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Experimental investigation of optical limiting and thermal lensing in toluene solutions of C₇₀

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Abstract. Optical limiting and thermal lensing studies are carried out in C₇₀–toluene solutions. The measurements are performed using 9-ns pulses generated from a frequency-doubled Nd:YAG laser at 532 nm. Optical limiting studies in fullerene molecules lead to the conclusion that reverse saturable absorption is the major mechanism for limiting. Analysis of thermal lensing measurements showed a quadratic dependence of thermal lens signal on incident laser energy, which also supports the view that optical limiting in C₇₀ arises due to sequential two-photon absorption via excited triplet state (reverse saturable absorption).

PACS: 78.40 Ri; 42.65 Jx; 36.40 Vz; 42.62 Fi

The story of the discovery of buckminsterfullerene and the birth of fullerene science started in 1985 when Smalley, Kroto, and co-workers evidenced a self-assembled spontaneous C₆₀ molecule from a hot nucleating carbon plasma [1]. The triggering of the activity of the exciting field of fullerene science started especially after it became possible to synthesise and isolate them in macroscopic quantities using simple and straightforward methods [2]. Amongst the initially unexpected properties of fullerenes is their interesting and sizeable nonlinear optical activity [3–5]. Probably the most promising application of nonlinear optical activity is optical limiting, i.e. the increase of optical absorption with light intensity. This can be used in broad-band laser safety devices and for optical sensor protection. Numerous investigators [6–13] have demonstrated the optical properties of fullerenes. A systematic spectroscopic study of the effects of different fullerene cage functionalisations on the photophysical properties and optical limiting responses of the C₆₀ derivatives have been discussed [6]. Photophysical and excited-state kinetic properties of fullerenes, including fluorescence have been studied at low temperature [14, 15] as

well as at room temperature [16, 17]. Because of the very high rate of intersystem crossing to the excited triplet state at room temperature, the fluorescence emission spectra of these molecules are very weak with an extremely low fluorescent quantum yield [17]. The small singlet–triplet splitting, the very low rate of fluorescence rate constant and expected large spin–orbital interaction in these molecules indicate the occurrence of intersystem crossing as a dominant process. Early reports [14] revealed that C₆₀ has a higher excited-state absorption cross-section than the ground-state absorption cross-section over the complete visible spectrum. This information implied that the fullerenes are reverse saturable absorption (RSA) materials and may have application to optical limiting for sensor protection [19]. Reverse saturable absorption (RSA) generally arises in a molecular system when the excited-state absorption cross-section is larger than the ground-state absorption cross-section. A detailed theoretical approach on RSA [20] and its applications [21] are given elsewhere. But a few authors reported that apart from RSA some other nonlinear mechanisms such as nonlinear refraction, nonlinear scattering, two-photon absorption etc. also play a major role in the optical limiting properties of these molecules [22, 23].

In this paper we report optical limiting and thermal lensing measurements done in toluene solutions of C₇₀. We employed thermo-optic techniques such as pulsed thermal lens method for investigating the role of any nonlinear absorption processes that are taking place in these molecules.

1 Experimental set-up

C₇₀ used in our experiment was prepared by following the Krätschmer–Huffman technique, and employing high-purity liquid chromatography further purified the sample. The extract of C₇₀ has the characteristic colour and its electronic absorption spectrum was identical with that reported in the literature [24].

We have carried out optical limiting measurements in toluene solutions of C₇₀. The solution is taken in quartz cu-

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vettes of pathlength 5 mm and 10 mm. 532-nm, 9-ns pulses from a frequency-doubled Nd:YAG laser are used for these measurements. The cuvette is kept slightly away from the focal spot of the laser beam. A long-focal-length lens is used for focusing the laser beam so that the spot size inside the cuvette remains more or less constant and is about 500 μm in radius. The input and output pulse energies are measured using a laser energy meter. This set-up essentially avoids nonlinear refraction, as only the nonlinear absorption is important in this case contrary to the measurements done with a point detector to measure the transmitted laser energy.

Figure 1 shows the schematic diagram of the thermal lens spectrophotometer, consisting of a frequency-doubled Q-switched Nd:YAG laser as the heating source and intensity-stabilised He-Ne laser as the probe beam. The sample solution taken in a 5-mm cuvette is placed in the pump beam path. The pump and probe beams are focused onto the sample cell and made to pass collinearly through it using suitable convex lenses and by the use of a dichroic mirror. The excitation beam is blocked after the sample cuvette by a filter. As the 532-nm radiation is passed through the sample-containing cuvette, the molecules absorb some of the incident energy and get excited to higher energy levels. The subsequent de-excitation processes can occur radiatively or nonradiatively. It is the nonradiative part that gives rise to thermal lens (TL) formation. The resulting refractive index gradient follows the intensity distribution of the exciting pump beam. The TL signal is detected by sampling the intensity of the centre portion of the probe beam through a small aperture. In the present work the intensity of the centre portion of the transmitted probe beam is detected by using an optical fibre. The polished tip of a long graded index optical fibre (200- μm core, NA 0.22) serves both as an aperture and as a light guide for the probe beam to a monochromator–photomultiplier tube (PMT) assembly. Since the optical fibre is used in the detector system the method is useful for telemetric measurements as well as for multiplexed transmission of data. It also reduces the influence of mode and pointing variations in the probing laser. The monochromator–photomultiplier assembly tuned to the probe beam wavelength (632.8 nm) provides further filtering of the signal. The TL signal is detected as the relative change in the intensity of the probe beam centre and recorded using a 100-MHz digital averaging oscilloscope (Tektronix TDS 220) which provides a complete time domain representation of the signal. A synchronous trigger pulse from the Nd:YAG laser operated at 5 Hz is used to trigger the oscilloscope.

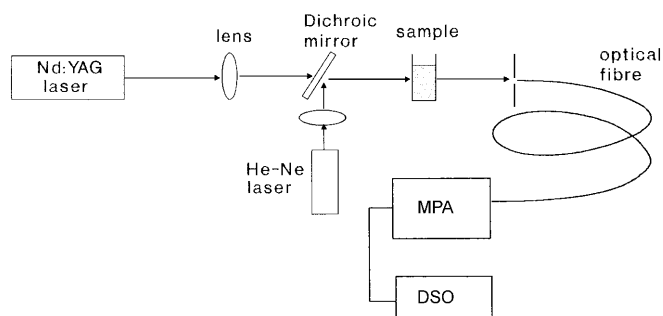


Fig. 1. Schematic diagram of the thermal lens experimental set-up (MPA – monochromator – PMT assembly, DSO – digital storage oscilloscope)

2 Results and discussion

2.1 Optical limiting in C_{70}

The ability to control the intensity of light in a predetermined and predictable manner is one of the most fundamental and important aspects of optical manipulations, with applications ranging from optical communications to optical computing. An ideal optical limiter is one which is perfectly transparent at low intensities up to a predetermined intensity level, above which the transmitted intensity remains clamped at a constant value. Several mechanisms have been suggested and used for optical limiting. Among these are reverse saturable absorption (RSA), multiphoton absorption, free carrier absorption in semiconductors, nonlinear refraction and optically induced scattering [19]. Multiphoton-absorption-induced optical limiting has desirable features such as low attenuation at low incident intensities and an instantaneous response to the incident light. Two-photon absorption for optical limiting has been studied predominantly in semiconductors [25] and in novel organic molecules [26, 27]. With increasing order of nonlinearity, the probability of the transition drastically reduces and it takes higher intensities to induce sufficient nonlinear absorption for optical limiting.

The optical limiting property in fullerene molecules was first reported by Tutt and Kost [28] using 532-nm, 8-ns pulses. These authors attributed the limiting action mainly to RSA. Transient excited-state absorption spectroscopy measurements of higher lying singlet and triplet states of these molecules lend support to the RSA hypothesis. Recently, Riggs and Sun [8] proposed a RSA mechanism that includes both unimolecular and bimolecular excited-state processes of fullerenes. Joshi et al. [22] observed a reduction in pulse width and steepening of the falling part of the pulse for input energies well into the limiting region and suggest that the multiphoton absorption from the excited-state rather than the ground state might be operative. Mclean et al. [23], who also reached a similar conclusion, found that their nonlinear transmission measurements with 8-ns and 30-ps, 532-nm pulses departed from the results of a rate-equation analysis for input fluences greater than 1 J cm^{-2} indicating initiation of some other nonlinear mechanism. According to them, RSA yields reasonable explanation of the low-fluence behaviour in both ns and ps cases, but unusual large nonradiative relaxation rates for higher lying singlet states must be assumed in the ps case. Even though much attention has been given to the limiting property of these fascinating molecules; a clear-cut picture for the underlying physics behind this phenomenon has not yet emerged.

The optical limiting studies were carried out for different limiting concentrations of C_{70} in toluene. The optical limiting is obtained by varying the input energy of the laser and measuring the energy transmitted by the sample. The variation of transmitted energy with input energy is given in Fig. 2 for different concentrations of C_{70} in toluene for pathlength 5 mm and 10 mm. At very low laser energies the transmission obeys the Beer–Lambert law. The transmitted intensity varies with increasing input energy with a slope equal to $\exp(-N_0\sigma_1L)$, where σ_1 is the absorption cross-section of the ground state, N_0 is the number density of the C_{70} molecules, and L is the cuvette length. At high input intensity the transmittance decreases with input intensity and we observe an

optical limiting property with saturated or clamped output intensity. For a pathlength of 5 mm, the 48% linear transmitting solution gets clamped at 7.5 mJ and the 30% linear transmitting one is clamped at 6 mJ. This data show that as the concentration increases, a reduction is observed in linear transmittance (LT) as well as in the clamping level. It is also noted that the saturated output intensity decreases with increasing pathlength. For the same concentration, the clamping levels are 6 mJ for 30% and 3.3 mJ for 16% LT, respectively, with a pathlength of 10 mm. This indicates that the number density of C_{70} molecules in the beam path is the main factor affecting the clamped level. From the threshold intensity for optical limiting for each sample it can be seen that the threshold is inversely proportional to the concentration. It has been reported that the concentration dependence in the optical limiting performance of fullerenes in solution is likely due to concentrational effects on optical limiting contributions that are associated with bimolecular excited-state processes in fullerenes [8].

Several mechanisms have been proposed for optical limiting in fullerenes including RSA, nonlinear scattering, multiphoton absorption etc. The RSA with a 5-level energy diagram yields a reasonable explanation for optical limiting in the ns regime of a π -electron conjugated system such as C_{60} and C_{70} . When a C_{70} molecule is photoexcited using 532-nm, 9-ns pulses, it gets excited from the ground state S_0 into one of the vibrational rotational states of the first excited singlet state S_1 . This level relaxes very rapidly either to the ground state or to the triplet state T_1 . But the triplet production yield is found to be nearly unity at 532-nm excitation for the C_{70} molecule [29]. Hence the molecules in the excited singlet state get transferred predominantly to the lower level of the triplet state due to high triplet yield and small singlet-triplet splitting. The molecules in the S_1 and T_1 states can be excited to higher S_n and T_n states (where $n \geq 2$). Relaxation from these S_n and T_n states is in the form of heat and extremely short (<ps). The relaxation of T_1 to S_0 is forbidden and therefore very slow. The triplet state which has a long lifetime

(11.8 ms for C_{70} [30]) and higher absorption cross-section than the ground state will accumulate significant population and eventually become the dominant absorption source.

For explaining the optical limiting property of polyacene-based oligomer Kojima and co-workers [31] have shown that in the case of pure RSA the incident laser energy I_0 and the transmitted laser energy I obey the relation

$$\ln\left(\frac{I_0}{I}\right) = k(I_0 - I) + A_g, \quad (1)$$

where k is a constant that depends on the absorption cross sections and lifetimes of the ground, excited singlet and excited triplet states, and A_g is the ground-state absorbance. The above equation says that the plot of $\ln(I_0/I)$ vs $(I_0 - I)$ should be a straight line with slope k and the intercept A_g . Figure 3 shows such a plot for C_{70} . The plot of $\ln(I_0/I)$ vs $(I_0 - I)$ looks almost linear in the desired energy ranges of interest. This is a clear indication that RSA is one of the limiting mechanisms in the case of C_{70} .

2.2 Thermal lensing in C_{70} -toluene solutions

Thermal lens (TL) spectroscopy is an effective and efficient method to monitor nonradiative relaxations in a medium. Very weak optical absorption processes can be studied using this method. Recently, TL technique has been successfully used for the determination of nonlinear processes such as two-photon absorption and three-photon absorption in a dye medium [32,33]. The other important applications of TL spectroscopy are trace detection, measurement of absolute absorption coefficient, thermal diffusivity measurements, and determination of absolute fluorescence quantum yield [34–37]. An excellent review by Snook and Lowe [38] gives a detailed account of the applications of TL spectroscopy. Terazima and Azumi [39] have demonstrated that TL technique is very powerful in investigating the properties of

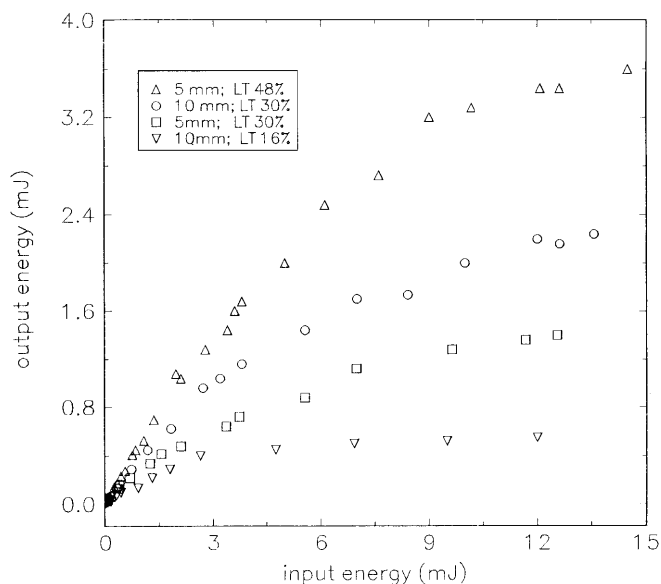


Fig. 2. Variation of transmitted energy with respect to input laser energy for C_{70} for pathlength of 5 mm and 10 mm (LT – linear transmittance)

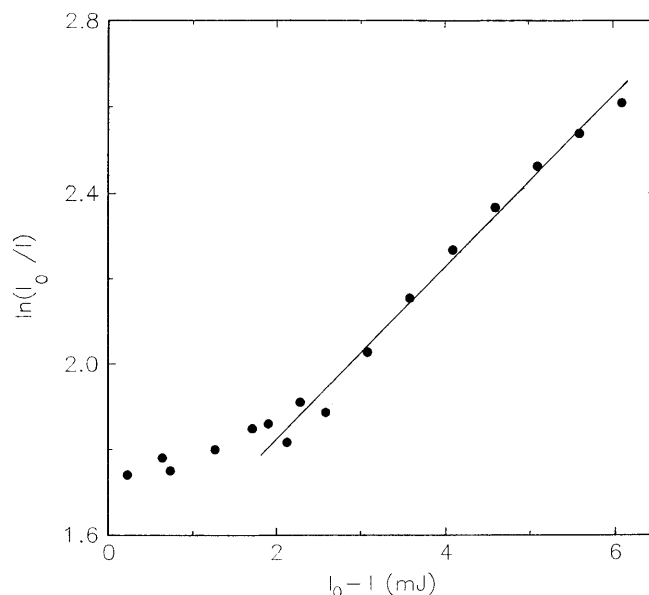


Fig. 3. Plot of $\ln(I_0/I)$ vs $(I_0 - I)$ for C_{70} in toluene

the excited-state. Terazima and co-workers [40] have also used this method for studying photophysical properties of triplet states of C_{60} clusters. They investigated time dependence of the TL signal by considering the quenching and decay of the triplet state and triplet-triplet absorption processes.

Methods classified as TL spectroscopy are based upon thermal change in the optical properties of a sample on the absorption of laser energy. This leads to a temperature rise in the sample and consequently to the formation of an inhomogeneous spatial profile of the refractive index. The heat released by the nonradiative relaxation processes generates a volume expansion in the sample and a density change within the excitation region. The refractive index caused by the heat evolution due to the radiationless processes turns in most cases the solution into a divergent lens, which defocuses the laser beam. The magnitude S , that is the change in intensity at the probe beam centre relative to its stationary value, is given by [41, 42]

$$S = \frac{I(t=0) - I(t=\infty)}{I(t=0)} \propto E^m, \quad (2)$$

where E is the incident laser energy, m is the number of photons involved in the generation of TL signal, $I(t=0)$ and $I(t=\infty)$ are the TL signal amplitude at time $t=0$ (before the pump laser pulse, ie, the base line) and $t=\infty$ (steady state), respectively. Hence by monitoring the dependence of TL signal amplitude on pump energy, one can identify the occurrence of different processes such as one-photon absorption ($m=1$) and multiphoton absorption ($m \geq 2$).

We have measured TL signal produced from solutions of C_{70} in toluene at different concentrations and various input energies. Log-log plots of TL signal amplitude against laser energy are plotted for each sample and some of them are given in Fig. 4. Figure 5 gives the dependence of slope obtained from the log-log plots on the concentration of C_{70} -toluene solution. The occurrence of slope 2 in these curves is an indication of two-photon absorption (TPA). However, the optical limiting action of C_{70} can be explained in terms of transient reverse saturable absorption, although some other mechanisms such as nonlinear refraction, nonlinear scattering etc. may also play a role under certain experimental conditions. The participation of instantaneous or simultaneous TPA in C_{60} or in C_{70} has not yet been demonstrated under laser excitation in the ns range. The TPA from the triplet state in these molecules is less likely since considerable triplet-triplet absorption cross-section is reported at 532 nm [40]. Another potentially effective nonlinearity is sequential TPA where the excited-state absorption cross-section is larger than the ground-state absorption cross-section. So the observation of slope 2 in the double logarithmic plot of these molecules could be due to sequential TPA. That is, instead of absorbing two photons simultaneously and exciting the molecules to a higher level, which is a multiphoton resonant one, the photons are absorbed one after the other. In the power limiting region, the leading part of the laser pulse excites most of the molecules to the vibrational levels of the excited singlet state S_1 . The reported quantum yield for intersystem crossing rate to the lowest triplet T_1 for C_{70} is equal to unity [28]. As the intersystem crossing is very fast for C_{70} (≈ 1 ns), the triplet state T_1 gets populated rapidly. The

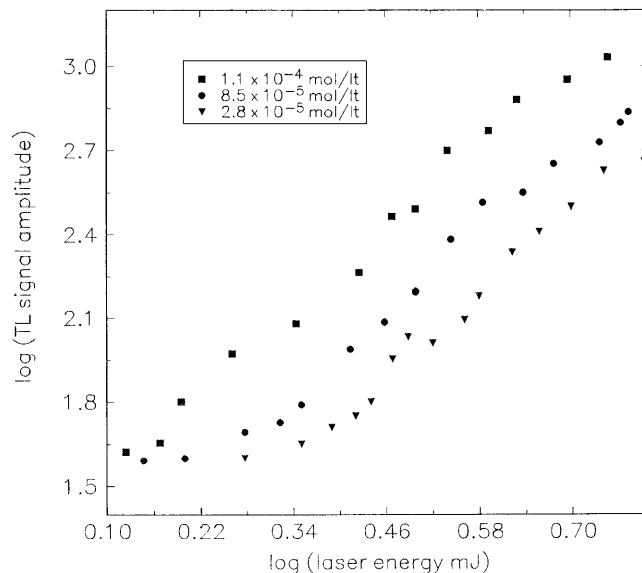


Fig. 4. Log-log plots of thermal lens signal amplitude as a function of input laser energy for C_{70} at different concentrations

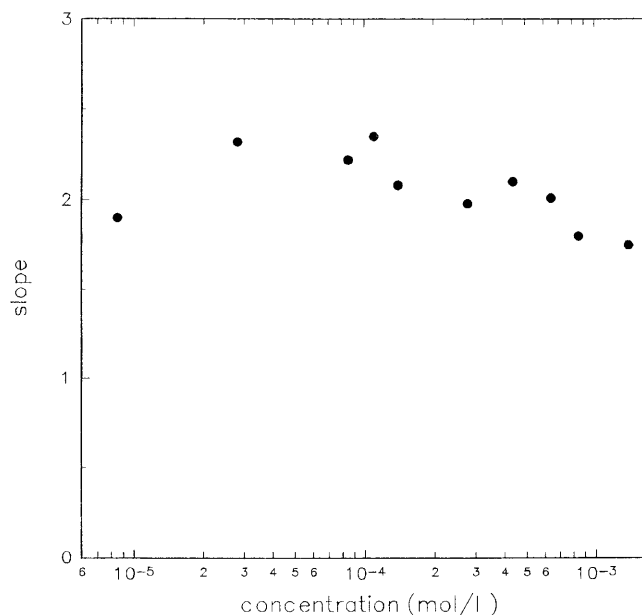


Fig. 5. The slope curve as a function of concentration of C_{70} in toluene

triplet state T_1 has a long lifetime and higher absorption cross-section than that of the ground-state [29]. After resonantly absorbing a single photon, the molecule in the triplet state goes to a higher excited-state T_n , the lifetime of which is considered to be in the ps region due to fast internal conversion. Therefore the molecules can relax to the lower excited triplet level by collisional energy transfer to the surrounding solvent molecules. This process occurs within the duration of a ns pulse. Thus the nonradiative decay from T_n gives rise to appreciable TL signals with quadratic dependence on laser energy. It has also been observed that, for a particular concentration, the thermal lens signal amplitude is greater in C_{70} compared to C_{60} . This is because at 532 nm, the ground-state absorption cross-section for C_{70} is much greater than for C_{60} . But in both cases the TL signal amplitude varies quadrati-

cally with laser energy indicating the presence of sequential two-photon absorption [43].

For C_{70} , the absorption from the excited singlet states is negligible for ns pulses. The variation of light intensity $I(\lambda)$, at laser wavelength λ , along the beam propagation direction in a cell containing these solutions will be given, at an instant t during the laser pulse and by taking intersystem crossing rate equal to unity, by the following expression [44]:

$$\frac{dI(\lambda)}{dI} = -\alpha_0[S_0]I(\lambda) - \alpha_1\alpha_0[S_0]I(\lambda)I(\lambda) = -\alpha I(\lambda), \quad (3)$$

where S_0 is the ground-state concentration at instant t , and α_0 and α_1 are the linear absorption coefficients from the S_0 and T_1 states, respectively. $\alpha = -\alpha_0[S_0] - \alpha_1\alpha_0[S_0]I(\lambda)$ can be considered as an intensity-dependent absorption coefficient. This α represents the absorption coefficient for the sequential TPA with effective sequential TPA parameter $\beta_{\text{eff}} = \alpha_1\alpha_0[S_0]$. The above equation is formally similar to $\alpha = \alpha_0 + \beta I$ for the case of instantaneous TPA. The quantity β_{eff} is intensity-dependent through the $[S_0]$ term whereas in the instantaneous TPA case β is constant. The dependence of the effective sequential TPA β_{eff} as a function of the incident laser intensity I_0 is given in Fig. 6. It is noted that the value of β_{eff} decreases with respect to increasing intensity of radiation. The fall-off of β_{eff} with increasing I_0 is a consequence of sequential TPA. With increasing intensity the total absorption of the C_{70} approaches asymptotically the value of α_1 , i.e. the absorbance of the triplet state.

The triplet-triplet absorption spectrum [45] shows that C_{70} has absorption at 632 nm (the probe-beam wavelength). So during the TL measurements there is a probability of triplet-triplet absorption of the probe He-Ne laser light. Hence the effect of triplet-triplet absorption by the probe beam should be taken into account. Since TL is detected as the decrease of the probe beam intensity, there is further decrease of intensity by the triplet-triplet absorption. The contribution of this effect is given by [40]

$$I_{\text{TL}} = AI_{\text{ex}}I_p\varepsilon_{TT}\phi_{\text{isc}}e^{-k_T t}, \quad (4)$$

where A is a constant that depends on experimental configuration, I_{ex} is the pump-beam intensity, I_p is the intensity of the probe beam, ε_{TT} is an extinction coefficient of the triplet-triplet absorption, k_T is the lifetime of the triplet state. In the present experiment we used a low-power He-Ne laser (2 mW) for probing the TL. We expect that triplet-triplet absorption is not serious at least at the power of the probe beam used in the present experiment. Furthermore, even if there is an effect of the TT absorption due to the He-Ne laser, it is possible to eliminate this by measuring the TL signal as a function of the He-Ne laser power and extrapolating to zero power. More than that we have verified our present results by repeating the experiments using a semiconductor laser (675 nm) for probing the TL. We obtained similar results using a semiconductor laser as the probe indicating that triplet-triplet absorption of the probe beam does not affect our experimental observations.

3 Conclusions

Optical limiting properties of C_{70} molecules in toluene were studied using 532-nm, 9-ns pulses from a frequency-doubled

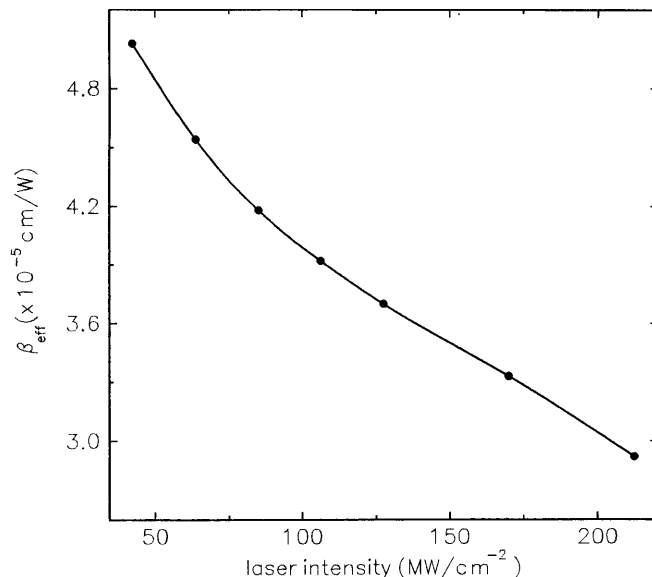


Fig. 6. Effective sequential two-photon absorption parameter β_{eff} as a function of the incident laser intensity for C_{70}

Nd:YAG laser. Because of large excited singlet as well as triplet absorption cross-sections compared to ground-state absorption cross-sections, the major mechanism for the limiting behaviour of these molecules is expected to be due to reverse saturable absorption. Optical limiting measurements showed that as the concentration increases a reduction in linear transmittance as well as the clamping level was observed. It was also noted that the saturated output intensity decreases with increasing pathlength. From the threshold intensity for optical limiting for each sample it can be seen that the threshold is inversely proportional to the concentration.

Thermal lensing studies in these solutions showed a quadratic dependence of thermal lens signal amplitude vs input laser energy. The occurrence of instantaneous TPA is less probable in the present context, since we are using ns laser pulses for pumping. So triplet-state absorption via sequential TPA is the process behind the observation of slope 2 in the log-log plots. Hence thermal lensing studies in fullerenes lead to the conclusion that sequential TPA (RSA), which gives a value of slope 2, is playing the leading role in the optical limiting properties of C_{70} .

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