

Semi-Classical Treatment of Matter-Light Interaction
 Light Electromagnetic radiation
 Electric field $\mathcal{E}$ is taken into consideration

Let us consider $\Psi(x, y, z, t) = \psi(x, y, z) \phi(t) = \psi \cdot \phi$

$$\hat{H}^{(0)} = -\frac{\hbar^2}{2m} \nabla^2 + V(x, y, z)$$

Time Independent

$$\hat{H}^{(0)} \Psi = -\frac{\hbar}{i} \frac{\partial}{\partial t} \Psi$$

$$\hat{H}^{(0)} [\psi \phi] = -\frac{\hbar}{i} \frac{\partial}{\partial t} [\psi \phi]$$

$$\phi \hat{H}^{(0)} \psi = \left[\frac{\hbar}{i} \frac{\partial \phi}{\partial t} \right] \psi$$

$$[\div \psi \phi] \Rightarrow \frac{\hat{H}^{(0)} \psi}{\psi} = \left[-\frac{\hbar}{i} \frac{\partial \phi}{\partial t} \right] / \phi$$

$$\Rightarrow -\frac{\hbar}{i} \frac{\partial \phi}{\partial t} = \frac{E \psi}{\psi} \cdot \phi$$

$$\Rightarrow \frac{\partial \phi}{\partial t} = -\frac{i E \phi}{\hbar}$$

$$\boxed{\phi = e^{-i E t / \hbar}}$$

$$\text{So, } \Psi = \psi e^{-i E t / \hbar}$$

Spectroscopy means transition from one state to the other.

One photon rule: one photon brings about only one transition.

A single photon interacts with only one molecule in a chemical reaction.

E_m — Ψ_m Two level system

Superposition of mixing of states

E_L — Ψ_L

$$\Psi = C_L \Psi_L + C_m \Psi_m$$

Mixing coefficients C_L, C_m

At $t \rightarrow 0$, $C_L = 1$, $C_m = 0$

No light, $t=0$, $\hat{H} = \hat{H}^{(0)}$, $\Psi = \Psi_L$

In presence of light, $\hat{H} = \hat{H}^{(0)} + \hat{H}^{(1)}$, $\Psi = C_L \Psi_L + C_m \Psi_m$

$$\hat{H} = -\mu x E x$$

We are considering that it is an electrostatic interaction of electric field and electric dipole. We limit to only one axis.

$$E_x = 2 E_x^0 \cos(2\pi \nu t), \nu = \text{frequency}.$$

$$[\hat{H}^{(0)} + \hat{H}^{(1)}] \Psi = -\frac{\hbar}{i} \frac{\partial}{\partial t} \Psi$$

$$[\hat{H}^{(0)} + \hat{H}^{(1)}] [C_L \Psi_L + C_m \Psi_m] = -\frac{\hbar}{i} \frac{\partial}{\partial t} [C_L \Psi_L + C_m \Psi_m]$$

$$\Rightarrow C_L \hat{H}^{(0)} \Psi_L + C_m \hat{H}^{(0)} \Psi_m + C_L \hat{H}^{(1)} \Psi_L + C_m \hat{H}^{(1)} \Psi_m = -\frac{\hbar}{i} \frac{\partial}{\partial t} [C_L \Psi_L + C_m \Psi_m]$$

$$= -\frac{\hbar}{i} \left[C_L \frac{\partial \Psi_L}{\partial t} + \frac{\partial C_L}{\partial t} \Psi_L + C_m \frac{\partial \Psi_m}{\partial t} + \frac{\partial C_m}{\partial t} \Psi_m \right]$$

$$C_L \hat{H}^{(1)} \Psi_L + C_m \hat{H}^{(1)} \Psi_m = -\frac{\hbar}{i} \left[\frac{\partial C_L}{\partial t} \Psi_L + \frac{\partial C_m}{\partial t} \Psi_m \right]$$

Now, multiply with Ψ_m^*

$$C_L \langle \Psi_m | \hat{H}^{(1)} | \Psi_L \rangle + C_m \langle \Psi_m | \hat{H}^{(1)} | \Psi_m \rangle = -\frac{\hbar}{i} \frac{\partial C_m}{\partial t}$$

$$\frac{\partial C_m}{\partial t} = -\frac{i}{\hbar} \langle \Psi_m | \hat{H}^{(1)} | \Psi_L \rangle$$

$$= -\frac{i}{\hbar} \langle \Psi_m | \hat{H}^{(1)} | \Psi_L \rangle \exp \left[\frac{i(E_m - E_L)t}{\hbar} \right] \exp \left[\frac{2\pi i(E_m - E_L)t}{\hbar} \right]$$

$$\underline{\hat{H} = \hat{H}^{(0)} + \hat{H}^{(1)}} \quad \hat{H}^{(1)} = -\mu_x E_x \quad E_x = 2E_2^0 \cos 2\pi \nu t$$

$$= -\mu_x E_2^0 (\cos 2\pi \nu t)$$

$$\hat{H}^{(1)} = -\mu_x \cdot 2 \cdot E_2^0 \cdot \frac{1}{2} \left[\exp(2\pi i \nu t) + \exp(-2\pi i \nu t) \right]$$

$$= -\mu_x E_2^0 \left[\exp(2\pi i \nu t) + \exp(-2\pi i \nu t) \right]$$

$$= -\mu_x E_2^0 \left[\exp\left(\frac{2\pi i \hbar \nu t}{\hbar}\right) + \exp\left(-\frac{2\pi i \hbar \nu t}{\hbar}\right) \right]$$

$$\frac{\partial C_m}{\partial t} = i E_2^0 \langle \Psi_m | \mu_x | \Psi_L \rangle \left[\exp\left\{ \frac{2\pi i(E_m - E_L + \hbar \nu)t}{\hbar} \right\} + \exp\left\{ \frac{2\pi i(E_m - E_L - \hbar \nu)t}{\hbar} \right\} \right]$$

$$\hat{H}^{(1)} = -\mu_x E_x$$

dipole moment
of the molecule

The amplitude of the electric
field

$$E_x = \underbrace{2 E_x^0}_{\text{Maximum amplitude of the electric field}} \cos 2\pi \underbrace{\nu}_{\text{frequency of radiation}} t$$

The interaction between
a dipole moment and
electric field gives the
perturbing
potential.

$$\frac{dC_m}{dt} = + \frac{i E_x^0}{\hbar} \langle \psi_m | \mu_x | \psi_L \rangle \left[\exp \left\{ \frac{2\pi i}{\hbar} (E_m - E_L + h\nu) t \right\} + \exp \left\{ \frac{2\pi i}{\hbar} (E_m - E_L - h\nu) t \right\} \right]$$

$$C_m = \frac{i E_x^0}{\hbar} \langle \psi_m | \mu_x | \psi_L \rangle \left[\frac{1 - \exp \frac{2\pi i}{\hbar} (E_m - E_L + h\nu) t}{\frac{2\pi i}{\hbar} (E_m - E_L + h\nu)} + \frac{1 - \exp \frac{2\pi i}{\hbar} (E_m - E_L - h\nu) t}{\frac{2\pi i}{\hbar} (E_m - E_L - h\nu)} \right]$$

$$= E_x^0 \langle \psi_m | \mu_x | \psi_L \rangle \left[\frac{1 - \exp \left\{ \frac{2\pi i}{\hbar} (E_m - E_L + h\nu) t \right\}}{E_m - E_L + h\nu} + \frac{1 - \exp \left\{ \frac{2\pi i}{\hbar} (E_m - E_L - h\nu) t \right\}}{E_m - E_L - h\nu} \right]$$

For absorption,

$$E_m - E_L \approx h\nu$$

Emission,

$$E_m - E_L \approx -h\nu$$

so this term becomes
significant

this term significant

$$C_m = \langle \psi_m | \mu_x | \psi_L \rangle \left[\frac{1 - \exp \left\{ \frac{2\pi i}{\hbar} (E_m - E_L - h\nu) t \right\}}{E_m - E_L - h\nu} \right]$$

The probability of a system existing in a given state having a wavefn ψ is proportional to $\psi^* \psi$.

$$\int \psi^* \psi dz = \int (C_l^* \psi_l^* + C_m^* \psi_m^*) (C_l \psi_l + C_m \psi_m) dz$$

$$= C_l^* C_l + C_m^* C_m$$

$$C_m = \frac{\pi t}{h} E_2^0 \langle \psi_m | \mu_x | \psi_l \rangle \left[\frac{1 - \exp \left\{ \frac{2\pi i}{h} (E_m - E_l - h\nu) t \right\}}{\pi (E_m - E_l - h\nu) \cdot t} \right]$$

$$= \frac{\pi t}{h} E_2^0 \langle \psi_m | \mu_x | \psi_l \rangle \left[\frac{1 - \exp i2A}{A} \right]$$

$$C_m^* C_m = \frac{\pi^2 t^2}{h^2} E_2^0 \langle \psi_m | \mu_x | \psi_l \rangle^2 \left[\frac{2 - e^{-i2A} - e^{i2A}}{A^2} \right]$$

Euler

$$e^{\pm iy} = \cos y \pm i \sin y$$

$$= \frac{\pi^2 t^2}{h^2} E_2^0 \langle \psi_m | \mu_x | \psi_l \rangle^2 \left[\frac{2 - \cos 2A + i \sin 2A - \cos 2A - i \sin 2A}{A^2} \right]$$

$$= \frac{\pi^2 t^2}{h^2} E_2^0 \langle \psi_m | \mu_x | \psi_l \rangle^2 \left[\frac{2 - 2(1 - \sin^2 A)}{A^2} \right]$$

$$= \frac{\pi^2 t^2}{h^2} E_2^0 \langle \psi_m | \mu_x | \psi_l \rangle^2 \left[\frac{\sin^2 A}{A^2} \right]$$

Natural Line width

- 1) Collision broadening
- 2) Doppler broadening
- 3) Heisenberg uncertainty principle

$$\Delta E \times \Delta t \simeq \frac{h}{2} = \frac{h}{4\pi} \quad 10^{-34} \text{ JS}$$

$$\delta \nu = \frac{\delta E}{h} \simeq \frac{h}{4\pi h \delta t} \simeq \frac{1}{2\pi \delta t}$$

excited electronic state lifetime 10^{-8} s .

$$\delta \nu \simeq 10^8 \text{ Hz}$$

Usual radiation frequency $10^{14} - 10^{16}$

electronic spin state lifetime 10^{-7} s

$$\delta \nu \simeq 10^7 \text{ Hz}$$

Usual radiation frequency $10^8 - 10^9 \text{ Hz}$

Intensity of spectral lines

- 1) Transition probability
- 2) Population of states
- 3) Path length of sample

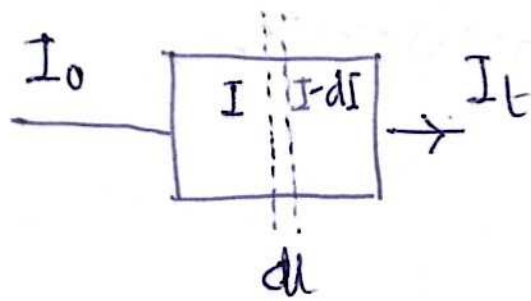
$$\frac{I}{I_0} = e^{-\epsilon \cdot c \cdot l}$$

Beer-Lambert Law

Molecular Spectroscopy

Absorption spectroscopy: Absorbance $A = \log \frac{I_0}{I_t}$

Emission spectroscopy: Emission quantum yield $= \frac{I_{em}}{I_{abs}} = \phi_{em}$



$$-dI \propto I, c, dl$$

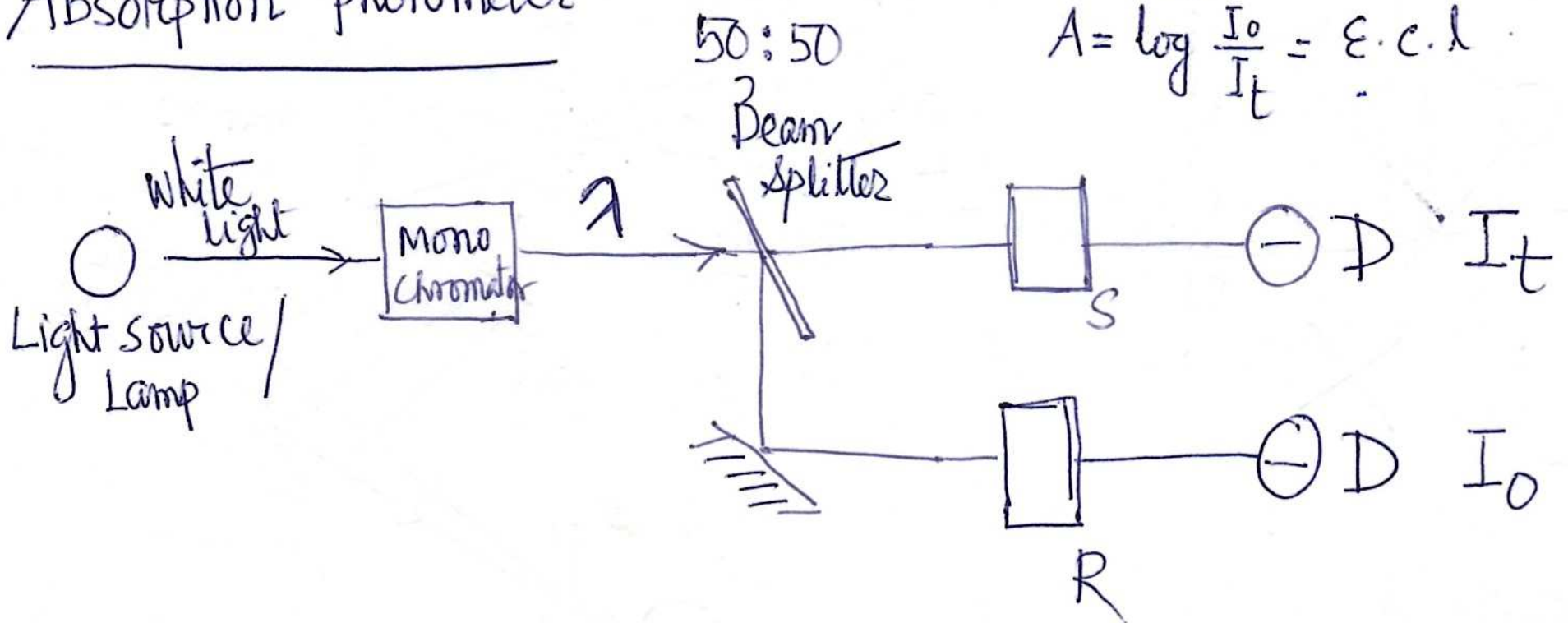
$$-dI = a \cdot I \cdot c \cdot dl$$

$$-\frac{dI}{I} = a \cdot c \cdot dl \Rightarrow \int_{I_t}^{I_0} \frac{dI}{I} = a \cdot c \cdot \int_0^l dl$$

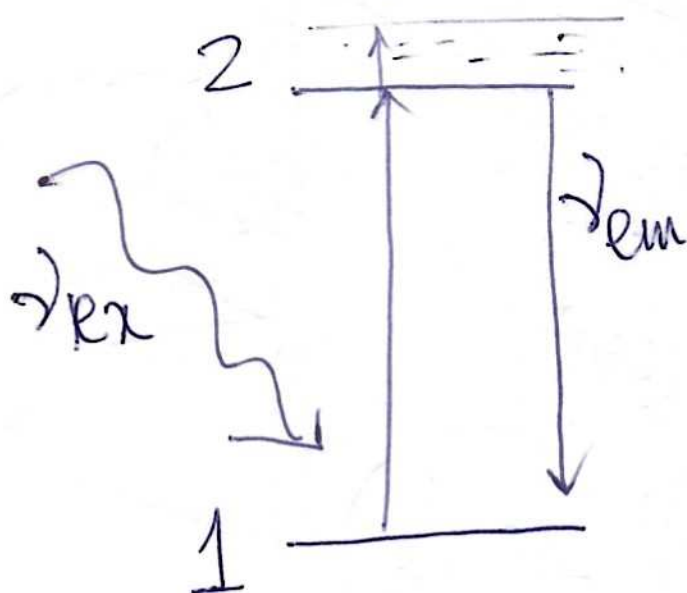
$$\ln \frac{I_0}{I_t} = a \cdot c \cdot l$$

$$A = \log \frac{I_0}{I_t} = \epsilon \cdot c \cdot l$$

Absorption photometer

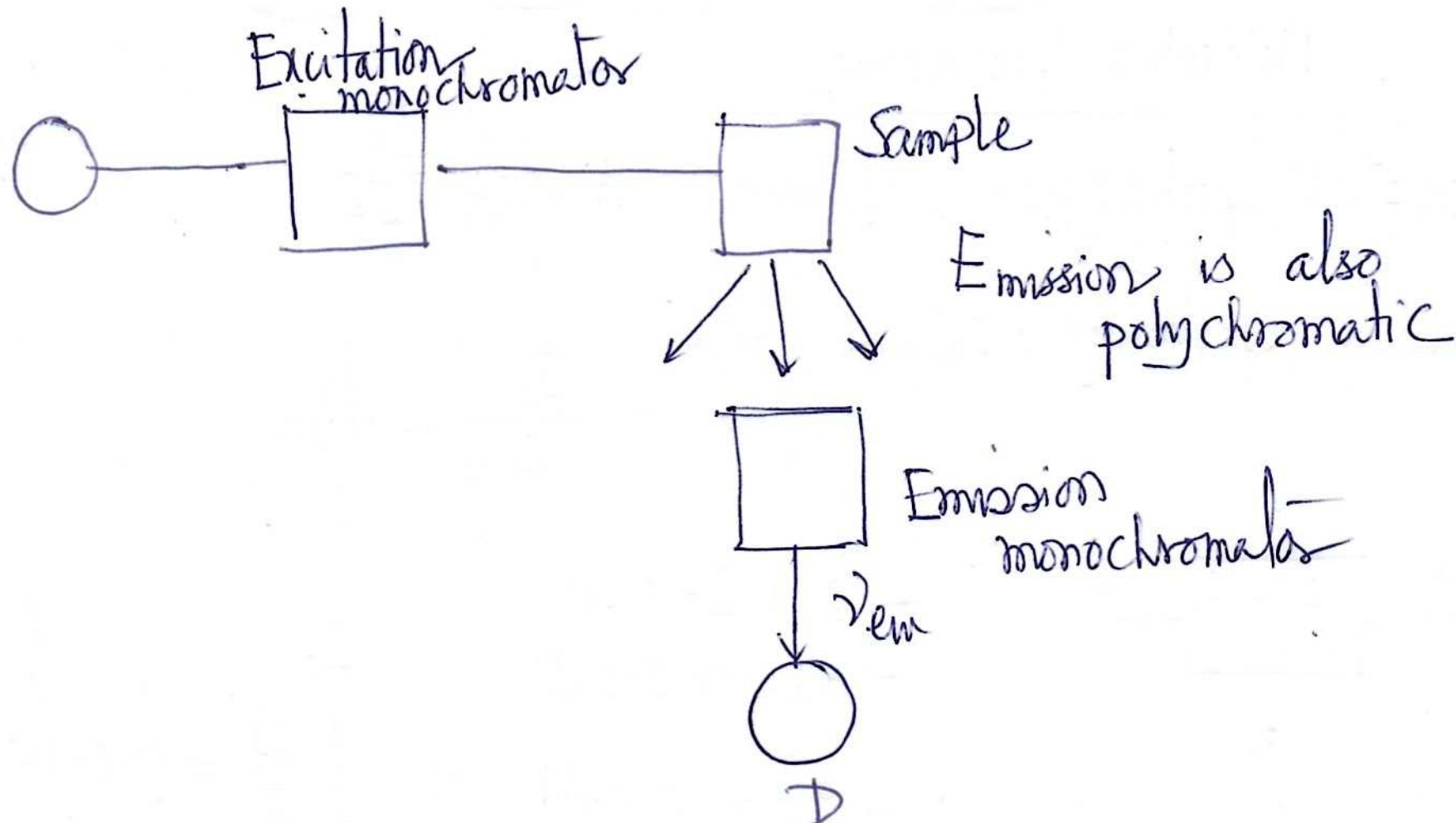


Emission photometer

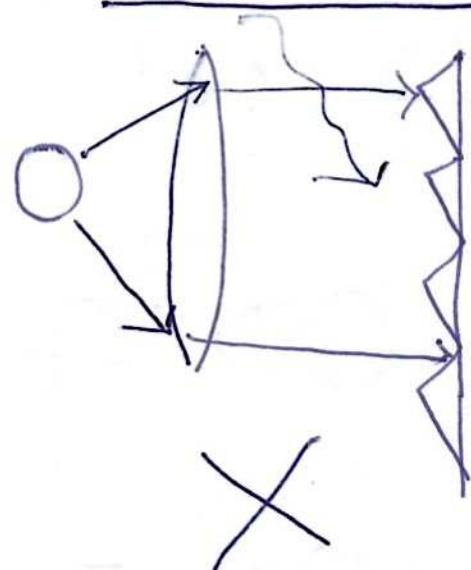


Generally λ_{ex} & λ_{em} are different
 λ_{ex} should be chosen in such a way that the sample is excited from state 1 to state 2.

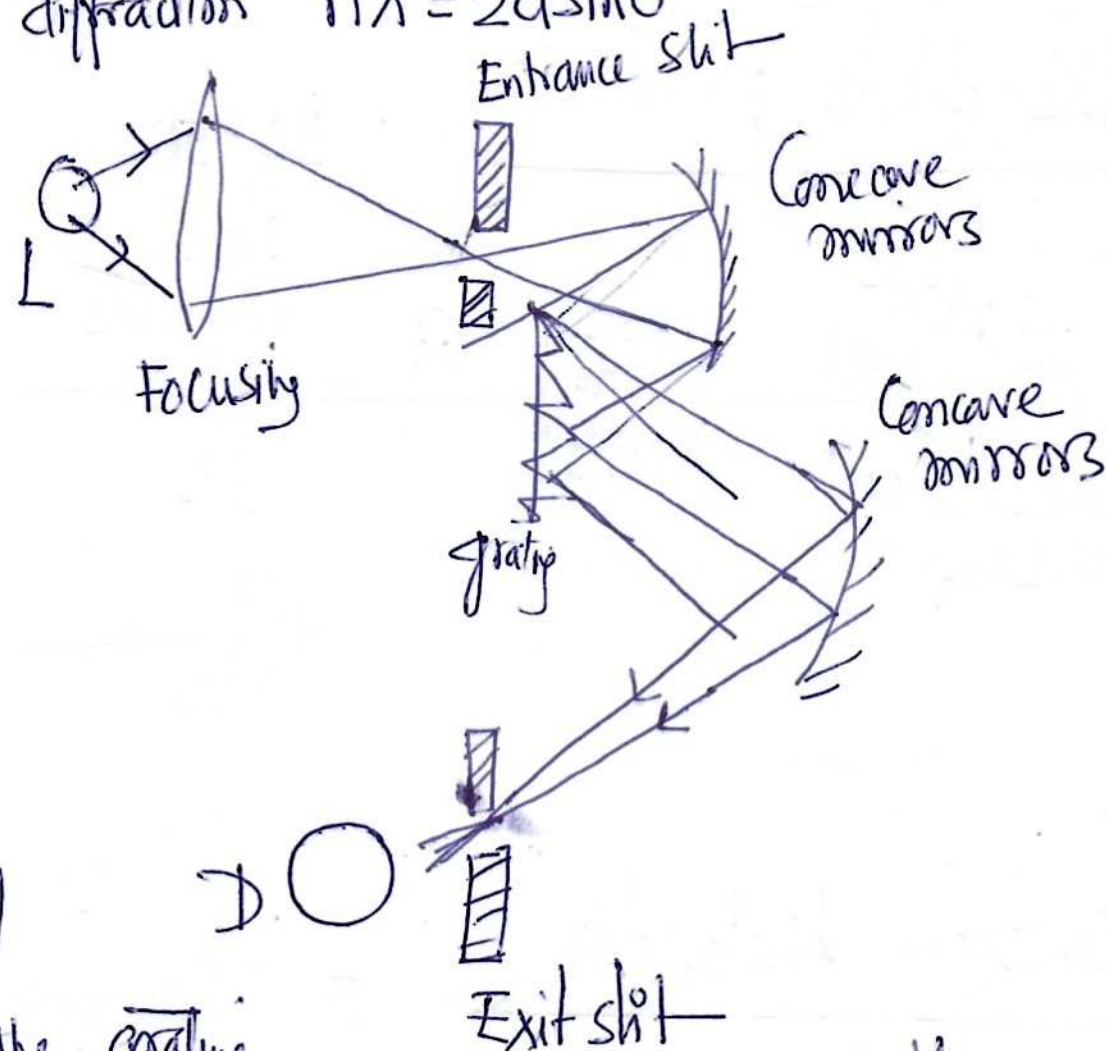
Generally, energy which is emitted is lower than the excitation.



Monochromator



Bragg's diffraction $n\lambda = 2d \sin \theta$



Smaller d
better resolution

We can only tilt the angle of the grating

Too good is no good

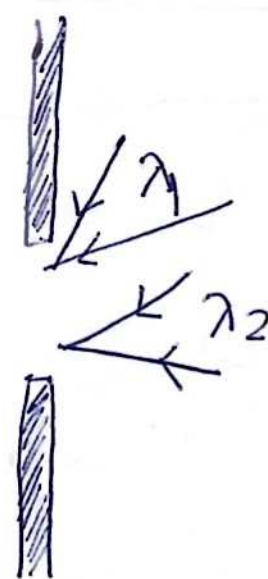
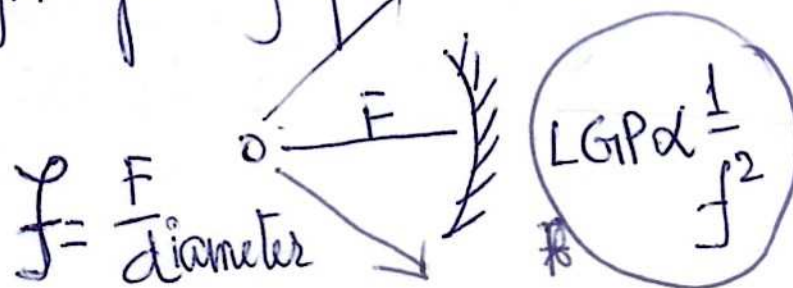
$$\lambda_1 = 2d \sin \theta_1$$

$$\lambda_2 = 2d \sin \theta_2$$

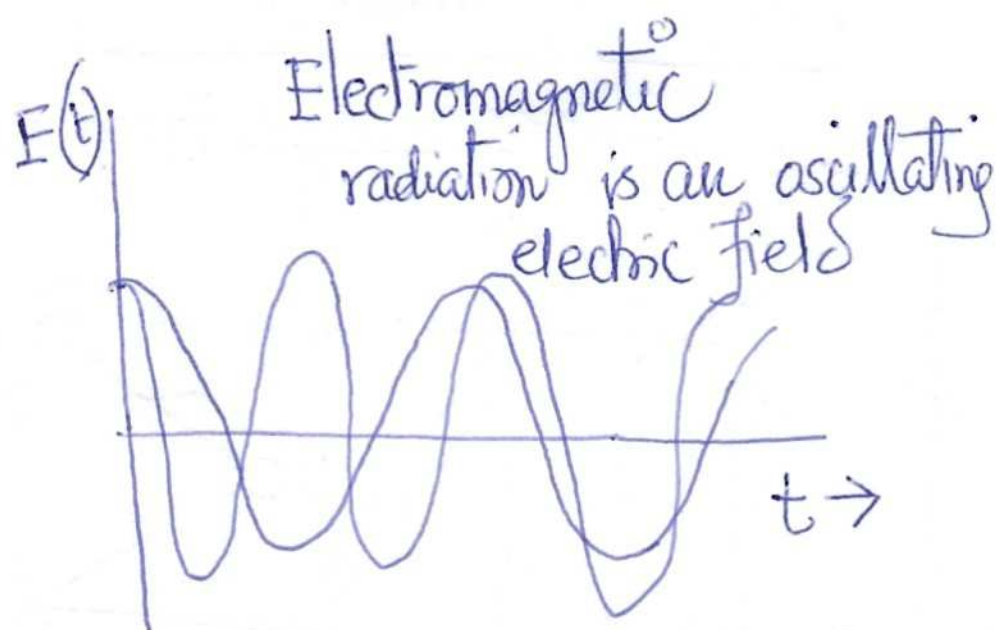
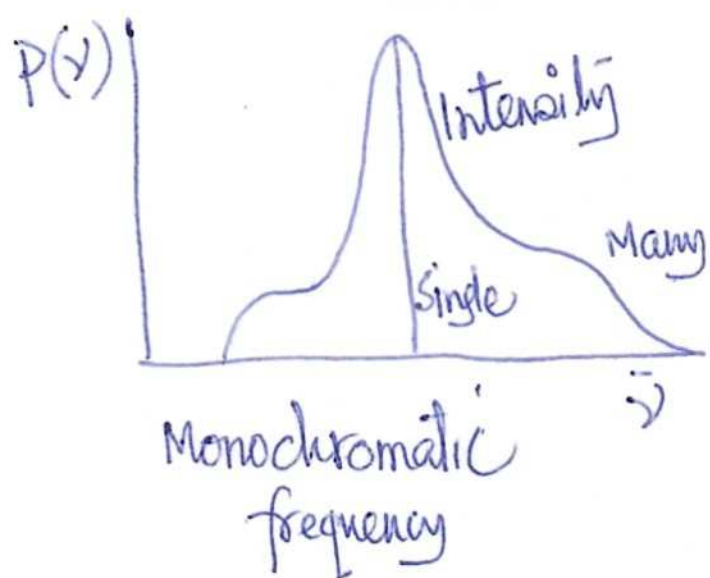
$$\lambda_2 - \lambda_1 = 2d \Delta(\sin \theta)$$

$$\left. \begin{aligned} \Delta \lambda \\ \frac{\Delta(\sin \theta)}{\Delta \lambda} = \frac{1}{2d} \end{aligned} \right\}$$

Light gathering power (LGP)



Time domain spectroscopy



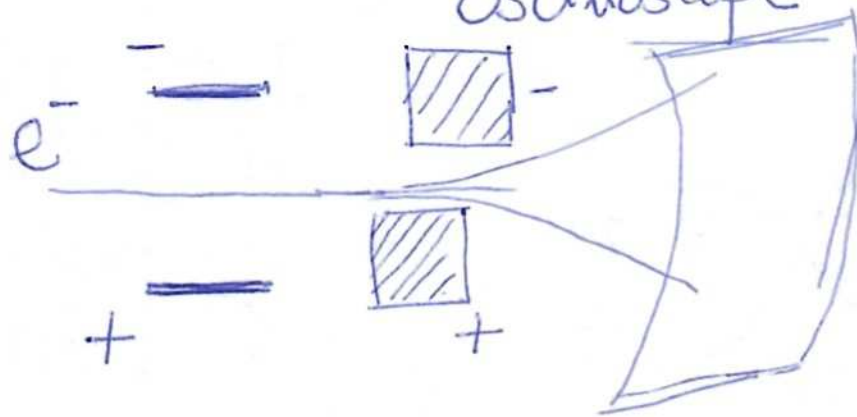
At a particular time, information of all frequencies are present.

Advantages of time domain

1. Jacquinot (throughput advantage)
2. Resolution
3. multiplex detection (all wavelengths together) S/N ratio is better

Detectors

to detect a time domain oscilloscope



$$c\bar{\nu} = \nu$$

$$1000 \text{ cm}^{-1} = \bar{\nu}$$

$$\nu = 3 \times 10^8 \times 10^2 \text{ cm}^{-1} \times 10^3 \text{ cm}^{-1}$$

$$= 3 \times 10^{13} \text{ s}^{-1}$$

Time period $\tau = \frac{1}{\nu} = 3.3 \text{ ps}$

We do not have faster oscilloscope.

wavelength
 $= \lambda$

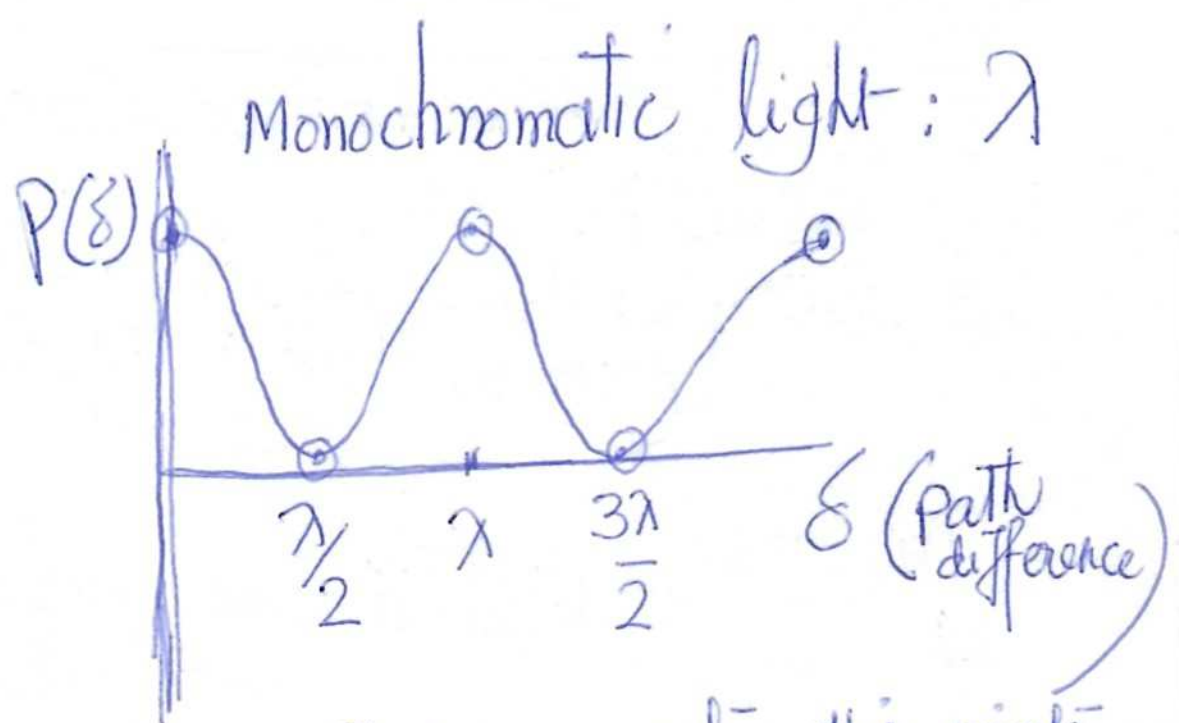
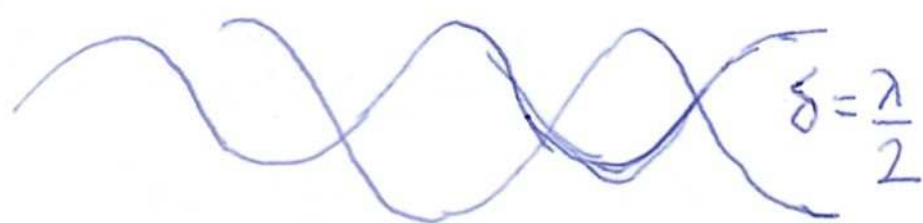
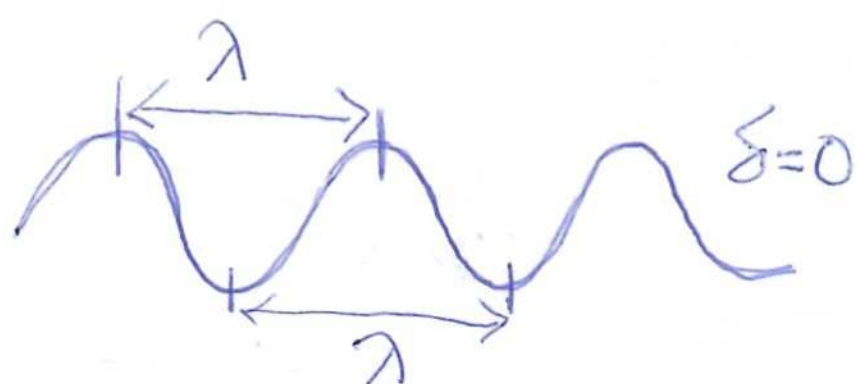
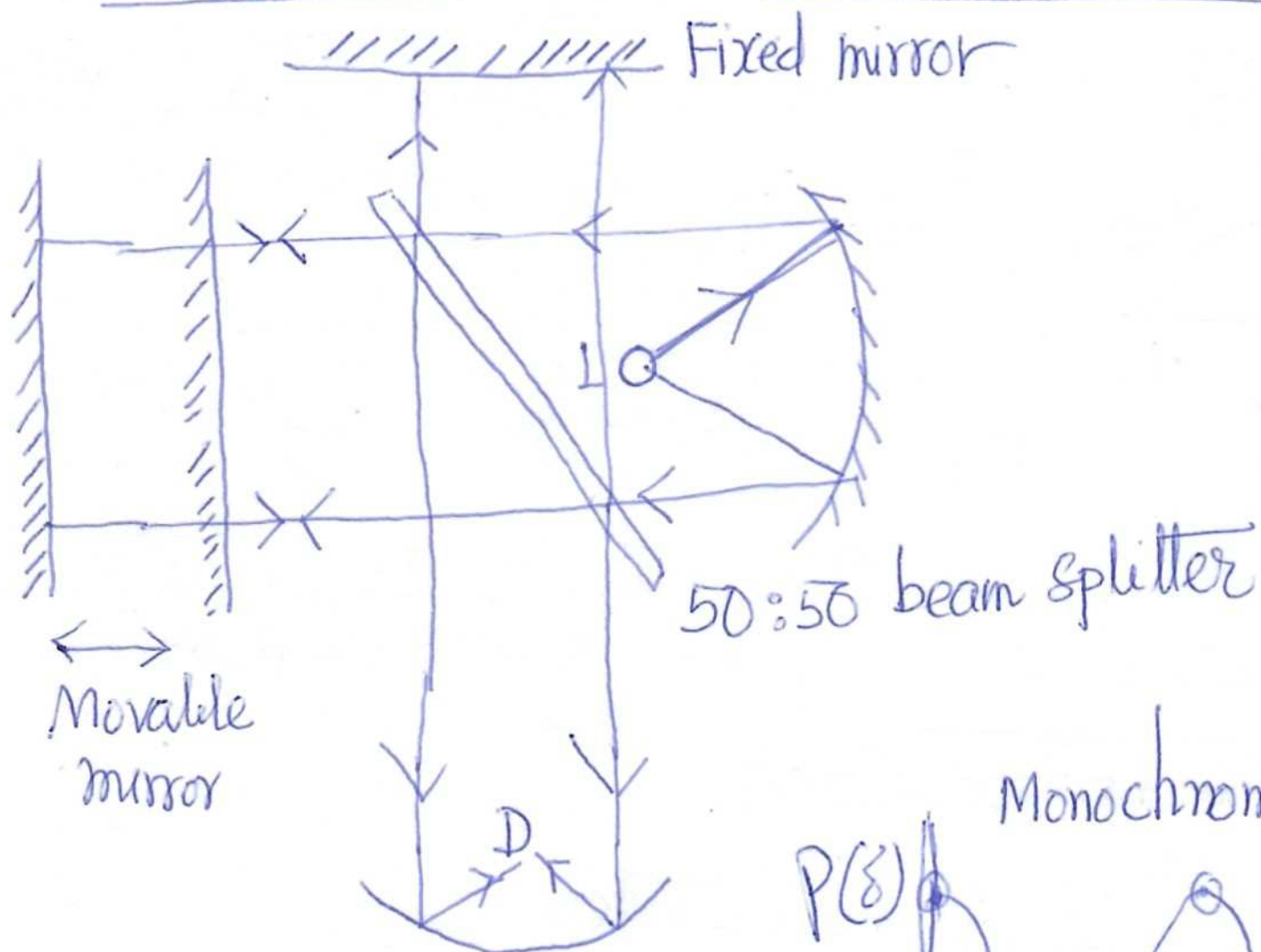
wave number
 $= \frac{1}{\lambda}$
 $= \bar{\nu}$

$$E = h\nu$$

$$= h \cdot \frac{c}{\lambda}$$

2022

Frequency modulation for Time domain



I can generate this points in δ in ~~real~~ measurements of practical timescale of a detector.

V_M = velocity of the mirror (M)
 τ = Time for mirror to travel $\frac{\lambda}{2}$

$$V_M \cdot \tau = \frac{\lambda}{2}$$

$$\tau = \frac{\lambda}{2V_M}$$

$$f = \frac{1}{\tau} = \frac{2V_M}{\lambda \text{ light}} = \frac{2V_M}{c} \nu$$

frequency of signal.

How do we get resolution?

No monochromator
 No grating
 No slit

$$f = \frac{2V_M}{c} \nu$$

Mirrors
Collimators
Filter
Modulators
lock-in amplifier

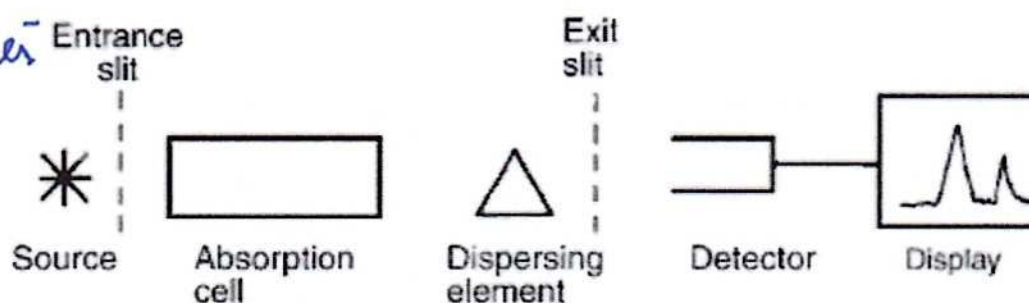
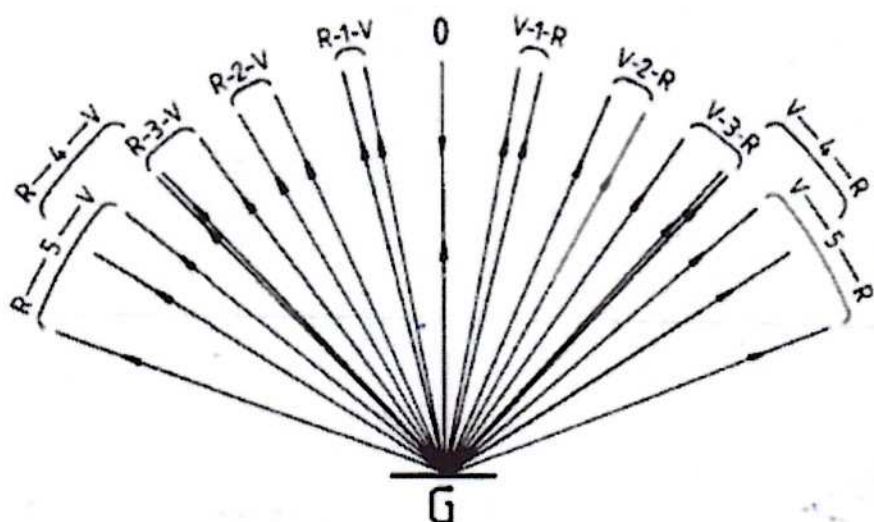


Figure 3.2 The components of a typical absorption experiment

$$m\lambda = d(\sin i + \sin \theta)$$



i = angle of incidence
 θ = angle of reflection
 d = groove distance
 $m = 0, 1, 2, 3, 4$
 λ = wavelength

Region	Source	Absorption cell window	Dispersing	Detector
Microwave	Klystron	Mica	None	Crystal diode
Mid Near IR	Nernst glower filament Globar (SiC) Nichrome wire	NaCl or KBr	Grating Interferometer	Transducers DTGS MCT
Vis. UV	(vis) Tungsten-halogen (uv) Deuterium (uv-vis) Xenon arc lamp	Glass Quartz (uv) Plastic	Prism Grating	photo multiplier

vis

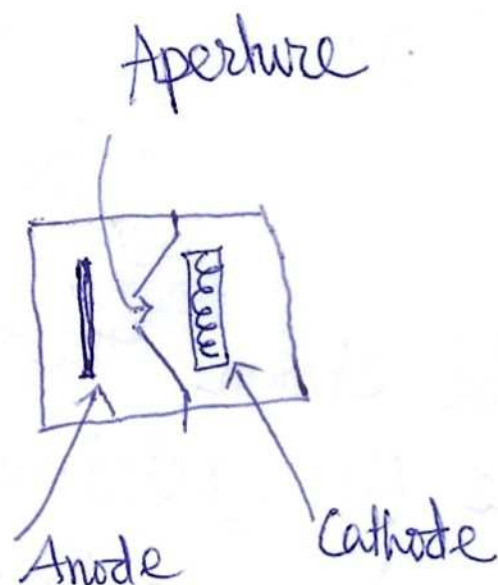
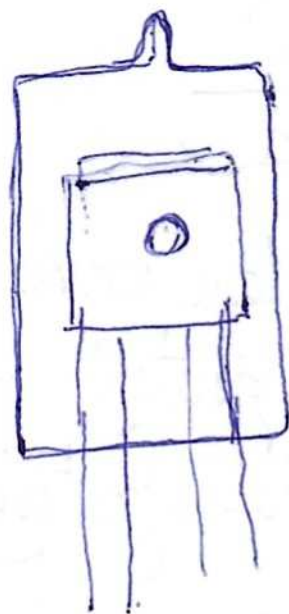
1 cm^{-1} wave number

$3 \times 10^{10} \text{ Hz} = 3 \times 10^4 \text{ MHz}$ (Frequency)

400 nm $\equiv$ 25000 cm^{-1}

800 $\equiv$ 12500 cm^{-1}

$$\tilde{\nu}(\text{cm}^{-1}) = \frac{10^7}{\lambda(\text{nm})}$$



Deuterium lamps 190 nm - 400 nm

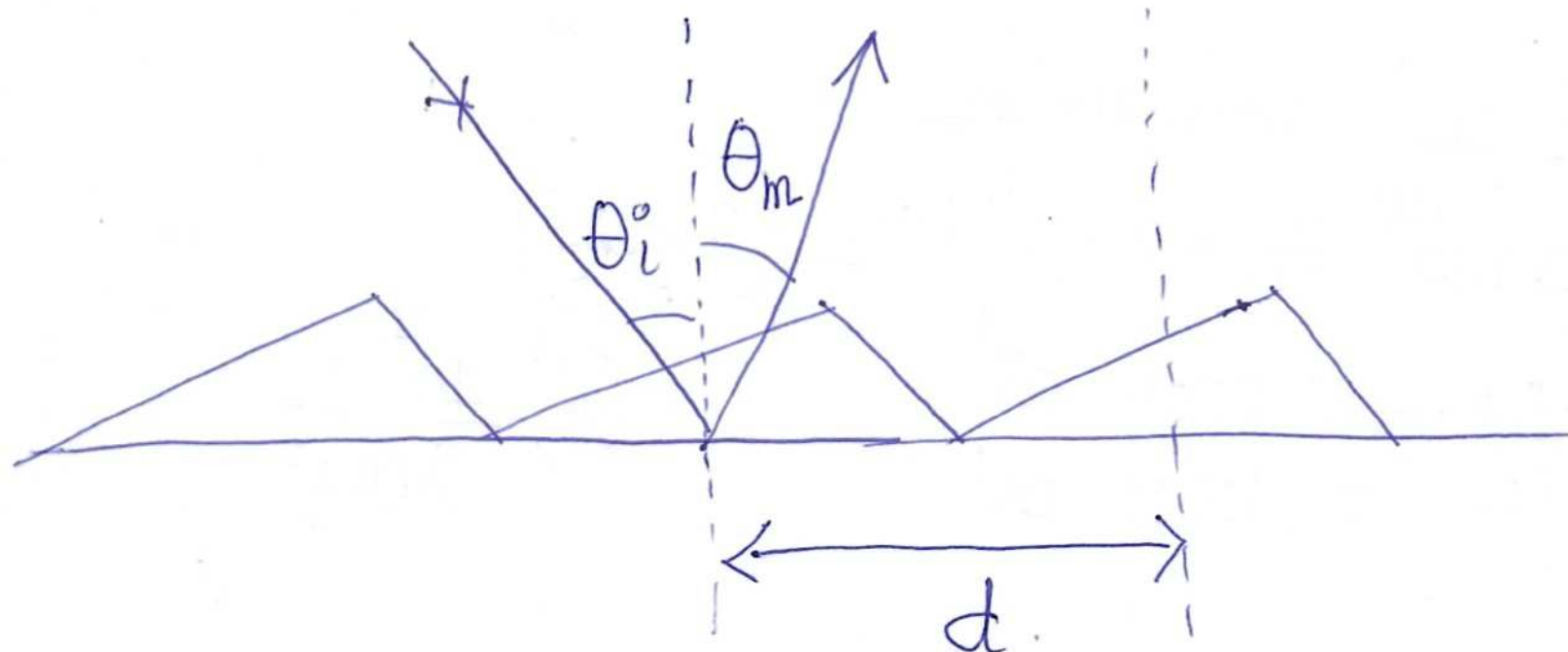
Tungsten Halogen lamp 320 nm - 2500 nm

Xenon arc lamp 190 nm - 1100 nm

Resolution : describes the smallest distance between two distinct points that can be seen/observed clearly.
" Smallest detectable difference in wavelength. "

The resolution of a spectrometer defines its ability to distinguish between two closely spaced spectral peaks or wavelengths.

$$R.P. = \frac{\lambda}{\Delta\lambda}$$



$$\sin \theta_m = \frac{m\lambda}{d}$$

It can be shown that if the plane wave is incident at angle θ_i relative to the grating normal in the plane orthogonal to the grating periodicity the grating eqn. becomes

$$\boxed{n\lambda = d(\sin \theta_i + \sin \theta_m)} \quad \sin \theta_i + \sin \theta_m = \frac{m\lambda}{d \sin \gamma}$$

$$\theta_m = \sin^{-1} \left(\sin \theta_i - \frac{m\lambda}{d \sin \gamma} \right)$$

A grating consists of a series of equally spaced parallel grooves formed in a reflective coating deposited on a suitable substrate.

Spectroscopy can be primarily classified into two categories → 1) Absorption Spectroscopy
2) Emission Spectroscopy

IR
microwave
UV/vis

← our syllabus

These are all absorption spectroscopy

If you look at the output/final representation spectrum of
pure rotational (microwave)
vibrational (IR)
electronic (UV/vis)

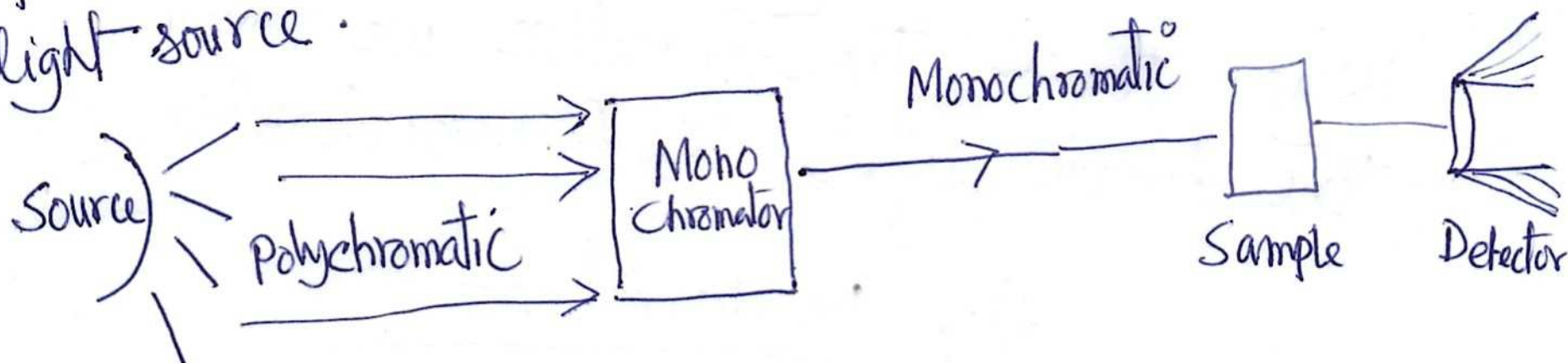
all are frequency domain spectrum.

which means, the X-axis contains energy/frequency/wavelength/
wave number

If you need to record frequency domain spectroscopy we need to send specific frequency of light at a time and record signal & thus vary frequency/wavelength and so on.

How do you do it?

In UV/vis spectroscopy, we use an optical component called monochromator that ~~can~~ separates/filters a particular wavelength/frequency of the polychromatic light source.



Now question?

* Do you use monochromator in microwave spectroscopy?

Answer: NO

* Then how you send/scan various frequencies?

Answer: Microwave spectroscopy typically uses coherent microwave sources like klystrons which are monochromatic electronic oscillators that output precisely one well-defined frequency at a time.

* Do you use monochromator in IR spectroscopy?

Answer: NO

We actually record interferogram in IR, which is like frequency-modulated time domain spectroscopy

A To record time-domain signal we need very fast oscilloscope which is scarce and difficult.

Rather if we use Michelson interferometer (moving mirror) to convert time domain signals to frequency modulation, ~~we can record time domain signals in measurable~~ as interferogram. [Intensity vs optical path difference]

Using Fourier Transformation, we convert time domain signals to frequency domain.

See the derivations

Electronic spectroscopy

How do we define an electronic state?

Born-Oppenheimer Approximation

$$\Psi = \Psi_{es} \Psi_v \Psi_r$$

$$E = E_{es} + E_v + E_r$$

— S_1 — T_1

— S_0

$\alpha(1)\alpha(2)$
 $\beta(1)\beta(2)$

HOMO
↑↓

Singlet

↓

↑

Singlet

↑

↑↓

Triplet

$\alpha(1)\beta(2) + \beta(1)\alpha(2)$ } symmetric with exchange.
 $\alpha(1)\beta(2) - \beta(1)\alpha(2)$

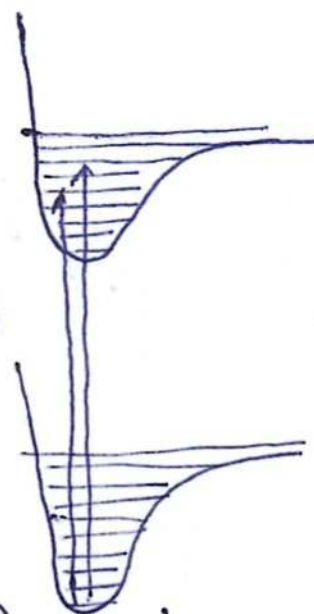
Triplet state is a combination of 3 wavefns.
Singlet " " a single wavefn.

(can we experimentally see?
Yes, by applying magnetic field)

$$\Psi = \Psi_{es} \Psi_v$$

$$E = E_{es} + E_v$$

The resulting state is called a Franck-Condon state, and the transition involves a vertical transition.



Franck-Condon Principle

* James Franck 1926
* Edward Uhler Condon
Classically the Franck-Condon principle is the approximation that an electronic transition is most likely to occur without

$$\begin{aligned} TMI &= \langle \Psi_{es}^{(2)} \Psi_v^{(2)} | (\mu_N + \mu_e) | \Psi_{es}^{(1)} \Psi_v^{(1)} \rangle \\ &= \langle \Psi_{es}^{(2)} \Psi_v^{(2)} | \mu_N | \Psi_{es}^{(1)} \Psi_v^{(1)} \rangle + \langle \Psi_{es}^{(2)} \Psi_v^{(2)} | \mu_e | \Psi_{es}^{(1)} \Psi_v^{(1)} \rangle \\ &= \langle \Psi_{es}^{(2)} | \Psi_{es}^{(1)} \rangle \langle \Psi_v^{(2)} | \mu_N | \Psi_v^{(1)} \rangle + \langle \Psi_{es}^{(2)} | \mu_e | \Psi_{es}^{(1)} \rangle \langle \Psi_v^{(2)} | \Psi_v^{(1)} \rangle \end{aligned}$$

changes in the positions of the nuclei

Zero electronic wavefns of same molecule

different vibrational manifolds
Non-zero

$$TM1 = \langle \psi_e^{(2)} | \psi_e^{(1)} \rangle$$

Franck-Condon factor

If good overlap, then

$$\psi_{es} = \psi_e \cdot \psi_s$$

$$\langle \psi_e^{(2)} | \mu_e | \psi_e^{(1)} \rangle \langle \psi_s^{(2)} | \psi_s^{(1)} \rangle$$

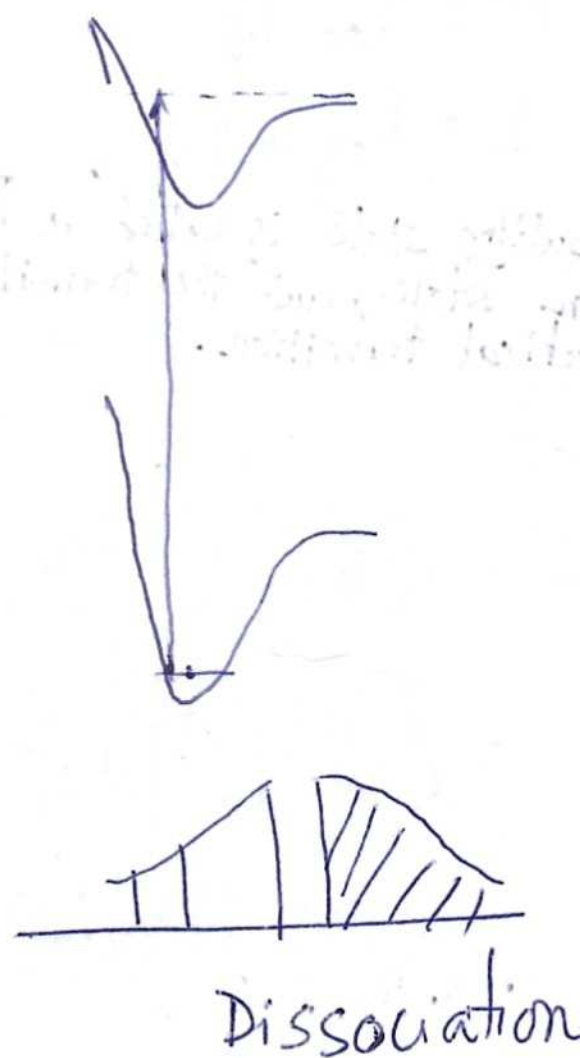
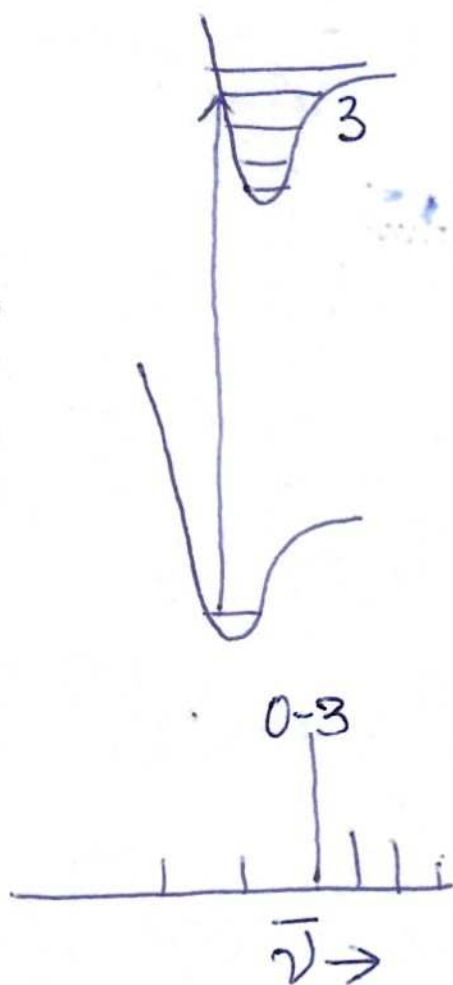
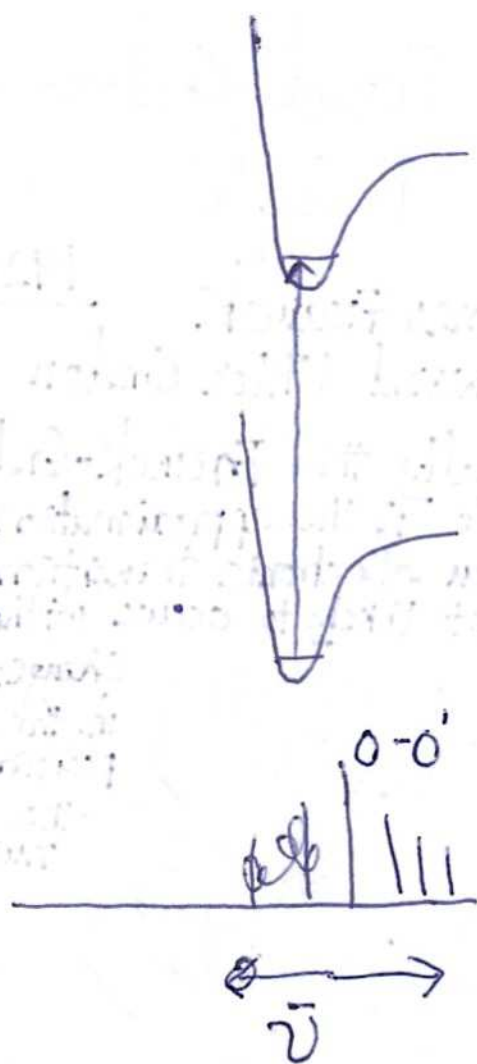
↓ symmetry
of electronic
wave-fns.

Orbital forbidden/allowed

↓ $\Delta S = 0$, $\Delta m_s = 0$
Spin forbidden/allowed.

* Orbital forbidden transitions can be vibronically allowed.

* Spin forbidden transitions can become allowed.
How? Spin-orbit splitting.



The quantum mechanical formulation of this principle is that the intensity of a vibronic transition is proportional to the square of the overlap integral between the vibrational wave functions of the two states involved in the transition.

Electronic Spectroscopy: Franck-Condon Factor

Born-Oppenheimer $\Psi = \Psi_{es} \Psi_v \Psi_r$

$$\downarrow$$

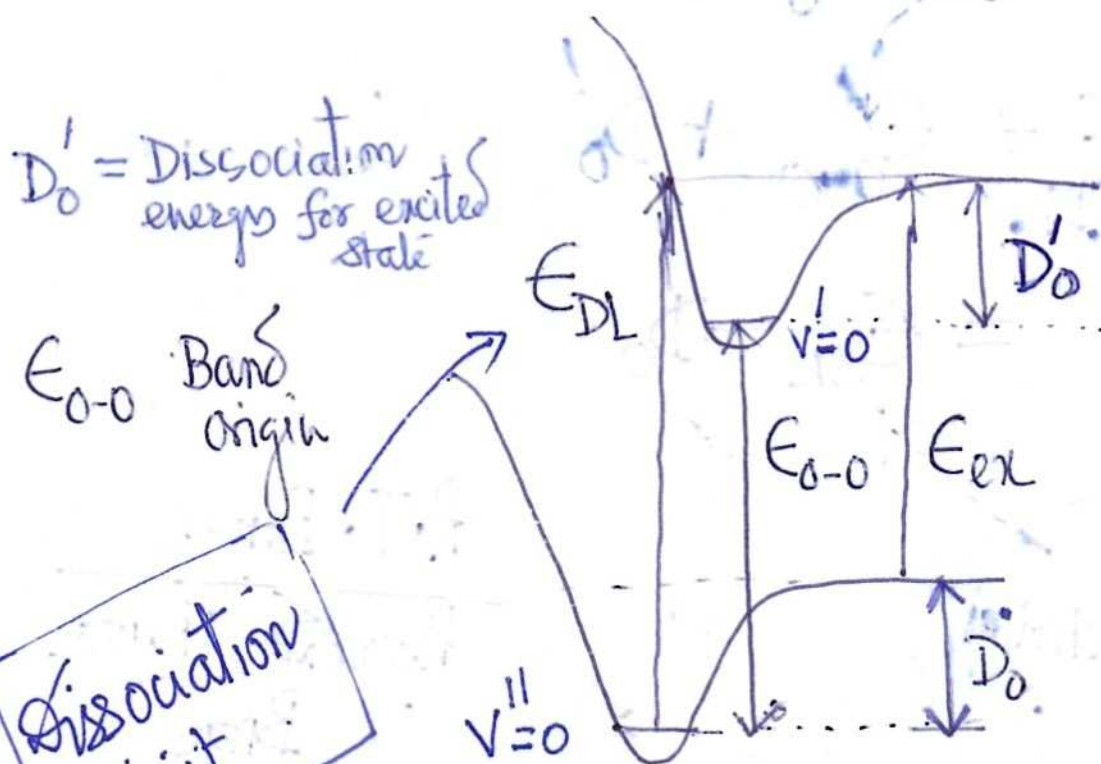
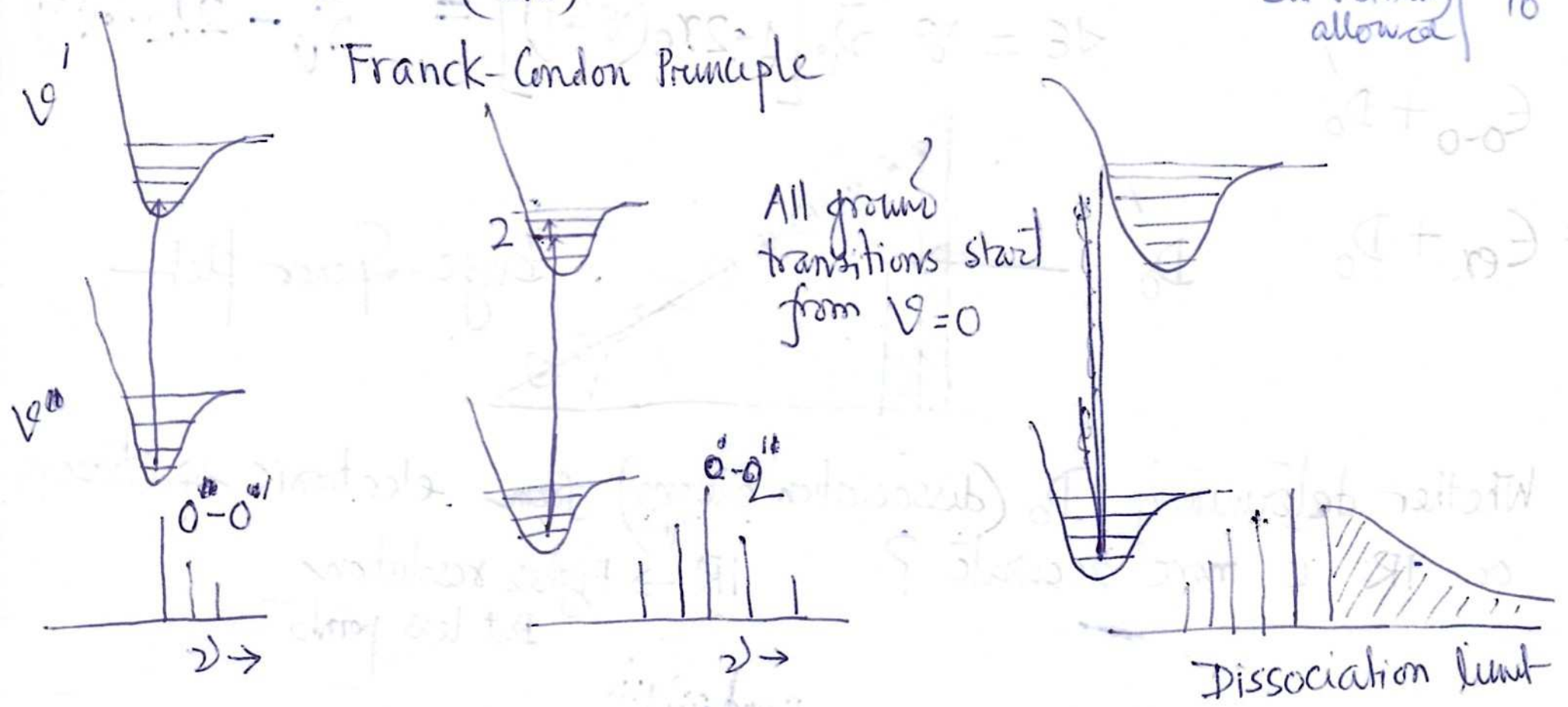
$$\Psi_e \cdot \Psi_s$$

$$TMI = \underbrace{\langle \Psi_v^{(2)} | \Psi_v^{(1)} \rangle}_{\text{Franck-Condon factor } \chi(\chi_i)} \underbrace{\langle \Psi_{es}^{(2)} | \mu | \Psi_{es}^{(1)} \rangle}_{\text{Orbital Selection}} \underbrace{\langle \Psi_s^{(2)} | \Psi_s^{(1)} \rangle}_{\text{Spin selection}}$$

Spin & orbitally allowed	10^3 to 10^5
Spin allowed but orbitally forbidden	10^0 to 10^3
Spin forbidden but orbitally allowed	10^{-5} to 10^{-10}

Franck-Condon Principle

All ground transitions start from $v=0$



$$E_{DL} = E_{0-0} + D'_0$$

If dissociation limit is very well-defined and E_{0-0} is clear we can determine D'_0 . But usually it is not the case.

Thermochemically we can measure directly, the excited state energy

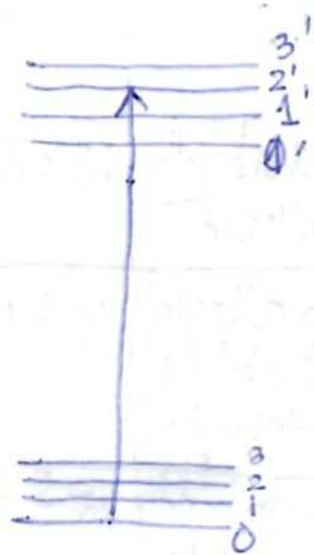
$$E_{DL} = E_{ex} + D_0$$

Find value experimentally with IR

E represents energy in cm^{-1}

Dissociation limit

If we do not have dissociation limit in the spectrum, then how can we determine



$$\epsilon = \epsilon_{es} + \epsilon_v$$

$$\Delta\epsilon = \epsilon_{00} + \Delta\epsilon_v$$

Born-Oppenheimer approximation

$$\epsilon_v = \left[\left(v + \frac{1}{2} \right) \bar{\nu}_v x_e - \left(v + \frac{1}{2} \right)^2 x_e \bar{\nu}_v \right]$$

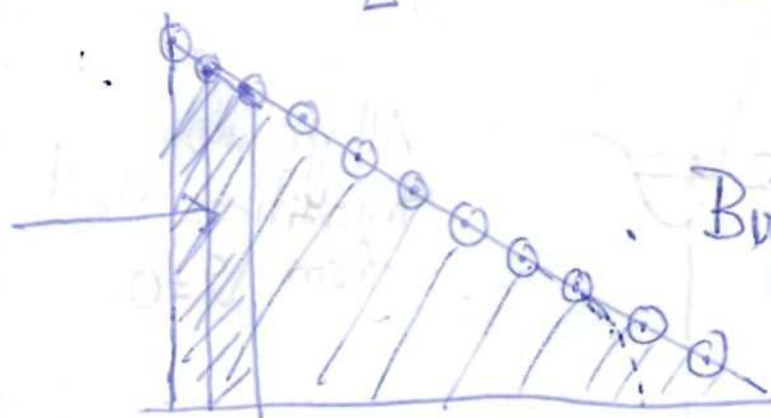
$$\left. \begin{array}{l} 0 \rightarrow v' \\ 0 \rightarrow v'+1 \end{array} \right\} \text{Two transitions}$$

$$\Delta\epsilon = \bar{\nu}_v \left[1 - 2x_e(v'+1) \right] = \bar{\nu}_v - 2x_e \bar{\nu}_v (v'+1)$$

$$\epsilon_{0-0} + D_0$$

$$= \epsilon_{ex} + D_0$$

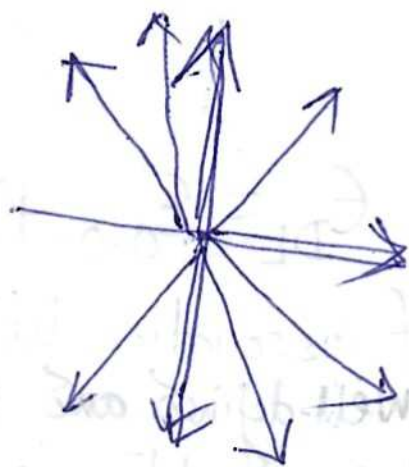
D_0



Birge-Sponer plot

Whether determining D_0 (dissociation energy) from electronic spectroscopy or IR is more accurate?

IR $\rightarrow$ Higher resolution
But less points



Band origin

$$\epsilon_{DL} = \epsilon_{0-0} + D_0$$

$$= \epsilon_{ex} + D_0$$

Can be determined from thermochemical

R.T. Birge

Raymond Thayer Birge

Hertha Sponer

w/o James Franck

Rotational Fine structure

$$\Delta E = \bar{\nu} = \bar{\nu}_{e,v} + \Delta [B J(J+1)]$$

$$\begin{aligned} \bar{\nu}_Q &= \bar{\nu}_{e,v} + B' J'(J'+1) - B'' J''(J''+1) \\ &= \bar{\nu}_{e,v} + (B' - B'') J(J+1) \end{aligned}$$

$$(7.2) (8.0) \text{ cm}^{-1}$$

The rotational constants in ground state & in the excited state might be different because the equilibrium bond length.

$$B \propto \frac{1}{r^2}$$

$$\Delta J = 0, J = 1, 2, 3, \dots \quad J=0 \text{ value not allowed}$$

The eqn is a parabola,

it is half parabola because -ve values of J is not possible.

Q branch

$$\Delta J = -1 \quad \text{Q branch} \quad J' = J'' - 1 \quad J'' = 1, 2, 3, \dots$$

$$\bar{\nu} = \bar{\nu}_{e,v} + B' (J'' - 1)(J'' - 1 + 1) - B'' J''(J'' + 1)$$

$$\begin{aligned} \bar{\nu}_P &= \bar{\nu}_{e,v} + (B' - B'') J''^2 - B' J''^2 - B'' J''^2 - B'' J'' \\ &= \bar{\nu}_{e,v} + (B' - B'') J''^2 - (B' + B'') J'' \end{aligned}$$

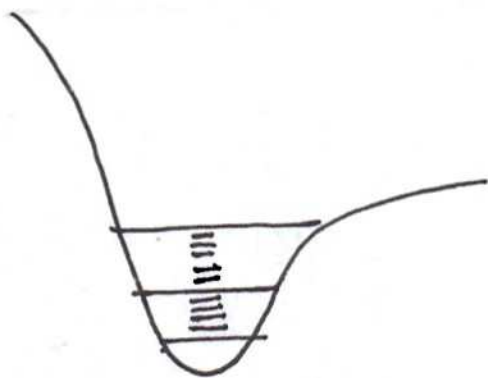
$$\bar{\nu}_R = \bar{\nu}_{e,v} + (B' - B'') J''^2 + (B' + B'') J''$$

$\Delta J = +1$ R branch

$$\bar{\nu}_{P,R} = \bar{\nu}_{e,v} + (B' - B'') J''^2 \mp (B' + B'') J''$$

Alternative representation,

$$\bar{\nu}_{P,R} = \bar{\nu}_{e,v} + (B + B') m \pm (B' - B'') m^2$$



$$\Delta J = \pm 1 \quad \text{for} \quad {}^1\Sigma \rightarrow {}^1\Sigma$$

Singlet sigma

$$= 0, \pm 1$$

provided $J''=0 \rightarrow J'=0$ not allowed



Electronic levels are associated with sublevels of vibrational level & rotational levels.

~~not~~ Unlike vibrational levels, the ground state ^{rotational} vibrational level should not be necessarily the most populated one.

René Fortrat - French physicist - 1914

Plotting the wave numbers of spectral lines versus their serial number creates a parabolic shape.

This is called Fortrat diagram / parabole.