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Cite as: Journal of Applied Physics **47**, 64 (1976); <https://doi.org/10.1063/1.322296>  
Published Online: 28 August 2008

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# Theory of the photoacoustic effect with solids

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(Received 24 July 1975)

When chopped light impinges on a solid in an enclosed cell, an acoustic signal is produced within the cell. This effect is the basis of a new spectroscopic technique for the study of solid and semisolid matter. A quantitative derivation is presented for the acoustic signal in a photoacoustic cell in terms of the optical, thermal, and geometric parameters of the system. The theory predicts the dependence of the signal on the absorption coefficient of the solid, thereby giving a theoretical foundation for the technique of photoacoustic spectroscopy. In particular, the theory accounts for the experimental observation that with this technique optical absorption spectra can be obtained for materials that are optically opaque.

PACS numbers: 78.20.H, 43.35., 07.45.

## I. INTRODUCTION

In 1880, Alexander Graham Bell<sup>1</sup> discovered that when a periodically interrupted beam of sunlight shines on a solid in an enclosed cell, an audible sound could be heard by means of a hearing tube attached to the cell. Motivated by Bell's discovery, Tyndall<sup>2</sup> and Röntgen<sup>3</sup> found that an acoustic signal can also be produced when a gas in an enclosed cell is illuminated with chopped light. Bell<sup>4</sup> subsequently experimented with a variety of solids, liquids, and gases and his work generated a brief flurry of interest. The photoacoustic effect was evidently regarded as a curiosity of no practical value and was soon forgotten. Fifty years later the photoacoustic or photoacoustic effect with gases was reexamined. It has since become a well-established technique for gas analysis and is well understood. Photons absorbed by the gas are converted into kinetic energy of the gas molecules, thereby giving rise to pressure fluctuations within the cell. The photoacoustic effect with solids, however, was apparently ignored for 90 years and a satisfactory theoretical explanation of the effect with solids was never published.

Recently, interest in the photoacoustic effect with solids has been revived with the development of a very useful technique for spectroscopic investigation of solid and semisolid materials.<sup>6-9</sup> The name change from photoacoustic to photoacoustic has been instituted to reduce confusion with the acousto-optic effect in which a laser beam is deflected by acoustic waves in a crystal.

In photoacoustic spectroscopy of solids, or PAS, the sample to be studied is placed inside a closed cell containing a gas, such as air, and a sensitive microphone. The sample is then illuminated with chopped monochromatic light. The analog signal from the microphone is applied to a tuned amplifier whose output is recorded as a function of the wavelength of the incident light. In this way photoacoustic spectra are obtained and these spectra have been found to correspond, qualitatively at least, to the optical absorption spectra of the solids.

One of the principal advantages of photoacoustic spectroscopy is that it enables one to obtain spectra similar to optical absorption spectra on any type of solid or semisolid material, whether it be crystalline, powder, amorphous, smear, gel, etc. This capability is based on the fact that only the absorbed light is converted to sound. Scattered light, which presents such a

serious problem when dealing with many solid materials by conventional spectroscopic techniques, presents no difficulties in photoacoustic spectroscopy. Furthermore, it has been found experimentally that good optical absorption data can be obtained, with the photoacoustic technique, on materials that are completely opaque to transmitted light.<sup>9</sup> Photoacoustic spectroscopy has already found some important applications in research and analysis of inorganic, organic, and biological solids and semisolids.<sup>6-9</sup> It furthermore has very strong potential as a spectroscopic technique not only in the study of bulk optical properties, but also in surface studies and deexcitation studies.<sup>9</sup> With the rapid growth of interest in PAS, a quantitative understanding of the production of the acoustic signal is of utmost importance. In this paper we lay the groundwork for this analysis. In addition we have, for the first time, been able to account for the capability of the photoacoustic technique to derive optical absorption spectra from systems that are completely opaque to transmitted light.

Bell<sup>4</sup> attributed the photoacoustic effect observed with spongy solids such as carbon black to a cyclic driving off of pulses of air from, and reabsorption onto, the pores of the solid in response to the cyclical heating and cooling of the solid by the chopped light. He also supported the theory of Rayleigh<sup>10</sup> who concluded that the effect is also probably due to a mechanical motion of the solid. However, Preece<sup>11</sup> inferred from his experiments that the solid does not undergo any substantial mechanical motion, and suggested that the effect was due to an expansion and contraction of the air in the cell. Mercadier<sup>12</sup> who also experimented with the effect concluded that the sound is due to "vibratory movement determined by the alternate heating and cooling produced by the intermittent radiations, principally in the gaseous layer adhering to the solid surface hit by these radiations."

We have found, from experiments in which we first thoroughly evacuated the photoacoustic cell and then refilled it with nonadsorbing noble gases and from experiments with two-dimensional solids and other materials with weak surface adsorption properties, that absorbed gases do not play a significant role in the production of the acoustic signal. Furthermore, it can be readily shown that thermal expansion and contraction of the solid, and any thermally induced mechanical vibration of the solid are generally too small in magnitude to account for the observed acoustic signal. From

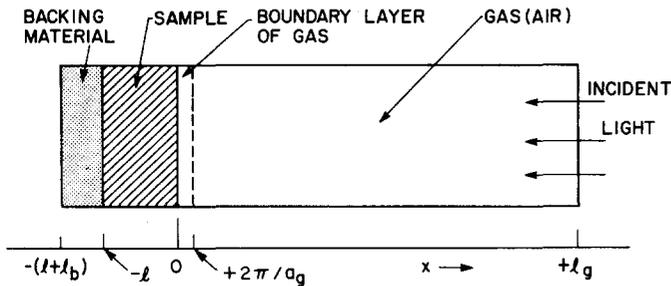


FIG. 1. Cross-sectional view of a simple cylindrical photoacoustic cell, showing the positions of the solid sample, backing material, and gas column.

both experimental and theoretical considerations we feel that the primary source of the acoustic signal in the photoacoustic cell arises from the periodic heat flow from the solid to the surrounding gas as the solid is cyclically heated by the chopped light.<sup>13</sup> Only a relatively thin layer of air ( $\sim 0.2$  cm for a chopping rate of 100 Hz) adjacent to the surface of the solid responds thermally to the periodic heat flow from the solid to the surrounding air. This boundary layer of air can then be regarded as a vibratory piston, creating the acoustic signal detected in the cell. Since the magnitude of the periodic pressure fluctuations in the cell is proportional to the amount of heat emanating from the solid absorber, there is a close correspondence between the strength of the acoustic signal and the amount of light absorbed by the solid.

## II. HEAT-FLOW EQUATIONS

Any light absorbed by the solid is converted, in part or in whole, into heat by nonradiative deexcitation processes within the solid. We formulate a one-dimensional model of the heat flow in the cell resulting from the absorbed light energy. Consider a simple cylindrical cell as shown in Fig. 1. The cell has a diameter  $D$  and length  $L$ . We assume that the length  $L$  is small compared to the wavelength of the acoustic signal and the microphone (not shown) will detect the average pressure produced in the cell. The sample is considered to be in the form of a disk having diameter  $D$  and thickness  $l$ . The sample is mounted so that its front surface is exposed to the gas (air) within the cell and its back surface is against a poor thermal conductor of thickness  $l_b$ . The length  $l_g$  of the gas column in the cell is then given by  $l_g = L - l - l_b$ . We further assume that the gas and backing materials are not light absorbing.

We define the following parameters:  $k_i$ , the thermal conductivity of material  $i$  (cal/cm sec °C);  $\rho_i$ , the density of material  $i$  (g/cm<sup>3</sup>);  $C_i$ , the specific heat of material  $i$  (cal/g °C);  $\alpha_i = k_i / \rho_i C_i$ , the thermal diffusivity of material  $i$  (cm<sup>2</sup>/sec);  $a_i = (\omega / 2\alpha_i)^{1/2}$ , the thermal diffusion coefficient of material  $i$  (cm<sup>-1</sup>);  $\mu_i = 1/a_i$ , the thermal diffusion length of material  $i$  (cm).  $i$  can take the subscripts  $s$ ,  $g$ , and  $b$  for the solid, gas, and backing material, respectively, and  $\omega$  denotes the chopping frequency of the incident light beam in radians per second.

We assume a sinusoidally chopped monochromatic light source with wavelength  $\lambda$  incident on the solid with intensity

$$I = \frac{1}{2} I_0 (1 + \cos \omega t),$$

where  $I_0$  is the incident monochromatic light flux (W/cm<sup>2</sup>). Let  $\beta$  denote the optical absorption coefficient of the solid sample (in cm<sup>-1</sup>) for the wavelength  $\lambda$ . The heat density produced at any point  $x$  due to light absorbed at this point in the solid is then given by

$$\frac{1}{2} \beta I_0 \exp(\beta x) (1 + \cos \omega t),$$

where  $x$  takes on negative values since the solid extends from  $x=0$  to  $x=-l$  with the light incident at  $x=0$ . Note also from Fig. 1 that the air column extends from  $x=0$  to  $x=l_g$  and the backing from  $x=-l$  to  $x=-(l+l_b)$ .

The thermal diffusion equation in the solid taking into account the distributed heat source can be written

$$\frac{\partial^2 \phi}{\partial x^2} = \frac{1}{\alpha_s} \frac{\partial \phi}{\partial t} - A \exp(\beta x) [1 + \exp(j\omega t)],$$

for  $-l \leq x \leq 0$ , (1)

with

$$A = \beta I_0 \eta / 2k_s,$$

where  $\phi$  is the temperature and  $\eta$  is the efficiency at which the absorbed light at wavelength  $\lambda$  is converted to heat by the nonradiative deexcitation processes. In this paper we shall assume  $\eta=1$ , a reasonable assumption for most solids at room temperature. For the backing and the gas,<sup>14</sup> the heat diffusion equations are given by

$$\frac{\partial^2 \phi}{\partial x^2} = \frac{1}{\alpha_b} \frac{\partial \phi}{\partial t}, \quad -l-l_b \leq x \leq -l \quad (2)$$

$$\frac{\partial^2 \phi}{\partial x^2} = \frac{1}{\alpha_g} \frac{\partial \phi}{\partial t}, \quad 0 \leq x \leq l_g. \quad (3)$$

The real part of the complex-valued solution  $\phi(x, t)$  of Eqs. (1)–(3) is the solution of physical interest and represents the temperature in the cell relative to ambient temperature as a function of position and time. Thus the actual temperature field in the cell is given by

$$T(x, t) = \text{Re}[\phi(x, t)] + \Phi,$$

where  $\text{Re}$  denotes the “real part of” and  $\Phi$  is the ambient (room) temperature.

To completely specify the solution of Eqs. (1)–(3), the appropriate boundary conditions are obtained from the requirement of temperature and heat-flux continuity at the boundaries  $x=0$  and  $x=-l$ , and from the constraint that the temperature at the cell walls  $x=+l_g$  and  $x=-l-l_b$  is at ambient. The latter constraint is a reasonable assumption for metallic cell walls but in any case it does not affect the ultimate solution for the acoustic pressure.

Finally, we note that we have assumed the dimensions of the cell are small enough to ignore convective heat flow in the gas at steady-state conditions.

## III. TEMPERATURE DISTRIBUTION IN THE CELL

The general solution for  $\phi(x, t)$  in the cell neglecting transients can be written

$$\begin{aligned}
\phi(x, t) &= (1/l_b)(x + l + l_b)W_0 + W \exp[\sigma_b(x + l) + j\omega t], \\
&\quad -l - l_b \leq x \leq -l \\
&= e_1 + e_2x + d \exp(\beta x) + [U \exp(\sigma_s x) + V \exp(-\sigma_s x) \\
&\quad - E \exp(\beta x)] \exp(j\omega t), \quad -l \leq x \leq 0 \\
&= (1 - x/l_g)\theta_0 + \theta \exp(-\sigma_g x + j\omega t), \quad 0 \leq x \leq l_g,
\end{aligned} \tag{4}$$

where  $W$ ,  $U$ ,  $V$ ,  $E$ , and  $\theta$  are complex-valued constants,  $e_1$ ,  $e_2$ ,  $d$ ,  $W_0$ , and  $\theta_0$  are real-valued constants, and  $\sigma_i = (1 + j)\alpha_i$  with  $\alpha_i = (\omega/2\alpha_i)^{1/2}$ . In particular it should be noted that  $\theta$  and  $W$  represent the complex amplitudes of the periodic temperatures at the sample-gas boundary ( $x=0$ ) and the sample-backing boundary ( $x=-l$ ), respectively. The dc solution in the backing and gas already make use of the assumption that the temperature (relative to ambient) is zero at the ends of the cell. The quantities  $W_0$  and  $\theta_0$  denote the dc component of the temperature (relative to ambient) at the sample surfaces  $x=-l$  and  $x=0$ , respectively. The quantities  $E$  and  $d$ , determined by the forcing function in Eq. (1), are given by

$$d = -\frac{A}{\beta^2}, \tag{5a}$$

and

$$E = \frac{A}{(\beta^2 - \sigma_s^2)} = \frac{\beta I_0}{2k_s(\beta^2 - \sigma_s^2)}. \tag{5b}$$

In the general solution, Eq. (4), we have omitted the growing exponential component of the solutions to the gas and backing material, because for all frequencies  $\omega$  of interest the thermal diffusion length is small compared to the length of the material in both the gas and the backing. That is,  $\mu_b \ll l_b$  and  $\mu_g \ll l_g$  ( $\mu_g \sim 0.02$  cm for air when  $\omega = 630$  rad/sec), and hence the sinusoidal components of these solutions are sufficiently damped so that they are effectively zero at the cell walls. Therefore, the growing exponential components of the solutions would have coefficients that are essentially zero in order to satisfy the temperature constraint at the cell walls.

The temperature and flux continuity conditions at the sample surfaces are explicitly given by

$$\theta = \frac{\beta I_0}{2k_s(\beta^2 - \sigma_s^2)} \left( \frac{(r-1)(b+1) \exp(\sigma_s l) - (r+1)(b-1) \exp(-\sigma_s l) + 2(b-r) \exp(-\beta l)}{(g+1)(b+1) \exp(\sigma_s l) - (g-1)(b-1) \exp(-\sigma_s l)} \right), \tag{9}$$

where

$$b = \frac{k_b \alpha_b}{k_s \alpha_s}, \tag{10}$$

$$g = \frac{k_g \alpha_g}{k_s \alpha_s}, \tag{11}$$

$$r = (1-j) \frac{\beta}{2\alpha_s}, \tag{12}$$

and as stated earlier  $\sigma_s = (1+j)\alpha_s$ . Thus, Eq. (9) can be evaluated for specific parameter values yielding a complex number whose real and imaginary parts  $\theta_1$  and  $\theta_2$ , respectively, determine the in-phase and quadrature components of the periodic temperature variation at the

$$\phi_g(0, t) = \phi_s(0, t), \tag{6a}$$

$$\phi_b(-l, t) = \phi_s(-l, t), \tag{6b}$$

$$k_g \frac{\partial \phi_g}{\partial x}(0, t) = k_s \frac{\partial \phi_s}{\partial x}(0, t), \tag{6c}$$

and

$$k_b \frac{\partial \phi_b}{\partial x}(-l, t) = k_s \frac{\partial \phi_s}{\partial x}(-l, t), \tag{6d}$$

where the subscripts  $s$ ,  $b$ , and  $g$  identify the solution to Eq. (4) for the temperature in the solid, backing, and gas, respectively. These constraints apply separately to the dc component and the sinusoidal component of the solution. From Eqs. (6), we obtain for the dc components of the solution

$$\theta_0 = e_1 + d, \tag{7a}$$

$$W_0 = e_1 - e_2 l + d \exp(-\beta l), \tag{7b}$$

$$-(k_g/l_g)\theta_0 = k_s e_2 + k_s \beta d, \tag{7c}$$

$$(k_b/l_b)W = k_s e_2 + k_s \beta d \exp(-\beta l). \tag{7d}$$

Equations (7) determine the coefficients  $e_1$ ,  $e_2$ ,  $W_0$ , and  $\theta_0$  for the time-independent (dc) component of the solution. Applying Eqs. (6) to the sinusoidal component of the solution yields

$$\theta = U + V - E, \tag{8a}$$

$$W = U \exp(-\sigma_s l) + V \exp(\sigma_s l) - E \exp(-\beta l), \tag{8b}$$

$$-k_g \sigma_g \theta = k_s \sigma_s U - k_s \sigma_s V - k_s \beta E, \tag{8c}$$

and

$$\begin{aligned}
k_b \sigma_b W &= U \exp(-\sigma_s l) - k_s \sigma_s V \exp(\sigma_s l) \\
&\quad - k_s \beta E \exp(-\beta l).
\end{aligned} \tag{8d}$$

These equations together with the expression for  $E$  in Eq. (5b) determine the coefficients  $U$ ,  $V$ ,  $W$ , and  $\theta$ . Hence the solutions to Eqs. (7) and (8) allow us to evaluate the temperature distribution, Eq. (4), in the cell in terms of the optical, thermal, and geometric parameters of the system. The explicit solution for  $\theta$ , the complex amplitude of the periodic temperature at the solid-gas boundary ( $x=0$ ), is given by

surface  $x=0$  of the sample. Specifically, the actual temperature at  $x=0$  is given by

$$T(0, t) = \Phi + \theta_0 + \theta_1 \cos \omega t - \theta_2 \sin \omega t,$$

where  $\Phi$  is the ambient temperature at the cell walls and  $\theta_0$  is the increase in temperature due to the steady-state component of the absorbed heat.

#### IV. PRODUCTION OF THE ACOUSTIC SIGNAL

As stated in Sec. I, it is our contention that the main source of the acoustic signal arises from the periodic heat flow from the solid to the surrounding gas. The

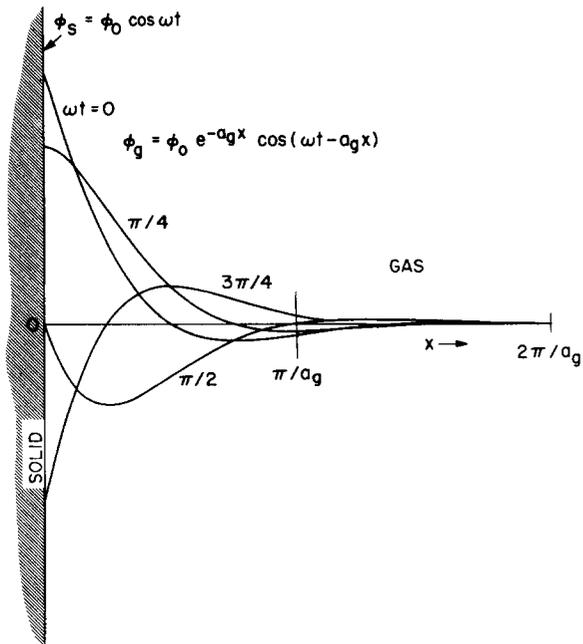


FIG. 2. Spatial distribution of the time-dependent temperature within the gas layer adjacent to the solid surface.

periodic diffusion process produces a periodic temperature variation in the gas as given by the sinusoidal (ac) component of the solution, Eq. (4),

$$\phi_{ac}(x, t) = \theta \exp(-\sigma_g x + j\omega t). \quad (13)$$

Taking the real part of Eq. (13), we see that the actual physical temperature variation in the gas is

$$T_{ac}(x, t) = \exp(-\alpha_g x) [\theta_1 \cos(\omega t - \alpha_g x) - \theta_2 \sin(\omega t - \alpha_g x)], \quad (14)$$

where  $\theta_1$  and  $\theta_2$  are the real and imaginary parts of  $\theta$ , as given by Eq. (9). As can be seen in Fig. 2, the time-dependent component of the temperature in the gas attenuates rapidly to zero with increasing distance from the surface of the solid. At a distance of only  $2\pi/\alpha_g = 2\pi\mu_g$ , where  $\mu_g$  is the thermal diffusion length, the periodic temperature variation in the gas is effectively fully damped out. Thus we can define a boundary layer, as shown in Fig. 1, whose thickness is  $2\pi\mu_g$  ( $\approx 0.1$  cm at  $\omega/2\pi = 100$  Hz), and maintain to a good approximation that only this thickness of gas is capable of responding thermally to the periodic temperature at the surface of the sample.

The spatially averaged temperature of the gas within this boundary layer as a function of time can be determined by evaluating

$$\bar{\phi}(t) = (1/2\pi\mu_g) \int_0^{2\pi\mu_g} \phi_{ac}(x, t) dx.$$

From Eq. (13) this gives

$$\bar{\phi}(t) \cong (1/2\sqrt{2}\pi)\theta \exp[j(\omega t - \frac{1}{4}\pi)], \quad (15)$$

$$Q = \frac{\beta I_0 \gamma P_0}{2\sqrt{2} k_s l_g a_g T_0 (\beta^2 - \sigma_s^2)} \left( \frac{(r-1)(b+1) \exp(\sigma_s l) - (r+1)(b-1) \exp(-\sigma_s l) + 2(b-r) \exp(-\beta l)}{(g+1)(b+1) \exp(\sigma_s l) - (g-1)(b-1) \exp(-\sigma_s l)} \right), \quad (21)$$

where  $b = k_g a_b / k_s a_s$ ,  $g = k_g a_g / k_s a_s$ ,  $r = (1-j)\beta / 2a_s$ , and  $\sigma_s = (1+j)a_s$  as previously defined. At ordinary tem-

using the approximation  $\exp(-2\pi) \ll 1$ .

Because of the periodic heating of the boundary layer, this layer of gas expands and contracts periodically and thus can be thought of as acting as an acoustic piston on the rest of the gas column, producing an acoustic pressure signal that travels through the entire gas column. A similar argument has been used successfully to account for the acoustic signal produced when a conductor in the form of a thin flat sheet is periodically heated by an ac electrical current.<sup>15</sup>

The displacement of this gas piston due to the periodic heating can be simply estimated by using the ideal gas law,

$$\delta x(t) = 2\pi\mu_g \frac{\bar{\phi}(t)}{T_0} = \frac{\theta\mu_g}{\sqrt{2} T_0} \exp[j(\omega t - \frac{1}{4}\pi)], \quad (16)$$

where we have set the average dc temperature of this gas boundary layer equal to the dc temperature at the solid surface,  $T_0 = \Phi + \theta_0$ . Equation (16) is a reasonable approximation to the actual displacement of the layer since  $2\pi\mu_g$  is only  $\sim 0.1$  cm for  $\omega/2\pi = 100$  Hz and even smaller for higher frequencies.

If we assume that the rest of the gas responds to the action of this piston adiabatically, then the acoustic pressure in the cell due to the displacement of this gas piston is derived from the adiabatic gas law

$$PV^\gamma = \text{const},$$

where  $P$  is the pressure,  $V$  the gas volume in the cell, and  $\gamma$  the ratio of the specific heats. Thus the incremental pressure is

$$\delta P(t) = \frac{\gamma P_0}{V_0} \delta V = \frac{\gamma P_0}{l_g} \delta x(t),$$

where  $P_0$  and  $V_0$  are the ambient pressure and volume, respectively and  $-\delta V$  is the incremental volume. Then from Eq. (16)

$$\delta P(t) = Q \exp[j(\omega t - \frac{1}{4}\pi)], \quad (17)$$

where

$$Q = \frac{\gamma P_0 \theta}{\sqrt{2} l_g a_g T_0}. \quad (18)$$

Thus the actual physical pressure variation,  $\Delta P(t)$ , is given by the real part of  $\delta P(t)$  as

$$\Delta P(t) = Q_1 \cos(\omega t - \frac{1}{4}\pi) - Q_2 \sin(\omega t - \frac{1}{4}\pi), \quad (19)$$

or

$$\Delta P(t) = q \cos(\omega t - \psi - \frac{1}{4}\pi), \quad (20)$$

where  $Q_1$  and  $Q_2$  are the real and imaginary parts of  $Q$  and  $-\psi$  are the magnitude and phase of  $Q$ , i. e.,

$$Q = Q_1 + jQ_2 = q \exp(-i\psi).$$

Thus  $Q$  specifies the complex envelope of the sinusoidal pressure variation. Combining Eqs. (9) and (18) we get the explicit formula

peratures  $T_0 \approx \Phi$  so that the dc components of the temperature distribution need not be evaluated. Thus Eq.

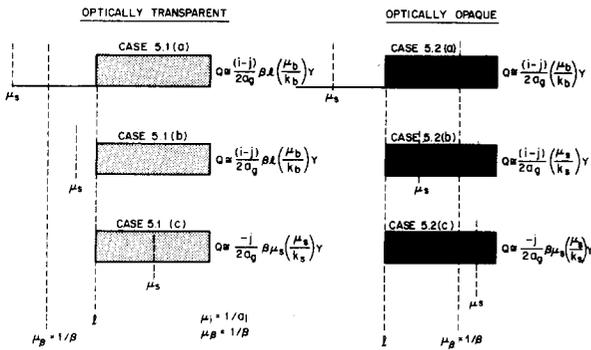


FIG. 3. Schematic representation of special cases discussed in the text.

(21) may be evaluated for the magnitude and phase of the acoustic pressure wave produced in the cell by the photoacoustic effect.

### V. SPECIAL CASES

The full expression for  $\delta P(t)$  is somewhat difficult to interpret because of the complicated expression for  $Q$  as given by Eq. (21). However, physical insight may be gained by examining special cases where the expression for  $Q$  becomes relatively simple. We group these cases according to the optical opaqueness of the solids as determined by the relation of the optical absorption length,

$$\mu_\beta = 1/\beta$$

to the thickness  $l$  of the solid. For each category of optical opaqueness, we then consider three cases according to the relative magnitude of the thermal diffusion length  $\mu_s$ , as compared to the physical length  $l$  and the optical absorption length  $\mu_\beta$ . For all of the cases evaluated below, we make use of the reasonable assumption that  $g < b$  and that  $b \sim 1$ , i. e., that  $k_g a_g < k_b a_b$  and  $k_b a_b \sim k_s a_s$ .

The six cases are illustrated in Fig. 3. It is convenient to define

$$Y = \frac{\gamma P_0 I_0}{2\sqrt{2} l_g T_0}, \quad (22)$$

which always appears in the expression for  $Q$  as a constant factor.

#### A. Case 5.1: Optically transparent solids ( $\mu_\beta > l$ )

In these cases, the light is absorbed throughout the length of the sample.

##### 1. Case 5.1 (a): Thermally thin solids ( $\mu_s \gg l$ ; $\mu_s > \mu_\beta$ )

Here we set  $\exp(-\beta l) \cong 1 - \beta l$ ,  $\exp(\pm \sigma_s l) \cong 1$ , and  $|r| > 1$  in Eq. (21). We then obtain

$$Q = \frac{lY}{2a_g a_b k_b} (\beta - 2a_s b - j\beta) \cong \frac{(1-j)\beta l}{2a_g} \frac{\mu_b}{k_b} Y. \quad (23)$$

The acoustic signal is thus proportional to  $\beta l$  and, since  $\mu_b/a_g$  is proportional to  $1/\omega$ , the acoustic signal has a  $\omega^{-1}$  dependence. For this thermally thin case of  $\mu_s \gg l$ , the thermal properties of the backing material come into play in the expression for  $Q$ .

##### 2. Case 5.1 (b): Thermally thin solids ( $\mu_s > l$ ; $\mu_s < \mu_\beta$ )

Here we set  $\exp(-\beta l) \cong 1 - \beta l$ ,  $\exp(\pm \sigma_s l) \cong (1 \pm \sigma_s l)$ , and  $|r| < 1$  in Eq. (21). We then obtain

$$Q = \frac{\beta l Y}{4k_s a_g a_s^3 b} [(\beta^2 + 2a_s^2) + j(\beta^2 - 2a_s^2)] \cong \frac{(1-j)\beta l}{2a_g} \left(\frac{\mu_b}{k_b}\right) Y. \quad (24)$$

The acoustic signal is again proportional to  $\beta l$ , varies as  $\omega^{-1}$ , and depends on the thermal properties of the backing material. Equation (24) is identical to Eq. (23).

##### 3. Case 5.1 (c): Thermally thick solids ( $\mu_s < l$ ; $\mu_s \ll \mu_\beta$ )

In Eq. (21) we set  $\exp(-\beta l) \cong 1 - \beta l$ ,  $\exp(-\sigma_s l) \cong 0$ , and  $|r| \ll 1$ . The acoustic signal then becomes

$$Q \cong -j \frac{\beta \mu_s}{2a_g} \left(\frac{\mu_s}{k_s}\right) Y. \quad (25)$$

Here the signal is now proportional to  $\beta \mu_s$  rather than  $\beta l$ . That is, only the light absorbed within the first thermal diffusion length  $\mu_s$  contributes to the signal, in spite of the fact that light is being absorbed throughout the length  $l$  of the solid. Also, since  $\mu_s < l$ , the thermal properties of the backing material present in Eq. (24) are replaced by those of the solid. The frequency dependence of  $Q$  in Eq. (25) varies as  $\omega^{-3/2}$ .

#### B. Case 5.2: Optically opaque solids ( $\mu_\beta \ll l$ )

In these cases, most of the light is being absorbed within a distance small compared to  $l$ .

##### 1. Case 5.2 (a): Thermally thin solids ( $\mu_s \gg l$ ; $\mu_s \gg \mu_\beta$ )

In Eq. (21) we set  $\exp(-\beta l) \cong 0$ ,  $\exp(\pm \sigma_s l) \cong 1$ , and  $|r| \gg 1$ . We then obtain

$$Q \cong \frac{(1-j)}{2a_g} \left(\frac{\mu_b}{k_b}\right) Y \quad (26)$$

In this case, we have photoacoustic "opaqueness" as well as optical opaqueness, in the sense that our acoustic signal is independent of  $\beta$ . This would be the case of a very black absorber such as carbon black. The signal is quite strong, [it is  $1/\beta l$  times as strong as that in case 5.1(a)], and depends on the thermal properties of the backing material, and varies as  $\omega^{-1}$ .

##### 2. Case 5.2 (b): Thermally thick solids ( $\mu_s < l$ ; $\mu_s > \mu_\beta$ )

In Eq. (21) we set  $\exp(-\beta l) \cong 0$ ,  $\exp(-\sigma_s l) \cong 0$ , and  $|r| > 1$ . We obtain

$$Q \cong \frac{Y}{2a_g a_s k_s \beta} (\beta - 2a_s - j\beta) \cong \frac{(1-j)}{2a_g} \left(\frac{\mu_s}{k_s}\right) Y. \quad (27)$$

Equation (27) is analogous to Eq. (26), but the thermal parameters of the backing are now replaced by those of the solid. Again the acoustic signal is independent of  $\beta$  and varies as  $\omega^{-1}$ .

##### 3. Case 5.2 (c): Thermally thick solids ( $\mu_s \ll l$ ; $\mu_s < \mu_\beta$ )

We set  $\exp(-\beta l) \cong 0$ ,  $\exp(-\sigma_s l) \cong 0$ , and  $|r| < 1$  in Eq. (21). We obtain

$$Q = \frac{-j\beta Y}{4a_g a_s^3 k_s} (2a_s - \beta + j\beta) = \frac{-j\beta \mu_s}{2a_g} \left(\frac{\mu_s}{k_s}\right) Y. \quad (28)$$

This is a very interesting and important case. Optically we are dealing with a very opaque solid ( $\beta l \gg 1$ ). However, as long as  $\beta\mu_s < 1$ , i. e.,  $\mu_s < \mu_\beta$ , this solid is not photoacoustically opaque, since, as in case 5.1(c), only the light absorbed within the first thermal diffusion length,  $\mu_s$ , will contribute to the acoustic signal. Thus even though this solid is optically opaque, the photoacoustic signal will be proportional to  $\beta\mu_s$ . As in case 5.1(c), the signal is also dependent in the thermal properties of the solid and varies as  $\omega^{-3/2}$ .

## VI. CONCLUSIONS

A theoretical analysis of the photoacoustic effect with solids has been performed. In this analysis we have assumed that the primary source of the acoustic signal arises from the periodic heat flow from the solid to the surrounding gas. This periodic heat flow causes an oscillatory motion of a narrow layer of gas at the solid-gas boundary, and it is this motion of the gas layer that produces the acoustic signal detected in the photoacoustic cell. We have derived the exact solutions for the acoustic pressure produced in the cell due to the process and have evaluated explicit formulas for certain cases of physical significance.<sup>16</sup> The formulas developed for the special cases have been found to give numerical results for magnitude and phase of the acoustic signal that are in good agreement with the experimental data. This agreement supports our explanation for the mechanism underlying the photoacoustic effect with solids. A full comparison of theory and experiment will be published in a later paper.

Our formulas show that the photoacoustic signal is ultimately governed by the magnitude of the thermal diffusion length of the solid. Thus even when a solid is optically opaque, it is not necessarily opaque photoacoustically and, in fact, as long as  $\beta\mu_s < 1$ , the photoacoustic signal will be proportional to  $\beta$ , even though

the optical thickness  $\beta l$  of the sample may be much greater than unity. Since the thermal diffusion length  $\mu_s$  can be changed by changing the chopping frequency  $\omega$ , it is therefore possible, with the photoacoustic technique, to obtain optical absorption spectra on any, but the most highly opaque, solids. This capability of the PAS technique together with its insensitivity to scattered light makes its use as a spectroscopic tool for the investigation of solid and semisolid materials highly attractive. In particular, these features give the photoacoustic technique a unique potential for noninvasive *in vivo* studies of human tissues, a potential which may have important implications in biological and medical research and in medical diagnostics.

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<sup>10</sup>Lord Rayleigh, Nature 23, 274 (1881).

<sup>11</sup>W. H. Preece, Proc. R. Soc. London 31, 506 (1881).

<sup>12</sup>M. E. Mercadier, C.R. Acad. Sci. (Paris) 92, 409 (1881).

<sup>13</sup>A recent treatment of the photoacoustic effect with solid by Parker [Appl. Opt. 12, 2974 (1973)] also assumes that the signal is produced by heat conduction from solid sample to surrounding gas. His treatment, however, assumes an anomalously high absorption coefficient for a thin surface layer of the solid.

<sup>14</sup>A more exact treatment for the gas can be derived using equations of fluid dynamics. However, the approximate treatment given here gives results consistent with the more exact method, and has the advantage of presenting a simpler physical description of the process.

<sup>15</sup>H. D. Arnold and I. B. Crandall, Phys. Rev. 10, 22 (1917).

<sup>16</sup>It should be noted that we have not considered here the effects of reflection losses at the surface.