Chapter 1

Introduction

Ultrafast interaction of light with matter is important for both fundamental and applied science. Ultrafast phenomenon characterized at high peak intensity leads to interesting nonlinear optical (NLO) interactions in various materials which include multi-photon absorption (MPA), frequency conversion, self-phase and cross-phase modulation, solitons generation, self-focusing and phase conjugations, which provide the phenomenal capability to control ‘light with light’ that is necessary to realize ultrafast all-optical (AO) information processing [Gubler and Bosshard (2002), Forchel (2003), Steinmeyer (2003), Gust et al. (2006), Christodoulides et al. (2010), Dudley (2010), Sansone et al. (2011), Ferreira (2015)].

Femtosecond (fs) high intensity pulses not only allow time resolutions comparable with the speed of changes at the molecular level, they also deliver unique experimental capabilities and present a new range of unexplored basic phenomena. They are an indispensable tool for studying ultrafast interaction of light with matter, laser controlled chemistry, frequency metrology (stabilized frequency combs for high-precision frequency metrology and for investigations of precision optical clocks), high-speed electrical testing, laser-plasma interactions, short-wavelength generation, optical communications (signal processing, optical computing, wavelength-division-multiplexing and data detection), biomedical applications (imaging and surgery) and materials processing (cutting or drilling) [Steinmeyer (2003), Hu et al. (2003, 2005), Smirnova and Ivanov (2010), Gamaly and Rode (2013), Sinclair et al. (2014), Krausz and Stockman (2014), Panagiotopoulos et al. (2015)].

The ability to generate and control ultrashort light pulses has exciting implications for the design of future communication networks, hence ultrashort light pulses are a potential signal source in future high bit rate optical communication systems. The uses of high intense ultrashort light pulses combined with all-optical switching (AOS) and signal processing will allow future light wave communication systems to take advantage of tremendous bandwidth capacity of optical fiber transmission [Wada (2004), Dudley et al. (2007), Idachaba et al. (2014)].
Future bandwidth demand for high speed signal processing and optical communication systems will soon exceed 100 Gbits/s [Hommelhoff and Kling (2015)]. However, such systems cannot be realized without introducing ultrafast AO devices and circuits such as light sources, wavelength converters and all-optical logic (AOL) gates, since existing optoelectronic and electronic devices and integrated circuits would not be able to function at a bit rate exceeding 100 Gbits/s, because of the speed limit of conventional semiconductor materials and devices [Wada (2004), Ishikawa (2008), Hommelhoff and Kling (2015)].

Light-matter interaction forms the basis of emerging technology of new photonics based materials that can be used in all aspects of information processing: acquisition of information (through optical sensors and scanners); transmission of information (through optical fibers and erbium doped fiber amplifiers); storage of information (through optical discs and holographic memories) and processing of information (through integrated optics and opto-electronic integration) [Saleh and Teich (1991), Ghatak and Thyagarajan (1998), Menzel (2001), Peyghambarian and Norwood (2005), He et al. (2008), Clark and Lanzani (2010), Marquardt (2011), Roy (2011), Smit et al. (2012), Kuramochi et al. (2014), Fang et al. (2015)]. However, the present challenge is to increase the processing speed and storage capacity of optical systems. The electronic parts at the transmitter and receiver end limit both the speed and bit rate capacity of present-day lightwave communication systems [Roy (2011)]. On the computing front, the conventional Very Large Scale Integration (VLSI) technology is fast approaching its fundamental limits in the sub-micron miniaturization process due to continuous shrinking of the transistor dimensions on a silicon chip. Extreme ultraviolet lithography is still the main candidate for patterning integrated circuits and reaching sub-10 nm resolution at 13.5 nm within less than a decade [Tallents et al. (2010), Tucker (2011), Mojarad et al. (2015)]. Further, lithographical miniaturization introduces several problems such as hot carriers, dielectric breakdown, signal errors, cross-talk and short channel effects [Abdeldayem et al. (2008)]. As the trend towards still faster and higher capacity systems continue, it has become more necessary to perform signal processing operations with AO components that possess an ultrahigh bandwidth and can perform parallel processing functions to eliminate the electronic
bottleneck [Roy (2011)].

On the other hand, projected limits of miniaturization in electronics, energy efficiency and the exponentially growing demand for faster computing speeds and information processing has led to the evolution of new computing strategies that include, bio, molecular, quantum and optical computing [Adleman (1994), Garzon and Deaton (1999), Raymo and Giordini (2001, 2002), Raymo (2002), Raymo and Tomasulo (2006), Balzani et al. (2007), DeSilva (2008), Caulfield and Dolev (2010), Miller (2010), Carell (2011), Roy (2011)]. Among all these alternative strategies, optical computing is advantageous as it offers excellent features such as parallelism, high speed and temporal bandwidth, low signal dispersion, non-interactive behavior and high speed interaction via material [Kaku (2000), Abdeldayem (2003), Brown et al. (2004), Fleischhauer (2011), Langford et al. (2011)]. Thus, for ultrafast and ultrahigh bandwidth information processing i.e. communication and computing, it is essential to perform various functions such as generation, transmission, amplification, routing and detection of optical signals in the optical domain itself [Cotter et al. (1999), Bishop et al. (2001), Dawes et al. (2005), Sahu et al. (2011)]. To fulfill the basic requirement to realize AO information processing, it is necessary to discover new materials or to tailor the NLO molecular response of existing extremely photosensitive and efficient NLO materials. In general, the application of NLO phenomena for practical device applications is limited by the lack of high performance optical materials that exhibit various requirements such as fast response, strong nonlinearities to facilitate low-power switching, broad wavelength range, high damage threshold, low optical loss, high efficiency, low cost, flexibility to reconfigure and tune its characteristics and also ease to fabricate and integrate them into photonic systems [Prasad and Reinhardt (1990), Tutt and Bogges (1993), Fischer et al. (1995), Arivuoli (2001), Abdeldayem et al. (2003), Wada (2004), Belousova (2007), Dudley et al. (2007), Der et al. (2007), Anusha et al. (2010), Christodoulides et al. (2010), Clark and Lanzani (2010), Dudley (2010), Haque and Nelson (2010), Suresh et al. (2012), Imakita et al. (2012), Lu et al. (2015)].

A light beam does not affect the properties of another light beam when it interacts with it in free space. However, in materials under certain conditions a light beam can modulate
another light beam. This is the domain of non-linear optics where many new NLO effects are observed [Bloembergen (1996), Marder et al. (1997) Menzel (2001), Sutherland (2003), Boyd (2003), Kivshar (2008), Wiersma (2008)]. Recently, the interaction of ultra-intense ultrafast laser pulses with atoms and molecules at nanometer scale has attracted considerable attention to overcome the future demand of bandwidth and computational challenges.

NLO materials have a nonlinear response to the electric field associated with the light of a laser beam, leading to a variety of optical phenomenon such as the alteration of optical properties of the materials or the generation of new light frequencies, excited-state absorption (ESA), nonlinear absorption (NLA), nonlinear refraction (NLR), two-photon absorption (TPA) and three-photon absorption (3PA) [Balu et al. (2004), Chopra (2013), Zongo et al. (2015)]. Among these, NLA which refers to the change in the frequency dependent transmittance of a material as a function of light intensity or fluence is an important NLO phenomenon that produces many effects that form the basis of several applications in science and technology such as NLO spectroscopy, optical limiting and optical computing [Sutherland (2003), Haque and Nelson, (2010)]. Since the invention of the laser, simultaneous multi-photon absorption has been observed in different materials. At higher intensities, the probability of a material absorbing more than one photon before relaxing to the ground state gets enhanced. At sufficiently high intensities, besides MPA, the population redistribution leads to interesting counter plays of absorption and stimulated emission, complicated energy transitions in complex molecular configurations, and free carriers generation in solids. These phenomena are manifested optically in a reduced absorption i.e. saturable absorption (SA) or an increased absorption i.e. reverse saturable absorption (RSA) [Reddy (1991), Sutherland (2003), Hales et al. (2010), Chen et al. (2003, 2015), Huang et al. (2015), Singh and Bindra (2015)].

Nonlinear processes occur in abundance in nature [Christodoulides et al. (2010)]. At high input optical intensities, intensity dependent changes occur in materials due to change in the referactive index of the materials [Wang et al. (2014)]. High intensity NLA is an important NLO phenomenon that plays a vital role in ultrafast nonlinear spectroscopy. It leads to many important phenomena such as; TPA, 3PA, NLA in two level systems and ESA. The TPA, 3PA
and ESA are important fundamental phenomena for characterization of any optical materials in laser spectroscopy.

Two-photon absorption involves simultaneous absorption of two photons from an incident radiation field that results in a transition from the ground state of a system to a higher-lying state. This process involves different selection rules than those of single-photon absorption. Hence TPA spectroscopy complements linear absorption spectroscopy in studying the excited states of systems. Two possible situations are illustrated in Figure 1.1. In the first, two photons from the same optical field oscillating at frequency $\omega$ are absorbed to make the transition, which is approximately resonant at $2\omega$. In the second situation, two optical fields at frequencies $\omega_e$ and $\omega_p$ are present, and one photon from each field is absorbed for the transition, which is approximately resonant at $\omega_e + \omega_p$. The first field in this case can be thought of as the pump or excitation beam with a subscript e, while the second can be thought of as the probe beam with a subscript p [Sutherland (1996)]. In both cases, the intermediate state is not real i.e. it is virtual. Hence, the system had to absorb the two photons simultaneously, making the process sensitive to the instantaneous value of optical intensity [Sutherland (1996), Ghatak and Thyagarajan (1998), Menzel (2001)].

![Figure 1.1](image)

**Figure 1.1** Schematic diagram for TPA. (a) Self TPA and (b) Pump-probe TPA.

Although the transition does not involve a real intermediate state, there are often impurities present, which produce a small amount of linear absorption and contributes to an
additional loss mechanism [Sutherland (1996)]. Two-step absorption involving a single photon pumped intermediate state is called ESA. Single beam TPA and two beam TPA are the important part of TPA. Single beam TPA has been studied in detail in this thesis. In single beam TPA, the nonlinear absorption is proportional to the square of the instantaneous intensity. The differential equation describing the optical loss is given by,

\[
\frac{dl}{dz} = -\alpha l - \beta l^2
\]  

(1.1)

where \(\alpha\) is the linear absorption coefficient due to the presence of impurities and \(\beta\) is the TPA coefficient. The TPA coefficient \(\beta\) is a macroscopic parameter characterizing the material that is of considerable interest and is described by the TPA cross-section \(\sigma_2\). The relation between \(\beta\) and \(\sigma_2\) is given by,

\[
\sigma_2 = \frac{\hbar \omega \beta}{N}
\]  

(1.2)

where \(N\) is the number density of molecules in the system and \(\hbar \omega\) is the energy of photons in the incident optical field. The TPA coefficient is also related to the third order susceptibility and is given by,

\[
\beta = \frac{3\pi}{\varepsilon_0 c \lambda n^2} \text{Im} \left[ \chi^{(3)} \right]
\]  

(1.3)

TPA coefficient is the imaginary part of \(\chi^{(3)}\) that determines the strength of NLA. Three-photon absorption is also an important phenomenon. It is illustrated in Figure 1.2. 3PA is related to the following equation,

\[
\frac{dl}{dz} = -\alpha l - \gamma l^3
\]  

(1.4)

where \(\gamma\) is the 3PA coefficient [Sutherland (1996)]. It is a fifth-order nonlinear process and \(\gamma\) is related to the fifth-order susceptibility by the equation,

\[
\gamma = \frac{5\pi}{\varepsilon_0 c^2 \lambda n^2} \text{Im} \left[ \chi^{(5)} \right]
\]  

(1.5)
Figure 1.2  Schematic diagram of 3PA.

The excitation of a material by ultrafast intense light populates its excited-state significantly. In semiconductors and polyatomic molecular systems, there is a high density of states near the state involved in the excitation [Li et al. (1994)]. The excited electron can quickly make a transition to one of these states before it eventually transitions back to the ground state [Sutherland (1996)]. There are also a number of higher-lying states that may be radiatively coupled to these intermediate states, and for which the energy differences are in near-resonance with the incident energy of the photon [Stamplecoskie et al. (2015), Sutherland (1996)]. Therefore, before the electron completely relaxes to the ground state, it may experience absorption that promotes it to higher lying states [Christodoulides et al. (2010)]. This important process is called *Excited State Absorption*. It is observable when the input incident intensity is adequate to deplete the ground state [Sutherland (1996), Ghatak and Thyagarajan (1998), Menzel (2001)].

On the basis of absorption cross-section of excited-state, absorption processes can be classified in two types: SA and RSA. To explain the SA, a simplified energy-level diagram of a polyatomic molecule is given in Figure 1.3. It is usually involved a five energy-levels that are distinct electronic states. This model is adequate to explain the NLA over different values of incident intensities. Each electronic state involves dense vibrational-rotational states. On being excited from one electronic state to another, an electron makes a transition to one of these vibrational-rotational states. However, with very little energy transfer, collisions rapidly thermalize the electron, and it drops to the lowest-lying vibrational-rotational level within the
electronic manifold of states [Sutherland (1996)]. From this state, it can either experience absorption of another photon or relax to any of a number of lower-energy states. The ground electronic state is called a single-state [Sutherland (1996)]. These states have a pair of electrons with antiparallel spins. Selection rules disallow any radiative energy transition for which one of these spins would flip, producing a pair of electrons with parallel spins. Thus absorption from the ground state causes a transition only to another singlet electronic state [Sutherland (1996)]. This is also the case when absorption of fluorescence from a higher-lying singlet state takes place. It is possible to flip the spin by external processes such as collisions with paramagnetic ions, or internal processes such as strong spin-orbit coupling [Sutherland (1996), Ghatak and Thyagarajan (1998), Menzel (2001)].

Under such conditions, the first excited electronic state may make a radiation-less transition to a lower-lying triplet state (i.e., a state with a pair of electrons having parallel spins). (The symmetric spatial factor of the singlet two-electron wave function results in an electron pair at equal molecular co-ordinates along the symmetry axis of the molecule, but residing in upper and lower lobes of the π-orbital. This close proximity results in a higher energy state than that of the antisymmetric triplet spatial wave function, which preferentially places the electrons at unequal molecular coordinates). A radiative transition from this state is allowed by selection rules only to another triplet state. Hence, singlet-singlet and triplet-triplet radiative transitions are analysed in such molecular systems [Sutherland (1996), Ghatak and Thyagarajan (1998), Menzel (2001)].

In a five-level system, absorption of an incident photon excites an electron to the first excited singlet state. From this state, there are three possibilities. The electron can either relax to the ground state by a radiative or nonradiative transition, or it can undergo a spin-flip transition to a triplet-state, which is called intersystem crossing and has a rate constant $k_{isc}$. The third possibility is that the molecule may absorb another photon, which promotes the electron to a higher-lying singlet state, from which it then relaxes back to the first excited singlet state. For an electron in the lowest triplet state, two possibilities exist [Sutherland (1996)]. It may relax by another spin-flip transition to the ground state. This occurs by a process called phosphorescence
and has an associated rate constant $k_{ph}$. The other possibility is that the molecule absorbs another photon, promoting the electron to a higher-lying triplet state from which it then relaxes back to the lowest triplet-state [Sutherland (1996), Ghatak and Thyagarajan (1998), Menzel (2001)].

![Figure 1.3 Schematic diagram of a five level system.](image)

The lifetimes of the higher-lying singlet and triplet states are generally very large. It is normally assumed that the corresponding relaxation rates are so large that the population densities of these states, designated by $S_n$ and $T_n$ can be neglected. As the absorption normally promotes the electron to vibronic levels well above the bottom of the manifold, and relaxation to the bottom vibronic level is very fast, stimulated emission from excited states is also not taken into account.

In general, in a material exhibiting SA, the excited-state absorption cross-sections are smaller than the ground state absorption cross-section. Whereas in a material exhibiting RSA, the excited-state absorption cross-sections are larger than the ground state absorption cross-section. SA and RSA in the same molecule have been observed. Higher-order singlet-singlet absorption has to be considered in order to explain this phenomenon [Sutherland (1996), Ghatak and Thyagarajan (1998), Menzel (2001)].

For SA and RSA transition TPA induced ESA is an important phenomenon, in which strong TPA in a material can lead to significant population of a two-photon allowed state. There
are often allowed radiative transitions from this state to higher-lying states of the system (i.e., ESA can be induced from the two-photon pumped state.) This occurs both in polyatomic molecules and in semiconductors. The attenuation and excited-state population equations are given by,

\[
\frac{dl}{dz} = -\alpha l - \beta l^2 - \sigma NI \tag{1.6}
\]

and

\[
\frac{dN}{dt} = \frac{\beta l^2}{2\hbar \omega} - \frac{N_1}{\tau_1} \tag{1.7}
\]

where \( \alpha \) is the linear absorption coefficient for impurity absorbers, and \( \tau_1 \) represents the lifetime of two-photon excited states. The nonlinear transmittance of the system is determined by numerical solution of these equations.

In the case of an incoherent resonant interaction the nonlinear behavior can be described by the change of the absorption coefficient as a function of the incident intensity of the light beam by the equation,

\[
a = f(I) = f\{I(r, \lambda, t, \psi)\} \tag{1.8}
\]

Under stationary conditions and for optically thin samples, the absorption coefficients can be given analytically as rational polynomials of the intensity. However, the intensity equation also be solved analytically only for simple cases. The nonlinear incoherent absorption is a consequence of the change in population of absorbing or emitting energy states of the matter. Thus the absorption coefficient \( a \) for a given light beam is written as:

\[
a = \sum \pm \sigma_m(\lambda, \psi, r)N_m(I, r, t) \tag{1.9}
\]

where \( \sigma_m \) is the cross-section of the \( m^{th} \) energy level of the material and \( N_m \) is its population density. All possible transitions that lead to absorption (+ sign) and emission (- sign) have to be summed. A strong pump beam produces nonlinear effect, which populates excited states in the sample. This excited sample has a variety of new properties generated by the pump. The choice of the pump beam parameters allow the appropriate population of all kinds of special material states with different new absorption characteristics, with life times from a few fs to hours. The
exciting beam can comprise two or more different light beams for multiple excitation of the sample. However, the probe beam intensity has to be weak so that it does not induce absorptions in the sample itself [Ghatak and Thyagarajan (1998), Sutherland (1996)]. The nonlinear interaction of a light beam with matter can be modeled with rate equations.

Hence, there is tremendous research interest in finding molecules possessing SA and RSA characteristics as these characteristics can be useful for a variety of applications that include Q-switching, mode locking, optical pulse shaping, power limiting, pulse shortening, pulse smoothing, spatial light modulation, pulse compression, optical switching and data processing [Reddy (1991), Sreekumar et al. (2009), Xing et al. (2010), Hirata et al. (2014), Huang et al. (2015)].

The phenomenon of ESA can be used to control one light beam by another light beam through a NLO material using the pump-probe spectroscopic technique. It is a fundamental technique to study the molecular dynamics; absorption or scattering that can be used for all-optical switching as shown in Figure 1.4. The basic requirement for any switch is high speed, high contrast and low-power operation. An optical switch can be designed based on the change in different properties of light, i.e., intensity, polarization, phase, direction, wavelength or frequency.

![Figure 1.4](image)

**Figure 1.4** Pump-probe set up for AOS.

The transmission of a continuous-wave (cw) probe signal beam, corresponding to the peak absorption wavelength of an excited-state [Singh and Roy (2004)], can be modulated or switched by modulating the population density of the excited-state or absorption of the sample, by exciting it with cw or pulsed pump laser beam around the peak absorption wavelength of the
ground state. Initially in the absence of the pump pulse, all the molecules are in the ground state [Singh and Roy (2004)]. Hence, the probe beam transmission is high due to either no absorption or low absorption by the ground state. However, when the pump pulse is incident, the molecules get excited and populate the excited-states for a specific time depending upon the lifetime of the excited-state and hence, the probe beam now gets absorbed by these excited molecules and its transmission is low or gets switched off. Higher the intensity, higher is the absorption and the contrast of the switched probe beam. The contrast depends on the absorption spectra of ground and the excited-states. This occurs when the absorption cross-section of the excited-state at probe wavelength is higher than that of the ground state and is called RSA. However, in case the probe beam is near the pump wavelength, its transmission increases due to less absorption, as the ground state is depleted, which leads to SA. The transmission of the probe beam depends on the pump intensity, pump and probe wavelengths and spectral and kinetic parameters of the intermediate states.

Recent technological advances in fabrication, design and control of the size and shape of small structures, such as thin films, quantum wells, optical fibers, integrated optical waveguides etc. have facilitated the observations and applications of NLO phenomena at low light intensities [Saleh and Teich (1991), Ghatak and Thyagarajan (1998), Li et al. (2008 a, 2008 b), Ma et al. (2010)]. More recently, nano organic photonics has emerged as a highly prospective area to manipulate, fabricate, design, synthesis, and characterization of novel materials and structures that exhibit an efficient NLO response, which can be utilized for designing organic molecular photonic devices [Lipson (2004), Clark and Lanzani (2010), Li et al. (2014), Yan and Zhao (2014), Agranovich and Rocca (2015)]. In addition to the advantages of small size and weight, fast response, strong nonlinearity and low power dissipation, their properties can be tailored by chemical, physical and genetic engineering methods to suit specific device applications [Henari et al. (1996), Henari (2001), Hu et al. (2003, 2005), He et al. (2007), Kong et al. (2009), Haque and Nelson (2010), Hales et al. (2010), Wurtz et al. (2011), Hales et al. (2014), Roy and Yadav (2014)]. Thus, these powerful capabilities provide the tremendous impetus for studying ultrafast NLO phenomenon of new novel nonlinear materials
for AO information processing applications.


Organic materials are emerging as the most promising NLO materials for state of the art optical device applications due to their unique properties and advantages [Zerbi (1993), Bredas et al. (1994), Said et al. (1994), Roy and Kulshrestha (2005), Muccini (2006), Samuel and Turnbull (2007), Terenziani et al. (2008), Jazbinsek et al. (2008), Bandyopadhyay et al. (2010), Clark and Lanzani (2010), Perry (2010), Gong et al. (2010), Graydon (2012), Yan et al. (2013), Bredas (2014), Hales et al. (2014), Kaur et al. (2014), Goldschmidt and Fischer (2015), Simon and Weder (2015)], which include the following:
(i) Ultrafast response times and efficient NLO response.

(ii) Potentially large NLO susceptibilities (allowing for low light intensities and small device dimension).

(iii) Broad spectral tunability, in order to choose the optimized excitation wavelength to tailor their properties to suit specific device requirements.

(iv) Ease of fabrication/modification and ability to form thin films or to process with conventional devices.

(v) Flexibility to alter and optimize molecular structure to maximize NLO properties by physical, chemical and genetic engineering methods.

(vi) Potential to integrate into device structures.

(vii) Large hyperpolarizability and low fabrication costs.

(viii) High singlet and triplet ESA.

(ix) High stability and damage threshold.

Organic materials are generally based on molecular structures containing a conjugated \( \pi \)-electron moiety, with electron donor and acceptor groups located at adequate positions in the molecule [Sreekumar et al. (2009), Gadalla et al. (2010), Haque and Nelson (2010), Clark and Lanzani (2010)]. Certain organic molecules behave like molecular switches [Xue and Forrest (2003), Silva and Uchiyama (2007), Szacilowski (2008), Virgili et al. (2010), Fuentes et al. (2011)]. Their electronic and structural properties can be adjusted when stimulated with chemical, electrical or optical inputs [Raymo (2002), Marder (2006)]. The above properties can be selectively enhanced by using genetic engineering techniques that provide sophisticated control and manipulation of large molecules for optimized device designs. The potential for using organic molecules for ultrafast AO information processing appears to be novel, unique, fascinating, environmentally safe and cost effective preposition. The relatively new exciting area of Ultrafast Organic Nonlinear Optics and Nano Photonics investigates the use of native as well as modified organic molecules (phthalocyanines, porphyrins, dyes, graphene, GO, GO-metal composites and natural photoreceptor proteins etc.) in place of inorganic molecules [Pospischil et al. (2013), Pradeep et al. (2014), Rakovich et al. (2014), Sun et al. (2014), Song
et al. (2014), Yin et al. (2014), Bao et al. (2015), Fitzgerald et al. (2015)].

On the other hand, the prospect of photonic and optoelectronic applications using state of the art ultra-sensitive natural photoreceptor proteins, discovered in broad range of plants and organisms that exhibit an efficient NLO response in a broad spectral range, which has been optimized over centuries of evolution, is extremely fascinating [Vsevolodov (1998), Birge (1990, 1992, 1994, 1995, 1999), Beja et al. (2000, 2001, 2002), Ebrey (2002), Berthoumieu et al. (2012)]. Integration of these photochromic biomolecules with metal nanoparticles, semiconductor quantum dots (QDs) and nanostructures provides a powerful capability to meet present challenges to achieve ultrafast low-power AO computing [Biesso et al. (2008, 2009), Roy et al. (2010, 2012), Rakovich et al. (2013), Mohammadpour and Janfaza (2015)].

Thus, the study of ultrafast NLO response of new class of organic and bio molecules would form the basis for the design of various AO devices and provides a fundamental understanding of light activated processes in them. The ultimate aim of the study is to find suitable materials for ultrafast low power AOS and NLA based devices which satisfy the condition of broad band spectral response, high damage threshold, large dynamic range, cost effective and practically feasible.

1.1 Ultrafast Nonlinear Optical Response of Organic Molecules

Extraordinary progress in the development of NLO materials during the last three decade has rendered photonic technologies an essential part of our daily life as we enter the 21st century of information age. To further improve the performance of photonic technologies, researchers have sought for materials with enhanced third order NLO properties and low optical loss due to absorption, including inorganic materials, polymeric systems and organic molecules. Organic molecules recently appeared as a potentially viable candidate for the future photonic technologies of telecommunication, optical computing, optical interconnects, high density data storage, sensors, image processing and switching due to facile tunability of their optical properties and ability to modulate, transmit and detect light in an architecture that is flexible, low cost, lightweight and robust.
On the other hand, the basic ideology in information processing so far has been to mimic the way nature processes information through semiconductor electronics, present day capabilities are no way near to the complex tasks performed in natural processes whether in a small cell or the human brain. Driven by the fundamental need of understanding natural information processing and adopting a cost-effective and environmentally safe technology that has the potential to meet our future needs, has provided tremendous impulse to investigate natural photosensitive biomolecules for a variety of high performance photonic applications. Most photosensitive biomolecules that has been the subject of great interest are the rhodopsin and heme proteins.

Rhodopsins and chlorophylls are the most well-known and widespread photosensitive biomolecular light energy converters on earth. Rhodopsins are the second most abundant photosensitive proteins in nature [Vsevolodov (1998), Beja et al. (2000, 2001, 2002), Ebrey (2002)]. Rhodopsins are currently known to belong to two distinct protein families, i.e., visual rhodopsins found in the eyes throughout the animal kingdom that are photosensory pigments, and archael rhodopsins found in extreme halophiles, which function as light driven proton pumps (bacteriorhodopsins), chloride-ion pumps (halorhodopsins), or photosensory receptors (sensory rhodopsins). Extremely high quantum yield, high molecular extinction coefficient and low isomerization time, make rhodopsins potential candidate for molecular photonic and optoelectronic applications [Vsevolodov (1998)].

Naturally occurring porphyrins are also one of the well-known photosensitive biomolecules [Beja et al. (2000)]. It serves as a functional group in a wide variety of biological systems, the most known being heme proteins i.e. iron-porphyrin complexes [Boni et al. (2010)]. Heme proteins that contain heme, iron and its variants are of particular interest due to their diverse range of biological activities such as oxygen transport and storage, ligand binding and ability to transfer charge in a controlled and stable fashion from the environment to the active site of the protein [Boni et al. (2010)]. High nonlinear effects, ability to form thin films and flexibility in modifying its properties by the conjugation with nanoparticles and graphenes make them prospective candidate for bioelectronic and biophotonic devices.
1.1.1 Copper-Phthalocyanine (CuPc)

Phthalocyanines with large number of delocalized π-electrons are versatile and ubiquitous class of macro molecules because of their interesting third order NLO properties, high optical absorption cross-section and ultrafast response times that find extensive applications in AOS, signal processing, optical storage and optical power limiting. Phthalocyanines have been considered excellent optical limiter materials due to strong RSA in ns regime as they exhibit relatively low linear absorption and high excited-state to ground state absorption cross-section ratio in visible range. The main limitation in the use of phthalocyanines is low solubility in common solvents, which results in a drastic decay in the optical properties [Yüksek et al. (2010)]. Hence, more recently, metallophthalocyanines (Cu/Zn phthalocyanine etc.) have been emerged as an ideal NLO materials compared to metal free phthalocyanines due to several key properties [De La Torre et al. (2004), Rahimi (2004), Li et al. (2008), Terenziani et al. (2008 b), Yüksek et al. (2010), Li F. and Li X. (2012), Vivas et al. (2012), Manjunatha et al. (2013 b), Chen et al. (2014), Li et al. (2014), Swain et al. (2014), Yang et al. (2014), Fashina and Nyokong (2015)], which include the following:

(i) High two-photon and three-photon absorption (3PA) coefficients.

(ii) Strong nonlinear refractive index (n₂) in picosecond (ps) and fs regime.

(iii) Large optical cross-sections (typically 10⁻¹⁵ cm² for peak absorption).

(iv) Excellent chemical and thermal stabilities.

(v) Easy dissolution in most of the common solvents.

(vi) Broad spectral tunability and flexibility to tailor the NLO response.

(vii) Ease of preparation/purification.

(viii) Good conductivity.

(ix) Low propagation delay and power dissipation.

(x) Electronic response time in ps and fs regime.

In recent years, NLO spectroscopy has shown that intensity dependent SA to RSA or RSA to SA transition takes place from nanosecond (ns) to fs domain on changing the pulse intensity in phthalocyanines and metallophthalocyanines thin films and solutions which include,
sub-phthalocyanines [Dini et al. (2005)], alkoxy and alkyl phthalocyanines [Venkatram et al. (2008), Rao et al. (2009)], copper-phthalocyanine (CuPc)-doped polymethylmethacrylate (PMMA) [Li et al. (2008 b)], unsymmetrical phthalocyanine [Rao et al. (2010)], multilevel organic molecular system [Li F. and Li X. (2012)], meso-tetraphenylporphyrins and meso-tetraphenylporphyrins derivatives [Ao et al. (2015 a, 2015 b)] and phthalocyanine cobalt [Chen et al. (2015)]. Most of the studies have focused on characterization of their NLO properties by the single beam Z-scan technique to understand the NLA mechanisms for potential application in optical power limiting.

1.1.2 Graphene, Graphene-Oxide and its Metal Porphyrin Composites

Graphene, a two-dimensional form of graphite, was isolated in 2004 using simple Scotch tape method by Kostya Novoselov and Andre Geim of Manchester University, UK [Novoselov et al. (2004), Geim and Novoselov (2007), Rao et al. (2009), Novoselov et al. (2012), Sur (2012)]. Graphene, a single atom-thick sheet of sp²-bonded carbon structure has become an emerging star on the horizon of physics, chemistry and material science. It has also considered an extremely prospective NLO material for photonic and optoelectronic applications due to several properties [Bonaccorso et al. (2010), Lim et al. (2011), Bao and Loh (2012), Sur (2012), Jariwala et al. (2013), Raccichini et al. (2015)], which include the following:

(i) Thinnest material in the universe (thickness ~ 0.33 nm i.e. almost 1 millionth the thickness of human hair).
(ii) Strongest and lightest material (harder than Diamond and 300 times harder than Steel).
(iii) Excellent electrical, mechanical, thermal, electronic, and optical properties.
(iv) High specific surface area.
(v) High Young’s modulus.
(vi) Extraordinary thermal conductivity.
(vii) Giant charge carrier mobility.
(viii) Highly efficient electrical conductivity.
(ix) High optical transparency and light absorption in the visible spectrum.
High elasticity and porosity. 

Tunable band gap. 

High chemical stability and biocompatibility. 

Flexibility in tuning its properties by chemical functionalization.

Due to these extraordinary properties of graphene, it has been realized that graphene is the only material which has a potential to compete with silicon based technology and may overtake it in the next coming years [Novoselov et al. (2012), Zhao et al. (2013)].

One specific branch of graphene research deals with GO. GO can be considered as the insulating and disordered analogue of the highly conducting crystalline graphene, synthesized by either chemical or thermal reduction processes [Eda et al. (2008), Loh et al. (2010)]. It comprises of a single-layer of graphite oxide and is usually produced by the chemical treatment of graphite through oxidation processes. Chemical reduction of GO by treating GO with hydrazine hydrate produces new form of GO that is called reduced graphene-oxide (rGO). GO has emerged as an important photonic material due to its unique properties and advantages [Loh et al. (2010)], that include (i) heterogeneous electronic and chemical structures [Roy and Yadav (2013 a)], (ii) interacts with a broad range of inorganic and organic molecular configurations that enables synthesis of functional hybrids and composites with outstanding properties [Roy and Yadav (2013 a), Yadav and Roy (2015)], (iii) can be processed in thin films and solutions, (iv) can be made into an insulating, semiconducting or semi metallic material by just tuning the oxidation and reduction parameters [Roy and Yadav (2013 a)], and (v) its band gap can be changed by controlling the sp² and sp³ fractions to alter its optical, electrical and chemical properties [Loh et al. (2010), Roy and Yadav (2013 a)].

A large number of applications have been projected for graphene, GO and rGO by exploiting their unique physicochemical properties which include (i) transparent electrodes for photovoltaic solar cells [Liu et al. (2013 a), Srivastava et al. (2015)], (ii) liquid crystal displays [Loh et al. (2010)], (iii) Organic light emitting devices (OLEDs) and touch screens [Loh et al. (2010), Han et al. (2012), Roy and Yadav (2013 a)], (iv) conducting plates of ultra supercapacitors [Liu et al. (2013 b), Roy and Yadav (2013 a)], (v) wireless communications
(Loh et al. (2010)), (vi) radar [Sur (2012)], (vii) security systems [Sur (2012)], (viii) sensing and drug delivery [Loh et al. (2010)], (ix) rGO channel field effect transistors [Trung et al. (2014)], (x) fs mode locking and Q-switching of erbium doped ring cavity fiber lasers [Xu et al. (2012), Roy and Yadav (2013 a)], (xi) broadband polarisers, and (xii) optical limiters [Jiang et al. (2012)].

The NLO response of graphene and GO has been experimentally investigated for ns to fs pulse excitation basically for broadband optical power limiting applications [Liu et al. (2009, 2011), Roy and Yadav (2013 a), Jiang et al. (2012, 2015)]. In GO thin films, increase in intensity results in a transition from SA to RSA with increase in contrast [Jiang et al. (2012)]. At low pump intensities NLO response is dominated by the charge carriers with SA from the sp²-hybridized domains whereas at high pump intensities, the influence of the TPA from the sp³-hybridized domains on the transient absorption signal becomes stronger [Loh et al. (2010), Liu et al. (2011), Roy and Yadav (2013 a), Yadav and Roy (2015)].

Despite many potential applications that graphene and GO promise to offer, the processability of graphene and GO is of vital importance in facilitating their functionalization with materials having high nonlinear coefficients and optical absorption cross-sections such as polymers, organic and inorganic materials to improve the electrical and optical properties for future photonic device applications [Krishna et al. (2011), Wang et al. (2011), Yin et al. (2015)]. Some recent spectroscopic characterization reports based on integration of graphene and GO with porphyrins, fullerenes, Fe₃O₄ nanoparticles, phthalocyanines and metal porphyrin composites show that hybrid materials exhibit interesting NLO properties in ns, ps and fs regime that can lead to extensive applications in AOS and optical power limiting [Zhao et al. (2013), Fraser et al. (2015), Zhang et al. (2015)].

1.1.3 Ruthenium (Ru) Dioxolene Complex

Recently, bipyridine-containing ligands and their transition-metal complexes have attracted considerable attention as promising NLO and photonic materials [Zhang and Rodgers (1995), Tian et al. (2005)]. Transition-metal complexes that exhibit metal to ligand charge transfer (MLCT) transitions can lead to large NLO responses due to high degree of electron
delocalization, possibility for stabilization of metal complexes in different oxidation states and flexibility of structure and function beyond the available traditional organic materials [Cassano et al. (2005)]. Ruthenium complexes have been well studied for NLO properties due to large tunability in photo-physical properties, strong optical absorption in visible region, variation in metal oxidation state, high chemical stability, ease of fabrication, ground and excited-state stability, long-lived emissive excited-states and formation of a Franck-Condon singlet MLCT excited-state which undergoes sub-ps intersystem crossing to the long lived (~600 ns) triplet MLCT excited-state [Thompson et al. (2001), Marin et al. (2003), Cassano et al. (2005), Tarnovsky et al. (2006), Manjunatha et al. (2013 a)].

The NLO properties of ruthenium complexes have also been experimentally studied in ns and ps regime for its application in optical limiting and computing. [Chao et al. (2004), Cassano et al. (2005), Manjunatha et al. (2013 a)]. A transition from RSA to SA in ruthenium complex $\{[\text{Ru (bipy)}_2]_2\text{L}]\text{[PF}_6\}$ has been experimentally observed using ps laser pulses at 532 nm. The ESA cross-sections and life times have also been calculated by the theoretical fitting of the experimental data [Cassano et al. (2005)]. Nanosecond Z-scan single beam and pump-probe technique has been used to study the third-order NLO properties and AOS of novel (2-thioxo-1,3-dithiole-4,5-dithiolato) triphenylphosphine Ru (III) [RuL] in solid form and solution [Manjunatha et al. (2013 a)]. It has been shown that ruthenium complexes exhibit RSA and self-defocusing with large third-order NLO susceptibility of the order of $10^{-11}$ esu. These studies suggest that ruthenium complexes can serve as a promising material for photonic devices [Cassano et al. (2005), Manjunatha et al. (2013 a, 2013 b)].

### 1.1.4 Bacteriorhodopsin Protein

Bacteriorhodopsin (bR), a photodynamic protein complex was discovered in 1970 by Dieter Oesterhelt [Oesterhelt and Stoeckenius (1971), Stoeckenius (1976)]. It is found in the purple membrane fragments of *Halobacterium salinarum*, which grows in the harsh conditions of salt marshes, where the concentration of salt is approximately six times that of seawater [Oesterhelt and Stoeckenius (1971), Lozier (1975), Khorana (1988), Kobayashi et al. (2001)]. bR has been the focus of intense research as it serves as a model to understand the basic
transport processes fundamental to all forms of life and due to its unique extraordinary properties and advantages [Oesterhelt and Stoeckenius (1971), Birge (1990, 1995), Shen et al. (1993), Birge et al. (1999), Hampp (2000), Stuart et al. (2002), Singh and Roy (2003 a, 2003 b) Han et al. (2008), Roy et al. (2010, 2012), Roy and Yadav (2014)], which include the following:

(i) Long-term stability and resistance to thermal and photochemical degradation over years; chemical stability over a wide pH range from 0-12, and high thermal stability ~ 80 °C in water and ~140 °C in dry form.

(ii) Unique photochromic and photoelectric responses [Roy and Yadav (2014)].

(iii) High quantum yield (~64%) of converting light into a state change [Roy and Yadav (2014)].

(iv) Large extinction coefficients and high two-photon cross-sections (nonlinearities).

(v) Large shift in absorption spectrum that permits accurate and reproducible state assignment.

(vi) Large change in refractive index that yields thin films with good holographic efficiencies.

(vii) Capability to form thin films in polymers and gels with excellent properties.

(viii) Capability of processing in crystalline form with high optical quality and of sufficiently large areas.

(ix) Flexibility in modifying its properties by physical, chemical and genetic engineering methods.

(x) Environmental friendliness, as its synthesis and processing does not require use of hazardous chemicals leading to environmental pollution.

(xi) Low production cost.


On excitation with 570 nm light, the bR molecule undergoes several transformations in a photocycle ($B_{570} + h\nu \rightarrow J_{625} (~\text{ps}) \rightarrow K_{610} (~\mu\text{s}) \rightarrow L_{550} (~\mu\text{s}) \rightarrow M_{410}^I (~\mu\text{s}) \rightarrow M_{410}^{II} (~\text{ms})$)
→ N_{520} (\sim ms) → O_{640} (\sim ms) → B_{570}) is clearly shown in Figure 1.5 [Birge (1990, 1994, 1995), Oesterhelt et al. (1991), He et al. (1999), Vought and Birge (1999), Birge et al. (1999), Hampp (2000), Roy et al. (2001), Roy and Yadav (2014)]. An interesting feature of its photocycle is that it can be terminated by shining light near the peak absorption wavelength of any intermediate or the intermediate can be photochemically switched back to the initial B-state [Hampp (2000), Stuart (2002), Wise et al. (2002), Singh and Roy (2003 b), Topolancik and Vollmer (2006, 2007), Roy et al. (2010), Roy and Yadav (2014)].

In the main photocycle of bR, a branching reaction can take place under certain conditions from the O-state. The excitation of O state with red light (640 nm), leading to the formation of the P-state that relaxes in the dark to the Q-state [Roy and Yadav (2014)]. The P and Q states are very long lifetime states as there is no thermal decay from these states to the initial B state. The initial B state can be generated only through photochemical excitation of these states by using blue light. The very long life time P and Q states can be used for permanent optical data storage that leads to bR based 3D volumetric memories [Downie et al. (1998), Birge et al. (1999), Millerd et al. (1999), Timucin and Downie (2000), Hampp (2000)].

The light-driven proton transport through bR is accompanied by a cyclic series of spectroscopically distinguishable molecular changes, as shown in Figure 1.6.

![Figure 1.5](image_url)  
**Figure 1.5** Photocycle of bR molecule [Roy et al. (2001)]. Subscripts indicate peak absorption wavelengths of intermediates in nm.
The absorption spectra exhibit RSA at wavelengths at which the absorption cross-section of excited intermediate state is higher than that of the initial bR state. This special feature has been used to design spatial light modulators, switches and logic gates with bR, based on ESA using the pump-probe configuration [Roy et al. (2002), Singh and Roy (2002a, 2002b, 2003a, 2003b), Fabian et al. (2010)].

**Figure 1.6** Absorption spectra of different intermediate states of bR span the entire visible region [Birge et al. (1999), Stuart et al. (2002)].

A large number of applications have been proposed with bR [Hampp (2000), Singh and Roy (2003)]. Its proton pumping and photoelectric properties have been used for instance, in desalination of sea water [Oesterhelt (1976), Singh and Roy (2003)], conversion of sunlight to electricity [Keszthelyi et al. (1990), Singh and Roy (2003)], ultrafast light detection [Trissl et al. (1989, 1990), Singh and Roy (2003)], chemo and bio sensors [Lee et al. (1991), Singh and Roy (2003), Vengadesh et al. (2006)], artificial retinas [Miyasaka (1992), Chen et al. (1993), Saeedi et al. (2011), Singh and Roy (2003), Ignatov and Mosin (2014)], photon counters, photovoltaic converters [Bertoncello (2003), Singh and Roy (2003), Xu et al. (2003), Li et al. (2004)] and photo-transceiver [Shin et al. (2004)]. Its unique photo-chromism property has resulted in applications such as information recording, associative and three dimensional memories [Chen et al. (1991), Birge (1992, 1995), Birge et al. (1997, 1999), Fischer et al. (2003)], second

Various designs of AOL gates have been reported with bR by utilizing its photochromic properties that include two-wave mixing [Chen et al. (2009 b), Roy and Yadav (2014)], degenerate four wave mixing [Rao et al. (1996)], photoinduced birefringence and dichroism [Joseph et al. (1997)], degenerate multiwave mixing [Li et al. (2003), Roy and Yadav (2014)], complementary modulated suppression transmission [Zhang et al. (2000), Roy and Yadav (2014)], and nonlinear intensity-induced ESA [Roy et al. (2001, 2010), Roy and Yadav (2014)]. However, the main limitation with optical processing with bR has been the switching speed (~ms-ns) as M_{410}, O_{640} or K_{610} intermediate states have been used [Rao et al. (1993, 1996), Hampp (2000), Wu et al. (2002), Singh and Roy (2003 a, 2003 b), Huang et al. (2004 a), Topolancik and Vollmer (2006), Roy et al. (2010), Fabian et al. (2010), Mathesz et al. (2013)].
AOS in μs regime have been reported with bR-coated high-Q silica microresonators to design arithmetic logic operations [Topolancik and Vollmer (2006), Roy et al. (2010, 2012)]. Recently, Fabian et al. have reported ultrafast AOS with a bR coated 1D photonic crystal on a thin film waveguide by utilizing K610 and I460 intermediates [Fabian et al. (2011), Roy and Yadav (2014)]. Hence, based on this photosensitive protein, the present challenge is to have devices with faster switching speed (fs-ps) and contrast that operate at very low powers.

1.1.5 Cytochrome-c Protein

Cytochrome-c (cyt-c) is a photoactive iron storage multifunctional protein of organisms that consists of a chain of approximately 100 amino acids in its primary structure [Andrade et al. (2003, 2004), Boni et al. (2010)]. It is used for transporting electrons in the mitochondria of the cells that is important for the energy transfer process. The photoactive charge transfer in the cyt-c is attributed to the presence of covalent heme group linked to the polypeptide chains [Boni et al. (2010)]. In order to work as an electron carrier during cellular respiration, iron-ion present in the heme group can change its oxidation state from reduced to oxidised, which possesses different optical properties [Andrade et al. (2003, 2004), Boni et al. (2010)]. It is one of the most widely studied proteins due to its stability and high solubility (~100 g/L) in water [Choi et al. (2001)]. Its peroxidase activity is stable upto 60 °C in the pH range of 6.4 to 10.1 [Ogawa et al. (2004), Fujita et al. (2007)]. Cyt-c molecules retain their function and structure with more than 40 different species and maintain bioactivity without any denaturation under plasmon excitation [Zhu et al. (2009), Zaidi et al. (2014)]. It undergoes conformational changes under various conditions of pH, temperature, ionic strength and storage time and it becomes partially unfolded upon adsorption onto the surface of nanoparticles [Sahoo et al. (2011), Kim et al. (2015)].

A variety of applications have also been proposed with cyt-c [Choi et al. (2001, 2002), Choi and Fujihira (2004), Zhu et al. (2009), Lee et al. (2010 a, 2010 b, 2015), Alwarappan et al. (2010), Li et al. (2011), Nam et al. (2012), Simsikova et al. (2013), Wu et al. (2014)]. Efficient integration of cyt-c with graphenes, semiconductor QDs and metal nanoparticles has been shown to improve its photocurrent response and optical properties for hybrid nano-biosystems.
based biotechnological and biomedical applications [Choi and Fujihira (2004), Alwarappan et al. (2010)]. Nano scale cyt-c hetero films on ITO and quartz have been fabricated to measure the photoelectric response for its application in bioelectronic devices, namely, photodiodes and switches [Choi et al. (2001, 2002), Choi and Fujihira (2004), Lee et al. (2010a, 2015)]. A metal insulator metal structured device has been fabricated with cyt-c hetero films to measure the photoelectric response for designing a biomolecular photodiode [Choi et al. (2002)]. Heterolayer structure of green fluorescent protein/cyt-c can function as a biomolecular photodiode with a photo-switching function and rectifying property at the molecular scale [Choi and Fujihira (2004)]. Redox properties of cyt-c have been used to store information [Lee et al. (2010a)]. Cyt-c heterolayer has been used to construct an electrochemical biosensor and a non-volatile memory device because of high durability and stability [Lee et al. (2015)]. Cyt-c on ITO glass substrates has been used to generate extremely slow photocurrents under white light illumination [Nam et al. (2012)]. CdSe/ZnS quantum dot-cyt-c bioconjugates have been used to design a fluorescent probe with high sensitivity and specificity in living cells without interference from other reactive oxygen species and relevant intracellular components [Li et al. (2011)].

Optoelectronic and chemophotonic logic gates have also been proposed with cyt-c [Deonarine et al. (2003), Zhu et al. (2009)]. Plasmon induced charge separation based on Au nanoparticles deposited on a TiO$_2$ nanoneedle film coupled with cyt-c has been used to obtain switchable photocurrents for realizing logic gate function [Zhu et al. (2009)]. The folding and unfolding transitions of cyt-c have been used to perform variety of logic functions such as YES, NOT, AND, OR and XOR [Deonarine et al. (2003)]. Cyt-c accepts input signals in the form of denaturants that can include unfolding of the protein. These conformational changes lead to alterations of the protein fluorescence intensity which is used as the output signal [Deonarine et al. (2003)]. Recently, multiple output logic circuits based upon the fluorescence results of bovine serum albumin and cyt-c and Pb$^{2+}$ and Pd$^{2+}$ ions have also been constructed [Bhalla et al. (2012)]. The designs proposed in the literature with cyt-c based on plasmon-induced photocurrents, fluorescence and folding and unfolding transitions of cyt-c have slower response
time [Deonarine et al. (2003), Zhu et al. (2009), Bhalla et al. (2012)]. The dialysis-based set up particularly has extremely slow (~min) response time as the solvent exchange involves molecular diffusion through a porous membrane [Deonarine et al. (2003)]. The other difficulty encountered for chemophotonic logic gates is the different nature of the input and output signals. Hence, with this protein, it would be important to design fs AOL gates.

1.2 Ultrafast All-Optical Computing

Any operation in which an optical device or phenomena can be used for numeric and symbolic computation can be categorized as optical computing [Karim and Awwal (1992), Caulfield and Dolev (2010), Benson (2011)]. Optical computer is a device that uses photons instead of electrons, thin films, tiny crystals, laser diodes and optical fibers to perform digital computations [Abdeldayem and Frazier (2007)], which will make the systems more efficient, compact, lighter and cost effective. Optical computing is the most viable technology that can replace electronics, and promises faster processor speeds, parallelism, non-interactive behavior and higher bandwidth that can enhance data transmission rate [Orrit (2009), Ambs (2010), Clark and Lanzani, (2010), Haque and Nelson (2010), Caulfield and Dolev (2010), Smith et al. (2011), Eggleton et al. (2011), Lin et al. (2012)]. Optical components i.e. optical integrated circuits are immune to electromagnetic interference, and free from short circuits. Photons of different colors can move simultaneously through same optical fiber without any interference or cross talk, offering optical devices to process multiple streams of data concurrently. This means that optical computing can enhance the computing speed by more than $10^7$ times faster than the currently exist fastest electronic systems [Abdeldayem and Frazier (2007)].

Various techniques have been proposed such as optical bistability, polarization, electron trapping, NLA, symbolic substitution and photorefractive effects to realize various functionalities for development of the optical computing technology [Saleh and Teich (1991), McAulay (1991), Karim and Awwal (1992), Efron (1995)]. The efforts in trying to avoid the optoelectronic and electro-optic conversion and build an AO system that enhances the communication performance and serves very well the optical computing technology [Miller...
(2010), Caulfield and Dolev (2010)]. Although much progress have been shown on all aspects of information processing in the fields of optics, still there are certain fundamental limitations to be resolved in optical computing, namely, (i) cascadability i.e., output of one stage must be in a correct form to drive the input of the next stage, so there should be compatibility between output and input wavelengths, beam and pulse shapes (ii) fanout i.e., output of one stage should be able to drive the input of the next stage, and a small input power change should result in larger output power changes (iii) logic level restoration i.e., quality of the logic signal should be restored (iv) input/output isolation i.e. the device should have separate input and output beams, otherwise the design of the system becomes difficult (v) logic level should be independent of loss, and (vi) integration of components. Recent progress in developing AO processors, ultrafast AO switches, optical materials and optical data storage media have brought AO systems close to reality. To meet the future demand of high speed AO computing devices, we need to realize ultrafast AOL gates, ultrafast optical switches, optical interconnects, optical memory, spatial light modulators and efficient optical materials which are the key components necessary to build an ultrafast optical computing system.

Hence, ultrafast AO information processing i.e. communication and computing, which uses photons rather than electrons to modulate a signal, is an active field of research [Hwang et al. (2009), Haque and Nelson (2010), Fleischhauer (2011)]. Novel techniques of AO signal processing are based on NLO phenomena such as self-phase modulation, cross phase modulation, cross gain modulation, stimulated Raman scattering, four-wave mixing, optical bistability, photorefractive effect, NLA etc.[Agarwal (2006), Ezra et al. (2009), Christodoulides et al. (2010), Benson (2011)].

Logic gates are the basic building blocks of any digital computing system [Abdeldayem and Frazier (2007)]. An AOL gate is a switch that controls one light beam by another light beam without introducing the electrical signal. Ultrafast logic gates can be realized using SA and RSA based on multiple pump pulse and single beam excitations. Using multiple pump pulse excitations, SA and RSA can be used to design AOL gates, OR and AND based on SA and NOT, NOR and NAND based on RSA. Since, SA and RSA occur at either different
wavelengths or at different lifetimes of the excited-states, different logic gates are realized with different samples [Singh and Roy (2003 a, 2003 b), Roy et al. (2010, 2012)]. Recent ultrafast NLO spectroscopy of organic thin films and solutions has shown that SA to RSA transition in the transmission of a pulse takes place in the same sample on changing the pulse intensity [Jiang et al. (2012), Singh and Bindra (2015)]. This facilitates simultaneous realization of different logic gates in parallel using the same sample with laser pulses at one wavelength only.

1.3 Motivation

The study of ultrafast NLO response of recently characterized organic molecules is of fundamental importance for basic as well as applied science. Experimental ultrafast (fs and ps) spectroscopic characterization of CuPc-doped PMMA, GO and GO-metal porphyrin composites and ruthenium-dioxolene complexes in solutions and thin films have been undertaken in detail to study the NLA, ESA, third and fifth order nonlinear effects etc. using Z-scan technique [Cassano et al. (2005), Li et al. (2008 b), Jiang et al. (2012)]. Various new features have been observed such as intensity dependent SA to RSA and RSA to SA transitions. However, the basic mechanism is not clearly understood in different organic systems and it is important that accurate theoretical model be developed to provide insights into these novel NLO responses in organic molecules. The unique properties of these organic molecules, such as ultrafast response, large third and fifth-order nonlinear coefficients, high stability and damage threshold, broad spectral tunability and ease of integration with other organic/inorganic and nano materials seem to extremely useful to optimize the molecular response to design ultrafast AO devices based on these intensity dependent SA to RSA or RSA to SA transition. Key elements of ultrafast AO information processing such as AO switches and logic gates, can be designed with these organic molecules by just controlling the input pulse intensity with the same sample and setup. To the best of our knowledge, no device applications have been proposed with GO and GO-metal porphyrin composites with fs switch off/on time to date. Hence, we were motivated to analyse the ultrafast AO SA to RSA or RSA to SA transitions with these materials in detail and to investigate their device applications based on fs or ps NLA.
Recently, ultrafast NLO response of photosensitive biomolecules such as bR and cyt-c protein has been experimentally studied using pump-probe and Z-scan technique respectively [Abramczyk (2012), Boni et al. (2010)]. In these proteins SA and RSA has been observed on different wavelengths. Excitation of bR with fs pulses around 570 nm triggers the formation of I_{460} state before the J state. Hence, based on the early sub-ps transitions in the bR photocycle, it is important to propose accurate theoretical model to understand the ultrafast AOS with bR. The outstanding properties of bR, such as extremely high quantum yield, low isomerization time, high molecular extinction coefficient and high chemical and thermal stability seem to be extremely useful to design AO devices based on sub-ps AOS. Integration of bR with semiconductor QDs and gold nanoparticles open up the prospect of low power ultrafast AOS. Hence, it would also be important to realize ultrafast AOS with bR-QDs and bR gold nanoparticles for low power AOL devices. Femtosecond spectroscopic characterization of cyt-c protein based on ESA has revealed SA and RSA at different wavelengths for its application in optical limiting. But the fs NLO response has not been explored for AOL operations. Hence, it would be important to optimize the NLO response to realize the different AO logic gates with fs switch off/on time with this protein. To the best of our knowledge, no device applications have been proposed with bR and cyt-c protein with sub-ps switch off/on time to date. Hence, we were motivated to analyse the sub-ps AOS and NLA with bR and cyt-c protein in detail and to investigate their device applications.

The proposed research work is very fundamental as it helps in understanding the ultrafast NLO and AOS response of these fascinating and extremely useful organic and biomolecules and also their applicability to some basic device applications for ultrafast AO information processing.
1.4 Thesis Objectives

The objective of the research work was to investigate ultrafast NLA (SA and RSA) and switching in the recently characterized organic molecules, namely, Phthalocyanines, Graphene, Graphene-oxide, Ruthenium complexes, Bacteriorhodopsin and Cytochrome-c protein and to design different AOL gates. The specific objectives of the study that had been outlined were as follows:

1. To conduct a detailed theoretical analysis of ultrafast NLA (SA and RSA) and switching in the recently characterized organic molecules, namely,
   (i) *Copper-phthalocyanines*
   (ii) *Graphene*
   (iii) *Ruthenium-dioxolene*
   (iv) *Bacteriorhodopsin, and*
   (v) *Cytochrome-c*

2. To analyze the effect of the following parameters on the switching and the NLA characteristics:
   (i) *Third and fifth order nonlinear coefficients*
   (ii) *Pump pulse width and intensity*
   (iii) *Concentration*
   (iv) *Pulse frequency*
   (v) *Absorption cross-sections and life times*

3. To derive optimized conditions for fs pulse absorption and propagation in organic samples and design the following AO ultrafast logic gates:
   (i) *NOT*
   (ii) *OR*
   (iii) *AND*
   (iv) *XOR*
   (v) *NOR*
   (vi) *NAND*

4. To compare the performance of various organic molecules.
1.5 Thesis Outline

The proposed research objectives have been successfully achieved and reported in the thesis as follows:

Chapter 1 is the introduction of the thesis which gives an overview of the significance of the research topic. The importance of ultrafast AO NLA (SA and RSA) and switching for realization of ultrafast and ultrahigh bandwidth AO devices, namely, logic gates have been discussed in detail. The advantages of organic, inorganic and nano-bio hybrid molecular configurations to overcome the present challenges of ultrafast, low power and compact AO devices and circuits have also been addressed.

Studies were initiated with a detailed theoretical analysis of fs intensity dependent SA and RSA characteristics in CuPc-doped PMMA thin films, the results of which are presented in Chapter 2. As described earlier, the next generation information processing systems require the design of AO ultrafast devices. This can be achieved by designing an efficient AO switch that fulfills the requirement of ultrahigh speed, high contrast and low-power operation as well as photo and thermal stability. Logic gates and computing circuits based on switches or NLA (SA to RSA) are necessary for digital information processing. Earlier studies have shown that logic gates can be designed by using SA and RSA characteristics respectively. In a variety of molecular configurations, the SA have been exploited to realize AO AND and OR logic gates whereas RSA have been utilized for NOT and the universal NAND and NOR logic gates, in a pump-probe configuration [Roy and Yadav (2011)]. These designs of AOL gates require different samples that exhibit either wavelength dependent or excited-state life time dependent SA or RSA and also suffer from speed of operation (~ns-ms) due to longer lifetime value of the triplet states in organic molecules. In order to achieve fast switching (fs-ps), it would be advantageous to realize various AOL gates with the same sample and experimental setup with a single laser pulse at the same color. Hence, we have taken the next level of complexity to efficiently design the ultrafast AOL gates based on SA to RSA or RSA to SA transition at same wavelength by just regulating the input pulse intensity. For this a four level energy diagram has
been presented to understand the fs transition from SA to RSA or RSA to SA in CuPc-doped PMMA thin films. The transition has been optimized with respect to TPA and 3PA coefficients, pulse intensity, pulse frequency, pulse width and concentration of the sample to design various AOL gates using the same films and single wavelength [Roy and Yadav (2011)]. Side humps in the SA and RSA characteristics that leads to XOR logic gates, has been realized by just changing the value of third-order nonlinear coefficients ($\beta^{(3)}$). Logic gates have been optimized by just controlling the input pulse frequency for optimum pulse interval of 15 fs that can lead to 66 Tbits/s repetition rates. The present study demonstrates the feasibility of using CuPc-doped PMMA thin films, for fs AOL devices.

In Chapter 3, a detailed analysis of SA and RSA in graphene, GO and graphene and GO-metal porphyrin composites in ps and fs regime has been presented. In graphene and GO-metal porphyrin composites, only RSA has been observed with ps and fs pulses at 532 and 800 nm respectively. Higher contrast (94%) has been achieved in graphene in comparison to GO and GO-metal porphyrin composites. RSA in graphene and GO-metal porphyrin composites has also been optimized to design NOT and the universal NAND and NOR logic gates. More interestingly, a theoretical model based on the recently reported experimental results by Jiang et al. (2012), has been proposed for GO to understand the turnover from SA to RSA or RSA to SA with fs laser pulses at 800 nm. Theoretical simulations successfully reproduce the experimental results. Turnover from SA to RSA by increasing the pulse intensity or RSA to SA by increasing the concentration has been realized. Transition intensity is sensitive to TPA and 3PA coefficients i.e. the SA to RSA transition intensity mainly depends on TPA and 3PA coefficients. The performance of SA to RSA or RSA to SA has also been studied over a range of intensity, concentration and TPA and 3PA coefficients. Hence, to explore the advantages of the unique properties of GO, SA to RSA or RSA to SA conversion have been optimized with respect to pulse intensity and frequency, concentration, pulse width and TPA and 3PA coefficients to design high speed AOL gates using the same setup and film by only changing the output threshold level. These designs would be advantageous to realize different logic operations simultaneously in parallel with the same set up [Roy and Yadav (2013 a, 2015)].
Interestingly, changeover from RSA to SA on increase in intensity have been experimentally realize in Ru-dioxolene complex with ps laser pulses at 532 nm by Cassano et al. (2005). It would be important to understand the mechanism of these RSA to SA transition for designing AOL gates. In Chapter 4, a detailed theoretical analysis of RSA to SA transition in Ru dioxolene complex has been presented for designing the ultrafast AOL gates. At low intensity values NOT, NAND and NOR logic gates can be realized.

AOS with bR protein has been widely studied experimentally and theoretically using pump-probe configurations [Hampp (2000), Singh and Roy (2003 a, 2003 b), Huang et al. (2004 a), Topolancik and Vollmer (2006), Roy et al. (2010), Fabian et al. (2010, 2011), Mathesz et al. (2013)]. However, the main limitation so far has been the switching speed (~ns-ms) as M\(_{410}\), O\(_{640}\) or K\(_{610}\) states have been used [Rao et al. (1993), Wu et al. (2002), Singh and Roy (2003 a, 2003 b), Huang et al. (2004 a), Fabian et al. (2010), Topolancik and Vollmer (2006), Roy et al. (2010), Mathesz et al. (2013)], or even in bR-coated high-Q silica microresonators [Topolancik and Vollmer (2006), Roy et al. (2010)]. Fabian et al. (2011) have recently reported ultrafast AOS with a bR deposited above a 1D photonic crystal on a thin film waveguide by utilizing K\(_{610}\) and I\(_{460}\) state [Fabian et al. (2011), Roy and Yadav (2014)].

Recent experimental elucidation of early sub-ps transitions in the bR photocycle opens up the possibility of ultrafast AOS and computing with this protein [Petrich et al. (1987), Logunov et al. (1994), Kobayashi et al. (2001), Biesso et al. (2008), Fabian et al. (2011), Abramczyk (2012), Cheng et al. (2012)]. Recently, nano-bioengineering technologies based on the efficient integration of metal nanoparticles and semiconductor quantum dots with bR protein have opened up possibilities for optimization of the photoresponse [Li et al. (2007), Biesso et al. (2008), Griep et al. (2010), Rakovich et al. (2010, 2013)]. The life time of I\(_{460}\) state in bR photocycle can be varied with QDs and metal nanoparticles [Biesso et al. (2008)]. This can lead to ultrafast AOS with bR based hybrid materials. In Chapter 5, we have proposed a theoretical model to analyze the high contrast sub-ps AOS in bR and bR-gold nanoparticles. Simultaneous realization of different logic gates in parallel have been designed based on this analysis with 100% modulation at MW/cm\(^2\) pump intensities with bR-gold nanoparticles [Roy and Yadav...
In Chapter 6, designs of fs AOL gates based on NLA at different wavelengths in cyt-c protein have been presented. The designs are based on the optimization of NLA in cyt-c protein. NLA behavior switches from SA to RSA on decrease in wavelength. Theoretical results match successfully with the reported experimental results by Boni et al. (2010). The designs are important as they are the first AO implementation with this cyt-c protein in sub-ps regime. The analysis demonstrates the applicability of the theoretical model to study the ultrafast NLO response of cyt-c and the possibility of using it for AO ultrafast photonic device applications.

The conclusion of the thesis is presented in Chapter 7. Detailed study of ultrafast AOS and NLA (SA and RSA) has been undertaken in novel organic and bio materials. The effects of various parameters such as peak pulse intensity and frequency, pump pulse width, concentration, thickness, absorption cross-sections, TPA and 3PA nonlinear coefficients and lifetimes of different states have been studied in detail. The switching and NLA characteristics have been optimized in terms of speed, low power and high contrast to efficiently design various ultrafast AOL gates.

The research work presented in the thesis opens up exciting new possibilities of using novel organic materials and ultrasensitive biomolecules for the design of various photonic devices for ultrafast and ultrahigh bandwidth AO information processing. In addition to that bR-gold nanoparticles based sub-ps AOL gates show the applicability of bR based hybrid materials with unique electronic and photonic properties for novel nano-bio-photonic applications.

The above research work has resulted in publications in five international Journals and six Conference Proceedings. Research work has also received recognition in terms of citations and awards. The detailed description is mentioned in APPENDICES-A and B.