Orientation Determination of the OH⁻ Dipole in Minerals under Fourier Transform Polarized Infrared Microspectroscopy

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(With 16 Figures)

Abstract

Polarized infrared absorbance spectrum of an optically anisotropic crystal was formulated for the crystallographic analysis of the hydrous component in the crystal under Fourier transform polarized infrared absorbance spectroscopy (pol-mFTIR). The adequacy of the formulation was confirmed by comparison of calculated interference fringes with those identical to the observed one in polarized absorbance spectra of an optically anisotropic crystal. The formulation of the spectrum, therefore, proposes an experimental constraint for correct measurements of polarized absorbance spectra under pol-mFTIR, which requests us to set the optically anisotropic crystal at its extinction position under an IR polarizing microscope. Under this experimental constraint, pleochroic distribution of absorbance due to an oriented absorber of light such as the OH⁻ dipole against IR light was also formulated for the purpose of determining the orientation of the OH⁻ dipoles in topaz and quartz. The results indicate that the OH⁻ dipoles in topaz predominantly lie in the (010) plane and are inclined 27.3° from the c-axis, which is in good agreement with the results of X-ray and neutron studies. The OH⁻ dipoles in quartz lie almost perpendicular to the c-axis. The formulation of absorbance distribution enables us to specify the hydrous components in nominally anhydrous minerals as well as in stoichiometrically hydrous minerals.

Key Words: polarized IR absorbance spectrum, orientation of the OH⁻ dipole, optical anisotropy, interference fringes, pol-mFTIR, topaz, quartz

1. Introduction

Hydrogen atoms in minerals are frequently bonded to oxygen atoms. The resultant hydrous components, which exist in various chemical states in crystal structure, affect significantly the physical properties of minerals. Since the first discovery of the anomalous weakness of synthetic quartz containing trace amounts of hydrous components (GRIGGS and BLACIC, 1965), the hydrolytic weakening of minerals such as quartz and olivine has been extensively studied by many researchers (GRIGGS, 1967; KEKULAWALA et al., 1978; DOUKHAN & TRÉPIED, 1985; KARATO et al., 1986; ROVETTA et al., 1986; CORDIER & DOUKHAN, 1989). Trace amounts of hydrous components also promote recrystallization of quartz (HOBBS, 1968). Although hydrous components have been considered as acting like catalysts to promote the mobility of atoms in crystal structure during deformation and recrystallization of minerals, the detailed mechanism of these processes under the

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control of hydrous components has not been known. For the precise analysis of the role of hydrous components in crystal structure during these processes, the chemical and crystallographic examinations of hydrous components are required.

Infrared absorption spectroscopy is one of the most useful methods of detecting hydrous components in crystal structure, because the OH bond strongly interacts with IR light. Numerous attempts to analyze precisely the water-related components in rock-forming minerals have been carried out by IR spectroscopy, and nominally anhydrous minerals such as quartz, olivine, and pyroxene have been seen to contain minor amounts of hydrous species (e.g. Aines & Rossman, 1984a). However, sufficient analyses of hydrous components in rock-forming minerals at regions as small as 10–100 \( \mu \text{m} \) in diameter have not been carried out, because a dispersive-type IR spectrometer is not capable of measuring absorbance spectra at such small regions. In recent years, Fourier transform infrared microspectroscopy (micro-FTIR) has been developed and applied to earth sciences taking advantage of an FTIR spectroscopy over a dispersive-type IR spectrometer. Micro-FTIR is constructed by installing an IR microscope which is equipped with a sensitive IR detector to the FTIR spectrometer, was generally reviewed by McMillan & Hofmeister (1988). Kronenberg & Wolf (1990) quantitatively measured the intragranular water contents of quartz and feldspar in various kinds of rocks by an FTIR spectrometer, in order to examine the potential hydrolytic weakening of rock-forming minerals. Nakashima et al. (1989) analysed the chemical state and spatial distribution of hydrous species in minerals from geochemical points of view under micro-FTIR by mapping analyses. However, crystallographic approaches to examine the positions of hydrogen atoms in crystal structures have not been sufficient.

From crystallographic viewpoints, the orientations of the OH\(^-\) dipole and the positions of hydrogen atoms in the crystal structure of minerals such as lawsonite (Labotka & Rossman, 1974), olivine (Beran & Putnis, 1983), danburite and labradorite (Beran, 1987), and quartz (Cordier & Doukhan, 1991) have been studied by the measurements of polarized IR absorbance spectra. Many researchers (Labotka & Rossman, 1974; Beran & Putnis, 1983; Beran, 1987; Cordier & Doukhan, 1991) observed pleochroism of polarized IR absorbance in thin sections of a crystal whose crystallographic orientation was known, and discussed the orientation of the OH\(^-\) dipole in the crystal. However, they failed to analyze quantitatively the pleochroism of polarized IR absorbance. They simply regarded that the OH\(^-\) dipole points to the orientation of the maximum of absorbance among the pleochroic distribution of absorbance, whether the pleochroism of absorbance is strong or weak. Therefore, a quantitative explanation should be given to the pleochroism of absorbance in order to examine the orientation of the OH\(^-\) dipole quantitatively.

Recently, Fourier transform polarized infrared microspectroscopy (pol-mFTIR) has been used to determine the chemical state of the hydrous component in minerals. Such a crystallographic approach as orientation determination of the
OH\textsuperscript{−} dipole is possible in principle under the pol-mFTIR. However, optical consideration must be made in measuring polarized IR spectra of an optically anisotropic crystal, because interference fringes, which confuse measurements of polarized IR spectra, are brought about by optical anisotropy of the crystal under pol-mFTIR. For correct measurements of polarized absorbance spectra, optical explanation of the interference fringes must be precisely given under pol-mFTIR. In this study, interference fringes are revealed in measuring polarized IR absorbance spectra of an optically anisotropic crystal under pol-mFTIR, and given the optical explanation by formulating the polarized absorbance spectrum. Using this spectrum, an experimental constraint for the correct measurement of polarized IR absorbance spectra under pol-mFTIR is proposed. Under the experimental constraint, the pleochroism of absorbance due to the OH\textsuperscript{−} dipoles in optically anisotropic crystals is formulated for quantitative analysis of the orientation of the OH\textsuperscript{−} dipole. Then, as applications to minerals, the orientations of the OH\textsuperscript{−} dipoles in quartz and topaz are quantitatively examined.

2. Polarized IR absorbance spectrum under pol-mFTIR

2.1. Fourier transform polarized infrared microspectroscopy (pol-mFTIR)

An FTIR spectrometer is an interference-type spectrometer which is based on the principle of the Michelson interferometer. IR light from its source (Globar) is collimated by mirrors, enters a beamsplitter (Ge-coated KBr) and splits into transmitted and reflected light. One light goes to a fixed mirror, which reflects the light back; the other goes to a moving mirror, which also reflects the light back. The light through the two paths recombine at the beamsplitter, are converted into interfered IR light depending on the position of the moving mirror, and go on to an IR light's detector. This brings about the interferogram of intensity vs. time. The IR spectrum of intensity vs. energy is obtained through Fourier transformation of the interferogram. The position of the moving mirror is precisely determined by using a laser beam, and the intensity of IR light over whole wavenumbers is simultaneously measured.

The pol-mFTIR system used in the present study consists of an FTIR spectrometer (Shimadzu FTIR4200) and an IR polarizing microscope (Shimadzu IMS-1) which is equipped with an IR polarizer in it. The instrumental arrangement in the IR polarizing microscope is schematically shown in Fig.1. IR light admitted from the FTIR spectrometer is focussed on and transmits a sample on a sample stage, and recondensed by means of Cassegrainian mirrors. The light then passes through a masking aperture, transmits the IR polarizer and goes on to an IR detector (MCT; Hg\textsubscript{1−x}Cd\textsubscript{x}Te). The masking aperture mechanically limits the measuring area of an IR absorbance spectrum. Measurement of IR absorbance spectra in high Signal/Noise ratio at the selected area as large as 50\textmu m in diameter is available under this...
system. Observation by visible light (VIS) under crossed polars in order to search for a sample is also capable under the polarizing IR microscope, just as under a conventional polarizing microscope. An IR polarizer allows IR light oscillating in a specific direction to pass through. The angular marks are plotted on the IR polarizer every 2.5° from 0° to 180°. They correspond to the angle in a counterclockwise rotation from N-S on the sample stage. In the present system, vertical and lateral orientations relative to an observer are labelled north-south (N-S) and east-west (E-W), respectively, with reference to the conventional use in an optical microscopy. By setting the IR polarizer to \( \theta \), only IR light oscillating in a \( \theta \) from N-S on the sample stage is permitted to go on to the MCT detector.

2.2. Partial polarization of incident IR light under pol-mFTIR

In an FTIR spectroscopy, the incident IR light into a sample is partially polarized, and can be regarded as an assemblage of incoherent plane polarized light oscillating in all directions. The incoherency is produced by the incoherent IR source (Glober). The partial polarization of incident IR light results from the refraction at the beamsplitter.
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Fig. 2. continued
Fig. 2. Intensity distribution of partially polarized incident IR light (a) ; 4000cm$^{-1}$, (b) ; 3500cm$^{-1}$, (c) ; 3000cm$^{-1}$, and (d) ; 2500cm$^{-1}$, respectively. Filled circles are observed intensity of polarized component of IR light. Open circles are plotted after symmetrical consideration. Curves are least square fitting curves with a function of $a_\kappa + b_\kappa \cos2\theta$. Constants $a_\kappa$ and $b_\kappa$ are calculated from maximum $(a_\kappa + b_\kappa)$ (0° ; N-S) and minimum $(a_\kappa - b_\kappa)$ (-90° ; E-W) values of the intensity.

and the reflection at the various mirrors under the FTIR system. Figs. 2(a)-(d) show that the intensity distributions of the incident IR light of 4000, 3500, 3000, and 2500cm$^{-1}$ on the sample stage can be exactly fitted with a symmetrical function around N-S ; $(a_\kappa + b_\kappa \cos2\theta)$ (where $\kappa$ is wavenumber). Such an IR intensity distribution is produced by combining fully polarized IR light with an intensity distribution of $2b_\kappa \cos^2\theta$ with unpolarized IR light which has constant intensity distribution of $a_\kappa - b_\kappa$ in all directions. The degree of polarization of partially polarized incident IR light is represented as $2b_\kappa/(a_\kappa + b_\kappa)$. The degree of polarization under this system decreases with increasing wavenumber (Fig. 3). The partial polarization of incident IR light and its wavenumber dependence will be taken into account in discussing the calculated polarized IR absorbance spectra.

2.3. Interference fringes brought about by birefringence under pol-mFTIR

Examined specimens are synthetic quartz cut parallel to the $c$-axis with thickness of 3.05 mm, (sample #1), synthetic quartz cut parallel to the $c$-axis with thickness of 1.10 mm, (#2), and natural zircon from Brazil cut parallel to the $c$-axis with thickness of 1.10 mm, (#3). Polarized and unpolarized IR absorbance spectra of three specimens (#1, #2, and #3) were measured under pol-mFTIR (Figs. 4 (a), (b), and (c)). In Fig.4, spectra A, which are measured with unpolarized IR light, show intrinsic absorption of each specimen. Spectra B and C are polarized IR absorbance spectra, measured with the angle of 45° between the $c$-axis and IR polarizer. The $c$-axis of the three specimens is parallel to N-S in B (extinction position with reference to the conventional use of a
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Fig. 3. Degree of polarization \( \frac{2b_y}{a_x + b_y} \) between 4000 and 2500 cm\(^{-1} \) under the present pol-mFTIR system. Light is unpolarized or fully polarized when degree of polarization is 0 \( (b_y = 0) \), or 1 \( (a_x = b_y) \), respectively.

polarizing microscope), and NW-SE in C (diagonal position). The three spectra B show almost the same IR absorption as spectra A. However, periodic absorption appears in spectra C, even though the relative angle between the c-axis and IR polarizer are set to 45 as in spectra B. Such a periodic absorption always appears in polarized IR absorbance spectra of an optically anisotropic crystal which is not set at the extinction position in IR microscope observation. Contrastingly, optically isotropic materials such as glass, optically isotropic crystals, and optically anisotropic crystals that are cut normal to the optic axis show no such periodic absorption in any optical setting condition. Therefore, the periodic absorption is a specific phenomenon in measuring polarized IR spectra of optically anisotropic crystals. The periodicity in absorbance is different between the same kinds of crystals with the different thickness (#1 and #2), and between the different kinds of crystals with the same thickness (#2 and #3). The amplitude of periodic absorbance commonly decreases in the higher wavenumber region in the three spectra. Judging from the periodicity and amplitude of the absorbance in Fig.4, the periodic absorption strongly depends on the thickness of the specimens and wavenumber, and also depends on the birefringence of the specimens, since birefringence of zircon is considered to be different from that of quartz in the IR region as well as in the visible light region.

2.4. Birefringence of synthetic quartz and natural zircon in the IR region

The periodic absorption from an optically anisotropic crystal depends on the birefringence. Then, the birefringence of synthetic quartz and natural zircon from Brazil in their \( \text{OH}^- \) absorption regions are directly obtained by measuring the refractive indices in the \( \text{OH}^- \) regions. The average refractive index \( (n) \) is measured by means of channel spectra (RANDALL & RAWCLIFF, 1967) which are produced by multiple reflection
Fig. 4. IR absorbance spectra of (a) ; synthetic quartz plate parallel to the c-axis (thickness 3.05mm), (b) ; synthetic quartz plate parallel to the c-axis (1.10mm), and Brazilian zircon plate parallel to the c-axis (1.10mm). Three spectra are measured for each plate under the different conditions as A ; without IR polarizer, B ; with setting IR polarizer to 45° (NW-SE) and the c-axis to 0° (N-S) (extinction position), and C ; with setting IR polarizer to 0° (N-S) and the c-axis to 45° (NW-SE) (diagonal position).
Fig. 5. Polarized IR absorbance spectra of (a) synthetic quartz (thickness 0.019 mm), and (b) Brazilian zircon (0.049 mm). Both the specimens are cut parallel to c-axis. The two spectra are measured as A; c-axis perpendicular to E and B; c-axis parallel to E.

of light between the faces of a flat specimen. The average refractive index between $\kappa_1$ and $\kappa_2$ is simply derived from the following equation,

$$n = \frac{m}{2l(\kappa_1 - \kappa_2)},$$

where $l$; thickness of the sample (cm), $m$; the number of the period between $\kappa_1$ and $\kappa_2$ (cm$^{-1}$). To compensate for the instrumental errors, the average refractive indices of synthetic quartz and natural zircon are measured under the same pol-mFTIR system.

Figs. 5 (a) and (b) show the polarized IR spectra of synthetic quartz ($l$= 0.019 mm) and Brazilian zircon ($l$=0.049 mm). Both the samples were cut parallel to the c-axis. Spectra A and B in Fig.5 were measured with the c-axis perpendicular and parallel to the electric vector of IR light (E), respectively. Average refractive indices in the OH$^{-}$ regions calculated from the channel spectra under pol-mFTIR are $n_o$=1.65 ($n_o$; refractive index of ordinary light), $n_e$=1.66 ($n_e$; extraordinary light) for synthetic quartz, and $n_o$=1.85, $n_e$=1.91 for Brazilian zircon, respectively. Therefore, the average
birefringences of synthetic quartz and natural zircon in the OH⁻ regions are 0.01 and 0.06, respectively.

3. Formulation of polarized IR absorbance spectrum under pol-mFTIR

3.1. Formulated polarized IR absorbance spectra of an optically anisotropic crystal

The periodic absorption interferes with the measurements of polarized IR absorbance spectra of an optically anisotropic crystal under pol-mFTIR. Although the periodic absorption observed in Fig. 4 is almost cancelled by setting a sample to its extinction position, a slight doubt is left whether the polarized IR absorbance spectra measured at the extinction position is correct or not. In this paragraph, polarized IR absorbance spectra of an optically anisotropic crystal under pol-mFTIR is formulated, and an experimental constraint for correct measurements of polarized IR absorbance spectra under pol-mFTIR is proposed (SHINODA & AIKAWA, 1993). Absorption intrinsic to the crystal is considered in the next paragraph.

Suppose a plate of an optically anisotropic crystal. Locate the crystal on the sample stage in such a way that the angular position of one principal direction in the plate (E₁) is at \( \theta \) with N-S, as shown in Fig. 6. In the three figures, the amplitude distribution of partially polarized incident IR light and the position of IR polarizer (\( \alpha \) with N-S) are also schematically shown in Fig. 6. Assume that a plane polarized light is expressed as:

\[ \Phi(\theta, v) = A(\theta, v)\exp(2\pi ivt), \]

where \( A(\theta, v) \) represents an amplitude of light (frequency \( v \) oscillating direction \( \theta \) with N-S, \( t \); time). Partially polarized incident IR light is regarded as an assemblage of incoherent IR light which oscillates in all directions. The plane polarized IR light, \( \Phi(\theta, v) \), breaks into two vibrational components (oscillating direction; \( E_1, E_2 \)) in the same phase just as it enters the crystal. One component is in the principal plane of the crystal (\( E_1 \)) and the other in the plane perpendicular to the principal plane (\( E_2 \)). These two polarized rays travel separately through an optically anisotropic crystal, and keep the phase difference between them on leaving the crystal. The phase difference, \( \delta \), is regarded as

\[ \delta = \frac{2\pi d(n_1 - n_2)}{\lambda_v}, \]

where \( \lambda_v \) is wave length, \( d \) is thickness of the plate, and \( n_1 \) and \( n_2 \) are refractive indices perpendicular to the plate. The two polarized rays leaving the crystal generally recombine into elliptically polarized light and go on to the IR polarizer. The IR polarizer allows a component of polarized light oscillating in an \( \alpha \)-direction to pass through.
polarized rays, $\Phi_{E_1}(\theta, v)$ and $\Phi_{E_2}(\theta, v)$, whose oscillating directions are $E_1$ and $E_2$, respectively, after passing through the IR polarizer are,

$$\Phi_{E_1}(\theta, v) = \Phi(\theta, v) \cos(\theta - \beta) \cos(\alpha - \beta) \exp\frac{2\pi i}{\lambda_1} (-dn_1/\lambda_v)$$

$$\Phi_{E_2}(\theta, v) = \Phi(\theta, v) \sin(\theta - \beta) \cos(\alpha - \beta) \exp\frac{2\pi i}{\lambda_2} (-dn_2/\lambda_v).$$

The phase difference, $\delta'$, between the two polarized components along the direction of the IR polarizer is regarded to be equal to $\delta$ when the two polarized components are in the same direction along an IR polarizer, or $\pi - \delta$ when in the opposite direction. Then, taking $\delta'$ into account, the intensity of $I(\theta, v)$ of the light composed of the two polarized lights $\Phi_{E_1}(\theta, v)$ and $\Phi_{E_2}(\theta, v)$ is expressed as;

$$I(\theta, v) = [\Phi_{E_1}(\theta, v) + \Phi_{E_2}(\theta, v)] [\Phi_{E_1}(\theta, v) + \Phi_{E_2}(\theta, v)]^*,$$

where * means complex conjugate.

Total intensity $J(v)$ passing through the IR polarizer can be obtained by the integration of the intensity $I(\theta, v)$, since plane polarized IR light $\Phi(\theta, v)$ is incoherent. Therefore,
Fig. 7. (A); Calculated absorbance spectra from formulated absorbance spectrum $L(\nu)$ and (B) differential spectra obtained by subtracting spectrum B from C in Fig. 4 (a), (b), and (c), respectively. In calculated spectra, the thickness and birefringence of the specimens are (a); 3.05 mm, 0.01, (b); 1.10 mm, 0.01, and (c); 1.10 mm, 0.06, respectively.

\[
J(\nu) = \int_0^{2\pi} I(\theta, \nu) d\theta
\]

The intensity spectrum when the sample is not set on the stage (reference spectrum
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$K(v)$ is expressed as;

$$K(v) = \int_0^{2\pi} \Phi(\theta, v)\Phi(\theta, v)^* \cos^2(\theta - \alpha) d\theta .$$

The intensity distribution of incident light is expressed as $a_v + b_v \cos 2\theta$ as observed in Fig. 2. Thus, the intrinsic intensity distribution $\Phi(\theta, v)\Phi(\theta, v)^*$ is derived from the equation;

$$a_v + b_v \cos 2\theta = \int_0^{2\pi} \Phi(\theta, v)\Phi(\theta, v)^* \cos^2(\theta - \alpha) d\theta .$$

Consequently,

$$\Phi(\theta, v)\Phi(\theta, v)^* = \left\{ A(\theta, v) \right\}^2 = \frac{a_v + 2b_v \cos 2\theta}{\pi} .$$

The absorbance spectrum $L(v)$ under pol-mFTIR can be formulated as;

$$L(v) = \log_{10} \left[ \frac{K(v)}{J(v)} \right] = \log_{10} \left[ \frac{a_v + b_v \cos 2\alpha}{a_v + (b_v/2)((1 - \cos \delta)\cos(2\alpha - 4\beta) + (1 + \cos \delta)\cos 2\alpha)} \right] .$$

Using this formulated absorbance spectrum, calculated absorbance spectra can be obtained by substituting practical values for $\alpha$, $\beta$, $d$, and $(n_1 - n_2)$ in $L(v)$. In Figs. 7 (a), (b), and (c), spectra A show calculated absorbance spectra of an optically anisotropic crystal of birefringence and thickness 0.01 3.05 mm, 0.01 1.10 mm, and 0.06 1.10 mm, respectively. In this calculation, the wavenumber dependence of the degree of polarization observed in Fig. 3 is taken into account. The amplitude of the calculated absorbance fringe decreases in the higher wavenumber regions. This is because the degree of polarization decreases in the higher wavenumber regions. The three spectra B in Fig. 7 are differential spectra which are obtained by substituting spectra B from spectra C in Fig. 4. Calculated spectra A show good accordance with the experimental one (spectra B) in the periodicity and in the amplitude variation of absorbance depending on the wavenumber. A slight difference of amplitude between calculated absorbance and observed one is considered to result from the optical construction of the IR polarizing microscope, where IR light is condensed by means of Cassegrainian mirrors and keep a solid angle on transmitting the plate of the specimen. In calculation, optical paths were assumed to be ideally perpendicular to the plate of the supposed crystal. Therefore, this proves that the formulation of polarized IR absorbance spectra under pol-mFTIR.
is correct.

According to the formulated absorbance spectrum, the periodic absorption is numerically brought about from a term, \( \cos \delta' \), and optically the interference fringes which result from the birefringence of an optically anisotropic crystal. The term, \( \cos \delta' \), can be cancelled by setting \( \beta = \pi \) or \( \alpha = \beta \). Under the setting of \( \alpha = \beta \), measurements of polarized absorbance spectra with changing the relative angle between a principal direction of an optically anisotropic crystal and the IR polarizer cannot be attained. Therefore, such a constraint to avoid the interference fringes as \( \alpha = \beta \) is neglected. Under the setting of \( \beta = \pi \), the interference fringes always can be cancelled, even though \( \alpha \) is set at any angular positions. The cancellation is experimentally attained by setting an optically anisotropic crystal to its extinction position under the visible light observation between crossed polars, since the intensity distribution of partially polarized incident IR light is symmetrical with N-S.

Consequently, an experimental constraint for correct measurement of the polarized absorbance spectrum under pol-mFTIR, the adequacy of which is confirmed by comparison of the calculated interference fringes with those identical to the observed one, can be proposed here.

3.2. Formulation of pleochroic distribution of absorbance due to the OH\(^-\) dipole under pol-mFTIR

In this paragraph, pleochroic distribution of polarized absorbance due to the OH\(^-\) dipole is formulated under the proposed experimental constraint for the purpose of quantitative examination of the orientation of the OH\(^-\) dipole in an optically anisotropic crystal (Shinoda & Aikawa, 1994).

Suppose that an oriented absorber of light of specific frequency \( v \) (absorption coefficient \( \mu_v \), when the oriented absorber is parallel to the electric vector of polarized light \( (E) \)) is in medium of complex refractive index, \( n_r = n_r - i \eta_r \). When the oriented absorber is inclined \( \gamma \) with the electric vector of polarized light, the complex refractive index \( (\hat{n}_r) \) against polarized light of frequency \( v \) is considered to be expressed as \( \hat{n}_r = n_r - i(\eta_r + \mu_v \cos \gamma) \) (Fig. 8). Suppose an optically anisotropic crystal plate with the thickness of \( d \), complex refractive indices perpendicular to the plate; \( n_1 - i \eta_1 \), and \( n_2 - i \eta_2 \). One principal direction in the plate is \( E_1 \), and the other principal direction \( E_2 \). The crystal has an oriented absorber inclined \( \gamma \) from \( E_1 \). The optical setting of the supposed optically anisotropic crystal and partially polarized incident light is schematically shown in Fig. 9. To complete the correct measurement of polarized IR absorbance spectra under pol-mFTIR, the orientation of \( E_1 \) and \( E_2 \) are just located at N-S and E-W direction on the sample stage. Assume that a plane polarized light is expressed as;

\[
\Psi(\theta, v) = A(\theta, v) \exp 2\pi i v t,
\]

where \( A(\theta, v) \) represents an amplitude of oscillating at \( \theta \) with N-S. Plane polarized
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\[ \mathbf{n}_v = n_v - i \left( \eta_v + \mu_v \cos \gamma \right) \]

Fig. 8. Schematic representation of complex refractive index of an oriented absorber of light (absorption coefficient \( \mu_v \)) in a medium of complex refractive index \((n_\nu-i\eta_\nu)\). The angle between electric vector of polarized light \((E)\) and the oriented absorber is \(\gamma\).

Fig. 9. Schematic diagram of optical setting among: IR polarizer \((x^\circ \text{ with N-S})\), one principal directions of an optically anisotropic crystal \((E_1)\) and the other \((E_2)\) \((0^\circ \text{ and } 90^\circ)\), an oriented absorber \((\gamma^\circ)\), and amplitude of polarized component \((A(\theta, \nu))\) \((\theta^\circ)\).
light $\Psi(\theta, v)$ (breaks into two vibrational components in the optically anisotropic crystal. Each polarized light is absorbed by host crystal structure with different absorption coefficient, $\mu_v \cos \gamma, \mu_v \sin \gamma$) through the crystal. After leaving the crystal, two polarized rays recombine and pass through a polarizer, which is fixed $\varphi_0$ with N-S during the following deviation of formula. The two polarized components, $\Psi_{E_1}(\theta, v)$ and $\Psi_{E_2}(\theta, v)$ are expressed as;

$$\Psi_{E_1}(\theta, v) = \Psi(\theta, v) \cos \theta \cos \varphi \exp(2 \pi i \left( - \frac{\hat{n}_1 v}{\lambda} \right))$$

$$\Psi_{E_2}(\theta, v) = \Psi(\theta, v) \sin \theta \sin \varphi \exp(2 \pi i \left( - \frac{\hat{n}_2 v}{\lambda} \right))$$

where $\hat{n}_1 v = n_{1v} - i(\eta_{1v} + \mu_v \cos \gamma)$, $\hat{n}_2 v = n_{2v} - i(\eta_{2v} + \mu_v \sin \gamma)$. The intensity of the recombining light $M(\theta, v)$ is expressed as;

$$M(\theta, v) = [\Psi_{E_1}(\theta, v) + \Psi_{E_2}(\theta, v)] [\Psi_{E_1}(\theta, v) + \Psi_{E_2}(\theta, v)]^*.$$ 

Considering the total integration $\theta : 0 \to 2\pi$, the total intensity of light which reaches to the detector is expressed as;

$$N(v) = \int_0^{2\pi} M(\theta, v) d\theta .$$

Intensity spectrum omitting the sample, $O(v)$, (reference spectrum) is expressed as;

$$O(v) = \int_0^{2\pi} \Psi(\theta, v) \Psi(\theta, v)^* \cos^2(\theta, v) d\theta .$$

Against the intensity distribution $a_\varphi + b_\varphi \cos 2\varphi$ of partially polarized light, $\Psi(\theta, v) \Psi(\theta, v)^*$ is given as;

$$\Psi(\theta, v) \Psi(\theta, v)^* = |A(\theta, v)|^2 = \frac{a_\varphi + 2b_\varphi \cos 2\theta}{\pi} .$$

Accordingly, polarized absorbance spectrum $P(v)$ is formulated as;

$$P(v) = \log_{10} \left[ \frac{O(v)}{N(v)} \right].$$

The angle $\varphi$ has been fixed during the above derivation. Experimentally, the term $\varphi$ is regarded as a variable, since polarized absorbance spectra is measured at various angular position of the polarizer. Hence, formula $P(v)$ is regarded as polarized absorbance distribution as a function of $\varphi$ and $v$, and formulated as;
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Since the terms \( \exp(-d\eta_{1,v}) \) and \( \exp(-d\eta_{2,v}) \) can be measured from the absorbance of background on a measured absorption peak, the formulated absorbance distribution contains two unknown parameters \( \mu^' \) and \( \gamma \). Consequently, quantitative determination of orientation of the OH⁻ dipole in an optically anisotropic crystal can be carried out from the least square method, where an observed distribution of polarized IR absorbance on a thin section in which crystal axis is known is fitted with the formulated absorbance distribution. At the same time, the absorption coefficient (\( \mu_v \)) of the oriented absorber can be derived from the calculation.

Using the formulated absorbance spectrum, the pleochroic distribution of absorbance due to the oriented absorber in an optically anisotropic crystal can be calculated by substituting practical values for each parameter. Calculated absorbance distributions by two degree steps with varying \( \gamma \) are shown in Fig. 10. Absorbance distributions (A),

\[
P(x,\gamma) = \log_{10} \left[ \frac{2(a_x + b_x \cos2\alpha)}{(a_x + b_x)(1 + \cos2\alpha)\exp\{-d(\mu^' \cos\gamma + \eta_{1,v})\} + (a_x - b_x)(1 - \cos2\alpha)\exp\{-d(\mu^' \sin\gamma + \eta_{2,v})\}} \right],
\]

where \( \mu^'_x = \frac{4\pi \mu_x}{\lambda_v} \), \( \mu^'_y = \frac{4\pi \mu_{1,v}}{\lambda_v} \), and \( \mu^'_z = \frac{4\pi \mu_{2,v}}{\lambda_v} \).

Fig. 10. Calculated distribution of absorbance which is brought about by an oriented absorber in optically anisotropic crystal under pol-mFTIR. The angle (\( \gamma^\circ \)) between the oriented absorber and N-S is as follows. A ; \( \gamma = 0^\circ \), B ; \( \gamma = 30^\circ \), C ; \( \gamma = 45^\circ \), D ; \( \gamma = 60^\circ \), E ; \( \gamma = 90^\circ \)
(B), (C), (D), and (E) are the cases that the angles between the oriented absorber and N-S are 0°, 30°, 45°, 60°, and 90°, respectively. In each case, the distribution of calculated absorbance is symmetrical as to \( E_1 \) or \( E_2 \) (N-S or E-W), and the pleochroism of distribution varies depending on the angle of \( \gamma \). The pleochroism is the strongest at \( \lambda = 0^\circ \) and 90°, become weaker at \( \gamma = 30^\circ \) and 60°, and is almost isotropic at \( \gamma = 45^\circ \). In all cases, the maximum and minimum of absorbance are either at \( E_1 \) or \( E_2 \), whether the oriented absorber is inclined to the principal direction of the optically anisotropic crystal or not. In other words, the formulated absorbance distribution proposes that the oriented absorber does not necessarily point to the direction of the maximum of absorbance, and that the oriented absorber is generally inclined to the principal direction of the optically anisotropic crystal when the pleochroic distribution of absorbance is observed. An additional thing to be noticed in Fig. 10 is that the pleochroism of absorbance A and E, or B and D are slightly different from each other in spite of the same angle between the oriented absorber and the principal direction. This results from the partial polarizability of incident light.

4. Application to the orientation of the OH\(^-\) dipole in minerals

4.1. Topaz

Topaz (\( \text{Al}_2\text{SiO}_4(\text{F, OH})_2 \)) is orthorhombic and has space group of \( \text{Pbmn} \). Optical orientation of topaz is \( x = a, \beta = b, \lambda = c, \text{OAP (010)} \). The sample examined in this study is colorless and euhedral single crystal of topaz from the Naegi district, Gifu prefecture, central Japan. The single crystal was cut into three thin sections as closely as possible perpendicular to the \( a(\#4), b(\#5), \) and \( c\)-axes (\#6) with aid of euhedral prismatic crystal planes and the perfect cleavage (001).

Polarized IR absorbance spectra of each thin section was measured at its extinction position so as to complete the experimental constraint which was confirmed in the previous sections for a correct measurement of polarized IR absorbance spectra under pol-mFTIR. A sharp absorption peak at 3650 cm\(^{-1}\) was observed in the polarized IR absorbance spectra of the sample (Fig. 11). In the three thin sections, polarized IR absorbance spectra were measured with changing the angle between the electric vector of IR light and the principal direction of each thin section in five degree steps. Figs. 12 (a), (b), and (c) show the absorbance distribution in polar coordinate of the thin sections \#4, \#5, and \#6, respectively. The crystal axes of the thin sections on the sample stage are located as the \( c\)-axis at NS, the \( b\)-axis at EW on thin section \#4, the \( a\)-axis at EW, the \( c\)-axis at NS on \#5, and the \( a\)-axis at NS, the \( b\)-axis at EW on \#6. As previously proposed by formulated absorbance distribution, the absorbance distribution of each thin section is symmetrical with the principal crystal axis, and the maximum and minimum absorbance are at the either of the principal crystal axes. The orthographic projections of the OH\(^-\) dipole which has a specific orientation in topaz onto the (100), (001), and (010) planes cause the absorbance distribution of thin sections \#4, \#5, and
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Fig. 11. Polarized IR absorbance spectrum of topaz from the Naegi district. The specimen was cut normal to the b-axis. E is parallel to c-axis.

\#6, respectively. From least square fitting of the three absorbance distributions with previously formulated absorbance distribution, the values of \(\gamma\) are calculated as 6.2 \((\sigma; 0.35, R; 0.996)\) in (100), 27.3° \((\sigma; 0.27, R; 0.995)\) in (010), and 9.9° \((\sigma; 0.25, R; 0.998)\) in (001).

Strong pleochroism of absorbance in (100) and (001) planes, and calculated \(\gamma\) (6.2° in (100) and 9.9° in (001)) consistently mean that the OH\(^{-}\) dipole is predominantly distributed in (010) planes and inclined from \(\langle 100 \rangle\) and \(\langle 001 \rangle\) directions. Weak pleochroism of absorbance distribution in (010) and calculated \(\gamma\) (27.3°) mean that the OH\(^{-}\) dipole is inclined at 27.3° with \(\langle 001 \rangle\). Therefore, the general orientation of the OH\(^{-}\) dipole in topaz is determined to be 27.3° from \(\langle 001 \rangle\) in (010) from the present polarized IR absorbance study.

ISETTI & PENCO (1967) observed an absorption peak at 3717 cm\(^{-1}\) in topaz, and suggested that the OH\(^{-}\) dipole lies on the (010) plane and inclined at 37° from the c-axis from two polarized IR absorbance spectra \((E/c\text{-axis and } E/a\text{-axis})\) in (010). Lying plane of the OH\(^{-}\) dipole determined in the present study is consistent with their study. However, the angle between the c-axis and the OH\(^{-}\) dipole and the wavenumber of the absorption peak obtained in their study are different from the present study. The different value of inclination angle of 37° by ISETTI & PENCO (1967) is those obtained in derived from only two measurements of polarized IR spectra, which are not precise measurements enough to determine the orientation of the OH\(^{-}\) dipole.

The position of the hydrogen atom in a single crystal of topaz was examined from a neutron diffraction study (PARISE \textit{et al.}, 1980) based on the positional parameters of X-ray diffraction (LADELL, 1965). From their studies, the OH\(^{-}\) dipole can be considered to lie predominantly in (010), and have an angle of 29° from the c-axis. The obtained angle \(\gamma\) in (010) in the present study is in good agreement with the result from the neutron diffraction. Therefore, the formulated absorbance distribution \(P(\alpha, \nu)\) is adequate for the orientation determination of the OH\(^{-}\) dipole in an optically anisotropic crystal.
Fig. 12. Anisotropic distribution of polarized IR absorbance of topaz from the Naegi district at 3650 cm⁻¹. Filled circles are observed absorbance. Open circles are plotted after symmetrical consideration. They are least square fitted (---) with the formulated distribution of absorbance. The sample #, the orientation of crystal axes on sample stage, and γ obtained from least square fitting is as follows.

(a) in (100) (#1) (c-axis/NS, b-axis/EW) γ = 6.2° (α = 0.35, R:0.996)
(b) in (010) (#2) (c-axis/NS, a-axis/EW) γ = 27.3° (α = 0.27, R:0.995)
(c) in (001) (#3) (a-axis/NS, b-axis/EW) γ = 9.9° (α = 0.25, R:0.998)
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4.2. Quartz

Two kinds of series of polarized IR absorbance spectra of quartz from Arkansas were measured so as to complete the proposed experimental constraint. Fig. 13 shows unpolarized IR absorbance spectra of quartz from Arkansas. Several kinds of absorption bands due to the OH\textsuperscript{-} dipole were observed between 3600–3300 cm\textsuperscript{-1}. One series of spectra were measured on quartz in plane. The c-axis was fixed at E-W, and the angular relation between the c-axis and E was changed from 0 to 170 in ten degree steps. IR absorbance about five absorption bands of 3508, 3482, 3440, 3402, and 3380 cm\textsuperscript{-1} was measured with respect to the relative angle between the c-axis and E. The other series of spectra were measured on quartz cut perpendicular to the c-axis, when IR polarizer was fixed and the specimen was rotated from 0 to 350 in 10 step. IR absorbance was measured with respect to the relative angle between the a-axis and E about the five absorption bands.

Figs. 14 (a)–(e) show absorbance distribution of the five absorption peaks in (10\overline{1}0) plane and the results of the least square fitting curve with the formulated pleochroic distribution of absorbance. From the results of the least square fitting of the five distribution of absorbance with the formulated distribution of absorbance, the values of \( \gamma \) were calculated as 0.8° (\( \sigma \); 1.1, R; 0.986) as to 3508 cm\textsuperscript{-1}, 7.7° (\( \sigma \); 0.7, R; 0.995) 3480 cm\textsuperscript{-1}, 7.1° (\( \sigma \); 1.1, R; 0.990) 3440 cm\textsuperscript{-1}, 7.4° (\( \sigma \); 0.8, R; 0.995) 3402 cm\textsuperscript{-1}, and 7.9° (\( \sigma \); 0.9, R; 0.993) 3380 cm\textsuperscript{-1}. These results suggests that the OH\textsuperscript{-} dipole in quartz is highly polarized perpendicular to the c-axis.

Figs. 15 (a)–(e) show absorbance distribution of the five absorption peaks in the (0001) plane. PANKRATH (1991) observed strong anisotropy of absorbance due to the OH\textsuperscript{-} dipole in (0001) plane by polarized IR spectra, and estimated the orientation of
Fig. 14-1. continued
Fig. 14. Pleochroic distribution of polarized IR absorbance in the (1010) plane of quartz from Arkansas, and the least square fitting curve with the formulated absorbance distribution. The observed absorption peaks are, (a) $\nu = 3508 \text{cm}^{-1}$, (b) $\nu = 3482 \text{cm}^{-1}$, (c) $\nu = 3440 \text{cm}^{-1}$, (d) $\nu = 3402 \text{cm}^{-1}$, and (e) $\nu = 3380 \text{cm}^{-1}$. The $c$-axis is along E-W. Filled circles are observed absorbance. Open circles are plotted after symmetrical consideration. They are least square fitted (---) with the formulated distribution of absorbance.

The $\text{OH}^-$ dipole with respect to the $a$-axis in synthetic smoky quartz. The five distributions of absorbance obtained in the present study are considered to be isotropic with respect to the $a$-axis within the angular resolution of $3^\circ$, because plane polarized light undergoes optical rotation of about $3^\circ$ through the specimen resulting from optical activity along the $c$-axis in quartz where specific rotation in the $\text{OH}^-$ absorption band is about $1^\circ/\text{mm}$. Based on an assumption that the $\text{OH}^-$ dipoles are governed by trigonal symmetry along the $c$-axis, three oriented absorbers, which are trigonal-symmetrically distributed should be considered as schematically shown in Fig. 16, where the distribution results in hexagonal symmetry because of no absorption difference depending on the orientation of an $\text{OH}^-$ dipole. In measuring absorbance in Fig. 15, the angle of the
IR polarizer was fixed at the N-S direction and the sample was rotated in order to avoid fluctuation background resulting from optical activity. Therefore, $\alpha$ in $P(\alpha, \nu)$ is regarded as $0^\circ$. The incident direction of IR light is along the optic axis of
quartz. Therefore, $\beta$ in $P(x, v)$ is regarded as 0. Supposing one of three absorbers is inclined at $\gamma^\circ$ with N-S, and absorption coefficient of an absorber is $\tau_v$, absorption coefficient effective to the polarized light (N-S) adds up to $\tau(|\cos\gamma| + |\cos(\pi/3 + \gamma)| + |\cos(\pi/3 - \gamma)|)$. Consequently, formula is $P(x, v)$ is modified into $Q(x, v)$ as

$$Q(O, v) = \log_{10} \left[ \frac{1}{\exp\left\{ -d\left(\eta'_v + \tau'_v\left(|\cos\gamma| + |\cos(\pi/3 + \gamma)| + |\cos(\pi/3 - \gamma)|\right)\right)\} } \right]$$

where $\eta'_v = \frac{4\pi \eta_v}{c}$, $\tau'_v = \frac{4\pi \tau_v}{c}$.

Hexagonal distribution slightly fluctuated is expected from the modified absorbance distribution. However, the observed pleochroism of absorbance (Fig.15) is almost
Fig. 16. Schematic figure of optical setting among IR polarizer ($x^\circ$ with N-S), trigonal-symmetrical oriented absorber ($\gamma^\circ$), and incident IR polarized component ($\Phi(\theta,v)$). 

isotopic. Since the incident IR light undergoes optical rotation resulting from optical activity through the sample, averaged absorbance in about 3° may be observed. However, the observed isotropic pleochroism of absorbance cannot be explained only by the optical activity of quartz. Distribution of OH⁻ dipoles in quartz may be more complicated in (0001) than simple trigonal-symmetrical distribution. Thus, the orientation of the OH⁻ dipole with respect to the a-axis was not clearly specified.

Kats (1962) revealed that absorptions in the 3000 cm$^{-1}$ region of quartz were due to hydrogen vibrations. Paterson's (1989) review showed that the OH⁻ dipole which occupies a specific site in quartz crystal structure is classified into the substitutional water defect denoted by (4H)$_{Si}$. This is produced by replacing a silicon atom by four hydrogen atoms as seen in hydrogarnets (Aines & Rossman, 1984b). Here the interstitial hydrogen defect is denoted by (H$_2$O)$_i$ or (2OH)$_o$ replacing an oxygen atom by (OH)$_2$ group, and the charge compensating the OH⁻ defect is coupled with substituting cation such as Al$^{3+}$. Four OH- dipoles in a (4H)$_{Si}$ defect are tetrahedrally distributed in the Si site of quartz structure (Weil, 1984). Cordier & Doukhán (1991) observed ambiguous anisotropic effect on near infrared (NIR) absorption bands of 4450 cm$^{-1}$ and 4545 cm$^{-1}$, and assigned the two peaks to the OH⁻ absorption bands due to the (4H)$_{Si}$ defects. The
four the OH⁻ dipoles in OH tetrahedron which may give the respective absorption in the near absorption bands must not show the same behaviour simultaneously in anisotropy of absorbance in (10\(\overline{1}0\)) plane, but should show the same in (0001) plane since they are governed by trigonal symmetry. However, all the five absorption peaks observed in the present study show the same strong anisotropy of absorbance in (10\(\overline{1}0\)) plane. Therefore, it is difficult to assign all the five peaks to absorption peaks due to the (4H)\(\text{Si}_i\) defects. PATTERSON (1986) predicted that the solubility of the interstitial water defects is very low and may be beyond the detection limit of IR spectroscopy based on thermodynamic considerations. On the other hand, natural quartz generally contains a small but significant amount of Al as solid solution. Therefore, the five peaks are considered to be assigned to the OH⁻ absorption bands due to charge-compensating the OH⁻ defects coupled with substituting cation such as Al\(^3+\). This kind of the OH⁻ dipole is considered to be highly polarized perpendicular to the c-axis.

CORDIER & DOUKHAN (1991) observed two ambiguous pleochroic distribution of absorbance on NIR absorption regions. However, they failed to give quantitative discussions about the orientation of the OH⁻ dipole in quartz. It is possible to obtain the orientation of OH⁻ dipole by applying the present formulation to their study. PANKRATH (1991) observed pleochroic distributions of absorbance due to the OH⁻ dipole in the (0001) plane of quartz, although the OH⁻ dipoles governed by the trigonal symmetry in the (0001) plane are considered to give rise to isotropic distribution of absorbance. Such a pleochroic distribution of absorbance due to the OH⁻ dipole in the (0001) plane of quartz means reduction of symmetry from the trigonal system, and suggests the ordering of the OH⁻ dipole in quartz. IR spectroscopy accompanied with the present formulation of pleochroic distribution of absorbance will make it possible that the orientation determination and the occupancy determination of the OH⁻ dipole in the theoretically anhydrous minerals, which is difficult by a neutron diffraction study.

5. Concluding Remarks

1. Polarized IR absorbance spectrum, \(L(v)\), under pol-mFTIR is formulated as;

\[
L(v) = \log_{10}\left[\frac{a_v + b_v \cos 2\alpha}{a_v + (b_v/2)(1 - \cos\delta')\cos(2\alpha - 4\beta) + (1 + \cos\delta')\cos 2\alpha}\right].
\]

The formulated absorbance spectrum suggests that interference fringes arise from birefringence intrinsic to an optically anisotropic crystal, and that the correct measurement of polarized IR absorbance spectrum to cancel the interference fringe can be attained by fixing an optically anisotropic crystal at its extinction position \((\beta = \pi\alpha/2)\). The problem in measuring polarized IR absorbance spectra under FTIR was solved by this formulation.

2. Pleochroic distribution of absorbance, \(P(\alpha, v)\), due to an oriented absorber in an optically anisotropic crystal is formulated under pol-mFTIR as;
$P(x, v) = \log_{10} \left[ \frac{2(x_a + b, \cos 2x)}{(a_x + b_x)(1 + \cos 2x) \exp \{-d(\mu_x' \cos \gamma + \eta_{1x}^z)\} + (a_x - b_x)(1 - \cos 2x) \exp \{-d(\mu_x' \sin \gamma + \eta_{2x}^z)\}} \right].$

The formulated distribution of absorbance suggests that observed pleochroic distribution of absorbance should be symmetrical with the principal direction of an optically anisotropic crystal, and that the maximum and minimum of absorbance should be at either of the principal directions of the crystal, even though the oriented absorber is inclined from the principal direction of the crystal. The OH$^-$ dipole is not generally oriented to the maximum direction of absorbance.

3. The general orientation of OH$^-$ dipoles in topaz lie in the (010) plane, and inclined at 27.3° from the c-axis. This is in good agreements with X-ray and neutron studies. Therefore, the adequacy of the formulated distribution of absorbance, $P(x, v)$, is confirmed from the comparison of the present study with the X-ray and neutron studies.

4. The orientation of the OH$^-$ dipole in quartz which compensates the charge balance coupled with substituting cation such as Al$^{3+}$ is almost perpendicular to the c-axis. The speciation of hydrous components in nominally anhydrous minerals as well as stoichiometrically hydrous minerals is made possible by the formulation of $P(x, v)$ under pol-mFTIR.

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**References**


