Optical limiting and thermal lensing studies in C_{60}

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Optical limiting and thermo-optic properties of C_{60} 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 C_{60}, otherwise known as fullerene, started in 1985 when Kroto and co-workers[1] evidenced a self-assembled spontaneous C_{60} 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 C_{60}. 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 C_{60} 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 $\simeq 1.45 \times 10^{-4}$ for C_{60} 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 reports[11] revealed that C_{60} 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 absorp (RSA) materials and may have application to optical limit for sensor protection.[15] But few authors reported that φ from RSA some other nonlinear mechanism like nonlin refraction, nonlinear scattering, two photon absorption, also play a major role in the optical limiting propertie these molecules.[16–19]

In this article, the optical limiting properties of $C_{\bullet}$ toluene are discussed along with its thermo-optic propert We used thermal lensing method to elucidate any nonli mechanisms in these liquids. C_{60} used in our experiment prepared by following Krätschmer–Huffman technique the sample was further purified by employing high p liquid chromatography. The extract of C_{60} has the chara istic color and its electronic absorption spectrum was in agreement with that reported in the literature.[20]

II. EXPERIMENTAL SETUP

We have carried out measurement of optical lim properties in C_{60} in toluene solutions with quartz cuvett path lengths 5 and 10 mm. The cuvette was kept sli away from the focal spot and a long focal length lens used so that the spot size inside the cuvette remains con and was about 500 μm in radius. The input and output energies were measured using a laser energy meter. setup essentially avoids nonlinear refraction as only the linear absorption is important in this case contrary t measurements done with a point detector to measure transmitted laser energy.

For thermal lens measurements, a 5 mm sample c was used. Figure 1 shows the block diagram of the th lens spectrophotometer, consisting of a frequency-do Q-switched Nd:YAG laser as the heating source and tensity stabilized He–Ne laser as the probe beam. sample solution taken in a quartz cuvette having pathle mm is placed in the pump beam path. The pump and beams are focused onto the sample cell and made t collinearly through it using suitable convex lenses and use of a dichroic mirror. The excitation beam was b after the sample cuvette by a filter.

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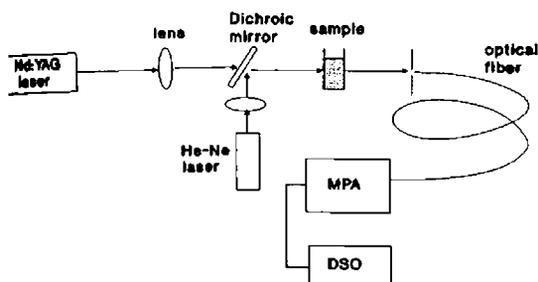[b]Electronic mail: photonix@md2.vsnl.net.in

G. I. Pulsed thermal lens setup used in the present experiment (MPA—mochromator—PMT assembly, DSO—digital storage oscilloscope).
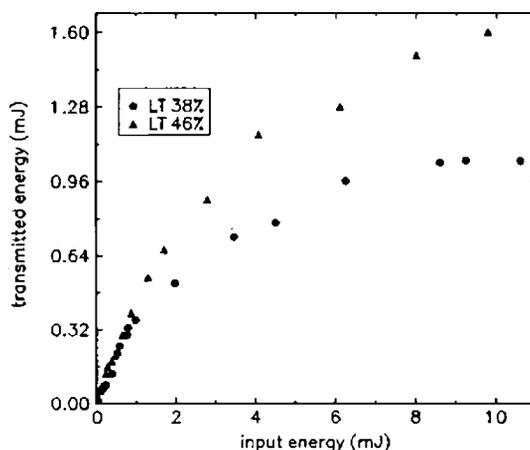

FIG. 2. Variation of transmitted energy with respect to input laser energy for C_{60} for an optical path length of 5 mm for a linear transmittance (LT) of 46% and 38%.

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 is adjusted to get maximum value for the TL signal. The signal was detected by sampling the intensity of the central 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. A polished tip of a long graded index optical fiber (200 μm, 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 the 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 imaging 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.

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 co-workers[10] using 532 nm, 8 ns pulses. These authors attributed the limiting action mainly to RSA in C_{60} resulting from the larger absorption from the photoexcited triplet state combined with that from the ground state. Transient excited state absorption spectroscopy measurements of higher lying singlet and triplet states of these molecules lend support to the hypothesis. Joshi et al.[16] did a numerical analysis of a three model incorporating the effect of higher excited state

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 $\exp(-N_0\sigma_1 L)$, 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
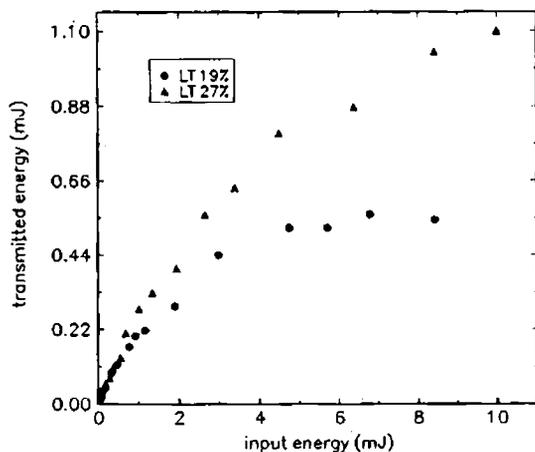
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FIG. 3. Variation of output energy vs input energy for an optical pathlength of 10 mm for C_{60} with a linear tansmittance (LT) of 27% and 19%.

FIG. 4. Plot of $\ln(I_0/I)$ vs (I_0-I) for C_{60} toluene solution showing app iamte linearity.

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 C_{60} 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 C_{60} 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 C_{60} below the input fluence of 1 $J cm^{-2}$. When a C_{60} molecule is photoexcited using 532 nm, 9 ns pulse, it gets excited from the ground state S_0($\sigma_g=1.21 \times 10^{-18} cm^2$) into one of the vibrational rotational states of the first excited singlet state S_1. The molecule relaxes rapidly (≈ 1 ps) into an equilibrium state S_1 which releases 0.33 eV energy. This level relaxes either to the ground state with life time $\tau_0=16$ ns, or to the triplet state T_1 in $\tau_{s1}=650$ ps. The reported fluorescence quantum yield[11] for C_{60} in toluene is 1.45×10^{-4}. But the triplet production yield is found to be nearly unity for 532 nm excitation of C_{60} 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 C_{60}. The molecule in the S_1 and T_1 states can be excited to higher S_n and T_n states ($\sigma_{s1}=8.07\times 10^{-18} cm^2$ and $\sigma_{T1}=5.35\times 10^{-18} cm^2$). Relaxation from these S_n and T_n states is in the form of heat and is extremely short ($<$ps). The relaxation of T_1 to S_0 is forbidden and therefore very slow. The triplet state which has long lifetime (40 ± 4 μs for C_{60})[23] and higher absorption cross section than that of the ground state will accumulate significant population and eventually become the dominant absorp-
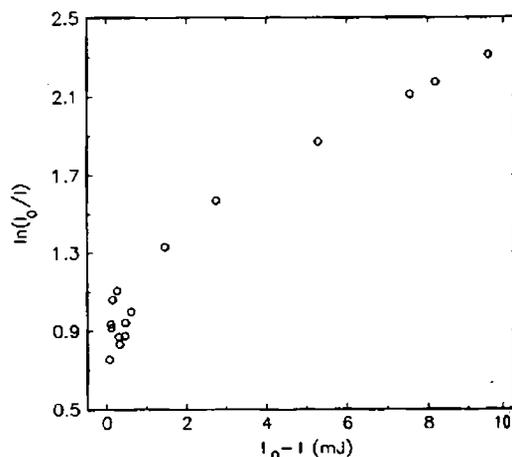
tion source. At very low laser energies, the transmission creases with increasing input energy with a slope equal $\exp(-N_0\sigma_g L)$, where N_0 the number density of the C_{60} molecules and L the optical path length. At higher laser energ taking into account the ground state absorption as well ESA the transmission varies at a rate $\exp(N_0\sigma_{s1}+N_1\sigma_T)$ where N_1 is the population density for the photoexcited let state. It has been found that[11] $\sigma_2 \approx 2.9\sigma_1$.

Kojima et al.[24] while explaining the optical limi property of π polyacene based oligomer have shown th the case of pure RSA the incident laser fluence I_0 and transmitted laser fluence I obeys the relation,

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

where k is a constant which depends on the absorption sections and lifetimes of the ground, excited singlet and cited triplet states and A_g is the ground state absorbance. above equation says that the plot of $\ln(I_0/I)$ vs (I_0-I) sh be a straight line with slope k and intercept A_g. Fig shows such a plot for C_{60}. The plot of $\ln(I_0/I)$ vs (I_0-I) approximately in the energy range of interest. This is a indication that RSA is one of the limiting mechanism i case of C_{60}.

Even though there are many reports exploring no earities and fluorescence of C_{60} molecules, its nonradi relaxations in solutions are not well investigated. Apart that, there is a controversy existing in the optical lim mechanism of these molecules. McLean et al.[18] sugg various mechanism other than RSA for the observati optical limiting in C_{60}. Joshi et al.[16] have found th optical limiting in C_{60} deviates from a theoretical based on a large excited state absorption cross section and they have attributed the discrepancy to the possibi multiphoton absorption (MPA) apart from ESA. The st MPA in absorbing media can very effectively be carri

ig the transient thermal lens technique.[25,26] We have ex-
ed the nonradiative relaxations in C_{60} in toluene solution
ig transient thermal lens technique.

THERMAL LENSING IN C_{60}

Thermal lens spectroscopy is an effective and efficient
bod to monitor nonradiative relaxations in a
ium.[27–30] Very weak optical absorption processes can be
lied using this method. Even though a few reports are
ilable[31] in literature on the thermo-optic properties of
, a more detailed study of thermo-optic properties of
e fullerene molecules has not been undertaken yet. In
section, thermal lensing studies in C_{60} are given.

Methods classified as thermal lens spectroscopy are
ed upon a thermal change in the optical properties of a
ple on the absorption of laser energy which leads to a
perature rise in the sample and consequently to the for-
tion of an inhomogeneous spatial profile of the refractive
ex. The heat released by the nonradiative relaxation pro-
es generates a volume expansion in the sample and a
ity change within the excitation region. The refractive
x caused by the heat evolution due to the radiationless
esses, turns the solution into a divergent lens in most
, which defocuses the laser beam. The change of irra-
ce at the probe beam intensity relative to its stationary
e S is given by[27,28]

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

re E is the incident laser intensity, m is the number of
ons involved in the generation of the thermal lens signal,
=0) and $I(t=\infty)$ are the thermal lens signal strength at
$t=0$ and $t=\infty$, respectively. Hence, by monitoring the
dence of the thermal lens signal amplitude on pump
gy, one can identify the occurrence of different pro-
es like one photon absorption ($m=1$) and multiphoton
ption processes ($m \geqslant 2$). We have measured thermal
signal produced from solutions of C_{60} in toluene at dif-
t input energies. Figure 5 gives a typical log–log plot
C_{60} in toluene. As is clear from the figure, a linear trans-
ce of a 30% C_{60} toluene solution gives a slope value

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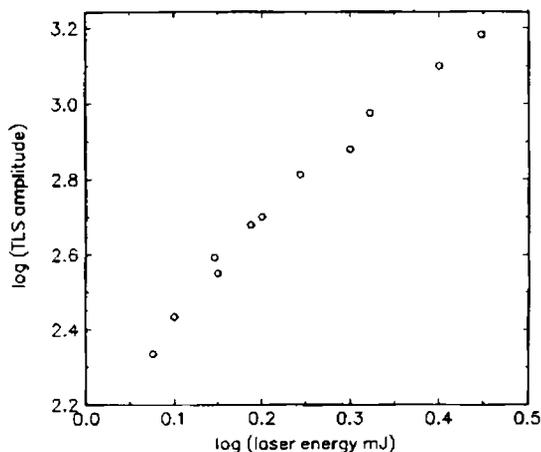of these molecules could be due to sequential two-

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 absorp-
tion of many photons and exciting the molecule to a higher
level which is multiphoton resonant, the photons are ab-
sorbed 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 cross-
ing rate to the lowest triplet T_1 for C_{60} is nearly unity.[23] As
the intersystem crossing is very fast for C_{60} ($\leqslant$ns) for ns
pulses, the triplet state T_1 gets rapidly populated. The triplet
state T_1 has a long lifetime (40 μs 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 collissional energy transfer to the sur-
rounding solvent molecules. This process occurs within the
duration of the nanosecond laser pulse. Thus, the nonradia-
tive 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]

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

where $S_0(t)$ and $T_1(t)$ are the ground and triplet state con-
centrations, respectively, at instant t, and α_0 and α_1 are the
linear absorption coefficients from the S_0 and T_1 states, re-
spectively.

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

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

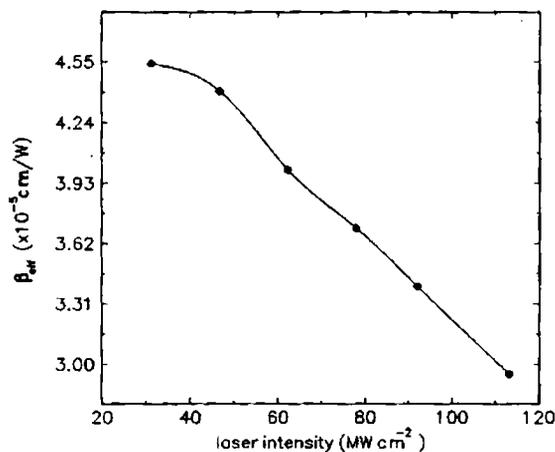1392   J. Appl. Phys., Vol. 86, No. 3, 1 August 1999

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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

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

$$= -\alpha I(\lambda), \qquad (5)$$

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 beh the observation of slope 2 in the log—log plots. This is a supported by the fact that the effective value of the t photon absorption cross-section decreases with increasing ser intensity. Hence, thermal lensing studies in fullere lead to the conclusion that sequential TPA (RSA), wh gives a slope of 2 is playing the leading role in the opti limiting properties of C_{60}.

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