Curvefitting Imaginary Components of Optical Properties: Restrictions on the Lineshape Due to Causality

C. Dale Keefe

Department of Physical and Applied Sciences, University College of Cape Breton, Sydney, Nova Scotia, Canada, B1P 6L2

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The Kramers–Kronig transformation has been extensively applied in optical spectroscopy to calculate the real component of an optical quantity from the imaginary component, such as the real refractive index from the imaginary component, or vice versa. In this paper, the traditional proof of the Kramers–Kronig transformation, and its application to the complex refractive index, complex dielectric constant, and complex molar polarizability, are reviewed. Often the imaginary components of these quantities are fitted with standard lineshapes such as the Gaussian, Lorentzian, or Classical Damped Harmonic Oscillator (CDHO) lineshapes. It is shown that the usual Gaussian and Lorentzian lineshapes do not meet the physical criteria of these imaginary components nor the conditions of the Kramers–Kronig transformation since they are not odd functions of wavenumber. However, the CDHO lineshape meets the physical criteria of the imaginary components of these optical quantities and the Kramers–Kronig transformation. Modifications are presented that make the Gaussian and Lorentzian odd. The Gaussian decays so fast that the modification is not needed in practice; however, the Lorentzian is much slower to decay and thus modification is necessary whenever fitting peaks below ~250 cm⁻¹. Since the computational difference between the usual Lorentzian and modified Lorentzian is negligible, the author recommends that only the modified Lorentzian be used when fitting bands with a Lorentzian lineshape. @ 2001 Academic Press

Key Words: Kramers-Kronig transformation; dielectric constants; optical constants; molar polarizability; curvefitting.

INTRODUCTION

The Kramers-Kronig transformation was developed independently by Kramers (1) and Kronig (2, 3) around 1927 and is widely used in optical spectroscopy (4-8). Even though it has been shown in the literature (1-3, 9-15) that causality (output cannot occur before input) ensures that for a linear response the conditions of the Hilbert and KK transformations are satisfied by the complex refractive index $(\hat{n}(\tilde{\nu}) = n(\tilde{\nu}) +$ $ik(\tilde{\nu})$) and complex dielectric constant $(\hat{\epsilon}(\tilde{\nu}) = \epsilon'(\tilde{\nu}) + \epsilon'(\tilde{\nu}))$ $i\epsilon''(\tilde{\nu})$) spectra, the criteria that a lineshape must meet in order to be a satisfactory lineshape to fit the imaginary components of these quantities have not been discussed. In this paper, it is shown that the commonly used Gaussian and Lorentzian lineshapes do not meet the criteria of the imaginary components of optical properties. Modifications to these lineshapes are suggested to correct this defect. This is especially important when fitting low-wavenumber bands. It is also shown that the Classical Damped Harmonic Oscillator (CDHO) lineshape (16), recently used to fit infrared absorption bands of liquids (17-21), meets the criteria of the imaginary components of the optical properties.

REVIEW OF THE TRADITIONAL PROOF

The traditional proof of the Kramers–Kronig transformation relies on the Cauchy–Goursat integral theorem (22, 23), which states

If a complex function f is analytic at all points interior to and on a simple closed contour C, then

$$\oint_C f(z)dz = 0.$$

Let

$$f(z) = g(z) + ih(z) = g(x, y) + ih(x, y),$$
[1]

where z = x + iy and g(x, y) and h(x, y) are real valued functions, such that f(z) is analytic (see appendix for a discussion of analytic functions) and $f(z) \rightarrow a$ as $|z| \rightarrow \infty$ in either the lower or upper half of the complex plane, where *a* is a constant which may be complex. Without loss of generality, it will be assumed here that this is true on the upper half of the complex plane. The lower half of the plane gives the same equations but with a negative sign. The positive sign is chosen since by convention both the real and imaginary components of the optical properties are positive on the real axis. The curve used in the proof is given in Fig. 1.

Consider the integral

$$\oint_C \frac{f(z) - a}{z - \omega} \, dz,$$
[2]





FIG. 1. The closed curve, *C*, in the complex *xy* plane, used to prove the Hilbert transform. The arrows give the direction of the integration. ρ is the radius of the semicircle centered at the origin and γ is the radius of the semicircle centered at ω .

where *C* is the closed curve defined in Fig. 1 and ω is the value of *x* at a specific point on the real axis. Since f(z) is analytic and $z-\omega$ is not zero on or interior to *C*, $(f(z) - a)/(z - \omega)$ is also analytic on and interior to *C* given in Fig. 1 and by the Cauchy–Goursat integral theorem the integral over this path is zero.

Consider the limit as $\rho \to \infty$, the integral over this part of the curve is 0 since $f(z) - a \to 0$. Therefore, the sum of the integral over the real axis and the semicircle centered about ω must also be zero:

$$\int_{-\infty}^{\omega-\gamma} \frac{f(x)-a}{x-\omega} \, dx + \int_{\omega+\gamma}^{\infty} \frac{f(x)-a}{x-\omega} \, dx + \int_{\pi}^{0} \frac{(f(\omega+\gamma e^{i\theta})-a)\gamma i e^{i\theta}}{\gamma e^{i\theta}} \, d\theta = 0 \quad [3]$$

$$\int_{-\infty}^{\omega-\gamma} \frac{f(x)-a}{x-\omega} \, dx + \int_{\omega+\gamma}^{\infty} \frac{f(x)-a}{x-\omega} \, dx + i \int_{\pi}^{0} (f(\omega+\gamma e^{i\theta})-a) d\theta = 0.$$
 [4]

Now consider the limit of this equation as $\gamma \rightarrow 0$,

$$\lim_{\gamma \to 0} \left[\int_{-\infty}^{\omega - \gamma} \frac{f(x) - a}{x - \omega} \, dx + \int_{\omega + \gamma}^{\infty} \frac{f(x) - a}{x - \omega} \, dx \right]$$
$$+ i \int_{\pi}^{0} \left(f(\omega + \gamma e^{i\theta}) - a \right) d\theta$$
$$= P \int_{-\infty}^{\infty} \frac{f(x) - a}{x - \omega} \, dx - i \pi (f(\omega) - a) = 0,$$
[5]

where P stands for the Cauchy Principal value of the integral (23). Separating the real and imaginary parts, one obtains

$$g(\omega) - \operatorname{Re}(a) = \frac{1}{\pi} P \int_{-\infty}^{\infty} \frac{h(x) - \operatorname{Im}(a)}{x - \omega} dx$$
 [6]

$$h(\omega) - \operatorname{Im}(a) = -\frac{1}{\pi} P \int_{-\infty}^{\infty} \frac{g(x) - \operatorname{Re}(a)}{x - \omega} dx.$$
 [7]

Usually, these equations are applied to the special case where *a*, the limit of f(z) as $|z| \to \infty$, is a real quantity and thus $\operatorname{Re}(a) = g_{\infty}$ and $\operatorname{Im}(a) = 0$, giving

$$g(\omega) - g_{\infty} = \frac{1}{\pi} P \int_{-\infty}^{\infty} \frac{h(x)}{x - \omega} dx$$
 [8]

$$h(\omega) = -\frac{1}{\pi} P \int_{-\infty}^{\infty} \frac{g(x) - g_{\infty}}{x - \omega} dx.$$
 [9]

These equations are called the Hilbert transforms in the chemistry and physics literature (11). If $f(x) = f^*(-x)$, where * represents the complex conjugate (in other words, g(x) is an even function and h(x) is an odd function), then Eqs. [6] and [7] become

$$g(\omega) - \operatorname{Re}(a) = \frac{2}{\pi} P \int_{0}^{\infty} \frac{x(h(x) - \operatorname{Im}(a))}{x^{2} - \omega^{2}} dx$$
 [10]

$$h(\omega) - \operatorname{Im}(a) = -\frac{2\omega}{\pi} P \int_0^\infty \frac{g(x) - \operatorname{Re}(a)}{x^2 - \omega^2} \, dx \qquad [11]$$

and the special case where *a*, the limit of f(z) as $|z| \to \infty$, is a real quantity gives

$$g(\omega) - g_{\infty} = \frac{2}{\pi} P \int_0^\infty \frac{xh(x)}{x^2 - \omega^2} dx \qquad [12]$$

$$h(\omega) = -\frac{2\omega}{\pi} P \int_0^\infty \frac{g(x) - g_\infty}{x^2 - \omega^2} dx.$$
 [13]

These are known as the Kramers–Kronig (KK) transforms in the chemistry and physics literature. The Hilbert transform does *not* require the real part of the function f to be even and the imaginary part to be odd. This is a requirement of the KK transform, but this has not been clear in the literature. The

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Hilbert transform is the more general transform and the KK is a special case of it. It should also be noted that the real part need only be even and the imaginary part need only be odd on the real axis, not over the entire upper half of the complex plane.

Extension of the Hilbert and KK Transforms to Nonanalytic Functions

If a function is analytic everywhere on and interior to a closed curve *C*, except for a finite number of singular points, z_1, z_2, \ldots, z_n , interior to *C*, then (22, 23)

$$\oint_C f(z)dz = 2\pi i \sum_{i=1}^n B_i,$$
[14]

where B_i is the residue (22, 23) of f(z) at z_i . If the sum of these residues is zero, then all the arguments developed above for an analytic function will apply to f(z) as well.

The requirements for the KK transform, given by Eqs. [12] and [13] to hold, can be summarized as follows:

(1) The function must be analytic over the upper half (or lower half) of the complex plane or the sum of the residues at the singular points must be zero.

(2) The function must go to a real constant as the complex variable z goes to infinity.

(3) The real part of the function must be even and the imaginary part must be odd on the real axis.

The Hilbert transform, given by Eqs. [8] and [9], only requires the first two criteria.

APPLICATION TO THE REFRACTIVE INDEX, DIELECTRIC CONSTANT, AND MOLAR POLARIZABILITY

As is mentioned in the introduction, it has been shown in the literature that causality (output can not occur before input) ensures that for a linear response, the conditions of the Hilbert and KK transformations are satisfied by the complex refractive index $(\hat{n}(\tilde{\nu}) = n(\tilde{\nu}) + ik(\tilde{\nu}))$ and complex dielectric constant $(\hat{\epsilon}(\tilde{\nu}) = \epsilon'(\tilde{\nu}) + i\epsilon''(\tilde{\nu}))$ spectra. The resulting equations for the Hilbert transform are

$$n(\tilde{\nu}_j) - n_\infty = \frac{1}{\pi} P \int_{-\infty}^{\infty} \frac{k(\tilde{\nu})}{\tilde{\nu} - \tilde{\nu}_j} d\tilde{\nu}$$
[15]

$$k(\tilde{\nu}_j) = -\frac{1}{\pi} P \int_{-\infty}^{\infty} \frac{n(\tilde{\nu}) - n_{\infty}}{\tilde{\nu} - \tilde{\nu}_j} d\tilde{\nu} \qquad [16]$$

$$\boldsymbol{\epsilon}'(\tilde{\nu}_j) - \boldsymbol{\epsilon}_{\infty} = \frac{1}{\pi} P \int_{-\infty}^{\infty} \frac{\boldsymbol{\epsilon}''(\tilde{\nu})}{\tilde{\nu} - \tilde{\nu}_j} d\tilde{\nu} \qquad [17]$$

$$\epsilon''(\tilde{\nu}_j) = -\frac{1}{\pi} P \int_{-\infty}^{\infty} \frac{\epsilon'(\tilde{\nu}) - \epsilon_{\infty}}{\tilde{\nu} - \tilde{\nu}_j} d\tilde{\nu} \qquad [18]$$

and the resulting equations for the KK transform are

$$n(\tilde{\nu}_j) - n_{\infty} = \frac{2}{\pi} P \int_0^\infty \frac{\tilde{\nu}k(\tilde{\nu})}{\tilde{\nu}^2 - \tilde{\nu}_j^2} d\tilde{\nu}$$
[19]

$$k(\tilde{\nu}_j) = -\frac{2\tilde{\nu}_j}{\pi} P \int_0^\infty \frac{n(\tilde{\nu}) - n_\infty}{\tilde{\nu}^2 - \tilde{\nu}_j^2} d\tilde{\nu} \qquad [20]$$

$$\epsilon'(\tilde{\nu}_j) - \epsilon_{\infty} = \frac{2}{\pi} P \int_0^\infty \frac{\tilde{\nu}\epsilon''(\tilde{\nu})}{\tilde{\nu}^2 - \tilde{\nu}_j^2} d\tilde{\nu}$$
[21]

$$\boldsymbol{\epsilon}''(\tilde{\nu}_j) = -\frac{2\tilde{\nu}_j}{\pi} P \int_0^\infty \frac{\boldsymbol{\epsilon}'(\tilde{\nu}) - \boldsymbol{\epsilon}_\infty}{\tilde{\nu}^2 - \tilde{\nu}_j^2} d\tilde{\nu}.$$
 [22]

The application of the KK and Hilbert transforms to the complex molar polarizability has not been previously shown. The Lorentz–Lorenz Formula (24) gives the connection between the dielectric constant and the polarizability

$$\frac{\hat{\epsilon} - 1}{\hat{\epsilon} + 2} = \frac{4\pi}{3} N\hat{\alpha},$$
[23]

where N is the number of molecules in unit volume. This relation is usually only applied where the substance is nonabsorbing but it is applicable at frequencies where absorption occurs as long as the complex dielectric constant and complex polarizability are used.

The complex polarizability, $\hat{\alpha}$, is a molecular quantity and one normally works with the more convenient complex molar polarizability, defined (*16*) as

$$\hat{\alpha}_m = N_A \hat{\alpha}, \qquad [24]$$

where N_A is Avogadro's number. The complex molar polarizability is related by $\hat{\alpha}_m = V_m \hat{C}$, to the complex local susceptibility, \hat{C} , that was defined by Clifford and Crawford (25), where V_m is the molar volume ($V_m = N_A/N$ for a pure liquid).

Equations [23] and [24] yield the equations through which the real and imaginary molar polarizabilities are calculated from \hat{e} , viz.:

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$$\alpha'_{m} = \frac{3V_{m}}{4\pi} \frac{[\epsilon' - 1][\epsilon' + 2] + \epsilon''^{2}}{[\epsilon' + 2]^{2} + \epsilon''^{2}}$$
[25]

$$\alpha_m'' = \frac{9V_m}{4\pi} \frac{\epsilon''}{[\epsilon'+2]^2 + \epsilon''^2}.$$
[26]

The complex molar polarizability will be analytic everywhere except where the denominator in Eqs. [23], [25], and [26] is zero. The denominator is zero if $\epsilon' = -2$ and $\epsilon'' = 0$. This is not a physically meaningful condition and the complex molar polarizability is an analytic function of $\tilde{\nu}$. Using $\hat{\epsilon}(\tilde{\nu}) \rightarrow \epsilon_{\infty} = n_{\infty}^2$ as $|\tilde{\nu}| \rightarrow \infty$, and Eqs. [25] and [26], one obtains

$$\alpha_{m,\infty} = \frac{3V_m}{4\pi} \frac{[\boldsymbol{\epsilon}_{\infty} - 1]}{[\boldsymbol{\epsilon}_{\infty} + 2]}.$$
[27]

Thus, the conditions of the Hilbert transform are satisfied by the complex molar polarizability and Eqs. [8] and [9] become

$$\alpha'_{m}(\tilde{\nu}_{j}) - \alpha_{m,\infty} = \frac{1}{\pi} P \int_{-\infty}^{\infty} \frac{\alpha''_{m}(\tilde{\nu})}{\tilde{\nu} - \tilde{\nu}_{j}} d\tilde{\nu}$$
[28]

$$\alpha_m''(\tilde{\nu}_j) = -\frac{1}{\pi} P \int_{-\infty}^{\infty} \frac{\alpha_m'(\tilde{\nu}) - \alpha_{m,\infty}'}{\tilde{\nu} - \tilde{\nu}_j} d\tilde{\nu}.$$
 [29]

Using the fact that $\hat{\epsilon}(\tilde{\nu}) = \hat{\epsilon}^*(-\tilde{\nu})$ and Eqs. [25] and [26], it is a matter of simple algebra to show that $\hat{\alpha}_m(\tilde{\nu}) = \hat{\alpha}_m^*(-\tilde{\nu})$. Thus, the conditions for the KK transform are satisfied and Eqs. [12] and [13] become

$$\alpha'_{m}(\tilde{\nu}_{j}) - \alpha_{m,\infty} = \frac{2}{\pi} P \int_{0}^{\infty} \frac{\tilde{\nu} \alpha''_{m}(\tilde{\nu})}{\tilde{\nu}^{2} - \tilde{\nu}_{j}^{2}} d\tilde{\nu}$$
[30]

$$\alpha_m''(\tilde{\nu}_j) = -\frac{2\tilde{\nu}_j}{\pi} P \int_0^\infty \frac{\alpha_m'(\tilde{\nu}) - \alpha_{m,\infty}}{\tilde{\nu}^2 - \tilde{\nu}_j^2} d\tilde{\nu}.$$
 [31]

FITTING THE IMAGINARY COMPONENT

The Gaussian, Lorentzian, and CDHO lineshapes are often used to fit the imaginary component of one of the optical properties (refractive index, dielectric constant, or molar polarizability, etc.). The application of the KK transform to these optical properties was reviewed above and when one chooses a function to fit experimental data, one must ensure that the function meets the requirements of the optical properties.

Application to the Gaussian Lineshape

The complex Gaussian lineshape can be defined as

$$h(z) = A_0 \operatorname{Re} \left\{ \exp \left(\frac{-(z - z_0)^2}{b} \right) \right\}$$

= $A_0 \exp \left(\frac{-(x - x_0)^2 + (y - y_0)^2}{b} \right)$ [32]
 $\times \cos(2(x - x_0)(y - y_0)),$

where A_0 , b, and z_0 are constants. This function gives the usual Gaussian lineshape when $y = y_0 = 0$:

$$h(x) = A_0 \exp\left(\frac{-(x-x_0)^2}{b}\right).$$
 [33]

The function given by Eq. [32] does not match the properties of the imaginary components of the optical quantities discussed above, since it is not odd and therefore is not a suitable function to use to represent the imaginary component of these optical properties. To make the function odd one needs to use the difference of two Gaussians centered at $z_0 = x_0 + iy_0$ and $-z_0 = -x_0 - iy_0$. Thus, Eq. [32] becomes

$$h(z) = A_0 \operatorname{Re} \left\{ \exp \left(\frac{-(z-z_0)^2}{b} \right) - \exp \left(\frac{-(z+z_0)^2}{b} \right) \right\}$$

= $A_0 \exp \left(\frac{-(x-x_0)^2 + (y-y_0)^2}{b} \right)$
× $\cos(2(x-x_0)(y-y_0))$ [34]
 $-A_0 \exp \left(\frac{-(x+x_0)^2 + (y+y_0)^2}{b} \right)$
× $\cos(2(x+x_0)(y+y_0)),$

which reduces to

$$h(x) = A_0 \left\{ \exp\left(\frac{-(x-x_0)^2}{b}\right) - \exp\left(\frac{-(x+x_0)^2}{b}\right) \right\}$$
[35]

when $y = y_0 = 0$.

It is a straightforward application to differentiate the function given in Eq. [34] twice and show that it is a harmonic function and therefore is suitable as the imaginary component of an analytic function (see appendix). This function goes to zero, as $|z| \rightarrow \infty$, and is odd on the real axis and therefore matches the properties of the imaginary components of the optical properties and is a suitable function to use to fit them. This does not address the question of whether the bandshapes of the experimental spectra are Gaussian; it simply means that the Gaussian function has the correct mathematical properties to be used as a fitting function. Since the real part that corre-



FIG. 2. The usual Gaussian as given by Eq. [33] and the modified Gaussian as given by Eq. [35] for a peak at 50 cm⁻¹ with a full width at half-height of 20 cm⁻¹. The two are superimposed.

sponds to Eq. [34] is calculated by the KK transform, it is forced to meet the requirements of the KK transform.

The Gaussian decays very quickly and thus for all practical purposes fitting the imaginary component for x > 0 with Eqs. [33] and [35] are equivalent, *even* when the peak is extremely close to zero. Figure 2 shows the plots of Eqs. [33] and [35] for a peak at 50 cm⁻¹ with a full width at half-height of 20 cm⁻¹. The two curves cannot be distinguished. Even for a peak at 1 cm⁻¹ with a FWHH of 0.1 cm⁻¹, the differences between the two equations are on the order of 10^{-20} % or less for positive *x* values. Thus, using the Gaussian defined by Eq. [33] to fit the imaginary component of one of the optical quantities for x > 0 is satisfactory with regard to meeting the criteria of the physical properties of the optical quantities discussed above.

Application to the Lorentzian Lineshape

h(z)

The complex Lorentzian lineshape can be defined as

$$= \operatorname{Re}\left\{\frac{A_{0}}{b^{2} + (z - z_{0})^{2}}\right\}$$
$$= \frac{A_{0}[(x - x_{0})^{2} - (y - y_{0})^{2} + b^{2}]}{[(x - x_{0})^{2} - (y - y_{0})^{2} + b^{2}]^{2} + 4(x - x_{0})(y - y_{0})},$$
[36]

where A_0 , b, and z_0 are constants. This function gives the usual Lorentzian lineshape when $y = y_0 = 0$:

$$h(x) = \frac{A_0}{b^2 + (x - x_0)^2}.$$
 [37]

As is the case for the Gaussian, the function given by Eq. [36] does not meet the requirements for the KK transformation, nor the properties of the optical quantities discussed above, since it is not odd. To make the function odd one needs to use the difference of two Lorentzians centered at z_0 and $-z_0$. Thus Eq. [36] becomes

$$= \frac{A_0[(x-x_0)^2 - (y-y_0)^2 + b^2]}{[(x-x_0)^2 - (y-y_0)^2 + b^2]^2 + 4(x-x_0)(y-y_0)} - \frac{A_0[(x+x_0)^2 - (y+y_0)^2 + b^2]}{[(x+x_0)^2 - (y+y_0)^2 + b^2]^2 + 4(x+x_0)(y+y_0)},$$
[38]

which reduces to

$$h(x) = A_0 \left\{ \frac{1}{(x - x_0)^2 + b^2} - \frac{1}{(x + x_0)^2 + b^2} \right\}$$
[39]

when $y = y_0 = 0$.

The function given in Eq. [38] has singular points in the upper half-plane at $z_1 = z_0 - ib$ and $z_2 = z_0 + ib$. It can be shown (22, 23) that if f(z) = P(z)/Q(z), where P(z) and



FIG. 3. The usual Lorentzian (upper curve) as given by Eq. [37] and the modified Lorentzian as given by Eq. [39], for a peak at 50 cm⁻¹ with a full width at half-height of 20 cm⁻¹.

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FIG. 4. The difference between the usual Lorentzian given by Eq. [37] and the modified Lorentzian given by Eq. [39], expressed as a percentage of the peak height of the usual Lorentzian, for the peaks shown in Fig. 3. The modified Lorentzian is always lower than the usual Lorentzian.

Q(z) are analytic and if z_1 is a singular point of f(z) and $Q'(z_1) \neq 0$, then the residue of f(z) at $z_1(B_1)$ is given by

$$B_1 = \frac{P(z_1)}{Q'(z_1)}.$$
 [40]

Let $P(z) = A_0$ and $Q(z) = b^2 + (z - z_0)^2$, thus $Q'(z) = 2(z - z_0)$ and

$$B_1 = \frac{-A_0}{2ib}$$
 and $B_2 = \frac{A_0}{2ib}$. [41]

Therefore, the sum of the residues is zero for the function given in Eq. [38]. The function goes to zero as $z \rightarrow \infty$ and is odd on the real axis. Thus, the function given in Eq. [38] is a suitable function to use to fit the imaginary component of the optical properties. Since the real part that corresponds to Eq. [38] is calculated by the KK transform, it is forced to meet the requirements of the KK transform.

Figure 3 shows the plots of Eqs. [37] (upper curve) and [39] (lower curve) for a peak at 50 cm⁻¹ with a full width at half-height of 20 cm⁻¹. The differences are obvious in the wings to low wavenumber of the peak, but there are also differences in the peak maxima and high wavenumber wings. Figure 4 shows the difference between the two curves as a percentage of the peak height of the curve given by Eq. [37]. The difference varies from 0.44 to 3.8% of the peak height,

with the usual Lorentzian given by Eq. [37] always higher. The difference between Eqs. [37] and [39] decreases if the peak is at higher wavenumber. Figures 5–8 show analogous plots to Figs. 3 and 4 for peaks at 100 and 250 cm⁻¹ both with a full width at half-height of 20 cm⁻¹. For the peak at 100 cm⁻¹ the differences are about a factor of 4 smaller with a maximum difference of 0.99%. For the peak at 250 cm⁻¹ the differences are <0.16%. Thus using a Lorentzian defined by Eq. [37] to fit the imaginary component of one of the optical properties is not satisfactory for peaks below 250 cm⁻¹. When fitting low wavenumber peaks, one needs to consider that the imaginary component is odd and therefore the peak will be asymmetric. Since the computational difficulty for Eq. [37] and [39] is essentially the same, the author recommends that only Eq. [39] be used for fitting with Lorentzian lineshapes.

Application to the CDHO Lineshape

The CDHO lineshape is defined (16) on the real axis by

$$f(x) = A_0 + \frac{B}{x_0^2 - x^2 - ixC},$$
[42]

where A_0 , B, and C are constants. The complex extension is

$$f(z) = A_0 + \frac{B}{z_0^2 - z^2 - izC}$$
[43]



FIG. 5. The usual Lorentzian, given by Eq. [37], and the modified Lorentzian, given by Eq. [39], for a peak at 100 cm^{-1} with a full width at half-height of 20 cm⁻¹. The two are superimposed on the scale shown.



FIG. 6. The difference between the usual Lorentzian given by Eq. [37] and the modified Lorentzian given by Eq. [39], expressed as a percentage of the peak height of the usual Lorentzian, for the peaks shown in Fig. 5. The modified Lorentzian is always lower than the usual Lorentzian.

with the real and imaginary components given by

$$g(x, y) = A_0 + \frac{B(x_0^2 - y_0^2 - x^2 + y^2 + yC)}{(x_0^2 - y_0^2 - x^2 + y^2 + yC)^2} + (2x_0y_0 - 2xy - xC)^2$$
[44]

$$h(x, y) = \frac{-B(2x_0y_0 - 2xy - xC)}{(x_0^2 - y_0^2 - x^2 + y^2 + yC)^2}, \qquad [45]$$
$$+ (2x_0y_0 - 2xy - xC)^2$$

which gives the usual CDHO lineshapes on the real axis ($y = y_0 = 0$):

$$g(x) = A_0 + \frac{B(x_0^2 - x^2)}{(x_0^2 - x^2)^2 + C^2 x^2}$$
[46]

$$h(x) = \frac{BCx}{(x_0^2 - x^2)^2 + C^2 x^2}.$$
 [47]

It is a relatively simple task to show that the functions given by Eqs. [44] and [45] satisfy the Cauchy–Riemann equations (see appendix), and thus the function given by Eq. [43] is analytic. Equation [43] goes to A_0 as $|z| \rightarrow \infty$, and by substituting -x into Eqs. [46] and [47], one can see that the real part, g(x), is even on the real axis and that the imaginary part, h(x), is odd on the real axis. Thus the CDHO bandshape matches the criteria of the optical properties and the KK transformation and is a suitable function to use to fit the imaginary components of these optical constants at any wavenumber.

SUMMARY

In this paper, the traditional proof of the Kramers–Kronig transformation and its application to the complex refractive index, complex dielectric constant, and complex molar polarizability were reviewed. The requirements for the KK transform to hold can be summarized as follows:

(1) The function must be analytic over the upper half (or lower half) of the complex plane or the sum of the residues at the singular points must be zero.

(2) The function must go to a real constant as the complex variable z goes to infinity.

(3) The real part of the function must be even and the imaginary part must be odd on the real axis.

The Hilbert transform only requires the first two criteria.

It has been shown in the literature that the complex refractive index and complex dielectric constant both satisfy these criteria. It was shown in this paper that the complex molar polarizability satisfies these criteria. Since the KK transform applies to these quantities, any lineshapes used to fit them must also meet these criteria. It was shown that the usual Gaussian and Lorentzian functions do not meet these criteria because they are not odd functions. This is not significant for the Gaussian lineshape but it is significant for low wavenumber



FIG. 7. The usual Lorentzian, given by Eq. [37], and the modified Lorentzian, given by Eq. [39], for a peak at 250 cm^{-1} with a full width at half-height of 20 cm⁻¹. The two are superimposed on the scale shown.



FIG. 8. The difference between the usual Lorentzian given by Eq. [37] and the modified Lorentzian given by Eq. [39], expressed as a percentage of the peak height of the usual Lorentzian, for the peaks shown in Fig. 7. The modified Lorentzian is always lower than the usual Lorentzian.

peaks for the Lorentzian lineshape. However, the Lorentzian lineshape can be made odd by considering the difference of two peaks centered at x_0 and $-x_0$. It was also shown in this paper that the CDHO lineshape meets all the criteria of the KK transformation and the optical quantities.

APPENDIX

Analytic Functions

This appendix presents a brief overview of analytic functions. For a more complete discussion, the reader is referred to a text on complex analysis such as Refs. (22) and (23). A function f(z), where z = x + iy, is *defined* to be analytic at a point z_0 if df/dz exists not only at z_0 but also at every point z in some neighborhood of z_0 . It should be noted that f(z) can always be considered to be the sum of two real valued functions g and h according to Eq. [1]. The fact that the partial derivatives of g and h with respect to x and y (i.e., $\partial g/\partial x$, $\partial g/\partial y$, $\partial h/\partial x$, $\partial h/\partial y$) exist is not sufficient to guarantee that df/dz exists and thus can not guarantee that f is analytic. For f to be analytic the functions g and h must satisfy the Cauchy– Riemann equations

$$\frac{\partial g}{\partial x} = \frac{\partial h}{\partial y}$$
[A1]

$$\frac{\partial g}{\partial y} = -\frac{\partial h}{\partial x}.$$
 [A2]

It can also be shown that for a function f to be analytic in a domain D, its component functions (g and h) must be *harmonic* in D, where a function, w(x, y), is defined to be harmonic if its satisfies Laplace's equation

$$\frac{\partial^2 w}{\partial x^2} + \frac{\partial^2 w}{\partial y^2} = 0.$$
 [A3]

If a function f(z) fails to be analytic at a point z_0 , but is analytic at some point in every neighborhood of z_0 , then z_0 is called a *singular point* of f.

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