Lineshape Functions

Four different mathematical descriptions of the lineshape for an absorptive transition are discussed below. These transitions may involve electronic, rotational, or vibrational (i.e. visible, microwave or infrared radiation) eigenstates.

δ-function Lineshape

In an ideal gas phase experiment where there is no Doppler broadening or lifetime broadening the energy at which transition occurs is unique. This implies that the line is infinitely narrow. How can we describe an infinitely narrow line. It turns out that this is done by defining the delta function \( \delta(x-x_0) \). The delta function has the useful property that the integral over all space (i.e. from minus infinity to plus infinity along the x axis) gives a single value \( x_0 \). We write this as

\[
\int_{-\infty}^{\infty} \delta{(x-x_o)}dx = x_o
\]

This integral is perhaps the hardest of all to grasp since according to its definition there is no finite extent along the x axis. The function defined is a line at \( x_0 \) that is infinitely narrow. But notice that if we define the variable as an energy \( e \) then the delta function returns a unique energy \( e_0 \).

\[
\int_{-\infty}^{\infty} \delta{(\epsilon-\epsilon_o)}d\epsilon = \epsilon_o
\]

This corresponds to our requirement for the idea line shape function of a transition with no broadening. Note that we observe a frequency (or wavenumber in an absorption spectrum). Therefore, we can also write the delta function in terms of the frequency \( \omega \).

\[
\int_{-\infty}^{\infty} \delta{(\omega-\omega_o)}d\omega = \omega_o
\]

Lorentzian Lineshape

Of course, real transitions always involve some line broadening. If nothing else there must be lifetime broadening since absorption of radiation always produces an excited state with a finite lifetime. Recall that the uncertainty principle states that there is a relationship between the lifetime and the energy width of the state. Usually, we describe the kinetic decay of an
excited state using an exponential function. This emerges directly from first order kinetics. Looking ahead this means that if we define the rate of disappearance of the excited state $E$ as

$$\frac{\partial [E]}{\partial t} = -\frac{[E]}{T_1}$$

Then we can solve this equation to find the $E(t) = E_0 e^{-t/T_1}$ where $(T_1)$ is the excited state life time and $(E_0)$ is the initial concentration of the excited state.

The uncertainty principle states that the conjugate energy width can be obtained from the Fourier transform of the life time function.

$$L(\omega) = \int_{0}^{\infty} e^{-t/T_1} e^{-i\omega t} dt$$

This Fourier transform is easily solved since the integral is nothing more than an exponential integral. The solution for this integral is

$$L(\omega) = \left[ \frac{1}{T_1} - i\omega \right]^{-1}$$

which is complex. We can calculate real and imaginary parts by multiplying both numerator and denominator by $(1/T_1 + i\omega)$. This gives

$$\Lambda(\omega) = \frac{1/T_1}{\pi((1/T_1)^2 + \omega^2)}$$

The real part of this integral is a Lorentzian line shape function. This is the line shape that will be observed for transitions that have no inhomogeneous broadening. Examples include, NMR spectra, Lamb dip spectra in the gas phase, etc. The normalized Lorentzian function is (i.e. the real part of the above function $L(\omega)$).

We can define the energy width $G$ as being $(1/T_1)$, which corresponds to a Lorentzian linewidth. Using this definition and generalizing the function so that it can be used to describe the line shape function centered about any arbitrary frequency $(\omega_0)$, we have

$$\Lambda(\omega) = \frac{\Gamma}{\pi((1/T_1)^2 + \omega^2)}$$

Note that this is a normalized function so that the integral from $(-\infty)$ to $(\infty)$ is equal to one.

**Gaussian Lineshape**

A Gaussian function is also a useful lineshape function. Any source of inhomogeneous broadening such as the Doppler shift or site differences of molecules in crystals or solution can be described as a Gaussian lineshape.

$$G(\omega) = \sqrt{\pi} e^{-\frac{\omega^2}{\Gamma^2}}$$

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In considering the appearance of spectra we observe that Franck-Condon progressions often have the appearance of a progression of different levels with Gaussian broadening for molecules in solution. The progression of levels arises from the discrete transitions among vibrational levels of the molecule and the Gaussian function is superposed on this discrete "stick" spectrum to represent the broadening due to lifetime and solvent origins. Since the inhomogeneous broadening is often significantly larger than the lifetime broadening, the Gaussian lineshape often dominates in solution.

The Gaussian distribution in frequencies can be thought of as corresponding to a Gaussian distribution in relaxation times of the excited state. The Gaussian distribution of relaxation times is usually assumed to arise from an inhomogeneous distribution of the molecules in the sample. The molecules experience different environments due to solvation or matrix effects and therefore they all have slightly different properties. Since the Fourier transform of a Gaussian is also a Gaussian, the distribution of the relaxation times gives rise to a distribution of energies (and therefore a distribution of frequencies in the observed spectrum).

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**Voight Lineshape**

The Voight lineshape is just a convolution of a Gaussian and a Lorentzian and can be interpreted as an inhomogeneous distributions of Gaussian lineshapes.

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