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ACCOUNT OF EVAPORATION IN PHOTOACOUSTICAL SPECTROSCOPY OF CONDENSED MEDIA

Abstract.

The Rosencwaig-Gersho theory of gas-microphone method of photoacoustical (PA) signal registration [1] is developed for the account of a sample material evaporation. For the case of quick inclusion of evaporating beam with constant intensity and exponential saturation of vapor concentration the relations derived describe the temporal dynamics of PA response.

Method of photoacoustical(PA) spectroscopy is often used at rather powerful excitation sources when transport phenomena on the sample boundaries[2-4] have a substantional effect on PA signal. In the general case of nonharmonic excitation account of these phenomena is a complex experimental and theoretical task.In the present report theory of gas-microphone method of PA signal registration [1] is developed for the case of account of a sample material evaporation.

Consider widespread scheme when two light beams fall on optically and thermally thick [1] sample.One of the beams is powerful with arbitrary dependence of intensity on time describing by dimensionless function f(t) and the other is probing with harmonic intensity modulation. Let us treat that evaporation of a sample material is caused only by the first beam. Supposing thermal flows additivity at beam absorption, temperature field in detector gas and a sample has 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 the temperature change caused by the first beam. Then T(x,t) definition task is divided into two

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

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

Here values without indexes and with index g refer respectively to the sample and detector gas, α, α_g and k are the coefficients of diffusivity and thermal conductivity, β is the light absorption coefficient,Q,Q_R are the thermal sources power densities in a sample for 1 and 2 beam respectively,T_0 is the ambient temperature,η=1cm is the dimentional factor, q is the vaporization specific heat, n(t) is the concentration of vapor formed which is considered to be independent on x coordinate (in the sample $x\leqslant 0$), ω is the probing beam modulation frequency. Here movement of gas-sample boundary is neglected.

The solution of task (2a) is considered to be known[1]. Consider task (2b). Assuming n(0)=0 and applying in a common way Laplace transformation we can get images of functions θ,θ^g:

$$\theta_L(x,s)=A(s)e^{\sigma x}+kQG(s)e^{\beta x}/(\sigma^2-\beta^2),\ \theta^g_L(x,s)=A_g(s)e^{-\sigma_g x}, \quad (3)$$

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

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

$$A_g(s) = (\rho/s^{1/2})\left\{QG(s)\left[\eta + 1/(\sigma + \beta)\right] - q_1 s n_L(s)\right\}, \quad (4)$$

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

From Eqs.(3) it is seen, that value $A_g(t)$ describes temperature change of gas near the sample surface (x=0), which is due to the influence of evaporating beam and is defined by the form of dependencies f(t) и n(t).

Let

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

Relations (5) at parameters $\lambda,n_0>0$ correspond to the case of quick inclusion of evaporating beam with constant intensity and exponential saturation of vapor concentration. In this case from (4) one can get an exact siolution [5] for $A_g(t)$

$$A_g(t) = \rho Q\left\{2(\eta+\beta^{-1})(t/\pi)^{1/2} + \beta^{-2}\alpha^{-1/2}\left[e^{\gamma t}\mathrm{ERFC}(\gamma t)^{1/2} - 1\right]\right\} - 2\rho q_1 n_0(\lambda/\pi)^{1/2}e^{-\lambda t}\int_0^{(\lambda t)^{1/2}} \exp(\zeta^2)d\zeta \quad , \quad (6)$$

where $\gamma=\alpha\beta^2$.

Further we would assume validity of approximations [1] and a piston model for PA signal calculation. Then amplitude q_{PA} of PA signal has the form

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

where notations [1] are preserved, $P(t)=\xi n(t)k_0T_0$ is the pressure change in the cell due to partial vapor pressure, k_0 is the gas constant, $\xi=1g^{-1}$ is dimentional factor, $\langle\theta^g\rangle$ is the average temperature change within the piston caused by evaporating beam. As a first approximation one may take

$$\langle\theta^g\rangle = A_g(t) \quad . \qquad (8)$$

Then from (7) we can finally get

$$Q_{PA} = -i\beta\mu^2\gamma_0 I_0 F/(2^{5/2}ka_g l_g) \;, \qquad (9)$$

where the following notations are adopted

$$F = \xi n_0 k_0(1 - e^{-\lambda t})+\left[P_0 + \xi n_0 k_0(1 - e^{-\lambda t})\langle\theta_R\rangle\right]/(T_0+A_g(t)),$$

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

Here $I_0=Q_R\beta^{-1}$, $I=Q\beta^{-1}$ are the intensities of 2 and 1 beams, μ is the thermal diffusion length [1].

Note that light intensity when account of evaporation is necessary can be evaluated from flows boundary condition (2b)

$$\left[Qf(t) - qdn/dt\right]_{x=0} > 0 \;. \qquad (10)$$

Hence it follows for t=0 at account of Eqs.(7)

$$I > q\lambda n_0\beta^{-1} \;. \qquad (11)$$

In Fig.1,2 dependencies of surface temperature $A_g(t)$ and amplitude of PA signal $q_{PA}(t)$, obtained from Eqs.(6),(9) at estimation data close to ethyl spirit constants for PA cell filled up with air at normal conditions (I_0=1 W/cm^2, Ω= 630 Hz, q=10^6 J/kg, and value n_0=2 kg/m^3 was estimated by concentration of saturated vapor) are presented. It is seen that at the evaporation essential change of PA signal amplitude characteristics occurs(Fig.2). At indicated data dependencies $q_{PA}(t)$ and n(t) (Fig.1,insert) coinside in form practically which is an evidence of predominant contribution into PA signal of partial pressure of occuring vapor compared to the contribution of temperature changes caused by the evaporating beam. At quick evaporation processes (Fig.1, curves 1,2, Fig.2, curve 5) surface temperature of a sample can decrease and PA signal amplitude goes through a small maximum.

Thus rather simple model describing dynamics of PA signal amplitude characteristics change at the presence of evaporation of a sample material is suggested.

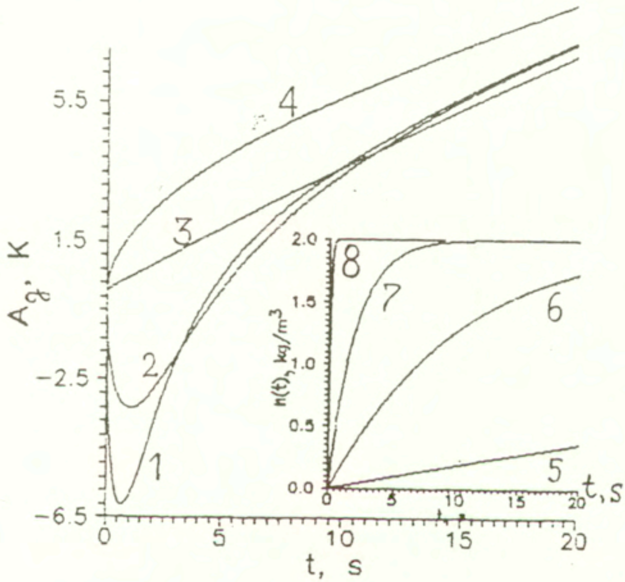

FIG.1 Dependencies of $A_g(t)$ and n(t)(on the insert) at λ= 0.01(4,5),0.1(2,6),0.5(3,7),1(4),10(8).

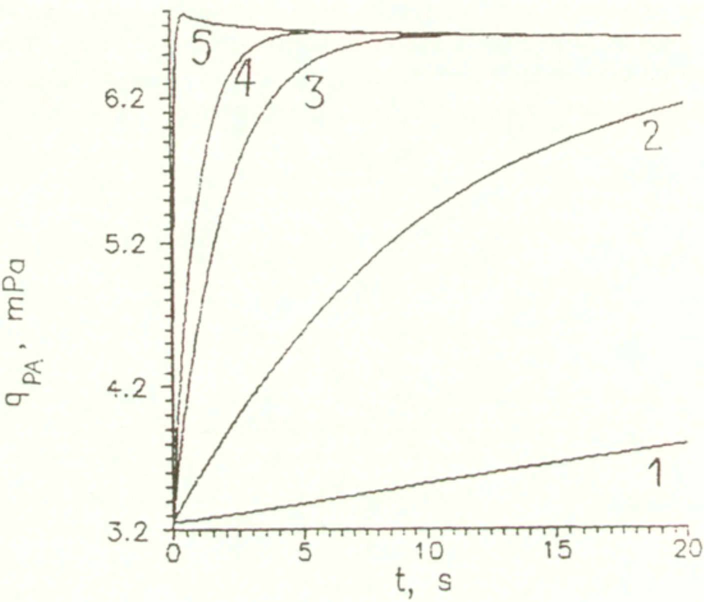

FIG.2 Dependence $q_{PA}(t)$ at $\lambda=0.01$(1), 0.1 (2), 0.5(3), 1(4), 10(5).

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