CHM 502 - Module 7 - Spectroscopy

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We will now determine the spectrum of frequencies of monochromatic radiation that absorbed by a molecule, using transition rates derived from time-dependent perturbation theory (TDPT).

We will show how the absorption spectrum is related to a quantity called the dipole correlation function. This all tees up the derivations of spectroscopic selection rules that we will cover in the next module. We will also consider how molecular absorption lineshapes are broadened by various homogeneous and heterogeneous processes.

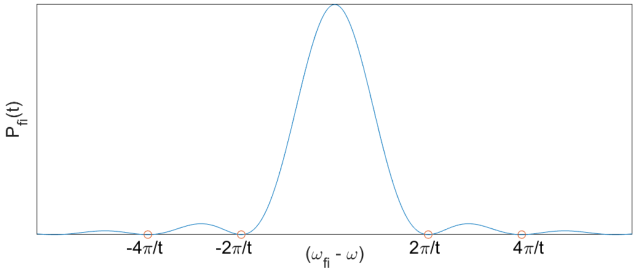
1 Recap: Transitions driven by monochromatic light

Let's first recap our major takeaway of TDPT. We consider a small perturbation to our Hamiltonian $\hat{H} = \hat{H}^{(0)} + \hat{H}^{(1)}(t)$. When $\hat{H}^{(1)}(t) = \hat{V}\cos(\omega t)$, we use TDPT to find the transition probability between two discrete eigenstates, $|\psi_i\rangle$ and $|\psi_f\rangle$ of $\hat{H}^{(0)}$:

$$P_{f\leftarrow i}(t) = \frac{|V_{fi}|^2}{\hbar^2} \cdot \frac{\sin^2(\frac{1}{2}(\omega_{fi}-\omega)t)}{(\omega_{fi}-\omega)^2} \tag{1}$$

where $\omega_{fi} = (E_f - E_i)/\hbar$ and $V_{fi} = \langle\psi_f|\hat{V}|\psi_i\rangle$.

The frequency-dependence of $P_{f\leftarrow i}$ is sharply peaked around $\omega = \omega_{fi}$:



$P_{f\leftarrow i}$ becomes increasingly sharply peaked over time, squeezing in about ω_{fi}. In this way, it approaches a δ function in the long-time limit:

$$\lim_{t\to\infty} \frac{\sin^2(\frac{1}{2}(\omega_{fi}-\omega)t)}{(\omega_{fi}-\omega)^2} = \frac{\pi t}{2} \cdot \delta(\omega_{fi}-\omega) \tag{2}$$

We can therefore write our long-time limit of the transition probability as:

$$P_{f\leftarrow i}(t) = \frac{\pi}{2\hbar^2} \cdot |V_{fi}|^2 \cdot \delta(\omega_{fi}-\omega) \cdot t \tag{3}$$

Since this probability is linear in t, we can consider instead the transition *rate*:

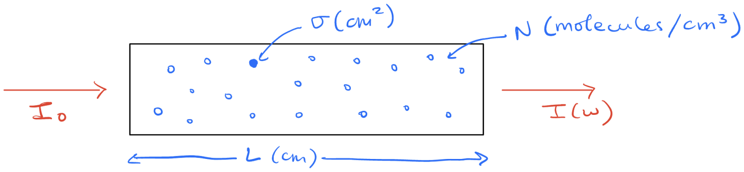
$$\boxed{\Gamma_{fi} = \frac{\pi}{2\hbar^2} \cdot |V_{fi}|^2 \cdot \delta(\omega_{fi} - \omega)} \tag{4}$$

2 Connecting the transition rate to an absorption cross section

Our task is to directly connect Eqn. 4 to the absorption cross section $\sigma(\omega)$ given by the Beer-Lambert law. The Beer-Lambert law states that the fraction of light transmitted through a sample with pathlength L is given by:

$$T(\omega) = \frac{I(\omega)}{I_0} = \exp\left[-\Delta N\, \sigma(\omega)\, L\right] \tag{5}$$

where I_0 is the initial intensity of light impinging on the sample, $I(\omega)$ is the frequency-dependent intensity of the transmitted beam, and $\Delta N = N_i - N_f$ is the difference in number densities between molecules in the initial and final quantum states of a given transition. If one were to assume that all molecules were in their ground state, then $\Delta N = N$, the total molecular number density.



$T(\omega)$ is a unitless fractional quantity, while we use cgs units for $N(\text{cm}^{-3})$, $\sigma(\text{cm}^2)$ and $L(\text{cm})$.

The absorption cross section $\sigma(\omega)$ is the important bit here, as it is intrinsic to the quantum mechanical properties of the molecules, rather than laboratory details like the sample density, pathlength, or light source. $\sigma(\omega)$ describes the rate of ***energy absorption per unit time per molecule*** relative to the intensity of light incident on the sample:

$$\sigma(\omega) \equiv \frac{\text{energy absorbed per unit time (energy / time)}}{\text{incident intensity (energy / time / area)}} \propto \text{area} \tag{6}$$

$$= \frac{\sum_{fi} \hbar\omega_{fi}\, \Gamma_{fi}\, p_i}{I_0} = \frac{\sum_{fi} \hbar\omega_{fi}\, \frac{\pi}{2\hbar^2}\, |V_{fi}|^2\, \delta(\omega_{fi} - \omega)\, p_i}{I_0} \tag{7}$$

Here, we have assumed that we are considering transitions between initial (i) and final (f) pairs of states where $\omega_{fi} = (E_f - E_i)/\hbar > 0$. We also define p_i as the probability that the system is found in initial state i.

To simplify the above, let's define:

$$\hat{V} = \underline{\hat{\mu}} \cdot E_0\, \underline{\xi} \tag{8}$$

where E_0 is the electric field amplitude, $\underline{\xi}$ is a unit vector along the electric field polarization, and $\underline{\hat{\mu}}$ is the dipole operator describing the spatial distribution of charges in the molecule. Therefore:

$$|V_{fi}|^2 = |\langle \psi_f | \underline{\hat{\mu}} \cdot E_0\, \underline{\xi} | \psi_i \rangle|^2 = |E_0|^2\, \langle \psi_f | \underline{\hat{\mu}} \cdot \underline{\xi} | \psi_i \rangle|^2 \equiv |E_0|^2\, |\mu_{fi}|^2 \tag{9}$$

We also note that the intensity of a beam of light is proportional to the squared amplitude of the electric field (in cgs units):

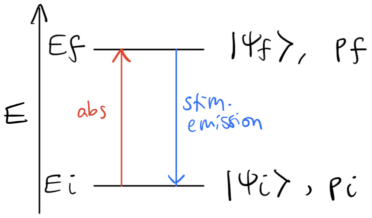
$$I_0 = \frac{c}{8\pi} \cdot |E_0|^2 \tag{10}$$

Now plugging Eqns. 9 and 10 back into Eqn. 7, we find:

$$\begin{aligned}
\sigma(\omega) &= \frac{\sum_{fi} \; \hbar\omega_{fi} \; \frac{\pi}{2\hbar^2} \, |E_0|^2 \, |\mu_{fi}|^2 \, \delta(\omega_{fi}-\omega) \; p_i}{\frac{c}{8\pi} \, |E_0|^2} \qquad (11) \\
&= \frac{4\pi^2}{\hbar c} \sum_{fi} \omega_{fi} \, |\mu_{fi}|^2 \, p_i \; \delta(\omega_{fi}-\omega) \qquad (12)
\end{aligned}$$

$\sigma(\omega)$ is indeed independent of the field amplitude, as we expect for an intrinsic molecular property.

Finally, let's introduce a second term in the sum that treats not just absorption of light ($f \leftarrow i$) but also the possibility of stimulated emission of light ($i \leftarrow f$). Stimulated emission occurs resonantly when $\omega = \omega_{fi}$, but instead *adds* energy $\hbar\omega_{fi}$ to the field rather than absorbs it.



The rate of stimulated emission depends on p_f rather than p_i. So we can amend $\sigma(\omega)$ to:

$$\sigma(\omega) = \frac{4\pi^2}{\hbar c} \sum_{fi} \Big[\omega_{fi} \, |\mu_{fi}|^2 \, p_i \; \delta(\omega_{fi}-\omega) \quad - \quad \omega_{fi} \, |\mu_{if}|^2 \, p_f \cdot \delta(\omega_{fi}-\omega) \Big] \tag{13}$$

Now, using the fact that $|\mu_{fi}|^2 = |\mu_{if}|^2$:

$$\boxed{\sigma(\omega) = \frac{4\pi^2}{\hbar c} \sum_{fi} \omega_{fi} \, |\mu_{fi}|^2 \; \delta(\omega_{fi}-\omega) \; \big[p_i - p_f\big]} \tag{14}$$

We therefore see that the absorption cross section depends on the population difference between the two states. This is expected since absorption (which can only occur out of lower state $|\psi_i\rangle$) will lead to a loss of transmitted intensity, while stimulated emission (which can only occur out of upper state $|\psi_f\rangle$) will lead to gain in transmitted intensity.

3 The Boltzmann distribution and the molecular lineshape

To evaluate in Eqn. 14 above, we usually consider a molecule thermalized to some temperature. The probability that the molecule is found in a given state is therefore determined by the Boltzmann distribution:

$$p_j = \frac{e^{-\beta E_j}}{Q(\beta)} \tag{15}$$

where $\beta = 1/k_B T$, k_B is Boltzmann's constant, T is temperature and $Q(\beta)$ is the molecular partition function.

We can therefore evaluate $p_i - p_f$ as:

$$p_i - p_f \quad = \quad \frac{e^{-\beta E_i} - e^{-\beta E_f}}{Q(\beta)} \quad = \quad \frac{e^{-\beta E_i}}{Q(\beta)} \left[1 - e^{-\beta(E_f - E_i)}\right] \quad = \quad p_i \left[1 - e^{-\beta\hbar\omega_{fi}}\right] \tag{16}$$

We can therefore rewrite Eqn. 14 as:

$$\sigma(\omega) = \frac{4\pi^2}{\hbar c} \sum_{fi} \omega_{fi} \, |\mu_{fi}|^2 \, \delta(\omega_{fi} - \omega) \, p_i \left[1 - e^{-\beta\hbar\omega_{fi}}\right] \tag{17}$$

The delta function inside the sum enforces the fact that only resonant transitions contribute to the absorption cross section. We can therefore replace ω_{fi} with ω wherever it appears outside $\delta(\omega_{fi} - \omega)$, and rewrite $\sigma(\omega)$ as:

$$\sigma(\omega) = \frac{4\pi^2}{\hbar c} \omega \left[1 - e^{-\beta\hbar\omega}\right] \sum_{fi} p_i \cdot |\mu_{fi}|^2 \cdot \delta(\omega_{fi} - \omega) \tag{18}$$

We can now cleanly reorganize the *absorption cross section* $\sigma(\omega)$ by defining $S(\omega)$ as the *molecular lineshape function*, which contains all information specific to the frequency response of the molecular system:

$$\sigma(\omega) = \frac{4\pi^2}{\hbar c} \omega \left[1 - e^{-\beta\hbar\omega}\right] S(\omega) \tag{19}$$

$$S(\omega) = \sum_{fi} p_i \, |\mu_{fi}|^2 \, \delta(\omega_{fi} - \omega) \tag{20}$$

4 The dipole correlation function

We will now go a step further and show how the molecular lineshape $S(\omega)$ can be related to another important quantity: the *time correlation function* of the molecular dipole.

We'll make two substitutions to Eqn. 20: (a) expand $|\mu_{fi}|^2$ and (b) make use the following definition of the delta function:

$$\delta(\omega - \omega_0) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt \, e^{i(\omega - \omega_0)t} \tag{21}$$

Aside: Why can we express the delta function this way? Because the Fourier transform of a sinusoid in time yields a delta function in frequency space.

Forging ahead and recalling our definition of μ_{fi}:

$$S(\omega) = \sum_{fi} p_i \ \langle \psi_i | \underline{\hat{\mu}} \cdot \underline{\xi} | \psi_f \rangle \ \langle \psi_f | \underline{\hat{\mu}} \cdot \underline{\xi} | \psi_i \rangle \cdot \frac{1}{2\pi} \int_{-\infty}^{\infty} dt \, e^{i(\omega_{fi} - \omega)t} \tag{22}$$

where we recall that $\underline{\hat{\mu}}$ is the dipole moment operator of the molecule and $\underline{\xi}$ is a dimensionless unit vector indicating the polarization axis of the electric field. Recalling also that $\omega_{fi} \equiv (E_f - E_i)/\hbar$, we can rearrange to write:

$$S(\omega) = \frac{1}{2\pi} \sum_{fi} p_i \int_{-\infty}^{\infty} dt \, e^{-i\omega t} \ \langle \psi_i | \underline{\hat{\mu}} \cdot \underline{\xi} | \psi_f \rangle \ \langle \psi_f | \underline{\hat{\mu}} \cdot \underline{\xi} | \psi_i \rangle \ e^{i(E_f - E_i)t/\hbar} \tag{23}$$

$$= \frac{1}{2\pi} \sum_{fi} p_i \int_{-\infty}^{\infty} dt \, e^{-i\omega t} \ \langle \psi_i | \underline{\hat{\mu}} \cdot \underline{\xi} | \psi_f \rangle \ \langle \psi_f | e^{iE_f t/\hbar} \, \underline{\hat{\mu}} \cdot \underline{\xi} \, e^{-iE_i t/\hbar} | \psi_i \rangle \tag{24}$$

Recalling the time evolution operator $\hat{U} = e^{-i\hat{H}t/\hbar}$, we know that we can equate:

$$e^{-iE_i t/\hbar} \ |\psi_i\rangle = e^{-i\hat{H}^{(0)} t/\hbar} \ |\psi_i\rangle = \hat{U} \ |\psi_i\rangle \tag{25}$$

$$\langle \psi_f | \ e^{iE_f t/\hbar} = \langle \psi_f | \ e^{i\hat{H}^{(0)} t/\hbar} = \langle \psi_f | \, \hat{U}^\dagger \tag{26}$$

Plugging these quantities back into Eqn. 24, we have:

$$S(\omega) = \frac{1}{2\pi} \sum_{fi} p_i \int_{-\infty}^{\infty} dt \, e^{-i\omega t} \ \langle \psi_i | \underline{\hat{\mu}} \cdot \underline{\xi} | \psi_f \rangle \ \langle \psi_f | \hat{U}^\dagger \cdot \underline{\hat{\mu}} \cdot \underline{\xi} \cdot \hat{U} | \psi_i \rangle \tag{27}$$

$$= \frac{1}{2\pi} \sum_{i} p_i \int_{-\infty}^{\infty} dt \, e^{-i\omega t} \ \langle \psi_i | \, \underline{\hat{\mu}} \cdot \underline{\xi} \left[\sum_f |\psi_f\rangle \langle \psi_f| \right] \hat{U}^\dagger \cdot \underline{\hat{\mu}} \cdot \underline{\xi} \cdot \hat{U} \, |\psi_i\rangle \tag{28}$$

We know that $\{|\psi_f\rangle\}$ is a complete basis set, and therefore that

$$\sum_f |f\rangle \langle f| = \hat{I} \tag{29}$$

Therefore:

$$S(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt \, e^{-i\omega t} \sum_i p_i \ \langle \psi_i | \underline{\hat{\mu}} \cdot \underline{\xi} \cdot \hat{U}^\dagger \cdot \underline{\hat{\mu}} \cdot \underline{\xi} \cdot \hat{U} | \psi_i \rangle \tag{30}$$

$$= \frac{1}{2\pi} \int_{-\infty}^{\infty} dt \, e^{-i\omega t} \sum_i p_i \ \langle \psi_i | \underline{\hat{\mu}}(0) \cdot \underline{\xi} \cdot \underline{\hat{\mu}}(t) \cdot \underline{\xi} | \psi_i \rangle \tag{31}$$

In the last step we used the fact that $\hat{U}^\dagger \cdot \underline{\hat{\mu}} \cdot \hat{U} \equiv \underline{\hat{\mu}}(t)$ within the Heisenberg picture. Recall that sandwiching an operator with time evolution operators represents a unitary transformation of that operator which serves to evolve it forward in time. Note that we've also defined $\underline{\hat{\mu}} = \underline{\hat{\mu}}(0)$ to underscore that the "bare" operator represents a measurement of this quantity at $t = 0$, again working within the Heisenberg picture.

Finally, we note that $\underline{\xi}$ is just a unit vector describing the polarization axis of the light's electric field. Let's assume (with no loss of generality) that our light is polarized along the z axis in the laboratory. In this case, Eqn. 31 evaluates to

$$\boxed{S(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt\, e^{-i\omega t} \sum_i p_i \, \langle \psi_i | \hat{\mu}_z(0) \cdot \hat{\mu}_z(t) | \psi_i \rangle} \tag{32}$$

where $\hat{\mu}_z$ is the component of the molecular dipole operator aligned along the lab-frame z axis.

The expression

$$\sum_i p_i \, \langle \psi_i | \hat{\mu}_z(0) \cdot \hat{\mu}_z(t) | \psi_i \rangle \equiv \langle \hat{\mu}_z(0) \cdot \hat{\mu}_z(t) \rangle \equiv C_{\mu_z \mu_z}(0, t) \tag{33}$$

is a ***quantum autocorrelation function***, which represents the equilibrium average of a product of a Hermitian operator with itself evaluated at two separate points in time.

Here, we're looking at the time autocorrelation function of the z component of the molecular dipole moment operator $\hat{\mu}_z$. We're asking how well $\hat{\mu}_z$ overlaps with itself as the wavefunctions of our collection of molecules evolve from time 0 to t. This quantity provides a statistical description of the time-evolution of $\hat{\mu}_z$ averaged over a thermalized ensemble of quantum states that our molecules might be in.

Qualitatively, a time autocorrelation function describes how long a property of the system persists until it is averaged out by microscopic motions and interactions with its surroundings. This is helpful to capture the inherent randomness of a molecular system at thermal equilibrium.

In the most compact form we can write the molecular lineshape as:

$$\boxed{S(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt\, e^{-i\omega t} \, \langle \hat{\mu_z}(0) \cdot \hat{\mu_z}(t) \rangle} \tag{34}$$

The absorption lineshape is therefore directly related to the Fourier transform of the dipole correlation function. It is from this expression that all spectroscopic selection rules arise! This expression for $S(\omega)$ ***will simultaneously produce all allowed transitions from all quantum states that are thermally occupied in the ensemble***.

The complexity in Eqn. 34 arises from the time dependence of $\hat{\mu}_z(t) = e^{i\hat{H}^{(0)}t} \, \hat{\mu}_z(0) \, e^{-i\hat{H}^{(0)}t}$. This quantity encodes (a) which pairs of molecular states are coupled by the molecular dipole, allowing light-induced transitions and (b) how resonant frequencies of the molecular system will appear in the absorption spectrum. If we add in some treatment of broadening mechanisms, $\hat{\mu}_z(t)$ also accounts for how finite state lifetimes, dephasing processes, and environmental inhomogeneities give rise to broadened experimental lineshapes.

Depending on what Hamiltonian we plug into Eqn. 34, we can consider the dynamics of all electronic, nuclear, and spin degrees of freedom of the molecule. Soon, we will use Eqn. 34 to derive the selection rules that govern light-induced transitions between rotational states in microwave spectroscopy and vibrational states in infrared and Raman spectroscopy.

5 Some qualitative examples of absorption lineshapes from the dipole correlation function

We will quickly look at two qualitative examples for how the molecular absorption lineshape behaves.

Let's first consider a system in which the dipole autocorrelation function oscillates sinusoidally at frequency ω_0:

$$\langle \hat{\mu}(0) \cdot \hat{\mu}(t) \rangle \sim \mu_0^2 \, \cos(\omega_0 t) \tag{35}$$

where μ_0 is some average permanent dipole moment. This behavior might arise in a harmonic oscillator model of a molecular vibration where the dipole moment oscillates with the bond length. We will revisit the exact details of this case later. But very qualitatively we have:

$$\begin{aligned} S(\omega) &= \frac{1}{2\pi} \int_{-\infty}^{\infty} dt \, e^{-i\omega t} \; \langle \hat{\mu}(0) \cdot \hat{\mu}(t) \rangle & (36) \\ &= \frac{\mu_0^2}{2\pi} \int_{-\infty}^{\infty} dt \, e^{-i\omega t} e^{\pm i\omega_0 t} \quad \propto \quad \frac{\mu_0^2}{2\pi} \, \delta(\omega \pm \omega_0) & (37) \end{aligned}$$

Thus, as we might expect, the spectrum consists of sharp absorption and emission lines at frequency ω_0. Because we have introduced no broadening mechanisms, these lines appear as arbitrarily narrow delta functions. Recall that we built up this framework beginning from Fermi's Golden Rule, derived in the long-time limit where the lineshapes of light-driven transitions approach delta functions!

Things gets more interesting if, for reasons we will explore shortly, the dipole autocorrelation function both oscillates sinusoidally and decays exponentially with time:

$$\langle \hat{\mu}(0) \cdot \hat{\mu}(t) \rangle \sim \mu_0^2 \, \cos(\omega_0 t) \, e^{-\gamma |t|} \tag{38}$$

This indicates a loss of correlation between $\hat{\mu}$ evaluated at time 0 and time t.

We won't do out the Fourier transform integral here as it involves complex analysis, but it turns out that the Fourier transform of $f(t) = e^{-i\omega_0 t - \gamma |t|}$ is a *Lorentzian* lineshape with

$$S(\omega) \propto \frac{\gamma - i(\omega - \omega_0)}{(\omega - \omega_0)^2 + \gamma^2} \tag{39}$$

The real part of this expression represents the experimentally observed broadened lineshape.

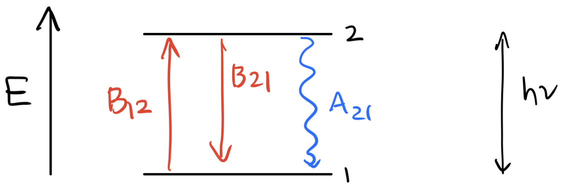
The Lorentzian absorption lineshape is ubiquitous and holds for any system whose dipole correlation function decays exponentially in time. This encompasses radiative decay, nonradiative decay, collisional broadening, and power broadening processes, which are collectively referred to as forms of *homogeneous* broadening.

The Lorentzian lineshape ultimately reflects a time-energy uncertainty relation. If some decay process limits the lifetime of a system in a given state to Δt, then we can't know the energy of the transition perfectly. The Lorenzian linewidth will be given by $\gamma \sim 1/\Delta t$.

6 Radiative lifetimes and Einstein coefficients

Let's be a bit more quantitative about the homogeneous radiative relaxation lifetimes of quantum states. We can use ***Einstein coefficients*** to describe the rates of stimulated absorption and emission of photons under laser illumination, as well as spontaneous emission, which describes the radiative decay of an excited state through emission of a photon.

Consider the energy diagram of a two-level system embedded in a radiation field. Einstein introduced three parameters which describe this situation: the A_{21} coefficient determines the rate of spontaneous emission, while B_{12} and B_{21} describe the absorption and stimulated emission rates. A_{21} has units of Hz, while B_{12} and B_{12} have units of m^3 Hz / J · s.



Our two-level system is interacting with a radiation field with energy density $\rho(\nu)$ per unit frequency. Here, we will work with $\rho(\nu)$ in units of J/m^3 per unit bandwidth in Hz, though it is not uncommon to see $\rho(\nu)$ in other units. Note that we are also working with frequency $\nu = \omega/2\pi$. This happens to be the convention when writing down Einstein coefficients.

The absorption coefficient B_{12} determines the rate with which upward transitions 1 → 2 occur in the radiation field. The number of photons of frequency ν *absorbed* per second is given by:

$$k_{1\to2} = N_1\, B_{12}\, \rho(\nu) \qquad [\mathrm{s}^{-1}] \tag{40}$$

where N_1 is the number of emitters initially in state 1.

The number of photons of frequency ν *emitted* per second comes from 2 → 1 downward transitions stimulated by the radiation field as well as from the field-independent spontaneous emission:

$$k_{2\to1} = N_2\, B_{21}\, \rho(\nu) + N_2\, A_{12} \qquad [\mathrm{s}^{-1}] \tag{41}$$

where N_2 is the number of emitters initially in state 2.

A_{12}, B_{12} and B_{21} are inherent properties of the emitter, independent of the radiation field. Thus, we can choose an arbitrary radiation field for the purposes of determining the relationships between these coefficients. It is mathematically convenient to consider a system at thermal equilibrium, where the radiation energy density at frequency ν is given by the Planck distribution:

$$\rho(\nu) = \frac{8\pi h\nu^3}{c^3}\frac{1}{e^{h\nu/k_BT} - 1} \qquad [\mathrm{J/m^3/Hz}] \tag{42}$$

We can now apply the principle of detailed balance (or microscopic reversibility) which states that at thermal equilibrium, the rate of upward transitions must exactly match the rate of downward transitions – otherwise we are not in equilibrium. Here, the relative populations in states 1 and 2 are given by the Boltzmann distribution:

$$\frac{N_2}{N_1} = \frac{g_2}{g_1} e^{-(E_2-E_1)/k_BT} \tag{43}$$

where g_i is the degeneracy of state i. Thus, we must have

$$k_{1\to 2} = k_{2\to 1} \tag{44}$$

$$= N_1\, B_{12}\, \rho(\nu) = N_2 B_{21}\, \rho(\nu) + N_2\, A_{12} = N_2\, [B_{21}\, \rho(\nu) + A_{12}] \tag{45}$$

$$\to \frac{N_2}{N_1} = \frac{B_{12}\, \rho(\nu)}{B_{21}\, \rho(\nu) + A_{21}} = \frac{g_2}{g_1} e^{-(E_2 - E_1)/k_B T} \tag{46}$$

where in the last step we used our result from Eqn. 43.

We now consider the resonant condition $h\nu = E_2 - E_1$. We will rearrange Eqn. 46 to solve for $\rho(\nu)$ and set it equal to the Planck distribution from Eqn. 49:

$$B_{12}\, \rho(\nu) = \frac{g_2}{g_1} e^{-h\nu/k_B T}\, [B_{21}\, \rho(\nu) + A_{21}] \tag{47}$$

$$\to \rho(\nu) \left[B_{12} - \frac{g_2}{g_1} e^{-h\nu/k_B T} B_{21} \right] = \frac{g_2}{g_1} e^{-h\nu/k_B T} A_{21} \tag{48}$$

$$\to \rho(\nu) = \frac{\frac{g_2}{g_1}\, e^{-h\nu/k_B T} A_{21}}{B_{12} - \frac{g_2}{g_1}\, e^{-h\nu/k_B T} B_{21}} = \frac{\frac{g_2}{g_1} A_{21}}{B_{12}\, e^{h\nu/k_B T} - \frac{g_2}{g_1} B_{21}} \overset{?}{=} \frac{8\pi h\nu^3}{c^3} \frac{1}{e^{h\nu/k_B T} - 1} \tag{49}$$

We must now define A_{12}, B_{12}, and B_{21} in terms of one another such that the equality in Eqn. 49 is enforced. I will write the solution down and you can check for yourself that it works:

$$A_{21} = \frac{8\pi h\nu^3}{c^3}\, B_{21} \qquad\qquad B_{12} = \frac{g_2}{g_1}\, B_{21} \tag{50}$$

The Einstein coefficients are therefore not independent quantities. Once you have one, all three are determined. They have straightforward relationships to other quantities which describe the likelihood of absorption of light, including the absorption cross section. These relationships are nicely laid out by Hilborn (*Am. J. Phys.* **50**, 982 (1982)) if you ever need to use them.

Let's briefly note some last takeaways regarding spontaneous emission in particular:

- $A_{21} \sim 1/\tau_{rad}$ represents the inverse of the radiative (or fluorescence) lifetime, and $N_2 A_{21}$ represents the number of photons spontaneously emitted per second by an ensemble. From Eqn. 50 we can see that A_{21} scales with ν^3.
- At frequencies corresponding to visible light, A_{21} can be quite large, resulting in short radiative lifetimes which can be the dominant mode of broadening (100 ns ↔ 100 MHz).
- At low frequencies, including the infrared regime, ν^3 is small, resulting in very slow fluorescence, and therefore extremely narrow natural linewidths, on the order of Hz. The slow emission rate at small frequencies is the reason that fluorescence measurements are routinely made at optical wavelengths, but are much more challenging in the infrared.

7 Other broadening processes

We have seen that the lineshape of the absorption cross section arises from the temporal dynamics of the molecular dipole operator. There are numerous processes that can influence this lineshape.

- *Molecular* effects arise from the dynamics of a single emitter
- *Ensemble* effects arise from disorder averaged across a population
- *Dynamic* processes and disorder lead to homogeneous broadening with *Lorentzian lineshapes*
- *Static* disorder leads to inhomogeneous broadening with *Gaussian lineshapes*

	molecule	ensemble
homogeneous (Lorentzian)	population relaxation	dephasing
inhomogeneous (Gaussian)	×	sample inhomogeneity

7.1 Population relaxation

Population relaxation is a homogeneous process causes Lorenzian broadening of the lineshape through exponential decay of the dipole correlation function due to a finite excited state lifetime. A finite state lifetime can have contributions from radiative decay (e.g. spontaneous emission) or non-radiative processes, which might include internal conversion, intersystem crossing, and intramolecular vibrational relaxation.

These decay processes are qualitatively described by a timescale T. If each decay is independent, the exponential decay rates add as:

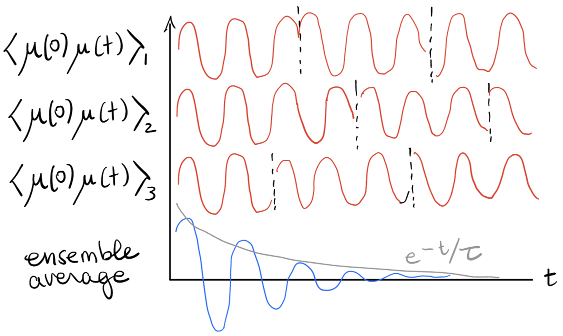
$$\frac{1}{T} = \frac{1}{T_1} + \frac{1}{T_2} + \ldots \tag{51}$$

If population relaxation is the only broadening mechanism, all members of the ensemble behave identically and the experimentally measured linewidth describes the state lifetimes of a single emitter.

7.2 Dephasing

Dephasing processes scramble the phase of oscillations of the dipole correlation function within an ensemble. This usually occurs as a result of interactions with the environment. This is a ensemble averaging effect in which the phase relationships of oscillations between members of the ensemble are slowly destroyed by dynamic disorder.

Examples of dephasing include fluctuations induced by collisions with solvent in a liquid phase sample. Each collision that an individual emitter experiences effectively “resets” its phase by introducing a random phase shift. This process causes destructive interference between emitters over time.

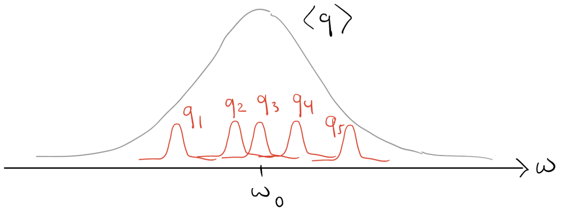


In gas phase samples, collisional broadening is known as pressure broadening, and is usually characterized phenomenologically with a pressure broadening coefficient γ (MHz/torr or cm^{-1}/torr), which describes how the pressure-broadened half-width-at-half-maximum scales linearly with gas pressure.

A related process is orientational relaxation. Since the dipole correlation function depends on the projection of the molecular dipole moment onto a fixed laboratory axis set by the polarization of the laser field, randomization of the initial dipole orientations is an ensemble-averaged dephasing effect. In solution, transition dipoles are often treated as having orientations which diffuse over time.

7.3 Sample inhomogeneity

Lineshapes can also be broadened by an inhomogeneous distribution of molecular absorption frequencies. If molecules in the ensemble are influenced by inhomogeneous environmental variations, the observed lineshape will appear Gaussian. This is an ensemble averaging effect which can obscure the dynamical processes encoded in the homogeneous linewidth.



Let's give a concrete example. In gases, inhomogeneous Doppler broadening arises due to the velocity distribution of the ensemble of emitters. Just like a pedestrian hears a Doppler shift in the siren frequency of a firetruck as it speeds past, the velocity of a molecule towards or away from the light source creates an optical Doppler shift:

$$\omega = \omega_0 \left(1 + \frac{v}{c}\right) \tag{52}$$

where ω is the observed frequency, ω_0 is the unshifted frequency, and v is the velocity of the emitter towards the light source. The distribution of molecular velocities therefore leads to a broadening in observed transition frequencies.

The velocity distribution for a sample of molecules with mass m thermalized to temperature T is given by the Maxwell-Boltzmann distribution:

$$P_v(v)dv = \sqrt{\frac{m}{2\pi k_B T}} \exp\left(-\frac{mv^2}{2k_B T}\right) \tag{53}$$

By combining Eqns. 52 and 53, one can find the distribution of observed frequencies:

$$P_\omega(\omega)d\omega = \sqrt{\frac{mc^2}{2\pi k_B T \omega_0^2}} \exp\left(-\frac{mc^2(\omega-\omega_0)^2}{2k_B T \omega_0^2}\right) \tag{54}$$

This is another Gaussian distribution centered about ω_0 with standard deviation

$$\sigma = \sqrt{\frac{k_B T}{mc^2}}\, \omega_0 \tag{55}$$

Doppler broadening therefore scales linearly with the transition frequency and dominates for small masses and at high temperatures.

7.4 Simultaneous homogeneous and inhomogeneous broadening

A final note is that the homogeneous and inhomogeneous linewidths can be comparable in scale for some systems. In this case, the lineshape is described by a *Voigt* profile, which is the convolution of a Gaussian and a Lorentzian:

$$V(x;\sigma,\gamma) = \int_{-\infty}^{\infty} dx'\, G(x';\sigma) L(x-x';\gamma) \tag{56}$$

There is no analytical form for the Voigt lineshape, so it must be calculated numerically.

Plotted below are Gaussian and Lorentzian lineshapes which are normalized with equal areas. A Gaussian lineshape has a higher maximum intensity, while the Lorentzian lineshape has more intensity in its wings. The Voigt profile falls in an intermediate regime between the Gaussian and Lorenzian lineshapes, and its shape depends on the relative scales of the Gaussian standard deviation σ and Lorentzian linewidth γ.