

Molecular spectroscopy refers to the field of looking at molecules using electromagnetic radiation. This technique is used both to detect and to manipulate and understand molecules. The information obtained from molecular spectroscopy relates to the energy levels and the shapes and charge densities of molecules. There are a few generic concepts and principles for all spectroscopy that we list below:

1. The energy of a molecule can be thought of as composed of different parts: Rotational Energy, Vibrational Energy and Electronic Energy. The energy spacing between rotational levels is smaller than that between vibrational levels which is smaller than that between Electronic levels.
2. The Electromagnetic spectrum can be thought of as divided into different regions based on the wavelength/frequency/energy of the light source used. The table below lists these energies and the transitions that are probed by these energies.
3. When light of a certain wavelength falls on a molecule, then the molecule will absorb light and go to an excited state such that the difference in energy between the ground state and the excited state is hc/λ , where λ is the wavelength of the light used. Alternatively, the molecule may emit light of a particular wavelength by going from the higher energy state to the lower energy state.

This condition is used to predict the wavelength of absorption of light.

$$hc/\lambda = \Delta E = h\nu = h\bar{\nu}$$

Where ν and $\bar{\nu}$ are frequency and wavenumber respectively

In addition to the energy and frequency criterion, there are some other conditions that are necessary in order for light to be absorbed. These refer to the symmetry of the molecule and the wavefunctions involved. They are referred to as selection rules. There are two kinds of selection rules - gross selection rules and specific selection rules for each type of transition. These rules can be developed using quantum mechanics supplemented with the quantum mechanical theory of interaction of radiation with matter.

The absorption spectrum refers to the absorption of light of different energies/wavelengths/frequencies/wavenumbers. Alternatively, there is also a possibility of stimulated emission, wherein light of a certain energy stimulates a transition of the same energy. We can think of a tunable light source which impinges on the sample and the transmitted/scattered light is collected by a detector.

Name of light	Frequency(Hz)	Motions of the molecules
Microwave	$10^9 - 10^{13}$	Rotations
Infrared	$10^{13} - 10^{14}$	Vibrations
Visible and Ultraviolet(UV-Vis)	$10^{14} - 10^{16}$	Electronic Transitions

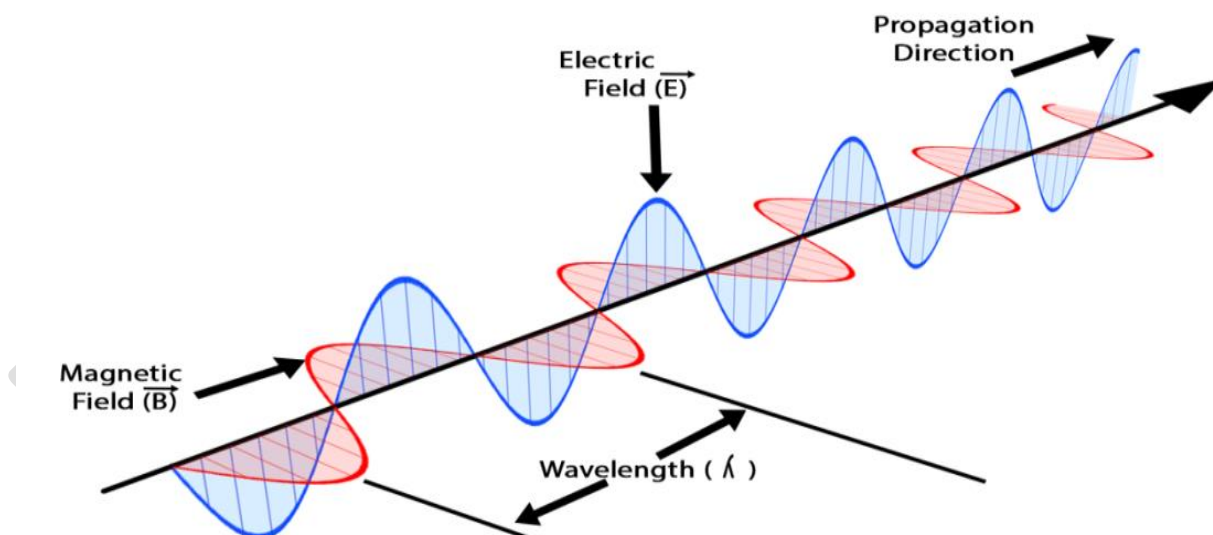
ELECTROMAGNETIC RADIATION

Spectroscopy: Spectroscopy is that branch of science which deals with the study of interaction of electromagnetic radiations with matter.

General Properties of all electromagnetic radiation: Electromagnetic radiation can travel through empty space. Most other types of waves must travel through some sort of substance. For example, sound waves need either a gas, solid, or liquid to pass through in order to be heard. The speed of light is always a constant. (Speed of light : $2.99792458 \times 10^8 \text{ m s}^{-1}$). Wavelengths are measured between the distances of either crests or troughs. It is usually characterized by the Greek symbol λ . The term electromagnetic radiation represents the radiant energy emitted from any source in the form of light, heat etc. Some important characteristics of these electromagnetic radiations are given below:

- I. 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.
- II. These waves are associated with electric and magnetic fields oscillating perpendicular to each other and also perpendicular to the direction of propagation.
- III. All electromagnetic radiations travel with the velocity of light.

Electromagnetic Wave

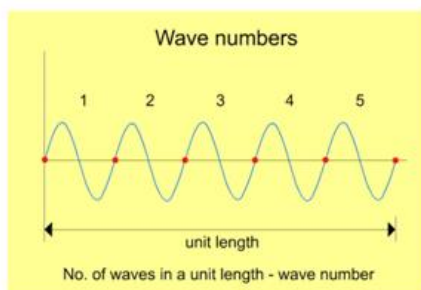
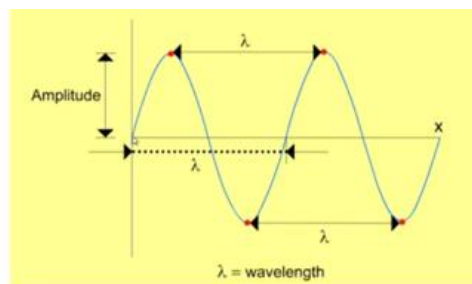
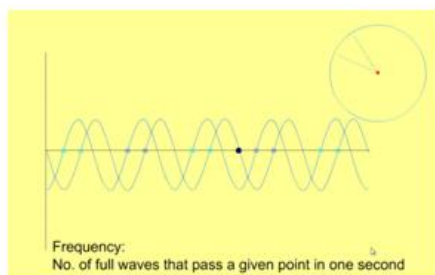


Energy of electromagnetic radiation is given by $E = h\nu$ where E is energy, h is Planck's constant, ($h = 6.625 \times 10^{-34} \text{ Js}$), and ν is frequency

Wavelength is related to frequency by $c = \lambda\nu$ Where, c is the speed of light, λ is wavelength, and ν is frequency. Wave number is related to wavelength by

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

since $\bar{\nu} = \frac{\nu}{c}$ Therefore, $E = hc\bar{\nu}$

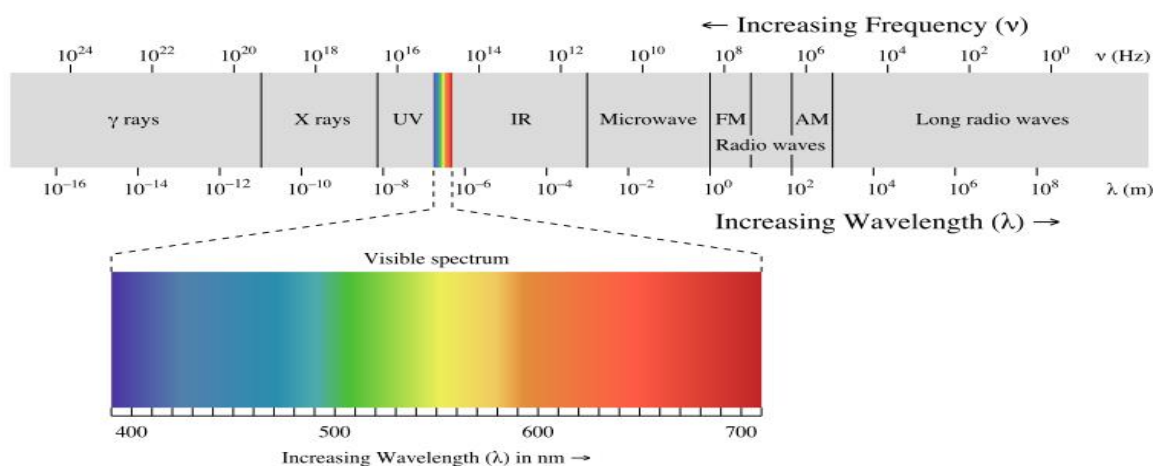


Frequency ν : unit: number per unit time t^{-1} .
 $1 \text{ s}^{-1} = 1 \text{ Hertz}$.

Wavelength λ : unit: length. meter or m

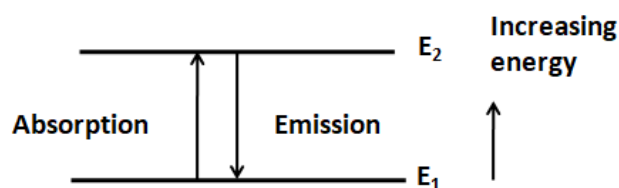
Wave number $\bar{\nu}$: unit: number per unit length m^{-1} .
 $c \rightarrow \text{speed of light in vacuum}$.

Electromagnetic spectrum:



QUANTISATION OF ENERGY:

- The energy levels are quantised.
- The frequency of light absorbed when there is a transition between two energy levels is the *difference* in energy between the two energy levels.
- When the molecule absorbs energy and moves from lower energy level to higher energy level absorption spectrum is observed.
- Similarly emission spectrum arises when molecule comes from higher energy level to lower energy level.



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

Difference between atomic spectra and molecular spectra

S.No.	Atomic spectra	Molecular spectra
1	The outer most electrons occupy valence the atomic orbital's and have its energy levels [K, L, M, N]	The outer most electrons occupy s, π or n electronic energy levels in ground state.
2	Upon excitation electrons are promoted to the higher atomic energy levels.	Upon excitation electrons are raised to π , π^* or σ , σ^* molecular orbital's.
3	Since there are no bonds there are no vibrational or rotational energy levels in either ground or excited state.	Since there are bonds, there are vibrational and rotational energy levels in both the ground and excited states.
4	The spectra are line spectra.	The spectra are band spectra due to the presence very close unresolved vibrational and rotational energy levels in the excited state.

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

Raman Spectroscopy

Raman spectroscopy is a vibrational spectroscopic technique used to study molecular vibrations, rotational, and other low-frequency modes. It is based on the inelastic scattering of light (Raman effect), discovered by C.V. Raman in 1928.

Principle

When monochromatic light (usually from a laser) interacts with a molecule:

1. Most photons are elastically scattered (Rayleigh scattering, no energy change).
2. A small fraction (~ 1 in 10^6 – 10^8) undergoes inelastic scattering (Raman scattering), where photons exchange energy with molecular vibrations.

This results in a shift in wavelength (Raman shift), providing information about vibrational energy levels of the molecule.

Types of Raman Scattering

Stokes Raman Scattering

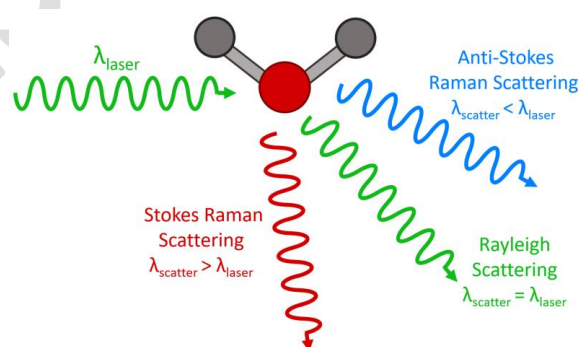
- Incident photon loses energy to the molecule → scattered photon has lower energy (longer wavelength). More intense than anti-Stokes.

Anti-Stokes Raman Scattering

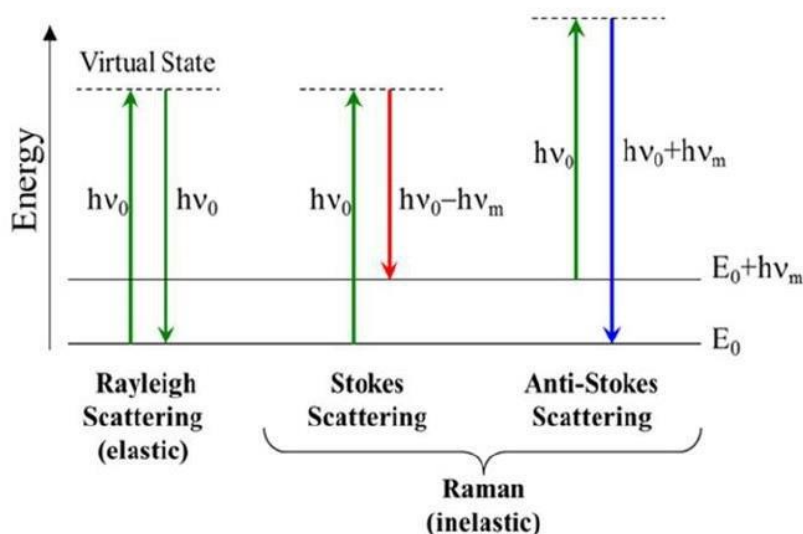
- Incident photon gains energy from the molecule (which was already in a vibrationally excited state) → scattered photon has higher energy (shorter wavelength).

Rayleigh Scattering (Elastic)

- No change in energy → scattered photon has the same wavelength as incident light.



Raman spectroscopy is a powerful tool for probing molecular vibrations and structures using the Raman effect. Its wide applications in chemistry, biology, and material science make it an essential spectroscopic technique.



1. Rayleigh Scattering (Elastic)

- The incident photon of energy $h\nu_0$ excites the molecule to a **virtual state**.
- The scattered photon has the **same energy** ($h\nu_0$) as the incident photon.
- No change in molecular vibrational energy → **elastic scattering**.

2. Stokes Raman Scattering (Inelastic)

- The incident photon excites the molecule to a virtual state.
- The molecule loses energy ($h\nu_m$) to a vibrational mode.
- The scattered photon has **lower energy** ($h\nu_0 - h\nu_m$) than the incident photon.
- This is more intense than Anti-Stokes scattering because most molecules are in the ground state.

3. Anti-Stokes Raman Scattering (Inelastic)

- The molecule is already in an **excited vibrational state**.
 - The incident photon excites it to a virtual state, and the molecule returns to the ground state.
 - The scattered photon has **higher energy** ($h\nu_0 + h\nu_m$) than the incident photon.
 - Less intense than Stokes scattering because fewer molecules are thermally excited.
- **Rayleigh scattering** → no energy change (elastic).
 - **Stokes scattering** → photon loses energy (longer wavelength).
 - **Anti-Stokes scattering** → photon gains energy (shorter wavelength).

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

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.

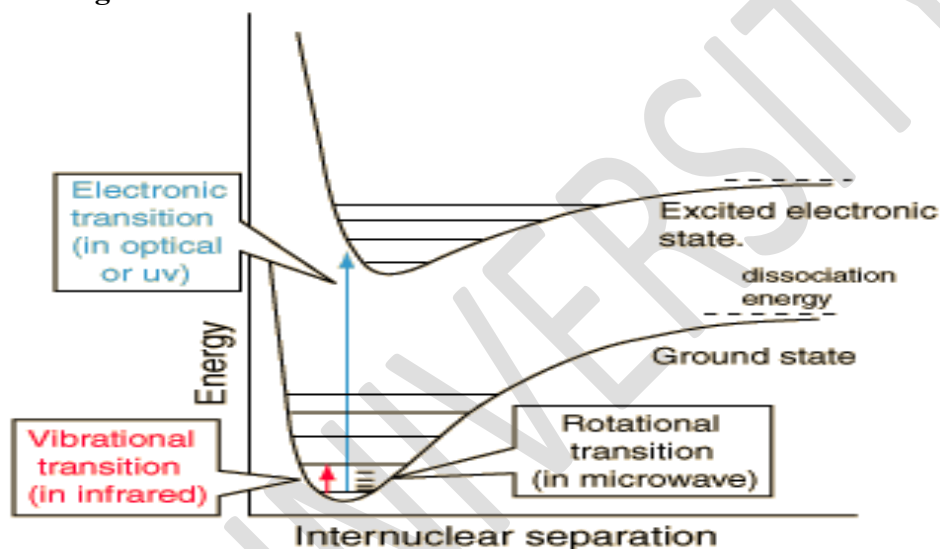
$$E = E_t + E_r + E_v + E_e$$

It is found that the translational energy is negligibly small. Hence Born-Oppenheimer approximation can be written as

$$E = E_r + E_v + E_e$$

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

Energy level diagram for a diatomic molecule:



TYPES OF MOLECULAR SPECTRA

1. Pure rotational (Microwave) spectra.
2. Vibrational rotational spectra
3. Electronic Band Spectra.
4. Raman Spectra.
5. Nuclear Magnetic Resonance (NMR)
6. Electron Spin Resonance (ESR) Spectra.

Rotational spectroscopy

Free atoms do not rotate or vibrate. For an oscillatory or a rotational motion of a pendulum, one end has to be tied or fixed to some point. In molecules such a fixed point is the center of mass. The atoms in a molecule are held together by chemical bonds. The rotational and vibrational energies are usually much smaller than the energies required breaking chemical bonds. The rotational energies correspond to the microwave region of electromagnetic radiation (3×10^{10} to 3×10^{12} Hz; energy range around 10 to 100 J/mol) and the vibrational energies are in the infrared region (3×10^{12} to 3×10^{14} Hz; energy range around 10 kJ/mol) of the electromagnetic radiation. For rigid rotors (no vibration during rotation) and harmonic oscillators (wherein there are equal displacements of atoms on either side of the centre of mass)

there are simple formulae characterizing the molecular energy levels. In real life, molecules rotate and vibrate simultaneously and high speed rotations affect vibrations and vice versa.

However, in our introductory view of spectroscopy we will simplify the picture as much as possible. We will first take up rotational spectroscopy of diatomic molecules.

A molecule undergoing rotation absorbs in the MW region.

- For a molecule to be rotationally active (MW active) the molecule has to possess a dipole moment.
- As a dipolar molecule rotates, the rotating dipole constitutes the transition dipole operator μ .
- 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.
- When the frequencies match, resonance occurs and the molecule absorbs energy and goes to the higher rotational levels and exhibits rotational spectrum.
- Molecules such as HCl and CO will show rotational spectra while H_2 , Cl_2 and CO_2 will not.

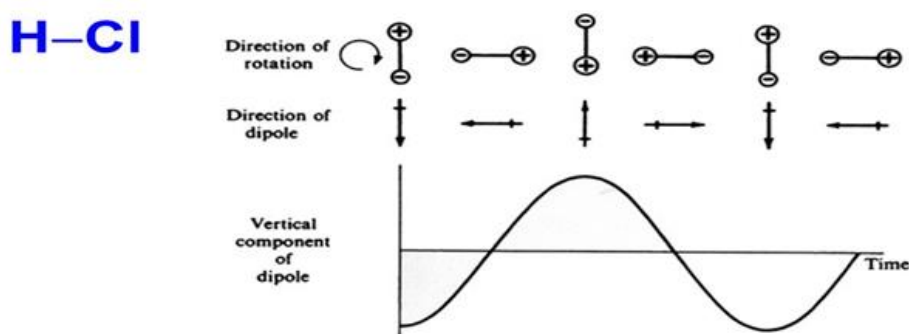
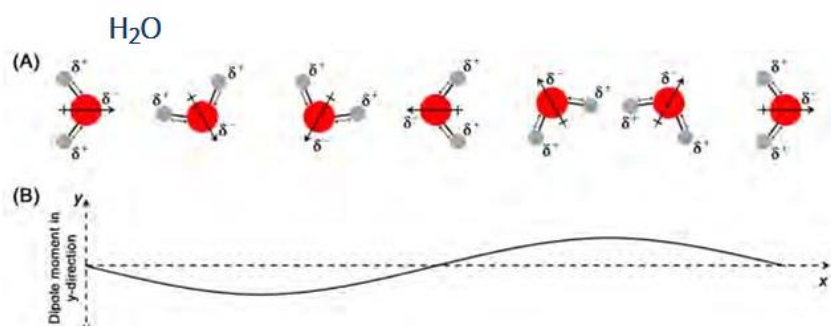
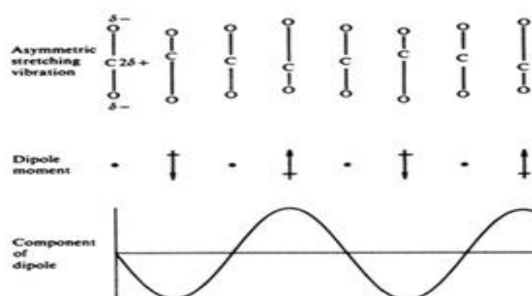
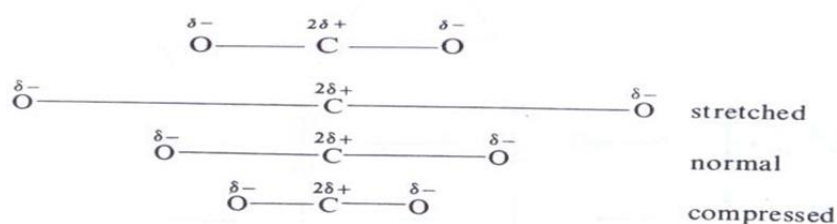


Fig. The rotation of a polar diatomic molecule, showing the fluctuation in the dipole moment measured in a particular direction

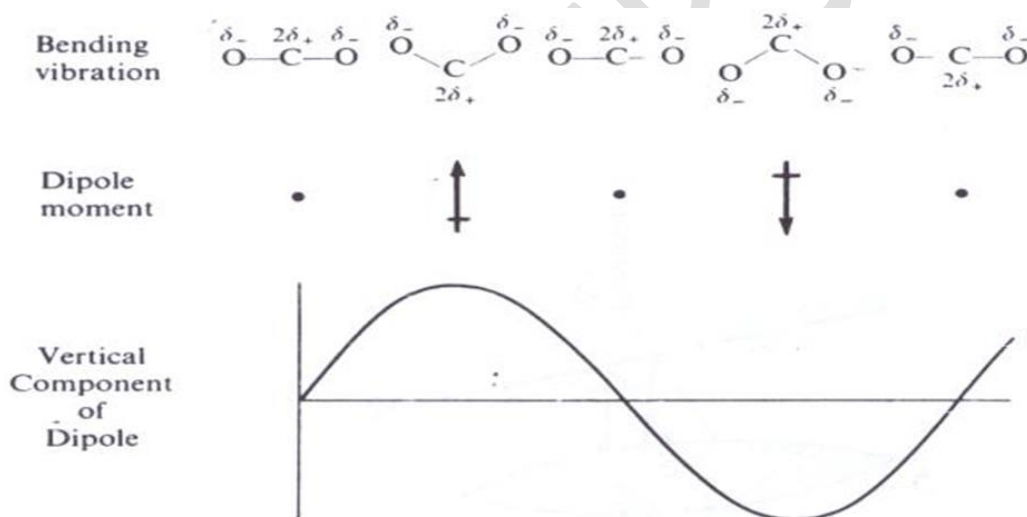
An electromagnetic wave is an oscillating electrical field and interacts only with molecules that can undergo a change in dipole moment. The oscillating dipole can be provided by the rotation of a permanent dipole like for example HCl. This type of interaction leads to microwave spectra.



Changes in the y-component of the dipole moment due to rotation of water molecule.



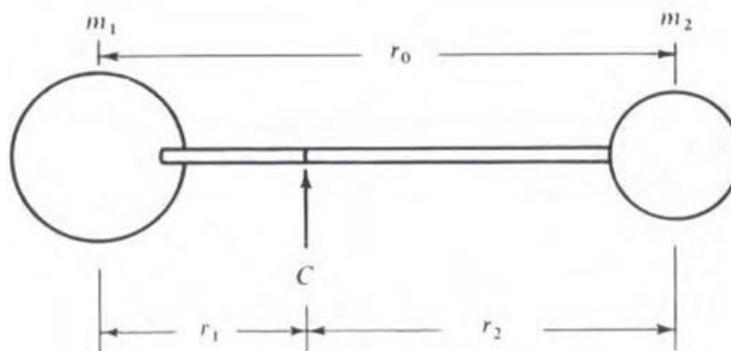
The asymmetric stretching vibration of the CO₂ molecule, showing the fluctuation in the dipole moment.



The bending motion of the carbon dioxide molecule and its associated dipole fluctuation.

In the above diagrams, one bond stretches while other is compressed and vice versa. As the figure shows, there is a periodic alteration in the dipole moment, and the vibration is infrared active. Further vibration is allowed to this molecule is known as the bending mode is also infrared active. In both the cases during motions center of gravity does not move.

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



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

The two independent rotations of this molecule are with respect to the two axes which pass through C and are perpendicular to the “bond length” r . The rotation with respect to the bond axis is possible only for “classical” objects with large masses. For quantum objects, a “rotation” with respect to the molecular axis does not correspond to any change in the molecule as the new configuration is indistinguishable from the old one. The center of mass is defined by equating the moments on both segments of the molecular axis.

The center of mass is defined by equating the moments on both segments of the molecular axis

$$m_1 r_1 = m_2 r_2$$

The moment of inertia about C is defined by:

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

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

therefore,

$$\begin{aligned} r_1 &= \frac{m_2 r_0}{m_1 + m_2} \quad \text{and} \quad r_2 = \frac{m_1 r_0}{m_1 + m_2} \\ I &= \frac{m_1 m_2}{m_1 + m_2} r_0^2 = \mu r_0^2 \end{aligned}$$

where we have written $\mu = m_1 m_2 / (m_1 + m_2)$, and μ is called the *reduced mass* of the system.

The rotation of a diatomic is equivalent to a “rotation” of a mass μ at a distance of r from the origin C. The kinetic energy of this rotational motion is $K.E. = L^2 / 2I$ where L is the angular momentum, $I\omega$ where ω is the angular (rotational) velocity in radians/sec.

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

Solving the Schrodinger equation for a rigid rotor shows that angular momentum is quantised and is given by, $L = \sqrt{J(J+1)}$ where J is the rotational quantum number. The quantity J which can take integral values from zero upwards $J=0,1,2,3,\dots$. Hence the rotational energy levels are quantised and given by the expression,

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

$h = \text{Plancks constant} = 6.626 \times 10^{-34} \text{ J}$ and I is moment of inertia

The energy differences between two rotational levels are usually expressed in cm^{-1} . The wave number corresponding to a given ΔE is given by $\nu = \Delta E / hc, \text{ cm}^{-1}$. The energy levels in cm^{-1} are therefore

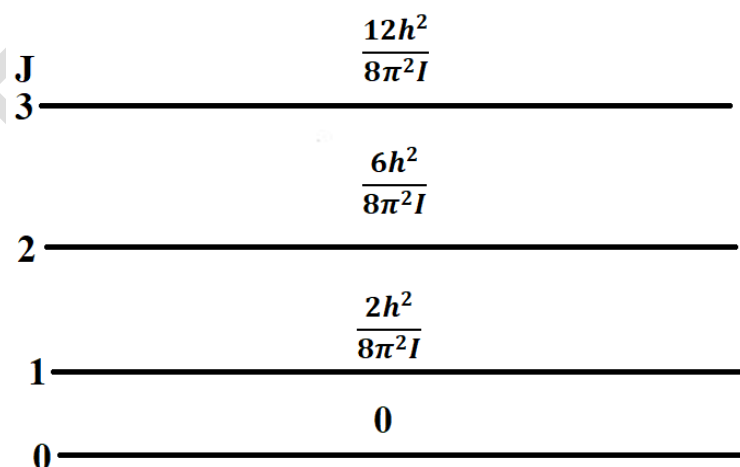
$$\epsilon_J = \frac{\Delta E_J}{hc} = BJ(J+1)$$

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

The selection rule for rotational transitions for a rigid rotor is, $\Delta J = \pm 1$.

For rotational transition of molecule from level J to J+1 the energy absorbed is given by (in cm^{-1}),

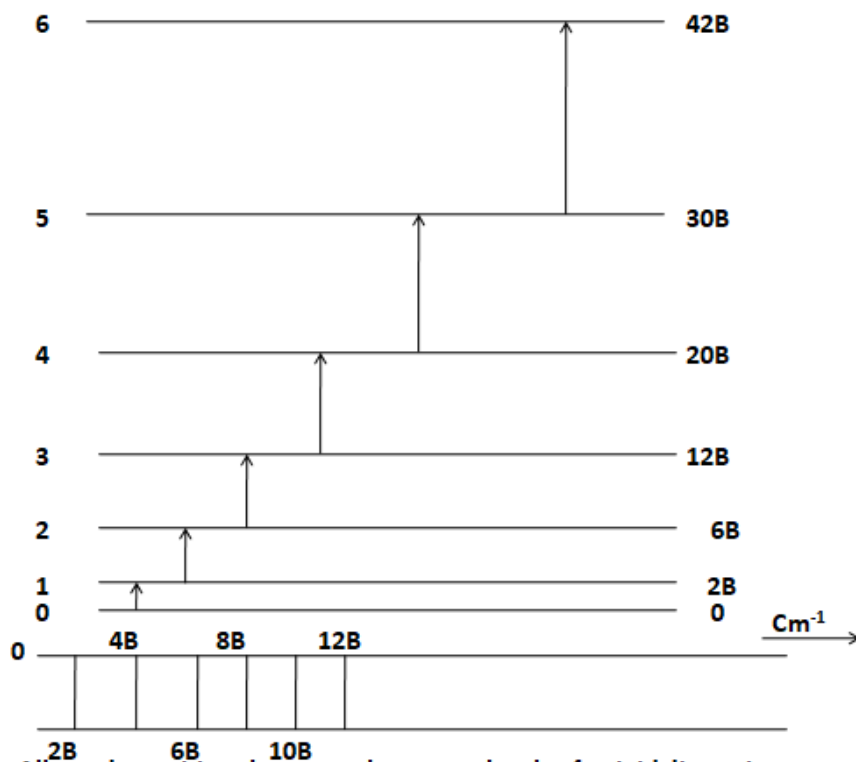
$$\Delta \epsilon_{J \rightarrow J+1} = \bar{\nu} = 2B(J+1) \text{ cm}^{-1}$$



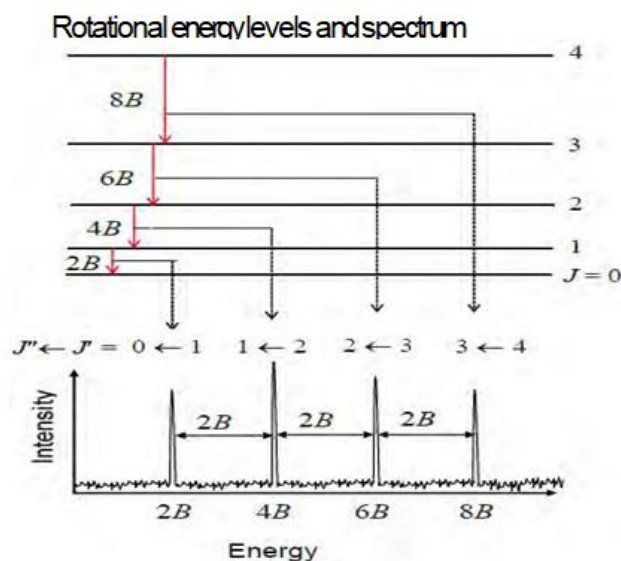
Rotational energy levels of a diatomic molecule treating it as a rigid rotator



The allowed rotational energies of a rigid diatomic molecule



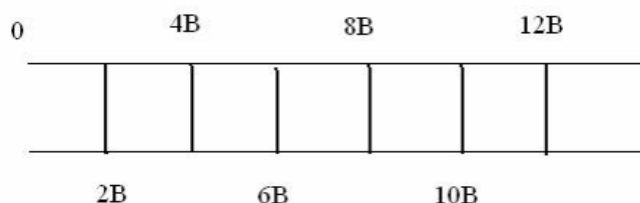
Allowed transitions between the energy levels of a rigid diatomic molecule and the spectrum which arises from them



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 $2B \text{ cm}^{-1}$

ROTATIONAL SELECTION RULES $\Delta J = \pm 1$

- A molecule must have a transitional dipole moment that is in resonance with an electromagnetic field for rotational spectroscopy to be used. *Polar* molecules have a dipole moment.
- A transitional dipole moment not equal to zero is possible.
- Only transitions are permitted in which there is an increase or decrease by unity in the rotational quantum number. It means that $J=0$ to $J=2$ transitions are not possible.
- In contrast, no rotational spectra are displayed by homonuclear diatomics; the same is true for spherical tops.
- Nevertheless, certain states of a such molecules allow unexpected interactions with the electromagnetic field; i.e. some vibrations, that introduce a time-dependent dipole moment high rotational speeds that cause some distortion of an originally spherical symmetry.
- A (weak) dipole moment emerges.
- The conservation of the angular momentum is fundamental for the selection rules that allow or prohibit transitions of a linear molecule:
- In addition to this requirement, the molecule has to possess a dipole moment. As a dipolar molecule rotates, the rotating dipole constitutes the transition dipole operator μ . Molecules such as HCl and CO will show rotational spectra while H_2 , Cl_2 and CO_2 will not.



Rotational spectrum of a rigid diatomic. Values of B are in cm^{-1} . Typical values of B in cm^{-1} are 1.92118 (CO), 10.593 (HCl), 20.956 (HF), $^1\text{H}_2$ (60.864), $^2\text{H}_2$ (30.442), 1.9987 (N_2).

- Let us apply the equation to the observed microwave spectrum of the molecule to calculate its moment of inertia and hence the bond length. The first line corresponding to $J=0$ appears in the rotational spectrum of Carbon monoxide at 3.84235 cm^{-1} . $\text{C}=12.0000 \text{ amu}$, $\text{O}=15.9949 \text{ amu}$.
- Calculate the value of I and r of CO. $B = 1.92118 \text{ cm}^{-1}$.

Solution:

$$I = h/(8\pi^2 Bc) = 6.626 \times 10^{-34} / (8 \times 3.1415^2 \times 1.92118 \times 3 \times 10^{10})$$

$$= 1.45579 \times 10^{-46} \text{ kg m}^2$$

Since the value of B is in cm^{-1} , the velocity of light c is taken in cm/s . $I = \mu r^2$. The atomic mass of $\text{C} \equiv 12.0000 \text{ amu}$, $\text{O} \equiv 15.9994 \text{ amu}$. $1 \text{ amu} = 1.6604 \times 10^{-27} \text{ kg}$. The reduced mass of CO can be calculated to be $1.13836 \times 10^{-27} \text{ kg}$.

$$\text{Therefore } r^2 = I/\mu = 1.45579 \times 10^{-46} / 1.13826 \times 10^{-27} \text{ m}^2$$

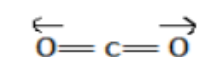
$$\text{Or } r = 1.131 \text{ \AA}$$

Vibrational spectroscopy

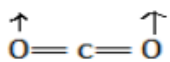
When system's molecular vibrations involve dipole moment changes, dipole-oscillators are going to form. These oscillators send EM waves to the space with certain frequency. External EM radiation with identical frequency supply system enough energy to generate a vibrational quantum jump of the system.

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 could interact with the electrical component of the electromagnetic radiation. 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 H_2O will show vibrational spectra while H_2 , Cl_2 will not.

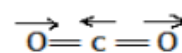
CO_2 molecule although does not possess permanent dipole moment is IR active because some of its vibrational modes are IR active: Symmetric stretch is IR inactive



ν_1 — symmetric
stretching (1330 cm^{-1})
IR inactive



ν_2 — symmetric
bending (667 cm^{-1})
IR active



ν_3 —Asymmetric
stretching (2349 cm^{-1})
IR active

The normal vibrations of CO₂ molecule:

Asymmetric Stretching Vibration of the CO₂

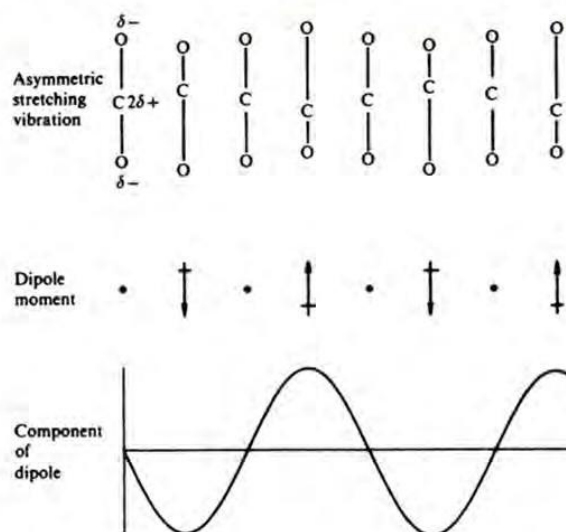
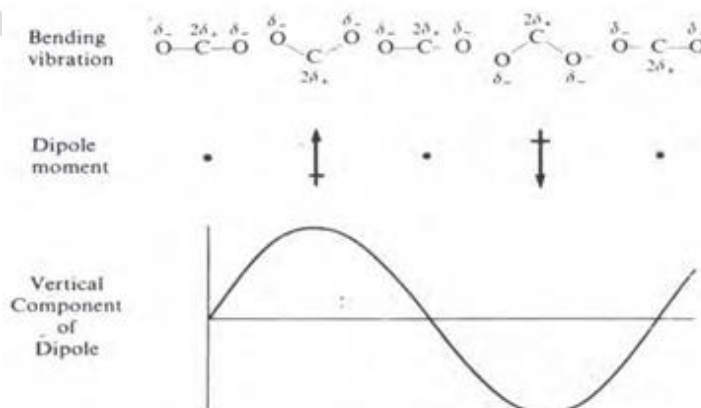
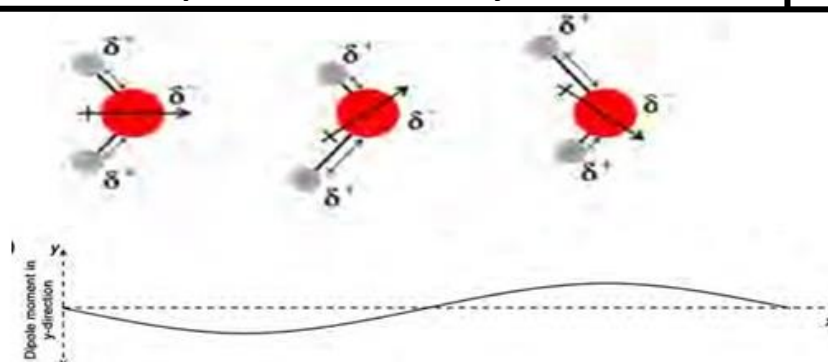


Fig. The asymmetric stretching vibration of the CO₂ molecule, showing the fluctuation in the dipole moment.

CO₂ Bending mode is IR active



H₂O



Changes in the y-component of the dipole moment due to vibration of water molecule.

Vibrational spectroscopy of diatomic molecule considered as 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.



Spring analogy of a bond vibration

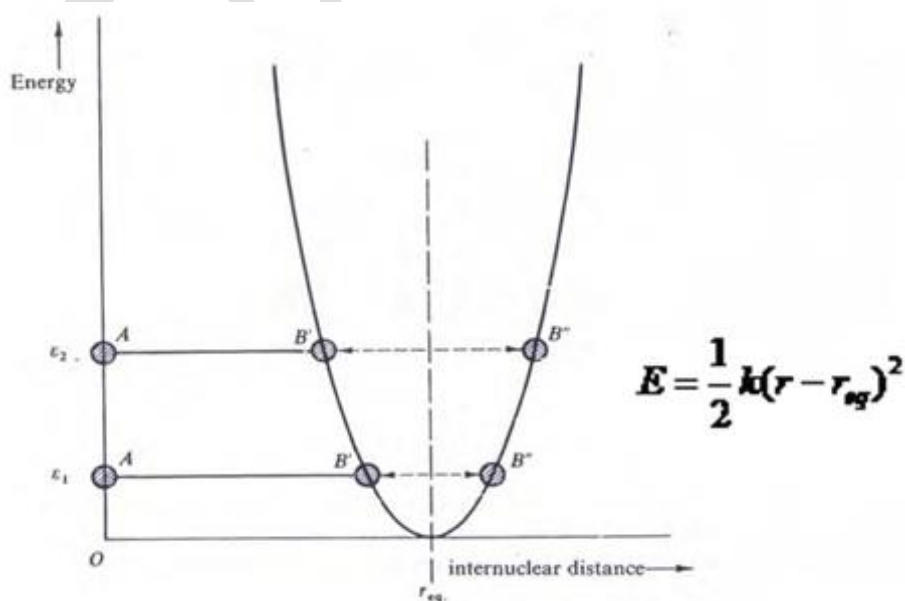
We have seen that the bonds are not static but vibrating in different ways. A vibrating bond can therefore be considered a spring with its ends tethered to two atoms as shown in the above figure and obeys Hooke's law., $F = -k(r - r_{eq})^2$

Where k is a force constant,

r is bond length,

r_{eq} is equilibrium internuclear distance.

Hence the energy curve is parabolic.



You have noticed in your earlier studies that simple pendulums or stretched strings exhibit simple harmonic motion about their equilibrium positions. Molecules also exhibit oscillatory motions. A diatomic oscillates about its equilibrium geometry. The quantized vibration energies E_v of a harmonic oscillator are $E_v = (v + \frac{1}{2}) h\nu$.

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

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

Where v = vibrational quantum number which can take up values zero upwards; $v=0, 1, 2, 3, \dots$

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

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

The energy levels will appear at, $v = 0$

$$\epsilon_0 = \frac{1}{2} \bar{\nu}_{osc} \text{ cm}^{-1}$$

This is called zero point energy $v = 1$

$$\begin{aligned} \epsilon_1 &= \frac{3}{2} \bar{\nu}_{osc} \text{ cm}^{-1} \\ v=2 \quad \epsilon_2 &= \frac{5}{2} \bar{\nu}_{osc} \text{ cm}^{-1} \end{aligned}$$

The difference between any two consecutive energy levels is equal to

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

Hence the energy levels are equally spaced. The selection rule for vibrational transition is $\Delta v = \pm 1$

Therefore transition between any two vibrational levels corresponds to absorption of frequency

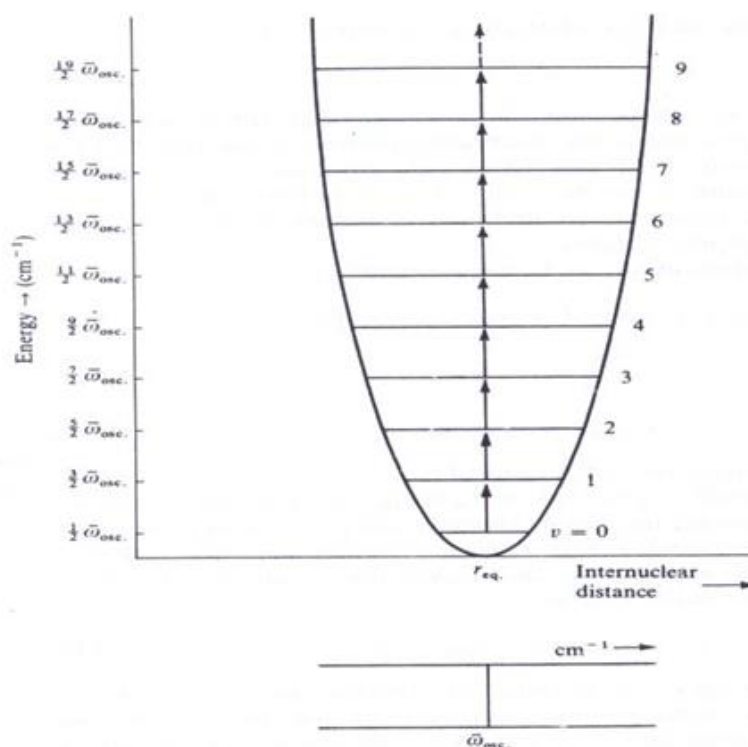
$$\bar{\nu}_{osc} \text{ cm}^{-1}$$

Hence only one line is observed in the spectrum at

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

Why only 1 line is seen in the vibration spectrum of a diatomic molecule?

All Transitions from any V to V+1 are the same. Therefore, the resulting spectrum contains only one line and is featureless.



Vibrational energy levels diagram for a diatomic molecule executing simple harmonic oscillation.

Anharmonic oscillator model

We have seen several equally spaced lines in SHM (spacing $h\nu$) corresponding to the transitions $0 \rightarrow 1$, $1 \rightarrow 2$, $2 \rightarrow 3$ and so on. The first transition will be the most intense as the state with $v = 0$ is the most populated.

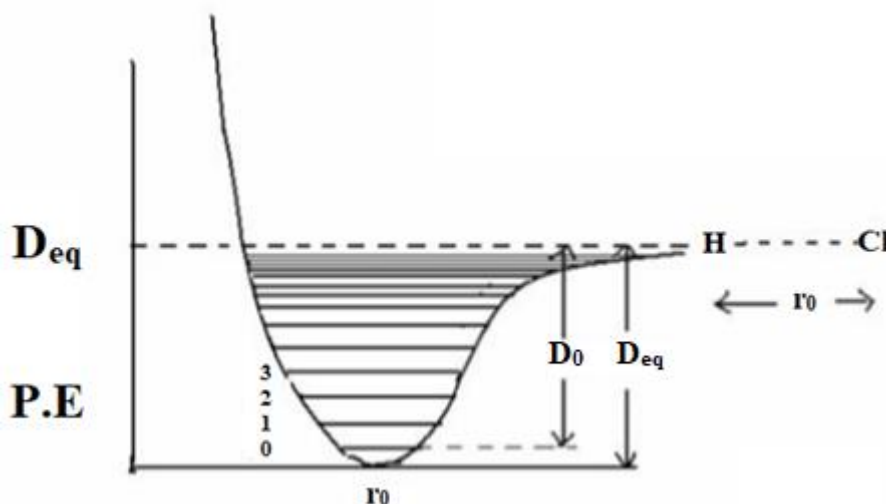
In actual diatomics, the potential is an anharmonic in actual diatomics, the potential is anharmonic because the bond when stretched beyond a point breaks and the molecule dissociates. Hence anharmonic oscillator model should be used. A good description of an anharmonic oscillator is given by the Morse function.

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

D_{eq} is the depth of the PE curve r_0 is the bond length. Solving the Schrodinger equation for anharmonic oscillator the vibrational energy levels are given by the expression;

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

Here x_e , is called the anharmonicity constant whose value is near 0.01.



The spacing between energy levels decreases for larger values of v , the vibrational quantum number

The selection rule for vibrational transition of anharmonic oscillator is $\Delta v = \pm 1, \pm 2, \pm 3, \dots$

All transitions start from $v = 0$ level because this state is most populated.

Vibrational spectrum

First line in the spectrum is called **fundamental frequency** and corresponds to transition from $v = 0$ to $v = 1$. The energy absorbed is given by,

$$\Delta \varepsilon_{1-0} = \bar{\nu}_e (1 - 2x_e) \text{ cm}^{-1}$$

Second line is called **first overtone** and corresponds to transition from $v=0$ to $v=2$. The energy absorbed is given by,

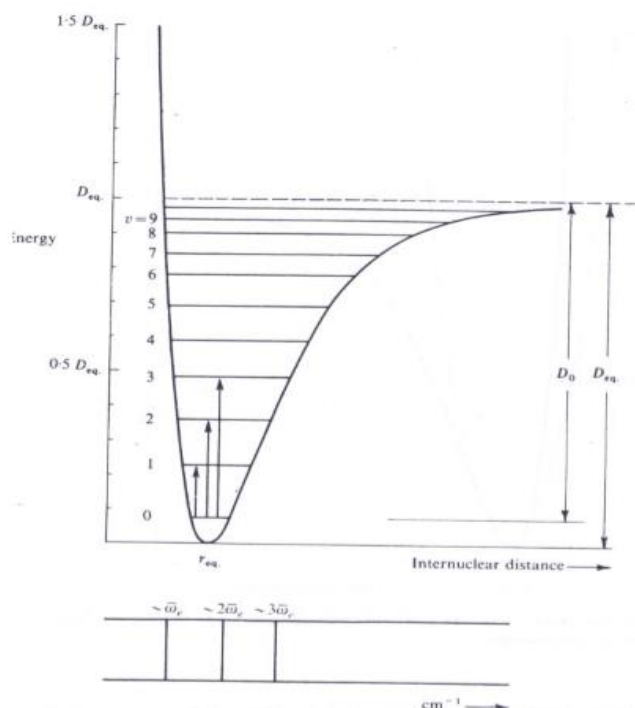
$$\Delta \varepsilon_{2-0} = 2\bar{\nu}_e (1 - 3x_e) \text{ cm}^{-1}$$

Third line is called **second overtone** and corresponds to transition from $v=0$ to $v=3$. The energy absorbed is given by,

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

The spacing between the lines in the spectrum decreases as we go to higher values of v . 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**. Ex: Energy absorbed for the transition from $v=1$ to $v=2$ is given by

$$\Delta \varepsilon_{2 \rightarrow 1} = \bar{\nu}_e (1 - 4x_e) \text{ cm}^{-1}$$



Vibrational transitions for diatomic molecule undergoing anharmonic oscillations

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

$$E = E_r + E_v + E_e$$

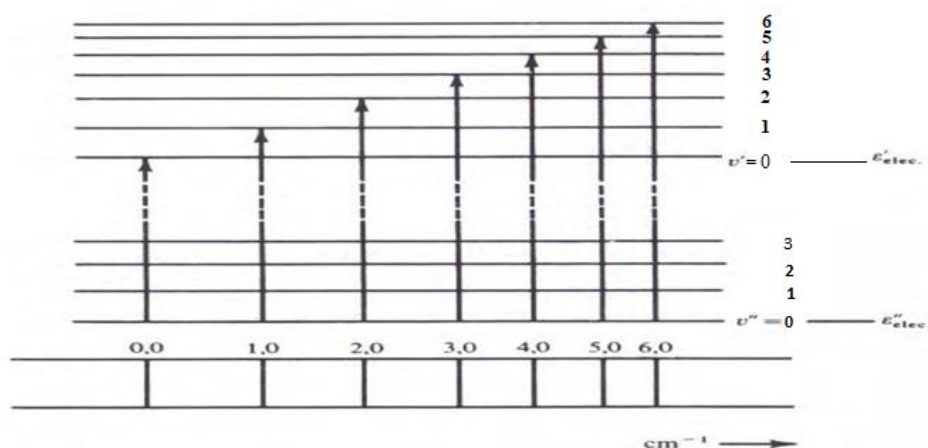
Which implies that the electronic, vibrational and rotational energies of a molecules are completely independent of each other. The change in total energy of the molecule is given by

$$\Delta E_{Total} = \Delta E_{Rot} + \Delta E_{Vib} + \Delta E_{Electronic}$$

Because $\Delta E_{Rot} \ll \Delta E_{Vib} \ll \Delta E_{Electronic}$

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 molecule can be obtained from their electronic spectra.

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

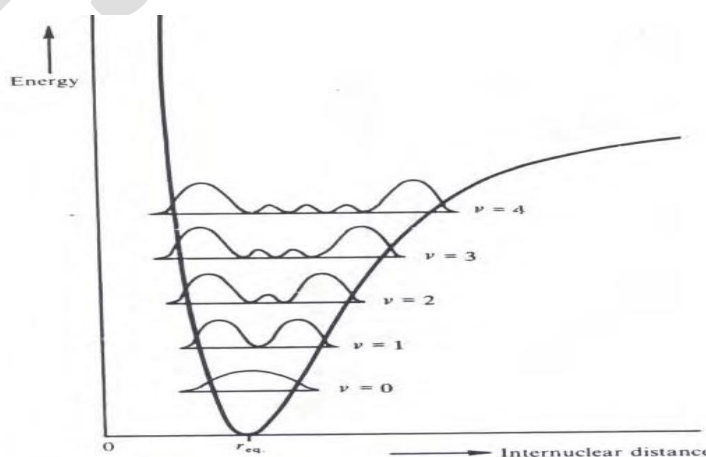


Franck-Condon principle:

All lines in the spectra are not of the same intensity though no selection rule for vibrational transitions exists. The excited state usually has longer internuclear distance because of antibonding character. The transitions arise from the centre of $v''=0$ because the maximum probability of finding the nuclei is at the centre of $v''=0$.

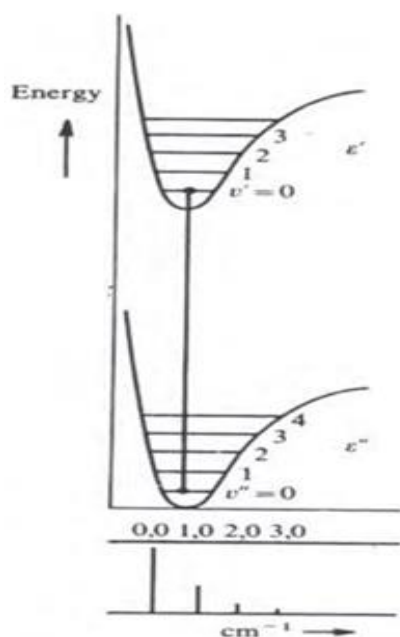
Statement of Franck Condon principle:

“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



Probability distribution for a diatomic molecule according to quantum theory

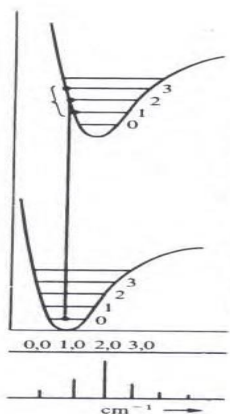
Intensity of vibrational-electronic spectra:



Three possibilities of vibrational - electronic transitions exist- (r_e'' and r_e' are internuclear distances of the ground and excited states respectively)

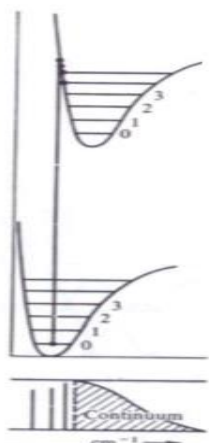
No change in internuclear distance $r_e'' = r_e'$ The spectrum shows maximum intensity for (0,0) line and intensity falls for the remaining lines as in fig.

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.

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.

- After studying molecular spectroscopy, you will be able to Calculate the bond lengths of diatomics from the value of their rotational constant.
- Outline the selection rules for rotational and vibrational spectra and rationalize the role of the molecular dipole moment in the selection rules.
- Distinguish between the energy levels of a rigid and a non rigid rotor.
- Distinguish between harmonic and anharmonic vibrations.
- Sketch qualitatively rotational-vibrational spectrum of a diatomic.
- Calculate the relative populations of rotational and vibrational energy levels.
- Identify the IR frequencies where simple functional groups absorb light.

References

- 1) nptel.ac.in
- 2) Banwell C N "Fundamentals of Molecular spectroscopy 4th edition, McGraw Hill Education (India) 2016.

Phase Equilibria

Statement:

phases are not influenced by gravity, or electrical, or magnetic forces, or by surface action but are influenced only by temperature, pressure and concentration, then the number of degrees of freedom (F) of the system is related to the number of components (C) and number of phases (P) by the following phase rule equation

$$F = C - P + 2$$

Explanation of terms:

Phase (P): A phase is defined as “a homogeneous, physically distinct and mechanically separable portion of system, which is separated from other such parts of the system by definite boundary surfaces”

Example:

1. Liquid phase: The number of liquid phases depends on the number of liquids present and their miscibility.

i) If two liquids are immiscible, they will form two separate liquid phases. Example: benzene and water

ii) If two liquids are miscible, they will form one liquid phase only. Example: alcohol and water

2. Solid phase: Each solid forms a separate phase. The number of solid phases depends on the number of solids present in it. Example: Many forms of sulphur can exist together, but these are all separate phases.

3. Gaseous phase: Since gaseous mixtures are thoroughly miscible in all proportions, it will form one phase only.

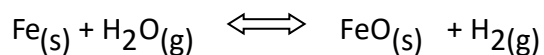
i) Example: a mixture of N_2 and H_2 forms one phase only.

ii) A solution of a substance in a solvent consists of one phase only, e.g. glucose solution.

iii) A heterogeneous mixture like: $CaCO_3 (s) \rightleftharpoons CaO (s) + CO_2 (g)$

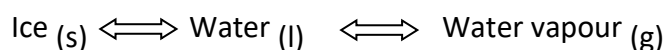
It consists of three phases (i.e., two solids and one gaseous).

iv) In the equilibrium reaction,



There are two solid phases, Fe and FeO and one gaseous phase consisting of $\text{H}_2\text{O}_{(g)}$ and $\text{H}_2_{(g)}$. Thus, three phases exist in equilibrium.

v) At freezing point, water consists of three phases:



vi) A homogeneous solid solution of a salt forms a single phase.

Example : Mohr's salt $[\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}]$ solution has a single phase.

Component (C): Component is defined as “the smallest number of independently variable constituents, by means of which the composition of each phase can be expressed in the form of a chemical equation”.

Example: i) In the water system,



The chemical component of all the three phases is H_2O and therefore it is one component system.

ii) Sulphur exists in four phases namely rhombic, monoclinic, liquid and vapour, but the chemical composition of all phases is S. Thus is a one component system.

iii) A system of saturated solution of NaCl consists of solid salt, salt solution and water vapour. The chemical composition of all the three phases can be expressed in terms of NaCl and H₂O. Therefore, it is a two-component system.

iv) In the thermal decomposition of CaCO₃,



The composition of each of the three phases can be expressed in terms of at least any two of the independent variable constituents, CaCO₃, CaO and CO₂. Suppose CaCO₃ and CaO are chosen as the two components, then the composition of different phases is represented as follows:

Phase: CaCO₃ = CaCO₃ + 0CaO

Phase: CaO = 0CaCO₃ + CaO

Phase : CO₂ = CaCO₃ – CaO

Thus, it is a two-component system.

v) In the equilibrium, Fe_(s) + H₂O_(g) → FeO_(s) + H_{2(g)}, the minimum components required to express the composition of each phase is three. Thus, it is a three-component system.

vi) In the dissociation of NH₄Cl, the following equilibrium occurs:



The system consists of two phases namely solid NH₄Cl and the gaseous mixture containing NH₃ + HCl.

When NH₃ and HCl are present in equivalent quantities the composition of both the phases can be represented by the same chemical compound NH₄Cl and hence the system will be a one component

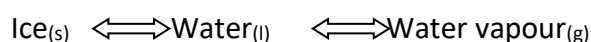
Degree of freedom:

Degree of freedom is defined as the minimum number of independent variable factors such as temperature, pressure and concentration of the phases, which must be fixed in order to define the condition of a system completely.

A system having 1,2,3 or 0 degrees of freedom is called univariant, bivariant, Trivariant and nonvariant respectively.

Example :

i) Consider the water system,



The three phases can be in equilibrium only at particular temperature and pressure.

Therefore, when all the three phases are present in equilibrium, then no conditions need to be specified. The system is therefore zero variant or invariant or has no degree of freedom.

In this system if pressure or temperature is altered, three phases will not remain in equilibrium and one of the phases disappears.

ii) Consider a system consisting of water in contact with its vapour,



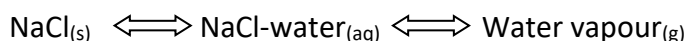
To define this system completely, we must state either the temperature or pressure. Thus, degree of freedom is one and the system is univariant.

iii) For a system consisting of water vapour phase only, we must state the values of both the temperature and pressure in order to define the system completely. Hence the system is bivariant or has two degrees of freedom.

iv) For a gaseous mixture of N_2 and H_2 , we must state both the pressure and temperature, because if pressure and temperature are fixed, the volume automatically becomes definite. Hence, for a gaseous system, two factors must be stated in order to define it completely and thus, it has two degrees of freedom or bivariant

system.

v) Consider a system consisting of



we must state either the temperature or pressure, because the saturation solubility is fixed at a particular temperature or pressure. Hence the system is univariant.

Merits of the Phase rule:

1. It is applicable to both physical and chemical equilibria.
2. It requires no information regarding molecular/micro-structure, since it is applicable to macroscopic systems.
3. It is a convenient method of classifying equilibrium states in terms of phases, components and degrees of freedom.
4. It helps us to predict the behaviour of a system, under different sets of variables.
5. It indicates that different systems with same degree of freedom behave similarly.
6. It helps in deciding whether under a given set of conditions:
 - a) various substances would exist together in equilibrium (or)
 - b) some of the substances present would be inter converted (or)
 - c) some of the substances present would be eliminated.

Limitations of Phase rule:

1. It can be applied only for system in equilibrium. Consequently, it is of little value in case of very slow equilibrium state attaining system.
2. It applies only to a single equilibrium system; and provides no information regarding any other possible equilibria in the system.
3. It requires at most care in deciding the number of phases existing in an equilibrium state, since it considers only the number of phases, rather than their amounts. Thus, even if a trace of phase is present, it accounts towards the total number of phases.
4. It conditions that all phases of the system must be present simultaneously under the identical conditions of temperature and pressure.
5. It conditions that solid and liquid phases must not be in finely-divided state; otherwise, deviations occur.

Derivation of Phase Rule:

- The phase rule was given by Williard Gibbs in 1876 is based on the principles of thermodynamics. It is a mathematical equation that relates the number of degrees of freedom, components and phases.
- It describe the mathematical relationship for determining the stability of the phases present in material at equilibrium condition.
- Degrees of the freedom of the system=Total number of independent variables.
- Mathematically it is stated as “for a heterogeneous system in equilibrium, the number of phases (P) plus the number of degrees of freedom (F) is equal to the number of components plus 2”
- We know that in a given phase involving C components at temperature T and pressure P, the chemical potential is determined by the molar fraction of the component present.
- However, for each phase the sum of mole fraction of all components is unity, implying that at most C-1 mole fraction can be independent. Therefore, for P phases, there are at P(C-1) independently variable mole fraction.

$$x_1^\alpha + x_2^\alpha + x_3^\alpha + \cdots + x_c^\alpha = 1$$

$$x_1^\beta + x_2^\beta + x_3^\beta + \cdots + x_c^\beta = 1$$

$$x_1^\gamma + x_2^\gamma + x_3^\gamma + \cdots + x_c^\gamma = 1$$

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$$x_1^P + x_2^P + x_3^P + \cdots + x_c^P = 1$$

- However, for each phase the sum of mole fraction of all components is unity, implying that at most C-1 mole fraction can be independent. Therefore, for P phases, there are at P(C-1) independently variable mole fraction.

Where μ = Chemical potential

- For the first component chemical potential must be same in every phase

$$\mu_1^\alpha = \mu_1^\beta = \mu_1^\gamma = \mu_1^P = P - 1$$

- For the second component chemical potential must be same in every phase

$$\mu_2^\alpha = \mu_2^\beta = \mu_2^\gamma = \mu_2^P = P - 1$$

- For the third component chemical potential must be same in every phase

$$\mu_3^\alpha = \mu_3^\beta = \mu_3^\gamma = \mu_3^P = P - 1$$

- For the Cth component chemical potential must be same in every phase

$$\mu_c^\alpha = \mu_c^\beta = \mu_c^\gamma = \mu_c^P = P - 1$$

- Therefore, for C components the total number of equations relating chemical potentials = C(P-1)

- In addition, the temperature and pressure are two intensive variables of the system
- Hence, the total number of independent variable properties of the system = P(C-1) + 2
- However, these P(C-1) + 2 variables are related to each other through C(P-1) equations

Total number of independent intensive variables

= Total Number of variables – Total number of equations

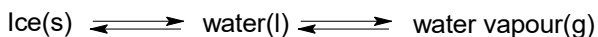
$$F = P(C - 1) + 2 - C(P - 1)$$

$$F = C - P + 2$$

This the Gibbs phase rule

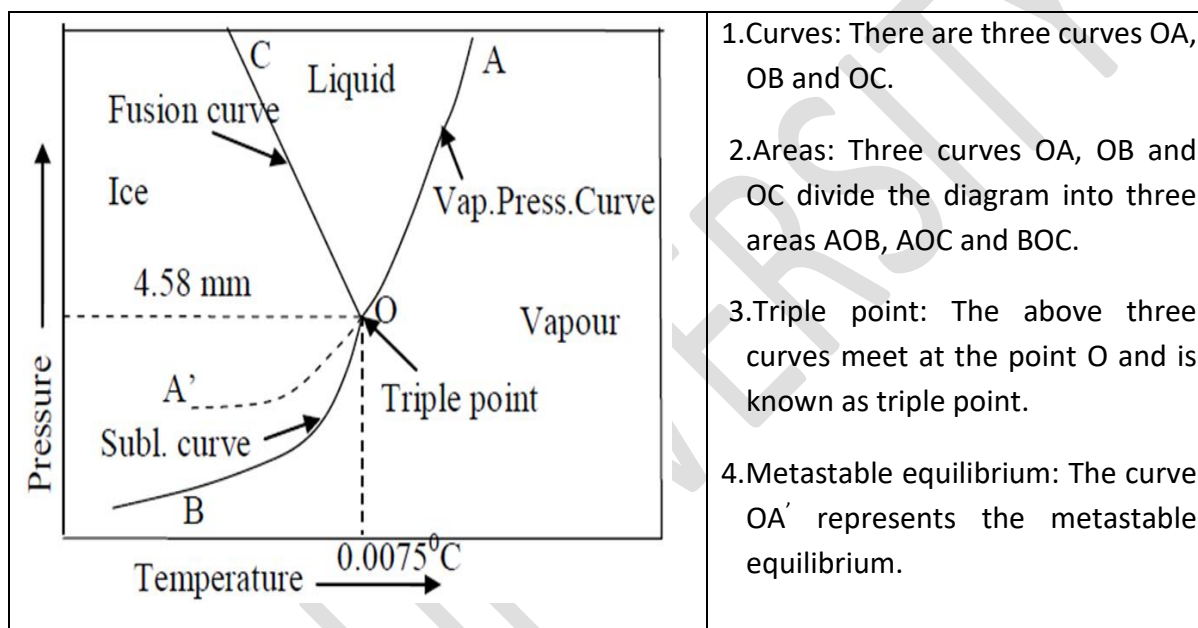
Applications of Phase rule to one component system (water system):

The water system is a one component system



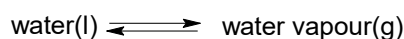
Since water exists in three possible phases such as solid, liquid and vapour, there are three forms of equilibria:

- Liquid – vapour
- solid - vapour
- solid - liquid
- Each equilibrium involves two phases. The nature of these phases which exist in equilibrium at any time depends on the conditions of temperature and pressure.



1) Curve OA

- The curve OA is called vaporization curve; it represents the equilibrium between water and vapour. At any point on the curve the following equilibrium will exist.



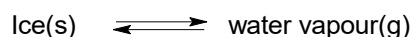
- The degree of freedom of the system is one, i.e. univariant. Thus, applying phase rule equation,

$$F = C - P + 2 = 1 - 2 + 2; F = 1$$

- This equilibrium (i.e., line OA) will extend up to the critical temperature (374°C). Beyond the critical temperature the equilibrium will disappear only water vapour will exist.

2) Curve OB

- The curve OB is called sublimation curve of ice; it represents the equilibrium between ice and vapour. At any point on the curve the following equilibrium will exist.



- The degree of freedom of the system is one, i.e., univariant.
- This is predicted by the phase rule.
 $F = C - P + 2$; $F = 1 - 2 + 2$; $F = 1$
- This equilibrium line will extend upto the absolute zero (– 273°C) where no vapour can be present and only ice will exist.

3) Curve OC

- The curve OC is called melting point curve of ice, it represents the equilibrium between ice and water. At any point on the curve the following equilibrium will exist.



- The curve OC is slightly inclined towards pressure axis. This shows that melting point of ice decreases with increase of pressure.
- The degree of freedom of the system is one. i.e., univariant.

4) Triple point (Point 'O')

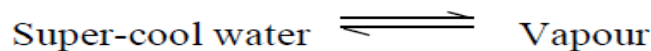
- At triple point all the three phases namely ice, water and vapour coexist. Thus, the value of P is 3. Applying phase rule equation, the degree of freedom at this point is zero. It means that three phases can coexist in equilibrium only at a definite temperature and pressure. The values are 0.0075°C and 4.58 mm respectively.

$$F = C - P + 2; F = 1 - 3 + 2 = 0$$

- At this triple point, neither pressure nor temperature can be altered even slightly without causing the disappearance of one of the phases. The triple point is not the same as the ordinary melting point of ice (i.e, 0°C). Its value has been increased due to the fact that 0°C is the melting point of ice at 760mm of mercury and a decrease of 4.58 mm will rise the melting point to 0.0075°C.

5) Curve OB (Metastable equilibrium)

- The curve OB is called vapour pressure curve of the super-cool water or metastable equilibrium.
- Where the following equilibrium will exist.



- Sometimes water can be cooled below 0°C without the formation of ice, this water is called super-cooled water. Super-cooled water is unstable and it can be converted into solid by 'seeding' or by slight disturbance.

6) Areas

- Area AOC, BOC, AOB represents water ice and vapour respectively. In order to define the system at any point in the areas, it is essential to specify both temperature and pressure. The degree of freedom of the system is two. i.e., Bivariant.
- This is predicted by the phase rule

$$F = C - P + 2; F = 1 - 1 + 2; F = 2 \quad \frac{dP}{dT} = \frac{\Delta H}{T\Delta V}$$

Clapeyron-Clausius Equation

For fusion of ice ΔH is +ve ΔV is -ve [ΔH Enthalpy of fusion is endothermic]

$$\frac{dP}{dT} = -ve$$

The change in volume is -ve when ice is converting into water, so ΔV is -ve, so melting curve has -ve slope.

Uses of Phase diagram

- From the phase diagram, it is possible to predict whether an eutectic alloy or a solid solution is formed on cooling a homogeneous liquid containing mixture of two metals.
- The phase diagrams are useful in understanding the properties of materials in the heterogeneous equilibrium system.
- The study of low melting eutectic alloys, used in soldering, can be carried out using phase diagrams.

Reduced phase rule or condensed phase rule:

We know the phase-rule equation,

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

Two component system

- For a two-component system, $C = 2$ and hence the above equation becomes,
- $F = 2 - P + 2 = 4 - P \dots\dots\dots (2)$
- The minimum number of phases in any system at equilibrium is one. It is clear from the equation (2), the maximum number of degrees of freedom is three.
- Thus, three variables – pressure, temperature and composition of one of the components must be specified to describe the system. This will lead to three dimensional figures which cannot be conveniently represented on a paper. To make this simple, one of the three variables is kept constant.
- In solid-liquid equilibrium of an alloy, practically there is no gaseous phase and the pressure will not have much influence. In the case of solid-liquid equilibrium, the experiments are generally carried out at constant pressure.
- Thus, the system in which only the solid and liquid phases are considered and the gas phase is ignored is called a condensed system. This reduces the degree of freedom of the system by one. The phase rule equation is then written as
 $F' = C - P + 1$

- This equation is called reduced phase rule or condensed phase rule. For a two-component system the phase rule equation is written as

$$F' = C - P + 1$$

$$= 2 - P + 1 = 3 - P \dots\dots\dots (4)$$

- The above equation is known as the reduced (condensed) form of phase rule for two component system.
- There are various types of solid-liquid equilibria of which only two of them are taken here.
- Those equilibria in which the components are completely miscible with one another in liquid state.
- They do not form any compound on solidification. They give rise to merely an intimate mixture known as eutectic.
- Some examples of this system are
 - 1) lead-silver system
 - 2) Lead-Antimony system
 - 3) Zinc-cadmium system
 - 4) Potassium iodide- water system

Classification of two component system:

The two component systems are classified into the following three types :

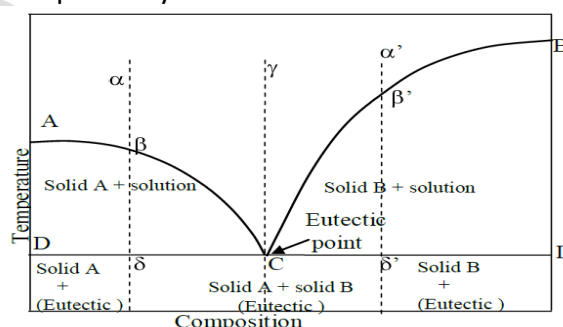
- i) Simple eutectic formation
- ii) a) Formation of compound with congruent melting point.
- b) Formation of compound with incongruent melting point.
- iii) Formation of solid solution.

i) Simple eutectic formation:

- A system with two substances which are completely miscible in the liquid state , but completely immiscible in the solid state is known as eutectic system. In this system the substances do not react chemically.
- Among the mixtures of different proportions of two substances, the mixture which has the lowest melting point is known as the eutectic mixture.
- The temperature and composition corresponding to the point eutectic point is called eutectic temperature and eutectic composition respectively.

Simple eutectic systems:

- The general phase diagram for binary alloy systems is shown in Fig. Here the pressure does not have the considerable effect. Hence, the other two variables viz, temperature and compositions are taken into account.
- Components A and B.
- When small quantities of B are added to A gradually, the melting point of A falls along the curve AC. In the same way when small quantities of A are added to B gradually, the melting point B falls along the curve BC. Hence, AC and BC are the freezing point curves of A and B respectively.

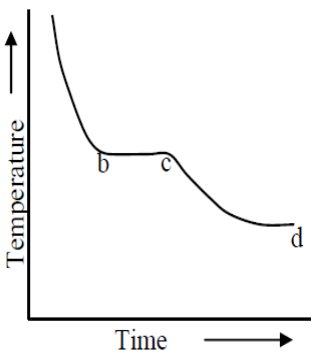
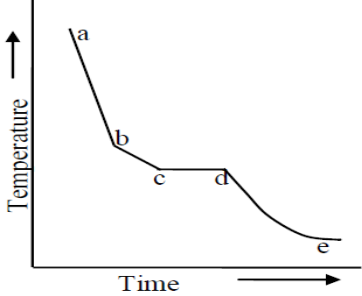


- The curves AC and BC meet at the point C. At this point the three phases solid A, solid B and their solution coexist. The degree of freedom is zero here and the system is therefore invariant. Also only at this point C, the liquid can exist at the lowest temperature. Since the mixture of components A and B of composition corresponding to the point C has the lowest melting point, the point C is called the eutectic point.

- The temperature and composition corresponding to the point C is called eutectic temperature and eutectic composition respectively.
- Consider a liquid mixture of composition represented by a point alpha cooled at constant pressure. The temperature falls without any change of composition until the point beeta on the curve AC is reached. At this temperature t_1 , the solid A will separate out. The system now consists of two phases and hence monovariant. As cooling continues, the component A keeps on separating out and the solution becomes relatively richer in B. The temperature and the solution composition both change along AC.
- Thus, at the temperature t_1 , solid A is in equilibrium with solution of composition X and at temperature t_2 , it is in equilibrium with solution of composition Y. It is clear therefore, in the area ACD, solid A is in equilibrium with solutions of varying composition given by the curve AC depending upon the temperature.
- When the temperature reaches a point delta represented by, the solid B also begins to separate out. On further cooling the system, solid A and B separate out together in constant ratio so that the composition of the solution remains constant. The temperature also remains constant for some time.
- When the liquid solution has been completely solidified and the system consists only of a mixture of solid A and B, it becomes monovariant. Further cooling will result in the fall of temperature below the line DD into the area in which only the two solids coexist as shown.
- In the same way, if the composition of liquid mixture is on the right of the eutectic point C, as represented by point “, similar series of changes will be obtained on cooling.
- In the same way, if the composition of liquid mixture is on the right of the eutectic point C, as represented by point ‘alpha’, similar series of changes will be obtained on cooling.

Construction of Phase diagram by Thermal analysis (or) cooling curve:

- Thermal analysis is a method involving a study of the cooling curves of various compositions of a system during solidification. The shape of the freezing point curves for any system, especially those involving metals can be determined by thermal analysis.
- The data obtained from thermal analysis along with recorded curves are called as thermogram.
- These thermograms are characteristic of a particular system composed of either single or multi component materials.
- Thermograms indicate the system in terms of temperature, dependencies of it's thermodynamic properties.
- Let us discuss in detail the cooling curves or time-temperature curves of some simple systems.

	<p>Example 1:</p> <ul style="list-style-type: none"> If a pure substance says x, in molten state is cooled slowly and the temperature is noted at different time interval. The graph plotted between temperature and time (the cooling curve) will be of the form shown in Fig. In this diagram 'ab' denotes the rate of cooling of molten liquid and the liquid starts solidifying at the freezing point 'b'. Now the temperature remains constant until the liquid melt is completely solidified. Solidification completes at the point 'c'. The horizontal line 'bc' represents the equilibrium between the solid and liquid melt. After the point 'c', the temperature of the solid begins to decrease along the curve 'cd'.
 <p>Fig shows the cooling curve of a mixture A+B</p>	<p>Example 2:</p> <ul style="list-style-type: none"> When a molten liquid containing two components (say A and B) is cooled slowly then the cooling curve is different and one such curve is shown in Fig. As before, initially the rate of cooling is continuous. When it reaches the point 'b' one substance (either A or B) begins to solidify out of the melt, which is indicated by a break and the rate of cooling is different. On further cooling at the break point 'c' the second compound also begins to solidify. Now the temperature remains constant until the liquid melt is completely solidified, which forms the eutectic mixture (line cd) . After the break point 'd' cooling of solid mass begins. The temperature of horizontal line 'cd' gives the eutectic temperature.

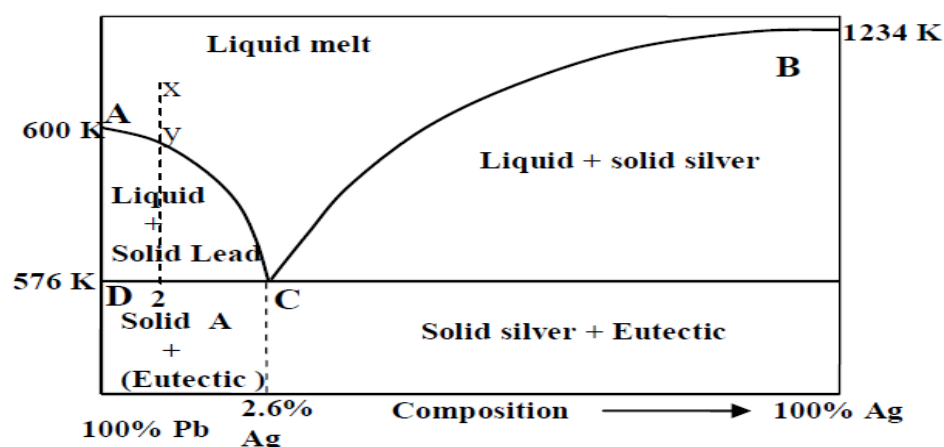
- A number of mixtures of A and B are taken with different composition.
- Each mixture is heated to the molten state and their cooling curves are drawn separately for each mixture.
- From the cooling curves of various compositions, the main phase diagram can be drawn by taking the composition in X-axis and temperature in Y-axis.
- Any point on this line indicates the appearance of the solid phase from the liquid. The area above this curve is only liquid phase.

Uses of Cooling curves:

- Cooling curves are used to find the percentage purity of the compounds.
- It is used to find the melting point of the compounds
- Thermal analysis is useful in derivation of phase diagram of any two component system
- Used to find the composition of the alloy.
- Used to analyse the behaviour of the compounds.

Lead –Silver system:

It is a two-component system. The two metals are completely miscible in liquid state and do not form any compound. There is almost no effect of pressure on this system. The temperature- composition phase diagram is shown in Figure. It contains lines, areas and the eutectic point.



The curve AC:

- The curve AC is the freezing point curve of pure lead. The melting point of lead decreases gradually along the curve AC, with the continuous addition of silver.
- Thus the curve AC is showing the effect of addition of silver on the melting point of pure lead.
- All along the curve AC two phases –solid lead and liquid are in equilibrium.
- According to reduced phase rule equation

$F' = C - P + 1; = 2 - 2 + 1; = 1$ i.e., $F' = 1$ i.e., the system is univariant.

The curve BC:

- Curve BC is the freezing point curve of pure silver and represents the effect of addition of pure lead on the melting point of pure silver. All along the curve BC two phases – solid silver and liquid are in equilibrium.
- According to reduced phase rule equation.
- $F' = C - P + 1; = 2 - 2 + 1; = 1$, i.e. $F' = 1$ (The system is univariant)

Point C (Eutectic point):

- Point C is the eutectic point where solid silver, solid lead and their solution coexist. The curves AC and BC meet at point C. Since the experiment is carried out at constant pressure, the number of degrees of freedom for the system at the eutectic point C is zero on the basis of reduced phase rule.
$$F' = C - P + 1; = 2 - 3 + 1 = 0; \text{ i.e., } F' = 0$$
- The system is non-univariant. Eutectic composition is 2.6% silver and 97.4% lead and the corresponding temperature is 576 K.

Areas:

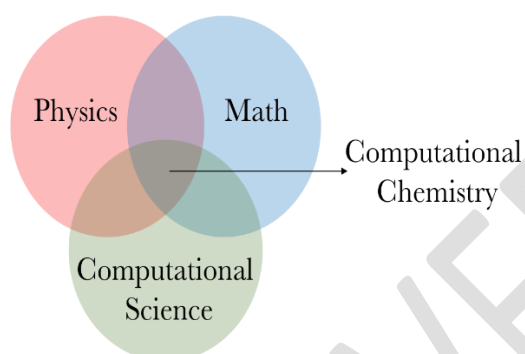
- The area above the line ACB has a single phase (molten Pb + Ag).
- According to reduced phase rule equation,
$$F' = C - P + 1; = 2 - 1 + 1 = 2; \text{ i.e., } F' = 2$$
- The system is bivariant. Both the temperature and composition have to be specified to define the system completely.
- The area below the line AC (solid Ag + liquid melt), below the line BC (solid Pb +liquid melt) and below the eutectic point 'C' have two phases and the system is univariant.
- According to reduced phase rule equation,
$$F' = C - P + 1; = 2 - 2 + 1 = 1 \text{ i.e., } F' = 1$$

Introduction to Computational Chemistry

Definition

Computational Chemistry is a branch of chemistry that uses **mathematical algorithms, statistics, and computer simulations** to study and solve chemical problems. It does not directly replace experimental chemistry but complements it by:

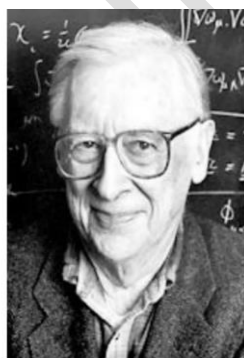
- Predicting molecular structures, properties, and reactions.
- Explaining experimental observations.
- Reducing the cost and time of experiments.



Computational chemistry refers to a collection of techniques used to investigate chemical problems with the aid of computers, rather than relying solely on laboratory experiments with chemicals. It applies the principles of theoretical chemistry through efficient computer programs to predict and calculate molecular properties. The earliest theoretical study in this field was carried out by Walter Heitler and Fritz London in 1927.



Walter Kohn



John A. Pople

In 1998, the Nobel Prize in Chemistry was awarded to:

- **Walter Kohn**, for his pioneering work in the development of **Density Functional Theory (DFT)**, a fundamental tool in computational chemistry.
- **John A. Pople**, for his contributions to the development of **computational methods in quantum chemistry**, which greatly advanced the practical applications of theoretical models.



Martin Karplus,

Michael Levitt

Arieh Warshel

In 2013, the Nobel Prize in Chemistry was awarded for the development of **computer-based methods to model and simulate complex chemical systems**, enabling a deeper understanding of molecular processes.

Objectives of Computational Chemistry

- ✓ **Prediction** – to estimate the structure, stability, reactivity, and properties of molecules.
- ✓ **Explanation** – to understand chemical phenomena in terms of fundamental principles.
- ✓ **Design** – to assist in the development of new materials, catalysts, and drugs.
- ✓ **Visualization** – to provide molecular-level insights into systems that are difficult to observe experimentally.

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

- ✚ **Small molecules** → geometry optimization, vibrational frequencies, reaction pathways.
- ✚ **Large biomolecules** → protein folding, drug–receptor interactions.
- ✚ **Materials science** → polymers, nanomaterials, surface chemistry.
- ✚ **Environmental chemistry** → atmospheric reactions, pollutant degradation.
- ✚ **Electrochemistry** → redox reactions, batteries, and fuel cells.

Applications

1. **Drug Design and Medicinal Chemistry** – predicting binding affinities, QSAR models.
2. **Catalysis** – mechanism and active site analysis.
3. **Spectroscopy** – simulating IR, NMR, UV-Vis spectra.
4. **Material Science** – designing semiconductors, nanostructures.
5. **Environmental Chemistry** – studying atmospheric pollutants and green chemistry processes.
6. **Energy Research** – modeling batteries, solar cells, and fuel cells.

Advantages

- Provides molecular-level insights not easily accessible experimentally.
- Saves time and cost compared to trial-and-error laboratory experiments.
- Enables prediction of new compounds and properties before synthesis.

Limitations

- Approximations are necessary → results may deviate from reality.
- Computational cost increases with system size.
- Requires validation with experimental data.

Conclusion:

Computational chemistry bridges theory and experiment, using mathematical models and computer simulations to study chemical systems. It covers a spectrum from highly accurate quantum calculations (small molecules) to large-scale molecular simulations (proteins, materials). With advancing computing power and algorithms, it is becoming an indispensable tool in research and industry.

Electronic Structure Determination – Illustration

1. Introduction

- **Electronic structure determination** → process of finding the arrangement of electrons in atoms and molecules.
- Important because **chemical bonding, reactivity, and properties** depend on electronic configuration.
- Achieved using **theoretical models + computational methods + spectroscopic techniques**.

2. Basis of Electronic Structure

- Governed by **Quantum Mechanics** (Schrödinger Equation).
- Wavefunction (Ψ) → contains complete information of a system.
- Electron density (ρ) → often used in modern methods (DFT).

3. Methods of Determination

(A) Theoretical/Computational Illustrations

1. **Ab Initio Methods** (first principles)
 - Solve Schrödinger Equation approximately.
 - Example: Hartree-Fock (HF), Post-HF methods (MP2, CI, CCSD).

- Provides orbital energies, electronic distributions.

2. Density Functional Theory (DFT)

- Uses **electron density $\rho(\mathbf{r})$** instead of wavefunction.
- Efficient and widely used for molecules and solids.

3. Semi-Empirical Methods

- Use experimental parameters + simplified QM.
- Faster but less accurate (AM1, PM3, MNDO).

4. Molecular Orbital (MO) Theory & Illustrations

- Electrons occupy molecular orbitals (bonding, anti-bonding, non-bonding).
- Orbital diagrams illustrate relative energy levels.

4. Illustration of Procedure

1. **Define the system** – molecule/atom with geometry.
2. **Select basis set** – mathematical functions (STO, GTO).
3. **Apply method** – ab initio / DFT / semi-empirical.
4. **Solve equations** → get wavefunction/electron density.
5. **Visualize electronic structure** → orbital diagrams, density maps, frontier orbitals (HOMO–LUMO).

5. Applications of Electronic Structure Determination

- Predicting **molecular geometry** and **bonding nature**.
- Understanding **spectroscopic transitions**.
- Explaining **reactivity** (HOMO–LUMO interactions).
- Designing **drugs, catalysts, and materials**.
- Studying **reaction mechanisms**.

6. Example Illustration

Ethylene (C_2H_4):

- Ethylene (C_2H_4) is the simplest **alkene** with a **C=C double bond**.
- Its electronic structure can be studied experimentally (spectroscopy) and theoretically (computational chemistry).
- Key interest: **σ - and π -bonding**, hybridization (sp^2), and molecular orbitals (MOs).

Hybridization and Bonding

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

Molecular Orbital (MO) Description

- σ system:
 1. Formed by overlap of sp^2 orbitals and H 1s orbitals.
 2. Strong, localized framework bonds.
- π system:
 1. Each carbon has an unhybridized p orbital (p_z).
 2. These overlap sideways to form:
 - π bonding MO (π) – lower energy, filled.
 - π antibonding MO (π^*) – higher energy, empty.

Computational Determination (Illustration)

- ✓ Step 1: Define system – Ethylene molecule geometry.
- ✓ Step 2: Select method – Hartree-Fock or DFT with basis set (e.g., STO-3G, 6-31G).
- ✓ Step 3: Solve equations – yields orbital energies + electron density.
- ✓ Step 4: Visualization – shows σ framework and delocalized π orbitals.
- ✓ Result: HOMO = π bonding orbital, LUMO = π^* antibonding orbital.

Orbital Energy Diagram (Summary)

- Filled orbitals:
 1. Core orbitals (C 1s, deep σ).
 2. $\sigma(\text{C-H})$, $\sigma(\text{C-C})$.
 3. π (HOMO).
- Unfilled orbital:
 1. π^* (LUMO).

Applications

- Explains reactivity of alkenes:
 - ✓ HOMO (π orbital) interacts with electrophiles.
 - ✓ LUMO (π^* orbital) interacts with nucleophiles in excited states.
- Basis of reactions: electrophilic addition, polymerization.
- Important in organic chemistry, catalysis, photochemistry.

Summary

- Ethylene electronic structure determined by MO theory + spectroscopy + computation.
- Bonding: sp^2 hybridization, C=C double bond ($\sigma + \pi$).
- HOMO = π orbital, LUMO = π orbital*.
- PES, UV-Vis, IR, NMR confirm orbital energies and transitions.
- Explains alkene reactivity via HOMO–LUMO interactions.

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