UNIT 1- Symmetry & Group Theory in Chemistry

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1.0 - INTRODUCTION

Group Theory is a mathematical method by which aspects of a molecules symmetry can be determined. The symmetry of a molecule reveals information about its properties (i.e., structure, spectra, polarity, chirality, etc…).

Group theory can be considered the study of symmetry: the collection of symmetries of some object preserving some of its structure forms a group; in some sense all groups arise this way.

It can be grouped into three categories:

- Getting to know groups — It helps to group theory and contain explicit definitions and examples of groups;
- Group applications — It helps to understand the applications of group theory. The mathematical descriptions here are mostly intuitive, so no previous knowledge is needed.
- Group history — It focuses on the history of group theory, from its beginnings to recent breakthroughs.

Electromagnetic Radiations are the radiations having electric field as well as magnetic field both are perpendicular to each other & are also perpendicular to the line of propogation. There are various electromagnetic radiations like radiowaves, microwaves, x-rays, uv-rays cosmic rays etc. Theses when interact with matter give rise to various different phenomenons like diffraction, interference, absorbtion, emission depending on the type of EMR & matter (energy).

1.1 - OBJECTIVES

By studying this unit we come across many of the things which you are not aware of :

1. The significance of group theory for chemistry is that molecules can be categorized on the basis of their symmetry properties, which allow the prediction of many molecular properties.
2. The process of placing a molecule into a symmetry category involves identifying all of the lines, points, and planes of symmetry that it possesses; the symmetry categories the molecules may be assigned to are known as point groups.
3. It allows you to determine that Which vibrational transitions are allowed or forbidden on the basis of symmetry.
4. How EMR interact to show different phenomenons like polarization, Dispersion, Refraction etc.
5. What is Transition & transition probability.

1.0.1 – Symmetry Elements & symmetry operation -

The term symmetry implies a structure in which the parts are in harmony with each other, as well as to the whole structure i;e the structure is proportional as well as balanced.

Clearly, the symmetry of the linear molecule A-B-A is different from A-A-B. In A-B-A the A-B bonds are equivalent, but in A-A-B they are not. However, important aspects of the symmetry of H_2O and CF_2Cl_2 are the same. This is not obvious without Group theory.

Symmetry Elements - These are the geometrical elements like line, plane with respect to which one or more symmetric operations are carried out.

- The symmetry of a molecule can be described by 5 types of symmetry elements. **Symmetry axis**: an axis around which a rotation by $\frac{360°}{n}$ results in a molecule indistinguishable from the original. This is also called an *n*-fold **rotational axis** and abbreviated C_n. Examples are the C_2 in water and the C_3 in ammonia. A molecule can have more than one symmetry axis; the one with the highest *n* is called the **principal axis**, and by convention is assigned the z-axis in a Cartesian coordinate system.
- **Plane of symmetry**: a plane of reflection through which an identical copy of the original molecule is given. This is also called a mirror plane and abbreviated σ. Water has two of them: one in the plane of the molecule itself and one perpendicular to it. A symmetry plane parallel with the principal axis is dubbed *vertical* (σ_v) and one perpendicular to it *horizontal* (σ_h). A third type of symmetry plane exists: if a vertical symmetry plane additionally bisects the angle between two 2-fold rotation axes perpendicular to the principal axis, the plane is dubbed dihedral (σ_d). A symmetry plane can also be identified by its Cartesian orientation, *e.g.*, (xz) or (yz).
- **Centre of symmetry** or **inversion center**, *i*. A molecule has a center of symmetry when, for any atom in the molecule, an identical atom exists diametrically opposite this center an equal distance from it. There may or may not be an atom at the center. Examples are xenon tetrafluoride (XeF_4) where the inversion cente is at the Xe atom, and benzene (C_6H_6) where the inversion center is at the center of the ring.
- **Rotation-reflection axis**: an axis around which a rotation by $\frac{360°}{n}$, followed by a reflection in a plane perpendicular to it, leaves the molecule unchanged. Also called an *n*-fold **improper rotation axis**, it is abbreviated S_n, with *n* necessarily even. Examples are present in tetrahedral silicon tetrafluoride, with three S_4 axes, and the staggered conformation of ethane with one S_6 axis.
- **Identity**, abbreviated to E, from the German 'Einheit' meaning Unity. This symmetry element simply consists of no change: every molecule has this element. It is analogous to multiplying by one (unity).

1.2.2- Symmetry Operations/Elements

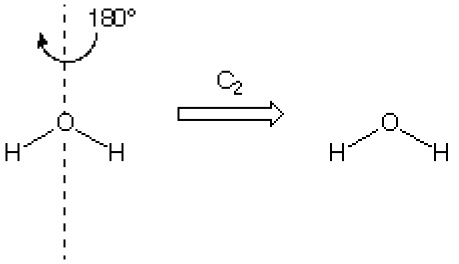
A molecule or object is said to possess a particular operation if that operation when applied leaves the molecule unchanged. Each operation is performed relative to a point, line, or plane - called a symmetry element. There are 5 kinds of operations -

1. Identity
2. n-Fold Rotations
3. Reflection
4. Inversion
5. Improper n-Fold Rotation

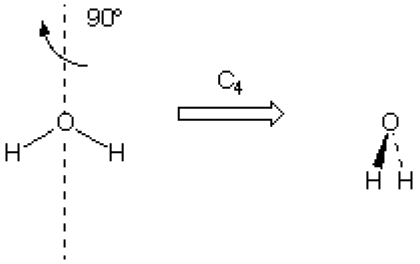
1. Identity is indicated as E

- does nothing, has no effect i;e this operation brings back the molecule to the original orientation
- all molecules/objects possess the identity operation, i.e., posses E.
- E has the same importance as the number 1 does in multiplication (E is needed in order to define inverses).

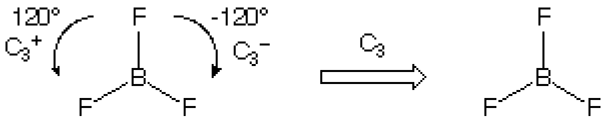
2. **<u>n-Fold Rotations</u>:** C_n, where n is an integer, rotation by 360°/n about a particular axis defined as the n-fold rotation axis.
C_2 = 180° rotation, C_3 = 120° rotation, C_4 = 90° rotation, C_5 = 72° rotation, C_6 = 60° rotation, etc.
Rotation of H_2O about the axis shown by 180° (C_2) gives the same molecule back.
Therefore H_2O possess the C_2 symmetry element.

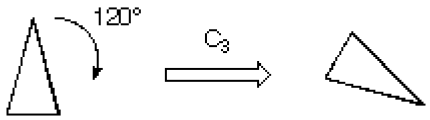


However, rotation by 90° about the same axis does not give back the identical molecule
Therefore H_2O does not possess a C_4 symmetry axis.

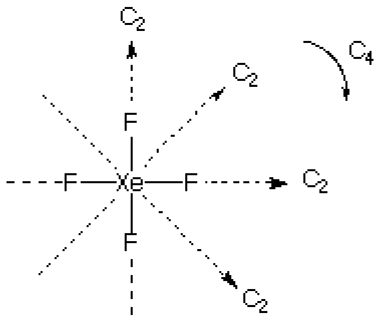


BF_3 posses a C_3 rotation axis of symmetry.



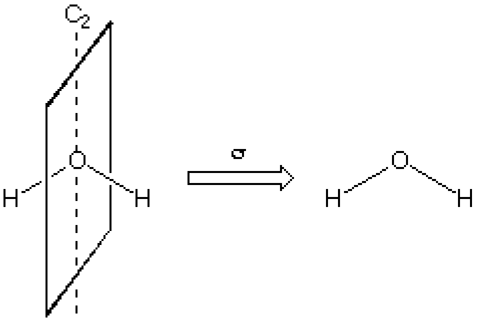


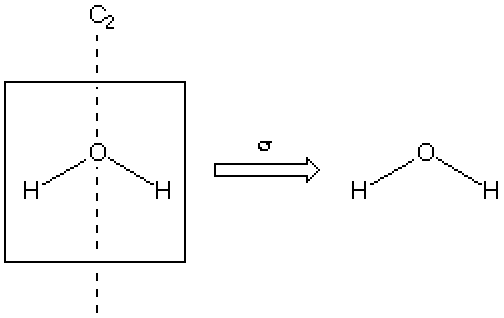
This triangle does not posses a C_3 rotation axis of symmetry.



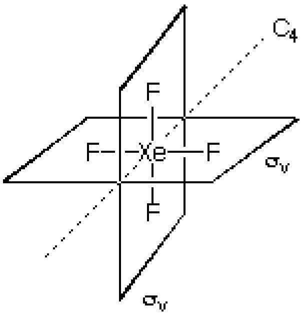
XeF_4 is square planar. It has four DIFFERENT C_2 axes . It also has a C_4 axis coming out of the page called the principle axis because it has the largest n. By convention, the principle axis is in the z-direction

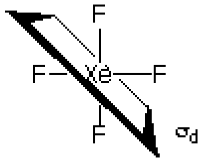
3. Reflection: σ (the symmetry element is called a mirror plane or plane of symmetry)
If reflection about a mirror plane gives the same molecule/object back than there is a plane of symmetry (σ).
If plane contains the principle rotation axis (i.e., parallel), it is a vertical plane (σ_v)
If plane is perpendicular to the principle rotation axis, it is a horizontal plane (σ_h)
If plane is parallel to the principle rotation axis, but bisects angle between 2 C_2 axes, it is a diagonal plane (σ_d)
H_2O posses 2 σ_v mirror planes of symmetry because they are both parallel to the principle rotation axis (C_2)

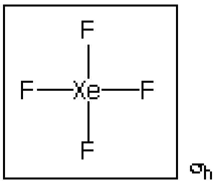




XeF_4 has two planes of symmetry parallel to the principle rotation axis: σ_v
XeF_4 has two planes of symmetry parallel to the principle rotation axis and bisecting the angle between 2 C_2 axes : σ_d
XeF_4 has one plane of symmetry perpendicular to the principle rotation axis: σ_h

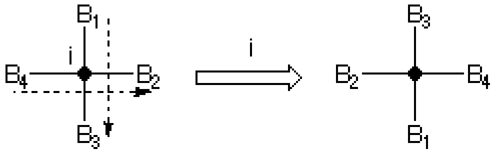






4. Inversion: i (the element that corresponds to this operation is a center of symmetry or inversion center) .

The operation is to move every atom in the molecule in a straight line through the inversion center to the opposite side of the molecule.

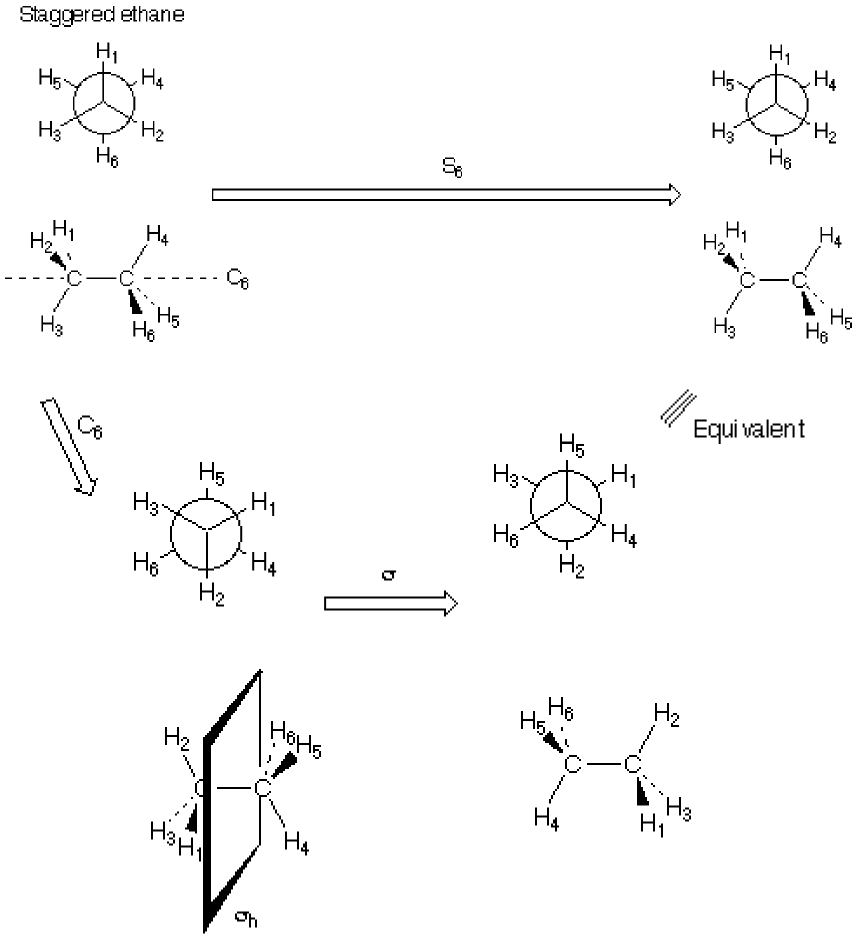


Therefore XeF_4 posses an inversion center at the Xe atom.

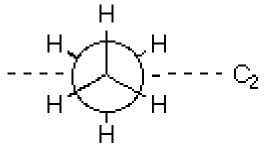
5. Improper Rotations: S_n

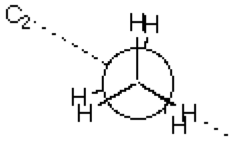
n-fold rotation followed by reflection through mirror plane perpendicular to rotation axis also known as Rotation Reflection axis. It is an imaginary axis passing through the molecule, on which when the molecule is rotated by $2\pi/n$ angle & then reflected on a plane perpendicular to the rotation axis then an equivalent orientation is observed.

Note: n is always 3 or larger because $S_1 = \sigma$ and $S_2 = i$.



These are different, therefore this molecule does not posses a C_3 symmetry axis.
This molecule posses the following symmetry elements: C_3, 3 σ_d, i, 3 $\perp$ C_2, S_6. There is no C_3 or σ_h.
Eclipsed ethane posses the following symmetry elements: C_3, $3\sigma_v$, 3 $\perp$ C_2, S_3, σ_h. There is no S_6 or i.





Compiling all the symmetry elements for staggered ethane yields a Symmetry Group called D_{3d}.

Compiling all the symmetry elements for eclipsed ethane yields a Symmetry Group called D_{3h}.

Importance of symmetry-

- It is an important concept in crystal morphology,crystal structure analysis.
- It helps in the classification of electronic states in a molecule.
- It is also useful in determining which atomic orbitals can combine to form molecules.
- It can be used in predicting the no of d-d absorption bands that are observed in coordination compounds.
- Ligand theory also depends on concept of symmetry.
- IR & Raman Spectroscopy used for structure illucidation also depends on symmetry.

CHECK YOUR PROGRESS - 1

Notes : i) Write your answer in the space given below.

ii) Compare your answer with those given at the end of the unit.

Q1.Name the symmetry element possessed by all the molecules.

Q2.Give an example of the molecule which contain C2 axis in addition to Cn axis of rotation.

Q3. Give an example of the molecule which contain horizontal plane of symmetry in addition to vertical plane of symmetry.

Q4.All the elements possessed by a molecule is represented by …………..

1.2.3- Groups & Subgroups

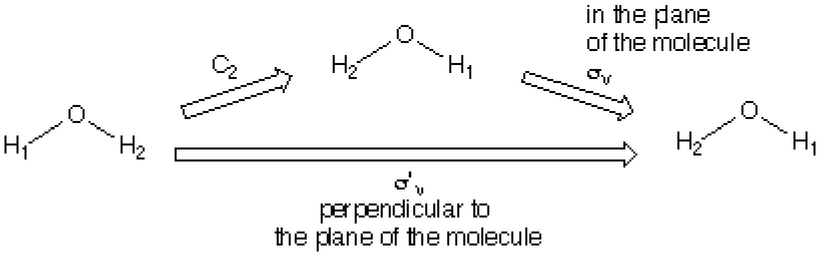
Each molecule has a set of symmetry operations that describes the molecule's overall symmetry. This set of operations define the group of the molecule.A group G is a finite or infinite set of elements together with a binary operation (called the group operation) that together satisfy the four fundamental properties of closure, associativity, the identity property, and the inverse property. The operation with respect to which a group is defined is often called the "group operation," and a set is said to be a group "under" this operation.

The study of groups is known as group theory.

A group is a set of operations which satisfies the following requirements-

1. Any result of two or more operations must produce the same result as application of one operation within the group.i.e., the group multiplication table must be closed

Consider H_2O which has E, C_2 and 2 σ_v's.



i.e., $\hat{C}_2\hat{\sigma}_v \equiv \hat{\sigma}'_v$ **of course** $\hat{C}_2\hat{C}_2 \equiv \hat{E}$ **etc…**

The table is closed, i.e., the results of two operations is an operation in the group i;e the elements are commutable.

2. Must have an identity ($\hat{E}$) such that AE = EA = A for any operation A in the group.

3. All elements must have an inverse i.e., for a given operation ($\hat{A}$) there must exist an operation ($\hat{B}$) such that $\hat{A}\hat{B}=\hat{E}$ or $AA^{-1} = A^{-1}A = E$
4. Each element has follows associative law

$$\mathbf{P(QR) = (PQ)R}$$

example, the point group for the water molecule is C_{2v}, with symmetry operations E, C_2, σ_v and σ_v'. Its order is thus 4. Each operation is its own inverse. As an example of closure, a C_2 rotation followed by a σ_v reflection is seen to be a σ_v' symmetry operation: $\sigma_v{*}C_2 = \sigma_v'$.

The group multiplication table obtained is therefore for water molecule:

	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

$\boldsymbol{\sigma_v . \sigma_{v} = E}$

$\boldsymbol{C_2 . \sigma_v = \sigma'_v}$

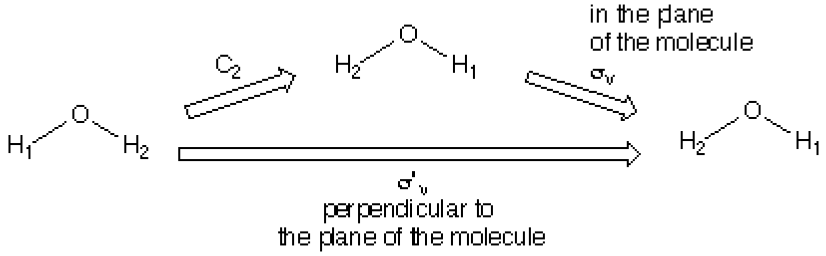
$\boldsymbol{C_2.E = E\ C_2 = C_2}$

$\boldsymbol{C_2\,(\sigma_v.\sigma'_v) = (C_2.\sigma_v)\sigma'_v}$

Another example is the ammonia molecule, which is pyramidal and contains a three-fold rotation axis as well as three mirror planes at an angle of 120° to each other. Each mirror plane contains an N-H bond and bisects the H-N-H bond angle opposite to that bond. Thus ammonia molecule belongs to the C_{3v} point group which has order 6: an identity element E, two rotation operations C_3 and C_3^2, and three mirror reflections σ_v, σ_v' and σ_v''.

Classification Of Group

1. **Abelian Group** – All elements are commutable. Example Water



2. **Non Abelian Group-** All elements do not commute with one another.

Example - Phosphine symmetry operations are E,C_1^3, C_3^4, σ_v^1, σ_v^2

$C_3 . \sigma_v \neq \sigma_v . C_3$

3.**Cyclic group-** In cyclic group all the elements of a group can be generated from one element .It is denoted by A^n. A represents identity element & n represents total no of elements & is called as order of group. Each cyclic group is abelian but each abelian group is not cyclic.
Example Trans 1,2 dichlorocyclopropane.

Classification of group on the basis of element-

1.Monoid - A group is a monoid each of whose elements is invertible.
2. Trivial Group- A group must contain at least one element, with the unique (up to isomorphism) single-element group known as the trivial group.
3. Finite group - If there are a finite number of elements, the group is called a finite group

Subgroups

Any subset of element which form a group is called as subgroup.
A subgroup is a subset H of group elements of a group G that satisfies the four group requirements. It must therefore contain the identity element. "H is a subgroup of G" is written $H \subseteq G$, or sometimes $H \leq G$. A subset of a group that is closed under the group operation and the inverse operation is called a subgroup.
The elements of a subgroup should obey the following conditions-If g is the order of the group & s is the order of the subgroup ,then g/s is a natural number. Example- water molecule has symmetry elements- $E, C_2, \sigma_{v,}\ \sigma_v{}^1$

GROUP - $E, C_2, \sigma_{v,}\ \sigma_v{}^1$

SUBGROUPS - E
E, C_2
$E, \sigma_{v,}$
$E,\ \sigma_v{}^1$

CLASSES – This is the subdivision of a group.
Two elements A & B in a group form a class if they are conjugate to each other. Conjugate elements are related by the equation

X-1AX = B

Where X is similarity transformation element .It is used to find whether a set of elements form a class.
Example- water molecule has symmetry elements- $E, C_2, \sigma_{v,}\ \sigma_v{}^1$

GROUP - $E, C_2, \sigma_{v,}\ \sigma_v{}^1$

CLASSES - $E^{-1} C_2 E = C_2$
$\sigma_v{}^{-1} C_2\ \sigma_v = C_2$
$\sigma_v{}^{-1}\ C_2\ \sigma_v{}^1 = C_2$
$C_2{}^{-1}\ C_2\ C_2 = C_2$

ORDER- The order of a class of a group must be an integral factor of the order of a group and the number of elements is called the group order of the group.

Method to find the class –

1.Symmetry operations which commutes with all symmetry operations forms a class.
$E,\ \sigma_{h,}$ I belongs to separate class
2.Rotation operation & its inverse forms a class like $C_2{}^{-1}$ & C_2
3. Improper axis & inverse forms a class $S_1 S_1{}^{-1.}$
4. Two rotation about different axis forms a class if there is a third operation which interchange the points of the axis.
5. Two reflection about different planes belongs to the same class if there is a third operation which interchange points on the two plane.
Example- Square Planar AB_4 molecule has
Symmetry operations- 16- E, i , $\sigma_{h,}\ C_2{}^1\ C_4{}^1\ C_4{}^3\ S_4{}^1\ S_4{}^3\ 4C_2{}^1 4\ \sigma_v$

No Of Elements - 13
Classes- (i) E, i , $\sigma_{h,}\ C_2$ (iv) 2 $C_2{}^1$operations about C_2 axis (reflection)
(ii) $C_4{}^1\ C_4{}^3$ (v) 2 $C_2{}^1$operations about $C_2{}'$ axis (reflection)
(iii) $S_4{}^1\ S_4{}^3$ (vi) 2 reflection operations in two σ_v planes
(vii) 2 reflection operations in two σ'_v planes

1.2.4 - Relation between orders of a finite group & its subgroup –

If there are a finite number of elements, the group is called a finite group and the number of elements is called the group order of the group.

- A subset of a group that is closed under the group operation and the inverse operation is called a subgroup. Subgroups are also groups, and many commonly encountered groups are in fact special subgroups of some more general larger group.
- A finite group is a group having finite group order. Examples of finite groups are the modulo multiplication groups, point groups, cyclic groups, dihedral groups, symmetric groups, alternating groups, and so on.
- The finite (cyclic) group C_2 forms the "Finite Simple Group of Order 2"
- A basic example of a finite group is the symmetric group S_n, which is the group of permutations (or "under permutation") of n objects.

Check your progress 2

Notes : i) Write your answer in the space given below.

ii) Compare your answer with those given at the end of the unit.

1. n-fold rotation followed by reflection through mirror plane perpendicular to rotation axis also known as ----------- .
2. Any subset of element which form a group is called as ------------- .
3. The order of a class of a group must be an integral factor of the order of a group and the number of elements is called the -------- of the group.

1.2.5 - Conjugacy Relation & Class

A complete set of mutually conjugate group elements. Each element in a group belongs to exactly one class, and the identity element ($I = 1$) is always in its own class. The conjugacy class orders of all classes must be integral factors of the group order of the group.

- A group of prime order has one class for each element.
- In an Abelian group, each element is in a conjugacy class by itself.
- Two operations belong to the same class when one may be replaced by the other in a new coordinate system which is accessible by a symmetry operation . These sets correspond directly to the sets of equivalent operations.
- Two elements A & B in a group form a class if they are conjugate to each other.Conjugate elements are related by the equation

  $$X^{-1}AX = B$$

  Where X is similarity transformation element .It is used to find whether a set of elements form a class.
- conjugacy is an equivalence relation. Also note that conjugate elements have the same order. The set of all elements conjugate to a is called the class of a.
- To find conjugacy class similarity transformations $X^{-1} A X = X^{-1} (A X)$ on A. Applying a similarity transformation gives

$$A^{-1} D A = E \qquad (6)$$

$$B^{-1} D B = E \qquad (7)$$

$$C^{-1} D C = E \qquad (8)$$

$$D^{-1} D D = D \qquad (9)$$

$$E^{-1} D E = D, \qquad (10)$$

so $\{D, E\}$form a conjugacy class.

1.2.6 - Point Symmetry Groups -

Each molecule has a set of symmetry operations that describes the molecule's overall symmetry. This set of operations define the **point group** of the molecule. Since all the elements of symmetry present in the molecule intersect at a common point & this point remains fixed under all symmetry operations of the molecule and is known as point symmetry groups.

1.2.7 - Schonflies notation

The point groups are denoted by their component symmetries. There are a few standard notations used by crystallographers. The **Schoenflies notation** or **Schonflies notation**, named after the German mathematician Arthur Moritz Schoenflies, is one of two conventions commonly used to describe crystallographic point groups. This notation is used in spectroscopy. The other convention is the Hermann-Mauguin notation, also known as the International notation. A point group in the Schoenflies convention is completely adequate to describe the symmetry of a molecule; this is sufficient for spectroscopy. The Hermann-Maunguin notation is able to describe the space group of a crystal lattice, while the Schoenflies notation isn't. Thus the Hermann-Mauguin notation is used in crystallography.

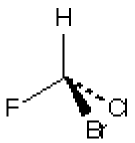
Schönflies notation

In Schönflies notation, point groups are denoted by a letter symbol with a subscript. The symbols used in crystallography mean the following:

- The letter O (for octahedron) indicates that the group has the symmetry of an octahedron (or cube), with (O_h) or without (O) improper operations .
- The letter T (for tetrahedron) indicates that the group has the symmetry of a tetrahedron. T_d includes improper operations, T excludes improper operations, and T_h is T with the addition of an inversion.
- The letter I (for icosahedron) indicates that the group has the symmetry of an icosahedron (or dodecahedron), either with (I_h) or without (I) improper operations.
- C_n (for cyclic) indicates that the group has an n-fold rotation axis. C_{nh} is C_n with the addition of a mirror (reflection) plane perpendicular to the axis of rotation. C_{nv} is C_n with the addition of a mirror plane parallel to the axis of rotation.
- S_n (for *Spiegel*, German for mirror) denotes a group that contains only an n-fold rotation-reflection axis.
- D_n (for dihedral, or two-sided) indicates that the group has an n-fold rotation axis plus a twofold axis perpendicular to that axis. D_{nh} has, in addition, a mirror plane perpendicular to the n-fold axis. D_{nv} has, in addition to the elements of D_n, mirror planes parallel to the n-fold axis.

Point Groups

Low Symmetry Groups

C_1: only E 

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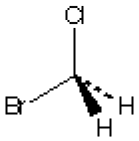
C_s: E and σ only



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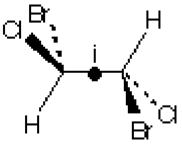
C_i: E and i only



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C_n, C_{nv}, C_{nh} Groups

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C_n: E and C_n only

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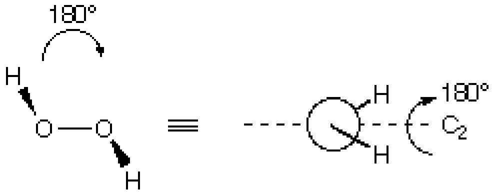
$C_{2:}$



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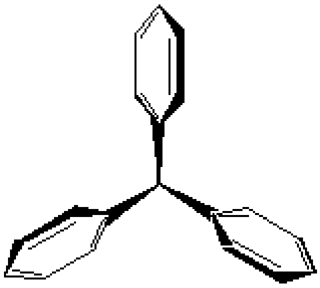
$C_{3:}$



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C_{nv}: E and C_n and n σ_v's

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C_{2v}: E, C_2, 2 σ_v H_2O

C_{3v}: E, C_3, 3 σ_v NH_3

Cσ $_v$: E, C , σ_v HF, HCN

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<tr><td>

C_{nh}: E and C_n and σ_h (and others as well)

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C_{2h}: E, C_2, σ_h, I

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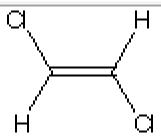
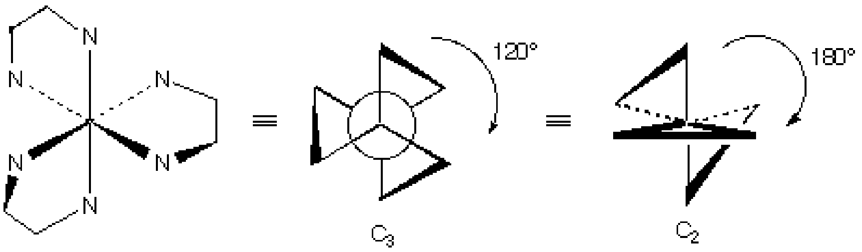
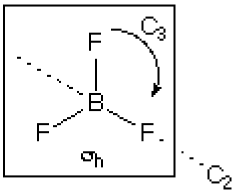
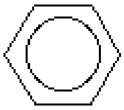


D_n, D_{nv}, D_{nh} Groups

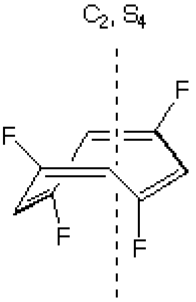
D_n: E, C_n, n C_2 axes to C_n
D_3: E, C_3, 3 C_2 $[Co(en)_3]^{3+}$ 

D_{nh}: E, C_n, n C_2 axes , σ_h
D_{3h}: E, C_3, 3 C_2, σ_h 
D_{3h}: E, C_3, 3 C_2, σ_h eclipsed ethane
D_{6h}: E, C_6, 6 C_2, σ_h 
$D\ _h$: E, C , C_2, σ_h  H_2

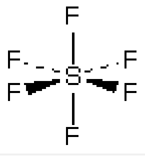
D_{nd}: E, C_n, n C_2 axes ⊥ to C_n,
D_{3d}: E, C_3, 3 C_2, 3 σ_d

staggered ethane

S_n Group

S_{2n}: E, C_n, S_{2n} (no mirror planes) S_4, S_6, S_8, etc. (Note: never S_3, S_5, etc.)
S_4: E, C_2, S_4 

High Symmetry Cubic Groups, T_d, O_h, I_h

T_d: E, 8 C_3, 3 C_2, 6 S_4, 6 σ_d Tetrahedral structures No need to identify all the symmetry elements - simply recognize T_d shape. methane, CH_4
O_h: E, 8 C_3, 6 C_2, 6 C_4, i, 6 S_4, 8 S_6, 3 σ_h, 6 σ_d Octahedral structures No need to identify all the symmetry elements - simply recognize O_h shape. 
I_h: E, 12 C_5, 20 C_3, 15 C_2, i, 12 S_{10}, 20 S_6, 15 σ Icosahedron
Other rare high symmetry groups are **T**, **T_h**, **O**, and **I**

Common point groups

Point group	**Symmetry elements**	**Simple description**, chiral if applicable	**Illustrative species**
C_1	E	no symmetry, chiral	CFClBrH, lysergic acid
C_s	$E\ \sigma_h$	planar, no other symmetry	thionyl chloride, hypochlorous acid
C_i	$E\ i$	Inversion center	*anti*-1,2-dichloro-1,2-dibromoethane
$C_{\infty v}$	$E\ 2C_\infty\ \sigma_v$	Linear	hydrogen chloride, dicarbon monoxide
$D_{\infty h}$	$E\ 2C_\infty\ \infty\sigma_i\ i\ 2S_\infty\ \infty C_2$	linear with inversion center	dihydrogen, azide anion, carbon dioxide
C_2	$E\ C_2$	"open book geometry," chiral	hydrogen peroxide
C_3	$E\ C_3$	propeller, chiral	triphenylphosphine
C_{2h}	$E\ C_2\ i\ \sigma_h$	planar with inversion center	trans-1,2-dichloroethylene
C_{3h}	$E\ C_3\ C_3^2\ \sigma_h\ S_3\ S_3^5$	Propeller	Boric acid
C_{2v}	$E\ C_2\ \sigma_v(xz)\ \sigma_v'(yz)$	angular (H_2O) or see-saw (SF_4)	water, sulfur tetrafluoride, sulfuryl fluoride
C_{3v}	$E\ 2C_3\ 3\sigma_v$	trigonal pyramidal	ammonia, phosphorus oxychloride
C_{4v}	$E\ 2C_4\ C_2\ 2\sigma_v\ 2\sigma_d$	square pyramidal	xenon oxytetrafluoride
T_d	$E\ 8C_3\ 3C_2\ 6S_4\ 6\sigma_d$	tetrahedral	methane, phosphorus pentoxide, adamantane
O_h	$E\ 8C_3\ 6C_2\ 6C_4\ 3C_2\ i\ 6S_4\ 8S_6\ 3\sigma_h\ 6\sigma_d$	octahedral or cubic	cubane, sulfur hexafluoride
I_h	$E\ 12C_5\ 12C_5^2\ 20C_3\ 15C_2\ i\ 12S_{10}\ 12S_{10}^3\ 20S_6\ 15\sigma$	icosahedral	C_{60}, $B_{12}H_{12}^{2-}$

Method of determination of point group of molecules- The process used to assign a molecule to a point group is straightforward with a few exceptions. It is a procedure. Here are set of steps to quickly guide you.

1. Look at the molecule and see if it seems to be very symmetric or very unsymmetric. If so, it probably belongs to one of the special groups (**low symmetry:** C_1, C_s, C_i or linear $C_{\infty v}$, $D_{\infty h}$) or high symmetry (T_d, O_h, I_h..).
2. For all other molecules find the rotation axis with the highest n, the highest order **Cn** axis of the molecule.
3. Does the molecule have any $\mathbf{C_2}$ axes **perpendicular to** the $\mathbf{C_n}$ axis? If it does, there will be n of such C_2 axes, and the molecule is in one of **D** point groups. If not, it will be in one of **C** or **S** point groups.

Does it have any mirror plane ($\boldsymbol{\sigma_h}$) perpendicular to the C_n axis? If so, it is $\mathbf{C_{nh}}$ or $D_{\mathbf{nh}}$.

Does it have any mirror plane ($\boldsymbol{\sigma_d},\boldsymbol{\sigma_v}$)? If so, it is C_{nv} or D_{nd}

1.2.8. Representation of groups by matrices-

Group actions, and in particular representations, are very important in group theory, & Also to physics and chemistry. Since a group can be thought of as an abstract mathematical object, the same group may arise in different contexts. It is therefore useful to think of a representation of the group as one particular incarnation of the group, which may also have other representations. Any symmetry operation about a symmetry element in a molecule involves the transformation of a set of coordinates x,y,z of an atom into a set of new coordinates x',y',z'.

$$\begin{pmatrix} x \\ y \\ z \end{pmatrix}$$

The two sets of coordinates can be related by a set of equation which is formulated in matrix notation. Thus each symmetry operation can be represented by special matrix which helps to solve structural problems in chemistry.

Matrix representation of symmetry operations- The matrices for the different symmetry operations can be obtained by considering the effect of these operations on the components of a two dimensional vector. The results can be extended to3 dimensions.

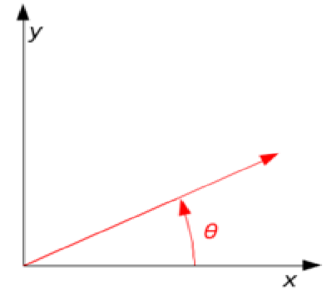
Rotations in two dimensions

Matrix representation for the Rotation operation – For 2D coordinate system X & Y , there is a vector r which can be represented by column matrix.

The symmetry operations can be **represented in many ways**. A convenient representation is by **matrices**. For any vector representing a point in Cartesian coordinates, left-multiplying it gives the new location of the point transformed by the symmetry operation. Composition of operations corresponds to matrix multiplication. In the C_{2v} example this is:

$$\underbrace{\begin{bmatrix}-1 & 0 & 0\\ 0 & -1 & 0\\ 0 & 0 & 1\end{bmatrix}}_{C_2} \times \underbrace{\begin{bmatrix}1 & 0 & 0\\ 0 & -1 & 0\\ 0 & 0 & 1\end{bmatrix}}_{\sigma_v} = \underbrace{\begin{bmatrix}-1 & 0 & 0\\ 0 & 1 & 0\\ 0 & 0 & 1\end{bmatrix}}_{\sigma_v'}$$

Although an infinite number of such representations exist, the irreducible representations (or "irreps") of the group are commonly used, as all other representations of the group can be described as a linear combination of the irreducible representations.



A counterclockwise rotation of a vector through angle θ. The vector is initially aligned with the x-axis.In two dimensions every rotation matrix has the following form:

$$R(\theta) = \begin{bmatrix}\cos\theta & -\sin\theta\\ \sin\theta & \cos\theta\end{bmatrix}$$
.

This rotates column vectors by means of the following matrix multiplication:

$$\begin{bmatrix}x'\\ y'\end{bmatrix} = \begin{bmatrix}\cos\theta & -\sin\theta\\ \sin\theta & \cos\theta\end{bmatrix}\begin{bmatrix}x\\ y\end{bmatrix}.$$

So the coordinates (x',y') of the point (x,y) after rotation are:

$$x' = x\cos\theta - y\sin\theta,$$
$$y' = x\sin\theta + y\cos\theta.$$

The direction of vector rotation is counterclockwise if θ is positive (e.g. 90°), and clockwise if θ is negative (e.g. -90°).

$$R(-\theta) = \begin{bmatrix}\cos\theta & \sin\theta\\ -\sin\theta & \cos\theta\end{bmatrix}$$

Common rotations

If C_n represents rotation about the axis by angle θ
r = C_n X r where C_n = R (-θ)
Particularly useful are the matrices for 90° and 180° rotations:

$$R(90^\circ) = \begin{bmatrix}0 & -1\\ 1 & 0\end{bmatrix}$$(90° counterclockwise rotation)

For C_2, θ= 180^0

$$R(180^\circ) = \begin{bmatrix}-1 & 0\\ 0 & -1\end{bmatrix}$$(180° rotation in either direction – a half-turn)

$$R(270^\circ) = \begin{bmatrix} 0 & 1 \\ -1 & 0 \end{bmatrix}$$ (270° counterclockwise rotation, the same as a 90° clockwise rotation)

Rotations in three dimensions

$$R_x(\theta) = \begin{bmatrix} 1 & 0 & 0 \\ 0 & \cos\theta & -\sin\theta \\ 0 & \sin\theta & \cos\theta \end{bmatrix}$$

$$R_y(\theta) = \begin{bmatrix} \cos\theta & 0 & \sin\theta \\ 0 & 1 & 0 \\ -\sin\theta & 0 & \cos\theta \end{bmatrix}$$

$$R_z(\theta) = \begin{bmatrix} \cos\theta & -\sin\theta & 0 \\ \sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{bmatrix}.$$

Each of these basic vector rotations typically appears counter-clockwise when the axis about which they occur points toward the observer, and the coordinate system is right-handed. R_z, for instance, would rotate toward the *y*-axis a vector aligned with the *x*-axis. This is similar to the rotation produced by the above mentioned 2-D rotation matrix.

2.Matrix for Reflection operation- Reflection on the xy-plane (analogous to a horizontal plane σ_h), coordinate z changes the sign.

$$\sigma_z = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix}$$

$$\begin{pmatrix} x \\ y \\ -z \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix}$$

The matrices which are applied for performing a reflection on the yz-plane and xz-plane are the matrices σ_x and σ_y respectively.

$$\sigma_x = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 0 \end{pmatrix} \qquad \sigma_y = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 0 \end{pmatrix}$$

3.Matrix for the inversion *i* operation- It relates the coordinates (x,y,z) with (-x,-y,-z) and is connected with the following matrix:

$$i = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix}$$

a two fold application of the inversion matrix yields the coordinates of the initial point (x,y,z) which is reflected by ***E = i*i***.

$$i \cdot i = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix}\begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} = E$$

4.Matrix for rotatory reflection $S_n(z)$ multiply the matrices for the fundamental operations σ_z and C_n.

$$S_n(z) = \sigma_z C_n = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix}\begin{pmatrix} \cos 2\pi/n & \sin 2\pi/n & 0 \\ -\sin 2\pi/n & \cos 2\pi/n & 0 \\ 0 & 0 & 1 \end{pmatrix} = \begin{pmatrix} \cos 2\pi/n & \sin 2\pi/n & 0 \\ -\sin 2\pi/n & \cos 2\pi/n & 0 \\ 0 & 0 & -1 \end{pmatrix}$$

5. Identity matrices- The most primitive symmetry operation is the identity and yields a final vector identical to the initial vector. It is the **unity matrix** or **identity matrix** which leaves all coordiates unaffected.

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

1.2.9.- Character of a Representation

The set of matrices for the various symmetry operations of a point group forms a representation. The set of vectors of the coordinate system,with respect to which the matrices are defined is called the basis of the representation

Example - C_{2h} point group

Four symmetry operation - E, **C_2, σ_{xy},i**

Matrix representation -

$$\underbrace{\begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}}_{C_2} \times \underbrace{\begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}}_{\sigma_v} = \underbrace{\begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}}_{\sigma'_v}$$

Reducible & Non reducible representation –

Reducible representation – A representation of higher dimension which can be reduced to representation of lower dimension is called reducible representation.

A reduclble representation & its reduction can be understood by carrying out a similarity transformation .Suppose A,B,C, D is a representation of a group in which [B] [C] = [D].If only the diagonal Elements of the matrix is shown & similarity transformation is done

$X^{-1}AX = A'$

$X^{-1} BX = B'$

$X^{-1}CX = C'$

$X^{-1}DX = D'$

Irreducible representation

Those representations which cannot be further reduced to representations of lower dimension are called irreducible representation.If it is not possible to find out similarity transformation matrix which will reduce the matrices of representation then the representation is said to be irreducible.All one dimensional representations are irreducible

Example - Matrices of transformation for z-coordinate of a Hydrogen atom in hydrogen molecule
Group - $D_{\infty h}$ group
Symmetry operation - E, C_{∞},, σ_v, σ_h, S_{∞}, C_2, *i*
The z-coordinate is unaffected by E, C_{∞},, σ_v operations
The equation for the transformation of z- coordinate of hydrogen atom by these operations are-

E.Z = 1Z	Ematrix = [1]
C_{∞}.Z = 1Z	$C_{\infty \text{matrix}}$ = [1]
σ_v.Z = 1Z	$\sigma_v$matrix = [1]

All the other operations of this group change the coordinate z of hydrogen atom into – z & the obtain equation for transformation are-

C_2.Z = - 1Z	$C_{2\text{matrix}}$ = [-1]
S_{∞}.Z = - 1Z	$S_{\infty \text{matrix}}$ = [-1]
σ_h.Z = - 1Z	$\sigma_h$matrix = [-1]
i.Z = - 1Z	imatrix = [-1]

The matrix representation thus obtained for z-coordinate of hydrogen atom in hydrogen molecule

	E	C_{∞}	σ_v	C_2	S_{∞}	σ_h	*i*
T	[1]	[1]	[1]	[-1]	[-1]	[-1]	[-1]

The representation T is irreducible since it is one dimensional.

Representation of the C_n, C_{nv}, C_{nh} D_{nh}

Q	**Cos Q**	**Sin Q**
90	**0**	**1**
120	**-1/2**	**√3/2**
180	**-1**	**0**
240	**-1/2**	**-√3/2**

Check your progress 3

Notes : i) Write your answer in the space given below.
ii) Compare your answer with those given at the end of the unit.

Q .1 The point groups are denoted by their component symmetries. There are a few standard notations used by crystallographers called ……… .
Q .2 In schonflies notations the letter *I* indicates that the group has the symmetry of an……… .
Q. 3 Those representations which cannot be further reduced to representations of lower dimension are called ……………. .
Q 4. Find the order of the point group C2V.
Q 5. - --- – is the subdivision of a group.
Q 6. Cite an example of a compound with Abelian group.
Q 7. Find the principal and the subsidiary axes of symmetry in benzene.
Q 8 State whether A1,A2, B1,B2 are **reducible representation or Irreducible representation.**
Q9.Cite an example of dihedral group.

1.2.10- Great Orthogonality Theorem (GOT)

This theorem is concerned with the elements of matrices constituting irreducible representation of a point group. The properties of irreducible representations can be obtained from this theorem.

The GTO states:

$$\sum_{G}[\Gamma_i(G)_{mn}]\,[\Gamma_j(G)_{m'n'}]^{*}=(h/\sqrt{l_i l_j})\,\delta_{ij}\delta_{mm'}\delta_{nn'}$$

Where,
1. ***h*****:** Order of the group: the number of elements of the group.
2. **i& j** are two irreducible representation of the group.

3. li **&** lj are the dimensions of these two irreducible representation.
3. Γi**:** i–th irreducible representation.
4. G**:** Generic element of the group.It represents particular symmetry operation in the group
5. $\Gamma i\ (G)mn$- : Matrix element at the intersection of the m–th row with n–th column of the matrix representing G in the i–th irreducible representation.
6. $\Gamma j\ (G)mn^*$ **-** The element in the mth& nth column of the matrix in the jth irreducible representation.
7. $\Gamma j(G)m'n'$ **-** The complex conjugate of the element in the mth row & nth column of a matrix in the jth irreducible representation.
8. $\delta ij\delta mm'\delta nn'$- Denotes Kornecker Delta symbol.The Kornecker Delta symbol δij has the meaning $\delta ij = 0$ **for** $i\neq j$ **&** $\delta ij=1 for\ i=j$.

It shows three cases

Case 1 - $i = j$, $m = m'$ **and** $n = n'$ **simultaneously. Under such restrictions, equation** reduces to

$$\sum_G [\Gamma i(G)mn]\,[\Gamma i(G)m'n']^* = \sum_G |[\Gamma i(G)mn]|^2 = h/li$$

this sum has as many terms as elements are in the group & the sum is over some matrix elements and their complex conjugate. In this case the numbers being multiplied by their complex conjugates can be considered as components of a vector, the result being the magnitude of the vector,hence the name given to the **orthogonality theorem**.

Case 2 - $i\neq j$ **,** $[\Gamma i(G)mn]$ **&** $[\Gamma j(G)m'n']$ represents two real elements in the mth row & nth column of a matrix for the operation G in the i&j representation

$$\sum_G [\Gamma i(G)mn]\,[\Gamma j(G)m'n']^* = (h/\sqrt{lilj})\,\delta ij = 0$$

It represents elements of corresponding matrices of different irreducible representation are orthogonal.

Case 3 - $m\neq m'$ & $n \neq n'$ If $\Gamma i\ (G)mn$ *is the* element in the mth row & nth column of the matrix for operation G in the ith irreducible representation & $\Gamma j(G)m'n'$ *is the* element in the m' th row & n' th column of the matrix for operation G in the same representation then

$$\sum_G [\Gamma i(G)mn]\,[\Gamma j(G)m'n']^* = (h/\sqrt{li})\,\delta ij\delta mm'\delta nn' = 0$$

It represents elements of different set of matrices of same irreducible representation are orthogonal.

Importance of Orthogonality Theorem

It defines the properties of irreducible representation. By considering the three classes , 5 corollaries can be derived & these gives the 5 rules about the irreducible representation of a group & their character.

Rules for the irreducible representation

Again, let's state them now and prove them later. In the following discussion $\chi i(G)$ is the character (trace) of the matrix representing G in Γi:
1.$\sum l2i = h$: The sum of the squares of the dimensions of the irreps equals The order of the group.
2.$\sum G\ |\chi i(G)|2 = h$: For a given irrep, the sum over all matrices of the squares of the magnitudes of the characters in the irrep equals the order of the group.
3.$\sum G\ \chi i(G)\chi j(G) = 0$: For any pair of irreps, the sum over all matrices of the products of the characters of the matrices representing the same element

Character tables

Sum of all the diagonal elements of a square matrix is known as character of matrix.

Symmetry operation	Character of matrix
Identity	3

Rotation	$2 \cos \theta + 1$
Inversion	-3
Improper rotation	$2 \cos \theta - 1$
Reflection	1

For each point group, a **character table** summarizes information on its symmetry operations and on its irreducible representations. As there are always equal numbers of irreducible representations and classes of symmetry operations, the tables are square.

The table itself consists of **characters** which represent how a particular irreducible representation transforms when a particular symmetry operation is applied. Any symmetry operation in a molecule's point group acting on the molecule itself will leave it unchanged. But for acting on a general entity, such as a vector or an orbital, this need not be the case. The Vector could change sign or direction, and the orbital could change type. For simple point groups, the values are either 1 or −1: 1 means that the sign or phase (of the vector or orbital) is unchanged by the symmetry operation (*symmetric*) and −1 denotes a sign change (*asymmetric*).

The representations are labeled according to a set of conventions:

- A, when rotation around the principal axis is symmetrical
- B, when rotation around the principal axis is asymmetrical
- E and T are doubly and triply degenerate representations, respectively when the point group has an inversion center
- the subscript g (German: *gerade* or even) signals no change in sign, and the subscript u (*ungerade* or uneven) a change in sign, with respect to inversion.with point groups $C_{\infty v}$
- $D_{\infty h}$ informs about how the Cartesian basis vectors, rotations about them, and quadratic functions of them transform by the symmetry operations of the group, by noting which irreducible representation transforms in t
  same way. These indications are conventionally on the right hand side of the tables.

This information is useful because chemically important orbitals (in particular *p* and *d* orbitals) have the same symmetries as these entities.

The character table for the C_{2v} symmetry point group is given below:

C_{2v}	**E**	**C_2**	**σ_v(xz)**	**σ_v'(yz)**		
A_1	1	1	1	1	*Z*	x^2, y^2, z^2
A_2	1	1	−1	−1	R_z	*Xy*
B_1	1	−1	1	−1	*x*, R_y	*Xz*
B_2	1	−1	−1	1	*y*, R_x	*Yz*

Example of water (H_2O) which has the C_{2v} symmetry . The $2p_x$ orbital of oxygen is oriented perpendicular to the plane of the molecule and switches sign with a C_2 and a σ_v'(yz) operation, but remains unchanged with the other two operations (obviously, the character for the identity operation is always +1). This orbital's character set is thus {1, −1,1, −1}, corresponding to the B_1 irreducible representation. Similarly, the $2p_z$ orbital is seen to have the symmetry of the A_1 irreducible representation, $2p_y$ B_2, and the $3d_{xy}$ orbital A_2. These assignments and others are noted in the rightmost two columns of the table.

1.2.11 Character Table & their uses

A finite group G has a finite number of conjugacy classes and a finite number of distinct irreducible representations. The group character of a group representation is constant on a conjugacy class. Hence, the values of the characters can be written as an array, known as a character table. Typically, the rows are given by the irreducible representations and the columns are given the conjugacy classes.A character table often contains enough information to identify a given abstract group and distinguish it from others. However, there exist nonisomorphic groups which nevertheless have the same character table, for example D_4 (the symmetry group of the square) and Q_8(the quaternion group).

For example, the symmetric group on three letters S_3 has three conjugacy classes, represented by the permutations $\{1, 2, 3\}$, $\{2, 1, 3\}$, and $\{2, 3, 1\}$. It also has three irreducible representations; two are one-dimensional and the third is two-dimensional:

1. The trivial representation $\phi_1(g)(\alpha) = \alpha$.
2. The alternating representation, given by the signature of the permutation, $\phi_2(g)(\alpha) = \operatorname{sgn}(g)\,\alpha$.
3. The standard representation on $V = \{(z_1, z_2, z_3) : \sum z_i = 0\}$with

$$\phi_3(\{a, b, c\})(z_1, z_2, z_3) = (z_a, z_b, z_c).$$

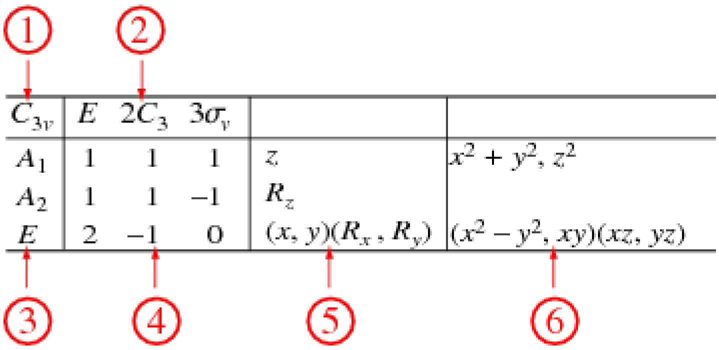
The standard representation can be described on $\mathbb{C}^2$via the matrices

$$\tilde{\phi}_3(\{2, 1, 3\}) = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}$$

$$\tilde{\phi}_3(\{2, 3, 1\}) = \begin{bmatrix} 0 & -1 \\ 1 & -1 \end{bmatrix},$$

and hence the group character of the first matrix is 0 and that of the second is -1. The group character of the identity is always the dimension of the vector space. The trace of the alternating representation is just the permutation symbol of the permutation. the character table for S_3 is shown below.

	1	2	3
S_3	e	(12)	(123)
Trivial	1	1	1
Alternating	1	-1	1
Standard	2	0	-1



C_{3v}	E	$2C_3$	$3\sigma_v$		
A_1	1	1	1	z	$x^2 + y^2, z^2$
A_2	1	1	-1	R_z	
E	2	-1	0	$(x, y)(R_x, R_y)$	$(x^2 - y^2, xy)(xz, yz)$

The numbered regions contain the following contents.

1. The symbol used to represent the group in question (in this case C_{3v}).
2. The conjugacy classes, indicated by number and symbol, where the sum of the coefficients gives the group order of the group.
3. Mulliken symbols, one for each irreducible representation.
4. An array of the group characters of the irreducible representation of the group, with one column for each conjugacy class, and one row for each irreducible representation.
5. Combinations of the symbols x, y, z, R_x, R_y, and R_z, the first three of which represent the coordinates x, y, and z, and the last three of which stand for rotations about these axes. These are related to transformation properties and basis of representations of the group. All square and binary products of coordinates according to their transformation properties.

Due to the crystallographic restriction theorem, *n* is restricted to the values of 1, 2, 3, 4, or 6. It is important to note that the 'plane' in the definition of the rotation-reflection (alternating) axis of symmetry is **not necessarily** a mirror plane of the group in which the axis exists. Consider S_4, for example.Due to the crystallographic restriction theorem, *n* = 1, 2, 3, 4, or 6 in 2 or 3 dimension space.

N	**1**	**2**	**3**	**4**	**6**
C_n	C_1	C_2	C_3	C_4	C_6
C_{nv}	$C_{1v}=C_{1h}$	C_{2v}	C_{3v}	C_{4v}	C_{6v}
C_{nh}	C_{1h}	C_{2h}	C_{3h}	C_{4h}	C_{6h}
D_n	$D_1=C_2$	D_2	D_3	D_4	D_6
D_{nh}	$D_{1h}=C_{2v}$	D_{2h}	D_{3h}	D_{4h}	D_{6h}
D_{nd}	$D_{1d}=C_{2h}$	D_{2d}	D_{3d}	D_{4d}	D_{6d}
S_n	$S_1=C_{1h}$	S_2	$S_3=C_{3h}$	S_4	S_6

D_{4d} and D_{6d} are actually forbidden because they contain improper rotations with n=8 and 12 respectively. The 27 point groups in the table plus T, T_d, T_h, O and O_h constitute 32 crystallographic point groups

An irreducible representation of a group is a representation for which there exists no unitary transformation which will transform the representation matrix into block diagonal form. The irreducible representations have a number of remarkable properties, as formalized in the group orthogonality theorem

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CHECK YOUR PROGRESS 4-

Notes : i) Write your answer in the space given below.
ii) Compare your answer with those given at the end of the unit.

Q.1 What is group orthogonality theorm?
Q.2 Sum of all the diagonal elements of a square matrix is known as……… .
Q3.The number of elements of the group is called the …… of the group

---

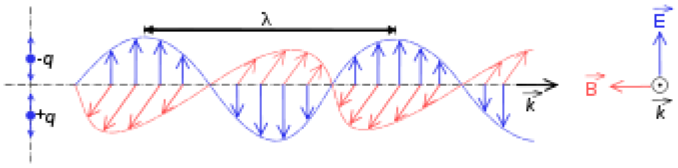
1.3 - UNIFYING PRINCIPLES

ELECROMAGNETIC RADIATION-

Electromagnetic radiation (often abbreviated **E-M radiation** or **EMR**) is a form of energy exhibiting wave-like behavior as it travels through space. EMR has both electric and magnetic field components, which oscillate in phase perpendicular to each other and perpendicular to the direction of energy propagation.

James Clerk Maxwell first formally postulated **electromagnetic waves**. These were subsequently confirmed by Heinrich Hertz. Maxwell derived a wave form of the electric and magnetic equations, thus uncovering the wave-like nature of electric and magnetic fields, and their symmetry. EM radiation exhibits both wave and particle properties at the same time.

Properties



1. Electromagnetic waves can be imagined as a self-propagating transverse oscillating wave of electric and magnetic fields. The electric field is in a vertical plane and the magnetic field in a horizontal plane.
2. Electric and magnetic fields obey the properties of superposition. Thus, a field due to any particular particle or time-varying electric or magnetic field contributes to the fields present in the same space due to other causes.
3. All magnetic and electric field vectors add together according to vector addition. For example, in optics two or more coherent light waves may interact and by constructive or destructive interference yield a resultant irradiance deviating from the sum of the component irradiances of the individual light waves.
4. Since light is an oscillation it is not affected by travelling through static electric or magnetic fields in a linear medium such as a vacuum. However in nonlinear media, such as some crystals, interactions can occur between light and static electric and magnetic fields — these interactions include the Faraday effect and the Kerr effect.
5. In refraction, a wave crossing from one medium to another of different density alters its speed and direction upon entering the new medium. The ratio of the refractive indices of the media determines the degree of refraction, and is summarized by Snell's law.
6. Different frequencies undergo different angles of refraction.
7. A wave consists of successive troughs and crests, and the distance between two adjacent crests or troughs is called the wavelength. Waves of the electromagnetic spectrum vary in size, from very long radio waves the size of buildings to very short gamma rays smaller than atom nuclei.
8. Frequency is inversely proportional to wavelength ,according to the equation.

   $$v = f\lambda$$

   where v is the speed of the wave , f is the frequency and λ is the wavelength.
9. As waves cross boundaries between different media, their speeds change but their frequencies remain constant. .
10. Interference is the superposition of two or more waves resulting in a new wave pattern.If the fields have components in the same direction, they constructively interfere, while opposite directions cause destructive interference.
11. The energy in electromagnetic waves is sometimes called radiant energy.

Wave model

Electromagnetic radiation is a transverse wave meaning that the oscillations of the waves are perpendicular to the direction of energy transfer and travel.The frequency of a wave is its rate of oscillation and is measured in hertz, the SI unit of frequency, where one hertz is equal to one oscillation per second.

Electromagnetic radiation is classified according to the frequency of its wave. The electromagnetic spectrum, in order of increasing frequency and decreasing wavelength, consists of radio waves, microwaves, infrared radiation, visible light, ultraviolet radiation, X-rays and gamma rays .The photon is the quantum of the electromagnetic interaction and the basic "unit" of light and all other forms of electromagnetic radiation and is also the force carrier for the electromagnetic force.

Electromagnetic radiation carries energy and momentum that may be imparted to matter with which it interacts.

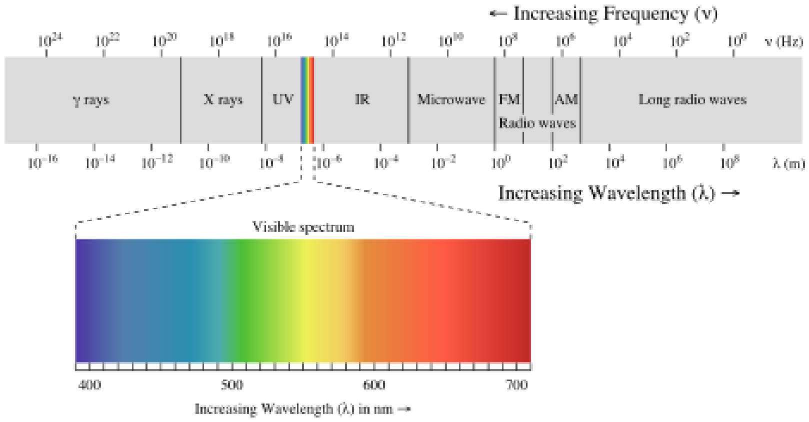
Particle model

Energy of an electromagnetic wave is quantized , electromagnetic energy is emitted and absorbed as discrete packets of energy, or quanta, called photons. The energy of the photons is proportional to the frequency of the wave.Conversely, in a first-quantized treatment, because a photon acts as a transporter of energy, it is associated with a probability wave with frequency proportional to the energy carried. The energy per photon is related to the frequency via the Planck–Einstein equation.

$$E = hf$$

where E is the energy, h is Planck's constant, and f is frequency. The energy is commonly expressed in the unit of electronvolt (eV). This photon-energy expression is a particular case of the energy levels of the more general *electromagnetic oscillator*, whose average energy, which is used to obtain Planck's radiation law, differ sharply from that predicted by the equipartition principle at low temperature, thereby establishes a failure of equipartition due to quantum effects at low temperature.

1.3.1 - Electromagnetic spectrum



The behavior of EM radiation depends on its wavelength. Higher frequencies have shorter wavelengths, and lower frequencies have longer wavelengths. When EM radiation interacts with single atoms and molecules, its behavior depends on the amount of energy per quantum it carries.

CHECK YOUR PROGRESS - 5

Notes : i) Write your answer in the space given below.
ii) Compare your answer with those given at the end of the unit.

Q1. EMR has both electric and magnetic field components, which oscillate in phase……… to each other and perpendicular to the direction of ……… .

Q.2 The ratio of the refractive indices of the media determines the degree of, and is summarized by …………… .

Q.3 Energy of an electromagnetic wave is quantized , electromagnetic energy is emitted and absorbed as discrete packets of energy called ……….. .

Q.4 When EM radiation interacts with single atoms and molecules, its behavior depends on the amount of ……… it carries.

1.3.2 - INTERACTION OF ELECTROMAGNETIC RADIATION WITH MATTER

As a photon is absorbed by an atom, it excites the atom, elevating an electron to a higher energy level. If the energy is great enough, so that the electron jumps to a high enough energy level, it may escape the positive pull of the nucleus and be liberated from the atom in a process called photoionisation.

Conversely, an electron that descends to a lower energy level in an atom emits a photon of light equal to the energy difference. Since the energy levels of electrons in atoms are discrete, each element emits and absorbs its own characteristic frequencies.

Together, these effects explain the emission and absorption spectra of light. The dark bands in the absorption spectrum are due to the atoms in the intervening medium absorbing different frequencies of the light. The composition of the medium through which the light travels determines the nature of the absorption spectrum . As the electrons descend to lower energy levels, a spectrum is emitted that represents the jumps between the energy levels of the electrons.

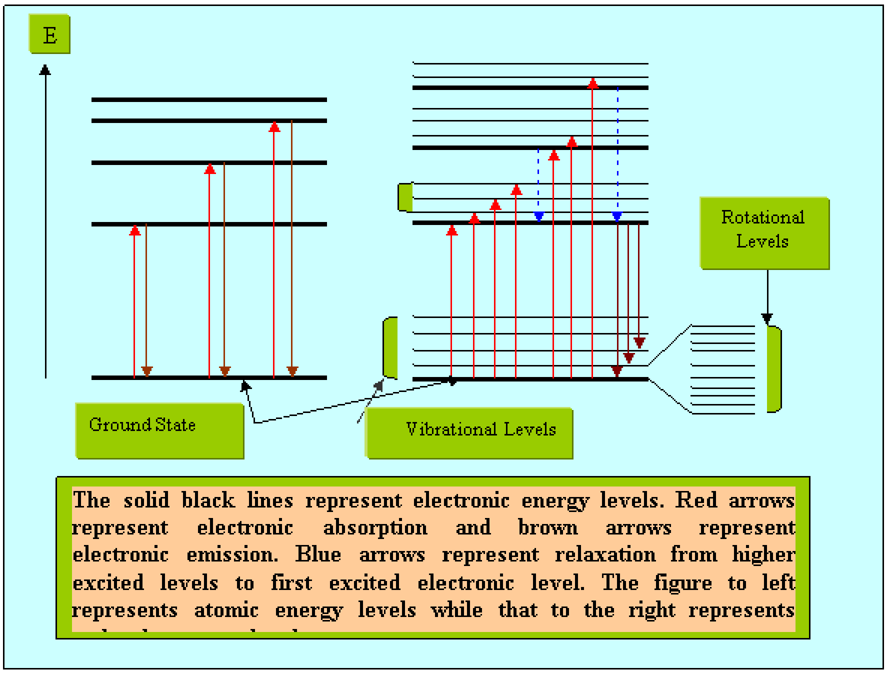
1.3.3 - Absorption of Radiation

Chemical species can absorb radiation when the energy of that radiation exactly match the energy for a transition to an excited state. At ordinary temperatures, the vast majority of chemical species are present in the ground state (lowest energy state). Two types of absorption will be emphasized:

1. **Atomic Absorption**: In this type of a process, atoms in the ground state can be transferred to a higher state (excited state) by absorption of an amount of energy equal to the difference of energy between the two states. This type of absorption involves transition of electrons and is thus called electronic transition.

2. **Molecular Absorption**: Beside electronic transitions , molecules can absorb energy and be transferred to higher vibrational or rotational levels. Vibrational and rotational transitions are the basis for infrared and microwave spectroscopy .

Only electronic transitions will be of interest to us for both atoms and molecules.



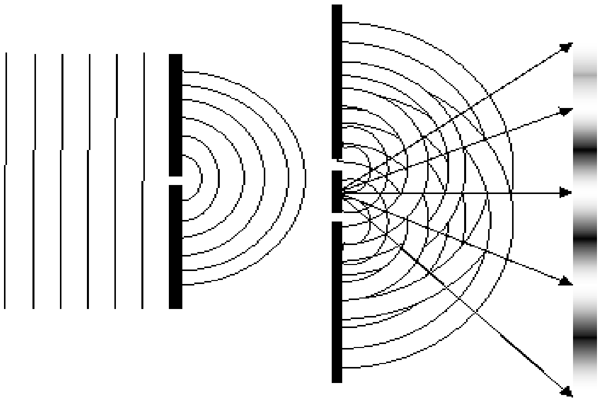
The solid black lines represent electronic energy levels. Red arrows represent electronic absorption and brown arrows represent electronic emission. Blue arrows represent relaxation from higher excited levels to first excited electronic level. The figure to left represents atomic energy levels while that to the right represents

1.3.4 - Emission of Radiation

An atom, ion, or molecule which absorbs radiation and is transferred to an excited state will lose this extra energy and is transferred back to the ground state. The process is the reverse of absorption, however, for atoms, only electronic emission is allowed since only electronic levels are present. In contrary, molecular species can transfer their extra energy by relaxation to electronic, vibrational or rotational levels. Usually, molecular species excited to an energy level higher than the first excited electronic level will initially relax to the first excited energy level without emission of radiation (nonradiative relaxation). This relaxation process is followed by another relaxation to ground state by either a nonradiative relaxation or through emitting a photon in a process called fluorescence(instantaneous emission) or phosphorescence(emission after some time lag).

Diffraction of Radiation

Diffraction is a characteristic of electromagnetic radiation. Diffraction is a process by which a parallel beam of radiation is bent when passing through a narrow opening or a pinhole. Therefore, diffraction of radiation demonstrate its wave nature. Diffraction is not clear when the opening is large.
However, when the opening is small enough (close to wavelength of radiation), the beam is bent as shown in the figure below:



Construction interference of beams exiting the two slits results in lighted regions while destructive interference gives opaque regions. The most intense constructive interference occurs at the point at the center of the region between the two slits where actually no light is emerging. However, at that point, light travels the same distance from both steps which results in 100% constructive interference and thus most intense lighted region. As the distance up and down that point increases, the intensity of lighted regions decrease.

Coherence of Radiation

Two beams of radiation are said to be coherent if they satisfy the following conditions:
1. Both have the same frequency and wavelength or set of frequencies and wavelength.
2. Both have the same phase relationships with time.
3. Both are continuous.

Only coherent radiation can result in the phenomenon of diffraction.

1.3.5- Transmission of Radiation

The velocity of radiation in any medium is less than that in vacuum. The velocity of radiation is therefore a function of the refractive index of the medium in which it propagates. The velocity of radiation in any medium can be related to the speed of radiation in vacuum (c) by the relation:

$$\mathbf{n_i = c/v_i}$$

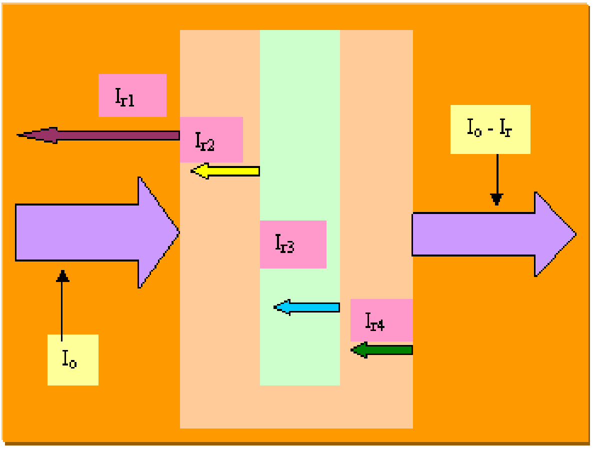
Where, v_i is the velocity of radiation in the medium I, and n_i is the refractive index of medium i.
The decrease in radiation velocity upon propagation in transparent media is attributed to periodic polarization of atomic and molecular species making up the medium. Polarization mean temporary induced deformation of the electronic clouds of atoms and molecules as a result of interaction with electric field of the waves.

1.3.6 - Reflection of Radiation

An incident beam hitting transparent surfaces (at right angles) with a different refractive index will suffer successive reflections. This means that the intensity of emerging beam will always be less than the incident beam. The relation governing the ratio between reflected and incident beams can be written as follows:

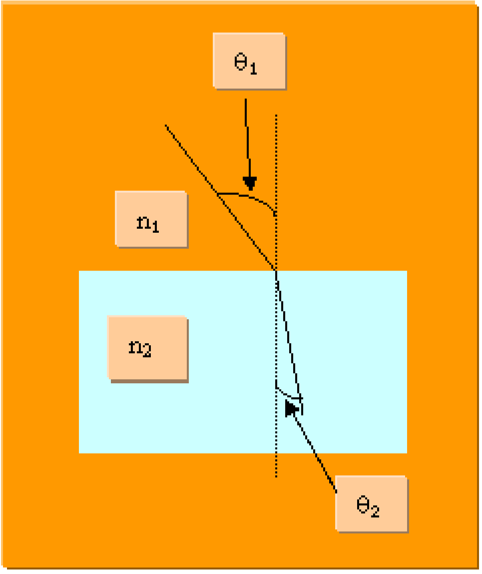
$$\mathbf{I_r/I_0 = (n_2 - n_1)^2/(n_2 + n_1)^2}$$

Where I_r is the intensity of the reflected beam, I_o is the intensity of the incident beam; n_1 is the refractive indices of the medium from which the incident beam emerges while n_2 is the refractive index of the other medium.



1.3.7 - Refraction of Radiation

When a beam of radiation hits the interface between two transparent media that have different refractive indices, the beam suffers an abrupt change in direction or refraction. The degree of refraction is quantitatively shown by Snell's law where:

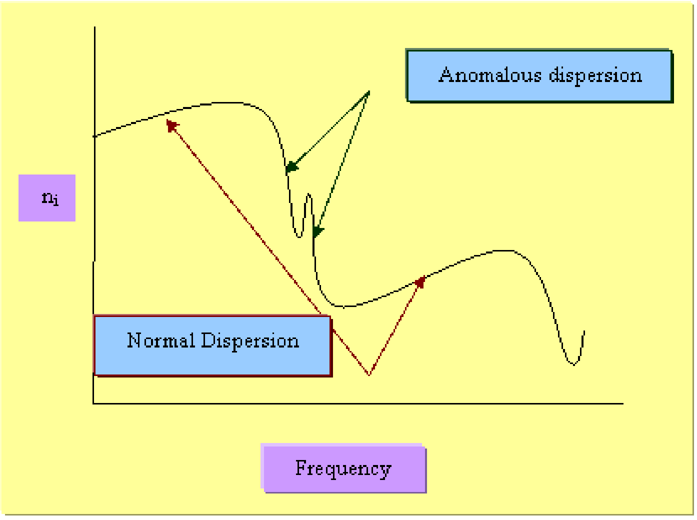


$$\mathbf{n_1 \sin \theta_1 = n_2 \sin \theta_2}$$

1.3.8 Dispersion of Radiation

The speed of radiation in vacuum is constant and independent on wavelength, and since the velocity of radiation in medium I is dependent on wavelength, therefore the refractive index of a substance should be dependent on wavelength. The variation of the refractive index with wavelength is called dispersion. **Transparent materials usually exhibit two types of dispersion phenomena**.**Normal dispersion-** where the variation of refractive index with wavelength is very small. Such substances which show normal dispersion are good materials for the manufacture of lenses and other optics which do not require dispersion.

Anomalous dispersion- reflects a large variation of refractive index with wavelength. Substances which show good anomalous dispersion are appropriate materials for the manufacture of dispersion elements like prisms. One substance can be used for the manufacture of both types of optical materials depending on the wavelength.



1.3.9 -Polarization

Polarization is a property of certain types of waves that describes the orientation of their oscillations. Electromagnetic waves, such as light, and gravitational waves exhibit polarization.

By convention, the polarization of light is described by specifying the orientation of the wave's electric field at a point in space over one period of the oscillation. When light travels in free space, in most cases it propagates as a transverse wave .The polarization is perpendicular to the wave's direction of travel. In this case, the electric field may be oriented in a single direction (linear polarization), or it may rotate as the wave travels (circular or elliptical polarization). In the latter cases, the oscillations can rotate either towards the right or towards the left in the direction of travel. Depending on which rotation is present in a given wave it is called the wave's chirality or handedness. In general the polarization of an electromagnetic (EM) wave is a complex issue.

For longitudinal waves such as sound waves in fluids, the direction of oscillation is by definition along the direction of travel, so there is no polarization. In a solid medium, however, sound waves can be transverse. In this case, the polarization is associated with the direction of the shear stress in the plane perpendicular to the propagation direction.

Polarization is significant in areas of science and technology dealing with wave propagation, such as optics, seismology, telecommunications and radar science. The polarization of light can be measured with a polarimeter .

1.3.10 B - Scattering of Radiation

When a beam of radiation hits a particle, molecule, or aggregates of particles or molecules, scattering occurs. The intensity of scattered radiation is directly proportional to particle size, concentration, the square of the polarizability of the molecule, as well as the fourth power of the frequency of incident beam. Scattered radiation can be divided into three categories:

1. Rayleigh scattering

This type of scattering is exhibited by molecules or molecular aggregates with dimensions significantly smaller than the wavelength of incident beam. The scattered radiation has the same wavelength as the incident beam. Therefore, radiation with smaller wavelengths are scattered more than that with longer wavelengths. This behavior explains the phenomenon of the blue color of the sky.

2. Tyndall Effect

Scattering by large particles is referred to as Tyndall effect. This behaviour is exhibited by particles in the colloidal dimensions and is routinely used in the detection of proteins and lipids as well as other species in the colloidal dimensions. Both the shape and size of colloidal species were determined by measurement of scattered radiation.

3. Raman Scattering

C. V. Raman in 1928 observed a new type of scattering where scattered radiation with wavelengths longer and shorter than that of the incident beam were detected. The scattered wavelengths were later realized to be related to the molecular structure and are a function of polarizability.

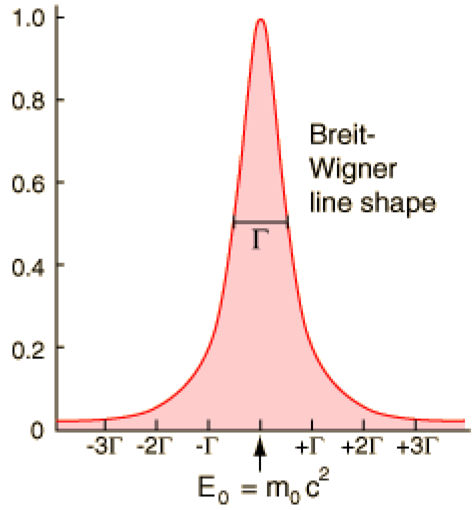
CHECK YOUR PROGRESS -6

Notes : i) Write your answer in the space given below.
ii) Compare your answer with those given at the end of the unit.

Q .1 Diffraction of radiation demonstrate …… nature of electromagnetic radiation.
Q.2 The most intense constructive interference occurs at the point at the center of the region between the two slits where actually ……..(most / less / no) light is emerges.
Q .3 The velocity of radiation in any medium is ……….. (More / less) than that in vacuum.
Q .4 The variation of the refractive index with wavelength is called ……………. .
Q.5 Explain polarization ?
Q.6 Tyndall effect is exhibited by particles in the ……….. dimensions.

1.3.11- The Uncertainty Principle

Werner Heisenberg, in 1927, introduced the uncertainty principle which states that: **Nature imposes limits on the precision with which certain pairs of physical measurements can be made**. This principle has some important implications in the field of instrumental analysis.



The Breit-Wigner distribution is similar to a gaussian near the peak, but the tails of the curve are flatter.

The uncertainty principle provides a tool for characterizing the very short-lived products produced in high energy collisions in accelerators. The uncertainty principle suggests that for particles with extremely short lifetimes, there will be a significant uncertainty in the measured energy. The measurement of the mass energy of an unstable particle a large number of times gives a distribution of energies called a Lorentzian or a Breit-Wigner distribution.

If the width of this distribution at half-maximum is labeled Γ , then the uncertainty in energy ΔE could be reasonably expressed as

$$\Delta E = \frac{\Gamma}{2} = \frac{\hbar}{2\tau}$$

where the particle lifetime τ is taken as the uncertainty in time τ = Δt.

In high energy scattering experiments, the energy uncertainty ΔE can be determined and the lifetime implied from it. In other cases, the lifetime is most conveniently measured and the "particle width" in energy implied from that lifetime measurement.

Γ is often referred to as the "**natural line width**" or Decay width. It is of great importance and provides the means for determining the ultra short lifetimes of particles produced. For optical spectroscopy it is a minor factor because the natural line width is typically 10^{-7} eV , about a tenth as much as the Doppler broadening. Another source of line width is the recoil of the source, but that is negligible in the optical range.

For nuclear transitions involving gamma emission in the 0.1-1 MeV range, the recoil width is typically much greater than the natural line width. The recoil of the emitting nucleus implies that the emitted gamma photon cannot be absorbed by an identical nucleus because its energy is reduced by an amount greater than the natural line width of potential absorbing levels. Mossbauer discovered that the absorption could be accomplished by putting the source on a rotating arm to give it enough speed to compensate for the recoil effect. The Mossbauer effect became a useful experimental tool when it was discovered that the recoil could be suppressed by putting the emitting nucleus in a crystal lattice. The emitted gammas then exhibited something close to the natural line width and could be absorbed by other identical nuclei.

1.3.12 - NATURAL LINE WIDTH & NATURAL LINE BROADENING

In an emission line, The line seems uniformly bright, but more careful study shows that its brightness is greatest at the center and tapers off toward either side. *line broadening* is caused by the *environment* in which the emission or absorption occurs, which often changes our perception of a photon's energy, and it tells us a lot about the physical state of the gas involved.

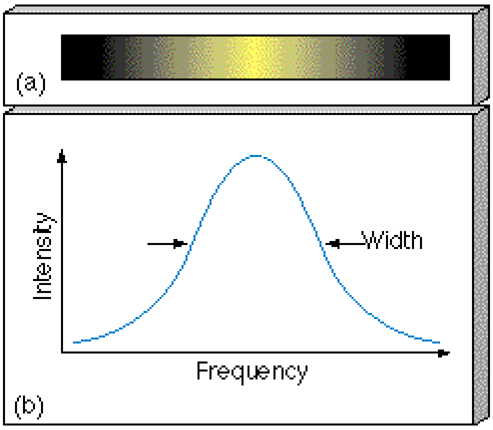


***Fig:** By tracing the changing brightness across a typical emission line (a) and expanding the scale, we obtain a graph of its intensity plotted versus wavelength (b).*

Several physical mechanisms can broaden spectral lines. The most important of these involve the Doppler effect. To understand how the Doppler effect can broaden a spectral line, imagine a hot gas cloud. Individual atoms are in random, chaotic motion. The hotter the gas, the faster the random *thermal motions* of the atoms, as illustrated in Fig. If a photon is emitted by an atom *in motion*, the wavelength of the detected photon is changed by the Doppler effect. For example, if an atom is moving away from our eye or from our detector while in the process of emitting a photon, that photon is redshifted. The photon is not recorded at the precise wavelength predicted by atomic physics but rather at a slightly longer wavelength. The extent of this redshift is proportional to the velocity away from the detector. Similarly, if the atom is moving toward us, its light is blueshifted.

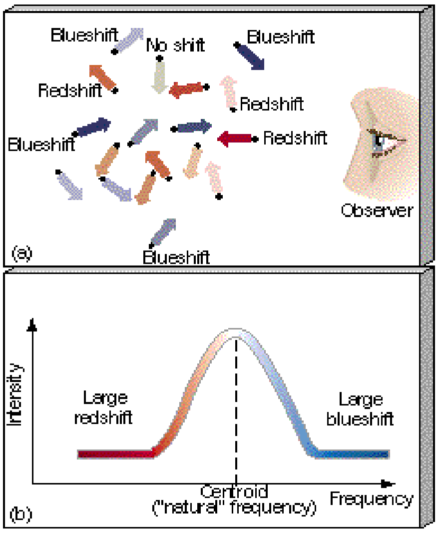


***Fig:** Atoms moving randomly (a) produce broadened spectral lines (b) as their individual redshifted and blueshifted emission lines merge in our detector.*

Throughout the whole cloud, atoms move in every possible direction. The result is that many atoms emit or absorb photons at slightly different wavelengths than would normally be the case if all the atoms were motionless. Most atoms in a typical cloud have very small thermal velocities. As a result, most atoms emit or absorb radiation that is Doppler-shifted only a little, and very few atoms have large shifts. So, the centre of any spectral line is much more pronounced than either of its "wings."

Thus, even if all atoms emitted and absorbed photons at only one specific wavelength, the effect of their thermal motion would be to smear the line out over a small range of wavelengths. The hotter the gas, the larger the spread of Doppler motions and the greater the width of the line. By measuring a line's width, astronomers can estimate the temperature of the gas producing it.

Several other physical mechanisms can also produce line broadening. One such mechanism is ***gas turbulence***, which exists when the gas in a cloud is not at rest or flowing smoothly but instead is seething and churning in eddies and vortices of many sizes. Motion of this type causes Doppler-shifting of spectral lines, but lines from different parts of the cloud are shifted more or less randomly.

Other broadening mechanisms do not depend on the Doppler effect at all. For example, if electrons are moving between orbitals while their parent atom is colliding with another atom, the energy of the emitted or absorbed photons changes slightly, thus "blurring" the spectral lines. This mechanism occurs most often in dense gases, where collisions are most frequent. It is usually referred to as *collisional broadening*. The amount of broadening increases as the density of the emitting or absorbing gas rises. Yet another cause of spectral-line broadening is *magnetism*. The electrons and nuclei within atoms behave as tiny, spinning magnets. As a result, the basic emission and absorption rules of atomic physics change slightly whenever atoms are immersed in a magnetic field. Generally, the greater the magnetic field, the more pronounced the spectral-line broadening.

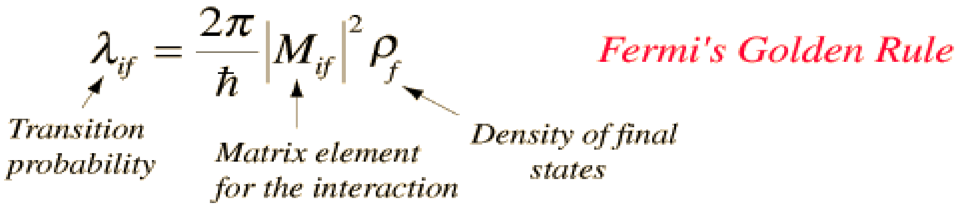
1.3.13 - TRANSITION PROBABILITY

The transition probability is defined as the probability of particular spectroscopic transition to take place. When an atom or molecule absorbs a photon, the probability of an atom or molecule to transit from one energy level to another depends on two things: the nature of initial and final state wavefunctions and how strongly photons interact with an eigen state. Transition strengths are used to describe transition probability. Selection rules are utilized to determine whether a transition is allowed or not.

1.3.14 -RESULT OF THE TIME DEPENDENT PERTURBATION THEORY

One of the prominent failures of the Bohr model for atomic spectra was that it couldn't predict that one spectral line would be brighter than another. From the quantum theory came an explanation in terms of wavefunctions, and for situations where the transition probability is constant in time, it is usually expressed in a relationship called Fermi's golden rule.

In general conceptual terms, a transition rate depends upon the strength of the coupling between the initial and final state of a system and upon the number of ways the transition can happen (i.e., the density of the final states). In many physical situations the transition probability is of the form



$$\lambda_{if} = \frac{2\pi}{\hbar} \left| M_{if} \right|^2 \rho_f$$

The transition probability λ is also called the decay probability and is related to the mean lifetime τ of the state by λ = 1/τ. The general form of Fermi's golden rule can apply to atomic transitions, nuclear decay, scattering ... a large variety of physical transitions.

A transition will proceed more rapidly if the coupling between the initial and final states is stronger. This coupling term is traditionally called the "matrix element" for the transition: this term comes from an alternative formulation of quantum mechanics in terms of matrices rather than the differential equations of the Schrodinger approach. The matrix element can be placed in the form of an integral where the interaction which causes the transition is expressed as a potential V which operates on the initial state wave function. The transition probability is proportional to the square of the integral of this interaction over all of the space appropriate to the problem.

$$M_{if} = \int \overset{\text{Wavefunction for final state}}{\Psi_f^*}\, \underset{\text{Operator for the physical interaction which couples the initial and final states of the system.}}{V}\, \overset{\text{Wavefunction for initial state}}{\Psi_i}\, dv$$

This kind of integral approach using the wavefunctions is of the same general form as that used to find the "expectation value" or expected average value of any physical variable in quantum mechanics. But in the case of an expectation value for a property like the system energy, the integral has the wavefunction representing the eigenstate of the system in both places in the integral.

1.3.15 - Transition Moment

In an atom or molecule, an electromagnetic wave (for example, visible light) can induce an oscillating electric or magnetic moment. If the frequency of the induced electric or magnetic moment is the same as the energy difference between one eigenstate Ψ_1 and another eigenstate Ψ_2, the interaction between an atom or molecule and the electromagnetic field is resonant (which means these two have the same frequency). The amplitude of this (electric or magnetic) moment is called the transition moment. In quantum mechanics, the transition probability of one molecule from one eigenstate Ψ_1 to another eigenstate Ψ_2 is given by $|\vec{M}_{21}|^2$, and $\vec{M}_{21}$is called the transition dipole moment, or transition moment, from Ψ_1 to Ψ_2. In mathematical form it can be written as

$$\vec{M}_{21} = \int \Psi_2 \vec{\mu} \Psi_1 d\tau$$

The Ψ_1 and Ψ_2 are two different eigenstates in one molecule, $\vec{M}_{21}$ is the electric dipole moment operator. If we have a system with n molecules and each has charge Q_n, and the dipole moment operator is can be written as

$$\vec{\mu} = \sum_n Q_n \vec{x}_n$$

the $\vec{x}_n$ is the position vector operator.

1.3.16 - Selection Rules

Electronic transitions in atoms

Atoms are described by the primary quantum number n, angular momentum quantum number L, spin quantum number S, and total angular momentum quantum number J. Based on Russell-Saunders approximation of electron coupling, the atomic term symbol can be represented as $^{2S+1}L_J$.

1. The total spin cannot change, $\Delta S=0$;
2. The change in total orbital angular momentum can be $\Delta L=0, \pm1$, but $L=0 \leftrightarrow L=0$ transition is not allowed;
3. The change in the total angular momentum can be $\Delta J=0, \pm1$, but $J=0 \leftrightarrow J=0$ transition is not allowed;
4. The initial and final wavefunctions must change in parity. Parity is related to the orbital angular momentum summation over all elections Σl_i, which can be even or odd; only even $\leftrightarrow$odd transitions are allowed.

Electronic transitions in molecules

The electronic-state configurations for molecules can be described by the primary quantum number n, the angular momentum quantum number Λ, the spin quantum number S, which remains a good quantum number, the quantum number Σ (S, S-1, ..., -S), and the projection of the total angular momentum quantum number onto the molecular symmetry axis Ω, which can be derived as $\Omega=\Lambda+\Sigma$. The term symbol for the electronic states can be represented as ${}^{2S+1}\Lambda^{(+/-)}_{\Omega,(g/u)}$.

Illustration of the possibility of electronic transitions via group theory.

1. The total spin cannot change, $\Delta S=0$; the rule $\Delta\Sigma=0$ holds for multiplets;

> If the spin-orbit coupling is not large, the electronic spin wavefunction can be separated from the electronic wavefunctions. Since the electron spin is a magnetic effect, electronic dipole transitions will not alter the electron spin. As a result, the spin multiplicity should not change during the electronic dipole transition.

2. The total orbital angular momentum change should be $\Delta\Lambda=0, \pm1$;

3. Parity conditions are related to the symmetry of the molecular wavefunction reflecting against its symmetry axis. For homonuclear molecules, the g $\leftrightarrow$ u transition is allowed. For heteronuclear molecules, + $\leftrightarrow$+ and - $\leftrightarrow$ - transitions apply;

> For hetero diatomic molecules with $C_{\infty v}$ symmetry, we can use group theory to reveal that $\Sigma^+ \leftrightarrow \Sigma^+$and $\Sigma^- \leftrightarrow \Sigma^-$transitions are allowed, while $\Sigma^+ \leftrightarrow \Sigma^-$ transitions are forbidden. Similarly, for a molecule with an inversion center, a subscript g or u is used to reveal the molecular symmetry with respect to the inversion operation, i.

Vibrational Selection rules

1. Transitions with $\Delta v=\pm1, \pm2$, ... are all allowed for an harmonic potential, but the intensity of the peaks become weaker as Δv increases.
2. v=0 to v=1 transition is normally called the fundamental vibration, while those with larger Δv are called overtones.
3. $\Delta v=0$ transition is allowed between the lower and upper electronic states with energy E_1 and E_2 are involved, i.e. (E_1, v"=n) $\rightarrow$ (E_2, v'=n), where the double prime and prime indicate the lower and upper quantum state.

The geometry of vibrational wavefunctions plays an important role in vibrational selection rules. For diatomic molecules, the vibrational wavefunction is symmetric with respect to all the electronic states. Therefore, the Franck-Condon integral is always totally symmetric for diatomic molecules. The vibrational selection rule does not exist for diatomic molecules.

For polyatomic molecules, the nonlinear molecules possess 3N-6 normal vibrational modes, while linear molecules possess 3N-5 vibrational modes. Based on the harmonic oscillator model, the product of 3N-6 normal mode wavefunctions contribute to the total vibrational wavefunction, i.e.

$$\psi_{vib} = \prod_{3N-6} \psi_1 \psi_2 \psi_3 ... \psi_{3N-6}$$

where each normal mode is represented by the wavefunction ψ_i. Comparing to the Franck-Condon factor for diatomic molecules with single vibrational overlap integral, a product of 3N-6 (3N-5 for linear molecules) overlap integrals needs to be evaluated. Based on the symmetry of each normal vibrational mode, polyatomic vibrational wavefunctions can be totally symmetric or non-totally symmetric. If a normal mode is totally symmetric, the vibrational wavefunction is totally symmetric with respect to all the vibrational quantum number v. If a normal mode is non-totally symmetric, the vibrational wavefunction alternates between symmetric and non-symmetric wavefunctions as v alternates between even and odd number.

If a particular normal mode in both the upper and lower electronic state is totally symmetric, the vibrational wavefunction for the upper and lower electronic state will be symmetric, resulting in the totally symmetric integrand in the Franck-Condon integral. If the vibrational wavefunction of either the lower or upper electronic state is non-totally symmetric, the Franck-Condon integrand will be non-totally symmetric.

We will use CO_2 as an example to specify the vibrational selection rule. CO_2 has four vibrational modes as a linear molecule. The vibrational normal modes are illustrated in the figure below:

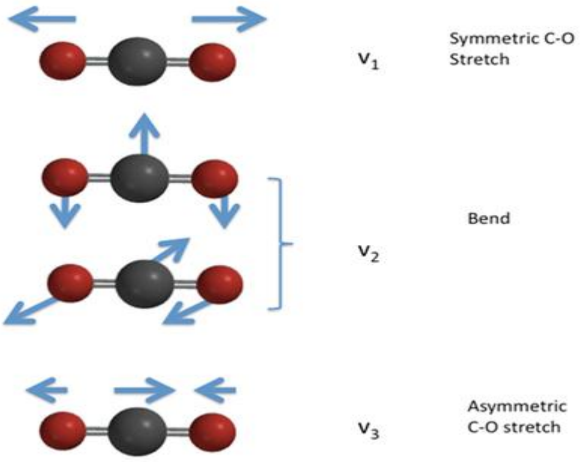


Fig. 1 Vibrational modes of CO_2

The vibrational wavefunction for the totally symmetric C-O stretch, v_1, is totally symmetric with respect to all the vibrational quantum numbers. However, the vibrational wavefunctions for the doubly degenerate bending modes, v_2, and the antisymmetric C-O stretch, v_3, are non-totally symmetric. Therefore, the vibrational wavefunctions are totally symmetric for even vibrational quantum numbers (v=0, 2, 4...), while the wavefunctions remain non-totally symmetric for v odd (v=1, 3, 5...).

Therefore, any value of Δv_1 is possible between the upper and lower electronic state for mode v_1. On the other hand, modes v_2 and v_3 include non-totally symmetric vibrational wavefunctions, so the vibrational quantum number can only change evenly, such as $\Delta v = \pm 2, \pm 4$, etc..

$$T_{2u} \times \{T_{1g} \times \ T_{1u} \times \ A_{1g}\} = T_{2u} \times \{A_{1u} + E_u + T_{1u} + T_{2u}\} = A_{1g} + \ldots$$

Since the t_{1u} and t_{2u} representation can generate the totally symmetric representation in the integrand. Therefore, we can see that t_{1u} and t_{2u} can couple with the electronic transition to form the allowed vibronic transition. Therefore, the d-d transition band for $Fe(OH_2)_6^{2+}$ complex can be observed through vibronic coupling.

Rotational Selection rules

1. Transitions with $\Delta J=\pm 1$ are allowed;

Photons do not have any mass, but they have angular momentum. The conservation of angular momentum is the fundamental criteria for spectroscopic transitions. As a result, the total angular momentum has to be conserved after a molecule absorbs or emits a photon. The rotational selection rule relies on the fact that photon has one unit of quantized angular momentum. During the photon emission and absorption process, the angular moment J cannot change by more than one unit.

Let's consider a single photon transition process for a diatomic molecule. The rotational selection rule requires that transitions with $\Delta J=\pm 1$ are allowed. Transitions with $\Delta J=1$ are defined as R branch transitions, while those with $\Delta J=-1$ are defined as P branch transitions. Rotational transitions are conventional labeled as P or R with the rotational quantum number J of the lower electronic state in the parentheses. For example, R(2) specifies the rotational transition from J=2 in the lower electronic state to J=3 in the upper electronic state.

2. $\Delta J=0$ transitions are allowed when two different electronic or vibrational states are involved: (X'', J''=m) $\longrightarrow$ (X', J'=m).

The Q branch transitions will only take place when there is a net orbital angular momentum in one of the electronic states. Therefore, Q branch does not exist for $^1\Sigma \leftrightarrow {}^1\Sigma$ electronic transitions because Σ electronic state does not possess any net orbital angular momentum. On the other hand, the Q branch will exist if one of the electronic states has angular momentum. In this situation, the angular momentum of the photon will cancel out with the angular momentum of the electronic state, so the transition will take place without any change in the rotational state.

The schematic of P, Q, and R branch transitions are shown below:

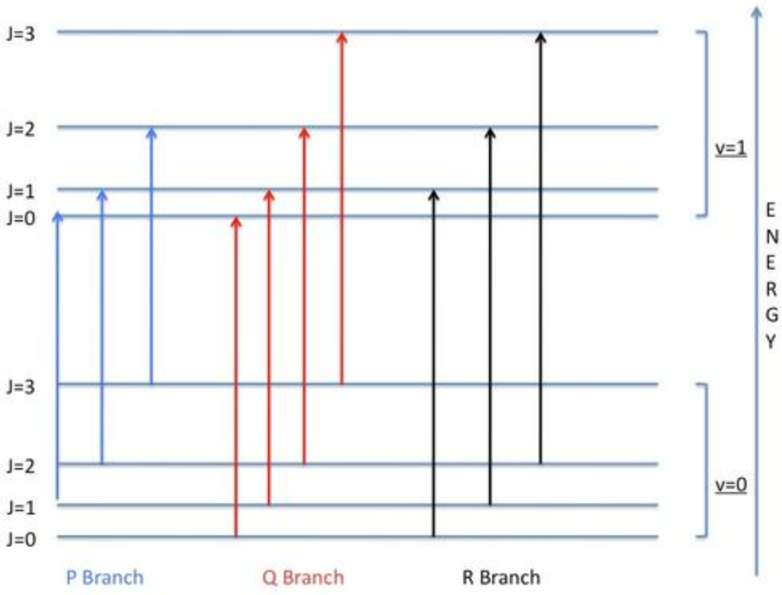


Fig. 6 Schematic diagram of P, Q, and R branch transitions

With regard to closed-shell non-linear polyatomic molecules, the selection rules are more complicated than diatomic case. The rotational quantum number J remains a good quantum number as the total angular momentum if we don't consider the nuclear spin. Under the effect of single photon transition, the change of J is still limited to a maximum of ± 1 based on the conservation of angular momentum. However, the possibility of Q branch is greatly enhanced irrelevant to the symmetry of the lower and upper electronic states. The rotational quantum number K is introduced along the inertial axis. For polyatomic molecules with symmetric top geometry, the transition moment is polarized along inertial axis. The selection rule becomes $\Delta K=0$.

1.3.17- INTENSITY OF SPECTRAL LINES

Because the intensity of a line is proportional to the number of photons emitted or absorbed by the atoms, the intensity of a particular line depends in part on the *number* of atoms giving rise to the line. The more atoms present to emit or absorb the photons corresponding to a given line, the stronger (brighter or darker, depending on whether it is seen in emission or absorption) that line is.

But intensity also depends on the *temperature* of the atoms—that is, the temperature of the entire gas of which the atoms are members—because temperature determines what fraction of the atoms at any instant are in the right orbital to undergo any particular transition. Consider the absorption of radiation by hydrogen atoms in an interstellar gas cloud or in the outer atmosphere of a star. If all the hydrogen were in its ground state—as it would be if the temperature were relatively low—the only transitions that could occur would be the Lyman series resulting in absorption lines in the ultraviolet portion of the spectrum. Thus, astronomers would observe no visible hydrogen absorption lines (for example, the Balmer series) in the spectrum of this object, not because there was no hydrogen, but because there would be no hydrogen atoms in the first excited state .

As the temperature rises, atoms move faster and faster. More and more energy becomes available in the form of collisions, and more and more electrons are boosted into an excited state. At any instant, then, some atoms are temporarily in an excited state and so are capable of absorbing at visible or longer wavelengths. As the number of atoms in the first excited state increases, lines in the Balmer series become more and more evident in the spectrum. Eventually, a temperature is reached at which *most* of the atoms are in the first excited state, simply because of their frequent, energetic collisions with other atoms in the gas. At this point the Balmer lines are at their strongest (and the Lyman lines are much weaker).

At even higher temperatures, most atoms are kicked beyond the first excited state into higher-energy orbital , and new series of absorption lines are seen, while the strength of the Balmer series declines again. Eventually, the temperature becomes so high that most hydrogen is *ionized*, and no spectral lines are seen at all.

Once an object's spectrum is measured, astronomers can interpret it by matching the observed intensities of the spectral lines with those predicted by the formulas. In this way, astronomers can refine their measurements of both the composition and the temperature of the gas producing the lines.

1.3.18 - Born–Oppenheimer (BO) approximation

In quantum chemistry, the computation of the energy and wavefunction of an average-size molecule is a formidable task that is alleviated by the **Born–Oppenheimer** (**BO**) **approximation**, named after Max Born and J. Robert Oppenheimer.

The BO approximation makes it possible to compute the wavefunction in two less complicated consecutive steps. This approximation was proposed in 1927, in the early period of quantum mechanics, by Born and Oppenheimer.

In basic terms, it allows the wavefunction of a molecule to be broken into its electronic and nuclear (vibrational, rotational) components.

$$\Psi_{\mathbf{total}} = \psi_{\mathbf{electronic}} \times \psi_{\mathbf{nuclear}}$$

In the first step of the BO approximation the *electronic* Schrödinger equation is solved, yielding the **wavefunction** $\boldsymbol{\psi_{\text{electronic}}}$ depending on electrons only.

The electronic energies, constituting the nuclear potential, consist of kinetic energies, interelectronic repulsions and electron–nuclear attractions. The BO approximation follows from the inertia of electrons being considered to be negligible in comparison to the atom to which they are bound.

Quantum concept - According to the Born-Oppenheimer approximation, the fast electronic motion can be separated from the much slower motion of the nuclei. As a result, the total wavefunction can be separated into electronic, vibrational, and rotational parts:

$$\Psi(r, R) = \psi_e(r, R_e)\psi_v(R)\psi_r(R)$$

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

According to born oppenheimer approximation transition energy is not quantised so total energy $E= E_r+ E_v+E_e$

The Born-Oppenheimer approximation assumes that the electronic wavefunction, ψ_e, is approximated in all electronic coordinates at the equilibrium nuclear coordinates (R_e). Since mass of electrons is much smaller than nuclear mass, the rotational wavefunction, ψ_r, only depends on nuclear coordinates. The rotational wavefunction could provide important information for rotational selection rules, but we will not consider the rotational wavefuntion any further for simplicity because most of the spectra are not rotationally resolved. With the rotational part removed, the transition moment integral can be expressed as

$$M = \iint \psi_e'(r, R_e) \cdot \psi_v'(R)(\mu_e + \mu_n)\psi_e''(r, R_e) \cdot \psi_v''(R) dr dR$$

where the prime and double prime represent the upper and lower states respectively. Both the nuclear and electronic parts contribute to the dipole moment operator. The above equation can be integrated by two parts, with μ_n and $\mu_e$respectively.

CHECK YOUR PROGRESS : 7

Notes : i) Write your answer in the space given below.

ii) Compare your answer with those given at the end of the unit.

Q .1 In an emission line, its brightness is greatest at the ……….and tapers off toward …………. .

Q .2 define transition probability ?

Q .3 A transition will proceed more rapidly if the coupling between the initial and final states is …………. (weaker/ stronger).

Q .4 transitions with larger Δv are called …………. .

Q .5 For polyatomic molecules, the nonlinear molecules possess normal---------- vibrational modes, while linear molecules possess------------ vibrational modes.(3N-5 , 3N-6)

1.3.19 – Let us sum up

Group Theory is a mathematical method by which aspects of molecular symmetry can be determined. The symmetry of a molecule reveals information about its properties like structure, spectra, polarity, chirality, etc…. **It** tells us about the allowed & forbidden transitions.

It tells us about the interaction of EMR with matter like polarization, dispersion, reflection , refraction etc. It tells us about the transition probability & transition moment.

1.3.20 - CHECK YOUR PROGRESS : KEYS

Key 1 1)Identity 2. $PtCl_4$ 3.Benzene 4.Point group

Key -2 - 1.)Rotation Reflection axis 2) subgroup. 3). group order

Key -3 – 1) Schoenflies notation 2) icosahedrons 3 irreducible representation 4) 1, 4
5) Classes 6) Abelian 7)Benzene (C_6 ,$6C_2$) 8) **Irreducible representation** 9) Benzene (D_6h)

KEY- 4 - 1) $\sum_G [\Gamma i(G)mn]\ [\Gamma j(G)m'\,n'\,]{*}=(h/\sqrt{lilj})\ \delta ij\delta mm'\ \delta nn'$

2) Character of matrix.

3) It defines the properties of irreducible representation. By considering the three classes , 5 corollaries can be derived & these gives the 5 rules about the irreducible representation of a group & their character.

Key – 5 1) (a) Perpendicular (b) energy propagation
2) (a) refraction (b) Snell’s law
3) photons 4) Energy per quantum

KEY -6 1) wave 2) no 3) less 4) dispersion 5) Property of certain types of waves that describes the orientation of their oscillations. 6)colloidal

Key 7- 1) (a) Center (b) either side
2) The transition probability is defined as the probability of particular spectroscopic transition to take place. 3) stronger 4) overtones 5) 3N-6 , 3N-5

1.3.21 - REFERENCES:

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Unit- 2.0 MICROWAVE AND VIBRATIONAL SPECTROSCOPY

Structure

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2.1- Objective
2.2- Microwave spectroscopy
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    2.2,2 – Rigid rotor model
    2.2,3 – Effect of isotopic substitution on the transition frequency
    2.2,4 – Non-rigid rotor
    2.2,5 – Stark effect
    2.2,6 - Nuclear and electron spin interaction
    2.2,7 - Application
2.3- Infrared Spectroscopy
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2.4- RAMAN SPECTROSCOPY
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2.6 - Check your Progress- The Key
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2.0- Introduction

Spectroscopy is the use of the absorption, emission, or scattering of electromagnetic radiation by matter to qualitatively or quantitatively study the matter or to study physical processes. The matter can be atoms, molecules, atomic or molecular ions, or solids. The interaction of radiation with matter can cause redirection of the radiation and/or transitions between the energy levels of the atoms or molecules.

In spectroscopy , we study the interaction of electromagnetic radiation with matter. When different types of electromagnetic radiations interact with matter, they also give different types of spectroscopy. For most electromagnetic radiation, wavelengths are too small to be conveniently expressed in meters and so they are usually expressed in **nanometers (nm), where**

The energy of a molecule has a number of separate components, each of which is quantized (each species has discrete molecule or atomic energy levels). Since absorption and emission are quantized, relationships between energy, frequency and wavelength can be established. We know,

$$E = hv$$

Where E is the energy of the photon emitted or absorbed in ergs. h is planck's constant = and v is the frequency in Hz. Frequency (V) is related to wavelength as

$$X\ v(Hz) = \lambda$$

Thus $E = hc/\lambda$

Frequency is directly proportional to energy but as energy increases the wave length decreases.

Atom, molecules or ions have limited number of discrete, quantized energy level. For absorption to occur, the energy of the exciting photon must match the energy difference between the ground state and one of the excited state of the absorbing species. These energy differences are different for different species. Hence frequency of absorbed radiation provides a means of characterizing the constituent of a sample of matter.

When a molecule emits or absorbs a photon, its energy is decreased or increased and one or more of the vibrational or rotational quantum number changes. Some important possibilities are

a)Rotational spectra- It arises when rotational quantum number changes and occur in microwave region.

b) Vibrational – rotational spectra- It arises when the vibrational quantum number changes possibly with a simultaneous change in the rotational quantum number. These spectra are found in near infra red region. In infrared region, the absorption of radiation by an organic compound cause molecular vibrations and so it is also known as vibrational spectroscopy. Infrared measurements permit the evaluation of the force constants for various types of chemical bonds. The wavelength of infrared absorption bands is characteristic of specific types of chemical bonds, and finds its greatest utility for identification of organic and organometallic molecules. The high selectivity of the method makes the estimation of an analyte in a complex matrix possible.

c) Raman spectra- These are concerned with change in the vibrational and rotational quantum number. Raman spectroscopy is the measurement of the wavelength and intensity of inelastically scattered light from molecules.

2.1- Objective

The main objective of this unit is to study the structure of molecules. After going through this unit you should be able to-

- Describe different types of spectra.
- Identify microwave active / inactive molecules
- Calculate force constant, bond length, moment of inertia etc. of microwave active molecules.
- Analyse IR spectra and identify the compound.
- Explain Raman effect.

2.2- MICROWAVE SPECTROSCOPY

Microwave spectroscopy deals with the part of electromagnetic spectrum which extends from 100 μm ($3x10^{13}$ Hz) to 1 cm. ($3x10^{10}$ Hz). This region of electromagnetic spectrum is known as microwave region which lies between far infrared and radiofrequency region. In most of the cases, absorption of microwave energy represent changes in rotational level of absorbing molecule therefore it deals with the rotational motion of molecule and is also known as rotational spectroscopy.

Condition –

Microwave spectra are shown by those molecules which possess permanent dipole moment. When a molecule having dipole moment rotates, it generates an electric field which can interact with the electric component of the microwave radiation. During this interaction energy can be absorbed or emitted and thus the rotation of the molecule gives like to a spectrum. Example - CH_3Cl, HCl, HBr, etc.They are also called microwave active. Homonuclear diatomic molecule such as H_2,N_2,O_2,Cl_2 etc. and linear polyatomic molecule such as CO_2, do not show microwave spectra because they do not possess permanent dipole moment. Such molecule are said to be microwave inactive.

2.2,1 - Classification of molecules:-

Microwave spectroscopy is mainly concerned with study of rotating molecules to understand rotational motion of a molecules, each molecule may be assigned three principal moment of inertia $I_{A.}$ $I_{B,}$ $I_{C.}$ According to the relative value of three principal moment of inertia molecules may be classified into following groups-

- Linear molecules.
- Symmetric top molecules
- Spherical top molecules
- Asymmetric top molecules
- **Linear molecules**:- In these molecules all the atoms are arranged in straight line eg.- HCN, HCl, OCS, $C_2H_{2,}$ CO_2 etc.

  H-Cl O=C=S O=C=0 $HC\equiv CH$

  In these molecules the rotation about the molecules axis will involve much lower moment of inertia, hence I_A is very small or zero.

  I_A=O and $I_B=I_C$

- **Symmetric top molecules**: - In these molecules two moment of inertia are equal and the third being different from these two.

  $I_B= I_c = I_A$ and I_A= O

  Example includes methyl halide (CH_3X), benzene, cyclobutane etc. In methyl halide, three hydrogen atoms are tetrahedrally bonded to the carbon, the end over end rotation in and out of the plane of the paper are identical ($I_B = I_C$). The moment of inertia about the C-X bond axis is not negligible because it involves the rotation of three of comparatively massive hydrogen atoms off this axis. Such a molecule spinning about this axis can be regarded as a Top.

  Molecules that have moment of inertia I_A less than $I_B = I_C$ are called prolate molecules. Example- CH_3CN. For these molecules $I_B = I_C > I_A$.

Molecules that have moment of inertia I_A greater than $I_B = I_C$ are said to be Oblate molecules eg. Benzene, BCl_3 etc. For these molecules $I_B = I_C < I_A$

- **Spherical top molecules**: - When a molecule has all the three moment of inertia identical, are called symmetric top molecules. eg. CH_4, SF_6 etc.

$$I_A = I_B = I_C$$

Spherical top molecules do not possess a permanent dipole moment hence do not give rotational spectra and are microwave inactive.

- **Asymmetric top molecules: -** These molecules have all the three moment of inertia different. eg. H_2O, vinyl chloride etc. $I_A \neq I_B \neq I_C$

CHECK YOUR PROGRESS: 1

Notes: 1) Write your answer in the space given below.
ii) Compare your answer with those given at the end of the unit.

Q.1) Which of the following molecules are microwave actives?

- HCl
- NO
- CO
- C_2H_4
- H_2
- Cl_2
- HBr

2.2,2 - Rigid rotor – A suitable model is dumb bell which consist of two balls of masses m_1 & m_2 representing two atoms connected by a rigid rod of length r that represent the chemical bond between the atoms. This is known as rigid rotor model. Consider the rotation of this rigid rotor about an axis perpendicular to the own axis passing through centre of gravity.

G

r_2

m_1 m_2

r_1

r

$r = r_1 + r_2$

r_1 & r_2 are the distance of atom A & B from centre of gravity G of the molecule AB. In this case moment of inertia is defined by

$I = m_1r_1^2 + m_2r_2^2$ --------------------------(1)

As the system is balanced about its centre of gravity G one may write –

$m_1r_1 = m_2r_2$ -- (2)

$r = r_1+r_2 = r_1$

And $r_1 =$

Similarly

$r_2 =$

on substituting these expression for r_1 & r_2 in eq. (1) & simplify we obtain

$I = {}^2$

= = = --------------(3)

Where is the reduced mass of the diatomic molecule and its value is

Eq.(3)defines moment of inertia in terms of atomic mass and bond length.

Rotating molecules having a permanent dipole or magnetic moment generate an electric field which can interact with the electric component of the microwave region. If it is assumed that a diatomic molecule behaves like a rigid rotator the rotational energy levels may in principal be calculated by solving the Schrödinger's equation for the system represented by that molecule.

Joules where J = 0,1,2 -------------------(4)

Where h = plank's constant ,I = moment of Inertia

J = Rotational Quantum Number, it takes integral values from 0 upwards & the square of the rotational angular momentum.

In rotational region, spectra are generally expressed in terms of wave number. So it becomes useful to consider energies in these units. Thus one may write

= -------------------- (5)

Where c is the velocity of light expressed in cm. per second . it is common to write B for so that eq. 5 becomes

------------------------------------(6)

Where B is called the rotational constant & may be expressed in cm per sec. or

-- (7)

From eq. (6) we can show the allowed energy level diagrammatically as in Fig.2, when J = 0 eq.(6) becomes

--------------------(8)

From eq.(8) it is evident that the molecule is not rotating at all. When J = 1 eq, (6) becomes

----------------(9)

J

5-------------------------30B

4-------------------------20B

3-------------------------12B

2----------------------------- 6B

1------------------------------ 2B

0----------------------------- 0

Fig-2 The allowed rotational energy level of a rigid diatomic molecule.

From eq. (9) it follows that a rotating molecule has its lowest angular momentum. Similarly one can calculate the value of for J= 1,2,3,….

Frequency of Rotational spectral lines- Consider there is a transition from rotational level of rotational quantum number J to the higher quantum number J', the energy difference between these two level will be given by-

----------------------------(10)

This energy is evolved when the molecule returns to the original rotational level of quantum number J from the excited rotational level of J'. According to quantum theory the energy evolved is then given out in the form of spectral lines. The frequency of these spectral lines expressed in wave number is given by-

-----------------------------(11)

When J= 1 , J' = 0 eq. ,11 becomes as

= 2B --------------------(12)

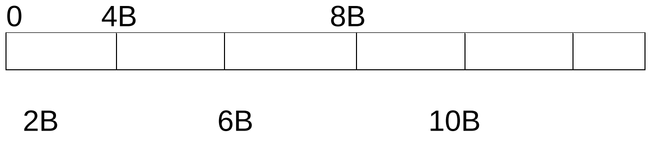
From eq. (12) it follows that an absorption line will appear at 2B . If the molecule is raised from J' = 1 to J = 2 level by the absorption of more energy in the microwave region eq. 11 becomes as

= B(6-2) = 4B

It means that absorption line will appear at 4B . In general when the molecule is

2B (J + 1)---------------------------------(13)

From eq. (13) it is clear that stepwise raising of the rotational energy gives rise to an absorption spectrum which consist of lines at 2B, 4B, 6B--- where a similar lowering would give rise to a similar identical emission spectrum.



6-----------------------------30B

5-----------------------------20B

4-------------------------------12B

3----------------------------6B
2----------------------------4B
1----------------------------2B

0------------------------------

Fig. 2.3 Allowed energy levels of a rigid diatomic rotor showing electric dipole transitions

Selection Rule for rotational spectra –

For a molecule to give rotational spectra it becomes essential that the molecule must have a dipole moment but all transition are not permitted there is a selection rule which is given as –

From the above rule it is evident that only those transition are permitted in which there is an increase or decrease by unity. In the rotational quantum number J =0 to J = 2 or J = 4 transition is not possible .

Validity of the theory –

This can be confirmed by considering following example-

CO molecule – Apply eq. (13) to microwave spectrum of the molecule. To calculate its moment of inertia & hence the bond length, the first line corresponding to J = 1 appear is the rotational spectrum of CO at 3.84235 ,

------------------(14)

From eq. 13

but J = 0

--------------(15)

2B = 3.84235 or B = --------------(16)

Also from eq. 7-

B = or I =

B =

In order to calculate the bond length one has to find out the value of reduced mass of CO molecule which is given by

=

m1 = 12.0000(C) & m2 = 15.9949g.(0)

=

from eq. (3) I =r^2

on substituting equation

From rotation absorption the calculated value of 2B for CO is found to be at 3.84235. This value for comes out to be 3.67337 and is designed as 2B' these data help us to calculate the exact mass of C- 13 isotope.

HCl molecule – from the microwave of HCl it is observed that the frequency difference to be & it is identified with 2B ie.

2B = 20.7 or B = 10.35

But , IHCl =

Reduced mass of HCl , molecule is given by

=

=

But , the bond length of HCl ie . r HCl is given by or

rHCl
The separation between energy level J = 0 & J = 1 will be given by

where 2B=20.7cm-1
= 0.405erg.

2.2,3 - Effect of Isotopic substitution on Transition frequencies -

Molecules having different isotopes of the same element show different spectra because the masses of the atoms are different and hence reduced mass as well as frequencies of vibration and rotation would be different.
The vibrational frequency of lighter species will be somewhat larger than that of heavies one. If we assume the harmonic vibrations for each species, the rotational constant (B) would also change because moment of inertia (I) would be different. As a consequence two species would give two superimposed band with their origins slightly shifted from one another and the lines in fine structure would appear as doublet. For example, there is a decrease in rotational constant and value in case of carbon monoxide, if we pass from $^{12}C\ ^{16}O$ to $^{13}C\ ^{16}O$, because of increase in mass. The rotational constant B' for ^{12}C is greater than the rotational constant B' for ^{13}C in CO (B>B'). Generally the spectrum of heavier species will show a smaller separation between the lines (2B') than that of evaluating the precise atomic weight for eg., the first rotational spectrum of $^{12}C\ ^{16}O$ and $^{13}C\ ^{16}O$ have been found to be at 3.84235 cm^{-1} and 3.67337 cm^{-1} respectively , the value of B and B' are found 1.92118cm^{-1} and 1.83669cm^{-1} respectively thus

= …………..(17)

Here μ and μ' are reduced masses of ^{12}C & ^{13}C atoms.
It is assumed that antinuclear distance remains unchanged by isotopic substitution. Taking mass of oxygen as 15.9994 and that of carbon -12 as 12.00, atomic weight of c-13 has been found to be 13.0007, which is in good agreement with the values obtained by the other methods.
Microwave spectra of molecules with isotopic substitution is useful in determining bond length in molecules.

2.2,4 - Non Rigid Rotor –

All bonds are elastic to some extent. The elasticity results in some changes which are as follows –
An elastic bond may have vibrational energy.
Another consequence of elasticity is that the quantities r & B vary during vibration.
When the spectrum of a non-rigid rotator is considered we must take into account the above two facts. For a non-rigid rotator schrodiagers wave eq. --------the following rotational terms –
Joules
Or Ej =(18)
Where B is rotational constant B = D is the centrifugal distortion constant & it's value is given by –
D =
In above eq. K is a force constant & is defined as the restoring force to bring the molecule to it's original position. The value of K is given by
K = ……………………(19)
Where is the vibrational fuquency expressed in .
From the value of B & D it may be shown that
D = -------------------------(20)

It is generally found that vibrational frequencies are of the order of and B has been found to be of the order of 10 it means that the value of D, according to eq. (20) is of the order 10^{-3} cm^{-1}which is very small compared to B. The selection rule for the non-rigid molecule is still .

2.2,5 - Stark effect

When the rotational spectrum is recorded in the presence of a strong electric field the line will generally split and get shifted. This is known as stark effect. This effect was first observed by stark in atomic spectra.

A molecule capable of exhibiting rotational spectrum also posses an electric dipole moment. If we consider a rotating linear molecule with angular momentum perpendicular to the electric field, the field tends to twist the dipole & gives it a faster rotation when the dipole is oriented in the direction of the field but a slower rate of rotation when it is opposite to the field. This minute difference between the dipoles pointing in the two directions causes the splitting of the energy levels. It the dipole moment has a component along the angular momentum J , a first order stark effect is observed and if one dipole moment is perpendicular to the angular momentum , J, a second order stark effect is observed.

In first order stark effect the splitting of the rotational level is directly proportional to the electric field E. symmetric top molecular exhibit first order Stark effect.

In second order stark effect, the splitting of the rotational level by an electric field E is proportional to E^2. This effect is exhibited by linear molecules.

The stark effect split the degeneracy of the J level into (2J+1) levels and thus multiplet structures has been observed for all the lines with J>0. Thus Stark effect is useful in the assignment of the observed rotational lines to particular J values. The Stark effect also one of the most accurate method for determining the dipole moment as can be measured on gas sample at very low pressure of the order of 10^{-13} torr and is not affected by solvent effect and molecular interaction etc.

2.2,6 - Nuclear and Electron Spin Interaction

In a molecule allowed rotational states are those for which the angular momentum is $\sqrt{J(J+2)}$ type multiple of $h/2\pi$. In addition to this molecular rotation angular momentum, some molecules also have angular momentum because of the nuclear spin of one or two of their nuclei, hence it is necessary to take into account both the molecular and nuclear spin angular momentum contribution to the total angular momentum for a complete characterization of rotational states of such molecules. The effect of nuclear spin has been observed in the hyperfine structure of rotational transition of some molecules.

The angular momentum of a nucleus results from the spinning of the nucleus is a characteristic of the nucleus. It is quantized in units of $h/2\pi$, and the spin angular momentum of a particular nucleus has one of the values.

$$\sqrt{I(I+1)}\, h/2\pi \text{ where } I= 0, \tfrac{1}{2},1,3/2,\text{---}$$

Here I represent the nuclear spin quantum number. If there is no coupling or interaction between the orientation of the nucleus and that of the molecule, the molecule will rotate and leave the spinning nuclei unchanged in orientation. The energy of a given molecular rotation state is represented by J, would be unaffected by the nuclear spin I.

But if there is interaction between the orientation of the nucleus and that of the molecule, the energy of the system will depend on the orientation of the nuclear spin relative to that of the molecular rotation. This dependence can be expressed by introducing a quantum number F for the total angular momentum of the system. The total angular momentum of the system is then given as

$$\sqrt{F(F+1)}\, h/2\pi$$

For a given value of J, various values of F, according to

$F=J+I,J+I-1,\ldots\ldots.J-I$

But the total angular momentum cannot be negative, and the J-I terms are not always realized for states with low J numbers.

The intensity of the rotational spectral lines can be determined by the population and degeneracy of the rotational level from which the transition takes place. According to Boltzman distribution law, the molecular population in each rotational level decreases exponentially with an increase in the value of J, but the number of degenerate levels available increases rapidly with increasing J values. The relative population at energy E_J is given by
Relative population = $(2J+1) \exp(-E_J/Kt)$

2.2,7- Applications-

- **Determination of molecular structure**: Microwave spectroscopy yields structures undistorted by intermolecular interactions in the crystalline state. Bond lengths can be measured upto 0.1 ppm(10^{-3}A°).
- **Determination of Bond angles and bond lengths**: a microwave spectrum can provide upto three moments of inertia,I for the molecule. Employing I's an dappropriate isotopic substitution, it is possible to calculate accurate bond angles and bond lengths.
- **The abundance of Isotopes:** since each molecule possesses a unique moment of inertia depending on particular isotopic nuclei present, so from the relative intensity of spectral lines, the abundance of these isotopes can be obtained. **Southern** et al., determined N^{15} in the range of 0.38 to 4.5% within $\pm$ 3% and C^{13} in the range of 1.1 to 10% within $\pm$ 2%.
- **Inversion Spectrum of ammonia:** it was the first molecule to be studied by m.sp by Bleaney and Townes. In the spectrum of NH_3 molecule each of the lines is split into a doublet due to inversion of the molecule.
- Microwave spectrum of xenon oxyfluoride is charachteristic of a symmetric top and consistent with C_{4v} symmetry of the molecule.
- Microwave spectroscopy can be useful in measuring the barrier heights of certain molecules like CH_3OH(C-O), CH_3OCH_3(C-O), $C_6H_5CH_3$(C-C) as 4.94,11.42 and 58.38 kj mol^{-1}.

CHECK YOUR PROGRESS – 2:

Notes: 1) Write your answer in the space given below.
ii) Compare your answer with those given at the end of the unit.

Q.) FILL IN THE BLANKS:

- J=O: J=2 transitions are spectroscopically-----------.
- Molecules having dipole moments are said to be Microwave-----------.
- The rotational energy levels are not quantized in ------------ phase.
- Microwave spectroscopy is also known as -------- spectroscopy.
- Spherical top molecule such as CH_4 or SF_6 is microwave -----------.
- Rotational energy are quantized in the gaseous state.

2.3 Infrared Spectroscopy

Vibrational spectra are given by diatomic molecule with permanent dipole moment and polyatomic molecule with and without permanent dipole moment. The molecular motion that is affected by the absorption of quanta of the infrared radiation is the vibrational motion. In a molecule in the gas phase, there will however be a simultaneous change in its rotational energy also.

Range of infrared radiation:

The infrared radiation lies between visible & microwave region. From instrumentation & applicant point of view this region has been subdivided as follow –

- Photographic region – this ranges from visible to 0.8µ.
- Near infrared region - 0.8µ to 2.5µ (12500 – 4000)
- Mid infrared region (vibration rotation region) - 2.5µ to 15µ (4000 - 667)
- Far infrared region (rotation region) – 15 to 200 µ (600 – 50)

Infrared spectra are usually plotted as percent transmittance rather than a absorbance as the ordinate. Thus absorption bands appear as a dips in the curve rather than a maxima. Each dip in the spectrum is called a band or peak, & represents absorption of infrared radiation at that frequency by the sample.

Condition for Infrared Radiation Absorption :

A molecule absorbs radiation only-

a) when the natural frequency of vibration of some part of a molecule is the same as the frequency of the incident radiation.

b) when its absorption cause a change in its dipole moment.

2.3,1 Simple Harmonic Oscillator & Vibrational energies of diatomic molecules:

The vibrating motion of the nuclei of a diatomic molecule can be represented to a first approximation as the vibration of a simple harmonic oscillator. Simple harmonic oscillator is regarded as the simplest modes for vibrating diatomic molecule.

An oscillator is one in which the restoring force is directly proportional to the displacement from the equilibrium position in accordance with Hooke's law. Consider the vibration of a mass attached to a spring that is hung from an immovable object. If the mass is displaced a distance x from its equilibrium position by applying a force along the axis of the spring, according to Hooke's law the restoring force F is proportional to displacement.

Thus

$$F = -kx \qquad \ldots\ldots(1)$$

Where F is the restoring Force and K is the Force Constant that depends upon the stiffness of the spring, i.e., it gives the restoring force for unit displacement from the equilibrium position. The negative sign indicates that F is restoring force. It means that as X increases in one direction the force increases, but is directed in the opposite direction.

Hooke's law implies that the potential energy of the particle increases parabolically as the particle moves in either direction from the equilibrium position (Fig-2.2). The potential energy of the mass and spring may be regarded as zero when the mass is in its rest or equilibrium position. The potential energy of the system increases by an amount equal to the work required to displace the mass, as the spring is compressed or stretched. If the mass is moved from, say, position x to (x+dx), the change in potential energy dE is equal to the force F times the distance dx. Thus,

$$dE = -F dx \qquad \ldots\ldots(2)$$

From equation (1) and (2), we have

$$dE = kx\,dx \qquad …….(3)$$

Integrating equation (3) between the equilibrium position (x = 0 and x), we get

E = ……(4)

The potential energy curve for a simple harmonic oscillator derived from equation (4) is shown in fig. It is clear from the figure that the potential energy is maximum when the spring is stretched or compressed to its maximum amplitude A and decreases parabolically to zero at the equilibrium position

According to Newton's law,

$$F = ma \qquad …….(5)$$

Where m is the mass and a its acceleration. The above equation expresses the motion of mass as a function of time t, but acceleration can be expressed as second derivative of distance w.r.t. time. Thus,

…..(6)

Putting these values in equation (1) we have

……(7)

of the solution of this equation is,

……(8)

Where A is the amplitude of the vibration, a constant, that is equal to maximum value of x. One complete cycle in a function involves a change of 2. Thus time needed to complete one cycle (the period of the motion) is given by a value of t such that the quantity in the parenthesis in equation (8) changes by 2 so,

……….(9)

The frequency of the vibration v is the reciprocal of its period. Thus

v_m … ……….(10)

v_m is the natural frequency of the mechanical oscillator. It depends upon the force constant of the spring and mass of the attached body. The natural frequency is independent of the energy imparted to the system. **Changes in energy merely cause a change in the amplitude A of the vibration.**

The equations can be readily modified to explain the behavior of a system made up of two masses m_1 and m^2 connected by a spring (as in a diatomic molecule). Here it is only necessary to substitute the **reduced mass** μ for the single mass m_1 where

$$\mu = \frac{m1m2}{m1+m2} \qquad \mu = \frac{m1m2}{m1+m2}$$

………………….. 11

Thus the vibrational frequency for such a system is given by,

$$v_m = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} = \frac{1}{2\pi}\sqrt{\frac{k\,(m1+m2)}{m1m2}} = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} = \frac{1}{2\pi}\sqrt{\frac{k\,(m1+m2)}{m1m2}}$$

……………………………………………12

Assuming the behavior of a molecular vibration analogous to the mechanical model just described, the frequency of the molecular vibration can be calculated from equation (12) where k becomes the force constant for the chemical bond containing two atoms of masses m_1 and m_2. The force constant is a measure of stiffness of chemical bond but not necessarily its strength.

It should be noted that quantized nature of molecular vibrational energies does not appear in the above equation. It is possible to use the concept of the simple harmonic oscillator for the development of the wave equation of quantum mechanics. Solution of these equation for potential energies are found when,

$$E = \left(v + \frac{1}{2}\right)\frac{h}{2\pi}\sqrt{\frac{k}{\mu}} \qquad E = \left(v + \frac{1}{2}\right)\frac{h}{2\pi}\sqrt{\frac{k}{\mu}}$$

………………….13

Where vv is the vibrational quantum number that can take only positive integer values, including zero. Thus quantum mechanics requires that only certain discrete energies are assumed by the vibrator. The term,

$$\frac{1}{2\pi}\sqrt{\frac{k\,1}{\mu 2\pi}}\sqrt{\frac{k}{\mu}}$$

appears in both mechanical as well as quantum mechanical treatment. From equation (12) and (13) we have,

$$E = \left(v + \frac{1}{2}\right)h \qquad E = \left(v + \frac{1}{2}\right)h_{V_m}$$

…………………….(14)

vv = vibrational quantum number

V_m = vibration frequency

To convert energy from Joule to wave number, divide it by hc.

$$\frac{Ev}{hc} = \varepsilon = \frac{Ev}{hc} = \varepsilon = \qquad V_v = \left(v + \frac{1}{2}\right)\omega = \left(v + \frac{1}{2}\right)\omega_e\ cm^{-1}\ cm^{-1}$$

…………(15)

Where $\omega\omega_e$ is the equilibrium vibrational frequency of oscillator. The expression gives the vibrational energy levels of a simple harmonic oscillator and applied successfully to express the vibrational energy level of a diatomic molecule.Above equation shows that such an oscillator retains the energy E_0=1/2 hv_0 in the lowest vibrational level v=0. This residual energy is called the **Zero point energy** of the oscillator and cannot be removed from the molecule even by cooling it to 0K.

Selection Rule for vibrational Transitions:

According to equation $\frac{Ev}{hc} = \varepsilon = \frac{Ev}{hc} = \varepsilon =$ $V_v = \left(v + \frac{1}{2}\right)\omega = \left(v + \frac{1}{2}\right)\omega_e\, cm^{-1}\, cm^{-1}$, vibrational quantum number $v\ v$ for a simple harmonic oscillator can have infinite number of values ranging from zero to infinity. But all these energy levels of diatomic molecule are not allowed. Permitted energy levels are given by selection rule between which transition can occur.

The application of Schrodinger wave equation leads to the simple selection rules for a harmonic oscillator undergoing vibrational changes as given by.

$$\Delta v = \pm 1 \qquad \Delta v = \pm 1$$

From the above selection rule it is evident that for a harmonic oscillator only those transitions are permitted in which vibrational quantum number or energy level changes by unity. It means transition can occur from given vibrational level to the next higher or next lower level only. +sign applies to absorption and –sign emission of radiation during vibrational transition. Vibration spectra are solely determined by absorption phenomenon, therefore the operative part of the selection rule for absorption spectra is $\Delta v = +1\ \Delta v = +1$. Selection rule $\Delta v = -1 \Delta v = -1$ is not used in vibrational transition.

Thus the vibration transition is only possible and restricted between the vibrational quantum number differing only by unity, i.e. , transition from v = 0 to v = 1 or v = 1 to v = 2 ….etc. , are only allowed and transition from v = 0 to v = 2 or v = 2 to v = 4 …etc., are not permitted. Hence each mode of vibration would give one band or one spectral line. Thus the vibrational energy change will only give rise to a spectrum if the vibration involves a change in the dipole moment of the molecule.

The energy difference between the two vibrational energy level can be written on

$$\Delta E_{vib} = hv$$

At ordinary temperature where molecules are in their lowest vibrational energy levels, the potential energy diagram approximate that of a harmonic oscillator. But at higher temperature deviation do occur.

Absorption of radiation with energy equal to the difference between two vibrational energy level (Δ E_{vib}) will cause a vibrational transition to occur. Transition from the ground state (v = 0) to the first exited state (v = 1) absorb light strongly & give rise to intense band called the **Fundamental bands**. The energy difference (Δ E_{vib}) between the lowest possible energy level of a bond & the next higher energy level (using selection rule) given as –

$$\Delta E_{vib} = E_{vib}(v = 1) - E_{vib}(v = 0)$$
$$= [1 + {}^{1}/_{2}]hv - [0 + {}^{1}/_{2}]hv = [1 + {}^{1}/_{2}]hv - [0 + {}^{1}/_{2}]hv$$
$$= {}^{3}/_{2}\,hv - {}^{1}/_{2}\,hv = hv = {}^{3}/_{2}\,hv - {}^{1}/_{2}\,hv = hv$$

…………………………(16)

Or

Because $\frac{Ev}{hc} = \bar{v}\frac{Ev}{hc} = \bar{v}_{v}$, the change in vibrational frequency in transition from v = v to v = v+1, is

$$\bar{v}\bar{v}_{v+1} - \bar{v} = \left(v + 1 + \frac{1}{2}\right)\omega\bar{v} = \left(v + 1 + \frac{1}{2}\right)\omega_{e} = \left(v + \frac{1}{2}\right)\omega = \left(v + \frac{1}{2}\right)\omega_{e}$$

$$\bar{v}\bar{v}_{(v+1)} \xrightarrow{} {}_{v} = \omega = \omega_{e}\, cm^{-1}\, cm^{-1} \qquad \ldots \quad \ldots\ldots\ldots\ldots\ldots\ldots(17)$$

Thus for a harmonic oscillator, the frequency of absorption between any two neighboring energy levels is equal or same to the frequency of oscillator ($\omega\omega_{e}$) or its own oscillating frequency. This is the requirement of IR spectrum.

Since the vibrational levels are equally spaced, transition between any two adjacent energy levels will give rise to the same energy change or frequency change. Hence each mode of vibration would give only one band or spectral line.

This gives the frequency of a **Fundamental band.** The word fundamental is used to specify that vibrational transition involved is only are step higher i.e. v - v' = 1 In actual practice. The nuclear vibrations are not harmonic and the change in the vibrational quantum number is rarely unity.

Transition from the ground state (v = 0) to the second exited state $(v = {}^{2}/_{3})(v = {}^{2}/_{3})$ with the absorption of infrared radiation give like to weak band called **overtones**. Thus the band corresponding to v = 0 &v' = 2 i.e. (v –v' = 2) are called first harmonics or overtones while those corresponding to v – v' = 3 are called second harmonic overtones. These band are fainter as compared to fundamental bands & appear in the region of shorter wave length. Assuming that all the vibrational bands are equally spaced, the energy of the first overtone is given by.

$$\Delta E_{vib} = E_{vib\,(v = 2)} - E_{vib\,(v = 0)}$$
$$= [2 + {}^{1}/_{2}]hv - [0 + {}^{1}/_{2}]hv = [2 + {}^{1}/_{2}]hv - [0 + {}^{1}/_{2}]hv$$
$$= 2hv = 2hv$$

2.3,2- Force constant & bond strength;

Atoms in a molecule which are joined by bands, are not at rest, but vibrate constantly. Consider a diatomic molecule AB. Atom A is joined to B by means of a bond. These atoms constantly vibrate with respect to their mean position behave like a harmonic oscillator and obey Hook's law.

For such a harmonic oscillator according to Hook's law, restoring force is directly proportional to the displacement.

$f \propto x$

Or $\qquad$ f = -kx

Where x is the displacement of one atom from its equilibrium position with respect to other.atom, f is the operating force on the atom. Negative sign shows that force is restoring force , K is a constant called **force constant**.

Since force constant is equal to the force per unit displacement ($f = {}^{k}/_{x} f = {}^{k}/_{x}$). It is the measure of the stiffness of the spring (bond) the value of K is given by

$$\omega = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}\omega = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$

Or $$k = 4\pi^2\omega^2\mu k = 4\pi^2\omega^2\mu \qquad \text{........(18)}$$

Where $\omega\omega$ is vibrational frequency

$$m_{\text{red}} = \frac{m_1 m_2}{m_1 + m_2} \equiv c \equiv c$$

$m_1 m_2$ are the masses of the oscillating atoms. The force constant for diatomic molecule can be obtained by using equation (18) provided the vibrational frequency is known. Its unit in CGS system is dyne/cm.

Force constant for polyatomic molecule cannot be determined directly. A method has been suggested by assuming that each valency bond has a certain definite value for the force constant which is characteristic of the band & independent of the molecule in which is occur.

Bond strength or bond energy is defined as the energy required to brake one mole (1 avogadro no.) of bonds of the substance under consideration in gaseous state. More energy of the bond indictes more stability & less reactivity.

force per unit displacement ($f = {}^{k}/_{x} f = {}^{k}/_{x}$) , it represent the resistance of the bond to stretching and every bond angle which measures resistance to deformation & stiffness of the bond between the atoms of the molecule.

A strong & rigid bond will have a large value of force constant. Force constant increases approximately in proportion to the multiplicity of the bond & so the former can be used to give an indication of the latter. For example the force constant for the carbon oxygen bond in CO_2 has been found to be $15.7 \times 10^5 15.7 \times 10^5$ dyne/cm. this value lie between c = 0 & c $\equiv 0 \equiv 0$ as shown in the table. This confirms the resonance struchture of CO_2, which is

$$\bar{o} - c \equiv o^+ \leftrightarrow o = c = o \leftrightarrow o^+ \equiv c - \bar{o}$$

<u>2.3,3- Anharmonicity:</u>

In harmonic vibration, the restoring force is directly proportional to the displacement x.The potential energy curve is parabolic and dissociation can never take place. But actual potential energy curves correspond to anharmonic vibration, and the restoring force is no longer directly proportional to the displacement.

The force is given by -$\partial v/\partial r \, \partial v/\partial r$, the slope of the potential energy curve and this decreases to zero at large values of r, so that dissociation can take place as a result of vibration of large amplitude. The anhamonicity term introduces an effect that decreases the spacing of the higher energy levels.

The anharmonic curves depart from harmonic behaviour to various degrees depending on the nature of the bond and the atoms involved. It should be noted that harmonic and anharmonic curves are almost alike at low potential energies.

In reference to potential energy curves, two heats of dissociation may be defined. The spectroscopic heat of dissociation D_e is the height from the asymptote to the minimum, and the chemical heat of dissociation, D_o, that is measured from the ground state of the molecule, at vv = 0, to the onset of dissociation. Thus,

$$D_e = D_o + \frac{1}{2} + \frac{1}{2} h v v_0$$

The energy levels corresponding to an anharmonic potential energy curve can be expressed as a power series in $\left(v + \frac{1}{2}\right)\left(v + \frac{1}{2}\right)$

$$E_v = h\nu\nu_o[\left(\nu+\frac{1}{2}\right)[\left(\nu+\frac{1}{2}\right) - x_e\left(\nu+\frac{1}{2}\right)\left(\nu+\frac{1}{2}\right)^2 + y_e\left(\nu+\frac{1}{2}\right)\left(\nu+\frac{1}{2}\right)^3 \text{-----}]$$

Considering the first anharmonic term, with anharmonicity constant x_e, we have

$$E_v = h\nu\nu_o\left(\nu+\frac{1}{2}\right)\left(\nu+\frac{1}{2}\right) - h\nu\nu x_e\left(\nu+\frac{1}{2}\right)\left(\nu+\frac{1}{2}\right)^2$$

The energy levels are not evenly spaced, but lie more closely together as the quantum number increases. Because a set of closely packed rotational levels is associated with each of these vibrational levels, it is sometimes possible to determine the energy level just before the onset of the continuum, and hence to calculate the heat of dissociation from the vibrational rotational spectra.

Anharmonicity leads to deviations of two kinds.

- At higher quantum numbers $\Delta E\ \Delta E$ becomes smaller, and
- The selection rules are not rigorously followed. As a result, transitions of $\Delta\nu = \pm 2 \Delta\nu = \pm 2$ or $\pm 3 \pm 3$ have been observed and these transitions are responsible for the appearance of overtones at frequencies approximately twice or three times that of the fundamental lines. The intensity of overtone absorption is often low and the peaks may not be observed.

2.3,4 - Morse potential energy diagram:

The **Morse potential**, named after physicist Philip M. Morse, is a convenient model for the potential energy of a diatomic molecule. The Morse Potential is an empirical potential that describes the stretching of a chemical bond. It is asymmetric indicating that it is harder to compress a bond than to pull it apart.

It is a better approximation for the vibrational structure of the molecule than the quantum harmonic oscillator because it explicitly includes the effects of bond breaking, such as the existence of unbound states. It also accounts for the anharmonicity of real bonds and the non-zero transition probability for overtone and combination bands. The Morse potential can also be used to model other interactions such as the interaction between an atom and a surface.

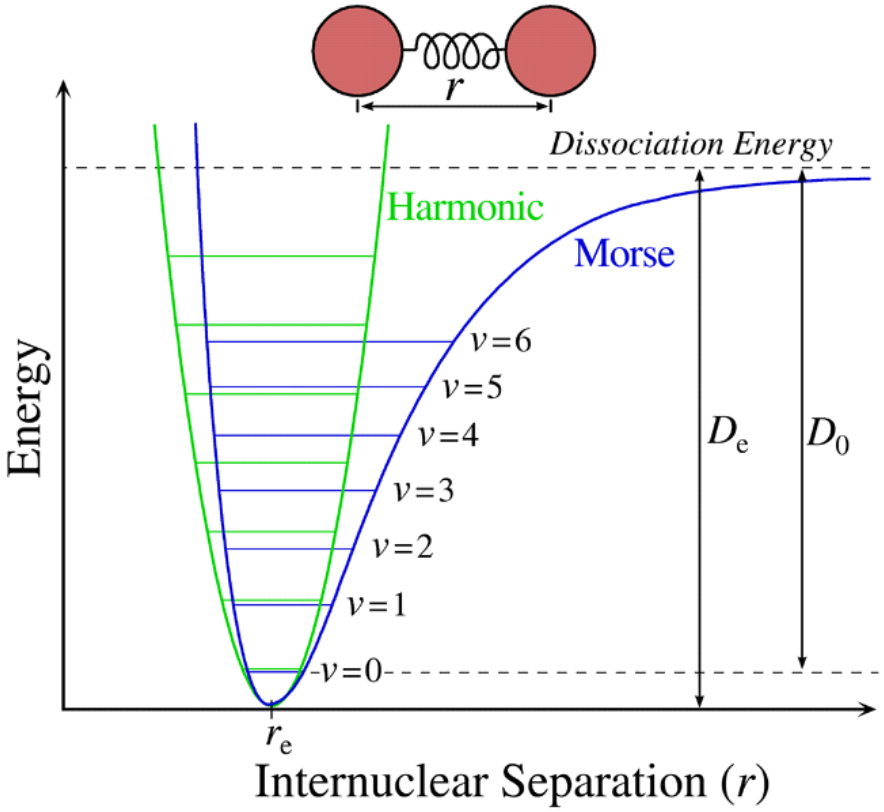


Fig: 2.2 The **Morse potential** and harmonic oscillator potential. Unlike the energy levels of the harmonic oscillator potential, which are evenly spaced by ħω, the Morse potential level spacing decreases as the energy approaches the dissociation energy. The dissociation energy D_e is larger than the true energy required for dissociation D_0 due to the zero point energy of the lowest ($v = 0$) vibrational level.

The Morse potential energy function is of the form

$$V(r) = D_e(1 - e^{-a(r-r_e)})^2$$

Here r is the distance between the atoms, r_e is the equilibrium bond distance, D_e is the well depth (defined relative to the dissociated atoms), and a controls the 'width' of the potential (the smaller a the larger the well). The dissociation energy of the bond can be calculated by subtracting the zero point energy $E(0)$ from the depth of the well. The force constant of the bond can be found by Taylor expansion of $V(r)$ around $r = r_e$ to the second derivative of the potential energy function, from which it can be shown that the parameter, a, is

$$a = \sqrt{k_e/2D_e},$$

where k_e is the force constant at the minimum of the well.

The zero of potential energy is arbitrary, and the equation for the Morse potential can be rewritten any number of ways by adding or subtracting a constant value. When it is used to model the atom-surface interaction, the Morse potential is usually written in the form

$$V(r) - D_e = D_e(e^{-2a(r-r_e)} - 2e^{-a(r-r_e)})$$

where *r* is now the coordinate perpendicular to the surface. This form approaches zero at infinite *r* and equals− D_e at its minimum. It clearly shows that the Morse potential is the combination of a short-range repulsion and a longer-range attractive tail.

In actual practice the molecule does not always vibrate as a simple harmonic oscillator and an anharmonicity may be present. The consequence of harmonicity is that the vibrational energy levels of simple harmonic oscillator are slightly lowered and the spacing between them is no longer constant and decreases steadily with increase in vibrational quantum number.

2.3,5 - P – Q – R Branches :

The vibrational rotational spectrum of a substance does not occur in the form of a single line, but a number of lines appear on either side of the expected position as shown in the fig.2.3 Since rotational transitions are also superimposed upon vibrational transition, the energy of rotation given by $EE_r = \frac{h^2}{8\pi^2 I} J = \frac{h^2}{8\pi^2 I} J$ must be added to or subtracted from the equation (17) Fundamental band due to one step change in vibrational transition, the second term, ie, $\pm\ h/8\pi^2 Ic \pm\ h/8\pi^2 Ic$ gives the rotational fine structure because of rotational transition. If J is positive, then a series of lines of higher frequency (shorter wave length) appear on the right side of the origin or band centre. These lines are known as **R – branch** of the vibration band. If J is negative, a series of lines corresponding to lower frequencies (longer wavelengths) appear on the left side of the band origin. These lines are known as **P – branch** of the vibration rotation band.

J may be close to zero, if the molecule has an angular momentum about the axis joining the nuclei. In this case vibrational transition is not accompanied by any significant rotational changes. This indicates that there must be some changes in rotational energy of these molecules. These changes give rise to a series of very closely spaced lines known as Q branch or Q band. This band is usually observed in polyatomic molecules.

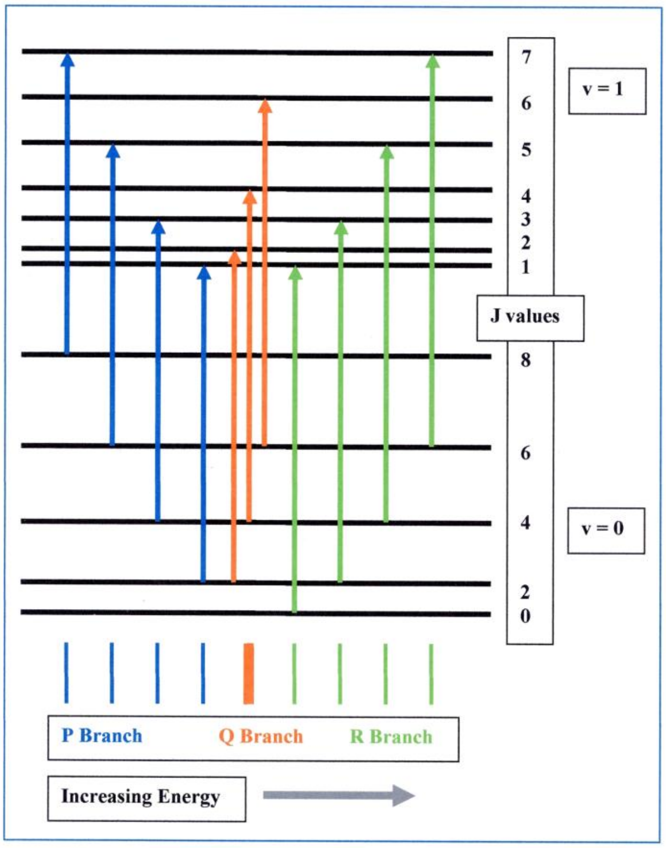


Fig. 2.3: PQR Branches

In general, a vibrational band may display three branches corresponding to three cases.

J' – J" = $\Delta J = +1 \Delta J = +1$ R - Branch

J' – J" = $\Delta J = -1 \Delta J = -1$ P - Branch

J' – J" = $\Delta J = 0 \Delta J = 0$ Q – Branch

2.3,6 - Vibrations Of Polyatomic Molecule:

In a polyatomic molecule each atom is having three degree of freedom in three directions which are at right angler to one another. Thus a polyatomic molecule of N atoms is said to have 3N degree of freedom.

3N degree of freedom = Transitional + Rotational + Vibrational

Rotational degree of freedom results from the rotation of a molecule about an axis through the centre of gravity.

Since only three co-ordinates are necessary to locate a molecule in space, so molecule has three translational degree of freedom. In case of linear molecule there are only two degree of rotation, it is due to the fact that the rotation of such a molecule about its axis of linearity does not bring about any change in the position of the atom while rotation about the other two axis change the position of the atoms.

Theoretically, there will be 3N-5 possible band for linear molecules. In case of non-linear molecule there are three degree of rotation, as the rotation about all the three axis (x,y,z) will result a change in the position of the atoms. Hence in non- linear molecules, there are (3N-6) fundamental bands.

Normal modes of vibration are generally of two types –

- **Stretching vibrations**: In this type of vibration, the atoms move along the bond axis, so that the bond length increases or decreases at regular intervals. But the atoms remain in the same bond axis. Such a mode of vibration does not cause any dipole change in the symmetrical molecules such as 0 = C= 0, and therefore it is **not IR active**.

Stretching vibrations are of two types:

a) Symmetric stretching: In this type of stretching with respect to a particular atom, other two atoms in a molecule move in the same direction. For example, in methylene group H-C-H, the two hydrogen atoms move away from the central carbon atom without change in the bond angle.

b) **Asymmetric stretching**: In this type of stretching one atom moves away from the central atom, while the other atom moves towards the central atom. For example, in methylene group one hydrogen atom approaches the carbon, while the other hydrogen atom moves away from the carbon atom.

(2) Bending or deforming vibrations: Such vibrations may consist of a change in bond angle between bonds with a common atom or the movement of a group of atoms with respect to the remainder of the molecule without movement of the atoms in the group with respect to one another. These are of four types:

Scissoring- In scissoring the two atoms joined to a center atom move towards and away from each other with deformation of the valency angle (in plane bending.)

Rocking: In rocking, the structural unit swings back and forth in the plane of the molecule (in plane bending.)

Wagging: In wagging, the structural unit swings back and forth out of the plane of the molecule (out of plane bending.)

Twisting: In twisting, the structural unit rotates about the bond which joins it to the remainder of the molecule (out of plane bending.)

In a molecule containing more than two atoms, all the four types of vibrations may be possible however only those vibrations that result in a rhythmical change in the dipole moment of the molecule are observed in the infrared. Some of the vibrations may be inactive in the IR region or the symmetry of the molecule may be such that two or more fundamental frequency are exactly identical these are called degenerate bonds.

HOT BANDS -

The selection rules for the anharmonic oscillator are,

$$\Delta v = \pm 1, \pm 2, \pm 3 \ldots\ldots \Delta v = \pm 1, \pm 2, \pm 3 \ldots\ldots$$

This shows that they are the same as for the harmonic oscillator with the additional possibility of larger jumps. In practice, however, these have been found to be rapidly decreasing probability and at the most only the lines of $\Delta v = \pm 1, \pm 2 \; and \pm 3 \Delta v = \pm 1, \pm 2 \; and \pm 3$ have observable intensity. Moreover, the spacing between the vibrational levels have been found to be of the order 10^3 cm^{-1} and at room temperature, it is possible to show that the population of the v = I state is nearly 0.01 or about 1% of the ground state population.

The Boltzmann distribution equation can be expressed as,

$$\frac{N\,upper}{N\,lower} = \frac{Nv = 1}{Nv = 0} = e^{-\Delta E/KT} = e^{-6.63\times10^{-34}\times3\times10^{10}\times10^{3}/1.38\times e10^{-23}\times300}$$
$$= e^{-4.8} = 0.008 = 0.01$$

Write $\Delta E = E \Delta E = E$ $_{upper}$ $- E - E$ $_{lower,}$ T is temperature and k is Boltzmann's constant $(1.38(1.38$x10^{-23} JK^{-1}).

Thus, in order to have a very good approximation, we may ignore all transitions originating at v=1 or more, and restrict to the following three transition.

- $v = 0 \rightarrow v = 1, \Delta v = +1. v = 0 \rightarrow v = 1, \Delta v = +1.$ It may have considerable intensity.

- $v = 0 \rightarrow v = 2, \Delta v = +2. v = 0 \rightarrow v = 2, \Delta v = +2.$ It would have small intensity.
- $v = 0 \rightarrow v = 3, \Delta v = +3. v = 0 \rightarrow v = 3, \Delta v = +3.$ It would have almost negligible intensity.

The spectrum of HCI, for example, shows a very intense absorption on at 2886 cm^{-1} .A weaker band at 5668 cm^{-1} and very weak band at 8347 cm^{-1} ,if the temperature is increased or if the vibration has a particularly low frequency, the population of the v=1 state may become appreciable. For example, at say 600k (i.e., about 300^0c),

$$\frac{Nv = 1}{Nv = 0} e^{-2.4} = 0.09$$

And transitions from v=1 to v=2 will be about 10% of the intensity of the transitions from v=0 to v=1. A similar increase in the excited state population would arise if the vibrational frequency changes from 1000 cm^{-1} to 500 cm^{-1}.

If such weak absorption arises, it would be found close to and at slightly lower wave numbers than the fundamental, because the vibrational levels crowd more closely together with increasing v. Such weak absorptions are generally known as **hot bands**. Hot bands may be confirmed by increasing the temperature of the sample. A true hot band will increase in intensity as a consequence of increase in temperature.

2.3,7 - Group Frequency & Factors Affecting Band Position & Intensities:

The vibrational frequency of absorption can be calculated by Hook's law. It has been found that the calculated value of frequency of absorption for a particular bond is never exactly equal to its experimental value. The difference is due to the fact that vibration of each group is influenced by the structure of the molecule in the immediate neighborhood of the band. The value of absorption frequency is also shifted since the force constant of a bond changes with its electronic structure.

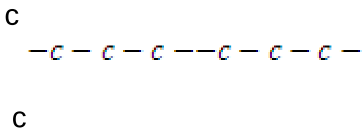
Normal mode of vibration may be classified as-

- Skeleton vibration.
- Characteristic group vibration.

Skeleton vibrations usually fall in the range of 1400-700 $cm^{-1} cm^{-1}$for organic molecules and these vibrations generally arise from linear or branched chain structure in the molecule. Most single bond gives rise to absorption bands at these frequencies. Strong interaction occurs between neighboring bonds, because their energies are about the same. The absorption bands are thus composites of these various interactions and depend upon the overall skeleton structure of the molecule.

For example, the groups such as

$-c - o - c --c - o - c -$



$$\overset{c}{\underset{c}{-c - c - c --c - c - c -}}$$

give rise to several skeleton modes of vibration, hence several absorption bands in the infrared..

The approximate frequency (or wave number) at which an organic functional group such as C$c = o, c = c, c - H, c \equiv c \; or \; o - Hc = o, c = c, c - H, c \equiv c \; or \; o - H$ etc. absorbs infrared radiation can be calculated from the masses of the atoms and the force constant of the bonds between them. These frequencies are known as **group frequencies**. Most group frequencies fall in the range of 3600 to 1250 $cm^{-1} cm^{-1}$.

Group frequency or group vibrations are usually almost independent of the structure of the molecule as a whole. It has been found that the vibration of light atoms in the terminal group such as – CH_3, - OH, $-C \equiv N - C \equiv N$, > $C = OC = O$ etc. are of high frequency, while those of heavy atoms such as $-C - Cl, -C - Cl, \; -C - Br - C - Br$, metal-metal etc. are low in frequency. The group frequencies and consequently their spectra are highly characteristic of the group present and hence can be used for analysis.

Following are some of factor responsible for shifting of the vibrational frequencies from their normal values –

(I)Physical state: A change in physical state may cause a shift in the frequency of a vibration, particularly in the case of polar molecule. In general, the more condensed phase gives a lower frequency.

$$V_{gas} > V_{liquid} = V_{solution} > V_{solid}$$

For example, a shift of about 100 $cm^{-1} \; cm^{-1}$ is obtained in polar molecule like HCl in passing from vapour to liquid and a further decrease of 20 $cm^{-1} cm^{-1}$ on solidification.

Non-polar CO_2 molecule shows almost negligible shifts in the symmetric vibrations, but a decrease of about 60 $cm^{-1} cm^{-1}$ on solidification.

(II)Resonance: The isolated multiple bonds such as $> C = C < or - C \equiv C -> C = C < or - C \equiv C -$ also have group frequencies which are highly characteristic. However, if two such groups which, in isolation, have comparable frequencies and occur together in a molecule, the group frequencies may be considerably shifted from the expected value because of the occurrence of resonance. For example, the isolated carbonyl in a ketone ($R_2C=O$) and the >C=C< double bond have group frequencies of 1715 $cm^{-1} cm^{-1}$ and 1650 $cm^{-1} cm^{-1}$ respectively. However, when the grouping,

$$>C=C-C=O$$

Occurs, their separate frequencies are shifted to 1675 $cm^{-1} cm^{-1}$ and about 1600 $cm^{-1} cm^{-1}$, respectively. Moreover, intensity of the $> C = C <> C = C <$ absorption increases to become comparable with that of strong $> C = O > C = O$ bond (This is due to Fermi resonance.) close coupling of two groups as in the species, $> C = C = O > C = C = O$ gives rise to absorptions at about 2100 $cm^{-1} cm^{-1}$ and 1100 $cm^{-1} cm^{-1}$, which are much far removed from the characteristic frequencies of the separate groups.

(III) Electronic Effect: Changes in the absorption frequencies for a particular group take place when the substituents in the neighbourhood of that particular group are changed. The frequency shifts are due to electronic effects which include:

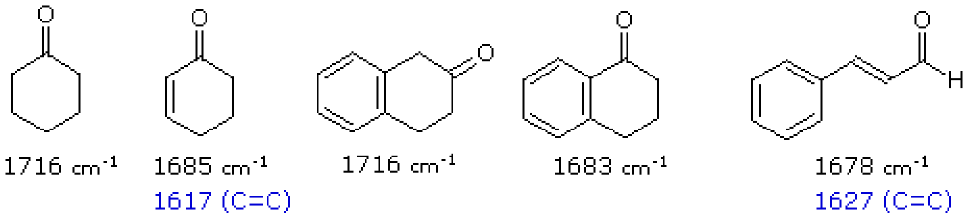
- Inductive effects,
- Mesomeric effects and
- Field effects etc.

These effects cannot be isolated from one another. Under the influence of these, the force constant or the bond strength changes and its absorption frequency shift from the normal value.

- **Inductive Effect:** The introduction of an electronegative atoms or group cause –I effect which results in the bond order to increase. The force constant increases and hence the wave number of absorption rises. Consider the wave numbers of absorption in the following compounds: (a) Acetone (CH_3COCH_3) 1715 cm^{-1} cm^{-1} (b) Chloroacetone (CH_3COCH_2Cl) 1725 cm^{-1} cm^{-1} , (C) Dichloroacetone ($CH_3COCHCl_2$) 1740 cm^{-1} cm^{-1} (d) Tetrachloroacetone ($ClCl$ $_2CH - CO - CHClCH - CO - CHCl$ $_2$) 1750, 1778 cm^{-1} cm^{-1} .

The introduction of alkyl groups causes +I effect which results in weakening of the bond. Hence, the force constant is lowered and wave number of absorption decreases. For example,the C=O stretching absorption of formaldehyde(HCHO) occurs at1735 cm^{-1} cm^{-1} and that of acetaldehyde at 1730 cm^{-1} cm^{-1} .

- **Mesomeric Effect:** It causes lengthening or the weakening of a bond leading to the lowering of absorption frequency. In most of the cases, mesomeric effect works along with inductive effect. In few cases. Inductive effect dominates over mesomeric effect. In case, where the lone pair of electrons present on an atom is in conjugation with the double bond of a group, the mobility of the lone pair of electrons matters. Conjugation with a double bond or benzene ring lowers the stretching frequency. The 30 to 40 cm^{-1} decrease in frequency is illustrated by the following examples. The stretching frequency of the conjugated double bond is also lowered (blue notation) and may be enhanced in intensity. The cinnamaldehyde example (far right) shows that extended conjugation further lowers the absorption frequency, although not to the same degree.



- **Field Effect:** In ortho substituted compounds, the lone pair of electrons on two atoms influence each other through space interactions and change the vibrational frequencies of both the groups. This effect is known as field effect. Consider ortho haloacetophenone.

  The non-bonding electrons present on oxygen atom and halogen atom cause electrostatic repulsions. This results in a change in the state of hybridisation of C=O group and also makes it to go out of the plane of double bond. Conjugation is diminished and absorption occurs at a higher wave number. Thus, for such substituted compounds, cis-isomer absorbs at a higher frequency (field effect) than the trans isomer.

(IV) **Relative masses of the atoms**: In general, increasing the mass of the atom undergoing oscillators within the group tends to decrease the frequency and increasing the strength of the bond and hence increasing the force constant, tends to increase the frequency.

For example, the intensities of the bands of the groups given below decreases in ,

$> C = O >> C = N- >> C = C <$

Similarly, intensities of the bonds of following groups decrease in the order,

$-OH >> NH >-OH >> NH >$ > CH

Because of this reason too, the vibrations of ionic crystal lattices often give rise to very strong absorption. We can say that the more polar a bond, the more intense will be the infrared spectrum arising from vibrations of that bond.

(V) **Hydrogen Bonding:** Hydrogen Bonding brings about remarkable downward frequency shifts. Stronger the H-bonding, greater is the absorption shift towards lower wave number than the normal value. Generally, bands due to intramolecular hydrogen bonds are sharp whereas intermolecular hydrogen bonds give rise to broad bands and these depend on concentration. On dilution, the intensities of intermolecular hydrogen bonds become independent of concentration. The absorption frequency difference between free and associated molecule is smaller in case of intramolecular H-bonding than that in intermolecular association.

Mostly non- associating solvents like $CHCl_3$, CCl_4, CS_2 are used because solvents like acetone and benzene etc. influence $O-HO-H$ and $N-HN-H$ compounds to greater extent. Since N-atom is less electronegative than O-atoms so hydrogen bonding in amines is weaker than that in alcohols. Thus amines show $N-HN-H$ stretching at 3500 $cm^{-1}cm^{-1}$ in dilute solutions while in condensed phase spectra, absorption occurs at 3300 $cm^{-1}cm^{-1}$. In aromatic amines, difference between intramoecularly and $N-HN-H$ bond absorption frequency are small and difficult to detect.

Spectra of pure alcohols show wide bond in the O-H stretching vibration as a result of extensive hydrogen bonding. In case of cyclohexanol, the O-H stretching vibration occur around 3330 cm^{-1} cm^{-1} (lower frequency) because of the lengthening of the original O-H bond on H- bonding. When hydrogen bonding is less extensive, a sharper and less intense bond is observed at higher frequency at about 3600 $cm^{-1}cm^{-1}$

Hydrogen bonding may be considered as a resonance hybrid as a result of which the bond gets weakened, its force constant is reduced and hence stretching frequency is decreased. Thus, stronger the hydrogen bond, lower the vibration frequency and broader and more intense will be absorption band.

Hydrogen bonding is strongest when the boded structure is stabilized by resonance.

The $O-HO-H$ group involved in chelation gives rise to broad absorptions between 3000 and 2500 cm^{-1} cm^{-1}. the vCO absorption in the enolic form occurs at 1630 cm^{-1} cm^{-1} and that in the keto form at 1725 $cm^{-1}.cm^{-1}$. infra –red spectrum of benzoic acid shows broad band at 3000 - 2500 $cm^{-1}cm^{-1}$ due to O-H stretching. Pi $(\pi)(\pi)$ cloud interactions are also noted when acidic hydrogen interacts with Lewis bases (nucleophiles) such as alkenes and benzene.

(VI) Vibrational Coupling:

The energy of a vibration and thus the wavelength of its absorption peak may be influenced by other vibration in the molecule. **The extent of coupling is influenced by the following important factors.**

- Strong coupling between stretching vibrations occurs only when the two vibrations have a common atom.
- Interaction between bending vibrations occurs only when a common bond is present between the vibrating groups.
- Coupling between a stretching and a bending vibration can occur if stretching bond forms one side of the angle that varies in the bending vibrations.
- Interaction is greatest when the coupled groups have individual energies that are approximately equal,

- If groups are separated by two or more bonds, little or no interaction occurs.
- Coupling occurs when vibrations are of the same symmetry species.

Consider the infrared spectrum of carbon dioxide which is a linear triatomic molecule. It has four normal modes, i.e. 4 (3N-5) or $3x3\ -53x3\ -5$ modes of vibrations. Two stretching vibrations are possible. Since the bonds involved are associated with a carbon atom, interaction between the two can occur according to the effect (1) **Hence one coupled vibration is symmetric and the other is asymmetric as shown in the Fig.**

Symmetric **Asymmetric**

As the symmetric stretching vibration produces no change in the dipole moment of the molecule, it is inactive (not seen) in the infrared spectra. Asymmetrical stretching vibration appears in the infrared spectrum in the region 2330 $cm^{-1.}$

The remaining two vibrational modes of carbon dioxide involve scissoring and are identical in energy, produce only one peak at 667 cm^{-1} It has also been confirmed experimentally that CO_2 exhibits two absorption peaks, the one at 2330 cm^{-1} and the other 667 $cm^{-1.}$If no coupling occurred between the two C= O bonds, an absorption peak would be expected at the same wave number as the peak for C = O stretching vibration in aliphatic ketone (about 1700 cm^{-1}).

− + − − + −

Scissoring vibration of CO_2

The following table lists some of the more common functional groups and their characteristic IR absorption energy.

Group	Bond	Approx. Energy (cm^{-1})
Hydroxyl	O-H	3610-3640
Amines	N-H	3300-3500
aromatic rings	C-H	3000-3100
Alkenes	C-H	3020-3080
Alkanes	C-H	2850-2960
Nitriles	C≡N	2210-2260
Carbonyl	C=O	1650-1750
Amines	C-N	1180-1360

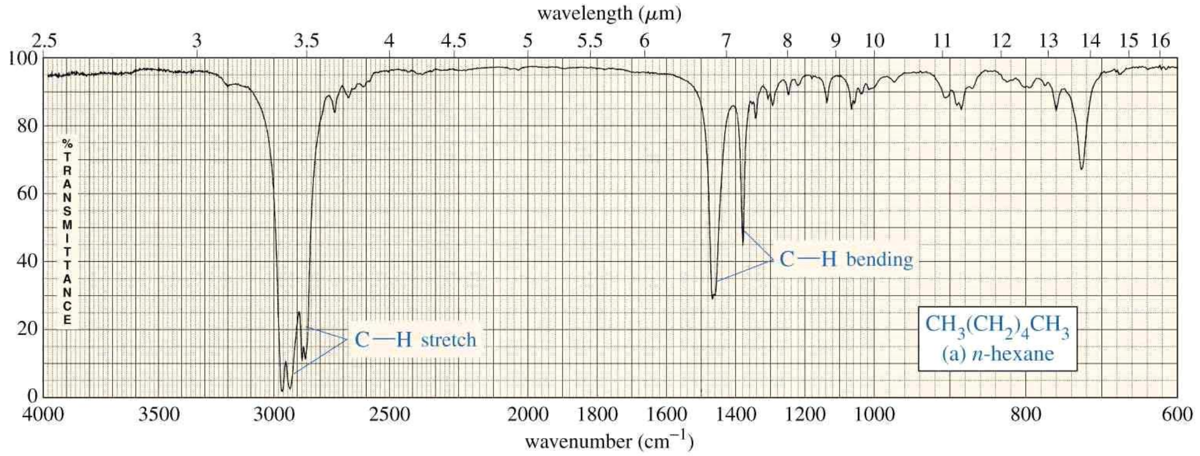
Carbon-Carbon Bond Stretching

- Stronger bonds absorb at higher frequencies:
  - C-C 1200 cm^{-1}
  - C=C 1660 cm^{-1}
  - CC 2200 cm^{-1} (weak or absent if internal)
- Conjugation lowers the frequency:
  - isolated C=C 1640-1680 cm^{-1}
  - conjugated C=C 1620-1640 cm^{-1}
  - aromatic C=C approx. 1600 cm^{-1}

Carbon-Hydrogen Stretching

- Bonds with more *s* character absorb at a higher frequency
  - sp^3 C-H, just below 3000 cm^{-1} (to the right)
  - sp^2 C-H, just above 3000 cm^{-1} (to the left)
  - *sp* C-H, at 3300 cm^{-1}

An Alkane IR Spectrum



CHECK YOUR PROGRESS-3

Q.1) In following molecules, the vibration will be active or inactive in the IR region?

- SO_2 – Symmetric stretching
- CH_3-CH_3 - C-C Stretching
- CH_2-CCl_3 - C-C Stretching
- CH_2=CH_2 - C-H Stretching

Q.2) TRUE/FALSE:

- The O-H Stretching is observed at higher frequency than the C-H Stretching.
- CO_2 Molecule has four fundamental vibrational modes
- A polyatomic molecule of N atoms has 3N degrees of freedom.
- Linear molecules have 3N-5 degrees of freedom.

2.3,8 - Far Infrared Region-

Far infrared region is particularly useful for inorganic studies, because absorption due to stretching and bending vibrations of bonds between metal atoms and both inorganic and organic ligands generally occur at frequencies lower than 650cm^{-1} .For example, heavy metal iodides generally absorb in the region below 100cm^{-1}. The bromides and chlorides have bands at higher frequencies. Absorption frequencies for metal organic bonds generally depend upon both the metal atom and the organic portion of the species.

Far infrared studies of inorganic solids provide useful information of the lattice energies of crystals and the transition energies of semiconducting materials. Molecules composed only of light atoms absorb in the far infrared, if they have skeletal bending modes involving more than two atoms other than hydrogen. For example, substituted benzene derivatives show several absorption peaks. Characteristic group frequencies also exist in the Far infrared region. Pure rotational absorption by gases has also been observed in the Far infrared region, if the molecules have permanent dipole moments. Examples include H_20, 0_3, HCl and AsH_3.

2.3,9 - Metal Ligand Vibrations:

Because of weak nature of metal ligand bond and also due to the relatively heavy mass of the metal atom, the vibrations involving metal ligand stretching and bending modes generally appear in the low frequency region. The metal ligand vibrations may also undergo coupling with other low frequency vibrations occurring in the metal complex.

Skeletal vibrations are very helpful in providing information regarding the nature of metal ligand bond as well as the special distribution of the donor atoms.

The most common linkage in coordination compounds are M-O,M-N,M-X(halogens) and M-S, and in general, the M-O stretching vibration gives a more intense and broad band than M-N stretching vibration, because of large dipole moment change taking place in M-O bond(O is more electronegative than N). In case of M-X stretching vibration, the frequency of vibration decreases with the increases in the mass of halogen atom, provided the mass of the structure complex remains unchanged.

Compounds containing bridge halogen atoms, it is expected that a bridging vibration is located at lower frequencies than those found for terminal vibrations due to the fact that sharing of halogen between two metals in a bridged structure causes the bond to be weaker than a terminal halogen bond.

Factors Affecting The Metal Ligand Vibrations:

- Higher the oxidation state of the metal higher is the frequency of vibration.
- Greater the mass of the metal and ligand lower is the frequency.
- Higher the coordination number of the metal, lower is the frequency
- Greater the basicity of the ligand, greater the freq for sigma bonding.
- Greater size of coubratinter ion, smaller is the frequency
- Non bridging ligands have higher frequency than the bridging ones.

2.3,10 - Normal Co-ordinate Analysis-

Normal co-ordinate analysis is the assignment of vibrational frequencies from infrared and Raman spectra to individual valency type vibrations and the calculations of relative amplitude of the symmetry co-ordinates in any normal mode.

It also provides the information about intramolecular force field. The procedure involves the framing up and solving of the vibrational secular equation. Force constant serves as abasis to calculate fundamental frequencies of larger polyatomic molecules. The intramolecular force constants are associated to the electronic structure and these canbe correlated with bond nature, interatomic repulsion and electron delocalization

CHECK YOUR PROGRESS- 4

Q-1 Give characteristic infrared absorption frequencies of the following-

- O-H carboxylic acid b) N-H amines
- Q-2 Why there is variation of frequency from double bond(C=C) to single bond(C-C).

2.4 - Raman effect

The Raman effect, named after Noble prize winner Chandrasekhara Venkata Raman, can be described as an inelastic light scattering process. When a strong light source (laser) is focused on a substance most of this energy will be scattered elastically. In this case the molecules of the substance are excited to a virtual electronic state and immediately fall back to their original state by releasing a photon (see figure 1). The photon energy of this scattered light is equal to that of the incoming light. This process is called Rayleigh scattering. A molecule may also fall back from an excited electronic state to an energy state that is higher (Stokes type scattering) or lower (anti-Stokes type scattering) than the original state. The difference in energy between the incoming and scattered photon (Raman shift) corresponds to the energy difference between vibrational energy levels of the molecule. The different vibrational modes of a molecule can therefore be identified by recognizing Raman shifts (or 'bands') in the inelastically scattered light spectrum.

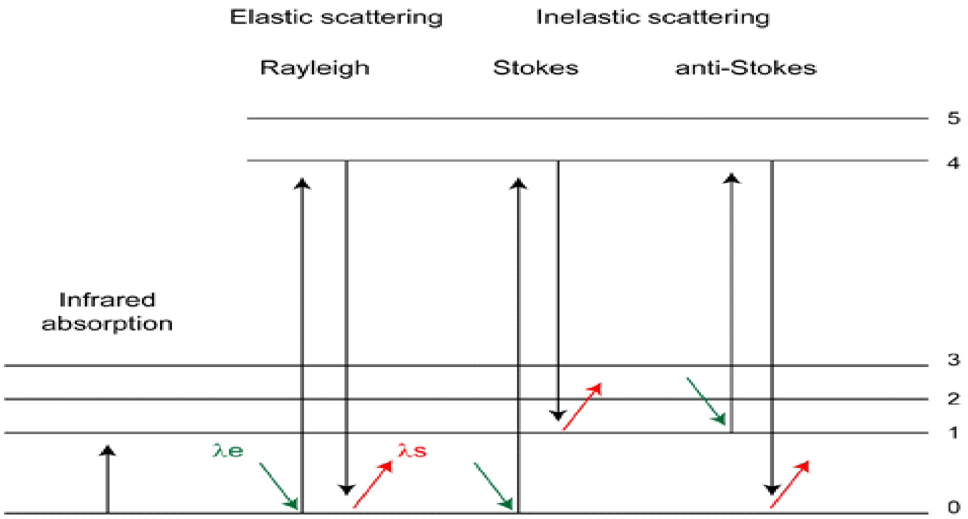


Figure 2.4. Simplified energy level diagram. The shift in wavelength between the excitation light (λe) and the scattered light (λs) is related to Raman shift (ΔV in cm-1) according to: ΔV = (1/ λe) + (1/ λs).

2.2 B-II-Classical Theory

In fact, Raman scattering is due to the oscillation of the induced electronic dipole moment when the molecules are put into an oscillating electric field. The relationship between the oscillating dipole moment and the field is described by the following equation:

$$\mu = \alpha E$$

Where μ is the induced electronic dipole moment, E is the external field, α is the polarizability of the molecules. This polarizability which is a kind of tensor is determined by the shape and also size of the electronic cloud of that molecule. So only the vibrational modes which can change the shape and size of the electronic cloud can be possibly Raman active.

Now, we come to a classical explanation of the Raman scattering. Assume that we have an incident light α whose electric field is like:

$$E = E_0 \cos(2\pi\nu t)$$

ν is the frequency of the light. Then the induced dipole moment is:

$$\mu = \alpha E_0 \cos(2\pi\nu t)$$

If the polarizability changes as the following expression due to the oscillation of the molecule:

$$\alpha = \alpha_0 + (\Delta\alpha)\cos(2\pi\nu_0 t)$$

where α_0 is the equilibrium polarizabilty, ν_0 is the frequency of that vibrational mode. So

$$\mu = [\alpha_0 + (\Delta\alpha)\cos(2\pi\nu_0 t)] * E_0 \cos(2\pi\nu t)$$

we can rearrange this equation into

$$\mu = \alpha_0 E_0 \cos 2\pi\nu t + \frac{1}{2}\Delta\alpha E_0[\cos 2\pi(\nu+\nu_0)t + \cos 2\pi(\nu-\nu_0)t]$$

This equation predicts that the induced dipole moment will oscillate with the following three frequencies: ν , $\nu + \nu_0$, $\nu - \nu_0$. So ν will be the Rayleigh scattering, $\nu + \nu_0$ is the anti-Stokes scattering, and $\nu - \nu_0$ is the Stokes scattering.

2.2 B-III--<u>**Quaqntum Theory**</u> - According to quantum theory, the virtual state is in fact the mixture of all the available vibronic states of the molecules, so Raman scattering is contributed by all the available vibronic states of the molecules. The interaction of light with matter in a linear regime allows the absorption and emission of a photon precisely matching the difference in energy levels of the interacting electron or electrons. It is assumed that the radiation of frequency v consists of stream of particles called quantum or photons of energy hv i.e., E=hv
Where h is Planks constant.
Raman effect arises from an exchange of energy between the instant photon and the molecules which scatter this photon on collision. A quantum of radiation hv of incident light collides with the molecule. There are three possibilities:

- No energy exchange between the incident photons and the molecules The phenomena is called **Rayleigh scattering**.
- Energy exchanges occur between the incident photons and the molecules. The energy differences are equal to the differences of the vibrational and rotational energy-levels of the molecule. In crystals only specific <u>phonons</u> are allowed (solutions, which do not cancel themselves, of the wave equations) by the periodic structure, so Raman scattering can only appear at certain frequencies. In amorphous materials like glasses, more photons are allowed and thereby the discrete spectral lines become broad.
    - molecule absorbs energy: Stokes scattering. The resulting photon of lower energy generates a <u>Stokes line</u> on the red side of the incident spectrum.
    - molecule loses energy: anti-Stokes scattering. Incident photons are shifted to the blue side of the spectrum, thus generating an anti-Stokes line.

These differences in energy are measured by subtracting the energy of the mono-energetic laser light from the energy of the scattered photons. The absolute value, however, doesn't depend on the process (Stokes or anti-Stokes scattering), because only the energy of the different vibrational levels is of importance. Therefore, the Raman spectrum is symmetric relative to the Rayleigh band. In addition, the intensities of the Raman bands are only dependent on the number of molecules occupying the different vibrational states, when the process began. If the sample is in thermal equilibrium, the relative numbers of molecules in states of different energy will be given by the Boltzmann distribution:

$$\frac{N_1}{N_0} = \frac{g_1}{g_0} e^{-\frac{\Delta E_v}{kT}}$$

where:

N_0: number of atoms in the lower vibrational state

N_1: number of atoms in the higher vibrational state

g_0: degeneracy of the lower vibrational state (number of orbitals of the same energy)

g_1: degeneracy of the higher vibrational state

ΔE_v: energy difference between these two vibrational states

k: Boltzmann constant

T: thermodynamic (absolute) temperature

Thus lower energy states will have more molecules in them than will higher (excited) energy states. Therefore, the Stokes spectrum will be more intense than the anti-Stokes spectrum.

CHECK YOUR PROGRESS –5

Q-1 Fill in the blanks:

a) Stokes lines are ------than antistokes lines.

b) Vibrations involving polar bonds are comparatively --------Raman scatterer.

c) For a bond to be allowed in Raman spectrum there must be change in the ---------- of the molecule.

2.2 B-IV- Pure Rotational Raman Spectra :

For a molecule to be Raman active its molecular rotation or the change in rotational energy must cause some change in the component of the molecular polarizability.

The expression for rotational energy levels of a linear diatomic molecule have already been derived in the previous pages of this chapter and is given by:

$$\epsilon_j = \epsilon_j = \frac{h}{8\pi^2 Ic} J(J+1) cm^{-1} \frac{h}{8\pi^2 Ic} J(J+1) cm^{-1}$$

Here in Raman spectroscopy transition between energy levels is different from transition between rotational levels in microwave spectroscopy.

$$\Delta J = 0, \pm 2$$

$$\Delta J = 0, \pm 2$$

ΔJ=0 corresponds to no change in rotational energy hence Rayleigh scattering only. ΔJ=±2 is the operative part of the selection rule for pure rotational Raman spectrum of a diatomic molecule. It means that in Raman spectrum rotational quantum number J changes by two units . For microwave spectroscopy selection rule is 1ΔJ=±1.the factor 2 comes in because during a complete rotation the polarizability ellipsoid rotates twice as fast as the molecule.

Using this selection rule (ΔJ=±2) energy level expression for diatomic molecule will be given by,

$$\Delta E_{rot} = \epsilon_{J+2} - \epsilon_J$$

Where J is the rotational quantum number in the lower state and (J+2) in the higher state.

Thus if the molecule gains rotational energy from the photon during collision a series of lines are produced to the low wave number or low wave frequency side of the exciting lines(Rayleigh lines). These lines obtained for ±2 are called S-branch lines or the Stokes lines. For $\Delta J=-2$, molecule loses energy to the photon, S-branch lines appear on the high wave number side of the exciting lines. These are called anti-stokes lines.

The frequency in wave number of the corresponding spectral lines are given by,

$$\Delta\overline{\upsilon} = \overline{\upsilon}_{ex} \pm B(4J+6)cm^{-1}$$

Where $\overline{\upsilon}_{ex}\overline{\upsilon}_{ex}$ is the frequency of existing radiation in wave number. Plus sign represents anti stoke lines and the minus sign for stokes lines.

If in equation we put J=0, it is seen that the separation of first line from the exciting line is $6Bcm^{-1}$ while the separation between successive lines is $4Bcm^{-1}$.

Pure vibrational raman spectra - Raman scattering occurs if –

- $\Delta v=\pm 1$, that the transition takes place when vibrational energy states differ by unity.

II) The polarizability changes with nuclear distance and change in bond length during vibrations.

The intensity of Raman lines are weak therefore no overtones are observed in Raman spectra. The energy for vibrational mode is

$E_v = (\upsilon\upsilon+1/2)h\,\upsilon\,\upsilon_e$ Where $\upsilon\upsilon_e$ is the vibrational frequency

Vibrational –rotational Raman spectra

selection rule for vibrational-rotational Raman spectra of a diatomic molecule is $\Delta v=\pm 1$ and $\Delta J=0, \pm 2$

This is to be noted here that selection rules involve the change in both vibrational and rotational energy levels . Hence both above equations refer to selection rule for vibrational raman spectra. This shows that transition can take place only to adjacent vibrational levels. Adjacent vibrational levels means from one level to next upper level giving Stokes lines or to the next lower level giving anti stokes. Anti stokes lines are weak because in the intial state there are very few excited molecules.

The transition with $\Delta J=0$ gives Q branch, those with $\Delta J=\pm 2$ forms a S-branch and for $\Delta J=-2$ we get an O-branch.

2.2 B-V - Mutual Exclusion Principle-

The mutual exclusion rule state that if a molecule has a centre of symmetry, then only those vibrations which are antisymmetric with respect to the centre can be infrared active and only those vibrations which are symmetric with respect to the centre of symmetry can be Raman active. If a molecule hs a centre of symmetry, then Raman active vibrations are infrared inactive and vice- versa. If there is no centre of symmetry then some vibrations may be both Raman and infrared active.

2.2 B-VI - Resonance Raman spectroscopy -

In resonance Raman spectroscopy, the energy of the incoming laser is adjusted such that it or the scattered light coincide with an electronic transition of the molecule or crystal. In most materials the incoming and outgoing electronic resonances are sufficiently broad that they can not be distinguished. So, rather than exciting the molecule to a virtual energy state, it is excited to near one of its excited electronic transitions. Since the energy of these transitions differ from one chemical species to the next, this technique did not become applicable until the advent of tunable lasers in the early 1970s. (Tunable lasers are those where the wavelength can be altered within a specific range.) When the frequency of the laser beam is tuned to be near an electronic transition (resonance), the vibrational modes associated with that particular transition exhibit a greatly increased Raman scattering intensity. This usually overwhelms Raman signals from all of the other transitions. For instance, resonance with a π-π* transition enhances stretching modes of the π-bonds involved with the transition, while the other modes remain unaffected.

This aspect of Raman spectroscopy becomes especially useful for large biomolecules with chromophores embedded in their structure. In such chromophores, the charge-transfer (CT) transitions of the metal complex generally enhance metal-ligand stretching modes, as well as some of modes associated with the ligands alone. Hence, in a biomolecule such as hemoglobin, tuning the laser to near the charge-transfer electronic transition of the iron center results in a spectrum reflecting only the stretching and bending modes associated with the tetrapyrrole-iron group. Consequently, in a molecule with thousands of vibrational modes, RR spectroscopy allows us to look at relatively few vibrational modes at a time. This reduces the complexity of the spectrum and allows for easier identification of an unknown protein. Also, if a protein has more than one chromophore, different chromophores can be studied individually if their CT bands differ in energy. In addition to identifying compounds, RR spectroscopy can also supply structural identification about chromophores in some cases.

The main advantage of RR spectroscopy over traditional Raman spectroscopy is-

Large increase in intensity of the peaks by as much as a factor of 10^6.

This allows RR spectra to be generated with sample concentrations as low as 10^{-8} M.

RR spectra usually exhibit only a few peaks, and different peaks can be selected for by targeting specific electronic transitions. The main disadvantage of RR spectroscopy is the increased risk of fluorescence and photodegradation of the sample due to the increased energy of the incoming laser light.

2.2 B-VII Coherent anti-Stokes Raman spectroscopy(CARS) - It is sensitive to the same vibrational signatures of molecules as seen in Raman spectroscopy, typically the nuclear vibrations of chemical bonds. Unlike Raman spectroscopy, CARS employs multiple photons to address the molecular vibrations, and produces a signal in which the emitted waves are coherent with one another. As a result, CARS is orders of magnitude stronger than spontaneous Raman emission. CARS is a third-order nonlinear optical process involving three laser beams: a pump beam of frequency ω_p, a Stokes beam of frequency ω_S and a probe beam at frequency ω_{pr}. These beams interact with the sample and generate a coherent optical signal at the anti-Stokesfrequency $(\omega_{pr}+\omega_p-\omega_S)$. The latter is resonantly enhanced when the frequency difference between the pump and the Stokes beams $(\omega_p-\omega_S)$ coincides with the frequency of a Raman resonance,

The CARS process can be physically explained by using either a classical oscillator model or by using a quantum mechanical model that incorporates the energy levels of the molecule. Classically, the Raman active vibrator is modeled as a (damped) harmonic oscillator with a characteristic frequency of ω_v. In CARS, this oscillator is not driven by a single optical wave, but by the difference frequency $(\omega_p-\omega_S)$ between the pump and the Stokes beams instead. The Raman oscillator is susceptible to the difference frequency of two optical waves. When the difference frequency $\omega_p-\omega_S$ approaches ω_v, the oscillator is driven very efficiently. On a molecular level, this implies that the electron cloud surrounding the chemical bond is vigorously oscillating with the frequency $\omega_p-\omega_S$. These electron motions alter the optical properties of the sample, i.e. there is a periodic modulation of the refractive index of the material. This periodic modulation can be probed by a third laser beam, the probe beam. When the probe beam is propagating through the periodically altered medium, it acquires the same modulation. Part of the probe, originally at ω_{pr} will now get modified to $\omega_{pr}+\omega_p-\omega_S$, which is the observed anti-Stokes emission. Under certain beam geometries, the anti-Stokes emission may diffract away from the probe beam, and can be detected in a separate direction.

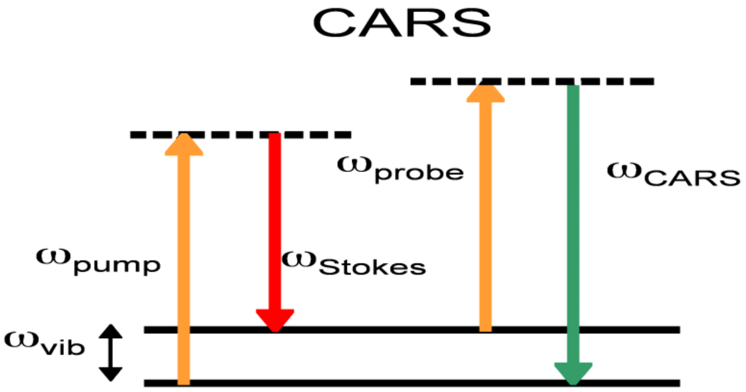


Fig. 2.5 – CARS process

Quantum mechanically, the CARS process can be understood as follows. Molecule is initially in the ground state,i.e. the lowest energy state of the molecule. The pump beam excites the molecule to a virtual state. A virtual state is not an eigenstate of the molecule and it cannot be occupied but it does allow for transitions between otherwise uncoupled real states. If a Stokes beam is simultaneously present along with the pump, the virtual state can be used as an instantaneous gateway to address a vibrational eigenstate of the molecule. The joint action of the pump and the Stokes has effectively established a coupling between the ground state and the vibrationally excited state of the molecule. The molecule is now in two states at the same time: it resides in a coherent superposition of states. This coherence between the states can be probed by the probe beam, which promotes the system to a virtual state. Again, the molecule cannot stay in the virtual state and will fall back instantaneously to the ground state under the emission of a photon at the anti-Stokes frequency. The molecule is no longer in a superposition, as it resides again in one state, the ground state. In the quantum mechanical model, no energy is deposited in the molecule during the CARS process. Instead, the molecule acts like a medium for converting the frequencies of the three incoming waves into a CARS signal (a parametric process). There are, however, related coherent Raman processes that occur simultaneously which do deposit energy into the molecule.

Theoretically Raman spectroscopy and CARS spectroscopy are equally sensitive as they use the same molecular transitions. However, given the limits on input power (damage threshold) and detector noise (integration time), the signal from a single transition can be collected much faster in practical situation (a factor of 10^5) using CARS. Imaging of known substances (known spectra) is therefore often done using CARS. Given the fact that CARS is a higher order nonlinear process. CARS signal from a single molecule is larger than the Raman signal from a single molecule for a sufficiently high driving intensity. However at very low concentrations, the advantage of the coherent addition for CARS signal reduces and the presence of the incoherent background becomes an increasing problem.

CHECK YOUR PROGRESS 6

Q-1) Fill in the blanks-

a- Vibrations involving relatively neutral bonds such as C-C, C-H, C= C, are --------- Raman scatterers but ----------- in infrared absorption.

b- Resonance Raman spectroscopy becomes especially useful for ……………….

c - Resonance with a π-π* transition …………….stretching modes of the π-bonds involved with the transition

d - CARS signal from a single molecule is larger/ shorter than the Raman signal for a sufficiently high driving intensity.

2.3 : Let Us Sum Up-

- The rotational energy of diatomic molecule or linear polyatomic molecule is given by-
- The separation between rotational lines gives the moment of inertia and hence interatomic distance for diatomic molecule.
- No two compounds except the enantiomers can have similar IR spectra.

- In IR spectroscopy ,the absorbed energy brings about predominant change in vibrational energy which depends upon-(a) masses of the atoms (b) strength of the bonds (c) arrangements of atoms within the molecule.
- Bending vibrations require lesser energy than stretching vibrations.
- An anharmonic oscillation does not obey Hook's law.
- Conjugation with olefinic or acetylinic group lowers the frequency and raises the intensity.
- In Raman spectrum, interaction of molecule takes place if the polarisability of the molecule is altered by vibrations.
- Generally stokes lines are predominant than antistokes lines.
- The enhanced intensity of few scattered frequencies give rise to Resonance Raman effect. It is used for studying biostructural problems and complex biological materials.
- CARS is the non-linear analogue of spontaneous Raman scattering. CARS signals are stronger than normal Raman lines by 8 to 10 orders of magnitude, so micro-quantities 10^{-5} to 10^{-7} can be detected by it.

2.4 : **Check Your Progress : The Key**

1- microwave active mol- HCl, CO, NO, HBr

2 – 1- forbidden 2- Microwave active 3- condensed

4- rotational 5- inactive. 6- quantized.

3-Q.1- a) Active b) Inactive c) Active d) Active e) Active
Q.2- f) True g) True h) True i) True.
4- Q-1 a) 2500-3000 cm^{-1} (broad)
b) 3300- 3500cm^{-1}
5- Q-1 a) more intense b) weak c) polarisability

6 – Q-1 a) strong , weak b) biomolecules c) enhance d) larger.

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UNIT III - ELECTRONIC SPECTROSCOPY

STRUCTURE:

3.0 - Introduction
3.1 - Objetives
3.2 - ATOMIC SPECTRA
  3.2.1 – Energies of Atomic Orbitals
  3.2.2 - Vector Representation of Momenta
  3.2.3 - Vector Coupling
  3.2.4 - Spectra of Hydrogen atom
  3.2.5 - Spectra of Alkali metal atoms

3.3 Molecular Spectroscopy
  3.3.1 - Energy Levels and Molecular Orbitals
  3.3.2 - Vibrionic Transitions and Vibrational Progression
  3.3.3 - Geometry of the Excited State
  3.3.4 – Frank Condon Principle
  3.3.5 - Electronic spectra of polyatomic molecules
  3.3.6 - Emission spectra
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  3.3.8 - Internal Conversion
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3.4 - PHOTOELECTRON SPECTROSCOPY
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3.5 - PHOTOACOUSTIC SPECTROSCOPY

  3.5.1 - Basic Principle
  3.5.2 - Instrumentation
  3.5.3 - PAS gases
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  3.5.8 - References

3.0 Introduction –

When a beam of polychromatic light is passed through a prism or grating , it is broken up into its constituent colors. This array of colors is known as spectrum. Atomic spectrum is obtained when the light emitting substance is in the atomic state. When the emitter in the molecular state is excited, each molecule emits bands which are characteristic of molecules then it is called **molecular spectrum**.

Photoelectron spectroscopy is based on **Einstein's photoelectric effect.** Photoelectron spectroscopy is based upon a single photon in/electron out process. A photon can ionize an electron from a molecule. By measuring the relative energies of the ground and excited positive ion states that are obtained by removal of single electrons from the neutral molecule the kinetic energy of the ejected (photo) electron is measured in the photoelectron spectrometer. Photoacoustic spectroscopy is the measurement of the effect of absorbed electromagnetic energy on matter by means of acoustic (sound) detection.

3.1 Objetives:

Atomic spectra

- To measure the wavelength of visible light emitted by atomic hydrogen and verify the measured wavelengths against those predicted by quantum theory.
- To identify elements through their emission spectra.
- To examine an absorption spectra.
- To learn about the bohr model of the atom.
- To use atomic spectroscopy to verify some predictions of bohr model and measure the rydberg constant.
- To understand relationship between energy levels and spectroscopy.
- Sketch absorption ,emission and ionization processes on an energy diagrams.
- Difference between dark line and bright line spectra.

Molecular spectra

- Identifying compounds & to understand the basic principles of molecular spectroscopy in terms of the quantization of molecular energy and transitions between molecular energy levels when matter interacts with radiation.
- Use the ‘particle in a box’ model to account for quantization in a one dimensional system.
- Use the Beer–Lambert law to find the amount of radiation absorbed at a given concentration or to find the molar absorption coefficient .
- Assign the type of molecular transition associated with radiation of a particular energy in the electromagnetic spectrum.
- Differentiate between absorption and transmission spectra and between absorption and emission spectra.
- Account for the relative populations of energy levels using the Boltzmann distribution.
- To understand the origin and appearance of rotational spectra.

Photoelectron spectroscopy

- radiation with a photon energy to examine valence levels.
- The kinetic energy distribution of the emitted photoelectrons
- the relationship of ionization energies to the molecular orbital model of electronic structure.
- quantitative analysis of the surface composition.

Photoacoustic spectroscopy

- Sensitive and selective detection of gases is done by PAS, vapours or particles under normal atmospheric pressure.
- Analytic examinations of liquids, solutions or suspensions
- Solid state- or powder analysis (e.g. photoacoustic microscopy).
- Photoacoustic examinations of collision processes in gases .

3.2 - Atomic Spectroscopy

When a beam of polychromatic light is passed through a prism or grating , it is broken up into its constituent colors. This array of colors is known as spectrum. The spectrum we see is only the visible region which extends from 4300 to 6900 A^o . However the complete spectrum may extend over wide range from γ-rays of wavelength 10^{-13} m to radiowaves of wavelengths 10^6 metres.There are two principal classes of spectrum , known as emission spectrum & absorbtion spectrum.

1. Emission Spectrum- This type of spectrum may be obtained , when the light coming after passing through a prism or a grating, is examined directly with a spectroscope. It is further classified into three categories according to their appearance.

(a) Continuous Spectrum – When the source emitting light is an incandescent solid, liquid or gas at a high temperature, the spectrum so obtained is continuous i.e whenever matter in the bulk is heated. example : hot filament, hot iron, hot Charcoal give the continuous spectrum.

Important characteristics are :

- *It* consists of a wide range of continuous wavelength lines red to violet which appear as continuous luminous band of light.
- The intensity of spectrum is not uniform over the entire spectrum. It becomes maximum at a particular wavelength & decrease on either side. The point of maximum intensity shifts towards the violet when the temperature of light emitting solid is raised.

- The general appearance of the Continuous Spectrum is independent of the nature of the light emitting substance.

(b) Line spectrum – This is obtained when the light emitting substance is in the **atomic state.** Therefore it is also called **Atomic Spectrum. Line** spectrum consists of discrete wavelengths extended throughout the spectrum & is a generally obtained from the light sources like mercury, sodium, neon discharge tube etc.

Important characteristics are :

- In it the spectral lines are regularly spaced.
- The wavelengths of the lines emitted are the characteristics of the element under consideration. It is independent of the compound in which the element may occur.
- Under a high resolving power instrument, the different lines are regularly spaced but they differ in their intensities.
- It can be observed against a dark or a faint continuous background.

(c) Band Spectrum – This type of spectrum arises when the emitter in the molecular state is excited. Each molecule emits bands which are characteristic of molecules therefore it is called **molecular spectrum** also. The sources of band spectrum are (i) carbon on arc with a metallic salt in its core (ii) Vaccum tubes

Important characteristics are :

- It consists of luminous bands separated by dark spaces.
- When each band is observed under a high resolving power apparatus, each band is seen to be composed of a large number of fine lines. These lines when observed along the long wave-length edge, becomes closer & closer until they coincide. This edge is known as ‘Band – head’.
- The lines of band constitute characteristic of the molecules & the method of their excitation.

2. Absorption Spectrum – When the light from a source emitting a continuous spectrum is first passed

Through an absorbing substance, & then observed through a spectroscope , it will be found that certain colors (or wavelength) are missing which leave dark lines or bands at their places. The observed spectrum is called **absorption spectrum.** The region of spectrum absorbed depends upon the nature of the absorbing material. It is also of three types as follows:

- Continuous absorption spectrum : This type of spectrum arises when the absorbing material absorbs a continuous range of wavelengths. Example: red glass absorbs all colors except red & hence, a continuous absorption spectrum will be obtained.

- Line absorption spectrum : In this type , sharp dark lines will be observed when the absorbing substance is a vapor or a gas. Example – The spectrum obtained from sun gives Fraunhofer absorption lines corresponding to vapors of different elements which are supposed to be present on the surface of sun.

- Band absorption spectrum : When the absorption spectrum is in the form of dark bands, this is known as band absorption spectrum. Example – Aqueous solution of $KMnO_4$ gives five absorption bands in the green region.

3.2.1 Energies of Atomic Orbitals

Electrons exist in different energy levels. Electrons have wave properties. These are added to the various orbitals , filling the higher energy levels as the size of the atom increases.

There are three orbital quantum numbers that describe an orbital. They are called n, l and m_l. The principal quantum number n determines the size of the atom. The second orbital quantum number l determines the shape of the orbital in a general way. The third quantum number m_l determines the orientation, with respect to an applied magnetic field.

The value of n can be any positive integer (1, 2, 3, 4, etc.) The value of l is from zero to n-1. Thus for $n = 1$, the value of l is 0. For $n = 2$, l can be 0 or 1. For $n = 3$, l can be 0, 1 or 2. For $n = 4$, l can have values of 0, 1, 2 or 3. The various shapes that correspond to the values of l are referred to as *s, p, d* and *f* orbitals.

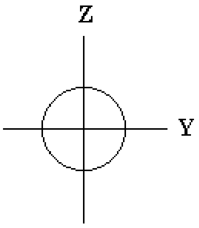
L	0	1	2	3
orbital	*s*	*p*	*d*	*f*

A given orbital can be described by combining the first and second quantum numbers n and l.1s, 2s, 2p, 3s, 3p, 3d, 4s, 4p, 4d, 4f, 5s, etc.The third quantum number has the range $-l$ to l. Thus for $l = 0$ there is only one value for m_l (0). For $l = 1$ there can be three values for m_l (-1, 0 or 1). For $l = 2$, m_l can have five values (-2, -1, 0, 1 or 2). For $l = 3$, m_l can have seven values (-3, -2, -1, 0, 1, 2 or 3). Thus for the *s* orbital there is only one value for m_l. For a *p* orbital there are 3 orientations. For a *d* orbital there are five orientations. For an *f* orbital there are 7 orientations.

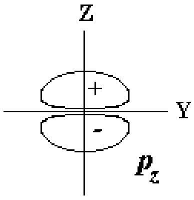
Orbital	*s*	*p*	*d*	f
orientations	1	3	5	7

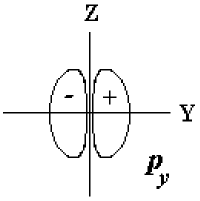
There is a fourth quantum number m_s. This is called the spin quantum number. It can have two values, 1/2 and -1/2. This is because an electron can orient in two ways in an applied magnetic field clockwise or counter clockwise. Thus an orbital specified by the first three quantum numbers can be occupied by only two electrons.

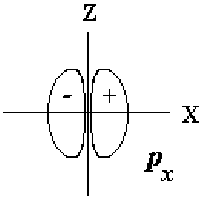
The shapes or orbitals are described by surfaces through regions of equal probability.An *s* orbital is spherical. An *s* orbital is shown below.



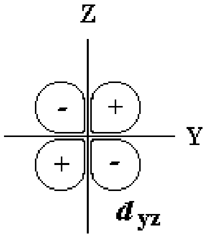
A *p* orbital has two parts separated by a nodal plane where the probability is zero. There are three orientations available for a *p* orbital. They are named p_z, p_y and p_x. These are shown below.

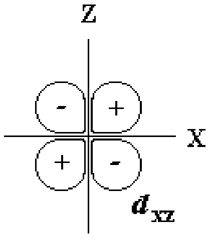


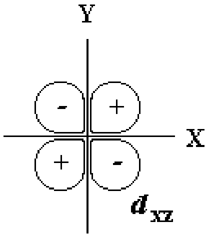


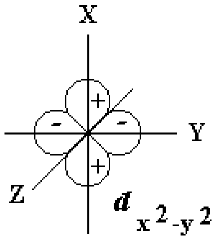


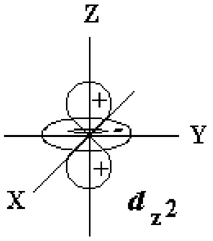
A *d* orbital has four lobes. The probability is zero between the lobes. There are five possible orientations. These are shown below.











The first quantum number determines the size, i.e., a 1*s* orbital is smaller than a 2*s* orbital which is smaller than a 3*s* orbital, etc. The energy of an orbital is determined mostly by the first two quantum numbers. The order in increasing energy is given below.

1s, 2s, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p, 7s, 5f , 6d

Electrons enter in the lowest energy orbitals .For hydrogen the single electron goes into the 1*s* orbital. This is the ground state, the state of lowest energy for the hydrogen atom. The electron may be elevated into higher energy orbitals by absorbing the energy of a photon of the right frequency. As the electron falls back to the ground state energy is released. The energy of the photon emitted depends on the energy difference between the orbits involved in the transition.

For helium the two electrons, one of spin 1/2 and the other of spin -1/2, are placed in the 1*s* orbital. The 1*s* orbital is filled with two electrons. This is represented as $1s^2$. The next electron (lithium) goes into the orbital with the next highest energy, the 2*s* orbital. This is written $1s^2 2s^1$. Similarly The carbon atom has six electrons. The lowest energy is achieved by placing the next electron in one of the unoccupied 2*p* orbitals. Furthermore the lowest energy is achieved if both the 2*p* electrons have the same spin (parallel spin). Such electrons are called *unpaired*. The lowest energy carbon atom electron configuration can be represented as $1s^2 2s^2\ 2p^2$ or $1s^2 2s^2\ 2p_x^1\ 2p_y^1$.

Orbital names : Orbitals are given names in the form : $X\ \mathrm{type}^y$

where *X* is the energy level corresponding to the principal quantum number *n*, **type** is a lower-case letter denoting the shape or subshell of the orbital and it corresponds to the angular quantum number *l*, and *y* is the number of electrons in that orbital.

For example, the orbital $1s^2$ has two electrons and is the lowest energy level ($n = 1$) and has an angular quantum number of $l = 0$. In X-ray notation, the *principal quantum number* is given a letter associated with it. For $n = 1, 2, 3, 4, 5, \ldots$, the letters associated with those numbers are *K*, *L*, *M*, *N*, *O*, ... respectively.

Atomic state specifies quantum numbers specially principal quantum number & orbital quantum number.The energies of each orbital varies from atom to atom & depend on two factors –

- Attraction between electrons & nucleus.
- Repulsion between electrons in the same atom.

The energy of electrons of an atom are known as terms of the atom & the corresponding energies expressed in wave numbers are called term values.

Example – Hydrogen atom having one electron does not experiences repulsion between electrons have energy levels corresponding to *l* is

l = 0 , 1, 2, 3
s, p, d, f terms

In atoms with a single electron (hydrogen-like atoms), the energy of an orbital is determined exclusively by *n*. The $n = 1$ orbital has the lowest possible energy in the atom. Each successively higher value of *n* has a higher level of energy, but the difference decreases as *n* increases. For high *n*, the level of energy becomes so high that the electron can easily escape from the atom. In single electron atoms, all levels with different ℓ within a given *n* are degenerate, and have the same energy.

In atoms with multiple electrons, the energy of an electron depends not only on the intrinsic properties of its orbital, but also on its interactions with the other electrons. These interactions depend on the its spatial probability distribution, and so the energy levels of orbitals depend not only on *n* but also on ℓ. Higher values of ℓ are associated with higher values of energy; for instance, the 2*p* state is higher than the 2*s* state. When $\ell = 2$, the increase in energy of the orbital becomes so large as to push the energy of orbital above the energy of the *s*-orbital in the next higher shell; when $\ell = 3$ the energy is pushed into the shell two steps higher. The filling of the 3d orbitals does not occur until the 4s orbitals have been filled.

The increase in energy for subshells of increasing angular momentum in larger atoms is due to electron-electron interaction effects, and it is specifically related to the ability of low angular momentum electrons to penetrate more effectively toward the nucleus, where they are subject to less screening from the charge of intervening electrons. Thus, in atoms of higher atomic number, the ℓ of electrons becomes more and more of a determining factor in their energy, and the principal quantum numbers *n* of electrons becomes less and less important in their energy placement.

The energy sequence of the first 24 subshells (e.g., 1s, 2p, 3d, etc.) is given in the following table. Each cell represents a subshell with *n* and ℓ given by its row and column indices, respectively. The number in the cell is the subshell's position in the sequence.

	S	***P***	***d***	***F***	*g*
1	1				
2	2	3			
3	4	5	7		
4	6	8	10	13	
5	9	11	14	17	*21*
6	12	15	18	*22*	
7	16	19	*23*		
8	*20*	*24*			

For S- orbital Schrodinger's equation for energy is

$$E_n = \frac{me^4}{8h^3c(E_0)^2n^2} = -\frac{R}{n^2} \quad (n = 1,2,3,4)$$

Where E_o – vaccum permittivity

R – Rydberg constant

m= mass , h – planck's constant

c- velocity of light.

for hydrogen p & d orbitals have same energy as s.

Lowest value of $E_n = -R\ cm^{-1}$ (n=1) represents stable or ground state. As n increases E_n also increases reaching to $E_n = 0$ for $n = \infty$. This represents ionization or complete removal of electron from nucleus. The closer the electron to the nucleus the more negative its energy due to the attraction between positive & negative charge particles.

3.2.2 - Vector Model of Atom - Vector Representation of Momenta

An electron moving in its orbital about a nucleus possesses orbital angular momentum given by *l* values & spin angular momentum given by spin quantum number s.
Total angular momentum = orbital angular momentumof electrons + spin angular momentum

Angular momentum is a vector quantity i;e it has magnitude as well as direction, therefore total angular momentum is also a vector quantity .This give rise to **vector model of the atom.**

Orbital angular momentum - The orbital angular momentum for an atomic electron is a vector model where the angular momentum vector is precessing about a direction in space. Since there is a magnetic moment associated with the orbital angular momentum, the precession can be compared to the precession of a classical magnetic moment caused by the torque exerted by a magnetic field. This precession is called Larmor precession and has a characteristic frequency called the Larmor frequency.

It is a special kind of vector because it's projection along a direction in space is quantized to values one unit of angular momentum apart. The possible values for the "magnetic quantum number" m_l for l=2 can take the values

$$m_\ell = -l, -l+1, \ldots, l-1, l\ .$$

$I = \sqrt{l(l+1)}.h/2\Pi$ & its Z component $l_z = m_I\, h/2\pi$

Where, l is orbital quantum number
$m_{I=}$ magnetic quantum number = l, l *-1, 0, -* l *+1, -l.*
l *is* always zero or positive hence so is I

l_z = 1 then l_z may be = +1, 0 ,-1
Similarly, l_z =2 then l_z may be = +2, +1 , 0, -1, -2

In general there are (2 l + 1) values of l_z for a given l. Thus , l_z is identified with the magnetic quantum number m, = m , Thus, m governs direction of an orbital.

In units of h/2π $I = \sqrt{l(l+1)}$. units
The orbital energy of the electron depends only on the magnitude & not on the direction of its angular momentum. Thus (2l + 1) values of l_z are all degenerate.

- The spin motion of the electron about an axis is designated by spin quantum number

The magnitude of spin angular momentum is - =
& its Z component $S_z = m_s$ h/2π
Where, s – spin quantum number & m_s is magnetic quantum number
S = + ½ then = units.
According to law of quantization for spin momentum the vector can point so as to have components in the reference direction which are half integral multiples of h/2π i;e S = S_z = h/2π where S_z = + ½ or -1/2.

Total Angular Momentum - It is the vector sum of orbital angular momentum & spin angular momentum

The magnitude & Z component of are specified by 2 quantum numbers j & $m_{j.}$

$$J_z = m_j \, h/2\pi$$

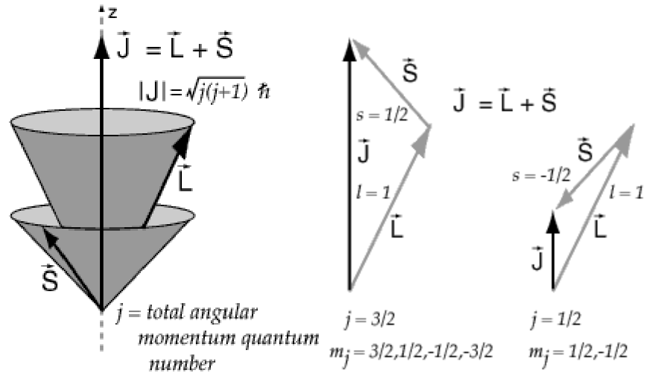
Where j is inner quantum number
m_j is magnetic quantum number
j is half integral since spin quantum number s is half integral for one electron atom.
J_z =
Possible values of m_z ranges from +j to –j in integral steps.
m_j = j, j-1…………….-j+1,

3.2.3 - Vector Coupling

Orbital Angular momentum & spin angular momentum couples with each other to give resultant momentum or total angular momentum. When orbital angular momentum **L** and electron spin angular momentum **S** are combined to produce the total angular momentum of an atomic electron, the combination process can be visualized in terms of a vector model. Both the orbital and spin angular momentua are seen as precessing about the direction of the total angular momentum **J**.

$\mathbf{J}_z = l_{z\ z}$
$m_z = m_1 + m_s$
Maximum value of m_j, $m_{I,}$ m_s are j, *l*, s respectively.
j= *l*
are all quantized, they can have only certain specific relative orientations.

For one electron atom, only two relative orientations possible,
j= *l* + so that
j= *l* – so that
The two ways in which can combine to form (when *l* =1, S = ½) are-



The angular momentum of the atomic electrons interact magnetically this is known as spin orbit interaction. The magnetic energy contribution is proportional to the component of total angular momentum along the direction of the magnetic field, which is usually defined as the z-direction.

If the atom is in free space so that no external torque acts on it, then conserved in magnitude as well as in direction. Thus the angle between would remain invariant.

$^{2} = {}^{2} + 2$ cos ((cosine law)

cos (= $\frac{^{2} - {}^{2} - {}^{2}}{2 +}$ = $\frac{j(j+1) - l\,(l+1) - S\,(S+1)}{2}$

The number of different possible orientations of & number of possible values of j is called multiplicity of the term. Multiplicity = 2S+1

Example For one electron system multiplicity = 2 X ½ +1 = 2

For s electron (ℓ = o) . The resultant s = = = or 1/2

As, s = -1/2 not allowed because quantum numbers cannot be negative only z component of vector can have negative values therefore state symbols is $S_{1/2.}$

For p electrons (ℓ =1) , therefore j = ½ represents $P_{3/2}$ .It occurs when I & S reinforce (same direction). If I & S oppose then j = 1/2 represents $P_{1/2}$ state as p split into two energies $P_{3/2}$ & $P_{1/2}$ known as doublet states, therefore, represented as $^2P_{3/2}$, $^2P_{1/2}$ and read as doublet P three halves or doublet P one half.
Similarly , If l =2 it produce $^2D_{5/2,3/2}$ states.
If l =3 it produce $^2F_{7/2,5/2}$ states.
If l =4 it produce $^2G_{9/2,5/2}$ states.
Transition between these states with different multiplicities are followed by selection rule.

Selection Rule - Δn = any integer , $\Delta\ell = 1$,

An electron in a lower state n_2 can undergo a transition into higher state n_1 with the absorption of energy $\Delta E = E_{n1} - E_{n2}$ cm^{-1}.

Coupling Schemes and Term Symbols

Term symbol gives the values of two angular momenta that may be coupled to give the total electronic angular momentum of a level (indicated by the J value). For configurations of more than one unfilled subshell, the angular momenta involved in the final coupling derive from two groups of electrons . These are often an inner group of coupled electrons and an outer group of coupled electrons, respectively. In any case the quantum numbers for the two groups can be distinguished by subscripts 1 and 2, so that quantum numbers represented by capital letters without subscripts are total quantum numbers for both groups. Thus, the quantum numbers for the two vectors that couple to give the final J are related to the term symbol as follows:

Coupling Scheme	**Quantum numbers for vectors that couple to give J**	**Term Symbol**
LS	L,S	${}^{2S+1}L$
$J_1\ J_2$	$J_1,\ J_2$	$(J_1,\ J_2)$
$J_1\ L_2(\rightarrow K)$	$K,\ S_2$	${}^{2S_2+1}[K]$
$LS_1(\rightarrow K)$	$K,\ S_2$	${}^{2S_2+1}[K]$

3.2.4 - Spectra of Hydrogen atom

The simplest atomic orbitals are those that occur in an atom with a single electron, such as the hydrogen atom. In this case the atomic orbitals are the eigenstates of the hydrogen Hamiltonian. An atom of any other element ionized down to a single electron is very similar to hydrogen, and the orbitals take the same form.

A given (hydrogen-like) atomic orbital is identified by unique values of three quantum numbers: n, l, and m_l. The stationary states (quantum states) of the hydrogen-like atoms are its atomic orbital. Electron states are best represented by time-depending "mixtures" (linear combinations) of multiple orbitals..

In modern quantum mechanics , n determines the mean distance of the electron from the nucleus; all electrons with the same value of n lie at the same average distance. For this reason, orbitals with the same value of n are said to comprise a "shell". Orbitals with the same value of n and also the same value of l are even more closely related, and are said to comprise a "subshell".

The atomic spectrum of hydrogen has played a significant role in the development of atomic structure. In the emission spectrum of hydrogen, when an electric discharge is passed through hydrogen gas, the molecules of hydrogen break into atoms. The hydrogen atoms get energized and go into an excited state. The excited atoms then return to the ground state by emitting light. Hydrogen atoms emit bluish light. On passing this light through a prism, a discontinuous line spectrum consisting of several sharp lines is obtained. This is the line spectrum of hydrogen.

Four sharp coloured lines were observed in the visible region of this spectrum by Balmer, in the ultra violet region by Lyman, in the infrared region by Paschen, Brackett and Pfund. These series of lines are named after these scientists who discovered them. Balmer expressed these lines in terms of inverse of their wavelength ($\bar{\nu}$) by a mathematical relation, which was later modified by Rydberg.

$$\bar{\nu}(\text{cm}^{-1}) = \frac{1}{\lambda(\text{cm})} = R_H\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

where 'R_H' is the Rydberg's constant and 'n_1', 'n_2' are integers with values equal to or greater than 3 and 'l' is the wavelength.

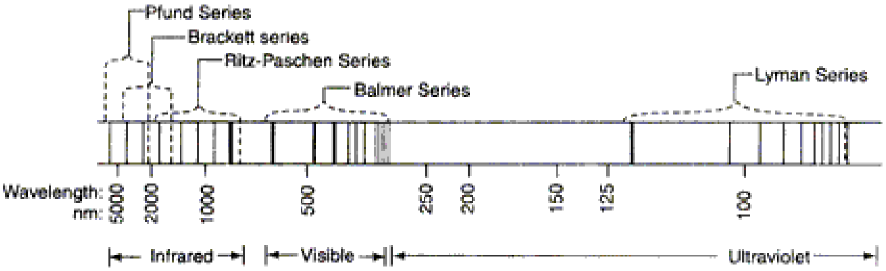
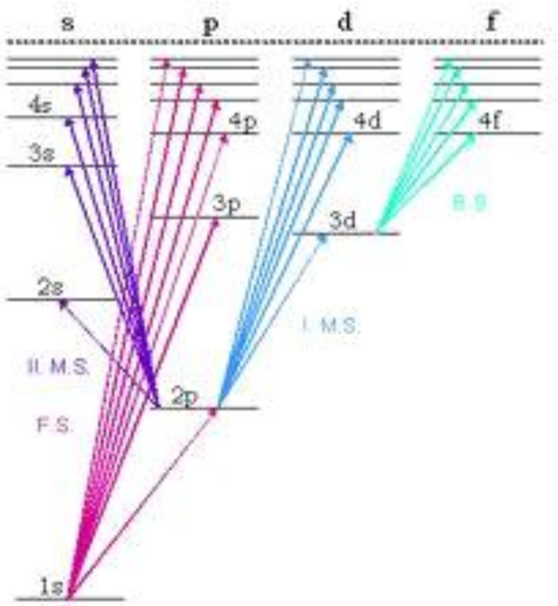


Fig: - Line spectrum of hydrogen atom

A particular *level* is denoted either by nl_j or by $nl\ {}^2L_J$ with $L = l$ and $J = j$. The latter notation is useful for more complex structures. The L values are written with the same letter code used for l values, but with roman capital letters. The *multiplicity* of the *L term* is equal to $2S + 1 = 2s + 1 = 2$. Written as a superscript, this number expresses the *doublet* character of the structure: each term for $L \geq 1$ has two levels, with $J = L \pm {}^1/_2$, respectively.

For, l = 0 , 1 , 2 , 3, 4
Energy levels = S , P , D , F, G
Lower Energy state = ${}^2s_{1/2}$
Higher energy state = ${}^2P_{1/2}{}^2P_{3/2}$

Selection rule Δn = any integer , $\Delta l = 1$,
Therefore allowed transitions are ${}^2S_{1/2}\ {}^2P_{1/2}$ $\Delta j = 0$
${}^2S_{1/2}\ {}^2P_{3/2}$ $\Delta j =$
j splitting decreases with increasing n & also with increasing l.
For S electron a doublet state is represented as ${}^2S_{1/2}$,transitions between ${}^2P$ & ${}^2D$
States are more complex. All lines in hydrogen should be close doublets if the transitions involve s levels & compound doublets if s electrons are not involved.



the largest energy separations are associated with levels having different *n*. The hyperfine splitting of the ^{1}H 1*s* ground level results from the interaction of the proton and electron magnetic moments . The separations of the 2*n* - 1 excited levels having the same *n* are largely determined by relativistic contributions, including the spin-orbit interaction, with the result that each of the *n* - 1 pairs of levels having the same *j* value is almost degenerate; the separation of the two levels in each pair is mainly due to relatively small (electron- electron interactions)Lamb shifts.

Transitions between orbitals

Under quantum mechanics, each quantum state has a well-defined energy. When applied to atomic orbitals, this means that each state has a specific energy, and that if an electron is to move between states, the energy difference is also very fixed.

Consider two states of the Hydrogen atom:

State 1) n=1, l=0, m_l=0 and s= $+{}^1\!/_2$
State 2) n=2, l=0, m_l=0 and s= $+{}^1\!/_2$

By quantum theory, state 1 has a fixed energy of E_1, and state 2 has a fixed energy of E_2.The electron need to gain an energy of exactly E_2 - E_1 to jump from E_1 to E_2. If the electron receives energy that is less than or greater than this value, it cannot jump from state 1 to state 2. Now, suppose we irradiate the atom with a broad-spectrum of light. Photons that reach the atom that have an energy of exactly E_2 - E_1 will be absorbed by the electron in state 1, and that electron will jump to state 2. However, photons that are greater or lower in energy cannot be absorbed by the electron, because the electron can only jump to one of the orbitals, it cannot jump to a state between orbitals. The result is that only photons of a specific frequency will be absorbed by the atom. This creates a line in the spectrum, known as an absorption line, which corresponds to the energy difference between states 1 and 2.

3.2.5- Spectra of Alkali metal atoms

For atoms with two or more electrons, there exists no angular-momentum coupling between a closed subshell and an electron outside the subshell, since the net spin and orbital angular momenta of the subshell are both zero. The *nlj* quantum numbers are, then, again appropriate for a single electron outside closed subshells. However, the electrostatic interactions of this electron with the core electrons and with the nucleus yield a strong *l*-dependence of the energy levels. The differing extent of "core penetration"" for *ns* and *np* electrons can in some cases, for example, give an energy difference comparable to or exceeding the difference between the *np* and $(n + 1)p$ levels. The spin-orbit fine-structure separation between the *nl* $(l > 0)$ levels having $j = l - {}^{1}/_{2}$ and $l + {}^{1}/_{2}$, respectively, is relatively small. .

Alkali metals like – Li, Na, K, Rb, Cs having atomic number Z consists of an inert gas core compound of nucleus & few complete subshells having Z-1 electrons, plus a single valence electron in the outermost subshells.

Example Li – $1s^2,2s^1$
Na – $1s^2,2s^22p^63s^1$

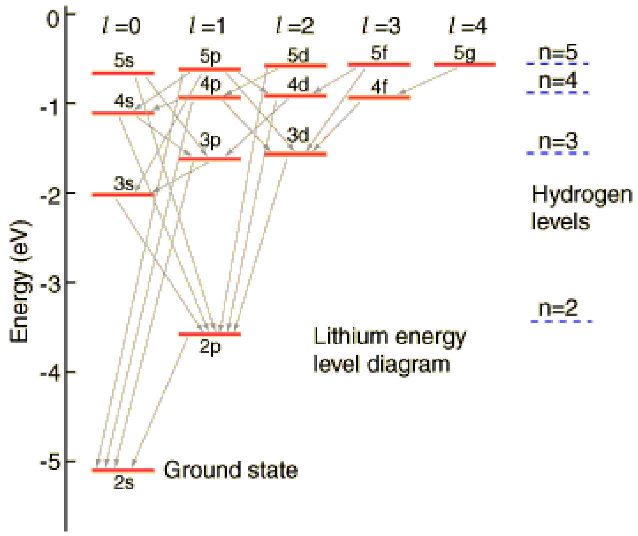
They resemble to hydrogen superficially, as 1s state is completely filled with 2 electrons which generally do not participate in transitions (angular momentum of the core can be ignored) .Only spin & angular momentum of the outer valence electron can be deal because much less energy is required to induce 2s electrons to undergo transitions.

1s electron may be promoted under high energy conditions. Like hydrogen atom, the selection rule for alkali metals are – Δn = any integer , $\Delta \ell = 1$,

Therefore their spectra are also expected to be similar to hydrogen atom. The transitions from Ground state of lithium ($1s^2,2s^1$) can occur to p- levels $^2S_{1/2}$ $^2P_{1/2,3/2}$ & a series of doublets similar to the lyman series will be formed converging to the same point from which ionization potential can be found. Two separate series of lines from 2p state are
$^2P_{1/2,3/2}$ n $^2S_{1/2}$ $^2P_{1/2,3/2}$ n $^2D_{3/2,5/2}$

The former transition will give rise to doublets & the later will yield compound doublets.Their frequencies will be different because the energies of s- & d- orbitals also differ.

Lithium Energy Levels



The lithium atom has a closed n=1 shell with two electrons and then one electron outside. Since the outer electron looks inward at just one net positive charge, it could be expected to have energy levels close to those of hydrogen. This is true for high angular momentum states, but the s and p states fall well below the corresponding hydrogen energy levels.

For other alkali metals j-splitting increase because of coupling between I & s increases significantly with increase in atomic number. Thus the doublet separation of lines in spectral series , which is almost non – observable for hydrogen atom, is less than 1 cm^{-1} for the 2p-level of lithium, about 17 cm^{-1} for sodium, & over 5000 cm^{-1} for cesium.

Except for lithium, the completed highest subshell is p-subshell & the next s- subshell is outermost one. In the optical or low energy excitation processes only valence electron is excited & so it is responsible for optical spectra.

The energy of electron in a completed p-subshell is quite more negative than energy of electron in next s- subshell consequently p electrons are not excited in low energy process . Thus the noble gas core, having a symmetrical distribution of charge does not play any role.

Example – Sodium whose normal outer configuration is 3s & the corresponding term is an S-term. The various possible excited configurations & the corresponding terms are

4s,5s,6s - - - S- terms
3p, 4p, 5p --- P terms
3d ,4d, 5d --- D- terms
4f , 5f, 6f - -- F- terms

The total energy of the core does not change in excitation. Thus, the total energy of the atom is a constant plus the total energy of the valence electron also known as optically active electron. For the sake of convenience, constant is taken as zero, so that the total energy of the atom in a certain state is equal to that of the optically active electron in that state.

The energy of an alkali metal atom in a certain state depends not only upon n but also *l* values of the optically active electron, because the probability of finding electron near the nucleus is largest for l=0 (s-electron) & decreases rapidly with increasing l. Thus for a given n, the energy is most negative for the s- electron which spends more time near the nucleus & feels almost the full nuclear charge & become less & less negative for the p,d,f --- electrons. In the case of sodium, the 4s level is more negative in energy than the 3d level. Thus, all alkali metal levels of a given n are shifted lower than the corresponding level of hydrogen , the shift being greatest for the s- level & becoming smaller & smaller for p, d, f --- levels.

When the sodium atom is excited by suitable means, the 3s electron is raised to be any of the excited levels 3p, 4s, 3d,4p,4d,4f,5s,5p---- etc. from which it comes back through any selected path governed by the selection rules, Δn = any integer , $\Delta l = 1$.

The observed series in the emission spectrum arise from the following transitions.

np	3s, n > 2	principal series
ns	3p, n > 3	sharp series
nd	3p, n > 2	diffuse series
nf	3d , n>3	fundamental series

All possible excited states are available for the transitions which take place through all the allowed paths because sodium source contains numerous atoms.

All four series are simultaneously emitted in the spectrum , as the electron returns to the ground state (which involves the principal series) , the lines of the principal series are most intense. Since for hydrogen atom, the energy in different states, S,P,D --- of the same n is same, the four different series observed in the spectra of alkali metal atoms become identical in the spectrum of hydrogen atom.

The sharp & diffuse series have the same convergence limit (3p level) , the limit corresponding to the jump of electron from infinity to the level 3p. The wave number difference between the limit (3p level) & principal series limit (3s level) is equal to the wave number of the first line (3p3s) of the principal series. Similarly, the wave number difference between the diffuse series limit (3p level) & the fundamental series limit (3d level) is equal to the wave number of the first line(3d3p) of the diffuse series.

CHECK YOUR PROGRESS - 1
Notes : i) Write your answer in the space given below.
ii) Compare your answer with those given at the end of the unit.

Q.1 Give the examples showing the continuous spectrum ?
Q.2 Continuous Spectrum is --------- (dependent / independent) of the nature of the light emitting substance.
Q.3 The orbital quantum number *l* determines the ------ (position / shape) of the orbital.
Q.4 Angular momentum is a --------- quantity . (vector /scalar)
Q..5 How can we find out the total angular momentum ?
Q.6 The probability of finding electron near the nucleus is ---------& rapidly with increasing l.
Q.7 The total energy of the core --------- change in excitation.

3.3- Molecular spectroscopy

It is the branch of Spectroscopy in which the interaction of electromagnetic radiation with matter deals with the transitions in a molecule between its energies (rotational, vibrational , electronic etc.) on the absorption of photon of suitable energy .It's an Absorption Spectroscopy because the temperature at which the molecules emit light very high at which the molecule decomposes therefore emission spectra is not observed.

Principle

A molecule is a collection of positively charged atomic nuclei surrounded by a cloud of negatively charged electrons. Its stability results from a balance among the attractive and repulsive forces of the nuclei and electrons. A molecule is characterized by the total energy resulting from these interacting forces. As is the case with atoms, the allowed energy states of a molecule are quantized.

Molecular spectra result from either the absorption or the emission of electromagnetic radiation as molecules undergo changes from one quantized energy state to another. In order to analyze molecular spectra it is necessary to consider simultaneously the effects of all the contributions from the different types of **molecular motions and energies**.

There are two primary sets of interactions that contribute to observed molecular spectra-

- The first involves the internal motions of the nuclear framework of the molecule and the attractive and repulsive forces among the nuclei and electrons.
- The other encompasses the interactions of nuclear magnetic and electrostatic moments with the electrons and with each other.

TYPES OF ENERGIES POSSESSED BY THE MOLECULE-

ELECTRONIC ENERGY - The electrons in a molecule possess kinetic energy due to their motions and potential energy arising from their attraction by the positive nuclei and their mutual repulsion. These two energy factors, along with the potential energy due to the mutual electrostatic repulsion of the positive nuclei, constitute the electronic energy of a molecule.

VIBRATIONAL ENERGY- Molecules are not rigid structures, and the motion of the nuclei within the molecular framework gives rise to vibrational energy levels.

ROTATIONAL ENERGY- In the gas phase, where they are widely separated relative to their size, molecules can undergo free rotation and as a result possess quantized amounts of rotational energy.

TRANSLATIONAL ENERGY- In theory, the translational energy of molecules through space is also quantized, but in practice the quantum effects are so small that they are not observable, and the motion appears continuous.

MOLECULAR SPECTRA-

Molecular spectra is observed when a molecule undergoes the absorption or emission of electromagnetic radiation with a resulting increase or decrease in energy. The first condition for the absorption of electromagnetic radiation by a molecule undergoing a transition from a lower energy state, E_{lo}, to a higher energy state, E_{hi}, is that the frequency of the absorbed radiation must be related to the change in energy by $E_{hi} - E_{lo} = h\nu$, where ν is radiation frequency and h is Planck’s constant.

Conversely, the application of electromagnetic radiation of frequency ν to a molecule in energy state E_{hi} can result in the emission of additional radiation of frequency ν as the molecule undergoes a transition to state E_{lo}. Also a molecule in an excited (high) energy state can spontaneously emit electromagnetic radiation, returning to some lower energy level without the presence of inducing radiation.

3.3.1- ENERGY LEVEL AND MOLECULAR ORBITALS

A quantum mechanical system or particle that is bound (confined spatially) can only take on certain discrete values of energy. These discrete values are called **energy levels**. The term is commonly used for the energy levels of electrons in atoms or molecules, which are bound by the electric field of the nucleus, but can also refer to energy levels of nuclei or vibrational or rotational energy levels in molecules. The energy spectrum of a system with such discrete energy levels is said to be quantized.

If the potential energy is set to zero at infinite distance from the atomic nucleus or molecule, the usual convention, then bound electron states have negative potential energy. If more than one quantum mechanical state is at the same energy, the energy levels are " degenerate ". They are then called degenerate energy levels.

Quantized energy levels result from the relation between a particle's energy and its wavelength. For a confined particle such as an electron in an atom, the wave function has the form of standing waves. Only stationary states with energies corresponding to integral numbers of wavelengths can exist; for other states the waves interfere destructively, resulting in zero probability density.

Assume there is one electron in a given atomic orbital in a hydrogen-like atom (ion). The energy of its state is mainly determined by the electrostatic interaction of the (negative) electron with the (positive) nucleus. The energy levels of an electron around a nucleus are given by :

$$E_n = -hcR_\infty \frac{Z^2}{n^2}$$

where R_∞ is the Rydberg constant , Z is the Atomic number, n is the principal quantum number h is Planck's constant, and c is the speed of light. For hydrogen-like atoms (ions) only, the Rydberg levels depend only on the principal quantum number n.

If there is more than one electron around the atom, electron-electron-interactions raise the energy level. These interactions are often neglected if the spatial overlap of the electron wavefunctions is low.There is an interaction energy associated with the magnetic dipole moment, μ_L, arising from the electronic orbital angular momentum, L, given by

$$U = -\boldsymbol{\mu}_L \cdot \mathbf{B}$$

Molecular Orbitals-

Chemical bonds between atoms in a molecule form because they make the situation more stable for the involved atoms, which generally means the sum energy level for the involved atoms in the molecule is lower than if the atoms were not so bonded. As separate atoms approach each other to covalently bond, their orbitals affect each others energy levels to form bonding and anti-bonding molecular orbitals. The energy level of the bonding orbitals is lower, and the energy level of the anti-bonding orbitals is higher. For the bond in the molecule to be stable, the covalent bonding electrons occupy the lower energy bonding orbital, which may be signified by such symbols as σ or π depending on the situation.

Corresponding anti-bonding orbitals can be signified by adding an asterisk to get σ* or π* orbitals. In polyatomic molecules, different vibrational and rotational energy levels are also involved.A molecular energy state, i.e. an eigenstate of the molecular Hamiltonian, is the sum of the electronic, vibrational, rotational, nuclear, and translational components, such that:

$$E = E_{\text{electronic}} + E_{\text{vibrational}} + E_{\text{rotational}} + E_{\text{nuclear}} + E_{\text{translational}}$$

Where $E_{\text{electronic}}$ is an eigenvalue of the electronic molecular Hamiltonian (the value of the potential energy surface) at the equilibrium geometry of the molecule.The molecular energy levels are labelled by the molecular term symbols.The specific energies of these components vary with the specific energy state and the substance.

Molecules can undergo transitions in their vibrational or rotational energy levels. Energy level transitions can also be non radiative, meaning emission or absorption of a photon is not involved.

If an atom, ion, or molecule is at the lowest possible energy level, it and its electrons are said to be in the *ground state*. If it is at a higher energy level, it is said to be *excited*, or any electrons that have higher energy than the ground state are *excited*.

An asterisk is commonly used to designate an excited state. An electron transition in a molecule's bond from a ground state to an excited state may have a designation such as σ→σ* or π→π* , meaning excitation of an electron from a σ bonding to a σ antibonding orbital or from a π bonding to a π anti bonding orbital.

3.3.2 -VIBRIONIC TRANSITION AND VIBRATIONAL PROGRESSION

Vibronic transitions are the simultaneous changes in electronic and vibrational energy levels of a molecule due to the absorption or emission of a photon of the appropriate energy.A transition in an energy level of an electron in a molecule may be combined with a vibrational transition and called a vibronic transition.

Some electronic-forbidden transitions as weak bands in spectrum can be explained by the interaction between the electronic and vibrational transitions. **The word "vibronic" is the combination of the words "vibrational" and "electronic**."

A vibrational and rotational transition may be combined by vibrational coupling. In vibronic coupling, electron transitions are simultaneously combined with both vibrational and rotational transitions. Photons involved in transitions may have energy of various ranges in the electromagnetic spectrum, depending on the type of transition. In a very general way, energy level differences between electronic states are larger, differences between vibrational levels are intermediate, and differences between rotational levels are smaller, although there can be overlap. Translational energy levels are practically continuous and can be calculated as kinetic energy using classical mechanics.

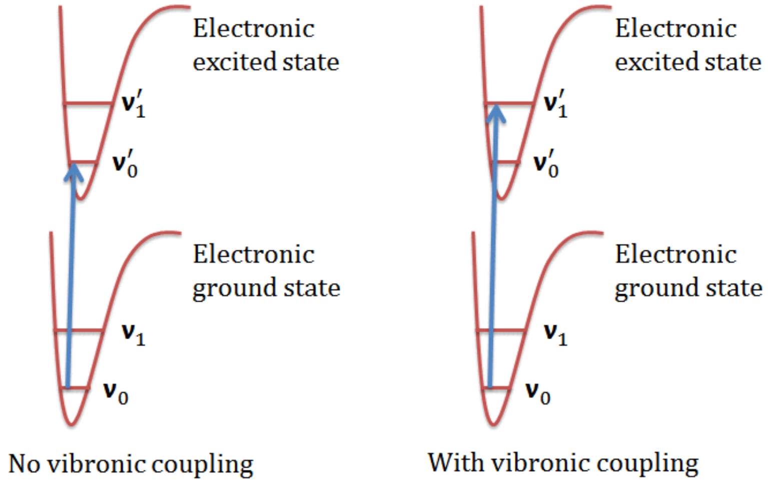


Fig. 4 Pure electronic transition and the electronic transition couples with the vibrational transition

Vibrational state may be regarded as the most likely state for the termination of electronic transition. The vibrational structure of the spectrum depends on the relative horizontal position of the two.

3.3.3 -Geometry of the molecule in excited state

In an excited electronic state ,a molecule may have a quite different shape from that in the ground state. for example ,the dimensions of acetylene in the ground state and first excited are –

	Normal (angstrom)	Excited(angstrom)
C-C bond length	1.208	1.385
C-H bond length	1.058	1.080
C-C-H angle(degree)	180	120

In ground state C_2H_2 molecule is linear but in excited state structure becomes bent. In the electronic excitation an electron is removed from a π orbital and placed in a sigma orbital.

3.3.4 -The Franck–Condon principle

Franck-Condon principle was proposed by German physicist James Franck (1882-1964) and U.S. physicist Edward U. Condon (1902-1974) in 1926.

This principle states that when an electronic transition takes place, the time scale of this transition is so fast compared to nucleus motion that we can consider the nucleus to be static, and the vibrational transition from one vibrational state to another state is more likely to happen if these states have a large overlap. It successfully explains the reason why certain peaks in a spectrum are strong while others are weak (or even not observed) in absorption spectroscopy.

Rule in spectroscopy and quantum chemistry that explains the intensity of vibronic transitions. Vibronic transitions are the simultaneous changes in electronic and vibrational energy levels of a molecule due to the absorption or emission of a photon of the appropriate energy.

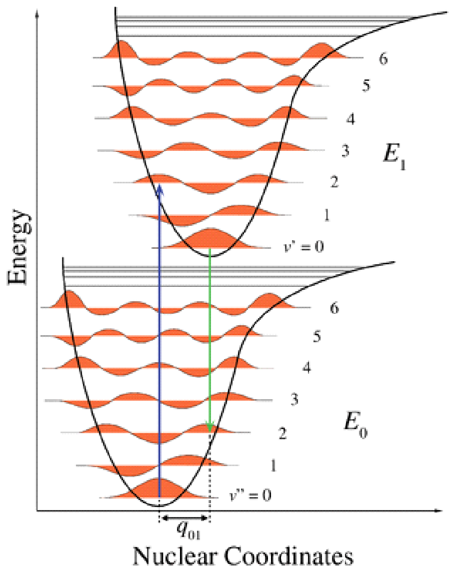


Fig . Franck–Condon principle energy diagram.

Since electronic transitions are very fast compared with nuclear motions, vibrational levels are favored when they correspond to a minimal change in the nuclear coordinates. The potential wells are shown favoring transitions between *v* = 0 and *v* = 2.

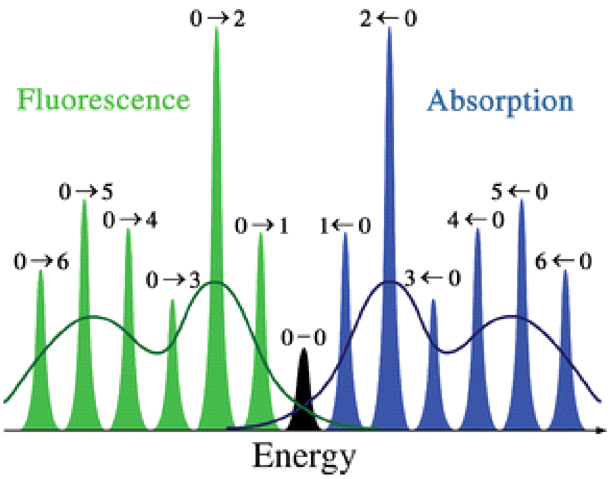


Figure. Schematic representation of the absorption and fluorescence spectra

The symmetry is due to the equal shape of the ground and excited state potential wells. The narrow lines can usually only be observed in the spectra of dilute gases. The darker curves represent the inhomogeneous broadening of the same transitions as occurs in liquids and solids. Electronic transitions between the lowest vibrational levels of the electronic states (the 0-0 transition) have the same energy in both absorption and fluorescence.

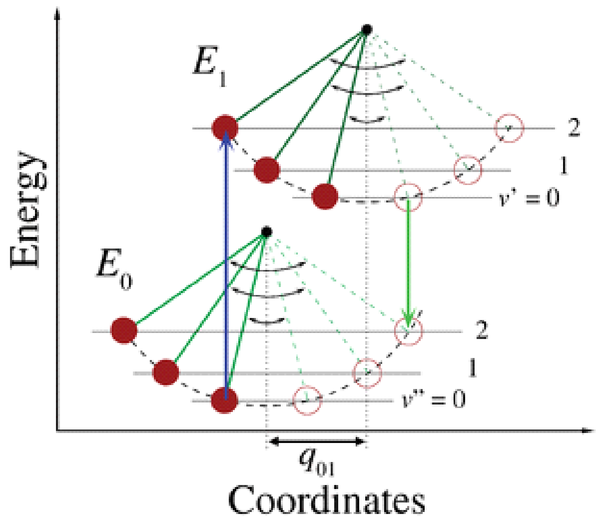


Fig. Semiclassical pendulum analogy of the Franck-Condon principle.

Vibronic transitions are allowed at the classical turning points because both the momentum and the nuclear coordinates correspond in the two represented energy levels. In this illustration, the 0-2 vibrational transitions are favored.

The Franck-Condon principle has a well-established semiclassical interpretation. Electronic transitions are essentially instantaneous compared with the time scale of nuclear motions, therefore if the molecule is to move to a new vibrational level during the electronic transition, this new vibrational level must be instantaneously compatible with the nuclear positions and momenta of the vibrational level of the molecule in the originating electronic state. In the semiclassical picture of vibrations (oscillations) of a simple harmonic oscillator, the necessary conditions can occur at the turning points, where the momentum is zero.

The Franck–Condon principle is the approximation that an electronic transition is most likely to occur without changes in the positions of the nuclei in the molecular entity and its environment. The resulting state is called a Franck–Condon state, and the transition involved, a vibrionic transition. The quantum mechanical formulation of this principle is that the intensity of a vibronic transition is proportional to the square of the overlap integral between the vibrational wavefunctions of the two states that are involved in the transition.

In the simplest case of a diatomic molecule the nuclear coordinates axis refers to the internuclear separation. The vibronic transition is indicated by a vertical arrow due to the assumption of constant nuclear coordinates during the transition. The probability that the molecule can end up in any particular vibrational level is proportional to the square of the (vertical) overlap of the vibrational wave functions of the original and final state. In the electronic excited state molecules quickly relax to the lowest vibrational level (Kasha's rule), and from there can decay to the lowest electronic state via photon emission. The Franck–Condon principle is applied equally to absorption and to fluorescence.

Applicability

The applicability of the Franck–Condon principle in both absorption and fluorescence, along with Kasha's rule leads to an approximate mirror symmetry . The vibrational structure of molecules in a cold, sparse gas is most clearly visible due to the absence of inhomogeneous broadening of the individual transitions. Vibronic transitions are narrow, equally spaced Lorentzian lineshapes. Equal spacing between vibrational levels is only the case for the parabolic potential of simple harmonic oscillators, in more realistic potentials, energy spacing decreases with increasing vibrational energy. Electronic transitions to and from the lowest vibrational states are often referred to as 0-0 (zero zero) transitions and have the same energy in both absorption and fluorescence.

3.3.5-Electronic Spectra of Polyatomic Molecules

The bound high energy electronic states in polyatomic molecules are not so abundant, because the energy of an electronically excited polyatomic molecule can usually be disturbed so as to break a weak chemical bond,one more consequence of this is that a sample usually cannot be heated to a temperature at which emission spectra can be obtained without danger of decomposition. Thus, the only transitions that are mostly obtained are those from the ground to an excited electronic state that can be seen in absorption spectra. Only a few bands arising from such transitions are usually obtained and the absorption bands are often broad and relatively structure less, because the samples under study are generally solutions or solids. Moreover ,a band doesn’t immediately reveal the nature of the electronic states involved in the transition.

The geometry of the molecule in excited states is not necessarily the same as that of the ground state. For example ,formaldehyde and ethylene are non planar in one or more of their excited state.

The absorption bands because of electronic transition, which usually occur in the ultraviolet or visible regions, play a important role in the analysis and characterization of organic and inorganic compounds.

There are polyatomic molecules that absorb radiation due to electronic transition which is essentially localized in a bond or group, of the molecule. The molecules containing conjugated π electron systems are other class of polyatomic compounds. Aromatic molecules are the most studied and largest group in this class.

Absorption spectra are also produced by systems containing a transition metal ion in a coordination compound .Many such systems are colored i.e. they have electronic transitions that result in absorption in the visible region. the spectrum of such a compound gives the characteristic of the material. Analysis of such absorption bands in terms of the electronic states involved leads to further understanding of the bonding in these coordination compounds.

3.3.6 -Emission Spectra

The **emission spectrum** of a chemical element or chemical compound is the spectrum of frequencies of electromagnetic radiation emitted by the element's atoms or the compound's molecules when they are returned to a lower energy state.

Each element's emission spectrum is unique. Therefore, *spectroscopy* ***can be used to identify the elements in matter of unknown composition***. Similarly, the emission spectra of molecules can be used in chemical analysis of substances.

Emission is the process by which a higher energy quantum mechanical state of a particle becomes converted to a lower one through the emission of a photon, resulting in the production of light. The frequency of light emitted is a function of the energy of the transition. Since energy must be conserved, the energy difference between the two states equals the energy carried off by the photon. The energy states of the transitions can lead to emissions over a very large range of frequencies.

For most substances, the amount of emission varies with the temperature and the spectroscopic composition of the object, leading to the appearance of color temperature and emission lines. Precise measurements at many wavelengths allow the identification of a substance via emission spectroscopy.

Origins of spectra

When the electrons in the atom are excited, for example by being heated, the additional energy pushes the electrons to higher energy orbitals. When the electrons fall back down and leave the excited state, energy is re-emitted in the form of a photon. The wavelength (or equivalently, frequency) of the photon is determined by the difference in energy between the two states. These emitted photons form the element's emission spectrum.

The fact that only certain colors appear in an emission spectrum means that only certain frequencies of light are emitted. Each of these frequencies are related to energy by the formula :

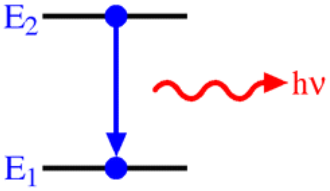
$$E_{\text{photon}} = h\,\nu,$$

where E is the energy of the photon, ν is its frequency, and h is Planck's constant. The principle of the atomic emission spectrum explains the varied colors in neon signs, as well as chemical flame test .

The frequencies of light that an atom can emit are dependent on states the electrons can be in. When excited, an electron moves to a higher energy level/orbital. When the electron falls back to its ground level the light is emitted.

Emission spectroscopy

Light consists of electromagnetic radiation of different wavelengths. Therefore, when the elements or their compounds are heated either on a flame or by an electric arc they emit energy in form of light. Analysis of this light, with the help of spectroscope gives us a discontinuous spectrum. A spectroscope or a spectrometer is an instrument which is used for separating the components of light, which have different wavelengths. The spectrum appears in a series of lines called the line spectrum. This line spectrum is also called the Atomic Spectrum because it originates in the element. Each element has a different atomic spectrum. The production of line spectra by the atoms of an element indicate that an atom can radiate only a certain amount of energy. This leads to the conclusion that electrons cannot have just any amount of energy but only a certain amount of energy.



Schematic diagram of spontaneous emission

Emission spectroscopy is a spectroscopic technique which examines the wavelengths of photons emitted by atoms or molecules during their transition from an excited state to a lower energy state. Each element emits a characteristic set of discrete wavelengths according to its electronic structure, by observing these wavelengths the elemental composition of the sample can be determined. Emission spectroscopy developed in the late 19th century and efforts in theoretical explanation of atomic emission spectra eventually led to quantum mechanics.

There are many ways in which atoms can be brought to an excited state. Interaction with electromagnetic radiation is used in fluorescence spectroscopy, protons or other heavier particles in Particle-Induced X-ray Emission and electrons or X-ray photons in Energy-dispersive X-ray spectroscopy or X-ray fluorescence. The simplest method is to heat the sample to a high temperature, after which the excitations are produced by collisions between the sample atoms. This method is used in flame emission spectroscopy, and it was also the method used by Anders Jonas Ångström when he discovered the phenomenon of discrete emission lines in 1850s.

Although the emission lines are caused by a transition between quantized energy states and may at first look very sharp, they do have a finite width, i.e. they are composed of more than one wavelength of light. This spectral line broadening has many different causes.

Emission spectroscopy is often referred to as **optical emission spectroscopy**, due to the light nature of what is being emitted.

In spectroscopy one can frequently find that atoms or molecules in the excited states dissipate their energy in the absence of any external source of photons. This is not spontaneous emission, but is actually nonradiative relaxation of the atoms or molecules caused by the fluctuation of the surrounding molecules present inside the bulk.

3.3.7 - Radiative & Non Radiative Decay

Radiative decay means that the quantum efficiency is 100%. Besides radiative decay, which occurs under the emission of light, there is a second decay mechanism ; nonradiative decay. To determine the total decay rate Γ_{tot}, radiative and nonradiative rates should be summed:

$$\Gamma_{tot} = \Gamma_{rad} + \Gamma_{nrad}$$

where Γ_{tot} is the total decay rate, Γ_{rad} is the radiative decay rate and Γ_{nrad} the nonradiative decay rate.

The rate of spontaneous emission (i.e., the radiative rate) can be described by Fermi's golden rule. The rate of emission depends on two factors: an 'atomic part', which describes the internal structure of the light source and a 'field part', which describes the density of electromagnetic modes of the environment. The atomic part describes the strength of a transition between two states in terms of transition moments. In a homogeneous medium, such as free space, the rate of spontaneous emission in the dipole approximation is given by:

$$\Gamma_{rad}(\omega) = \frac{\omega^3 n|\mu_{12}|^2}{3\pi\varepsilon_0\hbar c_0{}^3}$$

where ω is the emission frequency, *n* is the index of refraction, μ_{12} is the transition dipole moment, $\varepsilon_0$is the vacuum permittivity, $\hbar$ is the reduced Planck constant and c_0 is the vacuum speed of light. (This approximation breaks down in the case of inner shell electrons in high-Z atoms.) Clearly, the rate of spontaneous emission in free space increases with ω^3. In contrast with atoms, which have a discrete emission spectrum, quantum dots can be tuned continuously by changing their size.

In nonradiative decay, the energy is released as photons, more commonly known as heat. Nonradiative decay or transition occurs when the energy difference between the levels is very small, and these typically occur on a much faster time scale than radiative transitions.

For many materials (for instance, semiconductors), electrons move quickly from a high energy level to a meta-stable level via small nonradiative transitions and then make the final move down to the bottom level via an optical or radiative transition. This final transition is the transition over the bandgap in semiconductors. Large nonradiative transitions do not occur frequently because the crystal structure generally can't support large vibrations without destroying bonds .

3.3.8 -Internal conversion

Radioactive active process where an excited nucleus interacts with an electron in one of the lower atomic orbitals, causing the electron to be emitted from the atom. Thus, in an internal conversion process, a high-energy electron is emitted from the radioactive atom, but without beta decay taking place. For this reason, the high-speed electrons from internal conversion are not beta particles (β particles), since the latter come from beta decay.

Since no beta decay takes place in internal conversion, the element atomic number does not change, and thus no transmutation of one element to another is seen. Also, no neutron is emitted in internal conversion.

Internally converted electrons do not have the characteristic energetically-spread spectrum of β particles, which results from varying amounts of decay-energy being carried off by the neutrino (or antineutrino) in beta decay. Internally converted electrons, which carry a fixed fraction of the characteristic decay energy, have a well-specified discrete energy. The energy spectrum of a β particle is thus a broad hump, extending to a maximum decay energy value, while the spectrum of internally converted electrons is a sharp peak.

Mechanism

In the internal conversion process, the wave function of an inner shell electron penetrates the nucleus (i.e. there is a finite probability of the electron in an **s** atomic orbital being found in the nucleus) and when this is the case, the electron may couple to the excited state and take the energy of the nuclear transition directly, without an intermediate gamma ray being produced first.

As an electromagnetic quantum process, the process of imparting energy to the electron may be seen as taking place by means of a virtual photon, but in that sense the photon involved can be considered as a "virtual gamma ray", which never appears except as a feature of an equation, rather than a directly measurable particle. The kinetic energy of the emitted electron is equal to the transition energy in the nucleus, minus the binding energy of the electron.

Most internal conversion electrons come from the K shell as these two electrons have the highest probability of being found inside the nucleus. After the electron has been emitted, the atom is left with a vacancy in one of the inner electron shells. This hole will be filled with an electron from one of the higher shells and subsequently a characteristic x-ray or Auger electron will be emitted.

When the process is expected

Internal conversion is favoured when the energy gap between nuclear levels is small, and is also the primary mode of de-excitation for $0^+ \rightarrow 0^+$ (i.e. E0) transitions (i.e., where excited nuclei are able to rid themselves of energy without changing electric and magnetic moments in certain ways) with insufficient energy to decay by pair production. It is the predominant mode of de-excitation whenever the initial and final spin states are the same, but the multi-polarity rules for nonzero initial and final spin states do not necessarily forbid the emission of a gamma ray in such a case.

The tendency towards internal conversion can be determined by the internal conversion coefficient, which is empirically determined by the ratio of de-excitations that go by the emission of electrons to those that go by gamma emission.

The internal conversion process competes with gamma decay. This competition is quantified in the form of the internal conversion coefficient which is defined as $\alpha = e / \gamma$ where e is the rate of conversion electrons and γ is the rate of gamma-ray emission observed from a decaying nucleus.

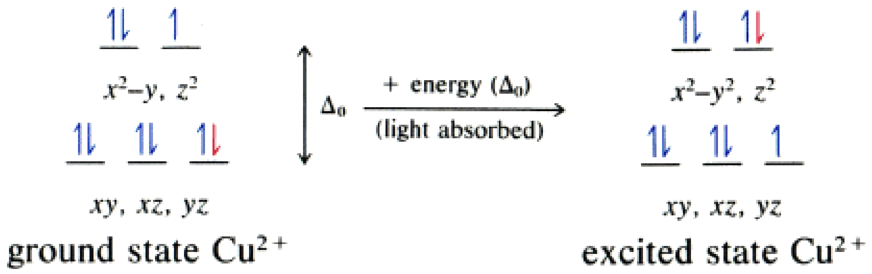
For example, in the decay of an excited state of the nucleus of ^{125}I, 7% of the decays emit energy as a gamma ray, while 93% release energy as conversion electrons. Therefore, this excited state of ^{125}I has an internal conversion coefficient of $\alpha = 13.6$. Internal conversion coefficients are observed to increase for increasing atomic number (Z) and decreasing gamma-ray energy.

The energy of the emitted gamma-ray is regarded as a precise measure of the difference in energy between the excited states of the decaying nucleus. However, this is not true in the case of conversion electrons. The energy of a conversion electron is given as $E = (E_i - E_f) - E_B$ where E_i and E_f are the energies of the nucleus in its initial and final states, respectively, while E_B is the binding energy of the electron.

3.3.9-Spectra of Transition Metal Complexes

The d-orbitals of a free transition metal atom or ion are degenerate (all have the same energy.) However, when transition metals form coordination complexes, the d-orbitals of the metal interact with the electron cloud of the ligands in such a manner that the d-orbitals become non-degenerate (not all having the same energy.) The way in which the orbitals are split into different energy levels is dependent on the geometry of the complex. Crystal field theory can be used to predict the energies of the different d-orbitals, and how the d-electrons of a transition metal are distributed among them. When the d-level is not completely filled, it is possible to promote and electron from a lower energy d-orbital to a higher energy d-orbital by absorption of a photon of electromagnetic radiation having an appropriate energy. Electromagnetic radiations in the visible region of the spectrum often possess the appropriate energy for such transitions.

For example - The solutions of most octahedral Cu (II) complexes are blue. The visible spectrum for an aqueous solution of Cu (II), $[Cu(H_2O_6]^{2+}$, shows that the absorption band spans the red-orange-yellow portion of the spectrum and green, blue and violet are transmitted.The absorption band corresponds to the energy required to excite an electron from the t_{2g} level to the e_g level.



the energy possessed by a light wave is inversely proportional to its wavelength. The Cu(II) solution transmits relatively high energy waves and absorbs the low energy wavelengths. This indicates that the band gap between the two levels is relatively small for this ion in aqueous solution.

3.3.10-Charge-transfer spectra

A **charge-transfer complex** (**CT complex**) or **electron-donor-acceptor complex** is an association of two or more molecules, or of different parts of one very large molecule, in which a fraction of electronic charge is transferred between the molecular entities. The resulting electrostatic attraction provides a stabilizing force for the molecular complex. **The source molecule from which the charge is transferred is called the electron donor and the receiving species is called the electron acceptor.**

The nature of the attraction in a charge-transfer complex is not a stable chemical bond, and is much weaker than covalent forces. The attraction is created by an electronic transition into an excited electronic state, and is best characterized as a weak electron resonance. The excitation energy of this resonance occurs very frequently in the visible region of the electro-magnetic spectrum, which produces the usually intense color characteristic for these complexes. These optical absorption bands are often referred to as *charge-transfer bands* (CT bands). Optical spectroscopy is a powerful technique to characterize charge-transfer bands.

Charge-transfer complexes exist in many types of molecules, inorganic as well as organic, and in all phases of matter, i.e. in solids, liquids, and even gases·A well-known example is the blue charge-transfer band exhibited by iodine when `combined with starch.

In inorganic chemistry, most charge-transfer complexes involve electron transfer between metal atoms and ligands. The charge-transfer bands in transition metal complexes result from movement of electrons between molecular orbitals (MO) that are predominantly metal in character and those that are predominantly ligand in character.

Ligand-to-metal charge-transfer (LMCT) complex- In it the electron moves from the MO with ligand like character to the metal.

Metal-to-ligand charge-transfer (MLCT) complex – In it the electron moves from the MO with metal like character to the ligand.

Thus, a MLCT results in oxidation of the metal center whereas a LMCT results in the reduction of the metal center. Resonance Raman Spectroscopy is also a powerful technique to assign and characterize charge-transfer bands in these complexes.

The charge-transfer association occurs in a chemical equilibrium with the independent donor (D) and acceptor (A) molecules:

$$D + A \rightleftharpoons DA$$

Quantum mechanically, this is described as a resonance between the non-bonded state |D, A> and the dative state $|D^+...A^->$. The formation of the dative state is an electronic transition giving rise to the colorful absorption bands.

The intensity of charge-transfer bands in the absorbance spectrum is strongly dependent upon the degree (equilibrium constant) of this association reaction. Methods have been developed to determine the equilibrium constant for these complexes in solution by measuring the intensity of absorption bands as a function of the concentration of donor and acceptor components in solution.

Identification of CT bands

Charge-transfer complexes are identified by

Color: The color of CT complexes is reflective of the relative energy balance resulting from the transfer of electronic charge from donor to acceptor.

Solvatochromism: In solution, the transition energy and therefore the complex color varies with variation in solvent permittivity, indicating variations in shifts of electron density as a result of the transition. This distinguishes it from the $\pi^* \leftarrow \pi$ transitions on the ligand.

Intensity: CT absorptions bands are intense and often lie in the ultraviolet or visible portion of the spectrum. For inorganic complexes, the typical molar absorptivities, ε, are about 50000 L mol^{-1} cm^{-1}, that are three orders of magnitude higher than typical ε of 20 L mol^{-1} cm^{-1} or lower, for d-d transitions (transition from t_2g to e_g). This is because the CT transitions are spin-allowed and Laporte-allowed. However, d-d transitions are only spin-allowed; they are Laporte-forbidden.

Ligand-to-metal charge transfer

LMCT complexes arise from transfer of electrons from MO with ligand like character to those with metal like character. This type of transfer is predominant if complexes have ligands with relatively high energy lone pairs (example S or Se) or if the metal has low lying empty orbitals. Many such complexes have metals in high oxidation states (even d^0). These conditions imply that the acceptor level is available and low in energy.

Consider a d^6 octahedral complex (example $IrBr_6^{3-}$). The t_{2g} levels are filled as shown in Figure 1. Consequently an intense absorption is observed around 250 nm corresponding to a transition from ligand σ MO to the empty e_g MO. However, in $IrBr_6^{2-}$ that is a d^5 complex two absorptions, one near 600 nm and another near 270 nm, are observed. This is because two transitions are possible, one to t_{2g} (that can now accommodate one more electron) and another to e_g. The 600 nm band corresponds to transition to the t_{2g} MO and the 270 nm band to the e_g MO.

Examples include:

- MnO_4^- : The permanganate ion having tetrahedral geometry is intensely purple due to strong absorption involving charge transfer from MO derived primarily from filled oxygen p orbitals to empty MO derived from manganese(VII).
- CdS: The color of artist's pigment cadmium yellow is due to transition from Cd^{2+} (5s) ← S^{2-}(π).
- HgS: it is red due to Hg^{2+} (6s) ← S^{2-}(π) transition.
- Fe Oxides: they are red and yellow due to transition from Fe (3d) ← O^{2-}(π).

Metal-to-ligand charge transfer

Metal-to-ligand charge-transfer (MLCT) complexes arise from transfer of electrons from MO with metal like character to those with ligand like character.[1][4] This is most commonly observed in complexes with ligands having low-lying π* orbitals especially aromatic ligands. The transition will occur at low energy if the metal ion has a low oxidation number for its d orbitals will relatively be high in energy.

Examples of such ligands taking part in MLCT include 2,2'-bipyridine (bipy), 1,10-phenanthroline (phen), CO, CN^- and SCN^-. Examples of these complexes include:

- Tris(2,2'-bipyridyl)ruthenium(II) : This orange colored complex is being studied as the excited state resulting from this charge transfer has a lifetime of microseconds and the complex is a versatile photochemical redox reagent.
- $W(CO)_4(phen)$
- $Fe(CO)_3(bipy)$

Color of charge-transfer complexes

Many metal complexes are colored due to d-d electronic transitions. Visible light of the correct wavelength is absorbed, promoting a lower d-electron to a higher excited state. This absorption of light causes color. These colors are usually quite faint, though. This is because of two selection rules:The spin rule: $\Delta S = 0$

On promotion, the electron should not experience a change in spin. Electronic transitions which experience a change in spin are said to be *spin forbidden*.

Laporte's rule: $\Delta l = \pm 1$

d-d transitions for complexes which have a center of symmetry are forbidden - *symmetry forbidden* or *Laporte forbidden*. Charge-transfer complexes do not experience d-d transitions. Thus, these rules do not apply and the absorptions are generally very intense.For example

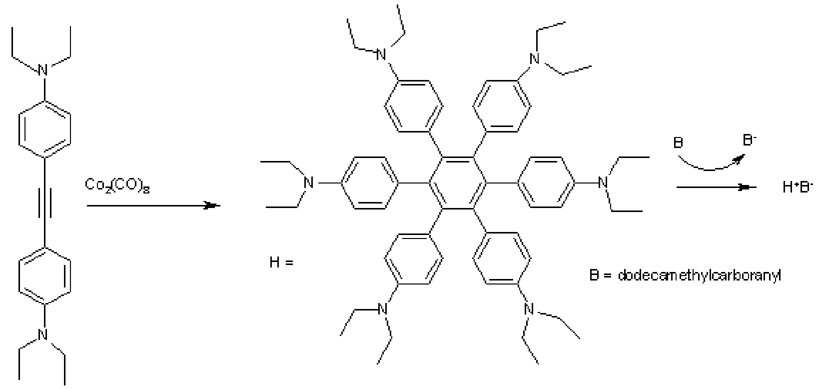


Fig. Synthesis of H^+B^- complex: Alkyne trimerisation of bisubstituted alkyne with dicobalt octacarbonyl, delocalization is favored with activating groups such as a di(ethylamino) group

The phenyl groups are all positioned in an angle of around 45° with respect to the central aromatic ring and the positive charge in the radical cation is therefore through space delocalised through the 6 benzene rings in the shape of a toroid. The complex has 5 absorption bands in the near infrared region.

Check Your Progress: 2

Notes : i) Write your answer in the space given below.
ii) Compare your answer with those given at the end of the unit.

Q.1 What is Molecular Spectroscopy?

Q.2 The process of internal conversion is favored when the energy gap between nuclear level is----?

Q.3 What are the two sets of interaction that contributes to observed molecular spectra?

Q.4 Why non radiative transitions do not occur frequently?

Q.5 When the molecular spectra is observed?

Q.6 What is emission spectroscopy?

Q.7 Give the examples of compounds showing metal to ligand charge transfer?

Q.8 What are vibrionic transitions?

Q. 9 The rate of spontaneous emission (radiative rate) can be described by ------------- rule.

Q.10 Write a note on charge transfer bands?

3.4 - PHOTOELECTRON SPECTROSCOPY

Photoelectron spectroscopy is based on **Einstein's photoelectric effect.** A photon can ionize an electron from a molecule if the photon has an energy greater than the energy holding the electron in the molecule. Any photon energy in excess of that needed for ionization is carried by the outgoing electron in the form of kinetic energy. The kinetic energy of the ejected (photo) electron is measured in the photoelectron spectrometer.

T*he difference between the photon energy (hv), which is known, and the electron kinetic energy (K.E.), which is measured, is the ionization energy (I.E)*Thus, photoelectron spectroscopy measures the relative energies of the ground and excited positive ion states that are obtained by removal of single electrons from the neutral molecule.

3.4.1 Basic Principle-

Photoelectron spectroscopy is based upon a single photon in/electron out process. The energy of a photon of all types of electromagnetic radiation is given by the following Einstein relation : $E = h\nu$

Where,

h - Planck constant (6.62×10^{-34} J s)
ν - frequency (Hz) of the radiation

Photoelectron spectroscopy uses **monochromatic** sources of radiation (i.e. photons of fixed energy).**Depending on the type of radiations and electron to be emitted, it can be of three major types.**

X- ray Photoelectron Spectroscopy-
Uses soft X-rays with a photon energy of 200-2000 eV to examine valence levels.

Ultraviolet Photoelectron Spectroscopy-
Uses vaccum UV radiation with a photon energy to examine valence levels

Auger Photoelectron Spectroscopy-
Uses X- rays and Energetic electrons.The kinetic energy distribution of the emitted photoelectrons (i.e. the number of emitted photoelectrons as a function of their kinetic energy) can be measured using any appropriate electron energy analyser and a photoelectron spectrum can thus be recorded.

Process of Photoionisation-The process of photoionization can be considered in several ways : one way is to look at the overall process as follows :

$$A + h\nu \rightarrow A^+ + e-$$

Conservation of energy then requires that :

$$E(A) + h\nu = E(A^+) + E(e-)$$

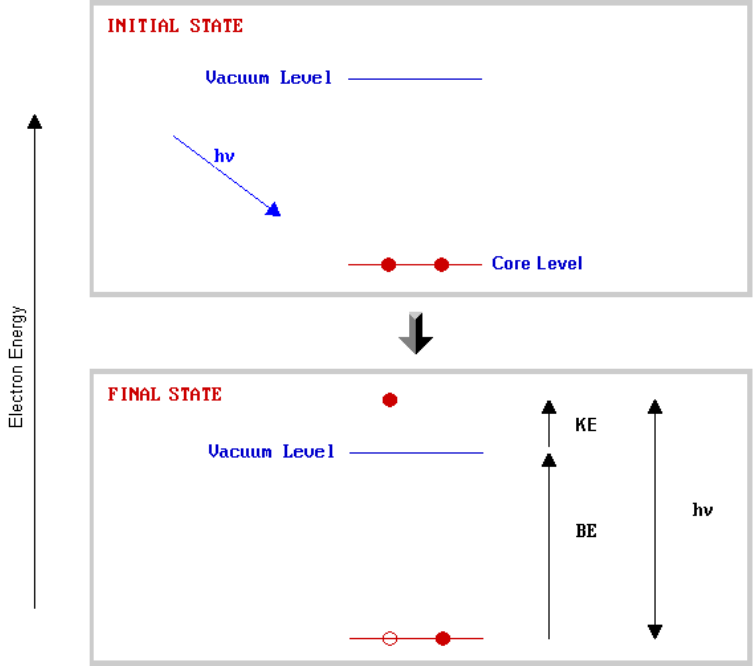
Since the electron's energy is present solely as kinetic energy (KE) this can be rearranged to give the following expression for the KE of the photoelectron:

$$KE = h\nu - (E(A^+) - E(A))$$

The final term in brackets, representing the difference in energy between the ionized and neutral atoms, is generally called the *binding energy* (BE) of the electron - this then leads to the following commonly quoted equation :

KE = $h\nu$ - BE

An alternative approach is to consider a one-electron model along the lines of the following pictorial representation.



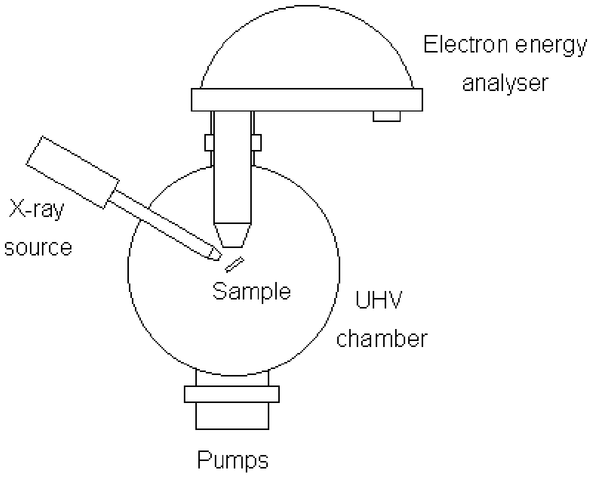
The BE is now taken to be a direct measure of the energy required to just remove the electron concerned from its initial level to the vacuum level and the KE of the photoelectron is again given by :

Instrumentation

The basic requirements for a photoemission experiment are:

1. A source of fixed-energy radiation
2. An electron energy analyser (which can disperse the emitted electrons according to their kinetic energy, and thereby measure the flux of emitted electrons of a particular energy)

a high vacuum environment (to enable the emitted photoelectrons to be analysed without interference from gas phase collisions)



There are many different designs of electron energy analyser but the preferred option for photoemission experiments is a concentric hemispherical analyser (CHA) which uses an electric field between two hemispherical surfaces to disperse the electrons according to their kinetic energy.

3.4.2 - The Photoelectric effect

The photoelectric effect is a process whereby light falling on a surface knocks electrons out of the surface. The photoelectric effect refers to the **emission, or ejection, of electrons from the surface of, generally, a metal** in response to incident light. To explain this effect, consider that light behaves like a stream of particles called photons.Each electron is ejected by a single photon or light quantum striking the surface.

In the quantum theory, the frequency, ν , of the light determines the energy, E, of the photons in that light beam.

$$E = h\nu$$

where h is Planck's constant ($h = 6.626069 \times 10^{-34}$ Joule seconds).

The energy of the emitted electron is given by the energy of the photon minus the energy needed to release the electron from the surface**. It thus depends on the frequency of light falling on the surface, but not on its intensity.**

Higher intensity light has more photons, and so will knock out more electrons. However, if the frequency of the light is such that a single photon is not energetic enough to release an electron from the surface, then none will be ejected no matter how intense the light.

The photoelectric effect is perhaps the most direct and convincing evidence of the existence of photons and the 'corpuscular' nature of light and electromagnetic radiation. That is, it provides undeniable evidence of the quantization of the electromagnetic field and the limitations of the classical field equations of Maxwell.

In Einstein's model, to increasing the number of incident photons per unit time (flux), while the energy of each photon remained the same (as long as the frequency of the radiation was held constant).

3.4.3 -IONISATION PROCESS

At the most fundamental level ionization energies are well-defined thermodynamic quantities related to the heats of protonation, oxidation/reduction chemistry, and ionic and covalent bond energies. Ionization energies are closely related to the concepts of electronegativity, electron-richness, and the general reactivity of molecules. The energies and other characteristic features of the ionization bands observed in photoelectron spectroscopy provide some of the most detailed and specific quantitative information regarding the electronic structure and bonding in molecules. Photoelectron spectroscopy has served as a particularly important basis for the bonding models used to describe organic, inorganic, and organometallic molecules because the energetics of ion formation from the neutral ground state are directly related to orbital electron configurations, oxidation states, charge distributions, and covalency.

The Orbital Model of Ionization

Ionization is explicitly defined in terms of transitions between the ground state of a molecule and ion states .Ionization of electrons occur from bonding molecular orbitals , lone pairs, antibonding molecular orbitals, or atomic cores. These descriptions reflect the relationship of ionization energies to the molecular orbital model of electronic structure.

Ionization energies are directly related to the energies of molecular orbitals by Koopmans' theorem, which states that the negative of the eigenvalue of an occupied orbital from a Hartree-Fock calculation is equal to the vertical ionization energy to the ion state formed by removal of an electron from that orbital, provided the distributions of the remaining electrons do not change. There are many limitations to Koopmans' theorem, but in a first order approximation each ionization of a molecule can be considered as removal of an electron from an individual orbital. The ionization energies can then be considered as measures of orbital stabilities, and shifts can be interpreted in terms of orbital stabilizations or destabilizations due to electron distributions and bonding. Koopmans' theorem is implicated whenever an orbital picture is involved, but is not necessary when the focus is on the total electronic states of the positive ions.

Ionization Intensity:

The probability of ionization is dependent upon the energy of the ionizing photon, the atomic character of the orbitals ionized, the angle at which photoelectrons are collected, and the polarized nature of the photons. These probabilities of photoionization are understood in terms of photoionization cross-sections. The dependence of photoionization cross-sections upon the energy of the ionization photon and the character of the molecular orbital has been particularly useful in the assignments of the spectra of multi-atomic molecules. The general trends that have been observed for photoionization behavior often lead to a clear and convenient differentiation between ionization from metal-based and ligand-based orbitals **in Photoelectron Spectroscopy .**

3.4.4 - Koopman's theorem

The principle that the ionization energy of a molecule is equal to the orbital energy of the ejected electron. It is the basis of the interpretation of spectra in photoelectron spectroscopy. Koopmans' theorem is an approximation in that it ignores any reorganization of electrons in the ion formed. It is named after the Dutch mathematition and economist Charles Koopmans.

Generalizations of Koopmans' theorem

While Koopmans' theorem was originally stated for calculating ionization energies from restricted (closed-shell) Hartree-Fock wavefunctions, the term has since taken on a more generalized meaning as a way of using orbital energies to calculate energy changes due to changes in the number of electrons in a system.

Ground-state and excited-state ions

Koopmans’ theorem applies to the removal of an electron from any occupied molecular orbital to form a positive ion. Removal of the electron from different occupied molecular orbitals leads to the ion in different electronic states. The lowest of these states is the ground state and this often, but not always, arises from removal of the electron from the HOMO. The other states are excited electronic states.

For example the electronic configuration of the H_2O molecule is $(1a_1)^2$ $(2a_1)^2$ $(1b_2)^2$ $(3a_1)^2$ $(1b_1)^2$ where the symbols a_1, b_2 and b_1 are orbital labels based on molecular symmetry. From Koopmans’ theorem the energy of the $1b_1$ HOMO corresponds to the ionization energy to form the H_2O^+ ion in its ground state $(1a_1)^2$ $(2a_1)^2$ $(1b_2)^2$ $(3a_1)^2$ $(1b_1)^1$. The energy of the second-highest MO $3a_1$ refers to the ion in the excited state $(1a_1)^2$ $(2a_1)^2$ $(1b_2)^2$ $(3a_1)^1$ $(1b_1)^2$, and so on. In this case the order of the ion electronic states corresponds to the order of the orbital energies. Excited-state ionization energies can be measured by photoelectron spectroscopy.

CHECK YOUR PROGRESS – 3
Notes : i) Write your answer in the space given below.
ii) Compare your answer with those given at the end of the unit.

Q.1 Photoelectron spectroscopy measures the ----------- of the ground & excited positive ion states that are obtained by removal of single electrons from the neutral molecules.
Q.2 Photo electric effect is a process whereby light falling on a surface knocks out ---------.
Q.3 Koopmann’s theorm is an approximation in that it ignores any reorganization of ---------- In the ion formed

3.4.5 - X-ray Photoelectron Spectroscopy (XPS) and Spectra of simple molecules

Also known as ESCA **(Electron Spectroscopy for Chemical Analysis**)

For each and every element, there will be a characteristic binding energy associated with each core atomic orbital i.e. each element will give rise to a characteristic set of peaks in the photoelectron spectrum at kinetic energies determined by the photon energy and the respective binding energies.

The presence of peaks at particular energies therefore indicates the presence of a specific element in the sample under study - furthermore, the intensity of the peaks is related to the concentration of the element within the sampled region. Thus, the technique provides a ***quantitative analysis of the surface composition*.**

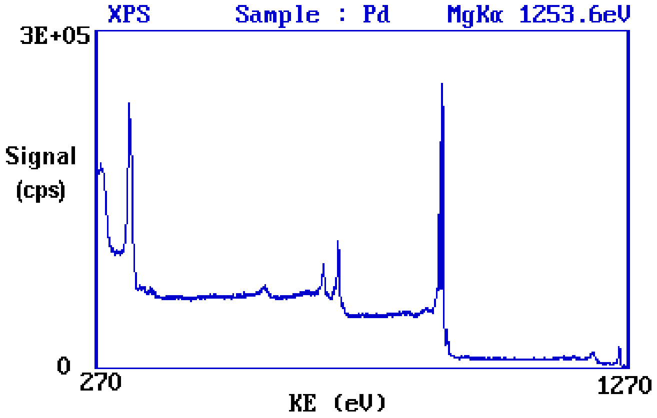
The most commonly employed x-ray sources are those giving rise to :

Mg K_α radiation : $h\nu$ = 1253.6 Ev   Al K_α radiation : $h\nu$ = 1486.6 eV

The emitted photoelectrons will therefore have kinetic energies in the range of *ca.* 0 - 1250 eV or 0 - 1480 eV . Since such electrons have very short IMFPs in solids , the technique is necessarily surface sensitive.

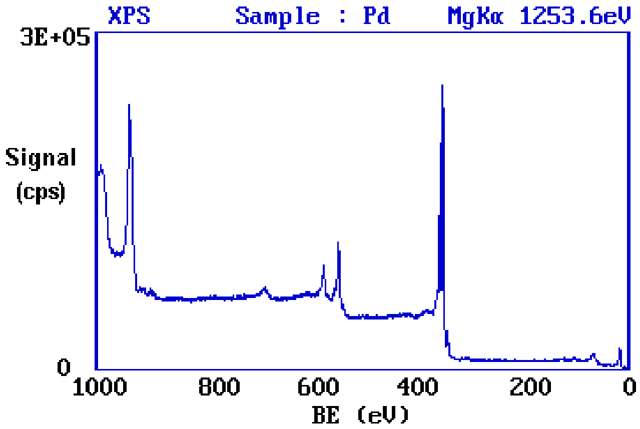
Example 1 - the XPS spectrum of Pd metal

The diagram below shows a real XPS spectrum obtained from a Pd metal sample using Mg K_α radiation



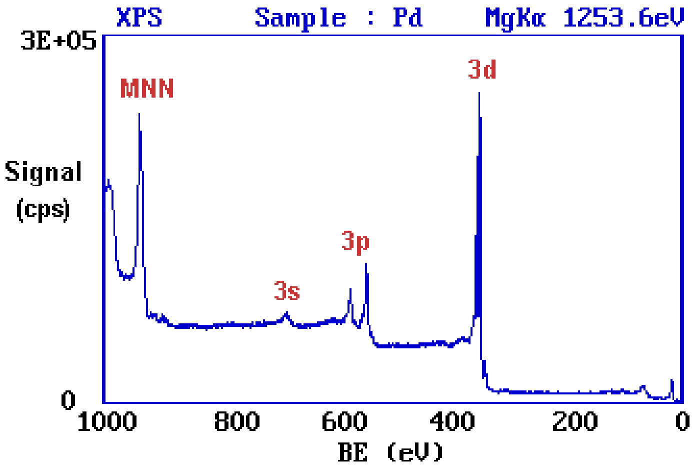
the main peaks occur at kinetic energies of 330, 690, 720, 910 and 920 eV.

Since the photon energy of the radiation is always known it is a trivial matter to transform the spectrum so that it is plotted against BE as opposed to KE.



The most intense peak is now seen to occur at a binding energy of 335 eV. The highest energy levels the valence band (4*d*, 5*s*) emission occurs at a binding energy of 0 - 8 eV (measured with respect to the Fermi level)

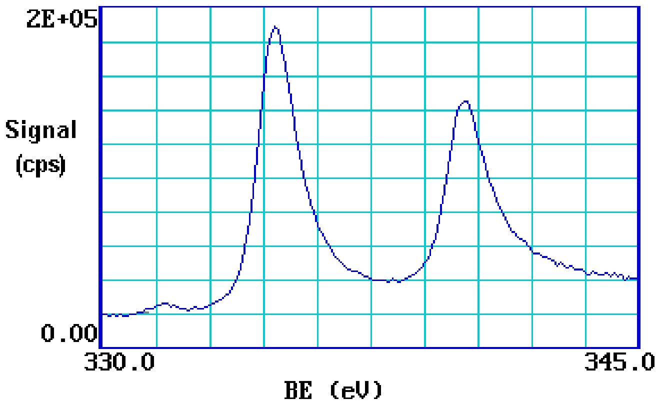
The emission from the 4*p* and 4*s* levels gives rise to very weak peaks at 54 eV and 88 eV respectively , the most intense peak at 335 eV is due to emission from the 3*d* levels of the Pd atoms, whilst the 3*p* and 3*s* levels give rise to the peaks at 534/561 eV and 673 eV respectively. The remaining peak is not an XPS peak at all , it is an Auger peak arising from x-ray induced Auger emission. It occurs at a kinetic energy of 330 eV (in this case it is really meaningless to refer to an associated binding energy).



It may be further noted that there are significant differences in the natural widths of the various photoemission peaks the peak intensities are not simply related to the electron occupancy of the orbitals

Spin-Orbit Splitting

Spectrum shows that emission from some levels (most obviously 3*p* and 3*d*) does not give rise to a single photoemission peak, but a closely spaced doublet. Example, the spectrum in the region of the 3*d* emission ...



The 3*d* photoemission is in fact split between two peaks,one at 334.9 eV BE and the other at 340.2 eV BE, with an intensity ratio of 3:2 . This arises from spin-orbit coupling effects in the final state. The inner core electronic configuration of the initial state of the Pd is :

$(1s)^2\ (2s)^2\ (2p)^6\ (3s)^2\ (3p)^6\ (3d)^{10}$ .... with all sub-shells completely full.

The removal of an electron from the 3*d* sub-shell by photo-ionization leads to a $(3d)^9$ configuration for the final state - since the *d*-orbitals ($l = 2$) have non-zero orbital angular momentum, there will be coupling between the unpaired spin and orbital angular momenta.

Spin-orbit coupling is generally treated using one of two models which correspond to the two limiting ways in which the coupling can occur - these being the *LS* (or Russell-Saunders) coupling approximation and the *j-j* coupling approximation.

If we consider the final ionised state of Pd within the Russell-Saunders coupling approximation, the $(3d)^9$ configuration gives rise to two states (ignoring any coupling with valence levels) which differ slightly in energy and in their degeneracy ...

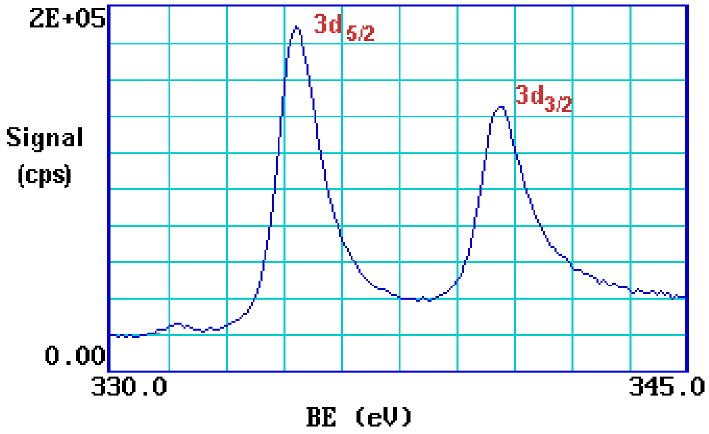
$^2D_{5/2}$ $g_J = 2x\{5/2\}+1 = 6$

$^2D_{3/2}$ $g_J = 2x\{3/2\}+1 = 4$

These two states arise from the coupling of the $L = 2$ and $S = 1/2$ vectors to give permitted J values of 3/2 and 5/2. The lowest energy final state is the one with maximum J (since the shell is more than half-full), i.e. $J = 5/2$, hence this gives rise to the "lower binding energy" peak. The relative intensities of the two peaks reflects the degeneracies of the final states ($g_J = 2J + 1$), which in turn determines the probability of transition to such a state during photoionization.

The Russell-Saunders coupling approximation is best applied only to light atoms and this splitting can alternatively be described using individual electron *l-s* coupling. In this case the resultant angular momenta arise from the single hole in the *d*-shell; a *d*-shell electron (or hole) has $l = 2$ and $s = 1/2$, which again gives permitted *j*-values of 3/2 and 5/2 with the latter being lower in energy.

The peaks themselves are indicated as



This spin-orbit splitting is of course not evident with *s*-levels (*l* = 0), but is seen with *p*,*d* & *f* core-levels which all show characteristic spin-orbit doublets.

Chemical Shifts - The exact binding energy of an electron depends not only upon the level from which photoemission is occurring, but also upon (1) the formal oxidation state of the atom (2) the local chemical and physical environment.

Changes in either (1) or (2) give rise to small shifts in the peak positions in the spectrum so called *chemical shifts* . Such shifts are readily observable and interpretable in XP spectra (unlike in Auger spectra) because the technique is of high intrinsic resolution .It is a one electron process (thus simplifying the interpretation)

Atoms of a higher positive oxidation state exhibit a higher binding energy due to the extra coulombic interaction between the photo-emitted electron and the ion core. *This ability to discriminate between different oxidation states and chemical environments is one of the major strengths of the XPS technique.*

In practice, the ability to resolve between atoms exhibiting slightly different chemical shifts is limited by the peak widths which are governed by a combination of factors ; especially the intrinsic width of the initial level and the lifetime of the final state the line-width of the incident radiation - which for traditional x-ray sources can only be improved by using x-ray monochromators .

3.4.6 ESCA Electron Spectroscopy for Chemical Analysis

It's a **Surface analysis technique** . It is used for obtaining chemical information about the surfaces of solid materials. The materials characterization method utilizes an x-ray beam to excite a solid sample resulting in the emission of photoelectrons. An energy analysis of these photoelectrons provides both elemental and chemical bonding information about a sample surface. The relatively low kinetic energy of the photoelectrons gives ESCA a sampling depth of approximately 30 Å.

The principal advantage of ESCA is its ability to look at a broad range of materials (polymers, glasses, fibers, metals, semi-conductors, paper, etc.) and to identify surface constituents as well as their chemical state.

3.4.7 Chemical information from ESCA:

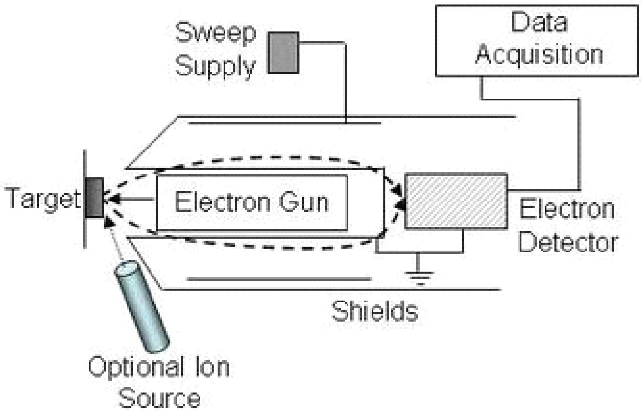
- elemental composition of the surface (top 1–10 nm usually)
- empirical formula of pure materials
- elements that contaminate a surface
- chemical or electronic state of each element in the surface
- uniformity of elemental composition across the top surface (or line profiling or mapping)
- uniformity of elemental composition as a function of ion beam etching.
- In the semiconductor industry, ESCA serves as a useful surface analysis tool for studying organics, polymers, and oxides.
- It also played a major role in the development of plasma etching techniques.
- ESCA is also a good FA technique for resolving issues related to oxidation, metal interdiffusion, and resin-to-metal adhesion.

3.4.8 -Auger Electron Spectroscopy

Auger Electron Spectroscopy (*Auger spectroscopy* or AES) was developed in the late 1960's , deriving its name from the effect first observed by Pierre Auger, a French Physicist, in the mid-1920's.

It is a surface specific technique utilizing the emission of low energy electrons in the *Auger process* and is one of the most commonly employed surface analytical techniques for determining the composition of the surface layers of a sample.

Instrumentation



AES experimental setup using a cylindrical mirror analyzer (CMA). An electron beam is focused onto a specimen and emitted electrons are deflected around the electron gun and pass through an aperture towards the back of the CMA. These electrons are then directed into an electron multiplier for analysis. Varying voltage at the sweep supply allows derivative mode plotting of the Auger data.

PHYSICAL BASIS

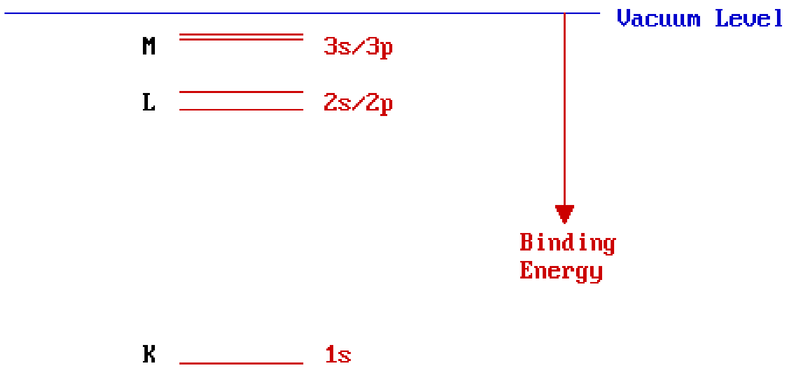
Auger spectroscopy can be considered as involving three basic steps :

(1) Atomic ionization (by removal of a core electron)
(2) Electron emission (the Auger process)
(3) Analysis of the emitted Auger electrons

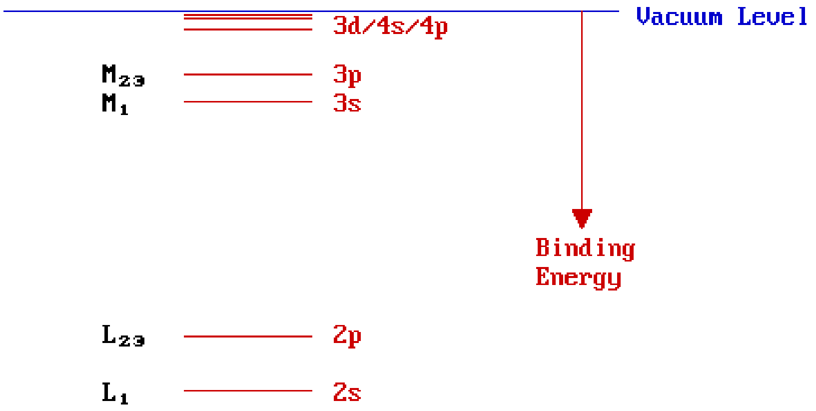
The last stage is simply a technical problem of detecting charged particles with high sensitivity, with the additional requirement that the kinetic energies of the emitted electrons must be determined.

Electronic Structure - Isolated Atoms.

The energies of the various electron energy levels in an isolated, multi-electron atom



The designation of levels to the K,L,M,… shells is based on their having principal quantum numbers of 1,2,3,… respectively. It is convenient to expand the part of the energy scale close to the vacuum level in order to more clearly distinguish between the higher levels ....

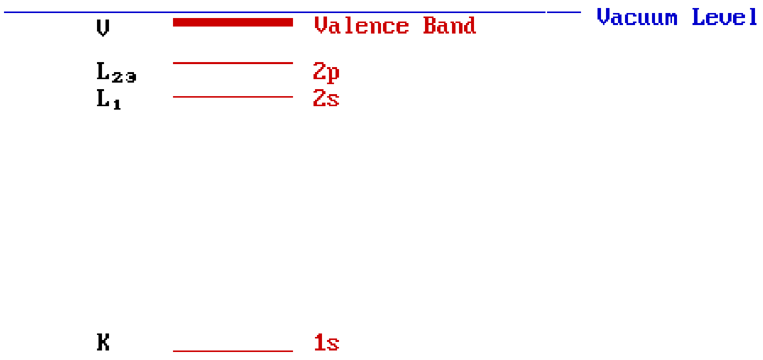


Levels with a non-zero value of the orbital angular momentum quantum number ($l > 0$), i.e. p,d,f,.. levels, show spin-orbit splitting. The magnitude of this splitting, however, is too small to be evident on this diagram - hence, the double subscript for these levels (i.e. $L_{2,3}$ represents both the L_2 and L_3 levels).

Electronic Structure - Solid State

In the solid state the core levels of atoms are little perturbed and essentially remain as discrete, localised (i.e. atomic-like) levels. The valence orbitals, however, overlap significantly with those of neighbouring atoms generating bands of spatially-delocalised energy levels. The energy level diagram for the solid is therefore closely resemblant of that of the corresponding isolated atom, except for the levels closest to the vacuum level.

The diagram below shows the electronic structure of Na metal :

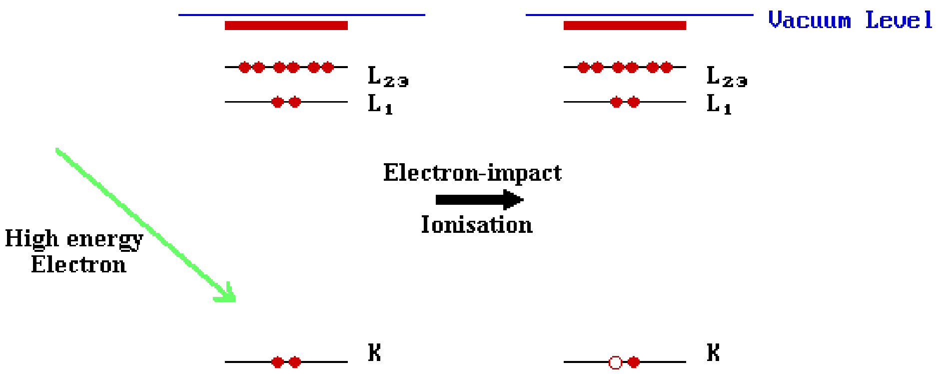


The Auger Process & Auger Spectroscopy

the Auger process is illustrated using the K, L_1 & $L_{2,3}$ levels. These could be the inner core levels of an atom in either a molecular or solid-state environment.

I. Ionization

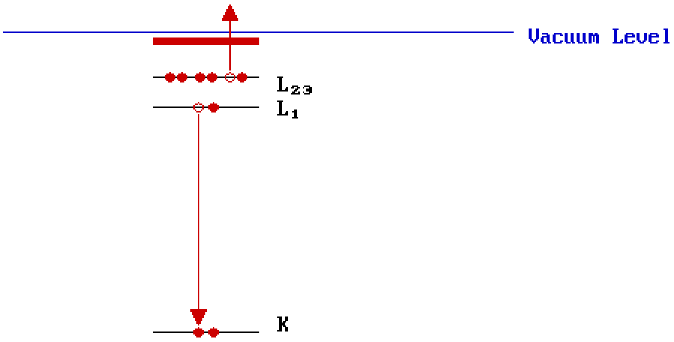
The Auger process is initiated by creation of a core hole - this is typically carried out by exposing the sample to a beam of high energy electrons (typically having a primary energy in the range 2 - 10 keV). Such electrons have sufficient energy to ionise all levels of the lighter elements, and higher core levels of the heavier elements.



In the diagram above, ionisation is shown to occur by removal of a K-shell electron, but in practice such a crude method of ionisation will lead to ions with holes in a variety of inner shell levels.

II. Relaxation & Auger Emission - The ionized atom that remains after the removal of the core hole electron is, of course, in a highly excited state and will rapidly relax back to a lower energy state by one of two routes :

X-ray fluorescence , or **Auger emission -** Considering the latter mechanism, an example of which is illustrated schematically below ....



In this example, one electron falls from a higher level to fill an initial core hole in the K-shell and the energy liberated in this process is simultaneously transferred to a second electron ; a fraction of this energy is required to overcome the binding energy of this second electron, the remainder is retained by this emitted *Auger electron* as kinetic energy. In the Auger process, the final state is a doubly-ionized atom with core holes in the L_1 and $L_{2,3}$ shells.

KE of the Auger electron from the binding energies of the various levels involved are

$$\mathbf{KE = (E_K - E_{L1}) - E_{L23}}$$

The expression for the energy can also be re-written in the form :

$$\mathbf{KE = E_K - (E_{L1} + E_{L23})}$$

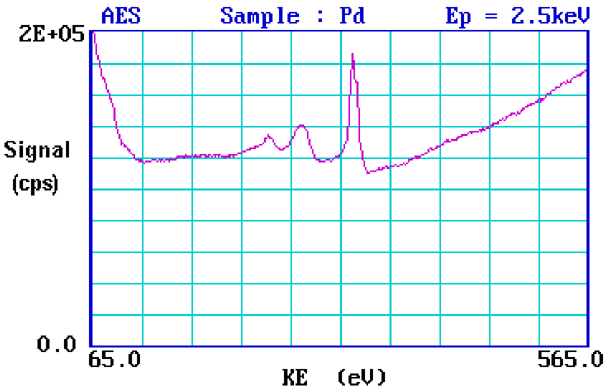
It should be clear from this expression that the latter two energy terms could be interchanged without any effect - i.e. it is actually impossible to say which electron fills the initial core hole and which is ejected as an Auger electron ; they are indistinguishable.

An Auger transition is therefore characterized primarily by :- the location of the initial hole ,the location of the final two holes although the existence of different electronic states (terms) of the final doubly-ionized atom may lead to fine structure in high resolution spectra. When describing the transition, the initial hole location is given first, followed by the locations of the final two holes in order of decreasing binding energy, i.e. the transition illustrated is a $KL_1L_{2,3}$ transition .

If we just consider these three electronic levels there are clearly several possible Auger transitions : specifically,

$K\ L_1\ L_1$ $K\ L_1\ L_{2,3}$ $K\ L_{2,3}\ L_{2,3}$

In general, since the initial ionisation is non-selective and the initial hole may therefore be in various shells, there will be many possible Auger transitions for a given element - some weak, some strong in intensity. AUGER SPECTROSCOPY is based upon the measurement of the kinetic energies of the emitted electrons. Each element in a sample being studied will give rise to a characteristic spectrum of peaks at various kinetic energies.



This is an Auger spectrum of Pd metal - generated using a 2.5 keV electron beam to produce the initial core vacancies and hence to stimulate the Auger emission process. The main peaks for palladium occur between 220 & 340 eV. The peaks are situated on a high background which arises from the vast number of so-called *secondary electrons* generated by a multitude of inelastic scattering processes.

Auger Electron Spectroscopy (AES) is a surface-sensitive spectroscopic technique used for elemental analysis of surfaces ; it offers

- high sensitivity (typically ca. 1% monolayer) for all elements except H and He.
- a means of monitoring surface cleanliness of samples
- quantitative compositional analysis of the surface region of specimens, by comparison with standard samples of known composition.

CHECK YOUR PROGRESS – 4

Notes : i) Write your answer in the space given below.
ii) Compare your answer with those given at the end of the unit.

Q.1 It is a surface specific technique utilizing the emission of-------- (low/ high) energy electrons in the *Auger process* and the most commonly employed techniques for determining the composition of the ------------ of a sample.

Q.2 What is the major strength of the XPS technique?

Q.3 The Russell-Saunders coupling approximation is best applied only to -------- (light / heavy) atoms.

Q.4 write the full form of ESCA ?

Q.5 Define chemical shifts?

3.5 Photoacoustic Spectroscopy (PAS) or Optoacoustic Spectroscopy

Photoacoustic spectroscopy (PAS) is a type of spectroscopy that uses light or other energy for “photo” and sound for “acoustic.”Spectroscopy by itself ,deals with emitting and absorbing light, matter and energy. PAS translates optical energy to mechanical energy through wavelengths during excitation. When the “ de-excitation process occurs it produces kinetic energy or heat”. Photoacoustic light spectrum is the wavelength of light used in Photoacoustic Spectroscopy.

Photoacoustic spectroscopy is the measurement of the effect of absorbed electromagnetic energy (particularly of light) on matter by means of acoustic detection.

HISTORY

The discovery of the photoacoustic effect dates to 1880 when Alexander Graham Bell showed that thin discs emitted sound when exposed to a beam of sunlight that was rapidly interrupted with a rotating slotted disk. The absorbed energy from the light is transformed into kinetic energy of the sample by energy exchange processes. This results in local heating and thus a pressure wave or sound. Later Bell showed that materials exposed to the non-visible portions of the solar spectrum (i.e., the infrared and the ultraviolet) can also produce sounds.

A photoacoustic spectrum of a sample can be recorded by measuring the sound at different wavelengths. This spectrum can be used to identify the absorbing components of the sample. The photoacoustic effect can be used to study solids, liquids and gases.

3.5.1 BASIC PRINCIPLE-

Photoacoustic spectroscopy is part of a class of photothermal techniques, in which an impinging light beam is absorbed and alters the thermal state of the sample. This "thermal state" can manifest itself as a change in temperature, density, or other measurable property of the sample.

A light beam is used and alters the thermal temperature as a result .When using solids in photothermal techniques ; the measurement of the thermal diffusivity of a solid sample is checked.One method of detection is to experimentally measure the temperature or density of the absorbing material. This is referred to as thermometric detection.

Other method is the incoming light is modulated, the absorbing sample warms and cools in a cycle. If the cycle is so fast that the sample does not have time to expand and contract in response to the modulated light, a change in pressure develops. This pressure "wave" can lead to the production of a sound wave. These sound waves can be detected by a sensitive microphone (for sample in gaseous state), piezoelectric devices, or optical methods . These techniques are more properly called photoacoustic techniques. It has been argued that photo-acoustic spectroscopy is as much a type of calorimetry as it is spectroscopy .

Factors affecting PA Spectra - A theoretical analysis of PA response based on the thermal and optical properties of the sample has been given by Rosencwaig and Gresho .

Thermal Properties & optical properties –

Heating up would depend on the (angular) chopping frequency w, the optical absorption coefficient b and the thermal diffusion coefficient of the sample. Two characteristic lengths may be defined as Lop = (1/b) and Lth = (1/v{2a/w}) which typically are measures of the lengths over which the optical and thermal effects can have their influence.

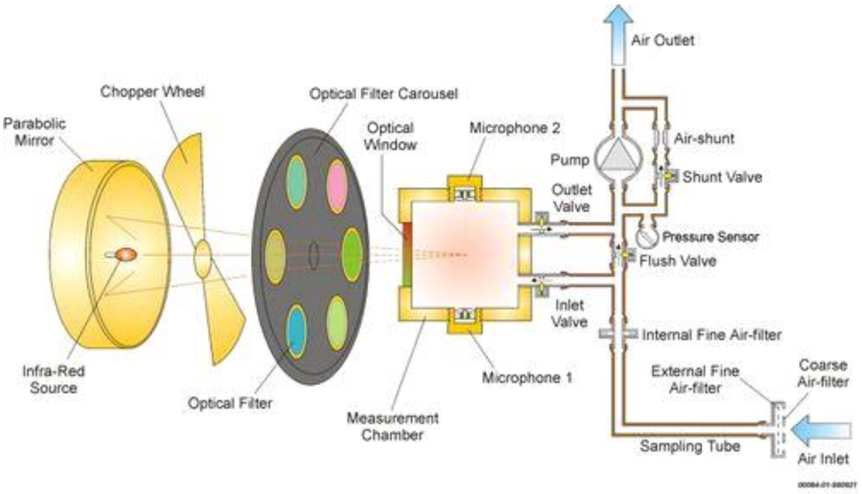
In the case of optically transparent samples, Lop is greater than the sample thickness d and hence light is absorbed by the entire length of the sample. Such samples are considered to be thermally `thin' if Lth is greater than both Lop and d. Then the PA signal intensity is directly proportional to (db/w) where w is the (angular) chopping frequency of incident light.

For thermally thick samples, only the light absorbed in the first layers of the sample contribute to the signal and the signal is proportional to at the product (b Lop)w. Thus by varying the chopping frequency we can actually probe different layers of the sample, thus offering the possibility for depth-profiling.

Frequency- By increasing the frequency thermal diffusion length can be increase and hence observing PA signal originating from a deeper layer within the sample. PA depth profiling opens up exciting possibilities such as studying layered and amorphous materials and determination of thickness of thin films. In the case of optically opaque (Lop<d) samples, the PA signal strength varies as w-1 . Even for opaque samples, b can be evaluated by analyzing the PA signal whereas conventional optical spectroscopy is not possible.

3.5.2 -INSTRUMENTATION

In Photoacoustic Spectroscopy (PAS) the gas to be measured is irradiated by modulated light of a pre-selected wavelength. The gas molecules absorb some of the light energy and convert it into an acoustic signal which is detected by a microphone.



The absorption (proportional to the concentration) is measured directly not relative to a background. This means that PAS is highly accurate, with very little unstability. Furthermore, with PAS all gases and vapours can be monitored simultaneously in a single measurement chamber as it is possible to detect each substance to be monitored individually.

Finally, the sample volume required is very small due to the small volume of the cell. Volumes down to 10 ml. can be measured**.**

The PAS Spectrometer can be single beam or Double Beam.

The Light Source - The type of light source most suited to gas detection and analysis is one, which emits radiation in the infrared region of the electromagnetic spectrum, particularly between 650 and 4000 cm-1.Sunlight is the most common & cheapest infrared light source used in photoacoustics.

An excellent and more dependable alternative to sunlight is an incandescent source. The simplest type is a wire filament heated to a high temperature. It has the major advantage of being stable, inexpensive and long lasting. The spectral output is continuous, with 70 to 80% of it in the infrared region. Xenon lamp, tungeston lamp, carbon arc lamp, Nernst glower (for mid and near IR) or lasers can be used as a source used for photcacoustic spectrometers.

Monochromator -the wavelength of the incident light is varied continuously using a scanning monochromator and the signal is monitored as a function of the wavelength. This spectrum has to be corrected for the spectral distribution of the light source and the dispersion of the monochromator. Filters are used for fixed wavelength irradiation. For continuous tunability, diffraction gratings, prisms or interferometry can be used.

Mechanical chopper- The incident light from a white light source is chopped at a desired frequency using a mechanical chopper. The absorption of chopped light by the sample causes periodic heating, which alters the size of the sample periodically, leading to alternate condensation and rarefaction in the coupling gas.

Sample - One advantage to photoacoustic spectroscopy is that it can be performed on all phases of matter. If the absorbing sample is gas, the sound wave can be directly picked by a microphone. If the sample is solid, the sonic waves are coupled in the solid to the microphones by immersing both in an enclosed space filled with a gas. As the wave crosses solid –gas boundary, there is a substantial loss of energy & this can be recovered by electronic amplification.The solid sample can also be attached to a piezoelectric transducer (PZT) by making use of an adhesive. Liquid samples can be handled either by air coupled microphones or by contact with a PZT in a closed system

Reference – Reference used in PAS is finely divided carbon or carbon black. It absorbs all the radiation that hits it, and thus provides a saturated response that is uniform at all the wavelengths.

PA cell or Matched Cell Or Transducers - It encloses the sample in a leak-free gas atmosphere at a desired pressure. Mostly, air at atmospheric pressure is used due to the simplicity of experimentation. However, better signals can be obtained if the coupling has a pressure slightly above the atmospheric pressure. The sample holder is designed such that light can be incident on the sample through a window. The cell volume is kept a minimum for better signal strength. The cell is to be isolated from possible acoustic disturbances.

In double beam instrument pair of transducers are present one contains the sample & other contains reference material.

Microphone- The pressure wave, normally in the acoustic frequency region, can be easily detected by a powerful microphone of sensitivity of more than 10 mV/Pa

Piezoelectric detector- A piezoelectric detector are used for the purpose of better acoustic impedance matching.

Lock-in amplification -The actual magnitudes of the temperature-rise and size-change of the sample are very small and hence the PA signal from the acoustic detector has to be amplified. Lock-in amplification is found to be very advantageous.

Sensitivity- Photoacoustic spectroscopy has become a powerful technique to study concentrations of gases at the part per billion or even part per trillion levels. To increase the sensitivity the following modifications have been made:

- Use of intense lasers instead of the sun to illuminate the sample since the intensity of the generated sound is proportional to the light intensity.
- The ear has been replaced by sensitive microphones. The microphone signals are further amplified and detected using lock-in amplifiers.
- By enclosing the gaseous sample in a cylindrical chamber, the sound signal is amplified by tuning the modulation frequency to an acoustic resonance of the sample cell.
- The IR-source is a spherical, heated black body. A mirror focuses the light onto the window of the PAS cell after it has passed the light chopper and the optical filter. The chopper is a slotted disk that rotates and effectively "switches" the light on and off. The optical filter is a narrow-band IR interference filter.

Technique- After passing through the window, the light beam enters the PAS-cell. If the frequency of the light coincides with an absorbtion band of the gas in the cell, the gas molecule will absorb part of the light. The higher the concentration of gas in the cell, the more light will be absorbed.

> As the gas absorbs energy, it is heated and therefore expands and causes a pressure rise. As the light is chopped, the pressure will alternately increase and decrease - an acoustic signal is thus generated. The acoustic signal is detected by two microphones. The electrical output signals from the two microphone signals are added in an amplifier, before they are processed.

3.5.3 - PAS Gases –Sample Gases

Photoacoustic spectroscopy is used when sampling gases. “An increase in the temperature of the gas leads to an increase in the pressure of an isochoric (constant volume) sample .If the incoming light is modulated –modulation frequencies can vary from single to several thousand hertz –the gas pressure increases and decreases accordingly, creating sound.”The different wavelengths effect sound through light received.

When a species absorbs some of the incoming light, one of several mechanisms of de-excitation is intermolecular colliding, which ultimately leads to increases in translation energy of the gas particles — that is, heating. Varying the wavelength of the incoming light will change the amount of light absorbed, the amount of pressure changes occurring, and the amount of sound produced, and a spectrum of loudness versus wavelength can be produced.

One useful aspect of photoacoustic spectroscopy of gases is that very bright light sources — lasers — can be used to detect very tiny concentrations of a particular gas, on the order of parts per *trillion*. This makes photoacoustic spectroscopy very useful in following the concentrations of trace gases in mixtures, like soot in diesel exhaust or NO_x in the atmosphere.

3.5. 4 - Condensed Systems

Photoacoustic Spectroscopy can be used with an accepted mechanism to have a photoacoustic effect. “The commonly accepted mechanism for the photoacoustic effect is called **RG theory** ,after its developers **Rosencwaig and Gersho**.The main source of the acoustic wave is the repetitive heat flow from the absorbing condensed –phase sample to the surrounding gas,followed by propogation of the acoustic wave through the gas column to microphone –based detector”.Radiant heat gets transferred through a solid vibrational mode reffered to as a phonon mode which is dependent on the size it is.

Condensed Phases

The mechanism of the photoacoustic effect in condensed samples is not as straightforward as it is for gas samples. For example, in 1973, Parker noticed a photoacoustic signal apparently coming from the windows of the sample cell, which should have been transparent to the incoming radiation.The exact mechanism of spectrum production depends on the type of detector used. The commonly accepted mechanism for the photoacoustic effect is called RG theory, after its developers Rosencwaig and Gersho . The main source of the acoustic wave is the repetitive heat flow from the absorbing condensed-phase sample to the surrounding gas, followed by propagation of the acoustic wave through the gas column to microphone-based detector.

However, a photoacoustic signal also can be detected piezoelectrically. Instead of being dissipated as heat, the absorbed radiant energy also can be transferred through the solid-state vibrational modes, or phonon modes, of the sample. The motions of these phonon modes are nondissipative (unlike heating), limited only by the size of the sample. A piezoelectric detector physically connected to the sample can detect absorbed energy in this manner. Although piezoelectric detection is about 100 times less sensitive than microphone detectors, it can be preferable for large samples or for samples that do not efficiently convert absorbed light to heat.

Limitation-

Source of energy must be sufficient.
Window of the sampling cell must be transparent.
Background noise can hamper the acoustic measurement
The analyte molecule must absorb some light from the source in order to be detectable.
Saturation effects can also cause problems .

Advantages of PAS

some important advantages of PAS over conventional techniques.
a) the basic simplicity of the experimental set up,
b) the convenience of studying samples in a variety of physical forms - crystals, powders, thin films, liquids etc.,
c) the possibility of investigating opaque materials,
d) the feasibility of direct measurement nonradiative lifetimes,
e) the ability to gather information from sub-surface layers,
f) the absence of stringent requirement on sample preparation and
g) the scope to obtain information on thermal parameters of the sample.

In fact this technique has been successfully used in a wide variety of applications ranging from semiconductor characterization to eye-lens degradation studies.

Scope and potential

PA response is widely used is a variety of scientific and technical applications. Spectroscopy of otherwise difficult samples (such as powders, opaque materials etc.) is an area of immediate interest to Chemists and Materials Scientists. This also provides a direct measurement for nonradiative lifetimes.

• -Chemical and surface Applications-

PAS has been used successfully as a spectroscopic tool for-

- investigating and characterizing colored inorganic as well as organic materials including transition metal complexes, semiconducting materials, liquid crystals and metals.
- for obtaining a more complete picture of the electronic processes in materials.
- It helps in the identification of species and their valence states in several situations such as catalysis and other chemical reactions.
- The effect of fluorescence quenchers can be studied by monitoring the PA and fluorescence signals simultaneously.
- In the study of photosynthesis and other photochemical reactions, quantum efficiency studies on organic dyes etc . The possibility of studying coloring agents such as cyctochrome and hemoglobin samples has attracted the attention of biologists.
- Some biomedical applications such as blood examination also have been demonstrated. Usually blood specimens have to be rendered transparent by smearing a thin layer on a glass plate after some processing in order to record the optical absorption spectrum. However, PA spectrum of whole blood as such can be recorded to get the same information as that obtainable with optical absorption .

- It is used to measure pollutants such as NO_x or soot in the atmosphere or in automobile exhaust.

- Medical applications of PAS include identification of bacterial states, study of animal and human tissues including teeth, bone, skin, muscle etc., analysis of drug in tissues, investigation of the photo-oxidative decay in human eye lenses etc.

- in obtaining visual information on a microscopic scale. This is done by focusing light onto a spot on the sample and scanning it over the sample while recording the PA signal. Any local change in the thermal or optical property shows up as a change in the PA signal at that point of scanning. Depth-profiling and subsurface imaging can be done by varying the chopping frequency. This has potential as both a general analytic tool as well as a process control instrument in semiconductor industry.

- A recent study on semiconductor nanostructures -Semiconductor nanostructures are of current topical interest due to the fact that their properties undergo considerable modification from those of the bulk due to quantum confinement effects. Nanoclusters of these materials embedded in dielectric hosts act are known to behave as quantum dots, described rightly as practical examples of `particle-in-a-box'. Such structures can be prepared by several chemical and physical methods such as ion-exchange reactions, molecular beam epitaxy, ion-implantation, sol-gel techniques etc .

- Quantum confinement leads to alterations in the band structure of the bulk. It also systematically shifts the band edge towards higher energy as the quantum dots get smaller and smaller. This is known as the signature `blue shift' in optical absorption and the process as `bandgap engineering'.

- It is a useful analytic and research technique in a variety of scientific, industrial and medical applications both as a spectroscopic tool as well as a nonspectroscopic probe for thermal and elastic properties.

- it is nondestructive to the sample; the sample does not have to be dissolved in some solvent or embedded in a solid-state matrix. Samples can be used "as is."

- Photoacoustic spectroscopy is not only used for depth profiling. Haisch and Niessner also list the analysis of textile dyes as another practical application of photoacoustic spectroscopy.

3.5.6 Let us Sum up

Atomic spectroscopy concerns only the properties of atoms. It helps to find the nature and the amounts of a given element in your sample but molecular spectroscopy concerns all the interaction of electromagnetic waves with the matter and gives you much more advice than atomic spectroscopy especially about chemical functions, structure of matter.

Molecular spectroscopy studies the interaction of electromagnetic radiation with molecules. Transitions between energy levels in molecules may be brought about by, for example, the absorption of light, but are subject to certain selection rules. By analyzing the shapes, frequencies, spacing and intensities of spectroscopic lines, molecular parameters such as the moments of inertia, bond lengths and symmetry, as well as temperature and concentration can be deduced.

Photoelectron spectroscopyhelps to find elemental composition of the surface (top 1–10 nm usually), empirical formula of pure materials ,elements that contaminate a surface, chemical or electronic state of each element in the surface

PAS has some advantages over conventional spectroscopic techniques (like e.g. mass spectrometers or NDIR-spectrometers):The specific advantages of PAS compared to other spectroscopic techniques are:

- It is an offset-free measurement technique. Smallest signals will be detected without background disturbance.
- No long absorption lengths are required which enables the use of small sample cells.
- Exploiting the acoustic resonance frequency of the sample cell will lead to a great signal increase and hence to a marked increase in sensitivity.
- The photoacoustic signal is linear over many orders of magnitude. No electronic linearisation of the measurement range is required.
- A reduction of absorption line widths by reducing the pressure is not required. Spectroscopic measurements can be performed under atmospheric pressure.
- In spite of using middle or far infrared radiation, no low-temperature cooling of the detector is required which which permits a particularly simple set-up.
- PAS is a cost efficient measurement technique, since simple microphones are much less expensive than infrared detectors.

CHECK YOUR PROGRESS- 4

Notes : i) Write your answer in the space given below.
ii) Compare your answer with those given at the end of the unit.
Q.1 What is photoacoustic spectroscopy?
Q.2 The commonly accepted mechanism for the photoacoustic effect is called----------- .
Q.3 What else do the name is given to photoacoustic spectroscopy?
Q.4 Full form of PZT
Q.5 ------- is referred to as a change in temperature, density, or other measurable property of the sample.
Q.6 The higher the concentration of gas in the cell, the --------- light will be absorbed.
Q.7 Piezoelectric detection is about------- less sensitive than microphone detectors.
Q.8 Piezoelectric detector is preferable for ----------- samples or for samples that ------ efficiently convert absorbed light to heat.

KEY -1

Ans.1 hot filament, hot iron, hot Charcoal give the continuous spectrum.
Ans.2 Independent

Ans.3 Shape
Ans.4 Vector
Ans.5 orbital angular momentum of electrons + spin angular momentum
Ans.6 (a) largest (b) decreases
Ans.7 does not

KEY - 2

Ans.1) Branch of Spectroscopy in which the interaction of electromagnetic radiation with matter deals with the transitions in a molecule between its energies (rotational, vibrational , electronic etc.) on the absorption of photon of suitable energy.

Ans. 2) Small
Ans.3) There are two primary sets of interactions that contribute to observed molecular spectra-The first involves the internal motions of the nuclear framework of the molecule and the attractive and repulsive forces among the nuclei and electrons.
The other encompasses the interactions of nuclear magnetic and electrostatic moments with the electrons and with each other.
Ans.4) The crystal structure generally can't support large vibrations without destroying bonds.
Ans.5) When a molecule undergoes the absorption or emission of electromagnetic radiation with a resulting increase or decrease in energy.
Ans.6) It is spectroscopic technique which examines the wavelength of photons emitted by atoms or molecules during their transition from an exited state to a lower energy state .
Ans.7) (a) Tris (2,2'-bipyridyl)ruthenium(II)
(b) $W(CO)_4$ (phen)
$Fe(CO)_3$ (bipy)
Ans. 8) Vibronic transitions are the simultaneous changes in electronic and vibrational energy levels of a molecule due to the absorption or emission of a photon of the appropriate energy.
Ans 9). Fermi's golden
Ans10). The excitation energy of this resonance occurs very frequently in the visible region of the electro-magnetic spectrum, which produces the usually intense color characteristic for these complexes. These optical absorption bands are often referred to as *charge-transfer bands* (CT bands).

Key -3

1.Relative energies
2. Electron
3. Electron

KEY -4

Ans.1 (a) Low (b) surface layers
Ans.2 The ability to discriminate between different oxidation states and chemical environments.
Ans.3 light
Ans.4 Electron Spectroscopy for Chemical Analysis
Ans.5 Change in either the formal oxidation state of the atom or local chemical and physical environment give rise to small shifts in the peak positions in the spectrum are known as chemical shifts .

KEY 5

Ans.1 Photoacoustic spectroscopy is the measurement of the effect of absorbed electromagnetic energy on matter by means of acoustic detection.
Ans.2 RG theory
Ans.3Optoacoustic Spectroscopy
Ans.4 Piezoelectric transducer
Ans.5 Thermal state
Ans.6 More
Ans.7 100 times
Ans.8 (a) Large (b) do not

Unit IV - Magnetic Resonance Spectroscopy

Structure

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4.1 Objectives
4.2 - Nuclear Magnetic Resonance Spectroscopy
    4.2.1 - Nuclear Spin
    4.2.2 - NMR active nuclei
    4.2.3 - Spinning Nuclei-Magnetic moments-Larmor Precision
    4.2.4 - Theory of NMR
    4.2.5 - Nuclear Resonance
    4.2.6 – Nuclear Saturation & Relaxation Process
    4.2.7 – Instrumentation
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    4.2.10 – Classification (ABK, AMX,ABC,A_2B_2)
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    4.4.10- Let us sum up
    4.4.11 – Check your progress - key
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4.0 INTRODUCTION –

Spectroscopy is a technique that uses the interaction of energy with a sample to perform an analysis.

Nuclear magnetic resonance spectroscopy, commonly referred to as NMR, has become the preeminent technique for determining the structure of organic compounds. Of all the spectroscopic methods, it is the only one for which a complete analysis and interpretation of the entire spectrum is normally expected. Although larger amounts of sample are needed than for mass spectroscopy, NMR is non-destructive, and with modern instruments good data may be obtained from samples weighing less than a milligram. NMR Can detect very fine structural components, works for organic and inorganic, qualitative and quantitative, versatile & reliable.

ESR is a microwave technique based on splitting electronic energy fields in a magnetic field. It is used to determine structures of samples containing unpaired electrons. **Electron paramagnetic resonance** (EPR) or **electron spin resonance** (ESR) spectroscopy is a technique for studying chemical species that have one or more unpaired electrons, such as organic and inorganic free radicals or inorganic complexes possessing a transition metal ion. EPR was first observed in Kazan State University by Soviet physicist Yevgeny Zavoisky in 1944, and was developed independently at the same time by Brebis Bleaney at the University of Oxford.

The NQR-spectrum is based on resonance between the nuclear quadrupole moment and a variable electric field gradient.

4.1 OBJECTIVES

A spectrum can be used to obtain information about-

- Nuclear & electronic spin
- Number & type of protons in a molecule
- Proton – electron interaction
- molecular geometries
- Nature & number of chemical bonds
- Interactions & processes related to molecules
- The components of a sample(qualitative analysis).
- the amount of material in a sample (quantitative analysis).

Nuclear Magnetic Resonance Spectroscopy

4.2 – Nuclear magnetic resonance spectroscopy or NMR spectroscopy or PMR spectroscopy or H^1NMR

It uses the magnetic properties of certain atomic nuclei to determine physical and chemical properties of atoms or the molecules in which they are contained. It provide detailed information about the structure, dynamics, reaction state, and chemical environment of molecules.

Branch of spectroscopy which deals with the study radio frequency waves by nuclei. Radio frequency waves induce transitions between magnetic energy levels of nuclei of an atom, by keeping the nuclei in a magnetic field. Radio waves are the lowest form of energy and frequency lies between 10^7 and 108 cps, sufficient to effect the spin of the nucleus of the atom of a molecule.

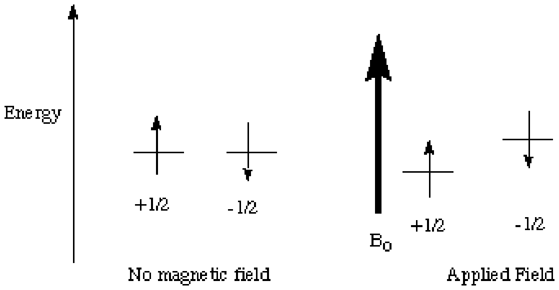
History

First described and measured by Isidor Rabi in 1938, and in 1944, Rabi was awarded the Nobel Prize in physics for this work. In 1946, Felix Bloch and Edward Mills Purcell expanded the technique for use on liquids and solids.

4.2.1 - Nuclear spin

All nucleons, that is neutrons and protons, composing any atomic nucleus, have the intrinsic quantum property of spin. The overall spin of the nucleus is determined by the spin quantum number *S.*

A nucleus must have a non-zero nuclear spin (I) to be observed in an NMR experiment. The most commonly observed nuclei have I=1/2 (^{1}H, ^{13}C, ^{19}F, ^{31}P). The nuclear spin, although not really a physical "spinning" has an associated magnetic moment vector that will interact with a magnetic field . The nucleus has spin states I, I-1, ..-I available. In the absence of a magnetic field, all of these spin states are degenerate. This degeneracy is removed when a magnetic field, B_0, is applied. The lowest energy state has the spin magnetic vector aligned parallel to the magnetic field. In the higher energy state, the vector is aligned antiparallel.



The splitting due to B_0 is dependent on the magnetic field strength

As, $\Delta E = \gamma(h/2\pi)B_0$

where gamma is a constant called the magnetogyric ratio, h is Plank's constant and B_0 is the strength of the applied field. The energy splitting induced by the magnetic field is not very large.

4.2.2 - NMR active nuclei

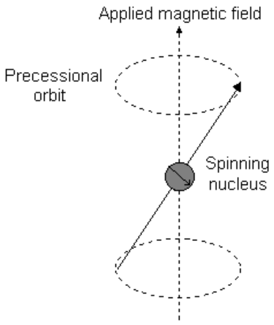
Subatomic particles spins on their axes. In many atoms (such as ^{12}C) these spins are paired against each other results in no overall spin. However, in some atoms (such as ^{1}H and ^{13}C) the nucleus does possess an overall spin. The rules for determining the net spin of a nucleus are as follows;

No.of protons	No. of neutrons	I	Examples
Even	Even	0	^{12}C, ^{16}O, ^{32}S
Odd	odd or Even	½	^{1}H, ^{19}F and ^{31}P
		3/2	^{11}B, ^{79}Br
E ven	odd	½	^{13}C
		3/2	^{127}I

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

4.2.3 A - Spinning Nuclei-Magnetic moments-Larmor precision

The spinning of electrically charged particle generates a magnetic field whose magnitude and direction is described by a vector quantity Magnetic Moment (μ) .



It also performs a slower waltz like motion in which the spinning axis of the top moves slowly around the vertical called precisional around the vertical axis of earth’s gravitational field. The precision arises from the interaction of spin with earth’s motion and the top is said to be precessing gravity acting vertically downwards called **Gyroscopic Motion.** Proton precesses about the axis of the external magnetic field same as spinning gyroscope precesses under the influence of gravity. Precessional motion observed by Larmor is known as **Larmor Precession.**

Nuclei when Placed in an external magnetic field rotates not in the plane of force of field but at right angles to the plane. The axis of rotating particle moves in a circular path around Magnetic field.

Larmor Precission

Defined as number of revolutions per second made by magnetic moment vector of the nucleus H_o i:e It is equal to the frequency of EMR in megacycles per second necessary to induce a transition from one spin state to another.

$$w/2\pi = vo = \gamma H_0/2\ \pi$$

where, ω is angular frequency

ν_0 is precessional frequency. It is just the frequency separation between two energy levels.

H_0 is applied magnetic field

γ **gyromagnetic ratio is the ratio of magnetic moment (μB) & angular moment Ih/2 π of nucleus.**

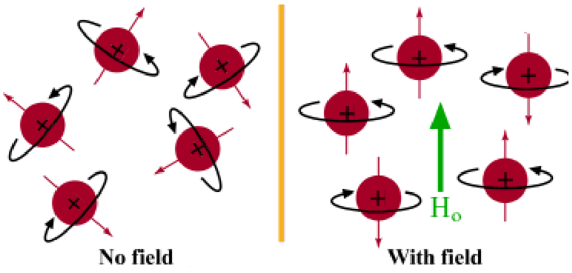
$$= 2\ \pi\ \mu B/\ Ih$$

Therefore precessional angular velocity $= \dfrac{\underline{2\ \pi\ \mu B\ .}H_o}{Ih} = \gamma.H_o$

If a proton is precessesing in the aligned orientation, it is in the lower energy state (+1/2). By absorbing energy it passes into the opposed orientation known as higher energy state against Ho called **flipping of proton.**energy required to flip the proton depends on the strength of the external magnetic field.**Stronger the magnetic field greater its tendency to keep nucleus aligned with it.**

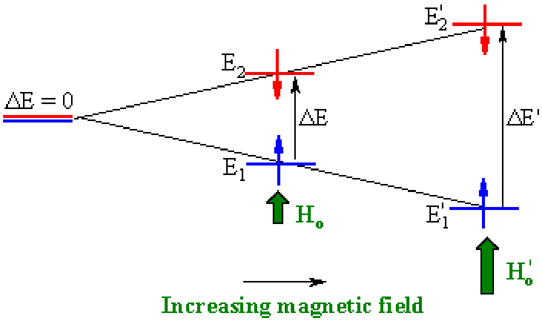
4.2.4 -Theory of NMR –

Since a nucleus is a charged particle in motion, it will develop a magnetic field. ^{1}H and ^{13}C have nuclear spins of 1/2 and so they behave in a similar fashion to a simple, tiny bar magnet. In the absence of a magnetic field, these are randomly oriented but when a field is applied they line up parallel to the applied field, either spin aligned or spin opposed. The more highly populated state is the lower energy spin state spin aligned situation.



In NMR, EM radiation is used to "flip" the alignment of nuclear spins from the low energy
higher energy spin opposed state. The energy required for this transition depends on the str
magnetic field but in is small and corresponds to the radio frequency range of the EM spect

e spin-flip depends on the magnetic field th no applied field, there is no energy n states, but as the field increases so does the he spin states and therefore so does the e the spin-flip, referred to as resonance.

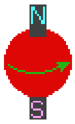


4.2.5 - NUCLEAR RESONANCE-

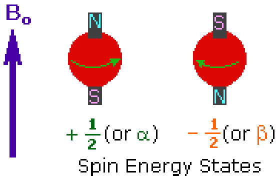
Larmor Mechanism is the actual mechanism in which the nuclear Spin can interact with a beam of EMR.

If the beam has same frequency as of precessing nucleus, it can interact coherently with the nucleus and energy can be exchanged and this phenomenon is known as *RESONANCE.*

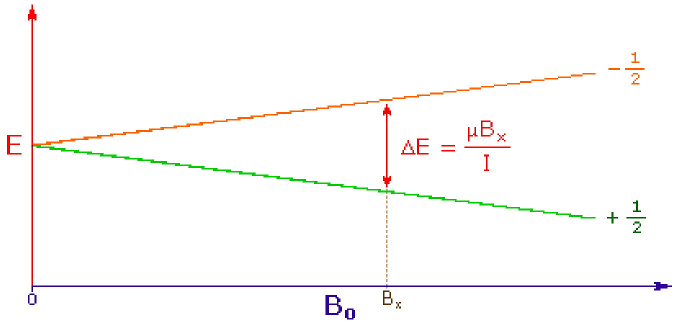
As far as nuclei is concerned, the process is called Nuclear Magnetic Resonance.



1. A spinning charge generates a magnetic field, .
   The resulting spin-magnet has a magnetic moment (μ)
   Proportional to the spin.
2. In the presence of an external magnetic field (B_0), two spin states exist, +1/2 and -1/2. The magnetic moment of the lower energy +1/2 state is aligned with the external field, but that of the higher energy -1/2 spin state is opposed to the external field.



3. The difference in energy between the two spin states is dependent on the external magnetic field strength, and is always very small. The two spin states have the same energy when the external field is zero, but diverge as the field increases. At a field equal to B_x a formula for the energy difference is given (I = 1/2 and μ is the magnetic moment of the nucleus in the field).



Strong magnetic fields are necessary for nmr spectroscopy. The international unit for magnetic flux is the tesla (**T**). The earth's magnetic field is not constant, but is approximately 10^{-4} T at ground level.
Irradiation of a sample with radio frequency (rf) energy corresponding exactly to the spin state separation of a specific set of nuclei will cause excitation of those nuclei in the +1/2 state to the higher -1/2 spin state.

Thus,when applied frequency from radio source becomes larmor/angular frequency of precession, two are said to be in resonance.as a result of this resonance some nuclei are excited from low energy state (m=+1/2) to high energy state (m= -1/2) by absorbance of energy. This transition is known as ***flipping of proton.***

Number of signals at different applied field strength is equal to different sets of equivalent protons. Different sets of equivalent protons requires slightly different applied field strength to produce absorption spectrum.

Transition energy

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

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

the *magnetogyric ratio* is a fundamental nuclear constant which has a different value for every nucleus. *h* is Plancks constant.The energy of a particular energy level is given by;

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

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

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

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

This means that if the magnetic field, *B*, is increased, so isΔ *E*. It also means that if a nucleus has a relatively large magnetogyric ratio, then ΔE is correspondingly large.

4.2.6 - Nuclear Saturation & relaxation process

When applied frequency from radio source becomes larmor/angular frequency of precession, two are said to be in resonance.as a result of this resonance some nuclei are excited from low energy state (m=+1/2) to high energy state (m= -1/2) by absorbance of energy.This transition is known as ***flipping of proton.***

But if number of nuclei in two states become equal, absorption signal decreases or approaches zero. Then the spin system is said to be saturated and process is known as ***saturation.***Then various non-radiative transitions takes place known as ***Relaxation Process***.To prevent saturation rate of relaxation must be greater than absorption.

Relaxation processes

Emission of radiation by photon is insignificant because the probability of re-emission of photons varies with the cube of the frequency. At radio frequencies, re-emission is negligible. Therefore varoius non-radiative relaxation processes takes place.

NMR relaxation rates should be fast - but not too fast. If the relaxation rate is fast, then saturation is reduced. If the relaxation rate is too fast, line-broadening in the resultant NMR spectrum is observed.

There are two major relaxation processes;

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

Spin - lattice relaxation

It involves the transfer of energy from the nucleus in its higher energy state to the molecular lattice. The sample in which the nuclei are held is called the *lattice*. Nuclei in the lattice are in vibrational and rotational motion, which creates a complex magnetic field. The magnetic field caused by motion of nuclei within the lattice is called the *lattice field*. This lattice field has many components. These components of the lattice field can interact with nuclei in the higher energy state, and cause them to lose energy (returning to the lower state). The energy that a nucleus loses increases the amount of vibration and rotation within the lattice .

The relaxation time, T_1 (the average lifetime of nuclei in the higher energy state) is dependant on the magnetogyric ratio of the nucleus and the mobility of the lattice. As mobility increases, the vibrational and rotational frequencies increase, making it more likely for a component of the lattice field to be able to interact with excited nuclei. However, at extremely high mobilities, the probability of a component of the lattice field being able to interact with excited nuclei decreases.

Spin - spin relaxation

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

CHECK YOUR PROGRESS - 1

Notes : i) Write your answer in the space given below.
ii) Compare your answer with those given at the end of the unit.

Q a. Why ^{12}C,^{16}O,^{18}O,^{32}S do not show NMR spectra.

Q b.The spin number of I of ^{35}Cl nuclei is _____________

Q c.A nuclei having spin quantum number (I) = 3/2 is –

- $_{17}Cl^{36}$ (ii) $_7N^{14}$ (iii) $_5B^{11}$ (iv) $_{13}Al^{27}$

Q d.The value of Transition energy between two spin states in NMR is ___________

Q e. The Spin Lattice relaxation is also known as ____________ & in it the spin/energy of the nuclei is transferred to ______________.

Q f.In NMR the EMR used are ______________ having frequency range lies between …………

____

4.2.7 - INSTRUMENTATION

A high resolution spectrometer contains a complex collection of electronic equipments. In this technique intense magnetic field is required along with precisely controlled power supplies as well as frequencies. Most of the power required by the instrument is dissipated as heat & very little of it (in microwatts) is obtained as a signal which has to be amplified by a complex electronic system. The simplest method is referred to as the continuous wave (CW) method.

The apparatus consists of the following essential components :

1.Sample Holder : sample holder should be chemically inert, durable &transparent to rf radiation. Generally glass tubes are employed which are sturdy, practical & cheap. They are generally about 7.5 cm long & approximately 0.3 cm in diameter.

2.Magnet : Permanent magnets or electromagnets can be used in a nuclear magnetic resonance instrument.

- **It** should give homogeneous magnetic field
- **The** strength & direction of the magnetic field should not change from point to point.
- Strength of the field should be very high, atleast 20,000 gauss (G) because the chemical shifts are proportional to the field strength.

Permanent magnets & electromagnets can give highly homogeneous fields by carefully machining & alignment of the pole faces. Homogeneity can be obtained with the help of current shims that consist of coils & are located at the pole faces. The current shims are used to produce field gradients in various directions so as to cancel out gradient inherent in the main field.

Permanent & conventional electromagnets are generally used in spectrometers operating upto 100 MHz. Superconducting magnets have been found to realise fields corresponding to 230 MHz.

3.Sweep Generator : In order for nucleus to resonate, the precession frequency of the nucleus should become equal to the frequency of the applied rf radiation. There are two methods to bring resonance in nuclei.

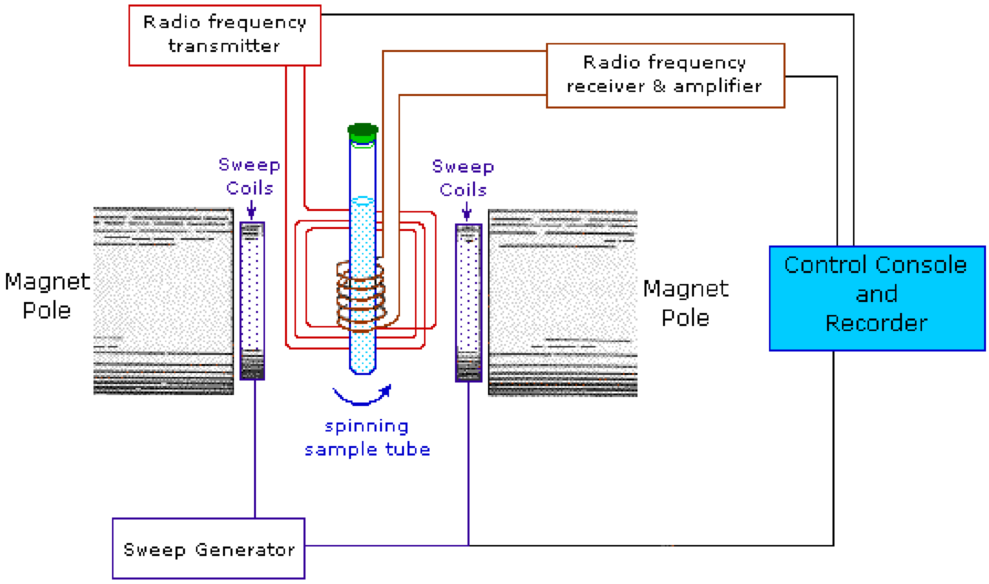
Frequency sweep method – If the applied magnetic field H_0 is kept constant, the precession frequency is fixed then the frequency of rf field is changed so that it become equal to the resonance frequency then this method is known as Frequency sweep method.

Field sweep method – If the rf radiation is kept constant, the resonance frequency of the nucleus must be changed by varying Ho. It is known as field sweep method.

4.**Sweep coils** – To vary the magnetic field of a large stable magnet a small variable magnetic field is superimposed on the main field. It is done by fixing a pair of Helmholtz coils in the pole faces of the main magnet known as sweep coils the magnetic field induced by these coils can be varied by varying the current flowing through them. The small magnetic field generated by the sweep coils is in the same direction as the main field therefore it is added to the main field.

5.**Radio Frequency Generator** – To generate radio frequency radiation , radio frequency oscillator is used. To achieve the maximum interaction of the rf radiation with the sample, the coil of oscillator is wound around the sample container. The oscillator irradiates the sample with a rf radiation.

The oscillator coil is wound perpendicular to the applied magnetic field so that the applied rf field should not change the effective magnetic field in the process of irradiation.



6. Radio Frequency Receiver : When the radio frequency radiation is passed through the magnetized sample, two phenomena, namely absorption & dispersion may occur. Interpretation of absorption spectrum is easier as compared to dispersion spectrum. The Detector should be capable of separating absorption signal from dispersion signal & from that of rf oscillator. There are two main methods of detection as follows – Using Radio Frequency Bridge – its network balances out the transmitter signal & allows the absorption & dispersion signal to appear as an out- of –emf across the bridge. In this method the coil used for surrounding the samples serves as both a transmitter & a receiver coil. Separate receiver coils- This method is known as crossed coil or nuclear induction method. In this method the two coils are fixed at right angles to each other as well as to the direction of static magnetic field, so that they will not be effectively coupled. Thus the transmitter signal is separated from the absorption & dispersion signal as they differ in phase by an angle of 90^0.

Detector – The phase sensitive detector which helps the operator to select the phase of the signal to be detected are used generally.

7.Read out System – The absorption signal received from radiofrequency receiver is extremely weak . Therefore, it requires considerable amplification before it is fed to a chart recorder. **Receiver subsystem:** This consists of the components: Preamplifier, Amplifier, Mixer and the Analog-to-Digital converter (ADC). The Mixer is used to subtract a reference frequency of specified phase from the observed signal, resulting a signal of lower frequency that can be easily digitized.

Technique - A solution of the sample in a uniform 5 mm glass tube is oriented between the poles of a powerful magnet. Radio frequency radiation of appropriate energy is incident on the sample . A receiver coil surrounds the sample tube, and emission of absorbed rf energy is monitored by dedicated electronic devices and a computer. An nmr spectrum is acquired by varying or sweeping the magnetic field over a small range while observing the rf signal from the sample. An equally effective technique is to vary the frequency of the rf radiation while holding the external field constant.

Reference compound - For ^{1}H NMR, the reference is usually tetramethylsilane, Si $(CH_3)_4$. the location of an nmr signal in a spectrum relative to a reference signal from a standard compound added to the sample. It is usually referred to as **TMS**.

A reference standard should be chemically –

1.unreactive
2. easily removed from the sample after the measurement
3.It should give a single sharp nmr signal that does not interfere with the resonances normally observed for organic compounds.
4. The hydrogen atoms in it are all structurally equivalent, averaged for fast conformational equilibria.Therefore it gives a single sharp resonance signal.
5.Relatively volatile & soluble in most organic solvents.

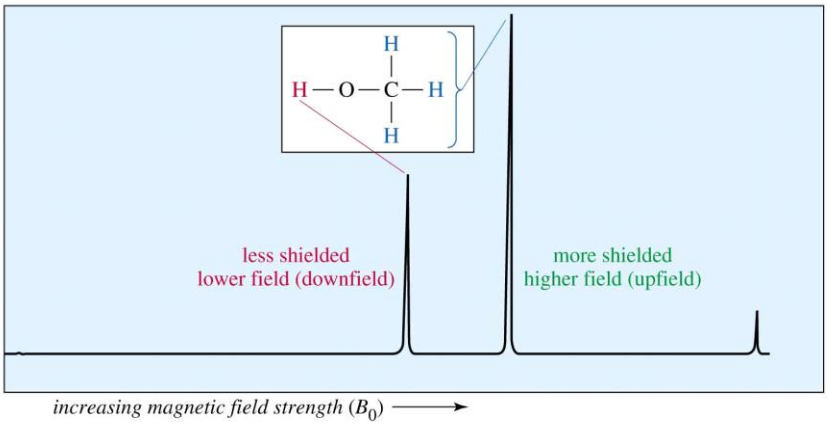
TMS is not soluble in aqueous solutions therefore for water soluble substances, DSS (2,2 dimethyl–2 silapentane-5-sulphonate) may be used as a reference. The protons in the methyl group of DSS give a strong line. The methylene protons of DSS give a series of small peaks.

Other used solvents are- Carbon tetrachloride - But it has no hydrogen that could introduce an interfering signal. CCl_4 is a poor solvent for many polar compounds and is also toxic. Deuterium labeled compounds, such as deuterium oxide (D_2O), chloroform-d ($DCCl_3$), benzene-d_6 (C_6D_6), acetone-d_6 (CD_3COCD_3) and DMSO-d_6 (CD_3SOCD_3) are now widely used as nmr solvents. Since the deuterium isotope of hydrogen has a different magnetic moment and spin, it is invisible in a spectrometer tuned to protons.

Various aspects of NMR spectrum –

- The plot of external field strength against absorption is called NMR (or PMR) spectrum.
- The various peaks of the spectrum represent different sets of equivalent protons with different environment.
- The number of signals which represents the number of sets of equivalent protons present in the molecule.
- The position of the signals (peaks) which gives us information about the electronic environment of each set of equivalent protons.
- The intensities of different signals which are proportional to the number of protons present in each set.
- Splitting of each peak (signal) into several peaks which tells us about the number of neighbouring protons.

Representation of NMR Signals



Check Your Progress-2

Notes : i) Write your answer in the space given below.

ii) Compare your answer with those given at the end of the unit.

Q a.Why the rf Oscillator coil is wound perpendicular to the applied magnetic field?

Q b. For what type of substances TMS is not suitable

Q c.Which sweep method is better & why?

Q d. List some other solvents used in NMR?

4.2.8 – **Shielding of magnetic nuclei**

In nuclear magnetic resonance (NMR), the chemical shift describes the dependence of nuclear magnetic energy levels on the electronic environment in a molecule. The magnetic field at the nucleus is not equal to the applied magnetic field; electrons around the nucleus shield it from the applied field. The difference between the applied magnetic field and the field at the nucleus is termed the *nuclear shielding*.

When the secondary field produced by the circulating electrons oppose the applied field at a particular nucleus in the molecule, the effective field experienced by the nucleus is less than the applied field.This is known as **positive shielding or upfield shielding or diamagnetic shift**.The value of applied field necessary to bring the resonance will be greater (low δ value) than that were no secondary opposing field .

If the secondary field produced by the circulating electrons reinforces the applied field , the position of resonance moves downfield. This is known as **negative shielding or paramagnetic shift (high δ value)**.

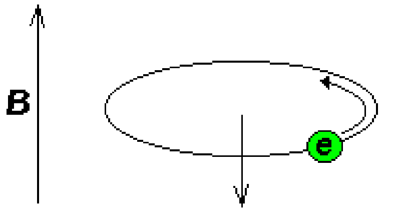
Chemical shift

This change in the effective field on the nuclear spin causes the NMR signal frequency to shift. The magnitude of the shift depends upon the type of nucleus and the electron motion in the nearby atoms and molecules. It is called a "chemical shift".

- In proton (^{1}H) NMR, p-orbitals play no part therefore a small range of chemical shift (10 ppm) is observed.
- It is measured relative to a reference compound.
- It is measured in units of parts-per-million (ppm), and designated by the symbol δ

Example - Consider the s-electrons in a molecule. They have spherical symmetry and circulate in the applied field, producing a magnetic field which opposes the applied field. This means that the applied field strength must be increased for the nucleus to absorb at its transition frequency. This *upfield shift* is termed as *diamagnetic shift*.

The variations of nuclear magnetic resonance frequencies of the same kind of nucleus, due to variations in the electron distribution, is called the chemical shift.



Magnetic field produced
by circulating electron

Electrons in p-orbitals have no spherical symmetry. They produce comparatively large magnetic fields at the nucleus, which give a *low field shift*. This "deshielding" is termed *paramagnetic shift*. In it the induced field produced by the electrons aligns with the applied field therefore applied field strength must be decreased for the nucleus to absorb its transition frequency.

Diamagnetic shielding

In real molecules protons are surrounded by a cloud of charge due to adjacent bonds and atoms. In an applied magnetic field (B_0) electrons circulate and produce an induced field (B_i) which opposes the applied field. The effective field at the nucleus will be $B = B_0 - B_i$. The nucleus is said to be experiencing a diamagnetic shielding

Some rules about chemical shifts are as follows

·Nulcei in different chemical environments absorb radiation of different frequencies (barring coincidence) called non equivalent protons

·Nuclei in the same chemical environment absorb radiation at the same frequency (chemical shift equivalency) are called equivalent protons.

Measurement of Chemical shift

The position of the peaks in an NMR spectrum relative to the reference peak is expressed in terms of chemical shift. The effective magnetic field at the nucleus can be expressed in terms of the externally applied field B_0 by the expression

$$B = B_0(1-\sigma)$$

where σ is called the shielding factor or screening factor. The factor σ is small - typically 10^{-5} for protons and $<10^{-3}$ for other nuclei (Becker).

In practice the chemical shift is usually indicated by a symbol δ which is defined in terms of a standard reference.

$$\delta = \frac{(\nu_S - \nu_R)x10^6}{\nu_R} \qquad \textit{quoted as ppm}$$

Chemical shift δ is usually expressed in parts per million (ppm) by frequency, because it is calculated from:

$$\delta = \frac{\text{difference between a resonance frequency and that of a reference substance}}{\text{operating frequency of the spectrometer}}$$

Since the numerator is usually in hertz, and the denominator in megahertz, delta is expressed in ppm.

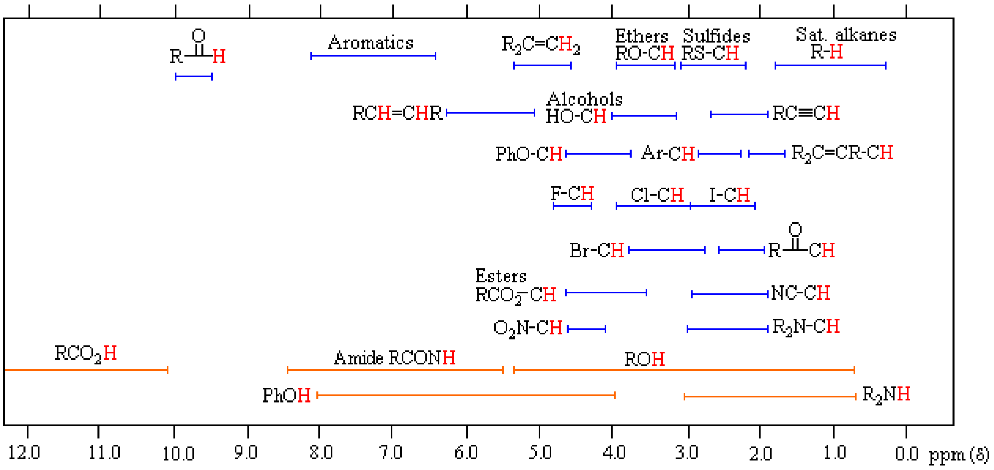
In terms of field strength- $\delta = \frac{H_0(\text{reference}) - H_0(\text{sample})}{H_0(\text{reference})} \text{ X } 10^6\text{ppm}$

- The detected frequencies (in Hz) for ^{1}H, ^{13}C, and ^{29}Si nuclei are usually referenced against TMS (tetramethylsilane) or DSS, which is assigned the chemical shift of zero. A small numericalvalue of δ indicates a small downfield shift while larger value indicates a large downfield shift.
- The chemical shift is independent of the applied field. On the other hand the resolution of NMR will increase with applied magnetic field resulting in ever increasing chemical shift changes.
- An alternative method used for defining the position of the resonance relative to the reference is tau (τ) scale. On this scale the reference is assigned the arbitrary position of 10 & the values of other resonances are given by

  $\tau = 10 - \delta$

On τ scale the TMS is assigned a value of 10.0ppm & most chemical shifts have value between
0 & 14.A small value of τ represents a lowfield absorption & a high value indicates a high field absorption. Thus, larger value of δ means smaller value of τ

For example, for the ^1H-NMR spectrum for ethanol (CH_3CH_2OH), one would expect three specific signals at three specific chemical shifts: one for the CH_3 group, one for the CH_2 group and one for the OH group. A typical CH_3 group has a shift around 1 ppm, a CH_2 attached to an OH has a shift of around 4 ppm and an OH has a shift around 2–3 ppm depending on the solvent used.



Proton chemical shift

For samples in $CDCl_3$ solution. The δ scale is relative to TMS at $\delta = 0$

Factors influencing Chemical shifts

1.**Inductive Effect & electron density**- If the electron density about a proton nucleus is relatively high, the induced field due to electron motions will be strong. Therefore The shielding effect will be larger, and a higher external field (B_o) will be needed for the rf energy to excite the nuclear spin. Such nuclei are said to be shielded.

If the electron density around the protons decreases, and they resonate at lower field strengths i:e they are deshielded. Elements that are more electronegative than carbon should exert an opposite effect i;e reduce the electron density at nucleus & deshielding will takes place i;e smaller value of applied field will be needed to bring the proton to resonance.

Example – substituted methanes, CH_3X. As X becomes increasingly electronegative , so the electron density around the protons decreases, & they resonate at lower field strengths. This chemical shift differences in proton resonance due to presence of electronegative group is known as inductive effect. The chemical shift of the methyl protons increase in the order I < Br < Cl < F from 2.16 ppm to 4.26 ppm.Thus greater the electronegativity of the atom or group, greater will be the shielding effect on a proton.

2.Vander – waal's deshielding – In overcrowded molecules, some protons may be occupying sterically hindered position. Electron cloud of a bulky group (hindering position) will tend to repel the electron cloud surrounding proton. Such proton will be deshielded & will resonate at slightly higher value of chemical shift than expected in the absence of this effect.

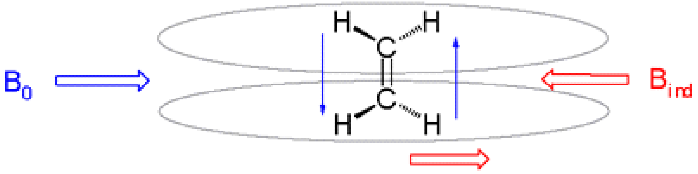
3. Anisotropic Effects or π-Electron Functions

The low field resonance of hydrogens bonded to double bond or aromatic ring carbons causes low field signal. But the hydrogen atom of a terminal alkyne, appears at a relatively higher field. It is due to the hydrogens bonded to pi-electron systems, as pi-electrons interact with the applied magnetic field.

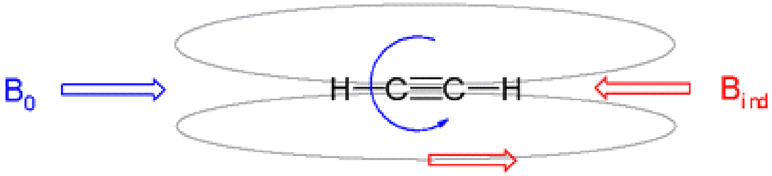
Pi-electrons are more polarizable than are sigma-bond electrons.The field induced pi-electron movement produces strong secondary fields that perturb nearby nuclei.

Example - The pi-electrons associated with a benzene ring .The electron cloud above and below the plane of the ring circulates in reaction to the external field so as to generate an opposing field at the center of the ring and a supporting field at the edge of the ring. This kind of spatial variation is called **anisotropy**, and it is common to nonspherical distributions of electrons.The local symmetry of such molecular orbitals is very high leading to "isotropic" shift, the shielding effect will depend on the orientation of the molecule with respect to the external field (**B_0**) . The protons in aromatic compounds are shifted downfield with a signal for benzene at 7.73 ppm as a consequence of a diamagnetic ring current.

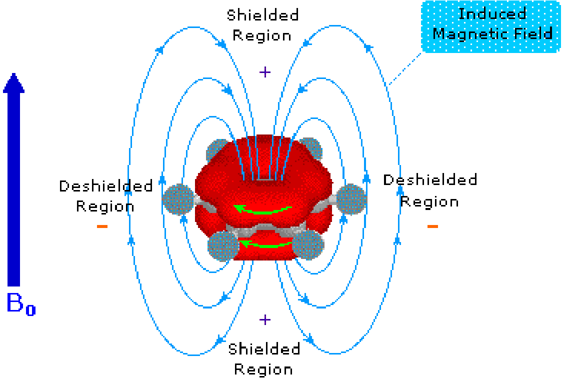
Anisotropic induced magnetic field effects are the result of a local induced magnetic field experienced by a nucleus resulting from circulating electrons that can either be paramagnetic when it is parallel to the applied field or diamagnetic when it is opposed to it. It is observed in alkenes where the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



Alkyne protons by contrast resonate at high field in a 2–3 ppm range. For alkynes the most effective orientation is the external field in parallel with electrons circulation around the triple bond. In this way the acetylenic protons are located in the cone-shaped shielding zone hence the upfield shift.



Regions in which the induced field supports or adds to the external field are said to be **deshielded**, because a slightly weaker external field will bring about resonance for nuclei in such areas. However, regions in which the induced field opposes the external field are termed **shielded** because an increase in the applied field is needed for resonance. Shielded regions are designated by a **plus sign**, and deshielded regions by a **negative sign**.
The anisotropy about the triple bond nicely accounts for the relatively high field chemical shift of ethynyl hydrogens.

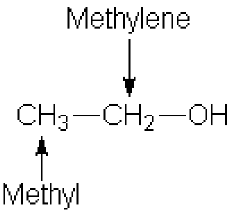


4.Hydroxyl Proton Exchange and the Influence of Hydrogen Bonding
Hydrogen bonding shifts the resonance signal of a proton to lower field higher frequency . Because the H-bonded proton being attached to highly electronegative atom will have smaller electron density around it. Therefore the field felt by such proton will be more & resonance will occur downfield.The downfield shift depends upon the strength of hydrogen bonding.
Intramolecular Hydrogen bonding does not show any shift in absorption due to the change in concentration.

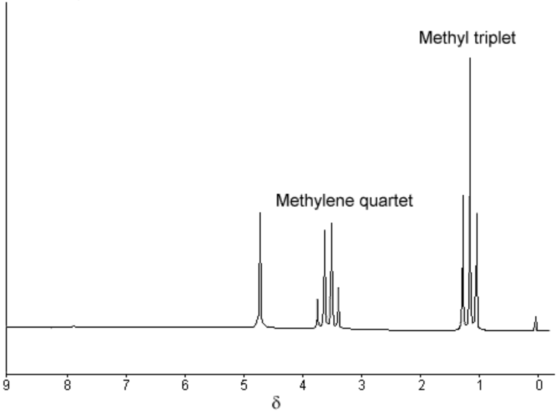
Check Your Progress -3
Notes : i) Write your answer in the space given below.
ii) Compare your answer with those given at the end of the unit.
Q a.As the distance of the proton from the electronegative atoms increases, the deshielding effect because of it _____________.
Q b.The higher the electronegativity of the atom, ________ is the deshielding caused to proton.
Q c .Write the relation between δ & τ scale?
Q d.Shielding & deshielding are associated with : (i) circulation of electrons (ii) spinning of proton (iii) spinning of neutron.

4.2.9 - Spin - spin interactions

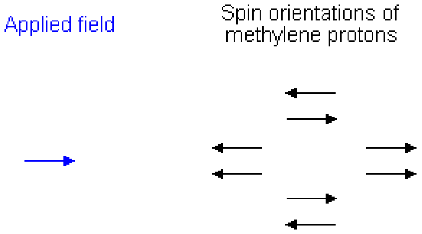
Consider the structure of ethanol;



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

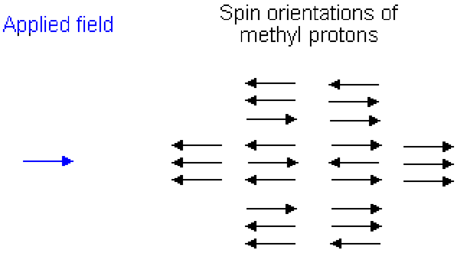


The methyl peak is split into a triplet,as the **methylene** protons can have one of two possible orientations (aligned with or opposed against the applied field). This gives a total of four possible states;



In the first possible combination, spins are paired and opposed to the field. This has the effect of reducing the field experienced by the **methyl** protons; therefore a slightly higher field is needed to bring them to resonance, resulting in an upfield shift. Neither combination of spins opposed to each other has an effect on the methyl peak. The spins paired in the direction of the field produce a downfield shift. Hence, the methyl peak is split into three, with the ratio of areas 1:2:1.

Similarly, the effect of the methyl protons on the methylene protons is such that there are eight possible spin combinations for the three methyl protons;



Out of these eight groups, there are two groups of three magnetically equivalent combinations. The methylene peak is split into a quartet. The areas of the peaks in the quartet have the ration 1:3:3:1.

In a *first-order* spectrum (where the chemical shift between interacting groups is much larger than their coupling constant), interpretation of splitting patterns is quite straightforward;

The multiplicity of a multiplet is given by the number of equivalent **protons** in **neighbouring** atoms plus one, i.e. *the n + 1 rule*

Equivalent nuclei do not interact with each other. The three methyl protons in ethanol cause splitting of the neighbouring methylene protons; they do not cause splitting among themselves

The coupling constant is not dependant on the applied field. Multiplets can be easily distinguished from closely spaced chemical shift peaks.

Coupling Constant - J

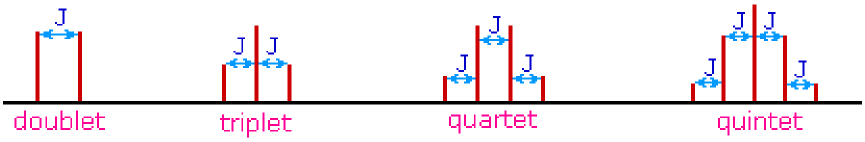
Multiplicity	**Intensity Ratio**
Singlet (s)	1
Doublet (d)	1:1
Triplet (t)	1:2:1
Quartet (q)	1:3:3:1
Quintet	1:4:6:4:1
Sextet	1:5:10:10:5:1
Septet	1:6:15:20:15:6:1

J-coupling or **scalar coupling** arises from the interaction of different spin states through the chemical bonds of a molecule and results in the splitting of NMR signals. These splitting patterns can be complex or simple.

- Coupling to *n* equivalent (spin ½) nuclei splits the signal into a *n*+1 **multiplet** with intensity ratios following Pascal's triangle.
- Coupling to additional spins will lead to further splittings of each component of the multiplet e.g. coupling to two different spin ½ nuclei with significantly different coupling constants will lead to a *doublet of doublets* .
- The coupling between nuclei that are chemically equivalent (that is, have the same chemical shift) has no effect of the NMR spectra and couplings between nuclei that are distant (usually more than 3 bonds apart for protons in flexible molecules) are usually too small to cause observable splittings.
- *Long-range* couplings over more than three bonds can often be observed in cyclic and aromatic compounds, leading to more complex splitting patterns.

Example, in the proton spectrum for ethanol the CH_3 group is split into a *triplet* with an intensity ratio of 1:2:1 by the two neighboring CH_2 protons. Similarly, the CH_2 is split into a *quartet* with an intensity ratio of 1:3:3:1 by the three neighboring CH_3 protons. In principle, the two CH_2 protons would also be split again into a *doublet* to form a *doublet of quartets* by the hydroxyl proton, but intermolecular exchange of the acidic hydroxyl proton often results in a loss of coupling information.

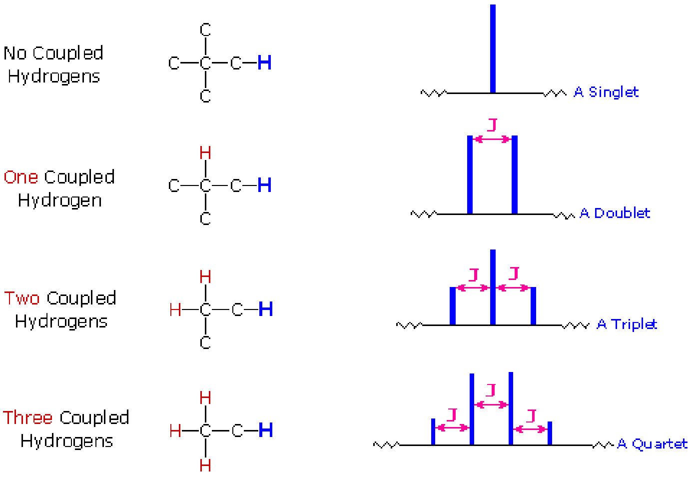
- Signals are known as doublet (two equal intensity signals), triplet (three signals with an intensity ratio of 1:2:1) and quartet (a set of four signals with intensities of 1:3:3:1). The line separation is always constant within a given multiplet, and is called the coupling constant (J).
- The magnitude of J, usually given in units of Hz, is magnetic field independent.

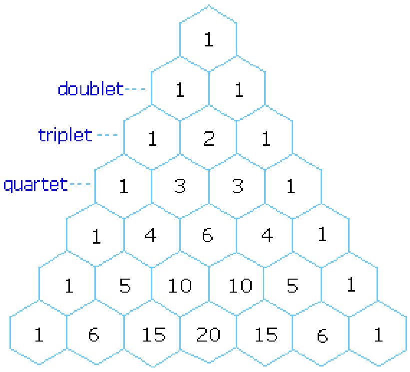


The splitting patterns shown above display the ideal or "**First-Order**" arrangement of lines. This is usually observed if the spin-coupled nuclei have very different chemical shifts (i.e. $\Delta\nu$ is large compared to J)

Reporting Coupling Constants

- The magnitude of coupling is independent of field strength, so coupling constants are reported in Hz.
- Peak positions on NMR printouts are usually reported in ppm, so the coupling constants need to be converted into Hz. This can be done by multiplying the coupling in ppm by (probe frequency/ 10^{6}).
- Coupling constants are reported in the form $^{X}J_{AB}$, where A and B designate the type of nuclei involved in the coupling (i.e. ^{1}H) and X is the number of bonds between the nuclei A and B.





Pascal's Triangle

If a given nucleus is spin-coupled to two or more sets of neighboring nuclei by different J values, the n+1 rule does not predict the entire splitting pattern. Instead, the splitting due to one J set is added to that expected from the other J sets.

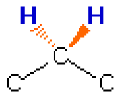
Factors affecting Coupling Constant & Various types of coupling constants

- **Bond angle - Geminal coupling**

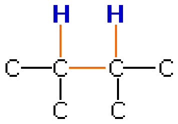
In case of germinal protons (protons attached on the same carbon having different chemical environment) of a saturated compound the value of J depends on bond angle.
J can have any sign. Geminal protons are separated by 2 bonds.(- CH_2). If these protons are in different environments, then coupling is usually strong. When bond angle is 105^{0},J is approximately - 25cps.

J becomes nearly -12 cps when bond angle increases to 109^0.When bond angle increases to 125^0 the value of J increases to zero. As bond angle increases j value becomes positive. J_{HH} depends on hybridization of carbon atom and the bond angle and the substituent such as electronegative atoms. When S-character is increased, Geminal coupling constant is increased : $J_{sp1} > {}^2J_{sp2} > {}^2J_{sp3}$ The bond angle(HCH) gives rise to change ${}^2J_{HH}$ value and depend on the strain of the ring in the cyclic systems. Geminal coupling constant determines ring size.

Example – The value of J for methane is -12.2 cps,while that for ethylene is +2.3cps.



Geminal Hydrogens



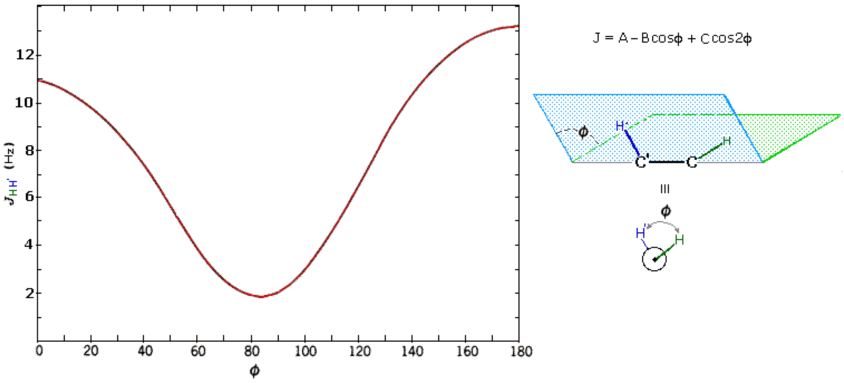
Vicinal Hydrogens

- **Dihedral angle – vicinal coupling**

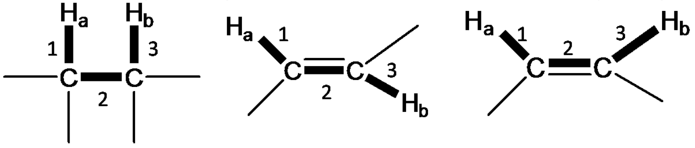
For vicinal protons, J varies with dihedral angle. **Vicinal protons are the protons which are separated by three bonds.**when the dihedral angle is 0^0 or 180^0 j values are more when dihedral angle is 90^0 the values of J is slightly negative.

The structures of cis and trans-4-tert-butyl-1-chlorocyclohexane, illustrate how the coupling constant changes with the dihedral angle (φ) between coupled hydrogens. The inductive effect of chlorine shifts the resonance frequency of hydrogen to a lower field (δ ca. 4.0). The preferred equatorial orientation of the large tert-butyl group holds the six-membered ring in the chair conformation . In the trans isomer the hydrogen in an axial orientation; whereas for the cis isomer it is equatorial. Vicinal coupling constant depending on the dihedral angle is given by the Karplus equation

$$^3J = 7.0 - 0.5cos\phi + 4.5cos^2\phi$$



Geminal couplings are most commonly observed in cyclic structures, but are also evident when methylene groups have diastereomeric hydrogens.



The coupling constant increases with the decrease of bond length. Electronegative atoms affect vicinal coupling constants so that electronegative atoms decrease the vicinal coupling constants.

3. Long – range coupling – usually no coupling is observed if the distance between the two absorbing nuclei is more than three covalent bonds .But if unsaturated compounds or in fluoro compounds, appreciable coupling is observed with the help of high resolution spectrometers even if the concerned nuclei are three bonds apart . It is called as long – range coupling.

4.Second-order (or strong) coupling

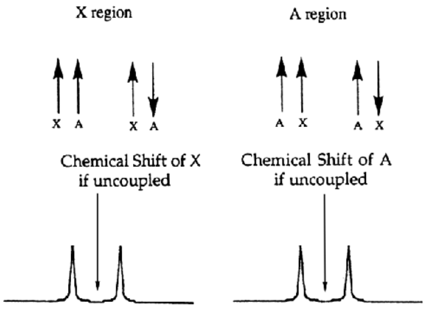
If the shift separation decreases (or the coupling strength increases), the multiplet intensity patterns are first distorted, and then become more complex and less easily analyzed (especially if more than two spins are involved). Second-order effects decrease as the frequency difference between multiplets increases, so that high-field (i.e. high-frequency) NMR spectra display less distortion than lower frequency spectra. Early spectra at 60 MHz were more prone to distortion than spectra from later machines typically operating at frequencies at 200 MHz or above.

4.2.10- Classification

Pope classify NMR active species or molecules on the following basis –
Protons having same chemical shift or separated by small chemical shift are kept in one set are designated by letters A,B,C
Sets separated by large δ are designated by X,Y,Z.
Sets having intermediate δ are designated by M,N,O.
Nuclei which are chemically identical but magnetically non equivalent are differentiated as AA′, BB′.
Nuclei having large δ difference as compare to J (ΔV/J ~10) are represented by AX, AMX.
If δ difference approaches J then the letter adjacent in the alphabet is used.
AX becomes AB system.
AMX becomes ABC System
If ΔV/J >10 then AX system is used
If ΔV/J <10 then AB system is used.

Proton system

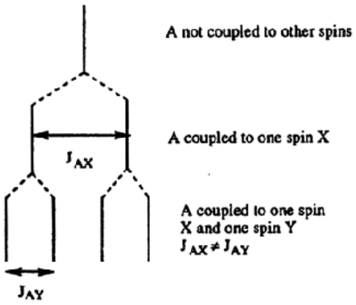
AX system – For two I = 1/2 nuclei coupled to each other (call one A, the other is X), there are two different possible orientations of the magnetic moments for both the X and A nuclei. The energy of the X transition depends on the spin-state of the A nucleus to which it is coupled; likewise, the energy of the A transition depends on the spin state of the X nucleus to which it is coupled. Accordingly, the signals for both the A and X nuclei appear as two lines, equally displaced above and below the respective frequency for the uncoupled nucleus . The splitting between these lines (usually expressed in Hz, **NOT** ppm) is referred to as the coupling between A and X and is denoted as J_{AX}



AX system and spectrum.

The more spins to which a group is coupled, the more complex the splitting patter for the signal of that group. The number of lines observed for a peak is called the multiplicity, M, which is a function of the number of equivalent nuclei to which the signal is coupled (n) and the spin (I) of the n nuclei: M = 2nI + 1

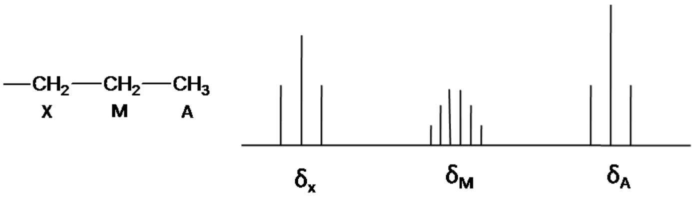
If a group of spins is coupled to more than one set of nuclei, the rule above is followed for each set. For example, splitting of a group of protons by two in equivalent protons, would yield a doublet of doublets. If J_{AX} and J_{AY} were equal (this would be true if X and Y were in the same group), then the observed pattern would have three lines, with the central line having twice the intensity of the other two lines following Pascal's triangle relationship .



- First-order splitting pattern

The chemical shift difference in hertz between coupled protons in hertz is much larger than the J coupling constant:

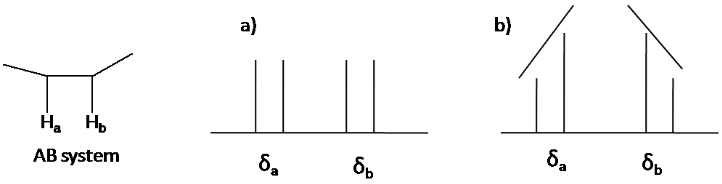
v is the difference of chemical shift. In other word, the proton is only coupled to other protons that are far away in chemical shift. The spectrum is called first-order spectrum. The splitting pattern depends on the magnetic field. The second-order splitting at the lower field can be resolved into first-order splitting pattern at the high field. The fist-order splitting pattern is allowed to multiplicity rule (N+1) and Pascal's triangle to determine splitting pattern and intensity distribution. example. In $A_3M_2X_2$ H_a and H_x has the triplet pattern by H_m because of N+1 rule. The signal of H_m is split into six peaks by H_x and Ha . The First order pattern easily is predicted due to separation with equal splitting pattern.



example of splitting pattern

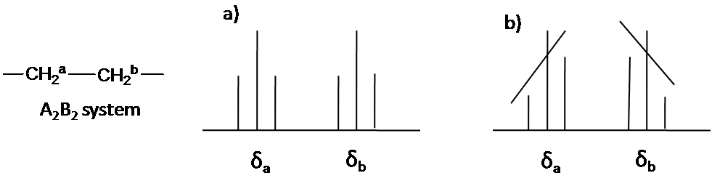
- b. High-order splitting pattern

High-order splitting pattern takes place when chemical shift difference in hertz is much less or the same that order of magnitude as the j coupling i;e the inner peaks are taller and the outer peaks are shorter in case of AB system. This is called the "roof effect."



. a) first-order pattern and b) second-order pattern of AB system

Here is other system as an example: A_2B_2 . The two triplet incline toward each other. Outer lines of the triplet are less than 1in relative area and the inner lines are more than 1. The center lines have relative area 2.



a) first-order pattern and b) second-order pattern of A_2B_2 system

4.2.11 - Spin Decoupling

Decoupling is the process of removing ^{13}C-^{1}H coupling interaction to simplify a spectrum and identify which pair of nuclei is involved in the J coupling. The decoupling ^{13}C spectra shows only one peak(singlet) for each unique carbon in the molecule. Decoupling is performed by irradiating at the frequency of one proton with continuous low-power RF.

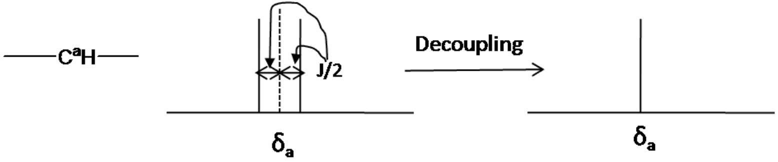


Fig . Decoupling in the ^{13}C NMR

When a given set of nuclei is irradiated with strong rf energy at its characteristic Larmor frequency, spin saturation and rapid interconversion of the spin states occurs. Neighboring nuclei with different Larmor frequencies are no longer influenced by specific long-lived spins, so spin-spin signal splitting of the neighbors vanishes.

Example - If H_a & H_b are the non equivalent protons on two different adjacent carbon atom in a compound .Two doublets corresponding to each proton should be observed at different field strengths. But if we irradiate H_a with correct frequency , then due to rapid transitions between the two spin states H_b will have one time average view of H_a & hence H_a will come to resonance only once & H_b will appear as a singlet & similarly when H_b will be irradiated with correct frequency then H_a will appear as a singlet.

eing observed by the spectrometer are of the
lear decoupling. It is also possible to decouple
ound having both hydrogen and fluorine as part
-coupling between their nuclei, and one may be
termed **heteronuclear decoupling**.
^{13}C nmr spectroscopy.

---

en below.
iven at the end of the unit.
t in the following compounds?
i) $CH_2=CH_2$ (iv) CH_3-CH_2-CH_3
ectrum of ethyl chloride & ethyl alcohol?
exhibit splitting of PMR signals
ate (iv) 1,2- dichloroethane

ect from (a) p- xylene (b) Benzene

---

than proton ^{13}C,^{19}F & ^{31}P –

approximately 1%. It is stable to nuclear decay.

and metabolic studies

chemical shift, yields sharp signals in a magnetic field of 23,500 gauss.

couplings and makes the spectrum appear less crowded. Slow relaxation
ion times are used.

essed relative to the ^{13}C resonance of TMS.

to the values of the relaxation times T1 and T2.

0-100 MHz, for typical spectrometers.

issolved in 0.4 - 2 ml of solvent (normally
trum would be obtained in 64 - 6400 scans.

pin coupled not only to the directly attached
wo to four bonds away.

. J is greater than 125 cps for C^{13} absorption
ly attached to it & it is nearly 20 cps when

unresolved long range couplings. Each signal

s

n atoms &

group in the organic compound.
l coupled spectra are recorded, but the latter with
nance proton decoupling";

he number of unique types of carbon atoms in the
yl group has **four** unique carbon atoms)

many hydrogen atoms are attached to each
oublet=1, singlet=none).

n, much information about the environment of

naturally occurring isotope.
chemical shift.

the standard.
y fluorine containing compound is 0- 200 ppm

nances are well separated on the spectrum.

nges from 43-370 cps.
es from 0 – 39 cps.
ries from 0- 58 cps while in case of trans
6 – 148 cps.
m 42-80 cps, while vicinal H-F has J between 1.3

while for trans isomer J = 11 – 52 cps.
so couples with protons on the ring.
J = 7.4 to 11.8 cps.
plings J ranges from 4.3 – 8.0 cps & 0.2 – 2.7 cps

z.

Spectrometer. Most applications of NMR involve full NMR spectra, that
methods involved irradiating simultaneously with more than one
(centered at the middle of the NMR spectrum) therefore it is also

contains" a range of frequencies centered about the carrier frequency,
l to the pulse duration. The restricted range of the NMR frequencies
iofrequency (RF) pulses to excite the entire NMR spectrum.

es all the single-quantum NMR transitions. It varies in conversion of time
e handled directly because they are on the time scale & so the interference

s

μS) powerful (100-1000 V) rf pulses. The rf pulses should have short rise

e coil & the sample coil to the receiver.
or less) from transmitter overloads.
& to measure the FID amplitude.

adiofrequency energy.
oscillator frequency, the band width depends on the duration of the pulse.
field) continue to emit signals at their characteristic larmor frequency.
on Decay (FID). It contains the vector-sum of the NMR responses from

nterferogram can be converted to useful form by a computer program to

entially decaying sine wave of frequency $\nu = |\upsilon_L - \upsilon_C|$ where, υ_L
y.
MR spectrum (NMR absorption intensity vs.
ensity vs. time) must be FTed.
ulse (FT) NMR and won a Nobel Prize in
nd his development of multi-dimensional NMR

nducting solenoids are used. High magnetic
erred for high resolution, high sensitivity NMR
magnetic fields provide higher signal to noise
esolution NMR spectrometers use
ectrometers with lower resolution may use

em – It is used to lock the magnetic field or
of a negative feedback loop that keeps the

ted & monitored at a frequency corresponding to
ngth of the magnet, provided by Deuterium in
the frequency for Deuterium.

ome changes in the magnetic field by carefully
oils.
agnetic field homogeneity has to be better than
the magnetic field created by the primary

ts longitudinal axis to counteract some of the

of spinning is that the magnetic field is
nay lead to sidebands on each side of absorption

er is responsible for coupling the radio frequency
nsmitter to the sample. It is also responsible for
) and passing it to the receiver for amplification

nd was used to generate a homogeneous RF
nuous RF or pulses of coherent RF radiation
in the sample. The precession of this transverse
cond coil known as the receiver coil. The
on coil.

ystal oscillator a gate to switch the pulse on &
lse to perhaps 50 – 100 W.

controlling the MR transceiver, magnetic field
, temperature of the sample (VT), and an
ing instructions and to transmit the digitized

independent subsystem. Magnetic field
rough coils of appropriate geometry. Static
ng.

ystems: The transmitter and the receiver

synthesizers and amplifiers. This subsystem is
ontaining RF pulses of specified frequency,
fied times. Recent systems works on DDS

he Transmitter or the Receiver subsystem to the
r subsystem is not overloaded with the high
ter system. Also, the receiver is 'blanked' during
rward.
ponents: Preamplifier, Amplifier, Mixer and the
xer is used to subtract a reference frequency of
ulting a signal of lower frequency that can be

nals is split & fed to two identical detectors. In
al manner, carrier signal is subtracted from
ector the carrier signal is altered 90^0 before

r phase, the first produce cosine waves while the are digitized, transformed ,separated into luce spectrum. The folded signals disappears sine wave forms.

to CW-NMR .

ntional continuous wave spectrometers (CW instead of minutes.

a brief intense pulse of a range of radio under study into resonance at the same time.

stribution, the frequencies of energy losses are computer memory.

tored signals possible.

mputer averaged i;e a process which averages nsities of the real signals . Thus here signal to

me domain i;e intensity is a function of time quency domain i;e intensity of radiation at

sive, time consuming, spectra take long time to

gonosis

lpful in magnetic resonance imaging for medical ttings, however, it is also widely used in 13 NMR, deuterium NMR and phosphorus-31 btained from living tissue (e.g. human brain magnetic resonance spectroscopy or chemical

nts from biological fluids to obtain information

r Protein nuclear magnetic resonance

technique in structural biology to obtain high tein. In this technique isotopically label the t method used for structure determination of e distances between pairs of atoms within the es are used to generate a 3D structure of the blem.

ful for analyzing samples non-destructively. r penetrate many types of matter example,

s nucleic acids, including RNA and DNA, or
tic resonance .

ver X-ray crystallography is that it can be used
uding the low-frequency collective motion in
almodulin system. The low-frequency internal
cal functions have been discussed by Chou.

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sed therefore it is known as --------------

NMR

– ESR

or **Electron Magnetic Resonance** (EMR). It is a
radiation having frequency in microwave region
uce transition between magnetic energy level of
splitting is done by applying a static magnetic

y in 1944, and was developed independently at
rsity of Oxford

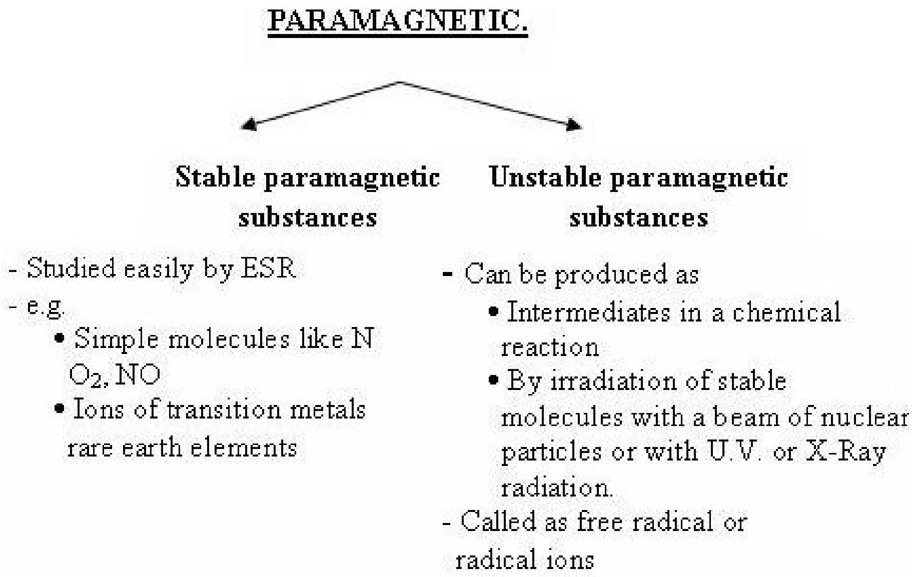
Types of substances with unpaired electrons (ESR active species)

- Atoms having an odd number of electrons.
- Ions having partly filled inner electron shells.
- Molecule that carry angular momentum of electronic origin.

- Free radicals having unpaired electrons.
- Molecule with paired electrons and zero magnetic field

-Diamagnetic

- Molecules with unpaired electrons and magnetic moment- **Paramagnetic**



PARAMAGNETIC.

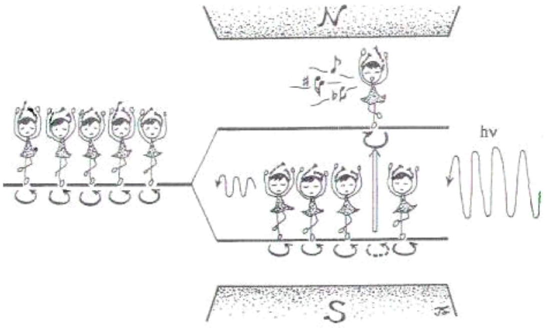
Stable paramagnetic substances

- Studied easily by ESR
- e.g.
  - Simple molecules like N O_2, NO
  - Ions of transition metals rare earth elements

Unstable paramagnetic substances

- Can be produced as
  - Intermediates in a chemical reaction
  - By irradiation of stable molecules with a beam of nuclear particles or with U.V. or X-Ray radiation.
- Called as free radical or radical ions

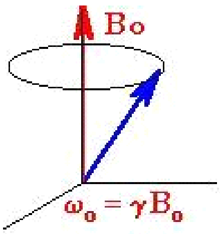
4.3.2 - Basic Principle Of ESR……………



The unpaired electrons are excited to a high energy state under the magnetic field by the absorption of microwave . The excited electron changes its direction of spin and relaxes into the ground state by emitting phonons .

Microwave absorption is measured as a function of the magnetic field by ESR spectroscopy. Theory & Working Of ESR

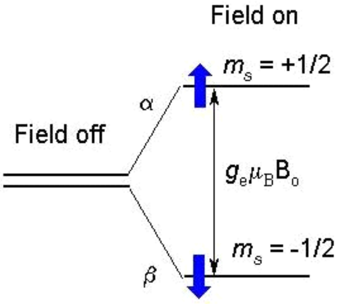
Electron is a charged particle with angular momentum and hence possess magnetic moment.



By virtue of it’s charge and spin electron act as a bar magnet and can interact with an external magnetic field B. If field is zero magnetic moment of odd electron have randomized direction, but in presence of B individual magnetic moment arising due to electron spin of the unpaired electron can be oriented in two ways.

- It will have a state of lowest energy when the moment of electron, μ is aligned along the magnetic field (parallel) and a state with highest energy when μ is aligned against the magnetic field (antiparallel).

- The two states are labelled by the projection of electron spin, M_s, on the direction of the magnetic field. Because the electron is a spin 1/2 particle, the parallel state is designed as $M_s= -1/2$ and the antiparallel state is $M_s = + 1/2$.
  $E = g\mu_B BM_s = \pm 1/2\ g\mu_B B$
  $DE = E_H – E_L = 1/2\ g\mu_B B_0 – (-1/2\ g\mu_B B)= g\mu_B B$

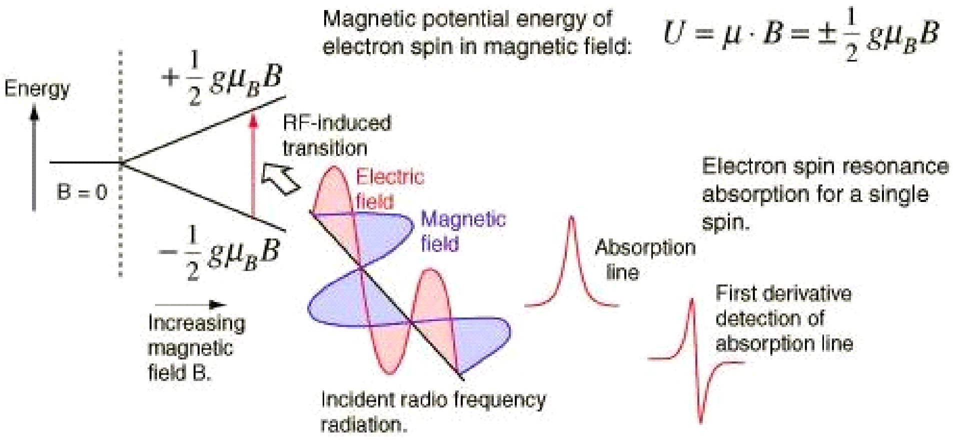


The equation describing the absorption (or emission) of microwave energy between two spin states is
$\Delta E = hv = g\mu_B B$
where: ß is the Bohr magneton = 9.274×10^{-24} J T^{-1}
ΔE is the energy difference between the two spin states
h is Planck constant Its value is 6.626×10^{-34} J s^{-1}
v is the microwave frequency
g is the proportionality factor which is a function of electron’s environment.
It is called as Zeeman splitting factor, Spectroscopic splitting factor, Lande’s splitting factor, Gyromagnetic ratio.
B_0 is the applied magnetic field measured in Tesla

The energy differences studied in EPR spectroscopy are due to the interaction of *unpaired electrons* in the sample with an external magnetic field produced by the EPR spectrometer. This effect is called Zeeman Effect.
A strong magnetic field B is applied to a material containing paramagnetic species.

Now if radiation is supplied to sample of frequency such that energy of each quantum is equal to the difference in energy between the electron state resonance occurs. For a given magnetic field the spin can be made to flip to opposite direction when they absorb radiation at a corresponding resonant frequency. These spin flips can be considered as transition between states that become separated in energy when the magnetic field is applied.

↓



Check your progress -6

Notes : i) Write your answer in the space given below

ii) Compare your answer with those given at the end of the unit

Q a. Will Cu^+ ion show ESR spectrum

Q b. Which EMR are used in ESR spectroscopy & what is their frequency range?

Q c. Is Graphite can also be studied by ESR why or why not?

Q d.In NMR spectroscopy , the two different energy states are produced as a result of alignment of ______________ relative to the applied field ,while in ESR spectroscopy , the two different energy states are produced due to alignment of the ____________ relative to the applied field.

4.3.3 - g values & factors affecting g

g is the proportionality factor which is a function of electron’s environment.
It is called as Zeeman splitting factor, Spectroscopic splitting factor, Lande’s splitting factor, Gyromagnetic ratio. g is also known as the g-factor. The g-factor is a unitless measurement of the intrinsic magnetic moment of the electron. It is a tensor quantity.

Factors affecting g

Value of g is not constant. It depends on the type of specie containing unpaired electron.

- For a free electron its value is 2.0023
- In a group of free electrons ,each electron is a magnetic dipole of magnitude β (ergs/gauss).Then value of g varies from 2.0023 for radicals, transition metal ions & other bodies containing unpaired electrons.
- For electron in molecules value 2.0023 slightly modifies.
- For free radicals & ionic crystal g values modified by +0.003 b’ze in free radicals the electrons behaves in very much ways as an electron in free space.
- In ionic crystals g varies from 0.2 to 0.8 because the unpaired electron is localised in a particular orbital about the atom .
- Orientation of molecules.-

G values also depends on orientation of molecules because in absence of field magnetic moment of odd electron in a sample have random direction but in presence of field the electronic moments are aligned parallel or antiparallel to the field.This effect is known as anisotropy.

- In case of gas or solutions the molecules have free motion & the value of g is averaged over all directions.
- In crystals , movement of electrons are not free.

Example-(i) In paramagnetic ion or radical situated in perfectly cubic crystal site g is same in all directions because in cubic crystal $gx = gy = gz = 2.0036$.
(ii) Paramagnetic ion or radical situated in a crystal of low symmetry depends on orientation of crystal as there are 3 axis in a crystal *gx* , *gy* , *gz respectively.*
(iii)In case of tetragonal site $gx = gy$ & is referred as $g_\perp$ .It is obtained when external H_0 is perpendicular to z axis. $gx = gy \neq gz$

Value of g_z is obtained when H is parallel to z- axis g_z is denoted by g_{II}
If θ is the angle between H & z-axis then for a system possessing axial symmetry $g^2 = g\,II^2 \cos^2\theta + g_\perp \sin^2\theta$

$$g_{avg} = 1/3\, gII + (2\, g_\perp)$$

(iv)The deviation of g from 2.0023 depends on the ability of H_0 flux density to induce local currents in free radical. Thus its value gives information about electronic structure.
The value of g vary, with B (magnetic field strength) according to following equation
$g = h\nu / ßB$
Since h, *v*, and *ß* should not change during an experiment, g values decrease as B increases. The concept of g can be roughly equated to that of chemical shift in NMR

Anisotropy

The *g* factor of many paramagnetic species, including Cu(II), is anisotropic, meaning that it depends on its orientation in the magnetic field. The *g* factor for anisotropic species breaks down generally into three values of *g* following a Cartesian coordinate system which is symmetric along the diagonal: *gx*, *gy*, and *gz*. There are four limits to this system:
i) When $gx = gy = gz$ the spectrum is considered to be isotropic, and is not dependent on orientation in the magnetic field.
ii) When $gx = gy > gz$ the spectrum is said to be axial, and is elongated along the z-axis. The two equivalent *g* values are known as $g_\perp$ while the singular value is known as $g_\parallel$. It exhibits a small peak at low field and a large peak at high field.
iii) When $gx = gy < gz$ the spectrum is also said to be axial, but is shortened in the xy plane. It exhibits a large peak at low field and a small peak at high field.
iv) When $gx \neq gy \neq gz$ the spectrum is said to be rhombic, and shows three large peaks corresponding to the different components of *g*.
Condition ii corresponds to Cu(II) in a square planar geometry with the unpaired electron in the $d_{x^2-y^2}$ orbital. Where there is also hyperfine splitting involved, *g* is defined as being the weighted average of the lines.
*g-value is isotropic in solutions due to free rotating motion Isotropic means average of 3 g-values in x,y & z directions.

4.3.4 - Determination of g- values

1.Experimental method –

$$E = g\beta H_{ms} \quad ----(1)$$
$$E = h\nu \quad -----(2)$$
$$h\nu = g\beta H_{ms}$$

therefore $g = h\nu / g\beta H_{ms}$

Putting values of $h = 6.626 \times 10^{-34}$ J s^{-1} , $ß = 9.274 \times 10^{-24}$ J T^{-1} & knowing values of v & H_{ms} g can be calculated.
Example - for methyl radical H = 0.3290 T, & $v = 9.230 \times 10^9$ Hz

$$g = 2.0036$$

2.Alternative method -
In this method a reference material is used like the organic salt DPPH (diphenyl-picryl-hydrazyl, $(C_6H_5)_2N\text{-}NC_6H_2(NO_2)_3$), (free radical) which has a very strong and narrow line, with a g factor very close to the value for free electrons i;e 2.0036.

Properties of DPPH

- It is not an internal standard for free radicals.
- It contains 1.53×10^{21} unpaired electrons per gram
- DPPH shows the dependence of the resonant magnetic field on the microwave frequency.
  The width of the resonant peak also provide valuable information regarding the local environment of the electron.
- In 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 & its g value is 1.4

Technique to measure g –
In this method the field separation between centre of unknown spectrum & that of reference substance whose g-value is accurately known. First of all ESR spectrum of DPPH is obtained & then same magnetic field is applied to sample & its ESR spectrum is obtained. For this standard substance is placed along with unknown in same chamber of dual cavity cell. The ESR spectrum will show two signals with field separation of ΔH.
The centre of ESR spectrum for sample may be obtained before or after the DPPH centre & therefore value of ΔH may be positive or negative.

g-value for unknown is -

$$g = g_s(1 - \Delta H/H)$$
$$g = 2.0036(1 - \Delta H/H)$$

where, H is resonance frequency, g_s is g-factor of sample
$\Delta H = +ve$ if $g < 2.0036$
$\Delta H = -ve$ if $g > 2.0036$
In a powdered sample, magnetic susceptibility measurements lead only to an average g-value, whereas ESR measurements can give the individual components of g-tensor.

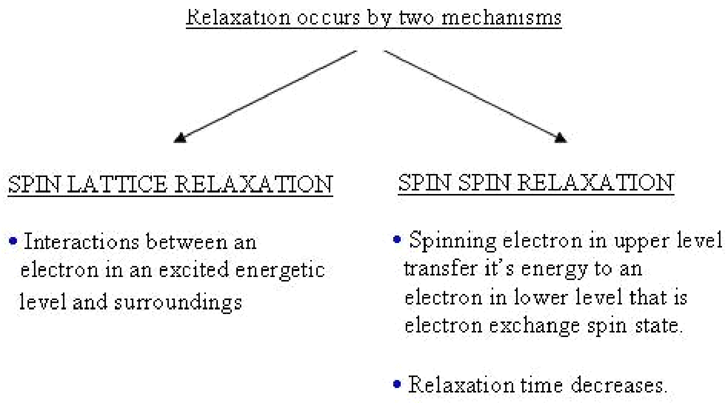
4.3.5-Relaxation And Saturation

If the number of electrons in both energy levels become equal then further no absorption of radiation occur & no resonance signal would be observed. This is known as Saturation.

Saturation Condition.
§ No further absorption.
§ No further resonance.
§ No further signal.
§ Broadening in signal.

In order to maintain steady state conditions there must be some mechanism known as **relaxation**.

By this electrons that have been exited to higher energy level can lose energy and return to lower level.In absence of relaxation saturation occurs in which continuous absorption of energy by electron present in lower state leads to equal population in both state – **Saturation Condition.**



Relaxation occurs by two mechanisms

SPIN LATTICE RELAXATION

- Interactions between an electron in an excited energetic level and surroundings

SPIN SPIN RELAXATION

- Spinning electron in upper level transfer it's energy to an electron in lower level that is electron exchange spin state.
- Relaxation time decreases.

·Relaxation time should be sufficiently rapid to prevent saturation of upper energetic level at the same time sufficiently slow to yield narrow spectral peaks.

·Ratio of numer of electrons in upper energy level to those in lower energy level is given by BOLTZMANN LAW. $n1/n2 = \exp - DE / kT = \exp - g\mu_B B / kT$

Check your progress – 7

Notes : i) Write your answer in the space given below

ii) Compare your answer with those given at the end of the unit

Q a .The paramagnetic effect is much _____________ than the diamagnetic effect arising from the orbital motion of electrons.

Q b . Calculate the ESR frequency of an unpaired electron in a magnetic field 0.33 T . Given for free electron $g = 2$ & $\beta = 9.273 \times 10^{-24}\ JT^{-1.}$

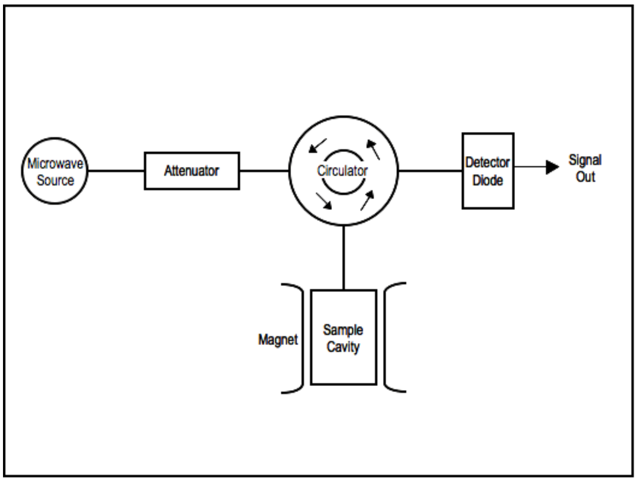
Q c .What is the value of g in the case of (i) organic radicals (ii) Free electron (iii) Transition metal ions.

(iv)DPPH powder

Q d .Which is one of the best known free radicals used in calibrating ESR spectra

4.3.6 -Instrumentation -

Electron Spin Resonance (ESR) provides a powerful tool for studying the unpaired electrons in condensed matter systems.



I . Source -EPR spectrometers work by generating microwaves from a source like klystron. A Klystron oscillator is generally operated at 9500 Mc/sec. It is stabilized against temperature fluctuations by immersion in an oil bath or by forced air cooling. It is kept at fixed frequency by an automatic frequency control circuit.

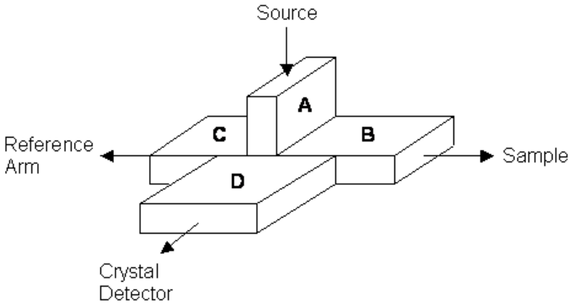
Its various components are -

- **Wave guide-** It is a hollow, rectangular brass tube having silver or gold plating inside to produce a highly conducting flat surface, used to convey the microwave radiation to the sample & crystal.
- **Attenuators, phase shifters -** It lies between wavemeter & circulator it attenuates (decreases) the power traveling through it without changing the frequency. A phase shifter; can be used as an attenuator by combining a reflected wave out of phase with the source wave.
- **Isolator**- It is a non reciprocal device used to prevent reflection of microwave power back into the radiation source. It is a strip of ferrite material which allows microwaves in one direction only.
- **Resonant cavities** - Two resonant cavities are used in this experiment.

  Wavemeter – It is put in between isolator & attenuator to know the frequency of microwaves produced by klystron oscillator. It is used for measuring the microwave frequency in (megahertz).

  Sample chamber or sample cavity - contain the sample being studied. In most of the ESR spectrometers, dual sample cavities are used for simultaneous observation of a sample & a reference material. This is done to compare relative signal heights.
- **Samples** for EPR can be gases, single crystals, solutions, powders, and frozen solutions. For solutions, solvents with high dielectric constants are not advisable, as they will absorb microwaves. For frozen solutions, solvents that will form a glass when frozen are preferable. A sample volume of 0.15 to 0.5 ml can be used with samples which do not possess a high dielectric constant. For samples having high dielectric constant flat cells with a thickness of 0.25 mm & sample volume of 0.05 ml.
- **Magic-T or Circulator -** The heart of the microwave spectrometer is the bridge circuit, and its primary component is the “magic-T.” A bridge circuit is used in the spectrometer is for sensitivity.

  The magic-T is a four port device.The microwave power is flowing in from port A through a waveguide by a loop of wire which couples with oscillating magnetic field & sets up a corresponding field in the waveguide. The microwave radiations enter through arm A. Arm B is connected to resonant cavity & sample. Arm C generally have a terminating load, it absorbs any power which might be reflected from the detector arm. Arm D is attached to the detector.



Magic-T.

This microwave energy should be equally divided between ports B, C and D. The power is not equally divided between ports B, C, and D. The microwave power flowing in from port A can branch into B and C but not into D. On the other hand, power which flows back, (reflected) from B and C can flow into D and is split equally between A and D. Therefore if we can match the power flowing back from ports B and C, they will superimpose at D to give a null output. Thus in this spectrometer, we will have the sample arm of the bridge off port B and a reference arm off port C. Match the impedance of arm C with that of the arm off port B which contains the sample. Therefore, as long as the arms are balanced and the magnetic field is far from the ESR resonance, the output of the detector located on port D will be zero.

IV **Magnet system** – The resonant cavity is placed between the pole pieces of an electromagnet.This provides a homogeneous magnetic field & can be varied from zero to 500 gauss. The field should be stable & uniform over the sample volume.

Magnets The ESR system utilizes three electromagnets. The primary magnet will be used to produce a field on the order of a few kilogauss. This will require a source current capable of producing a large amount of heat in the magnet over a period of time, and therefore the magnet must be water cooled. The secondary magnet is smaller and consists of Helmholtz coils found between the two sides of the primary magnet. The third source of magnetic fields is the set of coils in the sample cavity which will be used for the production of a few tenths of a gauss.

Diode Detector or Crystal Detectors - The microwave detector is the commonly used “crystal diode,” which consists of a silicon crystal in contact with a fine tungsten wire, known as a “cat's whisker.”It acts as a microwave rectifier. It converts microwave power into a direct current output. The DC voltage output of the detector circuit is proportional to the incident microwave power.

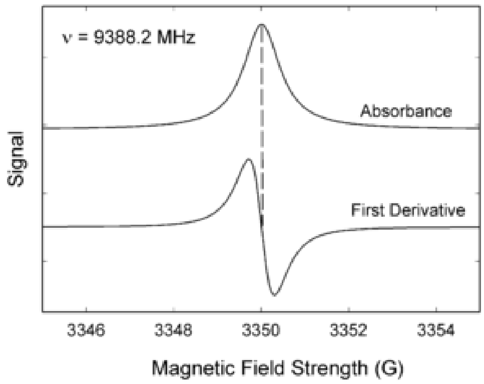
- **Autoamplifier & Phase Sensitive Detector** – After detection, the signal undergoes narrow-band amplification. But the amplified signal contains a lot of noise. The reduction in noise is achieved by rejection of all noise components by the operation of the phase sensitive detector.
- **Oscilloscope & Pen recorder – Finally**, the signal from phase sensitive detector & sweep unit is recorded by the oscilloscope or pen recorder.

Working – The sample, whose ESR is to be recorded, is kept in the resonant cavity in which waves are reflected to & fro thousand of times.

The klystron oscillator is set to produce microwaves which after passing through the isolator, wavemeter & attenuator are received by circulator through arm A. The microwave power entering through arm A will divide between arm B & C. The arm B is generally having a balancing load. If the impedances of arm B & C are same, microwave power is absorbed completely & no power will be received by the detector through arm D.

If the impedance of arm B (the sample cavity) changes because of some ESR resonance absorption by a sample in it, some microwave power will enter into detector through arm D. The detector acts as a rectifier, converting the microwave power into direct current.

If the magnetic field around & resonant cavity having the sample is changed to the value required for resonance , the recorder will show an absorption peak. But If the main magnetic field is swept slowly over a period of several minutes, the recorder will show the derivative of the microwave absorption spectrum against magnetic field. Due to instrumental considerations associated with the signal-to-noise ratio, the ESR spectra are generally recorded as first derivative spectra.



Sensitivity of ESR Spectrometer – The sensitivity of an ESR spectrometer is expressed as

$$N_{min} = 1 \text{ X } 10^{11} \frac{\Delta H}{\tau}$$

N_{min} = minimum number of detectable spins per gauss,
ΔH = width between deflection points on the derivative absorption curve, &
τ =time constant of the detecting system; this is inversely proportional to the bandwidth of the detection circuit.

Working at higher magnetic field strength increases the sensitivity of ESR spectrometers

Concentration of the sample – For a sample having a very small dielectric loss, the concentration should be of the order of 10^{-9} M. In case of aqueous solutions, the concentration should not be less than 10^{-7}M.When the structure determinations & quantitative analysis are to be carried out, the concentration should be about 10^{-6}M.

Choice of the solvent – In most of the ESR studies, water, alcohol & other high dielectric constant solvents are not used because they strongly absorb microwave power. But if the sample has a strong absorbance & is contained in a specially designed cell (very narrow sample tube) then these solvents can be used.

4.3.7 Spin Spin Splitting (Hyperfine Splitting)

Magnetic resonance can also occur without an external magnetic field from interaction of the electron and nuclear spin. Such resonance produces fine and hyperfine structure of atomic spectra. The nuclei of atoms in a molecule or complex often have magnetic moment which produces a local magnetic field at the electron. The interaction between an unpaired electron an nuclei with non zero nuclear spin is called the *hyperfine interaction*. This leads to splitting of the ESR line and is known as *hyperfine spectrum*

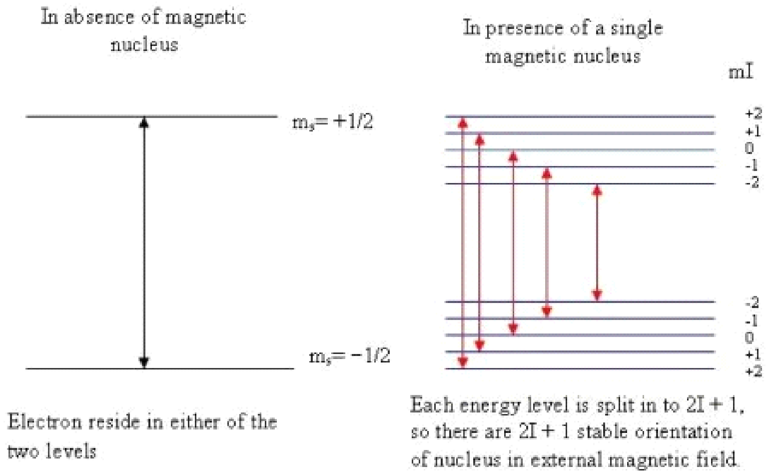
There are two kinds of hyperfine coupling: 1) coupling of the electron magnetic moment to the magnetic moment of its own nucleus; and 2) coupling of the electron to a nucleus of a different atom, called super hyperfine splitting.

The interaction of an unpaired electron, with nearby nuclear spins, results in additional allowed energy states and, in turn, multi-lined spectra.The spacing between the EPR spectral lines indicates the degree of interaction between the unpaired electron and the perturbing nuclei.

The number of splittings = 2nI + 1
Where I spin Quantum number , n is equivalent nuclei
It gives following important informations –

- It tells about the environment of molecule & distribution of electron density within the molecule
- It allows identification of paramagnetic substance

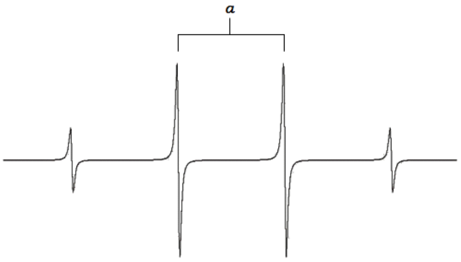
Energy levels of an unpaired electron that is coupled to a single magnetic nucleus with spin quantum number 2.



Diagrammatic presentation of hyperfine splitting due to one proton.

Both types of hyperfine coupling cause a splitting of the spectral lines with intensities following Pascal’s triangle for I = 1/2 nuclei.

Example 1- spectrum of the methyl radical.The line is split equally by the three hydrogens giving rise to four lines of intensity 1:3:3:1 with hyperfine coupling constant *a* =22.5 gauss.



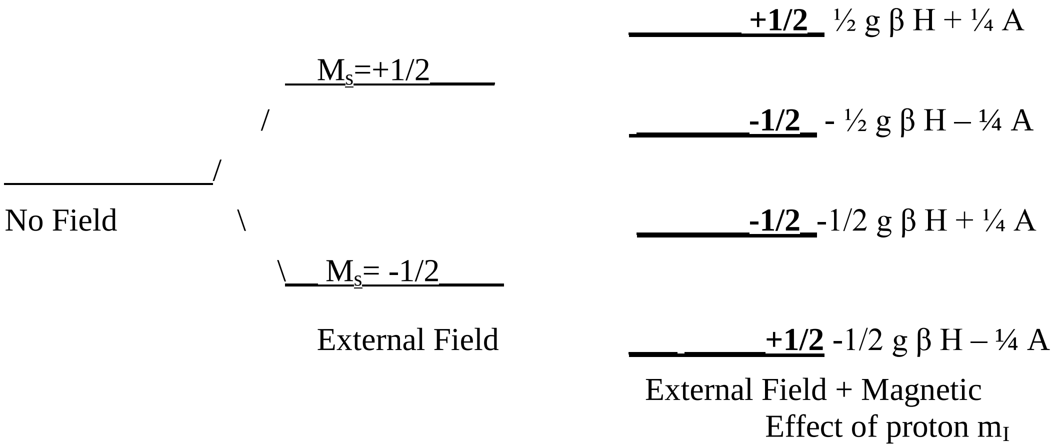
Simulated spectrum of CH_3 radical with hyperfine coupling constant *a*.

Example 2 - Hyperfine splitting of hydrogen atom

It has one unpaired electron & one proton . The energy of electron will be affected by orientation of magnetic moment of proton which can be parallel or antiparallel to H_0.

In absence of magnetic field the single electrons give rise to double degenerate spin energy state , when magnetic field is applied degeneracy is removed & two energy levels are obtained. This splitting is due to spin of electrons.Since this electron is not free therefore due to the interaction with nucleus further splitting occurs giving rise to four energy levels.

The relative orientation of nuclear magnetic moment & electron magnetic moment causes splitting of original two levels to four levels.



Only two transitions are found between these two states because nuclear moment remains fixed during electronic transitions so that transitions occur between I = ½ & I = -1/2 states.

The selection rule are $\Delta m_s = \pm 1$ & $\Delta m_I = 0$

Where, **Δm_I is** magnetic quantum number of nucleus **$\pm$1/2 for proton.**

Thus two possible transitions satisfying selection rules i;e two hyperfine lines are observed & energy difference between two values of field at which lines occur is called as **hyperfine splitting constant (a or A).**It is measured in Gauss or MHz or cm^{-1} or millitesla (1mT = 10 gauss).Proton hyperfine splitting for free radicals occur in range 0.30 gauss. For hydrogen atom a = 509 gauss.

When proton points in same direction as H_0 the electron finds the appropriate resonance at lower value of H_0.But when proton magnetic moment opposes the field, higher value of H_0 is required for resonance to occur.

If interaction between electron & nucleus is more value of A is more, it doesn't depend on magnetic field strength. The energy of splitted energy levels can be calculated as –

$E = g\beta H + A\ M_sM_I$

Where g is lande's splitting factor , β is Bohr's magneton , H is applied magnetic field, A is hyperfine splitting constant, M_s is spin quantum number of electron,M_I is magnetic quantum number of nucleus.

The energy of four energy levels are as follows :-

$E_{1/2,1/2} = \frac{1}{2} g \beta H + \frac{1}{4} A$ $E_{\frac{1}{2},-1/2} = -\frac{1}{2} g \beta H - \frac{1}{4} A$

$E_{-1/2,-1/2} = -1/2\ g \beta H + \frac{1}{4} A$ $E_{-1/2,1/2} = -1/2\ g \beta H - \frac{1}{4} A$

Example 3 – Deuterium ($_1{}^2H$)

I = 1, $M_s = \underline{+}1/2$, $M_I = \underline{+}\,1,0$. According to 2nI + 1 = 2 x 2x1/2 +1 = 3

Thus, corresponding to m_s= +1/2 there are three values of m_I = -1,0,+1.Similarly corresponding to m_s= -1/2 there are three values of m_I = -1,0,+1.The energy levels of all six energy levels are as follows :

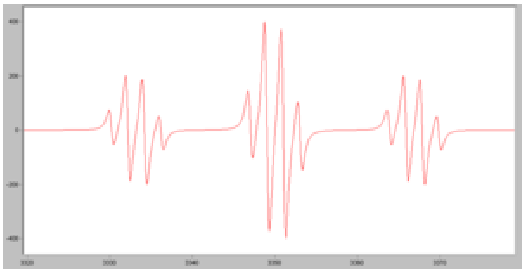
$E_{1/2,1} = \frac{1}{2} g \beta H + 1/2\ A$ $E_{-1/2,-1} = -\frac{1}{2} g \beta H + 1/2\ A$

$E_{\frac{1}{2},0} = \frac{1}{2} g \beta H$ $E_{-1/2,0} = -\frac{1}{2} g \beta H$

$E_{1/2,-1} = 1/2\ g \beta H - 1/2\ A$ $E_{-1/2,1} = -1/2\ g \beta H - 1/2\ A$

By virtue of the selection rules $\Delta m_s = \underline{+}1$ & $\Delta m_I = 0$ there are three allowed transition & thus three lines corresponding to these transitions in the ESR spectrum of deuterium.These lines will be of equal intensity , since all the states are non degenerate.

For a radical having M_1 equivalent nuclei, each with a spin of I_1, and a group of M_2 equivalent nuclei, each with a spin of I_2, the number of lines expected is $(2M_1I_1 + 1)\ (2M_2I_2 + 1)$. As an example, the methoxymethyl radical, $H_2C(OCH_3)$, has two equivalent ^1H nuclei each with $I = 1/2$ and three equivalent ^1H nuclei each with $I = 1/2$, and so the number of lines expected is $(2M_1I_1 + 1)\ (2M_2I_2 + 1) = [2(2)(1/2) + 1][2(3)(1/2) + 1] = [3][4] = 12$.



In the specific case of Cu(II), the nuclear spin of Cu is I = 3/2, so the hyperfine splittingwould result in four lines of intensity 1:1:1:1. Similarly, super hyperfine splitting of Cu(II) ligated to four symmetric I = 1 nuclei, such as ^{14}N, would yield nine lines with intensities would be 1:8:28:56:70:56:28:8:1.

Isotropic & Anisotropic hyperfine coupling constant

Two common mechanisms by which electrons and nuclei interact are the **Fermi contact interaction** and by dipolar interaction. The former applies largely to the case of isotropic interactions (independent of sample orientation in a magnetic field) and the latter to the case of anisotropic interactions (spectra dependent on sample orientation in a magnetic field). Spin polarization is a third mechanism for interactions between an unpaired electron and a nuclear spin, being especially important for π-electron organic radicals, such as the benzene radical anion. The symbols "*a*" or "*A*" are used for isotropic hyperfine coupling constants while "*B*" is usually employed for anisotropic hyperfine coupling constants.

In many cases, the isotropic hyperfine splitting pattern for a radical freely tumbling in a solution (isotropic system) can be predicted.

The hyperfine splitting constant, known as *a*, can be determined by measuring the distance between each of the hyperfine lines. This value can be converted into Hz (A) using the *g* value in the equation:

$$hA = g\,\beta a$$

Isotropic hyperfine splitting constant is the measure of separation between two ESR signals. Its value is same in all directions

$$A = [\ \{ g\beta H + \tfrac{1}{2} A\} - \{g\beta H - \tfrac{1}{2} A\}]$$

It occurs in the case where rotation of spinning species are free.

Anisotropic hyperfine splitting constant – B or Aiso or A_0 arises in the crystalline state or in the frozen solution.

Its value varies along different directions.

Its value is calculated as **- A_{av}** $= 1/3(A_{||||} + 2A_{\perp})$

Where $A_{||}$ is the value of A in Z axis & $A_{\perp}$ is the value of A in x & Y axis.Magnitude of A is determined by (a) size of nuclear magnetic moment (b) density of unpaired electron at nucleus.

Check your progress – 8
Notes : i) Write your answer in the space given below.

ii) Compare your answer with those given at the end of the unit

Q a. Why water & alcohol are not suitable solvents for ESR studies.
Q b. Why electron spin resonance is also called as electron para magnetic resonance?
Q c.Why the instrumentation of ESR is quite different from those of NMR, while basic principles of ESR are closely related to those of NMR?
Qd. The intensity of absorption line is ____________ to the number of unpaired electrons.
Q e .why C-12 & O-16 nuclei do not interact with the electron
Qf. Predict the number of lines in the ESR spectrum of naphthalene negative ion in solution.
Qg. The p-benzosemiquinone radical ion gives no splitting from carbon & oxygen . Why?

4.3.8 -Zero-field splitting (zfs)

Just like the spin of nucleus affects the spin of electron causing hyperfine lines in the similar manner the spin of unpaired electron of the same or adjacent atom affects the ESR spectrum i;e **when two unpaired electrons of the same atom or on the adjacent atom of diatomic molecule the spinning motion of these electrons influence each other & causes zero field splitting which results in ESR spectrum.**

For such substance value of S = 1
$M_s = +1,0 -1$

In the absence of magnetic field the three values of M_s are degenerated but when the magnetic field is applied to it then it get splits up into three energy levels.

It is the removal spin microstate degeneracy for systems with S > 1/2 in the absence of an applied field. That is, the degeneracy is removed as a consequence of molecular electronic structure and/or spin density distribution.

4.3.9-Kramer's Degeneracy –

AS the number of electrons increases from one to two zero field splitting occurs which give rise to fine structure in ESR spectrum.

If the even number of unpaired electrons are present the resultant spin quantum number M_s contains $M_s = 0$ state.

____________$M_s = 1$

________ ____________$M_s = 0$
S = 1

____________$M_s = -1$

But if odd number of unpaired electrons is present then the resultant spin quantum number does not contain $M_s = 0$ state i;e For odd-electron systems, axial zfs (the “*D*” zfs parameter) removes the microstate degeneracy and produces Kramer’s doublets.

Example for n=1, S = ½ , $M_s = \underline{+}$ ½

_____________$M_s = +1/2$

____
S = 1/2

_____________$M_s = -1/2$

Thus by knowing the fine structure the number of unpaired electrons can be calculated. If zero state is present then even number of unpaired electrons are present. If zero state is absent then odd number of electrons are present.

- Rhombic zfs (the “*E*” zfsparameter) splits the Kramer’s doublets.
- Zero-field splitting causes magnetic anisotropy, and has profound effects on magnetic *properties*. For example, magnetic hardness is related to the magnetoanisotropy.
- At the molecular level, understanding zfs is essential for rational design of single-molecule magnets since the energy barrier separating the +ms and –ms microstates is equal to |S2*D*|,where D is the energies of spin microstates .
- Orbital angular momentum can be of primary contributor to zfs, and can make the zfs quite large (≈1-10 cm-1)compared to spin-dipolar contributions (≈10-3 - 10-1 cm-1). There are two scenarios in which orbital angular momentum manifests itself in zfs: in-state orbital angular momentum (*e.g.*, orbital T states in *O*h symmetry), and out-of state orbital angular momentum (*e.g.*, spin-orbit mixing of certain excited states into the ground state).
- In-state orbital angular momentum can give rise to very large zfs.
- Spin-Orbit Coupling Splits spin multiplet by mixing with orbital multiplet. "ZFS" large,
- Out-of state orbital angular momentum can also give rise to zfs, but not alone and the degeneracy is retained.
- Spin-Orbit Coupling **does not** remove degeneracy of spin multiplet (D = 0) Any distortion that removes the degeneracy of t1g will work. Thus, the spin-orbit coupling plus the distortion combine as perturbations to allow the ground state “feel” the excited state splitting. The result is zero-field splitting.

4.3.10 -Spin Hamiltonian

Energy levels have been represented in terms of Hamiltonian as, electron spin resonance is concerned with electron & nuclear spin , the scheme of energy levels is called as spin Hamiltonian. It is represented by H_s.

$$H_s = g\beta HS_z + aS_z - g_N\beta_N HI_z$$

Where, a is hyperfine coupling constant for some magnetic nucleus
g_N is g – factor of hyperfine coupling constant
β_N is magnetic moment of coupling constant
S_z &I_z are electron & nuclear spin operators.

1st term in the equation represents energy of interaction of magnetic moment of odd electrons with field.
2nd term indicates the interaction between the moments of electrons & magnetic nucleus & is responsible for nucleus hyperfine structure.
3rd & last term is small in value & can be neglected as it represents the energy of magnetic nucleus in the field.
In case of free radicals ,g-factor slightly depart from the free spin value of 2.0023,therefore Hamiltonian is quite adequate for free radicals in solution. Interpretation of ESR spectra is difficult for free radical due to coulomb repulsion between d or f electrons & spin spin orbit coupling combine to give g-factor for electrons & resonance lines depart widely from 2.0023. Spin orbit couping couples the spin angular momentum of unpaired electrons with their orbital angular momentum.
Ions & complexes of transition metals & rare earth metals contain unpaired electrons in d & f orbitals therefore can be studied by ESR.

Spin densities & Mc Conell Relationship

Hyperfine splitting is observed in case of those nucleus where unpaired electron has some s-character at the nucleus & the numerical value of the splitting indicates the amount of s-character possessed by the nucleus.

But there is no mechanism by which unpaired spin density could appear at the ring protons, because there is nodal plane in the plane of the molecule. Mc.Conell (1956) proposed a mechanism for the appearance of hyperfine structure from ring protons in π-radical systems due to configuration interaction. According to wave mechanics , the unpaired electron in the π – orbital polarizes the electrons in the covalent C-H bond. As a result, a small unpaired spin density takes place at the proton.
The Mc.Conell relation is

$$a = Q\rho$$

where, a=Hyperfine splitting from the proton, & is proportional to unpaired π spin density ρ, on the adjacent carbon atom.
Q is constant.
Example - The value of Q is taken as 22.5 gauss from the spectrum of benzene negative ion, Charge density is 1/6 at each carbon atom & proton hyperfine splitting is 3.75 gauss.
This relationship allows the unpaired spin density distribution on the carbon skeleton of a free radical to be obtained from the experimental proton splitting constant.

4.3.11 –Applications

All application of ESR is based on three aspects, which are,
- Study of free radicals,
- Investigation of molecules in the triplet state, and
- Study of inorganic compounds.

Study of free radicals

Even in very low concentration of sample ESR can study via free radicals. It is also applied in determination of structure of organics and inorganics free radicals. The intensity of ESR signal is directly proportional to the no. of free radicals present. Hence using ESR we can measure relative concentration of free radicals.

Investigation of molecules in the triplet state

A triplet state molecule has a total spin S=1 so that, its multiplicity can be given as 2S+1=3. While free radicals with S=½ has an odd no. of unpaired electrons. A triplet state molecule has an even no. of electrons two of them unpaired. In triplet state molecule the unpaired electrons must interact whereas in diradical, the unpaired electrons do not interact for they are a great distance apart.

Study of inorganic compounds

ESR is very successful in the study of inorganic compounds. The ESR studies may be used in knowing the exact structures of solvated metal ions , in the study of catalysts, in the determination of oxidation state of metal. eg. Copper is found to be divalent in copper protein complexes whereas it is found to be monovalent in some biologically active copper complexes. The information of unpaired electrons is very useful in various aspects in applications of ESR. Like, Spin labels, Structural determination, and Reaction velocities and reaction mechanisms.

Spin labels:

Groups with unpaired electron can be attracted to macromolecules such as protein and membranes to obtain a great deal of information obtain their structure. The *nitroxide molecules* bound to macromolecules are called spin labels. This spin labels are stable molecules that possessing an unpaired 2p electrons. A commonly used **TEMPOL** (2,2,6,6-tetramethyl piperidinol-n-oxyl. The hyperfine structure of an ESR spectrum is a kind of fingerprint that helps to identify the free radicals presents in the sample. Spin labels give very useful information about the molecules to which they are bound.

Also, we get information like, The rate of motion of macromolecules to which they are bound, or the amount of thermal motion in a membrane in which they have been inserted. The spin label can give information about the polarity of its environments.

Structural determination

It does not tell us about the arrangement of the atoms in the molecule although the symmetry of the molecule can be sometimes deduced from the sets of equivalent nuclei. In certain cases ESR is able to provide useful information about the shape of the radicals.

Reaction velocities and reaction mechanisms:

A large no of organic reactions are known which proceed by a radical mechanism. Most of the radicals formed during organic reaction are not stable but are very reactive. The ESR spectroscopy can be used to study very rapid electron exchange reactions.

The various applications of ESR spectroscopy are grouped into two categories.
1.Analytical applications
2.Biological applications

Analytical applications:

Mn+^{2} ions can be measured and detected even when present in trace quantities. The method is very rapid and can be measured in aqueous solution over the range from 10-6 M to 0.1M. ESR method has proved to be a rapid and convenient method for determination of Vanadium in petroleum products. ESR can also be used to estimate Cu(II), Cr(II), Gadolinium(III), Fe(III) and Ti(III). The ESR spectroscopy has been used to estimate polynuclear hydrocarbons, which are first, converted in to radical cations and then absorbed in the surface of an activated silica-alumina catalyst.

Biological systems:

From the ESR studies of variety of biological system such as, leaves, seeds, and tissue preparation, it is found that a definite, correlation exists between the concentration of *free radicals* and the metabolic activity of the plant material. ESR has studied the presence of *free radicals* in healthy and diseased tissues. Most of the oxidative enzymes function via one electron redox reaction involving the production of either enzyme bound *free radicals* or by a change in the valence state of transition metal ion. This has been conformed by ESR studies. Much of the ESR work on photosynthesis has been carried out with photosynthetic bacteria. The oxidation of bacteriochlorophyll in vitro produces an ESR signal.

Modern biotechnology:

ESR being effectively used to revealed both structure and functional information. It is very useful in modern biotechnology. There are three branches of modern biotechnology in which ESR is applied,
a) Molecular biotechnology
b) Medical biotechnology
c) Classical biotechnology

Specific features of ESR in modern biotechnology are: Selectivity, Specificity ,Non-invasiveness
& Sensitivity

ESR in molecular biotechnology :

DNA: ESR is used to- investigate the nucleotide-centered free radicals in DNA, to analyse DNA hydration and the process of the hole or electron transfer from the hydration layer to DNA due to water ionization, and to the analysis of DNA repair by DNA photolyase, by detection of flavin radical formation. ESR is useful in analysis of Reverse Transcriptase (RT) inhibition by polynucleotide.

RNA: ESR was employed to structure dependent molecular dynamics of Trans Activator Responsive (TAR) RNA of HIV-1. ESR is also used to determine the map of protein-RNA interactions between RNA and ribonuclease P from E.coli.

Protein structure and dynamics: ESR helps to find the interactions between ligands and target protein example in the study on the ion siderophore complex and it's binding to site directed spin labeled ferric enterobactin receptor responsible for iron uptake by enterobacteria.

Activity of enzymes: ESR is used in the analysis of enzymatic activity of nitric oxide synthetase (NOS), the main enzymes delivering NO in biological systems.

Membranes: The Fluid Mosaic model of membrane has proved by the recent ESR evidence of the existence of structural domains stabilized by membrane proteins in the form of "rafts".

Glycobiology: Spin labeled sugars, sugar residues, and spin labeled components interacting with sugar applied in two basic fields of carbohydrate research: Sugar metabolism (degradation and transport), Structural biochemistry of glycoproteins and membranes.
o ESR is employed to analyze the process of sugar transport in bacteria.
o ESR was applied to the analysis of the influence of diabetes on the properties of erythrocytes showing the decrease in erythrocyte deformability due to the non-enzymatic glycation of hemoglobin.
oThus, structural investigation often reveals medical aspects.

ESR in medical biotechnology:

Activation and transport of drugs: ESR is useful in several pharmacological investigations like interactions between DNA binding drugs and DNA. ESR may be used to characterize some herb derived products which act by increasing the level of free radicals and other reactive species produced during light induced oxidative stress of the cell.

Imaging: ESR imaging is a valuable tool for spatially resolved redox mapping of living tissues. Redox status of tumor tissues is significant for understanding tumor physiology, and for determining the effects of chemotherapy and radiation.

ESR in classical biotechnology:

Plant biotechnology: ESR is helpful even at developing artificial photosynthesis, which is biggest biotechnological challenge for the mankind.

Food production and storage: Commercially, ESR is used to analyze shelf life of beer and wine. It is based on free radicals generated in beer or wine due to the action of light, or spontaneously during the process of storage, contribute to the degradation and flavor changes of product. The level of free radical would depend on antioxidants presents in the solutions. Therefore antioxidant capacity of beer or wine helps to predict stability. Similar approach is applied to other food products, such as oils or milk.

4.3.12 B - ENDOR & ELDOR

ESR techniques are further categorized in two different types – ENDOR & ELDOR

	ENDOR	ELDOR
1	Electron nuclear double resonance technique	Electron double resonance technique
2	It is used to improve resolution of an ESR spectrum	It is used to study relaxation mechanism.
3	In ths technique sample is irradiated simultaneously with microwave frequency suitable for electron resonance & radio frequency suitable for nuclear resonance.The radio frequency is then swept while observing the ESR spectrum under conditions of microwave saturation.	In this technique sample is irradiated with two microwave frequencies.
4	Signal height of trace recorded is function of swept nuclear radio frequency	signal height is function of difference of two microwave frequencies.

Check Your Progress – 9

Notes : i) Write your answer in the space given below
ii) Compare your answer with those given at the end of the unit

Q a why ESR spectroscopy is widely used in the study of chemical, photochemical & electrochemical reactions, which proceed via free radical mechanism.

Qb. How many lines are expected in the ESR spectrum of radical anion derived from p-xylene

Qc. For hydrogen atom, the hyperfine coupling constant is ------------

Qd. Predict the number of lines in ESR spectrum when an unpaired electron interacts wuth three equivalent proton.

Qe. The ESR spectra of $FeCl_3$ & $FeCl_3.6H_2O$ are different.

4.4 -Nuclear quadrupole resonance spectroscopy

Introduction

Nuclear quadrupole resonance spectroscopy or NQR is a chemical analysis technique related to nuclear magnetic resonance (NMR). Nuclear quadruple resonance (NQR) is a resonance absorption of electromagnetic energy in crystals, caused by transitions between power levels, appearing as a result of interaction of kernels possessing an electric quadruple moment with the electric crystalline field.

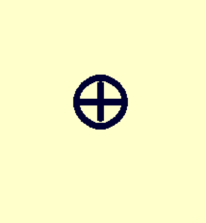
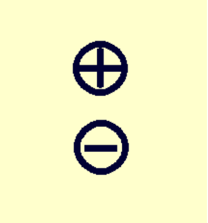
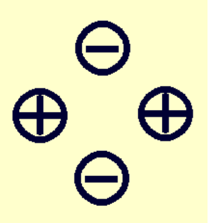
4.4.1Basics of NQR

- In NMR, nuclei with spin ≥ 1/2 have a magnetic dipole moment so that their energies are split by a magnetic field, allowing resonance absorption of energy related to the difference between the ground state energy and the excited state. But **In NQR, nuclei with spin ≥ 1 , such as ^{14}N, ^{35}Cl and ^{63}Cu, also have an electric quadrupole moment so that their energies are split by an electric field gradient, created by the electronic bonds in the local environment**.
- unlike NMR, NQR is done in an environment without a static (or DC) magnetic field, it is sometimes called "zero field NMR".
- NQR transition frequencies depend strongly upon temperature.
- Any nucleus with more than one unpaired nuclear particle (protons or neutrons) will have a charge distribution which results in an electric quadrupole moment.
- Allowed nuclear energy levels are shifted unequally due to the interaction of the nuclear charge with an electric field gradient supplied by the non-uniform distribution electron density (e.g. from bonding electrons) and/or surrounding ions.
- The NQR effect results when transitions are induced between these nuclear levels by an externally applied radio frequency (RF) magnetic field.
- The technique is very sensitive to the nature and symmetry of the bonding around the nucleus. The energy level shifts are much larger than the chemical shifts measured in NMR. Due to symmetry, the shifts become averaged to zero in the liquid phase, so NQR spectra can only be measured for solids.
- NQR Spectroscopy refers to that branch of spectroscopy in which energy is absorbed by various atomic nuclei in the region from 1-1000 **Mc/s.**

A quadrupolar nucleus is one that has a quantum spin number greater than ½. Such nuclei have a lower symmetry than spin-½ nuclei. The quadrupole moment that varies between nuclei is a measure of this asymmetry.Examples- Isotopes of Cl, Br, I, N, As, Antimony, tin.

4.4.2 - Nuclear Electric Quadrupoles

Any distribution of electric charge is the sum of simpler charge distributions. This is known as the superposition principle. In many cases it is useful to use "multipole moment" distributions.

Moment:	**Monopole**	**Dipole**	**Quadrupole**
Example distribution:			

Since Nuclei have a state of definite parity, a nuclear charge distribution cannot have an electric dipole contribution. Likewise they will not have a magnetic monopole or quadrupole contribution. (Magnetic contributions come from moving or spinning charges).

When a nucleus is in its equilibrium position in a crystal, the net force on it is zero . Hence, the Monopole Electric moment (which is the charge of the nucleus, giving the force on it due to neighboring charges) will not lead to energy level splittings.

On the other hand, deviations from spherical symmetry for both the nucleus and of the electric charges in the environment surrounding the nucleus can provide a torque on the nucleus and hence energy levels which depend on orientation. That is known as an electric quadrupole coupling.

Not all nuclei have an electric quadrupole moment. Due to symmetry considerations, for example, all nuclei which have a nuclear spin quantum number of 0 or 1/2 cannot have such a moment. Within the periodic table such spin quantum numbers are not all that common, but included are the common isotopes of Hydrogen, Oxygen, and Carbon. The most common isotope of Nitrogen

CHECK YOUR PROGRESS- 10

Q a. NQR spectra are observed for nuclei with I 1. What would happen if I <1
Q b. The nuclei having …………… & ………..nuclear spins possess nuclear electric quadrupole moment
Q c. s-orbitals bring their electrons close to the nucleus , but they are ineffective in orienting the nucleus
Q d. For , the I = ………….. & for , I = …………..

4.4.3 - Theory of NQR

The nuclei with spin ≥ 1possess an electric quadrupole moment which interacts with the electric field gradient created at nuclei due to assymetric charge distribution of charges arising from extranuclear electrons or bonding electrons in the molecule of which the nuclei form a part.

Energies of such nuclei are split by an electric field gradient, created by the electronic bonds in the local environment. Their energies split upon the application of a magnetic field into multiple levels . By comparison, spin-½ nuclei split into only two levels. The number of levels is given by 2*n* + 1 where is the spin number. The different splitting patterns can be seen in their coupling with other nuclei

The NQR energy levels of a nuclear magnetic moment I with quadrupole moment **Q** in an inhomogeneous electrostatic field are given by

$$E_m = \frac{e\,^{k}QV_{zz}}{4I(2I-1)}\left(3m^2 - I(I+1)\right).$$

$$E = A\,[3m^2 - I(I+1)]$$

Where, m being the magnetic quantum number –I,-I+1………..,+I eQ is the nuclear quadrupole moment &

V_{zz} or q electric field gradient

The selection rules for magnetic dipole transitions

$$\Delta m = \pm 1$$

4.4.4 - Electric field gradient q or V

The **electric field gradient** (**EFG**) measures the rate of change of the electric field at an atomic nucleus generated by the electronic charge distribution and the other nuclei.

It is created at the nuclei by asymmetric distribution of charge arising from extranuclear electrons or nonbonding electrons of which nuclei form a part.

- The EFG couples with the nuclear electric quadrupole moment of quadrupolar nuclei (those with spin quantum number greater than one-half) to generate an effect which can be measured using several spectroscopic methods.
- The EFG is non-zero only if the charges surrounding the nucleus violate cubic symmetry and therefore generate an inhomogeneous electric field at the position of the nucleus.
- A given charge distribution of electrons and nuclei, $\rho(\mathbf{r})$, generates an electrostatic potential $V(\mathbf{r})$. The derivative of this potential is the negative of the electric field component E generated. The first derivatives of the field, or the second derivatives of the potential, is the electric field gradient.
- EFG is a tensor quantity having 9 components.
- The nine components of the EFG are thus defined as the second spatial derivatives of the electrostatic potential, evaluated at the position of a nucleus

$$E_x = -\frac{\partial V}{\partial x} \quad E_y = -\frac{\partial V}{\partial y} \quad E_z = -\frac{\partial V}{\partial z}$$

Where, E is electric field gradient
V is electronic potential

$q_{xx} = -\partial E_x / \partial x = \partial^2 V / \partial X^2$

$q_{xy} = -\partial E_x / \partial y = \partial^2 V / \partial X \partial y$

……………………………..

……………………………

$q_{zz} = -\partial E_x / \partial z = \partial^2 V / \partial z^2$

- Nucleus is created at the origin of an arbitrarily oriented coordinate system (x,y,z).The time average electronic potential V is produced at the nucleus by all charges outside it.

  Therefore, Electric field of all charges E = $E_x i + E_y j + E_z k$

  Where , i ,j, k are unit vectors which specify the directions of X,Y,Z respectively.

$$V_{ij} = \frac{\partial^2 V}{\partial x_i \partial x_j}.$$

- For each nucleus, these components are combined as a symmetric 3 × 3 matrix.

$$\begin{matrix} q_{xx} & q_{xy} & q_{xz} \\ q_{yx} & q_{yy} & q_{yz} \\ q_{zx} & q_{yz} & q_{zz} \end{matrix}$$

- Diagonal component obeys Laplace equation,as the charge distribution generating the electrostatic potential is external to the nucleus, the matrix is traceless, for in that situation Laplace's equation, $\nabla^2 V(\mathbf{r}) = 0$, holds. Relaxing this assumption, a more general form of the EFG tensor which retains the symmetry and traceless character is

$$q_{xx} + q_{yy} + q_{zz} = 0$$

$$\nabla^2 V = 0$$

Thus components reduces from 9 to 5 B'ze cross components $q_{ij} = 0$
This type of cordinate system is known as Principal axis system & EFG components q_{xx}, q_{yy}, q_{zz} in principal axis system are represented as ABSOLUTE VALUE OF q_{xx}, q_{yy}, q_{zz}

- The traceless character, only two of the principal components are independent. Typically these are described by V_{zz} and the **asymmetry parameter**, η, defined as

  $$\eta = \frac{V_{xx} - V_{yy}}{V_{zz}}.$$

  η lies between 0 & 1

  the asymmetry parameter η defines the powder lineshape and eq is related to the linewidth.

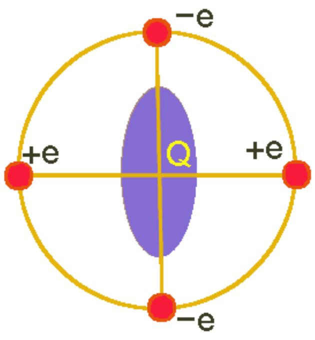
- If $\eta = 0$ There will be axial symmetry around z-axis
  Then $q_{xx} = q_{yy} = 1/2 q_{zz}$

- If $q_{xx} = q_{yy} = q_{zz}$, there is no interaction of nuclear quadruple moment Q with electronic charge distribution & EFG is spherical.
- If $q_{xx} \neq q_{yy} \neq q_{zz}$ EFG is unsymmetrical or non symmetrical.

CHECK YOUR PROGRESS – 11
Notes : i) Write your answer in the space given below
ii) Compare your answer with those given at the end of the unit
Q a. The electric quadrupole moment is negative for tangerine shaped nuclei.(True/ False)
Q b. The asymmetric parameter η lies between ………… & …………
Q c. The electric field gradient in NQR arises from the ………… & …………external to the nucleus under investigation.
Qd. The field gradient is said to be spherical if $q_{xx} \neq q_{yy} \neq q_{zz}$. In this case there is no interaction of ……..With the electronic charge distribution.

4.4.5 - Quadrupole moments-Q/eQ

Quadrupole nuclei with a half-integer spin larger than 1/2 possess a **quadrupole moment Q,** which interacts with the **electric-field gradient (EFG)** generated by their surroundings.



$Q = 1/e \int \rho r^2 (3 \cos^2\theta - 1)\, d\tau = Z (3Z^2 - r^2)$ Av

Where, e is fundamental charge,
ρ is nuclear charge density
τ is distance from centre of gravity of charge to element of volume $d\tau$.
θshows angle between r & spin axis z
Z atomic number
Av is average taken over nuclear state with m=I

Magnetic quantum number m represents orientation of I with respect to Z axis.Even if charge density within nucleus is constant, distorted or oriented shape give rise to charge distribution (non spherical).

Types of Quadrupole moments-Q/eQ

- Positive quadrupole moment – Prolate charge distribution with its axis parallel to Z axis give rise to positive quadrupole moment.
- Negative quadrupole moment – Oblate charge distribution flattened along spin axis give rise to negative quadrupole moment.

4.4.6 - Quadrupole coupling constant (QCC)

The coupling of Q (a property of the nucleus) with an EFG (a property coupling constant.)

QCC = Q * eq = eQq

Or eQ * eq = e^2Qq

The coupling of Q (a property of the nucleus) with an EFG (a property of a sample) is called the quadrupole interaction .The product of eq with eQ divided by Planck's constant is called the **quadrupole coupling constant (Cq).**

4.4.7 - Instrumentation of NQR

NQR Spectroscopy refers to that branch of spectroscopy in which energy is absorbed by various atomic nuclei in the region from 1-1000 **Mc/s.** The precise position of the absorption depends upon the electron density about the nucleus and the number of allowed absorption bands upon the nuclear spin chemically distiguishable nucleus.

The technique is very sensitive to the nature and symmetry of the bonding around the nucleus.NQR is a particular case of nuclear magnetic resonance (NMR) in crystals. Pure NQR is observed in the absence of a static magnetic field.

Resonance absorption of electromagnetic energy in a crystal owing to transitions between energy levels that are formed as a result of the interaction of nuclei that have an electric quadrupole moment with the crystal electric field.

The interaction of the quadrupole moment of a nucleus with the inhomogeneous electric field E in a crystal results in the appearance of energy states that correspond to various orientations of the nuclear spin S relative to the crystallographic axes. The quadrupole interaction energy varies over a wide range from hundreds of kilohertz to thousands of megahertz. The location of the energy levels does not depend on the orientation of the crystal axes with respect to an instrument, making it possible to use polycrystalline specimens. The equipment used to investigate NQR is not fundamentally different from NMR spectrometers.

- Sample requirements – Sample must be –
- Solid – crystalline
- Sample is cool upto 77 °K
- Sample size required depends on strength of resonance.
- Radio Frequency Oscillator – It provides balance to a balanced bridged circuit.
- Autodyne - The oscillations in the measuring LC circuit are supported by autodyne.
- Amplifier - High frequency (HF) signal are amplitude by amplifier in LC circuit is proportional to the NQR response signal.
- Synchronous detector (SD) demodulates this signal. The detected SD signal is processed by ADC.

In the investigation of NQR, measurements made in the absence of a static magnetic field H_0 are supplemented by measurements made in a field H_0. Depending on the relation between the energy of the nuclear quadrupole interaction with the field E and the energy of the magnetic interaction with the field H_0, a distinction is made between quadrupole splitting of NMR lines and Zeeman splitting in NQR.

Technique –

Any nucleus with more than one unpaired nuclear particle (protons or neutrons) will have a charge distribution which results in an electric quadrupole moment. Allowed nuclear energy levels are shifted unequally due to the interaction of the nuclear charge with an electric field gradient supplied by the non-uniform distribution electron density (e.g. from bonding electrons) and/or surrounding ions. The NQR effect results when transitions are induced between these nuclear levels by an externally applied radio frequency (RF) magnetic field. The spectra obtained is called as pure quadrupole resonance spectra.

4.4.8 - Splittings in NQR

In NQR the nuclear energy levels get splits up due to interaction of nuclear charge with an electric field gradient appears due to electron charge distribution.

Examples 1 - $^{14}{}_{7}N$

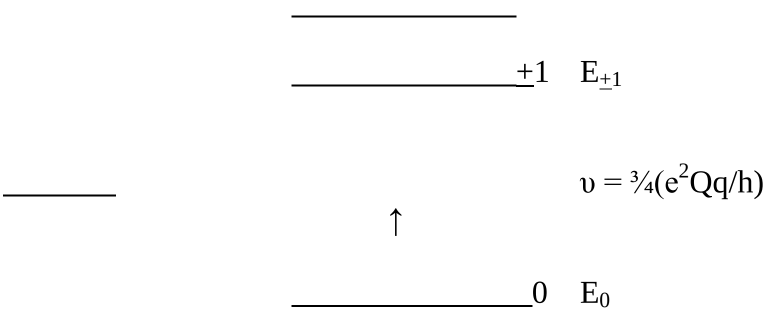
Value of $I = 1$, $2I + 1 = 3$
$m = -1 , 0 , +1$

According to

$$E_m = \frac{e\,{}^{k}QV_{zz}}{4I(2I-1)}(3m^2 - I(I+1)).$$

$E_0 = -(2/4)\, e^2Qq$ $\qquad$ $E_{\pm 1} = (1/4)\, e^2Qq$

$\upsilon = (E_{\pm 1} - E_0)/h$



$\Delta m_I = \pm 1$ Only one transition is possible.

The energy level shifts are much larger than the chemical shifts measured in NMR. Due to symmetry, the shifts become averaged to zero in the liquid phase, so NQR spectra can only be measured in solids

Examples 2 - $^{11}{}_{5}B$

Value of $I = 3/2$, $2I + 1 = 4$

$m = -3/2 , -1/2 , +1/2, +3/2$

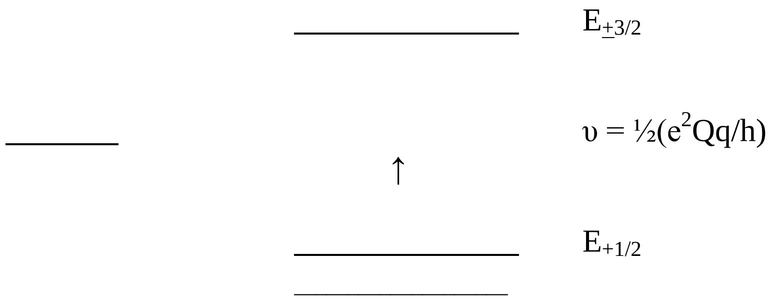
Two doubly degenerate pairs of sublevels are formed.

According to

$$E_m = \frac{e\,{}^{k}QV_{zz}}{4I(2I-1)}(3m^2 - I(I+1)).$$

$E_{\pm 1/2} = -(1/4)\, e^2Qq$ $\qquad$ $E_{\pm 3/2} = (1/4)\, e^2Qq$

$\upsilon = (E_{\pm 3/2} - E_{1/2})/h$



$\Delta m_I = \pm 1$ Only one transition is possible.

4.4.9 Applications

1. NQR is used in nuclear physics to determine the quadrupole moments of nuclei.

2. It is also used to investigate the symmetry and structure of crystals, the extent of ordering in macromolecules, and the nature of chemical bonds. Investigations of crystals are based on the relation between crystal structure and the values of gradients of the field *E*.

3.Nature of chemical Bond – NQR is used to determine electronic structure of molecules.It provides information regarding extent of hybridization & ionic character of bond by comparing Nuclear quadrupole coupling constant in atomic & molecular state of some nuclei.

4.Halogens have been extensively studied by NQR- Coupling constant increases with increase in number of halogen atoms due to an effective increase in electronegativity.

5. To detect Explosives – It is used to detect landmines & explosives concealed in luggage .A detection system consists of a radio frequency (Rf) power source, a coil to produce the magnetic excitation field & a detector circuit which monitors for a Rf NQR response coming from the explosive component of the object.

6.To measure the water/gas/oil coming out of an oil well in realtime. This particular technique allows local or remote monitoring of the extraction process,calculation of the well's remaining capacity & the water / detergents ratio the input pump must send to efficiently extract oil.

7. Structural information about group III halides- NQR is used for studying group III halides of type MX_3
(eg. $AlBr_3$). In the basic halogen spectrum , three resonance lines are observed two are closely spaced together & are far from third.It shows that 3 halogen atoms are not chemically equivalent.It is supported by X-Ray data also which shows that these halides exist as dimmers & there are 2 halogen atoms corresponding to bridge & end positions.

8. Study of charge transfer compounds-
When equimolar CBr_4 & p-xylene are brought together charge transfer compounds are formed.
Hooper studied frozen solution of these mixtures & reported resonance frequency of halogens are not different from those in pure state.This shows that charge transfer compounds are not formed in ground state.

Limitations
1. NQR can be obtained only for solids.
2. It requires moderately large samples.

CHECK YOUR PROGRESS -12
Notes : i) Write your answer in the space given below
ii) Compare your answer with those given at the end of the unit
Q a. What are the limitations of NQR
Q b. What structural information is provided by NQR in the study of group III halides.
Q c Can NQR is used for studying charge transfer compounds? Give reasons.

4.4.10 Let us sum up

Study of NMR gives detailed information about the molecular structure of the compound as –

- The number of signals in it represents the number of sets of equivalent protons present in the molecule.
- The position of the signals gives us information about the electronic environment of each set of equivalent protons.
- The intensities of different signals are proportional to the number of protons in each set, &
- Splitting of each peak into several peaks tells us about the number of neighboring protons.

Study of ESR gives detailed information about the structure of the compound as –

- It shows the site of unpaired electron(s) - The total area covered by either the absorption or derivative is proportional to the number of unpaired electrons in the sample.
- The number of line components decide the number & type of nuclei present in the vicinity of the odd electron.
- Hyperfine splitting shows interaction between the electron spin & the nuclear spin of the adjacent magnetic nuclei.
- Zero field splitting shows the number of unpaired electrons on the adjacent atom.

4.4.11 CHECK YOUR PROGRESS – KEYS

---

1. a) Because they have even number of p & n (I;e charge & mass are even) therefore there spin is zero.

b) 3/2

c) (iii) $_5B^{11}$

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

e) Longitudenal relaxation , molecular lattice

f) Radiowaves, $10^7 – 10^8$ cps.

2. a) So that the applied rf field should not change the effective magnetic field in the process of irradiation.

b) For aqueous solutions

c) Field sweep method

d) DSS, CCl_4 , D_2O etc.

3. a) decrease b) greater c) $\tau = 10 - \delta$ (d) - (i) Circulation of electrons

4. a) (i) 2 (ii) 4 (iii) 1 (iv) 2

b) for ethyl chloride - one triplet for methyl protons & one quartet for methylene protons.

For ethyl alcohol - at high resolution for impure alcohol shows one triplet for methyl protons ($-CH_3$) , one Quartet for methlene protons ($-CH_2$) & one singlet for –OH group

But impure alcohol shows - one triplet for methyl protons ($-CH_3$) , one pentate for methylene protons ($-CH_2$) & one triplet for –OH protons.

c) (i) Toluene d) p- xylene shows two singlets & benzene shows one singlet.

5. a) magnetic property of nucleus

b) Felix Bloch & E.M.Purcell

c) (iii) 1:1:1 triplet

d) short, pulsed

e) FTNMR

6. a) no

b) microwaves , $10^9 – 10^{12}$ cps

c) It shows evidence of unpaired electron.

d) nuclear spin, electronic spin.

7. a) larger

b) 9000 MHz

c) (i) 2.0043 (ii) 2.0023 (iii) more or less than 2.0023 (iv) 2.0036

d) DPPH

8. a) Because they strongly absorb in the microwave region.

b) Because it is shown by those substances which contains paramagnetic (unpaired electrons.

c) In ESR , transitions occur in microwave region while in NMR transitions occur in rf region.

d) Proportional

e) Because they have zero spin or no nuclear spin.

f) (m+1) (n+1) = (4+1) (4+1) = 5X5 =25

g) The ion $[O.C_6H_4O]^-$ contains four equivalent protons. So it exhibits (4+1) = 5 lines . There will be no splitting from C^{12} & O^{16}as these species have no nuclear spin.

9. a) Because the interaction between the unpaired electrons & magnetic nuclei in the paramagnetic species give rise to hyperfine structure.
   b) 35 lines
   c) 508 gauss
   d) According to (n+1) rule (3+1) = 4 lines
   e) Because bonding in the two species is differnt

10. a) When I<1, the nuclei donot possess eQ & so there is no nuclear quadupole interaction with eq
   b) Integral , half integral
   c) Due to their spherical symmetry
   d) 3/2 ,2

11. a) True
   b) 0 & 1
   c) Electrons, nuclei
   d) Quadrupole moment

12 a) NQR can be obtained only for solids.
   It requires moderately large samples.
   b) NQR is used for studying group III halides of type MX_3 (eg.$AlBr_3$)
   c) Yes

4.4.12 – References

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Unit V –X RAY DIFFRACTION

STRUCTURE

5.0–Introduction
5.1- Objective
5.2. – X-Ray Diffraction
  5.2.1 – Bragg Condition
  5.2.2 – Bragg law and method
  5.2.3 - Technique for x ray structure analysis of crystals
  5.2.4 – Laue method
  5.2.5 – Debye scherrer method of x-ray analysis
  5.2.6 - Miller Indices
  5.2.7 - Identification of unit cell
  5.2.8 - Structure of Simple lattices
  5.2.9 – Structure factor & its relation to intensity & electron density
  5.2.10- Phase problem
  5.2.11- Description of the procedure of x-ray structure analysis
  5.2.12 - Absolute configuration of molecule
  5.2.13- Ramchandran diagram
  5.2.14 – Let us sum up

5.3. Electron Diffraction

  5.3.1- Objectives of electron diffraction
  5.3.2- Instrumentation
  5.3.3 - Scattering angle
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  5.3.5- Wierl Equation
  5.3.6- Measurement Technique
  5.3.7- Elucidation of structure of simple gas phase molecules
  5.3.8- Low Energy Diffraction
  5.3.9- Determination of structure of surfaces
  5.3.10-Applications of Electron diffraction
  5.11 -Let us sum up

5.4 .- Neutron Diffraction
  5.4.1 Objectives of Neutron Diffraction
  5.4.2 Principle of neutron diffraction
  5.4.3 Scattering of Neutrons by solids & liquids
  5.4.4 Magnetic Scattering
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  5.4.6- Applications
  5.4.7 - Let us Sum Up
  5.4.8- Check Your Progress :Key
  5.4.9-References

5.0.- Introduction

Electromagnetic radiation, X-ray may be described in terms of their electric and magnetic components. These components are considered to oscillate transversely and sinusoidally in directions that are normal to the direction of propagation of the photon and normal to each other. When X-ray photons collide with matter, the oscillating *electric field* of the radiation causes the *charged components* of the atoms to oscillate with the same frequency as the incident radiation & provide information about the structural arrangement of atoms and molecules in a wide range of materials.

Electron diffraction is the electron microscopy techniques. Unlike other types of radiation used in diffraction studies of materials, such as X-rays and neutrons, electrons are charged particles and interact with matter through the Coulomb forces. This means that the incident electrons feel the influence of both the positively charged atomic nuclei and the surrounding electrons .Electron diffraction is a collective scattering phenomenon with electrons being (nearly elastically) scattered by atoms in a regular array (crystal). The incoming plane electron wave interacts with the atoms, and secondary waves are generated which interfere with each other. This occurs either constructively or destructively

Neutron diffraction or elastic neutron scattering is the application of neutron scattering to the determination of the atomic and/or magnetic structure of a material. Neutrons are neutral particles and interact principally with the atomic nuclei in a sample. Their scattering properties depend upon the complex neutron-nucleus interaction; as a consequence, isotopes of the same element can have very different neutron scattering properties

X-Ray Diffraction

5.1 – Objectives of X-ray diffraction studies

The Objectives of this unit are:

- To give a solid background in the basics in crystallography;
- To give a solid background in diffraction techniques;
- To highlight modern advances in XRD instrumentation and techniques;
- Phase identification problem;
- Structural problem in ordered solid.

It mainly focuses on crystallography and diffraction techniques. It is divided into three parts:

Part 1: From crystal lattice to crystal symmetry: symmetry, crystallographic point groups, symmetry classes, crystalline structure, space groups.

Part 2: Radiation interactions with matter: X ray, electron beam, synchrotron radiation, neutron sources, diffraction, Bragg law, direct and reciprocal lattice, structure factor, single crystal structure refinement.

Part 3: X-ray diffraction on powder: instrumentation, phase identification, quantitative analysis, crystallite size.

5.2 X-ray Diffraction

Discovered by Wilhelm Conrad Röntgen in 1895. X-rays are electromagnetic radiation with typical photon energies in the range of 100 eV - 100 keV.

X-ray Generation & Properties

For diffraction applications, only short wavelength x-rays (hard x-rays) in the range of a few angstroms to 0.1 angstrom (1 keV - 120 keV) are used. Because the wavelength of x-rays is comparable to the size of atoms, they are ideally suited for probing the structural arrangement of atoms and molecules in a wide range of materials. The energetic x-rays can penetrate deep into the materials and provide information about the bulk structure.

General Scattering Theory

Electromagnetic radiation, X-ray may be described in terms of their electric and magnetic components. These components are considered to oscillate transversely and sinusoidally in directions that are normal to the direction of propagation of the photon and normal to each other.

When X-ray photons collide with matter, the oscillating *electric field* of the radiation causes the *charged components* of the atoms to oscillate with the same frequency as the incident radiation. Each oscillating dipole returns to a less energetic state by emitting an electromagnetic photon that can, in general, travel in any outward direction.

John William Strutt (Lord Rayleigh) derived a formula that describes the intensity of coherent scattering. If the incident radiation is not polarized, then

$$I(2\theta) \propto I^{o} \cdot (T_f)^2 \cdot 1/r^2 \cdot [(1 + \cos^2 2\theta)/2]$$

where T_f is the cross section of the classical electron (e^2 / m c^2), r is the distance from the sample to the detector and 2θ is the angle between the incident and scattered photon. The last term describes the polarization of the scattered photon.

This theory presumes that the electrons that are bound in an atom would oscillate with a natural frequency, ω_0, when they are perturbed. It is also presumed that the frequency of the incident radiation ω is much larger than ω_0, but not so large that relativity corrections become important. Under these conditions, the electrons will scatter radiation exactly out of phase of the incident radiation. Hence this theory presumes that photons scattered from free electrons experience a phase shift of π radians from the phase of the incident photons.

5.2.1 -BRAGG'S CONDITION

Two beams with identical wavelength and phase approach a crystalline solid and are scattered off two different atoms within it. The lower beam traverses an extra length of $2d\sin\theta$. Constructive interference occurs when this length is equal to an integer multiple of the wavelength of the radiation.

Bragg diffraction occurs when electromagnetic radiation or subatomic particle waves with wavelength comparable to atomic spacings are incident upon a crystalline sample, scattered in a specular fashion by the atoms in the system, and undergo constructive interference in accordance to Bragg's law. For a crystalline solid, the waves are scattered from lattice planes separated by the interplanar distance d. Where the scattered waves interfere constructively; they remain in phase since the path length of each wave is equal to an integer multiple of the wavelength. The path difference between two waves undergoing constructive interference is given by 2dsinθ, where θ is the scattering angle. This leads to Bragg's law which describes the condition for constructive interference from successive crystallographic planes (h,k,l) of the crystalline lattice:

$$2d\sin\theta = n\lambda,$$

where n is an integer determined by the order given, and λ is the wavelength. A diffraction pattern is obtained by measuring the intensity of scattered waves as a function of scattering angle. Very strong intensities known as Bragg peaks are obtained in the diffraction pattern when scattered waves satisfy the Bragg condition.

5.2.2 –BRAGG LAW AND METHOD-

Bragg diffraction was first proposed by William Lawrence Bragg and William Henry Bragg in 1913 in response to their discovery that crystalline solids produced surprising patterns of reflected . They found that these crystals, at certain specific wavelengths and incident angles, produced intense peaks of reflected radiation (known as Bragg peaks).

W. L. Bragg and his father, Sir W. H. Bragg, were awarded the Nobel Prize in physics in 1915 for their work in determining crystal structures beginning with NaCl, ZnS, and diamond.

X-rays primarily interact with electrons in atoms. When x-ray photons collide with electrons, some photons from the incident beam will be deflected away from the direction where they originally travel.two things can happen-

If the wavelength of these scattered X-rays did not change (meaning that x-ray photons did not lose any energy), the process is called **Rayleigh scattering or Elastic scattering** (Thompson Scattering). Only momentum is transferred in the scattering process. *These x-rays carry information about the electron distribution in materials.*

On the other hand, in the **inelastic scattering process (Compton Scattering),** x-rays transfer some of their energy to the electrons and the scattered x-rays will have different wavelength than the incident x-rays.

Diffracted waves from different atoms can interfere with each other and the resultant intensity distribution is strongly modulated by this interaction. If the atoms are arranged in a periodic fashion, as in crystals, the diffracted waves will consist of sharp interference maxima (peaks) with the same symmetry as in the distribution of atoms. Measuring the diffraction pattern therefore allows us to deduce the distribution of atoms in a material

In Bragg's construct, the planes in the crystal are exposed to a radiation source at a glancing angle θ and X rays are scattered with an angle of reflection also equal to θ. The incident and diffracted rays are in the same plane as the normal to the crystal planes.

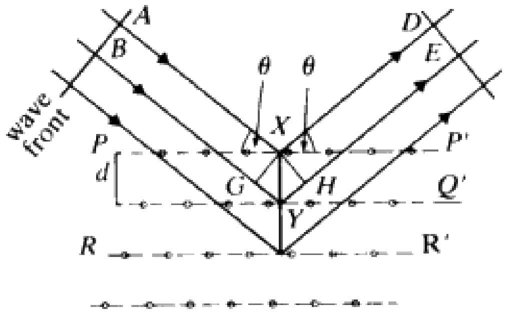


Figure : Bragg's Law.

Bragg reasoned that *constructive interference* would occur only when the path length difference between rays scattered from parallel crystal planes would be an integral number of wavelengths of the radiation. When the crystal planes are separated by a distance d, the path length difference would be 2d sin θ. Thus, for constructive interference to occur the following relation must hold true.

$$n\lambda = GY + YH$$

$$GY = YH = XY \text{ Sin } \theta$$

$$n\,\lambda = 2\,d \sin\theta \qquad (XY = d)$$

This relation is known as **Bragg's Law**. Thus for a given d spacing and wavelength, the first order peak ($n = 1$) will occur at a particular θ value. Similarly, the θ values for the second ($n = 2$) and higher order ($n > 2$) peaks can be predicted.

The above derivation assumes that phase differences between wavelets scattered at different points depend only on path length differences. It is assumed that there is no intrinsic phase change between the incident and scattered beams or that this phase change is constant for all scattering events.

5.2.3 -Technique for x-ray structural analysis of crystal – The apparatus consists of an X ray tube from which a narrow beam is allowed to fall on the crystal mounted on a rotating table .The rotating table is provided with scale and vernier ,from which the angle of incidence θ can be measured .

An arm which is rotating about the same axis as the crystal table carries an ionization chamber .The rays reflected from the crystal enter the ionization chamber and ionize the gas present inside. Due to the ionization ,current is produced which is measured by an electrometer. The current of ionization is the direct measure of intensity of reflected beam from the crystal. For different angle of incidence ,the corresponding ionization current is measured from the electrometer .The values are plotted in the form of a graph.

5.2.4 -LAUE METHOD FOR CRYSTAL ANALYSIS

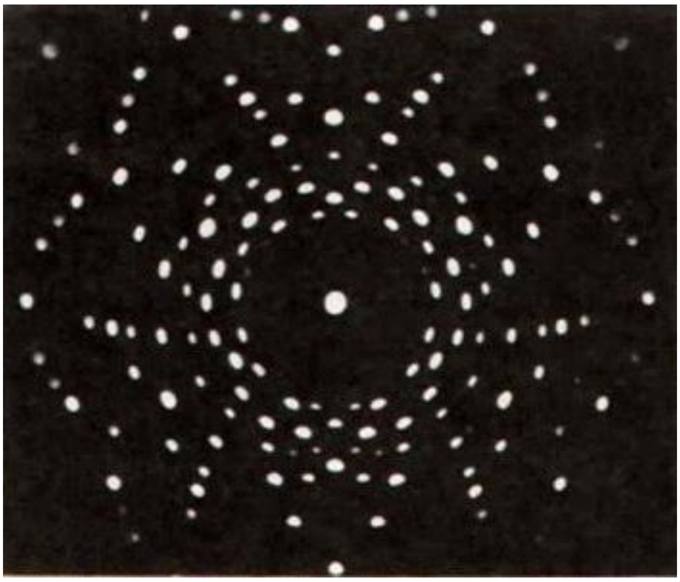
PRINCIPLE- In 1912 Laue suggested that crystal can act as a natural three dimensional diffraction grating for X rays because atoms in a crystal are orderly arranged with a distance between them equal to 10^{-8} cm.The Laue method is mainly used to determine the **orientation** of large single crystals. White radiation is reflected from, or transmitted through, a fixed crystal.

Laue won the Nobel Prize in Physics in 1914 for his work.

Max von Laue used continuous radiation (with all possible wavelengths) to impact on a stationary crystal. With this procedure the crystal generates a set of diffracted beams that show the internal symmetry of the crystal. In these circumstances, and taking into account Bragg's Law, the experimental constants are the interplanar spacings **d** and the crystal position referred to the incident beam. The variables are the wavelength **λ** and the integer number **n**:

$$n\,\lambda = 2\,d_{hkl} \sin\theta_{nh,nk,nl}$$

Thus, the diffraction pattern will contain (for the same spacing **d**) the diffracted beams corresponding to the first order of diffraction (**n=1**) of a certain wavelength, the second order (**n=2**) of half the wavelength (**λ/2**), the third order (**n=3**) with wavelength **λ/3**, etc. Therefore, the Laue diagram is simply a stereographic projection of the crystal.



Laue diagram of a crystal

TECHNIQUE- Laue diffraction pattern, in X rays, a regular array of spots on a photographic emulsion resulting from X rays scattered by certain groups of parallel atomic planes within a crystal. When a thin, pencil-like beam of X rays is allowed to impinge on a crystal, those of certain wavelengths will be oriented at just the proper angle to a group of atomic planes so that they will combine in phase to produce intense, regularly spaced spots on a film or plate centered around the central image from the beam, which passes through undeviated .Number of white spots obtains around central spot against black background due to diffracted beam.By careful study of intensities and position of the spots ,it is possible to deduce the geometrical arrangements of atoms or ions in the crystals.

There are two different geometries in the Laue method, depending on the crystal position with regard to the photographic plate: transmission or reflection:

Back-reflection Laue

In the back-reflection method, the film is placed **between** the x-ray source and the crystal. The beams which are diffracted in a backward direction are recorded. One side of the cone of Laue reflections is defined by the transmitted beam. The film intersects the cone, with the diffraction spots generally lying on an hyperbola

TECHNIQUE- Laue diffraction pattern, in X rays, a regular array of spots on a photographic emulsion resulting fro
by certain groups of parallel atomic planes within a crystal. When a thin, pencil-like beam of X rays is allowed to impi
those of certain wavelengths will be oriented at just the proper angle to a group of atomic planes so that they will comb
produce intense, regularly spaced spots on a film or plate centered around the central image from the beam, which pass
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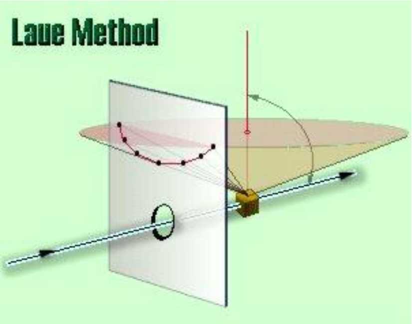
intensities and position of the spots ,it is possible to deduce the geometrical arrangements of atoms or ions in the crysta

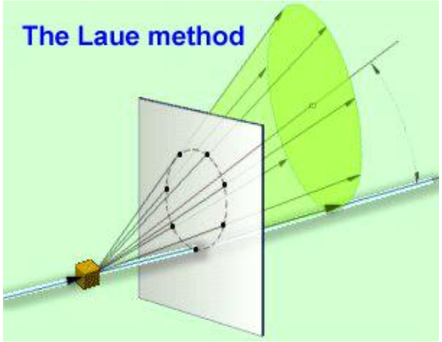


.

The Laue method in Reflection mode

Transmission Laue

In the transmission Laue method, the film is placed **behind** the crystal to record beams which are transmitted through t of the cone of Laue reflections is defined by the transmitted beam. The film intersects the cone, with the diffraction spo on an ellipse.



The Laue method in transmission mode

5.2.5 -Powder Diffraction(Debye Scherrer Method)

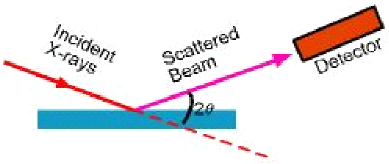
This method is known as Debye Scherrer method as it was first proposed by Debye & Scherrer.

Powder XRD (X-ray Diffraction) is the most widely used **x-ray diffraction technique for characterizing materials**. studying particles in liquid suspensions or polycrystalline solids (bulk or thin film materials).

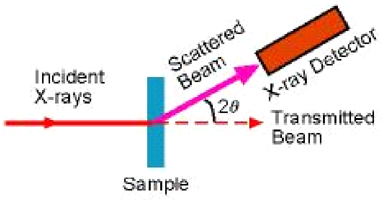
As the name suggests, the sample is usually in a powdery form, consisting of fine grains of single crystalline material t

The term 'powder' really means that the crystalline domains are randomly oriented in the sample. Therefore when the 2 pattern is recorded, it shows concentric rings of scattering peaks corresponding to the various d spacings in the crystal l positions and the intensities of the peaks are used for identifying the underlying structure (or phase) of the material. Fo diffraction lines of graphite would be different from diamond even though they both are made of carbon atoms. This ph is important because the material properties are highly dependent on structure .

Powder diffraction data can be collected using either transmission or reflection geometry. Because the particles in the p randomly oriented, these two methods will yield the same data.



Reflection



Transmission

A powder XRD scan from a $K_2Ta_2O_6$ sample is a plot of scattering intensity vs. the scattering angle or the correspondin peak positions, intensities, widths and shapes all provide important information about the structure of the material.

Two important points to remember in regard of crystallographic axis-

- The lengths of the crystallographic axes are controlled by the dimensions of the unit cell upon which the crysta
- The angles between the crystallographic axes are controlled by the shape of the unit cell.

  As the relative lengths of the crystallographic axes control the angular relationships between crystal faces. Thi crystal faces can only develop along lattice points. The relative lengths of the crystallographic axes are called

ation of Miller Indices

ed as the relative lengths of the crystallographic axes. They are normally taken as of the b crystallographic axis. Thus, an axial ratio is defined as follows:

/b : c/b

length of the a crystallographic axis, b, is the actual length of the b crystallographic al length of the c crystallographic axis.By determining the size of the unit cell, the crystallographic axes can be determined. For orthorhombic sulfur the unit cell red by x-rays are:

2.87Å ,c = 24.39Å

for orthorhombic sulfur is:

12.87 : 24.39/12.87 or 0.813 : 1 : 1.903

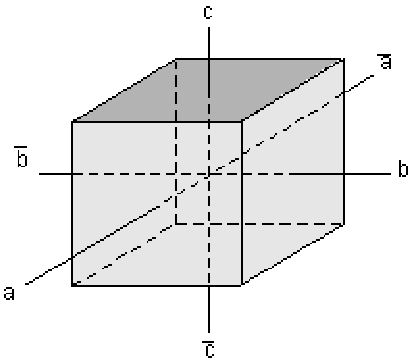
s develop along lattice points, the angular relationship between faces must depend s of the axes. Long before x-rays were invented and absolute unit cell dimensions ystallographers were able to determine the axial ratios of minerals by determining rystal faces. So, for example, in 1896 the axial ratios of orthorhombic sulfur were rly exactly the same as those reported above from x-ray measurements.

l Faces (Weiss Parameters)

defined by their intercepts on the crystallographic axes. For non-hexagonal crystals,

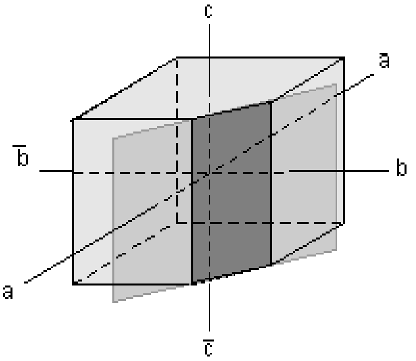
e intersects only one of the crystallographic

le the top crystal face shown here intersects t does not intersect the a or b axes. If we he face intercepts the c axis at a distance of 1 hen the intercepts, sometimes called Weiss re: ∞**a,** ∞**b, 1c**



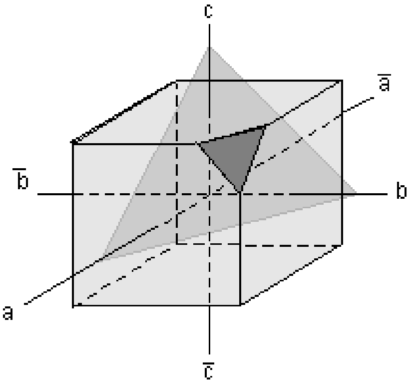
- A crystal face intersects two of the crystallographic axes.

  As an example, the darker crystal face shown here intersects the a and b axes, but not the c axis. Assuming the face intercepts the a and c axes at 1 unit cell length on each, the parameters for this face are: **1 a, 1 b, ∞c**



- A crystal face that intersects all 3 axes.

  In this example the darker face is assumed to intersect the a, b, and c crystallographic axes at one unit length on each. Thus, the parameters in this example would be:
  1a, 1b, 1c

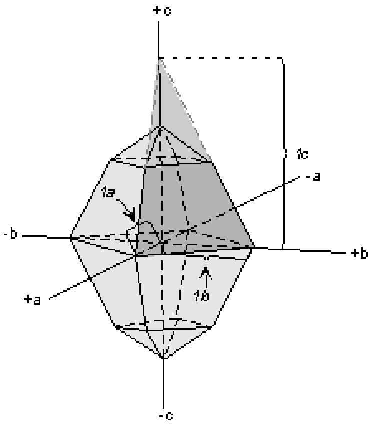


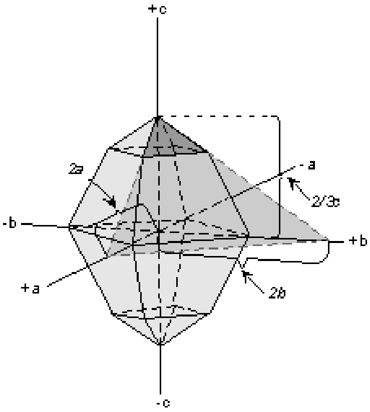
very important points about intercepts of faces:

- **The intercepts or parameters are relative values, and do not indicate any actual cutting lengths.**
- **Since they are relative, a face can be moved parallel to itself without changing its relative intercepts or parameters**.

face is chosen arbitrarily to have intercepts of 1. Thus, the convention is to assign the **largest face intersects all 3 crystallographic axes the parameters - 1a, 1b, 1c. This face is called the *unit***
.

example, in the orthorhombic crystal shown here, the large shaded face is the largest face that cuts all three axes. It is nit face, and is therefore assigned the parameters 1a, 1b, 1c.





e the unit face is defined, the intercepts of the smaller face can etermined. These are 2a, 2b, 2/3c. Divide these parameters he common factor 2, resulting in 1a,1b,1/3c. Moving a face llel to itself does not change the relative intercepts. Since cepts or parameters are relative, they do not represent the al cutting lengths on the axes.

pecifying the intercepts or parameters of a crystal face, each face of a crystal can be idemtified. But, notation is cumbersome, so crystallographers have developed another way of identifying or indexing s. This conventional notation called the Miller Index is our next topic of discussion.

ler Indices

Miller Index for a crystal face is found by

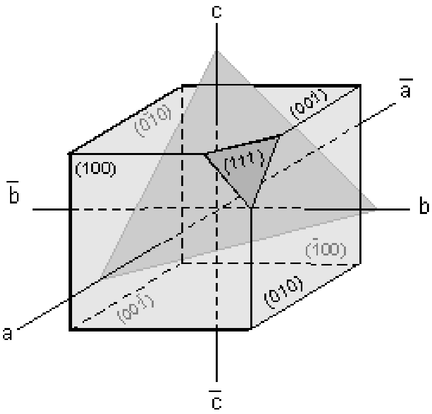
- first determining the parameters
- second inverting the parameters, and
- third clearing the fractions.

nple, if the face has the parameters 1 a, 1 b, ∞c, inverting the parameters would be 1/1, 1/1, 1/ ∞ would become 1, 1, 0. The Miller Index is written inside parentheses with no commas - thus (110)

nple let's look at the crystal shown here. All of the faces his crystal are relatively simple. The face [labeled (111)] cuts all three axes at 1 unit length has the parameters 1a, c. Inverting these, results in 1/1, 1/1, 1/1 to give the er Index (111).

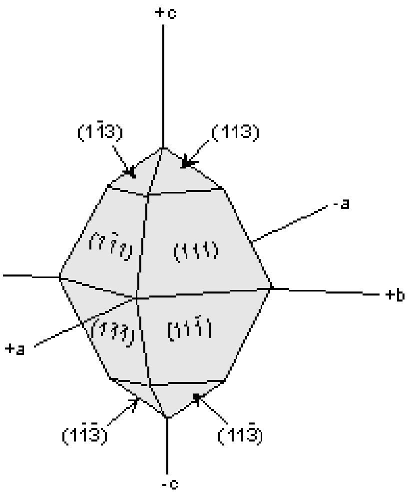
square face that cuts the positive a axis, has the meters 1 a, ∞ b, ∞ c. Inverting these becomes 1/1, 1/∞to the Miller Index (100).

face on the back of the crystal that cuts the negative a has the parameters -1a, 1 b, 1 c. So its Miller Index is). Note how the negative intercept is indicated by putting nus sign above the index. This would be read "minus one, one". Thus, the other 4 faces seen on this crystal ld have the Miller Indices (001), (00$\bar{1}$), (010), and (0$\bar{1}$0).



mple In a crystal the small triangular face near the top that all three axes had the parameters 1a, 1b, 1/3c.   Inverting e becomes 1/1, 1/1, 3/1 to give the Miller Index for this face 13).

larly, the small triangular face the cuts the positive a axis and egative b axis, would have the Miller Index (1$\bar{1}$3), the similar on the bottom of the crystal, cutting positive a, positive b, egative c axes would have the Miller Index (11$\bar{3}$

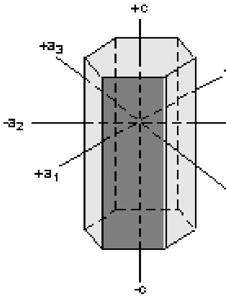


efer to a general face that intersects all three crystallographic axes where the parameters are not vn, we use the notation (hkl). For a face that intersects the b and c axes with general or unknown cepts the notation would be (0kl), for a face intersecting the a and c axis, but parallel to b the tion would be (h0l), and similarly for a face intersecting the a and b axes, but parallel to c we would he notation (hk0).

Miller Index notation applies very well to crystals in the Triclinic, Monoclinic, Orthorhombic, agonal, and Isometric systems, but requires some modification to be applied to the Hexagonal tal system.

ller Bravais Indices

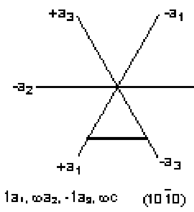
e the hexagonal system has three "a" axes perpendicular to the "c" axis, both the parameters of a face he Miller Index notation must be modified. The modified parameters and Miller Indices must ct the presence of an additional axis. This modified notation is referred to as Miller-Bravais Indices, the general notation (hkil)



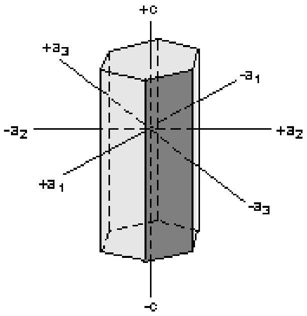
mple- look at the dark shaded face in the hexagonal crystal shown. This face intersects the positive a_1 axis at 1 unit th, the negative a_3 axis at 1 unit length, and does not intersect the a_2 or c axes. This face thus has the parameters:

$\infty\ a_2$, -1 a_3, ∞ c

rting and clearing fractions gives the Miller-Bravais Index:(100)$\bar{1}$. An important rule to remember in applying this tion in the hexagonal system, is that whatever indices are determined for h, k, and i,



k + i = 0



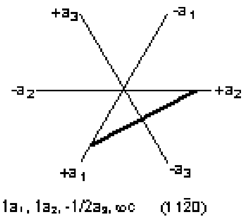
a similar hexagonal crystal, this time with the shaded face cutting all three axes, we would for the shaded face in the diagram that the parameters are 1 a_1, 1 a_2, -1/2 a_3, ∞ c. rting these intercepts gives:

1/1, -2/1, 1/∞

lting in a Miller-Bravais Index of

$\bar{2}$0)

e how the "h + k + i = 0" rule applies here!



stal Forms

er Index notation are used to designate crystal forms. A ***crystal form*** is **a set of crystal faces that related to each other by symmetry.** To designate a crystal form we use the Miller Index, or Miller-vais Index notation enclosing the indices in curly braces, i.e.

} or {hkil} Such notation is called a ***form symbol***.

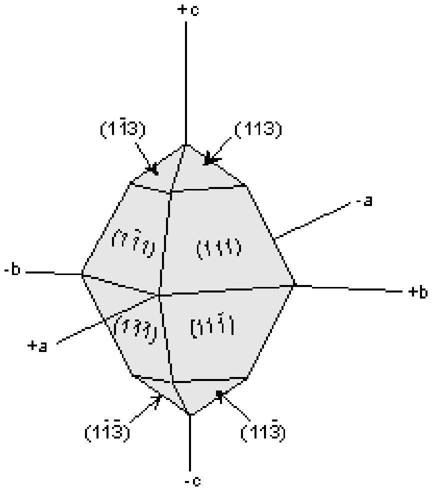
s crystal is the same orthorhombic crystal. It has two forms. form {111} consists of the following symmetrically 8 related s:

), (11$\bar{1}$), (1$\bar{1}$1), (1$\bar{1}\bar{1}$), ($\bar{1}$11), ($\bar{1}$1$\bar{1}$), ($\bar{1}\bar{1}$1), and ($\bar{1}\bar{1}\bar{1}$).

form is called a rhombic-dipyramid.

other form is also a rhombic-dipyramid, but consists of the gular shaped faces similar to the face (113). The form ool for this form is {113} and consists of the following 8 s:

), (1$\bar{1}$3), (11$\bar{3}$), (1$\bar{1}\bar{3}$), ($\bar{1}$13), ($\bar{1}$1$\bar{3}$), ($\bar{1}\bar{1}$3), and ($\bar{1}\bar{1}\bar{3}$).



5.2.7 - UNIT CELL AND ITS IDENTIFICATION

Crystals are solids that often have well-defined, smooth faces and straight edges. The angles between similar faces of d a crystalline substance are always constant. These properties led Haüy and others to suggest that crystals are made of m that are stacked in a 3-dimensional array related by simple translation.

Thus, crystals are defined as solids with long-range, 3-dimensional internal order. Each unique piece of the 3-dimensio ***unit cell.***

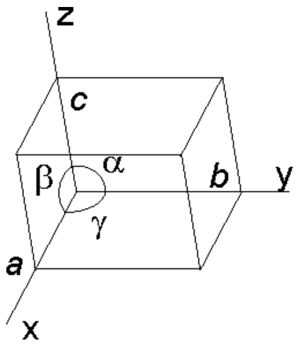


Fig: Unit cell

The shape of any unit cell is described by six parameters. These six parameters are three axial lengths, designated *a*, *b*,
interaxial angles, α, β, and γ. The angle α is the angle between *b* and *c*; β is the angle between *a* and *c*; and γ is the angl
Mostly the axial lengths are expressed in terms of **Å (Ångströms**), and the interaxial angles are expressed in terms of °

By convention the unit cell edges are chosen to be right-handed (*a* × *b* is the direction of *c*), to have the highest symme
smallest volume. If symmetry does not override then the cell is chosen so that $a \leq b \leq c$, and α, β, and γ all < 90 ° or all
of cell is called the *reduced cell*.

Some possible 2-dimensional lattices are shown below for a 2-dimensional array of commas.

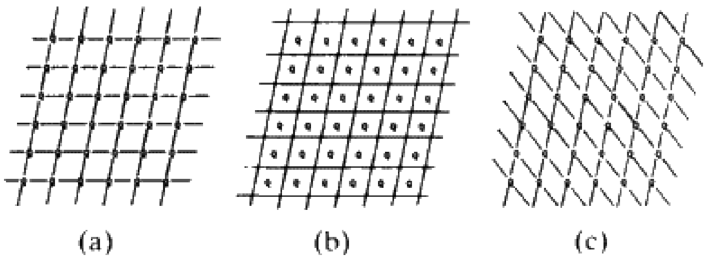

(a) (b) (c)

Fig: Various 2 dimensional lattices

In many lattices, both the choice of origin and the choice of lattice vectors are arbitrary.

5.2.8 - STRUCTURE OF SIMPLE LATTICES

Consider the sets of parallel planes that intersect all of the points in a lattice. Some examples of these lattice planes in a
lattice are shown below.

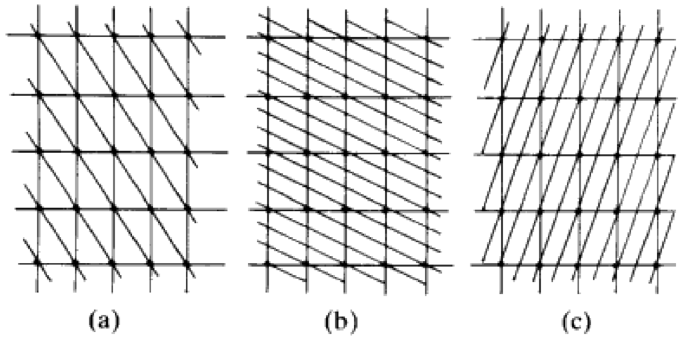

(a) (b) (c)

Figure . Various families of planes.

The intercepts of the planes with the cell edges must be fractions of the cell edge. Thus cell intercepts can be at 1/0 (=
1/n. The conventional way of identifying these sets of planes is by using three integers that are the denominators of the
the 3 axes of the unit cell (*hkl*). Thus if a set of planes had intercepts at 1/2, 1/3, 1/1 then the planes would be referred t
of planes.

Particular directions in a unit cell are described with the nomenclature [nmp] where n, m, and p are integers. The *a*, *b*,
be described as [100], [010], and [001], respectively. Symmetry-equivalent sets of directions would be described as {n
cubic axial directions [100], [010], and [001], which are all equivalent in this crystal system, can be described simply a

directions should not be confused with the nomenclature for sets of planes (*hkl*) shown above.

Crystallographers use a special way to denote negative integers. The negative sign is placed over the integer rather thar the left of the number. Thus the value for "-1" is pronounced as Europe 1 is pronounced "bar 1" in Euorpe in the Unitec pronounced "1 bar."

Reciprocal Lattice

The scattering of radiation and interference between scattered photons produces a resulting pattern called a *diffraction* Bragg's Law there is a reciprocal relationship between the distances between rows of scattering centers d and the scatte there is a reciprocal relationship between the unit cell of the crystal and the lattice pattern of the diffracted spots.

Consider normals to all possible direct lattice planes (*hkl*) to radiate from some point taken as the origin. Terminate ea a distance 1/d*hkl* from this origin, where d*hkl* is the perpendicular distance between planes of the set (*hkl*). The set of p constitutes the *reciprocal lattice*.

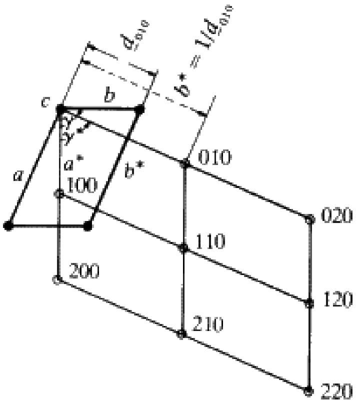


Fig. Real and reciprocal lattices.

Note that a short axis in real space (the space of the crystal) leads to a large separation between spots in reciprocal (diff that a long real axis of the unit cell leads to a short separation between spots. Also note that obtuse angles in the real un angles in the reciprocal cell, and vice versa.The dimensions and orientation of the crystal determine the positions of the diffraction pattern.

Lattice Relationships

Let the real cell vectors *a*, *b*, and *c* be represented by the basis set a_1, a_2, and a_3. There exists another set of vectors b_1, the following relations must hold:

$a_i \cdot b_i = 1$

$a_i \cdot b_j = 0, \quad i \neq j$

These b_i are called the reciprocal basis set. The first expression above states that the b_i are reciprocal in length to the expression above requires that the b_j are normal to the a_i. The b_i are typically referred to as a^*, b^*, and c^*.

Thus the reciprocal lattice can be represented by vectors of the form:

$\mathbf{R}hkl = ha^* + kb^* + lc^*$,
$|\,\mathbf{R}hkl\,| = K / dhkl$

where *h, k,* and *l* are the indices of sets of planes in the crystal, and K can assume the value of 1, λ, or 2πλ, depending c convention (crystallography, solid-state physics, etc).

5.2.9 -Structure Factor & its relation to intensity & electron density

In Crystallography , the **static structure factor** (or **structure factor**) is a mathematical description of how a material radiation. The structure factor is a particularly useful tool in the interpretation of interference patterns obtained in X-ra neutron diffraction experiments.It is measured without resolving the energy of scattered photons/electrons/neutrons. En measurements yield the dynamic structure factor.

The structure factor describes the way in which an incident beam is scattered by the atoms of a crystal unit cell, taking different scattering power of the elements through the term f_j. Since the atoms are spatially distributed in the unit cell, difference in phase when considering the scattered amplitude from two atoms. This phase shift is taken into account by exponential term. The atomic form factor, or scattering power, of an element depends on the type of radiation considere electrons interact with matter through different processes than for example X-rays, the atomic form factors for the two same.

To compute structure factors for a specific lattice, compute the sum above over the atoms in the unit cell. Since crystal described in terms of their Miller indices, it is useful to examine a specific structure factor in terms of these.

Consider that an atom j is located at $\mathbf{r}_i$ from the origin in a unit cell of a crystal. This shift in origin from the center of th means that the distance $\mathbf{r}$ in the equation for the scattering by an atom becomes $\mathbf{r} + \mathbf{r}_j$. Thus the scattering by atom j bec

$\mathbf{f}_j = \int \rho(\mathbf{r}) \exp[2\pi i\, (\mathbf{r} + \mathbf{r}_j) \cdot \mathbf{S}]\, dv$

$\mathbf{f}_j = f_j \exp(2\pi i\, \mathbf{r}_j \cdot \mathbf{S})$

where $f_j = \int \exp(2\pi i\, \mathbf{r} \cdot \mathbf{S})\, dv$

This last expression is called the atomic scattering factor for atom j.The term **S** is called the scattering vector.

$|S| = 2 \sin \theta / \lambda = 1/d_{hkl}$.

Bragg's Law requires that the phase difference between the waves scattered by successive unit cells must be equal to an of $2\pi / \lambda$. Since the scattered wave may be considered as coming from $1/n$ multiples of the cell edge vectors $\boldsymbol{a}$, $\boldsymbol{b}$, and $\boldsymbol{c}$,

$(2\pi / \lambda)\, (\boldsymbol{a} \cdot \mathbf{S}) = 2\pi\, h / \lambda$

$(2\pi / \lambda)\, (\boldsymbol{b} \cdot \mathbf{S}) = 2\pi\, k / \lambda$

$(2\pi / \lambda)\, (\boldsymbol{c} \cdot \mathbf{S}) = 2\pi\, l / \lambda$

These equations are known as the *Laue equations* and are a 3-dimensional representation of Bragg's Law.

The coordinates of atoms, given as the center of the nuclei, are usually represented as fractions of the unit cell edges, a are labelled x_j, y_j, and z_j. The $\mathbf{r}_j$ vector may be written as:

$\mathbf{r}_j = \boldsymbol{a}x_j + \boldsymbol{b}y_j + \boldsymbol{c}z_j$

The product $\mathbf{r}_j \cdot \mathbf{S}$ may be written as:

$\mathbf{r}_j \cdot \mathbf{S} = x_j\boldsymbol{a} \cdot \mathbf{S} + y_j\boldsymbol{b} \cdot \mathbf{S} + z_j\boldsymbol{c} \cdot \mathbf{S}$

$= h\, x_j + k\, y_j + l\, z_j$

Finally, the total scattering power for all of the atoms in the unit cell may be written as:

$\boldsymbol{F}(hkl) = \sum f_j \exp 2\pi\, i\, (h\, x_j + k\, y_j + l\, z_j)$

The relation above is known as the *structure factor expression*. This relation may be recast in terms of its amplitude, $|F$ angle, $\varphi(hkl)$ or in terms of its real, A, and imaginary, B components in the following expressions.

$\boldsymbol{F}(hkl) = |F(hkl)| \exp[2\pi i\, \varphi(hkl)]$

$\boldsymbol{F}(hkl) = A + iB$

Electron Density relation with structure factor

If the structure factor expression is rewritten as a continuous summation over the volume of the unit cell then the expre

$\boldsymbol{F}(\mathbf{S}) = \int \rho(\mathbf{r}) \exp 2\pi\, i\, \mathbf{r}_j \cdot \mathbf{S}\, dv$

By multiplying both sides by $\exp -2\pi\, i\, \mathbf{r}_i \cdot \mathbf{S}$ and integrating over the volume of diffraction space, dv_r, we get an expres electron density of the unit cell.

$\rho(\mathbf{r}) = \int \boldsymbol{F}(\mathbf{S}) \exp -2\pi\, i\, \mathbf{r}_j \cdot \mathbf{S}\, dv_r$

Since $\boldsymbol{F}(\mathbf{S})$ is nonzero only at the lattice points, The integral may be written as discrete sums over the three indices h, k

$\rho(xyz) = 1/V \sum \sum \sum \boldsymbol{F}(hkl) \exp -2\pi\, i(h\, x + k\, y + l\, z)$

$\rho(xyz) = 1/V \sum \sum \sum |F|(hkl) \exp -2\pi\, i[h\, x + k\, y + l\, z - \varphi(hkl)]$

where the three summations run over all values of x, y, and z.

5.2.10 - Phase Problem

The interaction of the electric vector of the incident radaition with charged matter in atoms generates dipoles in these c charged species then release this additional energy by emitting X-ray photons with the same energy as the incident radi is found experimentally to be proportional to the square of the structure factor amplitudes. Since $\boldsymbol{F}(\mathbf{S})$ is complex, then by $\boldsymbol{F}(\mathbf{S}) \times \boldsymbol{F}^*(\mathbf{S})$, where $\boldsymbol{F}^*(\mathbf{S})$ is the complex conjugate of $\boldsymbol{F}(\mathbf{S})$.

$$I(\mathbf{S}) \propto \boldsymbol{F}(\mathbf{S}) \cdot \boldsymbol{F}^*(\mathbf{S}) \propto |\boldsymbol{F}(\mathbf{S})|^2$$

Although the structure factor amplitudes may be measured directly from the diffraction experiment, all information co of the data are lost.

In the electron density expression, the structure factor term can be rewritten into its amplitude and phase angle giving

$$\rho(xyz) = 1/\mathrm{v} \sum \sum \sum F(hkl) \exp 2\pi\, i\, \varphi(hkl) \exp -2\pi\, i\, (h\,x + k\,y + l\,z)$$

If both the structure factor amplitudes and the phases were known, then the electron density could be directly calculate expression above. But, since the phases are lost during measurement, the electron density cannot be directly calculated knowledge of the phases is termed the *phase problem* in crystallography.

Phase angles can be estimated in a variety of ways. Often maps are calculated with measured structure factor amplitud estimated phases to see if other features of the map can be observed phase problem.

In x-ray crystallography, integrated intensities of the diffraction peaks are used to reconstruct the electron density map in the crystal. To achieve high accuracy in the reconstruction, which is done by Fourier transforming the diffraction int appropriate phase assignment, a high degree of completeness as well as redundancy in diffraction data is necessary, me possible reflections are measured multiple times to reduce systematic and statistical error. The most efficient way to do area detector which can collect diffraction data in a large solid angle. The use of high intensity x-ray sources, such as s radiation, is an effective way to reduce data collection time.

One of the central difficulties in structural determination using x-ray crystallography is referred to as the "phase proble from the fact that the diffraction data contains information only on the amplitude but not the phase of the structure fact many methods have been developed to deduce the phases for reflections, including computationally based direct meth replacement, and multi-wavelength anormalous diffraction (MAD) methods.

5.2.11 - Description of X ray analysis-

Max von Laue, in 1912, discovered that crystalline substances act as three-dimensional diffraction gratings for X-ray w to the spacing of planes in a crystal lattice. X-ray diffraction is now a common technique for the study of crystal struct spacing.

X-ray diffraction is based on constructive interference of monochromatic X-rays and a crystalline sample. These X-ray cathode ray tube, filtered to produce monochromatic radiation, collimated to concentrate, and directed toward the samp of the incident rays with the sample produces constructive interference (and a diffracted ray) when conditions satisfy B $\sin \theta$). This law relates the wavelength of electromagnetic radiation to the diffraction angle and the lattice spacing in a These diffracted X-rays are then detected, processed and counted. By scanning the sample through a range of 2θangles diffraction directions of the lattice should be attained due to the random orientation of the powdered material. Conversi diffraction peaks to d-spacings allows identification of the mineral because each mineral has a set of unique d-spacing comparison of d-spacings with standard reference patterns.

All diffraction methods are based on generation of X-rays in an X-ray tube. These X-rays are directed at the sample, a rays are collected. A key component of all diffraction is the angle between the incident and diffracted rays.

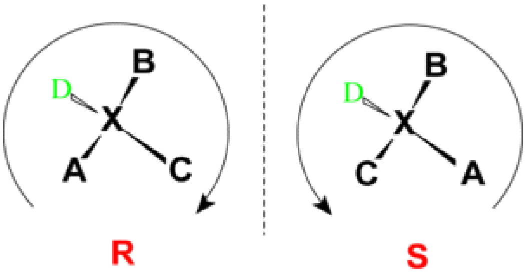
INSTRUMENTATION

X-rays are generated in a cathode ray tube by heating a filament to produce electrons, accelerating the electrons towar applying a voltage, and bombarding the target material with electrons. When electrons have sufficient energy to dislod electrons of the target material, characteristic X-ray spectra are produced.

These spectra consist of several components. The specific wavelengths are characteristic of the target material (Cu, Fe by foils or crystal monochrometers, is required to produce monochromatic X-rays needed for diffraction. Copper is the target material for single-crystal diffraction. These X-rays are collimated and directed onto the sample. As the sample a rotated, the intensity of the reflected X-rays is recorded. When the geometry of the incident X-rays impinging the samp Bragg Equation, constructive interference occurs and a peak in intensity occurs. A detector records and processes this converts the signal to a count rate which is then output to a device such as a printer or computer monitor.

Peak positions occur where the X-ray beam has been diffracted by the crystal lattice. The unique set of d-spacings deri
pattern can be used to 'fingerprint' the mineral.

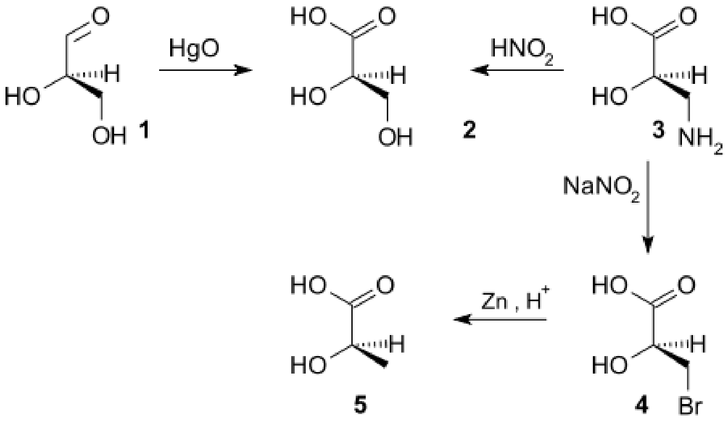
5.2.12 -Absolute configuration



An **absolute configuration** in stereochemistry is the spatial arrangement of the atoms of a chiral molecular entity (or g
stereochemical description e.g. **R** or **S**. Absolute configurations for a chiral molecule (in pure form) are most often obta
crystallography. When the absolute configuration is obtained the assignment of R or S is based on the Cahn-Ingold-Pre

Absolute configurations are also relevant to characterization of crystals.

The configuration of other chiral compounds is related to that of (+)-glyceraldehyde (R)-enantiomer by sequences of c
For example (+)- glyceraldehyde (**1**) was related to (-)-glyceric acid **2** (oxidation by mercury oxide) which in turn was
isoserine **3** (nitric acid oxidation) and bromide **4** and (-)-lactic acid **5** (zinc reduction). Because the chemical transforma
the asymmetric carbon atom, this sequence demonstrated that (-)-lactic acid was also a (R)-enantiomer.

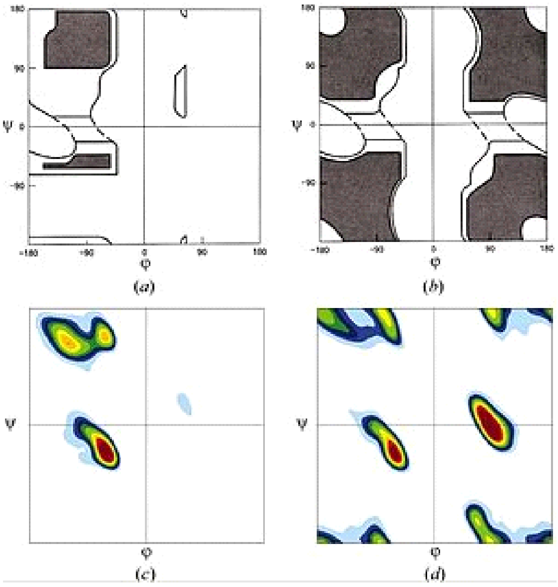


In 1951 Bijvoet for the first time used X-ray crystallography and a new property was discovered by him that he called
dispersion now referred to as resonant scattering .It is used to determine absolute configuration .The compound investi
sodium rubidium tartrate and from its configuration (R,R) it was deduced that the original guess for (+)-glyceraldehyd

5.2.13 -Ramachandran plot

**A Ramachandran plot (also known as a Ramachandran map or a Ramachandran diagram or a [φ,ψ] plot), deve
Gopalasamudram Narayana Ramachandran and Viswanathan Sasisekharan is a way to visualize dihedral angl
amino acid residues in protein structure. It shows the possible conformations of ψ and φ angles for a polypeptid**

Also known as a **Ramachandran map** or a **Ramachandran diagram** or a **[φ,ψ] plot**).A peptidic bond has two degr
dihedral angles named φ and ψ by Ramachandran.



The classical version of the Ramachandran plot for (a) alanine and (b) glycine

According to Ramachandran & Sasisekharan (1968). The fully allowed regions are shaded; the partially allowed region solid line. The connecting regions enclosed by the dashed lines are permissible with slight flexibility of bond angles. T arrived at by stereo-chemical modelling. Although some overall features of these plots are correct, the details differ fro experimentally observed Ramachandran plots for (c) all 19 non-glycines and (d) glycine.

The most remarkable differences are that most regions show a 45 degree slope rather than being parallel to any of the a region is split into two distinct maxima and the two most populated regions (red) for glycine seen in (d) were predicted permissible as shown in (b). There are five areas in the glycine plot; two with psi 0 and three with psi 180.

CHECK YOUR PROGRESS : 1

Notes : i) Write your answer in the space given below.
ii) Compare your answer with those given at the end of the unit

Q1.- X-rays are ----------with typical photon   in the range of--------- .
Q2.What are Bragg peaks?
Q3.Differentiate between elastic and inelastic scattering?
Q4.Write a note on phase problem?
Q5. What is Ramchandran plot

5.2.14 -Let sum up:

By the end of neutron diffraction you will be able to:

- Gain an appreciation of crystallography as a technique;
- Recognize the differences between small molecules and protein crystallography ;
- Distinguish between spectroscopy and diffraction;
- Understand the concept of the unit cell, and of the asymmetric unit in a crystal lattice.
- X-ray crystallography as a technique has certainly not caused the premature death of chemical research; instead it has greatly influenced and contributed to our knowledge and understanding of the

world around us, and will doubtless continue to do so.

- It helps to know that crystal of table salt consists of sodium and chloride ions arranged in a cubic close-packed structure or how is it known that graphite and diamonds are both simply carbon atoms arranged differently
- How Watson, Crick, and Wilkins determined that the basic building block of life, DNA (deoxyribonucleic acid), consists of a double helix structure. The answers to these questions lie in X-ray crystallography, an analytical technique that uses X-rays to identify the arrangement of atoms, molecules, or ions within a crystalline solid.

5.3 -Electron Diffraction

Electron diffraction is one of the major electron microscopy techniques.

Electron diffraction is a collective scattering phenomenon with electrons being (nearly elastically) scattered by atoms in a regular array (crystal). This can be understood in analogy to the Huygens principle for the diffraction of light. The incoming plane electron wave interacts with the atoms, and secondary waves are generated which interfere with each other. This occurs either constructively (reinforcement at certain scattering angles generating diffracted beams) or destructively .Electron diffraction represents a valuable tool in crystallography.

Apart from the study of crystals i.e. electron crystallography, electron diffraction is also a useful technique to study the short range order of amorphous solids, and the geometry of gaseous molecules.

Most electron diffraction is performed with high energy electrons whose wavelengths are orders of magnitude smaller than the interplanar spacings in most crystals. For example, for 100 keV electrons 3.7 x 10^{-12} m. Typical lattice parameters for crystals are around 0.3 nm.

Electron diffraction is most frequently used in solid state physics and chemistry to study the crystal structure of solids. Experiments are usually performed in a transmission electron microscope (TEM), or a scanning electron microscope (SEM) as electron backscatter diffraction. In these instruments, electrons are accelerated by an electrostatic potential in order to gain the desired energy and determine their wavelength before they interact with the sample to be studied.

The periodic structure of a crystalline solid acts as a diffraction grating, scattering the electrons in a predictable manner. Working back from the observed diffraction pattern, it may be possible to deduce the structure of the crystal producing the diffraction pattern. However, the technique is limited by the phase problem.

It has been used for phase identification , foil thickness measurement, lattice parameter measurement, disorder and defect identification.

Recent development has significantly improved the quantitative analysis of electron diffraction intensities and has brought new types of highly accurate electron diffraction techniques for structure refinement and structure factor measurement .

The recent development in the new generation of field of emission electron microscopes and energy filter promise further development in single atomic column scattering and include diffraction from nanometer sized molecules ,clusters ,wires and other two dimensional objects.

5.3.1 Objectives of Electron Diffraction studies:

- determination of the lateral arrangement of the atoms in the topmost layers of the surface, including the structure of adsorbed layers.
- To deduce the periodicity of the atomic arrangement parallel to the surface.

- Apart from the study of crystals i.e. electron crystallography, study the short range order of amorphous solids, and the geometry of gaseous molecules can be understood.
- Solid state physics and chemistry to study the crystal structure of solids. to deduce the structure of the crystal producing the diffraction pattern.
- To study phase identification , foil thickness measurement, lattice parameter measurement ,disorder and defect identification, structure refinement and structure factor measurement .

5.3.2 -INSTRUMENTATION:

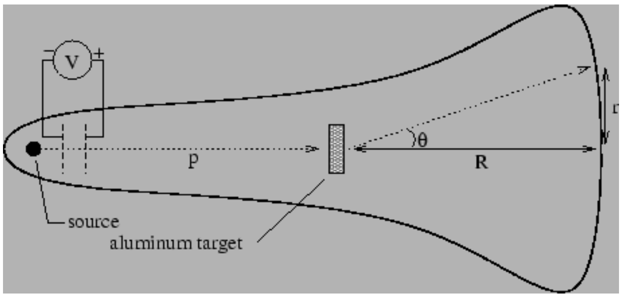


Figure : Schematic of electron diffraction experiment

The experiment takes place in a cathode ray tube. tube is filled with vacuum and has on one end a source of electrons a end an observation screen coated with a chemical which gives a little flash of light at the location where each electron l the source emits electrons at such a high rate that we do not perceive the individual flashes; we just see a glow with bri proportional to the rate or, equivalently, *probability* at which electrons arrive at each point.

After emerging from the source, the electrons pass through a parallel plate capacitor, made from two metal screens rath so that the electrons can pass through. A knob controls the voltage V across the capacitor so that the electrons can be a different speeds, ultimately picking up a kinetic energy equal to the electron charge e times the voltage V,

$$KE = \frac{1}{2}mv^2 = eV.$$

Some additional equipment focuses the accelerated electrons into a narrow beam which impinges on a target of alumin Finally, after interacting with the aluminum metal, the electrons travel off to the observation screen at a distance $R =$ target.

Aluminum metal is generally *polycrystalline*, consisting of many tiny *crystallites* of aluminum stuck together at all diff angles, where each little crystal is a nearly perfect periodic array of atoms of aluminum. Fig illustrates a tiny portion of showing five crystallites stuck together. Aluminum forms a so-called face centered cubic (fcc) crystal in which the aton tightly into planes of spacing $d = 2.34$ Å.

Upon sending the electrons through this series of slits, we observed something truly remarkable . The probability of fin arranges itself into thin circles of narrowly defined radii. The geometry of the experiment , means that the narrowly def of these circles implies that electrons emerging from each crystallite come out at certain specific highly preferred angle arrangement into circles coming from the fact that the crystallites occur at all possible angles. The radii which we see, very narrowly defined, also always seem to occur in multiples: if there is a circle of radius r, we also find circles of ra

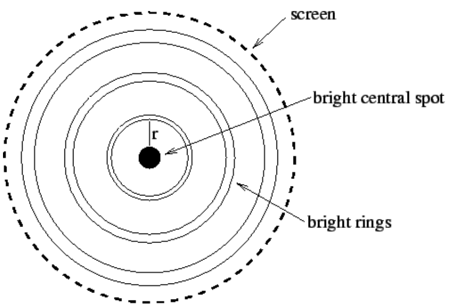


Fig: Image on surface of cathode ray tube

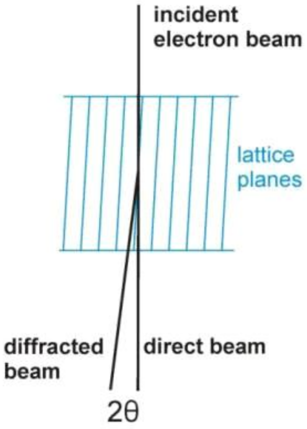
The radii of the different sets of rings correspond precisely to the spacings of the various planes of atoms .

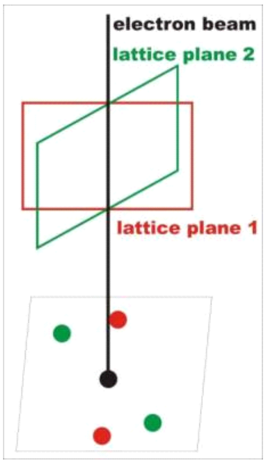
5.3.3 - Scattering angles

λ_{el} = 0.00197 nm (1.97 pm) for 300 kV electrons. A typical value for the interplanar distance is d = 0.2 nm. If these values are put in the Bragg law, then the scattering angle is: = 0.28°.

As a rule, the scattering angles in ED are rather small : $0 < \theta < 2$.

From this follows that
(i) the reflecting lattice planes are almost parallel to the direct beam (left figure),
(ii) the incident electron beam is the zone axis of the reflecting sets of lattice planes (right figure).





5.3.4 - Scattering Intensity & theory of Electron diffraction

Unlike other types of radiation used in diffraction studies of materials, such as X-rays and neutrons, electrons are charg interact with matter through the Coulomb forces. This means that the incident electrons feel the influence of both the p atomic nuclei and the surrounding electrons. In comparison, X-rays interact with the spatial distribution of the valence neutrons are scattered by the atomic nuclei through the strong nuclear forces. In addition, the magnetic moment of neut and they are therefore also scattered by magnetic fields. Because of these different forms of interaction, the three types suitable for different studies.

Intensity of diffracted beams

In the kinematical approximation for electron diffraction, the intensity of a diffracted beam is given by:

$$I_{\mathbf{g}} = |\psi_{\mathbf{g}}|^2 \propto |F_{\mathbf{g}}|^2$$

Here $\psi_{\mathbf{g}}$ is the wavefunction of the diffracted beam and $F_{\mathbf{g}}$ is the so called structure factor which is given by:

$$F_{\mathbf{g}} = \sum_i f_i e^{-2\pi i \mathbf{g}\cdot\mathbf{r}_i}$$

where $\mathbf{g}$ is the scattering vector of the diffracted beam, $\mathbf{r}_i$ is the position of an atom i in the unit cell, and f_i is the scatte atom, also called the atomic form factor. The sum is over all atoms in the unit cell.

The structure factor describes the way in which an incident beam of electrons is scattered by the atoms of a crystal unit account the different scattering power of the elements through the term f_i. Since the atoms are spatially distributed in th will be a difference in phase when considering the scattered amplitude from two atoms. This phase shift is taken into ac exponential term in the equation.

The atomic form factor, or scattering power, of an element depends on the type of radiation considered. Because electro matter though different processes than for example X-rays, the atomic form factors for the two cases are not the same.

Wavelength of electrons

The wavelength of an electron is given by the de Broglie equation

$$\lambda = \frac{h}{p}$$

Here h is Planck's constant and p the relativistic momentum of the electron. λ is called the de Broglie wavelength. The accelerated in an electric potential U to the desired velocity:

$$v = \sqrt{\frac{2eU}{m_0}}$$

m_0 is the mass of the electron, and e is the elementary charge.The electron wavelength is then given by:

$$\lambda = \frac{h}{p} = \frac{h}{m_0 v} = \frac{h}{\sqrt{2m_0 eU}}$$

However, in an electron microscope, the accelerating potential is usually several thousand volts causing the electron to appreciable fraction of the speed of light. An SEM may typically operate at an accelerating potential of 10,000 volts (1 electron velocity approximately 20% of the speed of light, while a typical TEM can operate at 200 kV raising the electr the speed of light. We therefore need to take relativistic effects into account. It can be shown that the electron waveleng according to:

$$\lambda = \frac{h}{\sqrt{2m_0 eU}} \frac{1}{\sqrt{1 + \frac{eU}{2m_0 c^2}}}$$

c is the speed of light. We recognize the first term in this final expression as the non-relativistic expression derived abo term is a relativistic correction factor. The wavelength of the electrons in a 10 kV SEM is then 12.3 x 10^{-12} m (12.3 pm TEM the wavelength is 2.5 pm. In comparison the wavelength of X-rays usually used in X-ray diffraction is in the orde kα: λ=154 pm).

According to energy $E = eV$ (where e is electron charge and V is potential difference), two major techniques of structur electron beams are distinguished:

low-energy electron diffraction (LEED) [$E \simeq$ 5–500 eV] and

high-energy electron diffraction (HEED) [$E \simeq$ 5–500 keV].

In addition, electrons generated in condensed matter by incident electrons or x-ray photons are diffracted. Unlike neutr electrons penetrate matter only for a very short distance before they lose energy (by inelastic scattering) or are scattere (diffracted).

5.3.5 -WIERL EQUATION (relation between Scattering intensity and Scattering angle)

There are two types of collisions which takes place between a beam of electron and a jet of gas molecules**.** These are:

- Elastic Collision – Which produce coherent scattering .
- Inelastic Collisions- Which produce incoherent scattering

In other words , scattering of electrons may be divided into two types viz coherent & inherent. The coherent scattering made up of different components .

- Atomic coherent scattering
- Molecular coherent scattering

It should be noted that incoherent scattering plus the atomic component of the coherent scattering are responsible for th background while molecular coherent scattering gives rise to concentric rings. The molecular coherent scattering deper structure of the molecule.

The coherent or elastic scattering is represented by an equation devised by Mark and Wierl similar to that applicable to intensity of molecular coherent scattering given by Wierl equation .The Wierl equation expresses the diffracted intensi separation of nuclei (Rij), the scattering angle and the electronic scattering factors f.

Wierl equation : $I(\theta) = \sum fi.\ fj\ (\sin sRij) / sRij$

with $s = 4\pi/\lambda \sin 1/2\ \theta$.

Where λ is the wavelength of electron beam and θ is the angle between incident and scattering beams.

The $\sum$ has been carried out over all pairs of atoms in the molecule ,irresponsible of whether or not the atoms are linke .

5.3.6 -MEASUREMENT TECHNIQUE

Electrons are boiled off from the hot filament made up of tungsten and accelerated through potential difference of 40,0 produces a wavelength of about 0.06 angstrom) which is then allowed to pass through the stream of gaseous sample a fluorescent screen.

The sample being gaseous , presents all possible orientations of the scattering atom –atom separations to the diffraction pattern is the superimposition of the scattering due to entire range of orientation. This appears in the diffract series of concentric undulations on a decreasing background. The undulation can be ascribed to the sharply defined sca nuclear positions and the background ascribed to contributions from the continuous distribution of electron density in way of eliminating the unwanted background is to insert a rotating heart shaped disc in front of the screen, this exposes more than the inner and helps to emphasize the undulations

5.3.7 - ELUCIDATION OF STRUCTURE OF SIMPLE GAS PHASE MOLECULES

Electron diffraction in gases and liquids is similar in principle to that in solids; the differences arise from the lack in ga any highly regular arrangement of the component atoms. In gases the low density makes it possible to study diffraction atoms and molecules. The results obtained from monatomic gases represent the density of electronic charge in the atom the distance from the nucleus. The results from gaseous polyatomic molecules represent the equilibrium distances betw nuclei and the average amplitudes of vibration associated with these distances.

The gaseous sample presents all possible orientations of atom-atom separations to the electron beam and the resulting like an X-ray powder photograph. The intensity of the diffracted beam decreases steadily with increasing scattering a pattern consists of a series of concentric undulations on a background . The undulations are due to the sharply defi nuclear positions, and the background is due to scattering from the less.

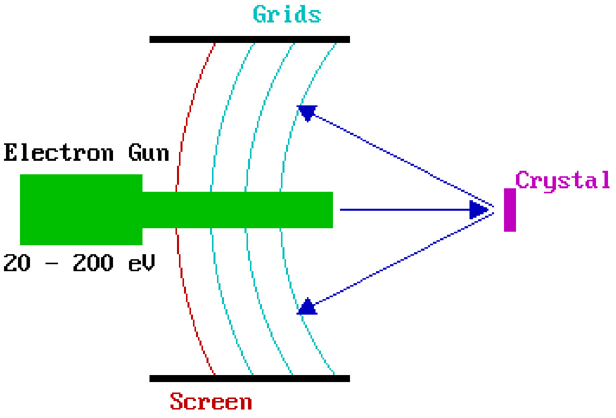
5.3.8 - LOW ENERGY ELECTRON DIFFRACTION (LEED)

LEED is the principal technique for the determination of surface structures. It may be used in one of two ways:

- Qualitatively : where the diffraction pattern is recorded and analysis of the **spot positions** yields information o symmetry and rotational alignment of the adsorbate unit cell with respect to the substrate unit cell.
- Quantitatively : where the **intensities** of the various diffracted beams are recorded as a function of the incident energy to generate so-called I-V curves which, by comparison with theoretical curves, may provide accurate in atomic positions.

Experimental Details

The LEED experiment uses a beam of electrons of a well-defined low energy (typically in the range 20 - 200 eV) incid sample. The sample itself must be a single crystal with a well-ordered surface structure in order to generate a back-scat diffraction pattern. A typical experimental set-up is shown below.



Only the elastically-scattered electrons contribute to the diffraction pattern ; the lower energy (secondary) electrons are energy-filtering grids placed in front of the fluorescent screen that is employed to display the pattern.

Basic Theory of LEED

By the principles of wave-particle duality, the beam of electrons may be equally regarded as a succession of electron w normally on the sample. These waves will be scattered by regions of high localised electron density, i.e. the surface ato therefore be considered to act as point scatterers.

The wavelength of the electrons is given be the de Broglie relation :

Wavelength, $\lambda = \boldsymbol{h} / \boldsymbol{p}$ (where p - electron momentum)

Now ,

$p = m.\mathrm{v} = (2mE_k)^{1/2} = (2m.e.V)^{1/2}$

Where
m - mass of electron [kg]
v - velocity [m s^{-1}]
E_k - kinetic energy
e - electronic charge
V - acceleration voltage (= energy in eV)

⇒ Wavelength, $\boldsymbol{\lambda = h / (2m.e.V)^{1/2}}$

5.3.9 -DETERMINATION OF STRUCTURE OF SURFACE

LEED is used mainly for the study of the structure of single-crystal surfaces and of processes on such surfaces that are changes in the lateral periodicity of the surface.

A monochromatic, nearly parallel electron beam, of 10^{-4} to 10^{-3} m (4 × 10^{-3} to 4 × 10^{-2} in.) in diameter, strikes the sur normal incidence. The elastically backscattered electrons are separated from all other electrons by a retarding field and suitable movable collector or, more frequently on a hemispherical fluorescent screen with the crystal in its center. The diffraction spots can be measured as a function of the energy of the incident electrons .

The most important contribution of LEED is to the understanding of chemisorption, which precedes corrosion . not onl many adsorption systems, mainly of gases on metals, or metals on other metals and semiconductors, has been studied, of the adsorption and desorption process as well as changes in the adsorption layer upon heating. The combination of L electron spectroscopy (AES) and with work-function measurements has proven particularly powerful in these studies, methods give the coverage and information on the location of the adsorbed atoms normal to the surface. Combining LE other complementary techniques such as ion scattering spectroscopy, electron energy loss spectroscopy, or photoelectr become increasingly popular and can enable the elimination of ambiguities in the interpretation of many LEED results.

The use of LEED ensures that the principle feature of the diffraction pattern related to the surface characteristics of the to its bulk.

The diffraction pattern is sharp if the surface is well ordered for distances long enough to be compared with the wavel incident electron, in practice this means that sharp patterns are obtained for surface ordered for about 20 nm .Diffused s either a poorly ordered surface structure or the presence of strong coulomb potential. as results ,electron interact very s very sensitive to matters valence electron or bonding electrons

HIGH ENERGY ELECTRON DIFFRACTION

HEED is used mainly for the study of the structure of thin foils, films, and small particles (thickness or diameter of 10 10^{-8} to 4 × 10^{-5} in.), of molecules, and also of the surfaces of crystalline materials. A monochromatic, usually nearly pa beam with a diameter of 10^{-3} to 10^{-8} m (4 × 10^{-2} to 4 × 10^{-7} in.) is incident on the target. The forward-scattered electro (backscattering is negligible) are detected by means of a fluorescent screen, a photoplate, or some other current-sensiti without the inelastically scattered electrons being eliminated.

Similar to LEED, reflection HEED (RHEED) can be used for the determination of the lateral arrangement of the atoms the topmost layers of the surface, including the structure of adsorbed layers. Although it is more convenient to deduce t the atomic arrangement parallel to the surface from LEED patterns than from RHEED patterns, LEED frequently beco inapplicable when the surface is rough. This usually occurs in the later stages of corrosion or in precipitation. In such i RHEED is far superior to LEED because the fast electrons can penetrate the asperities and produce a transmission HE pattern. RHEED has become particularly important for thin-film growth monitoring via the specular beam intensity os monolayer-by-monolayer growth.

5.3.10 - APPLICATIONS OF ELECTRON DIFFRACTION-

1.The diffraction pattern clearly distinguishes between cis and trans form

2.The configuration of triazo group and diazo group in aliphatic compound have also been studied.

3.In carbon di oxide molecule C-O bond length is observed is found to be 1.13 angstrom which is intermediate betwee
triple bond.

4. In benzene C-C bond length is found to be 1.39 angstrom which is intermediate between C-C double bond and singl

5.3.11 - Let US sum up:

In electron diffraction spectroscopy, atomic and molecular energy levels are studied by accurate measurement of the fl
relativistic energy-monochromated electrons scattered in angle with analysed energy loss. The measurements are expre
Bethe and Born approximations in terms of generalized oscillator strengths, which can be calculated from known wave
which serve as a sensitive test of the quality of wave-functions. Total as well as differential cross-sections are useful in
Energy loss spectra can also be measured at the threshold of excitation.

Low impact energy (1–20 eV) spectra show up the existence of resonances, or compound states of electron and atom o
appearing as structure in the cross-section functions. Spectroscopic constants and assignments of these resonances can
differential cross-sections for excitation of available channels.

CHECK YOUR PROGRESS -2

Notes : i) Write your answer in the space given below.
ii) Compare your answer with those given at the end of the unit

Q.1 What do you mean by electron diffraction?
Q.2 Give full form of the following:
a) TEM b) SEM
Q.3 What is the formula for the intensity of diffracted beam?
Q.4 Give the formula for Wierl equation?
Q.5 What do you mean by LEED?

5.4 - NEUTRON DIFFRACTION

Introduction

Neutron diffraction or elastic neutron scattering is the application of neutron scattering to the determination of the a
magnetic structure of a material: A sample to be examined is placed in a beam of thermal or cold neutrons to obtain a d
that provides information of the structure of the material. The technique is similar to X-ray diffraction but due to the di
properties of neutrons versus x-rays complementary information can be obtained.

History

The first neutron diffraction experiments were carried out in 1945 by Ernest O. Wollan using the Graphite Reactor at C
Ridge & Clifford Shull, together established the basic principles of the technique, and applied it successfully to many
addressing problems like the structure of ice and the microscopic arrangements of magnetic moments in materials.

5.4.1 Objectives of Neutron Diffraction

- Establishment the structure of low atomic number materials like protein a d surfactants much more easily with
- Determination of the atomic and / or magnetic structure of a material.
- Determination of the static structure factor of gases ,liquid or amorphous solids.
- Employed to give insight into the 3D structure of novel molecules such as nanoparticles ,

  nanorods ,nanotubes and fullerenes.
- Investigation of antiferromagnetic and ferromagnetic substance .

5.4.2 Principle

Neutrons are particles found in the atomic nucleus of almost all atoms, but they are bound. The technique requires free
normally do not occur in nature, because they have limited life-time. In a nuclear reactor, however, neutrons can be set
nuclear decay particularly when fission occurs. All quantum particles can exhibit wave phenomena typically associate
sound. Diffraction is one of these phenomena; it occurs when waves encounter obstacles whose size is comparable wit
the wavelength of a quantum particle is short enough, atoms or their nuclei can serve as diffraction obstacles. When a b
emanating from a reactor is slowed down and selected properly by their speed, their wavelength lies near one Ångströn
the typical separation between atoms in a solid material. Such a beam can then be used to perform a diffraction experim
a crystalline sample it will scatter under a limited number of well-defined angles according to the same Bragg's law tha
diffraction.

Neutron diffraction provides similar structural information as electron diffraction. Neutron beams interact more strong
do X-rays and neutron diffraction is more useful than X-ray diffraction for determining proton positions. The two mai
scattering are in refining molecular structures that have been mostly determined by X-ray diffraction and in polymer c
using small-angle neutron scattering (SANS).

The de Broglie wavelength associated with a beam of particles of mass m, speed v & energy E is-

$$\lambda= h/mv = h / (2mE)^{1/2} \qquad \ldots\ldots\ldots(1)$$

As neutrons are scattered from the nucleus of atoms in the crystal the Bragg’s law hold good for neutron scattering or c

$$n\lambda = 2d\sin\theta \qquad \ldots\ldots\ldots(2)$$

where n = order of interference.
d= spacing of lattice planes
θ = Glancing angle for the incident & diffracted beams with reference to lattice planes.

Combining Equation 1 & 2

$$E = \frac{n^2h^2}{8\,md^2\sin^2\theta} \qquad \ldots\ldots\ldots(3)$$

Highly monochromatic beams of neutrons after diffraction from a crystal at various angles can be obtained, if a collim
containing a spread of energies falls on a crystal oriented so that
Equation 3 is satisfied. The energy may be changed simply by changing the angle θ. This method also gives the structu
terms of its lattice spacing & miller indices. This method is most suitable for low atomic mass nuclei with small atomi
which X-ray diffraction becomes insensitive.

5.4.3 Scattering of neutrons by solids & liquids

Neutrons interact with a solid to a much lesser degree than X-rays and therefore have advantages in studying materials
by X-rays and in cases where a large penetration depth is desired. For the three types of diffraction methods, neutrons a
they have a magnetic moment and are therefore sensitive to magnetic ordering in a solid.

Neutrons & Generation of neutrons

According to the wave-particle dualism ($\lambda = h/mv$, de Broglie) neutrons have wave properties

As X-rays neutrons have a wavelength on the order of the atomic scale (Å) and a similar interaction strength with matt
depth from μm to many cm)

Neutrons generate interference patterns and can be used for Bragg diffraction experiments
Same scattering theory for neutrons and X-rays

Generation of neutrons
Neutron must be released from the atomic nuclei, two possibilities:Fission reactor235U nuclei break into lighter eleme
3 neutrons for every fissioned element
Spallation sourceproton bombardment of lead nuclei, releasing spallation neutrons
Properties of neutrons
Fission process: 1 MeV – too high for practical use
Neutrons are slowed down (moderated in water or carbon)hot neutrons:
moderated at 2000°C 0.1-0.5 eV, 0.3-1 Å, 10 000 m/s
thermal neutrons: moderated at 40°C 0.01-0.1 eV, 1-4 Å, 2000 m/s
cold neutrons: moderated at -250°C 0-0.01 eV, 0-30 Å, 200 m/s

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- Wavelength:
- – At 10 meV, λ = 2.86 ***Å***
- – ***Similar length scales as structures of interest***
- ***➔ Interference effects***
- ● Energy:
- – Thermal sources: ~ 5-100 meV
- – Cold sources: ~ 1-10 meV
- – Spallation sources: thermal + epithermal neutrons
- (> 100 meV)
- – Comparable to excitation energies in solids and
    - liquids

Intense beams of monochromatic neutrons can be produced by following methods:

- By reflection from crystals (like calcite or lithium fluoride crystal) according to Bragg’s law. This Technique s energy neutrons whose de – Broglie wavelengths are within the Bragg’s reflecting limit.

- By total reflection from highly polished surfaces, in a manner analogous to X-rays at angles smaller than their used. In this technique low energy neutrons of longer wavelengths are totally reflected. Mirrors of graphite , al ,Beryllium ,Copper, nickel etc. produce intense reflected beams at glancing angles upto 10 mins of arc.

Neutron-matter interaction
Neutron Interactions
● Zero charge
– No interaction with charge densities (electrons)
● Nuclear force
– The interactions that bind neutrons to nuclei also scatter neutrons
● Magnetic dipole moment
– μn = 1.04x10-3 μB
– Neutrons scatter from magnetic moments
● Interactions are weak
– Neutrons penetrate deeply into samples
– Samples can be enclosed during experiments
– Sample size an important consideration

Scattering cross section σ:

Scattering associated with Bragg’s reflections is called coherent scattering. The rate at which neutrons are scattered in directions is determined by a coherent scattering cross section $\boldsymbol{\sigma}_{\mathbf{coh}}$. In an ideal case (perfect crystals of one isotope on dependence of the scattering & no thermal motion.) the scattering is all coherent & the measured total cross section wil amplitude of the peaks depend upon $\boldsymbol{\sigma}_{\mathbf{coh}}$ for the crystal. The amount of scattering between the peaks can be measured quantities can be deduced from the diffraction patterns. Because of chemical bond effect in the crystal , the cross secti scattering of neutrons in the crystal will not be exactly the same as in a free state.

If we consider crystals made of several isotopes of one element , & if we recognize possible spin dependence of the sca allow the crystal temperature to be different than OK, some neutrons are scattered in all directions. There are only a fe in allowed Bragg directions. This is called diffuse scattering.

Area which represents probability that a neutron will interact with a nucleus.σ varies “randomly” from element to elem isotope to isotope.Typical σ ~ 10-24 cm2 for a single nucleus. Total nuclear cross section for several isotopes.

Neutron source sends neutrons to sample.
– Some neutrons scatter from sample.
– Scattered neutrons are detected.

- Number of scattered neutrons as a function of (**Q**,ω).
- Our parameter space is 4-dimensional

Types of Scattering -

- **Coherent Scattering**

Scattering from individual atoms is angle-independent.
Interference effects: – Scattering sites are spatially correlated
– Phase of scattered neutrons are correlated
Coherent scattering -is angle-dependent
– Angular dependence reveals spatial correlations

(1) Elastic Coherent Scattering

- If the time-averaged pair correlation function is periodic (such as for a crystal), then the Fourier transform will form a reciprocal lattice which is also periodic.
- S(**Q**,0) for a perfect crystal consists of delta functions at periodic **Q** positions. Each delta function corresponds to a B
- Bragg's Law: $n\lambda = 2d \sin\theta$

– Constructive interference when distance for two paths is multiple of wavelength
- gives an intuitive picture of S(**Q**,0)

(2) Inelastic Coherent Scattering

Phonons: quantized lattice vibrations

- Motion of atoms ➔ Inelastic scattering
- Correlated motion ➔ Interference effects (coherent scattering)

Phonon properties: - Frequency depends on propagation vector **q**
– ω(**q**) is dispersion relation

- Energy is quantized: E = hω
- Neutron scattering: S(**Q**=**q**,ω(**q**))

Inelastic Magnetic Scattering
Magnetically ordered systems:
– Magnetic moments coupled to neighbors.
– Rotating one spin from equilibrium will exert torque on neighboring moments.

– Spin waves: excitations in magnetic order.
Inelastic neutron scattering can measure spin wave dispersion.

B. Incoherent Scattering

Every particle has perfect instantaneous correlation with itself. Its self correlation function is therefore a delta function in space. Sinc(**Q**) is independent of **Q. This contribution to the scattering at all transfers is the primary source of background in many experiments.**

(1) Elastic Incoherent Scattering

For a perfectly stationary particle, the self-correlation function is constant in time.Sinc(**Q**,ω) for a stationary particle is a delta function in energy ω**. If atoms do not move, all incoherent scattering is elastic (ω = 0).**

(2)Quasielastic Incoherent Scattering

If an atom is moving, then neutrons which scatter from it may gain or lose energy.
Example: random diffusion Quasielastic incoherent scattering (broad in energy but centered at ω=0) can contain useful
Diffusion rates, molecular reorientations, relaxations

(3)Inelastic Incoherent Scattering

Local excitations (no spatial correlations):
– Q-independent scattering
– Periodic correlations in time
– Examples: crystal field levels, molecular vibration
Inelastic incoherent scattering:
– scattered neutrons can gain or lose energy ω0

Coherent vs. Incoherent
● Coherent cross section represents average scattering from that element.
● Incoherent cross section represents standard deviation in scattering.
● Deviations come from different isotopes of same element as well as nuclear spin state variations of single isotopes.For most elements, scattering is primarily coherent.
● Hydrogen is a very significant exception.
● Isotope selection can change cross section significantly.
Individual atomic scattering depend on Coherent Incoherent
isotope and nuclear spin state.

Interactions of Neutrons with Matter

- Neutrons are electrically neutral, they penetrate matter more deeply than electrically charged particles of comp energy; therefore they are valuable probes of bulk properties.
- Neutrons interact with atomic nuclei and magnetic fields from unpaired electrons. The neutrons cause pronoun and energy transfer effects in scattering experiments. Unlike an x-ray photon with a similar wavelength, which electron cloud surrounding the nucleus, neutrons interact with the nucleus itself. The interaction is described b pseudopotential. Neutron scattering and absorption cross sections vary from isotope to isotope.
- Depending on isotope, the scattering can be incoherent or coherent. Among all isotopes, hydrogen has the high scattering cross section. Also, important elements like carbon and oxygen are well visible in neutron scattering contrast to X-ray scattering where cross sections systematically increase with atomic number. Thus neutrons c analyse materials with low atomic numbers like proteins and surfactants. This can be done at synchrotron sour intensities are needed which may cause the structures to change. Moreover, the nucleus provides a very short r potential varying randomly from isotope to isotope, making it possible to tune the nuclear scattering contrast t experiment.
- The scattering almost always has an elastic and an inelastic component. The fraction of elastic scattering is giv Waller factor or the Mössbauer-Lamb factor. Depending on the research question, most measurements concent elastic or the inelastic scattering.

Basic Scattering Theory

Neutrons can be produced in a range of wavelengths from tenths to tens of angstroms and hence are useful for probing magnitude of dimensions relevant in biological structures: from ~1 to 103 A. Neutrons are neutral particles and interact the atomic nuclei in a sample. Their scattering properties depend upon the complex neutron-nucleus interaction; as a co isotopes of the same element can have very different neutron scattering properties. In addition to the coherent compone and hence yield structural information the scattering of neutrons by atoms can have a significant incoherent component component is only significant for nonzero spin nuclei , and in elastic scattering experiments it gives rise to isotropic sca contributes to the background. The incoherent scattering is very large for the hydrogen atom, and consequently for man biology applications of elastic neutron scattering it is optimal to minimize the amount of hydrogen in a sample by isoto with deuterium. Alternatively, investigators have used the incoherent, inelastic scattering from neutrons to probe the dy biomolecules .

Nuclear scattering

Neutrons interact with matter differently than x-rays. X-rays interact primarily with the electron cloud surrounding eac contribution to the diffracted x-ray intensity is therefore larger for atoms with a large atomic number (Z) than it is for a Z. On the other hand, neutrons interact directly with the *nucleus* of the atom, and the contribution to the diffracted inte each isotope; for example, regular hydrogen and deuterium contribute differently. It is also often the case that light (lo contribute strongly to the diffracted intensity even in the presence of large Z atoms. The scattering length varies from is rather than linearly with the atomic number. An element like vanadium is a strong scatterer of X-rays, but its nuclei ha neutrons, which is why it often used as a container material. Non-magnetic neutron diffraction is directly sensitive to th nuclei of the atoms.

A major difference with X-rays is that the scattering is mostly due to the tiny nuclei of the atoms. That means that there atomic form factor to describe the shape of the electron cloud of the atom and the scattering power of an atom does not scattering angle as it does for X-rays. Diffractograms therefore can show strong well defined diffraction peaks even at particularly if the experiment is done at low temperatures. Many neutron sources are equipped with liquid helium cooli allow to collect data at temperatures down to 4.2 K. The superb high angle (i.e. high *resolution*) information means tha very precise values for the atomic positions in the structure. On the other hand, Fourier maps (and to a lesser extent dif maps) derived from neutron data suffer from series termination errors, sometimes so much that the results are meaning

5.4.4 Magnetic scattering

Although neutrons are uncharged, they carry a spin, and therefore interact with magnetic moments, including those aris electron cloud around an atom. Neutron diffraction can therefore reveal the microscopic magnetic structure of a materi

Magnetic scattering does require an atomic form factor as it is caused by the much larger electron cloud around the tin intensity of the magnetic contribution to the diffraction peaks will therefore dwindle towards higher angles.

5.4.5 - Measurement Technique

Instrumental requirements

A neutron diffraction measurement requires a neutron source (e.g. a nuclear reactor or spallation source), a sample (the studied), and a detector. Samples sizes are large compared to those used in X-ray diffraction. The technique is therefor as powder diffraction. At a research reactor other components such as crystal monochromators or filters may be neede desired neutron wavelength. Some parts of the setup may also be movable. At a spallation source the time of flight tech sort the energies of the incident neutrons (Higher energy neutrons are faster), so no monochromator is needed, but rath aperture elements synchronized to filter neutron pulses with the desired wavelength.

Instrumentation

The Debye – Scherrer Hull X- ray technique for powdered samples can be used for neutron diffraction.

Source - Neutrons are produced by fission reactions in a nuclear reactor or by irradiating a metal target with high-energ accelerator, which is called spallation. Reactor sources produce a continuous spectrum of neutron energies and require crystal to select a particular energy. Accelerator sources are usually operated in a pulsed mode and neutron wavelength time-of-flight methods, that is, data is taken at a fixed Bragg angle as a function of neutron energy. Multiple detectors a at different angles in parallel to speed data acquisition.

Crystal- The neutron beam from the atomic pile falls on a crystal which is oriented to yield a diffracted beam of certain

Sample – The monoenergetic beam falls on the sample

Counter – A BF_3 counter always pointing towards the sample, is rotated slowly about it.The counter readings , correcte as a function of angle of rotation are the diffraction patterns.

Photographic plate – the scattered beam of neutrons by a crystal is allowed to fall on a photographic film. Since neutro photographic film, the film is coated with a thin film of indium, which is capable of capturing the neutrons. The unstab produced , emit β-particles which register dark spots on the film.This pattern is called Laue pattern.

The Laue photographs have also been obtained with thermal neutrons from nuclear reactor beam at Oak Ridge (1948). experiments , thermal neutrons from a reactor are collimated by cadmium slits & then diffracted by a large size calcite crystal.The neutron intensities are recorded by BF_3 counter.

The peaks occur at angles for which Bragg's condition holds good for various places.The diffraction of neutrons is due scattering by atomic nuclei in the crystal.

For a crystalline sample – Bragg's equation $n\lambda = 2d\sin\theta$ will be satisfied for just a few directions. Here there will be a r scattering. In other directions there will be destructive interference & no scattering. Scattering associated with these Br called coherent scattering. The rate at which neutrons

5.4.6 - Applications

1. Neutron Diffraction is used to determine the crystal structure of ice & the location of hydrogen atoms. It shows that t are not located midway between oxygen atoms.

2.It leads to the refractive index of various materials for a neutron beam. Regular reflection of neutrons from various cr that (μ -1) is of the order of 10^{-6} & that it is negative in sign (i;e $\mu < 1$) for majority of elements (condition of total refle (ie $\mu > 1$) for some elements like manganese.

3.X-ray intensities depend upon scattering from the elements shell, while neutron diffraction studies depend largely up nuclei. This indicates that neutron diffraction can supplement X-ray diffraction where the sample contains elements wh close together in atomic number or very far apart. If they are very close as in KCl, the X-ray scattering will nearly be t In case they are far apart, as in PbO or anything containing hydrogen the strong X-ray scattering of the heavier element lighter one.

4. The relative scattering power of the scattering centers making up the crystal is of great importance in studying the c Neutrons, having no charge can be scattered only by the atomic nuclei, because of the fact that they are not affected by electrons of atoms. Nuclear scattering cross section measurements have shown that there is a significant difference bet ray scattering.

The X-ray scattering cross sections vary regularly with increasing electron content of heavier atoms, but there i for the neutron scattering cross section .Example- In the study of the ice crystal the effects with X-ray are almost entire oxygen atoms in the crystal. Therefore, X-ray scattering cross section of hydrogen is extremely small compared with t a consequence the scattering effects due to hydrogen are not detectable.But with neutrons , if the **deuterated form, hea** scattering cross section of the deuterium atoms & the oxygen atoms are very close & a direct measure of the positional these atoms in the crystal.

5. For crystals containing two or more elements (each having only one isotope) the relative intensities of the Bragg ref generally influenced by the relative signs of the scattering amplitudes. The X-ray diffraction peaks that have odd Mille (111),(113) etc are weak (eg in NaCl type of structure) and strong in those with even Miller indices (200), (220) etc**.**

Neutron diffraction yield structural information on biological molecules and their complexes at multiple levels of re diffraction and scattering methods generally complement X-ray methods and other structural techniques, frequently off of information that enable one to put together the final jigsaw puzzle picture of how a biological molecule or complex v

6.A shift in the muons spin-relaxation rate in MnO is observed around 540 K, i.e. about 4.5 times T_N. This result confi observations using spin-polarized electron diffraction of a significant change in the paramagnetic spin system taking pl temperature. This change might be caused by the transition from a state with correlated magnetic clusters to independe spins. Furthermore, we have confirmed previous findings that at low temperature, the implanted muons are situated at s manganese ions and that, as the temperature is increased, they diffuse and are trapped at manganese vacancies. In addit observed that the muons are detrapped and start to diffuse again at temperatures above 800 K.

5.4.7 -Let sum up :

- Neutron diffraction is a technique which is more similar to x-ray diffraction and applicable particularly to l particulate structure.
- It is an exceptional tool for studying the structure and dynamics of materials at the molecular level.
- Mainly aims at the structure of the crystalline solids makes neutron diffraction an important tool of crystall
- The main practical application of neutron diffraction is that the lattice constant of metals or other crystallin accurately measured.
- One major advantage of neutron diffraction over X-ray diffraction is that the latter is rather insensitive to tl hydrogen in the structure where as the nuclei ^{1}H and ^{2} H are strong scatterer for neutrons.

Check Your Progress:-3

Notes : i) Write your answer in the space given below.

ii) Compare your answer with those given at the end of the unit

Neutrons are----------- particles and interact principally with the atomic------ in a sample .

Neutrons interact with a solid to a much-------- degree than X-rays.

According to the wave-particle dualism ($\lambda = h/mv$, de Broglie) neutrons have -------properties.

Neutrons are produced by --------reactions in a nuclear reactor or by irradiating a metal target with high-energy protons accelerator, which is called---------.

The photographic film is coated with a thin film of--------, which is capable of capturing the neutrons.

Neutron diffraction and scattering methods generally complement-----------.

Neutrons are particles found in the -------of almost all atoms.

The rate at which neutrons are scattered in the allowed directions is determined by a…… .

5.4.8 -Check your progress:

Key 1

Ans 1.(a) Electromagentic radiation (b)10 0 eV - 100 keV.

Ans 2.Crystalline solids, at certain specific wavelengths and incident angles, produced intense peaks of reflected radiat were given the name Bragg peaks.

Ans 3. If the wavelength of scattered X-rays did not change (meaning that x-ray photons did not lose any energy), the **Elastic scattering** while in **inelastic scattering process (Compton Scattering),** x-rays transfer some of their energy

Ans 4. Since the phases are lost during measurement, the electron density cannot be directly calculated. This lack of kn phases is termed the ***phase problem*** in crystallography.

Ans 5. A Ramachandran plot is a way to visualize dihedral angles ψ against φ of amino acid residues in protein structu possible conformations of ψ and φ angles for a polypeptide.

Check Your Progress : Key 2

- (a) neutral (b) atomic nuclei
- Lesser
- Wave
- (a) fission (b) spallation
- Indium
- X-ray methods
- atomic nucleus
- coherent scattering cross section $\boldsymbol{\sigma_{coh}}$

CHECK YOUR PROGRESS : KEY 3

Ans .(1) Electron diffraction is one of the major electron microscopy techniques.Its a collective scattering phenomen being scattered by atoms in a regular array

Ans.(2) Transmission electron microscope b) Scanning electron microscope

Ans.(3) The intensity of diffracted beam is given by-

$$I_{\mathbf{g}} = |\psi_{\mathbf{g}}|^2 \propto |F_{\mathbf{g}}|^2$$

Ans.(4) Wierl equation : $I(\theta) = \sum f_i . f_j (\sin sR_{ij}) / sR_{ij}$

Ans.(5) It is a technique for determining structure surfaces. The full form of LEED is low energy electron diffraction.

5.4.9 References

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