

Studies on the Enhancement of Photoacoustic Signals from Non-Porous Solids in the Presence of Volatile Liquids^{*}

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Abstract. Studies have been carried out on the enhancement of photoacoustic signals from non-porous solids in the presence of volatile liquids in order to understand the mechanism of enhancement. Dependence of enhancement on equilibration time, absorption coefficient, length of gas phase, illumination intensity, coupling gas together with influence of wall temperature, and relative vapour pressure have been presented. Experimental results are discussed in terms of existing theories and the role of the adsorbed liquid layer in the enhancement has been emphasized. A brief theoretical discussion has been presented to show that the enhancement is due to the more efficient transfer of heat to the gas phase from the solid.

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We have earlier reported the enhancement of photoacoustic (PA) signals from powdered solids by the introduction of vapours of a volatile liquid into the cell [1, 2]. Typically this was done by introducing the liquid itself into the cell without the liquid actually wetting the sample. The observed enhancement was found to be proportional to the vapour pressure of the liquid introduced. We have attributed this enhancement to a periodic evaporation and condensation of the molecules of the liquid adsorbed on the surface of the solid. In analogy with the acoustic piston effect of Rosencwaig and Gersho [3] and the mechanical piston of McDonald and Wetsel [4], we termed this effect an "adsorbed piston" effect. Further analyses of the effect with powdered samples led us to believe that the enhancement (E) is due to two processes [5]. One, which we termed $E_{\text{pressure}}(E_p)$, is due to an increase in the number of molecules in the gas phase and is operative mainly when the thermal diffusion length (μ_s) or the optical absorption length μ_β ($\mu_\beta = 1/\beta$; β : optical absorption coefficient) of the sample is greater than the

particle size d . Under these conditions, it was postulated that there will be evaporation of molecules of the liquid adsorbed in the voids between the particles. It was proposed that E_p leads to a decrease in the value of the exponent n in the relationship $I_{\text{PA}} \propto f^{-n}$ (f being the chopping frequency). E_p was considered to be responsible for the increased enhancement found for amorphous selenium (a-Se) or amorphous As_2S_3 powders at higher wavelengths [1, 5]. The second mechanism of enhancement, which we termed $E_{\text{thermal}}(E_T)$ was operative when μ_β or μ_s is smaller than d . This leads to a frequency-independent enhancement, and we have associated this with a more efficient heat transfer mechanism involving the adsorbed phase which is liquid like.

Recently Korpiun [6] has calculated the change in pressure (in presence of volatile liquid) inside the cell using the Clausius-Clapeyron equation, which relates the increase in pressure to an increase in temperature δT . The numbers thus obtained agree reasonably well with the enhancements reported by us earlier for some powdered samples. The increase in pressure is thus simply related to the increase in the number of vapour molecules in the gas phase and is similar to the

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mechanism E_p , proposed by us. Korpiun termed the enhancement as due to an oscillatory mass transfer effect [6]. Korpiun's model completely ignores the thickness of the adsorbed layer of the liquid. It does not account for several features of the enhancement observed with powders.

A serious test of any theory has to have data from non-porous solids. With this in mind, we have carried out experiments on flat polished samples such as graphite single crystals, amorphous selenium, CdS single crystal, etc. The studies include the dependence of the enhancement on the optical absorption coefficient, length of the gas phase, nature of the ambient gas, intensity of radiation, etc. Our results cannot be described by Korpiun's model. The results show that the thickness of the adsorbed layer is critical in understanding the enhancement. In this paper we present the results of our studies. A part of this data has been quantitatively discussed in an accompanying paper by Srinivasan et al. [7]. We shall present a semiquantitative theoretical examination in a subsequent communication.

1. Experimental

The experimental set-up used in this study has already been described in detail elsewhere [1, 5, 8]. We have made some modifications which are described below. We have modified the sample chamber (Fig. 1) such that an aluminium cup filled with the desired liquid (~ 1 cc capacity) could be placed inside the aluminium cell. An aluminium sample holder was placed on the top of the cup. The sample was kept in a cylindrical groove of 1 mm depth and 8 mm diameter. Two holes (~ 1.5 mm dia) in the sample holder provided the

communication between the cup and the space above the sample. The liquid was introduced by opening the cell, filling the cup to the desired level using a micro syringe and closing it again without spilling the liquid into the microphone/sample chamber. Care was taken such that no error in beam alignment or dead volume was introduced while doing these operations which took less than a minute. Temperature of the liquid was same as that of the cell. Background contributions to the PA signal due to scattered light both in the presence and absence of the liquid were subtracted. These contributions in any case were small and negligible. For experiments with different coupling gases, an identical cell was used except that provisions were made for passing the gases using glass capillaries and stopcocks.

In the absence of liquid, the PA signal intensity (I_{PA}) did not depend upon whether the cup was filled (with inert solid) or not. Despite the large increase in the volume, the cup does not seem to couple with the active region of pressure variation. This aspect is being further investigated. l_g was maintained at 3.5 mm for all experiments except for those involving its variation.

Time dependence studies were carried out immediately after the introduction of the liquid by closing the cell and recording both in-phase and quadrature components. Only after the stabilization in I_{PA} were enhancement values taken. Constant room temperature was maintained for a related series of experiments. Two thermocouples were used to measure the sample and wall temperatures (not shown in the figure). Ice cubes and hot air were used for rapid cooling and heating of the cell, respectively. In order to vary relative vapour pressure x , air-vapour mixtures in various molar ratios were passed through the cell by bubbling air through the liquid (kept outside the cell)

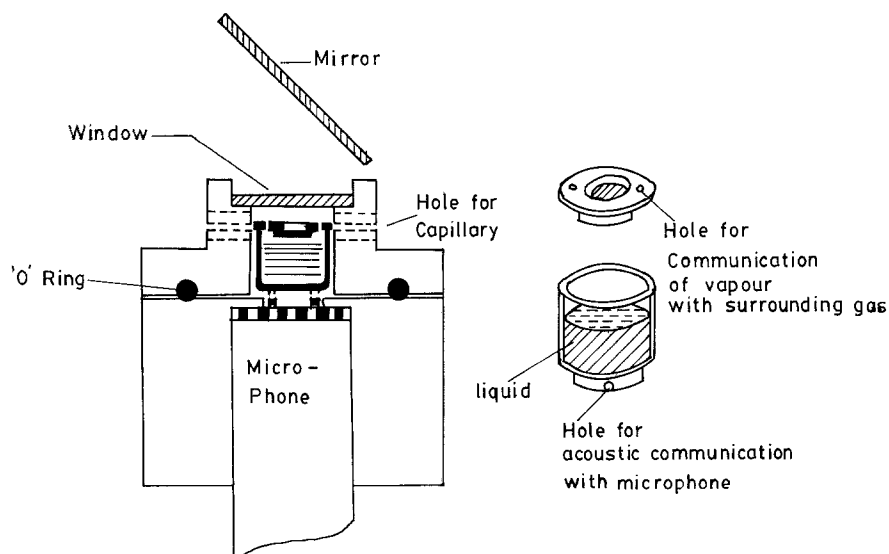


Fig. 1. Design of the cell, sample holder and liquid cup used for the enhancement studies. An identical cell was used with capillaries and stopcocks (shown by dotted lines) for gas passing experiments

at temperatures yielding the desired vapour pressure of the liquid. The relative vapour pressure in the air-vapour mixture was determined both by spectroscopic and gas-chromatographic techniques [9]. External sound was generated by a conventional loud speaker at desired frequencies and introduced into the cell through a glass tube.

2. Results and Discussion

As already shown by us the enhancement from powdered samples shows a strong dependence on β , d , and μ_s . In order to avoid such complications it is necessary, therefore, to study the enhancement from non-porous solids. We have carried out various studies mentioned earlier and discuss them one by one.

2.1. Time Dependence

On the introduction of a liquid in the cell, the signal increases initially as a function of time. It is difficult to reproduce the exact time dependence as several factors are involved. The most important of these seems to be the height of the liquid in the reservoir. However, with little practice the changes are more or less reproducible unless some liquid falls on the sample holder or within the cell. In Fig. 2, we show the time dependence of I_{PA} in a typical experiment. I_{PA} initially increases as a function of time, the rate decreasing as the height of the liquid level in the reservoir decreases (see for example, traces *a* and *b* of Fig. 2). There seems to be a dependence on the chopping frequency also, as seen in traces *a* and *c* which are obtained for the same experiment. After some time the PA signal is independent of

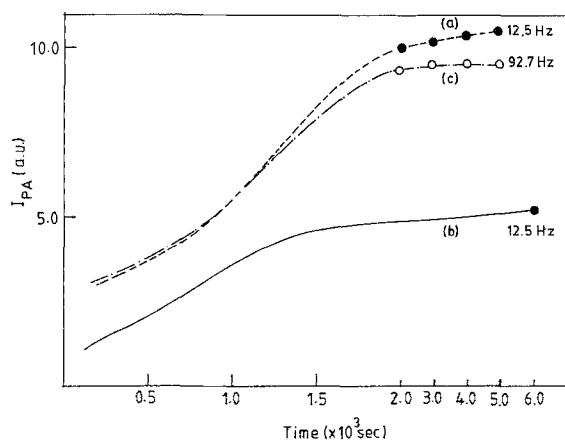


Fig. 2. Variation of I_{PA} with time for a-Se/teflon of $1 \mu\text{m}$ thickness at 20°C after introduction of the liquid into the cup. λ : 470 nm; f : 12.5 and 92.7 Hz. *a* 0.8 cc of acetone in the cup, *b* 0.6 cc of acetone, and *c* 0.8 cc of acetone. Note the change in time scale after 2000 s

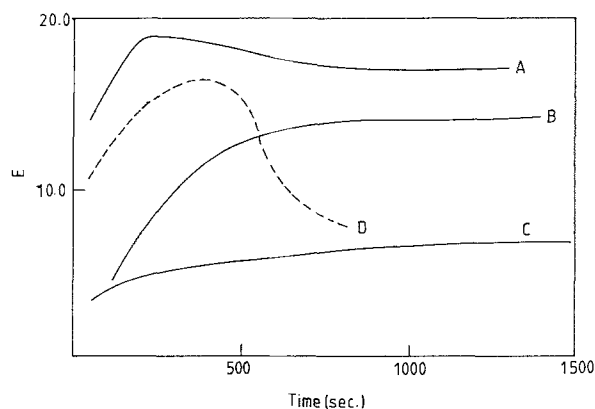


Fig. 3. Variation of E with time for a-Se/teflon at 29°C for various liquids. λ : 470 nm; f : 37 Hz; amount of liquid: 0.8 cc. *A* ether, *B* CS_2 , *C* methanol, and *D* CH_2Cl_2 . *D* shows variation of E when small amount of liquid fell on the sample/microphone

time over extended periods (typically one hour). A PA spectrum may therefore be recorded during this time. The enhancements reported by us correspond to this period. On prolonged standing there seems to be a decrease in the signal. The maximum is observed very quickly at elevated temperatures for liquids with high vapour pressures (see, for example, Fig. 3) or when some liquid is accidentally dropped on a part of the sample holder as seen in the case of trace (*D*) in Fig. 3. We have presented the above results to emphasize that relatively time-independent signals are obtained when the temperature of the liquid is well below its boiling point. In our early experiments [5] the cell design was different and the amount of liquid taken in the cell was very small never being more than $100 \mu\text{l}$. The enhancement measured could have been in error especially for liquids with high vapour pressure.

2.2. Changes in Signal to Noise Ratio (S/N)

One of the problems that had to be resolved was whether there was a change in the microphone's sensitivity during the enhancement experiment. In order to test this, we introduced an external acoustic signal into the cell by means of a glass tube. The amplitude of the external acoustic signals did not change on the introduction of the liquid showing that the microphone sensitivity was not affected. This was further confirmed by the lack of any increase in the noise level in the presence of liquid.

That the microphone sensitivity is not affected is also seen from the marked improvement in the S/N ratio in the presence of vapour. A typical example is given in Fig. 4. Such remarkable improvements in the S/N ratio should be of immense use in the practice of PA spectroscopy if only to improve the range of

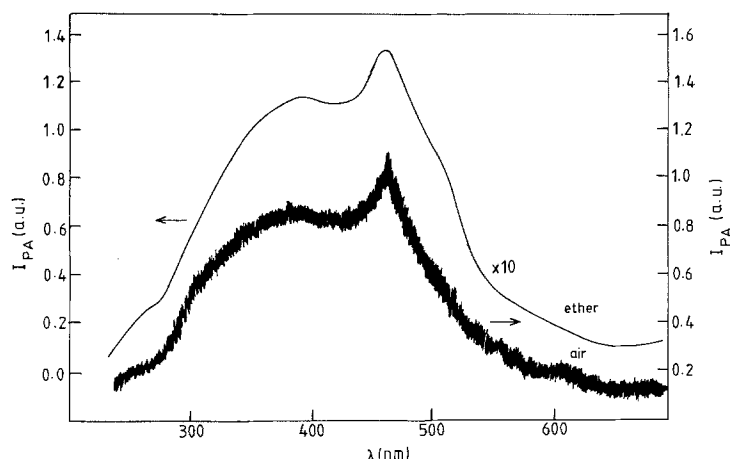


Fig. 4. Unnormalized PA spectra of CdS single crystal in presence of air (noisy line) and ether (smooth line). f : 30 Hz; T.C.: 300 ms; $\Delta\lambda$: 10 nm; wavelength drive: 100 nm/min

frequencies that may be studied since S/N ratio is poor in the low- and high-frequency regimes in most laboratories.

2.3. Length of the Gas Phase (l_g)

Dependence on l_g was studied earlier by us using carbon black [5]. A maximum was observed in the signal as a function of l_g . There was a considerable decrease in the value of l_g at which the maximum was observed in the presence of ether. We have repeated these experiments with a non-porous solid as well as an aqueous solution of methylene blue. The results with the aqueous solution are shown in Fig. 5. The results are similar to those obtained with carbon black (see Fig. 2 of [5]) with the maximum in I_{PA} shifting to a lower value of l_g in the presence of ether when compared to that in air. Such changes cause the enhancement to be more pronounced at lower l_g values (Fig. 5c) decreasing nearly as l_g^{-1} as mentioned by us earlier [5]. The results with the aqueous solution are

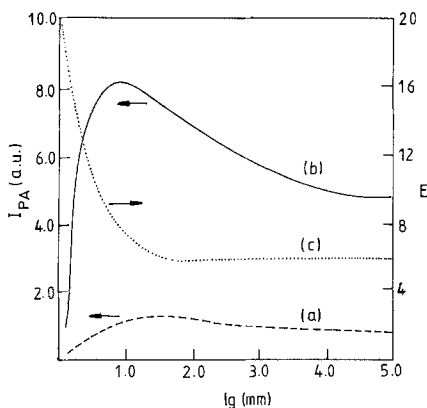


Fig. 5. Variation of I_{PA} with l_g in presence of *a* air and *b* ether for an aqueous methylene blue solution (2×10^{-3} M). *c* shows variation of E with l_g for the same solution. f : 30 Hz; λ : 605 nm

significant in the sense that when the vapour pressure of the liquid (used for enhancement) is low, the maximum is observed at a value closer to that in air. The change in the maximum corresponds to the change in thermal properties accompanying the replacement of air by the vapour.

2.4. Influence of Relative Vapour Pressure of Liquid (x)

In order to examine the influence of relative vapour pressure of the liquid, we passed air mixed with various mole fractions of the vapours of the liquid. We found it difficult to measure the actual vapour pressure inside the cell under the experimental conditions. We therefore, measured the amplitude of the PA signal from the absorption bands of the liquid molecules as a function of the vapour pressure. In Fig. 6 (inset) we show the variation of the PA amplitude of the 286 nm band (I_{286}) of acetone as a function of the predetermined value of x . The linear dependence especially at low x suggests that the expected vapour pressure was obtained inside the cell. The enhancement of a-Se was also measured at the same time and is shown in Fig. 6. The enhancement in the case of a non-porous sample becomes significant only when saturated vapour pressure condition is approached suggesting that a considerable number of monolayers is necessary. With a powdered sample E is significantly higher for $x < 1$. Condensation of liquids can take place in the voids in powders when $x < 1$ because of capillary condensation. These results seem to suggest that a thick liquid like layer is necessary for the enhancement to become appreciable. In these experiments, for non-porous solids at $x=1$ the enhancement was less than that observed under ambient conditions and we have to go to super saturated vapour pressures to achieve the same E observed under normal conditions. In a related experiment we bubbled air through acetone kept at

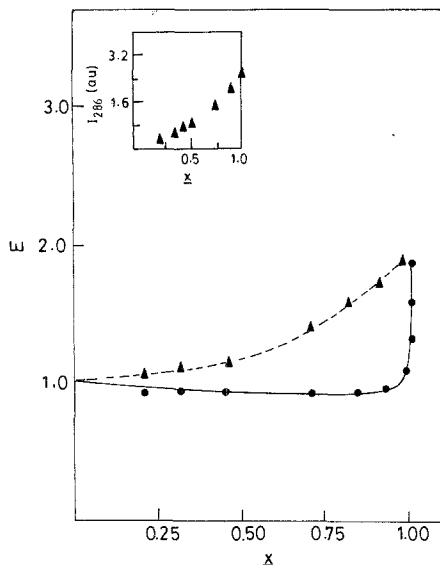


Fig. 6. Dependence of E on relative vapour pressure, x , of acetone for non-porous a-Se (circles) and powder sample of diameter $<25 \mu\text{m}$ (triangles) in presence of acetone at 19°C . Inset shows variation of the intensity of acetone band I_{286} with x

ambient temperature and measured I_{286} as well as the enhancement at 470 nm (E_{470}) from a-Se as a function of time. The values of E_{470} vs. I_{286} obtained at different times are shown by triangles in Fig. 7. I_{286} does not increase beyond the maximum value, for these experiments, as shown by the filled triangle in Fig. 7. At the maximum, the value of I_{286} (I_{286}^v) is close to that shown in the inset of Fig. 6. In these experiments also E becomes significant only when I_{286} is close to the maximum value.

A different situation is obtained when acetone is introduced directly into the cell. In this case E is more

pronounced and I_{286} in the presence of liquid (I_{286}^l) is considerably more than that at saturated vapour pressure conditions. There seems to be a linear relationship between I_{286}^l and E_{470} . Similar results were found for other non-porous solids. The implication is that the increased value of I_{286}^l is due to contributions from an adsorbed layer. The difference between I_{286}^v and I_{286}^l could perhaps be attributed to an adsorbed acetone layer. This is also supported by studies on the changes in the phase angles ϕ_{286} and ϕ_{470} . We find that on introduction of acetone into the cell the experimental values of ϕ_{286} increases from 187° to 193° while ϕ_{470} decreases from 209° to 201° . ϕ_{286} does not change for values of x (up to 0.95) in the experiments in which the relative vapour pressure is changed. Signals from the gas phase in our cell have always a lower value of ϕ than that from a solid. Our results thus seem to show that I_{286} is becoming more "solid-like" or is becoming adsorbed on the surface. On the other hand, I_{470} becomes more gas like which seems to suggest the involvement of the adsorbed layer in enhancing the signal.

Because of the possibility of adsorption on the window itself at least half the difference ($I_{286}^l - I_{286}^v$) could be attributed to the physically adsorbed layer on the sample. It turns out that this is roughly equal to the intensity from the saturated vapour. One could then calculate the thickness of the adsorbed layer. However, the intensity of the PA signal from molecules in a physically adsorbed multilayer is complicated by contributions due to evaporation of the molecules. For the same amount of energy absorbed, the PA signal from the adsorbed layer would be expected to be less than that from the gas phase because of the possibility of heat transfer to the adsorbent. The maximum possible signal per unit excitation energy from acetone

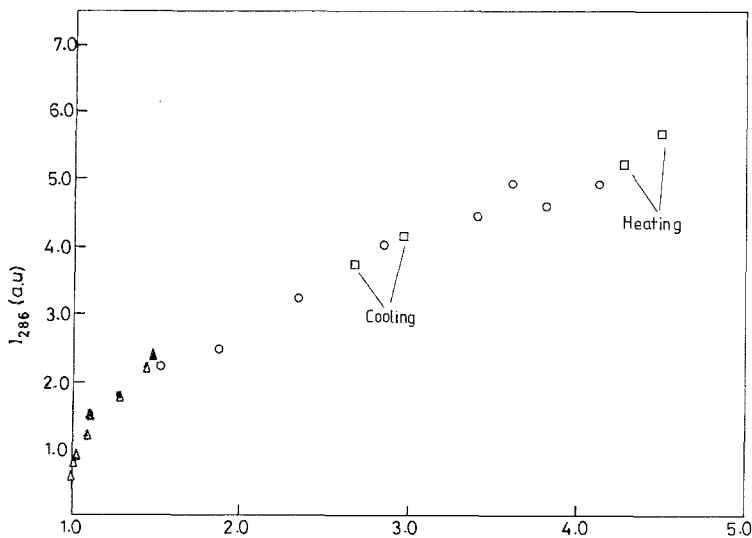


Fig. 7. Variation of I_{286} with E_{470} for a-Se under various conditions. (Open triangles: acetone kept at room temperature is bubbled through the cell at various times; closed triangle: maximum value of I_{286} under acetone bubbling condition; open circles: when acetone is introduced within the cell; open squares: when the cell is cooled or heated rapidly, see Fig. 8)

in an adsorbed layer may then be assumed to be that from acetone molecules in the gas phase itself. Since the absorption coefficient is proportional to the number of molecules per unit area, the minimum thickness of the adsorbed layer may then be calculated. Since the area of the slit is 0.15 cm^2 and l_g is 0.3 cm the thickness of the adsorbed layer works out to be $2 \times 10^4 \text{ \AA}$ which at the chopping frequency employed (37 Hz) is $0.06\mu_L$ (thermal diffusion length of the liquid) of acetone. It is to be noted that a horizontal plate at a height H above a reservoir level when exposed to a vapour and covered by a wetting film has a thickness $\sim 300 \text{ \AA}$ when $H=1 \text{ cm}$, but for $H \approx 0$, the thickness could be as high as $10 \mu\text{m}$ [10]. In our experiments the height H is usually $2\text{--}3 \text{ mm}$ so that thicknesses of the order calculated may be anticipated.

2.5. Influence of Wall Temperature

In Fig. 8 we have shown the changes in I_{PA} when the walls are rapidly heated or cooled as a function of sample temperature. In the inset of Fig. 8 we show the changes in I_{PA} with the difference between the wall and the sample temperature. When the system is cooled

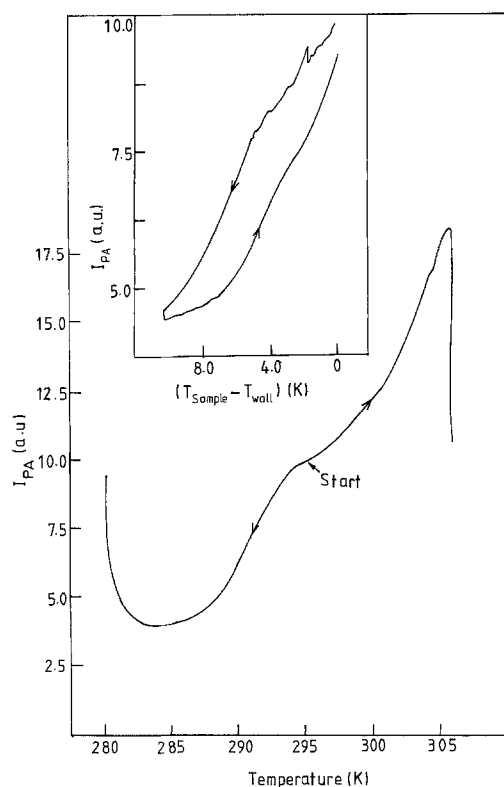


Fig. 8. Variation of I_{PA} from a-Se with temperature when the cell is cooled or heated rapidly. The extrema are reached within two minutes. Inset shows variation of I_{PA} with difference between temperature of the wall and the sample

rapidly, the wall temperature is less than that of the solid. We thus note that the anomalous behaviour is due to a difference in temperature between the wall and the sample. The enhancements obtained at various temperatures are also far different from those expected from the vapour pressure consideration. In order to explore further, we have studied the spectra of a-Se in presence of acetone and followed I_{286} and enhancement E_{470} . It was found that, I_{286} and E_{470} simultaneously increased on heating and decreased on cooling. The values of I_{286} and E_{470} fall well on the plot given in Fig. 7. We note that when the wall is hotter than the sample the molecules adsorbed on the wall would be desorbed and could readsorb on the sample while when the wall is cooler than the sample, the molecules adsorbed on the sample may get desorbed and readsorb on the wall. Thus these results are consistent with the assumption that the thickness of the adsorbed layer is important for the enhancement process.

2.6. Influence of Intensity of Radiation

We have studied the enhancement process as a function of the intensity of the illuminating radiation (white visible light filtered with water). With carbon black powder we have found the enhancement to be independent of the intensity of the lamp. However, the results are quite different when a single crystal of graphite is used. At low intensities the ratio $I_{\text{PA}}(\text{carbon black})/I_{\text{PA}}(\text{graphite}) \approx 70$ for the same intensity. At high intensities of illumination there is a marked dependence on the illumination intensity from graphite single crystal although I_{PA} was actually less than that of carbon black. We must add immediately that where an intensity dependence was obtained the level of the PA signal was much more than that normally encountered while recording PA spectra using monochromatic light. On closer examination we find that the I_{PA} is initially high, as soon as light is introduced into the cell and it rapidly decreases (within seconds) to a steady value (Fig. 10). By taking the shortest possible time constant (30 ms) we find that the intensity at zero time ($I_{t=0}$) against I_{PA} fits to a straight line (Fig. 9, dashed line). It would be difficult to account for these changes if the thickness of the adsorbed layer was not important.

2.7. Influence of the Coupling Gas

In Table 1 we show E of the PA signal from a-Se at 470 nm for various coupling gases in the presence of ether, as well as the ratios of the PA signal for various gases. The results with various coupling gases are compared with some of the values given in the

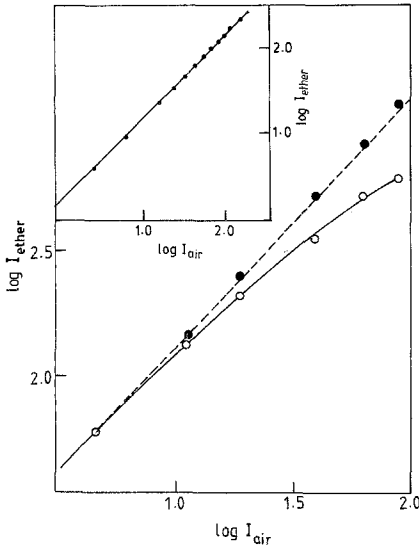


Fig. 9. Plot of $\log I_{\text{air}}$ vs. $\log I_{\text{ether}}$ for a flat piece of graphite single crystal using white light (full line). Plot of $\log I_{\text{air}}$ vs. $\log I_{\text{ether}}$ at $t = 0$ (see text) for the same conditions (dashed line). Inset shows the variation of $\log I_{\text{air}}$ with $\log I_{\text{ether}}$ for carbon black powder

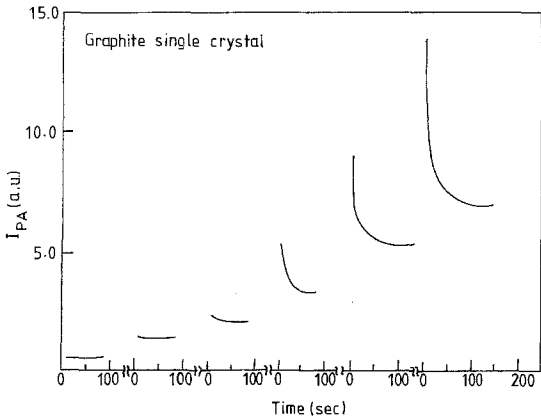


Fig. 10. Variation of I_{PA} with time immediately after allowing the light to impinge on the sample for various lamp intensities

literature; our results are close to those of Wong [11]. We see from the table E is nearly independent of the coupling gas.

2.8. Influence of the Optical Absorption Coefficient (β)

In our earlier studies non-porous a-Se samples have shown near independence of enhancement on wavelength although there seemed to be more E for higher β (lower λ). This behaviour is quite different from that of powders. In order to test this aspect we have to study E from both single crystal and powdered CdS. The results are shown in Fig. 11. We have reexamined the enhancement from a-Se and shown in the same figure. We note that a distinct enhancement (well outside experimental errors) at shorter wavelengths compared to that at longer wavelengths for the non-porous samples which is opposite to that observed for powders

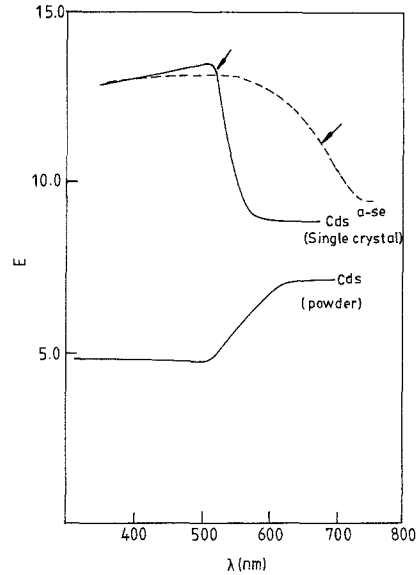


Fig. 11. Plot of E vs. λ for CdS single crystal, CdS powder and a-Se piece. Arrows show the points at which $\mu_s = \mu_\beta \cdot \Delta\lambda = 10$ nm. The thermal and optical properties are obtained from the literature [13]

Table 1

Coupling gases	$I_{\text{gas}}/I_{\text{air}}$			Enhancement	
	Our results	Predicted value [3]	Literature value [11]	E_{air} (relative to I_{air})	E_{gas} (relative to I_{gas})
Air	1.00	1.00	1.00	4.60	4.60
N ₂	1.00	1.00	1.01	4.60	4.60
H ₂	2.13	2.66	2.19	8.47	3.98
Ar	1.23	1.25	0.99	5.98	4.86
He	2.09	3.66	2.66	9.47	4.53
CO ₂	0.82	0.78	0.70	3.78	4.60

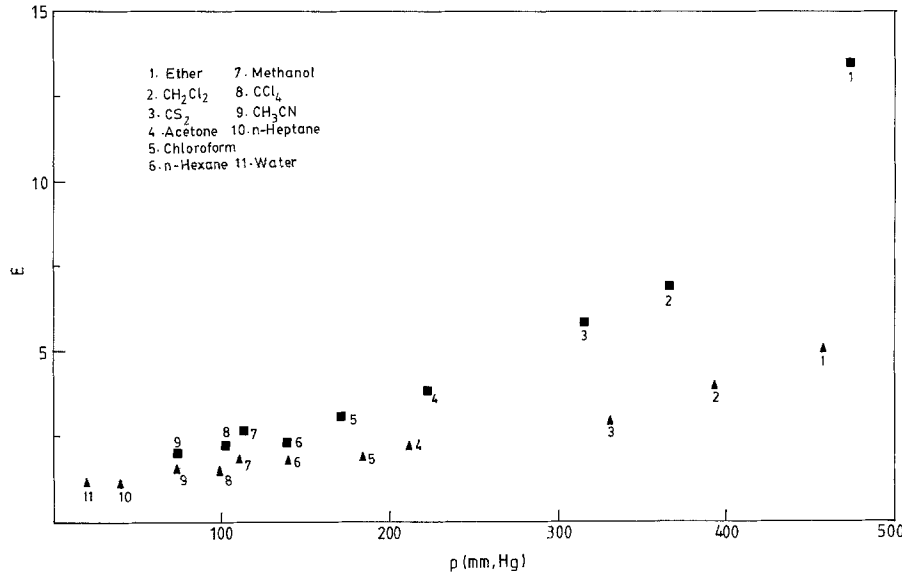


Fig. 12. Plots of E vs. vapour pressure for various liquids at ambient temperatures for CdS single crystal (squares) and CdS powdered sample (triangles)

[5]. For the non-porous samples we find that the wavelength dependence of E becomes more pronounced when the thermal diffusion length of the sample become close to μ_β , as indicated by arrows in Fig. 11.

2.9. Influence of Various Liquids

So far we have listed all the precautions that have to be taken to ensure that any change in the enhancement on introduction of different liquids into the cell is not due to other factors. In order to study the influence of various liquids for enhancement studies we have to choose the wavelength regions where the PA signal is saturated, allow for sufficient time for equilibration, choose chopping frequencies so that the length of the gas phase is more than $2.5\mu_g$, and see that wall temperature is same as that of the sample and operate at low intensities. With all these precautions, E obtained from a non-porous sample of a CdS single crystal, is shown for various liquids in Fig. 12.

The dependence on the saturated vapour pressure is far from linear, especially at high vapour pressures. Instead we obtain a better linear relationship of E with $x/(1-x)$, where x is the mole fraction of the vapour in the gas phase. We have also shown in the same plot the enhancement from powdered CdS. In this case E is less and seems to show a more linear dependence on the vapour pressure.

3. Some Theoretical Considerations

In the light of our recent studies, there are some important points that have to be considered. In the first instance we note that an enhancement has to mean that

more heat is given up to the gas phase. This obvious fact is shown in the following way: In the RG model [3] the PA signal is produced by the heating up of the air molecules by collision with hot solid surface. This causes an increase in the pressure δP . We assume an average increase of temperature by δT in the region of importance (δT is similar to the average temperature $\bar{\theta}$ of RG model given by [Ref. 3, Eq. (15)]). In the usual notation we may therefore write that

$$\delta P = nR\delta T/V. \quad (1)$$

We may consider another situation in which we inject a number of moles δn into the cell without changing T , to cause the same increase δP in pressure,

$$\delta P = RT\delta n/V. \quad (2)$$

Thus from (1, 2) we obtain

$$\delta n/n = \delta T/T. \quad (3)$$

If for the situation corresponding to (1), Q is the quantity of heat required to increase the temperature of the gas molecules by a temperature δT then

$$Q = nC_g^M \delta T, \quad (4)$$

where C_g^M is the molar specific heat. Since we are concerned only with the enhancement and hence ratios of the heat taken up by the gas phase, this expression is sufficient.

If the same amount of heat, Q , is available to the liquid, too, then the maximum number of moles $\delta n'$ that can be evaporated without an increase in the temperature is given by

$$Q = L\delta n', \quad (5)$$

where L is the molar latent heat of vaporization of the liquid. From (4, 5) we obtain

$$\delta n' = n C_g^M \delta T / L. \quad (6)$$

If $\delta p'$ is the increase in pressure due to an increase $\delta n'$ in the number of moles then

$$\delta P / \delta p' = \delta n / \delta n' = L / C_g^M T. \quad (7)$$

For all liquids at room temperature this ratio is greater than unity so that if Q , the quantity of heat flowing to the gas phase, is conserved, there can never be an enhancement. This is understandable, as some quantity of heat has to be consumed to overcome the forces of attraction between the liquid molecules before evaporation.

An enhancement of the magnitude given by Korpiun [Ref. 6, Eq. (11)] can be obtained if we assume that the liquid layer in contact with the sample surface has its temperature increased by the same average temperature δT as in (1). This assumption seems to be implicit in [Ref. 6, Eq. (8)]. Applying the Clausius-Clapeyron equation to the liquid layer we obtain the increase in pressure $\delta p''$ as

$$\delta p'' / \delta T = p'' L / RT^2, \quad (8)$$

where p'' is the pressure of the vapour in equilibrium with the liquid. From (1, 8) we thus obtain

$$\delta p'' = p'' L \delta P / PRT \quad (9)$$

using the relationship $PV = nRT$. We add δP to $\delta p''$ as in Korpiun model to obtain E , i.e.,

$$E = (\delta P + \delta p'') / \delta P \quad (10)$$

$$= 1 + p'' L / PRT. \quad (11)$$

This equation is then of the same form as the enhancement given by Korpiun if it is assumed that the mass diffusion length is the same as the thermal diffusion length. The justification for the increase in temperature of the liquid layer by δT , however, seems to be without foundation so that Korpiun's result may be fortuitous.

We note that an enhancement should mean a more efficient heat transfer from the solid to the gas phase. If $\delta n''$ is the increase in the number of moles in the gas phase, then the minimum amount of heat Q^{\min} required to evaporate these molecules would be given by

$$Q^{\min} = L \delta n'' \quad (12)$$

since $\delta n''$ is proportional to $\delta p''$ we find from (5, 7, 10, and 12)

$$Q^{\min} / Q = (E - 1) \frac{L}{C_g^M T}. \quad (13)$$

If A is the area of the sample we may define a minimum length l_L^{\min} , of the liquid layer such that

$$Q^{\min} = l_L^{\min} A C_L \rho_L \delta T, \quad (14)$$

where C_L is the specific heat per gram of the liquid and ρ_L is the density. Similarly we may write for Q from (4) as

$$Q = l_g A C_g \rho_g \delta T, \quad (15)$$

where l_g is the effective length of the gas phase that is important for the generation of the signal, C_g and ρ_g are the specific heat and density of the gas phase.

We thus obtain for l_L^{\min} the value

$$l_L^{\min} = [(E - 1) l_g C_g \rho_g / C_L \rho_L] \times \frac{L}{C_g^M T}. \quad (16)$$

$L / C_g^M T$ is of the order of 3–4 for most liquids. Equating l_g to be of the order of μ_g we find that at 10–100 Hz, l_L^{\min} for ether is roughly 2×10^{-3} and 7×10^{-4} cm compared to the thermal diffusion length for liquid ether of $\sim 10^{-2}$ – 10^{-3} cm, respectively. These thicknesses seem to be too large compared to what is known for adsorption under saturated vapour conditions. We note, however, that for our estimates on the thickness of the acetone we obtain a value close to what we obtain here. As mentioned by us earlier, this thickness is comparable to what is expected for horizontal plates kept above a liquid reservoir.

Such thick layers could affect the effective thermal diffusion length of the solid and make the technique more surface sensitive. Our studies with the enhancement of signals from aqueous solutions pointed to such an effect [12]. Since saturation effects which limit the PA amplitude begin to manifest itself when μ_β become less than μ_s [13], our results in Fig. 11 where E increases close to μ_s would imply that with non-porous solids μ_s is reduced in the presence of a layer of volatile liquid on the surface. How this happens is not clear to us. One possibility is that while considering the flow of heat to the gas phase in the presence of such a liquid layer, the thermal diffusion length of relevance would have to include the liquid layer, too. When this new thermal diffusion length μ_{LS} is greater than the length l_L of the liquid layer, the effective thermal diffusion length of the solid $\mu_s^{\text{eff}} (= \mu_{LS} - l_L)$, would be expected to be less than μ_s . A second consideration is that evaporation of the liquid molecules from the surface would cause a cooling which could affect the thermal diffusion processes in the solid.

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