(A) Excited State Radiative "Lifetime" 
(Einstein A Coefficient)

Consider any two states of a molecule within a container in equilibrium with electromagnetic radiation. States 1 & 2 are populated with numbers of molecules $N_1$ & $N_2$ according to Boltzmann:

$$\frac{N_2}{N_1} = e^{\frac{- (E_2 - E_1)}{kT}} = e^{\frac{-\hbar \nu}{kT}}$$

State 2, $N_2$ molecules

$\Delta E = \hbar \nu$

\[ \begin{array}{ccc}
\text{Absorption} & \text{Spontaneous Emission} & \text{Stimulated Emission} \\
\text{Rate} = N_1 B \nu \rho(\omega) & \text{Rate} = N_2 A & \text{Rate} = N_2 B_{21} \rho(\omega) \\
\end{array} \]

State 1, $N_1$ molecules.

At equilibrium: $N_1 B \nu \rho(\omega) = N_2 B_{21} \rho(\omega) + N_2 A$

The energy density $\rho(\omega) = \frac{8\pi^2 \hbar \nu^3}{c e^{\frac{\hbar \nu}{kT}} - 1}$

Planck's Blackbody Law

But the kinetics requires another expression for $\rho(\omega)$

$N_1 B \nu \rho(\omega) - N_2 B_{21} \rho(\omega) = N_2 A$

$\rho(\omega) = \frac{A}{N_1 B - B_{21}} = \frac{A}{\frac{\hbar \nu}{kT B_{12} - B_{21}}} = \frac{\frac{\hbar \nu}{kT B_{12} - B_{21}}}{\frac{\hbar \nu}{kT}}$
Einstein's brilliance here was postulating stimulated emission (not confirmed until the 1960s).
The last equation shows that:

\[ B_{12} = B_{21} = B' \]
\[ A = 8 \pi h \frac{2}{3} B' \]

but \( B = \) was defined by: \( \text{rate} = B \rho(\omega) = B' \rho(\omega) \)

\[ B = \frac{4 \pi |M_{fi}|^2}{\hbar^2 \epsilon_0} \]

\[ \rho(\omega) = \frac{d \rho}{d \omega} \quad \rho'(\omega) = \frac{d \rho}{d \omega} \]

So \( \rho(\omega) = \frac{d \rho}{2\pi \cdot d \omega} = \frac{1}{2\pi} \rho'(\omega) \)

\[ B \rho(\omega) = B' \rho'(\omega) = B' \rho(\omega) \cdot B' = \frac{B}{2\pi} \]

\[ B' = 2 \frac{|M_{fi}|^2}{\hbar^2 \epsilon_0} \]

\[ A = 8 \pi h \frac{2}{3} \frac{2|M_{fi}|^2}{(\frac{\hbar}{2\pi})^2 \epsilon_0} = \frac{64 \pi^3}{3} \frac{2}{3} \frac{|M_{fi}|^2}{\hbar \epsilon_0} \]

The rate of spontaneous emission depends on the transition dipole squared \( \times \) (frequency)\(^3\).
Lifet ime

rate = \frac{dN}{dt} = -A N

\frac{N(t)}{N(0)} = e^{-At} = e^{-\frac{t}{\tau}}

where \( \tau = \text{"lifetime"} = \frac{1}{A} \)

Exercise: (a) Find the lifetime for an excited state for which the transition dipole length = 1Å at a wavelength of 500 nm.

(b) Compare your result to a transition at \( \bar{\jmath} = 1 \text{cm}^{-1} \) with the same \( \mu \).


B) The lifetime of a coherently excited superposition.

\[ H = H_0 + W \]

\[ H_0 |n\rangle = E_n |n\rangle \quad H_0 |m\rangle = E_m |m\rangle \]

\[ \langle n/W/m \rangle = 0 = W_{nm} \]

Molecular Eigen states = \[ \Psi_i = b_{ni} |n\rangle + \sum_m b_{mi} |m\rangle \]
So a band of eigenstates is observed whose spectrum will look like:

\[
\text{absorbance} \uparrow \quad \text{width} \to |W_{nm}|^2
\]

rate of absorption to state \( \psi_i \) is \( \alpha = |\langle g|\mu|\psi_i \rangle|^2 \)

\[
\alpha = \left| \langle g|\mu| (b_{ni}|n\rangle + \frac{m}{M} b_{ni}|m\rangle \rangle \right|^2
\]

\[
\alpha = b_{ni}^2 |\langle g|\mu|n\rangle|^2
\]

For equally spaced levels of \( \hbar \omega \) and a constant interaction \( W_{nm} \)

\[
b_{ni} = \frac{\Delta^2}{\Delta^2 + (\bar{\omega}_i - \bar{\omega}_n)^2} \quad \text{(a lorentzian)}
\]

Note half width at half maximum = \( \Delta \)

Now if a pulse of radiation is applied such that the spectral width is \( \Delta \omega >> 2\Delta \), centered at \( \bar{\omega}_n \)

\( \bar{\psi}_i \) are coherently excited, producing the wave packet

\[
\left\{ \Phi(t) = \sum_i \langle g|\mu|n\rangle b_{ni} \psi_i e^{-i\omega_i t} \right\}
\]
Now, the rate of spontaneous emission from the coherent superposition is:

\[
\text{Rate} \propto \left| \langle g | \mu | \psi_i(t) \rangle \right|^2 \\
= \left| \langle g | \mu | \sum_i \langle g | \mu | n \rangle n_i (\langle n_i | n \rangle + \sum_m b_{n_i m}^* \delta_{n_i m} - i \omega_i t) \rangle \right|^2 \\
= \left| \langle g | \mu | n \rangle \sum_i \sum_{n_i} |n_i\rangle b_{n_i} e^{-i \omega_i t} \right|^2 \\
= \left| \langle g | \mu | n \rangle \sum_i b_{n_i} e^{-i \omega_i t} \right|^2 \\
\propto |\mu_n|^2 \text{ at time } t = 0 \text{ since } \sum_i b_{n_i} = 1
\]

Dephasing occurs as time increases and the different \( \psi_i \) parts get out of phase.

Note that because of close spacing:

\[
\sum_i b_{n_i} e^{-i \omega_i t} \Rightarrow \int b_n(\omega_i) e^{-i \omega_i t} d\omega_i
\]

= Fourier transform of a Lorentzian

\[
\int_{-\infty}^{\infty} \frac{\cos \omega t}{1 + \omega^2} = \pi e^{-t} \text{ exponential}
\]

\[
\int \frac{\Delta^2 \cos \omega t d\omega}{\Delta^2 + \omega^2} = \Delta \int \frac{\cos \frac{\omega \Delta t}{\Delta}}{1 + (\omega_0 - \omega)^2} = \Delta e^{-\Delta t}
\]
So emission decays exponentially
\[ \dot{\psi} = -e^{-\frac{\Delta t}{\tau}} \]

\[ \Delta \propto \frac{|W_{nm}|^2}{\hbar} \]

\( W_{nm} \) can be interaction with radiation field, in which this describes spontaneous and stimulated emission.

or \( m \) may be high vibrational levels of a lower electronic state. Then \( \mu^{-1} \) = a non-radiative rate.

\[ \boxed{\text{OSCILLATOR STRENGTH } = f} \]

This goes back to Drude's theory for a harmonically bound electron.

\[ x_c = \text{Classical turning point,} \]
\[ = \frac{1}{2} K x^2 \]
\[ E = V = \frac{1}{2} K x^2 \]
\[ \omega = 2\pi f = \sqrt{\frac{K}{m}} \]
\[ K = m \omega^2 \]
\[ \frac{1}{2} \hbar \omega = \frac{1}{2} m \omega^2 x_c^2 \]
\[ x_c^2 = \frac{\hbar}{m \omega} \]
Classical turning point when \( n = 0 \) is like the "Bohr radius" of the harmonic osc.

\[ x_c = \sqrt{\frac{\hbar}{m\omega}} \]

Rate of absorption for \( 0 \rightarrow 1 \) is \( e^2 x_c^2 \)

Can show that \( x_{01} = \frac{1}{2} x_c \)

So rate \( \propto \frac{e^2}{2} \frac{x_c^2}{2 \hbar \omega} = \frac{1}{\mu_{01}}^2 \cdot \frac{e^2}{2 \hbar \omega} \cdot \frac{\hbar}{\hbar} \)

Oscillator strength for any transition \( m \rightarrow n \) is defined as the ratio:

\[ F = \frac{|\mu_{mn}|^2}{|\mu_{01}|^2} = \frac{2m\omega/|\mu_{mn}|^2}{e^2 \hbar} = \frac{2m\omega |x_{mn}|^2}{e^2 \hbar} \]

Exercise 2.2: Find the oscillator strengths for the transitions in Exercise 1a & 1b.

\((p.3)\)
Finding $|\mu_{mn}|^2$ from $\varepsilon$

rate = $4 \times 10^{-19} \varepsilon F = 4 \times 10^{-19} \varepsilon \frac{I}{h\nu}$

= $4 \times 10^{-19} \varepsilon \frac{c}{h\nu}$

so $B = \frac{4 \times 10^{-19} \varepsilon c}{h\nu} = \frac{4\pi}{h^2 c^0} |\mu_{mn}|^2$

But typically $\varepsilon(\nu)$

\[ \nu \to \]

So $|\mu_{mn}|^2 = \frac{4 \times 10^{-19} c^2 \varepsilon_0}{4\pi h^2} \int \frac{\varepsilon(\nu) d\nu}{\nu}$

$\sigma = \frac{4 \times 10^{-19} c \varepsilon_0}{16\pi^3} \text{ (Area in (M cm$^{-1}$) cm$^{-1}$)}$

$\frac{1}{2} \text{ave.}$

A "good" problem would be to find the proportionality constant that changes $\sigma$ into $= $
MULTI PHOTON ABSORPTION & SCATTERING

\[ \omega' \]

\[ \omega \]

2 photon abs.

\[ \Delta E = h(\omega + \omega') \]

Raman Scattering.

\[ \Delta E = \hbar \omega - \hbar \omega' \]

Both processes involve the same non-stationary state which is often described as the molecule with 1 photon of energy \( \hbar \omega \) "absorbed" even though no stationary (energy even) state exists at \( E = E_i + \hbar \omega \).

For 2-photon abs., a 2nd photon is absorbed by the "virtual state" and a stationary state, \( |f\rangle \), is reached.

For Raman scattering, a 2nd photon with energy \( \hbar \omega' \) is spontaneously emitted.
Sketch of 2nd order time dependent perturbation theory: The KDH equation.

\[ W(t) = W \cos wt = \frac{W}{2} (e^{iwt} - e^{-iwt}) \]

\[ b(t) = \frac{-i}{2\pi} \int_0^t W_k \left( e^{iwt} - e^{-iwt} \right) b(0) e^{i\omega_k t'} dt' \]

[we start with \( \psi = 1g \) at \( t = 0 \)]

At very short times, the "uncertainty" in energy is large, and all states \( |k\rangle \) will get amplitude \( b_k \approx W_{kg} = \mu_{kg} \)

Integrating gives:

\[ b(t) = \frac{-i}{2\pi} \int_0^t W_k \left[ e^{i(w_k-w)t'} - e^{i(w_k+w)t'} \right] dt' \]

2nd order:

\[ b(t) = \sum_k \frac{-i}{2\pi} \int_0^t W_{tk}(e^{i\omega_k t'} - e^{-i\omega_k t'}) b(0) e^{i\omega_k t'} dt' \]
$$\frac{\partial f}{\partial t} = \frac{-i}{\hbar} \int \sum_{k} W_{fk}(e^{-i(W_{fk} - \omega)t} + e^{i(W_{fk} + \omega)t}) \left(\frac{-1}{2\pi}\right)i(W_{kg} - \omega) + \ldots$$

$$= \frac{-i}{\hbar} \int \sum_{k} W_{fk} W_{kg} \left[ e^{-i(W_{fk} + W_{kg} - \omega - \omega')t} \right] \frac{e^{-iW_{kg}t}}{W_{kg} - \omega} + \ldots$$

leads to resonance when $W_{fk} + W_{kg} = \omega + \omega'$

$W_{fk} - W_{kg} = W_{f} - W_{k} + W_{k} - W_{g} = W_{f} - W_{g}$

i.e. $\Delta E = \hbar(\omega + \omega')$

$$\frac{\partial f}{\partial t} = \sum_{k} \left[ \frac{W_{fk} W_{kg}}{W_{kg} - \omega} + \frac{W_{fk} W_{kg}}{W_{kg} + \omega'} \right]$$

- for 2PA
  + for Raman.

Kramers-Heisenberg-Dirac Formula.