SPECTROSCOPY

— Absorption transition
— Emission transition

$$E = h\nu = h\omega = h\frac{c}{\lambda} = h\tilde{\nu}c \text{ , where } \tilde{\nu} = \frac{1}{\lambda} \text{ (in cm}^{-1}\text{), how}$$
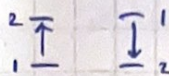many wavelengths fall in one centimeter.

Describing spectroscopic techniques using Q.M.:

Recall that the most general form of Schrödinger's Equation:

$$i\hbar \frac{\partial \Psi}{\partial t} = \hat{\mathcal{H}}\Psi = E\Psi$$

$\underbrace{\qquad}_{TISE}$

For a wave transition b/w 2 states:
$$\Psi_1 \rightarrow \Psi_2$$

For Ψ_1: $i\hbar \frac{\partial \Psi_1}{\partial t} = \hat{\mathcal{H}}\Psi_1$, $\Psi_1(t) = \Psi_1(0)e^{-\frac{i}{\hbar}E_1 t}$

Ψ_2: $i\hbar \frac{\partial \Psi_2}{\partial t} = \hat{\mathcal{H}}\Psi_2$, $\Psi_2(t) = \Psi_2(0)e^{-\frac{i}{\hbar}E_2 t}$

$\left.\begin{array}{l}\end{array}\right\}$ $\underbrace{\quad}_{TPSE}$ How can we force the transition $\Psi_1 \rightarrow \Psi_2$? → Change hamiltonian.

"Unperturbed hamiltonian" - before any force is applied to system.

Changing the hamiltonian involves applying some force, such that at $\Delta t = 0$, $\hat{\mathcal{H}}_o = \hat{\mathcal{H}}$

and at $\Delta t > 0$, $\hat{\mathcal{H}}_o + \hat{\mathcal{H}}_{int}(t) = \hat{\mathcal{H}}$ (total hamiltonian)

Force applied on system, interaction hamiltonian. → Note that this term is time-dependent!

$$\hat{\mathcal{H}}_o = \hat{R} + \hat{U}_o = \hat{\mathcal{H}} \text{ , and } \hat{\mathcal{H}}_o + \hat{\mathcal{H}}_{int}(t) = \hat{\mathcal{H}}$$

It follows that
$$-i\hbar \frac{\partial \Psi_1}{\partial t} = \hat{\mathcal{H}}_o \Psi_1 \text{ and } -i\hbar \frac{\partial \Psi_2}{\partial t} = \hat{\mathcal{H}}_o \Psi_2.$$

The terms may be written as a linear combination:
$$\Psi = b_1(t)\Psi_1(t) + b_2(t)\Psi_2(t) + ...$$
Ψ_1: $b_1(t) = 1$, $b_2(t) = 0$, $b_3(t) = 0$, ...
Ψ_2: $b_2(t) = 1$, $b_1(t) = 0$, $b_3(t) = 0$, ...

Since the coefficients are representation of the probabilities. We need to find a way to make b_2 nonzero and $b_1 = 0$ for $\Psi_1 \rightarrow \Psi_2$ after a perturbation.

$$\Psi = b_1\Psi_1(t) + b_2\Psi_2(t) + ... \rightarrow \text{TDSE}:$$
$$i\hbar \frac{\partial \Psi}{\partial t} = \hat{\mathcal{H}}\Psi \text{ when } \cancel{\Delta t}$$
$$\Psi = b_1(t)\Psi_1(t) + b_2(t)\Psi_2(t)$$
(Ignore all terms except $b_1\Psi_1$ & $b_2\Psi_2$)

$$= i\hbar \left[(\frac{d}{dt}b_1(t))\Psi_1(t) + b_1(t)\frac{d}{dt}\Psi_1(t) + \frac{d}{dt}b_2(t)\Psi_2(t) + b_2(t)\frac{d}{dt}(\Psi_2 t)\right]$$
$$= \underbrace{b_1\hat{\mathcal{H}}_o\Psi_1 + b_2\hat{\mathcal{H}}_o\Psi_2}_{\text{Unperturbed}} + \underbrace{b_1\hat{\mathcal{H}}_{int}\Psi_1 + b_2\hat{\mathcal{H}}_{int}\Psi_2}_{\text{Perturbed}}$$

Since $b_1(t)\frac{\partial}{\partial t}\Psi_1(t) = b_1\hat{\mathcal{H}}_o\Psi_1$ and $b_2(t)\frac{\partial}{\partial t}\Psi_2(t) = b_2\hat{\mathcal{H}}_o\Psi_2$, then we can state

$$i\hbar\Psi_1\frac{db_1}{dt} + i\hbar\Psi_2\frac{db_2}{dt} = b_1\hat{\mathcal{H}}_{int}\Psi_1 + b_2\hat{\mathcal{H}}_{int}\Psi_2$$

$\cdot \int \Psi_2^* dx$ (to eliminate $i\hbar\Psi_1\frac{db_1}{dt}$

$$i\hbar\frac{db_2}{dt} = b_1 \int \Psi_2^* \hat{\mathcal{H}}_{int}\Psi_1 dx + b_2 \int \Psi_2^* \hat{\mathcal{H}}_{int}\Psi_2 dx$$

For the initial state, $b_1 = 1$, $b_2 = 0$.
$\therefore b_2 \int \Psi_2^* \hat{\mathcal{H}}_{int}\Psi_2 dx = 0$

Therefore, $i\hbar\frac{db_2}{dt} = \int \Psi_2^* \hat{\mathcal{H}}_{int}\Psi_1 dx$,

$~~~~~~~~~~~~~~~~~~~$ ~~$\frac{d}{dt}\Psi\Psi_2^*$~~

$$b_2(t) = \frac{1}{i\hbar}\int dt \int \Psi_2^* \hat{\mathcal{H}}_{int}\Psi_1 dx, ~~~ \hat{\mathcal{H}}_{int}(t) = \hat{U}_{int}\cdot\cos\omega t$$

$$\therefore b_2(t) = \frac{1}{i\hbar}\iint \Psi_2^*\hat{\mathcal{H}}_{int}\Psi_1 dx dt$$

In order for $b_2(t) \neq 0$, both the time dependent and the time independent terms must not $= 0$.

$\left(\begin{array}{l} b_2(t) = \frac{1}{i\hbar}\int \Psi_2^*(0)U_{int}\Psi_1(0)dx \cdot \int_0^t e^{i\frac{E_2}{\hbar}t}e^{-i\frac{E_1}{\hbar}t}\cos\omega t\, dt \end{array}\right.$

$\underbrace{\qquad\qquad\qquad}_{\text{Time independent terms: does not depend on operator}}$ $\underbrace{\qquad\qquad\qquad}_{\text{Time dependent terms: depend on operator.}}$

Focusing on $\int_0^t e^{i\frac{E_2}{\hbar}t} e^{-i\frac{E_1}{\hbar}t} \cos\omega t \, dt$, how can we make this term $\neq 0$?

$\Delta E = E_2 - E_1$, so $\int_0^t e^{i\frac{E_2}{\hbar}t} e^{-i\frac{E_1}{\hbar}t} \cos\omega t \, dt = \frac{1}{2}\int_0^t e^{i\left(\frac{\Delta E + \hbar\omega}{\hbar}\right)t} + e^{i\left(\frac{\Delta E - \hbar\omega}{\hbar}\right)t} \, dt$

$\hookrightarrow \frac{1}{2}(e^{i\omega t} + e^{-i\omega t})$

$= \int_0^t e^{i\left(\frac{\Delta E - \hbar\omega}{\hbar}\right)t} \, dt = \frac{e^{i\left(\frac{\Delta E - \hbar\omega}{\hbar}\right)t} - 1}{i\left(\frac{\Delta E - \hbar\omega}{\hbar}\right)} = \frac{e^{iat} - 1}{ia}$, where $a = \frac{\Delta E - \hbar\omega}{\hbar}$.

$e^{i\frac{a}{2}t} \cdot \frac{e^{i\frac{a}{2}t} - e^{-i\frac{a}{2}t}}{2ia/2} = 2e^{i\frac{a}{2}t}\left(\frac{\sin(a/2)t}{a/2}\right)$. Relating back to $|b_2|^2$, we find that

$|b_2|^2 = \frac{1}{\hbar^2}\left|\int \Psi_2^* \hat{U}_{int} \Psi_1 \, dx\right|^2 \cdot \frac{1}{4}\left(\frac{\sin\left(\left(\frac{\Delta E - \hbar\omega}{2\hbar}\right)t\right)}{\frac{\Delta E - \hbar\omega}{2\hbar}}\right)^2$, let $\beta = \frac{\Delta E - \hbar\omega}{2\hbar}$, so $\frac{\sin\beta t}{\beta}$ may

be estimated using l'Hôpital's:
  • As β increases, frequency of oscillation increases but the amplitude decreases → lower probability (not useful)
  • As β decreases, frequency of oscillation decreases, the amplitude increases.
$\lim_{\beta \to 0} \frac{\sin\beta t}{\beta} \longrightarrow t$. For energy transition, the energy must be conserved in $\Delta E = \hbar\omega$
$\hookrightarrow$ Therefore for any meaningful term in probability, $\beta = 0$ $\quad \sin\left(\frac{\Delta E - \hbar\omega}{2\hbar}\right) = 0$

"Fermi Golden Rule" - Finding the transition and energy per unit time, is:

$$\approx \quad W = \frac{2\pi}{\hbar}\rho(\Delta E) \cdot \left|\int \Psi_2^* \hat{U}_{int} \Psi_1 \, dx\right|^2$$
$\hookrightarrow$(Probability density) $\quad \hookrightarrow$ if $\hat{U}_{int}\Psi_1 = \lambda\Psi_1$, then $\lambda\int \Psi_2^* \Psi_1 \, dx = 0$.

Therefore, the value of $\hat{U}_{int}\Psi_1$ should NOT result in an eigenfunction of Ψ_1. Specifically, $\hat{U}_{int}\Psi_1 = \Psi_2 = b_1\Psi_1 + b_2\Psi_2 + \ldots$, since $\hat{U}_{int}\Psi_1 = \lambda\Psi_1$ would result in $\left|\int \Psi_2^* \hat{U}_{int}\Psi_1 \, dx\right|^2 = 0$. How can we make sure that this is not the case?
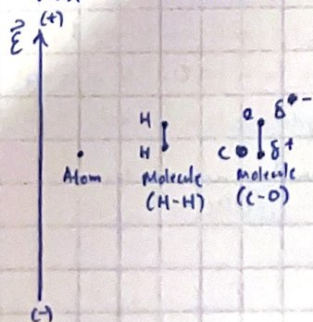
(An aside - introduction to different types of spectroscopy):
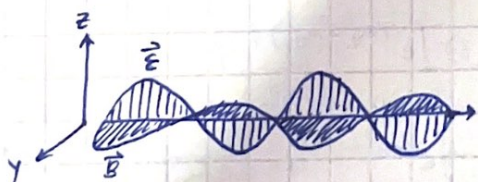
$\vec{E}$ = electric field
$\vec{B}$ = magnetic field

What happens when we place an atom in an electric field?
What about a molecule?

- Depends on the molecule:
a molecule with no net dipole, such as H–H, will not react. However, C–O will begin to orient: The dipole moment between C and O should be considered.

Physics of Interaction	Designation	λ
Electronic Transition	UV/Vis Spectroscopy	UV: $\lambda < 400$nm Vis: $400\mu < \lambda < 750$nm
Vibrational States	Infrared Spectroscopy	$750 < \lambda < 1\mu m$
Rotational States	Microwave Spectroscopy	$1mm < \lambda < 10$cm
Electron spin Electron orbital (EPR, ESR) Resonance	Microwave Spectroscopy	,,
Nuclear magnetic Resonance	Radio Frequencies	$\lambda > 10$cm

The dipole moment of a molecule, defined as $\vec{\mu}$, is related to the charge of the particles and the distance between the particles:
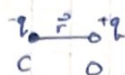
$$\underset{C}{q_\bullet} \vec{r} \underset{O}{\overset{+q}{\bullet}} \qquad \vec{\mu} = q\vec{r}.$$

The potential is related to the electric field:

$$U = -\vec{E} \cdot \vec{\mu}$$

Rotations and vibrations are caused by a molecule's interaction with $\vec{E}$. These interactions cause a dipole moment which may then be measured through spectroscopy. Let us consider both of these interactions for spectroscopy:

→ Rotations - energy associated with rotational motion is quantized, where

$$E_r = \frac{\hbar^2}{2I} \ell(\ell+1), \text{ where } \ell = 0, 1, 2, \ldots \qquad \text{and } I = \mu r^2.$$
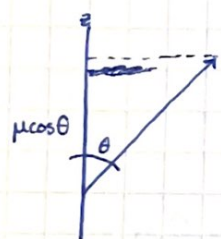
In spectroscopy, ℓ is synonomous with J (Just to make things confusing lol) We can modify the equation:

$$E_J = hc \frac{\hbar^2}{2Ihc} J(J+1), \text{ where } \frac{\hbar^2}{2Ihc} = B, \text{ the rotational constant. Then}$$

$$E_J = hcB J(J+1), \quad \psi_{J,m_J}(\theta, \phi) = T_{J,m_J}(\theta) e^{-im_J\phi}$$

$\hookrightarrow$ Normalization coefficient

If we consider that $\left| \int \psi_2^* \hat{U}_{int} \psi_1 dx \right|^2$, then for this case

$$\vec{E} \int \psi_2^* \vec{\mu} \psi_1 dx = \vec{E} \vec{\mu}_{2,1}. \text{ If } U = -\vec{E} \cdot \vec{\mu}, \text{ then } U = -[E_z\mu_z + E_x\mu_x + E_y\mu_y]$$

We are interested in the transition from $J_1 \to J_2^\circ$.

The dipole moment, $\mu_{21} = \int T_{J_2,m_{J_2}}(\theta) \cos\theta T_{J_1,m_{J_1}}(\theta) \underbrace{\sin\theta d\theta}_{\text{Jacobian}}$ since the wave functions are multiplicative.

$\underbrace{}_{\text{Assumes } \theta \text{ is along } Z.}$

θ represents the angle between the bond of the molecule and the field.

$\mu\cos\theta$, θ

Refining this statement to include ϕ, we get:

$$\mu_{2,1} = \langle \mu_i \rangle \int T_{J_2,m_{J_2}}(\theta) \cos\theta T_{J_1, m_{J_1}}(\theta) \sin\theta d\theta \int e^{i(m_{J_1} - m_{J_2})\phi} d\phi$$

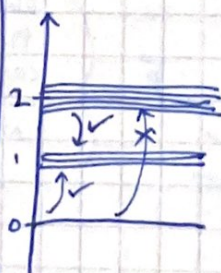From the dipole moment $\uparrow$ $\mu_{2,1} \neq 0$. In order for this to be true:

1) $\mu \neq 0$:

Molecules which do not have a net dipole cannot be measured: these are microwave inactive.

Ex.) H_2, N_2, O_2, etc.

2) $\int T_{J_2,m_{J_2}}(\theta)\cos\theta T_{J_1,m_{J_1}}(\theta)\sin\theta d\theta \neq 0$

This can only be the case when $J = J \pm 1$, or $\Delta J = \pm 1$. This is to say, the transition $J=0 \to J=2$ is impossible:

$2 \underline{\qquad}$

$\underset{1}{2\nu} \quad *$

$\underset{0}{\nu}$

3) $\int e^{i(m_{J_1} - m_{J_2})\phi} d\phi \neq 0$

This is only the case when $m_J = m_J'$:

$$\int e^{i(m_{J_1}-m_{J_2})\phi} d\phi = \frac{1}{i(m_{J_1}-m_{J_2})}\left(e^{i(m_{J_1}-m_{J_2})2\pi}\right)$$

Since m_{J_1} and m_{J_2} are both integers, Δm_J must also be an integer. Then, $e^{i2\pi n}$, where $n = 1, 2, 3, \ldots$ would result in $=1$, which makes the entire term $=0$. If $m_J = m_J'$, however, l'hôpital's rule is invoked,

$$\frac{e^0 - 1}{i(0)}, \text{ and a nonzero term results.}$$

So far, just $E_z \mu_z$ has been considered. What about $E_x \mu_x$?
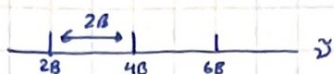
$$E_x \mu_x = E_x \mu \sin\theta \cos\theta$$

$$\underbrace{\frac{e^{i\phi}, e^{-i\phi}}{2}} \rightarrow e^{i(m_{J_i} - m_{J_a} \mp \pm 1)2\pi} - 1 . \quad \text{In this case,} \quad \Delta m_J = 0, \pm 1 , \text{ and}$$

a transition between different rotational states of each J is possible:
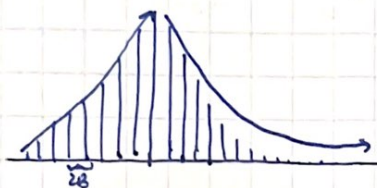

For $J \rightarrow J' = J+1$,

$$\Delta E = E_{J+1} - E_J = hcB[(J+1)(J+2) - J(J+1)] = 2hcB(J+1) = hc\tilde{\nu}, \text{ where } \tilde{\nu} = 2B(J+1)$$

If $J = 0$, then $\tilde{\nu} = 2B$. The transition between $J = 0$ to $J = 1$ results in a peak at $2B$.

Given this relationship, $\tilde{\nu} = 2B = \frac{2h^2}{2\mu r^2}\frac{1}{hc}$, the bond length may be calculated if μ is known.

In actuality, however, the intensity is not the same:

- The number of transitions increases as $(2J+1)3$, where J is the base level.
$$J_0 \rightarrow J_1 = 3 \text{ transitions}$$
$$J_1 \rightarrow J_2 = 9 \text{ transitions}$$

The intensity of the peaks is determined by the number of interacting photons, and since this term is related as $Ne^{-\frac{kBJ(J+1)}{kT}}$, the intensity tapers down after reaching a peak.
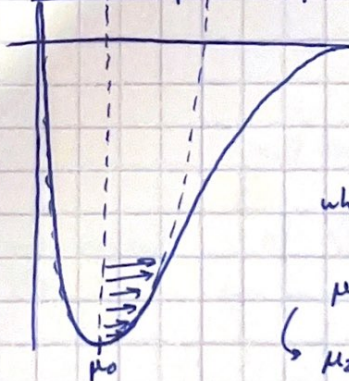
Another note on microwave activity:
Molecules with >2 atoms are generally microwave active, unless there is very specific symmetry in the molecule. For example,

CO_2 O=C=O   microwave inactive

CH_4 microwave inactive

$H_2O + \delta$ microwave ACTIVE

Vibrational Spectroscopy:

Recall that
$$E_{HO} = h\nu(n+\tfrac{1}{2})$$
$$\psi_n = A_n H_n(x\sqrt{a})e^{-\frac{ax^2}{2}}$$

If we consider the transition from $n \rightarrow n'$, what happens to $U = -E_z\mu_z = -E_z\mu_z\cos\theta$?

$$\mu_{z,1} = \mu \int_{-\infty}^{\infty} \psi_{n'}(x) \cancel{\text{...}} \cos\theta \psi_n(x) dx$$

$$\rightarrow \mu_{z,1} = \mu\cos\theta \int_{-\infty}^{\infty} \psi_{n'}(x)\psi_n(x) dx$$

$$\underbrace{\qquad\qquad}_{=0} \rightarrow \text{Therefore, a permanent dipole is not sufficient for vibrational motion to be detected.}$$

In an actual molecule, there is both rotational & vibrational motion:

$$E_z \cdot \underbrace{(\mu_0 + \delta\mu(x))}\cos\theta$$
$$\underbrace{\qquad}_{\text{Vibrational}} \rightarrow \text{Rotational property}$$

Property depending on x, estimated: $\mu = \mu_0 + \frac{d\mu}{dx}\Big|_{eq}\cdot x + \underbrace{\frac{d^2\mu}{dx^2}\Big|_{eq}x^2 + ...}_{\text{Ignored terms}}$

$\underbrace{\qquad}_{\text{Estimation is linear, meaning } \Delta n = \pm 1.}$

Remember that
$$\psi = \underbrace{\psi_n(x)}_{\text{Vibrational}} \cdot \underbrace{Y_{J,m_J}(\theta,\phi)}_{\text{Rotational}}$$

If we represent the dipole moment with J and m_J considered, we get:

$$\mu_{J,m_J} = \int \psi^* \mu \psi d... \text{ (Rotational terms)} \qquad \text{We can separate this integral to receive:}$$
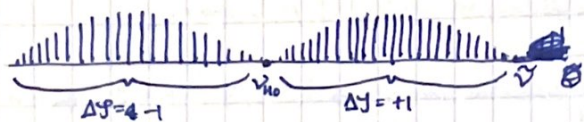
$$\int \psi^* \mu \psi \, d\ldots \longrightarrow \mu_0 \underbrace{\int \psi_{n1} \cdot \psi_n \, dx}_{\Delta n = 0} \underbrace{\iint \psi^*_{\cos\theta} \psi \sin\theta \, d\theta \, d\phi}_{\Delta J = \pm 1} + \underbrace{\int \psi_{n1} \delta\mu(x) \psi_n \, dx}_{\Delta n = \pm 1} \underbrace{\iint Y^*_{\cos\theta} \psi \sin\theta \, d\theta \, d\phi}_{\Delta J = \pm 1}$$

(From)

$E_z \cdot (\mu_0 + \delta\mu(x))\cos\theta$

The result of this integration tells us that we cannot jump from, say $n=0$, $J=0$ to $n=1$, $J=0$, as this kind of transition induces no change in J (i.e. $\Delta J = 0$) which is physically impossible as seen from the equation.

Resultantly, the spectroscopy of this would appear as such:

$\Delta J = -1$ ν_{no} $\Delta J = +1$

Raman Spectroscopy - Detection of molecules such as N_2, depends on scattering effects:

$\rightarrow \Delta E = 0$: "Elastic scattering"

$\rightarrow \Delta E \neq 0$: "Inelastic scattering"