

A DISSERTATION
ON
**THEORETICAL STUDY OF
EXCITED-STATE ABSORPTION
IN GRAPHENE OXIDE AND ITS APPLICATION IN
PHOTONIC SWITCHING**

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE
AWARD OF THE DEGREE
OF
**MASTER OF TECHNOLOGY
IN
NANOSCIENCE AND TECHNOLOGY**

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DECLARATION BY THE CANDIDATE

I hereby declare that the work presented in this dissertation entitled “**Theoretical study of excited-state absorption in grapheme oxide and its application in photonic**” has been carried out by me under the guidance of *Dr. Parag Sharma*, Scientist, National Physical Laboratory, Delhi and *Dr. A. Srinivasa Rao*, Associate Professor, Department of Applied Physics, Delhi Technological University, Delhi and hereby submitted for the partial fulfillment for the award of degree of Master of Technology in Nanoscience and Technology at Applied Physics Department, Delhi Technological University, Delhi.

I further undertake that the work embodied in this major project has not been submitted for the award of any other degree elsewhere.

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CERTIFICATE

This is certified that the P.G dissertation entitled “**Theoretical study of excited-state absorption in grapheme oxide and its application in photonic**” submitted by **Kaushal Upadhyay**, Roll no: 2K12/NST/08, is a bonafide record of the student’s own work. He has worked under my guidance and supervision at **National Physical laboratory, New Delhi** in the Quantum Phenomena and Applications division for a period of six months from **2nd December, 2013** to **2nd June, 2014** for fulfilling the requirements for the submission of this dissertation.

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The matter embodied in this dissertation is original and has not been submitted in part or full for the award of any other degree or certificate in this or any other university or institute.

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CONTENTS

Acknowledgement	i
Declaration by the candidate	ii
Certificates	iii
Abstract	vii
CHAPTER-1 INTRODUCTION	
1.1 Photonics	1
1.2 Nonlinear Optics	3
1.2.1 Nonlinear interactions between light and matter	4
1.2.1.1 General Classification	5
1.2.1.2 Incoherent Interaction	6
1.2.2 Nonlinear Absorption	8
1.2.2.1 Two-Photon Absorption (TPA)	8
1.2.2.2 Transient Absorption: Excited State Absorption	9
1.2.3 Nonlinear Transmission	12
1.3 Applications of Nonlinear Optics	13
1.4 All-Optical Switching	14
1.5 Nonlinear optical materials	17
CHAPTER-2 LITERATURE SURVEY OF GRAPHENE OXIDE	
2.1 Graphene	19
2.1.1 Properties of grapheme	19
2.1.1.1 Structure	19
2.1.1.2 Mechanical	20
2.1.1.3 Chemical	20
2.1.1.4 Electronic	20
2.1.1.5 Thermal	21
2.1.1.6 Optical	21
2.2 Graphene Oxide	22
2.2.1 Nonlinear optical properties of Graphene Oxide	23

2.2.2 Surveyed Results	25
CHAPTER-3 NONLINEAR ABSORPTION IN GRAPHENE OXIDE	
3.1 Introduction	28
3.2 Basic Model	28
3.3 Steady state analysis – Continuous Wave (CW) pump beam excitation	30
3.4 Time dependent analysis	36
3.4.1 Nanosecond Pulse Beam Excitation	36
3.4.2 Picosecond Pulse Beam Excitation	41
3.4.3 Femtosecond Pulse Beam Excitation	45
CHAPTER-4 CONCLUSION	
CHAPTER-4 CONCLUSION	50
REFERENCES	52

ABSTRACT

Ever since it was realised that the silicon based electronics (semiconductor) industry will reach to saturation in near future, there has been a tremendous search for novel materials that might be able to replace silicon, particularly in applications related to switching and computation. In this thesis, one such novel material i.e. Graphene Oxide has been theoretically studied and its nonlinear optical properties have been thoroughly explored using the phenomenon of excited state absorption and the technique of rate equations. The results have been simulated using computer software and explanations are provided based on population and transmittance curves. The phenomena of saturable absorption and reverse saturable absorption have also been discussed in regards with the population curves for GO when excited by pulses of different width.

Switching is the basic operation of establishing or breaking connection between two points in circuit. This is the basis for digital electronics that has revolutionalized the whole computer industry. GO shows all-optical characteristics that are desirable from a material useful for switching. So, the all-optical switching operation has been studied based on pump-probe method where one beam is used to modulate the intensity of the other and the possibility of GO being used in such applications has also been discussed. GO has proven to be a very interesting material that shows fascinating nonlinear optical properties. These properties if harvested properly, can help in developing all-optical switches based on GO that will be way faster, less power consuming and smaller than their silicon based electronic counterparts.

Chapter-1

INTRODUCTION

1.1 PHOTONICS

In the recent years, photonics has attracted a large number of researchers because of tremendous possibilities of developing novel materials that can be used in different areas of technology. The science of photonics [1] came into existence as a result of the growing similarities and co-dependence of electronics and optics on each other. This is evident by the ever growing involvement of semiconductor materials and devices in the field of optical communications and image processing. The two areas may seem different at first, but a close observation clearly indicates that electrons often control the flow of photons and, similarly, photons control the flow of electrons. Just as electronics deals with the flow of electrons and controlling the flow of charge inside a medium or in vacuum, photonics deals with the control of the flow of photons inside a medium or in vacuum.

Since we already have utilized and developed devices based on semiconductor electronics on a very large scale, so, one might wonder as to what was the need for exploring photonics. First and foremost, the speed of a photon is far more than an electron. Photon being a light particle travels with the speed of light whereas an electron can never reach that speed. This predicts that a device based on photons will be far much superior to its counterpart based on electrons in terms of speed of operation especially in the areas like computation and image processing.

Photonics is the science and technology of generating and controlling the flow of light, and specifically using light for carrying information. Photonics includes the emission, modulation, amplification, transmission, detection and switching of light. A photon (which is an elementary particle of light and all other electromagnetic radiations) can be viewed as a quantum or discrete packet of energy. The energy of a photon is given by:

$$E = \hbar\omega = h\nu \quad (1.1)$$

Here, ' h ' is the Planck's constant, ' ω ' is the angular frequency ($\omega = 2\pi\nu$), ' ν ' is frequency and ' \hbar ' is the reduced Planck's constant ($\hbar = h/2\pi$).

Just like any other elementary particle, a photon also exhibits the wave-particle duality. So, there are various applications which utilize the particle nature of photons while there are many others that rely on the wave nature of photons for their implementation.

The importance of photonics can be understood by the devices which base their operations on photons, like ‘Lasers’ that are used for drilling, welding and cutting of metals, cutting of fabrics and human tissues (in cosmetic surgery and cornea correction in human eye). These coherent beams of light (lasers) have a high bandwidth and can carry far more information than radio frequency and microwave signals. On the other hand, fiber optics allow light to be “tunneled” through cables. Photonics also plays an important role in the spectral analysis techniques that provide positive identification and quantifiable concentrations of gases and solid substances.

Photonics creatively uses lasers, optics, fiber-optics, and electro-optical devices in numerous and diverse fields of technology. The interdisciplinary nature of photonics presents tremendous opportunities in the fields of manufacturing, information technology and telecommunications, environmental monitoring, homeland security, aerospace, health care and the life sciences– Biophotonics, optical sensing, lighting, energy and displays optics and many others.

Nanophotonics is the sub-branch of photonics that deals with the interaction of light and nanomaterials or nanostructures. Nanomaterials are defined as materials having at least one dimension measuring less than 100 nanometers, or billionths of a meter. At such a small scale, the properties characterized by larger systems are not necessarily applicable and the nanomaterials respond differently to the changes in size, conductivity or temperature. This explicit behavior gives unique properties to the nanophotonics devices. Nanophotonics [2] can conceptually be divided into three parts. One way to induce interactions between light and matter on a nanometer size scale is to confine light to nanoscale dimensions that are much smaller than the wavelength of light. The second approach is to confine matter to nanoscale dimensions, thereby limiting interactions between light and matter to nanoscopic dimensions. This defines the field of nanomaterials. The last way is nanoscale confinement of a photoprocess where we induce photochemistry or a light-induced phase change. This approach provides methods for nanofabrication of photonic structures and functional units.

The recent advancements in the general field of nanotechnology have created a lot of opportunities for the utilization of these materials and methods to fabricate and develop nanophotonic devices. These nanophotonics devices largely comprise of structures that can confine light and can slow down, enhance and manipulate light-matter interactions. As a result, nanophotonics can provide high speed, high bandwidth

and ultra-small optoelectronic components. This technology has a great potential to revolutionize different industries like computation, telecommunications and sensing.

1.2 NONLINEAR OPTICS

Optics is the science of studying the interaction between matter and electromagnetic radiations such as light. Since the introduction of laser as an intense coherent source of light, a fascinating new field of research termed “nonlinear” optics was introduced to the scientific and engineering community. Nonlinear optics is a broad field of research and technology that encompasses subject matter in the fields of physics, chemistry, biology and engineering.

Simply put, nonlinear optics is the study of phenomena that result from a field-induced modification in the optical properties of a material system. Formally, the branch of optics that deals with the interaction of light within a nonlinear dielectric medium is described as being the ‘Nonlinear Optics’ (NLO). It deals with the light-matter interaction in situations under which the linear superposition principle is no longer followed.

A linear dielectric medium shows a linear relationship between the polarization density, P and the electric field, E given by:

$$P = \epsilon_o \chi E \quad (1.2)$$

Here, ϵ_o is the permittivity of free space and χ is the electric susceptibility of the medium.

The polarization density is in turn given by the product of the individual dipole moment ρ induced by the applied electric field E and the number density of dipole moments N .

$$P = N \rho \quad (1.3)$$

The nonlinear behavior may arise because of the effect of either N or ρ [3]. The relationship between P and E is considered to be linear only when the applied electric field E is small. This is done so as to simplify the problem but it is not completely correct. Since externally applied optical electric fields are typically small in comparison with characteristic interatomic or crystalline fields, even when focused laser light is used, the nonlinearity is usually weak. But when E is of the order of interatomic electric fields ($\sim 10^5 - 10^8$ V/m), which is observed at very high light intensities, the relation

between P and E acquires a nonlinear behavior. So, P can be expressed in the form of Taylor's series [4] expanded about $E = 0$:

$$P = \epsilon_o [\chi^{(1)} E + \chi^{(2)} E^2 + \chi^{(3)} E^3 + \dots] \quad (1.4)$$

Here, $\chi^{(1)}$ is the linear susceptibility, $\chi^{(2)}$ is the second-order susceptibility and so on. In general, the coefficient $\chi^{(n)}$ is the n -th order susceptibility of the medium and the presence of such a term is generally referred to as an n -th order nonlinearity. $\chi^{(n)}$ is a tensor since it represents the relationship between the polarization, which itself is a vector and the product of several electric field vectors.

1.2.1 Nonlinear Interactions between Light and Matter

Light can be generated or manipulated in almost any manner by using nonlinear effects in optics. The best example to support this statement is the laser itself, which produces light that is not available naturally, but produces profound effects in regards to light-matter interaction. So, we can say that nonlinear interactions are the basis of photonics. Since, the photon-photon interaction cross-section is extremely small, the direct influence of one light beam on another cannot be practically studied with the current light sources. As a result, the nonlinearity has to be achieved by the nonlinear interaction of light with matter.

This nonlinear interaction [5] may be resonant or non-resonant based on whether the matter is absorbing or non-absorbing (i.e. transparent). Non-resonant interactions are useful in applications like wavelength conversion of laser light, wave mixing and optical phase conjugation. In this type of interactions, almost no energy will be stored in the material as there is negligible absorption. Hence, these interactions can be applicable for high average powers with high efficiencies obtained by exploiting the high damage threshold of the applied materials.

At least some absorption is shown by all matter in almost all spectral regions as a consequence of electronic transitions. The effects of the resonant nonlinear interaction can often be neglected when the absorption coefficient is smaller than about 10^{-6} cm^{-1} . There are many photonic applications that are based on resonant nonlinear interactions such as stimulated emission in lasers or passive Q-switching and mode locking. Applications, such as optical switching and storage that are based on nonlinear absorbing devices, are being seen as the technology of future. It is generally observed that the non-resonant nonlinear effects with strongly increased nonlinear coefficients

can be used to promote resonance enhancement with very weak absorption. This implies that a detailed knowledge about nonlinear absorption, nonlinear transmission and transient absorption effects, and their experimental and theoretical evaluation, is essential for successful operation of nonlinear photonic devices in both resonant and non-resonant cases. There has not have been much investigation about nonlinear absorption up till now, and thus it is much less well known along with the experimental and theoretical methods.

1.2.1.1 General Classification

While dealing with small absorption with little structure as a function of the light frequency in the required spectral range, the relations based on the nonlinear polarization of matter as a function of the electric field strength can generally be used to describe the nonlinear interaction between light and matter if all values are taken to be complex values. But there have to be other descriptions to be used when the nonlinear absorption effects are dominant. In those cases, the detailed structure of the energy levels of the matter needs to be considered along with their transition moments and the relaxation times between them.

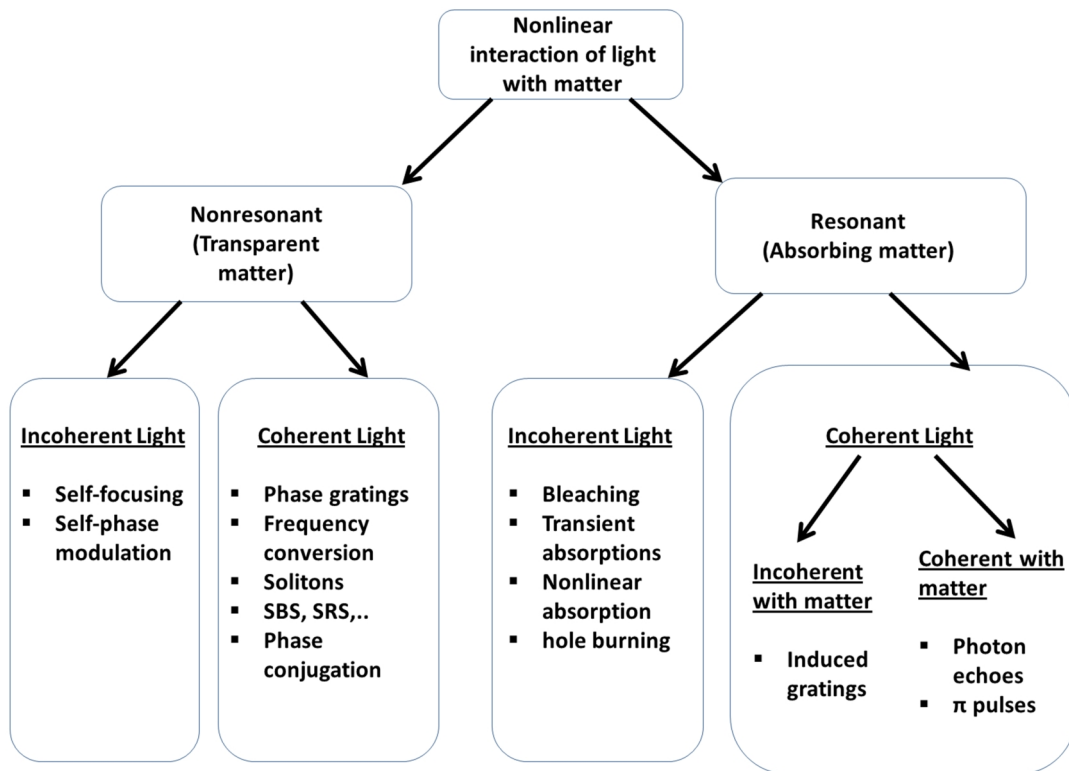


Fig. 1.1 Scheme of nonlinear interactions [5] of light with matter which may be transparent or not at the required wavelengths

The general classification of nonlinear interactions along with the distinctions between coherent and incoherent interactions has been schematically listed in Fig. 1.1.

Two levels of coherence can be observed with regards to nonlinear interactions in absorbing matter: First, the used light fields can be coherent and thus they can produce nonlinear absorption gratings. Second, the induced dipole moment in the matter can oscillate in phase with the applied electric field resulting in the quantum effects such as the generation of π -pulses and photon echoes. The essential requirement for this complete coherent interaction is that the internal phase coherence time of the matter must be longer than the relevant experimental time, e.g. the pulse width.

In case of incoherent light the non-diagonal elements of the density matrix can be set to zero and the solution can be based on a system of rate equations containing space, time, frequency and polarization in a phenomenological manner but considering the quantum structure of the involved matter. These equations can be extended for considering coherent light effects such as, e.g., induced gratings if the matter reacts incoherently as a consequence of fast coherence decay time.

The resonant coherent light-matter interaction can be described with density matrices. However, usually this is only possible if not too many optical transitions of the matter are involved. In most cases only one transition can be considered. In all cases it is widely assumed that the interaction does not change the energy eigen states of the matter and thus the energy levels and the resonance frequencies can be computed separately.

1.2.1.2 Incoherent Interaction

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

$$\text{Nonlinear absorption, } a = f\{I\} = f\{I(r, \lambda, t, \varphi)\} \quad (1.5)$$

In simple cases such as, e.g. under stationary conditions and for optically thin samples these absorption coefficients can be given analytically as rational polynomials of the intensity. But only in the simplest cases can the intensity equation also be solved analytically.

The nonlinear incoherent absorption results from the change in population of absorbing or emitting energy states of the matter. Thus the absorption coefficient a for a given light beam may be written as:

$$a = \sum_m \pm \sigma_m(\lambda, \varphi, r) N_m(I, r, t) \quad (1.6)$$

where σ_m is the cross-section of the m th eigenstate (or energy level) of the matter and N_m is its population density. All possible absorption (+ sign) and emission (– sign) transitions have to be summed.

In the most trivial approach the nonlinear absorption coefficient can be written as the first term of the series:

$$\text{0th approach} \quad a(I) = a_0 \left\{ 1 - \frac{I}{I_{n1}} \right\} \quad (1.7)$$

with the nonlinear intensity $I_{n1} = \frac{h\nu}{2\sigma\tau}$ and $a_0 = \sigma N_{total}$ and

$$I_{n1} = \frac{I_{n1}}{h\nu} = \frac{1}{2\sigma\tau} \quad (1.8)$$

where σ is the cross-section of the active transition, τ is the recovery time of the absorption of this transition, ν its frequency and N total the population density of the absorbing state without excitation. The intensity I_{n1} is measured as the photon flux density in photons $\text{cm}^{-2} \text{s}^{-1}$. In the case of a two-level scheme this approximation (1.7 and 1.8) is useful for intensities small compared to I_{n1} but in more complicated cases it may fail completely. Therefore the structure of the nonlinear absorption should be analyzed in detail to avoid fundamental errors in discussing the experimental results.

The nonlinear absorption can easily be measured if the necessary excitation intensities are available. For typical cross-sections of $10^{-16} - 10^{-20} \text{ cm}^2$ and recovery times of ns– μ s for molecular or atomic systems the resulting non-linear intensities are in the range of $10^{22} - 10^{27} \text{ photons cm}^{-2} \text{ s}^{-1}$ or kWcm^{-2} to GWcm^{-2} which can easily be realized with pulsed lasers. The following effects can be obtained:

- bleaching;
- general nonlinear transmission including darkening;
- transient absorptions – excited state absorptions (ESA);
- stimulated emission – super-radiance – laser action;
- spectral hole burning.

Although nonlinear absorption or transmission can be determined with high accuracy the evaluation of the experimental results for obtaining material parameters such as the transition moments or cross-sections and the decay times of all participating

matter states can be very difficult. Firstly, it can be difficult to determine which states are involved in the experiment and secondly, the population densities N_m of these states can be very difficult to work out. Sometimes the calculation with numerical models can be helpful. Simple rate equations can be sufficient but for safe results some experimental strategy has to be used.

1.2.2 NONLINEAR ABSORPTION

A number of significant changes can be induced by the intense monochromatic radiation from a laser in the optical properties of a material. The change in transmittance of a material as a function of intensity (or fluence) is referred to as the nonlinear absorption [6]. With considerably high beam intensities, there is a high probability of a material absorbing more than one photon before it relaxes to the ground state. The invention of the laser has not only led to the study of the simultaneous absorption of two photons in a wide variety of materials but also has contributed to expand this research into three photons and multiphoton absorption in various matters. Moreover, the population redistribution induced by intense laser fields leads to interesting effects of stimulated emission and absorption, complicated energy transitions in complex molecular systems, and the generation of free carriers in solids. These phenomena are optically exploited in a reduced (saturable) or increased (reverse saturable) absorption.

1.2.2.1 Two-Photon Absorption

Two-photon absorption (TPA) involves a transition from the ground state of a system to a higher-lying state by the simultaneous absorption of two photons from an incident radiation field or fields. 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 Fig. 1.2. In the first, two photons from the same optical field oscillating at frequency ω are absorbed to make the transition, which is approximately resonant at 2ω . In the second situation, two optical fields at frequencies ω_e and ω_p are present, and one photon from each field is absorbed for the transition, which is approximately resonant [4] 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 subscript p. In both cases, the intermediate (or virtual) state is not real (i.e., does not involve a real stationary state of the system). Hence the system must absorb the two photons simultaneously. This makes the process sensitive to the instantaneous optical intensity.

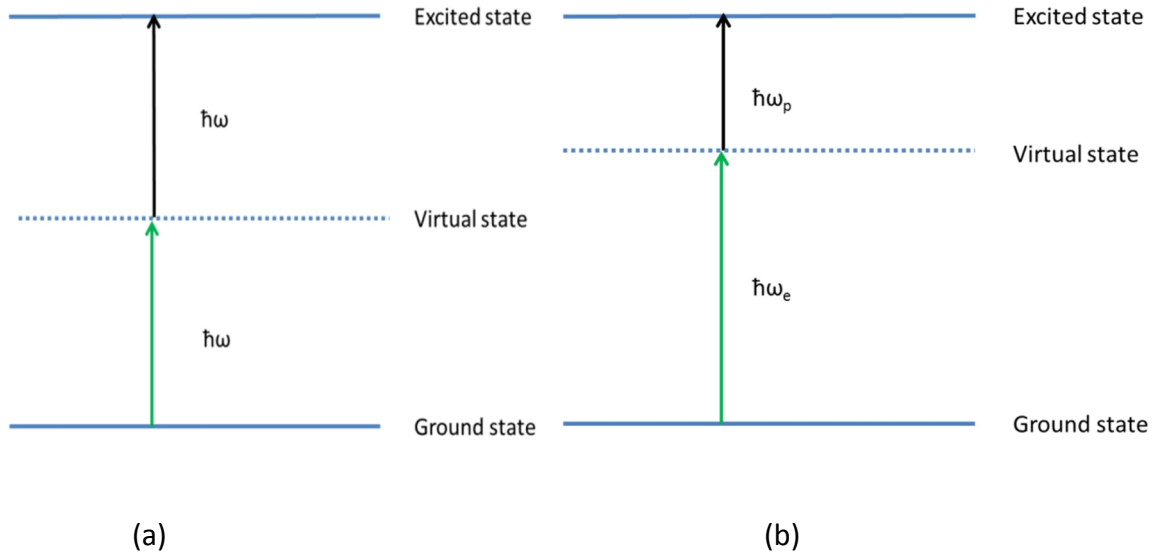


Fig. 1.2 Schematic diagram of two-photon absorption (TPA) (a) Self-TPA. (b) Pump-probe TPA.

Although the transition does not involve a real intermediate state, often there are impurities present that will produce a small amount of linear absorption. It should be understood that this absorption does not contribute to the transition to the final state of the process but only serves as an additional loss mechanism. Two-step absorption involving a single photon pumped intermediate state is described as excited state absorption.

1.2.2.2 Transient Absorption: Excited State Absorption (ESA)

When the incident intensity is well above the saturation intensity, then the excited state can become significantly populated. In systems such as polyatomic molecules and semiconductors, there is a high density of states near the state involved in the excitation. The excited electron can rapidly make a transition to one of these states before it eventually transitions back to the ground state. 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 photon energy.

Therefore, before the electron completely relaxes to the ground state, it may experience absorption that promotes it to a higher-lying state [7]. This process is called excited state absorption. It is observable when the incident intensity is sufficient to deplete the ground state significantly. When the absorption cross-section of the excited state is smaller than that of the ground state, the transmission of the system will be increased when the system is highly excited. This process is called saturable absorption (SA). It is similar to, but more complex than, saturable absorption in a simple two-level system. Generally, two-level saturable absorption will be approximated when the incident pulse is shorter than the decay time for any energy relaxation channel available to the excited electron, and when the transition to any higher lying state is not resonantly enhanced. When the absorption cross-section of the excited state is larger than that of the ground state, then the system will be less transmissive when excited. This gives the opposite result as saturable absorption and is thus called reverse saturable absorption (RSA).

In semiconductors, the absorption of a photon with energy greater than the band gap will promote an electron to the conduction band, where it is a free carrier and can contribute to current flow when a field is applied. The excited electron will rapidly thermalize and relax to the bottom of the conduction band. From there it will recombine with an excited hole in the valence band after a characteristic recombination time. However, at sufficiently high intensities, it can with high probability absorb another photon while it is still in the conduction band. This process is called free carrier absorption. It has similar qualitative characteristics to reverse saturable absorption. As photons from the incident light pump electrons into the upper energy level, the ground state becomes depleted. Population of the upper state also leads to spontaneous and stimulated emission of photons. The net result is that the system cannot absorb as large a fraction of the incident light as it can under low-intensity conditions. This process is called saturable absorption.

There is a tremendous research interest in finding molecules possessing this important RSA characteristic as it can be useful for a variety of applications that include pulse energy limiting, pulse shortening, power limiting, pulse smoothing, mode-locking, spatial light modulation and pulse compression etc.

The phenomena of ESA can be used to control one light beam by another light beam through a nonlinear optical material using the pump-probe technique. A large variety of nonlinear absorption effects can be obtained in pump-probe experiments with at least two beams (see Fig. 1.3).

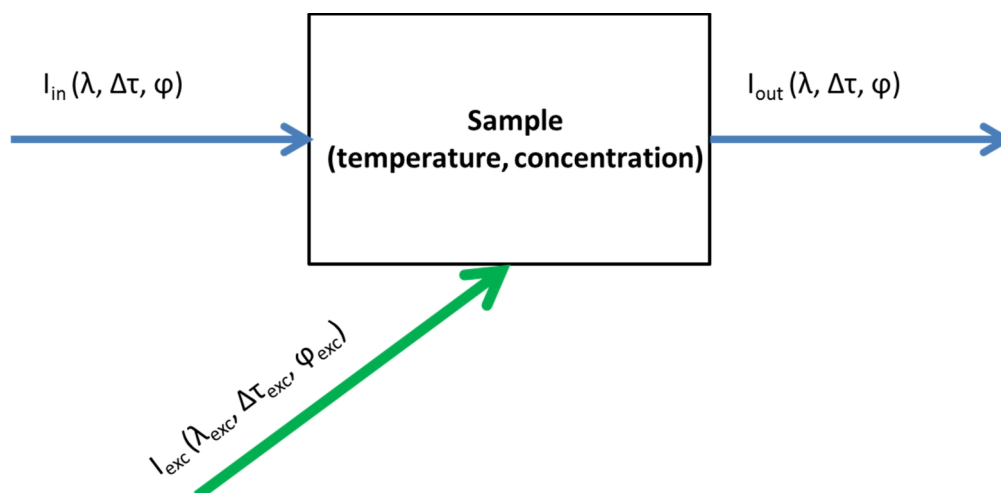


Fig. 1.3 Pump and probe technique for observing transient absorption (ESA spectroscopy)

The pump beam corresponding to the peak absorption wavelength of the ground state excites the molecules to the excited-state, which results in an increase in the absorption of a weak probe beam passing through the sample at the wavelength corresponding to the peak absorption wavelength of the populated excited-state. Thus, the transmission of a weak CW probe beam corresponding to the absorption peak of the excited-state would get modulated due to the intensity-induced changes in the population of the excited-state by a CW or pulsed pump beam.

The nonlinear effect is produced by a strong pump beam which populates excited states in the sample. This alteration of the sample has a large variety of new properties generated by the exciting light. The choice of the pump light parameters allows the appropriate population of all kinds of special material states with different new absorption characteristics, with life times from a few fs to hours, and so on.

The population densities of different intermediates depend upon the pump intensity, pump wavelength, lifetimes and absorption cross-section values of different states. The pump-probe technique can be used to effectively use this switching mechanism with different intermediates for all-optical light modulation. The transmission of the probe beam depends on the pump intensity, pump and probe wavelengths and spectral and kinetic parameters of the intermediate states.

The transmission of the sample can be determined from the intensities of the transmitted beam I_{out} and the incident beam I_{in} as:

$$\text{Transmission} \quad T = \frac{I_{out}(t_m)}{I_{in}(t_m)} \quad (1.9)$$

The conventional transmission as described in this expression (1.9) measuring both intensities at the same time is commonly used in nonlinear experiments as long as the pulse length is not too short. It is especially useful if steady-state conditions are realized. In experiments with *ps* or *fs* pulses the temporal pulse shape cannot be measured electronically and thus time-integrated intensities which are the pulse energies are then used.

The exciting light can be built from two or more different light beams for multiple excitation of the sample. But in any case the probe light intensity has to be small enough not to disturb the sample itself.

1.2.3 Nonlinear Transmission

The basic objective of a nonlinear transmission experiment is to measure the incident and transmitted laser pulse energies and to form their ratio to obtain the sample transmittance. The nonlinear transmission of absorption bands especially of organic materials can be much more complicated. In many cases an excited state absorption (ESA) occurs in the same wavelength range as the ground state absorption (GSA) with sometimes an even stronger cross-section than the GSA. The combination of bleaching and new transient absorptions can lead to quite complicated functions of the transmission as a function of the incident intensity in the nonlinear range.

It is observed that all kinds of transmission graphs as functions of the intensity with maxima, minima and plateau [8] are possible. The evaluation of the nonlinear transmission curve allows the identification of excited state absorption. Very often, at least, one transient absorption is present in the wavelength range of the investigated ground state absorption band and the use of a two-level scheme for modeling the experimental results is than not sufficient. Thus the detailed investigation of new samples with simple nonlinear transmission measurements can yield remarkable knowledge about the involved energy states, their parameters and finally about the nonlinear behavior of the material.

1.3 APPLICATIONS OF NONLINEAR OPTICS

Nonlinear optics has a wide range of applications [9]-[10] based on various nonlinear optical processes namely:

- Frequency doubling
- Parametric amplifiers
- Parametric up and down-converters
- Optical parametric oscillators or OPOs
- Waveguides
- Spontaneous parametric down converters
- Switching and optical computing

Switching is an essential operation in communication networks. It is also a basic operation in digital computers and signal processing systems. The digital circuits use data to switch between 0 and 1 (i.e. either high input or low input). The current rapid development of high-data-rate fiber-optic communication systems has created a need for high-capacity repeaters and terminal systems for processing optical signals and, therefore, a need for high-speed photonic switches. Similarly, the potential for optical computing can only be realized if large arrays of fast photonic gates, switches, and memory elements are developed. For that purpose, two types of switches have been proposed. One is an electro-optic switch which utilizes the conversion of energy between photons and electrons. Optical signals may be switched by the use of these switches: the optical signals are converted into electrical signals using photodetectors, switched electronically, and then converted back into light using LEDs or lasers. These optical/electrical/optical conversions introduce unnecessary time delays and power loss (in addition to the loss of the optical phase caused by the process of detection). The other is an all optical switch which carries the function of switching using photons only with no losses for energy conversions. Direct optical switching is clearly preferable to electronic switching. We will be discussing all-optical switch in details in the following section.

1.4 ALL-OPTICAL SWITCHING

In an all-optical (or opto-optic) switch, light controls light with the help of a nonlinear optical material. Nonlinear optical effects may be direct or indirect. Direct

effects occur at the atomic or molecular level when the presence of light alters the atomic susceptibility or the photon absorption rates of the medium. The optical Kerr effect (variation of the refractive index with the applied light intensity) and saturable absorption (dependence of the absorption coefficient on the applied light intensity) are examples of direct nonlinear optical effects. Indirect nonlinear optical effects involve an intermediate process in which electric charges and/or electric fields play a role.

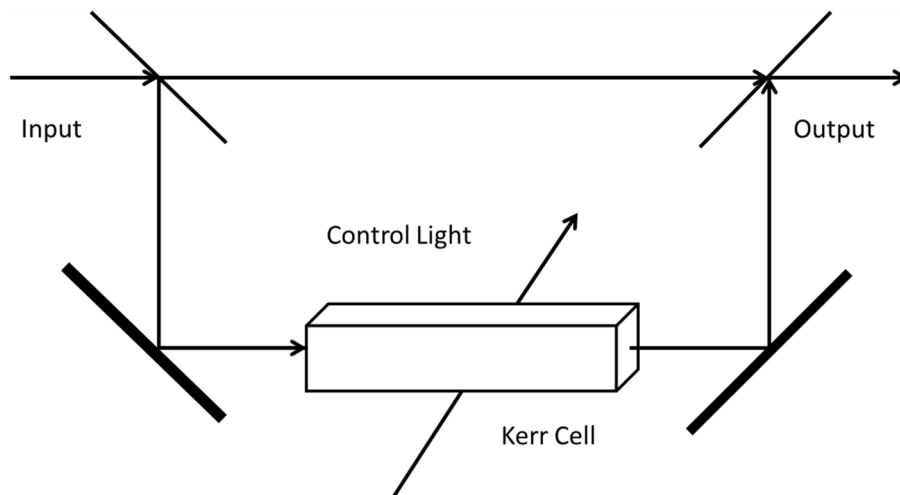
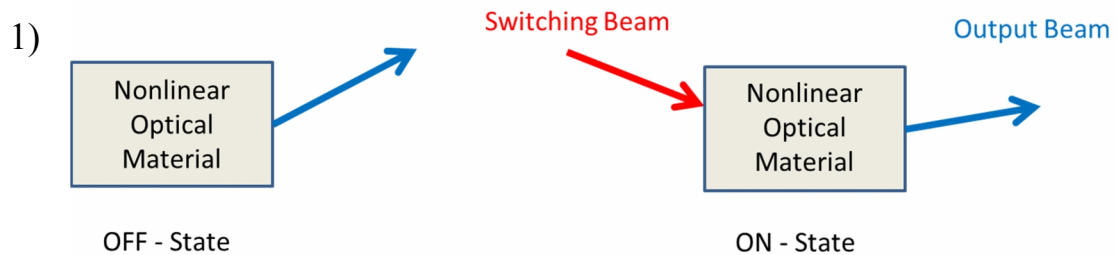


Fig. 1.4 An all-optical on-off switch using a Mach-Zehnder interferometer and a material exhibiting the optical Kerr effect

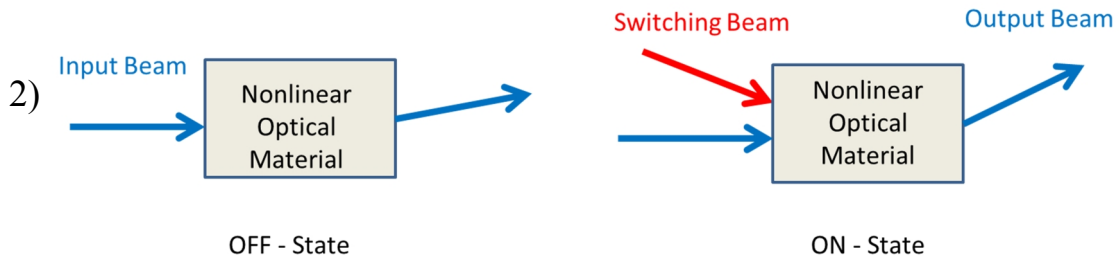
Nonlinear optical effects (direct or indirect) may be used to make all-optical switches. The optical phase modulation [11] in the Kerr medium, for example, may be converted into intensity modulation by placing the medium in one leg of an interferometer, so that as the control light is turned on and off, the transmittance of the interferometer is switched between 1 and 0. Fig. 1.4 illustrates this scheme.

An all optical switch is a device that allows one optical signal (modulating beam) to control another optical signal (signal or probe beam), i.e. control of light by light. This definition of an all-optical switch is rather general, encompassing many possible devices. Here we will illustrate three types [12] of all-optical switches:



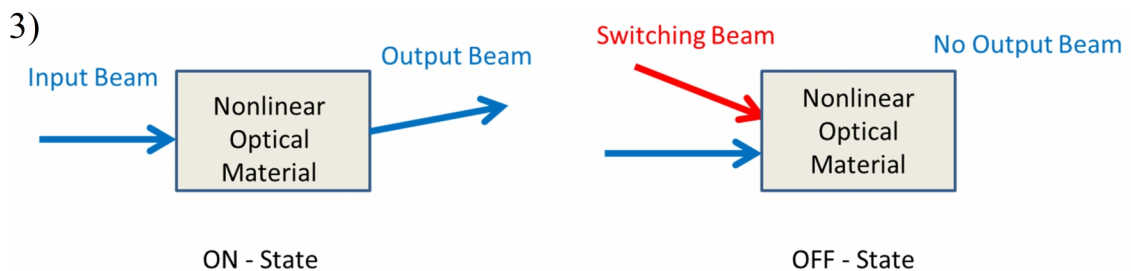
Schematic of an all-optical switch that changes the direction of output light.

In this type of device, a single beam of light (blue) is emitted from a nonlinear material and exits in a certain direction. This is one of the two states of the switch; we call it the "off" state. The switch is turned to the "on" state, when a second light beam, the switching beam (red), is injected into the nonlinear optical material. As a result, the output beam (blue) is emitted in a different direction.



Schematic of an all-optical switch that redirects light.

In the second type, a single beam of light (blue) passes through a nonlinear material and exits in a certain direction. This is the "on" state of the switch. The "off" state of the switch is achieved when a weak switching beam (red) is injected into the nonlinear optical material changes the direction of the output beam (blue).



Schematic of an absorptive all-optical switch.

The last case illustrates the behaviour of a third type of an all-optical switch. In this device, a single beam of light (blue) passes through a nonlinear material and exits in a certain direction. This is one of the two states of the switch; let's call it the "on" state. The switch is turned to the "off" state, when a second light beam, the switching beam [12] (red), is injected into the nonlinear optical material. In this case, the light of both the first beam (blue) and the switching beam (red) is absorbed by the material and there is no output light at all.

Electrical switches have been used as long as electricity has been used. The most basic electrical switch is simply a pair of wires that can be separated or put in contact; "off" or "on" respectively. In an all-electrical switch, electrical signals are

used to open or close the switch. An all-optical switch performs the same function but instead of electrical signals, it controls optical signals: light.

Without any doubt, all-electrical switches are extremely useful. It is great to be able to turn appliances "on" and "off" electronically and to use switches to direct electronic signal-streams around a network. Arguably, even more important is the use of all-electrical switches like the transistor as a building block for digital logic circuits. The idea is that the two states of a switch ("on" and "off") can be used as a physical representation of the binary integers or logic levels (0 and 1) and that logic rules used for computation can be implemented all-electronically because the state of the switch is controlled by another electrical signal.

All-optical switches can in principle fulfill the same functions as all-electronic switches, e.g. direct signal-streams around optical networks or serve as building blocks for optical computers. Would this be useful? An area for which all-optical switches are very important is communications, because nowadays most long-distance telephone and Internet communication is carried on optical fibers. These thin strands of glass let large amounts of information travel long distances at nearly the speed of light. At any point where data signals change fibers to get to their destination (like your car changing highways), the signal has to be turned from light into electricity so the destination address can be read and your data can be pointed in the right direction. The process of converting signals from light to electricity and back uses extra power (and generates extra heat) that can be expensive if the conversion has to happen quickly or many times in a row. The efficiency of optical communications can be increased if devices (like our all-optical switch) are designed to guide signals while they are in optical form.

1.5 NONLINEAR OPTICAL MATERIALS

A nonlinear optical material is one in which the interaction of the electromagnetic field of light and the electric field of the optical material is not proportional to the induced polarization. The advantages of using nonlinear optical materials for replacing the current electro-optic devices are – small size and weight, high intrinsic speed, extremely low propagation delay and power dissipation and the ability to tailor properties to suit specific applications. NLO materials typically have a distinct crystal structure [10]-[11], which is anisotropic with respect to electromagnetic radiation. Some materials change light passing through them, depending upon

orientation, temperature, light wavelength etc. (red light, lower wavelength) releasing one photon of accumulated higher energy (blue and green light, higher wavelength).

Depending upon the order of the nonlinearity expressed by the material, we can have a second-order nonlinear optical materials, third-order nonlinear optical materials or higher order nonlinear optical materials. On the basis of the three types of cohesive forces that bind the charges and polarization together, the NLO materials can be classified into the following cases: ionic crystals, which essentially consist of oxygen-polyhedra based solids, covalent crystals essentially dealing with semiconductors and molecular crystals that with organic materials, disordered and amorphous solids, in particular glasses and polymers and composites and inhomogeneous artificial solids.

Many kinds of gases, liquids, solutions and solids are useful for nonlinear optical applications based on nonlinear absorption and emission. The main categories of NLO materials [6] that are potentially useful in various nonlinear optical applications are listed below along with examples:

1. Wide bandgap insulator materials: - These include mostly crystals but also some glasses. Examples - Aluminum oxide, Arsenic trisulfide glass, Barium fluoride, Barium titanate, Calcium carbonate, Cadmium fluoride, Cadmium sulfide selenide-doped glass (OG550, RG610), Calcium fluoride, Cerium-doped barium titanate, Chromium-doped LiSGaF, Diamond, Fused silica, Germanium sulfide glass, Germanium-doped silica, Herasil glass (Heraeus), Lithium fluoride, Potassium bromide, Potassium chloride, Potassium iodide, Potassium niobate, Potassium titanyl phosphate, Rubidium bromide, Rubidium chloride, Rubidium iodide, Titanium dioxide.

2. Inorganic Crystals:- Aluminum nitride, Ammonium dideuterium arsenate (AD*A), Ammonium dihydrogen arsenate (ADA), Ammonium dideuterium phosphate (AD*P), Ammonium dihydrogen phosphate (ADP), Antimony niobate, Antimony tantalite, Barium–sodium borate, β -Barium borate (BBO), Cesium dihydrogen phosphate (CDP) CsLiB₆O₁₀ (CLBO), Potassium dihydrogen arsenate (KDA), Potassium dihydrogen phosphate (KDP), Cesium titanyl arsenate, CsTiOAsO₄ (CTA), Copper gallium arsenide, LaCa₄O(BO₃)₃ (LaCOB), Lead niobate, Lithium indium sulfide, Lithium triborate (LBO), K₂Al₂B₂O₇ (KABO), Silver gallium selenide, Zinc trissulfate (thiurea)

(ZTS), 2-Adamantylamino-5-nitropyridine (AANP), m-Bromonitroaniline (BNB), m-Chloronitrobenzene (CNB).

3. Organic materials: - 2,5-Benzothiazole 3,4-didecyloxy thiophene in tetrahydrofuran, Dialkyl-amino-nitrostilbene side-chain polymer (DANS), 66 wt-% symmetrically substituted tri-azo dye in partially fluorinated alkyl backbone main chain polymer (PSTF66), p-toluene sulfonate, Benzene, Canthaxanthin tetrahydrofuran, Carbon disulfide, 1-Chloronaphthalene Cyclohexane, Diphenylbutadiene, Fluorescein, Mesitylene, Methylene iodide, Rhodamine B, Poly(4,6-deadiyne-1, 10-diol bis{(n)-urethane}) [poly(3BCMU waveguide)], Poly-[2,4 hexadiyne-1,6 diol-bis-(p-toluene sulfonate)].

4. Nonlinear semiconductor materials:- Aluminum gallium arsenide, Gallium phosphide, Cadmium selenide, Cadmium sulfide, Cadmium telluride, Copper bromide, Copper chloride, Copper iodide, Gallium arsenide (GaAs), ZnSe, Gallium nitride, Indium antimonide (InSb), Indium phosphide (7nm crystals in porous Vycor glass, Silver gallium selenide, Zinc oxide, Zinc selenide (ZnSe) and Zinc telluride.

5. Frequency conversion materials: - Ammonium dihydrogen arsenate (ADA), Ammonium dihydrogen arsenate (ADP), Cesium dihydrogen arsenate (CDA), Lithium iodate, Lithium niobate, Potassium dideuterium phosphate (KD*P), Potassium dideuterium phosphate (KD*P), Potassium dihydrogen arsenate (KDA), Prousite (Ag_3AsS_3), Quartz ($\alpha\text{-SiO}_2$), Rubidium dihydrogen arsenate (RDA), Rubidium dihydrogen arsenate (RDP).

6. Nonlinear Absorber Materials: - Aluminum phthalocyanine, Asymmetric penta-azadentate porphyrin-like metal complexes (APPC), Buckminsterfullerene, C_{60} , Cadmium texaphyrin, Chloroaluminum phthalocyanine, Cubane clusters, Cyclopentadienyliron carbonyl tetramer, King's complex $[(\text{C}_5\text{H}_5)\text{Fe}(\text{CO})]_4$, Gallium phthalocyanine, Germanium phthalocyanine, Polymethine dyes, Tetrabenzporphyrine, Silicon naphthalocyanine.

Chapter-2

LITERATURE SURVEY OF GRAPHENE OXIDE

2.1 GRAPHENE

Since the discovery of graphene, it has been one of the favourite materials for researchers across different branches of science and engineering. Graphene is a pure form of carbon in the form of a two-dimensional single layer of carbon atoms with a hexagonal packed structure as shown in Fig. 2.1. Graphene [12] (2D) is one of carbon's allotropes, the other being 3D - diamond, graphite, charcoal, 1D - nanotube and 0D - fullerene. In fact, it can be considered to be the basic building block for all other allotropic forms. Graphene has gained immense popularity recently due to its superior properties, which include [13] extremely high thermal conductivity, high intrinsic breaking strength and very high charge carrier mobility. Moreover, it is nearly transparent to light. Graphene is seen as the only material which can compete with silicon based technology and may even overtake it in the next coming years.

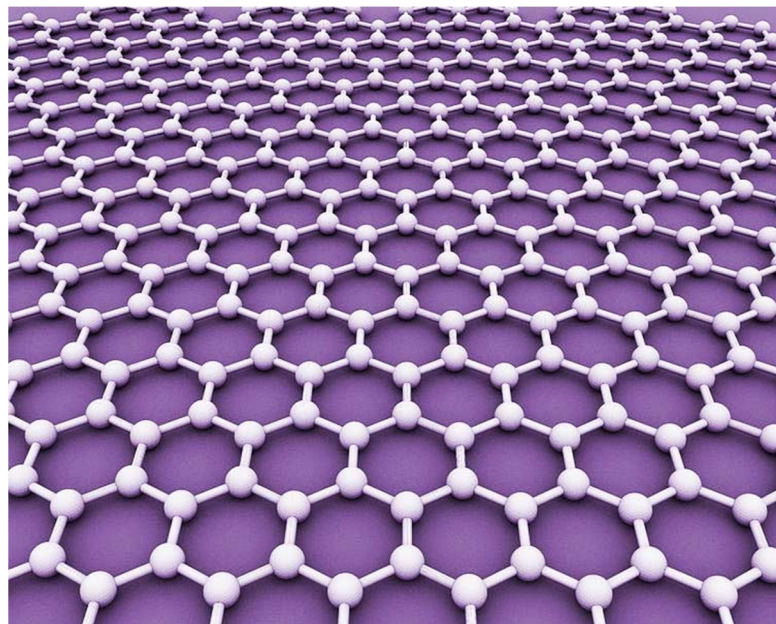


Fig. 2.1 Graphene in an atomic-scale honeycomb lattice made of carbon atoms.

2.1.1 Properties of Graphene

2.1.1.1 Structure

Graphene's stability is due to a tightly packed, periodic array of carbon atoms and an sp^2 orbital hybridization [14]. Graphene sheets in solid form usually show evidence in diffraction for graphite's (002) layering. This is true of some single-walled

nanostructures. However, unlayered graphene with only rings has been found in the core of presolar graphite onions. TEM studies show faceting at defects in flat graphene sheets [15] and suggest a role for two-dimensional crystallization from a melt.

Graphene can self-repair holes in its sheets, when exposed to molecules containing carbon, such as hydrocarbons. Bombarded with pure carbon atoms, the atoms perfectly align into hexagons, completely filling the holes.

2.1.1.2 Mechanical

The carbon–carbon bond length in graphene is about 0.142 nanometers. Graphene sheets stack to form graphite with an interplanar spacing of 0.335 nm [16]. Graphene is highly impermeable and is highly elastic.

Graphene is one of the strongest materials known with a breaking strength over 100 times greater than a hypothetical steel film of the same (thin) thickness, with a Young's modulus (stiffness) of 1 TPa (150,000,000 psi) [16]. Its spring constant was in the range 1–5 N/m and the stiffness was 0.5 TPa, which differs from that of bulk graphite. These high values make graphene very strong and rigid. These intrinsic properties could lead to using graphene for NEMS applications such as pressure sensors and resonators.

2.1.1.3 Chemical

Graphene is the only form of carbon (and generally all solid materials) in which each single atom is in exposure for chemical reaction from two sides (due to the 2D structure). It is known that carbon atoms at the edge of graphene sheets have special chemical reactivity, and graphene has the highest ratio of edgy carbons (in comparison with similar materials such as carbon nanotubes). In addition, various types of defects within the sheet, which are very common, increase the chemical reactivity.

2.1.1.4 Electronic

Graphene is a semi-metal or zero-gap semiconductor. Electron waves in graphene propagate within a single-atom layer, making them sensitive to the proximity of other materials such as high- κ dielectrics, superconductors and ferromagnetics. Experimental results from transport measurements show that graphene has remarkably high electron mobility at room temperature, with reported [16] values in excess of $15,000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.

Additionally, the symmetry of the experimentally measured conductance indicates that hole and electron mobilities should be nearly the same. The mobility is nearly independent of temperature between 10 K and 100 K, which implies that the dominant scattering mechanism is defect scattering. Scattering by the acoustic phonons of graphene intrinsically limits room temperature mobility to $200,000 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ at a carrier density of 10^{12} cm^{-2} , which is greater than copper.

2.1.1.5 Thermal

Graphene is a perfect thermal conductor. Its thermal conductivity was measured at room temperature and it is much higher than the value observed in all the other carbon structures as carbon nanotubes, graphite and diamond ($> 5000 \text{ Wm}^{-1}\text{K}^{-1}$). The ballistic thermal conductance of graphene is isotropic, i.e. same in all directions. Graphite, the 3 D version of graphene, shows a thermal conductivity about 5 times smaller ($1000 \text{ Wm}^{-1}\text{K}^{-1}$). The phenomenon is governed by the presence of elastic waves propagating in the graphene lattice, called phonons. The study of thermal conductivity in graphene may have important implications in graphene-based electronic devices. Even on a substrate, thermal conductivity reaches $600 - 5000 \text{ Wm}^{-1}\text{K}^{-1}$.

2.1.1.6 Optical

Graphene's unique optical properties produce an unexpectedly high opacity for an atomic monolayer in vacuum. Graphene's band gap can be tuned from 0 to 0.25 eV (about 5 micrometre wavelength) by applying voltage to a dual-gate bilayer graphene field-effect transistor (FET) at room temperature. The optical response of graphene nanoribbons is tunable into the terahertz regime by an applied magnetic field. Graphene/ graphene oxide systems exhibit electro-chromical [16] behavior, allowing the tuning of both linear and ultrafast optical properties.

A graphene-based Bragg grating (one-dimensional photonic crystal) has been fabricated and demonstrated its capability for excitation of surface electromagnetic waves in the periodic structure by using 633 nm He–Ne laser as the light source.

Graphene can be saturated readily under strong excitation over the visible to near-infrared region, due to the universal optical absorption and zero band gap. This has relevance for the mode locking of fiber lasers, where fullband mode locking has been

achieved by graphene-based saturable absorber. Due to this special property, graphene has wide application in ultrafast photonics. Moreover, the optical response of graphene/graphene oxide layers can be tuned electrically. Saturable absorption in graphene could occur at the Microwave [17] and Terahertz band, owing to its wideband optical absorption property. The microwave saturable absorption in graphene demonstrates the possibility of graphene microwave and terahertz photonics devices, such as microwave saturable absorber, modulator, polarizer, microwave signal processing and broad-band wireless access networks.

Under more intensive laser illumination, graphene could also possess a nonlinear phase shift due to the optical nonlinear Kerr effect. Based on a typical open and close aperture Z-scan measurement, graphene possesses a giant non-linear Kerr coefficient of $10^{-7} \text{ cm}^2\text{W}^{-1}$, almost nine orders of magnitude larger than that of bulk dielectrics. This suggests that graphene may be a nonlinear Kerr medium, paving the way for graphene-based nonlinear Kerr photonics such as a soliton.

2.2 GRAPHENE OXIDE

Graphite oxide is a layered material consisting of hydrophilic oxygenated graphene sheets (graphene oxide sheets) bearing oxygen functional groups on their basal planes and edges. Recently, tailoring band gap and electrical and optical properties of graphene has become a subject of intensive research in the context of nanoscale optoelectronics. Hence, researchers are increasingly drawn to chemically derived graphene oxide (GO) because of its heterogeneous chemical and electronic structures, along with the fact that it can be processed in solution. The presence [14] of oxygen-containing groups in graphene oxide makes it strongly hydrophilic and water soluble

GO is synthesized [18] by the oxidation of graphene, and its unique atomic and electronic structure has been elucidated so that small sp^2 carbon clusters are isolated by the sp^3 matrix. The presence of pristine graphitic nano islands, that is, sp^2 -hybridized domains, makes GO hold some characteristics of ultrafast carrier dynamics in the graphene. The tunable fluorescence in GO has been observed as a result of the heterogeneous atomic and electronic structure. Herewith, it is expected that there are a heterogeneous optical transition and nonlinear dynamic in GO. However, very little is known about the nonlinear properties and the carrier dynamics of GO, whereas they are

key issues for understanding and developing their optoelectronic properties. Furthermore, in contrast with well-established electronic structure of graphene as a zero-gap semiconductor with sp^2 -hybridized carbon atoms, it is still a challenge to determine the fundamental properties of GO such as energy band gap, optical properties, and electronic structure due to its nonstoichiometric chemical composition.

Graphene oxide (GO) and reduced graphene oxide (rGO) have attracted great attention due to promising applications [19], such as conducting thin films, supercapacitors composites, biosensing devices and nonlinear optical materials. Recently, more characteristics of GO and rGO have been revealed. Investigation of optical properties of GO is very important for understanding the fundamentals of the structure and the electronic transitions. Previously, the broad visible fluorescence has been observed in GO prepared by various strategies, where the origin of fluorescence has also been discussed based on both steady-state and time-resolved fluorescence measurements. Particularly, the carrier dynamics in rGO has been found to be dependent on the degree of oxygen reduction. Meanwhile, the main absorption bands of GO have been found in the ultraviolet spectral region. Transient absorption measurements of GO have revealed the various carrier decay processes.

2.2.1 Nonlinear Optical Properties of Graphene Oxide

Materials with excellent photophysical properties and large optical nonlinearities have many potential applications including fast optical communications, all-optical switching, and optical limiting. As a novel carbon-based material, pristine graphene [20] shows remarkable optoelectronic properties and optical nonlinearities with ultrafast response times and a broad spectral range. Graphene-based compounds also offer the advantage of tailorability: fine-tuning of the NLO properties can be achieved by rational modification of the chemical structure. Many NLO effects such as SA, TPA, RSA, FWM and optical limiting can be observed in graphene-based materials. All of these chemical variations, including oxidation and functionalization, can alter the electronic structure of the graphene, and therefore they allow fine-tuning of the nonlinear response and make more extensive applications easier because of the multiple NLO mechanisms. Graphene exhibits a unique chemical structure, and outstanding electronic and optical properties for optoelectronic and photonic applications. Large optical nonlinearities, including SA, FWM, and TPA have been

observed in pristine graphene. Excellent NLO properties combined with a fast response and broad wavelength range make graphene an ideal saturable absorber in mode-locked ultrafast laser systems. For example, it can be optically visualized, despite being only a single atom thick. Its transmittance can be expressed in terms of its fine-structure constant. Broadband saturable absorption was also observed as a consequence of Pauli blocking caused by the linear dispersion of the Dirac electrons in graphene, which makes it suitable for application to ultrafast mode-locked lasers. Also, nonequilibrium carriers and chemical or physical treatment of graphene can lead to luminescence. These properties make it an ideal photonic and optoelectronic material. Consequently, there is growing interest in graphene optoelectronics and initial demonstrations of graphene-based photodetectors, optical modulators, plasmonic devices and ultrafast lasers have been reported.

Recently, it has been predicted that graphene's linear dispersion properties should lead to strongly nonlinear optical (NLO) behavior at microwave and terahertz frequencies. At higher optical frequencies, one can also expect enhanced optical nonlinearity because of the graphene band structure, because interband optical transitions occur at all photon energies. Materials with excellent photophysical properties and large optical nonlinearities have many potential applications including fast optical communications, all-optical switching, and optical limiting. Graphene shows remarkable optical nonlinearities with ultrafast response times and a broadband spectral range.

The NLO properties of GO have also been investigated at 532 nm in the picosecond regime [12] and at 800 nm in the femtosecond regime [14]. The results show that TPA dominates the nonlinear absorption at high intensities, while SA dominates at low intensities. In contrast to bilayer graphene, TPA in GO arises from the introduction of the sp^3 hybridized domains caused by oxidation. Thus, we can conclude that the heterogeneous nonlinear dynamics of GO are governed by SA in the sp^2 domains and TPA in the sp^3 domains.

Graphene derivatives e.g. GO and graphene hybrid materials have been produced with various synthesis methods to meet increasing requirements for thin film processing, composite incorporation, and device integration. The NLO properties of these functional hybrid materials depend not only on the individual component materials, but also on the interactions between them. For GO, the unique chemical structure along with the heterogeneous electronic structure caused by the presence of

sp^2 and sp^3 [21] bonding confers intriguing properties that offer exciting prospects for tailoring of NLO properties. For most graphene hybrids, great importance is attached to electron or energy transfer by functionalizing graphene, which plays an important role in improving limiting performance. In general, covalent functionalization of graphene materials leads to better limiting performance than noncovalent functionalization. This is because the covalent link can more effectively improve energy or electron transfer from the functional moiety to the graphene nanomaterial, which results in enhanced limiting performance.

2.2.2 Surveyed Results

It has been a major challenge to design an all-optical ultrafast device that can fulfill the demands of next generation ultrahigh bandwidth information processing. So, a nonlinear optical (NLO) material is desired which can exhibit fast response, strong nonlinearity, broad wavelength range, low cost, low optical loss, high damage threshold, low-power consumption and ease of integration into optical systems. This has led to the search of novel NLO materials and graphene oxide has emerged as one such attractive photonic material because of its unique properties i.e. [22] (i) heterogeneous chemical and electronic structures, (ii) can be processed in solution, (iii) interacts with a wide range of organic and inorganic materials that facilitates synthesis of functional hybrids and composites with unusual properties, and (iv) its band gap can be tuned by controlling the sp^2 and sp^3 fractions to tailor its electrical, optical and chemical properties.

Graphene-oxide (GO) and reduced graphene oxide (rGO) can be used to propose a large number of applications. One of the most fascinating properties of GO is its high transparency in the visible spectrum that can be applied in transparent conductor applications such as a possible replacement for indium-tin oxide (ITO) in organic solar cells, organic light-emitting devices (LEDs), and displays. Its intrinsic tunable fluorescence in the visible and near infrared (NIR) has led to biological applications for bio-imaging, sensing, and drug delivery. GO films with very high dielectric constant have been used as spacers to realize thin film super capacitors. rGO obtained from chemical vapor deposition or thermal reduction of GO has been used as one electrode in diode-based memories, solar cells, and LEDs. The strong modulation conductance by strain has been used to fabricate rGO channel field-effect transistors for

ultrasensitive strain sensing. The strong saturable absorption (SA) of GO has also been used for Q-switching and femtosecond (fs) mode-locking of erbium-doped ring-cavity fiber lasers.

Both 1D CNT [14] and 0D fullerene have been reported to have good optical nonlinear properties. Single-walled CNTs (SWCNTs) and multiwalled CNT suspensions have been reported to have strong optical limiting effects in nanosecond regime. However, fullerenes have large excited state absorption (ESA) in nanosecond and picosecond regimes, which is a different nonlinear absorption (NLA) mechanism from CNT. It is essential for applications of materials to make clear the mechanism of nonlinear optical (NLO) properties. Due to unique and large 2D π -electron conjugation systems of graphene, much like that in fullerene and CNTs, we expect that GO would exhibit good NLO properties.

The NLO properties of GO have been experimentally investigated in the nanosecond (ns), picosecond (ps), and femtosecond (fs) regimes at different wavelengths, primarily for broadband optical limiting. These studies show that the NLO properties of GO are determined by the combined action of the sp^2 and sp^3 domains. For ns and ps pulse excitation at 532nm and also for fs pulse excitation at 800nm in GO dispersed in different solvents and thin films, a transition from SA to reverse saturable absorption (RSA) takes place on increase in intensity with increased contrast. The charge carriers with SA from the sp^2 – hybridized domains dominate the NLO response at low pump intensities while the influence of the two-photon absorption (TPA) from the sp^3 – hybridized domains on the transient absorption signal becomes stronger on increase in pump intensity.

The ultrafast relaxation dynamics and nonlinear optical response in single and few layered graphene oxide (GO) were studied [23]-[24] by ultrafast optical differential transmission spectroscopy and Z-scan technique using various pump intensities. It was found that charge carriers with subpicosecond-to-picosecond dynamics from sp^2 -hybridized domains dominate the ultrafast response at low pump intensities, like graphene. Surprisingly, the influence of two-photon absorption from sp^3 -hybridized domains on the transient absorption signal becomes increasingly strong with pump intensities. . With increasing pump intensities, the transient optical response exhibits a crossover from bleaching to enhanced absorption as two-photon absorption (TPA) of sp^3 domains [21] becomes more prominent. Because of the nonstoichiometric nature of GO, manipulation of the size, location, and relative fraction of the sp^2 domains of GO

by chemical methods provides opportunities for tailoring its nonlinear optical properties.

There are generally two mechanisms responsible for optical-limiting effects: nonlinear scattering and nonlinear absorption. The development of thin film optical-limiting material for femtosecond laser pulses with low thresholds is very challenging because of lack of contribution from nonlinear scattering. Most materials generally display saturable absorption in the near-UV region. The GO films, in particular, the partially reduced GO films, display very strong two-photon absorption at 400 nm (with huge effective two-photon absorption coefficient of $768000 \text{ cm}\cdot\text{GW}^{-1}$) and strong two- and three-photon absorption at 800 nm, which make them excellent candidates for broadband (from UV to near-infrared) optical-limiting materials [25]-[26] for femtosecond laser pulses. It has to be noted that excellent flexible plastic optical-limiting materials could be developed using these partially reduced GO films.

The broadband nonlinear optical properties of GO thin films and their optical limiting activity for femtosecond laser pulses at 800 and 400 nm were investigated [26] which could be tuned by the extent of reduction. The as-prepared GO films were found to exhibit strong broadband optical-limiting behaviors, which were significantly enhanced upon partial reduction by using laser irradiation or chemical reduction methods. The laser-induced reduction of GO could result in the enhancement of an effective two-photon absorption coefficient at 400 nm by up to ~ 19 times and effective two- and three-photon absorption coefficients at 800 nm by ~ 12 and ~ 14.5 times, respectively. Highly reduced GO films prepared by using chemical method displayed strong saturable absorption behavior. The optical-limiting thresholds of these partially reduced GO films are significantly lower than those of previously reported π -conjugated organic molecules and metal nanoparticles. These thin films could be easily fabricated on glass and even plastic substrates by using solution processing methods on a large scale. Low cost, easy preparation, and excellent nonlinear optical properties make these GO materials promising candidates for practical applications as broadband femtosecond optical limiters or saturable absorbers.

Chapter-3

NONLINEAR ABSORPTION IN GRAPHENE OXIDE

3.1 INTRODUCTION

There has been a growing interest in studying and developing the nonlinear optical properties of graphene oxide (GO). This material has a great potential to be used in widespread applications in future optical limiting, optical switches and optical data storage. There nonlinear absorption (NLA) phenomena can broadly be classified into two different types [27]. One is saturable absorption (SA) that is described by the decrease in absorption coefficient with increasing intensity, and the other is reverse saturable absorption (RSA), in which the absorption coefficient increases with increasing intensity. RSA can occur when the absorption cross-section of excited states exceeds the ground state cross-section, while for SA to happen at least one of the excited state cross-sections has to be smaller than the ground state cross-section.

In this chapter, we will be investigating the process of NLA in GO molecules first under steady state and then when excited by laser pulses with different pulse widths. We will be looking at the different cases of NLA under different regimes and their characterization of the phenomena of SA and RSA and the transition of SA to RSA or RSA to SA. For this purpose, a multi-level energy model is considered and the dynamic process of NLA is then investigated by the rate equation approach. While considering the multi-level energy model, we will have to take into account the different contributions of each excited state to the NLA for the excitation by laser with nanosecond (*ns*), picosecond (*ps*) and femtosecond (*fs*) pulse or under steady state.

The tool that has used for computer simulation of rate equations and analysis of graphs with variations in different parameters throughout this text is Wolfram Mathematica[®] 8.

3.2 BASIC MODEL

The energy-level model for excited state absorption is usually described by a five-level model that describes the dynamic process of state transitions, as shown in Fig. 3.1. There are both singlet and triplet states. S_0 is the ground state and S_1 and S_x [6] are the first excited state and upper excited state, respectively. Both S_0 and S_1 comprise the singlet states. T_1 and T_x are the first excited state and upper excited state in triplets, respectively. Additionally, each electronic level [28] consists of several vibrational sublevels.

The incident laser beam has a power density flux I_m (i.e. the ratio of the incident intensity I_{mp} to the photon energy $h\nu$). When the incident laser strikes the sample, the photons are absorbed by the molecules in the ground state due to which there is a transition from the ground state S_0 to a vibronic sublevel S_v with an absorption cross section σ_0 .

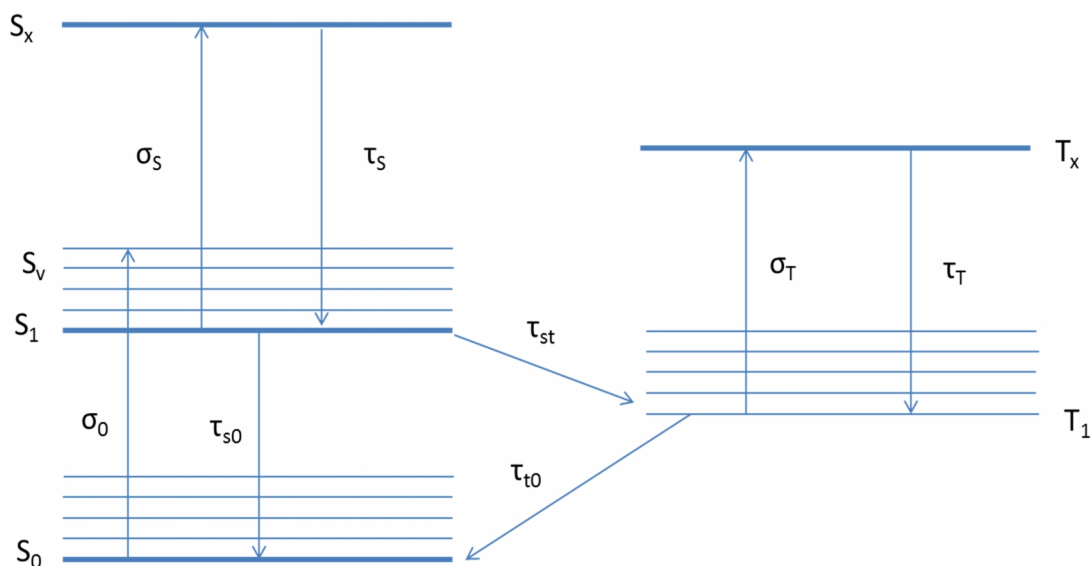


Fig. 3.1 [27] Five-level energy diagram for describing the excitation of an organic molecular system. S_0 : the ground state; S_1 : the first excited singlet state; S_v : the vibrational state of first excited singlet state; S_x : the upper excited singlet state; T_1 : the first excited triplet state; T_x : the upper excited triplet state; σ_0 and σ_s are the ground-state absorption cross sections and the excited state absorption cross sections from states S_0 and S_1 respectively; σ_t , the excited state absorption cross sections from state T_1 ; τ_{s0} , τ_{t0} , τ_s and τ_t are the states lifetime from S_1 , T_1 , S_x and T_x , respectively; and τ_{st} : the intersystem-crossing lifetime.

There is a rapid decay from S_v to S_1 with a lifetime of a few picoseconds because of the overlap between vibronic sublevels. Most of the molecules quickly transit from S_1 to T_1 with a short nonradiative intersystem crossing lifetime τ_{st} . The molecules in S_1 and T_1 can be excited to S_2 and T_2 with absorption cross sections σ_s and σ_t , respectively but the lifetimes in S_x and T_x are extremely short (< 1 ps). The molecules in S_2 can return [29] to the ground state either by fluorescence emission or by the nonradiative transition with the lifetime τ_{s0} and similarly, the molecules in T_1 can also return to the ground state either by phosphorescence emission or by the nonradiative transition with the lifetime τ_{t0} .

3.3 STEADY STATE ANALYSIS - CONTINUOUS WAVE PUMP BEAM EXCITATION

Usually, the intersystem-crossing lifetime τ_{st} in most organic molecular systems is of the order of nanoseconds. Also, the lifetimes in S_x and T_x are extremely short (< 1 ps) so that the contribution of S_x and T_x in the continuous wave pump beam model need not be considered. Therefore, the process can then be described using a three-level energy diagram [29] for describing the excitation of GO using a continuous wave (CW) pump laser beam.

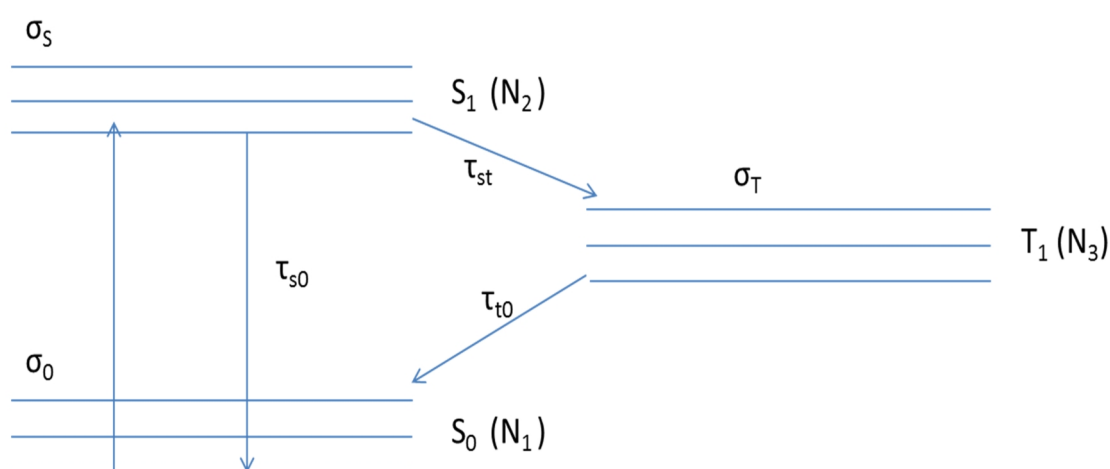


Fig. 3.2 Energy level diagram for describing the excitation of GO using a continuous wave pump beam. S_0 : the ground state; S_1 : the first excited singlet state; T_1 : the first excited triplet state.

The above energy level system consists of three energy states to describe the state transitions between ground and excited states. It consists of singlet and triplet states. S_0 is the ground state and S_1 is the first excited state. Both S_0 and S_1 comprise the singlet states. T_1 is the first excited state in triplet. Additionally, each electronic level consists of several vibrational sublevels.

We are considering the transmission of a CW signal (probe) light beam of intensity I_{np} modulated by the absorption due to different intermediate states that get populated due to excitation of GO molecules by both the pulsed modulating laser (pump) and the signal beams. We have taken the probe beam power density flux as I_n (the ratio of the probe beam intensity I_{np} to the photon energy $h\nu$). The incident laser beam being used as a pump beam has a power density flux I_m (i.e. the ratio of the incident intensity I_{mp} to the photon energy $h\nu$).

We use the rate equation approach to study and simulate the transmission characteristics of our theoretical model [30]. Hence, using the three-level energy diagram in Fig. 3.2, the rate equations for describing the time variation of the population density in each energy level can be written as:

$$\frac{dN_1}{dt} = -(I_m\sigma_0 + I_n\sigma_{0p})N_1 + \frac{N_2}{\tau_{s0}} + \frac{N_3}{\tau_{t0}} \quad (3.1)$$

$$\frac{dN_2}{dt} = (I_m\sigma_0 + I_n\sigma_{0p})N_1 - \frac{N_2}{\tau_{s0}} - \frac{N_3}{\tau_{st}} \quad (3.2)$$

$$\frac{dN_3}{dt} = \frac{N_2}{\tau_{st}} - \frac{N_3}{\tau_{t0}} \quad (3.3)$$

where N_1 , N_2 and N_3 are the number densities (or population densities) of states S_0 , S_1 and T_1 respectively. Also, σ_0 and σ_s are the ground-state absorption cross sections and the excited state absorption cross sections from states S_0 and S_1 respectively and σ_t , the excited state absorption cross sections from states T_1 corresponding to the pump beam wavelength. Similarly, corresponding to the probe wavelength, σ_{0p} and σ_{sp} are the ground-state absorption cross sections and the excited state absorption cross sections from states S_0 and S_1 , respectively and σ_{tp} correspond to the excited state absorption cross sections from states T_1 . Here, the subscript p is used to denote the value at probe wavelength.

Considering steady state,

$$\frac{dN_1}{dt} = \frac{dN_2}{dt} = \frac{dN_3}{dt} = 0 \quad (3.4)$$

And since, the total population density of all the states must remain conserved and hence, should be a constant [6] we have -

$$N_1 + N_2 + N_3 = N \quad (3.5)$$

where N is the sum total of all the population densities in the considered molecular system.

When the laser light propagates through the molecular system, the intensity through the sample is given by

$$\frac{dI_{np}}{dz} = -\alpha_p I_n = (\sigma_{0p}N_1 + \sigma_{sp}N_2 + \sigma_{tp}N_3)I_{np} \quad (3.6)$$

where Z is the propagation length.

Solving the above sets of equations, we calculate the populations N_1 , N_2 and N_3 as follows:

$$N_1 = \frac{m}{x} \left(\frac{1}{i_m \sigma_0 + i_n \sigma_{0p}} \left(\frac{1}{\tau_{s0}} + \frac{1}{\tau_{st}} \right) \right) \quad (3.7)$$

$$N_2 = \frac{m}{x} \quad (3.8)$$

$$N_3 = \frac{\tau_{t0}}{\tau_{st}} \left(\frac{m}{x} \right) \quad (3.9)$$

Here, m is a constant providing the multiplication factor

$$\text{and } x = \left(\frac{1}{i_m \sigma_0 + i_n \sigma_{0p}} \left(\frac{1}{\tau_{s0}} + \frac{1}{\tau_{st}} \right) + 1 + \frac{\tau_{t0}}{\tau_{st}} \right) \quad (3.10)$$

We can express the output intensity in terms of input intensity as

$$I_{np(out)} = I_{np} \text{Exp}[-(\alpha_p L)] \quad (3.11)$$

The non-linear intensity-dependent absorption coefficient for the signal beam is written as

$$\alpha_p = (\sigma_{0p}N_1 + \sigma_{sp}N_2 + \sigma_{tp}N_3) \quad (3.12)$$

and L is the thickness of the sample.

The dynamic process of NLA can be revealed theoretically by taking the above energy level model into consideration and carrying out the rate equation analysis to obtain the intensity dependence of level population densities. The laser wavelength of modulating beam is set as 300 nm and the signal beam wavelength is taken as 500 nm. The GO molecular system is having the photophysical parameters as follows:

$$\tau_{s0} = 4.5 \text{ ns};$$

$$\tau_{st} = 1.5 \text{ ns};$$

$$\tau_{t0} = 8.2 \text{ } \mu\text{s}$$

$$\begin{aligned}\sigma_0 &= 2.8 \times 10^{-15} \text{ cm}^2; \\ \sigma_p &= 2.7 \times 10^{-18} \text{ cm}^2; \\ \sigma_{sp} &= 3.5 \times 10^{-18} \text{ cm}^2; \\ \sigma_{tp} &= 2.6 \times 10^{-16} \text{ cm}^2;\end{aligned}$$

The variations for population densities N_1 , N_2 and N_3 of states S_0 , S_1 and T_1 , respectively are simulated in Fig. 3.3. When the pump beam is varied from 0 to 100 W/cm^2 , we see that the population in S_0 decreases exponentially whereas there is an exponential rise in the population in state T_1 . The population of state S_1 remains almost a constant. This implies that in steady state, there is a transfer of states from ground state to the first excited triplet state and almost no transition occurs involving the first excited singlet state.

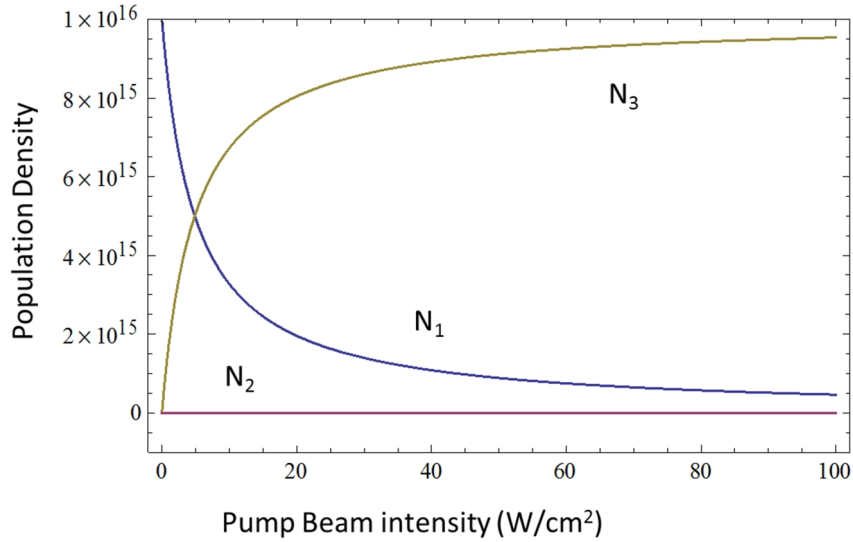


Fig. 3.3 Populations in S_0 , S_1 and T_1 when the intensity of pump beam is varied from 0 to 100 W/cm^2

The normalized transmitted intensity [31] of the probe beam is given by

$$T = \frac{I_{np(out)}}{I_{np}} = \text{Exp}\left[-\frac{\beta_p}{x} \left(\frac{\sigma_p}{i_m \sigma_0 + i_n \sigma_p} \left(\frac{1}{\tau_{s0}} + \frac{1}{\tau_{st}} \right) + \sigma_{sp} + \frac{\tau_{t0}}{\tau_{st}} \right)\right] \quad (3.13)$$

where $\beta_p = mL$ and x is as given in (3.10).

The transmission characteristics i.e. the variation of normalized transmitted intensity ($I_{np(out)} / I_{np}$) versus the modulating pump intensity, have been simulated using computer software. The changes in T with variation in modulating pump intensity for different values of normalized small-signal absorption coefficient (β_p) [32], are shown in Fig. 3.4.

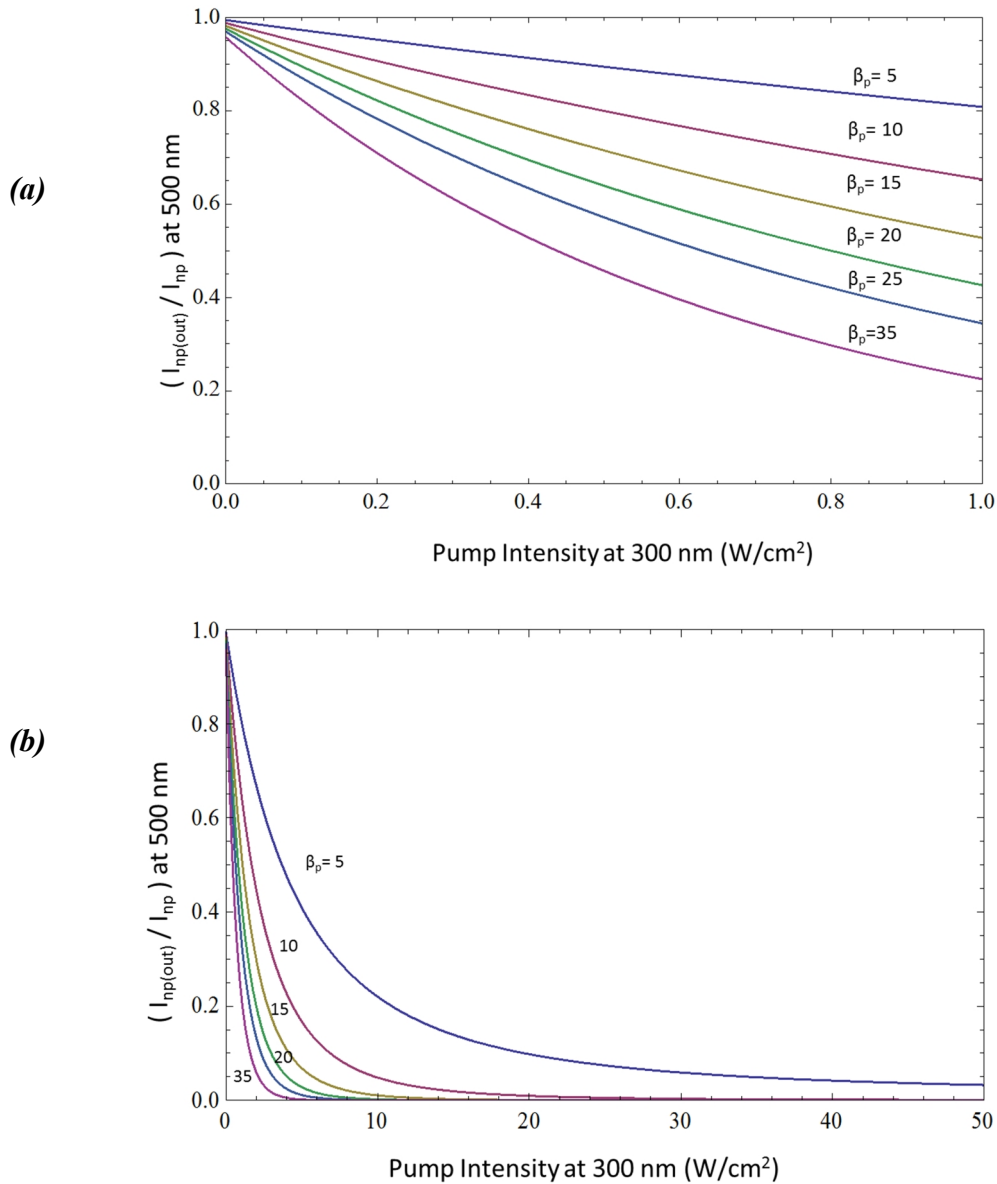


Fig. 3.4 Variation of normalized transmitted intensity of probe beam at 500 nm in GO with pump laser beam intensity at 300 nm for various values of the normalized small-signal absorption coefficient (β_p). (a) Corresponding variation when modulating pump intensity is varied from 0 to 1 W/cm^2 . (b) Corresponding variation when modulating pump intensity is varied from 0 to 50 W/cm^2 .

The output intensity when expressed as a function of input intensity is obtained in Fig. 3.5. It is observed that there is a monotonic decrease in the output intensity as the input intensity is increased.

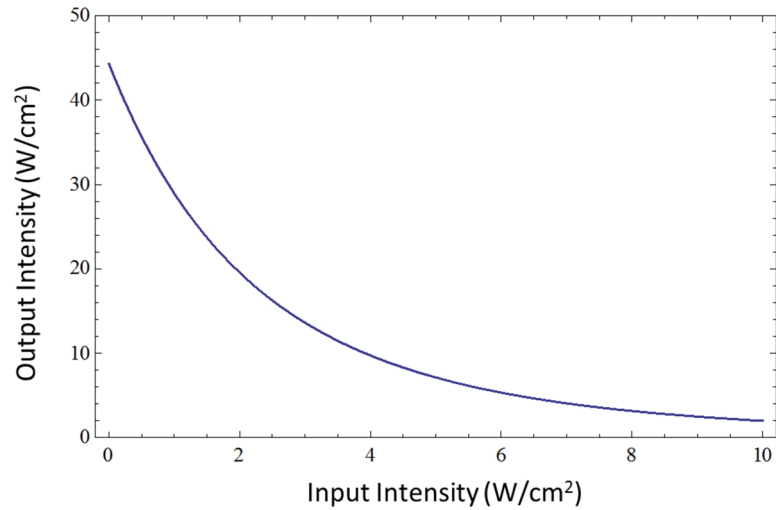


Fig. 3.5 Output intensity as a function of input intensity when the intensity of pump beam is varied from 0 to 10 W/cm²

These results are very close to what is desired from an all-optical switch (especially an inverter). It can be used to construct a NOT gate where the output is low when input is high and vice versa.

3.4 TIME DEPENDENT ANALYSIS

So far we have discussed the steady state absorption i.e. not considering the time variations. Now, we look forward at the cases when the input beam is in the form of a pulse with width in different regimes (i.e. ns, ps, fs). In the following sections, we consider each regime one by one and look at the effect of pulse width on population densities of various levels and the kind of phenomenon (SA or RSA) observed at different intensities.

3.4.1 Nanosecond Pulse Beam Excitation

As stated in the previous case, the intersystem-crossing lifetime τ_{st} in most molecular systems is of the order of nanoseconds and the lifetimes in S_x and T_x are extremely short (< 1 ps) so that the lifetime of S_x and T_x are much shorter [14] than the width of excited laser pulse and hence their contribution in the energy-level model need not be considered. Therefore, the process can then be described using a three-level energy diagram as given in Fig. 3.6.

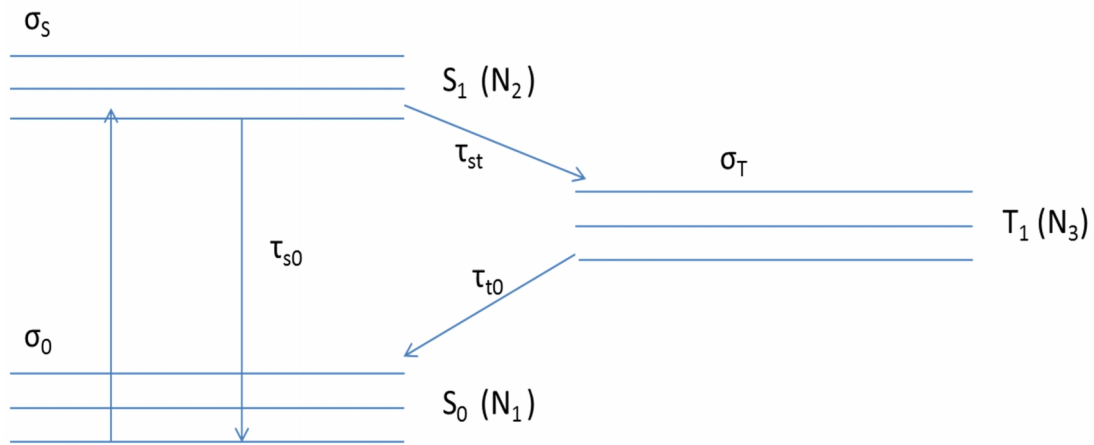


Fig. 3.6. Energy level diagram for describing the excitation of GO using a continuous wave pump beam. S_0 : the ground state; S_1 : the first excited singlet state; T_1 : the first excited triplet state.

Using this three-level energy diagram in Fig. 3.6, the rate equations for describing the time variation of the population density in each energy level can be written as:

$$\frac{dN_1}{dt} = -I_m \sigma_0 N_1 + \frac{N_2}{\tau_{s0}} + \frac{N_3}{\tau_{t0}} \quad (3.14)$$

$$\frac{dN_2}{dt} = I_m \sigma_0 N_1 - \frac{N_2}{\tau_{s0}} - \frac{N_3}{\tau_{st}} \quad (3.15)$$

$$\frac{dN_3}{dt} = \frac{N_2}{\tau_{st}} - \frac{N_3}{\tau_{t0}} \quad (3.16)$$

where N_1 , N_2 and N_3 are the number densities (or population densities) of states S_0 , S_1 and T_1 respectively. The incident laser beam has a power density flux I_m (i.e. the ratio of the incident intensity I_{mp} to the photon energy $h\nu$). σ_0 and σ_s are the ground-state absorption cross sections and the excited state absorption cross sections from states S_0 and S_1 respectively and σ_t , the excited state absorption cross sections from states T_1 .

When the laser light propagates through the molecular system, the intensity through the sample [28] is given by:

$$\frac{dI_{mp}}{dZ} = -\alpha_p I_{mp} = (\sigma_0 N_1 + \sigma_s N_2 + \sigma_t N_3) I_{mp} \quad (3.17)$$

where Z is the propagation length.

The time dependent rate equations given in Eq. (3.14)-(3.16) have been solved numerically by computer simulation by considering the pump laser pulse profile given by

$$i_{mp}' = i_{mp} \exp[-c_p (\frac{t-t_m}{\Delta t})^2] \quad (3.18)$$

where t_m is the time at which the respective pulse maxima occur, $c_p = 4 \ln(2)$ is the pulse profile parameter and Δt is the pulse width.

The rate equation analysis based on the above energy model has been carried out to obtain the intensity dependence of level populations. The laser wavelength has been set to 532 nm and laser pulse width is set as 20 ns. We have taken the molecular system of GO and the photophysical parameters of GO are taken as follows:

$$\begin{aligned} \tau_{s0} &= 15 \text{ ns}; \\ \tau_{t0} &= 10 \text{ ns}; \\ \tau_{st} &= 0.15 \text{ ns}; \\ \sigma_0 &= 2 \times 10^{-18} \text{ cm}^2; \\ \sigma_s &= 3.5 \times 10^{-17} \text{ cm}^2; \end{aligned}$$

$$\sigma_t = 3 \times 10^{-18} \text{ cm}^2;$$

The resulting curves obtained by solving the above set of rate equations for populations using simulation through computer software are shown in Fig. 3.7. The curves are plotted for two different intensities.

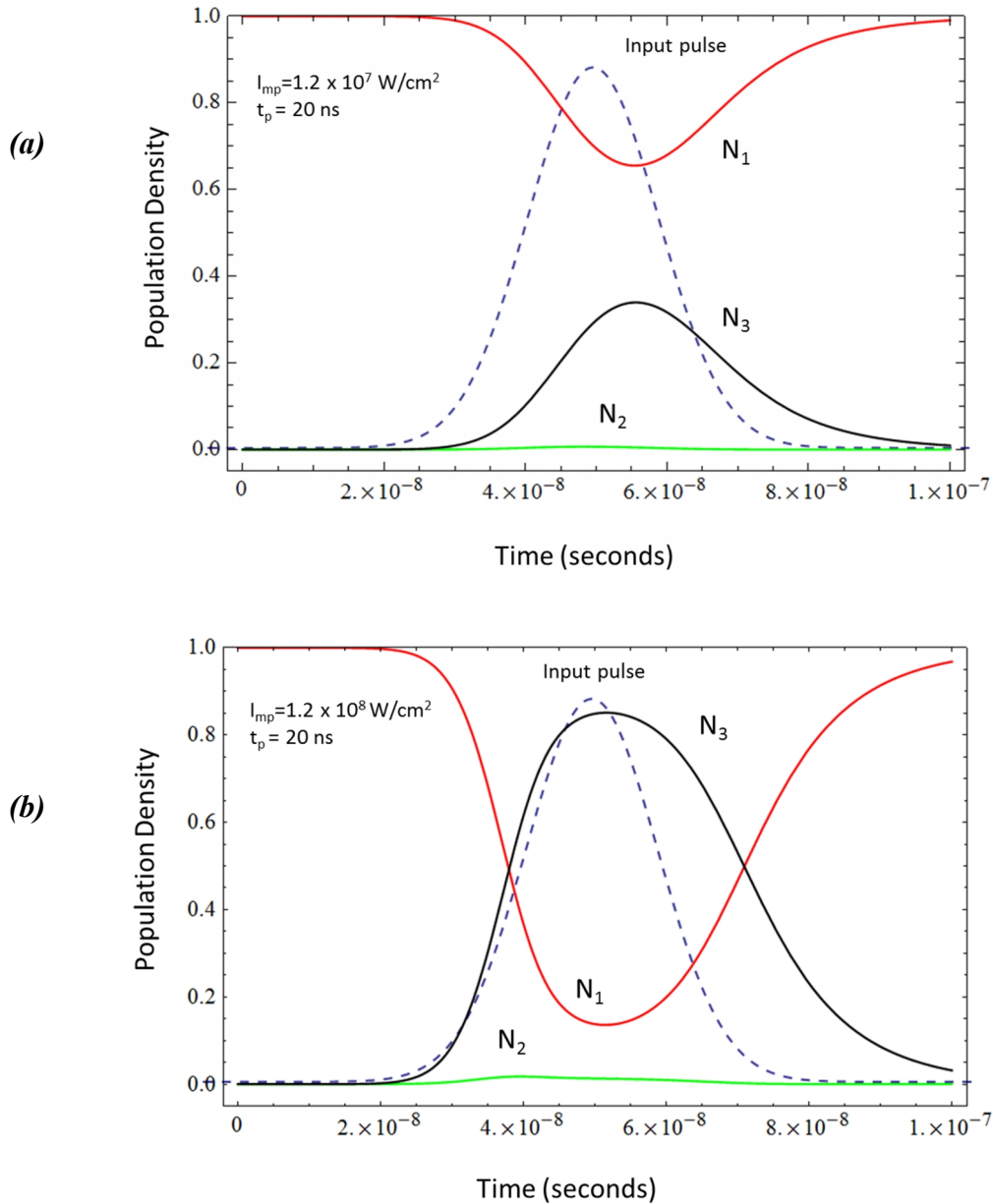


Fig. 3.7 Populations in S_0 , S_1 and T_1 versus the time during a single light pulse with a width of 20 ns under two excitation intensities: (a) $I = 1.2 \times 10^7 \text{ W/cm}^2$ and (b) $I = 1.2 \times 10^8 \text{ W/cm}^2$.

These curves show populations N_1 , N_2 and N_3 versus the time during a single light pulse using laser with two different excitation intensities. All the molecules get populated in the ground state S_0 only after a sufficiently long time has passed after the

pulse was applied. In the first case in Fig. 3.7(a), the excitation intensity has been taken to be $1.2 \times 10^7 \text{ W/cm}^2$ and we observe that most molecules are populated in the ground state S_0 , some molecules are populated in the first triplet state T_1 and only a few molecules are populated in the first singlet state S_1 . So, the phenomenon of SA would be observed in this case. When the excitation intensity is taken to be $1.2 \times 10^8 \text{ W/cm}^2$ in the second case, then as shown in Fig. 3.7(b), we find that most molecules are populated in the first triplet state T_1 , some molecules are populated in the ground state S_0 and only a few molecules are populated in the first singlet state S_1 . This shows that the phenomenon observed in this case would be of RSA.

Now, we look at the transmittance curves [27] for nanosecond pulse laser beam. The curves for transmittance versus time are shown in Fig. 3.8.

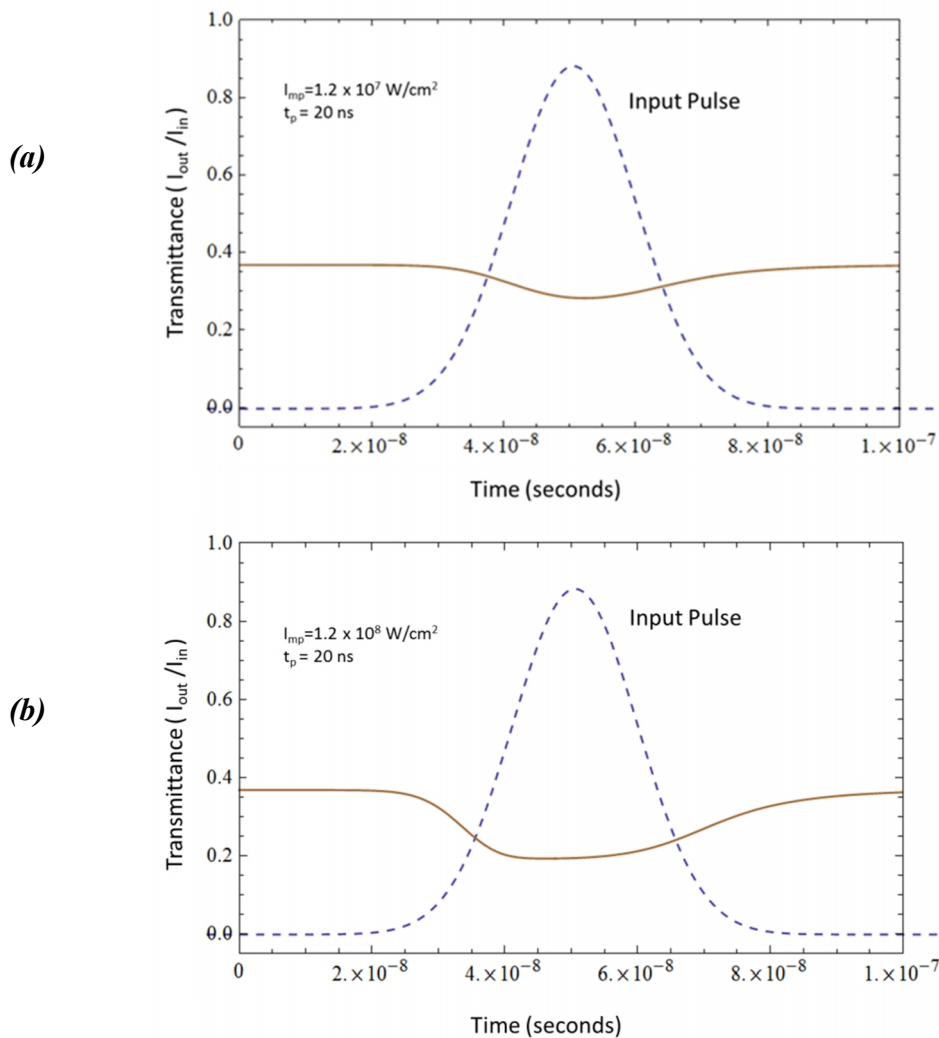


Fig. 3.8 Transmittance (I_{out}/I_{in}) versus the time during a single light pulse with a width of 20 ns under two excitation intensities: (a) $I = 1.2 \times 10^7 \text{ W/cm}^2$ and (b) $I = 1.2 \times 10^8 \text{ W/cm}^2$.

As defined earlier, the transmittance is the ratio of output intensity to the input intensity. Fig. 3.8(a) shows the curve when the intensity was $1.2 \times 10^7 \text{ W/cm}^2$ and Fig. 3.8(b) illustrates the curve for intensity $1.2 \times 10^7 \text{ W/cm}^2$. We observe that the transmittance decreases slightly with the application of the pulse and then regains the previous value as soon as the pulse vanishes. The dip in the curve is more pronounced in the second case when the intensity was more, thus showing the dependence of transmittance on the input intensity.

3.4.2 Picosecond Pulse Beam Excitation

In this case, we consider the excitation of GO molecules by the picosecond laser pulse whose width is much shorter than the intersystem-crossing lifetime τ_{st} . So, here we can neglect the contribution of the triplet states as well. Since the upper singlet state lifetime is in *ps* regime, so we have to take into consideration the upper singlet state's contribution. As a result, the process under *ps* pulse beam excitation can therefore be described using a three-level energy diagram similar to as given in Fig. 3.9.

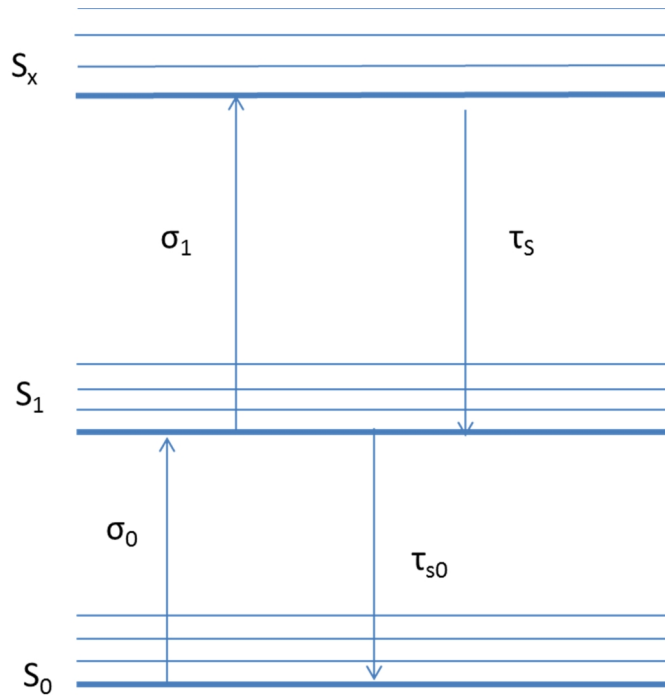


Fig. 3.9 Three-level energy diagram for describing the excitation of an organic molecular system in picosecond regime, S_0 : the ground state; S_1 : the first excited singlet state; S_x : the upper excited singlet state; σ_0 and σ_1 are the ground-state absorption cross sections and the excited state absorption cross sections from states S_0 and S_1 respectively; τ_{s0} and τ_s are the states lifetime from S_1 and S_x respectively.

Using this three-level energy diagram in Fig. 3.9, the rate equations for describing the time variation of the population density in each energy level [33] can be written as:

$$\frac{dN_1}{dt} = -I_m\sigma_0N_1 + \frac{N_2}{\tau_{s0}} \quad (3.19)$$

$$\frac{dN_2}{dt} = I_m\sigma_0N_1 - I_m\sigma_1N_2 - \frac{N_2}{\tau_{s0}} + \frac{N_3}{\tau_s} \quad (3.20)$$

$$\frac{dN_3}{dt} = I_m \sigma_1 N_2 - \frac{N_3}{\tau_s} \quad (3.21)$$

where N_1 , N_2 and N_3 are the number densities (or population densities) of states S_0 , S_1 and S_x respectively. The incident laser beam has a power density flux I_m (i.e. the ratio of the incident intensity I_{mp} to the photon energy $h\nu$). σ_0 and σ_1 are the ground-state absorption cross sections and the excited state absorption cross sections from states S_0 and S_1 respectively.

When the laser light propagates through the molecular system, the intensity [28] through the sample is given by:

$$\frac{dI_{mp}}{dz} = -\alpha_p I_{mp} = (\sigma_0 N_1 + \sigma_1 N_2 + \sigma_n N_3) I_{mp} \quad (3.22)$$

where σ_n is the absorption cross section, and Z is the propagation length.

The time dependent rate equations given in Eq. (3.19)-(3.21) have been solved numerically by computer simulation by considering the pump laser pulse profile given by

$$i_{mp}' = i_{mp} \exp[-c_p \left(\frac{t-t_m}{\Delta t}\right)^2] \quad (3.23)$$

where t_m is the time at which the respective pulse maxima occur, $c_p = 4 \ln(2)$ is the pulse profile parameter and Δt is the pulse width.

The rate equation analysis based on the above energy model has been carried out to obtain the intensity dependence of level populations. The laser wavelength has been set to 532 nm and laser pulse width is set as 80 ps. We have taken the molecular system of GO and the photophysical [34] parameters of GO are taken as follows:

$$\begin{aligned} \tau_{s0} &= 15 \text{ ns}; \\ \tau_s &= 47 \text{ ps}; \\ \sigma_0 &= 2 \times 10^{-18} \text{ cm}^2; \\ \sigma_s &= 3.5 \times 10^{-17} \text{ cm}^2; \\ \sigma_t &= 3 \times 10^{-18} \text{ cm}^2; \end{aligned}$$

The resulting curves obtained by solving the above set of rate equations for populations using simulation through computer software are shown in Fig. 3.10.

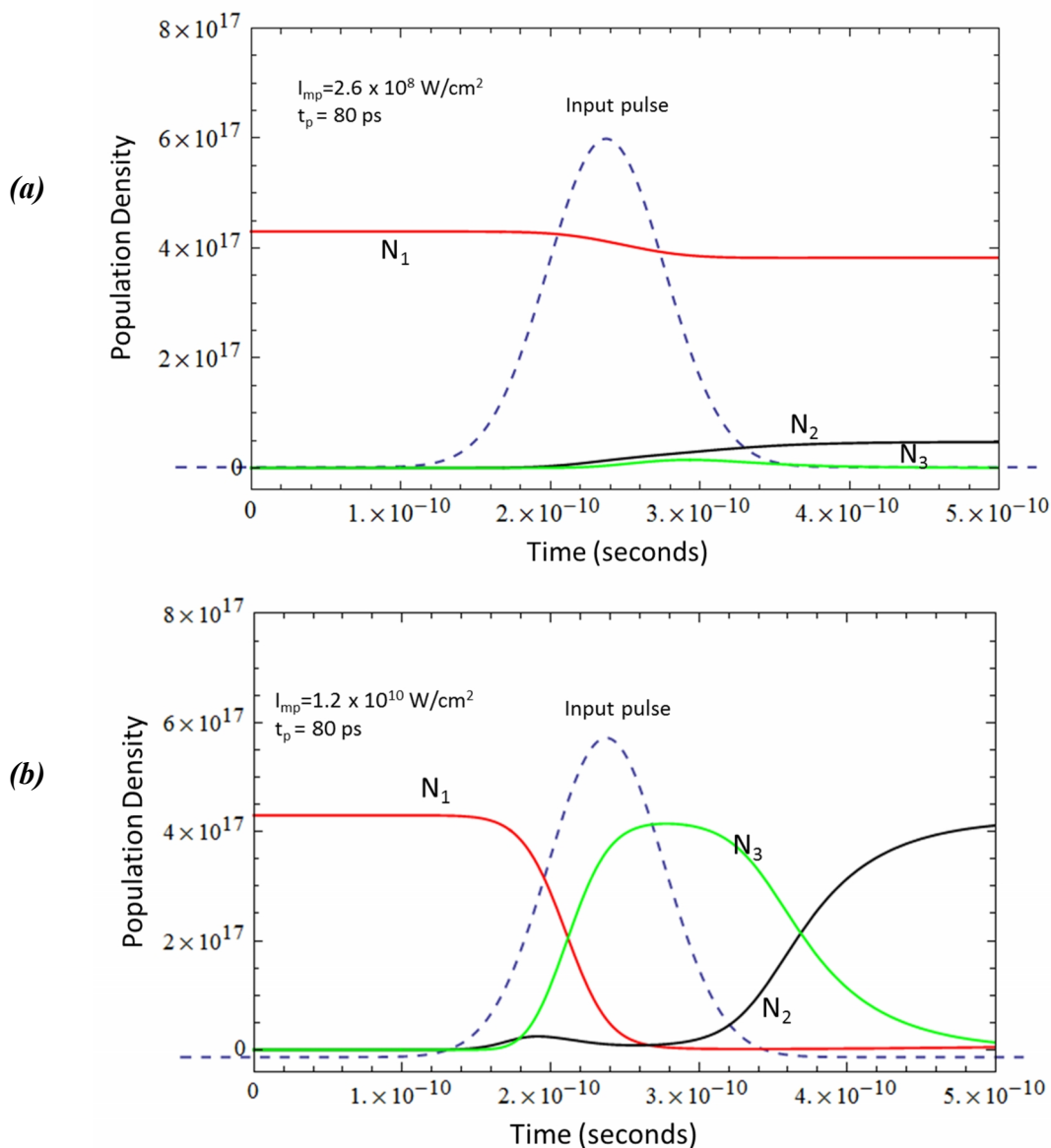


Fig. 3.10 Populations in S_0 , S_1 and S_x versus the time during a single light pulse with a width of 80 ps under two excitation intensities: (a) $I = 2.6 \times 10^8 \text{ W/cm}^2$ and (b) $I = 1.2 \times 10^{10} \text{ W/cm}^2$.

These curves show populations N_1 , N_2 and N_3 versus the time during a single light pulse using laser with two different excitation intensities. All the molecules get populated in the ground state S_0 only after a sufficiently long time has passed after the pulse was applied. In the first case in Fig. 3.10(a), the excitation intensity has been taken to be $2.6 \times 10^8 \text{ W/cm}^2$ and we observe that most molecules are populated in the ground state S_0 , only a few molecules are populated in the first singlet state S_1 and even lesser number of molecules are populated in the upper excited singlet state S_x . So, the phenomenon of SA would be observed in this case. When the excitation intensity is taken to be $1.2 \times 10^{10} \text{ W/cm}^2$ in the second case, then as shown in Fig. 3.10(b), we find

that most molecules are populated in the upper excited singlet state S_x , some molecules are populated in the ground state S_0 and only a few molecules are populated in the first singlet state S_1 . This shows that the phenomenon observed in this case would be of RSA.

The transmittance curves are shown in Fig. 3.11. The first curve in Fig. 3.11(a) shows that when the intensity was $2.6 \times 10^8 \text{ W/cm}^2$, the transmittance decreases steeply with the application of the pulse and approaches zero and remains at this value even after the pulse has passed. Fig. 3.11(b) shows that when the intensity is increased to $1.2 \times 10^{10} \text{ W/cm}^2$, the dip in the curve is steeper and there is a small hump in the curve at the middle of the pulse but this hump gradually approaches zero.

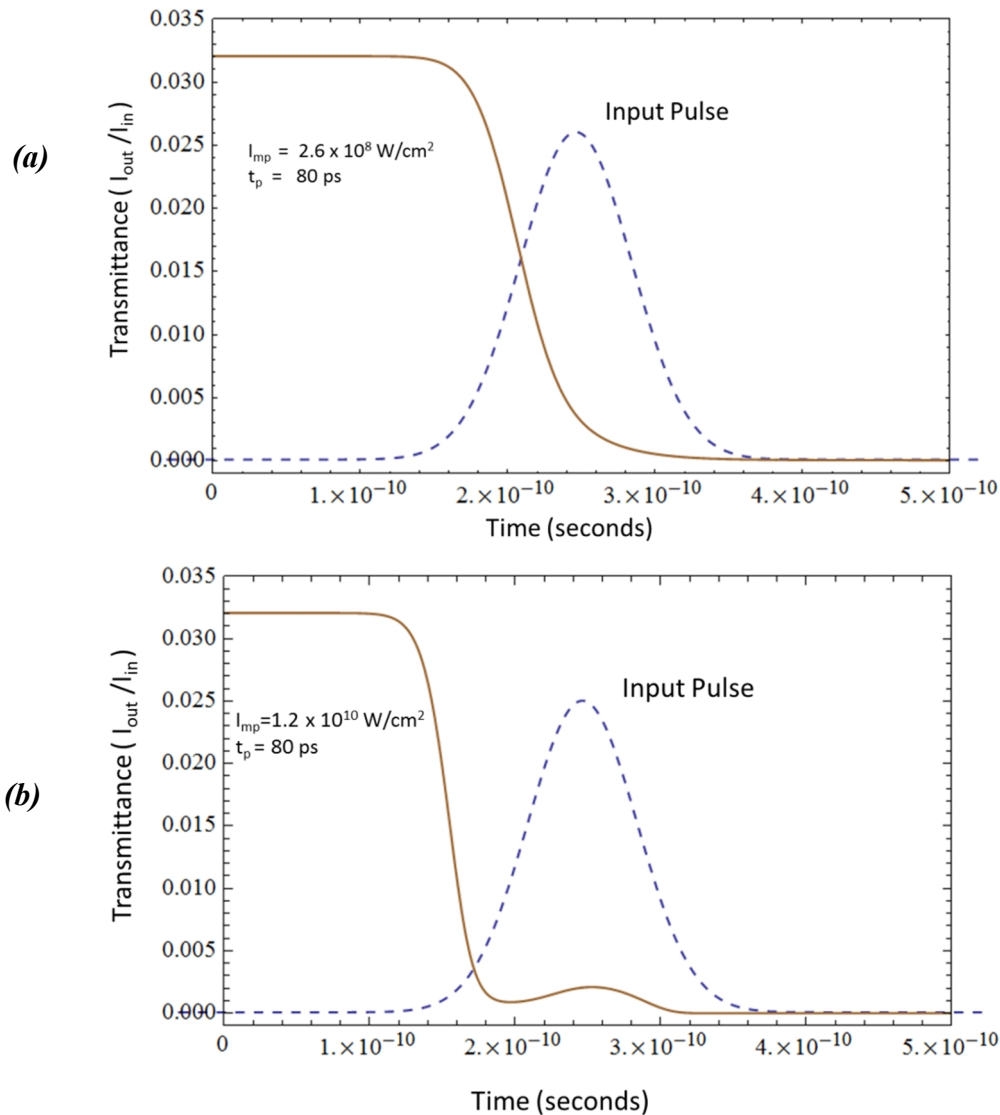


Fig. 3.11 Transmittance (I_{out}/I_{in}) versus the time during a single light pulse with a width of 80 ps under two excitation intensities: (a) $I = 1.2 \times 10^9 \text{ W/cm}^2$ and (b) $I = 1.2 \times 10^{10} \text{ W/cm}^2$.

3.4.3 Femtosecond Pulse Beam Excitation

When compared to the nanosecond or picosecond laser pulse, the femtosecond laser pulse has width comparable to the lifetimes of the higher upper excited states. So when the organic molecular system is excited by femtosecond laser pulse, the higher upper excited states play an important role in the NLA. So the contribution of the higher upper excited state becomes significant and therefore, we cannot neglect it. As a result, the process under f_s [35] pulse beam excitation can therefore be described using a four-level energy diagram as shown in Fig. 3.12 below:

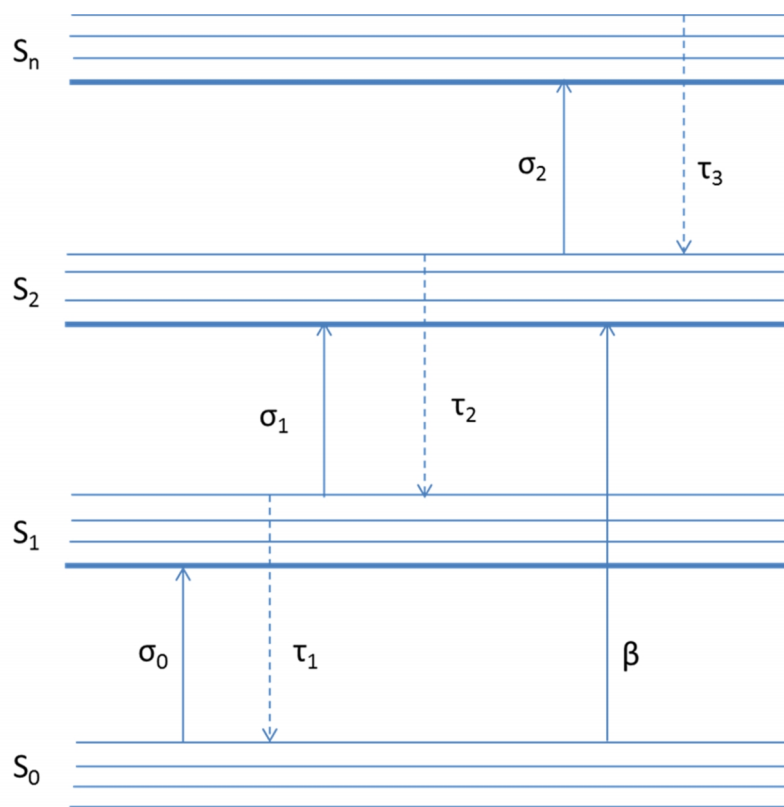


Fig. 3.12 Four-level energy diagram for describing the excitation of an organic molecular system in femtosecond regime, S_0 : the ground state; S_1 : the first excited singlet state; S_2 : the second excited singlet state; S_n : the upper excited singlet state; σ_0 is the ground-state absorption cross sections; σ_1 and σ_2 , the excited state absorption cross sections from states S_1 and S_2 respectively; β , the two-photon-absorption coefficient, and τ_1 , τ_2 and τ_3 are the states lifetime from S_1 , S_2 and S_n respectively.

Fig. 3.12 describes the four-level model, in which the ground state S_0 , the first excited singlet state S_1 , the second excited singlet state S_2 and the higher excited singlet state S_n are considered and all triplet states are ignored. When a femtosecond laser pulse with frequency ν excites this molecular system, it would cause ultrafast transitions [37]-[38]

through one-photon-absorption (OPA) by molecules in the ground state S_0 , which may either induce the transition of molecule from S_0 to S_1 with an absorption cross section σ_0 or the transition of molecule from S_0 to S_1 with a two-photon-absorption (TPA) [39] coefficient β . The molecules in S_1 and S_2 may absorb a photon and transit to S_2 and S_n with an absorption cross section σ_1 and σ_2 , respectively. The system mainly simultaneously absorbs two photons, promoting an electron from S_0 to S_2 . Subsequently, from S_2 , the electron will be promoted to S_n by absorbing another single photon, resulting in excited-state-absorption (ESA) induced by TPA.

Using this four-level energy diagram in Fig. 3.12, the rate equations for describing the time variation of the population density in each energy level can be written as:

$$\frac{dN_1}{dt} = -I_m\sigma_0N_1 + \frac{N_2}{\tau_1} - \frac{\beta I_m^2}{2} \quad (3.24)$$

$$\frac{dN_2}{dt} = I_m\sigma_0N_1 - I_m\sigma_1N_2 - \frac{N_2}{\tau_1} + \frac{N_3}{\tau_2} \quad (3.25)$$

$$\frac{dN_3}{dt} = I_m\sigma_1N_2 - I_m\sigma_2N_3 - \frac{N_3}{\tau_2} + \frac{N_4}{\tau_3} + \frac{\beta I_m^2}{2} \quad (3.26)$$

$$\frac{dN_4}{dt} = I_m\sigma_2N_3 - \frac{N_4}{\tau_3} \quad (3.27)$$

where N_1 , N_2 and N_3 are the number densities (or population densities) of states S_0 , S_1 and S_n respectively. The incident laser beam has a power density flux I_m (i.e. the ratio of the incident intensity I_{mp} to the photon energy $h\nu$). σ_0 and σ_1 are the ground-state absorption cross sections and the excited state absorption cross sections from states S_0 and S_1 respectively.

If we neglect the linear absorption at the considered wavelength and assume only two photon absorption from S_0 to S_1 and OPA from S_2 to S_n , then as the laser light propagates through the molecular system, the intensity through the sample is given by:

$$\frac{dI_{mp}}{dz} = -\alpha_p I_{mp} = -\beta I_{mp}^2 - \frac{\sigma_2\beta\tau}{2h\nu} I_{mp}^2 \quad (3.28)$$

where τ is the pulse duration, $h\nu$ is the incident photon energy σ_2 is the absorption cross section and Z is the propagation length. The first-term on the right-hand side is corresponding to the third-order nonlinear effect because it varies as I^2 . The TPA contributes to the intensity variation with an absorption coefficient β [40]. The second-term arises from ESA. Since this term varies as I^3 , ESA is related to the fifth-order nonlinearity.

The time dependent rate equations given in Eq. (3.24)-(3.27) have been solved numerically by computer simulation by considering the pump laser pulse profile given by

$$i_{mp}' = i_{mp} \exp[-c_p (\frac{t-t_m}{\Delta t})^2] \quad (3.29)$$

where t_m is the time at which the respective pulse maxima occur, $c_p = 4 \ln(2)$ is the pulse profile parameter and Δt is the pulse width.

The rate equation analysis based on the above energy model has been carried out to obtain the intensity dependence of level populations. The laser wavelength has been set to 800 nm and laser pulse width is set as 50 fs. We have taken the molecular system of GO [22] and the photophysical parameters of GO are taken as follows:

$$\begin{aligned} \tau_1 &= 15 \text{ ns}; \\ \tau_2 &= 47 \text{ ps}; \\ \tau_3 &= 100 \text{ fs}; \\ \sigma_0 &= 2 \times 10^{-18} \text{ cm}^2; \\ \sigma_1 &= 3.5 \times 10^{-17} \text{ cm}^2; \\ \sigma_2 &= 7.41 \times 10^{-19} \text{ cm}^2; \\ \beta &= -3.22 \times 10^{-9} \text{ cm/W}; \end{aligned}$$

The resulting curves obtained by solving the above set of rate equations for populations using simulation through computer software are shown in Fig. 3.13. These curves show populations N_1 , N_2 , N_3 and N_4 versus the time during a single light pulse using laser with three different excitation intensities. All the molecules get populated in the ground state S_0 only after a sufficiently long time has passed after the pulse was applied. In the first case in Fig. 3.13(a), the excitation intensity has been taken to be $2.83 \times 10^{12} \text{ W/cm}^2$ and we observe that most molecules are populated in the ground state S_0 .

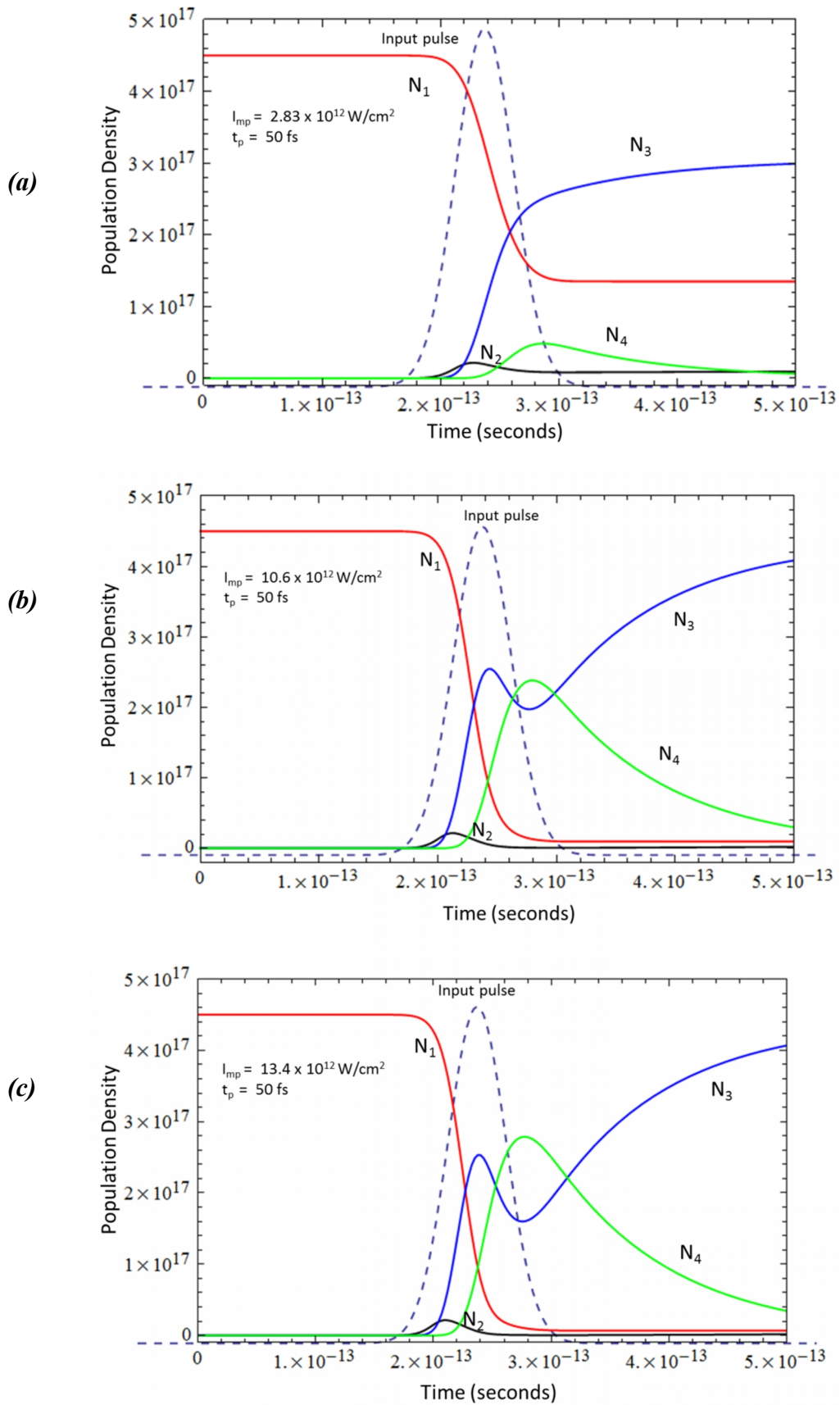


Fig. 3.13 Populations in S_0 , S_1 , S_2 and S_n versus the time during a single light pulse with a width of 50 fs under three excitation intensities: (a) $I = 2.83 \times 10^{12} \text{ W/cm}^2$, (b) $I = 10.6 \times 10^{12} \text{ W/cm}^2$ and (c) $I = 13.4 \times 10^{12} \text{ W/cm}^2$.

So, the phenomenon of SA would be observed in this case as the contribution of ground state is dominant in NLA. When the excitation intensity is taken to be 10.6×10^{12} W/cm² in the second case, then as shown in Fig. 3.13(b), we observe that many molecules are excited to the second excited singlet state S₂ from the ground state S₀ and a significant number are populated in the higher excited singlet state S_n. So, it marks the transition from SA to RSA [41]. In the third case, as shown in Fig. 3.13(c), when the intensity is increased to 13.4×10^{12} W/cm², more molecules are excited to the higher excited singlet state S_n from the second excited singlet state S₂. Since, the contribution of the higher excited singlet state S_n to NLA is being predominating, so RSA response is observed.

Chapter-4
CONCLUSION

In this thesis, all-optical light modulation in graphene oxide (GO) was analyzed using the technique of rate equations formulation and simulation of the results using computer software. First, the dynamics of GO were studied using continuous wave laser beam in steady state only. GO shows very interesting nonlinear optical properties based on intensity induced excited state absorption. The effect of changing pump beam intensity was observed on the dynamics of population, output intensity and transmittance of the probe beam.

Then, the analysis was applied to study the modulation of the transmission of probe beams at different pulse widths by varying the intensity of the modulation beam intensity. The nonlinear absorption properties of GO in nanosecond, picosecond and femtosecond regime were theoretically investigated by rate equations based on different efficient energy level models. The population curves for different states for the varying pump beam intensities were used to demonstrate the phenomena of saturable absorption (SA) and reverse saturable absorption (RSA) and their transition to one another with variations in the probe beam intensities.

In the ns, ps and fs regime, the SA would be observed under low excited laser intensity and the RSA could be observed under high excited laser intensity. And the SA is mainly due to the absorption contribution of ground state S_0 , while the RSA in ns regime is mainly due to the absorption contribution of triplet first excited state T_1 , the RSA in ps regime is mainly due to the absorption contribution of the singlet first excited state S_1 , both of which are a third-order nonlinear phenomena. The RSA in fs regime is mainly due to the excited state absorption (ESA) induced by two-photon absorption (TPA), which is a fifth-order nonlinear phenomenon. It was found that appreciable modulation can be achieved by varying the pump beam intensity and other parameters like the small-signal absorption coefficient. Apart from the intensity and β_p , the absorption cross sections and the lifetime of different intermediate states also play a significant role in the modulation curves.

The transmission characteristics show monotonic exponential decrease for continuous wave beam. For the ns and ps regimes, the transmittance exhibits a dip in the characteristics. The transmission characteristics are seen to be more profound when a probe beam of higher intensity is used suggesting that the resolution can be improved by increasing the intensity of input.

These results suggest the possibility of GO to be used as an efficient all-optical switching material. The NLO properties of GO can be tailored over a wide wavelength

range by various techniques that include, varying the number of layers and the chemical composition or covalently functionalizing it with materials with large optical nonlinearities to form hybrid materials.

In conclusion, there is a great scope of research and development on the proposed all-optical switch based on GO as it would be advantageous due to its small size, simplicity, low power consumption, small absorption coefficients, parallel operation, speed and flexibility in design. It can prove to be better than majority of other organic molecules studied so far in terms of low intensity operation, better modulation efficiency and faster response due to small lifetimes. Further study on GO and its properties can make it possible to use this material for switching and computation applications in near future.

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