VI. OPTICAL AND INFRARED SPECTROSCOPY*

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A. ON THE DIELECTRIC RESPONSE FUNCTION

1. Introduction

Many of the interactions of electromagnetic radiation with matter can be expressed most concisely in terms of a linear dielectric response function. Consequently, when studying the properties of a solid by means of its interaction with electromagnetic radiation, it is instructive to delimit the applicability of the dielectric response function, $\epsilon(\omega)$, by deriving it.

Such a procedure will show that it can be applied to the processes of reflection, transmission, absorption, and elastic scattering of electromagnetic radiation, but cannot be applied directly to those processes in which the frequency of the scattered radiation differs from that of the incident radiation, as in Raman scattering. Moreover, by considering $\epsilon(\omega)$ to be an analytic function the following derivation makes explicit the characteristic parameters of the dielectric response function, which can be completely specified by a scaling coefficient ϵ and the locations of all of its poles and zeros in the complex frequency domain. Finally, upper and lower bounds can be placed on the estimates of the characteristic frequencies of $\epsilon(\omega)$ based upon the experimentally determined values of $\epsilon(\omega)$.

2. Derivation of the Linear Dielectric Response Function

From Maxwell's equations,

$$\vec{D}(\vec{r},t) = \vec{E}(\vec{r},t) + 4\pi\vec{P}(\vec{r},t). \tag{1}$$

If we are working with "small" electric fields, we may approximate $\vec{P}$ and $\vec{D}$ by linear functions of $\vec{E}$. Using the most general form for the linear operator $\mathscr{L}_{sq}$, we have

$$D_s(\vec{r},t) = \sum_{q=1}^{3} \int_{-\infty}^{\infty} dt' \int_{\text{All space}} d^3r' \, \mathscr{L}_{sq}(\vec{r},\vec{r}',t,t') \, E_q(\vec{r}',t'), \tag{2}$$

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where

$$\vec{D}(\vec{r},t) = \sum_{s=1}^{3} \hat{s} D_s(\vec{r},t),$$

and $\mathscr{L}_{sq}(\vec{r},\vec{r}',t,t')$ is an element of the general linear operator relating $\vec{D}(\vec{r},t)$ to $\vec{E}(\vec{r}',t')$. Moreover, since we must work with physically realizable quantities, the Fourier transforms of $\vec{D}$, $\vec{E}$, and $\vec{P}$ must all exist. Therefore, we may define

$$D_s(\vec{r},t) = (2\pi)^{-1/2} \int_0^\infty \left[A_s(\vec{r},\omega)\cos\omega t + B_s(\vec{r},\omega)\sin\omega t)\right] d\omega,$$

where D_s, A_s, and B_s are all REAL coefficients. $D_s(\vec{r},t)$ may be more compactly expressed in terms of its complex Fourier amplitude.

$$D_s(\vec{r},t) = (2\pi)^{-1/2} \int_{-\infty}^{+\infty} d\omega\, \mathscr{D}_s(\vec{r},\omega)\, e^{-i\omega t},$$

where

$$\mathscr{D}_s(\vec{r},\omega) = \frac{1}{2}\left[A_s(\vec{r},\omega) + i B_s(\vec{r},\omega)\right] \qquad \omega \geq 0$$

and

$$\mathscr{D}_s(\vec{r},-\omega) = \mathscr{D}_s^*(\vec{r},\omega).$$

But the spatial Fourier transform must also exist. Therefore, we may define

$$D_s(\vec{r},t) = (2\pi)^{-2} \int_{-\omega}^{\infty} d\omega \int_{\substack{\text{reciprocal}\\ \text{space}}} d^3k\, \mathscr{D}_s(\vec{k},\omega)\, e^{i\vec{k}\cdot r - i\omega t}. \tag{3}$$

Likewise

$$E_s(\vec{r},t) = (2\pi)^{-2} \int_{-\infty}^{\infty} d\omega \int_{\substack{\text{reciprocal}\\ \text{space}}} d^3k\, \mathscr{E}_s(\vec{k},\omega)\, e^{i\vec{k}\cdot\vec{r} - i\omega t}, \tag{4}$$

where

$$\mathscr{D}_s(\vec{k},\omega) = \mathscr{D}_s^*(-\vec{k},-\omega)$$

and

$$\mathscr{E}_s(\vec{k},\omega) = \mathscr{E}_s^*(-\vec{k},-\omega)$$

in order that D_s and E_s be REAL functions. Substituting the Fourier expressions for D_s and E_s in (2), we obtain

$$(2\pi)^{-2} \int_{-\infty}^{\infty} d\omega \int d^3k\, \mathscr{D}_s(\vec{k},\omega)\, e^{i\vec{k}\cdot\vec{r}-i\omega t} =$$

$$\sum_{q=1}^{3} (2\pi)^{-2} \int_{-\infty}^{\infty} d\omega \int d^3k\, \mathscr{E}_q(\vec{k},\omega) \int_{-\infty}^{\infty} dt' \int d^3r'\, \mathscr{L}_{sq}(\vec{r},\vec{r}\,',t,t')\, e^{i\vec{k}\cdot\vec{r}\,'-i\omega t'}. \tag{5}$$

Consider first the integral over t':

$$\int_{-\infty}^{\infty} dt'\, \mathscr{L}_{sq}(\vec{r},\vec{r}\,',t,t')\, e^{i\vec{k}\cdot\vec{r}\,'-i\omega t} = \mathscr{L}^1_{sq}(\vec{r},\vec{r}\,',t,\omega)\, e^{i\vec{k}\cdot\vec{r}\,'}.$$

If $\mathscr{L}_{sq}$ is not explicitly dependent upon some absolute time, and g(t) is the result of applying $\mathscr{L}_{sq}$ to f(t'), then g(t+Δ) must be the result of applying $\mathscr{L}_{sq}$ to f(t'+Δ). But $\mathscr{L}_{sq}$ is a LINEAR operator,

$$\therefore \int_{-\infty}^{\infty} dt'\, \mathscr{L}_{sq}(\vec{r},\vec{r}\,',t,t')\, e^{i\vec{k}\cdot\vec{r}\,'-i\omega(t'+\Delta)} = e^{-i\omega\Delta}\, \mathscr{L}^1_{sq}(\vec{r},\vec{r}\,',t,\omega)\, e^{i\vec{k}\cdot\vec{r}\,'}$$

$$= \mathscr{L}^1_{sq}(\vec{r},\vec{r}\,',t+\Delta,\omega)\, e^{i\vec{k}\cdot\vec{r}\,'}.$$

Define

$$\mathscr{L}^2_{sq}(\vec{r},\vec{r}\,',\omega) = \mathscr{L}^1_{sq}(\vec{r},\vec{r}\,',0,\omega),$$

then it follows that

$$\int_{-\infty}^{\infty} dt'\, \mathscr{L}_{sq}(\vec{r},\vec{r}\,',t,t')\, e^{i\vec{k}\cdot\vec{r}\,'-i\omega t'} = e^{-i\omega t}\, \mathscr{L}^2_{sq}(\vec{r},\vec{r}\,',\omega)\, e^{i\vec{k}\cdot\vec{r}\,'}.$$

Applying the same argument to each of the spatial coordinates implies that

$$\int d^3r'\, \mathscr{L}^2_{sq}(\vec{r},\vec{r}\,',\omega)\, e^{i\vec{k}\cdot\vec{r}\,'} = e^{i\vec{k}\cdot\vec{r}}\, \mathscr{L}^3_{sq}(\vec{k},\omega),$$

where

$$\mathscr{L}^3_{sq}(\vec{k},\omega) = \int d^3r'\, \mathscr{L}^2_{sq}(0,\vec{r}\,',\omega)\, e^{i\vec{k}\cdot\vec{r}\,'},$$

$$(2\pi)^{-2}\int_{-\infty}^{\infty} d\omega \int d^3k\, \mathscr{D}_s(\vec{k},\omega)\, e^{i\vec{k}\cdot\vec{r}-i\omega t} =$$

$$\sum_{q=1}^{3} (2\pi)^{-2}\int_{-\omega}^{\omega} d\omega \int d^3k\, \mathscr{E}_q(\vec{k},\omega)\, \mathscr{L}^{3}_{sq}(\vec{k},\omega)\, e^{i\vec{k}\cdot\vec{r}-i\omega t}$$

where

$$\mathscr{L}^{(3)}_{sq}(\vec{k},\omega) = \int_{-\infty}^{\infty} dt' \int d^3r'\, \mathscr{L}_{sq}(0,\vec{r}\,',0,t')\, e^{i\vec{k}\cdot\vec{r}\,'-i\omega t'} \tag{6}$$

Taking the inverse Fourier transform of both sides, we get

$$\mathscr{D}_s(\vec{k},\omega) = \sum_{q=1}^{3} \mathscr{L}^{(3)}_{sq}(\vec{k},\omega)\, \mathscr{E}_q(\vec{k},\omega) \tag{7}$$

for a linear operator $\mathscr{L}_{sq}$ which is not explicitly dependent upon either an absolute time or space coordinate.

If we introduce a boundary at which the dielectric response function changes, we may mix different values of $\vec{k}$. If the change is discontinuous in a plane, Fresnel's equations describe the interaction. There is no way to mix different frequency components, however, unless we change $\mathscr{L}_{sq}$ as a function of time, or include terms that are nonlinear in E and D. Thus the $\epsilon(\omega)$ defined below will describe ordinary reflectance, transmittance, and elastic scattering processes, but will not include nonlinear interactions as harmonic generation or Raman scattering. Also, since

$$\mathscr{D}_s(\vec{k},\omega) = \mathscr{D}^*_s(-\vec{k},-\omega)$$

and

$$\mathscr{E}_s(\vec{k},\omega) = \mathscr{E}^*_s(-\vec{k},\omega),$$

it follows that

$$\mathscr{L}^{(3)}_{sq}(\vec{k},\omega) = \mathscr{L}^{(3)*}_{sq}(-\vec{k},-\omega), \tag{8}$$

in order that $\vec{D}$ and $\vec{E}$ be REAL functions.

If we restrict our attention to propagating electromagnetic disturbances in nonmagnetic materials, Maxwell's equations put very severe limitations on the frequencies, ω, associated with a given wave vector, $\vec{k}$. For isotropic (or cubic) materials $k^2 = \omega^2 c^2 \mathscr{L}(\vec{k},\omega)$, and $\vec{k}$ is an implicit function of ω. In this case, the isotropic dielectric response function $\epsilon(\omega)$ is defined as the value of $\mathscr{L}(\vec{k},\omega)$ such that $\mathscr{L}(\vec{k},\omega) = k^2/\omega^2 c^2$.

A similar, but much more complicated, expression can be defined for the general dielectric response function tensor, $\epsilon_{sq}(\omega)$, but the remainder of this discussion may be limited to the isotropic dielectric response function, $\epsilon(\omega)$, without loss of generality. For an isotropic material,

$$\mathscr{D}_s(\vec{k},\omega) \rightarrow \mathscr{D}_s(\omega)$$

$$\mathscr{E}_s(\vec{k},\omega) \rightarrow \mathscr{E}_s(\omega).$$

Since $\mathscr{D}_s(\omega)$ and $\mathscr{E}_s(\omega)$ can have no essential singularities, $\epsilon(\omega)$ can have no essential singularities. All of the poles and zeros of $\epsilon(\omega)$ must be isolated, and in order that $\epsilon(\omega) = \epsilon^*(-\omega)$, they must be symmetrically distributed about the imaginary axis of the ω-plane. Consequently, a pole or a zero of $\epsilon(\omega)$ must either lie on the imaginary ω axis or be paired with a complementary pole or zero of $\epsilon(\omega)$. In other words, if there is a pole or a zero of $\epsilon(\omega)$ at $\omega_1 = \omega_r + i\omega_i$, there must be a complementary pole or zero at $\omega_2 = -\omega_r + i\omega_i$. Moreover, the poles and zeros of $\mathscr{D}_s(\omega)$ must occur at frequencies such that the magnitude of the time-dependent term $\mathscr{D}_s(\omega)\, e^{-i\omega t}$ is constant or exponentially damped. Therefore, the imaginary component of the frequencies of any poles or zeros of $\mathscr{D}_s$ must be less than or equal to zero. That is, all of the poles and zeros of $\mathscr{D}_s(\omega)$ are in the lower half of the ω-plane. Consequently, any pole or zero contributed to $\mathscr{D}_s$ by $\epsilon(\omega)$ must also be in the lower half of the ω-plane. Since

$$\mathscr{D}_s(\omega) = \epsilon(\omega)\, \mathscr{E}_s(\omega)$$

or

$$\mathscr{E}_s(\omega) = \epsilon^{-1}(\omega)\, \mathscr{D}_s(\omega) = \eta(\omega)\, \mathscr{D}_s(\omega), \tag{9}$$

a zero of $\epsilon(\omega)$ and a pole of $\eta(\omega)$ occurs whenever there exists a frequency, ω_ℓ, such that $\mathscr{D}_s(\omega) \equiv 0$, although $\mathscr{E}_s(\omega) \neq 0$. Likewise, a pole of $\epsilon(\omega)$ and a zero of $\eta(\omega)$ occurs whenever there exists a frequency, ω_t, such that $\mathscr{E}_s(\omega) \equiv 0$, although $\mathscr{D}_s(\omega) \neq 0$.

We are now in a position to determine the limits on the frequencies of the poles and zeros of $\epsilon\omega)$.

3. Properties of the Poles and Zeros of $\epsilon(\omega)$

One may express the dielectric response function, $\epsilon(\omega)$, in terms of a product of complementary poles and zeros. For single-mode behavior,

$$\epsilon(\omega) = \epsilon_\infty \frac{(\omega-\omega^\ell)\left(\omega-\left(-\omega_\ell^*\right)\right)}{(\omega-\omega_t)\left(\omega-\left(-\omega_t^*\right)\right)}$$

or

$$\epsilon(\omega) = \epsilon_\infty \frac{\left(\omega_L^2 - \omega^2 - i\omega\Gamma_L\right)}{\left(\omega_T^2 - \omega^2 - i\omega\Gamma_T\right)},$$

where

$$\epsilon_\infty = \epsilon(\omega\to\infty)$$

$$\omega_L^2 = |\omega_\ell|^2$$

$$\Gamma_L = -2 \text{ Im } [\omega_\ell]$$

$$\omega_T^2 = |\omega_t|^2$$

$$\Gamma_T = -2 \text{ Im } [\omega_t]$$

and all coefficients are REAL.

This formula can also be written

$$\epsilon(\omega) = \epsilon_\infty + \epsilon_\infty \left\{ \frac{\left(\omega_L^2 - \omega_T^2\right) - i\omega(\Gamma_L - \Gamma_T)}{\omega_T^2 - \omega^2 - i\omega\Gamma_T} \right\}$$

which is analogous to the expression commonly derived for a damped classical oscillator, except that the numerator of this expression (oscillator strength) can be complex if $\Gamma_L \neq \Gamma_T$.

It can be shown that in order that the magnitude of a plane wave propagating through a dielectric either remain constant or be exponentially damped with time, Im $[\epsilon(\omega)] \geq 0$ and Im $[\eta(\omega)] \leq 0$, for $\omega \geq 0$. Therefore, for single-mode behavior

$$\text{Im } [\epsilon(\omega)] \geq 0 \qquad \text{as } \omega \to \infty \text{ or } \omega \to 0$$

$$\epsilon(\omega) = \epsilon_\infty \left(\frac{\omega_L^2 - \omega^2 - i\omega\Gamma_L}{\omega_T^2 - \omega^2 - i\omega\Gamma_T} \right) \underset{\omega\to\infty}{\longrightarrow} \epsilon_\infty \left(\frac{\omega + i\Gamma_L}{\omega + i\Gamma_T} \right)$$

$$\epsilon(\omega) \underset{\omega\to\infty}{\longrightarrow} \epsilon_\infty \left(\frac{\omega^2 - \Gamma_T\Gamma_L + i\omega(\Gamma_L - \Gamma_T)}{\omega^2 - \Gamma_T^2} \right)$$

$$\epsilon(\omega) \xrightarrow[\omega\to\infty]{} \epsilon_\infty \left[1 + i\,\frac{\Gamma_L - \Gamma_T}{\omega}\right].$$

$\therefore$ Since ϵ_∞ is REAL, $\Gamma_L - \Gamma_T \geq 0$, or

$$\boxed{\Gamma_L \geq \Gamma_T} \tag{10}$$

$$\epsilon(\omega) \xrightarrow[\omega\to 0]{} \epsilon_\infty \left(\frac{\omega_L^2 - i\omega\Gamma_L}{\omega_T^2 - i\omega\Gamma_T}\right)$$

$$\epsilon(\omega) \xrightarrow[\omega\to 0]{} \frac{\omega_L^2\omega_T^2 + \omega^2\Gamma_L\Gamma_T - i\omega\left[\Gamma_L\omega_T^2 - \Gamma_T\omega_L^2\right]}{\omega_T^4 - \omega^2\Gamma_T^2}$$

$$\epsilon(\omega) \xrightarrow[\omega\to 0]{} \epsilon_\infty \frac{\omega_L^2}{\omega_T^2}\left[1 + i\omega\left(\frac{\Gamma_T}{\omega_T^2} - \frac{\Gamma_L}{\omega_L^2}\right)\right]$$

$$\therefore\ \frac{\Gamma_T}{\omega_T^2} - \frac{\Gamma_L}{\omega_L^2} \geq 0, \text{ or}$$

$$\boxed{\frac{\Gamma_T}{\omega_T^2} \geq \frac{\Gamma_L}{\omega_L^2}}. \tag{11}$$

For a general dielectric response function, which is expressed as a product of poles and zeros,

$$\epsilon(\omega) = \epsilon_\infty \prod_{j=1}^{N} \frac{\omega_{Lj}^2 - \omega^2 - i\omega\Gamma_{Lj}}{\omega_{Tj}^2 - \omega^2 - i\omega\Gamma_{Tj}} \tag{12}$$

(in order that $\epsilon(\infty)$ be bounded as $\omega \to 0$ and $\omega \to \infty$ there must be the same number of zeros as there are poles), these relations generalize to

$$\text{(a)}\quad \Gamma_{Tj} \geq 0, \quad \Gamma_{Lj} \geq 0 \tag{13}$$

$$\text{(b)}\quad \sum_{j=1}^{N} \Gamma_{Lj} \geq \sum_{j=1}^{N} \Gamma_{Tj} \tag{14}$$

$$\text{(c)}\quad \sum_{j=1}^{N} \frac{\Gamma_{Tj}}{\omega_{Tj}^2} \geq \sum_{j=1}^{N} \frac{\Gamma_{Lj}}{\omega_{Lj}^2} \tag{15}$$

as the necessary conditions for a physically possible component of the dielectric response function.

4. Locating the Poles and Zeros of $\epsilon(\omega)$

If one has a dielectric response function exhibiting single-mode behavior, the value of ω_T^2 and Γ_T can be estimated from the behavior of the Im $[\epsilon(\omega)]$ and ω_L^2 and Γ_L can be estimated from the behavior of Im $[\eta(\omega)]$.

Consider

$$\epsilon(\omega) = \epsilon'(\omega) + i\epsilon''(\omega) = \epsilon_\infty\left(\frac{\omega_L^2 - \omega^2 - i\omega\Gamma_L}{\omega_T^2 - \omega^2 - i\omega\Gamma_T}\right)$$

$$\text{Im}\,[\epsilon(\omega)] = \epsilon''(\omega) = \epsilon_\infty\omega\left(\frac{\Gamma_T\left(\omega_L^2 - \omega\right) - \Gamma_L\left(\omega_T^2 - \omega^2\right)}{\left(\omega_T^2 - \omega^2\right)^2 + \Gamma_T^2\omega^2}\right).$$

The peak in ϵ'' occurs when $\partial\epsilon''/\partial\omega = 0$. Evaluating $\partial\epsilon''/\partial\omega$ at $\omega = \omega_T$, we have

$$\left.\frac{\partial\epsilon''}{\partial\omega}\right|_{\omega=\omega_T} = -2\epsilon_\infty \frac{\left(\omega_L^2 - \omega_T^2\right)}{\Gamma_T\omega_T^2} + 2\epsilon_\infty \frac{(\Gamma_L - \Gamma_T)}{\Gamma_T^2}.$$

But for single-mode behavior,

$$\Gamma_L \geqslant \Gamma_T \geqslant 0 \quad \text{and} \quad \frac{\Gamma_T}{\omega_T^2} \geqslant \frac{\Gamma_L}{\omega_L^2}.$$

$$\therefore \left.\frac{\partial\epsilon''}{\partial\omega}\right|_{\omega=\omega_T} \leqslant 0 \qquad \text{for all values of } \omega_T^2,\ \Gamma_T,\ \omega_L^2,\ \Gamma_L$$

the equality holds for $\Gamma_L = \Gamma_T \dfrac{\omega_L^2}{\omega_T^2}$. Consequently, the peak of ϵ'' occurs at a lower frequency than ω_T.

Similarly,

$$\left.\frac{\partial(\omega\epsilon'')}{\partial\omega}\right|_{\omega=\omega_T} = 2\epsilon_\infty\omega_T \frac{\Gamma_L - \Gamma_T}{\Gamma_T^2}.$$

$$\left.\frac{\partial(\omega\epsilon'')}{\partial\omega}\right|_{\omega=\omega_T} \geqslant 0 \qquad \text{for all allowed values. The equality holds for } \Gamma_L = \Gamma_T$$

and the peak of $\omega\epsilon''$ occurs at a higher frequency than ω_T. Therefore, if we define ω_1 as the frequency at which the peak in ϵ'' occurs and ω_2 as the frequency at which the peak in $\omega\epsilon''$ occurs, then

$$\boxed{\omega_1 \leqslant \omega_T \leqslant \omega_2} \qquad \text{for single-mode behavior.} \tag{16}$$

$$\omega_1 = \omega_T \qquad \text{for } \Gamma_L = \Gamma_T \frac{\omega_L^2}{\omega_T} \quad (\text{Upper limit on } \Gamma_L)$$

and

$$\omega_2 = \omega_T \qquad \text{for } \Gamma_L = \Gamma_T \quad (\text{Lower limit on } \Gamma_L).$$

Moreover, since $\eta(x) = \epsilon^{-1}(x)$ inverts the behavior of ω_L and ω_T, one can easily show that

$$\boxed{\omega_3 \leqslant \omega_L \leqslant \omega_4} \qquad \text{for single-mode behavior,} \tag{17}$$

where ω_3 is defined as the frequency at which the minimum of η'' occurs and ω_4 as the frequency at which the minimum of $\omega\eta''$ occurs.

$$\omega_3 = \omega_L \qquad \text{for } \Gamma_L = \Gamma_T \frac{\omega_L^2}{\omega_T^2}$$

and

$$\omega_4 = \omega_L \qquad \text{for } \Gamma_L = \Gamma_T.$$

Γ_T and Γ_L can be estimated from the half widths of ϵ'' and η'', respectively, and all four values can be iterated in the single-mode formula for $\epsilon(\omega)$ in order to achieve higher precision.

Furthermore, the relations for ω_T and ω_L will hold approximately for nearly isolated modes in a multimode dielectric response function. In this case, ϵ_∞ is replaced by an effective ϵ_∞ which incorporates the effect of all modes at a higher frequency than the desired ω_L and ω_T pair.

$$\epsilon_\omega(\text{effective}) = \epsilon_\infty \prod_{j=m+1}^{N} \frac{\omega_{Lj}^2}{\omega_{Tj}^2} \qquad \text{for the } m^{\text{th}} \text{ mode.}$$

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