

# Brewster-Angle Reflection—Absorption Infrared Spectrometry of Organic Films on Metallic Substrates

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Reflection—absorption spectrometry has been used to obtain infrared spectra of micrometer thick films on metals. The theory and practice of this method with very thin films is well understood, but with thicker films the bulk properties of the material must be taken into account. The influence of incidence angle and polarization on the spectra that are obtained from this method has been investigated, from both an experimental and theoretical viewpoint. An incidence angle of the pseudo-Brewster angle of the film ( $\sim 60^\circ$ ) with p-polarized radiation produces spectra that are the most faithful to what is obtained via transmission spectrometry.

## Introduction

Reflection—absorption infrared spectrometry (RAIRS) has been used for many years to study thin films on metal surfaces. However, there has been surprisingly little investigation into the influence of the polarization of the radiation used to observe the properties of films of moderate thickness on metal surfaces.

It has been observed<sup>1</sup> that the absorption of certain bands in the spectrum of polystyrene behaved in quite different ways when the angle of incidence was changed from  $40^\circ$  to  $60^\circ$ , depending on the polarization of the radiation. Specifically, bands measured with p-polarized radiation exhibited increasing absorbance upon going from  $40^\circ$  incidence to  $60^\circ$ , whereas the opposite behavior was observed with s-polarized radiation.

Greenler<sup>2</sup> investigated the properties of molecules adsorbed onto metal films and metal islands, and Allara *et al.*<sup>3</sup> did similar work, but most of these studies involved investigating the properties of very thin (1 nm to 1  $\mu\text{m}$ ) films. As a consequence of the boundary conditions imposed on the reflection from a conductor, s-polarized radiation does not interact with thin layers of adsorbed molecules on a conducting substrate, due to the presence of a node in the electric field at the surface of the metal. Conversely, p-polarized radiation can be absorbed, with the absorbance generally increasing with the angle of incidence.

Suëtaka<sup>4</sup> has surveyed the field of RAIRS and noted that for films that exceed the linear approximation limit the angle of maximum sensitivity is significantly less than the grazing angle applicable for extremely thin films. He also presented some data taken of a 1- $\mu\text{m}$  layer of mercaptobenzothiolate Cu(I) on a copper substrate which indicate that an incident angle of  $70^\circ$  provides maximum sensitivity. However, no explanation or analysis of the data was provided, nor was any mention made of possible effects of the polarization of the radiation on the observed spectra.

Suëtaka also discussed the distortion of relatively strong bands in the spectra of relatively thick films. Such distortions in the spectra of 1.5- $\mu\text{m}$  films were first noted by Allara *et al.*<sup>3</sup> Suëtaka<sup>4</sup> reported that strong bands in polymer films with thickness greater than approximately 1  $\mu\text{m}$  showed obvious distortion. It was even noted that this distortion could be

diagnosed by changing the polarization of the incident radiation, but no theoretical analysis was made of this phenomenon, and no way of overcoming it was proposed.

Suëtaka<sup>4</sup> discussed the C—O—C stretching band of poly(2,6-dimethyl-1,4-phenylene oxide) on copper, from the standpoint of both experimental data and computational models. He discussed the types of band distortions that can take place as a function of film thickness. However, he made no mention of the angle of incidence of the radiation nor of the polarization.

Ishino and Ishida<sup>5</sup> studied the external reflectance of polymer films and established the superiority of using p-polarized radiation at Brewster's angle when obtaining the spectra of a polymer on a dielectric substrate, but they did not investigate metallic substrates. Harrick<sup>6</sup> investigated the use of Brewster's angle spectrometry in transmission to eliminate the artifacts caused by the reflection at the analyte/air interface, and Miller and Johnson<sup>7</sup> described the influence of incident angle on the spectra of semiconductors. In all these reports, however, little or no theoretical analysis was carried out.

Anomalies induced by the optical behavior of a film on a metal can greatly change the appearance of a spectrum. Automated spectral interpretation techniques depend on having an artifact-free spectrum; anomalies in the spectrum that cannot be accounted for in a chemometric training set will make it impossible for the system to correctly characterize and classify the spectrum of the material being observed. Thus an understanding of the factors that affect a reflection—absorption spectrum is necessary if a spectrum is to be measured that matches a standard transmission spectrum as closely as possible.

## Theoretical Treatment

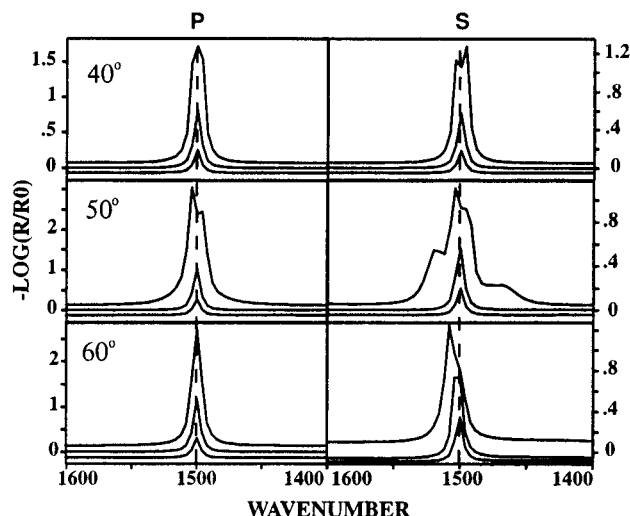
The theory behind the behavior of reflected light at the surface of a dielectric-coated metal substrate has been treated extensively by Heavens,<sup>8</sup> Born,<sup>9</sup> and others. The relevant equations were incorporated into a FORTRAN program by Dluhy,<sup>10</sup> and a slightly modified version of this program was used to perform the calculations reported below.

Calculations were performed for a three-layer stratified medium, consisting of air, an absorbing dielectric, and a metal. The real and imaginary components of the refractive index used for air were 1.0 and 0, respectively, and the values for silver ( $n = 4.2$ ,  $k = 42.5$ ) were used for the substrate. The values of  $n$  and  $k$  for a Lorentzian band in the absorbing dielectric were

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**Figure 1.** Calculated absorbances for a band centered at 1500  $\text{cm}^{-1}$  in a 10- $\mu\text{m}$  film on a silver substrate at 40°, 50°, and 60°, with s- and p-polarized radiation, for bands with  $k_{\text{max}} = 0.02, 0.06$ , and 0.2.

calculated according to the following formulas as adapted from Osawa:<sup>11</sup>

$$\epsilon_1 = \frac{B\gamma\nu}{(\nu_0^2 - \nu^2)^2 + \gamma^2\nu^2} \quad (1)$$

$$\epsilon_2 = m^2 + B \frac{\nu_0^2 - \nu^2}{(\nu_0^2 - \nu^2)^2 + \gamma^2\nu^2} \quad (2)$$

where  $\epsilon_1$  and  $\epsilon_2$  are the real and imaginary components of the complex dielectric function  $\hat{\epsilon} = \epsilon_1 + i\epsilon_2$ .  $B$  is the oscillator strength,  $\gamma$  is the full width at half-maximum of the band,  $\nu_0$  is the band center, and  $\nu$  is the wavenumber being evaluated.  $\hat{\epsilon}$  is related to the real and imaginary components of the complex refractive index in the following manner:

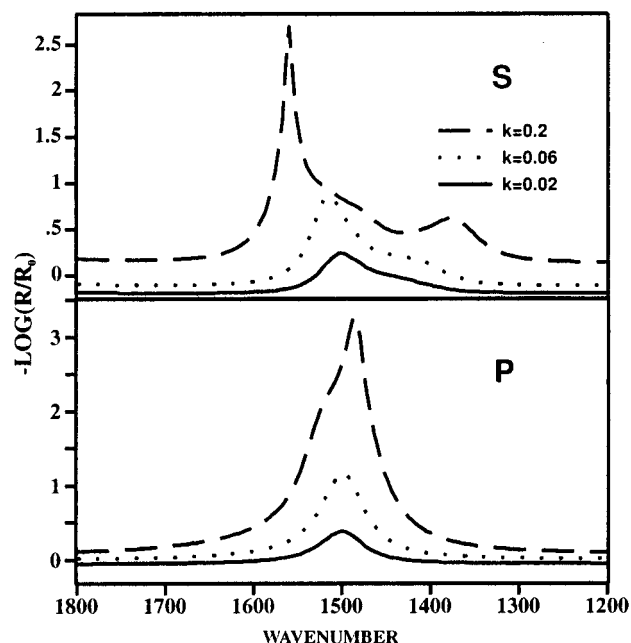
$$\hat{n} = (\hat{\epsilon})^{1/2} \quad (3)$$

where the complex refractive index,  $\hat{n}$ , is defined as  $\hat{n} = n + ik$ . The complex refractive index was evaluated over the interval from 1000 to 2000  $\text{cm}^{-1}$  at 4- $\text{cm}^{-1}$  intervals. The calculations were performed using Mathcad<sup>12</sup> for a variety of combinations of band strength and full width at half-height (fwhh). Band intensities were classified as strong ( $k_{\text{max}} = 0.2$ ), average ( $k_{\text{max}} = 0.06$ ), weak ( $k_{\text{max}} = 0.02$ ), while the widths were classified as broad (fwhh = 60  $\text{cm}^{-1}$ ), medium (fwhh = 20  $\text{cm}^{-1}$ ), and narrow (fwhh = 6  $\text{cm}^{-1}$ ).

The synthetic  $n$  and  $k$  spectra thus generated were then used to calculate reflectance spectra at 40°, 50°, and 60° incidence for 10-, 30-, and 100- $\mu\text{m}$  thick films for s- and p-polarized radiation and a total of 162 spectra. We have analyzed and will discuss these data with regard to the effects of polarization and incident angle on observed spectra as a function of band strength, band width, and film thickness.

## Theoretical Results

**General.** The results of the calculations for a narrow absorption band centered at 1500  $\text{cm}^{-1}$  in a 10- $\mu\text{m}$  film on a metal are shown in Figure 1, for both s- and p-polarized radiation at several angles for strong, medium, and weak bands. In the case of p-polarized radiation, some distortion is seen in the strong bands at 40° and 50°, but is absent at 60° incidence. For



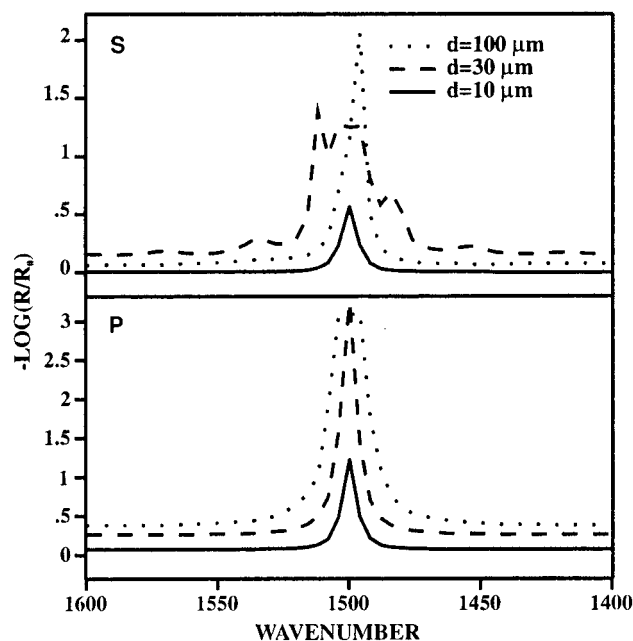
**Figure 2.** Reflectance calculations for a broad band (fwhh = 60  $\text{cm}^{-1}$ ) at 60° incidence, for band absorptivities of 0.02, 0.06, and 0.2, for s-polarized radiation and for p-polarized radiation.

s-polarized radiation, strong bands become distorted in all cases, with either inverted band centers, excessively broadened bands, or shifts of band center. From this evidence it can be concluded that the use of p-polarized radiation at 60° incidence maintains the best fidelity of band shape for a 10- $\mu\text{m}$  film.

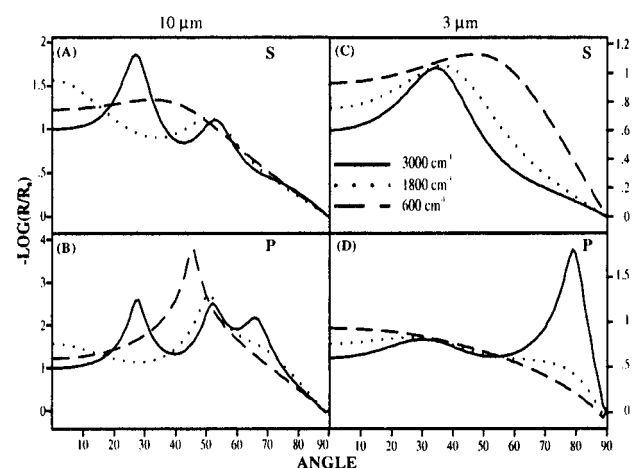
It has been noted<sup>13</sup> that broader absorption bands exhibit larger distortions. Our calculations indicate that the use of p-polarized radiation at Brewster-angle incidence on 10- $\mu\text{m}$  films gives relatively undistorted spectra even for broad (fwhh = 60  $\text{cm}^{-1}$ ) bands at absorbance values as high as 1.25, as shown in Figure 2 (lower). While the strong band, with a calculated absorbance of over 3.0, shows a moderate shift of band center and alterations in band contour, these are minor effects compared to what is observed in the case of s-polarized radiation, where a strong, broad band exhibits substantial wings 200  $\text{cm}^{-1}$  to either side of the band center (see Figure 2 (upper)). These distortions can be attributed to the anomalous dispersion of the complex refractive index over a broader portion of the spectrum; we believe that the use of Brewster-angle reflection spectrometry reduces this effect.

**Effect of Film Thickness.** Thicker films can be expected to exhibit greater anomalies, partly due to stronger absorption of the infrared radiation and partly due to interference effects caused by the film itself. Calculations for a narrow band of average strength (fwhh = 6  $\text{cm}^{-1}$ ,  $k_{\text{max}} = 0.06$ ) indicate that the distortions that can be seen in the Brewster-angle reflectance spectrum of a 100- $\mu\text{m}$  film are still small compared to those observed in the calculated spectrum for s-polarized radiation (see Figure 3). Note particularly the interference fringes visible on the wings of the band. In the calculated spectra for broader bands, the effects are even larger. It should be remembered that when the absorption band is strong enough and the film is sufficiently thick, no radiation reaches the surface of the metal, and the spectrum obtained in the region of that band will be a specular reflectance spectrum of bulk material. In this case, no choice of angle or polarization will produce a spectrum that resembles a transmission spectrum of the film.

**Calculations with Respect to Angle.** Relative intensities for bands of equal absorptivity at different frequencies were calculated as a function of angle for 3- and 10- $\mu\text{m}$  thick films.



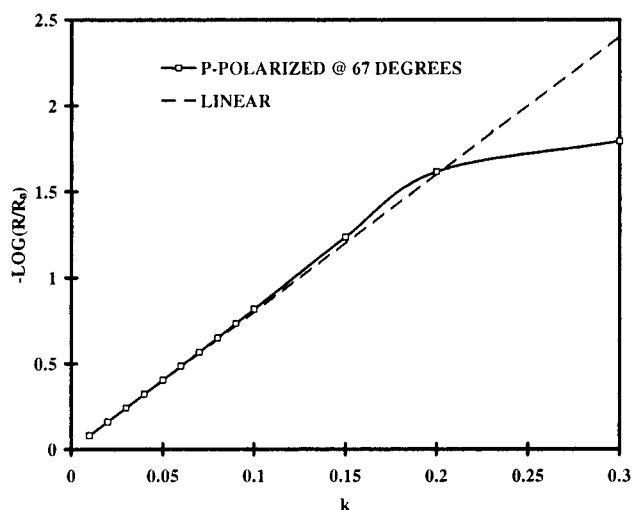
**Figure 3.** Calculated absorbance for "average, narrow" bands (fwhm = 6  $\text{cm}^{-1}$ ,  $k_{\text{max}} = 0.06$ ), centered at 1500  $\text{cm}^{-1}$  in 10-, 30-, and 100- $\mu\text{m}$  films, for s-polarized radiation at 40° incidence and p-polarized radiation at 60° incidence.



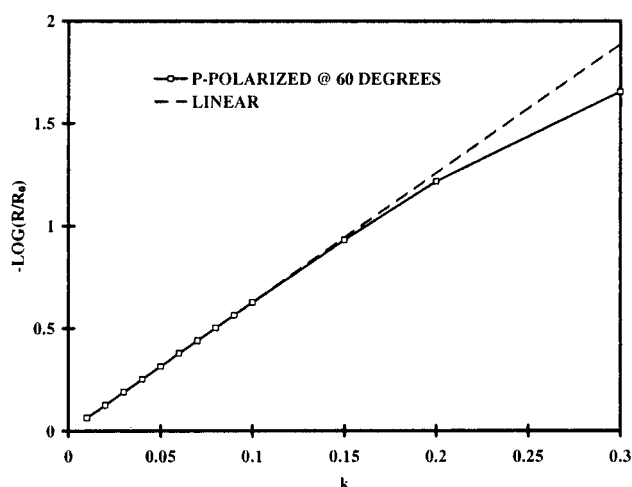
**Figure 4.** Calculations of reflectance as a function of angle for bands with the same absorptivity at 600, 1800, and 3000  $\text{cm}^{-1}$ : (A) 10- $\mu\text{m}$  film, s-polarized radiation; (B) 10- $\mu\text{m}$  film, p-polarized radiation; (C) 3- $\mu\text{m}$  film, s-polarized radiation; (D) 3- $\mu\text{m}$  film, p-polarized radiation.

The results for a 10- $\mu\text{m}$  film are shown in Figure 4A,B, where it appears that incident angles of approximately 20° and 55° would provide acceptable results with either s- or p-polarized radiation, as the  $-\log(R/R_0)$  curves all intersect, or nearly intersect, near these angles. In Figure 4C,D, the results of these calculations for a 3- $\mu\text{m}$  film are shown. With s-polarized radiation, the only condition where the reflectances have approximately the same value is for an incident angle of roughly 35°, while at the 55° optimum that we observed with the 10- $\mu\text{m}$  film, the values for low- and high-frequency bands differ by a factor of roughly 3. The 35° optimum for the 3- $\mu\text{m}$  film also gave strongly divergent results for a 10- $\mu\text{m}$  film.

The results for p-polarized radiation are shown in Figure 4D. The low-, medium-, and high-wavenumber curves meet at approximately 55° incidence, just as they do with the 10- $\mu\text{m}$  film. Furthermore, the value that they take at this angle in the 3- $\mu\text{m}$  film is roughly one-third that calculated for the 10- $\mu\text{m}$  film, indicating that the response is approximately linear with film thickness under these conditions.



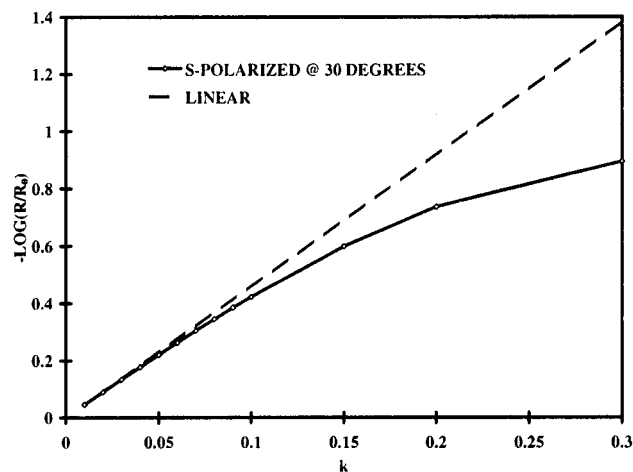
**Figure 5.** Calculated Beer's law adherence for a band centered at 1500  $\text{cm}^{-1}$  in a 3- $\mu\text{m}$  film with p-polarized radiation at 67° incidence. The extrapolated straight line calculated for  $k = 0.01$  is also shown.



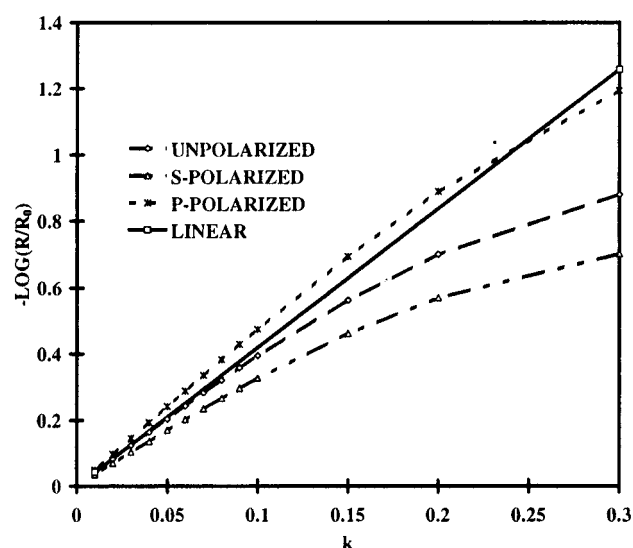
**Figure 6.** Calculated Beer's law adherence for a band centered at 1500  $\text{cm}^{-1}$  in a 3- $\mu\text{m}$  film with p-polarized radiation at 60° incidence. The extrapolated straight line calculated for  $k = 0.01$  is also shown.

**Determination of Adherence to Beer's Law.** Calculated reflectance values at a range of angles and  $k$  values demonstrate the consequences of polarization and incident angle with respect to adherence to Beer's law. Calculations were made for a 3- $\mu\text{m}$  film at 1500  $\text{cm}^{-1}$ , with  $k$  varying from 0.01 to 0.3, and  $n$  remaining a constant of 1.49. The optical constants used for the substrate were those of silver ( $n = 4.5$ ,  $k = 42.5$ ). The calculations were performed for s- and p-polarized radiation, with the angle varying from 0° to 90° in 1° increments.

The relationship between  $k$  and  $-\log(R/R_0)$  at 67° and 60° is shown in Figures 5 and 6; the straight line is the value extrapolated from the  $-\log(R/R_0)$  value for  $k = 0.01$ . The calculation for 67° shows little deviation from linear behavior until  $k$  approaches 0.2; there is then first a small positive deviation, and subsequently a strong negative deviation. This is a consequence of the angle of incidence exceeding the pseudo-Brewster angle for the film with  $k = 0.3$ . As the imaginary part of the refractive index becomes non-negligible, the pseudo-Brewster angle moves to lower values. In the 60° calculation, however, while the deviation from linearity sets in at lower  $k$ , the positive deviation is not present and the deviation for  $k$  larger than 0.2 is not as pronounced. By contrast, the deviation from linearity grows monotonically with  $k$  in the calculated reflection spectrum at 30° incidence for s-polarized radiation, as shown in Figure 7.



**Figure 7.** Calculated Beer's law adherence for a band centered at  $1500\text{ cm}^{-1}$  in a  $3\text{-}\mu\text{m}$  film with s-polarized radiation at  $30^\circ$  incidence. The extrapolated straight line calculated for  $k = 0.01$  is also shown.



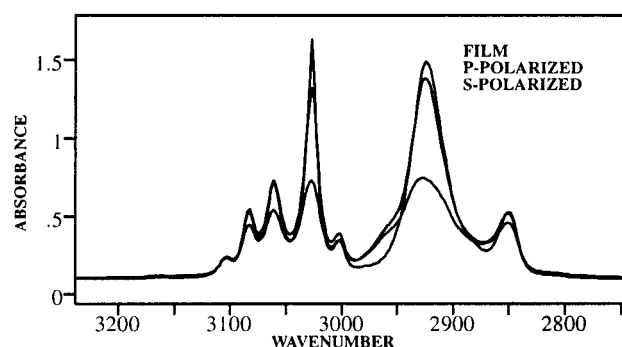
**Figure 8.** Calculated Beer's law adherence for a band centered at  $1500\text{ cm}^{-1}$  in a  $3\text{-}\mu\text{m}$  film with s-, p-, and unpolarized radiation at  $45^\circ$  incidence. The extrapolated straight line calculated for  $k = 0.01$  is also shown.

Allara<sup>3</sup> has suggested that reasonably good results could be obtained with the use of unpolarized radiation at  $45^\circ$  incidence. While our calculations, as shown in Figure 8, show that the deviation from linearity is predictable, the behavior exhibited with an incidence angle of  $45^\circ$  is nonetheless inferior to the calculated results for the use of p-polarized radiation at or near Brewster's angle.

In summary, from optical theory we have demonstrated that obtaining reflection-absorption spectra that are linear with respect to  $k$  is dependent on the polarization and the angle of incidence of the radiation. Our calculations have shown that the use of p-polarized radiation at or near Brewster's angle gives optimum results.

### Experimental Section

**General.** Spectra were obtained with a Bio-Rad (Cambridge, MA) FTS-60A FTIR spectrometer equipped with a Pike Veemax variable-angle specular reflectance accessory at angles of incidence from  $35^\circ$  to  $75^\circ$  at  $5^\circ$  intervals. Background spectra were obtained using a gold front-surface mirror. Spectra were obtained with s- and p-polarized radiation, as well as without polarization.



**Figure 9.** Reflection-absorption spectra of the C-H stretching region of a polystyrene film on aluminum obtained with p- and s-polarized radiation at  $60^\circ$  incidence, and a transmission spectrum of a  $50\text{-}\mu\text{m}$  polystyrene film, scaled so that the  $3110\text{-cm}^{-1}$  bands are of equal intensity.

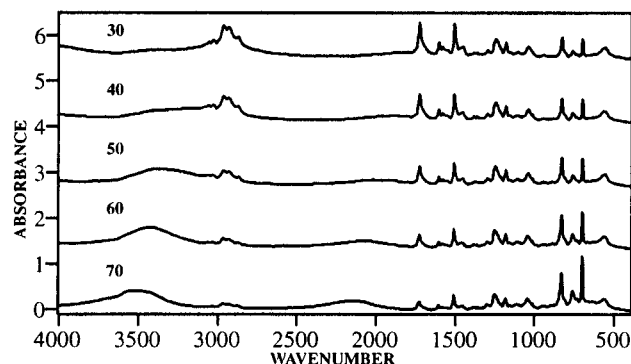
**Polystyrene Films.** Solutions of polystyrene (Aldrich, Milwaukee, WI, MW 45 000) in toluene (Fisher, Pittsburgh, PA) were deposited on a gold mirror (Edmund, Barrington, NJ) and allowed to evaporate. They were then placed in a vacuum oven and heated to approximately  $200^\circ\text{C}$  *in vacuo* to remove any residual toluene and to allow the surface of the film to relax to smoothness under the influence of surface tension. A sample of polystyrene was also prepared on a polished aluminum plate, with a somewhat thicker film than on the gold mirror. Specular reflectance spectra were also obtained of bulk polystyrene.

**Beverage Can Lining Film.** A sample of a thin polymer film on a metallic substrate was obtained by slicing out a section of a beverage can with a razor. A transmission spectrum of the can-lining film was obtained by scraping away the paint from a portion of the outside surface of the can and immersing the section in 1 M hydrochloric acid until the aluminum had been etched away, leaving a window of approximately 1 cm diameter. The spectrum of the film was then obtained in transmission in the usual manner. While the precise composition of coatings typically used to line aluminum beverage cans is usually proprietary, they generally are some form of a phenolic epoxide,<sup>14</sup> and our spectra discussed below are consistent with such an assignment.

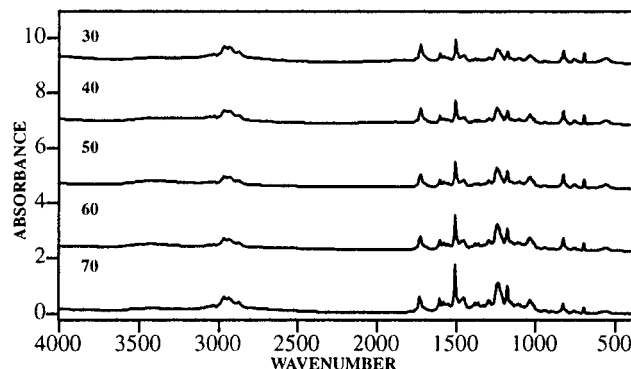
### Results and Discussion

**Results of Polystyrene Samples.** Inspection of the spectra of the C-H stretching region supports the results of our model calculations with respect to band-shape fidelity and adherence to Beer's law. Superimposed on the transmission spectrum of a  $50\text{-}\mu\text{m}$  polystyrene film are the reflection spectra for the film cast on aluminum obtained at  $60^\circ$  incidence for s- and p-polarized radiation, which have been scaled so that the bands at  $3110\text{ cm}^{-1}$  are of equal intensity in all three spectra (see Figure 9). Apart from the two strongest bands in this portion of the spectrum, the p-polarized spectrum closely resembles the transmission spectrum, and even for the strong bands the agreement is reasonable. By contrast, the spectrum measured with s-polarized radiation does not reproduce the line shape observed in the transmission spectrum.

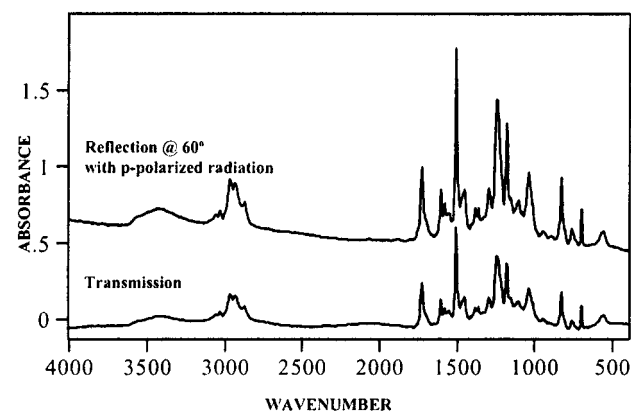
**Beverage Can Samples. Changes with Respect to Angle.** Reflection-absorption spectra of the soda can lining obtained with s-polarized radiation, with the angle of incidence increasing at  $10^\circ$  intervals from  $30^\circ$  to  $70^\circ$ , are shown in Figure 10. The relative intensities of the C-H stretching bands and the bands at  $1500$  and  $700\text{ cm}^{-1}$  change as the angle of incidence is increased. At  $30^\circ$  incidence, the  $1500\text{-cm}^{-1}$  band is the more intense, while at  $70^\circ$ , the  $700\text{-cm}^{-1}$  band is the stronger. The spectra obtained with p-polarized radiation (Figure 11) also show



**Figure 10.** s-Polarized reflection-absorption spectra of soda can lining, obtained at 30°, 40°, 50°, 60°, and 70° incidence.



**Figure 11.** p-Polarized reflection-absorption spectra of soda can lining, obtained at 30°, 40°, 50°, 60°, and 70° incidence.

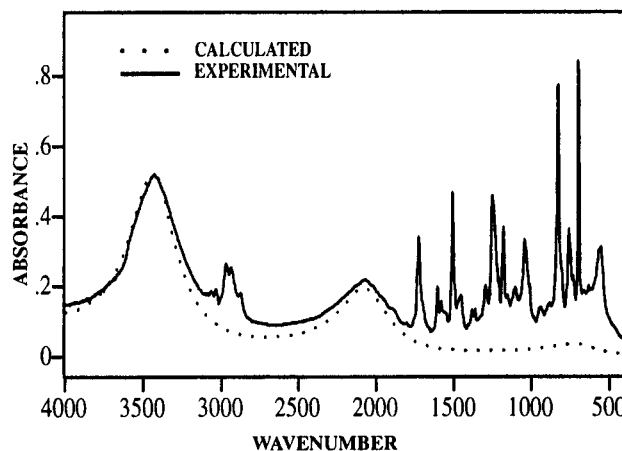


**Figure 12.** p-Polarized reflection-absorption spectrum of soda can lining obtained at 60° incidence and a transmission spectrum of this lining.

changes in relative band intensity as a function of angle (particularly for the 1500-cm<sup>-1</sup> and 1700-cm<sup>-1</sup> bands). These bands are of nearly equal intensity at 30° incidence, with the 1500-cm<sup>-1</sup> band becoming more intense as the incident angle is increased. These changes, however, are smaller than those observed in the spectra obtained with s-polarized radiation. The p-polarized spectra also lack the broad features visible in the s-polarized spectra obtained at large angles of incidence. From this it can be concluded that spectra obtained with p-polarized radiation generally show less variability with angle and fewer artifacts than those obtained with s-polarized radiation.

**RAIRS vs Transmission Spectra.** The RAIRS spectrum of the soda can lining at 60° incidence with p-polarized radiation and the transmission spectrum obtained from a sample of this film are shown in Figure 12. Note the excellent agreement of band location, shape, and relative intensity.

**Analysis of s-Polarized Spectra.** The spectra obtained with s-polarized radiation at high incidence angles exhibit large



**Figure 13.** s-Polarized reflection-absorption spectrum of soda can lining obtained at 60° incidence, and a calculated spectrum for a 3-μm film with  $n = 1.49$  and  $k = \bar{\nu}4.3 \times 10^{-6}$ .

features at 3300 and 2100 cm<sup>-1</sup>. Although the feature at 3300 cm<sup>-1</sup> could possibly be assigned to an O-H stretching mode, the broad band at 2100 cm<sup>-1</sup> does not readily correlate to any functional group. In addition, the changes in location and intensity of these features as the angle of incidence is changed are not consistent with assignment to a vibrational frequency, but seem more likely to arise from an optical property of the film itself.

The behavior with respect to angle for bands at different frequencies with s-polarized radiation fits the behavior that we have modeled computationally for a 3-μm film in that low-frequency bands will tend to become relatively stronger at larger incidence angles. Combined with the nonlinear behavior with respect to absorption index that we have modeled computationally, this appears to explain the lack of fidelity to relative band intensity that is observed in spectra obtained with s-polarized radiation.

The large baseline features observed in the s-polarized spectra can be reproduced in our calculations. We calculated spectra for a 3-μm film with  $n = 1.49$  and a small, empirically determined, frequency-dependent absorption coefficient,  $k = \bar{\nu}4.3 \times 10^{-6}$ . The calculated spectrum (Figure 13) shows good agreement in amplitude, shape, and location of the features at 3600 and 2100 cm<sup>-1</sup>. We do not yet have a complete explanation for this behavior, but the frequency dependence of this leads us to suspect that this is due to interference effects, the magnitude of which is increased by absorption or scattering, either from within the film or from the surface of the aluminum.

## Conclusions

Reflection-absorption spectra have been calculated for a range of film thicknesses and band strengths using varying angles of incidence for s- and p-polarized radiation. These calculations have shown that for films of moderate thickness the use of p-polarized radiation at an incidence angle of 60° (Brewster's angle) should provide RAIRS spectra that closely match spectra obtained in transmission. Spectra of polystyrene films cast on aluminum and gold substrates exhibit this behavior, as do the spectra of a commercially available material.

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