CHAPTER 1: INTRODUCTION

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1.1 Introduction to Photoacoustic Spectroscopy

The term "photoacoustics" (PA) or "optoacoustics" (OA) usually refers to the generation of acoustic waves by modulated optical radiation. Both terms are in common usage and have the same meaning. In its broader sense, photoacoustics can mean the generation of acoustic waves or other thermoelastic effects by any type of energetic radiation, including electromagnetic radiation from radio frequency to x-ray, electrons, protons, ions, and other particles [1].

The photoacoustic (PA) effect can be simply understood, when light is absorbed by a material, the material gets warm, which produces an increase in pressure and/or volume of the material and its surroundings. If the intensity of the light is modulated, the increase in temperature is periodic. The resulting periodic variation in pressure and/or volume can be detected as sound. This conversion of light to sound is the PA effect. The photoacoustic spectroscopy (PAS) utilizes the PA effect to detect how much light has been absorbed by a material, when a monochromatic intensity modulated light source is used. The spectra are obtained simply by scanning the wavelength of this light source while monitoring the output of the photoacoustic detector to observe variations in light absorption by the sample. PAS can also be used to investigate thermal and physical properties of the sample since the PA effect depends on these properties as well as light absorption. PAS is also called optoacoustic spectroscopy [2].

1.2 Principle and Theory of Photoacoustic Spectrometer

1.2.1 Principle

Photoacoustic spectroscopy is based on the absorption of electromagnetic radiation by analyte molecules. Non-radiative relaxation processes (such as collisions with other molecules) lead to local warming of the sample matrix. Pressure fluctuations are then generated by thermal expansion, which can be detected in the form of acoustic or ultrasonic waves. In other words, the transformation of an optical event to an acoustic one takes place in photoacoustic spectroscopy [3]. A fraction of the radiation falling upon the sample is absorbed and results in excitation, the type of which being dependent upon the energy of the incident radiation. Non-radiative de-excitation (relaxation) processes which normally occur give rise to the generation of thermal energy within the sample. If the
incident radiation is modulated then the generation of thermal energy within the sample will also be periodic and a thermal wave/pressure wave will be produced having the same frequency as this modulation. Energy is transferred by the thermal wave/pressure wave towards the sample boundary, where a periodic temperature change is generated. The periodic variation in the temperature at the surface of the sample results in the generation of an acoustic wave in the gas immediately adjacent and this wave propagates through the volume of the gas to the detector (microphone, piezoelectric transducers or optical method) where an electrical signal is produced. This detector or microphone signal, when plotted as a function of wavelength, will give a spectrum proportional to the absorption spectrum of the sample [4].

In photoacoustic spectroscopy, the sample to be studied is often placed in a closed cell or chamber. For the case of gases and liquids, the sample generally fills the entire chamber. In the case of solids the sample fills only a portion of the chamber, and the rest of the chamber is filled with a non-absorbing gas such as air. In addition, chamber also contains a microphone. The sample is illuminated with a monochromatic light that either passes through an electromechanical chopper or is intensity modulated in some other fashion. If any of the incident photons are absorbed by the sample, the internal energy levels within the sample are excited. Upon subsequent de-excitation of these energy levels, all or part of the absorbed photon energy is then transformed into heat energy through non-radiative de-excitation process. In a gas this heat energy appears as kinetic energy of the gas molecules, while in a solid or liquid, it appears as vibrational energy of atoms or ions. Since the incident radiation is intensity modulated, the internal heating of the sample is also modulated at the same frequency.

Since photoacoustics measures the internal heating of the sample, thus the periodic heating of the sample from the absorption of the optical radiation results in a heat flow from the sample to the gas, which itself does’t absorb the optical radiation. This in turn produces pressure and volume changes in the gas that drive the microphone, the output of which can be suitably amplified and directed. This technique is extremely sensitive and therefore offers the detection of pressure variation corresponding to $10^{-6}$ °C rise of temperature at the sample-gas interface [5].
1.2.2 Rosencwaig and Gersho Theory (R-G Theory)

The photoacoustic effect was discovered by A. G. Bell in 1880 [6]. He found that thin discs emit sound when exposed to a rapidly interrupted beam of sunlight [7]. By placing different absorbing substances in contact with the ear using a hearing tube, he was able to detect absorption in both the visible and the invisible regions of the solar spectrum. This spectrophone was used in his experiments on wireless transmission of sound. After additional experiments by Tyndall and Rontgen, and some initial analytical applications in the 1930 and 1940, interest in the photoacoustic effect was declined over the following decades. The first applications of the effect to trace gas monitoring were reported in the late 1960 [8]. The important steps leading to this rediscovery of the effect for analytical purposes were the invention of the laser as an intense light source, the development of highly sensitive sound detectors (such as condenser microphones and piezoelectric transducers), and the first comprehensive theoretical description of the photoacoustic effect in solids by Rosencwaig and Gersho: the so-called RG theory [9].

In conventional PAS of solids, a gas-microphone detector is used. The photoacoustic cell is a sealed cell of low volume (~1 cm³) containing the sample, a microphone, and an optical window through which chopped monochromatic light illuminates the sample. Heat produced in the sample warms the gas in the cell causing a pressure rise that is detected by the microphone as sound. A chopping (acoustic) frequency of 40-400Hz and light intensity of 100 mW is desirable to produce acoustic waves. This version of PAS was first applied in the UV-visible spectral region. Recently PAS has been extended to the infrared (IR) and to other types of spectroscopy. Variations on gas-microphone detection, which utilize other aspects of the PA effect, have also been developed. A general description of PAS techniques is provided by various authors [10-20]. The theory of the gas-microphone PA detector has developed in stages. The importance of heat flow from the solid to the gas was identified by Parker [21]. Rosencwaig & Gersho [22, 23] proposed a one dimensional model that attributes signal generation to the action of the heated layer of gas at the surface of the sample. This "thermal piston" model successfully describes the dependence of the PA signal on acoustic frequency, the optical and thermal properties of the sample, and the thermal properties of the gas. Various extensions of the thermal piston models have appeared [24, 25]. A similar model was proposed by McClelland & Kniseley [26]. Rosencwaig [10-12] also describes the thermal piston model and reviews some of the later developments in
PA theory. A number of authors have contributed to the further development of PA theory, but the R-G theory has been found to be very successful in interpreting the most of the experimental observations on PA studies [22, 23]. Temperature variations in the gas medium which directly depends on the light absorption by the sample could be exactly predicted by this theory. And hence a world-wide rebirth of interest in PA method could thus be triggered by the R-G theory and since then, a real boom in the growth of this field has been seen. Followed by this, Bennett and Forman [27] gave a theory based on linearised hydrodynamic equations for nearly transparent sample which included both acoustic and thermal diffusion terms. Bennett claims that the acoustic term is dominant in the intermediate frequency range which is the one currently encountered experimentally.

An extension to R-G theory has been done by McDonald and Wetsel [28] to include mechanical vibration of the sample. This is particularly important for liquid samples. which infact led Quim [29] to make appropriate changes in the RG theory by making use of the three dimensional heat flows at relatively low chopping frequencies. Then in the year 1982, a theory was formulated by Guli [30] based on thermo-elastic considerations in the sample which is in agreement with RG theory. However, these refinements did not change the basic results of the RG theory under most of the experimental conditions.

**A. Rosencwaig-Gersho Theory**

The significant feature of RG theory is its simplicity and straightforwardness in its approach to provide a basic understanding of the various physical processes in the generation of PA signal. This treatment is essentially based on the thermal diffusion through the sample which in turn produces the acoustic signal. Most of the experimental observations on PA studies can be interpreted on the basis of this theory.

RG theory is a one dimensional analysis of the production of a PA signal in a simple cylindrical cell as shown in Fig.(1.1). The cell has a diameter D and length L. It is assumed that the length L is small compared to the wavelength of the acoustic signal and the microphone detects the average pressure in the cell. The solid sample is considered to be in the form of a disc having a diameter d thickness l_s and length l. The sample is mounted so that its rear surface is supported against a poor thermal conductor (backing
material) of thickness $l_b$. The length of the gas column in the cell is given by $l_g$. It is also assumed that the gas and the backing material are not absorbers of light. The following parameters which are important in the theoretical formulation are defined as:

- $k =$ the thermal conductivity (cal. cm$^{-1}$ sec$^{-1}$ 0°C$^{-1}$)
- $\rho =$ the density (gm cm$^{-3}$)
- $c =$ the specific heat (cal. gm$^{-1}$ 0°C$^{-1}$)
- $\alpha = k/\rho c =$ the thermal diffusivity (cm$^2$ sec$^{-1}$)
- $a = [\frac{\alpha}{2\alpha}]^{1/2} =$ the diffusion co-efficient (cm$^{-1}$)
- $\mu = 1/a =$ the diffusion length (cm).

$\omega$ denotes the modulating frequency of the incident light beam in radians per second. In the following treatment the sample parameters are represented by unprimed symbols, the gas parameters by singly primed symbols and backing material parameters by doubly primed symbols.

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**Fig. 1.1** Production of photoacoustic signal
The intensity of a monochromatic light beam modulated at a frequency $\omega$ incident on the sample is given by

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

Where $I_0$ is the incident intensity of the light flux. If the absorption coefficient of the sample is $\beta$ for the wavelength $\lambda$, then the heat density $H$ produced at a point 'x' due to light absorbed at this point in the solid is given by

$$H = \frac{\beta}{2} I_0 \exp(\beta x) (1 + \cos\omega t) \quad --- \ (2)$$

where 'x' takes negative values since the solid extends from $x = 0$ to $x = -l_s$, with the light intensity at $x = 0$. Note also from Fig.1 that the gas column extends from $x = 0$ to $x = l_g$ and the backing from $x = -l_s$ to $x = -(l_s + l_b)$

**B. Temperature Distribution**

The heat generated in the sample represented by equation (2) warms up the sample, gas and backing by an amount $\theta(x,t)$ above the ambient temperature $T_0$. Therefore, the rise in temperature can be expressed as

$$\theta(x,t) = T(x,t) - T_0 \quad --- \ (3)$$

As soon as the heat is generated in the sample due to the absorption of light, it starts conducting to the gas and backing and the amount of heat transfer depends on the thermal conductivity of these media. Therefore, the thermal diffusion equation for the sample taking into account the distributed heat source due to illumination can be written as

$$\frac{\partial^2 \theta_s}{\partial x^2} - \frac{1}{\alpha_s} \frac{\partial \theta_s}{\partial t} + A e^{\beta x} (1 + e^{i\omega t}) = 0 \quad --- \ (4)$$

with $A = \frac{\beta I_0}{2K_s} \eta$ for $-l_s \leq x \leq 0$

where $K_s$ is the thermal conductivity of the sample, $\alpha_s$ thermal diffusivity of the sample given by
\[ \alpha_s = \frac{k_s}{\rho_s C_p} \]  

--- (5)

\( C_p \), being the specific heat capacity of the sample at constant pressure and \( \rho_s \) the density of the sample. \( \eta \) is the efficiency at which the absorbed light at wavelength \( \lambda \) is converted into heat through non-radiative deexcitation processes. The value of \( \eta \) is taken as unity, a reasonable assumption for most solids at room temperature. The last term in the equation (4) represents the heat generated in the sample. Since the heat generated in the sample is transferred to the air and the backing material, the temperature rise in these media will be entirely due to the heat transfer from the sample. The thermal diffusion equations for the gas and the backing material are respectively given by:

\[
\frac{\partial^2 \theta_g}{\partial x^2} - \frac{1}{a_g} \frac{\partial \theta_g}{\partial t} = 0
\]  

--- (6)

Where \( 0 \leq x \leq l_g \) and

\[
\frac{\partial^2 \theta_b}{\partial x^2} - \frac{1}{a_b} \frac{\partial \theta_b}{\partial t} = 0
\]  

--- (7)

Where \(- (l_s + l_g) \leq x \leq -l_s \)

The real part of the complex valued solution \( \theta (x, t) \) of equations (4), (6) and (7) is the solution of physical interest and represents the temperature in the cell relative to ambient, as a function of position and time.

The general solution for \( \theta_s(x,t) \) in the sample neglecting transients can be written as

\[
\theta_s(x,t) = b_1 + b_2 e^{\beta x} + \left[ U e^{\sigma_g x} + V e^{-\sigma_g x} - E e^{\beta x} \right] e^{i \omega t} \]

--- (8)

where \(-l_s \leq x \leq 0 \)

Similarly in the gas medium

\[
\theta_g(x,t) = (1 - \frac{x}{l_g}) F + \theta_0 e^{-\sigma_g x + i \omega t}
\]  

--- (9)

Where \( 0 \leq x \leq l_g \) and the temperature at the backing material is
\[ \theta_b(x,t) = \frac{1}{l_b} (x + l_s + l_b) W_0 + W e^{\sigma_b(x + l_s) + i\omega t} \quad --- \quad (10) \]

Where \(- (l_s + l_b) \leq x \leq -l_s\).

Here, \(W, U, V, E\) and \(e_0\) are complex valued constants, \(b_1, b_2, b_3, W_0\) and \(F\) are real valued constants, and \(\sigma = (1+i)a\), where 'a' is the thermal diffusion coefficient represented by

\[ a = \left[ \frac{\omega}{2\alpha} \right]^2 \]

\(\theta_0\) and \(W\) represent the complex amplitudes of the periodic temperature at the sample-gas boundary (\(x=0\)) and the sample-backing boundary (\(x = l_s\)) respectively. The term with amplitude \(U\) represents a temperature wave propagating to the left and \(V\) represents a temperature wave propagating in the opposite direction in the sample. These waves will be effectively attenuated when they start propagating through the gas medium. The distance up to which these waves can propagate through the gas medium without any appreciable change in its amplitude is approximately one wavelength of this wave which is represented by

\[ \lambda_g = 2\pi \mu_g \quad --- \quad (11) \]

Where \(\mu_g\) is the thermal diffusion length in the gas. The quantities \(E\) and \(b_3\), are given by

\[ b_3 = -\frac{l_0}{2\beta \kappa_s} \quad \text{and} \quad E = \frac{\beta l_0}{2\kappa_s(\beta^2 - \sigma_s^2)} \]

In order to solve the thermal diffusion equations, it is necessary to apply proper boundary conditions. Here the boundary conditions for the temperature and heat flux at the sample surface are given by

\[ \theta_s(0, t) = \theta_s(0, t) \quad --- \quad (12) \]

\[ \theta_b(-l_s, t) = \theta_s(-l_s, t) \quad --- \quad (13) \]

Similarly,
Using the above conditions in the equations (8), (9), (10), the constants can be determined and those solutions are essential for evaluating the temperature distribution in the cell in terms of optical, thermal and geometric parameters of the system. Therefore, the temperature at the sample gas interface (at \( x = 0 \)) is given by

\[
\theta_0 = \frac{\beta l_0}{2K_s(b^2-a_s^2)} \frac{[(r-1)(b+1)e^{\sigma s l_s}-(r+1)(b-1)e^{-\sigma s l_s})+2(b-r)e^{-\beta l_s}]}{[(g+1)(b+1)e^{\sigma s l_s}-(g-1)(b-1)e^{-\sigma s l_s})]
\]

--- (16)

Where \( b = \frac{k_b a_b}{K_s a_s} \); \( g = \frac{k_g a_g}{K_s a_s} \); \( \gamma = \frac{(1-i)\beta}{2a_s} \); \( \sigma_s = (1+i) a_s \)

From the above relations it is evident that \( a_s, a_g \) and \( a_b \) play an important role on the heat transfer process in the sample, gas and backing material respectively. The thermal diffusion coefficient

\[
a = \frac{1}{\mu} = \left[ \frac{\pi f \rho C_p}{K} \right]^{\frac{1}{2}}
\]

--- (17)

where \( \mu \) is the thermal diffusion length, ‘\( f \)’ represents the modulation frequency, \( \rho \) denotes the density, \( C_p \) is the specific heat and \( K \) is the thermal conductivity. Therefore the thermal diffusion length in a medium is inversely proportional to the square root of the modulation frequency which means that at higher chopping frequencies, the amount of heat transferred from the inner layer of the sample to the gas medium is much less. This causes a decrease in PA signal at higher chopping frequencies.

C. Production of Acoustic Signal

The periodic temperature variation at the sample surface as governed by equation (16) causes thermal waves to diffuse into the gas. This periodic diffusion process produces a periodic temperature variation in the gas as is given by the ac component of the solution of equation (9)
\[
\theta_{ac}(x,t) = \theta_0 e^{-\sigma_g x + i\omega t}
\]

--- (18)

The term \(e^{-\sigma_g x}\) denotes the damping of temperature wave when it propagates through the gas medium. The time dependent component of the temperature in the gas given by the equation (18) attenuates rapidly to zero with increasing distance from the surface of the solid. Since the thermal diffusion coefficient \(a_g\) represents the wave number of the temperature diffusion wave, the corresponding wavelength in the gas medium is

\[
\lambda_g = \frac{2\pi}{a_g} = 2\pi \mu_g
\]

Consequently at a distance of \(2\pi \mu_g\) which corresponds to one wavelength of acoustic wave in the gas medium, (where \(\mu_g\) is the thermal diffusion length in the gas), the periodic temperature variation in the gas is assumed to be fully damped out. Thus the spatially averaged temperature of the gas within this boundary layer as a function of time can be determined by

\[
\theta(t) = \frac{1}{2\pi \mu_g} \int_0^{2\pi \mu_g} \theta_{ac}(x,t)dx
\]

--- (19)

\[
\theta(t) = \frac{1}{2\pi \mu_g} \int_0^{2\pi \mu_g} \theta_0 e^{-\sigma_g x + i\omega t} dx
\]

--- (20)

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

--- (21)

using the relations \(\sigma_g = \frac{(1+i)}{\mu_g}\) and \((1+i) = \sqrt{2} e^{i\frac{\pi}{4}}\)

and the approximation made was \(e^{-2\pi} \ll 1\)

Because of the periodic heating, this boundary layer of gas expands and contracts periodically and thus can be thought of as an acoustic piston on the rest of the gas column, producing an acoustic signal that travels through the entire gas column. The displacement of this gas piston due to the periodic heating can be estimated by the ideal gas law as,
\[ \partial x(t) = 2\pi \mu_\theta \frac{\theta(t)}{\tau_\theta} \] 
--- (22)

Substituting the values from equation (21) for \( \theta(t) \)

\[ \partial x(t) = \frac{\theta_0 \mu_\theta}{\sqrt{2\tau_\theta}} e^{i(\omega t - \frac{\pi}{4})} \] 
--- (23)

Where \( T_0 \) is the temperature at the sample surface. This displacement of the acoustic piston therefore makes an adiabatic change in the gas pressure. Thus the corresponding acoustic pressure in the cell due to the displacement of this gas piston is derived from the adiabatic gas law

\[ P V^\gamma = \text{Constant.} \] 
--- (24)

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

\[ P(t) = \frac{\gamma P_0}{V_0} \delta V = \frac{\gamma P_0}{V_0} \delta x(t) \] 
--- (25)

where \( P_0 \) and \( V_0 \) are the ambient pressure and volume respectively. Therefore substituting values for \( \delta x(t) \) from equation (23)

\[ P(t) = \frac{\gamma P_0 \theta_0}{\sqrt{2l_g a_g T_0}} e^{i(\omega t - \frac{\pi}{4})} \] 
--- (26)

where

\[ \frac{\gamma P_0 \theta_0}{\sqrt{2l_g a_g T_0}} = Q \] 
--- (27)

\( Q \) specifies the complex envelope of the sinusoidal pressure variation in the gas medium which is detected by microphone placed in the cavity. Thus the actual physical pressure variation \( \Delta P(t) \) is given by the real part of the \( \delta P(t) \) as

\[ \Delta P(t) = Q_1 \cos(\omega t - \frac{\pi}{4}) - Q_2 \sin(\omega t - \frac{\pi}{4}) \] 
--- (28)

\[ \Delta P(t) = q \cos (\omega t - \psi - \frac{\pi}{4}) \] 
--- (29)

where \( Q_1 \) and \( Q_2 \) are the real and imaginary parts of \( Q \), and \( q \) and \( \psi \) are the amplitude and phase of \( Q \), that is,
\[ Q = Q_1 + iQ_2 = qe^{-i\psi} \]  

--- (30)

Explicit formula for \( Q \) is obtained by combining (16) and (26)

\[
Q = \frac{\beta I_0 \gamma P_0}{2\sqrt{2K_T \tau_0 \sigma g (\beta^2 - \sigma_s^2)}} \frac{[(\tau - 1)(b + 1) e^{\sigma_s l_s} - (\tau + 1)(b - 1) e^{-\sigma s l_s} + 2(1 - \tau)e^{-\beta l_s}]}{[(\tau + 1)(b + 1) e^{\sigma s l_s} - (\tau - 1)(b - 1) e^{-\sigma s l_s}]} \]  

--- (31)

The above equation gives the amplitude and phase of the acoustic pressure wave generated in the cell by photoacoustic effect. Because of the complexity of equation, it is somewhat difficult to interpret the results obtained. However, a physical insight may be gained by examining special cases where the expression for \( Q \) becomes relatively simple. Rosencwaig and Gersho considered its application to a variety of special cases. In all these special cases the prominent term is nothing but optical absorption coefficient \( l_\beta \), defined by \( l_\beta = 1/\beta \), where \( \beta \) is the optical absorption coefficient. The special cases mainly treat with the relative magnitude of \( l_\beta \) with respect to the sample thickness \( l_s \) and the variation of thermal diffusion length of the sample \( \mu_s \) with respect to the sample thickness \( l_s \). According to these conditions sample can be classified into mainly two groups. They are optically transparent samples in which the optical absorption length exceeds the sample thickness and optically opaque samples in which the optical absorption length must be smaller than the sample thickness. The sample can be again divided into two categories by considering its thermal properties. They are thermally thin samples in which the thermal diffusion length exceeds the sample thickness and thermally thick samples in which thermal diffusion length is smaller than the sample thickness.

A clear physical insight into the PA process can be easily obtained by choosing these special conditions. These conditions and their significances are discussed in the following section.

1.2.3 Special Cases

I. Optically Transparent Solids (\( l_\beta > l_s \))

In this case light is absorbed throughout the length of the sample and part of the light is transmitted through the sample. Hence also three special cases are to be considered depending on the thermal diffusion length and length of the solid sample.
A. Thermally Thin Solids

This is the case when $\mu_s > l_s$ and $\mu_s \gg l_\beta$ so that $e^{-\beta l_s} \cong (1 - \beta l_s)$; $e^{\pm \sigma l_s} \cong 1, \mid r \mid >$ in equation (31). Therefore Q can be expressed as

$$Q = \frac{Y}{2a_g a_b K_b} (\beta - 2a_s b - i \beta) \cong \frac{(1-i)\beta l_s}{2a_g}\left[\frac{\mu_b}{K_b}\right]^{\frac{1}{2}}$$  

$$\text{where } Y = \frac{\rho_{p_0}}{2\sqrt{2\pi}l_g}$$  

It is evident from the above expression that the acoustic signal is proportional to $\beta l_s$ and since $\frac{\mu_b}{a_g}$ is proportional to $\omega^{-1}$, Q has an inverse chopping frequency dependence. For this case where $\mu_s \gg l_s$ the thermal properties of the backing material play an important role on the PA signal.

B. Thermally Thin Solids

Here we set $\mu_s > l_s$ and $\mu_s < l_\beta$ so that $e^{-\beta l_s} \cong (1 - \beta l_s), e^{\pm \sigma l_s} \cong (1 \pm \sigma l_s)$

and $\mid r \mid <$ in equation (31) therefore,

$$Q \cong \frac{(1-i)\beta l_s}{2a_g}\left[\frac{\mu_b}{K_b}\right]^{\frac{1}{2}} Y$$  

The acoustic signal is again proportional to $\beta l_s$, which varies as $\omega^{-1}$ and also depends on the thermal properties of the backing material.

C. Thermally Thick Solids

Here, $\mu_s < l_s$ and $\mu_s \ll l_\beta$ therefore $e^{-\beta l_s} \cong (1 - \beta l_s), e^{-\sigma l_s} = 0$ and, $\mid r \mid \ll 1$

The acoustic signal then becomes

$$Q \cong \frac{-i\beta \mu_s}{2a_g}\left[\frac{\mu_s}{K_s}\right]^{\frac{1}{2}} Y$$  

Here, the signal is proportional to $\beta \mu_s$ rather than $\beta l_s$, i.e., only the light absorbed within the first thermal diffusion length contributes to the signal, inspite of the fact that light is being absorbed throughout the length $l_s$ of the solid. Also, since $\mu_s < l_s$, the thermal
properties of the backing material do not have any influence on the signal and it mainly depends on the thermal properties of the sample itself. Since the equation contains $\mu_s^2 \mu_g$, the frequency dependence of $Q$ in equation (35) varies as $\omega^{-2}$.

The above mentioned optically transparent sample demonstrate a unique capability of PA technique which enable one to obtain a depth profile of the optical absorption within a sample.

II. Optically Opaque Solids ($l_\beta \ll l_s$)

In this case most of the light is absorbed within a distance that is small compared to $l_s$ and consequently no light is transmitted into the sample, depending on the sample geometry and thermal diffusion length there exist three special cases which are described below.

A. Thermally Thin Solids

Here $\mu_s >> l_s$ and $\mu_s >> l_\beta$ and using the approximations $e^{-\beta l_s} \approx 0$; $e^{\pm \sigma l_s} \approx 1$, $|r| \gg$ in equation (31), the expression, for $Q$ is obtained as

$$Q \approx \left( \frac{1-i}{2\alpha_g} \frac{\mu_b}{K_b} \right) Y \quad --- \,(36)$$

In this case, the acoustic signal is independent of $\beta$. This would be the case for a very black absorber such as carbon black. Since the sample possesses large absorption coefficient the acoustic signal is quite strong. The signal depends on the thermal properties of the backing material because the heat generated in the sample can be transferred to the backing material owing to its large diffusion length. Here also the signal varies as $\omega^{-1}$

B. Thermally Thick Solids

In this case, $\mu_s < l_s$ and $\mu_s > l_\beta$ and setting $e^{-\beta l_s} \approx 0$; $e^{-\sigma l_s} = 0$ and $|r| > 1$. in equation (31),

$$Q \approx \left( \frac{1-i}{2\alpha_g} \frac{\mu_s}{K_s} \right) Y \quad --- \,(37)$$
Equation (37) is similar to (36) except that the thermal parameters of the backing material are now replaced by those of the sample. Also, the acoustic signal is independent of $\beta$ and varies as $\omega^{-1}$.

C. Thermally Thick Solids
Here the condition is $\mu_s << l_s$ and $\mu_s < l_\beta$ consequently $e^{-\beta l_s} \equiv 0$; $e^{-\sigma l_s} = 0$ and $|r| < 1$.

Therefore by incorporating these simplifications, the final expression (31) then becomes

$$Q \cong \frac{i\beta \mu_s}{2\alpha_g} \left[ \frac{\mu_s}{K_s} \right] Y$$

--- (38)

This is a very interesting and important case because even though the sample is optically opaque, it is not photoacoustically opaque as long as $\mu_s < l_\beta$, that is the acoustic signal is proportional to $\beta$. The signal also depends upon the thermal properties of the sample and varies as $\omega^{-3}$. The complete illustration of these special cases has been schematically represented in Fig.(1.2). One of the most obvious and important predictions of the theory is that the photoacoustic signal is always linearly proportional to the power of the incident photon beam, and that this dependence holds for any sample or cell geometry [5].

1.3 Applications of Photoacoustic Spectroscopy

Photoacoustic spectroscopy has become a widely used spectroscopic tool during the past decade. There are four general classes of applications of PA methods.

a. PA spectroscopy
b. PA monitoring of de-excitation processes
c. PA probing of thermoelastic and other physical properties of materials
d. PA generation of mechanical motions

a. PA spectroscopy

In this class of application, the PA signal amplitude is measured for a range of optical excitation wavelength, producing a PA spectrum; other factors (e.g., efficiency in thermal deexcitation and in acoustic wave generation) are usually kept or assumed fixed while the
PA spectrum is obtained. This is actually an "excitation spectrum" based on acoustic detection.

b. PA monitoring of de-excitation processes
Here, the thermal decay branch is monitored to provide information on a competing decay branch. After optical excitation, four decay branches are generally possible: luminescence, photochemistry, photoelectricity, and heat that may be generated directly or through energy-transfer processes. For example, if luminescence and heat are the only two competing branchings, PA monitoring of the heat branch can provide the quantum efficiency of luminescence under suitable circumstances.

c. PA probing of thermoelastic and other physical properties of materials
Various information can be obtained conveniently with the help of the optical generation of thermal waves or acoustic waves. Such information includes sound velocity, elasticity, temperature, flow velocity, specific heat, thermal diffusivity, thickness of a thin film, subsurface defects, and so on.

d. PA generation of mechanical motions
This is a small area of application now; PA effects can produce motions like liquid droplet ejection or structural vibrations. It has proved to be important in the investigation of the thermal and optical properties of a wide variety of samples, and in probing non-radiative de-excitations that follow a variety of excitations in matter. Since the PA signal is a function of the thermal propagation within the sample, it is possible to determine the thermal properties like thermal diffusivity, specific heat and thermal conductivity with great accuracy normally not attainable with other techniques. Therefore the study of thermal wave propagation through various layers of the sample provides the thermal properties of the sample in a non-destructive fashion. Using PA technique, the specific heat and thermal diffusivities of [NaNO$_2$], [TiNO$_3$]$^5^\circ$, [CsNO$_3$]$^5^\circ$, [NH$_4$NO$_3$]$^5^\circ$, [BaTiO$_3$]$^5^\circ$, and other polymer samples [31-32] have been determined precisely and these measurements provide the method of measuring absolute value of thermal diffusivity of samples with temperature. Since the thermal parameters of a material generally vary when the material undergoes a phase transition, monitoring the PA signal as a function of temperature should provide information on the occurrence of phase transitions. Thus first and second- order phase transition measurements have been carried out in materials like K$_2$SnCl$_6$, NaN$_2$, thiourea and 4,4’-dichlorobenzophenone[33-35] and subsequent
studies reveal that the application of PA technique to phase transition studies should constitute a useful complementary technique to the conventional calorimetric methodology.

I. Application to Solids
In the recent years substantial progress has been made in the fabrication of low loss optical material for use in the visible and infrared spectral regions. The absorption studies carried out in the infrared transmitting materials like ZnSe and uncoated sapphire could reveal the absorption co-efficients at 10.6 µm and the influence of thickness. The studies revealed that the ThF₄ layer acts as an antireflection coating on these materials at this wavelength region [36] this in turn brings out the developments of precision optics which can improve the CO₂ laser efficiency.

Similarly the methods for the accurate determination of photophysical parameters are of considerable importance. The quantum efficiency measurement of ruby crystal shows its utility as material for laser active medium [37]. The studies on the visible region PA spectra of silicon samples under open circuit and loaded conditions provide the detailed information regarding the wavelength dependence of solar cell performance [38]. The PAS method has been effectively utilized to measure optical absorption as low as 10⁻⁶ cm⁻¹ with a cell volume of 3cm³ using a laser of 1mj energy of 1µsec duration for excitation.

II. Application to Weak Absorption Gases
The main application of gas phase PAS is in the online gas monitoring of atmospheric pollutants such as sulphur oxides (SO₂), nitrogen oxides (NO₂), carbon oxides (CO and CO₂), hydrogen sulfide, ammonia, methane and aerosol particles (such as soot) which have potential impact on the atmospheric environment due to gaseous pollutant emissions from these anthropogenic sources such as air pollutant gases emitted from vehicles power plants and exhaust of industries etc [39-40]. Another important aspect of this technology is in situ measurement of absorption in the optical fibres which is highly useful for the development of low loss optical fibres needed for optical communications, similarly absorption in transparent solids and liquids [41-43] provides the development of various optics to be used in laser technology. Molecular alignment of linear molecules (O₂,
N$_2$CO$_2$ and CO) is determined photoacoustically in the gas phase [44]. The basic understanding of the molecular structures and photokinetics is provided by the overtone absorption measurements [45]. Furthermore this novel technique might allow the study of the details of absorption spectra of rare earth oxides. From these measurements it is found that the non-fluorescent levels of the rapidly ionized rare earth atoms are easily detected by this novel technique [46].

III. Application to Thin films
The use of PA techniques for measuring absorption in thin films, monolayers, or even multilayers has been reported [47-48]. The PA method has been successfully employed in the investigation of far-infrared PA spectra of four different four-and-five-ring aromatic hydrocarbons (tetracene, pentacene, perlene and pyrene) and have shown that the PA spectra contain many previously unobserved bands and complement the information already obtained from other types of vibrational spectra [49] consequently, this technique finds its application in obtaining the optical band-gap energy of the semi conductors GaAs, CdSe, Cds, ZnSe and Si doped with P at a concentration of 4x10$^{18}$ cm$^{-3}$ [50]. Since the study of thermal wave propagation through various layers of the sample provides the thermal properties of the sample in a non-destructive fashion. Hence the phase transitions of TiO$_2$ and poly (ethyleneterephthalate) PET thin films were detected [51-52] by using PA technique. Non-destructive testing of multilayer dielectric coating can be carried out using the photoacoustic technique [53]. Similarly, the depth profiling studies [54-55] in solids can be effectively utilized to obtain the physical properties at various layers in the sample by controlling the thermal wave propagation through the layers with great precision [56]

IV. Photoacoustic Microscopy (PAM)
PAM is a technique which provides information on the thickness of surface layers, depth of sub-layer, thermal diffusivity of a coating material, thermal barriers or irregularities below the surface and depth dependent optical absorption features by monitoring the signal amplitude and phase and by measuring the properties such as acoustic velocities, elasticity, density, thickness, specific heat, material discontinuities, crystallinity, phase transition etc [57].

The basic principle involved in PAM is the thermal wave analysis at each layer of the sample using PA technique. The PA signal amplitude and phase will vary rapidly due to the discontinuity in the heat flow through the layer of the sample. Thus the PA signal amplitude and phase directly reveal the detailed information regarding the nature and the location of the defect present in the material. If any irregularity of flaw is present in any of the layers of the sample, by controlling the thermal diffusion process through these layers of the sample very precisely, the nature and location of the defect can easily be identified using this method [58]. Therefore this method is a non-destructive tool for studying the defects and irregularities in a sample at the microscopic level.

Several research groups have actively investigated PAM as an exciting field that is very quickly expanding because of its potential application in thin film technology, chemical engineering, biology medical diagnostics etc. It provides a unique method for determining subsurface imaging of irregularities, flaws, doping concentrations etc., which cannot be obtained by other non-destructive methods. The remarkable attempt made in this direction is the pulsed imaging to obtain the subsurface holes in an aluminium cylinder using a piezoelectric transducer [59]. The subsurface inhomogeneities not visible with an optical microscope could be detected by the variations in the PA signal [60]. The PA imaging studies in multi-layer films on germanium substrate revealed the irregularities with a fairly high degree of resolution and the samples with inhomogeneities located by PAM will usually be damaged by sufficiently intense radiation at the positions where it is located. Therefore this method may actually be useful to predict the tendency towards the laser induced damages [61].

One of the most remarkable achievements in PAM technique is the demonstration of PA mapping of damages due to ion implantation and subsequent recrystallization due to annealing in Si or GaAs using continuous wave Nd:YAG laser operating at 1.06µm for excitation [62]. Recently, this method has been successfully used to detect the subsurface features of integrated circuits and this provides information on absolute spatial distribution of dopant concentration. This technique has been used for getting images of semiconductor structures [63-64]. Recently it has also been used for producing the three dimensional images of the material [65-66]. Excitations of the samples can be made either by modulated CW lasers or pulsed lasers or other energetic beams, and the detection of
the PAM signal is possible by sensitive microphone or piezoelectric transducer. PAM is considered as a promising non-destructive technique which has direct applications in the field of semiconductor industry which essentially influences the developments in every branch of technology.

To summarize, PAM techniques have been used for the following non-destructive imaging of various subsurface features: (i) detection of holes in materials (ii) flaws in ceramics (iii) absorption sites in laser windows (iv) water content in porous materials (v) inhomogenities in layered materials (vi) presence of foreign material inclusion in biological samples [67] (vii) defects in ICs and in substrate [68] (viii) compositional variations in alloys (ix) ion implantation damage in semiconductors [69] etc.

V. PAS in Biology and Medicine

Photoacoustic methods of determining the absorption of a material is widely being used in biological as well as in medical fields. Many of the above mentioned samples occur naturally in insoluble states, many others are membrane bound or part of bone or tissue structure, these materials are found to function biologically within a more or less solid matrix. PAS through its capability of providing optical data on intact biological matter, even with materials which are optically opaque, holds great promise both as a research tool and as a diagnostic tool in biology and medicine.

This novel technique has been effectively utilized for the spectroscopic studies of blood without the necessity of a preliminary separation of these large molecules as the conventional spectroscopy does not yield satisfactory spectra because of the string light scattering properties of the blood cells, protein and lipid molecules present [70]. This technique is applicable to the quantification of tissue chromophores such as oxyhaemoglobin (HbO₂) and deoxyhaemoglobin (HHb) for the measurement of physiological parameters such as blood oxygen saturation (SO₂) and total haemoglobin concentration with high spatial resolution [71].

PA spectroscopy has been shown to be able to discriminate between normal and athermatous areas of arterial tissue in the visible range (410nm-680nm) even when the blood is present. It is also possible to estimate the amount of 5-methylcytosine in
drosophila melanogaster DNA by obtaining a linear relationship between the contraction of 5-methylcytosine in DNA and staining intensity recorded by photoacoustic spectroscopy [72-73]. This method has been effectively utilized to study the optical absorption spectrum of the oxidized and reduced form of cytochrome-C in various aqueous solutions and the analysis shows the variation of its construction during cellular respiration [74]. Light absorption properties of urine and body tissue can be obtained more easily by PAS technique [75] because of its high sensitivity then the conventional techniques, measurement of thermal diffusivity of bone, hydroxyapatite and metals is possible by this technique for biomedical applications [76].

Photoacoustic signals can provide information about the depth profile of a sample, by monitoring differential interactions of drugs and other ligands with cells [77]. Photoacoustic spectroscopy has been employed to study the presence of aromatic amine acid in proteins [78]. Similarly one of the most exciting areas in PA studies lies in the field of medicine is that, the PAS provides optical data on medical specimens that are not amenable to conventional methods. An example of the use of PAS in medical studies is the identification of bacterial states [79].

PAS is a key technique in the investigation of nanosized magnetic particles for drug delivery systems [80]. PAS method is a promising tool for evaluating the elastic properties of tableting materials and the structural variations in tablets. PAS can be applied in order to quantify the brivudin and dithranol in Vaseline-I drug ointment. The PA spectroscopic investigations carried out makes it possible to monitor the spectral properties of abnormal or cancerous tissues and their molecular structure which helps in the early detection of such cancerous growth in the human body. The formation of tryp to phan and tyrosine residues which essentially cause cataract in human eye can be revealed by PA spectroscopic measurement [81-82]. PA studies in blood provide the absorption spectrum from which the concentration of haemoglobin, could be precisely determined [83].

The PA spectroscopy can be used to study the malarial parasites plasmodium chabavdi and plasmodium berghei their pigment and ferriprotoporphyrinix which is a byproduct of the haemoglobin that the parasite ingest [84], these result in turn reveal the
utility of this method in the field of medicine which is a direct application of PA effect in the day today life.

VI. Miscellaneous Applications
The main application of PAS is in the characterization of semiconducting materials. As the PA signal depends on heat diffusion, the thermal diffusivity can also be determined which is strongly sensitive to the structural quality of the semiconducting material using depth-resolved PAS, it is possible to estimate the thicknesses and moisture contents of varnish layers on waste papers. Furthermore, packaging materials have been characterized by PA measurements in the UV-visible range [85].

Laser photoacoustic spectroscopy helps to fight terrorism which is one of the burning problems of the current turbulent times with high sensitivity detection of chemical warfare agents and explosives. Among the explosives Wetsel, G. C. have demonstrated the capability of detecting homemade explosives such as triacetone triperoxide and its liquid precursor, acetone which is a common household liquid. This capability, deployed at airports and other public places, will go a long way towards increasing public safety and minimizing inconveniences faced in airline travel [86]. Photoacoustic spectroscopy plays a vital role in detecting the green house gases. PA spectroscopy meets the requirements that enable this technique to offer important advantages in pollutant gas monitoring [87].

Wheat heat damage is a grading factor that affects the commercial value of the crop and a number of method are developed to test the effect of heat damage on wheat protein functionality or solubility, the photoacoustic spectroscopy is simple and fast method to inspect grains. It is introduced to evaluate wheat heat damage due to post harvest drying or storage [88]. Another important area in the application of photoacoustic spectroscopy is in photosynthesis. The band gap energies of semiconductors can be obtained by photoacoustic spectroscopy [89-90]. Furthermore, PA techniques allow absorption spectra of solid samples (including powders, chips or large objects) to be determined, and they permit depth profiling of layered systems, these features mean that PAS can be used for on-line monitoring in technical processes without the need for sample preparation [91].
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