NONLINEAR SCATTERING OF INTENSE LIGHT BY COLLOIDAL SUSPENSIONS

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Passage of intense light through colloidal solutions containing particles with dimensions smaller than the light wavelength is considered. It is demonstrated experimentally that nonlinear scattering by bubbles formed around the absorbing particles is the main cause of attenuation of light in such solutions.

WHEN low-intensity light flux passes through absorbing colloidal solutions, the local changes of the refractive index of the medium around the absorbing centers, due to heating, are extremely negligible. These effects are usually not taken into account in the calculation of the scattering of light.

Askar'yan has shown,[1] however, that the principal role in the attenuation of intense radiation may be played by scattering by refracting aureoles, which are produced around absorbing particles. The refracting aureoles may be due either to the propagation of sound waves or directly to thermal effects. With increasing radiation intensity, vapor or gas bubbles are produced around the absorbing centers.[2] Scattering of light by vapor bubbles whose dimensions exceed the wavelength has been considered theoretically in [2]. Nonlinear attenuation of a powerful light flux by colloidal solutions was reported in [3,4].

The purpose of the present work was to study experimentally the attenuation of intense light fluxes by colloidal solutions as a result of scattering by vapor bubbles whose dimensions are much smaller than the wavelength.

POSSIBILITY OF FORMATION OF VAPOR BUBBLES

When radiation passes through a colloidal solution, each particle represents a thermal source, the power of which is determined by the absorption of the particle and by the density of the power of the incident radiation. Within certain limits, it is possible to assume that the absorption of a particle containing many molecules is directly proportional to the number of molecules. In this case, the unification of the particles should not influence the absorption of the solution.[1)] The distribution of the temperature around such a source is written in the following manner (the radiation pulse is assumed to be rectangular):

$$T(r,t)=\frac{I_0\sigma a}{\rho c_V 4\pi\chi r}\left[1-\Phi\left(\frac{r}{\sqrt{2\chi t}}\right)\right], \qquad (1)$$

where r is the distance from the center of the source, t is the time from the start of the pulse ($t < t_p$); ρ, c_V, and χ are the density, specific heat, and the temperature conductivity of the medium, Φ is the probability integral, I_0 is the intensity of the incident radiation, σ is the cross section for absorption of one molecule in the particle, and a is the number of molecules in the particle.

It is assumed here that the absorbed energy is lost only to heating of the surrounding medium, and is not consumed, for example, in dissociation or luminescence.

With increasing number of molecules in the particle, the temperature of the medium around the absorbing center increases and can reach the boiling temperature. Thus, at $I_0 = 25$ MW/cm^2, $a = 10^4$, $\sigma = 5.3\times10^{-17}$ cm^2, the temperature at a distance $r = 2\times10^{-6}$ cm from the particle reaches 350°, which greatly exceeds the boiling temperature of most organic solvents. The occurrence of a vapor bubble is facilitated by the fact that the particle itself is a center for the formation of the new phase. The produced bubble is in equilibrium with the liquid if the following condition is satisfied

$$R_{cr}=2\alpha/(p_s+p_g-p), \qquad (2)$$

where α is the coefficient of surface tension, p_s is the saturated-vapor pressure, p_g the pressure of the gases in the bubble, p the pressure in the liquid. If the radius of the bubble is $R < R_{cr}$, then the bubble collapses rapidly, otherwise it expands and can exist for an appreciable time. After the end of the radiation pulse, the vapor in the bubble condenses within a time on the order of $R^2/4\chi$, and R_{cr} increases. Now only the largest bubbles can "survive."

SCATTERING OF LIGHT BY VAPOR BUBBLES

The attenuation of low-intensity radiation by passage through a colloidal solution is the result of absorption and scattering of the light by the colloidal particles.

After formation of the vapor bubbles, the scattering by them can play the principal role in the attenuation of the light. Let us estimate the transmission of a colloidal solution in this case. Both the dimension of the particles and the dimension of the produced bubbles were assumed to be much smaller than the wavelength of the light. Then the cross section for the scattering of the light by the vapor bubble σ_{sc} [5] will be

$$\sigma_{sc}=\frac{3(\varepsilon_0-\varepsilon_1)^2}{2\pi(\varepsilon_0+2\varepsilon_1)^2}\frac{V^2}{\lambda^4}, \qquad (3)$$

where ϵ_0 and ϵ_1 are the dielectric constants of the liquid and of the vapor, respectively, V is the volume of

1) An example of such a solution may be an aqueous solution of copper phthalocyanine. Its absorption spectrum does not change in time, although continuous unification of aggregates proceeds in the solution.

the bubble, and λ is the radiation wavelength. The influence of the absorbing center on the scattering will be neglected. The loss occurring during the passage of a beam through an elementary layer of solution of thickness dx is written as follows:

$$dI(t, x) = -(\sigma_{sc} + \sigma_{abs}) nI(t, x) dx, \quad (4)$$

where σ_{abs} is the absorption cross section of the particle, n is the number of particles per unit volume. Expression (4) is valid only for single scattering. However, in the case of a parallel beam of light, under the condition that the scattering diagram has no maxima at angles close to zero, it is always possible to place the measuring device at a sufficiently large distance so that the multiply-scattered light is negligibly small compared with the directly transmitted beam.

In view of the small dimension of the particles, the heat conduction by thermal conductivity will have a characteristic time much shorter than the pulse duration. Consequently, the dimensions of the region around the absorbing center, with a temperature larger than the boiling temperature, will be determined by the radiation power density, and not by the total released energy, as in the case of larger particles. If it is assumed that the volume of the bubble is determined by the volume of the evaporating liquid, then the scattering cross section can be written in the form

$$\sigma_{sc} = \gamma I^2(t, x), \quad (5)$$

where γ is the proportionality coefficient. After integrating (4) we obtain

$$I(t,x) = \frac{I(t,0)\sigma_{abs}^{1/2} \exp(-\sigma_{abs} nx)}{\{\gamma I^2(t,0)[1 - \exp(-2\sigma_{abs} nx)] + \sigma_{abs}\}^{1/2}} \quad (6)$$

When the dimension of the bubble is larger than the wavelength then, as shown in [2],

$$\sigma_{sc} \infty \left(\int_0^t I\, dt\right)^{2/3}. \quad (7)$$

EXPERIMENT

We investigated the transmission of intense radiation of a ruby laser, operating in the Q-switched regime, through colloidal solutions. We measured both the transmitted and the scattered light. The working substances were colloidal solutions of phthalocyanine of aluminum chloride, phthalocyanine of copper, 1-2-naphthalocyanine of platinum, free perchlorophthalocyanine, 2-3-naphthalocyanine of copper, and also suspensions of gold, platinum, silver, and chlorophyll. The number of molecules in the particle was estimated with the aid of an ultramicroscope at a known dye concentration. For the associated form of phthalocyanine of aluminum chloride, there were approximately 10^4 molecules per particle.[2)] In all these solutions we observed an appreciable increase of the scattering at intensities on the order of several MW/cm^2. A photograph of the cell with the colloidal solution upon passage of a laser pulse is shown in Fig. 1.

Figures 2 and 3 show plots of the transmitted light and of the light scattered at 90° against the intensity of the incident radiation. The experimental dependences of the transmission for most solutions agree with the dependences calculated in accordance with (6) (the parameter γ was obtained from the experimental curve). This

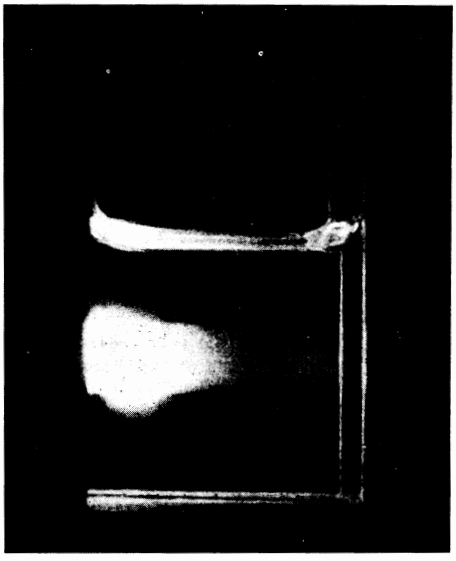

FIG. 1. Photograph of cell with colloidal solution, through which a giant pulse of laser radiation passes.

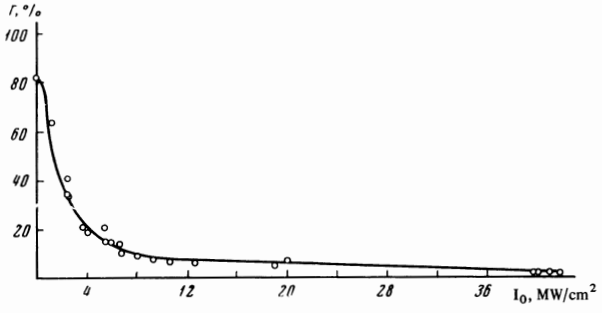

FIG. 2. Dependence of the transmission of the colloidal solution of phthalocyanine of aluminum chloride in dichlorobenzene on the intensity of the incident radiation. Points—experimental values, solid line—calculated curve.

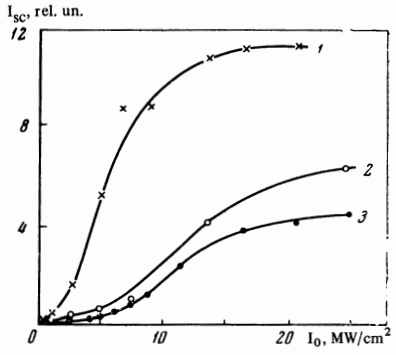

FIG. 3. Dependence of the light scattered at 90° on the intensity of the incident radiation for the following colloidal solutions: 1—adducts of phthalocyanine of aluminum chloride with aluminum bromide in dichlorobenzene, 2–2, 3—naphthalocyanine of copper in quiniline, 3–1, 2—naphthalocyanine of platinum in quiniline.

[2)] We have previously [3] assumed it to be a dimer, on the basis of the characteristic double-hump absorption spectrum of this compound.

agreement confirms the assumption that the dimensions of the produced bubbles are smaller than the wavelength of the light.

However, there is not always agreement between the experimental and the calculated curves. In particular, this case takes place for the transmission of the second harmonic of neodymium-laser radiation (λ = 530 nm) by a colloidal solution of phthalocyanine of aluminum chloride, although for a ruby laser and the same solution the agreement between the experimental and calculated relations is better. Apparently, scattering at the second harmonic of the neodymium laser is determined by vapor bubbles whose dimensions come closer to the wavelength of the light. Such bubbles are produced around relatively large particles. On the other hand, the bubbles produced around small particles, which played the principal role in the scattering of the ruby-laser light, are not produced in this case, since the absorption at λ = 530 nm is much smaller than at λ = 694.3 nm. In order to obtain a noticeable effect at the second harmonic of the neodymium laser, the concentration of the dye was chosen to be much higher than in the case of the ruby laser.

We also investigated the nonlinear scattering of solutions in which the particle dimensions varied with time, this being accomplished by mixing the dye solution with a solvent in which the dye is not dissolved. Figure 4 shows the dependence of the transparency of such a solution on the time elapsed after the mixing of the solutions, which characterizes the particle dimension and consequently also the dimension of the vapor bubbles. With increasing particle dimension, the nonlinear scattering reaches a maximum (minimum on the transmission curve), indicating that the scattering can no longer be regarded as Rayleigh scattering.

It was of interest to investigate the character of variation of the produced vapor bubbles with time. To this end, a probing weak-light beam was passed through the cell perpendicular to the ruby-laser beam. The change of the intensity of the probing beam was registered with a photomultiplier, and was observed on the screen of an oscilloscope. It is seen from the oscillogram of the probing beam (Fig. 5) that there are two types of bubbles. The first short pulse is produced by scattering of the probing beam from bubbles whose radius after the vapor condensation is smaller than the critical value. Such bubbles rapidly collapse after the passage of the radiation pulse. The series of succeeding broad pulses (10–20 μsec) is due to scattering by bubbles in which $R > R_{cr}$ after the condensation of the vapor; such bubbles, before they collapse, can compress and expand several times. With increasing intensity, the number of such bubbles decreases, and accordingly the broad pulses on the oscillogram of the probing beam first decrease and then disappear completely.

The dimensions of the produced vapor bubble depend very strongly on the properties of the solvent. It is clear, that in solvents with small heat of vapor production, low boiling temperature, and low specific heat, the dimensions of the bubbles will be larger and the nonlinear scattering will be stronger. Accordingly, the largest scattering was observed when chloroform and diethyl ether were used as solvents, and the smallest in the case of bromonaphthalene and trichlorobenzene.

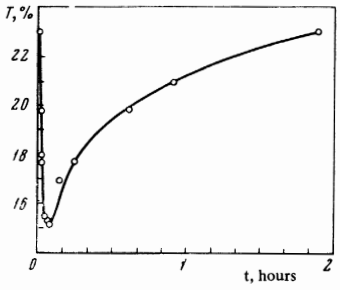

FIG. 4. Dependence of the transmission of a powerful light flux (I_0 = 30MW/cm^2) by a colloidal solution of phthalocyanine of aluminum bromide in water, in which particle unification takes place, on the time.

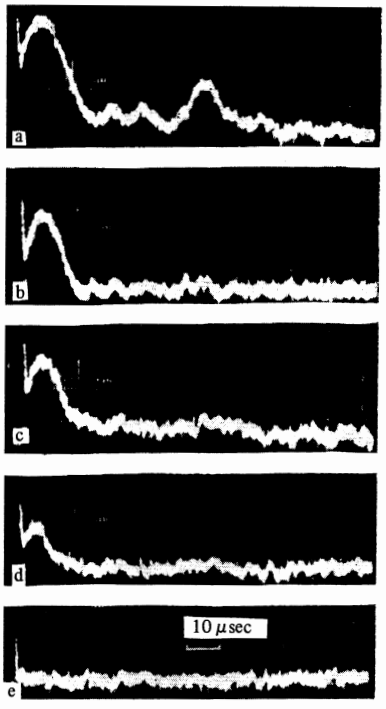

FIG. 5. Oscillograms of probing beam at different power densities of the laser radiation: a–40, b–30, c–25, d–18, e–9 MW/cm^2.

We investigated the spectral composition of nonlinear scattering of the light. At the employed dimensions of the absorbing particles, the time of occurrence and growth of the bubbles is of the order of 10^{-8} sec. Thus, in the scattering of monochromatic light by vapor bubbles, the half-width of the scattering line is 3.3×10^{-3} cm^{-1}. Measurements with the aid of a Fabry–Perot interferometer with polarization separation of the incident and scattered light[6] have shown that, accurate to 0.01 cm^{-1}, there is no broadening or frequency shift in the spectrum of the scattered light.

The considered effect can make an appreciable contribution to the attenuation of powerful light passing either through natural scattering media or through devices used in laser technology (passive shutters, working media of liquid lasers, etc.).

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