



ENGINEERING CHEMISTRY

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- *Interaction of electromagnetic radiation with matter*
- *Electromagnetic spectrum*
- *Born –Oppenheimer approximation*
- *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*

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*

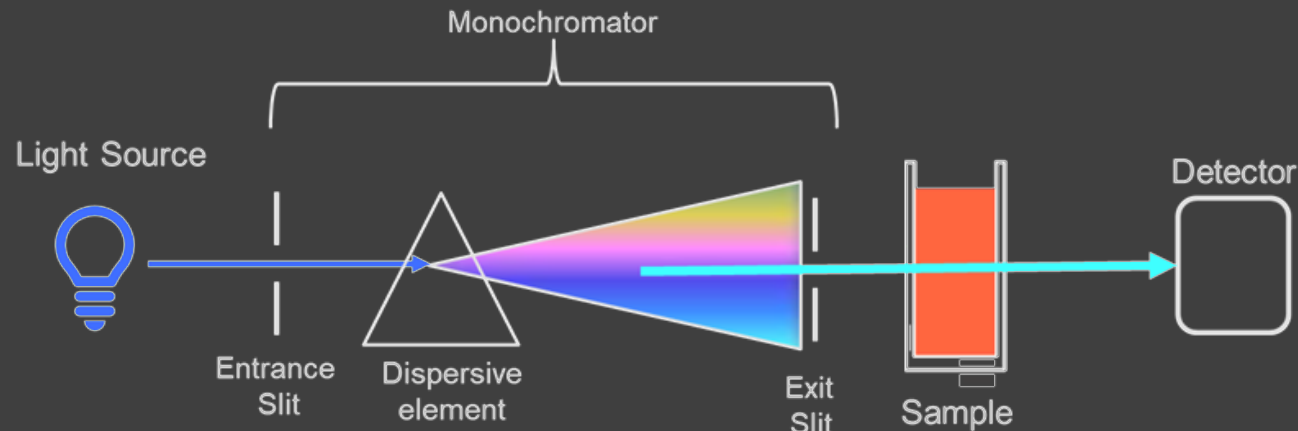
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Molecular Spectroscopy

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

idsdr

i dont see doctor



UV Vis Spectroscopy (<https://www.smacgigworld.com/>)

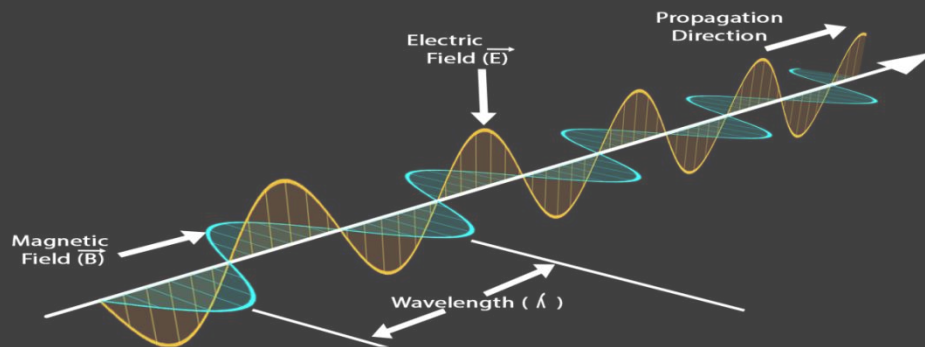
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Molecular Spectroscopy

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

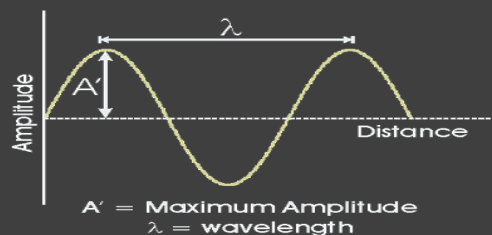


Source: <https://byjus.com/physics/characteristics-of-em-waves/>

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Molecular Spectroscopy

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



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

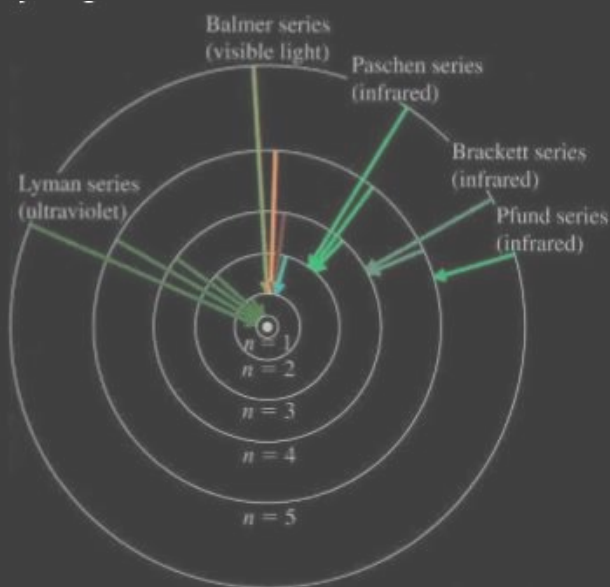
- **Wavelength** : The distance between two successive crests and troughs of the wave ; λ ; m , nm or \AA
- **Frequency** : The number of cycles completed in a certain amount of time ; ν ; Hz or s^{-1}
- **Wave number** : Number of complete waves or cycles contained in unit distance ; $\bar{\nu}$, cm^{-1}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

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

Comparison between atomic spectra and molecular spectra

Atomic spectra

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



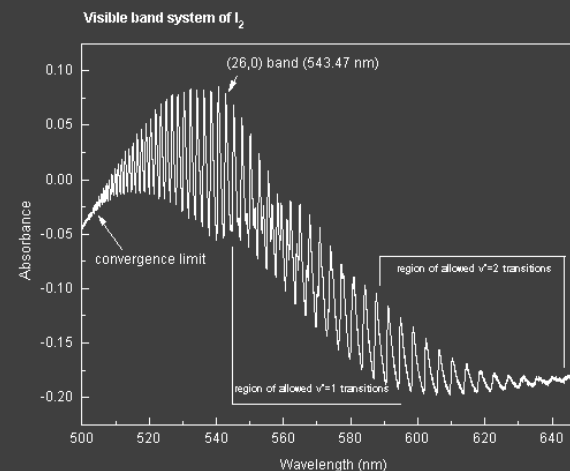
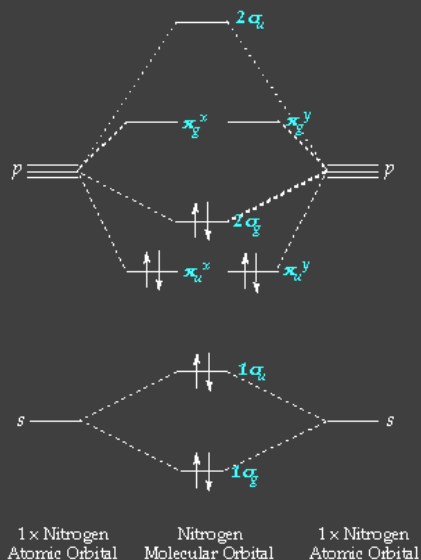
Source: <https://socratic.org/questions/what-happens-to-the-distance-between-energy-levels-at-higher-energy-levels>

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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](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

————— E_2

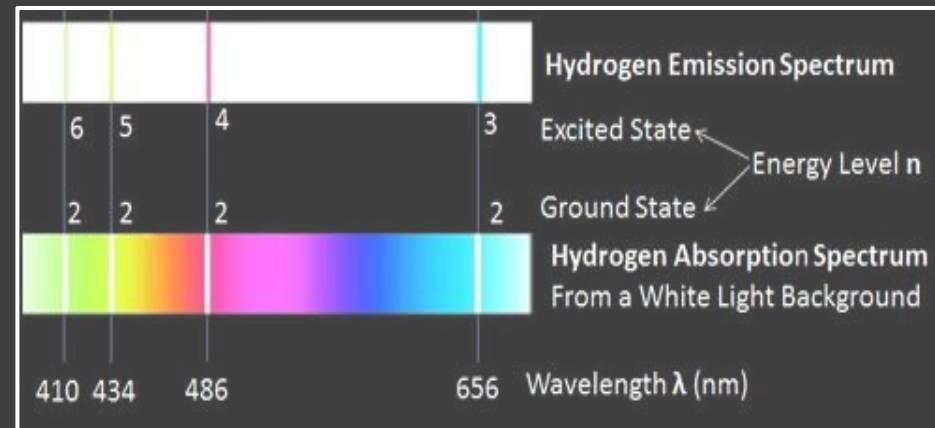
$$\Delta E = E_2 - E_1 = h\nu$$

————— E_1

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**

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



Spectroscopic units

$E=h\nu$ where Energy is expressed in Joules

Wave number is related to wavelength by $\bar{\nu} = \frac{1}{\lambda}$

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



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Module 1- Molecular spectroscopy



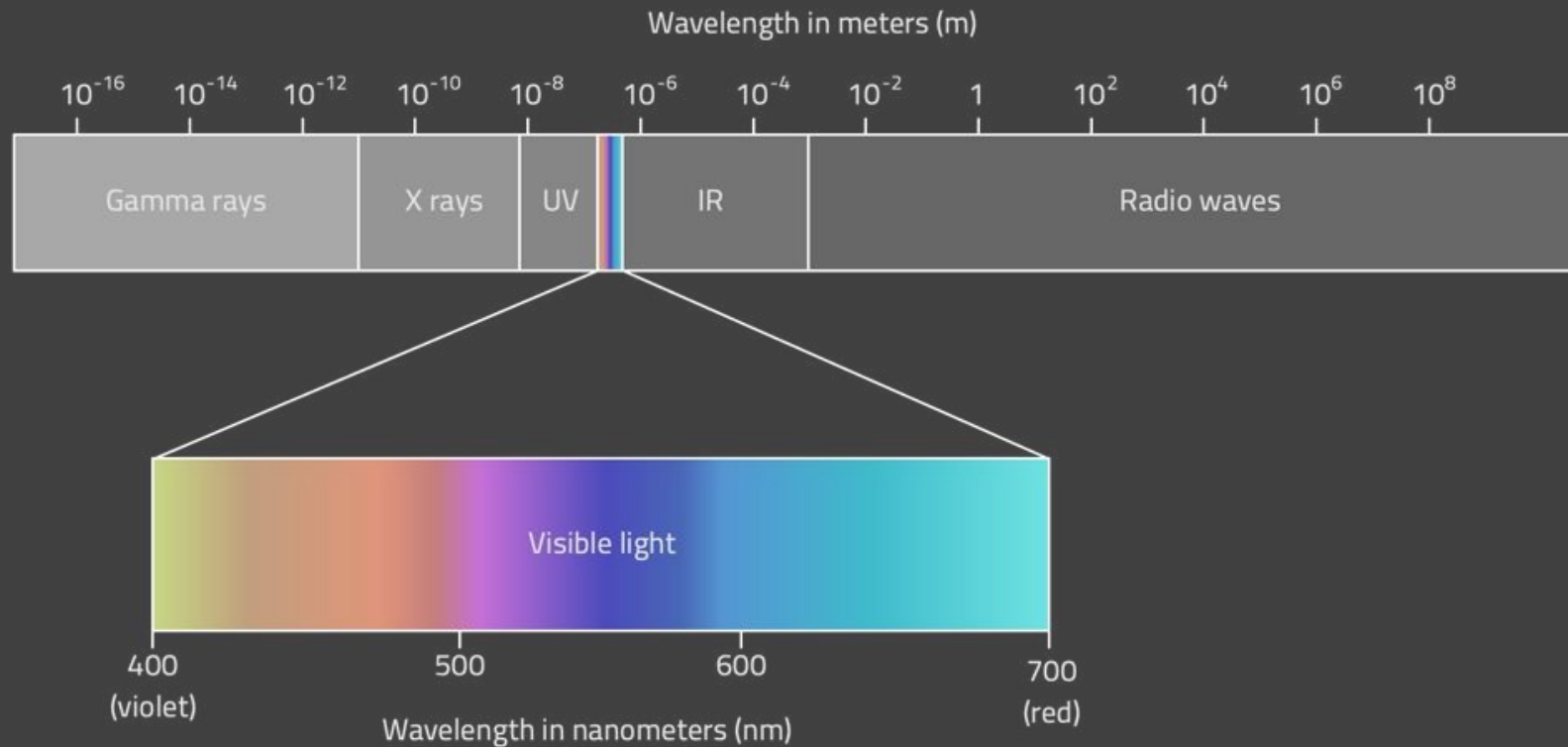
Class Content :

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

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Module I- Molecular Spectroscopy

Electromagnetic spectrum



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

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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-100 μ m) Rotational spectroscopy Rotational transitions
Infra Red region	Wavelength (100 μ m-1 μ m) Vibrational spectroscopy Vibrational transitions

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Module I- Molecular Spectroscopy



Information obtained from different regions of electromagnetic spectrum

Visible and Ultra-Violet region	Wavelength ($1\mu\text{m}$ -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

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Module I- Molecular Spectroscopy

Raman Spectroscopy: scattering of light

When monochromatic radiation is passed through a transparent medium:

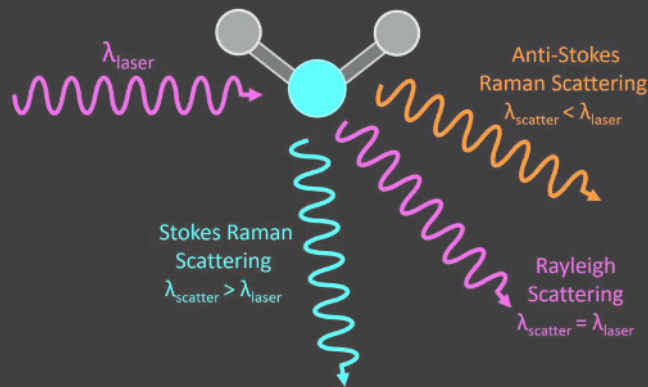
Most of the scattered radiation consists of radiation of incident wavelength –

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**

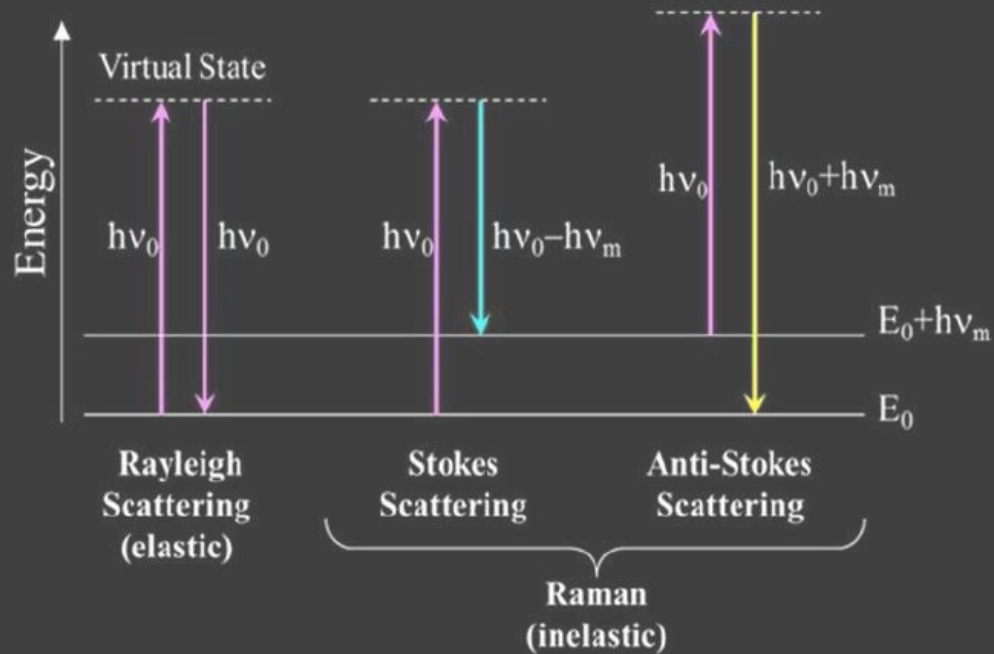
When the wavelength of scattered radiation is less than that of incident radiation – **anti-Stokes lines**



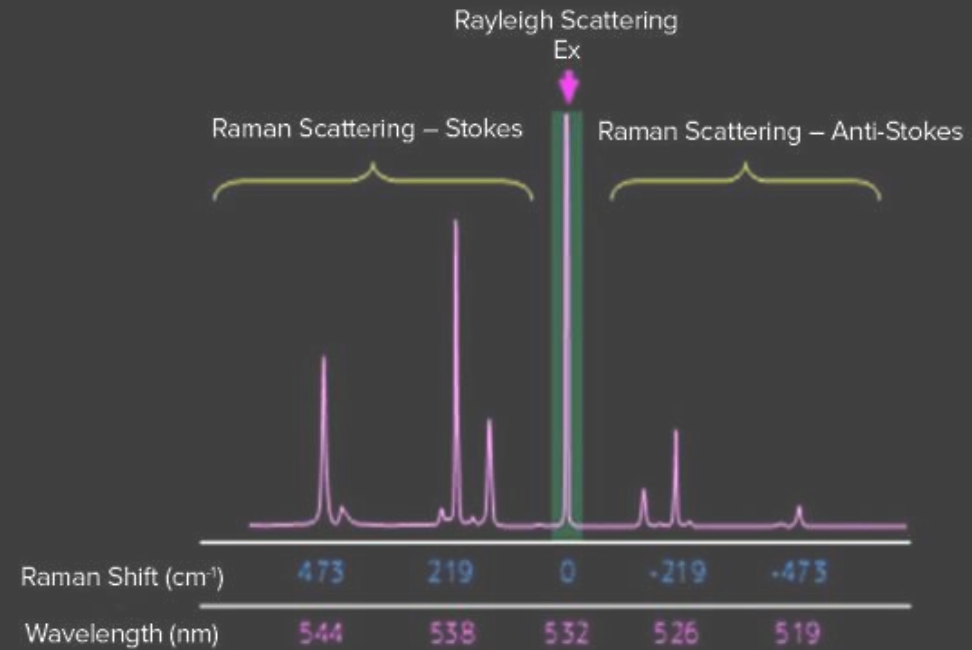
<https://www.edinst.com/blog/what-is-raman-spectroscopy/>

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



Source: <https://www.jasco-global.com>

Exchange of energy between the molecules and radiation
Homonuclear diatomic molecules which are microwave and
Infra-red inactive are Raman active

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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 μ 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>



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Module 1- Molecular spectroscopy



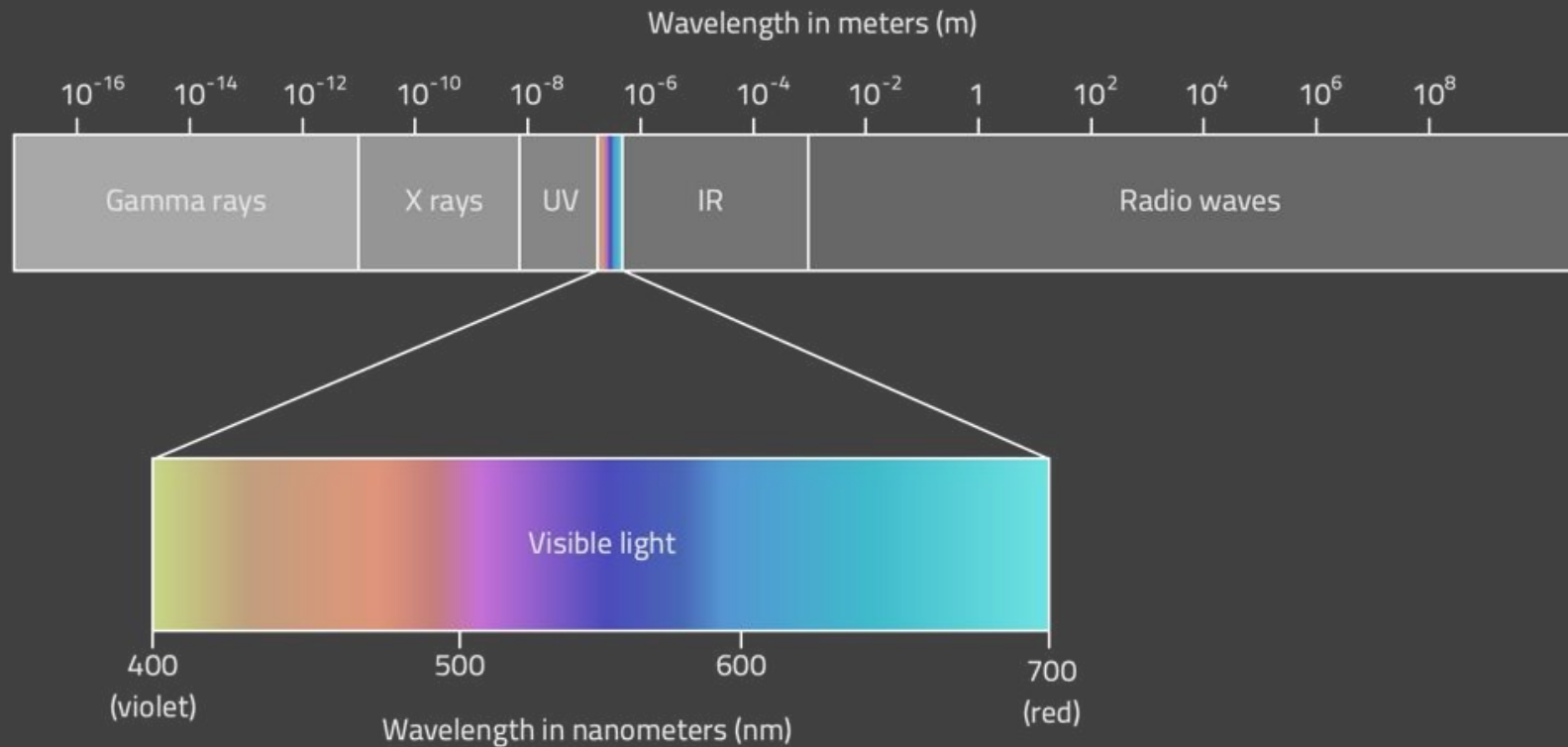
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Module I- Molecular Spectroscopy

Electromagnetic spectrum



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

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Module I- Molecular Spectroscopy



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Raman Spectroscopy: scattering of light

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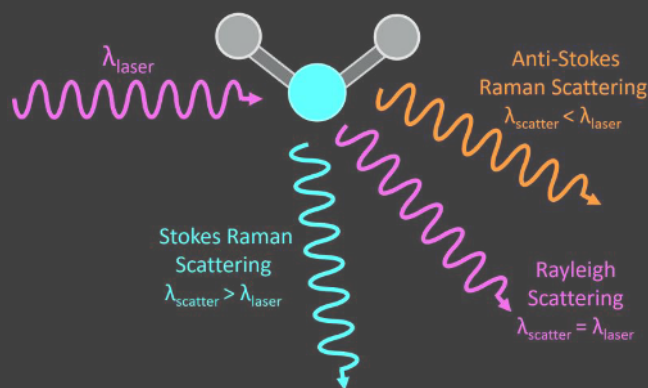
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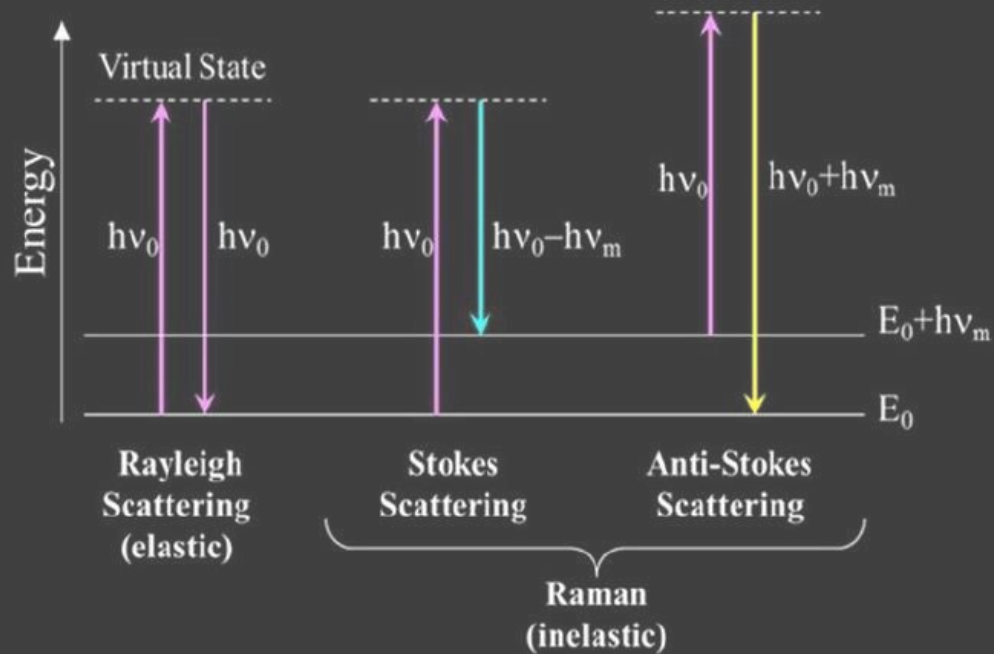
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<https://www.edinst.com/blog/what-is-raman-spectroscopy/>

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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

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Information obtained from different regions of electromagnetic spectrum

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



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Module I- Molecular Spectroscopy



Class content:

- *Born - Oppenheimer approximation*
- *Energy level diagram of a diatomic molecule*

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

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

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

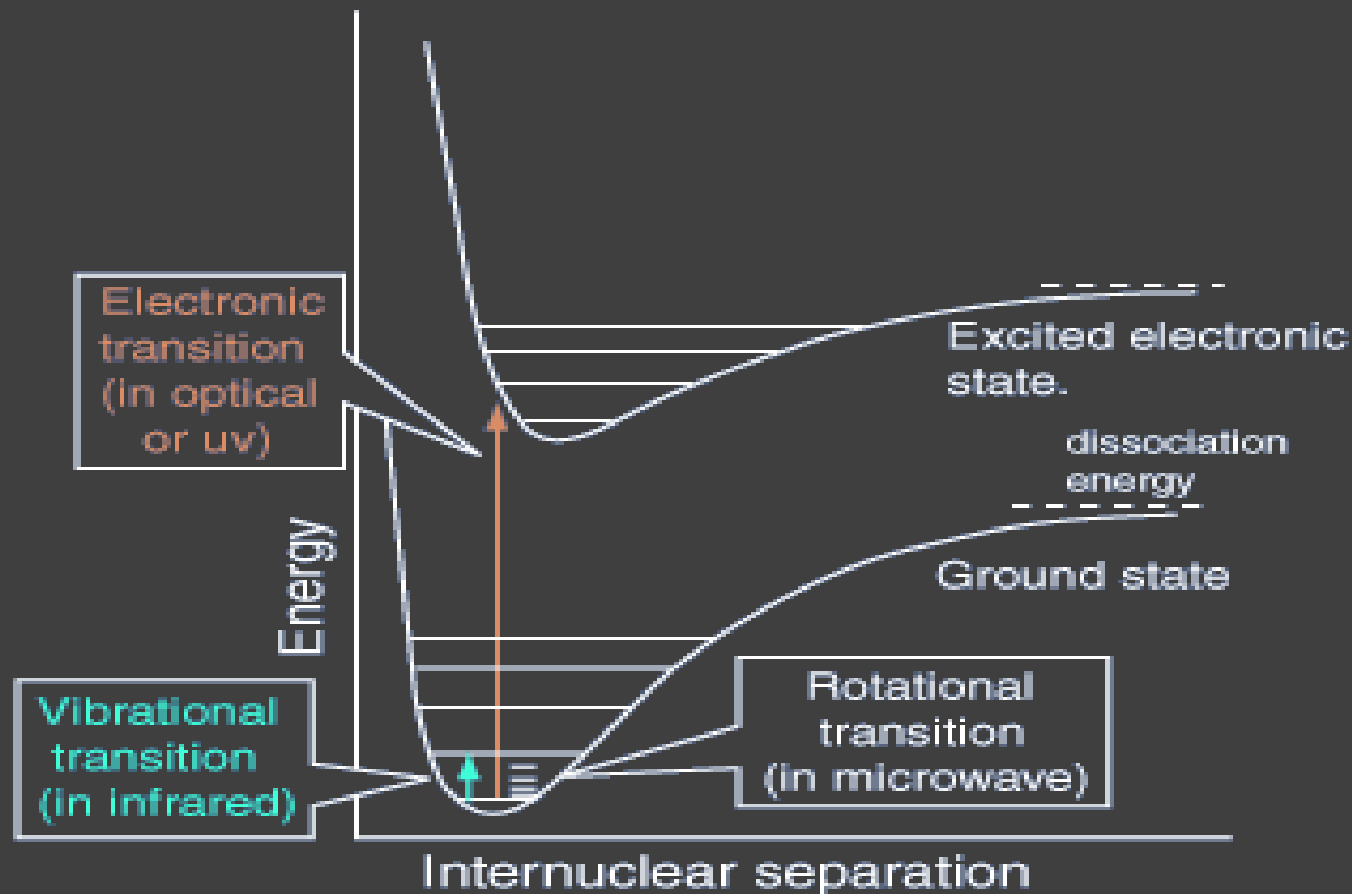
- Electronic, vibrational and rotational energies of a molecule are **completely independent** of each other
- Because the electronic energy levels are much farther apart than the vibrational energy levels which are again much farther apart than the rotational energy levels
- Can be written as

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

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Molecular Spectroscopy

Energy level diagram for a diatomic molecule



Source: <http://hyperphysics.phy-astr.gsu.edu/hbase/molecule/molec.html>



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Class content:

- *Introduction to rotational spectroscopy*
- *Expression for rotational energy levels of a diatomic molecule*

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

H-Cl

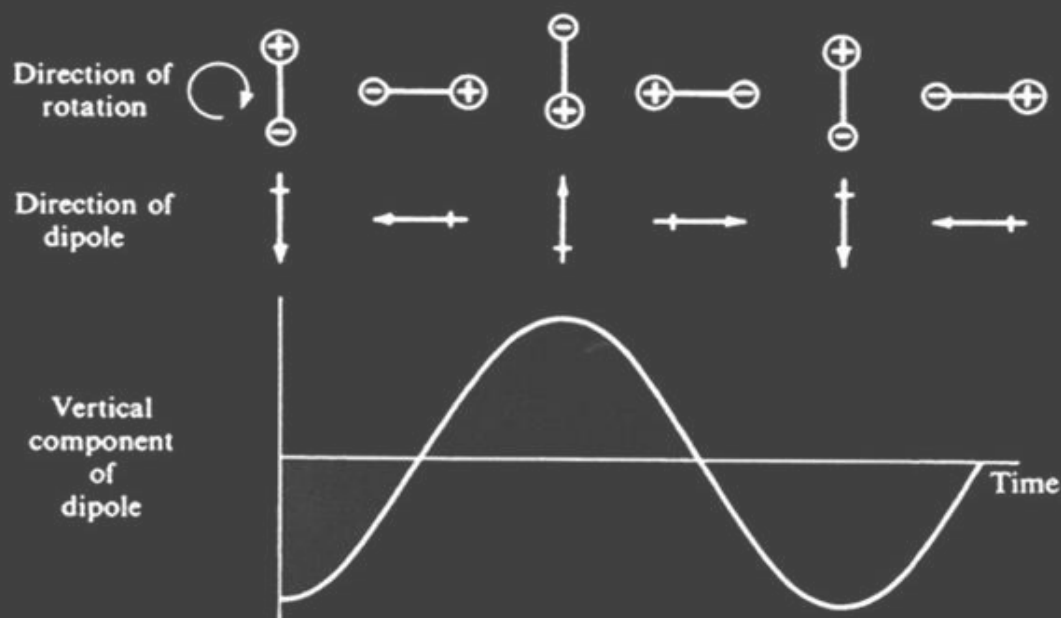


Fig. The rotation of a polar diatomic molecule, showing the fluctuation in the dipole moment measured in a particular direction

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

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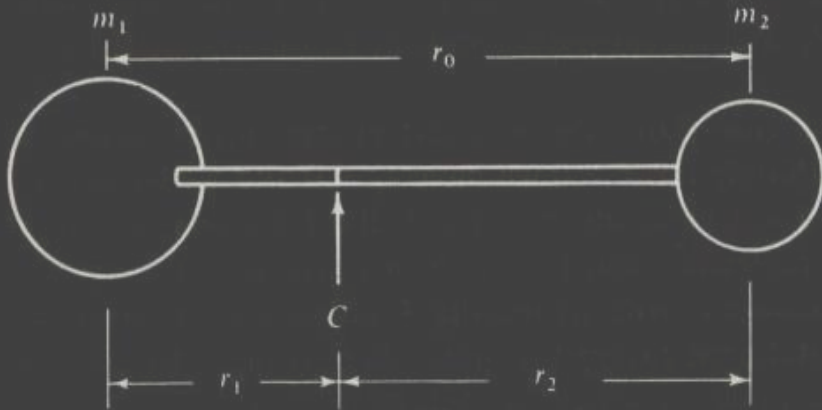
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- When the frequencies match, **resonance occurs** and the molecule absorbs energy and goes to the higher rotational levels and a **rotational spectrum** can be recorded
- Molecules such as **HCl and CO** show rotational spectra as they possess permanent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

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

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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

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

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,

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

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



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Module I- Molecular Spectroscopy



Class Content:

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

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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.

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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

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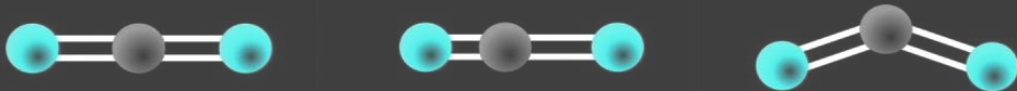
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CO₂ molecule although does not possess permanent dipole moment is IR active because some of its vibrational modes are IR active:

CO₂ **symmetric stretch** is IR inactive as there is no change in dipole moment when molecule vibrates in this mode.

CO₂ **asymmetric stretch** is IR active

CO₂ **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*

Source: <http://cepekmedia.co.nf>

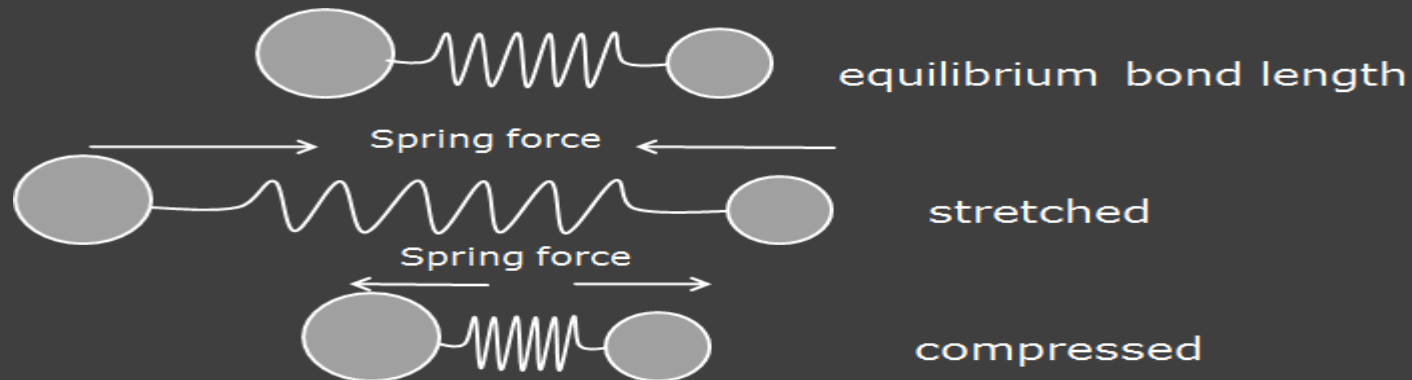
Source: <http://cepekmedia.co.nf>

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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.

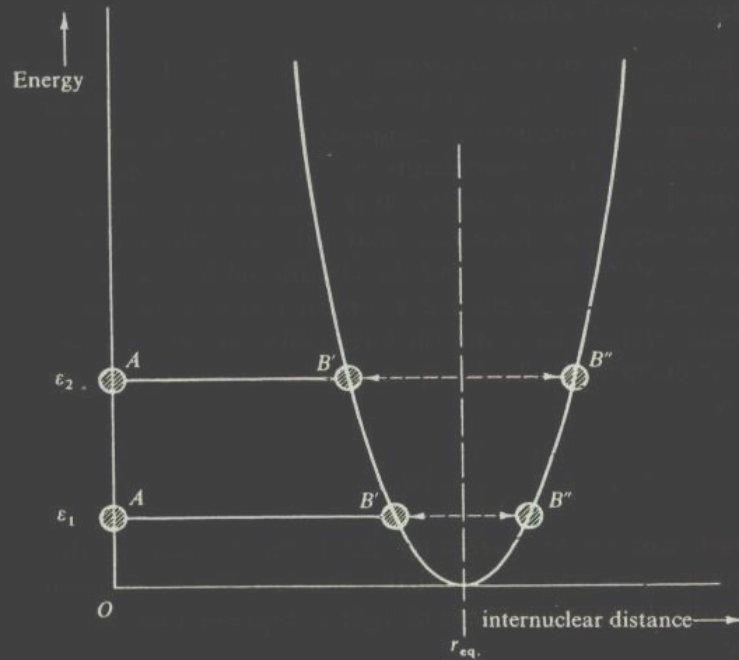
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The vibrating bond obeys Hooke's law, $F = -k(r - r_{eq})$

where k is a force constant, r is the inter nuclear distance, r_{eq} is equilibrium inter nuclear distance or bond length.

Energy is given by $E = \frac{1}{2} k(r - r_{eq})^2$ 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.

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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 wave number

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

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

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

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

Vibrational energy expressed in terms of wave number is given by,

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

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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**

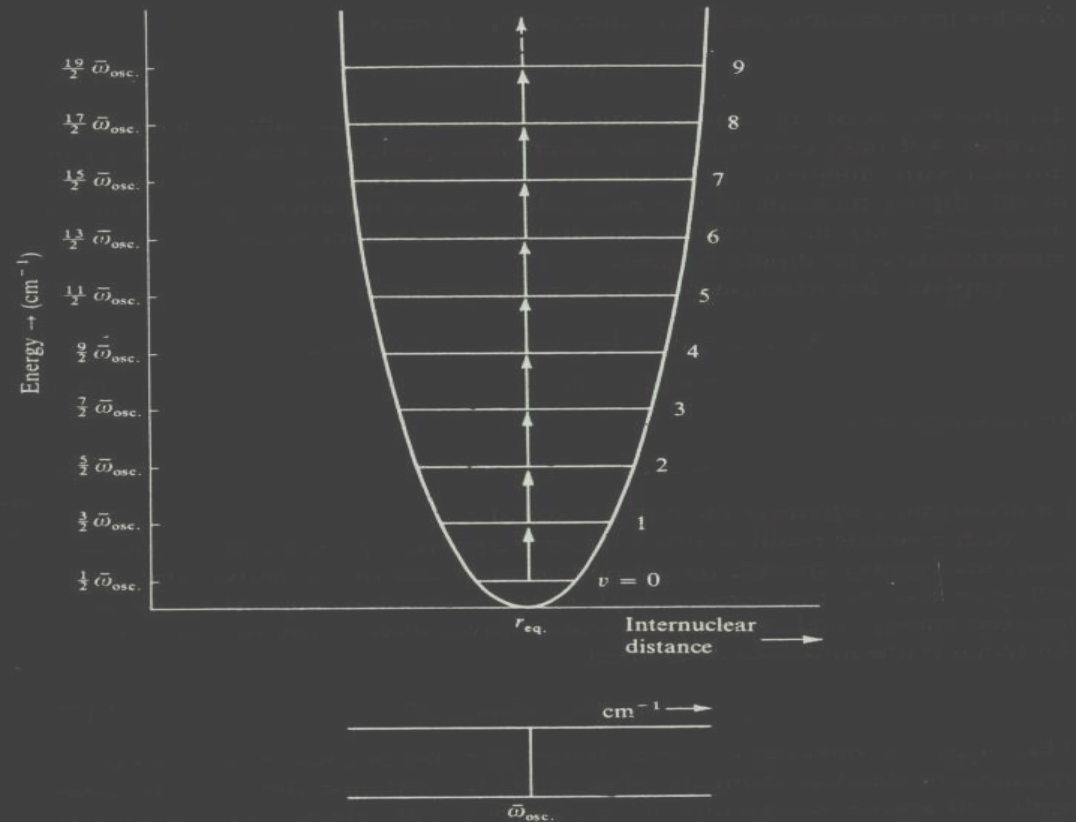
The **difference between any two consecutive energy levels** is equal to
Hence the energy levels are equally spaced.

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 $\bar{\nu}_{osc} cm^{-1}$

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

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

k can be determined which is the **bond strength (force constant)** of the molecule



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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*

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Module I- Molecular Spectroscopy

Vibrational spectroscopy-Anharmonic oscillator model

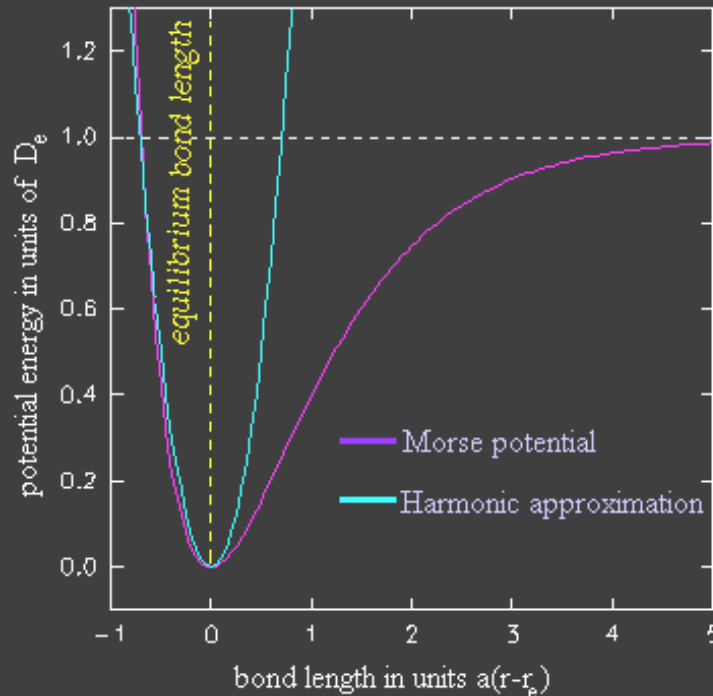
- In actual diatomics, the **potential is anharmonic** because the bond when stretched beyond a point breaks and the molecule dissociates
- A good description of an anharmonic oscillator is given by the Morse function

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

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>



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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

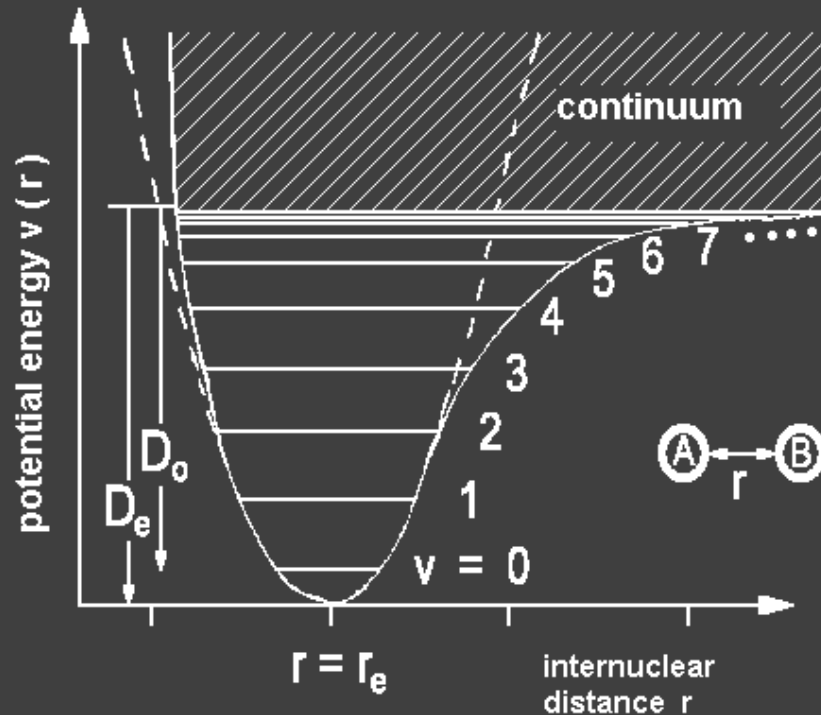
$$\varepsilon_v = \frac{E_v}{hc} = \left(v + \frac{1}{2}\right)\bar{\nu}_e - \left(v + \frac{1}{2}\right)^2 \bar{\nu}_e x_e \text{ cm}^{-1}$$

- 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

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Module I- Molecular Spectroscopy

Energy level diagram for a diatomic molecule showing anharmonicity



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

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

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- **Selection rules** for vibrational transition of anharmonic oscillator :
 - **Gross selection rule** : When a molecule vibrates there should be change in dipole moment
 - $\Delta v = \pm 1, \pm 2, \pm 3, \dots$
- 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**

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Module I- Molecular Spectroscopy

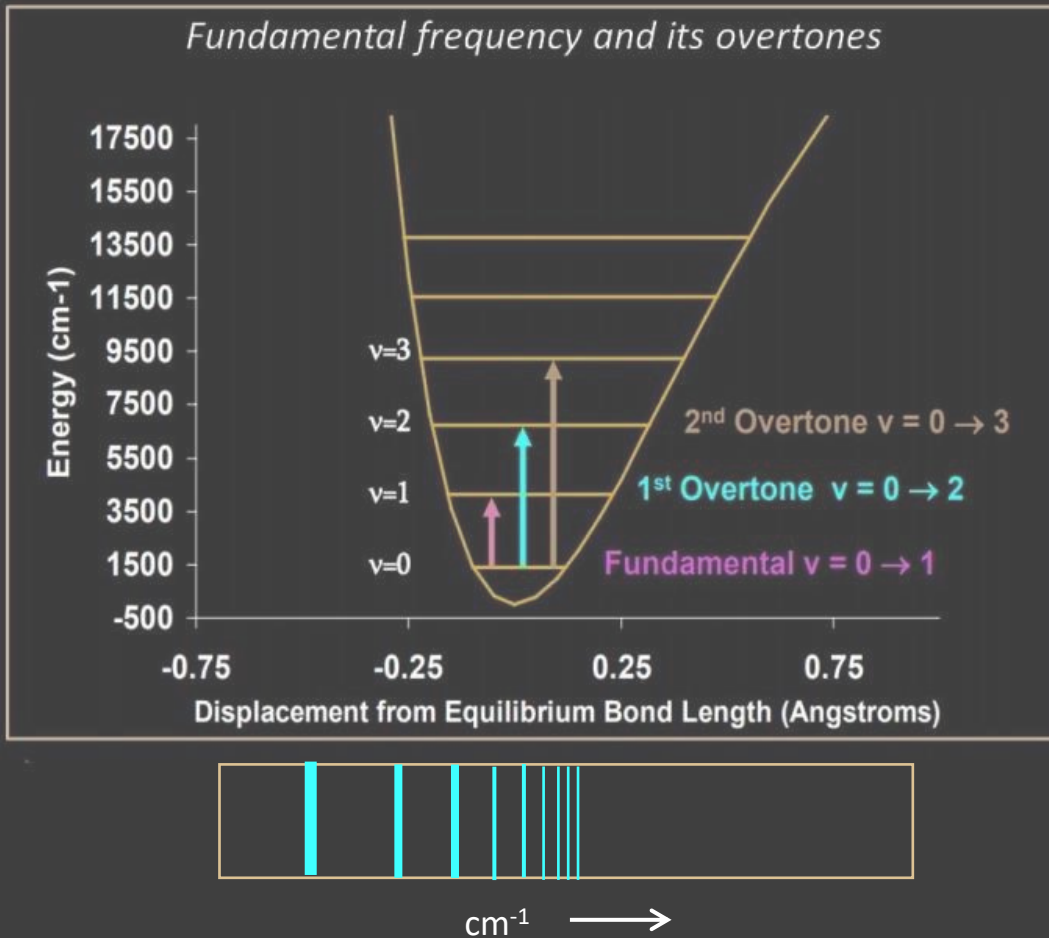
Substituting for values of v , we get the **energy gap** $\Delta\epsilon_{v+1 \leftarrow v}$

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 $v=2$	$\Delta\epsilon_{2 \leftarrow 0} = 2\overline{\nu}_e(1 - 3x_e)cm^{-1}$	First overtone
$v=0$ to $v=3$	$\Delta\epsilon_{3 \leftarrow 0} = 3\overline{\nu}_e(1 - 4x_e)cm^{-1}$	Second overtone

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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

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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,

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

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



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Module I- Molecular Spectroscopy



Class content:

- *Electronic spectroscopy*
- *Born – Oppenheimer Approximation*

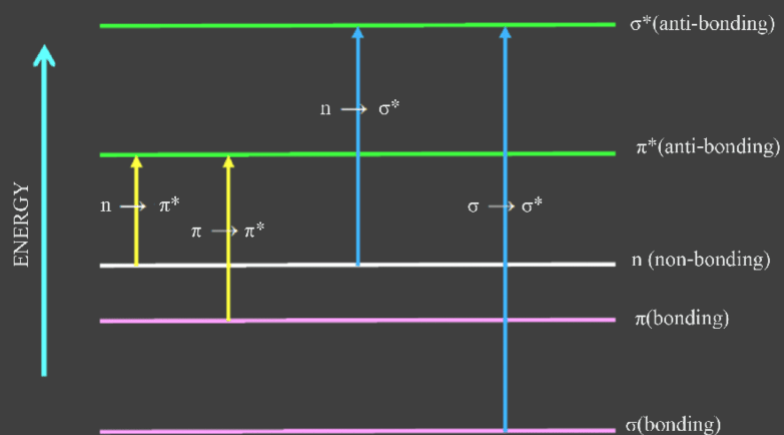
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Module I- Molecular Spectroscopy

Electronic spectroscopy

Electronic transitions :

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



- 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

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Module I- Molecular Spectroscopy

Electronic 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. $E_{\text{Total}} = E_t + E_r + E_v + E_e$

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

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

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

The approximate orders of magnitude are

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

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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 H_2 , N_2 which are inactive in IR and Microwave region can be obtained from their electronic spectra



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Module I- Molecular Spectroscopy



Class content:

- *Vibrational coarse structure-Progressions*

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Module I- Molecular Spectroscopy

Vibrational Coarse structure

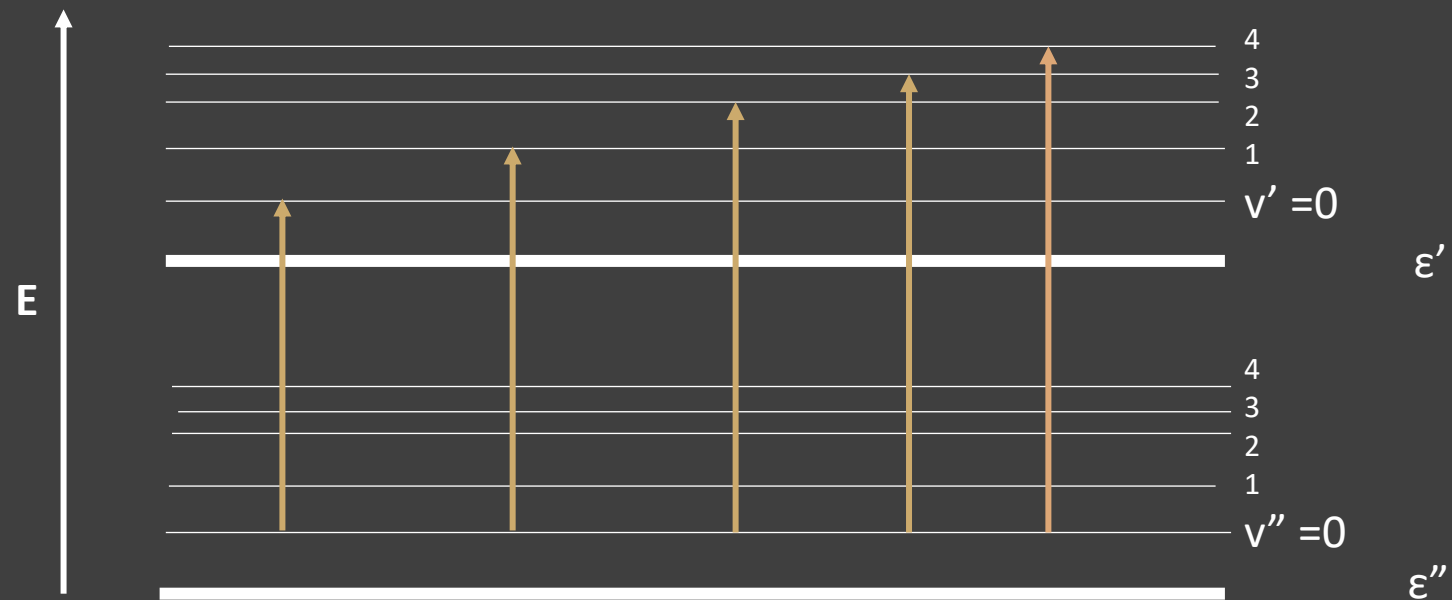
- The **ground state** energy levels are denoted by ϵ'' and v'' , while the **excited state** energy levels are denoted by ϵ' and v'
- There are **no selection rules** for vibrational transitions during electronic transition



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Module I- Molecular Spectroscopy

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

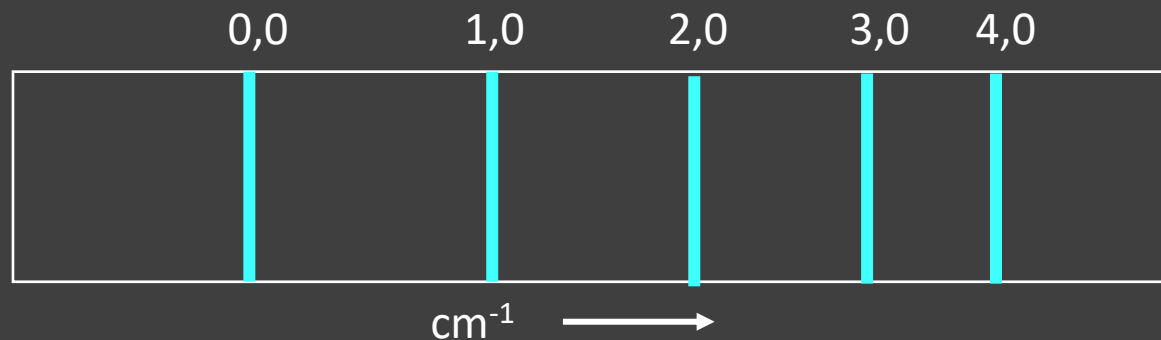


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Module I- Molecular Spectroscopy

- 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

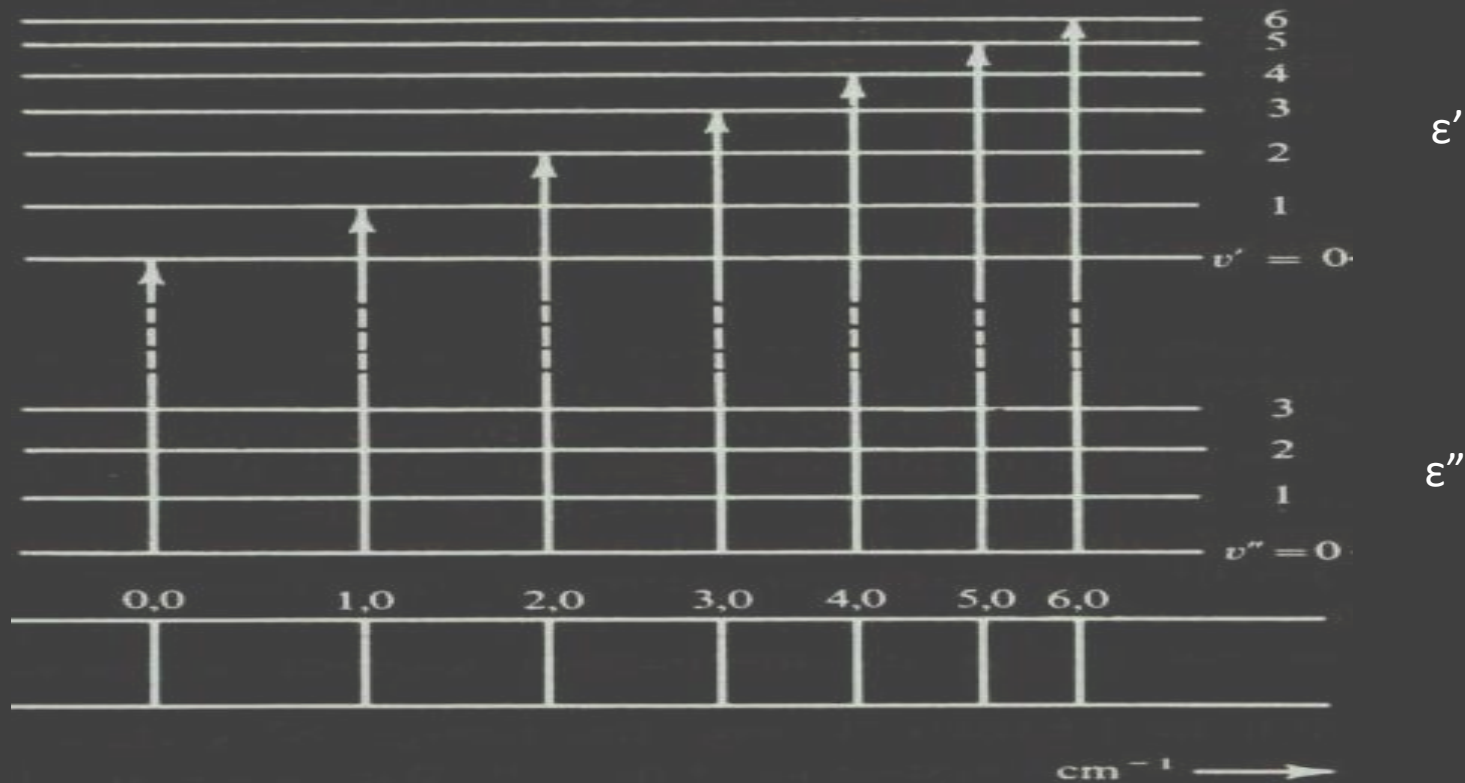
Spectrum showing Progression



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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.



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Module I- Molecular Spectroscopy



Class content:

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

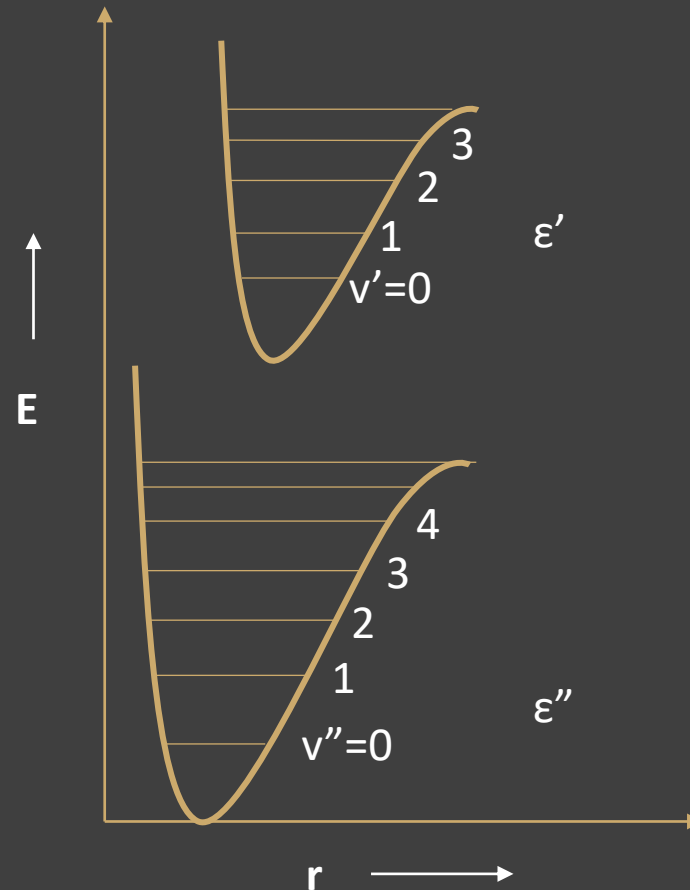
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Module I- Molecular Spectroscopy

Electronic spectroscopy

Intensity of spectral lines

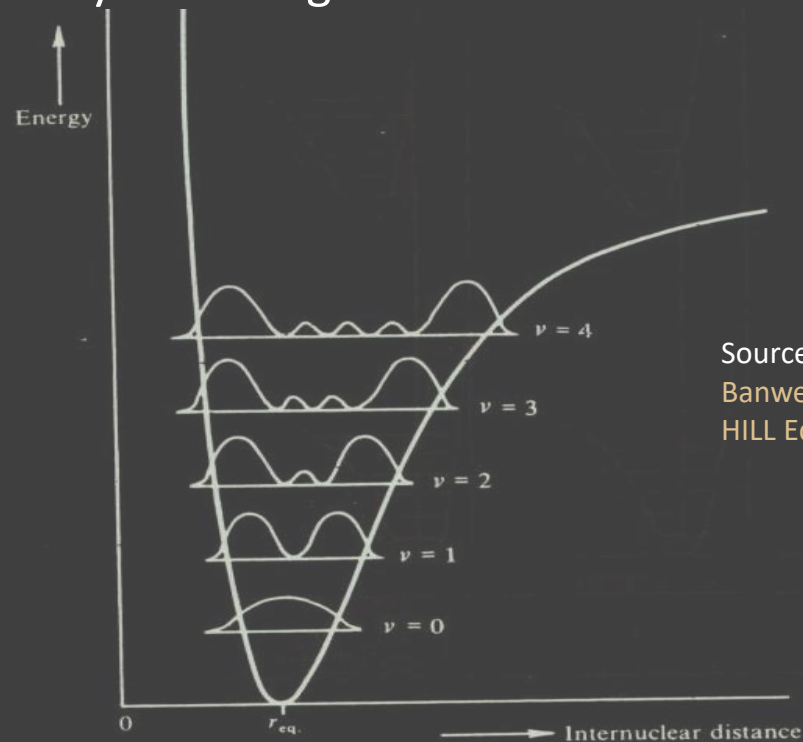
- There are **no selection rules** for vibrational changes during an electronic transition
- Most of the **transitions start from $v''=0$** as it is most populated level
- The excited state usually has **longer internuclear distance** because of antibonding character



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



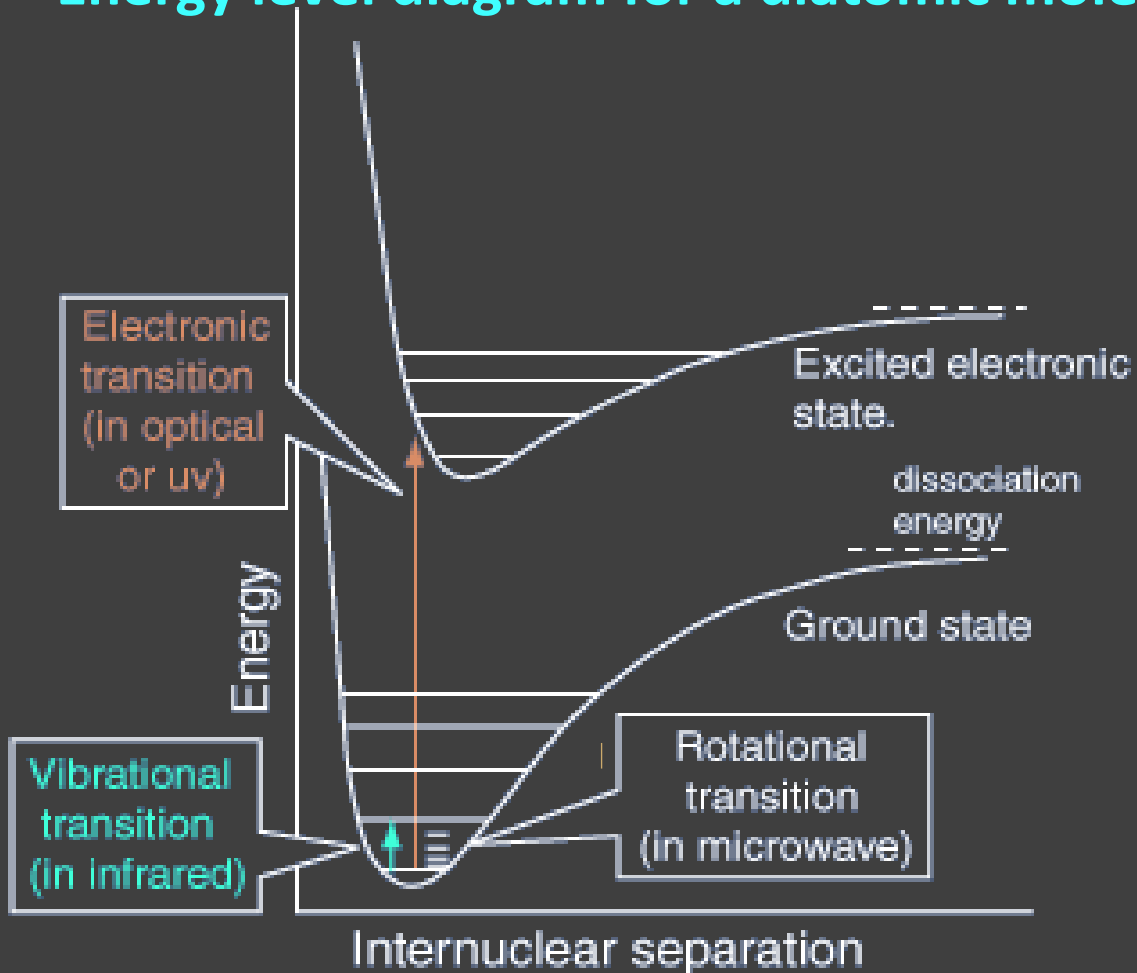
Source: Fundamentals of Molecular Spectroscopy: C. N. Banwell and Elaine M McCash, Fifth Edition, MCGRAW-HILL Education (India) Private Ltd.

Probability distribution for a diatomic molecule according to quantum theory

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Energy level diagram for a diatomic molecule



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Module I- Molecular Spectroscopy

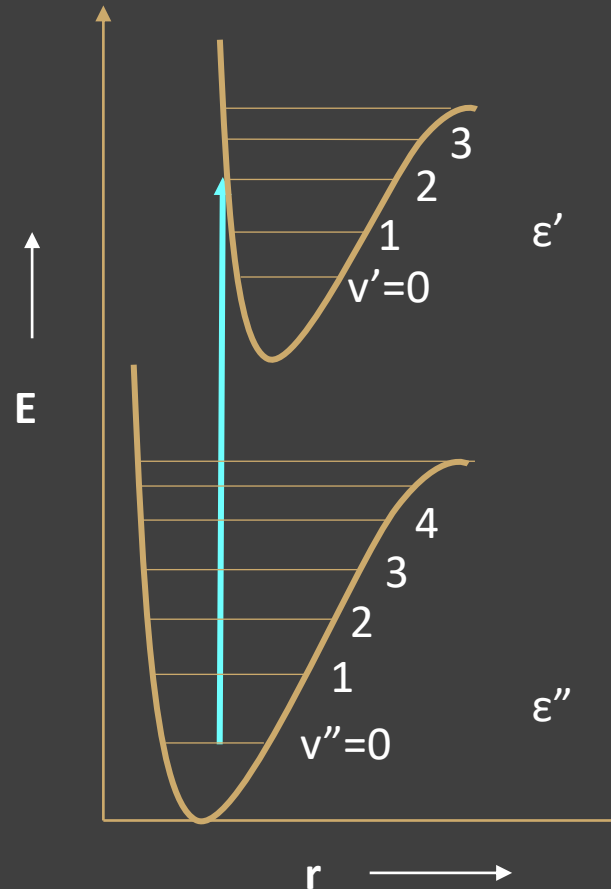
Franck-Condon principle

- 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**



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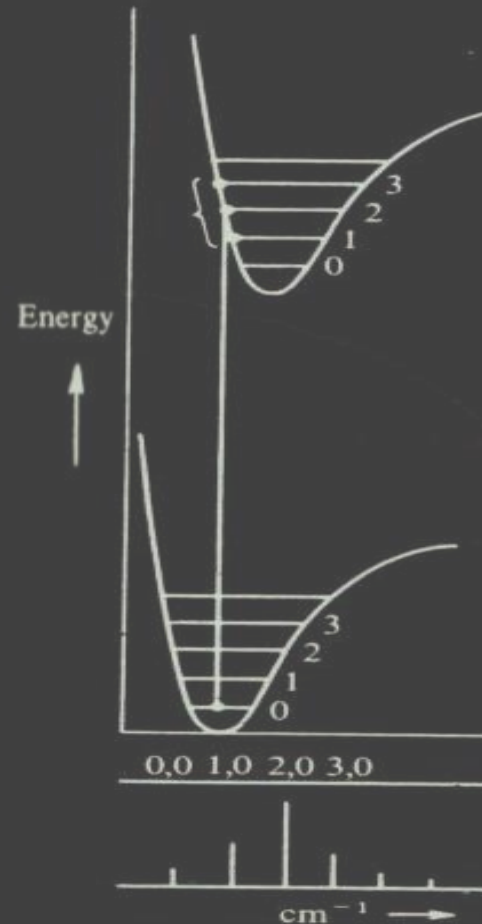
Module I- Molecular Spectroscopy

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.

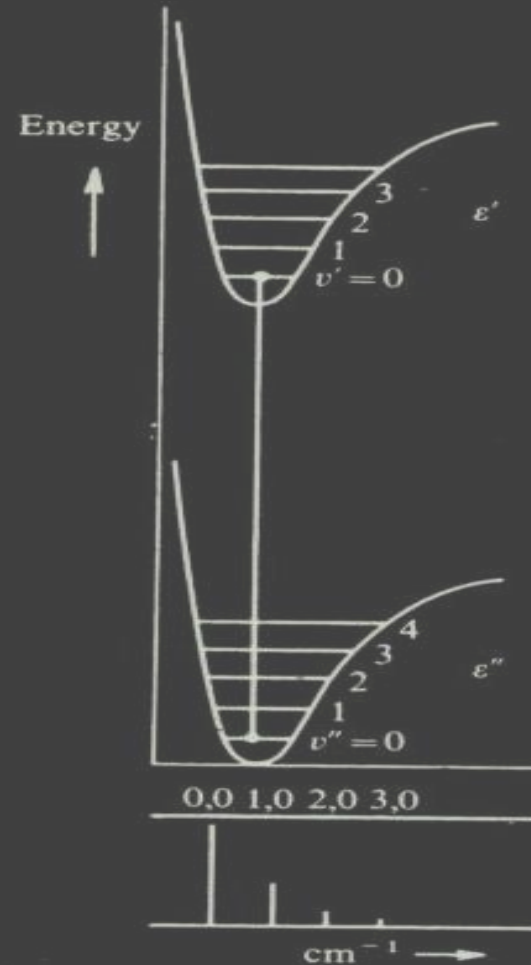
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- No change in internuclear distance

$$r_e'' = r_e'$$

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



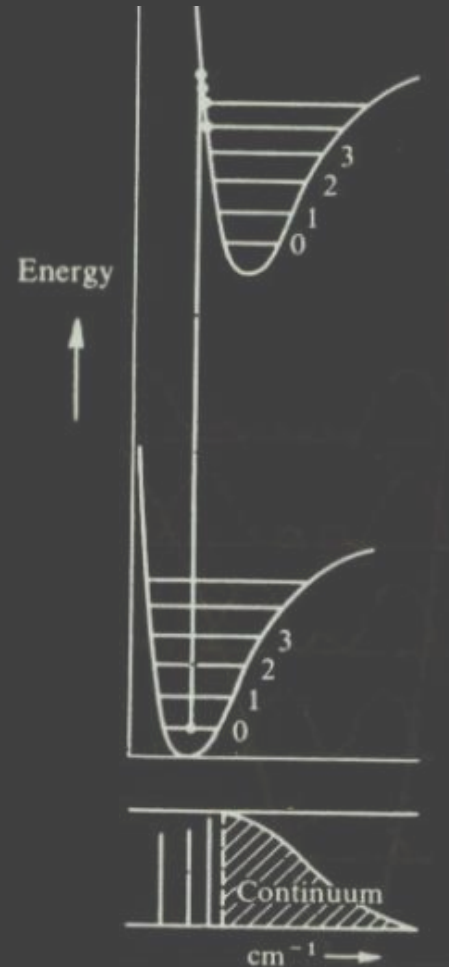
Source: Fundamentals of Molecular Spectroscopy: C. N. Banwell and Elaine M McCash, Fifth Edition, MCGRAW-HILL Education (India) Private Ltd.

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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.



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Class content :

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

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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, $c = 3 \times 10^8$ ms⁻¹, $h = 6.6 \times 10^{-34}$ Js)

Solution:

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

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

$$I = \mu r^2$$

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

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

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

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

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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 :

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

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

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

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

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

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Module 1- Molecular Spectroscopy



$$I = \mu r^2$$

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

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

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

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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 amu = $1.66 \times 10^{-27} \text{ kg}$, $h = 6.627 \times 10^{-34} \text{ Js}$, $c = 3 \times 10^{10} \text{ cms}^{-1}$, $N = 6.023 \times 10^{23} \text{ mol}^{-1}$, Gram molar mass of H = 1.0 and Br = 79.9)

Solution :

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

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

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Module 1- Molecular Spectroscopy



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

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

$$I = \mu r^2$$

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

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

$$x_e = 0.0171$$

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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 :

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

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

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

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

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

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

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

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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 :

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

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

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

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

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

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



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Module 2- Phase equilibria



Module content:

- *Phase equilibria*
- *Gibb's phase rule*
- *Phase diagram of 1-component system*
- *Phase diagram of 2-component system*

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Module 2- Phase equilibria



Class content:

- *Free energy in Phase equilibria*
- *Chemical potential*
- *Phase equilibria*
 - *Phase*
 - *Component*
 - *Degree of freedom*

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Module 2- Phase equilibria



Free energy in Phase equilibria

- All substances have tendency to **minimize their Gibbs energy** at constant temperature and pressure to attain stable state
- **Phase transformations** from one phase to another occur to reduce free energy of the system
- Gibb's energy is an **extensive property**

Chemical potential

- Chemical potential is defined as the **partial molar Gibb's energy** for a component i in a mixture , and is denoted by μ

$$\mu_i = \left(\frac{\partial G}{\partial n_i} \right)_{p, T, n_j \neq i}$$

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Module 2- Phase equilibria



Phase equilibria

- Phase equilibria between phases exist when **chemical potential of a component is equal in all the phases** in equilibrium

e.g. for water at triple point



The chemical potential of water will be equal in all the three phases

- For systems not at equilibrium, the chemical potential will point to the **direction in which the system can move** in order to achieve equilibrium viz. , the system moves from higher chemical potential to lower chemical potential
- When various phases are in equilibrium with one another in a heterogeneous system, there can be **no transfer of energy or mass** from one phase to another.
- For a system at equilibrium, the various phases must have the **same temperature and pressure and their respective compositions must remain constant** all along

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Module 2- Phase equilibria



Phase

A phase is defined as any **homogeneous and physically distinct part of a system** bounded by a surface and is mechanically separable from other parts of the system. It is denoted by P

- **Gaseous state** : $P = 1$ gases are completely miscible
- **Liquid state** : $P = \text{No. of layers when liquids are immiscible}$
 $P = 1$ when liquids are completely miscible
- **Solid state** : Each solid constitutes a separate phase
Each polymorphic form constitutes a separate phase
 $P = 1$ for solid solution

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Module 2- Phase equilibria



Counting the number of phases

1) **Solid \rightleftharpoons liquid \rightleftharpoons vapour** ; $P = 3$

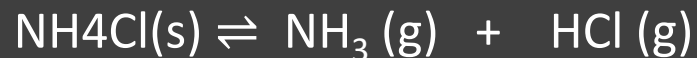
- Ice in the system is a single phase even if it is present as a number of pieces.

2) **Calcium carbonate undergoes thermal decomposition**



- $P = 3$; 2 solid phases, CaCO_3 and CaO and one gaseous phase, that of CO_2

3) **Ammonium chloride undergoes thermal decomposition**



- $P = 2$; one solid, NH_4Cl and one gaseous, a mixture of NH_3 and HCl

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Module 2- Phase equilibria



Components

- A component is defined as the **smallest number of independently varying chemical constituents** using which the composition of **each and every phase** in the system can be expressed
- When no reaction is taking place in a system, the number of components is the same as the number of constituents
- While expressing in terms of constituents **zero and negative values** are allowed

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Module 2- Phase equilibria

Counting the number of components:

- **1-component system**

e.g. **Pure water** ; **C = 1**

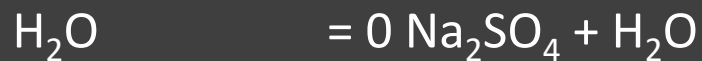
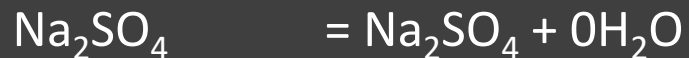
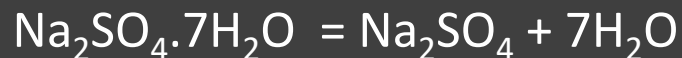
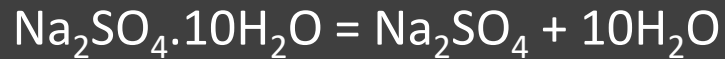
solid water \rightleftharpoons liquid water

All the different phases can be expressed in terms of the single constituent water

- **2-component system**

- **Salt hydrate system**

e.g. $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$; **C=2**



The composition of all the phases can be expressed in terms of 2 components

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Module 2- Phase equilibria

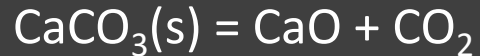


- Thermal decomposition of solid CaCO_3 in a closed container ; $C = 2$



- Though there are 3 species present, the number of components is only two
- Phases are : $\text{CaCO}_3(s)$, $\text{CaO}(s)$ and $\text{CO}_2(g)$
- Any two of the three constituents may be chosen as the components

- If CaO and CO_2 are chosen,



- If CaCO_3 and CO_2 are chosen,



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Module 2- Phase equilibria



- Thermal decomposition of ammonium chloride in a closed system ; **C = 1**



- Phases are : solid phase of $\text{NH}_4\text{Cl(s)}$ and gaseous phase of $\text{NH}_3\text{(g)}$ and HCl(g)

solid : $\text{NH}_4\text{Cl (s)} = \text{NH}_4\text{Cl}$

gas : $\text{NH}_3\text{(g)} + \text{HCl(g)} = \text{NH}_4\text{Cl}$

- The composition of both the solid and gaseous phase can be expressed in terms of NH_4Cl . Hence the number of components is one; $C=1$
- If additional HCl (or NH_3) were added to the system, then **C = 2**
- The decomposition of NH_4Cl would not give the correct composition of the gas phase
- A second component, HCl (or NH_3) would be needed to describe the gas phase, therefore $C=2$

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Module 2- Phase equilibria



Degrees of freedom (or variance)

The degrees of freedom or variance of a system is defined as the **minimum number of intensive variables** such as temperature, pressure, concentration, which must be fixed in order to define the system completely; it is denoted by F

OR

The degree of freedom of a system may also be defined as the number of variables, such as temperature, pressure and concentration that can be **varied independently** without altering the number of phases.

Example : water system

- **Only 1 phase** (solid , liquid or gas)
 - Both temperature and pressure need to be mentioned in order to define the system; **$F = 2$**

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Module 2- Phase equilibria



- **2 phases in equilibrium,**
 - Only one variable, either temperature or pressure need to be specified in order to define the system; **$F = 1$**
 - solid water \rightleftharpoons liquid water
 - If the pressure on the system is maintained at 1 atm, then the temperature of the system gets automatically fixed at 0°C, the normal melting point of ice
- **3 phases in equilibrium,**
 - No variable can be changed
 - temperature and pressure are fixed, **$F = 0$**
 - solid water \rightleftharpoons liquid water \rightleftharpoons water vapour
 - Three phases, ice, water, vapour can coexist in equilibrium at triple point of water at 0.0098°C and 4.58mm of Hg pressure only



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Module 2- Phase equilibria



Class content:

- *Gibb's Phase rule*
- *Derivation of Gibb's Phase rule*

Phase rule

- It was given by **Williams Gibbs** in 1874

- **Statement of Gibb's phase rule**

Provided the equilibrium in a heterogeneous system is not influenced by external forces (gravity, electrical or magnetic forces) , the number of degrees of freedom (F) of the system is related to number of components (C) and number of phases (P) existing at equilibrium to one another by the equation

$$F = C - P + 2$$

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Module 2- Phase equilibria



Derivation of the phase rule

- A system at equilibrium satisfies the following conditions:
 - **Thermal equilibrium** – Temperature is constant
 - **Mechanical equilibrium** – Pressure is constant
 - **Chemical or material equilibrium** – Chemical potential of a substance is same in all the phases
- Mathematically, $\mu_i^\alpha = \mu_i^\beta = \mu_i^\gamma = \dots$
- The system considered is: All C components distributed between P phases

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Module 2- Phase equilibria



- Total number of intensive variables that need to be ascertained to describe the system:

Temperature 1

Pressure 1

Composition mole fraction of each component in every phase

- For each phase, the sum of mole fractions equals unity

$$\chi_1^\alpha + \chi_2^\alpha + \chi_3^\alpha + \dots + \chi_c^\alpha = 1 \quad (\text{C-1})$$

$$\chi_1^\beta + \chi_2^\beta + \chi_3^\beta + \dots + \chi_c^\beta = 1 \quad (\text{C-1})$$

$$\chi_1^\gamma + \chi_2^\gamma + \chi_3^\gamma + \dots + \chi_c^\gamma = 1 \quad (\text{C-1})$$

.

.

.

$$\chi_1^P + \chi_2^P + \chi_3^P + \dots + \chi_c^P = 1 \quad (\text{C-1})$$

- In each phase (C-1) mole fraction terms need to be defined
- Number of phases : P
- Number of composition variables = P(C-1)
- **Total number of intensive variables = P(C-1) + 2**

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Module 2- Phase equilibria



Total number of equations(constraints) :

- At equilibrium the chemical potential of particular component is same in every phase in a system

$$\mu_1^\alpha = \mu_1^\beta = \mu_1^\gamma = \dots \quad (P-1)$$

$$\mu_2^\alpha = \mu_2^\beta = \mu_2^\gamma = \dots \quad (P-1)$$

$$\mu_3^\alpha = \mu_3^\beta = \mu_3^\gamma = \dots \quad (P-1)$$

⋮

$$\mu_c^\alpha = \mu_c^\beta = \mu_c^\gamma = \dots \quad (P-1)$$

- For C components $C(P-1)$
- Total number of equations or constraints = $C(P-1)$**

F = Total number of variables – total number of equations

$$F = P(C-1) + 2 - \{C(P-1)\}$$

$$\mathbf{F=C-P+2}$$

which is the **Gibb's phase rule**



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Module 2- Phase equilibria



Class content:

- *Phase diagram of a 1-component system*
- *Phase diagram of water*

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Module 2- Phase equilibria

Phase diagram

A diagram which represents the **conditions** under which a substance exists in **different phases** in a system

Phase diagram of a 1-component system

$$F = C - P + 2$$

For a 1-component system **$F = 3 - P$**

Single phase : $F = 2$; Area in a diagram

Two phases in equilibrium : $F = 1$; line in a diagram

Three phases in equilibrium : $F = 0$; point in a diagram

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Module 2- Phase equilibria



High pressure, low temperature: **solid phase**

High temperature, low pressure : **vapour phase**

In between : **liquid phase**

solid \rightleftharpoons liquid

liquid \rightleftharpoons vapour

vapour \rightleftharpoons solid

Solid \rightleftharpoons liquid \rightleftharpoons vapour

Source:http://abyss.uoregon.edu/~js/glossary/triple_point.html

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Module 2- Phase equilibria



Application of Gibb's phase rule $F = C - P + 2$ to 1-component system:

Water system

When only 1 phase is present :

$C = 1, P = 1; F = 2$; Temperature and Pressure can be varied independently

Bivariant system

When 2 phases are in equilibrium:

$C = 1, P = 2; F = 1$; Temperature or Pressure can be varied independently

Univariant system

When all 3 phases are in equilibrium:

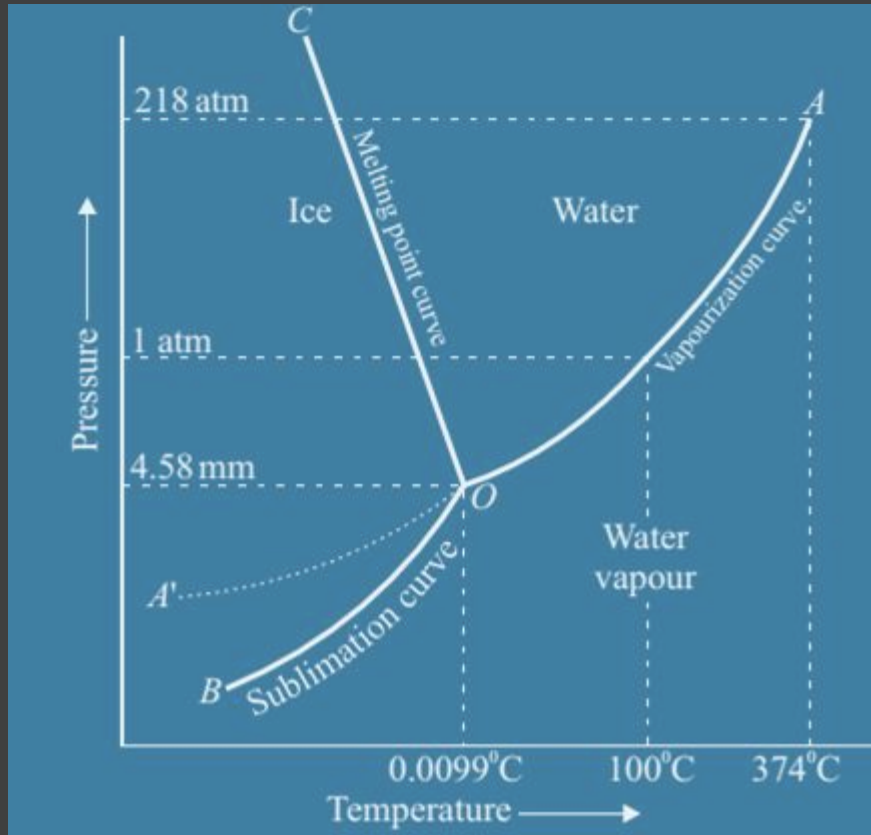
$C = 1, P = 3; F = 0$; Neither Temperature nor Pressure can be varied

Invariant system

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Module 2- Phase equilibria

Phase diagram of water



OC : Melting point curve

OA : Vaporisation curve

OB : Sublimation curve

O: Triple Point

A: Critical point

OA': Metastable equilibrium

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Module 2- Phase equilibria

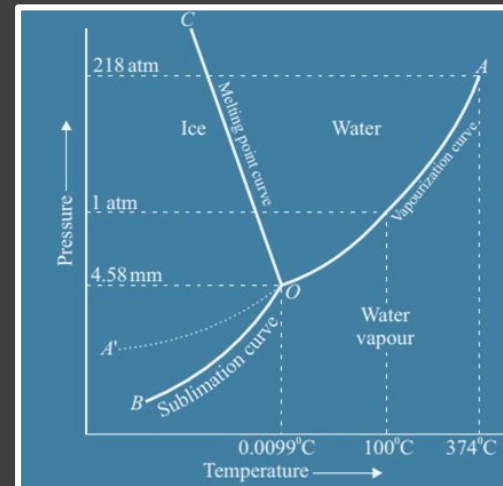
Equilibrium between solid and liquid (fusion curve OC)

- ice \rightleftharpoons water
- $F=1$, monovariant system
- variation of melting point of ice with pressure
- **slope is negative**; as ice melts its volume decreases or density increases
- Clausius-Clapeyron equation

$$\frac{dp}{dT} = \frac{\Delta H_{\text{Fusion}}}{T\Delta V} = \text{negative}$$

Where,

ΔV = decrease in volume as ice melts is -ve; ΔH_{fusion} = *endothermic*, +ve



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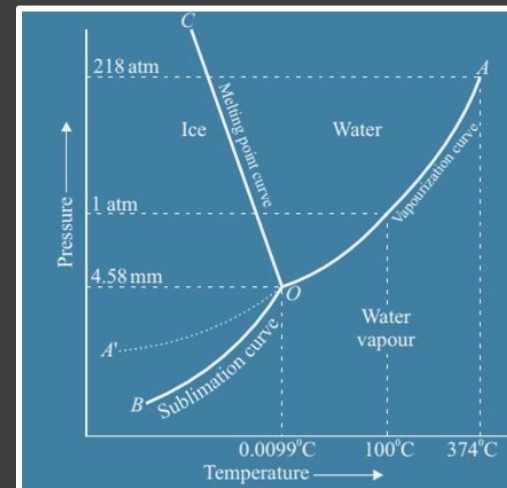
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Equilibrium between solid and vapour (sublimation curve OB)

- ice \rightleftharpoons water vapour
- $F=1$, monovariant system
- variation of sublimation temperature of ice with pressure
- slope is positive
- Clausius Clapeyron equation

$$\frac{dp}{dT} = \frac{\Delta H_{sub}}{T\Delta V} = \text{positive}$$

Where ,



ΔV = Increase in volume as ice sublimates, +ve ; $\Delta H_{sublimation}$ = endothermic reaction, +ve

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Module 2- Phase equilibria

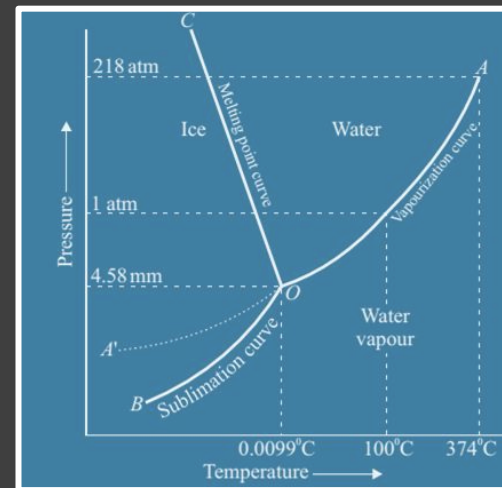
Equilibrium between liquid and vapour (vaporization curve OA)

- liquid water \rightleftharpoons vapour
- $F=1$, monovariant system
- variation of boiling temperature of water with pressure
- slope is positive
- Clausius - Clapeyron equation

$$\frac{dp}{dT} = \frac{\Delta H_{\text{vapourisation}}}{T\Delta V} = \text{positive}$$

Where,

ΔV = Increase in volume as liquid water vapourises, +ve; $\Delta H_{\text{vapourisation}}$ = endothermic reaction, +ve



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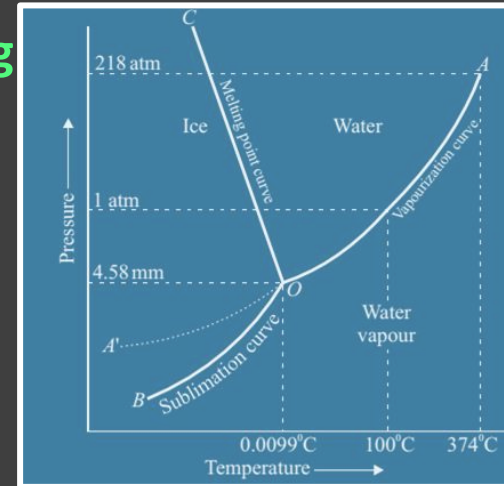
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Triple point “O”:

- Represents equilibrium between liquid, vapour and solid water (ice)
- All three phases are present together
- $F = 0$, **invariant system**
- Triple point for water lies at **0.0098°C and 4.58 mmHg**

Critical point “A”:

- the interface between liquid water and water vapour vanishes
- a point above which water does not exist in liquid state
- Critical point lies at **374°C and 218 atm** pressure

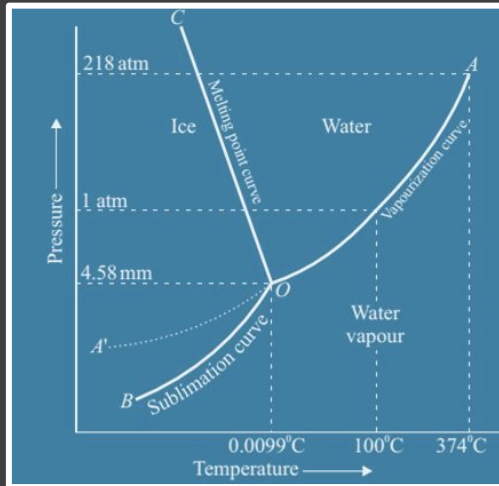


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Metastable equilibrium (OA'):

- Ice fails to form at the triple point and water continues to exist in liquid phase
- The vapour pressure of the liquid continues along OA'
- This is called **super cooled water** and represents metastable equilibrium involving liquid and vapour phases.
- Any disturbance will cause the system to go back to stable equilibrium (OB)
- The vapour pressure of the system in the metastable region is more than that of the stable system ice at the same temperature





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Class content:

- *Reduced phase rule for a 2-component system*
- *Phase diagram of a 2-component system*
 - *Phase diagram of Pb-Ag system*
- *Determination of solid-liquid equilibria*
- *Pattinson's process*

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Module 2- Phase equilibria



Phase diagram of a two component system

- The phase rule equation is $F = C - P + 2$
- For a 2 component system the ordinary phase rule cannot be used
- For a two component system, $C = 2$ then $F = 2 - P + 2 = 4 - P$
- The minimum number of phase is 1; $F = 4 - 1 = 3$
- This requires **3 dimensional space** which cannot be explained on the plane of paper
- **One of the three variables is kept constant**
- Measurements in these systems are generally carried out **at atmospheric pressure**
- Pressure may be considered constant ; degrees of freedom is reduced by 1,
- $F = C - P + 2 - 1$

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Module 2- Phase equilibria



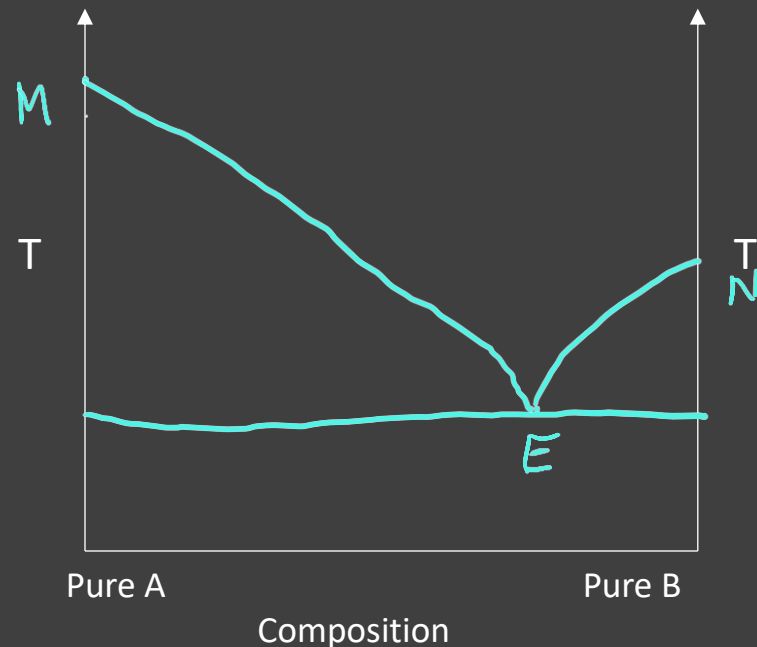
- The phase rule takes the form $F = C - P + 1$ and is known as the reduced phase rule
- Equilibria such as solid-liquid equilibria are such systems in which the gas phase is absent and hence are hardly affected by small changes in pressure
- Systems in which the gas phase is absent are called **condensed systems**
- $F = C - P + 1$ is also known as condensed phase rule

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Module 2- Phase equilibria

Phase diagram of a 2-component system

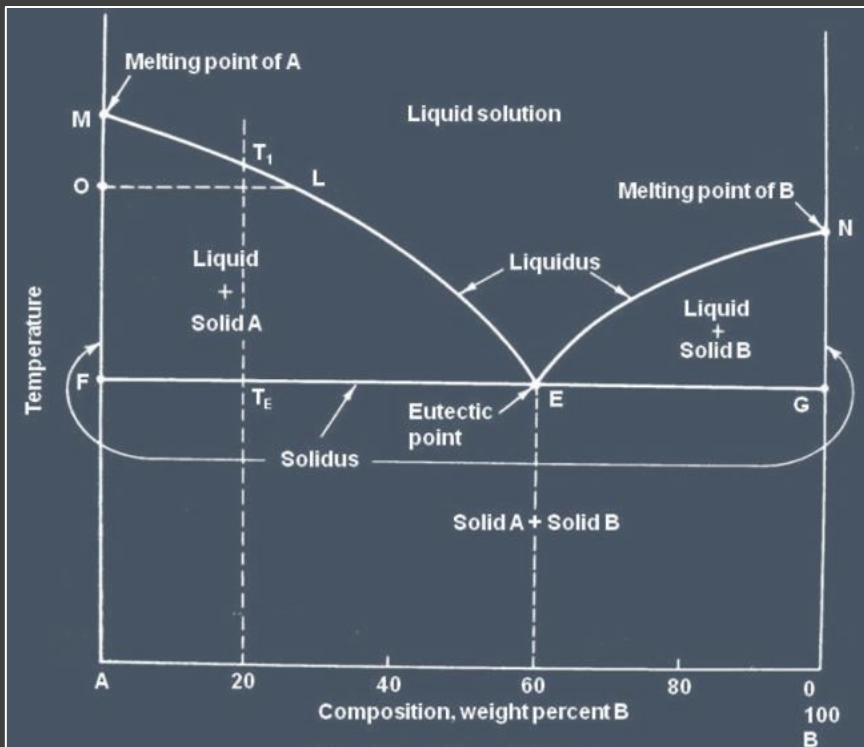
- Phase rule for a 2- component system : $F = C - P + 1$
- **Pressure is constant**
- Plot is between **Temperature and Composition**
- A and B are miscible in all proportions in the liquid (molten) state
- In solid state they are completely immiscible



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Module 2- Phase equilibria

Simple eutectic system



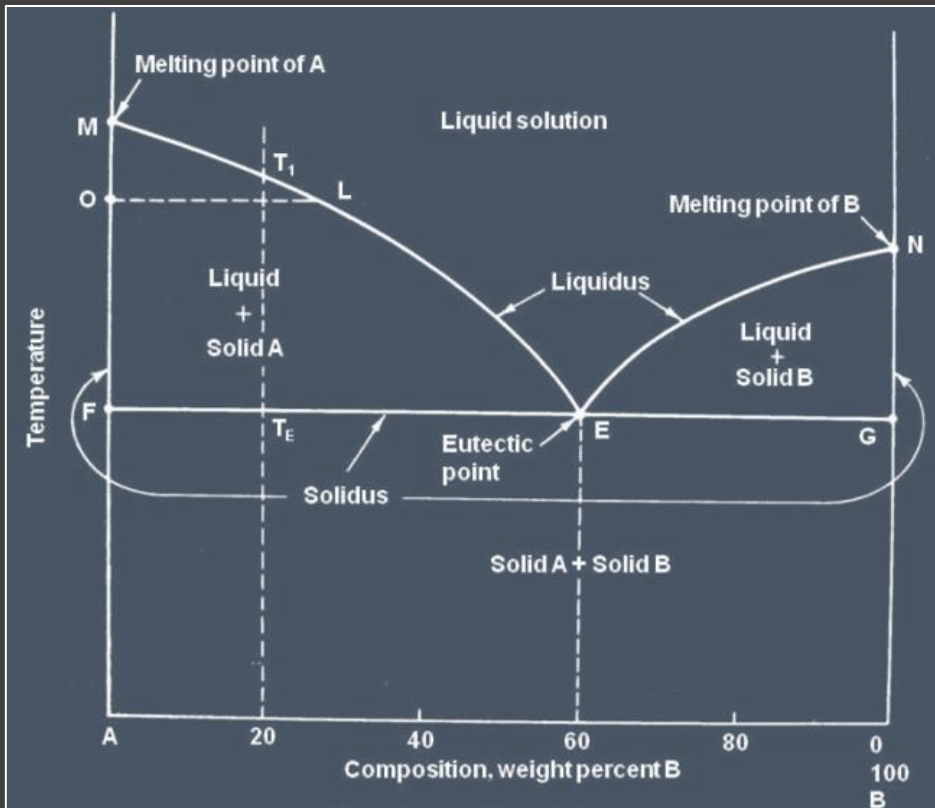
When a mixture of the 2 components is heated till the mixture melts and then cooled:

- First crystal of A is formed when **f.pt. of A in the mixture** is reached
- On further cooling more solid A precipitates and **liquid melt becomes richer in B**
- With decrease in temperature more and more solid A separates and the liquid melt moves along curve ME
- Finally when temperature reaches F, **solid B also starts precipitating**
- Three phases are present at E: **solid A, solid B and the liquid melt**
- Further cooling will just result in cooling of solid A & B

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Simple eutectic : Pb-Ag system



A-B system

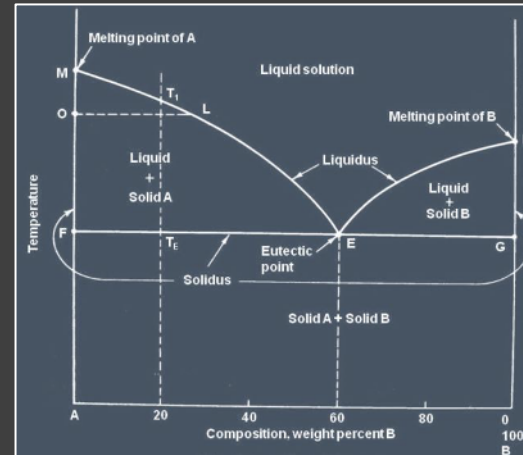
- A : 100% A
- B : 100% B
- Area above MEN: Liquid melt
- Area MEF : Solid A + Liquid melt
- Area NEG : Solid B + Liquid melt
- Below FEG : Solid A + Solid B
- Eutectic point – “E”
- Curves : ME and NE

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Eutectic point

- **Eutectic mixture:** A mixture of two components which has the lowest freezing point of all the possible mixtures of the components
- Number of phases at eutectic point = **3**
- $F = C - P + 1$; $C = 2$, $P = 3$, so **$F = 0$** ; invariant point
- It has a **definite composition** and a **sharp melting point**



For Pb-Ag system:

Melting point –

Ag : 961°C , Pb : 327°C

Eutectic temperature: **303°C**

Eutectic composition:

97.4 % Pb and 2.6 % Ag

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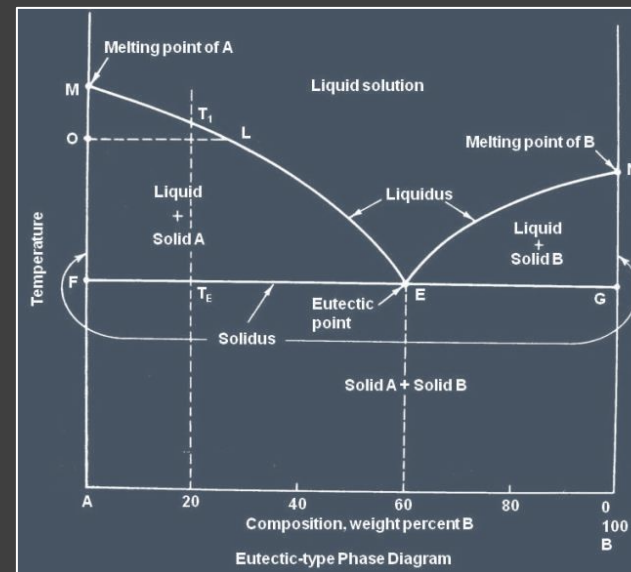
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CURVE ME : freezing point curve of A

- It shows decrease in freezing point / melting point of A due to the addition of B to A
- Solid A is in equilibrium with liquid melt of B in A
- Here $C = 2$ and $P = 2$, then the reduced phase rule is $F = C - P + 1 = 2 - 2 + 1 = 1$
- Hence the system is **univariant**

CURVE NE: freezing point curve of B

- It shows decrease in freezing point of B due to the addition of A to B
- Solid B is in equilibrium with liquid melt of A in B
- Here $C = 2$ and $P = 2$, then the reduced phase rule is $F = C - P + 1 = 2 - 2 + 1 = 1$
- Hence the system is **univariant**



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Module 2- Phase equilibria



Determination of solid-liquid equilibria

- For the determination of equilibrium conditions between solid and liquid phases – **Thermal Analysis**

Thermal analysis:

The study of the **cooling curves** of various compositions of a system during solidification

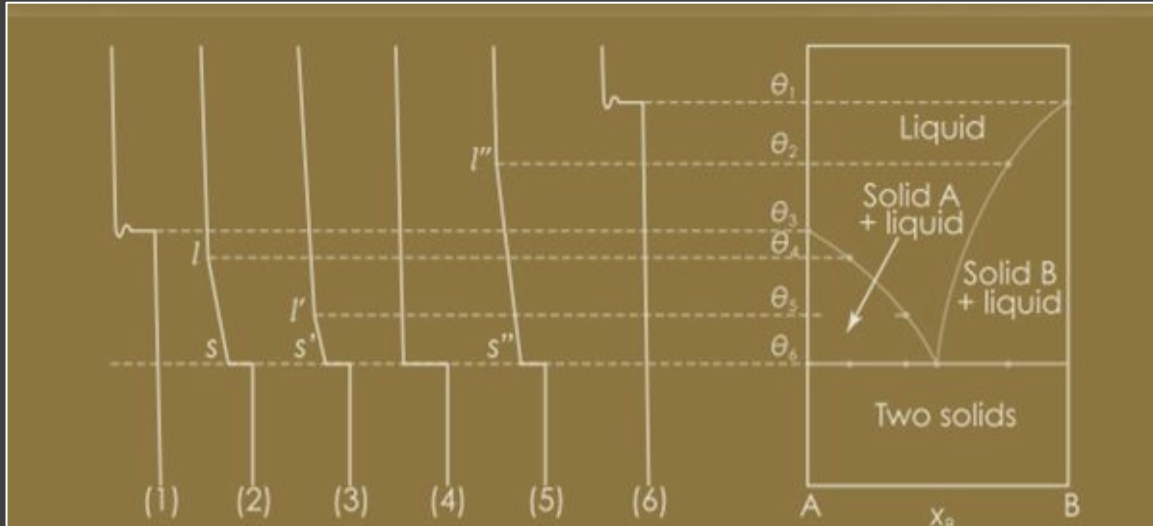
Cooling curves:

- Temperature versus time
- **Freezing point** and **eutectic point** can be determined from the cooling curves

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Module 2- Phase equilibria

Construction of phase diagram using cooling curves



Source: <http://www.mchmultimedia.com/PhysicalChemistry-help/clientstories/study-tips/digging-into-phase-diagrams-cooling-curves.html>

For pure solid: Initially the rate of cooling is continuous from 'a' till the point 'b' where solid begins to appear. Then the temperature remains constant until the liquid is fully solidified and solidification completes at the point 'c'.

For a mixture of solids: When crystallisation of one of the components starts, cooling curve exhibits a break. The temperature decreases continuously until the eutectic point is reached. Now the temperature remains constant, till the completion of solidification.



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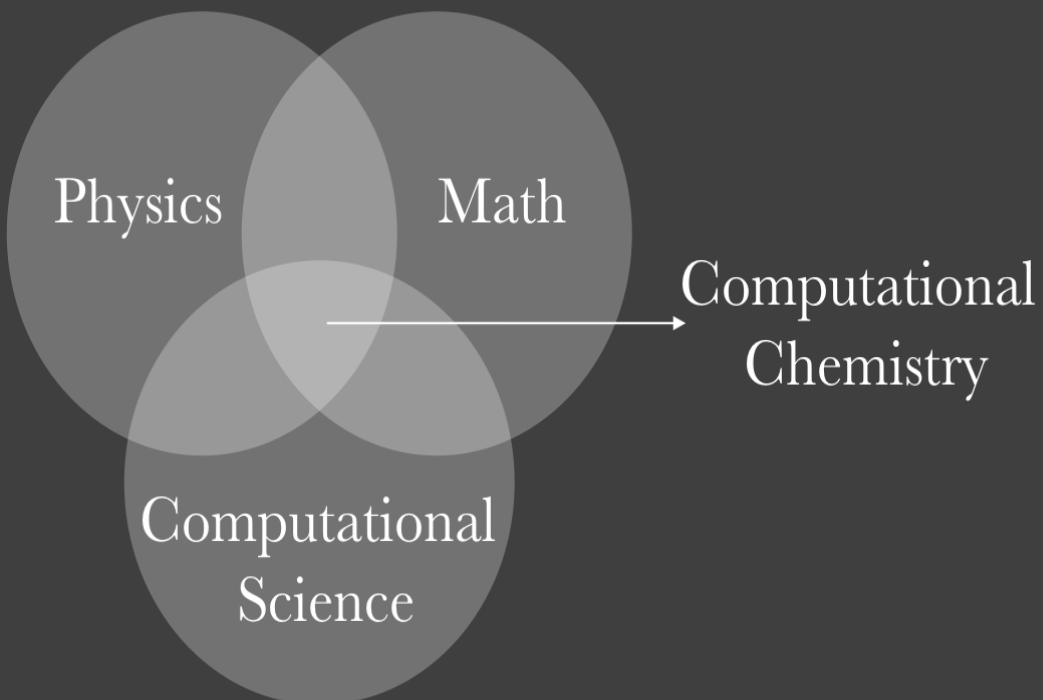
Module I- COMPUTATIONAL CHEMISTRY



- INTRODUCTION
- COMPUTATIONAL METHODS
- APPLICATIONS

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Module I- COMPUTATIONAL CHEMISTRY



Introduction

Computational chemistry is a set of techniques for the investigating chemical problems on a computer rather than using chemicals.

It uses the results of theoretical chemistry incorporated into efficient computer programs to calculate the properties of a molecule.

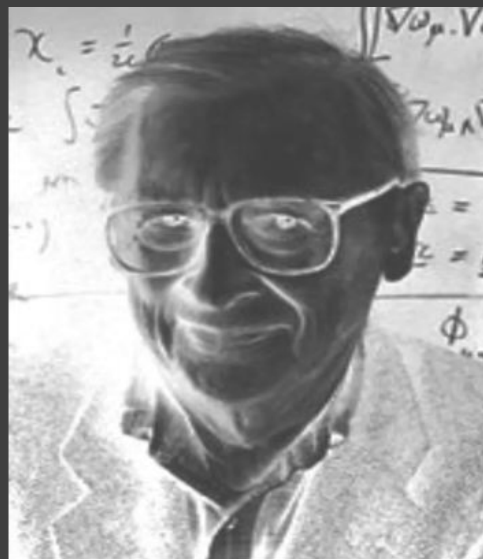
The first theoretical investigation was done by Walter Heitler and Fritz London in 1927

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Walter Kohn



John A. Pople

1998

Walter Kohn : For the development of density functional theory.

John A. Pople : For the development of computational methods in quantum chemistry.

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Module I- COMPUTATIONAL CHEMISTRY



Martin Karplus,



Michael Levitt



Arie Warshel

2013

For the development of computer based methods to model complex systems.

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Objective of computational chemistry:

To solve chemistry problems by simulating chemical systems (molecular, biological, materials) to provide reliable, accurate and comprehensive information at an atomic level.

Advantages of computational chemistry:

- Calculations are easy to perform than carrying experiments.
- Calculations are less costly, whereas experiments are becoming more expensive
- Calculations are safe than performing experiments.

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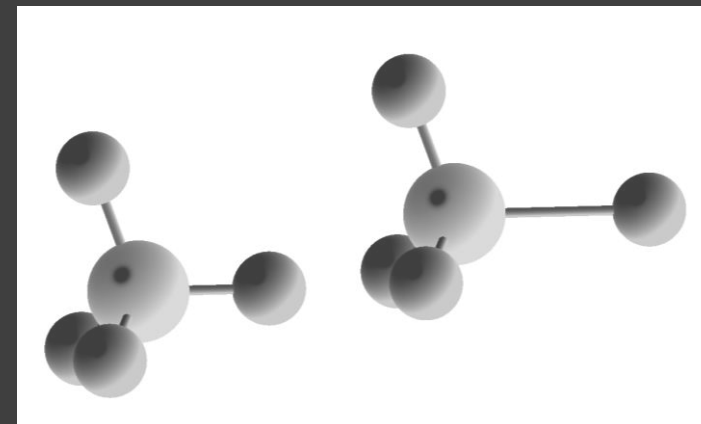
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Scope of computational modeling:

Molecular Properties:

Computational modeling can be used to accurately predict the physical and chemical properties of molecules, such as

- Bond lengths, Bond angles and HOMO/LUMO
- Can predict the spectra of UV-Vis, IR and NMR
- Thermodynamic and kinetic properties
- Electronic structure and mechanical properties



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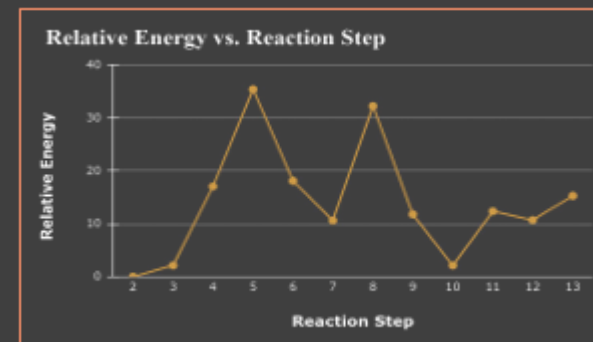
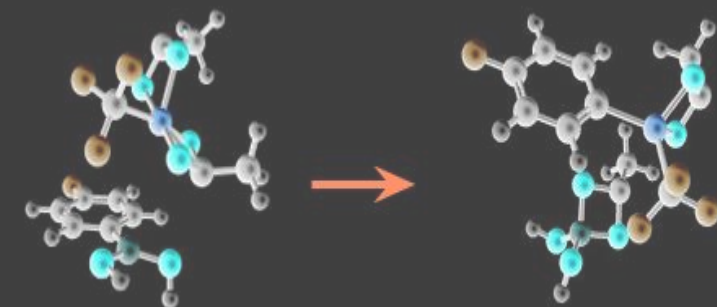
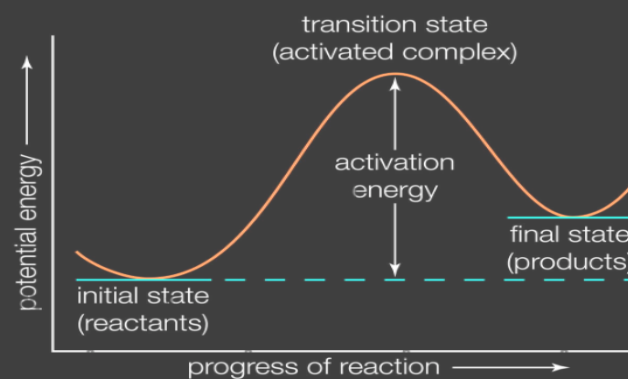
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Reaction mechanism:

To know the underlying reaction mechanism and the kinetics of a reaction, computational chemistry plays a vital role.

Material design:

Computational modeling enables the rational design of new materials with desired properties such as high electrical conductivity, thermal stability etc. This leads to the development of advanced materials for energy production and storage applications, electronics and much more.

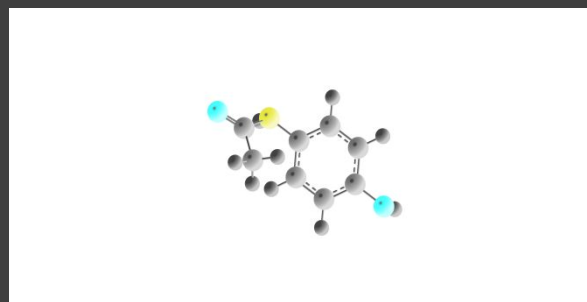


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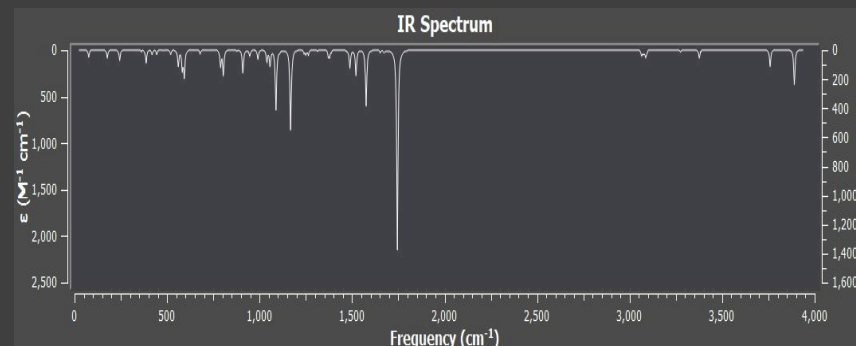
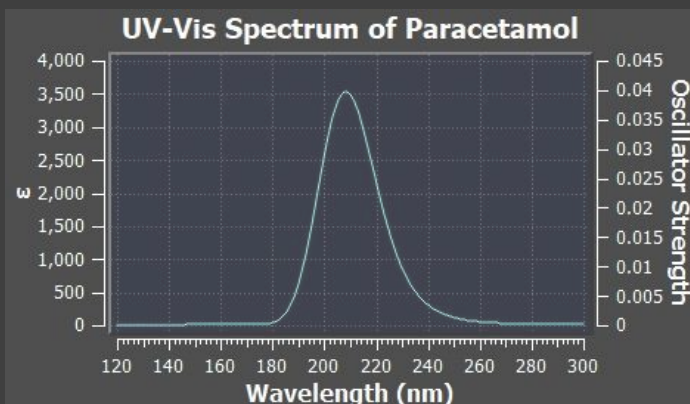
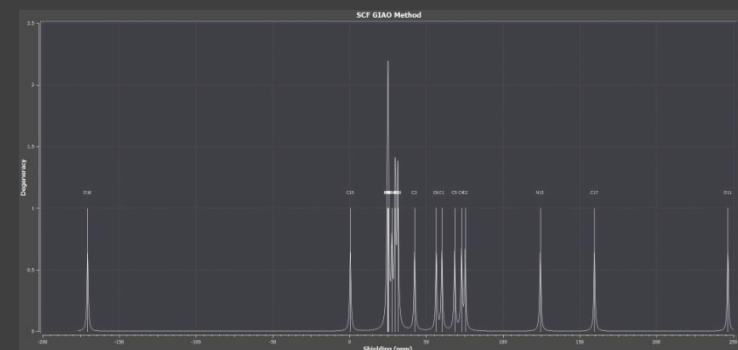
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Drug discovery:

Computational chemistry plays a pivotal role in design and screening of potential drug candidates by simulating the interactions between the drug molecules and biological targets.



Paracetamol



All these spectra are generated using Gaussian 16



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Computational methods:

There are two main methods depending on the starting point theory:

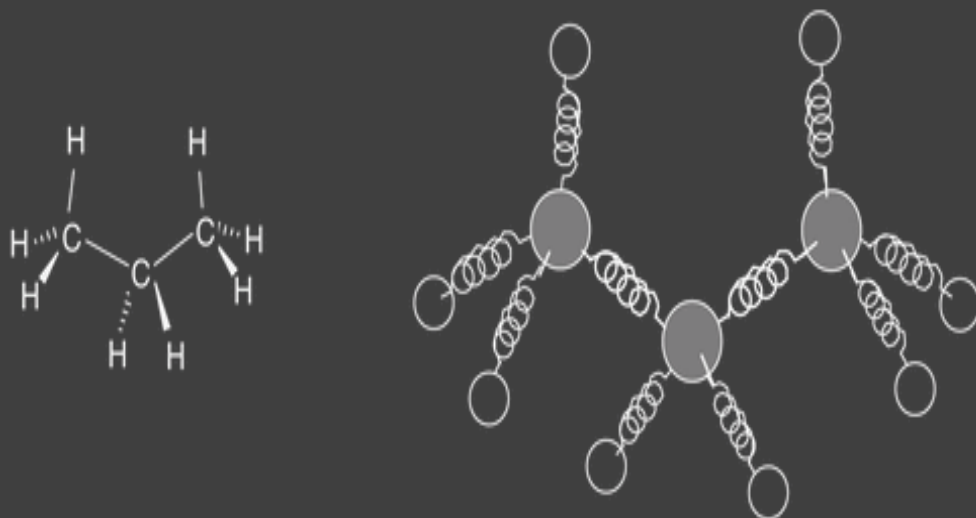
Classical method:	Quantum chemistry method :
<ul style="list-style-type: none">• These use Newton mechanics to model molecular system.• Atom – Sphere, Bonds – Springs and Electrons are ignored.• Total potential energy of a molecule is given by sum of all the energies of attractive and repulsive forces between atom in structure.	<ul style="list-style-type: none">• These use quantum mechanics to model the molecular system.• It is based on arrangement of electrons in molecules and interaction of these electrons with electron and nuclei of another molecule.• We consider that electron and all other particle exhibits both particle and wave nature.
<ul style="list-style-type: none">i. Molecular mechanicsii. Molecular dynamics	<ul style="list-style-type: none">i. Semi empirical methods.ii. Ab initio methodsiii. Density functional theory

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Molecular mechanics:

- Molecular mechanics programs use equations based on classical physics to calculate force fields.
- It is based on the model of a molecule as a collection of balls(atoms) held together by springs(bonds).
- Its too fast like a very large molecules like steroids can be optimized in seconds and allows geometry optimization .

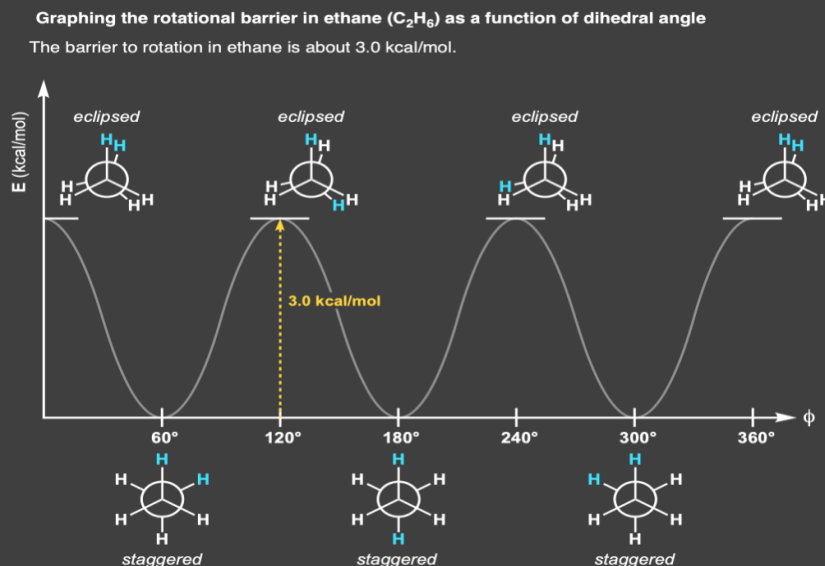


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Molecular dynamics:

- Molecular dynamics is a molecular mechanics program designed to mimic the movement of atoms within a molecule. The laws of motion to molecule is the base for it.
- Molecular dynamics can be carried out on a molecule to generate different conformation which on energy minimization.



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Semi empirical methods:

- Semi empirical calculations are based on Schrödinger equation.
- It represents a middle road between the mostly qualitative results available from molecular mechanics and the high computationally demanding quantitative results from Ab initio methods.
- Capable of calculating transition states and excited states.

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Ab initio calculations:

- Ab initio calculations are based on Schrödinger equation and it describes, among other things, how the electrons in a molecule behave.
- The wave function is a mathematical function that can be used to calculate the electrons distribution.

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Density functional theory

- DFT are like Ab initio and semi empirical calculations, based on Schrödinger equation.
- However, unlike the other two methods, DFT does not calculate a conventional wave function, but rather derives the electron distribution directly.
- Density functional calculations are usually faster than Ab initio, but slower than semi empirical method.

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Applications of computational chemistry

- Electronic structure predictions and energy minimizations.
- Finding transition structure and reaction paths and molecular docking: protein – protein, protein – ligand interactions.
- Thermochemistry : heat of reactions, energy of activation, etc.
- Calculation of many other molecular, physical and chemical properties.

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Conclusion:

- Computational chemistry plays a pivotal role in advancing our understanding of chemical systems and accelerating scientific discovery.
- Its advantages in cost-effectiveness, efficiency, safety, accessibility, versatility, and accuracy make it an indispensable tool in modern research and development.
- Computational chemistry is not a replacement for experimental studies, but plays an important role in enabling chemists to design and develop the desired chemicals/ products.

Ref. Book: Introduction to computational chemistry by Frank Jensen,
Wiley publications



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Electronic Structure Determination – Example: Ethylene (C_2H_4)

- ✓ Ethylene (C_2H_4) is the simplest alkene with a $C=C$ double bond.
- ✓ Electronic structure explains bonding, reactivity, and spectroscopy.
- ✓ Combines experimental (spectroscopy) and theoretical (MO theory, computation) approaches.

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Hybridization and Bonding

- Each carbon atom is sp^2 hybridized.
- 3 sp^2 orbitals \rightarrow 2 C–H σ bonds + 1 C–C σ bond.
- 1 unhybridized p orbital per C \rightarrow forms π bond.
- Double bond (C=C) = 1 σ bond + 1 π bond.

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Molecular Orbital (MO) Description

- σ system: strong localized framework bonds.
- π system: p-orbitals overlap to form π bonding and π^* antibonding orbitals.
- HOMO = π orbital, LUMO = π^* orbital.
- Basis for chemical reactivity of alkenes.

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Computational Determination

Steps:

1. Define geometry of C_2H_4 .
2. Select Basis set (Mathematical functions).
3. Apply Method \rightarrow orbital energies & density.
4. Solve Equations \rightarrow Get wave function/Electron Density
5. Visualize Electronic Structure \rightarrow Orbital diagrams, density maps, HOMO and LUMO orbitals.

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Application in Spectroscopy

- Photoelectron Spectroscopy (PES): measures σ and π orbital energies.
- UV–Vis: $\pi \rightarrow \pi^*$ transition ($\sim 165\text{--}180\text{ nm}$)
- IR: C=C stretch at $\sim 1650\text{ cm}^{-1}$
- NMR: Proton shifts

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Applications

- Explains electrophilic addition reactions.
- Basis of alkene polymerization.
- Important in organic, catalytic, and photochemistry.
- Provides HOMO–LUMO insight for reactivity.

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