

Optical limiting and thermal lensing studies in C₆₀

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Optical limiting and thermo-optic properties of C₆₀ in toluene are studied using 532 nm, 9 ns pulses from a frequency-doubled Nd:YAG laser. Optical limiting studies in these fullerene molecules lead to the conclusion that reverse saturable absorption is the major mechanism for limiting properties in these molecules. Thermal lensing measurements are also performed in fullerene solutions. The quadratic dependence of thermal lens signal on incident energy confirms that enhanced optical absorption by the sample via excited triplet state absorption may play a leading role in the limiting property. © 1999 American Institute of Physics. [S0021-8979(99)01715-6]

I. INTRODUCTION

The story of the discovery of C₆₀, otherwise known as fullerene, started in 1985 when Kroto and co-workers¹ evidenced a self-assembled spontaneous C₆₀ molecule from a hot nucleating carbon plasma. They exploited pulsed laser ablation of graphite in ambient helium as a reliable method for the production of C₆₀. Here, a pulsed laser beam is directed onto the surface of a rotating graphite disk. The power density delivered by the laser beam on to the target is sufficient to generate a plasma of carbon vapor over the irradiated spot in which temperatures over 10 000 °C are readily available.^{2,3} As the carbon atoms and small radicals are cooled in the ambient carrier gas (usually He) clustering reactions occur.⁴ The detailed nature of the carbon clusters can be studied using time-of-flight mass spectroscopy^{5,6} and laser spectroscopy.^{7,8} The technique developed by Krätschmer *et al.*⁹ for preparing and isolating macroscopic quantities of C₆₀ opened the way for exploring the molecular and bulk properties of these novel species. Fullerenes and their derivatives possess a number of potentially useful physical, biological and chemical properties.

The optical properties of fullerenes have been reported by numerous investigators.^{10–17} Photophysical and excited state kinetic properties of fullerenes, including fluorescence have been studied at low temperatures^{11,12} as well as at room temperature.¹³ Because of the very high rate for 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 of $\approx 1.45 \times 10^{-4}$ for C₆₀ at room temperature.¹⁴ The small singlet-triplet splitting, the very low value of fluorescent rate constant and expected large spin-orbital interaction in these nearly spherical molecules indicate the occurrence of intersystem crossing as a dominant process. Early literature reports¹¹ revealed that C₆₀ had 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.¹⁵ But few authors reported that apart from RSA some other nonlinear mechanism like nonlinear refraction, nonlinear scattering, two photon absorption, etc. also play a major role in the optical limiting properties of these molecules.^{16–19}

In this article, the optical limiting properties of C₆₀ in toluene are discussed along with its thermo-optic properties. We used thermal lensing method to elucidate any nonlinear mechanisms in these liquids. C₆₀ used in our experiment was prepared by following Krätschmer–Huffman technique⁹ and the sample was further purified by employing high purity liquid chromatography. The extract of C₆₀ has the characteristic color and its electronic absorption spectrum was in good agreement with that reported in the literature.²⁰

II. EXPERIMENTAL SETUP

We have carried out measurement of optical limiting properties in C₆₀ in toluene solutions with quartz cuvettes of path lengths 5 and 10 mm. The cuvette was kept slightly away from the focal spot and a long focal length lens was used so that the spot size inside the cuvette remains constant and was about 500 μm in radius. The input and output pulse energies were measured using a laser energy meter. The setup 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.

For thermal lens measurements, a 5 mm sample cuvette was used. Figure 1 shows the block diagram of the thermal lens spectrophotometer, consisting of a frequency-doubled Q-switched Nd:YAG laser as the heating source and an intensity stabilized He–Ne laser as the probe beam. The sample solution taken in a quartz cuvette having pathlength 5 mm 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 was blocked after the sample cuvette by a filter.

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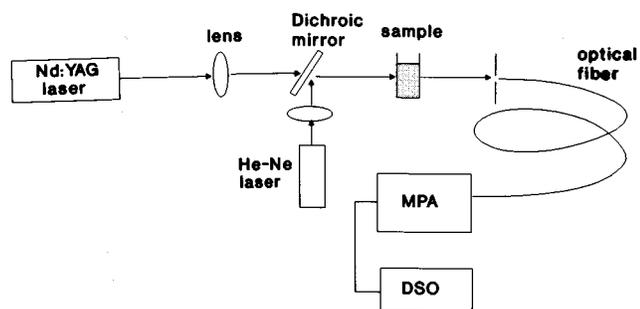


FIG. 1. Pulsed thermal lens setup used in the present experiment (MPA—monochromator—PMT assembly, DSO—digital storage oscilloscope).

As the 532 nm radiation was passed through the sample, the molecules absorb some of the incident energy and get excited to higher energy levels. The subsequent deexcitation process can occur radiatively or nonradiatively. It is the non-radiative part that gives rise to thermal lens formation. The resulting refractive index gradient follows the intensity distribution of the exciting pump beam. The TL effect was detected by monitoring the intensity fluctuations in the center of the probe He-Ne laser beam. The position of the cuvette was adjusted to get maximum value for the TL signal. The TL signal was detected by sampling the intensity of the center portion of the probe beam through a small aperture. In the present work, the intensity of the center portion of the transmitted probe beam was detected by using an optical fiber. The polished tip of a long graded index optical fiber (200 μm core, NA 0.22) serves both as an aperture and as a light guide for the probe beam to a monochromator—photomultiplier (PMT) assembly. Using optical fibers to transmit the laser beams makes the thermal lens technique amenable to remote, *in situ* analysis. It also reduces the influence of mode and pointing variations in the probing laser. Here, we used a multimode fiber which minimize alignment procedures and noise problems encountered with single mode fibers. The monochromator—photomultiplier assembly tuned to the probe beam wavelength (632.8 nm) provides further filtering of the signal. The TL signal was recorded using a digital averaging oscilloscope (100 MHz, Tektronix TDS 220) which provides a complete time domain representation of the signal. The oscilloscope was triggered by a synchronous trigger pulse from the Nd:YAG laser operated at 5 Hz.

III. OPTICAL LIMITING IN C_{60}

The discovery of optical limiting in fullerenes evoked considerable attention because of its comparatively lower threshold limiting fluence.^{15,21,22} Optical limiting property in these new found materials was first reported by Tutt and Kost¹⁰ using 532 nm, 8 ns pulses. These authors attributed the limiting action mainly to RSA in C_{60} resulting from the higher absorption from the photoexcited triplet state compared with that from the ground state. Transient excited state absorption spectroscopy measurements of higher lying singlets and triplet states of these molecules lend support to the RSA hypothesis. Joshi *et al.*¹⁶ did a numerical analysis of a simple model incorporating the effect of higher excited state

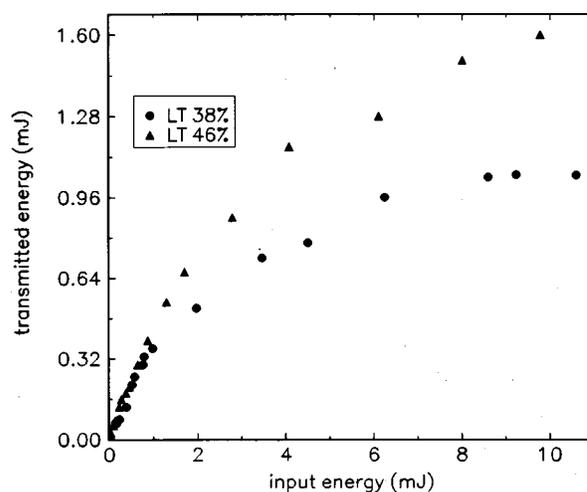


FIG. 2. Variation of transmitted energy with respect to input laser energy for C_{60} for an optical path length of 5 mm for a linear transmittance (LT) of 46% and 38%.

absorption and found that this model cannot explain their observations. They also observed a reduction in pulse width and steepening of the falling part of the pulse for input energies well into the saturation region and suggests that the multiphoton absorption from the excited state rather than the ground state might be operative. A similar conclusion was reached by McLean *et al.*,¹⁸ who 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 limiting mechanism. According to them, RSA yields a reasonable explanation of the low fluence behavior in both ns and ps cases, but unusually by large nonradiative relaxation rates for higher lying singlet states must be assumed in the picosecond case. Kost *et al.*²² reported that nonlinear transmission of C_{60} in PMMA was in agreement with the RSA mechanism and suggested the stronger limiting in C_{60} solutions could be due to nonlinear scattering. Even though large attention has been given for the limiting property of these molecules, a clear cut picture for the underlying physics behind this phenomenon has not yet emerged.

The optical limiting is obtained by varying the input energy and measuring the transmitted energy. The variation of transmitted energy with input energy is given in Fig. 2 for different concentrations of C_{60} in toluene for an optical path length of 5 mm. At very low laser energies, the transmission obeys Beer-Lambert law and 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 the number density of the C_{60} molecules, and L 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. With solutions showing low intensity linear transmittance (LT) of 46% and 38%, the outgoing laser intensities are saturated at energy levels of 6 and 4.5 mJ, respectively. These data show that as the concentration increases, a reduction in linear transmittance as well as the clamping level is

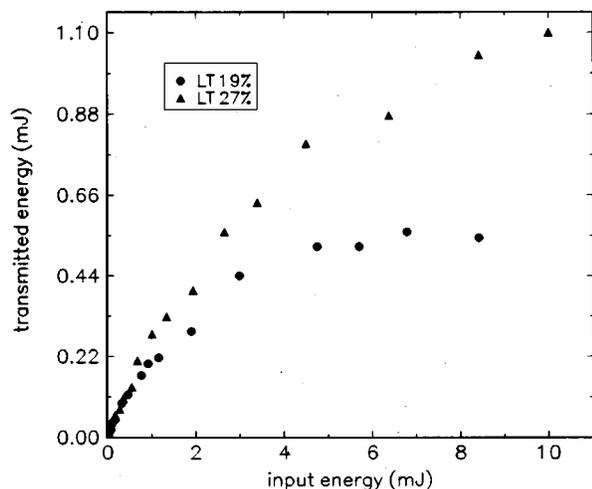


FIG. 3. Variation of output energy vs input energy for an optical path length of 10 mm for C₆₀ with a linear transmittance (LT) of 27% and 19%.

observed. It is also noted that the saturated output intensity decreases with increasing length of the optical path. Figure 3 gives the optical limiting properties of these solutions for a 10 mm cell path length. In this experiment, the low intensity linear transmittances of the solutions in a 10 mm path length cell are 27% and 19% with clamping energies at 4.6 and 3 mJ, respectively. This indicates that the number density of C₆₀ in the laser beam 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.

Several mechanisms have been proposed for optical limiting in C₆₀ including RSA, nonlinear scattering, multiphoton absorption, cyclic multiphoton absorption, etc. The RSA by a 5 level energy diagram yielded a reasonable explanation for optical limiting in the ns regime of a π -electron conjugated system such as C₆₀ below the input fluence of 1 J cm^{-2} . When a C₆₀ molecule is photoexcited using 532 nm, 9 ns pulse, it gets excited from the ground state S_0 ($\sigma_g = 1.21 \times 10^{-18} \text{ cm}^2$) into one of the vibrational rotational states of the first excited singlet state S_1 . The molecule relaxes rapidly ($\approx 1 \text{ ps}$) into an equilibrium state S_1 which releases 0.33 eV energy. This level relaxes either to the ground state with life time $\tau_0 = 16 \text{ ns}$, or to the triplet state T_1 in $\tau_{st} = 650 \text{ ps}$. The reported fluorescence quantum yield¹¹ for C₆₀ in toluene is 1.45×10^{-4} . But the triplet production yield is found to be nearly unity for 532 nm excitation of C₆₀ molecules. Hence, excited singlet state transfers dominantly to the lower level of the triplet state due to high triplet yield and small S - T splitting of 9 kcal/mol for C₆₀. The molecule in the S_1 and T_1 states can be excited to higher S_n and T_n states ($\sigma_{s1} = 8.07 \times 10^{-18} \text{ cm}^2$ and $\sigma_{T1} = 5.35 \times 10^{-18} \text{ cm}^2$). Relaxation from these S_n and T_n states is in the form of heat and is extremely short ($< \text{ps}$). The relaxation of T_1 to S_0 is forbidden and therefore very slow. The triplet state which has long lifetime ($40 \pm 4 \mu\text{s}$ for C₆₀)²³ and higher absorption cross section than that of the ground state will accumulate significant population and eventually become the dominant absorp-

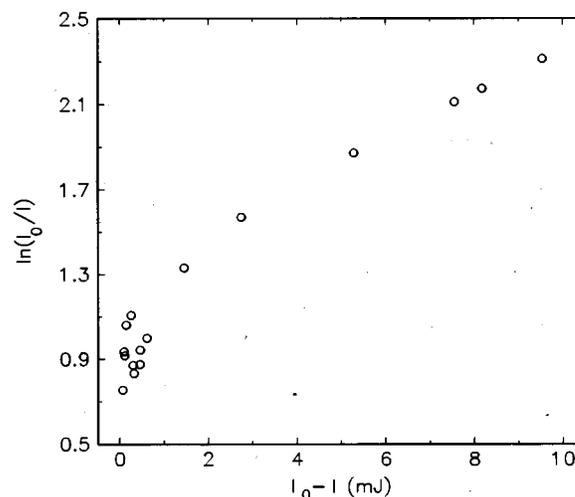


FIG. 4. Plot of $\ln(I_0/I)$ vs $(I_0 - I)$ for C₆₀ toluene solution showing approximate linearity.

tion source. At very low laser energies, the transmission increases with increasing input energy with a slope equal to $\exp(-N_0\sigma_g L)$, where N_0 the number density of the C₆₀ molecules and L the optical path length. At higher laser energies, taking into account the ground state absorption as well as ESA the transmission varies at a rate $\exp(N_0\sigma_{s1} + N_1\sigma_{T1})L$, where N_1 is the population density for the photoexcited triplet state. It has been found that¹¹ $\sigma_2 \approx 2.9\sigma_1$.

Kojima *et al.*²⁴ while explaining the optical limiting property of a polyacene based oligomer have shown that in the case of pure RSA the incident laser fluence I_0 and the transmitted laser fluence I obeys the relation,

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

where k is a constant which 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 intercept A_g . Figure 4 shows such a plot for C₆₀. The plot of $\ln(I_0/I)$ vs $(I_0 - I)$ is approximately in the energy range of interest. This is a clear indication that RSA is one of the limiting mechanism in the case of C₆₀.

Even though there are many reports exploring nonlinearities and fluorescence of C₆₀ molecules, its nonradiative relaxations in solutions are not well investigated. Apart from that, there is a controversy existing in the optical limiting mechanism of these molecules. McLean *et al.*¹⁸ suggested various mechanism other than RSA for the observation of optical limiting in C₆₀. Joshi *et al.*¹⁶ have found that the optical limiting in C₆₀ deviates from a theoretical model based on a large excited state absorption cross section alone and they have attributed the discrepancy to the possibility of multiphoton absorption (MPA) apart from ESA. The study of MPA in absorbing media can very effectively be carried out

using the transient thermal lens technique.^{25,26} We have explored the nonradiative relaxations in C_{60} in toluene solution using transient thermal lens technique.

IV. THERMAL LENSING IN C_{60}

Thermal lens spectroscopy is an effective and efficient method to monitor nonradiative relaxations in a medium.^{27–30} Very weak optical absorption processes can be studied using this method. Even though a few reports are available³¹ in literature on the thermo-optic properties of C_{60} , a more detailed study of thermo-optic properties of these fullerene molecules has not been undertaken yet. In this section, thermal lensing studies in C_{60} are given.

Methods classified as thermal lens spectroscopy are based upon a thermal change in the optical properties of a sample on the absorption of laser energy which 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 the solution into a divergent lens in most cases, which defocuses the laser beam. The change of irradiance at the probe beam intensity relative to its stationary value S is given by^{27,28}

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

where E is the incident laser intensity, m is the number of photons involved in the generation of the thermal lens signal, $I(t=0)$ and $I(t=\infty)$ are the thermal lens signal strength at time $t=0$ and $t=\infty$, respectively. Hence, by monitoring the dependence of the thermal lens signal amplitude on pump energy, one can identify the occurrence of different processes like one photon absorption ($m=1$) and multiphoton absorption processes ($m \geq 2$). We have measured thermal lens signal produced from solutions of C_{60} in toluene at different input energies. Figure 5 gives a typical log–log plot for C_{60} in toluene. As is clear from the figure, a linear transmittance of a 30% C_{60} toluene solution gives a slope value of 2.

The occurrence of slope 2 in these curves is an indication of two-photon absorption (TPA). However, the optical limiting action of C_{60} can be explained in terms of transient reverse saturable absorption, although some other mechanisms like nonlinear refraction, nonlinear scattering, etc. may also play a role under certain experimental conditions. The participation of instantaneous or simultaneous TPA in C_{60} has not yet been demonstrated under laser excitation in the nanosecond range. The two-photon absorption from the triplet state in these molecules is less likely since a considerable triplet-triplet absorption cross section is reported at 532 nm.³¹ Another potentially effective nonlinearity is sequential two-photon absorption where the excited state absorption cross section is larger than the ground state absorption cross section. The observation of slope 2 in the double logarithmic plot of these molecules could be due to sequential two-

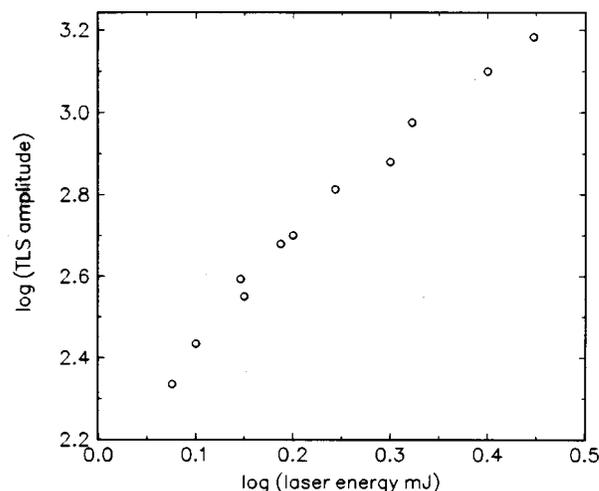


FIG. 5. Log–log plot of thermal lens signal (TLS) amplitude as a function of input laser energy for C_{60} .

photon absorption. That is, instead of simultaneous absorption of many photons and exciting the molecule to a higher level which is multiphoton resonant, 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 which rapidly decay nonradiatively to the lowest vibrational level of S_1 . The reported quantum yield for the intersystem crossing rate to the lowest triplet T_1 for C_{60} is nearly unity.²³ As the intersystem crossing is very fast for C_{60} (\ll ns) for ns pulses, the triplet state T_1 gets rapidly populated. The triplet state T_1 has a long lifetime (40 μ s for C_{60}) and a higher absorption cross section than that of the ground state. 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 picosecond region due to fast internal conversion. The molecule can relax to the lower excited triplet level by collisional energy transfer to the surrounding solvent molecules. This process occurs within the duration of the nanosecond laser pulse. Thus, the nonradiative decay from T_n gives rise to appreciable thermal lens signals with a quadratic dependence on laser energy.

For C_{60} , where 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, by the following expression:³²

$$\frac{dI(\lambda)}{dz} = -\alpha_0 S_0(t)I(\lambda) - \alpha_1 T_1(t)I(\lambda), \quad (3)$$

where $S_0(t)$ and $T_1(t)$ are the ground and triplet state concentrations, respectively, at instant t , and α_0 and α_1 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

$$T_1(t) = \alpha_0 S_0(t)I(\lambda)\Phi_{isc}, \quad (4)$$

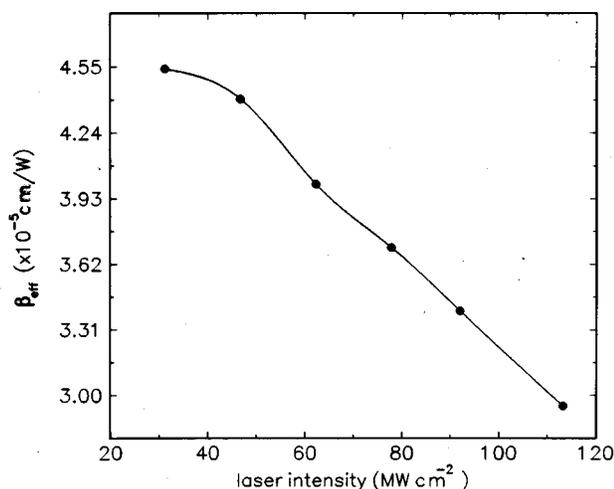


FIG. 6. Effective STPA parameter β_{eff} as a function of the incident laser intensity for C_{60} .

where Φ_{isc} is the intersystem crossing yield. For C_{60} , $\Phi_{\text{isc}} \approx 1$, so that

$$\begin{aligned} \frac{dI(\lambda)}{dz} &= -\alpha_0 S_0(t)I(\lambda) - \alpha_1 \alpha_0 S_0(t)I(\lambda)I(\lambda) \\ &= -\alpha I(\lambda), \end{aligned} \quad (5)$$

where $\alpha = -\alpha_0 S_0(t) - \alpha_1 \alpha_0 S_0(t)I(\lambda)$ can be considered as an intensity dependent absorption coefficient. This α represents the absorption coefficient for the sequential two-photon absorption (STPA) with an effective STPA parameter $\beta_{\text{eff}} = \alpha_1 \alpha_0 S_0(t)$. The above equation is formally similar to $\alpha = \alpha_0 + \beta I$ for the case of instantaneous two-photon absorption (ITPA). The quantity β_{eff} is intensity dependent through the $S_0(t)$ term, while in the ITPA case, β is constant. The dependence of the effective STPA parameter β_{eff} as a function of the incident intensity I_0 is depicted in Fig. 6 for C_{60} . It is noted that the value of β_{eff} decreases with respect to increasing intensity of radiation. The falloff of β_{eff} with increasing I_0 is a consequence of STPA. With increasing intensity, the total absorption of the C_{60} approaches asymptotically the value of α_1 , i.e., the absorbance of the triplet state.¹⁸

V. CONCLUSIONS

Optical limiting properties of C_{60} molecules in toluene are studied using 532 nm, 9 ns pulses from a frequency-doubled Nd:YAG laser. Because of large excited singlet as well as triplet absorption cross sections compared to ground state absorption cross section, the major mechanism for this limiting behavior of these molecules is reverse saturable absorption.

Thermal lensing studies in these solutions show a quadratic dependence of the thermal lens signal amplitude versus input laser energy. The occurrence of instantaneous TPA is less probable in the present context, since we are using ns laser pulses for pumping. Therefore, triplet state absorption

via sequential two-photon absorption is the process behind the observation of slope 2 in the log-log plots. This is also supported by the fact that the effective value of the two-photon absorption cross-section decreases with increasing laser intensity. Hence, thermal lensing studies in fullerenes lead to the conclusion that sequential TPA (RSA), which gives a slope of 2 is playing the leading role in the optical limiting properties of C_{60} .

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- ¹H. W. Kroto, J. R. Heath, S. C. O. Brien, R. F. Curl, and R. E. Smalley, *Nature (London)* **318**, 162 (1985).
- ²S. S. Harilal, C. V. Bindhu, R. C. Issac, V. P. Nampoori, and C. P. G. Vallabhan, *J. Appl. Phys.* **82**, 2140 (1997).
- ³S. S. Harilal, C. V. Bindhu, V. P. Nampoori, and C. P. G. Vallabhan, *J. Appl. Phys.* **72**, 167 (1998).
- ⁴S. S. Harilal, C. V. Bindhu, R. C. Issac, V. P. Nampoori, and C. P. G. Vallabhan, *Jpn. J. Appl. Phys., Part 1* **36**, 134 (1997).
- ⁵S. W. McElvany, M. M. Ross, and J. H. Callahan, *Acc. Chem. Res.* **25**, 162 (1992).
- ⁶R. E. Smalley, *Acc. Chem. Res.* **25**, 98 (1992).
- ⁷S. S. Harilal, R. C. Issac, C. V. Bindhu, V. P. Nampoori, and C. P. G. Vallabhan, *J. Appl. Phys.* **80**, 3561 (1996).
- ⁸S. S. Harilal, R. C. Issac, C. V. Bindhu, V. P. Nampoori, and C. P. G. Vallabhan, *J. Appl. Phys.* **81**, 3637 (1997).
- ⁹W. Krätschmer, L. D. Lamb, K. Fostiropoulos, and D. R. Huffman, *Nature (London)* **347**, 354 (1990).
- ¹⁰L. W. Tutt and A. Kost, *Nature (London)* **356**, 225 (1992).
- ¹¹J. N. Arbogast, A. P. Darmany, C. S. Foote, Y. Rubin, F. N. Diederich, M. M. Alvarez, S. J. Anz, and R. L. Whetten, *J. Phys. Chem.* **95**, 11 (1991).
- ¹²S. D. Sibley, S. M. Argentine, and A. H. Francis, *Chem. Phys. Lett.* **188**, 187 (1992).
- ¹³A. Andreoni, M. Bondoni, and G. Consolati, *Phys. Rev. Lett.* **72**, 844 (1994).
- ¹⁴D. Kim and M. Lee, *J. Am. Chem. Soc.* **114**, 4429 (1992).
- ¹⁵L. W. Tutt and T. F. Boggess, *Prog. Quantum Electron.* **17**, 299 (1993).
- ¹⁶M. P. Joshi, S. R. Mishra, H. S. Rawat, S. C. Mehendale, and K. C. Rustagi, *Appl. Phys. Lett.* **62**, 1763 (1993).
- ¹⁷S. R. Mishra, H. S. Rawat, M. P. Joshi, and S. C. Mehendale, *Appl. Phys. A: Mater. Sci. Process.* **63**, 223 (1996).
- ¹⁸D. G. McLean, R. L. Sutherland, M. C. Brant, D. M. Brandelik, P. A. Fleitz, and T. Pottenger, *Opt. Lett.* **18**, 858 (1993).
- ¹⁹S. R. Mishra, H. S. Rawat, M. P. Joshi, and S. C. Mehendale, *J. Phys. B* **27**, L157 (1994).
- ²⁰F. N. Diederich and R. L. Whetten, *Acc. Chem. Res.* **25**, 119 (1992).
- ²¹Y. Sun, Q. Gong, S. Yang, Y. H. Zou, L. Fei, X. Zhou, and D. Qiang, *Opt. Commun.* **102**, 205 (1993).
- ²²A. Kost, L. W. Tutt, M. B. Klien, T. K. Dougherty, and W. E. Elias, *Opt. Lett.* **18**, 334 (1993).
- ²³J. W. Arbogast and C. S. Foote, *J. Am. Chem. Soc.* **113**, 8886 (1991).
- ²⁴Y. Kojima, T. Matsuoka, N. Sato, and H. Takahashi, *Macromolecules* **28**, 2893 (1995).
- ²⁵A. J. Twarowski and D. S. Kliger, *Chem. Phys.* **20**, 253 (1977).
- ²⁶A. J. Twarowski and D. S. Kliger, *Chem. Phys.* **20**, 259 (1977).
- ²⁷C. V. Bindhu, S. S. Harilal, V. P. N. Nampoori, and C. P. G. Vallabhan, *Opt. Eng. (Bellingham)* **37**, 2791 (1998).
- ²⁸C. V. Bindhu, S. S. Harilal, V. P. N. Nampoori, and C. P. G. Vallabhan, *J. Phys. D (in press)*.
- ²⁹C. V. Bindhu, S. S. Harilal, V. P. N. Nampoori, and C. P. G. Vallabhan, *Mod. Phys. Lett. B* **9**, 1471 (1995).
- ³⁰C. V. Bindhu, S. S. Harilal, V. P. N. Nampoori, and C. P. G. Vallabhan, *Curr. Sci.* **75**, 167 (1998).
- ³¹M. Terazima, N. Hirota, H. Shimohara, and Y. Saito, *J. Phys. Chem.* **95**, 9081 (1991).
- ³²S. Couris, E. Koudoumas, A. A. Ruth, and S. Leach, *J. Phys. B* **28**, 4537 (1995).