Proceedings of The Institute of Acoustics

THE DESIGN OF A PHOTOACOUSTIC CELL AND ITS PRACTICAL PERFORMANCE

M ASHFAQ AHMED, W G B BRITTON AND R W B STEPHENS
PHYSICS DEPARTMENT, CHELSEA COLLEGE, PULTON PLACE, LONDON SW6 5PR

INTRODUCTION

Photoacoustic spectroscopy has become an extremely useful technique in the study of optical and thermal properties of condensed matter. In the present technique the specimen is placed inside a specially designed closed chamber, the photoacoustic cell, which contains a sensitive microphone and a dry gas coupling medium, such as air or a monoatomic gas. The specimen is irradiated by modulated electromagnetic radiation through a transmission window located in a cell wall. The energy absorbed by the specimen is converted into heat either partially, or fully in the absence of luminescent or photochemical reactions. Sequentially this periodic heating of the specimen gives rise to pressure pulsations in the gas and these are detected by a microphone suitably located in the cell. The output signal from the microphone is electronically processed and recorded as a function of the wavelength of the incident radiation. This provides the photoacoustic spectrum of the specimen and corresponds to its true optical absorption spectrum, being characteristic of the test material. A study of the phase of the photoacoustic signal as a function of modulation frequency could be used to obtain information about certain thermal parameters of the specimen. Other applications of the photoacoustic effect include the study of photochemical changes, of phase-transitions, as an indicator in imaging etc.

GENERAL CRITERIA FOR CELL DESIGN

The photoacoustic cell is the central part of the experimental system and the ultimate performance of the system ie. the signal to noise ratio, (SNR), and its optical resolution depend on the cell design. The design of the cell will depend mainly on the nature of the test specimen (i.e. powder, liquid, solid etc.) and the type of problem. The following factors are general considerations in the design of a cell.

(i) Volume:- The theory of the photoacoustic effect (1) predicts that the photoacoustic signal varies inversely with the volume of the filler-gas. However, there are certain physicsl limitations imposed by factors like diameter of the microphone and its location, which depends on :- whether it operates in the acoustically resonant or non-resonant mode; the size of the specimen; the thermal diffusion length of the filler-gas in keeping the volume to a minimum. The thermal diffusion length of the filler-gas is defined as $\mu_g = (2\alpha_g/\omega)^{\frac{1}{2}}$ where α_g = thermal diffusivity of the gas and $\omega = 2\pi f$ = modulation frequency. It is important to keep the distance between the specimen and transmission window $\ell_g > \mu_g$ within the operating range of modulation frequency. Aamodt and Murphy (2) have shown that the photoacoustic signal amplitude decreases with ℓ_g for the cell when $\ell_g < \mu_g$. Therefore this fact should be taken into account before minimizing the volume.

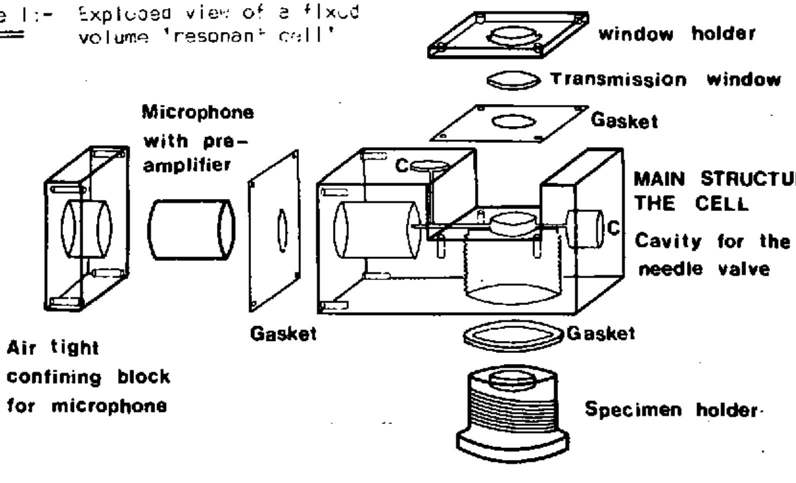
(ii) Background Noise:- This arises from the absorption of the direct and scattered radiation by the window and inner walls of the cell and should be minimized. Another precaution is to minimize the amount of thermal radiation

falling on the microphone diaphragm.
(iii) Acoustic Isolation:- The use of a lock-in amplifier for the analysis of the microphone signal eliminates the noise present in the photoacoustic signal at frequencies other than the modulation frequency. The acoustic isolation can be improved by using a modulation frequency absent from the frequency-spectrum of the environmental noise, but this may be unsuitable in situations where the dominant noise is of low frequency. As the photoacoustic signal amplitude varies as ω^{-1} or $\omega^{-3/2}$, depending on the relative optical and thermal properties of the specimen [1], so a high modulation frequency will yield a low SNR. For optical spectrum studies it is therefore necessary to employ a low modulation frequency and use acoustic methods to attenuate the external noise before it reaches the microphone. One method of achieving this objective is to use thick cell walls of a dense material.
By using a resonant-type photoacoustic cell with the appropriate modulation frequency the sensitivity of detection is increased and the SNR is consequently enhanced.

DESIGN OF PRESENT CELL

The present cell was designed to study powder specimens and to have a large illuminated surface area ie. 2cm diameter, but the total effective volume was kept as small as possible by appropriate geometry. Figure 1 shows the fixed-volume photoacoustic cell constructed from a single piece of brass and having an effective volume $\sim 2\ cm^3$. It is a cavity of cylindrical shape of diameter 2cm and depth 0.4cm. A 2.54cm diameter condenser microphone (B&K 4144) together with its matching preamplifier (B&K 2916T + DB 0375) are inserted into a side hole so that the microphone diaphragm is parallel with the central axis of cylindrical cavity. The microphone chamber is connected to the specimen cavity by means of a capillary of 0.12cm diameter and length 3.5cm. Two needle valves inserted into the cell walls permit the introduction of different gases into the cell. In order to minimize the background noise the inner walls of the cell are highly polished and an optically transparent window of CaF_2 used for transmitting the incident radiation.

Figure 1:- Exploded view of a fixed volume 'resonant cell'



THE DESIGN OF A PHOTOACOUSTIC CELL AND ITS PRACTICAL PERFORMANCE

RESULTS AND DISCUSSION

Only a lock-in amplifier (Brookdeal Model FL355) with the absence of phase shifting provision for the reference signal was available in the early stages of the work. Figure 2 shows the spectrum of 1kw Hg-Xe lamp obtained by PAS method using carbon powder as the irradiated specimen. The spectral energy distribution obtained closely resembles that for the standard data of this type of lamp. The mercury emission lines of the lamp can be seen clearly resolved at the expected values of wavelength.

In the case of a single-beam photoacoustic spectrometer, it is necessary to correct the observed spectrum of the specimen for the variation of the source intensity with wavelength. This is usually done by taking the ratio of the observed spectrum of the material and the power spectrum of the lamp. This manual method of correction proved tedious and inaccurate for the Hg-Xe lamp due to the presence of its strong mercury emission lines superimposed on the continuum spectrum. The problem was overcome by replacing this lamp by a 1kW Xe lamp which has a large wavelength region free from emission lines. Furthermore a recent design of lock-in amplifier (Brookdeal Model 9501) was acquired with a phase adjusting facility for the reference channel which improved signal detection. The photoacoustic spectrum of Xe lamp is shown in figure 3. The maximum noise (i.e. the acoustic signal registered by the microphone for cell without a test specimen at peak wavelength λ = 821nm) level measured was less than 20μV.

To study the dependence of photoacoustic signal amplitude on the incident intensity the wavelength of the monochromator was fixed at λ = 465nm and the widest slits i.e. 0.5cm of the monochromator were used. The input electrical power to the lamp was varied and the corresponding amplitude of the photoacoustic signal was measured keeping the modulation frequency constant. This process was repeated for different modulation frequencies. The average intnesity of the incident radiation is proportional to the product of input electrical power and reciprocal modulation frequency. The dependence of PA signal amplitude on this 'relative intensity' is shown in figure 4. The PA signal shows a saturation for higher values of intensity indicating the limit of the particular cell for detection. On the other hand the particular design could give the same sensitivity of detection but using only a low power lamp.

The modulation frequency dependence of PA signal for this cell is shown in figure 5. Two resonance peaks are seen at 194.2Hz and 365.4Hz. With the needle valves fitted to the cell, the inner geometry of the cell is quite complex for analysis by analogy with electrical circuits. However, for a simpler geometry shown on top right corner of figure 6, the analysis of equivalent electrical circuit under resonance conditions predicts the presence of two peaks. The frequency values of these peaks calculated by putting the relevent parameters for this cell were 254.2Hz and 1010.9Hz respectively. A close agreement was found with the experimentalresults shown in figure 6 for this geometry.

It is concluded that the theoretical study of the acoustic impedance as a function of frequency for various geometrical parameters can lead to the improved design of such resonant type systems and can be used for prediction of the frequency response of the cell.

REFERENCES

(1) A ROSENCWAIG AND A GERSHO 1976 J. Appl. Phys. 47, 64-69 Theory of the photoacoustic effect with solids.

(2) L C AAMODT, J C MURPHY AND J G PARKER 1977 J. Appl. Phys. 927-933 Size considerations in the design of cells for photoacoustic spectroscopy.

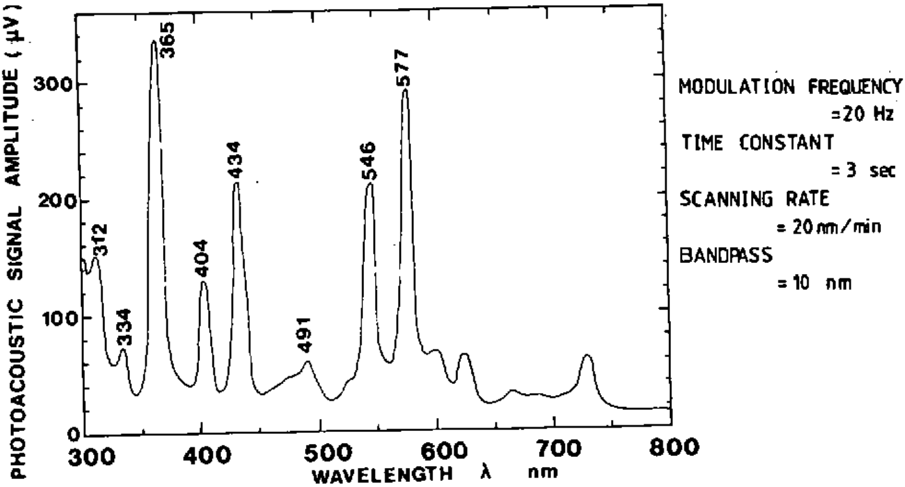


Figure 2:- Spectral energy distribution of a lkW Hg-Xe arc lamp as obtained by PAS using carbon powder as specimen.

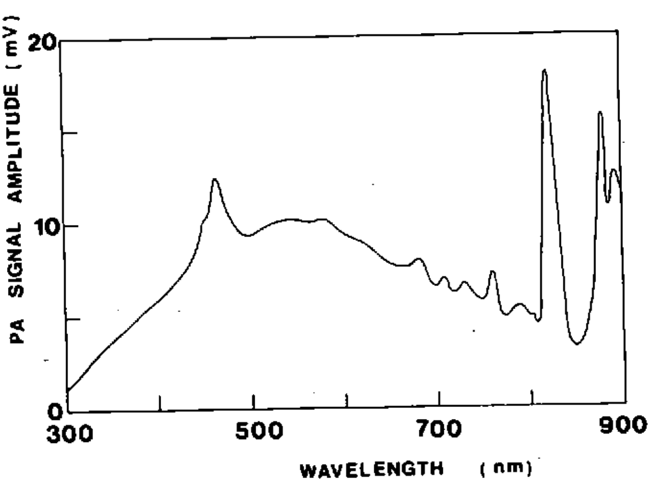


Figure 3:- Spectral energy distribution of a lkW Xe arc lamp as obtained by PAS method using carbon powder as specimen.

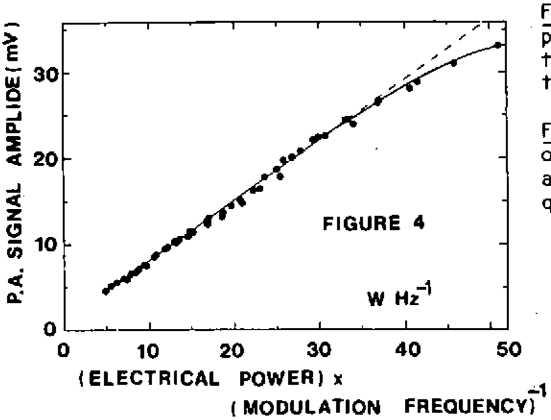
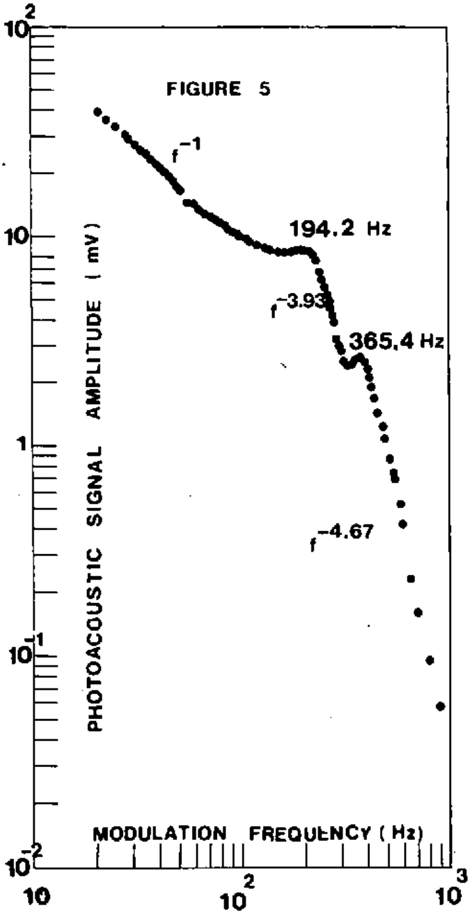


Figure 4:- Dependence of the photoacoustic signal amplitude on the 'relative radiation intensity'.

Figures 5 & 6:- Dependence of the photoacoustic signal amplitude on modulation frequency for resonant cell.



Inner geometry of cell A Incident modulated radiation; B cavity containing specimen; C specimen: D volume in front of microphone diaphragm; E Microphone.

FIGURE 6