

# Nonlinear refraction of silver hydrosols during their aggregation

S V Karpov, M K Kodirov, A I Ryasnyanskii, V V Slabko

**Abstract.** The relation between the degree of aggregation of silver hydrosols and their nonlinear refractive index  $n_2$  is studied experimentally. It is found that the sign of  $n_2$  at a wavelength of  $1.064 \mu\text{m}$  changes with increasing the aggregation degree, which corresponds to the replacing of self-focusing by self-defocusing. The observed effects are explained based on the analysis of a change in nonlinear dispersion of the medium, taking into account the interaction between phases and the photochromic effects, which are typical for colloidal structures with fractal geometry. It is shown that the change in the sign of the nonlinear refractive index of hydrosols upon irradiation by laser pulses of duration of less than  $10^{-7}$  s is caused by the perturbation of resonances of silver and water and by the competition between Kerr nonlinear polarisations involving these resonances.

**Keywords:** nonlinear refraction, silver hydrosol, self-defocusing.

## 1. Introduction

A search for new media with extremely high nonlinear optical parameters and a study of their properties is one of the basic problems of quantum electronics. These media can find broad applications in active integral elements in optoelectronics, which can be controlled by low-power semiconductor lasers. Sols of metals, in which nanoparticles of a dispersion phase form fractal structures, belong to such nonlinear optical media. The unique nonlinear optical properties of metal sols were demonstrated already in first experiments [1, 2], which confirmed the predictions of new physical theories (see references in [1]).

Silver colloids are the most convenient model medium for studying optical phenomena in metal sols. Their optical properties in the visible range are determined by an isolated surface plasmon resonance lying outside the interband absorption band. Coagulation of particles, both spontane-

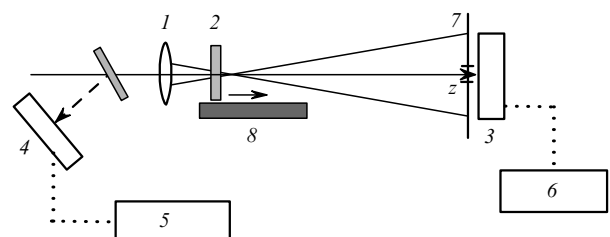
ous and photoinduced, results in a growth of colloidal structures with fractal properties (see references in [3]). The growth of fractal aggregates because of the electrodynamic interaction between particles is accompanied by a strong inhomogeneous broadening of the plasmon absorption spectrum of hydrosols [1, 3].

The relation between the degree of aggregation of solver colloids, the fractal dimensionality of the aggregates and nonlinear optical properties of these media has been found in a number of papers [1–6]. One of the simplest and convenient tools for studying nonlinear optical properties of materials is the  $z$ -scan method a new highly sensitive single-beam method for measuring the nonlinear refractive index  $n_2$ , which was proposed in paper [7].

The aim of this paper is to study by the  $z$ -scan method the variation in the refractive index  $n_2$  of silver hydrosols with increasing degree of their aggregation, to analyse the mechanisms of optical nonlinearity, and to estimate the role of accompanying processes. Note that in the case of cubic nonlinearity, the refractive index of the medium is related to  $n_2$  by the known expression [7]  $n = n_0 + 0.5n_2|E|^2 = n_0 + \Delta n$ , where  $n_0$  is the linear refractive index and  $E$  is the field amplitude.

## 2. Experimental

We used in our experiments a  $Q$ -switched Nd:YAG laser. The dynamics of variation of the refractive index  $n_2$  of silver hydrosols was studied at the emission wavelength  $1.064 \mu\text{m}$  of a Nd:YAG laser ( $W = 12 \text{ mJ}$ ,  $\tau = 15 \text{ ns}$ ). The experimental setup was assembled using the scheme with a limiting aperture [7] (Fig. 1). The aperture of diameter 1 mm, which transmitted  $\sim 1\%$  of laser radiation, was placed at a distance of 100 cm from the focal region. Behind the aperture, a photodiode (3) was placed whose output signal was measured with a digital voltmeter (6).



**Figure 1.** Scheme of the experimental setup: (1) focusing lens; (2) cell with hydrosol; (3, 4) photodiodes; (5, 6) digital voltmeters; (7) aperture; (8) micro precision translation stage.

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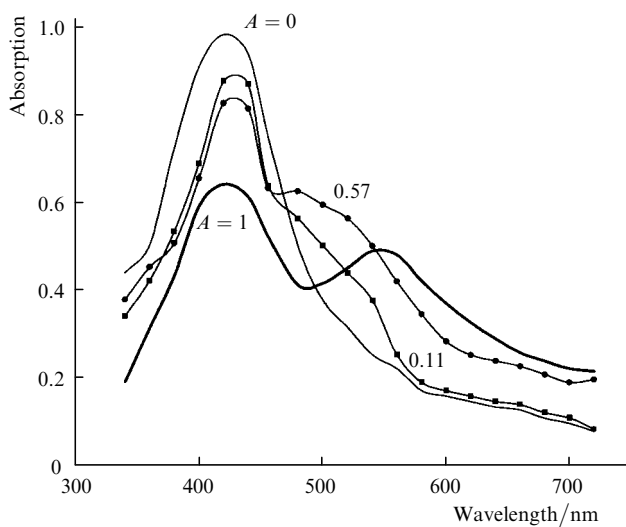
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To avoid the influence of the instability of output energy parameters of the laser on the results of measurements, a signal detected with a photodiode (3) was normalised to the corresponding signals from the second diode (4). Laser radiation was focused by a lens (1) with the focal distance 18 cm. A 2-mm thick quartz cell (2) containing silver hydrosol was moved along the optical axis  $z$  with the help of a micro precision translation stage (8), passing the focus and the regions in front of and behind the focus. The focal-spot size at the beam waist was 100  $\mu\text{m}$  and the maximum radiation intensity achieved 8  $\text{GW cm}^{-2}$ . The energy of laser pulses was measured with a calibrated photodiode (4) and recorded with a digital voltmeter (5). The scheme with a limiting aperture allowed us to measure both the sign and the absolute value of the nonlinear refractive index  $n_2$  of the medium under study.

A standard Ag hydrosol was prepared from collargol (methods of sol preparation are described in references in [3]). The dimensions of silver aggregates were within 100–1000 nm, the average size of silver particles being 4–20 nm and the volume fraction of silver being of the order of  $10^{-6}$ . The degree of aggregation was controlled by the absorption spectra of hydrosols. The determination of the degree of aggregation of sols by the broadening of their absorption spectra was proposed, in particular, in paper [3]. The absorption spectra of hydrosol detected during aggregation are shown in Fig. 2.

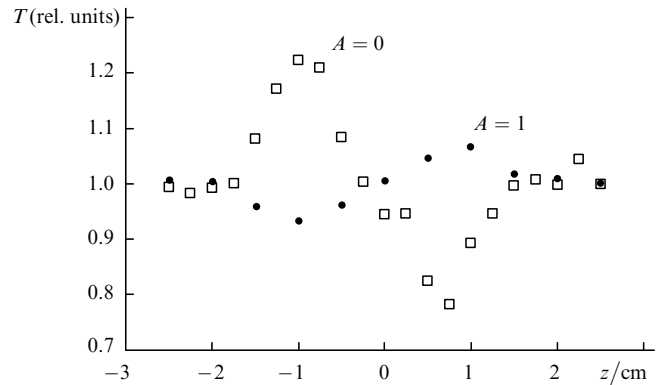


**Figure 2.** Absorption spectra of Ag hydrosols with different aggregation degrees  $A$ .

### 3. Results and discussion

Fig. 3 shows typical dependences  $T(z)$  of the transmission of a cell with Ag hydrosol on its position with respect to the point of laser radiation focusing. These dependences were obtained for the initial ( $A = 0$ , the intensity in the focal region is  $I \approx 10^9 \text{ W cm}^{-2}$ ) and final ( $A = 1$ ,  $I \approx 10^8 \text{ W cm}^{-2}$ ) degree of aggregation. We found that the sign of  $n_2$  changes with increasing  $A$ .

Nonlinear optical parameters of the medium were determined from optical transmission using the  $z$ -scan equation [7]



**Figure 3.** Normalised transmission  $T$  as a function of the position of a cell with Ag hydrosol in a scheme with a limiting aperture for different aggregation degrees  $A$ .

$$\Delta T_{\text{pv}} = 0.404(1 - S)^{0.25} \left| \frac{2\pi\Delta n_0 [1 - \exp(-\alpha L)]}{\lambda\alpha} \right|, \quad (1)$$

where  $\Delta T_{\text{pv}}$  is the normalised difference between the maximum and minimum transmission in the dependence  $T(z)$ ;  $\Delta n_0$  is the nonlinear addition to the refractive index  $\Delta n$  at the focus ( $z = 0$ );  $S$  is the geometrical transmission of the aperture (a fraction of radiation in a diverging Gaussian beam incident on the photodetector through the aperture 7 (Fig. 1) in the absence of nonlinear effects);  $\lambda$  is the radiation wavelength;  $L$  is the sample length;  $\alpha$  is the linear absorption coefficient. The nonlinear refractive index  $n_2$  of silver hydrosol calculated from equation (1) was from  $1.1 \times 10^{-11}$  ( $A = 0$ ) to  $3.2 \times 10^{-10}$  CGSE units ( $A = 1$ ).

An important experimental result obtained in this paper, which should be discussed separately, is the change of the sign of  $n_2$  with increasing  $A$ . In fact, the initial ability of the medium for self-focusing changes to its ability for self-defocusing with increasing  $A$ , because the nonlinear refractive index of the medium is related to the third-order nonlinear susceptibility as  $n_2 \propto n_0^{-2} \chi^{(3)}$  [8]. The fact of changing of  $\chi^{(3)}$  for hydrosols upon their aggregation is known [1, 2]; however, the models describing this effect do not predict the sign change (at least, upon irradiation at 1.064  $\mu\text{m}$ ). Therefore, this effect should be additionally analysed.

In this paper, we assume that nonlinear refraction in Ag hydrosols is caused by the high-frequency Kerr effect at the resonances existing in the medium, because, as follows from our estimates, the contribution from thermal expansion of the medium in the case of nanosecond pulses used in experiments is negligible. The Kerr nonlinear susceptibility  $\chi^{(3)}$  of a multicomponent system for the process  $\omega = \omega + \omega - \omega$  in the case of a simplest two-level system away from resonances can be written as (see, for example, Ref. [9])

$$\chi^{(3)}(\omega, -\omega, \omega) \propto \sum_i N_i \frac{d_{12i}^4}{(\omega_{12i} - \omega)^3}, \quad (2)$$

where  $d_{12i}$  is the matrix element of the electric dipole transition moment at the frequency  $\omega_{12i}$ ;  $N_i$  is the concentration of particles of the  $i$ th component of the medium (summation is performed over all the components).

One can see from expression (2) that the sign of  $n_2$  is determined by the sign of the resonance detuning. If the

condition  $\omega < \omega_{12}$  is fulfilled, self-focusing is observed in a one-component medium, while for  $\omega > \omega_{12}$ , self-defocusing is observed. If upon summation over components of the medium the partial contribution from some of the components dominates, then the sign of  $n_2$  will also depend on  $d_{12i}$  and the concentration of the  $i$ th component. The domination role of one of the resonances in the variation of nonlinear dispersion properties of the medium can result in the positive or negative nonlinear refraction. In our case, the main components of the medium are silver nanoparticles and water.

Consider the contribution from each of the main components of hydrosol to  $\chi^{(3)}$  at the laser emission wavelength 1.064  $\mu\text{m}$ , taking into account the resonances that are typical for such media. In the case of silver particles, a surface plasmon with the absorption band at  $\lambda_{\text{pl}} = 0.42 \mu\text{m}$  and the interband absorption band lying at  $\lambda < 0.35 \mu\text{m}$  play the main role in the formation of a nonlinear response. The frequencies of both these bands are higher than the laser frequency  $\omega_{\text{las}}$ , so that their contribution to nonlinear refraction will be positive.

The inhomogeneous broadening of the spectrum of a surface plasmon along with the effective red shift of the absorption band (Fig. 2) accompanying the aggregation of silver particles results in the increase of the positive contribution to nonlinear refraction. The negative contribution to nonlinear refraction can be introduced by discrete states, which are caused by the size quantisation of the electron energy in a small metal particle [10]. However, in our case, for Ag particles of diameter 10 nm the difference between the energies of nearest quantum states for allowed transitions is  $740 \text{ cm}^{-1}$  ( $\sim 13.5 \mu\text{m}$ ). For such a difference between the energies, it is unlikely that these resonances will make a substantial negative contribution to nonlinear refraction at the wavelength 1.064  $\mu\text{m}$ .

It follows from the above that the aggregation of Ag particles should not result in the change of the sign of nonlinear refraction because even in the case of maximum spectral broadening and partial absorption in the region  $\omega < \omega_{\text{las}}$ , the weight contribution to  $\chi^{(3)}$  of the resonances located in the region  $\omega > \omega_{\text{las}}$  dominates.

The Kerr susceptibility  $\chi^{(3)}$  of water is caused by the influence of the vibronic band ( $\lambda < 0.19 \mu\text{m}$ ) with the integrated  $d_{12}^{\text{ev}} \sim 10^{-18}$  CGSE units and of the vibronic band with the fundamental transition at 2.9  $\mu\text{m}$  and its first overtone at 1.45  $\mu\text{m}$  [11, 12]. The contributions from these bands to  $\chi^{(3)}$  have the opposite signs, and the total nonlinear refraction will be determined by the relation between  $d_{12}^{\text{ev}}$  and  $d_{12}^{\text{v}}$ . Our estimates show that the contribution from the short-wavelength transitions dominates, and nonlinear refraction of water at 1.064  $\mu\text{m}$  is positive, which is confirmed by the experimental data [13, 14]. This is explained by some excess of  $(d_{12}^{\text{ev}})^4 |\Delta\omega_{\text{ev}}|^{-3}$  over  $(d_{12}^{\text{v}})^4 \times |\Delta\omega_{\text{v}}|^{-3}$  ( $\Delta\omega_{\text{ev}}$  and  $\Delta\omega_{\text{v}}$  are the detunings of the corresponding resonances from  $\omega_{\text{las}}$ ).

Therefore, the contributions from both components of the medium to  $\chi^{(3)}$  are positive and should increase during the aggregation of particles. This contradicts to the experimental data and requires the model to be corrected.

### 3.1 Mechanisms of the change in optical characteristics of hydrosol in the laser radiation field

In our opinion, the optical characteristics of hydrosols are changed mainly due to the heating of particles. Thus, for the radiation intensity at the waist  $I = 8 \times 10^9 \text{ W cm}^{-2}$ , a

particle of size  $10^{-6} \text{ cm}$  absorbs  $10^{-10} \text{ J}$ . In this case, its temperature can increase to  $10^4 - 10^5 \text{ K}$  at a distance of 2 cm from the focus and to  $10^6 \text{ K}$  at the waist (neglecting the heat exchange with the environment). This means that, under these conditions, the effect of a plasmon resonance of silver particles on the dispersion properties of hydrosol is essentially different from that at room temperature.

The absorption of radiation increases with increasing  $A$  due to the approach of silver resonances to  $\omega_{\text{las}}$ , and the heating of silver particles is accompanied by a change in the hydrosol characteristics. We believe that the optical properties of hydrosol change due to a combined action of two processes. First, this is evaporation of silver particles and expansion of a plasma bunch during the laser pulse action to the size at which the plasma frequency  $\omega_{\text{pl}}$  decreases to  $\omega_{\text{pl}} < \omega_{\text{las}}$ , as well as  $d_{12}^{\text{pl}}$  (the latter occurs because of oxidation of silver ions during the destruction of a crystal lattice and electron solvation). Second, this is vibrational excitation of water molecules, which are in contact with silver particles, followed by the population of high vibrational states ( $v \gg 1$ ) of the molecules, whose dipole transition moment increases as  $v^{1/2}$  [15]. Both these mechanisms result in the increase of the negative contribution to nonlinear refraction.

The estimate of the minimum unperturbed value of  $d_{12}^{\text{pl}}$  based on the spectroscopic data for Ag sol with particles of size  $\sim 10 \text{ nm}$  gives the value  $2.5 \times 10^{-16}$  CGSE units. To estimate  $d_{12}^{\text{v}}$  for the vibrational transition of water ( $v = 0 - 1$ ) nearest to  $\omega_{\text{las}}$ , we can use optical constants of water at this frequency [11, 12] and the Lorenz–Lorentz formula. As a result, we obtained  $d_{12}^{\text{v}} \approx 10^{-20}$  CGSE units.

Using the above values of  $d_{12}^{\text{pl}}$  and  $d_{12}^{\text{v}}$ , the ratio  $|\Delta\omega_{\text{pl}}^3 / \Delta\omega_{\text{v}}^3| \approx 10^4$ , and the volume fraction of silver  $N_{\text{Ag}} \leq 10^{-6}$ , we obtain the ratio

$$P_{\text{Ag}}^{(3)} : P_{\text{H}_2\text{O}}^{(3)} \propto [N_{\text{Ag}} (d_{12}^{\text{pl}})^4 |\Delta\omega_{\text{pl}}|^{-3}] : [(d_{12}^{\text{v}})^4 |\Delta\omega_{\text{v}}|^{-3}] \quad (3)$$

of nonlinear polarisations at the transitions in silver and water for nonaggregated sol equal to  $\sim 10^7$ .

The experimental data show that the value of  $\chi^{(3)}$  for hydrosol is several orders of magnitude higher than that in pure water, although it is underestimated taking into account the large value of  $d_{12}^{\text{pl}}$ . This suggests that silver plays an important interceding role in the enhancement of optical nonlinearity of hydrosol and indicates the presence of processes in hydrolysis which reduce the relative contribution of dispersed silver to  $\chi^{(3)}$  of hydrosol and are characterised by the variation in parameters entering expression (2). Let us analyse these processes separately.

#### 3.1.1 Mechanisms of the enhancement of electric dipole transition moments in water

As was already mentioned, the effect of strongly heated dispersed silver particles on the nonlinear properties of water can be explained by a decrease in  $d_{12}^{\text{v}}$  caused by the population of high vibrational states of water molecules ( $d_{12}^{\text{v}} \sim v^{1/2}$  [15]), which are in contact either with silver particles heated by radiation or with a plasma being produced. A similar mechanism of self-focusing due to vibrational, rotational, and electronic excitation of molecules and atoms was discussed in paper [16].

Consider some examples describing the conditions for manifestation of this mechanism. The dissociation energy of

a water molecule is close to the energy of the upper vibrational state and is  $8.4 \times 10^{-20}$  J [17], which corresponds to the temperature  $6 \times 10^4$  K. The energy  $\sim 10^{-10}$  J absorbed by a particle is sufficient for thermal dissociation of  $\sim 10^8$  molecules, which occupy the volume  $3 \times 10^{-15}$  cm<sup>3</sup> and can be arranged around the particle in a spherical layer of thickness  $R = 10^{-5}$  cm. The time during which all the molecules in the layer will be dissociated is  $t = R/v_s \sim 10^{-10}$  s, where  $v_s$  is the sound speed in water.

This means that the volume occupied by thermally excited water molecules is at least  $10^3$  times larger than the volume of silver particles, although the fraction  $N_t$  of excited water molecules does not exceed  $10^{-3} - 10^{-2}$ . If we assume that  $d_{12}^V$  increases at least by one order of magnitude, then, taking into account the relation  $|\Delta\omega_{ev}|^{-3}/|\Delta\omega_v|^{-3} \approx 10^6$  and the above range of values of  $N_t$ , the contribution of vibrational transitions of water to its Kerr susceptibility  $\chi^{(3)}$  can be equal at least to the contribution of the vibronic band, by changing substantially the ratio (3).

### 3.1.2 Mechanism of a change in the resonance frequency of silver particles: dynamic resonances

During sol aggregation, the absorption spectrum is modified and a long-wavelength wing appears (Fig. 2). This is one of the reasons for the variation in dispersion properties of the medium. Another important mechanism is also based on the above estimates of the increase in the particle temperature in the field of laser pulses and on the possible change of  $\omega_{pl}$  under such conditions. The matter is that upon strong heating of particles followed by the plasma production, the particle volume increases, resulting in the decrease in the electron concentration  $n_e$ .

However, because  $\omega_{pl} \sim n_e^{1/2}$ , the plasma expansion is accompanied by the time-dependent red shift of  $\omega_{pl}$ . The evaporation of most particles during the pulse action should result in a strong dynamic increase in the density of surface plasmon resonances in the range  $\omega < \omega_{las}$ , which is responsible for self-defocusing. Thus, to observe during the plasma expansion the red shift of the frequency  $\omega_{pl}$  from  $c/0.42$   $\mu\text{m}$  to the frequency corresponding approximately to 1.1–1.2  $\mu\text{m}$ , at which the sign of nonlinear refraction can already change, the size of a plasma bunch should be approximately doubled. In this case, the rate of its expansion will be restricted by the sound speed in water, and, for the initial particle size  $\sim 10^{-8}$  m, the plasma-bunch size will be doubled for the time of the order of  $10^{-11}$  s, i.e., this effect can be observed using picosecond pulses. Obviously, it is in the aggregated sol with the initial red shift of the plasmon absorption band that the dynamic decrease in  $\omega_{pl}$  will lead to the maximum increase in the spectral density of plasmon resonances in the range  $\omega < \omega_{las}$ , which is responsible for self-defocusing.

When estimating dynamical frequency shifts, it is also necessary to take into account the correction for the shift of  $\omega_{pl}$  related to a change in the permittivity  $\epsilon_m$  of the environment when the vapour cavity is formed around a particle, because  $\omega_{pl} \sim (1 + 2\epsilon_m)^{-1/2}$  [18]. Such a correction  $\omega_{pl}^{\text{vapor}}/\omega_{pl}^{\text{water}}$  does not exceed 1.17.

### 3.1.3 Mechanisms of a change in the concentration of spectral components of a sol

When analysing the conditions of passing from self-focusing regime to self-defocusing in the process of aggregation, it is important to take into account the partial contributions

of the main components of hydrosol related to the possible variation in their volume concentration.

First of all, during the evaporation of particles, the destruction of a crystal lattice, and plasma expansion, the interband absorption band of the metal disappears, which facilitates self-defocusing. In addition, these mechanisms are directly related to sol aggregation. In particular, when a long-wavelength wing appears in the absorption spectrum of sol during the aggregation, the conditions are produced for photomodification of fractal aggregates and burning particles in them, which are in resonance with the field [5] (another photochromic effect—photoaggregation [19], will be absent because  $\omega_{las}$  lies beyond the red threshold of this process [3, 6]. However, the pulse intensity in our experiments exceeded the resonance photomodification threshold by a factor of  $\sim 10^3$ . In this case, the photomodification of aggregates in the field of IR pulses is strongly nonselective, and the fraction of particles involved in the process begins to increase sharply due to nonresonance particles. In the case of complete evaporation of all the particles in a sol during the action of the pulse, their interaction with radiation occurs only on dynamic plasmon resonances of silver (whose frequency changes during the pulse action).

In addition, the broadening of the absorption spectrum accompanied by its red shift during the aggregation provides a stronger absorption of laser radiation by particles, resulting in their stronger heating, because plasmon resonances approach the value of  $\omega_{las}$ . This leads, in particular, to the 30-fold increase in the magnitude of  $n_2$  for an aggregated sol compared to that for a nonaggregated sol.

### 3.2 Analysis of accompanying processes and of their kinetics

The destruction of particles in aggregates by nanosecond laser pulses as one of the reasons for the change in the sign of nonlinear refraction requires an additional analysis from the point of view of the kinetics of this process when experiments are performed with picosecond pulses. The question arises of whether silver particles will have time to evaporate (to cease the interaction with light) upon irradiation by a 30-ps pulse. To answer this question, we will use the dependences describing the development time  $t_p$  of photomodification in such Ag hydrosols [19].

It follows from [19] that  $t_p$  depends on the pulse energy density and decreases from 150 to 50 ps upon the fourfold increase of the energy density. Obviously, at higher energy densities, the time  $t_p$  can further decrease, and the particles can evaporate during one pulse, i.e., the role of this process in the Kerr nonlinearity seems to be realistic from the point of view of kinetics for picosecond pulses.

Note that the use of picosecond pulses in the  $z$ -scan method gave similar results: the sign of  $n_2$  changed and the magnitude of  $n_2$  increased with increasing  $A$ . This result shows that the contribution of the thermal component of nonlinearity caused by the heating of the medium by radiation and accompanied by the expansion of the heated region is negligible. The expansion reduces the medium density, resulting in the decrease in the refractive index.

The negligible contribution of the thermal mechanism to self-defocusing is confirmed by a negligible expansion of the heated region during irradiation by a nanosecond pulse even compared to the focal waist size. Indeed, the size of a thermal lens being formed is  $r_0 = v_s \tau$  ( $v_s \approx 10^5$  cm s<sup>-1</sup> is the sound speed in water), and for 15-ns pulses it does not

exceed  $\sim 10^{-3}$  cm. This is an order of magnitude less than the experimental size of the focal waist and at least two orders of magnitude less than the beam diameter outside the focus, where the self-defocusing is maximal (Fig. 3). For 30-ps pulses,  $r_0$  will be only  $\sim 10^{-6}d_b$ , where  $d_b$  is the beam diameter. At least for this reason, the conclusions made in paper [8] about the relation of negative nonlinear refraction of Au hydrosols to the formation of thermal lenses upon irradiation by 0.53- $\mu\text{m}$ , 35-ns pulses cast doubts.

When analysing the conditions for manifestation of nonlinear refraction, one should take also into account the scattering of laser radiation by metal hydrosols related to the formation of vapour bubbles around particles of the dispersed phase absorbing radiation [20] (the time of their formation and growth was  $\sim 10^{-8}$  s [20]). However, when a cell with hydrosol is located in front of the focus (Fig. 1), this effect will only prevent the Kerr self-defocusing. This means that the Kerr nonlinearity on dynamic plasmon resonances of silver and vibrational transitions in water makes a much greater contribution than under real experimental conditions.

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