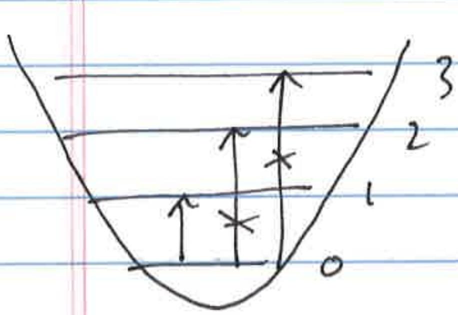
Optics & Spectroscopy — Lecture 14

~ useful example of perturbation theory...

Vibrational Overtones



harmonic oscillator selection rules

$\langle 0|\hat{x}|1\rangle \neq 0$

$\langle 0|\hat{x}|j\rangle = 0 \quad j > 1$

don't expect overtone transitions
(0→2, 0→3, .. not allowed)

~ however, overtones do exist

~ they occur b/c the pot^{l} is not purely harmonic: $\hat{H} = \hat{H}_0 + \hat{H}'$

$\hat{H}_0$: h.o. $\quad$ $\hat{H}'$: perturbation

~ our actual wavefunctions are mixtures of the "zeroth-order" wavefunctions

$$|n\rangle = |n^0\rangle + \sum_{i \neq n} \frac{H'_{in}}{E_n^0 - E_i^0} |i^0\rangle$$

where $H'_{in} = \langle i^0 | \hat{H}' | n^0 \rangle$

$\Rightarrow$ IR selection rule becomes:

$$\langle 0^0 | \hat{x} | n \rangle = \underbrace{\langle 0^0 | \hat{x} | n^0 \rangle}_{\substack{= \\ 0 \text{ for } n \neq 1}} + \langle 0^0 | \hat{x} \sum_{i \neq n} \frac{H'_{in}}{E_n^0 - E_i^0} |i^0\rangle$$

$$= \sum_{i \neq n} \frac{H'_{in}}{E_n^0 - E_i^0} \langle 0^0 | \hat{x} | i^0 \rangle$$

this is only $\neq 0$ for $i = 1$

$$\Rightarrow \langle 0^0 | \hat{x} | n \rangle = \frac{H'_{1n}}{E_n^0 - E_1^0} \langle 0^0 | \hat{x} | 1^0 \rangle$$

~ transition $0^0 \rightarrow n$ becomes allowed by mixing

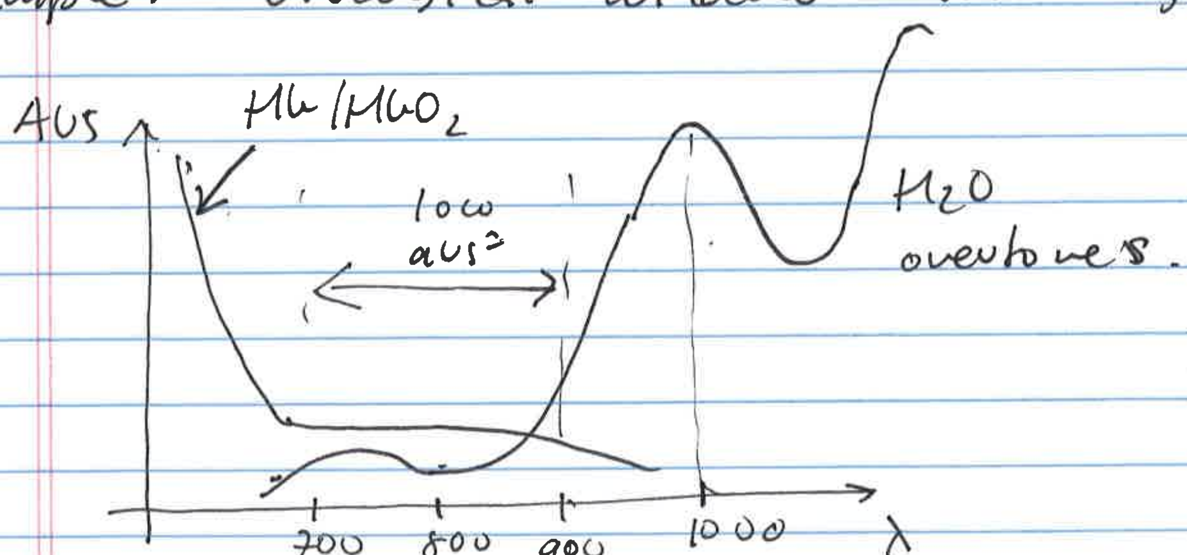
~ perturbation mixes $|n^0\rangle$ w/ all the other levels

~ transitions become allowed through the "$|1^0\rangle$" part of $|n\rangle$

~ mixing decreases as n increases ($E_n^0 - E_1^0$ becomes large)

~ intensity of overtone (transitions) decrease as n increases.

Example: "biological window" for light



Time-dependent S.E.

$$i\hbar \frac{\partial \Psi(\vec{r},t)}{\partial t} = \hat{H}(\vec{r},t)\Psi(\vec{r},t)$$

Dirac Notation: $$i\hbar \frac{\partial |n,t\rangle}{\partial t} = \hat{H}(t)|n,t\rangle$$

if $\hat{H}$ ~ time independent

$$\Rightarrow |n,t\rangle = e^{-iE_n t/\hbar}|n\rangle$$

~ include a time-dependent perturbation

$$\hat{H}(t) = \hat{H} + \hat{V}(t)$$

$$\Rightarrow (\hat{H} + \hat{V}(t))|\Psi(t)\rangle = i\hbar \frac{\partial |\Psi(t)\rangle}{\partial t} \quad \text{—}(*)$$

where $|\Psi(t)\rangle = \sum_n C_n(t)|n,t\rangle$

need to find the coefficients.

$$|n,t\rangle = e^{-iE_n t/\hbar}|n\rangle$$ ← solutions for $\hat{V}(t)=0$

~ solve time-independent S.E.

~ complete basis set

$$|\psi(t)\rangle = \sum_n c_n(t)\, e^{-iE_n t/\hbar}|n\rangle$$

as before: $c_n(t) = \langle n,t|\psi(t)\rangle$

(*) becomes $[\hat{H}+\hat{V}(t)]\sum_n c_n(t)\, e^{-iE_n t/\hbar}|n\rangle$

$$= i\hbar \sum_n \frac{\partial}{\partial t}\left(c_n(t)\, e^{-iE_n t/\hbar}|n\rangle\right)$$

$$\Rightarrow \sum_n c_n(t)\, e^{-iE_n t/\hbar}[E_n+\hat{V}(t)]|n\rangle$$

$$= i\hbar \sum_n \left[\frac{\partial c_n}{\partial t} e^{-iE_n t/\hbar}|n\rangle - \frac{iE_n}{\hbar} c_n(t)\, e^{-iE_n t/\hbar}|n\rangle\right]$$

$$\Rightarrow \sum_n c_n(t)\, e^{-iE_n t/\hbar}\hat{V}(t)|n\rangle$$

$$= i\hbar \sum_n \left[\frac{\partial c_n}{\partial t} e^{-iE_n t/\hbar}|n\rangle\right]$$

→ multiply b.s. by $\langle m|$ from the left

$$\sum_n C_n(t)\, e^{-iE_nt/\hbar} \langle m|\hat{V}(t)|n\rangle$$

$$= i\hbar \sum_n \frac{dC_n(t)}{dt} e^{-iE_nt/\hbar} \langle m|n\rangle$$

only ~~n=m~~ survives

$$\Rightarrow i\hbar \frac{dC_m(t)}{dt} e^{-iE_mt/\hbar} = \sum_n C_n(t)\, e^{-iE_nt/\hbar} \times \langle m|\hat{V}(t)|n\rangle$$

$$\Rightarrow \frac{dC_m(t)}{dt} = -\frac{i}{\hbar} \sum_n C_n(t)\, e^{-i(E_n-E_m)t/\hbar} \times \langle m|\hat{V}(t)|n\rangle$$

$$= -\frac{i}{\hbar} \sum_n C_n(t)\, e^{-i\omega_{nm}t} V_{mn}(t)$$

where $\omega_{nm} = (E_n - E_m)/\hbar$

$$V_{mn}(t) = \langle m|\hat{V}(t)|n\rangle$$

~ an exact, but not very helpful, sol^{n} that expresses the time-dependence of $C_m(t)$ in terms of all the other coefficients.

Weak Field Solution:

~ assume $C_a(0) = 1$

$C_n(0) = 0$ for all $n \neq 0$

all the population is initially in the ground state

$$\Rightarrow \frac{d\,C_m(t)}{dt} = -\frac{i}{\hbar}\, e^{-i\omega_{am}t} \langle m | \hat{V}(t) | a \rangle$$

~ formally integrate:

$$C_m(t) = C_m(0) - \frac{i}{\hbar} \int_0^t dt'\, V_{ma}(t')\, e^{-i\omega_{am}t'}$$

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population in $|m\rangle$ only comes from $|a\rangle$

for $m \neq a$

$$C_m(t) = -\frac{i}{\hbar}\int_0^t dt'\, V_{ma}(t) e^{-i\omega_{am}t'}$$

Note $|C_m|^2$ gives the prob^y of being in $|m\rangle$

~ prob^y of making a transition to $|m\rangle$ from $|a\rangle$ is

$$|C_m(t)|^2 = \frac{1}{\hbar^2}\left|\int_0^t dt'\, V_{ma}(t') e^{-i\omega_{am}t'}\right|^2$$

In spectroscopy: $\hat{V}(t) \propto \vec{E}(t) \cdot \vec{\mu}$

electric field

dipole moment of the molecule

write $\vec{E}(t) = \hat{\varepsilon}\,\frac{E_0}{2}\left[e^{-i\omega t} + e^{i\omega t}\right]$

polarization

amplitude

"Slowly varying amplitude" approximation

$$V_{ma}(t) = \langle m | \hat{\varepsilon} \frac{E_0}{2} (e^{-i\omega t} + c.c.) \cdot \vec{\mu} | a \rangle$$

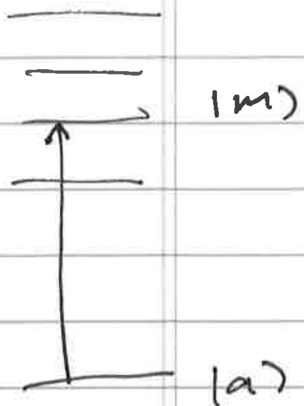
$$= \frac{E_0}{2} (e^{-i\omega t} + c.c.)\, \hat{\varepsilon} \cdot \underbrace{\langle m | \vec{\mu} | a \rangle}_{\substack{\text{transition-dipole} \\ \text{moment} \\ \vec{\mu}_{ma}}}$$

$$|C_m|^2 = \frac{1}{\hbar^2} \left| \int_0^t \frac{E_0}{2} (e^{-i\omega t'} + c.c.) e^{-i\omega_{am} t'} \times \hat{\varepsilon} \cdot \vec{\mu}_{ma} \, dt' \right|^2$$

$$= \frac{I_0}{4} \frac{|\vec{\varepsilon} \cdot \vec{\mu}_{ma}|^2}{\hbar^2} \left| \int_0^t dt' \left[e^{-i(\omega + \omega_{am})t'} + e^{i(\omega - \omega_{am})t'} \right] \right|^2$$

$$= (\quad) \left| \frac{e^{-i(\omega + \omega_{am})t} - 1}{-i(\omega + \omega_{am})} + \frac{e^{i(\omega - \omega_{am})t} - 1}{i(\omega - \omega_{am})} \right|^2$$

one of these is big, other small



$$\omega_{am} = \frac{E_a - E_m}{\hbar} < 0$$

~ write as ω_{ma} in our expression

$$|C_m|^2 = (\quad) \left| \frac{e^{-i(\omega-\omega_{ma})t} - 1}{-i(\omega-\omega_{ma})} + \frac{e^{i(\omega+\omega_{ma})t} - 1}{i(\omega+\omega_{ma})} \right|^2$$

$\omega - \omega_{ma}$ ~ small

$$\frac{1}{\omega-\omega_{ma}} \gg \frac{1}{\omega+\omega_{ma}}$$

$$\Rightarrow |C_m|^2 \simeq \frac{I_0}{4} \frac{|\;|^2}{\hbar^2} \left| \frac{e^{-i(\omega-\omega_{ma})t} - 1}{-i(\omega-\omega_{ma})} \right|^2$$

"Rotating wave" approximation, only take one part of

$$e^{-i\omega t} + e^{i\omega t}$$