Quantitative Analysis and Orientation of Langmuir–Blodgett Films by Photoacoustic Fourier Transform Infrared Spectroscopy

E. G. Chatzi, M. W. Urban, H. Ishida, and J. L. Koenig*  
Macromolecular Science Department, Case Western Reserve University, Cleveland, Ohio 44106

A. Laschewski and H. Ringsdorf  
Department of Organic Chemistry, University of Mainz, Mainz, West Germany

Received June 9, 1987. In Final Form: March 4, 1988

The use of Fourier transform photoacoustic IR spectroscopy for the semiquantitative study of Langmuir–Blodgett films is demonstrated for the first time. Data on 12 different film thicknesses for two compounds are reported. The Rosencweig–Gersho theory for the photoacoustic effect in solids is used to predict the magnitude of the photoacoustic signal as a function of modulation frequency and film thickness. Dignam–Roth's theory has been extended for the case of physisorbed molecules on flat surfaces in order to account for the dependence of band intensity on the polarizability of the coupling gas used in the photoacoustic attachment. The results obtained are in agreement with the orientational distribution of the bands of interest, as determined by using the Rosencweig–Gersho theory.

Introduction

Many water-insoluble amphiphiles can be spread at the air–water interface to form monomolecular layers.1 Under appropriate conditions, some monolayers can be transferred from the water surface to a solid support.2,3 Successive transfer of these monolayers leads to formation of so-called Langmuir–Blodgett (LB) multilayers. The thickness of these multilayer films is defined by the number of layers deposited. Such homogeneous layers with a defined thickness have a precise orientation of the amphiphiles within the layer. Molecules are packed in a two-dimensional hexagonal or monolentic lattice and are generally considered to occur in their maximally stretched conformation.

Due to the well-defined structure, the LB multilayers have been successfully used to obtain exact subnanometer spacing. For example, step gauges,3 X-ray gratings,4 and molecular assemblies for energy and electron transfer5 have been constructed by utilizing LB multilayers.

Quite often, however, a discrepancy between calculated and experimentally determined layer thickness is observed. This is related to a tilt of the molecules against the layer normal.7 Spectroscopic data also confirm this behavior.4,8

A unique surface technique is photoacoustic spectroscopy in which modulated radiation absorbed by a sample is released in the form of heat and transferred to the surrounding gas, resulting in pressure changes. These pressure changes are detected by a sensitive microphone and transformed to yield an absorption spectrum. Recently, we have utilized this technique to study orientation of the surface species.11 Using a highly polarizable coupling gas in the photoacoustic cell, one can make a distinction between species oriented parallel and perpendicular to the surfaces. The technique was also applied to study orientation of coupling agents on silicon,12 multilayer polymer films,13 PBT fibers,14 and the surface of the Kevlar fibers.15 Since this method offers the opportunity to obtain information regarding the orientation of the surface species, it is proper to apply the technique to Langmuir–Blodgett (LB) films deposited on PTFE surfaces. Depending on the relation between the thermal and optical properties of the sample and the sample thickness, the photoacoustic spectroscopy may be used to obtain depth profile information by changing the mirror; this approximates quite well an unconstrained cylindrical sample with uniform illumination of one complete surface.21

For such a sample, the Rosencweig–Gersho (R–G) theory may have potential for deriving quantitative information. This study is an attempt to analyze quantitatively the photoacoustic signal obtained at various mirror velocities for LB films deposited on PTFE disks. Furthermore, using a highly polarizable coupling gas, we determine the relative orientation of the LB films on the surface.

Experimental Section

Preparation of Monolayers. The amphiphilic compounds 1 and 2 were synthesized from (3-diocatadecylamino)prop-1-yl)-amine and p-nitrophenyl esters of β-adinepropionic acid and thyminepropionic acid, respectively.16 The hydrophilic groups

Photoacoustic IR Analysis of LB Films

**Figure 1.** Surface pressure–area diagram of amphiphile 1 at various temperatures: A, 10 °C; B, 20 °C; C, 30 °C; D, 40 °C.

**Figure 2.** Surface pressure–area diagram of amphiphile 2 at various temperatures: A, 10 °C; B, 20 °C; C, 30 °C; D, 40 °C.

of compounds 1 and 2 are adenine and thymine, respectively. Hereafter, these compounds will be termed D-18AD and D-18TH.

\[
\begin{align*}
\text{CH}_3-(\text{CH}_2)_7 &- \text{N}-(\text{CH}_2)_3-\text{NH}-\text{C}(\text{CH}_2)_2 \\
\text{CH}_3-(\text{CH}_2)_7 &- \text{C}(\text{CH}_2)_2
\end{align*}
\]

The monolayers were spread from chloroform (Alrich, HPLC grade; Merck, UVasol grade) solutions at concentrations about 0.5 mg/mL. Pure water subphase at pH 5.5 was used for all experiments. The water was distilled and purified by a Milli-Q water purification system (Millipore). The monolayer behavior of 1 and 2 is displayed in Figures 1 and 2.

The surface pressure–area diagrams show that both amphiphiles form stable monolayers between 0 and 50 °C. In this temperature interval, liquid analogous and solid analogous phases exist. At 20 °C, solid analogous phases are formed above 30 mN/m, thus enabling ordered deposition of the monolayers onto supports. The maximum packing density of both amphiphiles is ca. 0.4 nm²/molecule, corresponding to a tight packing of the two hydrocarbon chains. Poly(tetrafluoroethylene) PTFE (Huth, Germany) disks of thickness 1 mm and diameter 8 mm were used as a supporting material for the photoacoustic experiments. In UV measurements, multilayers were built on hydrophobized quartz slides (Heraeus-Schott, Germany). Polyester foil (Hostaphan RE 3.0, Kalle, Germany) was used for SAXS measurements. LB multilayers of both 1 and 2 were built up at 40 mN/m surface pressure, with dipping speeds of 20 mm/min downward and 10 mm/min upward. Deposition occurred at both downward and upward dip (Y-type deposition). Between subsequent dipping cycles, the samples were removed completely from the subphase and allowed to rest in the air for 1 min. Due to the sample geometry, the absolute transfer ratio could not be determined accurately. It was constant for all dips and was approximately 1 ± 20%.

**Spectral Measurements.** UV spectra were recorded on a Shimadzu U2400 Graphicon spectrometer. SAXS experiments were performed on a X-ray powder diffractometer, Siemens D 500, using Cu Ka radiation (λ = 0.1541 nm).

Photoacoustic FT-IR spectra were recorded by using a Digilab Model FTS-20E Fourier transform infrared spectrometer. A Digilab photoacoustic cell was used in the nonresonant mode by suitable choice of the sample cup. The instrument was purged with dry nitrogen to remove residual water vapor. The moving mirror in the Michelson interferometer was translated with five mirror velocities: 0.15, 0.5, 0.6, 0.9, and 1.2 cm/s. In a typical experiment 100–400 scans at a resolution of 4 cm⁻¹ were signal-averaged to increase the signal-to-noise ratio. The number of scans was chosen so that the measurement times are approximately 3 min. The carbon black reference spectra were recorded separately for each mirror speed. All spectra were stored on a VAX-11/780 computer for subsequent data processing. The film samples were loaded into a 3-mm sample cup which was purged with dried helium or xenon for 10 min. This sample cup yields a spectral profile that is almost flat between 4000 and 5000 cm⁻¹. The flow rate was adjusted to maintain the same pressure inside the cell, at approximately 0.2 psi. Since the PA detector is extremely sensitive to small changes in temperature and pressure, the PA cell was stabilized at the temperature of the sample compartment for approximately 1 h prior to use.

**Results and Discussion**

** Thickness Measurements of Langmuir–Blodgett Films.** In order to establish the reliability and reproducibility of the deposition experiments, the UV–vis spectra of a known number of layers deposited on the substrate were obtained. Figures 3 and 4 show the UV absorption spectra of D-18AD and D-18TH, respectively. The first compound exhibits an absorption maximum at 262 nm and the second at 268 nm. The UV absorbances are proportional to the number of deposited layers, thus verifying the regularity and reproducibility of the monolayer deposition (Figure 5).

The PTFE support, when examined by SEM, shows a planar surface interrupted by small rough arrays. Al-
Figure 4. UV–vis absorption spectra of multilayers of D-18TH deposited on quartz slides: (—) 4 layers; (⋯) 8 layers; (——) 12 layers; (—–) 16 layers.

Figure 5. UV intensities vs number of layers at the absorption maxima for D-18TH and D-18AD.

Table I

<table>
<thead>
<tr>
<th>compd</th>
<th>bilayer spacing, nm</th>
<th>calculated tilt angle, deg</th>
</tr>
</thead>
<tbody>
<tr>
<td>D-18AD</td>
<td>6.35 ± 0.03</td>
<td>7.2, 8.0</td>
</tr>
<tr>
<td>D-19TH</td>
<td>5.77 ± 0.03</td>
<td>7.7, 7.8</td>
</tr>
</tbody>
</table>

*Assuming maximally stretched conformation of the molecule and vertical orientation of the hydrophobic chains to the layer plane. **Assuming an orientation of the nucleobase parallel to the layer plane. ***Assuming an orientation of the nucleobase parallel to the hydrophobic chains.

Figure 6. Nonnormalized FT-IR PA spectra of D-18AD with coupling gas helium and mirror velocity 0.30 cm/s.

increasing number of layers of the deposited films.

In order to enhance the spectral features due to the deposited LB films, we subtracted the nonnormalized spectra (nonstretched to carbon black) of the neat PTFE substrate from the normalized spectra of 2–40 layers of both compounds deposited on PTFE. Figures 7A and 8A show the difference spectra for speed 0.15 cm/s and 1800–1200 cm⁻¹ and Figures 7B and 8B for 0.30 cm/s and 3500–1000 cm⁻¹. Three C–H stretching peaks can be seen in the difference spectra: 2957 cm⁻¹, CH₃ asymmetric stretching; 2920 cm⁻¹, CH₂ asymmetric stretching; and 2849 cm⁻¹, CH₂ symmetric stretching. The CH₃ symmetric CH stretching (2870 cm⁻¹) cannot be distinguished from the two strong symmetric and asymmetric methylene CH stretching peaks at 2920 and 2849 cm⁻¹. Lorentzian curve analysis gave only three peaks in that region, possibly because the contribution of the CH₃ symmetric CH stretching peak is very small.

Also, as the number of layers of D-18TH is increased, other features appear in the spectra: 3367 cm⁻¹, N–H stretching; 1703 cm⁻¹, imide (C=O stretching); 1671 cm⁻¹, secondary amides “free” amide I; and 1649 cm⁻¹, secondary amides “associated” amide I. However, for D-18AD we cannot distinguish any spectral features in the region below 2000 cm⁻¹, in particular no amide I modes. Both compounds have one amide group per molecule, and the amide I peaks can be clearly seen in the spectra of D-18TH but not in D-18AD. This indicates different orientations of
the amide group with respect to the electric vector of the normally incident IR radiation between the D-18AD molecule and D-18TH. Only those vibrations which have a dipole vibrating parallel to the plane of the surface interact with the IR beam and give rise to absorption peaks. So, in this case, the amide transition moment is parallel to the surface for D-18TH. Also in the case of D-18TH, the NH stretching peak at 3367 cm\(^{-1}\) can be seen, while for D-18AD the peak at about 3320 cm\(^{-1}\) cannot be distinguished.

In the following semiquantitative treatment we will only use the intensities of the methylene C-H stretching modes. For intensity measurements we used a Lorentzian curve fitting routine for the region 3100–2700 cm\(^{-1}\). Three peaks were considered, at 2849, 2920, and 2960 cm\(^{-1}\).

The peak intensities in the photoacoustic spectra also depend on the depth of penetration at the corresponding frequencies. The depth of penetration is a function of the thermal and optical properties of the sample. Rosencwaig\(^{21}\) has classified samples in four categories depending on the relative values of the thermal diffusion length, \(\mu\), optical absorption length, \(l_o\) and the sample thickness, \(t\): optically opaque or transparent and thermally thick or thin. A determination was made of the nature of the LB films from the PA properties. Most polymers have a thermal diffusivity, \(\alpha\), of approximately 10\(^{-3}\) cm\(^2\)/s.\(^{22}\) The thermal diffusion length is a function of the modulation frequency \(f\):

\[
\mu = (\alpha/\pi f)^{0.5} = (\alpha/2\pi V\nu)^{0.5}
\]

where \(V\) is the moving mirror velocity and \(\nu\) is the frequency. For this value of \(\alpha\) the range of the thermal

Table III

<table>
<thead>
<tr>
<th>V, cm/s</th>
<th>v, cm/s</th>
<th>f = 2Vω, Hz</th>
<th>μ × 10^{-3}, Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.15</td>
<td>2920</td>
<td>876</td>
<td>60</td>
</tr>
<tr>
<td>0.30</td>
<td>2849</td>
<td>854.7</td>
<td>61</td>
</tr>
<tr>
<td>0.60</td>
<td>2920</td>
<td>1772</td>
<td>43</td>
</tr>
<tr>
<td>0.90</td>
<td>2849</td>
<td>1709.4</td>
<td>43</td>
</tr>
<tr>
<td></td>
<td>2849</td>
<td>3504</td>
<td>30</td>
</tr>
<tr>
<td></td>
<td>2849</td>
<td>3418.8</td>
<td>31</td>
</tr>
<tr>
<td></td>
<td>2849</td>
<td>5235</td>
<td>25</td>
</tr>
<tr>
<td></td>
<td>2849</td>
<td>5128.2</td>
<td>25</td>
</tr>
</tbody>
</table>

diffusion length is given in Table II. However, the response of the microphone might not be flat at modulation frequencies outside the range f = 2100–300 Hz, which corresponds to thermal diffusion lengths of 39000–103900 Å.

The thickness, l, of the LB films varied from 60E to 1200E. So for any modulation frequency ω ≫ l, the LB films are thermally thin (cases 1a, 1b, or 2a of Rosencwaig’s theory21,22). However, only samples such as carbon black belong to case 2a. So our LB samples should be considered as optically transparent and thermally thin. The PTFE substrate used was 1 mm thick (δPTFE = 107 Å). Therefore the thermal diffusion length is always much smaller than l, and the substrate is considered a thermally thick material (μ ≪ δPTFE, simplified cases 1c, 2b, or 2c of Rosencwaig’s theory). However, only photoacoustically opaque samples, such as carbon black, belong to case 2b. For both cases 1c and 2c only the light absorbed within the first thermal diffusion length of the sample contributes to the photoacoustic signal. However, we were not able to use the intensity of the PTFE C–F stretching peaks in order to show the modulation frequency dependence, because the peaks are saturated. In the following discussion, we considered the PTFE substrate as the backing material for the thin films. The values of the thermal diffusion length are given in Table III. In order to avoid nonflat response of the microphone, for the two methylene CH stretching peaks, it is better to use only the speeds 0.15 and 3.30 cm/s.

For cases 1a and 1b the expressions of R–G theory for the photoacoustic signals (Q) are

\[ Q = \frac{(1 - j)}{2a_g} \frac{\mu_g}{k_b} Y \]

where \( \mu_g \) and \( k_b \) are the optical diffusion length and thermal conductivity of the backing material, \( \beta \) is the absorption coefficient, \( a_g \) and \( a_b \) are the thermal diffusion coefficients of the gas, backing, and sample, respectively, \( l \) is the sample thickness, and \( Y \) is a frequency-independent factor determined by the spectrometer and cell characteristics.

The magnitude of the photoacoustic response is

\[ q = 2^{1/2}Y(\beta l) \frac{1}{k_b} \frac{\mu_g}{\omega} \frac{1}{(\alpha_g \alpha_b)^{1/2}} \]

where \( \alpha_g \) and \( \alpha_b \) are the thermal diffusivities of the gas and backing material and \( \omega \) is the choppings frequency (rad/s).

The photoacoustic signal is dependent on the spectral output of the light source as modified by the spectrometer, \( Y \), and the observed peak heights must, therefore, be corrected for the different energy output in different spectral regions. A convenient approach to this correction is to replace the sample in the PAS cell by a black absorber which operates in the saturation range of the optical absorption coefficient and, therefore, yields a signal proportional to the incident light intensity.19 Impurities such as water vapor and CO2 adsorbed on the surface of the carbon black reference samples most commonly used will contribute spectral features to this intensity distribution and, consequently, perturb any reduced spectrum of the sample obtained with this reference.19 In order to reduce the problem we outgassed the carbon black for several days and immediately placed it in the PA sample cell and purged it with helium for at least 20 min.

In Figure 7 we compare the nonradiated spectra of two layers of D-18TH (A) to the spectra ratioed to carbon black (B) and graphite single crystal (C). The water vapor noise at 4000–3500 and 1800–1600 cm\(^{-1}\) is reduced by the use of the low surface area graphite single crystal. However, the graphite single crystal has very high reflectivity. In photoacoustic spectra, increasing reflectivity reduces the signal amplitude,20 while in absorption the amplitude is increased. (Above \( \beta = \beta_f \) full saturation the photoacoustic signal depends only on the sample’s reflectivity.) The decreased photoacoustic signal with graphite single crystal and the large difference between its reflectivity and the one of the PTFE sample introduce the increased noise in the saturated symmetric and asymmetric C–F stretching peaks (trace C of Figure 7). So for the intensity measurements it is preferred to ratio the spectra to carbon black.

For carbon black that is thermally thick and optically opaque (case 2b of R–G theory)

\[ Q = \frac{(1 - j)}{2a_g} \frac{\mu_g}{k_b} Y \]

\[ q = \frac{Y}{2^{1/2}} \frac{1}{a_g} \frac{\mu_g}{k_b} \]

where \( a_g = (2a_g/\omega)^{1/2} = (a_g/\pi f)^{1/2}, f = 2V\omega, a_g = (\omega/2\alpha_g)^{1/2}, \) \( \alpha_g \) is the thermal diffusion coefficient of the gas, and \( \alpha_g \) is the thermal diffusivity of the gas. Equation 2 can be also written

\[ q = 2^{1/2}Y(\alpha_g)^{1/2} \frac{1}{k_b} \frac{\mu_g}{\omega} \]

The photoacoustic magnitude for a sample is normalized to the magnitude of a perfectly opaque reference material to cancel the dependence on the beam intensity. The normalized magnitude \( q_n \) for the LB films is

\[ q_n = \frac{q}{q_{c-B}} = \frac{\beta l_{c-B}}{k_{PTFE}} \frac{\alpha_{PTFE}}{\alpha_{C-B}} \frac{1}{(\alpha_g \alpha_b)^{1/2}} \]

So the only frequency dependence of \( q_n \) comes from the absorption coefficient \( \beta \). \( q_n \) does not depend on the modulation frequency \( \omega \). So a plot of \( q_n \) vs \( l \) for a particular frequency \( \nu \) should give us a straight line with slope equal to

\[ \beta l_{c-B} k_{PTFE} \frac{\alpha_{PTFE}}{\alpha_{C-B}} \]

The sample thickness is \( l = N_i l_0 \), where \( N_i \) is the number of layers and \( l_0 \) is the monolayer thickness calculated from Table I.

Due to the multilayer formation method, LB films were deposited on both surfaces of PTFE, and so we had to determine if both faces contribute to the measured photoacoustic signal. The PTFE disks were fitted tightly in the sample cup in order to minimize gas penetration between the sample and the cell walls. This would allow only the sample front to serve as a thermal-transfer surface.20

Table IV

<table>
<thead>
<tr>
<th>( V, \text{ cm/s} )</th>
<th>( u, \text{ cm}^{-1} )</th>
<th>( L \times 10^{-3}, \text{cm} )</th>
<th>( V, \text{ cm/s} )</th>
<th>( u, \text{ cm}^{-1} )</th>
<th>( L \times 10^{-3}, \text{cm} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.15</td>
<td>2820</td>
<td>2.14</td>
<td>0.60</td>
<td>2820</td>
<td>1.07</td>
</tr>
<tr>
<td>0.30</td>
<td>2820</td>
<td>1.51</td>
<td>0.90</td>
<td>2820</td>
<td>0.87</td>
</tr>
<tr>
<td>0.30</td>
<td>2820</td>
<td>1.53</td>
<td>0.90</td>
<td>2849</td>
<td>0.88</td>
</tr>
</tbody>
</table>

Figure 9. FT-IR PA spectra of two layers of D-18TH with coupling gas helium and mirror velocity 0.60 cm/s: A, nonnormalized spectrum; B, spectrum ratioed to carbon black; C, spectrum ratioed to graphite single crystal.

Since PTFE is transparent to the incident radiation in the C–H stretching region, and the LB films are optically thin, the modulated IR light reaches the bottom of the cup and is absorbed by the multilayers deposited on the rear of the sample surface. However, since the PTFE substrate is thermally thick, the temperature wave generated by the lower absorbing layers is attenuated completely within a very short distance and does not contribute to the photoacoustic signal. Alternating thermal signals may reach the upper surface without appreciable attenuation only from an active depth \( u_a \) (thermal diffusion length). 21,21,46 This was also confirmed by obtaining the spectrum of six LB layers before and after cutting out a thin layer from the bottom of the PTFE disk, and so removing the layers deposited on the rear sample surface. So on this basis we use as the number of layers the ones deposited on one surface of the substrate.

According to McClelland and Knisley, 26 for samples with thicknesses \( l \) smaller than the thermally active layer thickness \( L \), the photoacoustic signal begins to saturate at \( \beta = 2\pi/l \). \( L \) is given by

\[
L = \frac{2\alpha}{\omega/2\alpha}^{1/2} = \left(\frac{2\alpha}{\omega V_u}\right)^{1/2}
\]

For \( \alpha = 10^{-3} \text{ cm}^2/\text{s} \) the value of \( L \) are given in Table IV. The thickness of 40 layers is \( 1.154 \times 10^{-6} \text{ cm} \) for D-18TH and \( 1.27 \times 10^{-6} \text{ cm} \) for D-18AD. So in the case of LB films \( l < L \) even for 40 layers and the PA signal at 2920 and 2849 cm\(^{-1}\) should begin to saturate at sample thickness \( l_{sat} = 2.37 \times 10^{-3} \text{ cm} \) for the 2920-cm\(^{-1}\) peak; \( l_{sat} = 4.17 \times 10^{-3} \text{ cm} \) for the 2849-cm\(^{-1}\) peak. So for the LB films of our study we do not expect to have onset of saturation for the methylene C–H stretching peaks.

Parts A and B of Figures 8 and 9 show plots of intensity vs number of layers for both compounds and both peaks. The plotted intensity values are the peak heights of Lorentzian peaks obtained by a Lorentzian curve fitting routine applied for the region 3100–2700 cm\(^{-1}\) with three peaks considered at 2849, 2920, and 2960 cm\(^{-1}\). These plots of photoacoustic signal vs number of layers are again independent of modulation frequency and linear, in agreement with the R–G theory (eq 3). The slopes of the intensities vs number of layers were calculated by a linear least-squares fitting routine using data for mirror velocities 0.30 and 0.15 cm/s. From the slope we can calculate the absorption coefficients, as shown in Table V.

The electric vector of the incident infrared radiation is parallel to the substrate surface. If the methylene CH stretching modes have dipoles vibrating at angles \( \theta \) with the plane of the surface, then the observed absorption intensity is \( A_{eff} = A/\cos \theta \). So if one knows the absorption coefficient of these modes in the case of molecules randomly oriented, it is possible to calculate the angles \( \theta \) as \( \cos \theta = \beta/\beta_{eff} \), where \( A_{eff} \) and \( \beta_{eff} \) are the effective (obscured) absorption intensity and absorption coefficient, respectively. The values used for the above calculations are \( A_{ptfe} = 0.000867 \text{ cm}^2/\text{s} \), \( \rho_{ptfe} = 2.2 \mu \text{g/cm}^3 \), \( k_{ptfe} = 9.56 \times 10^{-4} \text{ cal/(cm-s-K)} \), \( \rho_c = 2.403 \mu \text{g/cm}^3 \), \( C_p = 0.17 \text{ cal/(g-K)} \), and \( k_{c-B} = 0.04902 \text{ cal/(cm-s-K)} \).

\[
\frac{k_{c-B} \alpha_{ptfe}^{1/2}}{k_{ptfe} \alpha_c} = 1.3783
\]

A comparison of the values of the observed absorption coefficients for the two compounds shows that the transition dipoles of both the asymmetric and symmetric methylene CH stretching modes of D-18TH form a larger angle with the surface than those of D-18AD. This trend is in agreement with the calculated tilt angles of the chains.

According to Lambert’s law assumed in the R–G theory, a plot of intensity vs thickness should pass through the origin. However, our measurements show a non-zero Y-intercept. It is generally recognized that the increased absorption of a film-coated surface as compared to the bare substrate is due not only to the bulk of the film but also to the newly introduced film–substrate interface and the film-air interface. Becker and Temple 34–36 determined the absorption at the film–substrate interface by using a scanning adiabatic calorimeter from the Y-intercepts of plots of absorption intensity vs thickness. This interface absorption, hydrocarbon impurities in the PTFE substrate, or mirror contamination may be the cause of a non-zero Y-intercept in our intensity vs number of layers plots.

**Photoacoustic Data with Xenon as the Coupling Gas.** The nonnormalized spectra with coupling gas Xe and mirror velocity 0.30 cm/s for both compounds are shown in Figures 10 and 11. The Lorentzian peak heights for the 2920- and 2849-cm\(^{-1}\) peaks vs number of layers are plotted in parts A and B of Figure 12 for both compounds.
Figure 10. Intensity of the CH$_2$ asymmetric stretching peak vs number of layers for coupling gas He: (A, top) compound D-18AD, (B, bottom) D-18TH.

Figure 11. Intensity of the CH$_2$ symmetric stretching peak vs number of layers for coupling gas He: (A, top) compound D-18AD, (B, bottom) D-18TH.

Since we have shown with coupling gas He that the intensities of the normalized spectra are independent of modulation frequency (as R-G theory predicts), we only obtained spectra with Xe for one mirror velocity. In order to interpret these data, we used the Dignam model with minor modifications for the case of adsorbed species on a flat surface.

Figure 14. Intensity vs number of layers for coupling gas Xe: (A, top) CH₂ symmetric stretching peak, (B, bottom) CH₂ symmetric stretching peak.

Dignam\(^\text{21}\) derived expressions for the complex dielectric tensor components, \(\varepsilon_t\) and \(\varepsilon_n\), of a planar array of molecules on a flat surface:

\[
\begin{align*}
\varepsilon_t & = 1 + \frac{4\pi(N/d)\omega t}{1 - \theta_t(4\pi/3)(N/a)\omega t} \\
\varepsilon_n & = 1 + \frac{4\pi(N/d)\omega n}{1 - (4\pi/3)(2a/d - \theta_n)(N/a)\omega n}
\end{align*}
\]  

where \(t\) and \(n\) designate the tangential and normal component, respectively, \(\varepsilon_t\) is the dielectric constant of the ambient, \(d\) is the assumed (effective) film thickness of the adsorbed species (gas in our case), \(N\) is the mean number of molecules per unit area, and \(\omega t\) and \(\omega n\) are the components of the mean polarizability. The model also includes the simplifying approximations (i) that \(\alpha\) is constant, independent of the concentration and composition of the adsorbed layer, and (ii) that \(\theta = 1 = \theta_c\); \(\gamma_t\) and \(\gamma_n\) are defined according to

\[
\begin{align*}
\gamma_t & = (\varepsilon_t - \varepsilon_0) d \\
\gamma_n & = (1 - \varepsilon_t/\varepsilon_n) d
\end{align*}
\]

\(d\) may be given any value consistent with the condition \(d \ll \lambda_0\), where \(\lambda_0\) is the wavelength of light in vacuo. For frequency 3000 cm\(^{-1}\), \(d \ll 10^{-4}\) cm.

If the physically adsorbed molecules have isotropic polarizabilities, e.g., for He, or are randomly oriented on the surface, \(\alpha_t = \alpha_n = \alpha\), where \(\alpha\) is the gas-phase (or liquid-phase) molecular polarizability. The dielectric constant, \(\varepsilon_2\), for this “isotropic film” is

\[
\varepsilon_2 \approx 1 + \frac{4\pi(N/d)\alpha}{1 - (4\pi/3)(N/d)\alpha}
\]

where \(d\) (the effective film thickness) can be set equal to \(d^*\) (the molecular diameter). Dignam also assumed\(^\text{20}\) that \(\gamma_0\) (where \(u\) represents \(t\) or \(n\)) can be represented approximately by a Lorentzian function:

\[
\begin{align*}
\gamma_u & = \gamma_u^\infty + \frac{S_u}{1 - (\omega/\omega_u)^2 + i\Gamma_u(\omega/\omega_u)}
\end{align*}
\]

where \(\omega_u\) is the center frequency. Considering that \(K_u(4\pi/3)(N/a)\alpha_u^\infty\) and similar terms are small compared to unity,\(^\text{20}\) the expressions he derived for \(S_u\) and \(\gamma_u^\infty\) become

\[
\begin{align*}
S_u & \approx 4\pi N S_0 \\
\gamma_u^\infty & \approx 4\pi N\alpha_u^\infty
\end{align*}
\]

where \(S_u\) is the oscillator strength for a particular group and \(\alpha_u^\infty\) is the high-frequency contribution to the polarizability \(\alpha_u^\infty\), which is also approximated by a Lorentzian function. For \(\omega = \omega_u\), eq 6, 7, and 9 give

\[
\begin{align*}
\varepsilon_t & = 1 + \gamma_t^\infty \frac{S_t}{-i\Gamma_t} \\
\varepsilon_n & = 1 - \gamma_n^\infty + i[(S_n/d)/\Gamma_n]
\end{align*}
\]

The absorption coefficient is given by

\[
\beta = \frac{4\pi k}{\lambda} = \frac{4\pi Im\lambda^{1/2}}{\lambda}
\]

By substituting the expressions for \(S_u\) and \(\gamma_u^\infty\) from eq 10 and 11 into eq 12 and 13 we can calculate the extinction coefficients, \(k_u\), for modes oriented normal (n) or tangential (t) to the surface:

\[
\begin{align*}
k_t & = (1/2\Gamma)[(\varepsilon_t^2 + 8\varepsilon_t\pi(N/d)(s_t/\Gamma))^{1/2} - \varepsilon_t]^{1/2} \\
k_n & = \left[[\varepsilon_t^2 + 8\varepsilon_t\pi(N/d)(s_n/\Gamma)]\left(1 - 16\pi^2(N/d)^2[s_n/\Gamma]^2 - \varepsilon_t^2\right)\right]^{1/2} \\
\beta_t & = (4\pi/\lambda)k_t = 4\pi u k_t \\
\beta_n & = (4\pi/\lambda)k_n = 4\pi u k_n
\end{align*}
\]

where \(\varepsilon_t\) is the dielectric constant of the dielectric continuum (He or Xe) where the adsorbed species are immersed (dimensionless), \(\Gamma\) is the relative line width (dimensionless), and \(s_t\) and \(s_n\) are the oscillator strength in the normal and tangential direction, respectively (cm\(^2\)).

The relative values of the oscillator strength can be calculated from a knowledge of the orientational distribution of the related transition dipole moment. Thus, if the transition dipole moment makes an average angle \(\theta\) with the surface normal

\[
\begin{align*}
s_n & = \cos^2\theta s \\
s_t & = \frac{1}{2} \sin^2\theta s \\
s_n + 2s_t & = s
\end{align*}
\]

---


\(^{39}\) Krishnan, K. Appl. Spectrosc. 1981, 35(6), 549.

Table VI

<table>
<thead>
<tr>
<th>slope</th>
<th>(Y) intercept</th>
<th>correlation coeff</th>
<th>corrected slope</th>
<th>corrected (Y) intercept</th>
</tr>
</thead>
<tbody>
<tr>
<td>D-18TH</td>
<td>0.00057</td>
<td>0.0058</td>
<td>0.99</td>
<td>0.00126</td>
</tr>
<tr>
<td>D-18AD</td>
<td>0.00070</td>
<td>0.0093</td>
<td>0.84</td>
<td>0.00156</td>
</tr>
<tr>
<td>D-18TH</td>
<td>0.00037</td>
<td>0.0053</td>
<td>0.98</td>
<td>0.00083</td>
</tr>
<tr>
<td>D-18AD</td>
<td>0.00048</td>
<td>0.0062</td>
<td>0.95</td>
<td>0.00107</td>
</tr>
</tbody>
</table>

Table VII

<table>
<thead>
<tr>
<th>(\alpha) or (\beta) ((cm^{-1}))</th>
<th>(2920) cm(^{-1})</th>
<th>(2849) cm(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>4234</td>
<td>0.1154</td>
</tr>
<tr>
<td>D-18TH</td>
<td>3800.1</td>
<td>0.0809</td>
</tr>
<tr>
<td>D-AD</td>
<td>2836.9</td>
<td>0.0792</td>
</tr>
<tr>
<td>Xe</td>
<td>2562.4</td>
<td>0.0716</td>
</tr>
</tbody>
</table>

\(k_{2}\) = \((1/2^{1/2})[(e_{1}^{2} + 8\alpha_{\lambda}\pi/N/d_{S}(s_{L}/\Gamma))^1/2 - e_{1}]^{1/2}\)

\(\alpha_{\lambda}=4\pi/k_{2}L\)

where \(s_{L}\) is the oscillator strength of the transition.

For the quantitative analysis of our data we are going to use eq 14 and 15 for Xe, while for He

\[ k_{2} = \left(1/2^{1/2}\right)[(e_{1}^{2} + 8\alpha_{\lambda}\pi/N/d_{S}(s_{L}/\Gamma))^{1/2} - e_{1}]^{1/2} \]  

\[ \beta_{2} = 4\pi/k_{2} = 4\pi\tau k_{2} \]

where \(d_{S}\) is the molecular diameter and the subscript 2t means the tangential component for an isotropic adsorbed surface layer. By assuming monolayer coverage of the surface with He

\[ N/d_{S} = 0.55071E^{-3} \]

Also\(^{33}\)

\[ e_{1} = e_{\text{He}} = 1.00065 \]

By least-squares fitting the intensity vs number of layers with coupling gas Xe we can obtain the slopes and use the R–G theory to calculate \(k_{1}\), for the 2920- and 2849-cm\(^{-1}\) peaks and both compounds.

According to the R–G theory, the normalized PA spectrum does not depend on the thermal diffusivity of the coupling gas. However, in our case we ratioed the spectra with Xe to the spectra of carbon black with He, in order to avoid artifacts due to adsorbed surface species on carbon black. So we have to correct the intensity measurements obtained with Xe for this ratioing procedure. The depth of penetration does not depend on the nature of the coupling gas, and so we can use the peak of the PTFE substrate to evaluate a correction factor. This was done by least-squares fitting the corresponding spectra with Xe and He for the region 1350–1500 cm\(^{-1}\) for all the number of layers and both compounds and averaging the obtained values (the correction factor is 0.461 ± 0.05). Tables VI and VII show our results.

Using eq 21 we can calculate the values of \(s_{L}/\Gamma\), which are listed in Table VIII. From eq 18 and 19 we obtain

\[ s_{L}/\Gamma = 2(s_{L}/\Gamma) \cot\alpha^{2} (90 - \theta) \]

where \(\theta\) is the angle of the modes with the surface. If one knows the absorption coefficients of the modes for randomly oriented molecules, it is possible to determine \(\theta\) by using the R–G theory and subsequently to calculate the value of \(s_{L}/\Gamma\).

For the coupling gas Xe, using eq 14, we calculated the surface concentration \(N/d\) to be equal to 0.43\(^{-2}\). In this case \(e_{1} = e_{\text{Xe}} = 1.00123\). Then if one has calculated \(s_{L}/\Gamma\), by using eq 15, the values of \(k_{2}\) can be obtained for each mode.

The relative values of the corrected absorptive index obtained with coupling gas Xe show that the transition dipoles of both modes of interest for D-18TH form a larger angle with the surface than those of D-18AD. The same observation has been also made by independent calculations from the data with coupling gas He. The Digam theory predicts that for modes with the dominating components of the dipole moment parallel to the surface the absorptive index increases with Xe \((k_{2} > k_{1})\), whereas in contrast for modes with the dominating component of the dipole moment perpendicular to the surface the absorptive index with Xe is decreased as compared to the nonpolarizable He \((k_{2} < k_{1})\). From our calculations it is shown that the dominating components of the dipole moment of the methylene asymmetric C–H stretching of the compound D-18AD are parallel to the surface, whereas all the other modes considered are perpendicular to the surface.

Conclusions

In this work, we followed a new approach for obtaining quantitative orientation information on Langmuir–Blodgett films. The reliability and reproducibility of the deposition experiments were established by UV–vis, and the bilayer thickness was determined by SAXS. For the FT-IR PA measurements both a nonpolarizable and a polarizable coupling gas, He and Xe, respectively, were used in the photoacoustic cell for a sequence of samples with a different number of deposited layers and two almost identical compounds with different hydrophilic groups. For all the sample thicknesses the LB films are found to be thermally thin and optically transparent, while the PTFE substrate used was thermally thick. The normalized photoacoustic intensity was found to be independent of the chopper frequency and proportional to the sample thickness, as predicted by the R–G theory. The intensities of the two methylene CH stretching peaks of the long hydrophobic chains were used in order to calculate the effective absorption coefficients and relative differences of the average orientation of the vibrating dipoles with respect to the electric vector. The tilt angle, calculated from SAXS, of the molecules with respect to the plane of the support is smaller for D-18TH than for D-18AD. This is in agreement with the relative values of the effective absorption coefficients of the two methylene CH stretching modes, calculated from our photoacoustic data with coupling gas helium.

From the Digam–Roth theory for a planar array of molecules on a flat surface, we calculated the tangential components of the extinction coefficients for physically adsorbed molecules with isotropic and anisotropic polar-
izabilities, e.g., He and Xe, respectively. Our experimental data with both gases are consistent with this theoretical treatment. Also, the relative orientation of the dominating components of the dipole moment has been estimated by comparing the values of the tangential absorptive index obtained with Xe and He.

This model study shows the potential of photoacoustic FT-IR spectroscopy for obtaining at least semiquantitative data on the orientation of Langmuir–Blodgett films, and we believe that it serves to illustrate the general applicability of the Rosencwaig–Gersho theory and the Dignam–Roth treatment of the photoacoustic effect.

**Acknowledgment.** We gratefully acknowledge the Army Research Office for supporting this research under Grant DAAG29-85-K-0225 and the CWRU-MRL under Grant DMR-8119425.

**Registry No.** D-18AD, 114378-24-4; D-18TH, 114378-25-5.