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Photoacoustic Effect with Solids: A Theoretical Treatment

Abstract. *Chopped light impinging on a solid sample in an enclosed cell produces an acoustic signal within the cell. A derivation for the acoustic pressure supports the experimental observation that optical absorption spectra may be obtained from the acoustic signal even when the sample is completely opaque to transmitted light.*

Recently, a new technique has been developed for spectroscopic investigation of solid and semisolid materials. The method, photoacoustic spectroscopy (PAS), yields spectra similar to optical absorption spectra for any type of solid or semisolid material, such as crystals, powders, and gels (*1*). Because light scattering presents no severe difficulties with PAS and absorption spectra may be obtained, in many cases, from materials that are completely opaque optically, the technique has already found applications not only in physics and chemistry but also in biology and medicine (*2*). Because of the growing interest in this technique (*3*), a quantitative understanding of the underlying physical effect is essential.

The PAS technique is based on the effect originally discovered by Bell in 1880 (*4*), whereby chopped light impinging on a solid in an enclosed cell produces an acoustic signal within the cell. The periodic acoustic signal produced by this process can be detected with a microphone, and the analog signal recorded as a function of photon wavelength, giving a photoacoustic spectrum of the solid which bears a close correspondence to a true optical spectrum. Motivated by Bell's discovery, Tyndall (*5*) and Röntgen (*6*) found that a sound is also produced when chopped light is directed into a cell containing only a gas. The effect for gases has since become the basis for a well-established technique of gas analysis and is well understood (*7*). A completely satisfactory explanation for the effect with solids has not been published, though Bell (*8*), Rayleigh (*9*), Preece (*10*), Mercadier (*11*), and more recently Parker (*12*) have suggested various possible explanations.

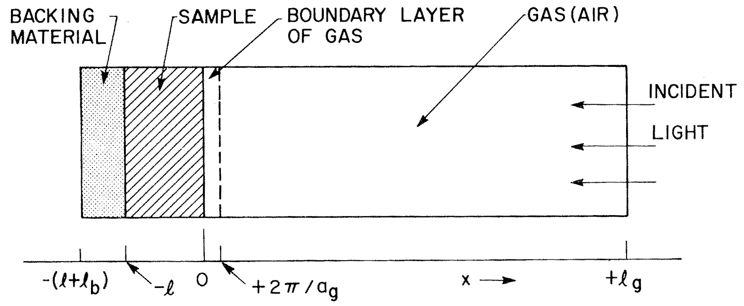
We believe the effect arises from the periodic heat flow from the solid to the surrounding gas as the solid is heated by the chopped light. A thin boundary layer of gas (~ 0.1 cm for air at a chopping rate of 100 hertz) adjacent to the surface of the solid responds thermally to the periodic heat flow from the solid. This layer may be regarded as a vibratory gas piston creating the acoustic signal detected in the cell.

Consider the simple cylindrical cell shown in Fig. 1. The sample is in the form of a disk with diameter D and thickness l. The optically transparent gas column (air) has length l_g, which is smaller than the wavelength of the acoustic signal. The backing material of thickness l_b is generally a poor thermal conductor and is assumed not to be light absorbing. Sinusoidally chopped monochromatic light of wavelength λ and flux I_0 (watt/cm^2) is incident on the sample. The heat density produced at a point x due to light absorbed at this point in the solid is given by $\frac{1}{2}\beta I_0 e^{\beta x}$ $(1 + \cos\omega t)$, where β (cm^{-1}) is the optical absorption coefficient at wavelength λ, ω is the chopping frequency (rad/sec), t is time, and x (cm) takes on negative values in the solid (see Fig. 1).

The thermal diffusion equation in the solid, taking into account the internal heat distribution, is then given by

$$\frac{\partial^2\phi}{\partial x^2} = \frac{1}{\alpha_s}\frac{\partial\phi}{\partial t} - Ae^{\beta x}(1 + e^{j\omega t})$$

where ϕ is temperature, $j = (-1)^{1/2}$, $A = \beta I_0/2k_s$, and α_s and k_s are, respectively, the thermal diffusivity and thermal conductivity of the solid. We assume here full efficiency in the conversion of the absorbed light into localized heat by nonradioactive de-excitation processes within the solid. For the backing and gas (*13*) we use the heat diffusion equations $\partial^2\phi/\partial x^2 = (1/\alpha_i)\phi$, where α_i takes on the appropriate value of thermal diffusivity α_b and α_g for the backing and gas, respectively.



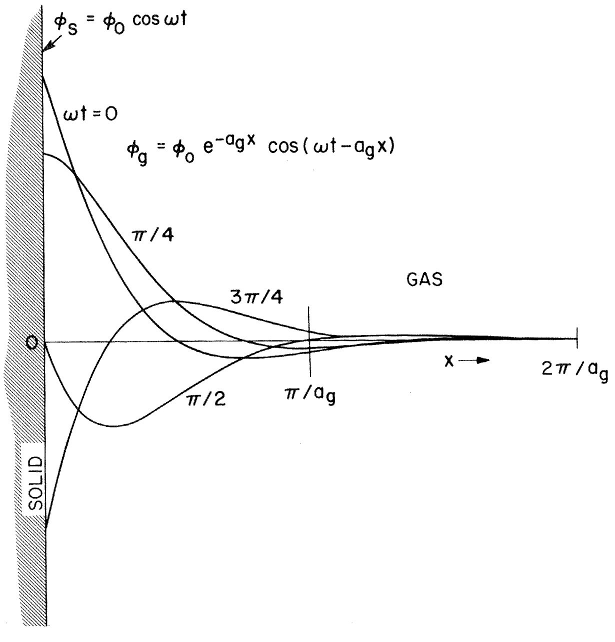


Fig. 1 (left). Cross-sectional view of a simple cylindrical photoacoustic cell, showing the positions of the solid sample, backing material, and gas column. Fig. 2 (right). Spatial distribution of the time-dependent temperature within the gas layer adjacent to the solid surface.

The complete solution for the temperature has the form $A(x) + B(x)e^{j\omega t}$ in each medium, neglecting transients. Applying the boundary conditions of temperature and heat flux continuity at the sample surfaces ($x = 0$ and $x = -l$) and an ambient temperature T_0 at the cell walls ($x = -l - l_b$ and $x = l_g$), we can obtain the full temperature distribution throughout the cell. In particular, the a-c component of the gas temperature distribution is given by

$$\phi^{g}_{a=c}(x, t) = \Theta e^{-\sigma_g x + j\omega t}$$

where Θ represents the complex amplitude of the time-dependent temperature of the solid sample at the solid-gas boundary ($x = 0$). The explicit expression for Θ is

$$\Theta = \frac{\beta I_0}{2k_s(\beta^2 - \sigma_s^2)} \left[\frac{(r-1)(b+1)e^{\sigma_s l} - (r+1)(b-1)e^{-\sigma_s l} + 2(b-r)e^{-\beta l}}{(g+1)(b+1)e^{\sigma_s l} - (g-1)(b-1)e^{-\sigma_s l}}\right] \quad (1)$$

where $a_i = (\omega/2\alpha_i)^{1/2}$ is the thermal diffusion coefficient for medium i, $b = k_b a_b/k_s a_s$, $g = k_g a_g/k_s a_s$, $r = (1 - j)\beta/2\alpha_s$ and $\sigma_i = (1 + j)a_i$, with the subscript i taking values b, s, and g for the backing, solid, and gas, respectively. The actual time-dependent temperature distribution in the gas is given by the real part of ϕ^{g}_{a-c} and, as shown in Fig. 2, it attenuates rapidly to zero with increasing distance from the solid surface. Since it is effectively zero at a distance of only $2\pi/a_g$, where $1/a_g$ is the thermal diffusion length, we can effectively consider that only this thickness responds thermally to the heating of the solid.

Because of the periodic heating within it, this layer expands and contracts periodically and thus can be thought of as an acoustic piston acting on the rest of the gas column, producing an acoustic pressure signal that travels through the entire gas column (*13*). The spatially averaged temperature of the gas within this boundary layer as a function of time is

$$\bar{\phi}(t) = \frac{1}{2(2\pi)^{1/2}} \Theta e^{j(\omega t - \pi/4)}$$

Using the ideal gas law, we can approximate the displacement of this gas piston by

$$\delta x(t) = 2\pi\bar{\phi}(t)/a_g T_0$$

where we have set the average d-c temperature of the boundary layer equal to the ambient temperature T_0.

Assuming that the rest of the gas column responds adiabatically to the action of this piston, the acoustic pressure in the cell due to the displacement $\delta x(t)$ is derived from the adiabatic gas law. 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 γ is the ratio of specific heats, P_0 and V_0 are the ambient pressure and volume, respectively, and $-\delta V$ is the incremental volume. Thus we get

$$\delta p(t) = Q e^{j(\omega t - \pi/4)}$$

for the acoustic pressure signal with the complex amplitude

$$Q = \frac{\gamma P_0 \Theta}{2^{1/2} l_g a_g T_0} \quad (2)$$

where Θ is given by Eq. 1. We therefore have a general expression for the acoustic signal in the photoacoustic cell as a function of the optical, thermal, and geometrical parameters of the system.

By applying the result to a variety of special cases we find that, for solids which are reasonably transparent to light ($\beta l < 1$), the pressure $\delta p(t)$ is proportional to βl unless the thermal diffusion length of the solid, $\mu_s = 1/a_s$, is less than l. In that case the pressure is proportional to $\beta\mu_s$.

For optically opaque solids ($\beta l \gg 1$), the pressure $\delta p(t)$ is independent of β when the thermal diffusion length μ_s is greater than the light absorption length $1/\beta$. In this case the sample, as well as being optically opaque, is also "photoacoustically opaque"—that is, the acoustic pressure is independent of the optical absorption coefficient β. However, when μ_s is less than $1/\beta$—that is, when $\beta\mu_s \ll 1$—the pressure amplitude is proportional to $\beta\mu_s$, irrespective of the magnitude of the optical absorptivity βl. Thus, even though the sample is optically opaque ($\beta l \gg 1$), it is not photoacoustically opaque—that is, the acoustic pressure is now dependent on the optical absorption coefficient β.

These results show that the photoacoustic signal is ultimately governed by the magnitude of the thermal diffusion length of the solid. Since the thermal diffusion length, μ_s, can be changed by changing the chopping frequency, ω, a solid that is completely opaque optically need not be photoacoustically opaque. It is therefore possible with the photoacoustic technique to obtain optical absorption spectra of any but the most highly opaque solids. This capability of PAS, together with its insensitivity to scattered light, makes its use as a spectroscopic tool for the investigation of solid and semisolid materials highly attractive. 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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7 July 1975

Laser-Excited Raman Spectroscopy for Nondestructive Partial Analysis of Individual Phases in Fluid Inclusions in Minerals

Abstract. *Laser-excited Raman spectroscopy has been successfully applied to the identification and partial analysis of solid, liquid, and gaseous phases in fluid inclusions. The procedure is no panacea for problems of analysis of fluid inclusions, but some unique features make it very useful. In particular, the measurement is performed in situ; it is nondestructive; and it can produce qualitative and quantitative data, some of which cannot be obtained otherwise, for samples as small as 10⁻⁹ gram.*

The analysis of fluid inclusions in minerals provides important data related to many mineralogical, geological, and geochemical processes. Inclusions represent samples of the fluids from which the host minerals have crystallized (*1*) or with which they have reacted (*2*). They may be trapped either during the growth of the host mineral or at one or more later times. Most samples thus contain more than one generation of inclusions, sometimes of greatly different ages and fluid compositions. During cooling, after the fluid has been trapped, two or more phases gener-