

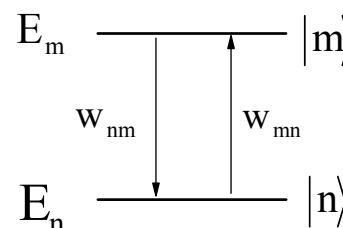
Time-Correlation Function Description of Absorption Lineshape

Let's express the absorption of radiation by dipoles as a dipole correlation function.

Start with the rate of absorption and stimulated emission between an initial state $|l\rangle$ and final state $|k\rangle$ induced by monochromatic field:

$$w_{k\ell} = \frac{\pi E_0^2}{2\hbar^2} \left| \langle k | \hat{\epsilon} \cdot \vec{\mu} | \ell \rangle \right|^2 \left[\delta(\omega_{k\ell} - \omega) \delta(\omega_{k\ell} + \omega) \right]$$

Let's consider a two-level system $|m\rangle$ and $|n\rangle$ with $E_m > E_n$.



The rate of energy absorption is proportional to the absorption rate and the transition energy: $-\dot{E}_{rad} = w_{nm} \cdot \hbar \omega_{nm}$. But more generally we need to consider the difference between the rates of absorption and stimulated emission, so the rates of transitions between these two states is

$$\begin{aligned} -\dot{E}_{rad} &= \sum_{\ell, k=m,n} p_\ell w_{k\ell} \hbar \omega_{k\ell} \\ &= \frac{\pi E_0^2}{2\hbar} \sum_{\ell, k=m,n} \omega_{k\ell} p_\ell \left| \langle k | \hat{\epsilon} \cdot \vec{\mu} | \ell \rangle \right|^2 \left[\delta(\omega_{k\ell} - \omega) + \delta(\omega_{k\ell} + \omega) \right] \end{aligned}$$

Here we have to sum over the rates of absorption from $|n\rangle \rightarrow |m\rangle$ and the rates of stimulated emission from $|m\rangle \rightarrow |n\rangle$.

$$\begin{aligned} -\dot{E}_{rad} &= \frac{\pi E_0^2}{2\hbar} \left[\omega_{mn} p_n \left| \langle m | \hat{\epsilon} \cdot \vec{\mu} | n \rangle \right|^2 \delta(\omega_{mn} - \omega) \right. && \text{absorption} \\ &\quad \left. + \omega_{nm} p_m \left| \langle n | \hat{\epsilon} \cdot \vec{\mu} | m \rangle \right|^2 \delta(\omega_{nm} + \omega) \right] && \text{stimulated emission} \end{aligned}$$

Note: $\delta(\omega_{nm} + \omega) = \delta(-\omega_{mn} + \omega) = \delta(\omega_{mn} - \omega)$ since $\delta(x) = \delta(-x)$

Also: the matrix elements squared are the same.

$$\omega_{mn} = -\omega_{nm}$$

$$-\dot{E}_{rad} = \frac{\pi E_0^2}{2\hbar} \omega_{mn} (p_n - p_m) \left| \langle m | \hat{\epsilon} \cdot \bar{\mu} | n \rangle \right|^2 \delta(\omega_{mn} - \omega)$$

At equilibrium $p_\ell = \exp[-\beta E_\ell] / Z$

$$p_n - p_m = p_n (1 - \exp[-\beta \hbar \omega_{mn}])$$

Now, the energy incident on the sample per unit time is

$$\dot{E}_{in} = \frac{c}{8\pi} E_0^2$$

So we can write the absorption coefficient, $\alpha(\omega) = \frac{\dot{E}_{rad}}{\dot{E}_{in}}$

$$\alpha(\omega) = \frac{4\pi^2}{\hbar c} \omega (1 - e^{-\beta \hbar \omega}) p_n \left| \langle m | \hat{\epsilon} \cdot \bar{\mu} | n \rangle \right|^2 \delta(\omega_{mn} - \omega)$$

Now this is written for two discrete states, but in general we will want to sum over all possible initial and final states. We can now separate α into a product of factors that represent the field, and the matter, where the matter is described by $\sigma(\omega)$ —the absorption lineshape.

$$\alpha(\omega) = \frac{4\pi^2}{\hbar c} \omega (1 - e^{-\beta \hbar \omega}) \sigma(\omega)$$

$$\sigma(\omega) = \sum_{m,n} p_n \left| \langle m | \hat{\epsilon} \cdot \bar{\mu} | n \rangle \right|^2 \delta(\omega_{mn} - \omega)$$

Now, since the delta function can be expressed as

$$\delta(\omega) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} dt e^{i\omega t}$$

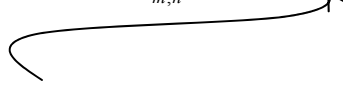
$$\begin{aligned}\sigma(\omega) &= \frac{1}{2\pi} \sum_{m,n} \int_{-\infty}^{+\infty} dt e^{-i(\omega_m - \omega)t} p_n \langle n | \hat{\epsilon} \cdot \bar{\mu} | m \rangle \langle m | \hat{\epsilon} \cdot \bar{\mu} | n \rangle \\ &= \frac{1}{2\pi} \sum_{m,n} \int_{-\infty}^{+\infty} dt e^{-i\omega t} p_n \langle n | \hat{\epsilon} \cdot \bar{\mu} | m \rangle \langle m | e^{i\omega_m t} \hat{\epsilon} \cdot \bar{\mu} e^{-i\omega_n t} | n \rangle\end{aligned}$$

Since $|m\rangle$ and $|n\rangle$ are states of system without radiation

$$\langle m | e^{i\omega_m t} = \langle m | e^{iHt/\hbar} = \langle m | U^\dagger(t)$$

$$e^{-i\omega_n t} |n\rangle = e^{-iHt/\hbar} |n\rangle = U(t) |n\rangle \quad U^\dagger \mu U = \mu(t)$$

$$\sigma(\omega) = \frac{1}{2\pi} \sum_{m,n} \int_{-\infty}^{+\infty} e^{-i\omega t} p_n \langle n | \hat{\epsilon} \cdot \bar{\mu}(0) | m \rangle \underbrace{\langle m | \hat{\epsilon} \cdot \bar{\mu}(t) | n \rangle}_{\substack{\text{sum over} \\ m: \text{unity}}}$$

 sum over n: equilibrium ensemble average

$$\sigma(\omega) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} dt e^{-i\omega t} \langle \langle \hat{\epsilon} \cdot \bar{\mu}(0) \hat{\epsilon} \cdot \bar{\mu}(t) \rangle \rangle$$

If we average over an isotropic system:

$$\sigma(\omega) = \frac{1}{2\pi} \cdot \frac{1}{3} \cdot \int_{-\infty}^{+\infty} dt e^{-i\omega t} \langle \langle \bar{\mu}(0) \bar{\mu}(t) \rangle \rangle$$

The absorption lineshape is the Fourier transform of the dipole correlation function.

The correlation function describes the time-dependent behavior or spontaneous fluctuations in the dipole moment in absence of E field and contains information on states of system and broadening due to relaxation.

Different spectroscopies are described by different forms of the dipole operator.

Rotational spectroscopy

The dipole operator is the permanent dipole moment: $\bar{\mu} = \bar{\mu}_0 = \mu_0 \hat{u}$

$$\sigma(\omega) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} dt e^{-i\omega t} \mu_0^2 \langle \hat{e} \cdot \hat{u}(0) \hat{e} \cdot \hat{u}(t) \rangle$$

The lineshape is the Fourier transform of the rotational motion of the permanent dipole vector in the laboratory frame. The frequency of the resonance would depend on the rate of rotation – the angular momentum and the moment of inertia. Collisions or other damping would lead to the broadening of the lines. Quantum mechanically we expect a distribution of resonances for different populated rotational states which we would sum over when performing the equilibrium ensemble average.

IR Vibrational Spectroscopy

We take the dipole operator to be weakly dependent on the displacement of nuclear coordinates

$$\bar{\mu} = \bar{\mu}_0 + \left. \frac{\partial \bar{\mu}}{\partial q} \right|_0 q + \dots$$

Here the first expansion term is the permanent dipole moment and the second term is the transition dipole moment. If we are performing our ensemble average over vibrational states, the lineshape now becomes the Fourier transform of a correlation function in the vibrational coordinate

$$\sigma(\omega) = \frac{1}{2\pi} \left| \frac{\partial \bar{\mu}}{\partial q} \right|^2 \int_{-\infty}^{+\infty} dt e^{-i\omega t} \langle q(0)q(t) \rangle$$

The vector nature of the transition dipole has been dropped here. So the time dependent dynamics of the vibrational coordinate dictate the IR lineshape.

Raman Spectroscopy

We can replace the dipole operator with an induced dipole moment, the polarizability tensor to get the correlation function for Raman spectroscopy.

$$\begin{aligned}\bar{\mu} &\Rightarrow \mu_{ind} = \bar{\alpha} \\ \hat{\epsilon} \cdot \bar{\mu} &\Rightarrow \hat{\epsilon}_s \cdot \bar{\alpha} \cdot \hat{\epsilon}_i\end{aligned}$$

$$\sigma(\omega) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} dt e^{-i\omega t} \langle \hat{\epsilon}_s \cdot \bar{\alpha}(0) \cdot \hat{\epsilon}_i \hat{\epsilon}_s \cdot \bar{\alpha}(t) \cdot \hat{\epsilon}_i \rangle$$

or

$$\sigma(\omega) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} dt e^{-i\omega t} \langle \bar{\alpha}(0) \bar{\alpha}(t) \rangle$$

where we have written the polarization components of the incident (i) and scattered (s) light. The polarizability tensor is a second rank tensor that tells you how well a light field polarized along i can induce a dipole moment (light-field-induced charge displacement) in the s direction. For cylindrically symmetric systems this usually takes the form

$$\bar{\alpha} = \begin{pmatrix} \alpha_{\parallel} & & \\ & \alpha_{\perp} & \\ & & \alpha_{\perp} \end{pmatrix} = \alpha \mathbf{I} + \frac{1}{3} \beta \begin{pmatrix} 2 & & \\ & -1 & \\ & & -1 \end{pmatrix}$$

where α is the isotropic polarizability and β is the anisotropic polarizability. The polarizability tensor can also be expanded in the nuclear coordinates

$$\bar{\alpha} = \bar{\alpha}_0 + \left. \frac{\partial \bar{\alpha}}{\partial q} \right|_0 q + \dots$$

where the leading term would refer to Rayleigh scattering and the second term would give vibrational Raman scattering.

ENSEMBLE AVERAGING and LINE BROADENING

An absorption lineshape can represent the dynamics of the dipole or energy relaxation (i.e., coupling to continuum). It can also reflect ensemble averaging effects.

Homogeneous broadening: dynamic

Inhomogeneous broadening: static

Homogeneous broadening (T_2): $\frac{1}{T_2} = \frac{1}{T_1} + \frac{1}{T_2^*} + \frac{1}{\tau_{or}}$

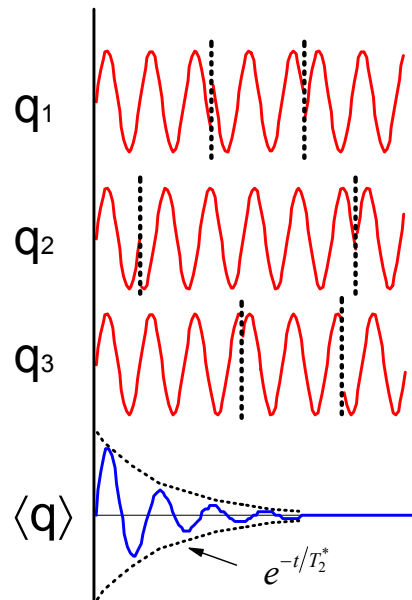
Population Relaxation (T_1): Amplitude decay due to finite lifetime.

This can have contributions from radiative decay or non-radiative processes (i.e., coupling to continuum) (IVR)

$$\frac{1}{T_1} = \frac{1}{\tau_{rad}} + \frac{1}{\tau_{NR}}$$

In this case, ensemble averaging doesn't change the measurement. All members of ensemble identical – measured decay is the microscopic lifetime.

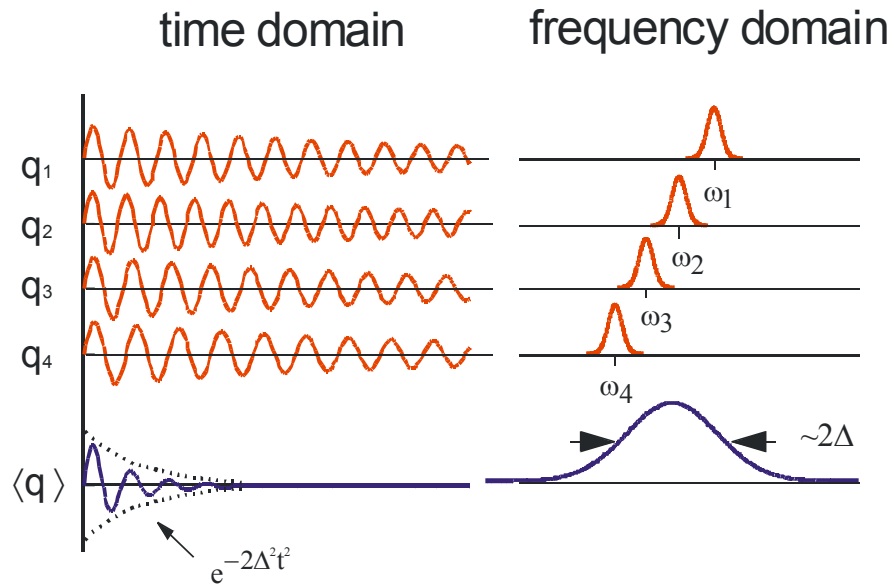
Pure Dephasing (T_2^*): Randomization of phase by molecular interactions → ensemble averaging effect.



Also, orientational dephasing—(τ_{or})

Inhomogeneous Broadening (Δ):

Line broadening arising from a static distribution of frequencies.
No dynamics: ensemble averaging effect.



The total broadening reflects the contribution of all of these effects:

$$\langle \mu(0)\mu(t) \rangle \sim e^{-t\left(\frac{1}{T_2} + \frac{1}{2T_1} + \frac{1}{\tau_{or}}\right)} e^{-2t^2\Delta^2} \equiv e^{-g(t)} \quad g(t): \text{lineshape function}$$

The lineshape for the broadening of a given transition can be written as the Fourier transform over the oscillating transition frequency damped and modulated by the lineshape function:

$$\sigma(\omega) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} dt e^{-i\omega t} e^{i\omega_m t - g(t)}$$