Fourier Transform Applications

Gaussian <-> Gaussian FT

Doppler broadening

Full Width at Half Maximum

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Gaussian broadening

There are kinetic models for solvent effects on spectra that include the recoil of molecules following an initial optical excitation. In these models the time-response function is Gaussian. We could call this an inertial response. There is some molecular inertia that delays the response.

$$G(\omega) = \frac{1}{\pi}\int_0^\infty exp\{-Dt^2\}exp\{-i\omega t\}dt$$

To calculate the Fourier transform we need to complete the square using exp(Aω^2)

$$G(\omega) = \frac{1}{\pi}exp\{A\omega^2\}\int_0^\infty exp\{-Dt^2 - i\omega t - A\omega^2\}dt$$

Gaussian broadening

In order for the perfect square to be a Gaussian it must have the form:

$$G(\omega) = \frac{1}{\pi} exp\{A\omega^2\} \int_0^\infty exp\{-(\sqrt{D}t + B\omega)^2\} dt$$

To evaluate the coefficients we expand the argument of the exponent and set it equal to the previous form:

$$Dt^2 + 2\sqrt{D}B\omega t + B^2\omega^2 = Dt^2 + i\omega t + A\omega^2$$

The cross term must be $i = 2\sqrt{D}B$ and A = B^2.
Therefore, $B = i/2\sqrt{D}$ and A = -1/4D. Thus, we see that:

$$exp\{-Dt^2\} \leftarrow FT \rightarrow \ exp\{-\omega^2/4D\}$$

Doppler broadening

The kinetic energy of a gas is:

$$E = \frac{1}{2} m s^2$$

The Maxwell distribution of speed is:c

$$exp\left\{-\frac{ms^2}{2k_B T}\right\}$$

The Doppler shift in the observed frequency is:

$$\nu_{obs} = \nu\left(\frac{1}{1 \pm s/c}\right)$$

$$s = \frac{(\nu_{obs} - \nu)c}{\nu}$$

Doppler broadening

The Doppler broadened line shape is:

$$I(\nu) = exp\left\{-\frac{mc^2(\nu_{obs} - \nu)^2}{2\nu^2 k_B T}\right\}$$

When written in standard form for a Gaussian:

$$exp\left\{-\frac{(\nu - \nu_0)^2}{2\sigma^2}\right\}$$

s is called the variance.

$$\sigma = \frac{\nu}{c}\sqrt{\frac{k_B T}{m}}$$

Full-width at half maximum for a Gaussian function

How does the variance, σ relate to the width of the band?
To examine this we can calculate the full-width at half maximum (FWHM). We set the value of a Gaussian equal to 1/2.

$$exp\left\{-\frac{(\nu-\nu_0)^2}{2\sigma^2}\right\} = \frac{1}{2}$$

$$\frac{(\nu-\nu_0)^2}{2\sigma^2} = ln(2)$$

$$(\nu-\nu_0) = \sigma\sqrt{2ln(2)}$$

$$FWHM = 2(\nu-\nu_0) = 2\sigma\sqrt{2ln(2)}$$