

Relation between s-Polarized and p-Polarized Internal Reflection Spectra: Application for the Spectral Resolution of Perpendicular Vibrational Modes

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Received: April 23, 2007

The orientation of chemical bonds in thin films is commonly probed with polarized internal reflection Fourier transform infrared spectroscopy. Here we demonstrate how the internal reflection spectra obtained using s-polarized light are related with the corresponding p-polarized spectra. The relation between s- and p-polarized internal reflection spectra is applied to resolve the absorption bands of vibrational modes with components oriented perpendicular to the substrate. This is successfully demonstrated using Langmuir–Blodgett films containing smectite clay minerals and a surfactant deposited on ZnSe and Ge internal reflection elements.

1. Introduction

Polarized infrared (IR) spectroscopy allows one to probe the orientation of chemical bonds.^{1–17} The features of polarized IR spectroscopy include (1) simultaneous probing of a wide variety of chemical bonds in organic, inorganic or hybrid materials, (2) sensitivity to measure films down to molecular thickness, (3) quantitative analysis and (4) widely available equipment.

Three optical configurations for polarized IR spectroscopy are usually applied: transmission, internal reflection and external reflection. Polarized transmission spectroscopy at normal and oblique incidence is a simple method but lacks sufficient sensitivity to study monolayers. In internal reflection spectroscopy (IRS), also called attenuated total reflection (ATR) spectroscopy, the sample material is in close contact with a high-refractive-index optical element (=internal reflection element or IRE; see Figure 1).^{1–3,18} This technique is well suited to study monolayers because the absorbance is proportional to the number of reflections inside the IRE. Using internal reflection spectroscopy, the s-polarized IR beam probes solely the components of the vibrational modes parallel within the plane of the film whereas the p-polarized beam probes the components of the modes parallel and perpendicular to the film. Spectra containing only the perpendicular components of the vibrational modes are not obtained using transmission or internal reflection spectroscopy. External reflection spectroscopy (ERS), also called infrared reflection absorption spectroscopy (IRRAS), is sensitive to bond orientation when the film is on a metal substrate and the IR beam is incident onto the film at a grazing angle (e.g., 80° to the surface normal). In this optical configuration the incident and reflected beam combine to a standing wave that is largely p-polarized. In ERS, only the perpendicular components of the vibrational modes absorb IR light.¹⁷

Many aspects of the theoretical principles behind internal reflection spectroscopy are summarized in the books by Mira-

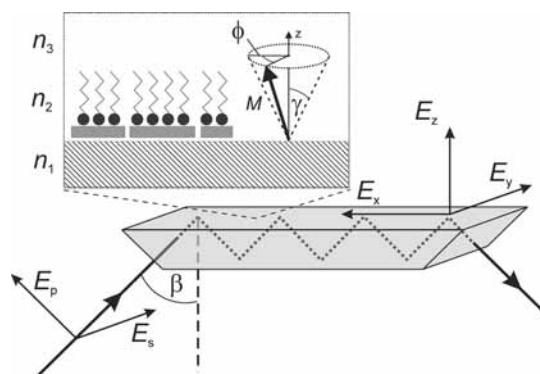


Figure 1. Schematic representation of internal reflection spectroscopy for the measurement of thin films. A thin, immobilized film of refractive index n_2 on the surface of an internal reflection element of refractive index n_1 is in contact with a rarer medium (i.e., air) of index of refraction n_3 . When measured with s-polarized light, only the y -component of the IR light probes the film. In the case of p-polarized light, the x - as well as the z -component of the electric field E are present. In uniaxially oriented films, the transition dipole moments M have a preferred tilt angle γ , but a random azimuthal angle ϕ . Biaxially oriented films have both preferred angles γ and ϕ .

bella & Harrick¹ and Fringeli.² About polarized internal reflection spectroscopy in particular, various theoretical models exist that relate the experimentally obtained absorbance to properties such as film thickness, the angle of transition dipole moments,^{3–13} the optical constants (i.e., complex refractive index)^{1,11,13} or the degree of monolayer coverage.¹⁴ In this paper, we describe an aspect concerning the theory of polarized internal reflection spectroscopy which remained unexplored, namely, how the s-polarized and p-polarized spectra are related to each other. Using this new theoretical finding, we develop a novel method to selectively resolve the absorption bands from perpendicular modes in an internal reflection spectrum. This method could potentially be used as an alternative for other spectral resolution methods such as curve fitting¹⁹ and Fourier self-deconvolution.²⁰

Clay mineral–surfactant hybrid thin films are chosen as materials to verify the applicability of the new method for spectral resolution. These hybrid clay films are made by the

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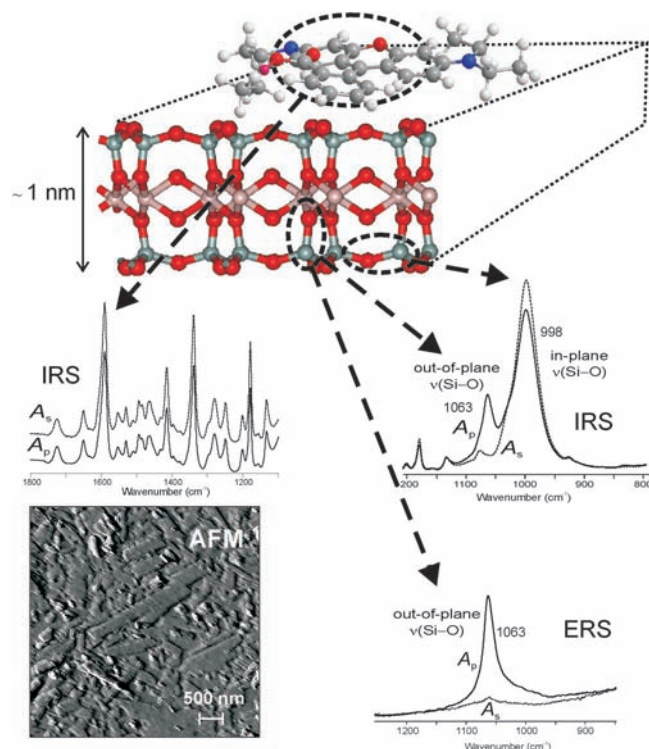


Figure 2. Polarized infrared spectroscopy (IRS and ERS) used to probe the nanoscale architecture of thin films containing clay minerals and dye molecules. The clay mineral has Si–O bonds with orientations in-plane and out-of-plane. The rhodamine dye molecules are oriented nearly parallel with the clay mineral surface. The substrate can be nearly fully covered by single layered clay lamellae, as shown by atomic force microscopy (AFM).

Langmuir–Blodgett method and have a well-defined structure consisting of a monolayer of single lamella of smectite clay combined with a cationic surfactant monolayer adsorbed on one side.^{14,21–26} Individual smectite particles are sheet-like lamellae with a high aspect ratio, on the order of 250–1000 to 1, with a thickness of 1 nm. The lamellae are highly oriented in the hybrid films with their 001 crystal plane oriented parallel with respect to the substrate.

Recent developments made on infrared spectroscopy on single lamellae of clay minerals are summarized in Figure 2 for the case of saponite.^{14,21,22,24} Two types of polarized infrared spectroscopies have been successfully applied to probe the nanoscale structure of these clay films: IRS and ERS. To avoid confusion on terminology, we first explain the difference between the terms “in-plane”, “out-of-plane” versus “parallel”, “perpendicular”. In-plane and out-of-plane refer both to the orientation of vibrational modes relative to the 001 plane in case of clay minerals or to the orientation relative to the chromophore plane in case of dye molecules. Parallel and perpendicular, on the other hand, refer to the orientation relative to the substrate, i.e., the IRE surface in the case of internal reflection spectroscopy, or the metal surface in the case of external reflection spectroscopy. Because the clay mineral lamellae are oriented with the 001 plane parallel to the substrate, the in-plane and out-of-plane modes correspond to respectively the parallel and perpendicular modes.

Internal reflection spectroscopy has been used to probe the in-plane modes and the out-of-plane modes of hybrid thin films.¹⁴ The absorption band near 998 cm^{-1} is assigned to the in-plane Si–O stretch, $\nu(\text{Si–O})$.²⁷ s-Polarized light has the y-component parallel to the IRE surface, p-polarized light has the x-component parallel to the IRE surface, and therefore the

in-plane $\nu(\text{Si–O})$ is observed in both spectra. p-Polarized light also has the z-component perpendicular to the IRE surface, unlike s-polarized light. This is why the out-of-plane $\nu(\text{Si–O})$ band at 1063 cm^{-1} is observed only in the p-polarized spectrum (Figure 2, spectra at top-right).

The cationic dye surfactants used to prepare the films have many absorption bands in the region from 1750 cm^{-1} to the cutoff of ZnSe near 630 cm^{-1} (Figure 2, spectra at top-left). On the basis of the intensity, shift, and dichroic ratio of the dye bands, it was recently shown that the dye molecules are densely packed in the film and oriented with the chromophore plane nearly parallel with the clay mineral surface.^{22,23}

External reflection spectroscopy on metal substrates selectively probes those transition dipole moments that have a component perpendicular to the surface.¹⁷ The p-polarized external reflection spectrum of a clay film on gold, therefore, only shows the out-of-plane $\nu(\text{Si–O})$ clay band (Figure 2, spectra at bottom-right).^{24,28} The in-plane $\nu(\text{Si–O})$ band is efficiently suppressed.

Polarized IR spectroscopy shows that these hybrid clay films contain certain vibrational modes that are perpendicular to the film surface (out-of-plane $\nu(\text{Si–O})$), and other vibrational modes that are mainly parallel with respect to the film surface (in-plane $\nu(\text{Si–O})$ and dye modes). Because perpendicular and parallel modes are both present in the same material, the hybrid clay films are applied for a case study to resolve the perpendicular components in the spectrum.

2. Materials and Methods

2.1. Clay Minerals. The clay mineral species used in this work was saponite (SapCa-1) obtained from the Source Clays Repository of the Clay Minerals Society. The clay minerals were Na^+ -saturated by repeated (three times) exchange with 1 M NaCl solutions followed by dialysis with water until a negative Cl^- test was obtained using AgNO_3 . The particle size fraction between 0.5 and 2.0 μm was obtained by centrifugation and freeze-drying of a salt-free, Na^+ -exchanged clay mineral dispersion.

2.2. Molecules. Octadecyl rhodamine B chloride (RhB18, Molecular Probes) and *N,N'*-dioctadecylthiacyanine (THIA18, gift from M. Vanderauweraer) were used as received and were dissolved in HPLC grade chloroform (99.9%, Aldrich, stabilized by 0.5–1% ethanol) to prepare a spreading solution of respectively 9.11×10^{-4} and 1×10^{-3} mol dm^{-3} .

2.3. Film Preparation. The thin clay films were prepared by the Langmuir–Blodgett (LB) method. LB films were prepared on a NIMA Technology model 611 LB trough at a temperature of 23 ± 1 $^\circ\text{C}$. Clay dispersions stirred for 24 h in Milli-Q water were used as the subphase. A microsyringe was used to spread 40 μL of the dye dissolved in chloroform over the subphase. After 15 min, the film was compressed at a rate of 30 $\text{cm}^{-2} \text{min}^{-1}$. Films were deposited in upstroke (lifting speed of 5 mm min^{-1}) on ZnSe and Ge internal reflection elements (IREs) at surface pressures of 2 mN m^{-1} or 5 mN m^{-1} and on gold substrates at surface pressures of 15 mN m^{-1} . The IREs were cleaned prior to each deposition by gently rubbing with a paper tissue soaked in methanol. The gold substrates were prepared by sputtering a 25 nm thick gold layer on a Si wafer.

2.4. Infrared Spectroscopy. The IREs were ZnSe and Ge trapezoidal-shaped crystals (Spectroscopy Central, UK) (50 mm \times 20 mm \times 2 mm) with 25 internal reflections and were measured in a vertical ATR cell. Because the IRE was not covered with film where it was attached to the dipper, there are

only 24 active reflections. The films on gold were measured in a monolayer/grazing incidence angle accessory P/N 19650 Series (Specac) at grazing incidence (80° with respect to the normal). The FTIR spectrometer was a Bruker IFS66v/S with an operating vacuum lower than 3 mbar inside the spectrometer. Polarized infrared spectra were obtained using a wire-grid polarizer. The FTIR spectrometer was equipped with a liquid nitrogen cooled MCT detector and a KBr/Ge beam splitter. A total of 512 scans were signal averaged using an optical resolution of 2 cm⁻¹.

The resolved z-polarized spectra, A_z , were calculated by subtraction of the s-polarized spectra, A_s , from the p-polarized spectra, A_p , according to eq 15. The subtraction was performed using the tool “spectral subtract—autosubtract” in Grams/32 AI software (version 7.02). This automated subtraction procedure is based on an iterative algorithm²⁹ that determines the factor k by minimizing the derivative of the resulting spectrum. The spectral region 1200–900 cm⁻¹ was used for determining the factor k . The derivative is related to the complexity of the spectrum. The measured p-polarized spectrum is the sum of the x-polarized spectrum and the z-polarized spectrum and is thus more complex than the z-polarized spectrum alone. The absolute area of the first derivative of the calculated z-polarized spectrum is at minimum when the x-polarized spectrum is removed.

3. Results and Discussion

3.1. Relation between the Absorbance Measured with s-Polarized and p-Polarized Light. Polarized internal reflection Fourier transform infrared spectroscopy allows one to probe the orientation of chemical bonds in thin films.^{3,6,8–10,12,13} s-Polarized light has the electric field component, E_s , perpendicular to the plane of incidence and results in an evanescent wave, E_y , parallel with the internal reflection element (IRE) surface (Figure 1). p-Polarized light has the electric field component, E_p , within the plane of incidence and results in an evanescent wave with components, E_x and E_z , respectively, parallel and perpendicular with the IRE surface and always mixed together. Spectra obtained using s-polarized light probe the chemical bonds that have components parallel with the plane of the IRE surface. On the contrary, spectra obtained using p-polarized light probe the chemical bonds with both parallel and perpendicular character. Spectra containing the perpendicular components of the vibrational modes only are not directly available by internal reflection spectroscopy.

Here we derive the relation between the absorbance measured with s-polarized light (A_s) and the absorbance measured with p-polarized light (A_p). The derivation is valid when the thin film approximation, developed by Harrick,¹ can be applied. The thin film approximation, sometimes also called the three-phase approximation,^{30,31} evaluates the evanescent wave electric field amplitudes that probe the film material. The criteria for application of the thin film approximation are based on two assumptions that warrant the reflectivity per internal reflection to deviate only slightly from that of a nonabsorbing medium.² First, the film must be very thin. Second, the absorption coefficient $\alpha < 10^4$ cm⁻¹.

The relation between the incident electric field components and the evanescent wave components at the surface of the IRE is given by eqs 1 and 2.^{1,2}

$$E_s^2 = E_y^2 \quad (1)$$

$$E_p^2 = E_x^2 + E_z^2 \quad (2)$$

The amplitudes of the electric field are determined by the refractive indices $n_1 = n_{\text{IRE}}$, $n_2 = n_{\text{film}}$, and $n_3 = n_{\text{air}}$ and by the angle of incidence β . The electric field components along x , y , and z according to the thin film approximation are given by^{1,2}

$$E_x^2 = \frac{4 \cos^2 \beta (\sin^2 \beta - n_{31}^2)}{(1 - n_{31}^2)[(1 + n_{31}^2) \sin^2 \beta - n_{31}^2]} \quad (3)$$

$$E_y^2 = \frac{4 \cos^2 \beta}{1 - n_{31}^2} \quad (4)$$

$$E_z^2 = \frac{4 \cos^2 \beta \sin^2 \beta n_{32}^4}{(1 - n_{31}^2)[(1 + n_{31}^2) \sin^2 \beta - n_{31}^2]} \quad (5)$$

with $n_{31} = n_3/n_1$ and $n_{32} = n_3/n_2$.

Equations 3 and 4 combine to

$$E_x^2 = kE_y^2 \quad (6)$$

with

$$k = \frac{\sin^2 \beta - n_{31}^2}{(1 + n_{31}^2) \sin^2 \beta - n_{31}^2} \quad (7)$$

According to eq 6, the evanescent wave electric field amplitudes parallel with the IRE surface, E_x and E_y , are proportional to each other.

The absorbance A_i (with $i = x, y$, or z) depends on the orientation of the transition dipole moment M relative to the electric field component E_i and can be expressed generally as

$$A_i = \int_{\gamma} \int_{\phi} \int_{\theta} M_i^2 E_i^2 N(\theta, \phi, \gamma) d\theta d\phi d\gamma \quad (8)$$

M_i is the projection of M along the i -direction. $N(\theta, \phi, \gamma)$ is the orientation distribution function of the transition dipole moments and in general three angles (θ , ϕ , and γ) can be considered of which γ is the tilt angle and ϕ is the azimuthal angle. A detailed description of this coordinate system is given by Ahn and Franses.⁶ The same authors have derived expressions for the absorbance A_i in case of specific distributions such as uniaxial orientation around the surface normal (eqs 9 and 10), in which the transition dipole moments have a preferred tilt angle γ_0 and no preferred angles θ and ϕ .^{6,32} N_0 is the population of transition

$$A_s = A_y = \frac{1}{2} N_0 M^2 E_y^2 \sin^2 \gamma_0 \quad (9)$$

$$A_p = A_x + A_z = \frac{1}{2} N_0 M^2 E_x^2 \sin^2 \gamma_0 + N_0 M^2 E_z^2 \cos^2 \gamma_0 \quad (10)$$

dipole moments with the orientation distribution $N(\theta, \phi, \gamma)$. Combination of eq 6 with eqs 9 and 10 results in the following equation, which shows how for uniaxially oriented thin films the absorbance measured with s-polarized light is related to the absorbance measured with p-polarized light.

$$A_p = kA_s + A_z \quad (11)$$

Similar expressions exist for the biaxial orientation distribution (eqs 12 and 13) in which the transition dipole moments have preferred angles γ_0 and ϕ_0 and no preferred angle θ .^{6,32}

$$A_s = A_y = N_0 M^2 E_y^2 \sin^2 \gamma_0 \sin^2 \phi_0 \quad (12)$$

$$A_p = A_x + A_z = N_0 M^2 E_x^2 \sin^2 \gamma_0 \cos^2 \phi_0 + N_0 M^2 E_z^2 \cos^2 \gamma_0 \quad (13)$$

Combination of eq 6 with eqs 12 and 13 results in the following equation, which shows how for biaxially oriented thin films the absorbance measured with s-polarized light is related to the absorbance measured with p-polarized light.

$$A_p = \frac{k}{\tan^2 \phi_0} A_s + A_z \quad (14)$$

The absorbance A_p is composed of parallel and perpendicular components. According to eqs 11 and 14, the parallel component of A_p is proportional to the absorbance A_s measured with s-polarized light. The proportionality factor is k for uniaxially oriented films and $k/\tan^2 \phi_0$ for biaxially oriented films.

The factor k varies only with the refractive index of the IRE, n_1 , and with the incident angle, β , and is thus constant for a given IRE. The reciprocal, $1/k$, can be interpreted as the theoretical dichroic ratio for vibrational modes that are uniaxially oriented parallel with the substrate ($DR = A_s/A_p = 1/k$ when $A_z = 0$). The value of factor $k = 0.791$ and $1/k = 1.26$ for a ZnSe IRE and $k = 0.933$ and $1/k = 1.07$ for a Ge IRE with 45° incident angle ($n_{\text{ZnSe}} = 2.406$ and $n_{\text{Ge}} = 4.004$ at 1000 cm^{-1} , ref 33).

3.2. Spectral Resolution of Perpendicular Vibrational Modes: Application to Clay Mineral–Surfactant Thin Films. In the previous section, we have shown theoretically that the s- and p-polarized internal reflection spectra are related to each other. Now we will convert this finding to a practical method for spectral resolution of absorption bands.

Equation 11 can be rearranged as

$$A_z = A_p - kA_s \quad (15)$$

Equation 15 shows that for uniaxially oriented thin films one can determine from the experimentally obtained s- and p-polarized spectra the z-polarized spectrum A_z , which contains only the vibrational modes probed by the perpendicular component of the electric field, E_z . In other words, using eq 15, one could resolve the perpendicular modes from the IRS spectra.

Thin hybrid films of clay minerals and surfactant are used as a case study to verify the applicability of the method to resolve perpendicular components from the p-polarized internal reflection spectrum. Equation 15 is deduced using a few assumptions: First, the film must be very thin. Second, the absorption coefficient $\alpha < 10^4 \text{ cm}^{-1}$. Third, the transition dipole moments are uniaxially oriented. The clay lamellae in the film are 1 nm thick and are randomly oriented parallel with the substrate.^{22,23} The first and third assumption are thus valid. The α_{max} value for clay minerals is $3.6 \times 10^4 \text{ cm}^{-1}$,^{14,15} which is slightly beyond the limit to satisfy the second assumption. A recent investigation on the $\nu(\text{Si}-\text{O})$ intensities of clay minerals was successful though in modeling the monolayer coverage using the thin film approximation.¹⁴

The A_z spectrum of the saponite film is obtained by subtraction of the s-polarized internal reflection spectrum from the p-polarized internal reflection spectrum (Figure 3), using the tool “spectral subtract–autosubtract”. In the case of ZnSe as IRE, the factor k was determined as 0.819, which is close to the theoretical value of 0.791 (see Table 1). In the case of Ge as IRE, the factor k was determined as 0.947, which is close to the theoretical value of 0.933 given by the model. The experimentally determined factor k corresponds well with the theoretical value in case of both types of IREs.

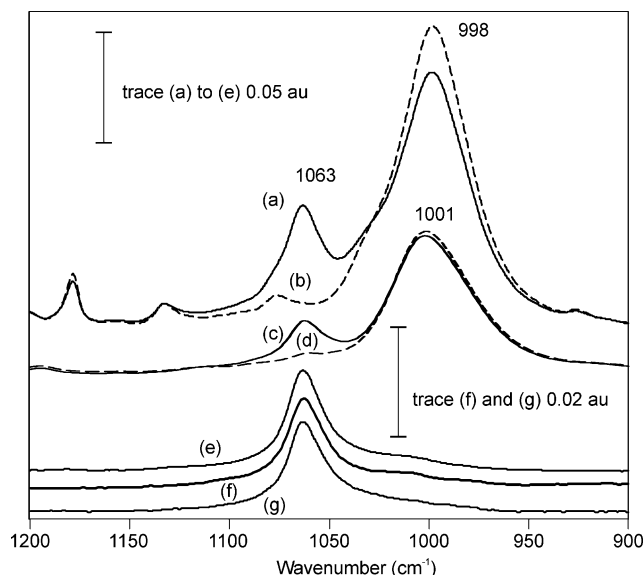


Figure 3. (a) p-Polarized and (b) s-polarized internal reflection spectrum of film on ZnSe, (c) p-polarized and (d) s-polarized internal reflection spectrum of film on Ge, (e) z-polarized internal reflection spectrum of film on ZnSe, (f) z-polarized internal reflection spectrum of film on Ge, (g) p-polarized external reflection spectrum of the saponite–RhB18 film.

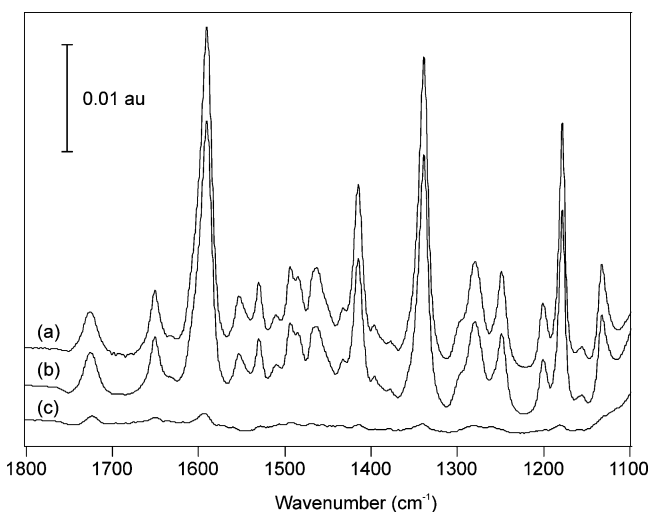


Figure 4. (a) s-polarized internal reflection spectrum, (b) p-polarized internal reflection spectrum, and (c) z-polarized internal reflection spectrum of the saponite–RhB18 film in the region from 1800 to 1100 cm^{-1} , where the organic dye absorbs. The validity of the model is confirmed by the nearly complete extinction of the dye absorption bands because the dye vibrational modes are oriented parallel with the IRE surface and are thus not probed by the z-component of the polarized light.

TABLE 1: Comparison of Theoretical and Experimental Values of k for ZnSe and Ge IREs

	ZnSe	Ge
$k(\text{theor})$	0.791	0.933
$k(\text{exp})$	0.819	0.947

Next, we check the validity of the method by comparison of the resolved A_z spectrum with the corresponding external reflection spectrum. External reflection spectroscopy is known to probe directly to perpendicular modes in thin films. The experimentally obtained s- and p-polarized internal reflection spectra of saponite films on ZnSe are shown in traces a and b and for Ge IRE in traces c and d of Figure 3. The resolved A_z spectra for ZnSe and Ge are shown in respectively trace e and

trace f. The A_z spectra for the ZnSe and Ge substrates compare well with the external reflection spectrum²⁴ (trace g).

Another feature supporting the spectral resolution method is the nearly complete suppression of the absorption bands from the dye molecules adsorbed on the clay mineral surface (Figure 4). The suppression is noteworthy as the $\nu(\text{Si-O})$ region (1200–900 cm^{-1}), and not the region of the dye bands, was used for determination of the factor k . It agrees with a recent study²³ in which we have shown that the chromophore plane is oriented nearly parallel with the clay surface and thus mainly has in-plane vibrations.

In summary, the validity of the method to resolve perpendicular components from internal reflection spectra is supported by three features from the clay mineral–surfactant spectra which are valid for different types of IREs: (1) good comparison with the external reflection spectra, (2) factor k close to the theoretical value, and (3) suppression of the in-plane dye bands.

4. Conclusion

We have reported a novel and general insight in polarized internal reflection spectroscopy showing how the spectra measured with s-polarized light are related to the spectra measured with p-polarized light. The relation is derived starting from the elementary principles of internal reflection spectroscopy and its validity is verified using experimental data. As a practical application, we have demonstrated its use for the spectral resolution of perpendicular vibrational modes. Such spectral resolution of selected modes is unique compared to other resolution methods such as curve fitting¹⁹ and Fourier self-deconvolution.²⁰ Furthermore, using the relation one can also determine for a given IRE the maximum value of the dichroic ratio A_s/A_p . The dichroic ratio is at maximum when the vibrational modes are oriented parallel with the substrate and in the case of uniaxial distribution the dichroic ratio cannot exceed the value of $1/k$.

References and Notes

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