GOVERNMENT ARTS AND SCIENCE COLLEGE
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STUDY MATERIAL B.Sc. CHEMISTRY

PHYSICAL CHEMISTRY-III

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DEPARTMENT OF CHEMISTRY

PHYSICAL CHEMISTRY –III

UNIT – I
SPECTROSCOPY- I

Introduction-various types of molecular spectra-electronic, vibrational and rotational energy levels-Born-Oppenheimer approximation. Rotation spectra of diatomic molecules- determination of bond length and moment of inertia from rotational spectra - numerical problems - selection rule, effect of isotopic substitution. UV-visible spectroscopy: theory - types of transitions in molecules - selection rules for electronic spectra - factors affecting absorption maximum and intensity – applications. IR spectroscopy: theory - stretching and bending vibrations - factors affecting vibrational frequencies - important spectral regions for the characterization of functional groups – fingerprint region - determination of force constant - qualitative relation of force constant to bond energies - selection rules - modes of vibrations in polyatomic molecules - vibrational modes of H2O and CO2 – applications - numerical problems.

UNIT - II
SPECTROSCOPY –II

Raman spectroscopy: Principle - Rayleigh and Raman scattering - Stokes and Anti-stokes lines - differences between IR and Raman spectroscopy - mutual exclusion principle – selection rule - applications.

NMR spectroscopy: Theory of NMR, modes of nuclear spin-relaxation process - shielding effect, hyperfine splitting, coupling constants, - chemical shift - factors affecting chemical shift - internal standard, δ and τ scale - pplications of NMR and limitations of NMR.

ESR spectroscopy: principle - energy level splitting - presentation of ESR spectrum for methyl and benzene radicals, deuterium - applications-Zerofield splitting &Kramer’s degeneracy –fine structure

UNIT III
GROUP THEORY

Concept of symmetry in chemistry - symmetry operations and symmetry elements - rotational axis of symmetry and types of rotational axes - planes of symmetry and types of planes - improper rotational axis of symmetry - identity element - groups and their basic properties – Abelian and cyclic groups -

classification of molecules into point groups - the symmetry operations of a molecule form a group – H_2O and NH_3 point groups - group multiplication ables.

UNIT IV
CHEMICAL KINETICS

Rate of reaction-Measuring rates of reaction-expressing reaction rates-factors influencing rate-rate constant-Rate laws, Stoichiometry, order and molecularity of reactionsFirst order, second order, third order and zero order reactions and example. Characteristics of I,II,III and Zero order reactions. Determination of order of reactions-expression for rate constant of first and second order reaction-derivation. Effect of temperature on rate constant. The activation energy - determination of Arrhenius frequency factor and energy of activation-The collision theory of reaction rates and its limitation. Lindemann theory of unimolecular reactions-The theory of Absolute reaction rates. Comparison of the collision theory with the Absolute reaction rate theory.

UNIT V
SURFACE CHEMISTRY AND SOLUTIONS.

Surface Chemistry: Adsorption - physisorption and chemisorption - adsorption of gases by solids - adsorption isotherms - Freundlich adsorption isotherm - derivation of Langmuir adsorption isotherm, statement and explanation of BET isotherm - applications of adsorption - determination of surface area – adsorption indicators.

Solution: Solutions of liquid in liquid– Binary liquid mixture - Ideal and on ideal solutions – Raoult's law. - deviation from ideal behavior – pressure – composition and temperature – Composition diagrams for completely miscible binary solutions-Fractional distillation –Azeotropic distillation—nature of azeotropic mixtures-partially miscible liquids— consolute temperature- critical solution temperature-system with upper CST, lower CST and upper and lower CST –Liquid crystals, Nematic, Semetic and cholestic types and their applications0.

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UNIT– I
SPECTROSCOPY- I

Molecular Spectroscopy

We know that when a matter is exposed to electromagnetic radiation, the electromagnetic spectrum of a series of wavelengths produces. Molecules absorb certain wavelengths to the higher electronic, vibrational, and rotational energy levels. So, the series of wavelengths, a molecule absorbs gives off a distinct molecular spectrum. A distinct molecular spectrum lies in the specific region of the electromagnetic spectrum.

Types of Molecular Spectra

As explained earlier, a molecule has different types of quantized energy levels i.e. translational, rotational, vibration and electronic. The molecular spectra arise due to the transitions taking place between these energy levels. The energy absorbed for any transition is equal to the difference in the energies of the two levels involved. It is found that these energies for transition are in the order

$$\mathbf{E_1 << E_r << E_v << E_e\ *}$$

In fact the difference between the successive translational energy levels is so small (10^{-60} J mol^{-1})that it cannot be observed experimentally. For this reason, for practical purposes, translational energy is considered as types of molecular spectra generally observed, depending upon the energies absorbed and the regions of the electromagnetic spectrum in which they are observed, are briefly explained below:

The three types of molecular spectra are:

1. Pure rotational spectra
2. Vibrational rotational spectra
3. Electronic band spectra

i. Pure rotational (Microwave) spectra.

If the energy absorbed by the molecules is so low the tit can cause transitionally form one rotational level to another within the same vibration level, the result obtained is called the rotational spectrum. These spectra are, therefore, observed in the far infra-red region or in the microwave reign whose energies are exceedingly small**.** The spectra is, therefore also called microwave spectra.

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ii. Vibration rotational spectra.

If the exciting energy is sufficiently large so that it can cause a transition form one vibration level to another witching the same electronic level then as the energies required for the transitions between the rotational levels are still less, bother types of transition will take place. The result is, therefore, a vibration-oration spectrum. Since such energies are available in the near infra-red region, these pectorals are observed in this region and are also called infra-red spectra.

iii. Electronic Band Spectra.

If the exciting energy is still higher such that it can result in a transition form one electronic level to another, then these will also be accompanied by vibration level changes and each of these is further accompanied by rotational level changes. For each vibration change, a set of closely spaced lines is observed due to rotational level changes. Such a group of closely spaced rotational lines is called a band. Thus for a given electronic transition, a set of bands is observed. This say of bands is called band group or a band system. such electronic transition gives a band system. The complete set of band systems obtained due to different electronic transition gives the electronic band spectrum of the gaseous molecule. Thus whereas atoms give line spectra, molecules give band spectra. As such high excitation energies are available in the visible and ultraviolet regions, these spectra are observed in the visible region (12,500-25,000 cm^{-1}) **and ultraviolet region** (25,000-70,000 cm-1)**.**

Born–Oppenheimer (BO) approximation

In quantum chemistry and molecular physics, the **Born–Oppenheimer (BO) approximation** is the best-known mathematical approximation in molecular dynamics. Specifically, it is the assumption that the wave functions of atomic nuclei and electrons in a molecule can be treated separately, based on the fact that the nuclei are much heavier than the electrons. Due to the larger relative mass of a nucleus compared to an electron, the coordinates of the nuclei in a system are approximated as fixed, while the coordinates of the electrons are dynamic.[1] The approach is named after Max Born and J. Robert Oppenheimer who proposed it in 1927,[2] in the early period of quantum mechanics.

The approximation is widely used in quantum chemistry to speed up the computation of molecular wavefunctions and other properties for large molecules. There are cases where the assumption of separable motion no longer holds, which make the approximation lose validity (it is said to "break down"),

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but even then the approximation is usually used as a starting point for more refined methods. In molecular infrared spectroscopy, using the **BO** approximation means considering molecular energy as a sum of independent terms, e.g.: These terms are of different orders of magnitude and the nuclear spin energy is so small that it is often omitted. The electronic energies {\displaystyle E_{\text{electronic}}} consist of kinetic energies, interelectronic repulsions, internuclear repulsions, and electron–nuclear attractions, which are the terms typically included when computing the electronic structure of molecules.

Rotational Spectra of Diatomic molecule

The rotation of a diatomic molecule can be described by the **rigid rotor** model. To imagine this model think of a spinning dumbbell. The dumbbell has two masses set at a fixed distance from one another and spins around its center of mass (COM). This model can be further simplified using the concept of reduced mass which allows the problem to be treated as a single body system.

Introduction

Similar to most quantum mechanical systems our model can be completely described by its wave function. Therefore, when we attempt to solve for the energy we are lead to the Schrödinger Equation. In the context of the rigid rotor where there is a natural center (rotation around the COM) the wave functions are best described in spherical coordinates. In addition to having pure rotational spectra diatomic molecules have rotational spectra associated with their vibrational spectra. The order of magnitude differs greatly between the two with the rotational transitions having energy proportional to 1-10 cm^{-1} (microwave radiation) and the vibrational transitions having energy proportional to 100-3,000 cm^{-1} (infrared radiation). Rotational spectroscopy is therefore referred to as microwave spectroscopy.

Rigid Rotor Model

A diatomic molecule consists of two masses bound together. The distance between the masses, or the bond length, (l) can be considered fixed because the level of vibration in the bond is small compared to the bond length. As the molecule rotates it does so around its COM (observed in Figure 11:. as the intersection of R1R1 and R2R2) with a frequency of rotation of νrotνrot given in radians per second.

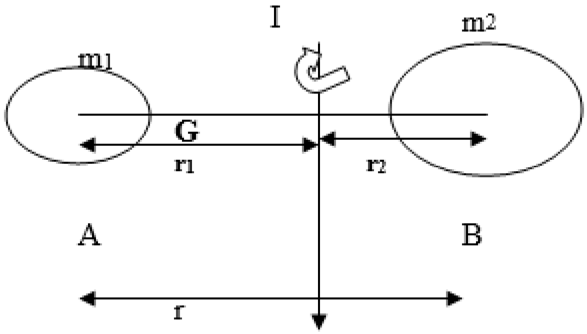
What is Rotational spectroscopy or microwave spectroscopy?

Rotational spectroscopy which is also called microwave spectroscopy provides information about the absorption or emission of electromagnetic radiation typically in the microwave region of the electromagnetic spectrum.

Heteronuclear diatomic molecules are microwave active.

- A Molecule, to give rotational spectra should possess a permanent dipole moment.
- Heteronuclear diatomic molecules possess a permanent dipole moment. This dipole moment gives rotational spectra.
- If the energy supplied is small enough during the rotation of molecules, the bond length of the molecule remains unchanged.
- The amount of energy required to change the rotational energy level is of the order of 0.05 ev (2.5×10^{-4} m) which corresponds to the energy of radiation in the microwave region.
- During rotation, these molecules generate an electric field that interacts with the microwave radiations giving rise to a spectrum.
- This absorption of radiation take place in the infrared or microwave region of the electromagnetic spectrum
- Due to the above reasons, Heteronuclear diatomic molecules are microwave-active, and Rotational spectra are **known as Microwave spectra.**
- Example: HCl, HBr, and CO are microwave active.

Expression for the moment of inertia in a simple diatomic molecule.



Rotational Spectroscopy

Consider a simple diatomic rigid polar molecule of masses **‘m_1’** and **‘m_2’** separated by an internuclear distance ‘r’. Let $\mathbf{r_1}$ and $\mathbf{r_2}$be the distances of these atoms from the center of gravity (G), about which the molecules rotate. Moment of inertia of a particle of mass ’**m**’ revolving around a fixed point at a distance ‘**r**’ is given by ‘**mr^2**’. For a diatomic molecule, the total moment of Inertia (**I**) is given by,

$I = m_1r_1^2 + m_2r_2^2$ ………………………………………………… i)

Since the system is balanced, the moments of both atoms are equal i.e.

$m_1r_1 = m_2r_2$...ii)

On substituting values from eq (ii) in eq (i), we get

$I = m_2r_2r_1 + m_1r_1r_2$

$I = r_1r_2 (m_1 + m_2)$..(iii)

But, $r = r_1 + r_2$

$r = r_1 + m_1r_1 / m_2$ ....(from eq ii)

$r = r_1(1 + m_1/m_2)$

$r = r_1(m_1 + m_2 /m_2)$

Therefore, $r_1 = m_2/m_1+m_2 . r$ ....(iv)

Similarly, $r_2 = m_1/m_1+m_2 . r$ ....(v)

On substituting the values of r_1 and r_2 in equation (iii) we get,

$I = r (m_2/ m_1+m_2) \times r (m_2/m_1+m_2) \times (m_1 + m_2)$

Therefore, $I = m_1m_2/ m_1+m_2 . r^2$ ……………………… eq (vi)

The term $m_1m_2/m_1+m_2 = \mu$ i.e. reduced mass of the system

Therefore, $I = \mu r^2$

The frequency separation (Δv) between two successive lines in the rotational spectrum is 2B i.e Δ v = 2B. The rotational spectrum of a diatomic molecule consists of equally spaced lines. The equation for the frequency separation of the lines in the rotational spectrum of a diatomic molecule.

The rotational energy E_J of a diatomic molecule is given by,

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

Where, **I** =moment of inertia of the molecule

h =Planck s constant

J =rotational quantum number which can have value 0,1,2,3……

Consider a rotational transition from a rotational energy level J to another level (J^1)

$$\therefore E_{J'} = \frac{h^2}{8\pi^2 I} J'(J'+1) \text{ ....(ii)}$$

(c) Now change its rotation energy (ΔE) is given as,

$\Delta E = E_J - E_{J'}$

$$\therefore \Delta E = \frac{h^2}{8\pi^2 I} J(J+1) - \frac{h^2}{8\pi^2 I} J'(J'+1)$$

$$\therefore \Delta E = \frac{h^2}{8\pi^2 I} [J(J+1) - J'(J'+1)] \text{ ....(iii)}$$

But accordingly, to the selection rule, $\Delta J = \underline{+}1$

i.e. $\Delta J = J - J' = +1$

Therefore $J' = J-1$

By substituting the equation of J' in eq (iii) we get,

$$\therefore \Delta E = \frac{h^2}{8\pi^2 I} [J(J+1) - (J-1)(J-1+1)]$$

$$\therefore \Delta E = \frac{h^2}{8\pi^2 I} \left(J^2 + J - J^2 + J \right)$$

$$\therefore \Delta E = \frac{h^2}{8\pi^2 I} \times 2J \text{ ....(iv)}$$

(d) According to quantum theory, energy changes are quantized by the equation,

$\Delta E = h\upsilon = h\bar{\upsilon}c$ ....(v)

$$\therefore \Delta E = h\bar{\nu}c = \frac{h^2}{8\pi^2 I} \times 2J \text{ ....(from eq (iv) \& (v))}$$

$$\therefore h\bar{\nu}c = \frac{h^2}{8\pi^2 I} \times 2J$$

$$\therefore \bar{\nu} = \left(\frac{h}{8\pi^2 I c} \times 2J \right)$$

But, $\frac{h}{8\pi^2 I c} = B$ i.e Rotational constant or Bjerrum's constant.

Therefore $\bar{\upsilon} = 2BJ$

Where $\bar{\upsilon}$ = frequency in wavenumbers of lines in the rotational spectrum.

(e) Thus, from eq(vi), the frequency of lines in the rotational spectrum can be found.

- When J=1, i.e for the transition from J=0 to J=1 (Transition from ground state J=0 to the first energy level J=1 takes place) Therefore $\bar{\upsilon}_1 = 2Bm^{-1}$
- When J=2, i.e for transition from J=1 to J=2 (Transition from the first energy level J=1 to second energy level J=2 takes place)

  $\bar{\upsilon}_2 = 4Bm^{-1}$
- When J=3, i.e for transition from J=2 to J=3

  $\bar{\upsilon}_3 = 6Bm^{-1}$

(f) The frequency separation between consecutive lines will be,

$$\Delta \bar{\upsilon} = \bar{\upsilon}_2 - \bar{\upsilon}_1 = 4B - 2B = 2B$$

$$\Delta \bar{\upsilon} = \bar{\upsilon}_3 - \bar{\upsilon}_2 = 6B - 4B = 2B \text{ \& so on .}$$

Thus the rotational spectrum of a diatomic molecule consists of a series of equidistance lines with the separation of 2B.

$$\triangle \bar{v} = 2B = \frac{h}{4\pi^2 I c}$$

Thus, the frequency difference between two successive lines in the rotational spectrum is 2B.

(g) From the Moment of Inertia (I) the equilibrium distance ‘r’ or bond length can be calculated

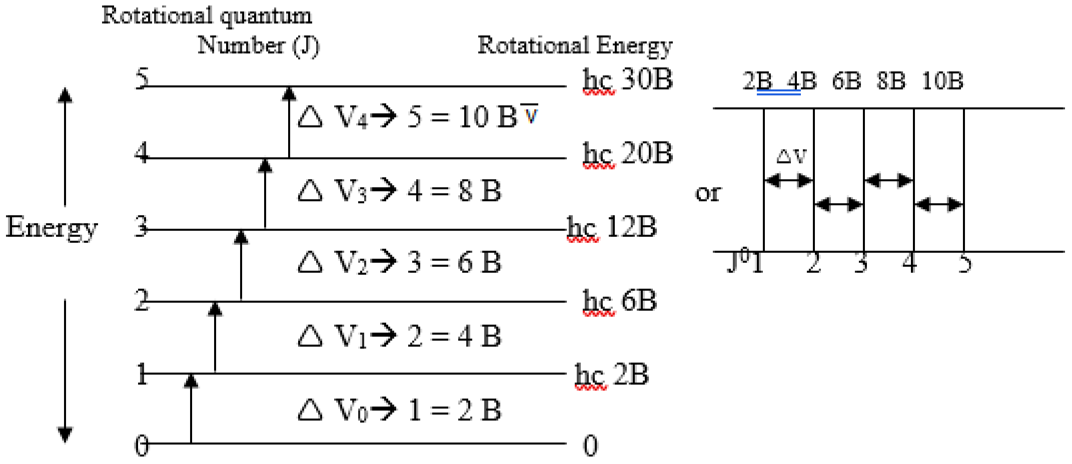
$$I = \left(\frac{m_1 m_2}{m_1 + m_2}\right) x\, r^2$$

Where m_1 and m_2 are masses of atoms in a diatomic molecule.

Diagram showing different rotational energy levels with permitted rotational transition in a domestic molecule

The nature of the rotational spectra:-

- The spectral lines are present in the microwave region.
- The spectrum consists of equally spaced lines.
- The spacing between any two successive lines is constant and is equal to $2B_0m^{-1}$.
- At room temperature, the rotational energy levels up to J = 5 are occupied by the molecules. Hence, all the transitions from $J_1 = 0$ to $J_1 = 5$ will be observed.



The effect of isotopic substitution on the rotational energy levels and rotational spectrum level of a diatomic molecule.

- The Presence of isotopes in a molecule will bring about a considerable change in the reduced mass (μ) of the molecules. However, the intermolecular distance (r) and geometry of the molecule remain unchanged. As reduced mass changes, it will bring about a change in the moment of inertia (I) and Rotational Constant (B).
- In the Relation $B = h/8\pi^2Ic$, the rotational constant B is inversely proportional to the moment of inertia.
- Therefore, the heavier isotopic molecule having a larger moment of Inertia will have a small value of B. As a result, the following frequency separation of successive lines which depends on B will be smaller for the heavier isotopic molecule than for the lighter isotopic molecule.
- These small differences in the frequency separation have been utilized to determine the isotopic masses.
- Consider two isotopic molecules A and B. Let I_A and I_B be their moment of inertia and π_A and π_B be their reduced masses. The rotational constants B_A and B_B will be given by.

$$B_A = \frac{h}{8\pi^2 I_A c}, \qquad B_B = \frac{h}{8\pi^2 I_B c}$$

$$\therefore \frac{B_A}{B_B} = \frac{I_B}{I_A} \quad \text{..............................(i)}$$

We know, $I = \mu r^2$ $\therefore I_A = \mu_A r^2$ and $I_B = \mu_B r^2$

$$\therefore \frac{I_B}{I_A} = \frac{\mu_B}{\mu_A} \quad \text{..............................(ii)}$$

But, the frequency separation $\Delta\bar{\nu} = 2B$ $\therefore \Delta\bar{\nu}_A = 2B_A$ $\Delta\bar{\nu}_B = 2B_B$

$$\therefore \frac{\Delta\bar{\nu}_A}{\Delta\bar{\nu}_B} = \frac{B_A}{B_B} \quad \text{..............................(iii)}$$

$\therefore$ From eqⁿ(i),(ii) and (iii) we have,

$$\frac{B_A}{B_B} = \frac{I_B}{I_A} = \frac{\mu_B}{\mu_A} = \frac{\Delta\bar{\nu}_A}{\Delta\bar{\nu}_B}$$

This relationship helps to calculate the abundance of isotopes by knowing the shifts in the spectral lines with the isotopic effect.

UV-Visible Spectroscopy

The wavelength range of UV radiation is 200 nm- 400 nm. There are mainly two types of UV region. 1. 200 nm - 400 nm that is called near ultraviolet region. 2. Below 200 nm that is called far ultraviolet region. The wavelength of visible radiation is 400 nm- 800 nm. Wavelength in UV and visible region is expressed in nanometers or in angstroms. Absorption is expressed in terms of wave number (cm-1). Absorption spectra arise from transition of electron or electrons within a molecule from a lower electronic energy level to a higher electronic energy level. Ultraviolet emission spectra arise from the reverse types of transition. For the radiation to cause electronic excitation, it must be in the UV region of the EMR spectrum. Radiation in this region is of sufficient energy to cause electronic transition of outer valence electrons. Both organic and inorganic species exhibit electronic transitions in which outermost or bonding electrons are promoted to higher energy levels. Electronic transitions are associated with vibrational as well as rotational transitions. A compound appears coloured if it selectively absorbs light in the visible region. The main function of absorbed energy is to raise the molecule from ground energy state (E0) to higher excited energy state (E1).

The difference is given by:

$\Delta E = E1 - E0 = hv = hc/\lambda$

ΔE depends upon how tightly the electrons are bound in the bonds and accordingly, absorption will occur in UV or visible range, for example; If the electrons of a molecule are tightly bound as in compounds containing sigma bonds (e.g. saturated compounds) no light of region will be absorbed. The light of UV region will only be absorbed and hence compound appears 4 colourless. If the electrons of molecule are loosely bound as in unsaturated compound. Such absorption may occur in visible region and substance will appear as coloured. Energy absorbed in the ultraviolet region produces change in the electronic energy of the molecule that is resulting from transitions of valance electrons in the molecule. There are three types of electrons in organic molecules.

a) **σ (sigma) electrons-** they are found in saturated systems like alkane. They require large amount of energy for their excitation and hence do not show absorption in UV region. Their absorption band is appeared in vacuum UV region. Hence, compounds containing σ- bonds do not absorb in near UV region. For example saturated hydrocarbons are transparent in near UV region and thus they can be used as solvents.

b) **∏ (pie) electrons-** they are found in multiple bonds. They are generally mobile electrons. Since ∏- bonds are weak bonds, the energy produced by UV radiation can excite ∏- electrons to higher energy levels.

c) **n (non-bonding) electrons**- valance electrons which do not participate in chemical bonding in molecule are called as non bonding electrons or nelectrons. These are located principally in atomic orbital of N, O, S and halogens(X) as a lone pair of electrons. They can be excited by UV radiation.

Principle of UV-Visible Spectroscopy:

The Principle of UV-Visible Spectroscopy is based on the absorption of ultraviolet light or visible light by chemical compounds, which results in the production of distinct spectra. Spectroscopy is based on the interaction between light and matter. When the matter absorbs the light, it undergoes excitation and de-excitation, resulting in the production of a spectrum. When matter absorbs ultraviolet radiation, the electrons present in it undergo excitation. This causes them to jump from a ground state (an energy state with a relatively small amount of energy associated with it) to an excited state (an energy state with a relatively large amount of energy associated with it). It is important to note that the difference in the energies of the ground state and the excited state of the electron is always equal to the amount of ultraviolet radiation or visible radiation absorbed by it

Beer's and Lambert's Law: When a light passes through absorbing medium at right angle to the plane of surface or the medium or the solution, the rate of decrease in the intensity of the transmitted light decreases exponentially as the thickness of the medium increases arithmetically. Accordingly, Lambert's law can be stated as follows:

"When a beam of light is allowed to pass through a transparent medium, the rate of decrease of intensity with the thickness of medium is directly proportional to the intensity of light." Mathematically, the Lambert's law may be expressed as follows.

$- dI / dt \alpha I$

$- dI / dt = KI$...................(1)

Where I = intensity of incident light

t = thickness of the medium

K= proportionality constant

By integration of equation (1), and putting $I=I0$ when $t=0$,

$I0/ It = kt$ or $It= I0\ e\ -kt$

Where, $I0$ = intensity of incident light

It = intensity of transmitted light

k = constant which depends upon wavelength and absorbing medium used

By changing the above equation from natural log,

we get, $It = I0\ e\ -Kt$...................(2)

Where $K = k/ 2.303$

So, It = I0 e -0.4343 kt

It = I010-Kt...................(3)

Beer's law may be stated as follows:

"Intensity of incident light decreases exponentially as the concentration of absorbing medium increases arithmetically."

The above sentence is very similar to Lambert's law.

So,

It = I0 e -k' c

It = I0 10-0.4343 k' c

It = I0 10 K' c...................(4)

Where k' and K'= proportionality constants

c = concentration

By combining equation (3) and (4), we get,

It = I0 10 -act

I0 / It = 10 act

Where, K and K' = a or ε c = concentration t or b = thickness of the medium

log I0 / It = εbc ....(5)

Where ε = absorptivity, a constant dependent upon the λ of the incident radiation and nature of absorbing material. The value of ε will depend upon the method of expression of concentration. The ratio I0 / It is termed as transmittance T, and the ratio log I0 / It is termed as absorbance A. formerly, absorbance was termed as optical density D or extinction coefficient E. the ratio I0 / It is termed as opacity.

Thus, A = log I0 / It .... (6)

From equation (5) and (6),

A = εbc .... (7)

Thus, absorbance is the product of absorptivity, optical path length and the concentration of the solution. The term E1% 1 cm or A1% 1 cm refers to the to the absorbance of 1 cm layer of the solution whose concentration is 1 % at a specified λ. According to equation (7),

A = log I0 / It

Transmittance T is a ratio of intensity of transmitted light to that of the incident light.

$T = I0 / It$

The more general equation can be written as follows:

$A = \log I0 / It = \log 1/ T = - \log T = abc = \varepsilon bc$

UV-VIS Spectroscopy Theory

When the interaction between incident radiation and the electron cloud in a chromophore results in an electronic transition involving the promotion of one or more of the outer shell or the bonding electrons from a ground state into a higher energy state, ultraviolet-visible (UV-Vis) spectra are derived.

Generally, the UV and visible spectral bands of substances are large. And may not exhibit a high degree of compound recognition accuracy. Nonetheless, they are sufficient for quantitative assays and are useful as an alternate means of detection for several substances. The radiation from typical hot solids consists of several wavelengths and depends primarily on the temperature of the solid and is predictable from the principle of chance, the energy released at each given wavelength.

More recently, using a version of this-the tungsten-halogen lamp-has become standard practice. Radiation is transmitted deep into the UV zone through the quartz envelope. The most popular source is the deuterium lamp for the UV region itself, and a UV-Visible spectrometer would normally have all types of lamps to fill the whole wavelength spectrum.

Factors Affecting UV-Vis Spectroscopy

Change in Absorption Spectrum of Solvent

UV-Vis spectroscopy is a quantitative laboratory technique used for the measurement of the absorbance of light by a chemical compound. It is performed through measurement of the intensity of light, which passes through a sample with respect to the intensity of light through a reference. It is used particularly in ultraviolet and visible regions. The obtained light intensity versus wavelength is called the spectrum.

Sometimes, the spectrum obtained from the UV-Vis spectrophotometer need not be the same every time. The result may be erroneous. Reproducibility is missing if any parameters like temperature, pH, concentration are changed. Hence, it is essential to study the factors influencing UV-Vis spectroscopy, so that a clear picture will be obtained for careful measurement of the spectrum. This blog takes you to the study of variables, which affect the spectrum obtained from UV-Vis spectroscopy.

List of factors affecting UV-Vis Spectroscopy

For measurement of absorbance and studies, there are numerous factors, which impact the results in ultraviolet visible spectroscopy. The factors are as follows:

1. Effect of sample temperature
2. Effect of sample concentration
3. Effect of sample pH
4. Effect of solvent
5. Effect of steric hindrance
6. Effect of conjugation

1. Effect of Sample Temperature

The change in temperature of the sample plays a role in the spectrum. With the decrease in temperature, the sharpness of absorption bands increases. With the decrease in temperature, the position of the peak (absorption maximum) moves very little towards the longer wavelength side. However, total absorption intensity is independent of the temperature. Simple thermal expansion of the solution can change the intensity of the absorption band. Rotational and vibrational energy states depend on the temperature. When the temperature is decreased, rotational and vibrational energy states of the molecules also get lowered. Fine absorption bands will be produced when absorption occurs at lower temperatures due to the smaller distribution of excited states.The position of the band maximum does not shift much with a decrease in temperature. Hence, for obtaining more accurate results, the spectrum needs to be taken at a constant or particular temperature. Influence of Temperature on Absorption Spectrum

2. Effect of Sample Concentration

The concentration of sample present is directly proportional to the intensity of light absorption, thus influencing the spectrum. At a high concentration of solvent, molecular interactions occur, which causes changes in the shape and position of absorption bands. For qualitative work, this effect needs to be identified and taken into consideration. The type of solvent used also affects the fineness of the absorption band in the UV spectra. Polar solvents provide broader bands, but non-polar solvents give better resolution. Removing the solvent gives the best resolution. These effects are all due to solvent-solute interactions. There are stronger solvent-solute interactions if the dielectric constant of the solvent is high. Water and ethanol, which are polar solvents, exhibit a stronger binding to solute through induced dipole-dipole interactions or hydrogen bonding. Through

London interactions in non-polar solvents, ground state and excited state will change and the frequency of absorbed photons can be changed. This leads to overlap of different transition energies in spectra, which broaden the absorption band.

3. Effect of Sample pH

The change of pH of the solution and the aquatic environment has an influence on the spectrum obtained from UV-Vis spectroscopy. If the pH of the solution is changed, absorption spectra of aromatic compounds like amines and phenols also change. Upon addition of a base, acidic compounds like phenols and substituted phenols undergo a change in absorption spectra. On removal of the phenolic proton, phenoxide ion is obtained, which increases the conjugation. This leads to a decrease in energy difference between LUMO and HOMO orbitals, resulting in a shift to a longer wavelength along with an increase in absorption intensity. If an aromatic amine gets protonated in an acidic medium, there is a disturbance of the conjugation system. The shift of peak towards shorter wavelength happens and a decrease in intensity also occurs. The acid-base indicators have an application due to their absorptions in the visible region of the UV-Vis spectrum. A minute change in the chemical structure of the indicator causes a change in the chromophore, which absorbs wavelength maximum at different values resulting in color change at different pH.

An example is a phenolphthalein. It is a weak acid, dissociating in water to give anions, which adds a negative charge to the oxygen atom, contributing a shift of absorption maximum to a longer wavelength. The anion of phenolphthalein is orange, while non-ionized phenolphthalein is colorless. At neutral and acidic pH, the equilibrium shifts towards the left and there will be a lesser concentration of anions and pink color is not observed. But at basic pH, equilibrium shifts towards the right, leading to a higher concentration of anions, and pink color is observed.

Hence, to maintain pH at a constant value, the UV-Vis spectrum should be measured in an appropriate buffer solution. Over the wavelength range of measurement, the buffer requires it to be transparent. The absorbance value is higher if the buffer solution also absorbs the light.

4. Effect of Solvent on UV-Vis Absorption Spectrum

Effect of Solvent

To an extent, the choice of solvent also affects the spectrum. The absorption spectrum is also dependent on the solvent in which the absorption molecule gets dissolved. The option of choosing a solvent can shift the absorption peak to longer or shorter wavelengths. It is based on the interaction of solvent with the chromophore of the desired molecule. When compared to hexane solution, ethanol gives absorption maximum at longer wavelengths. Alcohols and water can form hydrogen bonding with the substance, which shifts the absorption bands of polar molecules. As the polarities of ground and excited states of chromophore are different, a change in solvent polarity causes a change in the energy gap between the two states. Highly pure and non-polar solvents do not interact with the solute molecules either in the ground state or excited state. However, polar solvents impact the molecular orbitals at the ground state of the excited state. Hence, the spectrum recorded in non-polar solvent differs from that one recorded in the polar solvent.

5. Effect of Steric Hindrance

The configuration of molecules also has a say in the spectrum. When a molecule is planar in conjugation, electronic conjugation works well. The position of the absorption peak is dependent on the effectiveness and length of the conjugative system. If autochrome is there, it prevents the molecule to exist in a planar configuration and shift towards longer or shorter wavelengths depending on the distortion. Distortion of chromophore causes the absorption peak to shift, due to loss of conjugation. Steric hindrance can also be seen in geometric isomerism. Trans isomers exhibit absorption peaks at longer wavelengths and molar absorptivity is higher than the cis counterpart. Due to the steric effect, trans-stilbene absorbs with greater intensity at longer wavelengths.

6. Effect of Conjugation

Molecular conjugation plays a role in determination of spectrum. The absorption peak is shifted to a shorter frequency or longer wavelength when two or more chromophores are conjugated. Conjugation enhances the energy of the highest occupied molecular orbital and mitigates the energy of the lowest unoccupied molecular orbital. Hence, lesser energy is needed for an electronic transition to take place in a conjugated system. If the number of conjugated bands increases, the value of the absorption peak also increases. An increase in the double bonds of a conjugation leads to lesser energy needed for electronic transition. Conjugation of two chromophores also leads to an increase in molar absorptivity and intensity. An increase in the number of conjugated bonds leads to absorption of visible light and compounds will be colored. An example is beta carotene, which is a precursor compound of vitamin A. It has 11 conjugated bonds and the absorption peak is shifted from the UV region to the visible region (blue), giving it an orange color.

Conclusion

There are so many factors that impact the absorbance studies in UV-Visible spectroscopy. Choosing a proper solvent and buffer will make the reading accurate. At the same time, optimal temperature and concentration also provide the absorbance value with precision. Similarly, solvent pH should be optimized before taking the reading.

Applications:

1. Detection of Impurities
    - It is one of the best methods for determination of impurities in organic molecules.
    - Additional peaks can be observed due to impurities in the sample and it can be compared with that of standard raw material.
    - By also measuring the absorbance at specific wavelength, the impurities can be detected.

2. Structure elucidation of organic compounds
    - It is useful in the structure elucidation of organic molecules, such as in detecting the presence or absence of unsaturation, the presence of hetero atoms.

3. UV absorption spectroscopy can be used for the quantitative determination of compounds that absorb UV radiation.

4. UV absorption spectroscopy can characterize those types of compounds which absorbs UV radiation thus used in qualitative determination of compounds. Identification is done by comparing the absorption spectrum with the spectra of known compounds.

5. This technique is used to detect the presence or absence of functional group in the compound. Absence of a band at particular wavelength regarded as an evidence for absence of particular group.

6. Kinetics of reaction can also be studied using UV spectroscopy. The UV radiation is passed through the reaction cell and the absorbance changes can be observed.

7. Many drugs are either in the form of raw material or in the form of formulation. They can be assayed by making a suitable solution of the drug in a solvent and measuring the absorbance at specific wavelength.

8. Molecular weights of compounds can be measured spectrophotometrically by preparing the suitable derivatives of these compounds.

9. UV spectrophotometer may be used as a detector for HPLC

Infrared Spectroscopy

Introduction

Infrared (IR) spectroscopy is one of the most common and widely used spectroscopic techniques employed mainly by inorganic and organic chemists due to its usefulness in determining structures of compounds and identifying them. Chemical compounds have different chemical properties due to the presence of different functional groups.

Infrared (IR) spectroscopy is one of the most common and widely used spectroscopic techniques. Absorbing groups in the infrared region absorb within a certain wavelength region. The absorption peaks within this region are usually sharper when compared with absorption peaks from the ultraviolet and visible regions. In this way, IR spectroscopy can be very sensitive to determination of functional groups within a sample since different functional group absorbs different particular frequency of IR radiation. Also, each molecule has a characteristic spectrum often referred to as the fingerprint. A molecule can be identified by comparing its absorption peak to a data bank of spectra. IR spectroscopy is very useful in the identification and structure analysis of a variety of substances, including both organic and inorganic compounds. It can also be used for both qualitative and quantitative analysis of complex mixtures of similar compounds.

Diatomic Molecular Vibration

The absorption of IR radiation by a molecule can be likened to two atoms attached to each other by a massless spring. Considering simple diatomic molecules, only one vibration is possible. The Hook's law potential on the other hand is based on an ideal spring

$F=-kx$

$=-dV(x)dx$

this results in one dimensional space

$V(r)=1/2k(r-req)$

One thing that the Morse and Harmonic oscillator have in common is the small displacements ($x=r-reqx=r-req$) from the equilibrium. Solving the Schrödinger equation for the harmonic oscillator potential results in the energy levels results in

$Ev=(v+1/2)hv$

with $v=0,1,2,3,...,$infinity $v=0,1,2,3,...,$infinity

$v=1/2\pi\sqrt{}(k\mu)$

When calculating the energy of a diatomic molecule, factors such as anharmonicity (has a similar curve with the harmonic oscillator at low potential energies but deviates at higher energies) are considered. The energy spacing in the harmonic oscillator is equal but not so with the anharmonic oscillator. The anharmonic oscillator is a deviation from the harmonic oscillator. Other considered terms include; centrifugal stretching, vibrational and rotational interactions have to be taken into account. The first and third terms represent the harmonicity and rigid rotor behavior of a diatomic molecule such as HCl. The second term represents anharmonicity and the fourth term represents centrifugal stretching. The fifth term represents the interaction between the vibration and rotational interaction of the molecule.

The Deduction of Frequency

The second law of Newton states that

$F=ma$

where m is the mass and a is the acceleration, acceleration is a 2nd order differential equation of distance with respect to time. Thus "a" can be written as

$a=d^2y/dt^2$

Substituting this into Equation 11 gives

$md^2y/dt^2=-ky$

the 2nd order differential equation of this equation is equal to $-km-km$ displacement of mass and time can be stated as

$y=Acos2\pi\nu mt$

where ν_m is the natural vibrational frequency and A is the maximum amplitude of the motion. On differentiating a second time the equation becomes

$d^2ydt^2=-4\pi^2\nu^2mAcos2\pi\nu mt$

substituting the two equations above into Newton's second law for a harmonic oscillator,

$m*(-4\pi 2\nu 2mAcos\ 2\pi\nu mt)=-k*(Acos\ 2\pi\nu mt)$

If we cancel out the two functions y,

$4m\pi 2\nu 2m=k$

from above, we obtain the natural frequency of the oscillation.

$\nu m=1/2\pi\sqrt{}km$

$\nu m\nu m$ which is the natural frequency of the mechanical oscillator which depends on the force constant of the spring and the mass of the attached body and independent of energy imparted on the system. when there are two masses involved in the system then the mass used in the above equation becomes

$\mu=m1m2/m1+m2$

The vibrational frequency can be rewritten as

$\nu m=12\pi\sqrt{}k/\mu$

The Deduction of Wave Number

Using the harmonic oscillator and wave equations of quantum mechanics, the energy can be written as

$E=(v+12)h/2\pi\sqrt{}k/\mu$

where h is Planck's constant and v is the vibrational quantum number and ranges from 0,1,2,3 ....infinity.

$E=(v+12)h\nu m$

where $\nu m\nu m$ is the vibrational frequency. Transitions in vibrational energy levels can be brought about by absorption of radiation, provided the energy of the radiation exactly matches the difference in energy levels between the vibrational quantum states and provided the vibration causes a change in dipole moment. This can be expressed as

$oE=h\nu m=h/2\pi\sqrt{}k/\mu$

At room temperature, the majority of molecules are in the ground state v = 0, from the equation above

$Eo=1/2hvm$

following the selection rule, when a molecule absorbs energy, there is a promotion to the first excited state

$E1=3/2hvm$

$(3/2hvm-1/2hvm)=hvm$

The frequency of radiation v that will bring about this change is identical to the classical vibrational frequency of the bond v_m and it can be expressed as

$Eradiation=hv=oE=hvm=h/2\pi\sqrt{k}/\mu$

The above equation can be modified so that the radiation can be expressed in wave numbers

$\nu\tilde{}=h/2\pi c\sqrt{k}/\mu$

where

- cc is the velocity of light (cm s^{-1}) and
- $\nu\tilde{}\nu\sim$ is the wave number of an absorption maximum (cm^{-1})

1. **Stretching vibration**

It involves continuous change in the inner atomic distance (i.e. distance between 2 atoms increases or decreases) along the axis of bond between 2 atoms such that bond length changes without change in bond angle in regular interval. It requires more energy so appear at shorter wavelength. It occurs at higher frequency : 4000-1250 cm-1. It is further classified into 2:

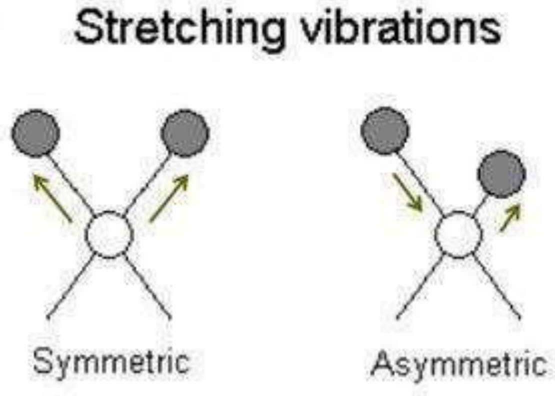
a) Symmetrical stretching
b) Asymmetrical stretching

- **Symmetrical stretching:**

The two atoms either move towards or away from central atom without change in bond angle or bond axis. Two bonds increase or decrease simultaneously.

- **Asymmetrical stretching:**

The 2 atoms move with respect to central atom such that one moves away & other moves towards the central atom. One bond length is increased & other is decreased.



2. **Bending vibration**

They involve movement of atoms which are attached to common central atom. These are characterized by change in the angle between two bonds. Also known as deformation vibration. It requires less energy so appear at longer wavelength. It occurs at lower frequency: 1400-666cm-1. It is further classified as:

a) In plane bending
  i. Scissoring
  ii. ii. Rocking
b) Out plane bending
  i. Wagging
  ii. Twisting

a) **In plane bending-**

In these types of vibrations, there is change in bond angle. This type of bending takes place within the same plane.

i. Scissoring:

Two atoms approach each other i.e. they move back & forth. Bond angles are decreased. Also known as symmetrical bending

ii. Rocking:

Movement of atoms takes place in the same direction i.e. they swing back & forth along the central atom.

b) **Out plane bending-**

This type of bending takes place outside of the plane of molecule.

- Wagging:

  Two atoms move to one side of the plane i.e. they oscillate back & forth. They move up & down of the plane.

- Twisting:

One atom moves above the plane & other move below the plane i.e. they rotate around the bond which joins the central atom of molecule.

FACTORS AFFECTING VIBRATIONAL FREQUENCIES

Vibrational frequency: A molecular vibration occurs when atoms in a molecule are in periodic motion while the molecule as a whole has constant translational & rotational motion. The frequency of the periodic motion is known as a vibrational frequency. The value of vibrational frequency of a bond calculated by Hooke’s Law is not always equal to their observed value. The force constant is changed with the electronic and steric effects caused by other groups present in the surroundings.

• There are number of factors that influence the precise frequency of a molecular vibration:

- Effect of bond order
- Vibrational coupling/ Coupled vibrations
- Hydrogen bonding
- Fermi resonance
- Electronic effects

a) Effect of bond order:

- Bond order affects the position of absorption bands. Higher the bond order larger is the band frequency.
- A C-C triple bond is stronger than a C=C bond, so a C-C triple bond has higher stretching frequency than does a C=C bond.
- The C-C bonds show stretching vibrations in the region from 1200-800 cm-1 but these vibrations are weak and of little value in identifying compounds.

- Similarly, a C=O bond stretches at a higher frequency than does a C-O bond and a C-N triple bond stretches at a higher frequency than does a C=N bond which in turn stretches at a higher frequency than does a C-N bond.

b) Coupled vibrations:

- Vibrations which occur at different frequencies of higher wave number are called coupled vibration.
- Strong coupling between stretching vibrations occurs only when the 2 vibrations have a common atom
- Interaction between bending vibrations occurs only when a common bond is present between the vibrating groups.
- Coupling between stretching & bending vibrations occurs. If stretching bond forms one side of angle that varies in bending vibrations
- Interaction is greatest when the coupled groups have individual energies that are approx. equal
- If groups are separated by 2 or more bonds, no interaction occurs
- Coupling occurs when vibrations are of same symmetry species.
- An isolated C-H bond has only one stretching vibrational frequency whereas methylene group shows 2 stretching vibrations- symmetrical & asymmetrical
- Asymmetric vibrations occur at higher frequencies or wave numbers than symmetric stretching vibrations.
- These are known as coupled vibrations because these vibrations occur at different frequencies than that required for an isolated C-H stretching

- A strong vibrational coupling is present in carboxylic acid anhydrides in which symmetrical & asymmetrical stretching vibrations appear in the region 1720-1825 cm-1.

- The interaction is very effective probably because of the partial double bond character in the carbonyl oxygen bonds due to resonance which also keeps the system planar for effective coupling.
- Asymmetrical stretching band in acyclic anhydride is more intense whereas symmetrical stretching band is more intense in cyclic anhydrides.
- For interaction to occur, the vibrations must be of same symmetry species.
- There must be a common atom between the groups for strong coupling between stretching vibrations.
- For coupling of bending vibrations, a common bond is necessary.
- Interaction is greatest when coupled groups absorb, individually near the same frequency.
- Coupling is negligible when groups are separated by one or more carbon atoms & vibrations are mutually perpendicular.

c) Fermi resonance:

- A vibration of large amplitude produced by a relatively small vibration coupling of 2 fundamental vibration modes produces 2 new modes of vibration, with frequencies higher & lower than that observed in absence of interaction. Interaction can also take place b between fundamental vibrations & overtones or combination tone vibration s & such interactions are known as Fermi Resonance.
- If 2 different vibrational levels, belonging to the same species, have nearly the same energy. • A mutual perturbation of energy may occur.
- Shifting of one towards lower & other towards higher frequency occur A substantial increase in intensity of respective bands occurs.
- In this, a molecule transfers its energy from fundamental vibrational level to overtone or combination tone level & back.
- Resonance pushes the 2 levels apart & mixes their character, consequently each level has partly fundamental & partly overtone or combination tone character.

- E.g.: symmetrical stretching vibration of CO_2 in Raman spectrum shows bands at 1337cm-1. The 2 bonding vibrations are equivalent & absorb at the same frequency of 667.3cm-1.
- The first overtone of this is 1334.6cm-1
- Fermi resonance occurs. • There is mixing of 1337.6cm 1 with intensity ratio 1:0.9 respectively.

d) Hydrogen bonding:

- It occurs in any system containing a proton donor group (X-H) & a proton acceptor.
- The stronger the hydrogen bond, the longer the O-H bond, the lower the vibration frequency & broader & more intense will be absorption band.
- The N-H stretching frequencies of amines are also affected by hydrogen bonding as that of hydroxyl group but frequency shifts for amines are lesser than that for hydroxyl compounds.
- Because nitrogen is less electronegative than oxygen so hydrogen bonding in amines is weaker than that in hydroxyl compounds.
- Intermolecular hydrogen bond gives rise to broad bands, while intramolecular hydrogen bonds give sharp & well defined bands.
- The inter & intra molecular hydrogen bonding can be distinguished by dilution.
- Intramolecular hydrogen bonding remains unaffected on dilution & as a result the absorption band also remains unaffected where as in intermolecular, bonds on dilution & as a result there is decrease in bonded O-H absorption.
- The strength of hydrogen bonding is also affected by:
  i) Ring strain
  ii) Molecular geometry
  iii) Relative acidity & basicity of proton donor & acceptor groups

e) Electronic effect:

- Changes in absorption frequencies for a particular group take place when the substituents in the neighbourhood of that particular group are changed. It includes:
  i) Inductive effect
  ii) Mesomeric effect
  iii) Field effect

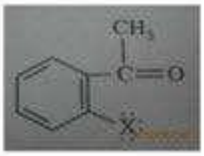
iv) Inductive effect-

- The introduction of alkyl group causes +I effect which results in lengthening or weakening of bond.
- Hence the force constant is lowered & wave number of absorption decreases.
- Let compare wave numbers of (C=O) absorptions for following compounds:
    a. Formaldehyde (HCHO)1750cm-1
    b. Acetaldehyde (CH3CHO) 1745cm-1
    c. Acetone (CH3COCH3) 1715cm-1
- Introduction of an electronegative atom or group causes –I effect which results in bond order to increase
- Hence force constant increases & wave number of absorption rises.

Mesomeric effect-

- It causes lengthening of weakening of a bond leading in lowering of absorption frequency.

- As nitrogen atom is less electronegative than oxygen atom, the electron pair on nitrogen atom in amide is more labile & participates more in conjugation.
- Due to this greater degree of conjugation, the C=O absorption frequency is much less in amides as compared to that in esters.
- Field effect-
- In ortho substituted compounds, the lone pair of electrons on 2 atoms influences each other through space interactions & changes the vibrational frequencies of both groups.
- This effect is called field effect.



Ortho halo acetophenone

VI. APPLICATIONS

1. Identification of functional group and structure elucidation

- Entire IR region is divided into group frequency region and fingerprint region. Range of group frequency is 4000-1500 cm-1 while that of finger print region is 1500-400 cm-1.
- In group frequency region, the peaks corresponding to different functional groups can be observed. According to corresponding peaks, functional group can be determined.
- Each atom of the molecule is connected by bond and each bond requires different IR region so characteristic peaks are observed. This region of IR spectrum is called as finger print region of the molecule. It can be determined by characteristic peaks.

Sr. No.	Functional Group	Characteristic Absorption(s) (cm^{-1})
1	Alkyl C-H Stretch	2950 - 2850 (m or s)
2	Alkenyl C-H Stretch Alkenyl C=C Stretch	3100 - 3010 (m) 1680 - 1620 (v)
3	Alkynyl C-H Stretch Alkynyl C≡C Stretch	~3300 (s) 2260 - 2100 (v)
4	Aromatic C-H Stretch Aromatic C-H Bending Aromatic C=C Bending	~3030 (v) 860 - 680 (s) 1700 - 1500 (m,m)
5	Alcohol/Phenol O-H Stretch	3550 - 3200 (broad, s)
6	Carboxylic Acid O-H Stretch	3000 - 2500 (broad, v)
7	Amine N-H Stretch	3500 - 3300 (m)
8	Nitrile C≡N Stretch	2260 - 2220 (m)
9	Aldehyde C=O Stretch Ketone C=O Stretch Ester C=O Stretch Carboxylic Acid C=O Stretch Amide C=O Stretch	1740 - 1690 (s) 1750 - 1680 (s) 1750 - 1735 (s) 1780 - 1710 (s) 1690 - 1630 (s)
10	Amide N-H Stretch	3700 - 3500 (m)

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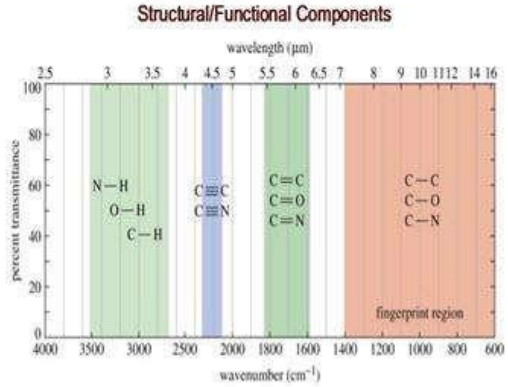
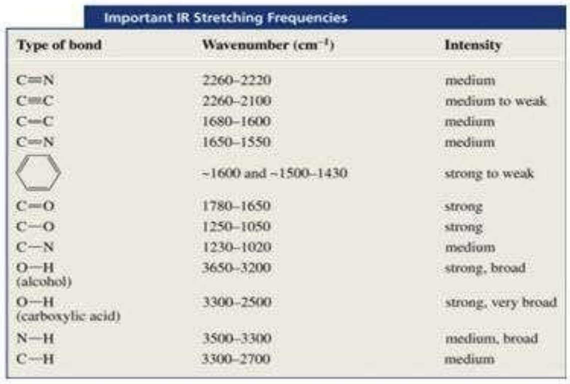
Table 1: IR Absorption

2. Identification of substances

- IR spectroscopy is used to establish whether a given sample of an organic substance is identical with another or not. This is because large number of absorption bands is observed in the IR spectra of organic molecules and the probability that any two compounds will produce identical spectra is almost zero. So if two compounds have identical IR spectra then both of them must be samples of the same substances.
- IR spectra of two enantiomeric compound are identical. So IR spectroscopy fails to distinguish between enantiomers.
- Criteria: sample & reference must be tested in identical conditions like physical state, temperature, solvent, etc.
- For example, an IR spectrum of benzaldehyde is observed as follows.
- C-H stretching of aromatic ring- 3080 cm-1
- C-H stretching of aldehyde- 2860 cm-1 and 2775 cm-1
- C=O stretching of an aromatic aldehyde- 1700 cm-1
- C=C stretching of an aromatic ring- 1595 cm-1
- C-H bending- 745 cm-1 and 685 cm-1

- No other compound then benzaldehyde produces same IR spectra as shown above.
- The Fingerprint Region (1200 to 600cm-1):
- Small differences in structure & constitution of molecule result in significant changes in the peaks in this region.
- Hence this region helps to identify an unknown compound.





Important IR Stretching Frequencies

Type of bond	Wavenumber (cm^{-1})	Intensity
C≡N	2260–2220	medium
C≡C	2260–2100	medium to weak
C═C	1680–1600	medium
C═N	1650–1550	medium
	~1600 and ~1500–1430	strong to weak
C═O	1780–1650	strong
C—O	1250–1050	strong
C—N	1230–1020	medium
O—H (alcohol)	3650–3200	strong, broad
O—H (carboxylic acid)	3300–2500	strong, very broad
N—H	3500–3300	medium, broad
C—H	3300–2700	medium

- Computer Search System:
- Newer IR instruments offer computer search systems to identify compounds from stored infrared spectral data.
- The position & magnitudes of peaks in the spectrum is compared with profile of pure compounds stored.
- Computer then compares profiles similar to that of the analyte & result is displayed.

Selection Rules of IR

In order for vibrational transitions to occur, they are normally governed by some rules referred to as selection rules.

1. An interaction must occur between the oscillating field of the electromagnetic radiation and the vibrational molecule for a transition to occur. This can be expressed mathematically as
   $(d\mu/dr)req\neq0$
   ov=+1 and oJ=+1
2. This holds for a harmonic oscillator because the vibrational levels are equally spaced and that accounts for the single peak observed in any given molecular vibration. For gases J changes +1 for the R branch and -1 for the P branch. oJ=0oJ=0 is a forbidden transition and hence a q branch for a diatomic will not be present. For any anharmonic oscillator, the selection rule is not followed and it follows that the change in energy becomes smaller.

This results in weaker transitions called overtones, then ον=+2ον=+2 (first overtone) can occur, as well as the 2nd overtone ον=+3ον=+3. The frequencies of the 1st and 2nd overtones provides information about the potential surface and about two to three times that of the fundamental frequency.

2. For a diatomic, since μμ is known, measurement of u_e provides a value for k, the force constant.
3. $k=(d^2V(r)/dr^2)$ req

where k is the force constant and indicates the strength of a bond.

Functional Group Identification – "Fingerprinting"

- Some groups give rise to distinctive frequencies no matter what molecule they are incorporated into, e.g. C=O stretch in metal carbonyls.
- Terminal = 1850-2125cm-1 Bridging = 1700-1860cm-1 (weaker due to back bonding)
- Fundamental associated with a specific group may be identified by their characteristic solvent variations.
- When the group vibration approach fails the most likely reason is Coupling and then the full vibrational analysis approach must be performed.
- Successful Group Vibrational analysis is typically with v > 1200cm-1. Vibrations with v < 1200cm-1 typically involve large parts of the molecule.
- Comparison with standard spectra allows identification of substances. Especially useful for more complex molecules with overlapping group vibrations.
- Identifies impurities (especially IR which is very sensitive).

Vibrational Spectra of polyatomic molecule

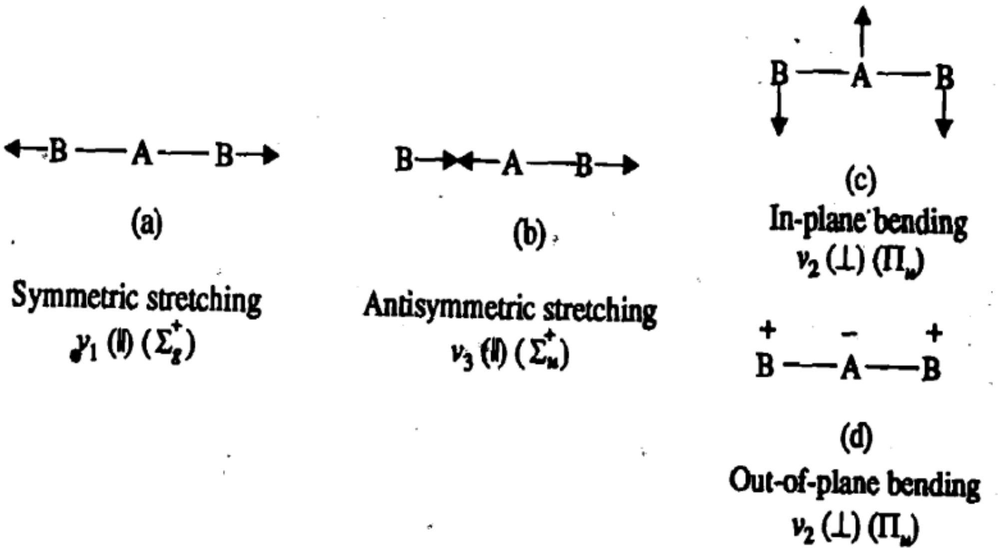
We have already seen in Unit 4 that a diatomic molecule has only one fundamental lku molecule an (3N-S). vibration or one vibrational coordinate. This arises due to the stretching and compres Gon of the bond connecting two atoms just like a spring (see Fig. 3.1 of Unit 3). Let us cdculate the vibrational degrees of freedom of a polyatomic molecule. First let us assume that each atom is free to move in three perpendicular directions (along x, y, and z axes) and thus has three degrees of freedom. The degrees of freedom are the number of directions in which an atom can move freely independent of other atoms in the molecule. Hence, for a molecule containing N atoms, the total degrees of freedom is 3N. We know that a molecule has translatigpal, rotational and vibrational motions. A molecule can have only three degrees of translational motion since centre of mass of the molecule can move only along three axial directions. That is, the whole molecule can mov$ along the three axes. In addition, when the molecule is nonlinear, there are three degree5 of freedom due to rotational motions about the three axes. Therefore, there remaid 3N - (3 +3) = (3N4) coordinates which account for vibrational degrees of freedom for nonlinear polyatomic molecules. For a linear molecule, there are two rotational degrees'of freedom as the rotations (Total degrees of freedom) - about two axes perpendicular to.internuclear bond axis only are allowed. The rotation (translational degrees of freedom +about the internuclear axis is not possible since the moment of inertia along the rotational delprcsof fmcdom) = internuclear axis is zero. Therefore a linear molecule possesses Vibntionaldegrea of frdom. 3N-(3 + 2) = (3N-5)vibrational degrees of freedom. Using Table 5.1, can you state the vibrational degrees of freedom of C02, H20 and NH3 molecules? It is worth recollecting that C02 is linear, H20 is angular and NH3 is pyramidal.C02 molecule has (3 x 3 -a= 4 vibrational degrees of freedom; H20 molecule has (3 x 3 - 6) = 3 vibrational degrees of freedom and Nq molecule has (3 x 4 - 6) = 6 vibrational degrees of freedom

Normal Modes Vibrations

A molecule can vibrate only in certain modes, known as normal modes. Each normal mode corresponds to a vibrational degree of freedom. A normal mode is an independent simultaneous motion of atoms or group of atoms that may be excited without leading to the excitation of any other normal mode. In general, a normal vibration is one in which all atoms in a molecule vibrate at the same frequency and in phase with each other.

(i) stretching vibrations

(ii) bending vibrations, the linear and nonlinear molecules have (N-1) stretching vibrations. The bending vibrations for linear and nonlinear molecules are (2N-4) and (2N-S), respectively.



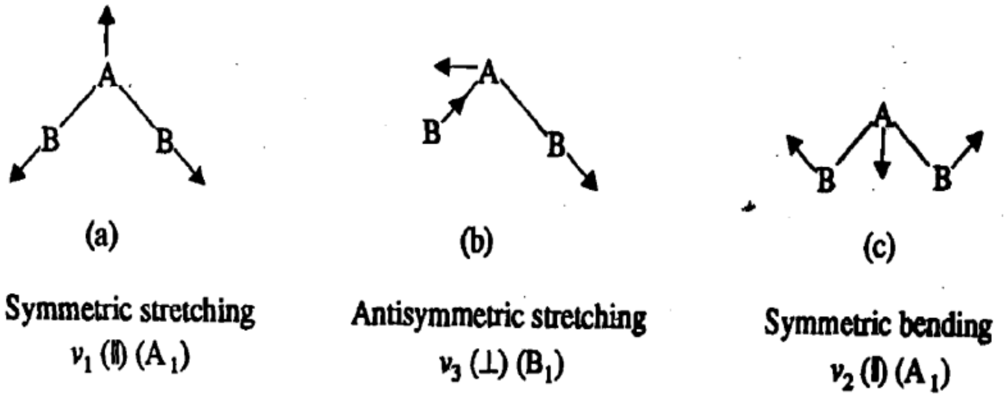
(a) Symmetric stretching ν_1 (∥) (Σ_g^+)

(b) Antisymmetric stretching ν_3 (∥) (Σ_u^+)

(c) In-plane bending ν_2 (⊥) (Π_u)

(d) Out-of-plane bending ν_2 (⊥) (Π_u)

Fig.5.1: **Normal modes of vibration of a triatomic linear molecule, AB_2 (e.g., CO_2). (a) symmetric stretching (ν_1) (b) antisymmetric stretching (ν_3) (c) in-plane bending and (d) out-of-plane bending ; both (c) and (d) are degenerate and hence these two give rise to only one band (ν_2);(+) sign shows that the atom is going above the plane while (–) sign indicates that the atom is going below the molecular plane. The ν_1 and ν_3 vibrations are parallel (∥) vibrations whereas the degenerate vibration ν_2 is a perpendicular (⊥) vibration.**



(a) Symmetric stretching ν_1 (∥) (A_1)

(b) Antisymmetric stretching ν_3 (⊥) (B_1)

(c) Symmetric bending ν_2 (∥) (A_1)

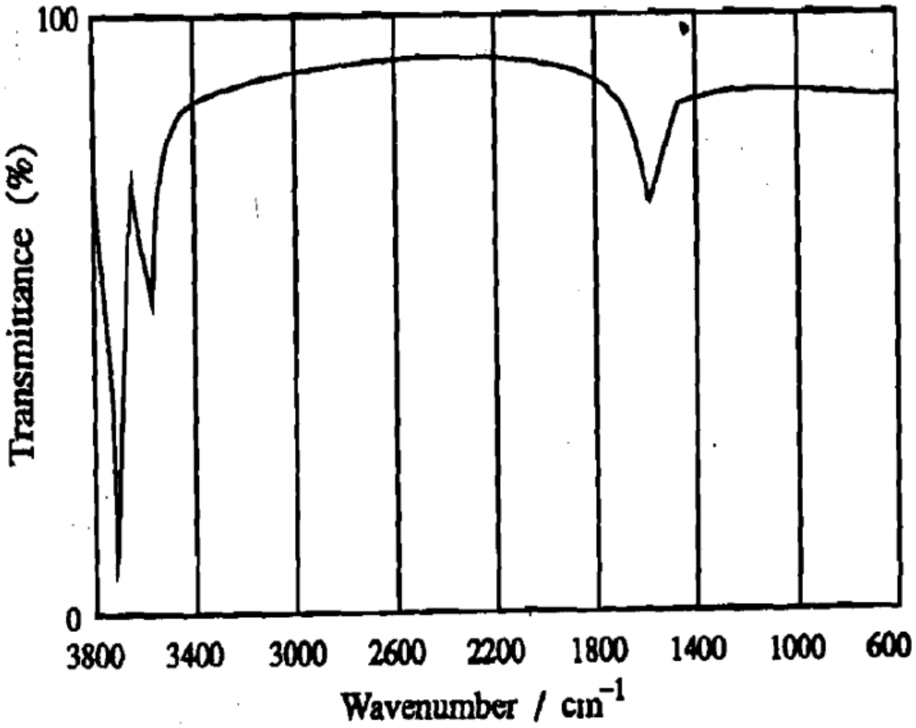
Fig.5.2: **Normal modes of vibrations of a triatomic angular molecule, AB_2 (e.g., H_2O). (a) symmetric stretching (ν_1) (b) antisymmetric stretching (ν_3) (c) symmetric bending (ν_2). ν_1 and ν_2 are parallel vibrations whereas ν_3 is a perpendicular vibration.**

In stretching vibrations, the atoms move along the bond axis so that the bond length increases or decreases at regular intervals. The stretching vibrations again are of two types. They are symmetric and antisymmetric stretchings. In symmetric stretching of a triatomic molecule, both the bonds connected to a common atom can simultaneously either elongate or contract. In the case of antisymmetric stretching, if one bond is lengthened, the other bond is shortened or, vice versa. These stretchings are shown in Figs. 5.la and b and Figs. 5.2a and b for linear and angular molecules of the type AB2. The arrows attached to each atom show the direction of its motion during half of the vibration. In Figs. 5.1 and 5.2, we indicate the type of each vibration mode as parallel (1l) or perpendicular (I). In a parallel vibration, the dipole change takes place along the line of the principal axis of symmetry. In a perpendicular vibration, the dipole change takes place perpendicular to the line of the principal axis of symmetry. The nature of vibration-rotation spectra of polyatomic molecules depends on the type of vibration - parallel or perpendicular. We shall discuss this in Sec. 5.3.4.

The bending vibrations occur when there is a change in bond angle between bonds connected to a common atom. In some cases, the movement of a group of atoms with respect to the remaining atoms in the molecule also causes bending vibrations and d) while a nonlinear triatomic molecule has only one bending vibration (5.2 c). Thus for a linear triatomic molecule (e.g., COJ, we could expect four vibrational modes, two stretching and two bending. Both these bending vibrations are identical in Depnerary of a vibrational mode all respects except the direction. Such vibrations have same frequency (and energy) is the number of normal modes and, are said to be degenerate. For instance, the two bending vibrations of C02 are which have same energy. For degenerate. As a result of this, only three absorption bands are found for C02 - two instance, the degeneracy of y corresponding to the stretching vibrations and one to the bending vibration. A mode Of '02 is two the two nonlinear angular triatomic molecule (e.g., H2O) also has three vibrational modes, two beading modes (in-plane and out of-plane) have same energy. being due to the stretching modes and one due to the bending mode. The difference between the linear and nonlinear triatomic molecules lies in the degeneracy of the bending mode of the former

IR Spectrum of H_2O Molecule

As mentioned in the last section, water, a nonlinear molecule, has three normal modes of vibrations. Fig.5.3 shows the IR spectrum of water in an inert solvent



We can notice two sharp bands at higher frequency region (at 3756 cm-' and 3652 cm-l) and one sharp band at lower frequency region (at 1595 cm-I). Group theory can be used in assigning vibrational modes to the observed IR absorption frequencies. Two examples (H@ and NH3) are discussed in the Appendix part of this unit. The frequencies at 3652 cm-I, 1595 cm-I and 3756 cm-I are associated with symmetric stretching, symmetric bending and antisymmetric stretchinn modes, respectively. All the three vibrations are associated with a change in dipole moment, wh3ch is a necessary condition for a vibration to be infrared active. It is also possible to draw vibrational energy level diagram corresponding to these three bands as in Fig. 5.4. The quantum numbers for each of the vibrational levels are shown below vl, v2 andv3. The quantum number notation is useful in identifying each of the energy sublevels. For instance, '000' means vl = v2 = v3 = 0; '010' means vl = 0, v2 = 1 and v3 = 0; ‘020' means vl = 0, v2 = 2 andv3 = 0 and so on. The notation mW means that the You can see that the wave number corresponding to the energy difference between isin tbevib*tiOnalenerW lcwl given by the qu~hun nwnb y E(100) and E(O00) is 3652cm-' ; the wave number corresponding to the energy (mo). difference between E(010) and E(000)is 1595 cm-l and the wave number corresponding to the energy difference between E(001)and E(000)is 3756 cm-l. The three vibrational modes which are associated with the three IR bands are similar to those shown in Fig.52.

IR Spectrum of CO2 Molecule

Among the four vibrations shown in Fig.5.1 for a triatomic linear molecule such as C02, the IR active vibrations are antisymmetric stretching (v3) and bending (vs but 2349 an-' not the symmetric stretching(vl) since it does not cause any change in the dipole (001) moment. The two IR bands of C02 at 2349cm-I and 667 cm-' correspond to v3 and v2 respectively. The band due to symmetric stretching (vl) at 1340 cm-' is not observed in IR spectrum. However the stretching band is Raman active. In the case of 1388 can-1 C02, the first overtone of v2 i.e., 2v2 (2 x 667 cm-' = 1334 cm-I) has the same rF symmetry as the symmetric stretching mode and hence interacts with this fundamental: vibration due to Fermi resonance giving rise to two bands. These two bands are not inokl :' observable in IR spectrum but both are observable in Raman spectrum which will be (loo) discussed in the next unit. In fact, the Raman spectrum shows two bands at 1388 and 1334 an-' 1286 cm-I; the mean of these two values (1337 cm-') is close to vl and 2v2. The (020), overtone 2v2 which would normally be weak borrows intensity from the fundamental \ , 1286m-i vl, and hence, two bands are observable in Raman spectrum. Earlier we stated the formula for the quantum mechanical vibrational energy of poly - atomic molecules. We can calculate the quantum mechanical vibrational energy of a - linear polyatomic molecule by carrying out summation over (3N-5)terms. But we leave .i it to you as an exercise in SAQ 2.

UNIT– II

SPECTROSCOPY- II

Introduction

Raman spectroscopy is another form of spectroscopy, which is used for structure determination. Unlike the other techniques, it is based on the scattering of light. When a beam of monochromatic radiation passes through a liquid or gas, it might be transmitted, absorbed or scattered. In the case of light scattering, nearly all of the scattered light is observed at the same frequency as the incident light (a phenomenon known as elastic or Rayleigh scattering). However, the great Indian physicist Sir C.V. Raman observed in 1928 that some of the scattered light also has discrete frequencies above and below the incident frequency. This phenomenon is known as inelastic or Raman Scattering. The Raman Effect comprises a very small fraction, about 1 in 107, of the incident photons. A powerful laser source in the visible or UV region is used as the light source. Figure 1 shows Rayleigh and Raman scattering. The lines at lower frequency than the incident radiation are known as Stokes lines, and those at higher frequency are called anti-Stokes lines.

Raman active is the molecular polarizability, which is a measure of the ease with which the electron cloud in a molecule can be distorted. This rule should be contrasted with that for IR and microwave activity, which states that the molecular motion must produce a change in the electric dipole of the molecule. Thus, Raman spectroscopy can be used on species with no dipole moment, e.g. H_2, Cl_2, etc., thus complementing microwave spectroscopy.

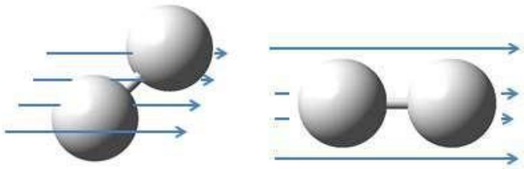
The Classical Theory of the Raman Effect (Molecular Polarizability)

When a static field is applied on a molecule, a polarization of charge takes place, the positively charged nuclei getting attracted to the negative pole of the field, and the electronic cloud to the positive pole. A dipole is induced in the molecule, even if it has no dipole moment initially, and the molecule is said to be polarized. The induced electric dipole moment, μ_{ind}, depends on both the magnitude of the applied field, E, and the ease with which the electron cloud of the molecule can be distorted.

Thus, $\mu_{ind} = \alpha E$ (1) where α is the polarizability of the molecule.

The polarizability is anisotropic, which means that the induced dipole moment is not the same in all directions. The polarizability is greater along the bond axis than across it since it is difficult to polarize in a direction perpendicular to the internuclear axis. The polarizability in various directions is conveniently represented by drawing a polarizability ellipsoid. The ellipsoid is a three dimensional surface whose distance from the electrical centre of the molecule is proportional to $1/\sqrt{\alpha_i}$, where α_i is the polarizability along the line joining point I on the ellipsoid with the electrical centre. Thus, where the polarizability is greatest, the axis of the ellipsoid is least (it is the minor axis of the ellipsoid).

Since the polarizability of a diatomic molecule is the same in all directions at right angles to the bond axis, the ellipsoid has a circular cross section in these directions (Fig. 2).



When a sample of diatomic molecules is subjected to a beam of radiation of frequency v, the electric field experienced by each molecule varies as follows: $E = E_0 \sin 2\pi \nu t$, (2) A time-dependent dipole moment is, therefore, induced in the molecule: $\mu ind = \alpha E = \alpha E0sin2\pi\nu t$ (3) where E0 is the strength of the applied field.

According to electromagnetic theory, an oscillating dipole emits radiation whose frequency is the same as its oscillation frequency. Equation (3) is, therefore, the classical explanation of Rayleigh scattering.

If, in addition, the molecule undergoes some internal motion, such as a vibration or a rotation, which changes the polarizability periodically, then the oscillating dipole will have superimposed upon the vibrational or rotational oscillation. The oscillating dipole has frequency $\nu \pm \nu vib$ as well as the exciting frequency v. It should be noted that if the vibration or rotation does not change the polarizability of the molecule, the dipole oscillates only at the frequency of the incident radiation.

Thus, we have the selection rule:

"In order to be Raman active, a molecular rotation or vibration must cause some change in a component of the molecular polarizability". A change in polarizability is reflected by a change in either the magnitude or direction of the polarizability ellipsoid.

4. The Quantum Theory of the Raman Effect

According to the Quantum Theory, radiation of frequency v can be pictured as a stream of particles (called photons) each having energy hv. These photons are imagined to undergo either inelastic or elastic collisions with molecules. Inelastic collisions result in energy exchange between the photon and the molecule, while elastic collisions result in no energy exchange at all.

If the molecule gains energy ΔE from the photon, the photon will be scattered with energy (hv - ΔE) and with frequency (v - ΔE/h). If, however, the molecule loses energy ΔE to the incident radiation, the scattered radiation will have a frequency of (v + ΔE/h). Radiation scattered with a frequency lower than that of the incident radiation is known as Stokes radiation, while that of a higher frequency is anti-Stokes radiation. Rayleigh scattering is the situation where the scattered radiation has the same frequency as the incident radiation (see Fig. 1).

NMR SPECTROSCOPY

1. INTRODUCTION

The interaction between the nuclei and the radiofrequency radiation is called nuclear magnetic resonance (NMR) spectroscopy. The nuclei of certain atoms or molecules are considered to be spin. In the absence of external magnetic field, the spin states of the nuclei are degenerate. (i.e) possess the equal energy levels. In the presence of external magnetic field, the degeneracy is removed and separate energy levels are possible. The nuclear transition between these energy levels can occur by the absorption of radio frequency radiation. Nuclear Magnetic Resonance spectroscopy is a powerful and theoretically complex analytical tool. On this page, we will cover the basic theory behind the technique. It is important to remember that, with NMR, we are performing experiments on the **nuclei** of atoms, not the electrons. The chemical environment of specific nuclei is deduced from information obtained about the nuclei.

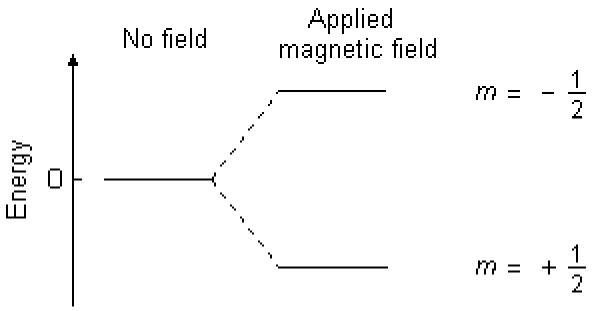
2. Nuclear spin and the splitting of energy levels in a magnetic field

Subatomic particles (electrons, protons and neutrons) can be imagined as spinning on their axes. In many atoms (such as ^{12}C) these spins are paired against each other, such that the nucleus of the atom has no overall spin. However, in some atoms (such as ^{1}H and ^{13}C) the nucleus does possess an overall spin. The rules for determining the net spin of a nucleus are as follows;

1. If the number of neutrons **and** the number of protons are both even, then the nucleus has **NO** spin.
2. If the number of neutrons **plus** the number of protons is odd, then the nucleus has a half-integer spin (i.e. 1/2, 3/2, 5/2)
3. If the number of neutrons **and** the number of protons are both odd, then the nucleus has an integer spin (i.e. 1, 2, 3)

The overall spin, I, is important. Quantum mechanics tells us that a nucleus of spin I will have 2I + 1 possible orientations. A nucleus with spin 1/2 will have 2 possible orientations. In the absence of an external magnetic field, these orientations are of equal energy. If a magnetic field is applied, then the energy levels split. Each level is given a magnetic quantum number, m.

Energy levels for a nucleus with spin quantum number 1/2



When the nucleus is in a magnetic field, the initial populations of the energy levels are determined by thermodynamics, as described by the Boltzmann distribution. This is very important, and it means that **the lower energy level will contain slightly more nuclei than the higher leve**l. It is possible to excite these nuclei into the higher level with electromagnetic radiation. The frequency of radiation needed is determined by the difference in energy between the energy levels.

3. Condition for NMR spectra:

The nuclei with a resultant nuclear spin are magnetically active and produces NMR spectra. The nuclear spin is described by the spin quantum number, I. The condition for the nuclei which exhibits NMR spectra have I > 0. The value of I for different nuclei can be predicted by the following empirical values,

i) Nuclei having even number of protons and neutrons have zero value of I. Example : ^{4}He, ^{12}C, ^{16}O and ^{32}S have I = 0. They are non magnetic and NMR inactive.

ii) Nuclei having odd number of protons and neutrons have integral value of I. Example $^{2}H$and ^{14}N have I = 1. They are magnetic and NMR active.

iii) Nuclei having odd value for the sum of protons and neutrons have half integral value of I. Example ^{1}H, ^{13}C, ^{15}N, ^{19}F and ^{31}P have I = ½. They are magnetic and NMR active.

At a time only one type of nucleus is used in NMR spectroscopy.

Example: all ^{1}H or ^{13}C or ^{19}F nuclei.

The ^{1}H (proton) nucleus is most commonly studied by NMR spectroscopy because of its high natural abundance (99.98%). Also proton is invariably present in the majority of organic compounds. Hence NMR spectroscopy is also known as proton compounds. Hence NMR spectroscopy is also known as proton magnetic resonance (PMR) or ^{1}H NMR spectroscopy.

Calculating transition energy

The nucleus has a positive charge and is spinning. This generates a small magnetic field. The nucleus therefore possesses a magnetic moment, μ, which is proportional to its spin,I.

$$\mu = \frac{\gamma I h}{2\pi}$$

The constant, μ, is called the magnetogyric ratio and is a fundamental nuclear constant which has a different value for every nucleus. h is Planck's constant. The energy of a particular energy level is given by;

Where B is the strength of the magnetic field **at the nucleus**.

The difference in energy between levels (the transition energy) can be found from

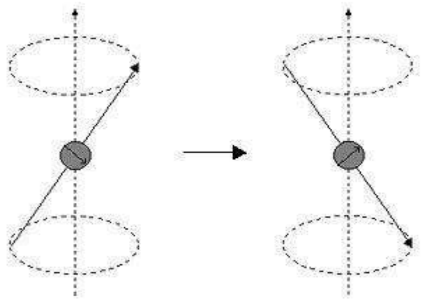
$$\Delta E = \frac{\gamma h B}{2\pi}$$

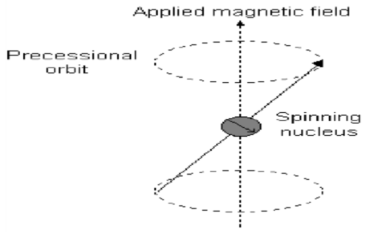
This means that if the magnetic field, B, is increased, so is ΔE. It also means that if a nucleus has a relatively large magnetogyric ratio, then ΔE is correspondingly large. If you had trouble understanding this section, try reading the next bit (The absorption of radiation by a nucleus in a magnetic field) and then come back.

The absorption of radiation by a nucleus in a magnetic field

In this discussion, we will be taking a "classical" view of the behaviour of the nucleus - that is, the behaviour of a charged particle in a magnetic field. Imagine a nucleus (of spin 1/2) in a magnetic field. This nucleus is in the lower energy level (i.e. its magnetic moment does not oppose the applied field). The nucleus is spinning on its axis. In the presence of a magnetic field, this axis of rotation will precess around the magnetic field.

Larmor Precession





The phenomenon of nuclear magnetic resonance can also be explained by the scientist Larmor called larmor precession. When a magnetic nucleus is placed perpendicularly in an external magnetic field of strength, BZ, it spins on its own axis. This is called Larmor precession (fig. 3). The angular frequency of the precession is known as Larmor frequency (ω) and it is directly proportional to the strength of the magnetic field BZ.

$\omega \alpha$ BZ $\omega = \gamma BZ$

where γ is the gyromagnetic ration of the nucleus. It is defined as the ratio of the nuclear magnetic moment μ and the nuclear spin angular momentum.

$I (h/2n\pi)$ i.e. $\gamma = \mu/I (h/2\pi)$ $(T\text{-}^{1}\ s^{-1})$

The frequency of precession is termed the Larmor frequency, which is identical to the transition frequency. The potential energy of the precessing nucleus is given by; $E = - \mu B \cos \theta$ where θ is the angle between the direction of the applied field and the axis of nuclear rotation. If energy is absorbed by the nucleus, then the angle of precession, θ, will change. For a nucleus of spin 1/2, absorption of radiation "flips" the magnetic moment so that it opposes the applied field (the higher energy state). It is important to realise that only a small proportion of "target" nuclei are in the lower energy state (and can absorb radiation). There is the possibility that by exciting these nuclei, the populations of the higher and lower energy levels will become equal. If this occurs, then there will be **no** further absorption of radiation. The spin system is saturated. The possibility of saturation means that we must be aware of the relaxation processes which return nuclei to the lower energy state.

4. Relaxation processes

How do nuclei in the higher energy state return to the lower state? Emission of radiation is insignificant because the probability of re-emission of photons varies with the cube of the frequency. At radio frequencies, re-emission is negligible. We must focus on non-radiative relaxation processes (thermodynamics!). Ideally, the NMR spectroscopist would like relaxation rates to be fast - but not too fast. If the relaxation rate is fast, then saturation is reduced. If the relaxation rate is too fast, linebroadening in the resultant NMR spectrum is observed. There are two major relaxation processes;

- Spin - lattice (longitudinal) relaxation
- Spin - spin (transverse) relaxation

5. 1Spin - lattice relaxation

Nuclei in an NMR experiment are in a sample. The sample in which the nuclei are held is called the lattice. Nuclei in the lattice are in vibrational and rotational motion, which creates a complex magnetic field. The magnetic field caused by motion of nuclei within the lattice is called the lattice field. This lattice field has many components. Some of these components will be equal in frequency and phase to the Larmor frequency of the nuclei of interest. These components of the lattice field can interact with nuclei in the higher energy state, and cause them to lose energy (returning to the lower state). The energy that a nucleus loses increases the amount of vibration and rotation within the lattice (resulting in a tiny rise in the temperature of the sample). The relaxation time, T_1 (the average lifetime of nuclei in the higher energy state) is dependent on the magnetogyric ratio of the nucleus and the mobility of the lattice. As mobility increases, the vibrational and rotational frequencies increase, making it more likely for a component of the lattice field to be able to interact with excited nuclei. However, at extremely high mobilities, the probability of a component of the lattice field being able to interact with excited nuclei decreases

4 .2 Spin - spin relaxation

Spin - spin relaxation describes the interaction between neighbouring nuclei with identical precessional frequencies but differing magnetic quantum states. In this situation, the nuclei can exchange quantum states; a nucleus in the lower energy level will be excited, while the excited nucleus relaxes to the lower energy state. There is no **net** change in the populations of the energy states, but the average lifetime of a nucleus in the excited state will decrease. This can result in line-broadening.

Chemical shift

The magnetic field at the nucleus is not equal to the applied magnetic field; electrons around the nucleus shield it from the applied field. The difference between the applied magnetic fieldand the field at the nucleus is termed the nuclear shielding. Consider the s-electrons in a molecule. They have spherical symmetry and circulate in the applied field, producing a magnetic field which opposes the applied field. This means that the applied field strength must be increased for the nucleus to absorb at its transition frequency. This upfield shift is also termed diamagnetic shift. Electrons in p-orbitals have **no** spherical symmetry. They produce comparatively large magnetic fields at the nucleus, which give a low field shift. This "DE shielding" is termed paramagnetic shift. In proton (^{1}H) NMR, p-orbitals play no part (there aren't any!), which is why only a small range of chemical shift (10 ppm) is observed. We can easily see the effect of s-electrons on the chemical shift by looking at substituted methane, CH_3X. As X becomes increasingly electronegative, so the electron density around the protons decreases, and they resonate at lower field strengths (increasing Δ_H values).

Chemical shift is defined as nuclear shielding / applied magnetic field.

Chemical shift is a function of the nucleus and its environment. It is measured relative to a reference compound. For ^{1}H NMR, the reference is usually tetramethyl lsilane, Si (CH3)4. The difference between the magnitudes of the magnetic field at which free nuclei and molecular nuclei resonate is called chemical shift. When an atom or molecule is placed in a magnetic field, the surrounding electron cloud induces a magnetic field at the nucleus will be slightly different from the applied field. The induced field is directly proportional to the strength of the applied field.

$B_{ind} \alpha\ B_{applied}$

$B_{ind} = \ | |B_{applied}$

where | | - shielding constant of screening constant.

The effective field strength experienced by the proton is

$B_{eff} = B_{applied} - B_{ind}$

$= B0 - | |\ B0$

$B_{eff} = B0\ (1 - | |)$ .... (2)

For two nuclei A and B,
BB = B0 (1- | | B) .... (3)
BA = B0 (1- | || |A) .... (4)
The difference is
BB – BA = B0 (1- | || |B) – [B0 (1 -
= B0 – B0| | |B – B0 + B0| || |A
= B0 – (| |A –| | B)
BB – BA = B0| |AB.......................... (5)

where AB is chemical shift of nucleus A with respect to B
| || |AB | | B B | |B A
B0.......................... (6)

The chemical shift can also be expressed in terms of frequency.
10 ppm

| | AB | | v B | |v A X 10^{6} PPM
v0
| | AB | | v Sample | |v reference X 10^{6} PPM.......................... (6)
v0
Reason for TMS used as a reference :

Tetra methyl silane (TMS) is used as reference compound in NMR, because,

i) It has 12 equivalent protons and gives a single sharp peak in its NMR spectrum.
ii) It has low boiling point 27ºC.
iii) It is chemically inert & non voluble.
iv) It is soluble in most of the organic solvents.
v) Its signal is appeared at the extreme end of the spectrum

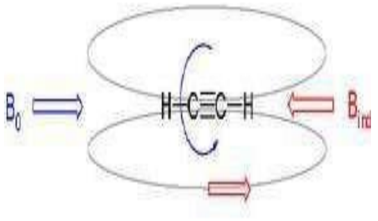
Factors affecting chemical shifts

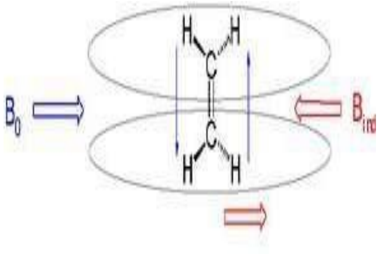
Important factors influencing chemical shift are electron density, electronegativity of neighbouring groups and anisotropic induced magnetic field effects.

Electron density shields a nucleus from the external field. For example, in proton NMR the electron-poor tropyliumion has its protons downfield at 9.17

ppm, those of the electron rich cyclooctatetraenylanion move upfield to 6.75 ppm and its dianion even more upfield to 5.56 ppm. A nucleus in the vicinity of an **electronegative_atom** experiences reduced electron density and the nucleus is therefore deshielded. Inproton NMR of methyl halides(CH_3X) the chemical shift of the methyl protons increase in the order I < Br < Cl < F from 2.16 ppm to 4.26 ppm reflecting this trend. Incarbon NMRthe chemical shift of the carbon nuclei increase in the same order from around –10 ppm to 70 ppm. Also when the electronegative atom is removed further away the effect diminishes until it can be observed no longer.

Anisotropic induced magnetic field effects are the result of a local induced magnetic field experienced by a nucleus resulting from circulating electrons that can either be paramagnetic when it is parallel to the applied field or diamagnetic when it is opposed to it. It is observed in alkeneswhere the double bond is oriented perpendicular to the external field with pi electrons likewise circulating at right angles. The **induced magnetic field** lines are parallel to the external field at the location of the alkene protons which therefore shift downfield to a 4.5 ppm to 7.5 ppm range. The three-dimensional space where a nucleus experiences diamagnetic shift is called the shielding zone with a cone-like shape aligned with the external field.





The protons inaromaticcompounds are shifted downfield even further with a signal forbenzeneat 7.73 ppm as a consequence of adiamagnetic ring current. Alkyneprotons by contrast resonate at high field in a 2–3 ppm range. For alkynes the most effective orientation is the external field in parallel with electrons circulation around the triple bond. In this way the acetylenic protons are located in the cone-shaped shielding zone hence the upfield shift.

Screening constant '□'

It is a dimensionless quantity. The value of |depends on the electron density around the proton (Fig. 4). Acetaldehyde has two types of protons CHO and CH_3protons. The three protons in $CH_3$are equivalent. Since the oxygen is more electronegative the electron density around the proton in CHO is less than that around the CH_3 proton.

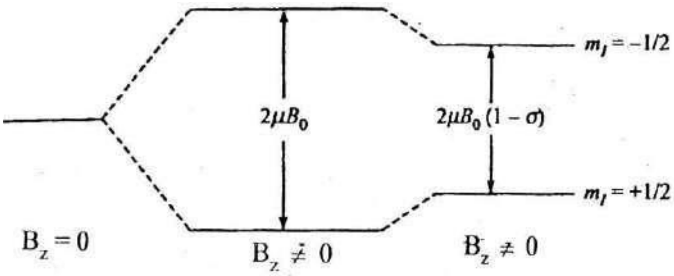


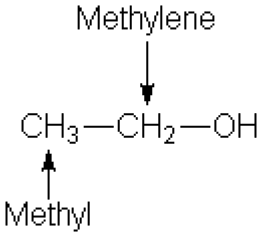
Fig 4. Bare and screened, spin ½ nucleus in B_Z

Therefore, the screening is more for the methyl protons.

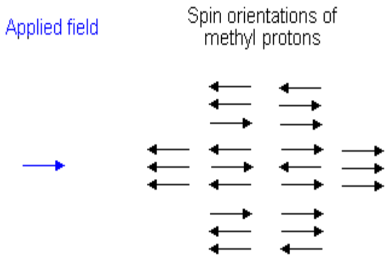
□CHO<□CH_3

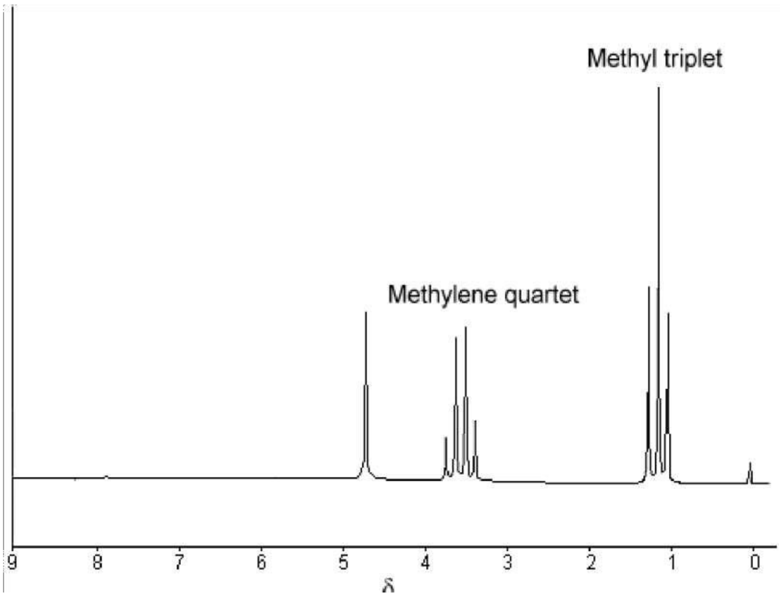
4.3.7 Spin - spin coupling

Consider the structure of ethanol;

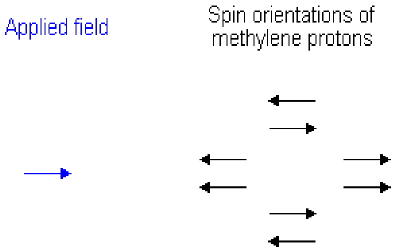


The ^1H NMR spectrum of ethanol (below) shows the methyl peak has been split into three peaks (a triplet) and the methylene peak has been split into four peaks (a quartet). This occurs because there is a small interaction (coupling) between the two groups of protons. The spacings between the peaks of the methyl triplet are equal to the spacings between the peaks of the methylene quartet. This spacing is measured in Hertz and is called the coupling constant, J.





To see why the methyl peak is split into a triplet, let's look at the **methylene** protons. There are two of them, and each can have one of two possible orientations (aligned with or opposed against the applied field). This gives a total of four possible states;



In the first possible combination, spins are paired and opposed to the field. This has the effect of reducing the field experienced by the **methyl** protons; therefore a slightly higher field is needed to bring them to resonance, resulting in an upfield shift. Neither combination of spins opposed to each other has an effect on the methyl peak. The spins paired in the direction of the field produce a downfield shift. Hence, the methyl peak is split into three, with the ratio of areas 1:2:1. Similarly, the effect of the methyl protons on the methylene protons is such that there are eight possible spin combinations for the three methyl protons; Out of these eight groups, there are two groups of three magnetically equivalent combinations. The methylene peak is split into a quartet. The areas of the peaks in the quartet have the ration 1:3:3:1. In a first-order spectrum (where the chemical shift between interacting groups is much larger than their coupling constant), interpretation of splitting patterns is quite straightforward;

- The multiplicity of a multiplet is given by the number of equivalent **protons** in **neighbouring** atoms plus one, i.e. the n + 1 rule
- Equivalent nuclei do not interact with each other. The three methyl protons in ethanol because splitting of the neighbouring methylene protons; they do not cause splittingamong themselves
- The coupling constant is not dependant on the applied field. Multiplets can be easily distinguished from closely spaced chemical shift peaks.

Theory : (Bloch and Purcell in 1946)

Atoms consists of nuclei and electrons. The nuclei have positive charges which are multiples of the protons. The nuclei have also angular momentum known as spin and characterised by the spin quantum number (I = 0, ½, 1, 1½) . The angular momentum associated with a nuclear spin is given by

[illegible] ½ . h/2

Since, a nucleus possesses an electric charge, the spinning nucleus gives rise to a magnetic field whose axis coincides with the axis of spin. Thus the nucleus can be regarded

as a micro magnet with the magnetic moment μ.

[illegible]

[illegible] $\vec{\mu}$ [illegible] spin, $\vec{I}$ -------(1)

$\vec{\mu}$ [illegible] g_N [illegible] $\vec{I}$

Where, gN is called nuclear g factor.

[illegible] is the nuclear magnetron = $\frac{eh}{4\pi mp}$ = 5.05 X 10 -27 JT-1

Where m_p – mass of proton; e- electronic charge

When the nucleus is placed in an external magnetic field B_z applied in the z-direction, the energy of interaction is

$E = -\vec{\mu} . \vec{B}_z$ ---------- (2)

Substituting the value of $\vec{\mu}$ from eqn 1 we get

$E = -g_N \mu_N . \vec{B}_z \vec{I}$

Since I is quantized in the presence of the magnetic field and the energy of nuclear spin is defined only by its components m1 then,

EmI = -gNμN. BZmI....................(3)
For a bare proton, I = ½, so that mI = ± ½;
i.e. m1 = +½; E½= ½ gNμN. BZ------- - (4)
m1 = -½; E½ = + ½ gNμN. BZ--------- (5)

$$m_I \quad = -1/2, E_{-1/2} = +\frac{1}{2}\ g_N\mu_N .B_Z$$

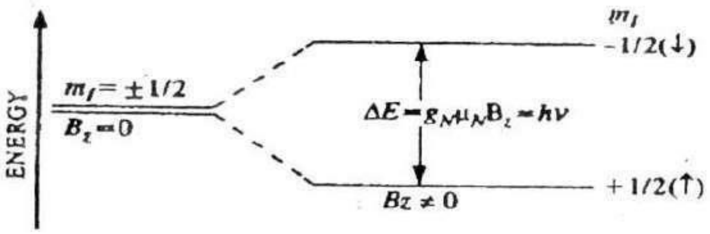


Fig. 1 Splitting of nuclear energy levels of a bare proton in a magnetic field (keeping BZ constant and frequency is varied)

From eqns (4) and (5) the energy difference is given by

ΔE = gNμN.BZ....................(6)

In order to flip the nucleus from the upward direction | || |to the downward direction (   ), oscillating radio frequency perpendicular to the direction of BZ is applied (of energy h| |)

ΔE = gNμN.BZ = h| | .... (7)

This is called Bohr frequency condition.

Thus, the NMR frequency of a bare proton is given by

| || | | | E/ h = g N| | N B Z / h | || |or | || | BZ

The NMR spectra can be recorded in two ways.

i) Keeping the magnetic field BZ fixed and varying the frequency | || |(fig. 1)

ii) Keeping | |fixed and varying the magnetic field BZ (fig. 2)

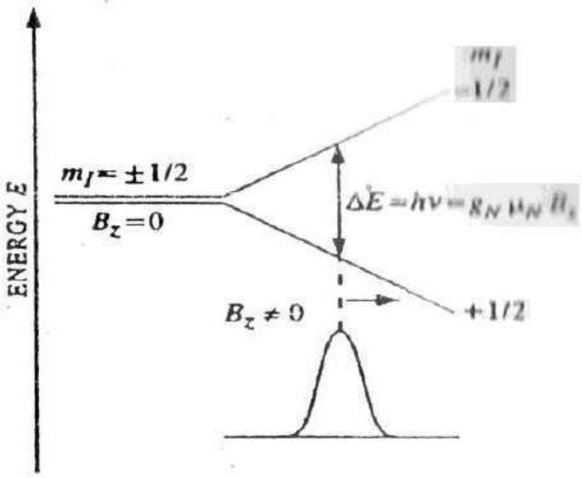
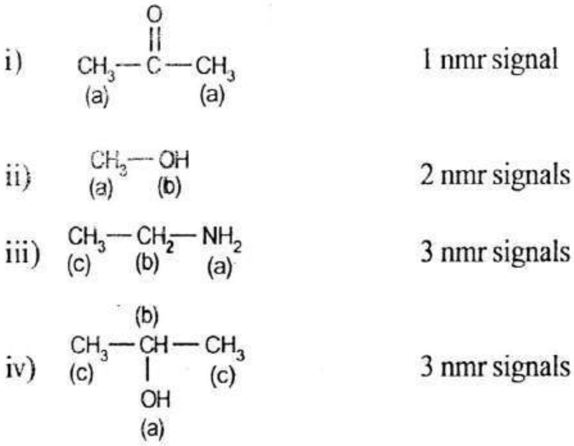


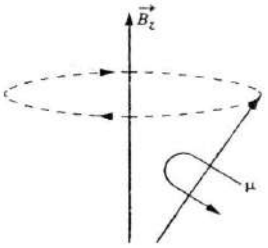
Fig. 2 Splitting of nuclear energy levels of a bare proton in a magnetic field (keeping constant and BZ frequency is varied)

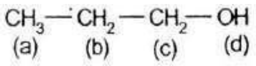
Signals

The number of signals explain the number of differentlysets of equivalent protons in a molecule. Each signal correspondsto a set of equivalent protons.

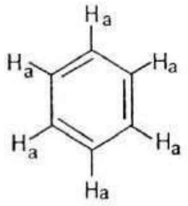
Example



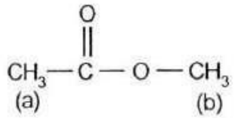


v)

$\underset{(a)}{CH_3}-\underset{(b)}{CH_2}-\underset{(c)}{CH_2}-\underset{(d)}{OH}$

4 nmr signals

vi)


2 nmr signals

vii)

$\underset{(a)}{CH_3}-\overset{\overset{O}{\|}}{C}-O-\underset{(b)}{CH_3}$

2 nmr signals

Applications of NMR spectroscopy:

i. Elucidation of molecular structure :

The most important application of NMR is the elucidation of molecular structure. The points of interest in this elucidation are.

a) Number of NMR signals, which gives the number of different types of protons such as methyl proton, methylene proton, hydroxyl proton, aldehydic proton and aromatic proton.

b) Position of the signal and chemical shifts: This decides the type of proton.

c) Intensities of signals: The intensity depends on the number of protons of a particular kind. The relative intensities of signals are measured by the areas under the different peaks obtained in the NMR spectrum.

d) Splitting of signals (under high resolution): This gives information about the number of equivalent protons which are near neighbours to the group under study.

The above points can be illustrated with a few examples:

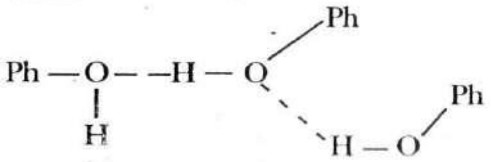
Compound	NMR Signals	Splitting pattern
CH3a – CH2b – Cl	2	a – triplet, b – quartet
CH3a – CO – CH3a	1	a – singlet
C6H6a	1	a – singlet

ii. Hydrogen bonding

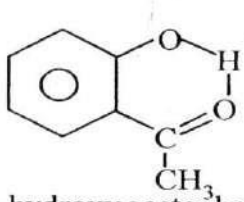
The NMR is used to study the nature of hydrogen bonding in compounds. If a proton in a compound is involved in hydrogen bonding, the resonance absorption peak occurs at a down field (higher | || |- value). This is due to decreased electron density around the proton by the hydrogen bond.

Intermolecular H – bonding is affected by concentration and temperature, but intermolecular H – bonding is unaffected by these factors.

Example : At ordinary concentration, phenols have –OH proton absorption at 6.0 to 7.7 | || |(down field) due to intermolecular H – bonding. At infinite dilution or at higher temperature their absorption at 4.0 to 5.0 | || |(up field) due to weakening of H – bonding.



Phenol



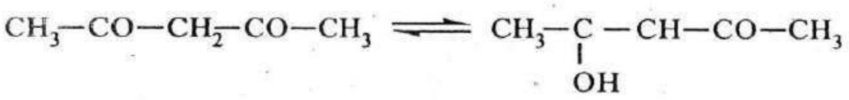
o - hydroxy acetophenone

O – hydroxy acetophenone has – intermolecular H – bonding. Its position is unaffected by dilution or temperature.

iii. Tautomerism :

NMR spectra are used in the study of keto-enol tautomerism.

Example : Acetyl acetone exists the following equilibrium.



$$CH_3-CO-CH_2-CO-CH_3 \rightleftharpoons CH_3-\underset{OH}{\underset{|}{C}}-CH-CO-CH_3$$

Keto form   Enol form

In its NMR spectrum, the areas of –CH2 – (keto form) and = CH – (enol form) peaks are carefully measured and found that the acetyl acetone contains 18.6± -.6% keto form at 25ºC.

iv. Study of water of crystallisation in solids:

In $CuSO_4, 2H_2O$. We would normally expect the two water molecules to be equivalent and hence only one NMR signal. Actually two signals are observed, each appearing as a doublet. This shows that the two water molecules have different orientation in space.

v. Kinetics of certain chemical reaction can be studied through NMR spectroscopy.

Rates of several exchange reactions. (Example: Proton exchange between ethanol and H_3O^+, acetic acid and water) have been evaluated from line broadening measurements.

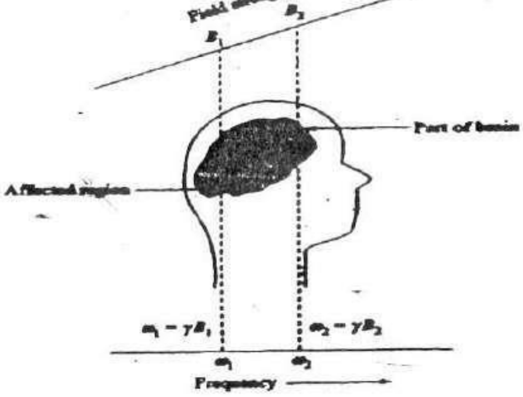
vi. Nuclear Magnetic Resonance Imaging (MRI)

Nuclear magnetic resonance imaging is nothing but Magnetic Resonance Imaging (MRI). It is also known as zeugmatography or tomography. NMR imaging is based on the principle that it is possible to create two and three – dimensional ―pictures‖ of objects, by proper adjustment of magnetic field at various depth in the sample, in the same way as a photograph or x-ray plate. In a normal NMR experiment the samples (in the mg range) are studied in a uniform

magnetic field with homogencity of none part in 109. But in the MRI experiment, the samples

are large and inhomogeneous such as human bodies, placed in uniform magnetic fields. The

applied fields are inhomogeneous so that different parts of the sample experience different fields and consequently have different resonance frequencies.



For example, when a narrow tube contains water as the sample is placed in a uniform magnetic field, the NMR spectrum displays a single sharp line. If the same simple is placed in a magnetic field a linear field gradient, the MRI spectrum displays ‗n' sharp lines at a various frequencies related directly to the magnetic fields at different parts of the sample. By taking profiles from different directions achieved by altering the directions of the magnetic fields and the linear field gradients, the images of the objects from different angles can be obtained. The profiles are then processed with the help of the image processing technique in a computer to obtain two or three dimensional images. A typical image with anotomical details is shown in the figure.

Electron Spin Resonance Spectroscopy

Introduction

Electron spin resonance (ESR), also called electron paramagnetic resonance (EPR), is a spectroscopic technique confined to the study of species having one or more unpaired electrons. Among the large number of systems having one or more unpaired electrons, i.e. paramagnetic system, the most important ones are free radicals, transition metal ions, ions and molecules having odd number of electrons.

Electron Spin Resonance (ESR) also known as Electron Magnetic Resonance (EMR) or Electron Paramagnetic Resonance (EPR) is a branch of absorption spectroscopy in which radiations having frequency in the microwave region (0.04 – 25 cm) is absorbed by paramagnetic substances to induce transitions between magnetic energy levels of electrons with unpaired spins.

ESR is based on the fact that atoms, ions, molecules or molecular fragments which have an odd number of electrons exhibit characteristic magnetic properties. An electron has a spin and due to spin there is magnetic moment. Since its discovery in 1944 by E.K. Zavoisky, EPR spectroscopy has been exploited as a very sensitive and informative technique for the investigation of different kinds of paramagnetic species in solid or liquid states.

Principle

The phenomenon of electron spin resonance (ESR) is based on the fact that an electron is a charged particle. It spins around its axis and this causes it to act like a tiny bar magnet. When a molecule or compound with an unpaired electron is placed in a strong magnetic field The spin of the unpaired electron can align in two different ways creating two spin states ms = ± ½. The alignment can either be along the direction (parellel) to the magnetic field which corresponds to the lower energy state ms = – ½ Opposite (antiparallel) to the direction of the applied magnetic field ms = + ½. The two alignments have different energies and this difference in energy lifts the degeneracy of the electron spin states. The energy difference is given by:

Δ E = E+ – E- = hv = gmßB

Where,

h = Planck's constant (6.626 x 10-34 J s-1)

v = the frequency of radiation

ß = Bohr magneton (9.274 x 10-24 J T-1) B = strength of the magnetic field in Tesla

g = the g-factor which is a unit less measurement of the intrinsic magnetic moment of the electron, and its value for a free electron is 2.0023.

An unpaired electron can move between the two energy levels by either absorbing or emitting a photon of energy {\displaystyle h\nu } hv such that the resonance condition, hv = Δ E, is obeyed. This leads to the fundamental equation of EPR spectroscopy

ESR SPECTRUM OF METHYL FREE RADICAL (• CH3)

In methyl free radical, an unpaired electron interacts with three equivalent protons

. The number of ESR signals expected for • CH3 is equal to four (2nI + 1 = 2×3 × 1 2 + 1 = 4). In fact, the experimental ESR spectrum of • CH3 displays four equally spaced signals with the intensity ratio 1 : 3 : 3 : 1. The energy of spin states of the unpaired electron in • CH3 coupled with three equivalent protons and allowed ESR transitions are shown in Fig. 6.11

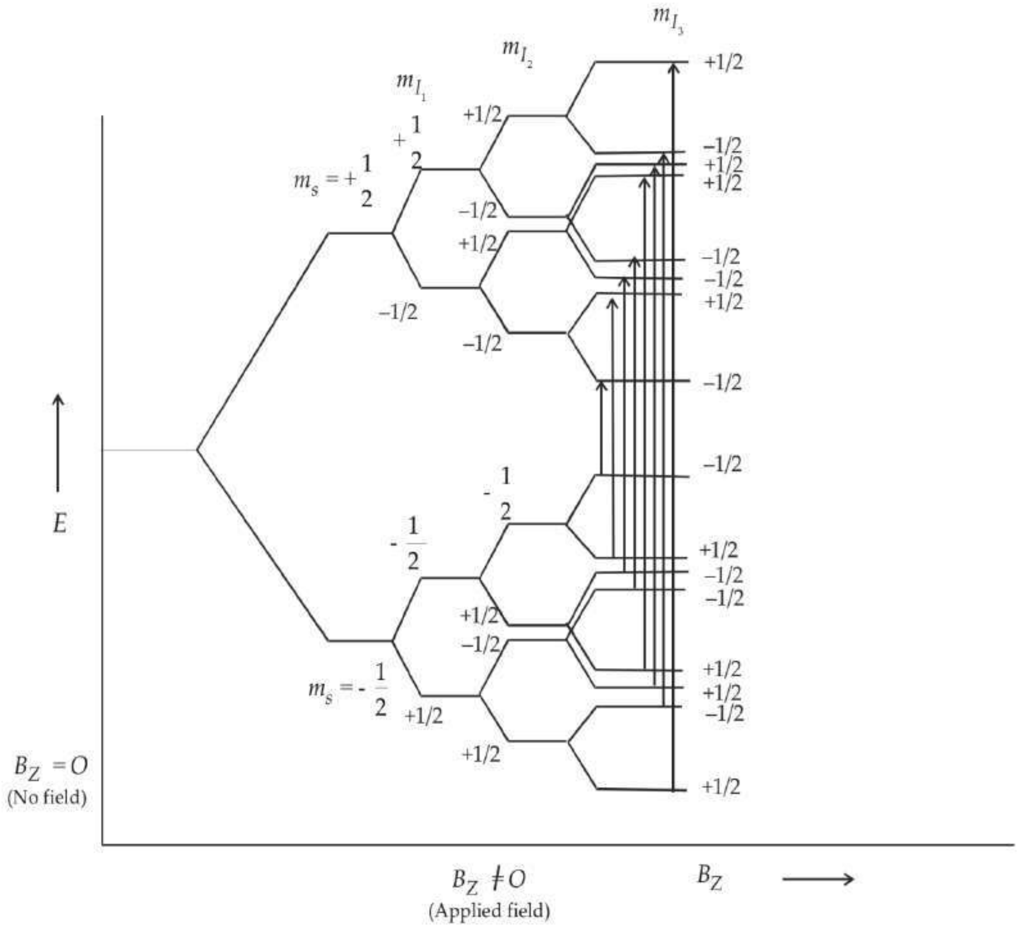


Fig.6.11. Interaction of electron spin of $\dot{C}H_3$ with nuclear spins of three equivalent protons and allowed ESR transitions.

The ESR spectrum of•CH3 is shown in Fig. 6.12.

Since the observed spectrum is symmetrical, the proton hyperfine couling constant is isotropic and the unpaired electron density is distributed equally among the protons in•CH3. The spacing between the ESR peaks gives hyperfine coupling constant (a) equal to 22.9 gauss.

ESR SPECTRUM OF BENZENE ANION

Benzene anion can be formed by the reaction of an alkali metal with benzene in asolvent such as tetrahydrofuran (THF). Benzene anion results when the alkali metal atom transfers an electron to the benzene molecule. The observed ESR spectrum of C_6H_6 (Fig.6.13) is symmetrical with seven peaks indicating that the unpaired electron density is distributed equally among the six protons in the system.

As there are six equivalent protons in benzene anion, the expected number of ESR signals = (2n I + 1) = 2 × 6 ×12+ 1 = 7 Seven lines with intensity ratio 1 : 6 : 15 : 20 : 15 : 6 : 1, are actually observed in the ESR spectrum of $\bullet C_6H_6$. The spacing between the lines gives the hyperfine coupling constant (a) of 3.76 gauss.

6.14 ZERO FIELD SPLITTING AND KRAMER' DEGENERACY

When a metal ion is placed in a crystal field, the degeneracy of d-orbitals is lifted by the electrostatic interactions, but the spin degeneracy remains, until a magnetic field is applied. However, when the species contains more than one unpaired electrons, the spin degenracy can also be destroyed by the crystal field. Thus, the spinlevels may be split even in the absence of a magnetic field. This phenomenon is called zero field splitting. For species with an odd number of unpaired electrons, the spin degeneracy of every level remains doubly degenerate. This is known as **Kramer's degeneracy.** For an even number of unpaired electrons, the spin degeneracy may be removed completely by the crystal field. Let us consider the case of a molecule or ion with two unpaired electrons, giving rise to a total spin of S=1. The two unpaired electrons per molecule or ion forming the triplet state can be treated for most ESR purposes as a single particle with spin 1. Thus, the angular momentum vector corresponding to S = 1 is given by :

$$\vec{S}=\sqrt{S(S+1)}\ \frac{h}{2\pi}$$

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

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

In the absence of a magnetic field, this vector orients itself randomly in space. When a magnetic field is applied, the vector can take up one of the three directions only -with, across or against the field direction. The components of the ngular momentum vector in the direction of the applied field (BZ) are ms =+1 ,0 and -1. In the applied field, the ms = +1 state is raised in energy, the ms= –1 state is lowered and ms = 0 state remains unaffected.

Applying the selection rule for spin allowed transitions, ms = ±1, only two transitions, ms =–t to ms = 0 and ms = 0 to ms = +1 are allowed, but both will have identical energy and hence give rise to only one spectral line. In fact, two spectral lines of different energy are invariably observed.

Reason for the unsymmetrical splitting of spin energy levels giving rise to two spectral lines :

Each state with S = 1 is made up of two electrons with parallel spins. We know that each spin produces a small magnetic field in the vicinity of the other affecting the net field experienced by its neighbour (dipolar spin spin coupling). Thus, both spins in ms = +1 state feel an applied field greater than the external field BZ and this state is raised in energy. For ms=–1, both feel a smaller field, which again raises their energy. In the case of ms=0, the dipolar field is across the main applied field, hence it is neither raised nor lowered in energy. Thus, the ms=0 state remains unaffected by the dipolar spin spin coupling.

The net effect of spin spin dipolar interaction is , then to raise both the ms= +1 and ms=–1 states with respect to ms= 0 state. Thus, the degeneracy of spin state is lifted due to spin spin dipolar interactions, even in the absence of applied agnetic field. This splitting of spin states in the absence of applied magnetic field is called zero field splitting (Fig. 6.17)

When a steadily increasing magnetic field is applied, the ms = ±1 levels diverge, the ms = +1 level is raised in energy while ms = –1 level is lowered (Fig. 6.18)

It is clear that there will be transitions at two different applied fields and he spectrum will consists of two fine structure lines

UNIT-III

GROUP THEORY

SYMMETRY IN CHEMISTRY

Symmetry is actually a concept of mathematics and not of chemistry. However, symmetry, and the underlying mathematical theory for symmetry, group theory, are of tremendous importance in chemistry because they can be applied to many chemistry problems. For example it helps us to classify the structures of molecules and crystals, understand chemical bonding, predict vibrational spectra, and determine the optical activity of compounds. We will therefore first discuss the general foundations of symmetry and group theory, and then apply them to chemical problems, in particular chemical bonding.

Let us first find a definition for symmetry. Symmetry is very familiar to us as we associate symmetry with beauty, but very familiar things are not necessarily easy to define scientifically. One common definition is that symmetry is the self-similarity of an object. The more similar parts it has the more symmetric it appears. For example, we would argue that the two wings of the butterfly depicted look similar. If the left wing was very different from the right wing the butterfly would look less symmetric.

Figure 2.1.1 Symmetry depicted through an image of a butterfly (Attribution: Chemlibretexts

How can we measure the self-similarity, or symmetry of an object quantitatively? We can do this using the concept of the symmetry operation. It is defined as a movement of an object into an equivalent indistinguishable orientation. The number and kind of symmetry operations that can be carried out defines the symmetry of the object.

Symmetry Operation

Movement of an object into an equivalent indistinguishable orientation. Symmetry operations are carried out around so-called symmetry elements. A symmetry element is a point, line, or plane about which a symmetry operation is carried out. Let us understand know what symmetry elements and operations exist.

Symmetry Element

A point, line or plane about which a symmetry operation is carried out

The Identity Operation (E)

The most simple operation is the identity operation. It can be denoted by the Schoenflies symbol E. Schoenflies symbols are the most common symbols to denote a symmetry operation. The identity operation says that each object is self-similar to itself when you do not move it in any way. This is a trivial statement, but as we will see later, the identity operation is necessary to make the mathematical framework of symmetry, group theory, complete. The identity operation is present in any object. In the example of the depicted snail shell it is the only operation (Fig. 2.1.2).

Figure 2.1.2 Snail shell

The Proper Rotation Operation

The proper rotation operation is a counter-clockwise rotation about a proper rotational axis by an angle of 360° over an integer number n. After that rotation the object must be indistinguishable from its original form. That means that the object after the rotation must superimpose the original object before the rotation. For example, when n=4, then we rotate around 90°, and after that the object must superimpose its original form. The proper rotational axis is the symmetry element associated with the proper rotation operation. It's Schoenflies symbol is C_n, whereby n is called the order of the rotational axis. A proper rotational operation has the symbol C_n^m, whereby m counts the number of times the operation is carried out. Overall we rotate by and angle of 360°× m/n when we carry out an operation C_n^m. This means that when m=n, then we have rotated around 360° (Fig. 2.1.3). Then all points in the object are at their original position. It is as though we had done nothing with the object. We can also say we have reached the identity E. In mathematical form we can say that $C_n^n=E$. If we rotated one more time, $C_n^{(n+1)}$, then this would be equal to rotating only one time, and thus $C_n^{(n+1)}=C_n^1$. For example if n=4, then rotating four times around 90° will produce the identity. We have rotated around 4 x 90°=360° which is the same a though we had not rotated at all, because all points in the object are in their original position after a 360° rotation. If we rotated 5 times around 90°, it would the same as rotating only one time.

Figure 2.1.3 Properties of the proper rotation operation

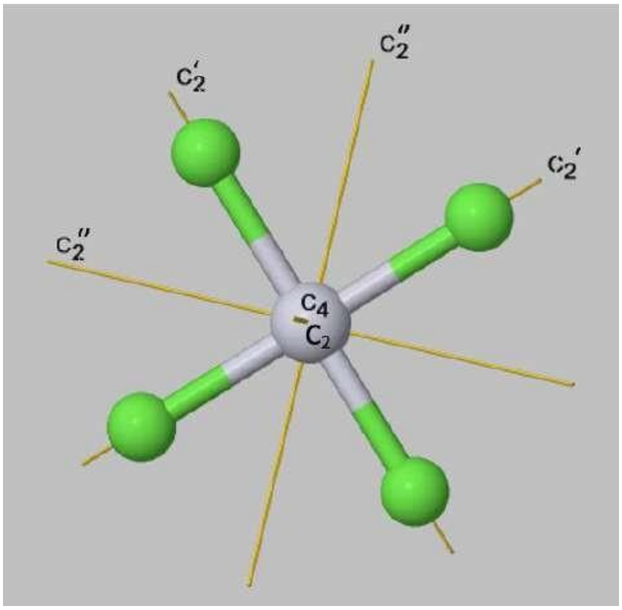
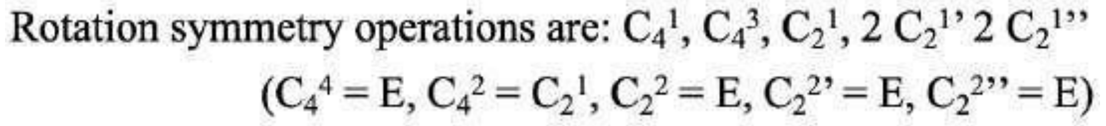


Figure 2.1.4 Proper rotational axes in the $PtCl_4^{2-}$ molecular anion. (Attribution: symotter.org/gallery)

If an object has several axes with different order n, then the one with the highest order is called the principal axis. If there is more than one axis of the same order, then they get distinguished by primes if they are not conjugate. We will learn about the exact definition of conjugation somewhat later, we can however often see by inspection if two axes are conjugate. This is usually the case when they pass through the object in a equivalent way, and rotate the object in an equivalent way. Axes that pass through less many bonds, get less many primes. This is just a convention, but you have to follow it. An additional rule is that an axis which is in the same position as the principal axis gets the least number of primes. For example, a square planar molecule such as $PtCl_4^{2-}$ has a C_4 principal axis standing perpendicular to the square plane of the molecule. There is an additional C_2 axis where the C_4 axis runs. It is present because one can also rotate around 180°, and not only around 90°. This C_2 axis does not get any prime. You an see that there are four additional C_2 axes, two of them are denoted C_2', and two others are denoted C_2''. You can see that the two axes which only have one prime pass through two Pt-Cl bonds, while the ones that have two primes, do not pass through any bonds. The two C_2' axes are conjugate, meaning that they transform the object in an equivalent way. The two C_2'' axes are also conjugate.

We can now think about how we can write out the axes and their associated proper rotational operations in a systematic way. Let us first look at the symmetry elements, the proper axes: We conventionally write the principal axis first, and then all other axes from their highest to their lowest order. When there are axes of the same order, those with the least number of primes get denoted first, and those with the highest number of primes last. If there are conjugate axes then their number is placed in front of their Schoenflies symbol. For the proper axes of the $PtCl_4^{2-}$ the notation would therefore be: C_4, C_2, $2C_2'$, $2C_2''$. Now let us see how to denote the rotation operations that are associated with these symmetry elements. The notation follows the same rules as for the symmetry elements. In addition, we have to consider that we must not count identical operations twice, we also do not denote the operations that are the same as the identity. For the C_4 axis there are four operations until we reach the identity. C_4^1, C_4^2, C_4^3, and C_4^4. For each of the C_2, C_2', and C_2'' elements there are two operations until the identity is reached. C_2^1, C_2^2, $C_2^{1'}$, $C_2^{2'}$, $C_2^{1''}$, $C_2^{2''}$. The C_4^4, the C_2^2, the $C_2^{2'}$, and the $C_2^{2''}$are the same as the identity and therefore we do not consider them. In addition we can see that the C_4^2 is the same as the C_2^1. This is because the C_4 and the C_2 axes are in the same location, and rotating two times around 90° is the same as rotating one time around 180°. By convention we eliminate the operation associated with the higher order, thus the C_4^2. The overall notation would then be: C_4^1, C_4^3, C_2^1, 2 $C_2^{1'}$ 2 $C_2^{1''}$ (Fig. 2.1.5).



Rotation symmetry operations are: C_4^1, C_4^3, C_2^1, 2 $C_2^{1'}$ 2 $C_2^{1''}$

($C_4^4 = E$, $C_4^2 = C_2^1$, $C_2^2 = E$, $C_2^{2'} = E$, $C_2^{2''} = E$)

Figure 2.1.5 Proper rotation operations in $PtCl_4^{2-}$

The Reflection Operations (σ)

Let us look at reflection operations which are carried out around reflection planes, or mirror planes. Mirror planes have the Schoenflies symbol σ. When we carry out a reflection operation, then we move any point of the object to the other side of the mirror plane. There are two types of mirror planes, so-called horizontal mirror planes and vertical mirror planes. A horizontal mirror plane always stands perpendicular to the principal axis. For example in the depicted BH_3 molecule there is a horizontal mirror plane that stands perpendicular to a C_3 principal axis (Fig. 2.1.6). A horizontal mirror plane has the Schoenflies symbol σ_h.

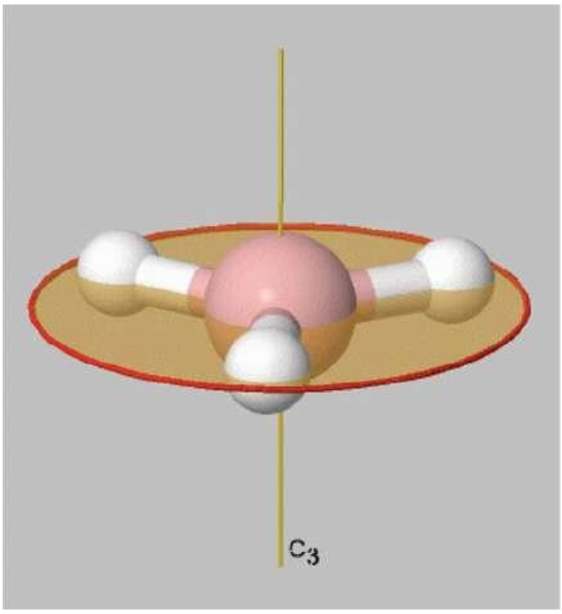


Figure 2.1.6 Visual depiction of the horizontal mirror plane of BH_3, σ_h (Attribution: symotter.org/gallery)

A vertical mirror plane has the property that it contains the principal axis, this means that it is part of the principal axis. It is denoted σ_v. The BH_3 molecule has three vertical axes that pass through the three B-H bonds. You can see that each of them contain the principal C_3 axis (Fig. 2.1.7). The three vertical mirror planes are conjugate, and therefore they are not distinguished by primes. We can write a coefficient 3 in front of the symbol σ_v to indicate that there are three conjugate vertical mirror planes.

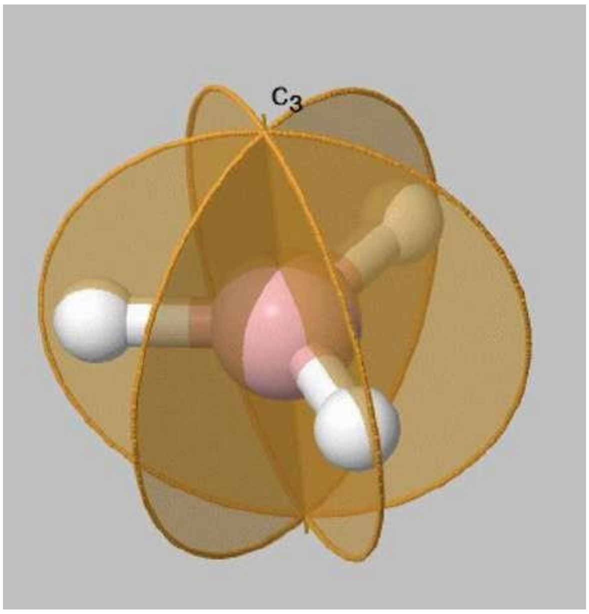


Figure 2.1.7 Visual depiction of the vertical mirror planes of BH_3, 3 σ_v (Attribution: symotter.org/gallery)

Now let us look at how many symmetry operations are associated with a particular mirror plane. Fortunately, things are simple here: There is only one reflection operation associated with one mirror plane. This because reflecting two times at a mirror plane produces the identity E: $\sigma_v^2=E$. More generally, when we reflect n times, and n is an even number then this is the same as the identity or, $\sigma_v^n=E$ (n is even). When n is odd the reflecting n times is the same a reflecting only one time or, $\sigma_v^n=\sigma_v^1$ (n=odd). The horizontal mirror plane of the BH_3 molecule deserves an additional comment. Carrying out the horizontal reflection does not change the position of any atom. It is important to understand why the operation does exist despite the fact it does not change the position of any atom. The criterion is not whether the position of an atom is changed, but whether the position of the points in the object changes. In the case of the BH_3 molecule the part of the molecule that is located above the mirror plane will be located below the mirror plane after the reflection operation has been carried out. Vice versa any part of the molecule that was formerly below the mirror plane will be located above the mirror plane after the reflection operation has been carried out. For example the lower half of the B atom with be above the mirror plane, and the half above the plane will be below the plane after the execution of the reflection operation.

Like non-conjugate proper rotations are distinguished by primes, also non-conjugate vertical mirror planes must be distinguished by primes. The smaller the number of bonds the vertical mirror plane contains, the larger the number of primes.

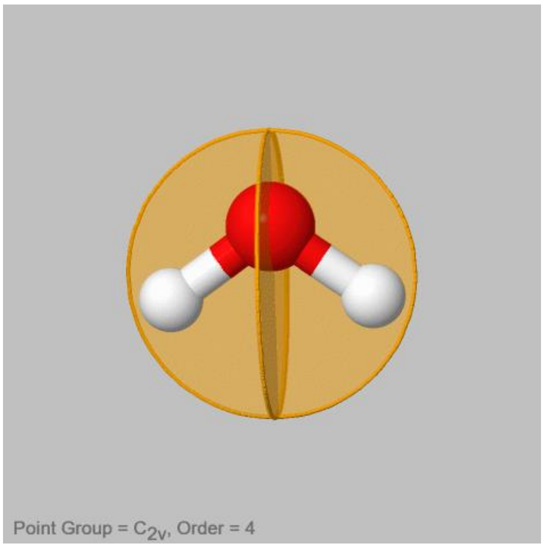


Figure 2.1.8 Non-conjugate vertical mirror planes of H_2O (Attribution: symotter.org/gallery)

For example in the water molecule (Fig. 2.1.8) there are two non-conjugate vertical mirror planes. One contains the two O-H bonds, the other stands perpendicular to the first mirror plane. It is easy to see that these two mirror planes will not move the points in the atom in an equivalent way, and therefore they are not conjugate. The first mirror plane does not change the position of any atom, while the second one swaps the positions of the two hydrogen atoms. Therefore, the second mirror plane not containing any O-H bonds gets one prime the one that contains the O-H bonds doe not get a prime.

Dihedral Reflection Planes (σ_d)

A special case of a vertical mirror plane is a dihedral mirror plane, denoted σ_d. A dihedral mirror plane bisects the angle between two conjugate C_2 axes.

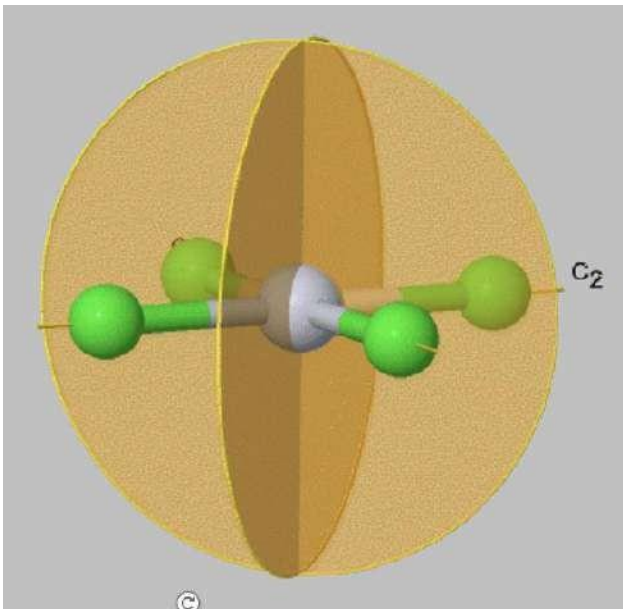


Figure 2.1.9 Dihedral mirror planes of $PtCl_4^{2-}$ (Attribution: symotter.org/gallery)

For example, in the $PtCl_4^{2-}$ anion (FIg. 2.1.9) there are two vertical mirror planes that bisect the angle between the two conjugate C_2 axes that pass through the Pt-Cl bonds. Therefore, these mirror planes are vertical mirror planes σ_d.

The Inversion Operation (i)

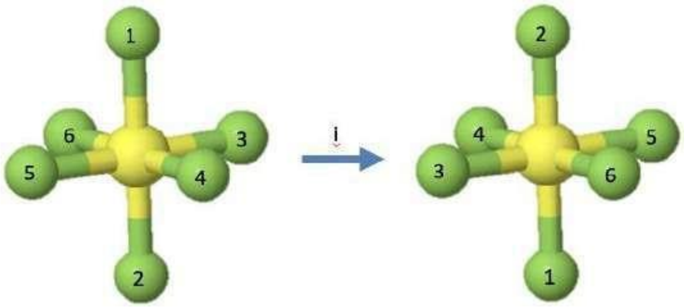


Figure 2.1.10 The inversion operation for SF_6 (Attribution: symotter.org/gallery)

Let us look next at the inversion operation which is symbolized by a Schoenflies symbol i. The symmetry element associated with an inversion, is the inversion center, also called center of symmetry. It is a single point. When an inversion operation is performed, then each point of the object is moved through the inversion center to the other side. Each coordinate in the object (x,y,z) is inverted into the coordinates (-x,-y,-z). For example, the octahedral molecule SF_6 has an inversion center in the center of the molecule (Fig. 2.1.10). When the inversion operation is carried out, then each fluorine atom is moved through the inversion center to the other side. This means that the fluorine atoms 1 and 2 swap up their positions, the fluorine atoms 3 and 5 swap up their positions, and so do the fluorine atoms 4 and 6. The sulfur atom does not change its position. There is only one inversion operation associated with each inversion center. Inverting two times, or more generally, an integer number of two times produces the identity. Inverting an odd number of times is the same as inverting one time.

The Rotation-Reflection Operation (S_n)

The rotation-reflection operation S_n is the most complex symmetry operation. It is carried out in two steps. First, a rotation around an improper axis is carried out. The angle is determined by the order n of the improper axis, and is 360°/n. This axis is called improper, because the object does not need to superimpose the original object after the rotation. Achieving superposition requires the second step which is the reflection at a mirror plane that stands perpendicular to the improper axis. Only after the second step the operation is complete. The presence of the rotation-reflection does not require a proper rotational axis or a regular mirror plane σ to exist, however it also do not preclude their existence.

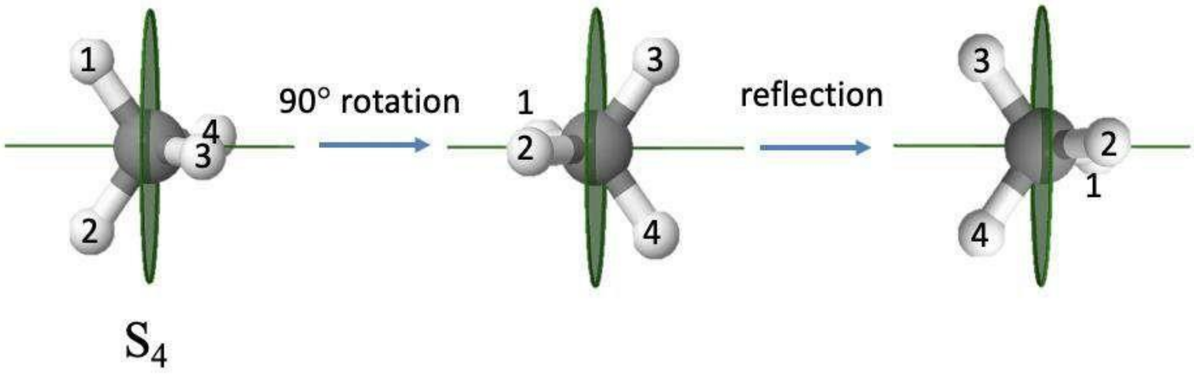


Figure 2.1.11 The improper S_4 rotation for CH_4 (Attribution: symotter.org/gallery)

An example of a molecule with an improper axis is the methane molecule (Fig. 2.1.11). It has an S_4 improper axis. The axis bisects the H-C-H tetrahedral bond angle. The order of the axis is four which requires that we rotate by 90° around this axis. You can see that after we carry out the rotation, the molecule does not superimpose the original molecule. Only after we reflect the rotated molecule at a mirror plane standing perpendicular to the improper axis the molecule superimposes the original molecule.

Properties of the Rotation-Reflection Operation (S_n)

The rotation-reflection has a number of interesting properties. One of the them is that an S_1 operation is the same as a reflection. This is because the order 1 implies a rotation around 360° which produces the identity, and all points within the object are in their original position. This is the same as though we had not rotated at all. This means actually we only did the second step, the reflection, and therefore the S_1 is identical to a “regular” reflection. The second property is that an S_2 operation is the same as an inversion. When you rotate around 180° and then reflect perpendicular to the improper axis of rotation, the positions of the points in the object change exactly the same way as they do when you invert through an inversion center.

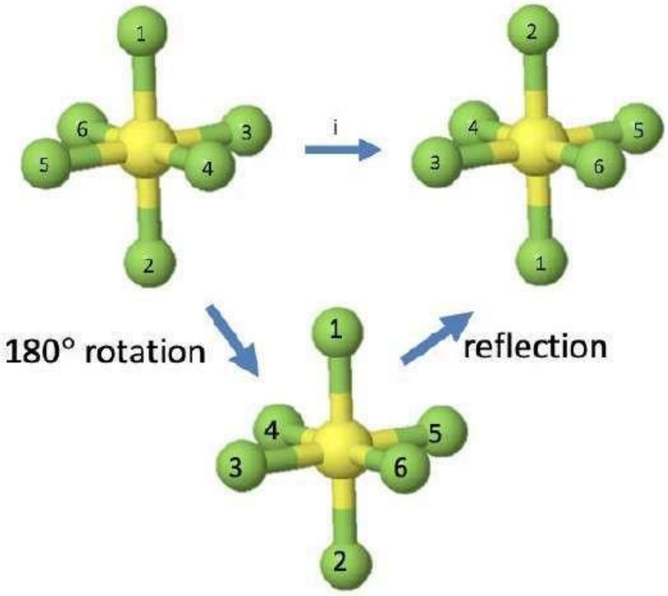


Figure 2.1.12 Rotation-Reflection operations for SF_6 (Attribution: symotter.org/gallery)

Look for example at the SF_6 molecule again (Fig. 2.1.12) which has an inversion center in the center of the atom. We previously saw that when we carry out the inversion, the atoms 1 and 2 swap their position, and so do the atoms 3 and 5, as well as the atoms 4 and 6. Let us carry out the rotation-reflection, and see if the atoms change the same way. Firstly we rotate 180° around an axis that goes through the atoms 1 and 2. This leaves the positions of the atoms 1 and 2 unchanged, but swaps up the positions of the atoms 3 and 5, as well as the atoms 4 and 6. Next we must do a reflection at a plane that stands perpendicular to the improper axis. It is the plane defined by the atoms 3, 4, 5, and 6. Reflection at this plane does not change the positions of the atoms 3, 4, 5, and 6, but it swaps up the positions of the atoms 1 and 2, which lie above and below the plane, respectively. We can see that the positions of the atoms are the same as after the inversion. The fact that we can express a reflection by an S_1 rotation-reflection, and an inversion by a S_2 rotation-reflection means that the reflection and the inversion are not independent symmetry operations, and we would not need them. The symmetry of an object could be fully described by the identity, proper rotations, and rotation-reflections. However, by convention, we use reflections and inversions instead of S_1 and S_2, simply because it is easier for the human mind to perform 1-step operations, rather than 2-step operations. Improper rotations have different properties depending on whether the order of the axis is even or odd. For even orders, the presence of an S_n improper rotational axis implies that there must also be a proper rotational axis with an order n/2. For improper axes of even orders n the identity is produced after n rotation-reflections (Fig. 2.1.13).

$$S_n \text{ with n even} \rightarrow \text{molecule contains } C_{n/2}$$

$$S_n^n = E$$

Figure 2.1.13 Properties of improper rotations with even order n

For improper axes of odd order n, carrying out the rotation-reflection n times is the same as carrying out a reflection at a horizontal mirror plane. We need to do the rotation-reflection 2n times to reach the identity (Fig. 2.1.4).

$$S_n \text{ with n odd} \rightarrow \text{molecule contains } C_n \text{ and } \sigma_h$$

$$S_n^n = \sigma_h$$

$$S_n^{2n} = E$$

Figure 2.1.14 Properties of improper axes of odd order n

Group and its properties

The number of elements in the group represents its order. It is a whole number only. Now we will see whether it is possible that smaller number of elements in the group constitute a group of lower order that satisfies al the four properties of a group. Can we divide further the group into smaller order groups? Smaller order groups in the main group are termed as sub groups.

3. Definition of group

According to the formal definition of a group, a group is a set /collection of elements, which are combined with certain operation *, such that:

1. The group contains an identity
2. The group contains inverses
3. The operation is associative

4. The group is closed under the operation or

In mathematical sense a group may be defined as, “collection/set of elements/numbers having certain properties in common i.e. these elements are bound by certain conditions, known as group properties/postulates”. The elements do not need to have some physical significance. My emphasis will be mainly on ‘‘symmetry operations as the collection of elements of the group”.

3.1 Basic properties of a group:

There are four basic properties/conditions/postulates/characteristics of a group .The elements belonging to the group should follow/adhere to these conditions in a true sense. Let us state these conditions and explain these by taking suitable examples. Let the elements of the group be [A, B, C, D, E X-].

i. In the collection (i.e. group) there must an element such when it combines/multiplies with each and every other elements of the group, it leaves them unchanged. This element is the identity element symbolized as ‘E’ and this property can be expressed as: AE=A, BE=B, CE=C, DE=D and so on. Further this type of combination with E is commutative (order ofcombination/product is immaterial) i.e. when order of combination is reversed the results, EA=A, EB=B, EC=C, ED=D are also true. Here mode of combination may be multiplication, addition, subtraction in mathematical sense or in symmetry sense one symmetry operation followed by another symmetry operation. There is only one identity element for every group.

ii. Each and every element in the group must have an inverse, say (X) , which is also the member of the group i.e. AX = XA = E . Here, X is the inverse of A and A is the inverse of X i.e. AX =XA=E or A=X-1, A-1=X ie AA-1= E.

Inverses are unique. It is to be noted that there exists only one identity for every single element in the group but each element in the group has a different inverse.

iii. Although the combination of two elements may or may not be commutative, but it must be associative. In group { A,B,C,D----X---} following relations are valid A(BC)=(AB)C=ABC. Provided the order of combination is not changed. This associative property can be extended to any number of elements of the group. This associative result of elements must be an element of the group.

iv. Closure: Results of combination (multiplication, addition, subtraction) of two or more elements or square of the element (the element is combined with itself) must be equivalent to an element of the group, which is also the member of the group. The group is closed under the given combination. In group [A, B, C, D---X-] these type of combinations and their results may be AB=C, AC=D, BC= another element of the group only. It is not necessary that combination AB= combination BA i.e. combination may be commutative or non-commutative. Order of combination matters in a group .This order of combination is very significant. This is true in case of symmetry product of symmetry operations.

Definition of group and its characteristics

Let us take the example of water molecule and find total symmetry elements in it and total symmetry operations generated by these symmetry elements. Figure 2 shows the various symmetry elements in structure of water molecule.

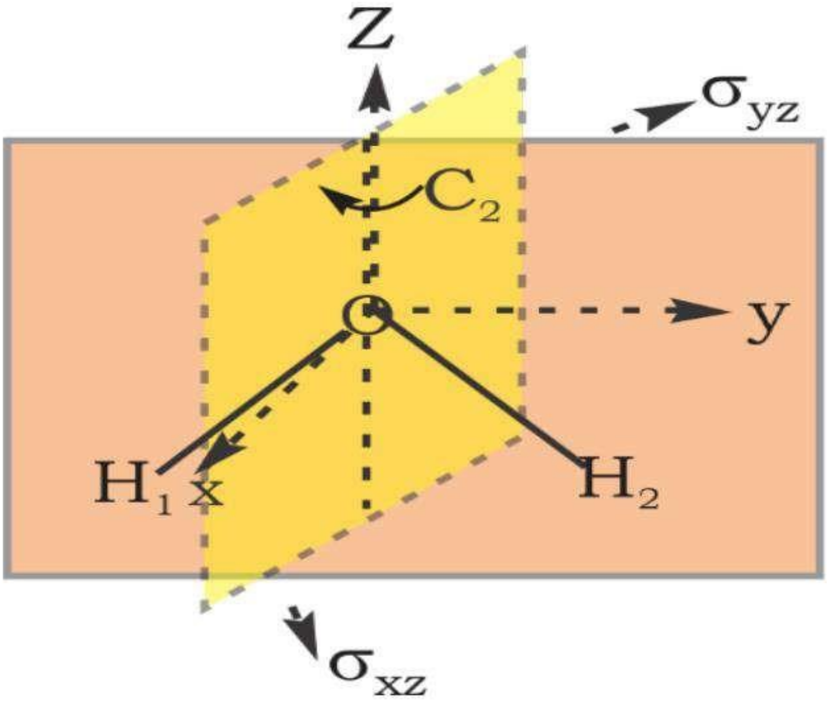


Figure 2: Various symmetry elements in H2O molecule

There are four symmetry elements σxz , σyz ,$C2$ and E in $H2O$ molecule. Total symmetry elements are four. Let us find the symmetry operations generated by each of these.

- E generates only one operation and it is E.

- σxz generates $\sigma xz1$ and $\sigma xz2 =E$ symmetry operations and these are σxz and E only.

- σyz generates $\sigma yz1$ and $\sigma yz2 =E$ symmetry operations and these are σyz and E only.

- $C2$ generates $C21$ and$C22=E$ symmetry operations and these are $C2$ and E only.

Thus total symmetry operations generated here: σxz, σyz , $C2$ and E in $H2O$ i.e. only four symmetry operations are generated by four symmetry elements. In case of $H2O$ molecule number of symmetry elements and symmetry operations are same. It is not same always.

These four symmetry operations constitute a group ie [σxz, σyz , $C2$, E] is a group of order four.

Number of elements in a group is its order. Now let us verify the four group properties.

1. Here E is the identity, $EE=E$, $EC2=C2E = C2$; $E\sigma xz= \sigma xzE = \sigma xz$; $E\sigma yz = \sigma yzE = \sigma yz$,thus group element remains unchanged. Figure 3 shows all these results. Symmetry operations are always carried out from right to left.

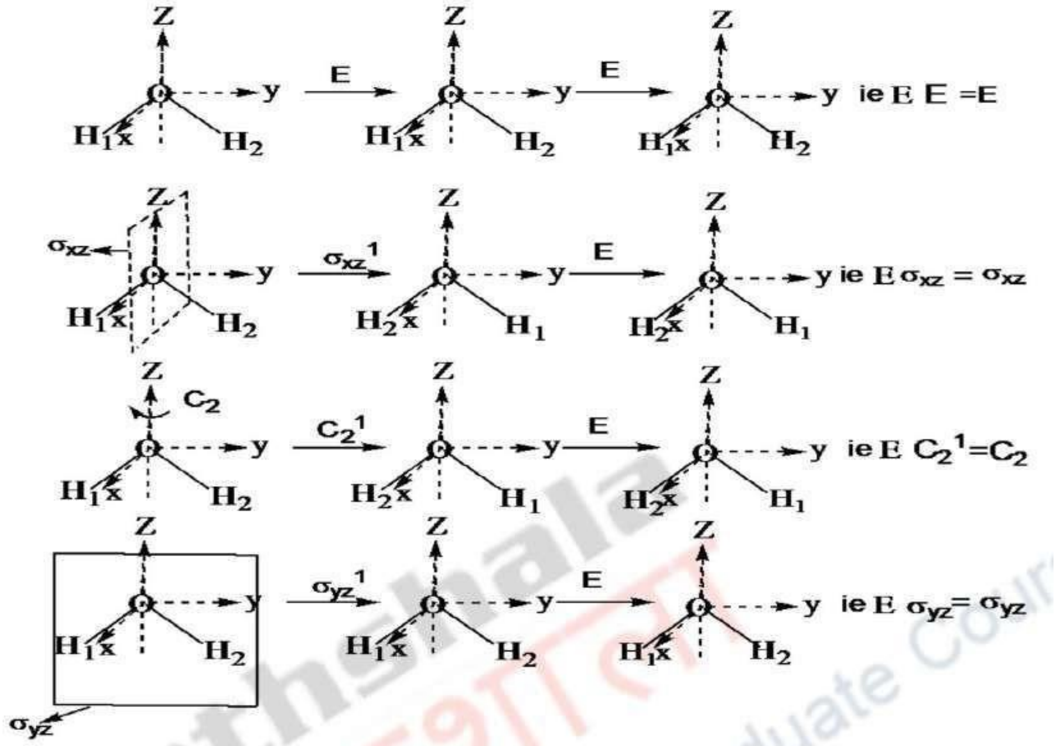


Figure 3: Combination of E with C_2, σ_{xz} , σ_{yz}

2. Every element has its reciprocal (i.e. inverse)

Here (σxz)-1 is (σxz) ; (σyz)-1 = σyz and (C2)-1 is C21. Symmetry operation and its reciprocal when combined give identity i.e.

σxz (σxz)-1 = E ; σyz (σyz)-1 =E; C21(C21)-1 =E

In Figure 4 we notice that the symmetry product C2.C2 =E, it means C2is its own inverse i.e. (C2)- 1 =C2. Similarly σxz =E , therefore, σxz is the inverse of itself and similarly inverse of σyz is σyz.. Thus in the group each element has a unique nverse. Here each and every group element (symmetry operation) is the inverse of itself.

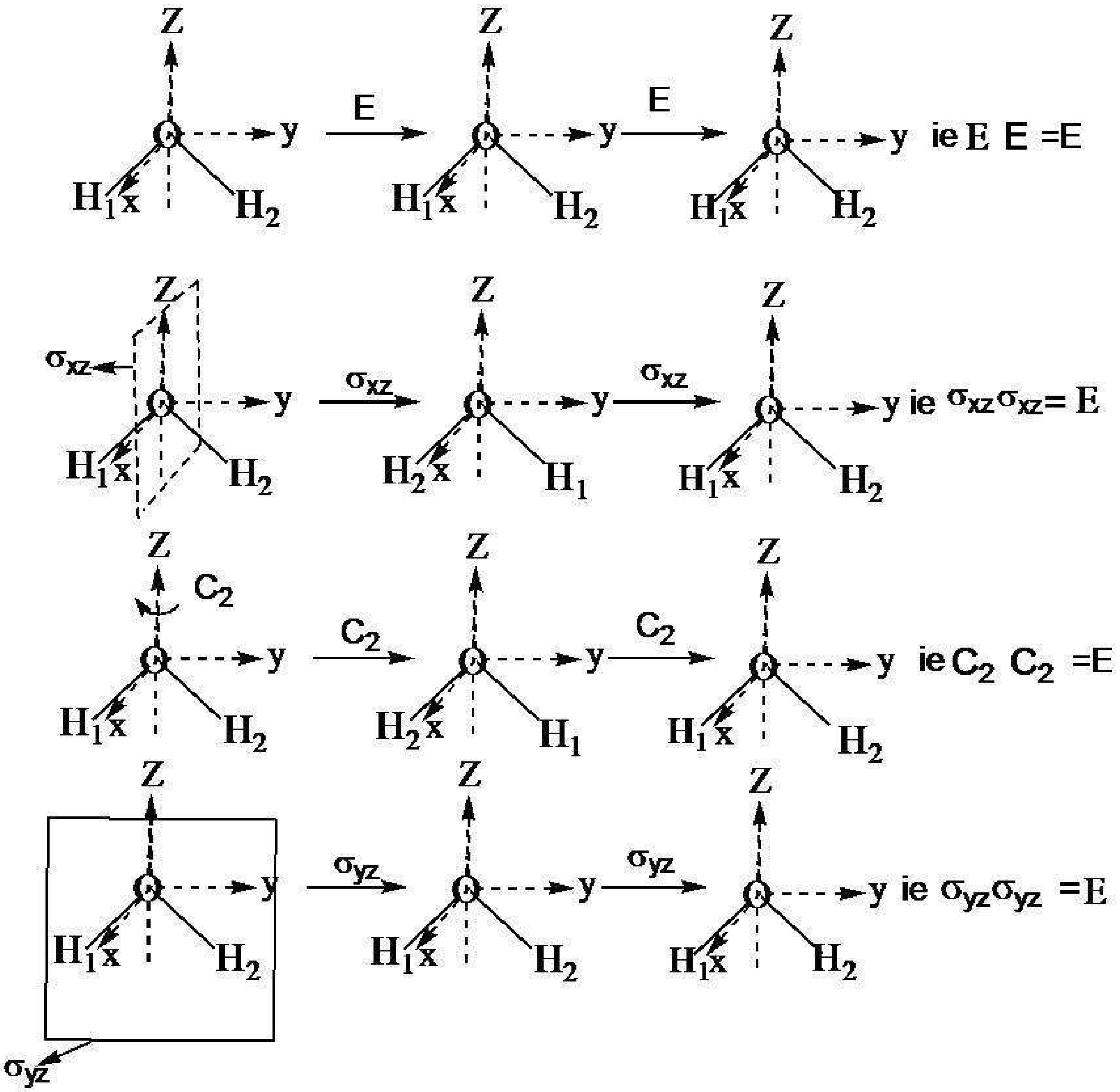


Figure 4: Combination of C2 with C2 , σxz withσxz , σyz with σyz

3. Law of associative multiplication (order of multiplication should not be changed). (C21 σxz) σyz = C21(σxz σyz) . These products are shown in the Figure 5.

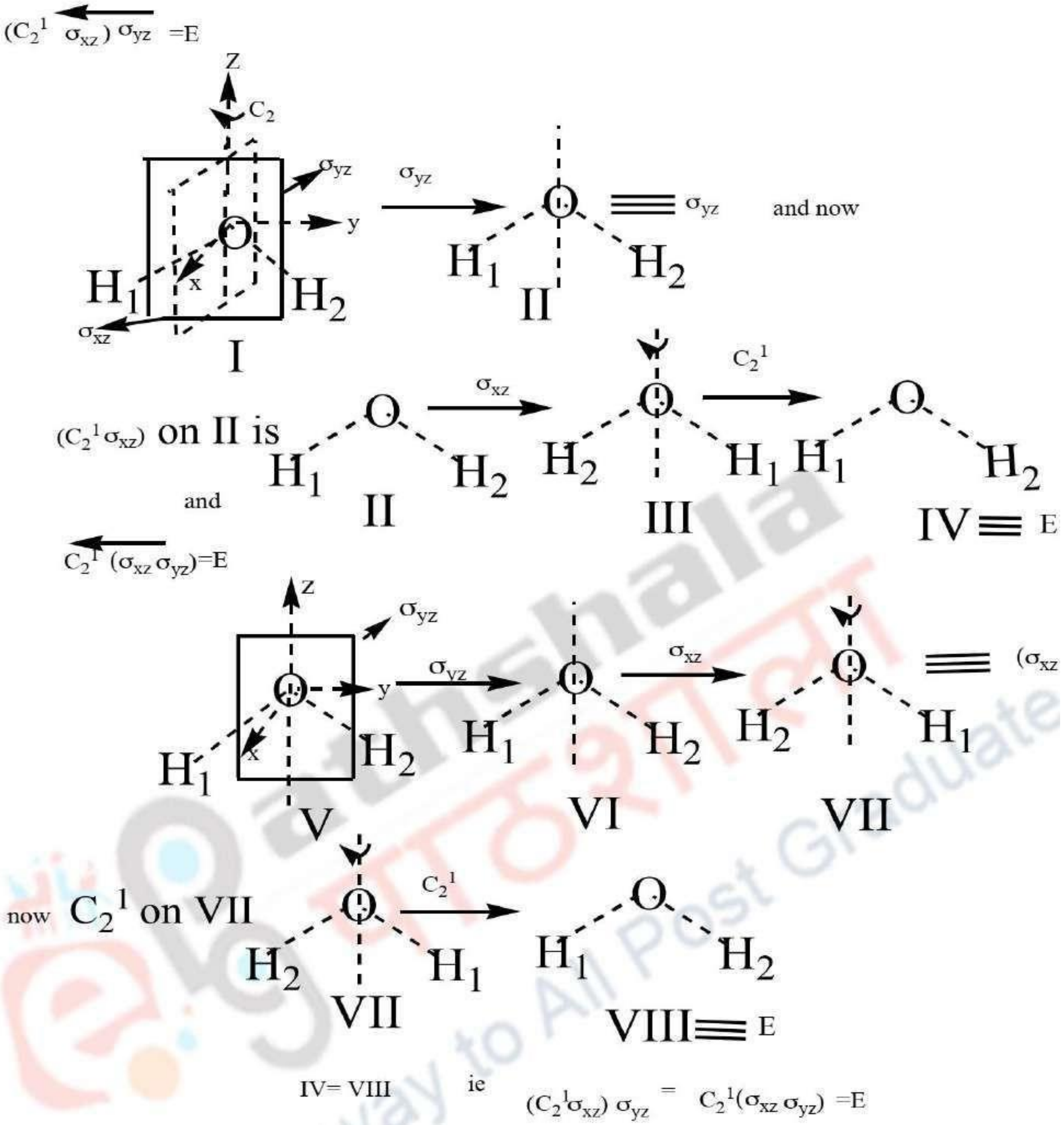


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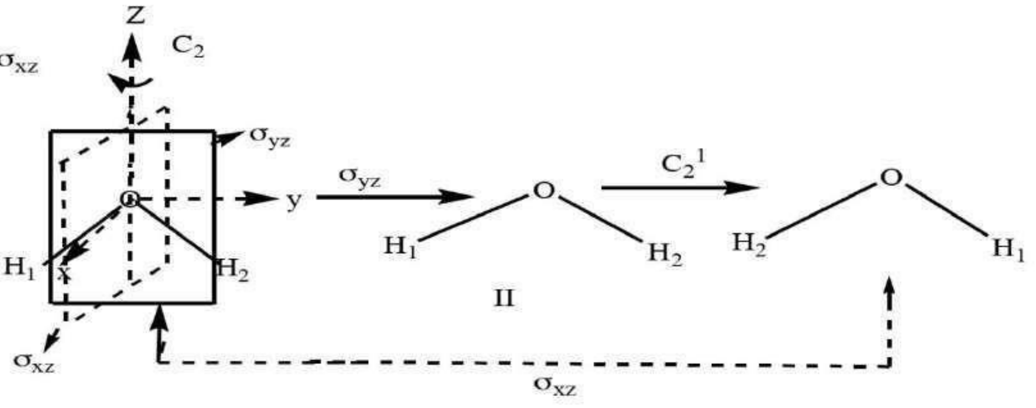
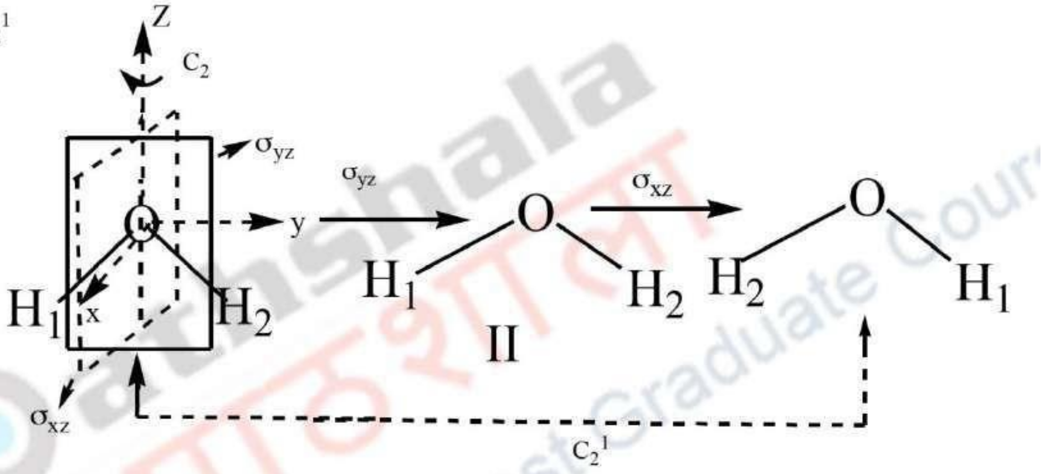
Figure 5: Associative products ($C_2\ \sigma_{xz}$) σ_{yz} = $C_2^1(\sigma_{xz}\ \sigma_{yz})$ for H_2O molecule

4. Product of two or more elements or square of the element must be an element of the group. The combinations of various symmetry operations are shown in figure 6

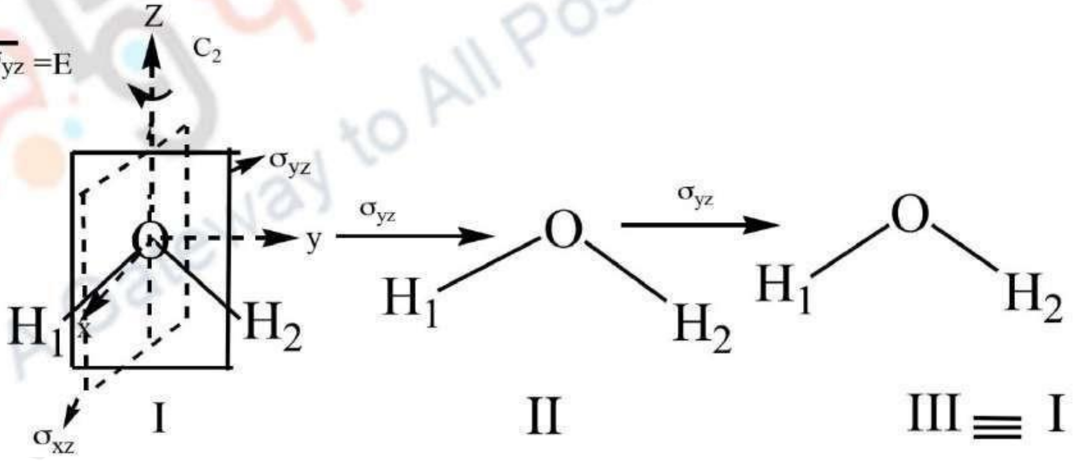
(ii) $\overleftarrow{C_2^1\sigma_{yz}}=\sigma_{xz}$



(i) $\overleftarrow{\sigma_{xz}\sigma_{yz}}=C_2^1$



(iii) $\overleftarrow{\sigma_{yz}\sigma_{yz}}=E$



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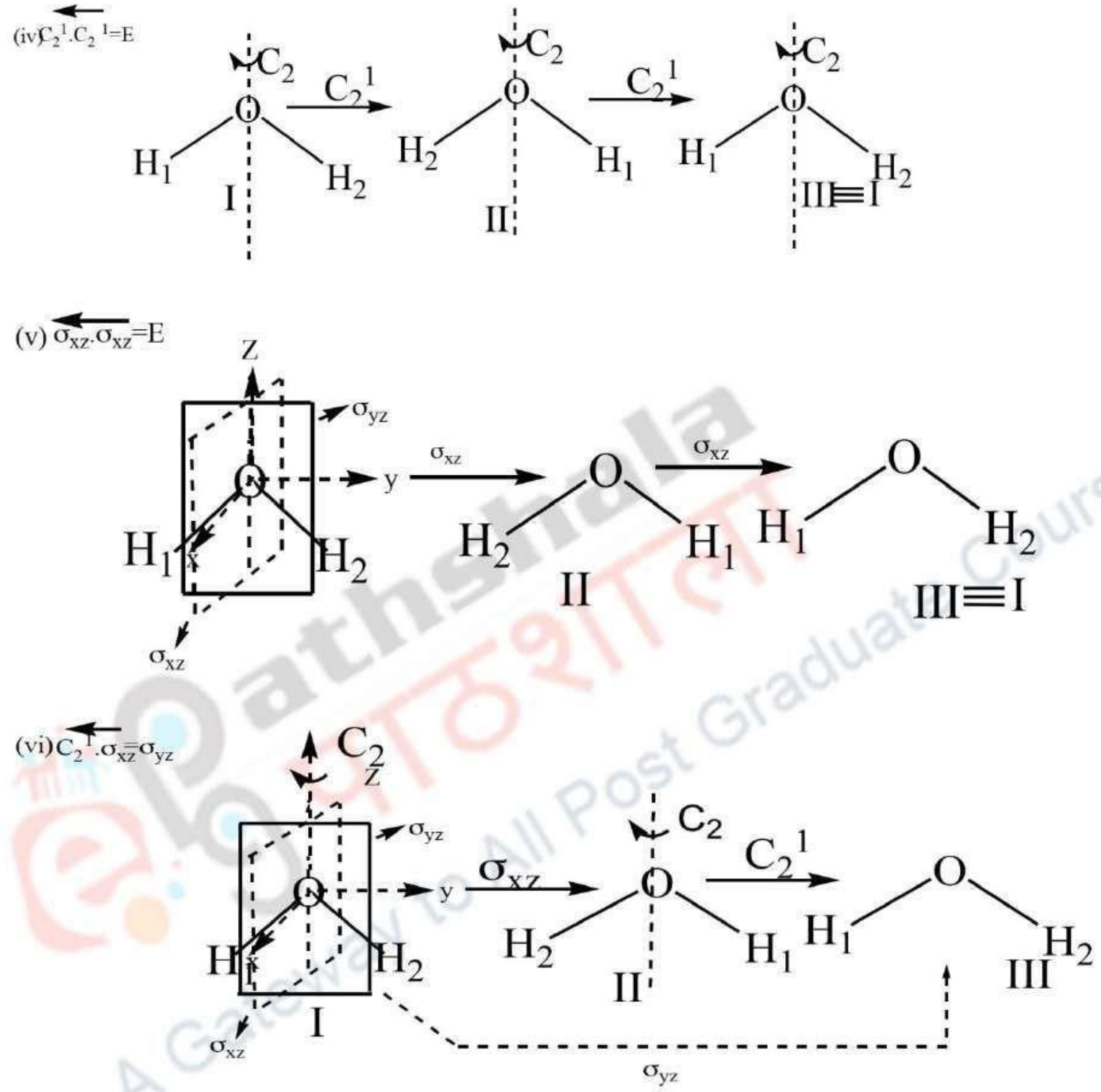

Figure 6: Effect of Combination of Symmetry Operations on H_2O Molecule

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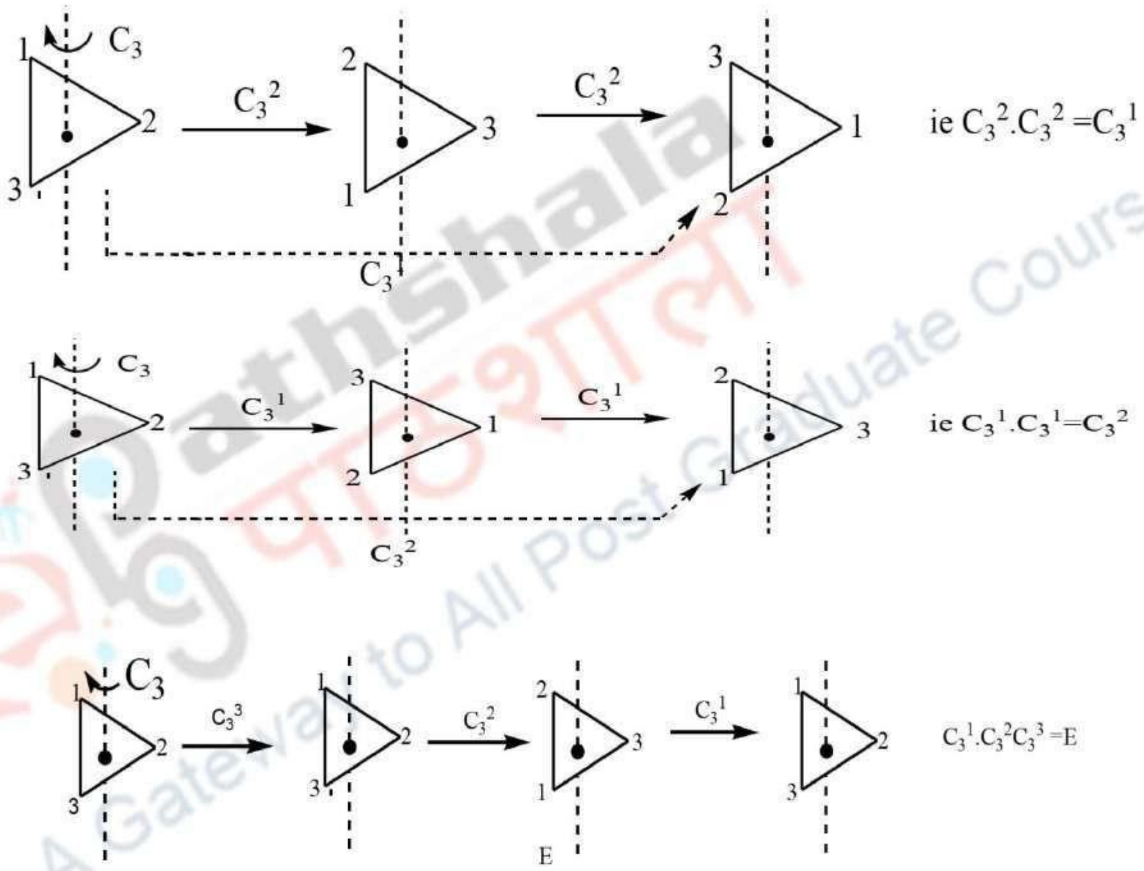
Thus all the four properties of a group [σxz , σyz ,C2 , E] have been verified. Let us take another example of C3 axis in an equilateral triangle and see that operations generated by C3 axis constitute a group.C3 axis generates the following symmetry operations: C31, C32, C33 =E i.e. in all three symmetry operations are generated. Various symmetry products are shown in Figure 7.

Similarly other symmetry products can be worked out and all the four properties of the group can be verified. Let us now find the following products or inverses.

C31.C32 =? ; (C31)-1=? C32.C32 =? C31.C31 =? ; (C31)[(C32)(C33)] = [(C31) (C32)](C33) Inverse of C31)-1=C32 so now show that C31.C32=E.



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igure 7: Various symmetry products of Total symmetry elements present in the given molecule symmetry operations C_3^1, C_3^2, C_3^3

Abelian group

In our previous discussion on group properties the order of combination of elements was stressed. In case of integers and addition as the mode of combination the order of combination does not matter but in symmetry operations as group elements it matters a lot. An abelian group is that group in which all elements when combine in either way give the same result. In a group [A, B, C, D] all combination products

AB=BA, AC=CA, BC=CB

are true i.e. the elements commute with each other. The integers [------- 3, -2, -1, 0, +1, +2, +3 ----] under the mode of combination as addition and zero as the identity element constitutes an abelian group of infinite order.

Cyclic group

In this group the elements are generated by taking the power of one group element. Let the element be X that generates all other group elements. Then the group elements are X1, X2, X3, X4---------Xn =E. There are n elements in the group and thus the order of the group is n. Cyclic group is always an abelian group as powers are additive and their order of combination does not matter.

X1+X2=X2+ X1=X3

Finite and infinite groups

The group which has infinite number of elements in it is called infinite group. All positive and negative integers with zero as the identity and addition as the mode of combination constitute an infinite order group ie [4, 3, 2, 1 0,-1,-1,-3,-4-------] with addition as mode is a n infinite group In finite group the number of elements is finite. The group (1,-1, i,-i) is a finite group of order **four**.

Introduction

In group theory, molecules or other objects can be organized into point groups based on the type and number of symmetry operations they possess. Every molecule in a point group will have all of the same symmetry operations as any other molecule in that same point group. The most common, and chemically relevant point groups are described below.

The Low Symmetry Point Groups

C_1 Point Group

Overall, we divide point groups into three major categories: High symmetry point groups, low symmetry point groups, dihedral point groups, and rotational point groups. Let us begin with the low symmetry point groups. As the name says, these point groups only have few symmetry elements and operations. The point group C_1 is the point group with the lowest symmetry. Molecules that belong to this point group only have the identity as symmetry element.

Figure 4.2.14.2.1 C_1 point group of bromochlorofluromethane (Attribution: symotter.org/gallery)

An example is the bromochlorofluromethane molecule (Figure 4.2.14.2.1). It has no symmetry element except the identity (E). The name C_1 comes from the symmetry element C_1. A C_1 operation is the same as the identity.

C_s Point Group

The point group C_s has a mirror plane in a addition to the identity. An example is the 1,2-bromochloroethene molecule (Figure 4.2.24.2.2).

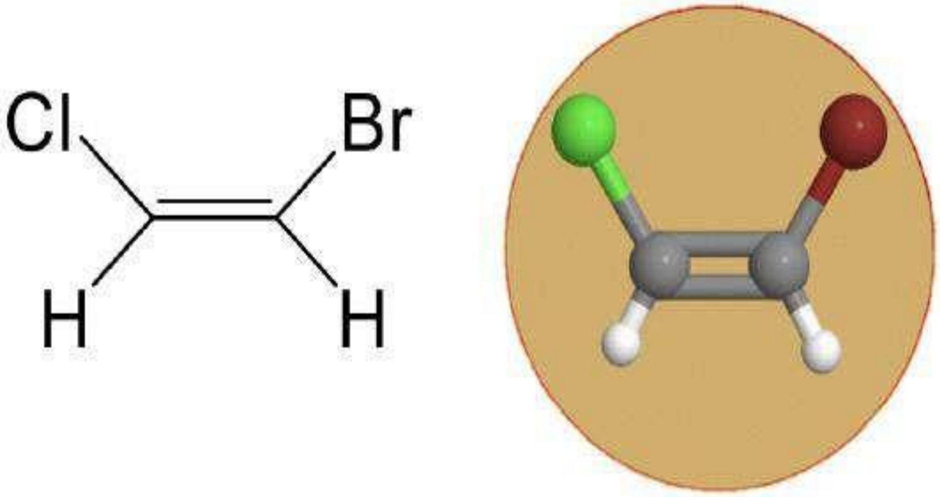


Figure4.2.24.2.2C$_s$ point group of 1,2-bromochloroethene (Attribution: symotter.org/gallery)

This is a planar molecule and the mirror plane is within the plane of the molecule. This mirror plane does not move any atoms when the reflection operation is carried out, nonetheless it exists because any point of the molecule above the mirror plane will be found below the mirror plane after the execution of the operation. Vice versa, any point below the mirror plane will be above the mirror plane. This mirror plane does not have a vertical or horizontal mirror plane designation because no proper rotational axes exist.

C$_i$ Point Group

The point group C$_i$ has the inversion as the only symmetry element besides the identity. The point group C$_i$ is sometimes also called S$_2$ because an S$_2$ improper rotation-reflection is the same as an inversion. An example is the 1,2-dibromo 1,2-dichloro ethane (Figure 4.2.34.2.3).

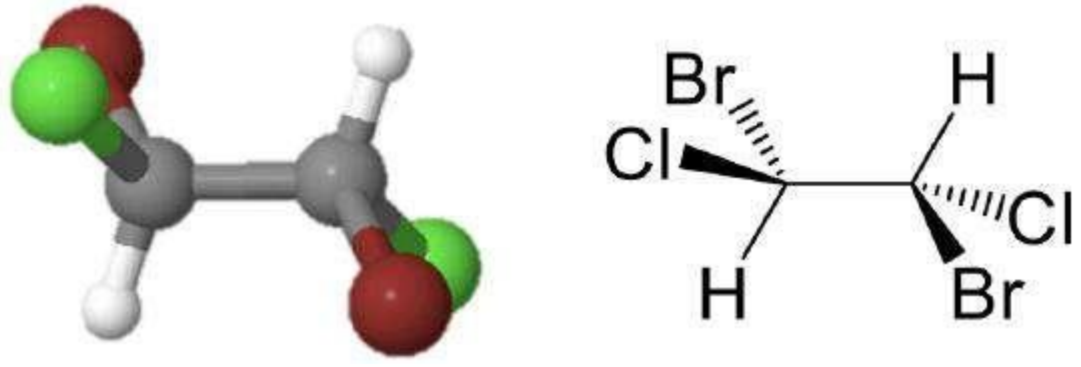


Figure 4.2.34.2.3 The C$_i$ point group: 1,2-dibromo-1,2-dichloroethane (Attribution: symotter.org/gallery)

This molecule looks quite symmetric, but it has inversion center in the middle of the carbon-carbon bond as the only symmetry element. Upon execution of the inversion operation, the two carbons swap up their positions, and so do the two bromine, the two chorine, and the two hydrogen atoms.

The High Symmetry Point Groups

The symmetry elements of the high symmetry point groups can be more easily understood when the properties of platonic solids are understood first. Platonic solids are polyhedra made of regular polygons. In a platonic solid all faces, edges, and vertices (corners) are symmetry-equivalent. We will see that this is a property that can be used to understand the symmetry elements in high symmetry point groups. There are only five possibilities to make platonic solids from regular polygons (Figure 4.2.44.2.4).

The first possibility is to construct a tetrahedron from four regular triangles. The second platonic solid is the octahedron made of eight regular triangles. The third possibility is the icosahedron made of twenty triangles. In addition, six squares can be connected to form a cube, and twelve pentagons can be connected to form a dodecahedron. There are no possibilities to connect other regular polygons like hexagons to make a platonic solid.

The T_d Point Group

The tetrahedron, as well as tetrahedral molecules and anions such as CH_4 and BF_4- belong to the high symmetry point group T_d (Note that only tetrahedral molecules where all four outer atoms/groups are the same will be in the T_d point group). Let us find the symmetry elements and symmetry operations that belong to the point group T_d. First, we should not forget the identity operation, E. Next, it is useful to look for the principal axes.

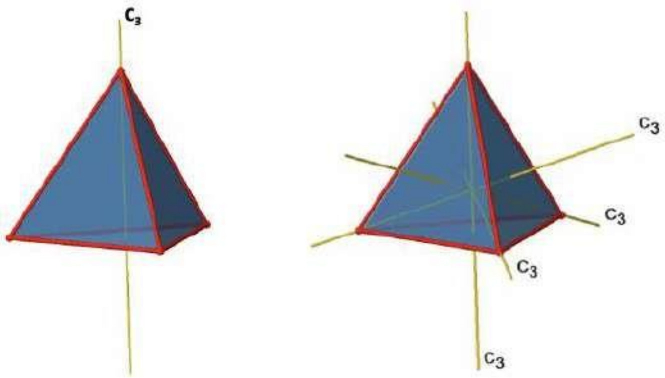


Figure 4.2.54.2.5 The C_3 axes in a tetrahedron (Attribution: symotter.org/gallery)

The tetrahedron has four principal C_3 axes (Figure 4.2.54.2.5). It is a property of the high-symmetry point groups that they have more than one principal axis. The C_3 axes go through the vertices of the tetrahedron. Because each C_3 axis goes through one vertex, there are four vertices, and we know that in a platonic solid all vertices are symmetry-equivalent, we can understand that there are four C_3 axes. How many unique C_3 operations are associated with these axes? After three rotations around 120° we reach the identity. Therefore $C_3^3=E$, and we only need to consider the C_3^1 and the C_3^2 rotation about 120 and 240° respectively. Because there are four C_3 axes, there are four C_3^1 and four C_3^2 operations and eight C_3 operations overall. In addition to the C_3 axes there are C_2 axes (Figure 4.2.64.2.6).

Figure 4.2.64.2.6 The C_2 axes in a tetrahedron belonging to the point group T_d (Attribution: symotter.org/gallery)

You can see that a C_2 axis goes through two opposite edges in the tetrahedron. Because a tetrahedron has six edges, and each C_2 axis go through two edges there are 6/2=3 C_2 axes. There is only one C_2 symmetry operation per C_2 axis because we produce the identity already after two rotations. Therefore there are three C_2^1 operations overall.

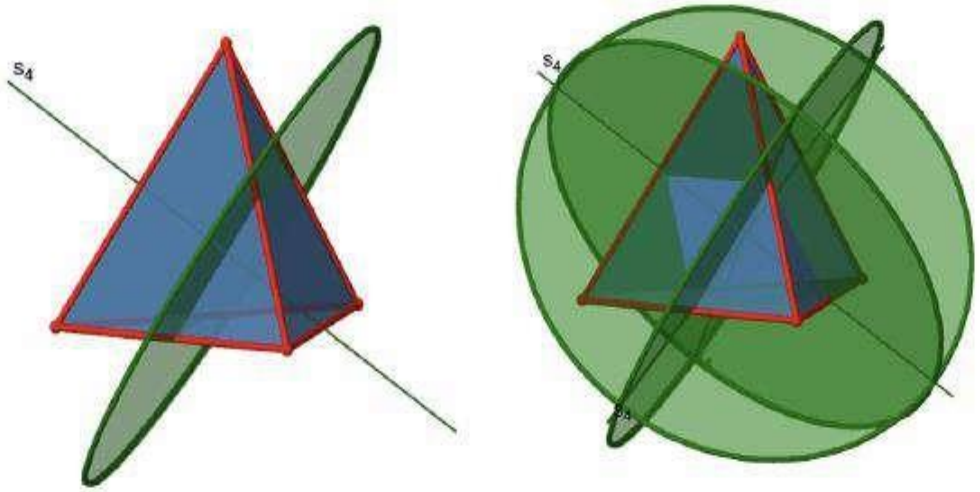


Figure 4.2.74.2.7 The S_4 axes in a tetrahedron (Attribution: symotter.org/gallery)

In addition, the T_d point group has S_4 improper rotation reflections. Like the C_2 axes, they pass through the middle of two opposite edges. This also means that they are superimposing the C_2 axes. Because there are six edges, and two S_4 axes per edge there are 6/2=3 S_4 axes (Figure 4.2.74.2.7). How many operations are associated with these S_4 axes? The order of the axes are even, and therefore we need four S_4 operations to produce the identity. The S_4^2 operation is the same as a C_2^1 operation because reflecting two times is equivalent to not reflecting at all, and rotating two times by 90° is the same as rotating about 180°. Therefore overall, only S_4^1 and S_4^3 operations are unique operations. S_4^2 and S_4^4 can be expressed by the simpler operations C_2^1 and E respectively. Because there are 3 S_4 axes, there are three S_4^1 and three S_4^3 operations. Overall there are six S_4 operations.

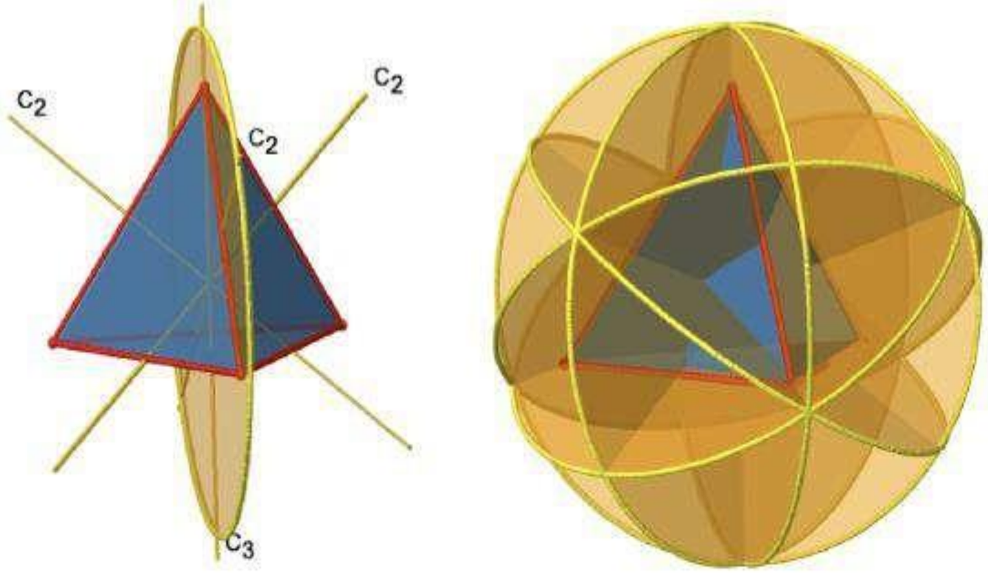


Figure 4.2.84.2.8 The mirror planes and C_2 axes in a tetrahedron belonging to the point group T_d (Attribution: symotter.org/gallery)

There are also mirror planes (Figure 4.2.84.2.8). The planes contain a single edge of the tetrahedron, thereby bisecting the tetrahedron. There a six edges in a tetrahedron, and therefore there are 6/1=6 mirror planes.These planes are dihedral planes because each plane contains a C_3 principal axis and is bisects the angle between two C_2 axes. Overall, there are three C_2 axes and three C_2 operations. There is one reflection operation per mirror plane because reflecting two times produces the identity. Therefore, there are six σ_d reflection operations.

Symmetry Operations in the T_d Point Group

Every molecule or object in the T_d point group has the following symmetry operations:

- E, 8 C_3, 3 C_2, 6 S_4, and 6 σ_d

The Octahedral Point Group O_h

Another high symmetry point group is the point group O_h. Both the octahedron as well as the cube belong to this point group despite their very different shape Figure 4.2.94.2.9. Because they belong to the same point group they must have the same symmetry elements and operations. There are many octahedrally shaped molecules, such as the SF_6.

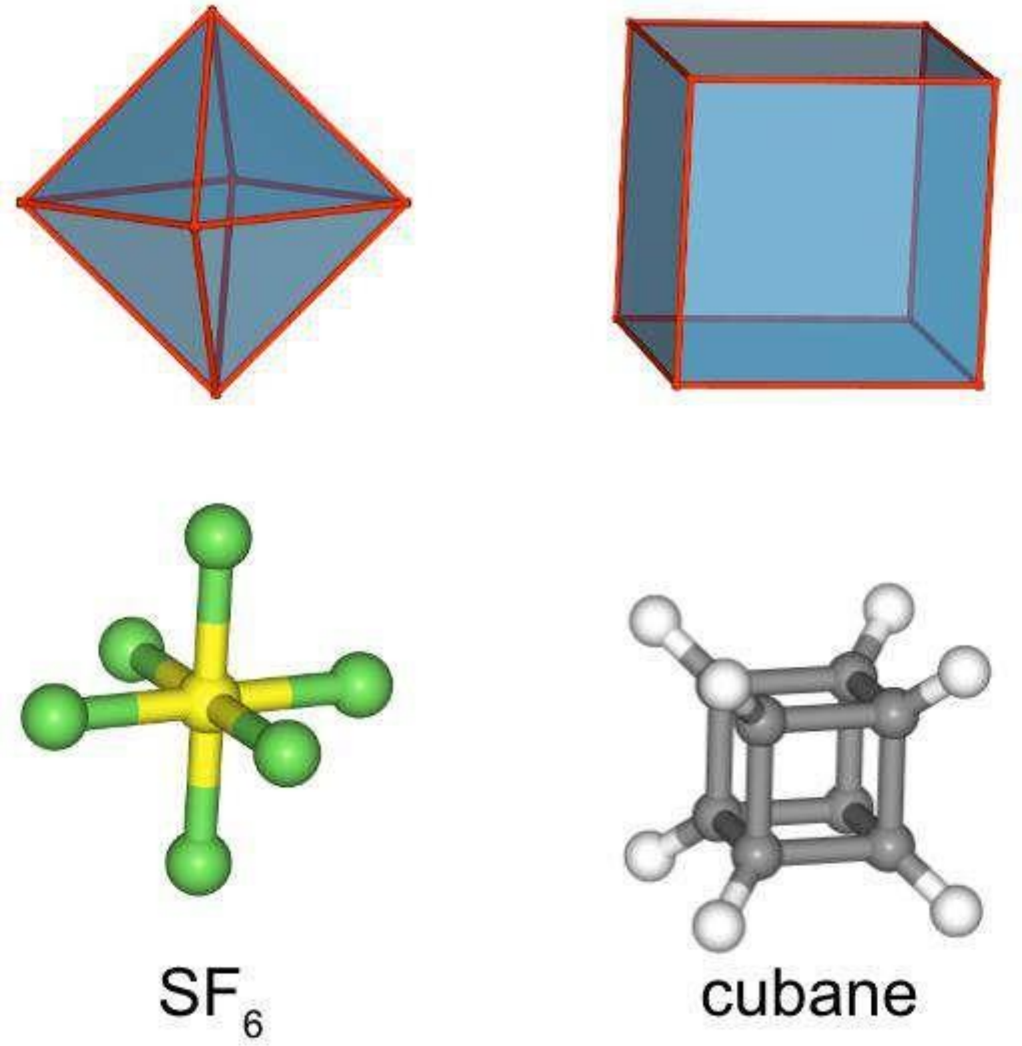


Figure 4.2.94.2.9: SF_6 and cubane with cubic and octahedral shape, respectively, belong to the point group O_h (Attribution: symotter.org/gallery)

Molecules with cubic shapes are far less common, because a cubic shape often leads to significant strain in the molecule. An example is cubane C_8H_8. Let us determine the symmetry elements and operations for the point group O_h using the example of the octahedron. If we used the cube, we would get exactly the same results.

There are three C_4 principal axes in the octahedron. They go through two opposite vertices of the octahedron (Figure 4.2.104.2.10). There are three C_4 axes because an octahedron has six vertices which are all symmetry-equivalent because the octahedron is a platonic solid.

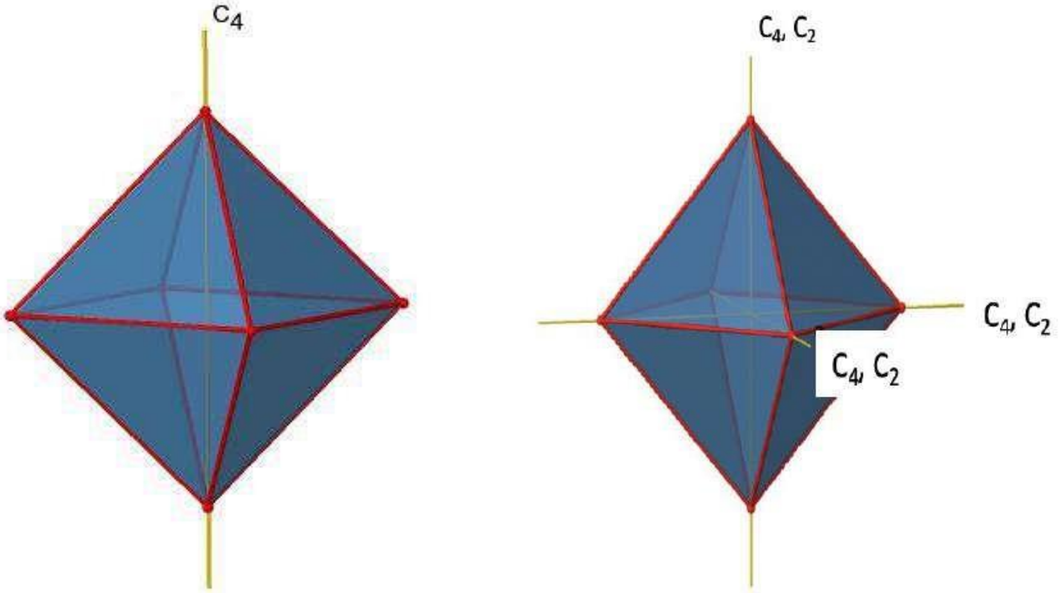


Figure 4.2.104.2.10: The C_4 and C_2 axes in the octahedral point group O_h (Attribution: symotter.org/gallery)

We can see that there are also C_2 axes where the C_4 axes run. This is because rotating two times around 90° is the same as rotating around 180°. What are the symmetry operations associated with these symmetry elements? Rotating four times around 90° using the C_4 axes produces the identity. So we have to consider the operations C_4^1, C_4^2, C_4^3 and C_4^4. How many of these are unique? C_4^4 is the same as the identity, so it is not unique, In addition a C_4^2 is identical to a C_2^1, and thus C_4^2 is also not unique, and can be expressed by the simpler operation C_2^1. That leaves the C_4^1 and the C_4^3 as the only unique symmetry operations. Because we have three C_4 axes, there are 2x3=6 C_4 operations, in detail there are $3C_4^1$ and three C_4^3 operations. In addition, there are the three C_2^1 operations belonging the three C_2 axes.

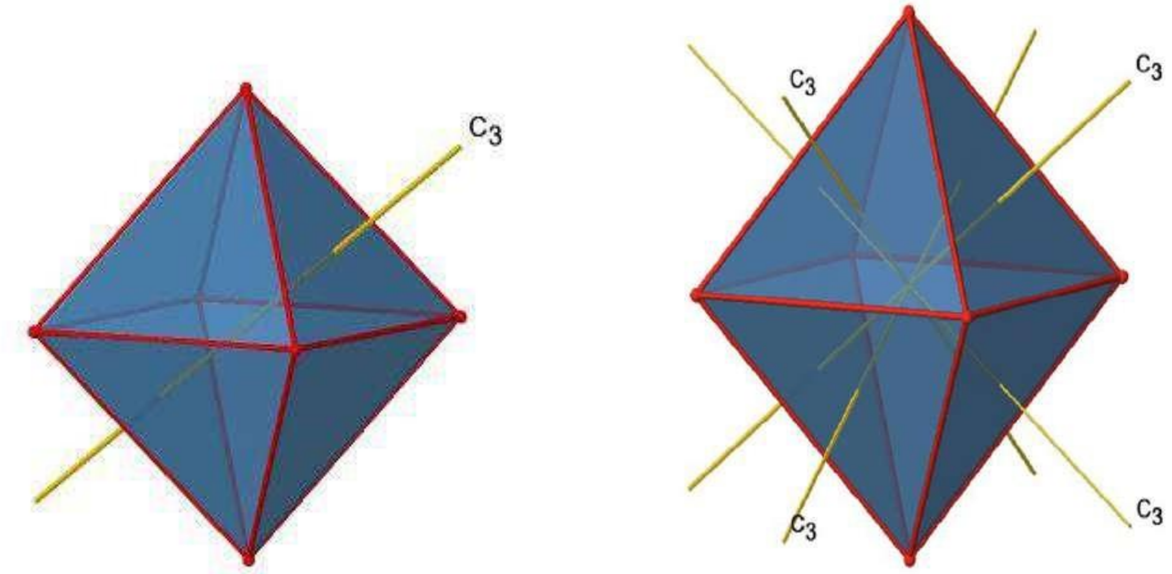


Figure 4.2.114.2.11: The C_3 axes in the octahedral point group O_h (Attribution: symotter.org/gallery)

In addition, there are four C_3 axes (Figure 4.2.114.2.11:). They are going through the center of two opposite triangular faces of the octahedron.You see above a single C_3 axis, and on the right hand side all four of these axes. How can we understand that there are four axes? An octahedron has overall eight triangular faces, and each C_3 axis goes through two opposite faces, so there are 8/2=4 C_3 axes. Each C_3 axis has the C_3^1 and the C_3^2 as unique symmetry operations. The C_3^3 is the same as the identity. So overall we have 4x2=8 operations, four of them are C_3^1, and four of them are C_3^2.

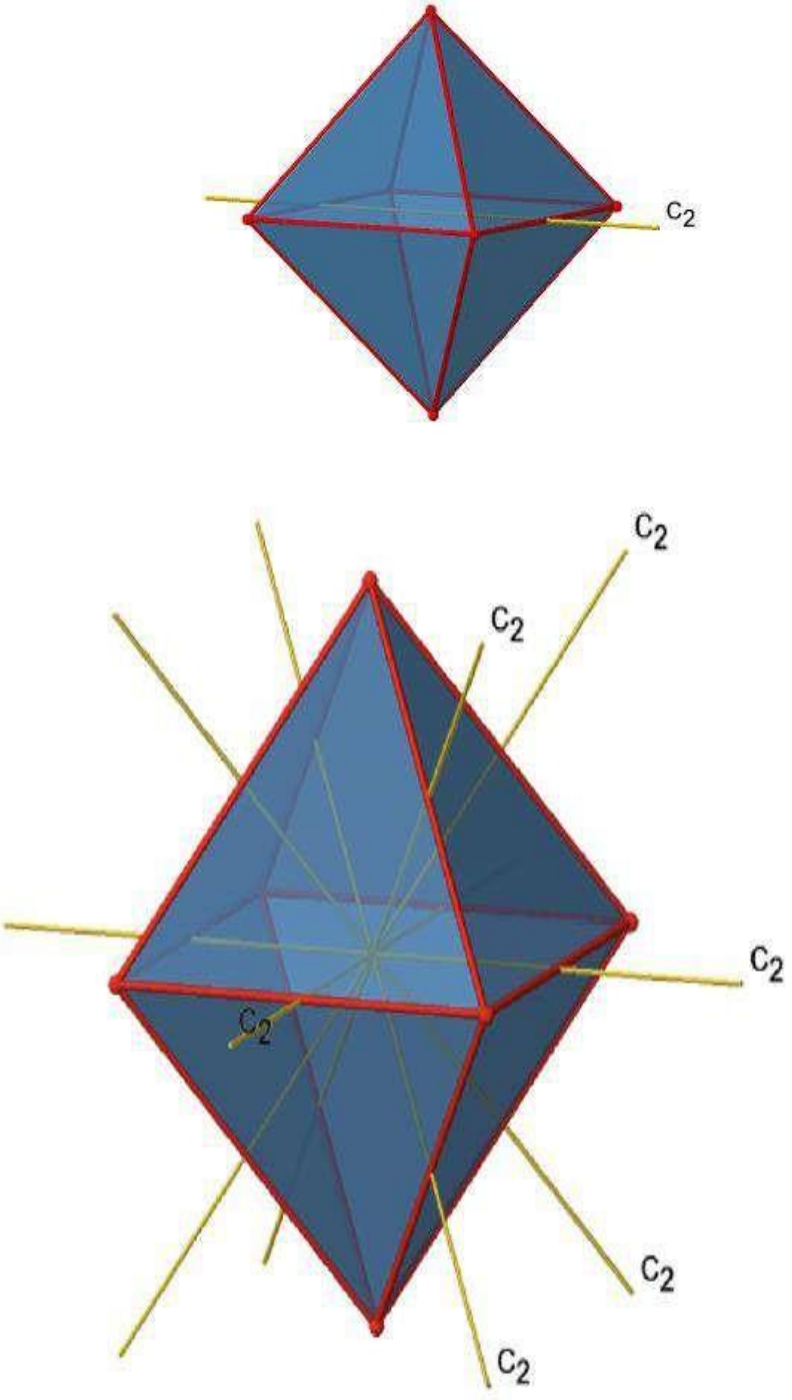


Figure 4.2.124.2.12: The C_2' axes in the octahedral point group O_h (Attribution: symotter.org/gallery)

In addition to the C_2 axes that superimpose the C_4 axes, there are C_2’ axes which go though two opposite edges of the octahedron (Figure 4.2.124.2.12:). How many of them are there? An octahedron has twelve edges, and because each C_2’ passes through two edges, there must be 12/2=6 C_2’ axes. These axes have primes because they are not conjugate to the C_2 axes that superimpose the C_4 axes. For each C_2’ axis there is only the C_2’ ^{1} as the unique symmetry operation, and therefore there are overall 6 C_2’^{1} symmetry operations.

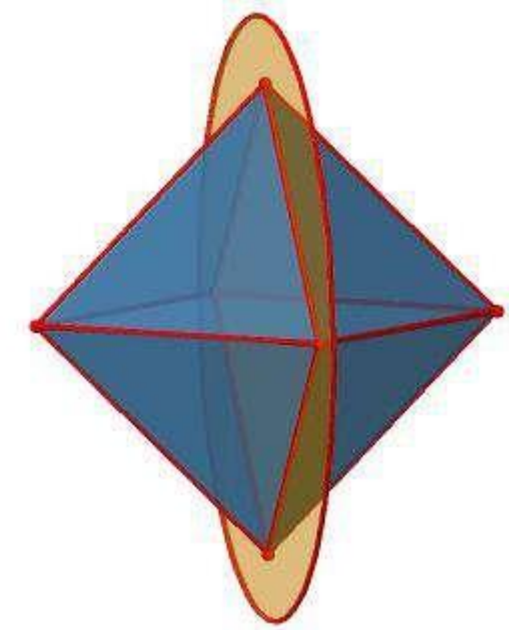
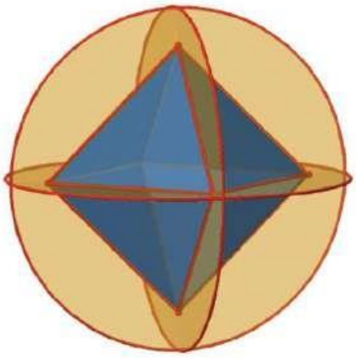


Figure 4.2.134.2.
octahedral point
group O_h (Attribution: s

Let us look at the
.134.2.13). There
are horizontal mirror pl
4 principal axes.
Note that this mirror pla
the one to which
it stands perpendicular.
axes, it has also
properties of a vertical
horizontal mirror



plane because it stands perpendicular to the third C_4. The horizontal properties trump the vertical ones, so to say. You can see that a single mirror plane contains four edges of the octahedron. Because there are twelve edges, there are 12/4=3 horizontal mirror planes. There is one mirror plane per principal C_4 axis. There are three horizontal reflection operations because there is always only one reflection operation per mirror plane

Figure 4.2.144.2.14: The vertical mirror planes in the octahedral point group O_h (Attribution: symotter.org/gallery)

Next let us look for vertical mirror planes (Figure 4.2.144.2.14). You can see that - contrast to the horizontal mirror planes - it does not contain any edges. Rather, it cuts through two opposite edges. You can see that this plane contains a C_4 axis, but it does not stand perpendicular to the other two C_4 axes. Therefore it has only the properties of a vertical mirror plane. You can see however, that the mirror plane bisects the angle between two C_2' axes which also depicted. This makes the vertical mirror planes dihedral mirror planes, σ_d. How may of them do we have? As previously mentioned, each mirror plane cuts through two opposite edges. There are twelve edges in an octahedron, and thus there are 12/2=6 dihedral mirror planes. You can see all of them on the right side of

Figure 4.2.144.2.14. Each mirror plane is associated with one reflection operation, therefore there are six dihedral reflection operations.

Next we can ask if the point group O_h has an inversion center? Yes, there is one in the center of the octahedron (Figure 4.2.154.2.15)!

Figure 4.2.154.2.15: The inversion center of the octahedral point group O_h (Attribution: symotter.org/gallery)

Each point in the octahedron can be moved through the inversion center to the other side, and the produced octahedron will superimpose the original one. There is always one inversion operation associated with an inversion center.

Next, let us look for improper rotations. You can see an S_6 improper rotation operation below (Figure 4.2.164.2.16, left).

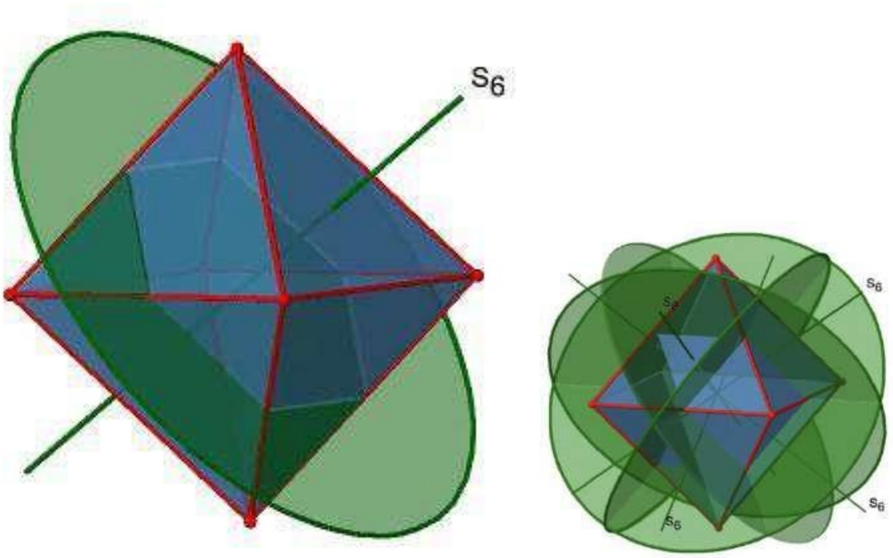


Figure 4.2.164.2.16: The S_6 improper rotation element of the octahedral point group O_h (Attribution: symotter.org/gallery)

The improper S_6 axis passes though the centers of two opposite triangular faces. One can see that rotation about 60° alone does not make the octahedron superimpose. The reflection at a plane perpendicular to the improper axis is required to achieve superposition. Overall, the rotation-reflection swaps up the position of the two opposite triangular faces. How many S_6 improper axes are there? Since each S_6 passes through two faces, and an octahedron has 8 faces there must be 8/2=4 S_4 axes. You can see all of them above (Fig. 2.2.31, right). Note that they are in the same position as the $4C_3$ axes we previously discussed. How many unique operations are associated with them? For an S_6 axis we need to consider operations from S_6^1 to S_6^6. S_6^6 is the same as the identity so it is not unique. The S_6^2 is the same as a C_3^1 because rotating two times round 60° is the same as rotating around 120°, and reflecting twice is the same as not reflecting at all. Similarly, an S_6^4 is the same as an C_3^2. Rotating four time by 60° is the same as rotating two times by 120° and reflecting four times is the same as not reflecting at all. Further, an S_6^3 is the same as an inversion. After three 60° rotations we have rotated by 180°. If we reflect after that, then this is the same as an S_2^1 operation which is the same as an inversion. Therefore, only the S_6^1 and the S_6^5 operations are unique, all other operations can be expressed by simpler operations.

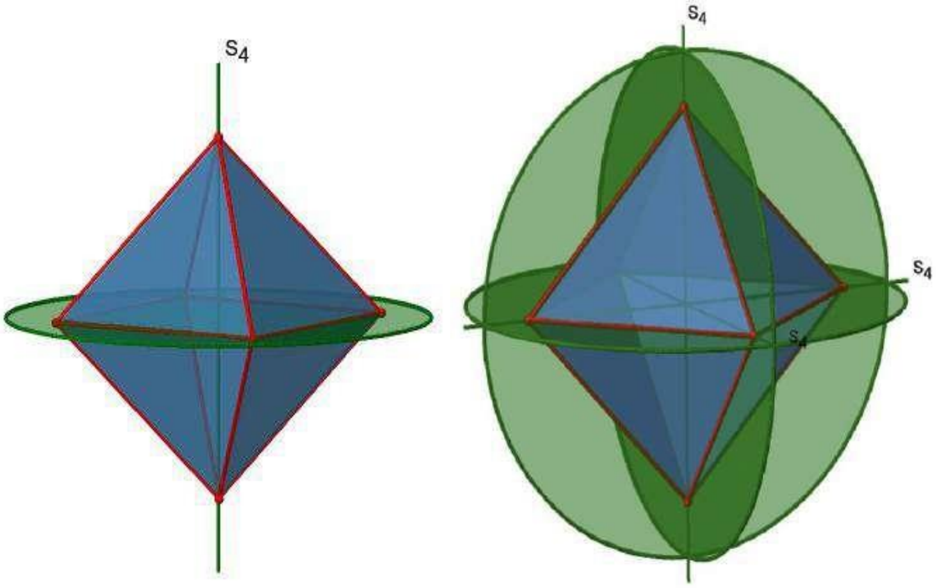


Figure 4.2.174.2.17: The S_4 improper axis of the octahedral point group O_h (Attribution: symotter.org/gallery)

The octahedron also has S_4 improper axes, and you can see one of them in Figure 4.2.174.2.17, right). It goes through two opposite corners of the octahedron. The S_4 improper axis seemingly does the same as the C_4 axis that goes through the same two opposite vertices, but actually does not. While rotating around 90° already makes the octahedron superimpose with its original form, executing the reflection operation after the rotation swaps up the position of the two vertices, and generally all points of the octahedron above and below the plane, respectively. Overall the S_4 moves the points within the object differently compared to the C_4 which makes it an additional, unique symmetry element. There are overall three S_4 improper axes because the octahedron has six vertices and one S_4 passes through two vertices.

Symmetry Operations in the O_h Point Group

Every molecule or object in the O_h point group has the following 48 symmetry operations:

- E, 8 C_3, 6 C_2, 6 C_4, 3 C_2 (C_4^2), i, 6 S_4, 8 S_6, 3 σ_h, and 6 σ_d

The I_h Point Group

The two remaining platonic solids, the icosahedron and the dodecahedron, belong both to the icosahedral point group I_h. This is despite they are made of different polygons. Because they belong to the same point group, they have exactly the same symmetry operations. An example for a molecule with icosahedral shape is the molecular anion $B_{12}H_{12}^{2-}$. Examples of molecules with dodecahedral shape include dodecahedrane ($C_{20}H_{20}$) and buckminsterfullerene (C_{60}). Let us determine the symmetry elements and symmetry operations for the example of the icosahedron. We could also use the dodecahedron, and the results would be the same. The principal axes of the icosahedron are the C_5 axes. You can see one of them, going through the center of the pentagon comprised of five triangular faces below (Figure 4.2.184.2.18).

You can understand that there is a C_5 when considering that there are five triangular faces making a pentagon. The C_5 axis sits in the center of the pentagon. We can see that when we rotate around this C_5 axis, then the produced icosahedron superimposes the original one. The C_5 axis goes through two opposite vertices of the icosahedron. Because an icosahedron has 12 vertices, there must be six C_5 axes overall. You can see all of them below (Figure 4.2.194.2.19). There are four unique symmetry operations associated with a single C_5 axis, namely the C_5^1, the C_5^2, the C_5^3, and the C_5^4. The C_5^5 is the same as the identity. Because there are six C_5 axes, there are overall 6x4=24 C_5 symmetry operations.

In addition, there are C_3 axes. One of them is shown below, and you can see that it passes through the centers of two opposite triangular faces (Figure 4.2.204.2.20). As one rotates by 120° the atoms on the triangular faces change their position, and the resulting icosahedron superimposes the original one. As the name icosahedron says, there are twenty faces overall. Because one C_3 passes through two opposite axes, there are 20/2=10 C_3 axes overall (Figure 4.2.214.2.21:). Each C_3 axis is associated with two symmetry operations, namely C_3^1, and C_3^2. Thus, there are overall 10x2=20 C_3 symmetry operations.

There are also C_2 axes (Figure 4.2.214.2.21). They pass through the centers of two opposite edges of the icosahedron. Rotating around the C_2 axis shown makes the icosahedron superimpose. An icosoahedron has overall 30 edges. Because one C_2 axis passes through the centers of two opposite edges, we can understand that there are 30/2=15 C_2 axes. There is one unique C_2 operation per axis, and therefore there are 15 C_2 operations.

We have now found all proper rotations. Let us look for mirror planes, next. You can see a mirror plane below (Figure 4.2.224.2.22).

It contains two opposite edges. It also bisects two other edges. An icosahedron has overall 30 edges, therefore there are 30/2=15 mirror planes. You can see all of them below (Figure 4.2.234.2.23)).

The icosahedron also has an inversion center in the center of the icosahedron (Figure 4.2.244.2.24). As we carry out the associated symmetry operation, all points in the icosahedron move through the inversion center to the other side.

Let us now look for improper rotations. The improper rotational axes with the highest order are S_{10} axes. They are located in the same position as the C_5 axes, and go through two opposite corners (Figure 4.2.254.2.25).

The S_{10} exists because in an icosahedron there are pairs of co-planar pentagons that are oriented staggered relative to each other. The rotation around 36° brings one pentagon in eclipsed position relative to the other, but superposition is only achieved after the reflection at the mirror plane perpendicular to the rotational axis. Because one S_{10} passes through two opposite vertices, and there are 12 vertices there are 6 S_{10} improper axes. For each axis there are four unique symmetry operations, the S_{10}^1, the S_{10}^3, the S_{10}^7, and the S_{10}^9. Therefore, there are overall 4x6=24 operations possible.

Are the lower order improper rotational axes? Yes, there are S_6 axes that pass through the centers of two opposite triangular faces (Figure 4.2.264.2.26). This symmetry element exists because the two triangular faces are in staggered orientation to each other. Rotation alone brings one face in eclipsed orientation relative to the other, but reflection at a mirror plane perpendicular to the axis is required to achieve superposition. The S_6 axes are in the same location as the C_3 axes. There are 10 S_6 axes because there are twenty faces and one axis passes through two opposite faces. Only the S_6^1 and the S_6^5 operations are unique S_6 operations, all others can be expressed by simpler operations. Therefore there are overall 10 S_6^1+10 S_6^5 = 20 S_6 operations.

We have now found all symmetry operations for the I_h symmetry. There are overall 120 operations making the point group I_h the point group with the highest symmetry.

Symmetry Operations in the I_h Point Group

Every molecule or object in the I_h point group has the following 120 symmetry operations:

- E, 24 C_5, 20 C_3, 15 C_2, i, 24 S_{10}, 20 S_6, and 15 σ

Rotational Point Groups

After having discussed high and low symmetry point groups, let us next look at rotational point groups. Unlike the high symmetry point groups, these only have a single proper rotational axis. The presence or absence of reflection planes further defines this class of point groups

C_n Point Groups

In the most simple case the point groups do not have any additional symmetry element such as mirror planes or improper rotations. These point groups are called pure rotation groups and denoted C_n whereby n is the order of the proper rotation axis. An example is the hydrogen peroxide molecule H_2O_2 (Figure 4.2.274.2.27). It has a so-called roof-structure due to its non-planarity. One hydrogen atom points toward us, and the other points away from us. This structure is due to the two electron-lone pairs at each sp^3-hybridized oxygen atom. These electron-lone pairs consume somewhat more space than the H atoms, and there is electrostatic repulsion between the electron lone pairs. Therefore, the electron lone pairs at the different oxygen atoms try to achieve the greatest distance from each other. This forces the H-atoms out of the plane, leading to the roof-structure of the hydrogen peroxide. Because the H_2O_2 molecule is not planar, it only has a single C_2 axis, but no other symmetry element besides the identity. The C_2 axis passes through the center of the O-O bond. Execution of the C_2 operation swaps up both the O and the H atoms.

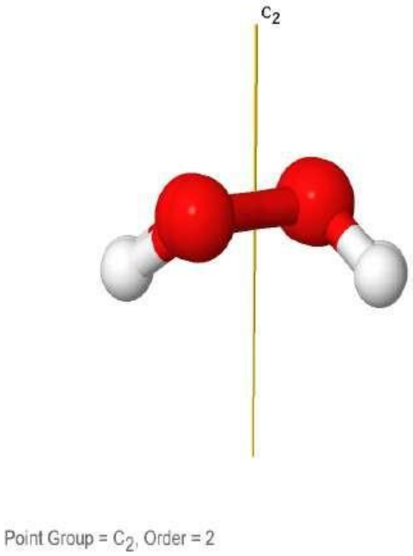


Figure 4.2.274.2.27: The C_2 rotational axis of hydrogen peroxide (Attribution: symotter.org/gallery)

C_{nv} Point Groups

Another class of groups are the pyramidal groups, denoted C_{nv}. They have n vertical mirror planes containing the principal axis C_n in addition to the principal axis C_n. Generally molecules belonging to pyramidal groups are derived from an n-gonal pyramid. An n-gonal pyramid has an n-gonal polygon as the basis which is capped. For example a trigonal pyramid has a triangular basis which is capped, a tetragonal pyramid has a square which is capped, and so on. The proper axis associated with a specific pyramid has the order n and goes through the tip of the pyramid and the center of the polygon. An example of a molecule with a trigonal pyramidal shape is the NH_3 (Figure 4.2.284.2.28).

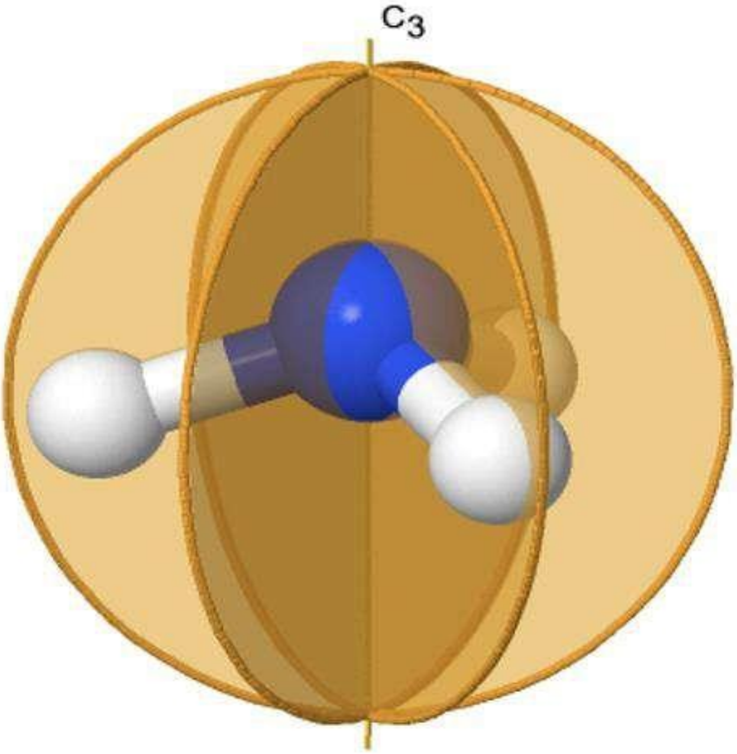


Figure 4.2.284.2.28: C_3 axis and vertical mirror planes in NH_3 (Attribution: symotter.org/gallery)

The three H atoms form the triangular basis of the pyramid, which is capped by the N atom. The NH_3 molecule belongs to the point group C_{3v}. The C_3 axis goes though the N atom which is the tip of the pyramid, and the center of the triangle defined by the H atoms. There are three vertical mirror planes that contain the C_3 axis. Each of them goes through an N-H bond.

C_{nh} Point Groups

If we add a horizontal mirror plane instead of n vertical mirror planes to a proper rotational axis C_n we arrive at the point group type C_{nh}. The presence of the horizontal mirror planes also generates an improper axis of the order n. This is because when one can rotate and reflect perpendicular to the rotational axes independently, then it must also be possible to do it in combination. An example of a molecule belong to a C_{nh} group is the trans-difluorodiazene N_2F_2 (Figure 4.2.294.2.29). It is a planar molecule with a C_2 axis going through the middle of the N-N double bond, and standing perpendicular to the plane of the molecule. The horizontal mirror plane stands perpendicular to the C_2 axis, and is within the plane of the molecule. There is an additional inversion center because an S_2 must exist which is the same as an inversion center. The inversion center is in the middle of the N-N bonds. Overall, the molecule has the symmetry C_{2h}.

Figure 4.2.294.2.29: C_2 axis and horizontal mirror plane in trans-N_2F_2 (Attribution: symotter.org/gallery)

S_{2n} Point Groups

The category of rotational point groups to be discussed are the improper rotation point groups. The only have one proper rotational axis, and an improper rotational axis that has twice the order of the proper rotational axis (Figure 4.2.304.2.30). There may be an inversion center present depending on the order of the proper and improper axes. Molecules that fall into these point groups are rare. An example the tetramethylcycloocta-tetraene molecule (Figure 4.2.304.2.30).

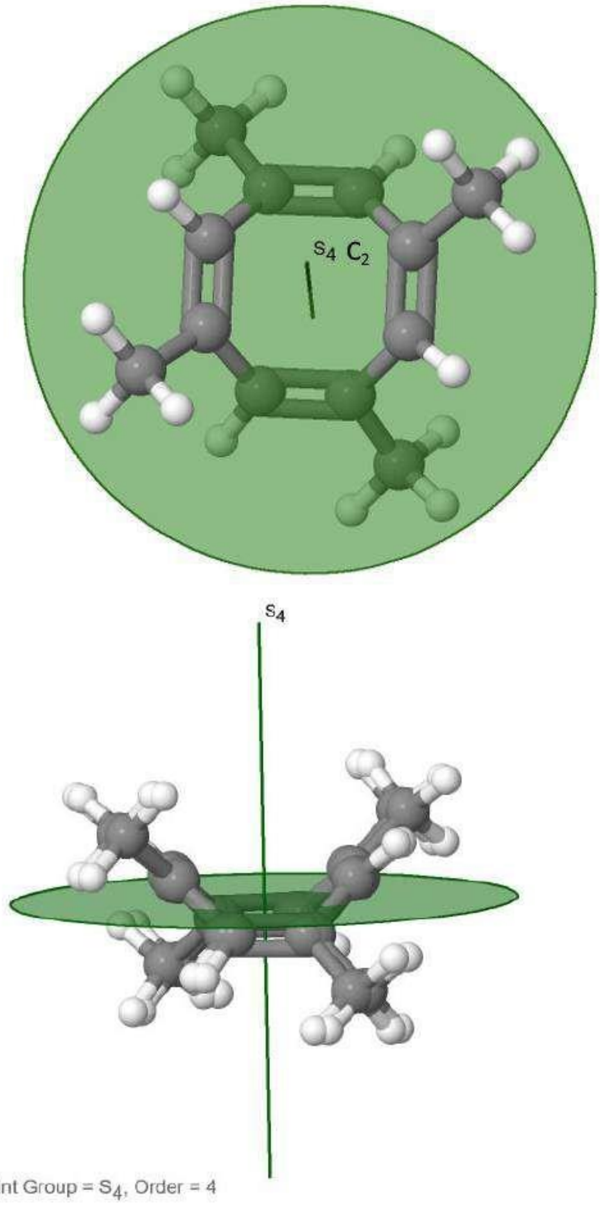


Figure 4.2.304.2.30: The S_4 and an C_2 axes of tetramethyl cycloocta-tetraene

It has an S_4 and an C_2 axis as the only symmetry elements besides the identity. Rotating by 90° alone does not superimpose the molecule because two C-C double bonds lie above the plane and two below the plane. In addition, two opposite methyl groups lie above and below the plane respectively. Therefore it needs the additional reflection to achieve superposition. There is also a C_2 axis which is in the same locations as the S_4 axis.

Dihedral Groups

D_n Point Groups

Dihedral groups are point groups that have n additional C_2 axes that stand perpendicular to the principal axis of the order n. If there are no other symmetry elements, then the point group is of the type D_n. For example in the point group D_3 there is a C_3 principal axis, and three additional C_2 axes, but no other symmetry element (Fig. 2.2.75). The tris-oxolatoferrate(III) ion belongs to this point group (Figure 4.2.314.2.31). You can see that the C_3 axis stands perpendicular to the paper plane, and there are three C_2 axes in the paper plane.

Figure 4.2.314.2.31: The tris-oxolatoferrate(III) ion and its symmetry elements. (Attribution: symotter.org/gallery)

D_{nh} Point Groups

If a horizontal mirror plane is added to the C_n axis and the n C_2 axes we arrive at the D_{nh} point groups. The addition of the horizontal mirror plane generates further symmetry elements namely an S_n and n vertical mirror planes.

An example for a molecule belonging to this class of point group is PF_5 (Figure 4.2.324.2.32). It has a trigonal bipyramidal shape. The C_3 axis goes through the axial F atoms of the molecule, and the three C_2 axes go through the three equatorial F atom. The horizontal mirror plane stands perpendicular to the principal C_3 axis and is located within the equatorial plane of the molecule. In addition, there are the vertical mirror planes that contain the C_3 axis, and go through the three equatorial P-F bonds. There is also an S_3 axis which superimposes the C_3 axis.

Figure 4.2.324.2.32: The PF_5 molecule belonging to the point group D_{3h} and its symmetry elements. (Attribution: symotter.org/gallery)

D_{nd} Point Groups

If we add n vertical mirror planes to the principal axis and the n C_2 axes, we arrive at the point group D_{nd}. The vertical mirror planes are dihedral mirror planes because they bisect the angle between the C_2 axes. An example is the ethane molecule in staggered conformation which has the symmetry D_{3d} (Figure 4.2.334.2.33:). The C_3 axis goes along the C-C bond, and the $3C_2$ axes pass through the middle of the carbon-carbon bond, and bisect the angle between two hydrogens and one carbon atom. The three dihedral mirror planes pass through the C-H bonds. In addition, the ethane molecule has an S_6 axis, and an inversion center.

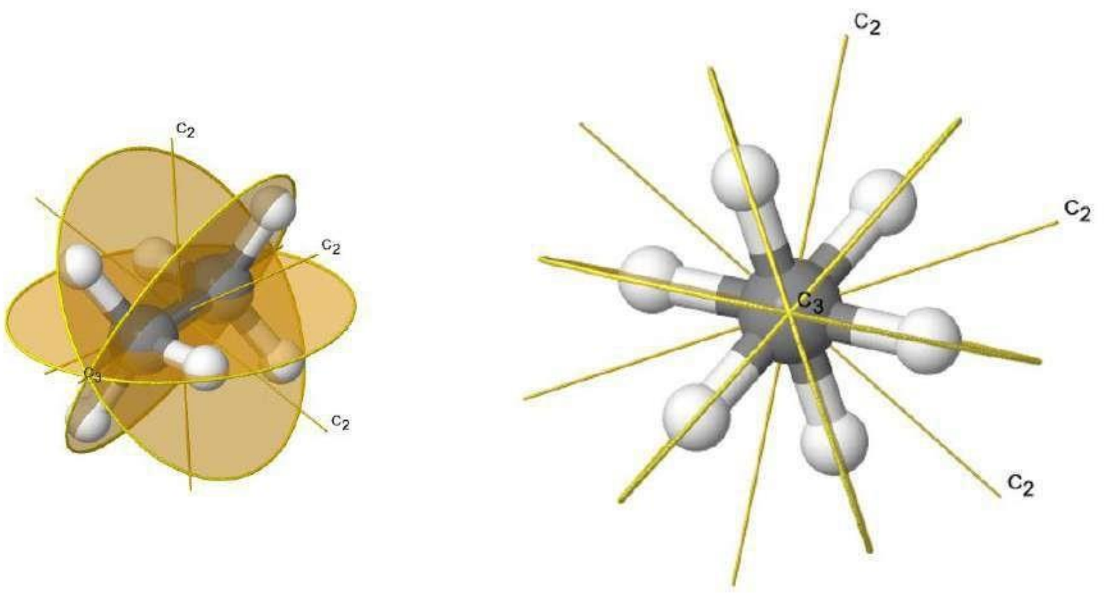


Figure 4.2.334.2.33: The ethane molecule in the staggered conformation belongs to the point group type D_{nd} (Attribution: symotter.org/gallery)

Linear Point Groups

The principal rotation axis in a linear molecule is a C_∞ axis, meaning the molecule can be rotated along its bond axis an infinitely small amount and remain unchanged. Linear molecules can be subdivided based on the presence or absence of a horizontal reflection plane and inversion center.

$C_{\infty v}$ point groups

A special n-gonal polygon is the cone. A cone can be conceived as an n-gonal pyramid with an infinite number n of corners at the base (Figure 4.2.344.2.34).

Figure 4.2.344.2.34: Cone having a proper rotational axis with infinite order.

In this case the order of the rotational axis that passes through the tip of the cone and the center of the circular basis is infinite. This also means that there is an infinite number of vertical mirror planes that contain the C_∞ axis. The point group describing the symmetry of a cone is called the linear point group $C_{\infty V}$. Polar, linear molecules such as CO, HF, N_2O, and HCN belong to this point group. You can see the HCN molecule with its C_∞ axis and its infinite number of vertical mirror planes below (Figure 4.2.354.2.35). The infinite number of mirror planes, shown in blue are forming a cylinder that surround the molecule.

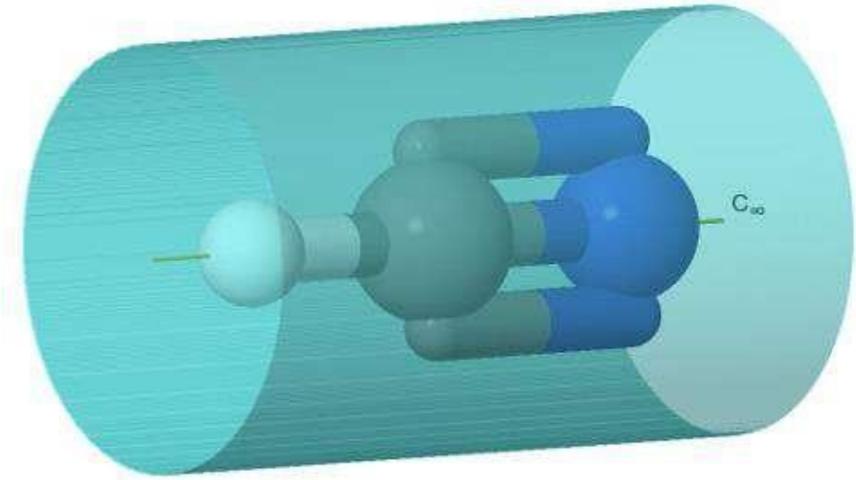


Figure 4.2.354.2.35: C_∞ axis of the HCN molecule.

$D_{\infty h}$ point groups

A special case of a D_{nh} group is the linear group $D_{\infty h}$. An object that has this symmetry is a cylinder. A cylinder can be conceived as a prism with an infinite number of vertices. Thus, the principal axis that passes through a cylinder has infinite order. Because of the infinite order of the principal axis, there is an infinite number of C_2 axes that stand perpendicular to the principal axis. You can see one such C_2 going though the cylinder (Figure 4.2.364.2.36:).

Figure 4.2.364.2.36: Cylinder as an example of linear group $D_{\infty h}$.

There is now also an improper axis of infinite order, as well as an infinite number of vertical mirror planes. Non-polar linear molecules like H_2, CO_2, and acetylene C_2H_2 belong to the point group $D_{\infty h}$. You can see the C_∞ axis passing through a CO_2 molecule below (Figure 4.2.374.2.37). You can see the infinite number of vertical mirror planes as a blue cylinder. The infinite number of C_2 axes is shown a yellow lines going around the molecule.

Figure 4.2.374.2.37: C_∞ in a CO_2 molecule.

Guide for the Determination of Point Groups

The symmetry operations a molecule possesses will determine which point group the molecule is in. The key to success is that you are able to see the symmetry elements in the molecule which takes practice. Luckily, especially for high symmetry point groups, you don't need to identify every single symmetry operation to correctly assign a point group. You can use a flow chart to identify a point group more easily. These flow charts ask systematic questions about the presence or absence of key symmetry elements. Eventually, after having answered enough questions the guide will lead you to the respective point group. You can see an example flow chart below (Figure 4.2.384.2.38:).

Figure 4.2.384.2.38: Flow chart for the determination of point groups. (CC BY-NC-SA; Catherine McCusker)

You can first ask if the molecule is linear (has a C_∞ rotation axis). Then we can ask next, if there is a high symmetry point group. This is the case when there are either $4C_3$, $3C_4$, or $6C_5$ rotational axes present, standing for tetrahedral, octahedral, and icosahedral symmetry, respectively. If there is are no C_n axes of any type present the molecule must be in a low symmetry point group. We ask if there are n ⍰C_2 axes in addition to the C_n principal axis. If this is so, then we must have a dihedral group of the D type. If there are no ⍰ C_2 axes in addition to the C_n, the group must be a rotational (C) group.

Example: Dibromonaphtalene

Let us practice the point group flow chart by example. Let us look at the dibromonaphtalene molecule (Figure 4.2.394.2.39).

Figure 4.2.394.2.39: Guide for determining the point group of dibromonaphtalene

After determining that the molecule is not linear or in a high symmetry group (having 2 or more C_3 rotation axes), the first question we ask is: Can you see at least one proper rotational axis? The answer is yes. There is a C_2 proper rotational axis that stands perpendicular to the plane of the molecule and goes through the center of the C-C bond that is shared by the two aromatic rings. Next we can think about if the there are $2C_2$ axes in addition to the C_2 axes we already found. The answer is no, so the point group cannot be a dihedral (D) group. Next, we would ask: Is there a horizontal mirror plane. This is indeed the case. There is a horizontal mirror plane in the plane of the molecule. It does not move any atoms around, but as we discussed before, a mirror does not need to do this to exist. This identifies the point group as C_{2h}.

UNIT – IV

CHEMICAL KINETICS

INTRODUCTION

Chemical kinetics, also known as **reaction kinetics**, is the study of rates of chemical processes. Chemical kinetics includes investigations of how different experimental conditions can influence the speed of a chemical reaction and yield information about there action's mechanism and transition states, as well as the construction of mathematical models that can describe the characteristics of a chemical reaction.

RATE OF REACTION

Define Rate of Reaction and also give its units.

The rate of reaction can be defined as the change in the concentration of any one of the reactants or products per unit time. The rate of the reaction depends on the molar concentrations of the reactants. The rate of the reaction means the speed with which the reaction takes place. This is expressed either in terms of decrease in the concentration of a reactant per unit time or increase in the concentration of a product per unit time. The rate of reaction varies with time.

Rate of reaction = decrease in the concentration of a reactant / Time interval = increase in the concentration of a product / Time interval Consider the reaction:

$$PCl_5 \longrightarrow PCl_3 + Cl_2$$

Suppose in a time interval Δt, decrease in concentration of PCl_5 is $\Delta [PCl_5]$ and increase in the concentration of PCl_3 and Cl_2 are $\Delta [PCl_3]$ and $\Delta [Cl_2]$ respectively, where square brackets indicate molar concentrations in moles / litre of the substances involved.

Hence,

$$\text{Rate of reaction} = -\Delta [PCl_5] / \Delta t = +\Delta [PCl_3] / \Delta t = +\Delta [Cl_2] / \Delta t$$

The minus sign along with the first term is used simply to show that the concentration of the reactant (PCl_5) is decreasing while plus sign along with the other two term is used simply to show that the concentration of the products (PCl_3 and Cl_2) is increasing.

Units of the Rate of Reaction:

As concentration is usually expressed in moles / litre and the time is taken in seconds or minutes, the unit of rate of reaction is moles litre^{-1} sec^{-1} or moles litre^{-1} min^{-1} **Order of reaction:**

The sum of concentration terms on which the rate of a reaction actually depends as observed experimentally is called the order of the reaction i.e. the sum of the powers or exponents to which the concentration or pressure terms are raised in order to determine the rate of the reaction.

Order of a reaction is an experimental quantity. A reaction is said to be of the zero order, first order, second order, and third order if some of concentration terms is equal to 0, 1, 2 and 3 respectively. Example: **Photosynthesis of HCl:**

H_2 (g) + Cl_2 (g) + hν ——————> 2HCl

Experimentally, it is found that the rate of reaction is independently of the concentration of H_2 and Cl_2. Hence it is a reaction of the zero order. Hence for such reactions: Rate = k

Dissociation of N_2O_5

2 N_2O_5 ————> 4 NO_2 + O_2

Experimentally, it is found that the rate of reaction is directly proportional to $[N_2O_5]$

i.e. it depends only on one concentration term. Hence the reaction is said to be of first order.

MOLECULARITY

In case of chemical reactions i.e. reactions involving a number of atoms, ions, molecules of the reactants in the balanced equation, the chances for all the atoms, ions or molecules of the reactants to come together and collide are very rare. Hence in such cases, the reactions are supposed to take place in a number of steps. The slowest step is the rate determining step.

The number of atoms, ions or molecules taking place in te slowest step i.e. the rate determining step is called the molecularity of the reaction of complex reactions.

Hence, the molecularity of the reaction must always be a whole number whereas the order of a reaction can be fractional.

Distinguish between order of a reaction and molecularity of a reaction?

The main difference between the order of a reaction and molecularity of a reaction are given below:

ORDER OF A REACTION	MOLECULARITY OF A REACTION
It is sum of the concentration terms on which the rate of reaction actually depends or it is the sum of the exponents of the concentrations in the rate law equation.	It is the number of atoms, ions or molecules that must collide with one another simultaneously so as to result into a chemical reaction.
It need not be a whole number i.e. it can be fractional as well as zero.	It is always a whole number.
It can be determined experimentally only and cannot be calculated.	It can be calculated by simply adding the molecules of the slowest step.
It is for the overall reaction and no separate steps are written to obtain it.	The overall molecularity of a complex reaction has no significance. It is only slowest step whose molecularity has significance for the overall reaction.
Even the order of a simple reaction may not be equal to the number of molecules of the reactants as seen from the unbalance equation.	For simple reactions, the molecularity can usually be obtained from the Stoichiometry of the equation.

RATE CONSTANT

Define Rate constant and also discuss its characteristics

Rate constant may be defined as the rate of the reaction when the concentration of each reactant is taken as unity. That is why the rate constant is also known as specific reaction rate.

Characteristics of rate constant:

Some important characteristics of the rate constant are as follows:

1. Rate constant is a measure of the rate of reaction. Greater is the value of the rate constant, faster is the reaction.
2. Each reaction has a definite value of the rate constant at a particular temperature.
3. The value of the rate constant for the same reaction changes with temperature.
4. The value of the rate constant of a reaction does not depend upon the concentrations of the reactants.
5. The units of the rate constant depend upon the order of reaction.

ORDER OF REACTION

"The order of reaction is defined as the sum of all the exponents of the reactants involved in the rate equation."

It should be noted down that all the molecules shown in a chemical equation do not determine the value of order of reaction but only those molecules whose concentrations are changed are included in the determination the order of a reaction. In other words:

"The number of reacting molecules whose concentration alters as a result of chemical reaction is termed as the order of reaction."

For example:

$2NO + O_2 \dashrightarrow 2NO_2$

$dx/dt = k[NO]^2[O_2]$, the reaction is of third order as 2 + 1 = 3 For a reaction maximum order is three and the minimum is zero.

FIRST ORDER REACTIONS

The reaction in which only one molecule undergoes a chemical change is called first order reactions.

Example: $N_2O_5 \dashrightarrow 2NO_2 + \frac{1}{2} O_2$

SECOND ORDER REACTIONS

The reaction in which two molecules undergo a chemical change is called second order reactions. Example:

$2CH_3CHO \text{-->} 2CH_4 + 2\,CO$

THIRD ORDER REACTIONS

The reaction in which only three molecules undergo a chemical change is called third order reactions. Example:

$2NO + O_2 \text{->} 2NO_2$

Rate and Order of Reactions

The rate **of a chemical reaction** is the amount of substance reacted or produced per unit time. The rate law is an expression indicating how the rate depends on the concentrations of the reactants and catalysts. The power of the concentration in the rate law expression is called the **order** with respect to the reactant or catalyst.

First-Order Reactions

A **first-order reaction** is a reaction that proceeds at a rate that depends linearly on only one reactant concentration.

The Differential Representation

Differential rate laws are generally used to describe what is occurring on a molecular level during a reaction, whereas integrated rate laws are used for determining the reaction order and the value of the rate constant from experimental measurements. The differential equation describing first-order kinetics is given below:

$$Rate=-d[A]/dt=k[A]^1=k[A] \quad (1)$$

The "rate" is the reaction rate (in units of molar/time) and k is the reaction rate coefficient (in units of 1/time). However, the units of k vary for non-first-order reactions. These differential equations are separable, which simplifies the solutions as demonstrated below.

Second-Order Reactions

Many important biological reactions, such as the formation of double-stranded DNA from two complementary strands, can be described using second order kinetics. In a second-order reaction, the sum of the exponents in the rate law is equal to two. The two most common forms of second-order reactions will be discussed in detail in this section.

Reaction Rate

Integration of the second-order rate law $d[A]/dt=-k[A]^2$ which is easily rearranged into a form of the equation for a straight line and yields plots similar to the one shown on the left below.

The half-life is given by $t_{1/2}=1/k[Ao]$

Notice that the half-life of a second-order reaction depends on the initial concentration, in contrast to first-order reactions. For this reason, the concept of half-life for a second-order reaction is far less useful. Reaction rates are discussed in more detail here. Reaction orders are defined here. Here are explanations of zero and first order reactions.

Case 1: Identical Reactants (A + A → P)

Two of the same reactant (A) combine in a single elementary step.

$A+A \longrightarrow P$

$2A \longrightarrow P$

The reaction rate for this step can be written as

$Rate=-1/2d[A]dt=+d[P]dt$ and the rate of loss of reactant A $dA/dt=-k[A][A]=-k[A]^2$

where k is a second order rate constant with units of M^{-1} min^{-1} or M^{-1} s^{-1}. Therefore, doubling the concentration of reactant A will quadruple the rate of the reaction. In this particular case, another reactant (B) could be present with A; however, its concentration does not affect the rate of the reaction, i.e., the reaction order with respect to B is zero, and we can express the rate law as $v=k[A]^2[B]^0$.

Case 2: Different Reactants ($A + B \rightarrow P$)

Two different reactants (A and B) combine in a single elementary step.

$A+B \longrightarrow P$

The reaction rate for this step can be written as $Rate=-d[A]/dt=-d[B]/dt=+d[P]/dt$ and the rate of loss of reactant A $d[A]/dt=-k[A][B]$

where the reaction order with respect to each reactant is 1. This means that when the concentration of reactant A is doubled, the rate of the reaction will double, and quadrupling the concentration of reactant in a separate experiment will quadruple the rate. If we double the concentration of A and quadruple the concentration of B at the same time, then the reaction rate is increased by a factor of 8. This relationship holds true for any varying concentrations of A or B.

Zero-Order Reactions

In some reactions, the rate is apparently independent of the reactant concentration. The rates of these **zero-order reactions** do not vary with increasing nor decreasing reactants concentrations. This means that the rate of the reaction is equal to the rate constant, k, of that reaction. This property differs from both first-order reactions and second-order reactions.

Origin of Zero Order Kinetics

Zero-order kinetics is always an artifact of the conditions under which the reaction is carried out. For this reason, reactions that follow zero-order kinetics are often referred to as pseudo-zero-order reactions. Clearly, a zero-order process cannot continue after a reactant has been exhausted. Just before this point is reached, the reaction will revert to another rate law instead of falling directly to zero as depicted at the upper left.

There are two general conditions that can give rise to zero-order rates:

1. Only a small fraction of the reactant molecules are in a location or state in which they are able to react, and this fraction is continually replenished from the larger pool.

2. When two or more reactants are involved, the concentrations of some are much greater than those of others

This situation commonly occurs when a reaction is catalyzed by attachment to a solid surface (heterogeneous catalysis) or to an enzyme.

Example 1: Decomposition of Nitrous Oxide

Nitrous oxide will decompose exothermically into nitrogen and oxygen, at a temperature of approximately 575 °C

$2N_2O-\rightarrow---> 2N_2(g)+O_2(g)$

This reaction in the presence of a hot platinum wire (which acts as a catalyst) is zero-order, but it follows more conventional second or derkinetics when carried out entirely in the gas phase.

$2N_2O\rightarrow 2N_2(g)+O_2(g)$

In this case, the N_2O molecules that react are limited to those that have attached themselves to the surface of the solid catalyst. Once all of the sites on the limited surface of the catalyst have been occupied, additional gas-phase molecules must wait until the decomposition of one of the adsorbed molecules frees up a surface site.

Enzyme-catalyzed reactions in organisms begin with the attachment of the substrate to the active site on the enzyme, leading to the formation of an enzyme-substrate complex. If the number of enzyme molecules is limited in relation to substrate molecules, then the reaction may appear to be zero-order.

This is most often seen when two or more reactants are involved. Thus if the reaction

$A+B\rightarrow$products (1) is first-order in both reactants so that

rate=k [A][B] (2)

If B is present in great excess, then the reaction will appear to be zero order in B (and first order overall). This commonly happens when B is also the solvent that the reaction occurs in.

Differential Form of the Zeroth Order Rate Law

$Rate=-d[A]/dt=k[A]^0=k=constant$ (3)

where Rate is the reaction rate and k is the reaction rate coefficient. In this example, the units of k are M/s. The units can vary with other types of reactions. For zero-order reactions, the units of the rate constants are always M/s. In higher order reactions, k will have different units.

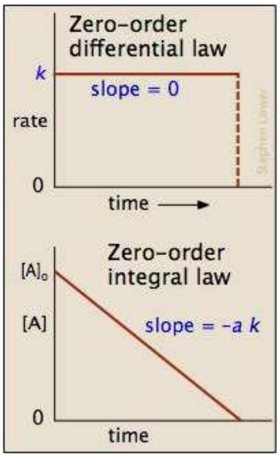


Figure: Rate vs. time (A) and Concentration vs. time for a zero order reaction.

FACTORS AFFECTING RATE OF CHEMICAL REACTION

Following are the main factors that influence the rate of a chemical reaction.

Different reactants have different energies of activation. Reaction between polar or ionic molecules is very fast. Oxidation-Reduction reactions are slower than ionic reactions because they involve transfer of electrons and bond rearrangement. The physical state of reacting substances are important in determining their reactivities. The reaction in which ionic solutions are involved also take place at high speed.

CONCENTRATION OF REACTANTS

The concentration of reactants plays an important role in chemical kinetics. It is usually true that by increasing the amount of reactants, the rate of reaction is increased. As we know that an increase in concentration of reactants increases the number of molecules. According to collision theory, the greater the number of molecules the higher is the collision ratio, consequently faster is the rate of reaction.

SURFACE AREA OF REACTANTS

In heterogeneous reactions, the rate of reaction depends upon the surface area of solid reactant. Greater the surface area, higher is the rate of reaction. For example finely divided calcium carbonate (marble) reacts more quickly with hydrochloric acid than calcium carbonate chips. It is due to the fact that powered calcium carbonate offers larger surface area to the reacting acid. In other words, by increasing the surface area of reactant, rate of reaction increases due to greater contact between individual particles and also due to the fact that the surface molecules reacts more quickly.

TEMPERATURE

The rate of reaction increases with the rise of temperature. It can be explain by the fact that at higher temperature, a greater fraction of colliding molecules posse the necessary energy of activation.Generally an increase of every 10°K in temperature doubles the rate.As the temperature increases the velocity of molecules also increases which results in the increase in the frequency of collision.The rise in temperature rises the kinetic energy of each molecule. It has been found that by raising the temperature by 10k, the fraction of molecule possessing threshold or activation energy becomes double. As a result the no of effective collision is also double, hence rate is doubled.

PRESENCE OF CATALYST

A catalyst is a substance, which controls the rate of reaction without itself undergoing a permanent chemical change. Catalysts are of two types

Positive catalyst:

A positive catalyst increases the rate of reaction by lowering the energy of activation. Thus in the presence of a positive catalyst, the greater fraction of the total molecule will posses lower energy of activation and collided successfully in a short period of time, there by increasing the rate of reaction

Negative catalyst or inhibitor:

A negative catalyst retards the rate of reaction. Negative catalyst do not lower the energy of activation rather they are combined with reactant molecule thus decreasing the number of colliding reactant molecules. This decreases the effective collisions, hence rate of reaction.

Role of positive catalyst

A positive catalyst functions by providing an alternate path to the reaction or by the formation of a transition (intermediate) compound having low energy of activation. The activation energy of this path is lower. As a result rate of reaction is increased.

Role of negative catalyst

A negative catalyst does not lower the energy of activation rather it combines with the reactant molecules, thus decreasing the number of colliding reactant molecules. This decreases the effective collisions, hence rate of reaction.

Not all reactions are affected by light or radiation but few reactions, which are usually free radicals, or photo chemical reactions are influenced by light. Light activates some of the reactant molecules producing free radicals. Since free radicals are very exited, therefore, they react immediately with other molecules to form products. The concentration of reactants does not influence the rate of such reactions, so they are zero order reaction. We know that that light consists of photon. When photons strike the reactant molecule, they provide necessary activation energy to the reactant molecules.

3.0 THE ARRHENIUS EQUATION

The actual dependence of the rate constant on temperature is given by the Arrhenius equation. k = Ae-Ea/RT

Where:

k is the rate constant

A is the Arrhenius factor (different for every reaction) e is the natural log base

Ea is the minimum energy required for a reaction to take place (known as the activation energy)

R is the universal gas constant (8.314 J kg^{-1} $^{o}C^{-1}$)

T is the absolute temperature in Kelvin

Arrhenius' constant, A - the pre-exponential factor

It is possible for colliding particles to possess enough energy for reaction, but still not have a successful collision (one that results in reaction). This is accounted for by the Arrhenius constant 'A' , also called the pre-exponential or frequency factor.

Imagine a collision between two cars; clearly more damage is going to be caused by a head on collision than a glancing scrape.

The Arrhenius constant (pre-exponential or frequency factor) is a number between 0 and 1, that reflects the proportion of successful collisions amongst those particles with enough energy for reaction.

For example, when A is very small, only a small proportion of collisions lead to reaction, regardless of the energy, When A = 1, all collisions with sufficient energy cause reaction.

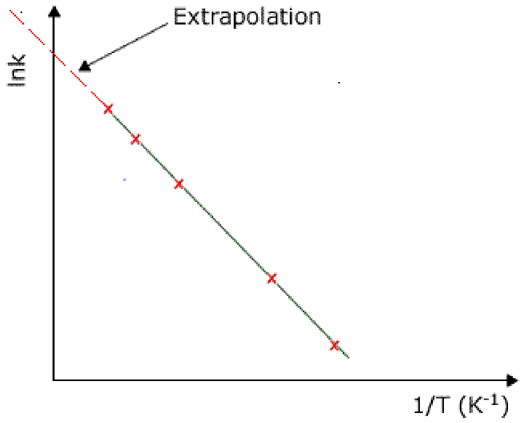
Using the Arrhenius equation

In reality, the basic form of the Arrhenius equation is not very convenient for graphing or analysing date. To analyse experiments at different temperatures we usually use the natural log form of the equation:

$k = Ae\text{-}Ea/RT$

Taking natural logs throughout this gives: $\ln k = \ln A - Ea/RT$

Thus a plot of lnk against 1/RT, 1/T or any variation, will allow us to find the activation energy of a specific reaction as a function of the gradient, and the Arrhenius constant as a function of the intercept to the y axis.



A typical plot used to calculate the activation energy from the Arrhenius equation.

In this graph the gradient of the line is equal to -Ea/R

Extrapolation of the line to the y axis gives an intercept value of lnA

When the temperature is increased the term Ea/RT gets smaller. This means in turn, that the term $e^{-Ea/RT}$gets bigger.

Alternatively two results may be analysed simultaneously to obtain values for Ea, the activation energy and the Orientation factor, A. This is not particularly reliable as only two values for the rate constant are used at two different temperatures. This can introduce large errors because of too little data.

ENERGY OF ACTIVATION

When gases or liquids are heated the particles gain kinetic energy and move faster increasing the chance of collision between reactant molecules and therefore the increased chance of a fruitful collision (i.e. one resulting in product formation).However! this is NOT the main reason for the increased reaction speed on increasing the temperature of reactant molecules because most molecular collisions do not result in chemical change. Before any change takes place on collision, the colliding molecules must have a minimum kinetic energy called the activation energy (denoted by E_a)..Its a sort of 'threshold' energy required before any bonds can be broken i.e. before a reaction can take place. Do not confuse activation energy with the overall energy change also shown in the energy profile diagrams below, that is the overall energy absorbed-taken in by the system (endothermic) or given out to the surroundings (exothermic).It does not matter whether the reaction is an exothermic or an endothermic energy change (see the pair of reaction profile diagrams below).Higher temperature molecules in gases and liquids have a greater average kinetic energy and so a greater proportion of them will then have the required activation energy to react on collision. The increased chance of higher energy collisions greatly increases the speed of the reaction because it greatly increases the chance of a fruitful collision forming the reaction products by bonds being broken in the reactants and new bonds formed in the reaction products. The activation energy 'hump' can be related to the process of bond breaking and making. Up the hump is endothermic, representing breaking bonds (energy absorbed, needed to pull atoms apart),down the other side of the hump is exothermic, representing bond formation (energy released, as atoms become electronically more stable).The 'reaction profile' diagrams below illustrate the course or progress of a reaction in terms of the energy changes taking place. Reaction profiles can be used to show the relative energies of reactants and products, the activation energy and the overall energy change of a reaction. Examples of an exothermic reaction profile and an endothermic reaction profile are shown below, with and without the activation energy - which must be reached on collision, before a reaction can occur.

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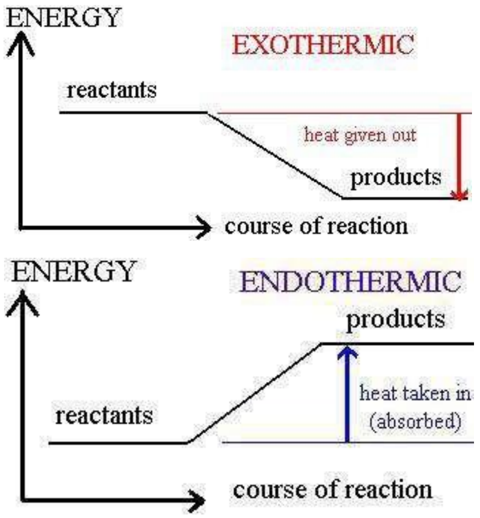
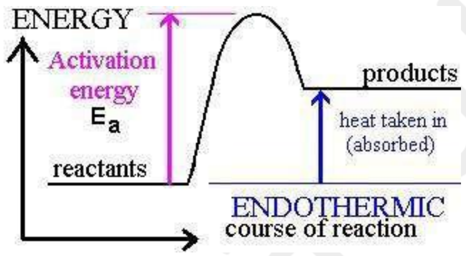


ENERGY PROFILES for chemical reactions Simple energy level diagrams for exothermic and endothermic reactions NOT showing the activation energy



ENERGY PROFILES for chemical reactions Energy level diagrams for exothermic and endothermic reactions showing the activation energy (E_a) 'hump' which must be overcome before a chemical reaction can take place

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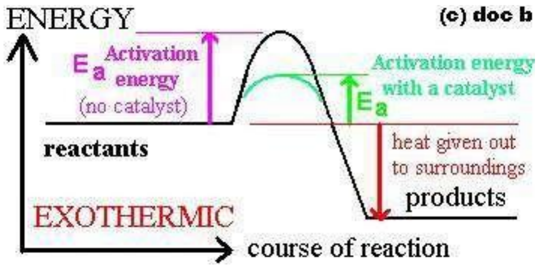
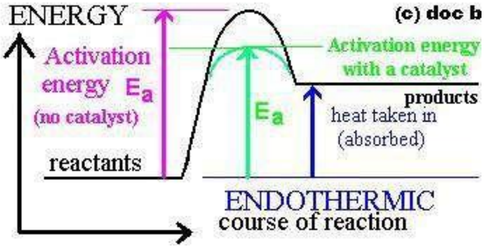


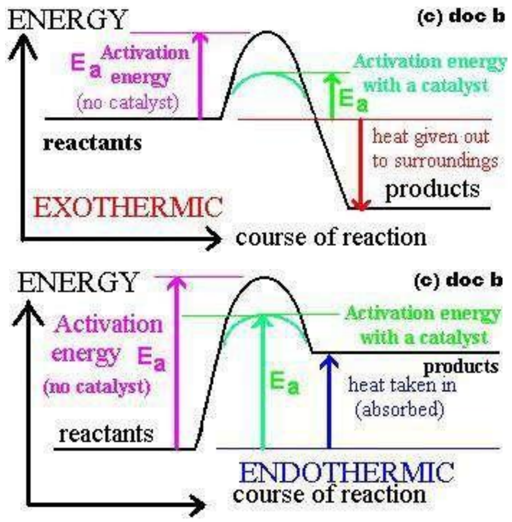


Note that the effect of a catalyst is to lower the activation energy E_a, enabling the reaction to go faster BUT it does NOT affect the overall energy change of the reaction. The catalyst provides a different pathway for the reaction that needs less energy to initiate it but it does NOT change the energy transfer value irrespective of whether it is an exothermic or an endothermic reaction.

Catalysts and activation energy

- Catalysts increase the rate of a reaction by helping break chemical bonds in reactant molecules.
- This effectively means the activation energy is reduced (see diagram 'humps' below). Therefore at the same temperature, more reactant molecules have enough kinetic energy to react compared to the uncatalysed situation and so the reaction speeds up with the greater chance of a 'fruitful' collision. Note that a catalyst does NOT change the energy of the molecules, it reduces the threshold kinetic energy needed for a molecules to react. The overall energy change for a catalysed reaction is identical to the energy change for the same uncatalysed reaction.
- Although a true catalyst does take part in the reaction, it does not get used up and can be reused with more reactants, it may change chemically on a temporary basis but would be reformed as the reaction products also form.
- However a solid catalyst might change physically permanently by becoming more finely divided, especially if the reaction is exothermic.
- Also note from the diagram that although the activation energy is reduced, the overall exothermic or endothermic energy change is the same for both

the catalysed or uncatalysed reaction. The catalyst might help break the bonds BUT it cannot change the actual bond energies.



ENERGY PROFILES for chemical reactions

TRANSITION STATE THEORY (TST) OR ABSOLUTE REACTION RATE THEORY (ARRT) OR ACTIVATED COMPLEX THEORY (ACT):

This theory was developed by H. Eyring, Polanyi and Evans in 1935.

Postulates:

i) The reactant molecules first excited to form an activated complex. This activated complex is in equilibrium with the reactants.

Reactants [Activated complex] ii) Activated complex is having four translational degree of freedom along the reaction coordinate and one vibrational degree of freedom less than that of the normal molecule. The extra translational degree of freedom is formed from one viberational degree. iii) The rate of the reaction is given by the rate of decomposition of products. [Activate complex] Products **Derivation:**

Let us consider a bimolecular reaction,

A+B -→Products

Rate = $k[A][B]$

According to ARRT the mechanism is

A+B-------- → [AB] Products

Reactants Activated complex

Where K is the equilibrium constant between the reactants and activated complex.

The rate of the reaction will depend upon two factors.

i) The concentration of [AB] (calculated by using statistical mechanics).

ii) The rate at which [AB] breaks upto yield products. A+B --→[AB]

On applying the law of mass action,

K =

Where K is the equilibrium constant between the reactants and activated complex. From classical mechanics,

Energy of vibration = $_{RT}$ k_BT

$\overline{N_A}$

Where k_B is Boltzmann constant, R/N From quantum mechanics,

Energy of vibration = hv

Where h is Planck's constant and v-frequency of the vibration Comparing eqns (3) and (4), we get.

hv = v = (or)

v =

The vibrational frequency v is the rate at which the activated complex molecules move across the enery barrier. The rate constant _k' can be identified with v. rate = v[(AB)]

Substituting the value of [(AB)] from eqn (2), we get rate = v [A] [B] K

Comparing eqns (1) and (7) we get

k[A][B] = v [A] [B] K k = vK

Substituting the value of v from eqn (5) and (5a) we get

k= K (or) K

The equilibrium constant K can be expressed in terms of the standard Gibbs free energy for the activation process.

$(\Delta G^0)^{\neq} = -RT\ell nK^{\neq}$

and $(\Delta G^0)^{\neq} = (\Delta H^0)^{\neq} - T(\Delta S^0)^{\neq}$

From eqn (10) we get,

$\frac{(\Delta G0)^{\neq}}{RT} = \ell n K^{\neq}$

$K^{\neq} = (\Delta G0)\neq / RT$

Substituting the value of (G)from eqn (11) we get

$K^{\neq} = (\Delta G0)\neq / RT\ .\ (\Delta S0)\neq / R$

Eqn (9) becomes

k =

Equation (14) is known as Eyring equation

When $(\Delta G^0)^{\neq}$ is standard entropy of activation,

$(\Delta G^0)^{\neq}$ is standard free energy of activation, and

$(\Delta G^0)^{\neq}$ is standard enthalpy of activation, **Significance of the equation of APRT:** We know that,

k =

The equation (1) involves two factors,

ie k =

i) The first factor is constant at constant temperature. ii) The second factor $^{(\Delta G0)\neq\ /\ RT}$ contains a negative sign. Hence the rate of the reaction depends on the free energy of activation. i.e. At particular temperature, greater the value of the $e^{(\Delta G0)\neq}$ the slower will be the reaction.

Comparison with Arrhenius equation: We know that according to ARRT

k = k =

But according to Arrhenius equation

$k = A.e{-}Ea/RT$

Taking ℓn on both sides of eqn (1), we get

$\ell nk = \ell n\,[\frac{k_B T}{h} e^{(\Delta H^0)^{\neq}/RT}\ .\ e^{(\Delta S^0)^{\neq}/R}] = \ell n \frac{k_B T}{h} + \ell n\, e^{(\Delta H^0)^{\neq}/RT} + \ell n\, e^{(\Delta S^0)^{\neq}/R}$

$\ell nk = \ell n\ + \ell nT\ -$

Differentiating both sides w.r.t T.

Both ℓn on both sides of eqn (2) we get,

ℓnk = ℓn (A. $e^{-Ea/RT}$

ℓnk = ℓn A -

Differentiating both sides w.r.t.T

(ℓnk) =

E_a= RT + $(\Delta H^0)^{\neq}$ or $(\Delta H^0)^{\neq}$ = E_a - RT

Comparison with the collision theory

According to ARRT, k = But according to

collision theory,

k = p.Z . $e^{-Ea/RT}$

Assume $^{(\Delta H0)\neq}$= E_a in equation (1)

Comparing eqn (1) and eqn (2), we get

= p.Z . $e{-}Ea/RT$

pZ = $\frac{k_B T}{h}$. $e^{(\Delta S^0)^{\neq}/\mathrm{R}}$

Advantages of transition state theory ARRT over collision theory:

i) Collision theory is based on less accurate classical mechanics and kinetic theory. While ARRT is based on more accurate statistical mechanics and thermodynamics.

ii) Collision theory considers effective collision, but ARRT considers the formation and decomposition of activated molecule $[AB]^{\neq}$.

iii) Collision theory considers only translational energy whereas ARRT considers all degrees of freedom.

iv) The steric factor ‗p‘is introduced arbitrarily in collision theory. While $\Delta S^{\neq}$ is included in ARRT.

UNIT – V

SURFACE CHEMISTRY AND SOLUTIONS

Adsorption: Dip a chalk piece in coloured solution for one minute. Cut the chalk piece and observe? Yes, you will watch wet chalk with the colour present only on the outer surface. In this activity, water is absorbed, and the colour is adsorbed. In this article, let us understand everything about adsorption, its types, properties, etc.

What is Adsorption?

When charcoal is dipped in the coloured solution, the solution decolorizes due to the adsorption of coloured particles by the charcoal.

The process in which molecular, atomic, decolorizing ionic species of one substance get accumulated at the surface of another is called adsorption.

Adsorption is also defined as the phenomenon of attracting and retaining the molecules of a substance on the surface of a liquid or a solid, resulting in a higher concentration of the molecules on the surface.

Components of Adsorption

1. **Adsorbate:**
   The substance which gets adsorbed on any surface is called adsorbate. For example, if gas gets adsorbed on a solid surface, then the gas is termed as the adsorbate.
2. **Adsorbent:**
   The substance on the surface of which adsorption takes place is called adsorbent. Adsorbents may be a solid or a liquid. Metal powders, powdered charcoal, silica powder, etc., are the commonly used adsorbents. Activated charcoal, silica, alumina, etc., are very effective adsorbents due to their large surface area.
3. **Desorption**
   The removal of the adsorbed substance from the surface is called desorption. Heating and lowering of pressure favour desorption.
4. **Sorption**
   The process in which adsorption and absorption take place simultaneously is called sorption.
5. **Occlusion**
   The adsorption of gases on the surface of the metal is called occlusion.

Adsorption is Exothermic Process

During adsorption, the surface energy of the adsorbent decreases. This decrease in energy appears in the form of heat of adsorption. Hence, adsorption is an exothermic process, i.e., ΔH adsorption ΔH adsorption is always negative. During adsorption, entropy (randomness of the system) also decreases, i.e., ΔS is negative. For the spontaneity of the adsorption, free energy should be negative.

$$\Delta G=\Delta H-T\Delta S$$

As ΔS is negative, $\Delta G \Delta G$ can be negative only if ΔH is negative and $\Delta H>T\Delta S$ in magnitude.

Factors Affecting Adsorption

1. **Nature and surface area of adsorbent:**
   Different adsorbents have different absorbing power. The greater the surface area greater is the adsorption. For example, porous and finely powdered charcoal absorbs more as compared to the hard non-porous charcoal.

The surface area per gram of the adsorbents is called the specific surface area of the adsorbent. The greater the ease of liquefaction of gas, the greater is the adsorption.

For example, adsorption on charcoal is in the order:

$H_2<N_2<CO<CH_4<CO_2<HCl<NH_3<SO_2$.

2. **Temperature**
   Adsorption is an exothermic process. Therefore, as temperature increases the adsorption decreases at a constant pressure. The relationship between the extent of adsorption and the temperature at any constant pressure is called adsorption isobar.
3. **Pressure:**
   Adsorption increases with the increase of pressure at a constant temperature. The effect is greater at a lower temperature.
4. **Activation of solid adsorbent:**
   This is done by increasing the adsorbing surface area by subdividing solid adsorbents are by removing the gases already adsorbed.

Types of Adsorption

Depending on the nature of the force existing between the adsorbate and adsorbents molecule, the absorption is classified into two types, i.e., physisorption and chemisorption.

1. **Physical adsorption or physisorption:** If the adsorbate is held on the surface by weak forces such as van der Waals' force then the absorption is called van der Waals adsorption or physical adsorption or physisorption. **Example 1:** Adsorption of gases on animal charcoal. **Example 2:** Adsorption of water vapor on silica gel.

2. **Chemical adsorption or chemisorption:** If the adsorbate is held on the surface by the strong chemical bond, the adsorption is called chemical adsorption or chemisorption. Example: Rusting of iron.

Difference between Physisorption and Chemisorption

Physisorption	Chemisorption
1. The force which binds the adsorbate to the adsorbate the weak van der Waal's forces.	1. The force which binds the adsorbate to the adsorbate is as strong as a chemical bond.
2. Low heat of adsorption: usually in the range of 20–40kJ/mol.20–40kJ/mol.	2. High heat of adsorption: usually in the range of 50–400kJ/mol.50–400kJ/mol.
3. Usually occurs at low temperature and decrease with increasing temperature.	3. Usually occurs at higher temperatures.
4. It is reversible.	4. It is irreversible.
5. It is not specific in nature.	5. It is highly specific in nature.
6. It forms multimolecular layers on the surface of the adsorbent.	6. It forms monomolecular layers on the surface of the adsorbent.

Adsorption Isotherm

Definition

Adsorption Isotherm is a curve that expresses the variation in the amount of gas adsorbed by the adsorbent with pressure at constant temperature.

Freundlich Adsorption Isotherm

In 1909, German scientist Freundlich provided an empirical relationship between the amount of gas adsorbed by a unit mass of solid adsorbent and pressure at a particular temperature. It is expressed using the following equation

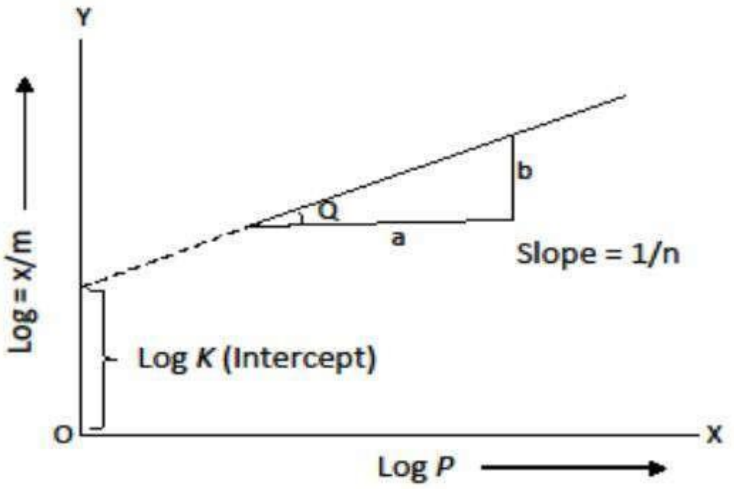
$$x/m = k.P^{1/n} \ (n > 1)$$

where 'x' is the mass of the gas adsorbed on mass 'm' of the adsorbent at pressure 'P'. 'k' and 'n' are constants that depend on the nature of the adsorbent and the gas at a particular temperature.

The mass of the gas adsorbed per gram of the adsorbent is plotted against pressure in the form of a curve to show the relationship. Here, at a fixed pressure, physical adsorption decreases with increase in temperature. The curves reach saturation at high pressure. Now, if you take the log of the above equation –

$$\log x/m = \log k + 1/n \log P$$

To test the validity of Freundlich isotherm, we can plot log x/m on the y-axis and log P on the x-axis. If the plot shows a straight line, then the Freundlich isotherm is valid, otherwise, it is not. The slope of the straight line gives the value of 1/n, while the intercept on the y-axis gives the value of log k.



Freundlich Isotherm

Limitations of Freundlich Isotherm

Freundlich isotherm only approximately explains the behaviour of adsorption. The value of 1/n can be between 0 and 1, therefore the equation holds good only over a limited range of pressure.

- When 1/n = 0, x/m is constant, the adsorption is independent of pressure.
- When 1/n =1, x/m = k P, i.e. x/m a P, adsorption is directly proportional to pressure.

Experimental results support both of the above-mentioned conditions. At high pressure, the experimental isotherms always seem to approach saturation. Freundlich isotherm does not explain this observation and therefore, fails at high pressure.

The Freundlich isotherm was followed by two other isotherms – Langmuir adsorption isotherm and BET adsorption isotherm. Langmuir isotherm assumed that adsorption is monolayer in nature whereas BET isotherm assumed that it is multi-layer.

Langmuir Adsorption Isotherms

Adsorption Isotherms are important for understanding adsorption techniques and dealing with other environmental issues. The following Langmuir Adsorption Isotherm study material will help you understand the processes.

Langmuir Adsorption Isotherm refers to the equilibrium between the adsorbent and the adsorbate system. In this method, adsorbate adsorption is always limited to one molecular layer. It happens at or before one reaches the relative pressure of unity. This equation is used in multiple systems with moderately low coverage. Most importantly, it is used to describe the behaviour of the binary absorption system. According to the Langmuir Adsorption Isotherm, the surface is homogeneous with the assumption that no lateral interaction takes place between the adjacent absorbed molecules. Even when a single molecule occupies a single surface site, this remains the same.

Assumptions of Langmuir Adsorption Isotherms

The Langmuir Adsorption Isotherm was derived using the kinetic energy of gases along with the following assumptions:

1. The adsorption includes a monolayer at the surface.
2. No interaction takes place between the molecules on different sites.
3. Each site can hold only a single adsorbed molecule.
4. The heat of adsorption is not dependent on the number of sites. It is equal for everyone.

Equation Derivations

Langmuir Adsorption Isotherm predicts linear adsorption at a maximum surface coverage and low adsorption densities. It happens at higher solute metal concentrations.

This isotherm takes the following form in the process:

$K_aC_e (1 – \theta) = K_d \theta$

Here,

Ka refers to the respective rate constant required for adsorption,

Kd refers to the respective rate constant required for desorption.

Θ stands for the fraction of the surface covered by an adsorbed molecule,

Calculation of Langmuir Adsorption Isotherm

Langmuir Adsorption Isotherm is calculated as follows:

$Ce/Qe = Ce/Qm + 1/(Qm*KL)$

Here,

Ce refers to the equilibrium concentration of the said adsorbate,

Qe refers to the adsorption capacity that gets adsorbed at equilibrium,

Qm refers to the maximum adsorption capacity,

KL refers to the Langmuir Adsorption Constant.

Langmuir Constant

The Langmuir Constant is commonly referred to as K. It indicates the level of interaction between the surface and the adsorbate. If the value of this constant is larger, it indicates a strong interaction between the adsorbent and the adsorbate. On the other hand, K having a smaller value indicates a weaker interaction between the surface and the adsorbate.

Position of the Equilibrium

The position of the equilibrium depends on the factors mentioned below:

1. The relative stability of the gas phase species and the adsorbed molecules.
2. The temperature of the said system (both the surface and the gas).
3. The pressure of the gas is calculated above the surface.

Derivation of Equilibrium Considerations

The Langmuir Isotherm is derived by treating the adsorption process as any other equilibrium process. However, the exceptional fact about this case is that the equilibrium happens between the gas phase molecules and the species adsorbed on the surface that also includes the vacant surface sites.

This equilibrium is always in a dynamic phase. It means that the equilibrium represents a state in which the rate of desorption of molecules counterbalances the rate of adsorption of molecules. According to the model of Langmuir Adsorption Isotherm, both desorption and adsorption are easily reversible processes.

Moreover, this model is also responsible for explaining the effects of pressure on the surroundings. That is why the adsorbent is assumed to be an ideal solid surface. It is composed of distinct sites that are capable of holding the adsorbate together. This binding is treated as a perfect chemical reaction that occurs between the gaseous molecules and a sorption site that is usually empty.

The most important thing to be kept in mind here is that the Langmuir Adsorption Isotherm is applicable only for monolayer adsorption. Moreover, this process takes place on a homogeneous surface when there is zero interaction between the already adsorbed species. Although this process was earlier suitable for describing only the chemisorption process, now it is followed in many systems, most of which have moderately low coverage.

Limitations of Langmuir Adsorption Isotherms

- The adsorbed gas is required to behave ideally in the vapour phase. Moreover, this condition can only be fulfilled under low pressure.
- Langmuir Adsorption Isotherms assume that adsorption is a monolayer. However, this formation is also possible only under low pressure. This assumption breaks down completely under high pressure. That is because gas molecules attract each other.
- The assumption held in this equation is that all sites present on the solid surface are equal in shape and size. It is also assumed that they have an equal affinity for the molecules that are adsorbed. In other words, the surface of a solid is considered homogeneous. However, it is heterogeneous.
- This equation also assumes that molecules do not interact with each other. However, that is not the case because all molecules have at least a weak force of attraction present among them.
- It further assumes that the adsorbed molecules must be localised. However, that is not true, as the adsorption liquefaction of gases results in a decrease in randomness. However, the value that remains is not zero.

Conclusion

Langmuir Adsorption Isotherms are based on a simple assumption. This theory holds that there is a homogeneous distribution of the reactive groups over the particulate’s surface. Moreover, no lateral interaction happens between these groups. So, it is possible to obtain only semi-empirical parameters.

This model explains the process of adsorption with another key assumption: that is the adsorbate always behaves like an ideal gas during isothermal conditions. An important fact about Langmuir Adsorption Isotherm is that it always assumes monolayer adsorption. The above study material notes on Langmuir Adsorption Isotherms will help you understand the entire equilibrium process in detail.

BET Adsorption Isotherm

This theory aims to explain the physical adsorption of gas molecules on a solid surface and serves as the basis for a vital analysis of the measurement of the specific surface area of the material.

Postulates:

1. The adsorption occurs only on well-defined adsorption active sides.
2. Adsorption is multilayer.
3. Adsorption is physical.
4. The uppermost layer is in equilibrium with its adsorbate molecules.

Summary

In this article, we learnt about Freundlich and Langmuir adsorption isotherms. Effect of temperature on adsorption, adsorption from solutions, and some applications of adsorption. The following are some examples of adsorption applications:

- When coal workers wear gas masks, poisonous gases are adsorbed to the mask’s surface, preventing them from coming into contact with them.
- Vacuum is created by adsorbing traces of air on charcoal and removing them from devices that are being evacuated.
- Moisture removal: Silica gel pellets are used to manage humidity in pharmaceuticals and new plastic bottles by adsorbing moisture.
- Removal of colour: To get a clear liquid solution, the juice collected from cane is treated with animal charcoal to remove the colouring ingredient.

- As Catalysts: Appropriate materials are employed as catalysts so that reactants attach to their surface, allowing the reaction to occur more quickly and increasing the rate of reaction.

Theory of BET Isotherm

The Langmuir theory relates the monolayer adsorption of gas molecules (Figure 2.3.52.3.5), also called adsorbates, onto a solid surface to the gas pressure of a medium above the solid surface at a fixed temperature to 2.3.12.3.1 , where θ is the fractional cover of the surface, P is the gas pressure and α is a constant.

$\Theta = \alpha \cdot P/1 + (\alpha \cdot P)$

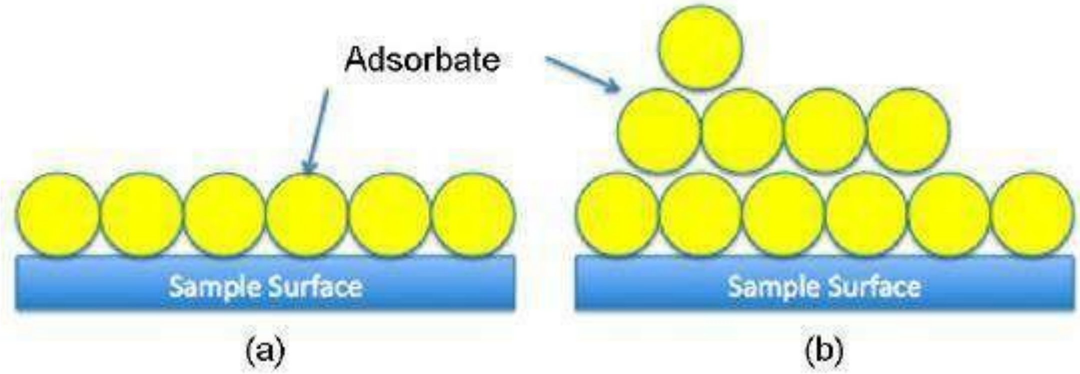


Figure 2.3.5 Schematic of the adsorption of gas molecules onto the surface of a sample showing (a) the monolayer adsorption model assumed by the Langmuir theory and (b) s the multilayer adsorption model assumed by the BET theory.

The Langmuir theory is based on the following assumptions:

- All surface sites have the same adsorption energy for the adsorbate, which is usually argon, krypton or nitrogen gas. The surface site is defined as the area on the sample where one molecule can adsorb onto.
- Adsorption of the solvent at one site occurs independently of adsorption at neighboring sites.
- Activity of adsorbate is directly proportional to its concentration.
- Adsorbates form a monolayer.
- Each active site can be occupied only by one particle.
- The Langmuir theory has a few flaws that are addressed by the BET theory. The BET theory extends the Langmuir theory to multilayer adsorption (Figure 2.3.12.3.1) with three additional assumptions:
- Gas molecules will physically adsorb on a solid in layers infinitely.

- The different adsorption layers do not interact.
- The theory can be applied to each layer.

How does BET Work?

Adsorption is defined as the adhesion of atoms or molecules of gas to a surface. It should be noted that adsorption is not confused with absorption, in which a fluid permeates a liquid or solid. The amount of gas adsorbed depends on the exposed surface are but also on the temperature, gas pressure and strength of interaction between the gas and solid. In BET surface area analysis, nitrogen is usually used because of its availability in high purity and its strong interaction with most solids. Because the interaction between gaseous and solid phases is usually weak, the surface is cooled using liquid N_2 to obtain detectable amounts of adsorption. Known amounts of nitrogen gas are then released stepwise into the sample cell. Relative pressures less than atmospheric pressure is achieved by creating conditions of partial vacuum. After the saturation pressure, no more adsorption occurs regardless of any further increase in pressure. Highly precise and accurate pressure transducers monitor the pressure changes due to the adsorption process. After the adsorption layers are formed, the sample is removed from the nitrogen atmosphere and heated to cause the adsorbed nitrogen to be released from the material and quantified. The data collected is displayed in the form of a BET isotherm, which plots the amount of gas adsorbed as a function of the relative pressure. There are five types of adsorption isotherms possible.

Calculations

The BET Equation, 2.3.2 , uses the information from the isotherm to determine the surface area of the sample, where X is the weight of nitrogen adsorbed at a given relative pressure (P/Po), X_m is monolayer capacity, which is the volume of gas adsorbed at standard temperature and pressure (STP), and C is constant. STP is defined as 273 K and 1 atm.

$$1/X[(P0/P)-1]=1/XmC+C-1/XmC(P/P0)$$

Multi-point BET

Ideally five data points, with a minimum of three data points, in the P/P_0 range 0.025 to 0.30 should be used to successfully determine the surface area using the BET equation. At relative pressures higher than 0.5, there is the onset of capillary condensation, and at relative pressures that are too low, only monolayer formation is occurring. When the BET equation is plotted, the graph should be of linear with a positive slope. If such a graph is not obtained, then the BET method was insufficient in obtaining the surface area.

- The slope and y-intercept can be obtained using least squares regression.
- The monolayer capacity X_m can be calculated with 2.3.3 .
- Once X_m is determined, the total surface area S_t can be calculated with the following equation, where L_{av} is Avogadro's number, A_m is the cross sectional area of the adsorbate and equals 0.162 nm^2 for an absorbed nitrogen molecule, and M_v is the molar volume and equals 22414 mL, 2.3.4 .

  Xm =1/s + i=C−1/Cs

  S =XmLavAm/Mv

Single point BET can also be used by setting the intercept to 0 and ignoring the value of C. The data point at the relative pressure of 0.3 will match up the best with a multipoint BET. Single point BET can be used over the more accurate multipoint BET to determine the appropriate relative pressure range for multi-point BET.

The Surface Area Determination of Metal-Organic Frameworks

The BET technique was used to determine the surface areas of metal-organic frameworks (MOFs), which are crystalline compounds of metal ions coordinated to organic molecules. Possible applications of MOFs, which are porous, include gas purification and catalysis. An isoreticular MOF (IRMOF) with the chemical formula Zn_4O(pyrene-1,2-dicarboxylate)$_3$ (Figure 2.3.12) was used as an example to see if BET could accurately determine the surface area of microporous materials. The predicted surface area was calculated directly from the geometry of the crystals and agreed with the data obtained from the BET isotherms. Data was collected at a constant temperature of 77 K and a type II isotherm (Figure 2.3.13) was obtained.

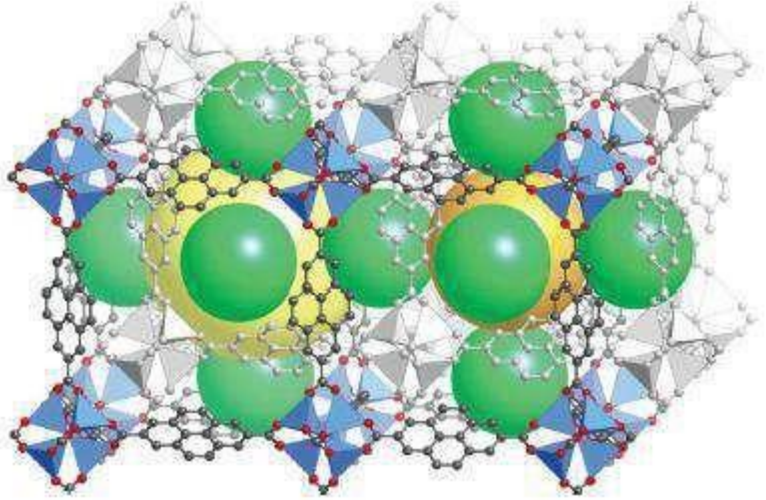
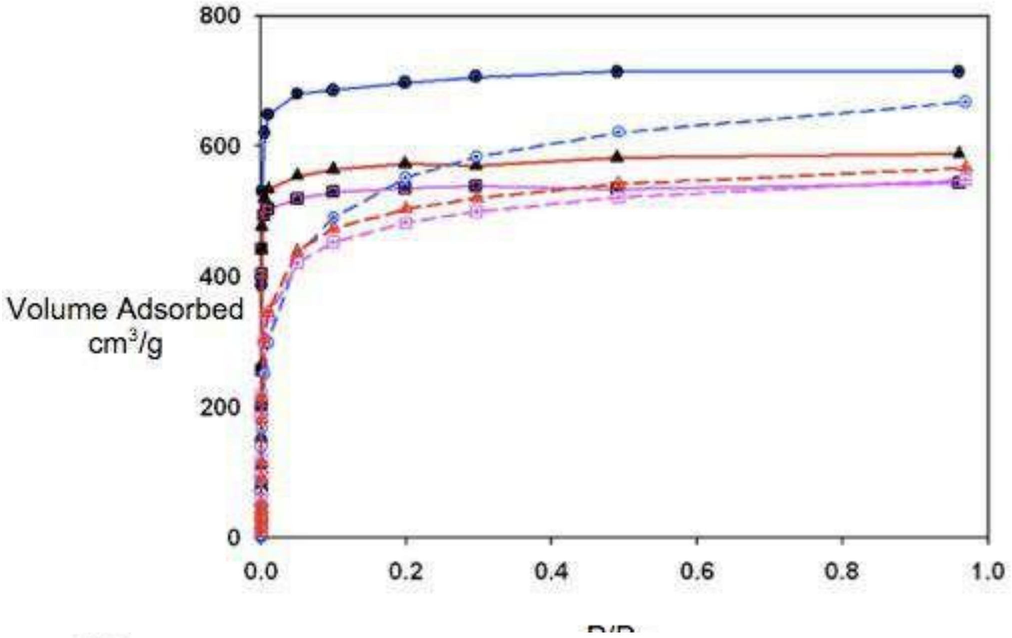
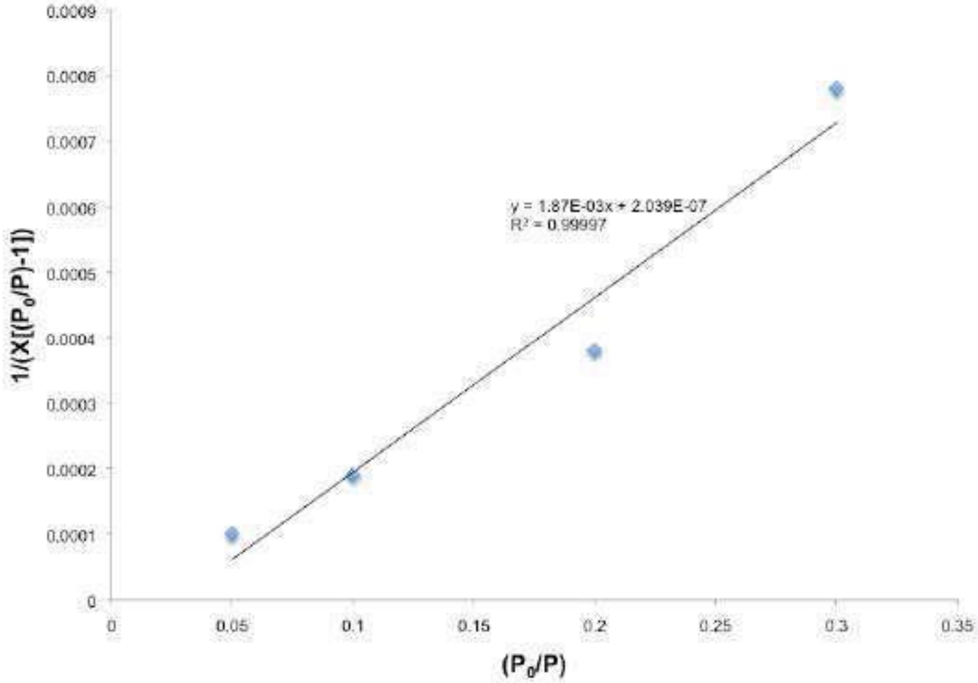


Figure 2.3.122.3.12 The structure of catenated IRMOF-13. Orange and yellow represent non-catenated pore volumes. Green represents catenated pore volume. Figure 2.3.132.3.13 The BET isotherms of the zeolites and metal-

organic frameworks. IRMOF-13 is symbolized by the black triangle and red line. Adapted from Y.S. Bae, R.Q. Snurr, and O. Yazaydin, Langmuir, 2010, **26**, 5478.





The isotherm data obtained from partial pressure range of 0.05 to 0.3 is plugged into the BET equation, 2.3.22.3.2 , to obtain the BET plot (Figure 2.3.142.3.14).

Figure 2.3.142.3.14 BET plot of IRMOF-13 using points collected at the pressure range 0.05 to 0.3. The equation of the best-fit line and R^2 value are shown. Adapted from Y.S. Bae, R.Q. Snurr, and O. Yazaydin, Langmuir, 2010, **26**, 5479.

Using 2.3.5 , the monolayer capactiy is determined to be 391.2 cm^3/g.

$X_m = 1/(2.66E - 3) + (-5.212E - 0.05)$

Now that X_m is known, then 2.3.6 can be used to determine that the surface area is 1702.3 m^2/g.

$S = 391.2 cm^2 * 0.162 nm^2 * 6.02 * 10^{23} / 22.414 : L$

Solution

Solutions of Liquids in Liquids

We know that some liquids mix with each other in all proportions; in other words, they have infinite mutual solubility and are said to be miscible. Ethanol, sulfuric acid, and ethylene glycol (popular for use as antifreeze, pictured in the figure below) are examples of liquids that are completely miscible with water. Two-cycle motor oil is miscible with gasoline.

Liquids that mix with water in all proportions are usually polar substances or substances that form hydrogen bonds. For such liquids, the dipole-dipole attractions (or hydrogen bonding) of the solute molecules with the solvent molecules are at least as strong as those between molecules in the pure solute or in the pure solvent. Hence, the two kinds of molecules mix easily. Likewise, nonpolar liquids are miscible with each other because there is no appreciable difference in the strengths of solute-solute, solvent-solvent, and solute-solvent intermolecular attractions. The solubility of polar molecules in polar solvents and of nonpolar molecules in nonpolar solvents is, again, an illustration of the chemical axiom “like dissolves like.”

Two liquids that do not mix to an appreciable extent are called **immiscible**. Layers are formed when we pour immiscible liquids into the same container. Gasoline, oil (see the figure below), benzene, carbon tetrachloride, some paints, and many other nonpolar liquids are immiscible with water.

The attraction between the molecules of such nonpolar liquids and polar water molecules is ineffectively weak. The only strong attractions in such a mixture are between the water molecules, so they effectively squeeze out the molecules of the nonpolar liquid. The distinction between immiscibility and miscibility is really one of degrees, so that miscible liquids are of infinite mutual solubility, while liquids said to be immiscible are of very low (though not zero) mutual solubility.

Two liquids, such as bromine and water, that are of moderate mutual solubility are said to be **partially miscible**. Two partially miscible liquids usually form two layers when mixed. In the case of the bromine and water mixture, the upper layer is water, saturated with bromine, and the lower layer is bromine saturated with water.

Since bromine is nonpolar, and, thus, not very soluble in water, the water layer is only slightly discolored by the bright orange bromine dissolved in it. Since the solubility of water in bromine is very low, there is no noticeable effect on the dark color of the bromine layer

Binary Solution

1. Solutions are the homogeneous mixtures of two or more substances that are mixed uniformly or are miscible in nature.
2. Solution consists of two components that are solute and solvent
3. Solute - They are present in less quantity.
4. Solvent - They are present in large quantities.
5. Thus, binary solutions also consist of two components (solute + solvent) in a homogeneous form that is mixed uniformly. However, the solvent may be gas or liquid.
6. For example, a solution of sugar, in which the two components are there one is solute- sugar and another is solvent - water.

Raoult's law

According to Raoult's law, "the vapour pressure of any solution containing a non-volatile solute in a volatile solvent is proportional to the mole fraction of the solvent in the solution."

Raoult's law was first given by French chemist François-Marie Raoult in the year 1887. It is applicable for a solution of two volatile liquids. It claims that the vapour pressure of the solution is proportional to the mole fraction of the solvent.

Thus, Raoult's Law formula is:

$P=P_0X$

Thus,

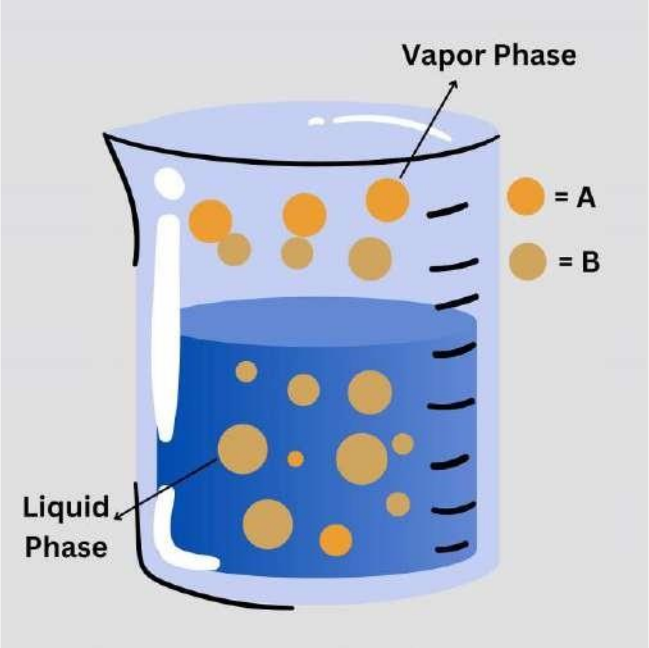
$P_{solution} = X_{solvent}.P_{solvent}$

Where,

- $P_{solution}$ = Vapor pressure of the solution
- $X_{solvent}$ = Mole fraction of the solvent
- $P_{solvent}$ = Vapor pressure of the pure solvent

Example of Raoult's Law

Assume a solution of volatile liquids A and B in a given beaker. Since both A and B are volatile, both particles A and B are in the vapour phase. Consequently, the vapour particles of A and B thus exert partial pressure, contributing to the total pressure above the solution.



Raoult's Law

Raoult's Law Also states that in **equilibrium**,

$\Rightarrow P_A = P°_A x_A,\ P_B = P°_B x_B$

Here,

- P_A = Partial pressure of A
- $P°_A$ = Vapour pressure of pure A at that temperature
- x_A = Mole fraction of A in the liquid phase

Ideal and Non-Ideal Solution

A homogeneous mixture composed of two or more components is called a Solution.

- The component which has the highest quantity in a solution is the solvent.
- The solvent helps determine the physical state of the solution.
- A solute is a substance, in a solution, found in a smaller amount.
- The solution that has two components is called a Binary Solution.
- The properties of a solution are further defined on basis of the Vapour Pressure, Boiling Point, Freezing Point and other Colligative Properties.

The binary liquid in liquid solutions can be further divided into two terms:

- Ideal Solution
- Non-ideal Solution

Ideal Solution

The solutions which follow Raoult's law at all temperatures and concentrations are called **Ideal Solution**. During its formation no change in enthalpy or volume takes place. In ideal solutions, the interaction between solute-solute and solvent-solvent molecules same as the interaction between solute and solvent molecules.

An ideal solution should possess the following characteristics:

- It should follow Raoult's law
- No heat or energy released during the formation of the solution means the enthalpy of mixing should be zero. e, $\Delta H_{(mix)} = 0$
- The volume of the solution should be constant means the volume of the solution will be equal to the volume of the components. $\Delta V_{(mix)} = 0$
- Practically, no solution behaves as an ideal solution. The substances of similar structure and **polarity** mix together to form an ideal solution.

Examples of Ideal Solution

The following examples of nearly ideal solutions:

- Benzene and Toluene
- n-hexane and n-heptane
- Chlorobenzene and Bromobenzene
- Ethyl bromide and ethyl iodide

Non-Ideal Solutions

The solutions which do not follow Raoult's law at all concentrations and **temperatures** are termed as non-ideal solutions. It is also termed **real solutions**.

The enthalpy of a non-ideal solution does not equal zero and it also changes **volume**. For example, when **sulphuric acid** is mixed in water then **heat** is released and a volume change is also observed. Thus, it is a non-ideal solution.

Non-Ideal solutions possess the following characteristics:

- It does not follow Raoult's law
- The enthalpy during the formation of the solution is not zero. $\Delta H_{(mix),}$ not 0
- The volume after mixing may not be constant. $\Delta V_{(mix)}$ not 0.
- The non-ideal solutions show deviation from Raoult's law.

Based on deviation the non-ideal solutions are of the following two types:

- Positive Deviation
- Negative Deviation

Positive and Negative Deviation from Raoult’s Law

Depending on the deviation of Non-ideal solutions,it can be further classified as:

- Positive Deviation
- Negative Deviation

Positive Deviation from Raoult’s Law

Most of the liquid mixtures form a non-ideal solution.

- In this solution, the interaction between solute and solvent is weaker than the interaction between solute-solute and solvent-solvent. Thus, A – B < A – A or B – B.
- $P_A > P_A \ x_A$ and $P_B > P \quad x$ (as total vapour pressure, i.e.$P\ ^0 x_A + P^0_B x_B$) is greater than predicted with respect to Raoult’s Law
- Sometimes the partial vapour pressure of a miscible liquid is greater than the expected vapor pressure as per Raoult's law.
- The total vapour pressure will be greater than the corresponding vapor pressure in the case of an ideal solution of the same composition.
- The **boiling point** of such solutions is lowered. This behaviour of a non-ideal solution shows a positive deviation from Raoult's law.

Deviations from ideal behavior

There are many cases when two miscible liquids mix with each other and form a non-ideal solution. Such solutions show two types of deviation from Raoult's law (ideal behavior): Positive and negative deviations. These deviations are due to the reason that both liquids have different molecular structures and so different intermolecular forces.

Positive deviation from Raoult's law

When two liquids A and B are mixed together, a solution is obtained. Cohesive forces between the molecules of the liquid (A and B) in a solution are weaker as compared to molecules of pure liquids (A-A or B-B). Consequently, liquids A and B have a high tendency to escape from the solution. Whereas, pure liquids (A-A or B-B) have a low tendency to escape. So, they have higher partial pressures than expected by Raoult's law. As a result, there is a positive deviation from ideal behavior.

Here are examples of liquids that show positive deviation:

- Acetone and carbon disulfide
- Acetone and ethyl alcohol
- Acetone and ether

In the above graph, dotted lines show the ideal behavior. Whereas, bold lines are the actual vapor pressure of the component and solution.

Negative Deviation from Raoult's law

When the molecules of A and B have a greater attraction for each other than pure liquids, then they have a lesser tendency to escape from the solution. They have less partial pressure as compared to partial pressure predicted by Raoult's law. This results in a negative deviation from Raoult's law.

The following are the examples of negative deviation of Raoult's law:

- Acetone and chloroform
- Acetone and methanol
- Acetic acid and pyridine etc.

The above graph shows bold and dotted lines. The dotted lines are indications of ideal behavior while bold lines are the actual vapor pressure of components.

Limitations of Raoult's law

- That solution which ideally behaves obeys Raoult's law
- They are applicable only for very dilute solutions
- That solution which contains nonvolatile solute obeys Raoult's law
- Those solutes that dissociate or associate with a solution do not obey Raoult's law

Azeotropic Distillation

Azeotropic Distillation can be defined as the process of separating the components of an azeotropic mixture by distillation.

An azeotropic mixture is a mixture containing two or more liquids that cannot be separated by simple distillation because the vapours formed from the boiling of azeotropic mixtures contain almost the same proportions of liquids as the liquid itself. Therefore, azeotropic distillation is a specialized type of distillation which involves the use of specific techniques to break the azeotropes.

The most common method of breaking an azeotrope involves the addition of a material separation agent that has the ability to change the molecular interactions between the components of the azeotrope. The addition of such a material separation agent tends to alter the activity of the activity coefficient of the components of the azeotropic mixture, thereby changing the relative volatility of the azeotropic mixture as a whole.

How can a Mixture of Ethanol and Water be Separated by Azeotropic Distillation?

Water and ethanol are known to form an azeotropic mixture. This mixture can be separated via the process of azeotropic distillation. In order to achieve this, material separation agents such as benzene, hexane, cyclohexane, pentane, diethyl ether, and acetone are commonly used. Historically, benzene was the most commonly used entrainer for this purpose. However, the discovery of the carcinogenic nature of benzene is believed to have caused a decline in the use of benzene in the azeotropic distillation of mixtures of water and ethanol. In modern practices, the ethanol-water azeotrope is usually broken with the help of toluene. Other suitable options for the dehydration of a mixture of water and ethanol include cyclohexane, isooctane, and even heptane.

Critical Solution Temperature And Its Applications

A phase diagram is a plot describing conditions of temperature and pressure under which two or more physical states coexist in dynamic equilibrium.

It means phase diagram is a graphical representation of chemical equilibrium. This diagram is also called as Pressure –Temperature graph.

In phase diagram of water there are three lines or curves that separate the area of each phase. Adjacent to each line there exist a different single phase of water. At any point on line there exist equilibrium between two phases shown by area i.e. solid/liquid, liquid/vapour and solid/vapour. The line OA, OB and OC represents equilibrium between liquid and vapour, solid and liquid and solid and vapour phases, respectively. The line OA represents vapourization curve and OC represent sublimation curve. For example, above line OA the liquid-water exist and below it water vapour exists. The liquid – vapour equilibrium curve has a top limit labeled as C in the phase diagram. This is known as critical point. Water has a critical point of 374°C. The temperature and pressure corresponding to this point is known as the critical temperature and critical pressure, respectively. The solid – liquid equilibrium line (m. p. line) slopes backwards (negative slope) rather than forward (positive slope). It means in case of water; the melting point gets lower at higher pressures. At solid – liquid equilibrium the ice is less dense than liquid water formed as it melts, and the water formed occupies a smaller space. At this equilibrium if pressure is increased the equilibrium move to reduce the pressure again. That means it moves to the side with smaller volume. To make the liquid water freeze again at this high pressure, we need to reduce the temperature. Higher pressure means lower melting point.

The transition temperature (TUCT) of a system helps to determine percent purity of substances. The change in TUCT is proportional to the concentration of substance added. For example, in phenol-water system addition of sodium chloride or potassium chloride changes its TUCT depending upon concentration of these substances. If known different concentration solutions of sodium chloride are prepared and added separately to phenol-water mixtures having composition say 50:50, then TUCT of the system is determined by plotting a phase diagram by taking concentrations of sodium chloride on x-axis and UCT on y-axis. An unknown solution of sodium chloride is then added to phenol – water (50:50) system and again TUCT is determined. It is plotted on curve to obtain its concentration by extrapolating on x-axis. The TUCT is mostly used as criterion to test the purity of substances that form conjugate system with some other liquid.

Phenol USP is a necrotic agent having freezing point 17ºC. Thus, at room temperature it exists in solid crystalline form. The corrosive characteristic and solid nature of phenol makes it difficult to handle. The Liquefied Phenol BP contains 80% w/w of phenol in water. The presence of other substance or impurities solidifies phenol approximately at about 10°C. The miscibility curve of phenol-water system suggest that 76% w/w of phenol should be used in the preparation. At this concentration freezing point of phenol is 3.5°C. Such preparations remain in liquid form that can be handled easily. In India, we have wide variety of climatic conditions with diverse temperatures ranging from 10 – 40°C during different seasons.

Hence, a preparation which is in dry powder state in winter or rainy season would become pasty during summer. The TUCT can also be used to determine percent compositions of each component in unknown mixtures. The temperature below which when system containing partially miscible liquids exist only as a single phase is known as lower consolute temperature (TLCT). For example, triethanolamine (TEA) - water system has TLCT of about 18.5°C at 13% w/w of TEA. The temperature – concentration plot of this system is shown in Fig. 1.12. Above 18.5°C mixture of these liquids forms two layers. The left upward curve shows decrease in miscibility of TEA in water whereas right upward curve shows decrease in miscibility of water in TEA with increase in temperature of system, respectively. At 50% by weight of TEA in water at 18.5°C forms single phase. This temperature is called TLCT of TEA – water system. The region outside the curve shows mutual solubility of TEA and water in each other. Other examples of liquid pairs that shows TLCT are dimethylamine – water (43°C, 13% w/w weight of dimethylamine), 1-methyl piperidine – water (48°C, 5% w/w of piperidine), polyethylene glycol – water, paraldehyde – normal saline, water – Tween 80, etc.

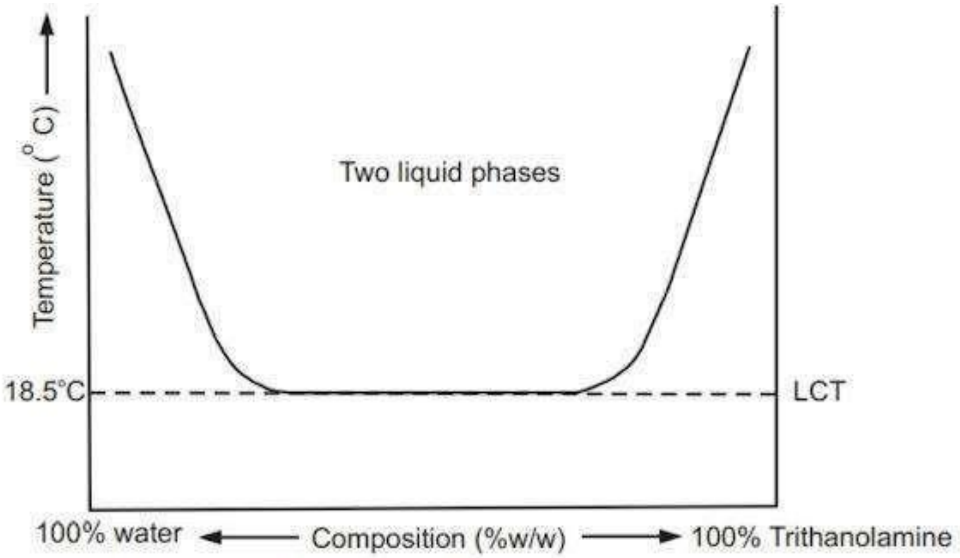


Figure 1.12: Phase Diagram of Triethanolamine – Water System

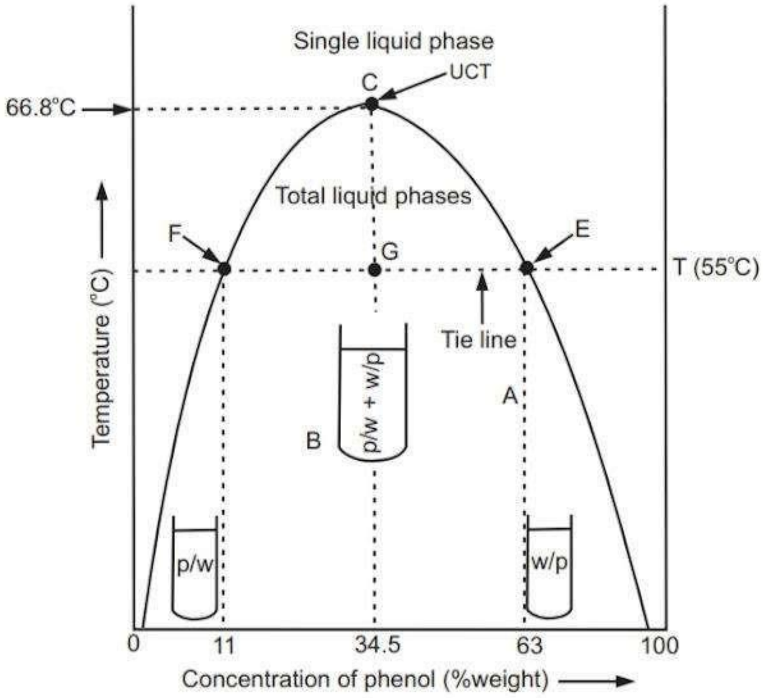


Figure 1.13: Phase Diagram of Phenol – Water System

Liquid Crystals

Liquid crystal is a term referring to substances that are not crystalline (solid) nor isotropic (liquid), but somewhere between the two. There are three main types, or what is scientifically known as mesophases, of liquid crystals which can be identified by their varying amounts of molecular order and positioning. This arrangement of molecules is what makes the substance either more solid or liquid.

Nematic

The nematic phase is the simplest form of liquid crystal and is the phase in which the crystal molecules have no orderly position and are free to move any which way. However, while they have no specific order, during this phase the molecules do tend to point in the same direction, which is what differentiates it from a pure liquid. Liquid crystal in this phase can be characterized by its thread-like appearance when looked at under a microscope. The use of nematic liquid crystal is common in telescope lenses as it allows for a clear image when researchers are confronted with atmospheric turbulence.

Smectic

The smectic phase of liquid crystal, which is defined as being equivalent to the slippery, thick residue found at the bottom of soap dishes, is characterized by a slight degree of translational order in the crystal molecules which is not found in the nematic phase. While keeping similar orientation and pointing in the same direction as the molecules in nematic liquid crystal do, in this phase the molecules tend to line themselves up into layers. While these layers as a whole move freely, movement within the layers is restricted; therefore, it creates a slightly more solid substance. Smectic liquid crystal has been found to have fast electro-optical response time and because of this is used, along with nematic liquid crystal, in producing liquid crystal display (LCD) screens.

Cholesteric

The cholesteric phase, also known as chiral nematic phase, is characterized by the molecules being aligned and at a slight angle to one another, stacked within very thin layers– it is the last phase before a substance becomes crystalline, or solid. This type of liquid crystal also has the characteristic of changing color when it is exposed to different temperatures. It is for this reason that cholesteric liquid crystal is used in common household items such as thermometers and mood rings.