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PHOTOACOUSTIC SPECTROSCOPY OF CONDENSED MEDIA WITH A PHASE TRANSITION

G. S. Mityurich and E. G. Starodubtsev

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The gas-microphone method of recording a photoacoustic (PA) Rosencwaig–Herschow signal is extended theoretically for consideration of material evaporation of a sample. For an excitation source of constant intensity and exponential saturation of vapor concentration, relations are derived to describe the transient dynamics of the PA response.

The method of photoacoustic (PA) spectroscopy is often employed for sufficiently high-power excitation sources when transport phenomena at the boundaries of the sample exert a pronounced influence on the PA signal [1-3]. In the general case of nonharmonic excitation, allowance for these phenomena is a complicated experimental and theoretical problem whose solution is necessary for correct interpretation of the data of PA measurements. In the present communication, one of the most verified experimental models [4] (the gas-microphone method of recording a PA signal) is developed to allow for material evaporation of a sample and to analyze numerically the dynamics of the PA response.

Consider the widely adopted scheme in which two light beams impinge on an optically and thermally thick [4] sample, namely, a high-power beam with an arbitrary dependence of intensity on time described by a dimensionless function $f(t)$ and a weak probing beam with harmonic intensity modulation. Assume that the material evaporation of the sample is caused only by the first beam. Assuming additivity of the heat fluxes emerging upon absorption of the beams, the temperature field in the region of the detection gas and the sample can be represented in the form

$$T(x, t) = \Theta_R(x, t) + \Theta(x, t), \tag{1}$$

where $\Theta_R(x, t)$ is the temperature field corresponding to the second beam: $\Theta(x, t)$ is temperature variation caused by the first beam. Then the problem of $T(x, t)$ determination is split into two:

$$\begin{gathered} \partial^2\theta_R/\partial x^2 = (1/\alpha)\,\partial\theta_R/\partial t - (Q_R/2k)\,(1 + \exp(i\omega t))\exp(\beta x), \\ \partial^2\theta_R^g/\partial x^2 = (1/\alpha_g)\,\partial\theta_R^g/\partial t,\ \ \theta_R(x, 0) = \theta_R^g(x, 0) = T_0, \end{gathered} \tag{2a}$$

$$\theta_R(0, t) = \theta_R^g(0, t),\ \ k\partial\theta_R(0, t)/\partial x = k_g\partial\theta_R^g(0, t)/\partial x;$$

$$\begin{gathered} \partial^2\theta/\partial x^2 = (1/\alpha)\,\partial\theta/\partial t - (Q/k)\,f(t)\exp(\beta x), \\ \partial^2\theta^g/\partial x^2 = (1/\alpha_g)\,\partial\theta^g/\partial t,\ \ \theta(x, 0) = \theta^g(x, 0) = 0, \\ \theta(0, t) = \theta^g(0, t),\ \ k\partial\theta(0, t)/\partial x - k_g\partial\theta^g(0, t)/\partial x = \eta\,(Qf(t) - q\,dn/dt). \end{gathered} \tag{2b}$$

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Here, the quantities without indices and those with the index "g" pertain to the sample and the detection gas, respectively; α, α_g, and k are the thermal diffusivities and thermal conductivity, respectively; β is the coefficient of light absorption; Q, Q_R are the power densities of the heat sources in the sample for the first and second beams, respectively; T_0 is the ambient temperature; $\eta = 1$ m is the dimensionality factor; q is the specific heat of vaporization; $\eta(t)$ is the concentration of the vapor formed, which is considered to be independent of the x-coordinate (in the sample, $x \leq 0$); ω is the modulation frequency of the probing beam. In system (2b) motion of the gas-sample interface is neglected.

Assume that a solution of problem (2a) is known [4]. Then consider problem (2b). Assuming $n(0) = 0$ and applying Laplace transformations in the traditional way, we arrive at transforms of the functions θ and θ^g:

$$\theta_L(x, s) = A(s) \exp(\sigma x) + kQG(s) \exp(\beta x)/(\sigma^2 - \beta^2),$$

$$\theta_L^g(x, s) = A_g(s) \exp(-\sigma_g x). \tag{3}$$

Here $\sigma = (s/\alpha)^{1/2}$, $\sigma_g = (s/\alpha_g)^{1/2}$, $G(s) = L(f(t))$ is the transform of $f(t)$. The constants A, A_g are determined from boundary conditions (2b):

$$A(s) = A_g(s) - kQG(s)/(\sigma^2 - \beta^2), \tag{4}$$

$$A_g(s) = (\rho/s^{1/2}) \left\{QG(s) [\eta + 1/(\sigma + \beta)] - q_1 s n_L(s)\right\},$$

where $\rho = (k/\alpha^{1/2} + k_g/\alpha_g^{1/2})$; $q_1 = \eta q$; $n_L(s) = L(n(t))$.

From (3) it is seen that $A_g(t)$ describes the change in the gas temperature near the sample surface ($x = 0$) due to the evaporating beam and is determined by the form of $f(t)$ and $n(t)$.

Let

$$f(t) = \begin{cases} 1, & t > 0, \\ 0, & t < 0, \end{cases} \quad n(t) = n_0 [1 - \exp(-\lambda t)]. \tag{5}$$

Relations (5) at λ, $n_0 > 0$ correspond to the case of quick switching of an evaporating beam of constant intensity and exponential law saturation of the vapor concentration. In this case, an exact solution [5] can be obtained for $A_g(t)$ from (4):

$$A_g(t) = \rho Q \left\{2(\eta + \beta^{-1})(t/\pi)^{1/2} + \beta^{-2}\alpha^{-1/2}\left[\exp(\gamma t)\operatorname{erfc}(\gamma t)^{1/2} - 1\right]\right\} -$$

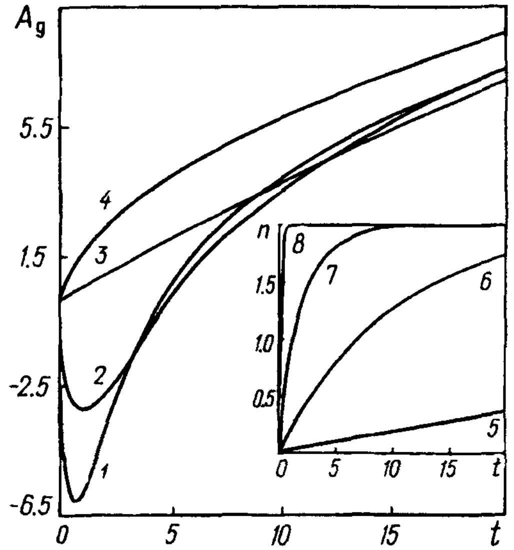
$$- 2\rho q_1 n_0 (\lambda/\pi)^{1/2} \exp(-\lambda t) \int_0^{(\lambda t)^{1/2}} \exp(\zeta^2)\, d\zeta, \tag{6}$$

where $\gamma = \alpha\beta^2$, $\operatorname{erfc}(z) = 2\pi^{-1/2} \int_z^\infty \exp(-\vartheta^2) d\vartheta$.

Next, we assume that the approximations [4] and the piston model are valid for calculation of the PA signal. Then the amplitude q_{PA} of the PA signal is as follows

$$q_{PA} = |Q_{PA}|, \quad Q_{PA} = \gamma_0 (P_0 + P(t))\, \theta_0 / [2^{1/2} l_g a_g (T_0 + \langle\theta^g\rangle)], \tag{7}$$

where the notation of [4] is preserved; $P(t) = \xi n(t) k_0 T_0$ is the pressure variation in a cell due to the partial vapor pressure; k_0 is the gas constant; $\xi = 1$ kg^{-1} is the dimensionality factor; $<\theta^g>$ is the mean temperature variation within the limits of the piston due to the evaporating beam. As a first approximation, we take



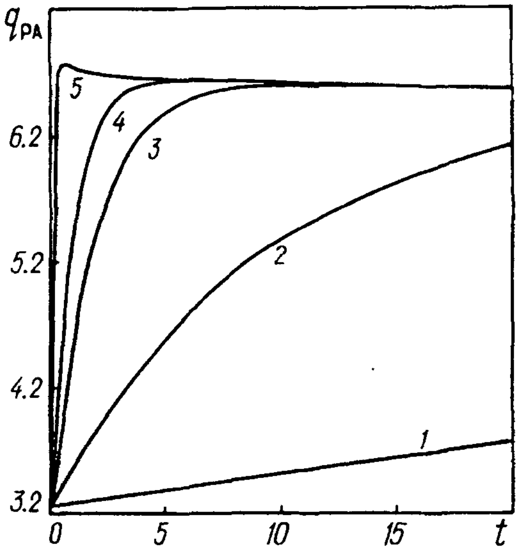


Fig. 1. Plots of $A_g(t)$ and $n(t)$ (inset) at $\lambda = 0.01$ (1, 5), 0.1 (2, 6), 0.5 (3, 7), 1 (4), 10 (8). A_g, K; n, kg/m^3; t, sec.

Fig. 2. Plot of $q_{PA}(t)$ at $\lambda = 0.01$ (1), 0.1 (2), 0.5 (3), 1 (4), 10 (5). q_{PA}, mPa.

$$\langle \theta^g \rangle = A_g(t) . \tag{8}$$

Then from (7) we finally obtain

$$Q_{PA} = -i\beta\mu^2 \gamma_0 I_0 F/(2^{5/2} k a_g l_g) , \tag{9}$$

where the following notation is adopted

$$F = \xi n_0 k_0 (1 - \exp(-\lambda t)) + [P_0 + \xi n_0 k_0 (1 - \exp(-\lambda t)) \langle \theta_R \rangle]/(T_0 + A_g(t)) ;$$

$$\langle \theta_R \rangle = -i(2^{7/2} \pi k)^{-1} \beta \mu^2 I_0 \exp(\omega t - \pi/4) .$$

Here $I_0 = Q_R \beta^{-1}$, $I = Q\beta^{-1}$ are the intensities of the second and first beams; μ is the thermal diffusion length [4].

Note that the light intensity at which evaporation must be taken into account can be evaluated from boundary condition (2b) for fluxes:

$$[Qf(t) - q\,dn/dt]_{x=0} > 0 . \tag{10}$$

Hence, for $t = 0$ with consideration of (7) we can write

$$I > q\lambda n_0 \beta^{-1} . \tag{11}$$

Figures 1 and 2 show dependences of the surface temperature $A_g(t)$ and the amplitude of the PA signal $q_{PA}(t)$ obtained from relations (6) and (9) with estimated data close to the constants of ethyl alcohol [6] for a PA cell filled with air under normal conditions ($I_0 = 1$ W/cm^2, $\omega = 630$ Hz, $q = 10^6$ J/kg, and $n_0 = 2$ kg/m^3 is evaluated by the concentration of the saturated vapor). It is seen that in the presence of saturation the amplitude characteristics of the PA signal change considerably (Fig. 2). For the above data, the dependences $q_{PA}(t)$ and $n(t)$ (Fig. 1, inset) almost coincide in form, which points to the predominant contribution of the partial pressure of the vapor formed to the PA signal as compared to the contribution of temperature changes caused by the evaporating beam. The saturation times of the quantities $q_{PA}(t)$ and $n(t)$ are also practically equal for the same λ values. The reported data illustrate the possibility of investigating the dynamics of evaporation processes, in particular, the time dependence of the concentration of the vapor formed by methods of PA spectroscopy.

In the case of fast processes of evaporation the surface temperature of the sample can decrease (Fig. 1, curves 1 and 2), which leads to a competing influence of the contributions determined by temperature variation and an increase in the partial vapor pressure on the PA signal. In this case, the amplitude of the PA signal passes through a small maximum (Fig. 2, curve 5).

Thus, based on an exact solution of a system of heat conduction equations, a fairly simple model is proposed which describes the dynamics of the amplitude characteristics of the PA signal in the presence of material evaporation of the sample. The results obtained can be used to choose regimes of PA measurements when evaporation is negligible as well as to determine thermophysical and other parameters of condensed media with an intense 1st-kind phase transition by the PA spectroscopy method.

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