Quantitative absorbance spectroscopy with unpolarized light: Part I. Physical and mathematical development

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ABSTRACT

A new approach to the use of spectroscopic absorbance measurements for anisotropic crystals allows results to be extracted using unpolarized light incident on random crystal orientations. The theory of light propagation in anisotropic absorbing crystals is developed from Maxwell’s equations to devise an expression for the transmittance of linearly polarized light traveling in an arbitrary direction in weakly absorbing media. This theory predicts the distribution of transmittance and absorbance as a function of direction and polarization angle of incident light. It is shown how a previously deduced empirical expression, commonly used in infrared spectroscopy, is a good approximation to the full theory under a wide range of conditions. The new theory shows that principal polarized absorbances correspond to the eigenvalues of an absorbance ellipsoid. An expression is derived for the unpolarized absorbance as a function of the angles describing incident light direction,

\[ A_{\text{unpol}}(\phi, \psi) = \frac{1}{2} \left[ A_a (\cos^2 \phi \cos^2 \psi + \sin^2 \psi) + A_b (\cos^2 \phi \sin^2 \psi + \cos^2 \psi) + A_c \sin^2 \phi \right]. \]

Integration of this expression over all incident angles leads to a simple relationship between total measured unpolarized absorbance and the three principal polarized absorbances. Using this theory, a procedure is proposed for estimating both total \( A_a + A_b + A_c \) and principal absorbances from spectroscopic measurements of absorbance using unpolarized light on a set of randomly oriented crystals.

Keywords: Absorption index theory, anisotropic media, unpolarized light, spectroscopy

INTRODUCTION

Optical indicatrix theory is well known and based on the work of Fletcher (1892). It provides a convenient mechanism for describing the optical properties of crystals, and allows calculation of refractive indices for light propagating through anisotropic media (Nesse 1986; Kliger et al. 1990). Phemister (1954) shows how the optical indicatrix theory is a direct consequence of Maxwell’s electromagnetic (EM) theory of light. In analogy with the optical case, an indicatrix ellipsoid is often used for analyzing measurements of absorbance of electromagnetic radiation in anisotropic minerals. Important mineralogical applications include using infrared (IR) spectroscopy to quantify water content of minerals like olivine and pyroxenes, and also to provide clues to the crystallography of water substitution. The solution of Maxwell’s equations for light propagation in media where both refractive index and absorption vary anisotropically has been largely neglected by modern researchers. Instead they have relied upon empirical evidence to determine relationships between various quantities, such as the angular dependence of absorbance, or transmittance on crystallographic orientation of polarized light in biaxial minerals. Consequently, there has been debate on the appropriate form of this relationship with several alternatives suggested (see Libowitzky and Rossman 1996). It has also been claimed that, in general, only polarized light can be used to recover principal and total absorbances and that use of unpolarized light cannot in general yield quantitative data (Libowitzky and Rossman 1996; Bell et al. 2003, 2004). Consequently, the belief has evolved that a major barrier to the practical use of IR spectroscopy (with polarized light) is the difficulty of performing the necessary orientation of fine-grained crystals (Asimow et al. 2006). A technique that avoided these difficulties altogether and used only unpolarized absorbance measurements would therefore have considerable appeal.

As has been shown by many (see references above), for practical purposes, analyses from absorption spectroscopy using polarized light can only be effected on crystal sections oriented parallel to the principal optical axes. The reason is that in addition to absorption, light traveling through other sections may undergo birefringence (splitting of light into two perpendicularly polarized waves propagated with different paths), the amount of path deviation depending on the refractive indices and the thickness of the section (see Nye 1957; Bloss 1961;
Born and Wolf 1980), resulting in complex relations. Optical activity will also cause additional complications (see Born and Wolf 1980). Finding suitably oriented crystals is often difficult in experimental run products, or natural samples with fine grain size, and instead mineralogists have sometimes tended to devote their efforts to large gem quality crystals that may not address the most important petrological problems. Here we show that simple analyses of unpolarized radiation permits quantitative information to be gleaned from a crystal with any orientation, allowing the recovery of the principal absorbances by standard statistical means from a population of crystals with unknown but random orientations. For crystals of orthorhombic or higher symmetry where orientations can be determined, for example by electron back-scattering diffraction (EBSD) or a universal stage, principal absorbances can be recovered from measurements on just three differently oriented grains. The statistical approach is particularly advantageous for the study of crystaline phases of low symmetry (i.e., monoclinic or triclinic) because it allows the principal absorbances to be determined without having to know their orientations relative to the crystal axes.

In this paper, we re-examine the early work on theory of light propagation (carried out in the latter part of the 19th and early 20th centuries) to arrive at a theory for transmittance (or absorbance) of both polarized and unpolarized radiation in anisotropic crystals. By returning to the fundamental theory based on solutions to Maxwell’s equations we are able to resolve the questions regarding the angular dependence of transmittance, as well as provide a useful self-consistent theory for absorption of polarized and unpolarized light in anisotropic crystals. In particular, we derive an expression for the dependence of transmittance on polarization angle for arbitrary directions in general biaxial crystals. The theory is valid in the case of weak absorbance (i.e., for minerals that are not opaque in thin section) for light propagation in a birefringent and absorbing anisotropic medium. The new theory leads to an expression for absorbance of unpolarized light, propagating in an arbitrary direction, in terms of the principal polarized absorbances. Using the theory we are able to derive a simple method for extracting quantitative information on total absorbance using unpolarized radiation measurements on randomly oriented minerals, i.e., without the need to align mineral samples in any special direction, or even knowing the positions of the principal axes of the indicatrix ellipsoid. We set out the theory in some detail for both polarized and unpolarized cases, verify the resulting formulae with a numerical test and describe the implications. In a companion paper (Kovács et al. 2008) we demonstrate the accuracy of the relationships derived here for real minerals. In addition, we compare the results of using the technique to estimate principal absorbances with those obtained with standard techniques and polarized light along principal directions.

**Theory**

In this section, we determine the relationship between transmittance (or absorbance) and polarization angle from the fundamental physics of light propagation in absorbing anisotropic media. First, we briefly review the case of light propagation in non-absorbing crystals with anisotropic refractive index, before dealing with the more general case.

### Light Propagation in Non-Absorbing Anisotropic Crystals

The theory of light propagation in non-absorbing anisotropic crystals was well understood by the early part of the 20th century. Seminal works are by Fresnel (1866), Voigt (1902), Pockels (1906), and Born (1933). Detailed accounts are given in Nye (1957), as well as section B2 of Ramachandran and Ramaseshan (1961) (hereafter referred to as RR), and Chapter 14.3 of Born and Wolf (1980). In short, Maxwell’s equations tell us that the optical properties of a medium are determined by the relationship between the displacement vector $D$ and the electric vector $E$ of the propagating electromagnetic wave. An anisotropic medium corresponds to the case where three components of $D$ and $E$ are linearly related through

$$D = [\varepsilon] E \quad (1)$$

where $[\varepsilon]$ is the dielectric tensor. Since $D$ and $E$ are 3 component vectors $[\varepsilon]$ is in general a $3 \times 3$ matrix (second-rank tensor) and Equation 1 represents a $3 \times 3$ system of equations. By inverting we have

$$E = [\alpha] D \quad (2)$$

where $[\alpha]$ is known as the index tensor (or matrix) and is equal to the inverse of the dielectric tensor

$$[\alpha] = [\varepsilon]^{-1} \quad (3)$$

As shown in RR, on their p. 61, the action of any second rank tensor can be represented as a surface in three dimensions. This fact together with Maxwell’s equations leads to the definition of an index ellipsoid describing all possible orientations of the displacement vector

$$\alpha_{ij}x^i x^j + \alpha_{13}x^2 + 2\alpha_{12}x^2 z + 2\alpha_{15}x z + 2\alpha_{35}y^2 = 1 \quad (4)$$

where $\alpha_{ij}$ are the components of the symmetric $3 \times 3$ index matrix $[\alpha]$. The index ellipsoid derived from Maxwell’s equations is the same as the optical indicatrix of Fletcher (1892) and provides a convenient geometric method for predicting many phenomena observed with the passage of light through anisotropic media. It can be shown that the refractive index experienced by the wave with displacement vector $D$ is given by the radius of the index ellipsoid parallel to $D$. (see RR, their p. 63–64.), i.e., we have

$$n(\phi, \psi) = \rho \quad (5)$$

where the angles $(\phi, \psi)$ are the spherical coordinates of a unit vector parallel to $D$.

The general theory leads to the conclusion that given any direction of the wave normal two waves can be propagated with their vibrations linearly polarized along the principal axes of the elliptic section on the index ellipsoid normal to the wave normal. (Note that in anisotropic media, the wave normal and the ray direction are not parallel, as they are in isotropic media.) The plane perpendicular to an arbitrary incident light direction cuts the ellipsoid and creates a cross-sectional ellipse. The principal
axes of this ellipse define the electric vector directions of the two propagating waves possible in the crystal. In general the particular paths (rays) that each wave can follow are not the same, a phenomenon known as birefringence. The thicker the sample the more separated the two rays will become, since they have different refractive indices. (In uniaxial crystals, these are known as the ordinary and extraordinary ray, since the latter does not obey Snell’s law at the crystal interfaces.) Bloss (1961) explains how the index ellipsoid may be used to predict the speeds and polarization of each wave for birefringence materials, including the special cases of light incident along principal and optic axes. (An optic axis is defined as those directions for which the cross section of the index ellipsoid is circular. In uniaxial crystals, this will be along the principal c-axis. In biaxial crystals, two optic axes exist inclined to all three principal axes.)

The equation of the index ellipsoid in Equation 4 may be written in terms of an x, y, and z coordinate system oriented along its principal axes

\[
\frac{x^2}{a^2} + \frac{y^2}{b^2} + \frac{z^2}{c^2} = 1
\]  

(6)

where a, b, and c are the semi axes of the index ellipsoid (see Fig. 1a) and depend on the index tensor \([\alpha]\). Using spherical coordinates \((\phi, \psi)\) of the vibration direction (defined with respect to the principal axes in Fig. 1b) we have

\[
x = r \sin \phi \cos \psi;
\]

\[
y = r \sin \phi \sin \psi;
\]

\[
z = r \cos \phi
\]

(7)

where \(r\) is the radius of the ellipsoid in the direction given by the spherical angles \((\phi, \psi)\). Substituting Equation 7 into Equation 6 and rearranging we get the equation of the index ellipsoid in terms of spherical coordinates

\[
\frac{1}{r^2} = \frac{1}{a^2} \sin^2 \phi \cdot \cos^2 \psi + \frac{1}{b^2} \sin^2 \phi \cdot \sin^2 \psi + \frac{1}{c^2} \cos^2 \phi.
\]

(8)

Since the radius is equal to the refractive index \(n(\phi, \psi)\), we get

\[
n(\phi, \psi) = \left( \frac{1}{a^2} \sin^2 \phi \cdot \cos^2 \psi + \frac{1}{b^2} \sin^2 \phi \cdot \sin^2 \psi + \frac{1}{c^2} \cos^2 \phi \right)^{-1/2}
\]

(9)

which is Equation 9.2 on p. 155 of Bloss (1961).

**Light propagation in absorbing anisotropic crystals**

The theory of light propagation in absorbing anisotropic media is described in detail by Pancharatnam (1955) and extended by RR; see also Chapter 14.6 of Born and Wolf (1980). Here we present the essential elements for the results needed below. The above summary of light propagation in non-absorbing anisotropic media provides the setting for an extension to absorbing media. In an absorbing medium light propagation may be described by two parameters, the refractive index \(n\) and the absorption coefficient, \(k\). For example, an electric vector of a plane polarized wave traveling a distance \(z\) is given by

\[
E_z = E_o \exp \left\{ -kz \right\} \exp \left\{ -\frac{2\pi i n z}{\lambda} \right\}
\]

(10)

where \(\lambda\) is the wavelength. Due to absorption, the wave reduces to \(1/e\) of its amplitude after traveling a distance \(1/k\) in the medium.

We can rewrite Equation 10 as

\[
E_z = E_o \exp \left\{ -\frac{2\pi i n z}{\lambda} \right\}
\]

(11)

where \(n\) is a complex refractive index, \(\bar{n} = n - ik\), \(k = (\omega A)/(2\pi)\) is the extinction coefficient, and \(i\) is the imaginary constant \(-1\). Therefore an absorbing medium corresponds to a complex refractive index. To extend this to anisotropic media we follow the same approach as in the previous section but add an imaginary component to the dielectric tensor, i.e., we replace the 3 × 3 matrix \([\varepsilon]\) with a 3 × 3 complex matrix \([\varepsilon] + i[\eta]\). In this case, the index tensor also becomes complex, which we write with real and imaginary parts as \([\alpha] + i[\beta]\). Therefore Equation 3 in absorbing media becomes

\[
[\alpha] + i[\beta] = ([\varepsilon] + i[\eta])^{-1}.
\]

(12)

After rearranging and equating real and imaginary parts, we obtain

\[
[\alpha] = (I - [\varepsilon]^{-1}[\eta][\varepsilon]^{-1}[\eta])^{-1}[\varepsilon]^{-1}
\]

(13)
\[ \beta = (I - [\varepsilon]^{-1}[\eta][\varepsilon]^{-1}) [\varepsilon]^{-1}[\eta][\varepsilon]^{-1} \]  

where \( I \) is the identity matrix. In this case, \([\alpha] \) is still the index tensor (matrix) and just as before will govern the refractive index of light (and birefringence), and \([\beta] \) is known as the absorption tensor (matrix), which will determine the extinction coefficient (governing dichroism). As in the previous case, both \([\alpha] \) and \([\beta] \) are second-rank tensors and can be represented by ellipsoids, \([\alpha] \) giving the index ellipsoid and \([\beta] \) giving the absorption ellipsoid. However, in this case things are more complicated as both the real and imaginary components of the dielectric tensor influence both the index and absorption tensors. The absorption tensor also depends on wavelength, but here we develop the theory for a single wavelength \( \lambda \).

To proceed, we make the assumption that the absorption is weak, i.e., that the imaginary part of the complex dielectric tensor is small compared to unity, hence terms in \([\varepsilon]^{-1}[\eta] \) are small compared to the identity matrix, \( I \). (This will be true for most non-metallic transparent materials, and is quantified further below.) In this case we may neglect second-order terms and get

\[ [\alpha] = [\varepsilon]^{-1} \]

and

\[ [\beta] = [\varepsilon]^{-1}[\eta][\varepsilon]^{-1} \]

which gives first-order accurate expressions for the index and absorption tensors in terms of the dielectric tensors. As before an index ellipsoid is defined by the index tensor, but now we also have an absorption ellipsoid defined by the absorption tensor. The nature of light propagation in the absorbing medium will depend on the degree to which the two sets of principal axes coincide, which in turn depends on the crystallographic symmetry of the medium. For the most general case of triclinic absorbing media, none of the principal axes of the index and absorption ellipsoids are required to coincide, and for light incident in an arbitrary direction the nature of the wave propagation is determined by the cross sections of both the index and absorption ellipsoids perpendicular to the incident wave normal. (Here the effect of optical activity has been neglected. Optical activity results in a rotation of linearly polarized light on passage through a medium. Neglecting optical activity is equivalent to assuming that the absorption tensor \([\beta] \) is symmetric.) However, for orthorhombic and higher order symmetries the index and absorption principal axes are coincident.

In contrast to the non-absorbing case where incident light splits up into two linearly polarized light waves that propagate through an anisotropic crystal, Pancharatnam (1955) showed that when the principal axes of the index and absorption ellipsoids do not coincide, then the solution to Maxwell’s equations permits two elliptically polarized waves to propagate without distortion through the crystal (see Fig. 2a). (Note elliptical polarization is the most general form, and has circular and linear polarization as special cases. In elliptical polarization, the electric vector \( \mathbf{E} \) rotates about the direction of light and traces out an ellipse when viewed by an observer looking along the direction of light propagation. See Born and Wolf (1980) for more details.) In general, any type of incident light in any direction will be split
up into these two non-orthogonal elliptical polarizations upon entering the crystal. Each will propagate through the crystal with its own refractive indices and absorption coefficients. At the exit surface the two beams will combine. Our interest is in the intensity of the combined (output) light beam and how it depends on the polarization angle of incident linearly polarized light, which we denote as \( \theta_p \).

Before the theory can be developed further, an explanation is required of a geometrical construction known as the Poincaré sphere (see Fig. 2b). This is useful because any type of polarized light (elliptical, circular, or linear) can be represented as a unique point on the Poincaré sphere. The general case of elliptical polarization is determined by two angles. The first, \( \phi_{ps} \), is the ellipticity of the ellipse formed by the rotation of the \( E \)-vector and the second, \( \psi_{ps} \), is the angle between the semi-major axis of this ellipse with the reference \( x \)-axis in the cross sectional plane to the direction of incident light (see Fig. 2a). Any elliptical polarization is then uniquely represented by the point with latitude \( \psi_{ps} \) and longitude \( \phi_{ps} \), lie on the equator. Hence \( PP_{ps} \) (18) represents the first main result of this paper. It is convenient to redefine the polarization variable \( \theta_p \) by writing

\[
\theta = \theta_p - \psi_{ps},
\]

where now \( \theta \) measures the polarization of the incident light with respect to the major axis of the elliptical vibration \( P \), in the cross sectional plane (see Fig. 2a). Hence we have

\[
\frac{I_1}{I_0} = \frac{\sin^2 \theta_{ps} + \cos^2 \left( \frac{\psi_{ps} - \theta_p}{2} \right)}{\cos^2 \phi_{ps} + \cos^2 \psi_{ps}},
\]

\[
\frac{I_2}{I_0} = \frac{\sin^2 \phi_{ps} + \sin^2 \left( \frac{\psi_{ps} - \theta_p}{2} \right)}{\cos^2 \phi_{ps} + \cos^2 \psi_{ps}}.
\]

(21)

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\[
\frac{I_1}{I_0} = \frac{\sin^2 \theta_{ps} + \cos^2 \theta}{\cos^2 \phi_{ps} + \cos^2 \psi_{ps}},
\]

\[
\frac{I_2}{I_0} = \frac{\sin^2 \phi_{ps} + \sin^2 \theta}{\cos^2 \phi_{ps} + \cos^2 \psi_{ps}}.
\]

(23)

Therefore the initial intensity of the light beams depends on both the polarization angle, \( \theta_p \), of incident light and the positions of the two elliptical waves on the Poincaré sphere. The latter depend on principal absorbances and refractive indices in the cross sectional ellipses formed from the intersection of the direction of light with the index and absorption ellipsoids (Fig. 3). The splitting of the incident light will also induce a phase difference between the two resulting waves, \( \delta \), which is also a function of \( \theta \), details of which can be found in section 4 of RR.

The next step is propagation through the crystal a distance \( z \), after which the intensities will be reduced by factors \( e^{-2ik_1z} \) and \( e^{-2ik_2z} \), respectively (see Eq. 10), where \( k_1 \) and \( k_2 \) are the absorption coefficients of the two waves. In addition, there will be another phase delay, \( \delta_p \), between the faster and slower moving wave (due to birefringence). As before each of the quantities \( k_1 \), \( k_2 \), and \( \delta \) depend on the light direction and the cross sections of the index and absorption ellipsoids. Full solutions for each can be obtained from Maxwell’s equations (see section 4 of RR). For our purposes it is important to note that none of these depend on \( \theta \). After transmission a distance \( z \) we can use Equation 69.1 of RR to determine the total intensity of the combined waves. This gives

\[
I = I'_1 + I'_2 + 2 \left( I'_{12} \right)^2 \cos \frac{\pi}{2} \cos \left( \phi_{ps} \right) \cos \left( \theta + \delta_p \right) \cos \left( \phi_{ps} \right) \cos \left( \theta + \delta_p \right)
\]

(24)

where \( I'_1 \) and \( I'_2 \) are the intensities of the two waves after transmission. Substituting in known quantities we get

\[
\frac{I}{I_0} = \left( e^{-2ik_1z} + e^{-2ik_2z} \right) \left( \frac{\sin^2 \theta_{ps} + \cos^2 \theta}{\cos^2 \phi_{ps} + \cos^2 \psi_{ps}} \right) \left( e^{-2ik_1z} \cos^2 \theta + e^{-2ik_2z} \sin^2 \theta \right)
\]

\[
+ 2e^{-i(\delta_1 + \delta_2)z} \left( \frac{\sin^2 \theta_{ps} + \cos^2 \theta}{\cos^2 \phi_{ps} + \cos^2 \psi_{ps}} \right) \left( \frac{\sin^2 \theta_{ps} + \sin^2 \theta}{\cos^2 \phi_{ps} + \cos^2 \psi_{ps}} \right) \cos \left( \phi_{ps} \right) \cos \left( \theta + \delta_p \right)
\]

(25)

Equation 25 represents the first main result of this paper. It shows how the ratio of the total intensity of the transmitted light depends on the incident polarization angle for an arbitrary direction of light through a general biaxial birefringent absorbing crystal (keeping in mind that the initial phase lag \( \delta \) also depends on \( \theta \).
The principal axes of absorbance, and if the incident light is appreciably inclined to both we have linear polarization along the principal axes of refraction in the cross sectional plane. These considerations each suggest the simplification $\phi_{ps} = 0$, so that Equation 25 becomes

$$\frac{I}{I_o} = e^{-2kz}\cos^2 \theta + e^{-2kz}\sin^2 \theta. \quad (26)$$

Since transmittance of the incident light, $T$, is defined as $I/I_o$, we have

$$T(\theta) = T_{\text{max}}\cos^2 \theta + T_{\text{min}}\sin^2 \theta \quad (27)$$

where

$$T_{\text{max}} = e^{-2kz}, \quad T_{\text{min}} = e^{-2kz}. \quad (28)$$

This expression is commonly cited in the literature as an empirically determined relationship between transmittance and polarization angle when the incident light direction is along a principal direction of the index ellipsoid (e.g., Libowitzky and Rossman 1996). The theoretical development here provides a proof of the relationship for arbitrary incident light direction in crystals with orthorhombic symmetry or higher, which is also appropriate for most directions in monoclinic or triclinic crystals. (As stated in RR section 4, for these crystals it will only break down in a small region immediately surrounding the optic axis, but not along it.) This result does not appear to have been obtained previously, although Turrill (1972) derived the same result (from Maxwell’s equations) for the special case of light incident along the $b$-axis of a monoclinic absorbing crystal.

All of the analytical expressions here also depend on an assumption of weak absorption. As pointed out by Born and Wolf (1980), this condition corresponds to the case where the extinction coefficient, $\kappa$, is much less than one. To give a specific example, $\kappa = 0.0899$ for the “Pakistan” olivine that we have used to test the theory of this paper in Kovács et al. (2008); hence for this mineral the condition is clearly met. In general this condition will be satisfied for crystals that are transparent in a standard petrographic thin section.

To summarize the results of this section: The elliptical cross sections of the index and absorption ellipsoids determine the wave propagation properties. An angular dependence of transmittance for linearly polarized light incident in any direction has been derived from fundamental physics. This expression (Eq. 25) is a generalization of one previously proposed (Eq. 27) for polarized light incident along principal crystallographic axes of a crystal. The conditions under which the full expression reduces to a simplified relationship (i.e., Eq. 25 becomes Eq. 27) have been discussed. In what follows, we show how the new theory leads to a convenient definition of an absorbance ellipsoid (or indicatrix) that is of practical use in spectroscopy of anisotropic minerals.

**THE ABSORBANCE ELLIPSOID FOR LINEARLY POLARIZED LIGHT**

In the previous section, we derived an expression for the angular variation of transmittance of linearly polarized incident...
light for an arbitrary angle of incidence, and showed that the simple relationship (Eq. 27) is appropriate for a wide range of conditions. However, spectroscopic measurements of IR radiation are often carried out using absorbance, $A$, rather than transmittance, $T$, where

$$A = -\log_{10} T.$$  \hspace{1cm} (29)

Using Equation 27 the dependence of absorbance on polarization angle is

$$A(\theta) = -\log_{10}\left(10^{-A_{\text{max}} \sin^2 \theta + 10^{-A_{\text{min}} \cos^2 \theta}}\right)$$  \hspace{1cm} (30)

where

$$T_{\text{min}} = 10^{-A_{\text{max}}}, \quad T_{\text{max}} = 10^{-A_{\text{min}}}. \hspace{1cm} (31)$$

A convenient approximation to Equation 30 (in common use) is to take

$$A(\theta) = A_{\text{max}} \sin^2 \theta + A_{\text{min}} \cos^2 \theta$$  \hspace{1cm} (32)

where we have now redefined the angle $\theta$ to be with respect to the direction of maximum absorbance rather than maximum transmission as it is in Equation 30 ($\theta \to \theta - \pi/2$). The accuracy of Equation 32 will depend on the principal values of absorbance in the cross sectional plane perpendicular to the direction of light, $A_{\text{min}}$ and $A_{\text{max}}$. In the appendix, we quantify the conditions under which Equation 32 may be used in place of Equation 30 and hence Equation 27 in more detail. The results show that the two produce the same absorbance as $A_{\text{min}} \to 0$, and also when $A_{\text{pol}} \to 1$. By combining Equations 31 and 28, we see that both $A_{\text{min}}$ and $A_{\text{max}}$ depend linearly on the thickness of the crystal section, $z$. In practice then the first condition can usually be met by making the section thin enough. In any case, given any principal values a simple numerical calculation gives the relative error in Equation 32 (see appendix). In what follows, we will assume that the conditions on $A_{\text{pol}}$ and $A_{\text{min}}$ are met and Equation 32 gives acceptable accuracy. From here on, the theory will be based on the simplified absorbance Equation 32, but because Equation 27 has the same form as Equation 32, i.e., the one is obtained from the other by exchanging each “$T$” with an “$A$,” the derivations below would apply equally well to transmission, as given by Equation 27. In each case, the more exact expressions are recovered by simply replacing each “$A$” with a “$T$,” and the mathematics is exactly the same.

It is straightforward to show that Equation 32 is the equation of an ellipse. Consider the cross sectional ellipse in the $x$-$y$ plane of Figure 1a, which has the equation

$$\frac{1}{a^2} + \frac{1}{b^2} = 1.$$  \hspace{1cm} (33)

Note this is the 2D equivalent of Equation 4 with a diagonal index matrix and $z = 0$. Using polar coordinates we write

$$x = r\cos \theta, \quad y = r\sin \theta,$$  \hspace{1cm} (34)

where $\theta$ is the angle between the polarization vector and the semi-major axis defined as the $x$ direction in Figure 1. Combin-
common experimental setup in IR spectroscopy is to align the direction of light incidence along one of the crystallographic axes (as in Fig. 1a) and measure the absorbance of linearly polarized IR radiation. By rotating the system through 360° (2π), absorbance measurements can be obtained as a function of relative polarization angle, \( A(θ₀) \). In this way, one can experimentally determine the maximum and minimum absorbance values, \( A_{\text{min}} \) and \( A_{\text{max}} \). Repeating for all three axes gives the three principal polarization absorbances, \( A_{\text{e}}, A_{\text{o}}, \) and \( A_{\text{i}} \). Next we show, contrary to previous assertions (e.g., Libowitzky and Rossman 1996), that absorbance measurements of unpolarized light on randomly oriented samples can be used for the same purpose.

**UNPOLARIZED LIGHT PROPAGATING AT AN ARBITRARY ANGLE**

By using the absorbance ellipsoid and analytical geometry, we now extend the above theory established for linearly polarized light to the general case of unpolarized light propagating in an arbitrary direction. Our aim is to show that, contrary to assertions in recent literature, absorbance measurements of unpolarized light may be used to determine the three principal absorbances and also the total absorbance of the sample.

The geometrical situation is shown in Figure 3. Here the direction of propagation of light is at an arbitrary angle to the three principal axes \((x, y, z)\) of the absorbance ellipsoid. We use two angles to describe the propagation direction. The first, \( φ \), is the angle between the incident light and the \( z \)-axis. The second \( ψ \), is the angle between the \( x \)-axis and the projection of the incident light onto the \( xy \)-plane. These angles are simply the spherical polar angles for any point along the line of the incident light. The angles \((φ, ψ)\) also define the plane perpendicular to the incident light, which we call the \( x'y' \)-plane. The intersection of this plane with the absorbance ellipsoid forms an ellipse (shown in Fig. 3). It is convenient to define a second set of axes, which we call \((x', y', z')\), such that \( z' \) is aligned with the direction to the incoming light, while \( x' \) and \( y' \) are perpendicular axes within the \( x'y' \)-plane. Both \( z' \) and the \( x'y' \)-planes are completely defined by the direction of light, but there remains some freedom in choosing the \( x' \) and \( y' \) axes, since any pair of perpendicular axes in the inclined plane will do. To make the new set of axes complete we introduce another angle, \( ζ \), which is the angle between the \( y' \)-axis and the line formed by the intersection of the \( xy \)- and \( x'y' \)-planes. The new axis system is inclined to the principal axes of the absorbance ellipsoid, but is more convenient as it aligns with the incoming light direction (see Fig. 3). This setup is exactly the same as considered before, with the absorbance for any polarization vector within the \( x'y' \)-plane given by Equation 32. Therefore if we sum the absorbances over all angles \( θ \) in the \( x'y' \)-plane we get the total unpolarized absorbance

\[
A_{\text{unpol}}(φ, ψ) = \frac{1}{2π} \int_0^{2π} A(θ) dθ.
\]  

**Equation 40**

Using Equation 32 we have

\[
A_{\text{unpol}}(φ, ψ) = A_{\text{max}} \frac{2π}{2π} \int_0^{2π} \cos^2 θ dθ + A_{\text{min}} \frac{2π}{2π} \int_0^{2π} \sin^2 θ dθ
\]  

**Equation 41**

and after integration we get

\[
A_{\text{unpol}}(φ, ψ) = \frac{1}{2} (A_{\text{min}} + A_{\text{max}}).
\]  

**Equation 42**

Hence, the total unpolarized absorbance is just the average in the extremal polarized absorbances defined by the inclined ellipse. Moreover we know by analogy to the 3-D case, that the extremal polarized absorbances \( A_{\text{min}}^{\text{polelliptic}} \) and \( A_{\text{max}}^{\text{polelliptic}} \) are equal to the eigenvalues of the 2 \( \times \) 2 matrix governing the inclined ellipse. Hence we have

\[
A_{\text{unpol}}(φ, ψ) = \frac{1}{2} (e_{\text{min}} + e_{\text{max}})
\]  

**Equation 43**

where \( e_{\text{min}} \) and \( e_{\text{max}} \) are now the eigenvalues of the inclined elliptical cross-section defined by the propagation direction \((φ, ψ)\).

Since Equation 43 is based on the approximate expression for angular dependence of absorbance Equation 32 rather than the more accurate Equation 30, this will introduce some error in the unpolarized absorbance. In the appendix, we show results quantifying this error as a function of \( A_{\text{min}}^{\text{polelliptic}} \) and \( A_{\text{max}}^{\text{polelliptic}} \).

Our aim is now to find the relationship between the absorbance of unpolarized light in the \((φ, ψ)\) direction and the three principal absorbances \((A_{\text{e}}, A_{\text{o}}, A_{\text{i}})\) of the full ellipsoid. Since the principal absorbances are equal to the eigenvalues of the matrix, \( M \), the problem to be solved is one of geometry, namely we require the relationship between the eigenvalues of the elliptical cross section \((e_{\text{min}}, e_{\text{max}})\) with those of the full ellipsoid \((A_{\text{e}}, A_{\text{o}}, A_{\text{i}})\) in Figure 3.

The key to solving the geometrical problem is to notice that if we were able to find the equation of the ellipsoid in terms of the \((x', y', z')\) coordinate system, then that of the required elliptical cross-section would be obtained by setting \( z'=0 \). A general method for relating the two coordinate axes systems is Euler’s theorem, which says that any set of orthogonal axes \((x, y, z)\) can be rotated onto any other \((x', y', z')\) using three Euler angles. The procedure is the following: First rotate the system about the \( z \)-axis through an angle \( ψ \), then rotate about the “rotated \( y' \)-axis” through angle \( ζ \), finally, rotate about the rotated \( z \)-axis through the angle \( ζ \) (see Zwillinger 1996 for full details). As can be seen from this description (and Fig. 3) the three Euler angles \((φ, ψ, ζ)\) are exactly those used above to define the coordinate axes \((x', y', z')\) in the first place.

Euler’s theorem tells us that the coordinates of any point in the old coordinate system, \( x \), can be converted into the new coordinate system, \( x' \), by

\[
x = Rx'
\]  

**Equation 44**

where \( R \) is known as the Euler rotation matrix given by

\[
R = \begin{pmatrix}
\cos ζ & \cos ψ & -\sin ζ \\
\sin ζ & \cos ψ & -\cos ζ \\
\cos ζ & -\sin ψ & \sin ζ
\end{pmatrix}
\]  

**Equation 45**

To see that the Euler matrix works, examine what happens to a point on the incident light axis, i.e., with coordinates \((x' = 0, y' = 0, z' = 1)\). Multiplying this vector with the \( R \) matrix in Equation 44 we see that the coordinates for the same point in the old \((x, y, z)\) system are just the third column of the matrix \( R \). These are just the spherical polar coordinates of a point on
the incident light axis given earlier in Equation 7, which is the correct result.

We are now in a position to derive the equation of the absorbance ellipsoid in the new coordinate system. We simply substitute Equation 44 into Equation 38 and get

\[(Rx')^T M(Rx') = 1 \rightarrow x'^T R^T M R x' = 1.\]  

(46)

This may be written in the form

\[x'^T S x' = 1\]  

(47)

where S is the governing matrix for the ellipsoid in the new \((x', y', z')\) coordinate system

\[S = R^T M R.\]  

(48)

Note that S is symmetric, but no longer diagonal, as it was in the original coordinate system. Since R is an orthogonal matrix, the coordinate transformation of Equation 44 does not change the eigenvalues of \(M\), hence S and M have the same eigenvalues. (This can be verified quite simply from a geometrical perspective. Multiplication by matrix R only represents a rotation of coordinate axes, and so the lengths of semi-axes of the ellipsoid do not change. Hence its eigenvalues, which are determined by the semi-axes, also do not change.)

For convenience of notation we write the elements of the symmetric matrix S as

\[S = \begin{pmatrix} s_{11} & s_{12} & s_{13} \\ s_{12} & s_{22} & s_{23} \\ s_{13} & s_{23} & s_{33} \end{pmatrix}.\]  

(49)

As noted above, the equation of the inclined ellipse is found in the rotated coordinate system by setting \(z' = 0\) in Equation 47, which gives

\[\begin{pmatrix} x' & y' & 0 \\ s_{11} & s_{12} & s_{13} \\ s_{12} & s_{22} & s_{23} \\ s_{13} & s_{23} & s_{33} \end{pmatrix} \begin{pmatrix} x' \\ y' \end{pmatrix} = 1\]  

which we write as

\[\begin{pmatrix} x' & y' \end{pmatrix} S_{\text{sub}} \begin{pmatrix} x' \\ y' \end{pmatrix} = 1\]  

where S_{\text{sub}} is the \(2 \times 2\) sub-matrix in the upper left hand corner of S. The entries of S_{\text{sub}} determine the size and orientation of the inclined ellipse in Figure 3. We know from Equation 43 that the average of its eigenvalues \((e_{\text{min}}, e_{\text{max}})\) will be equal to the unpolarized absorbance measured in the direction \((\phi, \psi)\). Before proceeding we can simplify things by recalling that eigenvalues of matrices are unaffected by a rotation of axes. Therefore it does not matter where the \(x'\) and \(y'\) axes are positioned so long as they are in the \(x'-y'\) plane (see Fig. 3). This means that we can choose any convenient value for the Euler angle \(\zeta\), since it only rotates the new axis system within the \(x'-y'\) plane. Let us choose the value \(\zeta = 0\). In this case, the rotation matrix R simplifies to

\[R = \begin{pmatrix} \cos \phi \cdot \cos \psi & -\sin \psi & \sin \phi \cdot \cos \psi \\ \cos \phi \cdot \sin \psi & \cos \psi & \sin \phi \cdot \sin \psi \\ -\sin \phi & 0 & \cos \phi \end{pmatrix}.\]  

(53)

With this simplification we can evaluate each term in the sub-matrix S_{\text{sub}} using Equation 39 and 48 to get

\[s_{11} = A_0 \cos^2 \phi \cos^2 \psi + A_1 \cos^2 \phi \sin^2 \psi + A_2 \sin^2 \phi + A_3 \cos \phi \sin \phi \cos \psi.\]  

(54)

The eigenvalues of S_{\text{sub}} are the solutions of the equation

\[\det(S_{\text{sub}} - eI) = 0\]  

which leads to a quadratic equation for the eigenvalues, e

\[e^2 - (s_{11} + s_{22})e + s_1 s_2 - s_{12}^2 = 0.\]  

(57)

This has solutions

\[e = \frac{1}{2} (s_{11} + s_{22}) \pm \frac{1}{2} \sqrt{(s_{11} + s_{22})^2 - 4(s_1 s_2 - s_{12})^2}^{\frac{1}{2}}.\]  

(58)

and hence

\[e_{\text{min}} = \frac{1}{2} (s_{11} + s_{22}) - \frac{1}{2} \sqrt{(s_{11} - s_{22})^2 + 4s_{12}^2}^{\frac{1}{2}}\]  

(59)

\[e_{\text{max}} = \frac{1}{2} (s_{11} + s_{22}) + \frac{1}{2} \sqrt{(s_{11} - s_{22})^2 + 4s_{12}^2}^{\frac{1}{2}}.\]

Hence combining Equation 59 with 54 and substituting into Equation 43 we arrive at the required expression for the unpolarized absorbance as a function of the direction angles \((\phi, \psi)\):

\[A_{\text{unpol}}(\phi, \psi) = \frac{1}{2}[A_0 (\cos^2 \phi \cos^2 \psi + \sin^2 \psi) + A_1 (\cos^2 \phi \sin^2 \psi + \cos^2 \psi) + A_2 \sin^2 \phi + A_3 \cos \phi \sin \phi \cos \psi].\]  

(60)

As a check on the correctness of the expression, we can see if it reproduces the known solution in special cases. When light propagates along the z axis, we know from the earlier discussion that the unpolarized absorbance should be the average of \(A_a\) and \(A_b\). This direction corresponds to the case \(\phi = 0\). Substituting in Equation 60 we see that the \(\psi\) terms drop out and we recover the expected result

\[A_{\text{unpol}} = \frac{1}{2}[A_a + A_b].\]  

(61)

Similarly for light along the x-axis (\(\phi = \pi/2, \psi = 0\)) so that

\[A_{\text{unpol}} = \frac{1}{2}[A_b + A_a]\]  

(62)

and for light along the y-axis (\(\phi = \pi/2, \psi = \pi/2\)) so that
the integration we obtain $60$ over the sphere containing all angles $(\phi, \psi)$. The answer is found by integrating Equation 60 can be rearranged into

$$A_{\text{unpol}}(\phi, \psi) = \frac{1}{2}(A_a + A_c) \sin^2 \phi \cos^2 \psi + \frac{1}{2}(A_a + A_c) \sin^2 \phi \sin^2 \psi + \frac{1}{2}(A_a + A_c) \cos^2 \phi. \tag{64}$$

Comparison with Equation 8 shows that this is also the equation of an ellipsoid with principal values given by $A_a$, $A_b$, and $A_c$ along the x, y, and z axes, respectively. Hence the absorbance ellipsoid for polarized light leads naturally to an absorbance ellipsoid for unpolarized light [represented now in terms of the incident light direction $(\phi, \psi)$]. The principal (eigen) values of the polarized indicatrix are directly related to those of the unpolarized indicatrix through Equations 61 to 63. Together with the derivation of Equation 27 from fundamental physics, Equations 60 and 64 constitute the main results of this paper, and do not appear to have been obtained previously.

Thus far, the crystal property known as optical activity has been ignored in this paper. Optical activity occurs when the absorption tensor $[\beta]$ is not symmetric, and is possible in rock forming minerals (e.g., quartz). The theory of light propagation can be extended to deal with this case (details can be found in RR). The main effect of optical activity is to produce a rotation of linearly polarized light as it travels through a crystal, which would degrade its usefulness in absorption spectroscopy. However, because unpolarized light is the summation of linear polarized light over all polarization angles, it is invariant to a rotation within the polarization plane. Hence unpolarized measurements give average estimates over all polarization angles, thereby circumventing problems in absorption measurements due to light rotation in optically active crystals.

**ESTIMATING PRINCIPAL AND TOTAL ABSORBANCE FROM UNPOLARIZED MEASUREMENTS WITH RANDOM ORIENTATIONS**

With an expression for $A_{\text{unpol}}(\phi, \psi)$ in hand, we can now ask the question, “If many measurements of absorbance were taken using unpolarized light for samples with random orientations, what does our expression predict would be the average unpolarized absorbance?” The answer is found by integrating Equation 60 over the sphere containing all angles $(\phi, \psi)$, i.e., we have

$$A_{\text{unpol}}^{\text{avg}} = \frac{1}{4\pi} \int_{\phi=0}^{\phi=\pi} \int_{\psi=0}^{\psi=\pi} A(\phi, \psi) \sin \phi \cos \phi \sin \psi \cos \psi \, \sin \psi \cos \psi \, \mathrm{d} \phi \mathrm{d} \psi. \tag{65}$$

Substituting Equation 60 into Equation 65 and carrying out the integration we obtain

$$A_{\text{unpol}}^{\text{avg}} = \frac{1}{3}(A_a + A_b + A_c) = \frac{1}{3} A_{\text{tot}}. \tag{66}$$

In words, the ratio of the sum of the principal absorbances of the sample to the average of the measured unpolarized absorbance values over many random orientations is equal to $3$.

Equation 66 provides a direct means to estimate the sum of the principal absorbances in an anisotropic sample from many measurements of unpolarized absorbance over randomly oriented directions of light. However we can go further and ask whether it is possible to recover all three individual absorbances $(A_a, A_b, A_c)$ from unpolarized measurements on random samples? It turns out that this is indeed the case, and to see why we must first determine the maximum and minimum values of $A_{\text{unpol}}(\phi, \psi)$ over the sphere (i.e., all directions $\phi, \psi$). This can be done using standard methods of calculus (see Arfken 1985). The angles for which $A_{\text{unpol}}(\phi, \psi)$ reaches a maximum or minimum are those for which

$$\frac{\partial A_{\text{unpol}}}{\partial \phi} = 0,$$

$$\frac{\partial A_{\text{unpol}}}{\partial \psi} = 0. \tag{67}$$

The algebra is straightforward and omitted here. The result is that $A_{\text{unpol}}(\phi, \psi)$ has its extreme values when the light propagates along axis directions, which are the special cases considered in Equations 61–63. If we use the notation $A_i$ to describe the minimum of the three principal absorbances, $A_i$ for the middle value and, $A_i$ for the maximum value this gives

$$A_{\text{min}}^{\text{unpol}} = \frac{1}{2}(A_a + A_c),$$

$$A_{\text{max}}^{\text{unpol}} = \frac{1}{2}(A_b + A_c). \tag{68}$$

Rearranging Equations 66, 68, and 69 we get

$$A_a = 3A_{\text{avg}}^{\text{unpol}} - 2A_{\text{max}}^{\text{unpol}} - 3A_{\text{min}}^{\text{unpol}},$$

$$A_b = 2(A_{\text{min}}^{\text{unpol}} + A_{\text{avg}}^{\text{unpol}}) - 3A_{\text{avg}}^{\text{unpol}},$$

$$A_c = 3A_{\text{avg}}^{\text{unpol}} - 2A_{\text{min}}^{\text{unpol}}. \tag{70}$$

These expressions allow the three principal absorbances to be found in terms of quantities that can be determined experimentally. (Note that using this approach we obtain the three values of the principal absorbances, but without any information on their orientation.) Given a series of measurements of unpolarized absorbance on randomly orientated samples, $a_i (i = 1,...,n)$ with estimated errors, $e_i (i = 1,...,n)$, the minimum, $A_{\text{max}}^{\text{unpol}}$, maximum $A_{\text{min}}^{\text{unpol}}$, and average $A_{\text{avg}}^{\text{unpol}}$ can be calculated, and Equation 70 yields the principal components. The most useful quantity is likely to be the total absorbance, which can be found directly from the average observed absorbance (Eq. 66). To summarize, the theory presented in this section shows that the absorbance of unpolarized light in a single direction is related to the principal absorbances projected onto the corresponding cross sectional plane (through Eq. 60); therefore, by combining measurements from multiple light directions, both the total absorbance and the principal absorbances of the crystal can be resolved (through Eq. 70).

In any estimation procedure, it is worthwhile knowing how observational errors, $e_i (i = 1,...,N)$ propagate into the quantities of interest. For the average $A_{\text{avg}}^{\text{unpol}}$ we can use the minimum variance estimator (see Papoulis 1991) to take account of the observational
errors in forming the average, i.e., we get

$$A_{\text{avg}} = \frac{1}{N} \sum_{i=1}^{N} w_i a_i, \quad w_i = \frac{\epsilon_i^{-2}}{\sum_{j=1}^{N} \epsilon_j^{-2}}. \quad (71)$$

This has a corresponding standard error

$$\sigma_{\text{avg}}^2 = \sum_{i=1}^{N} \frac{w_i^2}{\epsilon_i^2} \sigma_i^4 \quad (72)$$

and gives an estimate of the total absorbance

$$A_{\text{tot}} = \frac{1}{N} \sum_{i=1}^{N} w_i a_i, \quad \sigma_{\text{tot}} = \left( \sum_{i=1}^{N} \frac{w_i^2}{\epsilon_i^2} \right)^{1/2}. \quad (73)$$

Hence we have a mechanism for estimating total absorbance and its error from individual measurements of unpolarized absorbance on randomly oriented samples. For the ordered principal absorbances $A_a$, $A_b$, and $A_c$, we write their standard errors as $\sigma_a$, $\sigma_b$, and $\sigma_c$. A straightforward analysis of error propagation gives the following expressions:

$$\begin{align*}
\sigma_a^2 &= 9 \sigma_{\text{avg}}^2 + 4 \sigma_{\text{max}}^2 - 12 \sigma_{\text{avg}} \sigma_{\text{max}} \sigma_{\text{min}} \\
\sigma_b^2 &= 9 \sigma_{\text{avg}}^2 + 4 (\sigma_{\text{max}}^2 + \sigma_{\text{min}}^2) - 12 \sigma_{\text{avg}} (\sigma_{\text{max}} + \sigma_{\text{min}}) \\
\sigma_c^2 &= 9 \sigma_{\text{avg}}^2 + 4 \sigma_{\text{min}}^2 - 12 \sigma_{\text{avg}} \sigma_{\text{min}} \sigma_{\text{max}} \quad (74)
\end{align*}$$

where $\sigma_{\text{min}}$ and $\sigma_{\text{max}}$ are the standard errors in the estimated minimum and maximum absorbance, respectively. It turns out that errors in maximum and minimum absorbance are often difficult to determine accurately. In the example below, we use a simple bootstrap procedure (see Efron and Tibshirani 1993) to estimate $\sigma_a$, $\sigma_b$, and $\sigma_c$, directly.

**A NUMERICAL EXAMPLE**

To complete this paper, we include a numerical example to illustrate how the theory presented here may be used in practice. We use a synthetic test involving fixed principal polarized absorbance values and demonstrate the procedure for recovering the total absorbance as well as the individual principal absorbances. For our synthetic test we choose values $A_a = 1.89$, $A_b = 45.60$, and $A_c = 80.94$ that gives $A_{\text{tot}} = 128.43$ (these integrated absorbance values in units of cm$^{-1}$, were measured on olivine by Kovács et al. 2008). We then simulate many random directions and calculate the unpolarized absorbance for each from Equation 60. This constitutes our synthetic data set. [Note that truly random light orientations ($\phi, \psi$) should be defined from spatially uniform points on a sphere, and not uniform random angles between $0 < \phi < \pi, 0 < \psi < 2\pi$, which would not give uniformly distributed points on a sphere.] Figure 4 shows a histogram of 10$^4$ absorbance values generated in this way. Note the increase in frequency near the middle of the distribution and the abrupt cut-offs at the tails.

By calculating the maximum, minimum and weighted average of the synthetic absorbance values we can determine total absorbance using Equation 73, and principal absorbances using Equation 70, as shown in Figures 5a–5c, where the calculated absorbances are plotted as a function of the number of synthetically generated data that were used. For the total absorbance the estimated error is determined from Equation 73, while for the principal absorbances standard errors are determined using the bootstrap (Efron and Tibshirani 1993) directly from the data values, $a_i (i = 1, \ldots, 10^4)$. In all cases, we see that the estimated total absorbance and the principal absorbances converge to their true values as the number of absorbance data increases. With 10 000 data, the recovered values are $A_{\text{tot}} = 128.36 \pm 007(1\sigma)$, and $A_a = 80.87 \pm 007(1\sigma)$, $A_b = 45.66 \pm 007(1\sigma)$, and $A_c = 80.87 \pm 007(1\sigma)$.

This number of data is much larger than would be achieved in practice, but it illustrates the correctness of the estimation procedure. (Here standard errors are determined by neglecting the errors in $A_{\text{min}}$, $A_{\text{max}}$, and $A_{\text{avg}}$, which would be extremely small at this number of samples.)

The important issue is how fast the error decreases as the number of measurements increase. As expected the total absorbance is the fastest to converge since it is based only on the mean of the distribution where many more random samples are likely to fall (see Fig. 4). Here the error estimate was evaluated with Equation 73 using input errors of 6% on each sample, i.e., $\epsilon_i = 0.06 \times a_i$, and a reasonably accurate recovery is achieved with between 10 and 50 measurements, and even at 10 samples errors are under 20%.

The principal absorbances are more difficult to estimate because they require sampling in the relatively unpopulated tails of the distribution. Nevertheless all three are recovered reasonably well with 10–50 measurements. With the approach outlined in this paper it should be possible, for example, to make sufficiently accurate estimates of total absorbance to quantify water contents of nominally anhydrous minerals with anisotropic crystal structures, avoiding technical difficulties involved in use of polarized light. This will be demonstrated empirically in the companion paper (Kovács et al. 2008), where the theory presented here is tested on actual measurements of absorbance with both polarized and unpolarized light.

![Figure 4. Histogram of 10000 absorbance values calculated with Equation 60 using uniformly random directions of light (defined by a uniform distribution of points on a sphere). From this distribution of absorbances the maximum, minimum and mean ($A_{\text{avg}}, A_{\text{min}}, A_{\text{max}}$) can be calculated and then inserted into Equation 70 to retrieve the principal polarized absorbances, $A_a, A_b$, and $A_c$.](image)
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Figure 5. (a) Total absorbance $A_{\text{tot}}$ calculated using Equation 73 as a function of the number of simulated measurements for random light incidence direction. The dashed line represents the target value of 128.43. The error bar shows the effect of propagating a 6% (1σ) error in the simulated absorbance values. As the number of samples increases the result converges to the correct solution and the error value decreases. (b) shows the calculated principal absorbance $A_a$; (c) is for $A_b$; and (d) is for $A_c$. For the principal absorbance calculations, the standard errors were determined using the bootstrap technique (see text). In all cases, the dashed lines represent the true values and error bars are three standard deviations. The estimation procedure clearly converges to the input values, with the total absorbance being the fastest.
APPENDIX

Accuracy of the A(θ) expression for polarized and unpolarized light

In this paper, we have developed the theory for unpolarized light in terms of absorbance rather than transmittance. This was done simply because absorbance is the quantity most convenient to use in IR spectroscopy (see Kovács et al. 2008 for a discussion). In doing so we made use of the simplified Equation 32 for absorbance over the more accurate Equation 30 for transmittance. As noted above this is unnecessary from a mathematical perspective since the entire theoretical development is unchanged if the transmittance Equation 27 is used rather than the absorbance Equation 32. We simply replace each “A” expression with a “T” expression. In the appendix we evaluate the error introduced in making use of Equation 32.

Appendix Figure 1a shows the percentage error in the polarized absorbance estimate produced by Equation 32 for a particular polarization angle of θ = 45°, as a function of the principal values of the absorbance ellipsoid in the cross sectional plane. More specifically, if we write $A_{\text{true}}(\theta, A_{\text{min}}, A_{\text{max}})$ for the absorbance given by Equation 30 and $A_{\text{approx}}(\theta, A_{\text{min}}, A_{\text{max}})$ for the value given by Equation 32 then the function contoured in is

$$\frac{1}{2} \left( A_{\text{max}} + A_{\text{min}} \right) - A_{\text{true}}(\theta, A_{\text{min}}, A_{\text{max}}) \times 100$$

(75)

where $\theta = 45°$ in Appendix Figure 1a and $\theta = 80°$ in Appendix Figure 1b. There are two influences on the error function. The first is the magnitude of the principal absorbances in the cross sectional plane, as $A_{\text{min}}$ and $A_{\text{max}}$ decrease the error decreases to zero. However as $A_{\text{min}} / A_{\text{max}} \rightarrow 1$, the error also decreases, and this is the more dominant influence. The lighter shaded contour of 10–20% error provides a marker for examining the influence of polarization angle, θ. The angle $\theta = 45°$ corresponds to the worst case, i.e., the error is larger for given values of $A_{\text{min}}$ and $A_{\text{max}}$ compared to any other angle. As the polarization angle tends to 90° (and also 0° by symmetry), we see that the error decreases everywhere. For a large part of the region, the error is less than 10% for a wide range of principal values. In the limit of $\theta = 0°$ or 90° it is clear from Equation 32 that the error will be zero for all values of $A_{\text{min}}$ and $A_{\text{max}}$.

Appendix Figure 1c shows a similar plot for the unpolarized case as a function of $A_{\text{min}}$ and $A_{\text{max}}$, i.e., the percentage error between the $A_{\text{unpol}}$ produced by Equation 42 and from the integration of full Equation 30 over θ. More specifically we plot the function

$$\frac{1}{2} \left( A_{\text{max}} + A_{\text{min}} \right) - A_{\text{unpol, true}} \times 100$$

(76)

A

B

C

APPENDIX FIGURE 1. Percentage error in polarized absorbance obtained from simplified Equation 32 compared to the more accurate Equation 30 as a function of principal absorbances A1 and A2, where $A_{\text{min}}$ is the smaller of A1 and A2, and $A_{\text{max}}$ is the larger. (a) Polarization angle θ = 45°; (b) for θ = 80°. As the principal absorbance values tend to zero, or each other, the error decreases. As the polarization angle tends to 0° or 90° the average error across the plane also decreases. (c) This is a similar plot for unpolarized absorbance found by integrating the expressions Equations 30 and 32 over polarization angle. These plots allow us to determine the experimental conditions under which Equation 32 accurately replicates Equation 30.
where

\[ A_{\text{unpol, true}} = -\frac{1}{2\pi} \int_0^{2\pi} \log_{10} \left( 10^{-A \sin^2 \theta} + 10^{-A \cos^2 \theta} \right) d\theta. \]

Since no analytical solution exists the latter integral may be evaluated numerically. For unpolarized light, the error lies somewhere between the two previous cases, but again the contour map has the same overall shape. To make use of the angular absorbance expression in Equation 42 for unpolarized light, we need to have experimental conditions that correspond to the low error region. Since both \( A_{\text{pol, min}} \) and \( A_{\text{pol, max}} \) depend linearly on thickness of the crystal section, then even in extreme cases one will be able to reduce thickness to the point where this condition is met for any light direction. Evaluation of these error functions is most conveniently achieved through a simple computer program, which is available upon request (to the authors).