Chapter 2

Photoacoustics : General Theory

Abstract

During the past decade, there has been substantial development in instrumentation and experimental methodologies related to photoacoustic technique mainly due to the availability of high-energy sources, sensitive detectors and equipment for data collection and processing. With its various spectroscopic and non-spectroscopic attributes, photoacoustics has already found many important applications in research and characterization of materials. The photoacoustic technique is based on strong theoretical background. Since the formulation of one-dimensional heat flow model by Rosencwaig and Gersho to explain the photoacoustic signal generation, a number of modifications and extended models have been reported. Eventhough several modifications are proposed, the basic result of Rosencwaig and Gersho (R-G) is valid for most of the experimental conditions. The R-G theory for reflection configuration and its extension to transmission configuration are presented in this chapter.
2. Photoacoustics

2.1. Introduction

One of the important photothermal phenomena, the photoacoustic effect was first observed in 1880 by Alexander Graham Bell (1). The term photoacoustic effect (PA) usually refers to the generation of acoustic waves by a sample as a result of interaction with modulated electromagnetic radiation. Even though the PA effect was discovered more than a century ago, Veingerov experimentally observed it in gaseous samples (2) only after the advent of microphones in 1938. Emergence of lasers in 60's gave a boost to the photoacoustic studies in gaseous samples. A general theoretical formulation for the photoacoustic effect in solids was given by Rosencwaig and Gersho in mid seventies (4) and is known as Rosencwaig-Gersho (RG) theory. Later on many scientists made modifications to the RG theory. Bennett and Forman (5) in 1976 and Aamodt et.al in 1977 (6) have modified the basic theoretical model by treating the acoustic wave transport in the gas using Navier-Stokes equations. McDonald and Wetsel (7) made modifications on the RG theory by taking into consideration the mechanical vibrations of the sample. Quimby (8) made additional changes to the theory by making use of the three-dimensional heat flow model. In 1982, Guli (9) formulated a theory based on thermoelastic considerations in the sample. Even though several modifications were made and new theories were proposed, basic results of RG theory remains the same for most of the experimental conditions and the predictions of R-G theory have been experimentally verified by others (10-18).
2.2. Photoacoustic effect in condensed media

The photoacoustic technique is essentially a closed cavity detection of energy liberated by atoms or molecules through non-radiative de-excitation mechanism, subsequent to light absorption by a sample. When a solid sample placed inside an air-tight cavity is irradiated with a modulated optical radiation, the energy liberated through non-radiative channels will result in the generation of thermal waves within the sample. The thermal waves diffuse through the sample to the gas in the cavity and will produce periodic pressure fluctuations in the cavity. This pressure variation can be detected using a microphone kept inside the cavity. If the sample to be analysed is in gaseous form, then the sample itself can act as the source of signal generation and the acoustic coupler to the microphone. In order to investigate liquid samples, a piezoelectric transducer is used. The piezoelectric transducer kept in contact with the liquid sample will detect the acoustic pulse propagating through the medium.

2.3. Rosencwaig –Gersho Theory

Rosencwaig-Gersho (RG) theory is sufficient to describe the photoacoustic signal generation in condensed media. It is a one-dimensional analysis of the production and flow of heat from a sample on irradiation. The theory which is being presented is for the reflection (front side illumination) configuration. According to this theory, for a gas-microphone detection scheme, the signal depends on the generation of acoustic pressure disturbance at the sample-gas interface, which in turn depends on the periodic temperature change at the gas-sample surface.
RG theory is formulated by considering the generation of photoacoustic signal in a simple configuration as in figure 1. The sample is considered to be in the form of a disc having diameter D and thickness \( l \) and it is mounted so that its back surface is against a poor thermal conductor of thickness \( l' \). The length \( l' \) of the gas column in the cell is then given by \( l' = L - l - l'' \). It is also assumed that the gas and the backing material are not light absorbing.

\[ l' = L - l - l'' \]

Figure 1. Schematic representation of the photoacoustic cell configuration

The parameters used in the theory are:

\[ \kappa : \text{the thermal conductivity (cal/cm-sec-°C)} \]

\[ \rho : \text{the density (g/cm}^3\text{)} \]

\[ C : \text{the specific heat (cal/g-°C)} \]
2. Photoacoustics:

\[ \alpha = \kappa / \rho C : \text{the thermal diffusivity (cm}^2/\text{sec}) \]

\[ a = (\omega/2 \alpha)^{1/2} : \text{the thermal diffusion coefficient (cm}^{-1}) \]

\[ \mu = \frac{1}{a} , \text{the thermal diffusion length (cm)} \]

\[ \omega = 2\pi f \] where 'f' denotes the chopping frequency of the incident light beam.

Sample parameters are denoted by unprimed symbols, gas(air) parameters by singly primed symbols and backing material parameters by doubly primed symbols.

Assume a sinusoidally chopped monochromatic light source with wavelength \( \lambda \) incident on the solid with intensity

\[ I = \left( \frac{1}{2} \right) I_0 (1 + \cos \omega t) \] (1)

where \( I_0 \) is the incident monochromatic light flux (W/cm\(^2\)) and \( \beta \) denotes the optical absorption coefficient of the solid sample (in reciprocal centimeters) for the wavelength \( \lambda \). The heat density produced at any point \( x \) due to light absorbed at that point in the solid is then given by

\[ \frac{1}{2} \beta I_0 e^{\beta x} (1 + \cos \omega t) \] (2)

where \( x \) takes on negative values since the solid extends from \( x = 0 \) to \( x = -l \), with the light incident at \( x = 0 \). The air column extends from \( x = 0 \) to \( x = l' \) and the backing material from \( x = -l \) to \( x = -(l + l') \).

The thermal diffusion equation in the solid, taking into account the distributed heat source, can be written as
\[
\frac{\partial^2 \theta}{\partial x^2} = \frac{1}{\alpha} \frac{\partial \theta}{\partial t} - Ae^{\beta x} (1 + e^{i\omega t}) \text{ for } -l \leq x \leq 0
\]  

(3)

with

\[A = \frac{\beta I_0 \eta}{2k}\]  

(4)

where \(\theta\) 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. For most solids at room temperature, \(\eta = 1\). For the backing and the gas, the heat diffusion equations are respectively given by

\[
\frac{\partial^2 \theta}{\partial x^2} = \frac{1}{\alpha} \frac{\partial \theta}{\partial t} \quad -l'' - l < x < -l
\]  

(5)

\[
\frac{\partial^2 \theta}{\partial x^2} = \frac{1}{\alpha} \frac{\partial \theta}{\partial t} \quad 0 < x < l
\]  

(6)

The real part of the complex valued solution \(\theta(x,t)\) of equations (3) –(6) 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

\[T(x,t) = \text{Re} \theta(x,t) + \varphi_0\]  

(7)

where \(\text{Re}\) denotes the "real part of" and \(\varphi_0\) is the ambient (room) temperature.
To completely specify the solution of (3), (5), and (6), 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 \(x=+l\) and \(x=-l-l''\) is at ambient. It is assumed that the dimensions of the cell are small enough to ignore convective heat flow in the gas at steady state conditions.

2.3.1. Temperature distribution in the cell

The general solution for \(\theta(x,l)\) in the cell, neglecting transients, can be written as

\[
\theta(x,t) = \begin{cases} 
\frac{1}{l}(x + l + l'')W_0 + We^{-\sigma(x+l)}e^{i\omega t} & \text{.........8(a)} \\
(b_1 + b_2 x + b_3 e^{\beta x} + (Ue^{-\sigma x} + Ve^{\sigma x} - Ee^{\beta x})e^{i\omega t}) & \text{.........8(b)} \\
(1 - \frac{x}{l'})F + \theta_0 e^{-\sigma'x}e^{i\omega t} & \text{.........8(c)} 
\end{cases}
\]

For 8(a), \(-l-l'' \leq x \leq -l\)
For 8(b), \(-l \leq x \leq 0\)
For 8(c), \(0 \leq x \leq l'\)

where \(W, U, V, E,\) and \(\theta_0\) are complex valued constants, \(b_1, b_2, b_3, W_0,\) and \(F\) are real valued constants, and \(\sigma = (1+i)\) \(a\) with \(a = (\alpha/2\alpha)^{1/2}\) \(\theta_0\) 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 d.c. solution in the backing and air make use of the assumption that the temperature (relative to ambient) is zero at the ends of the cell. The quantities
Wo and F denote the d.c components of the temperature (relative to ambient) at the sample surfaces $x = -l$ and $x = 0$ respectively. The quantities $E$ and $b_3$, determined by the forcing function in (3), are given by

$$b_3 = \frac{-A}{\beta^2}$$

$$E = \frac{A}{\beta^2 - \omega^2} = \frac{\beta I_0}{2k(\beta^2 - \omega^2)}$$

Since for all frequencies of interest, the thermal diffusion length is small compared to the length of the material in both the gas and the backing, the growing exponential component of the solutions to the gas and backing material are omitted in the general solution (8). That is, $\mu^- < l^-$ and $\mu^+ < l^+$, and hence the sinusoidal components of these solutions are sufficiently damped so that they are effectively zero at the cell walls. Therefore, to satisfy the temperature constraint at the cell walls, the growing exponential components of the solutions would have coefficients that are essentially zero.

The temperature and flux continuity conditions at the sample surfaces are explicitly given by the following set of relations.

$$\theta'(0, t) = \theta(0, t)$$

$$\theta'(-l, t) = \theta(-l, t)$$

$$k' \frac{\partial \theta''}{\partial x}(0, t) = k \frac{\partial \theta}{\partial x}(0, t)$$
\[ k' \frac{\partial \theta}{\partial X} (-l, t) = k \frac{\partial \theta}{\partial X} (-l, t) \]

These constraints apply separately to the d.c. component and to the sinusoidal component of the solution. From (11), the d.c. components of the solution can be obtained as

\[ F_0 = b_1 + b_3 \]

\[ W_0 = b_1 - b_2 l + b_3 e^{-\beta l} \quad (12) \]

\[ \frac{-k'}{l'} f_0 = k b_2 + k \beta b_3 \]

\[ \frac{-k'}{l'} w_0 = k b_2 + k \beta b_3 e^{-\beta f} \]

These equations determine the coefficients \( b_1, b_2, b_3, W_0, \) and \( F_0 \) for the time-independent (d.c.) components of the solution. Applying (11) to the sinusoidal component of the solution yields:

\[ \theta_0 = U + V - E \]

\[ W = e^{-\sigma U} + e^{\sigma V} - e^{-\beta E} \quad (13) \]

\[ -k' \sigma \theta_0 = k \sigma U - k \sigma V - k \beta E \]

\[ k'' \sigma'' W = k \sigma e^{-\sigma U} - k \sigma e^{\sigma V} - k \beta e^{-\beta E} \]
These quantities together with the expression for E in (10) determine the coefficients U, V, W, and \( \theta_0 \). Hence the solutions to (12) and (13) allow us to evaluate the temperature distribution (8) in the cell in terms of the optical, thermal, and geometric parameters of the system. The explicit solution of \( \theta_0 \), the complex amplitude of the periodic temperature at the solid-gas boundary (\( x = 0 \)) is given by

\[
\theta_0 = \frac{\beta I_0}{2k(\sigma^2 - \tau^2)} \left[ \frac{(r-1)(b+1)e^{\sigma_1} - (r+1)(b-1)e^{-\sigma_1} + 2(b-r)e^{-\beta_1}}{(g+1)(b+1)e^{\sigma_1} - (g-1)(b-1)e^{-\sigma_1}} \right]
\]

where

\[
b = \frac{k''a''}{ka} \quad (15)
\]

\[
g = \frac{k'a'}{ka} \quad (16)
\]

\[
r = (1-i)\frac{\beta}{2}\alpha \quad (17)
\]

and \( \sigma = (1+i)\alpha \). Thus equation (14) 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 surface (\( x=0 \)) for the sample. The actual temperature at \( x = 0 \) is given by

\[
T(0,t) = \varphi_0 + F_0 + \theta_1 \cos\omega t - \theta_2 \sin\omega t \quad (18)
\]
where \( \varphi_0 \) is the ambient temperature at the cell walls and \( F_0 \) is the increase in temperature due to the steady-state component of the absorbed heat.

### 2.3.2. Production of the acoustic signal

The main source of the acoustic signal arises from the periodic heat flow from the solid to the surrounding gas. The periodic diffusion process produces a periodic temperature variation in the gas as given by the sinusoidal (a.c.) component of the solution

\[
\theta_{a.c}(x,t) = \theta_0 e^{-\sigma' x} e^{i\omega t}
\]  

(19)

Taking the real part of (19), we see that the actual physical temperature variation in the gas is

\[
T_{a.c}(x,t) = e^{-\alpha' x} \left[ \theta_1 \cos(\omega t - \alpha' x) - \theta_2 \sin(\omega t - \alpha' x) \right]
\]  

(20)

where \( \theta_1 \) and \( \theta_2 \) are the real and imaginary parts of \( \theta_0 \), given by (14). 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

\[
\frac{2\pi}{\alpha'} = 2\pi \mu', \quad \text{where} \quad \mu' \quad \text{is the thermal diffusion length in the gas},
\]

the periodic temperature variation in the gas is effectively fully damped out. Thus we can define a boundary layer with thickness \( 2\pi \mu' \) (~0.1 cm at \( \omega/2\pi = 100 \text{ Hz} \)) and maintain to a good approximation that only this thickness of air 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.

\[
\overline{\theta}(t) = \frac{1}{2\pi \mu' \theta_{a,c}} \int_0^{2\pi} \theta_{a,c}(x,t) dx
\]  

(21)

\[
\overline{\theta}(t) \approx \frac{1}{2\sqrt{2\pi}} \theta_0 e^{i(\omega t - \pi/4)}
\]  

(22)

using the approximation \(e^{-2x}<1\).

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 air column, producing an acoustic pressure signal that travels through the entire air column.

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

\[
\delta x(t) = 2\pi \mu' \frac{\overline{\theta}(t)}{\theta_0 T_0} = \frac{\theta_0 \mu'}{\sqrt{2} T_0} e^{i(\omega t - \pi/4)}
\]  

(23)

Here, the average d.c. temperature of the gas boundary layer, equal to the d.c. temperature at the solid surface is \(T_0 = \varphi_0 + F_0\).

If it is assumed 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

\[PV^\gamma = \text{constant} \]  

(24)

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

\[
\delta p(t) = \frac{\gamma P_0}{V_0} \delta V = \frac{\gamma P_0}{l'} \delta x(t)
\]  

(25)
where $P_0$ and $V_0$ are the ambient pressure and volume, respectively, and $\delta V$ is the incremental volume. Then from (23),

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

(26)

where,

$$Q = \frac{\gamma P_0 \theta_0}{\sqrt{2l'a'T_0}}$$

(27)

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

$$\Delta p(t) = Q_1 \cos(\omega t - \frac{\pi}{4}) - Q_2 \sin(\omega t - \frac{\pi}{4})$$

(28)

or

$$\Delta p(t) = q \cos(\omega t - \psi - \frac{\pi}{4})$$

(29)

where $Q_1$ and $Q_2$ are the real and imaginary parts of $Q$, and $q$ and $-\psi$ are the magnitude and phase of $Q$, that is,

$$Q = Q_1 + iQ_2 = q e^{-i\psi}$$

(30)

Thus $Q$ specifies the complex envelope of the sinusoidal pressure variation.

Combining (14) and (27) we get the explicit formula (31),

$$Q = \frac{\beta l_0 P_0}{2\sqrt{2l_0 k' a'}(\beta^2 - \sigma^2)} \times$$

$$\left[ \frac{(r - 1)(b + 1)e^{\sigma l} - (r + 1)(b - 1)e^{-\sigma l} + 2(b - r)e^{-\beta l}}{(g + 1)(b + 1)e^{\sigma l} - (g - 1)(b - 1)e^{-\sigma l}} \right]$$
where \( b = \kappa''a'' \) / \( \kappa a \), \( g = \kappa'a' / \kappa a \), \( r = (1-i)\beta/2a \), and \( \sigma = (1+i)a \). At ordinary temperatures \( T_0 \geq \varphi_0 \) so that the d.c component of the temperature distribution need not be evaluated.

Equation (31) can be used to evaluate the magnitude and phase of the acoustic pressure wave produced in the cell by the photoacoustic effect. It is difficult to interpret the full expression for \( \Delta p(t) \) because of the complicated expression of \( Q \) as given by equation (31). Hence, some special cases, according to experimental conditions, have to be considered to get a clear physical insight. Different cases can be categorised according to the optical opaqueness of the solid. For each category of optical opaqueness, there are three different cases according to the relative magnitude of the thermal diffusion length \( \mu \), as compared to the physical length \( l \) and the optical absorption length \( l_{\beta} = 1/\beta \) where \( \beta \) is the optical absorption coefficient. For all the cases, it is assumed that \( g < b \) and \( b \approx 1 \). i.e., \( \kappa'a' < \kappa''a'' \) and \( \kappa a \approx \kappa''a'' \).

Depending on the experimental conditions, sample can be classified mainly into two groups. Samples are optically transparent when the absorption length exceeds the sample thickness and are optically opaque when the optical absorption length is less than the physical thickness. The sample can be again divided into two categories by considering its thermal properties. Samples are considered to be thermally thin when the thermal diffusion length exceeds the sample thickness and thermally thick when it is less than the sample thickness.

2.3.3 Special cases.

2.3.3.1 Optically transparent solids (\( l_{\beta} > l \))

When the sample is optically transparent, the light is absorbed throughout the length of the sample, and some light is transmitted through the sample.
Case 1(a): Thermally Thin Solids \((\mu >> l; \mu > l_\beta)\)

Setting \(e^{-\beta l} \approx 1 - \beta l\), \(e^{\pm \sigma l} \equiv 1\), and \(|r| > 1\) in equation (31), we get

\[
Q = \frac{Yl(\beta - 2ab - i\beta)}{2a a' \kappa} \equiv \frac{(1 - i)\beta l}{2a'} \left( \frac{\mu^*}{\kappa^*} \right) Y
\]  

(32)

with

\[
Y = \frac{\kappa^2 I_0}{2 \sqrt{2} I_0 l'}
\]

(33)

where \(\mu = \sqrt{\frac{2a}{\omega}}\) and \(a = \frac{1}{\mu}\). The acoustic signal is thus proportional to \(\beta l\) and has an \(\omega^{-1}\) dependence. Moreover, the signal is now determined by the thermal properties of the backing material.

Case 1(b): Thermally Thin Solids \((\mu > l; \mu << l_\beta)\)

Setting \(e^{-\beta l} \approx 1 - \beta l\), \(e^{\pm \sigma l} \equiv 1\), and \(|r| < 1\) in equation (31) we get,

\[
Q = \frac{\beta l Y}{4ka'a^3b} \left[ (\beta^2 + 2a^2) + i(\beta^2 - 2a^2) \right] Y
\]

\[
\equiv \frac{(1 - i)\beta l}{2a'} \left( \frac{\mu^*}{\kappa^*} \right) Y
\]

(34)

In this case also, the acoustic signal is proportional to \(\beta l\), varies as \(\omega^{-1}\), and depends on the thermal properties of the backing material. Equation (34) is identical to (32).
Case 1(c) Thermally Thick Solids \( (\mu<l, \mu<<l_{\beta}) \)

Setting \( e^{-\beta l} \approx 1 - \beta l, e^{-\sigma l} \approx 0 \), and \( |r|<<1 \) in equation (31), the acoustic signal becomes,

\[
Q \approx -i \frac{\beta\mu}{2a'} \left( \frac{\mu}{k} \right) Y
\]

Here, the signal is proportional to \( \beta\mu \) rather than \( \beta l \). That is, only the light absorbed within the first thermal diffusion length contributes to the signal, in spite of the fact that light is being absorbed throughout the length \( l \) of the solid. Also, since \( \mu<l \), the thermal properties of the backing material present in (32) are replaced by those of the sample and hence backing material does not have any contribution to the signal. The photoacoustic signal has a frequency dependence of \( \omega^{-3/2} \).

Cases 1a, 1b, and 1c for the so-called optically transparent sample demonstrate a unique capability of photoacoustic spectroscopy, the capability of obtaining a depth profile of optical absorption within a sample. By starting at a high chopping frequency we can obtain optical absorption information from a layer of material near the surface of the solid. For materials with low thermal diffusivity this layer can be as small as 0.1 \( \mu \)m at chopping frequencies of 10,000 – 100,000 Hz. Then by decreasing the chopping frequency, we increase the thermal diffusion length and obtain optical absorption data further within the material, until at \( \sim 5 \) Hz we can obtain data down to 10-100 \( \mu \)m for materials with low thermal diffusivities. This capability for depth-profile analysis is unique and opens up exciting possibilities in studying layered and amorphous materials and in determining thin film thicknesses.
2.3.3.2 Optically opaque solids ($l_\beta \ll l$)

In these cases, most of the light is absorbed within a distance that is small compared to $l$, and essentially no light is transmitted.

**Case 2(a): Thermally thin Solids ($\mu >> l; \mu >> l_\beta$)**

Setting $e^{-\beta l} \equiv 0$, $e^{\pm \sigma l} \equiv 1$, and $|r| >> 1$ in equation (31) we get,

$$Q \equiv \frac{(1-i)(\mu'' \kappa'')}{2a'} Y$$

(36)

Now the acoustic signal is independent of $\beta$, which is characteristic of a black absorber such as carbon black. The signal is $1/\beta l$ times as strong as that in case 1(a) and depends on the thermal properties of the backing material. The signal varies as $\omega^{-1}$.

**Case 2(b): Thermally thick solids ($\mu < l; \mu > l_\beta$)**

Setting $e^{-\beta l} \simeq 0$, $e^{\pm \sigma l} = 0$, and $|r| > 1$ in equation (31), we get,

$$Q = -\frac{Y}{2a' \alpha k \beta} (\beta - 2a - i\beta) \frac{(1-i)(\mu'' \kappa'')}{2a'} Y$$

(37)

Equation (37) is analogous to (36), but the thermal parameters of the backing are now replaced by those of the sample. Again the acoustic signal is independent of $\beta$ and varies as $\omega^{-1}$.
Case 2(c): Thermally Thick Solids ($\mu<<1$; $\mu<l_\beta$)

Setting $e^{-\beta l} = e^{-\sigma l} = 0$, and $|r|<1$ in equation (31) we get,

$$Q = \frac{-i\beta Y}{4a' a'^3 k} (2a - \beta + i\beta) = \frac{-i\beta Y}{2a'} \left( \frac{\mu}{k} \right) Y$$  (38)

In this case, even though the solid is optically opaque ($\beta l<<1$), as long as $\beta \mu<l$ (i.e., $\mu<l_\beta$), it is not photo-acoustically opaque. The light absorbed within the first thermal diffusion length $\mu$ alone will contribute to the acoustic signal. Thus even though this solid is optically opaque, the photoacoustic signal is proportional to $\beta$. The signal is also dependent on the thermal properties of the sample and varies as $\omega^{-3/2}$.

The different cases discussed so far can be made use of in the photoacoustic study of any type of sample. One of the important predictions of the R-G theory is that the photoacoustic signal is always linearly proportional to the incident light intensity, irrespective of the sample properties and cell geometry.

2.4. Heat transmission configuration

The heat transmission (rear side illumination) geometry used in the open cell configuration is a modified form of conventional photoacoustic cell. In this configuration the sample is mounted on the cell leaving a small volume of air in between the sample and the microphone (18-33). The back surface of the sample is free and is open to the ambient. The sample is illuminated from the rear side and the microphone detects the pressure variation from the front.
side. The major advantage of this configuration is that samples having large area can be studied, whereas in conventional PA cells sample size should be small enough to be enclosed within the cell cavity.

The R-G theory can be used to derive an expression for the periodic pressure variation produced in the air column inside the PA cell.

![Figure 2](image)

Figure 2. General schematic representation of open photoacoustic cell (OPC)


![Figure 3](image)

Figure 3. Schematic representation of the OPC geometry
Consider the OPC geometry as shown in figure 3. Assume that the sample is optically opaque and the incident energy is fully absorbed at the sample surface itself. Then according to R-G theory, we can show that the periodic pressure variation in the air chamber is given by,

$$Q = \frac{\gamma P_0 I_0 (\alpha_g \alpha_s)^{1/2}}{2\pi T_0 l_0 k_s f} e^{j(\omega t - \pi/2)} \frac{e^{-l_s \sqrt{\pi f/\alpha_s}}}{\sinh(l_s \sigma_s)}$$

(39)

Now, if the sample is thermally thin (i.e., $l_s \alpha_s << 1$), the equation (39) reduces to

$$Q \approx \frac{\gamma P_0 I_0 \alpha_g^{1/2} \alpha_s}{(2\pi)^{3/2} T_0 l_0 l_s k_s f^{3/2}} e^{j(\omega t - 3\pi/4)}$$

(40)

Here, the amplitude of the PA signal varies as $f^{-3/2}$. At high chopping frequencies, sample is thermally thick (i.e., $l_s \alpha_s >> l$) and the pressure variation in the air chamber is given by,

$$Q = \frac{\gamma P_0 I_0 (\alpha_g \alpha_s)^{1/2}}{\pi T_0 l_0 k_s} e^{-l_s \sqrt{\pi f/\alpha_s}} \frac{e^{-l_s \sqrt{\pi f/\alpha_s}}}{f} e^{j(\omega t - \pi/2 - l_s \alpha_s)}$$

(41)

For a thermally thick sample, the amplitude of the OPC signal varies exponentially with the modulation frequency as $\left(\frac{1}{f}\right) \exp(-b \sqrt{f})$, where

$$b = l_s \sqrt{\frac{\pi}{\alpha_s}}$$

and the phase decreases linearly with $\sqrt{f}$ with a slope of $b$.

Hence, the thermal diffusivity $\alpha_s$ of the sample can be easily evaluated either from the signal amplitude plot or from the phase plot. However, a necessary
condition to employ the OPC configuration is that the sample should be optimally opaque at the incident wavelength.

Investigations discussed in the subsequent chapters are based on the theoretical models described in this chapter.

References

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3. A.G.Bell, Philos. Mag., 11, 510 (1881)
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