Photoacoustic signal saturation and optical limiting in C_{70}-toluene solution

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Abstract. Pulsed photoacoustic studies in solutions of C_{70} in toluene are made using the 532-nm radiation from a frequency-doubled Nd:YAG laser. It is found that contrary to expectation, there is no photoacoustic (PA) signal enhancement in the power-limiting range of laser fluences. Instead, the PA signal tends to saturate during optical power-limiting phenomenon. This could be due to the enhanced optical absorption from the photoexcited state and hence the depletion of the ground-state population. PA measurements also ruled out the possibility of multiphoton absorption in the C_{70} solution. We demonstrate that the nonlinear absorption leading to optical limiting is mainly due to reverse saturable absorption.

Subject terms: photoacoustic and photothermal science and engineering; pulsed photoacoustics; fullerenes; optical limiting.

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1 Introduction

The success of the Krätschmer-Huffman process,[1] by which fullerenes, the molecular allotropic form of carbon, could be mass produced has opened up a new avenue for scientific studies of carbon clusters and their derivatives.[2–6] These molecules have unique properties such as relatively high temperature superconductivity,[7] photovoltaic response,[8] a high degree of hardness,[9] persistent photoconductivity,[10] the ability to trap anions inside the cage,[11] etc. It has been found that fullerenes exhibit optical nonlinearities leading to second-harmonic generation[12] and optical limiting[13,14] and self-defocusing of laser beams due to high values of third-order susceptibility.[15] Photophysical and excited state kinetic properties of fullerenes, including fluorescence, have been studied at room temperature.[16,17] 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 the order of 10^{-4} at room temperature.[16]

The discovery of optical limiting in fullerenes evoked considerable attention because of its comparatively lower threshold limiting fluence.[14,18,19] Joshi et al.[20] have found that their transmission measurements on C_{60} deviates substantially from the kinetic model based on large excited state absorption (ESA) and they have attributed the discrepancy to the possibility of multiphoton absorption and/or nonlinear scattering along with ESA.

Even though there are many reports exploring nonlinearities and fluorescence from these molecules, its nonradiative relaxations in solutions are not well investigated. Pulsed photoacoustics is a very effective technique for exploring the nonradiative relaxations and multiphoton processes in liquids.[21–25] In this paper, we report results from two sets of experiments. In the first case, we examined the photoacoustic (PA) signal and optical limiting simultaneously using a suitable PA cell. In another experiment, optical limiting alone is studied in a short-path-length cuvette.

2 Experiment

The C_{70} used in our experiment was prepared following the Krätschmer-Huffman technique and the sample was further purified employing high-performance liquid chromatography. The experimental arrangement used for PA measurements is almost the same as that used earlier.[23] The PA cell used is basically a stainless steel cylinder having glass windows on both ends, and it has an acoustic transducer screwed on one side. A solution of C_{70} in toluene is placed inside the PA cell. The 532-nm radiation from a *Q*-switched frequency-doubled Nd:YAG laser is focused into the center of the PA cell containing the solution. A dichroic filter separates out the fundamental radiation (1064 nm) from the second harmonic. The laser pulse width is 9 ns with a pulse repetition frequency of 16 Hz. The pump pulse energy is monitored using a laser energy meter and the strength of the PA signal is measured using a 200-MHz digital storage oscilloscope. The pulse energies were measured after averaging over 16 pulses and corrections for reflection losses at window and lens surfaces are made. The transmitted energy from the PA cell is measured with the same energy meter to study optical limiting in the solution.

In a separate experiment, the optical limiting alone is studied with the solution placed in a quartz cuvette of path length 10 mm. The cuvette is kept slightly away from the focal spot and a long-focal-length lens is used so that the spot size inside the cuvette is approximately constant and about 750 μm in radius. Again the input and output pulse energies are measured using a laser energy meter. The setup essentially avoids nonlinear refraction as only the nonlinear absorption is important in this case, contrary to measurements done with a point detector to measure the transmitted laser energy (see, for example, Ref. 26).

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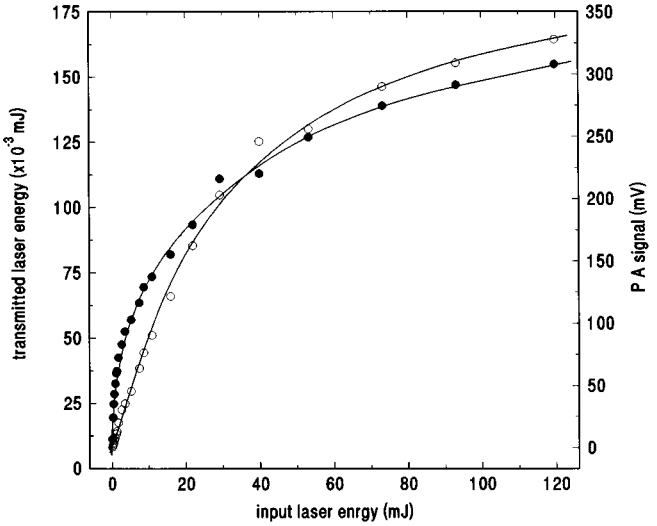

Fig. 1 Variation of transmitted laser energy (solid dots) and PA signal (open dots) as a function of input laser energy in a C_{70}-toluene solution with a low-intensity transmission of 16%. Both the curves show saturation effects at high laser fluences but the saturation thresholds are well separated.

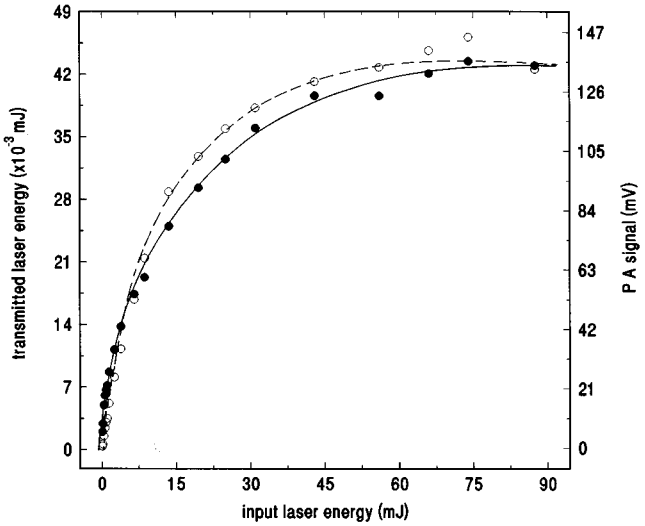

Fig. 2 Variation of transmitted laser energy (solid dots) and PA signal (open dots) amplitude as a function of input laser energy for a low-intensity transmission of 5% from C_{70} solution. The saturation thresholds almost coincides.

3 Results and Discussion

In general the pulsed PA signal amplitude $q(\nu)$ generated in an absorbing liquid media at input laser frequency ν can be written as[21]

$$q(\nu)=kA\sigma(\nu)L_{\text{eff}}N\tau\eta(\nu_m)I^m(\nu), \tag{1}$$

i.e., $q(\nu)$ is proportional to the m'th power of the incident laser power density $I(\nu)$, where m is the number of photons involved in the process. In Eq. (1), k is a constant determined by calibration factors that include cell geometry, acoustic transducer properties, etc.; $\sigma(\nu)$ is the absorption cross section at laser frequency ν; N is the density of absorbing molecules; L_{eff} is the effective optical path length in the cell, given by $L_{\text{eff}}=(1-e^{-\alpha L})/\alpha$, where α is the absorption coefficient in units of inverse centimeters; and A is the beam area at the focal spot. Therefore the slope of the plot of log $q(\nu)$ versus log $I(\nu)$ will give an indication of the number of photons involved in the process.

Figure 1 shows the variation of transmitted laser energy and PA signal as a function of input laser energy for a solution having a low-intensity transmission of 16%. For fullerenes the radiative deexcitation cross section of the excited molecules should be small, as seen from their low fluorescence quantum efficiencies.[16] Then one could expect an enhanced nonradiative relaxation and thereby a sudden jump in the PA signal in the laser fluences when optical limiting begins. In the case of C_{70}-toluene solution, this was not observed, as shown in Fig. 1. Instead, the PA signal also saturates at higher laser energies. In this case, the low-intensity transmission is about 16% and one can see that the PA signal saturation threshold and limiting threshold clearly separate. For high concentrations of C_{70} (5% transmitting solution) the PA saturation threshold decreases and the limiting threshold almost coincides with the PA saturation threshold, as shown in Fig. 2. That is, at higher concentrations there are enough C_{70} molecules in the solution so that almost all the photons are either absorbed from the ground state or from the excited state. At low concentrations of C_{70}, however, because of the depletion of both ground-state and the photoexcited triplet-state populations, the solvent toluene may be absorbing some of the laser light due to a two-photon resonance at the pump wavelength.

Figure 3 shows a plot of input laser energy and photoacoustic signal for both the C_{70} solution and the solvent toluene on a logarithmic scale. According to Eq. (1), the slope of the curve yields the number of quanta absorbed. In the case of pure toluene, the initial linear dependence of the PA signal on the input laser energy changes into a quadratic dependence after a threshold laser energy, thus giving evi-

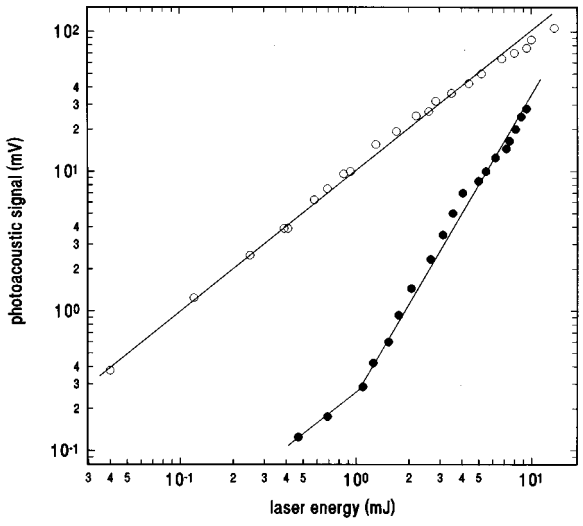

Fig. 3 PA signal strength as a function of input laser energy on a logarithmic scale for both solvent toluene (solid dots) and C_{70} solution (open dots) toluene.

dence of a two-photon transition corresponding to the (one-photon) absorption band at 266 nm due to the transition $^1A_1 \rightarrow {}^1B_2$. After C_{70} is dissolved in toluene, the intensity dependence of the PA signal is found to be linear and there is no tendency for it to change over to a higher order dependence greater than 1, which clearly indicates that a multiphoton transition does not contribute to optical limiting in C_{70}. Due to the influence of the solvent, the value of the slope gradually increases from 1 to 2 as we decrease the C_{70} concentration.

In a study of optical limiting in C_{60} solutions Wrang et al.[27] showed that about 100 to 150 photons are absorbed by a single molecule without decomposition. This type of many-photon process may be possible in the case of C_{70} also because of the similarity in the nonlinear properties of these two molecules. As is the case in C_{60} solution,[28] C_{70} also maintains linear behavior (slope equal to 1) in the PA signal. This is because the photons are not absorbed simultaneously to have a multiphoton effect, but all these photons are absorbed during the laser pulse, which lasts about 9 ns. In other words, instead of simultaneous absorption of many photons and exciting the molecule to a higher level, which is multiphoton resonant, the photons are absorbed sequentially. PA saturation beyond a threshold energy is an indication of such behavior. Above a threshold value of the input laser energy, the dominant absorption is due to excited state cyclic single-photon processes. In the power limiting region, the leading part of the laser pulse excites most of the molecules to the excited singlet state from which, due to intersystem crossing, the molecules cross over to the triplet state, which has a longer lifetime. After resonantly absorbing a single photon, the molecule in the triplet state goes to a higher excited state, whose lifetime is 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 repeats in cycles within the duration of the nanosecond laser pulse. The excited molecules deexcite to the ground state only after a few tens of microseconds (equal to the excited state lifetime) through nonradiative relaxation processes.

Figure 4 shows optical limiting in a C_{70}-toluene solution contained inside the quartz cuvette. Optical limiting is obtained by varying the input laser fluence and measuring both input and output fluences using a laser energy meter. At very low laser fluences, the transmission obeys the Beer-Lambert law and the transmitted fluence varies with increasing input fluence 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 is the number density of the C_{70} molecules, and L is the cuvette length. The curve shows that the solution has a low-intensity transmission of $\simeq$40% and the curve deviates from linearity at 0.35 J cm^{-2}. The intensity becomes completely saturated above an input laser fluence of 1.8 J cm^{-2}. Optical limiting due to reverse saturable absorption (RSA) can be explained using a five-level model. Kojima et al.,[29] discussing 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 obey the relation

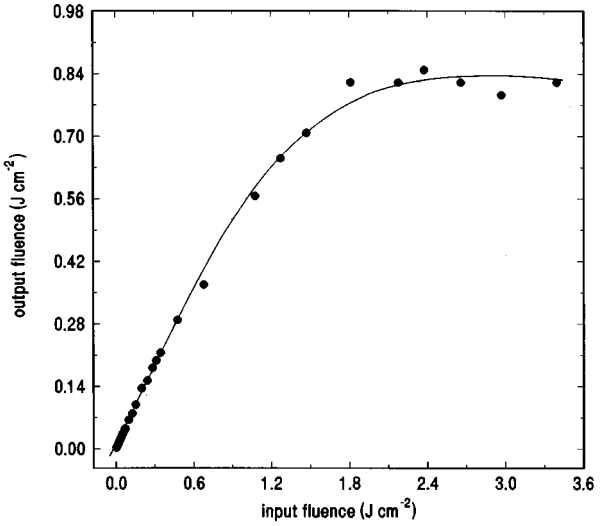

Fig. 4 Optical limiting in C_{70} solution placed inside a 10-mm-long quartz cuvette.

$$\ln\left(\frac{I_0}{I}\right) = k(I_0 - I) + A_g\,, \tag{2}$$

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. This equation implies that a plot of $\ln(I_0/I)$ versus $(I_0 - I)$ should be a straight line with slope k and intercept A_g. Figure 5 shows one such plot and it is almost linear in the fluence range of interest. This is a clear indication that the limiting mechanism in the case of C_{70} in toluene is RSA. Even though effects due to nonlinear refraction are reduced in our experimental arrangement, further investigations are required to test the possibility of nonlinear scattering from the solution.

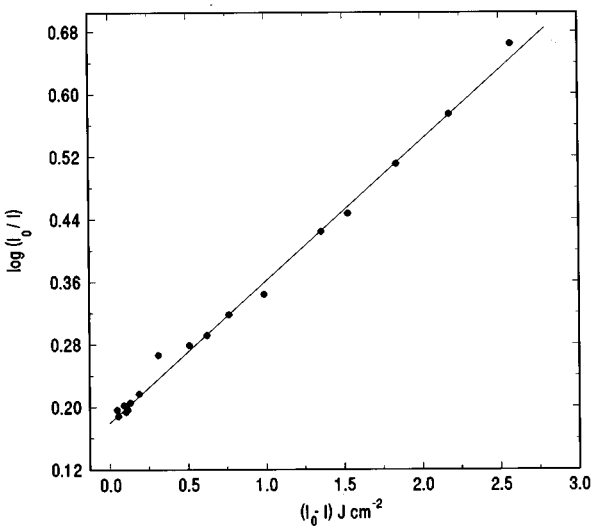

Fig. 5 Plot of log (I_0/I) versus $(I_0 - I)$ showing linearity in the entire fluence range.

In conclusion, we have explored the nonradiative relaxations in C_{70}-toluene solution and found, contrary to our expectations, that there is no PA signal enhancement in the power-limiting laser fluences. Instead, the PA signal tends to saturate in the power-limiting region. This is due to enhanced optical absorption from the photoexcited state and hence depletion of the ground-state population. PA measurements also ruled out the possibility of multiphoton absorption in the C_{70} solution. We also demonstrated that the nonlinear absorption leading to optical limiting is mainly due to RSA.

Acknowledgments

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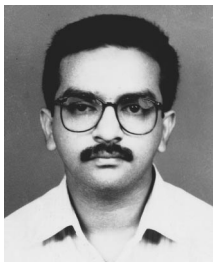

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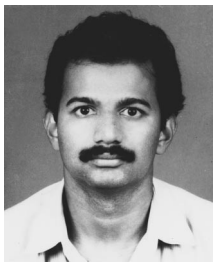

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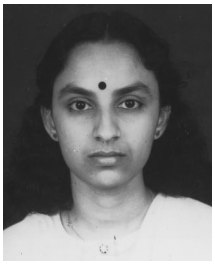

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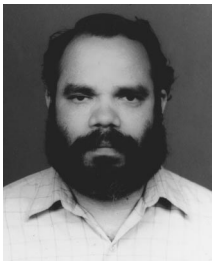

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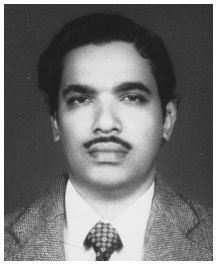

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