Chapter 7

PHOTOACOUSTICS: THEORY AND EXPERIMENT

7.1 Introduction

Spectroscopy deals with the study of interaction of energy with matter. In the field of high-energy physics, the radiation is sufficiently energetic to perturb and in some cases, even transform the matter with which it interacts. In the oldest form of spectroscopy, the energy is usually too low to perturb the material under study. In optical spectroscopy, the energy exists in the form of optical photons or quanta with wavelength ranging from 1 Å in the X-ray region to more
than $10^6$ A° in the far – infrared[1]. Because of its versatility, range and nondestructive nature, optical spectroscopy remains a most important and widely used tool for investigating and characterizing the properties of matter.

Conventional spectroscopy can be categorized into two.

a) That which involves the study of the photons that are transmitted through the material of interest; that is, the study of those photons that do not interact with the material.

b) That which involves the study of light that is scattered or reflected from the material, that is, those photons that have undergone some interaction with the material.

Almost all conventional optical methods are variations of these two basic techniques[2-12]. This has been a scientific tool for over a century, and it has proven invaluable in studies on reasonably clean media, such as solutions and crystals and on reflective surfaces. There are, however several instances where conventional transmission spectroscopy is inadequate even for the case of clear, transparent materials, such as to measure a very weak absorption. This problem occurs for all forms of matter. Over the years, various techniques have been developed to overcome this difficulty, such as derivative spectroscopy which has proven to be generally inadequate. In addition, there are substances, both organic and inorganic, that are not readily amenable to the conventional transmission or reflection modes of optical spectroscopy. These are usually highly light-scattering
materials, such as powders, amorphous solids, gels etc. There are a number of materials that are optically opaque and have dimensions that far exceed the penetration depth of the photons.

In recent years, thermal wave physics has emerged as an effective analytical tool for the characterization of such materials[13-16]. These methods are based on the generation of thermal waves due to a transient temperature change within the sample after illumination with a pulsed or chopped optical radiation[17-30]. During the past three decades, another optical technique called photoacoustic spectroscopy (PAS) has been developed to study those materials that are unsuitable for the conventional transmission or reflection methodologies. PAS is different from the conventional techniques chiefly in that even though the incident energy is in the form of optical photons, the interaction of these photons with the material under investigation is studied not through subsequent detection and analysis of some of the photons, but rather through a direct measure of the energy absorbed by the material as a result of its interaction with the photon beam[31-37].

In PAS, the sample is always placed in a closed cell or chamber. In the case of gases and liquids, the sample 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, the chamber also contains a sensitive microphone. The sample is illuminated with monochromatic light that passes through an electromechanical chopper for modulation. If any of the incident photons are absorbed by the sample 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 transformed into heat energy through non-radiative de-excitation processes. 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 ions or atoms. Since the incident radiation is intensity or frequency modulated, the internal heating of the sample is also modulated.

Since photo acoustics measures the internal heating of the sample, it is clearly a form of calorimetry, as well as a form of optical spectroscopy. There are many calorimetric techniques by which one can detect and measure the heat produced during the process. By employing a conventional calorimeter based on the usual temperature sensors such as themistors and thermopiles, one can measure the temperature rise. These classical techniques have several disadvantages compared to photo acoustic spectroscopy in terms of sensitivity, and speed at which measurements can be made. More suitable calorimetric techniques measure heat production through volume and pressure changes produced in the sample or in an appropriate transducing material in contact with the sample.

In gaseous samples, volume changes can be quite large as a result of internal heating. In these cases, a sensitive capacitor microphone proves to be an excellent detector. When dealing with liquids or bulk solid samples, it is possible to measure heat production through subsequent pressure or stress variations in the sample itself by means of
always, possible to employ a piezoelectric detector, as in the case of powdered or gel sample. In these cases, a gas is used as a transducing medium, coupling the sample to a microphone. The periodic heating of the sample from the absorption of the optical radiation results in a periodic heat flow from the sample to the gas, which itself does not absorb the optical radiation. This in turn produces pressure and volume changes in the gas that drive the microphone.

Photo acoustics is, much more than spectroscopy. Photo acoustics can be used to measure the absorption or excitation spectrum, the life time of excited states and the energy yield of radiative processes. These are all spectroscopic measurements. On the other hand, photo acoustics can also be used to measure thickness of layers and thin films and to perform a variety of other non-spectroscopic investigations. In such studies the calorimetric or acoustic aspect of photo acoustics plays a dominant role. Thus photo acoustic studies can be performed on all types of materials – inorganic, organic and biological and on all states of matter.

7.2 History of Photo Acoustic effect

The photo acoustic effect is the process of conversion of optical energy into acoustical perturbation when modulated light interacts with matter kept in a cavity. Light absorbed by the sample will excite a fraction of the ground state molecular population into higher energy levels. These excited states will subsequently relax through a combination of radiative and non-radiative path ways. The non-
region of the excitation light beam and create a pressure wave that propagates away from the source. The pressure wave is then detected with a suitable sensor such as microphone.

The photo acoustic effect in both nongaseous and gaseous matter was discovered by Alexander Graham Bell in the year 1880. He showed that the solar radiation, dispersed with a prism and chopped at an audio frequency is absorbed by different materials to varying amounts depending upon the wavelength and produced varying audio signals. One of the transmitters of Bell called as photo phone consisted of a voice-activated mirror (which was activated by sound waves of a voice), a selenium cell and an electrical telephone receiver [6]. The intensity modulated sunlight was then focused onto a selenium cell. Since electrical resistance of selenium varies with the intensity of light falling on it, the voice modulated beam of sunlight resulted in electrically reproduced telephonic speech.

Bell demonstrated that the photo acoustic effect in solids was dependent on the absorption of light and that the strength of the acoustic signal was in turn, dependent on how strongly the incident light was absorbed by the material in the cell. He concluded that “The nature of the rays that produces sonorous effects in different substances depends upon the nature of the substances that are exposed to the beam, and that the sounds in every case are due to those rays of the spectrum that are absorbed by the body”. Bell thus correctly deduced the intrinsic optical absorptive dependence of the photo acoustic effect.
Though Bell had prophesized the scope of his novel observation, after the initial flurry of interest generated by his original work, experimentation (for nearly 50 years) with the photo acoustic effect remained almost in a dormant state. The effect was obviously considered as being no more than an interesting curiosity of no great scientific or practical value. Further more, the experiments were difficult to perform and were quantitative since they required the investigator's ear to be the signal detector. After the advent of microphones, Veingerov of Leningrad was able to observe this effect in gaseous samples. Between 1950 and 1970, the photo acoustic gas analyzer employing a conventional light source gave way to the more sensitive gas chromatographs and the spectrograph was overtaken by the more versatile infrared spectrophotometer. During this period, the photo acoustic effect was primarily employed to study vibrational life times and other aspects of radiation less de-excitation in gases. The advent of lasers in the early 1970's paved a new way in the photo acoustic spectroscopy of gaseous samples. But the applications of this technique has been effectively and efficiently extended to liquids and solids only after the successful formulation of general theoretical model by Rosencwaig and Gersho in mid seventies [1, 37].

Subsequent developments in the theoretical aspects of photo thermal phenomena are mere extensions of the modifications of R-G model. Modifications to the R-G theory by McDonald and Wetsel in 1978, by taking into account the contribution from thermally
induced vibrations in the sample are somewhat intriguing. By this time, a new form of photo acoustic configuration, namely open photo acoustic cell (OPC) had emerged. This was a major renaissance in the field of PA technique. Thermal and optical characterization of materials in solid or liquid state becomes more simple, accurate and sensitive in OPC configuration. If the sample is in solid form, it can be mounted on the OPC and from the signal amplitude or phase dependence on the modulation frequency of the excitation beam, one can easily evaluate the thermal parameters such as thermal diffusivity of the sample.

7.3 Photo Induced Processes

The absorption of photons by atoms or molecules will result in a series of processes or effects in a material. The excited level may lose its energy by radiative processes, such as spontaneous or stimulated emission, and by non radiative processes which mainly results in heat generation. If the photon energy is high enough, direct photochemical changes may take place. Destructive changes may take place at very high power densities of the incident light. A schematic representation of various photo-induced processes and main channels of photo-induced changes that occur in condensed matter is given in the following figure.
In the figure $E_1$ and $E_2$ represent the energies of the lower and upper levels and

$$E_2 - E_1 = hv$$ is the energy of the absorbed photon. The absorbed power in the sample $I_{abs}$ is in accordance with

$$I_{abs} = I_0 [1 - \exp(-\infty L)] = \infty I L$$ ......................................................... (7.1)  

with $\infty L << 1$. Here $I$ and $L$ are the incident light intensity and the sample length respectively and $\infty$ is the absorption coefficient.

Now, the absorbed energy will be liberated through radiative, nonradiative or chemical processes and each of these processes has specific quantum yield [38-39].
If $n_r$, $n_{nr}$ and $n_{pc}$ are the quantum yields of radiative, nonradiative and photochemical processes respectively, the total quantum yield of all the channels of de-excitation is given by

$$n_r + n_{nr} + n_{pc} = 1 \quad \cdots \quad (7.2)$$

Accordingly, the intensity $I_{abs}$ of the laser radiation absorbed over all these channels is

$$I_{abs} = I_r + I_{nr} + I_{pc} \quad \cdots \quad (7.3)$$

where $I_r = n_r I_{abs}$, $I_{nr} = n_{nr} I_{abs}$ and $I_{pc} = n_{pc} I_{abs}$ are the amount of energy liberated through the radiative, nonradiative and photochemical processes respectively.

Measurement of the energy absorbed or that released through any of these relaxation channels facilitates the study of various properties and parameters of the sample.

### 7.4 Detection methods

Spectroscopy is the measurement and interpretation of EM radiation absorbed or emitted when the molecules or atoms or ions of a sample move from one state to another. The laser based spectroscopic techniques can be divided into

a) Absorption method

b) Radiative emission

c) Non Radiative emission
The absorption method is the basic and the simplest approach and by using this technique, information regarding the optical properties and composition of the sample can be obtained by varying different parameters such as intensity, wavelength, etc. of the light beam that passes through or get reflected from the sample. However a variety of external parameters such as surface quality, influence of stray light etc have a pronounced effect on the accuracy of the conventional absorption measurements. In such situations, radiative or non radiative emission measurements are more appropriate. The non radiative relaxation of photo-excited state usually results in heating of the sample. The liberated heat energy not only carries the information regarding the absorbed energy but contains details regarding the thermal properties of the sample as well. A group of such spectroscopic methods on the measurement of photo induced heating of the sample are called photo thermal methods.

Fig. 7.2 Schematic diagram of photo thermal effects
The thermalisation of a sample as a result of non radiative relaxation brings about changes in many parameters such as density, pressure, refractive index etc. If the temperature change occurs in a faster time scale, then it will result in a pressure change in the sample.

Pressure transducers such as microphones, piezo electric crystals etc are commonly used to monitor the pressure waves associated with rapid ample heating. The branch of photo thermal spectroscopy based on the pressure wave measurement is known as photo acoustic technique.

**Detection Techniques**

**Table 7.1** Various detection schemes

<table>
<thead>
<tr>
<th>Thermodynamic Parameter</th>
<th>Measured Property</th>
<th>Detection Technique</th>
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</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>Temperature</td>
<td>Calorimetry</td>
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<tr>
<td></td>
<td>InfraRed Emission</td>
<td>Photothermal Radiometry</td>
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<td><strong>Pressure</strong></td>
<td><strong>Acoustic Wave</strong></td>
<td><strong>Photoacoustic Spectroscopy</strong></td>
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<td>Density</td>
<td>Refractive Index</td>
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<td>Surface Deformation</td>
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<td>P T Diffraction</td>
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<tr>
<td></td>
<td></td>
<td>Surface Deflection</td>
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</table>
7.5 Photoacoustic effect in condensed media

Photoacoustic spectroscopy has been proved to be a powerful analytical tool for samples such as powders, opaque materials and even living tissues. In condensed matter, absorbed light is converted partially or totally into heat by non-radiative transitions. In the atoms or molecules, the excited level may lose its energy by spontaneous or stimulated emission. The non-radiative process mainly results in heat wave generation. For the heat wave generation, many excitation mechanisms can be used such as pulsed electrical heating or irradiation with laser etc. If the energy is high enough, direct photochemical changes such as photo decomposition, photo-ionization etc, of the excited molecule may take place. Destructive changes such as vaporization of the sample and plasma generation may take place as a result of photon-matter interaction at very high power densities of incident light.

The photo acoustic technique is essentially a closed cavity detection of energy liberated by atoms or molecules through non radiative de-excitation mechanisms subsequent to light absorption by a sample. When a solid sample is irradiated with a modulated optical radiation, the energy liberated through the non-radiative channel will result in the generation of thermal waves within the sample. The thermal waves diffused through the sample to the surrounding gas (say a cavity) carry information regarding the thermal properties of the sample.
The most widely used model for describing photo acoustic effect on condensed sample in a gas-microphone cell was originally developed by Rosencwaig and Gersho in 1976[37]. It is valid for acoustic wavelengths much greater than the dimensions of the sample and gas column.

7.6 Rosencwaig-Gersho theory

The Rosencwaig-Gersho theory is a one dimensional heat flow model for the analysis of the production of a photo acoustic signal in a cell [37]. This theory is sufficient to describe the photo acoustic signal generation in condensed media. According to R-G theory with gas-microphone detection, the signal depends on the generation of an acoustic pressure disturbance at the solid-gas interface. The generation of the surface pressure disturbance, in turn depends on periodic temperature at the sample-gas interface. The formulation of R-G model is based on the light absorption and thermal wave propagation in an experimental configuration as in figure 7.1.

Here a cylindrical cell of length $L$ and diameter $D$ is considered. Assume that the length $L$ is small compared to the wavelength of the acoustic signal. 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 a poor thermal conductor of thickness $l_b$. The length $l_g$ of the gas column in the cell is then given by $l_g = L - l - l_b$. Further assumption is that the gas and backing materials are not light absorbing.
Let $k_i$, $\rho_i$, $C_i$, and $\alpha_i$ represent the thermal conductivity, density, specific heat and thermal diffusivity respectively of the material $i$. Then $a_i = (\omega/2\alpha_i)^{1/2}$ is the thermal diffusion coefficient and $\mu_i = 1/a_i$ is the thermal diffusion length of the material. $i$ can be $s$, $g$ and $b$ for solid, gas and backing material respectively. $\omega$ denotes the chopping frequency of the incident light beam in radians per second.

Assume that the sinusoidally chopped monochromatic light with wavelength $\lambda$ is incident on the solid with intensity

$$l = (1/2) I_0 (1 + \cos \omega t) \quad \text{................................. (7.4)}$$

The thermal diffusion equation in the three regions can be written as[5]

$$\frac{\partial^2 \varphi}{\partial t^2} = \frac{1}{\alpha_b} \frac{\partial \varphi}{\partial t}, -l - l_b \leq x \leq -l \quad \text{Region III} \quad \text{............... (7.5)}$$

$$\frac{\partial^2 \varphi}{\partial t^2} = \frac{1}{\alpha_g} \frac{\partial \varphi}{\partial t}, 0 \leq x \leq -l_g \quad \text{Region I} \quad \text{............... (7.6)}$$
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\[ \frac{\partial^2 \varphi}{\partial t^2} = \frac{1}{\alpha_s} \frac{\partial \varphi}{\partial t} - A \exp(\beta t)[1 + \exp(j\alpha t)] \quad , \quad -l \leq x \leq 0 \text{ Region II} \quad \cdots \quad (7.7) \]

where \( A = \frac{\beta A_0 \eta}{2k_s} \quad \cdots \quad (7.8) \)

Here \( \varphi \) is the temperature and \( \eta \) is the light conversion efficiency. The real part of the complex-valued solution \( \varphi(x, t) \) of the above equations is the solution of physical interest and represents the temperature in the cell relative to the ambient temperature as a function of position and time. Thus, the actual temperature field in the cell is given by,

\[ T(x, t) = \text{Re}[\varphi(x, t)] + \phi \quad \cdots \quad (7.9) \]

where Re denotes "the real part of" and \( \phi \) is the ambient (room) temperature.

The complex amplitude of the periodic temperature distribution, \( \theta \) at the solid-gas boundary \((x=0)\) is given by

\[ \theta = \frac{\beta \theta_0}{2k_s \left( \beta^2 - \sigma_s^2 \right)} \left\{ \frac{(r - 1)(b + 1)\exp(\sigma_s) - (r + 1)(b - 1)\exp(-\sigma_s)}{(g + 1)(b + 1)\exp(\sigma_s) - (g - 1)(b - 1)\exp(-\sigma_s)} \right\} \cdots \quad (7.10) \]

Where

\[ b = \frac{k_s a_g}{k_s a}, \quad g = \frac{k_s a_g}{k_s a}, \quad \tau = (1 - j) \frac{\beta}{2a_s} \quad \text{and} \quad \sigma_s = (1 + j)a_s \quad \cdots \quad (7.11) \]

The main source of acoustic signal arises from the periodic heat flow from the solid to the surrounding gas. The periodic heating causes the boundary layer of gas to expand and contract periodically. This can
be thought of as the action of an acoustic piston on the rest of the gas column, producing an acoustic pressure signal that travels through the entire gas column. The displacement of the gas piston due to the periodic heating can be estimated using the ideal gas law,

$$\delta x(t) = 2\pi \mu g \frac{\phi(t)}{T_0} \frac{\partial p}{\sqrt{2T_0}} \exp \left[ j \left( \omega \tau - \frac{\pi}{4} \right) \right]$$

(7.12)

where the average dc temperature of the gas boundary layer is set as the dc temperature at the solid surface, $T_0 = \phi + \theta_0$, $\phi$ being the ambient temperature at the cell walls. Assuming that the rest of the gas responds to the action of the piston adiabatically, the acoustic pressure in the cell due to the displacement of the gas piston can be obtained from the adiabatic gas law $PV^{\gamma} = \text{constant}$, where $P$ is the pressure, $V$ is the gas volume in the cell, and $\gamma$ the ratio of the specific heats. Thus the incremental pressure is

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

(7.13)

where $P_0$ and $V_0$ are the ambient pressure and volume respectively and $-\delta V$ is the incremental volume. Then from equations (7.12) & (7.13)

$$\delta P(t) = Q \exp \left[ j \left( \omega \tau - \frac{\pi}{4} \right) \right]$$

(7.14)

where

$$Q = \frac{\gamma P_0 \theta}{\sqrt{2l g} a g T_0}$$

(7.15)
The actual physical pressure variation is given by the real part of $\delta P(t)$ and $Q$ specifies the complex envelope of the sinusoidal pressure variation.

Substituting for $\theta$

$$Q = \frac{\beta l_0 \rho_0}{2\sqrt{2k Lent_a T_0}} \left( \beta^2 - \sigma_s^2 \right) X \left[ \frac{(r-1)(b+1)\exp(\sigma_s l) - (r+1)(b-1)\exp(-\sigma_s l) + 2(b-r)\exp(-\beta l)}{(g+1)(b+1)\exp(\sigma_s l) - (g-1)(b-1)\exp(-\sigma_s l)} \right] \cdots \cdots (7.16)$$

Thus, equation (7.16) can be used to evaluate the amplitude and phase of the acoustic pressure wave produced in the cell by photo acoustic effect. It can be observed that interpretation of the full expression for $\delta P(t)$ is difficult because of the complex expression of $Q$. Some physical insight can be gained if certain special cases according to the optical opaqueness of solids are examined. For each category of optical opaqueness, 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 $\mu_\beta$ can be considered.

Defining $\gamma = \frac{\rho_1 l_0}{2\sqrt{2k Lent_a T_0}}$, \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdOTS
CASE I: Optically Transparent solids ($\mu_\beta > 1$)

1. **Case Ia: Thermally Thin Solids ($\mu_s >> 1 ; \mu_s >> \mu_\beta$)**

   We can set $e^{\beta l} \equiv 1 - \beta l$, $e^{\tau_0 l} \equiv 1$ and $|l| > 1$ in equation (7.17) and hence we obtain

   \[ Q = \frac{(1-i)\beta l}{2a_g} \left( \frac{\mu_b}{k_b} \right) Y \] ............................ (7.18)

   Thus the acoustic signal is proportional to $\beta l$ and varies as $l^{-1}$. In addition, the thermal properties of the backing material come into play in the expression for $Q$.

2. **Case Ib: Thermally Thin Solids ($\mu_s > 1 ; \mu_s < \mu_\beta$)**

   Here we can set $\exp(-\beta l) \equiv 1 - \beta l$, $e^{\tau_0 l} \equiv 1 \pm \sigma_s l$ and $|l| < 1$ in equation (7.17).

   Then \[ Q = \frac{(1-i)\beta l}{2a_g} \left( \frac{\mu_b}{k_b} \right) Y \] ............................ (7.19)

   This equation is identical with equation (7.18) and hence the acoustic signal behaves in the same fashion.

3. **Case Ic: Thermally Thick Solids ($\mu_s > 1 ; \mu_s << \mu_\beta$)**

   In this case we set $\exp(-\beta l) \equiv 1 - \beta l$, $e^{\tau_0 l} \equiv 0$ and $|l| << 1$ in equation (7.17)

   Now \[ Q = -j \frac{\beta l}{2a_g} \left( \frac{\mu_s}{k_s} \right) Y \] ............................ (7.20)
The acoustic signal is now proportional to $\beta \mu_s$ rather than $\beta l$. This means that light absorbed within the first thermal diffusion length contributes to the signal, although light is being absorbed throughout the length of the solid. Moreover, $\mu_s$ being less than the thickness $l$, thermal properties of the backing material will not influence the signal. Here the signal varies as $f^{3/2}$ with the modulation frequency.

CASE II: Optically Opaque Solids

Case II a: Thermally Thin Solids ($\mu_r > l ; \mu_s >> \mu_\beta$)

In equation (7.17), we set $\exp (-\beta l) \equiv 0$, $e^{+\alpha l} \equiv 1$ and $|r| >> 1$

Then we obtain

$$Q = \frac{(1-j)}{2a_g} \left( \frac{\mu_b}{k_b} \right) Y \quad \text{.......................................................... (7.21)}$$

Here the photo acoustic signal is independent of $\beta$, which is valid for a perfect black absorber. The signal depends on the thermal properties of the backing material and varies as $1/f$.

Case II b: Thermally Thick Solids ($\mu_r < l ; \mu_s > \mu_\beta$)

We set $\exp (-\beta l) \equiv 0$, $e^{-\alpha l} \equiv 0$ and $|r| > 1$ in equation (7.17)

We obtain

$$Q = \frac{(1-j)}{2a_g} \left( \frac{\mu_s}{k_s} \right) Y \quad \text{.......................................................... (7.22)}$$

Though equations (7.21) & (7.22) are similar, in the present case there is no contribution from the thermal properties of the backing material.
Case II c: Thermally Thick Solids ($\mu_s << l; \mu_s < \mu_\beta$)

We set $\exp(-\beta l) \equiv 0$, $e^{-\alpha l} \equiv 0$ and $|f| < 1$ in equation (7.17). Then we obtain

$$Q = \frac{-j\beta\mu_s}{2a} \left( \frac{\mu_s}{k_s} \right) Y \text{...................................................................................... (7.23)}$$

The photo acoustic signal will be proportional to $\beta\mu_s$. The signal is independent of the thermal properties of the backing material and varies as $t^{-3/2}$.

A theoretical analysis of the photo acoustic effect applied to different cases has been discussed and can be applied to the study of any kind of sample.

The photo acoustic measurements can be done in two different configurations (1) By heat transmission and (2) By heat reflection configurations. The photo acoustic cell can be designed for the two configurations. The simplest and convenient form of a cell that can be used for heat transmission configuration is the open photo acoustic cell.

7.7 Open photo acoustic cell configuration

Open photo acoustic cell (OPC) configuration is a modified form of conventional photo acoustic cell configuration. In the OPC, the solid sample can be mounted directly on top of the microphone, leaving a small volume of air in between the sample and microphone. It is an open cell detection configuration in the sense that the sample is placed on top of the detection system as in the case of piezoelectric and
pyroelectric detection. Consequently this configuration is a minimum volume detection scheme and hence the signal strength will be much greater than that in conventional PA configurations. The major advantage of this configuration is that samples having large sizes can also be studied, whereas in conventional PA cells, sample size should be small enough to be contained inside the PA cavity. A schematic representation of the typical OPC is shown in figure 7.4.

According to R G theory, the pressure variations in the acoustic chamber for an OPC detection configuration is given by,

\[
Q_{th} = \frac{\gamma P_0 I_0 (\alpha_g \alpha_s)^{1/2} e^{i(\alpha_g \Gamma/2)}}{2\pi T_0 l_g K_g f \sinh(l_g \sigma_s)} \tag{7.24}
\]

where \(\gamma\) is the ratio of specific heats of air, \(I_0\) is the intensity of incident light beam, \(P_0(T_0)\) is the ambient pressure (temperature), \(f\) is the modulation frequency, \(l_i, k_i\) and \(\alpha_i\) are the thickness, thermal conductivity
and thermal diffusivity of the medium $i$, where $i=g$ refers to the gas and $i=s$ refers to the sample under investigation. Also $\sigma_i = (1+i)a_i$, where thermal diffusion co-efficient, $a_i = \frac{\sqrt{\omega}}{2\alpha_i}$

For a thermally thin sample, ($l_s\alpha_s \ll 1$), the above equation reduces to,

$$Q_{th} \approx \frac{\mathcal{P}_0 (\alpha_g^{1/2}) \alpha_s e^{i(\alpha - 3\pi/4)}}{(2\pi)^{3/2} T_0 l_g l_s \kappa_s f^{3/2}}$$  \hspace{2cm} (7.25)

In this case, the amplitude of the photo acoustic signal varies as $f^{1.5}$

At higher modulation frequencies, the sample becomes thermally thick, ($l_s\alpha_s >> 1$), so that photo acoustic signal obeys the equation,

$$Q_{th} \approx \frac{\mathcal{P}_0 l_0 (\alpha_g^{1/2})^2 e^{-i2\pi f}}{\Pi T_0 l_k \kappa_s} e^{j(\alpha - n/2 - l_s)}$$  \hspace{2cm} (7.26)

From the last equation it is obvious that for thermally thick sample, the amplitude of photo acoustics signal varies as $(1/f)\exp(-b\sqrt{f})$, where $b=\sqrt{l_s\Pi/\alpha_s}$, whereas phase decreases linearly with $\sqrt{f}$, namely,

$$\Phi_{th} = -\pi/2 - b\sqrt{f}$$  \hspace{2cm} (7.27)

Hence the thermal diffusivity can be evaluated either from the amplitude or phase of the PA signal obtained under heat transmission configuration. A necessary condition that should be satisfied for employing OPC configuration is that the specimen under investigation should be opaque at the incident wavelength. Though the phase and
amplitude of the PA signal contains clear signature of the thermal transport properties of the specimen, phase data is more reliable for OPC since the amplitude data depends on many external parameters such as surface quality and detector response at different wavelengths.

However for plate shaped specimens, the contribution to the PA signal from the thermo elastic bending due to the temperature gradient existing in the specimen cannot be neglected, especially when the sample is in the thermally thick region. The existence of temperature gradient causes an expansion of the sample parallel to the sample surface, thereby inducing bending along the thickness direction. Such a vibrating sample acts as a mechanical piston; this is otherwise known as drum effect. For an optically opaque sample, in the thermally thick regime, the pressure fluctuation in the air chamber of the OPC detector from the thermo elastic displacement is given by[40],

$$Q_{el} = \frac{3\alpha_T R^3 \gamma \rho_0 l_0 \alpha_s \left[ \frac{1}{z} - \frac{1}{z^2} \right] \frac{1}{2} e^{i(\omega t + \Phi)} + \frac{1}{z^2}}{4\pi R_c l_s^2 l_s k_s f}$$

.................. (7.28)

Where \(z=b\sqrt{f}, \Phi=\tan^{-1}(1/(z-1))\) and \(\alpha_T\) is the sample thermal expansion co-efficient. \(R\) is the radius of the front hole of the microphone and \(R_c\) is the radius of the OPC air chamber. The above equation means that the thermo elastic contribution, at high frequencies varies as \(f^1\) and the phase \(\Phi\) follows the expression

$$\Phi_{el} = \Phi_0 + \tan^{-1}(1/(z-1))$$

........................................ (7.29)
Thus for thermally thick sample, if thermo elastic contribution is dominant, the thermal diffusivity value can be evaluated from the modulation frequency dependence of the signal phase.

In the next section of this chapter, the thermal diffusivity analysis of PANI (HCl) and PANI (HCl)-MWNT composites are carried out. The thermal diffusivities are calculated using thermo elastic bending formula applied to open photo acoustic technique in transmission configuration.

Experimental

7.8 Thermal diffusivity measurements on PANI (HCl) and PANI (HCl)-MWNT composites

Although PANI and its composites have been widely investigated over the years, their thermal properties have been unfortunately ignored. For the fabrication of devices capable of working in the high temperature region, the thermal behaviour of such materials has to be studied in detail.

In this section, thermal diffusivity measurements on PANI (HCl) and PANI (HCl)-MWNT composites with different aniline to MWNT feed ratios are described. The thermal diffusivity of the composite depends on the thermal conductivity as well as thermal diffusivity of its components[41-42].MWNT is a material with good thermal conductivity as already described in chapter5. So it is relevant to study the variation of thermal diffusivity of the composites with varying aniline to MWNT feed ratios.
7.9 Experimental Setup

The experimental setup consists of a) Laser source  b) Open Photoacoustic cell (OPC)  c) Mechanical chopper  d) Lock-in-amplifier.

a) The Laser source used in the present investigation is He-Ne laser (6328 Å) of power 20 mW. The original laser beam has a spot size of 0.7mm and is used without focusing to avoid lateral heat flow.

b) A conventional OPC made of stainless steel of radius 2cm (figure 7.5) is used in which the sample is placed directly on top of microphone by leaving a small volume of gas in between the two. Such OPC’s can be used only in the heat transmission configuration. The microphone used is a highly sensitive electret microphone (Knowles FG 3329). Shielded wires are used to take electrical connections directly from the microphone. The samples can be fixed on to the sample chamber by means of vacuum grease.

Fig. 7.5 Open photo acoustic cell
c) The model **SR 540 mechanical chopper** is used to square-wave modulate the intensity of the optical signal. The unit can chop light sources at rates from 4Hz-4 kHz. The choice of operating frequency is influenced by several factors. In general, phase jitter, background noise and lock-in-amplifier noise all degrade at low frequencies. For frequencies from 4Hz to 400Hz, the six slot blade is used whereas for frequencies from 400 Hz to 4 kHz, the thirty slot blade is used.

d) The **Lock-in amplifier** used in the present study is **Stanford Research model (SR 830)**. Lock-in amplifiers are used to detect and measure very small AC signals (upto nanovolts). Accurate measurement may be made even when the small signal is obscured by noise sources many thousands of times larger. Lock-in amplifiers use a technique known as phase-sensitive detection to single out the component of the signal at a specific reference frequency and phase. Noise signals at frequencies other than the reference frequency are rejected and do not affect the measurement. According to Fourier theorem any input signal can be represented as the sum of many sine waves of differing amplitudes, frequencies and phases. The lock-in amplifier multiplies the signal by a pure sine wave at the reference frequency. All components of the input signal are multiplied by the reference simultaneously. The average of the product of two sine waves is zero unless the frequencies are exactly the same. The product of this multiplication yields a DC output signal proportional to the component of the signal whose frequency is exactly locked to the reference frequency. The low pass filter, which follows the
multiplier, provides the averaging which removes the products of the reference with components at all the other frequencies. In the general case, the input consists of signal plus noise. Noise is represented as varying signals at all frequencies. The ideal lock-in only responds to noise at the reference frequency. Noise at other frequencies is removed by the low pass filter following the multiplier. This “bandwidth narrowing” is the primary advantage that a lock-in amplifier provides. Only inputs at frequencies at the reference frequency result in an output. A schematic of the experimental setup is shown in figure 7.6.

![Schematic of the experimental setup](image)

A: He-Ne laser, B: Mechanical Chopper, C: OPC, D: Lock-in-Amplifier E: Battery F: Chopper control

**Fig. 7.6** Photo acoustics setup

### 7.10 Experimental procedure

In the OPC, the solid plate like sample is fixed on the top of the microphone using vacuum grease at the edges, leaving a small volume
of air in between the sample and microphone and the sample is irradiated at its surface facing the ambient. This configuration is a minimum volume PA detection scheme and hence the signal strength is much greater than the conventional PA configuration. A cross-sectional view of the OPC used in the experiment is shown in the figure 7.6. Continuous-wave laser emission at 6328A from a He-Ne laser of 20 mW is used as the source of excitation. The original laser beam has a spot size of 0.7mm and is used without focusing to avoid lateral heat flow. The signal is detected using a highly sensitive electret microphone kept in the side chamber. A mechanical chopper is used to modulate the laser beam at the desired frequency. The PA signal is produced in a small volume of air in between the sample and microphone. The phase and amplitude as a function of modulation frequency is recorded using dual phase lock-in-amplifier.

Hence the thermal diffusivity $\alpha_s$ of the sample can be easily evaluated from either a signal amplitude plot or a phase plot. A necessary condition for employing the OPC configuration is that the sample would be optically opaque at the incident wavelength. Though the phase and amplitude of the PA signal contains clear signature of the thermal transport properties of the sample, phase data are more reliable since the amplitude data depend on many external parameters such as sample surface quality and the detector response at different modulation frequencies.

7.11 Analysis of thermal diffusivity results

Plots of phase vs frequency $^{1/2}$ plots of PANI (HCl) and PANI (HCl)-MWNT composites with various aniline to MWNT feed ratios are given in
figures 7.7-7.10. Samples are taken in the form of pressed pellets of 1mm thickness and 1.2cm diameter, applying uniform pressure.

**Fig. 7.7** Phase vs. square root of frequency plot of PANI (HCl)

**Fig. 7.8** Phase vs. square root of frequency plot of PANI (HCl)-MWNT (1:0.1) composite
Fig. 7.9 Phase vs. square root of frequency plot of PANI (HCl)-MWNT (1:0.3) composite

Fig. 7.10 Phase vs. square root of frequency plot of PANI (HCl)-MWNT (1:0.5) composite
The thermal diffusivity values calculated from the above plots are given in table 7.2.

**Table 7.2.** Table depicting the thermal diffusivity values of PANI (HCl) and PANI (HCl)-MWNT composites

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>THERMAL DIFFUSIVITIES (m²s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PANI(HCl)</td>
<td>0.1427e-5</td>
</tr>
<tr>
<td>PANI(HCl)-MWNT(1:0.1)</td>
<td>0.1742e-5</td>
</tr>
<tr>
<td>PANI (HCl)-MWNT(1:0.3)</td>
<td>0.269e-5</td>
</tr>
<tr>
<td>PANI (HCl)-MWNT(1:0.5)</td>
<td>0.1724e-5</td>
</tr>
</tbody>
</table>

The thermal diffusivity values of the composites increase with increase in MWNT loading up to 1:0.3 ratio. Obviously the enhancement in thermal diffusivity is due to the high thermal conductivity of MWNT as explained earlier. But thermal diffusivity value decreases for the PANI (HCl)-MWNT (1:0.5) composite. As MWNT feed ratio increases beyond a particular level, the following effects may come into play.

a) There are reports that MWNTs may act as dopant in PANI-MWNT composites [43]. So dopant induced phonon scattering may predominate at higher MWNT feed ratios, reducing the thermal diffusivity value.

b) There is a large difference in thermal diffusivity value between PANI and MWNT. This thermal diffusivity mismatch [44] may
play a major role in lowering the thermal diffusivity of the composite at high MWNT feed ratios.

c) At higher MWNT content, the thermal interfacial contact resistance and thermal barrier resistance increases, reducing the thermal diffusivity value of the composite [45].

Still the thermal diffusivity value of the PANI (HCl)-MWNT (1:0.5) composite is higher than that of PANI (HCl).

7.12 Conclusions

Thermal diffusivity measurements are performed on PANI (HCl) and PANI (HCl)-MWNT composites with varying aniline to MWNT feed ratios. It is found that the thermal diffusivity value for the composite increases with MWNT loading up to 1:0.3 ratio and thereafter decreases. The reasons for this anomalous variation are studied. The present study offers ample scope in tailoring the thermal diffusivity parameters of polyaniline composites according to device requirements.

References


Chapter 7


Photoacoustics: theory and experiment


