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Experiments with flowing gases in an open photoacoustic cell†

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Abstract. A simple gas-microphone photoacoustic cell is described in which there is no sizable loss of signal on opening the cell to the atmosphere or even under conditions of gas flow. Results obtained under different rates of flow of gases and chopping frequencies are reported. Except for carbon black, the photoacoustic signal is found to be independent of flow-rate for all the solid substances studied.

Keywords. Photoacoustic spectroscopy; open photoacoustic cell; flowing gases.

1. Introduction

The versatility of the photoacoustic (PA) technique for studying several phenomena is by now well-documented (Rosencwaig 1980; Ganguly and Rao 1981; Tam 1986). When gas-microphones are used as the detector, it is assumed that the cell should be closed as otherwise the flow of heat to the gas phase from the solid following a non-radiative de-excitation will not result in an increase in pressure. Efforts have been made, however, to construct open PA cells so that the ranges of application of the PA effect may be further extended (Dioszeghy *et al* 1985; Kanstad and Nordal 1978). These cells have limited applications. We have exploited the fact that when a PA cell is connected to the atmosphere by a tube, the fraction of transmitted acoustic wave depends on the dimensions of the tube. By a proper choice of the diameter, length and wall thickness of the capillary such that the acoustic impedance of the capillary is increased, a simple PA cell may be constructed in which there is no sizable loss of photoacoustic signal at ordinary chopping frequencies (f), even though the cell is open to the atmosphere, or more interestingly, when a gas is flowing through the cell. In this communication we describe the cell used by us and the results obtained for various solid samples under different gas flow conditions.

2. Experimental

The cell used by us earlier (Somasundaram and Ganguly 1984) has been modified as shown in figure 1. The arms of the glass capillaries could be varied in order to operate at various f. Glass stopcocks at the end of these arms allowed the cell to be

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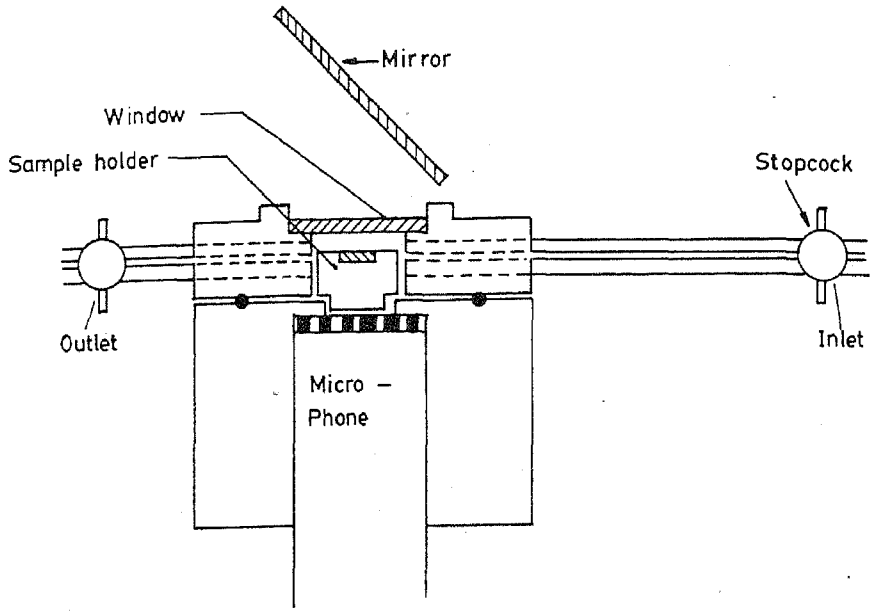

Figure 1. Schematic drawing of the open PA cell used for gas-flow studies.

closed or opened to the atmosphere. The capillaries used in these experiments were of 0·5 mm internal diameter and 2·5 mm wall thickness. Gases could be passed through these capillaries. In order to achieve high flow-rates and at the same time retain the signal strength, we have made the gas-inlet arm 12·5 cm and gas-outlet arm 4·5 cm in length. Flow-rates as high as 2 cc/sec could be achieved without affecting the signal to noise ratio. At higher flow-rates ~6 cc/sec or more, there is considerable noise within the cell, associated with the vibrations and rattling of the loosely mounted sample holder and sample. The length of the gas phase between the sample and the window is 3·5 mm and the internal diameter of the cell is 12 mm. The volume within the cell is ~0·3 cc so that at the rates of 2 cc/sec the entire volume of the gas in the cell would have been swept out within the chopping period for $f \sim 6{\cdot}7$ Hz. The microphone used was General Radio 1961-1 inch electret condenser microphone with a flat frequency response between 5–15,000 Hz. Nitrogen gas was used for the gas flow experiments with the flow-rates being measured by a soap bubble flow meter. The lock-in-amplifier, illuminating source, chopper etc. were the same as that described earlier by Ganguly and Rao (1981) and Somasundaram and Ganguly (1984).

3. Results and discussion

We show in figure 2a the changes in the PA signal (I_{PA}) from a flat single crystal of graphite at various chopping frequencies when the cell is closed, open and when nitrogen gas is passing through the cell at 1·2 cc/sec. The behaviour is similar even if the intensity of the illuminating source is varied by a factor of 40. I_{PA} is inversely related to f when the cell is closed, for the whole frequency range studied (6–300 Hz). We have shown in figure 2b the changes in I_{PA} when various arms are opened or closed. We see that for $f \geq 20$ Hz, I_{PA} is hardly changed under the

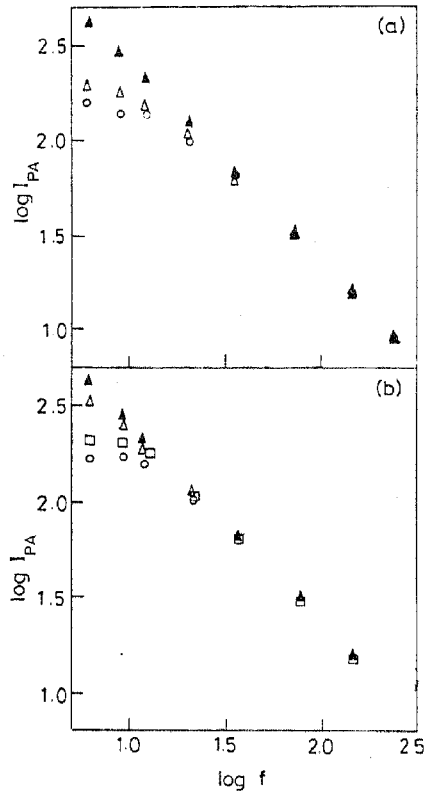

Figure 2. (**a**) Variation of I_{PA} with f for a single crystal of graphite using white light for illumination under various conditions. Inlet arm length ~12·5 cm, outlet arm ~4·5 cm. (▲): cell closed; (△): cell open with a gas flow (1·2 cc/sec) and (○): cell open with no gas flow. (**b**) Variation of I_{PA} with f for the same conditions as (a). (▲): both arms closed; (△): inlet arm open; (□): outlet arm open and (○) both arms open.

various conditions, at lower values of f, however, I_{PA} is considerably reduced. At these lower f I_{PA} seems to be proportional to a factor $[1-(B/l_1+B/l_2)]$ where l_i are the lengths of the capillary arms ($1/l_i=0$ when an arm is closed) and B is a constant for each frequency. It is interesting to note that when a gas is passing through the cell, there is a slight increase in I_{PA} at low frequencies, which is close to the value obtained when the inlet arm is closed. There is also considerable change in the phase of the signal. A complete theoretical analysis of this aspect is being further pursued. We note that one has to consider whether the acoustic losses in the capillaries are adiabatic or isothermal in nature (Kinsler and Frey 1950). In general the former is obtained when the diameter of the tube is $>2{\cdot}14/(f)^{1/2}$ (in cm) and the latter when the diameter is $<0{\cdot}214/(f)^{1/2}$ (in cm). Since the length of the gas phase in the cell is 3·5 mm, the adiabatic condition seems to be fulfilled in the cell only for $f>37$ Hz. In the capillary there could be isothermal or adiabatic conditions depending on the chopping frequency.

The other aspect is that even under gas flow conditions there is no change in amplitude of I_{PA} for various values of f. In order to understand this aspect further, we have studied the influence of flow-rate on the PA signal generated from various powdered as well as flat solid samples. The changes in I_{PA} from a single crystal of graphite at $f=6{\cdot}2$ Hz for two intensities (one being 40 times greater than the other) are shown in figure 3. At this f an equivalent volume of the entire gas in the cell

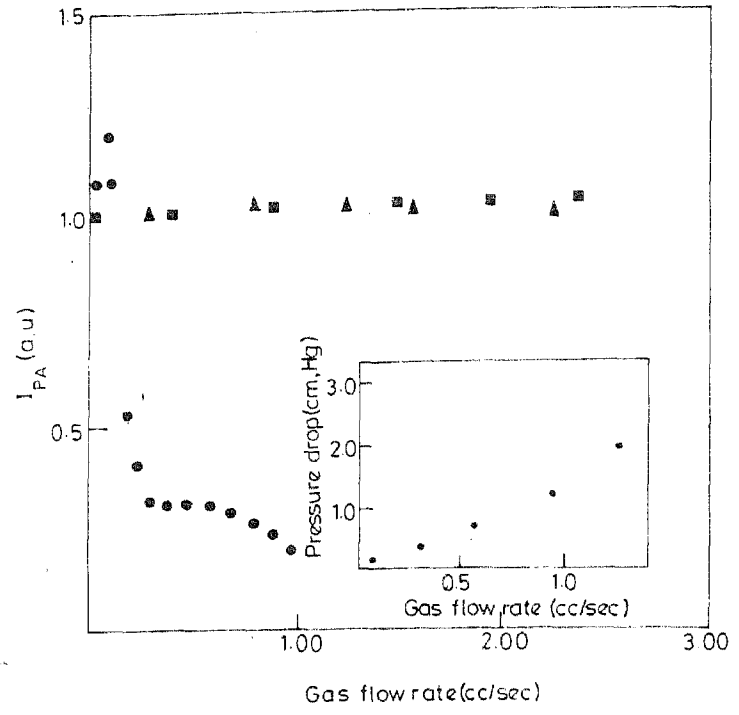

Figure 3. Variation of I_{PA} with gas flow-rate. I_{PA} is normalised to unity for no gas flow conditions. (■) & (▲) for single crystals of graphite using white light. (●) for carbon black powder. I_{PA} corresponding to (▲) when gas flow is zero is nearly the same as (●) but is 40 times larger than that corresponding to (■). Inset shows the measured pressure drop in a mercury manometer for various gas flow rates.

may be displaced during the chopping period for flow-rates ~2 cc/sec. The length of the gas phase is moreover nearly equal to the value at which a maximum in I_{PA} is expected from our earlier studies (Ganguly and Somasundaram 1987) at this chopping frequency ($l_g \sim 1{\cdot}0$ mm at 6·2 Hz). We see no decrease in the PA intensity even at the highest flow-rates. The slight increase may be accounted for the increase in the pressure within the cell. The changes in pressure within the cell was measured by a manometer attached to the cell, after the set of experiments were over. This value of pressure (in cm of Hg) for various gas flow-rates is given in the inset of figure 3. Similar results were obtained with other flat solids such as amorphous selenium deposited on teflon, CdS single crystals etc. as well as various powders such as a-Se, chromia-alumina catalyst. The only exception is, however, with carbon black where there is a marked change in the PA amplitude as a function of flow-rate as shown in figure 3. There is an increase in I_{PA} for small flow-rates followed by a rapid decrease. This behaviour is quite reversible with respect to flow-rate. At high flow-rates I_{PA} seem to be roughly inversely related to the flow-rate. At all flow-rates I_{PA} is however related inversely to f.

The present study throws up some questions which does not seem to be expected from some of the presently accepted theories of the PA effect (Rosencwaig and Gersho 1976). Carbon black is often used as a model substance. The very different behaviour of carbon black does not seem to be related simply to its thermal properties. All the other substances which include high surface area catalysts which have different thermal diffusivities show quite different behaviour. When the gas is

flowing through the cell, part of the heat given up to the gas phase must be carried out of the cell and hence there should be a reduction in I_{PA} with increasing flow-rate accompanied by a marked f dependence. In other words, under gas flow conditions there would be a decrease in the thermal diffusion length and according to the Rosencwaig-Gersho theory there should be a decrease in I_{PA} since it is proportional to the thermal diffusion length. It is therefore surprising that there is no dependence of I_{PA} from flat bulk single crystal of graphite on the flow-rate even at $f = 6{\cdot}2$ Hz when $l_g \sim 3{\cdot}5$ mm is sizably less than $2\pi\mu_g$ (the value at which thermal waves are nearly attenuated in the gas phase). This behaviour does not depend upon the location of the microphone, temperature and cell design. So a jet of gas entering the cell may be made to impinge directly on the sample or other parts of the cell without affecting the results. This behaviour does not seem to be related to the thermal properties of the solid or the powder-gas composite as we have found similar behaviour with a wide range of solids. Further study is now in progress in areas such as study of catalysts under catalytic conditions (Somasundaram and Ganguly 1987), transition from lamellar to turbulent flow etc.

4. Conclusion

The above data clearly demonstrate that a truly open photoacoustic gas-microphone cell may be used at rather high flow-rates of gas through the cell. Thus PA effect may now be extended to several areas such as spectroscopy of catalysts under catalytic conditions, the study of flowing systems as in effluents from reactors, gas-chromatograms, exhausts etc. The transition from lamellar to turbulent flow may perhaps be fruitfully studied by the technique.

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