

# Excited state dynamics of $C_{60}$ studied using incoherent light

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Received 22 September 1997; in final form 24 November 1997

## Abstract

Excited state dynamics of  $C_{60}$  have been studied using backward degenerate four wave mixing with incoherent light. Estimates of the population relaxation time  $T_1$  of the lower excited singlet state  $S_1$  and phase relaxation time  $T_2$  of the higher excited singlet state  $S_n$  are obtained. The vibrational dephasing in the  $S_1$  state is  $\sim 5$  ps. The results are in good agreement with those obtained using a fs laser. We also present Z-scan data at 600 nm. © 1998 Elsevier Science B.V.

## 1. Introduction

Over the last few years there has been tremendous interest in the optical, physical and chemical properties of fullerenes. It has been well established that organic molecules with highly delocalized  $\pi$ -electron systems exhibit large optical nonlinearities. Fullerenes are also found to have a high value of  $\chi^{(3)}$  [1] with a small absorption coefficient, fast nonlinear response and chemical stability. Although there is considerable variation in the reports on measurements of  $\chi^{(3)}$  values [1–6], fullerenes are found to have a high potential in device applications. Earlier studies indicate  $C_{60}$  and  $C_{70}$  as potential candidates for optical limiting, optical switching and optical bistability [7–11]. Owing to their unique electronic structure, fullerenes find applications in photoconductivity, electroluminescence, superconductivity, cancer therapy and in biological use [12]. Understanding the excited state dynamics in  $C_{60}$  is important, both from the fundamental point of view

and for the wide range of applications. In this Letter we present results of the studies of the excited state dynamics, both in the femtosecond and the picosecond domain, of  $C_{60}$  dissolved in xylene. Measurements of  $\chi^{(3)}$  also indicate high nonlinearity in these samples ( $\sim 1 \times 10^{-11}$  esu at 600 nm at a concentration of  $3.47 \times 10^{-4}$  M) which is attributed to two photon absorption.

## 2. Experimental details

Complete details of the experimental apparatus have been reported in our earlier publications [13,14]. An Nd:YAG laser (6 ns, 100 mJ at 532 nm) is used for pumping the home built rhodamine B dye laser. The laser linewidth (FWHM) is measured to be  $\sim 8$  nm with its maximum at 598 nm and this corresponds to a correlation time ( $\tau_c$ ) of  $\sim 170$  fs. Three beams of equal intensity are derived from the same beam and are focused into the sample with a beam waist of  $\sim 100$   $\mu$ m at the focus. Beam 1 ( $k_1$ ) is designated as the forward pump, beam 2 ( $k_2$ ) is the backward pump and beam 3 ( $k_3$ ) is the probe. The

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sample is placed in a 1 mm cuvette. Beam 1 is fixed, whereas beams 2 and 3 pass through variable delays. Beam 2 passes through a retro-reflector mounted on a micrometer which is delayed manually, whereas beam 3 passes through another retro-reflector mounted on a micrometer controlled by a stepper motor interfaced to a computer. For both the micrometers the resolution is  $\sim 5 \mu\text{m}$  which corresponds to  $\sim 33 \text{ fs}$  in time. Beam 3 makes an angle of  $\sim 10^\circ$  with the forward pump.  $\text{C}_{60}$  ( $> 99\%$  pure) was purchased from Strem Chemicals, USA and is used without further purification. The sample is dissolved in xylene. All the beams have same polarisation.

### 3. Results and discussion

Fig. 1 shows the absorption spectrum, recorded using a UV/VIS spectrometer, of the sample dissolved in xylene. An OD of  $< 0.05$  at 600 nm is chosen for recording the signals. Fig. 2 shows the phase conjugate signal as the probe beam is delayed with respect to beam 1, with beam 2 kept at delay of  $\delta$  with respect to beam 1 (Inset of Fig. 2 shows the schematic of the configuration). The signal is recorded for different values of  $\delta$  varying from  $-300$  to  $300 \text{ ps}$  and the observed linewidths are found to be same for all values of  $\delta$ . We see a sharp coherence peak at  $\tau=0$  due to beams 1 and 3 and another at  $\tau=\delta=9 \text{ ps}$  due to beams 2 and 3. It has

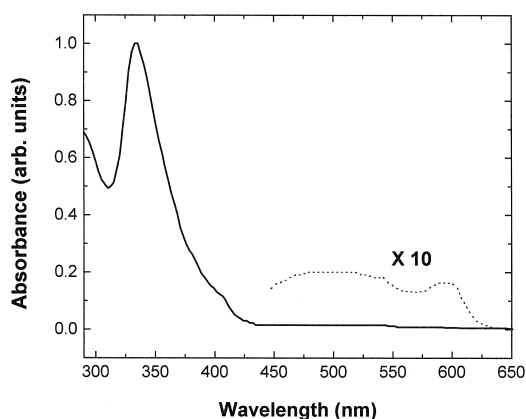


Fig. 1. Absorption spectrum of the sample,  $\text{C}_{60}$  dissolved in xylene.

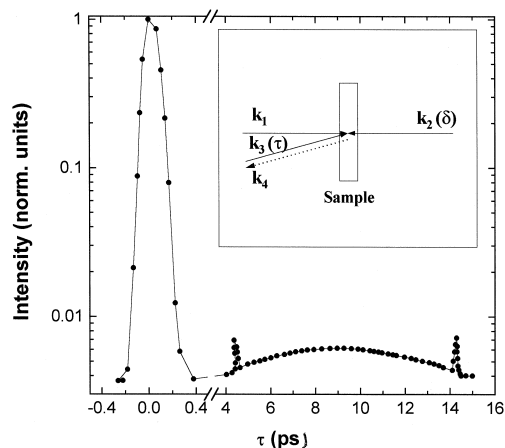


Fig. 2. Time resolved spectrum of the phase conjugate signal for  $\delta = 9 \text{ ps}$ . Inset shows the FWM apparatus in phase conjugate configuration.

been shown that the ratio of these peaks would give information on the population relaxation time of the lower excited state [15] and the linewidths give information on the dephasing of the  $S_n$  and  $S_1$  states [14]. The width (FWHM) of the first coherence peak at  $\tau=0$  is  $\sim 170 \text{ fs}$ , the width (FWHM) of the second peak at  $\tau=\delta$  is  $\sim 5 \text{ ps}$ , the ratio of these peaks  $\sim 430$ . Rosker et al. [16] employ the standard backward degenerate four wave mixing (DFWM) using  $150 \text{ fs}$  pulses at  $633 \text{ nm}$  and delay the backward pump beam to record the phase conjugate signal. They observe three different decay times,  $260 \text{ fs}$ ,  $4.6 \text{ ps}$  and  $64 \text{ ps}$  in the signal. In our present study, the three observed time scales are assigned to the relaxation processes in the upper and the lower excited states.

The intersystem crossing rate would not play an important role in the time scales of the present studies. Two photon and/or excited state absorption take the molecules from the vibrational manifold of the ground state to the upper states of  $S_n$ . The upper states  $S_n$  will relax back to the  $S_1$  state on fs time scale and in the process generate a vibrationally excited  $S_1$  state. Peak 1, which has a fast response time in fs, is attributed to the dephasing of the excited states  $S_n$ . The width of the second peak, of the order of few ps, is attributed to the vibrational dephasing of the  $S_1$  state. From the observed linewidths, we estimate the dephasing time of the  $S_n$

states to be less than 170 fs (which is the limit of the present resolution due to the 8 nm bandwidth of the dye laser) and the dephasing time of  $S_1$  state to be  $\sim 5$  ps. From the ratio of the two peaks we calculate the population relaxation time of  $S_1$  state to be  $\sim 70$  ps ( $430 \times \tau_c$ )

A wide range of values have been reported for the relaxation process in this molecule varying from 30 ps to 1.3 ns [17–22]. Cheville and Halas [17] have reported a carrier relaxation time of  $\sim 43$  ps in a  $C_{60}$  thin film on a sapphire substrate. Fleischer et al. [19] used 50 fs pulses at 625 nm and report the decay rate for solid  $C_{60}$  as  $\sim 30$  ps. Wasielewski et al. [22] report a decay rate of 33 ps for  $C_{60}$ . Lee et al. [23] report a value of 1.3 ns for the  $S_1$  state lifetime. In the present technique, the ratio of the two peaks depends on the lifetime of the lower excited state. For  $S_1$  states with a lifetime of few ns, the second peak would be three to four orders of magnitude weaker than for the ps relaxation components. This has been confirmed from the results on Rhodamine B and Rhodamine 6G solutions, where we do not observe the second peak as the lifetimes of the  $S_1$  states in these dyes are of the order of ns. Our results, therefore, reveal a fast relaxation component of the  $S_1$  levels in the  $C_{60}$  molecule and since the ratio of the two peaks a representation of the lower excited state lifetime, we attribute the calculated ratio of the two peaks to the fast relaxation component of the  $S_1$  state lifetime.

We have performed an open aperture Z-scan [24] with the broad band dye laser and find a valley (Fig. 3) in the scan indicating a two photon absorption

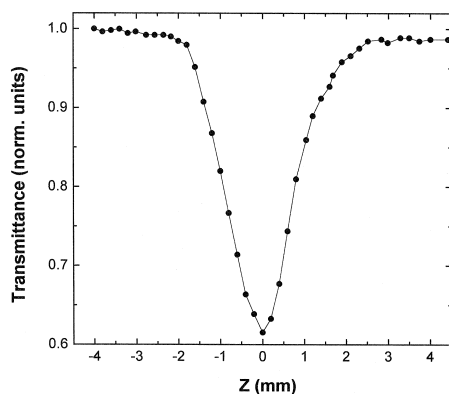


Fig. 3. Open aperture Z-scan of the sample.

(TPA) and/or excited state absorption (ESA). Lee et al. [23] have identified the energy of the singlet states in  $C_{60}$ .  $S_1$  falls in the  $\sim 16000$   $\text{cm}^{-1}$  range and the  $S_n$  state falls in the  $\sim 29000$   $\text{cm}^{-1}$  range. Two photon absorption, with fs pulses at 612 nm [25] and a CW beam at 633 nm [26], has been reported. We work at a wavelength of  $\sim 600$  nm ( $16600$   $\text{cm}^{-1}$ ) and the two photon energy corresponds to  $\sim 33000$   $\text{cm}^{-1}$ . It is likely that TPA may dominate in our present studies. Theoretical studies are in progress to determine the contribution of TPA and ESA in populating the  $S_n$  states.

Although there is a wide literature available [1–6] on the measurement of  $\chi^{(3)}$ , there are also a wide range of values reported ( $\sim 10^{-8}$  to  $10^{-12}$  esu). We have measured  $\chi^{(3)}$  using the same broad band laser (600 nm) and  $\text{CS}_2$  as a reference ( $\chi^{(3)}$  of  $\text{CS}_2$  is taken as  $6.8 \times 10^{-13}$  esu). Signals are recorded at low intensity levels, by observing the cubic dependence of the signal with input intensity variation. We observed a variation of 7–8 times in the signal intensity for a variation of input intensity by a factor of 2. Our results indicate a value of  $\sim 1 \times 10^{-11}$  esu (for a concentration of  $3.47 \times 10^{-4}$  M). This observed high value of  $\chi^{(3)}$  is attributed to the a possible strong TPA at 600 nm.

Apart from the two coherence peaks we also observed two sharp peaks overriding the broader peak (Fig. 2). These sharp peaks observed on the shoulders of the broad peak are found to be due to coherence of probe beam (beam 3) and the reflections of the backward pump (beam 2) from the surfaces of the cell. This was confirmed by using cuvettes of different size. The broader peak appears at  $\tau = \delta$  and therefore its position is dependant on the delay of second beam (beam 2) [16].

#### 4. Conclusions

In conclusion we have estimated the excited state life times of  $C_{60}$  in xylene solution. The results agree well with those obtained using a fs laser. Using a broad band dye laser we are able to estimate the dephasing times of the excited  $S_n$  states ( $< 170$  fs), the longitudinal relaxation time ( $\sim 70$  ps) and the vibrational dephasing time ( $\sim 5$  ps) in the  $S_1$  state.

The higher value of  $\chi^{(3)}$  at 600 nm is attributed to TPA.

### Acknowledgements

One of the authors, DNR acknowledges the financial support of DST (Government of India) for experimental facilities. SVR is thankful to UGC for financial support. We also duly acknowledge the help of Mr. G. Panda during the experiment.

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