

Absolute optical absorption coefficient measurements using transverse photothermal deflection spectroscopy

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Information about the optical absorption coefficient of solid materials in contact with a fluid phase can be obtained from photothermal deflection (PDS) measurements using both the signal amplitude and phase channels of the PDS response of a system to an optical excitation. This paper presents a theoretical model of photothermal processes in the transverse (TPDS) experimental configuration. The theory is used to determine the dependence of both signal channels on the optical absorption coefficient of the solid material and to define absorption coefficient ranges within which TPDS can be used as a spectroscopic technique. A method concerning the use of the combined amplitude and phase data for the absolute measurement of the absorption coefficient is presented for the experimentally important thermally thick limit.

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INTRODUCTION

Photothermal deflection spectroscopy (PDS) has recently emerged as a sensitive method for the study of solid-fluid interfaces. Boccara *et al.*,¹ Murphy and Aamodt,² and Jackson *et al.*³ have applied this technique to studies of solid-gas interfaces. Royce *et al.*⁴ have used PDS to study *in situ* the optical properties of solid (electrode)-liquid (electrolyte) interfaces. In a PDS experiment the probe laser beam deflection is usually detected in the collinear or in the transverse modes in the frequency domain.³ However, the collinear configuration has the disadvantage that it requires samples which are transparent to the probe beam. For this reason the transverse mode (TPDS) has been favored by many workers.^{1,2,4}

Murphy and Aamodt² have studied the PDS response from a solid sample subject to a harmonic optical excitation. They derived expressions for the dependence of both signal amplitude and phase on the probe beam offset and verified their theory for sample surface temperatures ranging between 30.3 and 94 °C. However, the usefulness of the PDS technique as a spectroscopic tool hinges on its success in providing a measurement of the absolute optical absorption coefficient of a material. Although Murphy and Aamodt's theory could in principle be used to provide expressions for the amplitude and phase dependence on the optical absorption coefficient, the derivation of such expressions is rather complicated, especially for certain limiting cases which are of interest to experimentalists. Complications in deriving explicit amplitude and phase expressions from the exact PDS theory presented by Murphy and Aamodt might arise because they considered acoustic transport phenomena similar to those which they reported in previous publications on the theory of photoacoustic spectroscopy (PAS).^{5,6} McDonald and Wetsel^{7,8} and Mandelis⁹ have shown that the acoustic transport phenomena in a PAS cell become unimportant for times greater than ca. 10^{-5} sec, or modulation frequencies below 10^4 Hz.

This paper is concerned with the development of one-dimensional theoretical model for the transverse PDS effect at a solid-fluid interface with emphasis on the relationship between signal amplitude/phase channels and the optical absorption coefficient of the solid sample under investigation. It is shown that under specific experimental conditions the combination of PDS amplitude and phase data can be used to determine the absolute value of the absorption coefficient.

THEORY

An idealized one-dimensional configuration is employed to determine the amplitude (TPDS) signal. The geometry of the system is shown in Fig. 1. A solid with optical

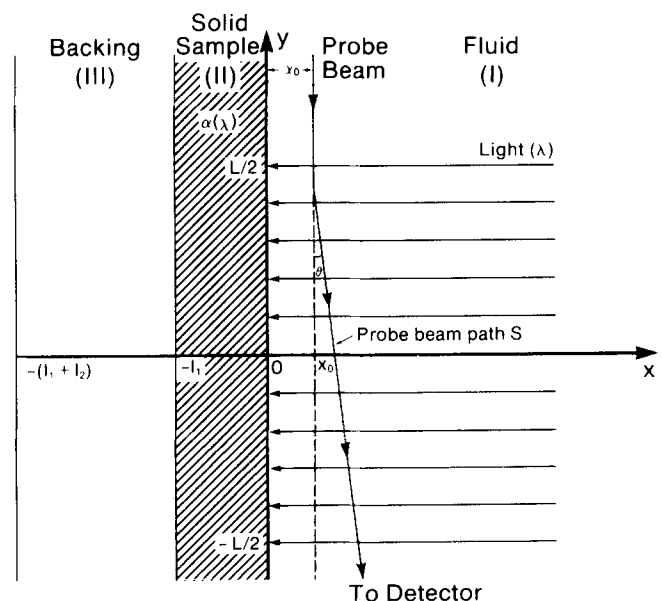


FIG. 1. Geometry of a one-dimensional TPDS system at a solid-fluid interface.

absorption coefficient $\alpha(\lambda)$ is illuminated uniformly with a light beam of wavelength λ , whose intensity is harmonically modulated in time at a frequency ω . The solid absorbs the incident radiation according to Beer's law and is in thermal contact with a transparent fluid (e.g., a liquid or a gas). The sample under investigation has thickness l_1 and is supported by a transparent backing material of thickness l_2 . It is further assumed that the extent of the solid surface along the y plane is large compared with the width L of the incident beam. Nonradiative deexcitations in the illuminated solid cause a harmonic modulation of the temperature at the sample surface and, through heat transfer, the temperature of the fluid layer adjacent to the surface. A laser probe beam passes through the fluid, parallel to the sample surface at a distance x_0 less than the thermal diffusion length in the fluid. It is deflected through an angle $\theta(\omega, \alpha)$ due to changes in the refractive index caused by the heat transfer from the absorbing solid.^{2,3}

In the three regions (I)–(III) shown in Fig. 1, the temperature rise satisfies the appropriate thermal diffusion equations:

$$\frac{\partial^2}{\partial x^2} T_i(x, t) = \frac{1}{\alpha_i} \frac{\partial}{\partial t} T_i(x, t) = \begin{cases} \frac{\dot{H}(x, t)}{k_s}, & \text{Region (II)} \\ 0, & \text{Regions (I), (III)}, \end{cases} \quad (1)$$

$i = f$ (fluid), s (solid), b (backing).

In the solid (s) region for which $-l_1 \leq x \leq 0$, the sample heating rate \dot{H} (W cm^{-3}) is given by

$$\dot{H}(x, t) = \frac{1}{2} \eta I_0 \alpha \exp(-\alpha|x|) \text{Re}[1 + \exp(i\omega t)], \quad (2)$$

where η is the quantum efficiency of nonradiative processes. In this work it will be assumed that $\eta = 1$ (Ref. 10). I_0 is the irradiance of the incident light (W cm^{-2}); k_i is the thermal conductivity of material i [$\text{cal cm sec}^{-1} \text{K}^{-1}$]; $\alpha_i = k_i / \rho_i C_i$, the thermal diffusivity of material i ($\text{cm}^2 \text{sec}^{-1}$); ρ_i and C_i are the density (g cm^{-3}) and specific heat [$\text{cal g}^{-1} \text{K}^{-1}$] of material i .

The quantity of interest is $T_f(x, t)$ which describes the departure of the temperature from its ambient value T_A in the fluid region. Thus the actual temperature profile in the fluid is given by

$$T_f(x, t)_{\text{Actual}} = \text{Re}[T_f(x, t)] + T_A. \quad (3)$$

The solution of the system of Eq. (1) can be separated into an ac and a dc (i.e., time-independent) component. The ac component of the solution in the fluid region is given by

where $A \equiv I_0 \alpha / 2k_s$, $\sigma_i \equiv (1 + i)\alpha_i$, $a_i = (\omega / 2\alpha_i)^{1/2} \equiv 1/\mu_i$ is the thermal diffusion coefficient of material i (cm^{-1}), and μ_i is the thermal diffusion length of material i ; $i = b, s, f$. The remaining parameters in Eq. (4) have been defined as

$$r \equiv (1 - i)(\alpha / 2\alpha_s), \quad (5)$$

$$b \equiv (a_b k_b / a_s k_s), \quad (6)$$

$$f \equiv (a_f k_f / a_s k_s). \quad (7)$$

The dc component of the solution in the fluid region can be obtained by making the assumption that the loss of heat at any position above the illuminated area of the y plane to that surrounding fluid is proportional to the temperature at that position.² Then the time independent component of the fluid temperature can be written

$$T_f^{(\text{dc})}(x) = -\frac{A}{\alpha^2} \left\{ \frac{(1 - e^{-\alpha l_1})(1 - F_{sb} \alpha l_2) - \alpha l_1}{1 + F_{fs} G l_1 + F_{fb} G l_2} \right\} \exp(-Gx), \quad (8)$$

where G is the inverse of the distance above the sample surface at which the fluid temperature has decreased to the $1/e$ of its value at the solid–fluid interface.² The remaining parameters in Eq. (10) have been defined as

$$F_{ij} \equiv k_i / k_j; \quad i, j = b, s, \text{ or } f. \quad (9)$$

The refractive index $n(x, t)$ of the fluid region (I) varies spatially and temporally with the heating of the illuminated fluid column from $(+L/2)$ to $(-L/2)$, Fig. 1. The trajectory of the probe beam is given by the equation of ray propagation in an optically inhomogeneous medium¹¹

$$\frac{d}{ds} \left[n(\mathbf{r}, t) \frac{d\mathbf{r}}{ds} \right] = \nabla n(\mathbf{r}, t), \quad (10)$$

where s is the distance along the ray measured from the entrance point, $y = L/2$, and \mathbf{r} is the position vector of a point along s . For small changes of the refractive index from its ambient temperature value n_0 along the illuminated column and for small angles θ in the transverse geometry of Fig. 1, Eq. (10) can be simplified

$$n_0 \frac{\partial^2 x}{\partial s^2} = \frac{\partial}{\partial x} n(x, t). \quad (11)$$

Integrating Eq. (11) once over the deflected beam path s^{12} gives the following expression for the beam deflection θ to a good approximation on the order of $\cos \theta$:

$$\theta(x_0, t) = -(L/T_0) \left[\frac{\partial}{\partial x} T_f(x, t) \right]_{x=x_0}, \quad (12)$$

where

$$T_f(x, t) = T_f^{(\text{ac})}(x, t) + T_f^{(\text{dc})}(x), \quad (13)$$

and we defined a material parameter T_0 as follows¹²

$$-\frac{1}{n_0} \frac{\partial n}{\partial T_F} \equiv \frac{1}{T_0}. \quad (14)$$

Equations (4), (8), and (12) indicate that the deflection θ

$$T_f^{(\text{ac})}(x, t) = \frac{A}{\alpha^2 - \sigma_s^2} \left\{ \frac{(r-1)(b+1)e^{\sigma_s l_1} - (r+1)(b-1)e^{-\sigma_s l_1} + 2(b-r)e^{-\alpha l_1}}{(f+1)(b+1)e^{\sigma_s l_1} - (f-1)(b-1)e^{-\sigma_s l_1}} \right\} \exp(-\sigma_f x + i\omega t), \quad (4)$$

decreases exponentially with x_0 for both ac and dc components of the fluid temperature. θ tends to zero for beam offset values x_0 such that

$$x_0 \gg \min(G^{-1}, \mu_f).$$

T_0 is a slowly varying function of the wavelength of the exciting radiation. Ignoring the slow variation with wavelength, T_0 will be assumed constant for small fluid temperature departures from the ambient value.

The deflection angle θ consists of ac and dc components, which can be written explicitly using Eqs. (12), (4), and (8):

$$\theta^{(dc)}(x_0) = \left(\frac{LGI_0}{2T_0k_s\alpha} \right) \left\{ \frac{\alpha l_1 - (1 - e^{-\alpha l_1})(1 - F_{sb}\alpha l_2)}{1 + F_{fs}Gl_1 + F_{fb}Gl_2} \right\} \times \exp(-Gx_0), \quad (15)$$

and, in the experimentally important thermally thick limit¹⁰

$$\theta^{(ac)}(x_0, t) = \left(\frac{LI_0\alpha}{2T_0k_s} \right) \times \operatorname{Re} \left\{ \left[\frac{\sigma_f}{(\alpha^2 - \sigma_f^2)} \right] \left[\frac{(r-1)}{(f+1)} \right] \right\} \times \exp(-\sigma_f x_0 + i\omega t). \quad (16)$$

The dc contribution to the deflection angle θ which is described by Eq. (15) is a constant deviation of the probe beam path due to the steady-state thermal flux from the solid surface out into the fluid column adjacent to the solid. At offset distances from the solid-fluid interface such that $x_0 \gg G^{-1}$ thermal losses to the fluid column due to heat conduction from the solid will rapidly attenuate the dc component of the θ deflection. Experimentally only relative deflections of the probe beam can be measured accurately by means of position-sensitive diode detectors and lock-in amplifiers.² Therefore, it is the phase and amplitude of the ac component of the TPDS signal which can be measured and analyzed to give optical absorption data. For this reason the dc component of the signal will not be considered further in this work.

The ac contribution to the deflection angle θ can be used for the measurement of absolute optical absorption coefficients in the special case of a thermally thick solid. In this limit, the thickness l_1 of the solid must satisfy the condition¹⁰

$$l_1 \gtrsim l_0 \equiv 2\pi\mu_s. \quad (17)$$

For a typical frequency of 100 Hz, $l_0 = 816.8 \mu\text{m}$ for KCl crystal¹³; 3.65 mm for crystalline Si (Ref. 14); and 167.6 μm for crystalline SiO_2 (Ref. 14). Therefore, condition (17) can be met easily in most experimental situations.

Using a polar coordinate method developed in Ref. 15, the phase of the ac thermally thick TPDS signal can be written as an explicit function of the product $(\alpha\mu_s)$:

$$\psi(x_0; \alpha\mu_s) \simeq \alpha_f x_0 - \tan^{-1} [2/(\alpha\mu_s)^2] - \tan^{-1} \left(\frac{\alpha\mu_s}{2 - \alpha\mu_s} \right). \quad (18)$$

The TPDS deflection amplitude is also a function of

$(\alpha\mu_s)$:

$$|\theta^{(ac)}(x_0; \alpha\mu_s)| = \frac{LI_0}{T_0k_s} \left(\frac{\alpha_s}{\alpha_f} \right)^{1/2} \times \left[\frac{\frac{1}{2}(\alpha\mu_s)^2 - (\alpha\mu_s) + 1}{(\alpha\mu_s)^2 + 4/(\alpha\mu_s)^2} \right]^{1/2} \exp(-\alpha_f x_0). \quad (19)$$

Equations (18) and (19) give functional dependences of the phase and amplitude of the transverse PDS signal on the probe beam offset x_0 and on the material parameter product $(\alpha\mu_s)$ between $\alpha\mu_s \gg 1$ (optically opaque limit¹⁰) and $\alpha\mu_s \ll 1$ (optically transparent limit¹⁰). From an experimental viewpoint the ranges of $(\alpha\mu_s)$ values near the TPDS signal saturation ($\alpha\mu_s > 1$) and the low optical absorption coefficient region ($\alpha\mu_s < 1$) are of considerable spectroscopic interest.¹⁶ Near signal saturation Eqs. (18) and (19) reduce to the following expressions:

$$\psi(x_0; \alpha\mu_s > 1) \simeq \alpha_f x_0 + \tan^{-1} \left(1 + \frac{2}{\alpha\mu_s} \right), \quad (20)$$

and

$$|\theta^{(ac)}(x_0; \alpha\mu_s > 1)| \simeq \frac{LI_0}{T_0k_s} \left(\frac{\alpha_s}{\alpha_f} \right)^{1/2} \left(\frac{1}{2} - \frac{1}{\alpha\mu_s} \right)^{1/2} \exp(-\alpha_f x_0), \quad (21)$$

where terms higher than $1/\alpha\mu_s$ were neglected. In the low absorption region, Eqs. (18) and (19) become

$$\psi(x_0; \alpha\mu_s < 1) \simeq \alpha_f x_0 - \tan^{-1} [2/(\alpha\mu_s)^2], \quad (22)$$

and

$$|\theta^{(ac)}(x_0; \alpha\mu_s < 1)| = \frac{LI_0}{2T_0k_s} \left(\frac{\alpha_s}{\alpha_f} \right)^{1/2} (\alpha\mu_s) \exp(-\alpha_f x_0). \quad (23)$$

In Eqs. (22) and (23) terms higher than $(\alpha\mu_s)$ were neglected.

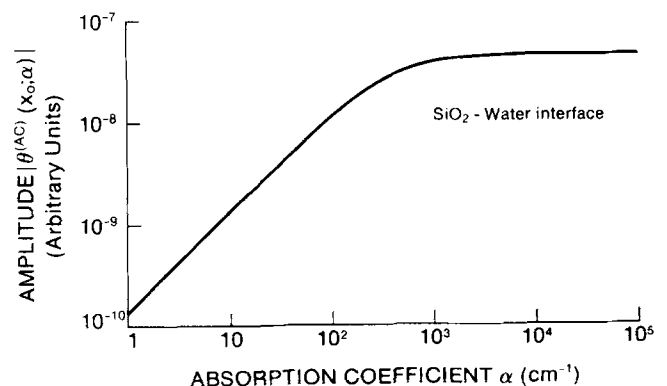


FIG. 2. Log-log plot of the transverse PDS amplitude as a function of the absorption coefficient of the solid. $\nu = 50$ Hz, $l_1 = 50 \mu\text{m}$, $b = 1$, $f = 1.13$, $\alpha_s = 1.95 \times 10^{-3} \text{ cm}^2/\text{sec}$, $\alpha_f = 1.465 \times 10^{-3} \text{ cm}^2/\text{sec}$, $x_0 = 5 \times 10^{-2} \text{ cm}$.

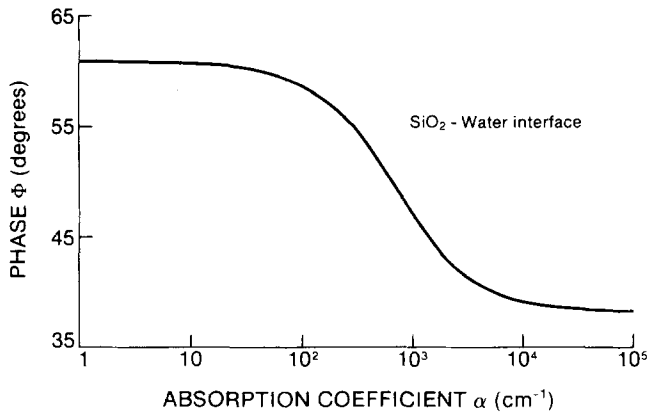


FIG. 3. Semi-log plot of the transverse PDS phase Φ as a function of absorption coefficient of the solid. $\nu = 50$ Hz, $l_1 = 50$ μm , $b = 1$, $f = 1.13$, $\alpha_s = 1.95 \times 10^{-3}$ cm^2/sec , $\alpha_f = 1.465 \times 10^{-3}$ cm^2/sec , $x_0 = 5 \times 10^{-2}$ cm.

DISCUSSION

A. General results of the theory

Full expressions for the TPDS deflection amplitude and phase were obtained from the polar coordinate model of Ref. 15 and evaluated numerically. Figure 2 shows the relative amplitude of the signal displayed as a function of $\ln(\alpha)$. In order to simulate PDS processes in an electrochemical environment, the system chosen was an SiO_2 -water interface at a modulation frequency of 50 Hz. Figure 2 indicates that photothermal saturation occurs in the amplitude response at large values of α ($\gtrsim 5 \times 10^3$ cm^{-1}). This range of amplitude saturation values of the absorption coefficient is similar to that for photoacoustic saturation.¹⁵ Figure 3 is a plot of the PDS phase Φ as a function of $\ln(\alpha)$, for the same set of param-

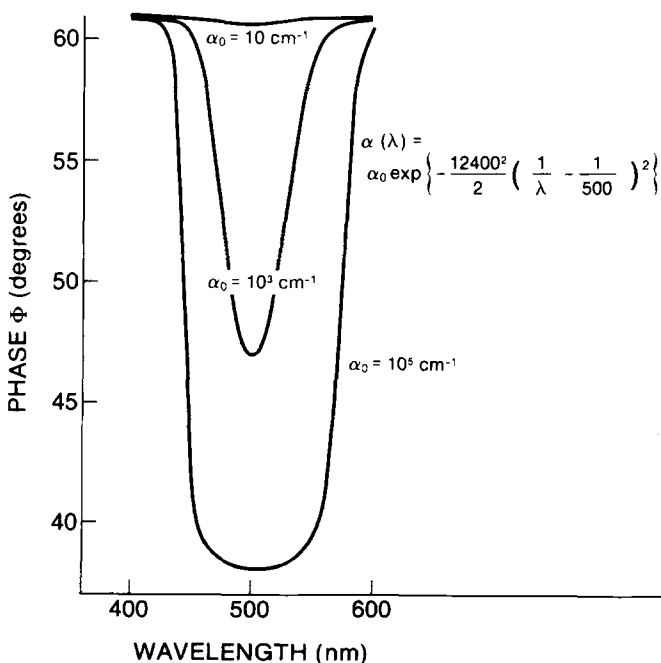


FIG. 4. Phase response in passing through a Gaussian absorption band having different values of $\alpha_{\text{max}} = \alpha_0$. ($\nu = 50$ Hz, $x_0 = 5 \times 10^{-2}$ cm.)

eters as that used in Fig. 2. Figure 3 shows that the phase anticorrelates with the PDS amplitude, in that it decreases with increasing α . Phase saturation occurs for both high and low values of α . The range of α values within which Φ exhibits sensitivity to changes in α lies approximately between 10 and 10^4 cm^{-1} . These features are similar to the behavior of the photoacoustic phase¹⁵ and indicate that Transverse PDS can be successfully used as a spectroscopic technique to measure absorption coefficients in the range $10 \lesssim \alpha \lesssim 10^4$ cm^{-1} . The effect of the phase dependence on the absorption coefficient of the solid is shown in Fig. 4, which exhibits the system response to a family of Gaussian lineshape absorption bands centered at 500 nm with linewidths of 0.1 eV. Saturation is seen to occur at large values of α , while Φ becomes essentially independent of the absorption coefficient for $\alpha < 10$ cm^{-1} .

Figure 5 is a plot of TPDS amplitude and phase in the thermally thick limit of Eqs. (18) and (19). $\theta^{(\text{ac})}$ and Φ have been plotted versus the product $(\alpha\mu_s)$ for a chopping frequency of 50 Hz. Figure 5 shows that under thermally thick conditions PDS can be used as a spectroscopic technique for values of $(\alpha\mu_s)$ such that $0.05 \lesssim \alpha\mu_s \lesssim 100$. Both phase and amplitude saturate at large values of $(\alpha\mu_s)$ and exhibit similar degrees of sensitivity to changes in this product. Equation (18) shows that absolute phase is a linear function of the probe beam offset x_0 . This behavior has been previously described by Murphy and Aamodt² who also carried out an experimental verification using a 100-nm-thick platinum metal film as the absorbing sample in contact with air and sputtered on a glass substrate. Equations (18) and (19) give a precise definition of the undefined parameters K and θ_0 presented by Murphy and Aamodt in the form²

$$\ln(S_{\text{opt}}) = K - (\omega/2\alpha_f)^{1/2} x_0, \quad (24)$$

$$\theta_{\text{opt}} = \theta_0 - (\omega/2\alpha_f)^{1/2} x_0, \quad (25)$$

where $S_{\text{opt}} \equiv |\theta^{(\text{ac})}|$ and $\theta_{\text{opt}} \equiv \psi$ of this work.

A comparison between Eqs. (24), (19), and (25), (18) identifies K and θ_0 as functions of $(\alpha\mu_s)$ in the thermally thick limit. It is, however, difficult to determine whether the experimental data presented in Ref. 2 in conjunction with Eqs. (24) and (25) satisfy the condition (17) because of the double layer structure of the sample-support system. If condition Eq. (17) is not satisfied, then general amplitude and

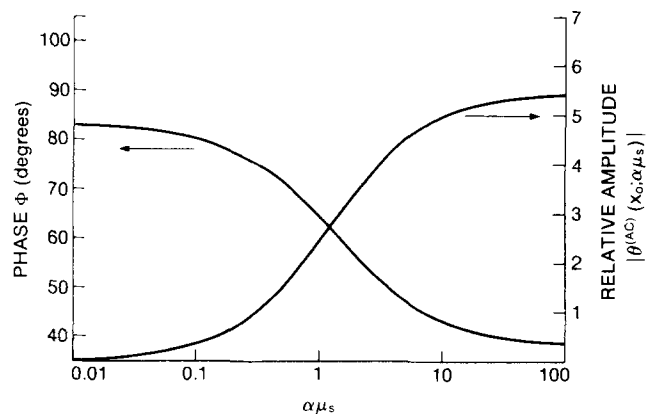


FIG. 5. Comparison between TPDS amplitude and phase as functions of the product $(\alpha\mu_s)$ in the thermally thick limit ($\nu = 50$ Hz, $x_0 = 5 \times 10^{-2}$ cm).

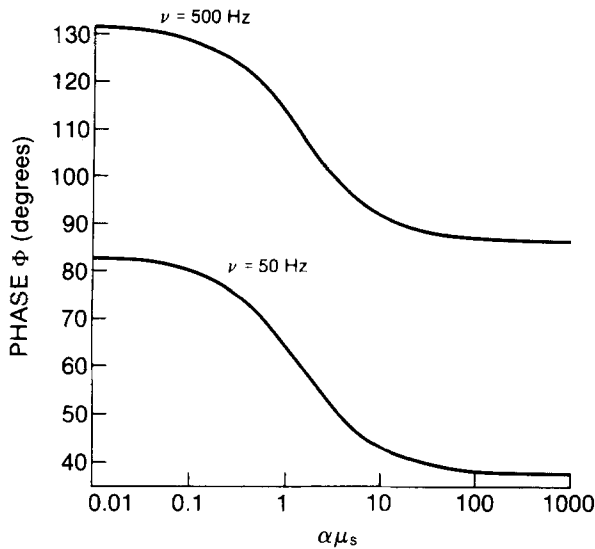


FIG. 6. TPDS deflection phase response as a function of chopping frequency in the thermally thick limit. $x_0 = 5 \times 10^{-2}$ cm; $\alpha_f = \alpha_{\text{water}} = 1.465 \times 10^{-3}$ cm²/sec.

phase equations must be used along the lines of those of Ref. 15, in which case the simple functional forms (24) and (25) are not strictly valid.

Figure 6 shows two TPDS phase plots as functions of $\ln(\alpha\mu_s)$ in the thermally thick limit for different chopping frequencies. The linear dependence of ψ on $a_f = (\omega/2\alpha_f)^{1/2}$, Eq. (18), effects a phase shift of ca. 48° between the curves with $\nu = 50$ Hz and $\nu = 500$ Hz. It is clear from Fig. 6 that, unless the probe laser beam is very precisely positioned, it might be difficult to make absolute phase measurements, as Φ is very sensitive to beam position and chopping frequency changes.

B. The absolute absorption coefficient

From the point of view of absolute spectroscopic measurements, the transverse PDS amplitude and phase can be convoluted to yield absolute optical absorption coefficient values in the thermally thick range near signal saturation ($\alpha\mu_s \gg 1$) and for optically transparent materials ($\alpha\mu_s \ll 1$). In an experiment, an unknown instrumental contribution Φ'_0 will be added to the variable phase $\Phi(x_0; \alpha)$ in a manner similar to that described by Teng and Royce,¹⁷ and by Roark *et al.*¹⁸ in their discussion of the photoacoustic phase. Φ'_0 is independent of α , and the measured phase ψ_{exp} is the sum of two terms.

$$\psi_{\text{exp}} = \Phi(x_0; \alpha) + \Phi'_0; \quad \Phi_0 = \Phi'_0 + \pi/4, \quad (26)$$

where $\psi(x_0, \alpha)$ is the theoretically determined TPDS phase.

Similarly, the experimental TPDS amplitude $|\theta^{(\text{ac})}|$ will include an instrumental contribution q'_0 , such as amplifier gain, semiconductor detector gain etc. Thus, the measured amplitude $|\theta^{(\text{ac})}|_{\text{exp}} = q_{\text{exp}}$ will be the product of two terms

$$q_{\text{exp}} = q'_0 |\theta^{(\text{ac})}(x_0; \alpha)|. \quad (27)$$

In the thermally thick limit near signal saturation Eqs. (26) and (27) can be combined with Eqs. (20) and (21) to give

$$\psi_{\text{exp}} \simeq \Phi_0 + a_f x_0 + \tan^{-1} \left(1 + \frac{2}{\alpha\mu_s} \right), \quad (28a)$$

and

$$q_{\text{exp}} \simeq q_0 \exp(-a_f x_0) \sqrt{\frac{1}{2} - \frac{1}{\alpha\mu_s}}, \quad (28b)$$

where $q_0 = q'_0(LI_0/T_0k_s)\sqrt{\alpha_s/\alpha_f}$ is also an unknown quantity. Upon inverting Eq. (28a), solving for $(\alpha\mu_s)$ and inserting the resulting expression in Eq. (28b), the following expression is obtained

$$q_{\text{exp}} = q_0 \exp(-a_f x_0) \left[1 - \frac{1}{2} \tan(\psi_{\text{exp}} - \Phi_0 - a_f x_0) \right]^{1/2}. \quad (29)$$

Equation (29) can be used with the Least-Squares Linear-Taylor Differential-Correction curve technique^{17,19} to determine the optimal values of q_0 and Φ_0 from a set of experimental data point pairs $[(q_{\text{exp}})_i, (\psi_{\text{exp}})_i]$. Then the product $(\alpha\mu_s)$ may be calculated from either Eq. (28a) or (28b), once Φ_0 or q_0 , respectively, are known, provided that μ_s is known.

In the low absorption coefficient region Eqs. (22) and (23) can be combined with Eqs. (26) and (27):

$$\psi_{\text{exp}} = \Phi_0 + a_f x_0 - \tan^{-1} [2/(\alpha\mu_s)^2], \quad (30a)$$

and

$$q_{\text{exp}} = q_0 \exp(-a_f x_0)(\alpha\mu_s). \quad (30b)$$

Equation (30) can be convolved in a way similar to the convolution of Eq. (28). The result is

$$q_{\text{exp}} = q_0 \exp(-a_f x_0) \left[\frac{2}{\tan(\Phi_0 + a_f x_0 - \psi_{\text{exp}})} \right]^{1/2}. \quad (31)$$

The numerical methods of Ref. 19 can be used with Eq. (31) to optimize the values of q_0 and Φ_0 . The latter can then be inserted into Eq. (30) to yield absolute values of the product $(\alpha\mu_s)$, and hence of the absorption coefficient $\alpha(\lambda)$.

CONCLUSIONS

A simplified one-dimensional theory of transverse mode photothermal deflection spectroscopy (TPDS) has been developed for a solid-fluid interface. Explicit expressions have been obtained for the ac and dc components of the signal, in terms of physical and geometrical parameters of the system. The amplitude and phase channels of the experimentally meaningful ac component were identified as carrying information about the optical absorption coefficient of the solid sample. Absorption coefficient ranges within which TPDS can be utilized as a sensitive spectroscopic tool have been defined, and expressions relating the experimental amplitude and phase have been obtained in the thermally thick limit in the regions of signal saturation and low absorption coefficient. These expressions can be used with optimizing fitting techniques to obtain absolute values of the absorption coefficient in the respective regions. Applications of the numerical methods will be discussed in a later publication.

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