

II Year
Paper VIII: Physical Chemistry - II

Unit I

Chemical Kinetics

Simple collision theory, absolute reaction rate theory (ARRT), thermodynamic treatment, potential energy surfaces, applications of ARRT to Simple bimolecular Processes; chain reactions - general characteristics, study of kinetics of chain reactions like H_2 -Br₂ reactions, decomposition of acetaldehyde and H_2O_2 ; study of H_2 -O₂ explosive reactions. Theory of unimolecular reactions - Lindemann, Hinshelwood, RRKM and Stator treatments; Steady state approximations, principles of microscopic reversibility and detailed balancing, kinetic isotope effect; Reactions in solution, factors influencing reaction rate in Solution, ARRT to reactions in solution, significance of volume of activation, primary and secondary salt effects.

Homogeneous catalysis, acid - Base catalysis, acidity function, Bronsted catalysis law. Fast reaction techniques - Chemical relaxation methods, temperature and pressure jump methods, ultrasonic absorption technique, reactions in flow system, continuous and stopped flow shock wave tube methods, chemical kinetics in crossed molecular Beam.

Unit II

Photochemistry and Radiation Chemistry

Physical properties of the electronically excited molecules - Excited state dipole moments, excited State Pka, excited state redox potentials. Photophysical processes in electronically excited molecules - Fluorescence, phosphorescence and other deactivating processes, Stern - volmer equation and its applications, electronic energy transfer mechanisms, photosensitisation and chemiluminescence. Experimental techniques in photochemistry - light sources, chemical actinometry, conventional photolysis procedure flash photolysis techniques. Study of photochemical reactions like H_2 - X₂ decomposition of photosynthesis, photochemical conversion and storage of Solar energy.

Radiation Chemistry - source of high energy, interaction of high energy radiation with matter, radiolysis of water, definition of G - value, mode of reactions of hydrated electrons, OH and H- Experimental techniques on radiation chemistry, dosimetry. Elementary aspects of radiation chemistry in biology and industry.

Unit III

Group Theory

Group Theory : Molecular symmetry elements and symmetry operations, vector and matrix algebra, symmetry operations and transformation matrices; group theory - definition and properties of a group symmetry. Point groups, representation of a group - reducible and irreducible representations, great orthogonality theorem, characters, construction of character, tables, direct product groups.

Symmetry of Normal modes of vibrations, applications of group theory to normal mode analysis, symmetry properties of integrals, application for spectral selection rules of vibrational Spectra - IR and Raman active fundamentals, symmetry of molecular orbitals and symmetry selection rule for electronic transitions in simple molecules (ethylene, formaldehyde, benzene and naphthalene), Group theory and quantum mechanics wave function as a basis of irreducible representations, group theory as applied to hybridisation, HMO theory and HMO calculation and delocalisation energy for ethylene, cyclopropenyl and butadiene systems.

Unit IV

Spectroscopy I

Elements of molecular spectroscopy: Absorption and emission of radiation, the time dependent schrodinger equation, interaction of EMR with matter, Einstein coefficient, induced emission and absorption, ultra wave, IR and Raman spectroscopy of diatomic molecules - Determination of molecular parameters, vibrational spectra of polyatomic molecules - definition of normal modes and normal coordinates, IR and Raman active fundamentals, overtone and combination bands - concept of group frequencies, coupling interaction bands Fermi resonance, Basic concept of FT-IR. Electronic Spectra of diatomic and polyatomic molecules, Born-oppenheimer approximations, Franck - condon principle, dissoci energy, Rotational fine structure and Fortrat diagram.

Unit V

Spectroscopy II

H^1 -NMR, Introduction, theory of splitting of Nuclear Zeeman levels in a magnetic field, chemical shift, spin-spin splitting, dipolar interactions, relaxation times, line shape and line width, experimental techniques - double resonance technique, ENDOR, overhauser, effect, FT - nmr spectroscopy - Lanthanide shift reagents.

ESR spectroscopy - hyperfine splitting, factors affecting the magnitude of the 'g' values, solid state epr, rate of electron exchange reactions, fine structure and hyperfine structures, electron density from esr, theory of esr spectra of free radicals.

Photoelectron spectroscopy - basic principles, instrumentation X-ray photoelectron and uv photoelectron spectra, core energy level studies - application of ESCA; laser, Raman spectroscopy theory of Raman Scattering, techniques and instrumentation, the laser source, applications of laser Raman Spectroscopy, structure determination.

References

1. K.J. Laidler, Chemical Kinetics, 2nd edn., Tata Mc Graw Hill, New Delhi, 15th reprint 1991.
2. K.J. Laidler, Theories of Chemical Reaction rates, Mc Graw Hill, New York, 1969.
3. K.K. Rohatgi - Mukerjee, Fundamentals of photochemistry.
4. J.N. Bradley, Fast Reaction.
5. N.J. Turo, Modern Molecular photochemistry.
6. F.A. Cotton, Chemical Application of Group theory.
7. C.N. Banewall, Spectroscopy.
8. Stangan and Walker, Spectroscopy, Vol. 1, 2, & 3.

M.Sc Chemistry – II year

Paper VII – Physical Chemistry - II

UNIT - I

CHEMICAL KINETICS

Simple collision theory

The collision theory has been developed to explain why certain factors, such as the nature of reactants concentrations and temperature affect the rate of a chemical reaction. According to this theory the rate of reaction is proportional to the number of collision per unit of time and the fraction of collisions that are effective in producing chemical change. Consider a bimolecular reaction involving two molecules



$$\text{Rate of reaction} = \left(\text{Number of colliding molecules per litre per cc} \right) \times \left(\text{fraction of the effective collision} \right)$$

$$\frac{dx}{dt} = Z_{AB} e^{-E_a/RT} \quad \dots (1)$$

where Z_{AB} is the number of bimolecular collision per second per cc and E_a is the activation energy. The number of collision of molecule A with that of B per second per cc in a bimolecular mixture is

$$Z_{AB} = N_A N_B \sigma_{AB}^2 \left[8\pi k_B T \left(\frac{1}{m_A} + \frac{1}{m_B} \right) \right]^{1/2} \quad \dots (2)$$

N_A, N_B = number of molecules of A and B in one cc

σ_{AB} = average diameter equal to the molecular diameter $\left(\frac{\sigma_A + \sigma_B}{2} \right)$ which is called the distance of closest approach of effective molecular diameter.

m_A and m_B = masses of the molecules A and B

Substitute the value of eqn. (2) in eqn. (1) we get

$$\frac{dx}{dt} = N_A N_B \sigma_{AB}^2 \left[8\pi k_B T \left(\frac{1}{m_A} + \frac{1}{m_B} \right) \right]^{1/2} e^{-E_a/RT} \quad \dots (3)$$

According to the fundamental postulate of chemical kinetics

$$\frac{dx}{dt} = k [A] [B] \quad \dots (4)$$

where k is the specific rate constant

The concentration of A and B are equal to N_A and N_B . we get

$$\frac{dx}{dt} = k N_A N_B \quad \dots (5)$$

compare eqn. (3) and (5) we get

$$k = \sigma_{AB}^2 \left[8\pi k_B T \left(\frac{m_A + m_B}{m_A m_B} \right) \right]^{1/2} e^{-E_a/RT} \quad \dots (6)$$

$$k = A T^{1/2} e^{-E_a/RT} \quad \dots (7)$$

$$\text{where } A = \sigma_{AB}^2 \left[8\pi k_B \left(\frac{m_A + m_B}{m_A m_B} \right) \right]^{1/2}$$

Taking the logarithm of eqn (7) we get

$$\ln k = \ln A + \frac{1}{2} \ln T - \frac{E_a}{RT} \quad \dots (8)$$

Differentiating this equation with respect to T gives

$$\frac{d \ln k}{dT} = \frac{E_a + \frac{1}{2} RT}{RT^2} = \frac{E_a}{RT^2} + \frac{1}{2T} \quad \dots (9)$$

In most cases $\frac{1}{2T}$ is small as compared to E_a/RT^2 . Therefore the above equation can be written as

$$\frac{d \ln k}{dT} = \frac{E_a}{RT^2} \quad \dots (10)$$

If the reaction involves two identical molecules



$$\frac{dx}{dt} = k [A]^2$$

$$= k N_A^2$$

The value of collision number given by

$$Z_{AA} = 4 N_A^2 \sigma^2 \left(\frac{\pi K_B T}{m_A} \right)^{1/2}$$

and

$$k = 4\sigma^2 \left(\frac{\pi K_B T}{m_A} \right)^{1/2} e^{-E_a/RT}$$

$$k = Z e^{-E_a/RT}$$

The collision number Z , is defined as "The number of collision per second when there is only one reactant molecules per cc of the gas. Thus the theory relates the frequency factor in Arrhenius equation with the collision number Z .

The rate of reaction can be theoretically calculated by determining the collision number Z from viscosity data and E_a from reaction rate measurements at two temperatures.

Absolute Reaction Rate Theory

The absolute reaction rate theory represents an alternative molecule approach to the collision theory to explain the mechanism of a reaction. The fundamental postulate of the theory is

1. The reacting molecules must form an activated complex before being converted into products.
2. There exists an equilibrium between the activated complex and the reactants (Fig. 1).

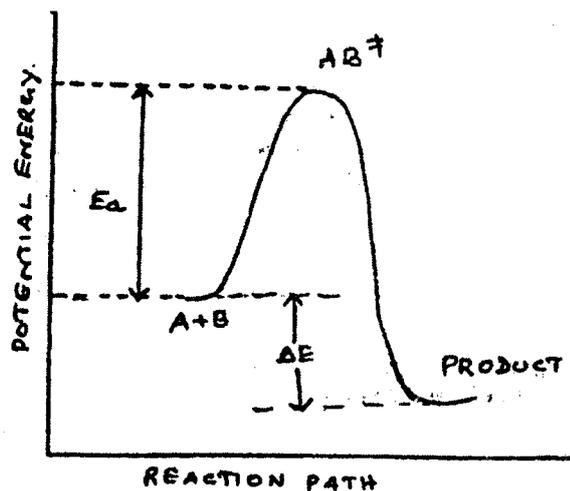


Fig. 1

3. The conversion of reactants to products is through the formation of a activated complex. The activated complex is a molecule in the processes of breaking or forming bonds. In the activated complex the atoms are linked together with large valence bonds. It is not stable because it exists at the top of the potential energy barrier.

Let us consider a biomolecular reaction between a molecule A and B



The rate of the reaction is equal to the concentration of the activated complex and the frequency of the decomposition of activated complex

$$\text{Rate} = [AB^*] \times \text{frequency of decomposition of activated complex}$$

Concentration of $[AB^*]$

If $[A]$, $[B]$ and $[AB^*]$ represent the concentration of A, B and AB^* at time t, then equilibrium constant K^* for the formation of the activated complex may be written as

$$K^* = \frac{[AB^*]}{[A][B]}$$

$$[AB^*] = K^* [A] [B] \quad \dots (2)$$

Frequency of the decomposition of activated complex

The activated complex must have one of its vibrational degree of freedom which would be quit unstable. If E_{vib} be the vibrational energy which causes the rupture of bond, then according to the Planks quantum theory

$$E_{vib} = h\nu \quad \dots (3)$$

This vibration is responsible for disrupting the complex into the product. The vibration in large enough in amplitude to decompose the complex. The frequency of such vibration will be low and the average energy E_{vib} will be of the order of classical vibrational energy kT .

$$E_{vib} = k_B T \quad \dots (4)$$

k_B = Boltzmann constant

compare equation (3) and (4) we get

$$h\nu = k_B T$$

$$\nu = \frac{k_B T}{h} \quad \dots (5)$$

substitute eqn. (5) and (2) in eqn. 1 we get

$$\frac{-d[A]}{dt} = K^\ddagger [A] [B] \cdot \frac{k_B T}{h} \quad \dots (6)$$

If k is the velocity constant of the reaction, the experimentally obtained rate law

$$\frac{-d[A]}{dt} = k [A] [B] \quad \dots (7)$$

compare eqn. (6) and (7) we get

$$k [A] [B] = K^\ddagger [A] [B] \cdot \frac{k_B T}{h}$$

we get

$$k = K^\ddagger \frac{k_B T}{h} \quad \dots (8)$$

The K^\ddagger can be expressed in thermodynamic term

$$\Delta G^\ddagger = -RT \ln K^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger$$

$$\ln K^\ddagger = \frac{-\Delta G^\ddagger}{RT}$$

$$K^\ddagger = e^{-\Delta G^\ddagger/RT} \quad \dots (9)$$

Substitute eqn. (9) in eqn. (8) we get

$$k = \frac{k_B T}{h} e^{-\Delta G^\ddagger/RT} \quad \dots (10)$$

where

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

$$k = \frac{k_B T}{h} e^{\Delta S^\ddagger/R} e^{-\Delta H^\ddagger/RT} \quad \dots (11)$$

This equation known as the Eyring equation.

According to ARRT

$$k = \frac{k_B T}{h} K^\ddagger \quad \text{(or)}$$

$$\ln k = \ln \frac{k_B}{h} + \ln T + \ln K^\ddagger \quad \text{(or)}$$

$$\frac{d \ln k}{dT} = \frac{1}{T} + \frac{d \ln K^*}{dT} \quad \dots (12)$$

Vant Hoff reaction isochore

$$\frac{d \ln K^*}{dT} = \frac{\Delta E^*}{RT^2} \quad \dots (13)$$

Substitute this value in eqn. (12) we get

$$\frac{d \ln k}{dT} = \frac{1}{T} + \frac{\Delta E^*}{RT^2} \quad \dots (14)$$

The Arrhenius equation is

$$k = A e^{-E_a/RT}$$

$$\ln k = \ln A - \frac{E_a}{RT}$$

$$\frac{d \ln k}{dT} = \frac{E_a}{RT^2} \quad \dots (15)$$

compare eqn. (14) and (15) we get

$$\frac{E_a}{RT^2} = \frac{1}{T} + \frac{\Delta E^*}{RT^2}$$

$$\frac{E_a}{RT^2} = \frac{RT + \Delta E^*}{RT^2}$$

$$E_a = RT + \Delta E^* \quad \dots (16)$$

The relationship between ΔE^* and ΔH^* is $\Delta H^* = \Delta E^* + P\Delta V^*$

Hence,

$$E_a = \Delta H^* - P\Delta V^* + RT$$

For reaction in solvents ΔV^* is small and hence

$$E_a = \Delta H^* + RT \quad \dots (17)$$

For a unimolecular reaction

$$k = e \left(\frac{k_B T}{h} \right) e^{\Delta S^*/R} e^{-E_a/RT}$$

For a bimolecular reaction

$$k = e^2 \left(\frac{k_B T}{h} \right) e^{\Delta S^\ddagger/R} e^{-E_a/RT}$$

Potential energy surfaces

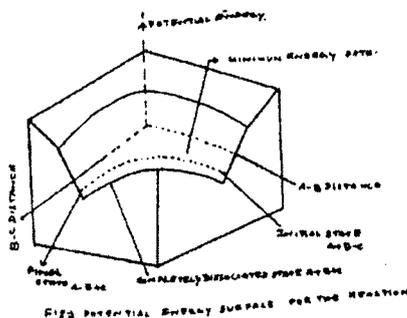
Consider one of the simplest reactions viz., $D + H_2 \rightarrow DH + H$. We need three spatial coordinates to describe the configuration of this reacting system at any point along the reaction path. These coordinates are the internuclear distance r_1 between H and H; the distance r_2 of D from the midpoint of the H-H bond and the angle θ between the H-H bond and vector from the midpoint of the bond to D. It is evident that one particular approach of D to H-H is energetically more favourable than any other. This in, infact, the path in which approaches H-H along the line of centres of the three body system, i.e. the angle θ is either 0° or 180° . The reason for this is that when D approaches H-H along the $\theta = 0$ direction, the D-atom feels appreciable repulsion from any one of the H-atom whereas in an approach from any other direction the D-atom is under the influence of repulsive field from both H atom.

The potential energy surface of a reaction presents the potential energy as a function of the relative position of all the atom taking part in the reaction.

Consider the reaction between atom A and molecule BC.



The potential energy surface of the above reaction is the plot of potential energy for all relative locations of the three atoms A, B and C. The detailed calculation show that the approach of an atom along the B-C axis requires less energy for reaction than any other approach and hence the treatment is confined to collinear approach. Two parameters are required to define the atom separation, one in the A-B separation and the other in the B-C separation. At the start of the reaction A-B distance is infinite and B-C distance is the BC equilibrium bond length. At the end of the reaction A-B distance is equal to the equilibrium bond length A-B and B-C distance is infinite. The total energy of the three atom system depends on their relative separations and can be fixed by doing a potential structure calculation using the Born-oppenteious approximation. The plot of the total energy of the system against each value of A-B and B-C distances gives the potential energy surface of this collinear reaction (Fig. 2).



Chain reactions

A chain reaction is one in which the products of the reaction carry on the reaction on the part of the reacting molecules and thus a long series of self-repeating steps is started.

Ex. Chemical chain reactions are oxidation processes, combustion, explosion, breaking, polymerization etc.

Characteristics of chain reaction

1. The rates of chain reactions are markedly affected by exposure of the reaction mixture to radiation of a certain wavelength.
2. Some chain reactions are followed by an induction period before any measurable change in pressure or concentration occurs. The rate of such reactions may increase rapidly or slowly depending on the type of reaction (Fig. 3).

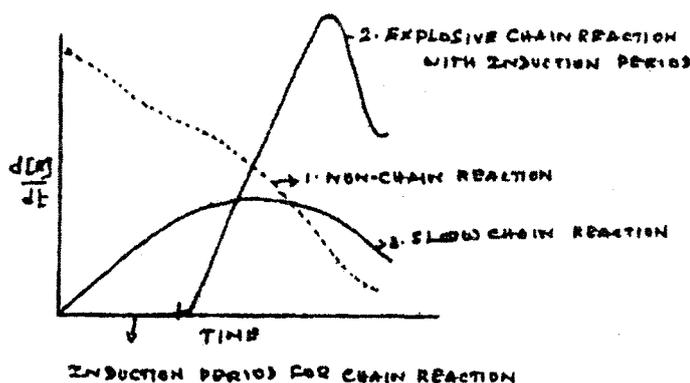


Fig. 3.

3. The speed of a chain reaction is greatly affected by the traces of other substance. It may accelerate or retard the reaction.
4. Inert gases accelerate the rate of chain reactions.
5. Reactions are sensitive to inhibitors
6. Some chain reactions exhibit complex kinetics. They very often show this fractional reaction orders.
7. Free radicals and atoms have been detected in many chain reactions

1. Hydrogen-Bromine reaction

The reaction between hydrogen and bromine can be written as



The rate law for the above reaction can be written as

$$\frac{d[\text{HBr}]}{dt} = \frac{k[\text{H}_2][\text{Br}_2]^{1/2}}{1 + k' \frac{[\text{HBr}]}{[\text{Br}_2]}}$$

The mechanism for the above reaction can be written as

1. $\text{Br}_2 \xrightarrow{k_1} \text{Br}\cdot + \text{Br}\cdot$; Initiation
2. $\text{Br}\cdot + \text{H}_2 \xrightarrow{k_2} \text{HBr} + \text{H}\cdot$; Propagation
3. $\text{H}\cdot + \text{Br}_2 \xrightarrow{k_3} \text{HBr} + \text{Br}\cdot$
4. $\text{H}\cdot + \text{HBr} \xrightarrow[k_5]{k_4} \text{H}_2 + \text{Br}\cdot$; Initiation
5. $2\text{Br}\cdot \longrightarrow \text{Br}_2$ Termination

In the above reaction Br-atom and H-atom are the active short-lived intermediates and must have a low concentration. The steady state concept can be applied to the rate law from this mechanism.

$$\frac{d[\text{H}]}{dt} = k_2[\text{Br}\cdot][\text{H}_2] - k_3[\text{H}][\text{Br}_2] - k_4[\text{H}][\text{HBr}] = 0 \quad \dots (6)$$

$$\frac{d[\text{Br}\cdot]}{dt} = k_1[\text{Br}_2] + k_3[\text{H}][\text{Br}_2] + k_4[\text{H}][\text{HBr}] - k_2[\text{Br}\cdot][\text{H}_2] - k_5[\text{Br}\cdot]^2 = 0 \quad \dots (7)$$

add eqn. (6) and (7) we get

$$[\text{Br}\cdot] = \left[\frac{k_1}{k_5} [\text{Br}_2] \right]^{1/2} \quad \dots (8)$$

and from eqn. (6) we get

$$[\text{H}] = \frac{k_2[\text{Br}\cdot][\text{H}_2]}{k_3[\text{Br}_2] + k_4[\text{HBr}]}$$

(or)

$$[H] = \frac{k_2 \left(\frac{k_1}{k_5} \right)^{1/2} [H_2] [Br_2]^{1/2}}{k_3 [Br_2] + k_4 [HBr]} \quad \dots (9)$$

Now HBr is formed in reaction (2) and (3) and disappears in reaction (4), so the net rate of formation of HBr is given by

$$\frac{d[HBr]}{dt} = k_2 [Br] [H_2] + k_3 [H] [Br_2] - k_4 [H] [HBr] = 0 \quad \dots (10)$$

From eqn. (6) we get

$$k_2 [Br] [H_2] - k_4 [H] [HBr] = k_3 [H] [Br_2]$$

substituting this in eqn. (10) we obtain

$$\frac{d[HBr]}{dt} = 2k_3 [H] [Br_2] \quad \dots (11)$$

substituting [H] from eqn. (11) we get

$$\frac{d[HBr]}{dt} = 2k_3 \left(\frac{k_2 (k_1/k_5)^{1/2} [H_2] [Br_2]^{1/2}}{k_3 [Br_2] + k_4 [HBr]} \right) [Br_2]$$

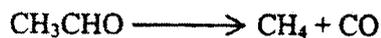
Dividing both numerator and the denominator of the above equation by $k_3 [Br_2]$ we get

$$\frac{d[HBr]}{dt} = \frac{2k_2 (k_1/k_5)^{1/2} [H_2] [Br_2]^{1/2}}{1 + \frac{k_4 [HBr]}{k_3 [Br_2]}}$$

$$(or) \quad \frac{d[HBr]}{dt} = \frac{k [H_2] [Br_2]^{1/2}}{1 + \frac{k^1 [HBr]}{[Br_2]}}$$

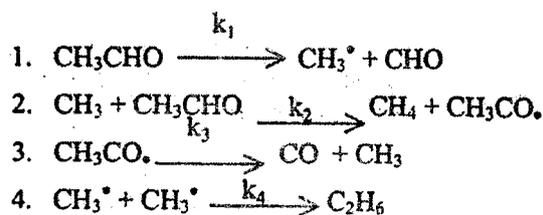
where $k = 2k_2 (k_1/k_5)^{1/2}$ and $k^1 = k_4/k_3$

2. Decomposition of acetaldehyde



$$\frac{d[CH_4]}{dt} = k [CH_3CHO]^{3/2}$$

The chain mechanism



The rate law

$$\frac{d[\text{CH}_4]}{dt} = k_2 [\text{CH}_3][\text{CH}_3\text{CHO}]$$

S.S.A.

$$\frac{d[\text{CH}_3]}{dt} = k_1 [\text{CH}_3\text{CHO}] - k_2 [\text{CH}_3][\text{CH}_3\text{CHO}] + k_3 [\text{CH}_3\text{CO}\cdot] - k_4 [\text{CH}_3]^2 = 0$$

$$k_1 [\text{CH}_3\text{CHO}] + k_3 [\text{CH}_3\text{CO}\cdot] = k_2 [\text{CH}_3][\text{CH}_3\text{CHO}] + k_4 [\text{CH}_3]^2$$

$$\frac{d[\text{CH}_3\text{CO}\cdot]}{dt} = k_2 [\text{CH}_3][\text{CH}_3\text{CHO}] - k_3 [\text{CH}_3\text{CO}\cdot] = 0$$

$$= k_2 [\text{CH}_3][\text{CH}_3\text{CHO}] = k_3 [\text{CH}_3\text{CO}\cdot]$$

$$[\text{CH}_3\text{CO}\cdot] = \frac{k_2}{k_3} [\text{CH}_3][\text{CH}_3\text{CHO}]$$

$$k_1 [\text{CH}_3\text{CHO}] + k_3 \left[\frac{k_2}{k_3} [\text{CH}_3][\text{CH}_3\text{CHO}] \right] = k_2 [\text{CH}_3][\text{CH}_3\text{CHO}] + k_4 [\text{CH}_3]^2$$

$$[\text{CH}_3]^2 = \frac{k_1}{k_4} [\text{CH}_3\text{CHO}]$$

$$[\text{CH}_3] = \left(\frac{k_1}{k_4} \right)^{1/2} [\text{CH}_3\text{CHO}]^{1/2}$$

$$\frac{d[\text{CH}_4]}{dt} = k_2 \left(\frac{k_1}{k_4} \right)^{1/2} [\text{CH}_3\text{CHO}]^{3/2}$$

Hydrogen-oxygen reaction

The reaction between hydrogen and oxygen proceeds at a measurable speed if the temperature is between 450° and 600°C. Below this range, the reaction becomes slow but above this range, explosion takes place.

Consider a mixture of O₂ and H₂ in the ratio of 1:2 which is maintained at a 550°C and at a pressure of about 2mm. When the pressure is slowly increased, the rate of the reaction also increases slowly. At a certain critical pressure of 50 mm the mixture explodes. The exact value of this critical pressure will depend upon the size and shape of the vessel. The limit at which it occurs is known as first explosion limit or lower explosion limit.

Let us maintain the mixture of O₂ and H₂ at 200 mm pressure. Again, the reaction proceeds at a steady rate. If the pressure is reduced, the rate of the reaction is also

reduced. But at about 100 mm the reaction mixture explodes. Thus, there is a pressure region between 50 and 100 mm within which explosion takes place. Above and below this pressure region, reaction proceeds at a normal rate. The pressure limit of 100 mm at which the explosion occurs is known as upper explosion limit or second limit.

There is a third limit of explosion which is at still higher pressures. Here explosion are due to the rise in the temperature of the reaction system. Such explosion are known as thermal explosion.

From the variation of explosion limits with the temperature it is found that explosion will taken place at all pressures above 600°C but no explosion will occur under any pressure condition below 460°C.

Explanation of explosion limits

At low pressures (2mm), the recombination of radicals will takes place at the surface when the pressure is increased, the rate of the recombination of radicals at surfaces will decreases and explosion will take place. (First).

When gases are maintained at higher pressures (200 mm), the recombination of radicals will occur in the gas phase. When the pressure is decreased, the rate of the removal of radicals in the gas phase is decreased, When the limit of pressure is reached, explosion will takes place. This limit of pressure (100 mm) is known as second explosion limit.

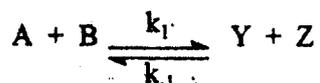
Principle of microscopic reversibility and detailed balance

The principle may be expressed as follows.

“In a system at equilibrium, any molecular process and the reverse of that process occur, on the average, at the same rate”.

For an elementary reaction the equilibrium constant must be the ratio of the rate constants in the formed and reverse directions.

Let us consider a process



The rate of forward reaction = $k_1 [A] [B]$

Rate of backward reaction = $k_{-1} [Y] [Z]$

If the system is at equilibrium, these rates are equal, hence

$$\frac{k_1}{k_{-1}} = \frac{[Y][Z]}{[A][B]} = K_c$$

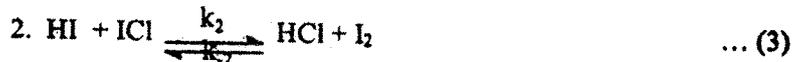
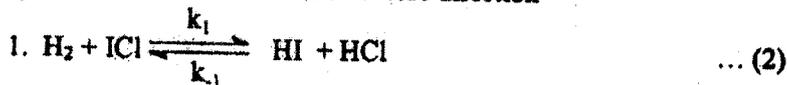
Where K_c is the equilibrium constant.

This argument can be extended to a reaction that occurred in two or more stages.

Consider, for example, the reaction



The above reaction occurs in two steps. At equilibrium the process are occurring at equal rates in the forward and reverse direction



Thus, at equilibrium

$$k_1 [\text{H}_2] [\text{ICl}] = k_{-1} [\text{HI}] [\text{HCl}] \quad \dots (4)$$

$$k_2 [\text{HI}] [\text{ICl}] = k_{-2} [\text{HCl}] [\text{I}_2] \quad \dots (5)$$

The equilibrium constant for each reaction is thus

$$K_1 = \frac{k_1}{k_{-1}} = \left(\frac{[\text{HI}][\text{HCl}]}{[\text{H}_2][\text{ICl}]} \right)_{\text{eq}} \quad \dots (6)$$

$$K_2 = \frac{k_2}{k_{-2}} = \left(\frac{[\text{HCl}][\text{I}_2]}{[\text{HI}][\text{ICl}]} \right)_{\text{eq}} \quad \dots (7)$$

The product of these two equilibrium constant is

$$K_1 K_2 = \frac{k_1 k_2}{k_{-1} k_{-2}} = \left(\frac{[\text{I}_2][\text{HCl}]^2}{[\text{H}_2][\text{ICl}]^2} \right)_{\text{eq}} = K_c \quad \dots (8)$$

Where K_c is the equilibrium constant for the overall reactions. For any mechanism, involving any number of elementary and consecutive steps, the overall equilibrium constant is the product of the equilibrium constants for the individual steps and is the product of the rate constants for the reaction in the forward direction divided by the product of those for the reverse reaction.

$$K_c = K_1 K_2 K_3 \dots = \frac{k_1 k_2 k_3 \dots}{k_{-1} k_{-2} k_{-3} \dots} \quad \dots (9)$$

If a reaction occurs by a composite mechanism, and we measure a rate coefficient k_1 for the overall reaction from left to right and also measure a rate coefficients k_{-1} for the overall reaction from right to left, at the same temperature the ratio k_1/k_{-1} is not necessarily the equilibrium constant for the overall reaction. The reason is that rate laws for composite reaction change with the experimental conditions such as reactant concentration, and the rate coefficients also change.

KINETICS OF FAST REACTIONS

The conventional methods for the study of reaction kinetics cannot be applied to fast reactions which go to equilibrium in a few seconds or less. A fast reaction is one whose half life ($t_{1/2}$) varies from 10^{-1} sec to about 10^{-15} sec. The methods have been developed to study the fast and very fast reaction in solution.

The methods used in the study of these fast and very fast reactions are:

1. Flow methods
2. Relaxation methods
3. Shock tubes methods

Flow methods

The flow technique is the first method for determining the rate constant of the fast reaction. In the flow method equal volumes of two reaction mixtures are made to flow through the separate tubes into a mixing chamber of appropriate design. Under condition of turbulence the mixing of the two solutions takes place in about 10^{-3} sec. The mixed solution then flows into an observation tube. With the flow of this solution at a constant rate, the composition of the mixed solution at each position along the observation tube corresponds to a particular extent of reaction that occurs. Hence within constant flow rate steady state concentration of reactants and products are established along the observation tube i.e., concentration at a particular point along the observation tube does not change. The concentration in the observation tubes are determined by a spectrophotometric method at various positions. Each position along the observation tube corresponds to the lapse of a definite time interval after mixing given by.

$$t = \frac{x \cdot a}{f}$$

where x is the distance along the tube from the mixing chamber, $a \text{ cm}^2$ is the cross-sectional area of the tube, and $f \text{ cm}^3 \text{ s}^{-1}$ is the total flow rate (Fig. 4).

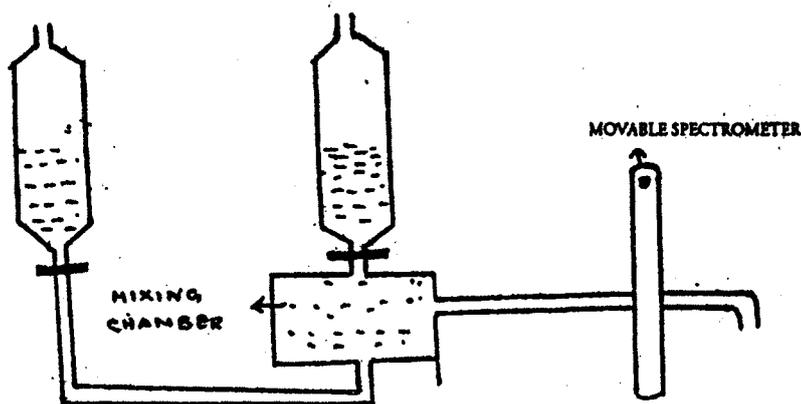


Fig. 4.

The reaction between Fe^{3+} and CNS^- in aqueous solution is the best example for fast reactions. Its rate law is

$$\text{Rate} = k_2 [\text{Fe}^{3+}] [\text{CNS}^-] \left[1 + \frac{a}{[\text{H}^+]} \right]$$

where k_2 is the second order rate constant and 'a' is an empirical constant which is related the dependence of reaction rate on pH. At 25°C the rate constant k_2 is 1271 litre mol⁻¹ sec⁻¹.

Relaxation methods

Flow techniques are not suitable for the study of reaction occurring in less than 10⁻³ sec. Relaxation techniques are employed to study some of the fastest reversible gaseous and solution reactions.

Kinetic study based on the measurement of rate of attainment of equilibrium is known as relaxation method. The reaction is allowed to reach equilibrium under controlled condition. The state of equilibrium is suddenly changed by rapid change of the physical parameters (temperature, pressure etc.). The time, called relaxation time (τ) which is necessary to cover a certain factor of the path towards its new equilibrium, is measured. The system tries to cover this path quite rapidly to reach the near equilibrium. This movement to equilibrium (known as relaxation) i.e. the rate of reaction from non-equilibrium state to the equilibrium state can be measured by a fast physical method. Photometric method is very often used.

Two important requirements of the method are

1. The physical parameter required to disturb the equilibrium must be changed very rapidly the time taken for the change must be of the order of half life time of the reaction.
2. The analytical method used (conductometry, spectrophotometry) must be capable of responding very quickly to the changes in the reaction mixture.

Let us consider a reaction



Now suppose the equilibrium is suddenly displaced to the right. Let a_0 and b_0 be the original concentration of A and B and let the concentration in the new equilibrium position be symbolized by a_e and b_e respectively. The concentration at time t are a and b . If the initial displacement from the new equilibrium position is x_0 and x is the displacement at time t , then

$$x = a - a_e = b_e - b \quad \dots (2)$$

The overall rate of the forward reaction leading to a state of new equilibrium position i.e. the rate of relaxation.

$$\frac{dx}{dt} = k_1 a - k_2 b \quad \dots (3)$$

substitute the value of a and b from eqn. (2) in the above equation

$$\begin{aligned} \frac{-dx}{dt} &= k_1 (x + a_e) - k_2 (b_e - x) \\ \frac{-dx}{dt} &= k_1 a_e - k_2 b_e + (k_1 + k_2) x \end{aligned} \quad \dots (4)$$

Taking into account the fact that at equilibrium the rates of two opposing reaction become equal, that is

$$k_1 a_e = k_2 b_e$$

Hence

$$\frac{-dx}{dt} = (k_1 + k_2) x \quad \dots (5)$$

on rearranging eqn. (5) we get

$$\frac{-dx}{x} = (k_1 + k_2) dt$$

on integration

$$\begin{aligned} \int \frac{-dx}{x} &= (k_1 + k_2) \int dt \\ -\ln x &= (k_1 + k_2) t + C \end{aligned}$$

when $t = 0$ $x = X_0$ and $C = -\ln X_0$

Hence

$$\ln \left(\frac{X_0}{x} \right) = (k_1 + k_2) t \quad \dots (6)$$

Eqn. (6) illustrates the important principle that the rate of relaxation depends on two rate constants the overall first order constant

$$k = k_1 + k_2$$

Eqn. (6) becomes

$$\ln \left(\frac{X_0}{x} \right) = kt$$

$$x = x_0 e^{-kt} \quad \dots (7)$$

Here x_0 signifies the departure from equilibrium concentration immediately after the initial conditions are changed.

The rates of relaxation processes are defined by relaxation time. Relaxation time is a quantity which is the inverse of the sum of the rate constants

$$(\text{app}) \tau = 1/k_1 + k_2 = 1/k$$

Eqn. (7) can be written as

$$x = x_0 e^{-t/\tau}$$

In numerical value τ is close to the half life period, $\tau_{1/2}$ since

$$\frac{\tau_{1/2}}{\tau} = \ln 2 = 0.6993$$

Thus by measuring x/x_0 at different intervals of time τ is obtained. From τ , the value of rate constant k_1 can be evaluated.

Determination of relaxation time

Relaxation time is determined by various methods such as temperature jump and pressure jump methods (used for times larger than 10^{-5} sec), the high electric/magnetic fields or ultrasonic vibration (used for times smaller than 10^{-5} sec).

In temperature jump method, a temperature change of several degree ($\approx 10^\circ\text{C}$) in 10^{-6} sec is created by a discharge of high voltage condenser (100 KV) through a small quantity of solution. Then the time dependence of concentration is followed by the absorption spectroscopy or by measuring electrical conductivity as a function of time. A temperature range of 1 degree centigrade (near room temperature) has been found to change the equilibrium concentration by about 3%.

An alternative approach to the problem of suddenly raising the temperature is to use a pulse of microwaves. The advantage of this method is that non-conducting solution may be used, though only a relatively small temperature rise can be obtained, generally less than 1°A .

The pressure jump method uses a sudden change in pressure to displace the equilibrium. The sensitivity of a reaction to pressure depends on the change in volume ΔV° and is represented quantitatively by the equation

$$\left(\frac{\partial \ln K}{\partial P} \right)_T = -\Delta V^\circ / RT$$

The sample is placed in a flexible cell which is contained in a pressure vessel filled with an inert liquid such as xylene. A pressure of about 65 atmospheres is set up in the vessel and this is reduced to atmospheric pressure within about 10^{-4} sec by punching a thin metal disc set into the wall of the vessel. The attainment of the new equilibrium is followed conductometrically.

SHOCK TUBES

The technique has been used for studying fast reactions in the millisecond – microsecond range at high temperature. The reactants are heated by shock wave traveling at supersonic speed, the high temperature. Stays approximately constant for hundreds of a microsecond or a few milliseconds in some cases and throughout this period the concentration of radicals is followed by one of the standard methods of detection.

The shock tube is a metal or glass pipe several centimeters in diameter and several meters long. A thin metal or plastic diaphragm divides the shock tube into two sections: one section contains the driver gas (usually hydrogen or helium) at pressure up to ten times atmospheric pressure, and the other section contains a reactant gas at a low pressure. At the end of the tube there is an observation point for measurement of radical concentration and also detectors for measuring the velocity of shock front. As soon as diaphragm is mechanically ruptured, the driver gas bursts out and rapidly forms a shock wave with a self-sustaining sharp shock front. The front is traveling with a supersonic speed compressing and heating the reactant gas as it proceeds.

As soon as the shock front reaches the observation point, the reactant gas is suddenly compressed and heated. The initial readings are recorded. After the reacting gases, the driver gas will reach the observation point. The time interval between the arrival of the shock front and arrival of the driver gas is the reaction time which is usually about a millisecond. The temperature in the reaction zone is calculated from the initial conditions in the reactant gas and the velocity of the shock wave. Optical spectroscopy and mass spectroscopy may be employed to follow changes in concentration of the reacting gases.

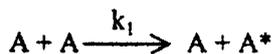
Ex:

Reaction between H_2 and O_2 . The course of the reaction is followed by measuring the absorption due to OH radical light is passed through two quartz windows set opposite each other into the side of the tube and is picked up by a photomultiplier. This light is particularly rich in OH spectral lines since it is produced by discharging a flash lamp containing range $1150^\circ - 1850^\circ C$ and pressure of a few atmospheres were achieved. By analyzing the change in absorption by the OH radicals as a function of the time behind the shock front, it was possible to deduce the relative importance of the various reaction paths for the recombination of the radicals produced with different $H_2:O_2$ ratios.

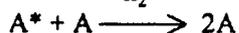
Lindemann theory

The reactant molecules acquire activation energy by collision with one another. The activated molecules do not decompose immediately, but more around in the activated form for a while. Thus, there is time by between activation and decomposition. The deactivation of the molecule takes place as result of collision with less energetic molecules.

Let us consider a reaction

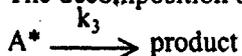


$$\text{Rate of activation} = k_1[A]^2 \quad \dots (1)$$



$$\text{Rate of deactivation} = k_2[A^*][A] \quad \dots (2)$$

The decomposition of activated molecules



$$\frac{d[P]}{dt} = k_3[A^*] \quad \dots (3)$$

$$\text{Rate of decomposition} = k_3[A^*] \quad \dots (4)$$

As the concentration of activated molecules is very small at any time during the process, the rate of their formation equals the rate of their disappearance establishing a steady state concentration of the activated molecules.

$$\frac{d[A^*]}{dt} = 0$$

$$\frac{d[A^*]}{dt} = k_1[A]^2 - k_2[A][A^*] - k_3[A^*] = 0$$

$$[A^*] = \frac{k_1[A]^2}{k_2[A] + k_3}$$

substituting the eqn. (3) we get

$$\frac{d[P]}{dt} = \frac{k_3 k_1 [A]^2}{k_2 [A] + k_3}$$

Case: 1 (high pressure)

When $k_2[A] \gg k_3$ i.e. when the rate of deactivation is very very large as compared to the rate of decomposition, the rate is given by

$$\frac{d[P]}{dt} = \frac{k_3 k_1 [A]}{k_2} = k^1 [A]$$

This expression obeys first order kinetics.

Case : II (low pressure)

If $k_3 \gg k_2[A]$ is the rate of decomposition is greater than the rate of deactivation.

$$\frac{d[P]}{dt} = k_1[A]^2$$

Hence the reaction is second order kinetics.

Hinshelwood's theory

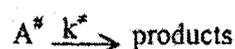
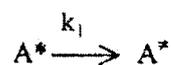
The first difficulty with the Lindemann's theory, that the first order behaviour is maintained down to lower concentration than the theory appeared to permit, reposes that k_1 must have a larger value than $Z e^{-E^*/RT}$. It was pointed out that this expression is actually only applicable to a molecule having one degree of vibrational freedom, a molecule having more degrees of vibrational freedom has a greater probability of acquiring the energy E^* since this energy may now be distributed amount all the degrees of freedom in the molecule. The

expression for $k_1 = \frac{Z}{(S-1)!} \left(\frac{E^*}{RT}\right)^{S-1} e^{-E^*/RT}$ S-degrees of vibrational freedom. If the experimental activation energy is taken as 40 k. cal for more and S as 12 the above expression gives rise to value of $k_1 = 9.9 \times 10^{-2}$.

RRKM Theory

Rice, Rampsberger, Kassel and Marcus defined theory by taking into consideration all vibrations and rotations of the energized molecule (A^*) in term of the actual vibrational frequencies and rotational constants under the basic frame work of the activated complex theory.

According to RRKM theory



where A^* refers to an energized species as before and must attain a critical configuration of the activated complex A^* enroute the reaction. It is possible to calculate k_1 by considering the relationship between the concentration of activated complexes and the energized molecules.

$$k_1 = f^* \frac{\int_0^c N_1(E_n^*)}{f_R N_1(E_c) h} dE_n^*$$

The critical energy E_c is equal to the from of E_1^* , for motion along the reaction coordinates, and E_n^* which gets related to vibrational modes and active rotation. $N_1(E_n^*)$ denotes the energy density of quantum states at energy E_n^* for vibrational modes f^*/f_R refers

to the ratio of partition function which allow for changes in momenta of inertia in the non-contributing rotations on forming the activated state from the energized molecule.

The Slater's treatment

Slater proposed a dynamic theory without energy flow. Vibrations are required to be simple harmonics C , which does not allow energy flow between modes, but when different modes come into phase, the vibrational amplitude is changed. For suitable phase relationships the vibrational amplitude may be extending beyond the critical length corresponding to the reaction.

Slater provided a classical treatment in 1939 and later a quantum mechanical derivation. The mathematical treatment is against complex but the variation of k_{uni} with $[A]$ can be calculated. The number of vibrational modes that may contribute to the critical reaction coordinate is selected to give the best fit with experimental data, and the result is generous approximately half the maximum possible modes of vibration.

Under high pressure condition, the rate constant k_{∞} may be

$$k_{\infty} = v^{exp} (-E^*/RT) \text{ (or) } v_e (-E^*/RT)$$

E^* refers to the minimum energy for the process as defined by the theory and v an average vibrational frequency.

Kinetic isotope effect

The variation of reaction rate on replacing an atom in a reactant by one of its isotopes provides information about the reaction mechanism. Such kinetic isotope effects are greatest when an ordinary hydrogen atom is replaced by deuterium or tritium, these substitution correspond to large relative change in the mass of the atom. The effect of changing an atom connected by the bond that is involved directly in the rate-controlling step of a reaction is known as primary kinetic isotope effect and otherwise it is called secondary kinetic isotope effect.

Primary kinetic isotope effect

When an atom, is replaced by an isotope, there is no change in the potential energy surface for the reaction. But there is a change in the zero point energy of the molecule leading to a change in the activation energy and hence the reaction rate.



The replacement of an atom by an isotope bands to no change in the potential energy surface but results in changes in vibrational frequencies and therefore zero point energies. On deuterium, the significant change is the reduction of the zero point energy of the bond. The zero point energies for the activated complexes are therefore the same for H and D.

Secondary kinetic isotope effect

When the isotopic substitution involves an atom that is not attached to the bond broken or formed during the reaction, the effects is small and is known as secondary kinetic

isotope effect. The secondary effect is due to changes in vibrational frequencies in the reactants and activated complexes. These changes affect the zero point levels and hence the activation energies.

Reaction in solution

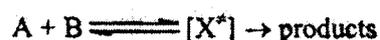
Reactions in solution are far more complex than reactions in gases. When a molecule dissolves in a solvent a chemical change take place wherein the solute molecules enter into a loose combination with a solution shell of the surrounding molecules. The kinetics of chemical reactions, therefore depend on the nature of this solvents shell. Mechanism of a given reaction is frequently altered when the solvent is changed.

Application of activated complex theory to reaction in solution.

Bronsted - Bjerrum equation

The theory of activated complex is very often employed to study the role of the medium in chemical kinetics.

Let us consider a molecular reaction



Where A and B are reactants and $[X^*]$ is an activated complex. According to the ARRT, the rate equation for this reaction is

$$\text{Rate} = \left(\frac{k_B T}{h} \right) [X^*] \quad \dots (1)$$

k_B - Boltzmann constant

If the activated complex exists in equilibrium with the reactions, then

$$[X^*] = K^* [A] [B] \frac{v_A v_B}{v_{AB}^*} \quad \dots (2)$$

$K^* \rightarrow$ equilibrium constant for the formation of the complex

v_A, v_B and v_{AB}^* - The activity coefficients of the reactants and activated complexes

substitute this value in eqn (1)

$$\text{Rate} = \left(\frac{k_B T}{h} \right) K^* [A] [B] \frac{v_A v_B}{v_{AB}^*} \quad \dots (3)$$

The rate law for the reaction

$$\text{Rate} = k[A] [B] \quad \dots (4)$$

compare (3) and (4) we get

$$k [A] [B] = \frac{k_B T}{h} K^\ddagger [A] [B] \frac{v_A v_B}{v_{AB}^\ddagger}$$

$$k = \frac{k_B T}{h} K^\ddagger \frac{v_A v_B}{v_{AB}^\ddagger} \quad \dots (5)$$

In the vapour phase, the activity coefficient of the reacting particles and of the activated complex may be taken as equal to unity.

The specific rate of reaction is this in the vapour phase

$$k_0 = \frac{k_B T}{h} K^\ddagger$$

and in the liquid phase

$$k = k_0 \frac{v_A v_B}{v_{AB}^\ddagger}$$

This equation is known as Bronsted and Bjerrum equation.

k_0 is the reaction rate constant under identical condition i.e. at low pressure for gaseous state and in extremely dilute dilution in liquid phase reaction.

Factors influencing reaction rate in solution

1. Effect of pressure on rate of reaction in solution

According to the activated complex theory, the rate constant k is related to the equilibrium constant by

$$k = \frac{k_B T}{h} K^\ddagger \quad \dots (1)$$

Taking logarithm of expression (1) we get

$$\ln k = \ln \left(\frac{k_B T}{h} \right) + \ln K^\ddagger \quad \dots (2)$$

Differentiating above equation with respect to P at a constant temperature T we get

$$\left(\frac{\partial \ln k}{\partial P} \right)_T = \left(\frac{\partial \ln K^\ddagger}{\partial P} \right)_T \quad \dots (3)$$

According to Van't Hoff isotherm

$$-\Delta G^\ddagger = RT \ln K^\ddagger \quad \dots (4)$$

$$\begin{aligned} \ln K^\ddagger &= \frac{-\Delta G^\ddagger}{RT} \\ &= \frac{-\Delta H^\ddagger}{RT} + \frac{\Delta S^\ddagger}{R} \quad \dots (5) \end{aligned}$$

where ΔG^\ddagger , ΔH^\ddagger , ΔS^\ddagger and the standard free energy, enthalpy and entropy changes respectively for the formation of transition state and K^\ddagger is the corresponds thermodynamic equilibrium constant

$$\Delta H^\ddagger = \Delta E^\ddagger + P\Delta V^\ddagger \quad \dots (6)$$

Therefore

$$\ln K^\ddagger = -\frac{\Delta E^\ddagger}{RT} - \frac{P\Delta V^\ddagger}{RT} + \frac{\Delta S^\ddagger}{R} \quad \dots (7)$$

The effects of pressure at constant temperature, the expression is partially differentiated with respect to P at constant, T, we get

$$\left(\frac{\partial \ln k^\ddagger}{\partial P} \right)_T = \frac{-\Delta V^\ddagger}{RT} \quad \dots (8)$$

ΔV^\ddagger in the change in volume or volume of activation.

The above equation reveals

- (1) The rate constant of a chemical reaction increases with increasing pressure when $\Delta V^\ddagger < 0$ the volume of the activated complex is less than the total volume of the reactants.
- (2) The rate constant decreases with increase in pressure when $\Delta V^\ddagger > 0$.
- (3) The reaction rate is almost independently of pressure when ΔV^\ddagger is negligibly small.

$$d \ln k = \frac{-\Delta V^\ddagger}{RT} \cdot dP$$

which an integration yields

$$\ln k = \frac{-\Delta V^\ddagger}{RT} P + \text{constant}$$

If applied pressure P is zero, $k = k_0$

Hence

$$\ln k = \ln k_0 - P \left(\frac{\Delta V^\ddagger}{RT} \right)$$

$$\ln k/k_0 = -P \left(\frac{\Delta V^\ddagger}{RT} \right)$$

when a plot of $\ln k/k_0$ versus applied pressure P , should be straight line passing through the origin. The value of ΔV^\ddagger can be determined from the slope $-\Delta V^\ddagger/RT$.

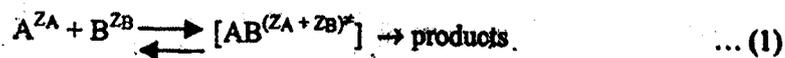
(4) Influence of ionic strength of solution on reaction rates

Salt effects

Primary salt effect

The effect of inert salts in the reaction rate is called primary kinetic salt effect.

Consider the reaction



The equilibrium between the reactants and the activated complex then

$$K^\ddagger = \frac{a_{AB^{(Z_A+Z_B)^\ddagger}}}{a_{A^{Z_A}} \cdot a_{B^{Z_B}}} \quad \dots (2)$$

It is necessary to express the equilibrium constant K in activities rather than concentration

$$K^\ddagger = \frac{\gamma_{AB^{(Z_A+Z_B)^\ddagger}} [AB^{(Z_A+Z_B)^\ddagger}]}{\gamma_{A^{Z_A}} \cdot \gamma_{B^{Z_B}} [A^{Z_A}] [B^{Z_B}]} \quad \dots (3)$$

$$[AB^{(Z_A+Z_B)^\ddagger}] = K^\ddagger [A^{Z_A}] [B^{Z_B}] \cdot \frac{\gamma_{A^{Z_A}} \cdot \gamma_{B^{Z_B}}}{\gamma_{[AB^{(Z_A+Z_B)^\ddagger}]}}$$

where a in the activities and γ are the activity coefficients.

According to the transition theory,

$$\begin{aligned} \text{Rate} &= [\text{AB}^{(Z_A + Z_B)^*}] \frac{k_B T}{h} \\ &= K^* [A^{Z_A}] [B^{Z_B}] - \frac{\gamma A^{Z_A} \cdot \gamma B^{Z_B}}{\gamma [\text{AB}^{(Z_A + Z_B)^*}]} \frac{k_B T}{h} \quad \dots (4) \end{aligned}$$

For a bimolecular reaction between A and B the experimental rate of reaction may be expressed as

$$\text{Rate} = k [A^{Z_A}] [B^{Z_B}] \quad \dots (5)$$

Equating eqn. (4) and (5) we get

$$\begin{aligned} k &= K^* \frac{k_B T}{h} \frac{\gamma A^{Z_A} \cdot \gamma B^{Z_B}}{\gamma [\text{AB}^{(Z_A + Z_B)^*}]} \\ k &= k_0 \frac{\gamma A^{Z_A} \cdot \gamma B^{Z_B}}{\gamma [\text{AB}^{(Z_A + Z_B)^*}]} \quad \dots (6) \end{aligned}$$

$$\text{where } k_0 = K^* \frac{k_B T}{h} \quad (\text{ZA})$$

$$(\text{ZB})$$

Taking logarithm on eqn. (6) we get

$$\log k = \log k_0 + \log \gamma_A^{Z_A} + \log \gamma_B^{Z_B} - \log \gamma_{\text{AB}^{(Z_A + Z_B)^*}}$$

According to the Debye-Huckel limiting law

$$\log \gamma_A = - A Z_i^2 \sqrt{\mu}$$

For an aqueous solutions at 25°C, the constant A = 0.509, then the have

$$\log \gamma_A = - 0.509 Z_i^2 \sqrt{\mu}$$

$$\log k = \log k_0 - (0.509 Z_A^2 + 0.509 Z_B^2 - 0.509 (Z_A + Z_B)^2) \sqrt{\mu}$$

$$\log k = \log k_0 + 1.018 Z_A Z_B \sqrt{\mu}$$

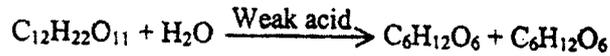
The above equation indicates that the rate constant of an ionic reaction in solution should depend on the ionic strength. This is the kinetic salt effect.

Secondary salt effect

The reaction rate depends on the effective concentration of the reacting species. The degree of dissociation of the reacting electrolyte varies with the ionic strength of the medium. The ionic strength influences concentration of the reacting ion. This is known as secondary salt effect.

If the reaction are catalysed by acids or bases i.e. H^+ or OH^- ions, the addition of inert salt effects the concentration of H^+ or OH^- ions. Since the rate of reaction is a function of the degree of ionization of acetic acid, it is proportional to the concentration of H^+ or OH^- ions. Thus the rate constant will be influenced by the salt concentration i.e. rate constant would depend on the ionic strength,

Let us consider the hydrolysis of cane sugar catalysed by a weak acid.



The rate of reaction $\propto [H^+]$

$$k_{\text{exp}} = k [H^+]$$

The catalyst comes from the dissociation of weak acid.



$$K^* = \frac{[H^+][A^-] \gamma[H^+]\gamma[A^-]}{[HA] \gamma_{HA}}$$

$$[H^+] = K \frac{[HA] \gamma[HA]}{[A^-] \gamma[H]\gamma[A^-]}$$

If the reaction is carried out at fixed ratio of $[HA]/[A^-]$ by making use of buffer solution

$$[H^+] = K^* \frac{\gamma[HA]}{\gamma[H]\gamma[A^-]} \quad \dots (2)$$

substituting $[H^+]$ in eqn. (2) we get

$$k_{\text{exp}} = k K^* \frac{\gamma[HA]}{\gamma[H]\gamma[A^-]}$$

$$k_{\text{exp}} = k_0 \frac{\gamma[HA]}{\gamma[H]\gamma[A^-]} \quad K_0 = kK^* \quad \dots (3)$$

$$\log k_{\text{exp}} = \log k_0 + \log \gamma [HA] - \log \gamma[H^+] - \log \gamma[A^-]$$

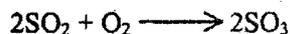
using the Debye-Huckel limiting law to get

$$\log k_{\text{exp}} = \log k_0 + 1.018 \sqrt{\mu} \quad \dots (4)$$

The above equation shows that k_{exp} increases with an increase in the ionic strength of the solution.

Homogenous catalysis

In Homogenous catalysis the reaction occurs in one phase and the rate is function of a catalyst concentration.



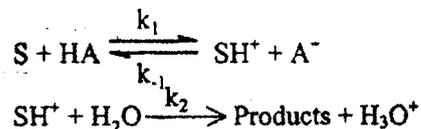
Acid-base catalysis

A large number of reactions are catalysed by either acid or base. If the reactions are catalysed by H^+ ion only, it is known as specific hydrogen ion catalysis. Similarly the reaction catalysed by OH^- ions only are known as specific hydroxyl ion catalysed reaction.

Acid-catalysed reaction generally proceed through protonation, transfer of a proton to a substrate.

Mechanism

The first step in the mechanism of acid-base catalysed reaction is a transfer of a proton from an acid to a substrate (S) or from a substrate (S) molecule to the base. Thus the reaction between an acid HA and substance S in



Applying steady-state approximation to the species SH^+ , we get

$$\frac{d[\text{SH}^+]}{dt} = 0 = k_1 [\text{S}][\text{HA}] - k_{-1} [\text{SH}^+][\text{A}^-] - k_2 [\text{SH}^+] \quad \dots (1)$$

Hence

$$[\text{SH}^+] = \frac{k_1 [\text{S}][\text{HA}]}{k_{-1} [\text{A}^-] + k_2} \quad \dots (2)$$

$$\frac{d[\text{P}]}{dt} = k_2 [\text{SH}^+] = \frac{k_1 k_2 [\text{S}][\text{HA}]}{k_{-1} [\text{A}^-] + k_2} \quad \dots (3)$$

Case : 1

If the rate constants of decomposition of the intermediate into the reactants is much more than that of its formation i.e.

$$k_2 \gg k_{-1} [A^-]$$

then

$$\frac{d[P]}{dt} = k_1 [S][HA]$$

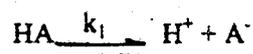
The rate of reaction is now directly proportional to the concentration of the catalyst and the reactants. This is the case of general acid catalysis.

Case: II

If $k_2 \ll k_{-1} [A^-]$, then all the intermediates transform into the products and the rate of reaction can be written as

$$\frac{d[P]}{dt} = k_2 \frac{k_1}{k_{-1}} [S] \frac{[HA]}{[A^-]} \quad \dots (3)$$

The dissociation of an acid HA is



and the dissociation constant of the reaction is

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

$$\frac{[HA]}{[A^-]} = \frac{[H^+]}{K_a}$$

substituting this value in eqn. (3) we get

$$\begin{aligned} \frac{d(P)}{dt} &= k_2 \frac{k_1}{k_{-1}} \frac{[S][H^+ A]}{K_a} \\ &= k_{H^+} [S] [H^+] \quad \dots (4) \end{aligned}$$

From the above equation that the reaction rate is directly proportional to the concentration of the $[H^+]$. In this case the reaction is said to be specific hydrogen ion catalysis. The constant k_{H^+} is known as the catalytic coefficient of hydrogen ion.

Bronsted catalysis law

In acid base catalysis the first step is the transfer of a proton from acid to the substrate molecule or from substrate molecule to the base. The effectiveness of a catalyst is to be related to the strength of acid or base. Bronsted proposed a relationship between the acid catalytic constant k_a and the dissociation constant of acid K_a i.e.

$$k_a = G_a K_a^\alpha$$

where G_a and α are constant of characteristic of the solvent. The values of α are usually less than unity.

Similarly for a base catalysis, Bronsted and Pederson proposed the equation

$$k_b = G_b K_a^\beta$$

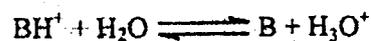
where k_b is the rate constant of base catalysis and K_b is the dissociation constant of the base.

The relationship between the catalytic constant of a base and the acid constant of conjugate acid may be obtained as follows:



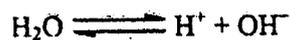
$$K_b = \frac{[BH^+][OH^-]}{[B]}$$

considering the reaction



$$K_a = \frac{[B][H_3O^+]}{[BH^+]}$$

We also know that



$$K_w = [H^+][OH^-]$$

$$K_b \times K_a = K_w$$

$$K_b = \frac{K_w}{K_a}$$

Insert the value of K_b in the equation.

$$K_b = G_b K_a^\beta$$

$$G_b = \frac{K_w}{K_a^\beta}$$

β is again always less than unity.

If an acid contains P protons bound equally strongly in the acid, and of is the number of positions in the conjugate base to which a proton may be attached, then for acid catalysis the Bronsted equation may be

$$\frac{K_a}{P} = G_a \frac{(q K_a)^a}{P}$$

and for base catalysis

$$\frac{K_b}{P} = G_b \left(\frac{P}{q K_a} \right)^b$$

Chemical kinetics in crossed molecular beam

The experiment techniques a studying molecular reaction dynamics includes the molecular beam method in which the reaction dynamics investigated by utilizing a mono-energetic beam of atoms or molecules.

In a molecular beam investigation of a bimolecular reaction, narrow beams of atoms or molecules are made to cross one another. The directions and speeds of the product molecules and of the unreacted species are determined by movable detectors. Experimental results are analyzed to yield detailed information about the distribution of energy and regular momentum among the reaction products, the dependence of overall kinetics on the states of the reactant molecules, the quantum states of the product molecules and other features of the elementary reaction event.

The schematic apparatus used in a molecular beam experiment is

The two essential features of this apparatus are

1. Device for producing extremely narrow beams of reactants with provision for controlling the speeds of the molecules and their rotational vibrational and electronic states.
2. Movable devices for the detection of the reaction products at various positions.

In the molecular beam experiments the beam were produced by taking the reactants in a small vessel with a very small opening allowing the atoms or molecules to effective into an evaluated vessel. A rectangular slit served on the orifice and a second small shift, placed close to it, made the molecules travel in the required direction. However, these early molecular beam experiments suffered from the fact that the beams produced had a very low intensity and also these was a thermal spread of molecular velocities.

UNIT - II

PHYSICAL PROPERTIES OF ELECTRONICALLY EXCITED MOLECULES

A molecule in the electronically excited state can be completely different chemical species with its own wave function and nuclear geometry. Since the charge densities are different, it shows a different geometry from the normal ground state molecule more so because it has excess energy but weaker bonds. The other physical properties like dipole moment, pK_a values, redox potentials also differ in comparison to the ground state values.

Excited state dipole moment

The effect of solvent on the absorption and emission spectra may give useful information regarding dipole moment changes and polarizability of the molecule in the two combining states. According to Frank-Condon principle, the energy shift between the (zero-zero) 0-0 band in absorption and emission is related to the dielectric constant D and the refractive index n of the solvent and the difference in dipole moments of the solute molecule in the two combining energy states given by the equation,

$$\Delta E = hv_a - hv_f = 2 \left[\frac{D-1}{2D+1} \cdot \frac{n^2-1}{2n^2+1} \right] \frac{(\mu_g - \mu_e)^2}{a^3}$$

μ_g - dipole moment of the ground state

μ_e - dipole moment of the excited state

a - the radius of the cavity in which the solute molecule resides.

The shift in 0-0 transition due to solvent interaction in the two states of different polarity can be explained with the help of Frank-Condon principle for absorption and emission processes.

In the ground state, a solute molecule having a dipole moment μ_g residing in a spherical cavity of radius a in a medium of static dielectric constant D polarizes the medium. The reaction field R_0 produced on such interaction is

$$R_0 = \frac{2\mu_g}{a^3} \left[\frac{D-1}{2D+1} \right]$$

If R_0 is the unperturbed vapour phase energy level of molecule in the ground state, in solution it is depressed by an amount proportional to R_0 . On excitation, the molecule is promoted to the Frank-Condon excited state (FC)*. In the excited state, the dipole moment may not only have a different magnitude, μ_e but different direction also. Since the electronic

transition is much faster than the dielectric relaxation time, the ground state solvent orientation will not have the time to change in the new situation. The reaction field in (FC)^{*} state is

$$R_{FC}^* = \frac{2\mu_g}{a^3} \frac{(n^2 - 1)}{(2n^2 + 1)}$$

where n is the refractive index

n^2 is equal to high frequency dielectric constant at the frequency of absorption.

The energy of absorption is

$$h\nu_0 = (h\nu_a)_0 + (R_{FC}^* - R_0) (\mu_e - \mu_g)$$

If the average life time T_f of excited state is greater than the dielectric relaxation time T_D then excited state dipole moment μ_e polarizes the solvent and the solvent molecules adjust to the new situation. A reaction field is produced

$$R^* = \frac{2\mu_e}{a^3} \left[\frac{D-1}{2D+1} \right]$$

The FC excited state (FC)^{*} is stabilized by this amount to give equilibrium excited state. The 0-0 fluorescence transition occurs from this energy state. Again a strained ground state (FC) is produced in accordance with the Frank-Condon principle in which solvent orientation does not have time to change. The Onsager's field is

$$R_{FC} = \frac{2\mu_e}{a^3} \left[\frac{n^2 - 1}{2n^2 + 1} \right]$$

The energy of the 0-0 transition in emission is given as

$$h\nu_f = (h\nu_f)_0 + (R_{FC} - R^*) (\mu_e - \mu_g)$$

The difference between 0-0 absorption and 0-0 fluorescence energies is obtained from the two relationships. Assuming $(h\nu_a)_0 \approx (h\nu_f)_0$.

$$h\nu \Delta \bar{\nu} = h\nu (\bar{\nu}_a - \bar{\nu}_f) = (R_{FC}^* - R_0 - R_{FC} + R^*) (\mu_e - \mu_g)$$

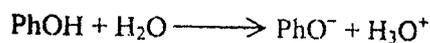
$\Delta \bar{\nu}$, the difference in the O-O energy in absorption and emission is obtained as

$$\Delta \bar{\nu} = \frac{2(\mu_e - \mu_g)^2}{hca^3} \left[\frac{D-1}{2D+1} - \frac{n^2 - 1}{2n^2 + 1} \right]$$

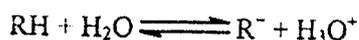
For a nonpolar solvent $D \approx n^2$ and the interaction energy is zero.

Excited state acidity constants – pK_a^* values

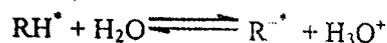
The acidity constants in the excited states provide rather direct measures of electron density distributions in the respective energy states. The charge distribution for phenol in the ground and excited state can be obtained from MO calculation. The high electron densities are observed on O-atom and *ortho* – and *para*-positions of the benzene ring. This distribution explains the weak acid character phenol and *ortho*-, *para*- directing property of the hydroxyl group. In the first excited singlet state, the charge density on oxygen is reduced and a reasonable charge density is found in *ortho* and *meta* positions. Therefore, excited phenol is more acidic and is also *ortho-meta* directing towards substitution in benzene ring. The protolytic equilibrium constant pK_a for the reaction is 10.0 and 5.7 in the ground and excited states respectively, a difference of 4.3 pK units.



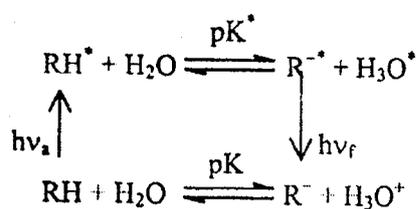
The equilibrium between an acid RH and its conjugate base R^- in the ground state is



and the equilibrium constant is expressed as pK_a values. In the excited state, the representation is



and the constant is pK^* . If $pK^* < pK$, it suggests that the equilibrium shifted towards the right on excitation.



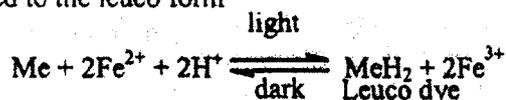
A molecule which is undissociated in the ground state at a given pH is dissociated on promotion to the higher energy state. If the ion R^{*-} is capable of emitting fluorescence. Therefore, within certain pH range fluorescence due to RH^* and R^{*-} both are observed. The pH value at which the two intensities are nearly equal give the approximate value for pK^* . Since absorption wavelengths for the acid and its ion are also different, the ground state pK can be calculated from absorption studies. Absorption and emission characteristics of RH and R^- must be different to utilize this method for the evaluation of pK and pK^* .

$$pK - pK^* = \frac{hc \Delta \bar{\nu}}{2.303 RT}$$

$\Delta \bar{\nu}$ is the difference in electronic transition frequencies (in cm^{-1}) of the acid and its conjugate base.

Excited state redox potential

Redox potentials between ground and triplet states are observed in the oxidizing powers of methylene blue and thionine. In the ground state the dyes cannot oxidize Fe^{2+} to Fe^{3+} , but in the excited state in the presence of Fe^{3+} , the colour of the dye is bleached. The colour returns on removal of the excitation source. In the long-lived triplet state, oxidation potential of the dye increases and the ferrous iron is oxidized to ferric state, the dye itself being reduced to the leuco form



The electron transfer in the excited state is reversed when the molecule returns to the ground state, the leuco dye being oxidized back by ferric ion.

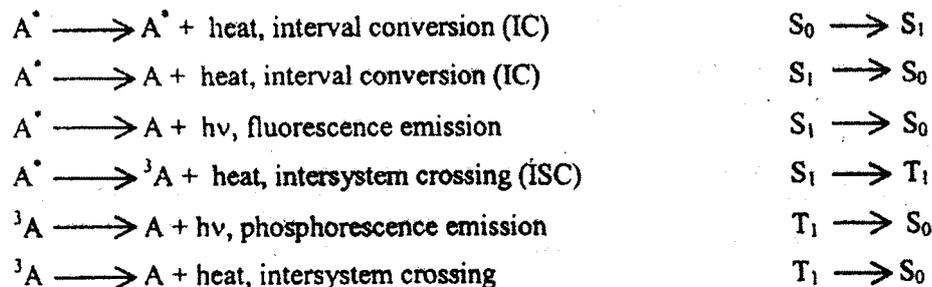
Photophysical processes in electronically excited molecules

A molecule excited to a higher energy state must return to the ground state, unless it gets involved in a photochemical reaction and loses its identity. In solution, liquids and solids at a reasonable pressures, there are more than one pathways available to the excited molecule for dissipation of excitational energy. These different pathways are grouped under photophysical processes in electronically excited molecules. All these photophysical processes must occur in a time period less than the natural radiative life time of the molecule and priorities are established by their relative rate constants. Let us consider

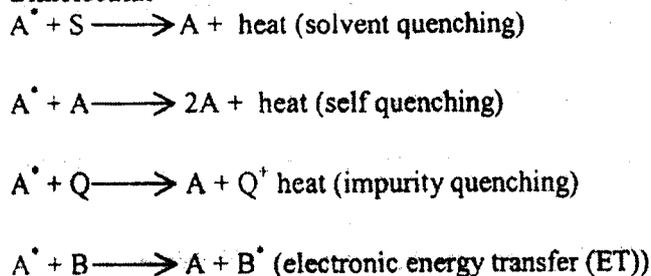


where A^* is an electronically excited molecule. The various photophysical processes that can occur in a molecule are:

Unimolecular reaction



Bimolecular



where A^* , 3A and A are molecules in first excited singlet state, molecules in triplet state and in the ground state respectively.

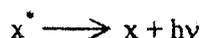
Fluorescence

When the incident light falls on certain substances, they emit visible radiation of the different frequency the phenomenon is known as fluorescence. Such substances are called fluorescence substance.

Fluorescence can be explained on the basis of quantum theory. When fluorescent substance absorbs light energy, its atoms or molecules set excited to higher energy levels by absorbing quantum of light ($h\nu$).



Since the life time of this excited singlet state is very very short (10^{-9} to 10^{-6} sec) a direct transition from this state back to the singlet ground state may take place with the emission of radiations. This kind of emission is gives the fluorescence.



Some characteristics of the phenomenon of fluorescence

1. This phenomenon is instantaneous and starts immediately after the absorption of light and stops as soon as the incident light is cut off.
2. Different substance fluorescence with light of different wavelengths. Thus fluorspar fluoresces with blue light, chlorophyll with red light, uranium glass with green light and so on.
3. According to Stoke's law, during fluorescence light is absorbed at a certain wavelength and should be emitted at a greater wavelength.
4. Fluorescence may be regarded as a secondary effect resulting from the primary process of absorption of a quantum of light by an atom or molecule.

Phosphorescence

When light radiation is incident on certain substances, they emit light continuously even after the incident light is cut off. This type of delayed fluorescence is called phosphorescence and substances are called phosphorescent substances.

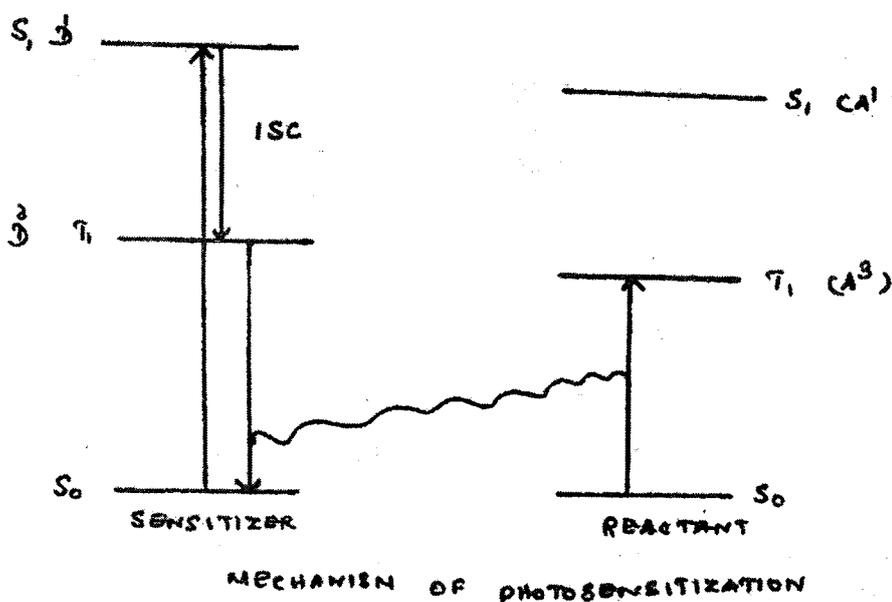
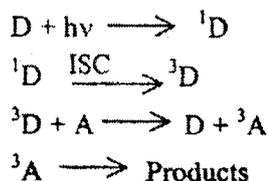
Some characteristics of phenomenon of phosphorescence

1. The phenomenon of phosphorescence is caused chiefly by the UV and violet parts of the spectrum.
2. The phenomenon of phosphorescence is shown mainly by solids.
3. The magnetic and dielectric properties of phosphorescent substances are different before and after illumination.
4. Different colours may be obtained by mixing different phosphorescent substances.

Energy transfer in photochemical reaction Photosensitization

Certain reaction are known which are not sensitive to light. These reactions can be made light sensitive by adding a small amount of foreign material which can absorb light and stimulate the reaction without itself taking part in the reaction such an added material is known as photosensitiser and the phenomenon is known as photosensitization.

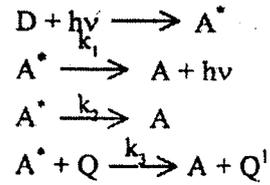
A general donor-acceptor system in which only the donor D, i.e. the sensitizer, absorbs the incident photon and the triplet state of the donor is higher energy than the triplet state of the acceptor A, i.e. the reactant. Absorption of the photon produces the singlet excited state of the donor, 1D which via intersystem crossing (ISC) gives the triplet excited state of the donor B. This triplet excited state then collides with the acceptor producing the triplet excited state of the acceptor, 3A and the ground state of the donor. If 3A gives the desired products the mechanism is called photosensitization.



Stern-Volmer equation

Fluorescence may be quenched when the excited state species undergoes collision with a normal molecule before it has chance to fluoresce. The quenching of fluorescence occurs because of the energy transfer from the excited state species to the molecule with which it collides. Quenching may also occur when the molecule changes from the singlet excited state to the triplet excited state. This phenomenon is called internal quenching. Quenching may also result from the presence of an externally added species

which takes up energy from the excited state molecule. This phenomenon is called external quenching. If Q is the quencher,



Apply steady state approximation to A^* we get

$$I_a = k_1[A^*] + k_2[A^*] + k_3[A^*][Q]$$

Where I_a is the intensity of light absorbed.

If I_f is the intensity of fluorescence, the quantum yield for fluorescence is given by

$$\begin{aligned} \phi_f = \phi_Q &= \frac{I_f}{I_a} \frac{k_1[A^*]}{k_1[A^*] + k_2[A^*] + k_3[A^*][Q]} \\ &= \frac{k_1}{k_1 + k_2 + k_3[Q]} \end{aligned}$$

In the absence of quenching i.e. when $[Q] = 0$ we get

$$\phi_0 = \frac{k_1}{k_1 + k_2}$$

Hence the ratio of two quantum yields

$$\begin{aligned} \frac{\phi_0}{\phi_Q} &= \frac{k_1 + k_2 + k_3[Q]}{k_1 + k_2} = 1 + \frac{k_3}{k_1 + k_2}[Q] \\ &= 1 + k_3 \tau [Q] = 1 + K_{SV} [Q] \end{aligned}$$

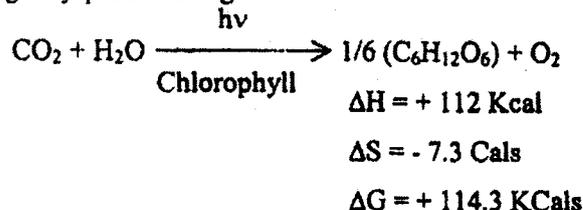
where $K_{SV} = k_3 \tau$ and $\tau = \frac{1}{k_1 + k_2}$

$$\frac{\phi_0}{\phi_Q} = 1 + K_{SV} [Q]$$

This equation known as Stern-Volmer equation in which K_{sv} is called the Stern-Volmer constant and τ in the life time of A^* in the absence of external quenching.

Photosynthesis

Photosynthesis is the most remarkable activity and the source of energy for all living organism. Photosynthesis is a process in which simple carbohydrates are synthesized from water and CO₂ in the chlorophyll containing tissues of plants in the presence of sunlight. Oxygen being a by-products is given set.



In this reaction the free energy is positive and hence it is not spontaneous and therefore, needs energy from an external source in order to proceed in forward direction. This energy is supplied by the light photons absorbed by photosensitized dye i.e. chlorophyll.

The glucose formed in photosynthesis may be partly converted into starch, cellulose, fats and proteins by the action of host of enzymes. Thus, photosynthesis is the key processes for synthesis of most of the compounds needed for life.

Chemiluminescence

Chemiluminescence is defined as the production of light by chemical reaction. To be chemiluminescence a reaction must provide sufficient excitation energy and at least one species capable of being transferred to an electronically excited state, hence $\Delta H = - 170 - 300 \text{ kJ/mole}$

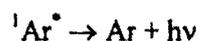
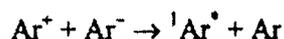
$$\phi_{\text{chemi}} = \frac{\text{Number of photon emitted}}{\text{Number of molecules of A or B consumed}} = \phi_r \phi_f$$

ϕ_{chemi} depends on the Chemical efficiency ϕ_r of the formation of excited product molecules and on the quantum yield of emission ϕ_f from this excited molecule.

Chemiluminescence is also generated by a radical ion recombination mechanism as observed when polycyclic aromatic hydrocarbons in solution are electrolyzed.

The anion contains an extra electron in the antibonding orbital whereas the cation is electron deficient in its highest bonding π -orbital.

When the electron is transferred from the anion to the antibonding orbital of the cation with proper spin configuration, a singlet excited state of the compound is formed which can be deactivated by emission.



The primary requirement of a chemiluminescent reaction is that it should have energy sufficient. If the energy of the reaction is not enough to promote the product to its first excited

singlet state, the system is said to be energy-deficient and molecules in the triplet states may be formed.

Ex:

Chemiluminescence has been observed in oxidation reactions of hydrazides of which luminol (3-amino cyclophthalhydrate) is an important example.

An inorganic chemiluminescent reaction system involves the reaction between alkaline solution of H_2O_2 and either Cl_2 gas or OCl^- .

Photochemical combination of hydrogen and chlorine

1. It has very high quantum yield whose rates various from 10^4 to 10^6 in absence of oxygen.
2. The radiation for the initiation of reaction is found to be in the range 4000 to 4360Å.
3. This reaction is followed by an increase in volume of constant pressure. This is called Draper's effect.

Mechanism



$$\frac{d[\text{Cl}]}{dt} = k_1 I_{\text{abs}} + k_3 [\text{H}][\text{Cl}_2] - k_2 [\text{Cl}][\text{H}_2] - k_4 [\text{Cl}] = 0 \quad \dots (1)$$

$$\frac{d[\text{H}]}{dt} = k_2 [\text{Cl}][\text{H}_2] - k_3 [\text{H}][\text{Cl}_2] = 0 \quad \dots (2)$$

Adding (1) and (2) we get

$$k_1 I_{\text{abs}} - k_4 [\text{Cl}] = 0$$

$$[\text{Cl}] = \frac{k_1}{k_4} \times I_{\text{abs}} \quad \dots (3)$$

From eqn. (2)

$$k_2 [\text{Cl}] [\text{H}_2] = k_3 [\text{H}][\text{Cl}_2] \quad \dots (4)$$

$$\frac{d[\text{HCl}]}{dt} = k_2 [\text{Cl}][\text{H}_2] + k_3 [\text{H}][\text{Cl}_2] \quad \dots (5)$$

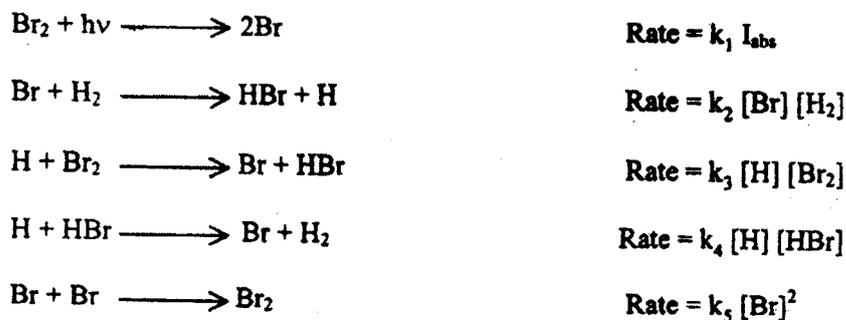
substitute the value of eqn. (4) in eqn. (5) we get

$$\frac{d[\text{HCl}]}{dt} = 2k_2[\text{H}_2][\text{Cl}] \quad \dots (5)$$

substitute values of [Cl] in the above a

$$\frac{d[\text{HCl}]}{dt} = 2 \frac{k_1 k_2}{k_4} I_{\text{abs}}[\text{H}_2]$$

Photocombination between hydrogen and bromine Mechanism



Rate of formation of HBr

$$\frac{d[\text{HBr}]}{dt} = k_2[\text{H}_2][\text{Br}] + k_3[\text{H}][\text{Br}_2] - k_4[\text{H}][\text{HBr}] = 0 \quad \dots (1)$$

$$\frac{d[\text{H}]}{dt} = k_2[\text{Br}][\text{H}_2] - k_3[\text{H}][\text{Br}_2] - k_4[\text{H}][\text{HBr}] = 0 \quad \dots (2)$$

$$\frac{d[\text{Br}]}{dt} = k_1 I_{\text{abs}} - k_2[\text{Br}][\text{H}_2] + k_3[\text{H}][\text{Br}_2] + k_4[\text{H}][\text{HBr}] - k_5[\text{Br}]^2 = 0 \quad \dots (3)$$

Adding (2) and (3) we get

$$k_1 I_{\text{abs}} - k_5 [\text{Br}]^2 = 0$$

$$[\text{Br}] = \left[\frac{k_1 I_{\text{abs}}}{k_5} \right]^{1/2} \quad \dots (4)$$

From eqn (2)

$$[\text{H}] = \frac{k_2 [\text{Br}][\text{H}_2]}{k_3 [\text{Br}_2] + k_4 [\text{HBr}]} \quad \dots (5)$$

substitute this values in eqn (1)

$$\frac{d[\text{HBr}]}{dt} = \frac{2k_2 \sqrt{k_1 \cdot I_{\text{abs}}/k_3} \cdot [\text{H}_2]}{1 + k_4 [\text{HBr}]/k_3 [\text{Br}_2]}$$

Actinometry

For the measurement of quantum yields, a knowledge of incident light flux, I_0 i.e. number of quanta falling per unit time is required. A number of methods are available for the standardization of light sources. The procedure is known as actinometry.

Chemical actinometry

A convenient method for the standardization of light sources in the lab in the use of suitable photochemical reaction whose quantum yields have been determined by a standard source.

The basic expression

$$\phi = \frac{\text{rate of reaction}}{\text{rate of absorption}}$$

$$\phi = \frac{\text{number of molecules decomposed or formed}}{\text{number of quanta absorbed}}$$

$$\phi = \frac{\frac{-dC}{dt} \text{ or } \frac{dx}{dt}}{I_0 \times \text{fraction of light absorbed}}$$

I_0 the incident intensity can be calculated in the units of Einstein $\text{cm}^{-3} \text{s}^{-1}$ falling on the reaction cell.

There are a number of photochemical reactions which have been found suitable as actinometers. They are useful within their specific wavelength respectively.

1. Ferrioxalate actinometer

Photodecomposition of K-ferrioxalate was developed into an actinometer. It is one of the most accurate and widely used actinometers which covers a wavelength range between 250 nm to 577 nm. Irradiation of ferrioxalate solution results in the reduction of Fe^{3+} to Fe^{2+} which is estimated colorimetrically by using *o*-phenanthroline as complexing agent. The OD at 510 nm of the deep red colour produced is compared with a standard.

The quantum yield for Fe^{2+} formation is nearly constant within the wavelength range and shown negligible variation with temperature solution composition and light intensity. The recommended actinometric solution, for wavelength upto 400 nm contains 0.006 M $\text{K}_3\text{Fe}(\text{ox})_3$ in 0.1 N H_2SO_4 . For longer wavelengths, a 0.15M solution is more convenient. Quantum yields vary between 1.2 to 1.1 at longer wavelength.

2. Reinecke's salt actinometer

The useful range for this actinometer extends from 316-735 nm and therefore is convenient in the visible region. Reinecke's salt is commercially available as ammonium salt

$(\text{NH}_4)_3 \text{Cr} (\text{NH}_3)_2 (\text{NCS})$. It should be converted into the potassium salt. The ligand field band extends from 400 nm to 735 nm. On irradiation a quation of the complex proceeds with release of thiocyanate. Quantum yields are calculated as moles of thiocyanate released per Einstein of light absorbed. The concentration of the actinometer solution should be such as to absorb nearly 99% of the incident light. The pH is adjusted between 5.3 – 5.5. The quantum yield for the reaction over the visible range lies between 0.27 to 0.3.

Solar energy conversion and storage

The photosynthetic membrane in green plant resembles a semiconductor electrode because it can separate the positive and negative charge carriers. The photon are absorbed from the sun light by chloroplast in the presence of magnetic field. Then it produce two different charge carriers that is one is positive and the other is negative, having different life times and different motilities. The capacity of such membranes to convert solar energy into chemical energy is an endoenergetic reaction ($\Delta G \gg 0$) in photosynthetic cycle has stimulated interest in development of such model systems for storage and utilization of solar energy by direct conversion of light quanta. In the photosynthesis solar energy is stored in two products, carbohydrates and oxygen. The energy is released when carbohydrates burn in air.

Solar energy quantum conversion are based on two objectives.

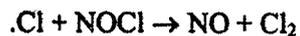
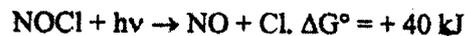
1. Conversion of light energy into thermal energy by suitable energy storing i.e., endergonic photochemical reactions.
2. Conversion of light energy into electrical energy by suitable photoelectro chemical devices.

The energy storing photoreactions occur with positive free energy change (+ ΔG) and the thermodynamically unstable. A simple photo rearrangement reactions which are governed by Woodward – Hoffman rules have been found useful. These rules provide the stereochemical course of photochemical rearrangement based on symmetry properties of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the molecule. A reaction which is photochemically allowed may be thermally forbidden. A reaction which can store about 260 cal/gram of material and has shown in valence isomerisation of norbornadiene (NBD) to Quadricyclene.

The disadvantages is that it does not absorb in the visible region and therefore the sunlight efficiency is poor. By attachment of chromophoric group or by use of suitable sensitizers it might be possible to shift the absorption region towards the visible for better utilization of solar energy.

Photodecomposition reaction in which photoproducts can store energy separately as fuels have been found to be more efficient systems. The stable products can be stored and then allowed to recombine releasing thermal electrical energy.

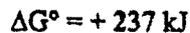
Photodecomposition of NOCl occurs with high quantum yield in the following two steps storing positive free energy $\Delta G^\circ = + 40 \text{ kJ}$



The products can be made to recombine in a fuel cell

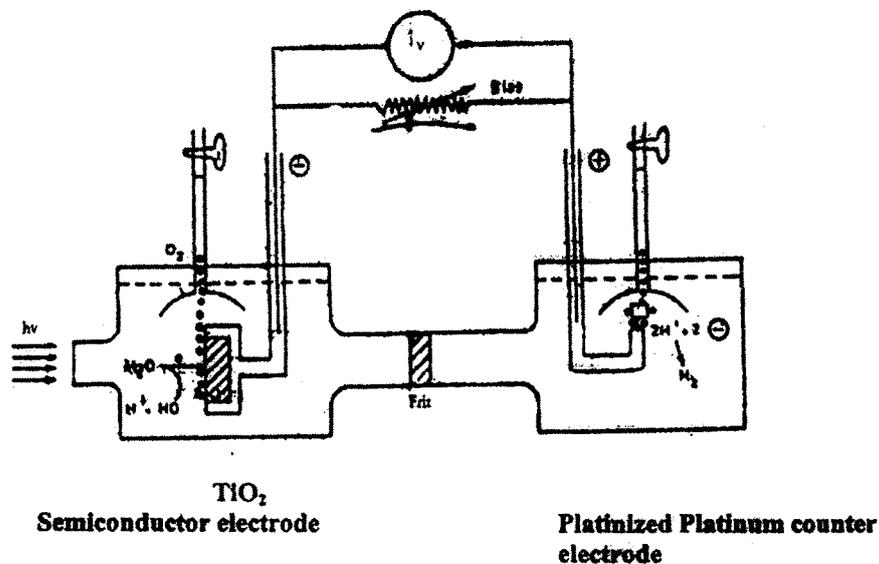


The photosensitized decomposition of water to H_2 and O_2 is a highly endothermic process.

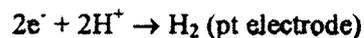
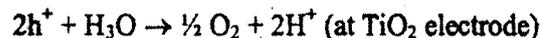
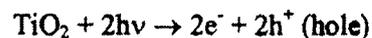


Hydrogen is a nonpolluting fuel which burns in air to produce water against releasing large amount of heat. Alternatively, H_2 and O_2 may be made to recombine in a fuel cell generates electrical energy.

On photolysis of water using n-type TiO_2 semiconductor electrode as the anode and a platinum electrode as the cathode, O_2 is evolved at the TiO_2 electrode on irradiation. At the pt electrode, H_2 is evolved (Fig. 2).



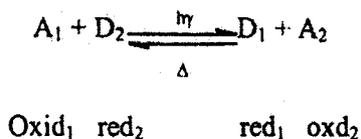
The steps involved in photoelectrolysis of water at the two electrode and



Hydrogen and oxygen can be collected separately and combined again in a fuel cell to obtain electrical energy.

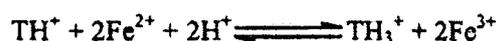
Photo electrochemical devices to convert light energy to electrical energy implies construction of a battery which undergoes cyclical charging and discharging process.

Light energy is converted into chemical energy by driving a suitable redox reaction against the potential gradient.



where D and A represent the reduced forms and oxidized forms of the donor -acceptor system respectively. The reaction reverses spontaneously in the dark using the external circuit for electron transfer. In the process chemical energy is converted into electrical energy and the cell is discharged.

Ex: The reversible photobleaching of thionine by Fe²⁺ ion. Thionine exists as a cation at low pH and can be represented on TH⁺ the overall reaction is



The efficiency of photogavanic devices for solar energy conversion is not very good mainly because of difficult in preventing the spontaneous back recombination reaction.

Flash photolysis

The ordinary photochemical techniques, the concentrations of atoms and free radicals produced are too small for detection even by the most sensitive methods. A technique was developed by Norrish in which the reaction system is illuminated with extremely intense flashes of light. This technique is known on flash photolysis.

The intensity of the flash is typically 2000 Joules or more and the duration of the flash about 10⁻⁴ sec. Absorption of this amount of light energy 6 × 10⁴ Einstein, can dissociate more than 50% of the molecules in a small gas sample. By using another flash, set off at a short interval after the first, it is possible to photograph of the absorption spectrum of dissociation products. The simpler line diagram for flash photolysis.

Not only have the absorption spectra of several free radical intermediates such as ClO, OH, CH, NH, etc. been obtained, but also by changing the time interval between the dissociation and observation flashes if is possible to follow the concentration time. Curve for a free radical intermediate in certain reaction. Example: In the explosion of a mixture of acetylene 10 mm Hg; oxygen, 10 mm Hg and NO₂, 1.5 mm Hg the radical concentration versus time curves were obtained.

Radiation chemistry

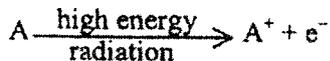
Radiation chemistry deals with physical, chemical and biochemical transformations in matter brought about by the absorption of nucleus radiation. The letter conventionally includes not only high energy electromagnetic radiation X-rays and γ-rays,

but also high energy charge particles as electrons, mesons, protons, deuterons, tritons, alpha particles, other accelerated heavy ions and fission fragments as well as neutrons.

Interaction of radiation with matter

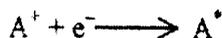
Radiolysis involves the following two stages

Primary stage: In the primary stage, the exposure of the substance to high energy radiations results in ionization of the substance to form ions and electrons.



Secondary stage : In the secondary stage, the ions and the electrons give rise to variety of reactions some of which are

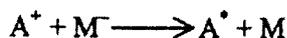
1. Formation of excited molecule



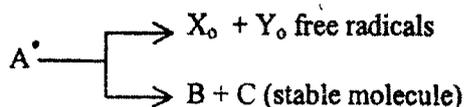
2. Capture of the released electron by a molecule M to form M⁻ ion



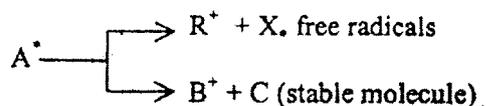
3. Interaction of ion A⁺ and M⁻ to give excited molecule



4. Decomposition of the excited molecule A* into free radicals X[•] and Y[•] or to give stable molecules B and C



5. Decomposition of ion A⁺ into another ion R⁺ and free radical X[•], or an ion B⁺ and a stable molecule C.



Linear energy transfer (LET)

The primary radiolytic products such e_{aq}⁻, H[•] and [•]OH interact in their turn in a variety of ways leading to different final products. The yields of final products depend on the nature of the radiation and its energy, as well as on the nature of the target substance, its atomic number and mass, or its ability to stop the radiation. This stopping power δ is defined as

$$\delta = -\left(\frac{\partial E}{dx}\right)^*$$

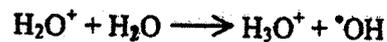
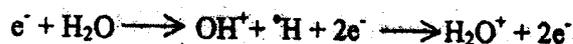
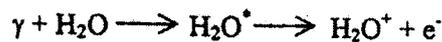
i.e. the rate of energy loss per unit length of matter. This is also referred to as the linear energy transfer (LET) of the substance for the given radiation.

Radiolysis of water vapour

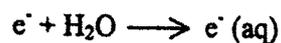
Radiolysis of water vapour by gamma radiation affords one of the best examples for the subject of radiation chemistry. The major products of radiolysis of water vapour are free radicals $\cdot\text{H}$, $\cdot\text{OH}$, $\cdot\text{HO}_2$, positive ions H_2O^+ , H_3O^+ , H^+ , OH^+ , hydrated electron e^-_{aq} and molecular species H_2 and H_2O_2 . The species formed initially by radiation give rise to other products by secondary reaction. The variety of products formed by radiolysis of water are

1. Formation of ionic products

Some of the ionic products produced during radiolysis of water are as follows



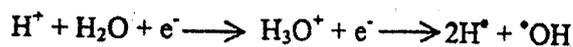
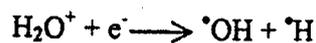
The electrons formed either recombine with possible ions as illustrated above or get solvated as



The various ionic products formed can be detected in a mass spectrometer. The relative abundance of the ionic products are: H_2O^+ (100), H_3O^+ (20), OH^+ (20), H^+ (28), and O^+ (2). Thus H_2O^+ is the main ionic product of radiolysis of water vapour.

Formation of free radicals

The ionic products obtained as above are very reactive. They recombine to yield free radicals.



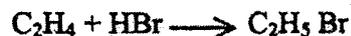
The perhydroxyl radical $^{\bullet}\text{HO}_2$ is also formed in the presence of dissolved air or oxygen



G value

In radiation chemistry the yields are expressed in terms of the G value of the product i.e. the number of molecules of product formed per 100ev energy absorbed.

Ex:



The purity is around 9.95% and the yield corresponds to a low energy absorption of 96 J/mol.

G value for ($\text{C}_2\text{H}_5\text{Br}$)

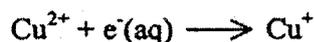
$$\frac{6 \times 10^{23} \times 100}{96 / 1.6 \times 10^{-19}} = 10^5$$

Hydrated electrons

Irradiation of water by X-rays or γ -rays results in the production of electrons of high energy. The lose of part of their energy in collosions and are said to become thermalised. The thermalized electrons get hydrated yielding intensity coloured hydrated electrons $e^{\bullet}(\text{aq})$ exhibiting a broad absorption spectrum with a maximum at about 7000Å



It acts as a reducing agent and gives the same products as given by H atoms in many cases



Radiation dosimetry

In order to understand fully a reaction induced by radiation, it is important to know the amount of energy consumed and the yield of the products. These data are essential for formulating a mechanism of the reaction. Let us consider the units that have been employed for expressing the dose viz., the amount of energy absorbed. These units are

1. The Rad : The rad is defined as follows

1 rad = Absorption of 100 ergs per gram of the substance

$$= 10^{-5} \text{ J g}^{-1} = 6.24 \times 10^{13} \text{ ev g}^{-1}$$

2. The Gray : The gray (Gy) is the unit of dose in SI system. It is defined as

$$1 \text{ gray (Gy)} = 1 \text{ J kg}^{-1} = 100 \text{ rad}$$

3. The Rontagen

This is defined as exposure of such a dose that would produce in 1 cm³ of dry air at STP = (0.001293 g) ions carrying 1 erg of electricity of either sign.

$$1R (\text{air}) = 0.87 \text{ rad} = 8.7 \text{ m Gy}$$

We can use any change, physical or chemical, induced by radiation in a substance a measure of the energy transformed to the substance provided the magnitude of the change is directly proportional to the dose and is independent of the dose rate and the nature of the radiation. The physical methods, employed for dosimetry involve measurement of ionization produced in a gas or direct colorimetry. This is called physical dosimetry. In chemical dosimetry, with which we are concerned here we investigate the yields obtained in chemical radiations induced by radiation. Two chemical dosimeters which are commonly used are:

1. The Fricke dosimeter

This dosimeter is based on the study of the oxidation of Fe²⁺ to Fe³⁺ ions. The Fricke solution is obtained by dissolving 0.4 g of Mohr salt (FeSO₄ (NH₄)₂SO₄ · H₂O), 0.06g NaCl and 22 ml of con. H₂SO₄ in distilled water and making the volume one litre. A portion of this solution is taken on a thick container and exposed to γ -radiation for a certain period of time. Fe²⁺ is oxidized to Fe³⁺ ions. The presence of NaCl only facilitates the oxidation reaction. The concentration of Fe³⁺ ions produced is determined spectrophotometrically at a wavelength of 3040 Å i.e. 304nm. The concentration of Fe³⁺ ions can also be determined by optical density versus concentration of Fe³⁺ ion. Knowing that the standard yield of Fe³⁺ ions is 15.5 ions per 100ev energy absorbed, the unknown dose can be estimated from the measured concentration of Fe³⁺ ions.

2. The ceric sulphate dosimeter

In this dosimeter, a 1-10mM solution of acidified ceric sulphate is exposed to γ -radiation for a given period of time. The Ce⁴⁺ is reduced to Ce³⁺. The fall in concentration of Ce⁴⁺ ions is determined spectrophotometrically at 320 nm. This dosimeter is particularly useful for measuring high doses. However, it is very sensitive to the presence of organic impurities. This dosimeter is generally calibrated against the Fricke dosimeter.

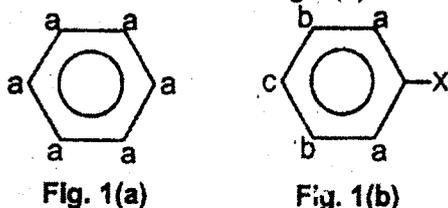
UNIT - III

GROUP THEORY

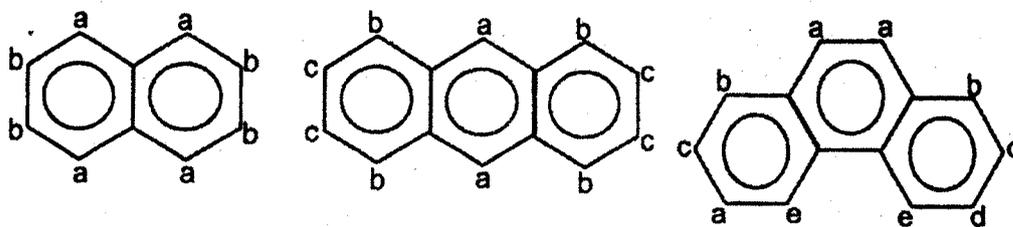
The most important properties of a molecule are its geometry and its electronic structure. These two are related. All physical and chemical properties can be inferred from these two properties. Although the electronic structure and geometry are correlated, the vibrational motions of a molecule do not significantly affect the energy of electrons. Hence the energy of electrons is considered to be independent of vibrations and rotations of the molecule. This approximation is known as the Born-Oppenheimer approximation and it enables one to neglect nuclear motions while considering electronic motions. Thus assuming fixed nuclear positions for a molecule it is possible to make successful predictions regarding the vibrational and electronic motions. Thus assuming fixed nuclear positions for a molecule it is possible to make successful predictions regarding the vibrational and electronic states of a molecule.

The word "symmetry" means that a certain part or portion of an object looks exactly like another part. In the non-mathematical sense, symmetry is associated with regularity in form, pleasing proportions, periodicity or a harmonious arrangement; thus it is frequently associated with a sense of beauty. In the geometry sense it may be analysed as an axis of symmetry, a centre of symmetry, or a plane of symmetry which define respectively the line, point, or plane about which the body is symmetrical.

Many advantages accrue to a chemist trained and experienced in the way of symmetry. One of the least sophisticated consists in the recognition of equivalent atoms in a molecule. For example, all the six carbon atoms in benzene Fig. 1(a) are occupying an equivalent position, but after the introduction of one substituent in the ring, there will be three sets of equivalent carbon atoms in benzene Fig. 1(b).



This leads to the formation of three different types of disubstituted benzene derivatives. In a similar manner the equivalent carbon atoms in naphthalene, anthracene and phenanthrene are indicated in the Figure 2.



Thus the fact there is only one possible monosubstituted ethane, two possible monosubstituted propanes, and so on, is the best example for symmetry considerations.

Definition of symmetry

If a molecule has two or more orientations in space that are indistinguishable, the molecule possesses symmetry. The two possible orientations for the hydrogen molecule are illustrated in Figure (3), only by labelling the two equivalent hydrogen atoms in this figures with prime double prime marks. Actually the two hydrogen atoms are indistinguishable, the two orientations are equivalent, and the molecule has symmetry.



Fig. 3.

The two orientations in figure (3) can be obtained by rotation of the molecule through 180° about an axis in the plane of the paper bisecting H-H bond. This rotation is referred to as a symmetry operation, and the rotation axis is called a symmetry element. The terms symmetry element and symmetry operation should not be confused or used interchangeably. The symmetry element is the line, point or plane about which the symmetry operation is carried out. The symmetry operation can be defined only with respect to element and the existence of the element can be shown only by carrying out the operation.

Symmetry elements and symmetry operations

In a molecule possessing a number of identical atoms in suitable positions it is possible to perform on them specific geometrical operations like reflections, rotations, inversions etc., so that the resulting geometric configuration is indistinguishable from the original geometric configuration such operations are referred to as symmetry operations.

Symmetry operation is the geometrical operation such as reflection, rotation, inversion etc., which leads to a configuration indistinguishable from the original configuration. It must be emphasised that the two configurations are not exactly identical, but they look alike in all respect so that one is not able to say whether any change has been effected or not. The various symmetry operations that can be performed on an object or molecule has been listed in Table -1 along with their symbol and symmetry elements.

Table - 1: Symmetry elements of symmetry operations

Symmetry operation	Symbol	Symmetry element
1. Identity	E	Does not arise
2. Rotation	C_n	Axis of symmetry (a line)
3. Reflection	σ	Plane of reflection (a plane)
4. Improper rotation	S_n	Rotation (C_n) about an axis respect to plane perpendicular to the rotation axis
5. Inversion	I	Centre of symmetry

Identity (E)

Identity is the operation of not doing anything. When we do not do anything we leave the system unchanged and identical to the original system in all respects. It is denoted by symbol E or I. Though E may appear to be a superfluous operation, it is mathematically necessary to include it as we shall see in character table formation.

The rotational axis

If an imaginary axis can be constructed in a molecule, around which the molecule can be rotated to produce an equivalent orientation, this molecule is said to possess a rotational axis. This is usually referred to as a proper rotation axis. If the angle through which the molecule must be rotated in order to secure a super imposable image is denoted by θ° , then the molecule is said to have a $360^\circ/\theta^\circ$ fold rotational axis, denoted by C_n where $n = 360/\theta$ and C stands for cyclic. Figure 4 illustrates the rotational axis of water molecule.

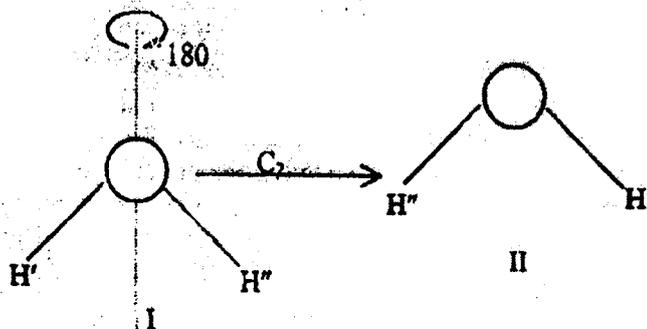


Fig. 4

In BCl_3 molecule the axis passing through the centre B atom and perpendicular to the plane of the molecule is a proper rotational axis (C_3). Rotation, which by convention is in a clockwise direction about this axis, twice through an angle of 120° each time produces two equivalent orientations is illustrated in Figure 5. The order, n, of the rotation is three and three rotations are needed to return to the original position.

Rotation of the molecule through $2\pi/n$ i.e., 120° produces equivalent orientations, and n operations produce the starting configuration referred to as identity. The symbol C_3^2 is employed to indicate a rotation of 240° around a C_3 axis. The C_3^2 operation is identical to a anticlockwise rotation of 120° which is indicated as C_3^1 .

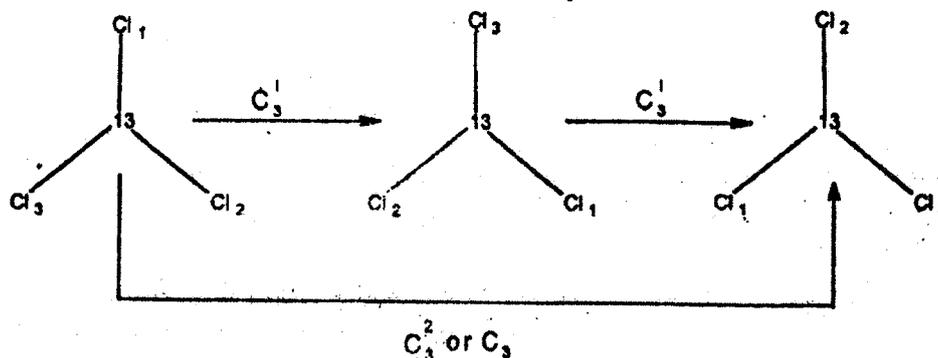


Fig. 5

The C_n^n operation gives not only an equivalent orientation but also an identical one. Further examination of BCl_3 molecule indicate the lack of centre of symmetry and the presence of three additional two fold rotation axes C_2 , each one is passing through B atom and one chlorine atom.

A linear molecule such as O_2 in which all the atoms lie on a straight line, can be rotated around the lengthwise axis passing through the center of all atoms by any angle imaginable and hence all such linear molecule have an axis with $n = \infty$ called C_∞ axis.

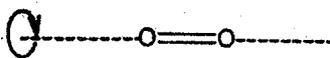


Fig. 6

This molecule is also having infinite number of C_2 axis which are passing through the centre of the molecule and perpendicular to O-O bond. As the next example we shall take a regular hexagon eg., benzene. The axis perpendicular to the plane (Z-axis) is a C_6 axis. Besides this there are six C_2 axes that lie in the plane of the molecule. These pass through pairs of opposite carbon atoms, and the other three pass through the centers of C-C bond.

The following are the general conventions to be followed for specifying coordinates.

Assignment of Z-axis

1. The rotational axis with the highest order is the principal axis and is the Z-axis.
2. If all the rotational axes are of the same order, the axis passing through the largest number of atoms must be taken as the Z-axis. If one does not find such an axis, Z is one passing through a large number of bonds.

Assignment of X-axis

3. If the molecule is planar and the Z-axis lies in this plane the X-axis is chosen to be axis normal to the plane.
4. If the molecule is planar and the Z-axis is perpendicular to the plane, the X-axis which must lie in the plane, is chosen, so as to pass through the largest number of atoms.
5. If non-planar, the plane containing the largest number of atoms, than any other plane is considered to be the plane of the molecule.

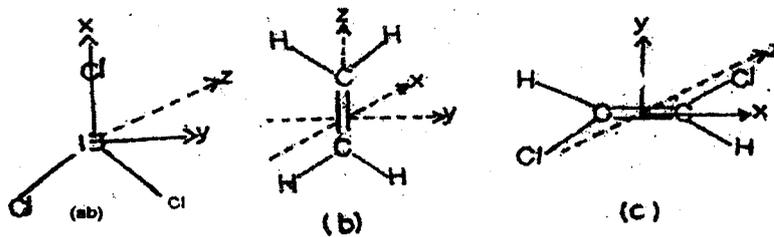
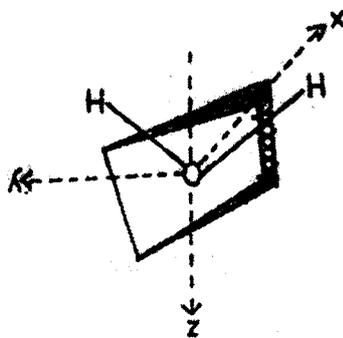


Fig. 7

Plane of symmetry

If in a molecule there exists a plane that separates the molecule into two halves that are mirror images of each other, the molecule possesses the symmetry element of a mirror plane. It is represented by σ . This plane cannot lie outside the molecule but must pass through it. For example, in the water molecule (Fig. 8) the XZ plane is a mirror plane. For water, yet there is another plane (YZ plane) which is perpendicular to XZ plane and containing all the three atoms. These two mirror planes include the C_2 axis and are known as vertical planes, denoted by σ_v . Note that the reflection in XZ plane, for example converts (x,y,z) to $(x,-y,z)$. The signs of points in the plane do not change by reflection in that plane; only the y changes on the operation of σ_{xz} .



For ammonia every NH bond is in a reflection plane which bisects the other HNH angle.

The same is true for all AB_3 molecules having the pyramidal geometry.

For a regular tetrahedron like CH_4 , the plane containing the central carbon atom and two other hydrogen atoms is a reflection plane. We get 6 such reflection planes associating the carbon with any two hydrogen atoms.

A linear molecule such as carbon monoxide $C=O$ has an infinite number of planes of symmetry all of which include the C_∞ rotational axis, the internuclear axis.

As our last example we take a four coordinate square planar complex. For such complexes there are five reflection planes. They are as follows:

1. The molecular plane
2. For different planes perpendicular to the molecular plane. Two of them cut the opposite sides (σ_d) and the other two pass through opposite atoms (σ_v).

In the above discussion we have used the following standard conventions to label the planes. The principal axis of the molecule is taken to be the vertical axis.

σ_v : Plane containing the principal axis

σ_d : Plane bisecting the dihedral angle between σ_v planes. Here 'd' stands for dihedral, though some authors call it diagonal.

σ_h : Plane perpendicular to the vertical (principal) axis. Here 'h' stands for horizontal.

Improper rotation S_n

It is a process of rotation (C_n) followed by reflection in a plane perpendicular to the axis of rotation (σ). Assume that a molecule is rotated around an axis and the resulting orientation is reflected in a plane perpendicular to this axis; if the resulting orientation is superimposable on the original, the molecule is said to possess a rotation reflection axis (the element). The operation is referred to as improper rotation and this axis is called an alternating axis, the symbol 'S' is used to indicate this symmetry element. The subscription in S_n indicates rotation through $2\pi/n$. If trans-dichloroethene (Fig. 9a) is rotated around the X-axis by 180° and the resulting orientation (9b) is then reflected in the YZ plane, the final orientation (9c) is equivalent to the original and hence the X-axis is a rotation reflection axis, since the rotation was by 180° $n = \frac{360^\circ}{180^\circ} = 2$ and the axis is S_2 axis.

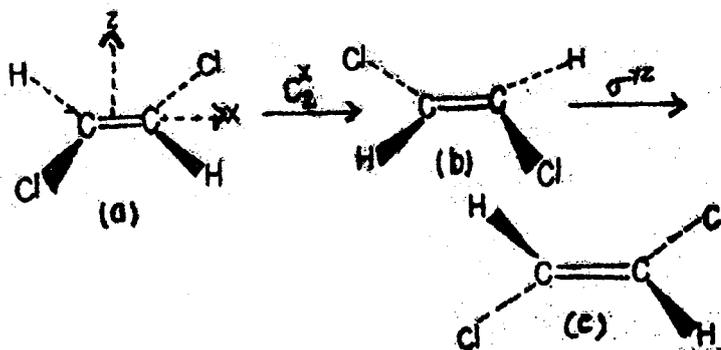


Fig. 9

If a molecule has center of symmetry, i , it must also necessarily possess an S_2 axis; we say then that 'i' implies S_2 because when one of the two is specified, the other is implied and need not be explicitly stated.

Similarly every molecule with a plane of symmetry has an S_1 axis perpendicular to the plane of symmetry.

Obviously, if an axis C_n exists, and there is a perpendicular to it, C_n will be an S_n . Now we shall consider a case in which S_n exists when neither C_n nor the mirror plane perpendicular to its axis separately. In the staggered form of ethane, Figure 10, the C-C bond defines a C_3 axis but there is no perpendicular mirror plane. However, if we rotate the molecule by 60° and then reflect it through a plane perpendicular to the C-C bond, we have an equivalent configuration, consequently an S_6 axis exists and clearly there is no C_6 .

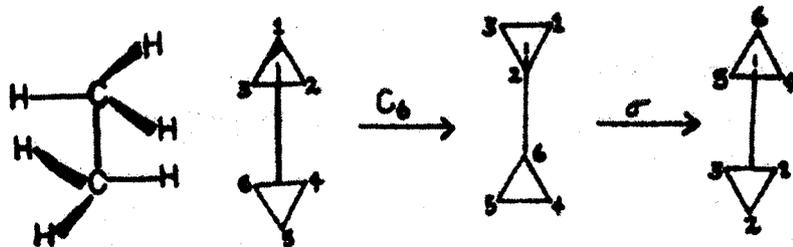


Fig. 10

Methane possess an S_4 axis (actually three of these; Figure 11) each of these axis passes through the center of the molecule and bisects pair of opposite HCH angles. Rotation of the molecule by 90° around the vertical axis followed by reflection in a plane perpendicular to this axis restores the molecule to an orientation superimposable on the original one. Since there are six equivalent faces to the cube in which the tetrahedral CH_4 may be inscribed three axis including the one already described are S_4 axes. Note that the each S_4 axis is also a C_2 axis.

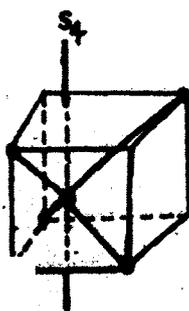


Fig. 11

Some differences in improper rotation axis of even and odd order may be considered here. With 'n' even S_n^m generates the set $S_n^1, S_n^2, S_n^3, \dots, S_n^n$. This is equivalent to $C_n^1 \sigma^1, C_n^2 \sigma^2, C_n^3 \sigma^3, \dots, C_n^n \sigma^n$. (Note: In carrying out $C_n^m \sigma^n$, one reflects first and then rotates, while in carrying out $\sigma^n C_n^m$, one rotates and then reflects). We have the relation $\sigma^m = \sigma$ when 'm' is odd; and $\sigma^m = E$ when 'm' is even. The latter leads to the identities $S_n^m = C_n^m E = E$ and $S_n^m = C_n^m$.

CENTRE OF SYMMETRY

OR

INVERSION CENTRE

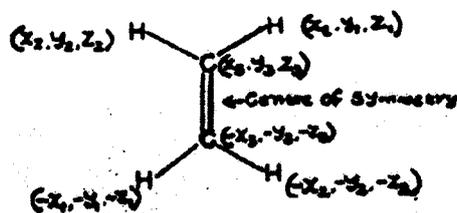


Fig. 12

In molecules like that in figure 12 if we join any atom to the centre of the molecule and extend the line of the other side by the same distance we meet a similar atom. Molecules where atoms and geometrically arranged in this manner are said to possess a center of symmetry or inversion center.

The other molecules having center of symmetry are shown in the Figure 13.



Fig. 13

Neither cis-dichlorethylene, nor tetrahedral molecule possesses an inversion center. It is important to realize that an inversion (operation) every atom converts every point (x,y,z) into a point $(-x,-y,-z)$ in shown in the Fig. 12.

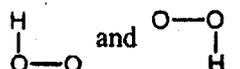
POINT GROUPS

It is possible to classify any given molecule into one of the point groups. Each point group is a collection of all symmetry operations that can be carried out on a molecule belonging to this group. We shall first present a general discussion in which molecules belonging to some of the very common, simple point groups are examine for the symmetry elements they possess. This will be followed by a general set of rules for assigning molecules to the appropriate point groups. It should be borne in mind that all groups to necessarily contain identity as the element.

I. Rotational point groups (C_n)

These groups contain (C_n) rotation as the sole symmetry element (besides identity, of course).

1. C_1 groups: This group contains only C_1 axis as the symmetry element. Note $C_1 = E$. In other words this point group has only identity as the element. This is also referred to as C_s group.
2. C_2 group: This group has E and C_2 as elements e.g. H_2O , F_2O_2 etc. Let us consider H_2O_2 molecule.

The planes  are inclined at an angle 110° (dihedral angle). C_2 axis bisects O-O bond.

3. C_3 group: E and C_3 are the elements e.g. CX_3-CY_3 (substituted ethane).

II. S_n groups (groups having S_n axis) ($n = \text{even}$)

S_2 : S_2 is same as inversion (i) i.e. $S_2 = i$. Hence this group is also referred to as C_i group. Any information of ethane with a center of inversion is a good example.

III. C_{nv} type groups

These contain a C_n rotational axis and 'n' number of vertical planes (σ_v). These do not have a center of inversion or σ_h .

1. C_{2v} : This contains a C_2 axis and two symmetry planes which contain this rotational axis. Recall that the plane containing the principal rotational axis is called the 'vertical plane'. Principal rotational axis is the rotational axis of the highest order and is specified to be the Z-axis by convention.

For C_{2v} we have E, C_2 and two σ_v planes as elements. These σ_v planes are YZ and XZ planes respectively.

IV. C_{nh} group

The group has a C_n axis (principal axis) and a horizontal plane (σ_h) perpendicular to C_n axis. If 'n' is even there is center of symmetry, e.g., trans-dichloroethylene. Z axis is the C_2 axis, xy plane is the σ_h .

V. D group

The symbol D_n is used for point groups that have in addition to C_n axis, n C_2 axes perpendicular to it. Therefore, the D_n point group has greater symmetry (i.e., more symmetry operations) than C_n group.

D_{nh} : A D_n molecule that also has a horizontal mirror plane to the C_n axis, belongs to the point group D_{nh} , and as a consequence will also have 'n' vertical mirror planes. The addition of a horizontal plane group C_{nv} necessarily implies the presence of n C_2 axis in the horizontal plane, and the result is the point group D_{nh} . BCl_3 is an example of a molecule belonging to the D_{3h} point group.

D_{nd} : D_{nd} molecules may also have σ_d plane that contain the principal axis but none of the perpendicular C_2 axis. These dihedral planes σ_d , bisect the angle between two of the C_2 axis. Such a molecule will contain an n-fold axis, n-two fold axis perpendicular to C_n and in addition n vertical planes of symmetry bisecting the angle between two fold axis and containing the n-fold axis. Allene $H_2C = C = CH_2$ is an example of a molecule belonging to D_{2d} point group.

VI. T group

There are four C_3 axis and three mutually perpendicular C_2 axis. There is no symmetry plane.

T_d group: All symmetry elements of T are present. Additionally six planes (σ_d) also exist. CH_4 , SO_4 and tetrahedral molecules are examples.

O_h group: All octahedral complexes belong to this point group.

Symmetry elements in some common point groups

Point group	Symmetry elements	Examples
C_1	No symmetry	SIBrClFI
C_2	One C_2 axis	H_2O_2
C_{nh}	One 'n' fold axis and a horizontal plane σ_h which must be perpendicular to n-fold axis	trans $\text{C}_2\text{H}_2\text{Cl}_2$
C_{2v}	One C_2 axis and two σ_v plane	H_2O , $\text{C}_2\text{H}_5\text{N}$, HCHO
C_{3v}	One C_3 axis and three σ_v plane	NH_3 , CHCl_3
D_{2h}	Three C_2 axis all perpendicular, two σ_v planes one σ_h plane and center of symmetry i	N_2O_4 (planar)
D_{3h}	One C_3 , three C_2 axis perpendicular to C_3 , three σ_v and one σ_h plane	BCl_3
D_{2d}	Three C_2 axis, two σ_d planes, and one S_4	$\text{H}_2\text{C}=\text{C}=\text{CH}_2$ (Allene)
T_d	Three C_2 axis perpendicular to each other, four C_3 axis σ and three S_4 containing C_2	CH_4 , SiF_4

All point groups possess the identity element E

The reader should examine the example for the presence of the symmetry elements required for each group and the absence of others. It is important to realize that although CHCl_3 has a tetrahedral geometry, it does not have a tetrahedral (T_d) symmetry, so it belongs to the point group C_{3v} and not T_d .

The following sequence of steps has been proposed for classifying molecules into point groups and is more reliable procedure than analogy.

1. Determine whether or not the molecule belongs to one of the special point groups, $C_{\infty v}$, $D_{\infty h}$, O_h or T_d . Only linear molecule belongs to $C_{\infty v}$, or $D_{\infty h}$.
2. If not, look for a proper rotational axis, if any are found, proceed to step (3); if not, look for a center of symmetry or a mirror plane. If the element 'i' is present. The molecule belongs to C_i , if a mirror is present the molecule belongs to C_s . If no symmetry other than E is present, the molecule belongs to C_1 .
3. Locate the principal axis, C_n . See if a rotation reflection axis S_{2n} exists that is coincident with the principal axis. If this element exists and there are no other elements except

Product or combination of symmetry operations

The products of any two symmetry operations, defined as their consecutive application, must be a symmetry operation. Hence the product of the C_2 and σ_v operations of a molecule with C_{2v} symmetry (e.g., H_2O) is σ_v (Recall that the C_2 axis is the Z axis, the plane of the molecule is YZ, and σ_v is the YZ plane). This can be written as:

$$C_2 \times \sigma_v' = \sigma_v \text{ or}$$

$$C_2\sigma_v = \sigma_v$$

Instead of the 'product', the term combination is a better description of the above operations. The order in which the operations are written (i.e., from left to right) is the reverse, of the order in which they are applied. In the above case, the σ_v operation is carried out first and is followed by C_2 to produce the same result as σ_v . In trans-dichloroethylene the combination of $C_{2z} \times \sigma_h$ is equivalent to i , and this is again readily verified by the fact that C_{2z} converts the point (x,y,z) into $(-x,-y,z)$ and σ^{xy} converts $(-x,-y,z)$ into $(-x,-y,-z)$ hence $\sigma_h \times C_{2z} = i$.

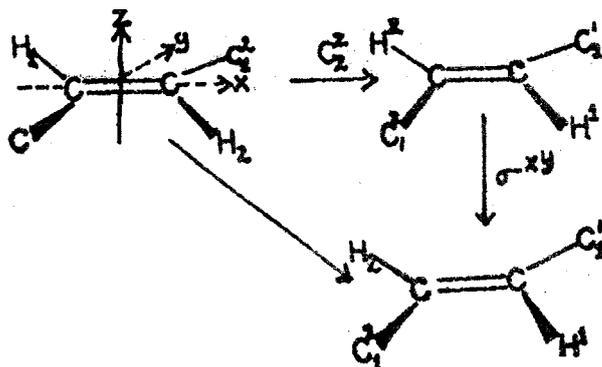


Fig. 15

In general the final result depends on the order in which the operations are carried out, but, in some cases it does not make any difference, i.e., $\sigma^{yz} \times \sigma^{xz} = \sigma^{xz} \times \sigma^{yz} = C_2^z$. In algebra, when $AB = BA$ we say multiplication is commutative. The groups for which it is true are called Abelian groups. In a D_{3h} molecule (e.g., BCl_3), the two operations C_3 and σ_v do not commute; i.e., $C_3\sigma_v \neq \sigma_v C_3$.

Properties of the multiplication tables

If we have a complete and non-redundant list of all the elements in a finite group, and we know all the products, then the group is completely and uniquely defined. This information can be summarized with a group multiplication table. This table is simply an array in which each column and row is headed by an element. The matrix format is employed here because it is a convenient way to insure that we have taken all possible permutations of products of the elements. The number of elements in the group is referred to as the order of the group, h ; the group multiplication table will consist of h rows and h columns; certain groups have infinite number of elements, e.g., H_2 belongs to $D_{\infty h}$.

In order to illustrate simply the rules of group theory we will consider a group of order four containing the symmetry elements E , C_2 , σ_h and i of trans-dichlorethylene molecule; their effect on the molecule was shown in the figure. One important property of the mathematical groups is that every possible product of two operations in the set is also an operation in the set. We place each of the operations in the first row and again in the first column of Table-2. Now, if we multiply an element in the row, say C_2 by an element in the column, say σ_h implying operation σ_h followed by C_2 we will always get another element in the set to which the product is equivalent, in the present example $C_2 \times \sigma_h = i$.

	E	C_2	σ_h	i
E	E	C_2	σ_h	i
C_2	C_2	E	i	σ_h
σ_h	σ_h	i	E	C_2
i	i	σ_h	C_2	E

Table - 2

The water molecule has the symmetry elements C_2 , σ_v , σ_v' and E . the multiplication table for this group C_{2v} in the Table-3.

	E	C_2	σ_v	σ_v'
E	E	C_2	σ_v	σ_v'
C_2	C_2	E	σ_v'	σ_v
σ_v	σ_v	σ_v'	E	C_2
σ_v'	σ_v'	σ_v	C_2	E

Table - 3

We shall consider the C_{3v} , ammonia molecule, whose point group contains the symmetry operations E , $2C_3$ and $3\sigma_v$. the three σ_v planes are labeled as in figure - 16.

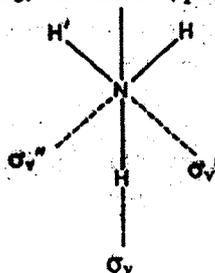


Fig. 16

C_{3v}	E	C_3	C_3^2	σ_v	σ_v'	σ_v''
E	E	C_3	C_3^2	σ_v	σ_v'	σ_v''
C_3	C_3	C_3^2	E	σ_v''	σ_v	σ_v'
C_3^2	C_3^2	E	C_3	σ_v'	σ_v''	σ_v
σ_v	σ_v	σ_v'	σ_v''	E	C_3	C_3^2
σ_v'	σ_v'	σ_v''	σ_v	C_3^2	E	C_3
σ_v''	σ_v''	σ_v	σ_v'	C_3	C_3^2	E

Table - 4

Character tables and their applications

Vectors

A vector in three dimensional space has a magnitude and a direction that can be specified by the lengths of its projections on the three orthogonal axis of Cartesian coordinate system. Vector properties may be more than three dimensional, so the above statement can be extended to p -dimensional space and p -orthogonal axis in p -space.

It is often necessary to take the product of vectors. One type of product that produces a number (i.e., scalar) is called the scalar or dot product. This is given by

$$\vec{A} \cdot \vec{B} = AB \cos \theta \quad \dots (1)$$

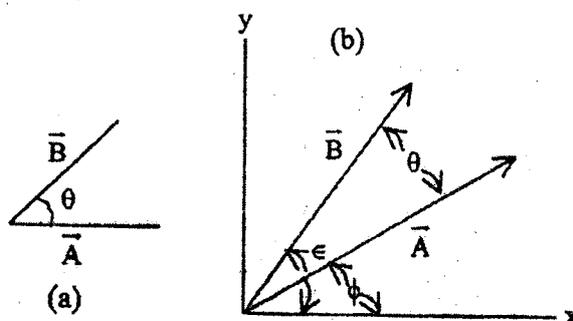


Fig. 17

Here the bold face \vec{A} and \vec{B} refer to two vectors, and the dot refers to their dot product right hand side of the equation, A and B refer to the lengths \vec{A} and \vec{B} vectors, and θ is the angle between them as shown in the figure 17(a). Accordingly, if the angle θ between two vectors is 90° , the dot product is zero ($\cos 90^\circ = 0$) and the vectors are orthogonal.

It is necessary to reference to vectors to a coordinate system. This is done for a two-dimensional example (i.e., the xy plane) in figure 17b. This angle θ is now seen to be $\epsilon - \phi$. So that the dot product becomes

$$\vec{A} \cdot \vec{B} = AB \cos (\epsilon - \phi) \quad \dots (2)$$

Thus, The dot product of two vectors in two dimensional space is the product of the components with all cross terms ($A_x B_y$ and so on) absent. In p -space, the result obtained.

$$\vec{A} \cdot \vec{B} = \sum_{i=1}^p A_i B_i$$

where, 'i' ranges over the p orthogonal axis in p -space. Accordingly, the scalar square of a vector is given by

$$\vec{A}^2 = \sum_{i=1}^p A_i^2$$

Matrices

A matrix is a rectangular array of numbers or symbols that has the following general form:

$$\begin{bmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{bmatrix}$$

The square brackets indicate that it is a matrix, as opposed to a determinant. The entire matrix is abbreviated with a script letter or by the symbol (a_{ij}) . The symbol a_{ij} refers to the matrix element in the i^{th} row and j^{th} column. The elements a_{ij} of a square matrix for which $i = j$ are called the diagonal elements, and the other elements are called off-diagonal. When all of off-diagonal elements of a matrix are zero, the matrix is called a unit matrix. The unit matrix is often abbreviated by the Kronecker delta.

$$\begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix} = \delta_{ij}$$

Unless $i = j$, δ has a value of 0. The trace or character of a square matrix, an important property, is simply the sum of the diagonal elements. A one row matrix can be conveniently written on a single line. In order to write a one column matrix on a single line it is enclosed in braces, $\{ \}$.

A vector is conveniently respected by a one column matrix. In three dimensional orthogonal coordinate system, a vector initiating at the origin of the coordinate system is completely specified by the x, y and z coordinates of the other end. Thus the matrix $\{x, y, z\}$ is a one column matrix that represents the vectors. In p -space, a play 1 column vector is needed. In both instances, the elements of the matrix give the projections of the vector on the orthogonal coordinates.

Matrices may be added, subtracted, multiplied or divided by using the appropriate rules of matrix algebra. In order to add or subtract two matrices A and B to give a matrix C the matrices must all be of the same dimensions, i.e., they must contain the same number of rows and columns, the elements of the C matrix are given by

$$C_{ij} = a_{ij} \pm b_{ij}$$

A matrix can be multiplied by a scalar (a singular number) when multiplying by a scalar, each matrix element is multiplied by this scalar.

$$[a_{ij}] = k a_{ij}$$

The ij^{th} matrix element of a product matrix is obtained by multiplying the i^{th} row of the first matrix by the j^{th} column of the second matrix, i.e., row by column. That is the matrix elements of C are given by

$$C_{ik} = \sum_{j=1}^n a_{ij} b_{jk}$$

where 'n' is the number of elements in the i^{th} row and in the j^{th} column. This matrix multiplication is equivalent to taking the dot product of two vectors.

It should be clear that, in order to multiply by another matrix the two matrices must be conformable, i.e., if we wish to multiply A by B to give C, the number of columns in A must equal to the number of rows in B. If the dimensionality of matrix A is i by j and that of B is j by k , the C will have a dimensionality of i by k . This can be seen by carrying out the following matrix multiplication.

$$\begin{bmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \\ a_{31} & a_{32} \end{bmatrix} \quad \begin{bmatrix} b_{11} & b_{12} & b_{13} \\ b_{21} & b_{22} & b_{23} \end{bmatrix} \quad \begin{bmatrix} c_{11} & c_{12} & c_{13} \\ c_{21} & c_{22} & c_{23} \\ c_{31} & c_{32} & c_{33} \end{bmatrix}$$

3 by 2 2 by 3 3 by 3

The number of columns (two) in A equals the number of rows (two) in B. the matrix elements of C are obtained by a row by column multiplication, i.e.,

$$\begin{aligned} C_{11} &= a_{11}b_{11} + a_{12}b_{21} \\ C_{12} &= a_{11}b_{12} + a_{12}b_{22} \\ C_{13} &= a_{11}b_{13} + a_{12}b_{23} \\ C_{21} &= a_{21}b_{11} + a_{22}b_{21} \\ C_{22} &= a_{21}b_{12} + a_{22}b_{22} \\ C_{23} &= a_{21}b_{13} + a_{22}b_{23} \\ C_{31} &= a_{31}b_{11} + a_{32}b_{21} \\ C_{32} &= a_{31}b_{12} + a_{32}b_{22} \\ C_{33} &= a_{31}b_{13} + a_{32}b_{23} \end{aligned}$$

Matrix multiplication always obeys the associative law, but is not necessarily commutative. Conformable matrices in the order AB may not be conformable in the order BA.

Division of matrices is based on the fact that A divided by B equals AB^{-1} where B^{-1} is defined as the matrix such that $BB^{-1} = \delta_j$. Thus the only new problem associated with division is the finding an inverse. Only square matrices can have inverses. The procedure for obtaining the inverse is not needed here.

Conjugated matrices deserve special mention. If two matrices A and B are conjugate, they are related by a similarity transform just as conjugate elements of a group are; i.e., there is a matrix R such that

$$A = R^{-1}BR$$

One advantage of matrices that will be significance to us is that can be used in describing transformations of points, functions, vectors and other entities in space. The transformation of point will be helpful in explaining how symmetry operations (elements) can be represented by matrices what advantages are thus obtained.

Representations

We have shown the relationship between various symmetry operations by examining changes produced on the molecules. The safest and most accurate method is to find out the effect each operation on the coordinates and express the changes in the form of a matrix. The matrix referred to as the transformation matrix expresses quantitatively the net effect of each operation. These matrices are combined observing the useful rules of matrix algebra, to obtain the matrix for successive symmetry operations.

Consider a point P with (x,y,z) coordinates of (1,1,1) corresponding to the projections of the point on these axes. The identity operation of this point corresponds to giving rise to a new coordinates that are the same as the old ones. The following matrix does this

$$\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} x' \\ y' \\ z' \end{bmatrix}$$

The matrix multiplication yields

$$\begin{aligned} x &= x' \\ y &= y' \\ z &= z' \end{aligned}$$

This unit matrix is said to be a representation of the identity operation.

Reflection

A reflection in the xz plane σ^{xz} changes the sign of y coordinate, but leaves x and z unchanged. The original coordinate x , y and z transform to x_1 , y_1 and z_1 . We now write

$$\begin{aligned}x_1 &= 1x + 0y + 0z \\y_1 &= 0x - 1y + 0z \\z_1 &= 0x + 0y + 1z\end{aligned}$$

or

$$\begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} x_1 \\ y_1 \\ z_1 \end{bmatrix}$$

This can be written as two matrix equations.

$$\begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \begin{bmatrix} x \\ y \end{bmatrix} = \begin{bmatrix} x_1 \\ y_1 \end{bmatrix}$$

and

$$[1] [z] = [z_1]$$

We note that in this operation the new coordinate x_1 depends on x only, y_1 on y only and z_1 on z only. We can thus say that for σ^{xz} , x transforms independently of y and z and finally z transforms independently x and y . The matrix representations of σ^{xz} is thus given by

$$\sigma^{xz} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

The matrix representation of yz is

$$\sigma^{yz} = \begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$x_1 = -x; y_1 = y \text{ and } z_1 = z$$

The matrix representation of xy is

$$6xy = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix}$$

$$x_1 = x; y_1 = y \text{ and } z_1 = -z$$

Rotations

Let us affect a rotation on the vector r (PO in figure 19) by θ . This rotation is done w.r.t the z -axis and hence the z -coordinates of the points do not change. The point $p(x_1, y_1, z_1)$ moves to (x_2, y_2, z_2) .

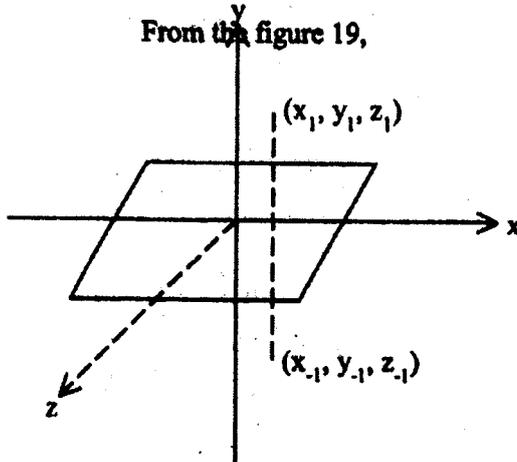


Fig. 18

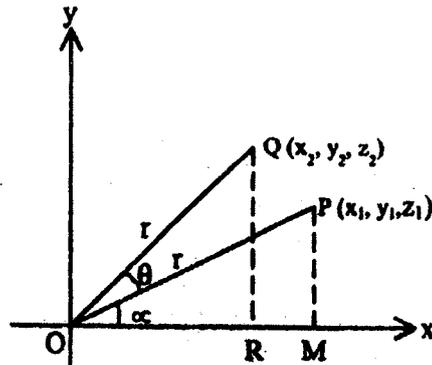


Fig. 19

$$OM = X_1 = r \cos \alpha$$

$$RM = Y_1 = r \sin \alpha$$

$$OR = X_2 = r \cos (QOR) = r \cos (\theta + \alpha)$$

$$OR = Y_2 = r \sin (QOR) = r \sin (\theta + \alpha)$$

$$x_2 = r \cos \theta \cos \alpha - r \sin \theta \sin \alpha = x_1 \cos \theta - y_1 \sin \theta$$

$$y_2 = r \cos \alpha \sin \theta + r \sin \alpha \cos \theta = x_1 \sin \theta + y_1 \cos \theta$$

$$z_2 = z_1$$

We can express the relationship between (x_2, y_2, z_2) and (x_1, y_1, z_1) as

$$x_2 = x_1 \cos \theta - y_1 \sin \theta + (0)Z_1$$

$$y_2 = x_1 \sin \theta + y_1 \cos \theta + (0)Z_1$$

$$z_2 = 0x_1 + 0y_1 + 1Z_1$$

In matrix form these equations are

$$\begin{bmatrix} \cos \theta & -\sin \theta & 0 \\ \sin \theta & \cos \theta & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} x_1 \\ y_1 \\ z_1 \end{bmatrix} = \begin{bmatrix} x_2 \\ y_2 \\ z_2 \end{bmatrix}$$

We also note that the same can be rewritten as

$$\begin{bmatrix} \cos \theta & -\sin \theta \\ \sin \theta & \cos \theta \end{bmatrix} \begin{bmatrix} x_1 \\ y_1 \end{bmatrix} = \begin{bmatrix} x_2 \\ y_2 \end{bmatrix}$$

[1] $[z_1] = [z_2]$ i.e., z does not change.

Notice that the value of x_2 depends on both x_1 and y_1 and similarly y_2 depends on x_1 and y_1 ; but $z_2 = z_1$ and they are independent of x and y . In other words, the 3×3 matrix is reducible to 2×2 matrix involving x and y a 1×1 matrix involving z . We list below the 2×2 matrix for different operations.

$$\begin{bmatrix} \cos \theta & -\sin \theta \\ \sin \theta & \cos \theta \end{bmatrix}$$

Operation	Angle θ	Matrix
C^2	0°	$\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$
C^2	180° or -180°	$\begin{bmatrix} -1 & 0 \\ 0 & -1 \end{bmatrix}$
$C_3^2 = C_3^{-1}$	240° -120°	$\begin{bmatrix} -1/2 & 3/2 \\ -3/2 & -1/2 \end{bmatrix}$
C_3	120°	$\begin{bmatrix} -1/2 & 3/2 \\ +3/2 & -1/2 \end{bmatrix}$

Reducible and Irreducible representations

It is an important fact that all the inter-relationships between symmetry operations are also valid for the corresponding transformation matrices. Let us illustrate this by showing that

$$\sigma_v \sigma_v^1 = C_2^*$$

Multiply the matrices for σ_v and σ_v^1 i.e., multiply the matrices for σ^{xz} and σ^{yz} defined above, by the usual matrix multiplication method and verify that the result is the matrix C_2^* .

$$\text{It is also easily verified that } \sigma_v^1 \cdot \sigma_v = C_2^*$$

All the interrelationship shown in the group multiplication table can be actually worked out employing matrices and matrix multiplication procedure. Let us take C_{2v} group. We can write the matrices for all four operations.

$$\begin{array}{cccc}
\text{E} & \text{C}_2 & \sigma^{xz} = \sigma_v & \sigma^{yz} = \sigma_v^1 \\
\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} & \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} & \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} & \begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}
\end{array}$$

We see

$$\begin{aligned}
C_2^2 &= (\sigma_v)^2 = (\sigma_v^1)^2 = E \\
C_2\sigma_v &= \sigma_v C_2 = \sigma_v^1 \\
\sigma_v^1 C_2 &= C_2 \sigma_v^1 = \sigma_v \\
\sigma_v \sigma_v^1 &= \sigma_v^1 \sigma_v = C_2
\end{aligned}$$

Thus the relation $C_2\sigma_v = \sigma_v^1$ is in matrix representation:

$$\begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} = \begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

All the above four matrices collectively form a set called representation.

Thus it is clear that we can generate for C_{2v} or for any point group several sets of matrices or quantities or numbers each one of which will obey the group multiplication table. Such a set of quantities or matrices obeying the group multiplication table of a point group is called representation of the group. The definite representations are basis and will not contain any other representations. These are called 'irreducible representations'. All the other representations obtained by combining these basis irreducible representations are called reducible representations. Reducible representations are linear combinations of irreducible representations. In higher point groups two or three vectors may jointly form a basis for an irreducible representation and such representations of dimension greater unity is called a degenerate representation. The sum of the diagonal elements of a matrix is called is character or trace.

The total representation describing the effect of all of the symmetry operations in the C_{2v} point group on the point with co-ordinates x, y and z is

$$\begin{array}{cccc}
\text{E} & \text{C}_2 & \sigma_v^{xz} & \sigma_v^{yz} \\
\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} & \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} & \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} & \begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}
\end{array}$$

Here each of the matrices is block diagonalized, i.e., the total matrix can be broken up into blocks of smaller matrices will number off diagonal elements between the blocks. The fact that it is block diagonalize indicates that the total representation described

must consist of a set of so called one dimensional representations. We can see this as follows: if we were to be concerned only with operations on a point that had only an x-coordinates, (i.e., column 'matrix' $\{x, 0, 0\}$) then only the first row of the total representation would be required (i.e., 1, -1, -1). This is an irreducible representations, or we shall call it as symmetry type; symmetry species. This is a set of one dimensional x-vector in the specified point group. The symbol B will be used to symbolize this irreducible representation. The irreducible representation of y is (1 -1 -1 +1) which is labeled as B₂ and that of z is (1 1 1 1) which is labeled as A₁.

The total representation – the four 3 by 3 matrices is a reducible representation. The trace or character of each of the total representation matrices is the sum of the characters of each of the component irreducible representation in order these are 3, -1, 1 and 1.

Character Table for the C_{2v} point group

C _{2v}	E	C ₂ ^z	σ _v ^{xz}	σ _v ^{yz}		
(Γ ₁) A ₁	+1	+1	+1	+1	z	z ² , y ² , x ²
(Γ ₂) A ₂	+1	+1	-1	-1	Rz	xy
(Γ ₃) B ₁	+1	-1	+1	-1	x, R _y	x ²
(Γ ₄) B ₂	+1	-1	-1	+1	y, R _x	y ²

The irreducible representations are labelled according to the following rules. Notation for irreducible representations: H. Bethe labelled the irreducible representations as Γ₁, Γ₂, Γ₃ etc., and these symbols were used previously R.S. Mulliken gave labels which denote symmetry properties of these irreducible representations and currently only Mullikens notations are in vogue. Mulliken notations are summarized below:

1. One dimensional representation is designated as A or B. Two dimensional (doubly degenerate) representations are designated by the letter E and three dimensional representations are designated by the letter T.
2. The irreducible representation symmetric ($\chi = +1$) with respect to the principal rotation and also to other rotations of the same order is termed as A and if it antisymmetric ($\chi = -1$) it is termed as B.
3. If there are several irreducible representations of the type A and B labels such as A₁, A₂, A₃, ... B₁, B₂, B₃ etc., are to be used. If there is only one A or one B, the number subscript is not necessary. Number subscripts are employed to differentiate between different T representations or E representations also.
4. In the case of a group where inversion is a symmetry operation subscript of (gerade) is appended if the representation is symmetric ($\chi = 1$) with respect to inversion and u (ungerade) is used for the representation antisymmetric ($\chi = -1$) with respect to inversion.

- The representation which is symmetric ($\chi\chi = 1$) with respect to all the symmetry operations of the point group is called totally symmetric irreducible representation. It is labelled as A_1 or A_{1g} .
- Single prime (') denotes that the IR is symmetric with respect to σ_h . Double prime (") implies that it is antisymmetric with respect to σ_h . For example in C_{2v} group Γ_1, Γ_2 would be labelled A while Γ_3 and Γ_4 would be labeled B.

Let us now discuss some of the most important theorems concerning the irreducible representations and their characters. These theorems are quite general and apply to all groups.

Some theorems and definitions concerning irreducible representations

Definitions

- A set of quantities or matrices or numbers obeying the group multiplication tables as the elements of a group form a representation.
- The irreducible representations of a point group are the sets of representations whose linear combinations express any representation of the group. a representation which can be expressed as a linear combination of two or more irreducible representations is therefore called a reducible representation.

Theorems on matrix representations

- The sum of the squares of the characters of any irreducible representations is equal to the order (h) of the group

$$\sum_{\text{operations}}^{\text{All}} \chi_i(\hat{o})^2 = h$$

$\chi_i(\hat{o})$ is the character of the operation \hat{o} for the irreducible representation designated as i .

For example, the characters of the A_1 representation of C_{2v} are 1.

	E	C_2	σ_v	σ_v'
χ_{A_1}	1	1	1	1

$$\text{Thus, } \sum \chi_{A_1}^2 = (1)^2 + (1)^2 + (1)^2 + (1)^2 = 4 = h$$

- The characters of any two irreducible representations of a group are orthogonal i.e.,

$\sum_{\hat{o}} \chi_i(\hat{o})\chi_j(\hat{o}) = 0$, where i and j are different one dimensional irreducible representations.

To illustrate, consider the Γ_1, Γ_2 and Γ_3 IR's C_{2v} group and their characters. Thus

$$\sum \chi_{\Gamma_3}(\hat{o})\chi_{\Gamma_2}(\hat{o}) = (1 \times 1) + (-1 \times -1) + (1 \times -1) + (-1 \times 1) = 0$$

Similarly we have $\sum \gamma \Gamma_1(\hat{o}) \gamma \Gamma_3(\hat{o}) = \sum \gamma \Gamma_2(\hat{o}) \gamma \Gamma_3(\hat{o}) = 0$

3. The total number of irreducible representations is equal to number of classes.

Application of the rules

- a. These rules can be utilized to check up the character tables of groups and for simple groups one can derive the character table using these rules.
- b. Rules 1 and 2 utilised to find out the composition in terms of IR's of any reducible representation.

Procedure

Let 'i' be a reducible representation composed of IR's j, k and l such that

$$i = aj + bk + cl$$

where a, b, c are coefficients.

Multiply the character of 'i' for operation o by the character of j for o i.e., $i^{(o)}$ $j^{(o)}$, and form the sum,

$$\text{Sum} = \sum_{\substack{a \\ \text{operations } \hat{o}}} \gamma_i(\hat{o}) \gamma_j(\hat{o})$$

By the orthogonality rule 2 above, only the 'j' term will survive on expanding i into its IR's.

$$\begin{aligned} \text{Sum} &= a \sum_{\text{all operations}} \gamma_j(\hat{o}) \gamma_j(\hat{o}) + b \sum_{\text{all operations}} \gamma_k(\hat{o}) \gamma_j(\hat{o}) + c \sum_{\text{all operations}} \gamma_l(\hat{o}) \gamma_j(\hat{o}) \\ &= ah + 0 + 0 = ah \end{aligned}$$

where 'h' is the total number of elements or order of the group, and we have used the rule 1.

Thus the coefficient of

$$\Gamma_j \text{ in } \Gamma_i = a = \frac{1}{h} \sum_{\substack{a \\ \text{operations } \hat{o}}} i(\hat{o}) \gamma_j(\hat{o})$$

we can find the k and l composition i.e., values of b and c by a similar procedure

For example, a reducible representation of C_{2v} is as follows:

E	C_2^z	σ_v	σ_v'
3	3	1	1

see the character table for C_{2v} . There are 4 IR's viz., A_1 , A_2 , B_1 and B_2 and $h = 4$. Coefficient of A_1 in given here is obtained as follows:

	E	C ₂	σ _v	σ _v '
γΓ =	3	3	1	1
γA ₁ =	1	1	-1	-1
γΓ ψA ₁ =	3	3	1	1

$$\text{Sum} = 3 + 3 + 1 + 1 = 8$$

The coefficient of A₁ in Γ = 8/h = 8/4 = 2, i.e., There are 2A₁ in A₂ composition

	E	C ₂	σ _v	σ _v '
γΓ =	3	3	1	1
γA ₁ =	1	1	-1	-1
γΓ γA ₂ =	3	3	-1	-1

$$\text{Sum} = 3 + 3 - 1 = 4$$

Sum/order = 4/4 = 1 i.e., There is one A₂ in

If we add 2A₁ + A₂ we get. Hence = 2A₁ + A₂. We shall also check for B₁ and B₂ and show that they do not contribute to. Thus

	E	C ₂	σ _v	σ _v '
γΓ =	3	3	1	1
γB ₁ =	1	-1	1	-1
γΓ γB ₁ =	3	-3	1	-1

$$\text{Sum} = 3 - 3 + 1 - 1 = 0$$

Coefficient of B₁ = 0/4 = 0.

Similarly we can show that B₂ is not contained in



This method is useful when we deal with one dimensional irreducible representations. Difficulties are encountered when try to employ these in the case of higher dimensional representations.

General theorems of representations theory

The matrices of the different irreducible representations possess certain well defined inter-relationships. By mathematics methods we can express the conclusions in the

form of general theorems. By using the theorems we can classify the groups and analyse their structures. These general theorems apply to degenerate and also non-degenerate groups.

Theorem 1:

Number of classes in a group is equal to the number of irreducible representations.

Theorem 2:

A group possessing k different irreducible representation $\Gamma_1, \Gamma_2, \Gamma_3, \dots, \Gamma_k$ of dimensions $n_1, n_2, n_3, \dots, n_k$ respectively obeys the equation,

$$\sum_{i=1}^k n_i^2 = n_1^2 + n_2^2 + n_3^2 + n_4^2 + \dots + n_k^2 = h$$

where 'h' is total number of elements (order) and k is the number of classes in the group.

Theorem 3:

The characters of irreducible representations of the elements forming a class are identical.

Proof:

Members of the class are conjugate, i.e., they are related by similarity transformation $X^{-1}AX = B$. Similarly transformation does not change the trace of the matrix. Hence A and B have same characters.

Theorem 4:

If $\gamma_i^{(\mu)}$ is the character of the irreducible representation with respect to the element i forming a class constituted by l_i elements, the following relationship are valid.

$$\text{If i. } \sum_{i=1}^k l_i \gamma_i^{(\mu)*} \gamma_i^{(\nu)} = h \delta_{\mu\nu}$$

where $\gamma_i^{(\mu)*}$ is the complex conjugate of $\gamma_i^{(\mu)}$; $\delta_{\mu\nu}$ the Kronecker delta, equal to zero for $\mu \neq \nu$, equal to 1 for $\mu = \nu$. Thus if μ and ν refer to different irreducible representations ($\mu \neq \nu$) then $\sigma_{\mu\nu} = 0$ and

$$\sum_{i=1}^k l_i \gamma_i^{(\mu)*} \gamma_i^{(\nu)} = 0 \text{ (orthogonality theorem)}$$

ii. if μ and ν refer to the same irreducible representation ($\mu = \nu$) the $\delta_{\mu\nu} = 1$ (normalization condition) and

$$\sum_{i=1}^k l_i \gamma_i^{(\mu)} \gamma_i^{(\nu)} = \sum_{i=1}^k l_i = h$$

These general theorems can be restated in a simpler form as applicable to non-degenerate groups.

Theorem 5:

(The great orthogonality theorem or the general key theorem of the theory of representations).

The elements of matrices of any two irreducible representation μ and ν satisfy the relationship,

$$\sum_R [A^{(\mu)}(R)]_{ij} [A^{(\nu)}(R)]_{pq} = \frac{h}{\sqrt{n_\mu n_\nu}} \delta_{\mu\nu} \delta_{jp} \delta_{iq}$$

Here $A^{(\mu)}(R)_{ij}$ is the $(i,j)^{\text{th}}$ element of the matrix A representing the symmetry operation R in the μ^{th} irreducible representation. n is the dimension of the μ^{th} irreducible representation. Note that the summation is non-vanishing and equal to h/n only when $\mu = \nu$; $i = p$ and $j = q$. The theorem means that the corresponding (i,j) elements of the matrices $A(R)$ for a given IR form the components of a set of vectors in an h dimensional space such that these vectors are orthogonal and normalized to a length of $h/n\mu$.

All the previous theorems are in fact derived from this theorem 5 and hence it is appropriately called the great orthogonality theorem.

Construction of character table

The two methods that are available for the construction of character table are (i) systematic method and (ii) deductive method. The deductive method consists in using all the well known theorems so far learnt and identifying the irreducible representations and their characters individually. The character tables can be obtained in the case of simple group using the following procedure.

1. Write down all the symmetry elements of the point group and group them into classes.
2. Remember that the total number of irreducible representations equals to the total number of classes.
3. Determine the dimensions of the IR's using theorem.
4. Remember the inter-relationships between various group operations and use this knowledge.
5. Use the orthogonality and normality theorems in fixing the characters.
6. Generate representations using certain basis vectors (x, y, z) Try out with x, y, z, R_x, R_y, R_z etc., a basis and check. We shall now derive the character tables of C_{2v} point group.

There are four operations $E, C_2^z, \sigma_v, \sigma_v'$ i.e., order of the group $h = 4$. Each one forms a class by itself thus there are four classes. Hence it should have 4 IR's. These are all one dimensional and hence

$$n_1^2 + n_2^2 + n_3^2 + n_4^2 = 4$$

and the solution in $n_1 = n_2 = n_3 = n_4 = 1$.

By taking a general point or vectors T_x, T_y, T_z or P_x, P_y, P_z we have already accounted three IR's and fourth one is obtained by considering R_z operation as $(1, 1, -1, -1)$. Thus we obtain the complete character table of C_{2v} point group (given already).

Character table for C_{2h} point group

C_{2h}	E	C_2	i	σ_h		
Ag	1	1	1	1	R_z	x^2, y^2, z^2, x^y
Bg	1	-1	1	-1	R_x, R_y	x^z, y^z
Au	1	1	-1	-1	T_x	
Bu	1	-1	-1	1	T_x, T_y	

Chemical applications of group theory

The concept of group theory have been employed to solve many problems. The various uses may be stated briefly as follows:

1. To classify functions and states according to their symmetry properties and correlate them.
2. To predict the allowed and non-allowed spectral transitions and chemical transformations.
3. To simplify the laborious procedures involved in constructing molecular orbital functions, vibrational modes etc.

Molar vibrations

Vibrational motion of a molecule is due to displacements of the constituent atoms in certain directions. When all the atoms are simultaneously displaced in the direction of x it is referred to as T_x or translational motion along x . In a molecule consisting of n atoms, complete specifications of the location in space of all the atoms require $3n$ coordinates the so called $3n$ degrees of freedom, i.e., the three Cartesian coordinates for each atom these $3n$ degrees of freedom three are needed and are sufficient to determine the position of the molecule. i.e., of its center of gravity in space. Three more degrees are needed to define the orientations of the molecule, two angles to locate the axis, and one more angle to define the rotational position about this axis. If the molecule is linear and only then different rotational

position about this principal axis are equivalent and the last angle is meaningless and unnecessary. This leaves $(3n-6)$ degrees of freedom (in a linear molecule $3n-5$) which define the positions of the atoms relative to one another, and hence the bond distances and angles and their changes i.e., their vibrations.

The reducible representation obtained would be a combination of the irreducible representations for translations, rotations and normal modes of vibrations.

Molecular vibrations of symmetrical AB_2 (Bent) molecule

A typical molecule of this system is H_2O . The four matrices constitute a reducible representation corresponding to the transformation of nine displacement coordinates. Thus the characters of this irreducible representations are:

Γ	$3N$	(3×3)	E	C_2	σ_v	σ'_v
			9	-1	1	3

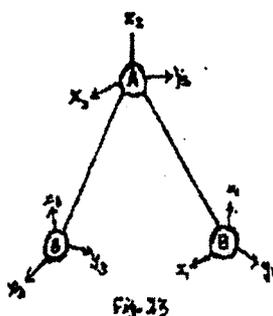
The characters can be obtained even without writing down the complete transformation matrix.

The following procedure can be used for this purpose:

1. Identify the atoms which are unshifted by the concerned operations and consider only their coordinates. That is, we ignore the vectors or coordinates which have changed their location since they do not contribute to the diagonal elements.
2. The total number of coordinates or vectors which have not changed their location and also direction minus the total number of coordinates or vectors that have not changed their location but have reversed their direction is the character of the operation.

Let us illustrate this for C_2 operation. Atoms designated B in Fig. 23 have shifted their positions and hence x_1, y_1, z_1, x_3, y_3 and z_3 have changed their locations.

Their contributions to the diagonal elements will be 0 and hence we ignore them. Z_2 is the only vector which is not shifted and which has not at the same time changed the direction. xz and yz have not changed their locations, but C_2 has reversed their directions. Hence $\chi(C_2) = 1-2 = -1$. The characters of σ_v and σ'_v may be verified using this simple procedure.



Having found the characters of the reducible representations, it is now necessary to find its composition in terms of IR's Thus

	E	C ₂ ^z	σ _v	σ _v '
γ(A ₁)	1	1	1	1
γ(A ₁)γ(Γ)	(1 × 9) 9	(1 × -1) -1	(1 × 1) 1	(1 × 3) -3

$$\text{Therefore, the number of } A_1 = \frac{9 + (-1) + 1 + 3}{4} = \frac{12}{4} = 3$$

$$\text{Similarly number of } A_2 = \frac{(1 \times 9) + (1 \times -1) + (-1 \times 1) + (-1 \times 3)}{4} = 1$$

$$\text{Number of } B_1 = \frac{(1 \times 9) + (-1 \times -1) + (1 \times 1) + (-1 \times 3)}{4} = 2$$

The rest is B₂. Number of B₂ is 9 - (3 + 1 + 2) = 3. This may be directly verified using the characters of B₂. The reducible representation is reduced as

$$\Gamma = 3A_1 + A_2 + 2B_1 + 3B_2$$

Since this contains translations, rotations, and vibrations, we must subtract from this the IR's of translations and rotations to find out those of vibrations. We note from C_{2v} character table the details regarding the symmetries of translations and rotations. Thus,

$$T_x (B_1); T_y (B_2); T_z (A_1); R_x (B_2); R_y (B_1); R_z (A_2)$$

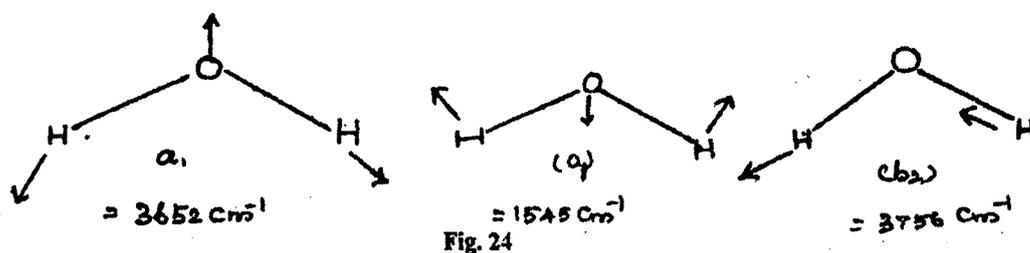
Hence

$$\Gamma_{(\text{trans} + \text{rot})} = A_1 + A_2 + 2B_1 + B_2$$

and

$$\Gamma_{\text{vib}} = \Gamma - \Gamma_{(\text{trans} + \text{rot})} = 2A_1 + B_2$$

These refer to the symmetries of fundamental modes, n = 1 (Fig. 24) gives a schematic representation of vibrations of H₂O which is a typical member AB₂ (bent) system.



It is needless to point out that all symmetrical (AB_2) bent type molecules will have two A_1 vibrational modes and one B_2 mode. If we perform the four group operations on the two A_1 vibrational modes, i.e., on the structures listed in Fig. 24. They are symmetric (+1) with respect to all the operations and the assignment A_1 is correct. If we perform the same four operations on the mode shown as B_2 we observe the following.

Identity leaves it indistinguishable. C_2 and σ_v^{xy} yield configurations in which the vectors are exactly turned into opposite directions and its is antisymmetric (-1). σ_v^{xz} leaves it unchanged and hence the mode is symmetric with respect to this operation. Thus the assignment B_2 is valid.

Selection rules for infrared spectra

The selection rules for infrared absorption is essentially the same as that of the electronic spectroscopy.

A fundamental will be infrared active if the excited normal mode belongs to one of the irreducible representations corresponding to X, Y and Z vectors, and will be inactive if it does not i.e., there should be non-zero transition dipole moment. If ψ_2 is the vibrational wave function of the state upper and ψ_1 , that of the lower state.

$$\mu = e \int \psi_1 \tau \psi_2 d\tau$$

For the fundamental absorption $n = 0$ to $n = 1$, note $n = 0$ state transforms like the totally symmetric representation. Atleast one of the three components viz., μ_x , μ_y or μ_z must have non-zero value for an allowed transition

$$\mu_x = e \int \psi_1 \bar{x} \psi_2 d\tau$$

$$\mu_y = e \int \psi_1 \bar{y} \psi_2 d\tau$$

$$\mu_z = e \int \psi_1 \bar{z} \psi_2 d\tau$$

$\mu_x \neq 0$ if direct product $\Gamma_1 \times \Gamma_x \times \Gamma_2$ contains totally symmetric representation or transforms like a totally symmetric representation.

Similar rules can be stated for μ_y and μ_z also. The transition is polarized along the direction for which the transition moment component has non-zero value.

We illustrate the use of this rule by discussing the infrared spectrum of H_2O . H_2O has three normal modes. $[(3 \times 3) - 6] = 3$ two of them are A_1 type and third one is of B_2 type.

A_1 mode; μ_z : Direct product is $\Gamma_1 \times \Gamma_2 \times \Gamma_2$

$$= A_1 \times A_1 \times A_1 = A_1$$

$$\mu_z \neq 0$$

μ_x : Direct products is $\Gamma_1 \times \Gamma_x \times \Gamma_2$

$$= A_1 \times B_1 \times A_1 = B_1$$

$$\mu_x = 0$$

$$\mu_y = \text{Direct product is } \Gamma_1 \times \Gamma_y \times \Gamma_2$$

$$= A_1 \times B_1 \times A_1 = B_2$$

$$\mu_y = 0$$

The two A_1 fundamentals are allowed and are polarized along z-direction

$$B_2 \text{ mode: } \mu_x: \text{Direct product } \Gamma_1 \times \Gamma_x \times \Gamma_2$$

$$= A_1 \times B_1 \times B_2 = A_2$$

$$\mu_x = 0$$

$$\mu_y: \text{Direct products is } \Gamma_1 \times \Gamma_y \times \Gamma_2$$

$$= A_1 \times B_2 \times B_2 = A_1$$

$$\mu_y \neq 0$$

$$\mu_z: \text{Direct product is } \Gamma_1 \times \Gamma_x \times \Gamma_2$$

$$= A_1 \times A_1 \times B_2 = B_2$$

$$\mu_z = 0.$$

B_2 mode is allowed and is y polarized.

Selection rules for Raman spectra

A vibration that causes a change in dipole moment is infrared active. On the other hand a vibration that causes a change in induced dipole moment is Raman active. A change in induced dipole moment results from the change in polarizability α of the molecule.

i.e., A fundamental transition will be Raman active if the corresponding normal mode belongs to the same irreducible representation as one or more of the components of the polarizability tensor.

The induced dipole moment μ (induced) is given by the expression.

$$\mu_{(ind)} = \alpha E$$

The components are given by the equations

$$\mu_x (ind) = \alpha_{xx} E_x + \alpha_{xy} E_y + \alpha_{xz} E_z$$

$$\mu_y (ind) = \alpha_{yx} E_x + \alpha_{yy} E_y + \alpha_{yz} E_z$$

$$\mu_z (\text{ind}) = \alpha_{zx}E_x + \alpha_{zy}E_y + \alpha_{zz}E_z$$

where E_x , E_y and E_z are the components of the electric field and $\alpha_{xx}, \alpha_{xy}, \alpha_{xz}, \dots, \alpha_{zz}$ are the components of the polarizability tensor.

For C_{2v} structure of SF_4 molecule, all the nine fundamental vibrations are Raman active and four modes will be polarized.

In the case of the molecules having a center of symmetry the infrared active modes are Raman inactive and Raman active modes are infrared inactive. This is known as mutual exclusion rule and can be stated as follows. In the case centrosymmetric molecules infrared active vibrational modes are Raman inactive and Raman active modes are infrared inactive.

Mutual exclusion principle can be deduced from the following observations:

- The direct product of the functions forming the transition moment must be 'g' for an allowed transition. If it is 'u' the transition moment is 0.
- The Cartesian coordinates x , y and z (occurring in the dipole moment vector $\vec{\mu}$ for infrared transitions) are of 'u' symmetry as

$$\begin{aligned} x & \text{---} \rightarrow -x; \\ y & \text{---} \rightarrow -y; \\ z & \text{---} \rightarrow -z \end{aligned}$$

on inversion. But the binary products of the Cartesian coordinates such as x^2 , xy , yz , etc., occurring in the polarizability tensor (for Raman spectra) are obviously of 'g' symmetry.

Thus, for the IR active modes,

$$\mu = \int \text{functions} \times \int \frac{d}{dt} = \int \text{functions} \times u$$

This must be 'g' for $\mu \neq 0$ hence $\int (\text{functions})$ must be 'u' But if $\int \text{functions} = \text{'u'}$

$$\int \text{functions} \times \int_a = u \times g = u$$

Therefore, the transition moment is zero, i.e., the IR mode is Raman active.

Furthermore spectroscopists know that the fundamentals belonging to the totally symmetric irreducible representations are seen polarized in the Raman spectrum. While all the three modes of water are infrared as well as Raman active, in the case of CO_2 the exclusion rule predicts that the Raman active modes For example in the case of MX_4 (square planar), a_{1g} and b_{2g} are Raman active while a_{2u} and b_{2u} are infrared active. In the case fumarate ion (C_{2h}) there are twelve infrared active modes ($4a_u + 8b_u$) and twelve Raman active modes ($9a_g + 3b_g$).

Symmetry of hybrid atomic orbitals

The structure and shape of molecules can often be well described by postulating that atoms use hybrids or mixed orbitals rather than atomic orbitals for binding. For example it can be shown that in the formation of methane molecule with its regular tetrahedral geometry, carbon utilizes one s-orbital and three p-orbitals to yield four new equivalent hybrid atomic orbitals. In this section we shall employ group theory and obtain the atomic orbitals that hybridise to give hybrid orbitals of specified spatial orientation such as tetrahedral, square pyramidal etc.

Tetrahedral hybridization

Let us take CH_4 . The four C-H bonds are directed towards the corners of a regular tetrahedron. This fact is well established by experiment. We can inscribe CH_4 in a cube. Let the four hybrid orbitals be designated as h_1, h_2, h_3 and h_4 respectively (Fig. 25).

Let us subject these four hybrid orbitals to the operations of TD group to which CH_4 belongs, and find the corresponding matrices. The operations are E, C_3 , C_2 and σ_d . For E we have obviously,

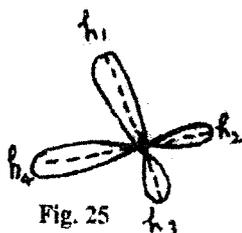


Fig. 25

$$E = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix}$$

character with respect to E is therefore 4.

If we subject the molecule to C_3 operation with respect to h_1 axis, we obtain the following results:

$$h_1 \longrightarrow h_1; h_2 \longrightarrow h_3; h_3 \longrightarrow h_4; h_4 \longrightarrow h_2$$

$$C_3 h_1 = 1h_1 + 0h_2 + 0h_3 + 0h_4$$

$$C_3 h_2 = 0h_1 + 0h_2 + 1h_3 + 0h_4$$

$$C_3 h_3 = 0h_1 + 0h_2 + 0h_3 + 1h_4$$

$$C_3 h_4 = 0h_1 + 1h_2 + 0h_3 + 0h_4$$

$$C_3 \text{ w.r.t. } h_1 \text{ axis} = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix}$$

The character is therefore equal to one.

We note that there are six σ_d planes. Each one is formed by a pair of C-H bonds. Let us take the plane formed by h_1 and h_2 effect reflections with respect to this plane. h_1 and h_2 are unchanged h_3 goes over to the position of h_4 and vice versa.

$$h_1 \rightarrow h_1; h_2 \rightarrow h_2; h_3 \rightarrow h_4; h_4 \rightarrow h_3$$

The transformation matrix for this is

$$\sigma_d = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix}$$

The character is two. Recall that we can down the characters even without explicitly writing down the transformation matrix. For identify all the four vectors (hybrids) are unchanged in position and sign and hence the character is equal to 4. For C_3 specified above only one vector is unchanged in position and sign and the rest have got shifted. Hence the character is equal to one. Similarly for σ_d we obtain the characters as 2 and for S_4 it is 0. We have thus shown that the four hybrids for a representation with the following characters.

	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$
Γ_h	4	1	0	0	2

Γ_h is the reducible representation obtained by the transformation of the four tetrahedral hybrid orbitals. Let the four pure atomic orbitals combining to yield the four hybrids h_1, h_2, h_3, h_4 . These are the atomic orbitals of carbon atom. Let $\Gamma_1, \Gamma_2, \Gamma_3$ and Γ_4 be the irreducible representations of T_d group corresponding to ϕ_1, ϕ_2, ϕ_3 and ϕ_4 respectively. Γ_h is easily reduced to $\Gamma_h = A_1 + T_2$. Thus it is clear that tetrahedral hybridization must result by a combination of a single pure atomic orbitals of A_1 symmetry and three degenerate orbitals jointly belonging to T_2 representation. Examining the character table for T_d group and identifying the transforming vectors we find the following. Any 's' type orbital being invariant transforms like A_1 (x, y, z) or (xy, yz, zx) act as bases for T_2 .

We also known that P_x, P_y and P_z transform like vectors x, y and z respectively and that d_{xy}, d_{yz} and d_{zx} transform like xy, yz and zx respectively. These can be proved in other ways also. Thus,

$p_x = \text{constant} \cdot \sin\theta \cos\phi$	$d_{xy} = \text{constant} \cdot \sin^2\theta \sin\phi \cos\phi$
$p_y = \text{constant} \cdot \sin\theta \sin\phi$	$d_{yz} = \text{constant} \cdot \sin\theta \cos\theta \sin\phi$
$p_z = \text{constant} \cdot \cos\theta$	$d_{zx} = \text{constant} \cdot \sin\theta \cos\theta \cos\phi$

d_{xy} can be expressed in terms of angle 2θ by remembering the fact that $\cos 2\theta = 2 \sin\theta \cos\theta$

We also know that the Cartesian coordinates (x, y, z) are transformed into polar coordinates by the following relations.

$$x = r \sin\theta \cos\phi$$

$$y = r \sin\theta \sin\phi$$

$$z = r \cos\theta$$

$$p_x = \text{constant } x$$

$$p_y = \text{constant } y$$

$$p_z = \text{constant } z$$

we see that

$$d_{xy} = \text{constant } (xy)$$

$$d_{yz} = \text{constant } (yz)$$

$$d_{xz} = \text{constant } (xz)$$

The exact constants in these equations are not needed here for considering the symmetry properties. Thus the tetrahedral hybrids are formed by the combination of one s -orbital and three p -orbitals viz., p_x , p_y and p_z . In a similar manner the hybridization in BF_3 and ethylene molecule may be discussed.

Symmetries of π -Mo's of

This belongs to D_{2h} point group, but we shall assume a lower point group like D_2 . The ten p_z orbitals located on carbon atoms numbered 1, 2, ..., 10 are referred to as $\phi_1, \phi_2, \dots, \phi_{10}$ respectively (Fig. 26).

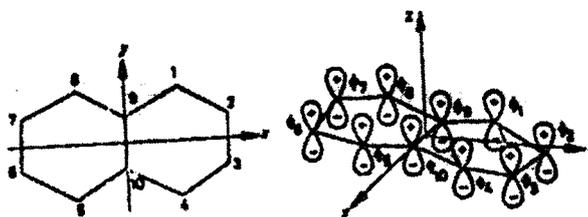


Fig. 26 Numbering and axis system for naphthalene

Let us subject all the ten p_z orbitals $\phi_1, \phi_2, \dots, \phi_{10}$ to the four operations of D_2 viz., E, C_{2x}, C_{2y} and C_{2z} . We recall the following rule for finding out the characters of the transformation matrices from reducible and irreducible representation. Assign zero to orbitals shifted, to each orbital unshifted in position and unchanged in sign is +1. To each orbital unshifted in position and changed in sign is -1. Add all these contributions to get the character. Thus T_ϕ will be as follows:

	E	C_{2x}	C_{2y}	C_{2z}
T_ϕ	10	0	-2	0

Reduction of T_ϕ into I.R.'s gives

$$T_\phi = 2A_1 + 3B_1 + 2B_2 + 3B_3.$$

The symmetries of π Mo's in D_{2h} point group are $\rho = 2A_u + 3B_{1u} + 2B_{2g} + 3B_{3g}$

Electronic Transitions in simple molecules :

Ex :Formaldehyde

Formaldehyde has three σ bonding MO's (two σ_{CH} and σ_{CO}) is an approximate "localized MO" scheme where we consider the electron pairs to be localized in bonds. For each bonding σ MO there is a higher energy antibonding σ^* MO.

There is a C - O π bond MO and a corresponding antibonding π^* MO. There are two different orbitals on oxygen accommodating non-bonding electrons (n -orbitals). Formaldehyde is planar and it belongs to C_{2v} point group. Let us find the symmetries of the orbitals of co group (Fig. 27).

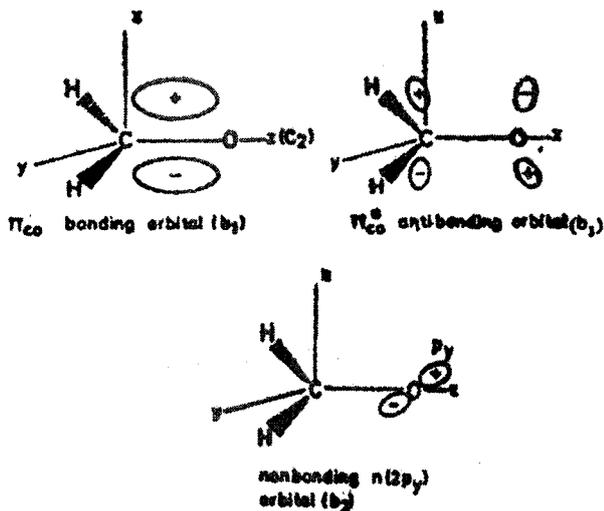


Fig. 27 Symmetries of the orbitals of formaldehyde

σ bonding orbital of co group (σ_{CO})

$$E \sigma_{CO} = \sigma_{CO}$$

$$C_2 \sigma_{CO} = \sigma_{CO}$$

$$\sigma_{xz} \sigma_{CO} = \sigma_{CO}$$

Hence σ_{CO} belongs to a_1 representations. Similarly π^* co (antibonding) orbitals also transforms like a_1 , π bonding orbital of co (π_{CO}) transforms as follows.

$$E \pi_{CO} = \pi_{CO}$$

$$C_2 \pi_{CO} = -\pi_{CO}$$

$$\sigma_{xz}\pi = \pi$$

$$\sigma_{yz}\pi = -1 \pi$$

Hence π_{CO} transforms as b_2

Similarly π^*_{CO} (antibonding π orbital) also belongs to b_1 symmetry. The non-bonding orbital $2P_y$ on oxygen atom transform like y and hence like b_2 .

Let us examine symmetries of excited state i.e. π, π^* state is the one obtained by exciting an electron from non-bonding orbital to π^* ($n - \pi^*$ transition). An other excited state, i.e., π, π^* state is the one obtained by exciting an electron from a π orbital π^* ($\pi^* \rightarrow \pi^*$ transitions)

$$n, \pi^* \text{ state} = (\sigma_{CO})^2 (\pi_{CO})^2 (n)^1 (\pi^*_{CO})^1$$

$$= a_1. a_1. b_2. b_1 = A_2$$

$$\pi, \pi^* \text{ state} = (\sigma_{CO})^2 (\pi_{CO})^1 (n)^2 (\pi^*_{CO})^1$$

$$= a_1. b_1. a_1. b_1 = A_1.$$

Thus it is seen that the configuration n, π^* and π, π^* have symmetries A_2 and A_1 respectively.

The Hückel Molecular Orbital (HMO) Theory

E. Huckel presented a simplified form of MO theory for π -systems by introducing the following set of approximations:

1. σ, π Separation

It is first assumed that π -electrons in a conjugated molecule do not interact with σ -electrons. The complete molecular wave function being,

$$\Psi = \Psi_{\sigma}, \Psi_{\pi}$$

and the molecular energy,

$$E = E_{\sigma} + E_{\pi}$$

This enables one to treat the π MO's independently of the σ MO's.

2. Free π electron approximation

It is further assumed that the total π -electron wave function, Ψ_{π} , is a angle product of one-electron functions (the Hückel MO's) and not a determinant. The total energy of the π -electrons is then the sum of the one electron (HMO) energies. For a system of n π -electrons in the ground state, (with n even)

$$\psi_x = \psi_1 (1) \bar{\psi}_1 (2) \bar{\psi}_x (3) \bar{\psi}_2 (4) \dots \bar{\psi}_{n/2} (n-1) \bar{\psi}_{n/2} (n) \quad \dots (1)$$

where ψ_x is the i th HMO.

The energy is given by the relation,

$$E_x = (n_1 E_1 + n_2 E_2 + \dots + n_n E_n) \quad \dots (2)$$

Where E_i is the energy of a single electron in ψ_i ; the factors n_i may be 1 or 2 or 0 depending upon whether the HMO ψ_i is singly or doubly occupied or unoccupied.

Each ψ is an approximate solution of a one-electron Schrodinger equation,

$$\hat{H} (t) \psi_i = E_i \psi_i \quad \dots (3)$$

3. LCAO π -MO

The equation (3) is never solved. Each HMO (ψ_i) is taken as a linear combination of the carbon $2P_z$; AO's,

$$\begin{aligned} \psi_i &= a_{i1} p_1 + a_{i2} p_2 + \dots + a_{in} p_n \\ &= \sum_{r=1}^n a_{ir} p_r \quad \dots (4) \end{aligned}$$

where ψ_i is the i th HMO of the π -system, p_r is the $2p$, AO of the r th carbon atom and a_{ir} is the coefficient of the r th AO in the i th HMO.

The HMO method is confined to carbon atoms only; orbitals of H atoms are not considered at all.

4. The energy of the HMO

The energy of the HMO is calculated by the formula,

$$E_i = \frac{\int \psi_i \hat{H} \psi_i d\tau}{\int \psi_i^2 d\tau} \quad \dots (5)$$

assuming ψ_i to be real

5. The Secular equation

Variation treatment leads to n Secular equations of the type

$$a_1 (H_{11} - ES_{11}) + a_2 (H_{12} - ES_{12}) + \dots + a_n (H_{1n} - ES_{1n}) = 0$$

$$a_1 (H_{21} - ES_{21}) + a_2 (H_{22} - ES_{22}) + \dots + a_n (H_{2n} - ES_{2n}) = 0$$

$$\dots \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots$$

$$\dots \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots$$

Thus for a linear conjugated chain the secular determinantal equation (7) now assumes the form,

$$\begin{vmatrix} \alpha - E & \beta & 0 & 0 & \dots & \dots & \dots & 0 \\ \beta & \alpha - E & \beta & 0 & \dots & \dots & \dots & 0 \\ 0 & \beta & \alpha - E & \beta & 0 & \dots & \dots & 0 \\ \dots & \dots \\ \dots & \dots \\ 0 & 0 & 0 & 0 & 0 & 0 & \beta & \alpha - E \end{vmatrix} = 0 \quad \dots (10)$$

(d) The equation (10) can be made still simpler if we divide each element by β and put $\frac{\alpha - E}{\beta} = x$. The determinant now becomes,

$$\begin{vmatrix} x & 1 & 0 & 0 & \dots & \dots & 0 \\ 1 & x & 1 & 0 & \dots & \dots & 0 \\ 0 & 1 & x & 1 & 0 & \dots & 0 \\ \dots & \dots & \dots & \dots & \dots & \dots & \dots \\ \dots & \dots & \dots & \dots & \dots & \dots & \dots \\ 0 & 0 & 0 & 0 & \dots & 0 & \dots & 1 & x \end{vmatrix} = 0 \quad \dots (11)$$

This determinant reveals some interesting features. It is seen that x appears on the principal diagonal. The number 1 appears in positions where the indices r and s correspond to bonded carbon atoms (e.g. H_{12} , H_{21} , H_{23} , etc.) and 0 appears where they are not bonded (e.g. H_{13} , H_{14} , etc.). This generalization enables one to write the Hückel determinant for an unsaturated conjugated hydrocarbon by looking at the structure of the molecule. The determinant may be constructed easily by the following procedure:

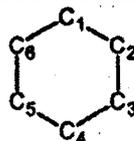
- (i) Sketch the framework of the hydrocarbon indicating the carbon atoms;
- (ii) Number the carbon atoms 1, 2, 3 n;
- (iii) Fill the $n \times n$ determinant with x 's on the principle diagonal, 1 in positions where row-column indicates correspond to neighbours and zero everywhere else; and
- (iv) Check that the determinant is symmetric with respect to reflection through the principal diagonal.

The following two examples of butadiene and benzene will serve to explain the procedure. The skeletal framework of the molecules is shown below along with numbering of the carbon atoms.



Butadiene (C_4H_6)

(I)



Benzene (C_6H_6)

(II)

The 4×4 determinant (I) in the first case and the 6×6 determinant (II) in second case will be obtained by following step (III):

	1	2	3	4
1	x	1	0	0
2	1	x	1	0
3	0	1	x	1
4	0	0	1	x

(I)

	1	2	3	4	5	6
1	x	1	0	0	0	1
2	1	x	1	0	0	0
3	0	1	x	1	0	0
4	0	0	1	x	1	0
5	0	0	1	x	1	1
6	1	0	0	0	1	X

(II)

(Hückel determinants for butadiene and benzene)

Application to simple π -system

Ethylene

The skeletal framework of ethylene is $\text{C}_1 - \text{C}_2$. The π -HMO may be written as,

$$\psi = a_1 p_1 + a_2 p_2 \quad \dots (12)$$

where p_1 and p_2 are the p_x AO's associated with the carbon atoms C_1 and C_2 , treating the molecular plane as the xy plane. For this system, the Hückel determinant equation is,

$$\begin{vmatrix} \alpha - E & \beta \\ \beta & \alpha - E \end{vmatrix} = 0$$

(or)

$$\begin{vmatrix} x & 1 \\ 1 & x \end{vmatrix} = 0 \quad \dots (13)$$

where

$$x = \frac{\alpha - E}{\beta}$$

(or)

$$x^2 - 1 = 0,$$

$$x = \pm 1 \quad \dots (14)$$

Corresponding to $x = -1$ and $+1$; the two HMO energies are,

$$E_1 = \alpha + \beta \quad \dots (15)$$

$$E_2 = \alpha - \beta \quad \dots (16)$$

E_1 , which is less than α (since β is negative), is the bonding and E_2 the antibonding energy level (Fig. 28).

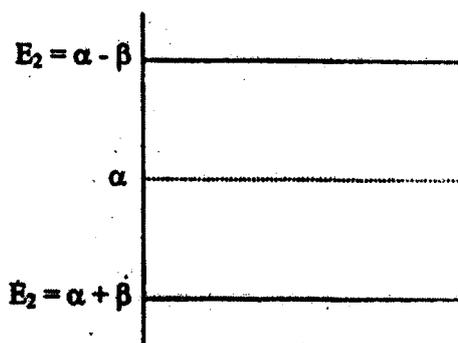


Fig. 28. The two HMO levels of ethylene.

The π -Bond Energy: In the ground state, the two electrons of ethylene were in the lower energy level (E_1) with a total energy $E_\pi = 2(\alpha + \beta)$. In the absence of bonding, the total

energy of the two electrons (lying in the two p_z AO's) would be 2α . The π bond energy is, therefore,

$$2(\alpha + \beta) - 2\alpha = 2\beta$$

The coefficients and the HMO functions: The secular equations are,

$$\left. \begin{aligned} a_1(\alpha - E) + a_2\beta &= 0 \\ a_1\beta + a_2(\alpha - E) &= 0 \end{aligned} \right\} \dots (17)$$

or,

$$\left. \begin{aligned} a_1x + a_2 &= 0 \\ a_1 + a_2x &= 0 \end{aligned} \right\} \dots (18)$$

For the bonding level ($x = -1$),

$$-a_1 + a_2 = 0 \quad \text{or} \quad a_1 = a_2$$

and $a_1^2 + a_2^2 = 1$ (by normalization condition).

Hence, $a_1 = a_2 = \frac{1}{\sqrt{2}}$, and

$$\psi_1 = \frac{1}{\sqrt{2}}(p_1 + p_2) \dots (19)$$

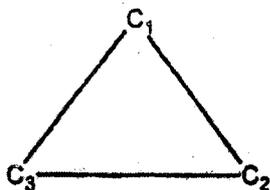
Similarly, for the antibonding level ($x = +1$)

$$a_1 = -a_2 = \frac{1}{\sqrt{2}}$$

and

$$\psi_2 = \frac{1}{\sqrt{2}}(p_1 - p_2) \dots (20)$$

Cyclopropenyl system. The skeletal framework for this molecule is,



The HMO function for this system is

$$\psi = a_1 p_1 + a_2 p_2 + a_3 p_3 \quad \dots (21)$$

The secular determinant in this case also is of their order, however, C_1 and C_3 here are neighbours, so

$$H_{12} = H_{21} = H_{13} = H_{31} = H_{23} = H_{32} = \beta$$

In terms of x ,

$$\begin{vmatrix} x & 1 & 1 \\ 1 & x & 1 \\ 1 & 1 & x \end{vmatrix} = 0 \quad \dots (22)$$

The determinant leads to the polynomial equation

$$x^3 - 3x + 2 = 0 \quad \dots (23)$$

This can be easily factorised into

$$(x + 2)(x^2 - 2x + 1) = 0$$

One of the roots of eq. (23) will be $x = -2$ while the other two roots will be identical i.e., $x = 1$.

$$x_1 = -2, x_2 = 1 \text{ and } x_3 = 1 \quad \dots (24)$$

The three corresponding π -energy levels are,

$$E_1 = \alpha + 2\beta, E_2 = E_3 = \alpha - \beta \quad \dots (25)$$

Thus, two of the levels (E_2 and E_3) are degenerate.

The ground state π -electron distribution in the three HMO's of the cyclopropenyl carbonium ion, radical and carbanion is show in Fig. 29.

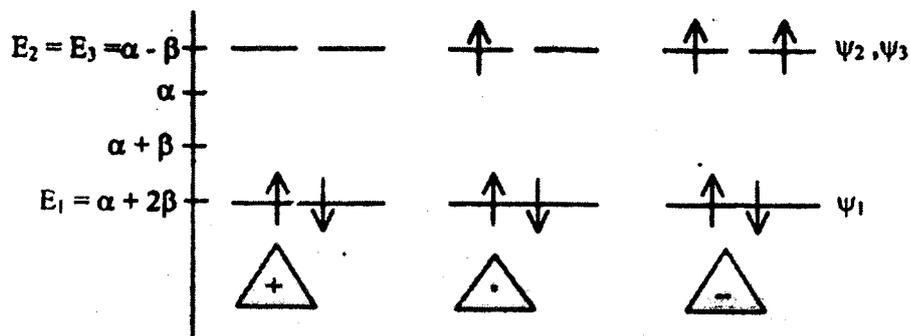


Fig. 29. π -electron distribution in the cyclopropenyl systems

The total energy, E_x , and the delocalisation energy for the three systems (Fig. 29) are,

Cyclopropenyl carbonium ion:

$$E_x = 2(\alpha + 2\beta)$$

$$\text{D.E.} = 2(\alpha + 2\beta) - 2(\alpha + \beta) = 2\beta$$

Cyclopropenyl radical:

$$E_x = 2(\alpha + 2\beta) + (\alpha - \beta) = 3\alpha + 3\beta$$

$$\text{D.E.} = (3\alpha + 3\beta) - (2\alpha + 2\beta) - \alpha = \beta$$

Cyclopropenyl carbanion:

$$E_x = 2(\alpha + 2\beta) + 2(\alpha - \beta) = 4\alpha + 2\beta$$

$$\text{D.E.} = (4\alpha + 2\beta) - (2\alpha + 2\beta) - 2\alpha = 0$$

This leads to the prediction that in the cyclopropenyl system, the carbonium ion will be more stable than the radical or the carbanion.

The HMO-coefficients: In terms of x , the secular equations for the cyclopropenyl are,

$$\left. \begin{aligned} a_1 x + a_2 + a_3 &= 0 \\ a_1 + a_2 x + a_3 &= 0 \\ a_1 + a_2 + a_3 x &= 0 \end{aligned} \right\} \dots (26)$$

For $x = -2$, we have

$$-2a_1 + a_2 + a_3 = 0 \dots (27)$$

$$a_1 - 2a_2 + a_3 = 0 \dots (28)$$

$$a_1 + a_2 - 2a_3 = 0 \dots (29)$$

From (27) and (29), we get $-3a_1 + 3a_2 = 0$

or

$$a_1 = a_2$$

Also, from (28) and (29), we get $-3a_2 + 3a_3 = 0$

or

$$a_2 = a_3$$

From the normalization condition,

$$a_1^2 + a_2^2 + a_3^2 = 1$$

or $3a_1^2 = 1$ or $a_1 = a_2 = a_3 = \frac{1}{\sqrt{3}}$... (30)

Thus,

$$\psi_1 = \frac{1}{\sqrt{3}}(p_1 + p_2 + p_3) \quad \dots (31)$$

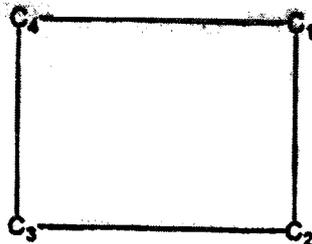
Similarly

$$\psi_2 = \frac{1}{\sqrt{2}}(p_1 - p_3) \quad \dots (32)$$

$$\psi_3 = \frac{1}{\sqrt{6}}p_1 - \frac{2}{\sqrt{6}}p_2 + \frac{1}{\sqrt{6}}p_3 \quad \dots (33)$$

Further, any linear combinations of the degenerate MO's which satisfy the orthogonality and normalization conditions, will be equally valid MO's

Cyclobutadiene



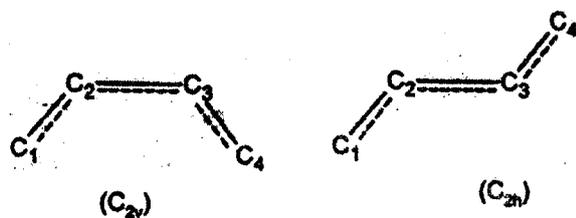
The HMO's are of the form

$$\psi = a_1p_1 + a_2p_2 + a_3p_3 + a_4p_4 \quad \dots (34)$$

since $H_{14} = H_{41} = \beta$, the secular determinant, in terms of x is

$$\begin{vmatrix} x & 1 & 0 & 1 \\ 1 & x & 1 & 0 \\ 0 & 1 & x & 1 \\ 1 & 0 & 1 & x \end{vmatrix} = 0 \quad \dots (35)$$

The *cis*-butadiene belongs to C_{2v} point group and the *trans* isomer to C_{2h} point group.



For the *trans* isomer (C_{2h}), the following reducible representation may be constructed.

$C_{2h}: E$	C_2	σ_h	i	Basis
$\Gamma_r: 4$	0	0	4	(p_1, p_2, p_3, p_4)

By eq. (), it reduces as

$$\Gamma_r = 2A_u + 2B_g \quad \dots (36)$$

We may construct one of the two SALC's of A_u type as follows.

$$\begin{aligned} \psi(A_u) &= \frac{1}{4} [X(E) \cdot E p_1 + X(C_2) C_2 p_1 + X(i) i p_1 + X(\sigma_h) \sigma_h p_1] \\ &= \frac{1}{4} [E p_1 + C_2 p_1 - i p_1 - \sigma_h p_1] \text{ (using the character table of } C_{2h}) \\ &= \frac{1}{4} [p_1 + p_4 - (-p_4) - (-p_1)] \\ &= \frac{1}{2} [p_1 + p_4] = \phi_1 \text{ (say)} \quad \dots (37) \end{aligned}$$

For the other SALC of A_u , we use p_2 in Eq. () and obtain,

$$\psi(A_u) = \frac{1}{2} (p_2 + p_3) = \phi_2 \text{ (say)} \quad \dots (38)$$

Similarly, using p_1 and p_2 , we obtain the SALC's of B_g type,

$$\psi(B_g) = \frac{1}{2} (p_1 - p_4) = \phi_3 \quad \dots (39)$$

$$\psi(B_g) = \frac{1}{2} (p_2 - p_3) = \phi_4 \quad \dots (40)$$

use of p_3 and p_4 , we will generate the same set of SALC's.

The linear combination of functions ϕ_1, ϕ_2, ϕ_3 and ϕ_4 will lead to the secular determinant

$$\begin{vmatrix} H_{11} - S_{11} E & H_{12} - S_{12} E & H_{13} - S_{13} E & H_{14} - S_{14} E \\ H_{21} - S_{21} E & H_{22} - S_{22} E & H_{23} - S_{23} E & H_{24} - S_{24} E \\ H_{31} - S_{31} E & H_{32} - S_{32} E & H_{33} - S_{33} E & H_{34} - S_{34} E \\ H_{41} - S_{41} E & H_{42} - S_{42} E & H_{43} - S_{43} E & H_{44} - S_{44} E \end{vmatrix} = 0 \quad \dots (41)$$

where

$$H_{ij} = \int \phi_i \hat{H} \phi_j d\tau, \quad \text{and } S_{ij} = \int \phi_i \phi_j d\tau$$

Now integrals will be zero if the functions ϕ_1 and ϕ_j belong to different symmetry type. This sets,

$$H_{13} = H_{32} = H_{24} = H_{41} = H_{23} = H_{32} = H_{24} = H_{42} = 0$$

$$S_{13} = S_{31} = S_{14} = S_{41} = S_{23} = S_{32} = S_{24} = S_{42} = 0$$

For example,

$$\begin{aligned} H_{13} &= \int \phi_1 \hat{H} \phi_3 d\tau = \frac{1}{4} \int (p_1 + p_4) \hat{H} (p_1 - p_4) d\tau \\ &= \frac{1}{4} \left[\int p_1 \hat{H} p_1 d\tau + \int p_4 \hat{H} p_1 d\tau - \int p_1 \hat{H} p_4 d\tau - \int p_4 \hat{H} p_4 d\tau \right] \\ &= \frac{1}{4} [\alpha + 0 - 0 - \alpha] = 0 \end{aligned}$$

$$\text{where } \alpha = \int p_1 \hat{H} p_1 d\tau$$

The determinant takes the form,

$$\begin{vmatrix} H_{11} - S_{11} E & H_{12} - S_{12} E & 0 & 0 \\ H_{21} - S_{21} E & H_{22} - S_{22} E & 0 & 0 \\ 0 & 0 & H_{33} - S_{33} E & H_{34} - S_{34} E \\ 0 & 0 & H_{43} - S_{43} E & H_{44} - S_{44} E \end{vmatrix} = 0 \quad \dots (42)$$

which is block-diagonalised or symmetry-factored. The equation (42) can be satisfied only if each block is equal to zero;

$$\begin{vmatrix} H_{11} - S_{11} E & H_{12} - S_{12} E \\ H_{21} - S_{21} E & H_{22} - S_{22} E \end{vmatrix} = 0, \quad \begin{vmatrix} H_{33} - S_{33} E & H_{34} - S_{34} E \\ H_{43} - S_{43} E & H_{44} - S_{44} E \end{vmatrix} = 0$$

(A₁)

(B₂)

... (43)

Thus, instead of the 4×4 determinant, we get two 2×2 determinants. It is easier to work with 2×2 determinants. In terms of Hückel parameters α and β , we get

$$H_{11} = H_{33} = \frac{1}{2} \alpha \quad H_{12} = H_{21} = H_{34} = H_{43} = \frac{1}{2} \beta$$

$$H_{22} = \frac{1}{2} (\alpha + \beta)$$

$$H_{44} = \frac{1}{2} (\alpha - \beta)$$

[For example, $H_{11} = \int \phi_1 \hat{H} \phi_1 d\tau$

$$= \frac{1}{4} \int (p_1 + p_4) \hat{H} (p_1 + p_4) d\tau$$

$$= \frac{1}{4} \left[\int p_1 \hat{H} p_1 d\tau + \int p_4 \hat{H} p_4 d\tau - \int p_4 \hat{H} p_1 d\tau - \int p_1 \hat{H} p_4 d\tau \right]$$

$$= \frac{1}{4} [\alpha + 0 - 0 - \alpha] = \frac{1}{2} \alpha$$

The integrals

$$S_{ij} = \frac{1}{2} \text{ and } S_{ij} = 0$$

The Eq (43) may be written as,

$$\begin{vmatrix} \frac{1}{2}(\alpha - E) & \frac{1}{2}\beta \\ \frac{1}{2}\beta & \frac{1}{2}(\alpha + \beta - E) \end{vmatrix} = 0 \quad \text{and} \quad \begin{vmatrix} \frac{1}{2}(\alpha - E) & \frac{1}{2}\beta \\ \frac{1}{2}\beta & \frac{1}{2}(\alpha - \beta - E) \end{vmatrix} = 0$$

(A₀) (B₀)

... (44)

or, putting $\frac{\alpha - E}{\beta} = x$, we get

$$\begin{vmatrix} x & 1 \\ 1 & x+1 \end{vmatrix} = 0 \quad \text{and} \quad \begin{vmatrix} x & 1 \\ 1 & x-1 \end{vmatrix} = 0$$

(A₀) (B₀)

... (45)

... (46)

On expanding, the determinant belonging to A₀ gives,

$$x^2 + x - 1 = 0 \text{ or } x = \frac{1 \pm \sqrt{5}}{2} = -1.618 \text{ and } 0.618$$

The other determinant (B₀) gives,

$$x^2 - x - 1 = 0, \text{ or } x = \frac{1 \pm \sqrt{5}}{2} = 1.618 \text{ and } -0.618$$

Using these values of x in equation (46), we obtain the four energy levels as

$$\begin{aligned} E_1 &= \alpha + 1.618 \beta & \dots (A_u) \\ E_2 &= \alpha + 0.618 \beta & \dots (B_g) \\ E_3 &= \alpha - 0.618 \beta & \dots (A_u) \\ E_4 &= \alpha - 1.618 \beta & \dots (B_g) \end{aligned} \quad \dots (47)$$

Where $E_1 < E_2 < E_3 < E_4$

We have seen earlier that SALC's of same symmetry type may be combined, so the HMO's are, $\psi = a_i \phi_i + a_j \phi_j$... (48)

We thus need to determine only two coefficients instead of four. Use of symmetry properties has simplified our job.

Corresponding to A_u symmetry, the HMO is,

$$\psi = a_1 \phi_1 + a_2 \phi_2 = \frac{1}{2} a_1 (p_1 + p_4) + \frac{1}{2} a_2 (p_2 + p_3) \quad \dots (49)$$

For $x = -1.618$, the HMO, ψ_1 , is

$$\begin{aligned} \psi_1 &= 0.744 \phi_1 + 1.204 \phi_2 \\ &= 0.372 p_1 + 0.602 p_2 + 0.602 p_3 + 0.372 p_4 \end{aligned} \quad \dots (56)$$

(in view of (37) and (38)).

The other value of x ($= +0.618$), similarly, yields another HMO of the same symmetry (A_u); but since this corresponds to the energy E_2 , we shall number it as ψ_3 ;

$$\psi_3 = 0.602 p_1 - 0.372 p_2 - 0.372 p_3 + 0.602 p_4 \quad \dots (57)$$

Using SALC's of B_g type (ϕ_3 and ϕ_4) we likewise construct the HMO's of the B_g symmetry, which are,

$$\psi_2 = 0.602 p_1 + 0.372 p_2 - 0.372 p_3 - 0.602 p_4 \quad \dots (58)$$

$$\psi_4 = 0.372 p_1 - 0.602 p_2 + 0.602 p_3 - 0.372 p_4 \quad \dots (59)$$

Corresponding to the energy levels E_2 and E_4 respectively.

Each HMO can accommodate two electrons so that the group theory notation for the ground state configuration of the π electrons is $A_u^2 E_g^2$.

Questions

1.
 - a. What are the different types of symmetry elements?
 - b. Explain the operation improper rotation S_n with an example.
2. Identify the symmetry elements present in the following cases and assign the point groups
 - i. ethane (staggered form)
 - ii. Ammonia
 - iii. trans-dichlorethylene
 - iv. carbon-dioxide
3.
 - a. What is meant by Abelian group? Given one example.
 - b. Discuss the construction of character table for C_{2v} point group.
4.
 - a. Discuss the selection rules of infrared active, and Raman active vibrations (from character table).
 - b. State and explain mutual exclusion principle
5.
 - a. Define symmetry and symmetry elements
 - b. Write a note on character table.
 - c. Discuss the orthogonality theorem and its consequences.
6.
 - a. What is meant by axis of symmetry?
 - b. Discuss the reducible representation of point group.
 - c. Give an account of character table in relation to Raman spectra.

UNIT - IV

ORIGIN OF MOLECULAR SPECTRA

The study of the interaction of the electromagnetic waves and matter is defined as molecular spectroscopy. The electromagnetic radiation is explained in terms of the wave number $\bar{\nu}$. This is the reciprocal of the wavelength expressed in cm.

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

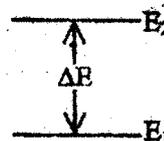


Fig. 1

Consider two possible energy state of a system E₁ and E₂ (Fig. 1). Transitions can take place between the levels E₁ and E₂ provided the appropriate amount of energy $\Delta E = E_2 - E_1$ can be either absorbed or emitted by the system. Such absorbed or emitted energy can take the respective region of electromagnetic radiation.

$$\Delta E = h\nu \text{ Joules (} h = 6.63 \times 10^{-34} \text{ Joules/molecule)}$$
$$\Delta E = hc \bar{\nu} \text{ cm}^{-1} (\because \nu = C \bar{\nu})$$

If you pass electromagnetic radiation of a single frequency ν , the molecule will absorb the energy and there will be a transition from E₁ to E₂. A detector placed to collect the radiation after the interaction with the molecule will show that its intensity has decreased. If we use a beam containing a wide range of frequencies the intensity of all other frequencies except ν remains undiminished. In this way we have produced an absorption spectrum.

If we analyse the radiation, when the molecule reverts from 2 to 1, then emission spectrum is obtained.

Regions of the spectrum

Based on the molecular or nuclear process and the range of the electromagnetic radiation. We classify different regions and different spectroscopic techniques.

Radio frequency region

The frequency of the electromagnetic radiation in this region lies in the range 3×10^6 to 3×10^{10} Hz. The spectroscopic techniques are nuclear magnetic resonance (NMR) and electron spin resonance (ESR) spectroscopy. In NMR spectroscopy the energy change involved is due to the reversal of spin of a nucleus. In ESR spectroscopy the energy change involved is due to the reversal of spin of an electron.

Microwave region

The frequency of the electromagnetic radiation in this region lies in the ranges 3×10^{10} to 3×10^{12} Hz. The technique is called rotational spectroscopy.

Infrared region

The frequency of the electromagnetic radiation in this region lies in the range of 3×10^{12} to 3×10^{14} Hz. The technique is called vibrational spectroscopy.

Visible and ultraviolet regions

The frequency of the electromagnetic radiation in this region lies in the range of 3×10^{14} to 3×10^{16} Hz. The technique is called electronic spectroscopy.

Rotational spectra-microwave spectroscopy

Microwave spectroscopy is concerned with the study of rotating molecules. For a molecule to be microwave active, it should have a permanent dipole moment. The rotation of a molecule is resolved into rotational components about 3 mutually perpendicular directions and hence a molecule has three moments of inertia (I_A , I_B and I_C). I_A refers to the direction of rotation about the bond axis. I_B and I_C refer to end-over-end rotations in the plane of the paper and at right angles to the plane respectively. Based on the values of I_A , I_B and I_C the molecules are classified into 4 types.

1. Linear molecules

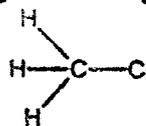
Examples: HCl, carbon oxysulphide

H-Cl, O-C-S: All the atoms are arranged in a straight line.

2. Symmetric tops

$I_A \neq 0$; $I_B = I_C$

Example, CH_3Cl



If $I_B = I_C > I_A$ then the molecule is called prolate symmetric top (CH_3Cl)

If $I_B = I_C < I_A$ then the molecule is called to be symmetric top (BCl_3).

3. Spherical tops

All the 3 moments of inertia are equal

$I_A = I_B = I_C$: Example; CH_4

Since the dipole moment is zero, rotation spectrum is not observable.

4. Asymmetric tops

All the 3 moments of inertia are different $I_A \neq I_B \neq I_C$

Example: H_2O , vinyl chloride

Rotation spectra of diatomic molecules – rigid rotator

The model for the diatomic molecule is called rigid rotator (Fig. 2). It consists of two masses m_1 and m_2 connected by a rigid bar of length r_0 .

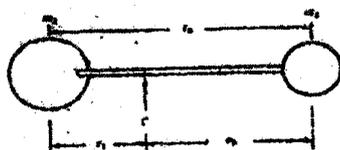


Figure 2. A rigid diatomic molecule treated as two masses m_1 , and m_2 , joined by a rigid bar of length $r_0 = r_1 + r_2$

A rigid diatomic molecule treated as two masses, m_1 and m_2 joined by a rigid bar of length $r_0 = r_1 + r_2$.

By the use of the Schrodinger equation we get the following equation for the allowed rotational energy levels

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

J is called the rotational quantum number. It can take integral values from zero upwards. Substituting the values of J the following energy level diagram is obtained. The allowed energy levels of a rigid diatomic molecule is given in Fig. 3.

J	ϵ_J
5	30B
4	20B
3	12B
2	6B
1	2B
0	0

Fig. 3.

In the equation $E_J = BJ(J + 1)$ where 'B' is called rotational constant

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

$$I = \mu r^2 \quad r = \text{bond length}$$

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \quad m_1, m_2 = \text{masses of the two atoms}$$

$$h = \text{Planck's constant}; C = 3 \times 10^{10} \text{ cm.}$$

μ is called the reduced mass of the system.

Selection rule

All transitions between various quantised rotational energy levels are not allowed. The allowed and forbidden transitions are explained by a result called the selection rule. The mathematical statement of the selection rule is given below

$$\Delta J = \pm 1$$

A molecule can move from a level to its immediate neighbour either above or below. Allowed transitions between the energy levels are given in the following diagram Fig. 4.

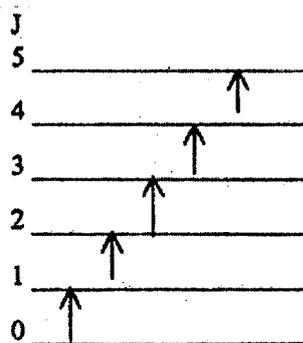


Fig. 4.

Fig. 4 shows the allowed transitions between the energy levels of a rigid diatomic molecule. The energy needed for any transition $J \rightarrow J + 1$ is given by the following equation.

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

Nature of the spectrum

The microwave spectrum of a rigid diatomic molecule consists of rotational lines with constant spacing between the successive lines. The constant spacing is equal to $2B$. The spectrum is given below Fig. 5.

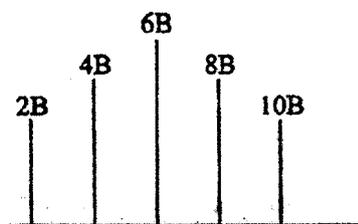


Fig. 5. Microwave spectrum of a rigid diatomic molecule

From the microwave spectrum, the value of 'B' is obtained. Substituting the values of C, μ and h the inter-nuclear distance of the molecule can be obtained.

$$B = \frac{h}{8\pi^2\mu r^2 C}; \quad r^2 = \frac{h}{8\pi^2 B \mu C}$$

Once we get B, r^2 and hence r can be obtained. Hence by recording the microwave spectrum of a diatomic molecule, the internuclear distance of the molecule is obtained.

Vibrational spectra-infrared spectroscopy

One of the most valuable spectroscopy regions for the chemist is vibrational spectroscopy. This region is concerned with the study of vibrating molecules. The molecule

need not have a permanent dipole moment but the vibration which produces a change in the dipole moment is said to be infrared active. The dipole moment of carbon dioxide is zero and the symmetric stretching vibration does not produce any change in dipole moment. Hence, symmetric stretching vibration is infrared inactive.

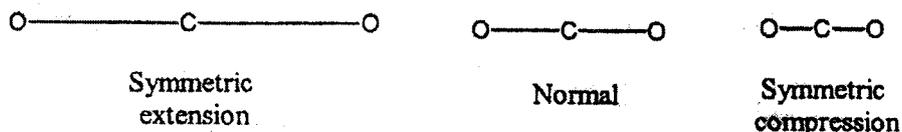


Fig. 6. Symmetric stretching of carbon dioxide

But the anti-symmetric stretching of carbon dioxide is infrared active (Fig. 7).

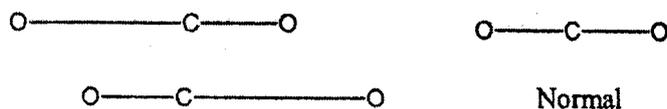


Fig. 7

Harmonic oscillator

The vibrational spectrum of a diatomic molecule is explained by a model called harmonic oscillator. The model consists of a ball and a spring (Fig. 8). One end of the spring is attached to a firm end and other end carries a ball.



Fig. 8. Harmonic oscillator

The vibrating motion of the nuclei of a diatomic molecule may be similar to the vibration of a linear harmonic oscillator.

In such an oscillator the force tending to restore an atom to its original state is proportional to the displacement of the vibratory atom from the original position (Hooke's law). The plot of energy versus internuclear distance for a harmonic system is a regular parabola.

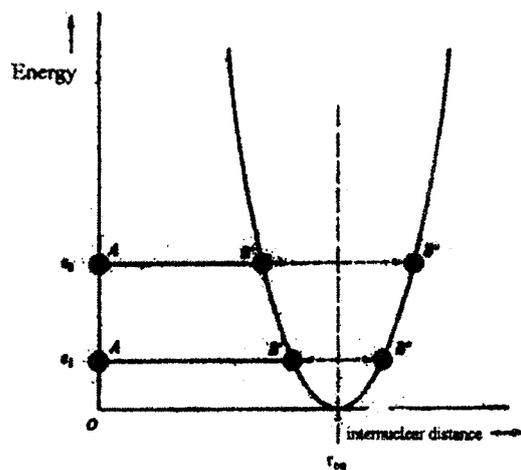


Figure.9 Parabolic curve of energy plotted against the extension or compression of a spring obeying Hooke's Law.

The compression and extension of a bond may be likened to the behaviour of a spring and we may extend the analogy by assuming that the bond like a spring, Obey's Hooke's law

$$f = -k (r - r_{eq}) \quad \dots (1)$$

f = restoring force; k = force constant

r = internuclear distance ; r_{eq} = equilibrium distance

In this case the energy curve is parabolic

$$E = \frac{1}{2} k (r - r_{eq})^2 \quad \dots (2)$$

An elastic bond, like a spring, has a certain vibration frequency dependent upon the mass of the system and the force constant, but independent of the amount of distortion.

The oscillation frequency is

$$\omega_{osc} = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \text{ Hz} \quad \dots (3)$$

where μ is the reduce mass of the system. To convert frequency into wave numbers eqn (3) becomes

$$\bar{\omega}_{osc} = \frac{1}{2\pi C} \sqrt{\frac{k}{\mu}} \text{ cm}^{-1} \quad \dots (4)$$

By using the Schrodinger wave equation the allowed vibrational energy levels are given by the following equation.

$$E_v = (v + \frac{1}{2})h \omega_{osc} \text{ Joules} \quad \dots (5)$$

($v = 0, 1, 2 \dots$)

where v is called the vibrational quantum number. Converting to the spectroscopic unit, cm^{-1} we have

$$\epsilon_v = \frac{E_v}{hC} = \frac{(v + 1/2)\omega_{osc}}{hC} = (v + 1/2)\bar{\omega}_{osc} \quad \dots (6)$$

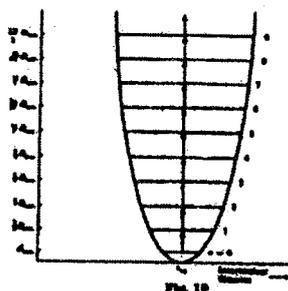
Selection rule

Selection rule for the harmonic oscillator undergoing vibrational changes

$$\Delta v = \pm 1 \quad \dots (7)$$

Since the vibrational energy levels are equally spaced any transition from $v \rightarrow v + 1$ needs the same energy ($\bar{\omega}_{osc} \text{ cm}^{-1}$).

The vibrational energy level diagram and the transitions between them for a harmonic oscillator are given below in the Fig. 10.



In the Fig. 10, vibrational levels are equally spaced, transitions between any two neighbouring state will give rise to the same energy change. Further, since the difference between energy levels expressed in cm^{-1} gives directly the wave number of spectral line absorbed or emitted.

$$\bar{\nu}_{\text{spectroscopic}} = \epsilon = \bar{\omega}_{osc} \text{ cm}^{-1} \quad \dots (8)$$

Since all transitions within the selection rule need the same energy, we get a single intense line at $\bar{\omega}_{osc}$ for a simple harmonic oscillator.

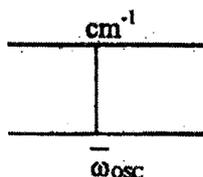


Fig. 11. Vibrational spectrum of a simple harmonic oscillator

From the wave number of the spectral line $\bar{\omega}$ is directly obtained.

Since $\bar{\omega} = \frac{1}{2\pi C} \sqrt{\frac{k}{\mu}}$, substituting C and reduced mass of the system (μ), the

force constant k is obtained.

Vibrating diatomic molecule-Anhormonic oscillator

If the diatomic molecule does not obey's Hooke's law then it is called anharmonic. The compressions and extensions during vibration are not equal on both sides.

Fig. 12 shows the energy curve for a typical diatomic real molecule which behaves as anharmonic oscillator and undergoes extensions and compressions. In the same figure, a dotted parabola is there which is due to an ideal diatomic molecule obeying ideal simple harmonic motion.

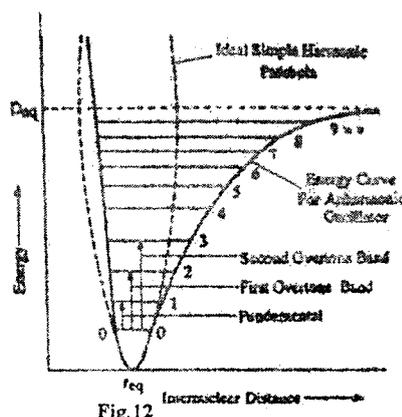


Fig. 12

Fig. 12: Morse curve: the energy of a diatomic molecule undergoing anharmonic extensions and compressions.

In order to explain the energy curve due to a real molecule. P.M. Morse invented a purely empirical expression known as Morse function which is as follows.

$$E = D_{eq} [1 - e^{-a(r - r_{eq})}]^2 \quad \dots (1)$$

where

D_{eq} = the dissociation energy for a particular molecule

a = constant for a particular diatomic molecule

r_{eq} = the value of internuclear distance which corresponds to a minimum of Morse curve.

With the use of Schrodinger equation the pattern allowed vibrational energy levels is found to be

$$\epsilon_v = (v + \frac{1}{2}) \bar{\omega}_e - (v + \frac{1}{2})^2 \bar{\omega}_e x_e \text{ cm}^{-1} \quad \dots (2)$$

$v = 0, 1, 2, \dots$

$\bar{\omega}_e$ – equilibrium oscillation frequency

x_e – anharmonicity constant

If we rewrite equation (2) for the anharmonic oscillator

$$\epsilon_v = \bar{\omega}_e \{1 - x_e (v + \frac{1}{2})\} (v + \frac{1}{2}) \quad \dots (3)$$

and compare with energy levels of the harmonic oscillator $\epsilon_v = (v + \frac{1}{2}) \bar{\omega}_{osc}$.. (4)

Substitute eqn. (4) in (3)

$$\bar{\omega}_{osc} = \bar{\omega}_e \{1 - x_e (v + \frac{1}{2})\} \quad .. (5)$$

Thus the anharmonic oscillator behaves like the harmonic oscillator but with an oscillation frequency which decreases steadily with increasing v .

Selection rules for an anharmonic oscillator

The selection rule for all transitions in anharmonic oscillator is given as $\Delta v = \pm 1, \pm 2, \pm 3 \dots$

The transition $v = 0$ to $v = 1$ of an anharmonic oscillator is called fundamental absorption (fundamental band). The energy needed for the transition $v = 0 \rightarrow v = 1$ is given below.

$$\Delta E = \bar{\omega}_e (1 - 2 x_e) \text{ cm}^{-1}$$

The vibrational lines due to transitions $v = 0 \rightarrow v = 2$ and $v = 0 \rightarrow v = 3$ are called first and second overtones respectively. The positions of the spectral lines due to overtones are given below.

$$v = 0 \rightarrow v = 2; \quad \Delta E = 2 \bar{\omega}_e (1 - 3 x_e) \text{ cm}^{-1}$$

$$v = 0 \rightarrow v = 3; \quad \Delta E = 3 \bar{\omega}_e (1 - 4 x_e) \text{ cm}^{-1}$$

Among the three transitions the intensity of the fundamental absorption is the strongest of all. The overtones are weak absorptions. The second overtone is weaker than first overtone.

The vibrational spectrum of an anharmonic oscillator indicating fundamentals and overtones is given in Fig. 13.

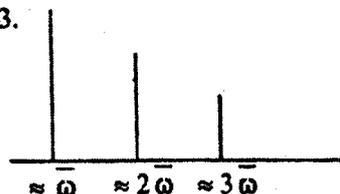


Fig. 13

Fundamental absorption ($\bar{\omega}$), first overtone ($2\bar{\omega}$), and second overtone ($3\bar{\omega}$).

The diatomic vibrating rotator

Typical diatomic molecule has rotational energy separations of 1-10 cm^{-1} . Vibrational energy separation of HCl were nearly 3000 cm^{-1} . Two motions are so different. A diatomic molecule can execute rotations and vibrations quite independently.

According to Born-Oppenheimer approximation the combined rotational - vibrational energy is simply the sum of separate energies.

$$E_{\text{total}} = E_{\text{rot}} + E_{\text{vib}} \text{ (joules)} \quad \dots (1)$$

$$e_{\text{total}} = e_{\text{rot}} + e_{\text{vib}} \text{ (cm}^{-1}\text{)} \quad \dots (2)$$

$$e_{J, v} = e_J + e_v \quad \dots (3)$$

$$= BJ(J+1) + (v + \frac{1}{2}) \bar{\omega}_e - x_e (v + \frac{1}{2})^2 \bar{\omega}_e \quad \dots (4)$$

The rotational levels are sketched in Fig. 14 for the two lowest vibrational levels $v = 0$ and $v = 1$.

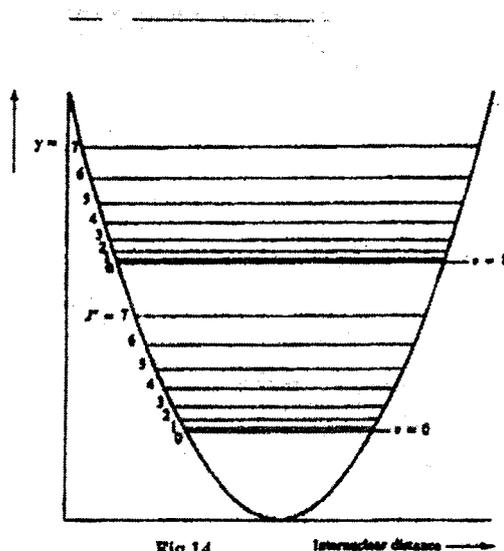


Fig.14
The rotational energy levels for two different vibrational states of a diatomic - molecule

The rotational constant B in equation (4) is taken to be the same for all J and v, the separation between two levels of given J is the same in the $v = 0$ and $v = 1$ states.

Selection rule

$$\Delta v = \pm 1, \pm 2, \text{ etc.}, \quad \Delta J = \pm 1$$

Applying selection rule to the energy levels in eqn (4).

$$\begin{aligned}
\Delta \epsilon_{J,v} &= \epsilon_{J',v=1} - \epsilon_{J'',v=0} \\
&= BJ'(J'+1) + 1/2 \bar{\omega}_c - 2/4 x_c \bar{\omega}_c - \{ BJ''(J''+1) + 1/2 \bar{\omega}_c - 1/4 x_c \bar{\omega}_c \} \\
&= \bar{\omega}_0 + B(J' - J'')(J' + J'' + 1) \text{ cm}^{-1} \quad \dots (5)
\end{aligned}$$

$$\bar{\omega}_0 = \bar{\omega}_c (1 - 2 x_c)$$

The value of 'B' to be identical in the upper and lower vibrational states is a direct consequence of the Born-Oppenheimer approximation-rotation is unaffected by vibrational changes.

If $\Delta J = \pm 1$

i.e. $J' = J'' + 1$ (or) $J' - J'' = +1$

$$\Delta \epsilon_{J,v} = \bar{\omega}_0 + 2B(J'' + 1) \text{ cm}^{-1}, \quad J'' = 0, 1, 2 \quad \dots (6)$$

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

$$\Delta \epsilon_{J,v} = \bar{\omega}_0 - 2B(J' + 1) \text{ cm}^{-1}, \quad J' = 0, 1, 2, \dots \quad \dots (7)$$

The eqn (6) and (7) conveniently combined into

$$\Delta \epsilon_{J,v} = \bar{\nu}_{\text{spect}} = \bar{\omega}_0 + 2Bm \text{ cm}^{-1}, \quad m = \pm 1, \pm 2, \dots \quad \dots (8)$$

where m, replacing $J'' + 1$ in eqn (6) and $J' + 1$ in eqn (7) has positive values for $\Delta J = +1$ and is negative if $\Delta J = -1$. m constant be zero since this would imply values of J' or J'' to be -1. The frequency $\bar{\omega}_0$ is usually called the band origin or band centre. Equation (8) represents combined vibration-rotation spectrum.

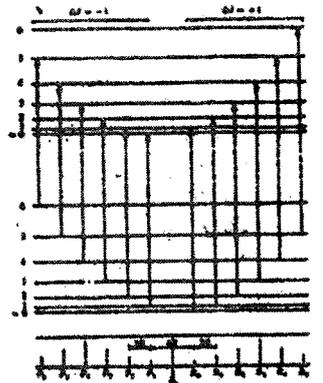


Fig. 15
Some transitions between the rotational - vibrational energy levels of a diatomic molecule together with the spectrum arising from them

The approximate orders at magnitude of these changes are

$$\frac{\Delta \epsilon_{\text{elec}}}{hC} \approx \frac{\Delta E_v}{hC} \times 10^3 \approx \frac{\Delta E_r}{hC} \times 10^{-6} \text{ cm}^{-1} \quad \dots (6)$$

Eqn (6) it follows that vibrational changes will produce a coarse structure and rotational energy changes fine structure on the spectra of electron transitions.

Vibrational coarse structure progressions

Ignoring rotational changes mean that we rewrite eqn (3) as follows

$$E_{\text{total}} = E_{\text{elect}} + E_{\text{vib}} \quad \dots (7) \text{ (or)}$$

$$\epsilon_{\text{total}} = \epsilon_{\text{elect}} + \epsilon_{\text{vib}} \text{ cm}^{-1} \quad \dots (8)$$

Use of Schrodinger eqn, the pattern of the allowed vibrational energy level is

$$\epsilon_{\text{vib}} = (v + \frac{1}{2}) \bar{\omega}_e - (v + \frac{1}{2})^2 x_e \bar{\omega}_e \text{ cm}^{-1} \quad (v = 0, 1, 2 \dots) \quad \dots (9)$$

Eqn (9) in (8)

$$\epsilon_{\text{total}} = \epsilon_{\text{elect}} + (v + \frac{1}{2}) \bar{\omega}_e - x_e (v + \frac{1}{2})^2 \bar{\omega}_e \text{ cm}^{-1} \quad \dots (10)$$

(v = 0, 1, 2 ...)

The energy levels of this equation are shown in Fig. 16 for two arbitrary values of ϵ_{elect} .

Lower states = v'', $\epsilon''_{\text{elect}}$, upper state = v', ϵ'_{elect}

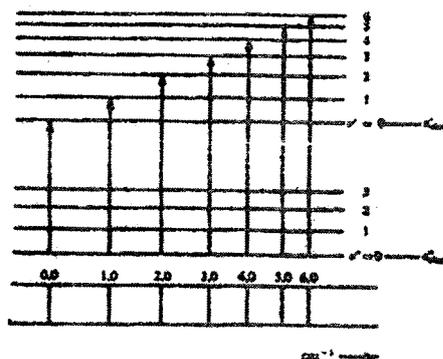


Fig. 16 the vibrational coarse structure of the band formed during electronic absorption from the ground ($v'' = 0$) state to a higher state.

The spacing between the upper vibrational levels is deliberately shown to be rather smaller than that between the lower. This is the normal situation since an excited electronic state usually corresponds to a weaker bond in the molecule and hence a smaller vibrational wave number $\bar{\omega}_e$.

There is essentially no selection rule for v when a molecule undergoes electronic transition i.e. every transition $v'' \rightarrow v'$ has some probability and a great many spectral lines would, therefore, be expected. Consider the electronic transition from $\epsilon'' \rightarrow \epsilon'$.

According to Maxwell Boltzmann distribution law, almost all the molecules (99%) are in the lowest vibrational level. Hence, consider the transition from $v'' = 0$ of ϵ'' . The transitions may reach 0, 1, 2, 3, 4 of v' in the excited electronic state ϵ' . The transition state given in Fig 16.

The transitions are labelled according to their v', v'' i.e (0, 0), (1, 0), (2, 0), (3, 0), (4, 0) ... such set of transition is called v' progressions, since the value of v' increases by one in each set.

The spectral lines (vibrational coarse structure)

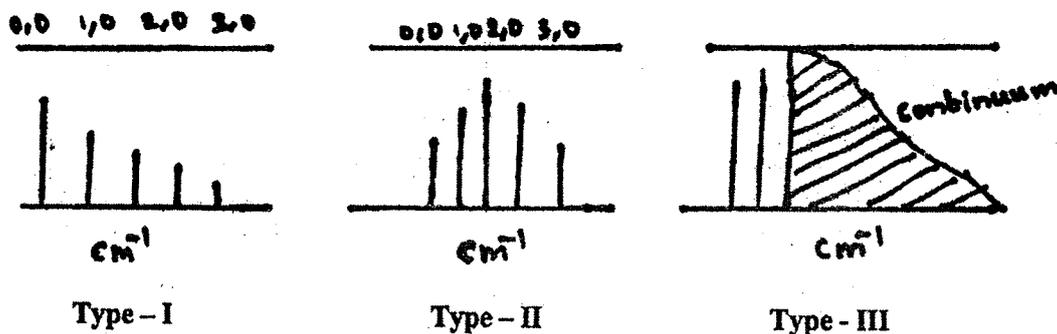
The diagram (Fig. 16) shows that the lines in a band crowd together more closely at high frequencies. This is a direct consequence of the anharmonicity of the upper state vibration which causes the excited vibrational levels to converge.

An analytical expression can easily be written for this spectrum. From eqn. (10) we have immediately

$$\Delta\epsilon_{\text{total}} = \Delta\epsilon_{\text{elect}} + \Delta\epsilon_{\text{vib}}$$

$$\therefore \bar{\nu}_{\text{spect}} = (\epsilon' - \epsilon'') + \left\{ (v' + \frac{1}{2})\bar{\omega}'_e - x'_e(v' + \frac{1}{2})^2 - \bar{\omega}'_e \right\} - \left\{ (v'' + \frac{1}{2})\bar{\omega}''_e - x''_e(v'' + \frac{1}{2})^2 - \bar{\omega}''_e \right\} \text{ cm}^{-1} \quad \dots (11)$$

There are three types of v' progression. They are given below fig. 17



In type I: (0, 0) line is the strongest of all the lines. The intensity decreases gradually.

In type II: The intensity gradually increases, reaches a maximum and then further decreases.

In type III: a few discrete lines are observed together with a continuous band. The continuous band is called a continuum. The intensity variation of vibrational electronic spectra is explained by Frank-Condon principle.

Frank-Condon principle

It states that an electronic transition takes place so rapidly that a vibrating molecule does not change its internuclear distance appreciably during the transition. In other words, during electronic transition the inter-nuclear distance of the molecule does not change appreciably. Based on the Frank-Condon principle and transition probability the intensity variation of v' progression is explained.

Transition probability and potential energy curve

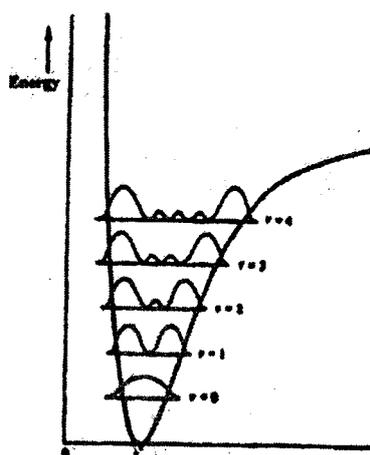


Fig. 18
The Probability distribution for a diatomic molecule according to the quantum theory. The nuclei are most likely to be found a distance apart given by the maxima of the curve for each vibrational state.

Energy of a diatomic molecule varies with internuclear distance. We recall the Morse curve, represents the energy when one atom is considered fixed on the $r = 0$ axis and the other is allowed to oscillate between the limits of the curve classical theory would suggest that the oscillating atom would spend most of its time on the curve at the turning point of its motion, since it is moving most slowly there. According to quantum theory, the most probable position is given by the maximum of the curve ($v = 0$). As v increases, the maxima move towards the extreme positions. The maximum (i.e.) the centre in $v = 0$ state is the most probable position from where the transition takes place. Other transitions are also possible in $v = 0$ state from the extreme position. So the curve explains the transition probability.

The operation of the Frank-Condon principle

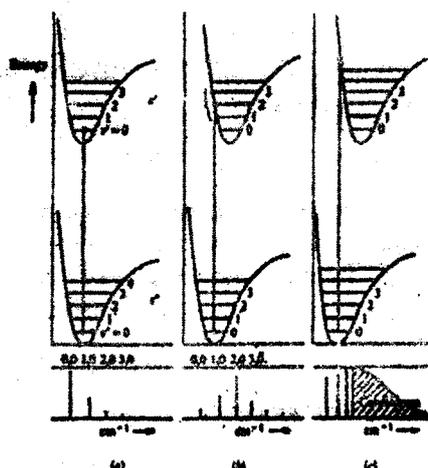


Fig. 19. The Operation of the Frank - Condon Principle for (a) internuclear distances equal in upper and lower states, (b) upper-state internuclear distance a little greater than that in the lower state, and (c) upper - state distance considerably greater.

- (a) Internuclear distance equal in upper and lower states
- (b) Upper-state internuclear distance a little greater than that in the lower state
- (c) Upper-state distance considerably greater

Each electronic state is explained by a Morse curve. The vibrational levels associated with each electronic energy level are given. There is an electronic transition from $\epsilon'' \rightarrow \epsilon'$. The molecule will move from the lowest vibrational energy level $v'' = 0$ of the electronic state ϵ'' . Since the most probable position is the centre, the transition will occur from the centre of $v'' = 0$. Draw a vertical line from the centre of $v'' = 0$, since during electronic transition there is no change in internuclear distance according to Frank-Condon principle. The vertical line meets the centre $v' = 0$ of the electronic state ϵ' fig. a.

Fig. a. Type I, vibrational coarse structure

In type I, the upper electronic state having same equilibrium internuclear distance as the lower, i.e. r' is equal to r'' . Hence the vertical transition from the centre of $v'' = 0$ reaches the centre of $v' = 0$. Hence (0, 0) transition is the most probable transition. Due to this (0, 0) line appears to be the strongest of all the lines. Transitions are also possible from $v'' = 0$ state and finishing in the $v' = 1, 2$ etc states. The (1, 0), (2, 0) etc., lines diminish rapidly in intensity shown in fig. a.

Fig. b. Type II vibrational coarse structure

The excited electronic state (r') has a slightly greater internuclear (r'') separation than the ground state. Hence, the vertical transition from the centre of $v'' = 0$ meets $v' = 2$ of the upper electronic state. Hence (2, 0) line is the strongest line. Depending upon the difference between r'' and r' , the vertical transition meets either 2, 3, or 4 of v' . Hence other than the first line is the strongest line, since r' is greater than r'' . Hence the intensity increases and reaches a maximum and then decreases gradually.

Fig. c. Type II vibrational coarse structure

The almost horizontal portion of the Morse curve indicates the dissociation limit. In type III, r' is far greater than r'' i.e. the upper state separation is drawn as considerably greater than that in the lower state. The transition from $v'' = 0$ meets the dissociation limit at the upper electronic state. Hence we get a continuous band called continuum. At the same time transitions from right extreme position of $v'' = 0$ meets the minimum of the Morse curve and hence discrete lines are also seen.

Raman spectroscopy

Raman spectroscopy deals with scattering of light. If the frequency of the incident electromagnetic radiation is equal to that of scattered radiation then it is called Rayleigh scattering. If the frequency of the scattered radiation is different from the incident radiation, then it is referred to as Raman scattering. In this technique certain frequencies above and below that of the incident beam will be scattered.

Raman scattering or Raman effect is explained by quantum theory as well as classical theory.

Quantum theory of Raman effect

The incident radiation consists of a stream of particles called photons. Photons undergo collisions with molecules. There are two types of collisions. Inelastic collisions energy is not exchanged between the photon and the molecules. Elastic collision leads to Rayleigh scattering.

If energy is exchanged between photon and molecule during the collision, such collisions are called inelastic. These collisions cause Raman scattering. The molecule can gain or lose in accordance with the quanta laws i.e. its energy change, ΔE joules, must be the difference in energy between two of its allowed states. That is to say, ΔE must represent a change in the vibrational and/or rotational energy of the molecule. If the molecule gains energy ΔE , the photon will be scattered with energy $h\nu - \Delta E$ and the equivalent radiation will have a frequency $\nu - \frac{\Delta E}{h}$. If the molecules loses energy ΔE , the scattered frequency will be

$$\nu + \frac{\Delta E}{h}.$$

Radiation scattered with a frequency lower than that of the incident beam is referred to as Stoke's radiation, the molecule gains energy by moving from lower energy level to higher level. When the molecule returns from a high energy level to a lower energy

level then the molecule loses energy. Hence the frequency of the scattered radiation is greater than the frequency of the incident radiation. This is called anti-stokes radiation.

Lines due to Stokes radiation are more intense than the anti stokes lines. Since the probability of transition from lower level to higher level is greater than a molecule from higher level to lower level, the Stoke's lines are more intense than anti-Stoke's lines. Thus Raman effect is explained by quantum theory.

Classical theory of Raman effect – Polarization and polarizability

When a molecule is put into a static electric field, the positively charged nucleus is attracted by the negative pole of the electric field and the negatively charged electron cloud is attracted to the positive pole. The molecule is said to be distorted. This distortion leads to charge separation and induced electric dipole moment. The molecule is said to be polarized. This distortion is called polarization. The following equation explains the relationship between the induced dipole and the magnitude of the electric field.

$$\mu = \alpha E$$

μ = Induced electric dipole moment ; E = Strength of the applied field

α = Polarizability of the molecule.

Polarizability is nothing but the ease with which the molecule can be polarized.

In H_2 polarizability is anisotropic, the electrons forming the bonds are more easily displaced by an electric field applied along the bond axis than one across this direction. We can represent the polarizability in various directions most conveniently by drawing a polarizability ellipsoid as in Fig. 20.

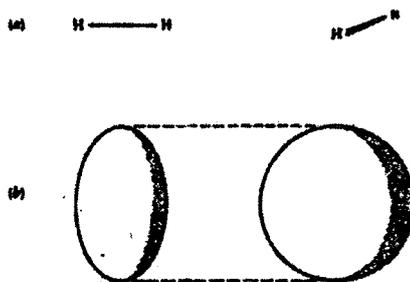


Fig. 20. The hydrogen molecule and its polarizability ellipsoid seen from two directions at the right angles.

All diatomic molecules, for example CO, HCl and linear polyatomic molecules for example CO_2 , $HC \equiv CH$ etc., having ellipsoids of the same general shape, differing in the relative sizes of their major and minor axes.

When a sample of such molecules is subjected to a beam of radiation of frequency ν the electric field experienced by each molecule varies according to the equation

$$E = E_0 \sin 2\pi\nu t \quad \dots (1)$$

and thus the induced dipole also undergoes oscillations of frequency ν

$$\mu = \alpha E = \alpha E_0 \sin 2\pi\nu t \quad \dots (2)$$

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, of course, reflected by a change in either the magnitude or the direction of the polarizability ellipsoid.

Rotational Raman spectra of linear molecule

The rotational energy levels of linear molecules

$$\epsilon_J = BJ(J+1) - DJ^2(J+1)^2 \text{ cm}^{-2} \quad (J = 0, 1, 2, \dots) \quad \dots (3)$$

but, in Raman spectroscopy, the precision of measurements does not normally warrant the retention of the term involving D , the centrifugal distortion constant. Due to this reason, on simplification of eqn (3), to represents the energy levels.

$$\epsilon_J = BJ(J+1) \text{ cm}^{-1} \quad (J = 0, 1, 2, \dots) \quad \dots (4)$$

Selection rule

Transition between these levels follow the formal selection rule

$$\Delta J = 0 \text{ or } \pm 2 \quad \dots (5)$$

The fact that in Raman work the rotational quantum number changes by two units rather than one is connected with the symmetry of the polarizability ellipsoid.

The transition $\Delta J = 0$ is trivial since this represents no change in the molecular energy and hence Rayleigh scattering only

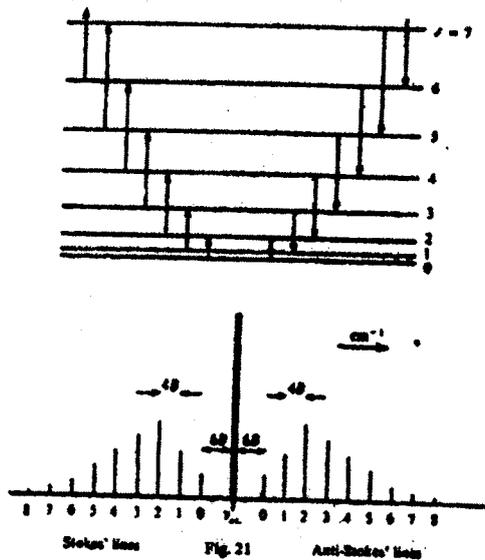
$$\Delta J = +2 \text{ with energy level in eqn (4) then } j' = 2; j'' = 0$$

$$\begin{aligned} \text{(i)} \quad \Delta\epsilon &= \epsilon_{j'} - \epsilon_{j''} = 0 \\ \Delta\epsilon &= B2(2+1) - B(0)(0+1) \\ \Delta\epsilon &= 6B \end{aligned} \quad \dots (6)$$

$$\begin{aligned} \text{(ii)} \quad j' &= 3 & j'' &= 1 \\ \Delta\epsilon &= B(3)(3+1) - B(1)(1+1) \\ &= 12B - 2B \\ &= 10B \end{aligned} \quad \dots (7)$$

$$\begin{aligned} \text{(iii)} \quad j' &= 4 & j'' &= 2 \\ \Delta\epsilon &= B(4)(4+1) - B(2)(2+1) \\ &= 20B - 6B \\ &= 14B \end{aligned} \quad \dots (8)$$

Where J is the rotational quantum number in the lower state. The rotational Raman spectrum appears as indicated below Fig. 21. The spacing between the successive lines is equal to $4B$.



For symmetric top molecules

Selection rule $\Delta J = 0, \pm 1, \pm 2$. The 'R' and 'S' branch lines, obtained

Vibrational Raman spectra

For every vibrational mode, the expression is

$$\epsilon = \bar{\omega}_e \left(v + \frac{1}{2} \right) - \bar{\omega}_e x_e \left(v + \frac{1}{2} \right)^2 \text{ cm}^{-1} \quad \dots (9)$$

$$v = 0, 1, 2, \dots$$

The selection rule for vibrational Raman spectra

$$\Delta v = 0, \pm 1, \pm 2, \dots$$

$$v = 0 \rightarrow v = 1 \quad \Delta \epsilon_{\text{fundamental}} = \bar{\omega}_e (1 - 2x_e) \text{ cm}^{-1}$$

$$v = 0 \rightarrow v = 2 \quad \Delta \epsilon_{\text{overtone}} = 2\bar{\omega}_e (1 - 2x_e) \text{ cm}^{-1}$$

$$v = 1 \rightarrow v = 2 \quad \Delta \epsilon_{\text{hot}} = \bar{\omega}_e (1 - 4x_e) \text{ cm}^{-1}$$

Rule of mutual exclusion

If a molecule has a centre of symmetry then Raman active vibrations are infrared inactive. Raman inactive vibrations are infrared active.

If a molecule has no centre of symmetry then some vibrations may be both Raman and infrared active.

Mode of vibration of CO ₂	Raman	Infrared
ν_1 : Symmetric stretch	Active	Inactive
ν_2 : Bending	Inactive	Active
ν_3 : Asymmetric stretch	Inactive	Active

Dissociation energy and dissociation products

Figure (21a) and (22b) shows two of the ways in which electronic excitation can lead to dissociation part (a) of the figure represents the equilibrium nuclear separation in the upper state is considerably greater than that in the lower. The dashed line limits of the Morse curves represent the dissociation of the normal and excited molecule into atoms, the dissociation energies being D_0'' and D_0' from the $\nu = 0$ state in each case. Already we have seen that the total energy of the dissociation products from the upper state is greater by an amount called E_{ex} than that of the products of dissociation in the lower state. This energy is the excitation energy of one of the atoms produced on dissociation. The lower wave number limit of this continuum must represent just sufficient energy to cause dissociation and no more and thus we have

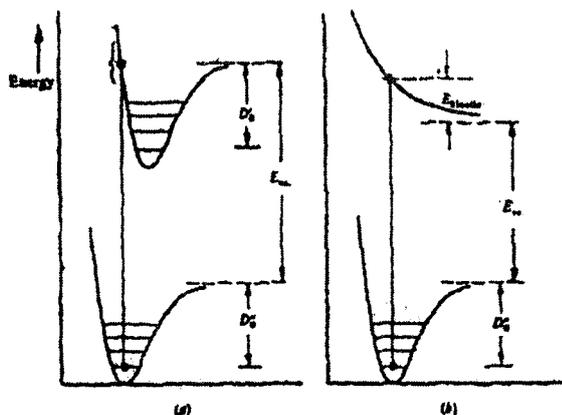


Fig. 22. Illustrating dissociation by excitation into (a) a stable upper state, and (b) a continuous upper state.

$$\bar{\nu}_{(\text{continuum limit})} = D_0'' + E_{ex}$$

we can measure D_0'' , the dissociation energy, if we know E_{ex} , the excitation energy of the products. Now, although the excitation energy of atoms to various electronic states is readily measurable by atomic spectroscopy, the precise state of dissociation products is not always

obvious. There are several ways in which the total energy $D_0'' + E_{ex}$ may be separated into its components.

In Fig (b) we illustrate the case in which the upper electronic state is unstable. There is no minimum in the energy curve and, as soon as a molecule is raised to this state by excitation, the molecule dissociates into products with total excitation energy E_{ex} . The products fly apart with kinetic energy $E_{kinetic}$ which represents the excess energy in the final state above that needed just to dissociate the molecule. Since $E_{kinetic}$ is not quantised the whole spectrum for this system will exhibit a continuum the lower limit of which will be precisely the energy $D_0'' + E_{ex}$. If E_{ex} can be found from the knowledge of the dissociation products, D_0'' can be measured with great accuracy.

Rotational fine structure of electronic – vibration transitions

The energy levels of a rotating diatomic molecule is

$$\epsilon_{rot} = \frac{h}{8\pi^2 I C} J(J+1) = BJ(J+1) \text{ cm}^{-1} \quad (J = 0, 1, 2, \dots) \quad \dots (1)$$

I – moment of inertia; B – rotational constant

J – rotational quantum number

By the Born-Oppenheimer approximation, the total energy of a diatomic molecule is

$$\epsilon_{total} = \epsilon_{ele} + \epsilon_{vib} + BJ(J+1) \text{ cm}^{-1} \quad \dots (2)$$

changes in the total energy may be written

$$\Delta \epsilon_{total} = \Delta \{\epsilon_{elect} + \epsilon_{vib}\} + \Delta \{BJ(J+1)\} \text{ cm}^{-1} \quad \dots (3)$$

and the wave number of a spectroscopic line corresponding to such a change becomes

$$\bar{\nu}_{spect} = \bar{\nu}_{(v', v'')} + \Delta \{BJ(J+1)\} \text{ cm}^{-1} \quad \dots (4)$$

$\bar{\nu}_{(v', v'')}$ represents the wave number of an electronic vibrational transition.

The selection rule for J depends upon the type of electronic transition undergone by the molecule. The movement we must simply state that if both the upper and lower electronic states are $^1\Sigma$ states (i.e. states in which there is no electronic angular momentum about the internuclear axis) this selection rule is

$$\Delta J = \pm 1 \text{ only for } ^1\Sigma \rightarrow ^1\Sigma \text{ transitions} \quad \dots (5)$$

From the above rule, it follows that for such transitions only P and R branches will occur. No Q branches will occur.

For all other transitions, which have either the upper or lower or both states having angular momentum about the intermolecular axis, the selection rule becomes.

$$\Delta J = 0 \text{ or } \pm 1 \quad \dots(6)$$

From the above rule, it follows that P and R branches along Q branches ($\Delta J = 0$) will occur.

For this later case there is the added restriction that a state with $J = 0$ cannot undergo a transition to another $J = 0$ state.

$$J = 0 \not\leftrightarrow J = 0 \quad \dots (7)$$

Thus we see that for transitions between $^1\Sigma$ states, P and R branches only will occur, while for other transitions Q branches will appear in addition.

Spectrum

If we represent the upper electronic state by B' and J' and lower electronic state by B'' and J'' , we may put eqn. (4) in the form

$$\bar{\nu}_{\text{spect}} = \bar{\nu}_{(v', v'')} + B'J'(J' + 1) - B''J''(J'' + 1) \text{ cm}^{-1} \quad \dots (8)$$

where B' and B'' refer to the upper and lower electronic states respectively as, generally, to different vibrational states and so they are very much different from one another. As B' and B'' are different from each other and also from B , one cannot take $B' = B'' = B$. Let us take P, R and Q branches in turn. Thus, we have

P branch

As $\Delta J = -1, J'' = J' + 1$, it means that

$$\Delta \epsilon = \bar{\nu}_P = \bar{\nu}_{(v', v'')} - (B' + B'')(J' + 1) + (B' - B'')(J' + 1)^2 \text{ cm}^{-1} \quad \dots (9)$$

where $J' = 0, 1, 2, \dots$

R-branch

As $\Delta J = +1, J' = J'' + 1$

$$\Delta \epsilon = \bar{\nu}_R = \bar{\nu}_{(v', v'')} + (B' + B'')(J'' + 1) + (B' - B'')(J'' + 1)^2 \text{ cm}^{-1} \quad \dots (10)$$

where $J'' = 0, 1, 2, \dots$

By combining eqn (9) and (10), we get combined equation in the form

$$\bar{\nu}_{P,R} = \bar{\nu}_{(v', v'')} + (B' + B'')m + (B' - B'')m^2 \text{ cm}^{-1} \quad \dots (11)$$

where $m = \pm 1, \pm 2, \dots$ In eqn (11), positive values result R branch ($\Delta J = \pm 1$) whereas negative values give rise to P branch ($\Delta J = -1$). It is important to remark here that m cannot be zero i.e., $m \neq 0$. Because in P branch zero value of m ($m = 0$) corresponds to $J_1 = -1$ which is

impossible. Some is true for R branch. Thus, we conclude that no line from P and R branches would appear at the band origin $\bar{\nu}_{(v', v')}$.

Q branch

As $\Delta J = 0$, $J' = J''$, so that

$$\bar{\nu}_Q = \bar{\nu}_{(v', v')} + (B' - B'') + (B' - B'') J''^2 \text{ cm}^{-1} \quad \dots (12)$$

where $J'' = 1, 2, 3 \dots$. As transition from $J = 0$ to $J = 0$ is not possible, it means that J' and J'' cannot be equal to zero i.e., $J' = J'' \neq 0$. In other words, it means that no line will appear at the band origin.

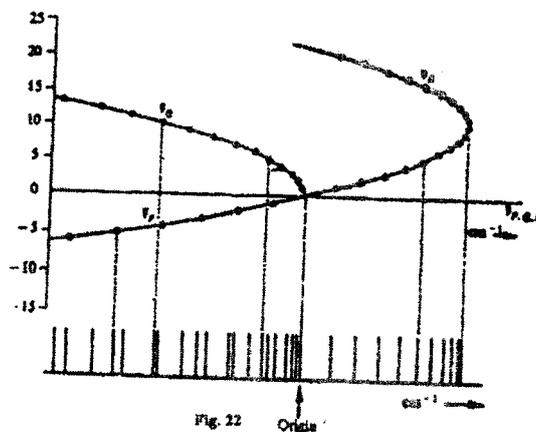
Fortrat Diagram

Equation 11 for the P and R branch lines and equation 12 for Q lines can be expressed in terms of variable parameters P and Q respectively.

$$\bar{\nu}_{P, R} = \bar{\nu}_{(v', v')} + (B' + B'') p + (B' - B'') p^2 \quad \dots (13)$$

$$\bar{\nu}_Q = \bar{\nu}_{(v', v')} + (B' - B'') q + (B' - B'') q^2 \quad \dots (14)$$

Both equations (13) and (14) represent parabola provided if we take both positive and negative values for p while positive values for q only. The sketches of the parabola obtained from equations (13) and (14) are called Fortrat parabola in which we have taken 10% difference between the upper and lower B values and also taken $B_1 < B_2$.



In the figure, regions of positive P values are labelled as $\bar{\nu}_R$ whereas those of negative P values as $\bar{\nu}_P$. Both p and q may take only integral values but not zero values. The allowed values of p and q have been indicated by drawing circles round the allowed points on the Fortrat's diagram. This fact helps us to read $\bar{\nu}$ values of spectral line directly from the group.

A useful property of Fortrat diagram is that the band head lies at the vertex of P and R parabola. The position of vertex can be obtained by differentiating equation (13) which is

$$\frac{d\nu_{P,R}}{dP} = B' + B'' + 2(B' - B'')P = 0 \quad \dots (15)$$

(or)

$$P = -\frac{B' + B''}{2(B' - B'')} \quad \dots (16)$$

From equation (16) two conclusions can be drawn

- (i) If $B' > B''$, band head will occur at positive P values in R branch
- (ii) If $B' < B''$, band head will occur at negative P values in P branch.

Coupled Vibrations and Fermi Resonance

We expect one stretching absorption frequency for an isolated C-H bond but in the case of methylene ($-\text{CH}_2-$) group, two absorptions occur which correspond to symmetric and asymmetric vibrations as follows:



In such cases, asymmetric vibrations always occurs at higher wave number compared with the symmetric vibrations. These are called coupled vibrations since these vibrations occur at different frequencies than that required for an isolated C-H stretching. Similarly, coupled vibrations of $-\text{CH}_3$ group take place at different frequencies compared to $-\text{CH}_2-$ group. For methyl group, symmetric vibrations are as follows:



Sometimes, it happens that two different vibrational levels have nearly the same energy. If such vibrations belong to the same species (as in the case of $-\text{CH}_2-$ group or $-\text{CH}_3$ group), then a mutual perturbation of energy may occur, resulting in the shift of one towards lower frequency and the other towards higher frequency. It is also accompanied by a substantial increase in the intensity of the respective bands.

Acid anhydrides show two $\text{C}=\text{O}$ stretching absorptions between 1850-1800 and 1790-1745 cm^{-1} with a difference of about 65 cm^{-1} . This can be explained due to the symmetric and asymmetric stretching. In Infra-red spectrum, absorption bands are spread over a wide range of frequencies. It may happen that the energy of an overtone level chances to coincide with the fundamental mode of different vibration. A type of resonance occurs as in the case of coupled pendulums. This type of resonance is called **Fermi Resonance**. This can be explained by saying that a molecule transfers its energy from fundamental to overtone and back again. Quantum mechanically, resonance pushes the two levels apart and mixes their character so that each level becomes partly fundamental and partly overtone in character. Thus, this type of resonance gives rise to a pair of transition of equal intensity.

This phenomenon was first observed by Enrico Fermi in the case of carbon dioxide. Carbon dioxide molecule (Triatomic) is linear and four fundamental vibrations are expected for it. Out of these, symmetric stretching vibration is Infra-red inactive since it produces no change in the dipole moment (D.M.) of the molecule.



For symmetric stretching, Raman spectrum shows a strong band at 1337 cm^{-1} . The two bending vibrations are equivalent and absorb at the same frequency of 667.3 cm^{-1} . The overtone of this is 1334.6 cm^{-1} (2×667.3) which is very close to 1337 cm^{-1} . Thus, Fermi Resonance takes place resulting in the shift of first level towards higher frequency. The mutual perturbation of 1337 cm^{-1} (Fundamental) and 1334.6 cm^{-1} (overtone) gives rise to two bands at 1285.5 cm^{-1} and 1388.3 cm^{-1} having intensity ratio of 1 : 0.9.

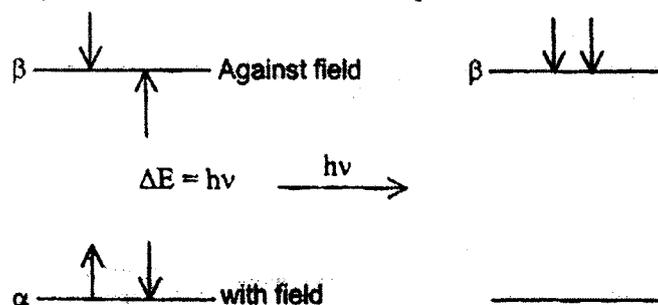
UNIT - V

SPECTROSCOPY - II

The nucleus of a hydrogen atom (proton) behaves as a spinning bar magnet because it possesses both electric and magnetic spin. Like any other spinning charged body, the nucleus of hydrogen atom also generates a magnetic field. Isotopes with nuclear spin, therefore have small magnetic fields, whose magnitude and direction can be described by a vector called a magnetic moment.

These magnetic moments are oriented in random fashion in field free space, but they have the important quantization property, that in a magnetic field only certain discrete orientations are allowed. ^1H , ^{13}C and ^{19}F , the nuclear spin can have only two alternative values associated with the quantum numbers, $+\frac{1}{2}$ (α) and $-\frac{1}{2}$ (β). When these nuclei are placed in a magnetic field which is designated as H_0 , their magnetic moments tend either to align with the field (α -spin) or against the field (β -spin). The energy difference between the proton α - and β -spin states is very small although α -spin state is of lower energy.

When the compound in the applied field is irradiated with electromagnetic radiation of the proper frequency, a nucleus with α -spin can absorb a light quantum and converted to the higher energy β -spin state, a process called flipping the spin. Thus energy is needed to flip, the proton from its lower-energy state to its higher-energy state. This energy in a NMR spectrometer is supplied by electromagnetic radiation in the radio frequency region. When this energy absorption occurs at the frequency that causes flips, the nuclei are said to be in resonance with electromagnetic radiation. This terminology is the origin of the name nuclear magnetic resonance. This can be represented via an energy diagram.



where ΔE is the energy difference between the two states and this quantity is directly proportional to the strength of the applied field H_0 and is given by the expression

$$\Delta E = 2\mu H_0 \quad \dots (1)$$

$$\Delta E = hv \quad \dots (2) \quad \nu = \text{frequency of radiation}$$

$h = \text{Planck's constant}$

$$\nu = \frac{2\mu H_0}{h} \quad \dots (3)$$

Here μ is the nuclear magnetic moment, which is a constant for a particular nucleus. Thus the greater the applied field the greater the energy gap between the two possible states of the proton. A proton in the lower energy state can be promoted to the higher state by supplying the exact quantity of energy ΔE . Conversely, if one has a source of energy ΔE available to the proton in a magnetic field H_0 it will be absorbed if equation (1) holds. According to equation (2), the excitation is possible only if $\Delta E = h\nu$. When expressed in terms of ν , H_0 , μ and h the equation (3) represents the resonance condition.

Instrumentation

Nuclear magnetic resonance spectrometers are used by chemists to measure e.g., the absorption of energy by hydrogen nuclei. These instruments use very powerful magnets and irradiate the sample with electromagnetic radiation in the radio frequency region. The sample is placed in a glass tube between the poles of a powerful magnet. Radio frequency input oscillator and receiver coils surround the sample. The sample is usually dissolved in a solvent that has no protons, like $CDCl_3$ to enable only the protons of the sample to be observed.

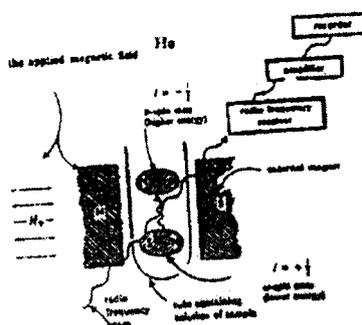


Fig. 1. ΔE = energy difference between α and β

The sample tube is rotated during spectral determination to average out the effects of nonuniformity. Nuclear magnetic resonance spectrometers are normally so designed so that they irradiate the compound with electromagnetic energy H_0 varies, so does ΔE . When the applied magnetic field H_0 reaches the correct strength ($h\nu/2\mu$), the ΔE matches the energy of the incident radiation. At this field strength, absorption of energy from the incident radiation will take place and transition from α -spin state to β will occur. Thus, when the nuclei absorb energy resonance occurs. This causes a tiny electrical current to flow in a coil surrounding the sample tube. The instrument then amplifies this current, which is displayed as a signal on the chart paper.

Chemical shift

The number of signals in an NMR spectrum tells the number of the sets of equivalent protons in a molecule.

When a molecule is placed in a magnetic field, its electrons are caused to circulate and thus they produce secondary magnetic fields i.e., induced magnetic field. If the induced field opposes the applied field, then proton is said to be shielded. But if the induced field reinforces the applied field, the proton feels a higher field strength and thus, such a proton is said to be deshielded. Shielding shifts the absorption upfield and deshielding shifts the absorption downfield to get an effective field strength necessary for absorption. Such shifts (compared with a standard reference) in the positions of NMR absorptions which arise due to the shielding or deshielding of protons by the electrons are called chemical shifts. For measuring chemical shifts of various protons in a molecule the signal for tetramethyl silane (TMS) is taken as a reference. This difference in the absorption position of the proton with respect to TMS signal is called chemical shift. The chemical shifts are measured in δ (Delta) or τ (Tau) scales.

$$\delta = \frac{\nu_{\text{sample}} - \nu_{\text{reference}}}{\text{Operating frequency in megacycles}}$$

ν_{sample} = Resonance frequency of the sample

$\nu_{\text{reference}}$ = Resonance frequency of TMS

The value of δ is expressed in parts per million (ppm). Most chemical shifts have δ values between 0 and 10. In the τ scale, signal for the standard reference, TMS is taken as 10 ppm. The two scales are related by the expression

$$\tau = 10 - \delta$$

NMR signal is usually plotted with magnetic field strength increasing to the right. Thus the signal for TMS appears at the extreme right of spectrum with $\delta = 0$ ppm. Greater the deshielding of protons, larger will be the value of δ . For most of the organic compounds signals appear downfield to the left of TMS signal.

Shielding and deshielding effects

Hydrogen nuclei in a molecule are surrounded by the electronic charge which shields the nucleus from the influence of the applied field. Thus, to overcome the shielding effect and to bring the protons to resonance, greater external field is required. Greater the electron density around the proton, greater will be the induced secondary magnetic field which opposes the applied field and thus greater external field will cause proton absorption. The extent of shielding is represented in terms of shielding parameter α . When absorption occurs, the field H felt by the proton is represented as

$$H = H_0 (1 - \alpha) \quad \dots (1)$$

H_0 – Applied field strength

Greater the value of α , greater will be the value of applied field strength which has to be applied to get the effective field required for absorption and vice versa.

$$\nu = \frac{\gamma H}{2\pi} \quad \dots (2)$$

From eqn. (1) and (2)

$$\nu = \frac{\gamma H_0 (1 - \alpha)}{2\pi} \quad \dots (3)$$

Equation (3) expressed that the protons with different electronic environments or with different shielding parameter can be brought into resonance by the following two ways.

- (i) The strength of the external field is kept steady and the radio-frequency is constantly varied.
- (ii) The radio frequency is kept steady and the strength of the applied field is constantly varied.

Factors influencing chemical shift

Inductive effect: A proton is said to be deshielded if it is attached with an electronegative atom or group. Greater the electronegativity of the atom, greater is the deshielding caused to the proton. If the deshielding is more for a proton, then its δ value will also be more.

The electronegativity of the halogens increases from iodine to fluorine. The chemical shift for the protons of a halomethane is directly related to the electronegativity of the halogen atom. Of the halogens, fluorine is the most effective at drawing electron density from the methyl group (-I effect). Therefore, one finds the protons in fluoromethane to be most deshielded than any of the protons in the series and thus their signal is found farthest downfield. Iodine is the least electronegative of the halogens thus the signal from the iodomethane protons is found the farthest upfield.

	CH ₃ -F	CH ₃ -Cl	CH ₃ -Br	CH ₃ -I
δ (ppm)	4.26	3.0	2.82	2.16

Van der Waal's deshielding : In overcrowded molecules, it is possible that some proton may be occupying sterically hindered position. Clearly electron cloud of a bulky group (hindering group) will tend to repel the electron cloud surrounding the proton. Thus, such a proton will be deshielded and will resonate at slightly higher value of δ than expected in the absence of this effect.

Anisotropic effects (space effect)

Electrons in the neighbouring bonds generate local magnetic fields. These magnetic fields may reinforce or oppose the applied field. The local magnetic field may be generated by π electrons or σ electrons. The effect due to σ electrons is less compared to that generated by π -electrons.

In benzene a magnetic field is generated by the circulating π electrons. This magnetic field reinforces the applied field in the case of protons which lie in the plane of the benzene ring and opposes the applied field for protons which lie above the plane of the benzene ring. Due to the magnetic anisotropic effect of the π -electrons protons of benzene absorb at 7.28 ppm.

The proton chemical shifts of hydrocarbons decrease in the order ethylene > acetylene > ethane. For protons in ethylene the magnetic field produced by the π electrons reinforce the applied field whereas for the protons in acetylene the magnetic field generated by the π electrons opposes the applied field. Therefore, the chemical shift of ethylene is greater than that of acetylene though acetylene is more acidic than ethylene. Aldehydic proton absorbs at about 9 ppm due to the deshielding caused by the magnetic anisotropic effect of the carbonyl group.

Hydrogen bonding

The hydrogen atom exhibiting property of hydrogen bonding in a compound absorbs at a low field in comparison to the one which does not. The hydrogen bonded proton being attached to a highly electronegative atom will have smaller electron density around it. Being less shielded, the field felt by such a proton will be more and hence resonance will occur downfield. The downfield shift depends upon the strength of hydrogen bonding.

Spin-spin splitting

Each signal in an NMR spectrum represents one kind or one set of protons in a molecule. It is found that in certain molecules, a single peak (singlet) is not observed, but instead, a multiplet (group of peaks) is observed.

Consider a molecule ${}^a\text{CH}_3{}^b\text{CH}_2\text{Br}$, ethyl bromide. This molecule has two kinds of proton in it and thus, two signals are expected in its NMR spectrum. The two signals are not singlets but a group of peaks are observed. For 'a' kind of protons (CH_3), a triplet i.e., a group of three peaks is observed and a quartet (group of four peaks) is noticed for 'b' kind of protons ($-\text{CH}_2-$). For 2-chloropropane ${}^a\text{CH}_3{}^b\text{CHCl}{}^a\text{CH}_3$, two signals are observed. For 'a' kind of protons, a doublet is observed while a septet (7 peaks) is noticed for 'b' kind of proton.

Spin-spin coupling

In order to understand the splitting patterns, we consider the molecule ethyl bromide ($\text{CH}_3\text{CH}_2\text{Br}$). The spin of two protons ($-\text{CH}_2-$) can couple with the adjacent methyl group ($-\text{CH}_3$) in three different ways relative to the external field. The three different ways of alignment are

- | | | |
|------|-----------------------|---------------------|
| i. | ↑↑ (Reinforcing) | ↑
External field |
| ii. | ↓↑ ↑↓ (Not effecting) | |
| iii. | ↓↓ (Opposing) | |

Thus, a triplet of peaks results with the intensity ratio of 1:2:1 which corresponds to the distribution ratio of alignment.

Similarly, the spin of three protons (CH_3-) can couple with the adjacent methylene group ($-\text{CH}_2-$) in four different ways relative to the external field.

i.	$\uparrow\uparrow\uparrow$	(Strongly reinforcing)	↑ External field
ii.	$\uparrow\uparrow\downarrow \uparrow\downarrow\uparrow \downarrow\uparrow\uparrow$	(Weakly reinforcing)	
iii.	$\downarrow\downarrow\uparrow \downarrow\uparrow\downarrow \uparrow\downarrow\downarrow$	(Weakly opposing)	
iv.	$\downarrow\downarrow\downarrow$	(Strongly opposing)	

Thus, quartet of peak results with an intensity ratio 1:3:3:1 which corresponds to the distribution ratio of all the alignments. The splitting of a signal is due to the different environment of the absorbing proton not with respect to electrons but with respect to the nearby protons.

Consider the compound 1,1,2-trichloroethane $^{(a)}\text{ClCH}_2^{(b)}\text{CHCl}_2$. This compound has two types of protons in it. The mutual magnetic influence between the protons 'a' and 'b' is not transmitted through space but through the electrons in the intervening bonds. The nuclear spin of protons 'a' first couples with the electron spin of C-H_a bonding electrons and these in turn couple with C-C bonding electrons and then with C-H_b bonding electrons. Thus, the coupling is eventually transmitted to the spin of H_b nucleus. The magnetic field that the proton 'a' feels at a particular instant is slightly increased (or) decreased by the spin of the neighbouring proton b. Thus, absorption by protons 'a' is shifted slightly, downfield for half the molecules and slightly upfield for other half of the molecules. Thus, the signal for a kind of protons is split into two peaks i.e., into doublet with equal peak intensities.

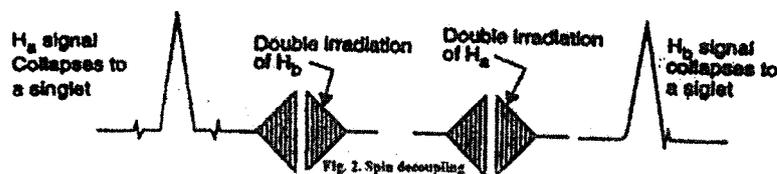
The signal from 'b' proton is effected by 'a' kind of proton. These two protons can be aligned with the applied field in three different ways and will consequently influence the proton 'b'. Thus a signal for 'b' proton will be split up into three peaks which are equally spaced with peak intensities 1:2:1. Thus, in the above compound, we observe 1:1 doublet which corresponds to 'a' protons ($-\text{CH}_2-$) and 1:2:1 triplet which represents 'b' proton ($-\text{CHCl}_2$).

Double resonance technique

This technique involves the irradiation of a proton or a group of equivalent protons with sufficiently intense radio frequency energy to eliminate completely the observed coupling to the neighbouring protons. A signal for a particular proton or a set of equivalent protons is split up into a multiplet under the influence of the neighbouring proton or protons under different environments. Consider the case of a compound, $\begin{array}{c} \text{---} \text{C} \text{---} \text{C} \text{---} \\ | \quad | \\ \text{H}_a \quad \text{H}_b \end{array}$ in which H_a and H_b are different environments. Clearly in its NMR spectrum, two doublets corresponding to each proton should be observed at different field strengths.

It has been observed that if we irradiate H_a with correct radio frequency energy so that the rate of its transitions between the two energy states becomes much larger than the life time of this nucleus in any one spin state will be too short to resolve coupling with H_b . In

such a case, H_b proton will have one time average view of H_a and hence H_a will come to resonance only once and H_b will appear as a singlet (not doublet). In the same way, if we irradiate H_b with sufficiently intense radio frequency energy, then due to its rapid transitions between the two spin states, H_a will have one time average view of H_b and H_b will come to resonance only once and H_a will appear as a singlet.



It may be noted that the time (dt) needed to resolve the two lines of a doublet is related to the separation between the lines i.e., coupling constant J . Thus, the formation of doublet in the above example is possible if each spin state of H_a has a life greater than dt . With double irradiation, the said life time becomes still less and thus, due to the increase in the rate of transition, coupling is not possible and thus, singlets result. In this technique, we make simultaneous use of two radio frequency sources. In addition to the normal NMR instrument, a second tunable radio frequency source is needed to irradiate H_a at the necessary frequency and the recording of the spectrum is done in the same way. It is called double resonance or double irradiation. Since multiplet collapses to a singlet in the process, it is also called spin decoupling.

FT-NMR

The common routine method of obtaining a NMR spectrum is to irradiate the sample with a constant frequency while the magnetic field is varied (field sweep). Other spectrometers operate by applying a constant magnetic field while the radio frequency is varied (frequency sweep). Either method gives the same spectrum. This is the normal, less expensive continuous wave nuclear magnetic resonance spectroscopy.

More recent technique is to irradiate the sample with all radio frequencies in the desired range (covering all H^1 frequencies) at once, while the magnetic field is held constant. The nuclei under study e.g. protons absorb at their individual frequencies. The interaction of all the frequencies gives an interferogram which can not be interpreted directly. It is converted by Fourier Transform (a mathematical technique) to the spectrum which shows absorption against frequency and the technique is called Pulsed-Fourier Transform nuclear magnetic resonance spectroscopy.

Lanthanide shift reagents

Shift reagents, provide a useful technique for spreading out NMR absorption patterns which normally overlap, without increasing the strength of the applied magnetic field. The NMR spectrum of *n*-hexanol is reproduced in Fig. 3-1, which is the normal record.

In this spectrum the high field triplet is distorted which represents the absorption of a methyl group adjacent to a $-CH_2-$ group. The low field broad multiplet is due to the methylene group adjacent to the hydroxyl group. The protons of the remaining methylene groups are all buried in the methylene envelope between δ 1.2 and 1.8. When the same spectrum is recorded after the addition of a soluble europium(III) complex, $Eu(DMP)_3$ i.e., the shift reagent, the spectrum is spread out over

a wider range of frequencies so that it is now simplified almost to first order, and the spectrum is given in Fig. 3-II.

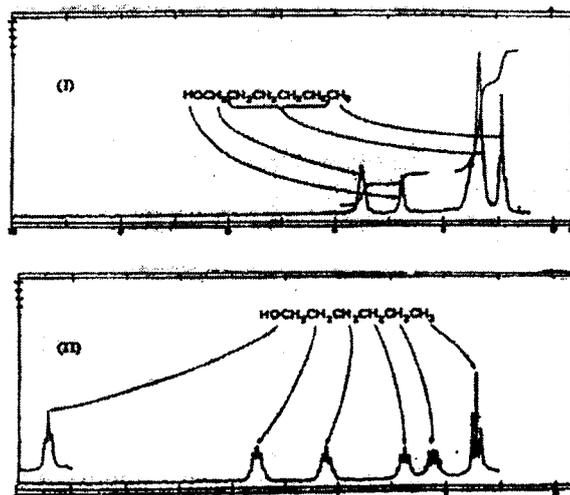


Fig. 3

In spectrum-II, the OH absorption signal is shifted too far to be observed. In complexes of this type, the lanthanide ion can increase its coordination by bonding interaction with lone pair electrons of groups like NH_2 , OH , $> \text{C}=\text{O}$, $-\text{O}-$, $-\text{COOR}$ and $-\text{CN}$. The magnetic field associated with the metal ion, which is a paramagnetic moiety, causes marked changes in the observed shifts of the protons in the substrate thus the name called shift reagent. Thus the paramagnetic europium(III) ion complexes with *n*-hexanol to induce dramatic downfield shifts in the *n*-hexanol resonances.

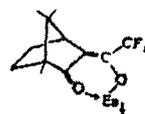
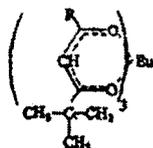


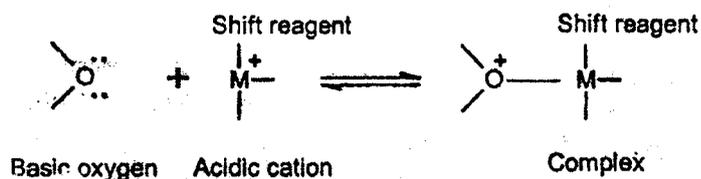
Fig. 4 a chiral lanthanide shift reagent

$\text{R} = t\text{-butyl} \equiv \text{Eu}(\text{DMP})_3$

tris-(dipivalomethanato)europium

$\text{R} = -\text{C}_3\text{F}_7 \equiv \text{Eu}(\text{FOD})_3$

tris-1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-3,5-octanedionateeuropium



As a result, a separate signal is now observed for each methylene group. It appears that the degree of shift is a function of the distance of the group from the coordination centre, the signals of the methylene protons closer to the OH group are moved downfield.

The shift reagents like $\text{Eu}(\text{FOD})_3$ are usually enolic B-dicarbonyl complexes of a rare earth metal and these complexes are mild Lewis acids. The mechanism by which these induce shifts is termed the pseudocontact interaction and originates from the fact that these are paramagnetic and substantially change the magnetic field in their immediate environment. Generally, europium complexes produce downfield shifts, while the praseodymium complexes produce upfield shifts. Ytterbium, erbium and holmium compounds tend to give greater shifts, but in the case of last two considerable line broadening also occurs and complicates the analysis of multiplets.

Coupling constant (J)

The distance between the centres of the two adjacent peaks in a multiplet is usually constant and is called the coupling constant. The value of the coupling constant is independent of the external field. It is measured in Hertz (Hz) or in CPS (cycles per second).

Now let us consider a compound $\begin{matrix} \text{a} & \text{b} \\ | & | \\ \text{CH} & - & \text{CH}_2 \end{matrix}$. In this compound two signals are expected in the NMR spectrum. Under the influence of two equivalent protons 'a' the signal for proton 'b' will appear as a triplet. The distance between any two adjacent peaks in a multiplet will be exactly the same. The triplet formed due to spin-spin coupling is shown below in Fig. 5.

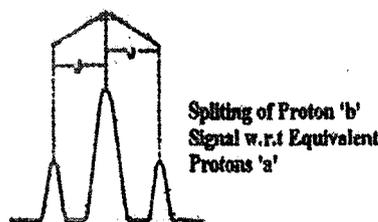


Fig. 5

Geminal coupling:

In the case of geminal protons (protons attached on the same carbon having different chemical environment) of a saturated compound, the value of J depends upon the bond angle. ($\angle < 120^\circ$) J can have any sign. Geminal protons are separated by two bonds. If these protons are in different environment, then the coupling is usually strong. When the bond angle is 105° , J is approximately -25CPS . J becomes nearly -12CPS when the bond angle increases to 109° . With the bond angle widened to 125° , the value of J increases to zero. If the bond angle is wider than 125° , we observe small positive values for the coupling constants. A plot showing the relationship between the values of J versus the bond angle is shown below in Fig. 6.

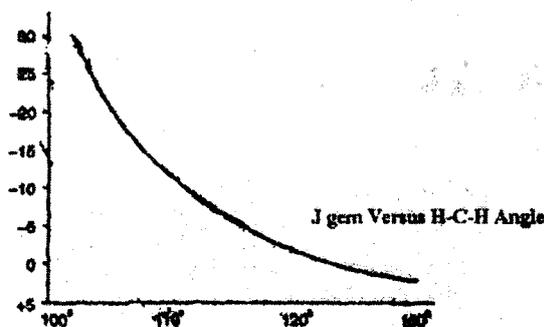


Fig. 6. Geminal Coupling Constants

Vicinal coupling

For vicinal protons, the value of coupling constant varies with the dihedral angle. Vicinal protons are the protons which are separated by three bonds. A plot for the values of J versus the dihedral angle for vicinal protons is shown below in Fig. 7.

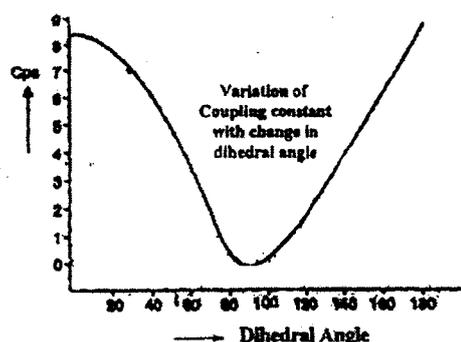


Fig. 7. Coupling Constants versus Dihedral Angles.

When the dihedral angle is 0° or 180° , we observe largest values for the coupling constants. The value of ' J ' is slightly negative when the dihedral angle is 90° .

INDOR spectroscopy

Probably the most powerful double resonance technique for the observation of the multiplicity of signals hidden by band overlap is Internuclear Double Resonance (INDOR). Here signals are only observed from coupled protons.

In the INDOR experiment the magnetic field (H_0) and the observation frequency (ν_1) are held fixed on one of the A signal lines in a spectrum where, for example, the X signal is obscured. The second weak perturbing frequency ν_2 is now swept through the spectrum. As ν_2 passes in turn through the hidden X lines a change in intensity of the A line may result, leading to a vertical movement of the recorder pen. Thus a negative or positive signal will result at positions corresponding to the X-resonance frequencies. The signals overlapping X will not register unless they too are coupled to proton A.

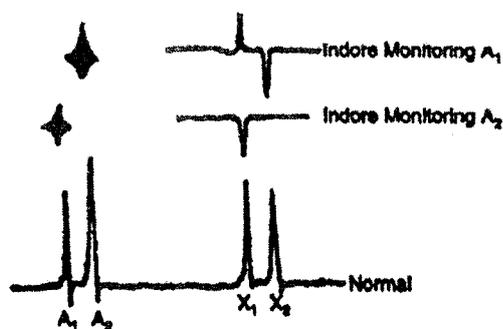


Fig. 8 : MHz Spectra of C₆H₅. CHBR.No2. 300 Hz scan, demonstrating the INDOR effect.

Spin-lattice relaxation

This relaxation time can be characterized as T_2 , which is a measure of the average lifetime of the nuclei in the higher energy state. The term lattice refers to the framework of molecules containing the precessing nuclei. A properly oriented small magnetic field due to motions induces a transitions in a particular precessing magnetic from an upper state to a lower state. The energy from this transition is referred to the components of the lattice as additional translational and vibrational energy, the total energy remaining unaltered. This maintains the excess of nuclei in the lower energy state. The time T_2 is dependent upon the gyromagnetic ratio of the absorbing nuclei and is strongly affected by the mobility of the lattice. The mobility increases, T_2 becomes shorter but at very high mobilities the probability of a suitable frequency for a spin-lattice transition again decreases because of the spreading of increased frequency over a broad range. The spin-lattice relaxation time is greatly influenced and becomes short in presence of an element with an unpaired electron, the spin of which produces a strong fluctuating magnetic field. This effect is also observed by nuclei of $I > \frac{1}{2}$. The great shortening of the relaxation time results in the broadening of the line.

Relaxation processes

As the collection of nuclei continuously absorb radio frequency radiation the excess of nuclei originally in a lower state may diminish, accordingly the intensity of the absorption signal may diminish and may, under certain circumstances, vanish entirely. When the population in both states becomes equal, the phenomenon is referred to as saturation. A very lengthy time would be required for the initial excess of nuclei in a lower state to be reformed but other mechanisms that are simultaneously occurring reduce this considerably. These various types of radiationless transitions responsible for the return of nuclei from higher to lower state are called relaxation processes which are of two kinds spin-spin relaxation and spin-lattice relaxation.

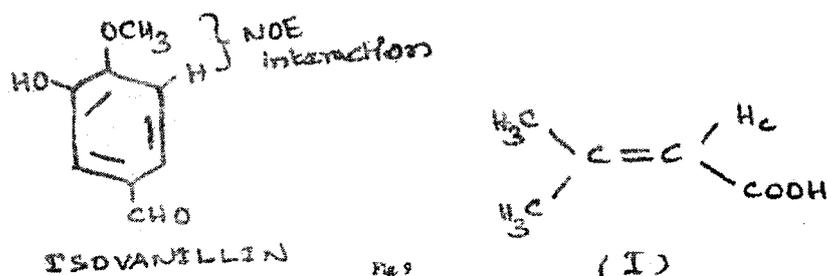
Spin-spin relaxation

This is effected by the mutual exchange of spins by two precessing nuclei in close proximity to one another. With each precessing nucleus there is an associated magnetic field vector component rotating in a plane perpendicular to the main field. If the two nuclei are extremely close this small rotating magnetic field is exactly what is required to induce a transition in the neighbouring nucleus? This mutual exchange of spins shortens the lifetime of an individual nucleus in the higher state, it contributes to a extent in the maintenance of the required excess of nuclei in a lower spin state. This relaxation time is denoted as T_1 and its

value is generally very small for crystalline solids or viscous liquids ($\sim 10^{-4}$ sec) and thus prevents the use of such samples for high resolution work.

Nuclear overhauser effect

A spin excited nucleus may undergo spin relaxation via the transfer of its spin energy to that of an adjacent nucleus. The efficiency of this energy transfer is directly related to the distance between the two nuclei. The nuclear overhauser effect takes advantage of this spin energy transfer. This interaction of magnetic nuclei through space does not lead to coupling and this NOE effect is only noticeable over short distances, generally 2-4Å. In a simple experiment of NOE normal NMR spectrum of the compound is recorded and the integral is determined. If one now irradiates (as in double resonance) one of the nuclei and records the NMR spectrum and its integral, the integrals of the nuclei closest in space to the irradiated nucleus will be enhanced in intensity relative to those for removed.



If one records the NMR of isovanillin normally and then while irradiating at the CH₃O frequency, the integral for the *ortho*-proton (doublet) is markedly increased i.e., this doublet then appears as a more intense signal. As a second example, if one irradiates the vinyl hydrogen in compound (I) and records the integral while doing so, the integral of the *cis* methyl group will be larger than that of the *trans* methyl group. This method is useful to determine stereochemical relationships in molecules.

Electron spin resonance spectroscopy

Electron spin resonance is a branch of absorption spectroscopy in which radiation having frequency in the microwave region is absorbed by paramagnetic substances to induce transitions between magnetic energy levels of electrons with unpaired spins. The main interest of electron spin resonance lies in the study of free radicals having unpaired electrons.

Types of substances with unpaired electrons

Stable paramagnetic substances. These include stable substances which can be studied very easily by ESR. The examples are simple molecules like NO, O₂ and NO₂, and the ions of transition metals and rare earth elements.

Unstable paramagnetic substances: These can be produced either as intermediate in a chemical reaction or by irradiation of stable molecules with a beam of nuclear particles or with UV or X-ray radiation. The substances so produced are also called free radicals or radical ions. These can be studied by ESR provided the life-times of such radicals are greater

than 10^{-6} second. If the life time are less than 10^{-6} second, they should produced at low temperatures in the solid state called matrix technique.

Theory of ESR

In ESR, the energy levels are produced by the interaction of the magnetic moment of an unpaired electron in a molecule ion with an applied magnetic field. The ESR spectrum results in due to the transitions between energy by absorbing radiations of microwave frequency.

For an electron of spin $s = \frac{1}{2}$ the spin angular momentum quantum number will have values of $m_s = \pm \frac{1}{2}$. In the absence of magnetic field, the two values of m_s , i.e. $+\frac{1}{2}$ and $-\frac{1}{2}$ will give rise to a doubly degenerate spin energy state. If a magnetic field is applied, this degeneracy is removed and this leads to two non-degenerate energy levels. The low energy state will have the spin magnetic moment aligned with the field and corresponds to the quantum number, $m_s = -\frac{1}{2}$. On other hand, the high energy state will have the spin magnetic moment opposed to the field and corresponds to the quantum number, $m_s = +\frac{1}{2}$. These energy states are illustrated in Fig. 10.

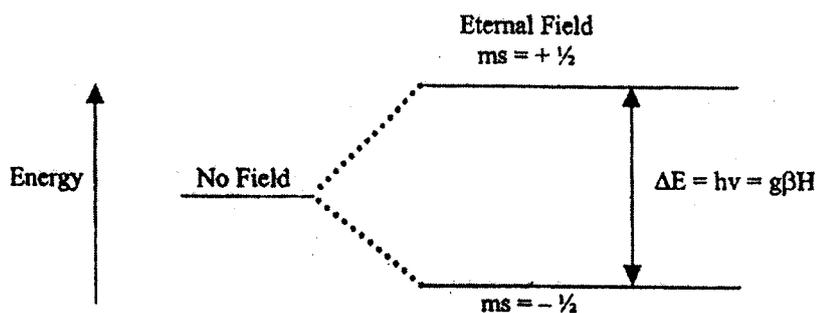


Fig .10.

These two states will posses energies that are split up from original state with no applied magnetic field by the amount $+\mu_e H$ and $-\mu_e H$ for the low energy and high energy states respectively; here H is the magnetic field acting on the unpaired electron and μ_e is the magnetic moment of the spinning electron. In ESR, a transition between the two different energy levels takes place by absorbing a quantum of radiation of frequency in the microwave region. Thus, the ESR spectrum of a free electron would consist of a single peak corresponding to a transition between these levels. When the absorption occurs, the following relation holds good, i.e.,

$$2\mu_e H = hv \quad \dots (1)$$

where ν is the frequency of the absorbed radiation in cycles per second. As the relation (1) holds good for a free electron, the energy (ΔE) of transition is more accurately given by the following relation:

$$\Delta E = hv = g\beta H \quad \dots (2)$$

In equation (2)

h is the Planck's constant ; H is the applied magnetic field

β is the magneton which is a factor for converting angular momentum into magnetic moment. The value of β is defined as follows:

$$\beta = \frac{eh}{4\pi mc} = 0.9723 \times 10^{-20} \text{ erg/gauss} \quad \dots (3)$$

where 'e' is the electronic charge, m the mass of electron and c the velocity of light.

'g' is the proportionality factor which is a function of the electron's environment. It is sometimes called the spectroscopic splitting factor or Lande's splitting factor.

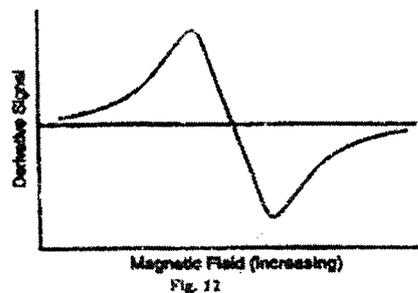
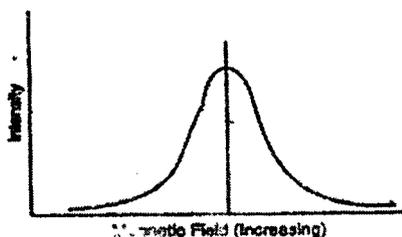
The values of g depend upon the orientation of the molecule having the unpaired electron with respect to applied magnetic field. In the case of a gas or solution, the molecules have free motion and the value of g is averaged over all orientations. But in the case of crystals, the movement of electron is not free. However, in the case of a paramagnetic ion or radical situated in a perfectly cubic crystal site, the value of g is same in all directions, i.e., the value of g does not depend upon the orientation of the crystal. On the otherhand, the value of a paramagnetic ion or radical situated in a crystal of low symmetry depends upon the orientation of the crystal. There are three axes in a crystal. The values of g along x, y and z axes are denoted by g_x , g_y and g_z respectively. In the case of a tetragonal site, the values of g_x and g_y are equal and referred to as g_{\perp} (g perpendicular). This value is generally attained when the external magnetic field is perpendicular to z-axis. The value of g is obtained when the magnetic field is parallel to z-axis. The value of g_z is obtained when magnetic field is parallel to z-axis. The value of g_z is denoted by g_{\parallel} (g-parallel).

Suppose θ is the angle between magnetic field and z-axis. The experimental value of g is defined by the following equation for a system possessing axial symmetry.

$$g^2 = g_{\parallel}^2 \cos^2\theta + g_{\perp}^2 \sin^2\theta \quad \dots (4)$$

Presentation of the ESR spectrum

The ESR spectrum, similar to NMR spectrum, may be obtained by plotting intensity against the strength of a magnetic field. However, the better way is to represent ESR spectrum as a derivative curve in which the first derivative (the slope) of the absorption curve is plotted against the strength of magnetic field. In Fig. 11 there is a single absorption peak having no fine structure. In Fig. 12, there is a derivative curve that corresponds to Fig. 11.



The results represented by derivative curves in ESR can be readily interpreted. Each negative slope in the derivative curve represents a peak or shoulder in the absorption spectrum. Every crossing of the derivative axis with a negative slope indicates a true maximum whereas a crossing with positive slope indicates minimum. It means that the number of peaks or shoulders in the absorption curve can be determined from the number of minima or maxima in the derivative curve.

The peak height of the absorption curve to derivative curve does not provide much information. However, the total area covered by either the absorption or derivative curve is proportional to the number of unpaired electrons in the sample. In order to calculate the number of electrons in an unknown sample, comparison is made with a standard sample having a known number of unpaired electrons and possessing the same line shape as the unknown. The most widely used standard is 1,1-diphenyl-2-picrylhydrazyl free radical (DPPH). DPPH is a chemically stable material having the splitting factor $g = 2.0046$. DPPH contains 1.53×10^{21} unpaired electrons per gram. DPPH cannot be employed as an internal standard for other free radicals. In the case of free radicals, an internal standard is a trace of Cr(III) entrapped in a tiny chip of ruby crystal cemented permanently to the sample cell. This standard shows a strong resonance and its g value is 1.4.

Hyperfine splitting

The ESR spectrum exhibits hyperfine splitting which is caused by the interactions between the spinning electrons and adjacent spinning magnetic nuclei. When a single electron interacts with one nucleus, the number of splittings will be equal to $2I + 1$, where I is the spin quantum number of the nucleus. In general, if a single electron interacts magnetically with n equivalent nuclei, the electron signal is split up into a $(2nI + 1)$ multiplet. Let us illustrate the hyperfine splitting by considering an example of a hydrogen atom having one proton and one electron ($I = \frac{1}{2}$ for the proton). In the absence of a magnetic field, the single electron of spin ($s = \frac{1}{2}$) gives rise to a doubly degenerate spin energy state. When a magnetic field is applied, the degeneracy is removed and two energy levels, one corresponding to $m_s = -\frac{1}{2}$ aligned with the field and the other corresponding to $m_s = +\frac{1}{2}$ aligned opposing the field, will be obtained (Fig. 13). The spectrum of a free electron would consist of a single peak corresponding to a transition between these levels. This is shown in Fig. 14.

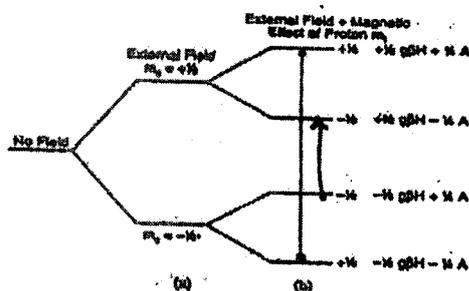


Fig. 13: a) Effect of external field on the energy states for an electron
b) Effect of a nuclear spin $\frac{1}{2}$ of proton on these states.

When the interaction between the two energy states and the nuclear spin due to proton is considered, each energy state is further split up into two energy levels corresponding to $m_1 = +\frac{1}{2}$ and $m_1 = -\frac{1}{2}$, where m_1 is the nuclear spin angular momentum quantum number. Thus, corresponding to two energy states, four different energy levels are obtained (Fig. 13). It means that ESR spectrum of hydrogen would consist of two peaks (Fig. 14) corresponding to two transitions shown by two arrows in Fig. 13.

The energies of four energy levels (Fig. 13) are as follows:

$$E_{\frac{1}{2}, \frac{1}{2}} = \frac{1}{2} g \beta H + \frac{1}{4} A \quad \dots (5)$$

$$E_{\frac{1}{2}, -\frac{1}{2}} = \frac{1}{2} g \beta H - \frac{1}{4} A \quad \dots (6)$$

$$E_{-\frac{1}{2}, -\frac{1}{2}} = -\frac{1}{2} g \beta H + \frac{1}{4} A \quad \dots (7)$$

$$E_{-\frac{1}{2}, \frac{1}{2}} = -\frac{1}{2} g \beta H - \frac{1}{4} A \quad \dots (8)$$

The general expression for all the four energy levels is as follows:

$$E = g \beta H m_s + A m_s m_l \quad \dots (9)$$

where A is termed as the hyperfine coupling constant. When the proper values of m_s and m_l are substituted in equation (9), the values of energies indicated in Fig. 13 are obtained. The selection rules in ESR are

$$\Delta m_s = 0 \text{ and } \Delta m_l = \pm 1$$

The deuterium (^2H) is simple example of a system with $I = 1$. Energy levels are computed in a similar manner as done in the case of hydrogen atom. Corresponding to $m_s = +\frac{1}{2}$, there are three values of $m_l = 1, 0, -1$. Similarly corresponding to $m_s = -\frac{1}{2}$, there are also the three values of m_l , i.e., $m_l = -1, 0$ and $+1$. The energy of all the six energy levels are as follows:

$$E_{\frac{1}{2}, 1} = \frac{1}{2} g \beta H + \frac{1}{2} h A \quad E_{-\frac{1}{2}, -1} = -\frac{1}{2} g \beta H + \frac{1}{2} h A$$

$$E_{\frac{1}{2}, 0} = \frac{1}{2} g \beta H \quad E_{-\frac{1}{2}, 0} = \frac{1}{2} g \beta H$$

$$E_{\frac{1}{2}, -1} = \frac{1}{2} g \beta H - \frac{1}{2} h A \quad E_{-\frac{1}{2}, 1} = \frac{1}{2} g \beta H - \frac{1}{2} h A$$

Let us now consider the case for $s = \frac{1}{2}$ and $I = 3/2$. An example of this is the methyl radical. When the interaction is considered between the sample unpaired electron on the carbon atom and three hydrogen nuclei, there are four values corresponding to $m_s = +\frac{1}{2}$. Similarly, there are four values corresponding to $m_s = -\frac{1}{2}$, i.e.

$$\text{For } m_s = +\frac{1}{2}, m_l = +3/2, +1/2, -1/2, -3/2$$

$$\text{and for } m_s = -\frac{1}{2}, m_l = -3/2, -1/2, +1/2, +3/2$$

On applying the selection rule $\Delta m_l = 0$ and $\Delta m_l = +1$ four transitions are possible, resulting four lines in the ESR spectrum of methyl radical. The observed relative intensities for the four lines are in the ratio 1:3:3:1. The four transitions that occur in the ESR spectrum of methyl radical are shown in Fig. 15. The derivative spectrum of methyl radical is shown in Fig. 16.

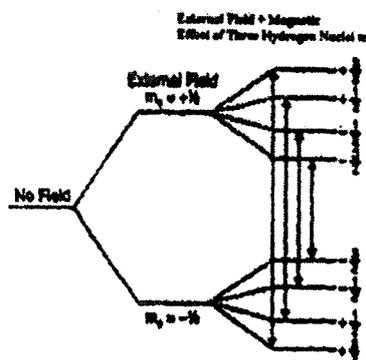


Fig. 15

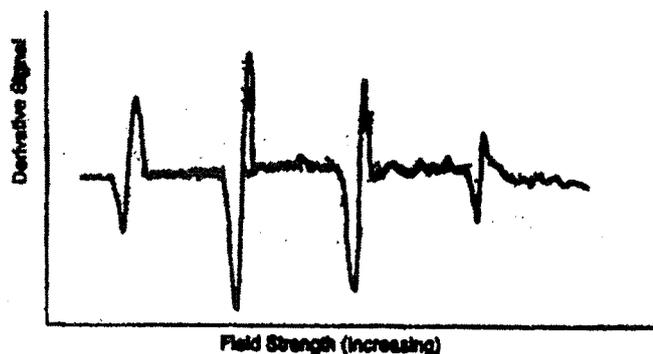


Fig. 16

In general, when the absorption spectrum of an unpaired electron undergoes interaction with n equivalent nuclei of equal spin I , the number of lines obtained in ESR spectrum will be given by $(2nI + 1)$. When the interaction involves a set of n equivalent nuclei of spin I , and a set of equivalent nuclei m of spin I_j , the number of lines will be given by $(2nI + 1)(2mI_j + 1)$.

Determination of g-value

In order to measure the value of g , the best method is to measure that field separation between the centre of the unknown spectrum and that of a reference substance whose g -value is accurately known. In most of the cases, DDPH is generally used as a standard whose g -value is 2.0036. In the ESR spectrometer, the standard substance is placed along with the unknown in the same chamber of a dual-cavity cell. The ESR spectrum will show two signals with a field separation of ΔH . The g -values for the unknown is given by

$$g = g_s \left(1 - \frac{\Delta H}{H} \right) \quad \dots (10)$$

where H is the resonance frequency. ΔH is positive if the unknown has its centre at higher field.

Line width

The width of an ESR resonance depends on the relaxation time of the spin state under study. For most of the samples, 10^{-7} sec is a relaxation time and if we substitute this value in the Heisenberg's uncertainty relation, we can calculate a frequency uncertainty (line width) which comes out to be ≈ 1 gauss. A shorter relaxation time will increase this width. Thus, there is a much wider line in ESR spectrum than in NMR where the width of a normal line for a liquid is 0.1 gauss.

The wider lines in ESR spectrum possess advantages and disadvantages. The advantage is that in ESR a lower magnetic field homogenous to 1 in 10^5 over the sample is employed whereas for NMR a figure of 1 in 10^8 is adequate. The major disadvantage of the wider lines is that these are more difficult to observe and measure than sharp lines. For this simple reason, ESR spectrometers are generally operated in the derivative mode.

The increase in width of spectral lines in ESR spectrum is termed as the broadening of the lines. The broadening becomes too much in those cases where the ground state has another orbital level above it, not having very different energy.

The broadening the spectral lines in ESR may also occur if the concentration of the paramagnetic species is very high. For this reason, the ESR spectrum is obtained for such a substance whose trace quantity is incorporated as an impurity on a diamagnetic compound, isomorphous with that under study.

The Heisenberg uncertainty-principle can be utilized to estimate line width from relaxation times. It states that the product of uncertainty in energy and the uncertainty in time is constant and equal to $h/2\pi$.

$$\Delta E \times \Delta t = h/2\pi$$

Photoelectron spectroscopy

The technique of photoelectron spectroscopy (PES) measures the ionization energies of molecules when electrons are ejected from different orbitals, and uses the information to infer the orbital energies.

Because energy is conserved when a photon ionizes a sample, the energy of the incident photon $h\nu$ must be equal to the sum of the ionization energy I of the sample and the kinetic energy of the photoelectron,

$$h\nu = \frac{1}{2} m_e v^2 + I \quad \dots (1)$$

This equation can be refined in two ways. First, photoelectrons may originate from one of a number of different orbitals, and each one requires a different ionization

energy. Hence, a series of different kinetic energies of the photoelectrons will be obtained each one satisfying.

$$h\nu = \frac{1}{2} m_e v^2 + I_i \quad \dots (2)$$

where I_i is the ionization energy for ejection of an electron from an orbital i . Therefore, by measuring the kinetic energies of the photoelectrons and knowing ν , these ionization energies can be determined. Photoelectron spectra are interpreted in terms of an approximation called Koppman's theorem which states that the ionization energy I_i is equal to the orbital energy of the ejected electron.

The second refinement is that the ejection of an electron may leave an ion in a vibrationally excited state. Then not all the excess energy of the photon appears as kinetic energy of the photoelectron, and we should write

$$h\nu = \frac{1}{2} m_e v^2 + I_i + E_{\text{vib}}^+ \quad \dots (3)$$

where E_{vib}^+ is the energy used to excite the ion into vibration. Each vibrational quantum that is excited leads to a different kinetic energy of the photoelectron, and gives rise to the vibrational structure in the photoelectron spectrum.

The ionization energies of molecules are several electronvolts even for valence electrons, so it is essential to work in at least the ultraviolet region of the spectrum and with wavelength of less than about 200 nm. A great deal of work has been done with radiation generated by a discharge through helium; the He(I) line ($1s^1 2p^1 \leftarrow 1s^2$) lies at 58.43 nm, corresponding to a photon energy of 21.22 eV. Its use gives rise to the technique of ultraviolet photoelectron spectroscopy (UPS). If the core electrons are being studied, then photons of even higher energy are needed to expel them; X-rays are used and the technique is denoted XPS.

Ultraviolet photoelectron spectroscopy (UPES)

If we consider the uv photoelectron spectrum of HBr, it gives two sets of lines at 11.88 eV and 15.2 eV. The lines at 11.88 eV are due to least tightly bound electrons are those in the non-bonding lone pairs of Br. The next ionization energy lies at 15.2 eV, and corresponds to the removal of an electron from the HBr σ bond. The HBr spectrum shows that ejection of a σ electron is accompanied by a long vibrational progression. The Frank-Condon principle would account for this progression if ejection were accompanied by an appreciable change of equilibrium bond length between HBr and HBr^+ because the ion is formed in a bond compressed state, which is consistent with the important bonding effect of the σ electrons. The lack of much vibrational structure in the two bonds labelled 2π is consistent with the non-bonding role of the $\text{Br} 2p\pi$ lone pair electrons, for the equilibrium bond length is little changed when one is removed.

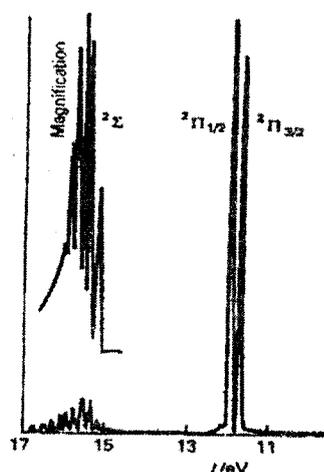


Fig. 17. The Photo electron spectrum of HBr.

X-ray photoelectron spectroscopy

In XPS, the energy of the incident photon is so great that electrons are ejected from inner cores of atoms. The cores ionization energies are characteristic of the individual atom rather than the overall molecule. Consequently, XPS gives lines characteristic of the elements present in a compound or alloy. For instance, the K-shell ionization energies of the second row elements are

Li	Be	B	C	N	O	F
50	110	190	280	400	530	690 eV

Detection of one of these values indicates the presence of the corresponding element. This chemical analysis application is responsible for the alternative name, electron spectroscopy for chemical analysis or ESCA. The technique is mainly limited to the study of surface layers because, even though X-rays may penetrate into the bulk sample, the ejected electrons cannot escape except from within a few nanometers of the surface. Consider the XPS spectrum of NaN_3 , the azide ion N_3^- gives the spectrum by the following way. Although the spectrum lies in the region of 400 eV, it has a doublet structure with splitting 6eV.

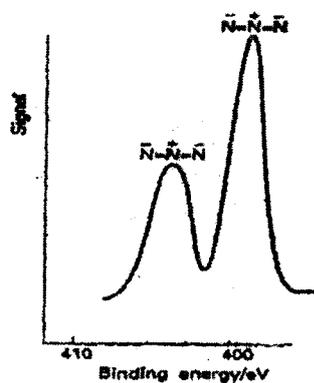


Fig. 18.

This splitting can be understood by noting that the structure of the ion is $\ddot{\text{N}}=\text{N}=\ddot{\text{N}}$ with charge distribution (-, +, -). Hence the presence of the negative charges on the terminal atoms lowers the core ionization energies, while the positive charge on the central atom raises it. This inequivalence of the atoms results in two lines in the spectrum with intensities in the ratio 2:1. Observations like this can be used to obtain valuable information about the presence of chemically inequivalent atoms of the same element.

Instrument for photoelectron spectroscopy

The essential components of a photoelectron spectrometer are:

(a) A source, (b) A target or a great chamber, (c) An energy analyzer for the ejected photoelectrons and (d) A detector for the energy analysed electrons.

In addition to these, appropriate electrical circuitry and good vacuum and differential pumping systems are also essential.

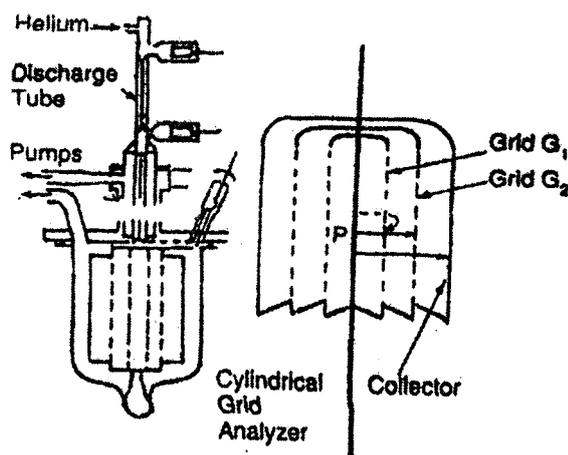


Fig.19 A simple photoelectron spectrometer.

(a) **Source:** The source of photon may be a monochromatic emission line or continuous emission spectrum fed through a vacuum monochromator. But monochromatic emission line is used in most of the work. The most common source of producing low energy photons is by passing electric discharge through an inert gas such as helium (giving the He I line at 584 Å or 21.22 eV and He II line at 373 Å or 40.80 eV) or neon (giving neon lines at 16.67 eV and 16.85 eV). High energy X-ray photons are obtained using different metals as a nodes. The most commonly used one K_{α} lines is obtained from magnesium ($\text{Mg } K_{\alpha} = 1254 \text{ eV}$) and aluminium ($\text{Al } K_{\alpha} = 1487 \text{ eV}$).

The synchrotron radiation is the most promising emission source in the intervening wavelength region for photoelectron spectroscopic studies. Synchrotron radiation is obtained from very high energy electrons and positrons moving in circular orbits as, for example, in accelerators and storage rings.

(b) Target: The arrangements for the target sample vary with its nature. For less volatile compounds with low source method, heated probes are usually employed.

(c) Electron energy analyzer: Two types of electron analysers are in use these days. These are retarding potential analyzer and the dispersive analysers. In the first method of energy analysis, the photoelectrons are subjected to a variable retarding potential and a photoelectron spectrum results due to differences in relative transmission of electrons of different energy at a given retarding field. In dispersive analyzer voltage sweep causes electrons of different velocities to reach an exit slit before passing into the detector.

(d) Detector: The detector is usually an electron multiplier of one type or the other with appropriate electronic amplification and recording. The detectors used in photoelectron spectroscopy vary a great deal in degree of sophistication. The most common instruments for low-energy photoelectron spectroscopy use a cylindrical electrostatic analyser. The detector is calibrated with known lines of argon, krypton or xenon, the recorded half-width of which gives a guide to the resolution.

Technique of photoelectron spectroscopy

A simple discharge tube and photoionization chamber used in one of the first photoelectron spectrometers is shown in Fig. 19. Photoionization occurs in the region P. The electron energy spectrum of the ejected photoelectron is then scanned by applying a retarding potential difference voltage between the grids G1 and G2. For He I radiation, the grid G2 is held at -20 volts, while G1 changes from this negative value to about zero, thus gradually inhibiting transmission of the high energy electrons. The grid G2-collector voltage difference is always kept greater than the grid G1-collector voltage difference. This prevents the movement of positive ion to the collector. After coming out of the grids the analysed photoelectrons are detected at the collector C. The retarding potential spectrum i.e. intensity of the collected electrons as a function of increasing retarding potential can be displayed as such or in a differentiated form. This is then recorded.

Applications of photoelectron spectroscopy

The applications of ESCA can be grouped in several types. First, the binding energy of a given level, such as 1s level, is different for different elements, and small shifts upto 10 eV of such an energy level for the same elements in different oxidation states or different molecular environments are also measurable. These shifts are similar in a sort of way to proton chemical shifts in NMR.

1. Core binding energy

Photoionization by high energy X-ray photons cause ejection of core electrons and an analysis of the consequent photoelectron spectra yields core electron binding energies. Deeper the location of the core electron, higher is the magnitude of the binding energy. Also, for a given core shell electron, the binding energy increases with the atomic number across a period.

The core electron shifts or the chemical shifts are due to the influence of the molecular charge distribution on the shielding of core electrons. The chemical shifts are correlated with oxidation number or charge of an atom in a molecule. In electrostatic model the electron binding energy shifts relative to a free neutral atom is equal to the charge of the electrostatic potential that all charges in the system cause at the considered atomic core. Thus, the chemical shift of an atom in a molecule is predominantly influenced by its nearest neighbour atoms. Similarly, chemical shifts are also influenced by the presence of substituents, called substituent shifts. This is due to the influence of atoms or groups at a distance farther than one atom away from the atom considered. The chemical shifts of binding energies for any given type of electron are very small, and are dependent on the nature of the neighbouring atoms. The latter determine the type of bonding and hence the nature of charge distribution in the atom, this causes small changes in the binding energy.

2. Element analysis

It is possible to carry out the elemental analysis by PES provided relative intensities of the electron lines are known for the elements one wishes to study.

3. Quantitative analysis

The relative amounts of zinc and copper in brass alloys have been estimated with a fair accuracy by means of ESCA. Quantitative analysis of many other elements have been successfully carried out by ESCA.

4. Gas analysis

ESCA seems also to have some potential in gas analysis. As an example ESCA spectra of the analysis of a mixture of methane, carbon monoxide and carbon dioxide is shown. In a mixture of CO, CO₂ and CH₄, there are well separated peaks due to two kinds of O(1s) (CO and CO₂) and three kinds of C(1s) (CO, CO₂, CH₄). Analysis of air can be made from O(1s), N(1s) and Ar(2p_{3/2}, 2p_{1/2}) peaks.

5. Structural analysis

The atomic character of core electron spectra makes it possible to probe specific parts of molecules. ESCA has therefore been very useful for structural analysis, in particular for linkage analysis. Spectra for alternative structural arrangements can be predicted with relative good accuracy. In this way to determine the correct structure in some cases where the structure was in doubt. The problem of distinguishing between the possible structures of doubly oxidized cystine is a typical example.

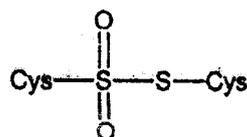
Cys-S-S-Cys

Cystine

Cys SO₂ SCys

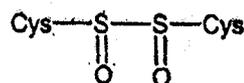
Doubly oxidized cystine

There are two possible structures for doubly oxidized cystine.



Thiosulphonate structure

and



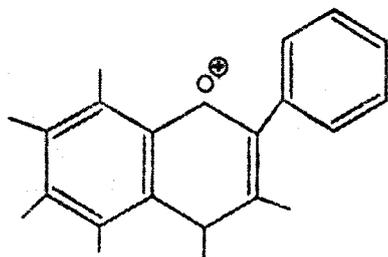
Disulphoxide structure

The thiosulphonate structure is expected to give two peaks of equal intensity corresponding to the two oxidation states in the molecule, whereas the disulphoxide structure should give only one peak.

6. Charge distribution in bonds and molecules

ESCA is useful also in the study of the polarity of bonds and charge distribution in molecules because the core electron binding energies are dependent on the charge.

- (a) The long standing controversy about the charge transfer in metal carbides has been finally settled with help of ESCA. The ESCA spectra conclusively prove that the charge transfer occurs from metal to carbon in metal carbides.
- (b) In metal complexes, the balance between σ - and π - back bonding has been studied by means of ESCA. ESCA spectrum has shown that P - Pt, σ -bonding and P \rightarrow Pt π -back bonding in a series of neutral triphenylphosphine platinum complexes are fully balanced.
- (c) The power of ESCA for probing the charge on individual atoms in complex systems has been demonstrated on the ring oxygen in flavylum compounds which are usually written as a comparison of the O (1s) shift with that of known oxygen groups showed that the oxygen is neutral or even slightly negative, the charge thus being strongly localized.



- (d) ESCA has also been applied to charge distribution in five-membered heterocyclic compounds, trithiopentalenes and related sulphur compounds, nucleic acids and hydrogen bonding.

Raman Spectroscopy

In 1928, Sir C.V. Raman discovered that when a beam of monochromatic light was allowed to pass through a substance in the solid, liquid or gaseous state, the scattered light contains some additional frequencies over and above that of incident frequency. This is known as Raman effect. The lines whose wavelengths have been modified in Raman effect are called Raman lines. The lines having wavelengths greater than that of the incident wavelength are called Stoke's lines and those having shorter wavelengths Anti-Stoke's lines.

If ν_i is the frequency of incident radiation and ν_s the radiation scattered by the given molecular species, then the Raman shift, $\Delta\nu$ is defined by the following relation.

$$\Delta\nu = \nu_i - \nu_s$$

The Raman shift does not depend upon the frequency of the incident light but it is regarded as a characteristic of the substance causing Raman effect. For Stoke's lines, $\Delta\nu$ is positive and for Anti-Stoke's lines $\Delta\nu$ is negative (Fig. 20).

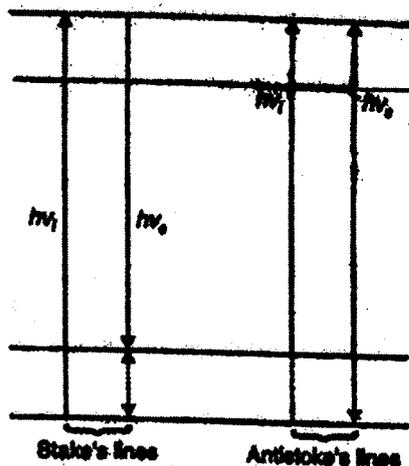


Fig. 20

Raman instrumentation

In Raman spectrometer the sample is irradiated with monochromatic light and the scattered light is observed at right angles to the incident radiation. Thus, the Raman spectrometer, us er spectrometer, employs as light source, a sample tube, a monochromator and a detector. Since the intensities of the scattered radiation and roughly 0.01 per cent of that of the incident radiation, intense source into radiation and high sensitive detector are usually built into a Raman spectrometer. The following Fig. 21 shows the schematic diagram of a Raman spectrometer

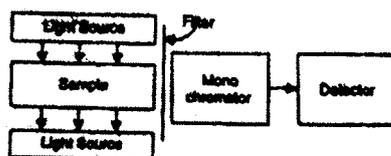


Fig. 21 Schematic diagram for a Raman spectrometer.

Raman source

Since the intensities of scattered radiation are very weak, roughly 0.01 per cent of that of the incident radiation, an extremely intense source of radiation must be used. Usually a mercury lamp shaped in the form of a helix or a bank of four to eight individual tubular mercury lamps of the H type surround the sample tube. The introduction of optical masers or lasers as Raman source the scope of Raman spectroscopy is greatly widened. For coloured solution argon-krypton mixed gas laser can be used.

The sample

The sample usually liquid, is taken in a sample tube provided with an optical window at the end. Gaseous samples can also be examined by Raman spectroscopy. Commercially available gas cells are used with the mercury source. With the development of laser, Raman spectrometer with double monochromators, powdered solid sample can also be examined and a good spectra can usually be obtained.

Filter

Liquid filters are placed between the source and the sample tube. Different filters are used for different excitation radiation, example for 4358Å excitation a saturated solution of NaNO_2 is used to remove the ultraviolet lines and the violet lines at 4047Å.

Monochromators

In the monochromator, both lenses, and mirrors have been employed. Most Raman spectrometer use a diffraction grating as a dispersing element. To avoid stray light problem from scattering by dust particle in the sample, from the cell wall or from the surface of the solid sample particles, a double monochromator is used.

Detectors

Raman spectrum can be photographed with an ordinary spectrograph. There are basically two different ways to detect and record the Raman lines. The easiest way is to gather the scattered light emerging through a glass window at the end of the Raman sample tube, allow to pass through the prism or grating and then focus on to a photographic plate. The plate is developed and both the line frequencies and intensities can be measured using external equipment. The other method is the photoelectric method of recording the Raman spectrum. Modern instruments have photomultiplier tubes for direct measurement and automatic scanning of a spectrum. The spectrum produced by the monochromator is passed through a slit which allows a narrow wavelength region to pass through, which is focussed on to a photomultiplier type detector. The photomultiplier type detector employs an amplifier and a recorder, which provides the Raman spectrum directly.

Uses of Lasers in Raman spectroscopy

The theory of Raman effect shows that the amount of Raman scattering from the sample is directly proportional to the intensity of the incident radiation at the sample, to the fourth power of the frequency of the exciting line and to the concentration of the scattering species. The total intensity overall directions of a Raman line with frequency $\nu_0 + \nu_{lm}$ is given by

$$I = Q_{lm} I_0$$

Where l and m are the two vibrational states between which transition occurs. The intensity of the incident light of frequency ν_0 is I_0 and Q_{lm} is the scattering cross section which depends on the polarization of the incident light. Earlier Raman work has been done employing the very intense blue line (435.8 nm) of mercury arc lamps. Photographic exposures of several hours duration were frequently required. The use of gas LASER'S (which is the acronym for light amplification by stimulated emission of radiation) for excitation in Raman spectrometers in the 60's has brought about the renaissance in Raman spectroscopy. The high degree of collimation, polarization and high power density of the

laser beam are usefully taken more advantage. The higher the power concentrated on a small volume of the sample, the more intense spectra will be obtained. Lasers are over a thousand times brighter than mercury arc source and which is superior to mercury source. Some of the commonly used lasers are helium-neon 632.8 nm, krypton ion 647.4, 568.4 nm and argon ion 488 and 514.5 nm. The most striking property of the laser ideally suited to Raman work is the laser light is highly monochromatic and plane polarized besides its extreme brightness, directionality and high degree of coherence.

Determination of molecular structure

Because of the considerable difficulties in detection and poor resolution, Raman spectroscopy technique has not been so widely used for compound identification as IR. IR and Raman techniques are complementary to each other. Vibrations which are forbidden in IR appear in Raman spectrum and vice versa. For example, OH and C=O absorb strongly in IR but show up weakly in Raman spectrum. NH, SH, C=C, C≡C etc., show strongly in the Raman spectrum but may be weak in the IR. Therefore, there are great advantages in applying both Raman and IR techniques to the same compound. Molecular vibrations which appear above 650 cm^{-1} are best studied by IR and for weak vibrations such as metal-ligand stretchings, lying below 600 cm^{-1} , Raman technique is most suited. Raman spectroscopy can be applied to investigate bond angles, structure, ionic equilibria, nature of bonding, analysis of strong acids and other aqueous solutions, the degree of dissociation of strong electrolytes and the corresponding activity coefficients.

The observed Raman frequencies can be used to calculate other vibrational frequencies. If there is agreement between the calculated and observed frequencies the model is a good representation of the molecule and the relative positions of the atoms in the molecule are known. At the same time information is obtained about the magnitude of the forces holding the atoms together in the molecule and conclusions can be drawn about the chemical bonds in the molecule.

Diatomic molecules

Let us consider molecules like H_2 , N_2 , O_2 , HCl, HBr, HI. The first three molecules are composed of identical atoms and therefore are known as homonuclear molecules. The last three belong to heteronuclear molecules since they are composed of non-identical atoms. Moreover, the first three molecules are non-polar and their vibrational energy is not influenced by alternative electric field of light. Hence they do not exhibit any vibration-rotation absorption band in the infrared which are necessarily found in polar molecules such as HCl, HBr and HI. Each of those has only one vibrational frequency and its value can be evaluated by studying the Raman spectra. The following table gives the natural frequency of vibration and restoring force per unit displacement.

	H_2	N_2	O_2	HCl	HBr	HI
$\nu_0 \text{ cm}^{-1}$	4156	2331	1556	2880	2558	2233
$f \times 10^{-5}$	5.1	22.4	11.4	4.8	3.8	2.9

From the above table that lighter the molecule, greater is the vibration frequency. The values of the restoring force per unit displacement are approximately in the

ratio of 3:2 for N_2 , and O_2 . This suggest that atoms in their respective molecules are held together by triple and double bonds.

Triatomic molecules: Carbon dioxide

Theoretically two very strong bands in the infrared absorption spectrum at 668 and 2349 cm^{-1} and one strong band in the Raman effect at 1389 cm^{-1} , if one tries to study the infrared and Raman spectrum of CO_2 . As none of these occurs both in the Raman and IR spectrum, it follows from the rule of mutual exclusion that the molecule has a centre of symmetry. Since it is triatomic molecule, its structure should, linear.

CS_2 resembles a similar structure gives by $S=C=S$, as obtained from the study of the IR absorption and Raman spectrum.

Code No. : 6133

Sub. Code: DCH 23

M.Sc. (DD & CE) DEGREE EXAMINATION

APRIL 2009

Second Year - Non-Semester

CHEMISTRY

PHYSICAL CHEMISTRY - II

(For those who joined in July 2003 and afterwards)

Time : Three hours

Maximum : 100 Marks

SECTION A - (5x5=25 Marks)

Answer any FIVE out of Eight

1. Explain briefly the primary and secondary salt effects.
2. Explain the process of photosensitization in terms of energy transfer between singlet and triplet states.
3. Write short notes on excimer and exciplex formation.
4. By using group theory, find normal mode analysis of H_2O molecule and their IR and Raman activity.
5. State and explain Franck - Condon principle.
6. Discuss the basic concepts of FT-IR spectroscopy.
7. Give short notes on :
 - (a) Lanthanide shift reagents
 - (b) Uses of ESCA
8.
 - (a) Draw an energy level diagram showing the ESR spectrum of an odd electron.
 - (b) Sketch the ESR spectrum of ethyl radical.

SECTION B - (5X15=75 marks)

Answer any FIVE out of Eight

9. (a) Describe the Lindemann theory of unimolecular reactions.
(b) Discuss the thermodynamic treatment of ARRT.
10. (a) Describe the pressure jump method in the study of fast reactions.
- Or
- (b) Write notes on :
(i) Dosimetry
(ii) Radiolysis of water
11. (a) Derive Stern-Volmer equation and its applications.
(b) Discuss on solar energy storage.
12. (a) Apply HMO to butadiene to calculate delocalisation energy and energy level diagram using group theory.
(b) Give the relationship between reducible and irreducible representations.
13. (a) Derive the expression for an anharmonic oscillator and also give at the expressions for fundamental, overtones and hot bands.
(b) Explain the concept of predissociation.
14. (a) Discuss the basic principles of laser Raman Spectroscopy.
(b) Write a brief note on the vibrational Raman spectra.
15. (a) Discuss the theory of FT-NMR spectroscopy.
(b) Explain spin-spin splitting in NMR spectroscopy.
16. (a) Give a detailed account on the basic concepts of ESR spectroscopy. Mention its applications.

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