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On the theory of nonlinear photoacoustic signal generation during gas-microphone detection

© T.Kh. Salikhov,[1] U. Madvaliev,[2] D.M. Sharifov,[3] H.Kh. Tuichiev[4]

[1] Tajik State National University,
734025 Dushanbe, Tajikistan
[2] S.U.Umarov Physical-Technical Institute of the National Academy of Sciences of Tajikistan,
734063 Dushanbe, Tajikistan
[3] L.N.Gumilyov Eurasian National University,
010008 Nur-Sultan, Kazakhstan
[4] Tajik State Pedagogical University,
734025 Dushanbe, Tajikistan
e-mail: tsalikhov@mail.ru

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A theory is proposed for of the generation of the first two harmonics of a nonlinear photoacoustic signal of a solids sample with an arbitrary value of thermal conductivity. For limiting cases (thermally thin and thick samples) has been obtained simple expressions for the dependence of the amplitude of the excited photoacoustic signal from the emissivity of the sample and the thermophysical parameters of the sample, gas and substrates, including their thermal coefficients.

Keywords: photoacoustics, thermal nonlinearity, second harmonic.

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Introduction

Various options of the linear theory of laser generation of sound waves by one- and two-layer samples in a photoacoustic (PA) chamber, when the signal is recorded by a microphone technique, are proposed in [1–4]. Numerous theoretical and experimental studies have shown that the parameters of the PA signal are saturated with information about the physical quantities of condensed media, including nanosystems (see, for example, [5–11]). The main mechanism of excitation of acoustic waves in this case is thermal, due to the periodic change in the heat flux coming from the sample into the gas layer, the thermal acoustic piston model [1]. It is known that when performing an PA experiment, as a rule, a laser beam is used, the spatial distribution of which is Gaussian, and with an increase in its intensity I_0, a significant increase in the temperature of the sample occurs, due to which all physical quantities of the medium become temperature-dependent, and this dependence is commonly called thermal nonlinearity (TN) [7].

The features of the excitation of nonlinear components of heat waves, including the second harmonic (SH), are studied in sufficient detail in [12–14]. Meanwhile, relatively recently it was shown [15] that the resolution of the PA microscope on the SH significantly exceeds the resolution of a conventional PA microscope on the fundamental harmonic (FH) and this allowed the authors to implement the visualization of biological samples. Essentially, a fundamentally new opportunity has emerged for the visualization of ultra-high resolution biological materials, which is a significant potential for the development of studies of nonlinear PA response of samples.

For the case when the registration of the PA signal is performed by the gas-microphone technique, the theoretical consideration is carried out in [16,17]. In [17] for a two-layer one-dimensional PA chamber model, the theory of generating a nonlinear PA response was developed when the sample is low heat conducting, but which is not acceptable for samples with moderate or high thermal conductivity. The purpose of this paper is to summarize the results of [17] and a detailed theoretical study of the contribution of the TN substrate to the characteristics of a nonlinear PA signal.

1. Mathematical model

Suppose that the intensity of the monochromatic beam incident on the PA chamber is modulated harmonically with the frequency ω, and the absorption coefficient of the incident beam of the sample is — β. As in [17], we consider a one-dimensional model of the PA chamber in which the buffer gas and the substrate are transparent for the incident beam, and then the following system of nonlinear heat conduction equations for all layers of the chamber takes place:

$$C_{pg}(T_g)\frac{\partial T_g'}{\partial t} = \frac{\partial}{\partial x}\left(\kappa(T_g)\frac{\partial T_g'}{\partial x}\right), 0 \le x \le l_g, \quad (1)$$

$$C_{ps}(T_s)\frac{\partial T_s'}{\partial t}=\frac{\partial}{\partial x}\left(\kappa_s(T_s)\frac{\partial T_s'}{\partial x}\right)$$
$$+0.5A(T)\beta I_0(1+e^{i\omega t})\exp(\beta x),\ -l\le x\le 0, \quad (2)$$
$$C_{pb}(T_b)\frac{\partial T_b'}{\partial t}=\frac{\partial}{\partial x}\left(\kappa_b(T_b)\frac{\partial T_b'}{\partial x}\right),\ -(l_b+l)\le x\le -l. \quad (3)$$

The temperature dependence of the values $C_{pi}(T)=\rho_i c_{pi}$ and $\kappa_i(T)$ — the heat capacity of the volume unit and the thermal conductivity coefficient of the corresponding layers in the PA chamber, as well as $A(T)$ — the degree of blackness of the sample is considered linear and let us imagine in the following form

$$C_{pi}=C_{pi}^{(0)}(1+\delta_i T'),\ \kappa_i=\kappa_i^{(0)}(1+\delta_{2i}T'),$$
$$A=A^{(0)}(1+\delta_3 T'),$$

where $C_{pi}^{(0)}=C_{pi}(T_0)$, $\kappa_i^{(0)}=\kappa(T_0)$, $A^{(0)}=A(T_0)$ — initial values, and $\delta_i=(1/C_{pi}^{(0)})(\partial C_{pi}/\partial T)$, $\delta_{2i}=(1/\kappa_i^{(0)})\times(\partial\kappa_i/\partial T)$, $\delta_3=(1/A^{(0)})(\partial A/\partial T)$ — thermal coefficients of the same values.

The temperature perturbation is represented as a sum

$$T_i'(x,t)=T_{0i}(x)+\Phi_{Li}(x,t)+\Phi_{1Ni}(x,t)+\Phi_{2Ni}(x,t),$$

where $T_{0i}(x)$ is locally equilibrium, and $\Phi_{Li}(x,t)$ and $\Phi_{Ni}(x,t)$ are linear and nonlinear components corresponding to the acoustic parts on the main and second harmonics. Then from (1)–(3) we obtain the following systems of equations for $T_{0i}(x)$, $\Phi_{1Ni}(x,t)$ and $\Phi_{2Ni}(x,t)$:

$$\frac{d}{dx}\left[\frac{dT_{0i}(x)}{dx}+0.5\delta_{2i}\frac{dT_{0i}^2(x)}{dx}\right]=H_i,\quad i=g,s,b, \quad (4)$$
$$\frac{\partial^2\Phi_{1Ni}}{\partial x^2}-\frac{1}{\chi_i^{(0)}}\frac{\partial\Phi_{1Ni}}{\partial t}=-\left(\delta_{2i}\frac{\partial^2}{\partial x^2}-\frac{\delta_{1i}}{\chi_i^{(0)}}\frac{\partial}{\partial t}\right)$$
$$\times\big(T_{0i}(x)\Phi_{Li}(x,t)\big)+H_{1i},\quad i=g,s,b, \quad (5)$$
$$\frac{\partial^2\Phi_{2Ni}}{\partial x^2}-\frac{1}{\chi_i^{(0)}}\frac{\partial\Phi_{2Ni}}{\partial t}=-\frac{1}{2}\left(\delta_{2i}\frac{\partial^2}{\partial x^2}-\frac{\delta_{1i}}{\chi_i^{(0)}}\frac{\partial}{\partial t}\right)$$
$$\times\big(\Phi_{Li}^2(x,t)\big)+H_{2i},\quad i=g,s,b, \quad (6)$$

where

$$H_g=H_b=0,$$
$$H_s=\frac{0.5\beta A^{(0)}I_0\big(1+\delta_{3s}T_{0s}(0)\big)e^{\beta x}}{k_s^{(0)}},$$
$$H_{1g}=H_{1b}=0,$$
$$H_{1s}=0.5A^{(0)}\beta I_0\delta_3\big[T_{0s}(0)e^{i\omega t}+\Phi_L(0,t)\big]e^{\beta x},$$
$$H_{2g}=H_{2b}=0,\ H_{2s}=-0.5A^{(0)}\beta I_0\delta_3\Phi_L(0,t)e^{i\omega t}e^{\beta x}.$$

Taking into account that $\Phi_L(t,x)=\Phi_L(\omega,x)\times\times\exp(i\omega t)$ [1], put $\Phi_{1Ni}(t,x)=\Phi_{1Ni}(\omega,x)\exp(i\omega t)$ and $\Phi_{2Ni}(t,x)=\Phi_{2Ni}(2\omega,x)\exp(i2\omega t)$. Then from (4)–(6) for functions $\Psi_{1i}(x,\omega)=\Phi_{1Ni}(x,\omega)+\delta_{2i}T_{0i}(x)\Phi_{Li}(x,\omega)$ and $\Psi_{2i}(t,x)=\Phi_{2Ni}(2\omega,x)+0.5\delta_{2i}\Phi_{Li}^2(\omega,x)$ we get the following system of equations:

$$\frac{d^2\Psi_{1i}}{dx^2}-\sigma_i^2\Psi_i=\sigma_i^2(\delta_i-\delta_{2i})T_{0i}(x)\Phi_{Li}(x,\omega)+G_i,$$
$$i=g,s,b, \quad (7)$$
$$\frac{d^2\Psi_{2i}}{dx^2}-\sigma_{2i}^2\Psi_{2i}=\frac{(\delta_i-\delta_{2i})}{2}\sigma_{2i}^2\Phi_{Li}^2(\omega,x)+G_{2i},$$
$$i=g,s,b, \quad (8)$$

where

$$G_g=G_b=0,\ G_s=-0.5A^{(0)}\beta I_0\delta_3[\Theta_0+\Phi_{Ls}(0,\omega)]e^{\beta x},$$
$$G_{2g}=G_{2b}=0,$$
$$G_{2s}==-0.5A^{(0)}\beta I_0\delta_3\Phi_{Ls}(0,\omega)e^{\beta x},$$
$$\Phi_{Lg}(x,\omega)=\Theta_L e^{-\sigma_g x},\ \Phi_{Lb}(x,\omega)=W_L e^{\sigma_b(x+l)},$$
$$\Phi_{Ls}(x,\omega)=U_L e^{\sigma_s x}+V_L e^{-\sigma_s x}-Ee^{\beta x}$$

are the linear components of temperature fluctuations, the amplitudes of which are determined by the expressions [1]:

$$U_L=\Delta_1/\Delta,\quad V_L=\Delta_2/\Delta,$$
$$\Delta_1=E[(g+r)(b+1)e^{\sigma_x l}-(g-1)(b-r)e^{-\beta l}],$$
$$E=0.5\beta A^{(0)}I_0[k_s^{(0)}(T_0)(\beta^2-\sigma_s^2)]^{-1},$$
$$\Delta_2=E[(g+1)(b-r)e^{-\beta l}-(b-1)(g+r)e^{-\sigma_x l}],$$
$$\Delta=[(g+1)(b+1)e^{\sigma_s l}-(g-1)(b-1)e^{-\sigma_s l}],$$

but $\sigma_i^2=i\omega/\chi_i^{(0)}$, $\sigma_i=(1+i)/\mu_i$, $g=\kappa_g^{(0)}\sigma_g/\kappa_s^{(0)}\sigma_s$, $b=k_b^{(0)}\sigma_b/k_s^{(0)}\sigma_s$, $r=(1-i)\beta\mu_s/2$, $\mu_i=(2\chi_i/\omega)^{1/2}$ — thermal diffusion length, $\chi_i^{(0)}=\kappa_i^{(0)}/C_{pi}^{(0)}$ — the initial value of the thermal conductivity of the corresponding layers. We emphasize that when deriving a system of equations (4)–(6) The fact was taken into account that the degree of blackness of the sample $A(T)$ characterizes the optical properties of its surface and is not a function of its thickness. This is due to the appearance of terms with $T_{0s}(0)$ and $\Phi_{0s}(0,\omega)$ in the right parts of the system of equations (4)–(6), and then in equations (7) and (8).

The conditions of continuity of temperatures and heat flows at the boundaries between the layers, as well as the absence of heating at the ends of the PA chamber, allow us to write the following boundary conditions for a joint solution (4)–(8):

$$T_{0g}(l_g)=T_{0b}(-1-l_b)=0,\quad T_{0s}(0)=T_{0g}=\Theta_0,$$
$$T_{0b}(-l)=T_{0s}(-l)=W_0, \quad (9)$$
$$\kappa_g(T_g)\frac{dT_{0g}(x)}{dx}\bigg|_{x=0}=\left[\kappa_s(T_s)\frac{dT_{0s}(x)}{dx}\right]\bigg|_{x=0},$$
$$\kappa_b(T_b)\frac{dT_{0b}(x)}{dx}\bigg|_{x=-l}=\left[\kappa_s(T_s)\frac{dT_{0s}(x)}{dx}\right]\bigg|_{x=-l}, \quad (10)$$

$$\Phi_{1Ns}(\omega,0)=\Phi_{1Ng}(\omega,0),\quad \Phi_{1Nb}(\omega,-l)=\Phi_{1Ns}(\omega,-l),$$

$$\left[\frac{\partial\Psi_{1g}(\omega,x)}{\partial x}\right]\bigg|_{x=0}=\frac{\kappa_s^{(0)}}{\kappa_g^{(0)}}\frac{\partial\Psi_{1s}(\omega,x)}{\partial x}\bigg|_{x=0}, \tag{11}$$

$$\Phi_{1Nb}(\omega,-l-l_b)=\Phi_{1Ng}(\omega,l_g)=0,$$

$$\frac{\partial\Psi_{1b}(\omega,x)}{\partial x}\bigg|_{x=-l}=\frac{\kappa_s^{(0)}}{\kappa_b^{(0)}}\frac{\partial\Psi_{1s}(\omega,x)}{\partial x}\bigg|_{x=-l}, \tag{12}$$

$$\Phi_{2Ns}(\omega,0)=\Phi_{2Ng}(\omega,0),\quad \Phi_{2Nb}(\omega,-l)=\Phi_{2Ns}(\omega,-l),$$

$$\left[\frac{\partial\Psi_{2g}(\omega,x)}{\partial x}\right]\bigg|_{x=0}=\frac{\kappa_s^{(0)}}{\kappa_g^{(0)}}\frac{\partial\Psi_{2s}(\omega,x)}{\partial x}\bigg|_{x=0}, \tag{13}$$

$$\Phi_{2Nb}(\omega,-l-l_b)=\Phi_{2Ng}(\omega,l_g)=0,$$

$$\frac{\kappa_s^{(0)}}{\kappa_b^{(0)}}\frac{\partial\Psi_{2s}(\omega,x)}{\partial x}\bigg|_{x=-l-l_b}=\frac{\partial\Psi_{2b}(\omega,x)}{\partial x}\bigg|_{-l-l_b}. \tag{14}$$

Boundary conditions (9)–(14) together with a system of equations (4)–(8) represent a mathematical model of the formulated problem and allow it to be solved.

2. Temperature field

Using the notation $T_i(x)=\delta_{2i}^{-1}g_{0i}(x)$, from the system (6) for a stationary temperature field we obtain the following expressions:

$$g_{0g}(x)=\left[1+\Theta_0\delta_{2g}(2+\Theta_0\delta_{2g})\left(1-\frac{x}{l_g}\right)\right]^{1/2}-1,$$

$$g_{0b}(x)=\left[1+W_0\delta_{2b}(2+W_0\delta_{2b})\left(1+\frac{x+l}{l_b}\right)\right]^{1/2}-1,$$

$$g_{0s}(x)=\Bigg\{1+\delta_{2s}\Theta_0(2+\delta_{2s}\Theta_0)\left(1+\frac{x}{l}\right) - \delta_{2s}W_0(2+\delta_{2s}W_0)\frac{x}{l}+\frac{A^{(0)}I_0\delta_{2s}(1+\delta_3\Theta_0)}{\beta\kappa_s^{(0)}} \times\left[1+\frac{x}{l}-\left(e^{\beta x}+E_0\frac{x}{l}\right)\right]\Bigg\}^{1/2}-1,$$

where $E_0=\exp(-\beta l)$. The conditions of continuity of heat flows allow us to write the following system of nonlinear algebraic equations to determine the values of Θ_0 and W_0:

$$\Theta_0^2(\delta_{2s}+d\delta_{2g})+2\Theta_0(1+d+U\delta_3)-W_0^2\delta_{2s}-2W_0+U=0, \tag{15}$$

$$\Theta_0^2\delta_{2s}+2\Theta_0(1+U_1\delta_3)-W_0^2(\delta_{2s}+d_1\delta_{2g}) - 2W_0(1+d_1)+U_1=0, \tag{16}$$

where

$$d=\frac{\kappa_g^{(0)}l}{\kappa_s^{(0)}l_g},\quad d_1=\frac{\kappa_b^{(0)}l}{\kappa_s^{(0)}l_b},$$

$$U=\frac{A^{(0)}I_0}{\beta\kappa_s^{(0)}}(1-E_0-\beta l), U_1=\frac{A^{(0)}I_0}{\beta\kappa_s^{(0)}}[(1-E_0(1+\beta l)].$$

The expressions for $g_{0i}(x)$ together with the system of algebraic equations (15), (16) determine the main features of the formation of a stationary temperature field in the PA chamber for the case under consideration. Obviously, due to the nonlinearity of the system (15), (16), its solution can be obtained only numerically. We performed this calculation for the case when the sample is quartz glass, and the role of the substrate is played by zirconium dioxide ZrO_2. The thermophysical parameters required for the calculation have the following values: $T_0=300\,K$, $\kappa_g^{(0)}$=0.025 W/(m·K), $\kappa_s^{(0)}$=1.36 W/(m·K), $\kappa_b^{(0)}$=1.7 W/(m·K), δ_{2g}=2.3910^{-3} K^{-1}, δ_{2s}=0.5610^{-3} K^{-1}, δ_{2b}=0.104·10^{-3} K^{-1} [18]. Thickness values l_g=5·10^{-3} m, $l_s=10^{-3}$ m, $l_b=10^{-3}$ m. The calculation results are illustrated in Figure 1, from which it can be seen that for small values of β not only the temperature increase is small, but also the nature of its dependence on intensity is linear. With the growth of β and the gradual transition from the condition $\beta<1$ to the condition $\beta>1$, the heating will increase significantly, and the dependence on I_0 goes to a power one. Numerical solutions of the system (15), (16) were also found for different values of δ_3, the results of which are shown in Figure 2. It can be seen that with an increase in the value of variable value and a change in its sign from negative to positive, the heating of the sample increases significantly, and the nature of its dependence on the intensity of the incident beam becomes close to quadratic. The decrease in the values of Θ_0 and W_0 at $\delta_3<0$ compared to their values at $\delta_3=0$ is due to a decrease in the absorption capacity of the system. And conversely, an increase in the values of these values for the case $\delta_3>0$ compared to the case is associated with an increase in the absorption capacity of the sample. The calculating results of the temperature increment for various substrates are illustrated in Figure 3, from which it can be seen that with the transition from substrates made of materials with low thermal conductivity to materials with higher thermal conductivity, the heating of the sample decreases significantly. This is due to the fact that with such a transition, the rate of heat transfer to the substrate increases, and then from it to the environment. It is obvious that with an increase in the thermal conductivity of the substrate, the values of Θ_0 and W_0 will decrease significantly. Meanwhile, as it was found in [16], only for small values of I_0 the dependencies $\Theta_0\sim I_0$, $W_0\sim 1$ are valid, and for moderate and higher values of I_0 this dependence goes from linear to a power one.

3. The fundamental harmonic

The expressions

$$\Psi_{1Ng}=\Theta_{1N}e^{-\sigma_g x}+R_{1g}S_{1g}(x)e^{\sigma_g x}-R_{1g}S_{2g}(x)e^{-\sigma_g x}, \tag{17}$$

$$\Psi_{1Ns}=U_{1N}e^{\sigma_s x}+V_{1N}e^{-\sigma_s x}+[R_{1s}S_{1s}(x)-\Omega_1(x)]e^{\sigma_s x} - [R_{1s}S_{2s}(x)-\Omega_2(x)]e^{-\sigma_s x}. \tag{18}$$

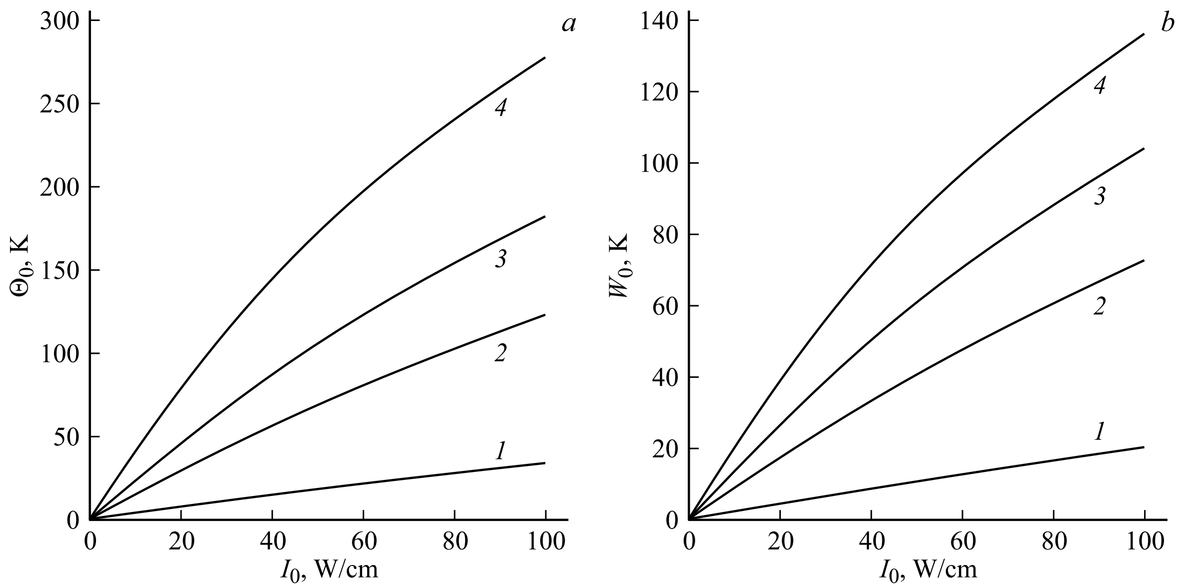

Figure 1. Dependence of the temperature of the irradiated (a) and rear (b) sides of quartz glass in contact with zirconium dioxide in the PA chamber on the intensity of the incident beam at values $A^{(0)} = 0.87$, $\delta_3 = -0.577 \cdot 10^{-3}\,\mathrm{K}^{-1}$, (integral values) [19] and $\beta = 1$, 5, 10, 50 cm^{-1} (curves *1–4* respectively).

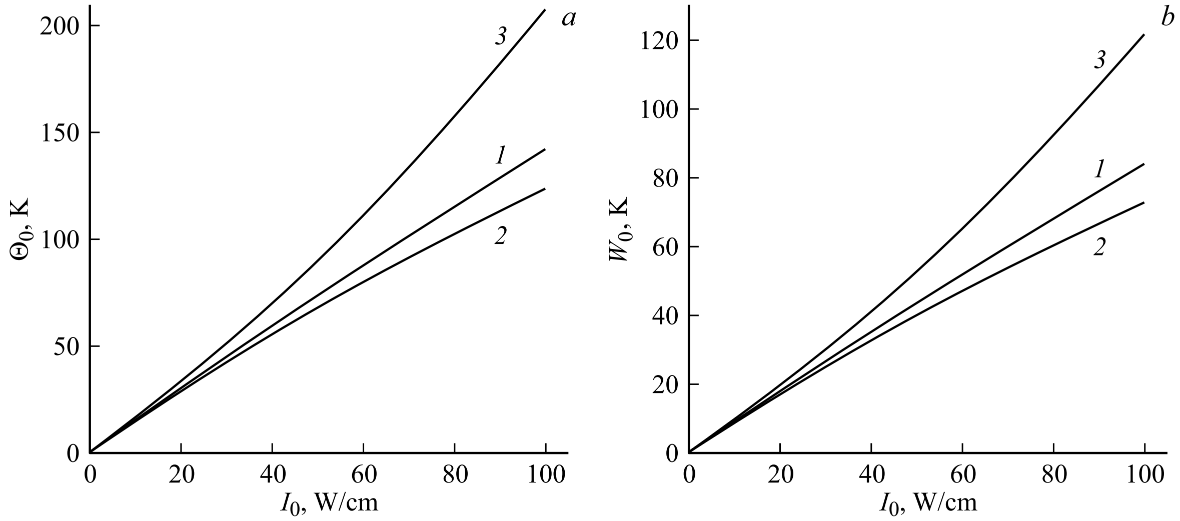

Figure 2. Dependence of the temperature of the irradiated (a) and rear (b) sides of quartz glass in contact with zirconium dioxide in the PA chamber on the intensity of the incident beam at values $A^{(0)} = 0.87$, $\delta_3 = 0$ (curve *1*), $\delta_3 = -0.577 \cdot 10^{-3}\,\mathrm{K}^{-1}$ (curve *2*) and $\delta_3 = 1.2355 \cdot 10^{-3}\,\mathrm{K}^{-1}$ (curve *3*).

$$\Psi_{1Nb} = W_{1N} e^{\sigma_b(x+l)} + R_{1b} S_{1b}(x) e^{\sigma_b(x+l)} - R_{1b} S_{2b}(x) e^{-\sigma_b(x+l)}, \tag{19}$$

are solutions of equations (7) for the corresponding layers. The following designations are used here: $R_{1i} = 0.5\delta_{2i}^{-1}\sigma_i(\delta_i - \delta_{2i})$,

$$S_{1g}(x) = \int g_{0g}(x)\Phi_{Lg}(x,\omega) e^{-\sigma_g x} dx,$$

$$S_{2g}(x) = \int g_{0g}(x)\Phi_{Lg}(x,\omega) e^{\sigma_g x} dx, \tag{20}$$

$$S_{1b}(x) = \int g_{0b}(x)\Phi_{Lb}(x,\omega) e^{-\sigma_b(x+l)} dx,$$

$$S_{2b}(x) = \int g_{0b}(x)\Phi_{Lb}(x,\omega) e^{\sigma_b(x+l)} dx, \tag{21}$$

$$S_{1s}(x) = \int g_{0s}(x)\Phi_{Ls}(x,\omega) e^{-\sigma_s x} dx,$$

$$S_{2s}(x) = \int g_{0s}(x)\Phi_{Ls}(x,\omega) e^{\sigma_s x} dx, \tag{22}$$

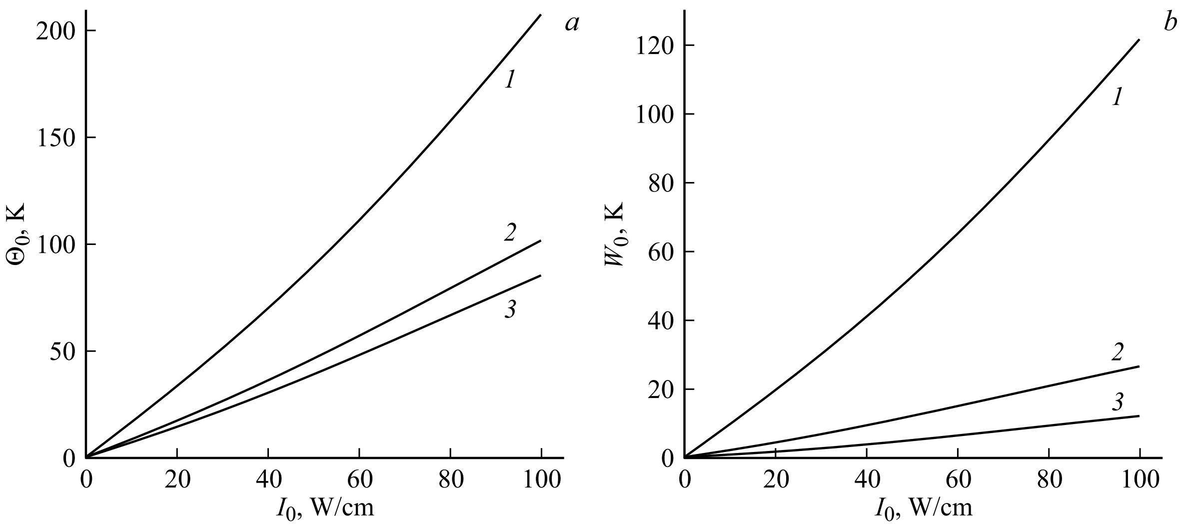

Figure 3. Dependence of the temperature of the irradiated (a) and the rear (b) side of the quartz glass ($A^{(0)} = 0.87$, $beta = 50\,\mathrm{cm}^{-1}$, $\delta_3 = 1.2355 \cdot 10^{-3}\,\mathrm{K}^{-1}$) for the case of substrates made of: zirconium oxide (curve *1*), polycrystalline bismuth $\kappa_b^{(0)} = 7\,\mathrm{W/(m\cdot K)}$, $\delta_2 = 2.38 \cdot 10^{-3}\,\mathrm{K}^{-1}$ [18] (curve *2*) and stainless steel $\kappa_b^{(0)} = 14.9\,\mathrm{W/(m\cdot K)}$, $\delta_2 = 0.94 \cdot 10^{-3}\,\mathrm{K}^{-1}$ [18] (curve *3*).

$$\Omega_{1s}(x) = (0.25A^{(0)}\beta I_0\delta_3)(\kappa_s^{(0)})^{-1}\sigma_x^{-1} \times \int [\Theta_0 + \Phi_{Ls}(\omega, 0)] e^{(\beta-\sigma_s)x} dx, \tag{23}$$

$$\Omega_{2s}(x) = (0.25A^{(0)}\beta I_0\delta_3)(\kappa_s^{(0)})^{-1}\sigma_x^{-1} \times \int [\Theta_0 + \Phi_{Ls}(\omega, 0)] e^{(\beta+\sigma_s)x} dx, \tag{24}$$

Substituting the functions $\Phi_{Li}(\omega, x)$ into the corresponding expressions (20)−(24) and by performing the integration according to the procedure proposed in [17], we will have

$$S_{1g}(x) \approx \frac{\Theta_L}{2\sigma_g}\left[1 - \sqrt{B_g} + \frac{b_g}{2l_g\sqrt{B_g}}\left(x + \frac{1}{2\sigma_g}\right)\right] e^{-2\sigma_g x},$$

$$S_{2g}(x) = -\left[\frac{2l_g}{2b_g} B_g^{3/2}\left[\sqrt{\left(1 - \frac{b_g x}{B_g l}\right)^3} - 1\right] + x\right]\Theta_L,$$

$$S_{1s}(x) \approx \left\{\frac{2l}{3(b_s - b_{s,b})} B_s^{3/2}\left[\sqrt{\left(1 + \frac{(b_s - b_{s,b})x}{B_s l}\right)^3} - 1\right] - x\right\} U_L + (1 - B_s^{1/2})\frac{V_L}{2\sigma_s}\exp(-2\sigma_s x),$$

$$S_{2s}(x) \approx \left\{\frac{2l}{3(b_s - b_{s,b})} B_s^{3/2}\left[\sqrt{\left(1 + \frac{(b_s - b_{s,b})x}{B_s l}\right)^3} - 1\right] - x\right\} V_L + (B_s^{1/2} - 1)\frac{U_L}{2\sigma_s}\exp(2\sigma_s x),$$

$$S_{1b}(x) = \left\{\frac{2}{3} B^{3/2}\frac{l_b}{b_b}\left[\sqrt{\left[1 + \frac{b_b}{l_b B_b}(x + l)\right]^3} - 1\right] - (x + l)\right\} W_L,\ S_{2b}(x) \approx \frac{W_L\sqrt{B_b} - 1}{2\sigma_b} e^{2\sigma_b(x+l)},$$

where $B_i = 1 + b_i$, $b_g = \delta_{2g}\Theta_0(2 + \delta_{2g}\Theta_0)$, $b_s = \delta_{2s}\Theta_0(2 + \delta_{2s}\Theta_0)$, $b_b = \delta_{2b}W_0(2 + \delta_{2b}W_0)$, $b_{sb} = \delta_{2s}W_0(2 + \delta_{2s}W_0)$. Taking into account the condition $l_g \gg \mu_g$ and equality $g_{0g}(0) = \delta_{2g}\Theta_0$, $\sqrt{B_g} = 1 + \delta_{2g}\Theta_0$, $\sqrt{B_s} = 1 + \delta_{2s}\Theta_0$, $g_{0s}(0) = \delta_{2s}\Theta_0$, $g_{0s}(-l) = \delta_{2s}W_0$, $g_b(-l) = \delta_{2b}\Theta_0$, we get that

$$S_{1g}(0) \approx -0.5\Theta_L\delta_{2g}\Theta_0\sigma_g^{-1},\ S_{2g}(0) = 0,$$

$$S_{1s}(0) \approx -0.5V_L\delta_{2s}\Theta_0\sigma_s^{-1},\ S_{2s}(0) \approx 0.5U_L\delta_{2s}\Theta_0\sigma_s^{-1}.$$

In expressions (17)−(19) there are four unknown parameters Θ_{1N}, U_{1N}, V_{1N} and W_{1N}, for finding which, using the boundary conditions (11), (12), we obtain the following algebraic system of equations:

$$\Theta_{1N} + R_{1g}[S_{1g}(0) - S_{2g}(0)] - g_{0g}(0)\Phi_{Lg}(0, \omega) = U_{1N} + V_{1N} + R_{1s}[S_{1s}(0) - S_{2s}(0)] - g_{0s}(0)\Phi_{Ls}(0, \omega) + \Omega_{2s}(0) - \Omega_{1s}(0), \tag{25}$$

$$g[R_{1g}(S_{1g}(0) + S_{2g}(0)) - \Theta_{N1}] = U_{1N} - V_{1N} + R_{1s}[S_{1s}(0) + S_{2s}(0)] - \Omega_{1s}(0) - \Omega_{2s}(0), \tag{26}$$

$$U_{1N}e^{-\sigma_s l} + V_{1N}e^{\sigma_s l} + [R_{1s}S_{1s}(-l) - \Omega_{1s}(-l)]e^{-\sigma_s l} - [R_{2s}S_{2s}(-l) - \Omega_{2s}(-l)]e^{\sigma_s l} - g_{0s}(-l)\Phi_{Ls}(-l) = W_{1N} + R_{1b}[S_{1b}(-l) - S_{2b}(-l)] - g_{0b}(-l)\Phi_{Lb}(-l), \tag{27}$$

$$U_{1N}e^{-\sigma_s l} - V_{1N}e^{\sigma_s l} + [R_{1s}S_{1s}(-l) - \Omega_{1s}(-l)]e^{-\sigma_s l}$$
$$+ [R_{1s}S_{2s}(-l) - \Omega_{2s}(-l)]e^{\sigma_s l}$$
$$= b\{W_{1N} + R_{1b}[S_{1b}(-l) + S_{2b}(-l)]\}. \quad (28)$$

Taking into account the smallness of $g \ll 1$, the equality

$$\Phi_{Ls}(0) = \Phi_{Lg}(0) = \Theta_L = U + V - E,$$
$$\Phi_{Ls}(-l) = \Phi_{Lb}(-l) = Ue^{-\sigma_s l} + Ve^{\sigma_s l} - Ee^{-\beta l} = W_L$$

and using the notation

$$\Psi = \Big\{\big[(1-b)S_{1s}(-l)e^{-\sigma_s l} + (1+b)S_{2s}(-l)e^{\sigma_s l}\big]R_{1s}$$
$$+ [g_{0s}(-l)\Phi_{Ls}(-l) - g_{0b}(-l)\Phi_{Lb}(-l) - 2R_{1b}S_{2b}(-l)]b\Big\},$$

for the value Θ_{1N}, we get the following expression:

$$\Theta_{1N} = \Big\{\Delta\Theta_L\Theta_0(\delta_{2g} - \delta_{2s}) + R_{1g}\Delta[S_{1g}(0) - S_{2g}(0)]$$
$$+ 2e^{\sigma_s l}(b+l)[\Omega_{2s}(0) - R_{1s}S_{2s}(0)] + 2(1-b)e^{-\sigma_s l}$$
$$\times [\Omega_{1s}(0) - R_{1s}S_{1s}(0)] + 2\Psi - 2[\Omega_{2s}(-l)e^{\sigma_s l}(b+1)$$
$$- \Omega_{1s}(-l)e^{-\sigma_s l}(b-1)]\Big\}\Delta^{-1}. \quad (29)$$

Taking into account the fact that $\Theta_0 \gg \Theta_L$, the type of functions $\Omega_{1s}(\omega, x)$ and $\Omega_{2s}(\omega, x)$ can be written in the form of

$$\Omega_{1s}(x) = (0.25A^{(0)}\beta I_0\delta_3)(\kappa_s^{(0)})^{-1}\sigma_s^{-1}\Theta_0(\beta-\sigma_s)^{-1}e^{(\beta-\sigma_s)x}, \quad (30)$$

$$\Omega_{2s}(x) = (0.25A^{(0)}\beta I_0\delta_3)(\kappa_s^{(0)})^{-1}\sigma_s^{-1}\Theta_0(\beta+\sigma_s)^{-1}e^{(\beta+\sigma_s)x}, \quad (31)$$

Expressions (30) and (31) together with the formula (29) allow us to determine the acoustic pressure perturbation in the buffer gas. To do this, using the ratio $\Phi_{1Ng}(x,t) = \Psi_{1g}(x,t) - \delta_{2g}T_{g0}(x)\Phi_{Lg}(x,t)$ and the expression (17), we find the form functions $\Phi_{1Ng}(x,\omega)$, and then $\delta p_{1N}(\omega)$ — the nonlinear part of the acoustic pressure fluctuation, for which it is necessary to integrate the expression

$$\delta p_{1N}(\omega) = \frac{\gamma p_0 2\pi\mu_g}{T_0 l_g}\overline{\Phi}_{1Ng}(\omega) = \frac{\gamma p_0}{T_0 l_g}\int_0^{2\pi\mu_g}\Phi_{1Ng}(\omega,x)dx. \quad (32)$$

The expression [17]

$$\delta p_N(\omega) = \frac{\gamma p_0}{T_o l_g \sigma_g}\left[\Theta_{1N} + R_{1g}\tilde{S}_{1g}(0) - g_{0g}(0)\Theta_L\right] \quad (33)$$

is the result of integration, where $\tilde{S}_{1g}(x) = S_{1g}(x)\exp(2\sigma_g x)$. Performing the necessary calculations, we obtain the expression

$$R_{1g}\tilde{S}_{1g}(0) - g_{0g}(0)\Theta_L = -0.25\Theta_L(3\delta_{2g} + \delta_g)\Theta_0,$$

considering which the expression (33) can be rewritten in the form

$$\delta p_{1N}(\omega) = \delta p_L\big[\Theta_L^{-1}\Theta_{1N} - 0.25(3\delta_{2g} + \delta_g)\Theta_0\big], \quad (34)$$

where $\delta p_L = \gamma p_0\Theta_L/T_0 l_g\sigma_g$ — is the linear component of the PA signal, the amplitude of which linearly depends on I_0. Due to the fact that the expression for Θ_{1N} is very complex, we will consider the limit cases that are implemented in the experiment. We will also assume that the system is strongly absorbing, for which the conditions are valid $\beta l \gg 1$ and $\exp(-\beta l) \approx 0$.

3.1. Thermally thin samples

The conditions $l \ll \mu_s$, $\mu_s \gg \mu_\beta$, $\exp(-\beta l) \approx 0$, $\exp(\pm\sigma_s l) \approx 1$, $|r| \gg 1$, $g \ll 1$, $b \gg g$, $r \gg g$, $\Delta \approx 2b$, $W_L = Er/b$, $\Delta_1 \approx r(1+b)E$, $\Delta_2 \approx r(1-b)E$, $E = b(r - -b)^{-1}\Theta_L$, $U_L = Er(b+1)/2b$, $V_L = Er(1-b)/2b$, $U_L + V_L = Er/b$, $U_L - V_L = Er$, are met for them, where $\mu_\beta = \beta^{-1}$ — is the photon path length in the sample.

It follows from the expression (29) that to define Θ_{1N}, it is necessary to have an explicit form of the functions $S_{1g}(0)$, $S_{2g}(0)$, $S_{1s}(0)$, $S_{2s}(0)$, $S_{1s}(-l)$, $S_{2s}(-l)$, $S_{2b}(-l)$. Performing the necessary calculations for these functions, we obtain the following expressions:

$$\Omega_{1s}(\omega,-l) \approx 0,\ \Omega_{2s}(\omega,-l) \approx 0,$$
$$\Omega_{1s}(\omega,0) \approx \Omega_{2s}(\omega,0) = 0.25A^{(0)}I_0\delta_3,$$
$$S_{1s}(0) \approx -\frac{V_L\delta_{2s}\Theta_0}{2\sigma_s},\ S_{2s}(0) \approx \frac{U_L\delta_{2s}\Theta_0}{2\sigma_s},$$
$$S_{2s}(-l) \approx \frac{V_L\delta_{2s}\Theta_0}{2\sigma_s}, S_{1s}(-l) \approx -\frac{V_L\delta_{2s}\Theta_0}{2\sigma_s},$$
$$S_{2b}(-l) = \frac{\delta_{2b}W_0W_L}{2\sigma_b},$$
$$S_{2s}(-l) - S_{1s}(-l) = -\frac{\delta_{2s}\Theta_0}{2\sigma_s}\frac{Er}{b},$$
$$S_{2s}(-l) + S_{1s}(-l) = \frac{\delta_{2s}\Theta_0}{2\sigma_s}\frac{Er}{b},$$
$$\Psi \approx bW_0W_L\left[\delta_{2s} - \delta_{2b} - \frac{\delta_b - \delta_{2b}}{2}\right].$$

Then from the expression (29) we get

$$\Theta_{1N} = \Theta_L\Big\{\Theta_0[\delta_3 + 0.25(\delta_g - \delta_{2g}) + \delta_{2g} - \delta_{2s}]$$
$$+ W_0[\delta_{2s} - \delta_{2b} + 0.5(\delta_{2b} - \delta_b)]\Big\}. \quad (35)$$

Further, substituting the expression (35) into (34) for the nonlinear PA signal on FH, we obtain

$$\delta p_{1N}(\omega) = \delta p_L(\omega)[K_{1(1)}\Theta_0 + K_{1(2)}W_0], \quad (36)$$

where $K_{1(1)} = \delta_2 - \delta_{2s}$, $K_{1(2)} = \delta_{2s} - 0.5(\delta_b + \delta_{2b})$. From (36) it is easy to see that in this case the dependence of the amplitude of the PA signal on the frequency is governed by the dependence $|\delta p_{1N}(\omega, l \ll \mu_s)| \sim \omega^{-1}$.

3.2. Thermally thick samples. Case I

In this case, these conditions come around $\mu_s < l$, $\mu_s > \mu_\beta$, $\exp(-\beta l) \approx 0$ and $\exp(-\sigma_s l) \approx 0$ and $|r| > 1$. Then the equalities are valid $\Delta_1 = Er(b+1)e^{\sigma_s l}$, $\Delta_2 \approx 0$, $\Delta = (b+1)e^{\sigma_s l}$, $U_L \approx Er$, $V_L \approx 0$, $\Theta_L = E(r-1) \approx rE$, $W_L \approx 0$, $E = A^{(0)} I_0 (2\beta k_s^{(0)})^{-1}$, accounting for which allows you to get the following expressions:

$$\Phi_{Ls}(-l) = W_L = 0, \Phi_{Lb}(-l) = W_L = 0, S_{1s}(0) \approx 0,$$

$$\Omega_{1s}(\omega, -l) \approx 0, \quad \Omega_{2s}(\omega, -l) \approx 0,$$

$$S_{2s}(0) \approx \frac{\Theta_0 \delta_{2s}}{\sigma_s} U_L, S_{1s}(-l) \approx -\frac{lU_L}{2} \delta_{2s}\Theta_0, S_{2s}(-l) \approx 0,$$

$$S_{2b}(-l) = 0, \Omega_{1s}(\omega, 0) \approx \Omega_{2s}(\omega, 0) = 0.25A^{(0)} I_0 \delta_3 \Theta_0 \sigma_s^{-1}.$$

Substituting these formulas in (29), we obtain the expression

$$\Theta_{1N} \approx \left[\delta_3 + \delta_{2g} + 0.25(\delta_g - \delta_{2g}) - 0.5(\delta_s + \delta_{2s})\right]\Theta_0\Theta_L,$$

which allows you to write the following expression for the FH acoustic pressure fluctuations in the buffer gas

$$\delta p_{1N} = \delta p_{1L} \Theta_0 K_{1(3)}, \qquad (37)$$

where $K_{1(3)} = \delta_3 - 0.5(\delta_{2s} + \delta_s)$. Rewriting the expression (37) as $\delta p_{1N}(\omega, l \gg \mu) = |\delta p_{1N}| e^{i\psi_{1N}}$, for the amplitude $|\delta p_{1N}|$ and the phase ψ_{1N} of the excited PA signal, we get

$$|\delta p_{1N}(l \gg \mu_s)| = \frac{\gamma p_s \mu_s^{(0)} \mu_g^{(0)} A^{(0)} I_0}{4T_0 l_g k_s^{(0)}} |K_{1(3)}| \Theta_0,$$

$$\psi_{1N(1)}(l \gg \mu_s) = \begin{cases} -\frac{\pi}{2}, & if\ K_{1(3)} > 0, \\ \frac{\pi}{2}, & if\ K_{1(3)} < 0. \end{cases} \qquad (38)$$

This expression shows that the dependence of the amplitude of the nonlinear PA signal on the frequency for thermally thick samples obeys the law $\propto \omega^{-1}$.

3.3. Thermally thick samples. Case II

Consider the case when the conditions are valid $\mu_s \lll$, $\mu_s < \mu_\beta$, $\exp(-\beta l) \approx 0$, $\exp(-\sigma_s l) \approx 0$, $|r| < 1$ and equality $\Delta_1 = Er(b+1)e^{\sigma_s l}$, $\Delta_2 \approx 0$, $\Delta = (b+1)e^{\sigma_s l}$, $U_L \approx Er$, $V_L \approx 0$, $W_L \approx 0$,

$$\Theta_L = E(r-1) \approx -E = A^{(0)} I_0 [2\kappa_s^{(0)} \sigma_s^2],$$

$$E = -A^{(0)} I_0 (2\sigma_s^2 k_s^{(0)})^{-1}, \Omega_{1s}(\omega, 0) \approx -\Omega_{2s}(\omega, 0),$$

$$\Omega_{2s}(\omega, 0) = 0.25A^{(0)} (\kappa_s^{(0)})^{-1} \beta l_0 \delta_3 \Theta_0 \sigma_s^{-2},$$

$$S_{2s}(0) \approx \frac{\Theta_0 \delta_{2s}}{\sigma_s} [0.5U_L - E] \approx \frac{\Theta_0 \delta_{2s} E}{\sigma_s} [0.5r - 1] \approx \frac{-\Theta_0 \delta_{2s} E}{\sigma_s}.$$

The other functions $S_{1s}(0)$, $S_{1s}(-l)$, $S_{2s}(-l)$, $S_{2b}(-l)$ and Ψ have the same form as above. Then from (29) we get the expression

$$\Theta_{1N} \approx \left[\delta_{2g} + 0.25(\delta_g - \Theta_{2g}) - 0.5(\delta_s + \delta_{2s}) - \delta_3\right]\Theta_0\Theta_L,$$

substitution of which into (34) will lead us to the expression

$$\delta p_{1N}(\omega, \mu \ll l, \mu_s < \mu_\beta) = \delta p_{1L} \Theta_0 K_{1(4)}, \qquad (39)$$

where $K_{1(4)} = -\delta_3 - 0.5(\delta_s + \delta_{2s})$. In this case, for the amplitude and phase of the signal, we get

$$|\delta p_{1N}(\omega, l \gg \mu_s,\ \mu_s < \mu_\beta)| = \frac{\gamma p_0 A^{(0)} I_0 \mu_g \mu_s^2}{4\sqrt{2} l_g T_{00} k_s^{(0)}} K_{1(4)} \Theta_0,$$

$$\psi_{1N}(\omega, l \gg \mu_s, \mu_s < \mu_\beta) = \begin{cases} \frac{\pi}{4}, & if\ K_{1(4)} > 0, \\ -\frac{3\pi}{4}, & if\ K_{1(4)} < 0. \end{cases} \qquad (40)$$

It follows from (40) that the amplitude of the generated PA signal depends on the frequency $|\delta p_{1N}(\omega, l \gg \mu_s, \mu_s < \mu_\beta)| \sim \omega^{-3/2}$.

It follows from (36), (38) and (40) that only for low values I_0, when $\Theta_0 \sim I_0$, $W_0 \sim I_0$, there is a dependence $|\delta p_{1N}(\omega, l \gg \mu_s, \mu_s < \mu_\beta)| \sim I_0^2$.

4. Second harmonic

The expressions

$$\Psi_{2g}(\omega, x) = \Theta_{2N} e^{-\sigma_{2g} x} + e^{\sigma_{2s} x} W_{1g}(\omega, x) - e^{-\sigma_{2g} x} W_{2g}(\omega, x), \qquad (41)$$

$$\Psi_{2s}(\omega, x) = U_{2N} e^{\sigma_{2s} x} + V_{2N} e^{-\sigma_{2s} x} + e^{\sigma_{2s} x}[W_{1s}(\omega, x) - Q_{1s}(x, \omega)] - e^{-\sigma_{2s} x}[W_{2s}(\omega, x) - Q_{2s}(x, \omega)], \qquad (42)$$

$$\Psi_{2b}(\omega, x) = W_{2Nb} e^{+\sigma_{2b}(x+l)} + e^{\sigma_{2b}(x+l)} W_{1b}(\omega, x) - e^{-\sigma_{2b}(x+l)} W_{2b}(\omega, x) \qquad (43)$$

are the solution of equation (8), where

$$W_{1g}(\omega, x) = R_{2g} \int e^{-\sigma_{2g} x} \Phi_{Lg}^2(\omega, x) dx,$$

$$W_{2g}(\omega, x) = R_{2g} \int e^{\sigma_{2g} x} \Phi_{Lg}^2(\omega, x) dx, \qquad (44)$$

$$W_{1b}(\omega, x) = R_{2b} \int e^{-\sigma_{2b}(x+l)} \Phi_{Lb}^2(\omega, x) dx,$$

$$W_{2b}(\omega, x) = R_{2b} \int e^{\sigma_{2b}(x+l)} \Phi_{Lb}^2(\omega, x) dx, \qquad (45)$$

$$W_{1s}(\omega, x) = R_{2s} \int e^{-\sigma_{2s} x} \Phi_{Ls}^2(\omega, x) dx,$$

$$Q_{2s}(\omega, x) = (0.25A^{(0)} \beta I_0 \delta_3)(\kappa_s^{(0)})^{-1} \sigma_{2s}^{-1} \times \int \Phi_{Ls}(\omega, 0) e^{(\beta + \sigma_{2s})x} dx, \qquad (46)$$

$$W_{2s}(\omega, x) = R_{2s} \int e^{\sigma_{2s} x} \Phi_{Ls}^2(\omega, x) dx,$$

$$Q_{1s}(\omega, x) = (0.25A^{(0)} \beta I_0 \delta_3)(\kappa_s^{(0)})^{-1} \sigma_{2s}^{-1} \times \int \Phi_{Ls}(\omega, 0) e^{(\beta - \sigma_{2s})x} dx. \qquad (47)$$

To determine the values of Θ_{2N}, U_{2N}, V_{2N} and W_{2N} from the boundary conditions (13), (14) we obtain the following algebraic system of four equations:

$$Q_{2N} + W_{1g}(\omega, 0) - W_{2g}(\omega, 0) = U_{2N} + V_{2N} + W_{1s}(\omega, 0) - W_{2s}(\omega, 0) + Q_{2s}(\omega, 0) - Q_{1s}(\omega, 0) + 0.5\Theta_L^2(\delta_{2g} - \delta_{2s}), \quad (48)$$

$$-Q_{2N} + W_{1g}(\omega, 0) + W_{2g}(\omega, 0) = g^{-1}\big[U_{2N} - V_{2N} + W_{1s}(\omega, 0) + W_{2s}(\omega, 0) + Q_{1s}(\omega, 0) - Q_{2s}(\omega, 0)\big], \quad (49)$$

$$U_{2N}e^{-\sigma_{2s}l} + V_{2N}e^{\sigma_{2s}l} + e^{-\sigma_{2s}l}[W_{1s}(\omega, -l) - Q_{1s}(\omega, -l)] - e^{\sigma_{2s}l}[W_{2s}(\omega, -l) - Q_{2s}(\omega, -l)] = W_{2N} + W_{1b}(\omega, -l - W_{2b}(\omega, -l) + 0.5\Phi_{Ls}^2(\omega, -l)(\delta_{2s} - \delta_{2b}), \quad (50)$$

$$U_{2N}e^{-\sigma_{2s}l} - V_{2N}e^{\sigma_{2s}l} + e^{-\sigma_{2s}l}[W_{1s}(\omega, -l) - Q_{1s}(\omega, -l)] + e^{\sigma_{2s}l}[W_{2s}(\omega, -l) - Q_{2s}(\omega, -l)] = b[W_{2N} + W_{1b}(\omega, -l) + W_{2b}(\omega, -l)]. \quad (51)$$

Here $g = k_g^{(0)}\sigma_{2g}/k_s^{(0)}\sigma_{2s} = k_g^{(0)}\sigma_g/k_s^{(0)}\sigma_s$, $b = k_b^{(0)}\sigma_{2b}/k_s^{(0)}\sigma_{2s} = k_b^{(0)}\sigma_b/k_s^{(0)}\sigma_s$. The expression is valid for the acoustic pressure fluctuation on the SH [17]

$$\delta p_{2N}(2\omega, t) = \frac{\gamma p_0 2\pi\mu_{2g}(\omega)}{T_{00}l_g}\overline{\Phi}_{2N}(\omega) = \frac{\gamma p_0}{T_0 l_g}\left[\frac{\Theta_{2N}}{\sigma_{2g}} - \frac{\Theta_L^2}{4\sigma_g}\left(\delta_{2g} + \frac{2R_{2g}\sigma_{2g}}{\sigma_{2g}^2 - 4\sigma_g^2}\right)\right]. \quad (52)$$

It follows from (52) that in order to find the features of generating the PA signal on the SH, it is necessary to have an expression only for Θ_{2N}, for which from the system of equations (48)–(51) we get

$$\Theta_{2N} = \Lambda(\omega)\Big\{(b+1)\Lambda_1(\omega)e^{\sigma_{2s}l} + (b-1)\Lambda_2(\omega)e^{-\sigma_{2s}l} + b\Phi_{Ls}^2(\omega, -l)(\delta_{2s} - \delta_{2b}) - 4bW_{2b}(\omega, -l) + \frac{\Theta_L^2}{2}(\delta_{2g} - \delta_{2s})\big[(b-1)e^{-\sigma_{2s}l} + (b+1)e^{\sigma_{2s}l}\big]\Big\}. \quad (53)$$

The following designations are used here:

$$\Lambda(\omega) = e^{\sigma_{2s}l}(b+1)(g+1) - e^{-\sigma_{2s}l}(b-1)(g-1),$$

$$\Lambda_1(\omega) = (1+g)W_{2g}(\omega, 0) + (g-1)W_{1g}(\omega, 0) - 2[W_{2s}(\omega, 0) - Q_{2s}(\omega, 0)] + 2[W_{2s}(\omega, -l) - Q_{2s}(\omega, -l)],$$

$$\Lambda_2(\omega) = (1-g)W_{2g}(\omega, 0) - (g+1)W_{1g}(\omega, 0) + 2[W_{1s}(\omega, 0) - Q_{1s}(\omega, 0)] - 2[W_{1s}(\omega, -l) - Q_{1s}(\omega, -l)].$$

Expressions (53) together with (52) are the solution of the formulated problem with respect to the SH of PA signal.

Substituting the functions $\Phi_{Lg}(x, \omega)$, $\Phi_{Ls}(x, \omega)$ and $\Phi_{Lb}(x, \omega)$ in expressions (44)–(47) and after completing the integration, we will have

$$W_{1g}(\omega, x) = -\frac{R_{2g}\Theta_L^2}{(\sigma_{2g} + 2\sigma_g)}\exp[-(\sigma_{2g} + 2\sigma_g)x],$$

$$W_{2g}(\omega, x) = -\frac{R_{2g}\Theta_L^2}{(2\sigma_g - \sigma_{2g})}\exp[-(2\sigma_g - \sigma_{2g})x],$$

$$W_{1b}(\omega, x) = -\frac{R_{2b}W_L^2}{(\sigma_{2b} - 2\sigma_b)}\exp[-(\sigma_{2b} - 2\sigma_b)(x + l)],$$

$$W_{2b}(\omega, x) = \frac{R_{2b}W_L^2}{(\sigma_{2b} + 2\sigma_b)}\exp[(\sigma_{2b} + 2\sigma_b)(x + l)],$$

$$W_{1s}(\omega, x) = R_{2s}\left\{\frac{U_L^2\exp[(2\sigma_s - \sigma_{2s})x]}{2\sigma_s - \sigma_{2s}} - \frac{2U_LV_L\exp(-\sigma_{2s}x)}{\sigma_{2s}} - \frac{V_L^2\exp[-(\sigma_{2s} + 2\sigma_s)x]}{\sigma_{2s} + 2\sigma_s} - \frac{2EU_L\exp[(\beta + \sigma_s - \sigma_{2s})x]}{\beta + \sigma_s - \sigma_{2s}} - \frac{2EV_L\exp[(\beta - \sigma_s - \sigma_{2s})x]}{\beta - \sigma_s - \sigma_{2s}} + \frac{E^2\exp[(2\beta - \sigma_{2s})x]}{2\beta - \sigma_{2s}}\right\},$$

$$W_{2s}(\omega, x) = R_{2s}\left\{\frac{U_L^2\exp[(2\sigma_s + \sigma_{2s})x]}{2\sigma_{2s} + 2\sigma_s} + \frac{2U_LV_L\exp(\sigma_{2s}x)}{\sigma_{2s}} + \frac{V_L^2\exp[(\sigma_{2s} - 2\sigma_s)x]}{\sigma_{2s} - 2\sigma_s} - \frac{2EU_L\exp[(\beta + \sigma_s + \sigma_{2s})x]}{\beta + \sigma_s + \sigma_{2s}} - \frac{2EV_L\exp[(\beta - \sigma_s + \sigma_{2s})x]}{\beta - \sigma_s + \sigma_{2s}} + \frac{E^2\exp[(2\beta + \sigma_{2s})x]}{2\beta + \sigma_{2s}}\right\},$$

$$Q_{1s}(\omega, x) = \frac{0.25A^{(0)}\beta I_0\delta_3\Theta_L}{\kappa_s^{(0)}\sigma_{2s}(\beta - \sigma_{2s})}e^{(\beta - \sigma_{2s})x},$$

$$Q_{2s}(\omega, x) = \frac{0.25A^{(0)}\beta I_0\delta_3\Theta_L}{\kappa_s^{(0)}\sigma_{2s}(\beta + \sigma_{2s})}e^{(\beta + \sigma_{2s})x}.$$

The bulkiness of the expression for $\Theta_i squiteobvious2N$, and in this connection, as above, we will consider the limiting cases that take place in a highly absorbing system.

4.1. Thermally thin samples

Here $\mu_s \gg l$, $\mu_s\beta \gg 1$, $\exp(-\beta l) \approx 0$, $\exp(\pm\sigma_s l) \approx 1$, $|r| \gg 1$ and $|r| \gg b$. Then the equalities are valid

$$Q_{1s}(\omega, -l) \approx Q_{2s}(\omega, -l) = 0,$$

$$W_{1s}(\omega, 0) - W_{1s}(\omega, -l) = 0,$$

$$W_{2s}(\omega, 0) - W_{2s}(\omega, -l) = 0.$$

$$\Lambda_1(\omega) = W_{2g}(\omega, 0) - W_{1g}(\omega, 0) + 2Q_{2s}(\omega, 0),$$

$$\Lambda_2(\omega) = W_{2g}(\omega, 0) - W_{1g}(\omega, 0) - 2Q_{1s}(\omega, 0),$$

$$Q_{1N} = 0.5\Big\{[\Lambda_1(\omega) + \Lambda_2(\omega)] + [\Lambda_1(\omega) - \Lambda_2(\omega)]b^{-1} + W_L^2(\delta_{2s} - \delta_{2b}) - 4W_{2b}(\omega, -l) + \Theta_L^2(\delta_{2g} - \delta_{2s})\Big\}.$$

Given that $\Theta_{1s}(\omega, 0) \approx Q_{2s}(\omega, 0)$, we get the expression

$$Q_{2N} = W_{2g}(\omega, 0) - W_{1g}(\omega, 0) + 2Q_{1s}(\omega, 0)b^{-1} + W_L^2(\delta_{2s} - \delta_{2b}) - 4W_{2b}(\omega, -l) + \Theta_L^2(\delta_{2g} - \delta_{2s}),$$

which will allow one to get the expression after performing the necessary calculations

$$\Theta_{2N} = 0.5\Theta_L^2\left[2\delta_{2g} - \delta_g - \frac{(\delta_b + \sqrt{2}\delta_{2b})}{1+\sqrt{2}} + \sqrt{2}\delta_3\right]. \quad (54)$$

Then from (52) for the acoustic pressure fluctuation on the SH we will have

$$\delta p(2\omega, \mu_s\beta \gg 1) = \frac{\gamma p (A_0 I_0)^2 \mu_{2g}\mu_b^2}{16\sqrt{2}T_0 l_g k_b^{(0)2}} e^{i\psi_2(l\ll\mu_3)}|K_{2(1)},$$

$$\psi_2(2\omega, l \ll \mu_s) = \begin{cases} -3\pi/4, & if\ K_{2(1)} > 0, \\ \pi/4, & if\ K_{2(1)} < 0, \end{cases} \quad (55)$$

where

$$K_{2(1)} = [(2\delta_{2g} - \delta_g) - (\sqrt{2}\delta_b + 2\delta_{2b})](2+\sqrt{2})^{-1} + \sqrt{2}\delta_3$$

— a nonlinear coefficient, which is determined by a combination of the thermal coefficients of the absorption capacity of the sample and the thermophysical parameters of the gas and substrate. It can be seen from (55) that in this case the dependence of the amplitude of the PA signal on the frequency obeys the law $\propto \omega^{-3/2}$.

4.2. Thermally thick samples. Case I

For them $\mu_s < l$, $\mu_s > \mu_\beta$, $\mu_{2s} > \mu_\beta$, $\exp(-\beta l) \approx 0$ and $\exp(-\sigma_s l) \approx 0$ and $|r| > 1$. Then the expressions are valid

$$W_{2b}(\omega, -l) = 0, \quad Q_{1s}(\omega, -l) \approx Q_{2s}(\omega, -l) = 0,$$

$$W_{1s}(\omega, -l) = 0, \quad W_{2s}(\omega, -l) = 0,$$

$$Q_{2s}(\omega, 0) = 0.25A^{(0)}I_0\delta_3\Theta_L[\kappa_s^{(0)}\sigma_{2s}]^{-1} = \beta\Theta_L^2\delta_3[2(r-1)\sigma_{2s}]^{-1},$$

that allow to obtain the expression from (52) are valid

$$\Theta_{1N} = \Lambda_1(\omega) + 0.5\Theta_L^2(\delta_{2g} - \delta_{2s}). \quad (56)$$

Further, considering the equality

$$W_{1s}(\omega, 0) = R_{2s}\left(\frac{U_L^2}{2\sigma_s - \sigma_{2s}} + \frac{2EU_L}{\sigma_{2s} - \sigma_s - \beta} + \frac{E^2}{2\beta - \sigma_{2s}}\right) \approx R_{2s}\left(\frac{U_L^2}{2\sigma_s - \sigma_{2s}} - \frac{2EU_L}{\beta} + \frac{E^2}{2\beta}\right),$$

$$W_{2s}(\omega, 0) = R_{2s}\left(\frac{U_L^2}{2\sigma_s + \sigma_{2s}} - \frac{2EU_L}{\sigma_{2s} + \sigma_s + \beta} + \frac{E^2}{\sigma_{2s} + 2\beta}\right) \approx R_{2s}\left(\frac{U_L^2}{2\sigma_s + \sigma_{2s}} - \frac{2EU_L}{\beta} + \frac{E^2}{2\beta}\right) \approx \frac{R_{2s}r^2E_L^2}{(2\sigma_s + \sigma_{2s})},$$

we will get

$$\Lambda_1(\omega) = W_{2g}(\omega, 0) - W_{1g}(\omega, 0) - 2[W_{2s}(\omega, 0) - Q_{2s}(\omega, 0)] \approx -\frac{\Theta_L^2}{2}\left[\delta_g - \delta_{2g} + \frac{\delta_{2s} - \delta_s}{1+\sqrt{2}} - \sqrt{2}\delta_3\right]. \quad (57)$$

Substituting (57) into (56) results in the expression

$$\Theta_{2N} = \frac{\Theta_L^2}{2}\left[2\delta_{2g} - \delta_g + \frac{\delta_{2s} - \delta_s}{1+\sqrt{2}} - \delta_3 + \sqrt{2}\delta_3\right],$$

considering which enables us to obtain from (52) for the desired value the following formula:

$$\delta p(2\omega, l > \mu_s) = \frac{\gamma p_0 \Theta_L^2}{2T_0 l_b \sigma_{2g}} K_{2(2)}, \quad (58)$$

where

$$K_{2(2)} = \left(2\delta_{2g} - \delta_g - 2\delta_{2s} - \sqrt{2}\delta_s\right)\left(2+\sqrt{2}\right)^{-1} + \sqrt{2}\delta_3$$

is a nonlinear coefficient for this case. It can be seen that in this case, the amplitude of the nonlinear PA signal on the SH depends on the temperature coefficients of the thermophysical quantities of the sample and gas, as well as the absorption capacity of the sample and does not depend on the parameters of the substrate. In view of the fact that for this case

$$Q_L = (r-1)E \approx rE = \frac{A^{(0)}I_0\mu_s(1-i)}{4\kappa_s^{(0)}},$$

the expression (58) can be written as

$$\delta p(2\omega, l > \mu_s) = \frac{\gamma p_0 (A^{(0)}I_0\mu_s)^2\mu_{2s}}{16\sqrt{2}T_0 l_g(\kappa_s^{(0)})^2} K_{2(2)} \times \exp[i\psi_{2N}(2\omega, l > \mu_s)].$$

For this case, the phase of the nonlinear PA signal at $K_{2(2)} > 0$ is (-135°), and at $K_{2(2)} < 0$ is 45°; the amplitude does not depend on β, and its frequency dependence obeys the law $\propto \omega^{-3/2}$.

4.3. Thermally thick samples. Case II

We believe that the conditions $\mu_s \ll l$, $\mu_s < \mu_\beta$, are valid $\exp(-\beta l) \approx 0$ and $\exp(-\sigma_s l) \approx 0$, $|r| < 1$. Then the following equalities take place: $W_{2b}(\omega, -l) = 0$, $Q_{1s}(\omega, -l) \approx Q_{2s}(\omega, -l) = 0$, $W_{1s}(\omega, -l) = 0$, $W_{2s}(\omega, -l) = 0$,

$$Q_{2s} = A^{(0)}\beta I_0\delta_3\Theta_L[4\kappa_s\sigma_{2s}^2]^{-1} = -\Theta_L^2\delta_3\sigma_s^2[2\sigma_{2s}^2(r-1)]^{-1} \approx \Theta_L^2\delta_3\sigma_s^2[2\sigma_{2s}^2]^{-1},$$

$$W_{2s}(\omega,0)=R_{2s}\left(\frac{U_L^2}{2\sigma_s+\sigma_{2s}}-\frac{2EU_L}{\sigma_s+\sigma_{2s}}+\frac{E^2}{\sigma_{2s}}\right)$$

$$=R_{2s}E^2\left(\frac{r^2}{2\sigma_s+\sigma_{2s}}-\frac{2r}{\sigma_s+\sigma_{2s}}+\frac{1}{\sigma_{2s}}\right)\approx\frac{R_{2s}E^2}{\sigma_{2s}},$$

accounting for which allows you to get expressions

$$\Theta_{1N}=\Lambda_1(\omega)+0.5\Theta_L^2(\delta_{2g}-\delta_{2s}), \quad (59)$$

$$\Lambda_1(\omega)=W_{2g}(\omega,0)-W_{2s}(\omega,0)-2[W_{2s}(\omega,0)$$

$$-Q_{2s}(\omega,0)]\approx 0.5\Theta_L^2[\delta_{2g}-\delta_g+\delta_{2s}-\delta_s+\delta_3]. \quad (60)$$

From (59) and (60) we will have

$$\Theta_{2N}=0.5\Theta_L^2(2\delta_{2g}-\delta_g-\delta_s+\delta_3).$$

Then for the acoustic pressure fluctuation on the SH we get the expression

$$\delta p(2\omega,\mu_s\beta<1)=\frac{\gamma p_0(I_0A^{(0)})^2\mu_{2g}\mu_s^4}{32\sqrt{2}T_0l_g\kappa_s^{(0)2}}K_{2(3)}e^{i\frac{\pi}{4}}, \quad (61)$$

where $K_{2(3)}=(2\delta_{2g}-\delta_g)(\sqrt{2}+2)^{-1}-\delta_s+\delta_3$ is a nonlinear coefficient for this case. It can be seen that this value depends on the temperature coefficients of the absorption capacity of the sample, as well as the thermophysical values of the gas and sample. Since the value of $K_{2(3)}$ can be both positive and negative, it is obvious that the phase of this signal is equal to $3\pi/4$ in one case and $-\pi/4$ in the other case. As it follows from (61) that for this case the frequency dependence of the amplitude obeys the law $\propto\omega^{-5/2}$. We note that for all the above cases, the dependence of the amplitude of the SH of PA signal on I_0 is quadratic.

Conclusion

A theory has been developed for the generation of the first two harmonics of a nonlinear PA signal by a solid sample with an arbitrary value of thermal conductivity, due to the TN of the emissivity of the sample, as well as the thermophysical parameters of the sample, gas layer and substrate. For the limiting cases (thermally thin and thick samples), quite simple expressions are obtained for the dependence of the amplitude of the excited PA signal on the emissivity of the sample and the thermophysical parameters of the sample, gas, and substrate, including their thermal coefficients. Obviously, measurements of the parameters of the first ghost harmonics of a nonlinear PA signal make it possible to determine the emissivity of the sample, as well as the thermophysical parameters of the sample, gas layer, substrate, and their thermal coefficients. As a result, a complete picture of the temperature dependence of these quantities will be obtained. It seems to us that it is very important to be able to determine the value of δ_3, which will allow one to establish the temperature dependence of the degree of emissivity of the sample, which is rather difficult to implement by traditional methods.

Conflict of interest

The authors declare that they have no conflict of interest.

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