

ENGINEERING CHEMISTRY

Module I- Molecular Spectroscopy



- *Module content:*
 - *Interaction of electromagnetic radiation with matter*
 - *Electromagnetic spectrum*
 - *Born –Oppenheimer approximation*
 - *Beer-Lambert's law*
 - *Microwave spectroscopy- diatomic rigid rotor model and the rotational spectrum*
 - *IR spectroscopy- diatomic harmonic oscillator and anharmonic oscillator model*
 - *Electronic spectroscopy- Vibrational coarse structure(Progressions), Franck Condon Principle*

ENGINEERING CHEMISTRY

Module I- Molecular Spectroscopy



Class content :

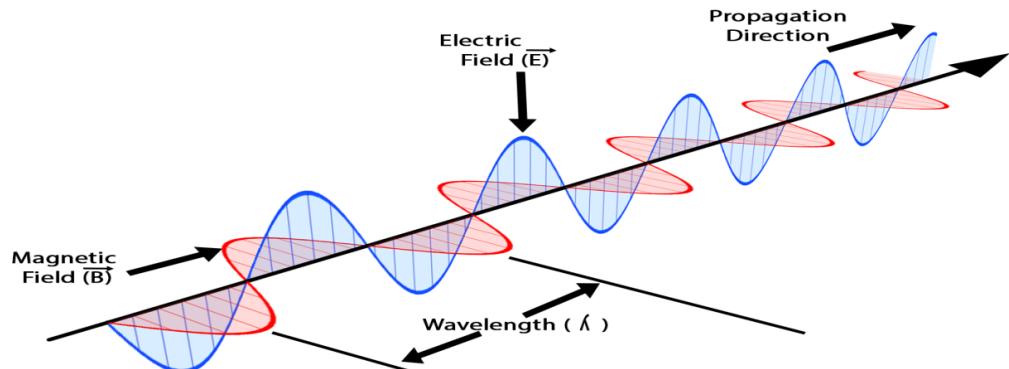
- *Definition of Molecular spectroscopy*
- *Interaction of electromagnetic radiation with matter*
- *Comparison between atomic and molecular spectra*
- *Quantisation of energy*
- *Absorption and emission spectra*
- *Spectroscopic units*

- **Molecular spectroscopy** is that branch of science which deals with the study of **interaction of electromagnetic radiation with matter(molecules)**
- **Incident radiation → sample → detector → diffraction grating → recorder(spectrum)**

Some important features of **electromagnetic radiations** are:

- They have **dual character** i.e. particle character as well as wave character, for example, a beam of light is a stream of particles called photons moving through the space in the form of waves
- These waves are associated with **electric and magnetic fields** oscillating perpendicular to each other and also perpendicular to the direction of propagation
- All electromagnetic radiations travel with the **velocity of light**

Electromagnetic Wave

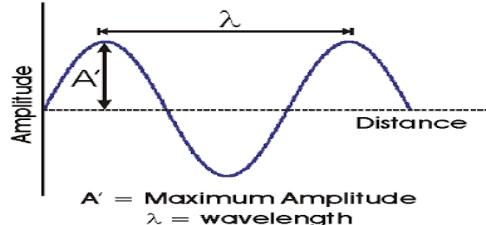


Source:<https://byjus.com/physics/characteristics-of-em-waves/>

ENGINEERING CHEMISTRY

Module I- Molecular Spectroscopy

Waves can be characterised by the following **properties** :



<http://www.chemistry.wustl.edu/~coursedev/Online%20tutorials/Waves.htm>

- **Wavelength** : The distance between two successive crests and troughs of the wave ; λ ; m , nm or A°
- **Frequency** : The number of cycles completed in a certain amount of time ; v ;Hz or s^{-1}
- **Wave number** : Number of complete waves or cycles contained in unit distance ; \bar{v} , cm^{-1}
- **Energy** of electromagnetic radiation is given by $E=hv$, where E is energy,h is Planck's constant,($h= 6.625 \times 10^{-34} \text{ Js}$), and v is frequency
- Wavelength is related to frequency by $c=\lambda v$, where c is the speed of light, λ is wavelength, and v is frequency
- Wave number is related to wavelength by $\bar{v} = \frac{1}{\lambda}$

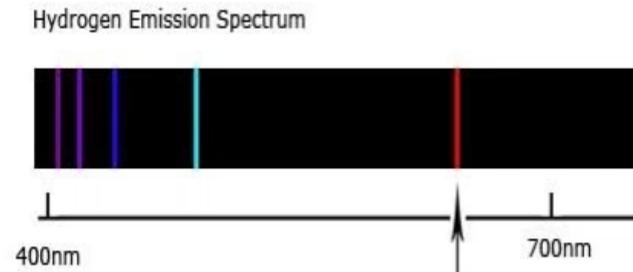
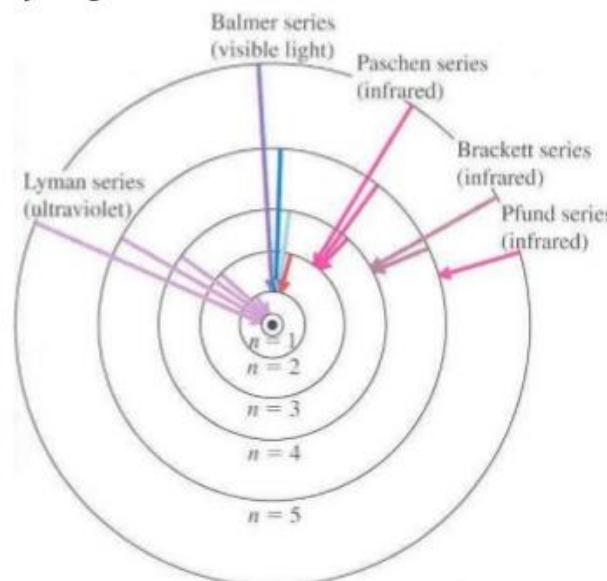
ENGINEERING CHEMISTRY

Module I- Molecular Spectroscopy

Comparision between atomic spectra and molecular spectra

Atomic spectra

- Due to electronic transitions from **one atomic orbital to another**
- Gives rise to **line spectra**



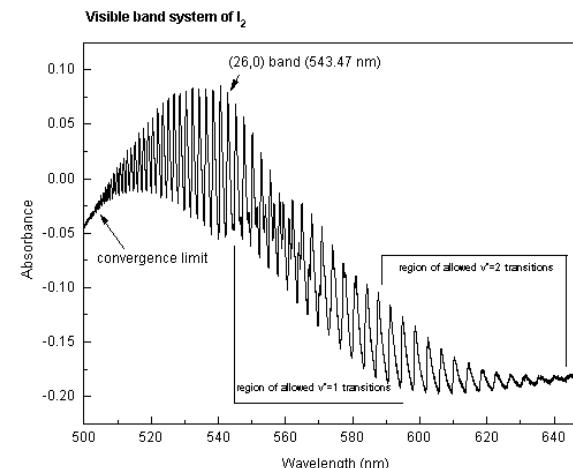
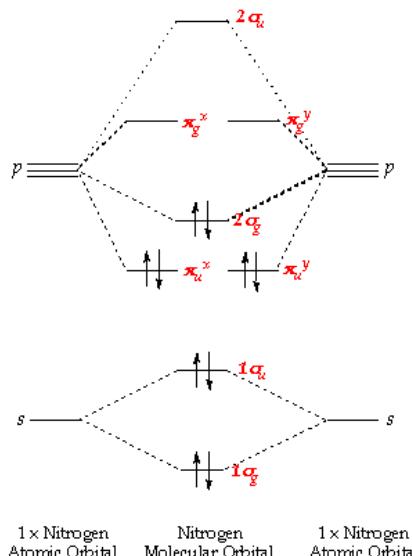
[Source:https://socratic.org/questions/what-happens-to-the-distance-between-energy-levels-at-higher-energy-levels](https://socratic.org/questions/what-happens-to-the-distance-between-energy-levels-at-higher-energy-levels)

ENGINEERING CHEMISTRY

Module I- Molecular Spectroscopy

Molecular spectra

- Due to electronic transitions from the **Highest occupied molecular orbital(HOMO)** to **Lowest unoccupied molecular orbital(LUMO)**
- Gives rise to **band spectra** due to rotational and vibrational transitions possible in molecules along with electronic transitions



Source:<https://socratic.org/questions/what-are-the-molecular-orbital-configurations-for-n-2-n-2-2-n-2-n-2-and-n-2-2>

Source:https://chem.libretexts.org/Courses/Pacific_Union_College/Quantum_Chemistry/13%3A_Molecular_Spectroscopy/13.06%3A_Electronic_Spectra_Contain_Electronic%2C_Vibrational%2C_and_Rotational_Information

Quantisation of energy

- Energy levels in atoms or molecules are discrete or **quantised**
- Energy can be absorbed only in packets called **quanta**
- Frequency of light absorbed when there is a transition between two energy levels depends on the **difference in energy** between the two energy levels
- If an atom or molecule in ground state absorbs energy there exists a higher energy level corresponding to the frequency of light absorbed

E₂

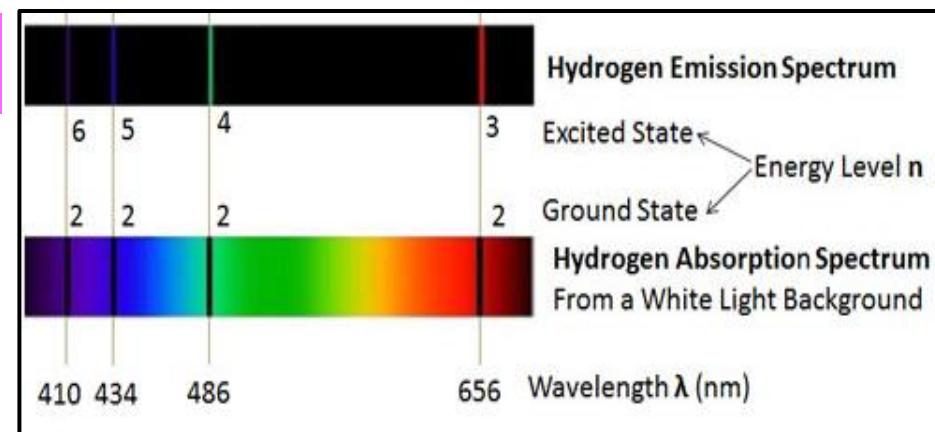
$$\Delta E = E_2 - E_1 = h\nu$$

E₁

Absorption and Emission spectrum

- **Absorption spectrum** is observed when an atom or molecule absorbs energy and moves from lower energy level to higher energy level
- **Emission spectrum** arises when molecule comes from higher energy level to lower energy level

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



ENGINEERING CHEMISTRY

Module I- Molecular Spectroscopy

Spectroscopic units

$E=h\nu$ where Energy is expressed in Joules
Wave number is related to wavelength by $\nu = \frac{1}{\lambda}$

since $c = \lambda\nu$, $\bar{\nu} = \frac{\nu}{c}$

Therefore $E = hc\bar{\nu}$ or $\bar{\nu} = \frac{E}{hc}$

- The **spectroscopic unit** for energy of a radiation is **cm⁻¹**
- It is **energy expressed in wave numbers**
- It is for **convenience** of using small numerals

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

ENGINEERING CHEMISTRY

Module 1- Molecular spectroscopy



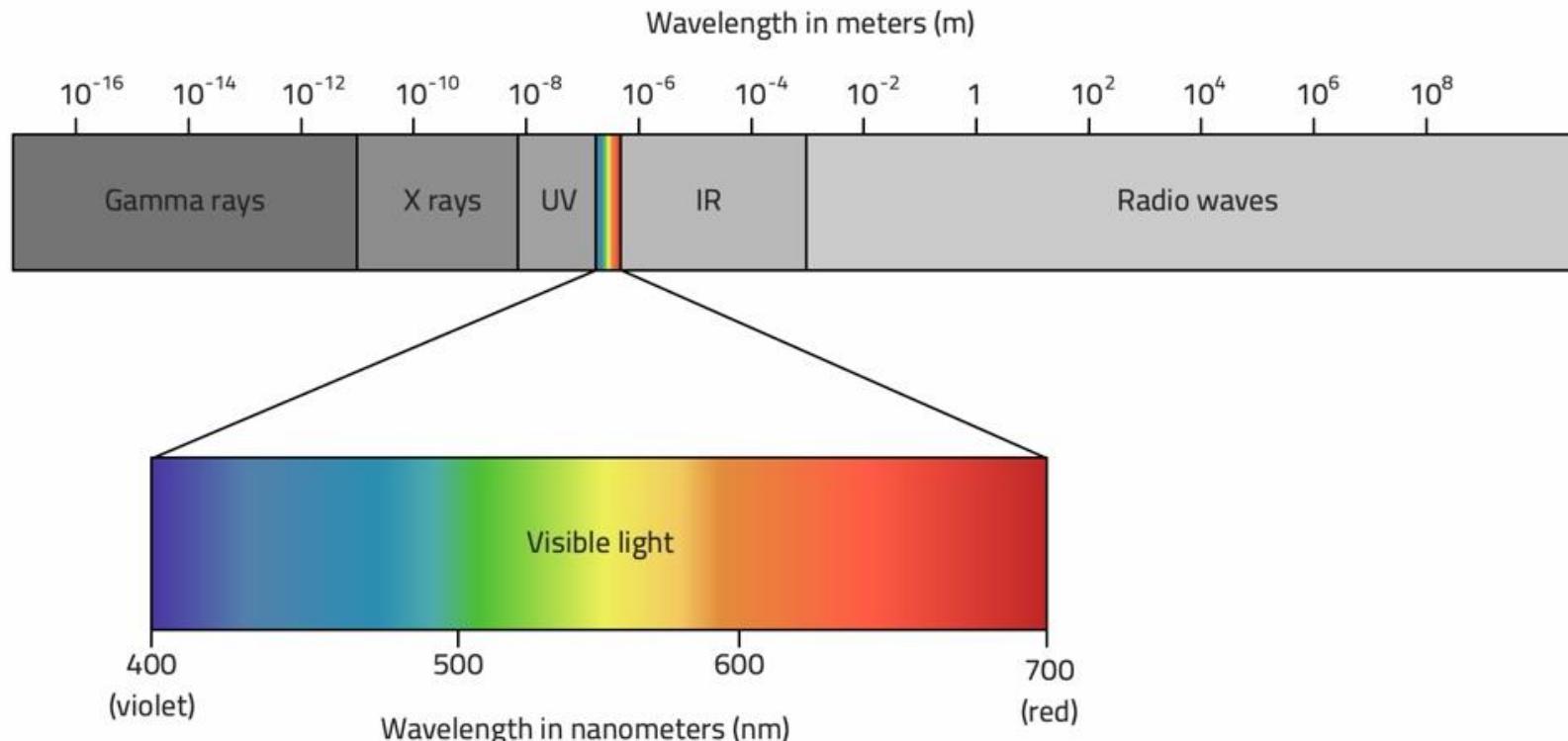
Class Content :

- *Electromagnetic spectrum*
- *Information obtained from each region of the spectrum*

ENGINEERING CHEMISTRY

Module I- Molecular Spectroscopy

Electromagnetic spectrum



Source: <https://www.radio2space.com/components-of-electromagnetic-spectrum/>

ENGINEERING CHEMISTRY

Module I- Molecular Spectroscopy

Information obtained from different regions of electromagnetic spectrum

Radiofrequency region	Wavelength (10m-1cm) NMR, ESR Nuclear and electron spin reversal
Microwave region	Wavelength (1cm-100μm) Rotational spectroscopy Rotational levels
Infra Red region	Wavelength (100μm-1μm) Vibrational spectroscopy Vibrational levels

ENGINEERING CHEMISTRY

Module I- Molecular Spectroscopy

Information obtained from different regions of electromagnetic spectrum

Visible and Ultra-Violet region	Wavelength (1μm-10nm) UV-Visible spectroscopy Electronic states Change in electronic distribution of valence electrons
X-ray region	Wavelength (10nm-100pm) X-ray spectroscopy Change in electronic distribution of inner electrons
γ- ray region	Wavelength (100pm-1pm) γ- ray spectroscopy Rearrangement of nuclear particles

ENGINEERING CHEMISTRY

Module I- Molecular Spectroscopy

Raman Spectroscopy: scattering of light

When monochromatic radiation is passed through a transparent medium:

Most of the scattered radiation consists of radiation of incident wavelength –

Rayleigh scattering

Some of the scattered radiation consists of radiation with different wavelength

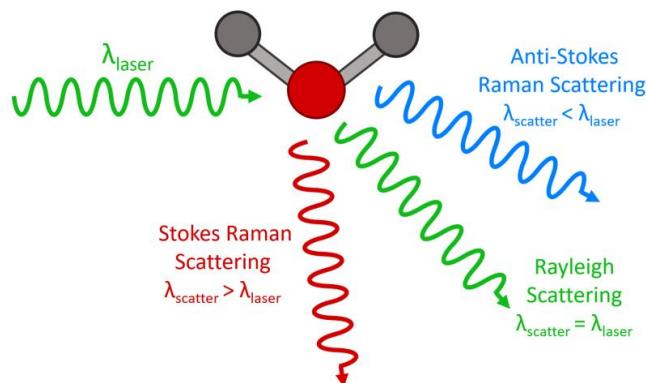
from incident wavelength – **Raman scattering**

When the wavelength of scattered radiation is more than that of incident radiation

– **Stokes lines**

When the wavelength of scattered radiation is less than that of incident radiation –

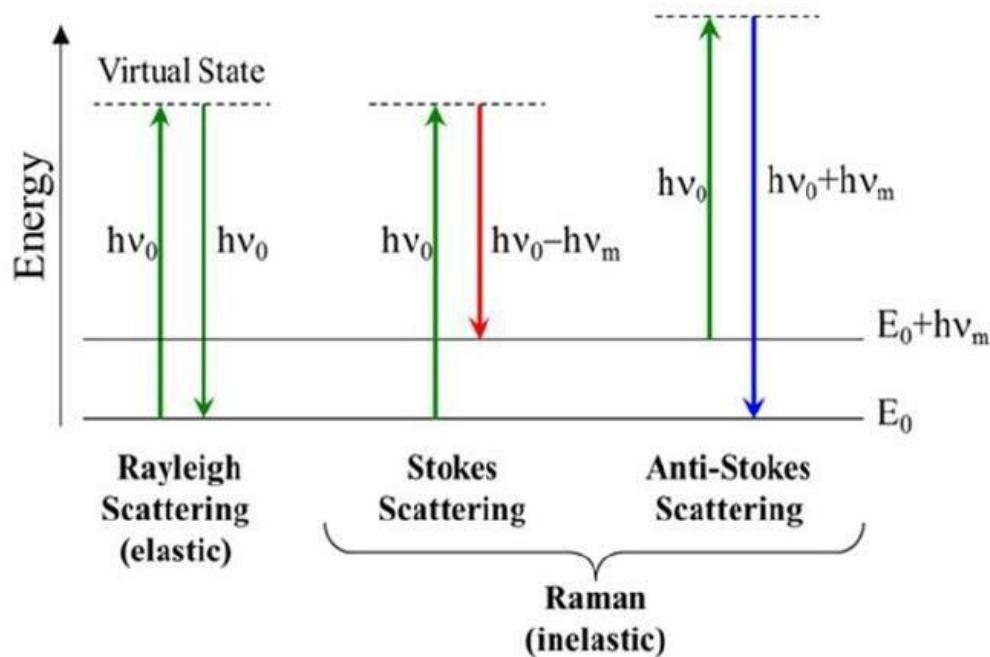
anti -Stokes lines



<https://www.edinst.com/blog/what-is-raman-spectroscopy/>

ENGINEERING CHEMISTRY

Module I- Molecular Spectroscopy



Source: https://www.researchgate.net/figure/A-simplified-diagram-of-energy-transitions-for-Rayleigh-and-Raman-scattering_fig7_327321311

Exchange of energy between the molecules and radiation

Homonuclear diatomic molecules which are microwave and Infra-red inactive are Raman active

ENGINEERING CHEMISTRY

Module I- Molecular Spectroscopy

Information obtained from different regions of electromagnetic spectrum

Spectral region	VHF	UHF	Microwave	Infrared	Visible	Ultraviolet	X-rays	γ-rays
Common usage	NMR	EPR	rotational transitions	vibrational transitions	electronic transitions	ionisation	nuclear effects	
Frequency (Hz)	5×10^8	3×10^{10}	3×10^{11}	3×10^{13}	6×10^{14}	1.2×10^{15}	3.0×10^{17}	1.5×10^{19}
Wavelength	0.6 m	1 cm	1 mm	$10 \mu\text{m}$	500 nm	250 nm	1 nm	20 pm
Wavenumber (cm^{-1})	0.017	1.0	10.0	1000	20,000	40,000	1.0×10^7	5.0×10^8

Source: <http://photobiology.info/Visser-Rolinski.html>

ENGINEERING CHEMISTRY

Module I- Molecular Spectroscopy



Class content:

- *Born - Oppenheimer approximation*
- *Energy level diagram of a diatomic molecule*
- *Beer-Lambert's law*
- *Introduction to rotational spectroscopy*

Different types of energies possessed by a molecule

- **Translational energy** (E_{trans}): by virtue of translatory motion of the molecule
- **Rotational energy** (E_{rot}) : by virtue of rotation of a molecule about its centre of gravity
- **Vibrational energy** (E_{vib}): by virtue of periodic displacement of the atoms of a molecule about its equilibrium position
- **Electronic energy**(E_{elec}) : due to the different electronic arrangements in the molecule

ENGINEERING CHEMISTRY

Module I- Molecular Spectroscopy

Born-Oppenheimer approximation

- **Total energy** of a molecule is the sum of translational, rotational, vibrational and electronic energies, i.e.

$$E = E_{\text{trans}} + E_{\text{rot}} + E_{\text{vib}} + E_{\text{elec}}$$

- Translational energy is negligibly small. Hence Born-Oppenheimer approximation can be written as

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

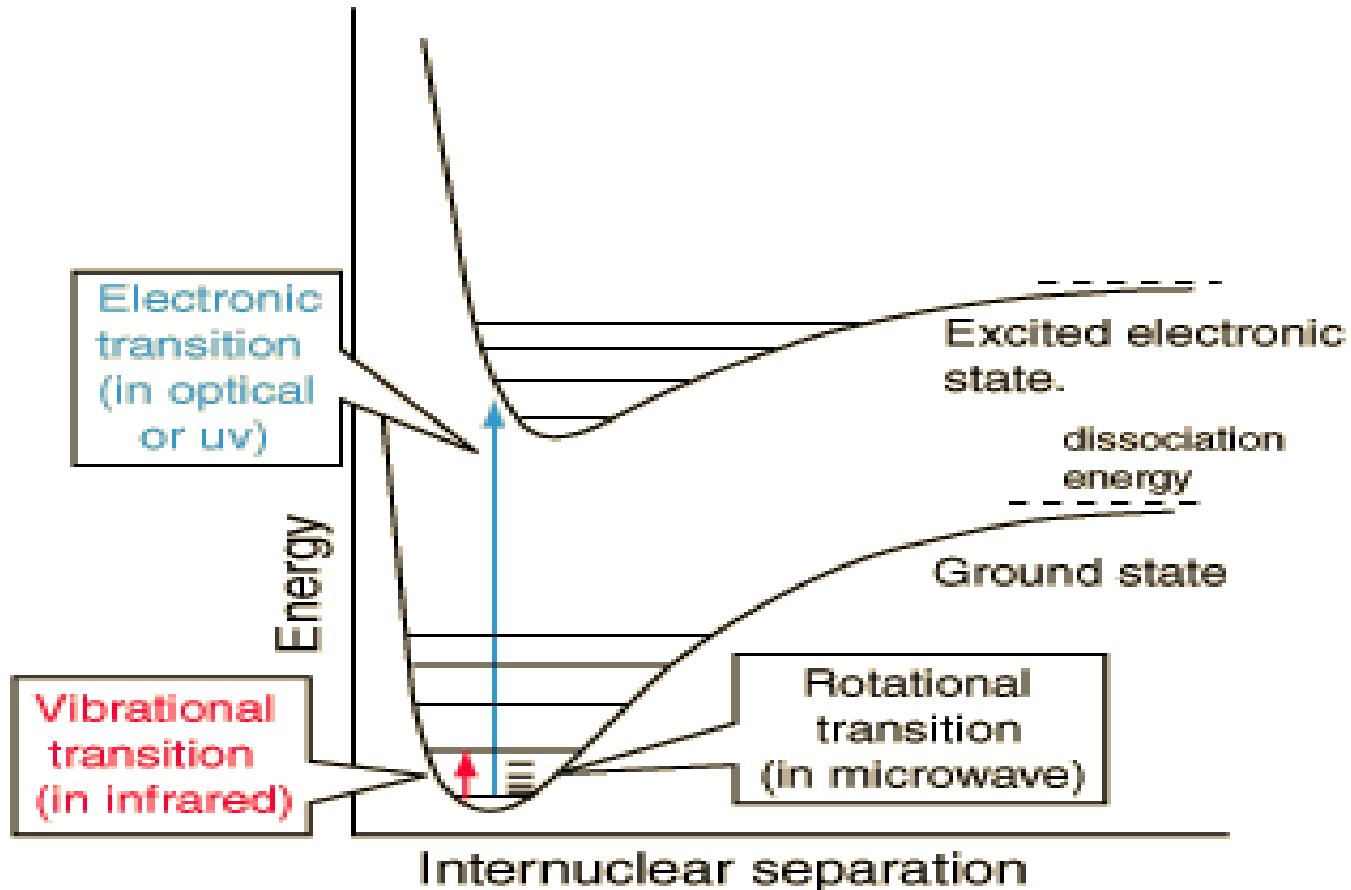
- Electronic, vibrational and rotational energies of a molecule are **completely independent** of each other
- Because the electronic energy levels are much farther apart than the vibrational energy levels which are again much farther apart than the rotational energy levels
- Can be written as

$$E_{\text{rot}} \ll E_{\text{vib}} \ll E_{\text{elec}}$$

ENGINEERING CHEMISTRY

Module I- Molecular Spectroscopy

Energy level diagram for a diatomic molecule



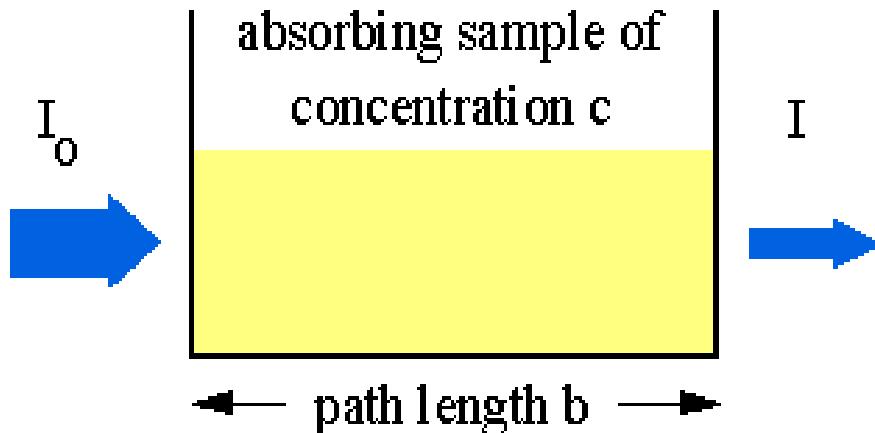
ENGINEERING CHEMISTRY

Module I- Molecular Spectroscopy

Lambert-Beer's law

When light falls on a homogeneous medium, a part of it is **absorbed**, part of it is **reflected** and the rest is **transmitted**

If I_0 is the incident light and I is the transmitted light,



Source:<http://life.nthu.edu.tw/~labcjw/BioPhyChem/Spectroscopy/beerslaw.htm>

Transmittance is given by

$$T = I/I_0$$

Absorbance is related to the % T by

$$A = -\log T = -\log (I/I_0)$$

ENGINEERING CHEMISTRY

Module I- Molecular Spectroscopy

Lambert's law:

When a beam of **monochromatic light** passes through a transparent medium, the decrease in intensity with **thickness of the medium** is proportional to intensity of incident radiation

$$I_t = I_0 e^{-k'l}$$

Beer's Law:

When a beam of **monochromatic light** passes through a transparent medium, the decrease in intensity with **concentration of the light absorbing species** is proportional to intensity of incident radiation.

$$I_t = I_0 e^{-k''c}$$

ENGINEERING CHEMISTRY

Module I- Molecular Spectroscopy

Lambert-Beer's law :

Combining the two laws we get

$$\log_{10} \frac{I_o}{I} = \epsilon l c$$

Greek letter, epsilon

concentration of solution
(mol dm⁻³)

length of solution the light
passes through (cm)

Source:[https://chem.libretexts.org/Bookshelves/Physical_and_Theoretical_Chemistry_Textbook_Maps/Supplemental_Modules_\(Physical_and_Theoretical_Chemistry\)/Spectroscopy/Electronic_Spectroscopy/Electronic_Spectroscopy_Basics/The_Beer-Lambert_Law](https://chem.libretexts.org/Bookshelves/Physical_and_Theoretical_Chemistry_Textbook_Maps/Supplemental_Modules_(Physical_and_Theoretical_Chemistry)/Spectroscopy/Electronic_Spectroscopy/Electronic_Spectroscopy_Basics/The_Beer-Lambert_Law)

which can also be written as

$$A = \epsilon cl$$

A	Absorbance	
ϵ	Molar absorption coefficient	M ⁻¹ cm ⁻¹
c	Molar concentration	M
l	optical path length	cm

Source: <https://www.edinst.com/blog/the-beer-lambert-law/>

ENGINEERING CHEMISTRY

Module I- Molecular Spectroscopy

Rotational spectroscopy

- A molecule undergoing rotation absorbs in the **microwave region**
- For a molecule to be rotationally active or microwave active the molecule has to possess a **permanent dipole moment**
- Rotations of a molecule having permanent dipole moment will cause changes in **electric dipoles** that will interact with the **electrical component** of the electromagnetic radiation

ENGINEERING CHEMISTRY

Module I- Molecular Spectroscopy

H-Cl

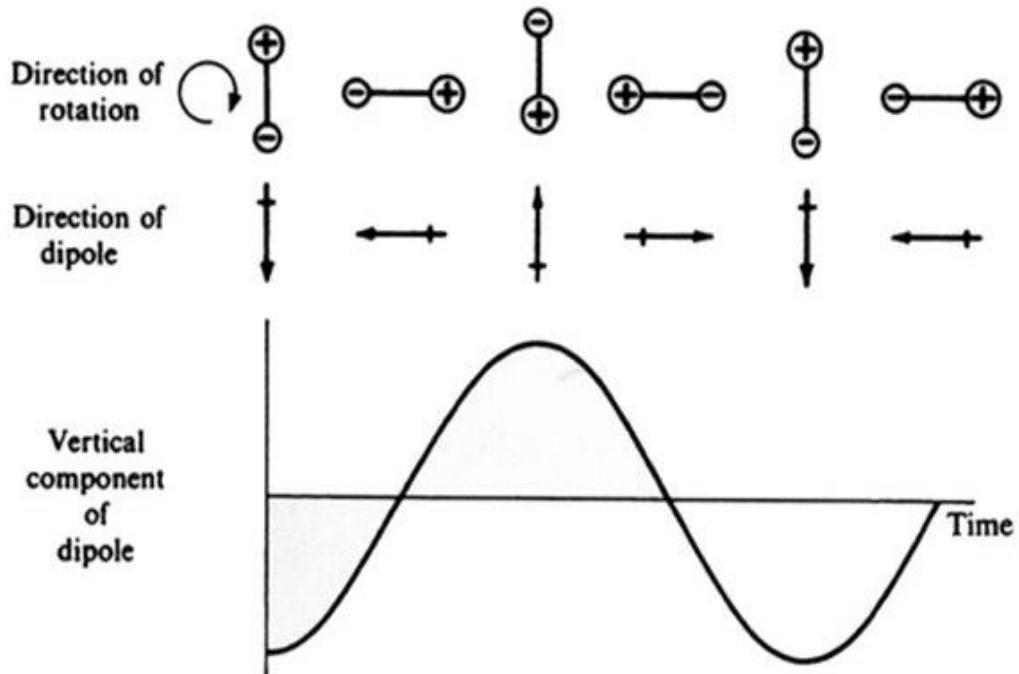


Fig. The rotation of a polar diatomic molecule, showing the fluctuation in the dipole moment measured in a particular direction

Source:Fundamentals of Molecular Spectroscopy: C. N. Banwell and Elaine M McCash, Fifth Edition, MCGRAW-HILL Education (India) Private Ltd.

ENGINEERING CHEMISTRY

Module I- Molecular Spectroscopy



- When the frequencies match, **resonance occurs** and the molecule absorbs energy and goes to the higher rotational levels and a **rotational spectrum** can be recorded
- Molecules such as **HCl and CO** show rotational spectra as they possess permanent dipole moment while **H₂, Cl₂ and CO₂** do not

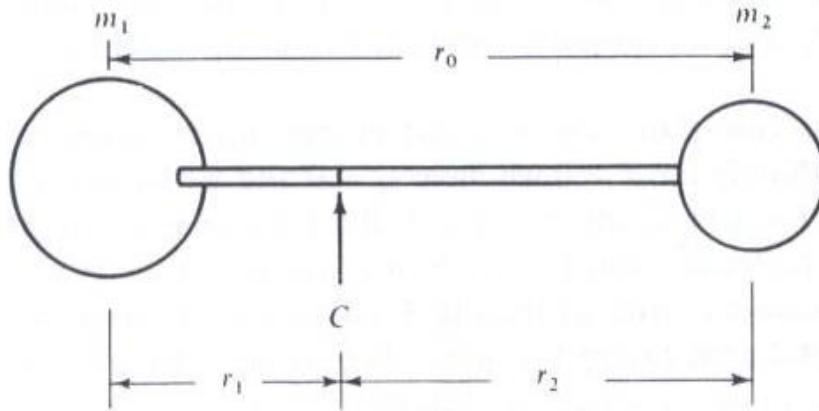
Class content:

- *Expression for rotational energy levels of a diatomic molecule*
- *Selection rules*
- *Rotational spectrum*

Module I- Molecular Spectroscopy

Expressions for rotational energy levels for a diatomic molecule

- Derivation of Moment of Inertia for a heteronuclear diatomic molecule- rigid rotor model



Source:Fundamentals of Molecular Spectroscopy: C. N. Banwell and Elaine M McCash, Fifth Edition, MCGRAW-HILL Education (India) Private Ltd.

A rigid diatomic molecule with masses m_1 and m_2 joined by a thin rod of length $r_0 = r_1 + r_2$. The centre of mass is at C

Module I- Molecular Spectroscopy

The molecule rotates end- over- end about a point C, the centre of gravity , this is defined by the moment, or balancing, equation:

$$m_1 r_1 = m_2 r_2$$

The **moment of inertia** about C is defined by

$$I = m_1 r_1^2 + m_2 r_2^2$$

$$I = m_2 r_2 r_1 + m_1 r_1 r_2$$

$$I = r_1 r_2 (m_1 + m_2)$$

Since $m_1 r_1 = m_2 r_2 = m_2 (r_o - r_1)$, $r_1 = \frac{m_2 r_o}{m_1 + m_2}$

Since $m_1 r_1 = m_2 r_2 = m_1 (r_o - r_2)$, $r_2 = \frac{m_1 r_o}{m_1 + m_2}$

Therefore $I = \frac{m_1 m_2}{m_1 + m_2} r_o^2 = \mu r_o^2$

Where μ is the reduced mass given by

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

Module I- Molecular Spectroscopy

Rotational energy $E_r = \frac{1}{2} I \omega^2 = \frac{L^2}{2I}$; Since $L=I\omega$

Solving the Schrodinger equation for a rigid rotor shows that angular momentum is quantised and is given by,

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

where J is the rotational quantum number.

The quantity J , **rotational quantum number**, which can take integral values from zero upwards; **J=0,1,2,3.....**

Hence the rotational energy levels are quantised and given by the expression,

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

h = Planck's constant= 6.626×10^{-34} Js and I is the moment of inertia

Module I- Molecular Spectroscopy

The energy expressed in spectroscopic units(cm^{-1}) is given by :

$$\varepsilon_J = \frac{h}{8\pi^2 I c} J(J+1) \text{cm}^{-1}$$

which can be written as

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

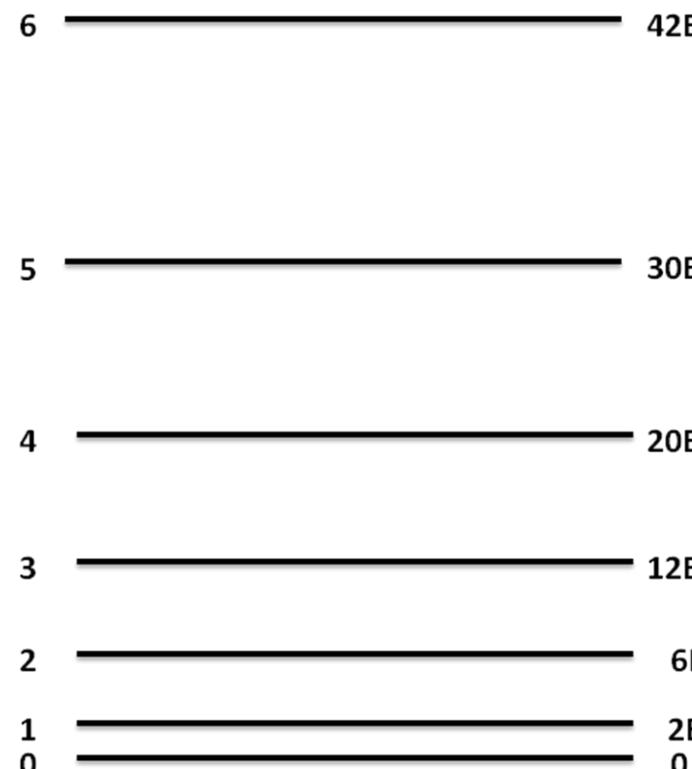
where $B = \frac{h}{8\pi^2 I c} \text{cm}^{-1}$

B is known as the **rotational constant**

Substituting for values of

$J = 0, 1, 2, 3, \dots$, we can get the energies for the rotational levels

J	ε_J
0	0
1	2B
2	6B
3	12B



Module I- Molecular Spectroscopy

The **selection rules** for rigid rotor model obtained after solving Schodinger equation is :

- **Gross selection rule – molecule should possess permanent dipole moment**
- $\Delta J = \pm 1$

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

For rotational transition of a molecule from level $J \rightarrow J + 1$, the energy absorbed is given by $\Delta\varepsilon_{J \rightarrow (J+1)} = \bar{\nu} = 2B(J + 1)cm^{-1}$

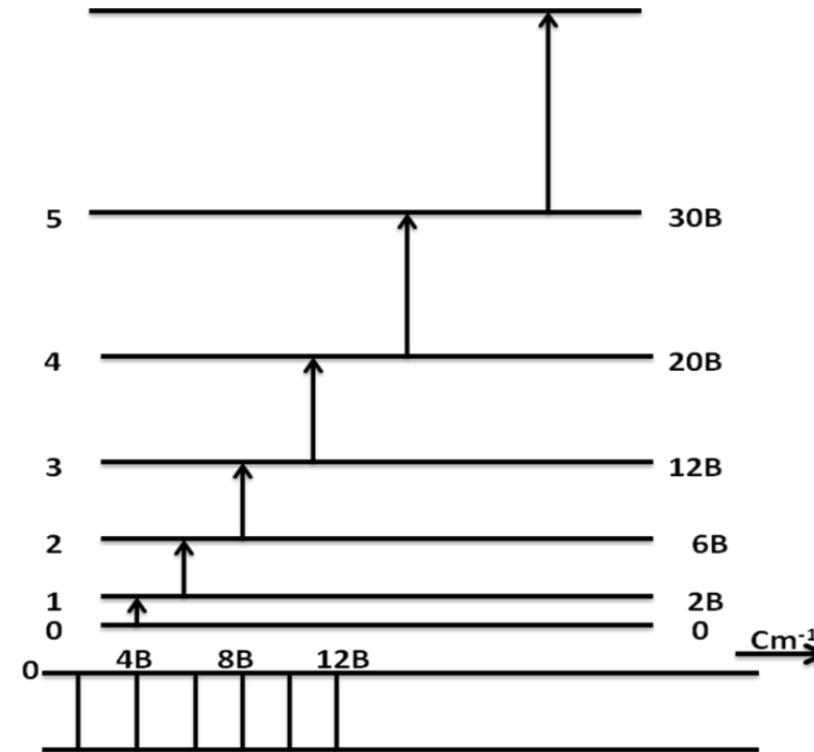
Substituting for values for $J = 0,1,2,3....$

J	$\Delta\varepsilon_{(J \rightarrow J+1)}$
0	$2B\text{ cm}^{-1}$
1	$4B\text{ cm}^{-1}$
2	$6B\text{ cm}^{-1}$

Module I- Molecular Spectroscopy

Rotational energy levels and spectrum

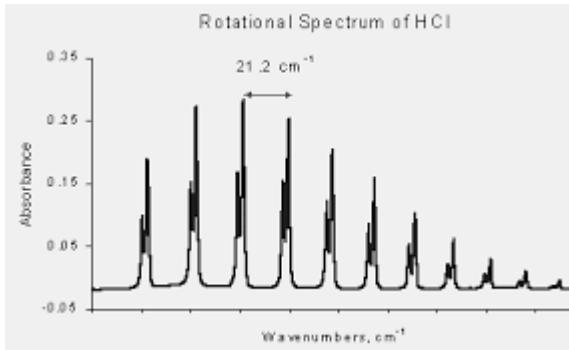
J	$\Delta\epsilon_{(J \rightarrow J+1)}$
0	2B cm^{-1}
1	4B cm^{-1}
2	6B cm^{-1}
3	8B cm^{-1}
4	10B cm^{-1}



Source:Fundamentals of Molecular Spectroscopy: C. N. Banwell and Elaine M McCash, Fifth Edition, MCGRAW-HILL Education (India) Private Ltd.

Module I- Molecular Spectroscopy

Information obtained from the rotational spectrum



Source:<http://www.physics.dcu.ie/~be/Ps415/Rotational1.pdf>

- The **first line in the spectrum** appears at $2B \text{ cm}^{-1}$ and the **distance between any two consecutive lines** is constant and is equal to $2B \text{ cm}^{-1}$. We can get value of 'B' from the spectrum and calculate I , the moment of inertia using the expression

$$B = \frac{h}{8\pi^2 I c} \text{ cm}^{-1}$$

Since $I = \mu r_o^2$, r_o can be determined ; $r_o = \sqrt{\frac{I}{\mu}}$
 r_o is the **bond length** of the molecule

- The spectrum also reveals that **some higher rotational levels are also populated at room temperature**

ENGINEERING CHEMISTRY

Module I- Molecular Spectroscopy



Class Content:

- *Vibrational spectroscopy*
- *Expression for vibrational energy levels
(Harmonic oscillator)*
- *Vibrational spectrum(Harmonic oscillator)*

ENGINEERING CHEMISTRY

Module I- Molecular Spectroscopy

Vibrational Spectroscopy



- When a molecule undergoes vibrational changes it absorbs **IR radiation**
- For a molecule to be vibrationally active (IR active) the vibration of a molecule must be associated with **change in dipole moment**
- Vibrations of molecules can result in changes in electric dipoles that can interact with the **electrical component** of the electromagnetic radiation.

ENGINEERING CHEMISTRY

Module I- Molecular Spectroscopy

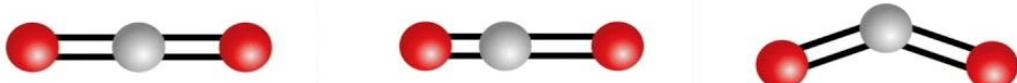
- When the frequencies match, **resonance occurs** and the molecule absorbs energy and goes to the higher **vibrational levels** and exhibits **vibrational spectrum**
- Molecules such as **HCl ,CO and H₂O** will show vibrational spectra while **H₂, Cl₂** will not
- **CO₂** molecule does not possess permanent dipole moment but **is IR active** as when it vibrates asymmetrically or in bending mode ,there is change in dipole moment

ENGINEERING CHEMISTRY

Module I- Molecular Spectroscopy

CO_2 molecule although does not possess permanent dipole moment is IR active because some of its vibrational modes are IR active:

- CO_2 **symmetric stretch** is IR inactive as there is no change in dipole moment when molecule vibrates in this mode.
- CO_2 **asymmetric stretch** is IR active
- CO_2 **bending** mode is IR active



Symmetrical stretching

No change in dipole moment therefore IR inactive

Asymmetrical stretching

Change in dipole moment therefore IR active

In plane bending

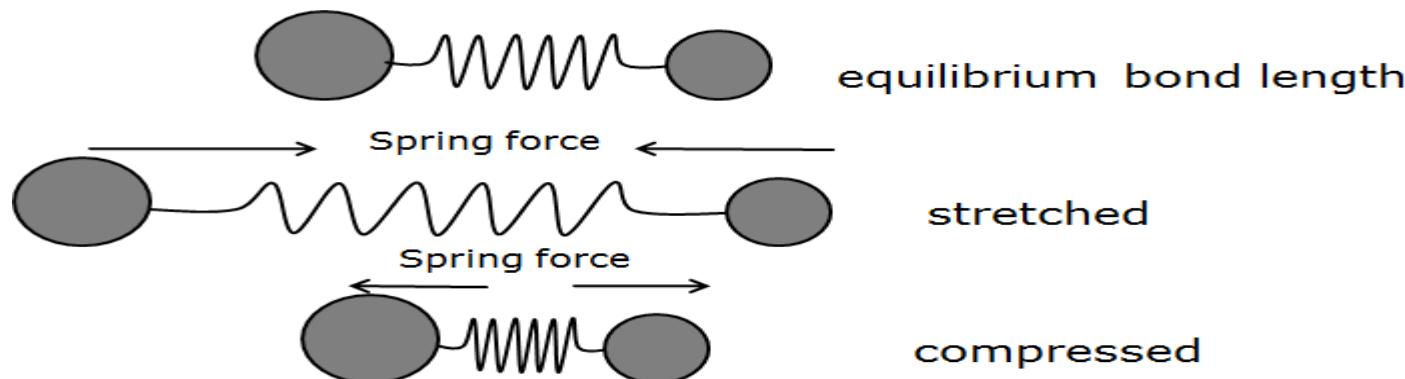
Change in dipole moment therefore IR active

ENGINEERING CHEMISTRY

Module I- Molecular Spectroscopy

Vibrational spectroscopy of diatomic molecule: simple harmonic oscillator (SHO) model

- Every type of bond in a molecule has a unique natural **vibrational frequency**
- Therefore the IR spectrum of every molecule is **unique** as much as the finger print of human beings
- Bonds are not static but **vibrating in different ways**
- A vibrating bond can therefore be considered a spring with its ends tethered to two atoms as in the figure and obeys **Hooke's law**



Source : Ramasahayam, Swathi & Roy Chowdhury, Shubhajit. (2016). Non Invasive Estimation of Blood Urea Concentration using Near Infrared Spectroscopy. International Journal on Smart Sensing and Intelligent Systems. 9. 10.21307/ijssis-2017-878.

ENGINEERING CHEMISTRY

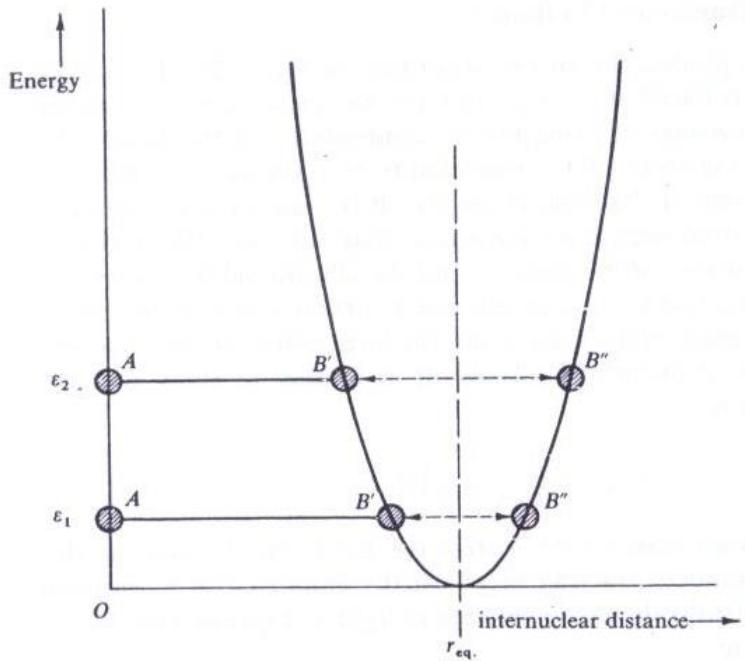
Module I- Molecular Spectroscopy

The vibrating bond obeys Hooke's law, $F=-k(r-r_{eq})$

where k is a force constant, r is bond length, r_{eq} is equilibrium internuclear distance

Energy is given by

$$E = \frac{1}{2} k(r - r_{eq})^2 \quad \text{Hence the energy curve is parabolic}$$



Source:Fundamentals of Molecular Spectroscopy: C. N. Banwell and Elaine M McCash, Fifth Edition, MCGRAW-HILL Education (India) Private Ltd.

ENGINEERING CHEMISTRY

Module I- Molecular Spectroscopy

The **oscillation frequency** is given by,

$$\nu_{osc} = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \text{Hz}$$

where μ is **reduced mass**

Expressing frequency of oscillation in terms of wavenumber

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

Solving **Schrodinger equation for harmonic oscillator** shows vibrational energy levels are quantised and are given by the expression

$$E_v = (\nu + \frac{1}{2}) h \nu_{osc} \text{Joules}$$

where **v= vibrational quantum number** which can take up values zero upwards;
v=0,1,2,3....

Vibrational energy expressed in terms of wavenumber is given by,

$$\epsilon_v = (\nu + \frac{1}{2}) \bar{\nu}_{osc} \text{cm}^{-1}$$

ENGINEERING CHEMISTRY

Module I- Molecular Spectroscopy

The energy levels will appear at,

v	ϵ_v
0	$\epsilon_0 = \frac{1}{2} \bar{\nu}_{osc} cm^{-1}$
1	$\epsilon_1 = \frac{3}{2} \bar{\nu}_{osc} cm^{-1}$
2	$\epsilon_2 = \frac{5}{2} \bar{\nu}_{osc} cm^{-1}$

ϵ_0 is called **zero point energy**

The **difference between any two consecutive energy levels** is equal to $\bar{\nu}_{osc} cm^{-1}$
Hence the energy levels are equally spaced.

The **selection rules** for vibrational transitions are

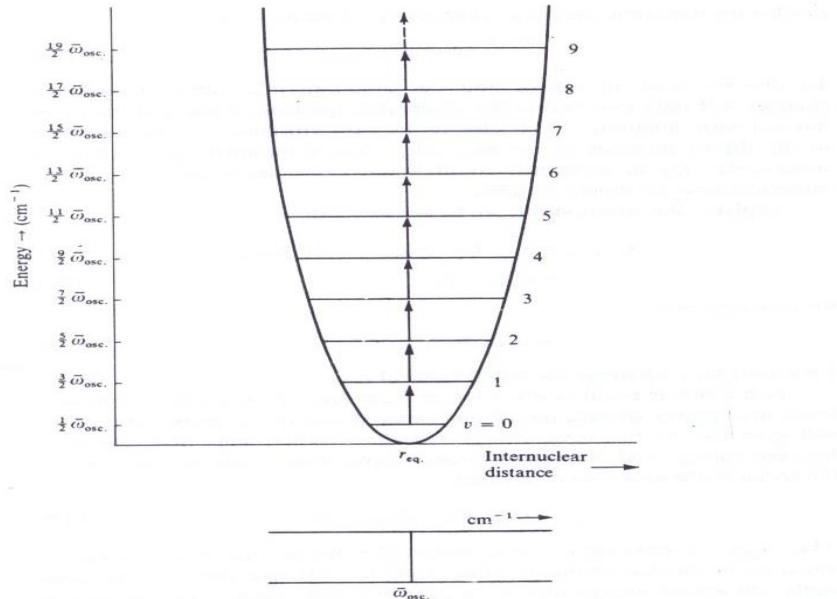
- **Gross selection rule** : When the molecule vibrates there should be a change in the dipole moment
- **$\Delta v = \pm 1$**

Therefore transition between any two consecutive vibrational levels are allowed and only **one line** is observed in the vibrational spectrum at $\bar{\nu}_{osc} cm^{-1}$

ENGINEERING CHEMISTRY

Module I- Molecular Spectroscopy

Vibrational energy levels and resulting spectrum for a diatomic molecule executing simple harmonic motion



Source:Fundamentals of Molecular Spectroscopy: C. N. Banwell and Elaine M McCash, Fifth Edition,
MCGRAW-HILL Education (India) Private Ltd.

From the spectrum $\bar{\nu}_{osc}$ can be obtained and using the expression

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

k can be determined which is the **bond strength** of the molecule

ENGINEERING CHEMISTRY

Module I- Molecular Spectroscopy



Class Content:

- *Vibrational spectroscopy-Anharmonic Oscillator*
- *Expression for vibrational energy levels for an Anharmonic oscillator*
- *Vibrational spectrum of an Anharmonic Oscillator*

ENGINEERING CHEMISTRY

Module I- Molecular Spectroscopy

Vibrational spectroscopy-Anharmonic oscillator model

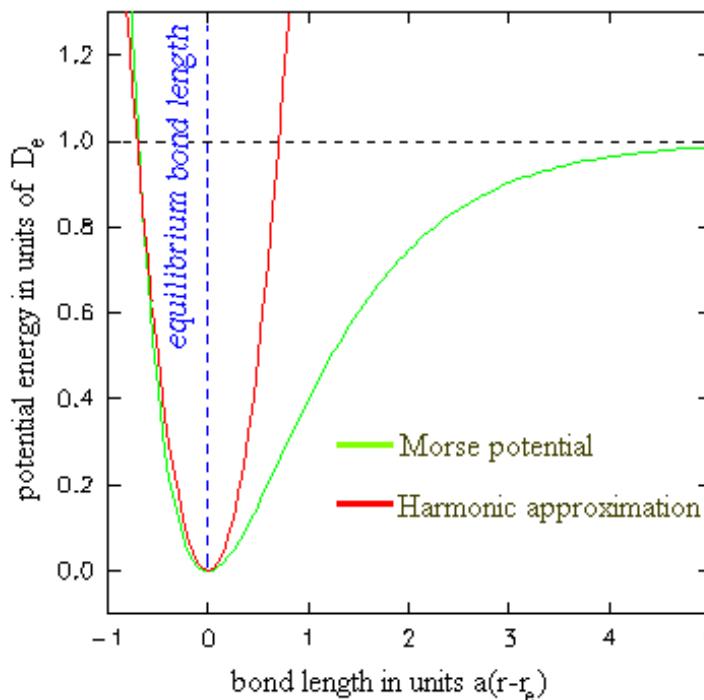
- In actual diatomics, the **potential is anharmonic** because the bond when stretched beyond a point breaks and the molecule dissociates
- A good description of an anharmonic oscillator is given by the Morse function

$$\text{P.E.} = D_{\text{eq}} [1 - \exp \{a(r_0 - r)\}^2]$$

D_{eq} is the depth of the PE curve

r_0 is the bond length

Source:<https://physics.stackexchange.com/questions/54814/why-is-there-a-global-minimum-for-the-morse-potential/55077>



ENGINEERING CHEMISTRY

Module I- Molecular Spectroscopy

Energy levels of an anharmonic oscillator:

- Solving the **Schrodinger equation** for anharmonic oscillator the vibrational energy levels are given by the expression

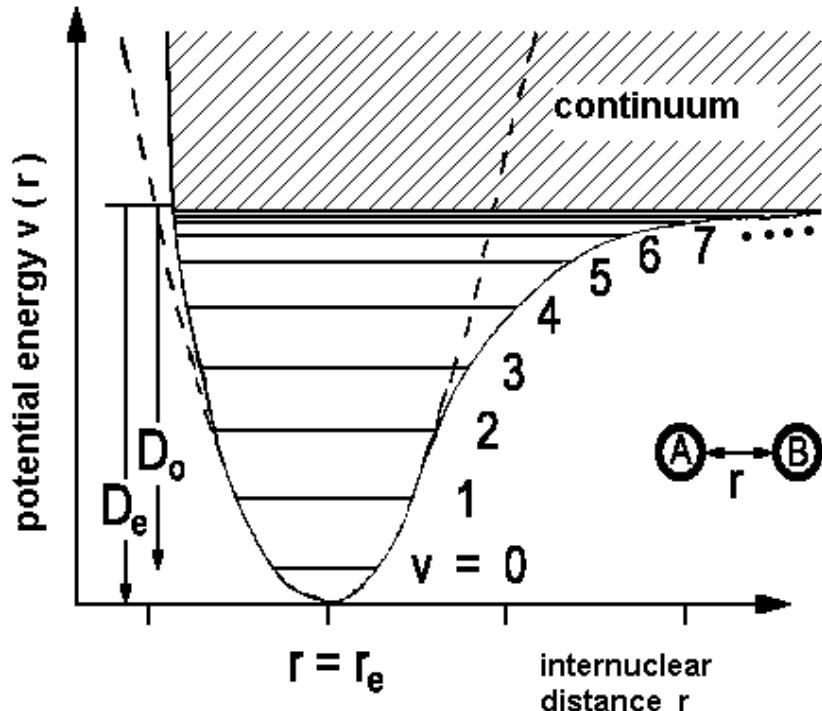
$$\varepsilon_v = \frac{E_v}{hc} = (v + \frac{1}{2})\bar{\nu}_e - (v + \frac{1}{2})^2 \bar{\nu}_e x_e \text{cm}^{-1}$$

- x_e , is called the **anharmonicity constant** whose value for bond stretching vibrations is always small and positive
- $\bar{\nu}_e$ is the **oscillation frequency** expressed in wavenumbers
- v is the **vibrational quantum number** which can take up values 0,1,2,3....
- Substituting values for v we get the energy levels for an anharmonic oscillator

ENGINEERING CHEMISTRY

Module I- Molecular Spectroscopy

Energy level diagram for a diatomic molecule showing anharmonicity



$$\varepsilon_v = \frac{E_v}{hc} = (v + \frac{1}{2})\bar{\nu}_e - (v + \frac{1}{2})^2 \bar{\nu}_e x_e \text{ cm}^{-1}$$

Source: http://www pci.tu-bs.de/aggericke/PC4e/Kap_III/Vibration.htm

The spacing between energy levels decreases as v , the vibrational quantum number, increases

ENGINEERING CHEMISTRY

Module I- Molecular Spectroscopy

- Selection rules for vibrational transition of anharmonic oscillator :
 - Gross selection rule : When a molecule vibrates there should be change in dipole moment
 - $\Delta v = \pm 1, \pm 2, \pm 3.....$
- Most of the transitions start from **v=0 level** because this state is most populated
- The transitions observed are :
 - $v=0 \rightarrow v=1$ **Fundamental absorption**
 - $v=0 \rightarrow v= 2$ **First overtone**
 - $v=0 \rightarrow v=3$ **Second overtone**

ENGINEERING CHEMISTRY

Module I- Molecular Spectroscopy

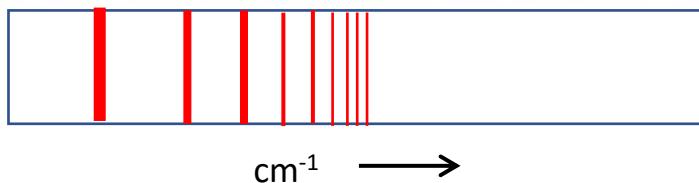
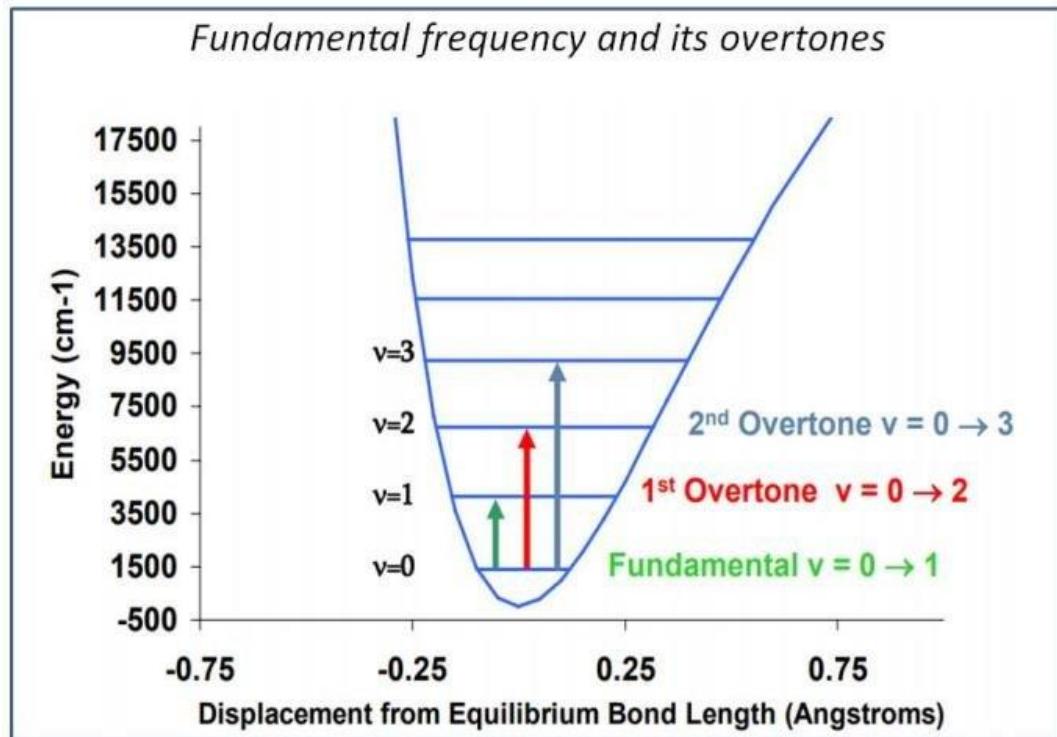
Substituting for values of v , we get the **energy gap** $\Delta\epsilon_{v+1 \leftarrow v}$

Transition	Energy gap	
$v=0$ to $v=1$	$\Delta\epsilon_{1 \leftarrow 0} = \overline{\nu_e}(1 - 2x_e) cm^{-1}$	Fundamental absorption
$v=0$ to $v=2$	$\Delta\epsilon_{2 \leftarrow 0} = \overline{2\nu_e}(1 - 3x_e) cm^{-1}$	First overtone
$v=0$ to $v=3$	$\Delta\epsilon_{3 \leftarrow 0} = \overline{3\nu_e}(1 - 4x_e) cm^{-1}$	Second overtone

ENGINEERING CHEMISTRY

Module I- Molecular Spectroscopy

Vibrational transitions for diatomic molecule undergoing anharmonic oscillations



Source: https://www.researchgate.net/figure/Fundamental-frequency-and-overtones-see-lecture-N-Antaris_fig2_331976119

The spacing between the lines in the spectrum decreases as we go to higher values of v

ENGINEERING CHEMISTRY

Module I- Molecular Spectroscopy



At **higher temperatures** additional lines are visible in the spectrum as higher vibrational levels may also get populated and these lines originating from the higher vibrational levels are called **hot bands**

e.g., Energy absorbed for the transition from **$v=1$ to $v=2$** is given by,

$$\Delta\epsilon_{2 \leftarrow 1} = \overline{\nu_e} (1 - 4x_e) \text{ cm}^{-1}$$

The expression shows that this line will appear to the left of the fundamental absorption in the spectrum

ENGINEERING CHEMISTRY

Module I- Molecular Spectroscopy



Class content:

- *Electronic spectroscopy*
- *Born – Oppenheimer Approximation*
- *Vibrational coarse structure-Progressions*

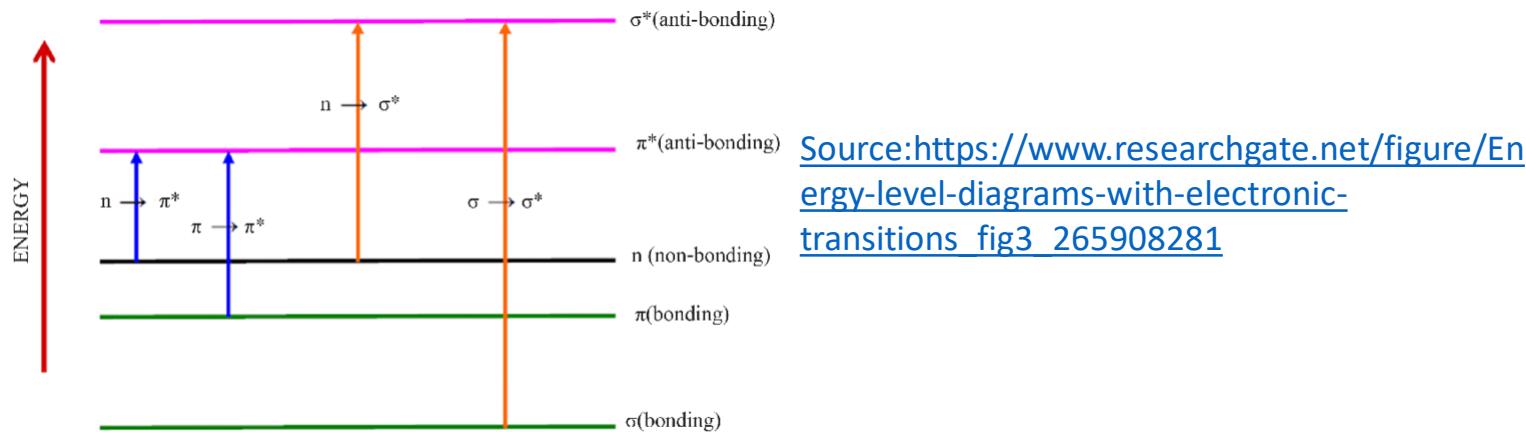
ENGINEERING CHEMISTRY

Module I- Molecular Spectroscopy

Electronic spectroscopy

Electronic transitions :

- Highest Occupied Molecular Orbitals (HOMO) → Lowest Unoccupied Molecular Orbitals(LUMO)



Source: https://www.researchgate.net/figure/Energy-level-diagrams-with-electronic-transitions_fig3_265908281

- Transitions in **UV-Visible region**
- $\sigma \rightarrow \sigma^*$, $\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$
- If transitions in visible region **colour** can be seen
- Electron redistribution causes **change in electric field**
- **All molecules** can undergo electronic transitions

ENGINEERING CHEMISTRY

Module I- Molecular Spectroscopy

Born-Oppenheimer approximation

According to Born-Oppenheimer approximation, the **total energy** of a molecule is the sum of translational, rotational, vibrational and electronic energies, i.e.

$$E = E_r + E_v + E_e$$

which implies that the electronic, vibrational and rotational energies of a molecule are **completely independent** of each other.

The change in total energy of the molecule is given by

$$\Delta E_{Total} = \Delta E_{Rot} + \Delta E_{Vib} + \Delta E_{Electronic} \quad \text{in Joules}$$

$$\Delta \varepsilon_{Total} = \Delta \varepsilon_{Rot} + \Delta \varepsilon_{Vib} + \Delta \varepsilon_{Electronic} \quad \text{in cm}^{-1}$$

The approximate orders of magnitude are

$$\Delta \varepsilon_{Rot} \times 10^6 \simeq \Delta \varepsilon_{Vib} \times 10^3 \simeq \Delta \varepsilon_{Electronic}$$

ENGINEERING CHEMISTRY

Module I- Molecular Spectroscopy

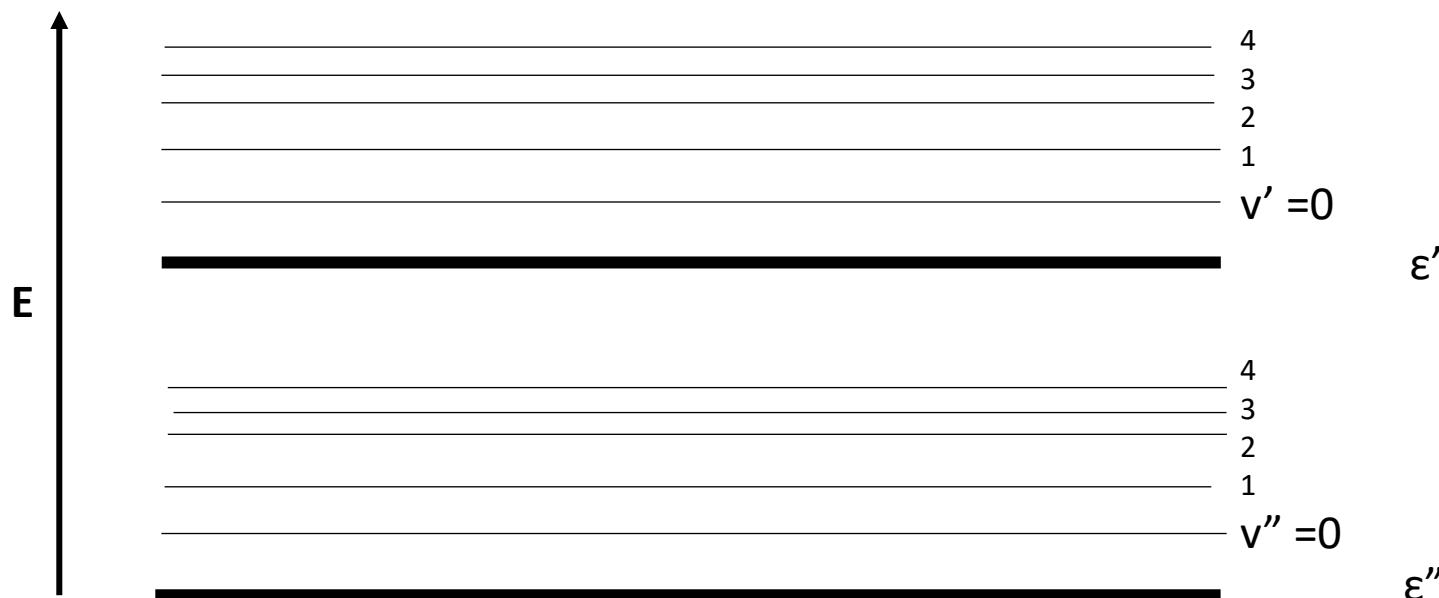
- Electronic transitions involve **electronic redistribution** hence electrostatic forces experienced by the molecule which **vibrates in response** and this in turn **affects rotation** of the molecule
- Electronic transitions are accompanied by vibrational and rotational changes. Hence vibrational changes will produce "**coarse structure**" and rotational changes will produce "**fine structure**" in the electronic spectra of molecules
- Information about vibrational and rotational structure of **homonuclear molecules** like H₂, N₂ which are inactive in IR and Microwave region can be obtained from their electronic spectra

ENGINEERING CHEMISTRY

Module I- Molecular Spectroscopy

Vibrational Coarse structure

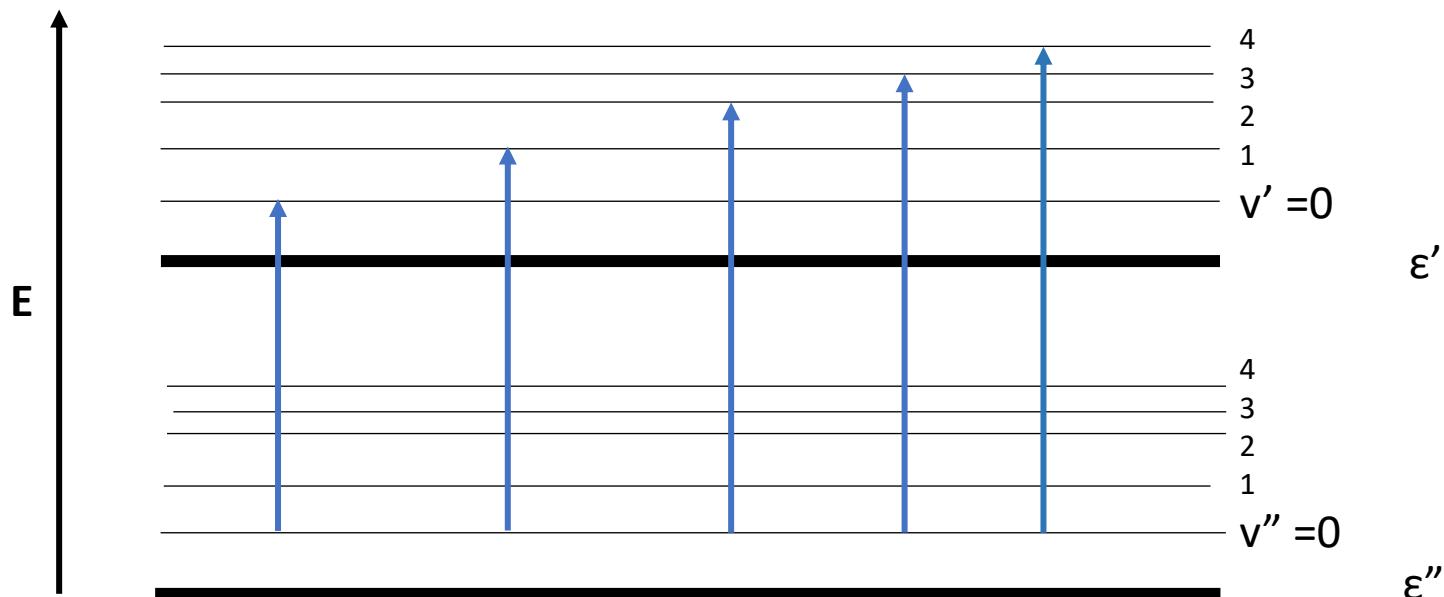
- The **ground state** energy levels are denoted by ϵ'' and v'' , while the **excited state** energy levels are denoted by ϵ' and v'
- There are **no selection rules** for vibrational transitions during electronic transition



ENGINEERING CHEMISTRY

Module I- Molecular Spectroscopy

Most of the transitions start from $v''=0$ as it is the most populated level



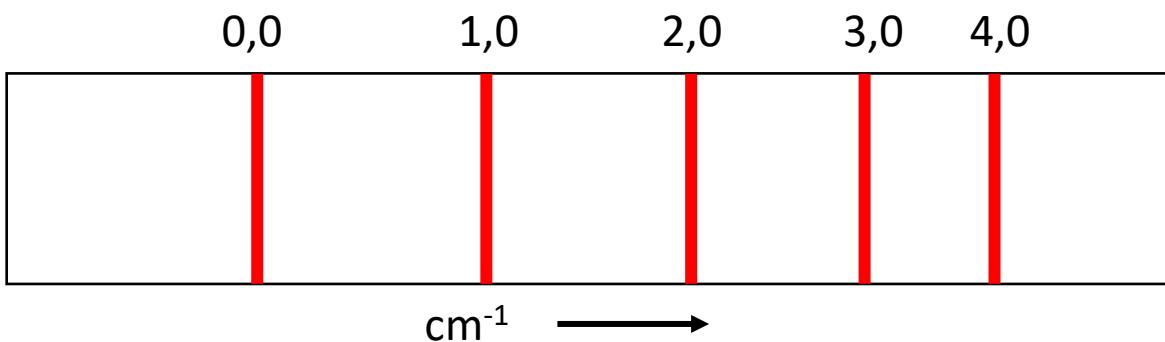
ENGINEERING CHEMISTRY

Module I- Molecular Spectroscopy



- The lines in the resulting spectrum are denoted by (v', v'')
- The resulting spectrum is called **progression**
- The lines **converge** at higher energy levels showing **anharmonicity** in the excited electronic state

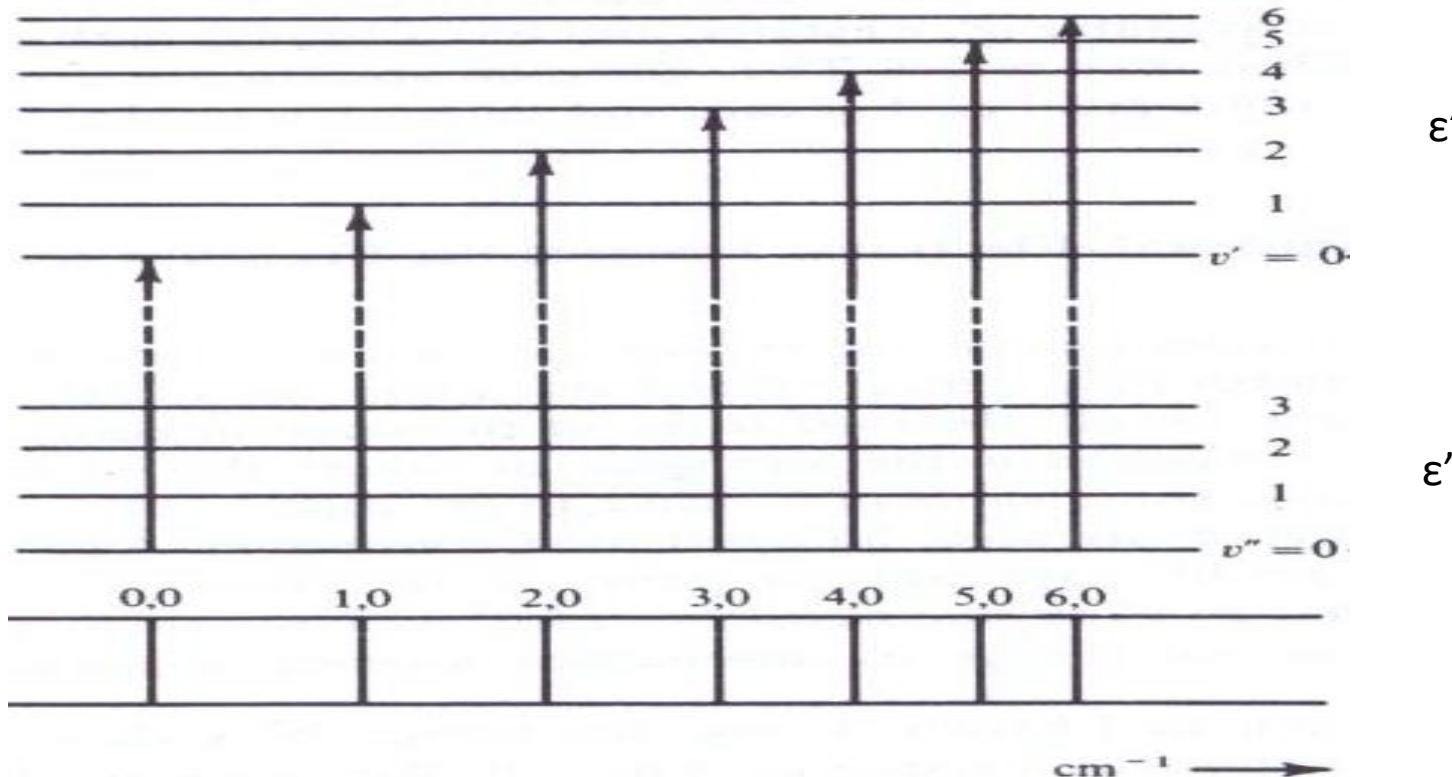
Spectrum showing Progression



ENGINEERING CHEMISTRY

Module I- Molecular Spectroscopy

Vibrational 'coarse structure' during electronic transition



Source:Fundamentals of Molecular Spectroscopy: C. N. Banwell and Elaine M McCash, Fifth Edition, MCGRAW-HILL Education (India) Private Ltd.

ENGINEERING CHEMISTRY

Module I- Molecular Spectroscopy



Class content:

- *Intensity of spectral lines*
- *Franck Condon Principle*

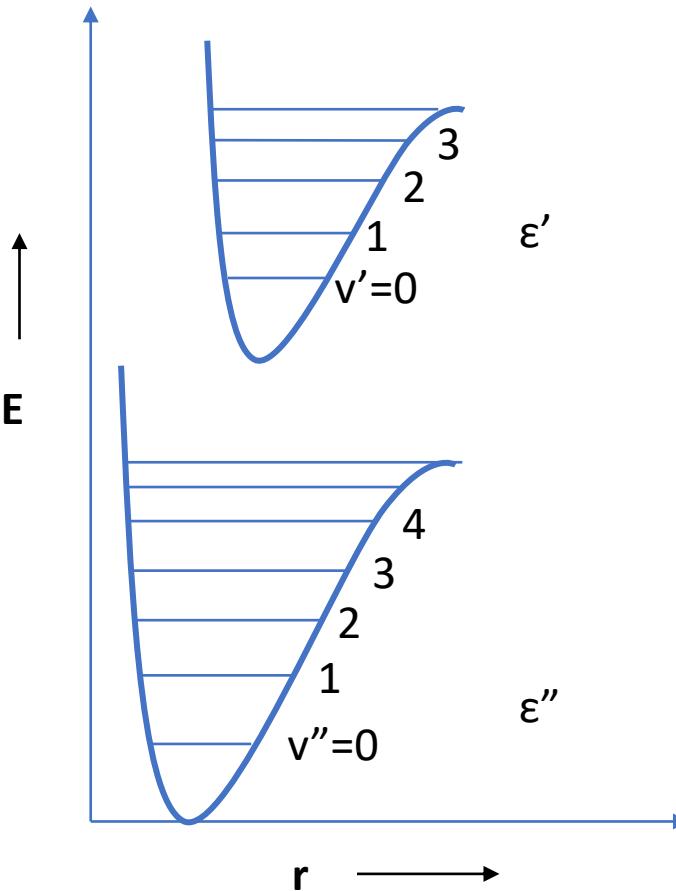
ENGINEERING CHEMISTRY

Module I- Molecular Spectroscopy

Electronic spectroscopy

Intensity of spectral lines

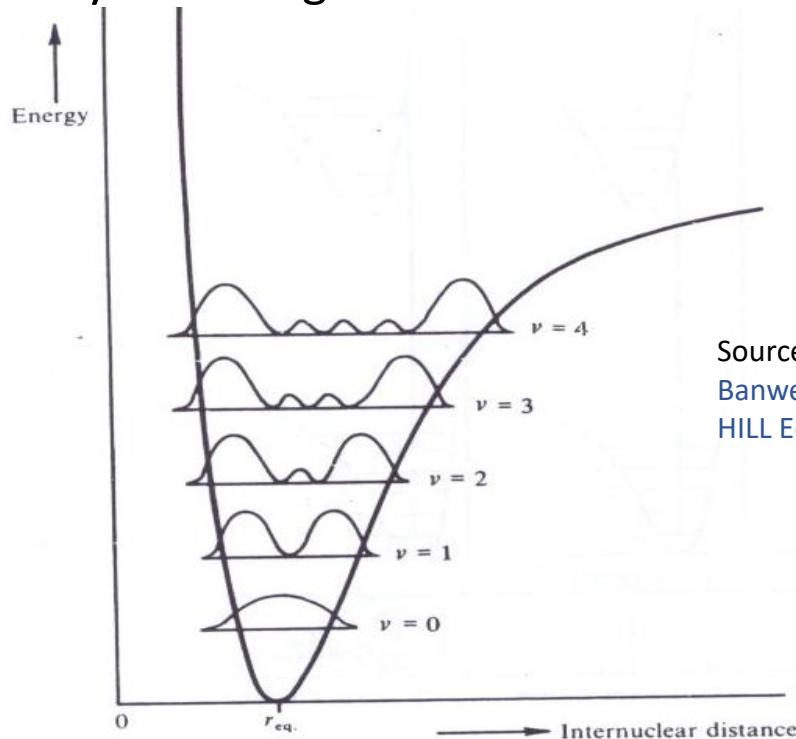
- There are **no selection rules** for vibrational changes during an electronic transition
- Most of the **transitions start from $v''=0$** as it is most populated level
- The excited state usually has **longer internuclear distance** because of antibonding character



ENGINEERING CHEMISTRY

Module I- Molecular Spectroscopy

The transitions arise from the **centre of $v''=0$** because the maximum probability of finding the nuclei is at the centre of $v''=0$



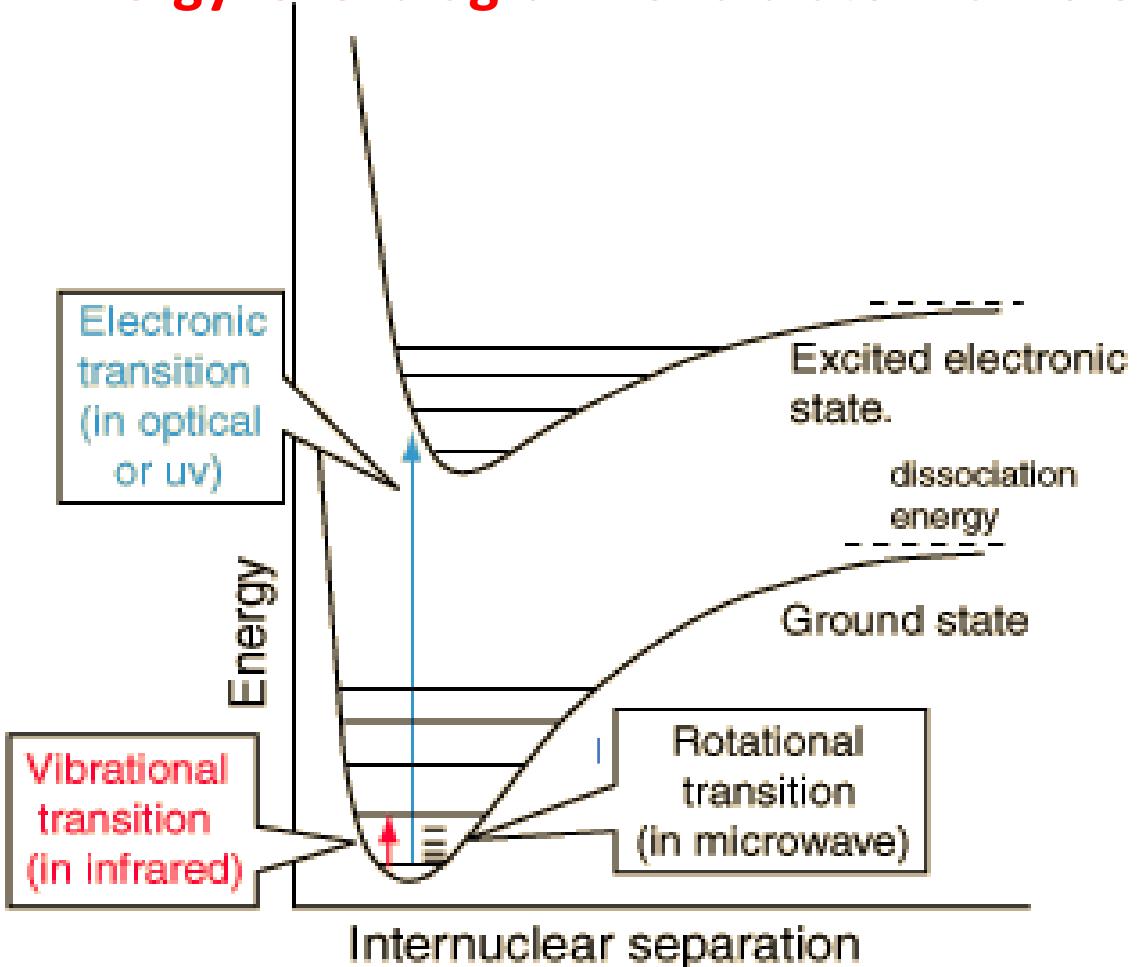
Source:Fundamentals of Molecular Spectroscopy: C. N. Banwell and Elaine M McCash, Fifth Edition, MCRAW-HILL Education (India) Private Ltd.

Probability distribution for a diatomic molecule according to quantum theory

ENGINEERING CHEMISTRY

Module I- Molecular Spectroscopy

Energy level diagram for a diatomic molecule



ENGINEERING CHEMISTRY

Module I- Molecular Spectroscopy

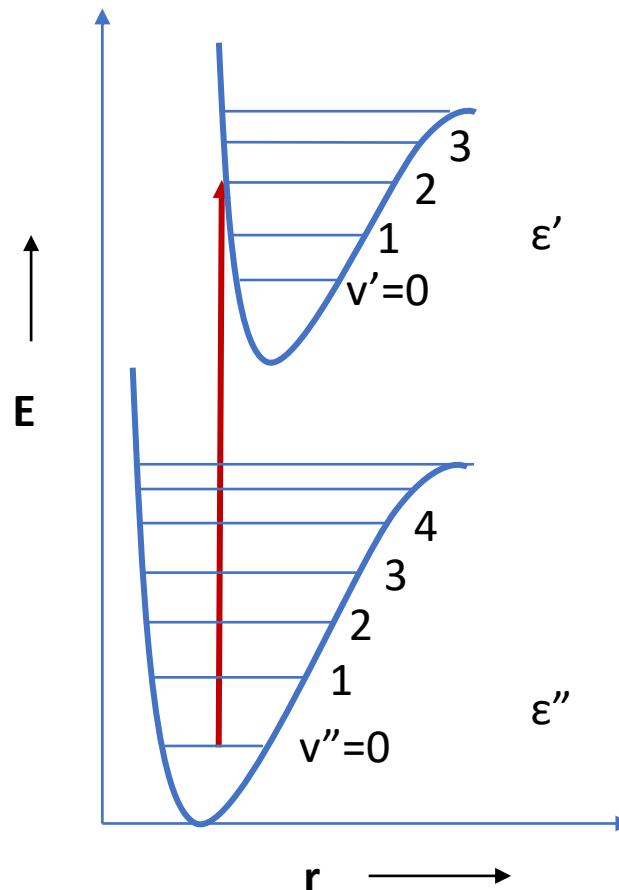
Franck-Condon principle

- All lines in the spectra are **not of the same intensity** though no selection rule for vibrational transitions exist

Statement of Franck Condon principle:

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

- This implies that the electronic transitions are always **vertical transitions**



ENGINEERING CHEMISTRY

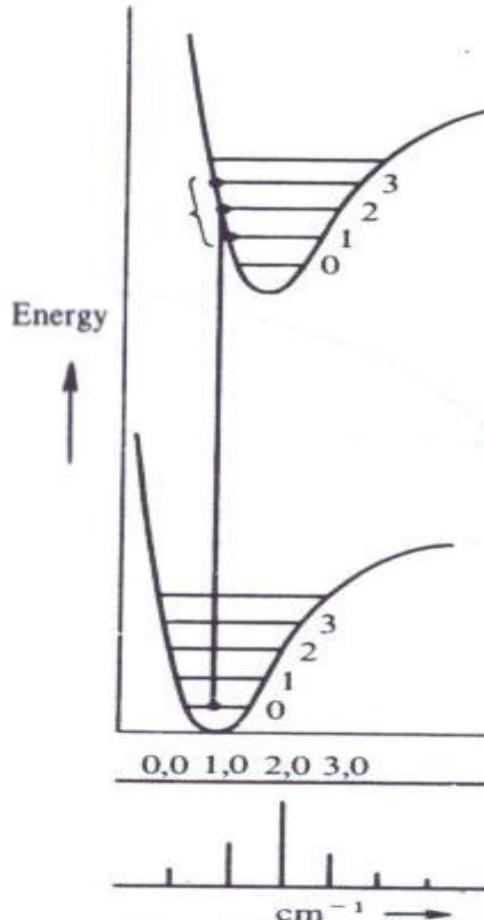
Module I- Molecular Spectroscopy

r_e'' and r_e' are the internuclear distances of the ground and excited states respectively

Three possibilities of vibrational - electronic transitions exist

- Internuclear distance of excited state is more than that of ground state $r_e'' < r_e'$

The spectrum shows **maximum intensity for ($v',0$) line** where v' is the vibrational level in the excited state to which electronic transition takes place



Source:Fundamentals of Molecular Spectroscopy: C. N. Banwell and Elaine M McCash, Fifth Edition, MCGRAW-HILL Education (India) Private Ltd.

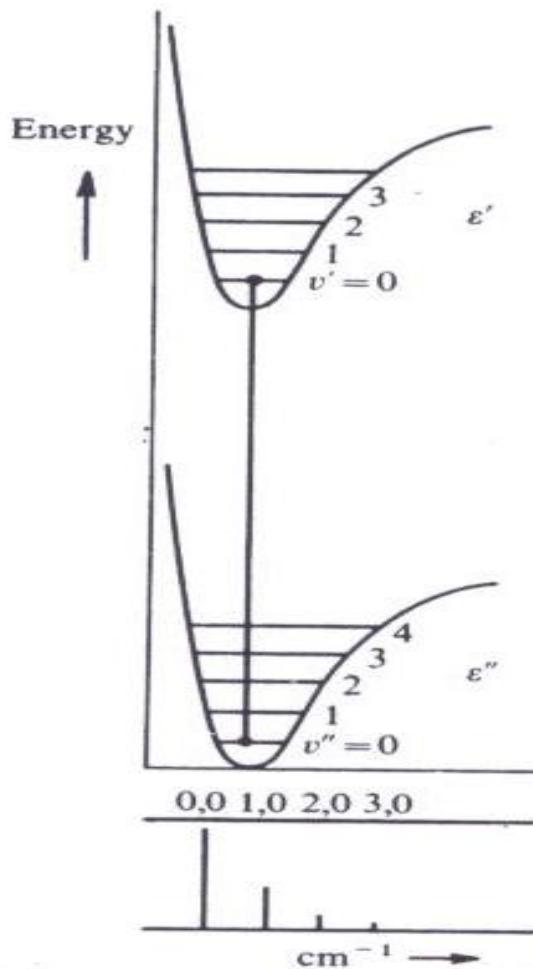
ENGINEERING CHEMISTRY

Module I- Molecular Spectroscopy

- No change in internuclear distance

$$r_e'' = r_e'$$

The spectrum shows **maximum intensity** for **(0,0) line** and intensity falls for the remaining lines



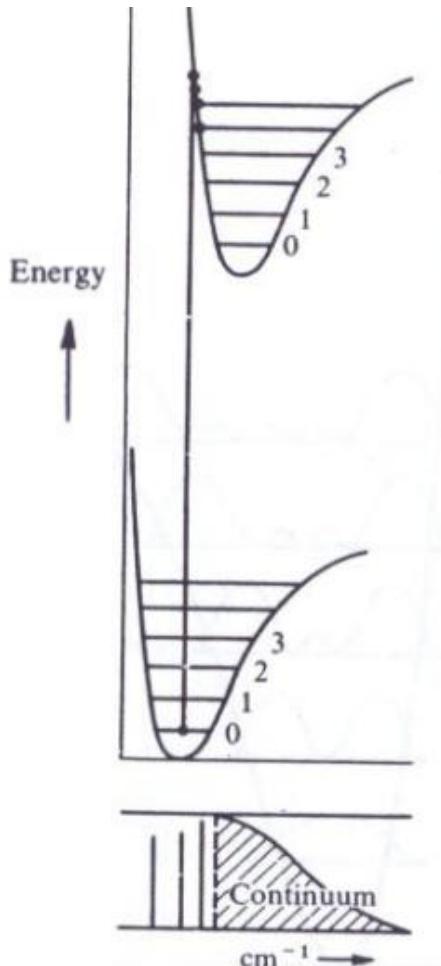
Source: Fundamentals of Molecular Spectroscopy: C. N. Banwell and Elaine M McCash, Fifth Edition, McGRAW-HILL Education (India) Private Ltd.

ENGINEERING CHEMISTRY

Module I- Molecular Spectroscopy

- Internuclear distance of excited state is considerably greater than that of ground state $r_e'' \ll r_e'$

The spectrum shows **continuum** since the transition results in the molecule going beyond dissociation energy. The molecule dissociates into atoms which gain kinetic energy. Since this energy is not quantised a continuum is seen in the spectrum



Source:Fundamentals of Molecular Spectroscopy: C. N. Banwell and Elaine M McCash, Fifth Edition, MCGRaw-HILL Education (India) Private Ltd.

ENGINEERING CHEMISTRY

Module I- Molecular Spectroscopy



END OF MODULE 1 – MOLECULAR SPECTROSCOPY

ENGINEERING CHEMISTRY

Module 1- Molecular Spectroscopy



Class content :

- *Numericals on Molecular Spectroscopy*
 - *Rotational Spectroscopy*
 - *Vibrational Spectroscopy*

ENGINEERING CHEMISTRY

Module 1- Molecular Spectroscopy

1. Calculate the rotational constant for an NO molecule. Given atomic masses of N and O are 14.004 amu and 15.9994 amu respectively. The bond length of NO is 115 pm.

(1 amu = 1.66×10^{-27} kg, c = 3×10^8 ms⁻¹, h= 6.6×10^{-34} Js)

Solution:

$$\mu = \frac{m_1 m_2}{m_1 + m_2} = \frac{(14.004 \times 1.66 \times 10^{-27} \text{ kg})(15.9994 \times 1.66 \times 10^{-27} \text{ kg})}{(14.004 \times 1.66 \times 10^{-27} \text{ kg}) + (15.9994 \times 1.66 \times 10^{-27} \text{ kg})}$$

$$\mu = 12.3963 \times 10^{-27} \text{ kg}$$

$$I = \mu r^2$$

$$I = 12.3963 \times 10^{-27} \text{ kg} \times (115 \times 10^{-12} \text{ m})^2 = 1.63941 \times 10^{-46} \text{ kg m}^2$$

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

$$B = \frac{6.6 \times 10^{-34} \text{ J.s}}{8 \times (3.14)^2 \times 1.63941 \times 10^{-46} \text{ kg m}^2 \times (3 \times 10^8 \text{ ms}^{-1})} = 170.13 \text{ m}^{-1}$$

$$B = 1.70 \text{ cm}^{-1}$$

ENGINEERING CHEMISTRY

Module 1- Molecular Spectroscopy

2. The first line in the pure rotational spectrum of HCl appears at 21.18 cm^{-1} . Calculate the bond length of the molecule. Given atomic masses of H and Cl are 1.008 amu and 35.45 amu respectively.
(1 amu = $1.66 \times 10^{-27} \text{ kg}$, c = $3 \times 10^8 \text{ ms}^{-1}$, h = $6.6 \times 10^{-34} \text{ Js}$)

Solution :

$$2B = 21.18 \text{ cm}^{-1}, B = 10.59 \text{ cm}^{-1} = 10.59 \times 10^2 \text{ m}^{-1}$$

$$\mu = \frac{m_1 m_2}{m_1 + m_2} = \frac{(1.008 \times 1.66 \times 10^{-27} \text{ kg})(35.45 \times 1.66 \times 10^{-27} \text{ kg})}{(1.008 \times 1.66 \times 10^{-27} \text{ kg}) + (35.45 \times 1.66 \times 10^{-27} \text{ kg})}$$

$$\mu = 1.627 \times 10^{-27} \text{ kg}$$

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

$$I = \frac{6.6 \times 10^{-34} \text{ J.s}}{8 \times (3.14)^2 \times 10.59 \times 10^2 \text{ m}^{-1} \times (3 \times 10^8 \text{ ms}^{-1})} = 2.634 \times 10^{-47} \text{ kg m}^2$$

ENGINEERING CHEMISTRY

Module 1- Molecular Spectroscopy

$$I = \mu r^2$$

$$r^2 = \frac{I}{\mu} = \frac{2.634 \times 10^{-47} \text{ kg m}^2}{1.627 \times 10^{-27} \text{ kg}}$$

$$r^2 = 1.619 \times 10^{-20} \text{ m}^2$$

$$r = 127 \text{ pm}$$

ENGINEERING CHEMISTRY

Module 1- Molecular Spectroscopy

3. For HBr molecule:

- i) The rotational spectrum shows the first line at 17.19 cm^{-1} . Calculate the bond length of HBr molecule(Use rigid rotor model)
- ii) The vibrational spectrum shows fundamental and first overtone at 2559.08 cm^{-1} and 5027.54 cm^{-1} respectively. Calculate the anharmonicity constant for the molecule. (Use anharmonic oscillator model). ($1 \text{ amu} = 1.66 \times 10^{-27} \text{ kg}$, $\hbar = 6.627 \times 10^{-34} \text{ Js}$, $c = 3 \times 10^{10} \text{ cms}^{-1}$, $N = 6.023 \times 10^{23} \text{ mol}^{-1}$, Gram molar mass of H = 1.0 and Br = 79.9)

Solution :

i) $2B = 17.19 \text{ cm}^{-1}$ $B = 8.595 \text{ cm}^{-1}$

$$\mu = \frac{m_1 m_2}{m_1 + m_2} = \frac{(0.001/6.023 \times 10^{23}) (0.0799/6.023 \times 10^{23})}{(0.001/6.023 \times 10^{23}) + (0.0799/6.023 \times 10^{23})} = 1.6395 \times 10^{-27} \text{ kg}$$

ENGINEERING CHEMISTRY

Module 1- Molecular Spectroscopy

$$I = \frac{h}{8\pi^2 B c} = \frac{6.627 \times 10^{-34}}{8(3.14)^2 \times 8.595 \times 3 \times 10^{10}}$$

$$I = 3.2583 \times 10^{-47} \text{ kgm}^2$$

$$I = \mu r^2$$

$$r = \sqrt{I/\mu} = 0.141 \text{ nm}$$

ii) $\frac{2\bar{\nu}(1-3x_e)}{\bar{\nu}(1-2x_e)} = \frac{5027.54}{2559.08} = 1.9646$

$$x_e = 0.0171$$

ENGINEERING CHEMISTRY

Module 1- Molecular Spectroscopy

4. For a KCl molecule undergoing simple harmonic motion the vibrational spectrum shows a fundamental frequency at 378 cm^{-1} .

- i) Calculate the reduced mass of KCl ii) Determine force constant of KCl
- iii) Determine zero point energy for KCl molecule. ($c = 3 \times 10^{10} \text{ cms}^{-1}$, $N = 6.023 \times 10^{23} \text{ mol}^{-1}$, Gram molar mass of K = 39 and Cl = 35.5)

Solution :

$$\text{i) } \mu = \frac{m_1 m_2}{m_1 + m_2} = \frac{(0.039 / 6.023 \times 10^{23}) (0.0355 / 6.023 \times 10^{23})}{(0.039 / 6.023 \times 10^{23}) + (0.0355 / 6.023 \times 10^{23})}$$

$$\mu = 3.085 \times 10^{-26} \text{ kg}$$

$$\text{ii) } \bar{\nu} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}}$$

$$k = 4\pi^2 \bar{\nu}^2 c^2 \mu$$

$$k = 4 \times (3.14)^2 \times (378 \times 10^2)^2 \times (3 \times 10^8)^2 \times 3.085 \times 10^{-26}$$

$$k = 156.313 \text{ Nm}^{-1}$$

$$\text{iii) Zero point energy} = \frac{1}{2} \bar{\nu} = \frac{1}{2} \times 378 = 189 \text{ cm}^{-1}$$

ENGINEERING CHEMISTRY

Module 1- Molecular Spectroscopy

5. The force constant of CO is 1840 Nm^{-1} . Calculate the oscillation frequency and wave number in cm^{-1} . (1 amu = $1.66 \times 10^{-27} \text{ kg}$, $c = 3 \times 10^8 \text{ ms}^{-1}$, Gram molar mass of C = 12.000 and O = 15.9994)

Solution :

$$\mu = \frac{m_1 m_2}{m_1 + m_2} = \frac{(12.000 \times 1.66 \times 10^{-27} \text{ kg}) (15.9994 \times 1.66 \times 10^{-27} \text{ kg})}{(12.000 \times 1.66 \times 10^{-27} \text{ kg}) + (15.9994 \times 1.66 \times 10^{-27} \text{ kg})}$$

$$\mu = 11.3827 \times 10^{-27} \text{ kg}$$

$$v = \frac{1}{2\pi} \sqrt{k/\mu} = \frac{1}{2 \times 3.14} \sqrt{\frac{1840 \text{ Nm}^{-1}}{11.3827 \times 10^{-27} \text{ kg}}}$$

$$v = 6.402 \times 10^{13} \text{ s}^{-1}$$

$$\bar{v} = \frac{v}{c} = \frac{6.402 \times 10^{13} \text{ s}^{-1}}{3 \times 10^8 \text{ ms}^{-1}} = 2.134 \times 10^5 \text{ m}^{-1}$$

$$\bar{v} = 2134 \text{ cm}^{-1}$$

ENGINEERING CHEMISTRY

Module 2- Nanomaterials



- *Module content:*
- *Nanomaterials (classification and deviation of properties from bulk)*
- *Properties of nanoparticles*

ENGINEERING CHEMISTRY

Module 2- Nanomaterials



Class content:

- *Nanomaterials*
- *Classification of nanoparticles*
- *Deviation in properties of nanomaterials from bulk material- reasons*

ENGINEERING CHEMISTRY

Module 2- Nanomaterials

- The prefix '**Nano**' is derived from the Greek word for dwarf
- $1\text{nm} = 10^{-9}\text{m}$
- 1nm is approximately the **length of 10 H or 5 Si atoms** aligned in a line
- Dimensions of nanomaterials lie in between bulk material and atoms/molecules
- Up to μm **bulk properties** are observed. For smaller sizes **quantum effects** are seen as the dimensions are closer to atoms or molecules

ENGINEERING CHEMISTRY

Module 2- Nanomaterials

• Properties of nanomaterials are different from bulk materials

- Au-bulk is **yellowish** in colour, and Au- nanoparticles are **red** in colour

- Al which is stable becomes **combustible** in the nanoparticle range and is used as solid fuel in rocket propulsion

- **Melting point** of materials is lower in nano-range

ENGINEERING CHEMISTRY

Module 2- Nanomaterials



- **Nanomaterials:** Materials with **at least one** external dimension between 1 and 100 nm
- **Nanoscience** is the study of phenomena and synthesis, characterisation , exploration and exploitation of nanostructured materials
- **Nanotechnologies** are the design, characterisation, production and application of structures, devices and systems by controlling shape and size at nanometer scale

ENGINEERING CHEMISTRY

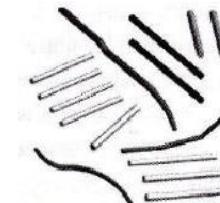
Module 2- Nanomaterials

Classification of Nanomaterials

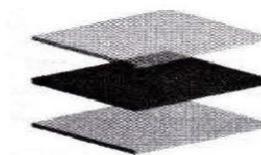
- **Zero dimensional nanomaterials (0D) :**
Materials having all the dimensions within the nanorange where no dimension is allowed to be outside of nanorange. Like quantum dots , nanoclustures eg. fullerene.
- **One dimensional nanomaterials(1D):**
Materials having one of their dimensions out of the nanorange eg. nanotubes , nanowires
- **Two dimensional nanomaterials (2D) :**
Materials having two of their dimensions out of the nanorange eg. Nanofilms, nanocoatings
- **Three dimensional nanomaterials (3D):**
Materials having all the three dimensions out of the nanorange eg. Dispersions of nanoparticles, bundles of nanowires



Cluster 0D



Nanotubes, fibers and rods 1D



Films and coats 2D



Polycrystals

ENGINEERING CHEMISTRY

Module 2- Nanomaterials

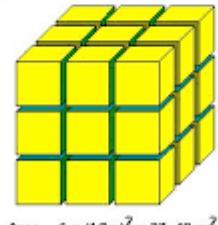
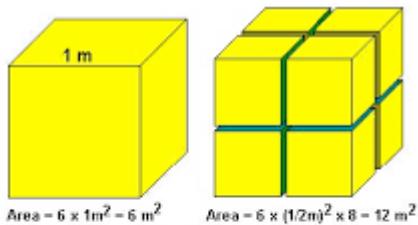
Nanomaterials possess specific properties which maybe significantly different from bulk properties

Reasons

Large fraction of surface atoms / unit volume:

Properties are dictated by surface atoms rather than bulk atoms

Eg Pt sheet versus Pt powder



[Source:https://nanosense.sri.com/activities/size matters/introduction/SM_Lesson1Student.pdf](https://nanosense.sri.com/activities/size_matters/introduction/SM_Lesson1Student.pdf)

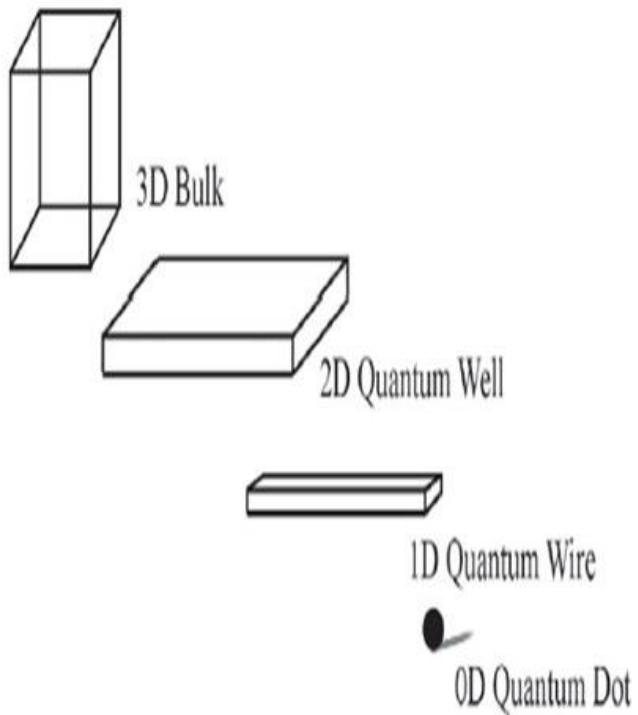
Large surface energy : Surface atoms are held with less force as compared to bulk. Surface activity high .Eg Al

ENGINEERING CHEMISTRY

Module 2- Nanomaterials

Spatial confinement- (quantum confinement)

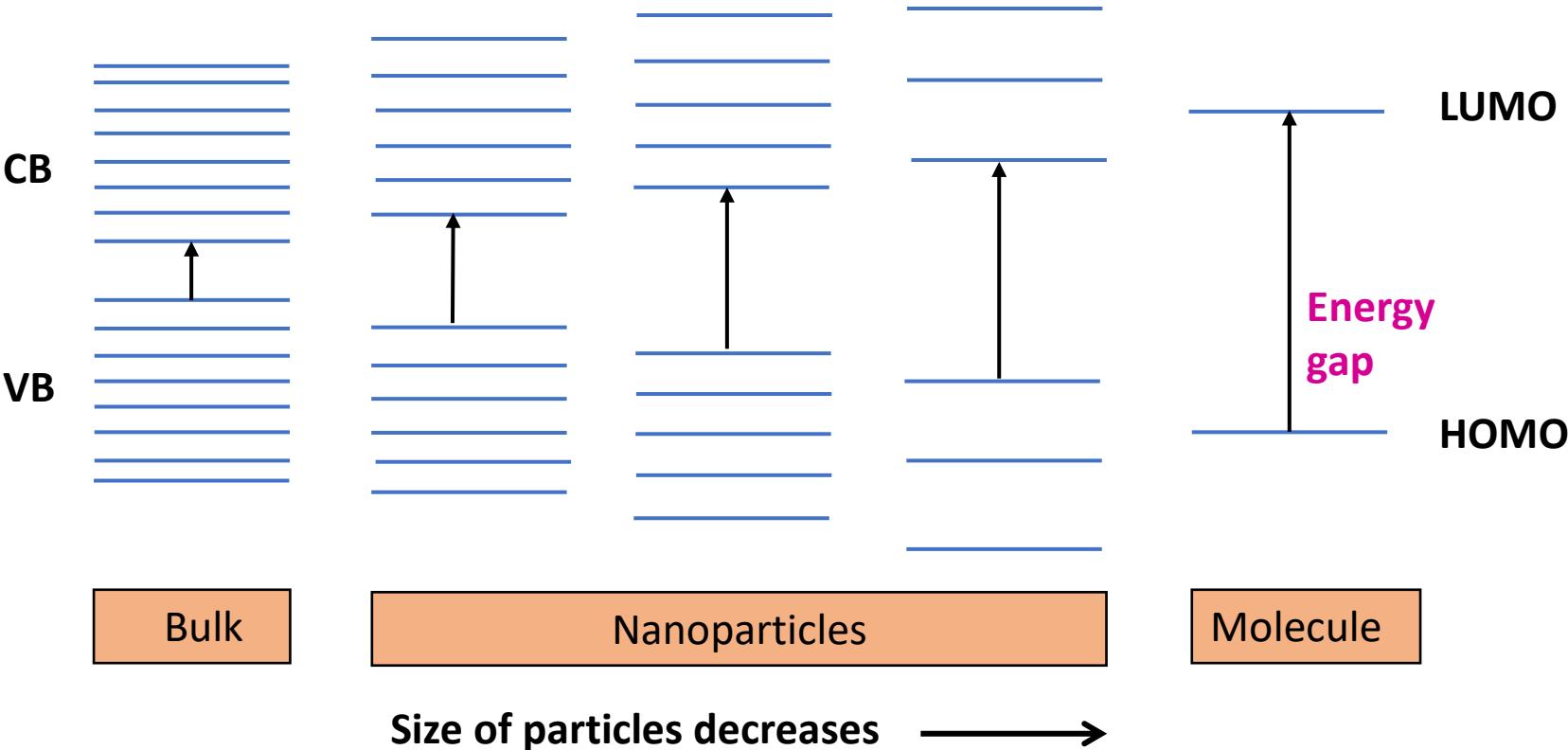
- 3-D
 - All carriers act as free carriers in all three directions
- 2-D or Quantum Wells
 - The carriers act as free carriers in a plane
 - First observed in semiconductor systems
- 1-D or Quantum Wires
 - The carriers are free to move down the direction of the wire
- 0-D or Quantum Dots
 - Systems in which carriers are confined in all directions (no free carriers)



ENGINEERING CHEMISTRY

Module 2- Nanomaterials

Bulk : 1 mole = 10^{23} atoms ; Nanomaterials : $10\text{-}1000$ atoms



ENGINEERING CHEMISTRY

Module 2- Nanomaterials



Reduced imperfections:

Bulk material- metal **lattice imperfections** like dislocations, kinks etc

Nanomaterial - **smaller lattice** so less possibility of imperfections

ENGINEERING CHEMISTRY

Module 2- Nanomaterials



Class content:

- **Properties of Nanomaterials**
 - Surface area dependant properties
 - Electrical properties
 - Optical properties

ENGINEERING CHEMISTRY

Module 2- Nanomaterials



Properties of Nanomaterials

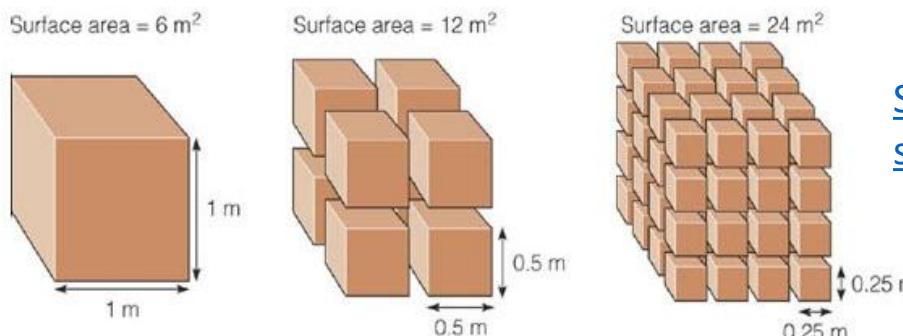
- Properties of any bulk material are independent of its size whereas properties of nanomaterials change with size
- Properties of a bulk material can be altered only by altering their structure and composition

ENGINEERING CHEMISTRY

Module 2- Nanomaterials

Surface Area dependant properties

- Many **physical and chemical properties** of a material depend on its surface properties
- Surface area is **enormously increased** on moving from bulk to nano scale.
- Nanomaterials have a **significant proportion of atoms** existing at the surface
- Properties like **catalytic activity, gas adsorption** depend on surface area
e.g. Bulk gold is catalytically inactive but gold nanoparticles are catalytically very active for selective redox reactions
- **Surface energy** is also high so **chemical reactivity** is high
e.g. Aluminum becomes combustible



[Source:https://niniti.wordpress.com/nano
scale-why-size-matter/](https://niniti.wordpress.com/nano-scale-why-size-matter/)

ENGINEERING CHEMISTRY

Module 2- Nanomaterials

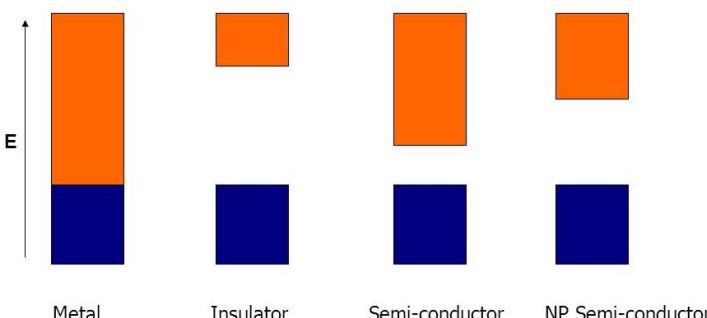
Electrical Properties

Electrical conductivity decreases for nanoparticles as compared to bulk material

- **Due to spatial confinement**

- The electronic bands in bulk material are continuous
- In nano size materials the **electronic bands become discrete** and the **band gap increases**
- Some metals which are good conductors in bulk become semiconductors and insulators as their size is decreased to nano

Band gap increases as particle size decreases



[Source:https://www.mknano.com/info-guide/what-are-nanoparticles.aspx](https://www.mknano.com/info-guide/what-are-nanoparticles.aspx)

ENGINEERING CHEMISTRY

Module 2- Nanomaterials

- **Due to surface scattering**

- Electrical conductivity decreases due to surface scattering
- Electrons have a mean free path
- If dimensions of the nanomaterial is smaller than the mean free path of the electron, **elastic or inelastic surface scattering** can happen
- Elastic scattering will not affect conductivity but when inelastic scattering happens, the **scattered electron loses its velocity** and electrical conductivity decreases

ENGINEERING CHEMISTRY

Module 2- Nanomaterials



Optical Properties

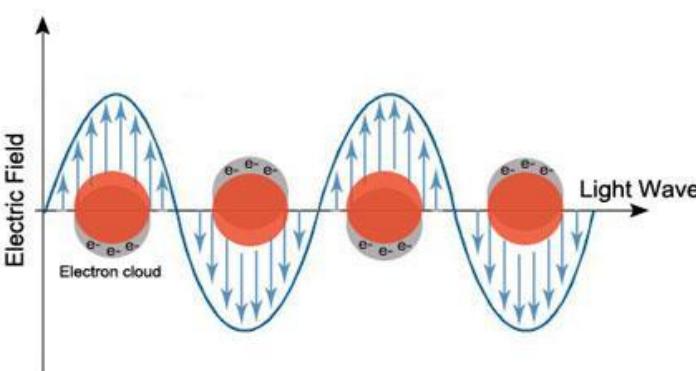
- Nanomaterials show unique optical properties
- Colour depends on the size of the particles
 - Due to Surface Plasmon Resonance
 - Due to increase in band gap

ENGINEERING CHEMISTRY

Module 2- Nanomaterials

Surface plasmon resonance (SPR)

- Metals have **positive lattice points** surrounded by a sea of electrons
- When radiation falls , the **surface electrons are polarised**
- These electrons oscillate with a frequency
- Collective oscillations of these electrons is called **Plasmons**
- When the plasmon frequency matches with the frequency of radiation falling, **resonance occurs** and radiation is absorbed and the material appears coloured
- Plasmon frequency** depends on size, shape and nature of metal
- As size of nanoparticle changes, **colour changes**



Source:<https://www.cytodiagnostics.com/pages/gold-nanoparticle-properties>

ENGINEERING CHEMISTRY

Module 2- Nanomaterials

Increase in Energy gap

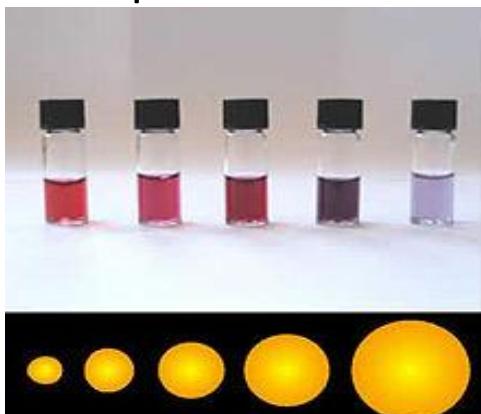
- Increases in energy gap between the **valence band and conduction band**
- As size of nanoparticles decreases the energy gap increases and the **wavelength of light absorbed** moves towards smaller values . This is referred to as '**blue shift**'

eg. colloidal suspensions of gold nanoparticles :

Gold spheres of > 50 nm absorb at $\lambda = 575$ nm

Gold spheres of 10- 20 nm absorb at $\lambda = 524$ nm

Gold spheres of 2-5 nm absorb at $\lambda = 517$ nm



Source::https://en.wikipedia.org/wiki/Colloidal_gold

ENGINEERING CHEMISTRY

Module 2- Nanomaterials



Class content:

- *Properties of Nanomaterials(contd.)*
 - *Mechanical properties*
 - *Thermal properties*
 - *Magnetic properties*
 - *Applications*

ENGINEERING CHEMISTRY

Module 2- Nanomaterials

Mechanical properties

Strength of nanomaterials is greater than bulk material

- Mechanical properties may reach theoretical strength , which is **one or two orders of magnitude higher** than that of the bulk materials.

e.g bending of bulk Cu happens readily but Cu particles < 50 nm are considered **super hard materials** that do not show same malleability and ductility as bulk Cu.

- The reason for this high strength is due to **reduced probability of defects** Large lattices in bulk materials have imperfections like **dislocations, kinks and vacancies** but for lattice with smaller cross-section, there is less probability of finding imperfections.

ENGINEERING CHEMISTRY

Module 2- Nanomaterials

Thermal properties

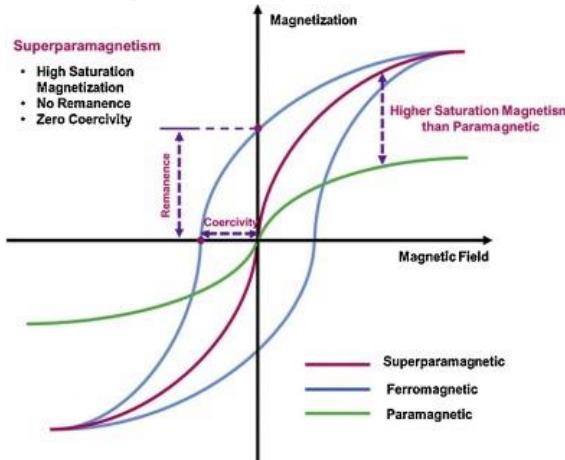
- Low melting point and phase transition temperature
 - Due to a **large fraction of surface atoms** compared to bulk.
 - Atoms or molecules on the surface are **bound by lesser number of bonds** as compared to the atoms in the bulk.
 - the number of bonds need to be broken per atom during melting is less in nanomaterials
- Decrease in thermal conductivity
 - Size of the particles is smaller than the path length of phonons arising due to lattice vibrations .
 - **Phonon scattering** results in decrease in thermal conductivity

ENGINEERING CHEMISTRY

Module 2- Nanomaterials

Magnetic Properties

- Magnetic properties of nanomaterials are distinctly different from that of the bulk materials.
- In ferromagnetic materials like Fe,Co,Ni , **ferromagnetism changes to superparamagnetism** in the nanometer scale due to the high surface energy. The domains can flip directions . In the presence of magnetic field ,they get magnetised with high susceptibilities.

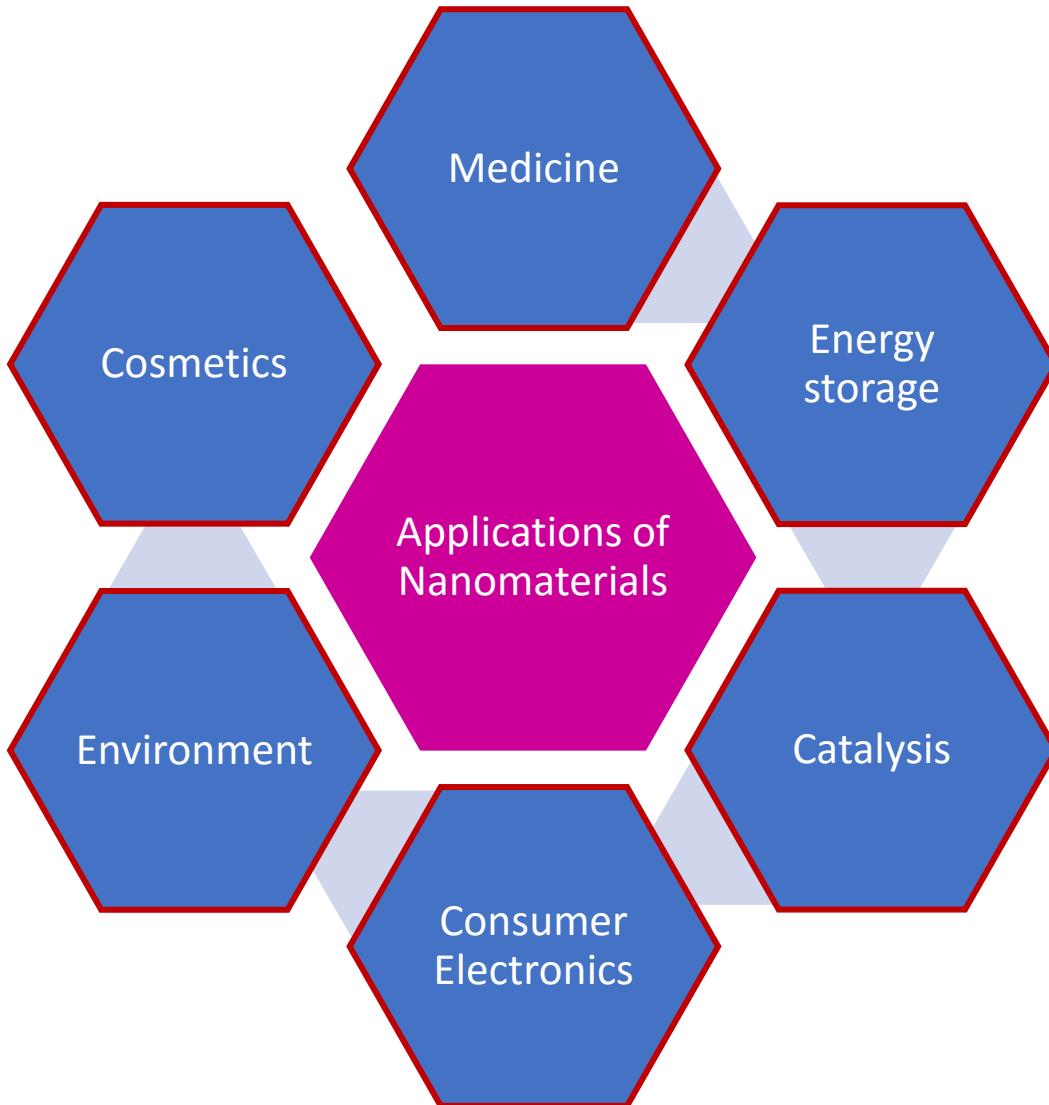


Source:<https://www.sciencedirect.com/science/article/pii/S1674200116300852>

- Bulk **gold and platinum** are non-magnetic but at the nanosize they act as magnetic particles

ENGINEERING CHEMISTRY

Module 2- Nanomaterials



ENGINEERING CHEMISTRY

Module 2- Nanomaterials

Applications

- **Medicine:**
 - for **targeted drug delivery** to enhance effectiveness, **injectible nanobots** which can serve as detectors, informers of early disease and perhaps repair metabolic defects
 - **antibacterial activity** - Ag nanoparticles
- **Energy storage:**
 - as **electrodes** in fuel cells- high surface area
- **Catalysis:**
- Nanocrystalline materials have very **large surface area** due to their small size. Therefore, they are very active with regards to their physical, chemical, and mechanical properties
 - Au, Ag nanoparticles – good catalysts
 - **Oxygen reduction reaction catalysts** for fuel cells & metal-air batteries
 - **CO oxidation catalyst**

ENGINEERING CHEMISTRY

Module 2- Nanomaterials

- **Consumer electronics:**

- **Nanophosphors for good resolution in HDTV-** The resolution of a monitor or television is subject to the size of the pixel. These pixels are fundamentally composed of materials known as “phosphors,” which glow when struck by a stream of electrons within the cathode ray tube (CRT). The resolution enhances with a reduction in the pixel size or the phosphors. Nanocrystalline zinc selenide, cadmium sulfide, zinc sulfide, and lead telluride are potential materials for enhancing the resolution of monitors
- **Nanophosphors in white light emitting diode**

ENGINEERING CHEMISTRY

Module 2- Nanomaterials

- **Environment:**

- Elimination of pollution using **catalytic converters** - Owing to their improved chemical activity, nanomaterials can be employed as catalysts to react with toxic and noxious gases such as nitrogen oxide and carbon monoxide, in power generation equipment and automobile catalytic converters, to avoid environmental pollution caused when gasoline and coal are burnt.
- **Water purification** by Carbon nanotubes

- **Cosmetics:**

- **ZnO and TiO₂** in sunblocks