CHAPTER 6

$C_{60}$: Studies of Third-order Nonlinearity, Excited State Dynamics using DFWM-IL and Dispersion of Nonlinear Absorption using Z-scan techniques

Third-order optical nonlinearity, excited state dynamics and dispersion studies of nonlinear absorption of $C_{60}$ have been studied using backward Degenerate Four Wave Mixing (both with incoherent light and coherent light) and Z-scan techniques. We observe a large nonlinearity at 600 nm and it is attributed to strong two-photon absorption. We estimate the population relaxation $T_1$ (of the lower excited singlet state $S_1$) and phase relaxation time $T_2$ (of the higher excited singlet state $S_n$) of the sample. The vibrational relaxation ($\tau_{vb}$) in the $S_1$ state is found to be $\sim 5$ ps. Our results are found to be in good agreement with those obtained using 150 fs pulses. We also present our open aperture Z-scan data at 600 nm using the broadband source and our experimental and theoretical results on the dispersion studies of non-linear absorption in $C_{60}$ solution. Open aperture Z-scans are performed over the visible region (440 nm to 660 nm) using an ns OPO and the obtained results are interpreted using a 5-level model taking into account both the excited state absorption and two-photon absorption processes. Results indicate that excited state absorption dominates in the shorter wavelength region (440 nm to 560 nm) whereas two-photon absorption dominates in the longer wavelength region (580 nm to 660 nm).

6.1 Introduction

The progress of modern optical technology for all-optical, electro-optical, acousto-optical, and opto-mechanical devices demands the ability to control the intensity of light in a predetermined and predictable manner. Some of the important requirements of materials for the realisation of photonic devices are a) Large nonlinearity b) Ultrafast response time (in ps and fs domain) c) Low dielectric constant and linear losses d) High resistance to laser radiation $\sim$ GW/Cm$^2$ e) Ease in chemical tailoring of physical and optical properties f) Ability to process into thin films, fibres g) Mechanical strength and flexibility h) Compatibility with semiconductor-integrated structures and i) Compactness and cost-effectiveness. Extensive research in recent years suggests organic and organo-metallic materials to be the best candidates for ‘tailoring’ the material properties. Since its discovery and availability in milligrams [1], fullerenes and their derivatives have received extraordinary attention from physicists, chemists and material scientists who have been extensively investigating their optical,
physical and chemical properties for fundamental understanding and technological applications. Fullerenes are fascinating owing to their chemistry and unique physics coupled with material science. It has been well established that organic molecules with highly de-localised π-electron system exhibit large optical nonlinearity [2]. Fullerenes are also found to have a very high value of $\chi^{(3)}$ with small absorption coefficient, fast nonlinear response and high chemical stability. Although there is considerable variation in the reports on measurements of experimental and theoretical $\chi^{(3)}$ values of fullerenes in solution/thin films [3-21], they are found to have very high potential in device applications. Earlier studies indicate $C_{60}$ and its derivatives (doped in glass matrix, sol-gels, polymers, etc.) as potential candidates for optical limiting [22-36], optical bistability [37] optical switching [38] and higher harmonic generation [39]. Owing to their electronic structure, fullerenes also find unique applications in photoconductivity, electroluminescence, ferromagnetism, superconductivity, cancer therapy, and in biological use [40]. Understanding the origin, magnitude of nonlinearity and excited state dynamics in such an exotic molecule is very important both from the fundamental point of view and its wide range of applications. We study the third order optical nonlinearity, excited state dynamics, which occur in fs and ps domain, and nonlinear absorption of $C_{60}$ dissolved in xylene/toluene.

6.2 Degenerate Four Wave Mixing

6.2.1 $\chi^{(3)}$ Measurements

Although there is wide literature available [3-21] on the measurement of $\chi^{(3)}$, there is also a wide range of values reported ($\sim 10^{-8}$ to $10^{-12}$ esu). Most of the nonlinearity measurements were performed in the NIR spectral region, far away from one-photon resonance. We have measured $\chi^{(3)}$ using a broad band laser peaking at 595 nm and having a width of $\sim 8$ nm. Complete details of the experimental set-up have been reported in earlier chapters. The laser line width (FWHM), when the mirror is present in the cavity, is found to be $\sim 8$ nm (RhB in methanol) [41]. This corresponds to a correlation time ($\tau_c$) of $\sim 170$ fs measured from the inverse of bandwidth as well as from the width of PC signal in RhB (since in RhB, $T_1$ is very large, $\sim$ few ns, we
see only a symmetric auto-correlation curve). When the mirror in the cavity is replaced by a dispersive element like a high resolution grating the line width is reduced and is found to be \(~1.3\) nm with the corresponding correlation time is \(~2.7\) ps (measured from the width of PC signal in RhB and CS\(_2\)). The correlation time measured by using the relation \(\Delta \nu \tau_c = 1\) is \(~900\) fs. Beam 1 (\(k_1\)) is forward pump, beam 2 (\(k_2\)) is backward pump and beam 3 (\(k_3\)) is the probe. The sample is placed in a 1-mm thick cuvette and different parts of the cell are exposed, for different measurements, to the laser beam to avoid any degradation of the sample. Beam 2 passes through a retro-reflector mounted on a micrometer which is delayed manually whereas beam 3 passes through another retro-reflector mounted on a micrometer controlled by a stepper motor interfaced to a computer. In both the cases the maximum resolution we could achieve (i.e. minimum distance that could be moved with this delay) is \(~5\) µm which corresponds to \(~33\) fs in time (with a retro-reflector). The sample is dissolved in spectroscopic grade, highly purified xylene/toluene. All the beams have same polarisation and the change in polarisation in each of the beams is achieved using a Half Wave Plate (HWP).

\(C_{60}\ (> 99\% \text{ pure})\) was purchased from Strem Chemicals, USA and is used without further purification. Fig. 6.1 (a) shows the absorption spectrum, recorded using a UV/VIS spectrometer (Jasco, model 7800), of the sample dissolved in xylene and it matches well with those reported in literature. The main features are a strong band around 335 nm, very small and almost constant absorption in the visible region. An OD of \(< 0.2\) at 600 nm is chosen for recording the signals in all measurements. The cubic dependence (at lower input intensities) of the PC signal with varying input is verified before each measurement. The PC signal plotted as a function of the sample concentration, shown in fig. 1 (b), clearly follows a linear dependence. \(\chi^{(3)}\) and \(\gamma\) are calculated using the standard relations as described in previous chapter. \(\chi^{(3)}\) value at a concentration of \(3.47*10^{-4}\) M is found to be \(~2.5*10^{11}\) esu (at 600 nm). \(\gamma\) is found to be \(5.388*10^{-30}\) esu using a \(\chi^{(3)}\) value for reference sample CS\(_2\) as \(1.7*10^{-12}\) esu. When the polarization of the probe beam is crossed with respect to pump beams, the PC signal dropped by 6-7 times indicating a part of thermal contribution to
Fig. 6.1 (a) Absorption spectrum of the sample C$_{60}$ (Xylene). (b) Concentration dependence of $\chi^{(3)}$. Solid dots are experimental data and line is a linear fit.
the nonlinearity (for pure electronic contribution the signal drops down by 3 times and for orientational type it drops down by three-fourths). This large value of $\chi^{(3)}$ could be also attributed to strong Two Photon Absorption (TPA) at this wavelength. As shown in the later part of this chapter there is a strong TPA at and around this wavelength, exciting the molecules directly into the $S_n$ states. Lee et. al. [41] have identified the energy of the singlet states in C$_{60}$. $S_1$ state falls in ~ 16,000 cm$^{-1}$ range and the $S_n$ state falls in ~ 29,000 cm$^{-1}$ range. We work at the wavelength of ~ 595 nm (16,800 cm$^{-1}$) and the two photon energy corresponds to ~ 33,600 cm$^{-1}$ leading the population directly into $S_n$ states. The measured nonlinearity, then, will have contributions from nonlinearities due to the ground state and the excited states. Moreover the singlet state excited state absorption is stronger than the ground state absorption forcing the population to be distributed among the different excited states. As argued in the earlier chapter this enhanced $\chi^{(3)}$ value could be a result of strong ESA/TPA with contribution from thermal part as well.

Comparing our value with those obtained in literature, Henari et al. [7] working with 5 ns pulses at 580 nm obtained a high value of ~ 8.8*10$^{-10}$ esu. Ji et al. [11] obtained a value of ~ 10$^{-10}$ esu for $\chi^{(3)}$ and ~ 10$^{-31}$ esu for $\gamma$ at 608 nm using 6 ns pulses for thin films and conclude that $\chi^{(3)}$ is dominated by its imaginary part (which again is due to excited state absorption). They assume a refractive index of 1.49 for the films. We assume a value of 2 for the solutions. Flom et al. [13] working with 1.2 ps pulses at 597 nm, and in the phase conjugate geometry, obtains a $\chi^{(3)}$ value of (38 ± 9)*10$^{-11}$ esu (in the xxxx configuration, where all the beams have same polarisation) for C$_{60}$ pure film. By looking at the temporal response of the PC signal the high value observed for $\chi^{(3)}$ is attributed to the participation of the excited states in the nonlinear process. They observe a short lifetime of ~ 43 ps which is due to the first excited singlet state occurring due to the exciton-exciton annihilation and a long lived component which is due to the triplet state. Flom et al. [13] again working with 1.2 ps pulses at 590.5 nm report a value of 52*10$^{-11}$ esu for $\chi^{(3)}$ in the xxxx configuration. J. Li et al. [21] working at a non-resonant wavelength, 810 nm, reports an upper limit for $\gamma$ as 9.0*10$^{-35}$ esu, which is very low.
6.2.2 Temporal response of the DFWM signal

We employ the standard DFWM in the phase conjugate geometry and delay the probe beam (beam 3) with backward pump and forward pump at zero delay. We observe two peaks in the phase conjugate signal when the probe is delayed with respect to the forward and backward pump beams. From the widths and ratio of these peaks we estimate \( T_1 \) and \( T_2 \) values for the \( S_1 \) and \( S_n \) states respectively [42]. We also estimate the vibrational relaxation time in the \( S_1 \) state. Fig. 6.2 shows the phase conjugate signal as the probe beam is delayed with respect to beam 1, with beam 2 kept at delay of \( \delta \) with respect to beam 1 (Inset shows the schematic of the configuration used, briefly). We see a sharp coherence peak at \( \tau = 0 \) due to beams 1 and 3 with beam 2 probing the grating, and another at \( \tau = \delta = 9 \text{ ps} \) due to beams 2 and 3 with beam 1 probing the grating. For different \( \delta \) values the broad peak shifted symmetrically across the first coherence peak. It has been shown that the ratio of these peaks would give information on the population relaxation time of the lower excited state and the line widths give information on the dephasing of the \( S_n \) and \( S_1 \) states [43]. From the width (FWHM) of the first coherence peak at \( \tau = 0 \) (\( \sim 170 \text{ fs} \)), the width (FWHM) of the second peak at \( \tau = \delta \) (\( \sim 5 \text{ ps} \)), the ratio of the two peaks (\( \sim 450 \)) we estimate the phase relaxation time \( T_2 \) of the \( S_n \) states as \( < 170 \text{ fs} \), vibrational relaxation in the \( S_1 \) state (\( S_{1v} - S_{10} \)) as \( \sim 5 \text{ ps} \), and population relaxation (\( T_1 \)) time as \( \sim 70 \text{ ps} \) (Ratio* \( \tau_c \)) respectively.

We compare our results with those obtained using 150 fs pulses at 633 nm and find that they are in excellent agreement with them. Rosker et al. [8] employ the backward DFWM using 150 fs pulses at 633 nm and recorded the PC signal by delaying the backward pump beam, with other two beams at zero delay, which would give information on the population relaxation time of the material [44]. They observe three different decay times, 260 fs, 4.6 ps and 64 ps, in the signal and could not account for their observation. The longer component was found to be sensitive to both the input intensity and the temporal overlap of the writing pulses suggesting that they are most likely due to presence of an excited state population grating. Also it was observed that the long-lived component vanishes for wavelengths longer
Fig. 6.2 Time resolved spectrum of the PC signal for $\delta = 9$ psec.
Inset shows the FWM schematic.
than 650 nm clearly suggesting the involvement of $S_1$ state. However, in our present study, the three different time scales could be successfully assigned to the different relaxation processes in the upper and the lower excited states.

Since the input pulses have a correlation time of $\sim 170$ fs, the intersystem crossing rate, which is $\sim 650$ ps, would not play an important role in these studies. Two photon / excited state absorption takes the molecules from the vibrational manifold of the ground state to the upper states of $S_n$. The upper states $S_n$ will relax back to the $S_1$ state on fs time scale and in the process generate a vibrationally excited $S_1$ state (Kasha’s rule). Peak 1, which has a fast response time in fs, is attributed to the dephasing of the excited states $S_n$. The width of the second peak, of the order of few ps, is attributed to the vibrational relaxation or the vibrational dephasing time within the $S_1$ state ($S_{1v}$ to $S_1$). The ratio of the peaks is related to the population relaxation time of the lower excited state. Thus from the observed line widths and the ratio of the DFWM signal, we estimate the dephasing time of the $S_n$ states to be less than 180 fs, the vibration relaxation time in the $S_1$ state as $\sim 5$ ps, the population relaxation time as $\sim 70$ ps ($450*\tau_c$). Apart from the two coherence peaks we also observed two sharp peaks overriding the broader peak (Fig. 6.2). These sharp peaks observed on the shoulders of the broad peak are found to be due to coherence of probe beam (beam 3) and the reflections of the backward pump (beam 2) from the surfaces of the cell. This was confirmed by using cuvettes of different size. The broader peak appears exactly at $\tau = |\delta|$ and therefore its position is dependant on the delay of second beam (beam 2). The PC signal recorded with a grating in the cavity of the dye laser is shown in fig. 6.3 (a). Since $\tau_c$ is now 2.6 ps, the ratio of the two peaks will be reduced. The widths of the first peak and the second peak remained same within the experimental errors. The width of first coherence peak is $\sim 2.7$ ps and there is no decay observed within experimental errors indicating that the value of $T_2$ is much smaller than $\tau_c$. The value of $T_1$ calculated in this case is $\sim 67.5$ ps ($25*2.7$ ps). This result corroborates our earlier result, of $T_1 \sim 70$ ps, on the same sample using pulses having $\tau_c$ of 170 fs. Both the measurements are performed under identical conditions of input intensity, concentration of the sample to avoid any other complications arising from these factors. The values quoted above have an error bar of
Fig. 6.3 (a) PC signal in the sample C60 with gratings in the cavity. $\tau_c$ in this case is $\sim 2.7$ psec. (b) Self diffracted signal in the $k_1 - 2k_2$ direction.

Dots are experimental data and line is a gaussian fit.
approximately 25%. The major sources of error arise from the calibration of the neutral density filters used, the stepper motor movement, linearity of the photodiode.

There are several reports on the $S_1$ excited state dynamics in $C_{60}$ in solution and thin film forms. As the excited singlet state has shorter lifetime compared to the metastable triplet state, different excited state populations are prepared if different pulse widths are used. Ishihara et al. [45] reports the relaxation dynamics of photoexcitations in polycrystalline $C_{60}$ thin films using fs pump-probe spectroscopy. They observe the decay times of self-trapped excitons and polarons as $570 \pm 120$ fs and $54 \pm 7$ ps respectively. Schell et al. [46] working with $C_{60}$-doped solid xerogel matrices observe a depopulation rate of $\sim 150$ ps for the $S_1$ state. They indicate the reason for the observation of short lifetime compared to intersystem crossing rate could be due to the increased interaction between the $C_{60}$ molecules and the surrounding glass matrix. Juhasz et al. [47] reports the dynamics of photoexcited carrier relaxation obtained through measurement of time-resolved transmissivity. They observe a decay time of $\sim 18$ ps at room temperature and $\sim 120$ ps at $5^0$ K. They indicate that carrier trapping plays an important role in the relaxation mechanism. Dexeheimer et al. [48] working with 60 fs at 620 nm observe the dynamics of $C_{60}$ in both solid and liquid forms using the time-resolved pump-probe technique. In the solid form, they observe a non-exponential decay of the induced absorption, which is intensity dependent. For $C_{60}$ in solution, because of the limited solubility, the molecules are well separated and the fast intensity dependent component is not observed. The dynamics are dominated by the intersystem crossing occurring on the time scale of few hundred ps.

Farztdinov et al. [49] report the slowing-down of ultrafast relaxation in $C_{60}$ thin films at high fs pump intensities and suggest that this slowing-down results from two-step photon absorption of the high-intensity pulse. Palit et al. [50] investigating the photophysical properties of $C_{60}$ and $C_{70}$ report the $S_1$ state lifetime in $C_{60}$ as 1.4 ns and is found to be solvent independent. Cheville et al. [51] report the time-resolved carrier relaxation in solid $C_{60}$ thin films at 605 nm and observe a decay time of 43 ps which is temperature independent. They identify the two processes, carrier trapping and carrier hopping, relevant for the understanding of carrier relaxation. Chekalin et al. [52]
performed fs measurements of relaxation in thin film and solution forms at different excitation intensities. They observe sharp differences in the relaxation mechanism in solid and solution forms. They do not observe any short-lived component in solution form (except for the 1.2 ps rise time, because of the disruption of the symmetry of the molecule as its structure changes). For thin films they observe the photo-induced absorption relaxes in a non-exponential way, at a rate which increases with increasing excitation intensity along with the spectral dependence peaking at 650 nm. Kardash et al. [53] reports their fs laser spectroscopic studies on ultrafast relaxation of photo-induced darkening in fullerite (C_{60} on a quartz substrate). They observe electronic-vibrational relaxation with time scales of ~ 1 ps and 30 ps. Wasielewski et al. [54] report first excited singlet state lifetime of ~ 34 ps observed from their transient absorption measurements. Yang et al. [55] performed time-resolved DFWM measurements with 32 ps pulses at 532 nm in the boxcar geometry. The time response was measured for different polarization configurations of the probe beam to extract the singlet S_1 state lifetime. They observe that dynamics exhibit a strong dependence on the incident energy. In the yxyy (probe polarization orthogonal to the pump beams) they observe a single decay in the DFWM signal with a decay time of ~ 650 ps. After excitation, the first excited state S_1 is populated, immediately opening up the S_1 to S_n transitions. At low pump intensities the lifetime of the S_1 state is mostly governed by the intersystem crossing rate from S_1 to T_1 state. They also argue that the most likely path for fast depletion of S_1 within a faster time scale (< 1 ns) is the strong singlet-singlet excited state absorption S_1 to S_n of the pump beams with subsequent non-radiative decay to the ground state. Flom et al. [56] performed time-resolved DFWM measurements on thin films of C_{60} and observed a lifetime of ~ 650 ps for the first excited singlet state. A non-exponential decay is observed for low laser fluences, which is consistent with the pump-probe studies. The dynamics exhibit strong dependence on the laser fluence with decay becoming much faster at higher fluences. They also suggest that lifetime of the singlet state is governed by the intersystem crossing and strongly dependent on the excited-state population density. At lowest excitation densities the decay of the NLO signal was consistent with the 43 ps lifetime previously reported at 605 nm. The shortening of the lifetime of the electronic excited state, observed at high fluence, is attributed to an excitonic singlet-singlet annihilation
mechanism. Sension et al. [57] reports the results of their transient absorption studies of C\textsubscript{60} in solution using second and third harmonics of a Nd: YAG laser. A 100 ps component and a 650 ps growth component were observed in kinetics measurement performed using a 600 nm probe. They indicate that the 100 ps component is possibly due to the relaxation of the low-lying singlet states contributing to the broad ground state absorption between 440 and 660 nm. Ebbesen et al. [58] reports their excited state properties using ns and ps laser flash photolysis. They obtain S\textsubscript{1} state lifetime as 1.2 ns. Tanigaki et al. [59] reports the S\textsubscript{1} state lifetime as \(\sim 670\) ps from their ps and ns laser flash photolysis studies. Brorson et al. [60] working with 80 fs pulses at 620 nm report their pump-probe investigations. In the forward FWM geometry (also known as self-diffraction geometry) they observe that the signal does not show any decay suggesting the phase relaxation time \(T_2\) to be < 100 fs. In our case we do observe two orders of the self-diffracted signals when the backward pump is blocked. The signal recorded by delaying the probe beam (beam 3 in this case) in either of \(2k_2 - k_1\) or \(2k_2 - k_1\) directions, shown in fig. 6.3 (b), does not show any decay again suggesting that \(T_2\) is less than correlation time, 170 fs. There are also several other reports [61-64] on the dynamics of excited states in C\textsubscript{60} and it’s derivatives studied using different techniques and pulse widths.

6.3 Z-scan studies

6.3.1 Reverse Saturable Absorption in C\textsubscript{60}

The ability to control the intensity of light in a predetermined and predictable manner is one of the most fundamental and important of manipulations, with applications ranging from optical communications to optical computing. There are many methods that can be used to switch, limit, amplify, or modulate the amplitude of an optical signal. All of these methods may be broadly categorised into two groups: dynamic and passive methods. In the dynamic methods, a device that uses some form of active feedback achieves control on the light intensity. For example a photo-sensor, which controls an iris that, restricts the intensity of light, incident on an optical system. There are an infinite number of schemes and devices that can be constructed to control
light in this manner. But all these dynamic devices suffer a number of disadvantages. One of them is higher complexity, which results from the need for multiple components that must communicate with one another. Passive control is typically accomplished using a nonlinear optical material in which the sensing, processing and actuating functions are inherent. The optical control function is part of the physical characteristics of the material, so the speed is not limited by communication between individual modules and the device can be potentially very simple and fast.

Two important and different types of passive devices used to control the amplitude of an optical signal are optical limiters and switches. Both have many realised and potential applications. An ideal passive optical switch is a nonlinear optical device that is activated at a set intensity or fluence (Energy/Unit Area) threshold, after that the device becomes completely opaque. Whereas the optical limiters exhibits linear response at low input levels and for inputs above some threshold level the output is clamped. For some materials, e.g., two photon absorbers, this transmittance may be near 100%, and the input-output curve would have a slope of 1. On the other hand, RSA materials require a certain amount of linear absorption, and thus the input-output slope in the linear regime would be less than 1. At certain critical intensity in an ideal optical limiter the transmittance changes abruptly and exhibits an inverse intensity or fluence dependence. Thus the output is clamped at some value that would be less than the amount required damaging the sensor. This critical point is known as threshold of the device, and the clamped output value is called as the limiting value of intensity or fluence. In a real material the transition is not so abrupt as in ideal optical limiter. In realistic conditions the definitions of threshold is not quite as precise and in a real material, the output is not always clamped at a constant value.

An optical limiter must provide protection over a wide range of incident intensity or fluence. To achieve this task the optical limiter should possess two desirable qualities, such as low threshold and wide dynamic range, which is the ratio of the damage threshold (ED) to the threshold limiting value (EL). One of the most important applications for optical limiters is eye and sensor protection in optical systems, such as direct viewing devices, night vision systems, etc. Such devices are
useful for the protection of human eye and optical sensors from intense laser beams. Development of materials for optical limiting is based on various mechanisms [65] such as free-carrier absorption and refraction in semiconductors, optical breakdown-induced scattering, thermal refractive beam spreading, two-photon absorption (TPA) and excited state absorption (ESA). C\textsubscript{60} was one of the first compounds to be identified as a potential candidate for optical limiting [22]. There have been series of other studies involving C\textsubscript{60} and it’s derivatives for realisation of optical limiter. The most important mechanisms responsible for limiting behaviour in C\textsubscript{60} are excited state absorption and scattering [22,30]. For realisation of practical devices a two-fold effort is necessary. In the first step one should identify and completely understand the underlying mechanisms responsible for optical limiting like the lifetimes of each state, different excited state cross-sections etc. The next step involves the structural/chemical modification of the material and to perform repeat studies for optimisation of the material properties. Among the different techniques for measuring the excited state parameters Z-scan [66] is a simple, single beam technique which provides deep insight into the nonlinear absorptive properties of the material.

The imaginary part of the third order nonlinear susceptibility is responsible for nonlinear absorption. Two-photon absorption, saturable absorption and reverse saturable absorption are the most relevant type of nonlinear absorption processes in our studies. In two-photon absorption process, a molecule makes a transition from its ground state to an excited state by the simultaneous absorption of two photons from the incident radiation field. TPA is an instantaneous nonlinearity, which involves the absorption of a photon from its initial state to a virtual intermediate state, followed by the absorption of a second photon that takes the electron to its final state [fig. 6.4 (a)]. Saturable absorption involves the saturation of a given transition [depicted in fig. 6.4 (b)]. If the excited state absorption is less than ground state absorption and a long-lived state, say T\textsubscript{1}, is involved in transition the material becomes transparent
Fig. 6.4 (a) Two-photon Absorption  (b) Saturable Absorption  
(c) Excited State Absorption
which was earlier absorbing. Reverse Saturable Absorption (RSA) generally arises in a molecular system when the excited state absorption cross section is larger than the ground state cross section. Keyes et al. and Guiliano et al. [67] reported the first observation of RSA. RSA is illustrated in Fig 5c for the materials in which energy states involved in three and five vibronically broadened electronic energy levels. $\sigma_0$ is the absorption cross-section from the ground state, $\sigma_1$ is absorption cross section from the first excited state to second excited state and $\sigma_2$ is absorption cross section from the first triplet state to excited triplet state. If $\sigma_1$ is larger than $\sigma_0$ then the total absorption increases and the material is known as reverse saturable absorber. In the five-level model the excited state 4 is usually a triplet or other long-lived state. It acts as a metastable state that accumulates population. The basic difference between TPA and ESA is that former involves intermediate extremely short-lived virtual states, whereas the latter involves intermediate real states whose lifetimes are determined by the electronic structure of the molecules in the material. TPA depends on intensity whereas ESA depends on fluence of the incident light. ESA involves a sequential process in which a photon is initially absorbed and the molecule remain in an excited state for a finite length of time so that a second photon that arrives during that time is absorbed to put the molecule in to an even higher excited state. For TPA, the material response is on the order of an optical cycle and is, therefore independent of the pulse width for a fixed intensity. The mechanism of TPA can be visualised in terms of three level RSA model for the case where lifetime of the intermediate state approaches zero and the ground state absorption cross-section is extremely low.

### 6.3.2 Dispersion studies of nonlinear absorption

Recent studies show very high performance ESA or reverse saturable absorption (RSA) behaviour in $C_{60}$ [22-36]. These materials are characterised by their strong excited state absorption ($\sigma_2$ and $\sigma_1$) compared to ground state absorption ($\sigma_0$). Most of these studies concentrated either at 532 nm or 600 nm and the models used to evaluate the photo-physical parameters are based on either 4-level (first excited singlet and triplet levels) or 3-level (singlet levels only) models. For fs and ps pulse excitation, triplet level contribution to the non-linear absorption can be neglected due to the
slower intersystem crossing (~ 650 ps). Whereas, with ns pulses the triplet levels do play an important role. Depending on the pump intensity and wavelength, the absorption could be (1) from ground state $S_0$ to the first excited singlet state $S_1$ and then to $T_1$ state through inter-system crossing (2) directly from $S_0$ to $S_n$ states (TPA) (3) from first excited singlet state $S_1$ to higher excited states $S_n$ (ESA/RSA) (4) from $T_1$ to $T_n$ states (ESA/RSA). One has to incorporate all these absorption phenomena in rate equations in order to obtain exact contribution from each of these processes. Earlier reports [68-72] on dispersion studies of non-linear absorption do not take into consideration the contribution of two-photon absorption. We have performed open aperture Z-scan of $C_{60}$ (in toluene) in the visible region from 440 nm to 660 nm. To fit our experimental data we consider a theoretical model where contribution to the non-linear absorption could be from $S_0$ to $S_n$ states (due to direct TPA), $S_1$ to $S_n$ states (due to ESA/RSA) or $T_1$ to $T_n$ states (due to ESA/RSA). Different curves are theoretically obtained by varying the ESA and TPA coefficients and the input intensity. The behaviour of the open aperture Z-scan curve with changes in the above parameters is investigated in detail.

We employ a commercial OPO (MOPO laser by Spectra Physics) pumped by the third harmonic (355 nm) from the Quanta Ray Nd: YAG laser with a repetition rate of 10 Hz and tunable in the range of 380-1000 nm for the open aperture Z-scan [66] studies. The pulse duration of the laser is 6 ns. The experimental set-up consists of a lens, sample, and a large area detector. The sample cell is moved along a rail, using a computer controlled stepper motor, to vary the intensity of light in the sample. An aperture of 1.4 mm is used at the output of the MOPO laser to obtain a smooth profile in the far field. Energy after the aperture varied from 0.2 to 2 mJ/pulse depending on the wavelength. The focal length of the lens used for focusing the beam into the sample is 50 mm. 1-mm glass cuvettes are used for the sample solutions. The input energy is monitored using a fast photo-diode and the total output collected using a large area lens is measured using a similar photo-diode. The data is collected from –40 mm to +40 mm in steps of 2 mm. Fig. 6.4 (c) details the 5-level model used for theoretical simulations and fitting of the data. $C_{60}$ dissolved in toluene is sonicated to obtain a clear solution. The concentrations used for the studies are in the range ~ $10^{-4}$
– 10⁻³ M. Open aperture Z-scans are obtained in the wavelength region covering from 440 nm to 680 nm. Immediate scans obtained in opposite direction (+Z to –Z) show similar structure verifying that there is no damage to the sample or the cell. The calculated values of beam waist at focus are ~ 30 - 50 µ and the corresponding peak intensities are ~ 10⁸ to 10⁹ W/cm². The Rayleigh ranges are ~ 6.5 to 8 mm depending on the wavelength. Rate equations for the 5-level model shown in fig. 6.4 (c) are:

\[
\frac{dN_0}{dt} = -\frac{\sigma_0 I N_0}{\hbar \omega} - \frac{\beta I^2}{2 \hbar \omega} \frac{N_1}{\tau_1} + \frac{N_3}{\tau_4} \tag{1}
\]

\[
\frac{dN_1}{dt} = -\frac{\sigma_1 I N_1}{\hbar \omega} + \frac{\sigma_0 I N_0}{\hbar \omega} - \frac{N_1}{\tau_1} \frac{N_1}{\tau_{ISC}} + \frac{N_2}{\tau_2} \tag{2}
\]

\[
\frac{dN_2}{dt} = \frac{\sigma_1 I N_1}{\hbar \omega} + \frac{\beta I^2}{2 \hbar \omega} \frac{N_2}{\tau_2} \tag{3}
\]

\[
\frac{dN_3}{dt} = -\frac{\sigma_2 I N_3}{\hbar \omega} \frac{N_3}{\tau_4} + \frac{N_1}{\tau_{ISC}} + \frac{N_4}{\tau_3} \tag{4}
\]

\[
\frac{dN_4}{dt} = \frac{\sigma_2 I N_3}{\hbar \omega} \frac{N_4}{\tau_3} \tag{5}
\]

and the intensity transmitted through the sample is given by

\[
\frac{dI}{dz} = -\sigma_0 I N_0 - \sigma_1 I N_1 - \sigma_2 I N_3 - \beta I^2 \tag{6}
\]

with

\[
I = I_{00} \ast \left( \frac{\omega_0^2}{\omega^2(z)} \right) \ast \exp\left( \frac{-I^2}{\tau_p^2} \right) \ast \exp\left( \frac{-2 * r^2}{\omega^2(z)} \right) \tag{7}
\]

and

\[
\omega(z) = \omega_0 \left\{ 1 + \left( \frac{z}{z_0} \right)^2 \right\} \frac{1}{2} ; \quad z_0 = \frac{\pi \omega_0^2}{\lambda}
\]

where σ₀ is the ground state absorption cross-section, σ₁ and σ₂ are the excited state absorption cross-sections from S₁ and T₁ states respectively, Nᵢ’s are the corresponding populations in the different states, τᵢ’s are the lifetimes of the excited states, z₀ is the
Rayleigh range, $\omega_0$ is the beam waist at focus, $I$ is intensity as a function of $r$, $t$, and $z$, $I_{00}$ is peak intensity at the focus of the Gaussian beam, $\tau_p$ is the input pulse width used, $\beta$ is the two-photon cross-section, and $\tau_{ISC}$ is the intersystem crossing rate. The differential equations are solved numerically using Runge-Kutta fourth order method. The equations are first de-coupled and then integrated over time, length, and along the radial direction. Assuming the input beam to be a Gaussian, the limits of integration for $r$, $t$, and $z$ are varied from 0 to $\infty$, $-\infty$ to $\infty$, and 0 to $L$ (length of the sample) respectively. Typical number of slices used for $r$, $t$, and $z$ are 60, 30, and 5 respectively. $\sigma_1$, $\sigma_2$, and $\beta$ are then estimated through least square fit of the experimental data.

Fig. 6.5 shows the experimental data (scattered points) and the theoretical fits (solid lines) obtained using the five level model for wavelengths ranging from 440 nm to 640 nm. Ground state absorption cross-sections for different wavelengths are calculated using $\sigma_0 = (\alpha/N)$ where $\alpha$ is the linear absorption and $N$ is the density of molecules per cm$^3$. Depending on the wavelength, $I_{00}$ is found to be $\sim 10^8 - 10^9$ W/cm$^2$, $\omega_0 \sim 30 - 50 \mu$m, $z_0 \sim 6.5 - 8$ mm. The relaxation time of the first excited singlet state $\tau_{S1}$, intersystem crossing time $\tau_{ISC}$, and the lifetime of the first excited triplet state $\tau_{T1}$ are taken as 70 ps, 650 ps, and 280 $\mu$s respectively. The relaxation times of $S_n$ and $T_n$ states are taken as $\sim 100$ fs. Excitation wavelengths are indicated for each Z-scan curve. In the wavelength region from 440 nm to 540 nm, experimental data fits better with $\beta = 0$ and in the wavelength region 580 nm to 640 nm, $\beta$ dominates with smaller contribution from $\sigma_2$ or $\sigma_1$. Effect of $\sigma_1$ on the Z-scan curves is shown in fig. 6.6 for two arbitrary wavelengths, one in 440 - 540 nm range and the other in 580 - 640 nm range.

Fig. 6.6 (a) shows the theoretical curves generated at 480 nm for $\sigma_0 = 3.0 \times 10^{-18}$ cm$^2$, $\sigma_1 = 15.0 \times 10^{-18}$ cm$^2$, $\sigma_2 = 12.0 \times 10^{-18}$ cm$^2$, $\beta = 0.0$ (solid line); $\sigma_0 = 3.0 \times 10^{-18}$ cm$^2$, $\sigma_1 = 0.0$, $\sigma_2 = 12.0 \times 10^{-18}$ cm$^2$, $\beta = 0.0$ (dotted line). Fig. 6.6 (b) shows the theoretical curves generated at 600 nm for $\sigma_0 = 1.65 \times 10^{-18}$ cm$^2$, $\sigma_1 = 6.60 \times 10^{-18}$ cm$^2$, $\sigma_2 =$
Fig. 6.5 Experimental data (open circles) and fitted curve (solid line) using the 5-level model for different wavelengths.
Fig 6.6 Theoretical curves showing the effect of $\sigma_1$ at two wavelengths
(a) $\sigma_0 = 2.99 \times 10^{-18}$ cm$^2$, $\sigma_2 = 12.0 \times 10^{-18}$ cm$^2$, $\beta = 0$, $I_{00} = 10^9$ W cm$^{-2}$
(b) $\sigma_0 = 1.65 \times 10^{-18}$ cm$^2$, $\sigma_2 = 2.40 \times 10^{-18}$ cm$^2$, $\beta = 2.25 \times 10^8$ cm W
$I_{00} = 4 \times 10^9$ W cm$^{-2}$. The scattered points are the experimental data.
$6.60 \times 10^{-18} \text{ cm}^2$, $\beta = 2.25 \times 10^{-8} \text{ cm/W} \text{ (solid line)}$; $\sigma_0 = 1.65 \times 10^{-18} \text{ cm}^2$, $\sigma_1 = 0.0$, $\sigma_2 = 6.60 \times 10^{-18} \text{ cm}^2$, $\beta = 2.25 \times 10^{-8} \text{ cm/W} \text{ (dotted line)}$. As we can see, there is very little effect on the open aperture Z-scan curves due to $\sigma_1$, which is mainly due to the fact that we have taken $\tau_{S_1}$ to be 70 ps. Lifetimes of $S_1$ state have been reported to be ~100 ps, ~650 ps and ~1.2 ns by several groups [44-56]. Our studies performed through incoherent laser spectroscopy [42] have shown a lifetime for the $S_1$ state as 70 ps. We could obtain a reasonably good fit for $\sigma_1$ varying from $15 \times 10^{-18} \text{ cm}^2$ to $20 \times 10^{-18} \text{ cm}^2$ with $\sigma_2$ around $12 \times 10^{-18} \text{ cm}^2$. Therefore, there could be larger error in the values of $\sigma_1$ compared to $\sigma_2$. If fs pulses are used for excitation we expect the contribution of $\sigma_1$ alone to the non-linear absorption as the intersystem crossing would be too slow compared to the pulse duration. From the fs data, one can then exactly find out the contribution of $\sigma_1$. Effect of varying $\tau_{S_1}$ on the Z-scan curves is shown in fig. 6.7. Simulated curves for $\tau_{S_1} = 1.2 \text{ ns}$ and 70 ps are shown in fig.'s 6.7 (a) for 480 nm and 6.7 (b) for 600 nm. Dotted line is the curve with $\tau_{S_1} = 1.2 \text{ ns}$ and solid line is the curve with $\tau_{S_1} = 70 \text{ ps}$ with all other parameters remaining same. We clearly see that for $\tau_{S_1} = 1.2 \text{ ns}$, the curves become very broad indicating that for the C$_{60}$ sample, that has been used in our system, $\tau_{S_1} = 70 \text{ ps}$. For longer wavelengths [fig. 6.7 (b)], the effect of $\tau_{S_1}$ is small because of the domination of TPA in this range. The present results are therefore consistent with our earlier studies reported through DFWM experiments done with a broad band laser [42]. The sample that has been used in both the experiments is from the same batch and company.

In the above theoretical calculations we have assumed that the scattering from the sample, responsible for nonlinear absorption, is minimum. Mishra et al. [30] reports nonlinear scattering as the main mechanism responsible for optical limiting in C$_{60}$ in their experiments performed at 527 nm using 30 ns pulses. They also argue that the scattering arises from the thermally induced inhomogeneities and has been observed for fluences larger than 4 J/cm$^2$ only. In our case the transmission measured with and without an aperture in the path of the transmitted remained almost the same, within experimental error, indicating the negligible contribution of scattering. Also the solution obtained by dissolving in toluene is a clear solution and visual
Fig. 6.7 Theoretical curves showing the effect of $S_1$, at two different wavelengths.

(a) $\sigma_0 = 2.99 \times 10^{-18}$ cm$^2$, $\sigma_1 = 0$, $\sigma_2 = 12.0 \times 10^{-18}$ cm$^2$, $\beta = 0$, $I_{00} = 10^9$ W/cm$^2$

(b) $\sigma_0 = 1.65 \times 10^{-18}$ cm$^2$, $\sigma_1 = 6.6 \times 10^{-18}$ cm$^2$, $\sigma_2 = 2.4 \times 10^{-18}$ cm$^2$, $\beta = 2.25 \times 10^{-8}$ cm/W, $I_{00} = 4 \times 10^9$ W/cm$^2$. The scattered points are the experimental data.
observation of the transmitted beam does not show any distortion in the beam profile.

\[ \sigma_1, \sigma_2, \text{ and } \beta \text{ obtained from our results are given in table 1 along with those } \]
reported in literature [74]. There is no contribution from TPA (\(\beta\)) to the non-linear absorption till 540 nm. From 580 nm to 640 nm the non-linear absorption appears to be dominated by TPA. Fig. 6.8 shows the influence of \(\sigma_2\) and \(\beta\) on the theoretical curves. Figure 6.8 (a) shows the theoretical curves with and without \(\sigma_2\) for 600 nm. Though both the fits can be seen to be close to the experimental data (open circles), curve generated with non-zero \(\sigma_2\) and \(\beta\) has lower chi-square value. \(\sigma_1\) has been taken as zero in this region as we see from fig. 6.8 (b) that the contribution of \(\sigma_1\) on the curves is negligible. \(S_0\) and \(S_1\) energies of \(C_{60}\) fall in the region of ~ 29,000 cm\(^{-1}\) and ~ 16,000 cm\(^{-1}\) respectively [41]. Excitations longer than 580 nm fall either on the lower edge of the absorption curve or below it. Since at such excitations, it is expected that the molecule remains localised without diffusing into the higher levels [75] eventually decaying into the \(S_0\) level through \(\tau_{S1}\) or crossover to \(T_1\) through \(\tau_{ISC}\). Under such circumstances \(\sigma_1\) and \(\beta\) would have the same effect. A complete reversal in the domination of \(\sigma\) and \(\beta\) are observed in the region of short wavelengths. Below 580 nm [fig. 6.8 (b) at 480 nm] introduction of a small value of \(\beta\) leads to a sharper valley in the curve, deviating from the experimental points. Dotted curve is obtained with non-zero values of \(\sigma_1, \sigma_2\) and \(\beta = 0.5*10^{-8}\) cm/W and dashed curve is obtained for \(\sigma_1 = \sigma_2 = 0.0\) and \(\beta = 2.25*10^{-8}\). This clearly shows the domination of \(\sigma_1, \sigma_2\) in the shorter wavelength region.

The values of different excited state parameters obtained by different groups, working with different pulse widths, are summarised in table 1. The value of \(\beta_{\text{eff}}\) obtained by Gu et al. [70] at 630 nm using CW beam is eight orders of magnitude larger than our value. Although they consider that large nonlinear absorption is dominated by triplet-triplet absorption, there is no experimental evidence that the triplet state \(T_1\) is actually populated. Moreover the ground state absorption of \(C_{60}\) is notably increased in thin films as compared with dilute solutions. They have
Fig. 6.8 Theoretical curves showing the effect of (a) $\sigma_2$ at 600 nm with $\sigma_0 = 1.65 \times 10^{-18}$ cm$^2$, $\sigma_1 = 0$, $\beta = 2.25 \times 10^{-8}$ cm/W, $I_{00} = 4.6 \times 10^8$ W/cm$^2$ (b) $\beta$ at 480 nm with $\sigma_0 = 2.99 \times 10^{-18}$ cm$^2$, $\sigma_1 = 12.8 \times 10^{-18}$ cm$^2$, $\sigma_2 = 9.6 \times 10^{-18}$ cm$^2$, $I_{00} = 9.5 \times 10^8$ W/cm$^2$ and for dashed curve $\sigma_1 = 0$. $\sigma_2 = 0.0$, $I_{00} = 9.5 \times 10^8$ W/cm$^2$. The scattered points are the experimental data.
also suggested that thermal effects play a crucial role in self-focusing observed for their thin-films using CW beams. Bezel et al. [71] working with 300 fs pulses at 612 nm report a $\beta$ value of $\leq 3 \pm 1.5 \times 10^{-8}$ cm/W which is in good agreement with our value. Henari et al. [72], using Z-scan measurements, report a value of $1.2 \times 10^{-3}$ cm/W at 488 nm for C$_{60}$-benzene/toluene solutions using CW beam, chopped at frequencies from 50 to 400 Hz, which is again five orders of magnitude larger than our value. The typical power density they used was $\sim 100$ W/cm$^2$. For longer duration pulses the population transfer to the triplet state is more efficient and therefore the optical limiting action will be observed at lower intensities. From viewpoint of practical optical limiting high-intensity pulse laser results are more relevant than the low-intensity chopped CW beams. The $\sigma_{ex}$ values reported by Henari et al. [73], working with 5 ns pulses, are two orders of magnitude large than our value. Their ground state cross-sections ($\sigma_0$) are also two orders of magnitude larger than most of the earlier reported values.

Ebbesen et al., Tanigaki et al., and Baroso et al. [58,59,69] report a value of $\sigma_1$ as $\sim 1.6 \times 10^{-17}$ cm$^2$ at 534 nm. We obtain a value of $1.82 \times 10^{-17}$ cm$^2$, which is in good agreement with theirs. The values reported by Chunfei Li et al. [38] also match well with our results. Kardash et al. [53] report $\beta$ value of $\sim 2.0 \times 10^{-8}$ cm/W for C$_{60}$ film on quartz substrate excited with light pulses of frequency $\sim 2.02$ eV corresponding to $\sim 600$ nm. Yang et al. [55] carried out Z-scan measurements using 32 ps pulses at 532 nm and found out that S$_1$ state is the dominant absorption intermediate, with triplet states playing minor role in nonlinear absorption. Justus et al. [32] investigated the C$_{60}$ solutions dissolved in 1-chloronaphthalene with Z-scan using 6 ns pulses at 532 nm. Nonlinear phase change of several radians was observed and concluded that both sequential TPA and thermally induced refraction contribute to the nonlinear response. They also suggest developing optical limiting materials based on hybrid mechanism involving both STPA and thermal lensing.

6.3.3 Z-scans at 532 nm and 600 nm using Nd: YAG laser

We have performed open aperture Z-scans at 532 nm [fig. 6.9 (a)] and
Fig. 6.9 (a) Open aperture Z-scan at 532 nm (6 ns pulses). Solid line is the fit to the data using 5-level model. (b) Open aperture Z-scan data at 600 nm using broadband dye laser. The solid line is fit to the data using 5-level model.
600 nm [fig. 6.9 (b)] using the Nd: YAG laser and the broadband dye laser (centred at 595 nm). The set-up is similar to the one described in earlier section. Input beam diameter in this case is ~ 2.5 mm and a lens of focal length of ~ 80 mm is used to focus the beam into the sample. The scans are obtained from –6 mm to +6 mm using solutions in the concentration range of $10^{-4}$ to $10^{-3}$ M. Typical peak intensities are again in the range of $10^8 - 10^9$ W/cm$^2$. The Rayleigh range is found to be ~ 3 mm, larger than the thickness of the sample (1-mm), validating the thin sample approximation. The obtained data is fitted to the above 5-level model [fig. 6.9 (a) and (b)] and the different excited state parameters evaluated are found to be of the same order. Two photon absorption coefficient, $\beta$, is found to be ~ $2.5 \times 10^{-8}$ cm/W at 600 nm with very small contribution from $\sigma_2 \sim 2 \times 10^{-18}$ cm$^2$. At 532 nm we obtain $\sigma_1$ as ~ $16.0 \times 10^{-18}$ cm$^2$ and $\sigma_2$ as ~ $10.0 \times 10^{-18}$ cm$^2$. Both the values match very well with those obtained using an OPO.
6.4 Conclusions

1. We observe large third-order nonlinearity at 600 nm ($\gamma \sim 5.388 \times 10^{-30}$ esu) obtained using broadband ns pulses. The high value is attributed to the strong TPA combined with contribution from the thermal part.

2. The excited state lifetimes measured using incoherent light are found to be $< 170$ fs, $\sim 5$ ps, and $\sim 70$ ps for the $S_n$ state dephasing, $S_{1v} - S_{10v}$ vibrational relaxation and the $S_1$ state population relaxation respectively. The above results match very well with those obtained using the DFWM technique with 150 fs pulses at 633 nm.

3. From the dispersion studies of nonlinear absorption and theoretical modelling of the experimental data we evaluate the different excited state parameters for $C_{60}$ in toluene. For the first time in the theoretical modelling we include the contribution of two-photon absorption, apart from excited absorption, to the total nonlinear absorption and solve the equations numerically. The values so obtained are in good agreement with those reported in literature.

4. From the dispersion studies we conclude that for optical limiting the main advantage of $C_{60}$, in comparison to porphyrins and phthalocyanines, is it shows RSA behaviour over the entire visible region, either through ESA in the shorter wavelengths or through TPA in the longer wavelength region. A proper chemical manipulation of this material could result in a practical optical limiter.
<table>
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* linear absorbance  + effective excited state cross-section

**Table 6.1** Comparison of the values obtained using our five-level model and those reported in literature
6.5 References


