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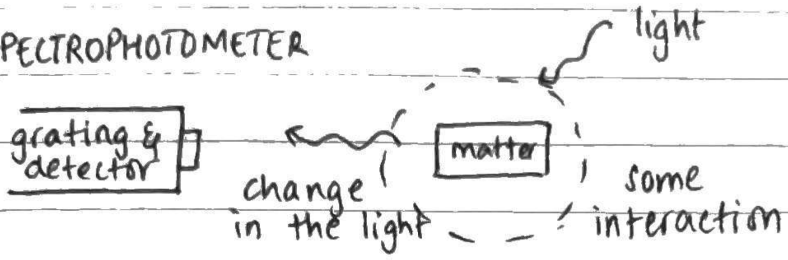
UNIT 1

Molecular Spectroscopy

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

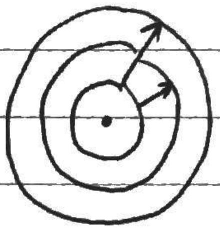
SPECTROPHOTOMETER



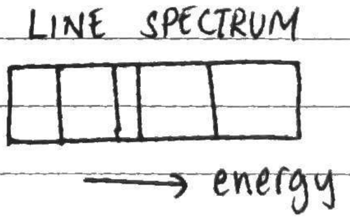
- Use the change and relate it to the structure of matter.
- Use quantum mechanics, not classical
- Get spectrum in detector
- Bond length, bond angle etc.

- 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



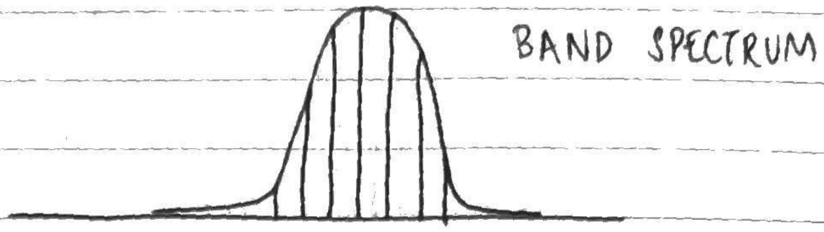
$E = h\nu$



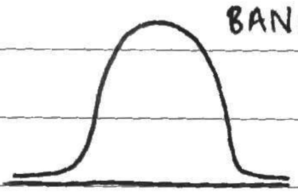
- Two energy levels with difference equal to energy of wavelength

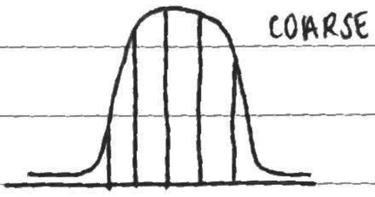
- Atoms have atomic orbitals, molecules have molecular orbitals (combination of atomic)
- $\sigma, \sigma^*, \pi, \pi^*$ etc.

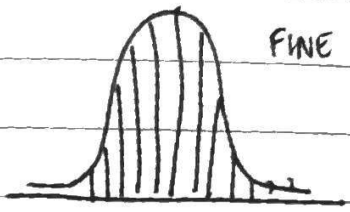
- Light incident on electrons in molecular orbitals may also cause them to move to higher energy levels
- Molecular spectra, therefore, must also exist
- Instead of lines, bands are seen



- Something else is also happening inside the molecule







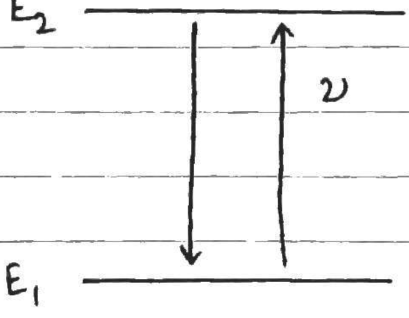
- Molecules can vibrate when energy falls
- Non-electronic transitions also possible
- Electronic levels & vibrational levels.

- Fine lines due to rotation of molecule
- Rotational levels.

- More complicated process, but more information out of it.

Quantisation of energy

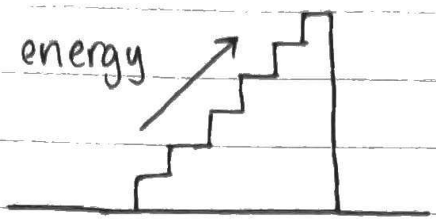
- Whenever energy is absorbed/emitted, it is always done in packets



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

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

- 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.

  - cm^{-1} ($1/\lambda = \bar{\nu}$) is a spectroscopic unit of energy.

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

A: $\Delta E = hc\bar{\nu} = (6.626 \times 10^{-34}\ \text{Js})(3 \times 10^{8}\ \text{ms}^{-1})(1\ \text{cm}^{-1})(100)$

$= 6.626 \times 3 \times 10^{-24}\ \text{J}$

$\Delta E = 1.9878 \times 10^{-23}\ \text{J} = 1\ \text{cm}^{-1}$

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

- If energy wasn't quantised, continuous spectrum would be formed, and no discreet lines.

- Band spectra: discreet, very close lines.

continuous

discreet

ELECTROMAGNETIC SPECTRUM

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

1. Radiowave region

$\lambda = 10 m - 1 cm$

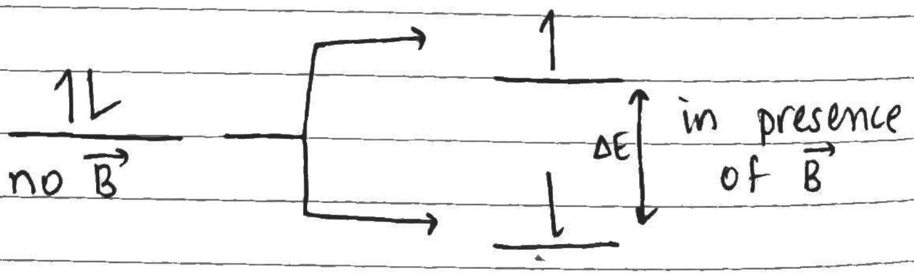
$E = 0.001 - 10 \text{ J mol}^{-1}$

- 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

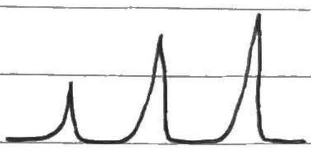
└ Nuclear Magnetic Resonance

- Nuclei also possess spin (particular ν_1)
- In presence of $\vec{B}$, splits into two levels (ν_2)
- Light incident also possesses particular ν
- Two levels - two spins
- Not all nuclei; usually for organic molecules.

- Proton NMR (^1H)
- ^{13}C NMR

Example:

CH_3CH_2OH
↑ ↑ ↑
all absorb different ν



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

2. Microwave region

$\lambda = 1cm - 100\mu m$

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

- Information on:
  - Rotational levels

- Spectroscopy:
  - Rotational spectroscopy or Microwave spectroscopy

- Molecule is rotating (dipole changes)
- Fluctuating $\vec{E}$ due to rotation
- If ν_{rot} matches ν_{light}, energy absorbed
- Molecule goes to next rotational level.

- Used interstellar; Mars

Example: $\overset{\delta+}{H} - \overset{\delta-}{Cl}$

- Polar molecule responds to rotational spectroscopy

$N \equiv N$

- No net dipole moment; no $\Delta \vec{E}_{field}$
- 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

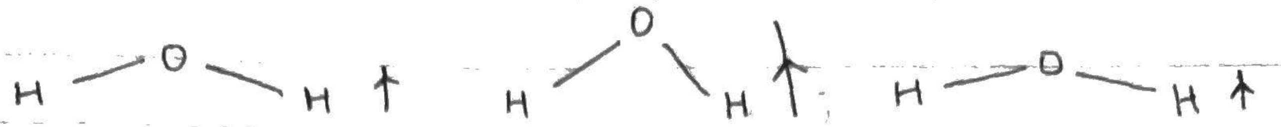
$\lambda = 100 \mu m - 1 \mu m$

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

- Information on:
  - vibrational levels

- Spectroscopy:
  - Vibrational spectroscopy or Infrared spectroscopy

- When dipole stretches, $\vec{E}$ fluctuates at certain ν
- 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 H_2O changes.

- CO_2 may bend while vibrating

- Depends on mode of vibration
- CO_2 is active in IR region even though it has no net dipole moment.

4. Visible & Ultraviolet region

$\lambda = 1 \mu m - 10 nm$

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

- Information on:
  - Electronic levels (valence e^-)

- Spectroscopy
  - Electronic spectroscopy / UV-vibrational spectroscopy

- $CuSO_4$ 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

$\lambda = 100 pm - 100 pm$
$E = 10^9$ ~~-10^{11}~~ $J\ g^{-1}\ atom^{-1}$

- 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. γ-Ray Region

$\lambda = 100 pm - 1 pm$
$E = 10^9 - 10^{14}\ J\ g^{-1}\ atom^{-1}$

- Information on
  - Nuclear rearrangement
- Spectroscopy
  - γ ray spectroscopy (GRS) used in astrophysics
- Used in Mars mission
- $$\begin{tikzcd} {}^{57}_{27}Co \arrow[r] & {}^{57}_{26}Fe \text{ (excited state)} \arrow[d, "\gamma"] \\ & {}^{57}_{26}Fe \end{tikzcd}$$
- Gieger counter
- Not molecules; nuclei & atoms
- Strong nuclear force requires γ 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

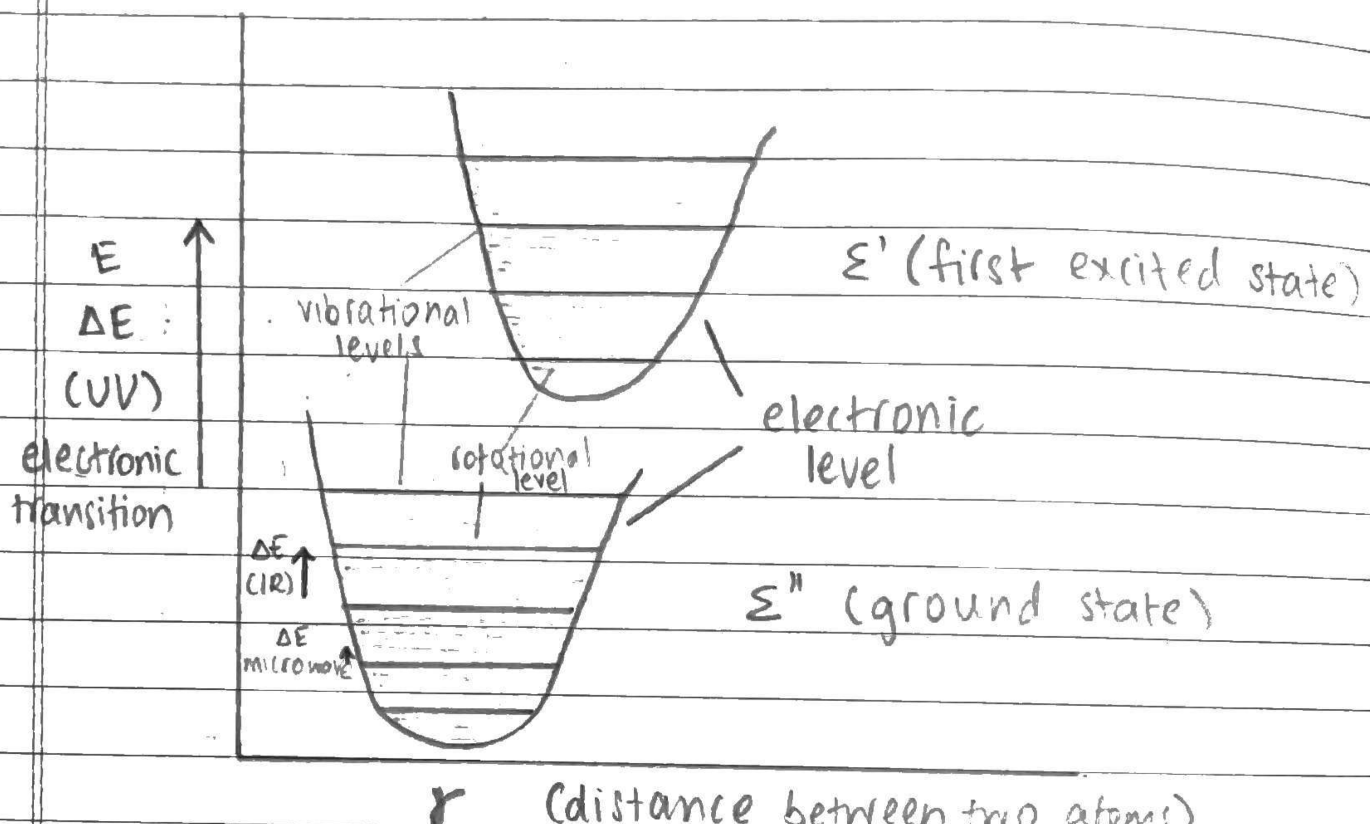
$$E_{total} = E_{trans} + E_{rot} + E_{vib} + E_{elec}$$

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

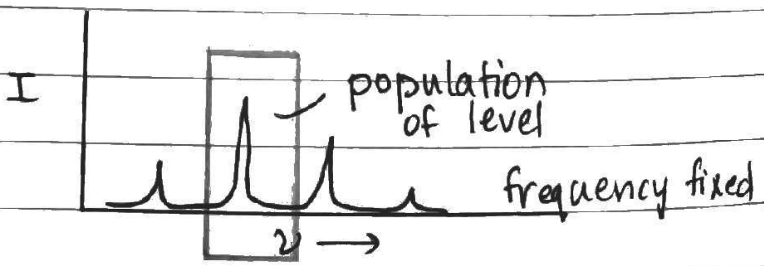
- Translational levels are extremely close to each other
- We don't have devices sensitive enough to see lines; we see a continuum

Energy level diagram for a diatomic molecule



BEER-LAMBERT'S LAW

- no. of transitions
- concentration of species
- talk about a fixed λ



- I_0 = incident light

$$I_0 = I_a + I_t + \boxed{I_r} \rightarrow \text{can be ignored (only turbid solution)}$$

reflection
absorbed
transmitted

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

— LAMBERT'S LAW

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

$$\boxed{I_t = I_0 \, 10^{-kl}}$$

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

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.

$$\boxed{I_t = I_0 \, 10^{-kc'}}$$

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

C = concentration of light-absorbing species

LAMBERT-BEER'S LAW

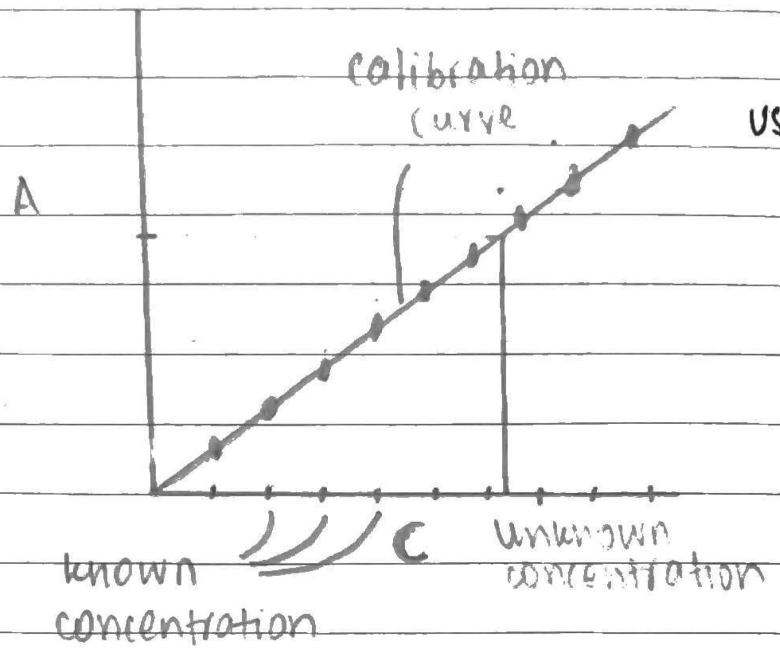
- Combining the two

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

- $A \propto l$, $A \propto c$, $A = \varepsilon c l$
- $\boxed{A = \varepsilon c l}$ — molar absorption coeffient

Lambert - Beer's Law

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



USING COLORIMETER

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

A: $A = \varepsilon c l$

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

$l = 9\ mm = 0.9\ cm$

$A = 0.14$

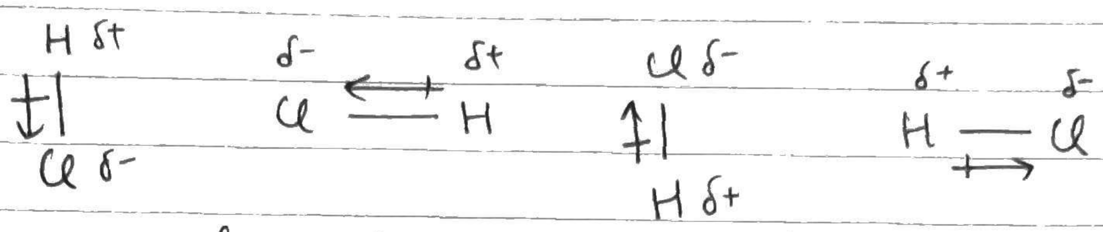
$0.14 = \varepsilon \times 0.5 \times 10^{-3} \times 0.9 = 45 \times 10^{-5} \times \varepsilon$

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

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

Rotational Spectroscopy

- Source of light - microwave region
- Constantly changing dipole



- frequency of rotation matches with microwave frequency (microwave active)

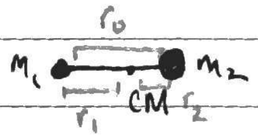
- Not possible for $N\equiv N$ (microwave inactive)

MICROWAVE ACTIVE	MICROWAVE INACTIVE
• HCl	• N_2
• CO	• CO_2
• $CHCl_3$	• homonuclear diatomic molecules
• $O=C=S$	• CH_4

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

$$m_1 r_1 = m_2 r_2 \quad (\text{torque about CM} = 0)$$
$$r_0 = r_1 + r_2$$
$$I = m_1 r_1^2 + m_2 r_2^2$$

$$I = m_1 r_1^2 + m_2 r_2^2$$
$$= m_2 r_2 r_1 + m_1 r_1 r_2$$
$$I = (m_1+m_2)\, r_1 r_2$$

$$m_1 r_1 = m_2 r_2 = m_2 (r_0 - r_1)$$
$$r_1 (m_1+m_2) = m_2 r_0$$

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

$$m_2 r_2 = m_1 (r_0 - r_2)$$
$$r_2 (m_1+m_2) = \frac{m_1 r_0}{\cancel{m_1+m_2}}$$

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

$$I = (m_1+m_2)\, r_1 r_2$$
$$= (m_1 \cancel{+m_2}) \frac{m_2 r_0}{(m_1+\cancel{m_2})} \frac{m_1 r_0}{(m_1+m_2)}$$

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

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

$$\boxed{I = \mu r_0^2}$$

└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

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

where J = rotational quantum number
J = 0, 1, 2, 3 . . .

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

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

$$\boxed{E_J = \frac{J(J+1)\ h^2}{8\pi^2 I}} \quad \text{where } J = 0,1,2\ldots$$

- ∴ rotational energy levels are quantised

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

$$\frac{E_J}{hc} = \underbrace{\frac{h}{8\pi^2 cI}}_{\text{constant}}\ J(J+1)$$

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

B = rotational constant

$$B = \frac{h}{8\pi^2 cI} \text{ in } cm^{-1} \text{ (Spectroscopic Units)}$$

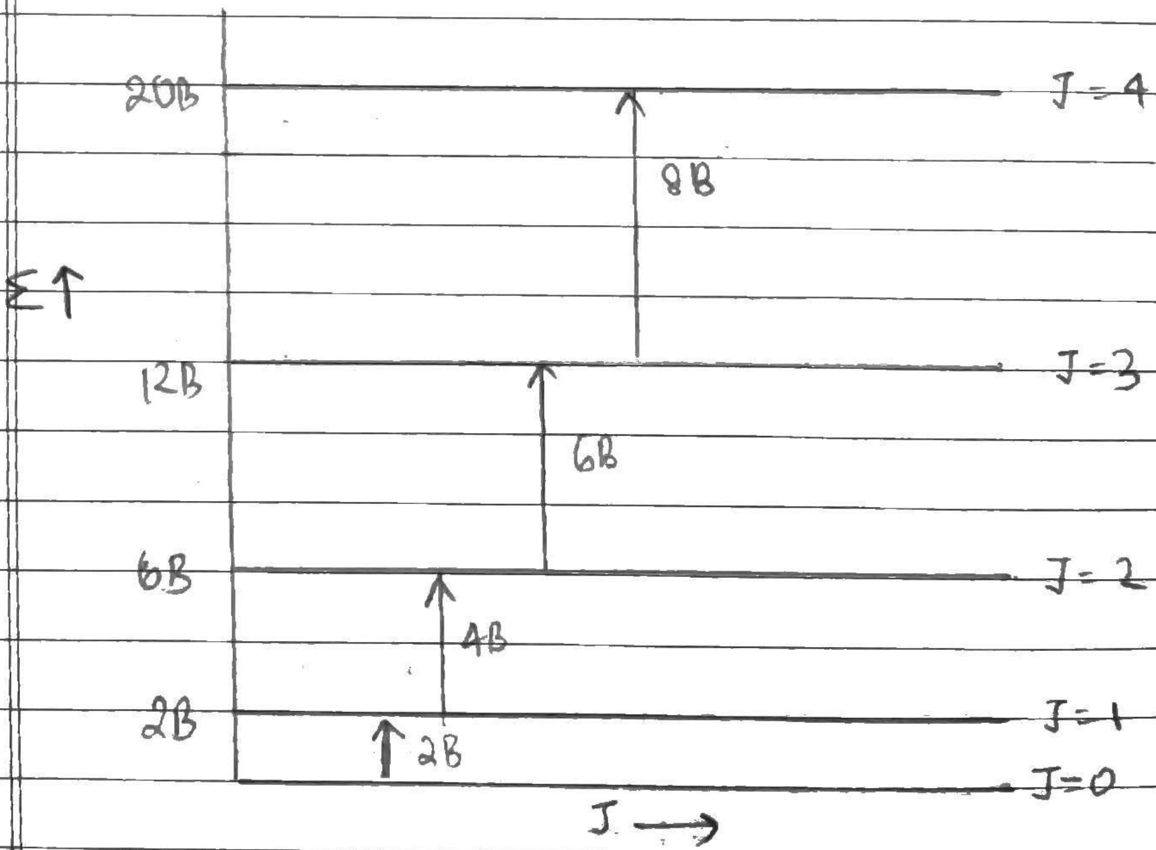
$$B = \frac{h^2}{8\pi^2 I} \quad \text{in Joules}$$

Energy level diagram for a diatomic molecule

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

$$\varepsilon_J = BJ(J+1)$$

$J = 0$, $\varepsilon_0 = 0$
$J = 1$, $\varepsilon_1 = 2B$
$J = 2$, $\varepsilon_2 = 6B$
$J = 3$, $\varepsilon_3 = 12B$
$J = 4$, $\varepsilon_4 = 20B$



- Energy level difference (consecutive levels)

$$\Delta\varepsilon_{J+1 \to J} = B(J+1)(J+2) - B(J)(J+1)$$
$$= B(J+1)(J+2-J)$$
$$= 2B(J+1) \ \text{cm}^{-1}$$

$$\Delta E_{1\to 0} = 2B$$
$$\Delta E_{2\to 1} = 4B$$
$$\Delta E_{3\to 2} = 6B$$
$$\Delta E_{4\to 3} = 8B$$

- Energy gap is increasing
- Energy gap is in the microwave range

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

A: $B = \frac{h}{8\pi^2 Ic}$ $I = \mu r_{CO}^2$ $\mu = \frac{m_C m_O}{m_C + m_O}$

$$\mu_g = \frac{(16)(12)}{(16+12)} \times \frac{1}{N_A} = \frac{(4)(12)}{(7)(N_A)} = \frac{48}{7N_A} = \frac{48\times10^{-23}}{7\times6.022}$$

$$\mu_{kg} = \frac{48\times10^{-26}}{7\times6.022} = 1.1387\times10^{-26}$$

$r_{CO} = 1.13\times10^{-10}$ m

$$I = \mu r_{CO}^2 = 1.14\times10^{-26}\times(1.13)^2\times10^{-20}$$
$$= 1.454\times10^{-46}$$

$$B = \frac{h}{I 8\pi^2 c} = \frac{(6.626)(10^{-34})}{(1.454\times10^{-46})(8\pi^2)(3)(10^8)}$$

$$B = \frac{(6.626)(10^4)}{(1.454)(3)(8)(\pi^2)} = 1.924\times10^2\ m^{-1}$$

$$B = 1.924\times10^2\ m^{-1}$$

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

In Joules,

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

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

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

Spectrum

└ selection rules

1. Gross selection rule
   - molecule should possess permanent dipole moment

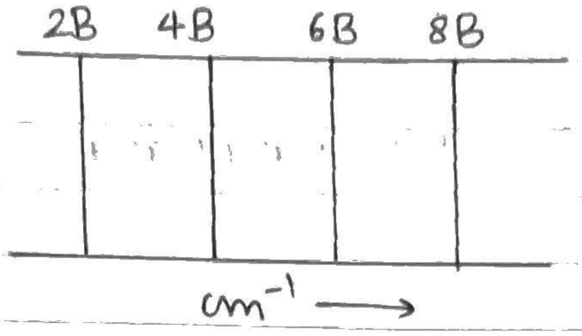
2. Specific rule for rigid rotor (Schrödinger equation)
   - $\Delta J = \pm 1$ (only consecutive transitions)

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

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

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

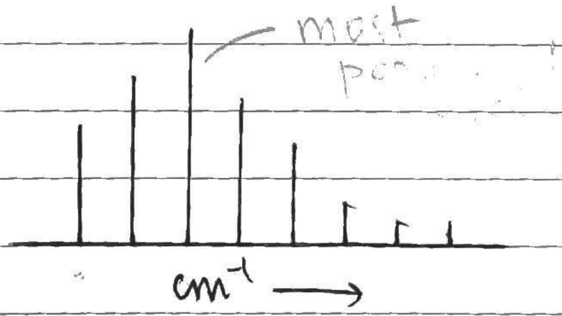
$J=3 \longrightarrow J=4 \qquad \Delta E_J = 8B$



- 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.

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



- Intensity due to population of energy levels
- More molecules are moving from $J=2$ to $J=3$
- 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 $^{12}C^{16}O$ molecule, first line appears at 3.842 cm^{-1}
Find out bond length (pm). $h = 6.626 \times 10^{-34}$ Js
$c = 3 \times 10^{8}$ ms^{-1}

A: First line: $2B = 3.842$ cm^{-1}
$B = 1.921$ cm^{-1} $= 1.921 \times 10^{2}$ m^{-1}

$$B = \frac{h}{8\pi^2 Ic} \quad \text{in m}^{-1}$$

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

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

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

$$I = \mu r_0^2 \qquad \mu = \frac{(12)(16)}{(12+16)} = \frac{\cancel{12}^{3} \times 16}{\cancel{28}_{7}} \text{ amu}$$

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

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

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

~~$r_0^2 = 12.8 \times 10^{-24}$~~

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

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

$$\boxed{r_0 = 113 \text{ pm}}$$

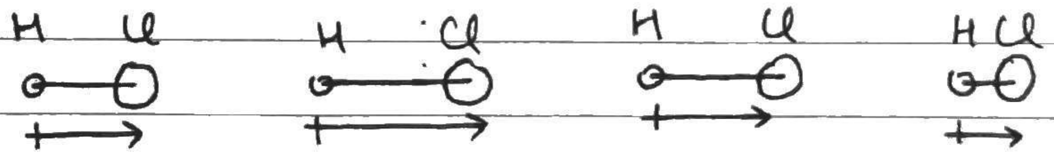
- Food in microwave oven
- Water molecules undergoes rotation
- Molecules coming back down give out thermal energy.
- Microwave radiation causes change in rotational levels.
- Food gets colder faster from microwave oven
- Why no metal?

- 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.

VIBRATIONAL SPECTROSCOPY

- Infrared radiation
- Vibration of molecule



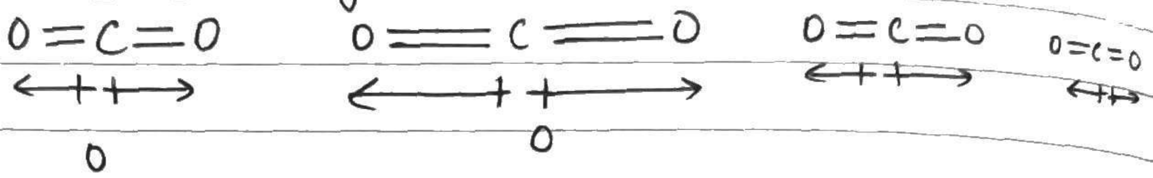
- Dipole moment continuously fluctuating for heteronuclear diatomic molecule.

- 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.

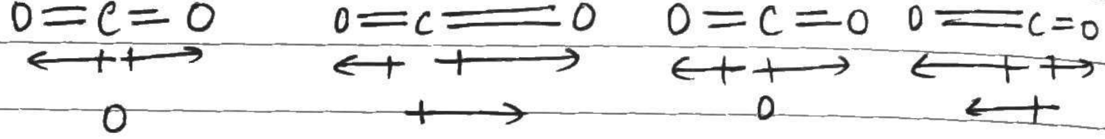
Exception: CO_2 modes of vibration

└ Symmetric stretching



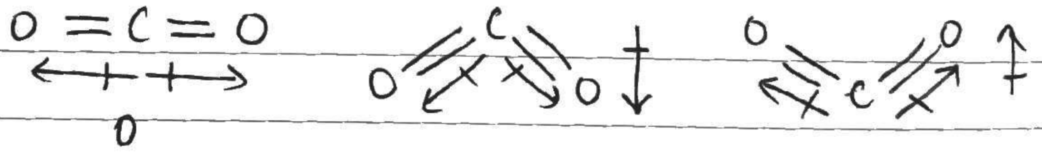
- IR inactive during symmetric stretching

└ Asymmetric stretching



- IR active during asymmetric stretching

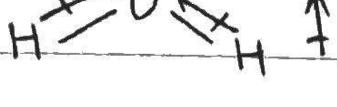
└ Bending vibration



- IR active during bending motion

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

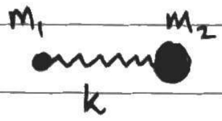
- H_2O is IR active in all modes of vibration (different frequencies)



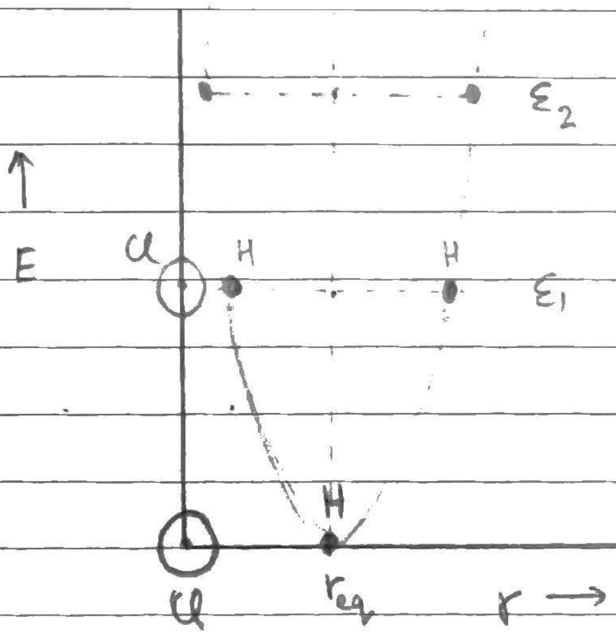
- Vibration of molecule must change the dipole moment

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

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

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

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

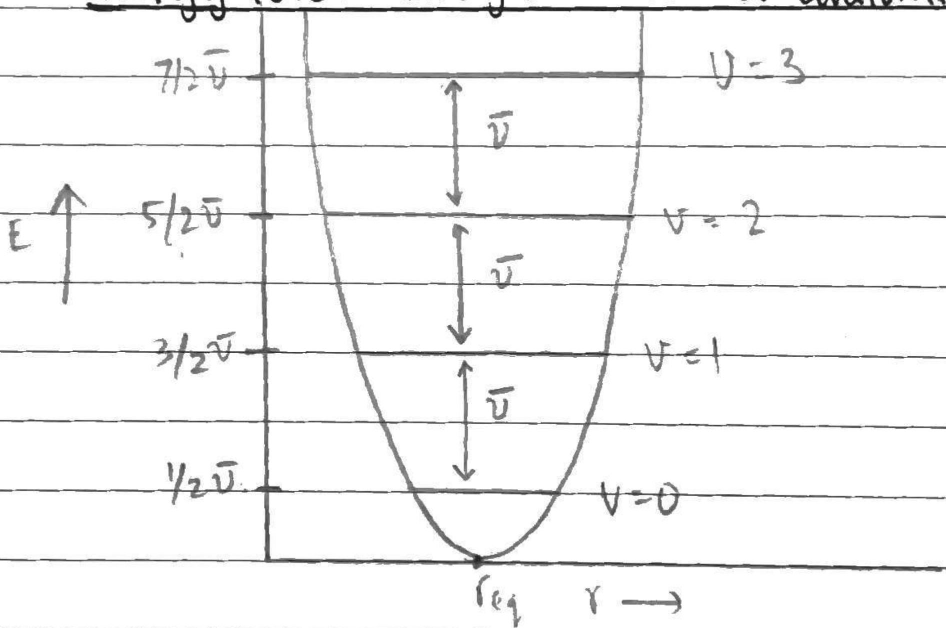
- If $\bar{\nu}$ is known, k can be calculated
- k represents bond strength
- Using vibrational spectrum, bond strength can be calculated

- Need to find solution of Schrödinger equation for simple harmonic oscillator.

- $E = (v + 1/2) h\nu$ (Joules)
  v = vibrational quantum number.
  $v = 0, 1, 2, 3 \ldots$

- Vibrational energy levels are quantised.
- $\varepsilon_v = (v + 1/2)\bar{\nu}$ (cm^{-1})

<u>Energy level diagram for a diatomic molecule (SHO)</u>



When $v=0$, $\varepsilon_0 = 1/2\,\bar{\nu}$
$v=1$, $\varepsilon_1 = 3/2\,\bar{\nu}$
$v=2$, $\varepsilon_2 = 5/2\,\bar{\nu}$
$v=3$, $\varepsilon_3 = 7/2\,\bar{\nu}$

- Energy gap between vibrational energy levels is constant

- $\Delta \varepsilon_v = (v+1+1/2)\bar{\upsilon} - (v+1/2)\bar{\upsilon}$

  $\Delta \varepsilon_v = \bar{\upsilon}\ \text{cm}^{-1}$

- Even at $v=0$ level, molecule possesses ~~teve~~ energy
- A molecule is never at rest; it is always vibrating.
- At $v=0$, $\varepsilon_v = 1/2\ \bar{\upsilon}$ (zero point energy)

- For macromolecules, μ is very high, and $\bar{\upsilon}$ is very low.

Spectrum

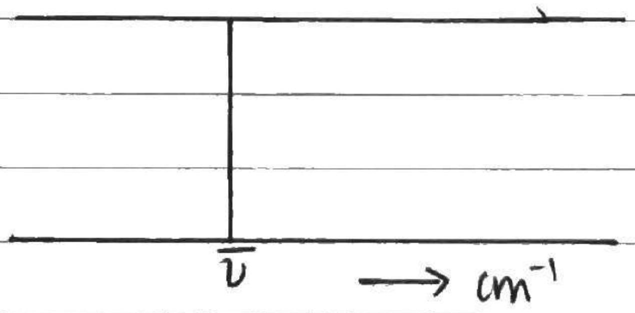
└ Selection rules

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

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

$v=0 \longrightarrow v=1$		$\Delta \varepsilon_v = \bar{\upsilon}$
$v=1 \longrightarrow v=2$		$\Delta \varepsilon_v = \bar{\upsilon}$
$v=2 \longrightarrow v=3$		$\Delta \varepsilon_v = \bar{\upsilon}$
$v=3 \longrightarrow v=4$		$\Delta \varepsilon_v = \bar{\upsilon}$



- Single spectrum line → 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 intence line is observed for HCl molecule at 2890 cm^{-1}. Find out the force constant in Nm^{-1} (bond strength).

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

H = 1.00g

Cl = 35.5g

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

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

$$\mu_{kg} = \frac{35.5 \times 10^{-3} \times 1}{36.5 \times 6.022 \times 10^{23}}$$

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

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

$$k = (28.9)^2 \times 4\pi^2 c^2 \mu \times 10^8$$
$$= 478773 \times 10^{16} \times 10^{-27} \times 10^8$$
$$= 4.79 \times 10^{21} \times 10^{-27} \times 10^8$$
$$= 4.79 \times 10^{-6} \times 10^8$$
$$\boxed{k = 479 \text{ Nm}^{-1}}$$

NOTE: 1 amu = 1.67×10^{-27} kg

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

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

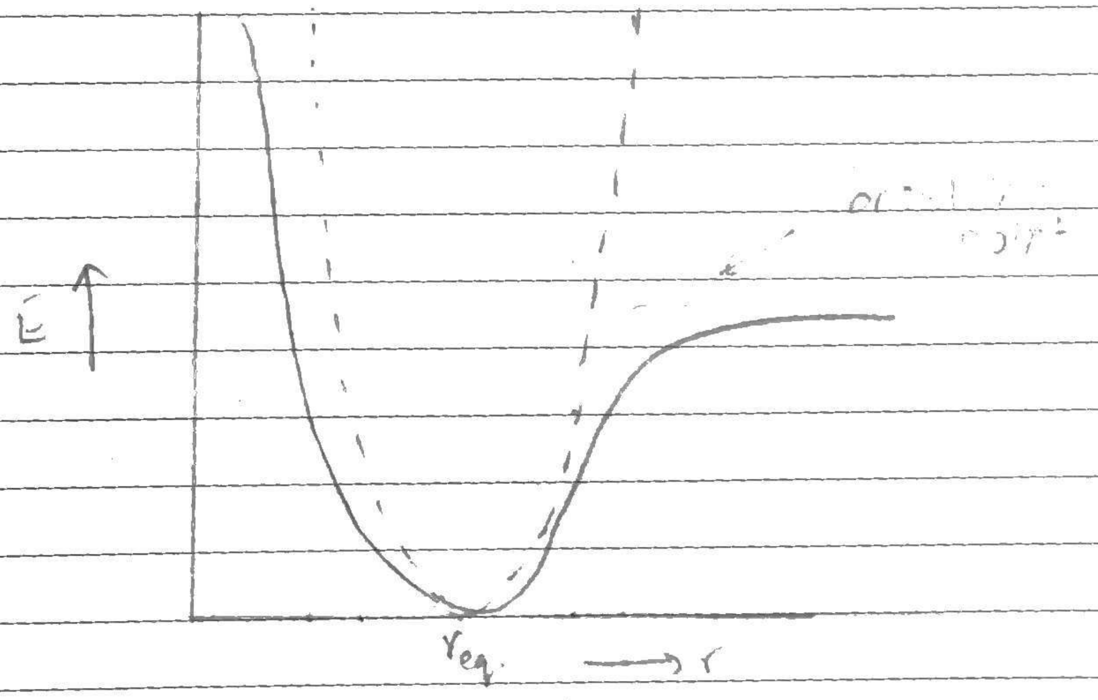
C≡C → $\bar{\upsilon}_1$ C–C → $\bar{\upsilon}_3$

C=C → $\bar{\upsilon}_2$

Eg: assume k is constant:
$\bar{\nu}_1 > \bar{\nu}_2 > \bar{\nu}_3 > \bar{\nu}_4$

C−F : $\bar{\nu}_2$
C−Cl : $\bar{\nu}_3$
C−H : $\bar{\nu}_1$
C−Br : $\bar{\nu}_4$

- 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.

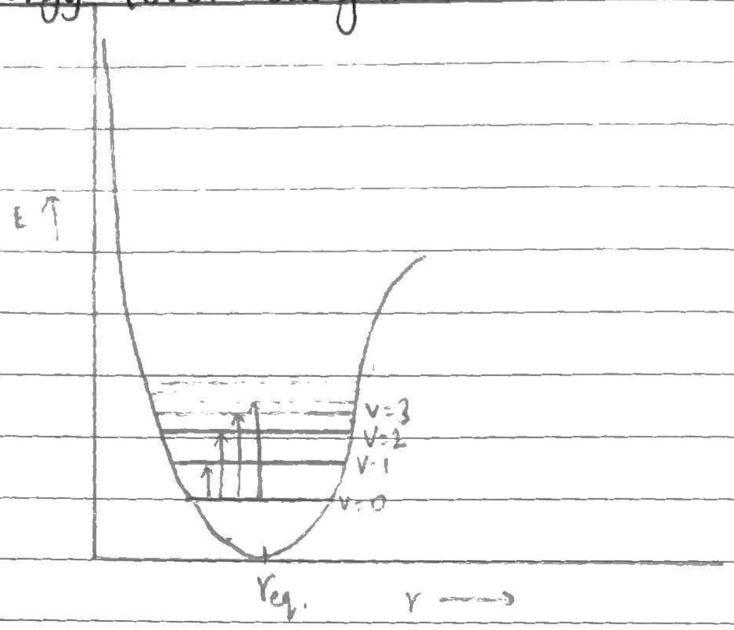
$$\varepsilon = (v+1/2)\bar{\nu}_e - (v+1/2)^2 \bar{\nu}_e x_e \quad cm^{-1}$$

x_e = anharmonicity constant
(small +ve value)

V= vibrational quantum number
V= 0, 1, 2, 3 ...

- Energy is quantised

Energy level diagram for Anharmonic Oscillator



- Energy of anharmonic oscillator slightly less than energy of harmonic oscillator
- subracted 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

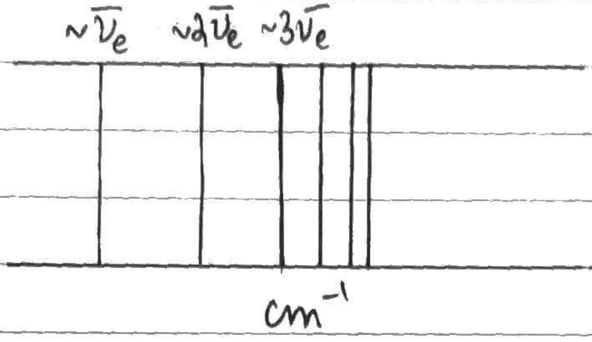
Spectrum

└ Selection rules

1. Gross selection rule
   - molecule should show a change in dipole moment as it vibrates

2. Specific selection rule
   $\Delta v = \pm 1, \pm 2, \pm 3 \ldots$

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



- V = 0 ⟶ V = 1 (fundamental absorption)
- V = 0 ⟶ V = 2 (first overtone)
- V = 0 ⟶ 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

$$\Delta E_{V=0 \to V=1} = (3/2)\bar{\nu}_e - (3/2)^2 \bar{\nu}_e x_e - (1/2)\bar{\nu}_e + (1/2)^2 \bar{\nu}_e x_e$$

$$= \bar{\nu}_e - 2\bar{\nu}_e x_e = (1-2x_e)\bar{\nu}_e$$

$$\boxed{\Delta E = \bar{\nu}_e (1-2x_e)}$$

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

Energy gap for first overtone

$$\Delta E_{V=0 \to V=2} = (5/2)\bar{\nu}_e - (5/2)^2 \bar{\nu}_e x_e - (1/2)\bar{\nu}_e + (1/2)^2 \bar{\nu}_e x_e$$

$$= 2\bar{\nu}_e - 6\bar{\nu}_e x_e$$

$$\boxed{\Delta E = 2\bar{\nu}_e (1-3x_e)}$$

Energy gap for second overtone

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

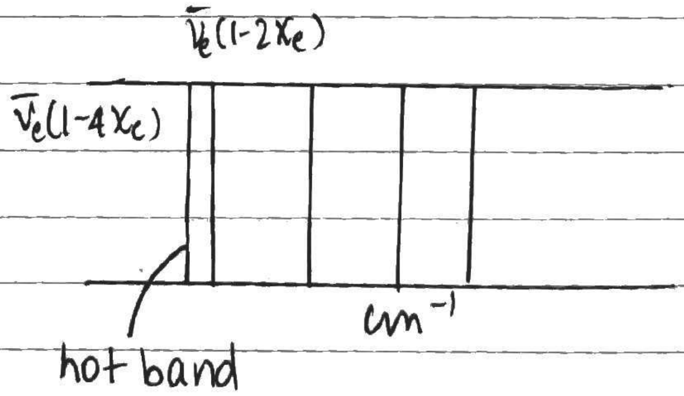
- At room temp, fundamental absorption is most frequent.
- At higher temperatures, V=1 can also get populate
- Ratio of transitions may increase tenfold.
- Lines appear from V=0 and V=1.
- Bands that are observed are called hot bands
- If observed, experiment is being carried out at a high temperature.

Hot Bands

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

$$= \bar{\nu}_e - 4\bar{\nu}_e\chi_e$$

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



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

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

Q: HCl molecule, $\bar{\nu}_e = 2990\ cm^{-1}$, $x_e = 0.0174$
$\bar{\nu}_{0\to1} = ?$ $\bar{\nu}_{0\to2} = ?$ $\bar{\nu}_{0\to3} = ?$ hot band = ? $(1\to2)$

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

A:
$$\Delta\varepsilon_{0\to1} = \bar{\nu}_e(1-2x_e)$$
$$= (2990)(1-2\times0.0174)$$
$$\simeq 2.89\times10^3\ cm^{-1} = 2886\ cm^{-1}$$
$$= 2886\ cm^{-1} \quad (\text{close to } \bar{\nu}_e)$$

$$\Delta\varepsilon_{0\to2} = 2\bar{\nu}_e(1-3x_e)$$
$$= 2(2990)(1-3\times0.0174)$$
$$= 5668\ cm^{-1}$$

$$\Delta\varepsilon_{0\to3} = 3\bar{\nu}_e(1-4x_e)$$
$$= 8346\ cm^{-1}$$

$$\Delta\varepsilon_{1\to2} = \bar{\nu}_e(1-4x_e)$$
$$= (2990)(1-4\times0.0174)$$
$$= 2782\ cm^{-1}$$

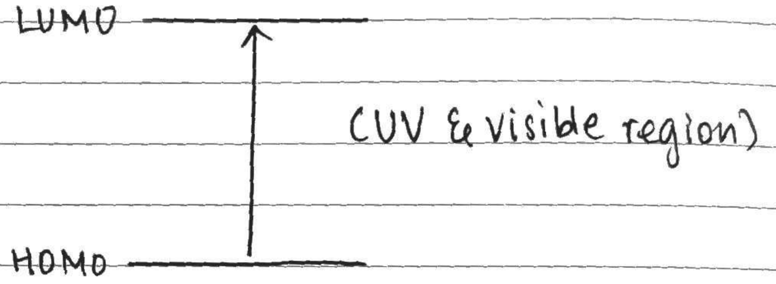
If HCl was harmonic oscillator, $\bar{\nu} = 2990\ cm^{-1}$ (energy gap is constant)

- 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 CO_2 used as greenhouse gas?
A: Absorbs IR radiation and emits radiation, keeping earth worm.

e^- 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.
- $\sigma \longrightarrow \sigma^*$ (UV)] usually
  $\pi \longrightarrow \pi^*$ (visible)]
  $n \nearrow$ (lone pair)
- energy gap more for $\sigma \rightarrow \sigma^*$

BORN-OPPENHEIMER APPROXIMATION

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

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

- A change in the total energy of the molecule

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

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

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

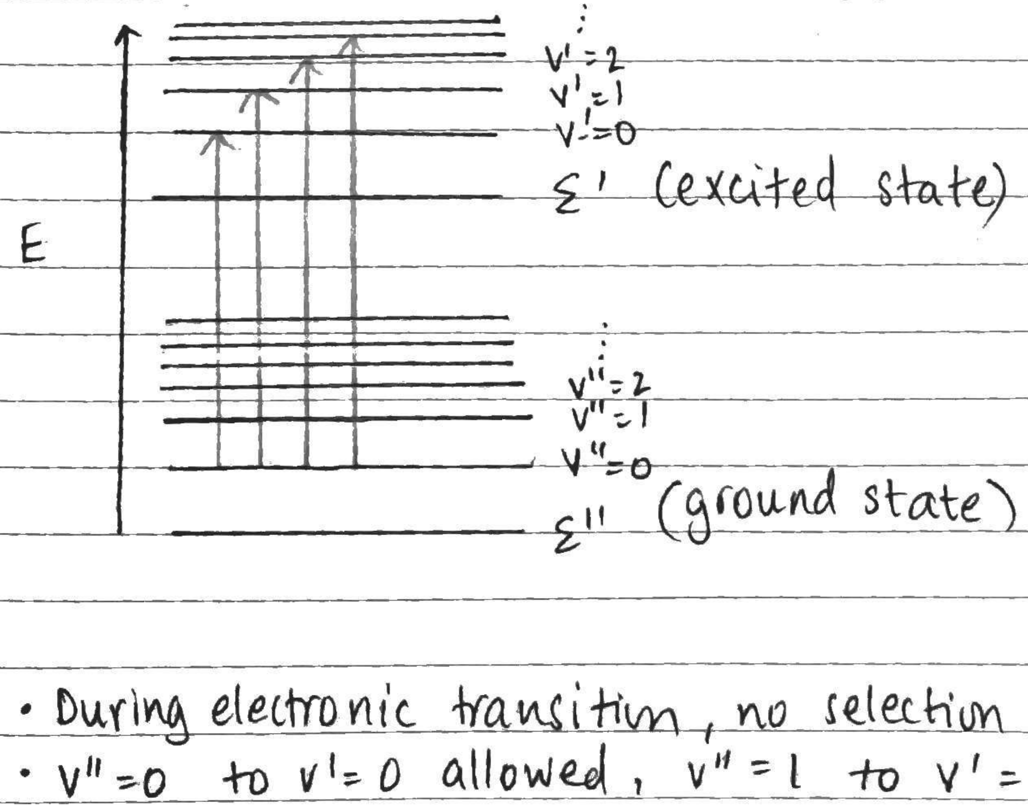
- can use vibrational coarse structure & rotational coarse structure to find bond strength and bond length for homonuclear diatomic molecules.

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

Born [illegible]

<u>Vibrational coarse structure : progression</u>

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



- During electronic transition, no selection rule for Δv
- 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 Δv in electronic transitions
2. Most populated state is $v''=0$; most transitio originate from $v''=0$.
3. The excited state vibrational levels' energy gap is lesser compared to ground state vibrational levels because excited state general has a weaker bond.

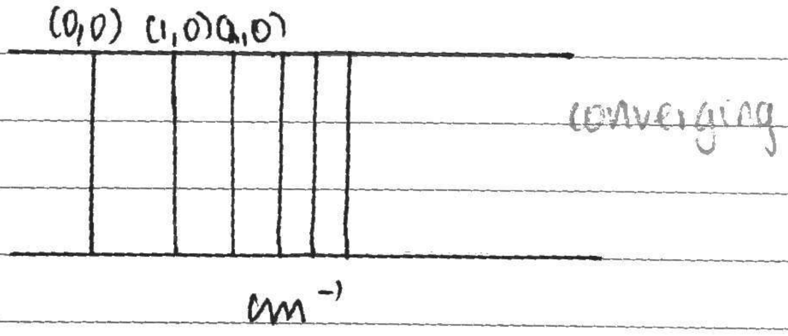
$$\bar{v} \propto \sqrt{k}$$

Spectrum

(v', v'')

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

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



- 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

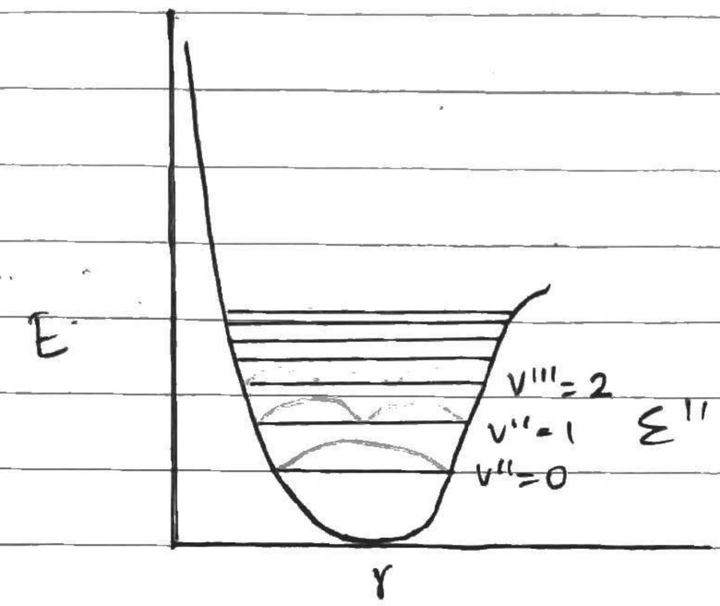
$v''=0 \rightarrow v''=1 \Rightarrow$ not UV/visible

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 ψ^2 (square of wavefunction)

- Probability of finding nuclei ~~or~~ molecules is given by ψ^2.



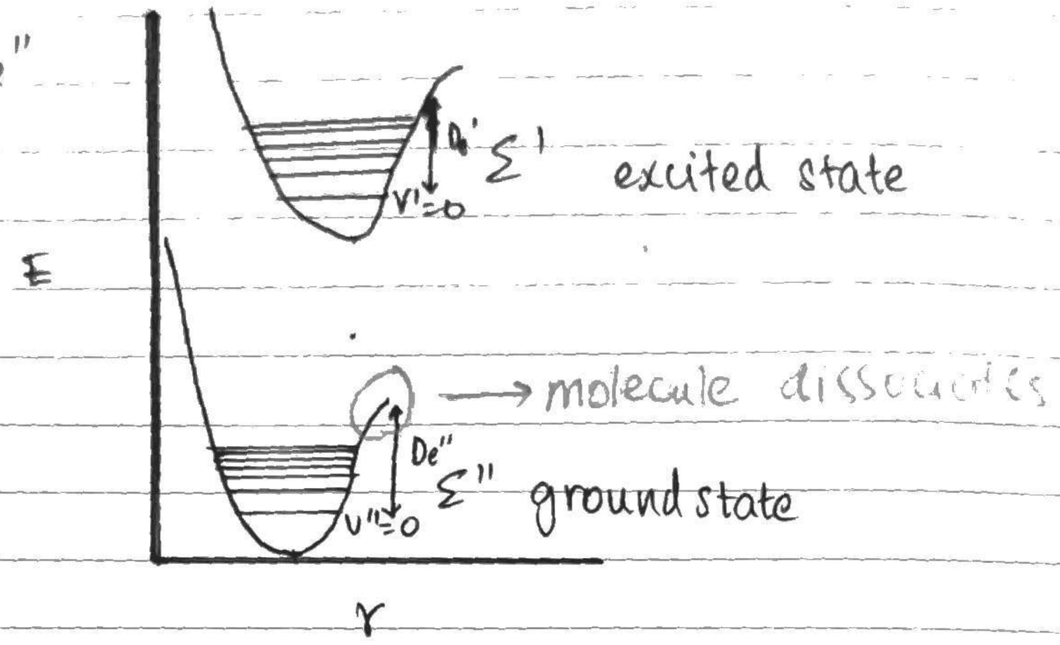
- Classically, probability of finding molecule is more at extremities (slows down near extremes)

- 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).

$r_e' > r_e''$



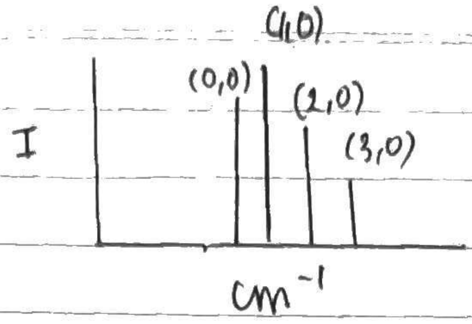
- J=0 is on the line of vibrational level, unlike v=0.
- Dissociation energy at any state can be calculat
- There are rotational levels everywhere

- Certain lines are more intense than others; depends on molecule.

FRANK-CONDON PRINCIPLE

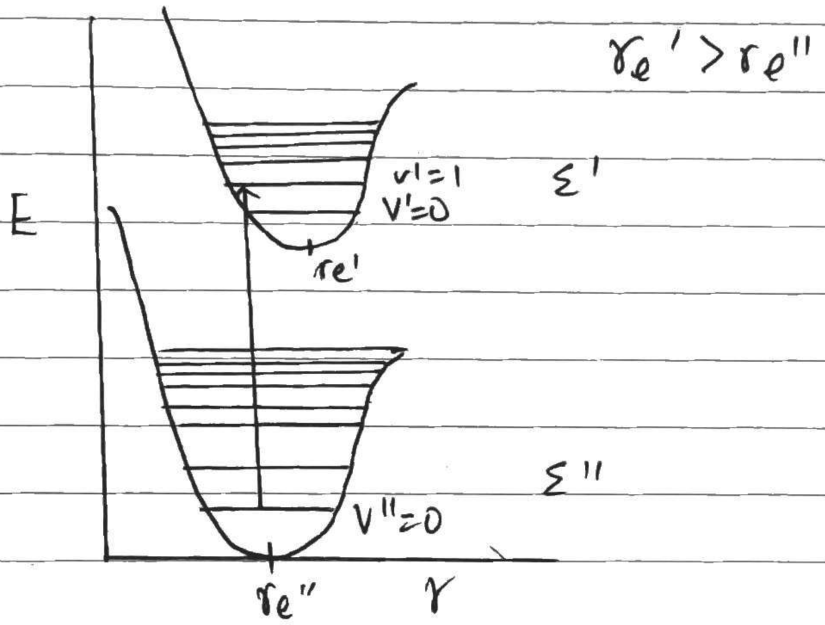
An electronic transition takes place so rapidly that a vibrating molecule does not change its internuclear distance appreciably during the transition.

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

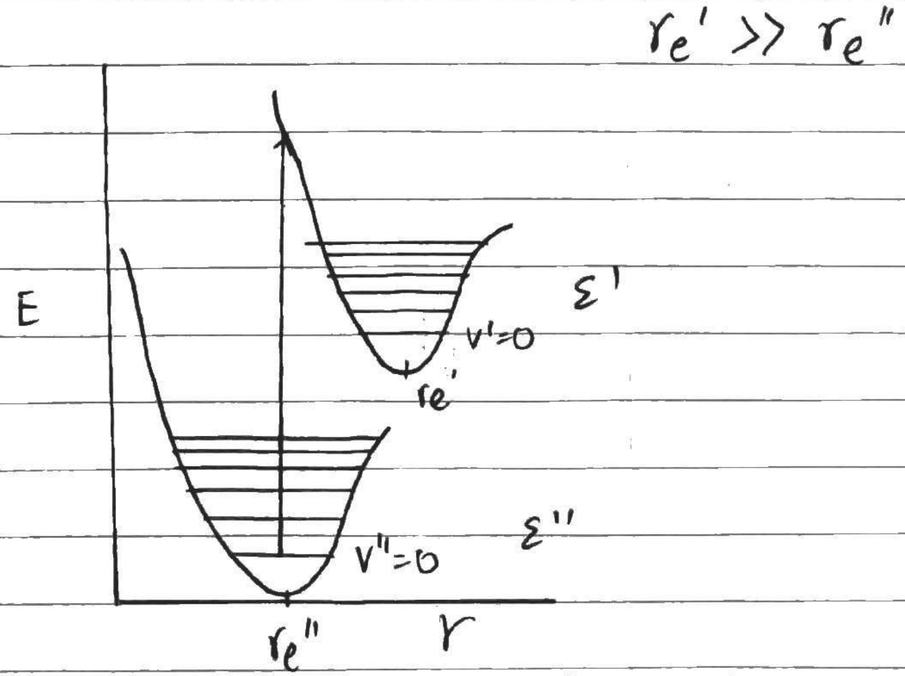


- Displacement depends on how antibonding the excited state is.
- Probability of extremities increases

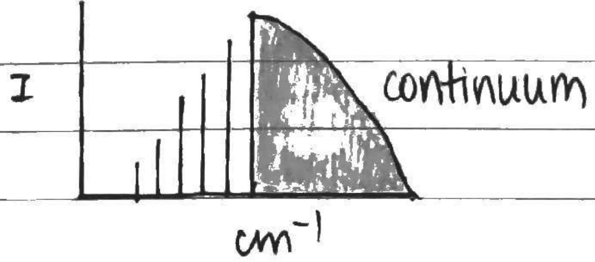
①.



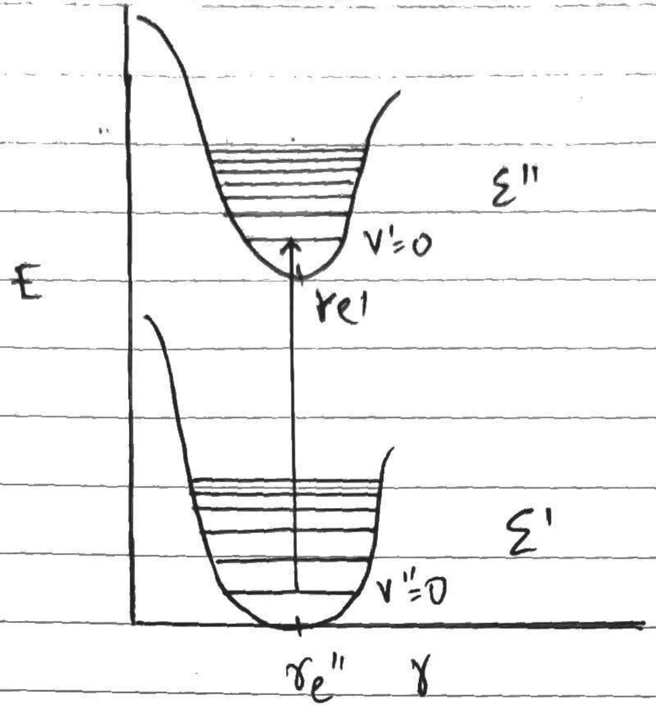
②



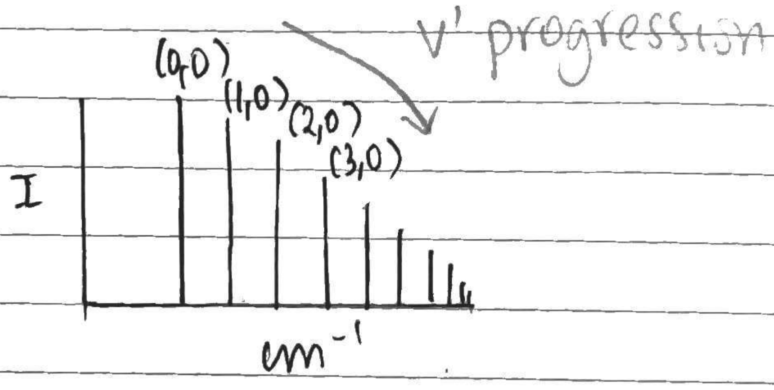
- Molecule will dissociate (beyond D·E); breaks into atoms, gains energy (kinetic, etc), which is not quantised.



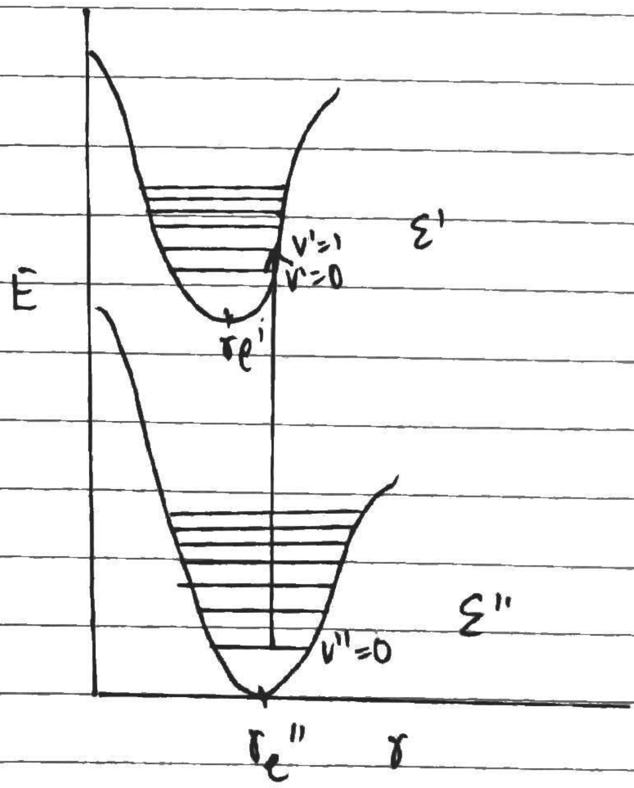
③



$r_e' = r_e''$

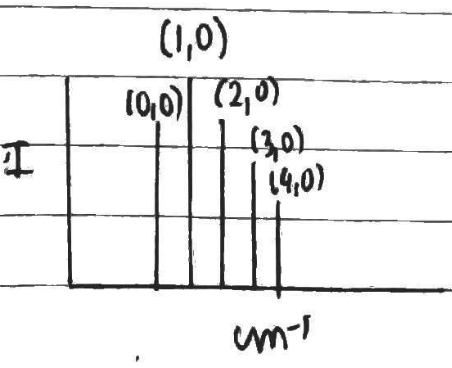


④



$r_e' < r_e''$

- antibonding to bonding also possible
- much rarer



⑤ Will never happen, super unlikely $r_e' \ll r_e''$
not a valid example ; just for concepts