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

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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 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 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 As2S3 was more for the smaller absorption coefficient \( \beta \) and higher chopping frequencies \( f \). It was felt that the relative ratios \( \mu_\beta / \delta \) or \( \mu_\beta / \beta \) \( \mu_\beta = 1/\beta \) = optical absorption length for an absorption coefficient \( \beta \), \( \delta = \) particle size, and \( \mu_\delta = \) thermal diffusion length could be of importance in explaining the dependence of the enhancement on \( \beta \) 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 \( \beta \), \( f \), and \( \delta \) on the enhancement observed from amorphous selenium (a-Se) whose optical absorption properties have been well characterized. 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. 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 \( [10–100 \text{ Hz}] \) and \( [250–1600 \text{ Hz}] \). 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 \( \pm 0.05 \text{ mm} \) 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 \( \phi_{PA} \) from carbon black in presence of air as a function of \( l_g \) for various chopping frequencies \( [10–100 \text{ Hz}] \) are shown in Fig. 2. The maximum in \( I_{PA} \) occurs at \( l_g \sim \mu_\text{air} \) where \( \mu_\text{air} \) is...
the thermal diffusion length in air, calculated using the thermal diffusivity given in the literature. The dependence of the intensity and phase is less marked for $l_s > 2\pi \mu_{\text{air}}$. 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 $E_{\text{obs}} (E_{\text{obs}} = I_{\text{air}} / I_{\text{air}}; I_{\text{air}} = I_{\text{PA}}$ 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 $l_s$ 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 $l_s$ is completely different from that in air, the maximum in the PA signal in presence of ether shifting to lower values of $l_s$. For small values of $l_s$, the enhancement $E_{\text{obs}}$ varies roughly as $l_s^{-1}$ while for higher values of $l_s$, $E_{\text{obs}}$ is independent of $l_s$. At higher values of $l_s$ enhancement increases with increasing chopping frequency.

B. Chopping frequency $f$ dependence

In terms of the Rosencaig–Gersho (RG) theory,6 the intensity of a PA signal varies with chopping frequency as $f^{-n}$. For optically opaque and thermally thin solids such as carbon black the log $I_{PA}$ vs log $f$ plots should give a straight line with a slope of $-1.0$ (or $n = 1$). The plots of log $I_{\text{air}}$ vs log $f$ for a fixed $l_s$ gives nearly straight lines with $n = 1.0$ when $l_s > 1.5$. In Fig. 3, we show the variation of the exponent $n$ obtained from log $f$ vs log $I_{\text{air}}$ plots for various $l_s$ values. The value of the exponent $n$ approaches 0.5 when $l_s$ tends to zero and reaches a value of 1.0 for $l_s = 1.5$ mm. The variation of $n$ as a function of $l_s$ in presence of ether (after four cycles of compression and expansion) is also shown. We note here also that as $l_s$ tends to zero, $n$ tends to 0.5, but for $l_s > 0.75$ mm the exponent $n$ levels off and approaches 0.9 with further increases in $l_s$.

C. Effect of optical absorption coefficient $\beta$ and particle size $\delta$

The enhancement for particular $l_s$ 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$_2$S$_3$ glass is more for smaller values of $\beta$. Since the intensity of PA signal is dependent on $\delta$, we have studied the enhancement of the PA signal from $\alpha$-Se in presence of air and ether as a function of $\delta$ (Figs. 4–6). We have chosen $\alpha$-Se as its thermal and optical properties have been well characterized.3,5 In Fig. 4, the results obtained with a flat disk of $\alpha$-Se of 1.6-mm thickness are shown. The data have been normalized such that

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

FIG. 2. (a) Variation of $I_{PA}$ and (b) $\phi_{PA}$ 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 $\mu_{\text{air}}$, $\mu_{\text{ether}}$, 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 $l_s$ in the presence of air and ether for carbon black in the frequency range 10–100 Hz.
FIG. 4. Variation of \( I_{\text{air}} \) (full line) \( I_{\text{ether}} \) (dotted line) and \( \beta \) (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 \( 10 \mu_B = \mu_e, \ f = 28.6 \text{ Hz} \).

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.\(^3\)

\[ I_{\text{air}}, I_{\text{ether}}, \text{ and } \beta \text{ [calculated using\(^3\) the relation } \beta = 7.35 \times 10^{-2} \exp(\phi_{\text{io}}/0.058) \text{ (eV cm}^{-1}\text{)] have the same value at 685 nm at which wavelength } \mu_B = \mu_e \text{ for the chopping frequency used. The observed enhancement is roughly independent of } \beta \text{ (Fig. 6) especially when } \mu_B > \mu_e. \text{ When } \mu_B < \mu_e \text{ there seems to be a slight increase in } E_{\text{obs}}. \]

With powdered samples, however, seemingly opposite results are obtained. This is seen from normalized PA spectra (Fig. 5) and \( E_{\text{obs}} \) (Fig. 6) obtained from powdered a-Se samples of different \( \delta \) 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 \( E_{\text{obs}} \) on \( \delta \). For higher values of \( \beta \), \( E_{\text{obs}} \) is roughly independent of \( \beta \). The range of \( \beta \) over which the independence is observed (shown by dashed line in Fig. 6) decreases as \( \delta \) decreases. \( E_{\text{obs}} \) is completely independent of \( \beta \) only when the PA signal is saturated.

The frequency dependence of the PA signal from a-Se for various values of \( \delta \) 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 \( n \) (\( I_{\text{PA}} \propto f^{-n}; n = n^0 \text{ for air and } n' \text{ in presence of ether} \)) calculated from the slopes are tabulated in Table I. The values of \( \mu_e / \delta \) and \( \mu_B / \delta \) are also given in Table I. It is seen from Table I that for the same gas phase and fixed \( \lambda \), \( n \) increases with decreasing \( \delta \), while for fixed \( \delta \), \( n \) increases with decreasing \( \beta \).

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 \( \delta \) and/or \( \beta \). 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

\[ E_n(\lambda) = \frac{I_{\text{air}}}{I_{\text{air}} \cdot f^{-n^0(\lambda)} - f^{-n'(\lambda)}} \]

or

\[ E_n(\lambda) = \frac{I_{\text{air}}}{I_{\text{air}} \cdot f^{-n^0(\lambda)} - f^{-n'(\lambda)}} \]

\[ E_n(\lambda) = \frac{I_{\text{air}}}{I_{\text{air}} \cdot f^{-n^0(\lambda)} - f^{-n'(\lambda)}} \]
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),

\[
Q \approx -\frac{1-i}{2\mu_s K_b} \left( \frac{\mu_s}{K_b} \right) \gamma \quad Y = -\frac{P_0 I_0}{2\gamma I_s T_0}
\]

(4)

where \( \mu_s = 1/\mu_s, T_0 \) 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 Wong\textsuperscript{12} 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 Waals constant for several gases and the observed enhancement over the RG theory as reported by Wong. We therefore believe that enhancement is due not 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.\textsuperscript{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.\textsuperscript{13} We shall refer to this process of enhancement as \( E_{\text{thermal}} \). 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.\textsuperscript{1,7,14} The enhancement due to \( E_{\text{thermal}} \) 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

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

\[
E_n = K_n f^{n(\lambda) - n(\lambda)}
\]

(2)

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

\[
R_n = \frac{E_n (600 \text{ nm})}{E_n (750 \text{ nm})} \quad \text{and} \quad R_0 = \frac{E_0 (600 \text{ nm})}{E_0 (750 \text{ nm})}
\]

for different values of \( \delta \) (Table 1). It is found that \( R_n \) is approximately equal to \( R_0 \) when \( \delta < \mu_s \), or \( \mu_s \), and \( R_0 \) is greater than \( R_n \) when \( \delta > \mu_s \), or \( \mu_s \). Thus for small particles \( \delta < \mu_s \), or \( \mu_s \) the additional enhancement observed for smaller values of \( \beta \) 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 \( I_{\text{air}} (\lambda) \) obtained for several wave lengths are plotted against log \( I_{\text{air}} (\lambda) \) values for the corresponding wavelength are indeed linear for smaller values of \( \delta \).

IV. DISCUSSION

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

\[
\delta P(t) = \frac{\gamma P_0}{V_0} \delta V = \frac{\gamma P_0}{I_g} \delta x(t)
\]

(3)

<table>
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<th>Particle size (( \delta \text{ cm} ))</th>
<th>( \mu_s / \delta )</th>
<th>( n_{\text{air}} )</th>
<th>( n_{\text{gas}} )</th>
<th>( f = 28.6 \text{ Hz} )</th>
<th>( f = 57.4 \text{ Hz} )</th>
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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.\textsuperscript{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 small\textsuperscript{15} (of the order of $10^{-5}$ K). The typical PA signal is of the order of 1 mV before amplification. The sensitivity of the microphore (GR 1961-1-in. electrophot) used by us is $-38$ dB re $1$V/N/m\textsuperscript{2}. Hence the average increase in pressure within the cell is of the order of 1 mbar. 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\textsuperscript{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 $l_s$ tends to zero has been reported earlier by Ganguly and Rao.\textsuperscript{5} The $f^{-1}$ dependence as predicted by RG theory is due to the product of two terms having a $f^{-1/2}$ dependence.\textsuperscript{15} 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 $\mu_s$ 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 $l_s$ 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 $l_s$ tends to zero.

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

The enhancement due to $E_{\text{pressure}}$ seems to be sufficient to account qualitatively the changes in $I_{\text{obs}}$ as a function of $\beta$, for small values of $\delta (\mu_s > \delta, \mu_B > \delta)$. When a solid is taken in the form of a powder of particle size $\delta$, the air in the voids (of average diameter $\delta_v$) between the particles are heated by the PA effect when $\mu_s > \delta$ or $\mu_B > \delta$. The efficiency of heat transfer from within the voids to the bulk gas is expected to be small since $\delta_v$ is usually much smaller than $\mu_s$ (the thermal diffusion length of gas phase). However, since there still may be a desorption from the void to the bulk phase, $E_{\text{pressure}}$ could be operative provided that $\delta_v$ is not so small that there is capillary condensation. We therefore expect that as $\delta$ decreases (and hence $\delta_v$ decreases) $E_{\text{pressure}}$ 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 (n0). The enhancement in the limit of very small particle size can be understood by examining the Eq. (2). When $\delta > \mu_B$ and $\mu_s$, only the illuminated surface is important so that the voids become unimportant. The enhancement would then be independent of $\alpha$ (or $B$) 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.

Acknowledgments

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\textsuperscript{6}A. Rosencauag and A. Gerbino, J. Appl. Phys. 47, 64 (1976).