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Concentration and wavelength dependence of the effective third-order susceptibility and optical limiting of $C_{60}$ in toluene solution

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Abstract. The optical limiting action of $C_{60}$ in toluene solution is mainly due to reverse saturable absorption (RSA). It is shown that the formalism describing nonlinear optical response due to instantaneous two-photon absorption can be used in the case of sequential two-photon absorption, yielding effective values of the relevant parameters of optical nonlinearity due to RSA. The effective two-photon absorption parameter $\beta_{\text{eff}}$ and the effective nonlinear refractive index parameter $\gamma_{\text{eff}}$, which are related respectively to the imaginary and real parts of the effective third-order susceptibility $\chi^{(3)}$, were measured by the z-scan technique as a function of fullerene concentration and of incident laser intensity and wavelength over the 420–640 nm region. The concentration dependence of these parameters indicates that the solution is optically thin as far as the ground state of $C_{60}$ is concerned, whereas the wavelength dependence confirms the applicability of the formalism used in the sequential two-photon absorption model. Comparisons are made with other z-scan results on $C_{60}$.

1. Introduction

The study of the intensity-dependent transmission and the third-order optical nonlinearity of $C_{60}$ have received considerable attention, in part because of the possible application of this fullerene as an optical limiter (Tutt and Kost 1992, Kost et al 1993, McLean et al 1993, Lin et al 1993, Justus et al 1993). The present experimental study concerns parameters which play a role in optical limiting processes in $C_{60}$. We determine two parameters:

(i) $\beta_{\text{eff}}$, an effective value of the two-photon absorption coefficient which, in the case of instantaneous two-photon absorption (ITPA) processes (electronic polarization response time $\approx$ fs), is related to the imaginary part of the third-order nonlinear susceptibility $\chi^{(3)}(-\omega; \omega, \omega, -\omega)$.

(ii) $\gamma_{\text{eff}}$, an effective value of the nonlinear refractive index which, in the case of an instantaneous nonlinearity induced by electronic polarization, is related to the real part of the third-order nonlinear susceptibility $\chi^{(3)}(-\omega; \omega, \omega, -\omega)$.

In our case we employ laser wavelengths in the 420–640 nm region, where $C_{60}$ absorbs, albeit weakly. In this region it has been shown that reverse saturable absorption plays a major role (Henari et al 1992), via populated real singlet ($\tau \leqslant 1$ ns) and triplet ($\tau \geqslant 40$ $\mu$s) states, in determining the nonlinear optical properties of $C_{60}$. Thus our measured parameters

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must be considered as effective values, $\beta_{\text{eff}}$, $\chi^{(3)}_{\text{eff}}$, and $\gamma'_{\text{eff}}$, which depend on the incident light intensity and, because they involve, at least in part, sequential two-photon absorption (STPA), they are excited-state population dependent and thus decay with a time dependence following pulsed excitation. Our measurements, using the z-scan technique (Sheik-Bahae et al. 1990, Said et al. 1992), concern the dependence of transmission on incident light intensity and wavelength and on C$_{60}$ concentration. This technique provides the information necessary for determining the above effective parameters which basically depend on the photophysical properties of C$_{60}$ such as absorption cross sections, inter-electronic state relaxation rates and yields and electronic state populations. These factors give rise to the dynamic response of the system studied.

The objective of our study is to investigate quantitatively the various parameters involved in optical limiting of C$_{60}$ solutions and to ascertain whether, under our experimental conditions, STPA is indeed the dominant mechanism in determining the nonlinear optical properties of C$_{60}$ over the spectral range 420–640 nm.

2. Theoretical preliminaries

2.1. Nonlinear response due to instantaneous two-photon absorption (ITPA)

For our study it is useful to begin by presenting the basic theoretical concepts involved in laser-induced modifications of the optical properties of a medium through instantaneous nonlinear response processes.

The simplest description of such a nonlinear response is in terms of a power expansion of the induced polarization due to a strong incident electric field $E$:

$$P_{\text{ind}} = \chi^{(1)}E + \chi^{(2)}E^2 + \chi^{(3)}E^3 + \cdots$$  \hspace{1cm} (1)

where $\chi^{(i)} (i > 1)$ is the $i$th-order nonlinear susceptibility, while $\chi^{(1)}$ is the linear susceptibility. In media with inversion symmetry, such as C$_{60}$, the third-order nonlinearity is the lowest-order nonlinear term allowed under the electric dipole approximation (Bloembergen 1965, Flytzanis 1975, Shen 1984).

On an atomic or molecular scale, the nonlinear response can be described in terms of the local electric field ($E_{\text{loc}}$) that the atom or the molecule experiences, which for isotropic media is related to the incident electric field $E$ by the equation (Shen 1984):

$$E_{\text{loc}} = (n_0^2 + 2)E/3$$  \hspace{1cm} (2)

where $n_0$ is the linear refractive index of the medium, and the factor $L = (n_0^2 + 2)/3$ is the Lorenz–Lorentz local field correction factor. The nonlinear induced polarization per molecule is then described by the microscopic susceptibilities, i.e. the hyperpolarizabilities. For third-order effects, the corresponding hyperpolarizability $\gamma$, which we will henceforth call the third-order polarizability, is related to the susceptibility $\chi^{(3)}$ by the equation

$$\gamma = \chi^{(3)}/NL^4$$  \hspace{1cm} (3)

where $N$ is the number of molecules per unit volume.

For a single incident radiation frequency $\omega$, the third-order term in equation (1) can generate polarizations at the third harmonic frequency $3\omega$ [$\chi^{(3)}(-3\omega; \omega, \omega, \omega)$], the second harmonic frequency $2\omega$ [$\chi^{(3)}(-2\omega; \omega, \omega, 0)$] and the fundamental frequency $\omega$ [$\chi^{(3)}(-\omega; \omega, \omega, -\omega)$]. The imaginary and real parts of this last term are related to the two-photon absorption process and the nonlinear refraction respectively. As a result of this
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polarization, the absorption coefficient $\alpha$ and the refractive index $n$ must be modified to include intensity dependent terms such that

$$\alpha = \alpha_0 + \beta I$$  \hspace{1cm} (4a)
$$n = n_0 + \gamma' I$$  \hspace{1cm} (4b)

where $\alpha_0$ (cm⁻¹) and $n_0$ are the linear terms, $I$ (W cm⁻²) is the incident radiation intensity, while the ITPA parameter $\beta$ (cm W⁻¹) and the nonlinear refractive index parameter $\gamma'$ (cm² W⁻¹) are related to the corresponding nonlinear susceptibility† by the equations (Mahr 1975, Prior and Vogt 1979, CRC 1988, Levenson 1982):

$$\text{Im} \chi^{(3)} \text{(esu)} = 10^{-7}c^2n_0^2\beta/96\pi^2\omega$$  \hspace{1cm} (5)
$$\text{Re} \chi^{(3)} \text{(esu)} = 10^{-6}cn_0^2\gamma'/480\pi^2$$  \hspace{1cm} (6)

where $c$ is the speed of light in cm s⁻¹ and $\omega$ is the fundamental frequency in cycles/s.

2.2. Nonlinear response due to sequential two-photon absorption (STPA)

The presentation in section 2.1 is valid for instantaneous polarization effects involving virtual or bound intermediate excited states. However, the optical limiting action of C₆₀ can be explained in terms of transient reverse saturable absorption (Tutt and Kost 1992, Kost et al 1993, McLean et al 1993, Li et al 1994a), although some other transient mechanisms, e.g. thermal blooming and nonlinear scattering, may also play a role under certain experimental conditions. The participation of instantaneous two-photon absorption has not yet been demonstrated under laser excitation in the nanosecond range.

Reverse saturable absorption in C₆₀, in a ns laser regime, can be described by a three-level system involving the ground $S_0$, the first excited singlet $S_1$ and the lowest triplet $T_1$ (Tutt and Kost 1992, Kost et al 1993, McLean et al 1993, Li et al 1994a), as indicated in figure 1. We note the relevant term scheme properties as follows: (i) the absorption cross section of $T_1$ is much larger than that of $S_0$ over the spectral region 400–1600 nm (Bensasson et al 1993); (ii) intersystem crossing to the triplet manifold is rapid, with a rate of the order of $10^9$ s⁻¹ (Ebbesen et al 1991); (iii) the intersystem crossing yield $\Phi_{\text{isc}} \approx 1$ (Bensasson et al 1993); the lifetime of the lowest triplet state $T_1$ is at least 40 µs in room temperature solution (Arbogast et al 1991), its value depending in part on the availability of triplet state quenchers such as oxygen.

For negligible absorption from singlet excited states (which will be the case for ns pulses), the variation of light intensity $I(\lambda)$, at laser wavelength $\lambda$, along the beam propagation direction in a cell containing C₆₀ in solution (see experimental set-up, figure 2) will be given, at an instant $t$ during the laser pulse, by the following expression:

$$dI(\lambda)/dz = -\alpha_0[S_0]I(\lambda) - \alpha_T[T_1]I(\lambda)$$  \hspace{1cm} (7)

where $[S_0]$ and $[T_1]$ are the ground and triplet state concentrations respectively, at instant $t$, and $\alpha_0$ and $\alpha_T$ are the linear absorption coefficients from the $S_0$ and $T_1$ states respectively.

The triplet state concentration at instant $t$ is, to a good approximation, given by

$$[T_1] = \alpha_0[S_0]I(\lambda)\Phi_{\text{isc}}.$$  \hspace{1cm} (8)

As mentioned above, the singlet–triplet radiationless intersystem crossing yield $\Phi_{\text{isc}} \approx 1$ (Bensasson et al 1993), so that

$$dI(\lambda)/dz = -\alpha_0[S_0]I(\lambda) - \alpha_1\alpha_0[S_0]I(\lambda)I(\lambda) = -\alpha I(\lambda)$$  \hspace{1cm} (9)

† The parameter $\gamma'$ is not to be confused with the hyperpolarizability $\gamma$ (see equation (3)).
where \( \alpha = \alpha_0[S_0] + \alpha_1\alpha_0[S_0]I(\lambda) \) can be considered as an intensity-dependent absorption coefficient formally similar to equation (4a) but where the effective STPA parameter is \( \beta_{\text{eff}} = [S_0]\alpha_0\alpha_1 \). Relation (9) will remain unchanged after temporal integration over the laser pulse duration and integration over the spatial distribution of the pulse; the final result will be ‘average’ values of \( \alpha \) and of \( \beta_{\text{eff}} \). However, the quantity \( \beta_{\text{eff}} \) is intensity dependent through the \( [S_0] \) term while in the ITPA case \( \beta \) is constant.

In the instantaneous nonlinear response model, the refractive index \( n \) is given by the expression \( n = n_0 + n_2|E|^2/2 \) \( (= n_0 + \gamma' I) \). In the case of \( C_{60} \), where there is an STPA sequential process involving the \( T_1 \) state, the refractive index can have a component due to the triplet state population and can be expressed as an intensity-dependent refractive index parameter, \( n = n_0 + \gamma_{\text{eff}}'I \), as in equation (4b). The parameter \( \gamma_{\text{eff}}' \) is proportional to the product \( \alpha_0'\alpha_1' \) where \( \alpha_0' \) and \( \alpha_1' \) are linear refractive index coefficients corresponding respectively to \( S_0 \) and \( T_1 \) state populations.

The expressions for \( \text{Im} \chi^{(3)} \) (equation (5)) and \( \text{Re} \chi^{(3)} \) (equation (6)) which contain respectively \( \beta \) and \( \gamma' \) can therefore be applied to the case of STPA induced nonlinear processes in \( C_{60} \). In our treatment of the optical limiting parameters we will therefore
conveniently use the formalism established for the instantaneous process but, as discussed above, refer to effective values of the parameters of nonlinear refractivity and two-photon absorption and its related third-order susceptibility. These effective parameters can be considered as key indicators of the propensity for optical limiting behaviour.

Modelization of the dynamic response of the $C_{60}$ system (in toluene solution) in terms of absorption cross sections and other photophysical parameters will be the subject of other studies.

3. Experimental details

3.1. Z-scan

Measurements of the effective third-order susceptibility of the $C_{60}$-toluene solution were performed using the $z$-scan technique (Sheik-Bahae et al 1990, Said et al 1992). This technique is based on the variation of transmitted radiation intensity by alteration of the geometrical parameters of the interaction region. This is achieved by gradually moving a sample along the axis of propagation ($z$) of a focused Gaussian beam through its focal plane and measuring the transmission ($T$) of the sample for each $z$ position. As the sample experiences different electric field strengths at different $z$ positions, the recording of the transmission as a function of the $z$ coordinate provides accurate information about the nonlinear effects present.

Two types of $z$-scan can be performed: (i) the open aperture $z$-scan, where all the transmitted light is detected, which provides information about the nonlinear absorption of the sample; and (ii) the closed aperture $z$-scan, where only the light transmitted through a pinhole placed in front of the detector is detected, which provides information about the nonlinear phase variations and hence the resulting focusing or defocusing of the transmitted beam.

The transmission of the sample as a function of its position on the $z$-axis can be described as follows.

3.1.1. Open aperture $z$-scans. Assuming a two-photon absorption effect such that the total absorptivity is given by an expression of the type $\alpha = \alpha_0 + \beta I$ and a laser beam which is Gaussian in space and time, the normalized transmission $T_{\text{norm}}(z)$ for an open aperture $z$-scan can be described by the equation (Sheik-Bahae et al 1990, Said et al 1992):

$$T_{\text{norm}}(z) = \frac{C}{\sqrt{\pi} q_0} \int_{-\infty}^{\infty} \ln(1 + q_0 e^{-t^2}) \, dt$$

(10)

where $C$ is a normalization constant and $q_0$ is given by the equation

$$q_0 = \frac{\beta I_0 (1 - e^{-\alpha_0 \ell})}{(1 + z^2/z_0^2) \alpha_0}$$

(11)

where $I_0$ is the maximum incident radiation intensity (for $z$, $t = 0$), $\ell$ is the pathlength of the sample, and $z_0$ is the Rayleigh length of the laser beam, defined by $z_0 = (\pi w_0^2/\lambda)$, where $w_0$ denotes the beam waist and $\lambda$ the laser wavelength (the equations being true for free space). The normalization of the transmission is essential in order to exclude linear absorption effects. The nonlinear absorption coefficient $\beta$ can then be determined by fitting equation (10) to the experimental data of $T_{\text{norm}}(z)$. 
3.1.2. Closed aperture z-scans. We assume a laser beam Gaussian in space and time, travelling in a nonlinear medium which experiences intensity-dependent phase shifts, such that the total refractive index is given by \( n = n_0 + \gamma' I \). In the case of negative nonlinearity the normalized transmission in a closed aperture z-scan shows a prefocal transmission maximum (called 'peak'), followed by a postfocal transmission minimum (called 'valley')\(^{\dagger}\) (Sheik-Bahae et al 1990). For a thin medium \( (\ell/n_0z_0 < 1 \text{, where } \ell \text{ is the medium length, } n_0 \text{ is the linear refractive index and } z_0 \text{ is the diffraction length}) \) and under the assumption that \( q_0(z, f = 0) \leq 1 \) and \( \text{Re } \chi^{(3)} > \text{Im } \chi^{(3)} \), one can estimate the effect of nonlinear refraction using the following procedure proposed by Sheik-Bahae et al (1990) and Said et al (1992): dividing the data of a closed aperture z-scan by that of an open aperture scan, both scans being performed at the same incident intensity, one can determine from the resultant curve the difference between the peak and the valley of the normalized transmission \( (\Delta T_{p-v}) \). The nonlinear refractive index parameter \( \gamma' \) can then be estimated by the equation:

\[
\gamma' = \frac{\Delta T_{p-v} \lambda \alpha}{0.812 \pi I_0 (1 - S)^{0.25} (1 - e^{-\alpha t})}
\]

where \( S = 1 - \exp(-2r_a^2/u_a^2) \) is the linear aperture transmission with \( r_a \) and \( u_a \) being the aperture and the beam radii respectively and \( \alpha \) is the total maximum absorption of the sample. For the calculation of \( \alpha \), the parameters \( \beta \) and \( I_0 \) can be estimated from the corresponding open aperture scan results.

3.2. Experimental set-up

The experimental set-up is schematically depicted in figure 2. An excimer pumped dye laser with output wavelengths within the three spectral regions 420–432, 490–520 and 620–640 nm, a pulse duration of 15 ns and a repetition rate of 10 Hz was used as the light source. The beam was split into two parts by means of a quartz plate beamsplitter, one part to be used as a probe beam and the other as a reference beam. The probe beam was focused by a 5 cm focal length lens into a 1 mm-pathlength quartz cell, containing the C60-toluene solution. The cell was moved by means of a stepper motor, with a displacement step of 0.3 mm. The excitation energy was adjusted in front of the beamsplitter by use of neutral density optical filters and was measured a few millimetres behind the focal plane of the lens, by means of a standard energy-meter, before and after each z-scan. The energy was always kept lower than 50 \( \mu \)J, as at higher energies flashing of the quartz cell windows was observed, the effect being more pronounced for higher concentrations of C60. Both beams were detected by two matched photomultipliers and the respective signals were averaged over 300 shots by boxcar integrators for each position of the cell in the z-scan. Nonlinear effects of the cell windows and/or the solvent (we will refer to these effects as ‘background effects’) were taken into account by calculating and normalizing the ratio \( T(C_{60}\text{-toluene})/T(\text{toluene}) \).

The beam waist and the Rayleigh length of the focused probe beam were found to be 22 \( \mu \)m and 2.9 mm respectively in air. These values were deduced by moving a linear diode array along the beam propagation axis \( z \) around the focal plane and recording the \( z \)-dependence of the \((1/e^2)\) beam radius.

The C60-toluene solutions were prepared using 99.9% pure C60, purchased from SYNCOM. The absorption spectra of the samples were measured with a Perkin–Elmer spectrophotometer and were in excellent agreement with the published spectra. The samples were checked before and after irradiation, verifying that no degradation of the fullerene had occurred.

\(^{\dagger}\) For media with positive nonlinearity one observes a valley before a peak in the transmission for increasing \( z \).
4. Results and discussion

4.1. Uncertainties in experimental parameters

Figure 3 shows a typical open aperture z-scan (full squares) of a 0.64 mM solution of C$_{60}$ in toluene at wavelength 520 nm and excitation energy 30 $\mu$J. The variation in $T_{\text{norm}}$ reflects nonlinear effects in the fullerene only, since any effects due to cell windows and to the solvent were found to be negligible as can be seen by the corresponding z-scan where $T_{\text{norm}}$ is approximately constant as a function of $z$ (full triangles). All data reported here have been corrected for background laser beam attenuation in the pure solvent.

![Figure 3](image)

Figure 3. Open aperture z-scan (full squares) of a 0.64 mM C$_{60}$-toluene solution for an incident energy of 30 $\mu$J at 520 nm. The full curve is the best fit of the data using equation (10), giving $\beta_{\text{eff}}$ and $w_{\text{eff}}$ values of $6.25 \times 10^{-8}$ cm W$^{-1}$ and 13 $\mu$m respectively. The broken curves are the best fit to the experimental data for two values of $w_{\text{eff}}$ differing respectively by $\pm 20\%$ from 13 $\mu$m. The full triangles represent the cell-toluene z-scan.

The full curve in figure 3 represents the best fit of equation (10) to the experimental $T_{\text{norm}}$ data, giving a value $\beta_{\text{eff}} = (6.25 \pm 0.94) \times 10^{-8}$ cm W$^{-1}$. The main uncertainties arise from fluctuations in laser intensity and in the determination of the transmission at maximum intensity. Repeating the z-scan 15 times gave a 5% variation of $T_{\text{norm}}$ at the maximum intensity.

Another uncertainty concerns the beam waist parameter. As stated above, the value of the waist parameter $w_0$, measured in air, was found to be 22 $\mu$m. The beam radius can be different in the C$_{60}$ solution because three media (air, quartz, solvent) possessing different refractive indices are involved and, furthermore, as will be shown in section 4.3, the probe beam experiences defocusing. The beam waist is an important parameter since it correlates with $\beta$ (equation (11)). It was thus treated as a variable in fitting equation (10) to the experimental data, and we therefore consider it as an effective value $w_{\text{eff}}$, the value of which was $w_{\text{eff}} = 13$ $\mu$m for the data in figure 3. A variation of $\pm 20\%$ of the value of $w_{\text{eff}}$ in fitting the experimental data (broken curves in figure 3) gave poor fits to $T_{\text{norm}}$ and would correspond respectively to a $+40\%$ and $-30\%$ variation of $\beta_{\text{eff}}$.

The necessity of treating the beam waist as a free parameter is also confirmed in the wavelength study of the optical nonlinearity of C$_{60}$ solutions in section 4.5. The observed defocusing is strongly wavelength dependent as illustrated in figure 4 which shows the beam waist as a function of wavelength over three spectral regions 420–432, 490–520 and...
620–640 nm for a 0.43 mM solution of C$_{60}$ in toluene for an incident radiation intensity of 120 MW cm$^{-2}$. The corresponding z-scan results are discussed in section 4.5.

**Figure 4.** Wavelength dependence of the effective beam waist $w_{\text{eff}}$. C$_{60}$ concentration in toluene is 0.43 mM. Incident laser intensity is approximately 120 MW cm$^{-2}$.

### 4.2. C$_{60}$ concentration and laser intensity effects on optical transmission and on $\beta_{\text{eff}}$

Figure 5 shows the normalized transmitted energy ($E_{\text{OUT}}$) as a function of the incident energy ($E_{\text{IN}}$) at 520 nm for three different concentrations of C$_{60}$–toluene solutions (0.94, 0.64 and 0.15 mM). At low incident energies the optical responses follow Beer's law (for normalized transmission $T = 100\%$). Deviations from Beer's law at higher energies indicate the occurrence of optical limiting. A constant transmitted energy regime was not attained at 520 nm with our range of increasing energy for the concentrations used. The values of these two experimental parameters are lower than in previously reported studies where constant transmission has been achieved at 532 nm (Tutt and Kost 1992, Kost et al 1993, McLean et al 1993). However, it is of interest that our intensity thresholds for the onset of nonlinear action, $I_{\text{TH}}$, for various concentrations, shown in figure 6, are consistent with those previously reported for the same solvent for similar pulse widths but for different C$_{60}$ concentrations. The $I_{\text{TH}}$ value decreases with increasing sample concentration and ranges between 25 and 5 MW cm$^{-2}$. For the highest concentration (0.94 mM) and the highest incident energy (47 $\mu$J), $T_{\text{norm}} \approx 37\%$.

The variation of the effective two-photon absorption parameter $\beta_{\text{eff}}$ as a function of the concentration of C$_{60}$ is shown in figure 7 for various incident energies. Increasing the concentration gives a linear increase of $\beta_{\text{eff}}$. The increase of $\beta_{\text{eff}}$ with fullerene concentration indicates that from the viewpoint of the ground state of C$_{60}$ the solution is optically thin. However, increasing incident energy results in diminishing $\beta_{\text{eff}}$ value, showing that $\beta_{\text{eff}}$ is indeed intensity dependent.

The dependence of the effective two-photon absorption parameter $\beta_{\text{eff}}$ as a function of the incident radiation intensity $I_0$ is depicted in figure 8 for three different concentrations of C$_{60}$. Increasing the intensity results in a decrease of $\beta_{\text{eff}}$. The fall-off of $\beta_{\text{eff}}$ with increasing $I_0$ is a consequence of the sequential two-photon absorption. With increasing intensity, the total absorption of the C$_{60}$ solution approaches asymptotically the value $\alpha_1$, that is the absorbance of the triplet state (McLean et al 1993, Li et al 1994b). Therefore, the $\beta_{\text{eff}}$ will
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Figure 5. Optical limiting action of three $C_{60}$-toluene solutions (0.15, 0.64 and 0.94 mM), using 15 ns laser pulses at 520 nm. The transmitted energy is normalized ($T = 100\%$) with respect to the linear transmission.

Figure 6. Intensity threshold, $I_{TH}$, for the onset of nonlinear optical action at 520 nm as a function of the concentration of the $C_{60}$-toluene solution.

be found reduced at least up to intensities where no other intensity-dependent processes are involved which can cause further reduction of transmission of the solution (McLean et al. 1993). The nature of such processes (such as higher-order absorption, scattering, triplet-triplet annihilation etc) requires further investigation. We remark that a decrease of $\beta_{eff}$ with increasing $I_0$ has also been reported for the optical limiting action of thiophene oligomers, where it is attributed to saturation of instantaneous two-photon absorption (Hein et al. 1994), and in p-toluene sulfonate crystal (Lawrence et al. 1994).

4.3. The nonlinear refractive index effective parameter $\gamma_{eff}$

A closed and open aperture z-scan, performed under the same experimental conditions, and their ratio, are presented in figure 9 for a 0.64 mM $C_{60}$-toluene solution (520 nm, $E_{IN} = 30 \mu J$). In order to fulfil the far field condition (Sheik-Bahae et al. 1990, Said et al. 1992) a 0.5 mm pinhole (corresponding to $S \approx 0.1$) was placed 25 cm from the focal plane of lens $L_1$. 
The ratio exhibits a clear peak–valley configuration corresponding to a negative nonlinearity of the C₆₀ solution. Using equation (12), a value of $\gamma'_{\text{eff}} = (-9.05 \pm 0.21) \times 10^{-13}$ cm² W⁻¹ was determined for the effective nonlinear refractive index parameter.

Figure 10 shows that $\gamma'_{\text{eff}}$, measured at two values of $E_{\text{IN}}$, exhibits a linear increase with increasing concentration. Moreover, at a given concentration, $\gamma'_{\text{eff}}$ is smaller at the higher $E_{\text{IN}}$ value. These two observations are similar to those found for the concentration and $E_{\text{IN}}$ dependence of $\beta_{\text{eff}}$. They probably have a similar physical origin but little direct relation since the determination of $\gamma'_{\text{eff}}$ through equation (12) is only weakly affected by variation of $\beta_{\text{eff}}$ (a 50% reduction of $\beta_{\text{eff}}$ introduces only 10% reduction of $\gamma'_{\text{eff}}$).
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4.4. Real and imaginary parts of the effective third-order susceptibility and the related polarizability $\gamma_{\text{eff}}$

From the results presented in figures 7 and 10, the real and the imaginary parts of the effective third-order susceptibility can be determined using equations (5) and (6). For a concentration of 0.64 mM and the lowest incident energy used (5 $\mu$J) the corresponding values are: $\text{Re} \chi_{\text{eff}}^{(3)} = (-3.4 \pm 0.7) \times 10^{-11}$ esu and $\text{Im} \chi_{\text{eff}}^{(3)} = (1.1 \pm 0.2) \times 10^{-11}$ esu respectively. Additionally, using the slopes of the lowest incident energy curves of figures 7 and 10, and equations (3), (5) and (6), the real and imaginary parts of the C$_{60}$ effective third-order polarizability $\gamma_{\text{eff}}$ were determined to be $\text{Re} \gamma_{\text{eff}} = (-1.7 \pm 0.3) \times 10^{-29}$ esu and $\text{Im} \gamma_{\text{eff}} = (0.6 \pm 0.1) \times 10^{-29}$ esu respectively.
4.5. Wavelength dependence of normalized transmission and of $\beta_{\text{eff}}$

Figures 11(a) and 11(b) depict respectively open and closed aperture z-scans of a 0.43 mM solution of C$_{60}$ in toluene for an incident energy of 4 $\mu$J and three different wavelengths, 420, 425 and 429 nm. Similar nonlinear action was observed at higher wavelengths in the same spectral region but the corresponding z-scans are not shown so as not to overburden figure 11. Nonlinear absorption and nonlinear refraction both become weaker with increasing wavelength, as indicated by the increase in $T_{\text{norm}}$ and the decrease in $\Delta T_{p-v}$ in the open and closed z-scans respectively.

It is interesting to note that, with decreasing wavelength, there is a tendency to suppression of the peak and enhancement of the valley for the closed aperture scans in figure 11(b). At 429 nm, the peak-valley configuration of the curve is almost symmetric with respect to the normalized transmission in the far field ($T_{\text{norm}} = 1$), whereas at shorter wavelength the curve becomes asymmetric, also indicating the presence of stronger nonlinear absorption (Sheik-Bahae et al 1990).

The observed peak-valley configuration of $T_{\text{norm}}$ in the closed aperture z-scans (figure 11(b)) indicates the presence of strong defocusing (Sheik-Bahae et al 1990, Said et al 1992) within the spectral region 420–429 nm. Since the $\Delta T_{p-v}$ values were found to be wavelength dependent, the defocusing varies with wavelength. This wavelength variation is also reflected in the observed change of the z-distance between the peak and the valley ($\Delta z_{p-v}$). Because $\Delta z_{p-v}$ is proportional to the diffraction length of the incident laser beam (Sheik-Bahae et al 1990), the change in its value indicates a modification of the beam parameters, due to varying defocusing. This is also consistent with the observed shift of the positions on the z-axis where maximum nonlinear absorption occurs, in figure 11(a), and the transmission peak related to the nonlinear refraction, in figure 11(b).
In the absence of nonlinearities in the refractive index, the position of the focusing plane of a Gaussian beam depends only on the focal length of the $L_1$ lens, the wavelength, and the linear refractive index of the medium. When negative nonlinear refraction is present, the beam waist increases and shifts to the left of the initial focus, i.e. closer to $L_1$ (Banerjee et al 1991). Furthermore, the position of the minimum beam radius (characterized by the position of the peak in the closed aperture $z$-scan) in the far-field observation also shifts to the left. Thus the variation of the $\Delta T_{p-v}$ and $\Delta z_{p-v}$ values, and the shift of the $z$-scan curves to the left, reveal a variation of the $C_{60}$ negative nonlinear refractive index as a function of the wavelength. This results in a wavelength-dependent modification of the beam radius within the sample, and therefore of the effective beam waist $w_{\text{eff}}$ (figure 4), which affects all nonlinear processes.

![Graph](image_url)

**Figure 12.** Normalized transmission, $T_{\text{norm}}$, as a function of wavelength for a 0.43 mM solution of $C_{60}$ in toluene, at constant energy (full squares) and constant intensity (full triangles).

Figure 12 depicts $T_{\text{norm}}$ at the focus in the solution as a function of wavelength for the three spectral regions studied. These regions of weak linear absorption from the ground state of $C_{60}$ correspond to forbidden electronic transitions that appear through Herzberg–Teller vibronic interactions (Leach et al 1992). Two cases of incident radiation conditions were examined for each spectral region: (i) constant incident energy and (ii) constant intensity at the focus. In both cases the smallest value of $T_{\text{norm}}$, and therefore the largest value of nonlinear absorption, occurs at the wavelength corresponding to the highest ground state absorbance within each region, i.e. 420, 520 and 620 nm respectively (figure 13). The different spectral regions present different slopes, in accordance with local absorbance trends (Leach et al 1992). In each region the wavelength variation of $T_{\text{norm}}$ for constant energy is weaker than for constant intensity. This is due to wavelength-dependent defocusing of the incident laser beam (cf figure 4). Keeping the energy constant and tuning to a wavelength
of increased ground state absorbance causes a decrease in the radiation intensity because of the greater beam radius within the sample. This results in a weaker nonlinear absorption effect than that corresponding to a non-defocused beam.

The spectral regions 420–432, 490–520 and 620–640 nm are of particular interest for the investigation of the relative contributions of the $S_0$ and $T_1$ electronic state absorptions to $C_{60}$ nonlinear absorption since they present different relative wavelength dependences (figure 13). In figure 14 we present the variation $\Delta$ of four parameters as a function of wavelength. These parameters are (i) $\sigma_g$, the $C_{60}$ ground state absorbance (broken curves), (ii) $\sigma_T$, the $C_{60}$ $T_1$ triplet state absorbance (dotted curves), (iii) the product $\sigma_g \times \sigma_T$ (full curves), (iv) $\beta_{\text{eff}}$, the effective nonlinear absorption parameter due to STPA. The $\beta_{\text{eff}}$ values (table 1) were measured at various wavelengths at the relatively low intensity of 120 MW cm$^{-2}$ in order to avoid the $\beta_{\text{eff}}$ 'saturation' regime and higher-order nonlinear processes. In addition, the incident beam intensity at focus was kept constant in order to eliminate defocusing effects.

![Figure 13. Ground state $S_0$ (full curve) and triplet state $T_1$ (broken curve) absorption of $C_{60}$ in toluene. The $T_1$ absorption spectrum is taken from Bensasson et al (1993).](image)

**Table 1.** Effective two-photon absorption parameter $\beta_{\text{eff}}$ of a 0.43 mM $C_{60}$–toluene solution, at various wavelengths, for 15 ns laser pulses and incident radiation intensity of approximately 120 MW cm$^{-2}$.

<table>
<thead>
<tr>
<th>$\lambda$ (nm)</th>
<th>$\beta$ ($10^{-8}$ cm W$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>420</td>
<td>6.03</td>
</tr>
<tr>
<td>425</td>
<td>2.74</td>
</tr>
<tr>
<td>429</td>
<td>2.05</td>
</tr>
<tr>
<td>432</td>
<td>1.74</td>
</tr>
<tr>
<td>490</td>
<td>6.64</td>
</tr>
<tr>
<td>505</td>
<td>8.51</td>
</tr>
<tr>
<td>520</td>
<td>9.12</td>
</tr>
<tr>
<td>620</td>
<td>3.90</td>
</tr>
<tr>
<td>630</td>
<td>3.14</td>
</tr>
<tr>
<td>640</td>
<td>1.91</td>
</tr>
</tbody>
</table>
Effective third-order susceptibility and optical limiting of C60

The variable $\Delta$ is defined as the relative ratio of each parameter value at wavelength $\lambda_f$ with respect to that of a reference value taken at a wavelength $\lambda_0$ corresponding to the smallest absorbance within the spectral region investigated. For example, the $\Delta$ value of $\sigma_g$ is given by the ratio $\Delta(\sigma_g) = (\sigma_g(\lambda_f) - \sigma_g(\lambda_0))/\sigma_g(\lambda_0)$, where $\lambda_0 = 432, 490$ and 640 nm respectively for the spectral regions studied.

It is seen from figure 14 that for the intensity used, the variation of $\beta_{\text{eff}}$ follows the product $\sigma_g \times \sigma_T$ much more closely than either $\sigma_g$ or $\sigma_T$ taken separately. This clearly demonstrates the validity of our sequential two-photon absorption (STPA) approach based on the theory initially developed for instantaneous two-photon absorption (ITPA) as discussed in section 2.

We remark that one of the usual figures of merit for reverse saturable absorption materials (McLean et al 1993, Perry et al 1994) is the ratio of triplet and ground state absorption cross sections, $\sigma_T/\sigma_g$. In principle, the larger the value of this ratio the lower are the fluence threshold and the asymptotic transmission. This ratio is 20.4 (420 nm), 8.3 (490 nm) and 7.5 (620 nm) at the wavelengths indicated in parentheses (cf Bensasson et al 1993). However, within each of the 420–432, 490–520 and 620–640 nm regions this ratio varies with wavelength in the same sense as the variation of $T_{\text{norm}}$ shown in figure 12 and in the opposite sense to the effective two-photon absorption coefficient $\beta_{\text{eff}}$ in figure 14, the variation of the $\sigma_T/\sigma_g$ ratio being most marked in the 620–640 nm region (22.9 at 640 nm). This indicates that $\sigma_T/\sigma_g$ alone is insufficient as a figure of merit for C60 as an optical limiter in the wavelength range investigated. Our results discussed above indicate that the product $\sigma_g \times \sigma_T$ is a valid indicator of the effective two-photon absorption coefficient $\beta_{\text{eff}}$. 

Figure 14. Relative variation $\Delta$ of (i) $C_{60}$ ground state absorption cross section $\sigma_g$ (broken curve), (ii) triplet state absorption cross section $\sigma_T$ (dotted curve), (iii) the product $\sigma_g \times \sigma_T$ (full curve), (iv) the effective nonlinear absorption parameter $\beta_{\text{eff}}$. See text for the definition of $\Delta$. 

\[ \frac{\sigma_T}{\sigma_g} \]

\[ \frac{\sigma_g \times \sigma_T}{\sigma_g} \]

\[ \frac{\sigma_T}{\sigma_g} \]

\[ \frac{\sigma_g \times \sigma_T}{\sigma_g} \]
in the case of STPA, which plays an important role in the optical limiting quality for this fullerene.

Finally, we compare our $\beta_{\text{eff}}$ values with those in the literature, limiting our comparisons to results obtained by the z-scan technique. Using a CW laser at 633 nm, Gu et al (1993) obtained $\beta_{\text{eff}} = 8.0 \text{ cm W}^{-1}$, which is eight orders of magnitude larger than our value $\beta_{\text{eff}} = 3.1 \times 10^{-8} \text{ cm W}^{-1}$ measured at 630 nm. Although Gu et al consider that their large nonlinear absorption is dominated by triplet-triplet absorption, this may be somewhat questionable in that no definitive experimental demonstration has been made that the $T_1$ state is actually populated in the case of a laser-illuminated $C_{60}$ film. Furthermore, the ground-state absorption of $C_{60}$ is notably increased in films as compared with dilute solutions (Bensasson et al 1994). The optical nonlinearity measured by Gu et al may therefore have its origin in effects other than STPA. It is of interest that Gu et al (1993) have suggested that thermal effects play a role in self-focusing observed for their $C_{60}$ films using a CW laser.

Henari et al (1993) have also used a 488 nm CW laser, with an average power 15 mW, chopped at frequencies from 50 to 400 Hz, to do z-scan measurements on $C_{60}$ in benzene ($10^{-3}$ M) and toluene ($10^{-5}$ M) solutions. The typical power density was 100 W cm$^{-2}$. Their value of $\beta_{\text{eff}} = 1.2 \times 10^{-3} \text{ cm W}^{-1}$ for the $C_{60}$-toluene solution is almost five orders of magnitude larger than our value at 630 nm. This marked difference seems to be consistent with the STPA model since, for longer pulse durations, the population transfer to the $T_1$ state is more efficient, therefore the optical limiting action will be observed at lower radiation intensities. The pulse duration effect on the optical limiting action of $C_{60}$ solutions is currently under investigation in our laboratory.

From the viewpoint of practical optical limiting, our high-intensity pulse laser results are more relevant than the low-intensity chopped CW laser observations. Furthermore, solution studies are of particular value since $C_{60}$ films have so far proven to be fragile, are subject to possible irreversible photochemical change under high intensity laser excitation (Bezel et al 1994), and possess significantly enhanced absorption in the visible, especially in the 450 nm region (Bensasson et al 1994).

The optical response of $C_{60}$-benzene ($10^{-5}$ M) solutions to high intensity visible laser pulses was studied by Henari et al (1992), using open-aperture z-scan measurements, with 5 ns pulses at a power density of the order of 100 MW cm$^{-2}$. They were thus able to determine $\text{Im } x_{\text{eff}}^{(3)} = 3330 \times 10^{-11} \text{ esu}$ at 520 nm, whereas our value for a 15 ns pulse, 120 MW cm$^{-2}$, at 520 nm is $\text{Im } x_{\text{eff}}^{(3)} = 0.54 \times 10^{-11} \text{ esu}$ for a 0.43 mM solution in toluene. Modelling studies of state population densities as a function of time (McLean et al 1993, Henari et al 1992, Li et al 1994a) clearly indicate that under our temporal and light power density conditions and of those of Henari et al (1992), the nonlinear response involves $T_1$ as the dominant relay state. Thus the origin of the very large difference between our results and those of Henari et al (1992) requires further investigation. Part of the discrepancy may be due to the use by Henari et al, in their model-dependent determination of $\text{Im } x_{\text{eff}}^{(3)}$, of ground and excited state absorption cross sections which differ somewhat from more directly measured experimental values (Leach et al 1992, Bensasson et al 1993).

Mishra et al (1994) have carried out z-scan studies of $C_{60}$-toluene solutions (0.24 mM), using 30 ns, 527 nm pulses at 200 MW cm$^{-2}$ focal plane irradiation intensity. The physical parameters of the observed optical nonlinearities were not evaluated from the z-scans but the transmission results were interpreted as being due to operative STPA mechanisms, with some additional induced nonlinear scattering. Thermally induced refractive index changes were considered to be negligible. If scattering effects are indeed present this would indicate significant aggregation of the fullerene in the solution; this could be tested by the appearance of additional absorption in the 450 nm region (Bensasson et al 1994).
Liquid solutions of C₆₀ in 1-chloronaphthalene were the subject of z-scan studies by Justus et al. (1993) at 532 nm with 6 ns pulses at a power density of about 60 MW cm⁻² at the focal plane. Nonlinear phase changes of several radians were observed, much larger than in our case. It was concluded that both STPA and thermally induced refraction contribute to the nonlinear response in this case, pointing to the interest of developing optical limiting materials based on a hybrid mechanism involving both STPA and thermal lensing. We note that the rise time for thermally induced refraction should be of the order of an acoustic wave transit time across the beam, which is of the order of 1 ns in the case of the tightly focused beam conditions of Justus et al.; we estimate the acoustic wave transit time to be of the order of 60 ns in the case of the 80 μm spot size conditions in the experiments of Mishra et al (1994), i.e. longer than the laser pulse duration.

Z-scan measurements on C₆₀-toluene solutions have also been carried out in the picosecond pulse range (32 ps) at 532 nm (Yang et al 1994). Under these conditions the excited S₁ state is the dominant absorption intermediate, with the triplet state playing little role in the nonlinear response of C₆₀.

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