Concurrent polarization IR analysis to determine the 3D angles and the order parameter for molecular orientation imaging

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Abstract

A non-tomographic analysis method is proposed to determine the 3D angles and the order parameter of molecular orientation using polarization-dependent infrared (IR) spectroscopy. Conventional polarization-based imaging approaches provide only 2D-projected orientational information of single vibrational modes. The newly proposed method concurrently analyses polarization angle-dependent absorptance of two non-parallel transition dipole moments. The relative phase angle and the maximum-to-minimum ratios observed from the two polarization profiles are used to calculate the 3D angles of the mean molecular orientation and the order parameter of the orientational distribution. Usage of those relative observables as intermediate input parameters makes the analysis results robust against variations in concentration, thickness, absorption peak, and absorption cross-section, which can occur in typical imaging conditions. This analysis is based on a single-step, non-iterative calculation that does not require any analytical model function of an orientational distribution function. This concurrent polarization analysis method is demonstrated using two simulation data examples, followed by associated error propagation analysis and discussion on the effect of absorption strength. Application of this robust spectral analysis method to polarization IR microscopy will provide a full molecular orientation image without tilting that tomographies require.

Keywords

(300.6340) Spectroscopy, infrared; (110.5405) Polarimetric imaging; (260.5430) Polarization

1. Introduction

Molecular anisotropy plays a critical role in nature, affecting not only the directionality of a bulk property but also creating new properties different from isotropic materials. Accurate measurement and proper characterization of the spatial heterogeneity and hierarchy in molecular orientation is important in the fundamental understanding of the effects of structured molecular anisotropy on the biological, chemical, and mechanical properties of macromolecular materials [1–3]. Various spectroscopic and optical imaging techniques for
orientation measurement are mostly based on polarization-controlled spectroscopy, such as IR absorption [3–5], fluorescence [6], confocal Raman [7], coherent Raman [8,9], and second harmonic generation [10]. Despite the diffraction-limited spatial resolution, these methods can only measure the molecular orientation projected onto the polarization rotating plane and the in-plane order parameters. 2D-projected orientation imaging can provide quantitative information for samples where the symmetry axis is pre-defined onto the polarization rotating plane, such as fibers [11] and stretched films [12]. However, for samples whose orientation can be out-of-plane, only qualitative information can be obtained by 2D-projected imaging methods. Recently, different imaging approaches have been developed to determine the out-of-plane component of molecular orientation by analyzing z-stacked images [13–16], interference patterns or intensity distributions of single molecule emissions [17–19], but those methods are applicable only to isolated chromophores or defects; thus, not appropriate for imaging of continuous materials. Alternatively, 3D orientation can be accurately determined by tomographical methods by tilting the sample while characterizing [20–22]. Despite their successful demonstrations for 3D orientation measurement of molecular orientation in polymer thin films, those tomographic approaches are very challenging to apply to high-resolution optical imaging due to spatial restriction of high magnification objective lenses. Therefore, these optical tomographic approaches have been demonstrated mostly for homogeneous thin samples.

Molecular orientation can be described either in the laboratory coordinate or in the molecular coordinate. For mathematical simplicity, the mean orientation direction is described with the 3D angles in the laboratory coordinate while the local orientational broadening is described in the molecular coordinate with respect to the mean orientation direction.

Molecular orientation is mathematically expressed by an orientational distribution function (ODF). For a molecular system with cylindrical symmetry, the ODF can be expressed by a series of Legendre polynomials with respect to the symmetry axis. Depending on the optical interaction mechanism, each measurement can determine a different number of coefficients in the Legendre polynomials [1,23]. For example, wide angle X-ray scattering (WAXS) is known to determine all coefficients. Nuclear magnetic resonance (NMR) can measure up to the eighth-order coefficients. Raman and fluorescence can provide the second- and fourth-order coefficients, and infrared (IR) absorption and second harmonic generation can measure the second-order coefficient [2,23]. Among the coefficients, in particular, the second-order coefficient, also known as the order parameter, is widely used to represent the broadening of an ODF. In this paper, the order parameter is used as a metric of orientational broadening of the ODF in the molecular coordinate.

In the previous paper [24], a new spectral analysis method was proposed to determine the 3D angles of molecular orientation, analyzing coherent anti-Stokes Raman scattering (CARS) susceptibilities of two non-parallel Raman modes observed by a single polarization scan. In the paper, the spectral analysis method determines the 3D orientation angles of molecular systems with different symmetries and orientational broadening. However, the previous approach requires an analytical model function for the ODF to determine the mean
orientation angles and the order parameter of the ODF. Its calculation is based on iterative computation, which potentially costs expensive computation time.

In this paper, a different approach based on polarization IR is proposed to determine the 3D angles and the orientational order parameter without assuming any model function for an ODF. This concurrent polarization IR analysis method can also calculate those output values by a single step without iterative computation. Similar to the approach developed for polarization CARS [24], this new IR analysis method takes advantage of dimensionless parameters observed from two polarization IR absorption profiles. The concurrent polarization IR analysis method can be easily implemented to conventional IR microscopy by a simple addition of polarization rotating optics in the beam path.

2. Theory
2.1. Polarization angle-dependent absorbance by aligned transition dipole moments

In literature, polarization angle dependence of light absorption by aligned molecules has been described with either absorbance $A \equiv - \log T$ [25–28], or absorptance $a = 1 - T$ [29–31], where $T$ is the transmittance. However, those expressions were used without thorough derivations or clarifications of underlying assumptions. Here, polarization angle-dependent light absorption is described for aligned molecules using classical electromagnetic wave theories. Figure 1 shows how linearly polarized light intensity is reduced by a collection of transition dipole moments that are aligned parallel to each other. In this scheme, the incident electric field is divided into the parallel and perpendicular electric fields with respect to the plane defined by the light propagation direction and the transition dipole moment direction. While the parallel electric field is reduced through the sample, the perpendicular electric field is unaffected. As derived in Fig. 1, the transmitted light intensity, $I^d$, is expressed with the incident light intensity, $I^0$, the polarization angle, $\eta$, and the transition dipole tilting angle, $\theta$, as

$$I^d = I^0 \left[ 1 - \left[ 1 - \exp\left(-2\varepsilon c d \sin^2 \theta \right) \cos^2 (\eta - \psi) \right] \right] \quad (1)$$

where $\psi$ is the azimuthal angle of the transition dipole moments on the $xy$ plane. Then, the polarization angle-dependent transmittance can be expressed as

$$T(\eta) \equiv I^d/I^0 = 1 - \left[ 1 - \exp\left(-2\varepsilon c d \sin^2 \theta \right) \cos^2 (\eta - \psi) \right] \quad (2)$$

Using Eq. (2) and the relation of $A = - \log T$, the absorbance can also be expressed as a function of $\eta$, but in a complex form as

$$A(\eta) = - \log \left[ 1 - \left[ 1 - \exp\left(-2\varepsilon c d \sin^2 \theta \right) \cos^2 (\eta - \psi) \right] \right] \quad (3)$$
which is far from the expression of \( \cos^2 \eta \) for absorbance, which is frequently used in literatures. In contrast, Eq. (2) can be rewritten into a simpler form of expression using absorptance, \( \alpha = 1 - T \) as

\[
\alpha(\eta) = \left[ 1 - \exp\left(-2ecd\sin^2 \theta\right) \right] \cos^2 (\eta - \psi) \tag{4}
\]

which shows that \( \alpha(\eta) \propto \cos^2 (\eta - \psi) \) and that the phase of \( \alpha(\eta) \) corresponds to the azimuthal angle \( \psi \). However, the tilting angle, \( \theta \), is still blended with the non-orientational quantities in the exponent, which makes it difficult to extract the orientation angles.

A Taylor series is a commonly used representation that transforms a nonlinear function into a series of polynomial terms. If the \( \exp() \) term in Eq. (4) is represented by a Taylor series, Eq. (4) can be rewritten as

\[
\alpha(\eta) = \left[ 1 - \left(1 - (2ecd\sin^2 \theta) + \frac{(2ecd\sin^2 \theta)^2}{2} - \cdots \right) \right] \cos^2 (\eta - \psi) \tag{5}
\]

When \( (2ecd\sin^2 \theta) \ll 1 \), or when light absorption is weak, the polarization angle-dependent absorptance, \( \alpha(\eta) \), can be simplified as

\[
\alpha(\eta) \approx (2ecd) \sin^2 \theta \cos^2 (\eta - \psi) \approx \alpha^\circ \sin^2 \theta \cos^2 (\eta - \psi) \tag{6}
\]

where \( \alpha^\circ \equiv (2ecd) \) contains all non-orientational quantities. In the simplified form of \( \alpha(\eta) \) in Eq. (6), \( \alpha^\circ \) corresponds to the maximum absorptance that can be measured when all transition dipole moments are parallel to the incident light polarization direction. Later in the last discussion section, more quantitative description is provided about the validness of the weak-absorption approximation in terms of the analysis results.

It is noted that in Eq. (6), the non-orientational term \( [\alpha^\circ = 2ecd] \) is separated from the orientational term \( [\sin^2 \theta \cos^2 (\eta - \psi)] \). Interestingly, the orientational term can be alternatively expressed as the inner product of the unit vector of the light polarization, \( \hat{e}_E \), and the directional unit vector of the transition dipole moment, \( \hat{e}_\mu \), as

\[
\alpha(\eta) = \alpha^\circ \left[ \hat{e}_E(\eta) \cdot \hat{e}_\mu(\psi, \theta) \right]^2 \tag{7}
\]

where \( \hat{e}_E(\eta) = (\cos \eta, \sin \eta, 0) \) and \( \hat{e}_\mu(\psi, \theta) = (\cos \psi \sin \theta, \sin \psi \sin \theta, \cos \theta) \). This expression of absorptance as the inner product is useful for an analytical description of absorptance using an ODF in the next section.
2.2. Polarization profiles of orientationally broadened transition dipole moments

Unlike conventional polarization analysis methods, this newly proposed analysis method uses polarization-dependent absorption profiles of two non-parallel transition dipole moments. Figure 2 shows a schematic presentation of broadening and rotation of a molecule represented by two orthogonal transition dipole moments. The primary transition dipole moment $\mu_1$ represents the main molecular axis with a high symmetricity, e.g., the main chain axis of a polymer. The secondary transition dipole moment $\mu_2$ represents a different vibrational mode that is orthogonal to $\mu_1$. If $\mu_1$ and $\mu_2$ are assumed to be broadened by the same degree, their local ODF with respect to the mean direction of each transition dipole moment will be represented by the same local ODF, $\rho(\beta)$. Rotation of a molecule from the molecular coordinate into the laboratory coordinate is represented by the Euler rotation matrix as

$$ R(\psi, \theta, \phi) = \begin{pmatrix} \cos \psi & -\sin \psi & 0 \\ \sin \psi & \cos \psi & 0 \\ 0 & 0 & 1 \end{pmatrix} $$(8)

where $\psi$, $\theta$, and $\phi$ are the azimuthal, axial, and rotational angles. Then, from Eq. (7), absorptance $\alpha_1(\eta)$ for $\mu_1$ can be expressed as

$$ \alpha_1(\eta) = \alpha^2_1 \int_0^{2\pi} \int_0^\pi \left[ \hat{e}_E(\eta) \cdot \hat{e}_{\mu_1} \right]^2 \rho(\beta) \sin \beta \sin \gamma \, d\beta \, d\gamma $$

(9)

where $\hat{e}_z = (0, 0, 1)$ is the unit vector of original $\mu_1$ direction in the molecular coordinate before broadening and rotation; and $\beta$ and $\gamma$ are the axial and rotational angles in the molecular coordinate, respectively.

If the local ODF is cylindrically symmetrical, $\rho(\beta)$ is independent of $\gamma$. Then, integration of Eq. (9) with respect to $\gamma$ becomes:

$$ \frac{\alpha_1(\eta)}{\alpha_1^2} = \frac{1}{2} \left[ 1 - \sin^2 \theta \cos^2 (\eta - \psi) \right] + \frac{1}{2} \left[ 3 \sin^2 \theta \cos^2 (\eta - \psi) - 1 \right] \int_0^\pi \cos^2 \beta \rho(\beta) \sin \beta \, d\beta $$

(10)

Derivation of the absorptance of the secondary transition dipole moment, $\alpha_2(\eta)$, is similar to that of $\alpha_1(\eta)$, but with an additional step. First, the secondary transition dipole moments is set along the $z$ axis and broadens by $\rho(\beta)$ with respect to the $z$ axis. The broadened $\alpha_2(\eta)$ is rotated by $R(\psi, \theta, \phi)$ around the $y$ axis toward the $x$ axis, followed by rotation by $R(\psi, \theta, \phi)$ into the laboratory coordinate. The analytical form of $\alpha_2(\eta)$ becomes:

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\[ \alpha_2(\eta) = \alpha_2^o \int_0^{2\pi} \int_0^{\pi} \left[ \mathbf{e}_z(\eta) \mathbf{R}(\psi, \theta, \phi) \mathbf{R} \left( \frac{\pi}{2} \right) \mathbf{e}_z \right] \rho(\beta) \sin \beta \, d\beta \, d\gamma \]  

(11)

where \( \mathbf{R} \left( \frac{\pi}{2} \right) \) denotes the rotation matrix around the \( y \) axis by \( \frac{\pi}{2} \). After the integration with respect to \( y \), Eq. (11) becomes:

\[
\frac{\alpha_2(\eta)}{\alpha_2^o} = -\frac{1}{2} \left\{ \left[ \cos \theta \cos \phi \cos (\eta - \psi) + \sin \phi \sin (\eta - \psi) \right]^2 - 1 \right\} 
+ \frac{1}{2} \left\{ [3\cos \theta \cos \phi \cos (\eta - \psi) + \sin \phi \sin (\eta - \psi)]^2 - 1 \right\} \times \int_0^{\pi} \cos^2 \beta \rho(\beta) \sin \beta \, d\beta
\]

(12)

For visualization of the polarization-dependent absorbance profiles of \( \alpha_1(\eta) \) and \( \alpha_2(\eta) \), an analytical function is used for \( \rho(\beta) \) in Eqs. (10) and (12). It should be noted that this analytical model function is used simply for data simulation, not used for data analysis. A von Mises-Fisher distribution function, \( \rho_{\text{vMF}}(\beta) \), shown in Fig. 3a, is widely used to represent a cylindrical ODF [24]. A von Mises-Fisher distribution function monotonically decreases from the maximum at \( \beta = 0 \), and its orientation broadening is represented by a parameter, called the concentration parameter, \( k \). When \( k \) increases, \( \rho_{\text{vMF}}(\beta) \) becomes narrower. For example, when \( k \) approaches to \( \infty \), the ODF has no broadening. Figure 3a shows two examples of \( \rho_{\text{vMF}}(\beta) \) plotted for two \( k \) values. Using the von Mises-Fisher distribution function for \( \rho(\beta) \), polarization-dependent absorbance profiles \( \alpha_1(\eta) \) and \( \alpha_2(\eta) \) are calculated from Eqs. (10) and (12) for two different Euler rotation angles, as shown in Figs. 3b and 3c. For comparison, they show \( \alpha_1(\eta) \) and \( \alpha_2(\eta) \) with an infinitely narrow ODF, represented as \( \rho_{\text{vMF}}(\beta) \) with \( k = \infty \). In the presence of broadening, the minimum absorbance becomes non-zero. The maximum values of \( \alpha_1(\eta) \) and \( \alpha_2(\eta) \) can either increase or decrease, depending on \( (\psi, \theta, \phi) \) and \( k \). These simulated polarization profiles are used for demonstration of 3D angles calculation and error analysis later in this paper.

### 2.3. Legendre polynomials for an orientation distribution function

For molecular orientation with cylindrical symmetry, the ODF can be expressed with a series of Legendre polynomials, \( P_n(\cos \beta) \), and the coefficients, \( \langle P_n \rangle \) as

\[
\rho(\beta) = \sum_{n=0}^{\infty} \left\{ n + \frac{1}{2} \right\} \langle P_n \rangle P_n(\cos \beta)
\]

(13)

Because of the symmetry with respect to the mirror plane perpendicular to the principal axis, all the odd-order terms in Eq. (13) are equal to zero. In addition, polarization-dependent IR absorbance signals are associated only with \( P_0(\cos \beta) \) and \( P_2(\cos \beta) \) terms because of the square dependence of the absorbance on the product of the electric field and the transition dipole moment [2,23]. The first two even-order Legendre polynomials, associated with polarization IR, are:

\[ P_0(\cos \beta) = 1 \]

\[ P_2(\cos \beta) = 3\cos^2 \beta - 1 \]
\[ P_0(\cos \beta) = 1 \]  \hspace{1cm} (14)

\[ P_2(\cos \beta) = \frac{1}{2}(3\cos^2 \beta - 1) \]  \hspace{1cm} (15)

While the zero-order coefficient, \( \langle P_0 \rangle \), is always equal to one, the second-order coefficient, \( \langle P_2 \rangle \), varies from \(-\frac{1}{3}\) to 1. \( \langle P_2 \rangle \), also called as the order parameter, is used as a metric of the breadth of an ODF. For an infinitely narrow distribution parallel to the symmetry axis, \( \langle P_2 \rangle \) is equal to one. For an isotropic distribution, \( \langle P_2 \rangle \) is equal to zero. For a distribution where all orientations are perpendicular to the symmetry axis, \( \langle P_2 \rangle \) becomes equal to \(-\frac{1}{3}\).

Now that an ODF is expressed as a generalized form of Legendre polynomials, the absorptance of the primary and secondary transition dipole moments in Eqs. (10) and (12), respectively, can be expressed by the Legendre polynomial coefficients. The integral term common in Eqs. (10) and (12) can be rewritten as

\[ \int_0^\pi \cos^2 \beta \rho(\beta) \sin \beta d\beta = \frac{2\langle P_2 \rangle + 1}{3} \]  \hspace{1cm} (16)

By inserting Eq. (16) into Eq. (10), the absorptance of the primary transition dipole moment is expressed as

\[ \frac{\alpha_1(\eta)}{\alpha_1^*} = \langle P_2 \rangle \sin^2 \theta \cos^2 (\eta - \psi) + \frac{1}{3}(1 - \langle P_2 \rangle) \]  \hspace{1cm} (17)

Similarly, by inserting Eq. (16) into Eq. (12), the absorptance of the secondary transition dipole moment is calculated as

\[ \frac{\alpha_2(\eta)}{\alpha_2^*} = \langle P_2 \rangle [\cos \theta \cos \phi \cos (\eta - \psi) + \sin \phi \sin (\eta - \psi)]^2 + \frac{1}{3}(1 - \langle P_2 \rangle) \]  \hspace{1cm} (18)

In a conventional non-tomographic approach to polarization scanning spectroscopy, the apparent order parameter, \( \langle P_2' \rangle \), is often determined by the maximum and minimum values of a polarization profile \([5,12,32]\). Using Eq. (17), the maximum and minimum absorptances, \( \alpha_{\text{max}} \) and \( \alpha_{\text{min}} \), respectively, are calculated and used to relate the apparent order parameter, \( \langle P_2' \rangle \), with the original order parameter, \( \langle P_2 \rangle \).
\[ \langle P_2 \rangle = \frac{\alpha_{\max} - \alpha_{\min}}{\alpha_{\max} + 2\alpha_{\min}} = \frac{\langle P_2 \rangle \sin^2 \theta}{1 - \langle P_2 \rangle \cos^2 \theta} \]  

(19)

Equation (19) shows that \( \langle P_2' \rangle \) becomes equal to \( \langle P_2 \rangle \) only when \( \theta = \pi/2 \). This is why the apparent \( \langle P_2' \rangle \) determined by the maximum and minimum values of a polarization-dependent measurement can be meaningful only when the mean orientation direction is already known to be parallel to the polarization plane; e.g., stretched films \([12]\) and fibers \([5, 11]\). However, if the mean direction of the molecular axis is unknown from the polarization plane, the apparent \( \langle P_2' \rangle \) cannot be used as the order parameter of the original ODF. This clearly shows that measurement of the order parameter is not separable from a measurement of the 3D angle of the mean molecular orientation.

2.4. Calculation of 3D angles (\( \psi, \theta, \phi \)) and order parameter \( \langle P_2 \rangle \)

This section describes how to determine the 3D orientation angles (\( \psi, \theta, \) and \( \phi \)) and the order parameter \( \langle P_2 \rangle \) using \( \alpha_1(\eta) \) and \( \alpha_2(\eta) \). First, the azimuthal angle \( \psi \) of the molecular main axis can be directly measured from the phase of the \( \alpha_1(\eta) \) profile, as shown in Eq. (17),

\[ \psi = \eta_{1,\max} \quad (0 \leq \psi \leq \pi) \]  

(20)

where \( \eta_{1,\max} \) is the polarization angle at \( \alpha_{1,\max} \). It is noted that because of inversion symmetry of the electric field of linearly polarized light, this linear polarization-based measurement can determine the azimuthal angle \( \psi \) only in the range of from 0 to \( \pi \) and cannot determine the absolute phase of the orientation. The other two angles, \( \theta \) and \( \phi \), cannot be directly measured from a single polarization profile, as discussed above. To calculate the other two angles, three intermediate parameters are defined using the phase angles and the maximum and minimum values of both polarization profiles.

The phase difference is defined as \( \Delta \eta \equiv \eta_{2,\max} - \eta_{1,\max} \), and its relation with \( \theta \) and \( \phi \) can be analytically expressed using the solution of \( \frac{d\alpha_2(\eta)}{d\eta} = 0 \) from Eq. (18), as

\[ \cos \phi \cos \theta \sin \Delta \eta = \sin \phi \cos \Delta \eta \]  

(21)

\[ \Delta \eta = \tan^{-1}(\tan \phi \sec \theta) \]  

(22)

The maximum and minimum values of \( \alpha_1(\eta) \) and \( \alpha_2(\eta) \) are expressed with \( \theta, \phi, \) and \( \langle P_2 \rangle \) from Eqs. (17) and (18) as
\[
\frac{\alpha_{1, \text{min}}}{\alpha_1^c} = \frac{1}{3}(1 - \langle P_2 \rangle) \quad (23)
\]

\[
\frac{\alpha_{1, \text{max}}}{\alpha_1^c} = \langle P_2 \rangle \sin^2 \theta + \frac{1}{3}(1 - \langle P_2 \rangle) \quad (24)
\]

\[
\frac{\alpha_{2, \text{min}}}{\alpha_2^c} = \frac{1}{3}(1 - \langle P_2 \rangle) \quad (25)
\]

\[
\frac{\alpha_{2, \text{max}}}{\alpha_2^c} = \langle P_2 \rangle (\cos^2 \phi \cos^2 \theta + \sin^2 \phi) + \frac{1}{3}(1 - \langle P_2 \rangle) \quad (26)
\]

Then, a modified form of the ratio of the minimum and maximum absorptance values of \( \alpha_1(\eta) \) is defined for the primary mode as \( M \)

\[
M \equiv \frac{(\alpha_{1, \text{max}}}{\alpha_{1, \text{min}}) - 1} = \frac{3\langle P_2 \rangle}{1 - \langle P_2 \rangle} \times \sin^2 \theta \quad (27)
\]

Similarly, for the secondary mode, a modified form of the ratio of the minimum and maximum absorptance values \( N \) is defined as

\[
N \equiv \frac{(\alpha_{2, \text{max}}}{\alpha_{2, \text{min}}) - 1} = \frac{3\langle P_2 \rangle}{1 - \langle P_2 \rangle} (\cos^2 \phi \cos^2 \theta + \sin^2 \phi) \quad (28)
\]

Using these three intermediate parameters (\( \Delta \eta, M, \) and \( N \)), the three remaining unknown variables, \( \theta, \phi, \) and \( \langle P_2 \rangle \), can be obtained from the three relations of Eqs. (22), (27), and (28). For simplifying the derivation, a temporary variable, \( P \), is defined on behalf of \( \langle P_2 \rangle \) as

\[
P \equiv \frac{3\langle P_2 \rangle}{1 - \langle P_2 \rangle} \quad (29)
\]

Then, Eq. (27) can be rewritten as

\[
\sin^2 \theta = M/P \quad (30)
\]
By inserting Eq. (30) into Eq. (28),

\[ \cos^2 \phi = \frac{(P - N)}{M} \]  

(31)

From Eqs. (21) and (28),

\[ \frac{N}{P} \cos^2 \Delta \eta = \cos^2 \phi \cos^2 \theta = \cos^2 \phi \left(1 - \sin^2 \theta \right) \]  

(32)

Insertion of Eqs. (30) and (31) into Eq. (32) leads to a quadratic equation with respect to \( P \) as

\[ (P - M)(P - N) = MN\cos^2 \Delta \eta \]  

(33)

The solution of the quadratic equation is:

\[ P = \frac{1}{2} \left[ (M + N) \pm \sqrt{(M + N)^2 - 4MN\left(1 - \cos^2 \Delta \eta \right)} \right] \]  

(34)

When this solution is inserted into Eq. (31),

\[ \cos^2 \phi = \frac{1}{2M} \left[ (M - N) \pm \sqrt{(M - N)^2 + 4MN\cos^2 \Delta \eta} \right] \geq 0 \]  

(35)

Because both \( M \) and \( N \) are positive, the condition \( \cos^2 \phi \geq 0 \) can be met only with the positive sign in front of the square root term in Eq. (35) as

\[ \cos^2 \phi = \frac{1}{2M} \left[ (M - N) + \sqrt{(M - N)^2 + 4MN\cos^2 \Delta \eta} \right] \]  

(36)

By inserting Eq. (36) back into Eq. (31), \( P \) can be expressed as a single-signed value as

\[ P = \frac{1}{2} \left[ (M + N) + \sqrt{(M - N)^2 + 4MN\cos^2 \Delta \eta} \right] \]  

(37)

Now that \( P \) can be determined with the three observables, \( \Delta \eta, M, \) and \( N \), Eq. (37) can be inserted into Eqs. (29), (30), and (31), providing the values of \( \langle P^2 \rangle, \theta, \) and \( \phi \), respectively.
\[ \langle P_2 \rangle = \frac{P}{P + \frac{3}{3}} \quad (38) \]

\[ \theta = \sin^{-1} \sqrt{M/P} \quad (0 \leq \theta \leq \pi) \quad (39) \]

\[ \phi = \cos^{-1} \left[ \pm \sqrt{(P - N)/M} \right] \quad (-\pi \leq \phi \leq \pi) \quad (40) \]

The sign in the brace of Eq. (40) is determined from the sign of \( \tan \Delta \eta \), from Eq. (21). It is important to know that a given set of observables (\( \Delta \eta, M, \) and \( N \)) will generate two sets of solutions for \( \theta \) and \( \phi \) from Eqs. (21) and (39). If the first solution pair is set as \( 0 \leq \theta_1 < \pi/2 \) and \( 0 \leq \phi_1 \leq \pi \), the second pair is its mirror image to the plane, as \( \theta_2 = \pi - \theta_1 \) and \( \phi_2 = -\phi_1 \). The existence of two solution pairs for \( \theta \) and \( \phi \) is because the transition dipole moments with a reflection symmetry to each other with respect to the polarization plane are indistinguishable in their polarization profiles.

Figure 4 summarizes how the six observables from the polarization profiles of two orthogonal IR absorption modes are used to simultaneously determine all 3D angles, \( \psi, \theta, \) and \( \phi \), and the order parameter, \( \langle P_2 \rangle \). It should be noted that the intermediate parameters, \( M, N, \) and \( \Delta \eta \), are dimensionless and are not affected by variation in sample conditions, such as concentration, thickness, absorption frequency, and absorption cross section. It should also be noted that the \( \langle P_2 \rangle \) value determined by this method is for the original molecular-coordinate ODF with respect to the mean molecular orientation direction, which is not affected by the out-of-plane tilting.

### 2.5. Error analysis

The earlier sections show that the analytical solutions of the 3D angles and the order parameter of molecular orientation can be obtained from a simple calculation with polarization dependent absorptances observed from two orthogonal IR modes. However, experimental data contains uncertainty or unwanted error in the measurement due to imperfect polarization optics, detector noise, and other system fluctuations. In this section, we examine how the errors in the input observables propagate to the intermediate parameters and to the outputs of the 3D angles and the order parameter. The uncertainty of each variable is represented by the standard deviation. The uncertainty of an output value is calculated from the uncertainties of the input values using the following error propagation relation assuming that there is no correlation between any input observables,

\[ \delta f(x_1, \ldots, x_n) = \sqrt{\left( \frac{\partial f}{\partial x_1} \right)^2 (\delta x_1)^2 + \cdots + \left( \frac{\partial f}{\partial x_n} \right)^2 (\delta x_n)^2}. \quad (41) \]
As expected from the complex relations among the input observables and the output variables, their error propagations are non-linear and complex. Instead of listing all error propagation equations of each output variable, the uncertainties in the output values are examined using simulation data generated with known input variables. The two examples of polarization profiles previously presented in Figs. 3b and 3c are used for this uncertainty analysis.

In actual experiments, measured transmittance may include non-negligible contributions from reflection from interfaces or scattering, resulting in an overestimation of absorptance \( [33] \). Because those factors can be both wavelength- and polarization-dependent, one may need to consider their effects into an analysis of polarization-IR absorptance measurements although those contributions are not discussed in this paper.

Table 1 shows how the input observables are converted to the intermediate parameters and then to the output values. The results confirm that the output results of this calculation correspond to the original input values used to generate the tested simulated data. It is also noted that the 3D angles of the mirror image of the original molecular orientation are also calculated as a complementary solution. In Table 1, the uncertainties (the standard deviations) of the intermediate parameters and the output values are computed based on the error propagation relation of Eq. (41).

The uncertainty in \( \psi \) is identical to the uncertainty in the input \( \eta_{1,\text{max}} \) from Eq. (20). Calculation of the uncertainties of \( \phi \) and \( \theta \) is more complicated but their output uncertainties are in the same order of magnitude with the input uncertainties. In these two specific examples, the output uncertainty in \( \langle P_2 \rangle \) is found to be 0.02 or lower, which can be considered as very small, compared to the whole range of \( \frac{1}{3} \leq \langle P_2 \rangle \leq 1 \). It should be noted that the calculated output uncertainties are for these two specific simulation data, and the resulting uncertainty will vary non-linearly with the input observables as well as their uncertainties.

### 2.6. Validity of the weak absorption approximation

Earlier in Eq. (4), polarization angle-dependent absorptances, \( a(\eta) \), of all parallel transition dipole moments is expressed as \( \cos^2(\eta - \psi) \) multiplied by an amplitude containing an exponential function. Then, the original form of \( a(\eta) \) is simplified as a product of a non-orientational term and an orientational term using the weak absorption approximation. The simplified form of \( a(\eta) \) is used to derive the following ODF-broadened absorptance into Eqs. (10) and (12) for the primary and the secondary modes, respectively. Here, the weak absorption approximation is examined in terms of the analysis outputs of 3D orientation angles and order parameters. For simplicity, the ODF-broadened absorptances calculated from the simple and the original forms of \( a(\eta) \) are denoted as \( a_{\text{ODF}}^{\text{simplified}}(\eta) \) and \( a_{\text{ODF}}^{\text{original}}(\eta) \), respectively. Unlike \( a_{\text{ODF}}^{\text{simplified}}(\eta) \), \( a_{\text{ODF}}^{\text{original}}(\eta) \) cannot be expressed as a simple analytical equation without integrals. Therefore, a numerical calculation is performed using a von Mises-Fisher function as a model ODF for \( a_{\text{ODF}}^{\text{original}}(\eta) \).
Figure 5 shows numerically calculated $\alpha_{\text{ODF original}}(\eta)$ for three different $\alpha^\circ$ values, which are compared with the corresponding $\alpha_{\text{ODF simplified}}(\eta)$. The shapes of the $\alpha_{\text{ODF original}}(\eta)$ curves correspond to an offset cosine function, which is similar to the shape of $\alpha_{\text{ODF simplified}}(\eta)$. Also, the phases are identical between $\alpha_{\text{ODF original}}(\eta)$ and $\alpha_{\text{ODF simplified}}(\eta)$. The only difference between the two curves is the amplitude and the offset. As $\alpha^\circ$ increases, $\alpha_{\text{ODF simplified}}(\eta)$ increases greater than $\alpha_{\text{ODF original}}(\eta)$, exhibiting the inadequacy of the weak absorption approximation for a large $\alpha^\circ$ case. However, the concurrent polarization analysis introduced in this paper is not performed based on the absolute absorptance values but on the phase angles and the maximum-to-minimum ratios, $M$ and $N$. Interestingly, $M$ values calculated from $\alpha_{\text{ODF original}}(\eta)$ and $\alpha_{\text{ODF simplified}}(\eta)$ are very close to each other even when $\alpha^\circ$ is close to one. The closeness in $M$ between $\alpha_{\text{ODF original}}(\eta)$ and $\alpha_{\text{ODF simplified}}(\eta)$ indicates that the formulation derived using the weak absorption approximation can still be useful for the concurrent polarization analysis. In addition, both $\alpha_{\text{ODF original}}(\eta)$ and $\alpha_{\text{ODF simplified}}(\eta)$ are not affected by $\alpha^\circ$, which suggests that the 3D angles and the order parameter determined by the analysis are not strongly influenced by variation in sample thickness, concentration, and absorption cross section, even when $\alpha^\circ$ is large. In Eq. (27), when $\alpha^\circ$ increases from 0.01 to 0.99 (corresponding to optical densities from 0.004 to 2), the relative variations in $M$ values are as low as 1.6% and 4% for $\theta = 60^\circ$ and $30^\circ$, respectively. This difference is comparable to or smaller than typical experimental uncertainty values in $M$. This unexpected insensitivity of intermediate parameters to sample variations even at a strong absorption condition demonstrates that the concurrent polarization analysis method based on dimensionless parameters can be effective for a wide range of absorptance.

3. Conclusion

A new non-tomographic approach based on polarization IR spectroscopy has been described to measure the 3D angles of the mean molecular orientation and the order parameter of the local molecular orientation. Six input observables from polarization profiles of two non-parallel transition dipole moments are converted into three intermediate, dimensionless parameters. Then, a single-step, non-iterative calculation using these parameters determines the 3D Euler angles ($\psi$, $\theta$, and $\phi$) and the order parameter, $\langle P_2 \rangle$, without requiring any analytical model function for the orientational distribution function. Usage of the relative intermediate parameters makes this concurrent polarization IR analysis method insensitive to variations in the sample concentration, thickness, and absolute absorption cross section. When applied to polarization IR microscopy, this concurrent polarization analysis method will provide a full orientational image map with a diffraction limited spatial resolution without tilting that tomographies require. The formulation in the paper is targeted for polarization IR imaging, but the same principle of this polarization analysis method can be applied to Raman imaging, which would expand the application systems of 3D orientation imaging.

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Fig. 1.
Polarization angle dependence of transmitted light intensity through a collection of aligned transition dipole moments. The incident light, \( I(0) \), propagating along the z axis, is linearly polarized with the polarization angle rotated by \( \eta \) from the x axis in the xy plane. All transition dipole moments are aligned parallel in the xz plane with the tilting angle of \( \theta \) from the z axis. The magnitude of the transition dipole moment, equivalent to the absorption cross section, is represented by \( \epsilon \). The terms \( d \) and \( c \) denote the sample thickness and the concentration, respectively. As the light passes through the sample, only \( E_x \) is reduced by absorption but \( E_y \) is unaffected.
Fig. 2.
Schematic presentation of broadening and rotation of molecular orientation. The orientational broadening is represented by $\rho(\beta)$, where $\beta$ denotes the axial angle of an individual $\mu$ from the mean orientation direction, $\langle \mu \rangle$. The molecular rotation is represented by the rotation matrix $R(\psi, \theta, \phi)$ from the molecular coordinate to the laboratory coordinate. The incident light propagates in the direction of the $z$ axis, and the light polarization plane is on the $xy$ plane. $\eta$ is the polarization angle with respect to the $x$ axis.
Fig. 3.
(a) Plots of the von Mises-Fisher function $\rho_{\text{vMF}}(\beta)$ for two different $k$ values. (b) and (c) Plots of absorptance calculated from Eqs. (10) and (12) for the primary (red) and the secondary (blue) transition dipole moments using two different sets of orientation angles of the mean orientation directions. The 3D angles used for calculation are indicated above each figure. For comparison, absorptance profiles from unbroadened ODF ($k = \infty$) are plotted as the solid lines. The dashed lines indicate absorptance profiles calculated from broadened $\rho_{\text{vMF}}(\beta)$ with $k = 10$ (b) and $k = 50$ (c). For both (b) and (c), $\alpha_1 = 0.9$ and $\alpha_2 = 0.8$. 
Fig. 4.
A flow chart of the concurrent polarization analysis method for determination of the 3D angles ($\psi$, $\theta$, and $\phi$) of the mean molecular orientation and the order parameter $\langle P_2 \rangle$ of the local orientation distribution using polarization profiles of two orthogonal IR modes. The intermediate parameters ($\Delta \eta$, $M$, and $N$) are calculated from the six input observables of the phase angles and the maximum and minimum absorptances of the two polarization profiles.
Fig. 5.
(a), (b), (c) Comparison of polarization angle-dependent absorptance calculated for ODF-broadened orientation based on the simplified and the original forms of $\alpha(\eta)$. The calculation is performed for the primary mode, and the axial angle $\theta = 60^\circ$. The von Mises-Fisher function with $k = 10$ is used as the model ODF for the numerical calculation. (d), (e) The maximum-to-minimum ratio, represented by $M$ in Eq. (27) is plotted as a function of $\alpha^\circ$ for different $\theta$. 

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Table 1.
Demonstration of determination of the 3D angles and $\langle P_2 \rangle$ using observables and intermediate parameters from the simulated polarization absorptance profiles shown in Fig. 3. The input uncertainties for phase angle $\eta$ and absorptance $\alpha$ are assumed to be 2° and 5%, respectively, for Fig. 3b, and 5° and 10% for Fig. 3c. The parentheses for $\theta$ and $\phi$ indicate the second solution for the 3D angles of the mirror image molecular orientation with respect to the polarization plane.

| Polarization IR Data | Input observables | Intermediate parameters | Output values |
|----------------------|-------------------|-------------------------|---------------|
| Fig. 3b              | $\eta_{\text{max}}$ | 45° ± 2°               | $\Psi$ 45° ± 2° |
|                      | $\eta_{\text{max}}$ | 161° ± 2°             | $\Delta \eta$ 116° ± 3° |
|                      | $\alpha_{1, \text{max}}$ | 0.68 ± 0.03         | $\theta$ 80° (100°) ± 1° |
|                      | $\alpha_{1, \text{min}}$ | 0.099 ± 0.004  | $\phi$ 160° (–160°) ± 1° |
|                      | $\alpha_{2, \text{max}}$ | 0.17 ± 0.01          | $\langle P_2 \rangle$ 0.67 ± 0.02 |
|                      | $\alpha_{2, \text{min}}$ | 0.088 ± 0.004        |               |
|                      | $\eta_{\text{max}}$ | 60° ± 5°               | $\Psi$ 60° ± 5° |
|                      | $\eta_{\text{max}}$ | 109° ± 5°             | $\Delta \eta$ 49° ± 7° |
|                      | $\alpha_{1, \text{max}}$ | 0.23 ± 0.02        | $\theta$ 30° (150°) ± 3° |
|                      | $\alpha_{1, \text{min}}$ | 0.018 ± 0.002  | $\phi$ 45° (–45°) ± 7° |
|                      | $\alpha_{2, \text{max}}$ | 0.67 ± 0.07          | $\langle P_2 \rangle$ 0.94 ± 0.007 |
|                      | $\alpha_{2, \text{min}}$ | 0.016 ± 0.002        |               |