

Transmission spectroscopy was once a standard against which all other spectroscopic techniques were compared. In the area of infrared (IR) spectroscopy, however, ATR has become more widely for all but gaseous samples.

The propagation of light through a homogeneous medium is easily understood within the framework of Maxwell's theory. The solution to Maxwell's equations is a plane wave. When the direction of propagation is along x-axis, the expression simplifies to:

$$\mathbf{E}(x, t) = \mathbf{E}(0, t)e^{2\pi inkx} e^{-2\pi k\kappa x} \quad (1)$$

where:

$$n_c = n + i\kappa \quad (2)$$

is the complex refractive index of the sample and:

$$k = \frac{1}{\lambda} \quad (3)$$

is the wavenumber of the propagating radiation. Since the radiation intensity $I(x)$ is proportional to the square of absolute value of the amplitude:

$$I(x) = I(0)e^{-4\pi k\kappa x} \quad (4)$$

The expression (4) is the law of transmission of radiation through an absorbing sample.

If light transmits through a sample of thickness d , the transmitted intensity is:

$$I(d) = I(0)e^{-4\pi k\kappa d} \quad (5)$$

ignoring the reflections at the two faces of the sample.

Transmittance is then defined as the fraction of incident light that transmits through the sample:

$$T = \frac{I(d)}{I(0)} \quad (6)$$

If the absorption bands are not too strong, the effects of reflections at the two faces of the sample could be eliminated by ratioing a measured spectrum of a sample to the transmission spectrum of a nonabsorbing sample of a similar refractive index (hence similar reflection losses). The result is:

$$\frac{T(\kappa)}{T(0)} = e^{-4\pi k\kappa d} \approx 1 - 4\pi k\kappa d \quad (7)$$

where the approximate part of the above relation holds only in the low absorption limit.

The equivalent expression in the low absorption limit for internal reflection (ATR) is:

$$R_i(\kappa) = 1 - \beta_i \kappa \quad (8)$$

where index i stands for the different polarizations and the coefficients β_i are functions of the refractive indices and the angle of incidence.

The fundamental similarity of these two expressions inspired the original introduction of ATR spectroscopy. In both cases, a negative logarithm (absorbance transform) of the measured spectroscopic observable is proportional to the absorption index. However, while for the transmission measurement this linear dependence holds even at high absorbance values, the linearity breaks down with increasing strength of absorbance in ATR. Furthermore, in the transmittance equations, the wavenumber is an explicit factor, distorting the result of the absorbance transform by artificially enhancing it at shorter wavelengths (i.e. higher wavenumbers). Thus, either multiplying the absorbance transform of the ATR spectrum by wavenumber, or dividing the absorbance transform of the transmission spectrum by wavenumber can achieve a superficial resemblance between the transmission and ATR spectra.