

Enhancement of photoacoustic signals from condensed materials in the presence of volatile liquids: Influence of optical absorption coefficient, particle size, length of the gas phase, and chopping frequency^{a)}

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The influence of the optical absorption coefficient, the particle size, the chopping frequency, and the length of the gas phase on the recently observed enhancement of photoacoustic signals in the presence of saturated vapors of ether has been investigated. Amorphous selenium has been used as the standard. The particle size plays a crucial role in understanding the enhancement as a function of optical absorption coefficient or chopping frequency. The enhancement is more when the optical absorption length is greater than particle size. The frequency dependence of the photoacoustic signal in the presence of ether is different from that in air when the thermal diffusion length of the solid is greater than the particle size. A qualitative interpretation of the results based on the "adsorbed" piston effect has been made.

I. INTRODUCTION

In earlier communications^{1,2} we have reported the enhancement of photoacoustic (PA) signals from solids and other condensed phases, on the introduction of a nonabsorbing volatile liquid into the cell without wetting the sample. Under these conditions the partial vapor pressure of the liquid within the cell is given by its saturated vapor pressure p_0 at the room temperature. We have observed^{1,2} that the enhancement from solids is roughly linearly related to the value of p_0 for different liquids at the ambient temperature. Typically two to tenfold enhancement of the PA signal could be obtained in the presence of diethyl ether at 20°C. We have been studying the enhancement in more detail in this laboratory. Of special interest to us was the observation that the enhancement of the PA signal from powdered solids such as amorphous As_2S_3 was more for the smaller absorption coefficient β and higher chopping frequencies f . It was felt that the relative ratios μ_β/δ or μ_s/δ ($\mu_\beta = 1/\beta =$ optical absorption length for an absorption coefficient β , $\delta =$ particle size, and $\mu_s =$ thermal diffusion length) could be of importance in explaining the dependence of the enhancement on β and f . In this paper we present further experimental results which throw more light on the mechanism behind the effect. We have studied the influence of the length of the gas volume above that sample l_g as well as other variables such as β , f , and δ on the enhancement observed from amorphous selenium (*a*-Se) whose optical absorption properties have been well characterized.³ The results obtained by us substantiates qualitatively the "adsorbed" piston effect proposed by us earlier.

II. EXPERIMENT

The details of the spectrometer used in these studies have already been described elsewhere.^{2,4} The spectrometer consisted of a 250-W tungsten lamp, Schoeffel 1/4-m GM250 monochromator, PAR model 163 chopper, PAR

model 124A lock-in amplifier, and GR 1961 1-in. electret condenser microphone with a flat frequency response in the 5 Hz–2 kHz region. The spectrometer showed the expected f^{-1} dependence for the signal from carbon black in the frequency range studied [(10–100 Hz) and (250–1600 Hz)]. The sample holder was modified such that it can hold, in addition to an inert nonabsorbing material such as alumina, silica gel which can be soaked with the desired liquid. The liquid was introduced into the cell through a microliter syringe without wetting the sample.

All the experiments except the l_g cycling were performed with a fixed l_g of 1.5 mm. Spectra were normalized with respect to carbon black. The variable temperature cell described in Refs. 2 and 4 has the sample in a variable temperature chamber which is connected by means of a glass capillary (1 mm diam) to the microphone chamber which is at room temperature. In the presence of the vapor, the PA signal is very sensitive to the ambient temperature. The time taken to obtain a steady signal is more for liquids with higher vapor pressure and is usually 20–30 min. Unless otherwise mentioned, all the experiments were performed only after the PA signal was found to be independent of time.

The variable l_g setup used by us is shown in Fig. 1. The sample holder is mounted on the top of the microphone while the window can be moved back and forth to get the desired l_g . The l_g 's are accurate to ± 0.05 mm and could be changed from 0.05 to 6.00 mm. Measurements were taken at intervals of 0.20 mm.

Amorphous selenium used in these studies was obtained from Koch light. Various particle sizes of *a*-Se were obtained by grinding and using sieves of appropriate mesh sizes.

III. RESULTS

A. Influence of l_g

The variation of the PA signal intensity I_{PA} and phase ϕ_{PA} from carbon black in presence of air as a function of l_g for various chopping frequencies (10–100 Hz) are shown in Fig. 2. The maximum in I_{PA} occurs at $l_g \sim \pi\mu_{air}$ where μ_{air} is

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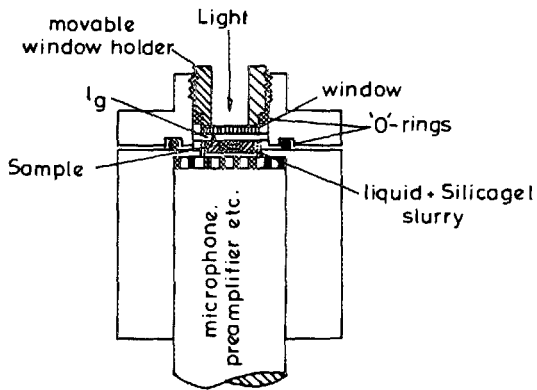


FIG. 1. Design of the photoacoustic cell used for varying length of the gas column l_g .

the thermal diffusion length in air, calculated using the thermal diffusivity given in the literature.⁵ The dependence of the intensity and phase is less marked for $l_g > 2\pi\mu_{\text{air}}$. We note that $2\pi\mu_{\text{air}}$ is roughly the length at which the thermal waves in the gas phase are attenuated.⁶⁻⁹

We have observed that on introduction of a liquid into the cell, the extent of enhancement E_{obs} ($E_{\text{obs}} = I_{\text{liq}}/I_{\text{air}}$; $I_{\text{liq}} = I_{\text{PA}}$ in presence of liquid and $I_{\text{air}} = I_{\text{PA}}$ in presence of air alone) depends initially on the number of cycles through which l_g has been changed [i.e., say from upper limit to lower limit (compression) and back (expansion)]. Three or four expansion and compression cycles are required for obtaining a reproducible behavior. The leak rate of ether into the microphone back volume seems to be unimportant for these experiments. The liquid ether in the cell replenishes any of the ether vapor that may have leaked out.

In Fig. 2(a), we have also plotted the variation of the PA signal from carbon black in the presence of ether after a reproducible behavior was obtained for the compression and expansion cycles. We note that the PA signal dependence on l_g is completely different from that in air, the maximum in the PA signal in presence of ether shifting to lower values of l_g . For small values of l_g the enhancement E_{obs} varies roughly as l_g^{-1} while for higher values of l_g , E_{obs} is independent of l_g . At higher values of l_g enhancement increases with increasing chopping frequency.

B. Chopping frequency f dependence

In terms of the Rosenzweig-Gersho (RG) theory,⁶ the intensity of a PA signal varies with chopping frequency as

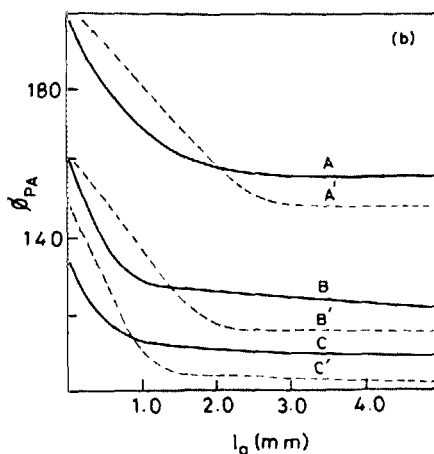
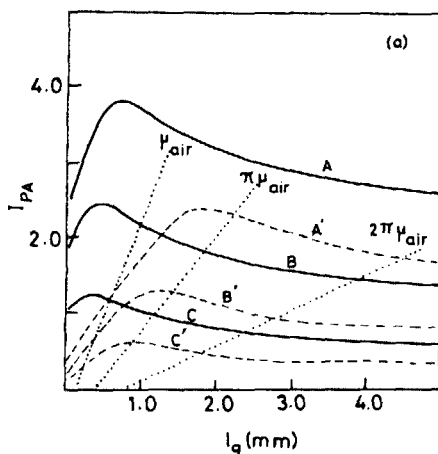


FIG. 2. (a) Variation of I_{PA} and (b) ϕ_{PA} in presence of air (dashed lines) and ether (full lines) for carbon black. A, A', B, B', and C, C' are the values obtained at 11.6, 28.6, and 73.4 Hz chopping frequencies. The values of μ_{air} , $\pi\mu_{\text{air}}$, and $2\pi\mu_{\text{air}}$ for these frequencies are obtained from the points at which the corresponding dotted lines intersect A', B', and C'.

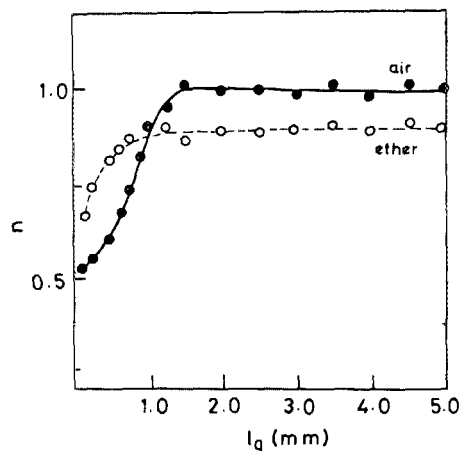


FIG. 3. Changes in the exponent n as a function of l_g in the presence of air and ether for carbon black in the frequency range 10–100 Hz.

f^{-n} . For optically opaque and thermally thin solids such as carbon black the $\log I_{\text{PA}}$ vs $\log f$ plots should give a straight line with a slope = -1.0 (or $n = 1$). The plots of $\log I_{\text{air}}$ vs $\log f$ for a fixed l_g gives nearly straight lines with $n = 1.0$ when $l_g > 1.5$. In Fig. 3, we show the variation of the exponent n obtained from $\log f$ vs $\log I_{\text{air}}$ plots for various l_g values. The value of the exponent n approaches 0.5 when l_g tends to zero and reaches a value of 1.0 for $l_g \approx 1.5$ mm. The variation of n as a function of l_g in presence of ether (after four cycles of compression and expansion) is also shown. We note here also that as l_g tends to zero, n tends to 0.5, but for $l_g > 0.75$ mm the exponent n levels off and approaches 0.9 with further increases in l_g .

C. Effect of optical absorption coefficient β and particle size δ

The enhancement for particular l_g and f from carbon black is always found to be independent of the intensity or wavelength in the visible region of the illuminating source. In our earlier communication,¹ we have noted that the enhancement of PA signals from powdered As_2S_3 glass is more for smaller values of β . Since the intensity of PA signal is dependent^{10,11} on δ , we have studied the enhancement of the PA signal from a -Se in presence of air and ether as a function of δ (Figs. 4–6). We have chosen a -Se as its thermal and optical properties have been well characterized.^{3,5} In Fig. 4, the results obtained with a flat disk of a -Se of 1.6-mm thickness are shown. The data have been normalized such that

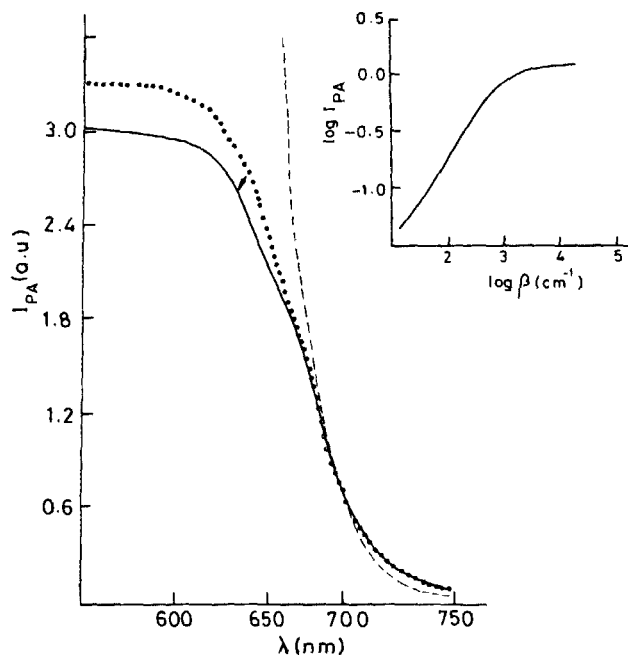


FIG. 4. Variation of I_{air} (full line) I_{ether} (dotted line) and β (dashed line) against wavelength for a flat disk of amorphous selenium. Inset shows the variation of $\log I_{\text{air}}$ vs $\log \beta$ for the same sample. The arrow indicates the point where $10 \mu_{\beta} = \mu_s$, $f = 28.6$ Hz.

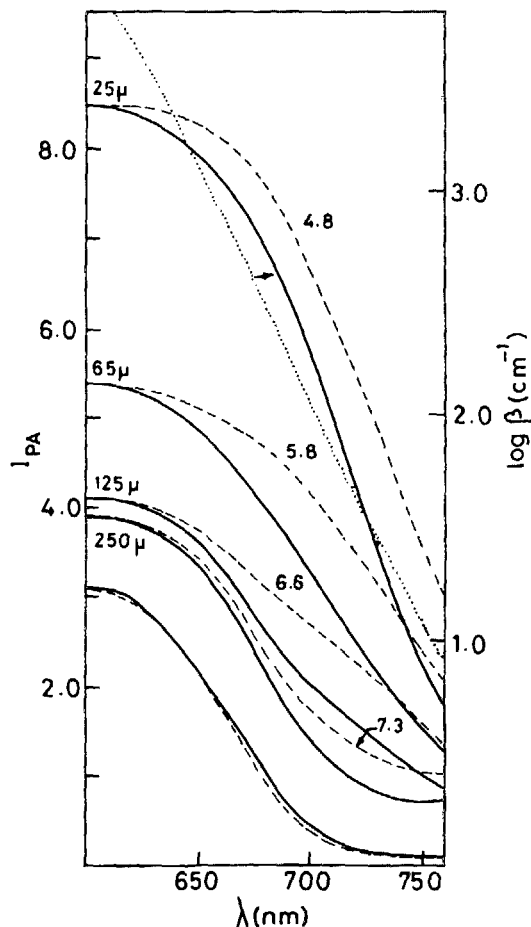


FIG. 5. Normalized PA signal from amorphous selenium in the presence of air (full line) and ether (dashed line) for various particle sizes as indicated. The enhancement for the various samples at 600 nm is shown against the corresponding curves. Variation of absorption coefficient as a function of wavelength is shown by dotted lines.³

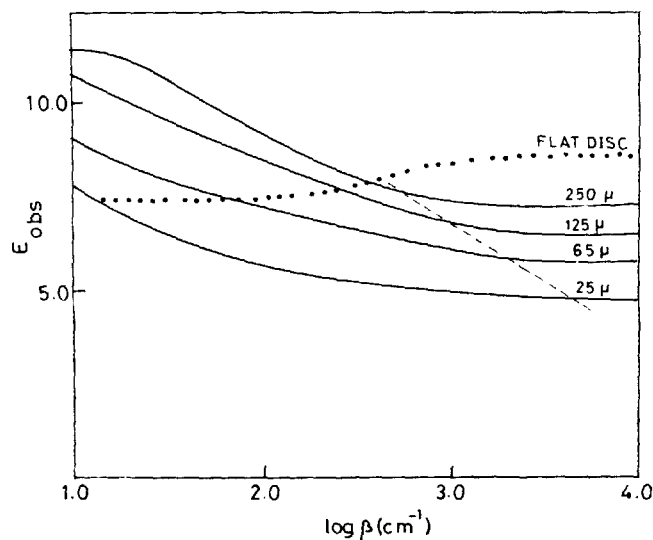


FIG. 6. Variation of enhancement E_{obs} in the presence of ether against $\log \beta$ for various particle sizes for amorphous selenium obtained from data in Figs. 4 and 5. The dashed line indicates the region over which E_{obs} is roughly independent of β . E_{obs} for the flat piece of a -Se is also shown (dotted line).

I_{air} , I_{ether} , and β [calculated using³ the relation $\beta = 7.35 \times 10^{-2} \exp(\hbar\omega/0.058) (\text{eV}) \text{ cm}^{-1}$] have the same value at 685 nm at which wavelength $\mu_{\beta} = \mu_s$ for the chopping frequency used. The observed enhancement is roughly independent of β (Fig. 6) especially when $\mu_{\beta} > \mu_s$. When $\mu_{\beta} < \mu_s$, there seems to be a slight increase in E_{obs} .

With powdered samples, however, seemingly opposite results are obtained. This is seen from normalized PA spectra (Fig. 5) and E_{obs} (Fig. 6) obtained from powdered a -Se samples of different δ in the presence of air and ether. However, since there may be loss in the effective surface area due to capillary condensation of liquids in small voids between particles we shall not comment the dependence of E_{obs} on δ . For higher values of β , E_{obs} is roughly independent of β . The range of β over which the independence is observed (shown by dashed line in Fig. 6) decreases as δ decreases. E_{obs} is completely independent of β only when the PA signal is saturated.

The frequency dependence of the PA signal from a -Se for various values of δ both in air and ether are shown in Fig. 7 for two wavelengths ($\lambda = 600$ and 750 nm corresponding to $\log \beta$ of 4.2 and 1.1, respectively). The values of the exponent n ($I_{\text{PA}} \propto f^{-n}$; $n = n^0$ for air and n' in presence of ether) calculated from the slopes are tabulated in Table I. The values of μ_s/δ and μ_{β}/δ are also given in Table I. It is seen from Table I that for the same gas phase and fixed λ , n increases with decreasing δ , while for fixed δ , n increases with decreasing β .

The values of the exponent n in the presence of ether (n') decreases when compared to that in air (n^0) (see Table I) especially for smaller values of δ and/or β . We note that this decrease in n could itself lead to an enhancement. Since $I_{\text{PA}} \propto f^{-n}$, we could write for the enhancement $E_n(\lambda)$, due to changes in the exponent at each wavelength, as

$$E_n(\lambda) = \frac{I_{\text{hq}}}{I_{\text{air}}} \alpha \frac{f^{-n'(\lambda)}}{f^{-n^0(\lambda)}} \alpha f^{n^0(\lambda) - n'(\lambda)} \quad (1)$$

or

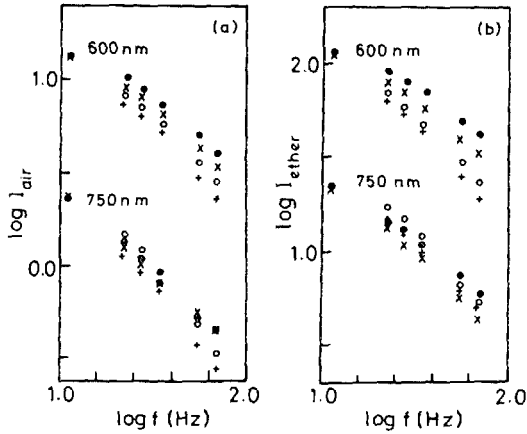


FIG. 7. (a) Plots of $\log I_{\text{air}}$ vs $\log f$ and (b) $\log I_{\text{ether}}$ vs $\log f$ for various values of δ at 600 and 750 nm. Filled circles: 250 μm ; crosses: 125 μm ; open circles: 65 μm , and plus signs: 25 μm . The plots have been normalized so that the intensities are same at 11.6 Hz for a particular wavelength.

$$E_n = K_n f^{n^0(\lambda) - n'(\lambda)}, \quad (2)$$

where $n^0(\lambda)$ and $n'(\lambda)$ are the values of the exponent for the wavelength λ . When $(n^0 - n')$ is greater than 1, E_n is greater than 1 as long as K_n is greater than 1. We have calculated the ratios,

$$R_n = \frac{E_n(600 \text{ nm})}{E_n(750 \text{ nm})} \text{ and } R_0 = \frac{E_{\text{obs}}(600 \text{ nm})}{E_{\text{obs}}(750 \text{ nm})}$$

for different values of δ (Table I). It is found that R_n is approximately equal to R_0 when $\delta < \mu_\beta$ or μ_s and R_0 is greater than R_n when $\delta > \mu_\beta$ or μ_s . Thus for small particles ($\delta < \mu_\beta$ or μ_s) the additional enhancement observed for smaller values of β is sufficiently accounted for by the changes in the exponent. In agreement with the above conclusion we have found that when the values of $\log I_{\text{ether}}(\lambda)$ obtained for several wavelengths are plotted against $\log I_{\text{air}}(\lambda)$ values for the corresponding wavelength are indeed linear for smaller values of δ .

IV. DISCUSSION

Enhancement of PA signals by adsorbed gases in the presence of volatile liquids is not expected in terms of the RG theory.⁶ These authors have obtained the acoustic pressure in the cell due to the displacement of the acoustic piston from the adiabatic gas law $PV^\gamma = \text{const}$, where γ is the ratio of specific heats. The incremental pressure $\delta P(t)$ is given by

$$\delta P(t) = \frac{\gamma P_0}{V_0} \delta V = \frac{\gamma P_0}{l_g} \delta x(t), \quad (3)$$

where P_0, V_0 are ambient pressure and volume, while $\delta x(t)$ is the displacement of the boundary layer. The term dp/dV for vapors of liquids below their boiling point is expected to be zero. For thermally thin and optically opaque materials such as carbon black, the PA signal is given by (Case 2a, Fig. 9. 3 of Ref. 7),

$$Q \approx -\frac{1-i}{2a_g} \left(\frac{\mu_b}{K_b} \right) Y; Y = -\frac{P_0 I_0}{2\sqrt{2} l_g T_0}, \quad (4)$$

where $a_g = i/\mu_g, T_0$ is ambient temperature, I_0 is intensity of the source, and K_b the thermal conductivity of the backing material. It has been argued by Wong¹² that the physically adsorbed gas could form a region of high density very close to the solid surface and hence could significantly enhance the pressure variation. The amplified pressure variation according to Wong is larger than the reduction in the thermal diffusion accompanying the increase in density. We have not found any correlation between the van der Waal's constant for several gases and the observed enhancement over the RG theory as reported by Wong. We therefore believe that enhancement is not due solely to factors related to changes in thermal diffusion length in the gas phase or enhanced pressure at the surface.

The observed enhancement of PA signals due to physically adsorbed vapors of liquids has been attributed to an "adsorbed" piston effect earlier.¹ In this model we have proposed that the periodic heat flow to the surface of the solid could cause a desorption of the physically adsorbed vapors of the liquid. In order that there be an enhancement of PA signals in the presence of vapors of volatile liquids, there should either be more efficient heat transfer to the gas phase, say, by reducing the extent of thermal diffusion into the bulk of the solid, or by reducing the thermal contact resistance at the solid gas interface.¹³ We shall refer to this process of enhancement as E_{thermal} . A second mechanism of enhancement would be the increase in the pressure inside the cell caused by an increase in the number of gas molecules following thermal desorption from the adsorbed layer. This is analogous to the "mechanical piston" effect proposed by McDonald and Wetsel.^{1,7,14} The enhancement due to this process will be referred to as E_{pressure} . Since the gas phase is already saturated with the vapors of the liquid an increase in the number of liquid molecules in the gas phase would make the vapor phase supersaturated. Hence enhancement due to E_{pressure} would be kinetically controlled and is expected to be more important for higher chopping frequencies. We may consider the increase in pressure dp in the gas phase (by desorption of molecules from adsorbed multilayer) due to an

TABLE I. The values of the exponent n , the ratio R_0 , and $R_n, \mu_s/\delta$, and μ_β/δ for various particle sizes of *a*-Se.

Particle size δ (cm)	μ_s/δ (f : 28.6 Hz)	n_{air}		n_{liq}		f : 28.6 Hz		f : 57.4 Hz		μ_β/δ			
		600 nm	750 nm	600 nm	750 nm	R_n	R_0	R_n	R_0	600 nm	650 nm	700 nm	750 nm
0.0250	0.160	0.86	1.00	0.76	0.94	1.433	0.7037	1.176	0.7065	0.0025	0.0325	0.330	3.25
0.0125	0.321	0.94	1.00	0.84	0.92	1.067	0.6822	1.084	0.8211	0.0050	0.065	0.665	6.50
0.0065	0.618	0.98	1.21	0.84	1.04	0.9044	0.7706	0.8655	0.6692	0.0097	0.125	1.28	12.50
0.0025	1.600	1.15	1.34	0.90	0.92	0.5683	0.6630	0.5060	0.7033	0.0252	0.325	3.33	32.50

increase dT of the surface temperature to be proportional to dp/dT of the bulk liquid. This would account for the linear relationship observed between the enhancement and the vapor pressure of the liquid in the cell.^{1,2}

It is important to note that the increase in surface temperature by dT over that of the ambient temperature implies that at the surface the relative vapor pressure of the liquid is minutely less than one. It is also important to note that dT itself is very small¹⁵ (of the order of 10^{-5} K). The typical PA signal is of the order of 1 mV before amplification. The sensitivity of the microphone (GR 1961-1-in. electret) used by us is -38 dB re 1V/N/m². Hence the average increase in pressure within the cell is of the order of $1 \mu\text{bar}$. If one considers the increase in pressure to be due to the desorption of molecules, then since the effective volume of the cell is 0.2 cm^3 , and a desorption of only 10^{+12} molecules into the gas would be sufficient to produce the observed enhancement. The changes in pressure and temperature are therefore only small perturbations.

The $f^{-1/2}$ dependence of PA intensity from carbon black when l_g tends to zero has been reported earlier by Ganguly and Rao.⁴ The f^{-1} dependence as predicted by RG theory is due to the product of two terms having a $f^{-1/2}$ dependence.¹⁴ One of these terms is associated with the heat flow from the bulk to solid gas interface which is determined by the thermal diffusion length μ_s of the solid. The second term is due to the heat flow from the surface to the gas phase which is determined by the thermal diffusion length of gas phase. When l_g tends to zero the acoustic piston model of RG theory is no longer operative and only pressure variations within the gas phase due to the periodic heat flow is important, so that one would expect a $f^{-1/2}$ dependence when l_g tends to zero.

We could therefore expect that PA signal in the presence of liquids for larger values of l_g would show an f^{-1} dependence if the PA signal is due entirely to E_{thermal} and an $f^{-1/2}$ dependence if the PA signal is due only to the changes in pressure due to desorption. When both E_{thermal} and E_{pressure} are responsible for the enhancement the value of $\exp(I_{\text{PA}} \propto f^{-n})$ is expected to be between that of 0.5 and 1.0. The fact that even for higher values of l_g , I_{ether} has a $f^{-0.9}$ dependence (Fig. 3) indicates that E_{pressure} could also be operative even for high values of l_g .

The enhancement due to E_{pressure} seems to be sufficient to account qualitatively the changes in E_{obs} as a function of β , for small values of δ ($\mu_s > \delta, \mu_\beta > \delta$). When a solid is taken in the form of a powder of particle size δ , the air in the voids (of average diameter δ_v) between the particles are heated by the PA effect when $\mu_s > \delta$ or $\mu_\beta > \delta$. The efficiency of heat transfer from within the voids to the bulk gas is expected to be small since δ_v is usually much smaller than μ_g (the thermal diffusion length of gas phase). However, since there still may be a desorption from the void to the bulk phase, E_{pressure} could be operative provided that δ_v is not so small that there

is capillary condensation. We therefore expect that as δ decreases (and hence δ_v decreases) E_{pressure} would become more important so that the value of the exponent n in the presence of ether (n') is expected to decrease compared to that in the presence of air (n^0). The enhancement in the limit of very small particle size can be understood by examining the Eq. (2). When $\delta > \mu_\beta$ and μ_s , only the illuminated surface is important so that the voids become unimportant. The enhancement would then be independent of λ (or β) as is observed in the case of thick flat disks or liquids.

The above discussion is admittedly speculative in nature. A quantitative theoretical modeling is difficult as there are several parameters for which we are not able to obtain a quantitative idea at present. These include a knowledge of the actual thickness of the multilayer and the nature of the interface between the physically adsorbed multilayer and the gas phase when the vapor pressure is close to that of saturated vapor pressure. We would like to caution once again that interpretation of results obtained by PA techniques including phase sensitive detection and determination of thermal diffusion lengths in gas phase should be made after the possibility of the presence of an adsorbed multilayer of a volatile liquid on the surface has been excluded.

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