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Near-Resonant Nonlinear Optical Response of Fullerene C_{60}

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Abstract Time-resolved degenerate four-wave mixing experiments were conducted on toluene solutions and film of C_{60} using the second harmonic generation of a 50 picosecond mode-locked Nd : YAG laser. A fast nonlinear optical response was observed from both C_{60} toluene solutions and C_{60} film, and another long-lived component was observed only from C_{60} toluene solutions. The near resonant third-order nonlinear optical susceptibility $\chi^{(3)}_{xxxx}(\omega,\omega,-\omega,\omega)$ of C_{60} estimated from the experimental result of the film is about $(3.6 \pm 1.4)\times 10^{-10}$ esu.

Key words fullerene C_{60}, nonlinear optics.

The availability of macroscopic quantities of C_{60} and C_{70}[1], together with the earlier theoretical predictions and experimental observations, allows for further systematic study on this new class of materials. Fullerenes possess highly delocalized π-electrons and are expected to exhibit large optical nonlinearity similar to conjugated polymers such as polydiacetylene and polydiacetylene which have received considerable interest in recent years.

Recent measurements of the third-order nonlinrear optical response of C_{60} solutions and thin films by non-resonant degenerate four-wave mixing (DFWM) or DC electric field induced second harmonic generation (EFISHG) technique were reported [2~5]. But the obtained values of $\chi^{(3)}$ of C_{60} scattered by over several orders which need to be clarified. Blau[2] performed the DFWM experiment at 1.06 μm on C_{60} benzene solution and obtained the $\chi^{(3)}$ value of 1×10^{-8} esu, while Kafafi[3] got the $\chi^{(3)}$ value of 7×10^{-12} esu on C_{60} film under the simiar conditions. From THG measurements on C_{60} film Y. Wang[4] obtained the $\chi^{(3)}$ value of 9×10^{-12} esu at 1.91 μm and 3×10^{-11} esu at 1.32 μm, and Hoshi[5] reported the value $\chi^{(3)}=2\times 10^{-10}$ esu at 1.06 μm. In this letter, DFWM experiment of C_{60} under near resonant conditions was reported using a picosecond laser with wavelength 532 nm which lay within the absorption band of C_{60} between 440 nm and 670 nm. Due to the absorption, the thermal contributions are inevitably involved and may overwhelm the pure electronic DFWM contribution as in nanosecond pulse case in our earlier experiments. In order to separate the contributions of different mechanisms, we choose a picosecond laser system as the excitation source.

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Buckminsterfullerene C_{60} was prepared and purified as described in the literature[1]. Magenta solutions up to a maximum concentration of 0.4 mg/ml in toluene were provided. C_{60} films were prepared in a vacuum chamber with C_{60} placed inside a crucible and vaporized by resistive heating at 500°C. The thickness of C_{60} films on quartz substrate is 0.2 μm.

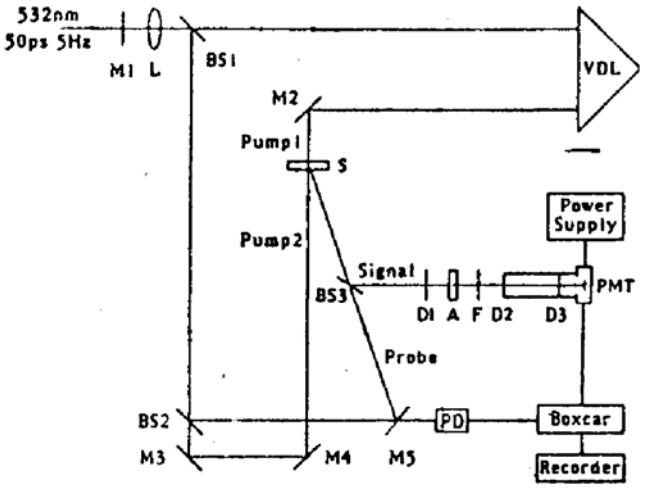

Fig. 1 The experimental setup of the ps DFWM measurement. M1, M2, M3, M4, M5- mirrors; L- lens; BS1, BS2, BS3- beam splitters; VDL-variable delay lines; S-sample; D1, D2, D3-diaphragm; A — attenuator; F-filter; PMT- Photomultiplier tube; PD-photodiode

A typical counter-propagating phase-conjugated DFWM set-up shown schematically in Fig. 1 was used to measure the nonlinear optical properties of C_{60} toluene solutions and films. The laser source was frequency doubled mode-locked Nd : YAG laser with a 50 ps duration and repetition rate of 5 Hz. The average energy per pulse was about 1 mJ. Time-resolved studies were conducted by inserting the time delay line in the backward pump beam. The cross angle of the probe and forward pump beams was 30 degrees. The diameter of the beams incident upon samples were about 300 μm. All beams were polarized horizontally. The generated DFWM signal was reflected by a beamsplitter and after passing several apertures was detected by a photomultiplier R446.

The temporal response of the phase conjugated signals of C_{60} film was measured as a function of the delay time of the back pumping beam which is shown in FIg. 2. A sharp peak with full width at half maximum (FWHM) 70 ps was observed. Similar peaks with the same FWHM were also observed from CS_2 and neat toluene liquid in 5 mm thick cells. Since both CS_2 and pure toluene have no absorption at 532 nm, we think these 70 ps signals represent the fast nonlinear optical response originating from distortion of electron clouds of the molecules. For the C_{60} case, the three-dimensional π-electron systems play an important role. Taking CS_2 as a reference ($\chi^{(3)}_{CS_2}=6.8\times10^{-13}$ esu) and considering the effects of refractive index, beam absorption and the beam-sample interaction lengths in the CS_2 and C_{60} film cases (the interaction length for the film is 0.2 μm, while in CS_2 case it was estimated from the beam diameter and the interaction angle to be about 2.4×10^{2} μm), the third-order nonlinear optical susceptiblity $\chi^{(3)}_{xxxx}(\omega,\omega,-\omega,\omega)$ of C_{60} is estimated to be $(3.6\pm1.4)\times10^{-10}$ esu. This value is about fifty times bigger than the value reported in reference 7 obtained under off-resonant condition (at 1.06 μm) with negligible absorption. So considering resonant enhancement effect, our result agree reasonably with the published data except the early result of Blau[2] with big error[6]. Recently, Marcy[7] reported the $\chi^{(3)}$ value of 2×10^{-10} esu measured by DFWM at 632.5 nm which is also in agreement with our result. The near-resonant enhanced factor of $\chi^{(3)}$ from 1.06 μm to 532 nm is about 50. It can also be seen from the THG results of Wang[4] and Hoshi[5] that the $\chi^{(3)}$ value becomes larger when the wavelength of the fundamental light decreases. Comparing the THG output frequency of 1.06 μm and 1.32 μm light with the absorption spectrum of C_{60} film, possibly we can attribute this augment to the three-photon resonance enhancement.

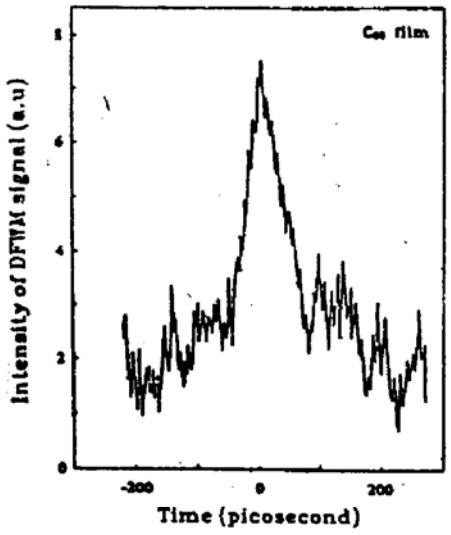

Fig. 2 Time dependence of the DFWM signal of C_{60} film. The thickness of the film was 0.2 μm. All four beams were polarized horizontally

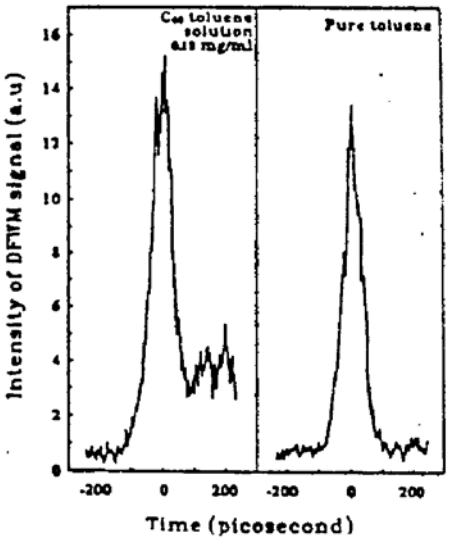

Fig. 3 Time dependence of the DFWM signal of C_{60} toluene and pure toluene. The concentration of C_{60} toluene solution was 0.18 mg/ml

The DFWM signals of C_{60}-toluene solutions with different concentrations were measured. Typical time behaviors of the DFWM signals of the C_{60} solution samples and neat toluene are shown in FIg. 3. Also at zero time delay, a sharp peak was present for C_{60}-toluene solution, but after that a long lived component was also observed. Because of the absorption, this signal of slow response may come from the population grating, or from the diffraction of the probe light by the thermal grating and the temperature variation in solution which causes a periodic change of the refractive index. Although the C_{60} content is low, its significant contribution to the tail signal is comprehensible if we notice its relatively large absorption to the 532 nm light. We did not observe such a tail in the C_{60} film, which may be due to its small thickness compared with the period of the grating. Thus, by using a ps laser source, the electronic and other contributions of the solution to DFWM signal can be distinguished which would otherwise be mixed in the ns experiment. The origin of the slow-response signal could be further studied if the delay time could be extended to the nanosecond scale. From Fig. 3, we can see that the DFWM signals of C_{60} solution at zero time delay is a little more intense than that of neat toluene because of the low concentration of C_{60} in solutions and light absorption. The calculated $\chi^{(3)}$ value from C_{60} solution with varied fiullerene concentrations agree with the result acquired from the film within a factor of 2, ignoring the local field factor.

In conclusion, we have measured the time dependence of the ps DFWM signals from C_{60} films and C_{60} toluene solutions. By using ps time-resolved measurement, the contributions from the pure electronic and other effects were separated. The nonlinear optical susceptibility determined from C_{60} films at 532 nm was $(3.6\pm1.4)\times10^{-10}$ ssu which was resonantly enhanced compared with the value at 1.06 μm.

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富勒烯 C_{60} 的近共振非线性光学响应

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摘 要 利用锁模 Nd：YAG 激光器的 50 ps 和倍频光输出对 C_{60} 甲苯溶液及 C_{60} 膜进行了时间分辨简并四波混频测量. 从溶液及膜都观察到一个很快的非线性光学响应. 而一个较长寿命的成分仅在溶液中见到. 由实验结果可以推算得 C_{60} 的近共振三阶非线性光学极化率 $\chi^{(3)}_{xxxx}(\omega,\omega,-\omega,\omega)$为$(3.6\pm1.4)\times10^{-10}$ esu.

关键词 富勒烯 C_{60}， 非线性光学.