Phase measurements in the frequency domain photoacoustic spectroscopy of solids

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Photoacoustic spectroscopy provides information about both the amplitude and phase of the response of a system to an optical excitation process. This paper presents a theoretical model of photoacoustic processes in the frequency domain which includes the relaxation time of the radiationless deexcitations and a two-layer absorbing system. Emphasis is placed on the effect of these conditions on the phase of the photoacoustic signal and the utility of this measurement in evaluating material parameters. Circumstances under which the phase may be used to measure the optical absorption coefficient of the solid and the nonradiative relaxation times are defined. The value of the phase measurement in the study of surface films is discussed.

PACS numbers: 78.20. — e, 78.65. — s, 42.80. — f, 07.65. — b

I. INTRODUCTION

Photoacoustic spectroscopy (PAS) provides information about both the amplitude and phase of the response of a photoacoustic system to an optical excitation process. The phase data contains contributions from a number of sources associated with the sample under study, the geometry of the photoacoustic cell, the response of the detecting system, etc. In an actual photoacoustic measurement many of the non-sample related parameters may be maintained constant and the phase data may therefore be used to provide information about the optical and thermal properties of the solid under study as well as the relaxation times associated with the non-radiative deexcitation processes that give rise to the PAS signal.

Measurements of the photoacoustic phase have been used with gaseous samples to obtain information about relaxation rates and photochemical processes. These measurements have been discussed in a recent review by Robin.[1] For the case of solids various contributions to the phase of the PAS signal have been considered by several authors.

In their one-dimensional theory of the photoacoustic response of solid samples, Rosencwaig and Gersho[2] discussed the effect of the optical absorption coefficient of the solid on the phase for the limiting cases of optically transparent and optically opaque specimens in which the nonradiative deexcitation processes occurred instantaneously. In a subsequent paper Rosencwaig[3] took the generalized expression for the photoacoustic signal from this initial paper and used it to obtain computer-generated curves for both the amplitude and the phase of the photoacoustic response as a function of the modulation frequency and the sample dimensions. The dependence of these signals upon the thermal properties of the sample support was also considered.

Aamodt et al.[4] developed a more exact one-dimensional model for the PAS response of a solid specimen which differs from the model of Rosencwaig and Gersho by using a thermal transport equation for the gas developed by Parker[5] which includes the finite velocity of sound. In this paper the effects of the dimensions of the photoacoustic cell on the phase of the signal are considered and it is shown that the phase is insensitive to cell length once the length of the gas in the cell is large compared to the corresponding thermal diffusion length at the chopping frequency of the radiation. Similarly the effect of the thermal properties of the sample backing on the phase was found to be unimportant in that range of chopping frequencies for which the thermal diffusion length in the solid was short compared to its thickness.

PAS phase has been discussed in a series of papers by Kirkbright and his co-workers.[6,7,8] These authors considered instantaneous nonradiative deexcitation processes and were largely concerned with the phase shifts in a multilayered sample which result from the thermal transit time through a transparent overlayer deposited on an absorbing substrate.

The use of PAS phase to measure the lifetime associated with the nonradiative deexcitation paths has been employed by Merkle and Powell.[9,10] These authors took the relationship between the nonradiative lifetime and the phase shift employed for a gaseous sample by Harshbarger and Robin[11] and used it to interpret radiationless relaxation rates of Eu^{2+} ions in a KCl matrix. A large relative phase shift was observed between the PAS signals resulting from excitation in the t_{2g} and e_g bands of the Eu^{2+} ion and was attributed to a long-lived excited state of the $4f^7$ configuration. Peterson and Powell[12] have employed the same analytical approach to compare the nonradiative decay modes for Cr^{3+} ions in Al_2O_3, MgO, $SrTiO_3$, and $BaTiO_3$ lattices.

Recently, Roark et al.[13] presented data on the absorption coefficient dependence of the photoacoustic phase. They suggested that measurement of the phase angle provides a means of computing the absolute optical absorption coefficient of a sample and indicated that the phase angle continues to be dependent upon the absorptivity of the sample after the PAS amplitude has saturated so that phase measurements provide a method of extending absorption coefficient determinations to higher values.

This paper is concerned with the extension of the Rosencwaig photoacoustic model to include the relaxation time of the radiationless deexcitation processes and two-layer absorbers supported on a nonabsorbing backing material. The emphasis is on the effects of these quantities on the phase of
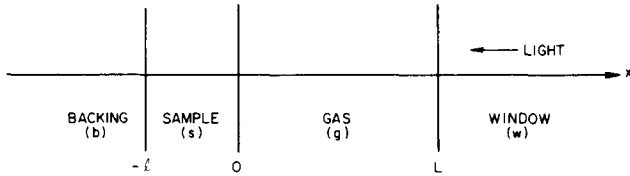
FIG. 1. Geometry of a single-layer PAS system.

the photoacoustic response and the utility of this measurement in obtaining material parameters. It is shown that the phase of the photoacoustic signal can be used to measure the optical absorption coefficient of a solid but that this measurement exhibits the same saturation behavior at high absorption coefficients as does the PAS amplitude. The phase may also be used to measure the relaxation time of the nonradiative deexcitation processes responsible for the PAS signal; however, the relaxation time is only proportional to the tangent of the phase angle in certain limiting cases. For a multilayer absorber the phase measurement provides useful information about both a transparent overlayer on an absorbing substrate and a two-layer system with widely differing optical absorption coefficients.

II. MODEL
A. Single-layer sample with a finite nonradiative relaxation rate

An idealized configuration of a photoacoustic system is shown in Fig. 1. The solid sample, of thickness l, contains a two-level optical absorption band which has an excited-state lifetime τ and a wavelength-dependent optical absorption coefficient β. The sample is supported by a transparent backing material of large thickness and is in thermal contact with a transparent gas. Heat transfer between the solid and the gas results in pressure fluctuations which constitute the PAS signal. The cell is closed by a nonabsorbing thick window. By choosing both the transparent cell window and sample backing to be infinitely thick the growing exponential solutions for the thermal transport equations in these components can be eliminated by application of the boundary conditions. This geometry is essentially the same as that used by other authors[2-4] but the system differs in that a finite relaxation time is associated with the nonradiative decay processes.

The light incident upon the solid is assumed to be modulated sinusoidally so that the irradiance at a distance x from the front surface is given by

$$I(x,t) = \tfrac{1}{2}[I_0 \, \beta \exp(-\beta |x|)](1 + \cos\omega_0 t)$$

$$= A(x) \, \text{Re}[1 + \exp(i\omega_0 t)],$$

where ω_0 is the modulation frequency. Absorption of this radiation by the electronic state gives rise to a time-dependent energy associated with the excited level and given by

$$\frac{dE(x,t)}{dt} = I(x,t) - \frac{E(x,t)}{\tau}.$$

Solving this equation for $E(x,t)$ gives

$$E(x,t) = A(x)\tau \, \text{Re}\!\left[S(t) - \left(1 + \frac{1}{(1 + i\omega_0\tau)}\right) \right.$$

$$\left. \times \exp\!\left(-\frac{t}{\tau}\right) + \left(\frac{\exp(i\omega_0 t)}{1 + i\omega_0\tau}\right) \right].$$

The first two terms are associated with the transient resulting from turning on the radiation at $t = 0$. Only the steady-state component of this solution is of interest for this paper so that

$$E(x,t) = A(x)\tau \, \text{Re}\!\left(\frac{\exp(i\omega_0 t)}{1 + i\omega_0\tau} \right).$$

The nonradiative decay of the excited-state population to the ground state provides a spatial- and time-dependent heat source in the solid

$$\dot{H}(x,t) = \frac{\eta}{\tau} E(x,t)$$

$$= \frac{\eta I_0 \, \beta \exp(-\beta |x|)}{2} \, \text{Re}\!\left(\frac{\exp(i\omega_0 t)}{1 + i\omega_0\tau} \right), \quad (1)$$

where η is the efficiency of the nonradiative processes. It is this alternating steady-state heat source that is responsible for the periodic temperature fluctuation of the sample. Thermal conduction processes then transfer energy to the sample backing and to the gas in the cell. In the approximation employed by Rosencwaig and Gersho[2] the appropriate thermal diffusion equations have the form

$$\frac{\partial^2}{\partial x^2} T_s(x,t) - \frac{1}{\alpha_s} \frac{\partial}{\partial t} T_s(x,t) = -\frac{\dot{H}(x,t)}{k_s} \quad (2)$$

for the solid in which the absorption of the incident radiation occurs, and

$$\frac{\partial^2}{\partial x^2} T_i(x,t) - \frac{1}{\alpha_i} \frac{\partial}{\partial t} T_i(x,t) = 0 \quad (3)$$

for the transparent window ($i = w, x \geqslant L$), gas ($i = g, 0 \leqslant x \leqslant L$), and backing ($i = b, x \leqslant -l$) regions of the cell. The quantities $\alpha_i = (k_i / \rho_i c_i)$ are the thermal diffusivities of various regions of the cell where ρ_i and c_i are the material densities and specific heats, respectively, and k_i is the corresponding thermal conductivity. These four coupled equations may be solved using Fourier transform techniques subject to the boundary conditions of temperature and heat flux continuity at each material interface so that

$$T_i(\text{boundary}, t) = T_j(\text{boundary}, t) \quad (4)$$

and

$$k_i \frac{\partial}{\partial x} T_i(\text{boundary}, t) = k_j \frac{\partial}{\partial x} T_j(\text{boundary}, t). \quad (5)$$

The resulting expression for the Fourier transform of the temperature distribution in the gas has the form

$$\hat{T}_g(x,\omega) = \left(\frac{\beta I_0 \eta}{2k_s(\beta^2 - \sigma_s^2)}\right) \mathrm{Re}\left[\left(\frac{\delta(\omega - \omega_0)}{1 + i\omega_0 \tau}\right)\right.$$

$$\times \left(\frac{(r-1)(b+1)\exp(\sigma_s l) - (r+1)(b-1)\exp(-\sigma_s l) + 2(b-r)\exp(-\beta l)}{(g+1)(b+1)\exp(\sigma_s l) - (g-1)(b-1)\exp(-\sigma_s l)}\right)$$

$$\left. \times \sum_{n=0}^{\infty} ((1+D)\exp[-\sigma_g(2nL + x)] - (1-D)\exp\{-\sigma_g[2(n+1)L - x]\})\right], \tag{6}$$

where

$$r = (1-i)\left(\frac{\beta}{2a_s}\right), \quad b = \left(\frac{a_b k_b}{a_s k_s}\right), \quad g = \left(\frac{a_g k_g}{a_s k_s}\right), \quad D = \left(\frac{a_g k_g}{a_w k_w}\right), \quad \sigma_j = (1+i)a_j, \quad \text{and} \quad a_j = \left(\frac{\omega}{2\alpha_j}\right)^{1/2}, \quad j = s,b,g,w.$$

The above relationship can be transformed from the frequency to the time domain and the presence of the multiplicative term $\delta(\omega - \omega_0)$ results in the frequency dependence implicit in the terms containing σ_i contributing only at $\omega = \omega_0$. The temperature distribution in the gas is then given by

$$T_g(x,t) = \left(\frac{\beta I_0 n}{2k_s}\right)\mathrm{Re}\left\{\left(\frac{1}{(\beta^2 - \sigma_s^2)}\right)\left(\frac{(r-1)(b+1)\exp(\sigma_s l) - (r+1)(b-1)\exp(-\sigma_s l) + 2(b-r)\exp(-\beta l)}{(g+1)(b+1)\exp(\sigma_s l) - (g-1)(b-1)\exp(-\sigma_s l)}\right)\right.$$

$$\left. \times \left[\left(\frac{1}{1+i\omega_0 \tau}\right)\sum_{n=0}^{\infty}((1+D)\exp[-\sigma_g(2nL + x)] - (1-D)\exp\{-\sigma_g[2(n+1)L - x]\})\right]\exp(i\omega_0 t)\right\}. \tag{7}$$

This periodic and spatially dependent temperature distribution generates a periodic but spatially uniform pressure in the gas given by

$$\langle p_g(t;\omega_0)\rangle = \frac{p_0}{T_0 L}\int_0^L T_g(x,t;\omega_0)\,dx, \tag{8}$$

where p_0 and T_0 are the initial pressure and temperature of the gas in the cell.

The PAS signal then has the form

$$\langle p_g(t;\omega_0)\rangle = \left(\frac{p_0 I_0 \eta \beta}{2k_s T_0 L}\right)\mathrm{Re}\left[\left(\frac{\exp[i(\omega_0 t - \frac{1}{4}\pi)]}{\sqrt{2}a_g(1 + i\omega_0 \tau)(\beta^2 - \sigma_s^2)}\right)\right.$$

$$\left. \times \left(\frac{(r-1)(b+1)\exp(\sigma_s l) - (r+1)(b-1)\exp(-\sigma_s l) + 2(b-r)\exp(-\beta l)}{(b+1)\exp(\sigma_s l) + (b-1)\exp(-\sigma_s l)}\right)\right] \tag{9}$$

since $\sigma_g^{-1} = [1/(2a_g)]^{1/2}\exp(-\frac{1}{4}i\pi)$ and where it has been assumed that $D < < 1, g < < 1$, and that $a_g L > > 1$ so that only the $n = 0$ term in the summation needs to be retained. Equation (9) is a generalization of Eq. (17) in Ref. 2 to include the effects of a noninstantaneous deexcitation process.

In order to separate the amplitude and the phase of the photoacoustice signal it is convenient to follow Rosencwaig and Gersho and define

$$\langle p_g(t;\omega_0)\rangle \equiv \mathrm{Re}\{Q\exp[i(\omega_0 t - \frac{1}{4}\pi)]\} \equiv \mathrm{Re}\{q\exp i[(\omega_0 t - \frac{1}{4}\pi) - \psi]\}$$

such that $Q = Q_1 + iQ_2 = q\exp(-i\psi)$.

The amplitude of the measured photoacoustic signal

$$|\langle p_g(t;\omega_0)\rangle| = |Q| = q = (Q_1^2 + Q_2^2)^{1/2}$$

and the phase lag of the signal with respect to the light source modulation

$$\Phi = (\tfrac{1}{4}\pi + \psi) \quad \text{with } \psi = \tan^{-1}[-(Q_2/Q_1)].$$

These quantities may be most conveniently evaluated by writing the components of Q in the polar notation for complex quantities so that

$$\beta^2 - \sigma_s^2 = Z_1 = |Z_1|\exp(i\phi_1) = \beta^2[1 + (\omega_0 \tau_\beta)^2]^{1/2}\exp(i\phi_1),$$

$$1 + i\omega_0 \tau = Z_2 = |Z_2|\exp(i\phi_2) = [1 + (\omega_0 \tau)^2]^{1/2}\exp(i\phi_2),$$

$$r - 1 = Z_3 = |Z_3|\exp(i\phi_3) = [(\omega_0 \tau_\beta)^{-1} + 1 - (2/\omega_0 \tau_\beta)^{1/2}]^{1/2}\exp(i\phi_3), \tag{10}$$

$$r + 1 = Z_4 + |Z_4|\exp(i\phi_4) = [(\omega_0 \tau_\beta)^{-1} + 1 + (2/\omega_0 \tau_\beta)^{1/2}]^{1/2}\exp(i\phi_4),$$

$$b - r = Z_5 = |Z_5|\exp(i\phi_5) = [(\omega_0 \tau_\beta)^{-1} + b^2 - b(2/\omega_0 \tau_\beta)^{1/2}]^{1/2}\exp(i\phi_5),$$

and

$$(b+1)\exp(\sigma_s l) + (b-1)\exp(-\sigma_s l) = Z_6 = |Z_6|\exp(i\phi_6) = [(b+1)^2\exp(2a_s l) + (b-1)^2\exp(-2a_s l)$$

$$+ 2(b^2 - 1)\cos(2a_s l)]^{1/2}\exp(i\phi_6),$$

where $\tau_\beta \equiv 1/\beta^2 \alpha_s$ is a characteristic relaxation time for the system corresponding to the thermal transit time from a depth μ_β ($\equiv 1/\beta$) within the solid.

Using these definitions the real and imaginary parts of Q can be evaluted and have the form

$$Q_1 = ReQ = K\,[(b+1)\,|Z_3|\,\exp(a_s l)\cos(\phi_1 + \phi_2 + \phi_6 - \phi_3 - a_s l) - (b-1)\,|Z_4|\,\exp(-a_s l)$$
$$\times\cos(\phi_1 + \phi_2 + \phi_6 - \phi_4 + a_s l) + 2\,|Z_5|\,\exp(-\beta l)\cos(\phi_1 + \phi_2 + \phi_6 - \phi_5)\,],$$

$$Q_2 = ImQ = -K\,[(b+1)\,|Z_3|\,\exp(a_s l)\sin(\phi_1 + \phi_2 + \phi_6 - \phi_3 - a_s l) - (b-1)\,|Z_4|\,\exp(-a_s l)$$
$$\times\sin(\phi_1 + \phi_2 + \phi_6 - \phi_4 + a_s l) + 2\,|Z_5|\,\exp(-\beta l)\sin(\phi_1 + \phi_2 + \phi_6 - \phi_5)\,],$$

(11)

where

$$K = \frac{p_0 I_0 \eta \beta}{2\sqrt{2}\,k_s T_0 L a_g\,|Z_1|\,|Z_2|\,|Z_6|}.$$

The amplitude of the photoacoustic signal is seen to be directly proportional to K and the relaxation time, τ, associated with the nonradiative decay process is contained in the term $|Z_2|$ in the denominator. For a modulation frequency $\omega_0 < < 1/\tau$ the PAS amplitude becomes independent of τ, as expected, and the expression for the pressure is identical to that obtained by Rosencwaig and Gersho.[2] When $\omega_0\tau$ cannot be neglected compared to unity, the PAS signal decreases as the relaxation time τ increases.

The variable contribution to the phase, $\psi = \tan^{-1}(-Q_2/Q_1)$, is seen to depend upon the optical absorption coefficient of the solid and its physical dimensions, the ratio of the thermal properties of the solid and the backing material, the relaxation time of the nonradiative deexcitation processes, the modulation frequency of the light, and the thermal properties of the solid and the gas in the cell. For certain limiting cases the expression for the phase can take on a particularly simple form.

For an optically opaque and thermally thick sample both the optical absorption depth, μ_β, and the thermal diffusion length, μ_s, are much less than the sample thickness. Under these conditions $\exp(-\beta l)\simeq 0$ and $\exp(-\sigma_s l)\simeq 0$ so that the variable component of the PAS phase is given by

$$\psi(\beta,\tau,\omega_0) = \tan^{-1}(-\omega_0\tau_\beta) + \tan^{-1}(\omega_0\tau)$$
$$-\tan^{-1}\left(\frac{-1}{1-(2\omega_0\tau_\beta)^{1/2}}\right).$$

(12)

At chopping frequencies for which $\mu_s > \mu_\beta$ and $\omega_0\tau_\beta \simeq 0$

$$\psi(\tau,\omega_0) = \tfrac{1}{4}\pi + \tan^{-1}(\omega_0\tau)$$

(13)

and the phase information provides a direct measure of the relaxation time, τ, of the nonradiative processes.

A similar expression is obtainable for an optically transparent thermally thick solid for which $\exp(-\beta l)\simeq(1-\beta l)$ and $\mu_s < l$. In this case

$$\psi(\tau,\omega_0) = \tfrac{1}{2}\pi + \tan^{-1}(\omega_0\tau).$$

(14)

Expressions (13) and (14) indicate that the PAS phase only provides a direct measurement of the relaxation time of the nonradiative processes in certain limiting cases. From an experimental viewpoint the preferred configuration would probably be that of Eq.(13) since the signal amplitude would be largest for this case.

The full expression for the phase may be evaluated numerically and Fig. 2 shows the dependence of the phase upon the modulation frequency of the light for a system in which the nonradiative relaxations are instantaneous. Fig. 2 is

equivalent to Fig. 2 in Ref. 3, however, an error of sign occurs in the expression for Q given in that paper and is responsible for the indicated nonsystematic dependence of the phase upon the properties of the backing material. If the data displayed in Fig. 2 of the present paper is plotted in terms of the the parameter $l/\mu_s \propto \omega_0^{1/2}$ it reduces to the form shown in Fig. 3 of Ref. 4. For this optically transparent sample the phase of the photoacoustic signal already displays a strong dependence upon the thermal properties of the backing at a modulation frequency for which $\omega_0\tau_l = 1$. τ_l may be considered to be a modified thermal diffusion time across the solid of thickness l and is defined by $\tau_l \equiv (k_s\,\rho_s c_s/k_b\,\rho_b c_b)$ $\times(l^2/\alpha_s) = (l/b)^2(1/a_s)$. The quantity l/b may be treated as an effective thickness of the sample which increases for a given sample as the thermal conductivity of the support material becomes smaller. When $\omega_0\tau_l \gtrsim 25$ the phase of the PAS signal is independent of the properties of the backing material. This is equivalent to a value of $l/\mu_s \simeq 5$. For very large values of b, e.g., in the case of a solid in contact with a good thermal conductor, the phase changes by more than 45° at experimentally realistic values of the chopping frequency, but tends asymptotically to the 45° value at very low frequencies ($\sim 10^{-3}$ Hz). However, in this limit, the signal is small and phase shifts may not be easy to measure accurately. For very small values of b, such as expected if the solid under study is a self-supporting film with a gas backing, the phase changes by less than 45° at intermediate values of the modulation frequency since the condition $\mu_s \sim l/b$ which determines the phase change is met at lower frequencies. In this case also the phase tends asymptotically to the 45° value at very low frequencies. In the limit of $b = 0$, there is no observable phase shift between the backing-independent frequency range and this intermediate region.

The amplitude of the PAS signal is also dependent upon the ratio of μ_s to this effective thickness and, as expected for
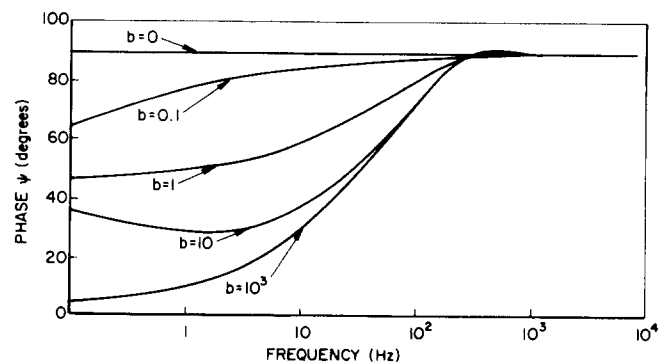

FIG. 2. Dependence of the PAS phase upon modulation frequency for various values of b, for an optically transparent solid ($\beta = 20$ cm^{-1}, $l = 50$ μm).
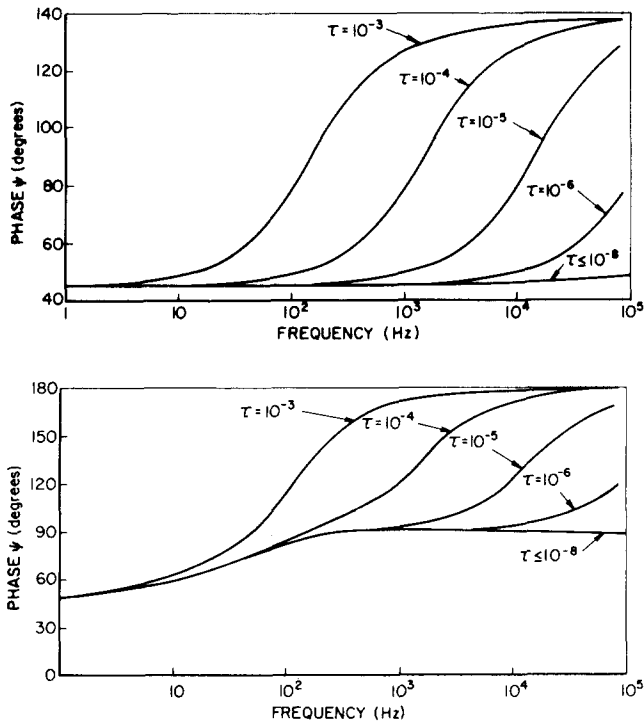
FIG. 3. (a) Frequency dependence of the PAS phase for various nonradiative lifetimes and an optically opaque thermally thick sample $(\mu_\beta < \mu_s, \mu_\beta < l)$. (b) Corresponding data for an optically transparent sample $(\mu_\beta > l, l = 50\mu m, b = 1)$.

a transparent solid, when μ_s is greater than the effective thickness for materials for which $b > 1$ the signal magnitude is reduced due to the large heat flux to the backing material.

Figure 3 shows the dependence of the phase upon the modulation frequency for solids in which the relaxation time of the nonradiative deexcitations is taken into account. In Fig. 3 it has been assumed that $b = 1$. As seen in Fig. 3a which applies to a material of high optical absorption coefficient $(\beta = 2 \times 10^5 \text{cm}^{-1})$, no contribution to the phase shift arises from the optical absorption depth since over the full range of modulation frequencies $\mu_s > \mu_\beta$. The complete phase shift displayed in this part of the diagram results from effects due to the nonradiative lifetime and, as expected, such processes become important for frequencies greater than that for which $\omega_0 \tau \simeq 1.0$. The phase shift produced by any given relaxation time is seen to saturate as the frequency increases. Figure 3b shows the response expected for a material of lower β (20 cm^{-1}). Two contributions to the phase are now seen to be involved. The phase shift of aproximately 45° associated with the instantaneous relaxation time curve results from a reversal of the relative magnitudes of μ_s and l as μ_s decreases with increasing ω. Superimposed on this contribution is that due to the relaxation time phenomena. As was shown in Eq. (14), in the limit of high frequencies for which μ_s is always less than l and the sample is therefore thermally thick, the additional increment of phase is directly related to the relaxation time.

In Figs. 2 and 3 the PAS signal is associated with a particular value of the absorption coefficient. In most actual PAS situations the wavelength of the exciting light is changed through a region associated with an absorption
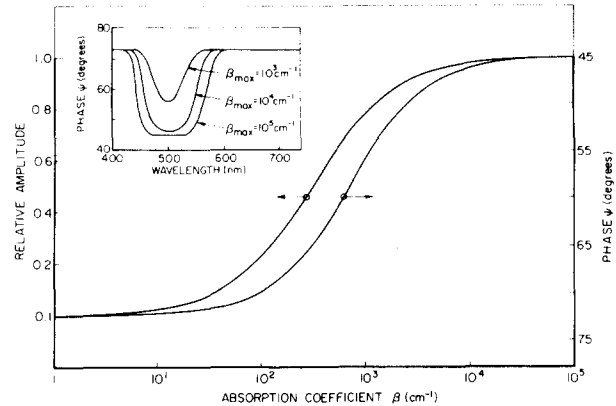

FIG. 4. Comparison between PAS amplitude and phase as a function of the absorption coefficient of the solid. $(f = 50 \text{ Hz}, l = 50\mu m, b = 1)$. Inset: Phase Response in passing through a Gaussian absorption band having different values of β_{max}.

band. The phase of the PAS signal will then depend upon $\beta(\lambda)$. This dependence is illustrated in Fig. 4, the phase lag and the relative amplitude of the signal being displayed as a function of log β. The inset in Fig. 4 shows the effect of this β dependence of the phase upon the system response to a Gaussian-shaped absorption band centered at 500 nm and with a full width at half-maximum of 0.1 eV. Both diagrams indicate that saturation occurs in the phase response at large values of β and the corresponding amplitude curve indicates that both phase and amplitude saturate at essentially the same value of β. As shown in the inset, for low values of β_{max} in an absorption band the phase response follows the form of the wavelength-dependent optical absorption coefficient and may therefore be used to measure this quantity. As $\beta(\lambda)$ increases, the phase angle decreases from an upper limit determined by the chopping frequency and by the coefficient b towards the 45° angle expected for a sample for which the optical absorption depth is less than the μ_s. "Phase saturation" therefore occurs for samples having high optical absorption coefficients.

The dependence of the thermal diffusion length, μ_s, upon the modulation frequency of the light means that for a sample with instantaneous nonradiative deexcitation processes the amplitude of the PAS signal has an ω^{-1} dependence at low modulation frequencies and an $\omega^{-3/2}$ dependence at high frequencies. For a sample in which the nonradiative processes have a finite relaxation time, the high-frequency slope is changed as is shown in Fig. 5. The
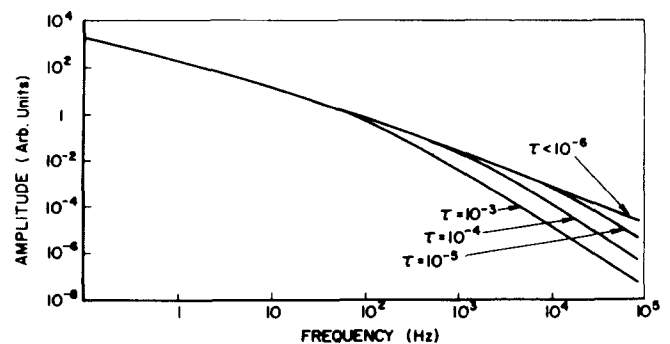

FIG. 5. Dependence of PAS amplitude on modulation frequency for different nonradiative lifetimes $(\beta = 20 \text{cm}^{-1}, b = 1, l = 50\mu m)$.

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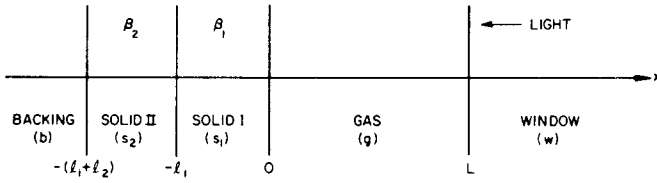
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FIG. 6. Geometry for a double-layer PAS system.

curves for the finite relaxation times break away from the instantaneous curve at a point for which $\omega_0 \tau \simeq 1.0$ and for all values of τ approach a limiting logarithmic slope higher by one than that of the instantaneous curve. For a material for which the instantaneous slope would be -1 that with relaxation is -2; for the case shown in Fig. 5 where the instantaneous slope is $-\frac{3}{2}$ that with relaxations is $-\frac{5}{2}$.

B. Two-layer sample with instantaneous nonradiative relaxations

Many systems of physical interest may be approximated by a two-layer model of a solid with each layer having independent optical absorption properties. Examples might be absorbing coatings on optical components, molecular films on an absorbing catalytic support, or biological systems such as the skin or a plant leaf. Such a system may be represented in the same approximation employed in Sec. II A as shown in Fig. 6. As before, the modulated light enters

the photoacoustic cell through a thick window at $x = L$. The surface of the first solid is at $x = 0$ and this material, with an absorption coefficient β_1, extends to $x = -l_1$. The second solid of thickness l_2 and optical absorption coefficient β_2 is supported on a transparent backing material that extends to $x = -\infty$. The finite thickness of the second solid makes the solutions for the two absorbing regions symmetric and avoids the problem of the second layer being optically opaque for all nonzero values of β_2.

Since only instantaneous nonradiative processes are being considered the distributed time-dependent heat source term associated with light absorption in the two solids has the form

$$\frac{\dot{H}(x,t)}{k_i} = \left(\frac{I\beta_i n_i}{2k_i}\right)\exp(-\beta_i y)\,\mathrm{Re}[1 + \exp(i\omega_0 t)], \quad (15)$$

where for solid 1, $i = 1, I = I_0$, the irradiance of the incident radiation, and $y = -x$. For solid 2, $i = 2$,
$I = I_0 \exp(-\beta l_1)$, and $y = -(x + l_1)$. There are now five coupled thermal diffusion equations for the system, two having the form of Eq. (2) but with Eq. (15) being substituted for $\dot{H}(x,t)/k_s$, and three having the same form as Eq. (3). As before these equations can be solved using Fourier transform techniques and invoking temperature and heat flux continuity at the boundaries between the various elements in the cell. It is only the ac component of the temperature in the gas that is of interest since this is responsible for the pressure fluctuations in the gas that are the PAS signal. In the general case this temperature is

$$T_g(x,t) = \left[\left(\frac{\eta_2\beta_2 I_0 b_1 \exp(-\beta_1 l_1)}{k_2(\beta_2^2 - \sigma_2^2)}\right)[(r_2 - 1)(b_2 + 1)\exp(\sigma_2 l_2) - (r_2 + 1)(b_2 - 1)\exp(-\sigma_2 l_2) + 2(b_2 - r_2)\right.$$

$$\times\exp(-\beta_2 l_2)] + \left(\frac{\eta_1\beta_1 I_0}{2k_1(\beta_1^2 - \sigma_1^2)}\right)\{(r_1 - 1)(b_1 + 1)(b_2 + 1)\exp(\sigma_1 l_1 + \sigma_2 l_2) - (r_1 + 1)(b_1 - 1)(b_2 + 1)$$

$$\times\exp[-(\sigma_1 l_1 - \sigma_2 l_2)] + (r_1 - 1)(b_1 - 1)(b_2 - 1)\exp(\sigma_1 l_1 - \sigma_2 l_2) - (r_1 + 1)(b_1 + 1)(b_2 - 1)$$

$$\times\exp(\sigma_1 l_1 + \sigma_2 l_2) + 2[(b_1 - r_1)(b_2 + 1)\exp(\sigma_2 l_2) + (b_1 + r_1)(b_2 - 1)\exp(-\sigma_2 l_2)]\exp(-\beta_1 l_1)\}\right]$$

$$\times\{(b_1 + 1)(b_2 + 1)\exp(\sigma_1 l_1 + \sigma_2 l_2) + (b_1 - 1)(b_2 + 1)\exp[-(\sigma_1 l_1 - \sigma_2 l_2)]$$

$$+ (b_1 + 1)(b_2 - 1)\exp[-(\sigma_1 l_1 + \sigma_2 l_2)] + (b_1 - 1)(b_2 - 1)\exp(\sigma_1 l_1 - \sigma_2 l_2)\}^{-1}$$

$$\times \sum_{n=0}^{\infty}((1 + D)\exp[-\sigma_g(2nL + x)] - (1 - D)\exp\{-\sigma_g[2(n + 1)L - x]\})\exp(i\omega_0 t)$$

or

$$T_g(x,t) = [N][M]^{-1}\sum_{n=0}^{\infty}[R(n)] \tag{16}$$

with $b_1 \equiv k_2 a_2/k_1 a_1$ and $b_2 \equiv k_b a_b/k_2 a_2$ and the other symbols having their previous meanings with the subscripts referring to solids 1 or 2. With either l_1 or l_2 zero this expression reduces to that for a single-layer system given in Eq. (13) of Ref. 2.

The modulated pressure in the gas is obtained by substituting Eq. (16) into Eq. (8). If L is large compared to the thermal diffusion length in the gas, only the $n = 0$ term in the summation $\sum_{n=0}^{\infty}[R(n)]$ is retained and the expression for the pressure is

$$\langle p(t;\omega_0)\rangle = \left(\frac{p_0 I_0 \exp[i(\omega_0 t - \frac{1}{4}\pi)]}{\sqrt{2}a_g T_0 L}\right)\frac{[N]}{[M]} \equiv Q_d \exp[i(\omega_0 t - \frac{1}{4}\pi)]. \tag{17}$$

By writing $[N]$ and $[M]$ in complex polar notation, as was done previously, this expression may be evaluated to obtain the amplitude and the phase of the photoacoustic response for the two-layer system.

For the case of a transparent overlayer on an absorbing substrate, as considered by Adams and Kirkbright,[7] $\beta_1 = 0$ and if $b_1 = 1$, then Q_d can be written as

$$Q_d = \left(\frac{p_0 I_0}{2\sqrt{2a_g T_0 L}}\right)\left(\frac{\eta_2 \beta_2}{k_2(\beta_2^2 - \sigma_2^2)}\right)\left(\frac{1}{\exp(\sigma_1 l_1) + \exp(-\sigma_1 l_1)}\right)$$

$$\times \left(\frac{(r_2 - 1)(b_2 + 1)\exp(\sigma_2 l_2) - (r_2 + 1)(b_2 - 1)\exp(-\sigma_2 l_2) + 2(b_2 - r_2)\exp(-\beta_2 l_2)}{(b_2 + 1)\exp(\sigma_2 l_2) + (b_2 - 1)\exp(-\sigma_2 l_2)}\right). \tag{18}$$

It is seen from the third term in Eq. (18) that Q_d, and hence the amplitude of the PAS signal, goes to zero as l_1 increases or as σ_1 increases due to an increased modulation frequency. Physically this is due to the thickness of the transparent overlayer on the absorbing substrate becoming considerably greater than the thermal diffusion length in that overlayer so that no ac component of the temperature fluctuation due to the absorbing substrate reaches the surface of the transparent overlayer. This modulated thermal signal from the absorbing underlayer decays to zero in the transparent overlayer in a distance of approximately $2\pi\mu_s$ from the intralayer boundary, just as occurs at the boundary between a single solid and the gas in a photoacoustic cell.

The phase of the PAS signal in the presence of a transparent overlayer can be written as

$$\psi = tan^{-1}(-\omega_0 \tau_{\beta 2}) + \left(\frac{\omega_0}{2\alpha_1}\right)^{1/2} l_1$$

$$- tan^{-1}\left(\frac{-1}{1 - (2\omega_0 \tau_{\beta 2})^{1/2}}\right). \tag{19}$$

When the absorption coefficient of the second layer is high and at normal modulation frequencies $(\omega_0 \tau_{\beta 2}) \to 0$, the phase becomes

$$\psi = \frac{\pi}{4} + \left(\frac{\omega_0}{2\alpha_1}\right)^{1/2} l_1. \tag{20}$$

This is the same expression given by Adams and Kirkbright.[8] When the second solid has a lower optical absorption coefficient, an additional contribution will be made to the phase by the thermal diffusion times in that material.

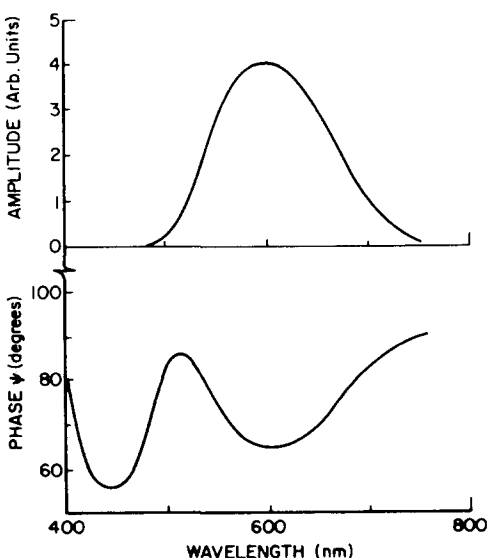Another case of interest is that of an absorbing thin film

FIG. 7. A comparison between the amplitude and the phase response of a double-layer PAS system [β_1(max) $= 50$cm^{-1}, β_2(max) $= 500$cm^{-1}, $l_1 = 10^{-4}$cm, $l_2 = 0.1$cm, $b_1 = b_2 = 1$].

with its absorption band overlapping the tail of the substrate absorption band. This case can be treated numerically using the full expressions for the PAS amplitude and phase derivable from Eq. (17). The results of such a calculation are shown in Fig. 7 for which it has been assumed that both the substrate and the film have Gaussian absorption bands situated at 600 and 500 nm respectively, with maximum absorption coefficients $\beta_2 = 10\beta_1 = 500$ cm^{-1} and full widths at half-maximum of 0.15 and 0.10 eV, respectively. As shown in Fig. 7 the presence of the surface film gives rise to a very small shoulder on the tail of the bulk PAS amplitude response. Provided the amplitude of the signal is large enough for the phase of the signal to be accurately measured this channel provides a clearer indication of the presence of the film. The wavelength dependence of the phase is, however, complex and depends upon both the amplitude and phase of the contributions from the two layers. As the wavelength of the light is scanned from short wavelengths the variable contribution to the phase of the signal changes from the 90° characteristic of a transparent material toward the value of 45° characteristic of an optically opaque material. Initially this signal is controlled in both amplitude and phase by the absorbing front solid. As the absorption coefficient of the back solid starts to become important, a contribution to the PAS signal is made by this second layer. The phase of this additional response is modified by the thermal transit time through the front film as well as by the changing absorption depth in the back solid. The amplitude of this signal also depends upon the absorption coefficients of both layers. Since for the case illustrated the second film has a much higher absorption coefficient than the surface film, the amplitude of the signal from this layer is much larger than that from the front solid and the phase of the response of the composite is finally dominated by the signal from the second layer. As the wavelength of the light is increased, the absorption coefficient of the front solid goes to zero and the phase of the signal depends only on the second solid and the thermal transit time characteristic of the first solid and is described by Eq. (19). Although this phase behavior does not provide a ready measure of the absorption coefficient of the front solid it does indicate the presence of such a solid and enables the correct interpretation to be made of the shoulder present in the amplitude signal. As has been pointed out by Rosencwaig and Gersho,[2] provided the PAS amplitude is high enough, the absorption behavior of the front solid can also be separated from that of an absorbing underlayer by making measurements at chopping frequencies for which $\mu_s \lesssim l_1$.

III. DISCUSSION

As indicated by the models outlined above, the phase data that is available in addition to amplitude information in frequency domain photoacoustic spectroscopy provides ad-

ditional insight into the properties of the system under study. The phase information, however, contains contributions from many sources and only in special limits of sample optical and thermal properties can the phase be unambiguously associated with one particular mechanism. In addition to phase contributions from the sample, the photoacoustic cell, the position of the sample within the cell, the preamplifier for the microphone, and the microphone itself will also produce phase shifts that will, in general, be dependent upon the modulation frequency of the radiation. It is therefore experimentally difficult to make accurate absolute phase measurements, however relative phase can be measured with considerable precision provided the signal-to-noise ratio of the PAS system is high enough and that calibration curves are available for those sources other than the sample.

For a sample in which the nonradiative relaxation processes are instantaneous the phase data can provide an alternate measure of the optical absorption coefficient of the solid. As this optical absorption coefficient increases, the phase lag of the PAS signal with respect to the modulated light source is reduced. As shown in the inset in Fig. 4 the phase data can replicate the shape of an optical absorption band, however phase saturation occurs at high optical absorption coefficients. It was suggested by Roark et $al.$[13] that the phase of the PAS signal enabled measurements to be extended to higher optical absorption coefficients than were measurable using the PAS amplitude. Both the theory presented above and measurements made in this laboratory suggest that this is not the case. Figure 4 also shows a comparison between the relative amplitude of the photoacoustic signal as a function of the absorption coefficient and the corresponding phase of the signal for a thermally thick sample. It is seen that the two measurements essentially coincide and the parallelism between the amplitude and phase response increases at higher chopping frequencies and sample thicknesses. At the low β limit both the phase and the amplitude depend linearly upon β. As β increases the curves pass through a region for which the amplitude and the phase have an approximately logarithmic dependence upon β after which saturation occurs. One advantage of the phase measurement however, is that it is insensitive to light intensity fluctuations whereas the amplitude will follow these fluctuations.

For optically thin samples the angular range of the phase measurement is dependent upon the relative values of the effective sample thickness and the thermal diffusion length in the solid. This behavior is indicated in Fig. 2 and shows that for modulation frequencies for which $\omega_0 \tau_I \lesssim 1$ the angular range of the phase response decreases as b decreases. The dependence of the phase change on sample thickness at a given modulation frequency is exactly analogous to the corresponding dependence of PAS phase on the length of the gas in the cell compared to the thermal diffusion length in the gas as discussed by Aamodt et $al.$[4] Once the sample thickness is greater than about five times the thermal diffusion length in the sample the photoacoustic phase is sample thickness independent (the thermally thick limit).

The measurement of the nonradiative lifetime can be made without contributions to the phase arising from the optical absorption coefficient of the solid only in the optical-

ly thick or the optically thin limit. At intermediate values of the optical absorption coefficient the phase will contain a contribution due to the optical absorption depth in the solid and this contribution must be subtracted from the total phase to obtain the correct value of the nonradiative lifetime. The optically thick limit for which $\mu_\beta < \mu_s$ seems to be the most satisfactory choice for experimental measurement since the amplitude of the PAS signal has saturated together with any phase contribution from the optical absorption coefficient. Only changes in the nonradiative lifetime will contribute to the sample related phase shift under these conditions.

In their measurements of radiationless relaxation processes in various solid systems Powell and co-workers[9,10,12] have used the gas phase relationship developed by Harshbarger and Robin[11] to obtain a measure of this lifetime. Although this expression is similar to that which applies for the case of an optically thick solid with $\mu_\beta < \mu_s$, Eq. (13), it is not clear from the data presented in their papers that this was the experimental situation. The photoacoustic amplitude data does not seem to show saturation, as would be expected in this limit, and consequently the optical absorption depth will be making a contribution to the measured relative phase angle. Only if this contribution was the same in the e_g and t_{2g} bands of the Eu^{2+} ions would the measured phase angle be directly related to the lifetime. Similar comments apply to the measurement of the relative lifetime for nonradiative processes of a given ion type in several host lattices. Only if all of the systems are studied in the optically thick region or if the absolute absorption coefficient of the host lattice plus the solute ion are the same in each case will it be possible to avoid contributions due to the absorption depth of the radiation. It would also seem to be fortuitous that the maximum response of the PAS signal occurred at 0° with the lock in amplifier since a $\frac{1}{4}\pi$ phase shift is to be expected due to the heat transfer process between the solid and the gas in the cell[2] and another $\frac{1}{4}\pi$ due to the fact that the heat flow leads the temperature wave by 45°.[14] These contributions are in addition to any phase shifts due to the optical absorption processes in the solid or contributions from the cell, sample position, and microphone. Such a zero phase shift cannot be correctly interpreted as an instantaneous relaxation process without detailed knowledge of these other contributions.

The phase calculations for the multilayer solid suggest that use of this information together with the PAS amplitude is a good method for detecting surface films. This was also suggested by Bennett and Forman.[15] Conversion of the phase data into a value of the optical absorption coefficient is complicated for this configuration since signals from an absorbing substrate will have both a phase shift due to the thermal transport time through the surface film and a phase shift due to the wavelength-dependent optical absorption coefficient of the substrate. In the limit of a transparent overlayer on a substrate of high optical absorption coefficient for which the β-dependent phase shift is saturated, the present calculations are in agreement with those of Adams and Kirkbright.[8] For a substrate of lower optical absorption coefficient a phase shift arising from the thermal transport time in the substrate will be added to the constant phase shift due to

transport through the transparent overlayer.

In conclusion, the phase of a photoacoustic signal from a solid sample can provide valuable information concerning its structure, thermal properties, optical absorption characteristics, and the lifetimes of the nonradiative transitions responsible for the photoacoustic signal. In the general case contributions to the measured phase will arise from all of these sources; however, for various limiting cases discussed above individual contributions may be isolated. The theory developed in this paper is applicable to samples having a planar form and in good thermal contact with their supporting substrate and consequently is applicable to liquid as well as solid specimens. Experimental measurements indicate that powdered specimens exhibit phase behavior, however, for certain conditions of powder size and optical absorption coefficient phase reversals can occur. This data will be discussed in a later paper.

ACKNOWLEDGMENTS

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