ATR Spectral Intensity: What is the Upper Limit of Weak Absorption?

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INTRODUCTION

The attenuated total reflection (ATR) technique is a powerful method for material characterization via Fourier transform infrared (FT-IR) spectroscopy. Due to the unique nature of the electric component of the electromagnetic radiation in the total internal reflection phenomenon, ATR/FT-IR spectroscopy is well known as a surface characterization and depth profiling technique.^{1–8} In contrast to transmission techniques, sampling depth in the ATR technique is defined not as the thickness of the sample but as the decay characteristic of the electric field. The depth ranges from submicrometer to several micrometers depending on experimental conditions and material characteristics. For an isotropic medium, material characteristics at the surface and those in the bulk are the same. As a result, the ATR technique also delivers bulk information as do the transmission techniques.⁹⁻¹⁸.

ATR/FT-IR spectroscopy has been employed for various applications such as qualitative and quantitative analyses,^{15–18} surface characterization,^{8,13,19} molecular orien-tation,^{11,20} and depth profiling.^{2–7,21} Since an ATR spectral intensity involves complex relationships between experimental conditions (i.e., angle of incidence, polarization, and number of reflection) and material characteristics [i.e., refractive index of internal reflection element (IRE) and complex refractive index of the absorbing medium], the quantitative-related analysis via ATR/FT-IR spectroscopy becomes complicated. In order to avoid difficulties, the mean square evanescent field (MSEvF) is employed instead of the mean square electric field (MSEF).^{1-3,12,18,19} As a result, the spectral intensity can be expressed as a linear function of the absorption coefficient. Although its applicability is restricted to bands with small absorption, there is no guideline for limitation of the ATR spectral intensity based on the MSEvF (i.e., how small is considered small?). It is the purpose of this paper to verify, theoretically and experimentally, the limit for quantitative analysis via ATR spectral intensity based on the MSEvF.

THEORY

Let's consider an interaction between incident beam and an isotropic medium under an attenuated total reflection condition. The medium has a complex refractive index of $\hat{n}_1(v) = n_1(v) + ik_1(v)$, where $n_1(v)$ and $k_1(v)$ are the refractive index and the absorption index, respectively. If there is no other cause for energy loss except absorption by the medium, the following expression is valid for an ATR/FT-IR spectrum:^{3,7,13,16}

$$A_{\bar{p}}(\theta, \mathbf{v}) = 1 - R_{\bar{p}}(\theta, \mathbf{v}) \tag{1}$$

where θ is the angle of incidence, \bar{p} is the degree of polarization, and $A_{\bar{p}}(\theta, \nu)$ and $R_{\bar{p}}(\theta, \nu)$ are *absorptance* and *reflectance*, respectively. It should be noted that the *absorptance* given in Eq. 1 is different from the absorbance one obtains from a spectrometer. An ATR spectral intensity in *absorptance units* with a single reflection is given in terms of experimental parameters and material characteristics by the following expression:^{9,10,16}

$$A_{\bar{p}}(\theta, \mathbf{v}) = \frac{4\pi \mathbf{v}}{n_0 \cos \theta} \int_0^\infty n_1(\mathbf{v}) k_1(\mathbf{v}) \langle E_{z\bar{p}}^2(\theta, \mathbf{v}) \rangle \, \mathrm{d}z \quad (2)$$

where n_0 is the refractive index of the IRE and $\langle E_{z\bar{p}}^2(\theta, \mathbf{v}) \rangle$ is the MSEF at depth z. The spectral intensity in *absorbance units* is defined in terms of the reflectance by^{9,10,16,22}

$$\mathbf{A}_{\bar{p}}(\theta, \mathbf{v}) = -\log[R_{\bar{p}}(\theta, \mathbf{v})]$$
(3)

Under a small absorption condition (i.e., reflectance is close to unity), the MSEF can be calculated from the MSEvF. Absorptance of an isotropic medium is given in terms of the MSEvF by^{9,10}

$$A_{\bar{p}}(\theta, \mathbf{v}) = \frac{4\pi \mathbf{v}}{n_0 \cos \theta}$$

$$\times \int_0^\infty n_1(\mathbf{v}) k_1(\mathbf{v}) \frac{1 + R_{\bar{p}}(\theta, \mathbf{v})}{2} \langle E_{z\bar{p}}^2(\theta, \mathbf{v}) \rangle_{k=0} \, \mathrm{d}z$$

$$2 \frac{1 - R_{\bar{p}}(\theta, \mathbf{v})}{1 + R_{\bar{p}}(\theta, \mathbf{v})} = \frac{4\pi \mathbf{v}}{n_0 \cos \theta} \int_0^\infty n_1(\mathbf{v}) k_1(\mathbf{v}) \langle E_{z\bar{p}}^2(\theta, \mathbf{v}) \rangle_{k=0} \, \mathrm{d}z$$

$$-\ln R_{\bar{p}}(\theta, \mathbf{v}) \cong \frac{4\pi \mathbf{v}}{n_0 \cos \theta} \int_0^\infty n_1(\mathbf{v}) k_1(\mathbf{v}) \langle E_{z\bar{p}}^2(\theta, \mathbf{v}) \rangle_{k=0} \, \mathrm{d}z$$
(4)

where $\langle E_{z\bar{p}}^2(\theta, v) \rangle_{k=0}$ is the MSEvF at depth *z* with a degree of polarization \bar{p} . Although the MSEvF is defined under a nonabsorbing condition, the above expression is still applicable since the decay characteristic of the MSEF under a weakly absorbing condition is similar to that of the MSEvF. According to Eqs. 3 and 4, an ATR spectral intensity in absorbance units is given in terms of experimental conditions and material characteristics by

$$\mathbf{A}_{\bar{p}}(\theta, \mathbf{v}) \cong \frac{4\pi \mathbf{v}}{\ln(10)n_0 \cos \theta} \int_0^\infty n_1(\mathbf{v}) k_1(\mathbf{v}) \langle E_{z\bar{p}}^2(\theta, \mathbf{v}) \rangle_{k=0} \, \mathrm{d}z \quad (5)$$

Since Eq. 5 is based on a weakly absorbing criterion, the following question is then raised: What is the maximum absorbance for which the equation is still valid? This is an important question for a quantitative analysis since the MSEF depends on experimental conditions and material characteristics. A nonlinear relationship between the spectral intensity and the absorption index is observed when the absorption is too strong. In order to demonstrate the limitation, the absorbance defined by Eq. 5 at various absorption indices is compared to $-\log[R_{\tilde{p}}(\theta, v)]$. The condition where the former deviates from the latter by 5% marks the upper limit for a small absorption criterion, and k_{limit} is then given for that particular experimental condition.

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FIG. 1. Comparisons between the absorbance obtained via the exact equation based on the MSEF (solid lines) and that via a simplified equation based on the MSEvF (broken lines). The upper pair represent those with *p*-polarization, the middle pair represent those with *s*-polarization. The table shows the upper limit for the small absorption approximation under a particular experimental condition. The simulated parameters are $n_{Ge} = 4.0$, $n_{ZnSe} = 2.4$, $n_1 = 1.5$, v = 1000 cm⁻¹, and number of reflection = 1.

There are several methods for the determination of a nonlinear relationship between an absorption index and an observed ATR spectral intensity of an *isotropic medium*.

(1) Using the condition $\mathbf{A}_p(45^\circ, \mathbf{v}) = 2\mathbf{A}_s(45^\circ, \mathbf{v})$. When the condition is not satisfied, the spectral intensity at that frequency exceeds the linear relationship under that experimental condition.

(2) Using the MSEvF ratio. According to Eq. 5, when $\mathbf{A}_{p}(\theta, \mathbf{v})/\mathbf{A}_{s}(\theta, \mathbf{v})$ is significantly different from $\int_{0}^{\infty} \langle E_{zp}^{2}(\theta, \mathbf{v}) \rangle_{k=0} dz / \int_{0}^{\infty} \langle E_{zs}^{2}(\theta, \mathbf{v}) \rangle_{k=0} dz$, the spectral intensity at that frequency is out of the linear range under that experimental condition. The MSEvF is characterized by its strength and decay characteristics. Since the decay characteristics for the MSEvF with *p*- and *s*-polarized radiation are the same,^{9,22} the above expression can then be further simplified.

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$$\frac{\int_{0}^{\infty} \langle E_{zp}^{2}(\theta, \mathbf{v}) \rangle_{k=0} \, \mathrm{d}z}{\int_{0}^{\infty} \langle E_{zs}^{2}(\theta, \mathbf{v}) \rangle_{k=0} \, \mathrm{d}z} = \frac{\langle E_{0p}^{2}(\theta, \mathbf{v}) \rangle_{k=0}}{\langle E_{0s}^{2}(\theta, \mathbf{v}) \rangle_{k=0}} \tag{6}$$

The expressions for $\langle E_{0p}(\theta, \mathbf{v}) \rangle_{k=0}$ and $\langle E_{0s}(\theta, \mathbf{v}) \rangle_{k=0}$ are given elsewhere.^{10,16,23} It should be noted that $\langle E_{0p}^2(45^\circ, \mathbf{v}) \rangle_{k=0} / \langle E_{0s}^2(45^\circ, \mathbf{v}) \rangle_{k=0} = 2$.

(3) Using a transmission spectrum. An ATR-like spectrum can be converted from a transmission spectrum of an isotropic medium with small absorption by the following expression.



FIG. 2. ATR spectrum of toluene collected by 45° ZnSe IRE using *p*-polarized radiation (the upper line) and *s*-polarized radiation (the lower line) with an effective number of reflections = 1.7.

$$\mathbf{A}_{\bar{\rho}}^{\mathrm{trans}\to\mathrm{ATR}}(\theta,\mathbf{v}) = \frac{n_{1}(\mathbf{v})d_{p}(\theta,\mathbf{v})\langle E_{0\bar{\rho}}^{2}(\theta,\mathbf{v})\rangle_{k=0}}{2n_{0}\cos\theta}\cdot\frac{N}{h}\cdot\mathbf{A}_{\mathrm{trans}}(\mathbf{v})$$
(7)

where $d_p(\theta, v)$ is the penetration depth, N is the effective number of reflections, and h is the thickness of the transmission cell. Spectral comparison, spectral subtraction, or spectral ratio between the converted spectrum and the observed ATR spectrum can be performed. Since Eq. 7 is valid for small absorption, any significant discrepancy between the two implies nonlinearity. There might be minor deviations at the shoulder of a peak due to refractive index dispersion.

RESULTS AND DISCUSSION

To theoretically verify the upper limit for the small absorption criteria of an ATR spectral intensity, one employs a spectral simulation. Spectral intensities at various absorption indices obtained via Eqs. 3 and 5 are compared. There are two systems being considered, those with a germanium IRE (30°, 45°, and 60° angles of incidence) and those with a zinc selenide IRE (45° and 60° angles of incidence). Figure 1 shows spectral intensities with a single reflection at various absorption indices. The experimental conditions with high spectral intensities (i.e., the angle of incidence close to the critical angle and the refractive index of the absorbing medium close to that of the IRE) have small values of k_{limit} . At highly absorbing conditions, the spectral intensity obtained via Eq. 5 deviates significantly from that via Eq. 3 [term $R_{\bar{n}}(\theta, v)$] in Eq. 3 is calculated via exact equation].⁹ This observation implies that Eq. 5 has limited applicability for quantitative analysis. Figures 1B and 1D also suggest limited applicability of the statement $A_{n}(45^{\circ}, v) =$ $2\mathbf{A}_{s}(45^{\circ}, \mathbf{v})^{1,14,18,21}$ in a highly absorbing region of an isotropic medium.

In order to obtain optical contact between the IRE and the isotropic media, liquid samples are employed. A multiple attenuated total reflection (MATR) accessory with a 45° zinc selenide IRE (Spectra Tech, USA) is utilized for all spectral acquisitions. All spectra are collected at a resolution of 4 cm⁻¹ and 64 scan coaddition using a Bruker Vector 33 FT-IR spectrometer equipped with a DTGS detector. Figure 2 shows ATR spectra of toluene acquired with *s*- and *p*-polarized radiation. Weak absorption bands follow the statement $A_p(45^\circ, v) = 2A_s(45^\circ, v)$, while strong absorption bands exhibit some degree of deviation depending on the absorption strength. A high absorption index is the major cause for the deviations; $k_{692 \text{ cm}^{-1}} =$



FIG. 3. Comparisons between observed ATR spectra and converted ATR spectra obtained from an observed transmission spectrum with nonpolarized radiation (A). The ATR spectra converted from the observed transmission spectrum (broken lines) are compared to the observed ATR spectra (solid lines) with *p*-polarized radiation (B) and *s*-polarized radiation (C). The experimental conditions for ATR spectra are the same as those in Fig. 2.

0.400 and $k_{725 \text{ cm}^{-1}} = 0.650$, while $k_{1030 \text{ cm}^{-1}} = 0.040$, $k_{1080 \text{ cm}^{-1}} = 0.031$, $k_{1495 \text{ cm}^{-1}} = 0.116$, and $k_{3026 \text{ cm}^{-1}} = 0.032$ with $n \cong 1.475$ in the mid-infrared region.²⁴

Figure 3 shows comparisons between observed ATR spectra and converted ATR spectra. The converted ATR spectra are calculated from an observed transmission spectrum via Eq. 7. The spectra agree quite well except in the region with a nonlinear relationship. The absorption band at 1495 cm⁻¹ shows some discrepancy since the complex refractive index is just at the borderline of linear/nonlinear relationship under the given experimental condition.

Equations 2 and 3 define the relationships between the ATR spectral intensity and the complex refractive index of the absorbing medium. The relationship is linear when the absorption is small. A nonlinear relationship is observed when the absorption becomes large. Equation 5 is

the simplified form of Eq. 2. The MSEvF is used instead of the MSEF for ease of quantitative analysis, since the MSEvF can be calculated only if the refractive index of the absorbing medium is known. Since it is derived on the basis of a weakly absorbing condition, Eq. 5 cannot be applied for quantitative analysis via strong absorption bands. As suggested by Eq. 2, when the weakly absorbing condition is not met, the MSEF is required for quantitative analysis. A method for MSEF calculation without knowing the complex refractive index is given elsewhere.²²

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