CHAPTER I

THE TECHNIQUE

1.1 ABSTRACT:

Photocoustic Spectroscopy is a newly emerged non-destructive absorption spectroscopic tool particularly suitable for studying solids, gels and biological materials. The photoacoustic signal contains information regarding the optical and thermal properties of the sample; information about the lifetime of the excited states and a depth profile of chromophores in the sample can also be obtained in some cases. The theoretical treatments of the photoacoustic effect, the effect of three dimensional heat flow and of the mechanical vibration of the sample on the PA signal are briefly described. Theoretical aspects of some nonconventional PA experiments, such as the measurement of nonradiative lifetimes of the excited states, dichroism and quantification of the PA signal are also briefly described. Some developments in the experimental techniques; the two commercial spectrometers used in the present study, and the modifications that we have incorporated in them for better performance are also described.
1.2 Introduction

Is is our aim in this chapter to provide a brief and contextual overview of the theoretical and experimental aspects of photoacoustic spectroscopy (PAS). Although we begin with the discovery and proceed towards the present state of the art of the technique, we would have certainly missed a few aspects or given lesser emphasis than what they deserve. This is largely due to our own interest, governed by the problems we set ourselves to tackle. Rosencwaig (1) has described the theoretical aspects of the technique in detail while its applications to problems of interest in biology (2, 3) and in the study of solids and surfaces (4) have been recently reviewed.

1.3 The discovery

Alexander Graham Bell's letter of 2nd November, 1880 to his associate, Summer Tainter, describes the first photoacoustic (PA) experiment. Bell had described the discovery of the effect in a brief account given to the American Association for Advancement of Science a few months earlier (5). This was followed by a series of papers published by Bell (6), Tyndall (7), Roentgen (8), Mercadier (9) and Preece (10).

Photophone is a device to communicate speech (sound) using light as carrier. Sound is converted to a light signal by deflecting a beam of sunlight, over a knife edge or a narrow slit, by a voice-activated mirror, making it possible to translate the pressure modulation of speech into an intensity modulation of light. Since the electrical conductivity of selenium changes with the intensity of light falling in it, this can be used to convert a light signal into an electrical signal, which in turn can reproduce the acoustic signal. While experimenting with such a system, Bell was able to hear sound without
any electrical means. An intensity modulated beam of light, upon impinging on a thin diaphragm, produces sound. This is the "sound produced by light" or the "photoacoustic phenomenon". Bell continued experimenting on this phenomenon (6) and found that such an effect could be realised with liquid and gas samples as well. He also inferred that this effect is due to the absorption of light, and proportional to the light intensity. Larger signals were produced from loose, porous materials, and those that have strong colors. Lampblack, the dark spongy solid gave a strong audible signal. Bell attempted to explain this phenomenon as follows:

"When a beam of sunlight falls upon the mass, the particles of lampblack are heated, and consequently expand, causing a contraction of the air-spaces or pores among them. Under these circumstances a pulse of air should be expelled, just as we would squeeze water out of a sponge. The force with which the air is expelled must be greatly increased by the expansion of the air itself, due to contact with the heated particles of lampblack. When the light is cut off, the converse process takes place. The lampblack particles cool and contract, thus enlarging the air spaces among them, and the enclosed air also becomes cool. Under these circumstances, a partial vacuum should be formed among the particles, and the outside air would then be absorbed as water is by a sponge when the pressure of the hand is removed. I imagine that in some such manner as this a wave of condensation is started in the atmosphere each time a beam of sunlight falls upon the lampblack, and a wave of rarefraction is originated when the light is cut off" (6).
However, the photophone effect remained for quite a while only a matter of scientific curiosity and the initial excitement of the discovery faded off soon. It was only about 50 years later, when sensitive microphones were available, that photoacoustic (PA) experiments were revived, but this time with only gaseous systems. Viengerov (11), Pfund (12) and Luft (13) were the first few pioneering workers in the field of gas phase PAS. Gorlik (14) was the first one to consider the possibility of extracting rate data from the phase of the PA signal. It was followed by Slobodskaya's (15) experimental realisation of obtaining the rates of energy transfer from the phase difference.

Although with gaseous samples the PA method appeared quite successful, it took a further 40 years for the 'rediscovery' of PA effect with solid samples. Though Bell's explanation of the PA effect is quite convincing, it turned out to be only partly true. Rosencwaig (1) considers that the explanations given by Mercadier (9) and Preece (10) were closer to the present day understanding of the effect. In the year 1973, Parker (16) observed a small signal from the cell windows in his gas PAS experiments and developed the theoretical basis for calculating the PA signal from transparent windows. Though Parker's theory was developed for a specific case, the modern theories for the PA effect have several common features with this theory.

1.4 Photoacoustic Effect - The Parker Theory

Parker (16) was investigating the collisional deactivation of singlet oxygen by the photophone technique. His system consisted of a closed high pressure gas cell with two windows and a microphone fixed on the side wall, half way between the ends of the cell, as shown in the Figure 1.1.
Figure 1.1 Cross-sectional view of Parker's Photoacoustic cell

$W_1$ and $W_2 =$ Cell windows; $M =$ Microphone.
Oxygen was contained in the cell and the pressure increase upon irradiation was monitored by the microphone. In the course of the study, it was observed that nonabsorbing gases like nitrogen and neon also gave strong audio signals. To isolate the source of the signal generation, Parker blocked the light entry into the cell by covering the front surface of the (side A) entrance window with a metal foil and found that there was no detectable signal. When the light entry was blocked by covering the same window, but from the rear surface (side B), one could detect a strong signal. Thus it was possible to recognise that the signal originates from the window, apparently due to heating caused by light absorption. Parker, subsequently carried out a theoretical analysis of this heat production and transport.

Heat equations can be applied to the glass (region I) and to the gas (region II) as

\[ -k_1 \nabla^2 T_1 + j_\omega \alpha C_1 T_1 = j_3 I_0 \]  

where \( K_1 \) is the thermal conductivity of the glass, \( C_1 \) is the specific heat per unit volume, \( j_\omega \) is the absorption coefficient and \( I_0 \) is the incident light intensity. In the region II, i.e., the gas phase,

\[ k_2 \nabla^2 T_2 - j_\omega C_{p2} T_2 = -j_\omega \alpha P_e \]

where \( K_2 \) is the thermal conductivity of the gas, \( C_{p2} \) is the specific heat at constant pressure per unit volume, and \( P_e \) is the differential pressure. The requirement of temperature and heat flux continuity defines the boundary conditions as:

\[ T_1 (c, t) = T_2 (0, t) \quad \& \quad k_1 \frac{dT_1}{dx} = k_2 \frac{dT_2}{dx} \]
Invoking the equation of state and imposing the boundary conditions, an expression for \( P_e \), the differential pressure, can be obtained in terms of the absorption coefficient, the intensity of the incident light, the modulation frequency, and the thermal properties.

\[
P_e \left( \frac{L}{2} \right) = -\left( \frac{\omega L}{k_1} \right)^{-1} \left( \frac{C_p}{C_v} \right)^{\frac{1}{2}} \left( \frac{\beta I_0}{C_1} \right)^{\frac{1}{2}}
\]

Equation 3 describes the differential pressure at the centre of the cell (the microphone is fixed mid way between the ends of the cell). This expression is derived with the assumption that \( \beta \), the optical absorption coefficient, is the same throughout the length of the window. \( P_e \) calculated from eq. 3 turned out to be much less than the experimental value. To account for this discrepancy, it was assumed that absorption at the surface is higher than that at the bulk, and that the heating must take place in a thin layer at the surface. The heat equations are altered accordingly and the expression for \( P_e \) is obtained as

\[
P_e \left( \frac{L}{2} \right) = -\frac{1}{2} \left( \frac{\omega L}{k_1} \right) \left( \frac{k_2 \rho_s}{k_1 C_1} \right)^{\frac{1}{2}} \beta_L I_0
\]

with \( \beta_L \), the absorption coefficient in a thin layer \( L \). Such an assumption gave a better agreement with the experimental value. In summary, the important features of the Parker theory are: 1. A thin layer of the sample absorbs light and converts it to heat; 2. the heat thus generated is communicated to the gas by thermal conduction; 3. the signal magnitude is predicted to vary as \( \omega^{-1} \) was so observed; 4. the role of the thermal properties of the filler gas on the signal is well described.
The Parker theory has been further extended to explicitly include the size of the PA cell and the finite thermal conductivity in the cell walls. The dependence of the PA spectrometer sensitivity to the cell size has been investigated; and the experimental results agree well with the extended Parker theory (17).

1.5 Photoacoustic effect; The Rosencwaig and Gersho (RG) theory (18):

When a sample is exposed to radiation of appropriate wavelength, optical excitation takes place. A molecule in its excited state has several options to return to ground state, the most general one being a nonradiative decay which deposits heat in the sample. The heat thus deposited diffuses to the sample surface and causes a small increase in the surface temperature. If the incident radiation is intensity modulated with a certain periodicity, the excitation, decay and the consequent surface temperature rise will also be modulated with the same periodicity. This periodic temperature changes at the surface will cause a thin layer of air surrounding it to expand and contract periodically, imposing a piston-like action on the rest of the gas in the cell; this leads to pressure oscillations in the closed cell. If the intensity modulation frequency is in the audiorange (say 40 Hz to 15 Khz), the resulting pressure oscillations can be measured by a gas microphone. The monitoring of this acoustic signal over a wavelength region of the incident light constitutes photoacoustic spectroscopy (PAS). A theoretical analysis of the PA effect can be divided into 3 stages. The first stage is an estimation of the heat deposited in the sample as a function of position and time, in terms of the optical absorption coefficient $\beta_i$ of the sample, the efficiency of the nonradiative decay $\gamma$ and the intensity of the incident radiation. The second stage is to set up and to solve the differential equations for the thermal diffusion from the
solid to the surface, to the backing material, and in the gas. The third stage is to calculate the volume changes in the thin layer of gas and the consequent pressure oscillations in the cell.

Rosencwaig and Gersho (18) use a one-dimensional heat flow model for the analysis in a cylindrical cell as given in Fig. 1.2. 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 that the microphone will detect the average pressure produced in the cell. The sample is considered to be in the form of a disk having a diameter D and length L. The length of the backing material is L, and the length of the gas column L, which is equal to L-L. The thermal diffusivity of the sample is defined as $\alpha = -k_i / \rho_i C_i$ where $k$ is the thermal conductivity of the material $i$. The damping of the heat waves is defined as thermal diffusion coefficient $a_i = (\omega/2\pi)$, where $CD$ is the modulation frequency. The inverse of the thermal diffusion coefficient $1/a_i$ gives the thermal diffusion length $\lambda_i$ in cm.

1.5.1 The production of heat: The heat produced in the sample is governed by the intensity of the incident radiation $I_o$, the optical absorption coefficient $\beta$ and the efficiency of the non radiative decay $\eta$: the expression for the heat density produced can be written as

$$H(x) = I_o \beta e^{\beta x} \eta$$

The intensity of the sinusoidally modulated monochromatic beam is given by

$$I = \frac{1}{2} I_o (1 + \cos \omega t)$$
Figure 1.2 Cross-sectional view of Photoacoustic cell (RG)

b = backing material, s = sample, g = gas column
where $I_0$ is the incident monochromatic light flux (watts/cm$^2$), and $\omega_5$ is the modulation frequency in radians. The heat density produced with the modulated light assuming $\eta = 1$, can be written as:

$$H(x, t) = \frac{1}{2} I_0 \beta e^{\beta x} (1 + \cos \omega t)$$

where $X$ takes on negative values since the soil extends from $x = 0$ to $x = -l$.

### 1.5.2 Thermal diffusion equations:

It follows from the Fourier heat conduction equation that the rate of change of temperature ($\partial \phi / \partial t$) is equal to the thermal diffusivity $\alpha_5$, times the derivative of the temperature gradient:

$$\frac{\partial^2 \phi}{\partial x^2} = \frac{1}{\alpha_5} \frac{\partial \phi}{\partial t}$$  \hspace{1cm} (8)

In the case of the PA effect the heat source is distributed in the soil; taking this distributed heat source into account thermal diffusion equation can be written as:

$$\frac{\partial^2 \phi}{\partial x^2} = \frac{1}{\alpha_b} \frac{\partial \phi}{\partial t} - A e^{\beta x} (1 + e^{i\omega t})$$ \hspace{1cm} (9)

Where $A = (\frac{\beta \tau_0 n}{2\alpha_5})$ and $\phi$ is the temperature. Similar equations can be written for the backing material and the gas, excluding the heat source term since there will be no light absorption and hence no heat production.

$$\frac{\partial^2 \phi}{\partial x^2} = \frac{1}{\alpha_b} \frac{\partial \phi}{\partial t} \hspace{1cm} -l - l_b \leq x \leq -l$$  \hspace{1cm} (10)

$$\frac{\partial^2 \phi}{\partial x^2} = \frac{1}{\alpha_g} \frac{\partial \phi}{\partial t} \hspace{1cm} 0 \leq x \leq l_g$$  \hspace{1cm} (11)

The real part of the complex valued solution of equation 9 to 11 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. These equations
are solved with appropriate boundary conditions, in terms of the optical and thermal properties of the sample. The explicit solution for $G$, the complex amplitude of the periodic temperature at the solid gas boundary, is given by:

$$\theta = \frac{\beta I_0}{2k_5(\beta^2 - \sigma_s^2)} \left\{ \frac{(r-1)(b+1)e^{\sigma_s l} - (r+1)(b-1)e^{-\sigma_s l} + 2(b-r)e^{-\beta l}}{(q+1)(b+1)e^{\sigma_s l} - (q-1)(b-1)e^{-\sigma_s l}} \right\} \quad \text{12}
$$

where $b = k_b a_b / k_s a_s$ ; $q = k_g a_g / k_s a_s$

$$r = (1 - j) \beta / 2a_s \quad ; \quad \sigma_s = (1 + j)a_s$$

Thus the above equations can be evaluated for specific parameters, 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 variations at the surface of the sample. The actual temperature at the surface as a function of time is given by:

$$T(0,t) = \Phi + \Theta_0 + \Theta_1 \cos \omega t - \Theta_2 \sin \omega t \quad \text{13}
$$

where $\Phi$ is the ambient temperature and $\Theta_0$ is the increase in temperature due to the steady state component of the absorbed heat.

1.5.3 Pressure oscillations: The temperature changes at the surface cause volume changes in a thin layer of gas surrounding it. This volume of air acts as a piston on the rest of the gas in the cell, resulting in pressure oscillations. The periodic temperature variations in the gas are given by the sinusoidal component of the solution (eq. 9 to 11)

$$\phi_{ac} = \theta \cdot e^{-\sigma_s} + j \omega t \quad \text{14}$$
It is shown, by plotting the real part of the solution of equation 14 as a function of $X$, that the thermal wave in the gas gets completely damped within a distance $2\pi \mu g$ from the surface of the sample. Hence the gas layer of thickness $2\pi \mu g$ can be considered as an acoustic piston. The displacement of this piston can be calculated from the spatially averaged temperature within $2\pi \mu g$ as a function of time and using the ideal gas laws. This spatially averaged temperature of the gas in the piston, as a function of time, is obtained by evaluating the integral

$$\Phi(t) = \frac{1}{2\pi \mu g} \int_0^{2\pi \mu g} \phi_{ac}(x,t) \, dx$$

substituting the solution for $\phi_{ac}(x,t)$, and integrating over the limits, one gets:

$$\Phi(t) = \frac{1}{2\pi \mu g} \cdot \Theta e^{j(\omega t - \pi/4)}$$

The displacement caused by this temperature change can be estimated by

$$\delta x = \frac{\Theta \mu g}{\sqrt{2} T_0} e^{j(\omega t - \pi/4)}$$

The rest of the gas responds to the action of the piston adiabatically. The acoustic pressure is derived from the adiabatic gas law $PV = K$,

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

where

$$Q = \frac{\rho_0 \Theta}{12 \mu g a T_0}$$

Thus $Q$ specifies the complex envelope of the sinusoidal pressure variation in the cell, which can be written as

$$G_1 = G_1 + jG_2 = Q e^{-j\psi}$$
where \( Q_1 \) and \( Q_2 \) are the real and imaginary parts of \( Q \), and \( q \) and \( \psi \) are the magnitude and phase of \( Q \). The complete expression for \( Q \) after substituting the expression for \( \theta \) is given by

\[
Q = \frac{\beta I_0 \gamma P_0}{2 \pi \kappa l q \alpha_0 T_0 (\beta^2 - \sigma^2)} \left\{ \frac{(\gamma-1)(b+1) e^{\sigma_0 l} - (\gamma+1)(b-1) e^{\sigma_0 l}}{(\gamma+1)(b+1) e^{\sigma_0 l} - (\gamma-1)(b-1) e^{\sigma_0 l}} \right\}
\]

Equation (21) may be evaluated for the magnitude and phase of the acoustic signal. The complexity of the expression for \( Q \) makes it difficult to get a physical insight of the phenomenon in terms of various parameters like \( J^3 \), \( \omega \) and \( \kappa \). These three parameters determine the optical absorption length \( \mu_3(J/\beta) \) and thermal diffusion length \( \mu_3[(\kappa/2\omega)^{1/2}] \) which in turn determine the PA signal phase and magnitude and their dependence on the modulation frequency \( OS \). Rosencwaig & Gersho have considered six special cases where the expression for \( Q \) can be made simple. Table 1.1 presents such simplified special cases.

1.6 Contribution of mechanical vibrations to the PA signal

Absorption of chopped light causes periodic heating in the sample: this causes the expansion and contraction of the sample itself depending on the thermal expansion coefficient of the sample. The simultaneous periodic heat flow to the gas also causes expansion and contraction within a thin boundary layer of gas next to the sample. The net pressure changes in the cell then can be attributed to the 'composite piston' which is the result of the superimposition of thermal and mechanical effects. McDonald and Wetsel, Jr. (19, 20) have considered this situation and extended the PA theory to include the contribution from the mechanical vibrations of the sample.
### TABLE 1.1

<table>
<thead>
<tr>
<th>Optical absorption length $\mu_a = \beta^{-1}$</th>
<th>Thermal diffusion length $\mu_s = (2\alpha/\omega)^{1/2}$</th>
<th>P.A. Intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Optically transparent</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(i) Thermally thin</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\mu_s &gt; L$; $\mu_s &gt; \mu_\beta$</td>
<td></td>
<td>$I_{PA} \propto \beta L$</td>
</tr>
<tr>
<td>(ii) Thermally thin</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\mu_s \geq L$; $\mu_s &lt; \mu_\beta$</td>
<td></td>
<td>$I_{PA} \propto \omega^{-1}$</td>
</tr>
<tr>
<td>(iii) Thermally thick</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\mu_s &lt; L$; $\mu_s &lt; \mu_\beta$</td>
<td></td>
<td>$I_{PA} \propto \beta \mu_s; \propto \omega^{-3/2}$</td>
</tr>
<tr>
<td>2. Optically Opaque</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(i) Thermally thin</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\mu_s \geq L$; $\mu_s &lt; \mu_\beta$</td>
<td></td>
<td>$I_{PA}$ Independent of $\beta$</td>
</tr>
<tr>
<td>(PA Saturation)</td>
<td></td>
<td>$I_{PA} \propto \omega^{-1}$</td>
</tr>
<tr>
<td>(ii) Thermally thick</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\mu_s \approx L$; $\mu_s &lt; \mu_\beta$</td>
<td></td>
<td>$I_{PA} \propto \mu_s; \propto \omega^{-3/2}$</td>
</tr>
<tr>
<td>(iii) Thermally thick</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\mu_s &lt; L$; $\mu_s &lt; \mu_\beta$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$\beta = \text{Optical absorption coefficient in cm}^{-1}$

$L = \text{Sample thickness}$

$\omega = \text{Modulation frequency}$

$\alpha = \text{Thermal diffusivity (=Thermal conductivity/density x specific heat)}$
The coupled equations are solved and the simplified expression for the gas pressure $P$ in the cell due to the combined effect of thermal and mechanical pistons for the thermally thick sample is obtained as:

$$P_g = - \frac{3 \tau_p \rho_c \sigma_c}{\omega l_q \rho_s \rho_p c_{ps}} \left[ \frac{\beta}{\sigma_q T_0 (q+1)(r+1)} + \beta_t (1 - e^{-\beta t}) \right]$$

where $\beta_t$ is the thermal expansion coefficient of the sample. The second term in the parentheses arises due to the mechanical vibrations. This treatment suggests that the acoustic coupling does not alter the linear relation between the PA signal and $\beta$, when $ft_i \ll 1$. The relative effect of coupling increases as $\omega_C^2$ if $\mu_\beta > \mu_s$. Increase in coupling effect with $\omega_C$ is due to the decrease in thermal diffusion length: only light absorbed within a thermal diffusion length can contribute to RG piston, whereas surface vibration is proportional to the total energy adsorbed in the sample. The relative contribution of the latter may be significant for thermally thick samples where $\mu_\beta > \mu_s$.

The composite piston model is applicable for liquids and solids. But, since the coefficient of thermal expansion is smaller for solids, the acoustic coupling becomes less significant. Nevertheless, including the acoustic coupling terms makes this theory more general and the interpretation of data becomes more accurate.

1.7 Effect of three dimensional heat flow

Both the RG and the McDonald and Wetsels' theories assume a one dimensional heat flow, which is found to be acceptable in most of the experimental situations. However, Powell et al. (21) and Quimby and Yen (22) have carried out experimental investigations and have observed departures
from the one-dimensional predictions, in regard to the frequency dependence of the PA signal and the phase change. Powell et al. (21) have observed a $\omega^{-\eta}$ dependence of the PA magnitude for a thermally thick sample where $n$ is less than $3/2$ and greater than $1$. Some theoretical ideas have been proposed by Quimby and Yen (23) and McDonald (24). McDonald has suggested that the one-dimensional model gives precisely the same result as that of the three-dimensional model provided the thermal waves, transverse to the incident beam, do not reach the cell wall. Quimby and Yen (23) also consider that the inclusion of the three-dimensional heat flow effect does not change the predicted PA signal, provided the thermal diffusion length in the gas is much less than the radius of the sample chamber.

Chow (25) has developed a rigorous theory of the three-dimensional photoacoustic effect, which imposes no restriction on the size of the sample, the geometry and the beam profile. For sufficiently high modulation frequencies, or for samples with large lateral dimensions, this signal is found to be smaller than its one-dimensional counterpart. Departure from one-dimensional theoretical predictions occur at modulation frequencies for which the thermal diffusion length of the gas is of the order of the lateral dimension of the sample. Beam spot size plays a relatively insignificant role in affecting the signal. McDonald (26) has extended the three-dimensional heat flow treatment to a situation in which thermal conduction to the side walls may be insignificant. The effect of this is to cause a decrease in the PA signal, when compared to the one-dimensional model, or to the three-dimensional model with the assumption that thermal waves do not reach the cell wall. Chow, in a latter publication (27), has presented a detailed study on the modulation frequency dependence of the PA signal in one-dimensional and three-dimensional cases.
McDonald (28, 29) has shown that PA signal is accurately given by one-dimensional model for short, wide cells, viz., cells with dimensions small compared to the acoustic wavelength, and radius large enough to avoid any appreciable thermal transport to the side wall.

1.8 Theoretical aspects of some nonconventional PA experiments

From the foregoing, it can be seen that the theory of PA signal generation is fairly well understood. In this section we describe briefly the theoretical aspects of a few nonconventional PA experiments which interest us.

1.8.1. Nonradiative lifetime measurements: PA signal originates after the decay of the excited state, and thus the delay between excitation and signal contains information regarding nonradiative lifetime. The relaxation times associated with radiationless decay processes have been studied using frequency domain PAS by Powell et al. (30-32) and the lifetime is calculated from the expression

\[ \tau = \tan \psi \]

The validity of this expression for solids is very limited. Mandelis and Royce (33) have developed theoretical treatment for time domain PAS. Aamodt and Murphy (34) have also considered excited state lifetime in their treatments for the time domain PAS. Royce and Mandelis (35) use one-dimensional model similar to that of RG and derive an expression for spatial and temporal temperature distribution in the gas, including the finite excited-state relaxation time in the sample.
A complex expression for the pressure change in the cell for a modulated light source is obtained, which shows that the phase depends on the optical absorption coefficient, the physical dimensions of the sample, the ratio of thermal properties of the sample and the gas, and the relaxation time. In the case of a thermally thick and optically opaque sample, the expression can be simplified to

$$\psi (T, \omega) \approx \frac{\pi}{4} + \tan^{-1} \left( \omega \tau \right)$$

which can be used to calculate $\tau$. The expression for the time-dependent temperature variation at the surface and the pressure in the cell are obtained for pulsed excitation. The plots of the computed pressure as a function of time show an inflection point at $t = T$, provided $\tau$, the lifetime, is short compared to the thermal transit time of the cell, but long compared to $\tau_p$, the duration of the pulse. This expression can be used to measure the relaxation times only after accounting for the transfer function of the microphone, which relates the electric output of the microphone to the pressure. Mandelis and Royce (33) have considered these effects and suggested a limitation on the range of the existed state lifetime measurements, the range being between $10^{-5}, 10^{-1}$ sec. However it may be possible to improve this by using a Piezo electric detector.

Malkin and Cahen have considered one and two step photochemical processes, with special emphasis on photosynthesis in green plants. The in phase component of the signal as a function of $\omega$ (in Hz) shows an inflection point, while quadrature component maximises at $\omega$ corresponding to the rate constant of the process: rate of the process equals to $\omega^{-1}(36)$. 


1.8.2 Quantitative PAS: One of the major drawbacks of the PAS technique is the difficulty in quantification. As it can be seen, the PA signal depends, apart from \( \beta \), on sample dimensions, and thermal properties of the sample and the coupling gas (and sometimes on the backing material). Empirical quantification methods (determining the standard plot for certain set of conditions and using it for determining the concentration of unknown samples under identical conditions) have met with reasonable success (37-45). Monahan and Nolle (46) have undertaken a systematic study of the dependence of PA signal on the optical absorption coefficient \( \beta \), with a known uniform particle size. They have shown that the PA signal is proportional to \( \beta \) if the sample is thermally thick and optically nontransparent. When the sample is thermally thin, Melamed's analysis of diffuse reflection absorption is to be applied for getting the correct \( \beta \) value. Many researchers could obtain the optical absorption coefficient by measuring PA signal as a function of \( \Theta \) (e.g. see 47-49).

Bennett and Forman (50) have shown that the phase lag between the PA signal with respect to light modulation can be used to distinguish surface and bulk absorption coefficients. As \( \beta \) increases, light penetration into the sample will decrease, and hence the heat deposited will be nearer to the surface. The time taken for this heat to diffuse to surface will be less, causing a decreased phase lag when compared to the phase lag obtained with the sample with low \( \beta \) • Roark et al. (51) have used the phase data to compute quantitative absorption spectra. They obtain, for thermally thick samples,

\[
\Psi = \tan^{-1} \left[ \frac{-B^3 + 2B - 4}{B^3 - 2B^2 - 2B} \right]
\]
where \( B = \beta \mu_s \). This equation enables one to calculate \( \beta \) (if the \( \mu_s \) is known) from \( \psi \). This equation gives satisfactory results even for samples with very high \( \beta \) values. It was noted that measured phase angle differs from theoretical one due to various problems associated with phase measurement. The experimentally determined phase lag, \( \psi_{exp} \), can be written as

\[
\psi = \psi_{th} + \psi_{app}
\]

\( \psi_{th} \) is obtained by measuring \( \psi_{exp} \) for a sample whose optical absorption is known. The PA phase angle spectrum is recorded for 0.2 M Fe\( \text{(bipy)}_3 \text{Br}_2 \) solution and \( \beta(\lambda) \) computed according to the equation 25. The computed \( \beta(\lambda) \) spectrum, at all modulation frequencies, agrees very well with the transmission data.

Poulet et al. (52) have developed a theoretical model within the framework of the RG theory and obtained an expression for the phase of the PA signal in terms of \( \beta \mu_s \) as

\[
\psi = -\pi + \tan^{-1}(\beta \mu_s 1)
\]

These authors also have realised that the experimental phase angle and theoretical value differ as:

\[
\psi_{exp} = \psi_{th} + \psi_{app}
\]

\( \psi_{app} \) is attributed to the three-dimensional heat flow and is estimated from the phase lag produced by a black body \((\beta \mu_s \gg 1)\) in which case \( \psi_{exp} \) is given by
Mechanical coupling suggested by McDonald and Wetsel (19, 20) complicates the situation at low $\beta$ values. For the samples with $\beta \mu_s < 1$ the present theory gives values of $\beta$, which are far from the experimental values. These authors suggest the use of the amplitude of the product of the PA signal and $\omega$ (i.e. $\Delta P(t) \omega$) for low values of $\beta \mu_s$ and phase of $\Delta P(t) \omega$ for high values of $\beta \mu_s$.

Teng and Royce (53) have used the magnitude data to compute the correction term, which can be used to calculate the correct phase angle $\psi(\beta)$. This $\psi'(\beta)$ can be used to compute $\beta(\lambda)$.

The optical absorption spectrum, i.e. $\beta(\lambda)$, is obtained from the measured phase and amplitude for 0.6 M potassium permanganate solutions, in the range of 300-600 nm. The spectrum thus obtained agrees well with the transmission spectrum. This method needs only a single scan at one modulation frequency, and no auxiliary measurement of $\beta$ at a chosen wavelength is necessary.

Burggraf and Leyden (54) have combined the phase and magnitude information to arrive at a combined response function given as

$$C \beta \mu_s = \frac{\sqrt{2} q_n}{\sin(\psi - \pi/4)}$$

where $C$ is a constant that depends on the thermal properties of the sample and gas. Thus by measuring $q_n$ and $\psi$ it is possible to measure $\beta$ provided $\mu_s$ and $C$ are known. This treatment has also been extended to include light scattering in particulate samples, by considering the light distribution in the sample.
From the foregoing, it appears that an adequate theory exists for quantitative PAS. But in all cases, the samples were assumed to be thermally thick and optically non-transparent. These assumptions are seldom valid in case of powder samples, where the particle diameter may become much smaller than $\mu$ or $\mu_5$.

We believe that the phase lag due to nonradiative relaxation should also be considered when one measures $\beta$ from $\psi$. Though this contribution is negligibly small, it is necessary for generalizing the theory and to interpret the data more precisely.

$$\psi_2 = \psi_{\gamma} + \psi_{\beta} + \psi_{\gamma}$$

where $\psi_{\gamma}$ is the experimental phase lag, $\psi_{\gamma}$ the phase lag due to the instrument, $\psi_{\beta}$ due to the finite nonradiative relaxation time, and $\psi_{\gamma}$ due to the optical absorption coefficient. The contribution of $\psi_{\beta}$ to $\psi_{\gamma}$ is recognised and accounted for by Royce et al. in deriving the expression for lifetimes in the time domain PAS. But in all the attempts to obtain $\beta$ from $\psi$, the contribution of $\psi_{\beta}$ is neglected. Though this is acceptable in many a case, there are, however, some instances where $\psi_{\beta}$ is not negligible. We have observed that the $\psi$ of naphthalene is altered significantly when benzophenone is added (optical absorption of benzophenone at the chosen wavelength is negligible). It could be due to the rapid and efficient energy transfer from the naphthalene singlet $S_1$ state to the benzophenone triplet ($T_1$) state, which relaxes to ground state slowly, leading to the increased phase lag. This observation points out the necessity of incorporating the $\psi_{\beta}$ term in the expression for $\psi_{\gamma}$, especially if an energy transfer phenomenon is under study. The difficulties associated with measuring accurate phase lag mask the significance of $\psi_{\beta}$ contribution to $\psi$. 
1.8.3 Dichroism measurements: If the sample is optically anisotropic, one can use polarized radiation to study the linear dichroism of the sample by PA method. We have incorporated a polarizer in the light path of the PA spectrometer which enabled us to obtain linearly polarized PA spectra. The details are discussed later in this thesis in Chapter 3. Fournier et al. (55) have constructed a PA spectrometer to measure linear and circular dichroic PA spectra of samples. In this system, light exhibits a periodic change of its polarization instead of intensity. PA signal then becomes proportional to $\Delta \beta = \beta_t - \beta_\perp$, where $\beta_t$ and $\beta_\perp$ are the absorption coefficients for the two orthogonal polarizations. They have demonstrated the performance of the setup by recording linear dichroic and magnetic circular dichroic spectra of a NdMoO$_4$ single crystal. The polarization modulation frequency was 300 Hz for linear dichroism and 3000 Hz for circular dichroism. Saxe et al. (56) have presented a theoretical analysis of the circular differential PA effect (CDPA). A polarization modulated beam may be considered as the superimposition of two intensity modulated beams which are phase shifted by 180°. Thus it is possible to treat the CDPA effect in terms of the superimposition of two conventional PA experiments, and the pressure changes in the cell $\Delta P(t)$ is given by:

$$\Delta P(t) = \Delta P_L(t) + \Delta P_R(t)$$

where

$$\Delta P_L = Re \left\{ Q_L \phi_L e^{i(\omega t - \frac{1}{4} \pi)} \right\}$$

and

$$\Delta P_R = Re \left\{ Q_R e^{i(\omega t - \frac{1}{4} \pi)} \right\}$$
These can be combined to write

\[ \Delta P(t) = \text{Re} \left\{ \Delta Q e^{j(\omega t - \phi \pi)} \right\} \]

where, \( \Delta Q = Q_L - Q_R \).

\( Q_L \) and \( Q_R \) both independently are equal to the value of \( Q \) given by the RG theory. Hence

\[ \Delta Q = \Delta Q_1 + j\Delta Q_2 \]

and the PA signal

\[ AP(t) = \Delta q e \]

The expression for \( \Delta Q \) is obtained from RG analysis and six limited cases as described by RG are considered. It was shown that in all the six cases \( AP(t) \) is proportional to \( \Delta \beta \), i.e., \( \beta_L - \beta_R \). Thus CDPAS can be used to obtain the CD spectrum of virtually any sample. The modulation frequency dependence of the signal can be used to further characterize the sample in terms of its thermal parameters. The signal varies as \( \omega^{-1} \) for optically transparent and thermally thin samples and as \( \omega \) for thermally thick samples. In the case of optically opaque samples, \( \omega \) dependence is expected for thermally thin samples and \( \omega^2 \) dependence for thermally thick samples. Fournier's sample (55) falls into the optically and thermally thick case and indeed shows \( \omega^{-3/2} \) dependence. CDPAS is expected to be extremely useful in the study of the conformation of membrane-bound proteins and similar matrix-embeded systems.
1.9 Developments in Experimental Techniques

Photoacoustics and photoacoustic spectroscopy are finding increasing applications in a wide variety of research and industrial problems. This has been mainly due to a better understanding of the technique and improvements in the experimental techniques. We briefly describe some of the significant improvements in the experimental techniques.

The detector for Bell's first PA experiment was the human ear, while the light source was the sun. The advent of sensitive microphones nearly half a century later has made PAS of gases more attractive. The PAS of gases is fairly well understood and is being extensively used. In regard to its experimental aspects, PAS has two major advantages over other spectral techniques. Firstly the PA signal is proportional to the intensity of incident radiation and hence the signal can be increased to very high levels, provided the sample is not photodamaged. The problem of detecting a small difference between large signals does not arise in PAS. Secondly the technique is not detector-limited, and can therefore be extended to some other parts of the electromagnetic spectrum with ease. There are significant developments in these two aspects. Tungsten lamps are replaced by high pressure arc lamps. With the advent of laser sources, the sensitivity of the technique has been greatly enhanced (for example see 44, 45, 57, 58). Horduik and Schlossberg (59) were the first to utilise a strain transducer directly in contact with the solid sample. They have used a PZT-5H piezoelectric device, a laser for light source and could detect optical absorption coefficients of $1 \times 10^{-5}$ to $10^{-6}$ cm, a truly enhanced sensitivity. They have also developed a theory to derive the functional dependence of the strain generated by light absorption. Wetsel (60) and Eyring et al. (61) have also considered the theoretical schemes for
piezoelectric PAS. Jackson and Amer (62) have developed the theory for piezoelectric PAS of condensed matter and experimentally verified their theoretical predictions. Tam and Patel (63) have used a pulsed dye laser, a piezoelectric transducer directly coupled to the sample, and gated PA detection. With this system the weak visible absorption band of benzene near 607 nm has been detected, and the sensitivity limit goes down to $10^{-7}$ cm$^{-1}$. Low temperature PAS (at 77° K) has been reported by Aamodt and Murphy (64), who dipped the whole PA cell in liquid nitrogen. A microphone which is kept outside is coupled to the cell by a narrow channel. Robin and Kuebler (65), Smith and Laguna (66) and Videl (67) have carried out of PA measurements at liquid helium temperatures while Durgaryan and Fahim have developed a PA cell for high temperature studies (68). A very high sensitivity superconducting microphone for low temperatures is a significant development towards low temperature PAS (69).

Boccara et al. (70) have developed a thermo-optical method wherein the microphone is replaced by a probe beam. The periodic temperature gradient in the gas near the surface of the sample gives rise to a refractive index gradient suitable for periodically deflecting a probe beam propagating along the surface of the sample. The magnitude of this deflection is proportional to the optical absorption in the sample and depends on the thermal properties of the sample and the gas. This has been termed as detection by the mirage effect.

In regard to the second aspect, namely, the possibility to extend to other regions of electromagnetic spectrum, some important developments are IRPAS, PA detection of micro wave absorption and PA Raman spectroscopy.
Low and Parodi (71) have carried out PA studies in infrared region. Fourier transform techniques have been developed for PAS in IR region to overcome the problems associated with the availability of intense IR sources (72-75). The detection of ferromagnetic resonance (FMR) in films of Fe, by the PA method was first reported by Nunes et al. (76). They have monitored the microphone signal while the sample was exposed to chopped microwave radiation of \( 11.6 \, \mu \text{T} \). The variation of the microphone signal as a function of the external magnetic field gives the FMR. Similar studies on Fe and Ni films using a Helmholtz resonant cell has also been reported (77), and paramagnetic resonance of DPPH (diphenyl-\( \beta \)-picryl-hydroxy-hydroxyl) crystals has been detected by the PA method (78). The piezoelectric and photothermal detection methods have also been introduced to enhance the sensitivity (79). Netzelmann et al. (80) have adopted a pulsed excitation mode for detecting EPR signals. The sensitivity of the PA method for detecting paramagnetic resonance is not greater than the conventional methods, but this method offers a depth profiling of paramagnetic species in the sample, which is not possible by conventional methods.

It has also been possible to carry out Raman spectroscopy of gaseous methane by the PA method (81). A laser beam of 514.5 nm wavelength (\( \omega_p \)) is chopped at 573 Hz and focussed in to the PA cell which contains methane gas. Another laser beam (\( \omega_s \)), is also focussed in to the PA cell, where the beams superimpose. \( \omega_s \) is chosen so as to make \( \omega_p - \omega_s = \Delta \omega = 2916.7 \, \text{cm}^{-1} \) (\( \nu_s \), symmetric stretch of methane). The PA signal was detected by the lock-in analyser tuned to 573 Hz; while \( \omega_p \) causes pulsed excitation due to chopping, \( \omega_s \) will stimulate the Raman scattering. The PA signal is detected only when \( \omega_s \) precisely equals \( \omega_p - \Delta \omega \). Thus monitoring the PA signal by scanning the \( \omega_s \) one obtains the Raman spectrum.
Wong et al. (82) have developed the scanning PA microscopy method. An intense laser beam is focussed to a point of diameter 30 μ and the PA signal is recorded as the beam scans the surface. Repeated scans, with the beam translation, will give the image of the sample. Important features of this technique are: it is non-destructive, locates chromophores of different characteristic absorption wavelengths, and a depth profiling of chromophore is possible by adding the third dimension, i.e. the modulation frequency. A high laser power density at the small point of excitation is necessary for a good signal to noise ratio, this requirement can be overcome by adopting the Hadamard transform technique (83).

Fourier transform PAS is a successful combination of the Bell's photoacoustic effect (1881) and Michelson's interferometer (1882) that was achieved in the year 1978. The recombined beam from the two arms of the interferometer may be in phase or out of phase, depending on the optical path difference achieved by translation of one of the mirrors. Each frequency comes in and out of phase at a characteristic optical path difference and the superimposition of all frequencies produces interferogram. The equivalent of an interferogram results if the beam is allowed to impinge on the PA cell and the PA signal is recorded as a function of optical path difference. This, upon Fourier transforming, gives the PA spectrum (uncorrected).

The output from the Michelson interferometer is focussed on to a PA cell. The PA signal is collected as a function of the path difference (which is twice the difference between the distance of the two mirrors from the beam splitters). This constitutes the interferogram.

\[ PA_{x} = \int_{\lambda}^{\infty} PA(\lambda) \cos(2\pi x \lambda) d\lambda \]
where $PA_0$ is the signal strength at wavelength $\lambda$ and $PA(x)$ the observed signal at a path difference $(x)$. This upon inverting gives the spectral distribution of $PA(\lambda)$, as:

$$PA_0 = \int_0^X PA(x) \cos(2\pi x \lambda) \, dx$$

The detected $PA_0$ signal is due to the composite effects of the spectral distribution at that $(x)$. Thus, FTPA spectrum is obtained after collecting $PA(x)$ at various discrete $X$ values, and transforming the data to $PA(\lambda)$. To achieve sampling at exact spacings in $x$, another interferometer is used, one arm of which is common with the source interferometer. The fringes from the second interferometer provide the trigger pulses for sampling. Farrow et al. (84) have reported the FTPAS for solids in the visible range using such a device.

Recently, single pulse PA technique has also been developed (85-86). The PA effect in water, using nanosecond and picosecond laser pulses has been reported by Sladky et al. (87). PA detection of nanosecond pulse-induced optical absorption (88, 89) and time resolved PAS in the picosecond region (90) are some of the significant developments in the time domain PA technique.

### 1.10 Instruments used in this study

We have used two commercial instruments in the present study, with some modifications and improvements in each, in order to suit our purposes.

#### 1.10.1 P.A.R. model 6001 Spectrometer: The EG&G Princeton Applied Research, model 6001 photoacoustic spectrometer, that we have used in our studies uses a 1 KW high pressure xenon arc lamp as the source in the uv, visible and
near infrared regions. The lamp current is sinusoidally modulated at a set frequency (40-2000 Hz) to achieve intensity modulation. The modulated light, reflected by an ellipsoidal reflector enters the grating monochromator through an entrance slit. Three concave holographic gratings, one each for the uv, visible and the near infrared regions, are mounted on a turret. The dispersion of the gratings used in the 200-800 nm region is 0.25 mm/nm, while the grating used in the region above 800 nm has a dispersion of 0.0625 mm/nm. Thus the minimum spectral bandwidth in the region below 800 nm is 2 nm with a 0.5 mm slit width, and 16 nm with a 4 mm slitwidth. The output from the monochromator passes through an order filter and is focussed on the sample by an off axis ellipsoidal reflector. About 8% of the beam is reflected back on to the centre of the reflector where the pyroelectric detector is located. The PA cell consists of an outer jacket with a fused silica window and a fused silica sample holder with a rectangular sample tray (4 mm x 8 mm x 2 mm), and coupled to a microphone. The preamplified signal from the microphone, is fed to a dual phase lock-in-amplifier, while the preamplified signal from pyroelectric detector is similarly fed to another dual phase lock-in-amplifier. A voltage controlled oscillator gives a sine wave at a set frequency, which is applied to the current modulator and to the lock-in amplifiers as the reference signal through a phase shifter which allows a phase shift of the reference signal with respect to the modulation signal through 360° in steps of 0.1°. The pyroelectric detector signal is used to compensate for the spectral distribution of the source intensity as well as for a real time correction for temporal fluctuation.
The inphase and quadrature components from the lock-in amplifiers are digitized by a 14 bit ADC and stored. A TMS 9900 microprocessor is used to carry out the computations and system controlling. It is possible to record the phase and magnitude of the signal as well as inphase and quadrature components separately (Figure 1.3).

The reference signal for the lock-in amplifier in the model 6001 spectrometer is derived from the voltage controlled oscillator, and the same signal is applied to the lamp current modulator. With this configuration it is possible to acquire correct magnitude spectra at any frequency. However, correct measurements of phase angle, and the magnitude of in phase and the quadrature components is possible only if there is no lag between the modulation of the lamp current and the lamp output. It can be safely assumed that the pyroelectric detector outputs the signal in phase with the modulation of the light intensity striking it. Thus it is possible to monitor the lag between the lamp current and the lamp output by measuring the phase lag between reference signal and pyroelectric signal. Figure 1.4 shows the plot of the phase as a function of the modulation frequency. It can be seen that this phase lag is appreciable even at 40 Hz and becomes very high at higher frequencies. This plot can be used to correct the measured phase angles. The correct phase angle is given by the sum of measured phase at a given frequency $\phi$ and the phase of pyroelectric signal at the same $\phi$.

We have incorporated an oriel uv standard polarizer (model no. 2540-2) mounted on a three axis precision rotator (model no. 1641) into the light path of the model 6001 PA spectrometer. Two separate spectra were recorded for orthogonal polarizations, the dichroism can be computed from this data.
Figure 1.3 Schematic diagram of PAR 6001 Photoacoustic Spectrometer
L = Lamp; M = Monochromator; C = Cell; VCO = Voltage controlled oscillator; PS = Phase shifter; LA = Lock-in-amplifier; P = Plotter;
IN = Input parameters; SC = System control; MIC = Microphone
MOD = Modulator.
Figure 1.4
Phase angle as a function of modulation frequency for the sample carbon black
Unfortunately, polarization of the beam is a common feature of many reflection optics. In the case of an optically isotropic sample, polarization in the monochromator makes very little or no difference. But for optically unisotropic samples the recorded spectrum depends on the optical absorption coefficient \( \beta(\lambda) \) and monochromator polarization \( P \), which is also wavelength dependent parameter. We have been able to obtain \( \beta(\lambda) \) by recording the source-compensated spectra for carbon black samples with orthogonal polarizations. An experimental situation encountered is described in Chapter 3.

In this instrument, two 12-bit digital-to-analog converters convert the digital memory contents to analog signals that drive the X, Y recorder; thus a monitoring of the signal with time is not possible. However, since one can extract the X and Y output from the instrument, we incorporated a Hitachi model 056-4006 stripchart recorder and could monitor the time profile of the signal. The example of a solid state photoreaction in this connection is described in Chapter 3.

1.10.2 EDT OAS 400 Spectrometer: The other commercial instrument used is the model OAS 400 made by Edt research, England. This is also a single beam PA spectrometer and employs a 300 W high-pressure short-arc xenon lamp with an integral parabolic reflector and a sapphire window. Radiation from the xenon source is focussed onto the plane of rotation of the chopper, which choppes the radiation at preset frequencies of 10, 20, 40, 80, 160 and 240 Hz. The monochromator employs two plane holographic gratings, one for the uv and visible region (1200 lines/mm) and the other for the near infrared region (300 lines/mm). The minimum spectral bandwidth below 800 nm at 0.5 mm slit is 2 nm. Fraction of the light is reflected onto the pyroelectric
detector while the remaining light impinges on the sample. The PA cell consists of a metal jacket with a fused silica window and incorporates a microphone and its preamplifier circuit. The sample holder is made of aluminium with a sample tray whose dimensions are 15 mm x 5 mm x 2 mm. The signal from the microphone is preamplified and fed to tuned amplifiers, the output of which is fed to a single phase lock-in-amplifier. The resultant output is ratioed against the pyroelectrical signal similarly treated, but without lock-in-detection. The ratioed signal is plotted against the wavelength in the manual operation mode. The OAS 400 also uses a CBM 4032 microcomputer along with a CBM 4020 dual floppy disc drive; in this computer assisted mode, the signal is digitised and sent to the computer through an IEEE 488 interface. Normalization of the spectra with a pre-recorded carbon black spectrum is necessary in this mode. This is because only the lock-in-output without ratioing against the pyroelectric signal is sent to the computer to avoid the problem of reference overloading around 750 nm. Thus on the OAS 400 spectrometer, with a CBM 4032 computer, it is possible to acquire the signal at one of the six frequencies at the set phase angle. Maximizing the signal at the peak absorption of the sample is recommended but this cannot be acceptable over a wide wavelength region, since phase angle is also a wavelength dependent parameter. In order to obtain a normalized magnitude spectrum, one has to acquire the spectrum in the required range with the phase set to 0° and store the data and then acquire the spectrum without altering any parameters, except setting the phase to 90° and store the data. Then one needs to compute the magnitude spectrum from the stored inphase (0°) and quadrature (90°) components, and normalize this with the carbonblack spectrum previously computed in the same way. The phase can be computed by taking the inverse tangent of the ratio of quadrature to inphase signals ( \( \tan^{-1} Q/I_n \) ), with a phase accuracy of about ± 3°.
And, acquiring the inphase or quadrature signal is not possible if the signal is negative with respect to the ground. To abviate these drawbacks, we have incorporated an absolute value operator circuit (figure 1.5) after the lock-in-amplifier and before the AD converter. This has enabled us to acquire the absolute value of the signal irrespective of its sign. (Since the computation of magnitude requires squaring the components, dropping the sign does not alter the magnitude data). In order to improve the sensitivity, phase resolution and to overcome the various problems mentioned earlier, we have incorporated a few more modifications in the OAS 400, as shown in figure 1.6. Firstly the pyroelectric detector is disengaged and the output from the microphone preamplifier is fed into a EG&G PAR dual phase lock-in-amplifier level. The output of the 5206 lock-in-analyzer is connected to the input of AD converter through the absolute value operator circuit. A high resolution graphics board is installed in the CBM 4032 in order to achieve a graphic display of the spectrum, and the entire system controlling software rewritten. With these modifications on line display of the normalized, magnitude spectrum was made possible, with several other improvements. Table 1.2 compares the performance of the OAS 400 spectrometer before and after our modifications.

Photoacoustics and photoacoustic spectroscopy are still in their formative stages. We hope that the next few years promise to be an exciting period of growth for the rediscovered spectroscopy.
Figure 1.5 Absolute value operator circuit

IC₁ and IC₂ = 741; R₁ = R₂ = R₄ = R₅ = 10 KΩ
R₃ = 5 KΩ; D₁ = D₂ IN 4001.
Figure 1.6 Schematic diagram of Edt OAS 400 Photoacoustic Spectrometer

L = Lamp; C = Chopper; M = Monochromator; BS = Beam splitter
TA = Tuned amplifier; R = Ratiometer; LA = Lock-in-amplifier
AO = Absolute value operator; HGR&S = High resolution graphics and system software; FL = Floppy disk drive. Dotted lines indicate our modifications.
| **TABLE 1.2** COMPARISON OF THE PERFORMANCE OF OAS 400 SPECTROMETER  
BEFORE AND AFTER MODIFICATIONS |
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<tr>
<td><strong>Before Modification</strong></td>
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<tr>
<td>1. It is possible to acquire signal at a preset phase (i.e. inphase or quadrature only one component at a time), provided the signal is not negative.</td>
</tr>
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| 2. Phase resolution is ± 3.0° (approx.)  
Phase setting: continuously variable, marking at 5° interval | 2. Phase resolution is ± 0.1°  
Phase setting: in steps of 0.025° |
| 3. Sensitivity maximum: 10 μA full scale | 3. Sensitivity: maximum 100 μA full scale |
| 4. Normalization to be done after acquiring and computing magnitude data by pre-recorded carbon black magnitude spectrum. | 4. On line normalization with pre-recorded carbon black magnitude spectrum. |
| 5. Displays spectral data in numbers. Intensity data displayed are only of one component of the signal along with the source spectral distribution. | 5. Graphic display of the (320 x 200 resolution) normalized magnitude spectrum. |
| 6. Minimum time required for recording a magnitude spectrum (in the range 200-800 nm) is 24 min. (+ computation time) | 6. Minimum time required is 3 min including computation time. |
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