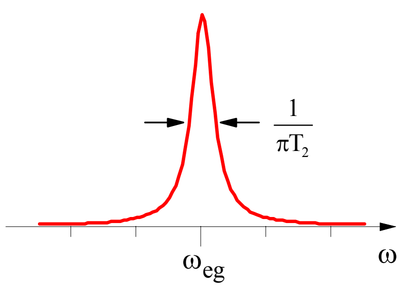
SPECTRAL DIFFUSION

We have discussed two limiting cases of line broadening:

Homogeneous:

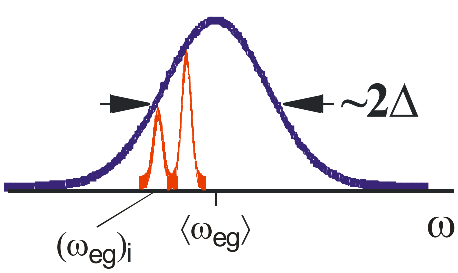


The absorption lineshape is dynamically broadened by variations in the amplitude, phase, or orientation of dipoles.

$\rightarrow$ Dephasing, Lifetime, Rotation $\rightarrow$ exponential decay time T_2

Note: Every molecule absorbs at same frequency.

Inhomogeneous:



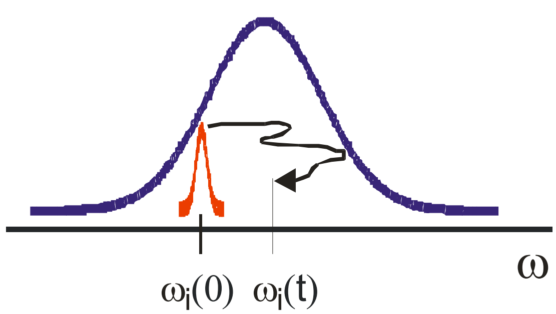
Static distribution of resonance frequencies.

Width of line represents distribution of frequencies (for instance structural environments).

More generally, every system lies between these limits. Imagine every molecule having a different "instantaneous frequency" $\omega_i(t)$ which evolves in time.

Spectral Diffusion

$\omega_i(t)$ evolves through a
Gaussian distribution of frequency.



Note: If $\omega_i(t)$ evolves slowly $\rightarrow$ inhomogeneous
If $\omega_i(t)$ evolves rapidly $\rightarrow$ homogeneous

This can be modeled through a Gaussian-Stochastic Model for random Gaussian fluctuations.

Gaussian-Stochastic Model for Spectral Diffusion

> The absorption lineshape derives from the dipole correlation function for the electronic or vibrational transition.

> This in turn depends on the energy gap between the ground and excited state → ω_{eg}.

> If ω_{eg} is a function of time due to random fluctuations in the environment surrounding the molecule:

$$\omega_i(t) = \langle\omega\rangle + \delta\omega_i(t)$$

Then the absorption lineshape will be related to the fluctuations in the frequency

$$\sigma_{abs} \propto \left\langle \int_{-\infty}^{+\infty} dt\, e^{i\omega t}\, e^{-i\omega_{eg} t} \right\rangle \Leftrightarrow \int_{-\infty}^{+\infty} dt\, e^{i\omega t}\, e^{-i\langle\omega_{eg}\rangle t}\, e^{-g(t)}$$

Let's find the lineshape function, *g(t)*.

Classical Description

To construct the effect of these random fluctuations on a spectrum, we can take the frequency fluctuations $\omega(t)$ to be coupled to the variation of an internal variable A.

$$A(t) \rightarrow \{\bar{\mu}(t); \bar{\alpha}(t); x(t)\ldots\}$$

$$\frac{\partial A}{\partial t} = i\omega(t) A(t) \quad \rightarrow \quad A(t) = A(0)\, exp\left[i \int_0^t d\tau\, \omega(\tau) \right]$$

$\omega(t)$ reflects random fluctuations about average value:

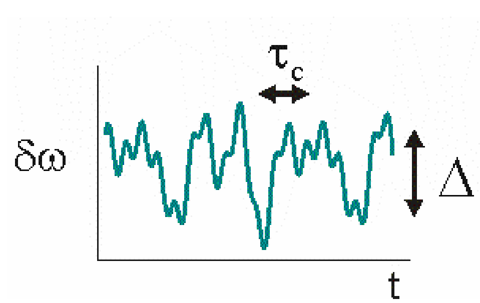
$$\omega(t) = \langle\omega\rangle + \delta\omega(t) \qquad \langle\delta\omega(t)\rangle = 0$$

The frequencies fluctuate randomly through a Gaussian distribution of frequencies by a variance:

$$\Delta = \left\langle \delta\omega^2 \right\rangle^{1/2}$$

The fluctuations are characterized by a correlation time:

$$\tau_c = \frac{1}{\Delta^2} \int_0^{\infty} dt \langle \delta\omega(t)\delta\omega(0) \rangle$$



$$A(t) = A(0)\,exp\left[i\int_0^t d\tau\ \omega(\tau) \right]$$

$$= A(0)\,exp\left[i\langle\omega\rangle t + i\int_0^t d\tau\ \delta\omega(\tau) \right]$$

$$C_{AA}(t) = \langle A(t)\,A(0)\rangle = \left\langle |A|^2 \right\rangle\ e^{i\langle\omega\rangle t}\ F(t)$$

where $F(t) = \left\langle exp\left[i\int_0^t d\tau\,\delta\omega(\tau) \right] \right\rangle$.

Note that $C_{AA}(t)$ looks similar to our typical dipole correlation function, $C_{\mu\mu}(t) = \left|\mu_{eg}\right|^2 e^{-i\omega_{eg}t - g(t)}$, with the dipole moment playing the role of our internal variable *A*, and our dephasing function $F(t) = exp(-g(t))$.

To simplify $F(t)$, we can expand it perturbatively: **<u>cumulant expansion of averages</u>**.

$$F(t) = exp\left[i\int_0^t d\tau_1 \langle\delta\omega(\tau_1)\rangle + \frac{i^2}{2!}\int_0^t d\tau_1 \int_0^t d\tau_2 \langle\delta\omega(\tau_1)\,\delta\omega(\tau_2)\rangle + \dots \right]$$

First term = 0

Stationary: $\langle\delta\omega(\tau_1 - \tau_2)\,\delta\omega(0)\rangle$

Only the second term survives for a system with Gaussian statistics to the fluctuations. This is a classical description, so there is no time-ordering to the exponential.

$$F(t) = exp\left[-\tfrac{1}{2}\int_0^t d\tau_1 \int_0^t d\tau_2 \langle\delta\omega(\tau_1 - \tau_2)\,\delta\omega(0)\rangle \right]$$

$F(t)$ can be rewritten through a change of variables ($\tau = \tau_1 - \tau_2$):

$$F(t) = exp\left[-\int_0^t d\tau\ (t-\tau)\langle\delta\omega(\tau)\,\delta\omega(0)\rangle \right]$$

So the frequency fluctuations are described by a correlation function

$$C_{\delta\omega\delta\omega}(t) = \langle \delta\omega(t)\,\delta\omega(0) \rangle$$

$$\Delta = \langle \delta\omega^2 \rangle^{1/2} \qquad \tau_c = \frac{1}{\Delta^2}\int_0^\infty d\tau\; C_{\delta\omega\delta\omega}(\tau)$$

Now, we will calculate the lineshape assuming that the $C_{\delta\omega\delta\omega}$ decays exponentially

$$C_{\delta\omega\delta\omega}(t) = \Delta^2\, exp\left[-t/\tau_c\right]$$

Then,

$$F(t) = exp\left[\Delta^2 \tau_c^2 \left(exp\left(-t/\tau_c\right) + t/\tau_c - 1\right)\right]$$

Let's look at the limiting forms of $F(t)$.

1) **<u>Long correlation times</u>** (or equivalently short t).

For $t < \tau_c$ we do short time expansion of exponential

$$e^{-t/\tau_c} \rightarrow 1 - t/\tau_c + \frac{t^2}{2\tau_c^2} + \ldots$$

$$F(t) = exp\left(-\Delta^2 t^2 / 2\right)$$

At short times, you have a Gaussian decay with a rate $\propto \Delta$. This is good since our dipole correlation function will be even $C_{\mu\mu}(t) = C_{\mu\mu}(-t)$.

Now the absorption lineshape is:

$$\sigma_{abs}(\omega) \propto \int_{-\infty}^{+\infty} dt\, e^{i\omega t}\, e^{-i\langle\omega\rangle t}\, F(t)$$

For long correlation times, the frequency fluctuations are very slow and we expect an effectively static ensemble

$$\sigma_{abs}(\omega) \propto \int_{-\infty}^{+\infty} dt\, e^{i(\omega - \langle\omega\rangle)t}\, e^{-\Delta^2 t^2/2} \qquad (t_c > t)$$

$$\approx exp\left(-\frac{(\omega - \langle\omega\rangle)^2}{2\Delta^2}\right) \qquad \textit{Gaussian shape}$$

Inhomogeneous lineshape.

2) **Very short correlation times** $\quad t >> \tau_c \quad\quad e^{-t/\tau_c} \rightarrow 0$

$$F(t) = e^{-(\Delta\tau_c)^2}\; exp\left[-\Delta^2\, \tau_c t\right]$$

↖ const

or defining $\Delta^2 \tau_c \equiv \frac{1}{T_2}$

$$F(t) \propto exp\left[-t/T_2\right]$$

Lineshape: For very small correlation times we will have very fast fluctuations

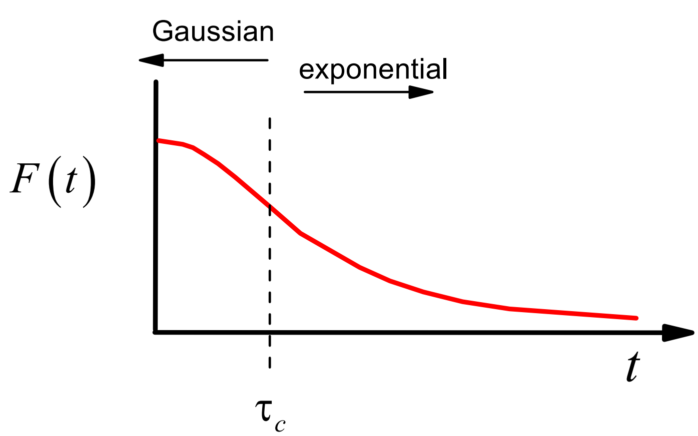
$$\sigma_{abs} \propto \int_{-\infty}^{+\infty} dt\; e^{i(\omega - \langle\omega\rangle)t}\; e^{-t/T_2}$$

$$\approx \frac{1}{\omega - \langle\omega\rangle - i\frac{1}{T_2}} \qquad \textit{Lorentzian shape}$$

homogeneous limit!

Overall Behavior:

The envelope of the dipole correlation function will look Gaussian at short times and exponential at long times.



(If this were derived quantum mechanically from Heisenberg equation of motion for A, then $F(t) = e^{-g(t)}$ with

$$g(t) = \left(\frac{-i}{\hbar}\right)^2 \int_0^t d\tau_2 \int_0^{\tau_2} d\tau_1 \quad \langle v(\tau_1) v(0) \rangle$$