Investigation of Nonlinear Effects Induced in Condensed Matter by Intense Laser Fields

by

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DECLARATION

I hereby declare that this thesis is composed independently by me at the Raman Research Institute, Bangalore, under the supervision of Dr. Reji Philip. The subject matter presented in this thesis has not previously formed the basis of the award of any degree, diploma, associateship, fellowship or any other similar title.

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CERTIFICATE

This is to certify that the thesis entitled **Investigation of Nonlinear Effects Induced in Condensed Matter by Intense Laser Fields** submitted by Anija M. for the award of the degree of DOCTOR OF PHILOSOPHY of Jawaharlal Nehru University is her original work. This has not been published or submitted to any other university for any other degree or diploma.

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To my teachers

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Table of Contents

Appendix I Rate equation analysis

Appendix II Light propagation through nonlinear media arranged in tandem

Preface

Interaction of electromagnetic radiation with matter has been an exciting field of study for several decades. In the past it was the frequency that was important but after the advent of lasers, the intensity of the electromagnetic field has started playing a decisive role in the interaction. A laser beam is primarily characterized by its spatial and temporal coherence. The coherence will allow spatial and temporal confinement of electromagnetic energy, leading to a myriad of nonlinear responses from the interacting medium. Modern lasers can be designed to give ultrafast light pulses as short as a few femtoseconds (10^{-15} seconds). It will be worth investigating their impact on novel forms of matter. The interaction of high intensity laser pulses with nanoparticles, carbon nanotubes, liquid crystals etc. are some examples. The interaction of laser pulses with plasma, which is a form of matter that normally exists only in stellar environments, can also be realized now in terrestrial laboratories.

In a broad sense, this thesis is an investigation of the interaction of electromagnetic radiation in the engineered form, viz. laser, with engineered forms of matter like nanoparticles and plasmas. Initially, the interaction of moderately intense laser pulses with metal nanoparticles contained in different hosts is investigated. Later, the focus of the study shifts to the application of intense laser pulses to create a plasma, and the response of the plasma to the laser pulse. Pulsed lasers emitting nanosecond (10^{-9} second) and femtosecond (10^{-15} second) pulses are employed for the investigations.

Chapter one gives a general introduction to the nonlinear response of matter in a strong laser field. Depending on the intensity of the input laser radiation, the response of the medium will be moderately nonlinear or extremely nonlinear. In this chapter, the nature of nonlinear optical phenomena in different ranges of input laser intensity is discussed in detail. Some laser sources used for the present studies are ultrashort, high power lasers. The generation of ultrashort laser pulses is a subject rich in physics, and chapter one gives a brief view of this interesting field also.

Chapter two is a study of the absorptive optical nonlinearity in gold and silver nanoparticles of different size, contained in different host materials. The nonlinear absorption of these nanoparticles is investigated using 7 nanosecond laser pulses in an automated zscan setup. A brief introduction to metal nanoparticles is given followed by a discussion of the physics of nonlinear light transmission. One group of samples investigated is the core-shell nanoparticles $Au@TiO_2$, $Au@ZrO_2$, $Au@SiO_2$ and $Ag@ZrO_2$, in the size range of 30–60 nm, at 532 nm. In this size range the surface plasmon resonance (SPR) will be very prominent in the linear absorption spectrum. These oxide-protected nanoparticles are found to be stable even at high input laser fluences of 20 Jcm^{-2} and intensities of 2.8 GW cm^{-2}. The z-scans obtained are peculiar in that an increase in transmission is seen at moderate laser fluences due to the plasmon band bleach while the transmission drastically decreases at higher fluences. The increase in transmission is more pronounced at higher concentrations. A significant amount of nonlinear light scattering also is observed from these samples. These results show that the samples can be used either as saturable absorbers or optical limiters in the appropriate concentration and laser fluence regimes. The nonlinear absorption coefficient is evaluated numerically to be of the order of 10^{-10} mW^{-1}, which is comparable to that of benchmark materials like C_{60}. Another set of samples studied is the core-shell alloy nanoparticles $Au_{0.18}Ag_{0.82}@ZrO_2$, $Au_{0.3}Ag_{0.7}@ZrO_2$ and $Au_{0.46}Ag_{0.54}@ZrO_2$, with an alloy core of average size 35nm and an oxide shell of size 2-3 nm. For these samples also an increase in transmission is seen at moderate laser fluences, and a decrease at higher fluences. The detailed features of the nonlinear transmission depend crucially on the alloy composition. The plasmon band bleach in the alloy system is dependent on its stoichiometry with a maximum saturation for $Au_{0.46}Ag_{0.54}@ZrO_2$, where the Au concentration is the largest. Significant nonlinear light scattering occurs in these core–shell alloys also, making these materials strong optical limiters. An advantage of core-shell structures is that they have a high laser damage threshold. We also investigated the nonlinear transmission of polymer films of pure Au, pure Ag, and Au:Ag composite in a PVA matrix using nanosecond laser pulses at the near-resonant wavelength of 532nm and off-resonant wavelength of 1064nm. Since these are free standing films with a thickness of 100μm, they are potential candidates for nonlinear optical applications, from a device point of view. For resonant excitation, the sign of the nonlinearity is dependent on sample composition and input laser fluence, while for off-resonant excitation the samples exhibit induced absorption caused by two-photon induced excited state absorption. Hence these materials can be used either as saturable absorbers or optical limiters at the appropriate wavelengths and pump intensities.

This chapter also includes nonlinear absorption studies and rate equation analysis of light propagation in small clusters of (≈ 1 nm) Au@hexanethiol and Au@dodacanethiol, which contain as small a number as approximately 140 atoms of gold per cluster. As the surface plasmon absorption band is almost absent in these clusters, plasmon bleach effects do not occur, and hence, the nonlinearity is exclusively of the optical limiting type. This reduced transmission fits numerically to a three-photon absorption process, which physically originates from a two-photon induced excited state absorption. The cluster properties are found to be semi-molecular, since their sizes fall in between those of nanoparticles and molecular clusters. Induced thermal scattering is not prominent. The lifetime of the optical limiting action in these clusters is estimated to be <2ps, from pump-probe experiments done at 400nm using 100 femtosecond laser pulses.

Chapter three discusses a novel idea for the design and implementation of a passive all-optical diode. Here, nonlinear absorbers are used for realizing the optical diode action. The hitherto proposed optical diodes include fluorescent dyes with a concentration gradient, absorbing multilayer systems, second harmonic generators with a spatially varying wavevector mismatch, Photonic crystals with structural asymmetries and liquid-crystal hetero junctions. In our new proposal we show that when a saturable absorber and a reverse saturable absorber are placed in tandem, the resulting axially asymmetric nonlinear configuration exhibits a spatially non-reciprocal transmittance at sufficiently high input laser intensities. If the laser beam passes through the saturable absorber first and through the reverse saturable absorber next, then we call the arrangement "forward biased". The inverse configuration is called "reverse biased". Such a device shows substantial transmission in the forward bias, but the transmission is limited in the reverse bias. In the reverse bias configuration, the reverse saturable absorber will initially bring down the intensity below the saturation intensity of the saturable absorber, so that the net transmittance through the device gets limited. The intensity dependent increase in the absorption of reverse saturable absorber makes the non-reciprocity prominent at higher laser intensities. An extensive numerical analysis is carried out for calculating the non-reciprocity of nonlinear materials with path lengths of 1mm and 1μm respectively. For experimental verification, the laser dye Rhodamine 6G is used as the saturable absorber, and C_{60} is used as the reverse saturable absorber. Nanosecond laser pulses at 532 nm are used for excitation. Similarly, combinations of R6G and LDS 867, Pyrromethene and C_{60}, and Pyrromethene and LDS 867 were investigated. Materials with higher nonlinearity (large saturable and reverse saturable absorption cross sections) are found to give better non-reciprocal transmission with a higher contrast.

Chapters four and five investigate the spectral characteristics of femtosecond laser-induced plasma from a thin planar jet of water. The jet has a thickness of 250 microns. The leading edge of a 100 femtosecond laser pulse (800nm central wavelength) is used to produce the plasma, and the interaction of the trailing edge of the pulse with the generated plasma is studied. Chapter four discusses the spectroscopic characteristics of the plasma generated when the water jet is irradiated at normal incidence. The input laser intensity is varied in the range of 8.1×10^{14} W/cm^2 to 3.9×10^{15} W/cm^2 to observe its effect on the emission characteristics. Emission in the 350-1100nm range is recorded using a fiber-optic spectrometer. For intensities beyond 1.4×10^{15} W/cm^2 a prominent H_α line is observed, along with the H_β line and singly ionized oxygen line (OII). The micrometer dimensions of a thin water jet allows us to observe the characteristic emissions, whereas only a spectroscopically featureless white light continuum was observed so far in femtosecond illumination experiments conducted in thicker water cells. The line emissions occur as a result of electron-ion recombination. At higher input laser intensities a spectral band is seen to emerge beyond 675nm. No spectrum is present on the stokes side of the excitation wavelength. This band is attributed to the spectral blueshift of the laser light as a result of the rapidly varying refractive index of the plasma. A polarization analysis of the observed spectra shows unpolarized emission from 350nm to 675nm, whereas the band beyond 675nm shows a polarization similar to that of the input laser pulse. This reaffirms the conjecture that this band originates from spectral blueshift of the scattered photons. The absence of Stokes emission in the spectrum supports the occurrence of plasma creation and the absence of Kerr nonlinearity from neutral molecules.

Chapter five discusses the spectroscopic characteristics of plasma generated when the water jet is irradiated at oblique incidence. In addition to the incoherent emission in the visible, the emission of second harmonic radiation of the exciting laser field also is observed in this case. In these experiments the 100 femtosecond laser pulse is focused on the water jet at an angle of 45^0 to the plane of the jet. Second harmonic (SH) emission is observed only in the specular reflection direction. The emitted spectra are collected at the reflecting angle for the oblique incidence. Polarization of the input laser pulse is changed from *s* to *p* in steps of 2^0 using an achromatic half wave plate, and corresponding variations in SH are studied. The SH intensity is found to be strongly dependent on the input laser pulse polarization, with a maximum yield for *p* polarized excitation. The incoherent visible emission also is studied for different input polarizations.

Chapter six describes the design and fabrication details of an experimental setup to study the interaction of ultrashort laser pulses with liquid droplets in vacuum. The major component in the setup is a vacuum chamber of approximately 300 litres volume, provided with a differential pumping arrangement. The chamber can be pumped using a turbo molecular pump with a pumping capacity of 2000 l/s to a pressure of 1x10^{-6} Torr. When an ethanol jet from a capillary tube of 10μm diameter is introduced into the chamber, the working pressure settles to 1x10^{-3} Torr. The 10μm diameter jet is produced by pressurizing ethanol in a stainless steel container with compressed nitrogen at a pressure of 7 bar. The ethanol jet in vacuum can be imaged using a CCD camera kept at a distance of more than 60cm, using appropriate imaging optics. The ultrafast laser-induced plasma emission from the ethanol droplets is expected to fall in the X-Ray frequency region. To observe this radiation, a Si-PIN detector (capable of detection in the range of 1-90 keV) and an NaI (Tl) detector (capable of detection in the ranges of 100 keV – 10 MeV) have been calibrated, using the radiation sources Am^{241} and Cs^{137} respectively. The NaI(Tl) detector is susceptible to background radiation emitted by ambient radioactive elements. Therefore to improve the signal to noise ratio, a time gate is applied to the Multi Channel Analyzer (MCA) unit. A precision function generator (SRS DS345) is used to derive the time gate signal in synchronization with the Q-switch output of the Nd:YAG pump laser of the femtosecond laser. Thus the detector will be recording the emission from the liquid droplet only for a desired time window (variable between 1μs to 1s) in synchronization with the femtosecond laser pulse. Time-synchronized operation ensures background free detection of the hard X-Ray produced in the laser-plasma interaction. This experimental setup will be used in future for investigating the plasma emitted by droplets of different liquids.

In Appendix I, a C programme developed for rate equation analysis (used in chapter two) is given. Appendix II is a Matlab programme that simulates the propagation of laser pulses through a saturable absorber and a reverse saturable absorber arranged in tandem (used in chapter 3).

The following publications contain work described in this thesis:

(1) Nonlinear light transmission through oxide-protected Au and Ag nanoparticles: an investigation in the nanosecond domain, ***M.Anija,*** *Jinto Thomas, Navinder Singh, A. Sreekumaran Nair, Renjis T.Tom, T.Pradeep and Reji Philip*, Chemical Physics Letters 380 (2003) 223.

(2) Observation of a fifth order optical nonlinearity in 29kDa Au@alkanethiol clusters excited in the visible, *Jinto Thomas*, **M. Anija**, *Jobin Cyriac, T. Pradeep and Reji Philip*, Chemical Physics Letters 403 (2005) 308.

(3) $Au_xAg_yZrO_2$ core-shell nanoparticles: synthesis, characterization, reactivity and optical limiting, *A.Sreekumaran Nair, V.Suryanarayanan, T.Pradeep, Jinto Thomas,* **M. Anija** *and Reji Philip*, Materials Science and Engineering B 117 (2005) 173.

(4) In situ synthesis and nonlinear optical properties of Au:Ag nanocomposite polymer films, *B. Karthikeyan,* **M. Anija** *and Reji Philip*, Applied Physics Letters 88, 053104 (2006).

(5) Passive all-optical diode using asymmetric nonlinear absorption*, Reji Philip,* ***M.Anija****, Chandra S. Yelleswarapu and D.V.G.L.N.Rao*, Applied Physics Letters (in press).

The following manuscripts, which are under preparation, also contain work reported in this thesis:

(1) Visible emission from femtosecond laser-induced plasma in a planar water jet, *M. Anija and Reji Philip* (in preparation).

(2) Features of nonreciprocal transmission in a passive all-optical diode based on asymmetric nonlinear absorption, *M. Anija, D.V.G.L.N. Rao and Reji Philip* (in preparation).

(3) Polarization dependent second harmonic and incoherent radiation from plasma generated in a planar water microjet, *M. Anija and Reji Philip* (in preparation).