

Extensions of the Kramers–Kronig transformation that cover a wide range of practical spectroscopic applications

Jennifer A. Bardwell and Michael J. Dignam

Citation: [The Journal of Chemical Physics](#) **83**, 5468 (1985); doi: 10.1063/1.449863

View online: <http://dx.doi.org/10.1063/1.449863>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/83/11?ver=pdfcov>

Published by the [AIP Publishing](#)

Articles you may be interested in

[A fast Fourier transform implementation of the Kramers-Kronig relations: Application to anomalous and left handed propagation](#)

[AIP Advances](#) **2**, 032144 (2012); 10.1063/1.4747813

[On the application of the Kramers-Kronig relations to the barrier interaction time problem](#)

[AIP Conf. Proc.](#) **458**, 932 (1999); 10.1063/1.57670

[Ultrasonic spectroscopy in polymeric materials. Application of the Kramers–Kronig relations](#)

[J. Appl. Phys.](#) **80**, 2728 (1996); 10.1063/1.363190

[Kramers–Kronig in two lines](#)

[Am. J. Phys.](#) **57**, 821 (1989); 10.1119/1.15901

[Kramers-Kronig Relations, Hilbert Transforms, Dispersion Relations, etc.](#)

[Am. J. Phys.](#) **32**, 713 (1964); 10.1119/1.1970960



Extensions of the Kramers–Kronig transformation that cover a wide range of practical spectroscopic applications

Jennifer A. Bardwell and Michael J. Dignam

Department of Chemistry, University of Toronto, Toronto, Ontario, Canada M5S 1A1

(Received 28 May 1985; accepted 23 August 1985)

The Kramers–Kronig (KK) transformation has been widely used for the determination of the spectra of the refractive and absorption indices from the normal-incidence reflectivity spectrum of solids. This paper considers the extension of this technique to *s*-polarized light at nonnormal incidence with a transparent incident medium of arbitrary, constant refractive index. While the KK transformation is known to be inapplicable under certain circumstances, we show that in all cases satisfactory corrections can be applied, and readily applied in most cases. As an example, for the experimentally important case of attenuated total internal reflection from an organic liquid in the infrared, only one additional piece of information is required, namely, the refractive index at a frequency where the absorption is low. The procedures are demonstrated using model systems consisting of sets of damped harmonic oscillators. All the KK transformations were done using the FT software of a commercial Fourier transform infrared spectrometer in order to demonstrate the considerable potential of this approach to the routine determination of optical constants.

I. INTRODUCTION

The Kramers–Kronig (KK) dispersion relationship has been used extensively to determine the spectrum of the complex refractive index from the reflection spectrum.¹ In the simplest and most widely used application, the reflectivity is measured at near-normal incidence, from air or vacuum ambient. In this case, the KK relationship takes the form

$$\theta(\omega_0) = \frac{2\omega_0}{\pi} P \int_0^\infty \frac{\ln[R(\omega_1)]^{1/2}}{\omega_1^2 - \omega_0^2} d\omega_1, \quad (1)$$

where R is the reflectivity (ratio of reflected to incident intensity), θ the phase shift defined in terms of the Fresnel reflection coefficient $\hat{r} = R^{1/2} e^{i\theta}$, and P implies taking the Cauchy principal value. For normal incidence from a vacuum, $\hat{r} = (\hat{n} - 1)/(\hat{n} + 1)$ and the complex refractive index $\hat{n} = n - ik$ may be calculated using the formulas

$$n = \frac{1 - R}{1 + R - 2R^{1/2} \cos \theta}, \quad k = \frac{-2R^{1/2}}{1 + R - 2R^{1/2} \cos \theta}. \quad (2)$$

Equation (1) is inapplicable under some conditions, as discussed by Young.² However, it is valid for materials whose optical properties can be fitted by a complex dielectric function $\hat{\epsilon} = n^2$ that can be expressed in the form of a set of damped harmonic oscillators, i.e.,

$$\hat{\epsilon} = \epsilon(\infty) + \sum_j \frac{S_j}{1 - (\omega/\omega_j)^2 + i\Gamma_j(\omega/\omega_j)}, \quad (3)$$

where $\epsilon(\infty)$ is the high frequency limit of $\hat{\epsilon}$ and S_j , Γ_j , and ω_j are the strength, relative linewidth, and center frequency of the J th oscillator, respectively. In this paper we consider only such materials.

The KK relationship is one expression of the causality condition. Another, mathematically equivalent to the KK equation, is the Fourier transform (FT) relationship^{3,4}

$$\theta(\omega_0) = -\frac{2}{\pi} \int_0^\infty dt \sin \omega_0 t \int_0^\infty \ln[R(\omega_1)]^{1/2} \cos \omega_1 t d\omega_1. \quad (4)$$

This relationship is computationally more efficient, and can be performed using software available with commercial Fourier transform infrared (FTIR) spectrometers,⁵ thus allowing routine determination of optical constants in the infrared region.

Several attempts have been made to extend the KK relationship to the following cases: (1) ambient medium refractive index, $n_0 > 1$; (2) nonnormal incidence, *s*-polarized light; (3) nonnormal incidence, *p*-polarized light.^{6–13} However, as far as the authors are aware, very few experimental applications of these extensions have appeared in the literature.^{14,15} In this paper, we consider extensions to cases (1) and (2) only, since case (3) does not yield further information for isotropic samples, and is somewhat more complicated than case (2).

The derivation of Eq. (1) depends on showing that $\ln \hat{r}(\omega)$ is analytic in the half of the complex frequency plane defined by $\omega_2 > 0$, where $\omega = \omega_1 - i\omega_2$. In our convention, this is the lower-half plane. For vacuum ambient and normal incidence where $\hat{r} = (\hat{n} - 1)/(\hat{n} + 1)$, the analyticity of \hat{r} is ensured since \hat{n} is analytic and $\hat{n} - 1 \neq 0$.¹⁵ The latter statement follows from the fact that \hat{n} is real valued only along the imaginary axis, where it is monotonically decreasing, from $n(-i0) > 1$ to $n(-i\infty) = 1$.⁶ For an incident medium with $n_0 > 1$, but real valued and constant,

$$\hat{r} = \frac{\hat{n} - n_0}{\hat{n} + n_0}, \quad (5)$$

and a singular point in $\ln \hat{r}$ is possible in the form of a logarithmic branch point on the imaginary axis where $\hat{n} = n_0$.

For *s*-polarized light incident at an angle α ,

$$\hat{r} = \frac{[\hat{n}^2 - n_0^2 \sin^2 \alpha]^{1/2} - n_0 \cos \alpha}{[\hat{n}^2 - n_0^2 \sin^2 \alpha]^{1/2} + n_0 \cos \alpha}, \quad (6)$$

and there exists the possibility of two singularities: a logarithmic branch point in $\ln \hat{r}$ if

$$n_0 \cos \alpha = [\hat{n}^2 - n_0^2 \sin^2 \alpha]^{1/2};$$

and a branch point in \hat{r} if

TABLE I. Definition of and phase correction terms for various reflection cases.

Case	α^a	η^b	τ^c	Ex ^d	In ^e	TIN ^f	$I(\omega_0)^g$
(1a)	0	∞	...	✓			0
(1b)	0	<0	...		✓		$-\pi$
(1c)	0	$0 < \eta < \infty$...	✓	✓		$-\pi + 2 \arctan(\eta/\omega_0)$
(2a)	>0	∞	∞	✓			0
(2b)	>0	<0	∞		✓		$-\pi$
(2c)	>0	$0 < \eta < \infty$	∞	✓	✓		$-\pi + 2 \arctan(\eta/\omega_0)$
(2d)	>0	<0	$0 < \tau < \infty$		✓	✓	$-\pi + M(\infty)[1 - 2/\pi \arctan(\tau'/\omega_0)]^h$
(2e)	>0	<0	<0			✓	$-\pi + M(\infty)$
(2f)	>0	$0 < \eta < \infty$	$0 < \tau < \infty$	✓	✓	✓	$+ (2/\pi) \arctan(\tau'/\omega_0)[M(0) - M(\infty)]^i$ $-\pi + 2 \arctan(\eta/\omega_0)$ $+ M(\infty)[1 - (2/\pi) \arctan(\tau'/\omega_0)]$

^a α = angle of incidence.^b η is the location of the logarithmic branch point on the imaginary axis.^c τ is the location of the branch point in r on the imaginary axis.^dEx = external reflection.^eIn = internal reflection.^fTIN = total internal reflection.^g $I(\omega_0)$ is the correction term which must be added to the phase resulting from transformation of the logarithm of the reflectivity.^h τ' is a parameter arising from the second mean value theorem, and satisfies $\infty > \tau' > \tau$.ⁱ $M(\infty) = 2 \arctan [[n_0^2 \sin^2 \alpha - n(\infty)^2]^{1/2} / n_0 \cos \alpha]$, $M(0) = 2 \arctan [[n_0^2 \sin^2 \alpha - n(0)^2]^{1/2} / n_0 \cos \alpha]$.

$$\hat{n}^2 - n_0^2 \sin^2 \alpha = 0.$$

Again, both types of singularities occur only on the imaginary axis, i.e., only for $\omega_1 = 0$, $\omega_2 \geq 0$. We now discuss the behavior of $\ln \hat{r}$ on the lower-half plane. Following the notation of Plaskett and Schatz,⁶ we denote the value of ω_2 at a logarithmic branch point by η , and its value at a branch point in \hat{r} by τ . For cases (1) and (2) above, the term “external reflection” refers to regions where $n > n_0$, while the term “internal reflection” refers to regions where $n < n_0$. For case (2), there is an additional regime where $n_0 \sin \alpha > n$, which is defined as “total internal reflection,” internal reflection referring to $n_0 \sin \alpha < n < n_0$. Along the real axis, these terms have meaning only in regions where $k \approx 0$, but are meaningful everywhere on the imaginary axis. Along the imaginary axis, the switch between external and internal reflection occurs at $\omega_2 = \eta$, while that between internal and total internal reflection at $\omega_2 = \tau$. Because \hat{n} decreases along the imaginary axis, $\tau > \eta$. For $k \approx 0$, and along the imaginary axis, it follows from Eqs. (5) and (6), that: $\theta = 0$ for external reflection; $\theta = -\pi$ for internal reflection; and $\theta = -\pi + 2 \arctan \{ [n_0^2 \sin^2 \alpha - \hat{n}^2]^{1/2} / (n_0 \cos \alpha) \}$ for total internal reflection.

Plaskett and Schatz⁶ showed that the following relationship holds generally:

$$\theta(\omega_0) = \frac{2\omega_0}{\pi} p \int_0^\infty \frac{\ln[R(\omega_1)]^{1/2}}{\omega_1^2 - \omega_0^2} d\omega_1 + I(\omega_0), \quad (7)$$

where

$$I(\omega_0) = \frac{2\omega_0}{\pi} \int_0^\infty \frac{\theta(-i\omega_2)d\omega_2}{\omega_2^2 + \omega_0^2}. \quad (8)$$

$I(\omega_0)$ represents a correction to the usual KK relationship. From the previous discussion, $I(\omega_0)$ is readily evaluated for the various cases. The resulting expressions for $I(\omega_0)$ are given in Table I, and were derived originally for cases (1a)–(2c) by Plaskett and Schatz,⁶ and for case (2d) by Makarova and

Morozov.¹² The expression $2 \arctan(\eta/\omega_0)$ is sometimes called a Blaschke term.^{1,17} Expressions for $I(\omega_0)$ in cases (2d)–(2f) are derived using the second mean value theorem, which introduces the parameter τ' , satisfying $\infty > \tau' > \tau$, and which can depend on ω_0 , a fact apparently unnoticed by Makarova and Morozov.¹² However, as we show later, these expressions for $I(\omega_0)$ can in fact be used to correct the KK relations, so that τ' is evidently not strongly dependent on ω_0 .

The preceding relations require reflectivity data over the complete frequency range, zero to infinity. In practice, of course, the reflectivity is known only over a limited frequency range, and moreover, the very meaning of the reflectivity at very high frequencies is in question.⁸ Thus, the “true” reflectivity must be replaced by a function equal to the reflectivity inside the experimental range, but, e.g., set constant outside the range. The nature of the KK integral is such that this approximation is expected to work well if the reflectivity is not changing too rapidly near the limits of the range, but not otherwise. However, a correction of some sort can be applied with some success to partially compensate for the finite frequency range. Several such procedures involve parameters which are chosen to make the extinction coefficient vanish at two or more chosen frequencies.^{18,19} Even with such corrections, the finite frequency range imposes a limitation on the accuracy achievable using the KK method. The goal of this work was to find practical methods that lead to errors in the phase spectrum arising from nonanalyticity in $\ln \hat{r}$ of the same order or less than those due to the finite frequency range. We have been successful in this goal, extending, therefore, the range of practical application of the KK method to include spectroscopically important cases, such as that of total internal reflection.

In the following sections we show how the expressions for $I(\omega_0)$, Table I, can be used to correct phase spectra. In the case of a total internal reflection spectrum for a typical organic compound, the correction takes a particularly simple

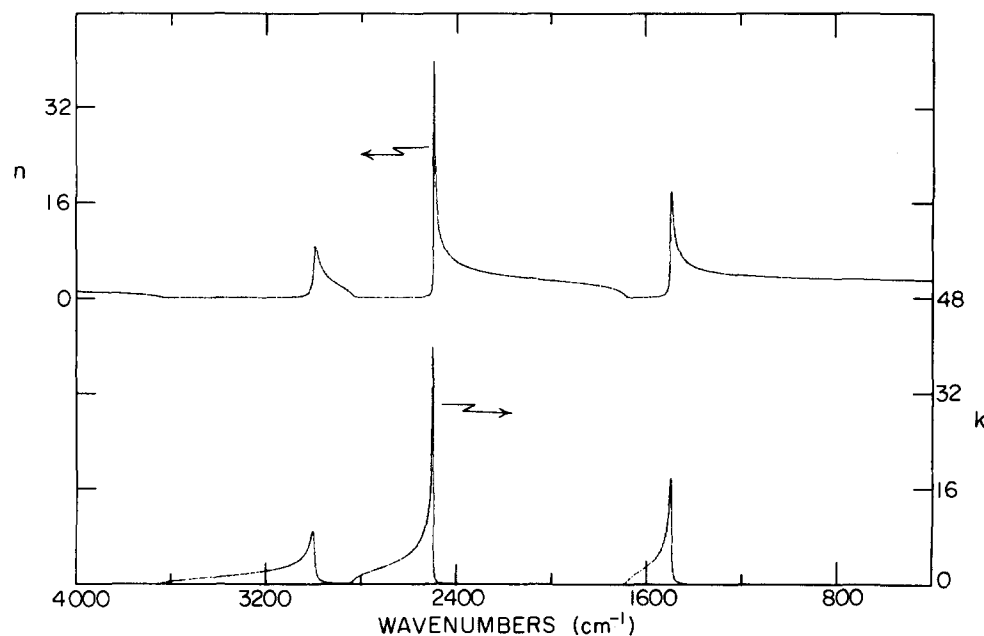


FIG. 1. Plots of n and k for inorganic system of harmonic oscillators, $n(\infty) = 2$.

form—an additive constant that is readily estimated. All of the transformations were performed using the FT software of a commercial FTIR spectrometer in order to demonstrate the potential of the procedures tested for routine applications.

II. METHOD

Two systems of oscillators were chosen for the tests. The first consists of three large bands, with n and k as shown in Fig. 1. $\hat{\epsilon}$ was first calculated using Eq. (3) from which $\hat{n} = \hat{\epsilon}^{1/2}$ was then determined. These data are meant to represent an inorganic, ionic solid with very strong bands ($k > 10$) in the infrared. Note that the bands, which are simple damped oscillators in $\hat{\epsilon}$, are highly asymmetric in \hat{n} , matching in shape, e.g., those observed in beryllium oxide.²⁰

The second system consists of relatively weak bands

($k < 1.5$) and is shown in Fig. 2. It was constructed to more or less reproduce the optical constants for benzene in the frequency range 400–4000 cm^{-1} .²¹ Because of the weakness of the bands, the damped harmonic oscillators of Eq. (3) were directly used to represent \hat{n} , rather than $\hat{\epsilon}$.

The spectra of R and θ were calculated from the n and k values using Eq. (4) or Eq. (5) and were transferred to FTIR files using the method described previously.⁵ The resolution was set at 2 cm^{-1} , the number of data points at 8192, the bandwidth at 7899 cm^{-1} , and the spectral range to 400–4000 cm^{-1} . This range was chosen to coincide with that covered by an FTIR instrument employing a KBr beam splitter. Below 400 cm^{-1} , R was set to its value at 400 cm^{-1} , while above 4000 cm^{-1} to its value at 4000 cm^{-1} . The function $\ln(R/R_\infty)$, rather than $\ln R$, was transformed, where R_∞ is equal to the value of R at 4000 cm^{-1} . The resulting function is continuous over the entire range of 0 to ∞ cm^{-1} , with a

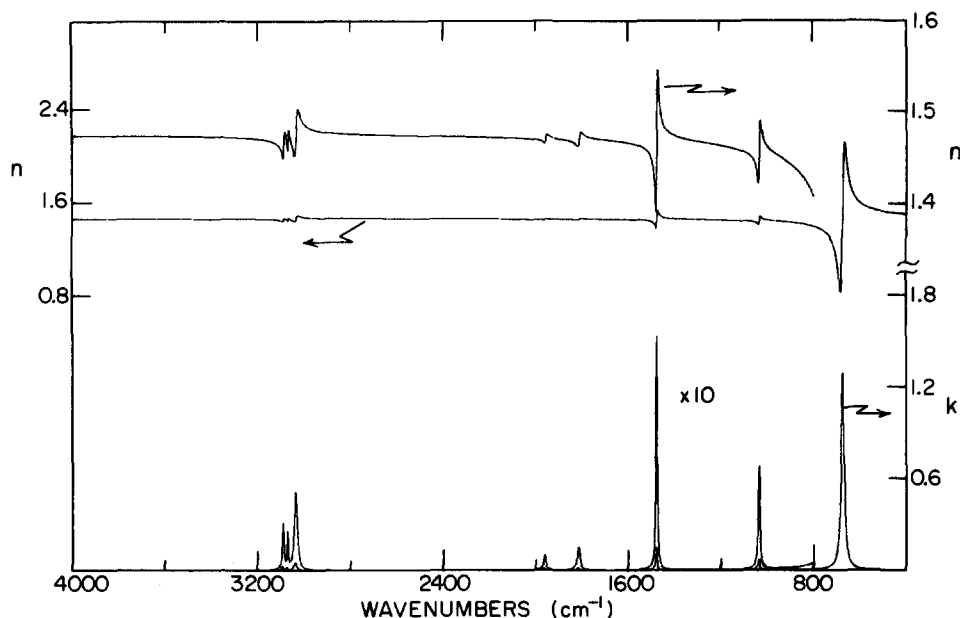


FIG. 2. Plots of n and k for benzene like system of harmonic oscillators, $n(\infty) = 1.475$.

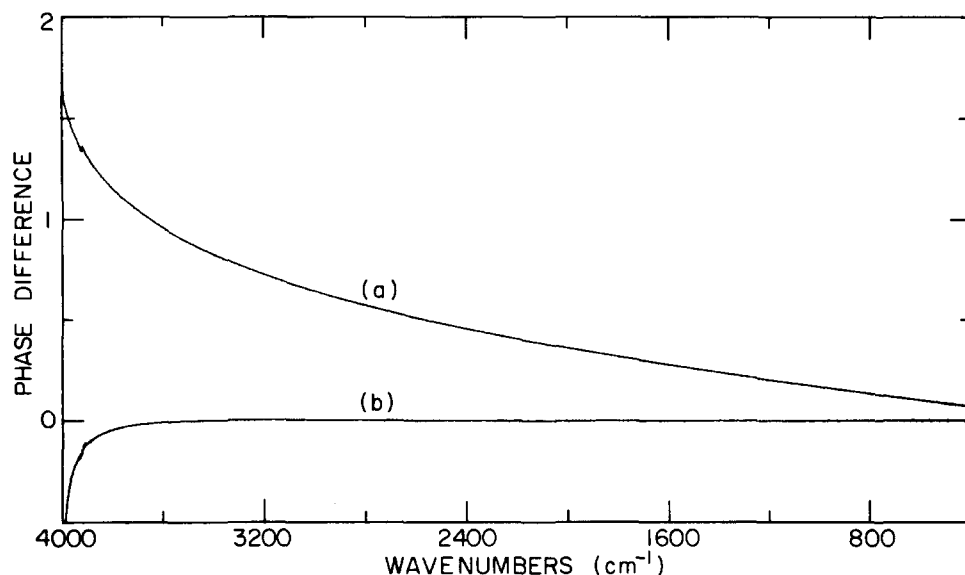


FIG. 3. Phase error spectra in radians for case (2a), inorganic system (a) uncorrected, (b) corrected.

value of 0 for $\bar{\nu} > 4000 \text{ cm}^{-1}$. Furthermore, it is square integrable, a requirement for the validity of the FT phase relationship,¹ Eq. (4).

The next step was the double Fourier transformation of $\frac{1}{2} \ln(R/R_\infty)$ to obtain the uncorrected phase spectrum θ' , using the method described previously.⁵ A difference spectrum, $\theta - \theta'$, representing the phase error due to both the correction term $I(\omega_0)$ and the finite frequency range was then plotted. Finally, a BASIC program with several branches was used to correct θ' to θ'' , and a plot of $\theta - \theta''$ made. If desired, n and k were also calculated from R and θ'' using for normal incidence the equations

$$\begin{aligned} n &= \frac{n_0(1-R)}{1+R-2R^{1/2}\cos\theta''}, \\ k &= \frac{-2n_0R^{1/2}\sin\theta''}{1+R-2R^{1/2}\cos\theta''}, \end{aligned} \quad (9)$$

while for *s*-polarized light, the equations

$$\epsilon_1 = n^2 - k^2 = \frac{n_0^2 \cos^2 \alpha [-8R + 4R^{1/2}(1+R)\cos\theta'']}{(1+R-2R^{1/2}\cos\theta'')^2} + n_0^2, \quad (10)$$

$$\epsilon_2 = 2nk = \frac{-4n_0^2 \cos^2 \alpha R^{1/2}(1-R)\sin\theta''}{(1+R-2R^{1/2}\cos\theta'')^2}, \quad (11)$$

$$n = 2^{-1/2} [\epsilon_1 + (\epsilon_1^2 + \epsilon_2^2)^{1/2}]^{1/2}, \quad (12)$$

$$k = \frac{\epsilon_2}{2n}, \quad (13)$$

where $\hat{\epsilon} = \epsilon_1 - i\epsilon_2$ were used. While relations similar to Eqs. (10) to (13) have been reported,^{14,15} they contain errors, presumably typographical.

III. RESULTS

Case (2a): $n_0 = 1$, $\alpha = \pi/4$, external reflection only. This case, where Eq. (1) is valid, is used to quantify the inherent errors in the KK (or FT) method due to the finite fre-

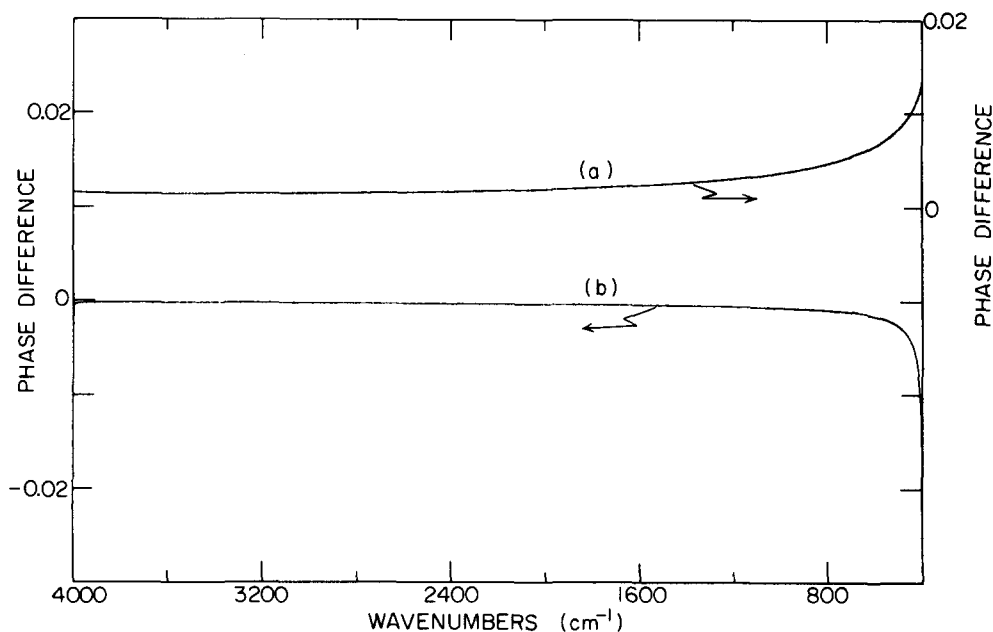


FIG. 4. Phase error spectra in radians for case (2a) benzene system (a) uncorrected, (b) corrected.

TABLE II. Accuracy of absorption parameters for the inorganic case.

Case ^a	$\bar{\nu}(\text{cm}^{-1})$	% error S^b	% error Γ^c
(2a) $n_0 = 1$ $\alpha = \pi/4$ two anchor point correction	1500	2.04	5.25
	2500	0.42	2.98
	3000	1.73	2.65
(2c) $n_0 = 2.5$ $\alpha = \pi/4$ three anchor point correction	1500	1.54	2.10
	2500	0.15	2.98
	3000	2.91	2.40
(2d) $n_0 = 3.5355$ $\alpha = \pi/4$ two anchor point correction	1500	6.60	10.53
	2500	14.0	24.60
	3000	2.65	2.14
(2e) $n_0 = 6$ $\alpha = \pi/4$ one anchor point correction	1500	0.09	0.53
	2500	17.80	14.92
	3000	9.19	2.66
(2e) $n_0 = 6$ $\alpha = \pi/4$ three anchor point correction	1500	0.50	0.53
	2500	0.49	1.51
	3000	0.17	0.26
(2e) $n_0 = 6$ $\alpha = \pi/4$ modified FT relationship one anchor point correction	1500	1.43	1.05
	2500	23.72	8.96
	3000	13.62	22.23

^a As defined in Table I, with n_0 the refractive index of the incident medium.

^b The % error in the absorption strength S compared to the initial value.

^c The % error in the relative linewidth Γ , compared to the initial value.

quency range. The “inorganic” system shows a very large error in the uncorrected phase spectrum, as shown in Fig. 3(a). This error is due to the fact that n , and therefore R , is changing at the high frequency end. When the spectrum of θ' is corrected using the method of Roessler,¹⁸ the error is reduced to <0.02 rad except very close to 4000 cm^{-1} as shown in Fig. 3(b). The corresponding results for the “benzene” system are shown in Fig. 4. Again, the correction for the finite frequency range results in a reduction of the error. In both cases \hat{n} or $\hat{\epsilon}$ were calculated from R and θ'' , and the peak heights and half-widths measured, allowing the parameters S and Γ to be extracted. For the inorganic case the errors in both S and Γ were less than 6%, for the benzene

case, less than 5%. The errors in $\hat{\epsilon}$ for the inorganic case are summarized in Table II for this and successive examples.

Case (2b): This is the case of internal reflection throughout the spectrum, and as expected from Table I, is similar to case (2a). Satisfactory results are obtained by merely subtracting π from the uncorrected spectra, and then applying the finite range correction.¹⁸

Case (2c): This case occurs when there are regions of both external and internal reflection in the spectrum. The correction is of the form of a Blaschke term resulting from a logarithmic branch point at $\omega_2 = \eta$. To provide an example of this case, n_0 must lie between $n(\infty)$ and $n(0)$, or in the present examples, between 2 and 3.099 for the inorganic sys-

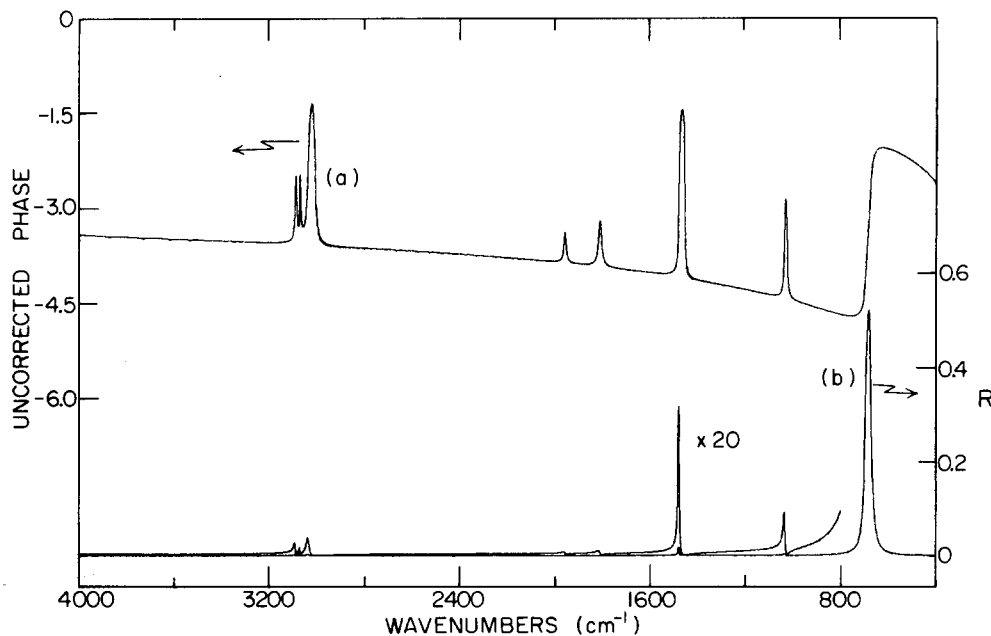


FIG. 5. (a) Uncorrected spectrum of $\theta - \pi$ in radians from transformation of R for case (2c) for benzene system, (b) spectrum of R .

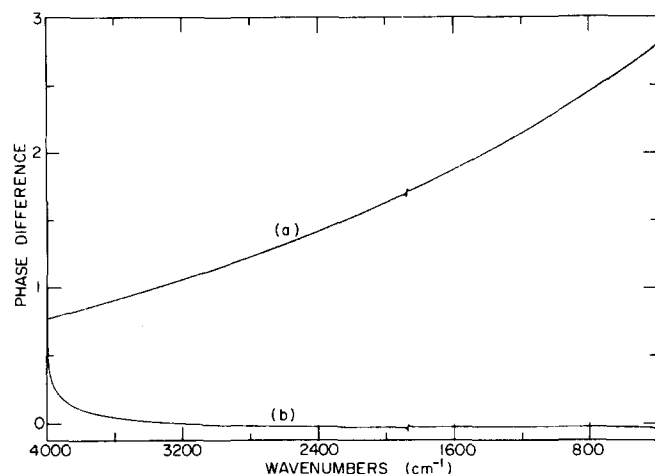


FIG. 6. Phase error spectra in radians for case (2c) inorganic system (a) uncorrected, (b) corrected.

tem and between 1.475 and 1.504 for the benzene system. Values of n_0 were chosen to be 2.50 and 1.49, respectively, with $\alpha = \pi/4$.

Figure 5 shows the reflectivity spectrum calculated for the benzene case and the resulting phase spectrum with a constant of π subtracted. The effect of the logarithmic branch point at $\omega_2 = \eta$ is clearly visible in the sloping base line. The phase spectra are corrected for both finite frequency range and the branch point using three points in the spectrum where $k \cong 0$ and therefore $\theta \cong 0$ or $\theta \cong -\pi$. The selection of these points can be done by inspection of the reflectivity and uncorrected phase spectra. For the finite frequency range correction alone,¹⁸ values of the parameters A and B are chosen so that

$$\theta(\bar{\nu}_i) = A \ln \left| \frac{\bar{\nu}_{\min} + \bar{\nu}_i}{\bar{\nu}_{\min} - \bar{\nu}_i} \right| + B \ln \left| \frac{\bar{\nu}_{\max} + \bar{\nu}_i}{\bar{\nu}_{\max} - \bar{\nu}_i} \right| + \theta'(\bar{\nu}_i),$$

where $\bar{\nu}_{\min}$ and $\bar{\nu}_{\max}$ are the end points of the frequency range, $\theta'(\bar{\nu}_i)$ is the phase resulting from the transformation,

and $\theta(\bar{\nu})$ is 0 or $-\pi$, for two points $i = 1, 2$. To correct for the finite frequency range and the logarithmic branch point simultaneously, three parameters, A , B , and η are determined by solving three simultaneous equations

$$\theta(\bar{\nu}_i) = \theta'(\bar{\nu}_i) + A \ln \left| \frac{400 + \bar{\nu}_i}{400 - \bar{\nu}_i} \right| + B \ln \left| \frac{4000 + \bar{\nu}_i}{4000 - \bar{\nu}_i} \right| + 2 \arctan(\eta/\bar{\nu}_i),$$

$i = 1, 2, 3$ by the half-interval method. The corrected phase, θ'' is then given by

$$\theta''(\bar{\nu}_0) = \theta'(\bar{\nu}_0) + A \ln \left| \frac{400 + \bar{\nu}_0}{400 - \bar{\nu}_0} \right| + B \ln \left| \frac{4000 + \bar{\nu}_0}{4000 - \bar{\nu}_0} \right| + 2 \arctan(\eta/\bar{\nu}_0) \quad (14)$$

for all points $\bar{\nu}_0$.

For the inorganic system the points chosen were $\bar{\nu}_1 = 500 \text{ cm}^{-1}$, $\theta(\bar{\nu}_1) = 0$; $\bar{\nu}_2 = 1000 \text{ cm}^{-1}$, $\theta(\bar{\nu}_2) = 0$; $\bar{\nu}_3 = 2250 \text{ cm}^{-1}$, $\theta(\bar{\nu}_3) = 0$; while for the benzene system they were $\bar{\nu}_1 = 500 \text{ cm}^{-1}$, $\theta(\bar{\nu}_1) = 0$; $\bar{\nu}_2 = 2400 \text{ cm}^{-1}$, $\theta(\bar{\nu}_2) = -\pi$; $\bar{\nu}_3 = 3500 \text{ cm}^{-1}$, $\theta(\bar{\nu}_3) = -\pi$.

The uncorrected and corrected phase error spectra for the two systems are shown in Figs. 6 and 7. In both cases, the corrections resulted in a satisfactory level of error when the parameters S and Γ were extracted from the spectra of \hat{n} and $\hat{\epsilon}$; the errors were less than 5% for the benzene case and are given in Table II for the inorganic case. An interesting feature of Fig. 7 is the presence of small spikes. These result from digitization error; in these areas R is close to zero, so that increases in R are represented in steps and thus peaks are produced in the transformed spectrum. In a practical case, these digitization errors would be much less than those resulting from signal noise. The larger features are in regions where R is very close to zero.

Case (2d): This case occurs when there are regions of both internal and total internal reflection in the spectrum; the singularity in the complex plane is due to a branch point at $\omega_2 = \tau$. To provide an example of this case, $n_0 \sin \alpha$ must

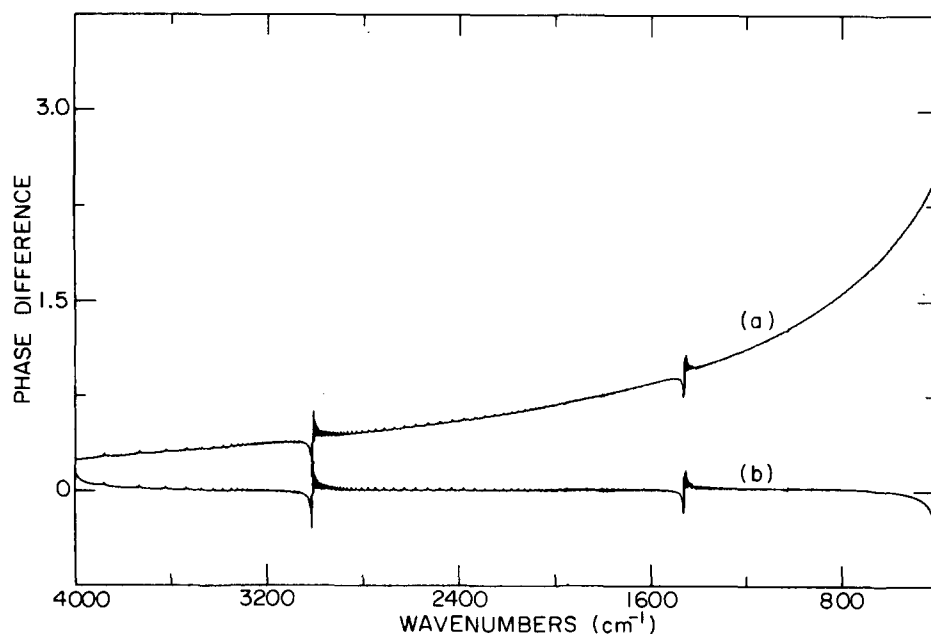


FIG. 7. Phase error spectra in radians for case (2c) benzene system (a) uncorrected, (b) corrected.

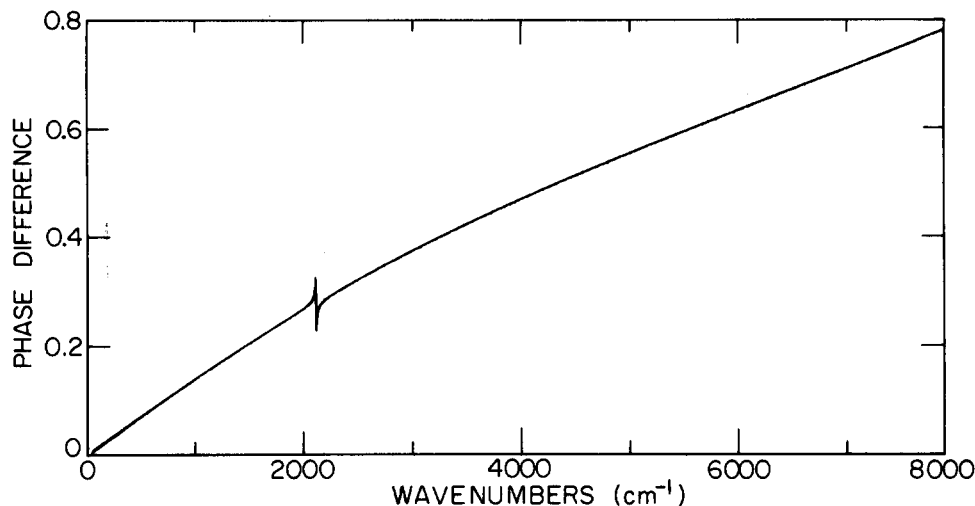


FIG. 8. Phase error spectrum in radians for a single oscillator, case (2d).

lie between $n(\infty)$ and $n(0)$. This case presents more problems than case (2c). First, in regions of total internal reflection $k \approx 0$ does not imply $\Theta \approx 0$ or $\Theta \approx -\pi$, and second, it is not clear that τ' can be treated as independent of $\bar{\nu}_0$ as noted earlier. The first problem can be avoided if one is able to select two anchor points in the region of internal reflection where $k \approx 0$ does imply $\Theta \approx -\pi$, but if this is not possible, an independent measurement of n at one or two points where $k \approx 0$ is required.

In our case, the value of the exact phase is known, so we are able to assess the utility of the correction term $M(\infty)[1 - (2/\pi) \arctan(\tau'/\bar{\nu}_0)]$ by fitting the $\theta - \theta'$ spectra to this function using $M(\infty)$ and τ' as adjustable parameters. A preliminary study was carried out using a single oscillator of the strength and linewidth of the band at 1500 cm^{-1} in the inorganic system, but located at 2500 cm^{-1} . The frequency range was $0\text{--}7899 \text{ cm}^{-1}$. Since $R \approx 1$ at the high frequency limit, this is a situation in which the effect of the finite frequency range is minimal. An example of the resulting phase error spectrum for this single oscillator is shown in Fig. 8. In this case, $n_0 \sin \alpha = 2.15$, $n(0) = 2.549$, and $n(\infty) = 2.0$. Two points are needed to determine τ' and $M(\infty)$; by varying the location of these two points the accuracy of the correction term can be assessed. As expected, τ' and $M(\infty)$ do depend on the location of the points, some examples being given in Table III. Despite the seemingly large variation in τ' and $M(\infty)$ with the choice of the anchor points, the data were fitted to within 0.03 rad as long as the points were chosen sufficiently far apart, with one of them above 6000 cm^{-1} . This method of correction thus appears to be satisfactory for a single oscillator system. Testing for the multiple oscillator systems follows.

TABLE III. Variation of the parameters τ' and $M(\infty)$ with location of the two points used to determine them.

$\bar{\nu}_1(\text{cm}^{-1})$	$\bar{\nu}_2(\text{cm}^{-1})$	$\tau'(\text{cm}^{-1})$	$M(\infty)$
4000	7850	7587.14	1.5260
1000	7000	5544.13	1.2406
1950	6000	5344.16	1.1820

Values for $n_0 \sin \alpha$ were chosen to be 2.50 and 1.49 for the inorganic and benzene systems, respectively, with $\alpha = \pi/4$. Figure 9 shows the spectra of R and θ' for the inorganic case. The spectrum for R clearly illustrates the need for phase information, as it would be difficult indeed to characterize the absorption properties of this system from the reflectivity spectrum alone. Plots of the uncorrected and corrected phase error spectra are shown in Figs. 10 and 11. The anchor points were chosen to be 850 and 3500 cm^{-1} for the inorganic system and 1000 and 3700 cm^{-1} for the benzene system. The calculated values of S and Γ are accurate to within 3% for the benzene system, but are not nearly as good for the inorganic system, as shown in Table II. Much of this error can be attributed to the finite frequency range. At the high frequency end of the range, this effect is expected to be small, since $R \approx 1$, but it is expected to be, and clearly is, significant at the low frequency end where the correction term is seen to do a relatively poor job of correcting the phase.

Case (2e): Total internal reflection only. This is a very common case in reflection spectroscopy involving an incident medium of high refractive index. It may be approached in three ways. First, we examine the correction term

$$I(\bar{\nu}_0) = -\pi + M(\infty) + (2/\pi) \arctan(\tau'/\bar{\nu}_0)[M(0) - M(\infty)] \quad (15)$$

and note that the factor $M(0) - M(\infty)$ is the difference in the phase at zero and high frequency. For relatively weak bands, $M(0) - M(\infty)$ is small compared to $M(\infty)$, so as a first approximation we may set $I(\bar{\nu}_0) = -\pi + M(\infty)$, which is a constant. To correct the phase spectrum in this approximation, the phase must be known at one point, e.g., n must be known at some frequency where $k \approx 0$.

A second approach is to determine the values of the three parameters $M(\infty)$, τ' , and $M(0)$ in Eq. (15) from values of n known at three frequencies where $k \approx 0$. Again, as in case (2d), the validity of this approach depends on τ' being only weakly dependent on $\bar{\nu}_0$.

A third approach has been developed by Plaskett and Schatz.⁶ Using a different contour integral, they developed a modified KK transformation, valid only for the case of total internal reflection:

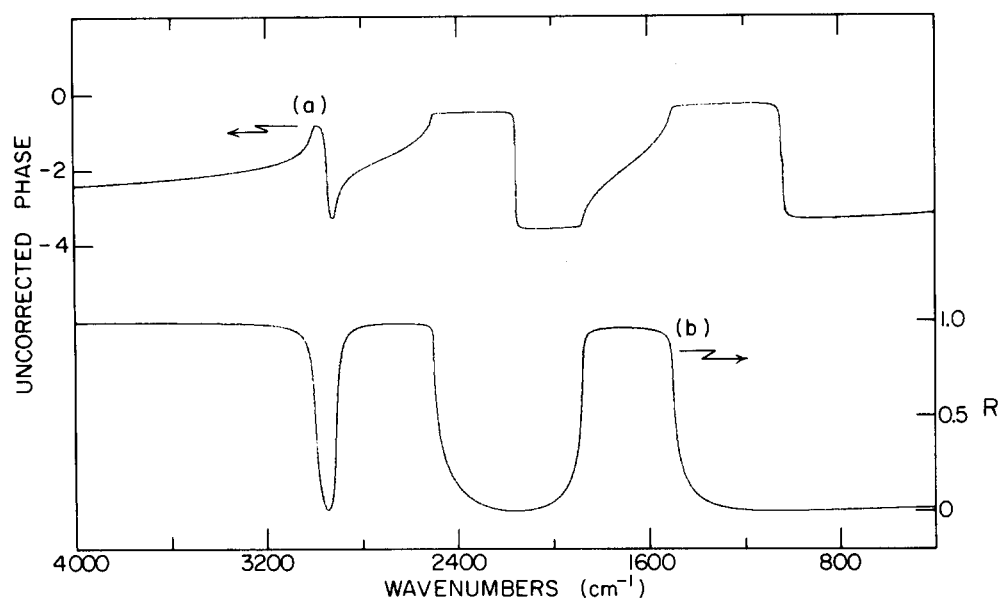


FIG. 9. (a) Uncorrected spectrum of $\theta - \pi$ in radians from transformation of R for case (2d) inorganic system, (b) spectrum of R .

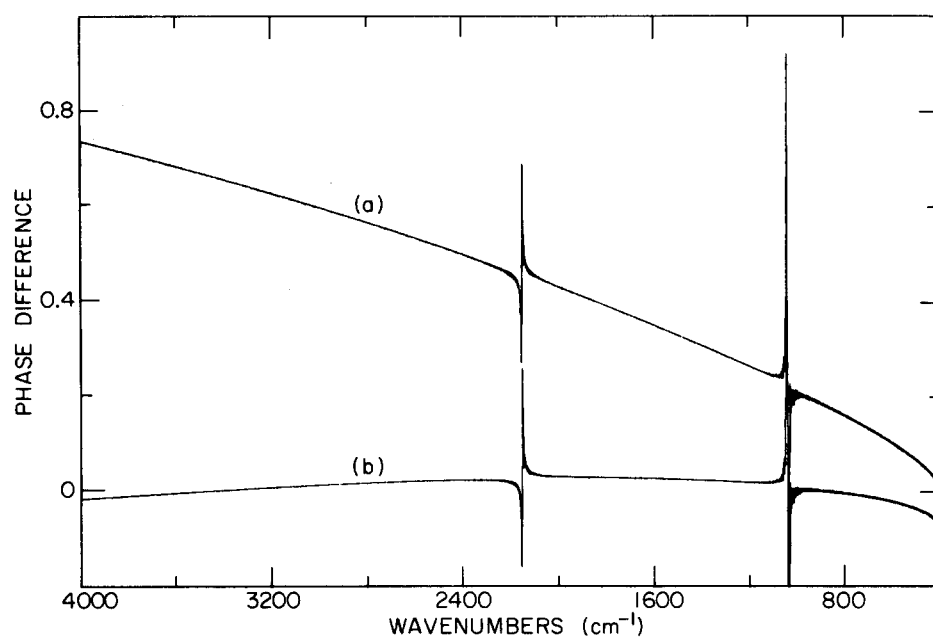


FIG. 10. Phase error spectra in radians for case (2d) inorganic system (a) uncorrected, (b) corrected.

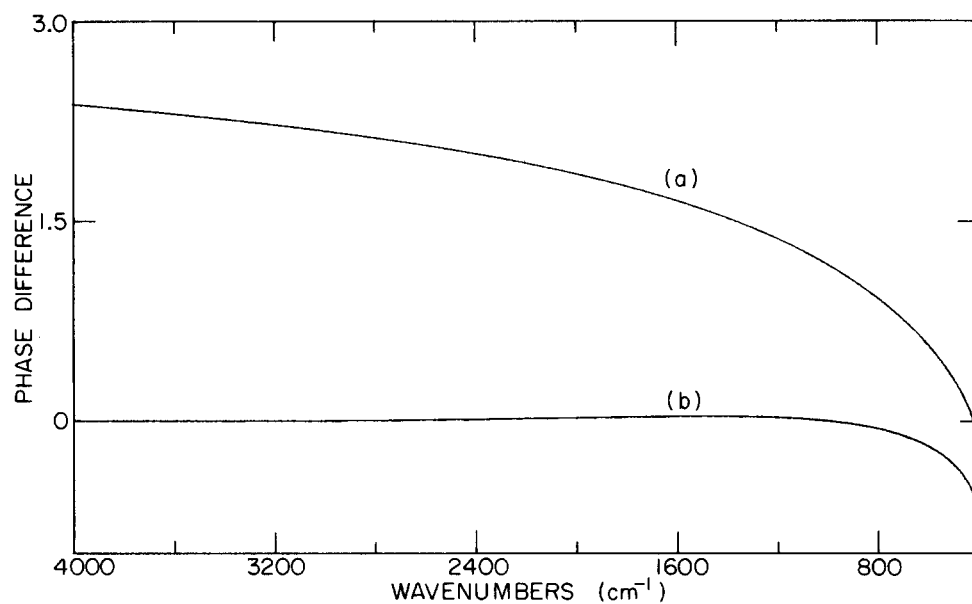


FIG. 11. Phase error spectra in radians for case (2d) benzene system (a) uncorrected, (b) corrected.

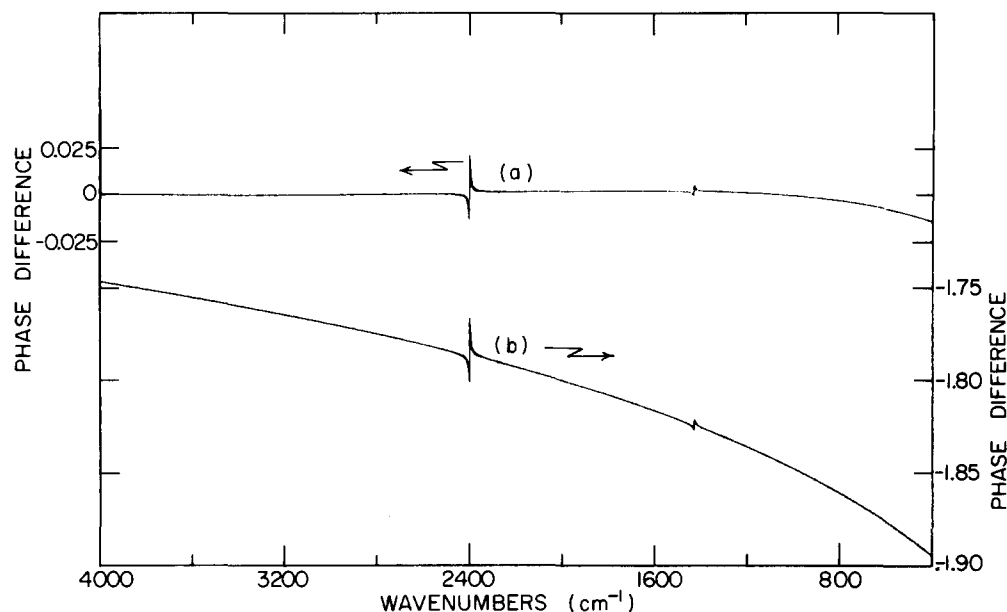


FIG. 12. Phase error spectra in radians for case (2e) inorganic system (a) corrected using three anchor point method, (b) uncorrected.

$$\theta(\omega_0) = \frac{2\omega_0}{\pi} \int_0^\infty \frac{\ln[R(\omega_1)]^{1/2} d\omega_1}{\omega_1(\omega_1^2 - \omega_0^2)} - \pi + 2 \arctan \left[\frac{[n_0^2 \sin^2 \alpha - n(0)^2]^{1/2}}{n_0 \cos \alpha} \right]. \quad (16)$$

Since the KK and FT relationships are mathematically equivalent, the FT relationship equivalent to Eq. (16) can be obtained by transforming, according to Eq. (4), the function $(1/\omega_1)\ln[R(\omega_1)]^{1/2}$ in place of $\ln[R(\omega_1)]^{1/2}$, then multiplying the result by ω_0 . Again, this approach requires knowledge of n at any one frequency.

To test these approaches, n_0 was chosen to be 6.0 and 4.0 for the inorganic and benzene systems, respectively, with $\alpha = \pi/4$. First, the normal FT transformation was carried out, and the phase error spectra determined. A constant phase error spectrum indicates that a single additive correc-

tion is adequate. The inorganic phase error spectrum [Fig. 12(a)] shows a significant deviation from constancy. Nevertheless, the spectra of $\hat{\epsilon}$ were calculated after adding a constant -1.82 to the phase. The results are tabulated in Table II. The error levels, while fairly large, are satisfactory for many purposes. On the other hand, the phase error spectrum for the benzene case is almost constant, varying only from -1.734 to -1.730 over the spectral range. A single additive correction gives very satisfactory results in this case, the errors in S and Γ being less than 1%. Of course, these results depend on the accuracy to which n is known at the anchor point. For organic materials, it is easy to estimate the value of n to within 5% or better. A 5% error in n at the anchor point was found to result in an error of 5% in the parameters S and Γ . This simple approach would clearly be useful for obtaining the absorption spectrum of typical organic compounds. Of course, an independent measurement of n at

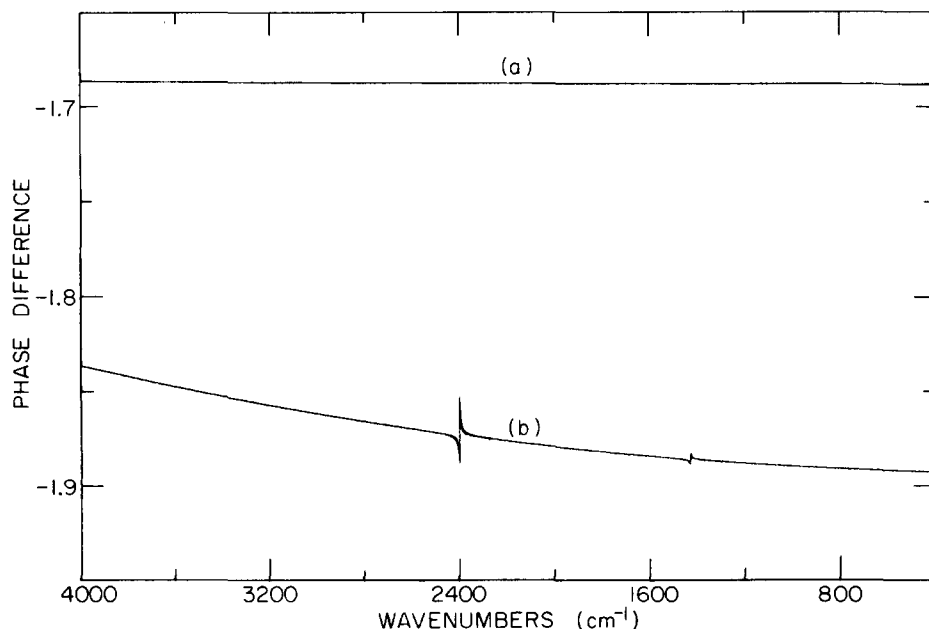


FIG. 13. Phase error spectra in radians obtained using modified FT method, case (2e) (a) benzene system, (b) inorganic system.

some frequency within the spectral range would be still better.

The second method, involving three anchor points, was tested on the inorganic system only. Anchor points chosen were at 1000, 2775, and 3800 cm^{-1} , from which the parameters were determined to be $\tau' = 2740.24$, $M(\infty) = 1.4908$, and $M(0) = 1.2372$. The corrected phase difference spectrum is shown in Fig. 12(b), and as might be expected from a three parameter fit, shows a very low phase error. The results for S and Γ are shown in Table II, and are excellent.

Finally, the modified KK relation of Eq. (16) was tested, the resulting phase difference spectra being shown in Fig. 13. Any nonconstancy in this case must be due to the finite frequency range. The phase difference is close to being constant for the benzene case, and values of S and Γ have errors of less than 2%. However, an appreciable slope appears in the phase difference spectrum for the inorganic case. The effect of finite frequency range is particularly serious for the modified KK relationship at the low frequency end, since division by a small frequency will increase the error due to the assumption that $\ln R^{1/2}$ is constant in this range. The consequences of this are seen in the large errors in the values of S and Γ , Table II. In both cases tested, the modified relationship performed marginally worse than the normal KK approach with only a single point correction, thus ruling out this approach as a practical possibility, unless data approaching zero frequency are available.

Case (2f): This case occurs when all three types of reflection: internal, external, and total internal, occur in different regions of the spectrum. It is very unlikely to occur in practice, except at grazing incidence, since both $n_0 \sin \alpha$ and n_0 must lie between $n(0)$ and $n(\infty)$; and so is not treated here.

Cases (1a)–(1c): These cases of normal incidence are special cases of, and are treated in an identical manner to, cases (2a)–(2c).

Finally we examined the effect of including an absorption band for the incident medium outside the spectral range so that it resulted in n_0 varying with frequency with k_0 very small. No additional difficulties were encountered when data so generated were transformed and n and k calculated setting $k_0 = 0$ but using the correct n_0 . Conceivably, such a situation could lead to two or more logarithmic branch points or branch points in $\hat{\gamma}$, and furthermore, they would not lie exactly on the imaginary frequency axis. However, on examining the problem we conclude that, in practice, such a difficulty is very unlikely to arise if the transformation is restricted to spectral regions where the incident or window material is commonly regarded as transparent, i.e., less than a few percent absorption in a pathlength of several mm or more.

V. SUMMARY AND CONCLUSIONS

The extension of the KK analysis to s -polarized light at nonnormal incidence from a transparent medium of arbitrary, constant refractive index is based on using anchor points where the phase is known. Two types of anchor points are used. The first are used when there are regions of external and/or internal reflection, where $k \approx 0$ implies $\theta \approx 0$ or $\theta \approx -\pi$, respectively. Use of this type of anchor point allows

the correction of the phase spectra without any independent knowledge of the optical properties of the material. The second type of anchor point must be used in regions of total internal reflection, and requires an independent measurement of n at a point where $k \approx 0$, or an estimate thereof, the latter often being sufficient as already noted.

For the system representing a typical organic material the extension is successful in all cases, allowing the optical constants to be determined to a comparable or better accuracy than is achieved with conventional KK analysis. The most difficult case to handle is where both internal and total internal reflection are present; here, two anchor points are required. For the particular choice of n_0 and α tested, both of the anchor points were of the second kind, a situation which would be quite unsatisfactory in practice. An important conclusion for this system is that for the case of total internal reflection only, even a fairly rough estimation of the value of n at a single anchor point results in reasonably accurate absorption parameters, making the method particularly useful for routine spectral measurements on organic liquids.

For the inorganic system of very strong bands, extension of the KK procedure was almost as satisfactory. The level of error introduced by the methods used is probably no larger than would be introduced experimentally, as R is often close to zero or one and thus the relative error in R or $\ln R$ is high. The least accurate results were obtained in the case where both internal and external reflection were present. Nevertheless, the resulting spectra are certainly a satisfactory first approximation; more accurate results could be obtained, e.g., by using oscillator functions to fit the reflectivity data,²² with the parameters obtained from KK analysis of the reflectivity providing starting values. Certainly, for these strong bands, the results of the corrected KK transformation give a much better understanding of the absorption properties of the system than do the spectra of R alone.

Experimentally, if the angle of incidence and/or n_0 may be varied, best results would be obtained using the KK method if total internal reflection were avoided in the case of very strongly absorbing materials.

Finally, we stress that the application of the software of commercial FTIR instruments makes the determination of optical constants by these techniques rapid and routine.

ACKNOWLEDGMENT

The authors thank the Natural Science and Engineering Research Council of Canada for supporting this work.

¹F. Stern, *Solid State Phys.* **15**, 299 (1963).

²R. H. Young, *J. Opt. Soc. Am.* **67**, 520 (1977).

³M. G. Sceats and G. C. Morris, *Phys. Status Solidi* **14**, 643 (1972).

⁴C. W. Peterson and B. W. Knight, *J. Opt. Soc. Am.* **63**, 1238 (1973).

⁵J. A. Bardwell and M. J. Dignam, *Anal. Chim. Acta.* **172**, 101 (1985).

⁶J. S. Plaskett and P. N. Schatz, *J. Chem. Phys.* **38**, 612 (1963).

⁷D. W. Berreman, *Appl. Opt.* **6**, 1519 (1967).

⁸A. A. Clifford, M. I. Duckels, and B. Walker, *J. Chem. Soc. Faraday Trans. 2* **68**, 407 (1972).

⁹G. M. Hale, W. E. Holland, and M. R. Querry, *Appl. Opt.* **12**, 48 (1973).

¹⁰M. R. Querry and W. E. Holland, *Appl. Opt.* **13**, 595 (1974).

¹¹W. G. Chambers, *Infrared Phys.* **15**, 139 (1975).

¹²E. G. Makarova and V. N. Morozov, *Opt. Spectrosc.* **40**, 138 (1976).

- ¹³W. N. Hansen and W. A. Abdou, *J. Opt. Soc. Am.* **67**, 1537 (1977).
¹⁴A. E. Tshmel and V. I. Vettegren, *Spectrochim. Acta. Part A* **29**, 1681 (1973).
¹⁵A. E. Tshmel, V. I. Vettegren, and V. M. Zolotarev, *J. Macromol. Sci. Phys. B* **21**, 243 (1982).
¹⁶B. Velicky, *Czech. J. Phys. B* **11**, 541 (1961).
¹⁷M. Cardona, in *Optical Properties of Solids*, edited by S. Nudelman and S. Mitra (Plenum, New York, 1969), p. 137.
¹⁸D. M. Roessler, *Br. J. Appl. Phys.* **16**, 1119 (1965).
¹⁹H. R. Phillip and E. A. Taft, *Phys. Rev. A* **136**, 1445 (1964).
²⁰E. Loh, *Phys. Rev.* **116**, 673 (1968).
²¹J. P. Hawranek and R. N. Jones, *Spectrochim. Acta. Part A* **32**, 111 (1976).
²²H. A. Verleur, *J. Opt. Soc. Am.* **58**, 1356 (1968).