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A STUDY OF PHOTOACOUSTIC EFFECTS AND OPTICAL LIMITING IN THE SOLUTION OF C_{60} IN TOLUENE

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Pulsed photoacoustic studies in solution of C_{60} in toluene have been made using the 532 nm radiation from a frequency doubled Nd:YAG laser. Though C_{60} is found to exhibit the phenomenon of optical limiting, the results on photoacoustic measurements do not give any indication of multiphoton transitions as suggested in some of the earlier works. Results of photoacoustic measurements show that excited state absorption is the dominant process responsible for optical limiting while phenomena like nonlinear scattering may contribute to a lesser extent.

1. Introduction

Discovery of high molecular weight stable carbon clusters called fullerenes[1] opened up a new and exciting field of research especially after it became possible to synthesize and isolate them in macroscopic quantities using simple and straight forward methods.[2] Many experiments on fullerene based materials point out to their unique properties like superconductivity, ferromagnetism, electroluminescence, high degree of hardness even higher than that of diamond etc.[3–5] It has been found that C_{60} exhibits optical nonlinearities leading to second harmonic generation[6] and optical limiting.[7] Photophysical[8] and excited state kinetic properties of fullerenes, including fluorescence have been studied at low temperatures[9,10] as well as at room temperature.[11] 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 of $\simeq 2 \times 10^{-4}$ for C_{60} at room temperature.[12] The small singlet–triplet splitting, the very low value of fluorescent rate constant and expected large spin-orbital interaction in these spherical molecules indicate the occurrence of intersystem crossing as a dominant process.

Kost *et al.*[13] studied optical limiting with C_{60} in solid polymer matrices like polymethyl methacrylate. They observed higher threshold for optical limiting in polymer matrices as compared to solutions and attributed this to increase in light scattering cross section in solid matrices. McLean *et al.*[14] suggested various mechanism other than excited state absorption (ESA) for the observation of optical limiting in C_{60}. Joshi *et al.*[15] have found that the optical limiting in C_{60} deviates from a theoretical model based on 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 pulsed photoacoustic (PA) technique[16,17] In this paper, we report the results of PA measurements in C_{60} solution in toluene carried out with a view to elucidate the role of multiphoton absorption process, if any, in optical limiting.

In general the pulsed PA signal amplitude $q(\nu)$ generated in an absorbing liquid media at input laser frequency ν can be written as[16]

$$q(\nu) = \frac{A}{\pi\omega_0^2}\,\sigma(\nu)L_{\mathrm{eff}}N\tau\eta(\nu_m)I^m(\nu) \tag{1}$$

i.e. $q(\nu)$ is proportional to the mth power of the incident laser power density $I(\nu)$, m being the number of photons involved in the process. In the above equation A is a constant determined by calibration factors which include cell geometry, acoustic transducer property etc., $\sigma(\nu)$ the absorption cross section at laser frequency ν, N the density of absorbing molecules, L_{eff} the effective optical path length in the cell given by $L_{\mathrm{eff}} = (1 - e^{-\alpha L})/\alpha$ where α is the absorption coefficient in units of cm^{-1} and ω_0 is the beam waist radius at the focal spot. Therefore assuming the dominance of m photon absorption, the slope of the plot of log $q(\nu)$ vs log $I(\nu)$ will give an indication of the number of photons involved in the process.

2. Experimental

C_{60} used in our experiment was prepared by following Krätschmer–Huffman technique[2] and the sample was further purified by employing high purity liquid chromatography. The extract of C_{60} has the characteristic color and its electronic absorption spectrum was identical with that reported in the literature.[18]

The schematic diagram and other details of the experimental set up used for PA measurements are given elsewhere.[17] Solution of C_{60} is taken 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 pulse repetition frequency of 16 Hz. The pump pulse energy is monitored using a laser power meter and the strength of PA signal is measured using a 200 MHz digital storage oscilloscope. The average amplitude of PA signal is monitored as a function of pump pulse energy.

Simultaneous measurement of the transmitted intensity of the excitation beam at 532 nm shows optical limiting in C_{60}. Figure 1 shows the transmitted laser energy as a function of the input laser energy. At lower energies the output varies nearly

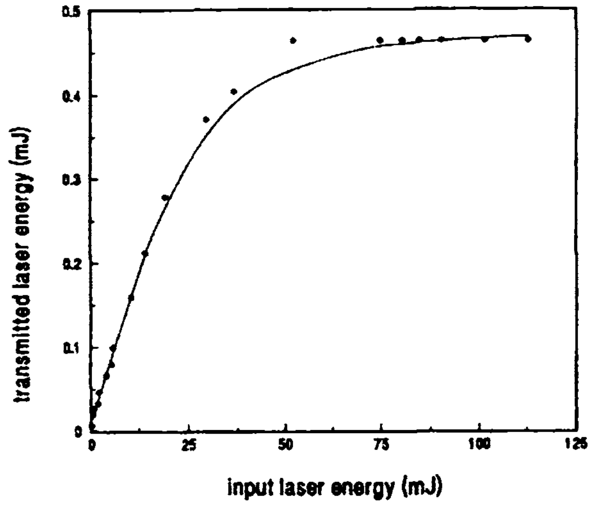

Fig. 1. Variation of output laser energy with input laser energy showing optical limiting in C_{60}.

linearly giving a low intensity transmission of $\simeq 8\%$ and at higher laser energies the transmission is virtually constant. The low percentage of transmission is evidently due to the longer path length of laser light through the solution (4.5 cm). The pump pulse energy and transmitted energy were measured by averaging over sixteen pulses and after making corrections for reflection at window and lens surfaces. The graphs show optical limiting beyond a threshold laser energy 30 mJ.

3. Results and Discussion

At very low laser energies the transmission increases with increasing input energy with a slope equal to $\exp(-N_0\alpha_1 L)$ 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 optical path length. From the above expression we estimate N_0 to be 4.36×10^{17} cm^{-3} for C_{60} solution with $L = 4.5$ cm and[15] $\alpha_1 = 1.25 \times 10^{-18}$ cm^2. At higher laser energies, taking into account the ground state absorption as well as ESA the transmission varies at a rate $\exp -(N_0\sigma_1 + N_1\sigma_2)L$ where N_1 and σ_2 are the population density and absorption cross section for the photoexcited triplet state respectively. It has been found that[8] $\sigma_2 \simeq 2.9\,\sigma_1$. Using the above expressions we estimate N_1 and it is plotted as a function of the input laser energy in Fig. 2. For lower laser energies the population at the excited state grows faster than that in the power limiting region which means that at higher laser energies most of the molecules are in the excited state and the dominant process involved in optical limiting arises mainly from the excited state.

The graph of PA signal as a function of laser energy shown in Fig. 3 exhibits a tendency of saturation at higher laser energies. Optical limiting has been attributed

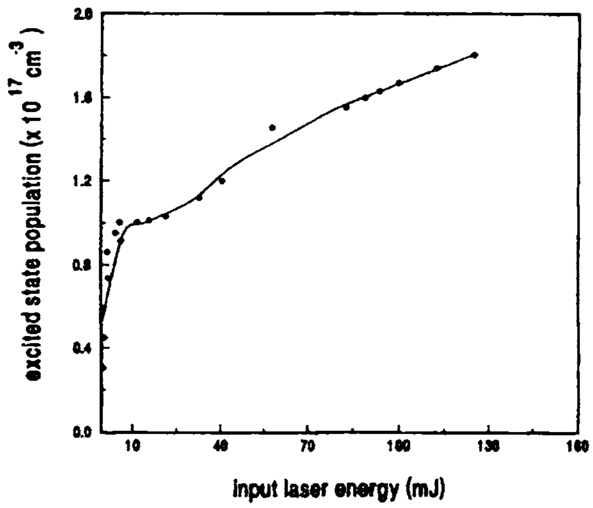

Fig. 2. Plot showing variation of excited state population with input laser energy.

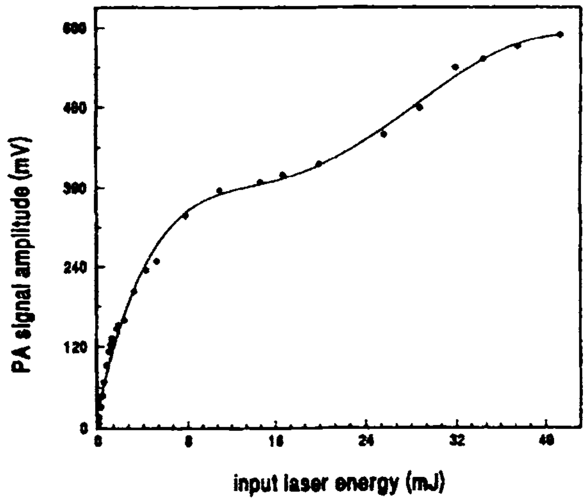

Fig. 3. Change in PA signal amplitude with input laser energy.

mainly to enhanced optical absorption by the sample at higher laser energies due to ESA.[15] The radiative de-excitation cross section of the excited molecules should be small as seen from very low fluorescence quantum efficiency of fullerenes.[12] Therefore one expects enhanced nonradiactive de-excitation probability, particularly at higher laser energies. This should logically result in a major enhancement in the PA signal amplitude in the range of laser energies exhibiting optical limiting. However, the experimental results as given in Fig. 3 do not show any indication of such a major enhancement of PA signal amplitude though a slight increase is observed at the limiting threshold followed by a saturation.

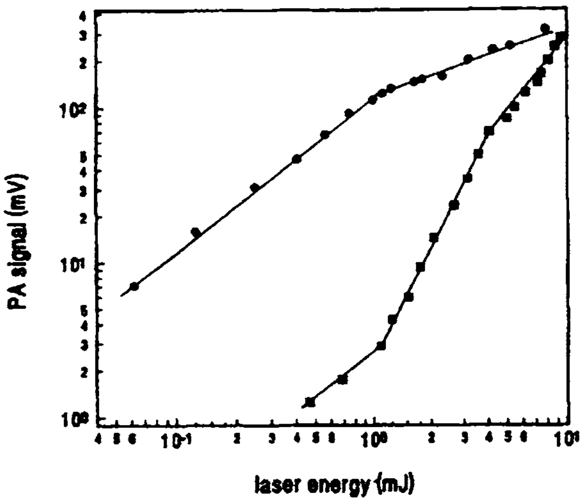

Fig. 4. PA signal strength as a function of input laser energy (■) toluene shows quadratic dependence and (•) C_{60} showing linear dependence.

Log–log plots of PA signal as a function of laser pulse energy for C_{60} and toluene are given in Fig. 4. In the case of pure toluene the initial linear dependence of PA signal on the input laser energy changes into a quadratic dependence after a threshold laser energy thus giving evidence of two photon transitions corresponding to the (one photon) absorption band at 266 nm due to the transition $^1A_1 \rightarrow {}^1B_2$. But after C_{60} is dissolved in toluene the intensity dependence of PA signal is found to be linear and there is no tendency for it to change over to a higher order dependence which suggests that multiphoton transition may not contribute to optical limiting as doubted by Joshi *et al.*[15]

In the power limiting region, the leading part of the laser pulse excites most of the molecules to the excited singlet state from where, due to intersystem crossing, the molecules cross over to the triplet state which has a longer life time. After resonantly absorbing a single photon, the molecule in the triplet state goes to a higher excited state, the life time 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 surrounding solvent molecules. This process repeats in cycles within the duration of the nanosecond laser pulse. Since single photon absorption alone is involved in these cycles the PA signal exhibits only a linear dependence on the laser pulse energy. Thus our PA measurements and determination of excited state populations support the mechanism of excited state cyclic photon absorption to be the major reason for optical limiting in C_{60}. This is further confirmed by the fact that at around the limiting threshold, the nature of variation PA signal as well as that of N_1 exhibits identical behavior. Though to a lesser extent, other nonlinear processes like photon induced chemical reactions, nonlinear scattering etc. also may contribute to the phenomenon of optical limiting in fullerenes along with excited state cyclic one photon absorption which evidently plays a major role in this process.

4. Conclusion

In conclusion, our PA studies show that simultaneous absorption of two photons is an unlikely mechanism for optical limiting in C_{60} solution. Phenomena of optical limiting, therefore, can be attributed to ESA, nonlinear scattering and cyclic photon absorption.

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