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Fourier Transform Infrared Surface Electromagnetic Wave Spectroscopy of Polymer Thin Films on Metallic Substrate

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FT-IR surface electromagnetic wave spectroscopy utilizing the Otto configuration is applied to the study of a thin film of poly(vinyl acetate) on a copper substrate. In order to determine optimal experimental conditions, a spectral simulation was made using the Fresnel formula. Some differences with respect to the angular dependence and air gap dependence between the calculation and experiment are found to be due to the angular spread of the incident beam. Calculations considering the angular spread of incident beam are also shown. Both a single reflection hemicylinder prism and a new multiple reflection modification of the Otto configuration are used. Sensitivity of the multiple reflection system is found to be better than the single reflection prism method.

A surface electromagnetic wave (SEW) is known as the electromagnetic wave propagating along the surface of the medium. A number of studies concerning the characteristics of SEW have been reported from both theoretical and experimental points of view (1-3). Experimentally, it was observed that the propagation length of SEW on the metal is on the order of a few centimeters in the mid-infrared region (4). Since a SEW propagating on the surface transmits through the surface species, SEW can be a sensitive probe for the metallic surface. Also, several experimental attempts have been shown to excite the SEW in the mid-infrared range by several coupling techniques including a prism (4), an edge (5), and a gap (6). In these studies, an IR laser was used because of its strong and coherent radiation and the low coupling efficiency of SEW. Advantages of this technique with respect to sensitivity were theoretically considered and demonstrated by experiment (7).

Therefore, SEW spectroscopy utilizing an IR laser is a very sensitive technique to investigate thin films on metallic substrates. However, even when both CO and CO₂ lasers are used for this spectroscopy, the measurable frequency range is only from 868 to 1086 cm⁻¹ (8), so that detectable chemical functional groups are limited. The discrete frequency of these lasers does not allow the spectrum to be continuous. Tunable IR lasers are still in their infancy for wide-range IR studies.

Alternately, Fourier transform infrared spectroscopy (FT-IR) provides several advantages such as Fellgett's and Jaquin's advantages to investigate sub-micrometer thin films. Also high sensitivity detectors such as a narrow band MCT detector and a copper-doped germanium detector are available for FT-IR to detect weak signals. Therefore, one of the alternative ways to perform SEW spectroscopy is to use FT-IR with a high sensitivity detector for a weak broad band source instead of a narrow band intensive laser. Few attempts of FT-IR SEW spectroscopy using broad band energy source have been reported (9,10). In these studies, grating coupling and edge coupling techniques were used. Since only vacuum evaporated metallic film can be used as the substrate in these techniques, the sample preparation is complicated and sample geometry is limited. In order to simplify the sample preparation and to measure a wide variety of samples, we applied the so-called

Otto configuration (11) to FT-IR spectroscopy. It is the purpose of this paper to compare the theoretical simulation and experimental results. Sensitivity of SEW spectroscopy is compared with that of the reflection-absorption spectroscopy.

EXPERIMENTAL SECTION

IR spectra were recorded on a Digilab FTS-20E FT-IR spectrophotometer equipped with a narrow band-pass, liquid-nitrogen-cooled mercury cadmium telluride (MCT) detector, and an ordinary broad band IR source at a resolution of 4 cm⁻¹ throughout the region 3800-700 cm⁻¹. Coadditions of 50 or 400 scans were used, depending on the film thickness. The spectrometer was purged with dry nitrogen to minimize atmospheric CO₂ and water vapor.

A copper film was coated on a glass microscope slide by vacuum evaporation. A dilute THF solution of poly(vinyl acetate) (PVAc) was deposited on the substrate with a microsyringe and the solvent was evaporated slowly in a nearly saturated THF environment. The thickness of the polymer film was estimated by the absorbance of the carbonyl band in the spectra of reflection-absorption spectrum and was compared to the simulated spectra calculated by exact optical theory.

For the Otto configuration (prism-air gap-metal configuration), Perkin-Elmer's variable-angle ATR attachment equipped with either a CaF₂ or a KRS-5 hemicylinder was used. A gold wire grid polarizer was placed between the optical attachment and the detector. Spectra were measured at different angles of incidence. Angular spread of the incident beam was measured with the same optical attachment equipped with the hemicylinder element without a sample. The angular dependence of reflectivity of the prism at a certain frequency was measured around the critical angle of the prism and was compared to the calculation. Multiple reflection modification of the Otto configuration was made by using modified Wilks' ATR attachment equipped with a specially designed trapezoidal KRS-5 prism. In these experiments, polymer films with different thicknesses were used as spacers to adjust the thickness of the air gap. In order to evaluate the sensitivity of SEW spectroscopy, single and multiple reflection reflection-absorption measurements were made with Harrick's external reflection attachment at 80° and Wilk's attachment at approximately 60°, respectively. Transmission measurement of PVAc film was made to determine the optical constants of the PVAc.

SIMULATION OF SEW SPECTRA

Computer simulation is useful to determine the optimal experimental conditions concerning the angle of incidence and the spacer thickness. Theoretically, the calculation of the field enhancement for the Otto configuration is a straightforward application of the multilayer Fresnel formula (12) when a polymer film is coated on a metallic substrate, the Otto configuration consists of the prism, air gap polymer film, and metallic substrate. Therefore, the Fresnel formula for a four-phase system (13) was used to simulate the SEW spectra. The Fresnel reflection coefficient is expressed as follows:

$$r = [r_1 + r_2 \exp(-2i\delta_1) + r_3 \exp(-2i(\delta_1 + \delta_2)) + \\ r_1 r_2 r_3 \exp(-2i\delta_1)]/[1 + r_1 r_2 \exp(-2i\delta_1) + \\ r_2 r_3 \exp(-2i\delta_2) + r_1 r_3 \exp(-2i(\delta_1 + \delta_2))]$$

where r_i is the reflection coefficient for the boundary between

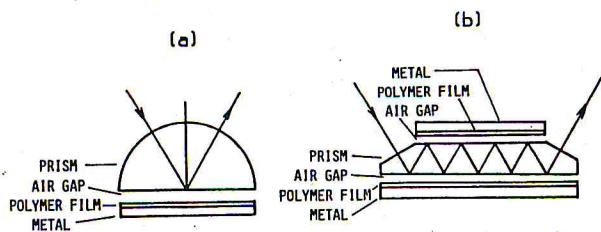


Figure 1. Experimental setup: (a) Otto configuration; (b) multiple reflection modification of the Otto configuration.

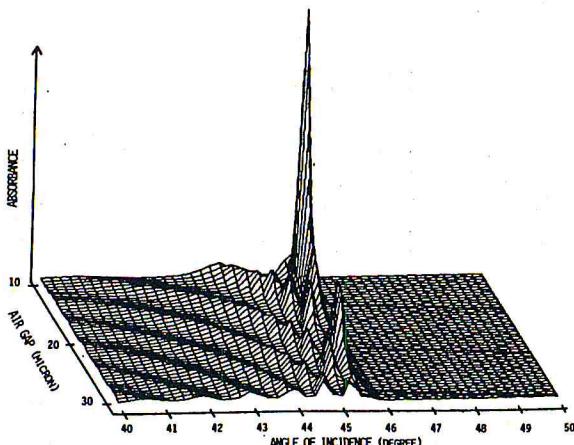


Figure 2. Simulation of SEW spectra as the three-dimensional plot. Absorbance due to carbonyl band (1747 cm^{-1}) of PVAc on copper is shown as a function of angle of incidence and spacer thickness. Critical angle of CaF_2 and air interface at 1747 cm^{-1} is 46.0° .

the i th and $(i-1)$ th phase, $\delta_i = 2n_i d_i \cos \varphi_i / \lambda$, n_i is the complex optical constant for the i th phase, d_i is the thickness of i th phase, and φ_i is the angle of incidence for i th phase. Optical constants for each layer are necessary to simulate the SEW spectra. The optical constant of copper in the mid-infrared region can be calculated by Drude free electron theory, where we used experimental values of the optical mass and relaxation time obtained by Johnson et al. (14). In order to determine the optical constant of PVAc, a transmission spectrum of uniform standing film was measured. The thickness and refractive index of the polymer film were determined by the interference fringe pattern using the method reported by Graf et al. (15). Kramers-Kronig analysis was used for the determination of refractive index $n(\nu)$ and absorption index $k(\nu)$ in the entire mid-infrared range. The refractive index of CaF_2 was calculated by Sellmeyer's empirical formula (16), where several constants derived by Malitson (17) are used for this calculation. The absorbance of a specific band was calculated as a function of angle of incidence, film thickness, and the thickness of air gap.

RESULT AND DISCUSSION

A. Spectral Simulation. Excitation of SEW using prism coupling techniques can be made either by the so-called Otto configuration or Kretschmann configuration (18). As shown in Figure 1a, the Otto configuration, which is used in this experiment, consists of a prism, an air gap, and a coated substrate. In this configuration, experimental variables are the angle of incidence, frequency, and the thickness of the spacer. No divergence of the infrared beam is considered at this point. Optimal conditions of these variables can be determined by computer simulation. Figure 2 shows the result of the simulation as the three-dimensional plot of absorbance due to the carbonyl band of PVAc. The two horizontal axes show the thickness of air gap and angle of incidence, respectively. As shown in Figure 2, the spectral intensity changes as a function of angle and air gap thickness. The

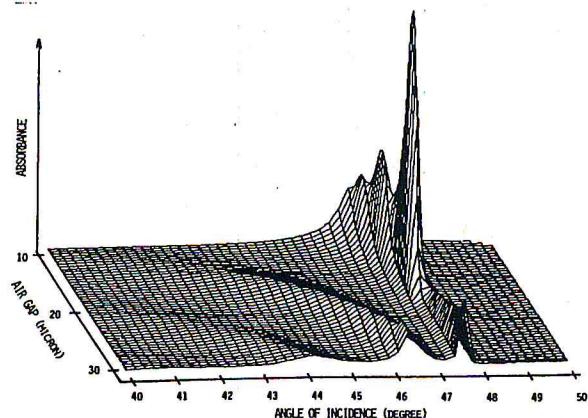


Figure 3. Absorbance due to ether band (1255 cm^{-1}) of PVAc on copper. Critical angle of CaF_2 and air interface at 1255 cm^{-1} is 47.8° .

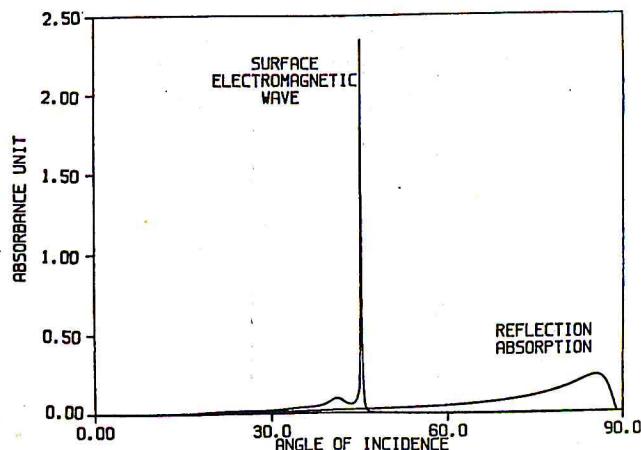


Figure 4. Simulation of SEW spectra compared to the simulated reflection-absorption spectra. Absorbance due to the carbonyl band of 20-nm PVAc film on copper is shown as a function of incident angle.

optimal angle of incidence is near the critical angle of prism and air interface, which is defined in the following equation:

$$\sin \Theta_c = 1/n_p(\nu)$$

where n_p is the refractive index of prism and Θ_c is the critical angle. Although there is no absorbance above the critical angle, the strongest peak appears near the critical angle. When the thickness of the air gap is approximately $12 \mu\text{m}$, the absorbance is maximum. This maximum peak shows the surface electromagnetic wave mode. Also, there are many wavelike peaks below the critical angle. They are due to the so-called Fabry-Perot mode (19), which is an interference effect caused by the existence of the air gap between the prism and metal. Also, Figure 3 shows the same type of three-dimensional plot but for the ether band of PVAc. According to the refractive index measurement of CaF_2 in the mid-infrared region, the refractive index of CaF_2 decreases as the wavenumber decreases, so that the critical angle of optical element becomes higher as the wavenumber decreases. Actually, as shown in the calculation (Figure 3), the optimum angle of incidence for the ether band is 2° higher than for the carbonyl band of PVAc. Thus the optimum angle for SEW varies as a function of the wavenumber. As shown in Figure 3, the optimum spacer thickness of the ether band is larger than the carbonyl band by several micrometers. This result shows that the optimum spacer thickness, which causes the maximum absorbance of the SEW mode, is different for each wavenumber. Hence as spacer thickness increases, longer wavelengths are excited.

Figure 4 shows the theoretical comparison of absorbance due to PVAc film on copper as a function of angle between SEW and the reflection-absorption spectroscopy. Clearly,

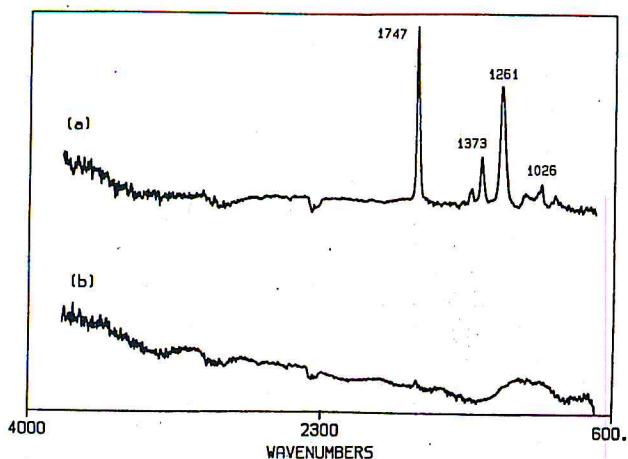


Figure 5. SEW spectra using Otto configuration of PVAc film on copper by a parallel polarized light (a) and a perpendicular polarized light (b).

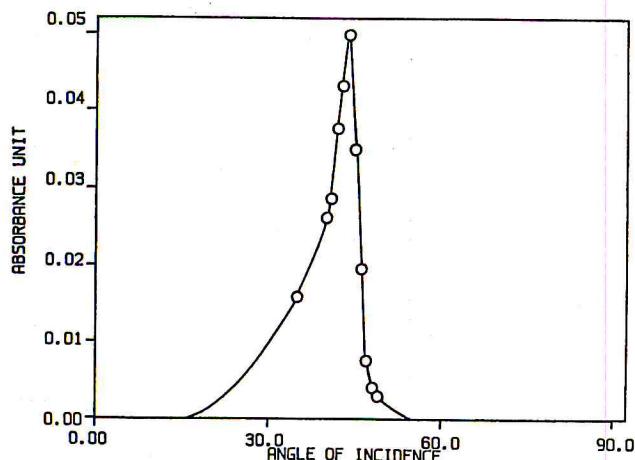


Figure 6. Experimental result of SEW using Otto configuration. Plot of absorbance due to carbonyl band of 50-nm PVAc film on copper vs. angle of incidence.

SEW shows greater absorbance at slightly below the critical angle than the reflection-absorption spectroscopy in which maximum absorbance is obtained near grazing angle. Theoretically, since the enhancement of SEW occurs as a sharp peak, the angular dependence of absorbance is very sensitive, which necessitates at least 0.1° as the angular accuracy of the reflection attachment.

B. Experimental Results Using Hemicylinder. In order to obtain SEW spectra, we used a hemicylinder as the optical element for the Otto configuration. The focal point calculated from the diameter and refractive index of the hemicylinder element was designed in front of the hemicylinder. Since in theory SEW is excited by only parallel polarized light, the spectrum of PVAc on copper was observed by using only parallel polarized light, while, as shown in Figure 5, almost no spectrum of PVAc was observed by using perpendicular polarized light. This great dependence on the polarized light shows that the SEW technique is quite different from the conventional ATR technique, although both techniques utilize either a prism or optical element. As expected in the spectral simulation, observed spectral intensity of SEW remarkably varies when the angle of incidence is changed. Figure 6 shows the absorbance of the carbonyl band vs. the angle of incidence. In this figure, the maximum absorbance is slightly below the critical angle of 46.0° and the angular distribution of the intensity is not as sharp as the theoretical prediction for the collimated beam. Furthermore, the maximum absorbance of PVAc is one-tenth of the calculated absorbance.

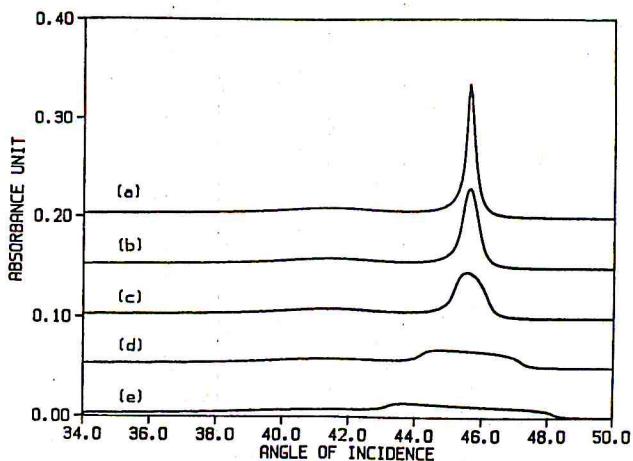


Figure 7. Simulation of SEW spectra considering angular spread of incident beam: (a) 0° , (b) 0.5° , (c) 1° , (d) 3° , (e) 5° angular spread.

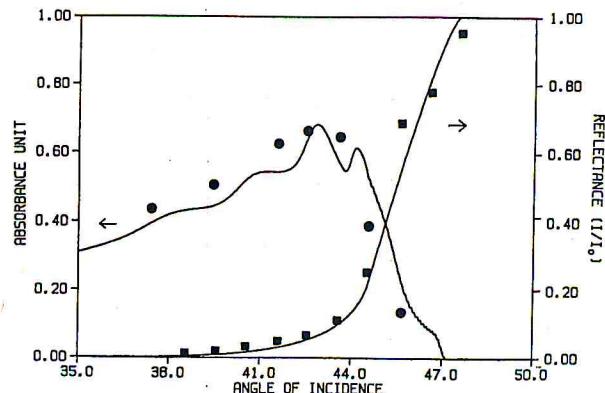


Figure 8. Experimental result of SEW using Otto configuration at 3-mm aperture. Plot of absorbance [●] due to carbonyl band of PVAc on copper and reflectance of hemicylinder prism [■] without a sample is compared to the simulation. Solid lines show the result of simulation.

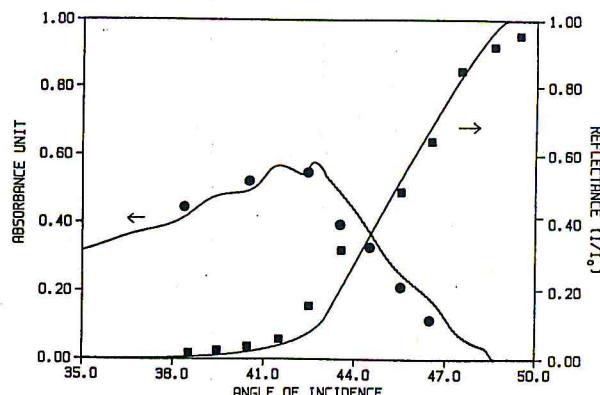


Figure 9. Experimental result of SEW using Otto configuration at 12-mm aperture.

This difference is explained as follows. Although we set the focal point in front of the prism to achieve a parallel beam, the size of incident beam is finite. This finite beam size causes angular spread of the incident beam in the hemicylinder even when a proper layout of the optical element is achieved. The effect of angular spread can be calculated by the integration of the theoretical absorbance in the region of angular spread. As shown in Figure 7, the calculation shows that the angular dependence of absorbance becomes broad as the angular spread of beam becomes wider. In this figure, the base line level has been shifted for a clarification purpose. Thus when the angular spread of incident beam becomes large, the Fabry-Pérot mode is mixed into the SEW mode and all modes

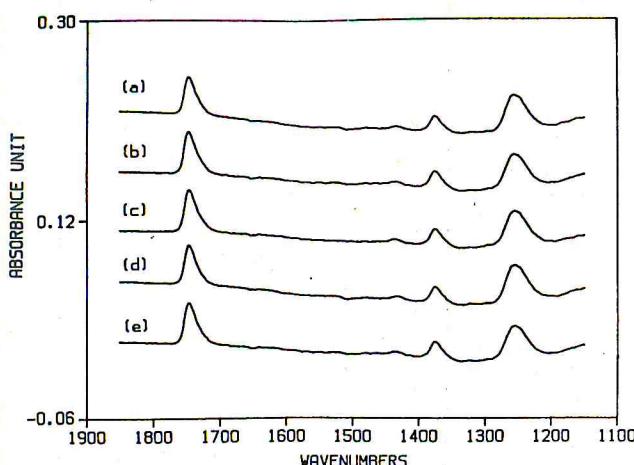


Figure 10. SEW spectra of 50-nm film on copper using different thicknesses of air gap: (a) 30 μm , (b) 20 μm , (c) 10 μm , (d) 3 μm spacer thickness, (e) without spacer.

contribute to a broad angular dependence of absorbance. Simultaneously, the intensive absorption of the SEW mode decreases.

This phenomenon can be proved as follows. Figure 8 and Figure 9 show the reflectance of the hemicylinder prism without a sample and the absorbance due to the carbonyl of PVAc film for different apertures. When the aperture size becomes large, the angular spread of the incident beam becomes broad. In Figure 8 the solid line is the theoretical curve considering the angular spread. Therefore, when we used a 3-mm aperture diameter at the energy source in our spectrometer, the angular spread was about 3° ($\pm 1.5^\circ$) (Figure 8). For a 12-mm aperture, the angular spread was 6° (Figure 9). As expected in the spectral simulation, the observed absorbance as a function of angle of incidence becomes broader, as the aperture size was increased. Also observed values of absorbance are in good agreement with the theoretical curve. Accordingly, the angular spread seems to cause the mixed mode of the SEW mode and Fabry-Perot mode, and in our system two modes are not distinguished. For the further discussion, we will use the word SEW spectra for this mixed mode spectra for the sake of convenience, unless otherwise mentioned.

With regard to the intensity of spectrum, smaller apertures yield higher absorbance of the PVAc film on copper. However, when a smaller aperture is used to obtain nearly a parallel beam, the energy throughput is reduced. Thus, in spite of a drastic effect of angular spread in SEW, the signal-to-noise (S/N) ratio worsens as one tries to increase the absorbance by utilizing a narrower beam. We might expect different optimum conditions for different spectrometers.

The angular spread of the incident beam also affects the dependence on the air gap size. As shown earlier, theoretically the air gap causes sharp changes in absorbance. In our experiment, however, when we change the thickness of the spacer, there was not a strong dependence observed. Figure 10 shows the spectra of 5-nm PVAc film on copper, by using several spacer thicknesses at the same angle of incidence. Only slight differences are observed. This phenomenon can also be explained by calculation considering the angular spread of the incident beam. Figure 11 is a three-dimensional plot of the intensity of the carbonyl band as a function of air gap and angle of incidence. In this calculation, the effect of an angular spread of 5° ($\pm 2.5^\circ$) was assumed. As shown in this figure, absorbance due to the carbonyl band shows only a slight change for the different thicknesses of the air gap and is in good agreement with the observed result. This phenomenon makes the thickness control of the spacer less critical for an

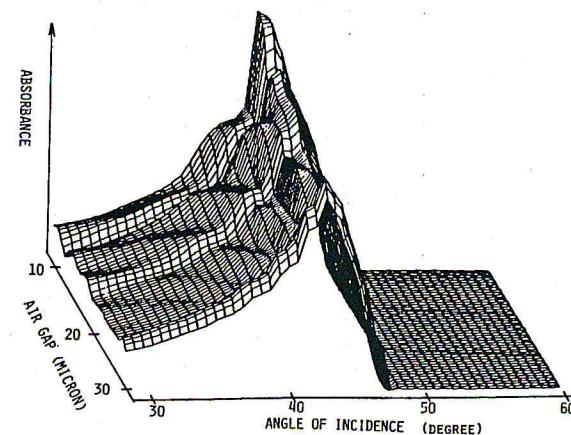


Figure 11. Simulation of SEW spectra considering the effect of angular spread. Absorbance due to carbonyl band of PVAc on copper is shown as a function of the incident angle and the thickness of air gap.

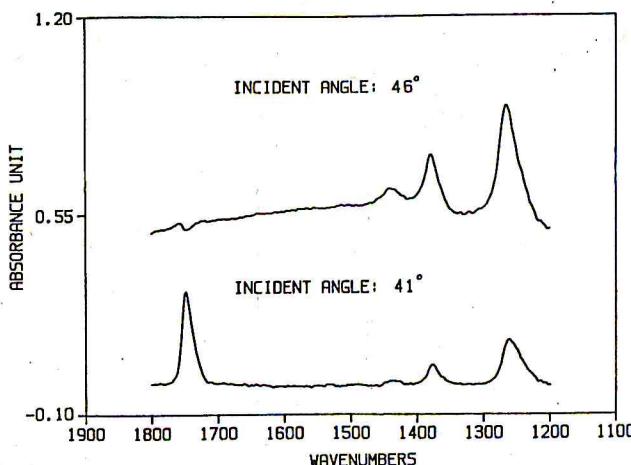


Figure 12. SEW spectra of PVAc film on copper using Otto configuration at different incident angles.

ordinary converged beam. In addition, because an air gap is used, tight optical contact between the sample and prism is not required so that wide variety of films can be measured by the SEW technique. This is a major advantage of the SEW technique compared to the conventional ATR, where optical contact is required.

Similar to that predicted by the simulation, remarkable frequency dependence of the spectra has been observed. Figure 12 shows the spectra of PVAc at the different angles of incidence. At a higher angle, the carbonyl stretching band almost disappears and the ether band is enhanced in this region. On the other hand, at a lower angle, the carbonyl band is enhanced. This is due to the fact that the critical angle of CaF_2 and air interface at 1747 cm^{-1} is lower than at 1261 cm^{-1} .

As predicted earlier in the simulation, the advantage of SEW spectroscopy is the improvement of the sensitivity. However, in this method the size of the sample is restricted by the diameter of the hemicylinder. In our system, the sample length that affects the spectra is approximately 5 mm, which is equal to the diameter of the hemicylinder. For the single reflection reflection-absorption measurement, a large sample with length in the range of 30–50 mm is used. When we compare the SEW spectra obtained by our experimental setup with a small substrate ($5 \times 10 \text{ mm}$) to reflection-absorption spectra of a large substrate ($10 \times 50 \text{ mm}$), the SEW spectra show a slightly worse S/N ratio compared to the reflection-absorption spectra. However, when we compared the spectra obtained by these two techniques on the same size of the small substrate slightly better S/N ratio can be observed on SEW spectra.

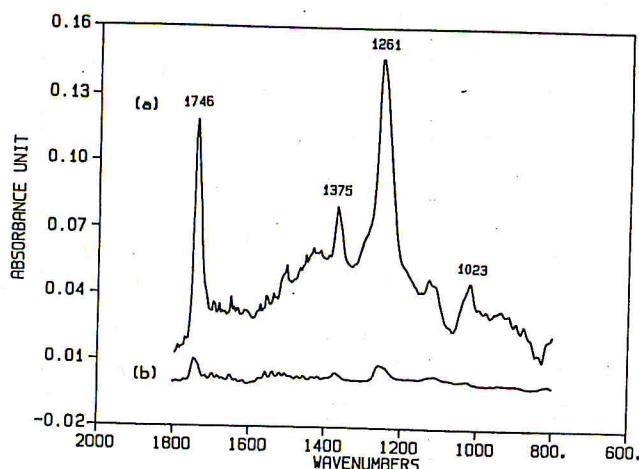


Figure 13. (a) SEW spectrum of 5-nm PVAc film on copper using multiple reflection modification of the Otto configuration. (b) Single reflection-absorption spectrum of the same sample as (a).

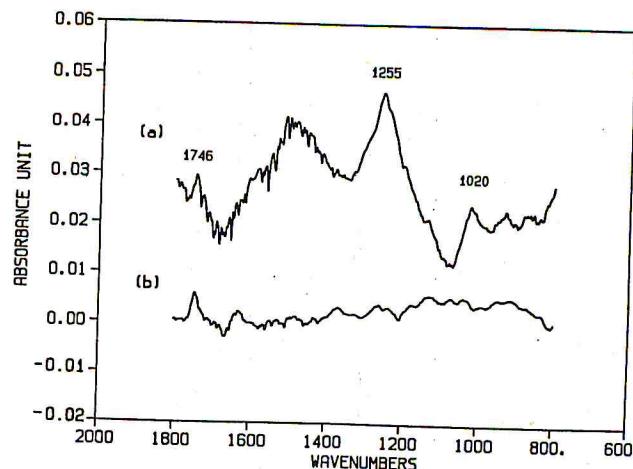


Figure 14. (a) SEW spectrum of submonolayer PVAc film on copper using multiple reflection modification of the Otto configuration. (b) Multiple reflection reflection-absorption spectrum of the same sample as (a).

C. Multiple Reflection Modification of the Otto Configuration. The result of the previous section indicates that a large hemicylinder is necessary to examine a large sample. Instead of using a larger hemicylinder, a trapezoidal element can be useful for such a sample. For this purpose, the Otto configuration was modified to a configuration referred to as the multiple reflection modification of the Otto configuration (Figure 1b). In our experiment a trapezoidal KRS-5 prism is used. The angle of the prism edge is 25° . This angle is nearly equal to the critical angle of KRS-5 in the mid-infrared region. The thickness of the prism is 4 mm and the number of reflections in the prism is 25 near the critical angle. The spectral measurement was carried out below the critical angle of the trapezoidal element. The SEW spectrum of 5.0-nm PVAc film on copper was obtained by this configuration and compared to the single reflection reflection-absorption spectrum of the same sample (Figure 13). The absorbance of the spectrum using the multiple reflection modification of the Otto configuration is 1 order of magnitude higher than the single reflection reflection-absorption spectrum at 80° . Therefore, multiple reflection modification of the Otto configuration can be applicable to the same size of sample as the reflection-absorption technique and also provides a better spectrum compared to the spectrum obtained by the single reflection reflection-absorption technique using a grazing angle.

On the other hand, in order to increase the absorbance of the spectrum, multiple reflection reflection-absorption was considered (20). Actually the multiple reflection reflection-absorption spectrum of 5.0-nm PVAc on copper shows a similar value of absorbance to the spectrum obtained by the multiple reflection SEW technique, where the same number of reflections was used for both techniques. However, the circular beam of the FT-IR spectrometer limits the energy throughput through the narrow gap of the multiple reflection mode of the reflection-absorption experiment. The new multiple reflection modification of the Otto configuration yields a higher number of reflections with a wider sample-to-sample gap and shorter sample size since the angle of incidence is much smaller than the reflection-absorption technique.

The advantage of sensitivity of the SEW technique becomes remarkable when the submonolayer film is measured as follows. In order to make a submonolayer film, we used a solution for the 5-nm film diluted to one-tenth its concentration and cast it on the substrate, where the average thickness of the film is expected to be 0.5 nm. When this film is measured by the multiple reflection reflection-absorption technique,

only the strongest carbonyl peak of PVAc is observed, whereas other peaks due to PVAc are hidden in the drifting base line (Figure 14 b). On the contrary, as shown in Figure 14a, a SEW spectrum of the same sample obtained by the same number of reflections shows at least three peaks due to PVAc, such as the bands at 1745 , 1255 , and 1020 cm^{-1} . Other bands are probably due to contamination. In this spectrum the peaks at lower wavenumbers seem to be enhanced, whereas enhancement of the carbonyl peak was also observed when the angle of incidence was slightly changed. This phenomenon is supported by the result of the spectral simulation which showed the strong angular dependence on the SEW spectra. Therefore, for measuring submonolayer films, the multiple reflection modification Otto configuration has an greater advantage in sensitivity compared to multiple reflection reflection-absorption spectroscopy.

As recently reviewed (21), the ATR technique can be a very sensitive technique. In order to obtain higher sensitivity, the ATR technique needs perfect optical contact between prism and film which is directly cast on the prism. Because of this, the interaction between substrate and surface species is difficult to study except for the case that the material for the substrate is transparent enough to be used as the prism. On the other hand, since SEW spectroscopy allows us to make an air gap whose size is several tens of micrometers, a wide variety of samples can be measured. It is expected that FT-IR SEW spectroscopy would be useful for studying the interfacial phenomena between the surface species and substrate.

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Registry No. PVAc, 9003-20-7; copper, 7440-50-8.

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