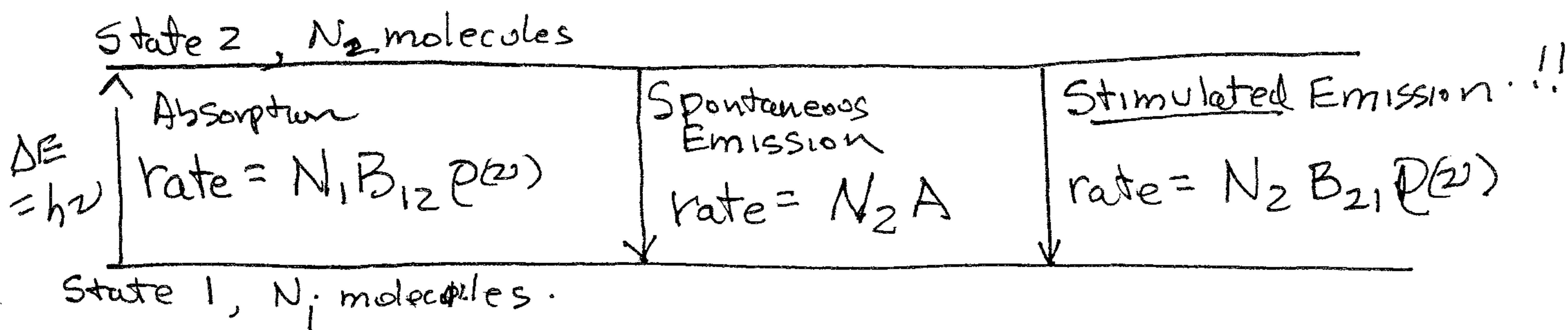


Lecture #22

(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

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


At equilibrium: $N_1 B_{12} \rho(\nu) = N_2 B_{21} \rho(\nu) + N_2 A$

The energy density $\rho(\nu) = \frac{8\pi h \bar{\nu}^3}{e^{\frac{h\nu}{kT}} - 1}$ ← $\bar{\nu} = \nu/c$
Planck's Blackbody Law

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

$$N_1 B_{12} \rho(\nu) - N_2 B_{21} \rho(\nu) = N_2 A$$

$$\rho(\nu) = \frac{A}{\frac{N_1}{N_2} B_{12} - B_{21}} = \frac{A}{e^{\frac{h\nu}{kT}} B_{12} - B_{21}} = \frac{A/B_{21}}{e^{\frac{h\nu}{kT}} \frac{B_{12}}{B_{21}} - 1}$$

Einstein's brilliance here was postulating stimulated emission (not confirmed until the 1960s)

The last equation shows that:

$$B_{12} = B_{21} \equiv B'$$

$$A = 8\pi h \bar{\nu}^3 B'$$

but $B =$ was defined by: rate = $B \rho(\omega) = B' \rho(\omega)$

$$B = \frac{4\pi |\mu_{fi}|^2}{\hbar^2 \epsilon_0}$$

$$\rho(\omega) = \frac{d\rho}{d\omega} \quad \rho(\omega) = \frac{d\rho}{d\omega}$$

$$\text{So } \rho(\omega) = \frac{d\rho}{2\pi d\omega} = \frac{1}{2\pi} \rho(\omega)$$

$$B \rho(\omega) = \frac{B}{2\pi} \rho(\omega) = B' \rho(\omega); \quad B' = \frac{B}{2\pi}$$

$$B' = \frac{2 |\mu_{fi}|^2}{\hbar^2 \epsilon_0}$$

$$A = \frac{8\pi h \bar{\nu}^3 \cdot 2 |\mu_{fi}|^2}{\left(\frac{\hbar}{2\pi}\right)^2 \epsilon_0} = \frac{64\pi^3 \bar{\nu}^3 |\mu_{fi}|^2}{h \epsilon_0}$$

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

Life time

$$\text{rate} = \frac{dN}{dt} = -AN$$

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

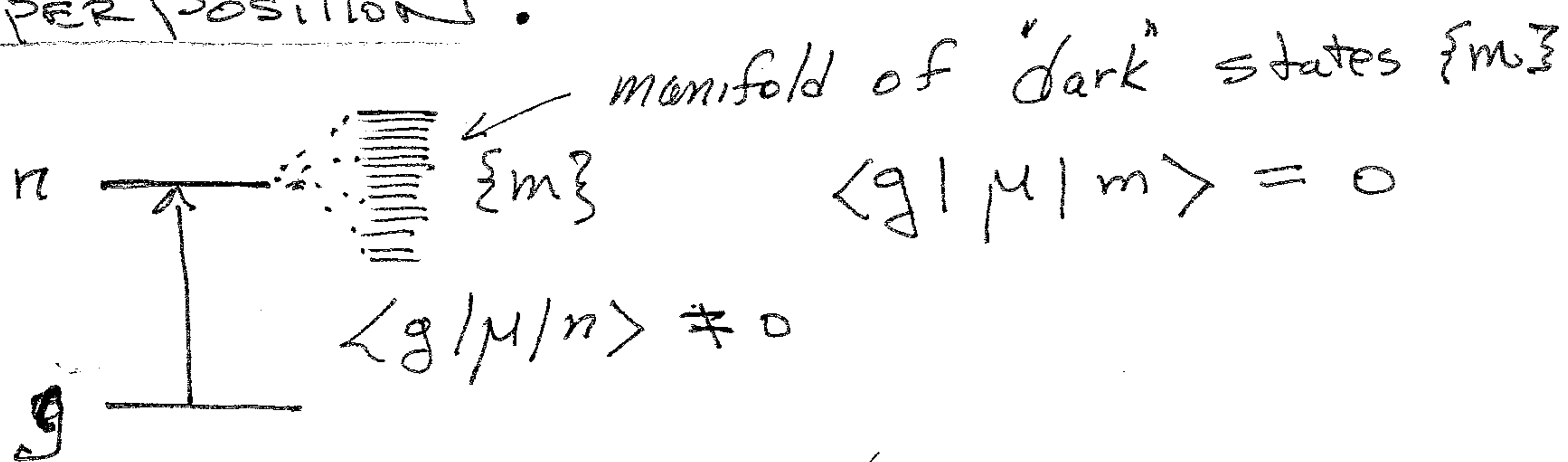
$$\text{where } \tau = \text{"lifetime"} = \frac{1}{A}$$

Exercise: (a) Find the ^{radiative} lifetime for an excited state for which the transition dipole length = 1 \AA at a wavelength of 500 nm .

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

From M. Byer, & J. Jortner, J. Chem. Phys. 40, 715-726 (1963)

(B) The LIFETIME OF A COHERENTLY EXCITED SUPERPOSITION.



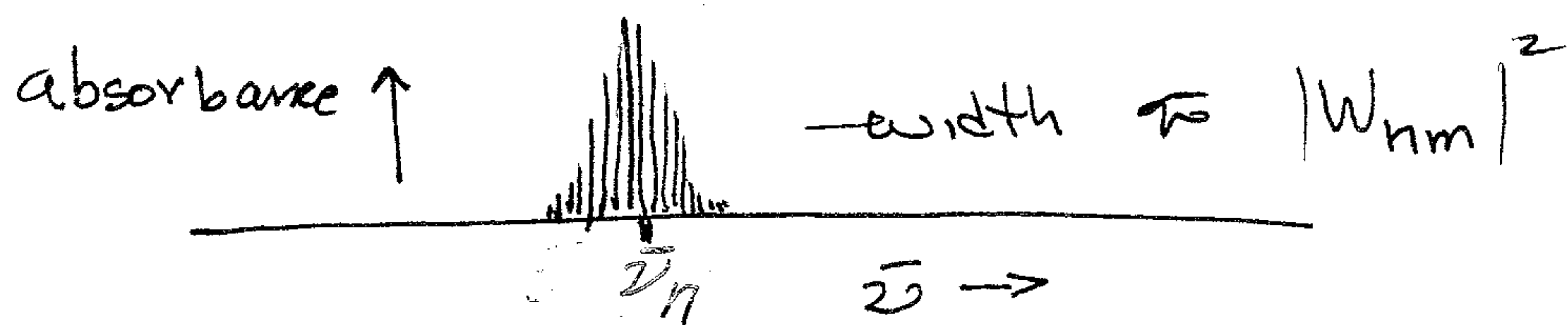
$$H = H_0 + W$$

$$H_0 |n\rangle = E_n |n\rangle \quad H_0 |m\rangle = E_m |m\rangle$$

$$\langle n | W | m \rangle \neq 0 = W_{nm}$$

$$\text{Molecular Eigen states} = \psi_i = b_{n_i} |n\rangle + \sum_m b_{m_i} |m\rangle$$

So a band of eigenstates is observed. whose spectrum will look like:



rate of absorption to state ψ_i is $\propto |\langle g | \mu | \psi_i \rangle|^2$

$$\propto |\langle g | \mu | (b_{ni} | n \rangle + \sum_m b_{mi} | m \rangle) |^2$$

$$\propto b_{ni}^2 |\langle g | \mu | n \rangle|^2$$

For equally spaced levels of $\{m\}$ and a constant interaction W_{nm}

$$b_{ni}^2 \propto \frac{\Delta^2}{\Delta^2 + (\bar{\omega}_i - \bar{\omega}_n)^2} \quad (\text{a Lorentzian})$$

Note half width at half maximum = Δ

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

all the ψ_i are coherently excited, producing the wave packet

$$\psi_{(\alpha)} = \sum_i \langle g | \mu | n \rangle b_{ni} \psi_i e^{-i\omega_i t}$$

Now, the rate of spontaneous emission from the coherent superposition is:

$$\begin{aligned} \text{rate} &\propto \left| \langle g | \mu | \psi(t) \rangle \right|^2 \\ &\propto \left| \langle g | \mu \left| \sum_i \langle g | \mu | n \rangle b_{ni} (b_{ni} |n\rangle + \sum_m b_{mi} |m\rangle) e^{-i\omega_i t} \right. \right|^2 \\ &\propto \left| \langle g | \mu | n \rangle \sum_i b_{ni} e^{-i\omega_i t} \right|^2 \\ &\propto |\mu_{gn}|^2 \quad \text{at time } t=0 \quad \text{Since } \sum_i b_{ni}^2 = 1 \end{aligned}$$

Dephasing occurs as time increases and the different ψ_i parts get out of phase.

Note that because of close spacing.

$$\sum_i b_{ni}^2 e^{-i\omega_i t} \Rightarrow \int b_n(\omega_i)^2 e^{-i\omega_i t} d\omega_i$$

= Fourier transform of a Lorentzian.

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

$$\int \frac{\Delta^2 \cos \omega t d\omega}{\Delta^2 + \omega^2} = \Delta \int \frac{\cos \frac{\omega}{\Delta} \Delta t \frac{d\omega}{\Delta}}{1 + (\frac{\omega_0 - \omega}{\Delta})^2} = \Delta e^{-\Delta t}$$

So emission decays exponentially

$$\text{rate } \propto e^{-\Delta t} = e^{-t/\tau} \quad \tau = \frac{1}{\Delta}$$

$$\Delta \propto \left| \frac{W_{nm}}{\hbar} \right|^2$$

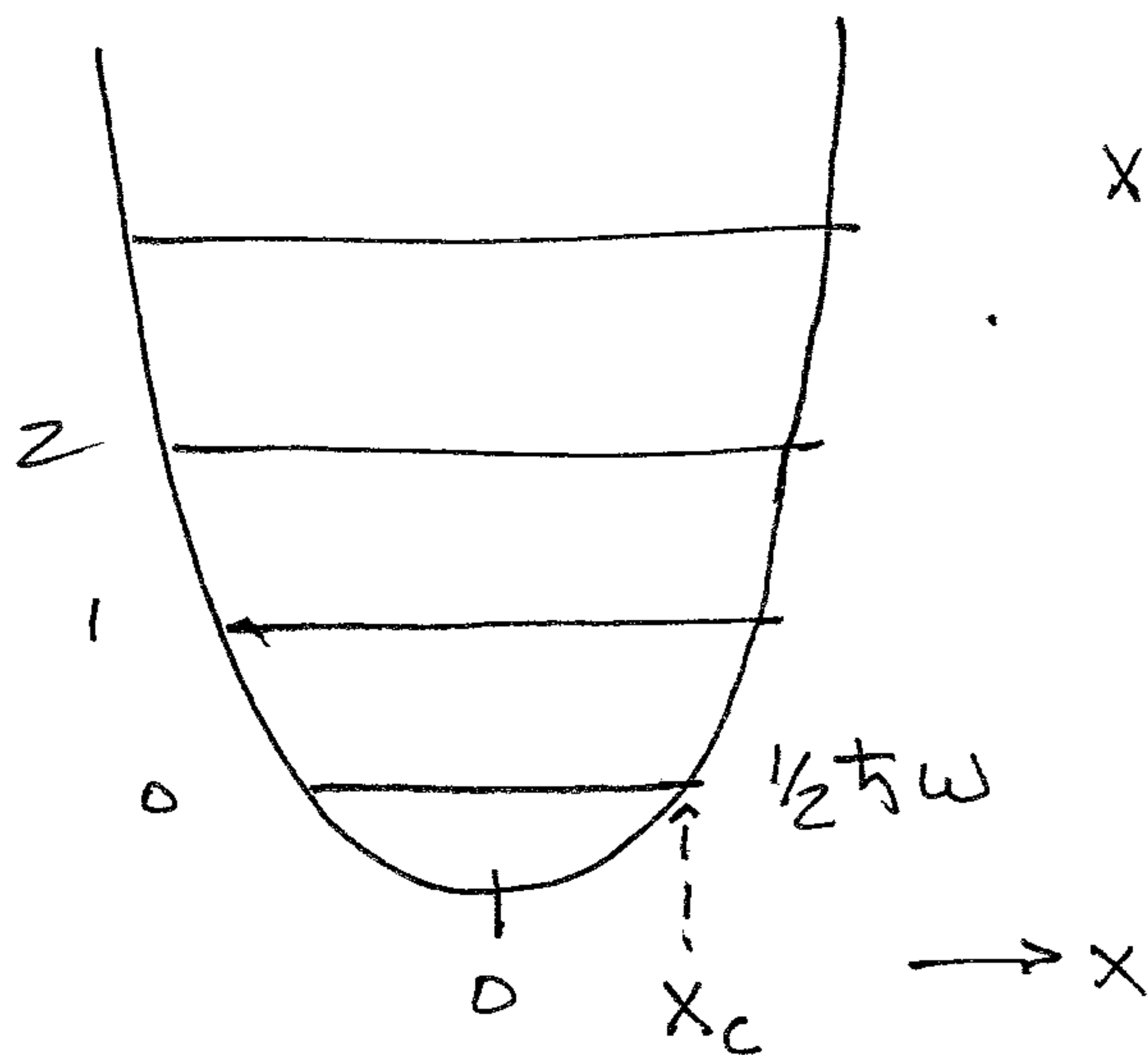
W_{nm} can be interaction with radiation field.
in which this describes spontaneous
and stimulated emission.

or m may be high vibrational levels of
a lower electronic state. Then

$\tau^{-1} = \text{a non-radiative rate.}$

(C) OSCILLATOR STRENGTH = f

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



$x_c = \text{Classical turning point.}$
= where $E = V = \frac{1}{2} K x^2$

$$\omega = 2\pi\nu = \sqrt{\frac{K}{m}}$$

$$K = m\omega^2$$

$$\frac{1}{2} \hbar \omega = \frac{1}{2} m \omega^2 x_c^2$$

$$x_c^2 = \frac{\hbar}{m\omega}$$

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 $e^2 x_{01}^2$

can show that $x_{01} = \frac{1}{\sqrt{2}} x_c$

$$\text{so rate is } e^2 \frac{x_c^2}{2} = \frac{e^2 \hbar}{2 m \omega} = |\mu_{01}^{H0}|^2$$

Oscillator strength for any transition $m \rightarrow n$ is defined as the ratio.

$$f = \frac{|\mu_{mn}|^2}{|\mu_{01}^{H0}|^2} = \frac{2m_e \omega |\mu_{mn}|^2}{e^2 \hbar} = \frac{2m_e \omega |x_{mn}|^2}{\hbar}$$

Exercise 2: Find the oscillator strengths for the transitions in exercise 1a & 1b.

(p3)

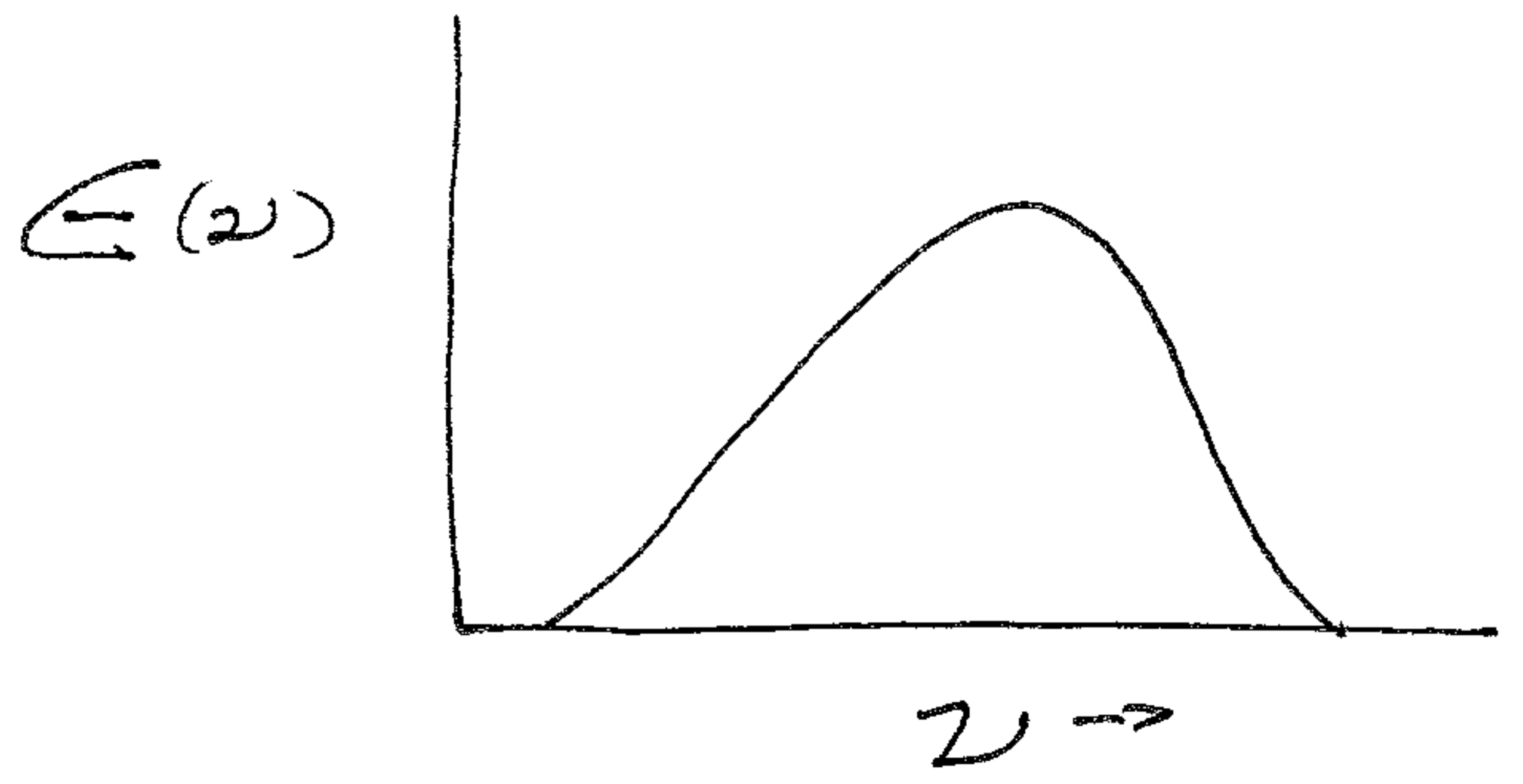
Finding $|\mu_{mn}|^2$ from ϵ

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

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

$$\text{so } B_{\omega} = \frac{4 \times 10^{-19} \epsilon c}{h\nu} = \frac{4\pi |\mu_{mn}|^2}{h^2 \epsilon_0}$$

But typically

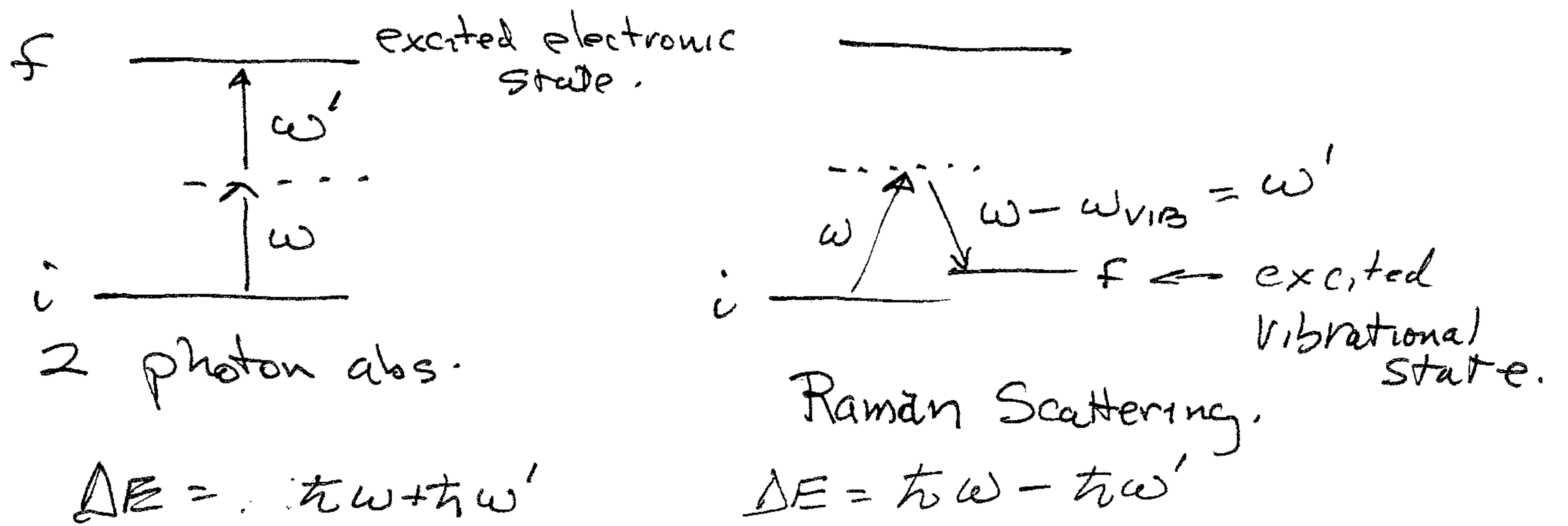


$$\text{so } |\mu_{mn}|^2 \approx \frac{4 \times 10^{-19} c h^2 \epsilon_0}{4\pi h} \int \frac{E(\omega) d\omega}{\omega}$$

$$\approx \frac{4 \times 10^{-19} c h \epsilon_0}{16\pi^3 \bar{\omega}_{ave.}} (\text{Area in } (\text{M}^{-1} \text{cm}^{-1}) \text{cm}^{-1})$$

A "good" problem would be to find the proportionality constant that changes ω into =

MULTI PHOTON ABSORPTION & SCATTERING



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 eigen) 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.

IF $W(t) = W \cos \omega t = \frac{W}{2} (e^{i\omega t} + e^{-i\omega t})$

$$b_k^{(1)}(t'') = \frac{-i}{2\hbar} \int_0^{t''} W_{kg} (e^{i\omega t'} + e^{-i\omega t'}) b_g^{(0)} e^{i\omega_{kg} t'} dt'$$

[we start with $\psi = |g\rangle$ at $t=0$]

At very short times, the "uncertainty" in energy is large, and all states $|k\rangle$ will get amplitude

$$b_k \propto W_{kg} = \mu_{kg}$$

Integrating gives.

$$b_k^{(1)}(t'') = \frac{-i}{2\hbar} W_{kg} \left[\frac{e^{i(\omega_{kg}-\omega)t''} - 1}{\omega_{kg}-\omega} + \frac{e^{i(\omega_{kg}+\omega)t''} - 1}{\omega_{kg}+\omega} \right]$$

2nd order:

$$b_f^{(2)}(t) = \sum_k \frac{-i}{\hbar} \int_0^t W_{fk} (e^{i\omega' t''} + e^{-i\omega' t''}) b_k^{(1)}(t'') e^{i\omega_{fk} t''} dt''$$

$$\begin{aligned}
 {}^{(2)}\psi_f^{(+)} &= \frac{-i}{\hbar} \int_0^t \sum_K W_{fK} \left(e^{i(\omega_{fK} - \omega')t''} + e^{i(\omega_{fK} + \omega')t''} \right) \left(\frac{-1}{2\hbar} \right) \left[\overset{W_{Kg}}{\downarrow} e^{\frac{i(\omega_{Kg} - \omega)t}{\hbar}} + \dots \right] \\
 &= \frac{-i}{2\hbar^2} \int_0^t dt'' \sum_K W_{fK} W_{Kg} \left[\frac{e^{i(\omega_{fK} + \omega_{Kg} - \omega - \omega')t''}}{\omega_{Kg} - \omega} + \dots \right]
 \end{aligned}$$

leads to resonance when $\omega_{fK} + \omega_{Kg} = \omega + \omega'$

$$\omega_{fK} + \omega_{Kg} = \omega_f - \omega_K + \omega_K - \omega_g = \omega_f - \omega_g$$

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

$${}^{(2)}\psi_f^{(+)} \propto \sum_K \left[\frac{W_{fK} W_{Kg}}{\omega_{Kg} - \omega} + \frac{W_{fK} W_{Kg}}{\omega_{Kg} + \omega'} \right]$$

- for 2PA

+ for Raman.

Kramers-Heisenberg-Dirac Formula.