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# PHOTOACOUSTIC SPECTROSCOPY OF CONDENSED MATTER

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## INTRODUCTION

The opto- or photo-acoustic effect was first observed by A.G.Bell in 1880(1).He found(2)that a modulated beam of electromagnetic radiation falling upon a solid inside a constant closed-volume gas cell can give rise to an acoustic wave.In this effect,the modulated electromagnetic radiation absorbed by the specimen is partially or fully converted into the kinetic energy of the molecules of the solid which in turn give rise to periodic pressure fluctuations within the gas cell.Photo-acoustic experiments on gases were reported by Tyndall(3)&Roentgen(4).

No further work was carried out until fifty odd years elapsed before further experiments were carried out by Veingerov(5)who used the effect to study infrared absorption in gases.Following the end of World War Second there was an increased activity in the photoacoustic spectroscopy of gases which is well documented in various reviews by Delany,Read and Colles et.al.(6,7,8).The introduction of laser as an optical source has enhanced the sensitivity of the photoacoustic spectrometer and has led to the development of a very sensitive air pollution monitor(9,10).

Despite Bell's initial experiments on condensed matter and the thorough development of the technique for gases,the photoacoustic effect in solids did not receive further attention until 1973(Rosencwaig(11)).The photoacoustic technique has now become a recognized tool for studying the optical and thermal properties of condensed matter for it possesses a number of advantages over the conventional absorption or reflectance spectroscopy(12).

## THEORY OF PHOTOACOUSTIC EFFECT IN CONDENSED MATTER

While studying the various materials Bell noted that,

"The loudest sounds are produced for substances in a loose,porous, spongy conditions and from those that the darkest or most absorbing colours" (Ref.2 p.515)

In order to explain these results,he postulated that cyclic expultion and re-adsorption of the air within the pores takes place following the periodic heating of the solid.For a solid in the form of a very thin disc Bell supported Rayleigh's theory which attributed the main source of sound to the mechanical vibrations of the disc arising from unequal heating(13).

Mercadier(14)also studied the phenomenon at the same time and concluded that the photoacoustic effect is a surface effect resulting from the direct action of the incident radiation and the amplitude of the acoustic signal is dependent on the intensity of the incident radiation. Preece(15)reached the similar conclution that acoustic signal is produced by the absorption of radiations by the solid and subsequent radiation of heat rays to the confined gas causing volume changes. Although the conclusions of Mercadier and Preece are very close to modern theories but lack the mathematical formulation.

A most common geometrical configuration of the photoacoustic cell is the cylinder ABCD shown in figure 1.The specimen is in the form of a disc having diameter "d" and thickness $l_s$.Theoretically it is generally assumed that $d \gg l_s$ i.e. the heat flux in the sample can be taken as one-dimensional.

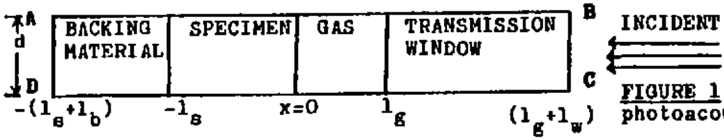


FIGURE 1:-Geometry of photoacoustic cell.

Rosencwaig-Gersho Theory:-This theory(16) assumes that the window is a perfect transmitter of the incident radiation and that the main source of the acoustic signal is the periodic heating of the solid by the modulated radiation.The periodic heat flow causes expansion and contraction of a thin layer of gas(of thickness the order of the thermal diffusion length)at the solid-gas boundary which acts as an acoustic piston for the rest of gas column and generates the photoacoustic signal.Although a simplified form of the general transport equation was used for gas region,the expression for the pressure variation within the cell is still complicated.However the solution for certain limiting cases indicates that the photoacoustic signal can be expressed in terms of the optical absorption coefficient of the specimen,modulation frequency,linear dimensions and thermal properties of the specimen and the gas.The calculated theoretical results for the magnitude and phase of the photoacoustic signal are in good agreement with the experimental data.This theory is widely used to interpret experimental results.

Afromowitz,Yeh and Yee(17) have successfully applied this theory to a layered medium.

Aamodt,Murphy and Parker Theory:-This model is based on the earlier work of Parker(18) and employs a more complete form of thermal transport equation taking into account the finite velocity of sound.An extension of Parker theory is used by AMP(19) to study the dependence of photoacoustic signal on the physical dimensions of a cell when the size was larger or smaller than the gas thermal diffusion length.In both cases the results depend on thermal properties of the gas and the sample.For the case of a large cell,the conclusions of AMP theory agrees with the simple Rosencwaig-Gersho(RG)model.

Generalized Theory:-This model as proposed by McDonald and Wetsel(20) takes into account the thermally generated mechanical vibrations of the sample.The coupled equations of fluid mechanics for thermal and acoustic waves are solved for the specimen and gas.It is found that the photoacoustic signal significantly depends on the mechanical vibrations of the solid in certain regions of modulation frequency and optical absorption coefficient.For the range of parameters generally encountered in PAS work this model is in reasonable agreement with RG model.

Bennett and Forman(21) used laser as energy source and introduced the effect of viscosity into their calculations.Although the above one-dimensional models give good agreement with the experimental data,but in some cases these models are not adequate.Therefore there is a need for a theory which can be applied to most practical situations.An acoustical theory of PAS has been reported by McQueen(22)which evaluates the PAS signal both for microphone(gaseous medium)and for hydrophone (liquid medium)

## EXPERIMENTAL TECHNIQUE

The block diagram of the experimental arrangement being used in our laboratory is shown in figure 2.The electromagnetic radiation from an air cooled 1kW high-pressure arc lamp is focussed onto the rotor of a variable speed mechanical chopper and is then filtered out by a grating monochromator before irradiating the specimen.This is placed inside a specially designed closed cell(figure 3).The periodic gaseous pressure fluctuations are detected by a one inch sensitive condenser microphone which are located within the cell.This photoacoustic signal is processed and amplified by a lock-in amplifier and recorded on a chart recorder as a function of the wavelength of the incident radiation.

Alternative to the above arrangement a beam splitter may be employed to correct for variation in source intensity by directing a known fraction onto a pyroelectric detector.In a recent improvement in technique use is made of a Fourier-transform photoacoustic spectrometer in which a conventional monochromator is replaced by a Michelson interferometer. This has reduced datd collection time and improved the S/N ratio.The design of the photoacoustic cell and S/N ratio are the important factors controlling the performance of the experimental system and currently its dependence on various parameters such as volume of the cell,filler gas,chopping frequency etc. is being carefully investigated with a view to improve the sensitivity of detection.

## APPLICATIONS

The PAS technique is currently applied to study,

(1)Optical properties(optical absorption spectra,absorption coefficient etc.)of a wide variety of solid or semi-solid materials with particular reference to its advantageous use with biological media.

(2)Thermal properties(thermal diffusivity etc.) of thin films.

(3)De-excitation processes(Flourescent and Photochemical studies).

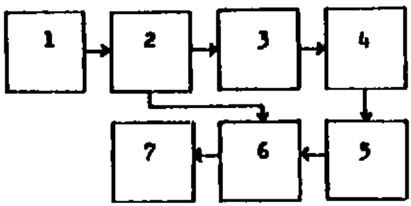


FIGURE 2:-Block diagram of single-beam spectrometer 1:Radiation source 2: Chopper 3:Monochromator 4:Photoacoustic cell with microphone 5:Preamplifier 6: Lock-in amplifier 6:Chart recorder.

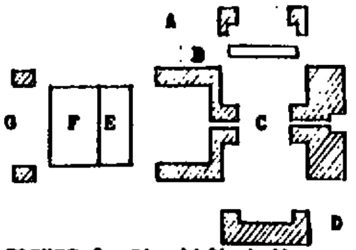


FIGURE 3:-Simplified diagram of a general purpose photo-acoustic cell. A:Transmission window holder B:Transmission window C:Main body of the brass cell D:Specimen holder E:Microphone F:Preamplifier G:Backing H:Needle-valve.

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