A novel technique for enhancing photoacoustic signals from solids[a)]

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Enhancement of the photoacoustic signal from condensed materials by several folds is achieved by the introduction of a liquid with high vapor pressure in the photoacoustic cell. The enhancement is especially marked for low absorption coefficients and high chopping frequencies. Typically the enhancement is two to nine times in the presence of diethyl ether at 293 K. A linear relationship is observed between the enhancement and the vapor pressure of the liquid.

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In the commonly accepted theory[1] of photoacoustic (PA) effect in solids, the role of adsorbed gases has been assumed to be negligible. During our investigations of the PA effect in solids we have indeed found that the PA signal is enhanced several folds in the presence of liquids with high vapor pressure placed in the cell. We present some of the significant results of our investigation in this letter.

The photoacoustic cells and the spectrometer used in this study are similar to those described by Ganguly and Rao.[2] These cells showed the normal f^{-1} dependence[1-3] of the PA signal from carbon black, where f is the chopping frequency. The sample holder was modified so that a liquid can be placed in the cell without wetting the sample but allowing its vapor to be present in the space between the sample and the window. For convenience the desired liquid was mixed with silica gel and kept as a slurry. The focusing optics was such that only the sample was illuminated by the intermittent beam.

PA spectra of a polycrystalline sample of $Nd_3Al_5O_{12}$ with and without diethyl ether in the cell at room temperature (293 K) are shown in Fig. 1(a). We notice a dramatic enhancement of the PA intensity in the presence of ether (more than five times). Frequency dependence of the PA signal at 580 nm from the same sample in the presence of ether and air indicates that the enhancement is greater at higher chopping frequencies [Fig. 1(b)]. This behavior is more pronounced at higher chopping frequencies (200–2000 Hz) as is shown in the case of carbon black in Fig. 2. We show a similar enhancement of the signal from As_2S_3 glass in Fig. 3(a). The enhancement is larger for smaller optical absorption coefficients β (longer wavelengths) as shown in Fig. 3(b); the phase dependence of the signal is entirely different in air and in ether [Fig. 3(c)]. Larger enhancements for smaller β are also evident from Fig. 1(a).

In order to investigate this phenomenon further we have studied the temperature dependence of the photoacoustic signal from $Nd_3Al_5O_{12}$ at 580 nm in the presence of water and air. At room temperature the intensity of the PA signal from the sample exposed to water vapor, I_{H_2O}, was 10% higher than that obtained in the presence of dry air, I_{air}. I_{air} decreases with increasing temperature as predicted from the Rosencwaig–Gersho (RG) theory.[1] However, I_{H_2O} increases with increasing temperature and the plot of I_{H_2O} against the vapor pressure P_{H_2O} of water at various temperatures is indeed linear (Fig. 4). A linear plot is also obtained when I_{H_2O} is plotted against the value of dp_{H_2O}/dT at various temperatures. Interestingly, the plot of the intensity of the PA signal, I_{liq}, obtained with various liquids in the cell at a fixed temperature (293 K) versus the vapor pressure of the liquid, P_{liq}, also falls on the same straight line. In general, the relationship $I_{liq}/I_{air} = 1 + Cp_{liq}$ seems to hold, where C is a constant for a given value of β and f. C increases with decreasing β and increasing f. Typically, C has values ranging from 0.003 to 0.02 so that enhancement of the PA signal by two to nine times can be observed in the presence of ether at 293 K ($p_{ether} = 430$ mm Hg). C is also dependent on lg, the length of the gas phase above the sample varying roughly as lg^{-1}.

The enhancement of the photoacoustic signal from condensed materials due to the presence of liquid vapors is quite universal and does not seem to depend on the surface area of the material. This technique should be rather useful in the practice of photoacoustic spectroscopy. The role of the liq-

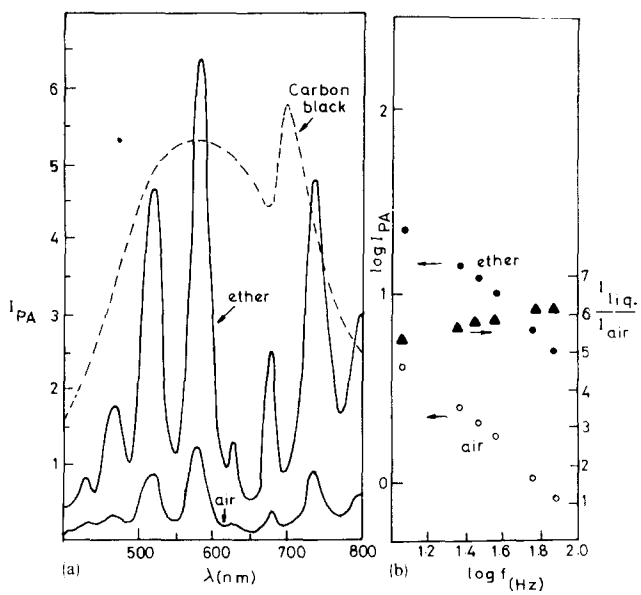

FIG. 1. (a) PA spectra of polycrystalline sample of $Nd_3Al_5O_{12}$ at 293 K in the presence of ether and air. The spectra are not normalized. The power spectrum of tungsten lamp and monochromator combination using carbon black is shown by dotted lines. $f = 28.6$ Hz, $\Delta\lambda = 10$ nm, wavelength drive = 100 nm/min, time constant = 1 s. (b) Frequency dependence of the PA signal for $\lambda = 580$ nm for low chopping frequencies (< 100 Hz) in the presence of air and ether at 293 K. The ratios I_{ether}/I_{air}, the intensity of the PA signal in the presence of ether to that in the presence of air is also shown.

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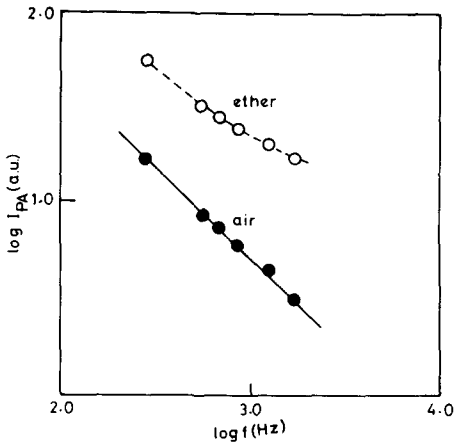

FIG. 2. Frequency dependence of the PA signal from carbon black between 200 and 2000 Hz in the presence of air and ether at 293 K.

uid itself may be to produce a physically adsorbed layer on the solid surface. Periodic heat flow to the surface of the solid could cause a periodic evaporation and condensation of a part of the physically adsorbed layer. The desorption and adsorption of the molecules in the physically adsorbed layer may be treated[4] as an "adsorbed piston." Since the physically adsorbed layer is liquidlike, the extent of evaporation would be proportional to dp/dT of the liquid at the ambient temperature when the surface temperature is increased by a small amount. The desorbed vapor could cause a momentary increase in pressure within the cell thus setting up an acoustic wave in the gas phase in addition to the usual thermal wave due to collisional heat transfer from the hot desorbed molecules to the gas phase. It would seem that a more efficient heat transfer to the gas phase is achieved in this fashion. The enhancement is thus expected to be more for small values of β where problems due to surface thermal contact resistance could be important in reducing the PA signal intensity.[5,6] Moreover, since the surface adsorbed layer is involved, PA signals generated close to the surface are likely to be more effective in the enhancement. There may thus be a change in the effective thermal diffusion length.

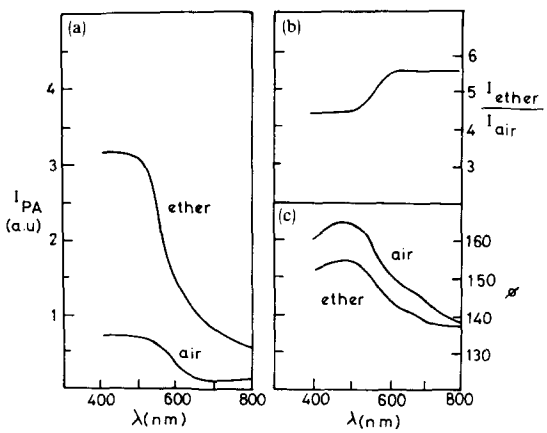

FIG. 3. (a) Normalized PA spectra of As_2S_3 glass in the presence of air and ether. Conditions are the same as that in Fig. 1(a). (b) Ratio I_{ether}/I_{air} for different wavelengths. (c) Phase dependence of the signal as a function of wavelength of As_2S_3 glass.

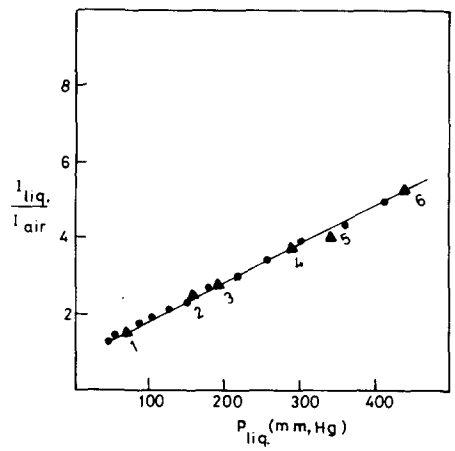

FIG. 4. Plot of PA intensity obtained from $Nd_3Al_5O_{12}$ at various temperatures in the presence of water vapor as a function of the vapor pressure of water at each temperature (circles). $f = 28.6$ Hz, $\lambda = 580$ nm. Triangles are the PA intensity obtained from various liquids placed in the cell at 293 K. 1 = acetonitrile, 2 = chloroform, 3 = acetone, 4 = carbon disulphide, 5 = methylene chloride, 6 = diethyl ether.

This aspect of the problem is being investigated theoretically and experimentally.

The acoustic wave due to the "adsorbed" piston may be similar to that from the "mechanical" piston proposed by McDonald and Wetsel[7] arising out of the bulk expansion and contraction of the solid. These latter authors set up coupled equations for pressure and temperature in the vapor phase and were able to demonstrate that the mechanical piston causes an enhancement of the PA signal over that predicted by the RG theory especially at high chopping frequencies and low absorption coefficients. This is precisely what is observed by us. It seems reasonable therefore to set up similar coupled equations to account for the adsorbed piston effect. We note that the effective thermal expansion coefficient of the adsorbed layer (because of desorption) would be much larger than the bulk thermal expansion coefficient of the solid employed for the mechanical piston effect by McDonald and Wetsel[7] so that contributions due to the acoustic effect would be much more important in the adsorbed piston effect. Indeed what seems to us more important is the fact that the mechanical piston effect may be entirely unnecessary to account for the observed phase and frequency dependence from solutions,[7] as a simple evaporation and condensation of the liquid would be sufficient to account for the results. We have indeed observed that the photoacoustic signal from liquids increases with temperature, being proportional to the vapor pressure of the liquid at each temperature.

The present study is of particular significance not only because of the ease with which the PA signal can be enhanced but also because of the fact that the effect of adsorbed gases has been ignored so far. This is especially true for studies involving lifetime measurements in which phase and frequency dependence is important and there could be considerable error if adsorbed gases are present.

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