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INVESTIGATION OF OPTICAL PROPERTIES OF PHOTOGRAPHIC EMULSIONS BY PULSE OPTOACOUSTIC METHOD

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Absorption and scattering of light in photographic emulsions at the wavelength of the fundamental ($\lambda = 1.06$ μm) and second ($\lambda = 0.53$ μm) harmonics of an Nd:YAG laser are investigated with the help of the pulse optoacoustic method. It has been found that the light absorption factor is much smaller than the scattering factor, while the extinction coefficient and the light absorption factor for emulsions with different sensitivity are close. It has been shown that the influence of latent image on optical characteristics of photographic emulsions is small.

1. INTRODUCTION

Photographic emulsions are an important and interesting object for investigation. In particular, the mechanism of latent image formation is still not completely understood. Earlier [1], basing on an analysis of experimental facts undertaken in view of contradictions between the accumulated experimental data and the Gurney–Mott photolytic theory of formation of latent image centers (LIC), a "photoacoustic" principle of LIC formation due to condensation of non-halide silver clusters was formulated [1]. For this principle to be verified, it is necessary to investigate optical characteristics of photographic emulsions and their changes under the effect of irradiation. In this paper we investigate the absorption of light by photographic emulsions.

Photographic emulsions are a heterogeneous scattering medium consisting of AgBr or AgCl microcrystals in gelatin. Therefore, for investigating their optical characteristics it is useful to employ a pulse optoacoustic effect [2] which makes it possible to measure the absorption of light in scattering objects with micron resolution per laser pulse [3–5].

AgBr and AgCl crystals are semiconductors with a forbidden bandwidth corresponding to quanta of the ultraviolet region (to 2.684 and 3.245 eV, respectively [6]). Therefore, two mechanisms of sound excitation by a laser can take place in them: a thermal mechanism and a concentration-deformation mechanism [2]. Since an increase in the concentration of electron-hole pairs leads to contraction of the silver halide lattice [7], these two mechanisms will compete. At short lifetimes of the electron-hole pairs (compared with the duration of a laser pulse) the thermal mechanism of sound generation will play the main role.

2. THEORETICAL MODEL OF PULSE OPTOACOUSTIC EFFECT IN A SCATTERING MEDIUM

The thickness of photographic emulsions (from a few to tens of micrometers) is, as a rule, much smaller than the diameter of a laser beam used for sound excitation. Therefore, it is sufficient to use a one-dimensional approximation in the problem of laser optoacoustics. The form of an acoustic signal can be represented as a convolution of the time dependence of the absorbed laser radiation intensity and of the spatial distribution of heat sources in the medium [2].

Photographic emulsions are characterized by strong scattering and weak transmission of light, even when the thickness of layers is tens of micrometers. Therefore, it will be reasonable to use the approximation of a semi-infinite medium occupying a half-space $z > 0$ and bordering with a transparent medium. Since the coefficient of light scattering μ_s is large (practically, $\mu_s > 103\ \text{cm}^{-1}$), and the depth of light penetration into the medium l is small as compared with the laser beam diameter, the incident beam may be assumed to be collimated. Because of a small depth of light penetration into the medium, the excited acoustic signals have a short duration (comparable with the duration of a laser pulse), and our consideration can be confined to one-dimensional acoustic and thermal problems. The distribution of light intensity $I(z,t)$ under various conditions of light scattering in the medium and its reflection at the boundaries was analyzed in [8–11]. We used the results reported in these publications for a collimated laser beam in an approximation of isotropic scattering.

If the light absorption factor μ_a is much less than the scattering factor: $\mu_a \ll \mu_s$ (this is true, as will be shown below, for photographic emulsions), then the pressure in an acoustic wave radiated into the scattering medium, has the form [12]

$$p\left(\tau = t - \frac{z}{c_0}\right) \cong \frac{c_0^2\beta^*}{2c_p} I_0 \int f(\tau-\theta)\mu_a \left\{-3\exp(-c_0\mu_s|\theta|) + 2\left(3 + \frac{2r_0}{1-r_0}\right)\exp\left(-2c_0\sqrt{\mu_a\mu_s}\,|\theta|\right)\right\} d\theta, \quad (1)$$

where $I_0 f(t)$ describes the time dependence of the envelope of the incident laser beam intensity, r_0 is the coefficient of light internal reflection from the boundary on the side of the scattering medium, c_0 is the velocity of sound propagation in the medium, c_p is the heat capacity of the medium, b^* is the coefficient of thermal expansion.

In our approximation ($\mu_a \ll \mu_s$) the light extinction coefficient $\mu_{\text{eff}} = 2\sqrt{\mu_a\mu_s} \ll \mu_s$, and, therefore, the shape of the acoustic signal is defined by the second addend in (1), which describes the generation of sound by the diffuse (scattered) component of the light field.

The spectrum of the acoustic pressure pulse in a laser excitation of sound $p(\omega) = I_0 f(\omega)K(\omega)$ [2], where $I_0 f(\omega)$ is the spectrum of the temporal envelope of the laser beam intensity, $K(\omega)$ is the transfer function of thermooptical sound excitation. From (1) it follows that

$$K(\omega) = \frac{c_0^2\beta^*}{c_p} \frac{1}{1 + (\omega/\mu_{\text{eff}}c_0)^2}\left(3 + \frac{2r_0}{1-r_0}\right). \quad (2)$$

Hence, the form of the transfer function is defined by the extinction coefficient μ_{eff}, and the amplitude of the thermooptically excited acoustic pulse is defined by the light absorption factor (see (1)). This provides an opportunity to measure $\mu_{\text{eff}} = 2\sqrt{\mu_a\mu_s}$ and μ_a (and, correspondingly, μ_s) separately for scattering media.

3. EXPERIMENTAL SETUP AND INVESTIGATED SAMPLES

A setup for investigating optical characteristics of photographic emulsions by the pulse optoacoustic method was connected in circuit with recording acoustic signals in an absorbing medium, and it was described in detail in [12]. We investigated optical properties of photographic emulsions on wavelengths of the fundamental harmonic ($\lambda = 1.06\ \mu$m; pulse energy, 20–30 mJ) and of the second harmonic ($\lambda = 0.53\ \mu$m; pulse energy, 0.7–2 mJ) of an Nd:YAG laser (pulse duration $2\tau_L \cong 10$ ns).

In this work we used an Ag(I, Br) emulsion with plane microcrystals; the preparation of photographic emulsion samples is described in [12]. The prepared emulsion was subjected to sulfur sensitization to the light-sensitivity levels of 0.85, 50, and 170 GOST units. The microstructure of photographic emulsions on a 2 mm-thick glass support, obtained in a scanning electron microscope, is illustrated in Fig. 1. One can clearly see silver bromide microcrystals with a mean size of $2R \sim 1\ \mu$m. Their volume concentration is too high: the distance between the crystals $d \cong 2$–$3\ \mu$m. The thickness of the microcrystals is on the order of $0.1\ \mu$m.

The efficiency of thermooptical sound excitation in AgBr crystals $\beta^* c_0^2/c_p \cong 2.2$ is close to the efficiency of thermooptical sound excitation in gelatin. Therefore, the photographic emulsion in terms of sound excitation efficiency can be regarded as a quasi-homogeneous medium. Since $c_0\tau_L \gg (R, d)$, the photographic emulsion could also be regarded acoustically homogeneous. No optoacoustic signal was recorded in pure gelatin.

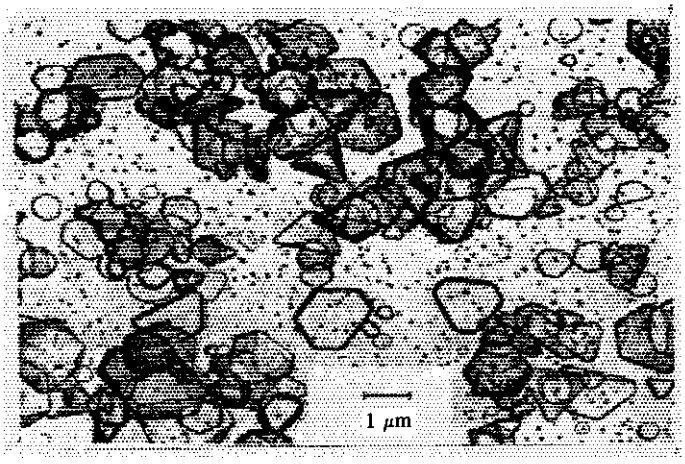

Fig. 1

Microstructure of photographic emulsion in a scanning electron microscope.

The thickness of photographic emulsions varied within 20–40 μm, and their transmittance did not exceed 8–10% (both at the fundamental frequency and at the frequency of the second harmonic). Therefore, the semi-infinite medium approximation employed in the derivation of formula (1) can also be regarded as fulfilled to sufficient accuracy. The photographic emulsions were pressed to a quartz acoustic duct of a broadband piezoelectric detector based on lithium niobate (time resolution not less than 3 ns). The photographic emulsions were irradiated through a transparent glass support, so that the surface of the absorbing medium could be regarded rigid and used in analyzing the experimental results of expressions (1)–(2).

4. EXPERIMENTAL RESULTS

We investigated an acoustic signal excited in the photographic emulsions by a single pulse emitted by an Nd:YAG laser at the fundamental frequency and at the frequency of the second harmonic. Both unexposed emulsions and emulsions exposed to a single second-harmonic radiation pulse or exposed to light were investigated. Exposed emulsions were not developed before measurements. In all cases the control unexposed samples did not display noticeable blackening (optical density $D < 0.02$) when being developed in a standard developer at 20°C during three minutes.

1°. Properties of Photographic Emulsions at a Wavelength $\lambda = 0.53$ μm

The shapes of optoacoustic signals excited in unexposed emulsions by radiation with $\lambda = 0.53$ μm and normalized to the energy density E_0 of the laser pulse applied to the emulsion are shown in Fig. 2*a*. The amplitudes of signals for three types of emulsions were close, and their variations remained within the scope of energy instability of second-harmonic radiation pulses.

The spectral transfer functions of laser sound excitation in unexposed emulsions (Fig. 3*a*) are close to those described by theoretical relation (2). The light extinction coefficient proved to be the same for unexposed emulsions of different sensitivity and amounted to

$$\mu_{\text{eff}}^{n}(\lambda = 0.53\ \mu\text{m}) = (1.39 \pm 0.05) \times 10^3\ \text{cm}^{-1}.$$

Using expression (1) and assuming that the form of the laser pulse is Gaussian, we find the light absorption factor from the measured efficiency of sound excitation $p_{\max}/E_0 = (90 \pm 15)$ atm·cm^2/J

$$\mu_a^n(\lambda = 0.53\ \mu\text{m}) = (2.2 \pm 0.4)\ \text{cm}^{-1},$$

which is also the same for emulsions with different sensitivity. (The light refraction indices in gelatin and glass are close, and for the light internal reflection coefficient it was assumed that $r_0 = 0$). Calculations of

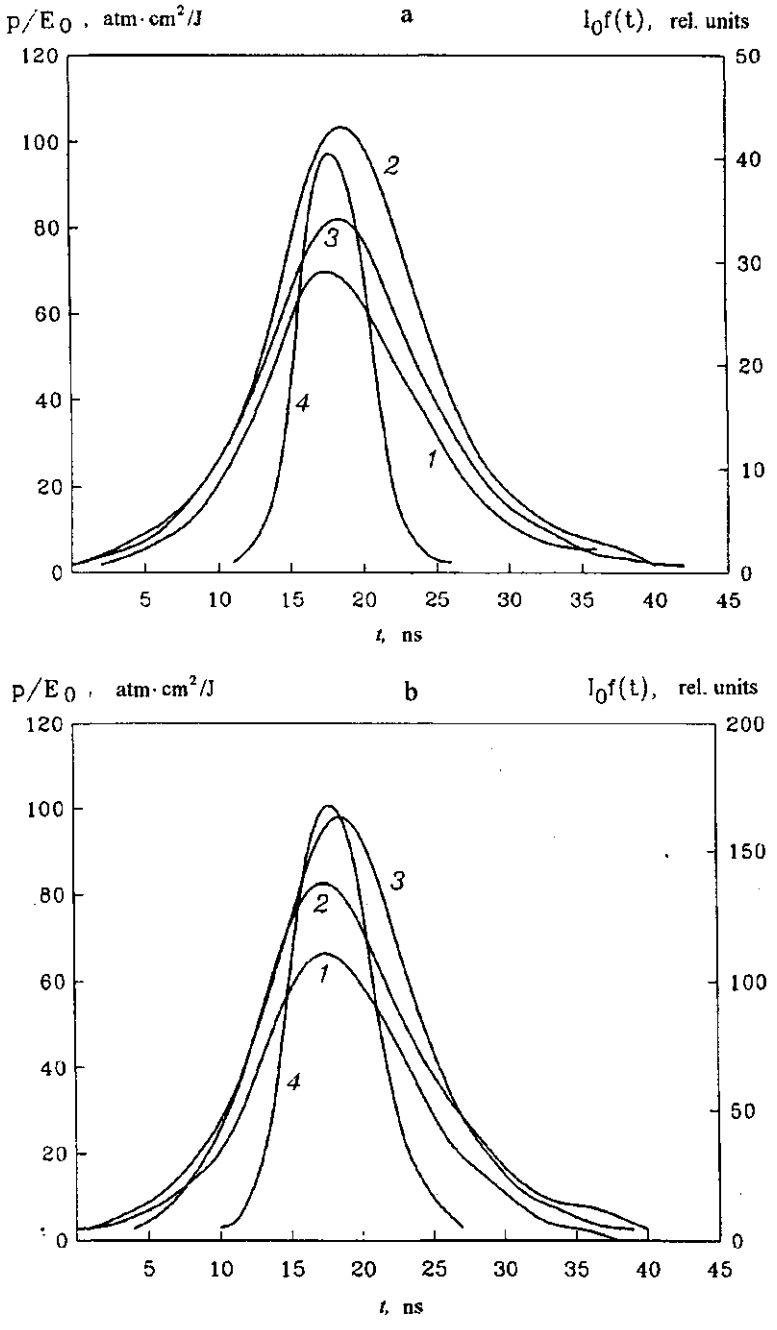

Fig. 2

Optoacoustic signals excited by radiation at $\lambda = 0.53$ μm in unexposed (*a*) and exposed to light (*b*) photographic emulsions with sensitivity of 0.85 (*1*), 50 (*2*) and 170 (*3*) GOST units. Curves *4* are the laser pulse shapes.

the light scattering factor yield

$$\mu_s^n(\lambda = 0.53\ \mu\text{m}) = (2.2 \pm 0.5) \times 10^5\ \text{cm}^{-1},$$

this corresponding to the inverse thickness of AgBr microcrystals in the emulsions. As can be seen, the condition of applicability of (1) $\mu_a \ll \mu_s$ is fulfilled sufficiently well.

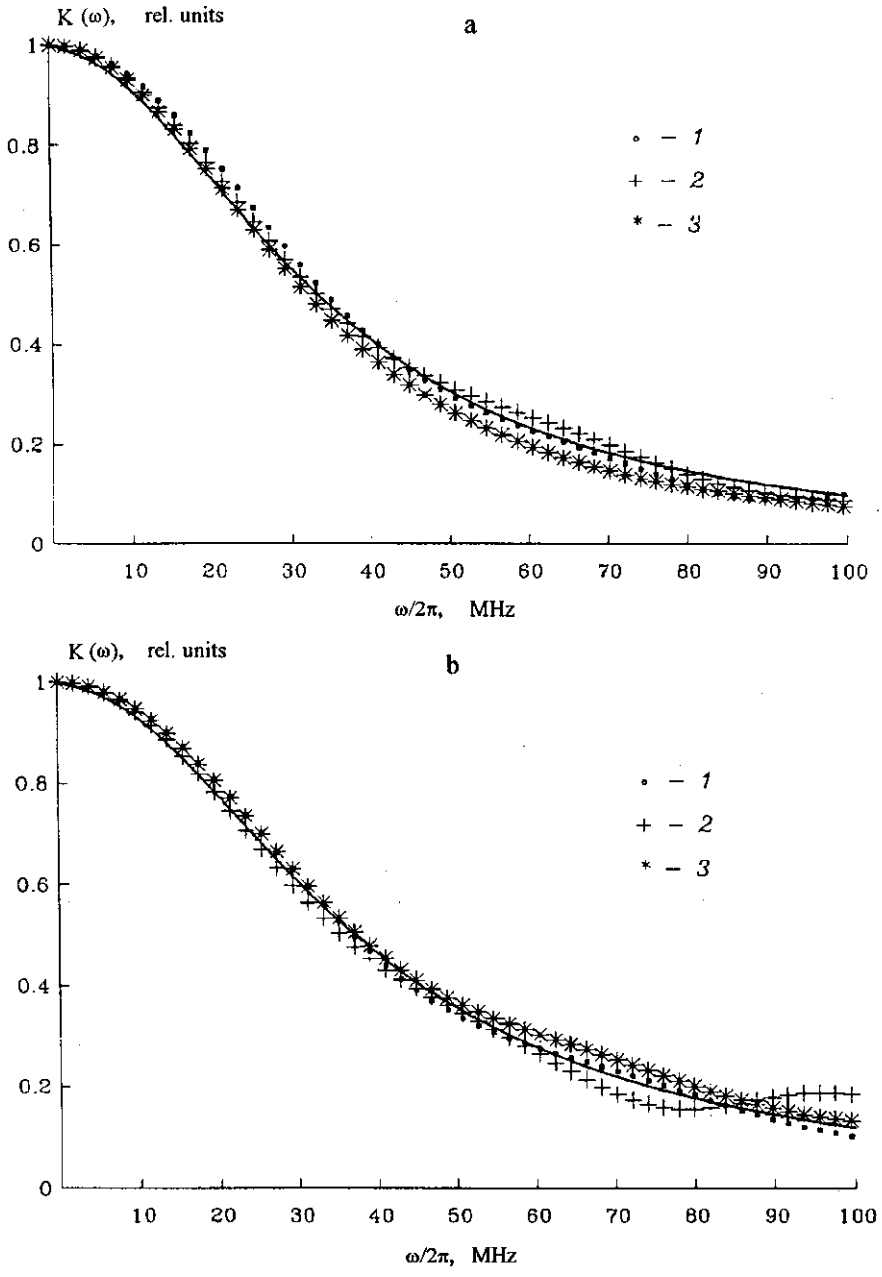

Fig. 3

Spectral transfer functions of laser excitation of sound ($\lambda = 0.53$ μm) in unexposed (*a*) and exposed to light (*b*) photographic emulsions with sensitivity of 0.85 (*1*), 50 (*2*) and 170 (*3*) GOST units. Approximations according to formula (1) are shown by solid lines.

The observed signals were the compression pulses. This is an indication that the influence of the concentration-deformation mechanism of sound excitation is scarce. In our case the concentration-deformation mechanism may manifest itself due to the presence of an AgI admixture, in which the forbidden bandwidth is smaller than the energy of the second-harmonic radiation quanta ($2\hbar\omega_L = 2.34$ eV). In AgBr crystals the relationship of energies is inverse, and electron-hole pairs cannot be generated in the bulk of the crystal. In any case, the predominance of a thermal mechanism of sound generation suggests that the concentration of electron-hole pairs is small or that the lifetime of photoexcited carriers is short (compared

with the laser pulse duration). These data correspond to direct measurements of the photoconductivity relaxation of emulsions [13, 14].

The optoacoustic signals excited by the second-harmonic radiation in emulsions exposed to light are close both in shape and in amplitude (Fig. 2*b*). Transfer functions for the three types of emulsions are close to one another (Fig. 3*b*), and the value of the light extinction coefficient

$$\mu_{\text{eff}}^{e}(\lambda = 0.53\ \mu\text{m}) = (1.55 \pm 0.05) \times 10^3\ \text{cm}^{-1}.$$

differs only little from the extinction coefficient of unexposed emulsions.

In emulsions exposed to light the efficiency of sound excitation is almost the same as in unexposed emulsions, $p_{\max}/E_0 = (80 \pm 15)$ atm·cm^2/J, and the light absorption factor

$$\mu_a^e(\lambda = 0.53\ \mu\text{m}) = (2.1 \pm 0.4)\ \text{cm}^{-1}.$$

The coincidence of optical characteristics of the unexposed and exposed to light emulsions is noteworthy and indicative of a slight latent-image effect on the optical properties of emulsions (the exposure of the emulsion to a single second-harmonic radiation pulse led to the formation of an image with optical density $D = 1.5$ under the above-stated development conditions).

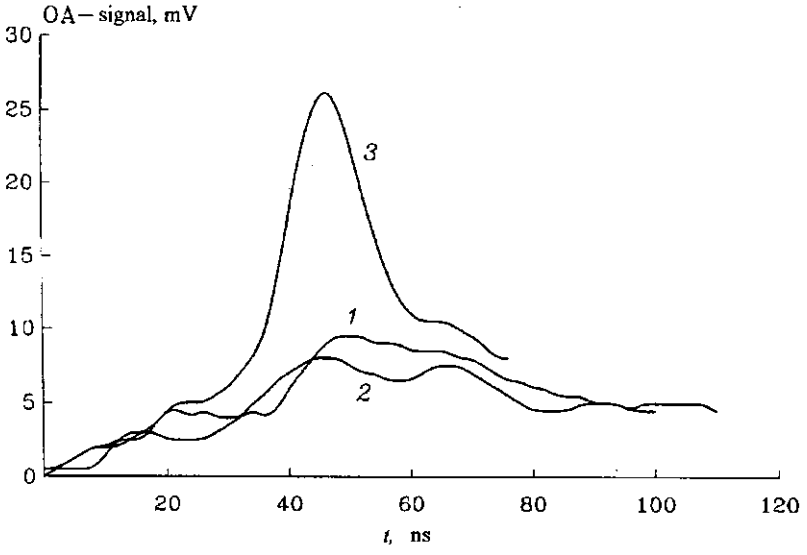

Fig. 4

Optoacoustic signals excited by radiation at $\lambda = 1.06$ μm in photographic emulsion with the sensitivity of 0.85 GOST units: *1*, unexposed emulsion, *2*, emulsion exposed to a single pulse $\lambda = 0.53$ μm ($E_0 = 3$ mJ/cm^2), *3*, emulsion exposed to light.

2°. Properties of Photographic Emulsions at a Wavelength $\lambda = 1.06$ μm

The shapes of optoacoustic signals excited by radiation with $\lambda = 1.06$ μm are shown in Fig. 4 for an emulsion with the sensitivity of 0.85 GOST units. The optoacoustic signals recorded in photographic emulsions with a different sensitivity differ only slightly in shape and in amplitude. For all emulsions the exposure to a single second-harmonic radiation pulse (which forms a latent image and leads to blackening of the emulsion after development) does not produce any noticeable change in the amplitude of the acoustic signal. This indicates that the light absorption factor remains constant. At the same time, in the emulsion exposed to light the amplitude of the signal increases markedly, and the shape changes.

The optoacoustic signals in the unexposed emulsion and in the emulsion exposed to a single pulse $\lambda = 0.53$ μm did not exceed the noise level considerably ($S/N \sim 5$ to 10), and, therefore, the light scattering

and light absorption factors can only be estimated. Since in this case we can assume that $\mu_{\text{eff}} c_0 \tau_L \ll 1$, the extinction coefficient can be estimated from the rate of acoustic signal wavefront rise [2]: $\mu_{\text{eff}} = (0.47 \text{ to } 0.56) \times 10^3 \text{ cm}^{-1}$. This is approximately one-third that for $\lambda = 0.53$ μm.

Estimates of the light absorption factor derived from the value of the normalized amplitude of the signal ($p_{\max}/E_0 \cong 0.4$ atm·cm^2/J) yield

$$\mu_a(\lambda = 1.06 \text{ μm}) = (0.06 \pm 0.02) \text{ cm}^{-1}.$$

Correspondingly, the light scattering factor has the same order of magnitude as at the second harmonic (see above). As can be seen, the light absorption factor is appreciably (by a factor of 30) smaller than at the second harmonic. Upon exposure of the emulsion to light (without development of the latent image), the light absorption factor at the fundamental harmonic increases 2.5 to 3 times. Thus, the forming latent image centers affect the absorption of the fundamental harmonic appreciably stronger than the absorption of the second harmonic.

5. DISCUSSION OF EXPERIMENTAL RESULTS AND CONCLUSIONS

The absence of a noticeable difference in the optical characteristics at the wavelength $\lambda = 0.53$ μm of unexposed and exposed to light photographic emulsions (see Item 4(1°)) appears to be the most unexpected result. This suggests that the forming latent image centers (blackening of emulsion upon development testifies unambiguously to their appearance even on irradiation by a single second-harmonic pulse) do not contribute materially to the absorption of light.

An unexpected feature is that the optical properties of photographic emulsions with strongly differing sensitivity (from 0.85 to 170 GOST units) are close for radiation both in visible and in UV region, in which photographic emulsions are not sensitive. This fact may count in favor of the idea of formation of latent image centers, set forth in [1].

The initial absorption of light with $\lambda = 1.06$ μm is small, so that its increase can be detected during the formation of silver clusters on latent image centers when the emulsion is exposed to light. However, latent image centers formed after a single exposure to a second-harmonic pulse do not bring about any noticeable change in the light absorption factor.

The observed shapes of the optoacoustic signals show that the contribution of the concentration-deformation mechanism of sound generation in photographic emulsions by radiation in the visible and UV regions is small. Therefore, the participation of photoexcited carriers in the generation of latent image centers deserves further verification.

We sum up the above discussion.

1. An optoacoustic procedure is proposed for measuring light scattering and absorption factors in heterogeneous media. The light absorption and scattering factors were measured at $\lambda = 1.06$ and 0.53 μm. It is found that at these wavelengths in photographic emulsions the light absorption factor is much smaller than the scattering factor.

2. It is found that the optical properties of photographic emulsions having the same composition but different photographic sensitivity are close.

3. It is shown that the influence of latent image centers on the optical characteristics of photographic emulsions is insignificant.

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