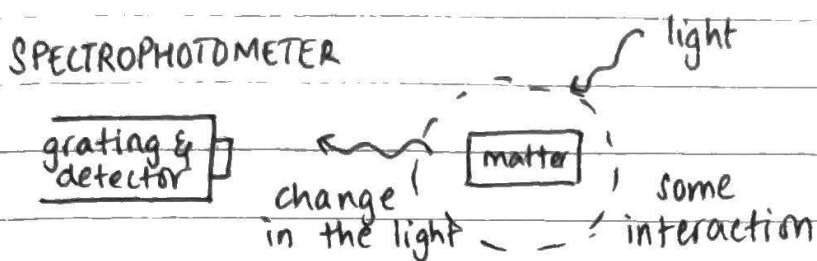


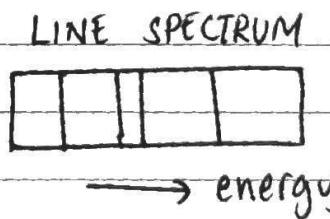
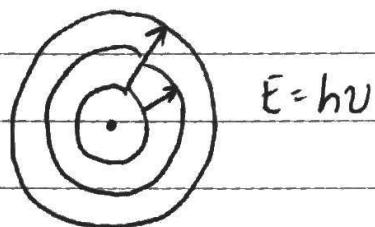
## UNIT 1

## Molecular Spectroscopy

- Using light as a probe to find out the structure of matter, in particular molecules.



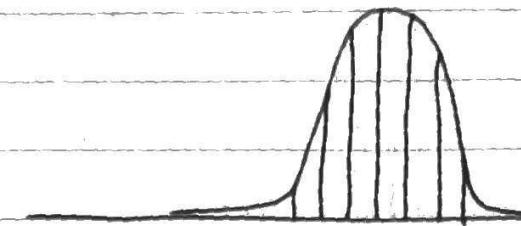
- Use the change and relate it to the structure of matter.
- use quantum mechanics, not classical
- Get spectrum in detector
- Bond length, bond angle etc.
- Molecular spectroscopy deals with interaction of EM radiation with matter (molecules) and is one of the richest probes into molecular structure.
- Atomic spectra tell us the difference in energy between electronic levels



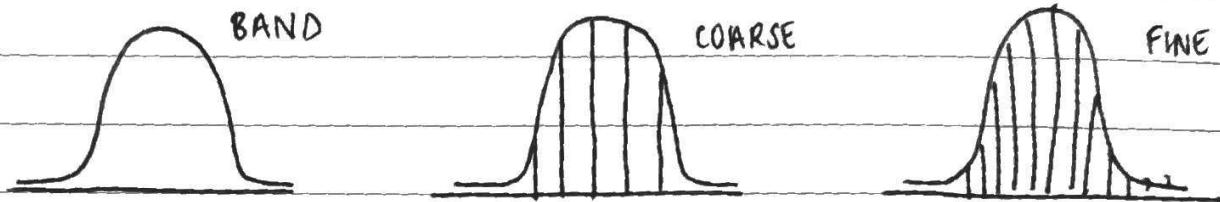
- Two energy levels with difference equal to energy of wavelength
- Atoms have atomic orbitals, molecules have molecular orbitals (combination of atomic)
- $\sigma$ ,  $\sigma^*$ ,  $\pi$ ,  $\pi^*$  etc.

- Light incident on electrons in molecular orbitals may also cause them to move to higher energy levels
- Molecular spectra, therefore, must also exist
- Instead of lines, bands are seen

BAND SPECTRUM



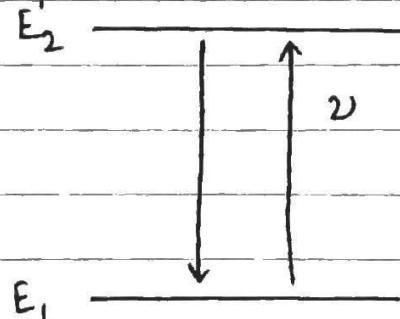
- Something else is also happening inside the molecule



- Molecules can vibrate when energy falls
- Non-electronic transitions also possible
- Electronic levels & vibrational levels.
- Fine lines due to rotation of molecule
- Rotational levels.
- More complicated process, but more information out of it.

### Quantisation of energy

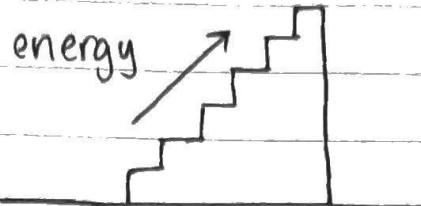
- Whenever energy is absorbed/emitted, it is always done in packets



$$\Delta E = E_2 - E_1 = h\nu$$

$$h = 6.626 \times 10^{-34} \text{ Js}$$

- Most times, absorption and not emission
- Always integer multiples of one quantum



- Difference in energy very small in fine spectra.
- Careful about units that are used in spectroscopy
- Wavenumber ( $\bar{\nu} = 1/\lambda \text{ cm}^{-1}$ ) is most commonly used.
- $\text{cm}^{-1}$  ( $1/\lambda = \bar{\nu}$ ) is a spectroscopic unit of energy.

Q: An absorption has  $\bar{\nu} = 1 \text{ cm}^{-1}$ . Calculate  $\Delta E$ .

$$\begin{aligned} A: \quad \Delta E &= hc\bar{\nu} = (6.626 \times 10^{-34} \text{ Js}) (3 \times 10^8 \text{ ms}^{-1}) (1 \text{ cm}^{-1}) (100) \\ &= 6.626 \times 3 \times 10^{-24} \text{ J} \\ \Delta E &= 1.9878 \times 10^{-23} \text{ J} = 1 \text{ cm}^{-1} \end{aligned}$$

$$1 \text{ cm}^{-1} = 1.99 \times 10^{-23} \text{ J}$$

- If energy wasn't quantised, continuous spectrum would be formed, and no discrete lines.
- Band spectra: discrete, very close lines.

continuous

discrete

## ELECTROMAGNETIC SPECTRUM

- Each region of EM spectrum tells us the scale of energy difference between energy levels.

### 1. Radiowave region

$$\lambda = 10\text{ m} - 1\text{ cm}$$

$$E = 0.001 - 10 \text{ J mol}^{-1}$$

- Information on:

- Nuclear spin reversal
- Electron spin reversal

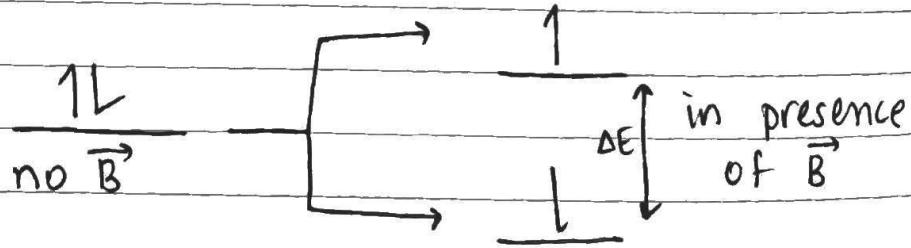
- Spectroscopy:

- Nuclear Magnetic Resonance (NMR)
- Electron Spin Resonance (ESR) or Electron Paramagnetic Resonance (EPR)

#### — Electron Spin Resonance

- In the presence of  $\vec{B}$ , orbital splits into two; one higher and one lower in energy (no longer degenerate)

- Electron spin changes; electron doesn't transition

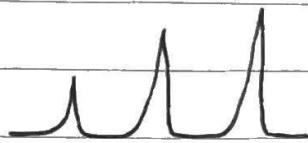
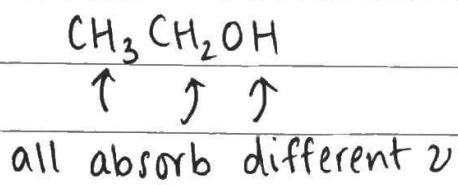


- Radio frequency causes these transitions
- Usually free radicals

## ↳ Nuclear Magnetic Resonance

- Nuclei also possess spin (particular  $\nu$ )
- In presence of  $\vec{B}$ , splits into two levels ( $\nu_1, \nu_2$ )
- Light incident also possesses particular  $\nu$
- Two levels - two spins
- Not all nuclei; usually for organic molecules.
- Proton NMR ( $^1\text{H}$ )
- $^{13}\text{C}$  NMR

Example:



- Proton spinning in  $\vec{B}$ , splits
- OH absorbs at one  $\nu$ ; splitting energy more/less.

## 2. Microwave region

$$\lambda = 1\text{ cm} - 100\mu\text{m}$$

$$E = 100 \text{ J mol}^{-1}$$

- Information on:
  - Rotational levels
- Spectroscopy:
  - Rotational spectroscopy or Microwave spectroscopy
- Molecule is rotating (dipole changes)
- Fluctuating  $\vec{E}$  due to rotation
- If  $\nu_{\text{rot}}$  matches  $\nu_{\text{light}}$ , energy absorbed
- Molecule goes to next rotational level.
- Used interstellar; Mars

Example:



- Polar molecule responds to rotational spectroscopy



- No net dipole moment; no  $\vec{E}$  field
- Does not respond to rotational spectroscopy
- As molecules become heavier, rotation reduces
- Will study further in detail.
- In some cases, instantaneous dipoles show spectra, but not as often.
- H replaced with O for better results.

### 3. Infrared region

$$\lambda = 100\mu\text{m} - 1\mu\text{m}$$

$$E = 10^4 \text{ J mol}^{-1}$$

- Information on:
  - vibrational levels
- Spectroscopy:
  - Vibrational spectroscopy or Infrared spectroscopy
- When dipole stretches,  $\vec{E}$  fluctuates at certain  $\nu$
- Absorbs IR radiation at resonance
- Vibrational levels separated by energy in the order of IR.
- Vibrational levels farther apart than rotational levels.



- Dipole moment of  $\text{H}_2\text{O}$  changes.

- $\text{CO}_2$  may bend while vibrating



- Depends on mode of vibration
- $\text{CO}_2$  is active in IR region even though it has no net dipole moment.

#### 4. Visible & Ultraviolet region

$$\lambda = 1\mu\text{m} - 10\text{ nm}$$

$$E = 100 \text{ kJ mol}^{-1}$$

- Information on:
  - Electronic levels (valence  $e^-$ )
- Spectroscopy
  - Electronic spectroscopy / UV-vibrational spectroscopy
- $\text{CuSO}_4$  absorbs at 620 nm; looks blue due to absorption of complement.
- Electronic levels much farther apart
- In bands, fine lines due to vibration & rotation
- Valence  $e^-$  undergo transitions
- UV/Visible spectrophotometer

## 5. X-Ray Region.

$$\lambda = 100 \text{ pm} - 1 \text{ pm}$$

$$E = 10^9 - 10^{11} \text{ J g}^{-1} \text{ atom}^{-1}$$

- Information on

- ~~Nuclear arrangement~~ Inner  $e^-$  electronic lev

- Spectroscopy

- X-ray Spectroscopy

- Not valence  $e^-$ ; inner shell  $e^-$

- Valence  $e^-$  may go for photoelectric emission

## 6. $\gamma$ -Ray Region

$$\lambda = 100 \text{ pm} - 1 \text{ pm}$$

$$E = 10^9 - 10^{14} \text{ J g}^{-1} \text{ atom}^{-1}$$

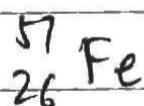
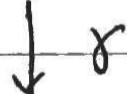
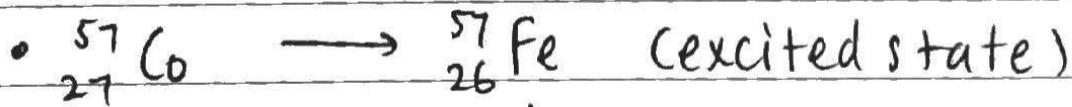
- Information on

- Nuclear rearrangement

- Spectroscopy

-  $\gamma$  ray spectroscopy (GRS) used in astrophysics

- Used in Mars mission



- Geiger counter

- Not molecules; nuclei & atoms

- Strong nuclear force requires  $\gamma$  to overcome attraction

## Types of Energies a Molecule Possesses

1. Translational energy -  $E_{trans}$

2. Rotational energy -  $E_{rot}$

- due to rotation of molecule about its COM

3. Vibrational energy -  $E_{vib}$

- due to periodic displacement of its atoms from their equilibrium position

4. Electronic energy -  $E_{elec}$

- due to the arrangement of electrons in the molecule

- Way too complicated to account for all these variables.
- Come up with an appropriate approximation.

### BORN-OPPENHEIMER APPROXIMATION

- The total energy of a molecule

$$E_{total} = E_{trans} + E_{rot} + E_{vib} + E_{elec}$$

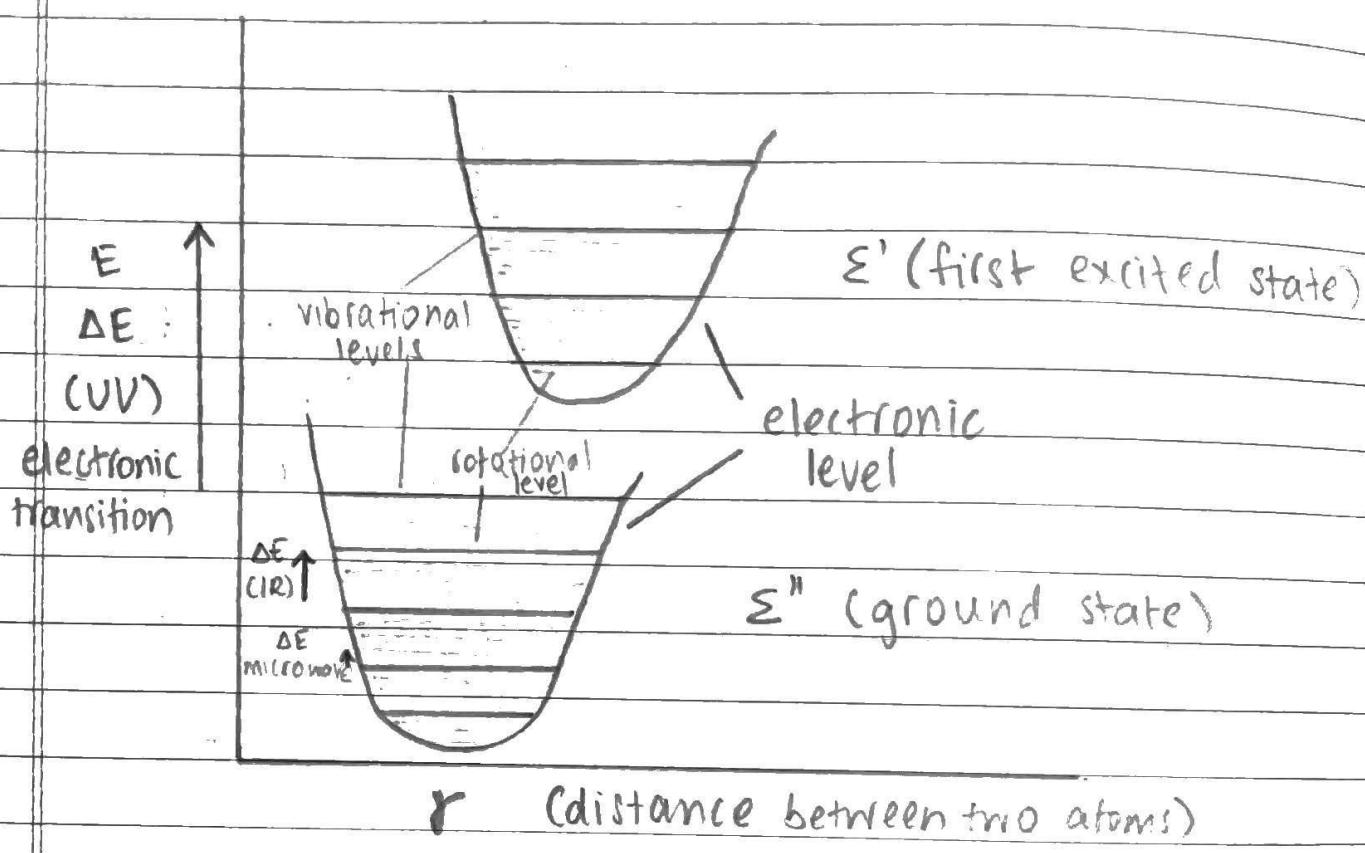
- Ignoring coupling
- Effects of rotation on vibration, vibration on translation etc
- All four energies are separate and independent
- Electronic levels are much farther apart than rotational, vibrational etc
- Nuclear rotation & vibration, NOT ELECTRONIC
- Electrons move much faster than nuclei
- From  $e^-$  point of view, nucleus is stationary

- Reasoning

$E_{\text{elec}} \gg E_{\text{vib}} \gg E_{\text{rot}} \gg E_{\text{trans}}$   
and can be treated independently

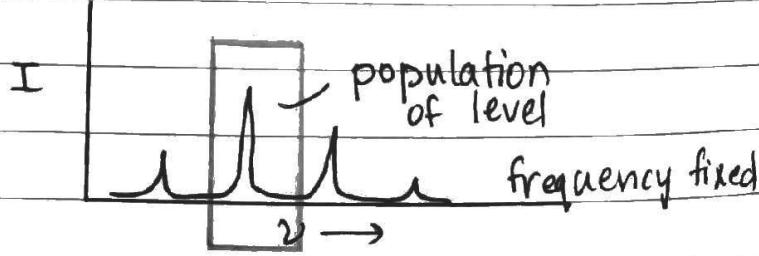
- Translational levels are extremely close to each other
- We don't have devices sensitive enough to see lines; we see a continuum

Energy level diagram for a diatomic molecule



### BEER - LAMBERT'S LAW

- no. of transitions
- concentration of species
- talk about a fixed  $\lambda$



- $I_0 =$  incident light reflection

$$I_0 = I_a + I_t + I_r \rightarrow \text{can be ignored}$$

absorbed transmitted

(only turbid solution)

- Transmittance =  $\frac{I_t}{I_0} = T$ ; Absorbance =  $-\log \frac{I_t}{I_0} = A$  or Optical density

### LAMBERT'S LAW

- When monochromatic light passes through a homogeneous medium, the rate of decrease in intensity with thickness is proportional to the intensity of light.

$$I_t = I_0 10^{-kl}$$

$$A = \log \frac{I_0}{I_t} = kl$$

$l$  = path length

- If path length more,  $A$  more
- $A \propto l$

### BEER'S LAW

- When monochromatic light passes through a homogeneous medium, rate of decrease in intensity with concentration is proportional to the intensity of light.

$$I_t = I_0 10^{-kc^2}$$

$$A = \log \frac{I_0}{I_t} = k'c$$

$c$  = concentration of light-absorbing species

### LAMBERT-BEER'S LAW

- Combining the two

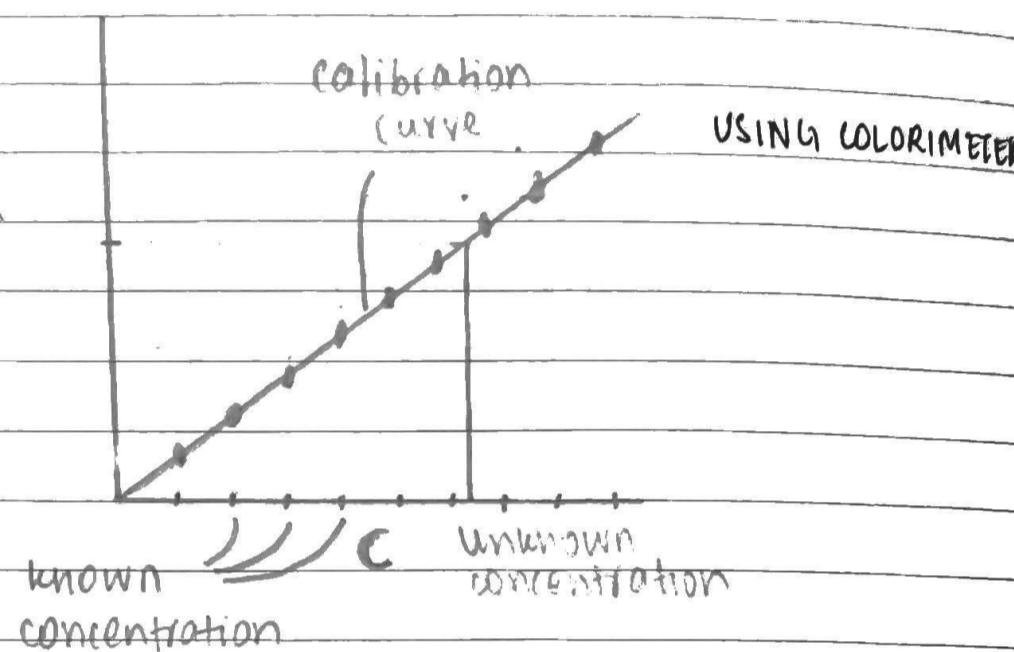
$$A = \log \frac{I_0}{I_t} = \Sigma cl$$

- $A \propto l$ ,  $A \propto c$ ,  $A = \epsilon cl$

- $A = \epsilon cl$  molar absorption coefficient

Lambert - Beer's Law

- Use it to determine concentration of unknown solution
- In the same sample holder, diameter of tube (cuvette) is path length  $\ell$  is constant
- $\therefore A \propto C$



Q: A sample of  $CuSO_4$  absorbs at 620 nm and absorbance is 0.14.  $[CuSO_4] = 0.5\text{ M}$ , path length is 9 mm. Find  $\epsilon$  in  $\text{cm}^2 \text{ mol}^{-1}$ .

A:  $A = \epsilon Cl$

$$C = 0.5 \text{ mol L}^{-1} = 0.5 \times 10^{-3} \text{ mol cm}^{-3}$$

$$\ell = 9 \text{ mm} = 0.9 \text{ cm}$$

$$A = 0.14$$

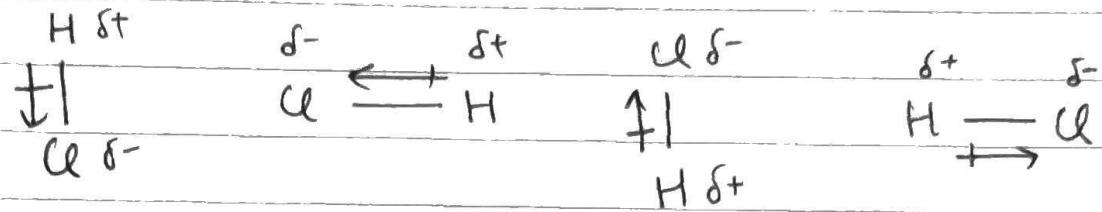
$$0.14 = \epsilon \times 0.5 \times 10^{-3} \times 0.9 = 45 \times 10^{-5} \times \epsilon$$

$$\epsilon = \frac{0.14 \times 10^3}{0.45} = 0.31 \times 10^3 \text{ cm}^2 \text{ mol}^{-1}$$

$$\epsilon = 3.1 \times 10^2 \text{ cm}^2 \text{ mol}^{-1}$$

## Rotational Spectroscopy

- Source of light - microwave region
- Constantly changing dipole



- frequency of rotation matches with microwave frequency (microwave active)
- Not possible for N≡N (microwave inactive)

### MICROWAVE ACTIVE

- HCl
- CO
- CHCl<sub>3</sub>
- O=C=S

### MICROWAVE INACTIVE

- N<sub>2</sub>
- CO<sub>2</sub>
- homonuclear diatomic molecules
- CH<sub>4</sub>

## Expression for rotational energy levels

- Simplest form - heteronuclear diatomic molecule
- Rigid rotator - rotation causes no distortion

rigid rod connecting the centres.

model for heteronuclear molecule

- Discussion of moment of inertia, angular momentum.

— Moment of inertia for a rigid rotor

$$m_1r_1 = m_2r_2 \quad (\text{torque about CM} = 0)$$

$$r_0 = r_1 + r_2$$

$$I = m_1r_1^2 + m_2r_2^2$$

$$\begin{aligned} I &= m_1 r_1^2 + m_2 r_2^2 \\ &= m_2 r_2 r_1 + m_1 r_1 r_2 \\ I &= (m_1 + m_2) r_1 r_2 \end{aligned}$$

$$\begin{aligned} m_1 r_1 = m_2 r_2 &= m_2 (r_0 - r_1) \\ r_1 (m_1 + m_2) &= m_2 r_0 \end{aligned}$$

$$r_1 = \frac{m_2 r_0}{m_1 + m_2}$$

$$\begin{aligned} m_2 r_2 &= m_1 (r_0 - r_2) \\ r_2 (m_1 + m_2) &= \frac{m_1 r_0}{m_1 + m_2} \end{aligned}$$

$$r_2 = \frac{m_1 r_0}{m_1 + m_2}$$

$$\begin{aligned} I &= (m_1 + m_2) r_1 r_2 \\ &= (m_1 + m_2) \frac{m_2 r_0}{(m_1 + m_2)} \frac{m_1 r_0}{(m_1 + m_2)} \end{aligned}$$

$$I = \frac{m_1 m_2}{m_1 + m_2} r_0^2$$

We define  $\mu = \frac{m_1 m_2}{m_1 + m_2}$  (reduced mass)

$$I = \mu r_0^2$$

## Energy levels of a rigid rotor

$$L = I\omega$$

$$E = \frac{1}{2} I \omega^2 = \frac{(I\omega)^2}{2I} = \frac{L^2}{2I}$$

- Use solution of Schrödinger equation for rigid rotor

$$L = \sqrt{J(J+1)} \frac{\hbar}{2\pi}$$

where  $J$  = rotational quantum number

$$J = 0, 1, 2, 3 \dots$$

- Angular momentum of rigid rotor is quantised; cannot take up all values.

$$E = \frac{L^2}{2I} = \frac{J(J+1) \hbar^2}{4\pi^2 \cdot 2I}$$

$$E_J = \frac{J(J+1) \hbar^2}{8\pi^2 I}$$

where  $J=0,1,2\dots$

- ∴ rotational energy levels are quantised

$$\text{To convert to } \text{cm}^{-1} : E = \frac{hc}{\lambda}$$

$$\frac{E_J}{hc} = \frac{h}{\frac{8\pi^2 c I}{\lambda}} J(J+1)$$

constant

$$\Sigma_J = B J(J+1) \text{ cm}^{-1}$$

$B$  = rotational constant

$$B = \frac{h}{8\pi^2 c I} \text{ in } \text{cm}^{-1} \text{ (spectroscopic units)}$$

$$B = \frac{h^2}{8\pi^2 I} \text{ in Joules}$$

Energy level diagram for a diatomic molecule

- Rotational levels; radius ( $r$ ) is constant.
- $\epsilon$  as a function of  $J$ , not  $r$ .

$$\epsilon_J = B J(J+1)$$

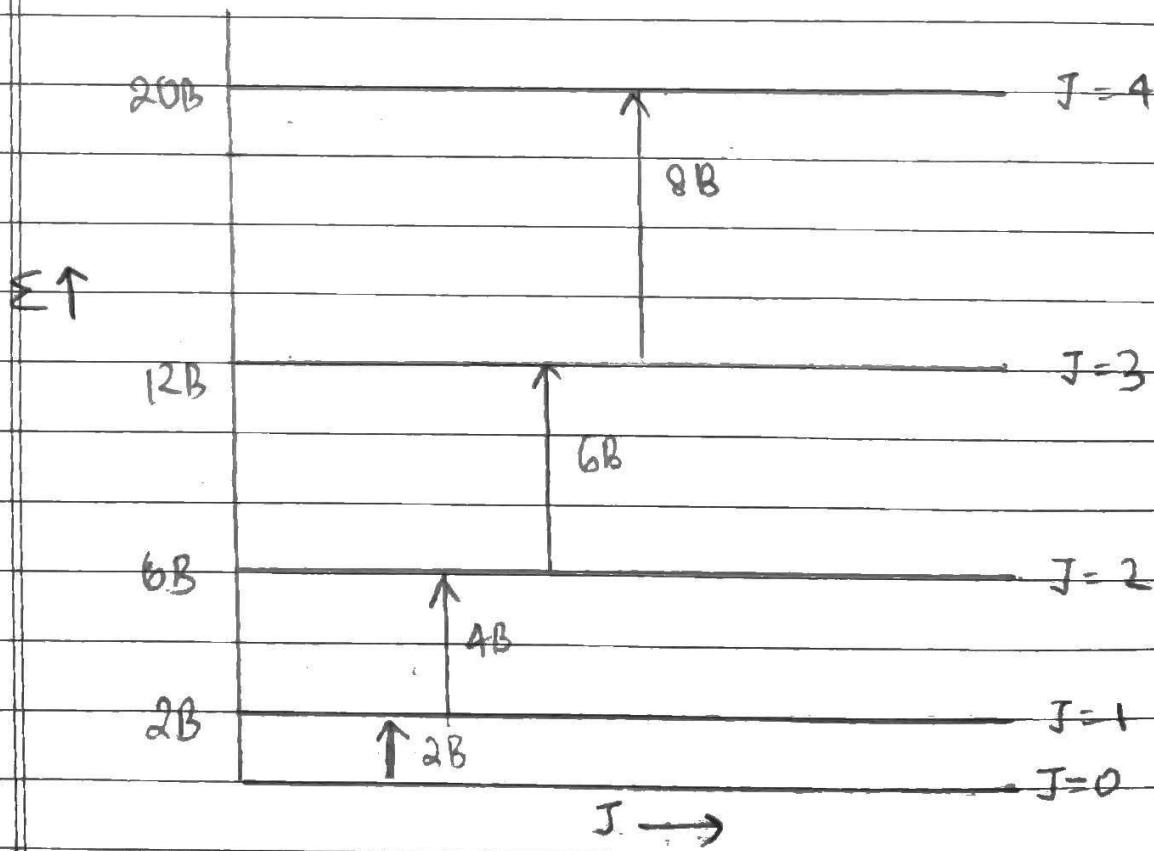
$$J=0, \epsilon_0 = 0$$

$$J=1, \epsilon_1 = 2B$$

$$J=2, \epsilon_2 = 6B$$

$$J=3, \epsilon_3 = 12B$$

$$J=4, \epsilon_4 = 20B$$



- Energy level difference (consecutive levels)

$$\begin{aligned}\Delta \epsilon_{J+1 \rightarrow J} &= B(J+1)(J+2) - B(J)(J+1) \\ &= B(J+1)(J+2-J) \\ &= 2B(J+1) \text{ cm}^{-1}\end{aligned}$$

$$\Delta \Sigma_{1 \rightarrow 0} = 2B$$

$$\Delta \Sigma_{2 \rightarrow 1} = 4B$$

$$\Delta \Sigma_{3 \rightarrow 2} = 6B$$

$$\Delta \Sigma_{4 \rightarrow 3} = 8B$$

- Energy gap is increasing

- Energy gap is in the microwave range

Q. Calculate rotational constant B for  $^{12}\text{C}^{16}\text{O}$  molecule if  $r_{\text{CO}} = 0.113 \text{ nm}$  in spectroscopic units.

Ans:

$$B = \frac{h}{8\pi^2 I c}$$

$$I = \mu r_{\text{CO}}^2$$

$$\mu = \frac{m_e m_o}{m_e + m_o}$$

$$\mu_g = \frac{(16)(12)}{(16+12)} \times \frac{1}{N_A} = \frac{(4)(12)}{(7)(N_A)} = \frac{48}{7N_A} = \frac{48 \times 10^{-23}}{7 \times 6.022}$$

$$\mu_g = \frac{48 \times 10^{-26}}{7 \times 6.022} = 1.1387 \times 10^{-26}$$

$$r_{\text{CO}} = 1.13 \times 10^{-10} \text{ m}$$

$$I = \mu r_{\text{CO}}^2 = 1.13 \times 10^{-26} \times (1.13)^2 \times 10^{-20} \\ = 1.454 \times 10^{-46}$$

$$B = \frac{h}{I 8\pi^2 c} = \frac{(6.626) (10^{-34})}{(1.454 \times 10^{-46}) (8\pi^2) (3) (10^8)}$$

$$B = \frac{(6.626) (10^4)}{(1.454) (3) (8) (\pi^2)} = 1.924 \times 10^2 \text{ m}^{-1}$$

$$B = 1.924 \times 10^2 \text{ m}^{-1}$$

$$B = 1.924 \text{ cm}^{-1}$$

In Joules,

$$\begin{aligned}
 B' &= (hc) (1.916 \text{ cm}^{-1}) (10^2) \\
 &= (6.626) (10^{-34}) (3) (10^{10}) (1.916) \\
 &= (6.626) (3) (1.916) (10^{-24}) \\
 &= 38.08 \times 10^{-24}
 \end{aligned}$$

$$B' = 3.808 \times 10^{-23} \text{ J}$$

$$B' = 3.8 \times 10^{-23} \text{ J}$$

## Spectrum

### — Selection rules

#### 1. Gross selection rule

- molecule should possess permanent dipole moment

#### 2. Specific rule for rigid rotor (Schrödinger equation)

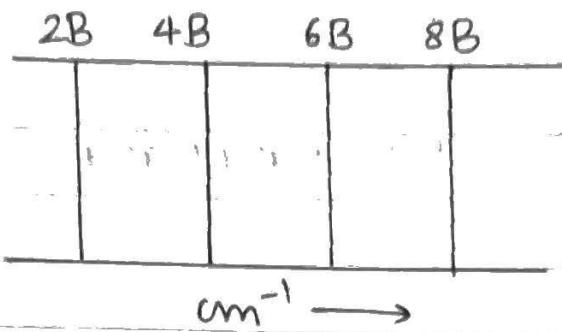
- $\Delta J = \pm 1$  (only consecutive transitions)

$$J=0 \longrightarrow J=1 \quad \Delta E_J = 2B$$

$$J=1 \longrightarrow J=2 \quad \Delta E_J = 4B$$

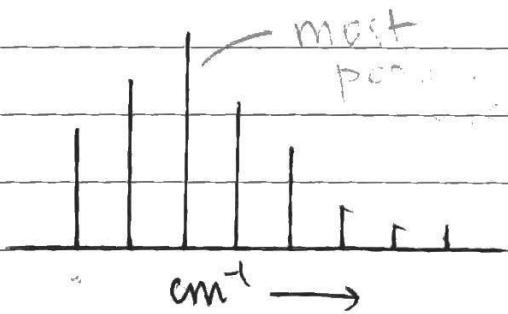
$$J=2 \longrightarrow J=3 \quad \Delta E_J = 6B$$

$$J=3 \longrightarrow J=4 \quad \Delta E_J = 8B$$



- In the spectrum, the spectral lines are equidistant
- Only the rotational spectral lines are, not the energy levels
- From spectrum can obtain gap =  $2B$
- calculate  $B$
- Then calculate  $I$
- Then calculate  $r_0$  (bond length)
- From rotational spectroscopy, bond length can be determined.

$$B = \frac{\hbar^2}{8\pi^2 I}$$



- Intensity due to population of energy levels
- More molecules are moving from  $J=2 \rightarrow J=3$
- Even higher levels are populated
- Thermal energy at room temperature sufficient for molecules to be at higher levels
- Energy levels closer together than vibrational
- Normally would expect  $J=0 \rightarrow J=1$  to be most populated.

Q: For  $^{12}\text{C}^{16}\text{O}$  molecule, first line appears at  $3.842\text{ cm}^{-1}$   
 Find out bond length (pm).  $\hbar = 6.626 \times 10^{-34} \text{ Js}$   
 $c = 3 \times 10^8 \text{ m s}^{-1}$

A: First line:  $2B = 3.842 \text{ cm}^{-1}$

$$B = 1.921 \text{ cm}^{-1} = 1.921 \times 10^2 \text{ m}^{-1}$$

$$B = \frac{\hbar}{8\pi^2 I c} \text{ in } \text{m}^{-1}$$

$$I = \frac{\hbar}{8\pi^2 c B} = \frac{6.626 \times 10^{-34}}{8 \times 3.14 \times 3.14 \times 3 \times B} \times 10^{-8}$$

$$I = \frac{0.028 \times 10^{-42}}{B} = \frac{2.8 \times 10^{-44}}{1.921} \times 10^{-2}$$

$$I = 1.458 \times 10^{-46} \text{ kg m}^2$$

$$I = \mu r_0^2$$

$$\mu = \frac{(12)(16)}{(12+16)} = \frac{12 \times 16}{28} \text{ amu}^3$$

$$\mu = \frac{3 \times 16}{7 \times N_A} = \frac{48}{7 \times 6.023} \times 10^{-23}$$

$$\mu = 1.138 \times 10^{-26} \text{ kg}$$

$$r_0^2 = \frac{1.458 \times 10^{-46}}{1.138 \times 10^{-26}} = 1.28 \times 10^{-20}$$

$$r_0^2 = 1.28 \times 10^{-24}$$

$$r_0 = 1.13 \times 10^{-10} \text{ m}$$

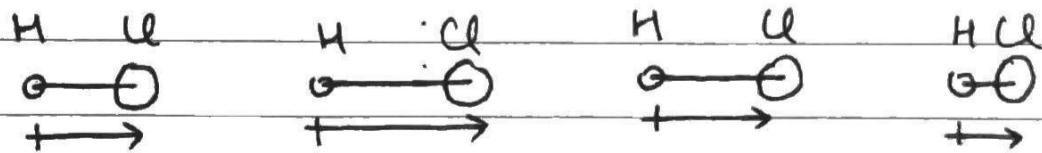
$$r_0 = 113 \times 10^{-12} \text{ m}$$

$r_0 = 113 \text{ pm}$

- Food in microwave oven
- Water molecules undergoes rotation
- Molecules coming back down give out thermal energy.
- Microwave radiation causes change in rotational levels.
- Food gets colder faster from microwave oven
- Why no metal?
  
- Metals reflect microwave radiation and if nothing absorbs it, the radiation can start a fire and pose as a hazard
  
- Synthesis of biodiesel in plant: 2 hours in microwave oven: 15 minutes.
- Greener way to synthesise
- Cryston - source of microwave
- Any experiment in microwave region should be moisture free as  $H_2O$  interferes with experiment by absorbing radiation.

### $\ddot{O}$ VIBRATIONAL SPECTROSCOPY

- Infrared radiation
- Vibration of molecule

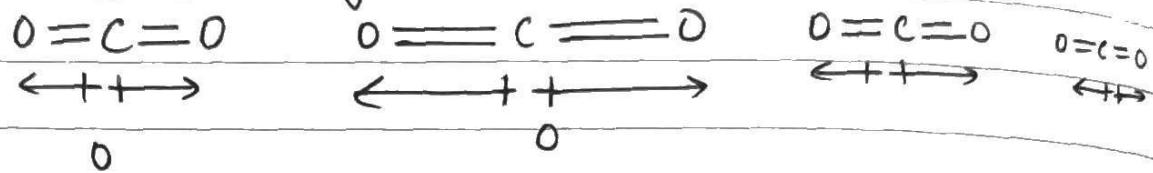


- Dipole moment continuously fluctuating for heteroatomic diatomic molecule.
- Has to be a change in the dipole moment during vibration

- For homonuclear diatomic molecules ( $N_2$ ,  $H_2$  etc), they will be IR inactive.

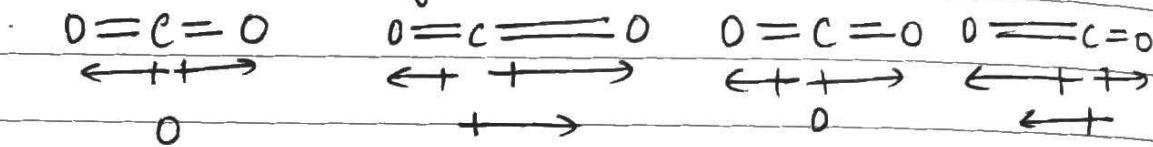
Exception:  $CO_2$  modes of vibration

← Symmetric stretching



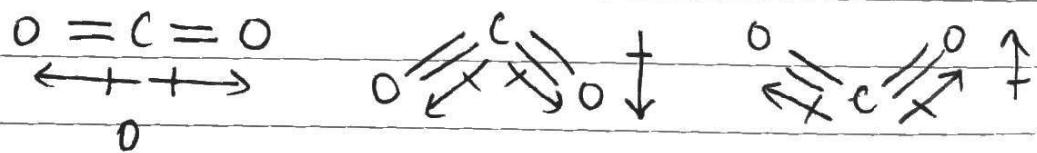
- IR inactive during symmetric stretching

← Asymmetric stretching



- IR active during asymmetric stretching

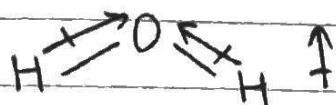
← Bending vibration



- IR active during bending motion

- A sample of  $CO_2$  is IR active (bending & asymmetric stretching) and microwave inactive
- Does not possess permanent dipole moment.

- $H_2O$  is IR active in all modes of vibration (different frequencies)



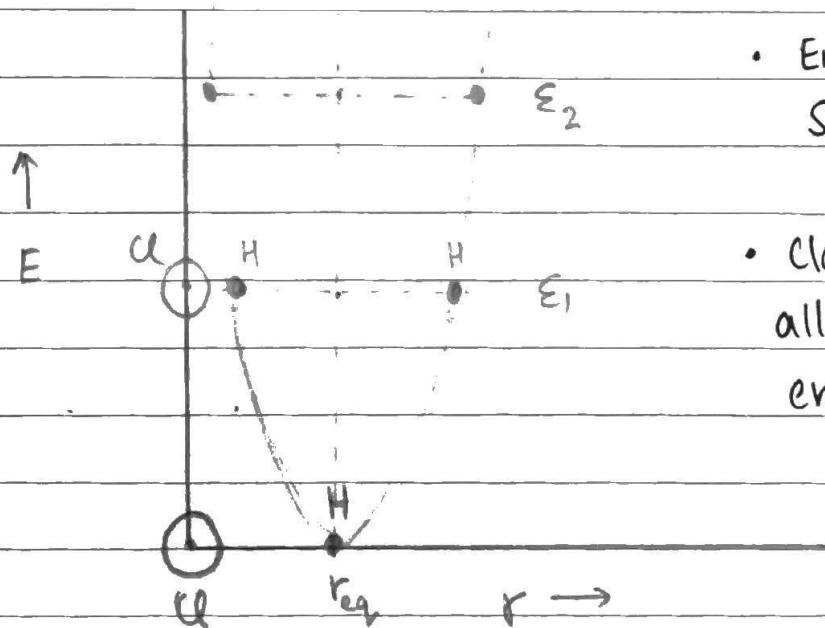
- Vibration of molecule must change the dipole moment

### Vibrational Energy levels in a diatomic molecule.

- Morse curve of energy of diatomic molecule
- Model to describe vibrational molecules
- Simple harmonic oscillator (ideal - follows Hooke's Law)



- Hooke's Law:  $F = -kx$ ;  $k = \frac{F}{x}$ ;  $E = \frac{1}{2}kx^2$
- If  $k$  is high, large amount of force required for minute displacement.



• Energy profile of SHO is a parabola

• Classical picture allows all possible energy values

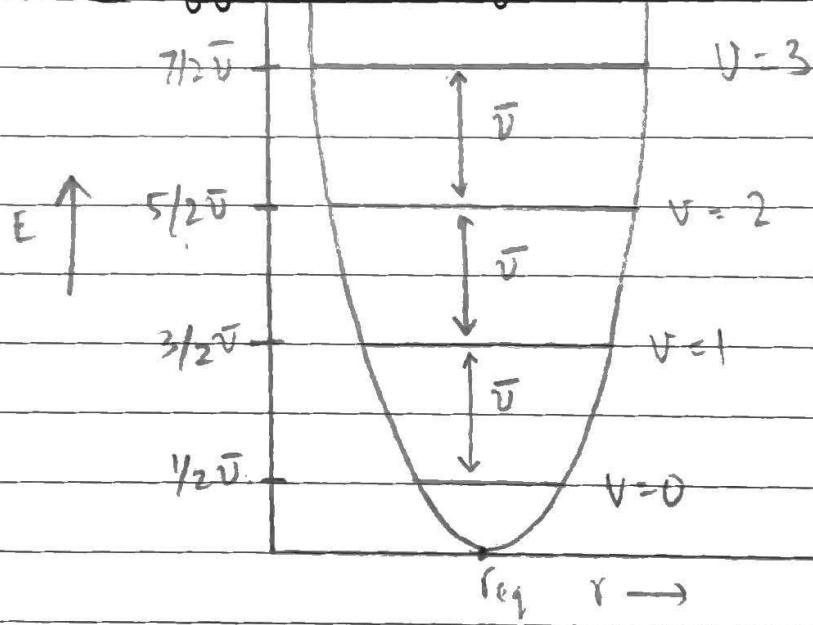
$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \text{ (Hz)}$$

- Every molecule vibrates with a characteristic frequency
- Adding energy does not alter the frequency; only amplitude

$$\bar{\nu} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}} \text{ (cm}^{-1}\text{)}$$

- If  $\bar{v}$  is known,  $k$  can be calculated
- $k$  represents bond strength
- Using vibrational spectrum, bond strength can be calculated
- Need to find solution of Schrödinger equation for simple harmonic oscillator.
- $E = (v + \frac{1}{2}) \hbar \bar{v}$  (Joules)
- $v$  = vibrational quantum number.
- $v = 0, 1, 2, 3 \dots$
- Vibrational energy levels are quantised.
- $\Sigma_v = (v + \frac{1}{2}) \bar{v}$  ( $\text{cm}^{-1}$ )

### Energy level diagram for a diatomic molecule (SHO)



$$\text{When } v=0, \Sigma_0 = \frac{1}{2} \bar{v}$$

$$v=1, \Sigma_1 = \frac{3}{2} \bar{v}$$

$$v=2, \Sigma_2 = \frac{5}{2} \bar{v}$$

$$v=3, \Sigma_3 = \frac{7}{2} \bar{v}$$

- Energy gap between vibrational energy levels is constant

$$\Delta \Sigma_v = (v+1+\frac{1}{2})\bar{\nu} - (v+\frac{1}{2})\bar{\nu}$$

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

- Even at  $v=0$  level, molecule possesses ~~zero~~ energy
- A molecule is never at rest; it is always vibrating.
- At  $v=0$ ,  $\Sigma_v = \frac{1}{2} \bar{\nu}$  (zero point energy)
- For macromolecules,  $\mu$  is very high, and  $\bar{\nu}$  is very low.

## Spectrum

### Selection rules

#### 1. Gross selection rule

- When the molecule undergoes vibration, there should be a change in the dipole moment

#### 2. Specific selection rule for simple harmonic oscillator

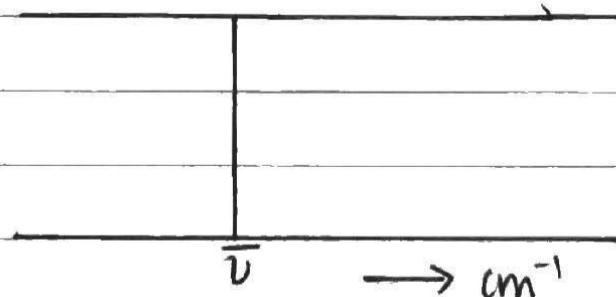
$$\Delta v = \pm 1 \text{ (only consecutive transitions)}$$

$$v=0 \longrightarrow v=1 \quad \Delta \Sigma_v = \bar{\nu}$$

$$v=1 \longrightarrow v=2 \quad \Delta \Sigma_v = \bar{\nu}$$

$$v=2 \longrightarrow v=3 \quad \Delta \Sigma_v = \bar{\nu}$$

$$v=3 \longrightarrow v=4 \quad \Delta \Sigma_v = \bar{\nu}$$



- Single spectrum line  $\rightarrow$  simple harmonic oscillator
- From spectrum, bond strength can be found
- $v=0$  most populated level

- Most transitions are  $v=0$  to  $v=1$

Q: A single intense line is observed for HCl molecule at  $2890 \text{ cm}^{-1}$ . Find out the force constant in  $\text{Nm}^{-1}$  (bond strength).

A:  $h = 6.626 \times 10^{-34} \text{ Js}$        $\bar{v} = 2890 \text{ cm}^{-1}$

$$M = 1.00 \text{ g}$$

$$\text{Cl} = 35.5 \text{ g}$$

$$M_{\text{amu}} = \frac{(1)(35.5)}{(36.5)}$$

$$\boxed{\bar{v} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}}}$$

$$\mu_{\text{kg}} = \frac{35.5 \times 10^{-3}}{36.5 \times 6.022 \times 10^{23}}$$

$$\mu_{\text{kg}} = \frac{35.5}{36.5 \times 6.022} \times 10^{-26} = 1.615 \times 10^{-27} \text{ kg.}$$

$$\bar{v} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}} \Rightarrow k = \bar{v}^2 4\pi^2 c^2 \mu$$

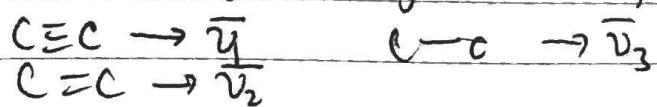
$$\begin{aligned} k &= (28.9)^2 \times 4\pi^2 c^2 \mu \times 10^8 \\ &= 478773 \times 10^{16} \times 10^{-27} \times 10^8 \\ &= 4.79 \times 10^{21} \times 10^{-27} \times 10^8 \\ &= 4.79 \times 10^{-6} \times 10^8 \end{aligned}$$

$$\boxed{k = 479 \text{ Nm}^{-1}}$$

NOTE: 1 amu =  $1.67 \times 10^{-27} \text{ kg}$

- $\bar{v} \propto \sqrt{k}$ ;  $\bar{v} \propto 1/\sqrt{\mu}$
- Energy of absorption increases with bond strength

Eg:  $\bar{v}_1 > \bar{v}_2 > \bar{v}_3$ , assign to C-C, C≡C, C=C.



Eg: assume  $k$  is constant:

$$\bar{v}_1 > \bar{v}_2 > \bar{v}_3 > \bar{v}_4$$

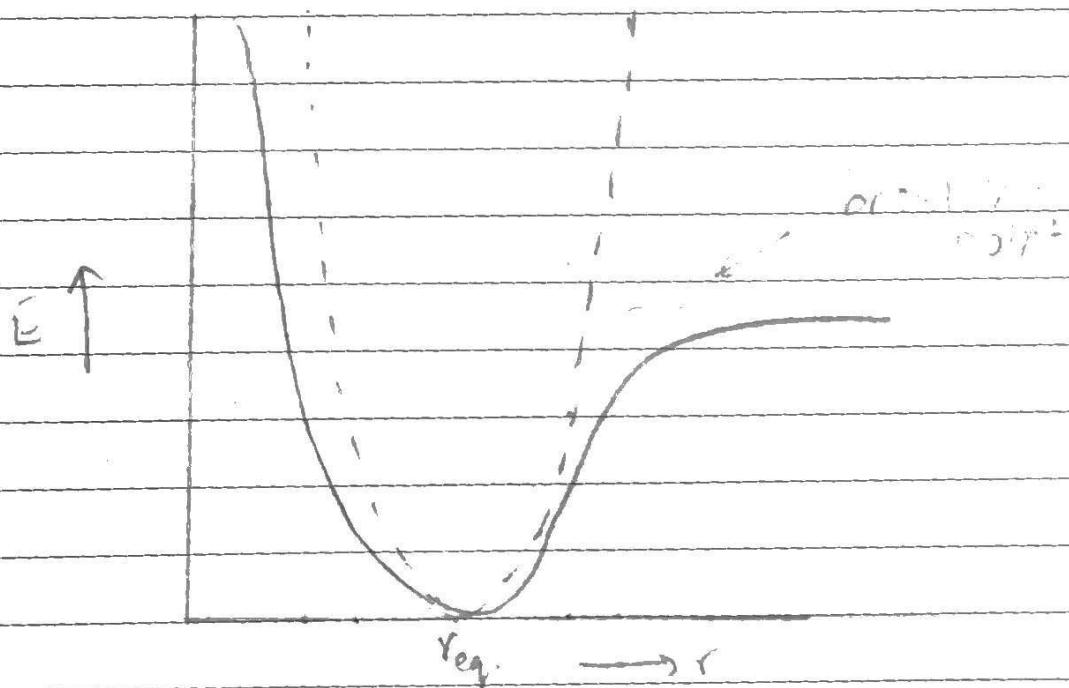
$$C-F : \bar{v}_2$$

$$C-Cl : \bar{v}_3$$

$$C-H : \bar{v}_1$$

$$C-Br : \bar{v}_4$$

- Simple harmonic oscillator is the ideal case
- If the oscillator stretches too much, it will break (not complete picture)
- All vibrations, therefore, are not elastic in nature.
- Need a better model; anharmonic oscillator.



### Anharmonic Oscillator Model

- Solve Schrödinger equation for anharmonic oscillator.

$$\Sigma = (v + 1/2) \bar{v}_e - (v + 1/2)^2 \bar{v}_e X_e \text{ cm}^{-1}$$

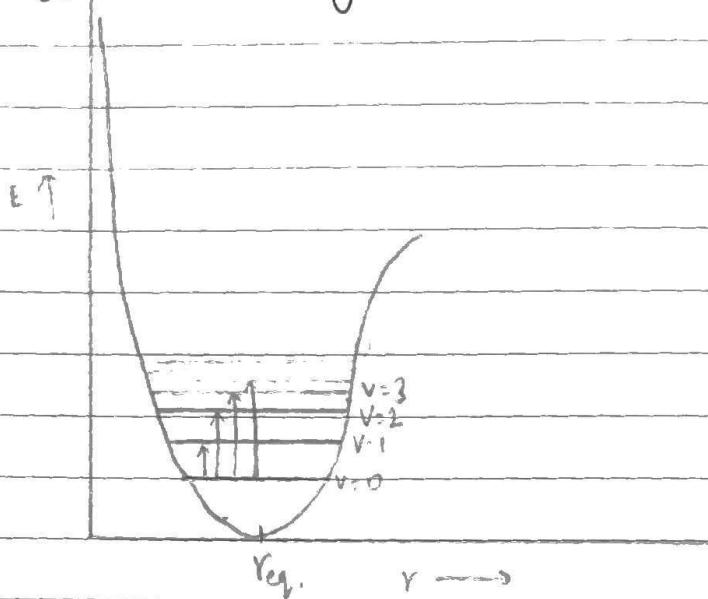
$X_e$  = anharmonicity constant  
(small +ve value)

$v$ : vibrational quantum number

$$v = 0, 1, 2, 3 \dots$$

- Energy is quantised

Energy level diagram for Anharmonic Oscillator



- Energy of anharmonic oscillator slightly less than energy of harmonic oscillator.
- Subtracted value of  $(v+1/2)^2 \bar{\nu}_e$  becomes larger.
- Energy gap reduces as the value of  $v$  goes up
- Higher energy levels closer together

### Spectrum

#### ↳ Selection rules

##### 1. Gross selection rule

- molecule should show a change in dipole moment as it vibrates

##### 2. Specific selection rule

$$\Delta v = \pm 1, \pm 2, \pm 3 \dots$$

- At room temperature,  $v=0$  is the most populated level. (Boltzmann distribution)
- All transitions start at  $v=0$  (most)

$$\sim \bar{v}_e \quad \sim 2\bar{v}_e \sim 3\bar{v}_e$$

$\text{cm}^{-1}$

- $v=0 \rightarrow v=1$  (fundamental absorption)
- $v=0 \rightarrow v=2$  (first overtone)
- $v=0 \rightarrow v=3$  (second overtone)

- Higher lines are closer together than lower lines
- Energy gap of higher levels much lower than that of lower levels
- Such a spectrum depicts anharmonicity.

### Energy gap for fundamental absorption

$$\begin{aligned}\Delta \epsilon_{v=0 \rightarrow v=1} &= (3/2)\bar{v}_e - (3/2)^2 \bar{v}_e \chi_e \\ &\quad - (1/2)\bar{v}_e + (1/2)^2 \bar{v}_e \chi_e \\ &= \bar{v}_e - 2\bar{v}_e \chi_e = (1-2\chi_e)\bar{v}_e\end{aligned}$$

$$\boxed{\Delta \epsilon = \bar{v}_e (1-2\chi_e)}$$

- Line is not at  $\bar{v}_e$ ; slightly less

### Energy gap for first overtone

$$\begin{aligned}\Delta \epsilon_{v=0 \rightarrow v=2} &= (5/2)\bar{v}_e - (5/2)^2 \bar{v}_e \chi_e \\ &\quad - (1/2)\bar{v}_e + (1/2)^2 \bar{v}_e \chi_e \\ &= 2\bar{v}_e - 6\bar{v}_e \chi_e \\ \boxed{\Delta \epsilon = 2\bar{v}_e (1-3\chi_e)}\end{aligned}$$

## Energy gap for second overtone

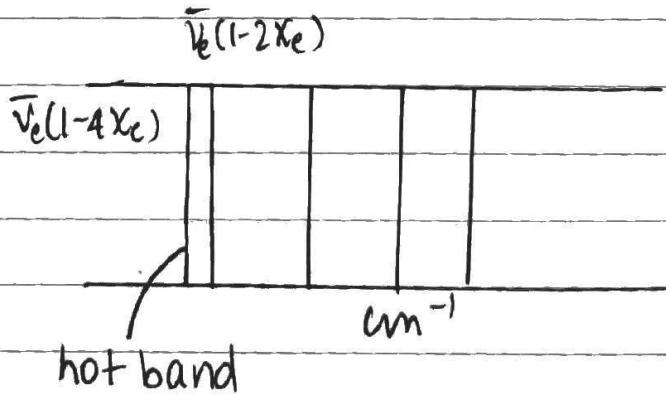
$$\Delta \Sigma = 3\bar{\nu}_e (1 - 4\chi_e)$$

- At room temp, fundamental absorption is most frequent.
- At higher temperatures,  $V=1$  can also get populated.
- Ratio of transitions may increase tenfold.
- Lines appear from  $V=0$  and  $V=1$ .
- Bands that are observed are called hot bands
- If observed, experiment is being carried out at a high temperature.

### Hot Bands

$$\Delta \Sigma_{V=1 \rightarrow V=2} = (5/2)\bar{\nu}_e - (5/2)^2 \bar{\nu}_e \chi_e - (3/2)\bar{\nu}_e + (3/2)\bar{\nu}_e \chi_e$$

$$\Delta \Sigma = \bar{\nu}_e (1 - 4\chi_e)$$



- Hot bands are not as intense as fundamental bands
- When the energy gap is less,  $V=1$  is populated at room temperature (Weaker bonds)

- $k \propto \bar{v}^2$  (Weaker bond  $\Rightarrow k$  is low)
- if  $\bar{v}$  is less, energy gap is less
- Possibility that room temperature is sufficient for hot bands to form

Q. HCl molecule,  $\bar{v}_e = 2990 \text{ cm}^{-1}$ ,  $\chi_e = 0.0174$   
 $\bar{v}_{0 \rightarrow 1} = ?$     $\bar{v}_{0 \rightarrow 2} = ?$     $\bar{v}_{0 \rightarrow 3} = ?$    hot band = ? ( $1 \rightarrow 2$ )

If HCl behaved like harmonic oscillator, what  $\bar{v}$  would it absorb?

A:

$$\begin{aligned}\Delta \Sigma_{0 \rightarrow 1} &= \bar{v}_e (1 - 2\chi_e) \\ &= (2990)(1 - 2 \times 0.0174) \\ &\approx 2.89 \times 10^3 \text{ cm}^{-1} = 2886 \text{ cm}^{-1} \\ &\approx 2886 \text{ cm}^{-1} \text{ (close to } \bar{v}_e)\end{aligned}$$

$$\begin{aligned}\Delta \Sigma_{0 \rightarrow 2} &= 2\bar{v}_e (1 - 3\chi_e) \\ &= 2(2990)(1 - 3 \times 0.0174) \\ &= 5668 \text{ cm}^{-1}\end{aligned}$$

$$\begin{aligned}\Delta \Sigma_{0 \rightarrow 3} &= 3\bar{v}_e (1 - 4\chi_e) \\ &= 8346 \text{ cm}^{-1}\end{aligned}$$

$$\begin{aligned}\Delta \Sigma_{1 \rightarrow 2} &= \bar{v}_e (1 - 4\chi_e) \\ &= (2990)(1 - 4 \times 0.0174) \\ &= 2782 \text{ cm}^{-1}\end{aligned}$$

If HCl was harmonic oscillator,  $\bar{v} = 2990 \text{ cm}^{-1}$   
 (energy gap is constant)

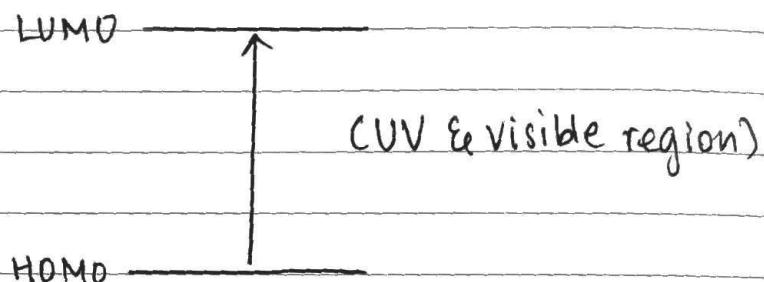
- For IR spectroscopy, chamber is filled with  $N_2$  as  $N_2$  is IR inactive and will not interfere.  $CO_2$  cannot be used.

Q: Why is  $\text{CO}_2$  used as greenhouse gas?

A: Absorbs IR radiation and emits radiation, keeping earth warm.

### $e^- \rightarrow$ ELECTRONIC SPECTROSCOPY

- Electron present in molecule absorbs UV/visible radiation



- Account for colour.
- Every molecule can undergo electronic transitions
- Homonuclear diatomic molecules are active; also show electronic spectrum.
- $\sigma \rightarrow \sigma^*$  (UV)  
 $\pi \rightarrow \pi^*$  (Visible) ] usually  
 n  
 (lone pair)
- energy gap more for  $\sigma \rightarrow \sigma^*$

### BORN-OPPENHEIMER APPROXIMATION

$$E_{\text{total}} = E_{\text{elec}} + E_{\text{vib}} + E_{\text{rot}}$$

- each independent of the other.
- $2e^-$  in the same electronic state can still have different energies (vibrational & rotational levels)

- A change in the total energy of the molecule

$$\Delta E_{\text{total}} = \Delta E_{\text{elec}} + \Delta E_{\text{vib}} + \Delta E_{\text{rot}} \text{ J}$$

$$\Delta \Sigma_{\text{total}} = \Delta \Sigma_{\text{elec}} + \Delta \Sigma_{\text{vib}} + \Delta \Sigma_{\text{rot}} \text{ cm}^{-1}$$

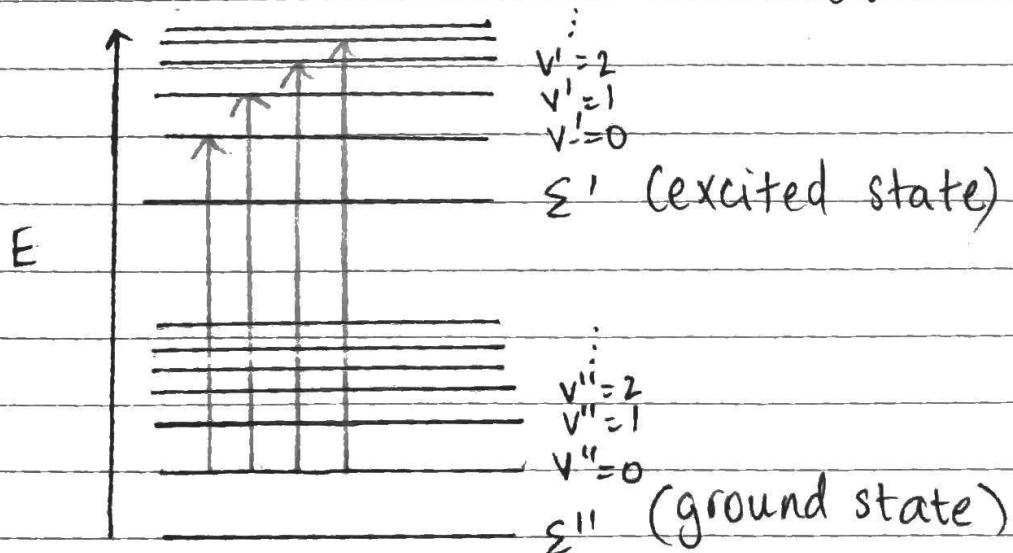
because  $\Delta \Sigma_{\text{elec}} \approx \Delta \Sigma_{\text{vib}} \times 10^3 \approx \Delta \Sigma_{\text{rot}} \times 10^6 \text{ cm}^{-1}$

- can use vibrational ~~coarse~~<sup>coarse</sup> structure & rotational coarse structure to find bond strength and bond length for homonuclear diatomic molecules.

- Electronic transitions cause nucleus to vibrate
- Response is slow
- Nuclei vibrate
- Bond length changes → rotation caused

### Vibrational coarse structure: progression

- UV / visible spectroscopy; electronic transition
- vibration occurs at lowest energy



- During electronic transition, no selection rule for  $\Delta v$
- $v''=0$  to  $v'=0$  allowed,  $v''=1$  to  $v'=3$  allowed
- has to go to next electronic level
- $v''=0$  is the most populated state

## Selection rules

1. No selection rule for  $\Delta v$  in electronic transitions
2. Most populated state is  $v''=0$ ; most transitions originate from  $v''=0$ .
3. The excited state vibrational levels' energy gap is lesser compared to ground state vibrational levels because excited state generally has a weaker bond.

$$\bar{v} \propto \sqrt{k}$$

## Spectrum

$(v', v'')$

$$v'' = 0 \longrightarrow v' = 0$$

$$v'' = 0 \longrightarrow v' = 1$$

$(0,0) (1,0) (0,1)$

Converging

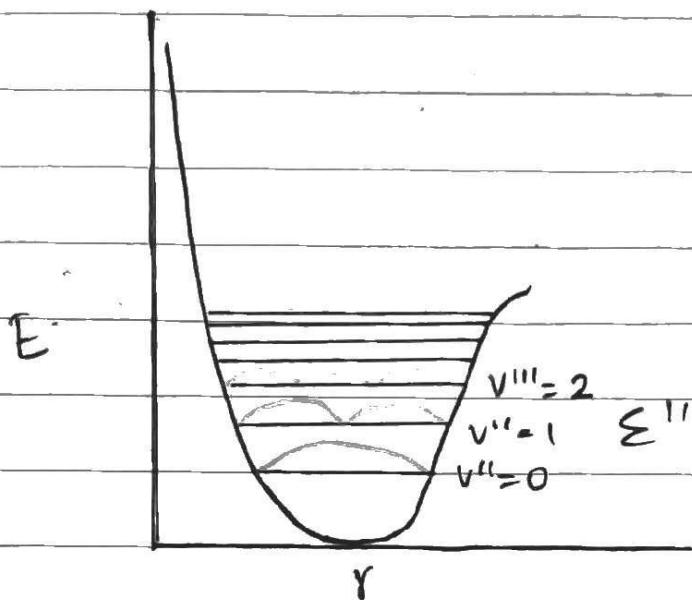
$\text{cm}^{-1}$

- Can conclude that the excited state shows anharmonicity
- Cannot make conclusions about the ground state
- Fundamental absorption has nothing to do with electronic transitions; only vibrational transitional  $v''=0 \rightarrow v''=1 \Rightarrow \text{not UV/VIS visible}$

## USES OF ELECTRONIC SPECTROSCOPY (APPLICATIONS)

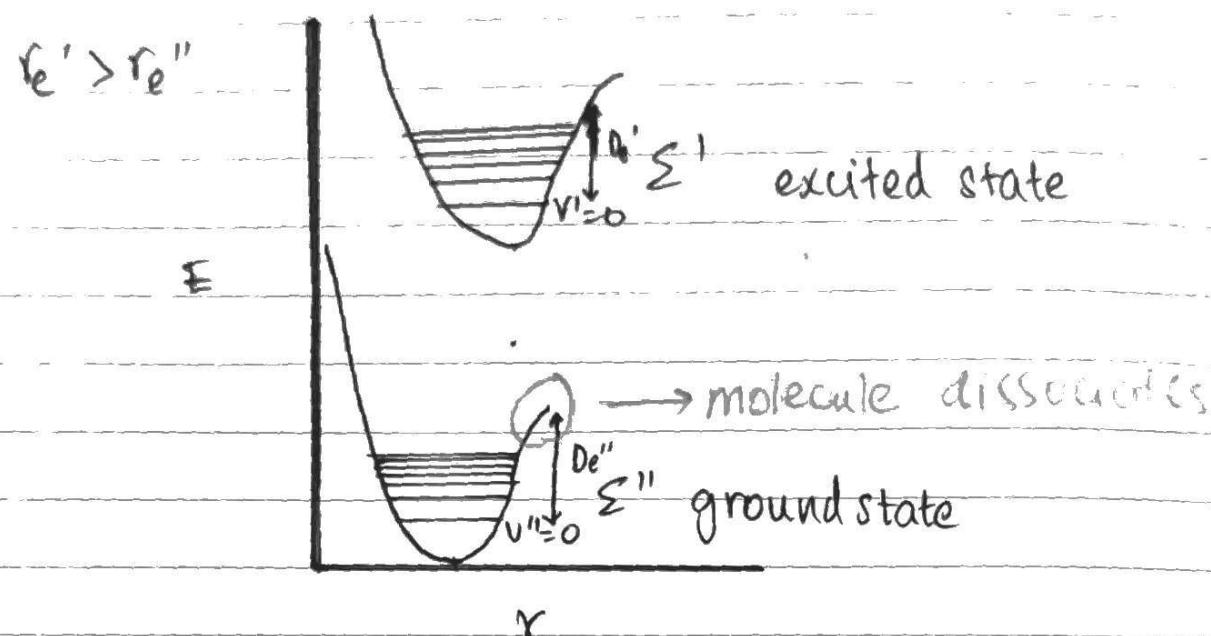
- Organic reactions: transition state (unstable)
- Information on bond length
- UV/visible spectrum on excited state
- Works for homonuclear diatomic molecules; vibration

- Difficult to get rotational fine structure.
- Rotation usually in gaseous state
- X-ray diffraction for solids.
- Probability of finding the electron in an atom is  $\psi^2$  (square of wavefunction)
- Probability of finding nuclei in molecules is given by  $\Psi^2$ .



- Classically, probability of finding molecule is more at extremities (slows down near extremes)
- Quantum mechanics, probability of finding molecules is maximum at centre ( $v''=0$ )
- Excited state has more antibonding character; bond order reduces, bond length increases.
- Displaced more to the right, indicates higher bond length.
- Transition: bonding to antibonding.

Energy level diagram for a diatomic molecule (anharmonic oscillator).

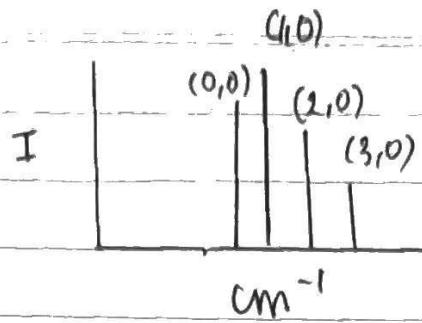


- $J=0$  is on the line of vibrational level, unlike  $v=0$ .
- Dissociation energy at any state can be calculated.
- There are rotational levels everywhere.
- Certain lines are more intense than others; depends on molecule.

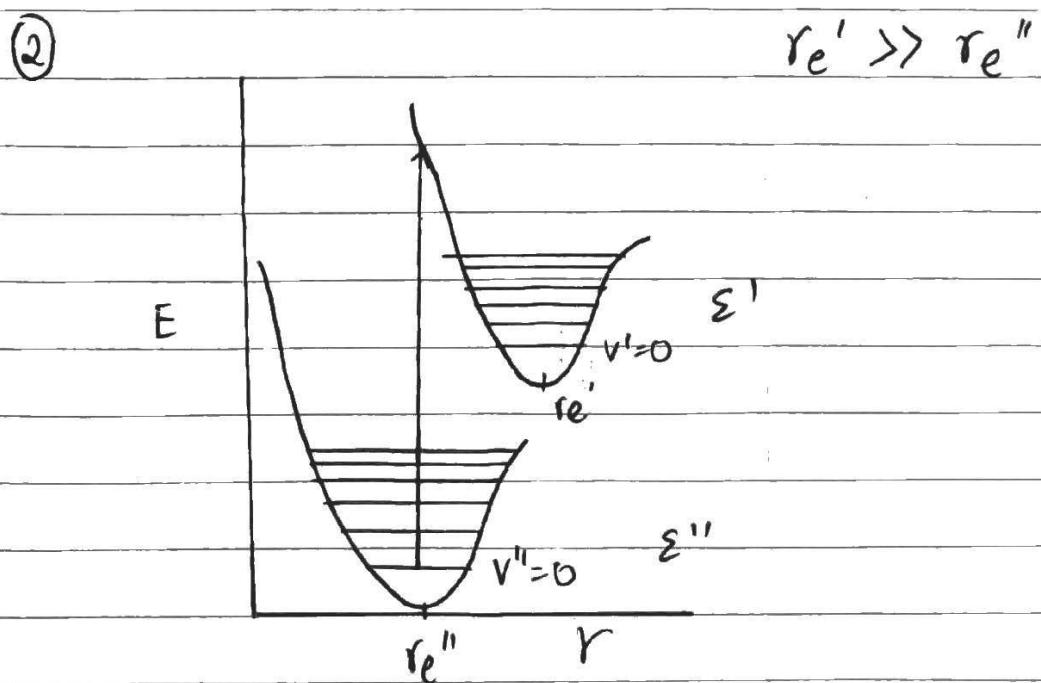
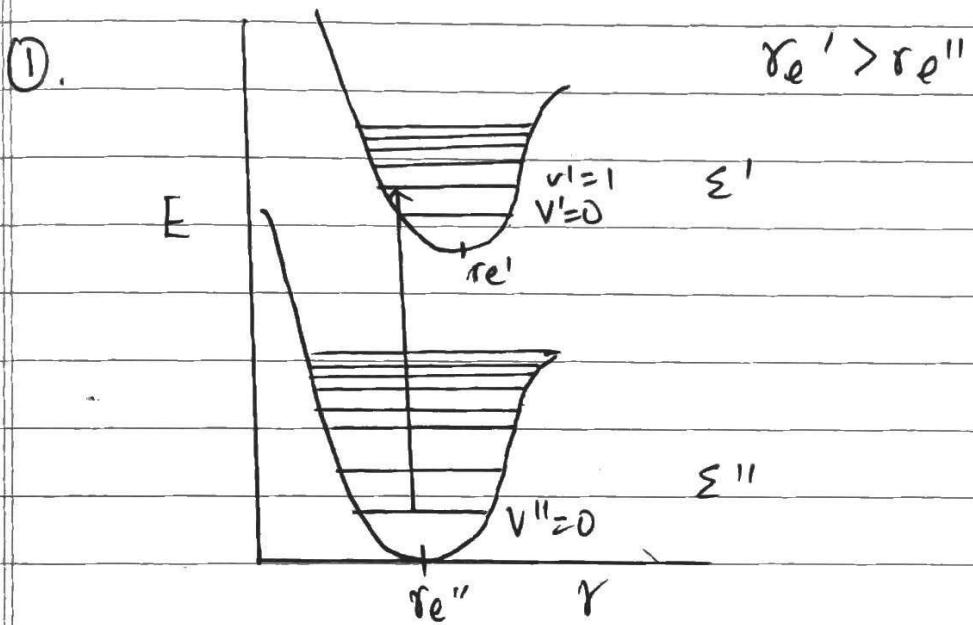
### FRANK-CONDON PRINCIPLE

An electronic transition takes place so rapidly that a vibrating molecule does not change its internuclear distance appreciably during the transition.

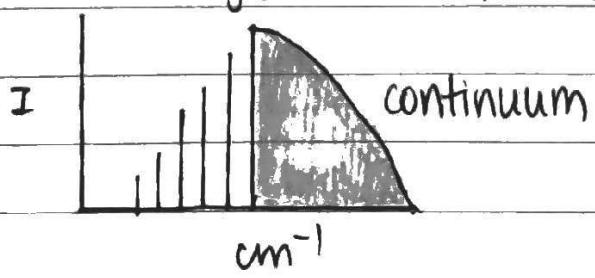
- Nuclei massive compared to electron.
- From the figure ① most common line is  $(1, 0)$  due to the position of  $\Sigma'$  with respect to  $\Sigma''$ .
- Electronic transitions are vertical transitions.



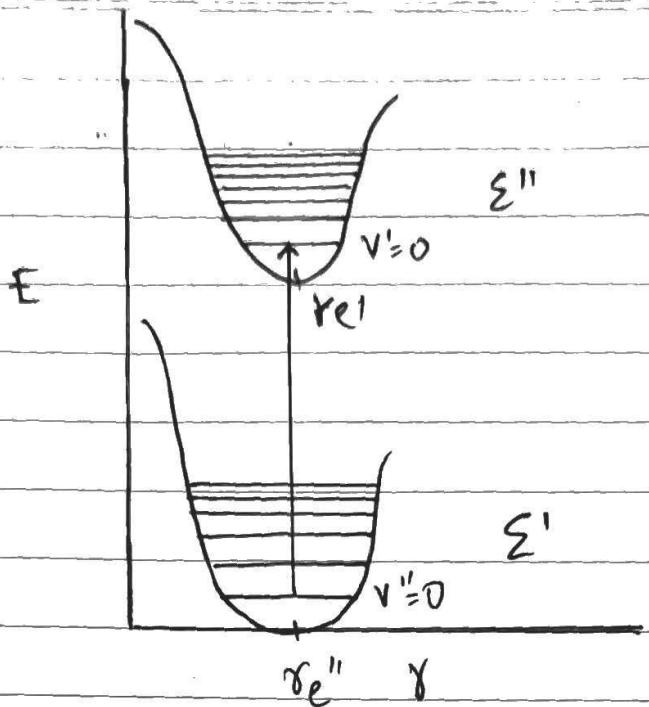
- Displacement depends on how antibonding the excited state is.
- Probability of extremities increases



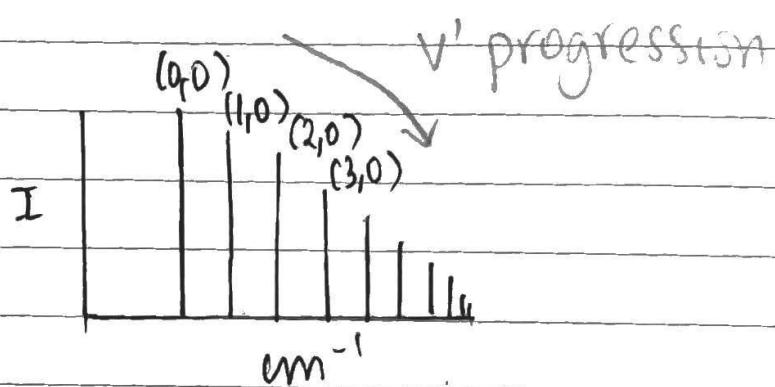
- Molecule will dissociate (beyond D-E); breaks into atoms, gains energy (kinetic, etc), which is not quantised



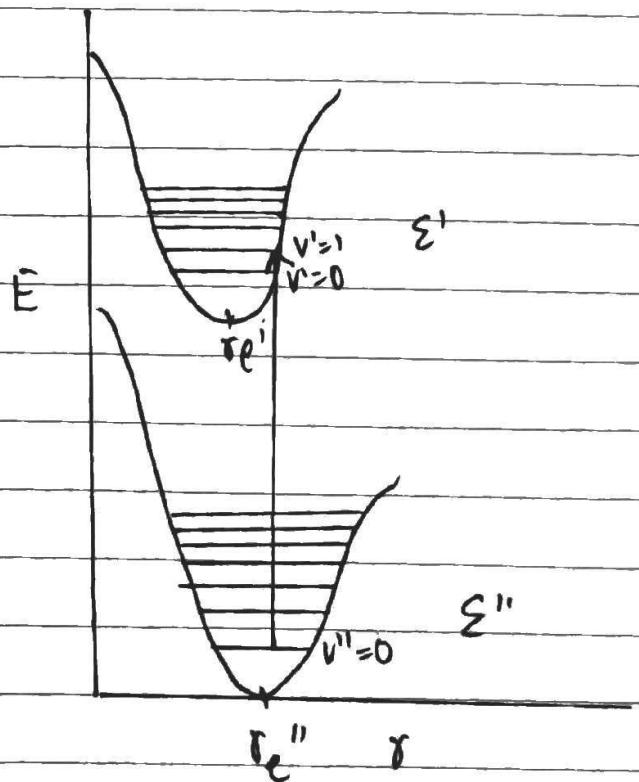
(3)



$$r_e' = r_e''$$

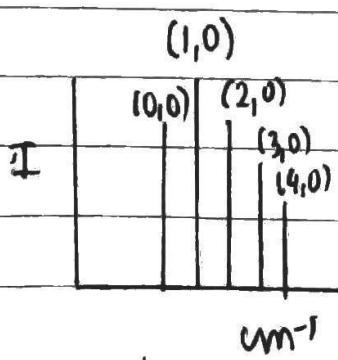


(4)



$$r_e' < r_e''$$

- antibonding to bonding also possible
- much rarer



- (5) Will never happen, super unlikely  $r_e' < r_e''$   
not a valid example ; just for concepts

