

# Chapter 47

## Infrared External-Reflection Spectroscopy

Takeshi Hasegawa

**Keywords** Vibrational spectroscopy · External reflection · Nonmetallic surface  
Thin film · Molecular orientation · Polarized IR rays

### 47.1 Principle

Infrared (IR) spectrometry is a representative un-destructive spectroscopic analytical technique, which provides rich molecular information such as molecular conformation, polymorph, packing and orientation. Another significant benefit of using IR spectroscopy is the sensitivity, which is good enough for analyzing monolayer-level thin films. Considering the great quantitative reproducibility, IR spectroscopy is one of the first choices to analyze an ultrathin film particularly of an organic compound. Here, IR reflection spectrometry on a *nonmetallic* surface, which is called “*external reflection*,” is described.

IR spectroscopy is one of the absorption spectroscopies, and the selection rules are deduced by solving Schrödinger equation with the perturbation theory. We have to note, however, that this is true of a single dipole moment (molecule) in vacuum. To discuss light absorption by a condensed matter, electrodynamics should be employed, since the collection of a huge number of dipole moment can conveniently be considered via the electric permittivity. The frequency response of IR absorption to the permittivity is theorized by Kramers–Kronig’s relationship via the convolution theory, which reveals that the permittivity must be a complex [1]. Since the magnetic permittivity can be ignored in IR spectroscopy, the electric relative permittivity,  $\epsilon_r$ , is simply related to the refractive index,  $n$ , by  $\epsilon_r = n^2$ , and therefore, the refractive index is also a complex:  $n \equiv n' + in''$ . Here,  $n'$  and  $n''$  are the real and imaginary parts of the refractive index, respectively.

---

T. Hasegawa (✉)

Institute for Chemical Research, Kyoto University, Uji, Kyoto-fu, Japan  
e-mail: htakeshi@scl.kyoto-u.ac.jp

By solving Maxwell equations without considering any optical interface, the absorbance spectrum,  $A$ , of a *bulk matter* with a thickness of  $z$  is deduced to be [1]:

$$A \equiv -\log_{10}\left(\frac{I}{I_0}\right) = \frac{1}{\ln 10} \frac{4\pi n''}{\lambda} z \equiv \frac{1}{\ln 10} \alpha z.$$

Here,  $I$  and  $I_0$  are the intensities of the incident and transmitted IR light, respectively, at the wavelength of  $\lambda$ . When the optical interface can be ignored, in this manner, the spectrum is simply driven by the “absorption index” of  $\alpha \equiv 4\pi n''/\lambda$ .

To discuss absorption spectroscopy *on a thin film*, the optical interface of the film/substrate boundary must be taken into account, i.e., the continuities of the electric and magnetic fields at boundaries must all be taken into account. If the p- and s-polarized IR rays are incident from Phase 1 (mostly air) to the sample (Phase 2) on the substrate (Phase 3), the absorbance spectra of both polarizations are finally obtained as follows [1].

$$A^{\text{ER,p}} = \frac{8\pi d_2}{\ln 10 \cdot \lambda} \frac{(\sin^2 \theta_1 - \varepsilon_3) \cdot \text{Im}(\varepsilon_{2,x}) + \varepsilon_3^2 \sin^2 \theta_1 \cdot \text{Im}(-1/\varepsilon_{2,z})}{\cos \theta_1 (\varepsilon_3 - 1)(\varepsilon_3 - \tan^2 \theta_1)} \quad (47.1)$$

$$\equiv \frac{8\pi d_2}{\ln 10 \cdot \lambda} (C_{\text{pTO}} \cdot \text{TO} + C_{\text{pLO}} \cdot \text{LO})$$

$$A^{\text{ER,s}} = \frac{-1}{\ln 10 \cdot \lambda} \frac{8\pi d_2 n_1 \cos \theta_1}{\varepsilon_3 - 1} \text{Im}(\varepsilon_{2,x}) \quad (47.2)$$

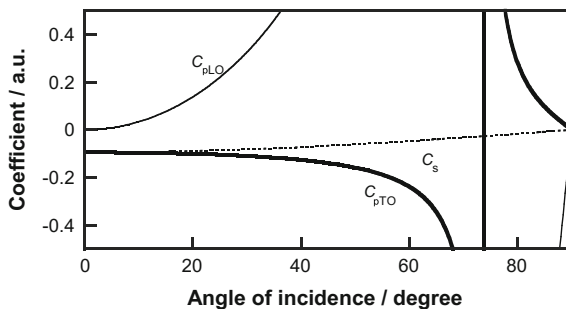
$$\equiv \frac{8\pi d_2}{\ln 10 \cdot \lambda} C_{\text{s}} \cdot \text{TO}$$

The subscript index,  $j$ , of the permittivity,  $\varepsilon_j$ , corresponds to the phase number. These equations simply imply that both polarized spectra are theorized by combinations of  $\text{Im}(\varepsilon_{2,x})$  and  $\text{Im}(-1/\varepsilon_{2,z})$ , which are often called TO (transverse optic) and LO (longitudinal optic) energy-loss functions, respectively. We have to pay attention that, therefore, we cannot directly compare ER spectra with a bulk spectrum especially for a strong IR absorber, represented by perfluoroalkyl compounds [2].

Since the TO and LO functions are driven by the  $x$ - and  $z$ -component of the electric permittivity, respectively, an s-polarized ER spectrum reveals only the surface-parallel component of a normal mode in the film, and the absorbance is always negative. On the other hand, the p-polarized ER spectrum depends on the molecular orientation via the  $x$ - and  $z$ -components, and the angle of incidence,  $\theta$ . Since the denominator involves  $\varepsilon_3 - \tan^2 \theta_1$ , the sign of absorbance changes at Brewster’s angle. To visually understand the complicated coefficients of the TO and LO functions,  $C_{\text{pLO}}$  and  $C_{\text{pTO}}$ , respectively, the calculated curves of the coefficients are presented in Fig. 47.1 [1]. As expected, both  $C_{\text{pLO}}$  and  $C_{\text{pTO}}$  overturn at the Brewster angle of silicon ( $\tan^{-1} n_3 = 73^\circ$ ).

These characteristics are interpreted as the *surface selection rules* of ER spectroscopy. Equations (47.1) and (47.2) are indeed very useful equations, and they

**Fig. 47.1** Coefficients calculated by using  $n_3 = 3.4$ .  $C_{pLO}$  and  $C_{pTO}$  are plotted by *thin* and *thick solid lines*, respectively; while  $C_s$  is given by the *dotted line*



also quantitatively reproduce the ATR and RA (Chap. 48) spectra. In this sense, the equations are the fundamental equations of IR *surface spectroscopy*.

Note that Eqs. (47.1) and (47.2) are deduced from the 3-layer model, which cannot be true of a double-side polished substrate, which requires a 5-layer model [1]. To keep the 3-layer model for using the surface selection rules, we have to employ a *single-side polished* substrate. A semiconductor wafer is useful for this purpose.

## 47.2 Features

- Vibrational modes in a monolayer-level thin film can be measured for quantitative discussion.
- Band intensity (absorbance) is rigorously reproduced by using the equations deduced from Maxwell equations.
- Surface selection rule of the p-polarized ER spectrum is a function of the molecular orientation and the angle of incidence.
- Both solid and liquid substrates can be employed.

## 47.3 Instrumentation

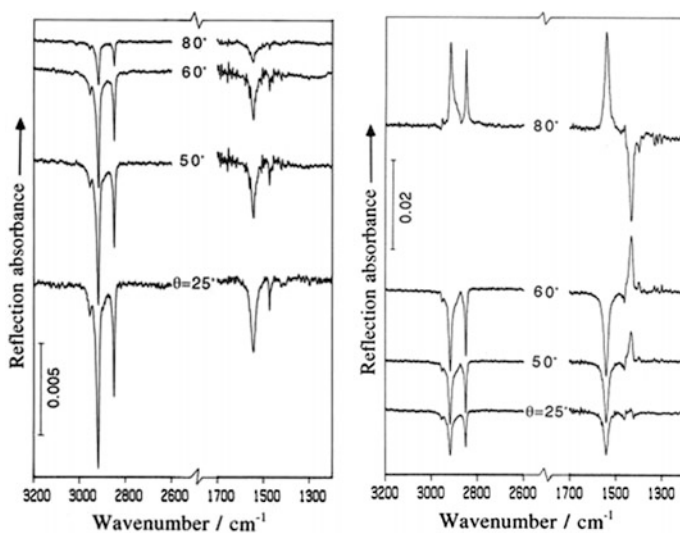
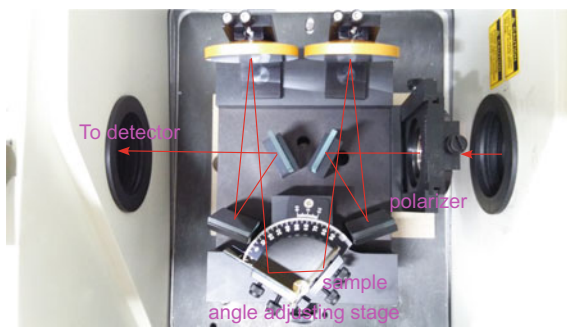
The measurements are performed on a normal FT-IR bench in laboratory. A reflection attachment (Fig. 47.2) must be used for setting the angle of incidence accurately.

## 47.4 Applications

### 47.4.1 Practical Measurements of a Thin Film

Figure 47.3 presents IR ER spectra of a 9-monolayer Langmuir–Blodgett (LB) film prepared on a GaAs water [3]. As theoretically expected, the s-polarized spectra

**Fig. 47.2** An overview of a reflector in the sample room of FT-IR

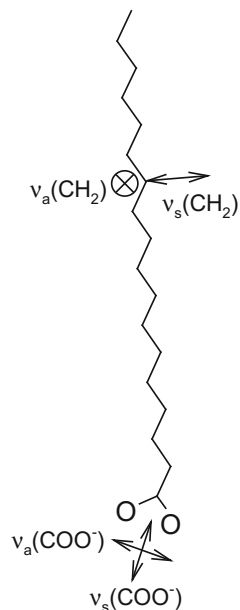


**Fig. 47.3** IR ER spectra of a 9-monolayer LB film of cadmium stearate on a GaAs wafer as a function of the angle of incidence. The *left* and *right* panels present results of the *s*- and *p*-polarizations, respectively

have negative bands only, and the intensity decreases with an increase of the angle of incidence.

On the other hand, the *p*-polarized IR ER spectra consist of positive and negative peaks, and they are overturned when the angle of incidence goes across the Brewster angle. When the angle of incidence is small, the negative bands appear for the antisymmetric and symmetric  $\text{CH}_2$  stretching vibration bands ( $\nu_a\text{CH}_2$  and  $\nu_s\text{CH}_2$  at  $2916$  and  $2850\text{ cm}^{-1}$ , respectively) and the antisymmetric  $\text{COO}^-$  stretching vibration ( $\nu_a\text{COO}^-$ ) band at  $1543\text{ cm}^{-1}$ . Judging from the surface selection rule (Fig. 47.1), the negative bands are attributed to the surface-parallel component. In this manner, the  $\text{CH}_2$  group is revealed to have a parallel orientation to the surface as illustrated in Fig. 47.4. As for the  $\text{COO}^-$  group, the symmetric

**Fig. 47.4** Averaged molecular orientation in the 9-monolayer LB film on Si revealed by the p-polarized IR ER spectrum



$\text{COO}^-$  stretching vibration ( $\nu_s\text{COO}^-$ ) band appears at  $1433\text{ cm}^{-1}$  as a positive peak in the p-polarized spectrum, which implies that the  $\text{COO}^-$  group takes a nearly perpendicular orientation to the surface as presented in Fig. 47.4.

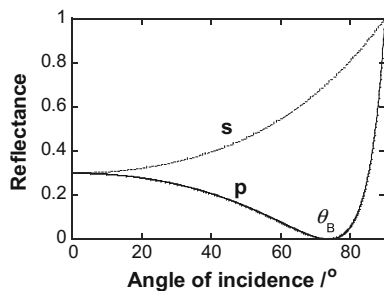
In this fashion, the p-polarized IR ER spectrum responds to the orientation of each normal mode as well as the angle of incidence. This surface selection rule is understandable by referring to Fig. 47.1, which can be calculated by using the permittivity of the substrate,  $\epsilon_3 (= n_{r,3}^2)$ , only.

#### 47.4.2 *Optimal Angle of Incidence for Obtaining High-Quality IR ER Spectra*

When we simply refer to the coefficient curves in Fig. 47.1, the sensitivity of the p-polarized spectrum would be very high at an angle of incidence near Brewster's angle, since the absorbance would also become significantly large. Here, we have to recall, however, another important fact that "reflectance" at the substrate surface becomes nil at Brewster's angle,  $\theta_B$ .

Figure 47.5 presents reflectance variations for s- and p-polarizations, which are plotted by the dotted and solid curves, respectively. At an angle near the Brewster angle, the reflectance of the p-polarization is very low, which makes the throughput very poor. Therefore, the spectral quality is determined by a balance of the band intensity and the throughput, which can be controlled by changing the angle of

**Fig. 47.5** Reflectance depending on the angle of incidence at the air/Ai interface



incidence. An angle apart from Brewster's angle by ca.  $10^\circ$  is recommended for the p-polarized ER measurements. For the s-polarization, on the other hand, we do not have to be concerned about the reflectance, and a small angle of incidence should be employed, so that the negative absorbance would become fairly large.

## References

1. Hasegawa, T.: *Quantitative Infrared Spectroscopy for Understanding of a Condensed Matter*. Springer, Tokyo (2017)
2. Hasegawa, T., Shimoaka, T., Shioya, N., Morita, K., Sonoyama, M., Takagi, T., Kanamori, T.: Stratified dipole-arrays model accounting for bulk properties specific to perfluoroalkyl compounds. *ChemPlusChem*. **79**, 1421–1425 (2014)
3. Hasegawa, T., Takeda, S., Kawaguchi, A., Umemura, J.: Quantitative analysis of uniaxial molecular orientation in Langmuir–Blodgett films by infrared reflection Spectroscopy. *Langmuir*. **11**, 1236–1243 (1995)