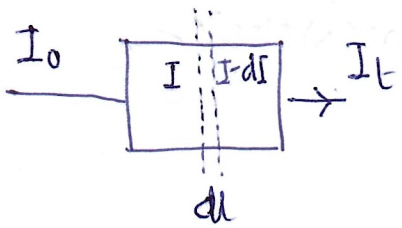
Molecular Spectroscopy

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

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



$-dI \propto I, c, dl$

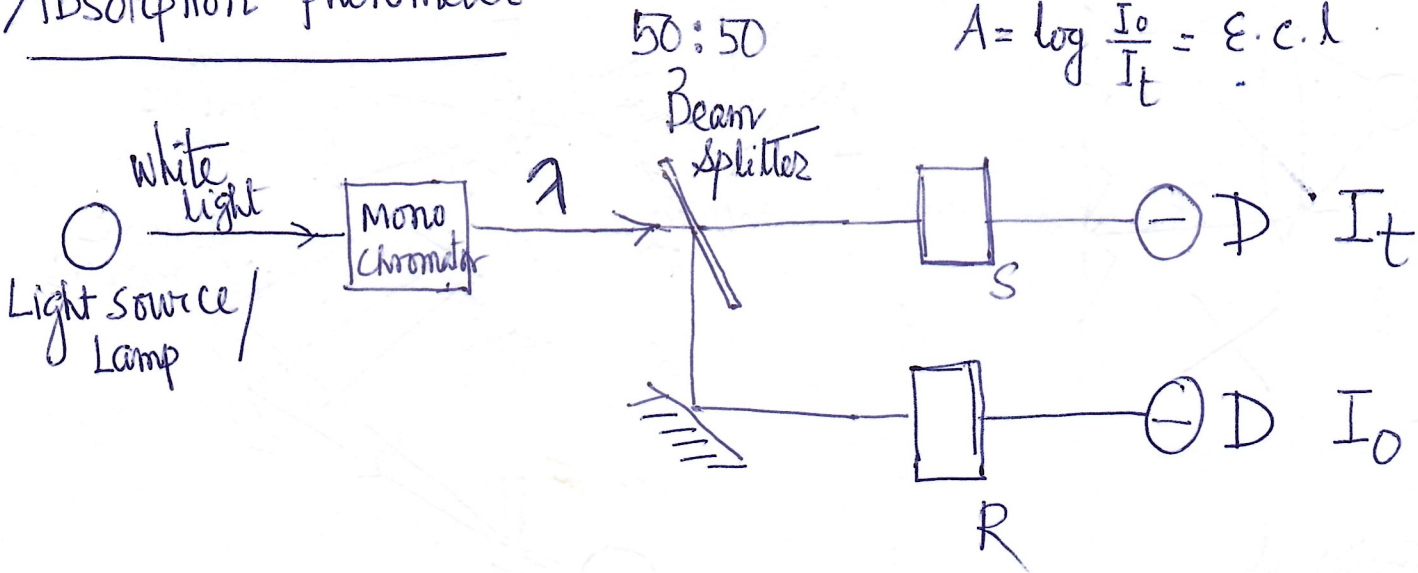
$-dI = a \cdot I \cdot c \cdot dl$

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

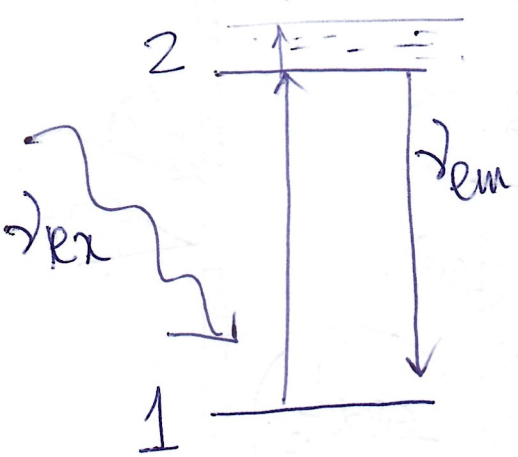
$\ln \frac{I_0}{I_t} = a \cdot c \cdot l$

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

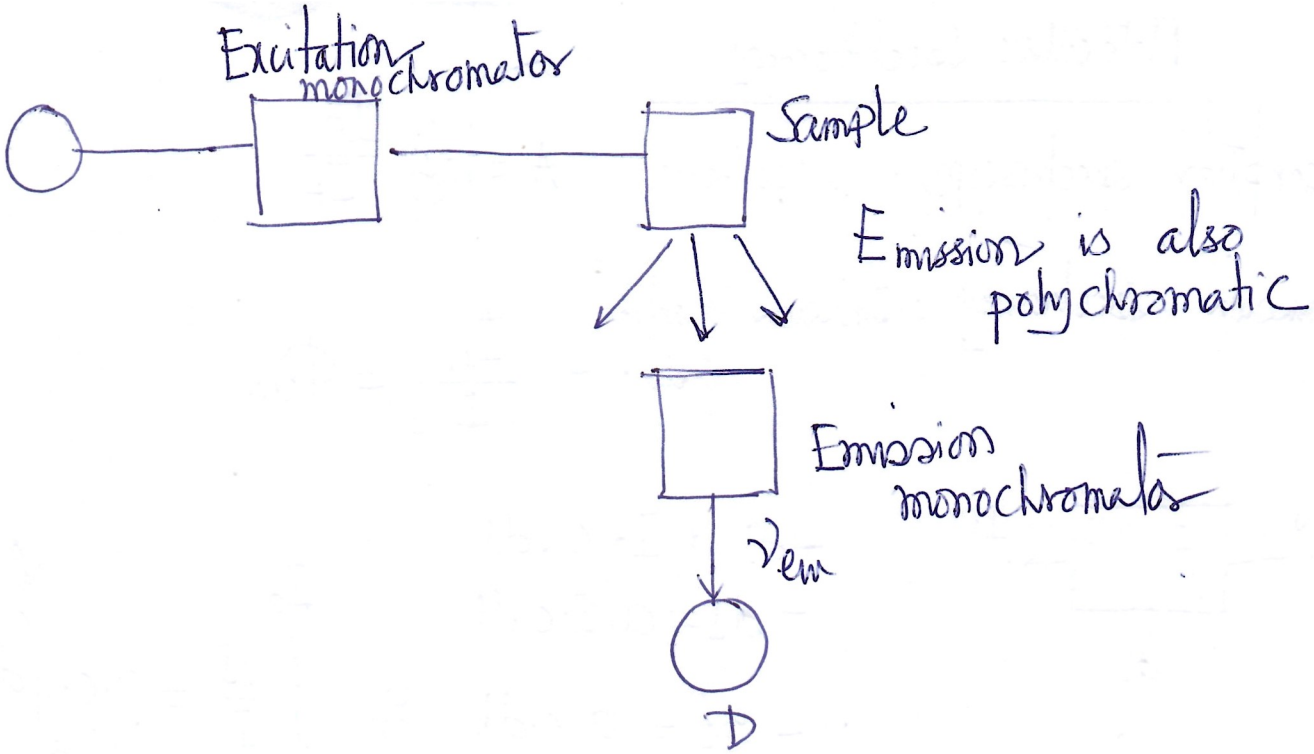
Absorption photometer



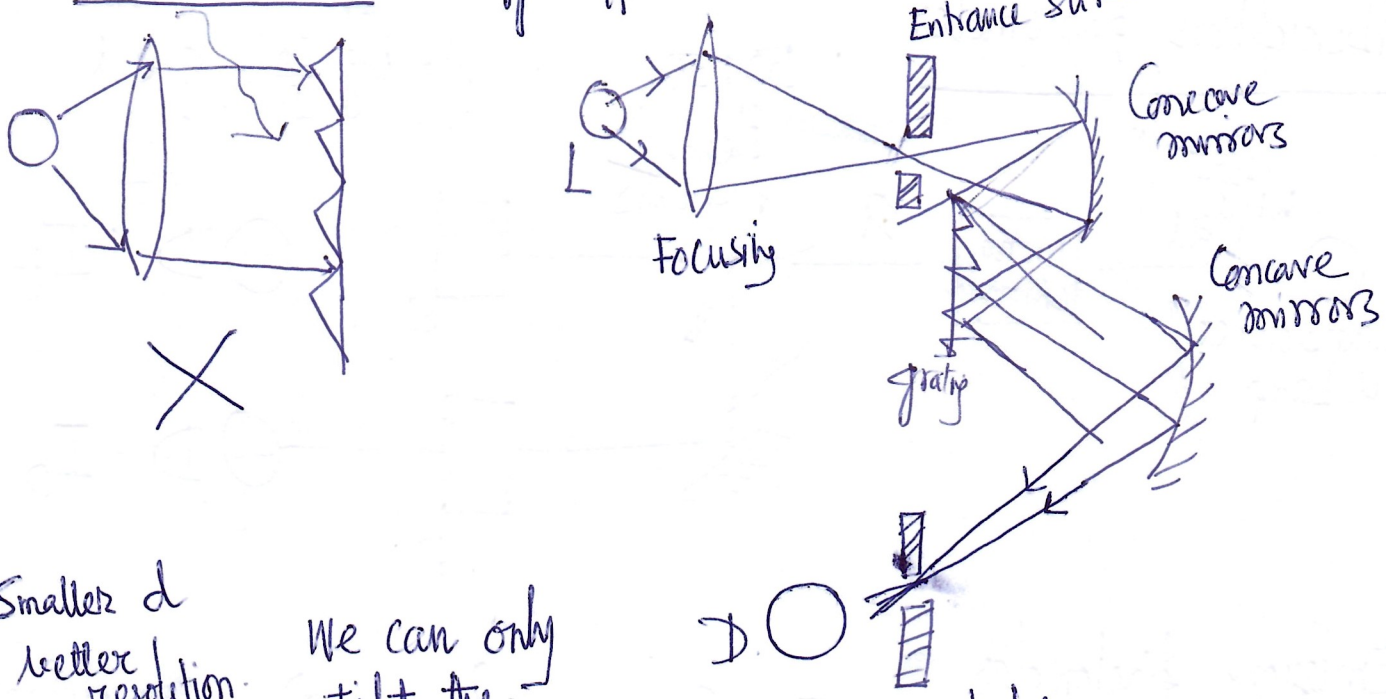
Emission photometer



- Generally ν_{ex} & ν_{em} are different
- ν_{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

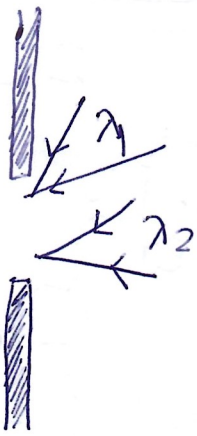
We can only tilt the angle of the grating

Too good is no good

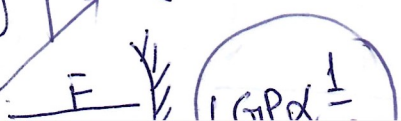
$\lambda_1 = 2d\sin\theta_1$

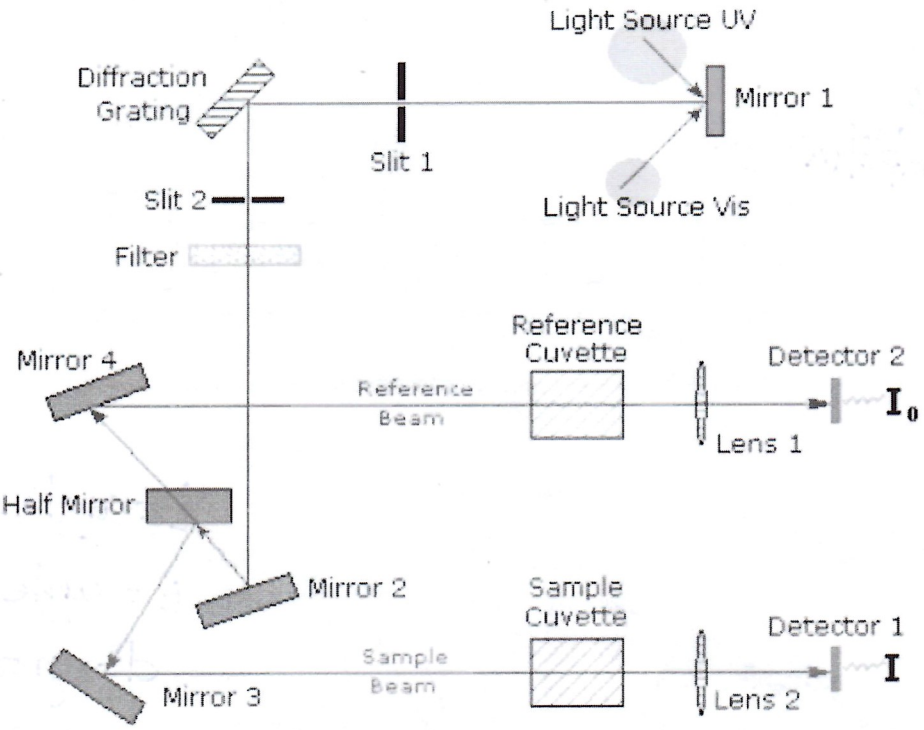
$\lambda_2 = 2d\sin\theta_2$

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

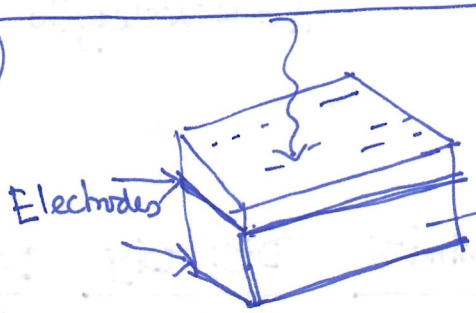


Light gathering power (LGP)





IR



DTGS Deuterated Triglycerine Sulphate (DTGS)

MCT Photoconductive
(Mercury Cadmium Telluride)

Resolution — The resolution of an instrument tells us how well two close-lying energies (or wavelength or freq. or masses) can be resolved.

Resolving power — The ~~spectral~~ resolving power of a spectrometer is a measure of its ability to resolve features

Mirrors
Collimators
Filters
Modulators
lock-in amplifier

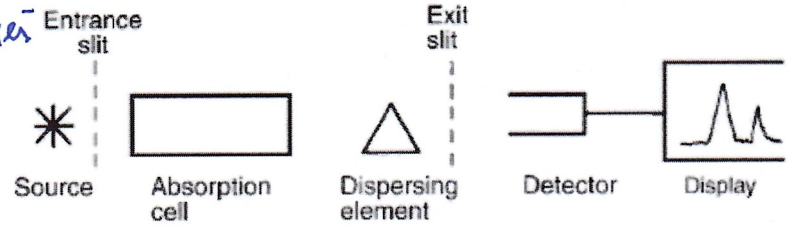
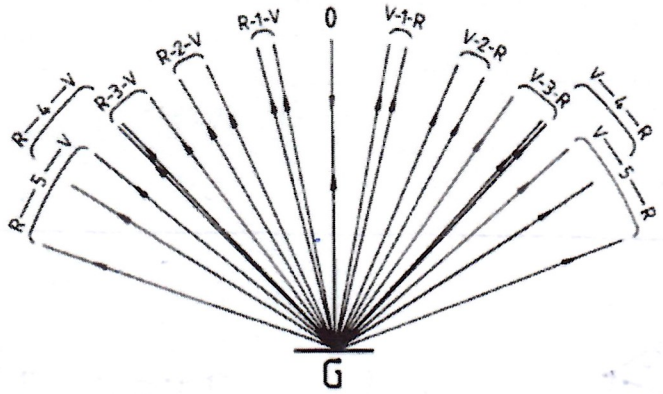


Figure 3.2 The components of a typical absorption experiment

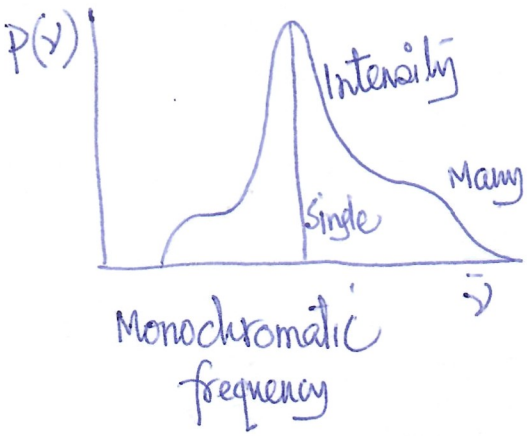
$$m\lambda = d(\sin i + \sin\theta)$$



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 IR Near IR	Nernst glower filament Globars (SiC) Nichrome wire	NaCl or KBr	Grating Interferometer	Transducers DTGS MCT
Vis. UV	(Vis) Tungsten-halogen (UV) Deuterium (UV-Vis) Xe arc lamp	Glass Quartz (UV) Plastic (Vis)	Prism Grating	photo multiplier

Time domain spectroscopy



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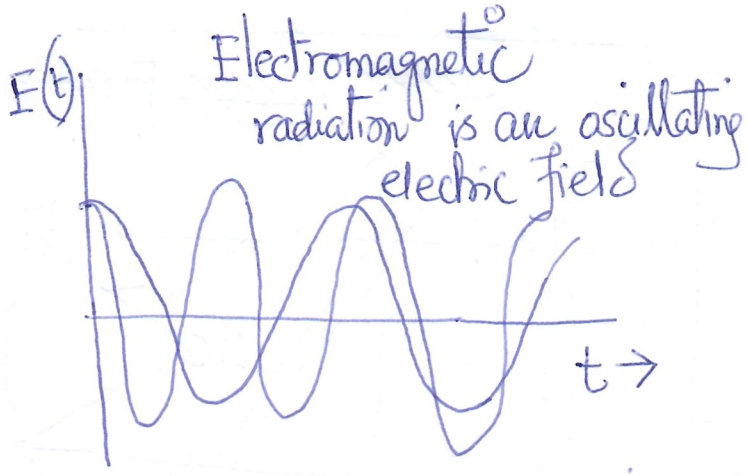


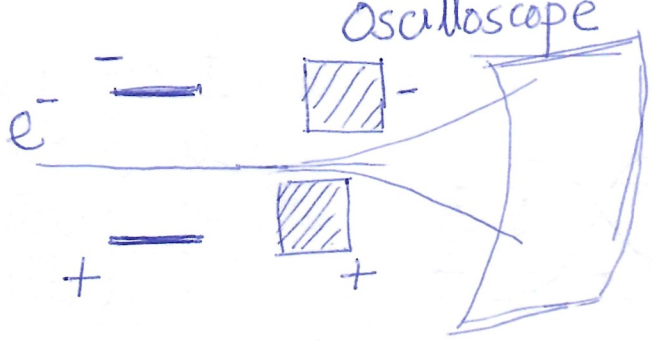
At a particular time, information of all frequencies are present.

Advantages of time domain

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

Detectors

to detect a time domain



$(\bar{\nu} = \nu)$

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

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

$10^{3}\ cm^{-1}$

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

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

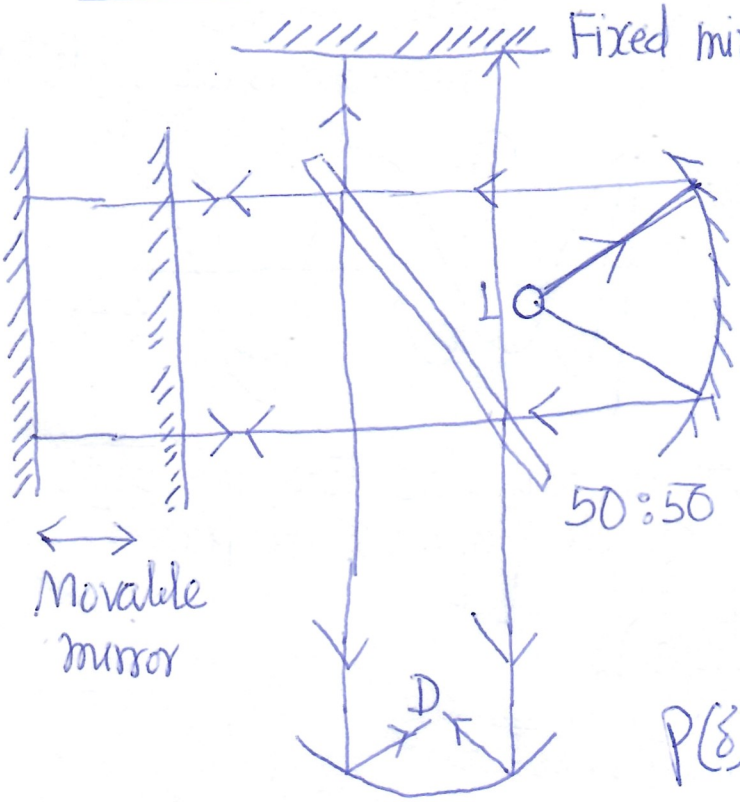
We do not have faster oscilloscope.

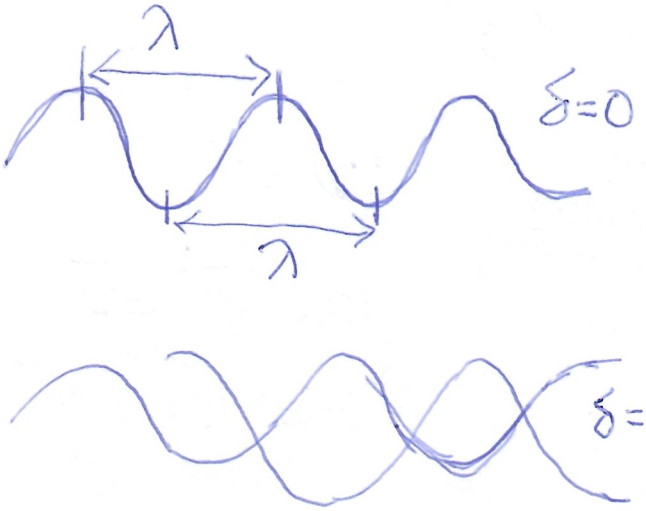
Wavelength $= \lambda$

Wavenumber $= \frac{1}{\lambda} = \bar{\nu}$

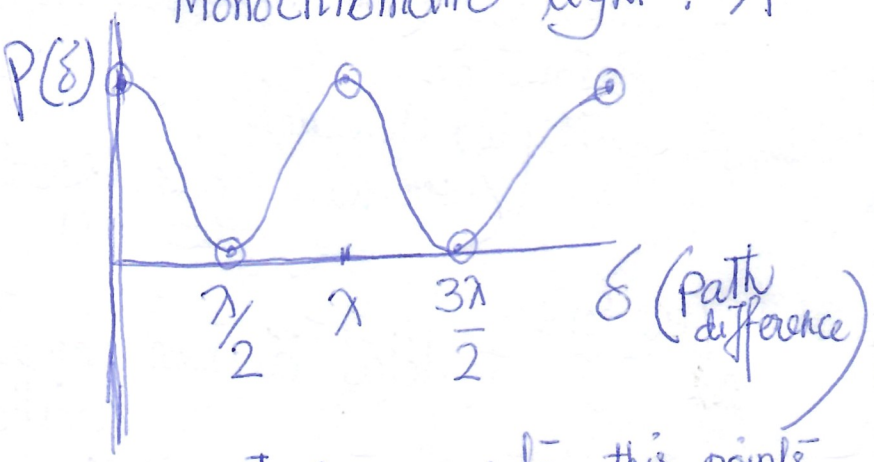
$E = h\nu = h \cdot \frac{c}{\lambda}$

Frequency modulation for Time domain





Monochromatic light: λ



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 $\lambda/2$

$V_M \cdot \tau = \lambda/2$

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

$f = \frac{1}{\tau} = \frac{2V_M}{\lambda}$ ← light

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

↑ frequency of signal.

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

How do we get resolution?

No monochromator
No grating
No slit

Semi-Classical Treatment of Matter-Light interaction

Light Electromagnetic radiation

Electric field 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

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

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

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

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

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

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

$$\boxed{\phi = e^{-iEt/\hbar}}$$

So, $\Psi = \psi e^{-iEt/\hbar}$

Spectroscopy means transition from one state to the other.

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

E_m —— ψ_m

E_l —— ψ_l

Two level system

Superposition of mixing of states

$$\psi = C_l \psi_l + C_m \psi_m$$

Mixing coefficients C_l, C_m

At $t \to 0$, $C_l = 1$, & $C_m = 0$

No light, $t=0$, $\hat{H} = \hat{H}^{(0)}$, $\psi = \psi_l$

In presence of light, $\hat{H} = \hat{H}^{(0)} + \hat{H}^{(1)}$, $\psi = C_m \psi_l + C_m \psi_m$

$$\hat{H} = -\mu_x E_x$$

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

$E_x = 2E_x^\circ \cos 2\pi\nu t$, ν = frequency.

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

$$\left[\hat{H}^{(0)} + \hat{H}^{(1)}\right]\left[C_l\psi_l + C_m\psi_m\right] = -\frac{\hbar}{i}\frac{\partial}{\partial t}\left[C_l\psi_l + C_m\psi_m\right]$$

$$\Rightarrow C_l\hat{H}^{(0)}\psi_l + C_m\hat{H}^{(0)}\psi_m + C_l\hat{H}^{(1)}\psi_l + C_m\hat{H}^{(1)}\psi_m = -\frac{\hbar}{i}\left[C_l\frac{\partial\psi_l}{\partial t} + \frac{\partial C_l}{\partial t}\psi_l + C_m\frac{\partial\psi_m}{\partial t} + \frac{\partial C_m}{\partial t}\psi_m\right]$$

$$C_l\hat{H}^{(1)}\psi_l + C_m\hat{H}^{(1)}\psi_m = -\frac{\hbar}{i}\left[\frac{\partial C_l}{\partial t}\psi_l + \frac{\partial C_m}{\partial t}\psi_m\right]$$

Now, multiply with ψ_m^*

$$C_l\langle\psi_m|\hat{H}^{(1)}|\psi_l\rangle + C_m\langle\psi_m|\hat{H}^{(1)}|\psi_m\rangle = -\frac{\hbar}{i}\frac{\partial C_m}{\partial t}$$

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

$$= -\frac{i}{\hbar}\langle \psi_m | \hat{H}^{(1)} | \psi_k \rangle \cdot \exp\left[\frac{i(E_m - E_k)t}{\hbar}\right] \exp\left[\frac{2\pi i (E_m - E_k)t}{h}\right]$$

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

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

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

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

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

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

Molecular Spectroscopy
Jack D. Graybeal

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

μ_x: dipole moment of the molecule

E_x: The amplitude of the electric field

$$E_x = 2E_x^\circ \cos 2\pi\nu t$$

E_x°: Maximum amplitude of the electric field

ν: frequency of radiation

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

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

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

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

For absorption, $E_m - E_k \cong h\nu$ — this term significant

Emission, $E_m - E_k \cong -h\nu$ — so this term becomes significant

$$C_m = E_x^\circ\langle\psi_m|\mu_x|\psi_k\rangle\left[\frac{1-\exp\left\{\frac{2\pi i^\circ}{h}(E_m-E_k-h\nu)t\right\}}{E_m-E_k-h\nu}\right]$$

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

$$\int \psi^* \psi \, d\tau = \int \left(C_l^* \psi_l^* + C_m^* \psi_m^*\right)\left(C_l \psi_l + C_m \psi_m\right) d\tau$$

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

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

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

Eulers

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

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

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

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

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

Natural Line width

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

$$\Delta E \times \Delta t \simeq \frac{\hbar}{2} = \frac{h}{2\pi} \qquad 10^{-34}\ JS$$

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

excited electronic state lifetime $10^{-8}\ s$

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

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

electronic spin state lifetime $10^{-7}\ s$

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

Usual radiation frequency $10^{8} - 10^{9}\ s\ H_2$

Intensity of spectral lines

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

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

Beer–Lambert Law

Electronic spectroscopy

How do we define an electronic state?

Born-Oppenheimer Approximation

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

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

LUMO ___ ↓ ↑

HOMO ___ ↑↓

singlet ↑ ↑ triplet

— S_1 — T_1

— S_0

singlet $\left.\begin{matrix}\alpha(1)\alpha(2)\\ \beta(1)\beta(2)\end{matrix}\right\}$ $\left.\begin{matrix}\alpha(1)\beta(2)+\beta(1)\alpha(2)\\ \alpha(1)\beta(2)-\beta(1)\alpha(2)\end{matrix}\right\}$ symmetric with exchange.

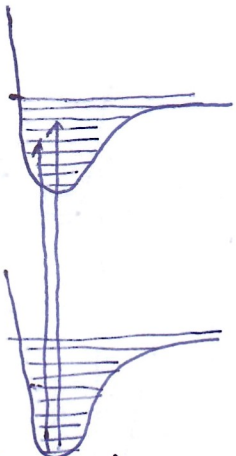
Triplet state is a combination of 3 wavefns.
Singlet " " a single wavefn

(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 involved a vertical transition.



Franck-Condon Principle

1926

* James Franck
* Edward Uhler Condon

Classically the Franck-Condon principle is the approximation that an electronic transition is most likely to occur without changes in the positions of the nuclei

$$TMI = \left\langle \Psi_{es}^{(2)}\Psi_v^{(2)} \middle| (\mu_N + \mu_e) \middle| \Psi_{es}^{(1)}\Psi_v^{(1)} \right\rangle$$

$$= \left\langle \Psi_{es}^{(2)}\Psi_v^{(2)} \middle| \mu_N \middle| \Psi_{es}^{(1)}\Psi_v^{(1)} \right\rangle + \left\langle \Psi_{es}^{(2)}\Psi_v^{(2)} \middle| \mu_e \middle| \Psi_{es}^{(1)}\Psi_v^{(1)} \right\rangle$$

$$= \left\langle \Psi_{es}^{(2)} \middle| \Psi_{es}^{(1)} \right\rangle \left\langle \Psi_v^{(2)} \middle| \mu_N \middle| \Psi_v^{(1)} \right\rangle + \left\langle \Psi_{es}^{(2)} \middle| \mu_e \middle| \Psi_{es}^{(1)} \right\rangle \left\langle \Psi_v^{(2)} \middle| \Psi_v^{(1)} \right\rangle$$

↑ electronic wavefns of same — different ⇑ zero

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~~Host: localhost~~

$$TMI = \langle \psi_v^{(2)} | \psi_v^{(1)} \rangle$$ Franck-Condon factor

If good overlap, then

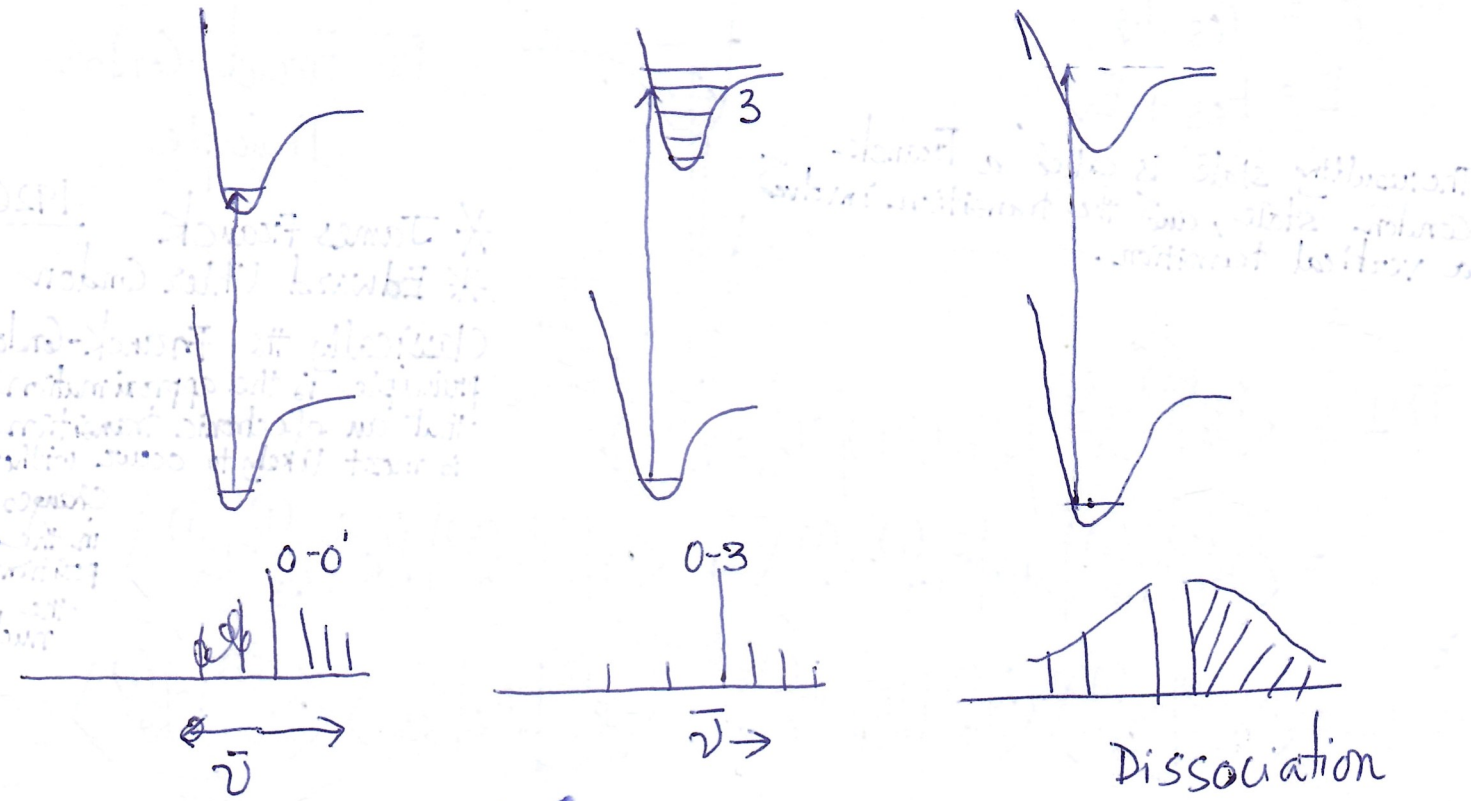
$$\psi_{es} = \psi_e \cdot \psi_s$$

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

↓ Symmetry of electronic wavefns. 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

Electronic Spectroscopy: Franck-Condon Factor

Born-Oppenheimer $\psi = \psi_{es}\,\psi_v\,\psi_r$

$\downarrow$

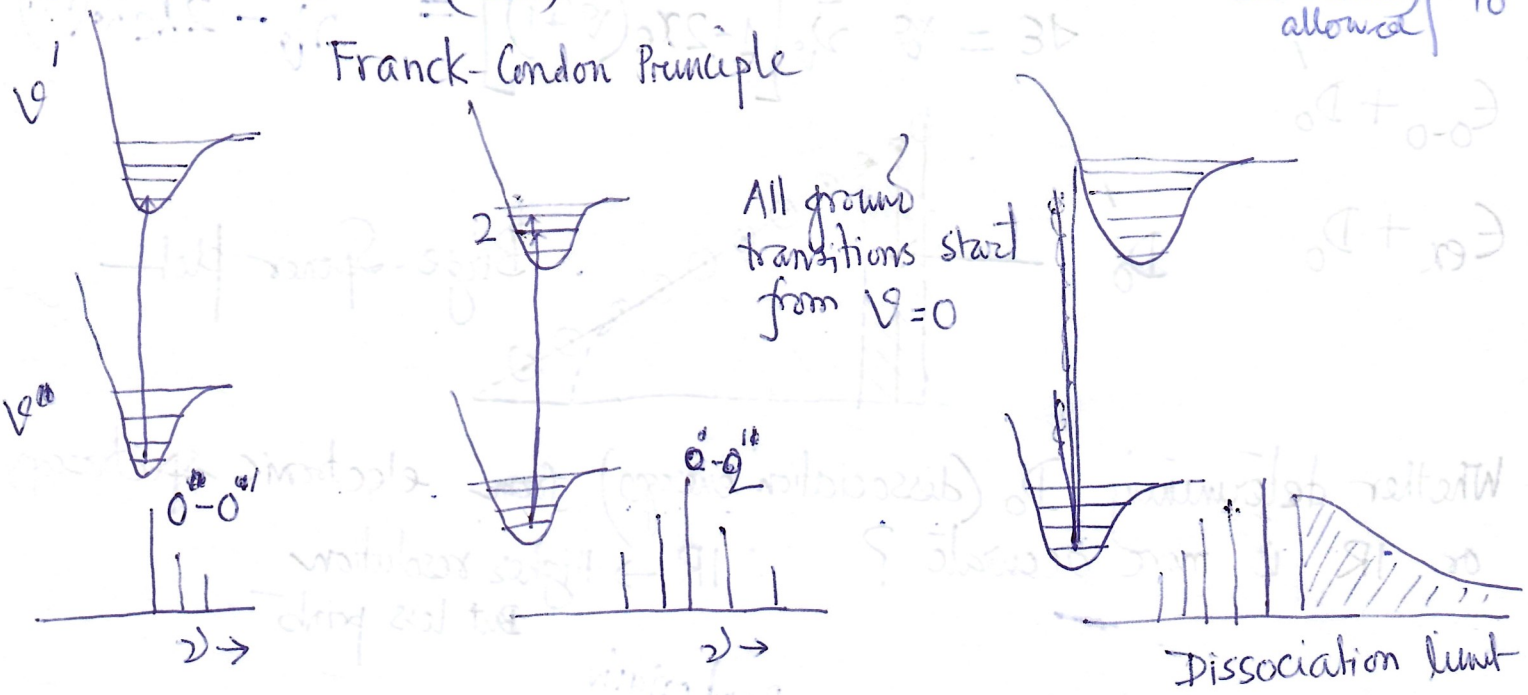
$\psi_e \cdot \psi_s$

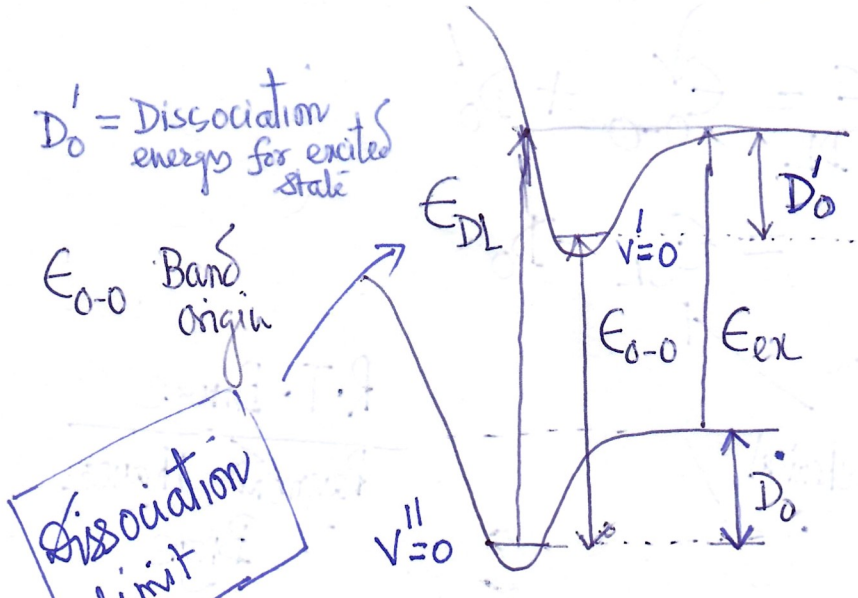
$$TMI = \langle \psi_v^{(2)} | \psi_v^{(1)} \rangle \langle \psi_{es}^{(2)} | \mu | \psi_{es}^{(1)} \rangle \langle \psi_s^{(2)} | \psi_s^{(1)} \rangle$$

Franck-Condon factor (χ (chi)) — Orbital selection — Spin selection

ε	
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 10^0

Franck-Condon Principle





ε represents energy

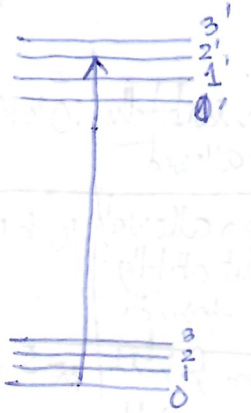
$$\epsilon_{DL} = \epsilon_{0-0} + D_0'$$

If dissociation limit is very well-defined and ϵ_{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

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

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



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

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

Born-Oppenheimer approximation

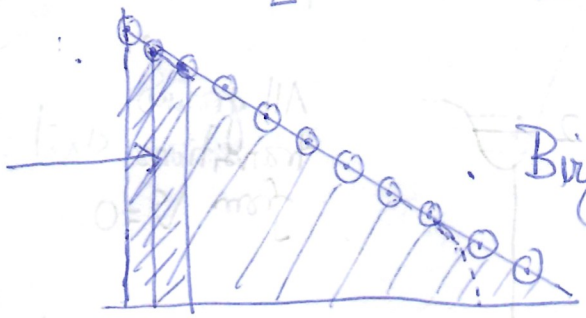
$$\epsilon_v = \left[\left(v+\tfrac{1}{2}\right)\bar{\nu}_v \chi_e - \left(v+\tfrac{1}{2}\right)^2 \chi_e \bar{\nu}_v\right]$$

$0 \rightarrow v'$
$0 \rightarrow v'+1$
} Two transitions

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

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

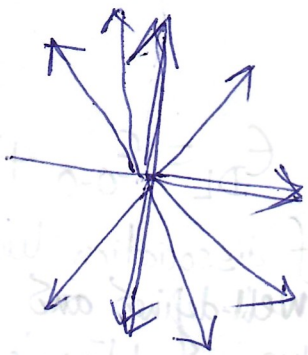
$= \epsilon_{ex} + D_0'$ $\quad D_0'$



. Birge-Sponer plot

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

IR → Higher resolution
But less points



Band origin

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

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

Can be determined from thermochemical

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