

Systematic errors in dispersive Fourier transform spectroscopy

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ABSTRACT

A description is given of some of the more significant systematic errors to which the technique of dispersive Fourier transform spectroscopy is susceptible, when used for transmission measurements. Most of the errors only manifest themselves in the refraction spectrum, as any effect in the absorption spectrum is generally at levels that are less than the random errors. It is shown that most of the errors can either be ignored as being too small, can be made negligibly small by good instrumental design, or can be corrected for the effects that are introduced. The exceptions to this are those that arise from the measurement of the thickness of the specimen. These can introduce errors that are as large as 10^{-4} into the derived values of the refractive index. These can be up to an order of magnitude larger than the corresponding random errors.

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1. INTRODUCTION

Many different techniques have been applied to the problem of determining the optical constants of materials in the near millimetre wavelength region of the electromagnetic spectrum. Each technique has generally brought particular measurement advantages with it. One may, for example, be a resonant technique that is well-suited to low loss solids, while another may be a channel spectrum method which, while only giving accuracy of a few percent in the refractive index, is a very simple technique. Whatever the method, however, it will be susceptible to systematic errors. Some of these will be significant, some will not. This will be determined by the overall measurement accuracy required, and by the level of random errors in the measurement.

It is generally the case that even the most significant of systematic errors are given little consideration in the literature on near millimetre wave optical constants. One can find wide ranges of values that have been assigned to the optical constants of particular materials. Indeed, in an intercomparison of dielectric measurements on the same specimens the refractive index values returned differed by up to 1%, while there was up to an order of magnitude spread in absorption coefficient values^(1,2).

The present work considers systematic errors in one such measurement technique, dispersive Fourier transform spectroscopy (DFTS)⁽³⁻⁵⁾, used in transmission measurements on solids. The technique determines the spectral variation of the optical constants of a specimen by measuring the attenuation and phase shift imposed on an electromagnetic field as it propagates through that specimen. It is apposite to make such a study, as DFTS is known for the low levels of random error that can be achieved by its use, particularly in the refraction spectrum. In transmission measurements on low loss solids, for example, random refractive index errors can be less than 10^{-5} . Under such circumstances it is important to be aware of the level of systematic errors in the values attributed to the optical constants.

2. DISPERSIVE FOURIER TRANSFORM SPECTROSCOPY

In a measurement technique such as DFTS, systematic errors may be considered to arise from practical deviations from the ideal model of the measurement. In the case of DFTS this would be a plane-parallel, homogeneous specimen which interacts with a plane electromagnetic wave at normal incidence, within the vacuum environment of a perfect two-beam interferometer. Aperture dimensions of the specimen and the interferometer optics will be sufficiently large for there to be no significant diffraction effects. The use of Fourier transform techniques to recover complex spectra is assumed to proceed perfectly. In this section this basic theory is introduced.

The optical constants of a medium, the real and imaginary parts of the complex refractive index, fully characterise the manner in which an electromagnetic wave propagates within that medium. At any frequency they determine the spatial variation of the amplitude and the phase of the wave. This can be seen by writing the complex refractive index in the form

$$\hat{n}(\nu) = n + ik$$

in which ν is vacuum wavenumber, n is the real refractive index, k is the absorption index, and $\hat{\cdot}$ indicates a complex quantity. In this equation, and the following ones, the dependent variables are all functions of wavenumber, although this is not always shown explicitly. Maxwell's equations can then be solved to give the following equation for a homogeneous plane wave propagating within the medium, attenuated in the propagation direction and with its phase delay increasing with propagation distance.

$$\hat{E}_d = \hat{E}_0 \exp(-2\pi\nu k d) \exp(i2\pi n \nu d)$$

In this $\hat{E}_d$ represents the complex electric field at a distance d from some arbitrary origin at which the complex field is $\hat{E}_0$, c is the speed of light in vacuum, and i is $\sqrt{-1}$. It is clear that the imaginary part, k , of the complex refractive index is the dissipative term, while the real part, n , is the dispersive term.

In DFTS it is usual not to work with k , but, instead, to use the power absorption coefficient, α , which is related to k by the equation

$$\alpha = 4\pi\nu k \quad (3)$$

Using equation 3 to rewrite equation 2 for a plane wave gives

$$\hat{E}_d = \hat{E}_0 \exp \frac{-\alpha d}{2} \exp(i2\pi n \nu d)$$

which allows the complex propagation factor, $\hat{a}$, to be defined as

$$\hat{a} = \exp \left(\frac{-\alpha d}{2} \right) \exp(i2\pi n \nu d)$$

It represents the complex transmission factor of a wave that has propagated over a distance d within a medium, and does not include interface effects between different media.

Consider now a lamella specimen of refractive index $\hat{n}_2$ immersed in a medium of refractive index $\hat{n}_1$ through which a plane wave propagates as shown in figure 1. The incident wave suffers multiple internal reflections between the two interfaces of the specimen. The resultant electric field amplitude transmitted through the specimen will be given by the infinite sum of all partial waves which emerge from its rear surface. Hence, the complex amplitude transmission coefficient, $\hat{t}_{121}$, of the specimen in this particular configuration will be given by

$$\hat{t}_{121} = \hat{t}_{12} \hat{a}_2 \hat{t}_{21} + \hat{t}_{12} \hat{a}_2^3 \hat{r}_{21}^2 \hat{t}_{21} + \hat{t}_{12} \hat{a}_2^5 \hat{r}_{21}^4 \hat{t}_{21} + \dots$$

In this $\hat{r}$ is the Fresnel amplitude reflection coefficient for the interface

between media 1 and 2, and $\hat{t}$ is the corresponding amplitude transmission coefficient. The subscript order ab indicates incidence from medium a onto medium b. It is important to note that this transmission coefficient, equation (6), is not the quantity measured in an ideal DFTS experiment. Instead, the first partial wave represented by the term $\hat{t}_{12}\hat{a}_2\hat{t}_{21}$ is measured. This is discussed in the following paragraph.

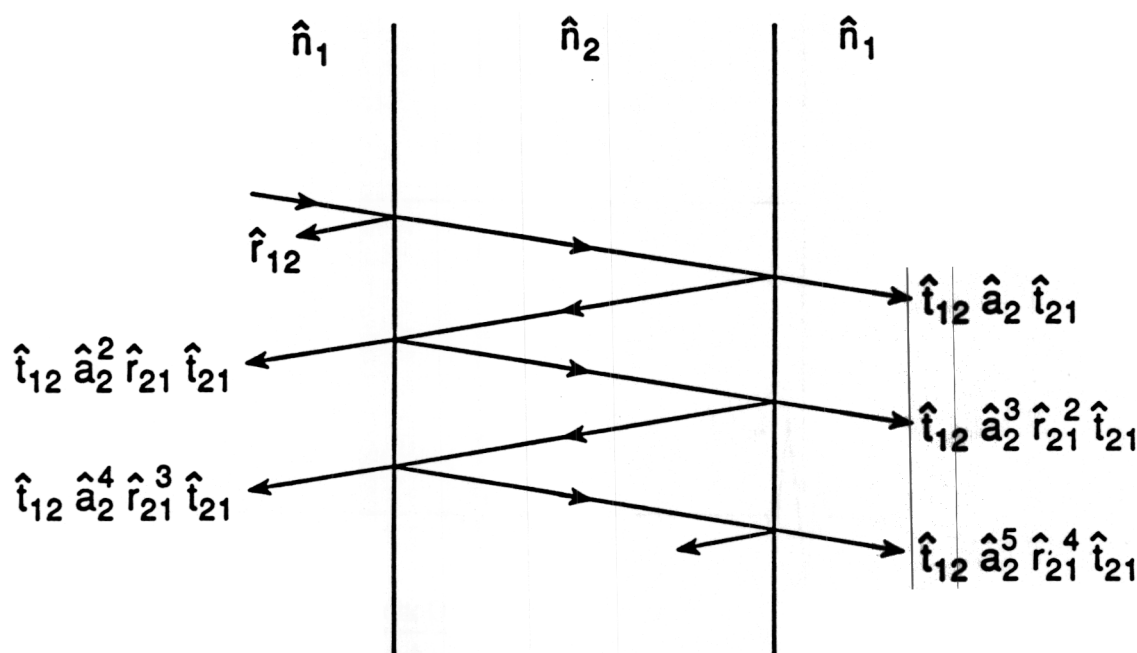


Figure 1. The internally reflected rays of a specimen of complex refractive index $\hat{n}_2$ immersed in a medium of complex refractive index $\hat{n}_1$.

DFTS determines the optical constants of a reasonably transparent specimen by measuring the attenuation and phase shift experienced by an em field that passes through that specimen. This is achieved by measuring interferograms obtained from a two-beam Michelson interferometer with and without the specimen in the fixed mirror arm. The geometry of the interferometer is such that the field in the specimen arm passes through the specimen twice, once before reaching the fixed mirror and once after reflection from it. Schematic interferograms corresponding to such a measurement are shown in figure 2. The reference measurement leads to an interferogram, $I_o(x)$, as a function of the path difference, x , between the two active arms of the interferometer, which is centred on the position of zero path difference. When the specimen is placed in the fixed mirror arm the nature of the interferogram changes as the optical length of that arm has increased. The phases of the partial waves within the specimen are progressively delayed by the increasing number of internal passes that each experiences. This gives rise to an interferogram, $I_s(x)$, which consists of a regular array of interference signatures each corresponding to one of the partial waves. These are separated from each other by a path difference amount of approximately $2\bar{n}d$, where $\bar{n}$ is the mean refractive index of the specimen, and d its thickness. In addition, the fringe which corresponds to the first partial wave is centered on a value of $2(\bar{n}-1)d$, where the term -1 comes from the thickness of vacuum displaced by the specimen. In the simplest experiment, the thickness and spectral resolution,

and possibly the absorption, are such that the second interference signature caused by the specimen, centred on $2(\bar{n}-1)d+2\bar{n}d$, does not contribute significantly to the dominant interference signature at $2(\bar{n}-1)d$.

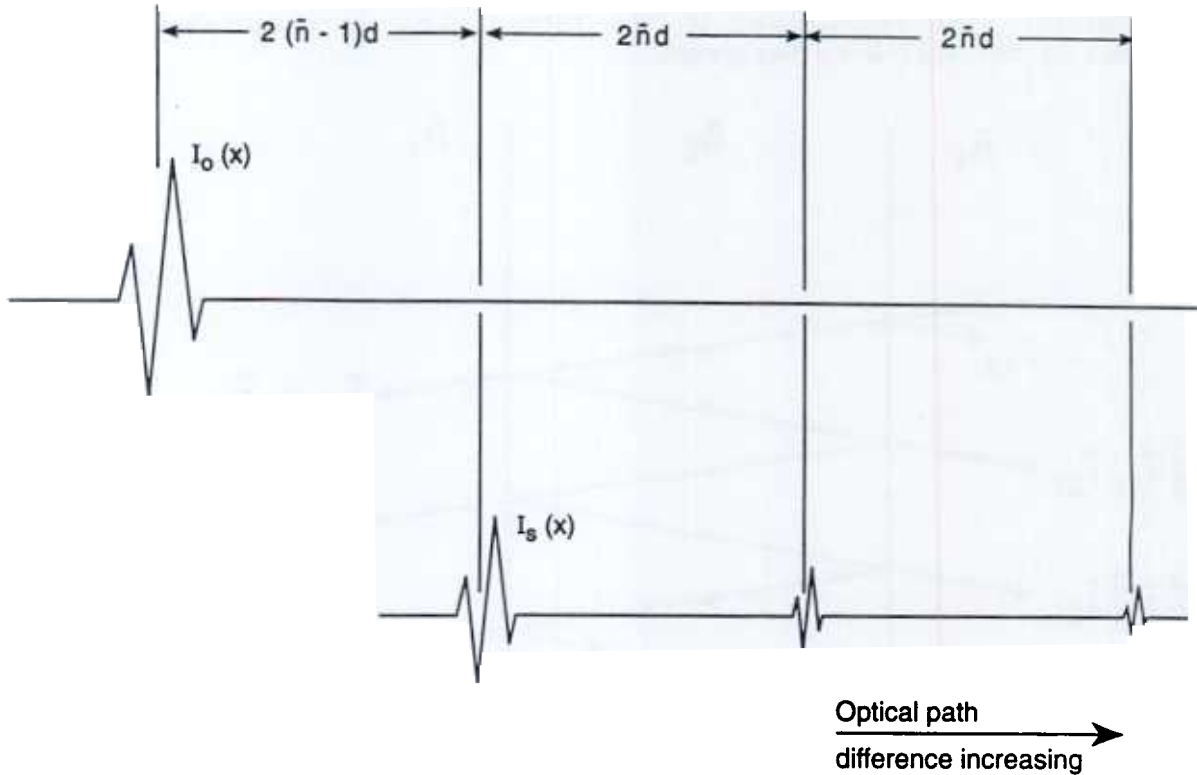


Figure 2. Representations of background and reference interferograms, $I_o(x)$ and $I_s(x)$, in a double pass transmission DFTS measurement on a specimen with a mean refractive index, $\bar{n}$, and a thickness, d .

Consider how the reference and specimen spectra are derived from the observed interferograms. If the real intensity spectrum giving rise to the reference interferogram, $I_o(x)$, is $S_o(v)$ then, under ideal conditions, the spectrum is related to the measured interferogram by the following Fourier integral

$$S_o(v) = \int_{-D}^D I_o(x) \cos(2\pi vx) dx$$

In this the interferogram has been recorded between path difference limits of $\pm D$. In a real interferometer the modulation technique, misalignment of optics and phase asymmetries lead to interferograms which may not be symmetric about $x=0$, and it is necessary to work with the complex spectrum

$$\hat{S}_o(v) = S_o \exp(i\phi_o) = \int_{-D}^D I_o(x) \exp(i2\pi vx) dx$$

When the specimen is placed within the interferometer, the main interference signature, $I_s(x)$, is shifted to a path difference position of $2(\bar{n}-1)d$. Under

these conditions the specimen spectrum, $\hat{S}_s(v)$, is found as follows. First, a shifted spectrum, $\hat{S}_s'(v)$, is computed from the observed specimen interferogram, $I_s(x')$, as the complex Fourier transform

$$\hat{S}_s'(v) = \int_{-D}^D I_s(x') \exp(i2\pi vx') dx' \quad (9)$$

This has its phase spectrum referred to the interferogram point taken as the origin of computation for the transform. In order to minimise phase branching this would normally be the point closest to the path difference value $2(\bar{n}-1)d$. The path difference variable x' refers to this origin. In order to compare specimen and reference phase spectra it is necessary that they refer to the same path difference position in the sampling combs that generate the recorded interferograms. Application of the Fourier transform shift theorem then leads to the desired specimen spectrum^(6,7)

$$\hat{S}_s(v) = \hat{S}_s'(v) \exp(i2\pi v\bar{x})$$

in which $\bar{x}$ is the path difference between the origins of computations used for the derivation of $\hat{S}_s'(v)$ and $\hat{S}_o(v)$. It corresponds to an integral number of sampling intervals and can in principle be determined exactly. However, dimensional drifts within the interferometer could cause this uniqueness to be lost, and lead to errors that could be random or systematic, depending on the nature of the drifts.

The complex ratio of the two complex spectra, $\hat{S}_s(v)$ and $\hat{S}_o(v)$, of equations (10) and (8) gives the measured attenuation and phase shift imposed on the detected radiation by the specimen. This can be expressed in terms of the first partial wave of equation (6) to give the following relationship between observed and unknown quantities

$$\frac{\hat{S}_s'(v) \exp(i2\pi v\bar{x})}{\hat{S}_o(v)} = (\hat{t}_{12}\hat{a}_2\hat{t}_{21})^2 \exp(-i4\pi vd)$$

In this the partial wave term on the right hand side is squared to indicate the radiation passes through the specimen twice. The phase term $\exp(-i4\pi vd)$ represents the phase effect of the vacuum that is displaced by the insertion of the specimen. Thus, substituting for equations (5) and (10) into equation (11) and equating modulus and phase terms on both sides of the result leads to the following relationships.

$$n_2(v) = 1 + \frac{\bar{x}}{2d} + \frac{1}{4\pi vd} (\text{ph}[\hat{S}_s'(v)] - \text{ph}[\hat{S}_o(v)] - 2 \cdot \text{ph}[\hat{t}_{12}\hat{t}_{21}]) \quad (12)$$

and

$$\alpha_2 = \frac{1}{d} \cdot \ln \frac{(\hat{t}_{12}\hat{t}_{21})^2}{|\hat{S}_s'(v)| |\hat{S}_o(v)|} \quad (13)$$

In these $\text{ph}[\]$ is taken to mean the phase of the complex quantity within the square brackets. Equations (12) and (13) are not tractable and cannot be solved exactly for n_2 and α_2 , as both contain terms on their right hand sides that are functions of n and α . At this stage an approximation is generally made to allow values for the refractive index and absorption coefficient to be derived. It is assumed that the absorption index, k , of medium 2 is sufficiently low for it to be ignored in the terms in the product $\hat{t}_{12}\hat{t}_{21}$ in equations (12) and (13). This has two consequences. First, the phase angle $\text{ph}[\hat{t}_{12}\hat{t}_{21}]$ in equation (12) goes to zero. Next, Fresnel's equations show that the modulus of the complex term, $|(\hat{t}_{12}\hat{t}_{21})^2|$, becomes real and takes the value

$$|(\hat{t}_{12}\hat{t}_{21})^2| = \frac{16n^2}{(1+n)^4} \quad (14)$$

Thus, equations (12) and (13) take their approximate forms

$$n_2(v) = 1 + \frac{\bar{x}}{2d} + \frac{1}{4\pi vd} (\text{ph}[\hat{S}'_s(v)] - \text{ph}[\hat{S}_o(v)]) \quad (15)$$

and

$$\alpha_2(v) = \frac{1}{d} \cdot \ln \frac{16n^2}{(1+n)^4 |\hat{S}'_s(v)| / |\hat{S}_o(v)|}$$

These can be used to calculate n and α values from the measurements. This would introduce systematic errors into the values assigned to the optical constants. An extension would be to use the values obtained from equations (15) and (16) as first step values in iterative calculations based on equations (12) and (13). This is considered in section 3.1.

3. SYSTEMATIC ERRORS

In this section a number of sources of systematic error in the determination of refraction and absorption spectra of solids by transmission DFTS are considered. Values for such errors are derived and compared with the typical random errors encountered in such measurements at near millimetre wavelengths ($\Delta n \sim 10^{-4}$ to 10^{-5} , $\Delta \alpha < 0.05 \text{ cm}^{-1}$). If these random errors are expressed in fractional form, the errors in refractive index are seen to be up to several orders of magnitude smaller than the absorption errors. Thus, most of the sources of systematic error in DFTS measurements only manifest themselves in the refraction spectrum. For them to be observed in the absorption spectrum would require gross departures from ideal measurement conditions. When it is necessary to introduce wavenumber values to illustrate the discussion, the near millimetre wavelength region from 10 to 50 cm^{-1} will be used, as it has been used for a large proportion of DFTS transmission measurements^(8,9).

3.1 Model approximations

These cover systematic errors introduced by the assumption that the absorption

allowing equations (15) and (16) to be derived from equations (12) and (13). The contributions that such errors make to the calculated values of the optical constants can be assessed by constructing an artificial spectrum, with a constant refractive index and an absorption spectrum that is a linear function of wavenumber that goes to zero at zero wavenumber. This is used, via complex arithmetic procedures, to calculate the modulus and phase of the complex spectrum that would be observed in a transmission DFTS measurement (equation (11)). These, in turn, are used, first in equation (15), to calculate the approximate refractive index spectrum resulting from the $k=0$ approximation, and then to obtain the approximate absorption spectrum resulting from equation (16).

The results of doing this for the refractive index spectrum in the spectral region from 10 to 50 cm^{-1} are summarised in figure 3. The curves plotted show the difference, $\Delta n = n_{\text{calc}} - n$, between the calculated refractive index values obtained from equation (15) and the real value, n , for $n = 1.5$ and 4 and a specimen thickness of 5 mm. In the following n refers to the refractive index of the specimen, the subscript 2 is not shown explicitly. Data are shown for three different absorption spectra, $\alpha = a_0 \nu$, each linearly dependent on wavenumber for $a_0 = 0.01, 0.1$ and 1. At a wavenumber value of 10 cm^{-1} , the first of these gives absorption coefficients that are of the order of those found in low loss polymers such as polyethylene, PTFE and TPX⁽¹⁰⁾, the second is characteristic of more lossy polymers such as Nylon and PMMA⁽¹⁰⁾, while the third gives values typical of more lossy media such as silicate glasses⁽¹¹⁾.

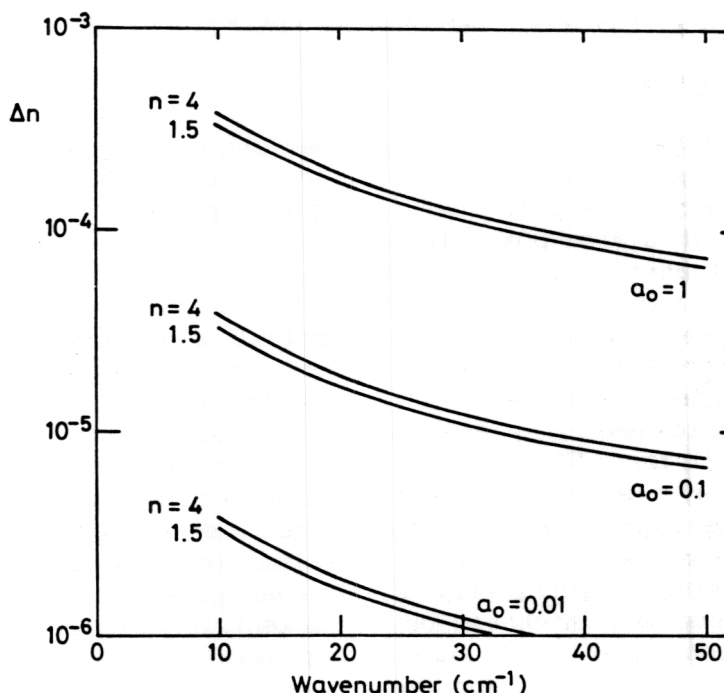


Figure 3. The error introduced into the derived refractive index spectrum by the use of the approximate expressions, equations (15) and (16), for refractive indices of 1.5 and 4, and a model absorption spectrum, $\alpha = a_0 \nu$.

The errors introduced by the use of the approximate equation (15) decrease with increasing wavenumber, reflecting the corresponding decrease in the absorption index, k , which largely determines the value of the phase angle, $\text{ph}[\hat{t}_{12}\hat{t}_{21}]$. There is not a strong dependence on the value of the refractive index, and the errors range in value from $2 \cdot 10^{-4}$ to $7 \cdot 10^{-5}$ for $a_0 = 1$, to less than $2 \cdot 10^{-6}$ for $a_0 = 0.01$. Such errors are of the order of, or less than, the random refractive index errors found in DFTS measurements on materials with corresponding absorption coefficients at such wavenumbers.

In the absorption spectra derived from the use of the second approximation, equation (16), the differences between the calculated values and the real values are typically at the level of 0.001 cm^{-1} , or less. The lowest random errors found in DFTS transmission measurements are of the order of 0.005 cm^{-1} . Thus, it would be adequate practice to use equations (15) and (16) to give the refraction and absorption spectra from the results of DFTS transmission measurements. It would, of course, be prudent to consider the possibility that this might not be so, and to use an iterative solution based on equations (15) and (16) providing first guess values.

3.2 Thickness-related errors

In this section systematic errors that arise from thickness-related effects are considered. The effects involved occur on a relatively small scale and, as such, their consequences are generally only observed in the refraction spectrum. These effects occur when the measured value of the thickness does not apply to the spectroscopic measurement, for whatever reason.

3.2.1 Thickness measurement

In most transmission DFTS measurements the specimen thickness is measured with some form of manually operated micrometer. The finest fiducial interval will probably be $10 \text{ }\mu\text{m}$ and, with practice, it might be possible to read thickness to $\pm 1 \text{ }\mu\text{m}$. Thus, it should be possible to know the thickness of a 10 mm thick specimen to about 1 part in 10^4 . This carries over into a similar systematic error in the derived value of the refractive index. While such an uncertainty may be more than adequate for many practical applications, it can be considerably greater than the random errors in the refraction spectrum, particularly for thinner specimens. It is important to be aware that errors in measuring the thickness of a specimen may be the source of the limiting systematic errors in the DFTS-derived refraction spectrum. It may be possible to improve on this by measuring the thickness at a number of points over the aperture of a specimen, and then averaging to get a mean value. Alternatively, one could use a more accurate way of determining thickness, such as a comparison with interferometrically calibrated gauge blocks. This would require that the specimen thickness be sufficiently well-defined for such a comparison to be meaningful. It might not be possible to use such an approach for soft materials. With such a specimen it would also be necessary to take care that any contacting thickness measurement did not compress the specimen and so lead to an over estimation of the refractive index.

If it were possible to reduce further the errors in the determination of the thickness of a specimen, one would ultimately arrive at the situation that the derived refractive index spectrum was limited by the random phase noise in the

measurement. When this would occur can be calculated. At 10 cm^{-1} , and for a thickness of 10 mm and a refractive index of 2, for example, the measured phase shift would be about 100 radian. The random phase noise in such a measurement would be about 1 milliradian. Thus, the fractional random phase noise would be at the level of 10^{-5} . If the measured refractive index is to be limited by this phase noise, then the specimen thickness must be known at the level of 1 part in 10^5 , or better. For a 10 mm thick specimen, this would correspond to knowing the thickness to better than $0.1\text{ }\mu\text{m}$. This can be achieved for hard specimens, but not for softer materials. Thus, in such measurements the overall level of the refraction spectrum may be in error because of an inability to define the geometry of the specimen.

A different approach to determining specimen thickness has been described in which the DFTS measurement itself was extended to include the interference signature of the second partial wave transmitted through the specimen. This introduces sufficient information to simultaneously determine both the optical constants and the thickness of the specimen^(12,13). Only preliminary results were obtained, but these showed that in measurements on a 2.7 mm thick silicon specimen the new method gave a value for the thickness that was within $1\text{ }\mu\text{m}$ of that obtained from a gauge block determination. If this performance is extrapolated to a 10 mm thickness, it would be similar to that of the micrometer discussed above.

3.2.2 Temperature

If the measurement of the thickness of the specimen and the DFTS measurement on it are made at different temperatures systematic errors in the refractive index will be present. These can be significant. Polyethylene, for example, has a coefficient of linear expansion of 2.10^{-4} K^{-1} ⁽¹⁴⁾. A temperature change of 1 K would therefore lead to a fractional thickness change of 2.10^{-4} . The refractive index should then be calculated from the measured phase spectrum using the new thickness value, but, instead, is calculated using the smaller measured value. This leads to a systematic change in the derived refractive index of 10^{-4} . Such an error would be significant in a DFTS measurement, and could be the dominant error. However, this is somewhat misleading as the temperature increase not only increases the thickness of the specimen. It also increases the volume and, hence, decreases the density. The refractive index will depend to some extent on the density, so its decrease will offset the positive systematic error introduced by the use of the incorrect small value.

The situation is different for the case of a harder material such as silicon. At 293 K this has a coefficient of linear expansion of $2.6 \times 10^{-6}\text{ K}^{-1}$ ⁽¹⁴⁾. As the far infrared refractive index of silicon is about 3.4, this implies that the error, Δn , for a 1 K change in temperature would be 6.2×10^{-6} , a much smaller error than for polyethylene, and one that would not be significant in relation to the level of random errors in a DFTS experiment.

These effects can be corrected for if the coefficient of linear expansion of the specimen is known. This will probably be the case for many established materials, but possibly not in the case of new materials. In such a situation it may be possible to use the non-contacting optical caliper approach referred to in section 3.2.1 to obtain values of the thermal expansion.

The best approach is to minimise such effects by attention to instrumental

design, using water cooling to remove heat from sources such as the mercury arc lamp and the stepper motor drive, if used, and to maintain the interferometer at a constant temperature. Control of the temperature of a small interferometer to within a few tenths of a degree over the short timescale of a near millimetre wave DFTS experiment should not be difficult to achieve. It may be important to filter out any visible and near infrared radiation from the source, to avoid any radiometric heating of the specimen.

3.2.3 Non-normal incidence

If the specimen is mounted in such a way that it is illuminated at non-normal incidence, another thickness-related systematic error contributes to the derived value of the refractive index. The radiation propagating through the specimen travels a longer path than it would at normal incidence. Thus, the refractive index should be calculated from the measured phase shift using the non-normal incidence path length, while it will, in fact, be calculated using the smaller (normal incidence) value of the thickness, resulting in an erroneously high refractive index. This can be quantified with reference to figure 4, which shows a lamellar specimen of thickness d illuminated at non-normal incidence. The angles of incidence, θ_i , and refraction, θ_r , are related by Snells Law

$$\frac{\sin \theta_i}{\sin \theta_r} = n$$

The internal path length, d' , travelled by the radiation is thus

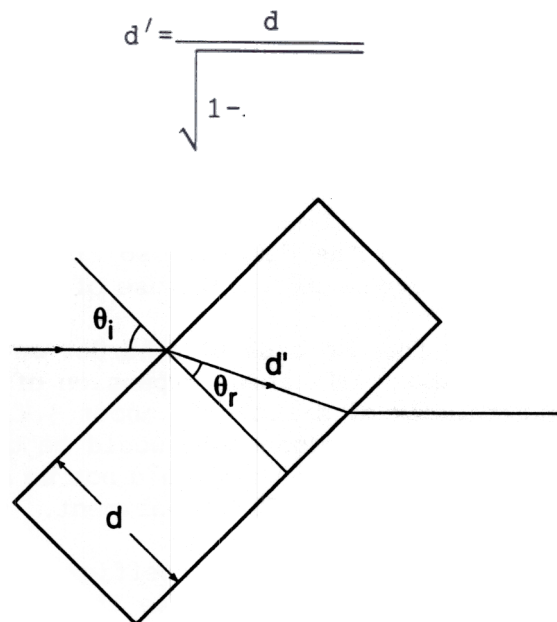


Figure 4. A specimen of thickness, d , illuminated at non-normal incidence.

Thus, the error due to non-normal incidence can be expressed as

$$\frac{\Delta n}{n-1} = \frac{1}{\sqrt{1 - \frac{\sin^2 \theta_i}{n^2}}} - 1 \quad (19)$$

Typical values are shown in figure 5 for refractive indices from 1.5 to 4, and for angles of incidence from 1 to 5°. The error is largest at low refractive indices, as these give the longest path through the specimen, and increases with increasing angle of incidence, for the same reason. The range of errors shown could all be significant in DFTS transmission measurements. The way to proceed is to have the specimen holder made to sufficiently good tolerances that the angle of incidence is zero to within a tenth of a degree, and reproducible so that it cannot be altered by change of specimen⁽¹⁵⁾.

In non-normal incidence measurements there is the potential for loss of interferometric modulation caused by lateral shear in the specimen measurement. This would lead to the derivation of an absorption spectrum that has larger values than the real spectrum. If the interferometer used for such measurements is a double pass instrument, the lateral shear introduced by the first passage through the specimen will be taken out on the second pass, leading to no effect in the absorption spectrum. This would not apply to a single pass interferometer. The two images of the lamp would not exactly overlap at the detector, giving a loss of interferometric modulation.

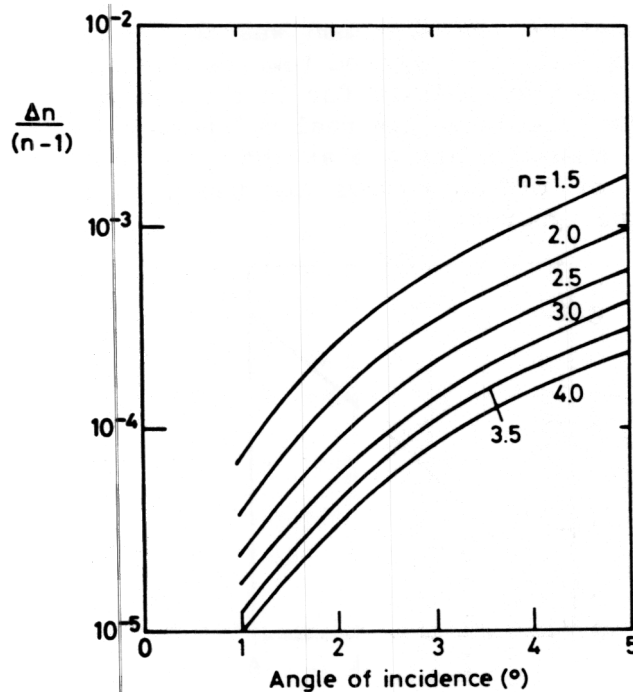


Figure 5. The refractive index error that results from measurement at non-normal incidence.

3.2.4 Off axis rays

Off axis rays will always be present in a DFTS instrument due to the finite size of the source, and may be a design feature in order to facilitate the study of small specimens. The effect of their presence in a DFTS measurement has been considered by Russell and Bell⁽¹⁶⁾, and by Chamberlain⁽¹⁷⁾. The analysis was developed by replacing the true thickness by an effective average thickness calculated for a geometry in which the specimen was illuminated by a cone of radiation of half angle, β , with the radiation uniformly distributed over the conical solid angle. This gave the result that the calculated value of the refractive index, n_{calc} , was related to the true value, n , by

$$n_{\text{calc}} = n[1 + \beta^2(1 - n^{-2})/4] \quad (20)$$

for an isotropic medium. Related expressions exist for uniaxial specimens studied with plane polarised radiation.

The interferometers most commonly used at NPL for transmission DFTS measurements are polarising interferometers which are based on the use of wire grid beamdividers^(18,19). For their particular geometries, the half angle of the cone of light incident on the specimen is 8.14×10^{-3} rad. This value was used in equation (20) to find the difference between the calculated and real values of the refractive index for values up to 4, with the results shown in figure 6. The difference increases monotonically with increasing refractive index to a value of about 6×10^{-5} by $n=4$. Such values, particularly those at the lower refractive indices, would only just be significant in the highest accuracy DFTS measurements. In the derivation of these results it was assumed that the cone of radiation incident on the specimen was uniformly illuminated. In practice, the illumination will be weighted towards the smaller angles close to normal incidence. If this were allowed for in the analysis it would reduce the difference between the calculated and real refractive index values. Thus, if random errors in DFTS measurements are at the levels of parts in 10^5 , or more, then the effects of off-axis rays on the derived values of the refraction spectrum can be ignored.

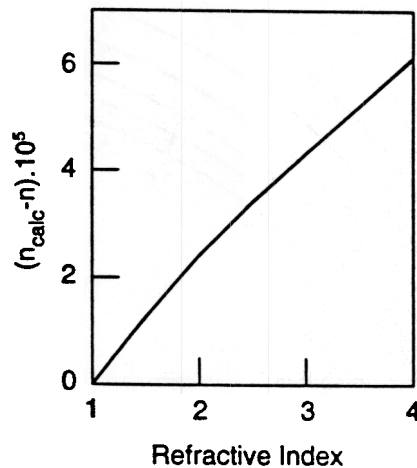


Figure 6. The difference between the calculated and real values of the refractive index in the presence of off axis rays.

Insertion of a sample into an off-axis geometry will also have an effect on the derived values of the absorption spectrum. This will arise from a defocussing of the source image at the detector. The effect, however, will be small because of the very small off-axis angles involved. In the NPL spectrometers, for example, the effect of a 10mm thick specimen on a 5° off axis ray is only to shift the focus at the detector by a few micrometres. This would not change the derived values of the absorption spectrum significantly in comparison with its relatively large random errors.

3.2.5 Elasticity

In most DFTS studies the specimen is measured within the interferometer in a vacuum environment. It therefore experiences almost zero hydrostatic pressure, and its elasticity causes the thickness to be larger than that that it exhibits under atmospheric pressure. If, as would normally happen, its thickness is measured under atmospheric pressure, the measured thickness will not be the value that applies to the DFTS experiment, and systematic errors will result.

The effect of hydrostatic pressure on an isotropic solid object is given by

$$\frac{\Delta l}{l} = -\frac{P}{E}(1-2\nu) \quad (21)$$

In this l is any linear dimension, Δl is the change in l caused by uniform hydrostatic pressure, P , E is Young's modulus, and ν is Poissons ratio. For a material like a heavy flint glass, $\nu = 0.25$ and $E = 60 \times 10^9 \text{ Nm}^{-2}$, and the fractional length change in reducing the hydrostatic pressure to zero ($P = -10^5 \text{ Nm}^{-2}$) becomes 8×10^{-7} , an amount that would not be significant in a DFTS transmission measurement. Its effect would be less than the usual level of random errors. The effect, however, is much larger for materials which have smaller Young's moduli. In high density polyethylene, for example, E can vary between 0.4 and $1.3 \times 10^9 \text{ Nm}^{-2}$, up to 2 orders of magnitude less than for the glass. Thus, the fractional extension that occurs on reducing the hydrostatic pressure to zero would be 2 orders of magnitude greater at 8×10^{-5} . This would be a significant amount in DFTS millimetre wave measurements on reasonably transparent media.

Thus, in an ideal measurement, the elastic properties of the medium, if known, would be used to calculate the extension that occurs when the hydrostatic pressure is removed. If they are not known, one can use the optical caliper method of section 3.2.1 to find the thickness under zero pressure.

3.2.6 Pseudocoherence

Pseudocoherence will be the last thickness-related source of systematic error in DFTS measurements that will be considered. It differs from all of the others that have been considered in that its effects are found in the absorption, rather than refraction, spectrum. In transmission DFTS pseudocoherence arises from a non-uniform optical thickness of a specimen. When this specimen is placed within one of the two active arms of the interferometer, any such non-uniformity causes the beam that passes through

the specimen to have a wavefront that is a mosaic of elemental waves, each with a distinct spatial phase. The beam from the other arm of the interferometer does not have this phase disorder. Thus, when the two waves interfere, interferometric modulation is lost, leading to transmission levels that are systematically low, and that can go to zero, resulting in corresponding absorption values that are systematically high^(26,27). Pseudocoherence-related absorption coefficient errors of greater than a factor of 3 have been seen⁽²⁷⁾.

Pseudocoherence effects are not observed in conventional FTS. Thus, if a non-uniform specimen has to be studied, pseudocoherence effects can be avoided by using a combination of DFTS to give the refractive index, and then using that refraction spectrum to derive the absorption spectrum from FTS measurements of the transmission spectrum.

3.3 Non-vacuum environment

Most DFTS measurements have been made using interferometers in which the optical path was evacuated to remove strong line absorptions due to atmospheric water vapour. There have been, however, a number of instruments in which this was not so. In these either the optical path was open to the normal laboratory environment⁽²⁰⁻²²⁾, or the specimen chamber was filled with gaseous helium⁽¹⁸⁾.

There are a number of possible consequences of such geometries. If the moving mirror arm is unevacuated, the wavenumber scale of the spectrometer will be incorrect, although the size of the effect will usually be small and possibly only matter in high resolution studies. More significant effects will be that both the overall level and the dispersion of the refractive index derived from such measurements could be incorrect.

When the specimen is inserted into one arm of an interferometer in a DFTS transmission measurement, it displaces a thickness equal to its own of the medium in that arm (vacuum, air, helium). The refractive index, $n_c(\nu)$, is usually derived from the measured total phase shift spectrum, $\Delta\Phi(\nu)$, at wavenumber, ν , using the following equation

$$n_c = 1 + \frac{\Delta\Phi(\nu)}{4\pi\nu d}$$

The first term on the right hand side of equation (22), unity, denotes that the analysis has proceeded with the assumption that the optical path of the interferometer was totally evacuated during the measurement, by representing the refractive index of the thickness, d , of vacuum displaced by the specimen.

If, instead, the interferometer were filled with a gas of refractive index, $n_g(\nu)$, the value of $n_c(\nu)$ calculated from equation (23) would be incorrect. The correct value would be given by

$$n_o = n_g + \frac{\Delta\Phi(\nu)}{4\pi\nu d}$$

Thus, if the refractive index spectrum of the gas is known (at the correct pressure and temperature) the correct refractive index spectrum of the unknown specimen can be derived from equation (23). Alternatively, previous measurements made with an incorrect assumption of a vacuum environment can be corrected using

$$n_o = n_c + n_g - 1 \quad (24)$$

It can be seen that, in general, $n_o > n_c$

Only two non-vacuum environments have been used in transmission DFTS measurements, air or gaseous helium. If one only considers the major constituents of air, N_2 and O_2 , then its refractive index is found to be 1.00027 from near-millimetre wave DFTS measurements on them⁽²³⁾. If, in addition, the effects of water vapour⁽²⁴⁾ are allowed for, then a term of up to 0.00008 needs to be added, depending on partial pressure, to allow for the water vapour refraction spectrum away from line centres. If measurements were to be made in the presence of water vapour, and near to line centres, the local values of the refraction spectrum of air would increase significantly⁽²³⁾. Overall, then, the effect on such DFTS measurements would be to introduce an error of up to -0.00035 into the derived values of the refractive index of the specimen. Such values would be significant in measurements on all but the most absorbing materials, and should, therefore, be allowed for.

The case of DFTS measurements in a helium environment reaches similar conclusions. The helium was present to provide a heat exchange medium in an interferometer designed for transmission DFTS measurements on solids at temperatures between 4.2 and 300 K⁽¹⁸⁾. At atmospheric pressure and room temperature the refractive index of helium gas at radio frequencies is 1.000035⁽¹⁴⁾, which would only introduce significant systematic errors into the derived values of the refraction spectrum of a specimen for a DFTS measurement of the highest accuracy. Significant systematic errors do begin to result, however, when the temperature of the exchange gas is lowered. At temperatures below 100 K, and especially below 10 K, the density of the helium gas increases rapidly with decreasing temperature, reaching values that are 0.0026 above the room temperature refractive index⁽²⁵⁾. These are significant, and it has been necessary to correct published data on the refractive index of some low loss polymers for the effect of the refractive index of helium gas⁽²⁵⁾.

3.4 Fourier effects

DFTS relies on the Fourier transformation to map from observed interferograms to desired spectra. It is, therefore, appropriate to ask whether any aspect of the Fourier process can introduce systematic error into the results of a DFTS study.

There will be a number of intensity related effects which will transform over into errors in the derived absorption spectrum. These will arise from effects such as detector non-linearity, drive non-linearity, choice of the interferogram weighting function, noise rectification etc. These, however, will not be unique to DFTS, and their consequences can largely be avoided by

good experimental practice. Indeed, if one takes a simplistic approach to Fourier effects in DFTS, only working with spectra in which structure is well-resolved, only computing optical constants in spectral regions for which the signal-to-noise ratio is high, then there is only one obvious source of Fourier derived systematic error, the question of phase branching.

3.4.1 Phase branching

The phase components of the complex spectra of equations (8) and (10) are the arc tangents of the ratio of the sine and cosine transforms of each interferogram. The computer used for such calculations will only return the principle value of the arc tangent, usually lying between $\pm\pi/2$ or $\pm\pi$ radians, depending on the procedures available, although the $\pm\pi/2$ can be extended to $\pm\pi$ by consideration of the signs of the transforms. This introduces the phenomenon of phase branching. There will be occasions when the physics of the measurement would require the phase of a complex spectrum to take values outside of the $\pm\pi$ limit. In such a circumstance the arc tangent procedure, instead of returning a real value of $(\pi + \Delta)$ would produce the principle value $(\pi + \Delta - 2m\pi)$, where m is the integer which shifts the phase angle into the $\pm\pi$ range. In general, m would be close to unity.

It is clear when branching has occurred, and it is easily corrected, or debranched, as can be seen from figure 7. The upper part of this shows a phase spectrum directly calculated from the sine and cosine transforms of an interferogram recorded with a mid-infrared FT spectrometer.

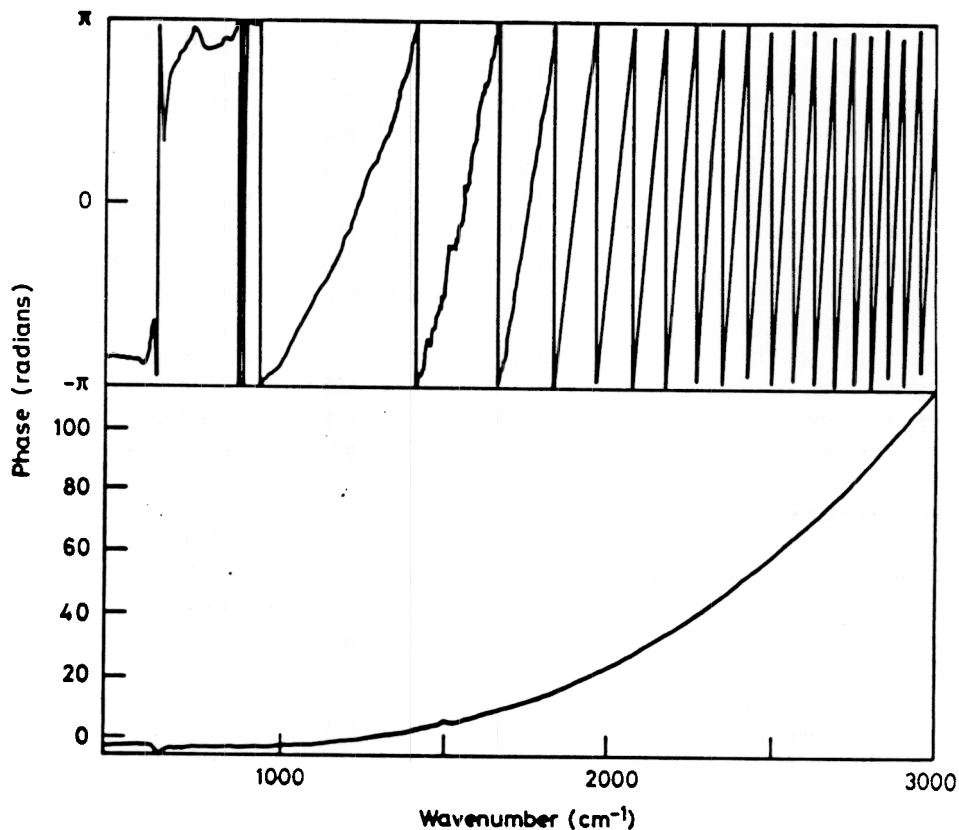


Figure 7. Examples of a branched phase spectrum (upper), and the corresponding debranched spectrum (lower).

It has clearly branched in a number of places. A simple algorithm will debranch this, as shown in the lower part of the figure. One begins by defining a pair of wavenumbers, or sets of pairs of wavenumbers, between which debranching is to be performed. This is important. If debranching is not restricted, the algorithm will debranch the large phase noise which occurs in regions of low signal and shift the overall level of the spectrum. If the phase at the next spectral point differs from the current phase by more than π radians, the branched phase angle is adjusted by $\pm 2\pi$, in increasing multiples if necessary, until it is within π of the previous point.

3.5 Interferometer stability

In an ideal measurement, the values ascribed to the refraction and absorption spectra would be limited by random uncertainty. In the refraction spectrum this would mean that the random uncertainties in the phase difference term of equation (12) should provide the limiting measurement errors. If they do not, then significant systematic errors could result. This can be discussed by recognising that a phase angle of 2π is equivalent to a length of one wavelength, and then transforming from phase noise to an equivalent dimension. At near millimetre wavelengths, DFTS measurements typically result in refraction spectra with random uncertainties of about 10^{-5} . Thus, at 10 cm^{-1} , and for a typical specimen thickness of 10 mm, the random uncertainty in the phase term would have been about 1 milliradian. This transforms over into a noise equivalent dimension of $0.15\text{ }\mu\text{m}$. This can be interpreted as meaning that such a determination of a refraction spectrum will be limited by systematic errors if the dimensions of the active arms of the interferometer change on the scale of $0.15\text{ }\mu\text{m}$, or more, during the course of a measurement. This can be avoided by the use of thermal insulation from the ambient laboratory environment, and of sensitive liquid helium cooled detectors to give short measurement times.

4 CONCLUSIONS

This consideration of possible sources of systematic error in transmission DFTS measurements at near millimetre wavelengths has identified a number of sources which could introduce errors into the derived refraction spectrum at levels of up to 3×10^{-3} . Given that random refractive index errors in such measurements can be smaller than 10^{-5} , it is clear that systematic errors can be the dominant errors, and need to be considered in the evaluation of the results of DFTS measurements. However, it turns out that some of the potential sources of the largest errors (temperature effects, non-normal incidence, off axis rays, interferometer instability) can be avoided by appropriate instrumental design and good experimental practice. Other potential error sources, such as those arising from working in a non-vacuum environment, can be corrected for if the refractive index of that environment is known. Elastic effects, arising from measuring the thickness under a different hydrostatic pressure (atmospheric) to that of the DFTS measurement (vacuum), can either be ignored for a hard specimen, or corrected for if the elastic moduli are known. The use of approximate expressions to derive the optical constants from the measured parameters can introduce refractive index errors, but these can be allowed for numerically. Possibly the only significant systematic errors that cannot be ignored or corrected are those that arise from an incorrect measurement of the thickness of a specimen having a non-ideal geometry. These can introduce errors as large as 10^{-4} into the derived values of the

refractive index, particularly for soft specimens. This can be up to an order of magnitude greater than the random errors in such measurements. It is important in DFTS studies to be aware of this, and to try to reduce the systematic error either by improved thickness measurements or by using specimens with better defined geometries.

Most of the systematic errors considered manifest themselves in the refractive index spectrum, and have very small effects in the absorption spectrum. The exception to this are pseudocoherence effects. These arise from departures of the specimen geometry from its ideal plane parallel form. They result in a loss of interferometric modulation, and lead to derived absorption spectra which are greater than the intrinsic spectrum of the specimen. The presence of such effects can, however, be monitored by a comparison of DFTS and FTS transmission measurements. The effect can be avoided by calculating the refraction spectrum from the DFTS phase spectrum and then calculating the absorption spectrum from the FTS transmission spectrum.

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