Application of Nonlinear Light Scattering in Nanocarbon Suspensions for Adjustment of Laser Pulse Duration

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It is shown that the scanning an optical cell containing the aqueous suspension of multiwalled carbon nanotubes with the focused laser beam along the optical axis leads to an increase of the nonlinear scattering. This is accompanied by a smooth change of the nanosecond laser pulse duration transmitted through the suspension. A pulse shortening occurs as the cell approaching the beam waist due to cutting off the trailing part of the incident laser pulse. Thus the full width at half maximum of the transmitted laser pulse through suspension decreases with the increase of the incident laser power density. In experiments the incident YAG: Nd3+ laser passive Q-switched pulses of 16 ns duration have been smoothly adjusted in the range of 16–10 ns.

Keywords: Optical Power Limiting, Laser Pulse Duration, Carbon Nanotube Suspension.

1. INTRODUCTION

The passive Q-switched lasers with outcoming pulses of nanosecond duration are often used in the different fields of experimental physics. An adjustment of the pulse duration of such lasers is possible by introduction into the laser resonator the additional losses by the electro-optic switches, the nonlinear absorbers or by a variation of length and configuration of the resonator. A shortening of the powerful nanosecond laser pulses can be carried outside the resonator using a stimulated Brillouin scattering or a stimulated Raman scattering in compressed gases. However, the stimulation of these types of scattering in gases can be excited only at a high power density, and the duration of obtained pulses of light is not regulated and is mainly determined by the length of the gas cells.

In recent years, a considerable effort has been devoted to investigations of the phenomenon of the optical limiting (OL) in various materials and media in order to use them in some applications. For instance, studying the OL in suspensions of carbon nanoparticles is interesting for creation of the reliable limiters of the laser radiation power in a broad spectral range and development the new methods of control over the parameters of the laser pulses. Conventionally, the OL is studied using the so called z-scanning technique, according to which the optical transmission coefficient of the cell filled with a suspension is measured for the cell various positions relative to the waist of a focused laser beam. According to a mechanism, responsible for the OL in the aqueous suspensions of carbon nanotubes (CNTs) is a nonlinear scattering on the vapor bubbles, which are formed due to the transfer of the absorbed energy from the CNTs to the liquid and due to the sublimation of the carbon nanoparticles. A nonlinear scattering can lead to a shortening of laser pulses. Although the number of publications devoted to OL in various suspensions and materials is very large, but no one has demonstrated the possibility of a smoothly adjustment of the nanosecond laser pulse duration. The aim of the present study was to fill this gap.

2. METHODOLOGY

We have studied the OL of laser radiation in the aqueous suspension of multiwalled CNTs. The CNTs were synthesized using the electric arc evaporation of graphite. In order to allow the CNTs to form the stable suspensions in water and to clean the CNTs from the glassy carbon nanoparticles, the as-synthesized material was chemically purified as described elsewhere. As a result of the oxidation of multiwalled CNTs in a solution of KMnO4 in a concentrated sulfuric acid (H2SO4), the oxygen-containing groups were formed on the carbon surface, those ensured...
the formation of a colloidal solution of CNTs in the water.\textsuperscript{16}

A deposition of carbon nanotubes was carried out using FeCl\textsubscript{3} solution. As a result of hydrolysis the iron hydroxide forming a composite with the oxidized CNTs was released. The air-dried composite was flooded with a small amount (~10 ml) of a concentrated sulfuric acid, and the mixture was kept in this state for several days to dissolve the iron hydroxide. The precipitate was washed on a filter to eliminate FeCl\textsubscript{3} with a 5% solution of the hydrochloric acid until a colorless filtrate was obtained, and then—with a distilled water—until a dark color of the filtrate appeared.

The obtained aqueous suspensions were stable for a rather long time (more than two years). The examination of nanoparticles of the colloidal solution in a transmission electron microscope confirmed an absence of the amorphous carbon and the glassy carbon nanoparticles in the samples. At the same time, the sample also contained no long CNTs. Most nanoparticles had a diameter of 15–20 nm and a length less than 1 \( \mu \)m.

3. EXPERIMENTAL DETAILS

The experiments were performed on an automated setup with a pulsed laser radiation source (\( \lambda = 1064 \) nm) operating at a repetition frequency of 1 Hz\textsuperscript{17} at a pulse duration of 16 ns. The initial coefficient of the optical transmission of the CNT suspension in a 1-mm-thick glass cell at 1064 nm was 45%. The OL in the CNT suspension was studied using a modernized \( \varepsilon \)-scanning scheme depicted in Figure 1.

A principal difference of this scheme from the conventional ones is that the photosensitive detector 1 (a first sensor) and the cell with a suspension 2 are arranged directly on the coordinate table 3 so, that the working surface of the sensor is always facing to the lateral side of the cell.\textsuperscript{18} This arrangement allowed us to study the amplitude and the temporal characteristics of the radiation scattered at a right angle when the cell was moved along the optical axis \( z \) with the zero-point at the waist of the focused laser beam. The focal distance of the collecting lens was 100 mm. The shapes of laser pulses incident on and transmitted through the suspension were studied using an another detector (a second sensor) arranged on the optical axis at position 4 or 5 as depicted in Figure 1. The role of sensors was played by the edges of the optic fibers with a core diameter of 200 \( \mu \)m, the other ends of which were connected to the input of a fast-response photodetector (SIR5-FC, ThorLabs) with a pulse rise time below 70 ps.

The photoelectric response pulses were measured with a digital oscilloscope (Tektronix 7704B) with a bandwidth of 7 GHz and an input impedance of 50 \( \Omega \). Thus, each pulse of a laser radiation produced two sequential electric pulses on the oscilloscope screen. The second pulse having a preset delay relative to the first one, which allowed us to study the temporal parameters of the incident pumping pulses, those scattered at right angle, and the transmitted pulses. It should be emphasized that the specially selected optical fibers did not distort the shapes of pulses on the nanosecond scale, which could be experimentally checked. Using the digital oscilloscope, it was possible to measure both the single response pulses and those averaged over a preset number of laser pulses. Owing to the highly stable scheme of the oscilloscope triggering (based on an avalanche photodiode detecting light leak from the laser cavity), the shapes of pulses could be monitored using a single sensor representing a short (0.6-m-long) optic fiber, which was sequentially arranged in positions 1, 4, and 5.

4. EXPERIMENTAL RESULTS

Figure 2 shows the measured transmittance \( T \) and energy \( \varepsilon _{in} \) as the functions of \( \varepsilon \) (a), and as the functions of a power density (b) in the logarithmic scale for the suspension moving along the optical axis at \( \varepsilon _{in} = 0.3 \) mJ. Power density is defined as: \( I = \varepsilon _{in}/\pi S \) where \( S = \pi r^2 \) is the

Fig. 1. A modernized scheme of \( \varepsilon \)-scanning: (1, 4, 5)—the positions of the optical sensors; (2)—a cell with CNT suspension; (3)—a coordinate table; (6)—a laser radiation source; (7, 13)—the infrared optical filters; (8)—a splitting mirror; (9, 11, 15)—the neutral filters; (10, 14)—matted glasses; (12)—the focusing lens.
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Fig. 2. The transmittance at the output of the cell filled with the suspension, \( T \), (curve 1), and a 90°-scattered laser pulse energy, \( e_s \), as a function of \( z \) at \( e_0 = 0.3 \text{ mJ} \) (curve 2) (a). The dependences \( T \) and \( e_s \) versus the incident power density \( I \) in a logarithmic scale (b).

The cross-sectional area of the laser beam and \( r \) is the Gaussian beam radius, which is determined by a well-known formula:

\[
r(z) = r_0 \left[ 1 + \left( \frac{\lambda z}{\pi T_0^2} \right)^2 \right]^{1/2}
\]

where \( r_0 \) is the beam waist radius.

As \( z \) approaches zero (the incident power density increases), the transmittance of the suspension, \( T \), decreases markedly (Fig. 2(a), curve 1) and, accordingly, the 90°-scattered laser pulse energy, \( e_s \), increases, i.e., the higher the \( e_s \), the lower the transmittance \( T \). Note that, away from the beam waist, the 90°-scattered laser light energy does not vanish, remaining roughly constant. Clearly, this is due to the Rayleigh scattering in the suspension, which is dependent on the nanoparticle concentration.

It is of interest to analyze the experimental data presented in Figure 2. To this end, consider the energy balance for the laser pulses incident on and transmitted through the cell when there is no OL:

\[
e_{in} = e_{out} + e_{ab} + e_r + e_{in}^{4\pi}
\]

where \( e_{ab} \), \( e_r \) and \( e_{in}^{4\pi} \) are the energies absorbed in the suspension, reflected from the cell wall and scattered in all directions through the Rayleigh scattering from the nanoparticles, respectively.

The initial transmittance of the cell filled with the suspension is then given by

\[
T_0 = \frac{e_{in} - e_{ab} - e_r - e_{in}^{4\pi}}{e_{in}}
\]

Under the assumption that OL is only due to a nonlinear scattering, the transmittance obtained in a \( z \)-scan measurements can be written in the form

\[
T = T_0 - k e_s
\]

where \( e_s^{4\pi} \) is the energy, scattered through the full \( 4\pi \) solid angle, which depends on the incident power density (or \( z \)). Clearly, the measured 90°-scattered pulse energy, \( e_s \) (in the relative units), is proportional to \( e_s^{4\pi} \). Consequently, the above relation can be rewritten in the form

\[
T = T_0 - k e_s
\]

where \( k \) is a proportionality factor.

Figure 3 presents the dependence \( T(e_s) \) data points derived from the \( T(z) \) and \( e_s(z) \) data in Figure 2(a). For this purpose, the small pedestal due to a Rayleigh scattering was subtracted from all the \( e_s \) values. Lines (1) and (2) represent, respectively, the linear and quadratic fits to the data. The linear fit is seen to represent poorly the experimental data, whereas the quadratic relation provides a good fit to the data points. Formula (5), being in a qualitative agreement with the experimental data in Figure 3, is insufficient. This, in turn, suggests that the OL takes place not only due to the nonlinear scattering but also due to the nonlinear laser light absorption, which

Fig. 3. The transmittance \( T \) versus 90°-scattered energy \( e_s \). The data points are derived from the experimental data in Figure 2(a). (1) a linear fit; (2) a quadratic fit.
is left out of the account in (4). The nonlinear absorption contribution to OL can be estimated using the $T(z)$ and $e_i(z)$ data in Figure 2.

Taking into account the energy balance, we find than the contribution of the nonlinear absorption to OL is $\sim 10\%$ and, hence, it is not a dominant process.

Figure 4 shows the shapes of laser pulses transmitted through the cell containing the CNTs suspension for the different coordinates $z$ at a fixed energy of incident pulse $e_{in} = 0.3$ mJ. For comparison, the same Figure shows the shape of an incident laser pulse (Fig. 4, curve 4) taking into account its linear attenuation after passing through the suspension. Its duration at a half of maximum is 16 ns. It is seen that the full width at half maximum of the transmitted laser pulse $\tau_{out}$ varies with $z$ and has a minimum when the cell is at the beam waist. The reduction in $\tau_{out}$ is due to the fact that a nonlinear scattering cuts off the trailing part of the pulse.

Consequently, the peak of the incident pulse is delayed relative to the peak of the transmitted pulse, and when the cell approaches the waist, the time delay $\Delta_{in-out}$ between these peaks increases (Fig. 5, curve 1). According to curve 3 (Fig. 5), the minimum duration of the laser pulses transmitted through the CNT suspension, is achieved in the beam waist at $z = 0$. As a result, at $z = 0$ the duration of the pulses at the cell output decreases by a factor of 1.6 in comparison to $\tau_{in}$.

The experimental data 2 and 4, included in Figure 5 show the character of changes in the rise time ($\tau_{ri}$) and the fall ($\tau_{f}$) times, defined in the standard way from 0.1 to 0.9 of the maximum of the light pulses transmitted through the suspension versus coordinate $z$. It is evident that $\tau_{ri}$ decreases while $z$ approaching zero and while the parameter $\tau_{f}$ experiences a failure at $z = 0$. It is noteworthy that, in accordance with the experimental curves 2 and 4, (Fig. 5), the rise time and the fall times of the laser pulses transmitted through the suspension at $z = 0$ are approximately equal to each other. Consequently, the passively Q-switched laser pulses with a protracted trailing edge, after passing the cell, positioned in location of the beam waist, become symmetric with respect to the time positions of their peak.

It should be noted that the decrease of $\tau_{hi}$ duration with a decrease of $|z|$ is accompanied by a corresponding decrease in the amplitude $A_{out}$ of the transmitted light pulses (see Fig. 6). This means that the shortening of pulses during OL in the CNT suspension (in contrast to compression during a stimulated Brillouin scattering and a stimulated Raman scattering) is accompanied by a corresponding decrease in the pulse power.

It is interesting to find a simple analytical function describing the amplitude $A_{out}$ of laser pulses at the output of the cell, containing the suspension, as a function on $z$. In the first approximation for this purpose the function can

\[ A_{out} \sim \frac{\Delta t_{in-out}}{\Delta t_{out}} \]

where $\Delta t_{in-out}$ is the duration of the peak of the transmitted pulse relative to the peak of an incident pulse, and $\Delta t_{out}$ is the time delay between the peaks of the transmitted pulse and the peak of the transmitted light pulses at the output.

**Fig. 4.** The form of the laser pulses at an energy $e_{in} = 0.3$ mJ at the exit of the optical cell with the suspension at $z = 0$ (1), 5 mm (2), 11 mm (3), as well as the form of the incident laser pulse with its linear attenuation with the suspension (4).

**Fig. 5.** The experimentally obtained dependences of (1) the advance time $\Delta t_{in-out}$ of the peak of a transmitted pulse relative to the peak of an incident pulse, (2) the rise time $\tau_{ri}$, (3, solid curve-approximation) duration $\tau_{out}$, (4) and the fall time $\tau_{f}$ of transmitted pulses on the coordinate $z$.

**Fig. 6.** The dependence of the amplitude $A_{out}$ of the transmitted pulses on the coordinate $z$. 

be used, obtained to describe the transmittance of a nonlinear medium at OL for the experiments with z-scanning (see, for example, Ref. [19]). For our case, it can be written as follows:

$$A_{\text{out}}(z) = A_{\text{in}} \frac{\ln(1 + \epsilon_{\text{in}}q/(1 + x^2))}{\epsilon_{\text{in}}q/(1 + x^2)} \quad (6)$$

Here $A_{\text{in}}$– an amplitude of the incident laser pulses (in rel. units); $x = z/z_0$, where $z_0$ is a Rayleigh length; $q \sim \sigma/(r_0^2h\omega)$ where $\sigma$ is a nonlinear scattering cross-section, $h$ is a Planck’s constant, $\omega$ is a laser radiation circular frequency.

Using the relation (6) to approximate the number of points of the experimental curve in Figure 6 yields the following values: $A_{\text{in}} = 0.99$, $q = 2 \ \text{mJ}^{-1}$, $z_0 = 5.3 \ \text{mm}$. Figure 6 shows that the formula (6) with these coefficients properly describes the experimental results.

To approximate the experimental dependence $\tau_{\text{out}}^{\text{in}}(z)$, (Fig. 5 dataset 3), the following similar function with three adjustable parameters $\tau_{\text{in}}^{\text{in}}$, $q$ and $z_0$ can be used:

$$\tau_{\text{out}}^{\text{in}}(z) = \tau_{\text{in}}^{\text{in}} \frac{\ln(1 + \epsilon_{\text{in}}q/(1 + x^2))}{\epsilon_{\text{in}}q/(1 + x^2)} \quad (7)$$

As a result of fitting, the obtained coefficients are: $\tau_{\text{in}}^{\text{in}} = 16.3 \ \text{ns}$, $q = 1.4 \ \text{mJ}^{-1}$, $Z_0 = 6.6 \ \text{mm}$. A formula (7) with the evaluated coefficients can approximately determine the duration of the laser pulses as a function of $z$ for a given value of the laser pulse energy $\epsilon_{\text{in}}$ (Fig. 5, a solid curve 3).

5. CONCLUSIONS

Thus, in this study we have demonstrated a possibility of continuously controlling the duration of the nanosecond laser pulses by the method of z-scanning of an optical cell filled with a CNT suspension. The shortening of the duration of Q-switched laser outcoming pulses with a prolonged tail part results from a nonlinear scattering and it is accompanied by a symmetrization of the time profile of the pulses.

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References and Notes


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