

A NOVEL TECHNIQUE FOR THE ENHANCEMENT OF PHOTOACOUSTIC SIGNAL*

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Résumé - Le signal photoacoustique se trouve renforcé par l'introduction de liquide volatile dans la cellule. Cette augmentation se remarque pour un coefficient faible d'absorption optique et une plus grande fréquence de coupure et est proportionnelle à la pression de la vapeur du liquide. Le signal PA des liquides se trouve renforcé avec la température qui, à son tour, est proportionnelle à la pression de la vapeur pour chaque température.

Abstract - The photoacoustic signal is found to be enhanced several fold by the introduction of a volatile liquid into the cell. The enhancement is more for lower optical absorption coefficient and higher chopping frequency and is proportional to the vapour pressure of the liquid. The PA signal from liquids increases with temperature being proportional to the vapour pressure at each temperature.

In the course of our investigations on the temperature dependence of photoacoustic spectra from solids we have observed in several cases an increase in the signal with increasing temperature reaching sometimes a maximum corresponding to the boiling point of water. We have also observed a slight enhancement of the PA signal on the adsorption of gases. On analysis of our results we have been able to show as a consequence that the photoacoustic signal could be enhanced several times by the introduction of a volatile liquid into the cell, the vapours of which presumably are adsorbed on the surface of the sample.

The cell and the spectrophotometer used for our studies have been described earlier¹. A schematic drawing of the cells used for room temperature and variable temperature studies are shown in Fig. 1a and 1b, respectively. The sample holder

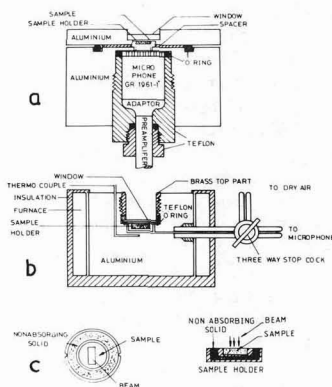


Fig. 1 - Cell design schematics for room temperature and variable temperature cells (a) and (b). (c) Details of the sample holder.

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(Fig. 1c) is such that the sample is placed in an aluminium cup (8mm dia, 0.8 mm depth) which in turn is placed on top of a non-absorbing solid (such as silica-gel or TiO_2) in a cavity inside the sample-holder. The image of the beam is incident only on the sample. A liquid is introduced in the cell by soaking the non-absorbing solid with the desired liquid with the help of a microsyringe. A GR 9602 electret microphone was used for the study. The illuminating source was a 200 W tungsten-halogen lamp.

In Fig. 2 we show the normalised PA spectra of As_2S_3 glass in the presence of air as well as diethyl ether in the cell. The intensity of the signal is found to be enhanced several fold in the presence of ether. It is however, found that the enhancement is higher for lower absorption coefficient (Fig. 2b). This dependence is general and

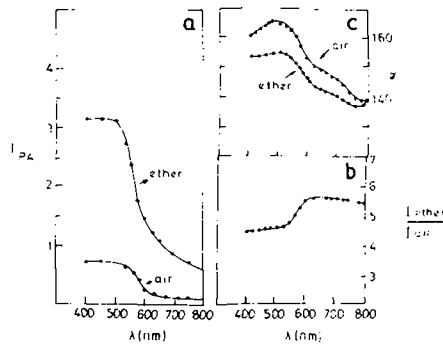


Fig. 2 -a) Normalised PA spectra of As_2S_3 glass in presence of ether and air.
 b) Ratio of I_{ether}/I_{air} for various wavelengths.
 c) Phase dependence of the signal as a function of wavelength.

is found in several cases. There is also a marked change in the phase dependence of the signal (Fig. 2c). The enhancement is found to be independent of the power of the irradiating source, nature of the sample holder (teflon or aluminium) slit width, or the geometry of the microphone with respect to the sample. There is a dependence on the length, l_g , of the gas phase above the sample, the enhancement being larger for smaller l_g .

In Fig. 3a we show the changes of the intensity of the PA signal (I_{liq}) at 600 nm for Cr_2O_3 in the presence of various liquids in the cell. A linear relation is observed between I_{liq} and the vapour pressure, p , of the liquid. In accordance with the above result the PA signal intensity from liquids also increases with temperature being proportional to the vapour pressure of the liquid at each temperature. Fig. 3b shows the results obtained during cooling from a .001 M aqueous solution of methylene blue the wavelength being 660 nm. The enhancement that is observed therefore seems to be linearly related to the vapour pressure of the liquid.

In Fig. 4 the enhancement observed from carbon black at various chopping frequencies (250 - 1600 Hz) is shown. While the signal in the presence of air (I_{air}) shows the normal ω^{-1} dependence, there is a change to an $\omega^{-1/2}$ dependence in the presence of ether. This dependence is most prominent at the highest frequencies. The approach to a $\omega^{-1/2}$ dependence seems to indicate that for high chopping frequencies the flow of heat into the gas phase by the usual RG mechanism is less important than the effects due to the heating of the adsorbed layer on the sample.

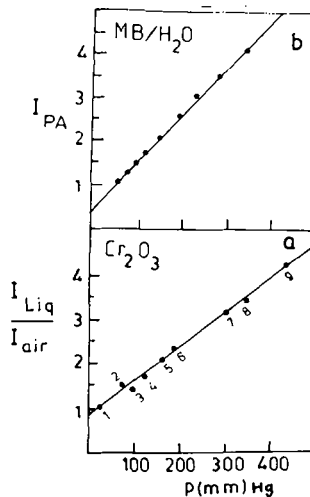


Fig. 3 - a) Plot of I_{liq} vs P for various liquids: 1= H_2O , 2= CH_3CN , 3=*n*-Hexane, 4= CH_3OH , 5= $CHCl_3$, 6= CH_3COCH_3 , 7= CH_2Cl_2 , 8= CS_2 , 9= $CH_3CH_2OCH_2CH_3$.
 b) Plot of I_{PA} vs P (vapour pressure at various temperatures for a 0.001 M aqueous solution of Methylene blue.

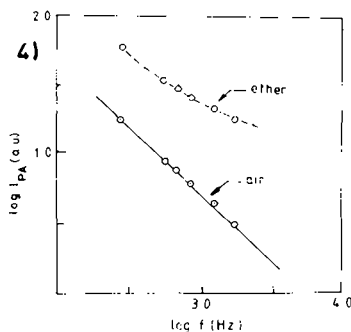


Fig. 4 - Frequency dependence of PA signal from carbon black in the presence of ether and air.

We see from above that the enhancement is dependent on β and ω . In general the relation between I_{liq} and I_{air} may be written as

$$I_{liq}/I_{air} = 1 + C(\beta, \omega)p$$

where p (in mm Hg) is the vapour pressure of the liquid, $C(\beta, \omega)$ is a constant for a particular optical absorption coefficient β and chopping frequency ω . C increases with decreasing β and increasing ω . Typically C has values ranging from 0.003 to 0.02 so that the enhancement in the presence of ether at 20° C ($p = 430$ mm) is 2 to 9 times.

The enhancement of the photoacoustic signal over that normally observed in air (adequately described by the RG theory²) could be attributed to the physically adsorbed layer (probably a multilayer) on the surface of the sample. Periodic heat flow to the surface of the solid could cause a periodic evaporation and condensation of a part of the physically adsorbed layer. Since the physically adsorbed layer is

liquid-like, the extent of evaporation would be proportional to dp/dT of the liquid at the ambient temperature (and hence essentially to the vapour pressure of the liquid) when the surface temperature is increased by a small amount dT . The desorbed vapour could cause a momentary (non-equilibrium) increase in the pressure within the cell thus setting up an acoustic wave. Moreover collisional heat transfer from the hot desorbed liquid molecules to the air molecules could also lead to a thermal wave. The problem then becomes one of solving coupled equations for pressure and temperature in the vapour phase. Essentially similar equations were solved by McDonald and Wetsel³ for their "mechanical" piston model. The model used by us, which we shall call the "adsorbed piston" model¹ is then expected to give the same dependence as those observed by McDonald and Wetsel³ namely a higher enhancement for low β and high ω . We note that the "adsorbed" piston effect would be much pronounced than the "mechanical" piston effect as the effective thermal expansion coefficient of the adsorbed layer on desorption is expected to be much larger than the bulk thermal expansion coefficient invoked by McDonald and Wetsel³ in their "mechanical" piston effect.

The enhancement of the photoacoustic signal from condensed materials due to the presence of liquid vapours is quite universal and is applicable not only to solids but also to biological systems such as gels, membranes, leaves etc., or to thin films and even to liquids. The technique should therefore be rather useful in the practice of photoacoustic spectroscopy. A consequence of this work is that it may be necessary to reexamine the interpretations of the phase and frequency dependence of photoacoustic signal especially where sufficient care has not been taken to remove physically adsorbed gases or for studies involving liquids and biological materials.

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References:

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