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Nonlinear optical parameters of films and solutions containing fullerenes

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Abstract. Nonlinear optical parameters of polyimide and toluene films containing fullerenes C_{60} and C_{70} are studied by the method of *Z*-scan. The nonlinear refractive indices of these structures are measured at the emission wavelength of a Nd : YAG laser at 1064 nm. The two-photon absorption and nonlinear susceptibility of solutions and films containing fullerenes are studied.

1. Introduction

Scanning of a sample through the focusing region, which was first proposed in papers [1, 2] and was called the method of *Z*-scan, permits the measurement of basic nonlinear optical parameters of many materials. The authors of papers [1, 2] realised for the first time a new, highly sensitive single-beam method of measurements of the nonlinear refractive index and the nonlinear absorption coefficient of optical media. The method is based on the study of the variation in the intensity of a Gaussian beam in the far-field zone during the movement of a sample in the region of beam focusing.

The main advantage of this method is that to measure the nonlinear parameters, it is sufficient to know only the transmission of radiation by the substance under study. Note also that this method permits the measurements of nonlinear parameters independently of each other, thereby allowing one to distinguish different nonlinear mechanisms that can be involved [2].

Nonlinear optical parameters of fullerenes have been actively recently studied in connection with the possibility of their using as elements for limiting optical transmission at a certain intensity level (optical limiting). Such materials have high nonlinear-optical coefficients and fast response [3 – 7]. Most studies of the nonlinear optical properties of fullerenes have been performed by the methods of degenerate four-wave mixing and third harmonic generation. Already first experiments [8] on phase conjugation in fullerene solutions have demonstrated a substantial increase in the reflection coefficient of the phase-conjugated wave near resonance transitions. The studies of degenerate four-wave scattering of light in fullerene films and solutions yielded the values of the nonlinear susceptibility $\chi^{(3)}$, which is responsible for phase conjugation at different wavelengths [8, 9]. In addition, the nonlinear responses of these systems related to the second [10 – 14] and third [10, 15, 16] harmonic generation have been investigated. The authors of these papers have found high nonlinear susceptibilities in films containing C_{60} at a wavelength of 1064 nm [$\chi^{(3)}(-3\omega;\omega,\omega,\omega) = 2\times10^{-10}$ CGSE units and $\chi^{(3)}(-2\omega;\omega,\omega,0) = 2.1\times10^{-9}$ CGSE units].

The inverse absorption saturation in fullerenes results in an increase in absorption with increasing intensity of laser radiation [5, 17]. It is known that this effect is explained by the fact that the cross section for absorption from excited states is higher than that from the ground state. Therefore, materials that exhibit the inverse saturated absorption are excellent candidates for using as optical limiters [18, 19].

We studied here the nonlinear optical parameters of fullerenes C_{60} and C_{70} in polyimide films and toluene by the *Z*-scan method using 35-ps pulses. We measured the nonlinear-optical refractive indices and susceptibilities caused by Kerr nonlinearities at the emission wavelength of a Nd : YAG laser and also studied nonlinear absorption coefficients of these samples.

2. Experimental setup

We used in our experiments a Nd : YAG laser emitting a train of picosecond pulses. A single 35-ps pulse, which was separated from the train, was amplified up to the energy 2.4 mJ. We studied nonlinear optical parameters of films and solutions of fullerenes at the emission wavelength of a Nd : YAG laser at 1064 nm. The laser radiation was focused by lens *1* with a focal distance of 25 cm (Fig. 1). A quartz

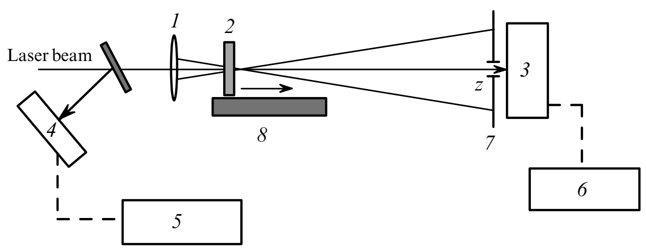

Figure 1. Scheme of experiments: (*1*) focusing lens; (*2*) sample; (*3, 4*) photodiodes; (*5, 6*) digital voltmeters; (*7*) aperture; (*8*) micropositioning table.

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cell *2* or a plate with a deposited fullerene film, which were placed on a micropositioning table *8*, were displaced along the optical axis Z, passing through the focusing region.

The size of the focused radiation region in the beam waist was 100 μm. The radiation intensity in this region was 5×10^{10} W cm^{-2} in experiments with fullerene films and 1.2×10^{11} W cm^{-2} in experiments with fullerene solutions, i.e., it was below the thresholds of optical breakdown and multiphoton ionisation of the samples ($I_{dc} = 8 \times 10^{10}$ and 3×10^{11} W cm^{-2}, respectively). The use of lenses with a lower focal distance (15 cm) resulted in the optical breakdown in the sample.

The laser radiation exhibited ~ 10 % fluctuations from pulse to pulse. The energy of individual laser pulses was detected with a calibrated FD-24K photodiode *4* equipped with a V4-17 digital voltmeter *5*. The laser radiation energy was varied using calibrated neutral filters.

At a distance of 150 cm behind the focusing region, aperture *7* of diameter 1 mm was placed (the so-called scheme with a limiting aperture), which transmitted about 3% of the laser radiation energy. Behind the aperture, an FD-24K photodiode *3* was placed, whose output signal was fed into a V4-17 digital voltmeter *6*. To eliminate the influence of instability of the laser output on the results of measurements, a signal detected with photodiode *3* was normalised to the signal detected with a second photodiode *4*. Each point in the experimental plots presented below was obtained by averaging over 10 laser pulses.

Using the scheme with a limiting aperture, we measured the nonlinear refractive index n_2 and its sign for solutions and films, as well as their nonlinear susceptibilities $\chi^{(3)}$. To determine the nonlinear absorption coefficient β, the aperture was removed and the dependence of the transmission of solutions and films on their position with respect to the focal spot was measured (the so-called scheme with an open aperture).

The dependence of the transmission of samples on the laser beam intensity was measured with a power meter, which had a sufficiently large detection area and was placed at such a distance from the focal point that provided the detection of all the radiation transmitted through the sample. Therefore, a decrease in the sample transmission measured in the scheme with an open aperture was caused by nonlinear absorption.

Spectral measurements were performed using a SF-26 spectrophotometer. We studied polyimide films doped with C_{70} and solutions of C_{60} and C_{70} in toluene. The film thickness was 1.25 μm. The weight concentration of C_{70} in films was 0.2% and 0.5%. Polyimide films containing fullerenes were deposited on glass substrates. We studied solutions of C_{60} in toluene at weight concentrations 0.5% and 0.05% and solutions of C_{70} in toluene at weight concentrations 0.1% and 1%.

3. Results and discussion

Fig. 2a shows the typical dependences of the transmission of the 0.5 % solution of C_{60} in toluene on the cell position with respect to the focusing point. Similar dependences were obtained for solutions and films with C_{70}. The nonlinear refractive index of all the samples had the negative sign. One can see the scatter of the experimental points in this and other figures, which is caused by the instability of the energy and (mainly) temporal parameters of the laser radiation. The dependences we observed are typical for the objects studied and are caused by Kerr nonlinearities that produce a change in the refractive index in the field of the intense wave.

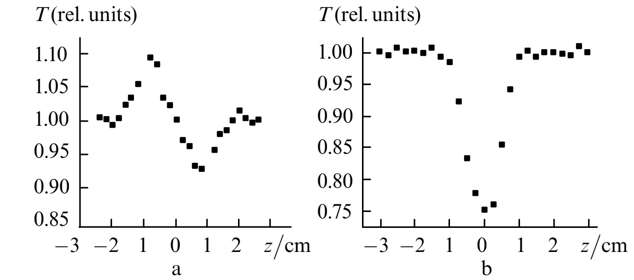

Figure 2. Normalised transmission T as a function of the position of a cell with the 0.5 % solution of C_{60} in toluene in a scheme with (a) limiting and (b) open aperture.

Cubic nonlinearities of the refractive index, which depend on the intensity, are determined by the known relation [2]

$$n = n_0 + 0.5n_2|E|^2 = n_0 + \gamma I, \quad (1)$$

where n_0 is the linear refractive index; I is the radiation intensity; and γ is the hyperpolarisability of the medium. The nonlinear refractive index n_2 and hyperpolarisability γ are related by the expression

$$\gamma = 40\pi n_2 c^{-1} n_0^{-1}, \quad (2)$$

where γ is measured in m^2 W^{-1}, n_2 and n_0 are measured in CGSE units, and the speed of light, c in m s^{-1}.

We chose the radiation intensity in our experiments so that to avoid the optical breakdown on the film surface or inside a cell with solution. In particular, the radiation intensity in experiments with films containing C_{70} achieved 5×10^{10} W cm^{-2}. This intensity was close to the optical breakdown threshold, which, according to our estimates, was 8×10^{10} W cm^{-2}.

We estimated the transmission of the samples and determined their nonlinear optical parameters using the equations of the theory of the Z-scan method [2]

$$\Delta T_{pv} = 0.404(1 - S)^{0.25}|\Delta\Phi_0|, \quad (3)$$

$$\Delta\Phi_0 = (2\pi/\lambda)n_2 I L_{eff}, \quad (4)$$

where ΔT_{pv} is the normalised difference of the maximum and minimum transmission for the dependence $T(z)$; S is the aperture transmission (the fraction of radiation incident on the photocathode); $\Delta\Phi_0$ is the phase shift of radiation transmitted through a cell; λ is the radiation wavelength;

$$L_{eff} = [1 - \exp(-\alpha L)]\alpha^{-1} \quad (5)$$

is the effective length of a sample; L is the sample length; and α is the linear absorption coefficient.

The linear absorption of the 0.5 % solution of C_{60}, 1 % solution of C_{70}, and a polyimide film containing 0.5 % of C_{70} was 1.2, 2, and ~ 500 cm^{-1}, respectively. The nonlinear refractive index of the 0.5 % solution of C_{60} in toluene calculated from expressions (3)–(5), taking into account the experimental data, is $n_2 = 1.3 \times 10^{-12}$ CGSE units.

The nonlinear susceptibility of each sample was determined from the expression [20]

$$\chi^{(3)} = \frac{\gamma n_0^2}{5.2 \cdot 10^{-6} K^{(3)}}, \tag{6}$$

where $K^{(3)}$ is a constant of about unity, and $\chi^{(3)}$ and γ are measured in the same units as in (3). For the 0.5 % solution of C_{60} in toluene, $\chi^{(3)} = 2 \times 10^{-12}$ CGSE units at 1064 nm.

It is known that the nonlinear refraction of a medium can be determined by different processes, such as Kerr focusing [21], thermal focusing [22], focusing caused by the movement of populations [23], etc. Because the radiation intensity in our case was rather high (5×10^{10} W cm^{-2} in experiments with films and 1.2×10^{11} W cm^{-2} in experiments with solutions), the contribution from hyperpolarisability resulting in the Kerr focusing should exceed the contribution from the rest two mechanisms.

The measurements of nonlinear absorption of samples showed that, within the error of measurements of the relative transmission (2 %), nonlinear absorption was distinctly observed only in the solution of C_{60} in toluene. Fig. 2b shows transmission of the 0.5 % solution of C_{60} in toluene measured using the scheme with an open aperture. One can see that the dependence of the normalised transmission of the solution on the position of a cell with respect to the focal point is typical for nonlinear absorption.

Nonlinear absorption in this case could be caused by inverse saturated absorption due to excitation of aggregates to higher-lying energy levels that have greater absorption cross sections compared to that from the ground level.

The inverse saturated absorption, which occurs due to a greater absorption from the excited stage than from the ground state, results in the increase in absorption with increasing the exciting radiation intensity [18]. The substances that exhibit the inverse saturated absorption are promising for the use in optical limiters for protecting eyes and other photodetectors against laser pulses.

The nonlinear absorption coefficient β can be determined from expressions [24]

$$\beta = q_0 I^{-1} L_{\text{eff}}^{-1}, \tag{7}$$

$$T_0 = q_0^{-1} \ln(1 + q_0), \tag{8}$$

where q_0 is a dimensionless parameter; T_0 is the minimal normalised transmission in the scheme with an open aperture. For the 0.5 % solution of C_{60} in toluene, $\beta = 1.5 \times 10^{-10}$ cm W^{-1} at 1064 nm.

Fig. 3 shows the absorption spectra of films and solutions of fullerenes. The absence of noticeable nonlinear absorption in films and solutions of C_{70} is explained by the fact that the resonance lines of C_{70} lie in the UV region, which reduces the probability of two-photon absorption at 1064 nm. In the case of C_{60}, the resonance line is located at 565 nm, which provides two-photon absorption.

The nonlinear optical parameters of other samples were determined in the same way. Fig. 4 shows the transmission of solutions of C_{70} at different fullerene concentrations, and Fig. 5 presents the transmission of polyimide films containing C_{70} at different concentrations. One can see that the difference between the maximum and minimum transmission for films containing C_{70} is somewhat greater than that for sol-

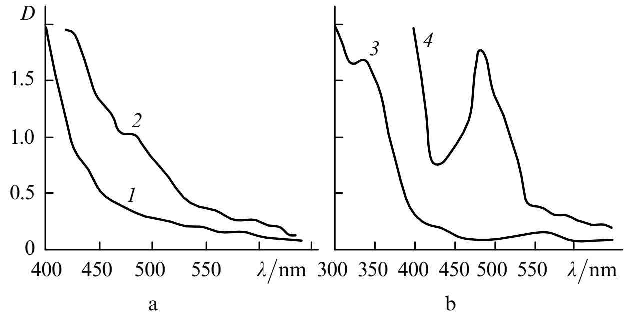

Figure 3. Absorption spectra D of (a) films and (b) solutions of fullerenes. (*1*) Polyimide film without fullerene; (*2*) film containing 0.5 % of C_{70}; (*3*) the 0.5 % solution of C_{60} in toluene; (*4*) the 1% solution of C_{70} in toluene.

utions of C_{70}. As the laser radiation intensity in the focus was decreased from 5×10^{10} (Fig. 5) to 2×10^{10} W cm^{-2}, the influence of nonlinear refraction on the dependence $T(z)$ for a pure polyimide film completely disappeared.

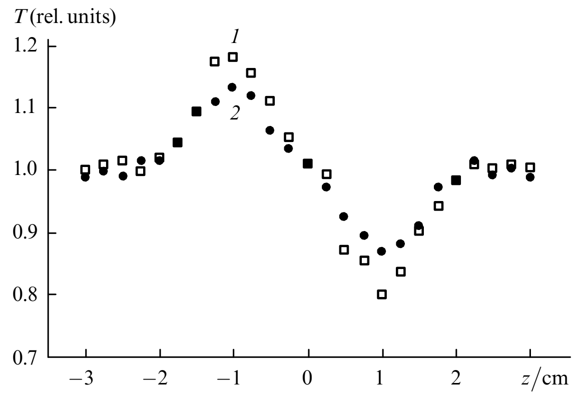

Figure 4. Normalised transmission T as a function of the position of a cell with (*1*) the 1 % and (*2*) 0.1 % solution of C_{60} in toluene in a scheme with a limiting aperture.

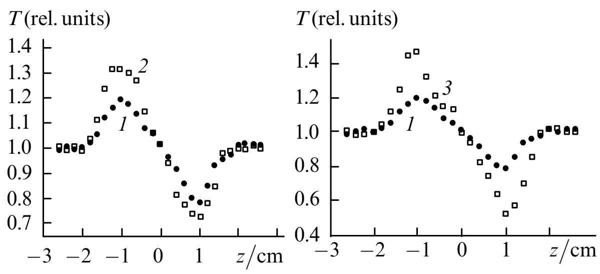

Figure 5. Normalised transmission T as a function of the position of plates with fullerene C_{70} films in a scheme with a limiting aperture for (*1*) a pure polyimide film and the polyimide film containing (*2*) 0.2 % and (*3*) 5 % of C_{70}.

The results of measurements of the nonlinear refractive index n_2, the nonlinear susceptibility $\chi^{(3)}$, and the two-photon absorption coefficient β of films and solutions of fullerenes at 1064 nm are summarised in Table 1.

As was mentioned above, the media that exhibit the inverse saturated absorption are promising for the use in optical limiters. This property of fullerenes was demonstrated earlier for films containing C_{60} and C_{70} [7] and fullerene sol-

Table 1. Nonlinear optical parameters of fullerenes

Substance	Weight concentration (%)	n_2/CGSE units	$\chi^{(3)}$/CGSE units	β/cm W^{-1}
Polyimide film with C_{70}	0.2	-1.2×10^{-9}	1.9×10^{-10}	–
Polyimide film with C_{70}	0.5	-1.4×10^{-9}	2.2×10^{-10}	–
Solution of C_{70} in toluene	0.1	-5×10^{-13}	8×10^{-14}	–
Solution of C_{60} in toluene	0.5	-1.3×10^{-12}	2×10^{-13}	1.5×10^{-10}

utions [5, 17, 21] at the wavelength 532 nm of the second harmonic of a Nd : YAG laser.

Below, we present the results of the study of optical limiting at 1064 nm in our samples. Fig. 6 shows the typical dependence of the transmission of a cell with the 0.5 % solution of C_{60} in toluene on the radiation intensity. The transmission did not change up to $I = 4 \times 10^{10}$ W cm^{-2} and began to decrease as the radiation intensity was further increased. The solution of C_{70} did not exhibit a similar dependence. Thus, solutions of C_{60} can produce optical limiting in the IR region.

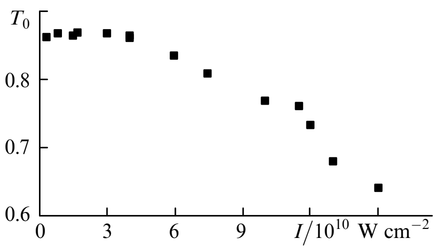

Figure 6. Dependence of the transmission of a cell with the solution of C_{60} in toluene on the radiation intensity at 1064 nm.

4. Conclusions

Films and solutions of C_{60} and C_{70} are of interest for applications in optical modulation and in optical limiters of laser radiation. Using the Z-scan method, we measured the third-order nonlinear optical susceptibility, which causes a change in the refractive index of these media, and the nonlinear refractive index, and studied the nonlinear absorption of these solutions. The samples studied have the negative refractive index at 1064 nm. The nonlinear absorption was only observed in solutions of C_{60} in toluene.

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