# **Optical Contact in ATR/FT-IR Spectroscopy**

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Optical contact between an internal reflection element (IRE) and a sample is crucial for obtaining a good spectrum in an attenuated total reflection (ATR) experiment. When an air gap is present between the IRE and the sample, the spectrum severely deteriorates. Two techniques for determining the goodness of contact are proposed—first, by making a comparison between polarized ATR spectra and, second, by making a comparison between ATR and transmission spectra. When the optical contact is achieved, the normalized *p*-polarized ATR spectrum is exactly the same as the normalized *s*-polarized ATR spectrum. Moreover, the ratio between the normalized absorbance measured in the ATR mode and the normalized absorbance measured in the transmission mode equals the ratio between the frequency being considered and the normalization frequency. Theoretical and experimental investigations have been performed in order to verify the proposed techniques.

Index Headings: Optical contact; ATR/FT-IR spectroscopy; Air gap; Electric field decay; Evanescent field.

## **INTRODUCTION**

Since the independent discovery of the technique by Harrick<sup>1,2</sup> and Fahrenfort<sup>3</sup> in the early 1960s, attenuated total reflection Fourier transform infrared (ATR/FT-IR) spectroscopy has been applied in various applications such as qualitative analyses,<sup>4,5</sup> quantitative analyses,<sup>6,7</sup> surface characterizations,<sup>8-14</sup> kinetic studies,<sup>15-17</sup> depth profiling,<sup>18-26</sup> environmental applications,<sup>27-30</sup> diffusion studies,<sup>31-34</sup> and molecular orientation studies.<sup>35,36</sup> The diverse applications of the technique are due to simplicity in sample preparation and availability of accessories designed for general and specific applications. ATR absorbance can be expressed in terms of material characteristics and experimental conditions. Various experimental parameters such as angle of incidence and polarization can be modified in order to gain specific information of the system. However, all equations expressing the relationship between ATR absorbance and material characteristics are defined under an assumption of the existence of optical contact between the internal reflection element (IRE) and the sample. The absorbance deteriorates significantly when an air gap presents itself between the IRE and the sample (i.e., the optical contact is not achieved). The characterization of solid samples, especially hard and rigid samples, normally encounters air gap problems. Severe absorbance deterioration is observed when the surface of the sample is not smooth and cannot be pressed against the IRE. If the air gap is thick enough, the spectrum of the sample may not be able to be observed. In general, an IRE with multiple reflection is employed in order to increase spectral intensity and improve the signal-to-noise (S/N) ratio. However, the surface area of a

large IRE associates with the local irregularity of the sample surface, contributing to the formation of the air gap. Even when a sample with a mirror-flat surface is employed, good contact between the IRE and the sample is difficult to obtain due to the local unevenness of the surfaces.

Solvent casting of polymer solution or hot pressing of polymer film onto the IRE has been employed in order to ensure optical contact. These approaches are, however, not applicable to various types of samples (i.e., surfacetreated polymers, polymer coatings, and insoluble polymers) since the required information may be destroyed during the preparation process. In general practice, applying pressure to the solid sample against the IRE is employed for improving the contact between the IRE and the solid samples.<sup>4,7,31,32</sup> This approach is, however, not generally applicable or not appropriate for soft IREs such as ZnSe and KRS-5 because excessive force may damage the surface of the IRE or the IRE itself. A hard and rigid sample can also damage the surface of a hard IRE such as germanium when it is under high pressure. A diamond IRE is normally employed when high pressure is necessary for the improvement of the contact. However, spectral information in 2500-1800 cm<sup>-1</sup> region is masked by diamond absorption.<sup>4,7</sup> Moreover, an infrared microscope is necessary when the diamond IRE is utilized because the IRE is very small.

Optical contact is generally assumed when performing quantitative analysis on the observed ATR spectrum of a solid sample. However, at the present, there is no theoretical consideration regarding the achievement of optical contact under various sampling procedures (i.e., hot pressing, solution casting, and force contacting). The purpose of this paper is to introduce techniques for determining from the observed spectra whether or not optical contact between the IRE and the solid sample has been achieved.

### THEORY

Consider a system where an isotropic sample is in optical contact with an IRE. The infrared transparent IRE has a refractive index of  $n_0$ , while the infrared absorbing sample has a complex refractive index at frequency  $\nu$ (cm<sup>-1</sup>) of  $\hat{n}_F(\nu) = n_F(\nu) + ik_F(\nu)$ , where  $n_F(\nu)$  is the refractive index and  $k_F(\nu)$  is the absorption index. Under a weakly absorbing condition, ATR absorbance can be expressed in terms of the experimental conditions and material characteristics by<sup>18-21</sup>

$$\mathbf{A}_{\rho}(\theta, \nu) = \frac{4\pi\nu}{\ln(10)n_0 \cos \theta} \\ \times \int_0^\infty n_1(\nu) k_1(\nu) \langle E_{\rho,z=0}^2(\theta, \nu) \rangle_{k=0} e^{-2z/d_{\rho}(\theta,\nu)} \, \mathrm{d}z \ (1)$$

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FIG. 1. Depth-dependent MSEvF at various angles of incidence with *p*-polarized radiation (**A**) and *s*-polarized radiation (**B**). The simulation parameters are  $n_0 = 4.0$ ,  $n_F = 1.5$ ,  $\nu = 1000$  cm<sup>-1</sup>, and  $\theta = 30^{\circ}$ ,  $35^{\circ}$ ,  $40^{\circ}$ ,  $45^{\circ}$ ,  $50^{\circ}$ ,  $55^{\circ}$ , and  $60^{\circ}$ .

where  $\bar{p}$  indicates polarization of the incident beam,  $\theta$  is the angle of incidence, z is the depth from an IRE/ sample interface,  $d_p(\theta, \nu)$  is the penetration depth, and  $\langle E_{\bar{\nu},z=0}^2(\theta,\nu)\rangle_{k=0}$  is the mean square value of the evanescent field or the mean square evanescent field (MSEvF) at the interface. Although the integration limit is defined from the depth equals zero (i.e., the interface) to the depth equals infinity, an ATR spectrum does not provide spectral information of the entire thickness of the sample due to the depth-dependent characteristic of the evanescent field. The field is strongest at the interface and exponentially decays to zero as a function of depth. The strength and decay characteristics of the evanescent field expressed in terms of the experimental parameters (i.e., angle of incidence, polarization, and frequency of the incident beam) and material characteristics (i.e., refractive indices of the IRE and that of the sample) are given elsewhere.37-41

The evanescent field depends strongly on the angle of incidence of the incident beam. The depth-dependent MSEvFs at various angles of incidence are shown in Fig. 1. The MSEvF at the interface becomes smaller as the angle of incidence becomes larger. The angle of incidence



FIG. 2. Depth-dependent MSEvF at various frequencies with *p*-polarized radiation (**A**) and *s*-polarized radiation (**B**). The simulation parameters are  $n_0 = 4.0$ ,  $n_F = 1.5$ ,  $\theta = 45^\circ$ , and  $\nu = 500$ , 1000, 1500, and 3000 cm<sup>-1</sup>.

also plays a major role in the decay characteristic of the field. The greater the angle of incidence, the faster the decay of the field. As a result, the evanescent field at a greater angle of incidence decays to zero at a shallower depth than that at a smaller angle.

The evanescent field also varies as a function of frequency of the radiation. The depth-dependent MSEvFs at various frequencies are shown in Fig. 2. If the refractive indices at two different frequencies are the same, their MSEvFs at the interface are the same. However, their decay characteristics are different. The greater the frequency, the faster the decay of the field. As a result, the evanescent field at a greater frequency decays to zero at a shallower depth than that at a lower frequency.

Due to the decay characteristic of the field, the spectral contributions from molecules at various depths to the total absorption in an ATR spectrum are not the same. The major contribution comes from molecules near the interface where the field strength is greatest. Those at further distance have a smaller contribution since the field strength becomes smaller. Only the molecules within the region where the field strength does not equal zero contribute to the absorption. Molecules situated beyond the



FIG. 3. ATR spectra of a simulated absorbing medium with *p*-polarized radiation (solid line) and *s*-polarized radiation (dotted line) at various thicknesses of the air gap: 0.00  $\mu$ m (**A**), 0.01  $\mu$ m (**B**), 0.05  $\mu$ m (**C**), and 0.50  $\mu$ m (**D**). The dashed lines indicate the ratio between *p*- and *s*-polarized spectra. The simulation parameters are  $n_0 = 4.0$ ,  $n_{air} = 1.0$ , and  $\theta = 45^{\circ}$ .

depth where the field decays to an insignificant level do not make any contribution to the spectrum. For an isotropic medium, the nonuniformity of the evanescent field in the depth direction does not have any influence on the quantitative characteristic of the spectrum unless the optical contact is not achieved. When there is an air gap between the IRE and the sample, anisotropy in the depth direction is introduced into the system (although the sample is isotropic). The evanescent field is greatly altered by the air gap. The relationship between the absorbance and material characteristics in such a system does not follow Eq. 1. As a result, the quantitative characteristic of the sample cannot be drawn from its spectrum. Absorbance of the system with an air gap is always smaller than that with the optical contact since the region near the IRE surface, where the field is strongest, is occupied by an air gap that does not involve any absorption. The sample, which is positioned at a distance far from the IRE, experiences a much smaller evanescent field compared to a system with optical contact. The absorption decreases as the air gap is widened.

Figure 3 shows simulated ATR spectra at a 45° angle of incidence with a Ge crystal as the IRE at various air gap thicknesses. The complete details for the spectral simulation and the employed equations are given elsewhere.<sup>39,42</sup> The complex refractive index spectrum of the absorbing medium is generated via a Lorentz model with the refractive index at an infinite frequency of  $1.5.^{43,44}$ The medium has three absorption bands at 700, 1600, and 3000 cm<sup>-1</sup> with an equally maximum absorption index of 0.1 and full width at half-height of 40. When the optical contact is satisfied, all bands have the same maximum absorption, and the absorbance with *p*-polarized radiation is twice that with *s*-polarized radiation (Fig. 3A). It should be noted that, since the spectra are simulated from a noise-free complex refractive index spectrum, the absorbance ratio can be calculated even at a frequency far away from an absorption band. A division by zero is not encountered due to a numerical dispersion of the complex refractive index.

When there is an air gap, spectral intensity at a high frequency decreases by a greater extent compared to that at a lower frequency. This is because the evanescent field at a higher frequency decays to an insignificant level at a shallower depth compared with that at a lower frequency. The field at a higher frequency loses more of its effectiveness for interacting with the sample. As a result, the absorption band at a higher frequency disappears before that at a lower frequency, as the air gap becomes thicker. Moreover, due to the changes in the strength and decay characteristic of the evanescent field, the absorbance ratio between p- and s-polarized absorbance is not the same as that of a system with optical contact. The greater the air gap thickness, the smaller the ratio. This phenomenon directly relates to the strength and decay characteristic of the evanescent field in the system. The evanescent field of the *p*-polarized radiation is affected more by the air gap compared to that of the s-polarized radiation (Fig. 4). Although there is a large increase in the field strength with *p*-polarized radiation near the IRE surface due to a refractive index mismatch, the field does not contribute to the absorption since it is in the air gap region. This is another contributing factor in the greater decrease of the absorbance when the air gap becomes wider.

The unusual behavior of the evanescent field of a system with an air gap is due to the refractive index mismatch between air  $(n_{air} = 1.0)$  and the solid sample  $(n_F = 1.5)$ . If the air gap is replaced by a liquid film (or a buffer layer) with a refractive index similar to that of the sample, the abrupt changes of the MSEvF at the interface in *p*-polarization are eliminated. Moreover, strengths and decay characteristics of the fields in the system are similar to those with an optical contact. The absorbance of the system can be expressed in terms of the absorbance of the liquid and that of the sample by<sup>45</sup>

$$\mathbf{A}(\theta, \nu) = (1 - e^{-2h/d_p(\theta, \nu)}) \mathbf{A}_{\text{buffer}}(\theta, \nu) + e^{-2h/d_p(\theta, \nu)} \mathbf{A}_F(\theta, \nu)$$
(2)

where *h* and  $\mathbf{A}_{\text{buffer}}(\theta, \nu)$ , respectively, are the thickness and the bulk absorbance of the liquid film, while  $\mathbf{A}_F(\theta, \nu)$ is the bulk absorbance of the solid sample.

Figure 5 shows noise-free ATR spectra of the simulated absorbing medium at various thicknesses of a nonabsorbing buffer layer. As the thickness of the buffer layer increases, the sample experiences smaller field strength and its associated absorption bands become smaller. Since the rate of decrease of the field strength is greater at a high frequency compared to that at a low frequency, absorbance at a higher frequency decreases faster with respect to the thickness of the buffer layer. An absorption band at a higher frequency disappears before that at a lower frequency, as the buffer layer becomes thicker. Unlike the case for a system with an air gap, absorbance with *p*-polarized radiation is always greater than that with *s*-polarized radiation. Although there is a fluctuation at



FIG. 4. Depth-dependent MSEvF at various air gap thicknesses with *p*-polarized radiation (**A**) and *s*-polarized radiation (**B**). The simulation parameters are  $n_0 = 4.0$ ,  $\theta = 45^\circ$ ,  $\nu = 1000 \text{ cm}^{-1}$ ,  $n_{\text{air}} = 1.0$ ,  $n_F = 1.5$ , and the air gap thicknesses are 0.0, 0.1, 0.2, 0.3, 0.5, and 1.0  $\mu$ m. Note: the broken lines indicate the MSEvFs with optical contact. The abrupt changes of the MSEvF with *p*-polarization indicate the air/absorbing medium interfaces. The insets are added for clarity.

the peak shoulder due to refractive index dispersion, the ratio of the p- and s-polarized absorbance is the same as that of a system with optical contact.

The above phenomena indicate that optical contact is necessary for acquiring a good ATR spectrum. Following are the proposed techniques for verifying whether or not optical contact is achieved in an ATR experiment (i.e., by comparing p- and s-polarized ATR spectra and by comparing ATR and transmission spectra). The major advantage of the proposed techniques is that the observed spectra, material characteristics, and experimental parameters are employed for the verification.

#### **TECHNIQUES**

**Comparison between ATR Spectra.** For an isotropic medium with optical contact, Eq. 1 can be simplified, and the ratio of absorbance at  $\nu_2$  to that at  $\nu_1$  is given by

$$\frac{\mathbf{A}_{\bar{p}}(\theta, \nu_{2})}{\mathbf{A}_{\bar{p}}(\theta, \nu_{1})} = \frac{\nu_{2}n_{F}(\nu_{2})k_{F}(\nu_{2})d_{p}(\theta, \nu_{2})\langle E_{\bar{p},z=0}^{2}(\theta, \nu_{2})\rangle_{k=0}}{\nu_{1}n_{F}(\nu_{1})k_{F}(\nu_{1})d_{p}(\theta, \nu_{1})\langle E_{\bar{p},z=0}^{2}(\theta, \nu_{1})\rangle_{k=0}}$$

$$= \frac{n_{F}(\nu_{2})k_{F}(\nu_{2})}{n_{F}(\nu_{1})k_{F}(\nu_{1})}$$
(3)



FIG. 5. ATR spectra of the same simulated absorbing medium shown in Fig. 6 with *p*-polarized radiation (solid line) and *s*-polarized radiation (dotted line) at various thicknesses of the buffer layer: 0.00  $\mu$ m (**A**), 0.01  $\mu$ m (**B**), 0.05  $\mu$ m (**C**), and 0.50  $\mu$ m (**D**). The dashed lines indicate the ratio between *p*- and *s*-polarized spectra. The simulation parameters are  $n_0 = 4.0$ ,  $n_{buffer} = 1.5$ ,  $k_{buffer} = 0.0$ , and  $\theta = 45^\circ$ .

The above equation indicates that the intensity of a normalized ATR spectrum is proportional to the ratio of the product of the refractive index and absorption index at a given frequency  $(\nu_2)$  to that at the normalization frequency  $(\nu_1)$ . Since the ratio is independent of polarization, normalized spectra of p- and s-polarization and nonpolarization spectra are exactly the same (Fig. 6A). Since the complex refractive indices at peak maxima (700, 1500, and 3000 cm<sup>-1</sup>) are the same, the normalized spectra (i.e., with the normalization frequency of 700  $cm^{-1}$ ) have the maximum value of unity. When optical contact is not achieved, the normalized spectra of p- and s-polarization and nonpolarized spectra are not identical (Fig. 6B). The degree of discrepancy depends on the thickness of the air gap. The greater the thickness of the air gap, the greater the difference among the normalized spectra.

When the air gap is replaced by a liquid film with a refractive index similar to that of the sample, the refractive index mismatch is eliminated. Due to frequency-dependent characteristics of the evanescent field, absorption bands at various frequencies experience different effects of the liquid film. Absorption bands associated with the sample are not the same as those of a system with optical contact, although the evanescent field in the system is similar to that of a system with optical contact. The magnitude of the difference is greatest at the high-frequency end of the spectrum. However, at the same frequency, the sample experiences the same decay pattern of p- and s-polarized radiation; the normalized p-polarized spectrum are exactly the same (Fig. 6C).

**Comparison between ATR and Transmission Spectra.** The existence of the optical contact may be verified by taking a ratio between the normalized ATR spectrum



FIG. 6. Normalized spectra of the simulated absorbing medium at various experimental conditions: ATR technique with optical contact (**A**); ATR technique with a 0.05  $\mu$ m air gap (**B**); ATR technique with a 0.05  $\mu$ m nonabsorbing buffer layer (**C**); transmission technique with 10  $\mu$ m film thickness (**D**); and the ratio of the normalized spectra (**E**). The simulation parameters are the same as those in Figs. 3 and 5. The normalized spectra of the *p*-polarized, nonpolarized, and *s*-polarized spectra in Figs. 9A, 9C, and 9D are exactly the same. The insets in Fig. 6B are added for clarity. The absorbance at 700 cm<sup>-1</sup> (indicated by asterisks) is used for normalization.

against the normalized transmission spectrum. Both polarized and nonpolarized spectra can be employed for the evaluation. Under a small absorption criterion, the absorbance ratio obeys the following relationship:

$$\frac{\mathbf{A}_{\text{Trans}}(\nu_{2})/\mathbf{A}_{\text{Trans}}(\nu_{1})}{\mathbf{A}_{\text{ATR}}(\theta, \nu_{2})/\mathbf{A}_{\text{ATR}}(\theta, \nu_{1})} = \frac{\left[\frac{\nu_{2}k_{F}(\nu_{2})}{\nu_{1}k_{F}(\nu_{1})}\right]}{\left[\frac{\nu_{2}n_{F}(\nu_{2})k_{F}(\nu_{2})d_{p}(\theta, \nu_{2})\langle E_{\vec{p},z=0}^{2}(\theta, \nu_{2})\rangle_{k=0}}{\nu_{1}n_{F}(\nu_{1})k_{F}(\nu_{1})d_{p}(\theta, \nu_{1})\langle E_{\vec{p},z=0}^{2}(\theta, \nu_{1})\rangle_{k=0}}\right]}$$
(4)

where  $\mathbf{A}_{\text{Trans}}(\nu)$  and  $\mathbf{A}_{\text{ATR}}(\theta, \nu)$ , respectively, are the absorbance of the transmission and ATR spectra. When a negligible refractive index variation over the spectral region is assumed, the above expression can be simplified to  $[\mathbf{A}_{\text{Trans}}(\nu_2)/\mathbf{A}_{\text{Trans}}(\nu_1)]/[\mathbf{A}_{\text{ATR}}(\theta, \nu_2)/\mathbf{A}_{\text{ATR}}(\theta, \nu_1)] = \nu_2/\nu_1$ . For the experimentally observed spectra, if the ratio significantly deviates from the theoretically predicted value, the ATR spectrum does not have optical contact. Figure 6E shows the absorbance ratio between the normalized transmission spectrum and normalized ATR spectrum.



FIG. 7. Nonpolarized ATR spectra of the thick mirror-flat PC sample at various experimental conditions: under applied pressure (A); with a thick methanol buffer layer (B); with a thin methanol buffer layer (C); with methanol buffer layer as air gap formation starts (D); and when methanol disappears (E). The asterisks indicate absorption bands associated with methanol.

Since the complex refractive indices of the simulated medium at peak maxima are all the same, the ratios given by Eq. 3 with  $\nu_1$  of 700 cm<sup>-1</sup> equal 4.29, 2.29, and 1.00 at 3000, 1600, and 700 cm<sup>-1</sup>, respectively. A small variation observed in Fig. 6E is due to refractive index dispersion.

#### EXPERIMENTAL

All spectra were acquired with a Bruker Vector33 FT-IR spectrometer equipped with a deuterated triglycine sulfate (DTGS) detector. The spectrometer was set to collect spectra at 64 scan coaddition with 4 cm<sup>-1</sup> spectral resolution. A multiple reflection ATR accessory (Spectra Tech, USA) with a 45° germanium IRE ( $50 \times 5 \times 2$  mm) was employed for all spectral acquisitions. Three samples were employed for the goodness-of-contact investigations: a hard and rigid solid sample (polycarbonate: PC), a soft and rubbery solid sample (polyvinylchloride: PVC), and a liquid sample (toluene).

#### **RESULTS AND DISCUSSION**

Figure 7 shows nonpolarized ATR spectra of a piece of thick PC. The sample was a virgin compact disc with mirror-flat surface. An ATR spectrum of the PC was not observed unless pressure was applied. In order to ensure the best possible contact, the ATR spectrum was taken as increasing pressure was applied to the sample. Figure



FIG. 8. Polarized ATR spectra of the thick mirror-flat PC sample at various experimental conditions: PC under applied pressure (A); PC after methanol buffer layer completely disappears (B); normalized spectra by the absorption at 1192 cm<sup>-1</sup> (C); and the ratio between the *p*-polarized spectrum and the *s*-polarized spectrum. Note: solid lines indicate the *p*-polarized spectra, while dotted lines indicate the *s*-polarized spectra.

7A shows a spectrum of the mirror-flat PC sample at the point where no further intensity change was observed as the pressure was increased. However, absorbance over the entire spectrum was still small. In order to verify optical contact, a small amount of methanol was introduced. The liquid was spread over the IRE as the mirror-flat PC sample was sandwiched onto the IRE. Pressure was then applied to the PC in order to squeeze out the excess methanol. The absorption bands associated with PC are greatly enhanced when a thin methanol film replaces the air gap. The higher the pressure, the thinner the methanol film and the greater the absorption bands associated with PC (Figs. 7B and 7C). The observed phenomena indicate the existence of an air gap in the system (Fig. 7A). Since the PC is thick, hard, and rigid, its surface is not perfectly adhered to the IRE. When the methanol evaporates, an air gap formation starts and the absorption bands associated with PC become smaller (Fig. 7D). When the methanol completely disappears, an air gap exists between the IRE and the PC. The air gap occurs although pressure is continuously applied to the sample. The greater absorbance in Fig. 7E compared to that in Fig. 7A indicates a thinner air gap after the methanol disappears. However, good optical contact cannot be achieved due to the rigidity and surface irregularity of the sample.

Polarized spectra of the system associated with Fig. 7A are shown in Fig. 8A, while those associated with Fig. 7E are shown in Fig. 8B. A greater absorbance with s-polarized radiation compared with that with p-polarized radiation in Fig. 8A confirms the existence of an air gap



FIG. 9. Nonpolarized ATR spectra of the thick soft PVC sample at various experimental conditions: under applied pressure  $(\mathbf{A})$ , with a thick iso-propanol buffer layer  $(\mathbf{B})$ , with a thin iso-propanol buffer layer  $(\mathbf{C})$ , and with a very thin iso-propanol buffer layer  $(\mathbf{D})$ . The asterisks indicate absorption bands associated with iso-propanol.

between the IRE and the PC sample. The opposite phenomena observed in Fig. 8B indicate an improvement in contact between the IRE and the sample. In order to verify the goodness of contact, the observed spectra in Fig. 8B were normalized by the absorbance at 1192 cm<sup>-1</sup>, and the results are shown in Fig. 8C. A minor discrepancy is observed in the high absorption region  $(1150-1300 \text{ cm}^{-1})$ of the normalized spectra. The goodness of contact was further examined by ratioing the *p*-polarized spectrum against the *s*-polarized spectrum, and the result is shown in Fig. 8D. The deviation from the theoretical prediction (i.e., Eq. 4) suggests that optical contact is not achieved. However, the PC has been brought closer to the IRE by the applied force together with the introduction of the thin methanol film.

ATR spectra of soft PVC are shown in Fig. 9. A high absorbance is obtained with little applied pressure (Fig. 9A). In order to verify the goodness of contact, a small amount of iso-propanol was deposited onto the IRE. The liquid was then spread over the IRE as the soft PVC sample was sandwiched onto the IRE. Pressure was continuously applied to the PVC until there was no observable change in the spectrum. Figures 9B and 9C show spectra of the system at two different thicknesses of the liquid film. The thicker is the iso-propanol film; the smaller, the absorption bands associated with PVC. However, there is no observable spectral enhancement as in the case of PC. Absorption bands associated with PVC in a three-phase system (i.e., PVC/iso-propanol/IRE; Figs. 9B and 9C) are always smaller than those in a twophase system (i.e., PVC/IRE; Fig. 9A). The observed phenomena suggest that the soft PVC has optical contact with the IRE.



FIG. 10. Spectra of toluene at various experimental conditions: ATR spectra at 45° angle of incidence (**A**) with *p*-polarized radiation (solid line) and *s*-polarization (dotted line); absorbance ratio of *p*-polarized spectrum over *s*-polarized spectrum (**B**); normalized ATR spectra (**C**); transmission spectrum (**D**); normalized transmission spectrum (**E**); and ratio of the normalized spectra (**F**). The triangles in **F** indicate peak positions, while the dashed line indicates the ratio between the frequency in the spectral region and the normalization frequency (1495 cm<sup>-1</sup>). Note: the normalized spectra of *p*-polarization and *s*-polarization in **C** cannot be differentiated by the graphical illustration.

ATR spectra at a  $45^{\circ}$  angle of incidence and the transmission spectrum of toluene are shown in Fig. 10. At a  $45^{\circ}$  angle of incidence, a factor of 2 is obtained (Fig. 10B) when the *p*-polarized spectrum is ratioed against the s-polarized spectrum. Although a small deviation from the theoretical prediction is observed, the discrepancy is due to spectral noise and baseline fluctuation. The ratio fluctuates a great deal in the very weak absorbing and nonabsorbing regions where noise dominates. When the p-polarized and s-polarized ATR spectra are normalized by absorbance at 1495 cm<sup>-1</sup>, a significant difference between the normalized spectra is not observed (Fig. 10C). The observed phenomena (Figs. 10B and 10C) indicate optical contact between the liquid sample and the IRE. Optical contact was further confirmed by comparing an ATR spectrum with a transmission spectrum. The ratio between the normalized transmission spectrum (nonpolarized) and the normalized ATR spectrum (*p*-polarized) was taken (Fig. 10F). The result at a certain frequency equals the ratio of the frequency being considered to the normalization frequency. The experimental results agree very well with the theoretical predictions (i.e., Eq. 4).

However, fluctuations due to noise and baseline are observed, especially in nonabsorbing and weakly absorbing regions.

#### CONCLUSION

Liquid samples always have optical contact with an IRE. Good contact in a soft and rubbery solid sample may be achieved with or without applied pressure. Hard and rigid solid samples, on the other hand, do not have good contact. The ATR spectra severely deteriorate when an air gap presents itself between the IRE and the sample. Two techniques are proposed for verifying the goodness of contact from the observed spectra: a comparison between polarized ATR spectra and a comparison between ATR and transmission spectra. When optical contact is achieved, a normalized p-polarized ATR spectrum is exactly the same as its counter s-polarized ATR spectrum. Furthermore, the ratio between a normalized transmission spectrum (polarized or nonpolarized) and a normalized ATR spectrum (polarized and nonpolarized), at any frequency, equals the ratio between the considered frequency and the normalization frequency. In a system where optical contact is difficult to achieve (i.e., a hard and rigid sample), a thin liquid index-matching organic film can be introduced between the IRE and the sample in order to enhance the absorption.

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