ ps}$ for intramolecular vibrational redistribution and $\sim 8.5\text{ ps}$ for intermolecular vibrational energy relaxation [27]. Several detailed spectroscopy based experiments have been performed to study the ultrafast excited state dynamics in energetic materials [29-32]. Transient absorption spectroscopy of sapphire (Al_2O_3) and explosives such as RDX, pentaerythritol tetranitrate (PETN) and polyvinyl nitrate (PVN)

under laser shock was studied by Moore's group [34]. In the case of RDX, they demonstrated an increase in the absorption after the shock stress at 23 GPa. They compared the absorption of sapphire and RDX immediately after the shock. Though the shock induced an electronic change building an absorption in both RDX and sapphire, the absorption did not prolong in the case of sapphire whereas absorption in RDX was clearly growing up. The possible reason for this increased absorption could be the chemical reactions and band gap changes in the material in the ps time scale under shock loading. Later they applied this shock loading to liquids like cyclohexane, acetylene, acetonitrile, carbon disulphide etc. [35, 36]. Dlott's group also developed experiments for probing fundamental mechanisms of energetic material initiation and ignition using ultrashort laser pulses [37]. They have also pioneered the experiments investigating the vibrational energy transfer, which is important in the dynamics of energetic materials whose fundamental mechanisms are poorly understood [38]. Very recently Dlott group characterized the vibrational energy relaxation processes and identified the daughter vibrations created from different parent excitations in liquid Nitromethane [39]. In summary, such ultrafast spectroscopic studies assist us in understanding the detonation/decomposition mechanisms of energetic materials and this data will potentially be useful for designing novel energetic materials with superior performance and higher stability. For example, one can design an energetic molecule such that the transfer of energy to one particular vibrational mode becomes faster resulting in a quicker reaction. Thus, one can tune the sensitivity of energetic molecule so as to use them in military as well as civilian applications. However, the experimental identification of decomposition and the formation of the final products is complex and challenging.

Understanding the electronic excited states of simple organic molecules can assist in the analysis of the excited state dynamics of any energetic molecule. Different types of time resolved spectroscopic techniques to be understood and optimized with the help of such molecular systems. The thesis focuses primarily to study the molecular excited states using time resolved experiments. A group of novel organic compounds such as corroles, naphthosapphyrins, porphyrins and phthalocyanines were studied to understand the behaviour of molecular excited states of organic moieties in ultrashort time scale. These advanced organic moieties

are from the family of porphyrins and has broad absorption in the visible region and are structurally diverse. Our efforts over the last five years were focused towards (i) setting up of pump-probe measurements in transmission as well as reflection geometry using ps and fs laser pulses in the visible spectral range (ii) improvising the degenerate pump-probe experimental set up to perform non-degenerate pump-probe experiments (iii) studying the excited state dynamics of the advanced organic materials (iv) investigating the interaction of porphyrin and phthalocyanine with explosive molecule of RDX, Cl-20, TNT using fs pump-probe and ns Z-scan techniques. The ps degenerate pump-probe measurements provided information on the transients which are in hundreds of ps to nanosecond (ns) whereas fs degenerate pump-probe measurements provided information on the transient transitions which are typically in hundreds of fs to ps timescale. The existing/functional non-degenerate pump-probe set up can later be improvised for (a) visible/IR pump and white light probe experiments (transient absorption) and (b) IR pump and visible probe experiments. We have successfully performed ps/fs pump-probe experiments (degenerate and non-degenerate) on a few selected novel organic materials.

1.2 Ultrafast process in organic molecules

In this section we discuss about the ultrafast process in organic molecules after photo excitation. This can be explained by using a Jablonski diagram which illustrates the life span of an excited electron starting from the instantaneous absorption to various processes while relaxing back to the ground state. A typical Jablonsky diagram is shown in figure 1.2. The absorption of photon excites the ground state electron from singlet ground state electronic state S_0 to excited electronic state S_1 (or $S_2 \dots S_n$). The timescale of absorption is instantaneous i.e., in femtosecond time scale. Assuming the presence of linear absorption (where excited state absorption or ESA is neglected), the excited state electrons relax back to the ground state through different channels. The absorption of the photon is governed by Beer-lambert's law. The transitions occur under Frank-Condon principle in which the nuclear position is unchanged in the ground state as well as in the excited state. The excited electrons relax from these Frank-Condon states to lowest vibrational state in the excited electronic state through non-radiative decay process. This vibrational relaxation occurs through intermolecular collision with a

time period of 10^{-12} seconds and a shift to the right in the potential energy curve is observed. There can be contribution from other processes such as reorientation relaxation when we consider individual molecule which are anisotropic, rather than considering them as an ensemble of molecules which are isotropic. The orientation of individual molecules has a random distribution. Hence, the absorption of light which is parallel to dipole of one molecule will be different to that of light perpendicular to the dipole of the molecule.

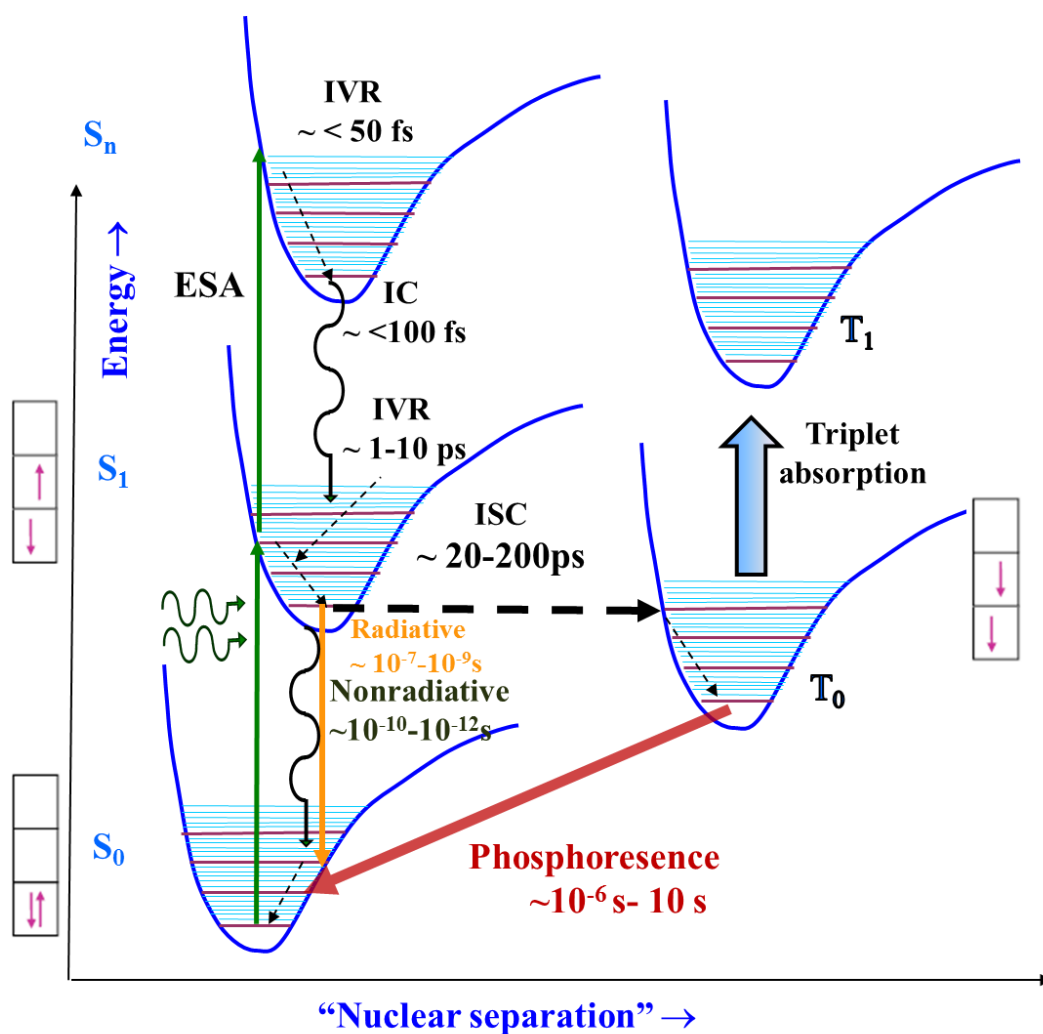


Figure 1.2 Jablonski diagram which shows various ultrafast process. The straight lines represent radiative transition. Wiggly lines and dashed lines represent non-radiative transitions.

The molecules reorient themselves with sufficient time dissipating energy to the solvent molecules. The dynamics of such reorientation relaxation helps to study the interaction of solvated and solvent molecules. If S_2 states were excited, the relaxation from S_2 states to S_1 states is called internal conversion (IC) and is followed by the internal vibrational relaxation (IVR). From the lowest vibrational

state in the first excited electronic state S_1 it can relax to ground state S_0 through radiative (fluorescence) or/and non-radiative decay according to Kasha's rule. It can also relax to triplet state T_0 by changing the spin of the electron in S_1 . This conversion is called inter system crossing (ISC) and occurs typically in a time scale of 20-200 ps. The decay from T_0 to S_0 is forbidden and therefore, it takes longer time which is called as phosphorescence [40, 41]. This non-radiative decay is also called collisional decay since the excited state disappears when the excited state population interacts with the surrounding atom or lattice and the energy is released as phonons (more generally as heat). The colliding atom receives the energy from the excited atom thereby ensures energy and momentum conservation [42]. Another aspect in the relaxation dynamics is the decay of coherence in the excited electronic states. This is called dephasing process in which the phase coherence of the excited system is lost through the interaction with environment but keeping the system in the particular quantum state and the time scale of the process changes from tens of fs to hundreds of fs [43,44]. In order to understand these ultrafast processes time-resolved spectroscopy has emerged with various techniques since the conventional detectors are not fast enough to measure the events. The following section discuss about the measurement of ultrafast dynamics using ultrashort pulses.

1.3 Ultrashort laser pulses - Characteristics

The key feature of a ultrashort pulse (USP) is its pulse duration (in ps and fs time scale) which makes it efficient in high temporal resolution measurements. Shorter the pulse duration larger will be the bandwidth according to uncertainty principle. For a 100 fs laser pulse, the bandwidth is 10 THz which is significant in optical communications. Another feature of USPs is the high spatial resolution. The spatial resolution of a 10 fs pulse is 3 μm which is much less than thickness of human hair. High peak intensity is one of the main characteristics of an USP. Peak intensities of 10^{14} - 10^{18} W/cm^2 can be achieved with normal focusing conditions which are commonly used in nonlinear optics, supercontinuum generation studies etc.. [43] Though the pulse duration (Δt) and spectral band width ($\Delta \nu$) are inversely proportional, there exists a finite relation which is based on Fourier transform analysis and is given as:

$$\Delta t \Delta \nu \geq c \quad (1)$$

where c is called as time-bandwidth product (TBP) which depends on the temporal and spectral profile of the pulse. The pulse is said to be transform limited if the equality is reached. The TBP measures the complexity of the pulse or the wave. It can be expressed in terms of coherence time ($\tau_c = 1/\Delta\nu$) which indicates the smallest temporal structure of the pulse. Hence $TBP = \Delta t / \tau_c$ implies the number of spikes in the pulse. Smaller the number of spikes, better the pulse. The value of c is smallest for Gaussian pulses since it can accommodate maximum amount of spectral components [45-46]. The spectra for pulse with same pulse width are shown in the figure 1.3 and the TBP values along with the intensity profiles are given in table 1.2.

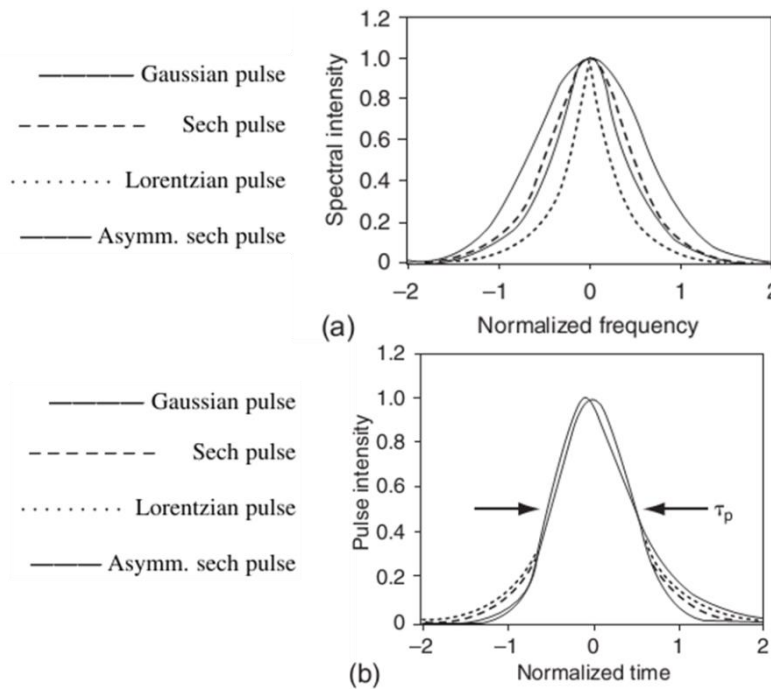


Figure 1.3 Spectra for pulses with same pulse duration (adapted from Reference [47])

Field envelope	Intensity profile	τ_p (FWHM)	TBP
Gauss	$e^{-2(t/\tau_G)^2}$	$1.177 \tau_G$	0.441
Sech	$\text{sech}^2(t/\tau_s)$	$1.763 \tau_s$	0.315
Lorentz	$[1 + (t/\tau_L)^2]^{-2}$	$1.287 \tau_L$	0.142
Asym. sech	$[e^{t/\tau_a} + e^{-3t/\tau_a}]^{-2}$	$1.043 \tau_a$	0.278
Square	1 for $ t/\tau_r \leq 1$, 0 otherwise	τ_r	0.443

Table 1.2 TBP and intensity profile of pulses with different field envelopes [47].

1.3.1 Development of the pump-probe techniques

Time-resolved spectroscopy started its journey from earlier flash photolysis experiments introduced by Porter and Norrish in which flash lamps in the time scales of milliseconds (ms) to microseconds (μ s) were used to study the transient spectrum [48, 49]. The experiments could explore many short lived radicals and intermediates in the time scale of ms and μ s. However, using ultrashort pulses, the pump-probe experiments could resolve the “fast moving pictures” of vibrating molecules in ps and fs time domain [50]. In a typical pump-probe technique, a short pump pulse excites the sample molecule of our interest, and induces a change in its optical properties through various ultrafast processes. After a definite time delay, another (weak) pulse called the probe arrives at the sample. The whole idea of pump-probe spectroscopy is to detect this probe pulse after its interaction with the excited sample molecule. By monitoring finite number of measurements of probe at various time delays, one can map the time dependence of the excited molecular processes. The probe pulse will be weak relative to the pump pulse such that probe itself does not create another process.

In degenerate pump-probe technique, the pump and probe pulses are identical in wavelength and the temporal information is obtained. The change in the probe transmittance $\Delta T/T$, is measured when the pump is on and off through a lock-in detection at various time delay. The sensitivity of the system depends on the repetition rate of the laser pulses. For 1 kHz, $\Delta T/T$ typically 10^{-4} - 10^{-5} and for 100 MHz oscillator, it is 10^{-6} - 10^{-7} . The sensitivity is achieved by using a lock in amplifier which measures a small signal out of noisy environment. It can measure the signal of nano-volt from a noise level which is 1000 times larger than the signal voltage. Lock-in measures signal at a reference frequency and discard all the other signals. The reference frequency is given through a chopper which modulates the pump beam. A schematic of chopped laser pulses to measure ΔT is shown in figure 1.4.

Higher is the chopper frequency better the number of samples to be averaged and higher the time constant to be used. The time constant of the lock-in amplifier defines the time during which it averages the samples. Hence, higher the

time constant better will be the signal to noise ratio. However, the time constant is compromised for a finite waiting time at one particular delay, since the waiting time should be at least five times the time constant [51, 52]. In non-degenerate experiments, the pump and probe possess different wavelengths. If the pump is a visible wavelength, the probe can be a broad band source such as Supercontinuum, infrared, terahertz, X-ray pulses etc. The use of a broad band source helps us to study spectrally resolved dynamics. Data acquisition is similar to that of degenerate case. However differential spectra are obtained in this case [43].

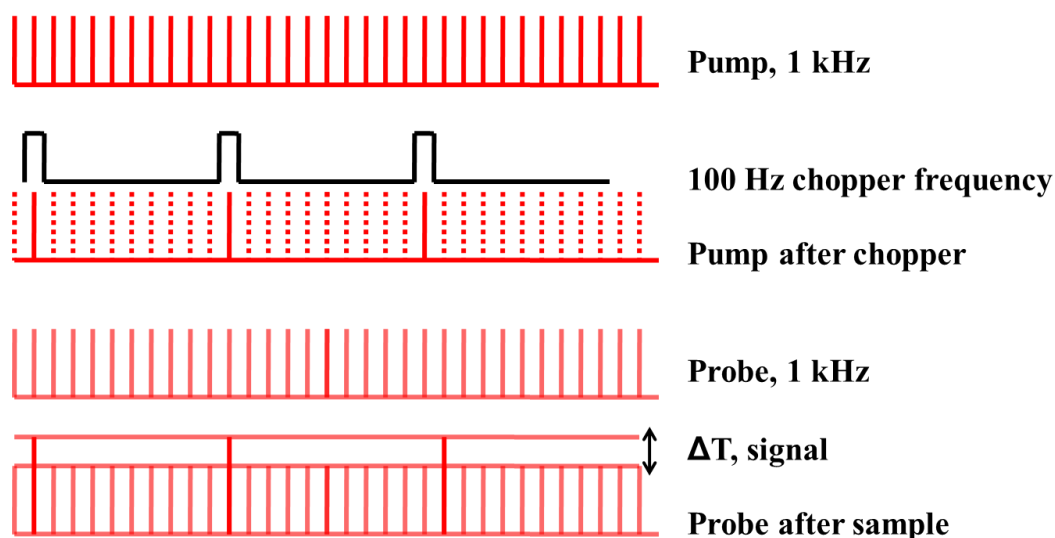


Figure 1.4 Pump modulation by a 100 Hz optical chopper assuming the repetition rate of pump to be 1 kHz.

Depending on the process to be examined, pump-probe technique has different types of probing methods. In the case to study the molecular relaxation dynamics, we choose time-resolved absorption measurement in which the differential transmittance of the probe is measured, whereas differential reflectance of the probe is measured to study the changes in the refractive index. The index change can also be detected by interferometric methods and by measuring the change in spatial profile of the output probe beam. In non-collinear geometry, transient grating is formed by refractive index gradient and the probe will get diffracted. By measuring the delay versus probe intensity we can measure the time in which coherence of excited state disappears, which is known as dephasing time. Reorientation time of anisotropic molecules can be studied using polarized pump and probe beams. Studying coherent vibrations is another

important goal of pump-probe spectroscopy. Resonant vibrational period of nuclei vary from 10-100 fs which corresponds to THz spectral range. These are measured through third order nonlinear polarization from the molecular vibrations. This is observed as the Raman shift in the output field. The time dependence of nonlinear refractive index measures the temporal response of these coherent vibrations [53].

1.4 Nonlinear absorption in organic molecules

The USPs are not only characterized by the short pulse duration but also by their high peak intensities which induces several nonlinear optical processes in materials. When the field of the electromagnetic wave is sufficiently large, the induced dipole moment in the material will no more linear to the field amplitude. The optical response can be expressed by the polarization P as a power series in the field strength E as follows:

$$P = \epsilon_0 (\chi^{(1)}E + \chi^{(2)}E^2 + \chi^{(3)}E^3 + \dots) \quad (2)$$

Where ϵ_0 is the permittivity of freespace, χ 's are the macroscopic susceptibilities : $\chi^{(1)}$ is the linear or normal or first order susceptibility, $\chi^{(2)}$ is the quadratic (second order) NLO susceptibility and $\chi^{(3)}$ is the cubic (third order) NLO susceptibility. The expansion is often written as the sum of two terms.

$$P = P^L + P^{NL} \quad (3)$$

where P^L is the linear polarization and P^{NL} corresponds to nonlinear polarization. The nonlinear absorption is associated with the imaginary part of macroscopic susceptibilities [54]. The absorption of the material changes nonlinearly under intense laser radiation. Figure 1.5 shows the probable NLA mechanisms. The NLA mechanisms mainly depend on the absorption cross section at the excitation wavelength and pump intensity and are explained in detail in the following sections.

1.4.1 Saturable Absorption (SA)

If the absorption of the sample decreases as the input laser intensity is increased, it is defined as saturable absorption (SA). SA occurs when the ground state cross section is generally higher than the excited state cross section. The saturation of excited state occurs owing to the long lifetime of the excited state S_1 .

The characteristic parameter for SA is the saturation intensity I_s which is related to the NLA as follows: $\alpha(I) = \alpha_0/(1+I/I_s)$ and is considered to be homogeneous saturation. In the case of inhomogeneous saturation i.e. if the absorption profile is inhomogeneous or Doppler broadened, the NLA becomes $\alpha(I) = \alpha_0/(1+I/I_s)^{1/2}$ where I_s is the saturation intensity which is estimated as $I_s = h\nu/\sigma_g\tau$, τ is the lifetime of S_1 state, $h\nu$ is the energy of photon and σ_g is the ground state cross section [56].

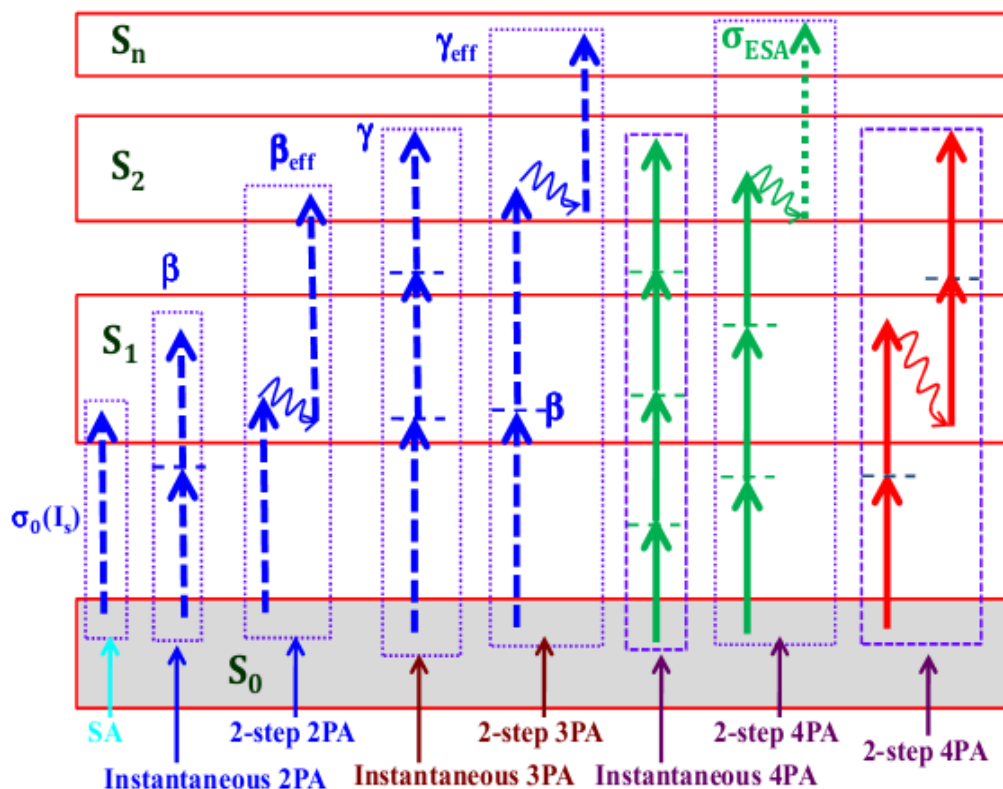


Figure 1.5 Various NLA processes in organic molecule (adapted from reference [55]). S_0 , S_1 , S_2 , S_3 and S_4 represent singlet electronic ground state and excited states. σ_0 is the ground state cross-section, I_s is the saturation intensity, β is the two photon absorption coefficient, β_{eff} is the effective two photon absorption coefficient or 2 step two photon absorption coefficient, γ is the three photon absorption coefficient, γ_{eff} is the effective three photon absorption coefficient or 2 step three photon absorption coefficient, σ_{ESA} is the excited state absorption coefficient.

1.4.2 Reverse Saturable Absorption (RSA)

If the absorption of the sample increases as the input intensity is increased, it is called as reverse saturable absorption (RSA) or induced absorption. RSA occurs when the excited state cross section is generally higher than the ground state cross section. It can also be observed as a result of excited state absorption, two photon absorption (2PA), three photon absorption (3PA) or combination of three of them which may lead even to four photon absorption [55]. It depends on the

excitation pulse duration, excited state lifetimes of singlet and triplets. In 2PA, the transition from S_0 to S_n occurs by simultaneous absorption of two photons. This is called instantaneous 2PA and is non-resonant i.e. in the presence of a virtual state. The transition can also occur from S_0 to S_n through S_1 . This is called sequential 2PA or 2 steps 2PA and is resonant i.e. in the presence of a real state. If the photo excited molecule relax in vibrational level of S_1 , the processes is called excited state absorption (ESA). The induced absorption is given by $\alpha(I) = \alpha_0 + \beta I$, where β is the two photon absorption coefficient [57]. The unit of 2PA coefficient is cm/W . In case of three photon absorption, the induced absorption becomes, $\alpha(I) = \alpha_0 + \gamma I^2$ where γ is the three photon absorption coefficient. The unit of 3PA coefficient is cm^3/W^2 . The 3PA can be instantaneous if the pulse duration is less than 100 fs. A two-step 3PA involves ESA followed by 2PA [58].

1.5 Importance of porphyrin and related compounds

Porphyrins are class of compounds from which many of the π conjugated molecules can be derived. The basic structure of theses compounds consist of tetra pyrrolic system. With the ease of synthesis and versatility in optical properties which depend on their structural diversities, molecular engineering has become inevitable part in organic optical materials. Phthalocyanines, corroles, porphyrins fit in the family of tetraprroles and whereas naphthosappyrins belong to expanded porphyrins and such class of compounds are used in chemo sensing, optical limiting, light harvesting etc. [62-65]. Sensors based on fluorescence quenching of these compounds are widely accepted methods to detect nitrated explosive molecules. However, steady state fluorescence measurements are not enough to understand the exact mechanism. Several physical processes like charge transfer, electro transfer, energy transfer, intersystem crossing, ground state complex formation contribute to the fluorescence quenching. Among these some of the process like electron transfer, charge transfer intersystem crossing etc. occur in ultrafast time scale [40, 41]. Besides, these compounds are prominent NLO materials with variable figures of merit and hence the nonlinear absorption is also affected by aforementioned processes. The origin of nonlinearity of these compounds is the presence of delocalized π electrons which are easy to get polarized under laser irradiation. In certain molecules, occupation of a central

metal atom enhances the nonlinearity of the material due to heavy atom effect. The different process occur due to nonlinearity are SA, ESA, multi photon absorption (MPA), etc. RSA is useful in making optical limiters. An optical limiter with low limiting threshold [59-62] is always preferred. Another class of application of these organic materials is in the field of light conversion as photosensitizers. Organic solar cells are considered to be third generation of photovoltaic cells since 1991 [63]. The organic dye, under photo excitation, transfers electron to an anode metal oxide and starts the circuit. The dye is restructured by electron transfer from the electrolyte in which the organic dye layer was placed. The injection of excited electron to the anode should be done faster (typically in few fs) for better efficiency. Moieties containing strong electron donating and accepting groups yield strong charge transfer [64, 65]. These fast processes in molecular level can be well understood only by using the techniques of ultrafast spectroscopy in which the temporal resolution is determined by the pulsed duration of ultrashort pulses and not by the response of the detector. The aim of present thesis is to explore the ultrafast dynamics of newly synthesized molecules which are derived from porphyrin moieties using time-resolved spectroscopy and NLO measurements. The compounds of interest include corroles, naphthosapphyrins (which are considered to be expanded porphyrins), phthalocyanines and porphyrins.

1.6 Outline of thesis

The thesis summaries the study of ultrafast dynamics and NLO properties of newly synthesized conjugate organic compounds such as corroles, naphthosapphyrins, porphyrins and phthalocyanines. Chapter wise discussions are given below:

Chapter 1 presents the background and motivation of the studies performed in this thesis. It provides information on various spectroscopic processes in an organic molecule after photo excitation. The interaction mechanism of these molecules with ultrashort laser pulses and a detailed discussion of various pump-probe measurements carried out by various research groups on energetic materials are highlighted. The time scales of these ultrafast processes are emphasized. Different ultrafast time resolved spectroscopic

techniques which are used to detect or measure these processes are discussed. The importance and characteristics of ultrashort pulses are being explained. The chapter ends with the details of evolution of fs pump-probe spectroscopy and important aspects of data acquisition involved in pump-probe technique.

Chapter 2 comprises of an overview of experimental methods and theoretical concepts of the techniques used in this thesis. Ultrafast laser sources used for the experiments and results from their characterization studies are presented. The principles of pump-probe technique and its artifacts are explained in detail. The Z-scan experiment for understanding the excited state absorption is explained based on the rate equations. Other methods such as degenerate four wave mixing, self-diffraction are explained which are used to study the dynamics of sample of interest. Schematic of all the experiments are explained in detail.

Chapter 3 comprises of two parts. The first part of the chapter contains the optimization of the ps/fs pump-probe experiments using semi-insulating gallium arsenide (SI-GaAs) and low temperature grown gallium arsenide (LT-GaAs) samples. Both the materials are used in terahertz (THz) generation and detection. The pump-probe experiments were performed in the reflection geometry. The temporal dynamics of carrier phonon interaction in semiconductors are discussed. The signal to noise ratio was calculated from these experiments. The second part of the chapter is dedicated to discussion on the optimization of Z-scan technique to understand the excited state absorption of phthalocyanine molecules. The NLO measurements were performed both in solution as well as thin film forms. Z-scan studies provided us with the information on excited state absorption, which was useful in analyzing the pump-probe data.

In **Chapter 4** ultrafast excited state dynamics of four novel corroles have been appraised with ps and fs degenerate pump-probe techniques using excitation wavelengths of 800 nm and 600 nm, respectively. Ultrafast NLO properties in the visible spectral range (660-800 nm) were evaluated using ps Z-scan technique. The excitation by 800 nm photons resulted in two-photon absorption, at adequately high peak intensities, thereby facilitating the access to higher excited states (S_n). The non-radiative relaxation mechanisms from these states, reflected in the pump-probe data, consisted of double-exponential decay with the slow

component in the range of 54-277 ps and the faster component in the range of 2.0-2.5 ps. When excited with 600 nm photons (unfocused) photo-induced absorption was observed with the first excited state S_1 being populated and as a consequence single decay was observed in the data of all molecules studied. These retrieved lifetimes were analogous to those obtained with ps pump-probe data at 800 nm. The long lifetime is attributed to non-radiative decay from the S_1 state with possible contribution from triplet states while the shorter lifetime is attributed to the internal conversion (S_2 to S_1^*) followed by vibrational relaxation (S_1^* to S_1) processes. Time-resolved fluorescence lifetime measurements revealed the magnitude of radiative lifetimes to be in the nanosecond regime. NLO coefficients were evaluated from the Z-scan data at wavelengths of 660 nm, 680 nm, 700 nm, 740 nm and 800 nm to understand the nonlinear absorption at different wavelengths. Large two-photon absorption coefficients (β)/cross-sections (σ_2) at 740 nm/680 nm were recorded for these molecules making them apposite for applications such as two-photon induced photodynamic therapy and lithography. NLO figure of merit, T , was <1 at 740 nm and 800 nm, suggesting these molecules find use in photonic device applications.

In **Chapter 5**, the ultrafast dynamics of two new series of freebase naphthobipyrrole-derived sapphyrins along with their various salts have been studied using ps degenerate and non-degenerate pump-probe studies. The degenerate ps pump-probe was performed at 800 nm at two energies. In non-degenerate ps pump-probe experiment, the sample was pumped by 400 nm wavelength and probed at 800 nm wavelength. One series of compound contained substituents at all of its β -positions, whereas the pyrrole unit opposite to the bipyrrrolic moiety remain unsubstituted in the other one. Effect of bipyrrrole fusion on the structure of sapphyrins was explored. The change in the lifetime of the excited states of the freebase and its salts with common acids were compared and the effect of anions on the third-order NLO properties of these Sapphyrins was explored in the salt form using Z-scan technique at 800 nm. The time scales of probable transitions are explained in a potential energy level diagram. A selective excitation is accomplished via non-degenerate pump probe technique. The non-radiative decay times were obtained from non-degenerate pump probe studies and the radiative life times were obtained from time correlated single photon counting.

It was found that due to the higher nonlinearity of free-bases, 2PA was observed even at lower peak intensities, whereas the sapphyrin salts needed higher peak intensities to achieve 2PA. The excited state dynamics studies using degenerate and non-degenerate pump-probe techniques revealed the decay times of high lying excited states in the ps and ns regimes.

In **Chapter 6**, the excited state dynamics of an octamethyl porphyrin (OMP) and free base tetra tert-butyl phthalocyanine (Pc) in the presence of energetic/explosive molecules such as 2,4,6-trinitrotoluene (TNT), 1,3,5-trinitroperhydro-1,3,5-triazine (RDX) and 2,4,6,8,10,12-Hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (CL-20) were studied using emission, nanosecond Z-scan and fs pump-probe techniques. The interaction of the fluorophore and the nitro-compounds (NC) was investigated by fluorescence spectroscopy which clearly demonstrated fluorescence quenching to varying degree depending on the fluorophore and the explosive molecule. The change in nonlinear absorption (saturable absorption mechanism in the case of OMP and reverse saturable absorption mechanism in case of PC) of these molecules was monitored using the standard open aperture Z-scan technique recorded with nanosecond (ns) pulses at 532 nm. The change in non-radiative decay time was studied by fs pump-probe measurements in the 600-700 nm spectral range. The experimental results obtained from these measurements suggest that the interaction of NCs with porphyrin and phthalocyanine moieties alters their nonlinear absorption properties and excited state dynamics in the ultrafast time scale. The results were verified qualitatively by simulating the open aperture Z-scan data with similar experimental conditions. The observed dynamics are explained using an effective three level energy diagram. These studies clearly reveal that the ultrafast decay times as well as the excited state cross-section play an important role in the interaction mechanism of NC's with porphyrin and phthalocyanine molecule. If the organic chromophores are designed and optimized thoroughly, open aperture Z-scan technique could possibly be used for screening the explosive molecules from others.

Chapter 7 concludes with the summary of results obtained in this thesis along with the scope for future work especially for studying high energy molecules. We have investigated the ultrafast dynamics of corroles,

naphthosapphyrins, phthalocyanine and porphyrins using degenerate and non-degenerate pump-probe experiments. Fs/ps pump-probe and Z-scan experiments were performed to understand the temporal dynamics and the NLO properties. Different geometries of pump- probe measurements have been investigated. Preliminary measurements, using fs degenerate pump-probe technique at 800 nm, have been performed on dicyclopentadiene (DCPD) which is used as binder in rocket propulsion applications. Our future works include developing the pump-probe set up for transient absorption spectroscopy in which a broadband probe is used. This helps to study not only time resolved dynamics but also spectrally resolved dynamics.



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CHAPTER 2

Experimental methods & Theoretical concepts

ABSTRACT

This chapter comprises of an overview of the experimental methods and theoretical concepts of various techniques used in this thesis. The principles of pump-probe technique and its artifacts are explained in detail. The details of ultrafast laser sources used for the experiments and results from their characterization studies are presented. Other methods to study the excited state dynamics through optical nonlinearity which including Z-scan, degenerate four-wave mixing, self-diffraction are also explained. The schematic of all the experiments used in the thesis are presented and explained in detail.

2.1 Introduction to pump-probe spectroscopy

With the recent development of ultrafast laser systems, time resolved studies have evolved immensely and helped scientists to understand the ultrafast phenomena in the field of physics, chemistry and biology using various spectroscopic techniques. Spectroscopy with ultrashort laser pulses has widely been used to elucidate the dynamics and physical mechanisms of intra and intermolecular energy redistribution, which could not be accessed through other experimental techniques. Pump-probe spectroscopy is a two beam experiment in which a strong ultrashort laser pump pulse and a weak probe pulse are sent to the sample with a definite time delay between them. The pump and probe beams are overlapped spatially (and temporally) at zero delay. The pump pulse excites the atomic/molecular species inducing particular transitions and the probe beam is used to monitor the process. For example, molecules or atoms in their excited states once excited tend to relax back to the ground state. The evolution of this process can be monitored by the delayed probe pulse through absorption or reflection and varying the delay time between pump and probe pulses. In case of transmission geometry one measures the change in transmittance ($\Delta T/T = T_{\text{pump on}} - T_{\text{pump off}}/T_{\text{pump off}}$) of probe due to pump whereas in the case of opaque samples reflection geometry is preferred, wherein one measures the change in reflectance ($\Delta R/R$) of probe beam. The pump excites the molecules and transmittance of the probe depends on various mechanisms occurring during the relaxation as shown in figure 2.1 (a).

For complete bleaching of the ground state and stimulated emission due to probe photons, the change in transmittance ΔT will be >0 . There will be an enhancement of transmittance followed by decay. In the case of excited state absorption or photo-induced absorption or transient absorption, the change in transmittance will be $\Delta T < 0$. If the pump-probe signal originates from ground state absorption, the graph can be overlapped with the linear absorption spectrum and if it is from stimulated emission the graph can be overlapped with the photoluminescence (PL) spectrum. The possible signatures of the time-resolved spectra in a typical pump-probe technique are demonstrated in figure 2.1 (b). From these dynamics we can understand the lifetime of high lying energy levels.

In the case of two photon absorption resonance, the observed signal will be due to the photo bleach and ΔT will be >0 . Experimentally, the pump beam is modulated with a lower frequency than probe using a chopper. The photodiode which measures the probe signal is connected to a lock-in amplifier and the lock-in amplifier measures ΔT or ΔR from photodiode at the frequency of pump. A large area photodiode is generally used for better collection of probe signal. The spot size of the probe beam is generally kept smaller than the pump beam so as to ensure the transmission of all the probe photons in the pumped region of the sample at various time delays during scanning of the delayed probe beam. The angle between the pump and probe is also kept low ($2-5^\circ$) to maximize the overlap of both the pulses [1-12].

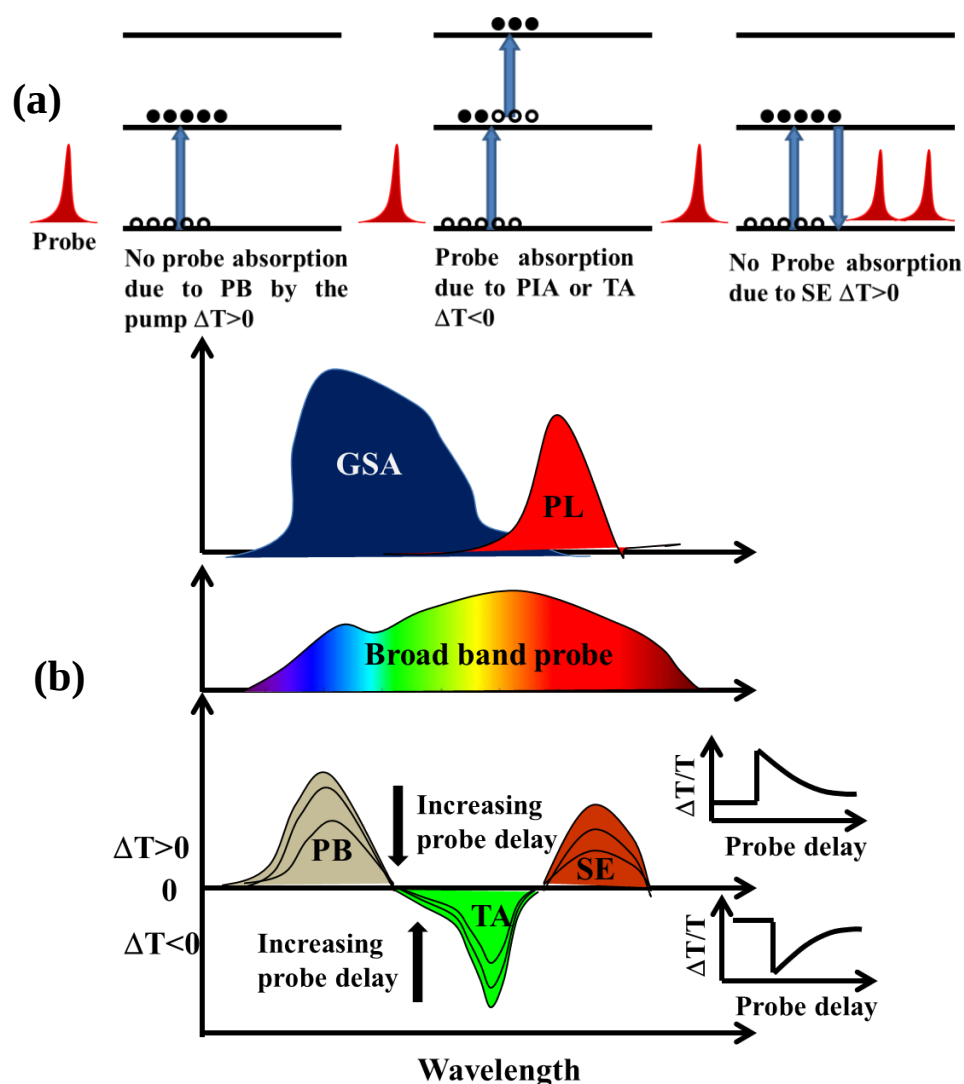


Figure 2.1 (a) Possible transitions in the pump-probe interaction in the sample and (b) typical transient absorption spectra. Here PB - Photo bleach, PIA - Photo-induced absorption, TA- Transient absorption, SE- Stimulated emission, GSA- Ground state absorption, PL- Photoluminescence.

2.1.1 Principle of pump-probe technique

In a typical pump-probe technique, an intense pump pulse with time dependence $I(t)$ interacts with the sample and the probe beam $I(t+\Delta t)$ which interrogates the population (which is not in equilibrium) after a time delay Δt . The measured pump probe signal $[F(\Delta t)]$ is proportional to the convolution of Gaussian function which is the cross-correlation of the two beams and exponential decay function, $f(t)$ which is the response from the excited sample. This can be written as:

$$F(\Delta t) \propto \int_{-\infty}^{\infty} I(t+\Delta t) f(t) dt \text{ where } f(t) = \sum_i A_i e^{-(t-t_0)/\tau_i} \quad (1)$$

The pump induced transmission change (ΔT) is measured by a lock-in amplifier by providing the reference frequency as modulation frequency of the pump beam using an optical chopper. Neglecting the ‘coherent artifacts’ which will be discussed in the next section, let’s consider the electronic transition between two levels i and j . According to Beer-Lambert relation, the absorption coefficient is $\alpha(\nu) = \sigma_{ij}(\nu)(N_i - N_j)l$ where σ_{ij} is the cross-section (cm^2), N_i, N_j are the populations in the initial and final states respectively. l is the thickness of the sample. The pump pulse acts on the sample by changing the level population as $N \rightarrow N + \Delta N$. The detector can measure the change in the probe intensity before and after the pump perturbation as $\Delta T/T$ ie.

$$\frac{\Delta T}{T} = - \sum_{i,j} \sigma_{ij}(\nu) \Delta N_j(t_d) l \quad (2)$$

The time dependence is reflected in $\Delta N_j(t_d)$ where t_d is the pump to probe delay. For a fixed pump to probe delay t_d , the dependence of $\sigma(\nu)$ and hence $\alpha(\nu)$ can be calculated so as to construct the transient absorption spectrum of the excited sample at time t_d . For a fixed ν , the change in the probe transmittance $\Delta T/T$ can be measured by varying t_d and is proportional to $\Delta N(t_d)$. Thus if the population N_j decays exponentially, the decay time τ , can be found from the equation:

$$\frac{\Delta T}{T} \propto \Delta N_j(t_d) \text{ where } \Delta N_j(t_d) \propto N_j(0) e^{-t_d/\tau} \quad (3)$$

For multi-component decay process, the signal can be fitted to the following equation:

$$\frac{\Delta T}{T} \propto \sum_i A_i \exp(-t_d / \tau_i) \quad (4)$$

Where A_i is the signal amplitude and τ_i is the lifetime of the i^{th} decay process [13-19].

2.1.2 The artifacts in pump-probe measurements

Though the signature of pump-probe signal has contributions from the population dynamics of the molecular system, there could be some unusual signals in the temporal region where pump pulse overlaps with the probe pulse (zero delay). This coherence artifact disturbs further analysis of pump-probe data and one has to eliminate these signals by appropriate methods. The main sources of these non-resonant contributions to the measurement are internal reflections of the pump pulse in an optical element, polarization of pump and probe beam, scattering from the surface of the sample in case of reflection geometry, nonlinear interactions of the pump and probe beam in the sample and group velocity dispersion (GVD) if the probe is broadband. The inner reflections from an optical elements cause the beam to travel extra path and form a delayed pulse. This will result a ‘ghost’ pump probe signal at the negative delay times [3,14].

In anisotropic medium, the transition moment of the excited species will be oriented according to the pump polarization and will start to reorient during the evolution of time. In such cases the measurements of probe whose polarization is parallel or perpendicular to the pump polarization can have the contribution from the lifetime of the population as well as the reorientation time. This can be avoided if the angle between pump polarization and probe polarization is maintained at 54.6° , which is called as magic angle [21]. The scattering of the pump light from the surface can cause interference pattern with probe beam throughout the overlapping region. A well-polished sample surface can avoid this artifact. Another major source of coherent artifact is diffraction of the pump beam along the probe beam by the transient grating formed by nonlinear processes and the detector can detect this diffracted signal along with the pump probe signal. The primal process responsible for this effect is $\chi^{(3)}$ which is the basic principle

for four wave mixing process. In most of the cases if the population dynamics is stronger than the coherent artifact, these effects can be neglected. These effects can be carefully eliminated by ensuring proper temporal delay steps in the data acquisition [20-25].

2.2 Ultrafast laser sources

In this section the technical specifications and operations of the various laser sources used in different experiments are explained in detail. The laser sources mainly include (1) Oscillator (MICRA; Coherent, USA) (2) Amplifiers (LEGEND; Coherent, USA) (3) Optical parametric Amplifiers (TOPAS & TOPAS-C; Light Conversion, Lithuania).

2.2.1 Oscillator (MICRA)

The Micra is a Ti: sapphire laser based oscillator system manufactured by Coherent, USA and is capable of producing mode locked pulses with bandwidths exceeding 100 nm. Ti: sapphire laser is based on Kerr lens modelocking. The top view of Micra Laser system is shown in figure 2.2. It is integrated with a pump laser (Verdi, Coherent, USA) which is a continuous wave green laser with power of 10W. The gain medium in Verdi is Neodymium Yttrium Orthovanadate (Nd:YVO_4 crystal), which generates a fundamental wavelength of 1064 nm. Frequency-doubling occurs within a lithium triborate (LBO) nonlinear crystal producing green light at 532 nm, allowing efficient absorption by the Ti:sapphire crystal. The doubling crystal is held at a particularly elevated temperature ($\sim 150^\circ\text{C}$) to achieve temperature tuned phase matching. The Nd:YVO_4 laser uses fiber array package (FAP) semiconductor diode (AlGaAs) CW lasers with wavelength of 808 nm as the pump source. Diode lasers directly convert electrical energy to laser light with high efficiency (60-80%).

The optical layout of Micra laser system is shown in figure 2.3. The Verdi pumps 532 nm to the Ti: sapphire crystal through a power track active mirror set (R1 & R2) to correct any long term drift associated with the pumping. The oscillator itself employs Kerr lens mode locking in combination with an intracavity adjustable prism pair (PR1 & PR2) to generate low-noise, large-bandwidth, and high peak power ultrafast laser pulses. The cavity also features automated mode locking initiation by means of a solenoid-driven movable mirror

mount at M4. The end mirrors M1 and M8 encompasses the entire cavity while M2-M7 are folding mirrors which configures the folding cavity.

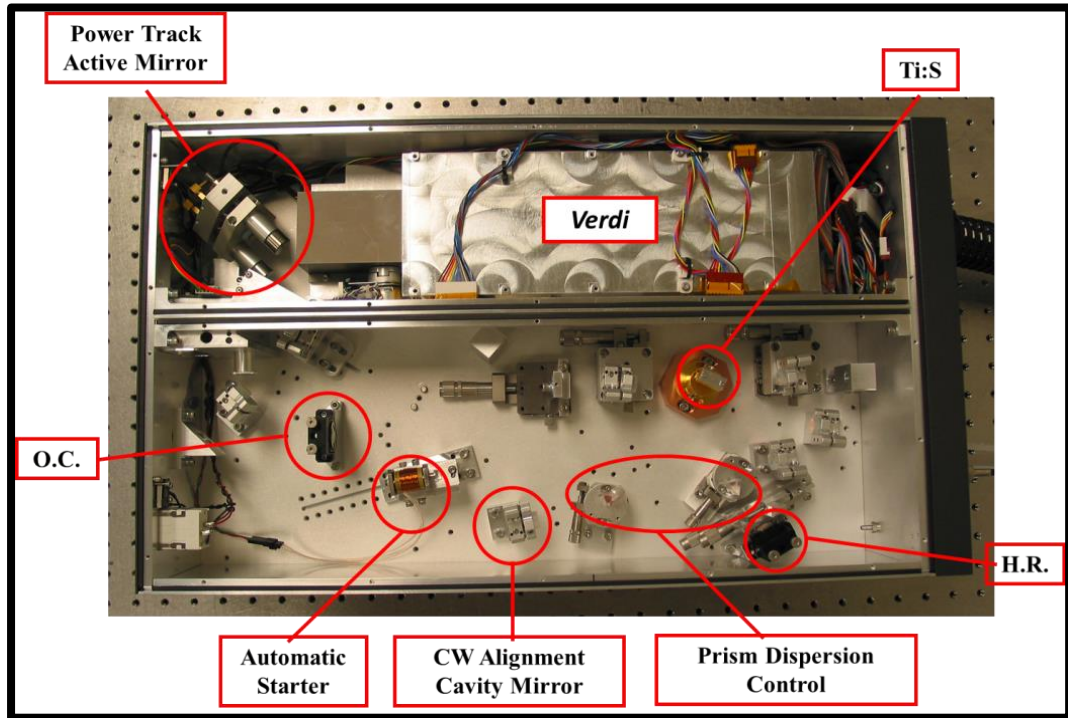


Figure 2.2 Top view of MICRA Laser system (Image adopted from Coherent MICRA manual) [33].

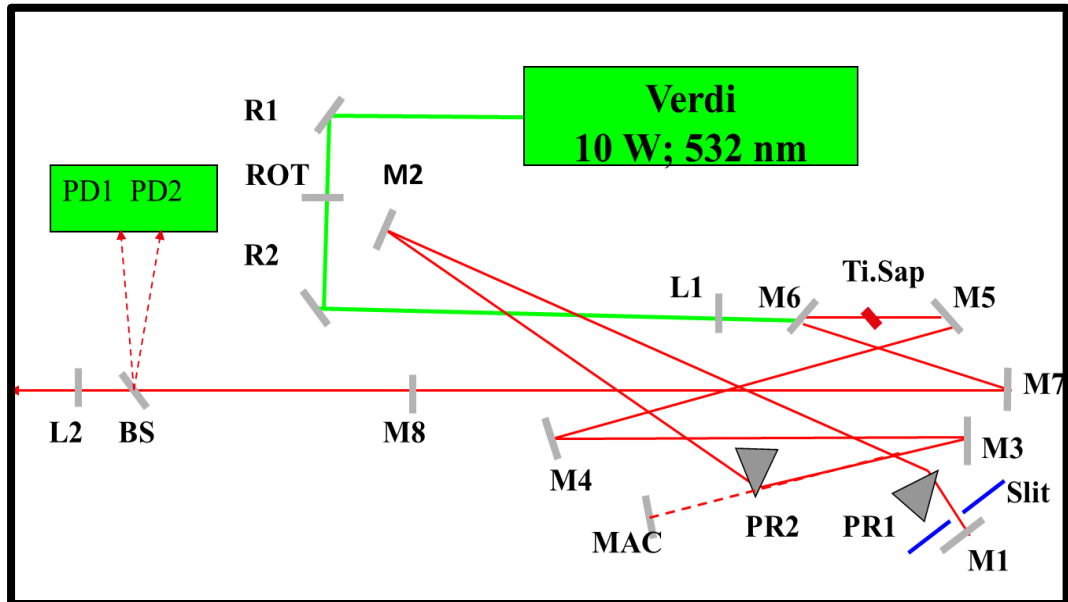


Figure 2.3 Optical layout of MICRA laser system (Image adopted from Coherent MICRA Manual) [33]. R1- Pump beam routing optic with Power Track beam steering actuators, ROT-Polarizer, R2-Pump beam routing optic, L1-Pump beam focusing lens, Titanium: sapphire laser crystal, M1-M8 Oscillator cavity mirrors, MAC- mirror in the auxiliary cavity for initial alignments, PR1&PR2- Prism pair, BS-Beam splitter, PD1&PD2-Fast and slow photodiodes, L2-Collimating lens.

Kerr lens mode locking is used for the generation of sub-100 fs laser pulses from Ti: sapphire crystal via optical nonlinear effect known as Kerr lensing. It is an intensity driven process by which the refractive index of the medium changes with the intensity as the following:

$$n = n_0 + n_2 I \quad (5)$$

where n_0 and n_2 are the linear and nonlinear refractive indices respectively, I is the input intensity. The subscript 2 in n_2 indicates the contribution of refractive index due to second order in electric field [32]. Due to the non-uniform intensity distribution of Gaussian beam, the crystal rod experiences different refractive index values at different positions and behaves like a focusing lens. Only those pulses with high intensity will be favored by the Kerr medium. The intensity maximum implies a fixed phase relationship between the modes in the cavity since the maxima of the stronger mode grow at the expense of the lesser maxima. As a result the bandwidth of output laser pulses increases and shorter pulses are generated [63].

2.2.2 Picosecond/ Femtosecond amplifier (LEGEND)

Legend-F is an industrial and scientific grade regenerative amplifier. It is a chirped pulse amplifier (CPA) laser system which is capable of delivering picosecond (ps) /femtosecond (fs) pulses with an average energy of typically >1 mJ/ pulse at a central wavelength of 800 nm and a repetition rate of 1 kHz. In our case, maximum energy provided by ps/fs amplifiers were ~2.0 mJ/~2.5 mJ, respectively. The amplifier is designed to amplify the ultrashort pulses in the near infrared similar to the one from MICRA. The optical layout is shown in figure 2.4.

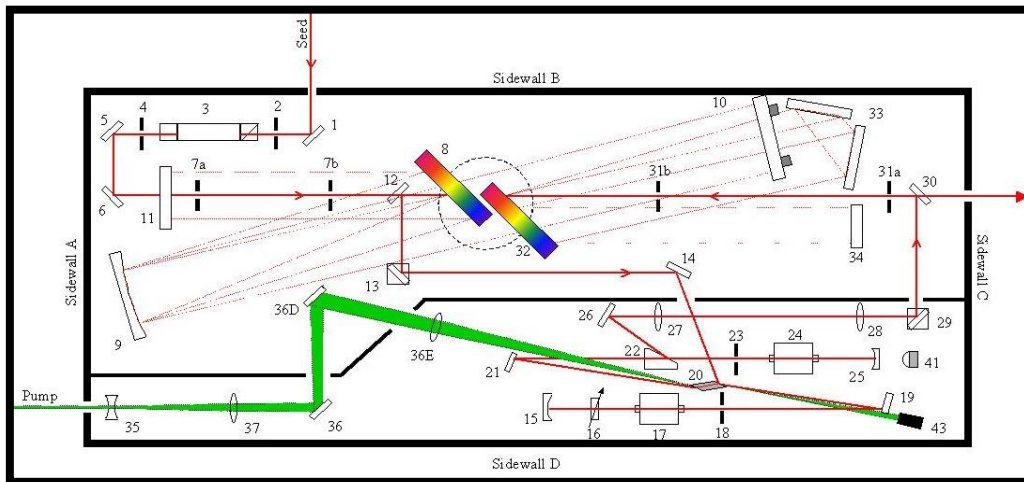


Figure 2.4 Optical layout of LEGEND amplifier (Image adopted from Coherent Manual) [34].

The amplifier consists of three main parts: (1) stretcher (2) regenerative amplifier (RGA) and (3) compressor. A proper synchronization and delay generator controls the precise timing for the regenerative amplification. The short seed pulse when amplified produces huge peak intensity which will destroy the optics inside the cavity. Hence the seed pulse is stretched in the temporal domain, before amplification and compressed to produce desired pulses.

2.2.2.1 Optical pulse stretcher and compressor

The optical layout of stretcher and compressor in LEGEND amplifier system are shown in figures 2.5 and 2.6 respectively. The stretcher (and compressor) has a single grating with a curved gold mirror which changes the GVD such that the pulse is positively chirped (negative chirping in case of compressor). The seed pulses enter to the stretcher grating (#8) which disperses the beam and directed towards the curved mirror (#9) and is focused at the end mirror (#10). The beam reverses its path towards the curved mirror (#9) and is sent back to grating. The end mirror is aligned such that this reflection takes a path towards the lower mirror of the vertical retro-reflector (#11). The beam path is now well above the input beam and is temporally stretched but dispersed spatially due to dispersion on the grating. The spatially broadened beam once again sends through the stretcher to re-collimate. The vertical height is retained after the double pass and is sent to the pick-off mirror (#13).

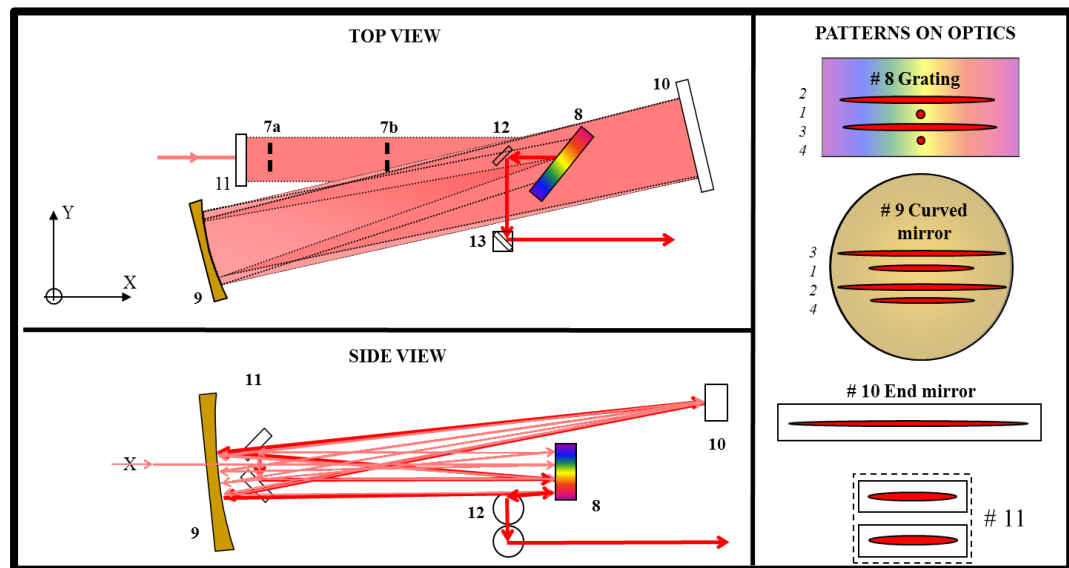


Figure 2.5 Optical layout of stretcher in LEGEND amplifier system (Image adopted from Coherent manual) [34].

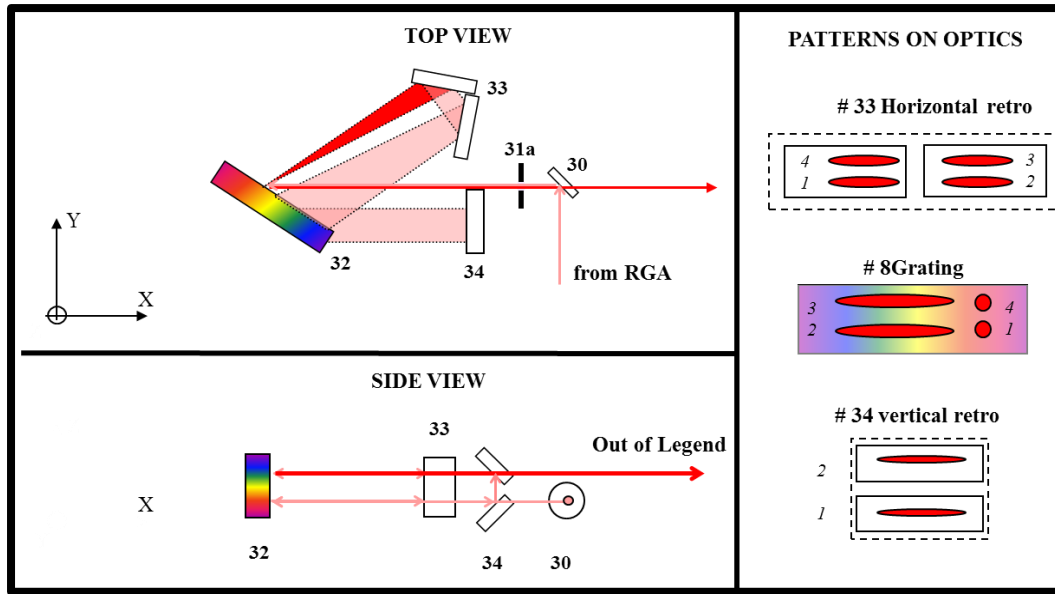


Figure 2.6 Optical layout of Compressor in LEGEND amplifier system (Image adopted from Coherent manual) [34].

The compressor has reverse effect of stretcher. The amplified pulse from the RGA is sent to the compressor grating (#32) by turning mirror (#30 in figure 2.6). The grating turns the beam towards the horizontal retro (#33) which reflects back the beam with horizontal shift from the input beam at the grating. The beam is now sent to the vertical retro (#31a) which increases the height of the beam and the beam is spatially broadened. A second pass to compressor from the retro compresses the pulse to its required pulse duration.

2.2.2.2 Regenerative Amplifier

A regenerative amplifier (RGA) is a multi-pass amplifier and has Ti:sapphire crystal rod pumped by green laser (second harmonic of Nd:YLF, Evolution, 527 nm, 20 W at 1 kHz repetition rate). The optical layout of RGA is shown in figure 2.7. Soon after the peak in the pump (Evolution) is reached, the gain in the Ti:sapphire medium reaches maximum and the amplification process begins. The seed pulse of 's' polarization (vertical) from the stretcher is sent to the Ti:sapphire rod and gets reflected to end mirror M2 by the mirror M1 through Pockel's cell 1 and a quarter wave plate ($\lambda/4$). Since the Pockel's cell (PC#1) is deactivated at this time, the polarization of the laser changes to circular because of the $\lambda/4$ plate. The beam is now retraced by the end mirror M2 through the $\lambda/4$ again and the polarization changes from circular to 'p' polarization (horizontal). Immediately after the pulse leaves the $\lambda/4$ plate, the PC#1 is

activated by applying a voltage of ~3.5 kV and the ‘p’ polarized pulse is trapped in the resonator and other seed pulses are rejected by Brewster’s reflection of Ti:sapphire rod. After certain number of round trips (usually about 8-10 passes) the voltage is applied to PC#2 which cause a half wave polarization rotation to the pulse after it double passes the PC#2. The polarization changes to ‘s’ polarization which is now ejected to the compressor.

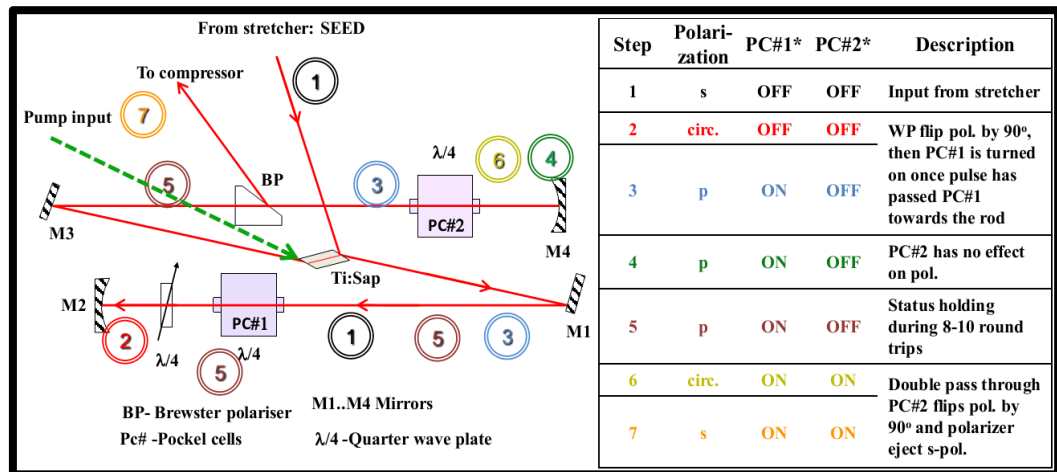


Figure 2.7 Optical layout of RGA in regenerative amplifier system (Image adopted from Coherent manual) [34].

2.2.3 Optical Parametric Amplifier (OPA)

Optical parametric amplifier (OPA) provides the wide range of tunability from deep ultraviolet to far infrared laser pulses through various second order nonlinear process. The commercially available systems TOPAS-C and TOPAS (Light Conversion) can deliver wavelengths from ~250 nm to 2600 nm. Both the OPAs use different amplifying configurations which are explained in the next section. Further, far IR pulses can be obtained by using nonlinear different frequency generation (NDFG) processes.

2.2.3.1 TOPAS-C

Travelling wave optical parametric amplifier-C (TOPAS-C) is a two stage amplifier with white-light continuum. The major units of TOPAS-C are white light continuum generator (WLG), pre-amplifier or first amplification stage (PA1) and the power amplifier or second amplification stage (PA2). The optical layout of TOPAS-C is shown in figure 2.8. The 800 nm pump beam from the

femtosecond amplifier is split into two beams. 80-98% is being sent to the power amplifier and the remaining is again split for WLG and PA1. About 1-3 μJ of the pump is used to generate white light continuum from a sapphire crystal. The generated continuum and the remaining part of the pump beam (30-50 μJ) are focused onto the pre-amplifier crystal (NC1: BBO crystal) non-collinearly where the parametric amplification takes place. The amplified signal is expanded, collimated and sent to the second stage of amplification (PA2). The power amplifier is pumped by bulk of the pump beam (800 nm). The pump and signal beams are overlapped collinearly in the second nonlinear crystal (NC2: BBO crystal) and a well collimated signal and idler are generated.

The wavelength tuning in the pre-amplifier is done by changing the delay of WLC pulse with respect to the first pump pulse and the NC1 crystal phase matching angle. In the power amplifier it is performed by first adjusting the pre-amplifier wavelength and then optimizing the NC2 angle and the signal delay with respect to the second pump beam. The pump beam should have good spatial as well as temporal coherence. An ideal pump is diffraction limited beam and transform limited with high contrast ratio. Tilted pulses or the pulses from improper compressor will result in poor functioning of the TOPAS. The seed pulses for RGA can be too weak due to low oscillator power, poor mode-locking or improper pockel cell timing. This also results in poor stability of the TOPAS.

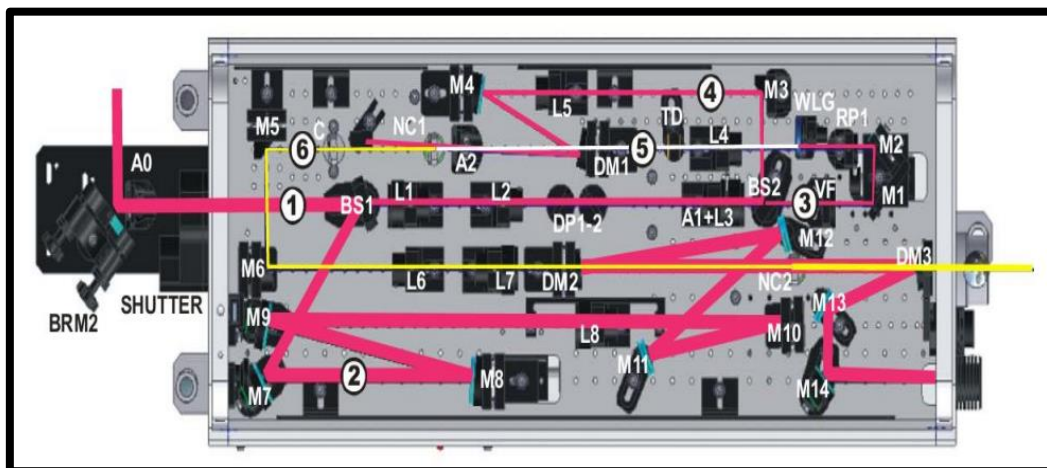


Figure 2.8 Optical layout of TOPAS-C (Image adopted from *Light Conversion Manual*) [35].

2.2.3.2 TOPAS-ps

TOPAS-ps has one stage of generator of superfluorescence (SFL) and four light amplification amplifier stages arranged in a single BBO crystal. Generator of SFL (first pass through the nonlinear crystal) serves as a seeder emitting broad band superfluorescence. The pre-amplifier (second and fourth passes through the nonlinear crystal) shapes the beam acting as a small amplifying aperture placed in the far field of the seeder. The amplification in the third pass is usually negligible. In the last stage amplification i.e., the fifth pass through the nonlinear crystal, the bulk of available pump is being used to boost the energy of the parametric pulse. The wavelength tuning is being done by rotating the nonlinear crystal (BBO) angle in the phase matching plane. Different mixers or wavelength separators are used to separate the required wavelengths.

2.3 Characterization of ultrashort pulses - Autocorrelation

Measurement of laser pulses whose pulse duration is less than 20 ps remains a challenge using conventional photo detectors. Several indirect methods such as autocorrelation, streak camera, frequency resolved optical gating (FROG), spectral phase interferometry for direct electric-field reconstruction (SPIDER) etc., for measuring ultrashort pulses have been developed. Among all, autocorrelation is the simplest and most affordable method to determine the pulse duration of ultrashort laser pulses. However, the phase information is not obtained using this technique. In this technique, the correlation of the same pulse in a second order nonlinear medium is recorded using a Michelson interferometer. A beam splitter splits the original incoming pulse into two identical pulses (beam 1 and beam 2). Thus the two beams $I(t)$ and $I(t+\tau)$, are variably delayed using proper delay line usually a translation stage, and allowed to overlap in some instantaneously responding nonlinear optical medium such as SHG crystal in a non-collinear geometry. The autocorrelation signal depends on the extent of overlap of both the beams. The temporal evolution of the autocorrelation (AC) signal is shown in figure 2.9(a). Under non-collinear phase matching conditions, a second harmonic signal is generated in the crystal. The AC signal appears in the middle of both the fundamental beams as shown in figure 2.9(b). The total

intensity of generated second harmonic signal is proportional to the extent of overlap of the two pulses or the autocorrelation function:

$$AC(\tau) = \frac{\int_{-\infty}^{\infty} I(t)I(t+\tau)dt}{\int_{-\infty}^{\infty} I(t)I(t)dt} \quad (6)$$

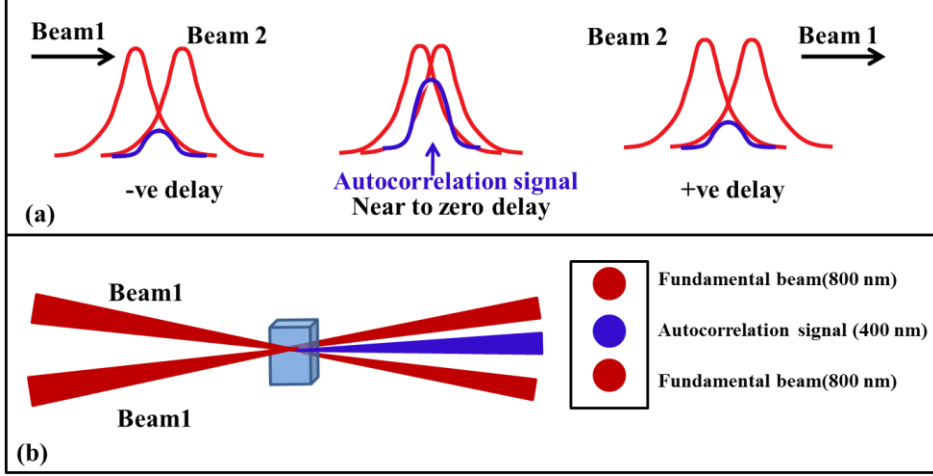


Figure 2.9 (a) Temporal evolution of autocorrelation signal. Here red and blue pulses represent fundamental and second harmonic respectively. Beam 2 remain fixed while beam 1 traverses beam 1. The intensity of the AC signal increases as the overlap of fundamental beams are increased. (b) Spatial appearance of AC signal satisfying the non-collinear phase matching condition.

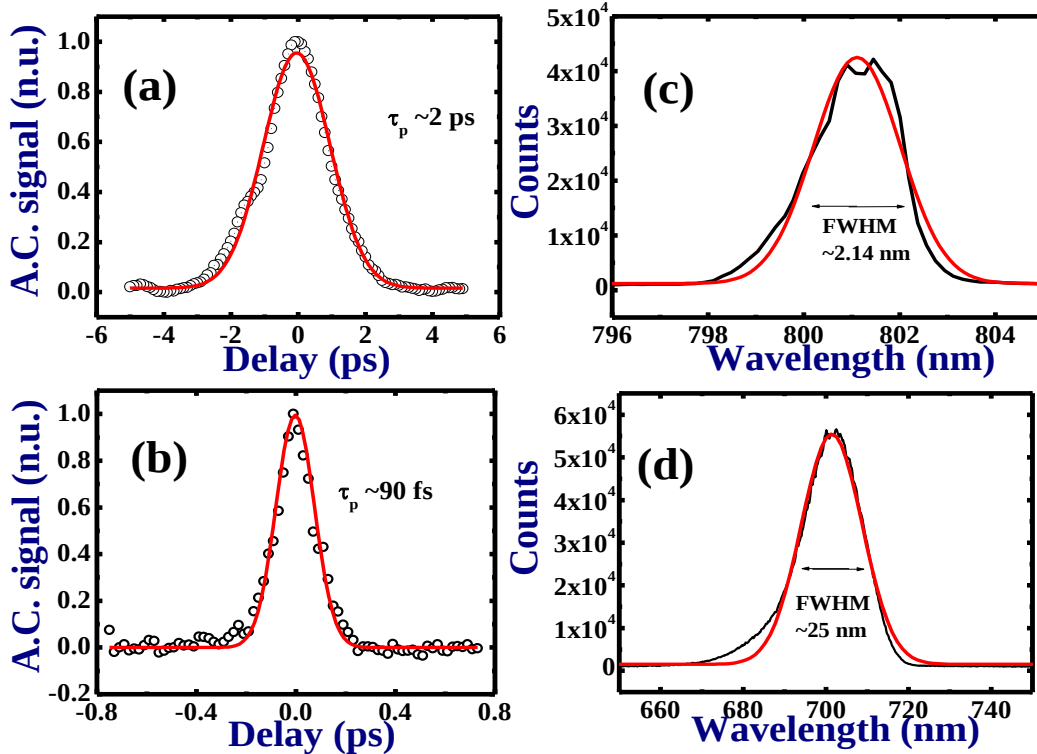


Figure 2.10 Autocorrelation trace of (a) 800 nm and (b) 700 nm pulses using a BBO crystal in non-collinear geometry. The open circles are the experimental data and the solid lines are the theoretical fits. The spectral profile of (c) ps pulses at 800 nm (d) fs pulses at 700 nm. The black solid lines and red solid lines are experimental and theoretical fits respectively.

Profile	Intensity profile $I(t)$	Autocorrelation function $G_2(\tau)$	Deconvolution factor ($\Delta\tau_{ac}/\Delta\tau_p$)*
Gauss	e^{-2t^2}	$e^{-2\tau^2}$	$\sqrt{2}$
sech	$\text{sech}^2(t)$	$\frac{3(\tau \cosh(\tau) - \sinh(\tau))}{\sinh^3(\tau)}$	1.543
exponential	e^{-t} for $t \geq 0$, 0 otherwise	$e^{- \tau }$	2
square	1 for $ t \leq 1/2$, 0 otherwise	1- $ \tau $ for $ \tau \leq 1$, 0 otherwise	1

Table 2.1 Autocorrelation functions and the deconvolution factors for different pulse shapes (adapted from reference [63]). * $\Delta\tau_{ac}$ and $\Delta\tau_p$ are the FWHM values.

For achieving shorter pulse duration, $\Delta\tau$, one has to negotiate for a larger bandwidth $\Delta\nu$ in Fourier space. The temporal and spectral bandwidth is related by the universal uncertainty relation in time and energy and can be written in the form of the inequality $\Delta\tau\Delta\nu \geq c$ where c is the constant which depends on the spatial and temporal profile of the pulse. The pulse is called Fourier transform limited when the equality is reached. It is also called the time-band width product. For a given band width, the pulse duration of the shortest pulse can be calculated from the time-band width product. However, there will be dispersion effects due to the phase change when these short pulses travel through any dispersive medium. The modified phase near a central frequency ω_0 as the pulse propagate through a medium of refractive index $n(\omega)$ and thickness L with a propagation vector k can be written as:

$$\Phi(\omega) = n(\omega)kL = k(\omega)L \quad (7)$$

The k - vector can be expanded in Taylor series:

$$k(\omega) = k(\omega_0) + k'(\omega_0)[\omega - \omega_0] + \frac{1}{2!}k''(\omega_0)[\omega - \omega_0]^2 + \frac{1}{3!}k'''(\omega_0)[\omega - \omega_0]^3 + \dots \quad (8)$$

The first term, $k(\omega_0)$ contributes to the phase velocity which is the speed at which the phase front propagates through the medium. The second term, $k'(\omega_0)$ contributes to the group velocity (v_g) which is first-order derivative of $\phi(\omega)$ with respect to ω evaluated at $\omega = \omega_0$. It is the speed at which the wave envelop propagate in the medium. The third term $k''(\omega_0)$ contributes to the group velocity dispersion (GVD) which is the first derivative of group velocity with respect to

ω [63]. The variation in group velocity with frequency or GVD cause time variation to different spectral components over the duration of the pulse, namely, frequency chirping. As a result, either the blue components travel slower (positive GVD) or the red components travel slower (negative GVD) which cause the pulse duration to broaden. A Gaussian pulse continues to be Gaussian in the medium but the pulse duration increases as it travel a distance L . The duration of broadened pulse can be calculated as:

$$\tau_{out} = \tau_{in} \sqrt{1 + \left(4 \ln 2 \frac{GVD}{\tau_{in}^2} \right)^2} \quad (9)$$

where t_{in} is the pulse duration of incoming un-chirped i.e., transform limited pulse. GVD can be calculated using standard procedure from Sellmeier's relation [27-32].

The autocorrelation technique provides information about the temporal width of the pulses whereas the phase information is unknown. The pulses from the fs amplifier at 800 nm were also characterized using multi-photon intra-pulse interference phase scan (MIIPS) using Silhouette (Coherent, USA) to study the phase properties [64]. A typical MIIPS data for the pulses from the fs amplifier is shown in figure 2.11. MIIPS has a spectrometer to measure the spectrum of NLO process such as SHG of the laser pulse. In autocorrelation technique, only the temporal axis is scanned. In FROG technique, both temporal and spectral axes are scanned. In MIIPS trace, the SH spectra of each phase is scanned. This is achieved by a liquid crystal mask in a dispersed ultrashort pulse to introduce a known phase delay. If $f(\omega)$ is the known reference phase and $\phi(\omega)$ is the unknown spectral phase, then the sum of $f(\omega)$ and $\phi(\omega)$ is $\Phi(\omega)$ and the SH spectrum of the pulse depends on $\Phi(\omega)$. Hence it is possible to find the unknown spectral phase $\phi(\omega)$ of the incoming pulse. The SHG is maximum when the second derivative of $\Phi(\omega)$ is equal to the negative of that of $f(\omega)$ [64]. A 2D plot can be constructed $\phi(\omega)$ vs ω . For transform limited pulses, a set of parallel lines separated by π can be constructed from the MIIPS trace.

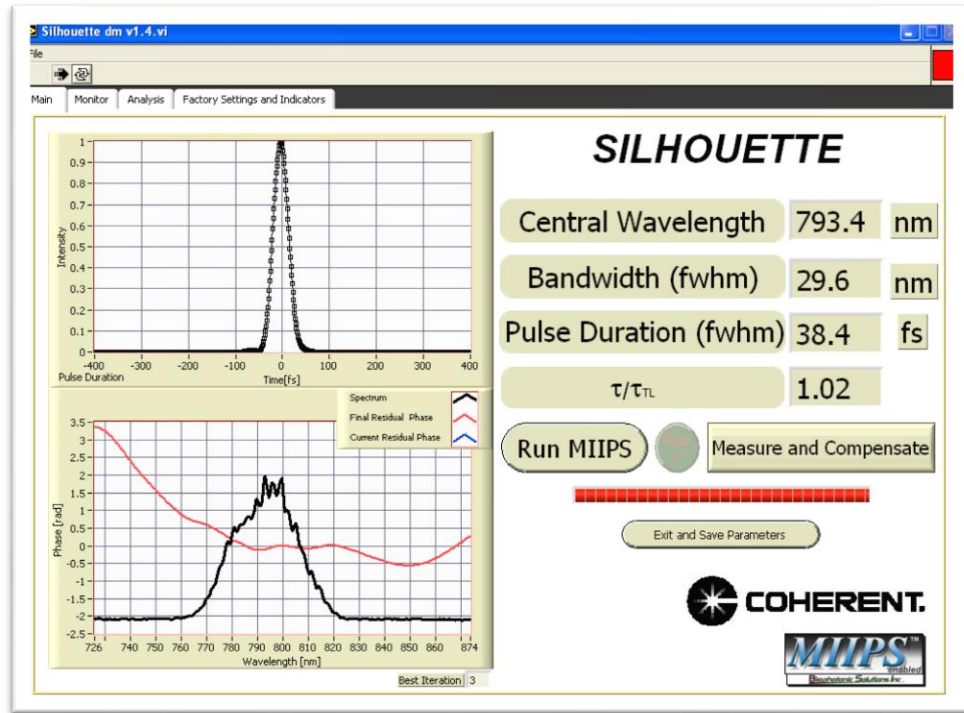


Figure 2.11 Pulse characteristics obtained using Silhouette and MIIPS (multi-photon intrapulse interference phase scan) technique. (Adopted from references [65,66])

2.4 Experimental details

2.4.1 Degenerate picosecond pump-probe experiment scheme

The degenerate ps pump probe experiments were performed using an amplified Ti:sapphire laser system delivering pulses of 800 nm (central wavelength) at a repetition rate of 1 kHz. Figure 2.12 shows a schematic diagram for the experimental set up. The amplifier was seeded with ~ 15 fs pulses (80 MHz, 800 nm central wavelength, typical bandwidth of ~ 55 nm FWHM) from the oscillator. The main beam was split with a 70:30 beam splitter into pump beam and probe beam. The probe beam was sent to the delay stage, Newport, ILS250PP which had a least count of $0.5 \mu\text{m}$. Being a retro reflection geometry, a move of $0.5 \mu\text{m}$ on delay stage corresponds to $1 \mu\text{m}$ of path length difference between the pump and probe. This corresponds to a least temporal step of 3.3 fs. The retro alignment was checked by measuring probe energy at zero delay position as well as 1.3 ns delay position (maximum delay) when the pump is blocked and the energies were found same indicating a good alignment over the entire delay. Both the pump and probe were focused to the sample in the 5 mm quartz cuvette using a 20 cm lens. Most of the samples were isotropic materials. The dynamics demonstrated by the samples with and without a $\lambda/2$ plate showed similar

signatures and hence the polarization of the pump and probe were insignificant. The angle between pump and probe was 75 mrad ($\sim 4^\circ$) to get proper spatial overlap. The intense pump (typically 22 μJ / pulse) was used to excite the molecule while a low power probe beam (typically 2 μJ / pulse) was used to monitor the transmittance of sample ensuring that there were no self-induced nonlinearities due to the probe beam. The pump to probe energy ratio was typically maintained at 10:1.

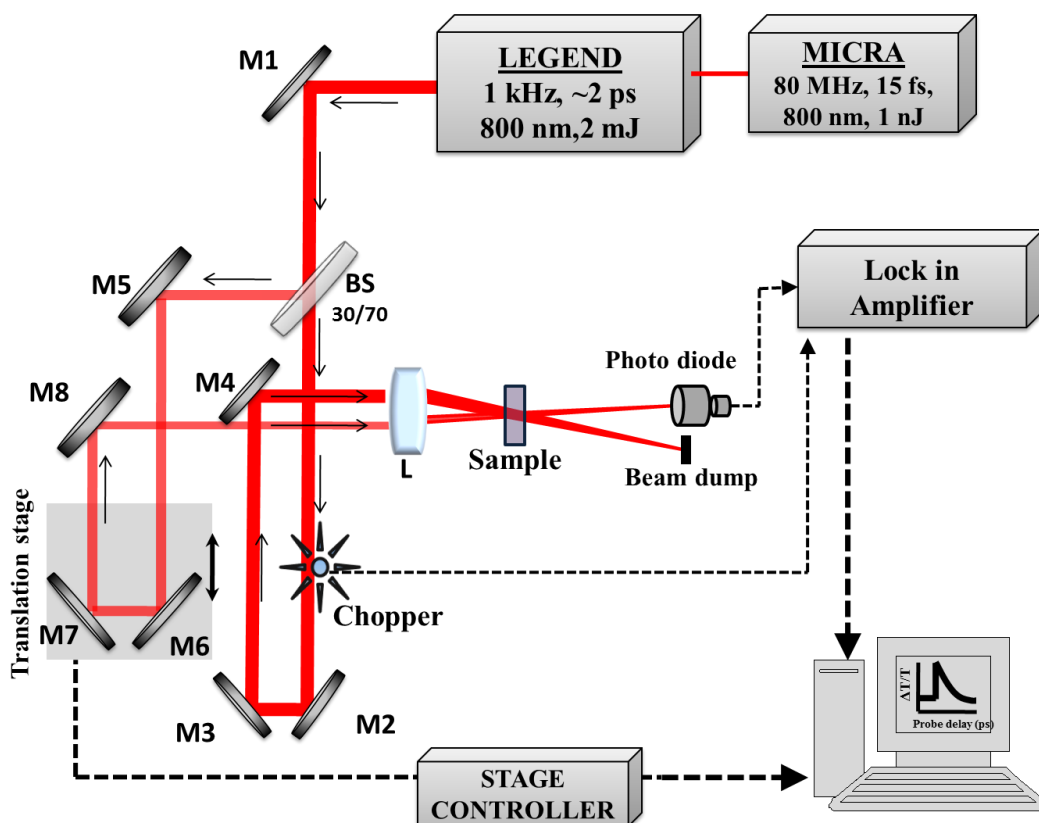


Figure 2.12 Schematic representation of degenerate picosecond pump-probe experimental set up. Here M1-M8, BS, L represent mirrors, beam splitter, lens respectively

The pulse duration was found to be ~ 2 ps measured with an autocorrelation technique using 2-mm thick BBO crystal (type I phase matching for SHG, cut at 29.1° for 800 nm to 400 nm conversion) in the non-collinear geometry which also suggested the zero delay between pump and probe beam. The pump was chopped at 109 Hz frequency. The translation stage which used for the probe delay was connected to a personal computer through ESP motion controller. The transmitted probe power was collected using Si photodiode (PS) (SM1PD2A, Thorlabs) in volts. The active area of the PD was 10 mm $\times$ 10 mm with a rise time of 45 ns measured using oscilloscope. Pump-probe signal being a

weak signal, a lock-in-amplifier (7265, Signal Recovery) was used to measure magnitude of signal at the modulation frequency (chopper frequency). The lock-in amplifier was used to measure phase sensitive detection i.e., it gives a maximum signal when the phase difference between the reference and signal frequency becomes zero. An appropriate time constant is used so as to give the lock-in enough time to integrate the samples. Higher is the time constant, better is the S/N ratio. Here, noise can be defined as the maximum deviation in the signal from the average value during the scan. However, one has to compromise the value of time constant at the expense of the delay time between the scan steps on the translation stage. The lock-in was set with a time constant of 1s. The translation stage was automated to acquire data from lock-in using a labview program.

2.4.2 Non-degenerate ps pump-probe experiment scheme

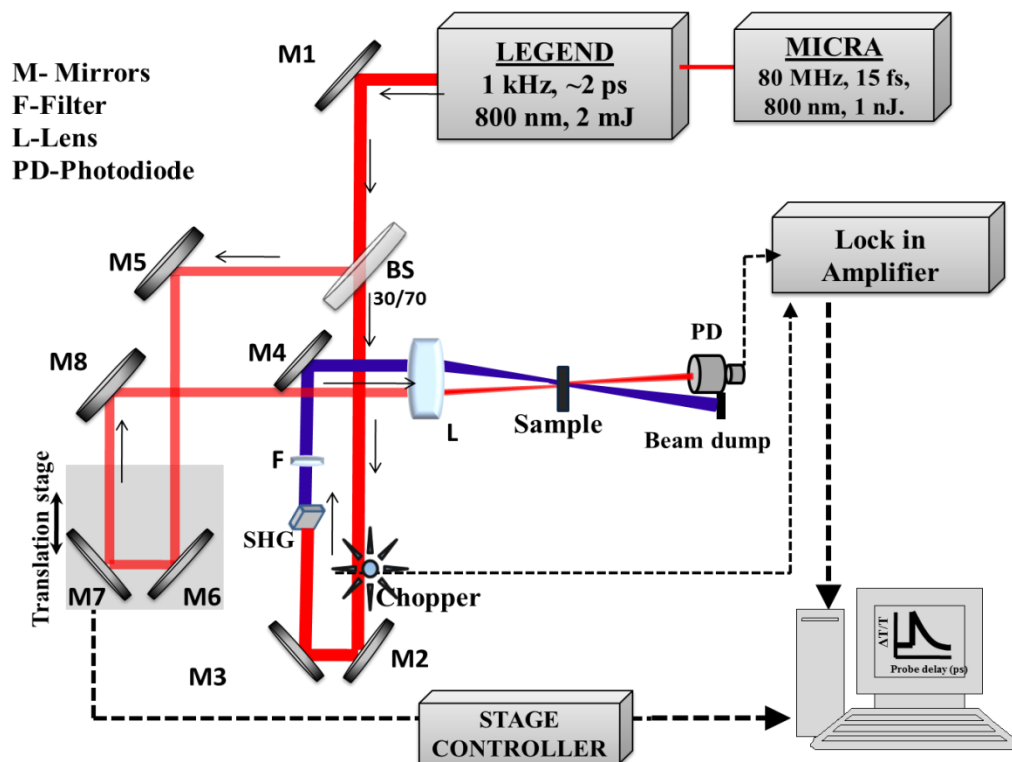


Figure 2.13 Schematic representation of non-degenerate pump-probe experiment.

In non-degenerate or two-color pump-probe experiments, a BiBO crystal with ~20% conversion efficiency was used to generate the 400 nm pump beam from the fundamental beam of 800 nm. Figure 2.13 shows the experimental schematic for non-degenerate pump probe experiment. The second harmonic was generated without focusing to the crystal. The crystal was cut in the optical yz

plane $\phi=90^\circ$ for type-I phase matching ($e + e \rightarrow o$) at an internal angle of $\theta=151.2^\circ$ at normal incidence. A notch filter was used to filter the fundamental 800 nm from the pump beam. Now the sample was pumped by 400 nm and probe was 800 nm laser pulses. The differential probe transmittance was measured using a lock-in amplifier (7265, Signal Recovery) connected to the PD (SM1PD2A, Thorlabs). The data acquisition was performed in the same procedure as that of degenerate pump-probe experiment.

2.4.3 Degenerate fs pump-probe experiment scheme

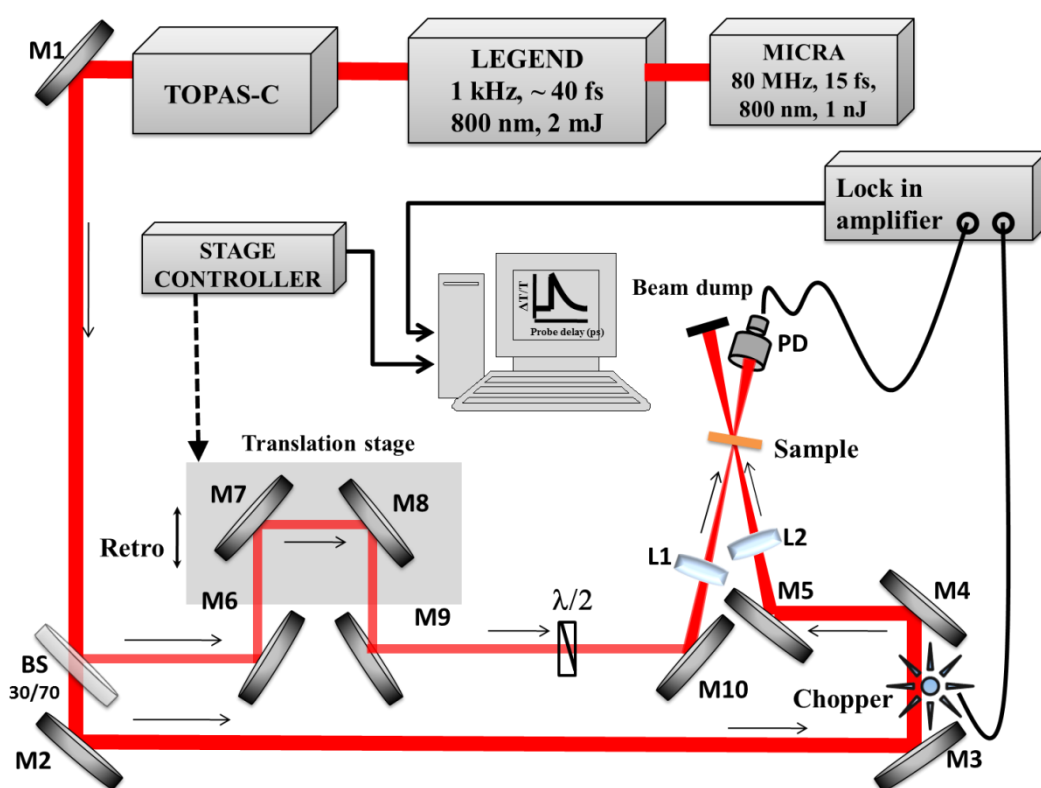


Figure 2.14 Schematic of the degenerate fs pump-probe experimental set up. Here M1-M10, BS, L1&L2, $\lambda/2$, PD represent mirrors, beam splitter, lenses, half wave plate and photodiode, respectively.

For all the fs degenerate pump-probe experiments other than 800 nm, we used an optical parametric amplifier (TOPAS-C, Light Conversion) pumped by a Ti:sapphire amplifier. The tuning range of TOPAS-C was from 260 nm to 2.6 μm . Further, higher wavelengths (2.6-20 μm) could be achieved by difference frequency generation when signal and idler pulses from TOPAS were mixed in a NLO crystal. Non-collinear difference frequency generator (NDFG) is used for

tuning in this infrared region. The intensity autocorrelation was performed at 700 nm and measured pulse duration was ~ 90 fs at 1 kHz repetition rate. The polarization of the pump and probe beam were made perpendicular using a half wave plate ($\lambda/2$). The pulse width at the sample was estimated which included the pulse broadening due to the optics and lenses involved. The pump and probe beams were focused using lenses of 30 and 20 cm focal length, respectively. The zero delay was confirmed by performing autocorrelation at 700 nm. The probe transmittance was collected using a Si photodiode (SM05R/M, Thorlabs) through lock-in amplifier. The data acquisition remained same to that used in ps pump-probe experiment. Figure 2.14 shows the schematic of the experimental set up.

2.5 Temporal resolution

Though the pulse duration can be obtained from autocorrelation technique, the actual temporal resolution is measured by the time duration of cross-correlation between the pump and probe beam within the sample. In degenerate pump-probe experiment this will be proportional to the autocorrelation of the applied pulse and can be recorded with the same pump-probe experimental set up by recording the probe transmittance in a cuvette with the solvent.

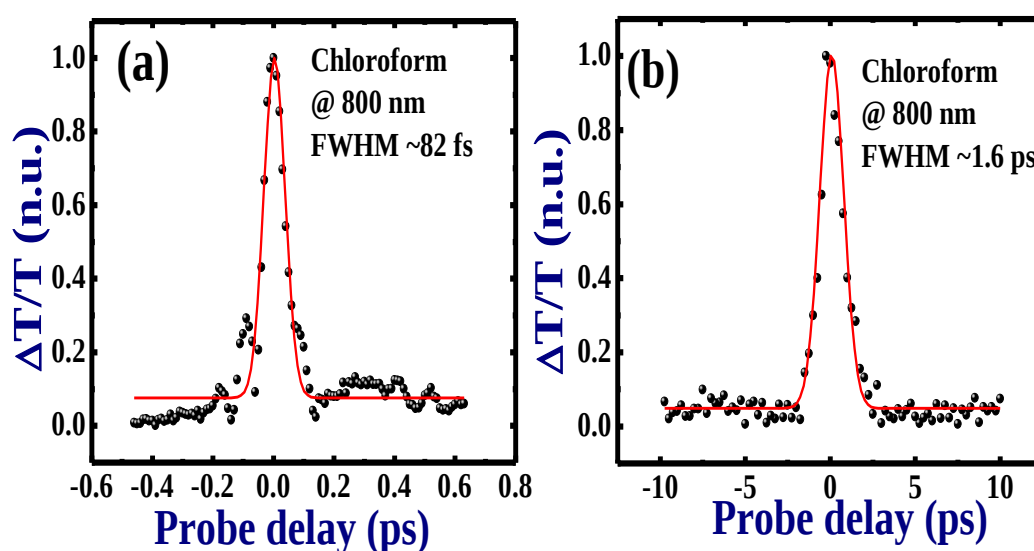


Figure 2.15 Degenerate pump-probe measurements in chloroform at 800 nm for laser pulses from **a)** fs amplifier **b)** ps amplifier. Solid line is a Gaussian fit and the scattered points are the experimental data.

Figure 2.15 shows the pump-probe data for chloroform performed with ~ 2 ps and ~ 40 fs laser pulses at 800 nm. The temporal resolution is also decided by the signal to noise ratio and the artifact at the fast timescale. The chirp induced pulse broadening also affects the temporal response and hence one has to pay attention for a proper compression. If the decay time is appreciably lesser than the pulse duration, the pump-probe signal follows the temporal profile of the pulse. If the decay time is comparable with the pulse duration the pump probe signal display slightly longer falling edge compared to the rising edge. In other case, where the decay time is much larger than the pulse duration, the pump-probe signal will be error function with rise time of the order of the time duration of cross-correlation of the pump and probe. In certain cases, the rise time will be longer than the pulse duration indicating a delayed response in the sample [36-38].

2.6 Z-scan studies to evaluate excited state properties

In order to probe different nonlinear processes occurring via nonlinear polarization when the laser pulses interact with the matter, Z-scan is a simple and sensitive experiment. This technique is generally used to study the transitions such as excited state absorption (ESA), multi-photon absorption (MPA), saturable absorption (SA), and free carrier absorption (FCA-in case of semiconductors) etc. Wei et al. used this technique to study the lifetime of high lying excited states [48]. While analyzing the excited state dynamics of molecules like porphyrins, phthalocyanines, and porphycenes etc. a proper understanding of nonlinear absorption which includes the aforementioned processes, is required. There are multitudes of reports in which this technique had been used to study excited state dynamics of organic, organo-metallic materials, nanoparticles, semiconductors, doped glasses etc.[39-47]. The experiment involves focusing a Gaussian beam onto an optically thin transparent sample and scanning it across the focal point of the lens along the propagation of the beam. The spatial beam distortion is measured by collecting the transmittance at a far field. This geometry is called open aperture Z-scan and is used to evaluate nonlinear absorption. If the transmittance is collected through a finite aperture, this technique can be used to study the nonlinear refraction. In this case the geometry is called as closed aperture Z-scan [43].

2.6.1 Open aperture Z-scan measurements

The OA Z-scan is used to measure the nonlinear absorption coefficients which results from a multitude of nonlinear process such as SA, MPA, ESA etc. The propagation of laser pulse through the medium can be written as:

$$\frac{dI}{dz'} = -\alpha(I) I \quad (10)$$

where $\alpha(I)$ is the intensity dependent absorption or the nonlinear absorption equation (10) can be considered as a nonlinear version of Beer-Lamberts law. Assuming a 3 level model as shown in fig. 2.16 (i), the rate equations describing absorptions and associated relaxation time rates of the population changes of each level involved are:

$$\frac{dN_0}{dt} = -\frac{\sigma_g I(t) N_0}{h\nu} + \frac{N_1}{\tau_1} \quad (11)$$

$$\frac{dN_1}{dt} = \frac{\sigma_g I(t) N_0}{h\nu} - \frac{\sigma_{ex} I(t) N_1}{h\nu} - \frac{N_1}{\tau_1} + \frac{N_2}{\tau_2} \quad (12)$$

$$\frac{dN_2}{dt} = \frac{\sigma_{ex} I(t) N_1}{h\nu} - \frac{N_2}{\tau_2} \quad (13)$$

$$\frac{dI}{dz'} = -\sigma_g I(t) N_0 - \sigma_{ex} I(t) N_1 \quad (14)$$

$$I(r, z, t) = I_0 \left(\frac{\omega_0}{\omega(z)} \right)^2 \exp \left(\frac{-2r^2}{\omega^2(z)} \right) \exp \left(-4 \ln 2 \frac{t^2}{\tau^2} \right) \quad (15)$$

Where N_0, N_1 , and N_2 are the population densities of ground singlet state S_0 , excited singlet states S_1 and S_2 , respectively. σ_g is the ground state cross section and σ_{ex} is the excited state cross section. τ_1 is the relaxation time of S_1 and τ_2 is the relaxation time of S_2 states. $I(r, z, t)$ is the input peak intensity with beamwaist ω_0 , and $\omega(z)$ is the spotsize at z , and τ is the pulse duration. Unlike the transitions shown in fig. 1.5 where the higher order processes are depicted in the present case 4PA was not considered in the analysis.

The propagation equation is:

$$\frac{dI}{dz'} = -\sigma_g I N_0 - \sigma_{ex} I N_1 = -\alpha(I) I \quad (16)$$

where $\alpha(I) = \sigma_g N_0 + \sigma_{ex} N_I = \alpha_0 + \beta I$, is the intensity dependent absorption and β is the nonlinear absorption coefficient.

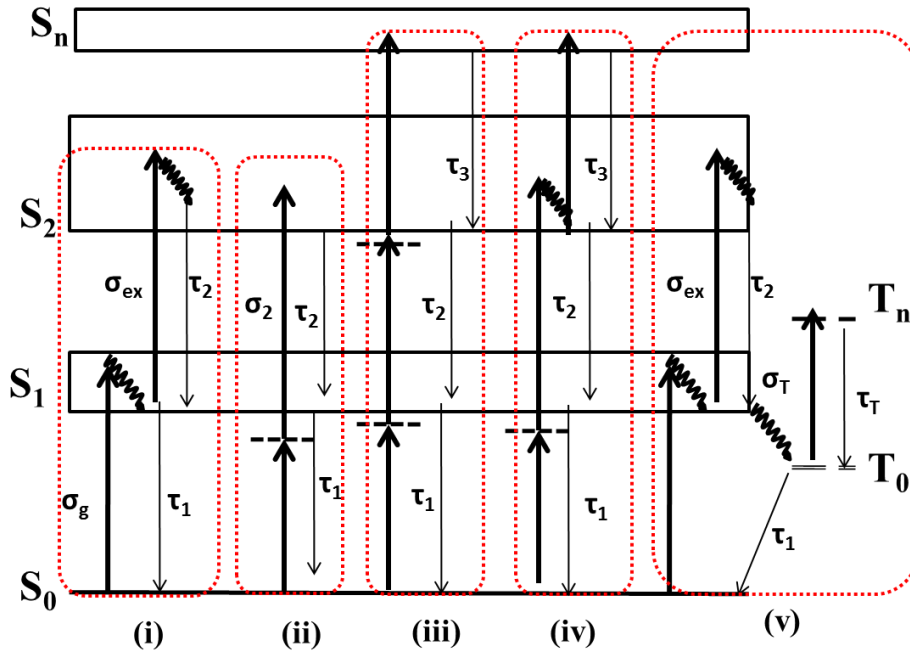


Figure 2.16 Schematic of the dynamics of various NLA process. (i) Sequential 2PA (ii) instantaneous 2PA (iii) Instantaneous 3PA (iv) 2-step 3PA (v) ESA involving triplet states .

In the case of instantaneous 2PA and instantaneous 3PA transitions, as shown in fig. 2.16 (ii) and 2.16 (iii), the rate equations will be modified accordingly. The additional term $\beta I^2/2h\nu$ and $\gamma I^3/3h\nu$ (where $\beta = \sigma_2 N_0/h\nu$ is the two photon absorption coefficient with two photon absorption cross section σ_2 and $\gamma = \sigma_3 N_0/(h\nu)^2$ is the three photon absorption coefficient with three photon absorption cross section σ_3) have to be considered in the rate equation. Here h is the plank's constant and ν is the frequency of the incident photon. In the case of excited state absorption induced two photon absorption $\gamma = \sigma_{ex}\beta\tau/2h\nu$. In this case the molecules are excited from S_0 states to S_2 states by simultaneous absorption of two photons and will be absorbed from S_2 states to S_n states via excited state absorption as shown in fig. 2.16 (iv). This process is considered to be fifth order process and the propagation equation can be simplified as:

$$\frac{dI}{dz} = -\alpha_0 I - \beta I^2 - \gamma I^3 \quad (17)$$

solving the above equation yields:

$$T_{OA}(z) = \frac{1}{\sqrt{\pi} q_0(z, 0)} \int_{-\infty}^{\infty} \ln(1 + q_0(z, 0) e^{-\tau^2}) d\tau \quad (18)$$

$$T_{OA}(z) = \frac{1}{\sqrt{\pi} p_0(z, 0)} \int_{-\infty}^{\infty} \ln \left[\sqrt{\ln(1 + p_0^2(z, 0) e^{-2\tau^2})} + p_0(z, 0) e^{-\tau^2} \right] d\tau \quad (19)$$

$T_{OA}(z)$ is the normalized open aperture transmittance as a function of z , $q_0 = \beta L_{eff} I_0$, $p_0 = (2\gamma L'_{eff} I_{00}^2)^{1/2}$, $\beta = 2PA$ coefficient and $\gamma = 3PA$ coefficient, I_{00} is the peak intensity at focus, $L_{eff} = \frac{1 - e^{-\alpha_0 L}}{\alpha_0}$, $L'_{eff} = \frac{1 - e^{-2\alpha_0 L}}{2\alpha_0}$ are effective path lengths

in the sample where L is the actual length of the sample for 2PA, 3PA respectively and α_0 is the linear absorption coefficient. In the case of Saturable absorption, the intensity dependent absorption becomes $\alpha(I) = \alpha_0 / (1 + I/I_s)^{1/2}$ where I_s is the saturation intensity which is estimated as $I_s = h\nu / \sigma_g \tau$, τ is the lifetime of S_1 state. If the excitation intensity I_0 is less than I_s the process said to be third order process with the absorption coefficient α_0/I_s [48-53]. In the case of transitions involving ESA involving triplet states as shown in fig 2.16 (v) a comprehensive five-level model has to be considered.

2.6.2 Closed Aperture Z-scan measurements

The closed aperture (CA) Z-scan is used to measure the nonlinear refractive index which is a real part of non-linear susceptibility by measuring the phase distortion $\Delta\Phi$ of the incoming electric field as it passes through the length of the medium L . Under slowly varying envelope approximation (SVEA) and thin sample approximation, the beam profile should not be changed within the nonlinear medium i.e, $L \ll z_0$ and $L \ll z_0 / \Delta\Phi_0$ where $\Delta\Phi_0$ is the maximum phase distortion due to nonlinearity of the material and z_0 is the Rayleigh range. The phase change with the propagation depth z' can be written as:

$$\frac{d\Delta\Phi}{dz'} = k\Delta n(I) \quad (20)$$

Where $\Delta n(I) = n_2 I$, n_2 being the nonlinear refractive index with units cm^2/GW and $k = 2\pi/\lambda$ where λ is the wavelength. Solving the equation (20) yields the phase change as:

$$\Delta\Phi(z, r, t) = \Delta\Phi_0(z, t) \exp\left(\frac{-2r^2}{\omega^2(z)}\right) \quad (21)$$

$$\Delta\Phi_0(z, t) = \frac{\Delta\Phi_0(t)}{1 + (z/z_0)^2} \quad (22)$$

with the on axis phase shift at focus, $\Delta\Phi_0(t) = kn_2 I_{00} L_{eff}$, where I_{00} is the on axis peak intensity. The complex electric field entering the sample can be written as :

$$E(r, z, t) = E_0(t) \left(\frac{\omega_0}{\omega(z)} \right) \exp\left(\frac{-r^2}{\omega^2(z)} - \frac{ikr^2}{2R(z)}\right) \exp(-i\Phi(z, t)) \quad (23)$$

Where $\omega(z)$ is the beam radius, ω_0 is the beam waist, $R(z)$ is the radius of curvature of wavefront at position z . The exiting electric field will have the phase change term $\Delta\Phi(z, r, t)$ and can be written as:

$$E_e(r, z, t) = E(r, z, t) \exp(-\alpha_0 L/2) \exp(-i\Delta\Phi(z, r, t)) \quad (24)$$

The far field pattern, E_a , of the beam at the aperture plane can be obtained from the zeroth-order Henkel transformation [55]. The far field pattern E_a can be integrated spatially from 0 to the aperture radius r_a to get the transmitted power through the aperture $P_T(\Delta\Phi_0(t))$. The normalized transmittance at z position can be written as:

$$T(z) = \frac{\int_{-\infty}^{\infty} P_T(\Delta\Phi_0(t)) dt}{S \int_{-\infty}^{\infty} P_i(t) dt} \quad (25)$$

where $P_i(t) = \pi\omega_0^2 I_{00}(t)/2$, the instantaneous input power and S is the aperture transmittance. The value of S can be in the range of 0.1 to 0.5 for the calculation of nonlinear refractive index (n_2). $S=1$ implies the OA Z-scan [39-55].

2.6.2.1 Experimental Details

Z-scan measurements were performed using an amplified Ti: sapphire laser system (LEGEND, Coherent) delivering nearly transform-limited pulses of ~ 2 ps with a repetition rate of 1 kHz at 800 nm. The amplifier was seeded with ~ 15 fs pulses from an oscillator (MICRA, Coherent, 1 W average power, 80 MHz repetition rate, 800 nm). Laser pulses with typically 2-5 μ J energy were used for the experiments. The beam was focused using 200 mm focal length lens into the

sample. The beam waist (ω_0) estimated was $\sim 30 \mu\text{m}$ with a Raleigh range of 4 mm. The sample was placed on the translation stage (Newport, ILS250PP), controlled by an ESP motion controller. The transmittance changes of the sample were measured with a photodiode (SM1PD2A) in the far-field. An aperture is placed in front of detector in the case of CA Z-scan. The aperture transmittance S was maintained to be 0.25. The photodiode via and a lock-in amplifier and the translation stage was interfaced to the computer as shown in figure 2.17. We established that the pulse energies remained low to avoid contribution from higher order nonlinearities. The experiments were repeated more than once and the best data were used for obtaining the nonlinear optical coefficients from the best fits. Other than 800 nm wavelength, TOPAS was used as the laser source.

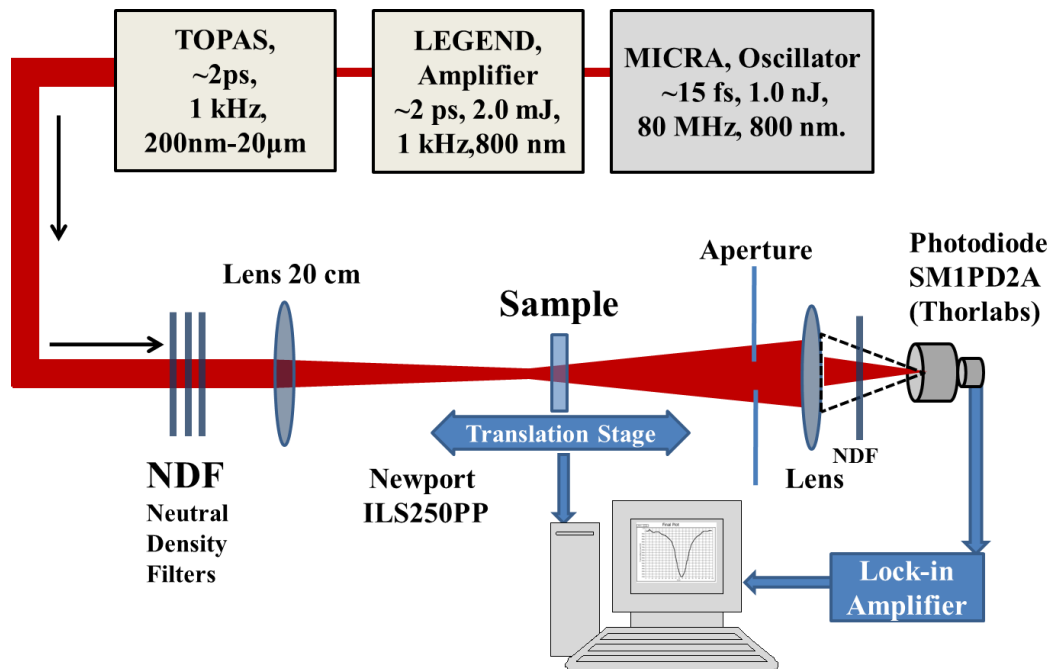


Figure 2.17 Schematic of the Z-scan experimental set up with ps pulses.

2.7 Excited state dynamics using four-wave mixing technique

Degenerate four wave mixing (DFWM) is the interaction of three input waves in a nonlinear medium to generate a fourth beam via third order polarization. The four wave mixing can be done in different geometries like phase conjugate geometry, BOXCAR geometry etc., with the selection depending on the experimental requirements and conditions. Using various combination of polarizations for the four beams, it is possible to measure all of the independent $\chi^{(3)}$ tensor components of an isotropic media [56]. In a FWM technique, multiple

laser pulses are used in order to extract the information of frequency and phase during an ultrafast relaxation process. Along with the electronic population relaxation, FWM signal also contains the information of vibrational coherence which comprised of the dephasing times, vibrational frequencies and phases of involved the Raman modes [57].

2.7.1 Phase conjugate geometry

In phase conjugate geometry, the generated fourth beam (resulting from third-order nonlinearity) has the phase which is conjugate to that of the third beam. Beam 1 and beam 2 are counter-propagating pump beams while beam 3 is the probe beam arriving at the sample at an angle to the forward pump. Beam 4 is the phase conjugate beam which contains the information about the magnitude and the time-response of the nonlinearity of the sample medium.

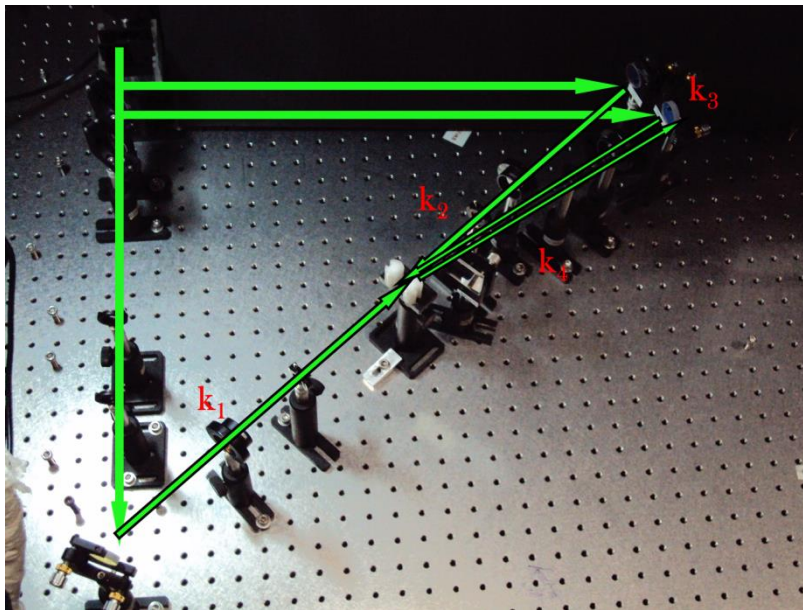


Figure 2.18 Experimental set up for DFWM in phase conjugate geometry.

Figure 2.18 shows the experimental set up of the DFWM set up in the phase conjugate geometry. The alignment sensitivity of the three beams is significant. The angle of beams and their overlap within the sample must be carefully checked. Three of the interacting laser pulses are aligned from the same laser (Q-switched Nd:YAG at 532 nm with ~ 7 ns pulse duration and repetition rate of 10 Hz) by appropriate use of beam splitters. The three beams are aligned as shown in the figure 2.18 such that the difference in the path length of the beams

at the sample position does not exceed the coherence length of the laser so that the beams may interact in the sample coherently to generate the PC signal. Proper care was taken to ensure the beams overlapped both spatially as well as temporally. The pump beams must be truly counter propagating and indistinguishable to avoid phase mismatch. The objective of the experiment is to measure the temporal response as well as the intensity of PC signal or equivalently phase conjugate reflectance.

2.7.2 BOXCAR geometry

In BOXCAR geometry, a third beam is sent to the third corner of a square plane containing the two beams from the autocorrelation experimental set up. Fig.. These three beams are focused to the nonlinear medium, and the FWM signal is formed in the fourth corner¹ when the phase matching condition $\vec{k}_4 = \vec{k}_3 - \vec{k}_2 + \vec{k}_1$ is satisfied. Hence, the momentum is conserved when $\vec{k}_1 + \vec{k}_2 - \vec{k}_3 - \vec{k}_4 = \Delta\vec{k} = 0$ and the process is perfectly phase matched as shown in figure 2.19 (c). A BiBO crystal (Bismuth Triborate, BiB_3O_6) was used in the present case. The crystal was cut in the optical yz plane $\phi = 90^\circ$ for type-I phase matching at an internal angle of $\theta = 151.2^\circ$ at normal incidence. Figures 2.19 (a) and (b) depict the DFWM signal in the fourth corner of the square made by the three fundamental beams.

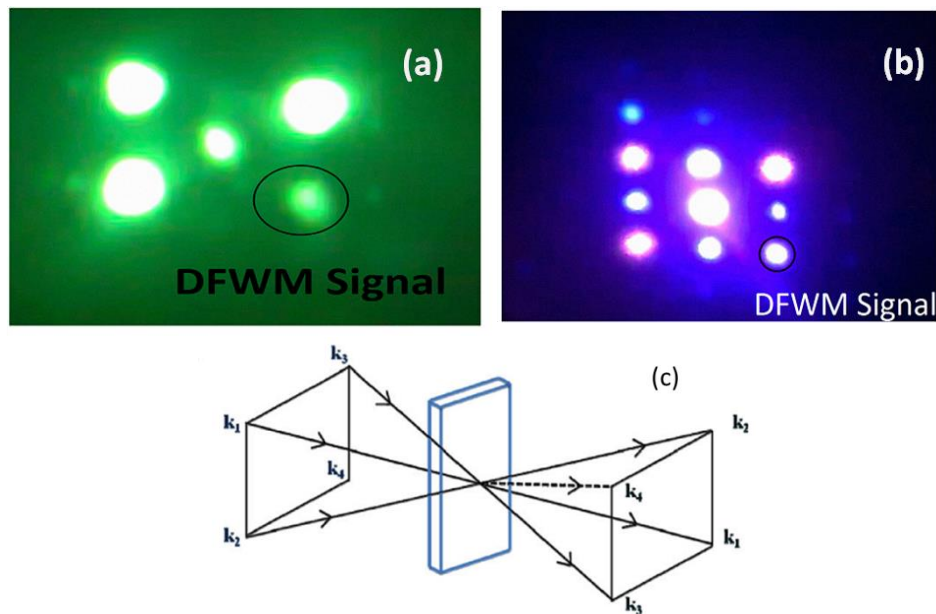


Figure 2.19 Photograph image DFWM signal in BOXCAR geometry with 800 nm, 2 ps (a) through an IR viewer (b) without IR viewer (c) wave vector diagrams of $\vec{k}_1, \vec{k}_2, \vec{k}_3, \vec{k}_4$

The experimental set up was calibrated using a reference sample whose $\chi^{(3)}$ value is known. The DFWM signal I_{ref} for the reference material was measured and compared with that of the sample as I_s . Usually carbon disulfide (CS_2) is used as the reference material. A value of $n_0=1.6$ for CS_2 was used and $\chi^{(3)}$ value of 1.7×10^{-12} e.s.u. for ns pulses and 4.0×10^{-13} e.s.u. for ps pulses were used [58]. The quantitative value of $\chi^{(3)}$ with respect to standard reference sample can be determined by the following relation:

$$\chi^{(3)} = \chi_{ref}^{(3)} \left(\frac{n_s}{n_{ref}} \right)^2 \left(\frac{I_s}{I_{ref}} \right)^{1/2} \frac{\alpha l \exp\left(\frac{\alpha l}{2}\right)}{1 - \exp(-\alpha l)} \quad (26)$$

where I_s and I_{ref} are the signal intensity from the sample and reference respectively n_s and n_{ref} are the refractive indices of the sample and reference respectively, l is the sample thickness, $\chi_{ref}^{(3)}$ is the third-order susceptibility of reference medium and α is the absorption coefficient of the sample. This is a direct measurement of $\chi^{(3)}$. Unlike in the case of Z-scan technique, the total magnitude of $\chi^{(3)}$ is obtained from the relation (26). In Z-scan technique, the magnitude of $\chi^{(3)}$ is calculated from its real and imaginary parts [41].

The non-degenerate four wave mixing process is used in CARS (Coherent Anti-Stokes Raman Spectroscopy) which is a third-order nonlinear optical process involving a pump beam of frequency ω_p , a Stokes beam of frequency ω_s and a probe beam at frequency ω_{pr} . All the three laser beams interact with the sample and generate the fourth coherent optical signal at the anti-Stokes frequency following the conservation relation $\omega_{CARS} = \omega_p - \omega_s + \omega_{pr}$. The strength of the signal is proportional to the difference in the population of ground state and the vibrationally excited state. A tunable laser source such as dye laser or OPA can be used to tune the frequency of pump beam so as to get efficient CARS signal [59].

2.7.3 Self-diffraction geometry

Self-diffraction is also referred as forward degenerate multi-wave mixing, When two coherent beams interact in a medium, additional waves are generated by diffraction from the refractive index gradient produced by the two beams within the nonlinear medium. The diffracted beams are the outcome of energy redistribution among the two incident beams interfering in the nonlinear media.

Here, the n^{th} order diffracted signal is a result of $2n+2$ wave mixing process which corresponds to an effective $2n+1$ order nonlinear susceptibility χ_{eff}^{2n+1} . Figure 2.20 show the formation of self-diffracted signal up to three orders in a BBO crystal. $A_1(0)$ and $A_2(0)$ are the amplitudes of fundamental input beam and $A_i(L)$ is the amplitude of the i^{th} diffracted signal.

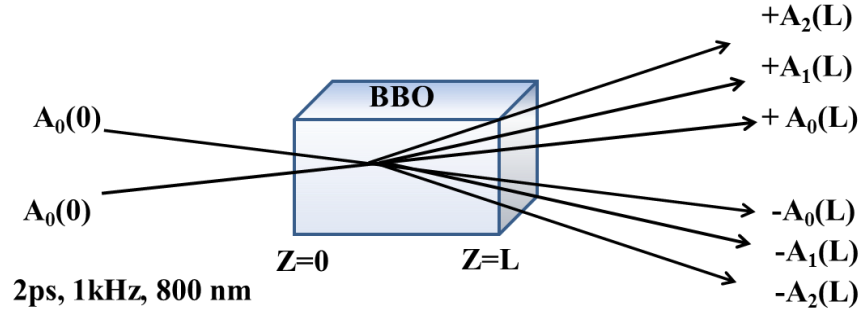


Figure 2.20 Schematic of self-diffraction process in BBO crystal (β Barium Borate, type I critically phase matching for SHG, 29.1° cut) using 800 nm, ~ 2 ps, 1 kHz pulses.

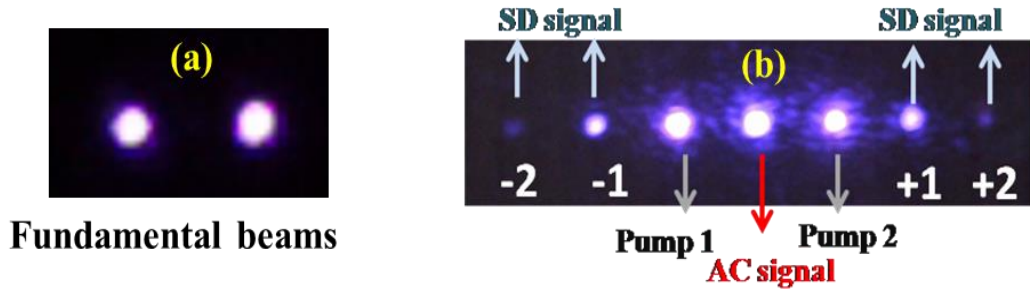


Figure 2.21 Photograph images of (a) pump beams (b) self-diffraction pattern obtained from BBO

The 1^{st} order diffracted signal (+1,-1) corresponds to the four-wave mixing phenomenon due to third-order susceptibility $\chi^{(3)}$ and can be found using equation 23. The beams are diffracted in the direction defined by phase matching relations $\vec{k}_3 = 2\vec{k}_1 - \vec{k}_2$ and $\vec{k}_3 = 2\vec{k}_2 - \vec{k}_1$. Similarly the 2^{nd} and 3^{rd} order diffracted signals (+2,-2 and +3,-3 in the figure 2.21) propagate in directions defined by $\vec{k}_5 = 3\vec{k}_1 - 2\vec{k}_2$, $\vec{k}_5 = 3\vec{k}_2 - 2\vec{k}_1$, $\vec{k}_7 = 4\vec{k}_1 - 3\vec{k}_2$ and $\vec{k}_7 = 4\vec{k}_2 - 3\vec{k}_1$ which are due to the 5^{th} and 7^{th} order nonlinear susceptibilities, $\chi^{(5)}$ and $\chi^{(7)}$ resulting in six and eight wave mixing processes respectively. One of the pump beams has the variable delay (say pump 1) and as both of the pump beams overlaps spatially and temporally the phase matching condition is satisfied and a clear, distinguished diffracted pattern is obtained. The thickness of the BBO crystal was approximately 2 mm. Figure

2.21(b) shows the self-diffraction pattern obtained from BBO crystal. Pump beams are also shown in figure 2.21 (a). Due to the nonlinearity of the crystal the autocorrelation signal also appeared. The ease of the experiment makes this technique to measure higher order nonlinearities [60-62].



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CHAPTER 3

Optimization of the Pump-Probe & Z-scan techniques using GaAs and Phthalocyanine

ABSTRACT

This chapter comprises two parts. The first part of chapter contains the details of experiments developed for optimization of the ps/fs pump-probe experiments using Semi-Insulating Gallium Arsenide (SI-GaAs) and Low-Temperature Gallium Arsenide (LT-GaAs). Both the materials are widely used in terahertz generation and detection. The pump-probe experiments were performed in the reflection geometry. The temporal dynamics of carrier phonon interaction in semiconductors are discussed in the light of obtained results. The signal to noise ratio was calculated from these experiments. The second part of the chapter is devoted to the experimental details for optimization of Z-scan technique to understand the excited state absorption of novel phthalocyanine molecules. The structurally different phthalocyanine molecules were investigated for their nonlinear optical properties and dynamics. The measurements were done both in solution form as well as in thin film form. Z-scan studies provide us with the information on excited state absorption which will be useful in analyzing the pump-probe data.

The chapter includes data from the following publications:

-  OSA Technical digest (online), Laser Science, paper LW5I.3 (LS, Florida, USA) **2013.**
-  OSA Technical Digest (online), International Conference on Fiber Optics and Photonics, paper TPo.5 (IIT Chennai, India), **2012.**
-  Material. Letters, 64, 1915-1917, **2010.**
-  Pramana – Journal Physics, 75(5), 1017-1023, **2010.**
-  Materials Science and Applications, 2, 299-306, **2011.**

3.1 Introduction

The pump-probe and Z-scan experiments with ultrashort laser pulses are prominent techniques to explore the excited state properties of different moieties. The natural question to address is how the excited state population relaxes back to the ground state after the instantaneous excitation. Here, one has to probe the relaxation to understand the temporal dynamics using ultrashort laser pulses. During the last few decades, pump-probe technique has been used to explore the temporal information. This is prominent experimental technique which has been used for investigating several compounds in the following chapters. It is important to optimize the pump-probe experimental set up for further characterization. We have used semi-insulating Gallium Arsenide (SI-GaAs) and low-temperature grown Gallium Arsenide (LT-GaAs) samples for optimizing the picosecond (ps) and femtosecond (fs) pump-probe experimental setup. These materials are generally used in terahertz generation and detection [19-21]. The Z-scan technique is used to understand the excited state dynamics by measuring the excited state population densities over the pulse duration and to measure the nonlinear optical (NLO) properties. The following sections discuss the optimization of the Z-scan technique using phthalocyanine molecules.

3.2 Optimization of pump-probe experimental set up (transient reflection measurements)

The experimental set up for degenerate ps pump-probe measurements was tested initially with SI-GaAs and LT-GaAs. Both the samples were reflecting and were opaque at 800 nm. Hence the pump-probe measurements were done in reflection geometry. The thickness of the sample was ~ 1 mm. The pump probe experimental set up is shown in figure 3.1. Both the pump, probe were focused using 50 cm lens. The diameter of the input beam was ~ 3 mm. The differential reflectivity ($\Delta R/R$) was measured by the same data acquisition technique which was used in the transmission geometry. The fs degenerate pump-probe measurements were performed at 600 nm (~ 70 fs) pulses. Unlike ps pump-probe measurements, the pump and probe beam were *unfocused* and the beam diameter was 3 mm at the sample position.

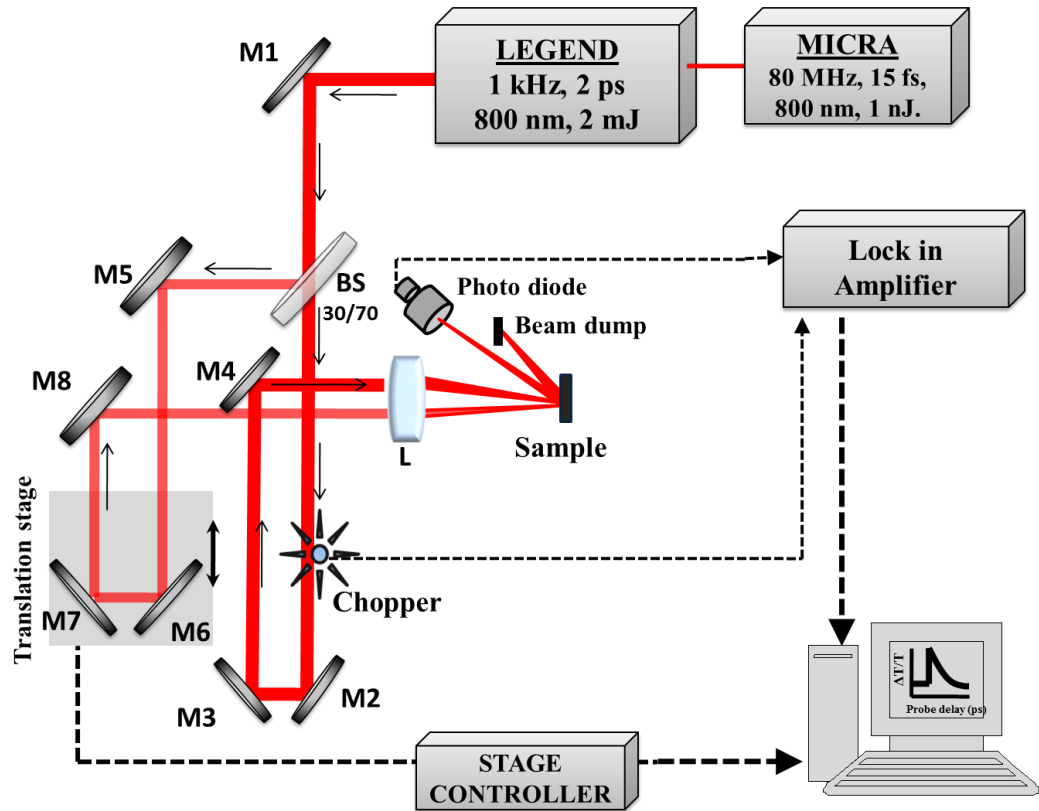


Figure 3.1 Schematic representation of degenerate picosecond pump-probe experimental set up in reflection geometry. Here M1-M8, BS, L represent mirrors, beam splitter, lens, respectively.

Microscopic Process	Characteristic time
Carrier-carrier scattering	$10^{-15} - 10^{-12}$ s
Intervalley scattering	$\geq 10^{-14}$ s
Intravalley scattering	$\sim 10^{-13}$ s
Carrier-optical phonon thermalisation	$\geq 10^{-12}$ s
Optical phonon-acoustic phonon interaction	$\sim 10^{-11}$ s
Carrier diffusion (0.1 μm)	$\sim 10^{-11}$ s
Auger recombination (carrier density 10^{20} cm^{-3})	$\sim 10^{-10}$ s
Radiative recombination	$\geq 10^{-9}$ s
Lattice heat diffusion (1 μm)	$\sim 10^{-8}$ s

Table 3.1 Fundamental processes and typical timescales involved in semiconductors (adapted from reference [1])

When a semiconductor is excited with photons of energy $h\nu > E_g$, electron-hole pairs are created with excess kinetic energy, $h\nu - E_g$. This excess energy will then redistribute among the electronic and lattice degree of freedom

until equilibrium is reached with the surroundings. The relaxation of these electrons and/or the redistribution of the excess energy (initially contained in these excited carriers) are then monitored with a time-resolved, weak probe and hence the transient reflectivity can measure the carrier dynamics of a semiconductor [1-15]. Various fundamental processes and their timescales in semiconductors are given in table 3.1. The optically generated carriers change the refractive index yielding a change in the reflectivity of the semiconductor. The reflectivity of a semiconductor at normal incidence is given by,

$$R = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2} \quad (1)$$

where n and k are real and imaginary parts of refractive index respectively. Since the change in reflectivity is very small, the imaginary part can be neglected and the change in reflectivity is given by,

$$\frac{\Delta R}{R} = \frac{4\Delta n(t)}{(n-1)^2} \quad (2)$$

where the ΔR is the difference in the reflectance of the probe when the pump is off and that when the pump is on, R is the sample reflectivity which is unperturbed by the pump i.e when the pump is off. $\Delta n(t)$ is given by $\Delta n(t) = \Delta n_{eh}N(t) + \Delta n_T T(t)$ where $N(t)$ is optically induced carrier density and $T(t)$ is the lattice temperature. The coefficients Δn_{eh} is the change in the real part of refractive index per electron-hole pair and Δn_T is the change in refractive index due to lattice heating per degree Celsius [16, 17]. LT-GaAs is usually grown at lower temperature and hence, the excess arsenic will form as impurity or defect in LT-GaAs. Depending on the temperature, the density of defects varies. The defect states may appear in the middle of valance band and conduction band of GaAs. These mid-gap states play important role in ultrafast absorption dynamics of LT-GaAs [18]. Ultrafast switching of photo-conducting antennas made from low temperature grown GaAs (LT-GaAs) has proven to be one of the efficient ways for generation of terahertz (THz) radiation with respect to both intensity and spectral bandwidth. This material has unique properties such as the ultrashort carrier lifetime, large resistivity, and relatively good carrier mobility. It is epitaxially grown on a semi-insulating GaAs (SI-GaAs) substrate. The bandwidth of photo-conducting antenna

is limited by the finite carrier lifetime or the momentum relaxation time of the carriers in the photo conducting substrates [19-23].

3.2.1 Results and Discussion

Figures 3.2 (a)-(b) show the typical pump-probe reflectivity measurements of LT-GaAs and SI-GaAs at 800 nm recorded with ~ 2 ps pulses and an average energy of ~ 5 μJ per pulse. Figures 3.3(a)-(c) show the fs pump probe reflectivity measurements of SI-GaAs at 600 nm using ~ 70 fs laser pulses delivered by TOPAS-C. At 600 nm, TOPAS-C delivered stable output and the beam quality was good which helped for the easy alignment. The measurements were performed without any focusing geometry for the pump and probe and the pump energies at ~ 8 μJ . There was no physical damage observed to the samples. Wang et al. reported the damage threshold of GaAs to be ~ 166 mJ/cm^2 [24]. The fluence in our experiments were calculated to be ~ 22.5 and ~ 0.14 mJ/cm^2 in the case of ps and fs measurements respectively, and evidently the fluence were much below the damage threshold value. In both cases, there is a clear increase in the reflectivity after the zero delay, which confirmed the excitation of carriers to occupy levels above the band-gap. The clear demarcation of zero delay spike shows increase in carrier density at the excited state. The exact number and the lattice temperature associated with it can be calculated using Drude model [3]. In order to extract the decay time constants of carrier relaxation, we fitted the experimental data using the equation:

$$\Delta R/R = A \exp[-(t-t_0)/\tau] \quad (3)$$

where ΔR is the time dependent change in probe reflection induced by the pump at time ' t ' after the excitation and R is the probe reflection in the absence of pump. τ is the decay constant or the relaxation time. The relaxation times obtained were ~ 20 ps for LT-GaAs and ~ 200 ps for SI-GaAs at pump energy of 5 μJ . The ps degenerate pump-probe measurements were repeated for SI-GaAs at higher pulse energies of ~ 10 μJ . The pump-probe data is shown in figure 3.2(c).

In the case of fs degenerate pump-probe, the data was fitted using single exponential function as described by equation (1) as shown in figure 3.3. The mean decay constant was ~ 20 ps. The instantaneous rise near zero delay time

implies that the photo generated free carriers quickly occupy the above band gap states to quench further absorption which is called as band filling (BF) [27,28]. After the excitation they quickly relax to reach the quasi-equilibrium with the lattice system through carrier-phonon interaction. Thus, the decrease in the transient differential reflection can be attributed to the free carriers consuming their kinetic energy via carrier –phonon scattering to the band edge or to form excitons.

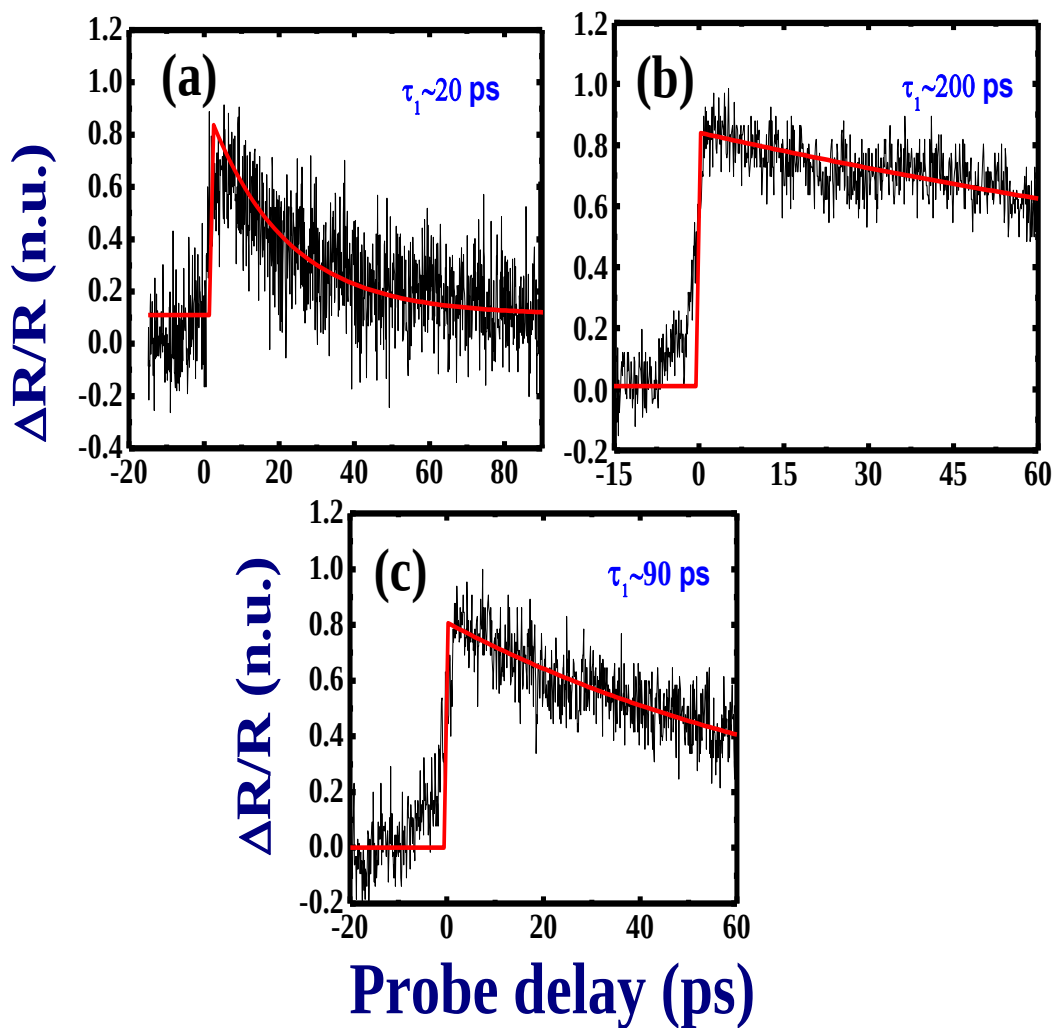


Figure 3.2 Degenerate ps pump-probe measurements of (a) LT-GaAs and (b) SI-GaAs at $\sim 5 \mu J$ (c) SI-GaAs at $\sim 10 \mu J$. The jagged line (black) represents experimental data, whereas the smooth line (red) represents best fit to a single-exponential decay function. (n.u) represent normalized units.

In the case of ps pump-probe measurements, it was found that the decay constant decreased from 200 ps to 90 ps. At higher pulse energies the analysis is complex in nature. As the intensity is increased, more numbers of electrons are

excited to conduction band (CB) and occupy the bottom of CB. However, if the concentration of these electrons are high enough (i.e. at higher peak intensities), the electron wave functions may overlap, forming a gas of interacting particles. Some of the electrons will repel by Columbic force and some lower energy to avoid same spin. This reduces the energy of CB resulting in band-shrinkage [25]. More spectroscopic tools are required to understand the actual mechanism. The experiment was repeated thrice for calculating the signal to noise ratio and the best data obtained was fitted for a single exponential function.

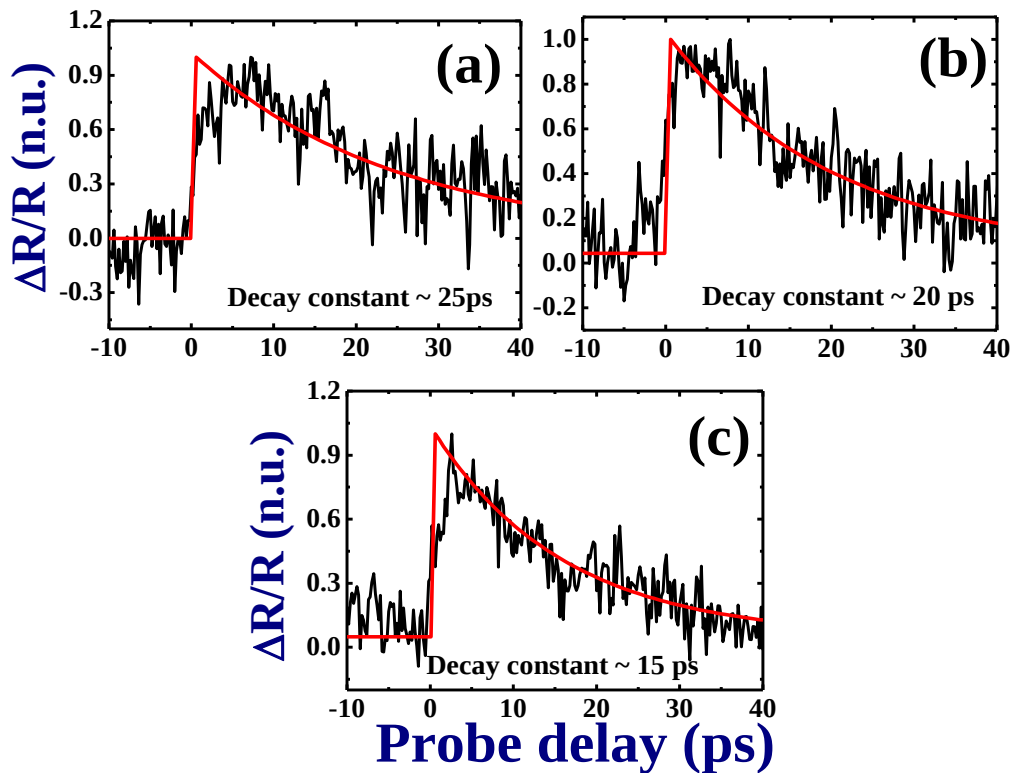


Figure 3.3 (a)-(c) Degenerate fs pump probe measurements at 600 nm of SI-GaAs for pump energies $\sim 8 \mu\text{J}$. The jagged line (black) represents experimental data, whereas the smooth line (red) represents best fit to a single-exponential decay function. n.u. represents normalized units.

3.2.1.1 Calculation of signal to noise ratio

During various experimental measurements noise can arise from many sources. Even though the environmental (temperature, humidity, mechanical vibrations etc.) and experimental (pulse energy, angle of data collection etc.) parameters are kept constant, the noise can still arise from variety of sources like laser stability, electronic device response, fluctuations in the ac line etc. The result obtained from one measurement may change slightly with the next measurement. Hence, a statistical analysis of the measurement is required to estimate signal to

noise ratio (SNR). SNR gives the minimum detectable change in the measurements. The SNR is calculated by evaluating the peak value of the signal and the noise value in the absence of the pump, measured from a series of experiments with identical conditions.

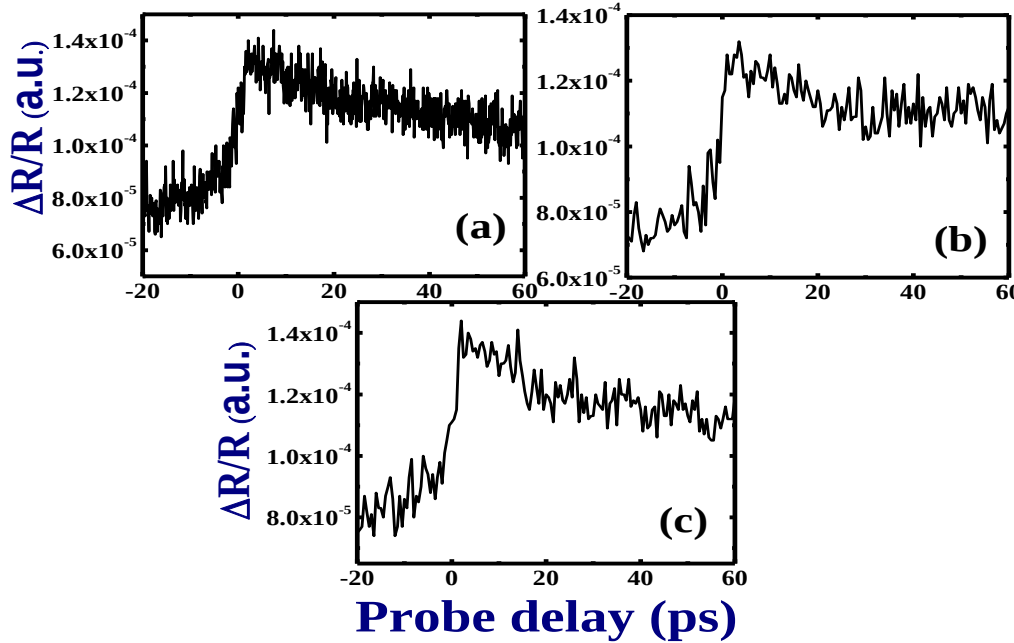


Figure 3.4 (a)-(c) Degenerate ps pump-probe measurements of SI-GaAs at $\sim 10 \mu\text{J}$ at 800 nm, ~ 2 ps laser pulses. $\Delta R/R$ is expressed in arbitrary units (a.u.)

In our case, a series of three experiments were performed on SI-GaAs at $10 \mu\text{J}$ energy per pulse in degenerate ps pump-probe set up at 800 nm. The sample was not removed after each scan to ensure the same angle of reflection and sufficient time was given after each scan to avoid long term exposure of laser to the sample. A commonly suggested procedure to calculate SNR is [8, 26]:

1. Measure the peak value of the signals in each measurement.
2. Measure the noise value in the absence of the pump i.e. before the arrival of the pump pulse.
3. Calculate the mean peak value of the signal and standard deviation (SD) of the noise value in the absence of pump pulse.
4.
$$SNR = \frac{\text{mean of the peak signal}}{SD \text{ of noise}} \quad (4)$$

Figure 3.4 (a)-(c) shows consecutive pump probe measurements on SI-GaAs. The values of peak maximum and the noise signal in the absence of pump are tabulated in table 3.2. The SD of noise was calculated as follows:

$$SD_{noise} = \left[\frac{\sum (x_i - \bar{x})^2}{N} \right]^{1/2} \quad (5)$$

The mean peak was calculated as 1.37×10^{-4} and the SD of noise was 0.34×10^{-5} . The estimated SNR was 40 for the measurements which can be improved by proper alignment of pump and probe beams. Our experimental setup was improved during the course of time and thereby the SNR.

Scan name	Peak max.	Noise in the absence of pump(x_i)	Decay constant from the fit
(a)	1.36×10^{-4}	7.60×10^{-5}	~ 87 ps
(b)	1.32×10^{-4}	7.30×10^{-5}	~ 100 ps
(c)	1.44×10^{-4}	8.10×10^{-5}	~ 81 ps

Table 3.2 The values of peak maximum and the noise in the absence of pump to calculate SNR.

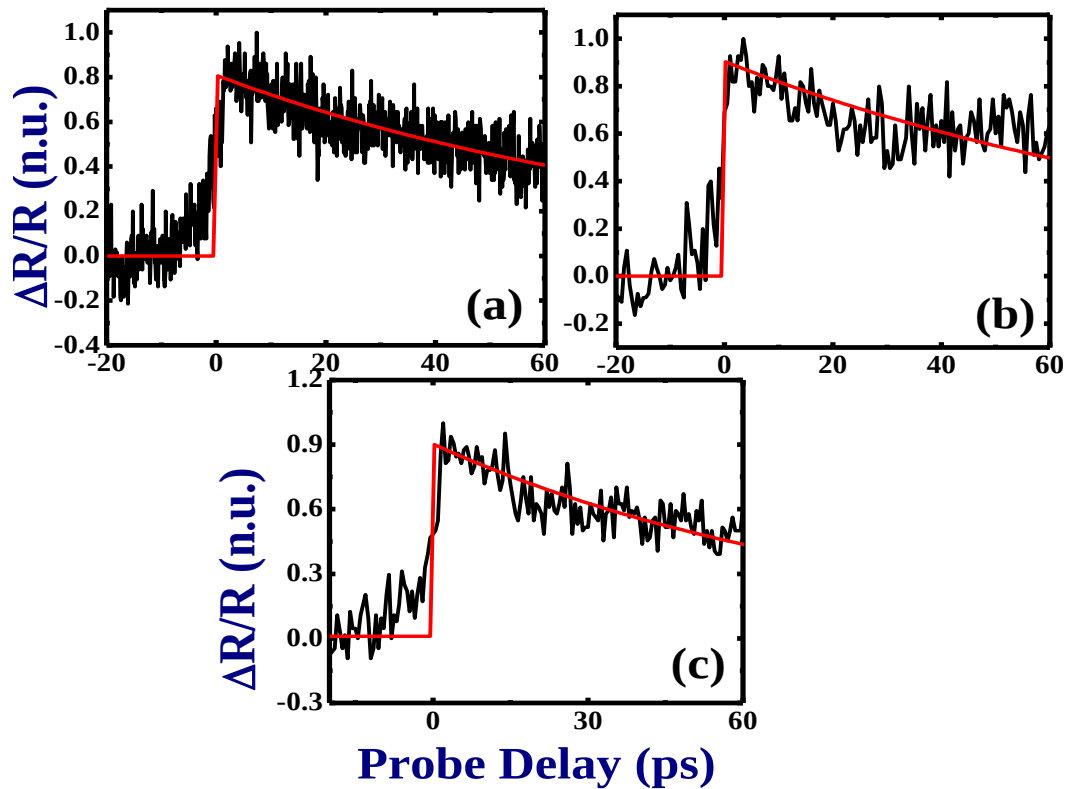


Figure 3.5 (a)-(c) Degenerate ps pump-probe measurements of SI-GaAs at $\sim 10 \mu\text{J}$ at 800 nm, ~ 2 ps laser pulses. The jagged line (black) represents experimental data, whereas the smooth line (red) represents best fit to a single-exponential decay function.

The data was fitted using a single exponential fit as shown in figure 3.5 and fitted values are summarized in table 3.2. The carrier lifetime of LT-GaAs depends on the density of defects in GaAs. The energy bands of LT-GaAs are

composed of defect states which act as electron trap levels [29]. Most of the carriers excited by the laser pulse reaching conduction band are considered to be captured by these defect levels. The trapping time of the carriers in conduction band is considered to be the carrier lifetime. The LT-GaAs was grown in relatively low temperature than the conventional way and there could be accumulation of impurities or defects during its growth. This defect density can be attributed to the fast decay of carriers in LT-GaAs than that of SI-GaAs. Thus in LT-GaAs the faster decay is attributed to carrier trapping process while the slower decay is characteristic of carrier-phonon interaction. The short carrier lifetime of LT-GaAs makes it a superior candidate for the generation of THz pulses.

3.3 Optimization of the Z-scan experimental set up

The Z-scan experimental set up was optimized with measurements on phthalocyanines both in solution and thin film form. Phthalocyanines have been examined by chemists, material scientists, and physicists alike since these are ubiquitous materials in which an alteration in molecular configuration allows the engineering of both linear and nonlinear optical (NLO) properties for specific applications. These organic systems contain conjugated π electron structure and demonstrate large third order optical nonlinearities combined with response time is in the fs and ps time domain [30-46]. The third order NLO properties of phthalocyanines are closely dependent on the central metal ion and other modifications to the core and peripheral substitution. However, phthalocyanines are hardly soluble in organic solvents and do not crystallize easily in matrices. Moreover, the molecule aggregation of phthalocyanines greatly influences the third order nonlinearity, $\chi^{(3)}$. To circumvent these problems modification of phthalocyanines such as the introduction of peripheral substitutions or attaching them to polymer chains have been carried out and NLO studies of novel phthalocyanines using cw, ns, ps and fs laser pulses were reported in literature [32-55].

In this chapter we present nonlinear absorption and the nonlinear refraction studies of phthalocyanines solutions as well as thin films achieved using ps pulses. The Z-scan technique was utilized to investigate the third order NLO properties of the film. The knowledge of ultrashort pulse n_2 aids in deciding appropriate materials for optical switching applications. Herein we present the results of our

investigations on the NLO properties of three solutions (2- (3-(Butane-1, 4- dioic acid) -9 (10), 16, (17), 23 (24)-tri tert-butyl Phthalocyanine Zinc(II) (unsymmetrical PCH001), 2- (3- (Butane-1, 4- dioic acid)-8, 11, 15, 18, 22, 25- hexakis- (butyloxy) Phthalocyanine Zinc (II) (unsymmetrical PCH003), and 2(3), 9(10), 17(18), 23(24) -[(1, 2- (dicarboxyethyl)]- phthalocyanato zinc(II) (Symmetrical ZnOCPC) and five thin films (Pc1-Pc5; the nomenclature of these compounds are mentioned in table 3.5) of phthalocyanines were studied using ~2 ps pulses.

3.3.1 Results and discussion

3.3.1.1 Nonlinear optical properties of Phthalocyanine in solution form

The linear absorption spectra of the phthalocyanines studied are shown in figure 3.6. Two main absorption bands were observed: a Q-band in the vicinity of 700 nm and a B-band in the 350 nm spectral region. The absorption spectra for PCH001/PCH003 and ZnOCPC were recorded with ethanol and water as the solvents, respectively. The linear absorption for all the molecules was <0.1 at the excitation wavelength of 800 nm. PCH001 and PCH003 was structurally unsymmetric and contain alkyl and alkoxy groups respectively. However, ZnOCPC is structurally symmetric. These materials have a window, between these two absorption bands, with high linear transmittance making them attractive as optical limiters for the visible spectral region (~420-650 nm).

Optical limiting (OL) is a phenomena observed when the transmission of a medium decreases with increasing input laser intensity (or fluence). An effective optical limiter will have low limiting threshold, high optical damage threshold and stability, fast response time, high linear transmittance throughout the sensor band width, optical clarity and robustness. One of the major mechanisms involved is reverse saturable absorption (RSA), usually observed with nanosecond pulse excitation. OL can be achieved through various nonlinear optical mechanisms such as multi-photon absorption (MPA), excited state absorption (ESA), free carrier absorption (FCA) self- focusing, self-defocusing, nonlinear scattering, photo-refraction etc. Coupling two or more of these mechanisms also cause OL like self de-focusing along with MPA.

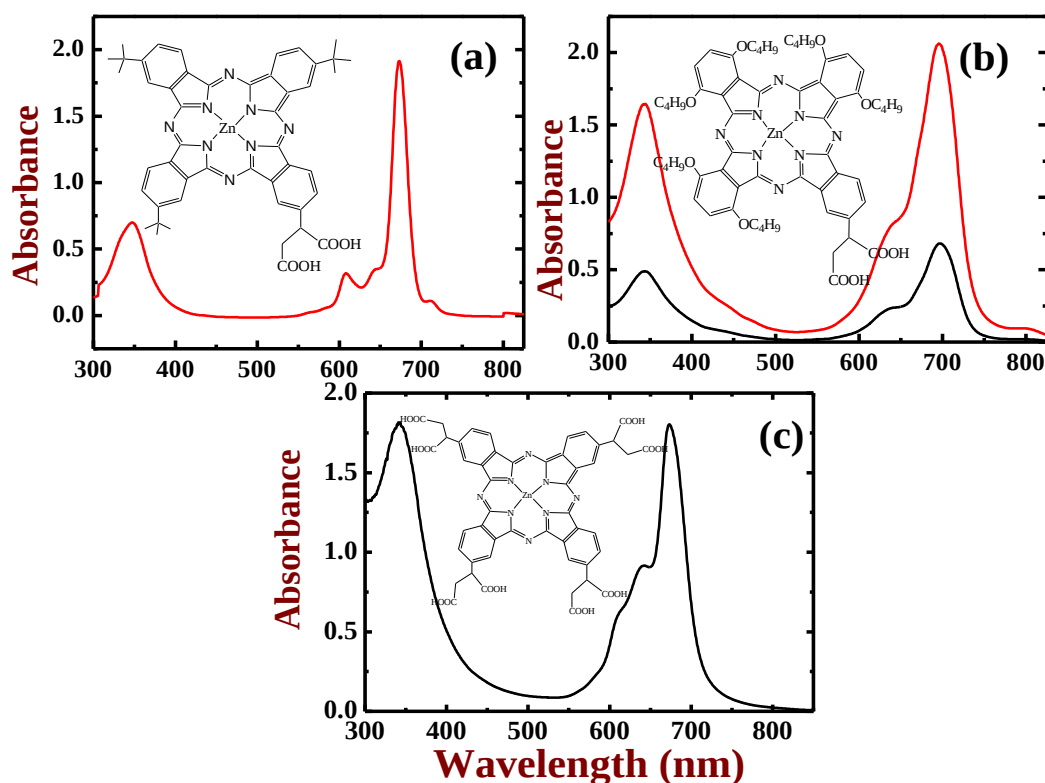


Figure 3.6 Absorption spectra and structure of (a) PCH001, 0.01 mM in ethanol (b) PCH003, 0.05 mM (red) and 0.01 mM (black) in ethanol and (b) ZnOCPC, 0.01mM in water.

Figure 3.7 (a) shows the closed aperture scans, along with the corresponding fits, for PCH001, PCH003 and the solvent ethanol recorded at $1 \times 10^{11} \text{ W/cm}^2$ intensity. Open circles represent the experimental data for solution and solid circles for the solvent while the solid lines are the theoretical fits [56]. In both cases of solution, the sign of nonlinear refraction n_2 was negative. We obtained the best fits for n_2 as $\sim 2.95 \times 10^{-15} \text{ cm}^2/\text{W}$ and $\sim 3.75 \times 10^{-15} \text{ cm}^2/\text{W}$ for PCH001 and PCH003, respectively. Similarly the closed aperture data along with fits for the sample ZnOCPC in water is also shown in figure 3.7(a). The open triangles ZnOCPC are the experimental data while solid lines are the theoretical fits. The peak-valley separation was $\sim 1.7 \times Z_0$, clearly suggesting the presence of Kerr type of nonlinearity. The peak followed by a valley (normalized transmittance obtained from the closed aperture Z-scan data) indicates that the sign of nonlinear refraction n_2 to be negative (self-defocusing) at 800 nm. Generally closed aperture scans contain contributions from both of the nonlinear absorption and the nonlinear refractive index. The saturation absorption (reverse saturable absorption) enhances (diminishes) the peak and diminishes (enhances) the valley of the transmittance. The closed aperture data was divided by open

aperture data to eliminate any contribution from nonlinear absorption and retrieve only the nonlinear refraction data.

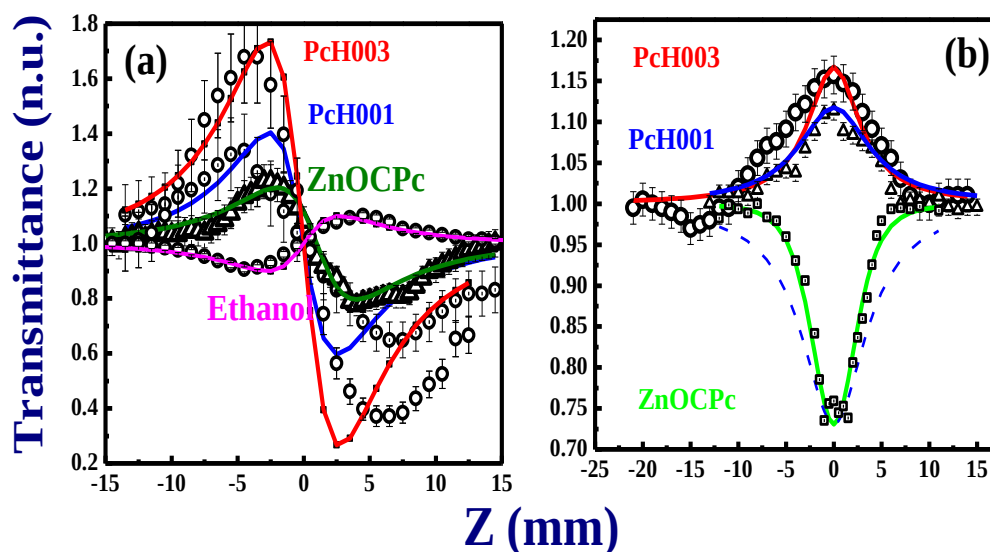


Figure 3.7 (a) Closed aperture Z-scan data for PcH001, PcH003 (in ethanol) and ZnOCPc (in water). Ethanol (solvent) did contribute to the n_2 but not to the nonlinear absorption. The sign of n_2 of ethanol was opposite compared to that of the samples. The scattered points are the experimental data and the solid lines are the theoretical fit (b) Open aperture Z-scan data for PcH001, PcH003 (in ethanol) and ZnOCPc (in water). The scattered points are the experimental data and the solid lines are the theoretical fit. The solid lines are fits to the experimental data. Dashed line is a 2PA fit to the OA scan (open squares) of ZnOCPc. 2% of error bar is considered.

We obtained the best fits for $n_2 = \sim 1.3 \times 10^{-15} \text{ cm}^2/\text{W}$ for ZnOCPc. In the present study all the samples were found to exhibit a negative nonlinearity except for pure solvent ethanol which displayed a positive nonlinearity ($n_2 = 1 \times 10^{-15} \text{ cm}^2/\text{W}$). The valley to peak curve indicates a positive optical nonlinearity as shown in figure 3.7(a). Hence the solvent contribution reduces the actual nonlinear refractive index of phthalocyanines (PCH001, PCH003 and ZnOCPc). The nonlinear refractive index values for the samples are actually higher than those calculated and presented here in table 3.3. The open aperture scan for ethanol did not indicate the presence of any significant nonlinear absorption. The nonlinear absorption and refraction observed from water was insignificant at the intensities used in present studies.

Figure 3.7 shows the open aperture Z-scan data for PCH001, PcH003, ZnOCPc at input energies of $\sim 1.9 \mu\text{J}$, $\sim 1.9 \mu\text{J}$ and $\sim 7 \mu\text{J}$ respectively. For ZnOCPc a valley was observed in the scan indicating strong 2PA/ESA behavior. For ps/fs pulse excitation, depending on the pump intensity and wavelength,

nonlinear absorption can be from (a) the ground state S_0 to higher excited singlet states S_n (two photon or multi-photon absorption), (b) the first excited singlet state S_1 to higher excited states S_n , [57]. The reduction in transmittance about the focus shows a positive nonlinear absorption coefficient. We obtained best fit for three-photon absorption coefficient, $\alpha_3 = 4.5 \times 10^{-22} \text{ cm}^3/\text{W}^2$. Typical peak intensities at the focus were $\sim 10^{11} \text{ W}/\text{cm}^2$. We tried fitting the data with two-photon absorption coefficient but the fit was better in the 3PA case. The open aperture profile for PCH003 showed an increase in transmission with increasing intensity is observed, which indicates the presence of saturation absorption (SA). A good fit was obtained for an effective nonlinear absorption coefficient of $\beta = 0.106 \text{ cm}/\text{GW}$ for PCH001 and $\beta = 0.275 \text{ cm}/\text{GW}$ for PCH003. The open aperture scan for ethanol did not indicate the presence of any significant nonlinear absorption.

Figure 3.8 shows the open-aperture data of (a) PCH001 ($\sim 3.15 \mu\text{J}$) and (b) PCH003 ($\sim 7.5 \mu\text{J}$) recorded at higher energies. Peak intensity of $\sim 154 \text{ GW}/\text{cm}^2$ was used for PCH001 while a peak intensity of $\sim 450 \text{ GW}/\text{cm}^2$ was used for PCH003. The cuvette was not damaged since the input fluence ($\sim 90 \text{ mJ}/\text{cm}^2$) was well below the damage threshold of quartz ($\sim 130 \text{ J}/\text{cm}^2$)[75]. It is evident that the saturable absorption (SA) behavior changed to reverse saturable absorption (RSA) and the nonlinear coefficients were obtained using the equation $\alpha = \alpha_0 I / [1 + (I/I_s)]$. The open-aperture scans were fitted by solving the propagation equation for homogeneous medium $dI/dz = \{-\alpha_0 I / [1 + (I/I_s)]\} - \beta I^2$. Both PCH001 and PCH003 have small absorbance near 800 nm resulting in SA at lower intensities. But, at higher intensities RSA dominated because of the excitation of population to the higher lying states. Such behavior was observed in similar molecules in our earlier studies using femtosecond pulses [58, 59]. In the case of ZnOCPC the absorption was almost negligible near 800 nm and we could observe RSA even at lower peak intensities. Considering all the unforced random experimental errors (arising from concentration measurement, input power measurement, data fitting, estimation of the spot size at focus etc.) we have estimated an overall error of $\pm 20\%$ in our calculations.

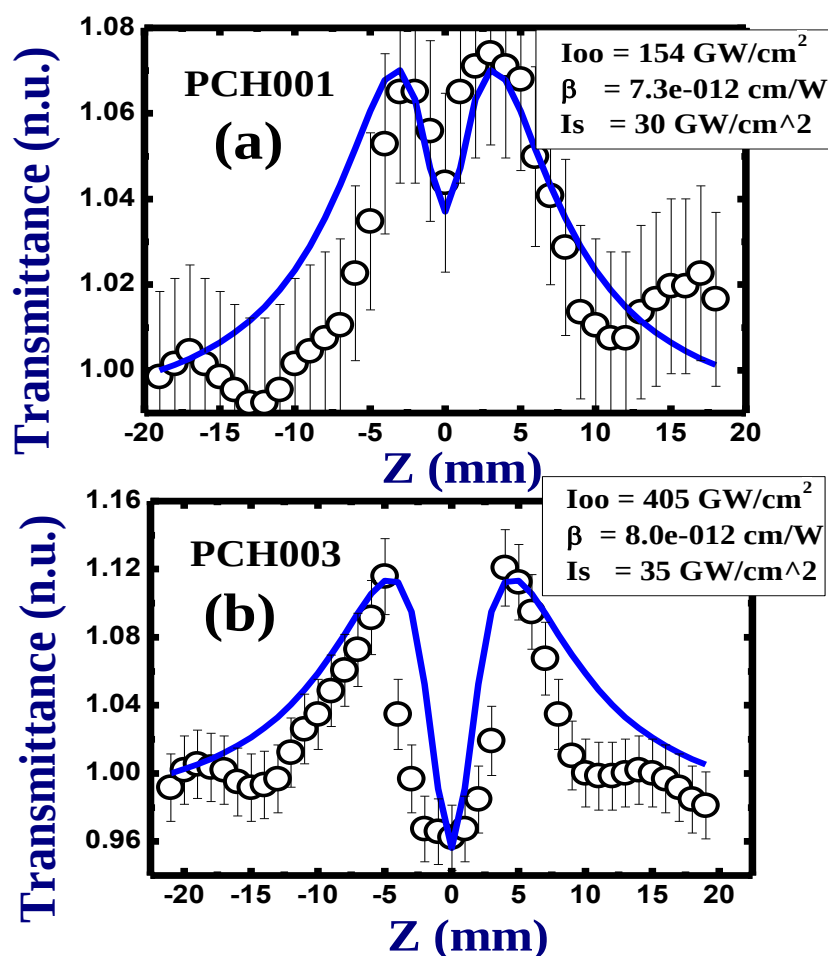


Figure 3.8 Open aperture Z-scan data for (a) PCH001 at a peak intensity of $\sim 154 \text{ GW/cm}^2$ (b) PCH003 at a peak intensity of $\sim 405 \text{ GW/cm}^2$. The solid lines are fits to the experimental data (open circles). 2% of error bar is considered.

PCH001 and PCH003 are unsymmetrical molecules while ZnOCPc is a symmetric molecule. PCH001 is an alkyl compound while PCH003 is an alkoxy compound. The NLO coefficients calculated for these compounds reveal interesting pattern. The unsymmetrical molecules (PCH001 and PCH003) had higher NLO coefficients compared to symmetrical molecules (ZnOCPc). Among the unsymmetrical molecules alkoxy substitution resulted in higher nonlinearity compared to the alkyl substitution. The higher value of NLO coefficient of PCH003 and PCH001 compared to ZnOCPc could be credited to the lack of symmetry in structure, resulting from the uneven peripheral substitution. It has been observed that the nonlinearity of a molecule increases with asymmetry if the excited states transition moments dominate [60]. Similar trends were observed in the nanosecond excitation case.

Sample	n_2 (m^2/W) $\times 10^{-19}$	n_2 (e.s.u.) $\times 10^{-12}$	$\text{Re} \chi^{(3)} $ (m^2/V^2) $\times 10^{-21}$	$\text{Re} \chi^{(3)} $ (e.s.u.) $\times 10^{-13}$	β (m/W) $\times 10^{-12}$	$\text{Im} \chi^{(3)} $ (m^2/V^2) $\times 10^{-21}$	$ \chi^{(3)} $ (m^2/V^2) $\times 10^{-21}$	$ \chi^{(3)} $ (e.s.u.) $\times 10^{-13}$	T	W
PcH001	-2.95	-0.95	-2.9	-1.3	1.06	2.90	2.90	2.13	4.6 (5.8)	92.8 (73.2)
PcH003	-3.75	-1.2	-3.69	-1.76	2.75	4.07	4.07	2.91	2.1 (2.7)	88.2 (65.8)
ZnOcPc	-1.3	-0.42	-1.2	-0.61	α_3 (cm^3/W^2) 4.5×10^{-22}	$\text{Im} \chi^{(5)} $ (m^4/V^4) 4.6×10^{-29}				

Table 3.3 Summary of the NLO coefficients obtained for different phthalocyanines in solution. 2% of error bar is considered.

Sample(s)	ZnPc(OBu) ₆ (NCS)	Fullerene Derivative 1 Derivative 2	Lead Pcs	Alkyl & Alkoxy Pcs	Titanium Pcs	Rare Earth Pcs in Polymer	Alkyl & Alkoxy Pcs
Details	130 fs, 800 nm	38 ps, 532 nm	90 ns, 532 nm	~100 fs, 800 nm	~500 ps, 532 nm	~25 ps, 532 nm	~2 ps, 800 nm
γ (esu)	2.35×10^{-31}	0.237×10^{-31} 0.202×10^{-31}	$\sim 10^{-34}$	$\sim 4 \times 10^{-31}$	$\sim 10^{-29}$	$\sim 10^{-29}$	6.5×10^{-31} 8.9×10^{-31}
Reference	61	62	73	74	63	64	This work

Table 3.4 Comparison of γ for various molecules studied recently.

With the intention of justifying the potential of these molecules we calculated the figures of merit (FOM) and later compared them with other potential molecules reported recently. The merit factor W is defined as [52]

$$W = \frac{n_2 I_{sat}}{\alpha_1 \lambda}, \text{ where } \lambda \text{ is wavelength, } I_{sat} \text{ is the light intensity at which } n_2 \text{ saturates.}$$

The pre-requisite for superior FOM is $W > 1$. The corresponding FOM for nonlinear absorption is $T^{-1} = \frac{n_2}{\lambda \alpha_2}$. For photonics device applications $T < 1$ is

desirable. For PCH001 (PCH003) the FOM calculated were $T = 2.7$ (5.8) and $W = 65.8$ (73.2). The corresponding values if the solvent contribution is eliminated are represented in the parentheses of table 3.3. It is apparent that FOM ‘ W ’ is $\gg 1$ and advocates potential applications in photonic devices. The second order hyper polarizability, γ values estimated were $\sim 6.5 \times 10^{-31}$ e.s.u. and $\sim 8.9 \times 10^{-31}$ e.s.u. for PCH001 and PCH003, respectively. These represent one of the best values reported recently (see table 3.4). Cheng et al. [62] studied two fullerenes with 38 ps pulses and observed γ values one order of magnitude lower than those presented here. However, higher γ values were obtained in titanium phthalocyanine [63] and rare earth phthalocyanines in polymer [64], possibly due to longer pulses (~ 500 ps) used in the former case and the polymer host (PMMA) along with excitation wavelength (532 nm) in the latter case enhancing the nonlinearity. The measurements with 100 fs gave a lower γ value [65]. We have been successful in doping these molecules in PMMA and studied the NLO properties and excited state dynamics using Z-scan and pump-probe technique. Preliminary data suggests the lifetimes are in the sub-100 ps range.

3.3.1.2 Nonlinear optical properties of phthalocyanine in thin film form

The IUPAC nomenclature for the compounds (films) is shown in table 3.5. Except PC3, all are symmetric in structure. In case of PC1 and PC2, the peripherals are substituted by alkoxy group and that of PC4 and PC5 are substituted by alkyl group. The central metal atom Zn is incorporated in PC2, PC3 and PC5. All the molecules were purified prior to NLO experiments. The molecules were dissolved in a sonicated PMMA+chloroform solution (crystal

clear). The phthalocyanine compounds were added to this solution by 1% weight. The solution was then transferred to clean microscopic slides and spin coated to achieve films of various thicknesses which depend on the spin speed. The typical thickness of the films measured using a profilometer were in the 8-12 μm range [47, 48].

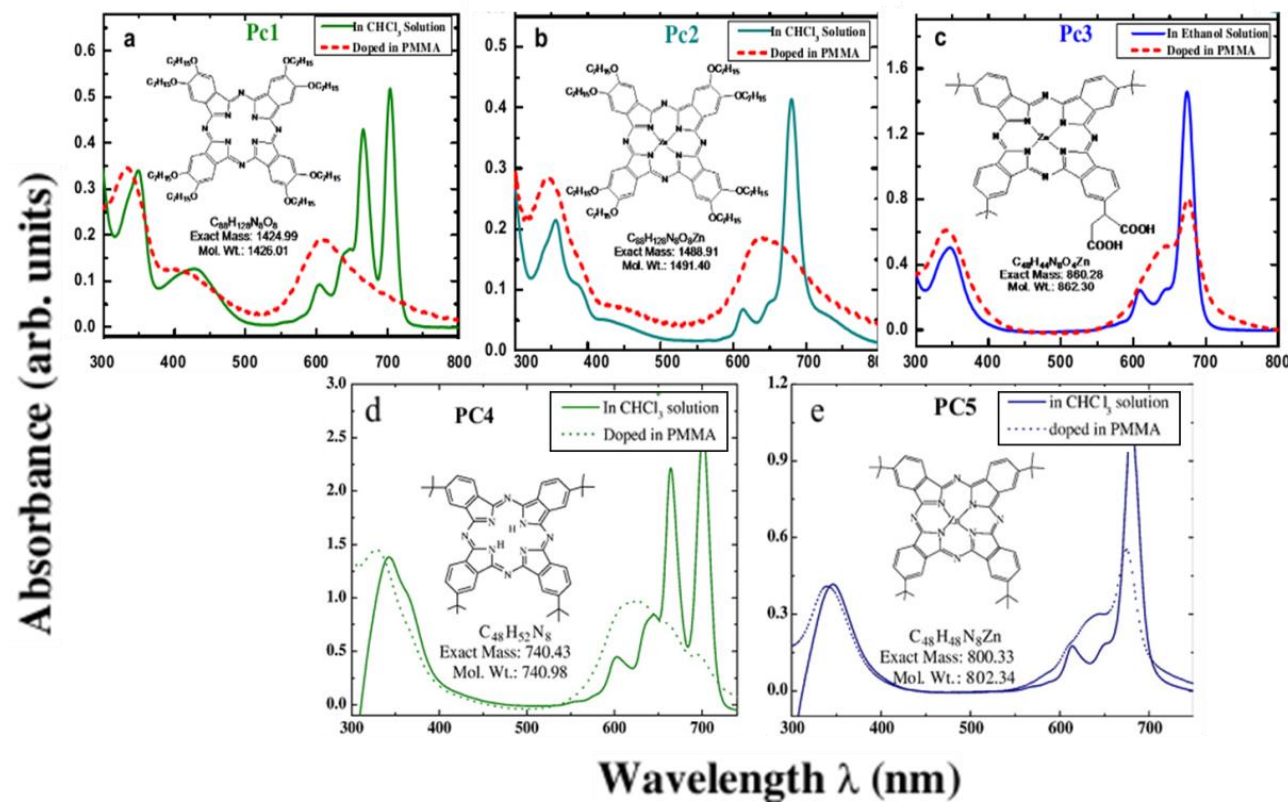
The absorption coefficients of all the films were estimated to be in the range of 10^4 m^{-1} for all the films. Linear absorption spectra of typical PC2 and PC3 thin films are shown in figure 3.9. The slight broadening and splitting observed in Q band (arising from electronic transitions) and broadening of Soret band in the thin film absorption spectra, compared to solutions, could be ascribed to the intermolecular interaction and molecular distortion/deformation [66,67]. In addition there is also the possibility of aggregation in solid state thereby slightly modifying the energy level configuration.

Sample	Nomenclature
PC1	2,3,9,10,16,17,23,24-octakis (heptyloxy)phthalocyanine
PC2	2,3,9,10,16,17,23,24-octakis-(heptyloxy)phthalocyanine Zinc(II)
PC3	(2-(3-(Butane-1,4-dioic acid)-9(10),16(17),23(24)-tri <i>tert</i> -butyl phthalocyanine Zinc(II)
PC4	2(3),9(10),16(17),23(24) tetra <i>tert</i> -butyl phthalocyanine
PC5	2(3),9(10),16(17),23(24) tetra <i>tert</i> -butyl Zinc phthalocyanine

Table 3.5 Nomenclature of compounds used in the present study.

Sample	n_2 (m^2/W) $\times 10^{-17}$	n_2 (e.s.u.) $\times 10^{-10}$	$\text{Re} \chi^{(3)} $ (m^2/V^2) $\times 10^{-19}$	α_2 (m/W) $\times 10^{-10}$	$\text{Im} \chi^{(3)} $ (m^2/V^2) $\times 10^{-19}$	$ \chi^{(3)} $ (m^2/V^2) $\times 10^{-19}$	$ \chi^{(3)} $ (e.s.u.) $\times 10^{-11}$	Figure of Merit W	Figure of Merit T	Limiting Threshold (J/cm^2)
PC1	4.30	1.53	5.06	6.00	4.50	6.78	4.86	3.7	11.2	0.164
PC2	6.94	2.47	8.17	18.0	13.5	15.8	11.3	7.3	20.7	0.137
PC3	14.4	5.12	17.0	20.0	15.0	22.6	16.2	2.6	11.1	0.112
PC4	2.18	0.78	2.57	6.00	4.50	5.18	3.71	2.3	22.0	0.131
PC5	2.30	0.82	2.71	1.50	1.13	2.93	2.10	3.1	5.2	0.550

Table 3.6 Summary of the nonlinear coefficients of Phthalocyanine thin films extracted from the present study.



Figures 3.10(a) to 3.10(e) show the open aperture data (open stars) of phthalocyanine thin films PC1 to PC5 recorded at 800 nm with 2 ps pulses and input peak intensities $\sim 200 \text{ GW/cm}^2$. Insets of figure 3.10 show the closed aperture data for all thin films. The peak followed by valley in the normalized transmittance data clearly suggests that the samples possessed negative type of nonlinearity and self-defocusing behavior. The n_2 values obtained from the fits to data for all the films were in the range of $2\text{-}15 \times 10^{-13} \text{ cm}^2/\text{W}$. In order to extract the information of nonlinear refraction alone, the experimental closed aperture Z-scan data was divided by the open aperture data. This greatly eliminated the influence of nonlinear absorption on the nonlinear refraction data. CA and OA data for all the films were fitted using conventional equations [56]. The presence of valley in normalized transmittance in open aperture (OA) scans indicates strong reverse saturation absorption (RSA) at these peak intensities. From all the fits to experimental data it is evident that 2PA is the dominant mechanism for the observed RSA kind of behavior. 2PA absorption coefficients estimated from the fits were in the range of $15\text{-}200 \text{ cm/GW}$. 3PA fits are also shown in the figures for comparison and undoubtedly the fits are off from the experimental data.

All the samples were checked for presence of any nonlinear absorption losses due to scattering. The transmitted light was devoid of any scattering in the far-field indicating that 2PA was the main mechanism contributing to nonlinear absorption. The values of nonlinear coefficients presented here are accurate within 15% and the errors arise due to uncertainties in the measurements of peak intensity, fitting procedures, unaccounted Fresnel losses, etc. The $\chi^{(3)}$ values, $\sim 10^{-10}$ e.s.u., obtained from our films are comparable to one of the highest reported nonlinearity for aluminum phthalocyanine films [43]. The best n_2 value was obtained for PC3 ($1.44 \times 10^{-16} \text{ m}^2/\text{W}$) is also comparable to the values obtained in self-assembled multilayer films containing tetrasulfonated iron phthalocyanine [68]. However, in their case due to the multi-layer nature of films the π -electron molecular orbits of macrocycles in the aggregates probably coupled with neighbors so strongly enough to enlarge the conjugation system, thus, changing the electronic structure of the Phthalocyanine molecule and improving the third-order optical response. Ma et al. [38] reported $\chi^{(3)}$ values of 10^{-10} esu for their titanyl phthalocyanine films which is again comparable to the

values obtained in present study. Furthermore, we observed strong 2PA in our molecules which find potential applications in bio-imaging and good optical limiting thresholds.

The solution studies of these molecules exhibited, strong 3PA in alkyl phthalocyanines (PC4 and PC5) [51]. In the case of alkoxy phthalocyanines (PC1 and PC2), a combination of excited state absorption, 2PA, and 3PA was found[50]. All these studies were performed with fs pulses. Saturable absorption behavior was observed with ps pulses in the asymmetric phthalocyanine (PC3) [53, 54]. However, all the films studies obviously pointed to the presence of strong 2PA. This could be explained with the changes in absorption spectra, and thereby the energy level configuration, corresponding to solutions and thin films. One has to consider the input peak intensities used for these studies too. With the broadening of Soret band there is a possibility of direct two-photon state existence for the molecule when excited with 800 nm photon in the bulk, unlike in solutions. PC3 in solution depicted SA (due to small absorption at 800 nm) when excited with lower peak intensities but immediately switched to RSA with increasing peak intensities [53, 54]. PC1 and PC2 also demonstrated similar behavior of RSA with increasing peak intensities. The nonlinear absorption in such molecules is indeed complex phenomena involving several excited state mechanisms such as 2PA/3PA induced excited state absorption, pure 2PA/ 3PA, single photon induced excited state absorption etc. [57, 69-72]. We have assessed the merit factors W and T for all the thin films studied and W was certainly >1 for all the films while T was also >1 . We strongly feel that these robust molecules are good for multi-photon absorption based applications due to the presence of strong 2PA. The nonlinear refractive index recorded was also high for these molecules compared to some the recently reported molecules of interest and furthermore the excitation wavelength was non-resonant. However, supplementary wavelength dependent studies will reveal the actual potency of these molecules for optical switching based applications which is strongly dependent on n_2 .

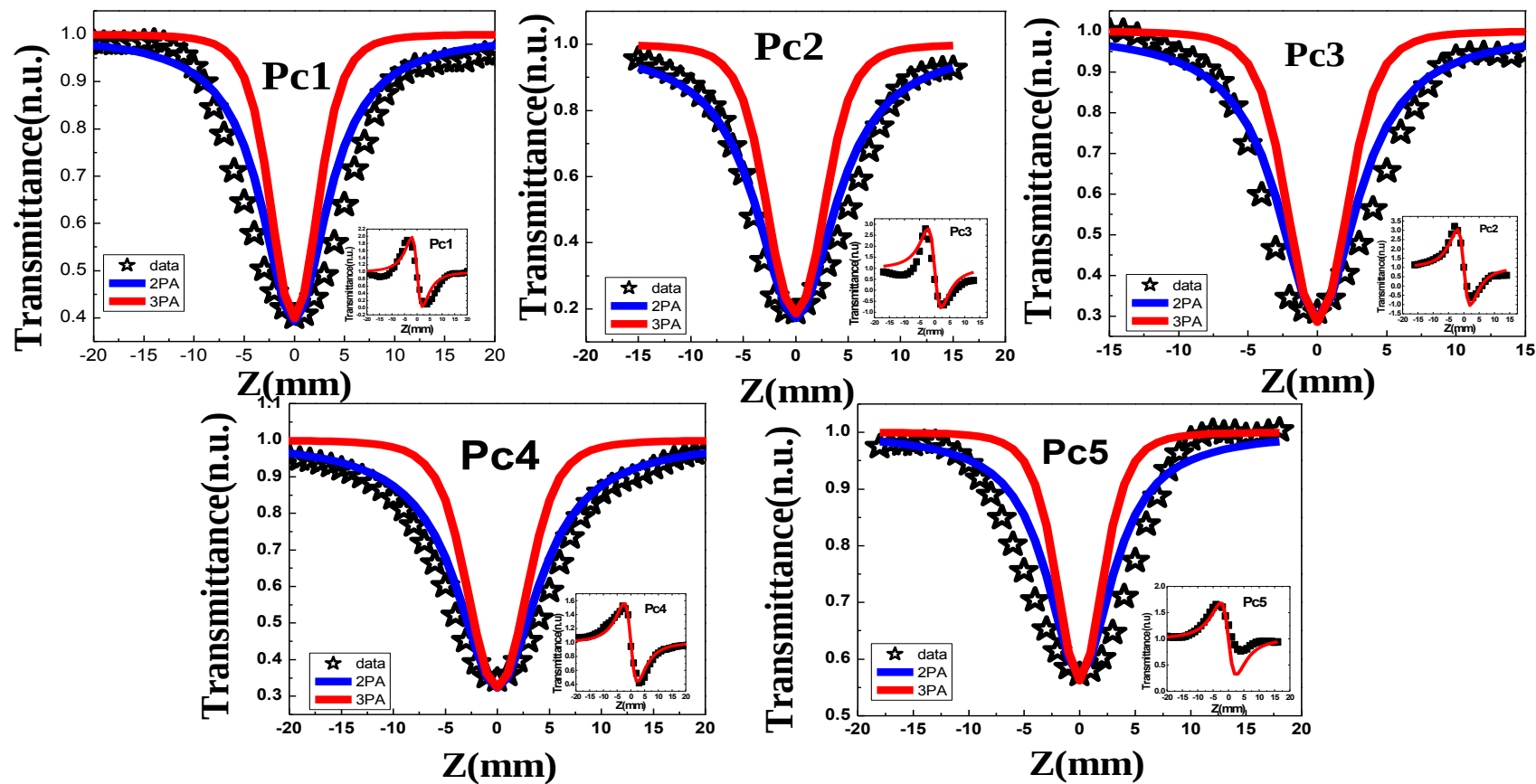


Figure 3.10 (a)-(e) OA Z-scan curves of PC1 to PC5 recorded with peak intensity of 200 GW/cm^2 . Open stars represent the experimental data while the solid lines are fits. Red (dotted) and blue (solid) lines represent theoretical fit for 3PA and 2PA, respectively. Inset shows CA data recorded at same intensities.

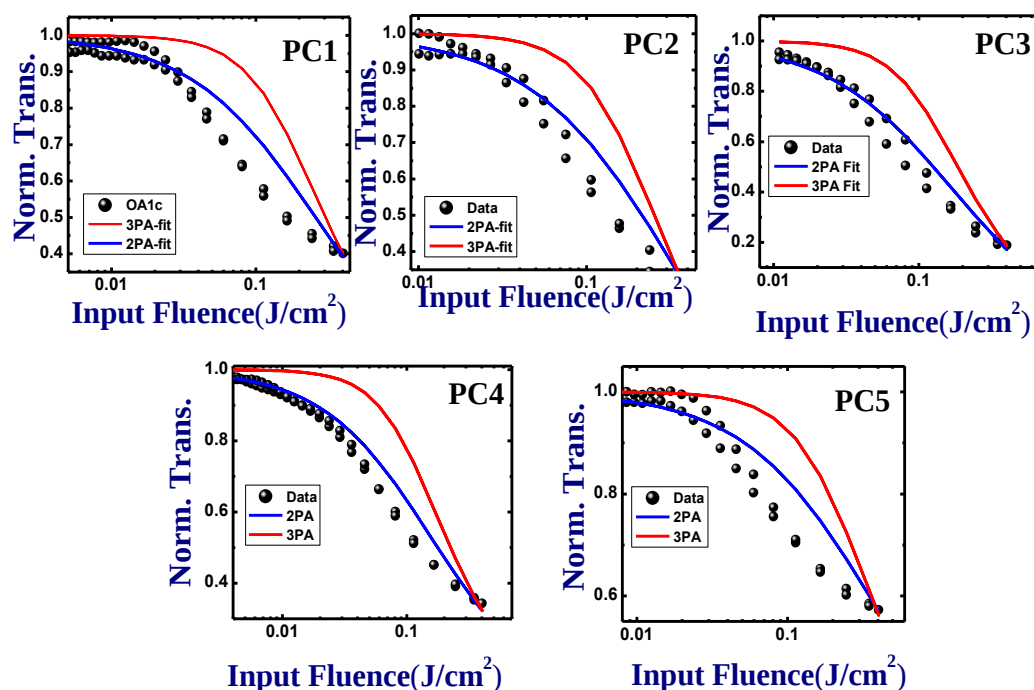


Figure 3.11 Optical limiting curve recorded for PC3 in PMMA. Blue (solid) line is the fit for 2PA while red (dotted) line is the fit for 3PA. Solid circles are experimental data points.

In the case of PC thin films it is observed that sample exhibits strong two-photon absorption and therefore is responsible for the limiting. Figure 3.11 shows a typical optical limiting curve depicting the sample transmission as a function of input laser fluence (i.e. energy per area). The input laser energy density was evaluated using the relation $E_{in} = 4\sqrt{\ln 2} E_{in} / \pi^{3/2} \omega(z)^2$, where E_{in} is the input laser pulse energy and $\omega(z)$ is the beam radius. It is evident that under strong irradiance the curve departs from Beer's law leading to optical power limiting in the thin film. The limiting thresholds evaluated from the data and fits were in the 0.1-0.6 J/cm² range. Table 3.6 summarizes the nonlinear coefficients of all the films extracted from the present study. The high nonlinearity of PC3 compared to other phthalocyanines can be ascribed to the asymmetry in structure compared to other symmetrical phthalocyanines and is consistent with our earlier results [50-55]. Metal phthalocyanine films exhibited higher nonlinearities when compared to free base phthalocyanine films for both, alkyl and alkoxy, cases whereas alkoxy phthalocyanine films displayed higher nonlinearity compare to alkyl phthalocyanine films. Our comprehensive studies strongly suggest these are potential molecules with strong nonlinearities and figures of merit.

3.4 Conclusions

In summary, it has been successfully optimized the experimental set up for ps/fs pump probe technique using LT- GaAs and SI-GaAs which can be used as the PC antenna substrate for the detection/generation of relatively low frequency THz radiation. SI-GaAs is important due to its high carrier mobility and long carrier lifetime whereas LT-GaAs has comparatively shorter lifetime which could be suitable for PC substrate. The carrier lifetime of SI-GaAs and LT-GaAs was measured to be ~200 ps and ~20 ps respectively. The Z-scan experiment was also optimized using series of structurally different phthalocyanines both in solution and thin film form. The nonlinear optical properties of phthalocyanine solutions ZnOCPc, PCH001, PCH003 and five different phthalocyanine thin films were studied and compared with the literature. All the samples were found to possess good n_2 values comparing to some of the recently reported values for similar molecules. The sign of the nonlinearity was confirmed to be negative. Open aperture studies demonstrated strong two photon absorption to be responsible for the nonlinear absorption. Figures of merit have been evaluated for the samples and the data suggests these molecules are good for multi-photon imaging and optical limiting applications.



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CHAPTER 4

Ultrafast excited state dynamics and third order optical nonlinearities in novel Corroles

ABSTRACT

Ultrafast excited state dynamics of four novel corroles have been appraised with picosecond (ps) and femtosecond (fs) degenerate pump-probe techniques using excitation wavelengths of 800 nm and 600 nm, respectively. Ultrafast NLO properties in the visible spectral range (660 - 800 nm) were evaluated using ps Z-scan technique. The excitation by 800 nm photons resulted in two-photon absorption, at adequately high peak intensities, thereby facilitating the access to higher excited states (S_n). The non-radiative relaxation mechanisms from these states, reflected in the pump-probe data, were extracted from bi-exponential decay fits to the experimental data. When excited with 600 nm photons (unfocused) photo-induced absorption was observed with the first excited state S_1 being populated and as a consequence single decay was observed. These retrieved lifetimes were analogous to those obtained with ps pump-probe data at 800 nm. The long lifetime is attributed to non-radiative decay from the S_1 state with possible contribution from triplet states while the shorter lifetime is attributed to the internal conversion (S_2 to S_1^) followed by vibrational relaxation (S_1^* to S_1) processes. S_1^* represent high lying vibrationally hot singlet excited states. Time-resolved fluorescence lifetime measurements revealed the magnitude of radiative lifetimes to be in the nanosecond regime. Large two-photon absorption coefficients (β)/cross-sections (σ_2) at 740 nm/680 nm were recorded for these molecules making them apposite for applications such as two-photon induced photodynamic therapy and lithography.*

The chapter includes data from the following publications:

-  *Journal of Physical Chemistry C*, 116, 17828-17837, **2012**.
-  *Proceedings of SPIE*, 8258, 82581C, **2012**.

4.1 Introduction

Novel moieties with strong two-photon absorption (2PA) and three-photon absorption (3PA) cross-sections/coefficients are imperative for potential applications in the fields of photonics, lasing, photodynamic therapy (PDT), and bio-imaging [1-7]. Studies on a variety of molecules with strong 2PA/3PA have established their relevance in fluorescence spectroscopy, 3D imaging, and lithography because of high spatial resolution achieved through intensity dependent processes [8-11]. Furthermore, they encompass potential in the fields of optical data storage and optical limiting [1,4]. Several organic materials with large number of π -electrons such as porphyrins, phthalocyanines, porphycenes possessing interesting nonlinear optical (NLO) properties and dynamics have been extensively investigated in recent times by several groups including rigorous efforts from our own research group [12-26]. Despite several studies being reported in literature many of them failed to embark upon some of the most important issues, for instance (a) wavelength dependent 3rd order optical nonlinearities (b) pulse width dependent nonlinearities (c) determination of third-order nonlinearity magnitude, especially the pure electronic contribution, combined with their temporal response. Corroles have recently been subjected to intense research activity due to their attractive properties finding numerous applications, straddling from antitumor therapeutic properties to catalytic and important sensor applications, for light energy conversion and generation of singlet oxygen [27-33]. Corroles possess stronger fluorescence properties than their porphyrin counterparts opening up the potential for their utility in diverse areas such as cancer diagnosis. LiLi et al. used tetraphenylporphyrin (TPP) whose fluorescence quantum yield was 0.00242 to calculate the quantum yield of corrole [34]. It was found that the quantum yield of corrole was 4.7% higher than that of TPP. The spectral, electro-chemical, and photo-physical properties make these compounds promising building blocks to be used in dye sensitized solar cells (DSSC) with superior conversion efficiency [35, 36]. Therefore, the investigation of photo-physical properties of corroles (and similar molecules) is imperative for the potential use of these compounds [37-41]. Furthermore, these properties enable the treatment of deeper penetration of light into human tissue when they used as an ideal photo sensitizer in PDT. Recent reports have suggested that

corroles are superior as PDT photosensitizers compared to porphyrin compounds [41].

Liu et al. demonstrated that the corroles (a) are non-planar with macrocycle framework which is rigid to yield sharp rising potential surface walls than that of metalloporphyrins (b) have a larger number of Franck–Condon active vibrations (c) comprise first excited singlet excited states S_1 with structural displacements (with respect to the ground state) which are smaller or similar to those of their metallo porphyrin counterparts and (d) possess 2nd excited singlet states S_2 which show, to some extent, larger displacements (with respect to the ground state) than those of the metalloporphyrins [42]. Although the first synthesis of Corroles was reported in 1965, important characterizations such as their optical nonlinearities and excited state dynamics are being investigated only recently [43-49]. Rebane et al. [43,44] and Cho et al.[45] studied the NLO properties and reported two-photon absorption (2PA) cross sections and spectra of Corroles. The NLO measurements of Tri-phenyl Corrole (TPC) and Tri-tolyl Corrole (TTC) were performed and found that the NLO coefficients were promising in the field of photonics [25, 26]. In this chapter, we present detailed results from the ultrafast nonlinear optical and excited state lifetime (non-radiative and radiative) measurements of four novel corroles: (a) TPC (b) TTC (c) Germanium substituted TTC (GeTTC) and (d) Phosphorous substituted TTC (PTTC) achieved using pump-probe/time-resolved fluorescence and Z-scan techniques, respectively. A summary of performance of these molecules in comparison with others is also presented.

4.2 Experimental details

Synthesis: Both TTC and TPC were synthesized and purified [28]. Synthesis of **[P(TTC)(OH)₂]**: 5,10,15-tri-(4-methyl phenyl) Corrole (100 mg, 0.19 mM) and POCl₃ (600 μ L, 6.45 mM) was dissolved in 20 ml of dry pyridine. The resulting reaction mixture was refluxed under N₂ atmosphere until the Q-bands of Corrole had changed. Then the solvent pyridine was removed under reduced pressure and obtained residue was dissolved in CH₂Cl₂ and filtered. The filtrate was washed with dilute HCl, dried and evaporated. The residue was subjected to silica gel column and eluted with CH₂Cl₂. The brown colour band was collected and re-crystallized from CH₂Cl₂/hexane to get the desired

compound. Elemental analysis $C_{37}H_{25}N_4O_2P$, (calculated mass % in parentheses): C = 75.40 (75.50); H = 4.30 (4.28) and N = 9.50 (9.52). **MS(ESI) m/z** 588 calculated for $C_{37}H_{25}N_4PO_2$. UV-visible. In CH_2Cl_2 (λ_{max} , ϵ , $dm^3 mol^{-1} cm^{-1}$) 647 (4.04), 616 (4.12), 575 (4.27), 415 (5.59). Synthesis of [**Ge(TTC)(OH)**]: 5,10,15-tri-(4-methyl phenyl) Corrole (100 mg, 0.19 mM) and GeI_4 (580 mg, 1.0 mM) was dissolved in 20 ml of dry DMF. The resulting reaction mixture was refluxed under N_2 atmosphere until the Q-bands of Corrole had changed. Then the solvent was removed under reduced pressure and obtained residue was dissolved in CH_2Cl_2 and filtered. The filtrate was washed with dilute HCl, dried and evaporated. The residue was subjected to silica gel column and eluted with CH_2Cl_2 . The brown colour band was collected and re-crystallized from CH_2Cl_2 /hexane to get the desired compound. Elemental analysis $C_{37}H_{25}N_4O_2P$, (calculated mass % in parentheses): C = 75.40 (75.50); H = 4.30 (4.28) and N = 9.50 (9.52). **MS(ESI) m/z** 588 calculated for $C_{37}H_{25}N_4PO_2$. UV-visible. In CH_2Cl_2 (λ_{max} , ϵ , $dm^3 mol^{-1} cm^{-1}$) 647 (4.04), 616 (4.12), 575 (4.27), 415 (5.59).

The UV-visible absorption spectra were recorded with a Shimadzu model 1700 spectrophotometer and steady state fluorescence spectra were recorded using a Spex model Fluorolog-3 spectrofluorometer. The optical densities of the solutions were ~ 0.15 at the excitation wavelength (λ_{ex}). Time-resolved fluorescence measurements have been carried out using HORIBA Jobin Yvon spectrofluorometer. The excitation wavelength was 405 nm and the emission decay was monitored at 605 nm, in each case. The count rates employed were typically $10^3 - 10^4 s^{-1}$. De-convolution of the data was carried out by the method of iterative re-convolution of the instrument response function (IRF) and the assumed decay function, with the help of DAS-6 software. The goodness of the fit of the experimental data to the assumed decay function was evaluated by the standard statistical checks (i.e. the values of reduced χ^2 , the autocorrelation function and random distribution of weighted residuals). The details of degenerate ps/fs pump probe experiments [23] were discussed in detail in chapter 2. The experimental set up used for measuring the nonlinear optical properties at 800 nm in the Z-scan [50] configuration were also discussed in detail in chapter 2 [21, 23, 25].

4.3 Results and Discussion

4.3.1 Picosecond NLO properties

The linear absorption spectra and structures of Germanium Tritolyl Corrole (GeTTC) and Phosphorus Tritolyl Corrole (PTTC) are shown in figure 4.1(a) and (b) and that of TTC and TPC are shown in figure 4.11(b) and (c). When compared with regular porphyrins, both GeTTC and PTTC exhibited two strong bands: one in the near ultraviolet spectral region ($\lambda_{\max} = 405$ nm) known as the Soret band ($\pi\text{-}\pi^*$) or B band and the other in the visible spectral region (500 nm-630 nm, $\lambda_{\max} = 590$ nm) known as Q-band. The absorption spectra were dominated by $\pi\text{-}\pi^*$ electronic transitions with strong and broader Soret band (B band) near 400 nm and $n\text{-}\pi^*$ electronic transitions with Q-bands higher than 500 nm. Figure 4.1(c) illustrates the emission spectra recorded for all molecules in dichloromethane. We noticed that PTTC molecules had the highest quantum yield (~ 0.25).

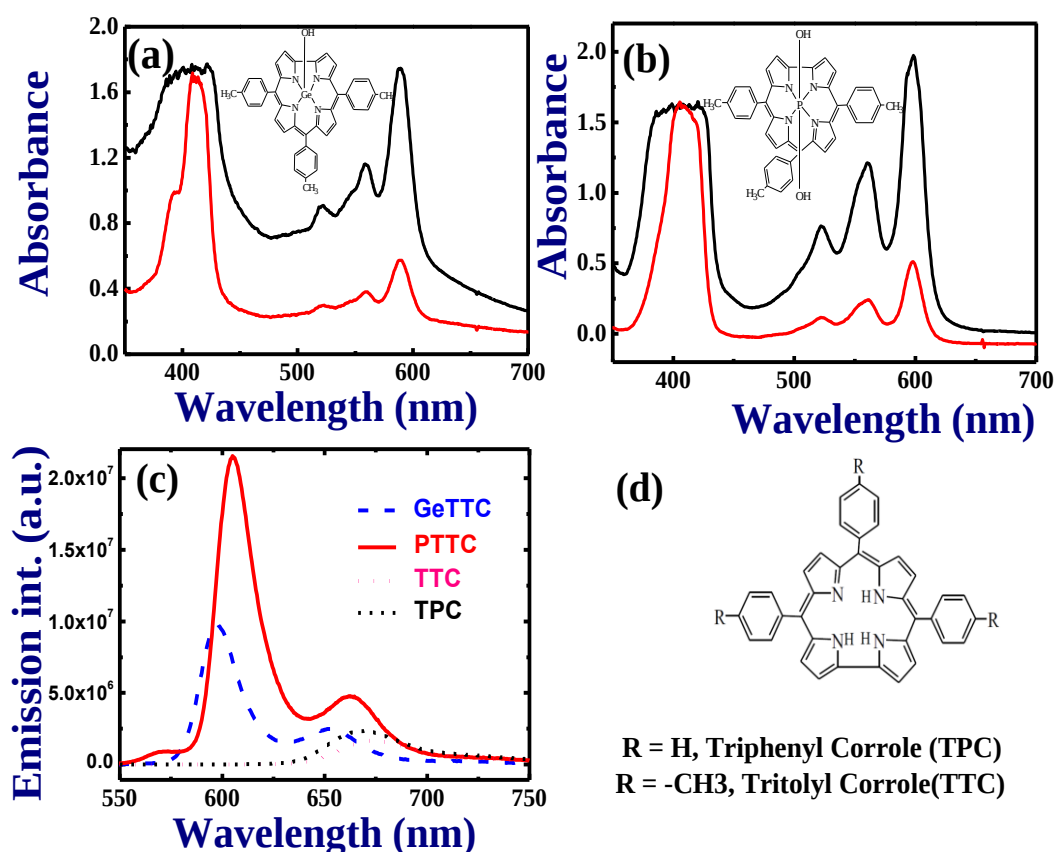


Figure 4.1 Absorption spectra of (a) GeTTC (b) PTTC in CH_2Cl_2 . Red (bottom) and black (top) solid lines are the absorption spectra recorded at low ($\sim 10^{-5} \text{ M}$) and high ($\sim 10^{-4} \text{ M}$) concentrations, respectively, (c) Emission spectra of (i) GeTTC (dashed) (ii) PTTC (solid) (iii) TTC (dotted) (iv) TPC in dichloromethane (short dashed). Inset of (a) and (b) depicts the structures of GeTTC and P-TTC. (d) Structures of TPC and TTC.

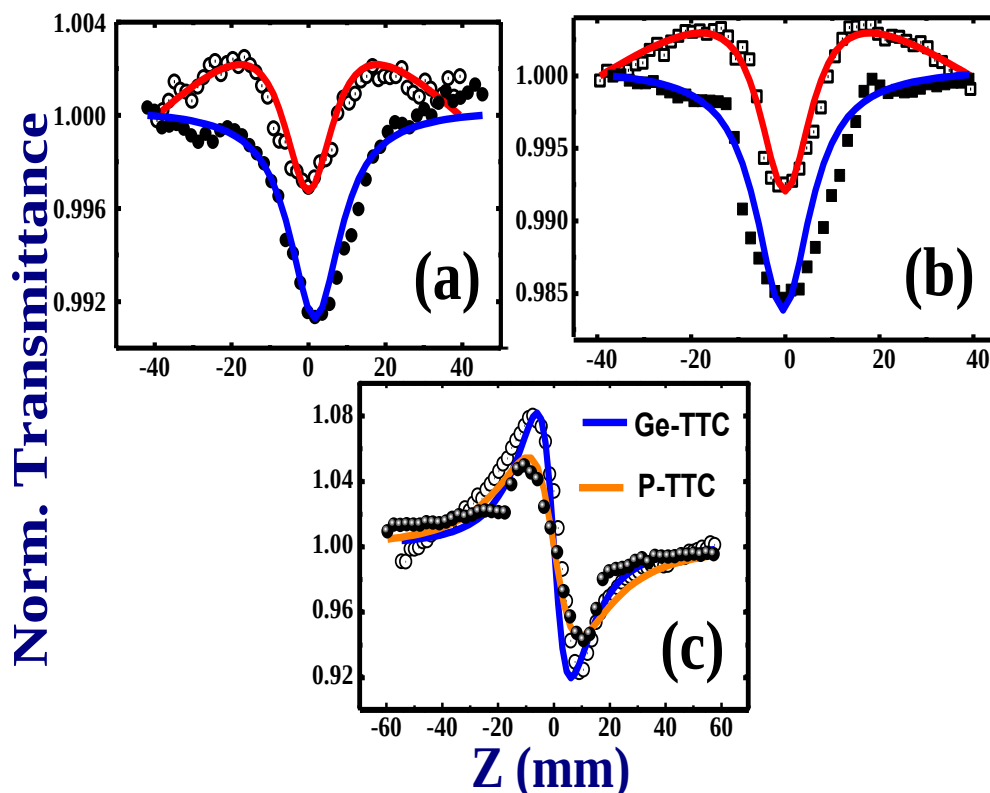


Figure 4.2 Open aperture Z-scan data of (a) GeTTC [$\sim 46 \text{ GW/cm}^2$ (open circles) and $\sim 86 \text{ GW/cm}^2$ (solid circles)] (b) PTTC [63 GW/cm^2 (open squares) and 83 GW/cm^2 (solid squares)] (c) Closed aperture data of GeTTC (empty circles) and PTTC (solid circles) recorded with peak intensity of 70 GW/cm^2 . Scattered points are experimental data and solid lines are the theoretical fits. Concentration of the solutions used was $\sim 1 \text{ mM}$.

Figures 4.2(a) and 4.2(b) show open and closed aperture Z-scan data of GeTTC and PTTC, respectively, obtained at 800 nm with a concentration of 1 mM . From the data presented in figures it is evident that both molecules exhibited strong reverse saturable absorption (RSA) for higher peak intensities and the magnitude of nonlinear absorption decreased for lower peak intensities due to the presence of saturable absorption (SA). The switching (SA to RSA) behavior observed was, probably, due to saturation (followed by absorption) from S_1 states ($20,400 - 15390 \text{ cm}^{-1}$). At higher peak intensities ($I_{00} \sim 86 \text{ GW/cm}^2$), the data was fitted with two photon absorption (2PA) [51, 52] and the fits obtained were good (least χ^2 was obtained). It is well established that such large molecules have intricate nonlinear absorption behavior heavily dependent on the excitation wavelength, peak intensity and the concentration of solute used [53, 54].

The 2PA mentioned here refers to one photon absorption followed by another photon absorption ($1+1$ photons). Since the pulse duration used was $\sim 2 \text{ ps}$ there is a possibility that a photon can excite the molecules to S_1 states can relax

back to the vibrationally cold states of S_1 before it can absorb another photon and arrive at S_2 states [53, 54]. The excitation from S_0 to S_2 is, thus, completed by the sequential absorption of two photons or in certain cases with simultaneous absorption. The presence of resonances in the spectral range of $23,100\text{ cm}^{-1}$ to $27,780\text{ cm}^{-1}$ (S_2 states) makes it possible for 2PA of 800 nm photons ($12,500\text{ cm}^{-1}$) at these intensities. We had earlier showed that with strong peak intensities one could even observe three-photon absorption (involving 1+2 or 2+1 photons kind of nonlinear absorption) [25]. The closed aperture Z-scan data demonstrated negative nonlinearity for the samples, which indicates self de-focusing phenomena. The magnitudes of NLO coefficients were obtained by solving the propagation equations and fitting the experimental data. The thermal nonlinearity (due to heating) will be minimal in the case of ps, 1 kHz excitation. The important thing to be noted is the time ($\sim 1\text{ ms}$) available between two successive ps laser pulses is sufficient to minimize any thermal effects. From the value of β/n_2 we have calculated the magnitudes of $\text{Im } \chi^{(3)}/\text{Re } \chi^{(3)}$. The magnitudes of 2PA cross-sections (σ_2) and figures of merit (T) were also evaluated. The obtained nonlinear coefficients are summarized in table 4.1. The obtained values of n_2 and β of GeTTC/PTTC were lower than those of TPC/TTC by one order of magnitude.

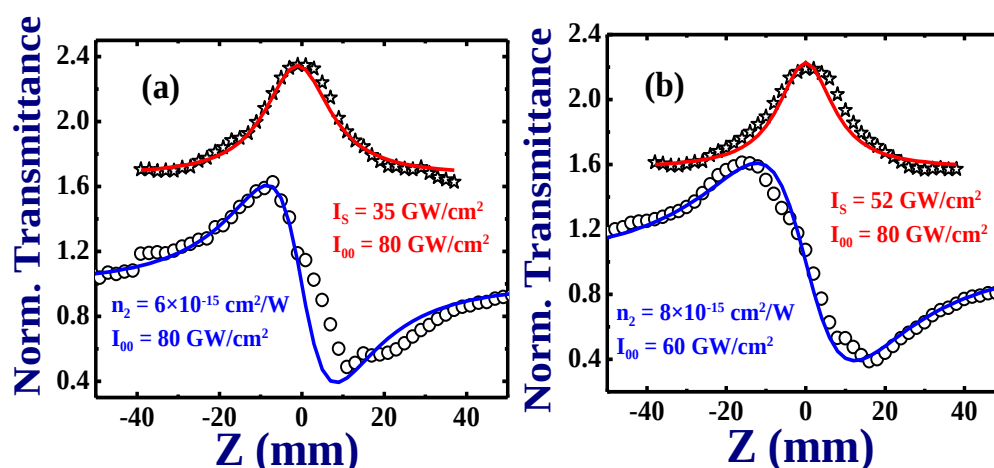


Figure 4.3 Picosecond open aperture (open stars) and closed (open circles) aperture data of (a) TPC and (b) TTC recorded with a peak intensity $I_{00} = 80\text{ GW/cm}^2$ at 660 nm for a concentration of 0.5mM. Open stars and circles represent experimental data while the solid lines are best fits.

To establish the efficacy of these molecules and understand the ESA properties in the visible spectral region (660– 800 nm) Z-scan data was recorded at different wavelengths. The data for TPC and TTC at wavelengths of 680 nm, 700 nm, and 740 nm was reported in reference [25]. Figures 4.4(a) and 4.4(b)

illustrate the open aperture data (stars) and closed aperture data (open circles) of TPC and TTC, respectively, recorded at a wavelength of 660 nm and a peak intensity of 80 GW/cm².

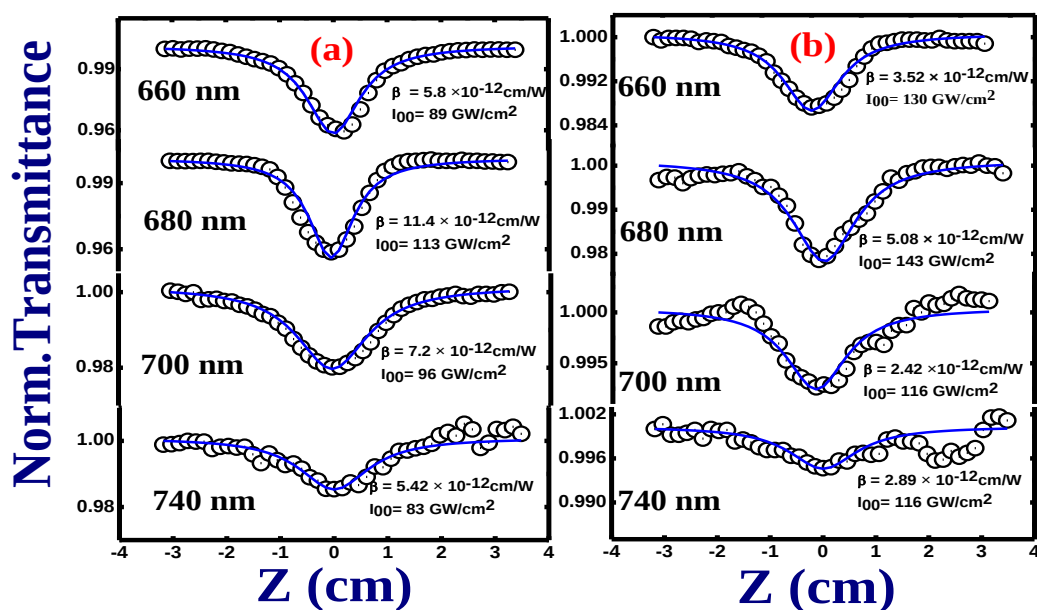


Figure 4.4 Open aperture Z-scan data and fits at different wavelengths for (a) PTPC and (b) GeTTC. Open (black) circles are the experimental data while solid (blue) lines are theoretical fits. Concentration of the solutions used was ~1 mM.

Figure 4.3 show the open aperture and closed aperture data of TPC and TTC at 80 GW/cm². SA was observed in this case. The concentrations of solutions used were 0.5 mM. The data was recorded for TPC and TTC at peak intensity levels where the contribution from solvent was insignificant which was confirmed by recording the Z-scan data of pure solvent. Obtained experimental data was fitted using the standard equations of Z-scan [51, 52]. The linear absorption for these molecules is slightly higher at 660 nm and therefore, we can expect saturation from the S₁ singlet state. For lower peak intensities population in the ground state is bleached initially (S₀ states to S₁ states). Generally, either the excited absorption cross-section (σ_{ex}) is smaller than the ground state absorption cross-section (σ_0) or the peak intensity is not sufficient to invoke σ_{ex} resulting in RSA. The saturation intensities (I_s) estimated (35 GW/cm² for TPC and 52 GW/cm² for TTC) were less than peak intensities used and, therefore, we did not calculate β . Both the samples showed negative nonlinearity as displayed by the peak to valley signature in the closed aperture data. The magnitudes of the nonlinear refractive indices (n_2) were assessed using the conventional procedure [52], and the calculated n_2 were 6×10^{-15} cm²/W for the TPC and 8×10^{-15} cm²/W

for TTC. The solvent nonlinearity was positive suggesting the actual values of n_2 estimated for the pure solute will be higher than those calculated and presented here. Figures 4.4(a) and 4.4(b) demonstrate the open aperture Z-scan data for PTTC and GeTTC, respectively, recorded at wavelengths of 660 nm, 680 nm, 700 nm, and 740 nm with a concentration of 1 mM and peak intensities in the range of 90-143 GW/cm². Unlike TPC and TTC (data recorded with 0.5 mM and little lower peak intensities) both the samples exhibited RSA kind of behavior. The values of nonlinear coefficient, β , extracted from the fits were in the range of 2.4-11.4 $\times 10^{-12}$ cm/W.

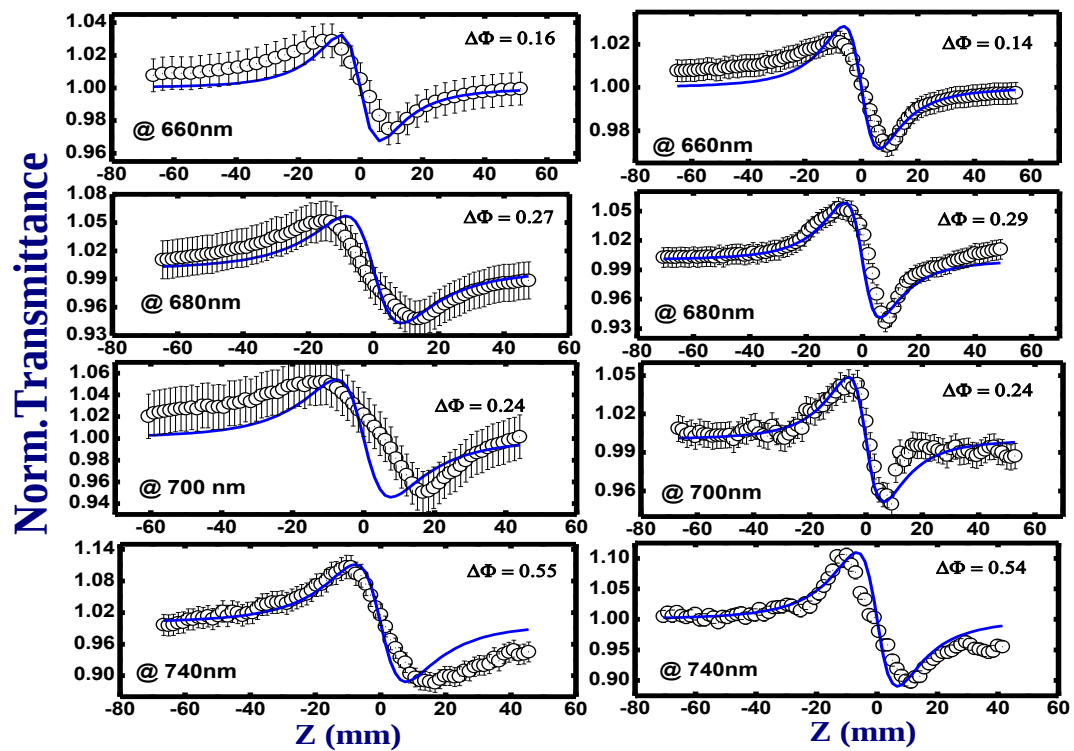


Figure 4.5 Closed aperture data of (a) GeTTC & (b) PTTC at different wavelengths. Typical peak intensity of ~ 70 GW/cm² was used.

Figure 4.5 shows the closed aperture data of GeTTC and PTTC at various wavelengths and the magnitude of n_2 (negative) was in the range of 1.8- 8.3 $\times 10^{-16}$ cm²/W. From the spectral data of NLO coefficients we deduced that TPC and TTC possessed similar magnitudes of NLO coefficients but they were superior when compared to GeTTC and PTTC. When the figures of merit (FOM) were calculated (taking into account the linear absorption) we again established that TTC/TPC were superior to GeTTC and PTTC. FOM defines the prerequisite for the material to be used in the photonic device applications. For photonic switching applications, the loss due to multi photon absorption (MPA) should be minimum.

The corresponding FOM is: $W = n_2 I_{sat} / \alpha_0 \lambda$, $T = \lambda \alpha_2 / n_2$, $V = \lambda \alpha_3 I_0 / 3 n_2$ where λ is wavelength, I_{sat} is the light intensity at which n_2 saturates, α_2 and α_3 are two and three photon absorption coefficients respectively. For successful operation of switching device, $T < 1$, $V < 0.68$, $W > 1$ is required. Here the T values of TTC and TPC were less than one for all the wavelengths.

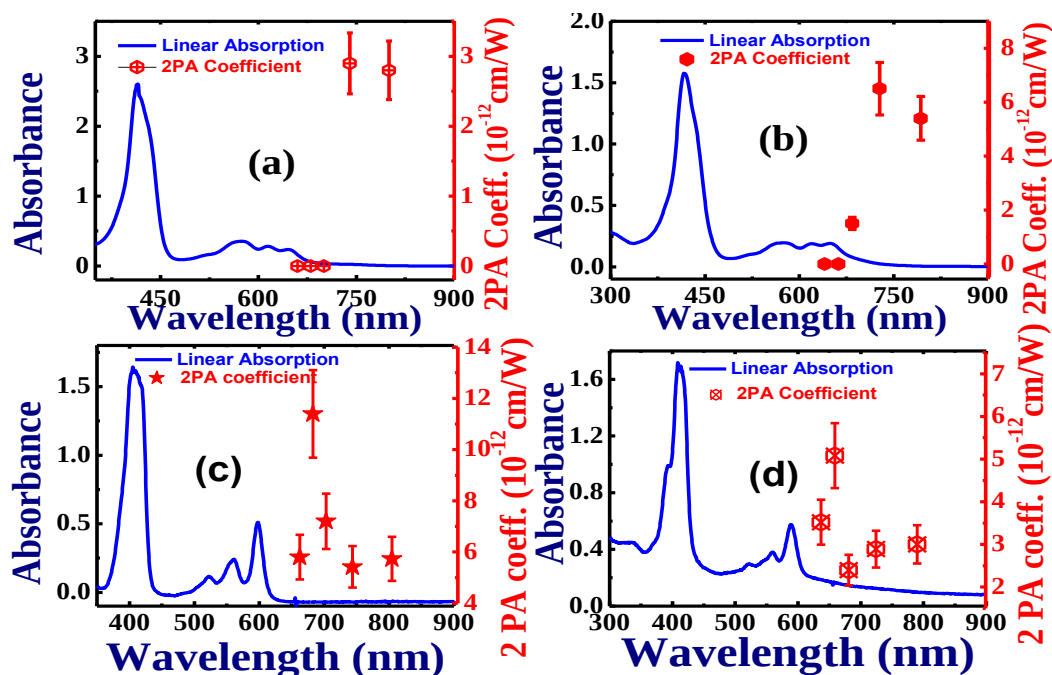


Figure 4.6 Linear (line) absorption spectra and two-photon absorption coefficients (symbols) of Corroles (a) TPC (b) TTC (c) PTTC and (d) GeTTC. Bottom X-axis presents wavelength and left Y-axis presents Absorbance (Linear Absorption), right Y-axis presents 2PA coefficients.

From these detailed studies we concluded that depending on the concentration and the peak intensities used one could easily achieve SA/RSA in such molecules, which, is extremely useful in designing photonic devices. The 2PA dispersion of Corroles (TPC, TTC, GeTTC, and PTTC) in CHCl_3 , measured over the wavelengths of 660 nm, 680 nm, 700 nm, 740 nm, and 800 nm are shown in figures 4.6(a)-4.6(d) collectively with the corresponding one photon absorption (1PA) spectra. The lower X-axis represents the wavelength which is common for both excitations. 1PA spectra of all molecules show a distinguishable and solid band in the B band region 400–450 nm, followed by three or four weaker bands in the Q band region, 520–680 nm. Interestingly the NLO coefficients [$\chi^{(3)}$ values] and the figures of merit were highest for 740 nm pumping for all the samples. This enhancement in nonlinearity could be due to the resonant contribution of available states in the B-band.

Sample	λ_{ex} (nm)	n_2 (cm^2/W) 10^{-16}	β (cm/W) 10^{-12}	$\text{Re} \chi^{(3)} $ (m^2/V^2) 10^{-22}	$\text{Im} \chi^{(3)} $ (m^2/V^2) 10^{-23}	$ \chi^{(3)} $ (m^2/V^2) 10^{-22}	$ \chi^{(3)} $ (e.s.u.) 10^{-14}	σ_2 ($\text{cm}^4 \text{ s}/\text{photon}$) 10^{-48}	δ (GM)	T
GeTTC	800	-7.60	3.00	8.36	2.10	8.36	5.99	1.22	122	0.31
	740	-8.30	2.89	9.13	1.87	9.14	6.53	1.27	127	0.26
	700	-2.60	2.42	2.86	1.48	2.86	2.05	1.12	112	0.65
	680	-3.16	5.08	3.47	3.02	3.49	2.50	2.39	239	1.01
	660	-2.30	3.52	2.53	2.03	2.54	1.81	1.73	173	1.01
PTTC	800	-5.10	5.73	5.61	4.01	5.62	4.03	2.33	233	0.89
	740	-6.80	5.42	7.48	3.51	7.49	5.36	2.37	237	0.59
	700	-3.00	7.20	3.30	4.41	3.33	2.38	3.33	333	1.68
	680	-3.30	11.4	3.63	6.79	3.69	2.64	5.43	543	2.34
	660	-1.80	5.80	1.98	3.35	2.01	1.43	2.85	285	2.12
TTC	800	-60	54 ($I_s = 31$ GW/cm^2)	66	37.8	66.1	47.3	44.30	4430	0.72
	740	-200	-61 ($I_s = 150$ GW/cm^2)	220.2	39.5	220.2	157.7	54.10	5410	0.22
	700	-100	15 ($I_s = 8$ GW/cm^2)	110.1	9.2	110.0	78.8	14.08	1408	0.10
	680	-70	0 ($I_s = 35$ GW/cm^2)	77.0	0	77.0	55.2	-	-	-
	660	-80	0 ($I_s = 52$ GW/cm^2)	88.0	0	88.0	63.0	-	-	-
TPC	800	-100	28 (2PA)	110.1	19.6	110.1	78.8	23.01	2301	0.22
	740	-100	-2.9 ($I_s = 200$ GW/cm^2)	110.1	18.8	110.1	78.8	25.76	2576	0.21
	700	-80	0 ($I_s = 28$ GW/cm^2)	88.0	0	88.0	63.0	-	-	-
	680	-50	0 ($I_s = 16$ GW/cm^2)	55.0	0	55.0	39.0	-	-	-
	660	-60	0 ($I_s = 35$ GW/cm^2)	66.0	0	66.0	47.3	-	-	-

Table 4.1 Summary of the NLO coefficients estimated for all four Corroles from the Z-scan data measured at wavelengths of 800 nm, 740 nm, 700 nm, 680 nm, and 660 nm.

4.3.2 Femtosecond NLO properties at 800 nm

To estimate the magnitude of pure electronic nonlinearities we performed the Z-scan studies of TTC and TPC at 800 nm using ~ 40 fs pulses. Open aperture scans for TPC and TTC recorded at 800 nm indicated SA behavior. The concentration of solutions used in this case was ~ 0.5 mM. Figures 4.7(a) and 4.7(b) illustrate the open aperture data (open stars) and closed aperture data (open circles) obtained with an intensity of 0.9 TW/cm^2 . The peak intensities were calculated considering the pulse duration to be ~ 70 fs due to broadening from the optical components (neutral density filters and lenses). An independent experiment performed for measuring the pulse duration indeed confirmed the value to be 70-75 fs. The experiment was performed using Silhouette (Coherent, USA) with optical components in the path. The Z-scan data was recorded for TPC and TTC at intensity levels where the contribution from solvent is again insignificant. We found the best fit was obtained with transmittance equation for SA. The fs pulses possessed large bandwidth (~ 27 nm FWHM) and in combination with linear absorption at 800 nm we can only expect saturation of the S_1 state. For pumping with higher peak intensities we observed Supercontinuum generation from the solvent chloroform.

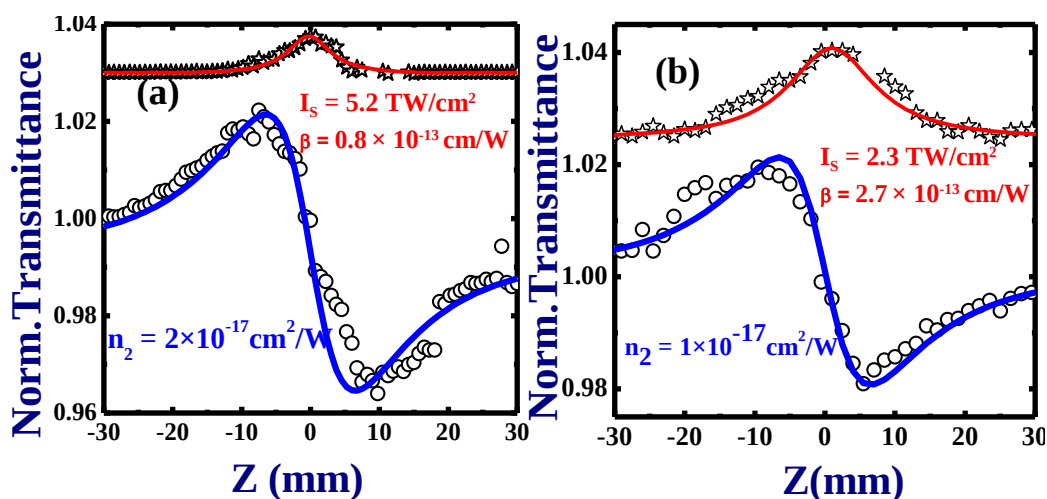


Figure 4.7 Femtosecond open aperture (open stars) and closed (open circles) of (a) TPC and (b) TTC with intensity of $I_{00} = 0.9 \text{ TW/cm}^2$ obtained at 800 nm for a concentration of $0.5 \times 10^{-3} \text{ M}$. Open stars and circles represent experimental data while the solid lines are best fits.

The peak to valley signature in the closed aperture Z-scan data further confirmed the negative nonlinearity or the self-defocusing property of the samples in fs domain also. The magnitudes of the nonlinear refractive indices (n_2) were assessed, using the conventional procedure [52], and the calculated n_2 values were

$2 \times 10^{-17} \text{ cm}^2/\text{W}$ for the TPC and $1 \times 10^{-17} \text{ cm}^2/\text{W}$ for TTC. We extracted the nonlinear absorption coefficients ($0.8 \times 10^{-13} \text{ cm/W}$ for TPC and $2.7 \times 10^{-13} \text{ cm/W}$ for TTC) for both the cases, because the saturation intensity I_s was greater than the peak intensity used. The values of NLO coefficients estimated and presented here are within an error of $\pm 10\%$ with contributions mainly from (a) uncertainty in spot size and thereby peak intensity measurements (b) errors in estimation of concentration (c) fitting errors etc..

The NLO coefficients of Tri-tolylCorroles and Tri-phenylCorrole (TTC and TPC) and metallocorroles (GeTTC and PTTC) obtained from Z-scan experiments at five different wavelengths (800 nm, 740 nm, 700 nm, 680 nm, 660 nm) using ps pulses are summarized in table 4.1. It is apparent that GeTTC had higher magnitude of $|\chi^{(3)}|$ compared to its phosphorous counterpart at 740 nm and 800 nm. Moreover, the magnitude gradually decreased as we moved from 800 nm to 660 nm. The figure of merit, T , was < 1 (for wavelengths up to 700 nm) for GeTTC making them worthy candidates for photonic applications (involving nonlinear refractive index) in these wavelengths. Interestingly, the substitution of germanium and phosphorous has changed the signature of nonlinear absorption in Corroles. The saturation absorption (SA) changed to a pure 2PA in the substituted cases. However, there was a sign of this switching behavior in the case of TTC at 700 nm [25]. PTTC exhibited superior 2PA coefficient and, therefore, a higher 2PA cross-section compared to GeTTC at 800 nm. The signature of closed aperture Z-scan trace demonstrated negative nonlinearity for all the Corroles. However, the solvent displayed a positive nonlinearity (with typical values of $\sim 10^{-17} \text{ cm}^2/\text{W}$). Hence, the NLO coefficients of these molecules are higher than those calculated and presented here. The magnitudes of NLO coefficients of metallo corroles were smaller compared to un-substituted Corroles. The nonlinearity could be enhanced further by doping these molecules in a polymer such as PMMA (Poly methyl methacrylate). In our previous NLO studies [18, 20] of phthalocyanines we observed that molecular aggregation in the case of thin films has greatly enhanced the nonlinearity when compared to solutions. This approach has an added advantage that a high concentration of chromophores can be incorporated into the polymer system thereby reducing the solvent effect and increasing the linear coefficient.

4.3.3 Time-resolved fluorescence studies

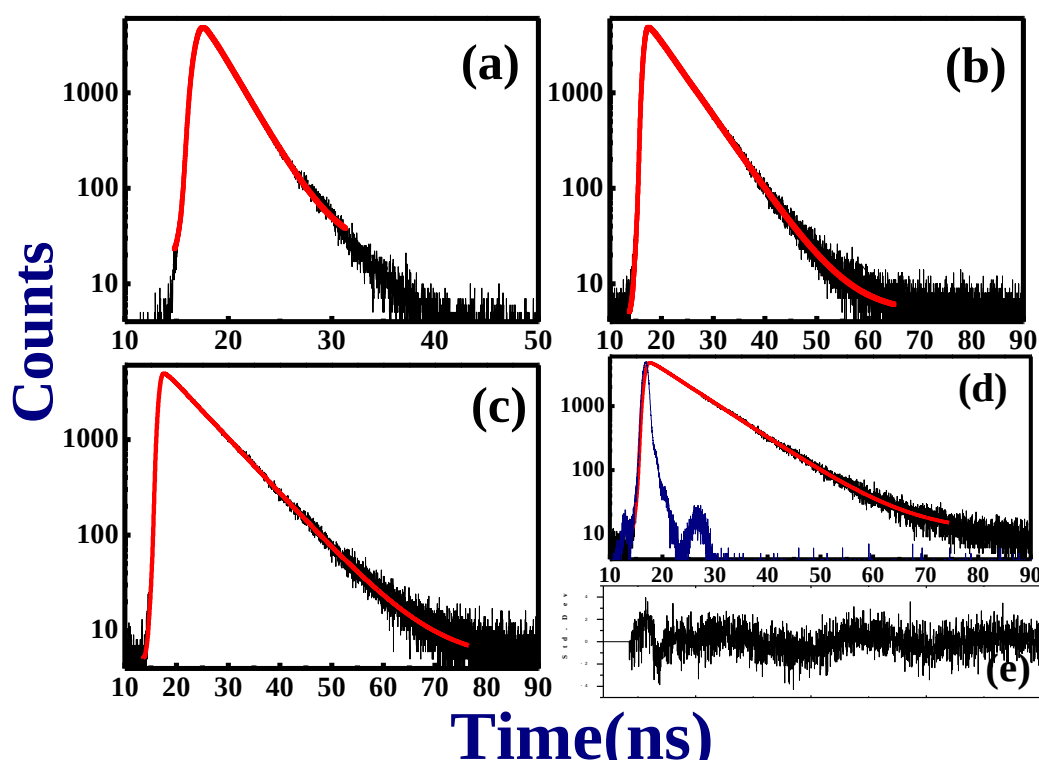


Figure 4.8 Fluorescence lifetime measurements of (a) GeTTC (b) PTTC (c) TTC (d) TPC in dichloromethane solvent. Wiggly lines (black) represent experimental data while the smooth lines (red) represent best fits. Excitation wavelength used was 405 nm. Concentration of the solutions used was $\sim 1 \mu\text{M}$. The blue line represent the instrument response function (IRF) (e) Distribution of residual of the fit of fluorescence decay profile of TPC solution.

The corroles studied in this work were fluorescent molecules with quantum yields of TPC, TTC, GeTTC, and PTTC being 0.19, 0.25, 0.14, and 0.31, respectively. Figures 4.8 (a)-(d) portray the dynamics of time-resolved fluorescence measured with time correlated single photon counting (TCSPC) experimental set up (FluoroLog3-Triple Illuminator, IBH Horiba Jobin Yvon). TCSPC technique is used to record radiative decay of fluorescent molecules. In TCSPC single photon is detected at time t after the excitation pulse. The probability of detecting the photon depends on the fluorescent intensity at that time. The time between excitation and the emission is measured by electronic clock. With periodic excitation, it is possible to construct the histogram over multiple cycles. The detector will not detect more than one photon because the detector and the electronics have a deadtime for at least some ns after a photon count. Hence TCSPC register only single photon per exciting pulse. The excitation pulse can be a flash lamp or mode-locked laser. The resolution depends on the detector and the electronics accuracy. The temporal profile of the exciting pulse or

instrument response function (IRF) was recorded under the same condition by replacing the sample with a scattering solution. Ludox (colloidal silica) or glycogen was used for this purpose. A picosecond light emitting diode laser (NanoLED, $\lambda_{\text{ex}} = 405 \text{ nm}$) was used as excitation source. The decay curves were recorded by monitoring the fluorescence emission maxima. Photomultiplier tube (R928P, Hamamatsu) was employed as the detector. The lamp profile was recorded by placing a scattered (dilute solution of Ludox in water) in place of the sample. The width of the instrument function was limited by the full width at half maximum (FWHM) of the excitation source, $\sim 635 \text{ ps}$ at 405 nm . Decay curves were analyzed by nonlinear least-squares iteration procedure using IBH DAS6 (version 2.3) decay analysis software. The quality of the fits was judged by the χ^2 (~ 1.1) values and distribution of the residuals. The radiative lifetimes (of S_1 state) estimated from the fits were $\sim 1.1 \text{ ns}$ for GeTTC, $\sim 2.7 \text{ ns}$ for PTTC, $\sim 3.6 \text{ ns}$ for TTC and $\sim 3.9 \text{ ns}$ for TPC. Figure 4.8 (e) shows the distribution of residual of the fit of fluorescence decay profile of TPC solution. The radiative lifetimes for PTTC and GeTTC were also measured in chloroform to check the solvent dependence. The retrieved lifetimes were similar to those observed in dichloromethane (DCM). The data is shown in figure 4.9. The lifetimes observed are radiative in nature. Under electronic excitation, the molecule is excited to vibrationally hot excited electronic state. The molecule relaxes to the lowest vibrational level in the upper electronic state by intermolecular collision followed by the decay from upper electronic state to ground state through radiative as well as nonradiative channel. In time resolved fluorescence measurements, only the emitted photon which has the information of radiative decay is monitored. Therefore, only τ_r is measured. However, in time resolved absorption measurements, the fast decay (τ_{nr}) of vibrational/ electronic levels can be measured depending on the probe wavelength. Liu et al studied the fluorescence decay times of gallium and aluminum corroles [42]. They observed that the S_2 excited states relaxed to the S_1 states on a sub-picosecond time scale. LiLi et al. studied the fluorescence dynamics of a series of hydroxyl Corroles and recorded lifetimes in the 1-4 ns range [34]. They also noticed that ISC transition time of these corroles decreased abruptly with the increase in the atomic weight and the number of halogen atoms. Ghosh et al.

similarly examined Phosphorus (V)–meso-Triaryl corroles and obtained emission lifetimes in the range of 2.1-3.7 ns range [27].

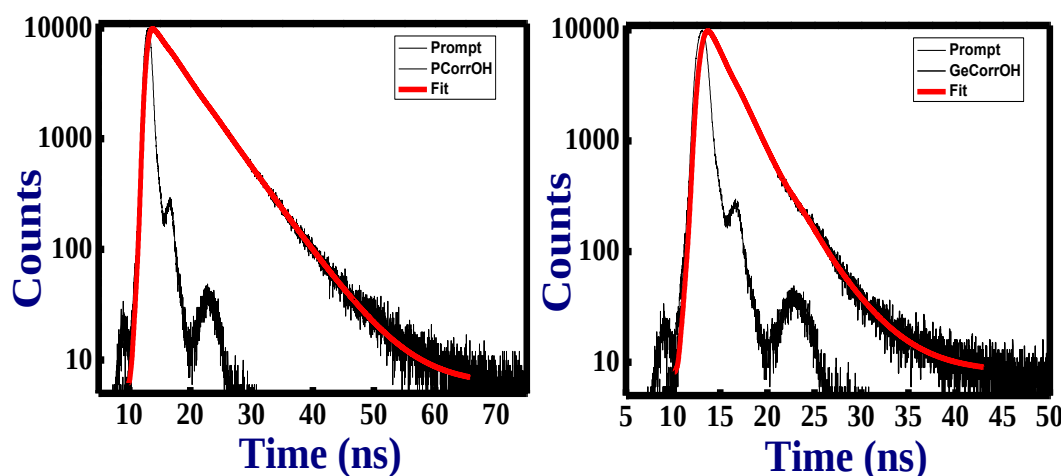


Figure 4.9 Radiative lifetimes of GeTTC and PTTC in solvent chloroform indicating similar lifetimes as observed in dichloromethane (DCM).

4.3.4 Degenerate picosecond and femtosecond pump-probe measurements

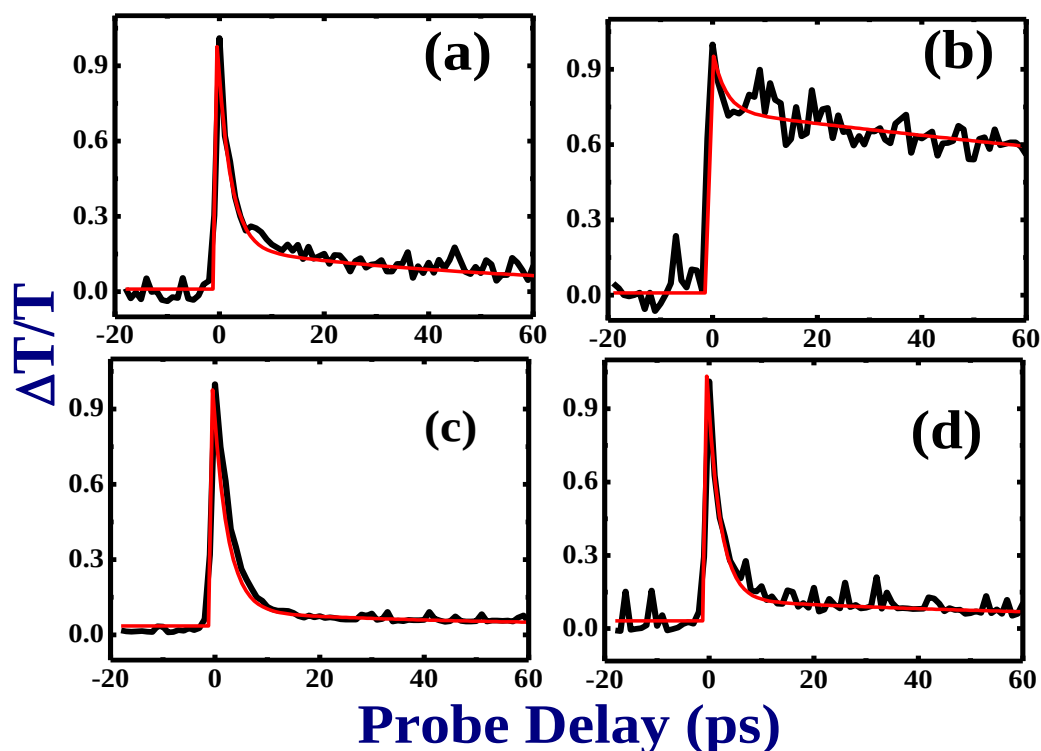


Figure 4.10 Picosecond degenerate pump-probe measurements at 800 nm of (a) GeTTC (b) PTTC (c) TTC (d) TPC. Wiggly lines (black) represent the experimental data while the smooth lines (red) represent the best fit to a double exponential decay function. Chloroform was used as solvent. Concentration of the solutions used typically was ≤ 1 mM.

In an effort to understand the dynamics following ultrafast excitation, a series of ps and fs pump probe experiments were performed. In the first set of

degenerate pump-probe experiments all the molecules were excited using 800 nm, 2 ps laser pulses. Figures 4.10 (a)-4.10 (d) depict the excited state dynamics of all corroles probed at a wavelength of 800 nm. At initial times after excitation, there was an ultrafast increase of the transmission of the probe beam, which indicated a ground state bleaching (GB) followed by a recovery process. A closer look at the data reveals that the relaxation dynamics or the bleaching recovery process of these molecules consisted of two components: a fast component (τ_1) at the early stages and a slow component (τ_2) that governed the later part of decay. The data was fitted using a double exponential decay function as follows:

$$\frac{\Delta T}{T} = y_0 + A_1 e^{-(t-t_0)/\tau_1} + A_2 e^{-(t-t_0)/\tau_2} \quad (1)$$

Figure 4.11 schematically explains the mechanisms involved in excitation and relaxation processes due to the 800 nm pump beam. Since the pump peak intensities ($< 85 \text{ GW/cm}^2$) used were sufficient to induce 2PA we expect the S_2 states to be populated. We propose the following mechanism for decay after excitation into the S_2 states. The first decay time (τ_1) is assigned to the combination of internal conversion from S_2 states to highest level of S_1 states (denoted by S_1^*) followed by intra-molecular vibrational relaxation in the S_1 states (S_1^* to S_1 states). S_1^* represent high lying vibrationally hot singlet excited states. For such molecules internal conversion occurs typically in few hundred fs and vibrational relaxation within few ps. Since the pulse duration used was ~ 2 ps we could not resolve those two components as we had done in the case of dinaphthoporphycenes [23]. From S_1 state population can come down to the ground state by radiative or non-radiative decay (τ_2). In addition to fluorescence one also comes across such *radiationless* processes where the excited state species may relax to the ground state without the emitting a photon, but dissipating all the energy through the solvent in the form of heat. This process is not well understood and its efficiency is very complicated to measure. Another possible channel of non-radiative decay is the transition from S_1 to T_1 states. There are multitudes of reports [55-63] of multi-exponential decays observed in the pump-probe dynamics in organic molecules similar to the ones investigated here. Kakade et al. [58] have shown that in a zinc phthalocyanine (similar molecules to ours), due to aggregation effects, a new non-radiative channel opens up with life times of < 100

ps recorded whereas the radiative lifetimes observed were few ns in magnitude. Jarota et al. [59] have also investigated tetra sulfonated phthalocyanines (again similar molecules to ours) and observed long lifetimes in the 150-500 ps range.

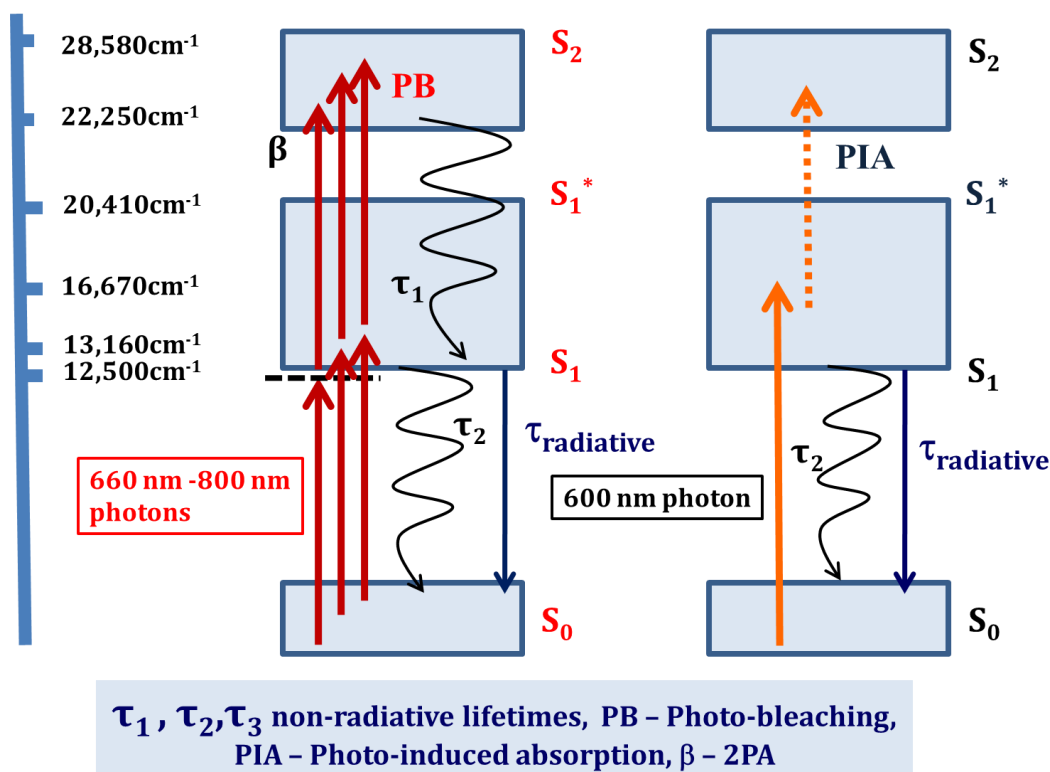


Figure 4.11 Energy level diagram of Corroles, PB is photo bleaching, PIA is photo induced absorption. Red lines represent 800 nm excitation, dark blue lines represent 600 nm excitation. Wiggly lines are for non-radiative transitions while the solid lines are for radiative transitions.

They have assigned it to the S_1 to S_0 non-radiative decay. Howe et al. [60] investigated phthalocyanine and zinc phthalocyanine tetrasulfonate using pump-probe spectroscopy, and explained the kinetics based on a three level model. According to their model, a fast decay of 10 ps was assigned to conversion from the 2nd to the 1st excited singlet state, which could be a vibrational relaxation in S_1 states. A small contribution from aggregates was also expected. They mentioned that 1st excited-state S_1 subsequently decayed with a decay time constant of 160 ps for ZnPcS₄ and 130 ps for PcS₄, respectively. This decay has contribution from radiative and non-radiative component of relaxation from S_1 to S_0 and of ISC from S_1 to the triplet state. In our case the radiative lifetimes are too long and we expect negligible contribution from them. We had checked for aggregation effects in our molecules since we recorded the pump-probe data at 1 mM concentration. The data is shown in the figure 4.12. We did observe slight changes and shift in

peak positions with slight peak broadening; in the absorption spectra (compared to the spectra recorded at 1 μM concentration) and, therefore, expect fractional contribution from aggregates resulting in shorter (non-radiative) lifetimes of S_1 .

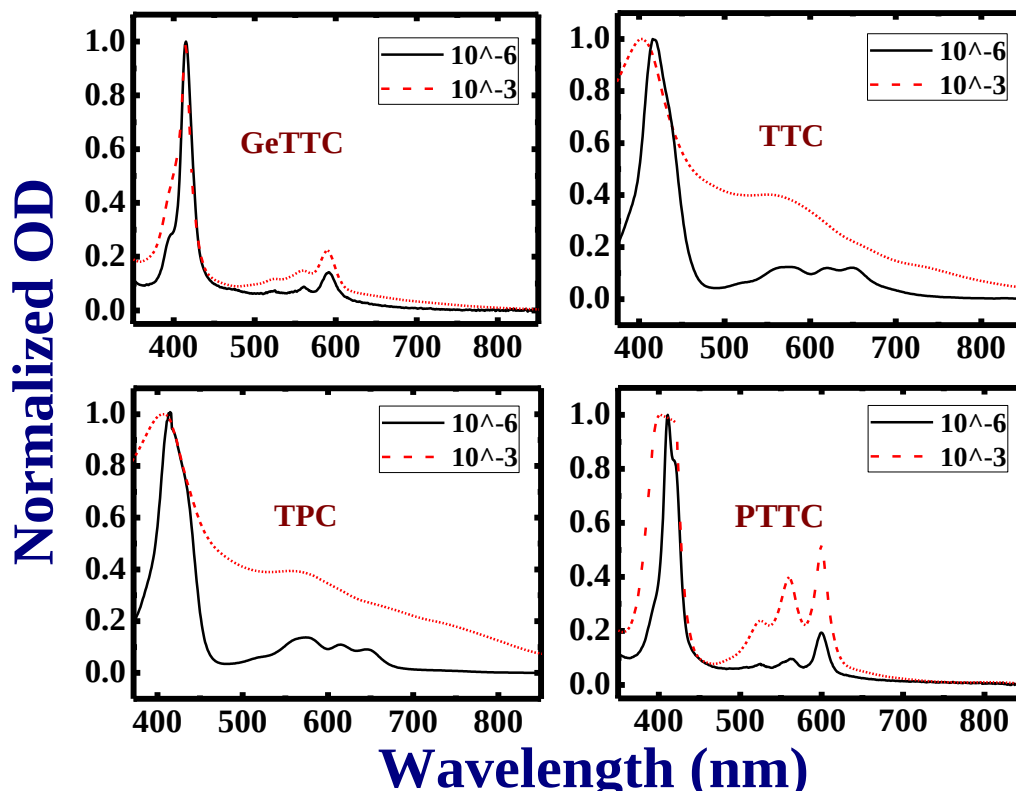


Figure 4.12 Absorption spectra of all the samples at two different concentrations. Red dash line represents 1 mM concentration while black line represents 1 μM concentration.

However, in the data reported by Kakade et al. [58] they observed nano-aggregates with strong shifts in the absorption peaks (by 40-50 nm) compared to monomers. They used strong hydrogen bonding solvents to create the nano-aggregates. In organic solvents, though, they did not observe aggregation. Fita et al. studied zinc phthalocyanines and observed 10-50 ps time scale dynamics which was attributed to the vibrational cooling (relaxation by transfer of heat to the solvent) from the S_1 state [61, 62]. That the molecule PTTC had the longest decay (of ~ 280 ps) among all the investigated ones could be due to its unique structure with OH groups in the axial position possibly affecting the aggregation.

Kullmann et al. [40] studied the dynamics of a bisporphyrin and figured out four different lifetimes for monomer. The fastest lifetime (few hundreds of fs) was attributed to intra molecular vibrational relaxation within the S_2 states, second fastest lifetime of few ps to the decay of S_2 , slower lifetime (few tens of ps) to the

cooling dynamics (non-radiative) in S_1 states. The longest lifetime of few ns was due to the emission decay. Liu et al. [42] observed S_2 lifetimes in the range of 0.28-2.71 ps for aluminum and gallium corroles. Similarly, fast decay times were observed in Soret-excited tetrapyrroles (MgTPP) where the internal conversion (S_2 - S_1 decay) was in few ps [55]. Figures 4.13 (a)-4.13(d) shows the degenerate pump-probe data of all molecules studies obtained using fs pulses at 600 nm. For 600 nm excitation, there is a clear reduction of probe transmittance at the zero delay and a slowly rising component (τ_1). At initial times, after excitation, there was an ultrafast decrease of transmission of the probe beam, which indicated photo-induced absorption. We fitted the data using the equation $\Delta T/T = A \exp[-(t-t_0)/\tau]$ where ΔT is the difference in the probe transmittance when the pump is on and off at delay time t and T is the probe transmittance when the pump is absent. Our data were fitted satisfactorily using a single exponential decay function since we used unfocused 600 nm pulses where we expect the excitation limited only to the first excited singlet state.

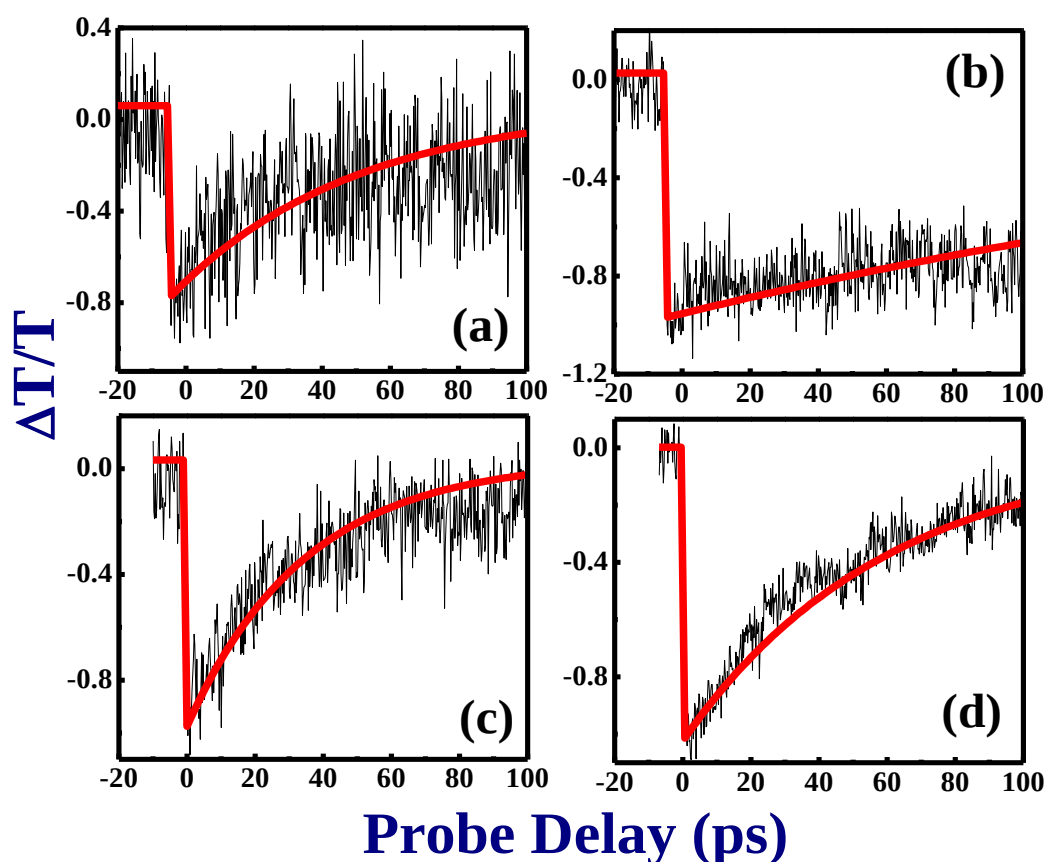


Figure 4.13 Femtosecond degenerate pump probe measurements at 600 nm of (a) GeTTC (b) PTTC (c) TTC (d) TPC. Wiggly lines (black) represent the experimental data while the smooth lines (red) represent the best fits. Chloroform was used as solvent. Concentration of the solutions used was ~ 1 mM.

The lifetimes estimated from the fits were ~ 53 ps for Ge-TTC, ~ 286 ps for P-TTC, ~ 60 ps for TTC and ~ 35 ps for TPC. The fact that the triplet contribution in our case is nominal can be understood from the fs data where the excitation is limited just to S_1 states. The recovery of PIA (photo-induced absorption) after crossing over to triplets (which could typically be few hundred ps) is remote. LiLi et al. [41] reported intersystem crossing times of few ns in a series of hydroxyl corroles. However, with the present data it is difficult to rule out triplet contribution to the non-radiative decay. Further experiments with white light probe and intensity dependent pump-probe studies will be undertaken in near future to elucidate the various contributions. We believe that focusing the fs pump and probe pulses could result in excitation into higher S_n states and thereby enabling us to resolve faster decay times (separate the internal conversion from 2nd excited singlet state S_2 to 1st excited singlet state S_1 and vibrational relaxation times in the 1st excited singlet state S_1) as was observed by us in the case of porphycenes whose data was recorded with similar experimental conditions [23]. The recovery times obtained with 600 nm and 800 nm excitations were similar which confirms the non-radiative decay of S_1 states in both the cases. The dynamics parameters are summarized in table 4.2. The error in the lifetime measurements was estimated to be $\pm 15\%$ incorporating the pulse to pulse fluctuations, spotsize calculations, fitting errors etc.

Sample	Picosecond data (non-radiative)		Femtosecond data (non-radiative) τ_2 (ps)	Radiative decay lifetime(ns)
	τ_1 (ps)	τ_2 (ps)		
GeTTC	2.0 (85%)	54 (15%)	53	1.1
PTTC	2.5 (30%)	277 (70%)	286	2.7
TTC	2.3 (93 %)	70 (7%)	60	3.6
TPC	2.4 (91%)	47 (9%)	35	3.9

Table 4.2 Summary of lifetimes retrieved from pump-probe and time-resolved emission experiments. The % is the weightage of each decay components.

4.4 Conclusions

Comparing the NLO coefficients of corroles with some of the recently reported molecules, Rebane et al. studied (2PA) cross sections and spectra of

corroles using a broad spectral range of wavelengths, 800–1400 nm for excitation. They retrieved much lower magnitudes of cross-sections in the range of 50-130 GM and this could be attributed to the non-resonant wavelengths used for excitation [43, 44]. Cho et al. [45] studied the 2PA cross sections of corrole dimers and recorded values of 1100-4600 GM. In our case we obtained $\sigma^{(2)}$ values in the range of 100-5400 GM comparable to that of dimers studied by Cho et al. [45]. Our studies on porphycenes indicated 2PA cross-sections in the 8000-21000 GM [23]. However, those molecules had strong two-photon resonances when pumped with 800 nm. Belfield et al. [64] studied 2PA of a new fluorine derivative using 200 fs pulses over a broad spectral range and recorded a maximum of 300 GM. Rebane et al. [65] investigated series of Fluorenyl-Based chromophores with electron donating or electron withdrawing substituents using fs pulses and demonstrated enhancements with 2PA cross-sections in the range of 10-80 GM. Morales et al. [66] studied unsymmetrical fluorenyl-based chromophores, with electron-acceptor and/or electron-donating groups on either side, separated by conjugated (π) moieties, and observed a cross-section of 1800 GM for one of the molecules near 300 nm wavelength. Belfield et al. [67] reported fs 2PA cross-sections of 650 GM and 1300 GM for fluorine derivatives.. Our molecules possess very good cross-sections compared to some of these molecules investigated.

Recently, a detailed study of photophysical properties of fluorinated derivatives of corrole was studied by Zhang et al. [68]. The transitions in fs to ns were directly measured by fs time resolved absorption spectroscopy. They observed SE at 655 nm which decayed faster than GB at 432 nm. This implies that the population of S_1 returned to S_0 state but the S_0 state was not recovered back, indicating a transition to excited triplet state. Further, they could resolve the decay from S_2 to S_1^* and then S_1^* to S_1 , followed by S_1 to S_0 . The substitution of fluoro phenyl accelerated S_2 relaxation ($S_2 \rightarrow S_1^*$). The ISC rate constants were also increased by heavy atom effect. However, the nonplanar distribution of the macromolecule accelerates $S_1 \rightarrow S_0$ transition than ISC. This is due to the increase in nonradiative decay rate by the nonplanarity induced by the peripheral substitution. The nonplanar distortion is caused by perfluorination of phenyl group through their electron withdrawing nature which accelerates decay of S_1 .

To summarize, the ps nonlinear optical properties of four novel corroles have been studied in detail and were found to be intensity dependent. At high peak intensities two photon absorption mechanism was observed contributing to the third order nonlinearity. The excited state dynamics of corroles, studied using degenerate ps pump-probe technique were found to possess double exponential decay constants with all the time scales in the ps domain. Femtosecond pump-probe data recorded at 600 nm corroborated the ps dynamics of S_1 state. The relaxation dynamics are explained by assuming a simple three level model consisting of S_0 , S_1 , and S_2 states. The observation of short lived excited state lifetime of S_1 , in the range of 54-286 ps, is important for applications in photodynamic therapy since short lived species or aggregates are likely to be inefficient in the generation of singlet-state oxygen. The measured fluorescence lifetimes were $\sim$ few ns. It is thus of interest to understand the NLO properties and excited state dynamics of these compounds which are expected to be the active species for PDT and can exist in organic solvents such as chloroform.



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CHAPTER 5

Ultrafast excited state dynamics and nonlinear optical properties of Naphthosapphyrins

ABSTRACT

The ultrafast dynamics of two new series of freebase naphthobipyrrole-derived sapphyrins along with their various salts have been studied using ps degenerate and non-degenerate pump-probe studies. The degenerate ps pump-probe was performed at 800 nm at two input energies. In non-degenerate ps pump-probe experiment, the sample was pumped by 400 nm wavelength and probed at 800 nm wavelength. One series of compound contained substituents at all of its β -positions, whereas the pyrrole unit opposite to the bipyrrolic moiety remain unsubstituted in the other one. Effect of bipyrrole fusion on the structure of sapphyrins was explored. The change in the lifetime of the excited states of the freebase and its salts with common acids were compared and the effect of anions on the third-order NLO properties of these sapphyrins was explored in the salt form using Z-scan technique at 800 nm. The time scales of probable transitions are explained in a potential energy level diagram. A selective excitation is accomplished via non-degenerate pump-probe technique. The non-radiative decay times were obtained from non-degenerate pump-probe studies and the radiative life times were obtained from time correlated single photon counting. It was found that due to the higher nonlinearity of free-bases, 2PA was observed even at lower peak intensities, whereas the sapphyrin salts needed higher peak intensities to achieve 2PA. The excited state dynamics studies using degenerate and non-degenerate pump-probe techniques revealed the decay times of high lying excited states in the ps and ns regimes.

The chapter includes the data presented in the following publications:

-  Chemistry: A European Journal, 20(47), 15561-15570, 2014.
-  OSA Technical Digest, Frontiers in Optics paper FW1A. 4(FIO, Florida, USA) 2013.

5.1 Introduction

Pump-probe experiments with ps/fs laser pulses are versatile experimental techniques for understanding the excited state dynamics since they not only provide the ability to measure population changes on ps/fs timescales, but also allow any excited state with an absorption transition to be probed, independent of whether such a state has a radiative decay pathway or not. The magnitude of the relaxation is given by slope of exponential decay curves. These studies have resulted in real-time viewing of transition states of the molecule as it relaxes back to the ground state. It is based on the use of two laser pulses to interact within the sample. The pump pulse interacts with the ground state population of a sample to generate photo excitations and the probe interrogates those excitations. By controlling the delay between the pump and probe pulses it is possible to investigate the changes in excited state population of the sample as a function of time [1-4]. Naphthosapphyrins are from the family of expanded porphyrins, which comprises a variety of cyclic systems with more than four pyrrole rings linked in a conjugated manner [6]. In the last two decades expanded porphyrins have emerged as a new class of attractive compounds because of their potential application in a variety of areas such as near infrared (NIR) dyes, two photon absorption (TPA or 2PA) materials, and photosensitizer in PDT. The efficacy of expanded porphyrins can be tailored by varying the degree of ring size, replacing one or more pyrrole rings or modifying the core and there by tailoring their electrochemical, optical properties. A qualitative relationship can be obtained between the excited state dynamics and various properties like aromaticity, number of π electrons, structural planarity etc. which are associated with static and dynamic polarizability [7].

Several reports have been published to study the dependence of nonlinear optical properties on the planarity and aromaticity of expanded porphyrins [8-14]. Sapphyrin being a porphyrins analogue, has 5 pyrrole rings and 4 connecting *meso* carbons which are arranged to contribute to 22 π -electron aromatic system and exhibiting greater affinity towards anions in diprotonated state [9]. Srinivasan et al. [15] have studied the ground and excited state dynamics of core- modified normal and expanded porphyrins and compared the triplet state properties of core

modified expanded thioporphyrins in freebase and protonated states. Yan et al. [5] have performed two color pump-probe experiments on a modified phthalocyanine to observe up conversion luminescence emission via two photon absorption process. We studied the third order nonlinear optical properties of naphthosappyrins, using the Z-scan technique with ~ 2 ps pulses and the effect of anions in their corresponding diprotonated salts. This was necessitated by the emergence of expanded porphyrins as a new class of attractive compounds for two-photon absorption (2PA) materials. The 2PA coefficients and cross-sections were estimated from the open aperture Z-scan data, and the nonlinear refractive indices n_2 from the closed aperture data. An extensive time-resolved characterization via degenerate and non-degenerate ps pump probe measurements, to study the excited state dynamics of the two series of naphthosappyrins and their various salts, have been carried out.

5.2 Experimental Details

Synthesis of naphthosapphyrin 1a and 1b: The new naphthosapphyrins were synthesized following a rational MacDonald type [3+2] approach, where β -dialkylated naphthobipyrrole dialdehyde **2** (employed to increase the solubility of the resultant macrocycles) [18, 25] was condensed with tripyrrane diacid **3a** or **3b** in acidified (*p*-TsOH) ethanol, in presence of oxygen to form the desired naphthosapphyrins **1a** and **1b** in 18 and 26% yield respectively as depicted in figure 5.1. Compound **3b**, previously not known, was synthesized following the synthetic route of **3a** [26, 27].

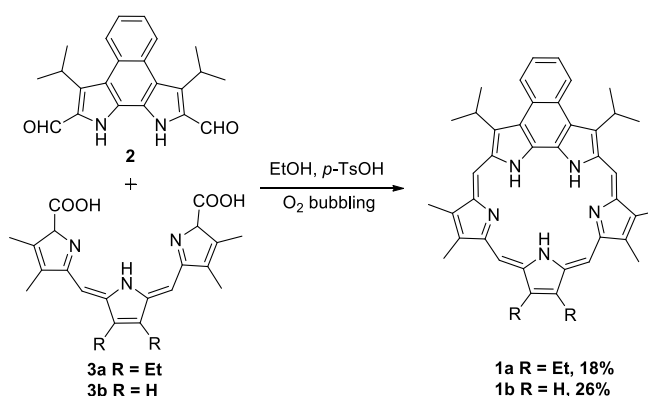


Figure 5.1 Synthesis of naphthosapphyrins **1a** & **1b**. (adapted from reference [16])

5.3 Results and Discussions

Various salts of two series of naphthosapphyrins (**1a** and **1b**) were prepared by washing a CHCl_3 solution of free base form with aqueous solution of different acids, namely hydrochloric acid (HCl), perchloric acid (HClO_4), sulphuric acid (H_2SO_4), and para-toluene sulfonic acid (p-TSA), respectively [16]. The structures of naphthosapphyrin **1a** and **1b** and their diprotonated salts from HCl , HClO_4 , H_2SO_4 and p-TSA are shown in figure 5.2.

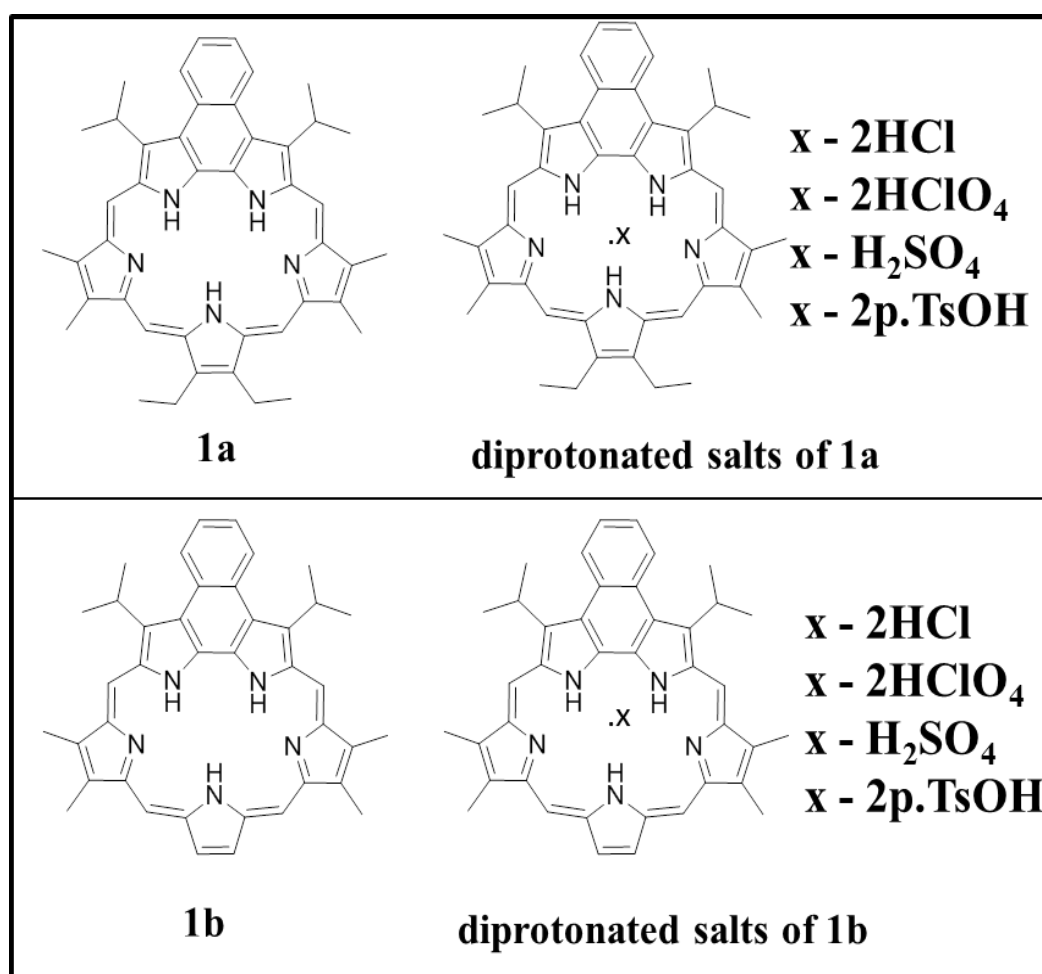


Figure 5.2 Structures of naphthosapphyrin **1a** and **1b** and the diprotonated salts from Hydrochloric Acid (HCl), Perchloric Acid (HClO_4), Sulphuric Acid (H_2SO_4), and para-Toluene Sulfonic Acid (p-TSA).

5.3.1 Ground state absorption and emission properties of naphthosapphyrins

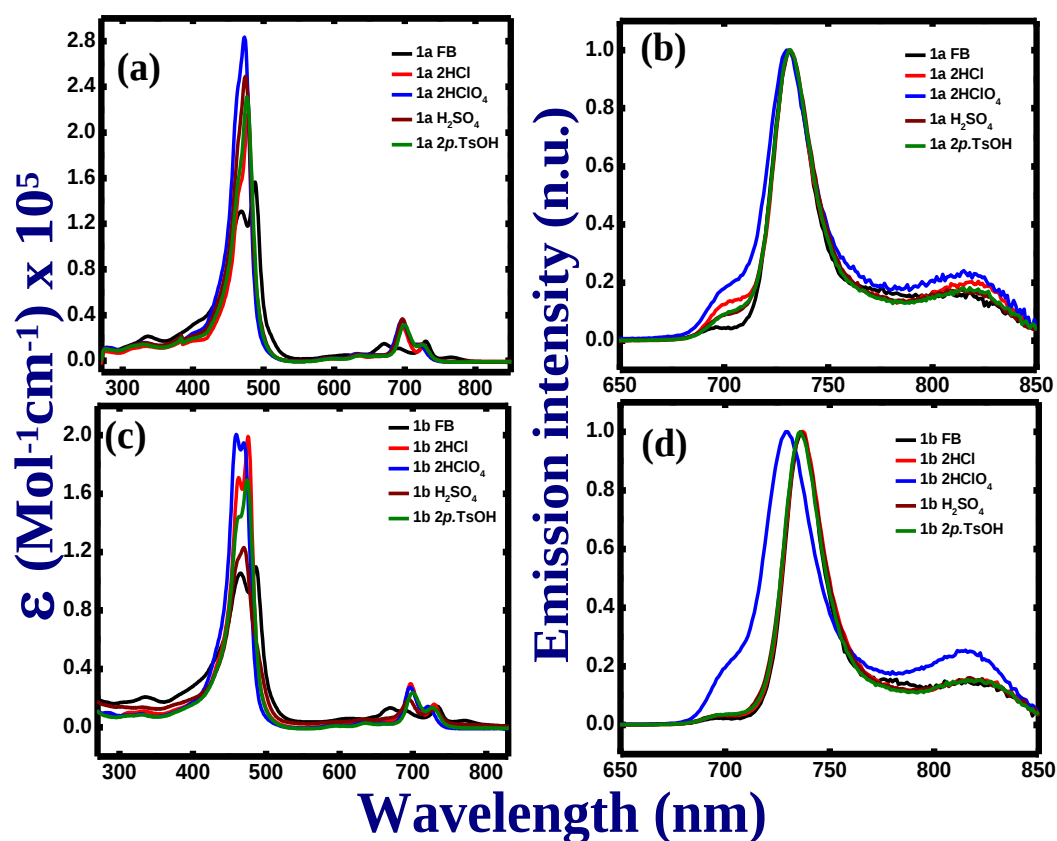


Figure 5.3 Top: (a) Linear absorption spectra and (b) normalized emission spectra of naphthosapphyrin **1a** and its diprotonated salts. (c) linear absorption spectra and (d) normalized emission spectra of naphthosapphyrin **1b** and its diprotonated salts measured in CHCl₃.

Figure 5.2 shows the molecular structure of **1a** and **1b**. Figure 5.3 shows the the absorption spectra and emission spectra of **1a** and **1b** series of compounds. In the absorption spectra of naphthosapphyrins, the strong Soret band or B band appears in the 400-500 nm range and a weak Q band appears in the 650-750 nm range as expected from porphyrin like moieties. However, there is splitting of the B bands at peak absorption for the free base **1a** and **1b** with the weak Q bands. The two bands within the soret band are produced due to the transition from ground state to two separate states in S₂ in case of freebase. On protonation, the B bands become intense than that of free base accompanied by a broad shoulder and the splitting was vanished indicating a degenerate level. The splitting of the B band was retained for protonated **1b** whereas the splitting disappeared for protonated **1a**. This may indicate that the energy states associated with the Soret band probably do not become degenerate on protonation of **1b** owing to large difference in the energies of the constituent pyrrolic units (alkylated versus non-

alkylated pyrroles). The emission bands of **1a** and **1b** are centred at 730 nm and 736 nm respectively, except for **1b**.2HClO₄ for which the emission is slightly blue shifted.

5.3.2 Nonlinear optical (NLO) studies of naphthosapphyrins

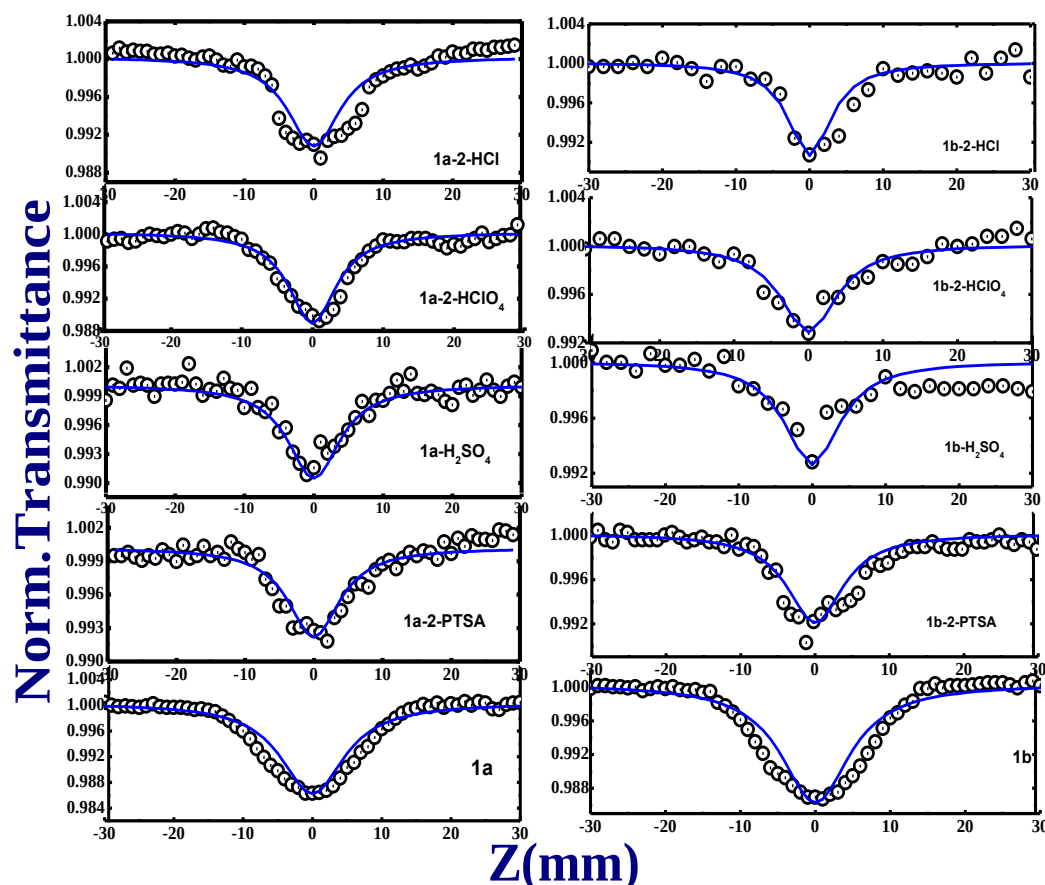


Figure 5.4 ps open aperture Z-scan data at 800 nm. The input peak intensity was $\sim 100 \text{ GW/cm}^2$ for freebases and $\sim 130 \text{ GW/cm}^2$ for the salt solutions. The open circles (black) represent experimental data while the solid lines (red) are 2PA fits.

Figure 5.4 presents the ps open aperture Z-scan data recorded at 800 nm for all the sapphyrins investigated and it is clear that two-photon absorption (2PA) or RSA is the dominant mechanism. An input peak intensity (I_{00}) of $\sim 100 \text{ GW/cm}^2$ for free-bases and $\sim 130 \text{ GW/cm}^2$ for the salt solutions was used. The presence of 2PA could be due to the available two-photon resonant states in the vicinity of B bands i.e. 400-505 nm (19800 cm^{-1} to 25000 cm^{-1}) range. It is interesting to note that at the same peak intensity where the free-base molecules demonstrated 2PA ($\sim 100 \text{ GW/cm}^2$), the salts did not display any nonlinearity and only at slightly higher peak intensities ($\sim 130 \text{ GW/cm}^2$) the salts started depicting

the nonlinear absorption behavior. Table 5.1 summarizes all the NLO coefficients retrieved from the Z-scan data. These values are within an error of $\pm 10\%$. The values of 2PA coefficients and cross-sections (200-1100 GM where GM is a unit of 2PA cross-section σ_2 ; $1\text{GM}=10^{-50}\text{ cm}^4\text{s/photon}$) obtained for the naphthosapphyrin derivatives are slightly lower compared to the σ_2 values of dihydrochloride salt of decaalkylsapphyrin reported by Yoon et al. [17]. Interestingly, the perchlorate salts displayed the largest σ_2 values in case of both the sapphyrin derivatives compared to their free-base and other salts.

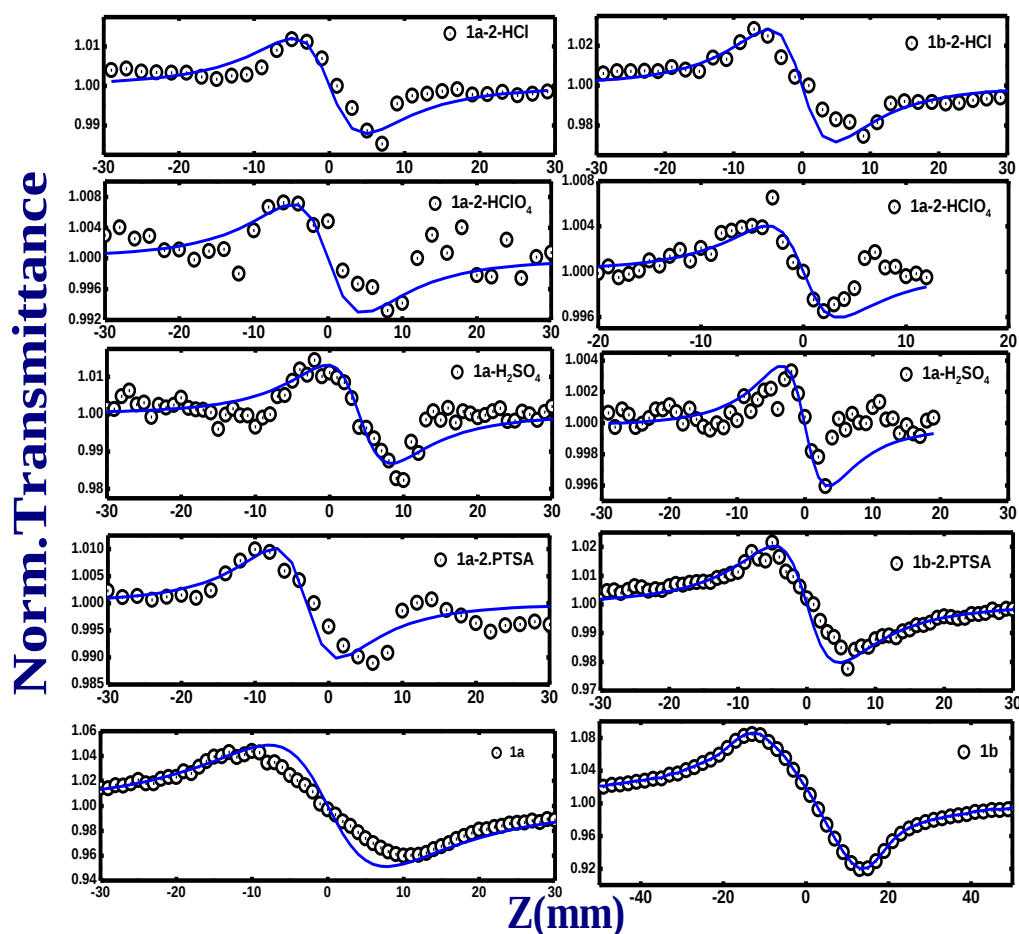


Figure 5.5 ps closed aperture Z-scan data at 800 nm. Open circles (black) represent experimental data while the solid lines (blue) are theoretical fits.

Figure 5.5 depicts the ps closed aperture Z-scan data of all the compounds investigated. All of them possess negative nonlinearity (n_2) as evident from the peak to valley structures in the Z-scan data. The values of n_2 retrieved from the fits were $\sim 10^{-16}\text{ cm}^2/\text{W}$. We could not de-couple the solvent contribution in the closed aperture case. As the n_2 value of chloroform is positive, therefore, the n_2

values of these molecules will be higher than those presented here. The solvent contribution in both open aperture data recorded at corresponding peak intensities is negligible. The experimental set up for Z-scan measurements are explained in chapter 2 [18,19]. The perchlorate salts of **1a** and **1b** demonstrated higher σ_2 value and the highest value of σ_2 was obtained for **1b.2HClO4**. This can be attributed with the intense solet band of **1b.2HClO4**. Moreover, the splitting in solet band of **1b.2HClO4** increases σ_2 value. This could be due to the nondegeneracy of S_2 states (solet band or B band) which are present in **1b** series. However, the $\chi^{(3)}$ values are ten fold higher for freebase than their protonated counter parts. Among the two free bases **1b** showed highest $\chi^{(3)}$. This is due to the higher n_2 value of the free bases and the real part contribution being more to the $\chi^{(3)}$ value. A concentration dependent and intensity dependent measurements have to be performed to identify the dependence of individual salts to $\chi^{(3)}$ value.

Sample	I_{00} (GW/cm ²)	Conc. (mM)	β (cm/W) $\times 10^{-12}$	n_2 (cm ² /W) $\times 10^{-17}$	σ_2 (GM)	$\text{Im } \chi^{(3)} $ (m ² /V ²) $\times 10^{-23}$	$\text{Re } \chi^{(3)} $ (m ² /V ²) $\times 10^{-23}$	$ \chi^{(3)} $ (m ² /V ²) $\times 10^{-23}$	$ \chi^{(3)} $ (e.s.u.) $\times 10^{-15}$
1a	97	0.33	4.00	39.3	498	2.80	43.2	43.3	31.0
1a.2HCl	131	0.27	2.00	6.12	302	1.40	6.73	6.88	4.92
1a.2HClO₄	131	0.14	2.40	2.50	694	1.68	2.75	3.22	2.31
1a.H₂SO₄	131	0.24	2.00	6.60	339	1.40	7.26	7.40	5.30
1a.2p-TsOH	131	0.29	1.70	3.75	238	1.19	4.12	4.29	3.07
1b	107	0.34	3.70	63.6	447	2.59	70.0	70.0	50.1
1b.2HCl	123	0.30	2.00	10.4	274	1.40	11.4	11.5	8.26
1b.2HClO₄	128	0.07	2.00	2.12	1090	1.40	2.40	2.77	1.99
1b.H₂SO₄	136	0.23	1.65	1.87	295	1.15	2.05	2.36	1.69
1b.2p-TsOH	118	0.25	1.70	11.4	272	1.19	12.5	12.6	9.03

Table 5.1 Nonlinear absorption coefficients of all the compounds used in this study obtained from Z-scan measurements at 800 nm.

5.3.3 Time-resolved fluorescence studies

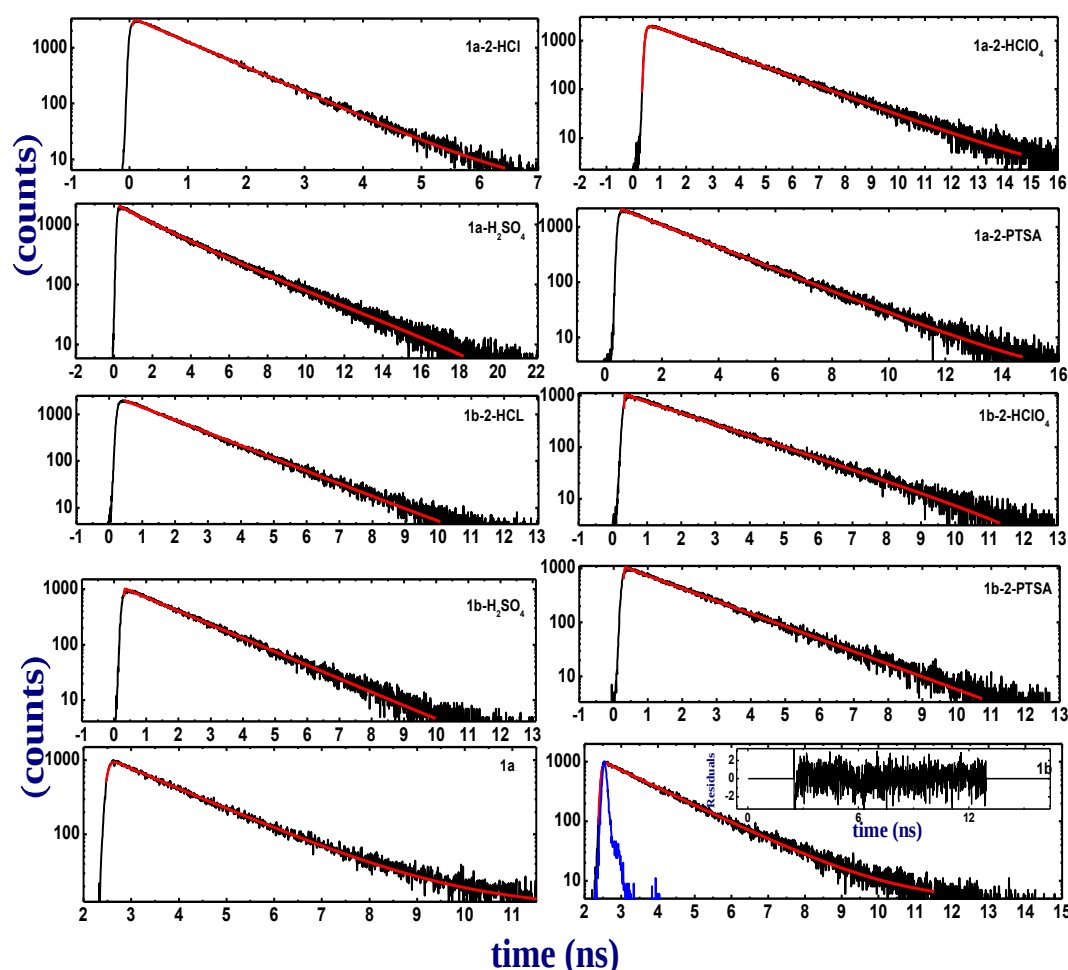


Figure 5.6 Radiative lifetime of naphthosapphyrins excited at 439 nm measured from time correlated single photon counting. Wriggly (Black) lines represent the experimental data while the solid (red) lines represent fits. The prompt (blue line in 1b) and the residuals are shown in the inset of 1b.

Figure 5.6 shows fluorescence lifetime measurements which were performed using a time correlated single-photon counting (TCSPC) spectrometer (Horiba JobinYvon IBH) [28]. The excitation wavelength λ_{exc} was ~ 439 nm from Nano LED source with a multichannel photomultiplier (Hamamatsu R3809U-50) as the detector. The width of the instrument response function (IRF), was limited by the pulse duration of the pulses (FWHM ~ 160 ps at 1 MHz repetition rate). The lamp profile was calibrated by placing a scatterer (dilute solution of Ludox in water) in place of the sample. The time resolved emission decay profiles were monitored at steady state emission maxima. Decay curves were fitted by nonlinear least-squares iteration procedure using IBH DAS6 (Version 2.2) decay analysis software. The quality of the fit was judged by the reduced χ^2 values ~ 1.1 and the uniform distribution of the residuals.

5.3.4 Degenerate pump-probe measurements

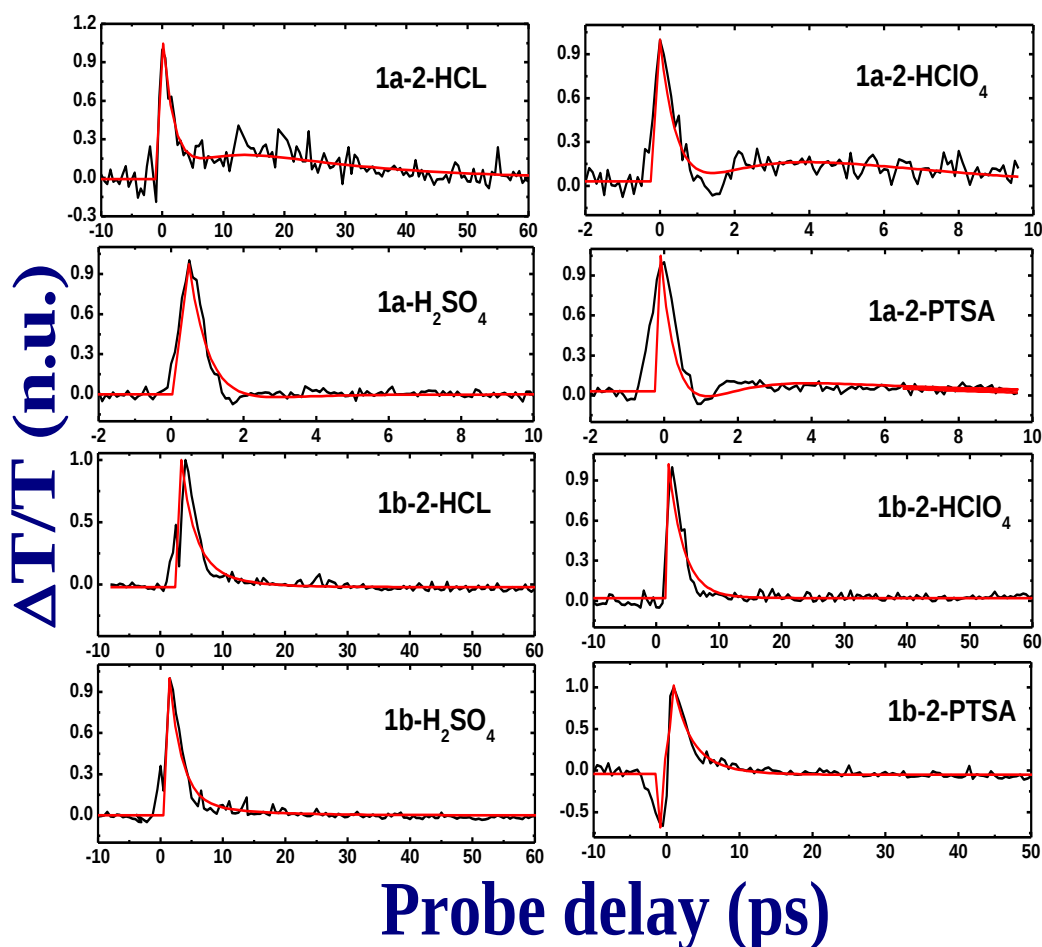


Figure 5.7 Degenerate pump-probe measurements (in normalized units) of the salt solution (concentrations are given in table.5.1) at 800 nm. The pump and probe intensities are 100 GW/cm² and 186MW/cm² respectively. The black line is experimental data and the red line is exponential fit.

Complete details of degenerate pump-probe experimental set up were explained in chapter 2 [20, 21]. The initial degenerate pump-probe measurements were performed with lower peak intensities (~ 100 GW/cm²) of the pump beam. The initial peak intensities were such that NLO effects were not involved. The data of degenerate pump-probe measurements of various salts are as shown in figure 5.7. All the pump-probe data were fitted using the equation $\Delta T/T = y_0 + \sum_i A_i e^{-(t-t_0)/\tau_i}$, where A_i are the weightage, τ_i are the decay constants and $i=1, 2, 3$ for single exponential, bi-exponential and triple exponential respectively. The fitted parameters were given in table 5.2. It was observed that differential probe transmittance depicted autocorrelation type of signal which suggests that there

could be either a faster relaxation than the pulse duration. In the case of freebase samples, the pump-probe signal showed a positive rise with double exponential decay. We believe that in this case the intensity was sufficient to excite the two photon resonant states (supported by Z-scan open aperture measurements) and the decay was comprised of two components. In order to excite the two photon resonant states of other compounds (i.e. the sapphyrin salts), the experiments were performed at slightly higher peak intensities of the pump beam.

Figure 5.8 shows the degenerate pump-probe data for compounds (a) **1a**.2HCl, (b) **1a**.2HClO₄, (c) **1a**.2*p*-TsOH, (d) **1b**.2*p*-TsOH and that for (e) **1a** at high intensities of 175 GW/cm² (f) **1b** at high intensities of 175 GW/cm² (g) **1a** at low intensities of 100 GW/cm² (h) **1b** at low intensities of 100 GW/cm². The differential probe transmittance was initially negative (especially for samples **1a**.2HClO₄, **1a**.2*p*-TsOH, **1b**.2*p*-TsOH) and subsequently became positive after a time delay of ~2 ps. The small negative component or the kink in the response could be due to the coherent artifact or coherent spikes [22,23]. This negative component is also visible in figure 5.7. The positive part decayed bi-exponentially. Similar behavior was observed for some of the corrole and cyclo[4]naphthobipyrrole derivatives studied earlier by our group [21,24]. The data was fitted with a bi-exponential function (Table 5.2) [21,24]. The slower component of the fits (1-2 ns, except for **1a** and **1b**) were almost comparable to the radiative lifetimes (typically few nanoseconds). In the case of **1a** and **1b** the slower decay components were ~184 and ~65 ps respectively. Similar slower decay times were observed even for stronger pumping (for higher peak intensities the decay values were ~150 and ~68 ps). These decay times probably have strong non-radiative components. The faster component (2-4 ps) can be attributed to the relaxation of population from high lying singlet states including the internal conversion (IC) from S₂ to S₁ states and intra-molecular vibrational relaxation within S₂ states. The two-photon excitation enables the population reach S₂ states and the slow decay includes relaxation of population from the excited singlet states S₁ to S₀.

The freebase sapphyrins **1a** and **1b** display relatively longer radiative life time (1.5-1.6 ns) compared to their *meso*-tetraaryl analog **9** derivatives (1.3 ns)

and this may be attributed to the relatively more structural flexibility in case of the latter due to the free rotation of the *meso*-aryl substituents.[8] Expectedly, the lack of tautomerization due to absence of internal proton transfer processes in case of the sapphyrin salts led to an increase in their radiative life times (Table 5.2). Except **1a**.H₂SO₄ all the sapphyrins, including the freebases displayed single exponential decay with lifetimes ranging from 1.50-2.18 ns, whereas the sulfate salt of **1a** exhibited double exponential decay with lifetimes of 1.90 and 3.60 ns.

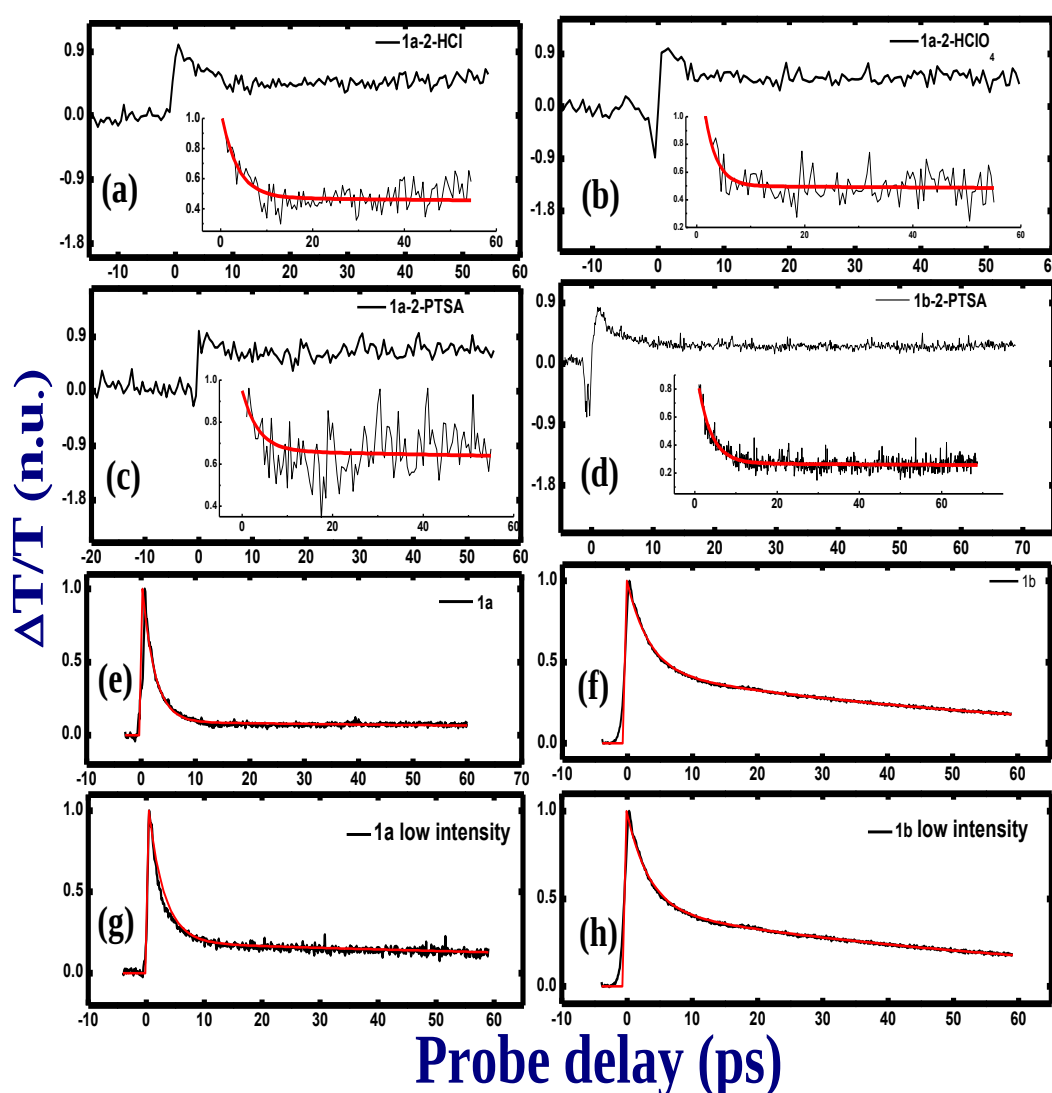


Figure 5.8 Degenerate pump-probe measurements (in normalised units) at 800 nm for (a) **1a** 2HCl, (b) **1a** 2HClO₄, (c) **1a**.2p-TsOH (d) **1b**.2p-TsOH at higher pump intensities ~ 175 GW/cm² (e) freebase solution **1a** and (f) freebase solution **1b** with pump intensity ~ 175 GW/cm² and probe intensity ~ 186 MW/cm². Degenerate pump probe measurements at 800 nm for (g) freebase solution **1a** and (h) freebase solution **1b** with pump intensity ~ 100 GW/cm² and probe intensity ~ 186 MW/cm². The concentration of freebase solutions were 0.3 mM. The black (wiggly) lines are experimental data while the red lines are exponential fits.

5.3.5 Non-degenerate pump-probe measurements

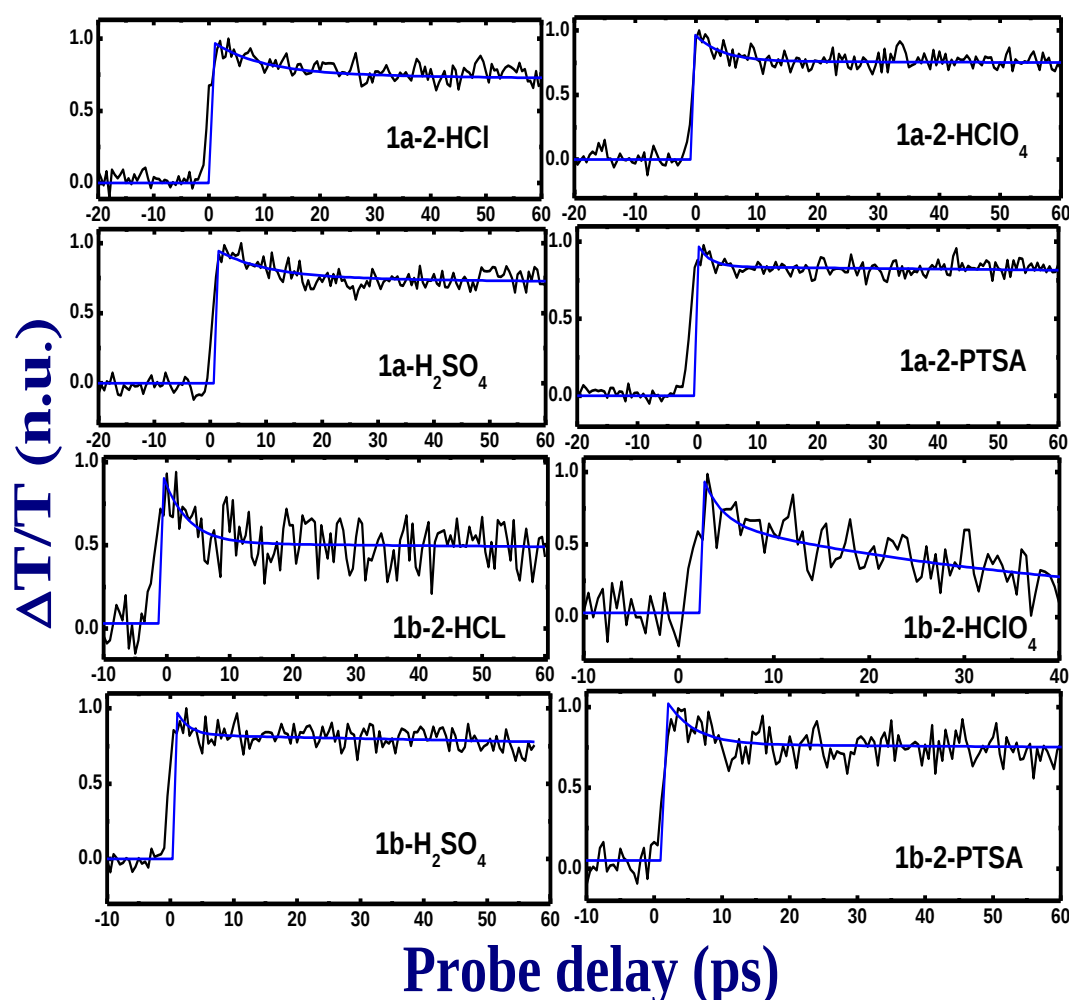


Figure 5.9 Non-degenerate pump-probe measurements (pump at 400nm and probe at 800nm). The pump and probe intensities were 440 GW/cm² and 186 MW/cm² respectively. The black wiggly line is experimental data and the red line is exponential fit.

The non-degenerate pump-probe measurements were performed by using the same experimental set up that was used for degenerate pump-probe measurements. However, a 2 mm β barium borate crystal was placed in the pump beam (no focusing of the pump beam was performed) and 400nm photons were generated. The schematic was given in chapter 2. Figure 5.9 shows the non-degenerate pump-probe data of **1a**.2HCl, **1a**.2HClO₄, **1a**.2p-TsOH, **1b**. 2p-TsOH, **1b**.2HCl, **1b**.2HClO₄, **1b**.H₂SO₄, and **1b**.2p-TsOH. The data (Table 5.2) depicted a positive rise in differential transmission with bi-exponential decay which, again, could be from the relaxation of population in the higher excited singlet states (S₂)

and IC from S_2 to S_1 . The faster lifetimes were 2-9 ps and the slower decay times were 1-2.2 ns, except for **1b**.2HClO₄ (~ 40 ps) and the longer decay time matches well with the radiative lifetimes recorded independently. Since these molecules emit at ~730 nm (from the emission spectra) second decay component could include contributions from both radiative and non-radiative processes.

The dynamics of naphthosapphyrins are understood in detail using the schematic presented in figure 5.10. The radiative decay from S_1 to S_0 is of the order of few ns. The fitted parameters of fluorescence decay curve are given in table 5.2. The lower energy excitations at 800 nm (degenerate case) were not sufficient to excite the molecules to S_2 states except for the freebase molecules. The higher energy excitation by 800 nm could access the two photon resonant states and the relaxation from S_2 to S_0 via S_1 was bi exponential as shown in figure 5.10 with a black solid curly line.

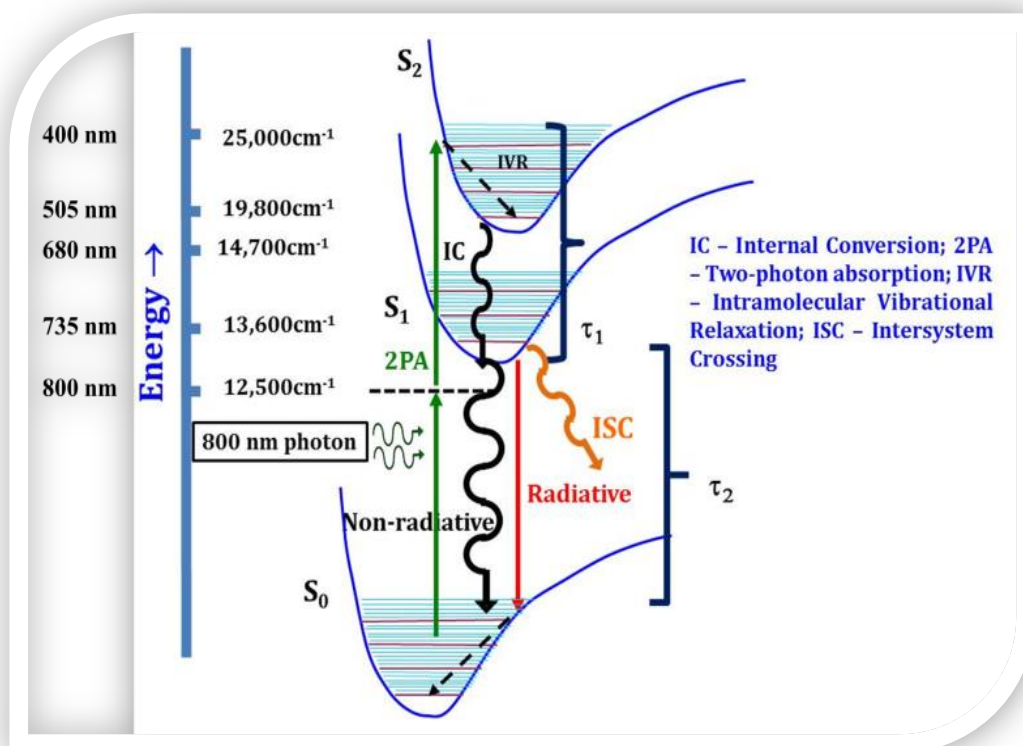


Figure 5.10 Energy level diagram describing the various transitions involved when the population is excited into S_2 states through 2PA.

Sample	Non-degenerate Pump probe data		Degenerate Pump probe data		Radiative lifetimes	
	τ_1 (ps)	τ_2 (ns)	τ_1 (ps)	τ_2 (ns)	τ' (ps)	τ_r (ns)
1a	-	-	2.2 (91%) * 2.7 (83%)	0.180 (9%), * 0.150 (16%)	-	1.60
1a.2HCl	9 (24%)	1.8 (76%)	* 3.5 (55%) 2 (74%)	* 1.500 (44%) 0.005 (25%)	-	1.90
1a.2HClO₄	5 (18%)	1.8 (82%)	* 2.1 (68%) 2 (78%)	* 2.000 (32%) 0.003 (21%)	-	2.18
1a.H₂SO₄	9 (21%)	1.9 (79%)	2 (90%)	0.009 (10%)	-	1.90 (47.7%), 3.60 (52.3 %)
1a.2p-TsOH	2 (13%)	2.2 (86%)	* 3.5 (31%) 1.9 (11%)	* 1.500 (69%) 0.004 (6%)	- 1.4 (82%)	2.17
1b	-	-	3.4 (55%) * 4.0 (55%)	0.065 (44%) * 0.068 (44%)	-	1.50
1b.2HCl	3.8 (48%)	1.4 (52%)	2.2 (52%)	0.021 (13%)	4.5 (34%)	1.59
1b.2HClO₄	2 (34%)	0.04 (65%)	0.5 (49%)	0.006 (17%)	1.5 (32%)	2.00
1b.H₂SO₄	2 (20%)	1.0 (80%)	0.5 (83%)	-	1.2 (16%)	1.78
1b.2p-TsOH	4 (30%)	2.0 (70%)	* 3.2 (79%) 0.48 (55%)	* 1.550 (21%) 0.003 (13%)	- 1.3 (31%)	1.90

Table 5.2 Summary of lifetime data of naphthosapphyrins τ_1 , τ_2 & τ' are the fitted parameters from the pump-probe data. τ_r (radiative lifetimes) were obtained from time correlated single photon counting measurements. The weightage (%) of decay constants are given in the bracket. τ' are the decay constants whose weightage is negative. * Data recorded with higher peak intensity of the pump ($\sim 175 \text{ GW/cm}^2$). Other degenerate pump probe data were recorded at about 100 GW/cm^2 . For non-degenerate pump probe data the peak intensity of the pump was $\sim 400 \text{ GW/cm}^2$.

Due to the optical nonlinearity of the free-base molecules, the lower energy excitations permitted access of two-photon resonant states. The decays at this energy were bi-exponential, which include intra molecular vibrational relaxation (IVR) and internal conversion (IC) followed by either radiative or non-radiative decay. However, stronger pumping allowed the population to be excited to S_2 states. In the non-degenerate pump-probe case since the pumping was at 400 nm, the excitation directly pumped the population into S_2 states and the double exponential decays τ_1 and τ_2 followed (see figure 5.10).

The data obtained from both degenerate and non-degenerate case matched very well within the experimental errors. For example, the value of τ_2 obtained for **1a**.2HClO₄ was 1.8 and 2.0 ns in non-degenerate and degenerate case, respectively. This value again matches with the radiative lifetime of 2.18 ns obtained from TCSPC studies. While the non-radiative de-excitation in case of freebase sapphyrins **1a** and **1b** can be attributed to the NH tautomerization processes, however, it is intriguing to find **1b**.2HClO₄ also follows a similar path unlike the other sapphyrin salts which undergo the de-excitation from S_1 state via radiative path and beyond our understanding at this stage.

5.4 Conclusions

It was found that due to the higher nonlinearity of free-bases, 2PA was observed even at lower peak intensities, whereas the sapphyrin salts needed higher peak intensities. The protonated sapphyrins need higher peak intensity to exhibit the nonlinear optical properties than their freebase counterparts. The excited state dynamics studies using degenerate and non-degenerate pump-probe techniques revealed the decay times of highly excited states in the ps and ns regimes. The degenerate pump probe measurements at higher intensities took longer decay time which are comparable with that obtained from the non-degenerate pump-probe measurements. Further, a broad band probe is required for analysing the deactivation channel of the sapphyrin moieties as performed and reported by Yan et al. [5].



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CHAPTER 6

Ultrafast excited state dynamics of Porphyrin & Phthalocyanine molecules in the presence of Explosive molecule

ABSTRACT

Nonlinear absorption (NLA) properties and excited state dynamics of an octamethyl porphyrin and free base tetratertbutyl phthalocyanine in the presence of explosive molecules of TNT, RDX and CL-20 were studied using the nanosecond Z-scan and femtosecond pump probe techniques, respectively. The NLA coefficients I_s and β increased in presence of explosive molecules. The change in NLA of these molecules was monitored using the open aperture Z-scan technique. The change in non-radiative decay times was calculated through degenerate fs pump probe measurements near 700 nm and it was observed that decay time decreased in presence of explosive molecules. The quenching of decay time and the increment in NLA coefficients varied with different molecules according to their absorption, emission and affinity towards the explosive molecule. The experimental results obtained from these measurements suggest that the interaction of explosive molecules with porphyrin, phthalocyanine moieties alters their excited state dynamics and, consequently, NLA properties.

The chapter includes the data presented in the following publications:

 *Chemical Physics Letters, 641, 23-28, 2015.*

6.1 Introduction

The scientific community over the last decade has been investigating various analytical methods rigorously to understand the interaction of conjugated organics with nitrated energetic moieties (or explosive molecules) with an aim to discover suitable molecules and methodologies for sensing applications [1-4]. A very recent review article articulates the various molecules used (polymers, small and large organic molecules, metal organic frameworks, etc.) and the methodologies developed for detection of explosive molecules [5]. Most of the conjugated organic moieties such as porphyrins, phthalocyanines, specific polymers etc. have been reported to demonstrate strong fluorescence quenching when they bind with the energetic moieties [9-23]. There are multitudes of mechanisms which occur during these interactions such as electron transfer, ground state complex formation, charge transfer etc. [5] which cause changes in the excited state lifetime, excited state cross-section and the formation of aggregates etc. Many of the organic compounds which are used in explosive sensing are highly active nonlinear optical (NLO) materials [6-8] and, therefore, any change in the aforementioned properties will directly affect the nonlinear absorption (NLA) properties such as excited state absorption (ESA), saturable absorption (SA) etc. Consequently, it is important to quantify the NLA properties of the fluorophore in the presence of nitrated compounds which helps to categorize the fluorophore according to the efficiency towards explosive sensing. Geng et al. reported detection of explosive vapours and taggants selectively using thin films of light-emitting dendrimers [43]. They observed that the fluorescence quenching was not observed for a range of common interferents. Using a combination of photophysical and other measurements they demonstrated that the origin of selectivity is primarily electronic in nature and not the diffusion kinetics of the analyte or its distribution in the film. It is, therefore, imperative to understand the dynamics of these sensing molecules in presence of the nitrated compounds for designing improved sensing molecules. The major mechanism in explosive sensing is the utilization of the electron withdrawing property of $-\text{NO}_2$ group present in the energetic molecule [9-12]. The presence of $-\text{NO}_2$ not only enables an energetic molecule to release large amount of energy but also alter the photo-physical parameters of the organic conjugates with which it interacts.

Several earlier studies were focused on monitoring the luminescence properties of different fluorophores in the presence of a variety of energetic molecules. In energetic molecules (or explosive molecules) the charges are strongly localized on the electron withdrawing nitro groups which favors the formation of several complexes in the presence of π electron rich compounds [13]. These effects vary according to the molecular structure and properties of central metal atom and peripheral moieties.

Venkatramaiah et al., for example, reported on peripherally modified dimethylamine substituted Zn(II)phthalocyanines [4] possessing both electron donating and electron withdrawing substituents at their periphery and investigated those molecules towards the detection of nitro-aromatic compounds (including trinitrophenol) in solution and vapour phase. Their detailed experimental studies and density functional theory calculations revealed that the fluorescence quenching behaviour occurred through photo-induced electron transfer from the excited state of phthalocyanines to trinitrophenol with static quenching as the predominant mechanism [4]. Gupta et al. recently reported the fluorescence quenching of Zn-Phthalocyanine triad {Zn[Pc(O-Bn-CH₃)₄] in the presence of explosive molecules of picric acid (PA) [24]. They observed that a charge-transfer complex from phthalocyanine derivative (donor) to picric acid (acceptor) was formed through nitrogen atoms. Their derivative demonstrated an efficient and selective fluorescence quenching toward picric acid, during which the compound exhibited a significant morphological change from round spheres to irregularly square-like aggregates [24]. Gupta et al. [25] also reported the fluorescence quenching of an electron-rich phthalocyanine–thiophene–phthalocyanine triad in the presence of PA molecules. They demonstrated that PA molecules interacted with the phthalocyanine molecules through intermolecular π – π interaction and that the photo-induced electron transfer complex arose from the electron-rich pendant phthalocyanine rings to the PA reagents, leading to an efficient fluorescence quenching mechanism. In general, the detection sensitivity can be enhanced by reducing the band gap, size of the molecule, increasing the rigidity of the structure, and possibility of strong intermolecular and π - π interactions with nitrated compounds [26, 27].

6.1.1 Mechanisms of interaction of nitrated compounds (NC's) to organic molecules

There are various types of mechanisms involved in the interactions of NC's with conjugated organic molecules which results in the change of different physical properties such as fluorescence intensity, wavelength, lifetime etc. Sometimes, non-fluorescent ground state complex is formed through the interaction of fluorophore and NC's which alters the ground state properties of the fluorophore molecule. This is called static quenching. In such cases, the molecules which were not bound to the quencher molecule decay with their natural lifetime and hence the fluorescence lifetime remains unchanged. If the quenching occurs at excited state, it is called dynamic quenching. Processes like photo-induced electron transfer, resonance energy transfer, electron exchange, and intersystem crossing etc. lead to dynamic quenching. Since the excited state of the fluorophore is interacting with the quencher, the average lifetime of that particular state get decreased [28, 29].

6.1.1.1 Photo-induced electron transfer (PET)

In PET, charge transfer complex is formed in the excited state between the fluorophore and the quencher. The electron withdrawing property of nitro groups in these binding compounds has been exploited for sensing. There is a possibility of excited state electron transfer from the electron rich fluorophore to the ground state of the explosive compounds and/or the formation of non-fluorescent charge transfer complex during the interaction of the fluorophore and oxidative binder [9-12].

6.1.1.2 Resonance energy transfer (RET)

The energy transfer occurs when the emission band of fluorophore matches with absorption band of the quencher. The photo-excited fluorophore transfers energy to the acceptor and returns to ground state. As the overlap of emission spectrum of donor and the absorption spectrum of acceptor increases, the rate of energy transfer increases. In explosive sensing, the fluorophore sensors are designed such that their emission band has more intersection with the absorption band of explosive molecule. [30-32]

6.1.1.3 Electron exchange (EE)

In EE, the excited electron in the lowest unoccupied molecular orbital (LUMO) of fluorophore get transferred to the acceptor and another electron from the highest occupied molecular orbital (HOMO) of the quencher returns back to the donor. EE is similar to RET but it is a short range interaction and requires high concentration. EE may occur but may not be observable if the spectral overlap is large due to the quenching by RET. Hence the EE is observable if the spectral overlap is small [29].

6.1.1.4 Inter system crossing (ISC)

Intersystem crossing occurs if the quencher has heavy atom which accelerates the spin orbit coupling. This interaction converts excited state singlet to excited state triplet from which the molecules returns to the ground state by non-radiative decay [29].

In this chapter we present the effect of nitrated energetic compounds on the NLA properties of the advanced organic conjugates of porphyrin and phthalocyanine. We present the results from detailed studies of NLA and excited state dynamics of an octamethyl porphyrin (OMP) and tetratertbutyl phthalocyanine (Pc) in the presence of explosive molecules [e.g. 2,4,6-trinitrotoluene (TNT), 1,3,5-trinitroperhydro-1,3,5-triazine (RDX) and 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (CL-20)] containing electron withdrawing groups using nanosecond (ns) Z-scan and femtosecond (fs) pump probe techniques, respectively. The ns Z-scan measurements revealed the presence, and changes, of saturable absorption and excited state absorption mechanisms whereas the fs pump probe data provided information on the first excited state decay rates (S_1). Such studies could *possibly* be extended towards the realization of a simple technique such as open aperture ns Z-scan to quantify the excited state properties in sub-picosecond time scales which ultimately leads to identification of an efficient fluorophore for screening explosive molecules. We also highlight some of the issues related to these and provide suggestions to improve and extent the present studies.

6.2 Experimental details

The ns Z-scan experiments were performed to investigate the interaction of Pc and OMP with nitro-rich compounds such as CL-20 (henceforth referred to as C for convenience), RDX (henceforth referred to as R for convenience) and TNT (henceforth referred to as T for convenience) molecules which are generally referred to as high energy materials/molecules (HEMs). The input laser source was a second harmonic of Nd:YAG laser with ~ 5 ns pulse duration delivering pulses at 10 Hz repetition rate. The input laser beam was focused to a spot size of ~ 14 μm with a ~ 10.5 cm focal length convex lens. A quartz cuvette of 1 mm thickness was used to hold the sample. The sample was translated using a linear translation stage interfaced to a computer. The fs degenerate pump-probe experiments were performed at 700 nm and 690 nm for Pc and OMP solutions, respectively. The laser source was an optical parametric amplifier (TOPAS-C, Light Conversion) pumped by a Ti:sapphire amplifier and tunable in the spectral range of 260 nm–20 μm delivering ~ 60 fs pulses at a repetition rate of 1 kHz. The polarization of the pump and probe beams were ensured to be perpendicular using a half wave plate (HWP). The pulse width at the sample was estimated to be ~ 90 fs including the pulse broadening due to the optics and focusing lenses involved. The pump and probe beams were focused to the sample in the 5 mm glass cuvette using lenses of ~ 30 cm and ~ 20 cm focal length. The zero delay was confirmed by performing autocorrelation in a BBO crystal at 700 nm. The probe transmittance was collected using a Si PD (SM05R/M, Thorlabs). The pump to probe energy ratio was typically maintained at 10:1. The intense pump (~ 960 nJ/pulse) was used to excite the molecule and the low power probe beam (~ 90 nJ/pulse) was used to monitor the transmittance of the sample ensuring that there were no self-induced nonlinearities due to the probe beam. The experiment was repeated after titrating with C, R, T solutions with a molar ratio of 1:10.

6.2.1 Sample preparation

6.2.1.1 Emission measurements

The fluorescence measurements were done for OMP and Pc titrating with C, R, T solutions. The excitation wavelength was so chosen that there should not be any change in the OD values when we add the HEM molecules and the OD should be less than 0.1 to avoid other artifacts

OMP:

2 μM of OMP solution is prepared by adding 6 μl of 1 mM solution to 3 ml of chloroform. Concentration of initial solution (C_{int}) $\times$ Vol. of initial solution (V_{int}) = Concentration of final solution (C_{fin}) $\times$ Vol. of final solution (V_{fin})

$$1\text{mM} \times 6\mu\text{l} = C_{\text{fin}} \times 3\text{ml}; C_{\text{fin}} = 2 \mu\text{M}$$

(a) For the first addition of C, R, T solutions:

To a total vol. of 3ml, 6 μl of quencher solutions of concentration 50 mM were added.

$$C_{\text{int}} \times V_{\text{int}} = C_{\text{fin}} \times V_{\text{fin}}$$

$$50 \text{ mM} \times 6 \mu\text{l} = C_{\text{fin}} \times 3 \text{ ml}; C_{\text{fin}} = 100 \mu\text{M} = 0.1 \text{ mM}$$

(b) For the second addition of C, R, T solutions

To a total vol. of 3 ml, 30 μl of quencher solutions of concentration 50 mM were added.

$$C_{\text{int}} \times V_{\text{int}} = C_{\text{fin}} \times V_{\text{fin}}$$

$$50 \text{ mM} \times 30 \mu\text{l} = C_{\text{fin}} \times 3 \text{ ml}; C_{\text{fin}} = 500 \mu\text{M} = 0.5 \text{ mM}$$

(c) For the third addition of C, R, T solutions

To a total vol. of 3 ml, 60 μl of quencher solutions of concentration 50 mM were added.

$$C_{\text{int}} \times V_{\text{int}} = C_{\text{fin}} \times V_{\text{fin}}$$

$$50 \text{ mM} \times 60 \mu\text{l} = C_{\text{fin}} \times 3 \text{ ml}; C_{\text{fin}} = 1000 \mu\text{M} = 1 \text{ mM}.$$

Pc:

2 μM of OMP solution is prepared by adding 10 μl of 0.6 mM solution to 3 ml of chloroform for C, R titration.

$$0.6 \text{ mM} \times 10 \mu\text{l} = C_{\text{fin}} \times 3 \text{ ml}; C_{\text{fin}} = 2 \mu\text{M}$$

(a) For the first addition of C R solutions:

To a total vol. of 3 ml, 10 μl of quencher solutions of concentration 50 mM were added.

$$C_{\text{int}} \times V_{\text{int}} = C_{\text{fin}} \times V_{\text{fin}}$$

$$50 \text{ mM} \times 10 \mu\text{l} = C_{\text{fin}} \times 3 \text{ ml}; C_{\text{fin}} = 165 \mu\text{M} = 0.165 \text{ mM}$$

(b) For the second addition of C, R, T solutions

To a total vol. of 3 ml, 50 μl of quencher solutions of concentration 50 mM were added.

$$C_{\text{int}} \times V_{\text{int}} = C_{\text{fin}} \times V_{\text{fin}}$$

$$50 \text{ mM} \times 50 \text{ }\mu\text{l} = C_{\text{fin}} \times 3 \text{ ml}; C_{\text{fin}} = \mathbf{816 \text{ }\mu\text{M} = 0.816 \text{ mM}}$$

(c) For the third addition of C, R, T solutions

To a total vol. of 3 ml, 100 μl of quencher solutions of concentration 50 mM were added.

$$C_{\text{int}} \times V_{\text{int}} = C_{\text{fin}} \times V_{\text{fin}}$$

$$50 \text{ mM} \times 100 \text{ }\mu\text{l} = C_{\text{fin}} \times 3 \text{ ml}; C_{\text{fin}} = \mathbf{1612 \text{ }\mu\text{M} = 1.612 \text{ mM}}$$

3 μM of Pc solution is prepared by adding 15 μl of 1 mM solution to 3 ml of chloroform for T titration. There are two reasons in increasing the concentration for titration with T solution. The first one is that the OD was changing at the excitation wavelength (370 nm) which was used for C, R titrations and hence we selected 597nm as the excitation wavelength. But the OD was below 0.05 with 2 μM . So in order to increase the OD the concentration was increased to 5 μM .

$$0.6 \text{ mM} \times 15 \text{ }\mu\text{l} = C_{\text{fin}} \times 3 \text{ ml}; C_{\text{fin}} = \mathbf{3 \text{ }\mu\text{M}}$$

(a) For the first addition of T solutions:

To a total vol. of 3 ml, 15 μl of quencher solutions of concentration 50 mM were added.

$$C_{\text{int}} \times V_{\text{int}} = C_{\text{fin}} \times V_{\text{fin}}$$

$$50 \text{ mM} \times 15 \text{ }\mu\text{l} = C_{\text{fin}} \times 3 \text{ ml}; C_{\text{fin}} = \mathbf{247 \text{ }\mu\text{M} = 0.247 \text{ mM}}$$

(b) For the second addition of C, R, T solutions

To a total vol. of 3 ml, 45 μl of quencher solutions of concentration 50 mM were added.

$$C_{\text{int}} \times V_{\text{int}} = C_{\text{fin}} \times V_{\text{fin}}$$

$$50 \text{ mM} \times 45 \text{ }\mu\text{l} = C_{\text{fin}} \times 3 \text{ ml}; C_{\text{fin}} = \mathbf{735 \text{ }\mu\text{M} = 0.735 \text{ mM}}$$

(c) For the third addition of C R T solutions

To a total vol. of 3 ml, 75 μl of quencher solutions of concentration 50 mM were added.

$$C_{\text{int}} \times V_{\text{int}} = C_{\text{fin}} \times V_{\text{fin}}$$

$$50 \text{ mM} \times 75 \text{ }\mu\text{l} = C_{\text{fin}} \times 3 \text{ ml}; C_{\text{fin}} = \mathbf{1213 \text{ }\mu\text{M} = 1.213 \text{ mM.}}$$

6.2.1.2 Z-scan measurements

OMP:

0.23 μM of OMP solution is prepared by adding 60 μl of 1 mM solution to 200 μl of chloroform for OMP alone measurement.

$$1 \text{ mM} \times 60 \mu\text{l} = C_{\text{fin}} \times 260 \mu\text{l}; C_{\text{fin}} = \mathbf{0.23 \text{ mM.}}$$

(a) For the first addition of quencher solutions:

Vol. of quencher solutions added= 24 μl of 50 mM

$$C_{\text{int}} \times V_{\text{int}} = C_{\text{fin}} \times V_{\text{fin}}$$

Concentration of quencher solutions:

$$50 \text{ mM} \times 24 \mu\text{l} = C_{\text{fin}} \times 284 \mu\text{l}; C_{\text{fin}} = \mathbf{4.2 \text{ mM}}$$

Concentration of OMP:

$$C_{\text{int}} \times V_{\text{int}} = C_{\text{fin}} \times V_{\text{fin}}$$

$$1 \text{ mM} \times 60 \mu\text{l} = C_{\text{fin}} \times 284 \mu\text{l}; C_{\text{fin}} = \mathbf{0.21 \text{ mM.}}$$

(b) For the second addition of quencher solutions:

Vol. of quencher solutions added= 45 μl of 50 mM

$$C_{\text{int}} \times V_{\text{int}} = C_{\text{fin}} \times V_{\text{fin}}$$

Concentration of quencher solutions:

$$50 \text{ mM} \times 45 \mu\text{l} = C_{\text{fin}} \times 305 \mu\text{l}; C_{\text{fin}} = \mathbf{7.3 \text{ mM}}$$

Concentration of OMP:

$$C_{\text{int}} \times V_{\text{int}} = C_{\text{fin}} \times V_{\text{fin}}$$

$$1 \text{ mM} \times 60 \mu\text{l} = C_{\text{fin}} \times 305 \mu\text{l}; C_{\text{fin}} = \mathbf{0.19 \text{ mM}}$$

Pc:

0.6 mM solution of PC was used for Z-scan measurements when PC was done alone.

(a) For the first addition of quencher solutions:

Vol. of quencher solutions added= 80 μl of 50 mM

$$C_{\text{int}} \times V_{\text{int}} = C_{\text{fin}} \times V_{\text{fin}}$$

Concentration of quencher solutions:

$$50 \text{ mM} \times 80 \mu\text{l} = C_{\text{fin}} \times 280 \mu\text{l}; C_{\text{fin}} = \mathbf{14 \text{ mM}}$$

Concentration of PC:

$$C_{\text{int}} \times V_{\text{int}} = C_{\text{fin}} \times V_{\text{fin}}$$

$$0.6 \text{ mM} \times 200 \text{ }\mu\text{l} = C_{\text{fin}} \times 280 \text{ }\mu\text{l}; C_{\text{fin}} = \mathbf{0.42 \text{ mM}}.$$

6.2.1.3 Pump-probe measurements

0.6 mM solution of Pc was used for Z-scan measurements when Pc was done alone.

(a) For the addition of quencher solutions:

Vol. of quencher solutions added = 400 μl of 10 mM

$$C_{\text{int}} \times V_{\text{int}} = C_{\text{fin}} \times V_{\text{fin}}$$

Concentration of quencher solutions:

$$10 \text{ mM} \times 400 \text{ }\mu\text{l} = C_{\text{fin}} \times 800 \text{ }\mu\text{l}; C_{\text{fin}} = \mathbf{5 \text{ mM}}$$

Concentration of OMP:

$$C_{\text{int}} \times V_{\text{int}} = C_{\text{fin}} \times V_{\text{fin}}$$

$$1 \text{ mM} \times 400 \text{ }\mu\text{l} = C_{\text{fin}} \times 800 \text{ }\mu\text{l}; C_{\text{fin}} = \mathbf{0.5 \text{ mM}}.$$

Concentration of Pc:

$$C_{\text{int}} \times V_{\text{int}} = C_{\text{fin}} \times V_{\text{fin}}$$

$$0.6 \text{ mM} \times 400 \text{ }\mu\text{l} = C_{\text{fin}} \times 800 \text{ }\mu\text{l}; C_{\text{fin}} = \mathbf{0.3 \text{ mM}}.$$

6.3 Results and Discussions

6.3.1 Absorption and Emission studies

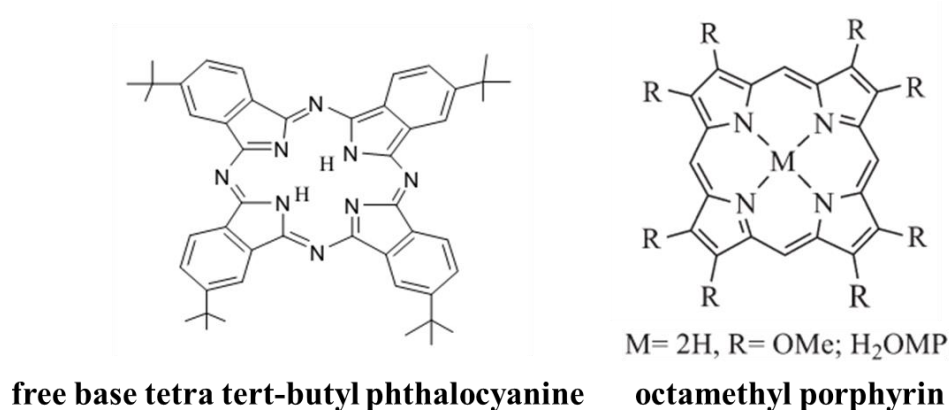


Figure 6.1 Structures of free base tetra-butyl phthalocyanine (Pc) and octamethyl porphyrin (OMP) adapted from reference [19, 41].

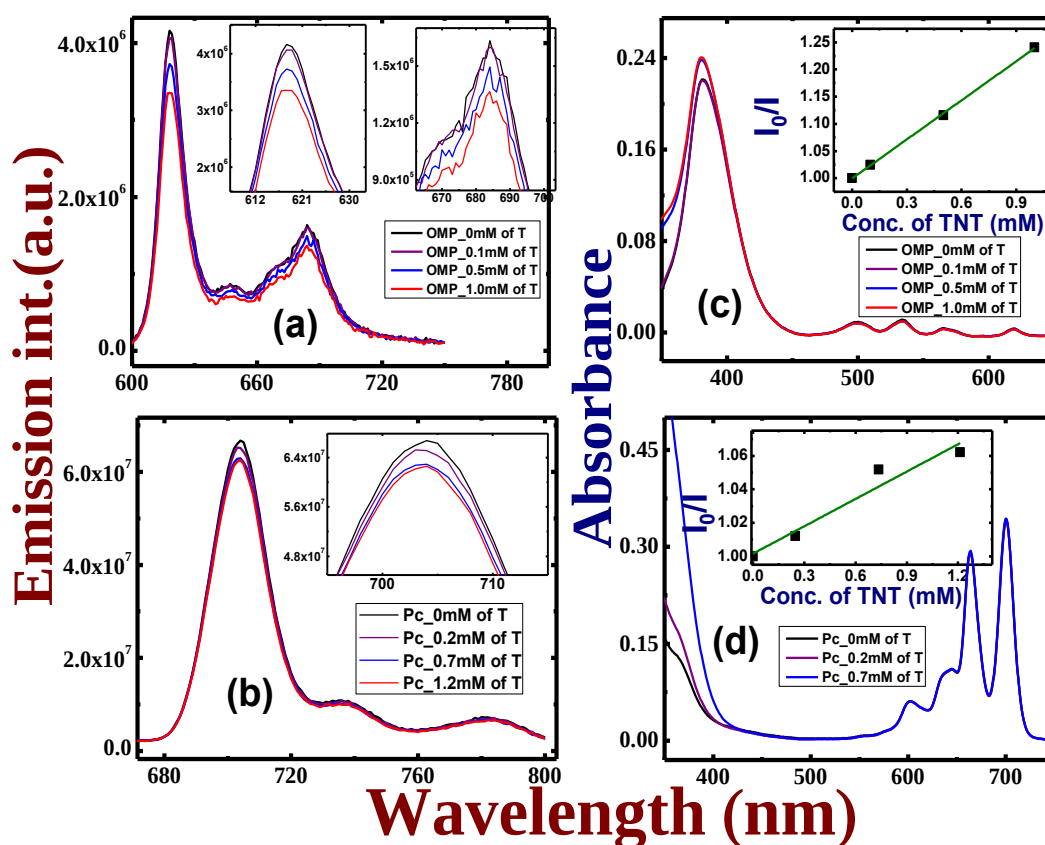


Figure 6.2 Emission measurements of (a) OMP and (b) PC and absorption measurements of (c) OMP and (d) PC in the presence of TNT solution. The inset of emission spectra shows the zoomed image of emission peaks. The inset of absorption spectra shows the Stern-Volmer plot for quenching.

The structures of the molecules used in the present study are shown in figure 6.1. The interaction of organic moieties with HEMs has been studied using steady state fluorescence and absorption. Figures 6.2(a), 6.2(b) depict the fluorescence data while figures 6.2(c), 6.2(d) illustrate the absorption data for OMP and PC, when titrated with TNT solutions of different concentrations. The excitation wavelength was chosen such that there was no change in the OD values after addition of the binder molecules and the OD was maintained to be < 0.1 [29]. $2 \mu\text{M}$ solution of OMP [figure 6.2(a)] was titrated with TNT solutions of 0.1 mM, 0.5 mM, and 1.0 mM concentration. The excitation wavelength used was 415 nm. The Stern-Volmer plots presented in the insets of figure 6.2(c) and 6.2(d) show the linear increase of quenching of fluorescence intensity as the concentration of quencher molecules are increased.

For emission measurements:	
Concentration of OMP	Concentration of T,C,R
1mM × 6μl = C_{fin} × 3ml; C_{fin} = 2 μM	0.1 mM
	0.5 mM
	1.0 mM
Concentration of PC	Concentration of T
0.6 mM × 15μl = C_{fin} × 3ml; C_{fin} = 3 μM	0.2 mM
	0.7 mM
	1.2 mM
Concentration of PC	Concentration of C,R
1mM × 10μl = C_{fin} × 3ml; C_{fin} = 2 μM	0.1 mM
	0.8 mM
	1.6 mM
For Zscan measurements:	
Concentration of OMP	Concentration of C,R,T
1mM × 60μl = C_{fin} × 260μl; C_{fin} = 0.23 mM (OMP1)	0
1st addition 1mM × 60μl = C_{fin} × 284μl; C_{fin} = 0.21 mM. (OMPA1)	4.2mM (OMPC1, OMPR1, OMPT1)
2nd addition 1mM × 60μl = C_{fin} × 305μl; C_{fin} = 0.19 mM. (OMPA')	7.3mM (OMPC', OMPR', OMPT')
Concentration of Pc	Concentration of C,R, T
0.6mM (Pc1)	0
1st addition 0.6 mM × 200μl = C_{fin} × 280μl; C_{fin} = 0.42 mM (PcA1)	50mM × 80μl = C_{fin} × 280μl; C_{fin} = 14 mM (PcC1, PcR1, PcT1)
For fs Pump-probe measurements:	
Concentration of OMP	Concentration of CRT
1mM (OMP2)	0
1st addition 1 mM × 400 μl = C_{fin} × 800 μl; C_{fin} = 0.5 mM.	10mM × 400μl = C_{fin} × 800μl; C_{fin} = 5 mM (OMPC2, OMPR2, OMPT2)
Concentration of Pc	Concentration of CRT
0.6mM (Pc2)	0
1st addition 0.6mM × 400 μl = C_{fin} × 800 μl; C_{fin} = 0.3mM.	10mM × 400μl = C_{fin} × 800μl; C_{fin} = 5 mM (PcC2, PcR2, PcT2)

Table 6.1 The concentrations and nomenclature used for all the measurements.

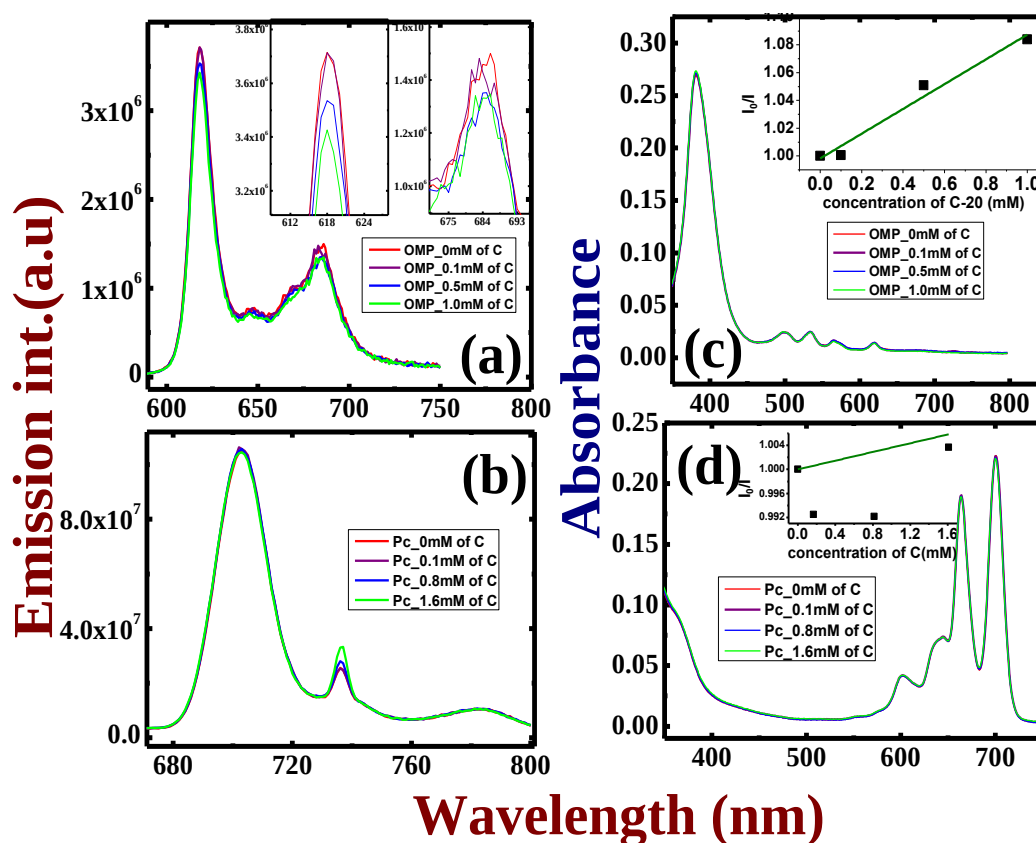


Figure 6.3 Emission measurements of (a) OMP and (b) PC and absorption measurements of (c) OMP and (d) PC in the presence of CL-20 solution. The inset of emission spectra shows the zoomed image of emission peaks. The inset of absorption spectra shows the Stern-Volmer plot for quenching.

In the case of PC, the excitation wavelength was 370 nm except for TNT solution and the binder molecules (RDX, Cl-20) were added in steps with the concentration in each addition as 0.1 mM, 0.8 mM and 1.6 mM, respectively. While performing the titration with TNT solution, we observed the OD of PC was changing at 370 nm. Hence, we selected the concentration of PC [figure 6.2(b)] such that the OD at 597 nm was above 0.05 and TNT solution was added in steps which yielded the concentrations as 0.2 mM, 0.7 mM and 1.2 mM respectively, in each addition. The measurements on titrations of Cl-20 and RDX solutions are shown in figures 6.3 and 6.4. The SV plot relates the quantity I_0/I versus the concentration of nitro compound solutions, where I_0 is the fluorescence intensity of the fluorophore and I is the fluorescence intensity of fluorophore for each addition of NCs. It was observed that SV plot of OMP with C, R, T solutions (OMP with R and T solutions as reported by Rana et al. [19]) and PC with T solutions were almost linear suggesting fluorescence quenching though the

interaction of Pc with C and R was not very significant. Figure 6.5 summarizes the quenching percentage recorded from the observed interactions.

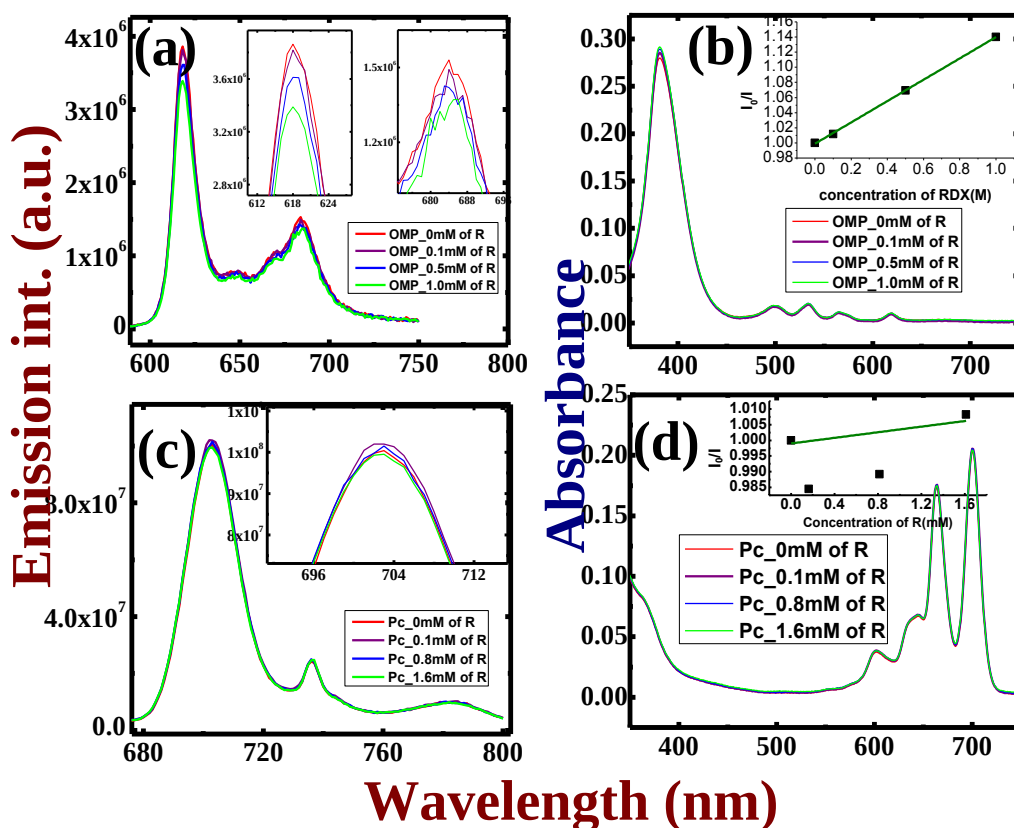


Figure 6.4 Emission measurements of (a) OMP and (b) PC and absorption measurements of (c) OMP and (d) PC in the presence of RDX solution. The inset of emission spectra shows the zoomed image of emission peaks. The inset of absorption spectra shows the Stern-Volmer plot for quenching.

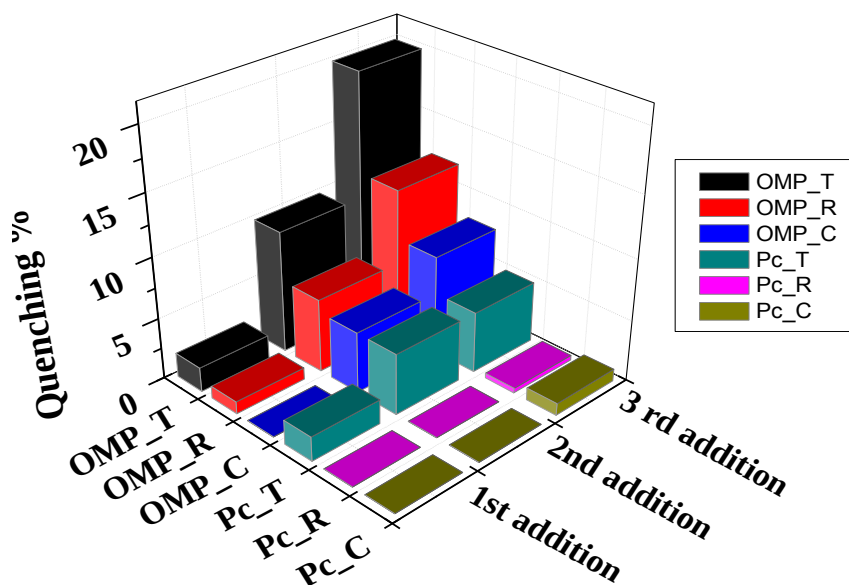


Figure 6.5 Quenching % for OMP titrated with consecutive three additions of TNT (OMP_T), RDX (OMP_R), Cl-20 (OMP_C) and Pc with TNT (Pc_T), RDX (Pc_R), Cl-20 (Pc_C) solutions.

6.3.2 NLO properties at 532 nm with ns pulses

The consequences of interaction of these nitro compounds in the nonlinear absorption properties were investigated by the Z-scan technique using ns pulses. The ns Z-scan experiment were conducted with 0.6 mM Pc solution titrated with C,R,T solutions in molar ratio 1:30 at two input peak intensities of $\sim 0.3 \text{ GW/cm}^2$ and $\sim 2.5 \text{ GW/cm}^2$. The open aperture Z-scan data obtained from these molecular solutions is presented in figures 6.6(a) and 6.6(b).

Pc1 represents the ns Z-scan measurements performed with 0.6 mM Pc solution without adding the quenching molecules. PcC1, PcR1, PcT1 and PcA1 indicated the ns Z- scan measurements of Pc after adding C, R, T solutions and acetonitrile solvent such that the molar ratio between Pc and the C, R, T solutions were 1:30. Due to dilution effects we could not do further titrations (which complicated the analysis). The concentrations of Pc and OMP were optimized so as to maintain a linear transmittance in the 55-65% range.

It is evident from the experimental data (represented by open circles) in figures 6.6(a) and 6.6(b) that the signature represents the presence of reverse saturable absorption (RSA) at both the peak intensities, typically observed with ns excitation in such molecules. However, the subtle changes observed in the data are retrieved from the theoretical fits (represented by solid lines) and the magnitude of two-photon absorption coefficient (β_{eff}) was obtained from all the fits. The nonlinear absorption coefficient β_{eff} in this case will be an '*effective* two photon absorption' taking into account the transitions occurring through (a) 1+1 photon absorption process (via excited state absorption either from singlet states or triplet states) and/or (b) instantaneous/pure two photon absorption.

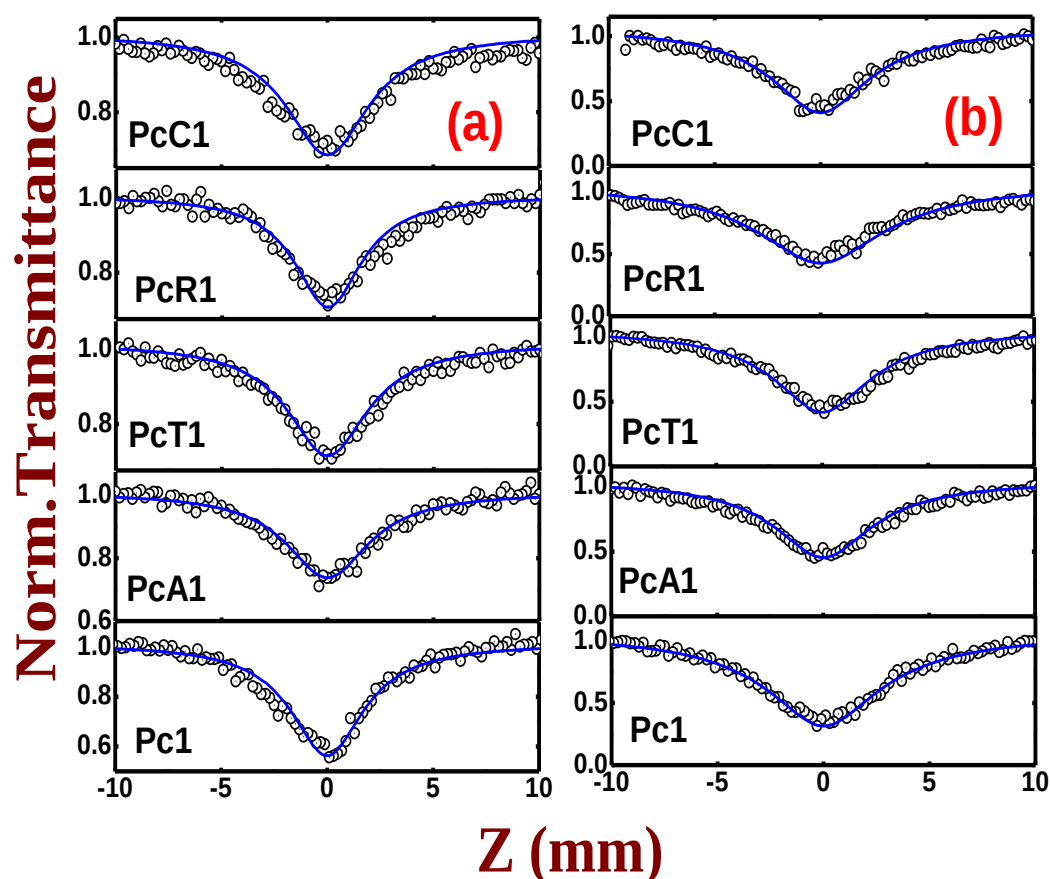


Figure 6.6 ns Z-scan measurements of Pc before and after the addition of C, R, T solutions and acetonitrile solvent which was the solvent for the NCs (denoted as Pc1, PcC1, PcR1, PcT1, PcA1, respectively) (a) data recorded at ~ 0.3 GW/cm² and (b) data recorded at ~ 2.5 GW/cm². The concentration Pc solution before the addition was ~ 0.6 mM. After addition of NCs, the concentration of Pc solution was ~ 0.43 mM and that of additives were ~ 14 mM in the mixture.

The NLA of Pc was found to be RSA and the nonlinear absorption coefficient was extracted by solving the propagation equation $dI/dz' = \alpha_0 I + \beta I^2$ where α_0 is the linear absorption coefficient and β is the NLA coefficient. To understand the concentration dependence, the experiment was performed by diluting the 0.6 mM Pc solution with the same volume of acetonitrile which used as solvent for making the C, R, T solutions. The β value was observed to be decreased as we diluted the Pc solution and similar observations have been reported in the literature [37]. However, post titration (PcC1, PcR1 and PcT1 with C, R, T solutions in 1:30 molar ratio) we observed a higher value for β which suggests the effect of interaction of these molecules with Pc molecule. The titration, PcA1, with solvent gave β value of ~ 4.4 cm/W and ~ 2.4 cm/W at 0.3 GW/cm² and 2.5 GW/cm² respectively. The addition of NCs enhanced the β values of (a) PcC1 to ~ 5.7 cm/GW and ~ 3.3 cm/W at 0.3 GW/cm² and 2.5

GW/cm², respectively (b) PcT1 to ~5.0 cm/GW and ~2.9 cm/W at 0.3 GW/cm² and 2.5 GW/cm², respectively (c) PcR1 to ~5.0 cm/GW and ~2.8 cm/W at 0.3 GW/cm² and 2.5 GW/cm² respectively.

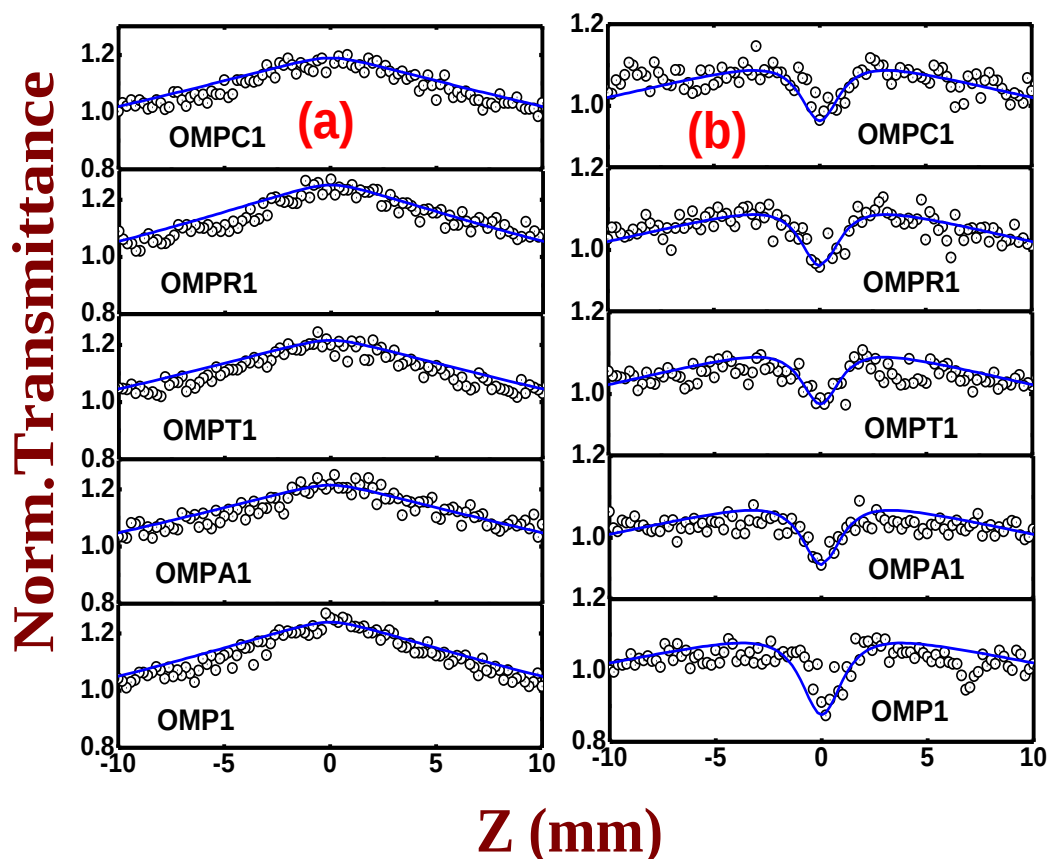


Figure 6.7 ns Z-scan measurements of OMP before and after the addition of C, R, T solutions and acetonitrile solvent which was the solvent for the NCs (denoted as OMP1, OMPC1, OMPR1, OMPT1, OMPA1, respectively) (a) data recorded at ~0.3 GW/cm² and (b) data recorded at ~2.5 GW/cm². The concentration OMP solution before the addition was ~0.2 mM. After addition of NCs, the concentration of OMP solution was ~0.2 mM and that of additives were ~4.2 mM in the mixture.

In the case of OMP, the ns Z-scan measurements were also performed with 0.23 mM [figures 6.7(a) and 6.7(b)]. The solutions of Cl-20, RDX, TNT (4.2 mM concentration) were added and the molar ratio between OMP and the Cl-20, RDX, TNT solutions were maintained at the ratio of 1:20. The data clearly suggested the presence of saturable absorption (SA) at lower peak intensities [figure 6.7(a)] whereas the behavior switched from SA to RSA at higher peak intensities [figure 6.7(b)]. The experiment was repeated for 1:40 molar ratio also to understand the concentration effect. Results from these measurements are shown in figures 6.8(a) and 6.8(b) wherein similar behavior to Pc was observed. At low intensity the Z-scan data was fitted by solving the propagation equation $dI/dz' =$

$\alpha_0 I / (1 + I/I_s)^{1/2}$ where I_s is the saturation intensity, α_0 is the linear absorption coefficient. At high intensity the data was fitted by solving the propagation equation $dI/dz' = \alpha_0 I / (1 + I/I_s)^{1/2} + \beta I^2$ where β is the nonlinear absorption coefficient. The change in NLO parameters upon the addition of nitro compounds was investigated further.

To understand the concentration dependence, the experiment was performed by diluting the OMP solution at lower (0.3 GW/cm^2) and higher peak intensities (2.5 GW/cm^2) indicated as OMPA1 in figure 6.7 (a) and 6.7 (b). The same volume of solvent (acetonitrile) was added and we found the NLO coefficients for OMPA1 were decreasing when compared to original solution OMP1. When the nitro compounds were added there was a reverse trend observed in the data. The I_s [37] value of OMP decreased from $3 \times 10^6 \text{ W/cm}^2$ (OMP1) to $2.0 \times 10^6 \text{ W/cm}^2$ (OMPA1) further to the addition of acetonitrile. The I_s value of OMP after the addition of acetonitrile was compared with that of OMP with the addition of C, R, T solutions and found that it increased from $2.0 \times 10^6 \text{ W/cm}^2$ (OMPA1) to $2.8 \times 10^6 \text{ W/cm}^2$ (OMPR1). At higher energies the I_s value increased whereas the β value decreased.

A similar trend was observed in the studies performed with 1:40 molar ratio solutions. The NLO parameters are given in table 6.2. The value of I_s changed from $1.8 \times 10^6 \text{ W/cm}^2$ (OMPA') to $3.0 \times 10^6 \text{ W/cm}^2$ (OMPR') at lower energies (peak intensities) and $7 \times 10^5 \text{ W/cm}^2$ (OMPA') to $9.0 \times 10^5 \text{ W/cm}^2$ (OMPR') at higher energies (peak intensities). The β value decreased from $8 \times 10^{-10} \text{ cm/W}$ (OMPA') to $7 \times 10^{-10} \text{ cm/W}$ (OMPT'). The values estimated from these measurements have an error of $\pm 5\%$ owing to the uncertainties in fitting procedures, laser fluctuations, etc. The changes in coefficients obtained were higher the error bars in these experiments.

Sample	1:30 (Molar Ratio)		Sample	1:20 (Molar Ratio)			Sample	1:40 (Molar Ratio)		
	$I_{00}=0.3 \text{ GW/cm}^2$	$I_{00}=2.5 \text{ GW/cm}^2$		$I_{00}=0.3 \text{ GW/cm}^2$	$I_{00}=2.5 \text{ GW/cm}^2$			$I_{00}=0.3 \text{ GW/cm}^2$	$I_{00}=2.5 \text{ GW/cm}^2$	
	β (cm/W) $\times 10^{-8}$	β (cm/W) $\times 10^{-8}$		I_s (W/cm ²) $\times 10^6$	I_s (W/cm ²) $\times 10^5$	β (cm/W) $\times 10^{-10}$		I_s (W/cm ²) $\times 10^6$	I_s (W/cm ²) $\times 10^5$	β (cm/W) $\times 10^{-10}$
PcR1	5.0	2.8	OMPR1	2.8	9.0	7.3	OMPR'	3.0	9.0	7.6
PcT1	5.0	2.9	OMPT1	2.1	9.0	6.7	OMPT'	2.2	9.0	7.0
PcC1	5.7	3.3	OMPC1	2.4	9.0	7.2	OMPC'	2.6	9.0	7.5
PcA1 (Acetonitrile)	4.4	2.4	OMPA1 (Acetonitrile)	2.0	8.0	9.4	OMPA' (Acetonitrile)	1.8	7.0	8.0
Pc1	10	5.5	OMP1	$I_s \text{ (W/cm}^2\text{)} = 3 \times 10^6 \text{ at } I_{00} = 0.3 \text{ GW/cm}^2,$ $\beta \text{ (cm/W)} = 12 \times 10^{-10}, I_s \text{ (W/cm}^2\text{)} = 9 \times 10^5 \text{ at } 2.5 \text{ GW/cm}^2$						

Table 6.2 Nonlinear optical coefficients obtained from ns Z-scan measurements

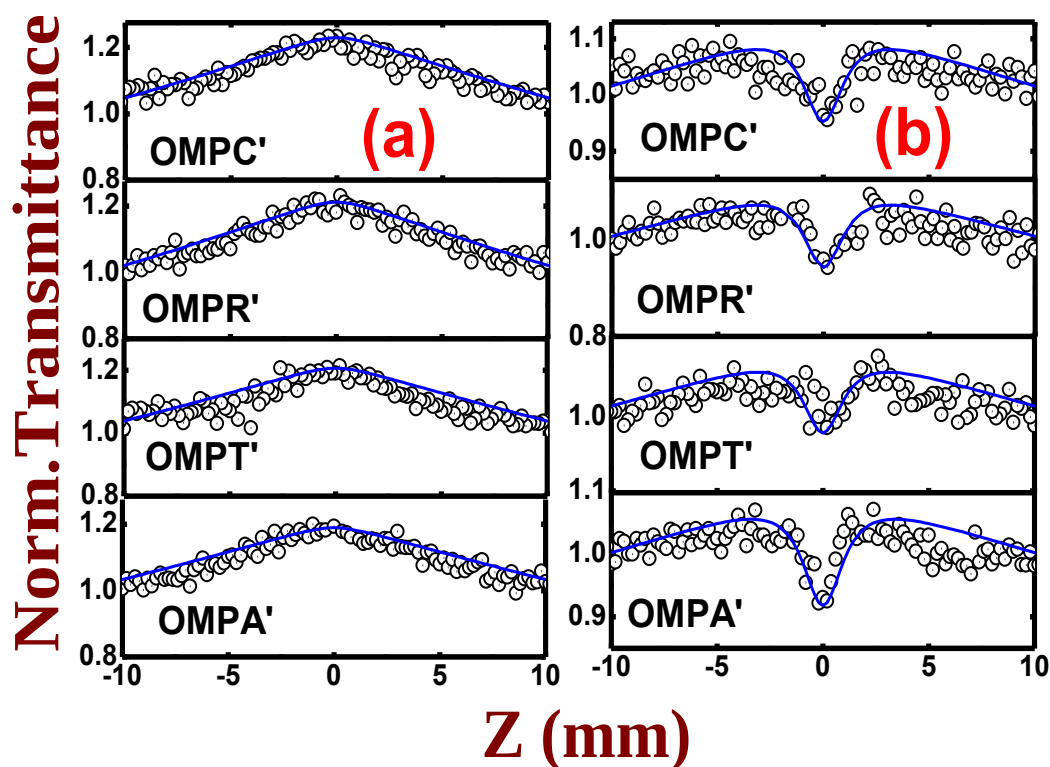


Figure 6.8 ns Z-scan measurements of OMP after the second addition of C, R, T solutions and acetonitrile solvent (denoted as OMPC', OMPR', OMPT', OMPA' respectively) (a) data recorded using $\sim 0.3 \text{ GW/cm}^2$ (b) data recorded using $\sim 2.5 \text{ GW/cm}^2$. After addition of NCs, the concentration of OMP solution was 0.19 mM and that of additives were $\sim 7.3 \text{ mM}$ in the mixture.

6.3.3 Fs degenerate pump-probe measurements

The degenerate pump probe measurements were performed at the emission band of the corresponding molecules. Figures 6.9 depict the fs pump probe measurements of Pc at 700 nm with and without the presence of the binder molecules. For a 300 ps scan range, at 0.5 ps step size, the time taken for the whole scan was 50 minutes. During this period, there could be fluctuations in the input laser power leading to fluctuations in the data collected near 100 ps and 280 ps in figure 6.9. However, the overall fit for the data was reasonably good. Pc2 represents the fs data of Pc solution of 0.6 mM concentration without adding the quencher solutions and PcR2, PcT2, PcC2 represent the measurements of Pc after adding C, R, T solutions, respectively. The differential transmittance demonstrated a positive rise followed by decay. Though the probe wavelength was within emission band, Pc still had resonance absorption at 700 nm which suggests that the pump probe signal had contribution from photo bleach as well as stimulated emission. Bellier et al. also observed similar observations in which the

one photon absorption is strongly dominated by stimulated emission [38]. The decay profile was fitted with single exponential function. The decay constant provided the rate of change of excited state population and it decreased as we added the quencher molecules. The decay constants are summarized in table 6.3. The Pc depicted a decay constant of ~ 1.9 ns (Pc2) which quenched to ~ 381 ps (PcT2) in the presence of TNT solution. Kumar et al. have reported that these phthalocyanine molecules possess radiative lifetime of ~ 6.31 ns [39]. The lifetime measured with our pump-probe experiments probably has predominant contribution from the radiative decay part (S_1 to S_0) with contribution from non-radiative part also [34].

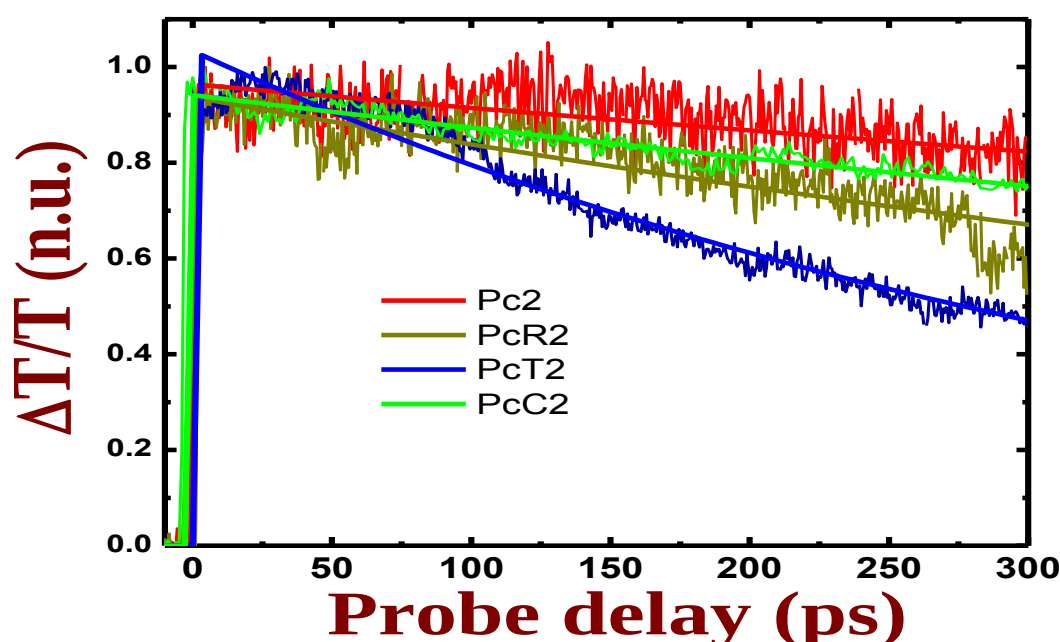


Figure 6.9 Degenerate fs pump probe measurements (near 700 nm) of Pc solution before and after adding C, R, T solutions (denoted as Pc2, PcC2, PcR2, PcT2, respectively). The concentration of Pc solution was ~ 0.6 mM (in Pc2) and after the addition of NCs the concentration of Pc was ~ 0.3 mM and that of NCs were ~ 5 mM. Wiggly lines are the experimental data while the solid lines are the theoretical fits.

Sample	τ_1 (ps)	τ_2 (ps)	Sample	τ_1 (ps)
OMP2	11(34%)	270(65%)	Pc2	1900
OMPR2	1.8(57%)	129(42%)	PcR2	896
OMPT2	2.0 (24%)	170(69%)	PcT2	381
OMPC2	9.0 (50%)	153(50%)	PcC2	1300

Table 6.3 The non-radiative decay constants (and their weights in the brackets) from fs pump probe measurements.

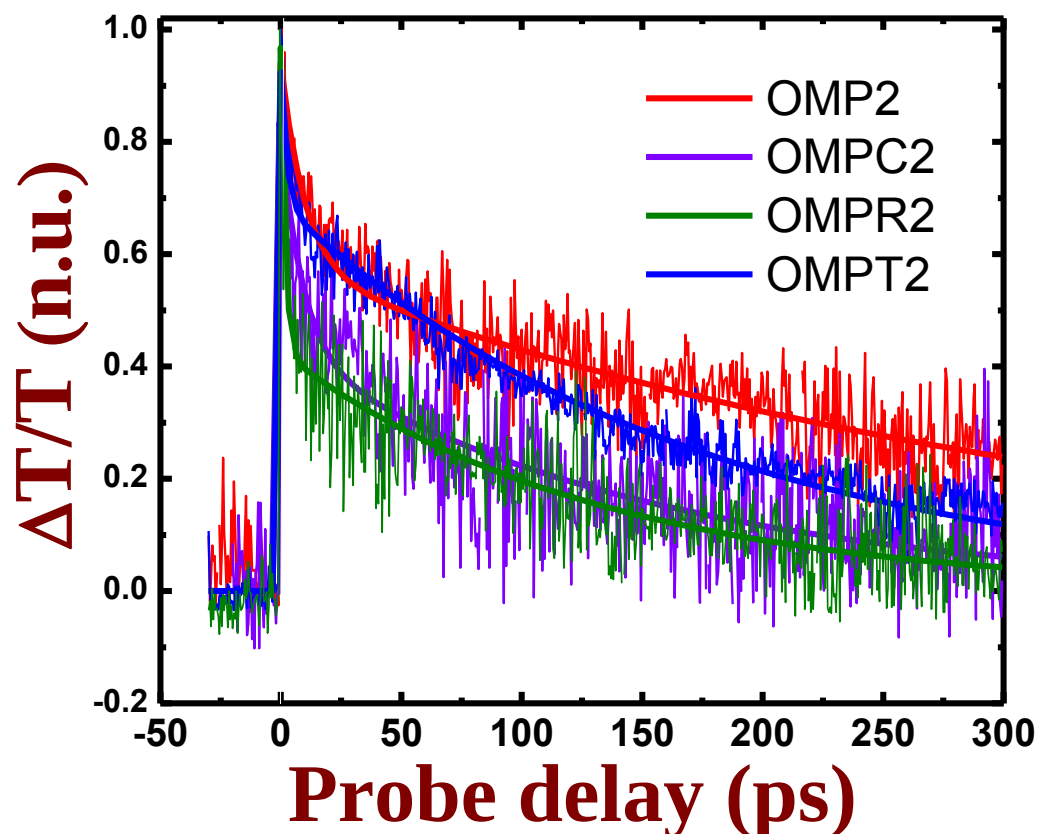


Figure 6.10 Degenerate fs pump probe measurements (near 690 nm) of OMP solution before and after adding C, R, T solutions (denoted as OMP2, OMPC2, OMPR2, OMPT2, respectively). The concentration of OMP solution was ~ 1 mM (in OMP2) and after the addition of NCs the concentration of OMP was ~ 0.5 mM and that of NCs were ~ 5 mM. Wiggly lines are the experimental data while the solid lines are the theoretical fits

Figures 6.10 illustrates the pump-probe data OMP solution before and after adding C, R, T solutions (denoted as OMP2, OMPC2, OMPR2, OMPT2, respectively). The data was fitted to a double exponential decay. The fast decay component could be attributed to the inter-molecular vibrational relaxation from high lying excited states to the lowest lying excited state and the slow decay component could be assigned to the relaxation from S_1 (first excited) states to the S_0 (ground) states either by (a) non-radiative decay directly to ground state or (b) to lowest triplet states and later to ground states. Both the decays were affected by the addition of nitro-compounds. The fast decay time was observed to be quenched from ~ 11 ps (OMP2) to ~ 1.8 ps (OMPR2) and the slow component was modified from ~ 270 ps (OMP2) to ~ 129 ps (OMPR2). Earlier we had reported the radiative lifetime of OMP to be ~ 3.77 ns [6]. Again, there could be a small component of radiative lifetime involved in these data, which we were unable to decouple from the present pump probe measurements. To comprehend and

explain the changes in NLA coefficient, we simulated ns Z-scan results with similar experimental conditions. Figure 6.11 shows the simulation data obtained for a typical molecule such as porphyrin or phthalocyanine. The simulation involved solving the rate equations and propagation equation [40]. Figure 6.12 shows all the possible transitions of the carrier population. Typically the ns pulse excitation involves transitions from S_0 levels to S_1 levels with cross-section σ_{s0} and S_1 states to S_n states with cross-section σ_{s1} . The subsequent relaxation may include transition from S_n states to S_1 states which is very fast compared to the duration of input pulse (ns) and from S_1 states the molecule may undergo internal conversion to S_0 through radiative and/or non-radiative transition. There is also a possibility of intersystem crossing from S_1 states to a triplet state, T_0 , depending on the spin orbit coupling. The triplet states (T_1) are generally populated through intersystem crossing from S_1 states to T_0 states. When the lifetime of S_1 quenches the population in S_1 state gets transferred to the new state. In other words, the excited state population is transferred to the triplet state or an intermediate state. Simplifying the above levels we considered three levels (level 1, level 2 and level 3) where level 1 involves the ground state S_0 , level 2 involves a combination of S_1 and the triplet state T_0 and level 3 involves all the high lying excited states. The ground state cross-section σ_g gives the probability of transition from level 1 to level 2 and the excited state cross-section σ_{ex} provides the probability of transition from level 2 to level 3 including the triplet states contribution. The relaxation time τ_2 from level 3 to level 2 is considered to be fast (typically <100 fs and can be ignored for ns excitation) and the decay time τ_1 from level 2 to level 1 was considered to encompass both radiative and non-radiative parts. The laser wavelength was chosen to be 532 nm with pulse duration of ~ 5 ns and input energy as 10 μ J.

Case I scenario:

Figure 6.11 (a) shows the simulated trace for following photo-physical parameters: $\sigma_g = 3.2 \times 10^{-17} \text{ cm}^2$, $\sigma_{ex} = 2.0 \times 10^{-17} \text{ cm}^2$, $\tau_1 = 2 \text{ ns}$, $\tau_2 = 2 \text{ ps}$. SA was observed since $\sigma_g > \sigma_{ex}$ and the saturation intensity I_s can be estimated as $I_s = h\nu/\sigma\tau$ where σ is the ground state cross-section and τ is the decay time of level 2. The dependence of I_s on τ is obvious from the above expression. The decrement of τ (due to quenching of fluorescence) in the presence of explosive molecules

causes an increase in I_s and it was observed experimentally from fs pump probe of measurements and ns open aperture Z-scan data, respectively in the OMP molecule (in the case of lower peak intensities). This presents only a qualitative elucidation of the observed results.

Case II scenario:

In case of RSA, the photo-physical parameters used for simulating the Z-scan data were $\sigma_g = 0.7 \times 10^{-17} \text{ cm}^2$, $\sigma_{ex} = 1.0 \times 10^{-17} \text{ cm}^2$, $\tau_1 = 2 \text{ ns}$, $\tau_2 = 2 \text{ ps}$. As the lifetime, τ_1 , was decreased the NLA was also found to decrease as shown in the data presented in figure 6.11 (b). However, experimentally we observed that the ' β ' value increased in the case of PcR1, PcT1 and PcC1 (i.e. in the presence of the quencher molecules) when compared with PcA1. We believe that the decay time of S_1 state and the excited state cross-sections play an equally important role in such interactions. In the presence of quencher molecules the lifetime of S_1 state was reduced (supported from the data of pump-probe measurements) which suggests the increase in possibility of population being transferred to triplet states. In such molecules it is well established that triplet state cross-sections are stronger than the singlet state cross-sections and moreover the excitation is with ns pulses in the present case [41, 42]. Therefore, the triplet cross-section influences the population and we observe an increase in the β value (here ' β ' is an *effective* nonlinear absorption coefficient). In such molecules two-photon absorption observed with ns excitation has contribution from singlet and excited states with predominant contribution from triplet states while with ps excitation the predominant contribution is expected from singlet states [41,42]. We simulated the open aperture Z-scan results by increasing the excited state cross-section using the parameters: $\sigma_g = 0.7 \times 10^{-17} \text{ cm}^2$, $\sigma_{ex} = 1.0 \times 10^{-17} \text{ cm}^2$, $\tau_1 = 2 \text{ ns}$, $\tau_2 = 2 \text{ ps}$ [data presented in figure 6.11 (c)] and found that the NLA coefficient was increasing which was in agreement with the observed experimental data.

Case III scenario:

In the case of higher peak intensity studies SA and RSA were simultaneously observed and the obtained parameters from the fits to experimental data were I_s and β . The I_s value increased and the β value decreased. Here, the formation of RSA is due to the transition of population from S_1 to S_2 at higher

intensities. However in the presence of quencher molecule, this transition gets weakened and the β value decreases with I_s value increasing simultaneously.

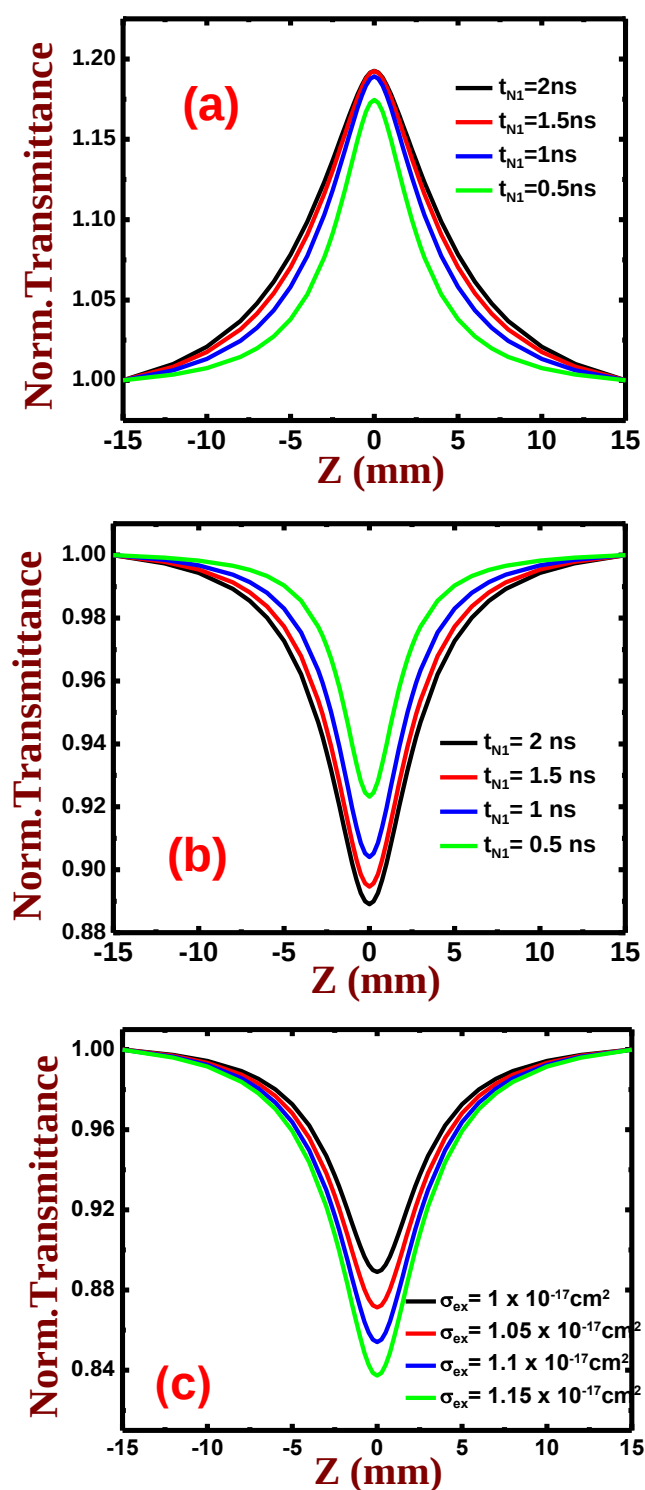
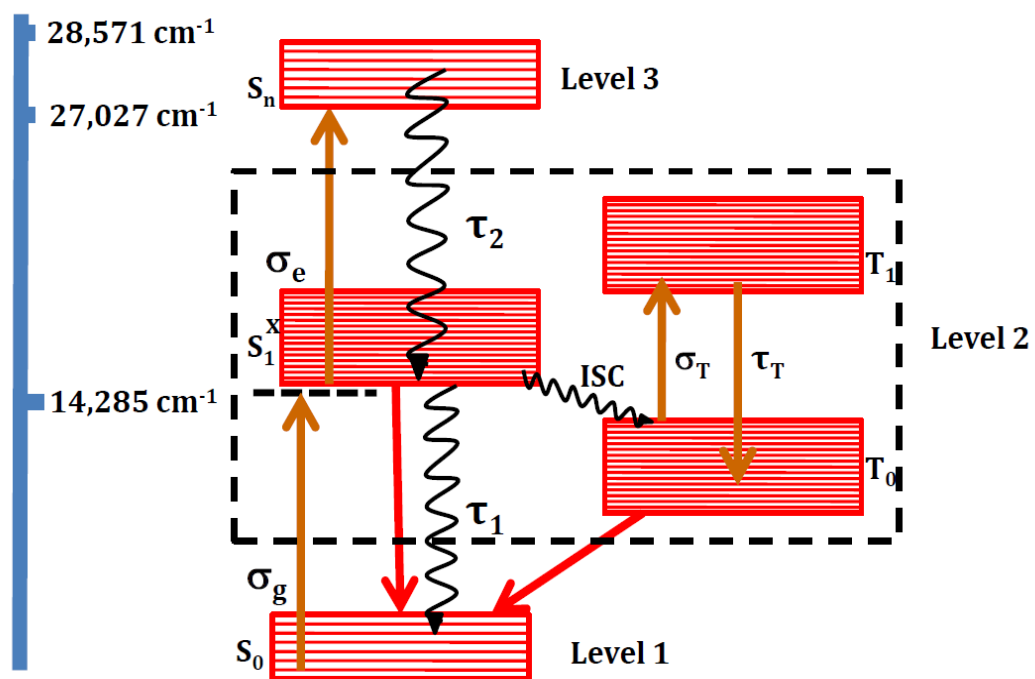
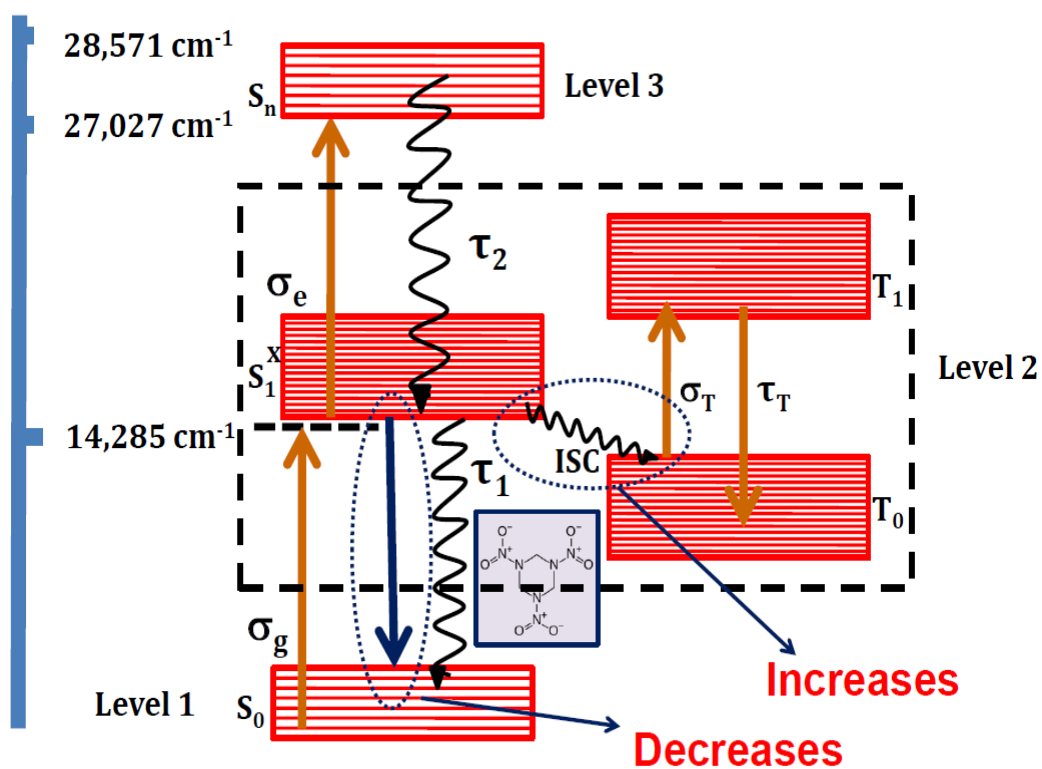


Figure 6.11 Simulated ns Z-scan results for (a) SA for $\sigma_g=3.2 \times 10^{-17} \text{ cm}^2$, $\sigma_{ex}=2.0 \times 10^{-17} \text{ cm}^2$, $\tau_1=2 \text{ ns}$, 1.5 ns , 1 ns , 0.5 ns , $\tau_2=2 \text{ ps}$ (b) RSA for $\sigma_g=0.71 \times 10^{-17} \text{ cm}^2$, $\sigma_{ex}=1 \times 10^{-17} \text{ cm}^2$, $\tau_1=2 \text{ ns}$, 1.5 ns , 1 ns , 0.5 ns , $\tau_2=2 \text{ ps}$ (c) RSA for $\sigma_g=0.71 \times 10^{-17} \text{ cm}^2$, $\sigma_{ex}=1 \times 10^{-17} \text{ cm}^2$, $1.05 \times 10^{-17} \text{ cm}^2$, $1.1 \times 10^{-17} \text{ cm}^2$, $1.15 \times 10^{-17} \text{ cm}^2$, $\tau_1=2 \text{ ns}$, $\tau_2=2 \text{ ps}$.



(a)



(b)

Figure 6.12 Energy level diagram involving transitions with ns pulse excitation.

We can summarize the following from our experimental data and a qualitative analysis.

- (a) We observed that the ' β ' value increased in the case of PcR1, PcT1 and PcC1 (i.e. in the presence of the quencher molecules) when compared with PcA1. We believe that the change in life time of S_1 state and the excited state cross-sections play an equally important role in such interactions. In the presence of quencher molecules the lifetime of S_1 state was reduced (supported by the pump-probe data) which suggests the increase in possibility of population being transferred to triplet states [see an effective energy level diagram (figure 6.12) of such molecules in the presence and absence of an explosive molecule]. In such molecules it is well established that triplet state cross-sections are stronger than the singlet state cross-sections and moreover the excitation is with ns pulses in the present case. Therefore, the triplet cross-section influences the population in excited state and we observe an increase in the β (an effective NLA coefficient) value. In the possible scenario of population coming back to ground state via non-radiative decay only (i.e. no triplet contribution) the NLA coefficient should decrease, which was not observed in our case.
- (b) The decrement of S_1 state lifetime (due to quenching of fluorescence) in the presence of explosive molecules causes an increase in I_s and it was observed experimentally from the open aperture Z-scan data for OMP molecule (lower peak intensities).
- (c) In the case of higher peak intensity studies for OMP, SA and RSA were simultaneously observed and I_s , β were obtained from the fits to experimental data. The I_s value increased and the β value decreased. Here, the formation of RSA could be due to the transition of population from S_1 to S_2 states (and T_0 to T_n states) since higher peak intensities are involved. However, in the presence of quencher molecule, this transition gets weakened and the β value decreases with I_s value increasing simultaneously.
- (d) From the data presented in tables 6.2 (life time data) and the table 6.1 (NLO coefficients) it is evident that the largest change in nonlinear absorption was observed for Pc molecules with the presence of TNT and CL-20 (both the input peak intensities) and, correspondingly, the largest change in life times

was also observed for PcT2 and PcC2 (though PcR2 also demonstrated large change in lifetime). Similarly, the largest change in NLO coefficients (for both lower and higher peak intensities) was observed for OMP with R and C and, consistently, the largest change in lifetime was observed for OMPR2 and OMPC2. This clearly suggests a strong correlation between the quenching dynamics and the nonlinear absorption in Pc and OMP in the presence of explosive molecules. We cannot rule out the possibility of fluorescence quenching and reduction in lifetimes of S_1 state due to aggregation related effects. With limited data at our disposal we cannot completely rule out the possibility of aggregation. Further detailed studies are essential, and will be taken up in future, for supporting these arguments.

- (e) We had performed simulation experiments as shown in figure 6.11 and the results could qualitatively explain the increase in NLA coefficients in the presence of explosive molecules.
- (f) From the steady-state fluorescence measurements of OMP and Pc, the fluorescence of OMP was quenching while titrating with T, R, C and was in accordance with the previous report [19] while the fluorescence quenching in Pc was not as significant as that of OMP. These experiments had been conducted only at lower concentrations of typically 6 μM . At higher concentrations (100 μM and above) the emission will also be quenched for different reasons (e.g. aggregation) and further there was an indication of non-fluorescent ground state complex formation thereby rendering the analysis to be convoluted. Further, at concentrations (similar to those used in Z-scan and pump-probe experiments) we could observe the formation of complexes [24] in these molecules rendering the data unfit for comparison and analysis.

It has been recently reported that the quantum of quenching depends on the type of explosive molecule [24]. Further studies with a range of explosive molecules (e.g. Picric acid where the quenching has been observed to be significant with different porphyrin and phthalocyanine molecules [24-25]) are required to completely understand the quenching mechanism. Detailed measurements with white light (transient absorption studies) are required to understand the complex dynamics thoroughly. Fluorescence quenching, Z-scan,

pump-probe measurements should be performed at similar concentrations (avoiding aggregation and other unwanted effects such as complex formation) and support from simulations will unquestionably provide an insight into the correlation between quantity and type of explosive molecule present and the nonlinear absorption changes. Furthermore, if these fluorophore (porphyrins, phthalocyanines) are appropriately designed and thoroughly optimized the Z-scan could be a potential technique for screening explosive molecules.

6.4 Conclusions

In summary, we have attempted studying the dynamics of fluorophore and nitro rich energetic molecules using ns Z-scan and fs pump probe techniques. Being a NLO active material, OMP found to exhibit SA at lower energies and RSA in SA at higher energies whereas tetra tert butyl Phthalocyanine was showing RSA. The nonlinear optical coefficients, I_s and β were observed to be changing in the presence of quencher molecules and the non-radiative decay was found to be reduced in all cases. The mechanisms of SA and RSA in the presence of quencher molecules were explained in detail. A deeper understanding of excited state dynamics is required for transforming these studies into sensing applications.



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CHAPTER 7

Conclusion and Future scope

7.1. Conclusions

To understand and elucidate the first few steps (sub-nanosecond time scales) of an explosion (or decomposition) process in a microscopic level is challenging and several attempts have been made in the past years. The decomposition/dissociation of energetic molecules into smaller molecules can be thoroughly understood only if we can probe these phenomena which occur in picosecond (ps) and femtosecond (fs) time scales using various time-resolved optical spectroscopic techniques. The use of time resolved studies such as pump-probe techniques, CARS, time-resolved IR spectroscopy can investigate these short lived phenomena. At ACRHEM our endeavor was to initiate these studies and towards this we started setting up simple pump-probe experiments and understand/interpret the dynamics of electronic excited states of simple organic molecules. Further we planned to extend these studies to IR-pump visible probe experiments which help us analyze the excited state vibrational dynamics of energetic molecules. We had initiated these studies by building indigenous time-resolved spectroscopic techniques and optimized those with the help of novel organic molecular systems. We are now confident of analyzing and interpreting the data obtained from these pump-probe experiments (including degenerate, non-degenerate, white light probe techniques etc.)

Several organic and organometallic compounds have been engineered with various structural modifications so as to achieve the required optical properties which are desired for particular photonic application such as explosive sensing, light harvesting etc. The key feature of all these applications is the interaction of the compounds with light and their fast response. Most of the organic conjugate compounds which are considered to the heart of the photonic devices, have large number of delocalized π electrons with which the NLO properties and excited state dynamics can be tailored. Thus it became pertinent to understand the photo excitation and subsequent relaxation of molecules (in liquid & solid form) in ultrafast time domain. In order to understand these ultrafast processes time resolved spectroscopy has been developed with various techniques since the conventional detectors are not fast enough to measure the events. In this context pump-probe spectroscopy, in ultrashort time domain, is the best choice in which

the temporal resolution depends on the duration of pump and probe pulses and the response time of detector is insignificant.

The motivation of the thesis was to develop and optimize the pump- probe and Z-scan techniques to explore the ultrafast dynamics of various molecules which provide information in understanding the excited state dynamics of different explosive molecule. In the absence of a transient absorption system, wherein a white light probe is present and provides the complete information on excited state absorption across the visible spectrum, Z-scan is a simple method to investigate the excited state processes. Further, with the Z-scan data one could evaluate the efficacy of organic materials towards various applications such as optical limiting and sensing. There are various types of pump probe techniques with which we can study electronically, vibrationally excited states of particular molecule. In the present thesis, we focused on understanding the electronic excitations and the following dynamics. Further, the interactions of novel organic molecules with prominent explosive molecules were studied. Some of the suggestions and future scope are discussed here to improve the current approach so as to develop efficient methods and engineer novel organic molecules towards screening the explosive molecule for sensing applications. The significant conclusions from the thesis can be summarized as follows:

- ✚ Ultrafast pump-probe techniques have been emerged in various configurations to understand the initial stages of molecular excitation and the subsequent decay dynamics. These techniques overtake the conventional electronic detectors through its powerful and sensitive measurements in sub-picosecond dynamic in materials. While pump probe measurements provide temporal information of particular excited state, Z-scan technique give the rate of change of the population of that particular state in the case of a nonlinear material. Hence both techniques can be used hand in hand to understand the various mechanisms occurring in a compound after photo excitation. In the view of end user of energetic materials, this information is important since the contribution of initial stages of decomposition of energetic materials can be explained with

photo-physics and the ultimate goal of such measurements help to design efficient energetic molecules or devices.

- ✚ The excited state dynamics of newly synthesized conjugate organic compounds such as corroles, Naphthosapphyrins, porphyrins and phthalocyanine were studied using ps/fs pump-probe technique and Z-scan technique. Phthalocyanines, Corroles, Naphthosapphyrins are tailored from the compounds belonging to the family of Porphyrins and expanded Porphyrins and such class of compounds can be used in chemo-sensing, organic photovoltaics, optical limiting, etc.
- ✚ The pump-probe experimental set up was optimized using SI-GaAs and LT-GaAs samples which possess ultrafast decay times and are widely used in preparing photo conducting antenna to generate terahertz pulses. The reflection geometry of ps and fs pump probe experimental set up was used. It was found that the relaxation time is in the order of ~ 100 ps for SI-GaAs and 20 ps for LT-GaAs and the setup was optimized to study the organic compounds. The pulse duration was measured by intensity autocorrelation using BBO crystal of 2 mm thickness. The GVD effects usually broaden the pulse duration of the actual pulses.
- ✚ In case of the Corroles, two-photon absorption was the dominant mechanism observed at higher peak intensities contributing to the third order nonlinearity. The excited state dynamics of Corroles, studied using degenerate ps pump-probe technique were found to possess double exponential decay constants with all the time scales in the ps domain. The observation of short lived excited state lifetime of S_1 , in the range of 54-286 ps. The resonant excitation with 600 nm photon, showed single exponential decay which corresponds to S_1 to S_0 transition.
- ✚ In the case of Naphthosapphyrins, non-degenerate pump-probe technique was employed in which the molecules were excited with 400 nm pump and probed with 800 nm. A selective excitation was accomplished via non-degenerate pump probe technique. The non-radiative decay times were

obtained from non-degenerate pump probe studies and the radiative life times were obtained from time correlated single photon counting indicating a significant contribution of non-radiative channel in the decay. The degenerate pump probe measurement at lower energies ($\sim 100 \text{ GW/cm}^2$), depicted autocorrelation type of signal which suggests that there could be either a faster relaxation than the pulse duration while at higher energies ($\sim 175 \text{ GW/cm}^2$), the intensity was sufficient to excite the two photon resonant states (S_2 states) and the decay was comprised of two components i.e. the transitions from S_2 to S_1 followed by S_1 to S_0 .

✚ The interaction of nitro compounds (NCs) with octamethyl porphyrin and tetratertbutyl phthalocyanine moieties altered their nonlinear absorption properties and excited state dynamics in the ultrafast time scale. These studies clearly revealed that the ultrafast decay times as well as the excited state cross-section play an important role in the interaction mechanism of NC's with Porphyrin and Phthalocyanine molecule. The change in nonlinear absorption (saturable absorption mechanism in the case of OMP and reverse saturable absorption mechanism in case of PC) of these molecules was monitored using the standard open aperture Z-scan technique recorded with nanosecond (ns) pulses at 532 nm. The change in non-radiative decay time was studied by fs pump probe measurements in the 600-700 nm spectral range. The nonlinear optical coefficients, I_s and β were observed to be elevating in the presence of quencher molecules while the non-radiative decay was found to be reduced in all cases.

✚ Dicyclopentadiene which has been used in rocket propulsion as a binder, found interest to explore the temporal dynamics (T. Goswami et al. Chem. Phys. Lett. 558, 1-7, 2013). Here, we have performed the preliminary measurements of fs degenerate pump-probe experiment at 800 nm and found that the decay time constant to be $\sim 97 \text{ fs}$. The data is shown in figure 7.1. Since the pulse duration is also within this time domain, it is clear that the decay is much faster. Further experiments (using transient absorption spectrometer) are required to analyze the dynamics completely.

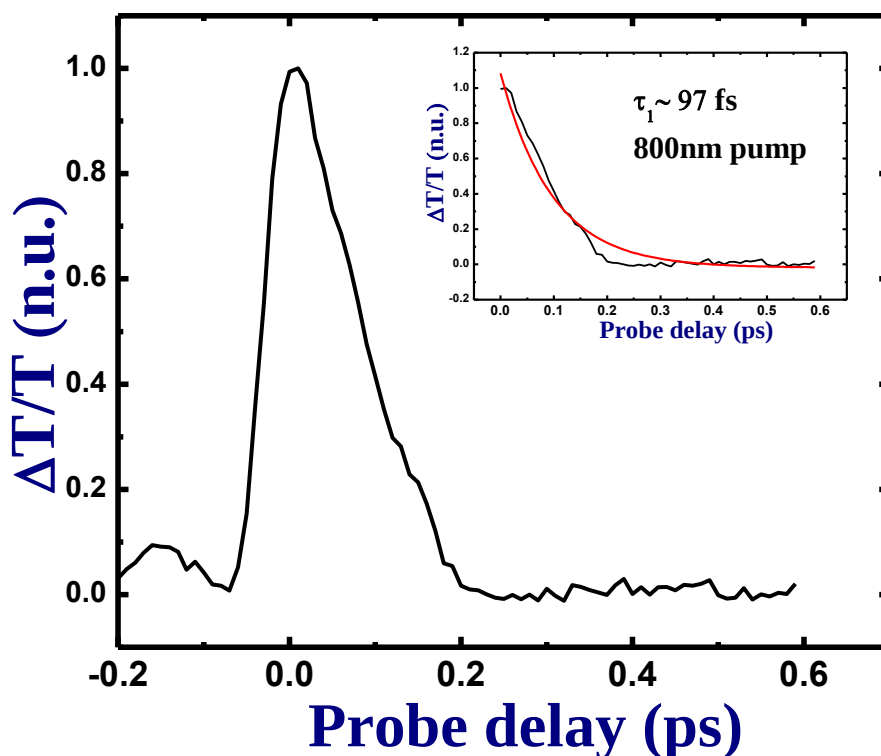


Figure.7.1 Femtosecond degenerate pump probe experimental data of DCPD at 800 nm.

7.2. Future challenges

Ultrashort laser pulses are widely utilized in ultrafast time-resolved spectroscopy which helps the scientists to unravel various quantum mechanical processes in condensed matter systems. However, these studies can only provide the temporal information which can be considered as one dimensional. Further multi-dimensional approach has to be undertaken to gather information on chemical dynamics, molecular structure, intra molecular energy transport, and many body interactions. For example, the improvisation of current pump-probe experimental set up to visible/IR pump and white light/IR or terahertz probe results time and frequency resolved pump-probe data could provide a complete photo physical picture of the excited states. Further, multiple laser pulses can be used to gather information on frequency as well as phase. The general form of this two dimensional (2D) spectroscopy is the three pulse transient four wave mixing. The scattered pulse or the fourth pulse is resolved in time with respect to a reference pulse. All these challenges open up new window to access the hitherto untapped information of chemical changes in molecular systems with unprecedented time resolution and energy scales. The second important aspect

which is an outcome from this thesis are some of the studies on the excited state dynamics of molecules which are extensively used in sensing explosives based on fluorescence quenching technique. Very recently (Nature Commun. 6, Article number: 8240, 2015; doi:10.1038/ncomms9240) it was pointed out that ultrafast spectroscopic studies are necessary to understand the quenching dynamics and such studies are essential for designing novel efficient sensing molecules. We could extend the studies carried out in this thesis further by performing transient absorption studies of all novel chromophores used in fluorescence quenching based detection.



“Science is an organized knowledge with no boundries so the search has to continue”

-Anonymous

Appendix I

Publications included in thesis:

1. **Anusha, P.T.**; Thomas, A.R.; Philip, R.; VenugopalRao, S.; *Chem. Phys. Lett.* **2015**, <http://dx.doi.org/10.1016/j.cplett.2015.10.049>.
2. Sarma, T.; **Anusha, P. T.**; Pabbathi, A.; Venugopal Rao, S.; Panda, P. K.; Naphthobipyrrole-derived sapphyrins: Rational synthesis, characterization, nonlinear optical properties, and excited state dynamics. *Chem. Eur. J.* **2014**, *20*(47), 15561-15570.
3. **Anusha, P. T.**; Sarma, T.; Panda, P. K.; Venugopal Rao, S.; Ultrafast dynamics of Naphthosapphyrins: Degenerate and Non-degenerate Pump-Probe Studies *OSA Technical digest, Frontiers in Optics 2013 paper FW1A*. 4(FIO, Florida, USA).
4. **Anusha, P.T.**; Tewari, S. P.; Venugopal Rao, S.; Ultrafast Dynamics of SI-GaAs and LT-GaAs by Degenerate Pump-Probe Studies *OSA Technical digest, Laser Science paper 2013 LW5I.3* (LS, Florida, USA).
5. **Anusha, P. T.**; Swain, D.; Hamad, S.; Giribabu, L.; Prashant, T. S.; Tewari, S. P.; Venugopal Rao, S.; Ultrafast excited state dynamics and third order optical nonlinearities of novel Corroles. *J. Phys. Chem. C*, **2012**, *116*, 17828-17837.
6. Venugopal Rao, S.; **Anusha, P.T.**; Tewari, S. P.; Ultrafast Dynamics of SI-GaAs and LT-GaAs *OSA Technical digest International conference on fiber optics and photonics 2012 TPo 5* (Chennai, India).
7. Venugopal Rao, S.; **Anusha, P.T.**; Prashant, T. S.; Swain, D.; Tewari, S. P.; Ultrafast Nonlinear Optical and Optical Limiting Properties of Phthalocyanine Thin Films Studied Using Z-Scan *Mat. Sci. and Applns.* **2011**, *2*, 299-306.
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9. **Anusha, P. T.**; Reeta, P. S.; Giribabu, L.; Tewari, S. P.; Venugopal Rao, S.; Picosecond nonlinear optical studies of unsymmetrical alkyl and alkoxy phthalocyanines *Mat. Lett.* **2010**, *64*, 1915-1917.

Other Publications: (Not included in the present thesis)

10. Swain, D.; **Anusha, P. T.**; Prashant, T.; Tewari, S. P.; Sarma, T.; Panda, P. K.; Venugopal Rao, S.; Ultrafast excited state dynamics and dispersion

- studies of nonlinear optical properties in Dinaphthoporphycenes. *Appl. Phys. Lett.* **2012**, *100*, 141109.
11. Sarma, T.; Panda, P. K.; **Anusha, P. T.**; Venugopal Rao, S.; Dinaphthoporphycenes: Synthesis and nonlinear optical properties. *Org. Lett.* **2011**, *13*, 188-191.
 12. Swain, D.; **Anusha, P. T.**; Sarma, T.; Panda, P. K.; Venugopal Rao, S.; Dispersion studies of optical nonlinearity and excited state dynamics in Cyclo[4]naphthobipyrroles. *Chem. Phys. Lett.* **2013**, *580*, 73-77.

International/National Conference Papers:

1. Theoretical and Experimental nonlinear absorption studies in the presence of High Energy Materials: A case study of Phthalocyanine.
Anusha, P.T.; Giribabu, L.; Venugopal Rao, S.; *9th International High Energy Materials Conference and Exhibits, 2014* (VSSC, Thiruvananthapuram, India) (*Oral presentation - Best Paper Award*).
2. Ultrafast dynamics of Naphthosapphyrins: Degenerate and Non-degenerate Pump-Probe Studies.
Anusha, P.T.; Sarma, T.; Panda, P. K.; Venugopal Rao, S.; *OSA Technical digest, Frontiers in Optics 2013 paper FW1A. 4*(FIO, Florida, USA) (*Selected for Oral presentation*).
3. Ultrafast Dynamics of SI-GaAs and LT-GaAs by Degenerate Pump-Probe Studies.
Anusha, P.T.; Tewari, S. P.; Venugopal Rao, S.; *OSA Technical digest, Laser Science paper 2013 LW5I.3* (LS, Florida, USA). (*Selected for Oral presentation*)
4. Ultrafast Degenerate Pump-Probe Studies of SI-GaAs & LT-GaAs.
Anusha, P.T.; Tewari, S. P.; Venugopal Rao, S.; *PHOTONICS 2012* (IIT Madras, Chennai, India), during 10th to 12th December.
5. Ultrafast excited state dynamics and third order optical nonlinearities of novel Corroles.
Anusha, P.T.; Debasis, S.; Hamed, S.; Giribabu, L.; Tewari, S.P.; Venugopal Rao, S.; *DAE-BRNS National Laser Symposium (NLS-21) 2012* (Anna University, Chennai, India) during 9th -12th January.
6. Femtosecond pump-probe spectroscopy of novel Corroles.
Dabasis, S.; **Anusha, P.T.**; Hamad, S.; Giribabu, L.; Tewari, S.P.; Venugopal Rao, S.; *AIP Conf. Proc. (FUNCTIONAL MATERIALS: Proceedings of the International Workshop on Functional Materials), 2012*, 1461, 363-366.
7. Ultrafast nonlinear optical studies of Cyclo [4] naphthobipyrroles.

- Anusha, P.T.;** Debasis, S.; Sarma, T.; Panda, P. K.; Venugopal Rao, S.; *Nonlinear Optics and Applications VI*, **2012**, *Proc. SPIE Vol. 8434* (SPIE, Bellingham, WA), 84341D 2012.
8. Ultrafast excited state dynamics and dispersion studies of third order optical non-linearities in novel Corroles.
Anusha, P.T.; Debasis, S.; Hamad, S.; Giribabu, L.; Tewari, S.P.; Venugopal Rao, S.; *International OSA Network of Students (IONS)*, **2012** (IIT Madras, Chennai, India) during 7th - 8th December (*Oral presentation*).
 9. Ultrafast Degenerate Pump-Probe Studies of SI-GaAs.
Anusha P.T.; Debasis, S.; Tewari, S. P.; Venugopal Rao, S.; *XXXVI Optical Society of India Symposium on Frontiers in Optics and Photonics*, **2011** (IIT-Delhi, Delhi, India), during 3rd -5th December (*Awarded as Excellence in Poster Presentation*)
 10. Multiphoton absorption studies in porphycenes using picosecond and femtosecond pulses.
Debasis, S.; **Anusha, P.T.;** Shuvan Prashant, T.; Tewari, S. P.; Sarma, T.; Panda, P.K.; Venugopal Rao, S.; *AIP conf. Proc.* **2011**, 1391, 674-676.
 11. Ultrafast nonlinear optical properties and excited state dynamics of phthalocyanine thin films. Venugopal Rao, S.; **Anusha, P.T.;** Shuvan Prashant, T.; Debasis, S.; Tewari, S.P.; *Organic Photonic Materials and Devices XIII*, **2011**, *Proc. SPIE* 7935 (SPIE, Bellingham, WA) 793517.
 12. Large three-photon absorption in porphycenes studied using Z-scan technique with picosecond pulses.
Venugopal Rao, S.; **Anusha, P.T.;** Sarma, T.; Shuvan Prashant, T.; Tewari, S. P.; Panda, P. K.; *DAE-BRNS National Laser Symposium (NLS-19)* **2010** (RRCAT, Indore, India) during 1st – 4th December.
 13. Picosecond optical nonlinearities in symmetric and asymmetric phthalocyanines studied using the Z-scan technique.
Anusha, P.T.; Giribabu, L.; Tewari, S. P.; Venugopal Rao, S.; *DAE-BRNS National Laser Symposium (NLS-19)*, **2010** (BARC, Mumbai, India) during 13th -16th January.
 14. Ultrafast nonlinear optical studies of phthalocyanine thin films using the z-scan and pump-probe techniques.
Anusha, P.T.; Shuvan Prashant, T.; Debasis, S.; Tewari, S.P.; Venugopal Rao, S.; *PHOTONICS-2010* (IIT-Guwahati, Guwahati, India) during 11th -15th December.

Appendix II

CURRICULUM VITAE

ANUSHA PULIPARAMBIL THILAKAN

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Education

➤ **Doctor of Philosophy (Ph.D in Physics)**

Thesis submitted in November 2015.

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Thesis Title : Studies of Ultrafast Excited State Dynamics of Corroles,
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➤ **Project Assistant (2009-2010):**

Title : Non-Linear Optical Characterization using Z-scan
and DFWM Techniques

Supervisor : Dr. Soma Venugopal Rao, Associate Professor,
ACRHEM, University of Hyderabad.

➤ **Master of Sciences (M.Sc in physics, June 2009)**

University : Mahatma Gandhi University, Kottayam, Kerala.

Specialization : Material science

Project : Non-Linear Optical Characterizations of Phthalocyanines
using Z-scan and DFWM Techniques (Supervisor: Dr.
Soma Venugopal Rao, Associate Professor, ACRHEM,
University of Hyderabad.)

Percentage : 69.2%

➤ **Bachelor of Sciences (B.Sc in Physics, April 2007)**

University : St. Thomas College, Thrissur, Kerala.
(affiliated to University of Calicut, Calicut, Kerala.)

Subject : Mathematics, Physics, Chemistry

Percentage : 93.9%

➤ **Higher secondary School (June 2004)**

School : St. Aloysius Higher Secondary School, Thrissur, Kerala

Board : Board of Higher Secondary, Govt. of Kerala.

Subjects : Mathematics, Physics, Chemistry with Computer Science

Percentage : 81.3%

➤ **Secondary school (June 2002)**

School : Infant Jesus Girls High School, Thrissur, Kerala.
Board : Board of Public Examination, Govt. of Kerala.
Percentage : 89.3%

Research Experience:

- Evaluation of ps/ fs excited state dynamics of various molecular systems like Corrole, Naphthosaphyrins, Porphyrin, Porphycene and Phthalocyanine using ultrafast pump-probe spectroscopy. Typical pump-probe experiments were deployed with ps/fs lasers in degenerate and non-degenerate configuration. Autocorrelation technique was used to measure the pulse duration. Other research activities include fluorescence spectroscopy, Z-scan and Degenerate four wave mixing techniques. The results are published in **9** peer reviewed journals and presented in **14** scientific conferences.

➤ **Technical Experience:**

- Expertise in picosecond and femtosecond laser system (MICRA oscillator, LEGEND ps and fs regenerative amplifiers from COHERENT) along with the Optical parametric amplifiers (TOPAS-ps and TOPAS-C from Light Conversion).
- Expertise in intensity/ single shot autocorrelation techniques using ps and fs laser pulses.
- Practical experience with Lock-in amplifiers, IR viewers, and Liquid nitrogen cooled Mercury cadmium Telluride detectors.
- Computational experience in Simphosoft package for Z-scan simulations.
- Experience in UV/Vis absorption measurements (Perkin Elmer lamda 750) and fluorescence measurements (Fluorolog-Spectrofluorometer).
- Expertise in Transient absorption spectrometer (HELIOS)

Research Awards/Achievements:

➤ **Best Poster Award:**

For the paper entitled “Ultrafast Degenerate Pump-Probe Studies of SI-GaAs”

P.T.Anusha, Debasis Swain, Surya P. Tewari, S. Venugopal Rao in XXXVI Optical Society of India Symposium on Frontiers in Optics and Photonics December 3-5, 2011 at IIT Delhi, New Delhi, India.

➤ **Best Paper Award:**

For the paper entitled “Theoretical and Experimental nonlinear absorption studies in the presence of High Energy Materials: A case study of Phthalocyanine”

P.T. Anusha, L.Giribabu and S. Venugopal Rao in 9th International High Energy Materials Conference and Exhibits-2014 at VSSC, Thiruvananthapuram, India.

➤ **CSIR, Govt. of India, Direct Senior Research Fellowship**

Technical Skills:

- Knowledge in programming with C, C++, MATLAB, Origin.

Other Activities/Achievements:

- Active member (membership # 1018859) of OSA (Optical Society of America) student chapter of University of Hyderabad.
- Position held: President (Feb, 2013-Jan, 2014), Vice-President (Jun, 2012- Jan, 2013) of OSA student chapter, University of Hyderabad.

Workshop Attended:

- SERC School on Laser Science and Technology, 12-30th March, 2012 at RRCAT, Indore and presented on 'Modelocked Fiber lasers' under the mentorship of Dr. P.K. Mukhopadhyay.

Personal Information:

Date of birth	: 18 th September 1986.
Gender	: Female
Nationality	: Indian
Mother tongue	: Malayalam
Languages known	: English, Hindi, Malayalam, Telugu
Marital status	: single
Permanent address	: Anusha P. T., D/o Thilakan puliparambil, Puliparambil House, Elthuruth P. O. Thrissur-680611, Kerala, India.

References:

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Declaration:

I hereby declare that all the information mentioned above is best of my knowledge.

Place: Hyderabad

Date: November, 2015

ANUSHA P.T.