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Theory of the photothermal radiometry with solids

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A quantitative derivation is presented for the production of the photothermal signal in solids. Both the frequency- and time-domain responses are discussed. Typical time response curves are presented and interpreted in terms of the physical processes occurring in the photothermal emission.

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I. INTRODUCTION

In recent papers,^{1,2} a new technique, namely the photothermal radiometry (PTR), has been proposed and experimentally demonstrated as an alternative method for spectroscopic analysis of solid and semisolid materials. Its basic principle consists essentially in the observation of the changes induced in the thermal radiation emittance of a sample as it is periodically heated by the absorption of chopped light. In Fig. 1, we show a typical PTR experimental arrangement, in which the monochromatic light from a tunable source, after being mechanically chopped, illuminates the sample. Any light absorbed by the sample is converted, in part or in whole, into heat by nonradiative de-excitation processes within the solid. Since this heating deposition depends, in principle, upon the optical absorption coefficient β of the solid, one should then expect that the induced changes in the total thermal emittance also depends on β . The thermal radiation from the illuminated area is then collected by means of an appropriate optical system and focused on an infrared detector. The analog signal from the detector is then applied to a tunable (lock-in) amplifier whose output is recorded as a function of the wavelength of the incident light. In this way, PTR spectra are obtained and these spectra have been found to correspond to the optical absorption spectra of solids. We note that, apart from being particularly suitable for surface studies, this new technique presents at least two great advantages over the otherwise quite similar photoacoustic spectroscopy. One of them is related to the ability of this technique to perform measurements at some distance. This feature is particularly attractive for remote analysis of samples under vacuum and/or at high temperatures. Secondly, since the photothermal emission occurs immediately upon thermalization of the absorbed energy (i.e., within typically $\sim 10^{-8}$ – 10^{-12} sec), the use of pulsed excitation allows us to perform spectral studies of transient states with a time resolution essentially determined by the response time of thermal radiation detectors ($\sim 10^{-7}$ sec).

In this paper we present a detailed theoretical discussion of the PTR signal production in the frequency domain, as well as of the time response to a signal light pulse excitation. Our theory very much resembles that of photoacoustic spectroscopy³⁻⁵ in the sense that a one-dimensional model for the heat flow in the solid-gas system is also used to find

the surface temperature fluctuation. The dependence of the surface temperature fluctuation δT upon the modulation frequency, the surface and bulk optical absorption coefficients, and the thermal properties are fully discussed. Once we know the surface temperature fluctuation δT , the increment in the thermal radiation emittance δW is given by the Stefan-Boltzmann law ($W = \epsilon \sigma T^4$) as

$$\delta W = 4\epsilon \sigma T_0^3 \delta T, \quad (1)$$

where $\sigma = 5.67 \times 10^{-12}$ W cm⁻², K⁻⁴ is the Stefan-Boltzmann constant, ϵ is the sample emissivity, and T_0 is the static surface temperature (i.e., $T_0 = T + \delta T_0$, T being the ambient temperature due to the steady-state component of the absorbed heat).

II. FORMULATION

Let us assume the one-dimensional model for the heat flow in the solid-gas system resulting from the absorbed light energy. This corresponds to the configuration illustrated in Fig. 2, where the solid of length l (cm) has a bulk optical absorption coefficient b (cm⁻¹) and a surface optical absorption coefficient β' . A sinusoidally chopped monochromatic light with wave length λ is incident on the solid with intensity $I = I_0(1 + \cos \omega t)/2$, where I_0 (W/cm²) is the incident monochromatic light flux and $\omega = 2\pi f$ is the chopping fre-

FIG. 1. Experimental arrangement for photothermal radiometry.

FIG. 2. Schematic diagram of the one-dimensional configuration.

quency. We further assume that the gas is not light absorbing. We define the following parameters: k_i is the thermal conductivity of material i (cal/cm sec K); c_i is the specific heat of material i (cal/gK); ρ_i is the density of material i (g/cm³); $\alpha_i = k_i/\rho_i c_i$ is the thermal diffusivity of material i (cm²/sec); $a_i = (\omega/2\alpha_i)^{1/2}$, is the thermal diffusion coefficient of material i (cm⁻¹); $\mu_i = a_i^{-1}$ is the thermal diffusion length of material i (cm). Here the subscripts $i = s$ and g denote the sample and gas material, respectively. Let $\phi_i(x, t)$ denote the temperature in material i relative to the ambient temperature (T_0).

Taking into account the distributed heat source resulting from the light absorption, the temperature distribution $\phi_s(x, t)$ is the solution to

$$\frac{\partial^2 \phi_s}{\partial x^2} = \frac{1}{\alpha_s} \frac{\partial \phi_s}{\partial t} - \frac{S(x, t)}{k_s}, \quad \text{for } l < x < 0, \quad (2)$$

where S is the net heat density produced at point x , given by the difference between the heat generated in the sample and the heat lost by it. The heat generated in the sample Q_s has two main contributions coming from the volume (β) and the surface (β') optical absorption,⁶⁻⁸ namely

$$Q_s(x, t) = [\beta(1 - \beta')I_0 e^{\beta x} + \beta'I_0 \delta(x) + \beta'(1 - \beta')I_0 e^{-\beta l} \delta(x + l)](1 + e^{j\omega t}). \quad (3)$$

As for the heat losses (by radiation) one has also two contributions; one from the volume (i.e., the heat lost through the lateral walls) and the other one due to the heat lost at the surface which is given by

$$H\phi_s(x, t)[\delta(x) + \delta(x + l)], \quad (4)$$

where $H = 4\sigma T_0^3$. Neglecting the heat loss through the lateral walls,⁹ the net heat source can be then be written as

$$S(x, t) = \beta(1 - \beta')I_0 e^{\beta x} + [\beta'I_0 - H\phi_s(0)]\delta(x) + [\beta'(1 - \beta')I_0 e^{-\beta l} - H\phi_s(-l)]\delta(x + l). \quad (5)$$

For the gas, the thermal diffusion equation is written as

$$\frac{\partial^2 \phi_g}{\partial x^2} = \frac{1}{\alpha_g} \frac{\partial \phi_g}{\partial t}, \quad \text{for } x > 0 \text{ and } x < -l. \quad (6)$$

The real part of the solution $\phi_i(x, t)$ to Eqs. (2) and (6) is, of course, the solution of physical interest. Thus, the actual surface temperature fluctuation is given by

$$\delta T = \text{Re}[\phi_s(0, t)]. \quad (7)$$

The complete specification of the solution ϕ_i depends upon the appropriate temperature and heat-flux boundary conditions. As has already been noted by Bennett and Forman,^{6,8}

one can work in Eq. (2) only with the volume heat source [namely, $\beta(1 - \beta')I_0 e^{\beta x}$] as the sole thermal source, provided we incorporate the surface terms in the boundary condition for the heat-flux conservation. The new heat-flux conservation boundary conditions are obtained by integrating Eq. (2) over x using Eq. (5) for S . One gets

$$k_s \phi_s'(0) = k_g \phi_g'(0) + \beta'I_0 - H\phi_s(0), \quad (8a)$$

$$k_s \phi_s'(-l) = k_g \phi_g'(-l) - \beta'(1 - \beta')I_0 e^{-\beta l} + H\phi_s(-l). \quad (8b)$$

Equation (8) states that the heat loss from the sample is divided into a radiation current and a conduction current through the gas. As for the temperature boundary condition we require the continuity condition, i.e.,

$$\phi_s(0) = \phi_g(0), \quad (9a)$$

$$\phi_s(-l) = \phi_g(-l). \quad (9b)$$

It could be argued that the transition from the sample to the gas involves not only a discontinuity in the derivative but also in the temperature itself due to a surface layer with a nonzero heat transfer coefficient. Such a thin layer may be important if its thickness is comparable to the gas thermal diffusion length $(2\alpha_g/\omega)^{1/2}$. This will not be considered in what follows.

III. FREQUENCY-DOMAIN PTR RESPONSE

Neglecting transients as well as the dc components, the solution $\phi_i(x, t)$ can be written as

$$\phi_s(x, t) = (Ue^{x\sigma_s} + Ve^{-x\sigma_s} - Ee^{\beta x})e^{j\omega t}, \quad (10a)$$

$$\phi_g(x, t) = \theta_1 e^{-x\sigma_g} e^{j\omega t}, \quad x > 0, \quad (10b)$$

$$\phi_g(x, t) = \theta_2 e^{x\sigma_g} e^{j\omega t}, \quad x < -l, \quad (10c)$$

where

$$\sigma_i = (1 + j)a_i, \quad (11)$$

and U, V, θ_1 , and θ_2 are complex-valued constants. The constant E is determined by forcing Eq. (10a) to satisfy Eq. (2) [with $S = \beta(1 - \beta')I_0 e^{\beta x} e^{j\omega t}$], and is given by

$$E = (1 - \beta')\beta I_0 / k_s (\beta^2 - \sigma_s^2). \quad (12)$$

Applying Eqs. (8) and (9) to Eq. (10), a set of algebraic equations for the coefficients U, V etc. is obtained. The solution to this set of equations, following the same procedures as in the photoacoustic theory, allows us to determine the temperature distribution in the sample. In particular, since the surface temperature fluctuation $\phi_s(0) = \theta_1$ is, in the general case, quite complicated we shall focus our attention only to the important case of optically opaque samples, for which the optical absorption length β^{-1} is much smaller than the sample thickness l . For this case, the surface temperature fluctuation reduces to

$$\begin{aligned} \phi_s(0) &= \left(\frac{(1 + g + h)(r - 1)e^{l\sigma_s} + (1 - g - h)(r + 1)e^{-l\sigma_s}}{(1 + g + h)^2 e^{l\sigma_s} - (1 - g - h)^2 e^{-l\sigma_s}} \right) E \\ &\quad + \left(\frac{(1 + g + h)e^{l\sigma_s} + (1 - g - h)e^{-l\sigma_s}}{(1 + g + h)^2 e^{l\sigma_s} - (1 - g - h)^2 e^{-l\sigma_s}} \right) \beta'I_0. \end{aligned} \quad (13)$$

Here $r = \beta/\sigma_s$, $r' = \beta'k_s\sigma_s$, $g = k_g a_g/k_s a_s$, and $h = H/k_s\sigma_s$.

Equation (13) tells us that the PTR signal depends on both the optical and the thermal opaqueness (i.e., $l\sigma_s$ and β/σ_s) of the sample. In other words, the surface temperature fluctuation probes not only the surface heating itself but also the heat generated within the volume and which later diffuses to the sample surface. To demonstrate this, for all cases of optical opaqueness ($\beta l \gg 1$), we shall consider two cases according to the relative magnitude of the thermal diffusion length a_s^{-1} as compared to the sample length l , and the optical absorption length β^{-1} . In all these cases, however, we shall assume that $g \ll 1$, which is reasonable for the common materials and gases. In particular, this assumption is especially true for the case of PTR under vacuum.

Case A: Thermally thin samples ($la_s \ll 1$)

This case describes the situation in which the thermal diffusion time in the sample is much smaller than the chopping period, namely, $f\pi l^2/\alpha_s \ll 1$. Hence, setting in Eq. (13) $\exp(\pm la_s) \simeq 1 \pm la_s$ and $|r| \gg 1$ one gets

$$\phi_s(0) \simeq \frac{I_0}{k_s\sigma_s(l\sigma_s + 2h)} \simeq \frac{I_0}{lk_s\sigma_s^2}, \quad (14)$$

since, in general, and for the common materials at room temperature, the condition $l\sigma_s \gg 2h$ ($f \gg H\alpha_s/lk_s$) is amply satisfied for all chopping frequencies of experimental interest. Equation (14) tells us that for optically opaque thermally thin solids, the PTR signal is independent of β and β' , varies inversely proportional to the chopping frequency, and depends on the thermal properties of the sample as the inverse of its heat capacity (α_s/k_s). The photothermal saturation observed in this case is a consequence of the fact that the heat generated within the optical penetration depth diffuses through the sample which entails that the signal becomes insensitive to the depth distribution of the irradiation heating (i.e., to β).

Case B: Thermally thick samples ($la_s \gg 1$)

In this case the thermal diffusion time in the sample is much greater than the modulation period, namely, $f\pi l^2/\alpha_s \gg 1$. Accordingly, we set in Eq. (13) $\exp(-l\sigma_s) \simeq 0$, $g \ll 1$. One gets

$$\phi_s(0) = \frac{(1 - \beta')\beta I_0}{k_s\sigma_s(\beta + \sigma_s)} + \frac{\beta' I_0}{k_s\sigma_s}, \quad (15)$$

which reduces to

$$\begin{aligned} \phi_s(0) &= \frac{I_0}{k_s\sigma_s}, \quad \text{for } \beta \gg \sigma_s \text{ or } f \ll \frac{\alpha_s \beta^2}{\pi} \\ &= \frac{(1 - \beta')\beta I_0}{k_s\sigma_s^2} + \frac{\beta' I_0}{k_s\sigma_s}, \quad \text{for } \beta \ll \sigma_s \text{ or } f \gg \frac{\alpha_s \beta^2}{\pi}. \end{aligned} \quad (16a)$$

$$(16b)$$

Equation (16a) tells us that for optically opaque thermally thick solids, and for modulation frequency such that $\beta \gg a_s$ ($f \ll \alpha_s \beta^2/\pi$), the PTR signal is independent of β and β' , varies inversely proportional to $f^{-1/2}$, and depends on the sample thermal properties as $(k_s \rho_s c_s)^{-1/2}$. On the other hand, at

the high modulation frequency limit such that $\beta \ll a_s$ ($f \gg \alpha_s \beta^2/\pi$), Eq. (16b) tells us that the PTR signal is represented by the sum of the bulk and the surface contributions, each of these contributions exhibiting, however, different modulation frequency dependences. The bulk contribution $(1 - \beta')\beta I_0/k_s\sigma_s^2$ varies linearly with β and f^{-1} , while the surface contribution varies linearly with β' and $f^{-1/2}$. Hence, in this high-frequency range, plotting the PTR signal versus the chopping frequency and performing adequate data fitting to an expression of the form $af^{-1} + bf^{-1/2}$ one should in principle be able to determine absolute optical absorption (bulk and surface) coefficients. We note that this high-frequency situation is the most important case for PTR since, even though the solid is optically opaque (large heat deposition), and PTR signal is proportional to the optical absorption coefficients. The reason for this is that in this case where the thermal diffusion length is smaller than the optical penetration depth, only the heat generated within the thermal diffusion length contributes to the photothermal signal.

Summarizing, we conclude that spectroscopic studies of solids via PTR are made possible by varying the modulation frequency, provided the conditions $\beta \ll a_s$ and $la_s \gg 1$ are satisfied simultaneously. Secondly, we remark that even though the case of a thermally thin solid [c.f., Eq. (14)] is unattractive as far the observation of optical properties are concerned, it can however, be used as an alternative optical detection method for phase transitions in solids at high temperatures since the PTR signal, in this case, varies as $(\rho_s c_s)^{-1}$. In other words, at the phase transition, the PTR signal of an optically opaque and thermally thin solid should exhibit a minimum.

IV. TIME-DOMAIN PTR RESPONSE

In this section we look at the PTR time response when the sample is excited by a light pulse in the form of a Heaviside function of duration τ_p (sec) and an irradiance of I_0 (W/cm²). The nonradiative de-excitation processes following light absorption in the solid are assumed to be instantaneous. Under these conditions, the thermal diffusion equations for both the sample and the gas are now written as

$$\begin{aligned} \frac{\partial^2 \phi_s}{\partial x^2} - \frac{1}{\alpha_s} \frac{\partial \phi_s}{\partial t} &= \frac{-(1 - \beta')\beta I_0}{k_s} e^{\beta x}, \quad 0 < t < \tau_p, -l < x < 0 \\ &= 0, \quad t > \tau_p, -l < x < 0 \end{aligned} \quad (17)$$

and

$$\frac{\partial^2 \phi_g}{\partial x^2} - \frac{1}{\alpha_g} \frac{\partial \phi_g}{\partial t} = 0, \quad \text{for all } t (x > 0, x < -l). \quad (18)$$

The Laplace transforms of Eqs. (17) and (18) have the form

$$\begin{aligned} \frac{\partial^2 \tilde{\phi}_s}{\partial x^2} (x, s) - \frac{s}{\alpha_s} \tilde{\phi}_s(x, s) &= - \frac{(1 - \beta')\beta I_0}{k_s} \frac{(1 - e^{-s\tau_p})}{s} e^{\beta x}, \quad -l < x < 0 \end{aligned} \quad (19a)$$

and

$$\frac{\partial^2 \tilde{\phi}_g}{\partial x^2}(x, s) - \frac{s}{\alpha_g} \tilde{\phi}_g(x, s) = 0, \quad x > 0 \text{ and } x < -l, \quad (19b)$$

where $\tilde{\phi}_i(x, s)$ are the Laplace transforms of the temperature fluctuations in the regions i . Equations (19) are solved subject to the conditions

$$\begin{aligned} \tilde{\phi}_s(0, s) &= \tilde{\phi}_g(0, s) \\ \tilde{\phi}_s(-l, s) &= \tilde{\phi}_g(-l, s), \\ k_s \tilde{\phi}_s'(0, s) &= k_g \tilde{\phi}_g'(0, s) + \beta' \tilde{I}_0 - H \tilde{\phi}_s(0, s) \\ k_s \tilde{\phi}_s'(-l, s) &= k_g \tilde{\phi}_g'(-l, s) - \beta'(1 - \beta') \tilde{I}_0 e^{-\beta l} + H \tilde{\phi}_s(-l, s) \end{aligned} \quad (20)$$

where $\tilde{I}_0 = I_0(1 - e^{-s\tau_p})/S$.

Defining $b_i(s/\alpha_i)^{1/2}$, the solution $\tilde{\phi}_i(x, s)$ can be written as

$$\tilde{\phi}_s(x, s) = U' e^{xb_s} + V' e^{-xb_s} - E' e^{\beta x}, \quad l < x < 0, \quad (21a)$$

$$\tilde{\phi}_g(x, s) = \theta_1' e^{-xb_g}, \quad x > 0, \quad (21b)$$

$$\tilde{\phi}_g(x, s) = \theta_s' e^{xb_g}, \quad x < -l, \quad (21c)$$

where

$$E' = \frac{(1 - \beta') \beta I_0}{k_s (\beta^2 - b_s^2)} \frac{(1 - e^{-s\tau_p})}{s}. \quad (22)$$

Substituting Eqs. (21) into (20), the general expression for $\tilde{\phi}_s(x, s)$ is obtained, and it turns out that it is very similar to its counterpart in the frequency domain [c.f. Eq. (13)]. In the following we shall restrict ourselves only to the important case of an optically opaque ($\beta l \gg 1$; largest heat deposition situation). Furthermore, we shall also assume that the sample is thermally thick (i.e., $lb_s \gg 1$) which entails that the observation times t_{obs} we are considering much smaller than the thermal diffusion time in the sample, namely,

$$t_{\text{obs}} \ll l^2/\alpha_s.$$

Under these circumstances the surface temperature fluctuation $\tilde{\phi}_s(0, s)$ can be written as

$$\tilde{\phi}_s(0, s) = \frac{\alpha_s(1 - \beta') \beta \tilde{I}_0}{k_s s^{1/2}(s^{1/2} + \tau^{-1/2})} + \frac{\alpha_s^{1/2} \beta' \tilde{I}_0}{k_s (s^{1/2} + \tau_h^{-1/2})}, \quad (23)$$

where

$$\tau^{-1/2} = \beta \alpha_s^{1/2} \quad \text{and} \quad \tau_h^{-1/2} = H \alpha_s^{1/2}/k_s. \quad (24)$$

Here τ is the thermal transit time from a depth β^{-1} and τ_h is the thermal radiation transfer time. We note that, in general, $\tau_h^{-1/2} \ll \tau^{-1/2}$. Inverting the expression for $\tilde{\phi}_s(0, s)$, using the theorems and the expression given in Table I, one gets the explicit expression for the surface temperature distribution as a function of time, namely

$$\delta T_{(t)} = \frac{\alpha_s(1 - \beta') \beta \tau I_0}{k_s} F_{(t)} + \frac{\alpha_s^{1/2} \beta' I_0 \tau_h^{1/2}}{k_s} G(t), \quad \text{for } t < \tau_p \quad (25a)$$

and

$$\delta T_{(t)} = [\delta T(t < \tau_p)]_t - [\delta T(t < \tau_p)]_{t = t - \tau_p}, \quad \text{for } t > \tau_p \quad (25b)$$

TABLE I. Expressions used in evaluating the PTR time response taken from Ref. 10.

$f(s)$	$F(t) = \mathcal{L}^{-1}[f(s)]$
$e^{-as}f(s)$	$F(t-a), t > a$ $0, t < a$
$\frac{f(s)}{s}$	$\int_0^t F(u) du$
$\frac{1}{s^{3/2}(s^{1/2} + \tau^{-1/2})}$	$2\left(\frac{t\tau}{\pi}\right)^{1/2} + \tau \left[e^{t/\tau} \operatorname{erfc}\left(\frac{t}{\tau}\right)^{1/2} - 1 \right]$
$\frac{1}{s(s^{1/2} + \tau^{-1/2})}$	$\tau^{1/2} \left[1 - e^{t/\tau} \operatorname{erfc}\left(\frac{t}{\tau}\right)^{1/2} \right]$

where

$$F_{(t)} = 2(t/\pi\tau)^{1/2} + [e^{t/\tau} \operatorname{erfc}(t/\tau)^{1/2} - 1] \quad (26)$$

and

$$G(t) = 1 - e^{t/\tau_h} \operatorname{erfc}(t/\tau_h)^{1/2}. \quad (27)$$

Equations (25) show that the PTR response depends directly upon β, β' , and I_0 . Its time development, however, is a rather complex function of the material parameters. In order to demonstrate the explicit dependence of the time evolution of the PTR response we have evaluated numerically Eq. (25) for a Ge sample ($\alpha_s = 0.35 \text{ cm}^2/\text{sec}$; $k_s = 0.60 \text{ W/cm K}$) illuminated at room temperature with a light pulse of 1 W/cm^2 intensity and pulse duration $\tau_p = 5 \times 10^{-6} \text{ sec}$. In Fig. 3 we show the response of a Ge sample for two different bulk absorption coefficients (β) for a given surface state. Finally, in Fig. 4 is presented the extreme situation where all the light is absorbed at the sample surface, namely, the case where $\beta' = 1.0$. In all these plots the temperature fluctuation of the sample surface $\delta T(t)$ is seen to increase during the pulse and to reach its maximum value at the end of the pulse, after which it decays to the background value via heat conduction. In the case of small bulk absorption (i.e., $\beta = 10 \text{ cm}^{-1}$), the PTR signal growth during the pulse duration is almost entirely dependent upon the surface absorption coefficient. In contrast, in the case of large bulk absorption (i.e., $\beta = 10^3 \text{ cm}^{-1}$) the growth of the PTR signal during the pulse dura-

FIG. 3. PTR time response for a thermally thick Ge sample ($l = 1 \text{ cm}$) with $\beta' = 0.20$ and for two different bulk absorption coefficients.

FIG. 4. PTR time response for a thermally thick Ge sample ($l = 1$ cm) considering only the surface optical absorption ($\beta' = 1.00$).

tion becomes sensitive to the bulk absorption coefficient. It is also follows from Figs. 3 and 4 that the time evolution of the PTR response to a pulsed excitation can be used to determine both β and β' by looking at its peak value at $t = \tau_p$. At the end of the pulse, noticing that $\tau_p \ll \tau_h$, one gets from Eq. (25a)

$$\delta T(t = \tau_p) = \frac{I_0 \tau_p^{1/2}}{(k_s \rho_s c_s)^{1/2}} \left(\frac{2}{\sqrt{\pi}} + \frac{(1 - \beta')}{z} (e^{z^2} \operatorname{erfc} z - 1) \right), \quad (28)$$

where $z = \alpha_s^{1/2} \tau_p^{1/2} \beta$. For $z \ll 1$, approximating $e^{z^2} \operatorname{erfc} z - 1$ by $-2z/\sqrt{\pi} + z^2$, Eq. (28) reduces to

$$\delta T(t = \tau_p) \simeq \frac{I_0 \tau_p^{1/2}}{(k_s \rho_s c_s)^{1/2}} \left(\frac{2}{\sqrt{\pi}} \beta' + (1 - \rho') \alpha_s^{1/2} \tau_p^{1/2} \beta \right). \quad (29)$$

This means that by varying the pulse duration in the region where $\alpha_s^{1/2} \tau_p^{1/2} \beta$ is smaller than unit, absolute evaluation of both β and β' can be accomplished by measuring the dependence of the peak value on the pulse duration setting; the surface contribution exhibits a $\tau_p^{1/2}$ dependence whereas the optical bulk absorption contribution should follow a linear variation with τ_p . On the other hand, for $z \gg 1$, approximating $e^{z^2} \operatorname{erfc} z$ by $(\sqrt{\pi} z)^{-1}$, Eq. (28) becomes

$$\delta T(t = \tau_p) \simeq \frac{I_0}{(k_s \rho_s c_s)^{1/2}} \left(\tau_p^{1/2} - \frac{(1 - \beta')}{\alpha_s^{1/2} \beta} \right). \quad (30)$$

Equation (30) tells us that the extrapolation at the origin of the plot of $\delta T(t = \tau_p)$ vs $\tau_p^{1/2}$ in the region of $\alpha_s^{1/2} \tau_p^{1/2} \beta \gg 1$ gives us $(1 - \beta')/\alpha_s^{1/2} \beta$.

Hence, as in the frequency domain case, the PTR re-

sponse to a pulse excitation is also capable to provide detailed information about the optical absorption properties of a material.

VI. CONCLUSIONS

In this paper we have presented a theoretical analysis of the PTR signal generation in both frequency and time domain. Our main assumption is that the primary source of the PTR signal arises from the temperature fluctuation at the sample surface, which in turn is a function of the relative size of the optical penetration depth and the thermal diffusion length as compared to the sample's length. We have derived that exact expressions for the surface temperature fluctuation and have evaluated explicit formulas for certain cases of physical significance. Particular emphasis was given to the large heat deposition situation, namely, that of an optically opaque sample.

In the frequency domain, our results show that the PTR signal is ultimately governed by the magnitude of the thermal diffusion length of the solid, and independent of the surrounding gas. This means that our predictions are equally applied to a sample under vacuum and that even when a solid is optically opaque, the PTR signal will be proportional to both β and β' as long as $\beta < \alpha_s$ and $l \alpha_s > 1$. As the thermal diffusion coefficient α_s can be varied by changing the modulation frequency, it is therefore possible, with the PTR technique to obtain optical absorption spectra on any solid. The same conclusion is also drawn from the time-domain PTR response. The only difference now is that in this case, to determine both β and β' one should look at the variation of the PTR peak value, at $t = \tau_p$, with the pulse duration. Finally, as noted at the end of Sec. III, in the low-modulation-frequency regime [i.e., thermally thin case, see Eq. (14)] the PTR technique can also be used as an alternative optical detection method for studying phase transitions in solids at high temperatures.

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