M.Sc. Previous Year
Chemistry, MC-04

GROUP THEORY, SPECTROSCOPY AND DIFFRACTION METHOD

मध्यप्रदेश भोज (मुक्त) विश्वविद्यालय – भोपाल
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SYLLABI-BOOK MAPPING TABLE

Group Theory, Spectroscopy and Diffraction Method

	Syllabi	Mapping in Book
Unit -I	**Symmetry and Group Theory in Chemistry** Symmetry elements and symmetry operation, definition of group, subgroup, relation belween orders of a finite group and its subgroup. Conjugacy relation and classes. Point symmetry group. Schonflies symbols, representations of groups by matrices (representation for the C_n, $C_{nv¢}$ $C_{nh'}$ D_{nh} etc. groups to be worked out explicitly). Character of a representation. The great orthogonality theorem (without proof) and its importance. Character tables and their use; spectroscopy. **Unifying Principles** Electromagnetic radiation, interaction of electromagnetic radiation with matter-absorption, emission, transmission, reflection, refraction, dispersion,polarisation and scattering. Uncertainty relation and natural line width and natural line broadening, transition probability, results of the time dependent perturbation theory, transition moment, selection rules, intensity of spectral lines, Born-Oppenheimer approximation, rotational, vibrational and electronic energy levels.	**Unit-1:** Symmetry and Group Theory in Chemistry **(Pages 3-58)**
Unit -II	**Microwave Spectroscopy** Classification of molecules, rigid rotor model, effect of isotopic substitution on the transition frequencies, intensities, non-rigid rotor. Stark effect, nuclear and electron spin interaction and effect of external field. Applications. **Vibrational Spectroscopy** **A. Infrared Spectroscopy:** Review of linear harmonic oscillator, vibrational energies of diatomic molecules, zero point energy, force constant and bond strengths; anharmonicity, Morse potential energy diagram, vibration-rotation spectroscopy, P,Q,R branches. Breakdown of oppenheimer approximation; vibrations of polyatomic molecules.Selection rules, normal modes of vibration, group frequencies, overtones, hot bands, factors affecting the band positions and intensities, for IR region, metal-ligand vibrations, normal co-ordinate analysis. **B. Raman Spectroscopy:** Classical and quantum theories of Raman effect. Pure rotational, vibrational and vibrational-rotational Raman spectra, selection rules, mutual exclusion principle. Resonance Raman spectroscopy, coherent anti Stokes Raman spectroscopoy (CARS).	**Unit-2:** Vibrational Spectroscopy **(Pages 59-98)**

Unit -III	**Electronic Spectroscopy** **A. Atomic Spectroscopy:** Energies of atomic orbitals, vector representation of momenta and vector coupling, spectra of hydrogen atom and alkali metal atoms. **B. Molecular Spectroscopy:** Energy levels, molecular orbitals, vibronic transitions, vibrational progression and geometry of the excited states, Franck-Condon principle, electronic spectra of polyatomic molecules. Emission spectra; radiative and non-radiative decay, internal conversion, spectra of transition metal complexes, charge-transfer spectra. **C. Photoelectron Spectroscopy:** Basic principles; photo-electric effect, ionization process, Koopman's theorem. Photoelectron spectra of simple molecules, ESCA, chemical information from ESCA. Auger electron spectroscopy basic idea. **Photoacoustic Spectroscopy** Basic principles of photoocoustic spectroscopy (PAS), PAS-gases and condensed systems, chemical and surface applications.	**Unit-3:** Electronic Spectroscopy **(Pages 99-126)**
Unit -IV	**Magnetic Resonance Spectroscopy** A. **Nuclear Magnetic Resonance Spectroscopy:** Nuclear spin, nuclear resonance, saturation, shielding of magnetic nuclei, chemical shift and its measurements, factors influencing chemical shift, deshielding, spin-spin interactions, factors influencing coupling constant 'J', Classification (ABX, AMX, ABC, A_2B_2 etc.) spin decoupling; basic ideas about instrument, NMR studies of nuclei other than proton –^{13}C, ^{19}F and ^{31}P, FT NMR, advantages of FT NMR, use of NMR in medical diagnostics. B. **Electron Spin Resonance Spectroscopy:** Basic principles, zero field splitting and kramer's degeneracy, factors affecting the 'g' value. Isotropic and anisotropic hyperfine coupling constants, spin Hamiltonian, spin densities and McConnel relationship, measurement techniques, applications. C. **Nuclear Quadrupole Resonance Spectroscopy:** Quadrupole nuclei, quadrupole moments, electric field gradient, copuling constant, splittings. Applications.	**Unit-4:** Magnetic Resonance Spectroscopy **(Pages 127-156)**
Unit -V	**X-ray Diffraction** Bragg condition, Miler indices, laue method, Bragg method, Debye-Scherrer method of X-ray structural analysis of crystals, index reflections, identification of unit cells from systematic absences in diffraction pattern. Structure of simple lattices and X-ray intensities, structure factor and its relation to intensity and electron density, phase problem. Description of the procedure for an X-ray structure analysis. absolute configuration of molecules, Ramchandran diagram. **Efectron Diffraction** Scattering intensity vs. scattering angle, Wierl equation, measurement technique, elucidation of structure of simple gas phase molecules. Low energy electron diffraction and structure of surfaces. **Neutron Diffraction** Scattering of neutrons by solids and liquids, magnetic scattering, measurement techniques. Elucidation of structure of magnetically ordered unit cell.	**Unit-5:** Diffractionx **(Pages 157-181)**

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  - 5.3.4 Elucidation of Structure of Simple Gas Phase Molecules
  - 5.3.5 Low Energy Electron Diffraction (LEED)
  - 5.3.6 Structure of Surface

5.4 Neutron Diffraction
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INTRODUCTION

NOTES

Quantum mechanics is a fundamental theory that provides a description of the physical properties of nature at the scale of atoms and subatomic particles. It is the foundation of all quantum physics including quantum chemistry, quantum field theory, quantum technology, and quantum information science. Quantum mechanics typically explains the aspects of nature at small (atomic and subatomic) scales. Principally, the quantum mechanics arose gradually, from theories to explain observations which could not be reconciled with classical physics, such as Max Planck's solution in 1900 to the black-body radiation problem, and the correspondence between energy and frequency in Albert Einstein's 1905 paper which explained the photoelectric effect. Early quantum theory was profoundly re-conceived in the mid-1920s by Niels Bohr, Erwin Schrödinger, Werner Heisenberg, Max Born and others.

Group Theory is one of the most powerful mathematical tools used in Quantum Chemistry and Spectroscopy. It allows the user to predict, interpret, rationalize, and often simplify complex theory and data. It is a set of Operations associated with the Symmetry Elements of a molecule constitute a mathematical set called a Group. This allows the application of the mathematical theorems associated with such groups to the Symmetry Operations.

Spectroscopy, in the electromagnetic spectrum, is a fundamental technique allowing the composition, physical structure and electronic structure of matter to be investigated at the atomic, molecular and macro scale and Diffraction refers to various phenomena that occur when a wave encounters an obstacle or opening. It is defined as the bending of waves around the corners of an obstacle or through an aperture into the region of geometrical shadow of the obstacle/aperture.

This book, *Group Theory, Spectroscopy and Diffraction*, is designed to be a comprehensive and easily accessible book covering the basic concepts of chemistry. It will help readers to understand the basics of elementary quantum mechanics, Plank's radiation law, photoelectric effect, de- Broglie hypothesis, Heisenberg's uncertainty principle, Hamiltonian operator, Schrodinger wave equation, Molecular Orbital (M.O.) theory, electromagnetic radiation, regions of the spectrum, Born- Oppenheimer approximation, rotational spectrum, Maxwell-Boltzmann distribution, the UV spectroscopy, electronic excitation, electronic spectrum, Raman spectrum, concept of polarizability, laws of photochemistry, Stark Law, polarization, nuclear magnetic resonance, electron spin resonance spectroscopy, X-ray diffraction, neutron diffraction, etc.

The book is divided into five units. It has been written in the Self-Instructional Mode (SIM) wherein each unit begins with an Introduction to the topic followed by an outline of the Objectives. The detailed content is then presented in a simple and an organized manner, interspersed with Check Your Progress questions to test the understanding of the students. A Summary along with a list of Key Terms and a set of Self-Assessment Questions and Exercises is also provided at the end of each unit for effective recapitulation.

UNIT 1 SYMMETRY AND GROUP THEORY IN CHEMISTRY

NOTES

Structure

1.0 INTRODUCTION

Group theory is a mathematical method by which aspects of a molecule's 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 understand various groups 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.

NOTES

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 propagation. There are various electromagnetic radiations like radio waves, microwaves, X-rays, UV-rays, cosmic rays etc. Theses when interact with matter give rise to various different phenomena like diffraction, interference, absorption, emission depending on the type of EMR & matter (energy).

1.1 OBJECTIVES

After going through this unit, you will be able to:

- Understand 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.
- Conceptualize 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.
- Able to determine that which vibrational transitions are allowed or forbidden on the basis of symmetry.
- Understand how EMR interact to show different phenomenon like polarization, dispersion, refraction etc.
- Differentiate between transition moment & transition probability.

1.2 SYMMETRY AND GROUP THEORY

Symmetry is very important in chemistry researches and group theory is the tool that is used to determine symmetry. In this section, you will learn about the relationship between symmetry and group theory.

1.2.1 Symmetry Elements and Symmetry Operations

Symmetry operations can be defined as the phenomenon of replicating an object's appearance and structure exactly the same, even when it has been carried out. For example, water molecule has one central oxygen molecule (O) between two hydrogen (H) molecules and if we even rotate this molecule to 180° at the axis passing through the centrally located O molecule, it will even appear exactly the same, as earlier.

Every even activity has a comparing symmetry operation, which is the hub, plane, line or point regarding which the balance activity is completed. The symmetry operation comprises of the multitude of focuses that stay in a similar spot when the symmetry operation is performed. In a turn, the line of focuses that stay in a similar spot establish an evenness pivot; in a reflection, the focuses that stay unaltered make up a plane of symmetry.

1.2.2 Groups and Subgroups

Every particle has a specific set of symmetry operations that portrays the atom's general symmetry. This arrangement of activities characterizes the group of the molecule. A group is a limited or boundless (finite or infinite) arrangement of components along with a double activity (called the group operation) that together fulfils the four key properties of conclusion, associativity, the character property, and the inverse property. The operation regarding which a group is characterized is regularly called the "group operation," and a set is supposed to be said as a group "under" operation. The investigation of gatherings is known as group theory.

Any subset of the component which structures a group is called a subgroup. A subgroup is a subset of group elements of a specific group that fulfils the four group prerequisites. It should thusly contain the identity element, "is a subgroup of" is composed, or now and then. A subset of a group that is shut under the group operations and the inverse activity is known as a subgroup. The components of a subgroup ought to submit to the accompanying conditions-If g is the order of the group and s is the order for the subgroup, then, at that point, g/s is a characteristic natural number. For example, the water molecule has symmetry elements E, C2, δv, δv1.

GROUP: E, C2, δ_v, δ_v^1

SUBGROUPS: E

E, C2

E, δ_v, E, δ_v^1

1.2.3 Relation between Orders of a Finite Group and its Subgroups

The order for a class of a group should be a fundamental variable of the group order and the number of elements is known as the group order of the specific group.

If there are a limited number of components, the group is known as a limited or finite group and the quantity of elements is known as the group order of the group.

- A subset of a group that is shut under the group activity and the inverse activity is known as a subgroup. Subgroups are also the groups, and many ordinarily experienced groups are the subgroups of some bigger groups.
- A limited or finite group is a group having a limited or finite group order. Instances of limited groups are the modulo multiplication groups, point groups, cyclic groups, dihedral groups, symmetric groups, substituting groups, etc.
- The limited (cyclic) group C2 structures the "Limited Simple Group of Order 2".
- An essential illustration of a limited group is the symmetric group Sn, which is the permutation group (or "under permutation") of n objects.

1.2.4 Conjugacy Relation and Classes

A total arrangement of mutual group elements. Every element in a group has a specific place with precisely one class, and the identity element (I=1) is generally in its own class. The conjugacy class order of all classes considered, should be vital elements of the group order of the group. A group of prime orders has a specific class for every specific element.

- In an Abelian bunch, every element is in a conjugacy class independently.
- Two operations are placed in a similar class when one might be supplanted by the other in another direction framework which is open by a symmetry operation. These sets compare straight-forwardly to the arrangements of equivalent operations.
- Two components A and B in a group form a class assuming they are conjugate to each other. Conjugate elements can be represented by the equation:

  $$X - 1AX = B$$

  Where, X is the comparability change component. It is utilized to observe whether a set of elements forms a class or not.
- Conjugacy is an equivalence connection. Additionally, note that conjugate elements have a similar order. The arrangement of all elements conjugate to a, is known as the class of a.

1.2.5 Point Symmetry Groups and Schoenflies Symbols

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.

Point groups are used to describe molecular symmetries and are a condensed representation of the symmetry elements a molecule may possess. This includes both bond and orbital symmetry. Knowing molecular symmetry allows for a greater understanding of the molecular structure and can help to predict many molecular properties.

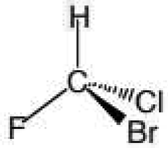
Point Symmetry: The symmetry of a molecule with respect to reflection, inversion, rotation, and improper rotation.

Point Symmetry Group: Collection of symmetry operations that arise because of the existence of symmetry elements in a molecule.

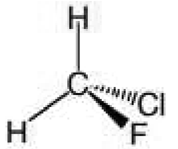
Point Groups and Their Operations

The common point groups and the operations associated with each group are listed below.

1. Point groups with very low symmetry; no rotational axis in the molecule.
   a. **C_1**: If a molecule has only the identity operation, E, and no other operations present, then the molecule belongs to the point group C1. An example is shown on the right.



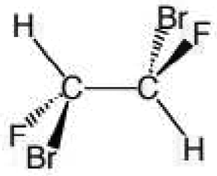
b. C_S: If the only operations in the molecules are a mirror plane and E, then its point group is Cs. Two examples are shown below.

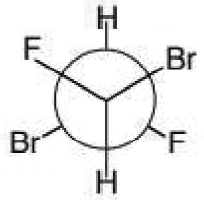


σ contains C,F,Cl

σ bisects H-N-H and contains N-Cl bond

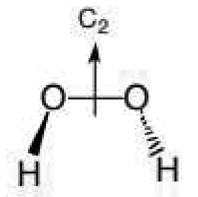
c. C_i: If the molecule only has the inversion operation, i, and E, then point group of the molecule is C_i. One example is 1,2-dibromo-1,2-difluoroethane in the staggered conformation shown below. The Newman projection of the molecule is also shown for clarity. The center of inversion of the molecule is located at the center of the C-C bond.



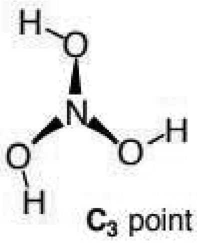


1. **Rotational Point Groups: C_n, C_{nh}, and C_{nv}**

a. C_n. The only operations in the C_n point groups are C_n (and its repetition) and E. The Cn point groups have a total of n operations: C_n, $C_{n\,2}$, $C_{n\,3}$, ... $C_{n\,n}$ = E. Examples of molecules that belong to the C_2 and C_3 point groups are shown below. Please note that there no other operations present in these molecules, such as mirror planes or inversion.



C_2 point group



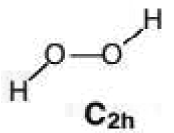
C_3 point group

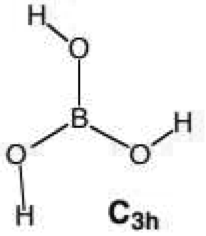
b. C_{nh}. This group has the operations of the C_n group with the addition of a horizontal mirror plane, σ_h, perpendicular to the C_n axis. Operations of the C_{nh} point groups:

- If n = even: C_n and its repetitions, σ_h, i, various S_n
- If n = odd: E, C_n and its repetitions, σ_h, various S_n

NOTES

The C_n axis "vertical", and horizontal mirror planes are always perpendicular to the C_n axis (or the C_n axis of highest order). Planar trans-HOOH is an example of a molecule that belongs to the C_{2h} point group. There is a C_2 axis perpendicular to the plane of the molecule and a mirror plane on the plane of the molecule. Additional operations present are i and E. Similarly, planar $B(OH)_3$ belongs to the C_{3h} point group.

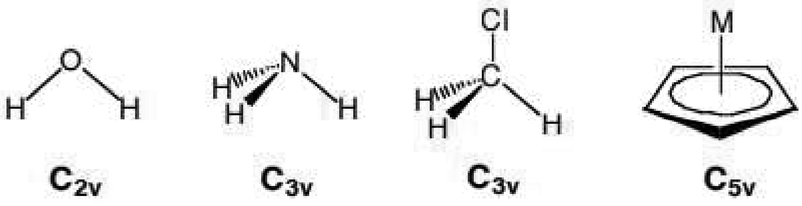




c. **C_{nv}:** This group has the operations of the C_n group with the addition of vertical mirror planes, σ_v (these are mirror planes that contain the C_n axis).

- The mirror plane σ_v is reproduced n times in the C_{nv} point group.
- The operations of the C_{nv} point group are: E, C_n and its repetitions, n σ_v.
- The C_{nv} point groups have a total of 2n operations.

Some examples of molecules that belong to the C_{nv} point groups are shown below.

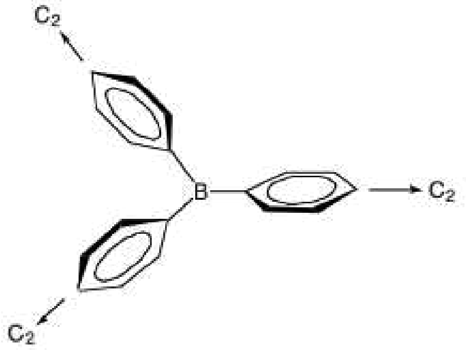


(2) Dihedral point groups: D_n, D_{nh}, D_{nd}

a. **D_n:** formed by the addition of a C_2 axis perpendicular to the C_n axis in the C_n point group These point groups are not very common, since there are no mirror planes or inversion center.

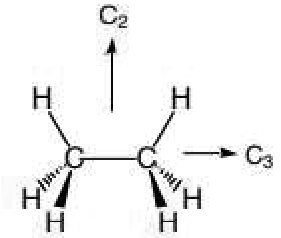
- There are n C_2 axes perpendicular to the C_n axis.
- There are a total of 2 n operations in the D_n point group.

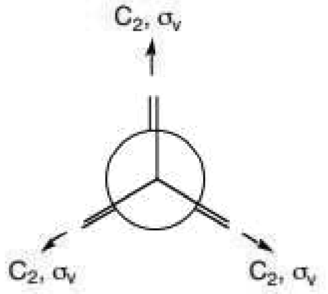
An example of a molecule that belongs to the D_3 point group is shown on the left, with a trigonal planar central B atom and three phenyl rings at 45° from the of the plane of the central atom. A C_3 axis is present from the central B atom, perpendicular to the trigonal plane defined around the central atom. C_2 axes are present perpendicular to the C_3 axis.



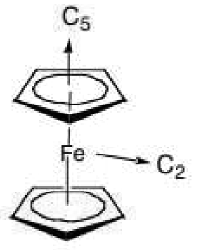
b. **D$_{nh}$:** Formed by the addition of σ_h to the D_n point group (where σ_h ¥” C_n axis). This is a very common point group. The D_{nh} point groups also have n σ_v mirror planes that contain both the C_n and C_2 axes, where an n number of C_2 axes are present in the group).

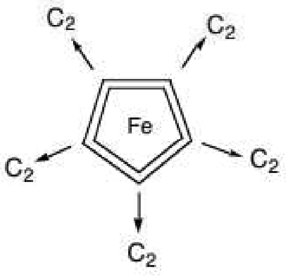
An example of a molecule that belongs to the D_{3h} point group is eclipsed ethane. As shown on the left, eclipsed ethane has a C_3 axis that contains the C-C bond and three C_2 axes perpendicular to C_3 with origin at the center of the molecule. A horizontal mirror plane, σ_h, is present, which contains all three C_2 axes and is perpendicular to the C_3 axis. In addition, vertical mirror planes, $\sigma_{v's}$, which contain both the C_3 axis and each C_2 axis are found.

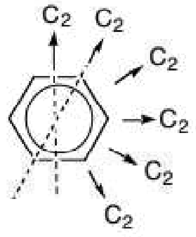




Eclipsed ferrocene, shown below, is similar to eclipsed ethane. Eclipsed ferrocene belongs to the D_{5h} point group. Benzene, with a C_6 axis, 6 C_2 axes perpendicular to C_6, and a σ_h mirror plane, belongs to the D_{6h} point group.



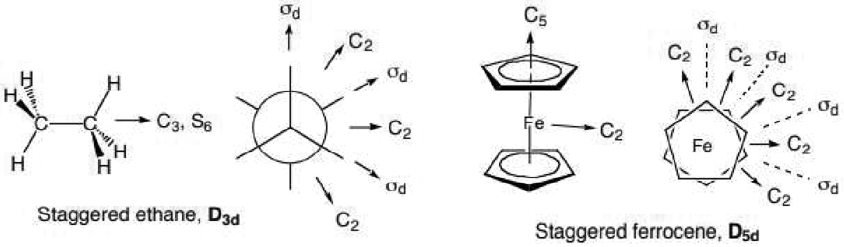




c. **D$_{nd}$:** Formed by the addition of dihedral mirror planes, σ_v, to the D_n point group. There are n σ_v mirror planes that contain the C_n axis and bisect adjacent C_2 axes. This point group is quite common. The most identifiable difference between the D_{nh} and D_{nd} point groups is that D_{nh} has a σ_h mirror plane and D_{nd} does not.

Operations: C_n and its repetitions, n $C_{2's}$, n $\sigma_{d's}$, i (if n is odd), various S_n.

An example of a molecule that belongs to the D_{3d} point group is staggered ethane. As shown below, staggered ethane has a C_3 axis that contains the C-C bond, however, it does not have a horizontal mirror plane perpendicular to the C_3 axis. The molecule has three C_2 axes that are perpendicular to C_3; these axes cross the center of the C-C bond. In addition, three dihedral mirror planes, σ_d, that contain C_3 but bisect adjacent C_2 axes are present. In addition, the molecule has a center of inversion, i, and an S_6 axis overlapping with the C_3 axis. In a manner similar to staggered ethane, staggered ferrocene belongs to the D_{5d} point group. Some of the operations of staggered ferrocene are shown below.



Each point group is associated with a specific combination of symmetry elements

Each point group has its own combination of symmetry elements.

The point group symmetry of a molecule can be described by 5 types of symmetry element:

- **Symmetry Axis:** An axis around which a rotation by 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 axis in water and the C_3 axis 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 aligned with 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 generated. This is also called a mirror plane and abbreviated σ (sigma = Greek "s", from the German 'Spiegel' meaning mirror). 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).

- **Center of Symmetry or Inversion Center:** It is abbreviated as *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. In other words, a molecule has a center of symmetry when the points (x,y,z) and (“x,”y,”z) correspond to identical objects. For example, if there is an oxygen atom in some point (x,y,z), then there is an oxygen atom in the point (“x,”y,”z). There may or may not be an atom at the inversion center itself. Examples are xenon tetrafluoride where the inversion center 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 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 as S_n. Examples are present in tetrahedral silicon tetra-fluoride, with three S_4 axes, and the staggered conformation of ethane with one S_6 axis. An S_1 axis corresponds to a mirror plane σ and an S_2 axis is an inversion center *i*. A molecule which has no S_n axis for any value of n is a chiral molecule.
- **Identity**: Abbreviated to *E*, from the German ‘Einheit’ meaning unity. This symmetry element simply consists of no change: every molecule has this element. While this element seems physically trivial, it must be included in the list of symmetry elements so that they form a mathematical group, whose definition requires inclusion of the identity element. It is so called because it is analogous to multiplying by one (unity). In other words, *E* is a property that any object needs to have regardless of its symmetry properties.

A point group contains all of the symmetry operations that can be performed on a given molecule, it is not necessary to identify all of these operations to determine the molecule’s overall point group. Instead, a molecule’s point group can be determined by following a set of steps which analyze the presence (or absence) of particular symmetry elements.

Point groups are a method of classifying the shapes of molecules according to their symmetry elements.

Before we can talk about point groups, we need to describe the basic elements of symmetry. These are the proper axis of symmetry (or just axis of symmetry), improper axis of symmetry, plane of symmetry, and inversion center (or point of symmetry).

- The proper axis of symmetry is an imaginary line through a compound. Rotation of the compound by an integral fraction of a circle around this axis (1/2, 1/3, etc.) brings the compound to superposition on itself. An axis of symmetry is represented by C_n, where *n* is the integral fraction. All shapes have at least a C_1 axis (the identity axis).
- The improper axis of symmetry is also an imaginary line through a compound. Rotation of the compound by an integral fraction of a circle around this axis (1/2, 1/4, etc.) followed by reflection through a plane perpendicular to this axis brings the compound to superposition on itself. An improper axis of

symmetry is represented by S_n, where n is the integral fraction (n must be even or 1).

- The plane of symmetry is a plane through a compound that relates its identical halves. A plane of symmetry is represented by σ and is the same as an S_1 axis.
- The inversion center (or point of symmetry) is an imaginary point in a compound. Reflection of the compound through this point brings the compound to superposition on itself. An inversion center is represented by i and is the same as an S_2 axis.

We can determine the symmetry operations of the point group for a specific molecule by considering the geometrical symmetry of its molecular model. However, when a point group is used to classify molecular states, the operations in it are not to be interpreted in the same way. Instead the operations are interpreted as rotating and/or reflecting the vibronic (vibration-electronic) co-ordinates and these operations commute with the vibronic Hamiltonian. They are "symmetry operations" for that vibronic Hamiltonian. The point group is used to classify by symmetry the vibronic eigenstates.

As it turns out, not every random combination of symmetry elements exist for any real object. In fact, only certain combinations of symmetry elements are possible for any real three-dimensional object. These combinations are called point groups. They are called this because all of the symmetry elements of the shape will intersect at (at least) a point. While technically there are an infinite number of point groups (for example, a rotational axis can have any number as its order), only a few are scientifically relevant. For example, in crystallography, it has been demonstrated that there are only 32 different ways that a crystal can fill three-dimensional space (this is known as the crystallographic restriction theorem and applies to true crystals, not quasicrystals).

If analysis of a molecule yielded a list of all present symmetry elements, such a list is the basis to form classes of molecules with common symmetry. Such a class is called a **symmetry point group**. Any molecule is unambiguously a member of one single point group. Though the point groups relevant in chemistry are numerous, we are able to work straightforward within this field as these groups are characterized by sets of increasingly complicated symmetry operations.

Two commonly used notations are, the Schoenflies system and the Hermann-Mauguin system. The former is more common in the discussion of individual molecules, the latter is used almost exclusively in the discussion of crystal symmetry. Note that both are expressions of one single system and they only differ with respect to semantics.

Schoenflies Symbols

The point groups are denoted by their component symmetries. There are a few standard notations used by crystallographers. The Schoenflies notation or Schoenflies 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. In Schoenflies 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 Cn 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.

1.2.6 Representation of Groups by Matrices

Group actions, and in particular representations, are very important in group theory and 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'.

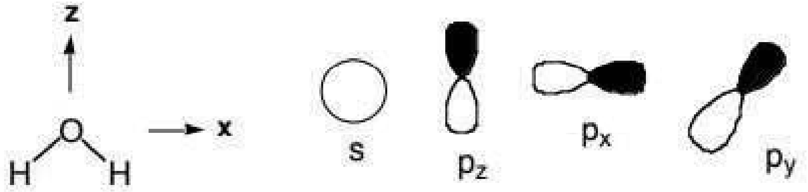
The symmetry of molecules is important in bonding, since only orbitals of the same symmetry are able to interact (or mix) to form bonds. Therefore, in order to know if two orbitals can combine to form a bond, one needs to be able to determine the symmetry of orbitals within molecules. Keep in mind that each molecule belongs to a point group and that the point group has a certain set of operations associated with it. In order to determine the symmetry of an orbital, one must follow what happens to each orbital in question when the operations of the group are performed on it.

For example, consider a H_2O molecule, which belong to the C_{2v} point group. In the C_2v point group, the operations present are:

$$C_{2v}: \{E, C_2, \sigma_x, \sigma_y\}$$

NOTES

The valence orbitals on the oxygen atom, the 2s and 2p orbitals using the coordinate system defined below:



For each of the point groups, the symmetry operations in a group can be represented by matrices. The concept of matrices in algebra can be applied to the elements in point groups. A set of number or matrices which is assigned to the elements of a group and represented the multiplication of the elements is said to constitute representation of a group (Ferraro & Ziomek, 1969). Here, each individual matrix is called a representative that corresponded to the symmetry operations of point groups, and the complete set of matrices is called a matrix representation of the group.

1.2.7 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, C2, 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:** A representation of a higher aspect that can be decreased to a comparatively lower dimension is called reducible representation. A reducible 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.

Those representations which cannot be further reduced to representations of lower dimension are called irreducible representation. If it is unimaginable to expect to discover a comparability change framework which will decrease the lattices of representation then the representation is supposed to be irreducible. Each of the one-dimensional representations is final.

1.2.8 The Great Orthogonality Theorem and its Importance

Great Orthogonality Theorem (GOT) summarizes a number of orthogonality relationships implicit in matrix representations of symmetry groups, and may be derived in a somewhat qualitative fashion by considering these relationships in turn. By making maximum use of molecular symmetry, we often greatly simplify problems involving molecular properties. For example, the formation of chemical bonds is strongly dependent on the atomic orbitals involved having the correct symmetries. To make full use of group theory in the applications we consider to develop a method to conceptualize easily them. For example, if a basic set of atomic orbitals is given, we need to find out:

1. How to determine the irreducible representations spanned by the basic functions?
2. How to construct linear combinations of the original basis functions that transform as a given irreducible representation/symmetry species?

The orthogonality theorem is concerned with elements of matrices constituting irreducible representation of a point group. 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.

1.2.9 Character Table and their Use

A more compact and self–explanatory representation table of a point group is said as 'character table'. The character tables of molecular point groups are important from the point of view of their application to chemical problems. The character of reducible and irreducible representation of symmetry operation of a point group are arranged in the character table and are used for understanding the various problems like atomic orbitals, hybrid orbitals, molecular orbitals in polyatomic molecules, crystal field theory of complex compounds, electronic and vibrational spectra of molecules.

Symbol for Irreducible Representation: The symbol for the irreducible representation was given by Mulliken and hence, called as Mulliken symbol. The rules are as follows:

(i) All uni-dimensional representations are represented either by A or B, two dimensional representations are represented by E and three-dimensional representations are represented by T.

(ii) All one-dimensional representations which are symmetrical with respect to the principal axis (i.e., character of Cn operation is +1) are designated as A while those anti-symmetric in this respect (i.e., character of Cn operation–1) are designated as B.

(iii) Those irreducible representations which are symmetrical with respect to the subsidiary axis, or in its absence to σv plane, subscript 1, (i.e., A1, B1, E1, T1) is used and for anti-symmetric subscript 2 (i.e., B1, A2, E2, T2) is used.

(iv) Primes and double primes are attached to all A, B, E or T to indicate the symmetric and antisymmetric with respect to σh. A' or E' appears forth σh having +1 and A'' or E'' appear for the σh having 1.

(v) Subscript g and u are used to indicate the symmetric and antisymmetric to the inversion. If the point group has no centre of symmetric, g or u are not used. Term g stands for gerade (centro symmetric) and u stands for ungerade (non– centro symmetric).

1.2.10 Spectroscopy

Spectroscopy is the investigation of the interaction between matter and electromagnetic radiation as an element of the frequency or recurrence of the radiation. So, Spectroscopy is a part of science that deals with the spectra of electromagnetic radiation as an element of its frequency or recurrence estimated by spectrographic instrumentation, and different strategies, to get information about the structure and properties of matter.

Spectral measurement devices are alluded to as spectrometers, spectrophotometers, spectrographs or spectral analyzers. Most spectroscopic investigation in the research facility begins with a sample to be analysed, then, at that point, a light source is looked over any ideal scope of the light range, and then, at that point, the light goes through the example to a scattering cluster (diffraction grinding instrument) and is caught by a photodiode.

Spectroscopy is utilized in physical and chemical science since molecules and atoms have novel spectra. Therefore, these spectra can be utilized to recognize, distinguish and evaluate data about the atoms and particles. Spectroscopy is an adequately expansive field that many sub-disciplines exist, each with various executions of explicit spectroscopic strategies.

Check Your Progress

1. Define group theory.
2. What do you understand by symmetry?
3. Define symmetry elements.
4. What do you understand by plane of symmetry?
5. Define rotation-reflection axis.
6. What do you understand by group?
7. Define group operation.

1.3 UNIFYING PRINCIPLES

In this section you will study about the basic unifying principles to make the concept more clear.

1.3.1 Electromagnetic Radiation and its Interaction with Matter

Electromagnetic radiation is a form of energy which is transmitted through space at an enormous velocity. Unlike sound energy, electromagnetic radiation does not require material media for its propagation. Light is the obvious example of electromagnetic radiation which occupies only a small region in electromagnetic spectrum.

An electromagnetic radiation has dual characteristics, behaving both as a particle and as a wave.

A wave is a kind of disturbance which originates from a vibrating source and travels onwards as a continuous sequence of alternating crest and troughs as shown in Figure 1.1.

It was James Clark Maxwell who proposed that radiant energy has a wave character. According to Maxwell's theory of electromagnetic radiation, light travels in space in the form of an oscillating electric field. An oscillating electric field generates magnetic field at right angles to itself as well as to the direction of propagation. The magnetic field oscillates in phase with the electric field and the magnetic vector is directed perpendicular to the electric vector (Refer Figure 1.2).

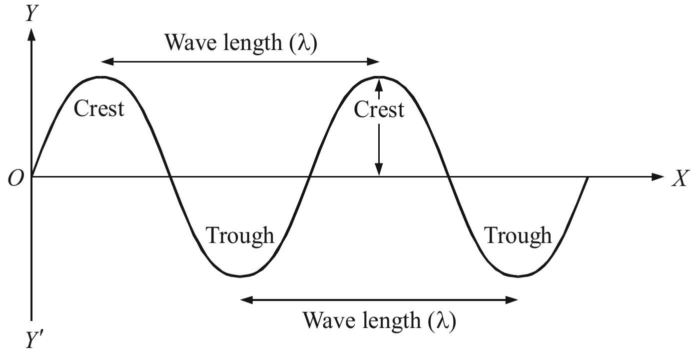


Fig. 1.1 *Wave Motion*

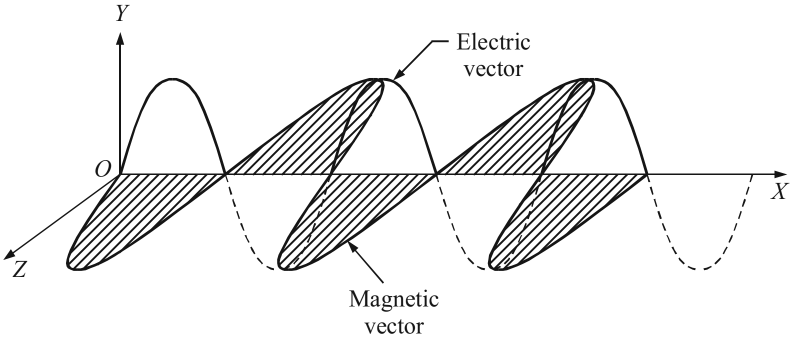


Fig. 1.2 *Representation of Electromagnetic Wave*

Characteristics of Electromagnetic Wave

(*a*) **Wave Length (λ):** It is the distance between the two adjacent crests or troughs in a particular wave. It is denoted by Greek letter Lambda (λ). The commonly used units are metres (m), centimetres (cm), millimetres (mm), micrometres (μm), nanometres (nm).

These units are related by,

$$1\ \mu\text{m} = 10^{-4}\ \text{cm} = 10^{-3}\ \text{nm} = 10^{-6}\ \text{m}$$
$$1\ \text{nm} = 10^{-6}\ \mu\text{m} = 10^{-7}\ \text{cm} = 10^{-9}\ \text{m} = 10\ \text{Å}$$
$$1\ \text{Å} = 10^{-8}\ \text{cm} = 10^{-1}\ \text{nm} = 10^{-10}\ \text{m}$$

Nanometre (nm) is also designated as millimicron (mμ).

(*b*) **Frequency (ν):** It is defined as the number of waves or cycles which pass through a given point in one second. It is expressed by the Greek letter, neu (ν). It is generally represented as cycles per second (S^{-1}) or Hertz (Hz)

Where $1\ \text{Hz} = 1\ \text{cycle sec}^{-1}$

(*c*) **Velocity:** It is the distance travelled by a wave in one second. It is represented by the letter C. The unit of velocity is ms^{-1}.

$$\text{Frequency} \propto \frac{1}{\text{Wave length}}$$

Or $$\nu = \frac{C}{\lambda}$$

Where C = Velocity of Electromagnetic Radiation = 2.998×10^{10} cm sec^{-1}

(*d*) **Wave Number ($\bar{\nu}$):** It is defined as the number of waves which can pass through a space of one centimetre i.e., number of waves per centimetre. It is thus the reciprocal of wavelength. It is denoted by ($\bar{\nu}$) (new bar).

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

The wave number notation is generally used in infrared spectroscopy.

(*e*) **Amplitude:** It is the maximum displacement of a wave. It is measured in terms of the height of crest or trough of a wave. It is denoted by the letter '*a*'.

(*f*) **Energy:** The energy of a wave of a particular radiation is given by,

$$E = h\nu = hC\bar{\nu} = \frac{hC}{\lambda}$$

Where h = Planck's Constant = 6.6256×10^{-27} erg sec

ν = Frequency of Radiation in Cycles Sec^{-1}

C = Velocity of Electromagnetic Radiation

λ = Wavelength of Radiation in Centimetre

$\bar{\nu}$ = Wave Number

C = Velocity of Light.

Characteristics of the Electromagnetic Spectrum

The characteristics of spectral regions can be given as follows:

(*i*) Cosmic rays ($\nu \approx 3 \times 10^{20}$ to infinity) originate from outer space and fall continuously on earth due to their great penetrating power

(*ii*) γ-rays [$\nu \approx 10^{20}$ Hz (0.2 to 1 Å)] emitted by radioactive substances

(*iii*) X-rays [$\nu \approx 10^{19}$ Hz (1 to 10 Å)] are emitted due to movement of electrons close to the nuclei of relatively heavy atoms.

(*iv*) Ultraviolet radiations [$\nu \approx 10^{16}$ Hz (1 - 380 nm)] are a component of sun's rays and can be produced from arc lamps containing mercury vapour, xenon or hydrogen gas, tungsten filament lamp and hydrogen-deuterium discharge lamp.

Ultraviolet regions have two components:

Vacuum Ultraviolet	1–180 nm
Ultraviolet	180–380 nm

(*v*) Visible radiations ($\nu \approx 4 \times 10^{14} - 8 \times 10^{14}$ Hz (380 nm to 760 nm) are a component of the sun's rays and are also produced from arc lamps, hot filaments of tungsten, etc.

(*vi*) IR radiations ($\nu \approx 10^{13}$ Hz) are emitted by incandescent objects. The other sources are Globar source (silicon carbide rod when heated emit IR), Nernst Glower (composed of Zirconia, Yttria, etc.), mercury arc lamps.

NOTES

The infrared regions are further divided into three sub-regions:

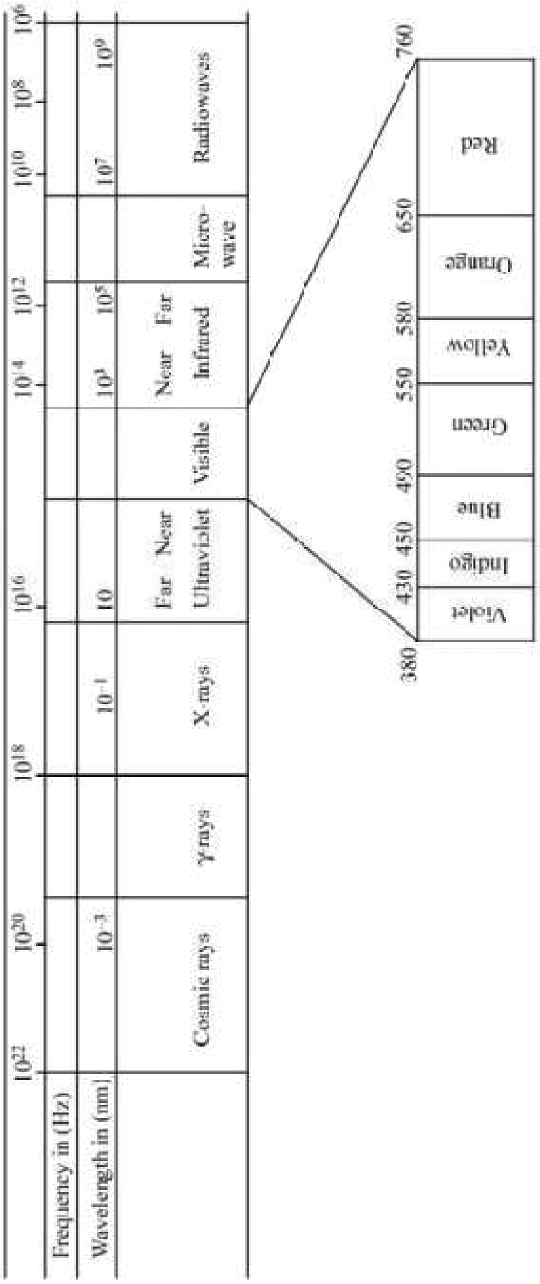


Fig. 1.3 Electromagnetic spectrum

Near Infrared	0.7–2.5 μ
Infrared	2.5–15 μ
Far Infrared	15–200 μ

All three regions of electromagnetic spectrum are associated with the changes in the vibrations of molecules.

(*vii*) Microwaves ($\nu \approx 10^{10}$ Hz (0.1 nm to 1 cm)) are produced by special generators such as Klystron tube. Microwave region corresponds to changes in the rotation of molecules.

(*viii*) Radio Waves ($\nu \approx 10^{4}$ Hz (10 mm^{-1} cm)) are generated from alternating electric currents of high frequencies. The energy change involved in this region arises due to the reversal of spin of nucleus or electron.

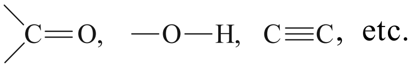
Although, all types of radiations travel as waves with the same velocity, yet they differ from one another in certain properties. For example, X-rays can pass through the muscle tissues but not the visible light. UV and IR radiation can be bent by reflection but not the γ-rays.

When light passes through a sample of a compound some portion of it is absorbed and some is transmitted. The absorption of light by a molecule is due to the changes in the electronic, vibrational or rotational energies of the molecule concerned. The energy absorbed corresponding to a particular wavelength is measured with the help of a spectrometer. If we plot the changes in absorption against wavelengths, certain absorption bands characteristics of a compound will be obtained and the technique provides an excellent tool to ascertain the molecular structure of an unknown substance.

In the visible and ultraviolet regions, the absorption of radiation causes the excitation of outer electrons. The transitions involved δ, π and *n* electrons; charge-transfer electrons as well as *d* and *f* electrons.

As far as organic compounds are concerned, the important transitions involved are *n* and π electrons to π* excited state as well as σ to σ* transitions. The ultraviolet and visible spectrum is therefore very useful for detection of conjugation, carbonyl group of an aldehyde or ketone, etc. However, it may not provide information about the remaining part of the molecule.

In case of IR radiations, the most useful region is 2.5 to 15μ (6.67–4000cm^{-1}). The energy in this region is much lower compared to UV and visible radiations. The absorption in this region by an organic compound causes molecular vibration. The changes in vibrational levels are accompanied by changes in rotational levels. The absorption of radiations is due to the characteristics stretching and bending vibrations of the molecule and thus help in structure elucidation and detection of functional groups having specific vibrational frequencies such as



$>C=O$, $—O—H$, $C\equiv C$, etc.

However, it does not reveal fully the environment effects in a molecule.

In case of NMR spectroscopic technique radio waves (10 nm^{-1} cm) are used. NMR spectroscopy provides a complete insight into the environment and the arrangement of atoms within a molecule. When a nuclei is placed in a strong magnetic field and exposed to radio waves the different nuclei (e.g., H^1, C^{13}, P^{31}) due to different environments around it will feel the applied magnetic field differently and will absorb radio frequency differently. The absorption thus becomes characteristic of the molecule.

Another slightly different principle in spectroscopic techniques, mass spectrometry can be employed for structural elucidation. Through electron beam impact (~ 70 eV) the molecule in the vapour state is ionised and fragmented and through spectrum of these fragmented ions the molecular weight and structure can be obtained.

1.3.2 Absorption and Emission

The field of spectroscopy consists of **emission** and **absorption spectroscopy**, but for organic molecules it is the absorption spectroscopy that is most important. Absorption spectra of a compound is obtained by keeping the substance between some source that provides electromagnetic radiations in the range being studied and the instrument examining the spectra (known as **spectrometer** or **spectrophotometer**).

Electromagnetic radiations of certain wavelengths are absorbed by the compound, while others are transmitted. It is the structure of compound, which determines the wavelengths to be absorbed. Thus knowledge of the absorbed wavelengths can give much information about the compound.

According to quantum theory the absorption of energy by a molecule is quantized (*i.e.*, energy is absorbed in discrete amounts or quanta or packets) and is given by the expression

$$E = \mathrm{h}\nu \quad \text{or} \quad E = \mathrm{h}\frac{c}{\lambda}$$

where E is the energy absorbed in ergs, h is Planck's constant (6.624×10^{-27} erg/sec.), ν is the frequency of radiations in cycle per second (cps), λ is the wavelength of radiations in cm; and c is the velocity of light (2.998×10^{10} cm/sec.).

In case of atoms, the absorption of energy corresponds to the excitation of electrons from one orbit to another. However, absorption of energy by molecules occurs not only by electronic excitations observed in atoms but also by changes in kinetic energy of the molecule due to rotational and vibrational motions of the atoms in the molecule. Apart from electronic excitations, these rotational and vibrational energies of the molecule are also quantized. Therefore, a molecule will absorb only those electromagnetic radiations, which correspond to these permissible electronic, vibrational and rotational energy changes. For a given excitation a molecule absorbs only a particular quantum of energy and therefore, should show sharp line corresponding to the wavelength of absorbed radiations. However in a given sample, group of molecules erist in a number of different vibrational and rotational energy states, which differ from one another in energy by comparatively smaller amounts. Thus, the compound absorbs energy over a small range resulting in the absorption bands instead of lines.

Electromagnetic radiations of different wavelength from X-rays to radio-waves have found some applications in the study of organic molecules. The spectrum of electromagnetic radiations and correlation between these regions and type of molecular excitation.

It may be pointed out here that as the wavelength increases the energy corresponding to radiations decreases. Thus absorption of electromagnetic radiations in ultraviolet or visible region result in electronic excitations whereas in the infrared region, because of relatively lower energy, absorption results in vibrational excitations. The absorbed energy is usually re-emitted in UV and visible region, while in the IR region it is released as heat.

1.3.3 Transmission

When light moves through a transparent (or semi-transparent) material, it can be transmitted, absorbed, or reflected. The transmission of a material is the proportion of the incident (approaching) light that moves all the way through to the other side.

Contrary to the absorption of light, transmission of light occur when the natural frequency of the vibration of electrons do not match the frequencies of the incident light. In such cases, when the light wave strikes the objects, the electrons of the object begin to vibrate. The electrons vibrate for a brief period of time with small amplitude after which the energy is re-emitted as a light wave.

1.3.4 Reflection and Refraction

In physics, the term reflection refers to the change in direction of a wavefront at an interface between two different media so that the wavefront returns into the medium from which it originated. Common examples include the reflection of light, sound and water waves. The law of reflection says that for specular reflection the angle at which the wave is incident on the surface equals the angle at which it is reflected. Mirrors exhibit specular reflection.

When a plane wave travels across a medium they may be reflected at the boundary of the medium and refracted after they cross the boundary. The amount of reflection and refraction depends on the following factors:

1. The type of medium in which the wave travels.
2. The angle of incidence of the wave.

Based on the angle of incidence, the incidence may be classified as:

1. Normal Incidence
2. Oblique Incidence

Reflection and Refraction of Plane Waves with Normal Incidence

When a plane wave is incident normally on a plane, or in other words, if a wave is incident on a plane perpendicular to the traveling wave, then they are said to represent normal incidence as shown in Figure (1.4).

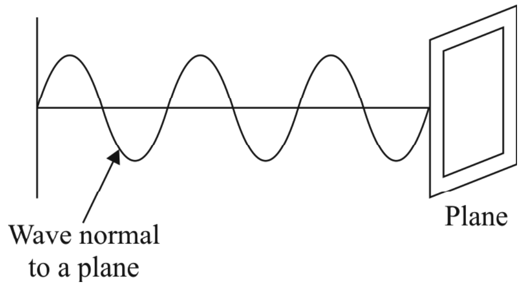


Fig. 1.4 *Normal Incidence*

Let the wave travel from Medium 1 to Medium 2. Medium 1 has the following properties σ_1, $\in_1$ and μ_1, and the Medium 2 has the properties σ_2, $\in_2$ and μ_2. The wave that is travelling has three stages and needs ti be represented uniquely. Hence the following subscripts will be used.

***Table 1.1**: Types of waves and their subscripts*

Wave	*Subscript*
Incident wave	i
Reflected wave	r
Refracted or transmitted wave	t

The EM wave is assumed to travel in the $+\overrightarrow{a_z}$ direction. Since the TEM waves are considered electric field, the magnetic field and direction of travel are mutually orthogonal. Following vectors identities should be recalled:

$$\vec{E} \times \vec{H} = \vec{k} \qquad [\vec{E} \perp \vec{H} \perp \vec{k}]$$

$$\vec{H} \times \vec{k} = \vec{E}$$

$$\vec{k} \times \vec{E} = \vec{H}$$

(a) Incident Wave

Let $\overrightarrow{E_i}$ and $\overrightarrow{H_i}$ travel in $+\overrightarrow{a_z}$ direction

$$\overrightarrow{E_i}(z) = E_{0_i} e^{-\gamma_1 z}\, \overrightarrow{a_x} = E_{0_i} e^{-(-\alpha_1 - j\beta_1)z}\, \overrightarrow{a_x}$$

$$\overrightarrow{E_i}(z) = E_{0_i} e^{-j\beta_1 z}\, \overrightarrow{a_x} \qquad [let\ \alpha_1 = 0] \qquad (1.1a)$$

$$\overrightarrow{H_i}(z) = H_{0_i} e^{-j\beta_1 z}\, \overrightarrow{a_y} \qquad (1.1b)$$

In Equations (1.1a) and (1.1b), the time harmonic term $e^{j\omega t}$ is removed for the sake of convenience and will be reinstated at the end of the derivation.

(b) Reflected Wave

The reflected wave consisting of $\overrightarrow{E_r}$ and $\overrightarrow{H_r}$ get reflected and travel in the $-\overrightarrow{a_z}$ direction.

$$\overrightarrow{E_r}(z) = E_{0_r} e^{j\beta_1 z}\, \overrightarrow{a_x} \qquad (1.2a)$$

$$\overrightarrow{H_r}(z) = H_{0_r} e^{j\beta_1 z}(-\overrightarrow{a_y}) \qquad [-\vec{k} \times \vec{E} = -\vec{H}]$$

$$\overrightarrow{H_r}(z) = -H_{0_r} e^{j\beta_1 z}\, \overrightarrow{a_y} \qquad (1.2b)$$

(c) Transmitted Wave

The transmitted wave, of $\overrightarrow{E_t}$ and $\overrightarrow{H_t}$ travel in the same direction as that of the incident wave, i.e., in the $+\overrightarrow{a_z}$ direction.

$$\overrightarrow{E_t}(z) = E_{0_t} e^{-j\beta_2 z}\, \overrightarrow{a_x} \qquad (1.3)$$

$$\overrightarrow{H_t}(z) = H_{0_t} e^{-j\beta_2 z}\,\overrightarrow{a_y}$$

The incident, reflected and transmitted waves are shown in Figure (1.5).

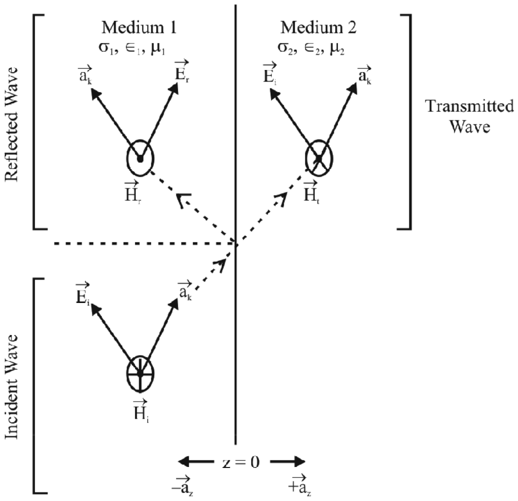


Fig. 1.5 *Reflection of Plane Waves at Normal Incidence*

The total field in Medium 1 includes the incident field and the reflected field. Similarly, total field in Medium 2 includes the transmitted field. Therefore,

In Medium 1,

$$\overrightarrow{E_1} = \overrightarrow{E_i} + \overrightarrow{E_r} \qquad (1.4a)$$

$$\overrightarrow{H_1} = \overrightarrow{H_i} + \overrightarrow{H_r} \qquad (1.4b)$$

In Medium 2,

$$\overrightarrow{E_2} = \overrightarrow{E_t} \qquad (1.5a)$$

$$\overrightarrow{H_2} = \overrightarrow{H_t} \qquad (1.5b)$$

Substituting Equations (1.1) and (1.2) in Equation (1.4), we have,

$$\overrightarrow{E_1} = E_{0_i} e^{-j\beta_1 z}\,\overrightarrow{a_x} + E_{0_r} e^{j\beta_1 z}\,\overrightarrow{a_x}$$

And

$$\overrightarrow{H_1} = H_{0_i} e^{-j\beta_1 z}\,\overrightarrow{a_y} - H_{0_r} e^{j\beta_1 z}\,\overrightarrow{a_y}$$

At the boundary, i.e., at $z = 0$,

$$\overrightarrow{E_1} = E_{0_i} + E_{0_r} \qquad (1.6a)$$

$$\overrightarrow{H_1} = H_{0_i} - H_{0_r}$$

$$= \frac{E_{0_i}}{\eta_1} - \frac{E_{0_r}}{\eta_1} \qquad (1.6b)$$

Similarly, substituting Equation (1.3) in Equation (1.5), we have,

$$\overrightarrow{E_t} = E_{0_t} e^{-j\beta_2 z}\,\overrightarrow{a_x}$$

$\overrightarrow{H_t} = H_{0_t} e^{-j\beta_2 z}\, \overrightarrow{a_y}$

At the boundary at $z = 0$,

$$\overrightarrow{E_2} = E_{0_t} \qquad (1.7a)$$

$$\overrightarrow{H_2} = H_{0_t} \qquad (1.7b)$$

$$= \frac{E_{0_t}}{\eta_2}$$

Across the boundary, the fields are continuous and hence,

$\overrightarrow{E_1} = \overrightarrow{E_2}$ and $\overrightarrow{H_1} = \overrightarrow{H_2}$

$$\therefore E_{0_i} + E_{0_r} = E_{0_t} \qquad (1.8a)$$

And

$$\frac{E_{0_i}}{\eta_1} - \frac{E_{0_r}}{\eta_1} = \frac{E_{0_t}}{\eta_2} \qquad (1.8b)$$

Multiplying Equation (1.8a) by $\frac{1}{\eta_1}$ and adding with eqn. Equation (1.8b),

we have $\left[\frac{1}{n_2}\text{Equation (1.8a)} + \text{Equation (1.8b)}\right]$

$$\left\{\left[\frac{E_{0_i}}{\eta_1} + \frac{E_{0_r}}{\eta_1}\right] + \frac{E_{0_i}}{\eta_1} - \frac{E_{0_r}}{\eta_1}\right\} = \frac{E_{0_t}}{\eta_1} + \frac{E_{0_t}}{\eta_2}$$

$$\frac{2}{\eta_1} E_{0_i} = E_{0_t}\left[\frac{1}{\eta_1} + \frac{1}{\eta_2}\right]$$

$$E_{0_t} = E_{0_i} \frac{2}{\eta_1}\left[\frac{\eta_1 \eta_2}{\eta_1 + \eta_2}\right]$$

$$E_{0_t} = E_{0_i}\left[\frac{2\eta_2}{\eta_1 + \eta_2}\right] \qquad (1.9)$$

Similarly, $\left[\frac{1}{n_2}\text{Equation (1.8a)} - \text{Equation (1.8b)}\right]$ implies,

$$\left\{\left[\frac{E_{0_i}}{\eta_1} + \frac{E_{0_r}}{\eta_1}\right] - \left[\frac{E_{0_i}}{\eta_1} - \frac{E_{0_r}}{\eta_1}\right]\right\} = \frac{E_{0_t}}{\eta_1} - \frac{E_{0_t}}{\eta_2}$$

$$\frac{2}{\eta_1} E_{0_r} = E_{0_t}\left[\frac{1}{\eta_1} - \frac{1}{\eta_2}\right]$$

$$E_{0_r} = E_{0_t}\left[\frac{\eta_2 - \eta_1}{2\eta_2}\right] \qquad (1.10)$$

Substituting Equation (1.9) in Equation (1.10),

$$E_{0_r} = E_{0_i}\left[\frac{2\eta_2}{\eta_1+\eta_2}\right]\left[\frac{\eta_2-\eta_1}{2\eta_2}\right]$$

$$E_{0_r} = E_{0_i}\left[\frac{\eta_2-\eta_1}{\eta_1+\eta_2}\right]$$

1.3.5 Dispersion

The variation of the refractive index with frequency is termed as dispersion. It is this property of a prism that effects the colour separation, or dispersion, of white light. An equation that connects the refractive index with frequency is called a dispersion relation. The dispersion relations describe the effect of dispersion in a medium on the properties of a wave traveling within that medium. Principally, a dispersion relation relates the wavelength or wavenumber of a wave to its frequency. From this relation the phase velocity and group velocity of the wave have convenient expressions which then determine the refractive index of the medium. Dispersion may be caused either by geometric boundary conditions (waveguides, shallow water) or by interaction of the waves with the transmitting medium. Elementary particles, considered as matter waves, have a nontrivial dispersion relation even in the absence of geometric constraints and other media.

For visible light the index of refraction increases slightly with frequency, a phenomenon termed normal dispersion. The degree of refraction depends on the refractive index. The increased bending of violet light over red by a glass prism is therefore the result of normal dispersion. If experiments are done, however, with light having a frequency close to the natural electron frequency, some strange effects appear. When the radiation frequency is slightly greater, for example, the index of refraction becomes less than unity (<1) and decreases with increasing frequency; the latter phenomenon is called anomalous dispersion. A refractive index less than unity refers correctly to the fact that the speed of light in the medium at that frequency is greater than the speed of light in vacuum. The velocity referred to, however, is the phase velocity or the velocity with which the sine-wave peaks are propagated. The propagation velocity of an actual signal or the group velocity is always less than the speed of light in vacuum.

All materials contain ions and electrons. These charged particles experience Lorentz force when exposed to electromagnetic fields. Except in plasmas (ionized gases), currents are predominantly caused by electron motion because ions are practically immobile. In conductors, conduction electron response to externally applied electric field is particularly strong, and the current induced by electron motion tends to prevent the external field from penetrating into conductors. This phenomena is known as skin effect. In dielectrics, electrons are bound to molecules and are thus not free as in conductors. However, those bound electrons can still react to external fields, and induce microscopic current. In an oscillating field, the effective permittivity becomes frequency dependent, and electromagnetic waves in dielectrics are strongly dispersive in contrast to waves in free space.

Dispersion occurs when pure plane waves of different wavelengths have different propagation velocities, such that a wave packet of mixed wavelengths tends to spread out in space. The speed of a plane wave, v, is a function of the wave's wavelength 'l' and is expressed as:

$$v = v\,(\lambda)$$

The wave's speed, wavelength, and frequency, f, are related by the identity,

$$v(\lambda) = \lambda\, f\,(\lambda)$$

The function $f\,(\lambda)$ expresses the dispersion relation of the given medium. Dispersion relations are more commonly expressed in terms of the angular frequency $\omega = 2\pi f$ and wavenumber $k = 2\pi/\lambda$. Rewriting the relation above in these variables gives,

$$\omega(k) = v(k).$$

Where 'f' is defined as a function of k. The use of $\omega(k)$ to describe the dispersion relation has become standard because both the phase velocity ω/k and the group velocity $d\omega/dk$ have convenient representations through this function.

The plane waves being considered can be described by,

$$A(x,t) = A_0 e^{2\pi i \frac{x-vt}{\lambda}} = A_0 e^{i(kx-\omega t)}$$

Where,

A = Amplitude of the Wave

$A_0 = A\ (0, 0)$

x = Position along the Wave's Direction of Travel

t = Time at which the Wave is described

For electromagnetic waves in vacuum, the angular frequency is proportional to the wavenumber and is expressed as,

$$\omega = ck$$

Normal Dispersion

When a white light, for example, sunlight, or light from an incandescent lamp is passed through a prism then the colour separation is observed. Since the 'Light' observes electromagnetic oscillations, therefore, the different colours have different wavelengths and different frequencies in vacuum for all of them move with the same speed 'c'. Our eyes can sense different wavelengths of visible spectrum only with different colours. The separation happens because the different wavelengths have different refractive indices. Whenever light enters a dielectric medium this separation happens and the phenomenon is known as 'Dispersion'. Basically, it is the variation of refractive index with the wavelength. Alternatively, the variation of the frequency with the wavelength in a medium is 'Normal Dispersion'. Cauchy explained dispersion and gave a formula which typically described the dispersion in the visible range. The following formula is known as Cauchy's dispersion formula,

$$n(\lambda) = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4}$$

Here A, B and C are constants which depend on the medium. Experimentally, the constants can be determined by measuring the refractive index for three wavelengths. In normal condition the first two terms would suffice to give an accurate value of ‘***n***’. The derivative of the refractive index is given by,

$$\frac{dn}{d\lambda} = \frac{B}{\lambda^3}$$

Since *A* and *B* both are positive, therefore the refractive index decreases increasing the wavelength.

Anomalous Dispersion

Anomalous dispersion refers to the dispersion of light in some refraction spectra in which the normal order of the separation of components is reversed in the vicinity of certain wavelengths, i.e., a sudden change in the refractive index of a material for wavelengths in the vicinity of absorption bands in the spectrum of the material. For material which are transparent to visible region the Cauchy’s formula works perfectly, but if there is further increase in the wavelength say to the Infra-Red (IR), then the refractive index suddenly decreases very fast and does not obey the Cauchy’s law. Thus it approaches the absorption region. Further increasing the wavelength once again the refractive index becomes big/large. Additionally, this behaviour is quite similar to the visible region for the increase in wavelength. If the range is increased further then again is observes another absorption band as shown in the Figure (1.6) below. The pattern may repeat further as shown, giving many absorption bands. This dispersion is known as ‘Anomalous Dispersion’.

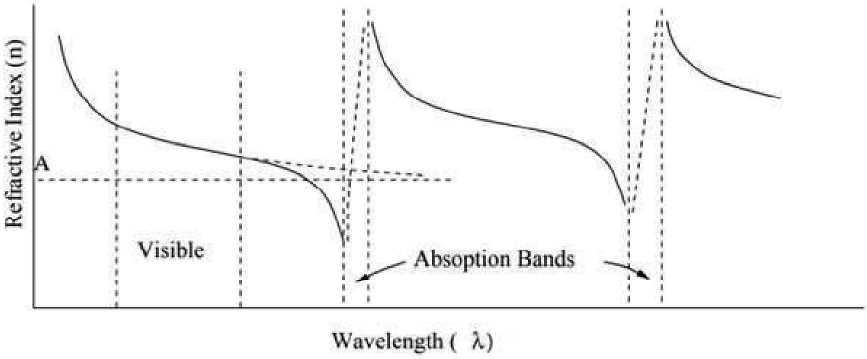


Fig. 1.6 *Normal and Anomalous Dispersion*

The first theory of it was proposed by Sellmeier who assumed that all elastically bound particles in the medium oscillate with a natural frequency ω_0 which correspond to a wavelength λ_0 in the vacuum. Sellmeir formula gave,

$$n^2 = 1 + \frac{\mathcal{A}\lambda^2}{\lambda^2 - \lambda_0^2} \quad n^2 = 1 + \frac{\mathcal{A}\lambda^2}{\lambda^2 - \lambda_0^2}$$

Where $\mathcal{A}$ is a constant. If one is away from λ_0 it can be expanded in powers of λ_0/λ and one would get a formula of the Cauchy type.

Dispersion in Gases

A dispersion is a system in which distributed particles of one material are dispersed in a continuous phase of another material. The two phases may be in the same or different states of matter.

Dispersions are classified in a number of different ways, including how large the particles are in relation to the particles of the continuous phase, whether or not precipitation occurs, and the presence of Brownian motion. In general, dispersions of particles sufficiently large for sedimentation are called suspensions, while those of smaller particles are called colloids and solutions.

IUPAC Definition: Material comprising more than one phase where at least one of the phases consists of finely divided phase domains, often in the colloidal size range, dispersed throughout a continuous phase.

Dispersions do not display any structure; i.e., the particles (or in case of emulsions: droplets) dispersed in the liquid or solid matrix (the 'dispersion medium') are assumed to be statistically distributed. Therefore, for dispersions, usually percolation theory is assumed to appropriately describe their properties.

Dispersion in gases can be explained using the propagation of electromagnetic waves in a dielectric or dilute gas in which the mutual interactions between the constituent particles are abandoned. When the wave passes through the gas, the electrons in the molecules are displaced from their equilibrium position such that the molecules are polarized. Because the gas has low density, hence the difference between the applied electric force and the local field can be neglected. Assuming that the electrons are bounded by a linear restoring force and also the damping is proportional to the velocity.

In physics, dielectric dispersion is the dependence of the permittivity of a dielectric material on the frequency of an applied electric field. Because there is a pause/delay between changes in polarization and changes in the electric field, the permittivity of the dielectric is a complicated function of frequency of the electric field. Dielectric dispersion is very important for the applications of dielectric materials and for the analysis of polarization systems.

This is one instance of a general phenomenon known as material dispersion: a frequency-dependent response of a medium for wave propagation.

When the frequency becomes higher, then:

- Dipolar polarization can no longer follow the oscillations of the electric field in the microwave region around 10^{10} Hz.
- Ionic polarization and molecular distortion polarization can no longer track the electric field past the infrared or far-infrared region around 10^{13} Hz.
- Electronic polarization loses its response in the ultraviolet region around 10^{15} Hz.

In the frequency region above ultraviolet, permittivity approaches the constant ε_0 in every substance, where ε_0 is the permittivity of the free space. Because permittivity indicates the strength of the relation between an electric field and polarization, if a polarization process loses its response, permittivity decreases.

Experimental Demonstration of Anomalous Dispersion in Gases, Solids and Liquids

Anomalous dispersion is the dispersion of light in some refraction spectra in which the normal order of the separation of components is reversed in the vicinity of certain wavelengths.

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Demonstration of Anomalous Dispersion in Liquid

When a beam of white light is refracted by an ordinary prism then it is not only redirected but it is also ***dispersed***. This dispersion happens since the index of refraction depends (slightly) on the wavelength of light being refracted. In maximum materials, the blue light is refracted more strongly as compared to the red light. Blue light is bent at a larger angle than red when a normal prism is used. Normal dispersion yields the accustomed rainbow of colours from white light.

Normal dispersion is assumed to occur because the atoms in the prism are capable of oscillating at natural resonant frequencies which are much higher than the frequency of visible light. Light with higher frequency (shorter wavelength) interacts more strongly with these atoms since it is nearby to the resonant frequency. As a result it has a larger index of refraction.

In a couple of materials, there is an atomic resonance whose frequency falls within the frequency range of visible light. A solution of potassium permanganate ($KMnO_4$) in water can be considered as the dispersing medium.

For his experiment, a hollow prism filled with ($KMn0_4$) solution was used and the apparatus was set as shown in Figure (1.7). White light is generated by the filament of a 500 watt incandescent lamp. A condensing lens collects much of this light and forms a small image of the filament. A collimating lens, with its focus on the image, produces a beam of parallel rays, roughly the same diameter as the lens.

This cylinder of light is converted to a sheet of light by a collimating slit. The sheet of light enters the prism and is refracted as shown in Figure (1.7). When water alone is in the prism, the light exits the prism in the usual (vertical) rainbow pattern.

In this experiment, the refracted light is passed through a spectral filter. This thin film filter allows blue wavelengths to pass on one end. The thickness of the film increases along the length of the filter, so that increasingly long wavelengths are allowed to pass. Red light passes through the end farthest from the blue-pass region. For normal dispersion in water, blue wavelengths are refracted through a greater angle, and thus strike the filter at a higher point.

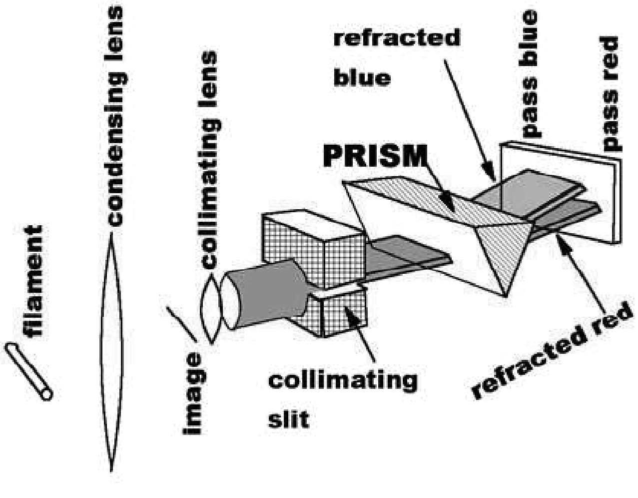

Fig. 1.7 *Experimental Setup*

This takes place for the entire length of the filter, but the blue light is only permitted at the right end of the apparatus. Using this method, the refraction for each wavelength can be displayed in graphical form for the expected curve for anomalous dispersion as shown in Figure (1.8). The angle at which the light is refracted is related to the index of refraction and the 'λ' is considered as the light wavelength.

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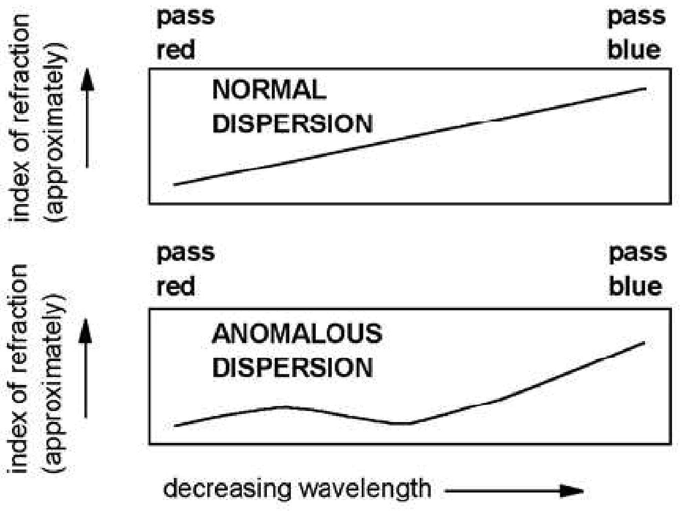

Fig. 1.8 *Index of Refraction*

For water, the index of refraction fluctuates/deviates by less than 1% throughout the visible range of wavelengths, such that the angles are approximately constant. Hence, as shown in Figure (1.9), it is a good approximation to state that 'the change of exit angle, 'ϕ' is proportional to the change in index of refraction, for a given change in wavelength'.

Consequently, the change in 'ϕ' is also proportional to the change in position at which the exiting ray of light hits the spectral filter. Accordingly the location of the light upon the filter is a reasonable representation of the index of refraction.

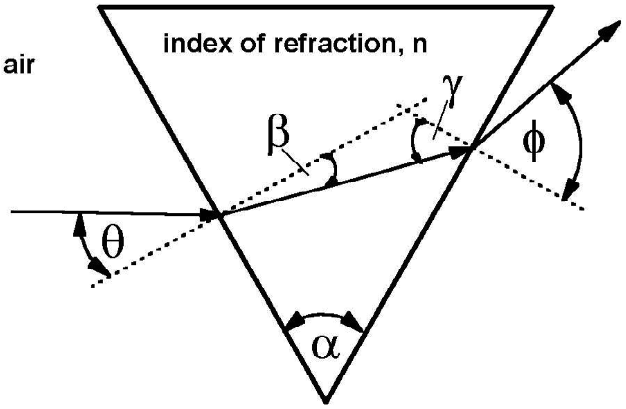

Fig. 1.9 *Index of Refraction and Angle 'ϕ'*

1.3.6 Polarization and Scattering

Electromagnetic waves are one of the best known and most commonly encountered forms of radiation that undergo scattering. Scattering of light and radio waves (especially in radar) is particularly important. Major forms of elastic light scattering including the negligible energy transfer are Rayleigh scattering and Mie scattering. Light scattering is one of the two major physical processes that contribute to the visible appearance of most objects, the other being absorption. Surfaces described as white owe their appearance to multiple scattering of light by internal or surface inhomogeneities in the object, for example by the boundaries of transparent microscopic crystals that make up a stone or by the microscopic fibers in a sheet of paper. More generally, the gloss of the surface is determined by scattering. Highly scattering surfaces are described as being dull or having a matte finish, while the absence of surface scattering leads to a glossy appearance, as with polished metal or stone.

Spectral absorption, the selective absorption of certain colours, determines the colour of most objects with some modification by elastic scattering. The apparent blue colour of veins in skin is a common example where both spectral absorption and scattering play important and complex roles in the colouration. Light scattering can also create colour without absorption, often shades of blue, as with the sky (Rayleigh scattering), the human blue iris, etc.

Models of light scattering can be divided into three domains based on a dimensionless size parameter, α which is defined as:

$$\alpha = \pi D_p/\lambda,$$

Where πD_p is the circumference of a particle and λ is the wavelength of incident radiation. Based on the value of α, these domains are defined as:

$\alpha << 1$: Rayleigh scattering, small particle compared to wavelength of light.

$\alpha \approx 1$: Mie scattering, particle about the same size as wavelength of light, valid only for spheres.

$\alpha >> 1$: Geometric scattering, particle much larger than wavelength of light.

Rayleigh scattering is a process in which electromagnetic radiation (including light) is scattered by a small spherical volume of variant refractive indexes, such as a particle, bubble, droplet, or even a density fluctuation. This effect was first modeled successfully by Lord Rayleigh, from whom it gets its name. In order for Rayleigh's model to apply, the sphere must be much smaller in diameter than the wavelength (λ) of the scattered wave; typically the upper limit is taken to be about 1/10 the wavelength. In this size regime, the exact shape of the scattering center is usually not very significant and can often be treated as a sphere of equivalent volume. The inherent scattering that radiation undergoes passing through a pure gas is due to microscopic density fluctuations as the gas molecules move around, which are normally small enough in scale for Rayleigh's model to apply. This scattering mechanism is the primary cause of the blue colour of the Earth's sky on a clear day, as the shorter blue wavelengths of sunlight passing overhead are more strongly scattered than the longer red wavelengths according to Rayleigh's famous $1/\lambda^4$ relation. Along with absorption, such scattering is a major cause of the attenuation of radiation by the atmosphere. The degree of scattering varies as a function of the ratio of the particle diameter to the wavelength of the radiation, along with many other factors including polarization, angle, and coherence.

For larger diameters, the problem of electromagnetic scattering by spheres was first solved by Gustav Mie, and scattering by spheres larger than the

Rayleigh range is therefore usually known as Mie scattering. In the Mie regime, the shape of the scattering center becomes much more significant and the theory only applies well to spheres and, with some modification, spheroids and ellipsoids. Closed-form solutions for scattering by certain other simple shapes exist, but no general closed-form solution is known for arbitrary shapes.

Both Mie and Rayleigh scattering are considered elastic scattering processes, in which the energy (and thus wavelength and frequency) of the light is not substantially changed. However, electromagnetic radiation scattered by moving scattering centers does undergo a Doppler shift, which can be detected and used to measure the velocity of the scattering center/s in forms of techniques, such as lidar and radar. This shift involves a slight change in energy.

At values of the ratio of particle diameter to wavelength more than about 10, the laws of geometric optics are mostly sufficient to describe the interaction of light with the particle, and at this point, the interaction is not usually described as scattering.

For modeling of scattering in cases where the Rayleigh and Mie models do not apply, such as irregularly shaped particles, there are many numerical methods that can be used. The most common are finite-element methods which solve Maxwell's equations to find the distribution of the scattered electromagnetic field.

Scattering of Electromagnetic Waves by Particles

Interaction between electromagnetic waves and particles produce unique scattering patterns that are wavelength and particle size dependent. As electromagnetic waves propagate through matter they interact with particles and locally perturb the local electron distribution. This variation produces periodic charge separation within the particle causing oscillation of the induced local dipole moment, this periodic acceleration acts as a source of electromagnetic radiation thus causing scattering. The majority of the scattered wave oscillates at the same frequency as the incident wave and is termed elastic scattering. Interaction with the incident beam may also lead to absorption in the form of thermal energy. The combination of scattering and absorption attenuate the incident beam leading to extinction.

Scattering of electromagnetic waves by particles can be explained using the following two theoretical frameworks:

1. Rayleigh scattering that is applicable to small, dielectric, non-absorbing spherical particles.
2. Mie scattering that provides a general solution to scattering independent of particle size. Mie scattering theory provide a generalized approach, has no particle size limitations and converges to the limit of geometric optics at large particle sizes.

Consequently Mie scattering theory can be used to describe most scattering by spherical particles, including Rayleigh scattering, but due to the complexity of implementation, Rayleigh scattering theory is often preferred.

Rayleigh scattering is strongly dependent upon the size of the particle and the wavelength of the illuminating radiation. The intensity of the Rayleigh scattered radiation increases rapidly as the ratio of particle size to wavelength increases

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and is identical in the forward and reverse directions. The Rayleigh scattering model breaks down when the particle size becomes larger than approximately 10% of the wavelength of the incident radiation at which point Mie theory must be applied. The Mie solution is obtained through an analytical solution of Maxwell's equations for the scattering of electromagnetic radiation by spherical particles in terms of infinite series rather than a simple mathematical expression.

Mie scattering differs from Rayleigh scattering in several respects. It is roughly independent of wavelength and it is larger in the forward direction than in the reverse direction, as shown in Figure (1.10). The greater the particle size, the more of the light is scattered in the forward direction. In addition to explaining many atmospheric effects of light scattering, applications of Mie scattering include environmental areas, such as dust particles in the atmosphere and oil droplet in water, etc. Figure (1.10) illustrates the electric field due to Mie scattering of incident wave in x direction showing enhanced scattering in forward direction.

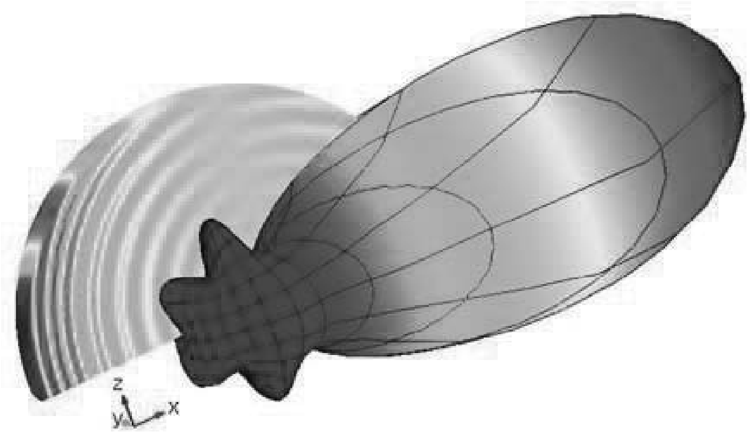

Fig. 1.10 *Electric Field due to Mie Scattering*

Analysis of Mie Scattering

It is a complex process to explain the Mie scattering by a particle or object and requires solution of Maxwell's equations to represent the incident, scattered and internal fields. These are not simple mathematical expressions and take the form of infinite series expansion of vector spherical harmonics that permits the cross sections, efficiency factors and distributions of intensity to be predicted. Additionally, the influence of particle geometry, incident of the incident wave and the particle's material properties can be examined.

In **electromagnetic wave** scattering problems, the total wave decomposes into the incident and scattered wave components:

$$E = E_{inc} + E_{sca}$$

$$H = H_{inc} + H_{sca}$$

Maxwell's wave equation can be solved with respect to scattered electric field as:

$$\nabla \times \left(\frac{1}{\mu_r} \nabla \times E_{sca} \right) - k_0^2 \left(\varepsilon_r - j \frac{\sigma}{\omega \varepsilon_0} \right) E_{sca} = 0$$

The scattered magnetic field is typically calculated from Faraday's law as:

$$H_{sca} = -\frac{1}{j\omega\mu}\nabla \times E_{sca}$$

The time-average Poynting vector for time-harmonic fields gives the energy flux as:

$$\mathscr{P} = \frac{1}{2}\text{Re}\left[E \times H^{-}\right], \left[w/m^{2}\right]$$

For an incident plane wave, the magnetic field is related to the electric field and is represented by:

$$H_{inc} = \frac{1}{\eta}\hat{k} \times E_{inc}$$

Where $\hat{k}$ is direction of the incident wave propagation, $\eta = (\mu/\varepsilon)^{1/2}$ is the characteristic impedance, ε is permittivity and μ is permeability of ambient medium. Hence, incident energy flux is calculated as,

$$\mathscr{P}_{inc} = \frac{1}{2\eta}\left|E_{inc}\right|^{2}\hat{k}$$

Significant physical quantities can be obtained from the scattered fields. One of these is the cross section, which can be defined as the net rate at which electromagnetic energy (*W*) crosses the surface of an imaginary sphere centered at the particle divided by the incident irradiation $(\mathscr{P}_{inc})$. To quantify the rate of the electromagnetic energy that is absorbed (W_{abs}) and scattered (W_{sca}) by the particle, the absorption (σ_{abs}), scattering (σ_{sca}) and extinction cross sections are defined as:

$$\sigma_{abs} = \frac{W_{abs}}{\mathscr{P}_{inc}}, \quad \sigma_{sca} = \frac{W_{sca}}{\mathscr{P}_{inc}}, \quad \sigma_{ext} = \sigma_{abs} + \sigma_{sca}$$

The total absorbed energy is derived by integrating the energy loss over the volume of the particle:

$$W_{abs} = \frac{1}{2}\iiint_{V_p}\text{Re}\left[(\sigma\mathbf{E} + j\omega\mathbf{D})\cdot\mathbf{E}^{*} + j\omega\mathbf{B}\cdot\mathbf{H}^{*}\right]dV, \quad [W]$$

The scattered energy is derived by integrating the Poynting vector over an imaginary sphere around the particle:

$$W_{sca} = \oiint_{S}\mathscr{P}_{sca}\cdot\mathbf{n}dS = \frac{1}{2}\oiint_{S}\text{Re}\left[\mathbf{E}_{sca} \times \mathbf{H}_{sca}^{*}\right]\cdot\mathbf{n}dS, \quad [W]$$

Where **n** is unit vector is considered normal to the imaginary surface *S*.

Due to the particulate nature of electromagnetic waves they also carry momentum $\mathscr{P}/c$ and exert a force on the particle, termed as the *radiation pressure* which can be obtained by integrating the Maxwell stress tensor over the surface of the sphere:

$$\sigma_{pr} = \sigma_{ext} - \langle \cos\theta \rangle \sigma_{sca}, \quad [m^2]$$

Where σ_{pr} is the *pressure cross-section*, and <cos θ> is the *asymmetry parameter*.

The radiation pressure cross section can be used to calculate force which the particle experiences in the incident direction:

$$\mathbf{F} = \frac{1}{c}\sigma_{pr}\mathcal{P}_{inc}, \quad [N]$$

The total time-averaged force **F** acting on a particle illuminated with light can also be calculated using surface integral of the time-averaged Maxwell's stress tensor $\hat{\mathbf{T}}$:

$$\mathbf{F} = \oiint_{S_p} \hat{\mathbf{T}} \cdot \mathbf{n} \, dS_p, \quad [N]$$

Where S_p is surface enclosing particle volume V_p and **n** is unit normal vector to surface S_p.

Scattering Parameters

Scattering parameters or S-parameters are the elements of a scattering matrix or S-matrix which define the electrical behaviour of linear electrical networks when undergoing various steady state stimuli by electrical signals. The parameters are used in different branches of electrical engineering, including electronics, communication systems design, and especially for microwave engineering.

The S-parameters are members of a family of similar parameters, other examples include Y-parameters, Z-parameters, H-parameters, T-parameters or ABCD-parameters. They differ from these, in the sense that S-parameters do not use open or short circuit conditions to characterize a linear electrical network; instead, matched loads are used. These terminations are easily used at high signal frequencies as compared to the open-circuit and short-circuit terminations. Moreover, the quantities are measured in terms of power.

Many electrical properties of networks of components (inductors, capacitors, resistors) may be expressed using S-parameters, such as gain, return loss, Voltage Standing Wave Ratio (VSWR), reflection coefficient and amplifier stability. The term 'Scattering' refers to the effect observed when a plane electromagnetic wave is incident on an obstruction or passes across dissimilar dielectric media. In the context of S-parameters, scattering refers to the way in which the traveling currents and voltages in a transmission line are affected when they meet a discontinuity caused by the insertion of a network into the transmission line. This is equivalent to the wave meeting an impedance differing from the line's characteristic impedance.

Although applicable at any frequency, S-parameters are mostly used for networks operating at Radio Frequency (RF) and microwave frequencies where signal power and energy considerations are more easily quantified than currents and voltages. S-parameters change with the measurement frequency, so frequency must be specified for any S-parameter measurements stated, in addition to the characteristic impedance or system impedance. S-parameters are readily represented in matrix form and obey the rules of matrix algebra.

Types of S-Parameters

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The S-parameters are of following types.

Small Signal S-Parameters: By small signal, we mean that the signals have only linear effects on the network, small enough so that gain compression or other non-linear effects do not take place. For passive networks, the small signal act linearly at any power level.

Large Signal S-Parameters: In this case, the S-matrix may vary depending upon the input signal strength.

Mixed-Mode S-Parameters: It refers to a special case of analysing balanced circuits.

Pulsed S-Parameters: These are measured on power devices so that an accurate representation is captured before the device heats up.

Cold S-Parameters: By cold, we refer to active devices that are not powered up. This can be an individual device, or an amplifier, or module, or anything active that is operated passively.

How S-Parameters Function

The scattering matrix is a mathematical construct that quantifies how Radio Frequency (RF) energy propagates through a multi-port network. The S-matrix is what allows us to accurately describe the properties of incredibly complicated networks as simple 'Black Boxes'. For an RF signal incident on one port, some fraction of that signal gets reflected back out of the incident port, some of it enters *into* the incident port and then exits at or ***scatters*** to some or all of the other ports, perhaps being amplified or attenuated. What is left of that incident power disappears as heat or even electromagnetic radiation. The S-matrix for an N-port contains N^2 coefficients (S-parameters), each one representing a possible input-output path.

S-parameters are complex numbers, having real and imaginary parts or magnitude and phase parts, because both the magnitude and phase of the incident signal are changed by the network. S-parameters are defined for a given frequency and system impedance, and vary as a function of frequency for any non-ideal network.

Additionally, the S-parameters are usually displayed in a matrix format with the number of rows and columns equal to the number of ports. For the S-parameter, S_{ij} the 'j' subscript stands for the port that is the input port and the 'i' subscript is for the output port. Thus, S_{11} refers to the ratio of the amplitude of the signal that reflects from port one to the amplitude of the signal incident on port one. Parameters along the diagonal of the S-matrix are referred to as reflection coefficients because they only refer to what happens at a single port, while off-diagonal S-parameters are referred to as transmission coefficients, because they refer to what happens at one port when it is excited by a signal incident at another port. Following are the examples of S-matrices for one, two and three-port networks:

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$$(S_{11}) \quad (one-port)$$

$$\begin{pmatrix} S_{11} & S_{12} \\ S_{21} & S_{22} \end{pmatrix} \quad (two-port)$$

$$\begin{pmatrix} S_{11} & S_{12} & S_{13} \\ S_{21} & S_{22} & S_{23} \\ S_{31} & S_{32} & S_{33} \end{pmatrix} \quad (three-port)$$

Etc.

Remember that each S-parameter is a complex number, so if actual data has to be presented in matrix format, then a magnitude and phase angle has to be presented for each S_{ij}. The input and output reflection coefficients of networks, such as S_{11} and S_{22} can be plotted on the Smith chart while the transmission coefficients (S_{21} and S_{12}) are generally not plotted on the Smith chart.

S-Parameters for Network Ports

S-parameters describe the response of an N-port network to signal(s) incident to any or all of the ports. The first number in the subscript refers to the responding port, while the second number refers to the incident port. Thus S_{21} means the response at port 2 due to a signal at port 1. The most common 'N-port' networks in microwaves are one-port and two-port networks.

Consider a two-port network. The signal at a port, say port 1, can be thought of as the superposition to two waves traveling in opposite directions. By convention each port is represented as two nodes so as to give a name and value to these opposite direction waves. The variable a_i represents a wave incident to port i and the variable b_j represent a wave reflected from port j. The magnitude of the a_i and b_j variables can be thought of as voltage-like variables, normalized using a specified reference impedance. This is very convenient since the square of these magnitudes are then equal to the power level of the waves. Remember, S-parameters can be used if the value of the reference impedance (frequently called Z_0) is known (Refer Figure (1.11)).

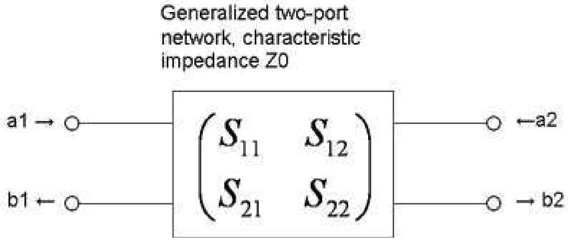

Fig. 1.11 *S-Parameters for Two-Port Network*

If we assume that each port is terminated in the reference impedance Z_0, we can define the four S-parameters of the 2-port as follows:

$$S_{11} = b1/a1$$
$$S_{12} = b1/a2$$
$$S_{21} = b2/a1$$
$$S_{22} = b2/a2$$

The above equations for S_{11} and S_{21} are derived from network analysis or measurements by setting the value of the incident signal $a_2 = 0$ and solving for the above S-parameter ratios as a function of a_1. Similarly, S_{12} and S_{22} are derived by setting the value of $a_1 = 0$ and solving for the other ratios.

The subscript precisely follows the parameters in the ratio, $S_{11}=b_1/a_1$, etc. The matrix algebraic representation of 2-port S-parameters is:

$$\begin{pmatrix} b_1 \\ b_2 \end{pmatrix} = \begin{pmatrix} S_{11} & S_{12} \\ S_{21} & S_{22} \end{pmatrix} \times \begin{pmatrix} a_1 \\ a_2 \end{pmatrix}$$

In order to measure S_{11}, a signal at port one is inserted to measure its reflected signal. In this case, no signal is injected into port 2, so a2 = 0; for almost all laboratory S-parameter measurements, only one signal is inserted at a time. To measure S_{21}, a signal at port 1 is inserted to measure the resulting signal power exiting port 2. For S_{12} a signal is inserted into port 2 to measure the signal power leaving port 1, and for S_{22} a signal is inserted at port 2 to measure its reflected signal.

All the 'a' and 'b' measurements can be complex numbers, hence for complex S-parameters these complex numbers are sometimes called vectors, therefore termed as the Vector Network Analyzers (VNA).

Polarization of Scattered Light

Polarization also occurs when light is scattered while traveling through a medium. When light strikes the atoms of a material, it will often set the electrons of those atoms into vibration. The vibrating electrons then produce their own electromagnetic wave that is radiated outward in all directions. This newly generated wave strikes neighboring atoms, forcing their electrons into vibrations at the same original frequency. These vibrating electrons produce another electromagnetic wave that is once more radiated outward in all directions. This absorption and reemission of light waves causes the light to be scattered about the medium. This scattered light is partially polarized. Polarization by scattering is observed as light passes through our atmosphere. The scattered light often produces a glare in the skies. Photographers know that this partial polarization of scattered light leads to photographs characterized by a *washed-out* sky. The problem can easily be corrected by the use of a Polaroid filter. As the filter is rotated, the partially polarized light is blocked and the glare is reduced.

How it Works

For example, when the unpolarized white light from a slide projector enters a fish tank of very slightly milky water. Some of the electromagnetic waves impinge on the colloidal particles and molecules in the water, are absorbed and re-radiated. The horizontal component of the polarization decreases as $\cos^2\theta$, where θ is the scattering angle (Refer Figure (1.12)) The maximum scattered intensity is perpendicular to the plane of oscillation of the molecule, where it is also totally plane polarized, $\theta = 90°$. At other angles the light is partially plane polarized.

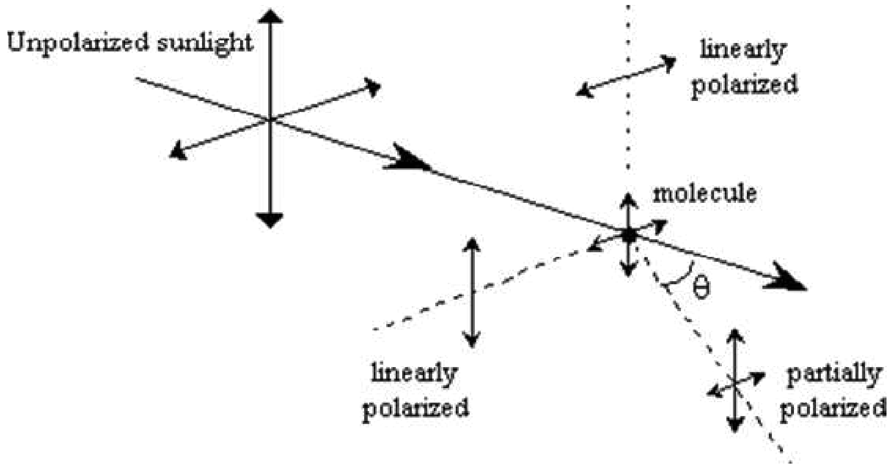

Fig. 1.12 *Polarization by Scattering*

This can be observed on the tank at right angles to the initial direction of propagation of the light. A mirror angled over the tank allows to view the phenomenon of scattered light emerging from two surfaces perpendicular to each other (Refer Figure (1.13)). By placing a Polaroid sheet between the projector and the tank with its polarizing axis horizontally, the scattered light from the side of the fish tank is blocked, whereas that from the top of the tank remains unaffected. Rotating the Polaroid 90° blocks the light from the top of the tank, but now the scattered light from the side of the tank reappears. Alternatively, let the scattering process polarize an unpolarized beam from the slide projector and let the Polaroid sheet be the analyzer, as shown in Figure (1.13).

Rayleigh scattering has a wavelength dependence of $1/(\lambda^4)$, so it affects blue light much more strongly as compared to red. By adding milk to the tank, the scattering can be increased because the milky water begins to develop a bluish tint and the un-scattered beam reddish.

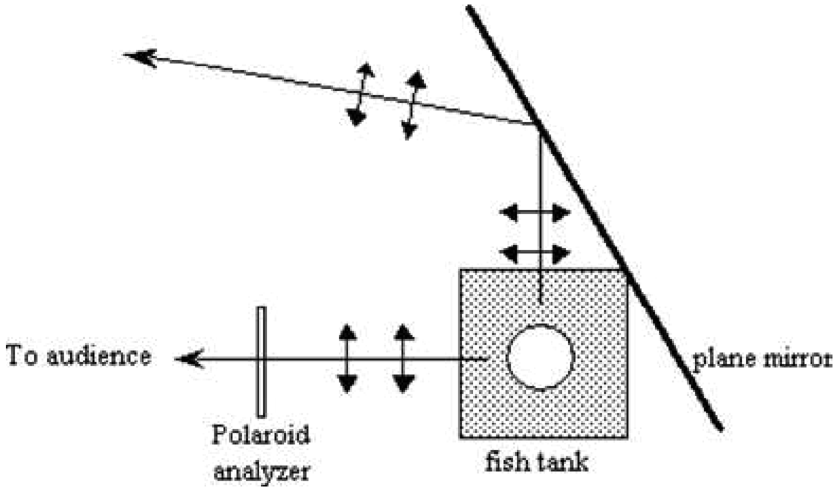

Fig. 1.13 *Fish Tank and Mirror Arrangement*

1.3.7 Uncertainty Principle

Werner Heisenberg, in 1927, presented the uncertainty principle which expresses that: Nature forces limits on the accuracy with which certain sets of actual estimations can be made. This principle has a few significant ramifications in the field of instrumental analysis.

The uncertainty principle gives an apparatus to portraying the exceptionally fleeting products produced in high energy collisions in accelerators. The uncertainty principle proposes that for particles with a very short lifetime, there will be a critical uncertainty in the deliberated energy. The estimation of the mass-energy of an unsteady molecule countless times gives dissemination 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, where the particle lifetime η is taken as the uncertainty in time $\eta = \Delta t$.

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.

Natural Line Width and Natural Line Broadening: An emission line appears to be consistently brilliant, yet a more cautious review shows that its splendour is most noteworthy at the centre and starts fading toward one or the other side. Line broadening is brought about by the environment where the emission or absorption happens, which regularly changes our view on photon's energy, and it enlightens us a great deal concerning the actual condition of the gas involved.

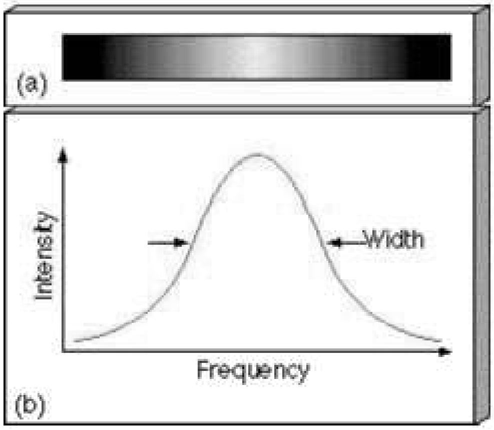

Fig 1.14 *By Tracing the Changing Brightness Across a Typical Emission Line (a) and Expanmding the Scale, We Obtain a Graph of its Intensity Plotted Versus Wavelength (b).*

A few actual instruments can widen spectral lines. The most significant of these include the Doppler Effect. To see how the Doppler impact can widen a spectral line, envision a hot gas cloud. Individual atoms are in irregular, turbulent movement. The more sultry the gas, the quicker the irregular warm movements of the atoms, as represented in Figure 1.15. Assuming a photon is emitted by a molecule moving, the frequency of the recognized photon is changed by the Doppler Effect. For instance, assuming a molecule is getting away from our eye or from our finder while during the time spent emitting a photon, that photon is redshifted. The photon isn't recorded at the exact frequency anticipated by nuclear material science yet rather at a somewhat longer frequency. The degree of this redshift is relative to the speed away from the identifier. Also, assuming the atom is advancing toward us, its light is blueshifted.

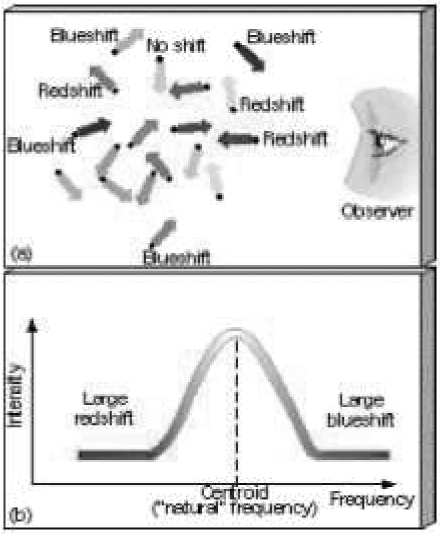

Fig 1.15: *Atoms Moving Randomly (a) Produce Broadened Spectral Lines (b) As Their Individual Redshifted and Blueshifted Emission Lines Merge in our Detector*

All through the entire cloud, particles movement in every conceivable direction. The outcome is that numerous atoms emanate or retain photons at marginally unexpected frequencies in comparison to would regularly be the situation assuming every one of the particles were not in motion. Most molecules in an average cloud have tiny thermal velocities. Accordingly, most molecules transmit or retain radiation that is Doppler-moved just a bit, and not many particles have enormous movements. Along these lines, the focal point of any phantom line is considerably more articulated than both of its wings.

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1.3.8 Transition Probability and Transition Moment

The transition probability is characterized as the likelihood of a specific spectroscopic change to occur. Whenever an atom or particle retains a photon, the probability of a molecule or atom to travel starting with one energy level then onto the next relies upon two things: the idea of introductory and final state wave capacities and how emphatically photons collaborate with an Eigen state. Transition strengths are utilized to depict change likelihood. Determination rules are used to decide if progress is permitted or not.

The transition moment between an underlying state m and a final state n is the electric dipole moment connected with the change between the two states. Overall the change dipole moment is an intricate vector amount that incorporates the stage factors related to the two states. It is normally signified by d_{nm}

The transition dipole moment is helpful for deciding whether changes are permitted under the electric dipole association. For instance, the progress from a bonding π orbital to an anti-bonding π^* orbital is permitted on the grounds that the basic characterizing the change dipole moment is nonzero.

1.3.9 Time Dependent Pertrubation Theory

In quantum mechanics, perturbation theory is a set of approximation schemes directly related to mathematical perturbation for describing a complicated quantum system in terms of a simpler one. The basic notion is to use a simple system for which a mathematical solution is known, and then adding an additional 'Perturbing' Hamiltonian representing a weak disturbance to the system. If the disturbance is not too large, then the various physical quantities associated with the perturbed system, for example its energy levels and eigenstates, can be expressed as 'Corrections' to those of the simple system. These corrections, being small compared to the size of the quantities themselves, can be calculated using approximate methods, such as asymptotic series. The complicated system can consequently be studied based on the simpler one.

Time dependent perturbation theory, developed by Paul Dirac, typically explains the effect of a time dependent perturbation $V(t)$ applied to a time independent Hamiltonian, H_0. Since the perturbed Hamiltonian is time dependent, accordingly are its energy levels and eigenstates. Thus, the goals of time dependent perturbation theory are slightly different from time independent perturbation theory. Following are the two significant quantities of the time dependent perturbation:

1. The time dependent expectation value of some observable A, for a given initial state.
2. The time dependent amplitudes of those quantum states that are energy eigenkets (eigenvectors) in the unperturbed system.

General Time Dependent Perturbations

Assume that the unperturbed energy eigenvalue problem is exactly of the form $H_0\phi_n = E_n\phi_n$.

To this is added a perturbation that depends on time, $\nu(t)$. To solve the time dependent problems we use the following time dependent Schrödinger equation.

$$(H_0 + \mathcal{V}(t))\,\psi(t) = i\hbar\frac{\partial\psi(t)}{\partial t}$$

Then we expand ψ in terms of the eigenfunctions as,

$$\psi(t) = \sum_k c_k(t)\phi_k e^{-iE_kt/\hbar} \text{ with } c_k(t)e^{-iE_kt/\hbar} = \langle\phi_k|\psi(t)\rangle\,.$$

The time dependent Schrödinger equations is then given as,

$$\begin{aligned}
\sum_k (H_0 + \mathcal{V}(t))\,c_k(t)e^{-iE_kt/\hbar}\phi_k &= i\hbar\sum_k \frac{\partial c_k(t)e^{-iE_kt/\hbar}}{\partial t}\phi_k \\
\sum_k c_k(t)e^{-iE_kt/\hbar}\,(E_k + \mathcal{V}(t))\,\phi_k &= \sum_k \left(i\hbar\frac{\partial c_k(t)}{\partial t} + E_kc_k(t)\right)e^{-iE_kt/\hbar}\phi_k \\
\sum_k \mathcal{V}(t)c_k(t)e^{-iE_kt/\hbar}\phi_k &= i\hbar\sum_k \frac{\partial c_k(t)}{\partial t}e^{-iE_kt/\hbar}\phi_k
\end{aligned}$$

Now dot $\langle\phi_n|$ into this equation to get the time dependence of one coefficient.

$$\begin{aligned}
\sum_k \mathcal{V}_{nk}(t)c_k(t)e^{-iE_kt/\hbar} &= i\hbar\frac{\partial c_n(t)}{\partial t}e^{-iE_nt/\hbar} \\
\frac{\partial c_n(t)}{\partial t} &= \frac{1}{i\hbar}\sum_k \mathcal{V}_{nk}(t)c_k(t)e^{i(E_n - E_k)t/\hbar}
\end{aligned}$$

Assuming that at $t = 0$, we are in an initial state $\psi(t = 0) = \phi_i$ and hence all the other c_k are equal to zero as $c_k = \delta_{ki}$.

$$\frac{\partial c_n(t)}{\partial t} = \frac{1}{i\hbar}\left(\mathcal{V}_{ni}(t)e^{i\omega_{ni}t} + \sum_{k\neq i}\mathcal{V}_{nk}(t)c_k(t)e^{i\omega_{nk}t}\right)$$

Next we calculate the transition rates. Considering that for the first order, all the $c_k(t)$ are small in comparison to $c_i(t) \approx= 1$, therefore the sum can be neglected.

$$\frac{\partial c_n^{(1)}(t)}{\partial t} = \frac{1}{i\hbar}\mathcal{V}_{ni}(t)e^{i\omega_{ni}t}$$

$$c_n^{(1)}(t) = \frac{1}{i\hbar}\int_0^t e^{i\omega_{ni}t'}\mathcal{V}_{ni}(t')dt'$$

This equation is used to calculate transition probabilities for a general time dependent perturbation. This can also be used as a basis to calculate the transition rates for the specific problem of harmonic potentials.

Assuming again that '*t*' is small enough hence the c_i may not have changed much.

Remember that, if there is a large energy difference between the initial and the final states, then a slowly varying perturbation can average to zero.

Subsequently we can find that the perturbation may require frequency components that are compatible with ω_{ni} in order to cause transitions.

If the first order term is zero or higher accuracy is required, then the second order term can be calculated. In second order, first a transition is made to an intermediate state ϕ_k and then a transition to ϕ_n . We simply put the first order $c_k^{(1)}(t)$ into the sum.

$$\frac{\partial c_n(t)}{\partial t} = \frac{1}{i\hbar}\left(\mathcal{V}_{ni}(t)e^{i\omega_{ni}t} + \sum_{k\neq i}\mathcal{V}_{nk}(t)c_k^{(1)}(t)e^{i\omega_{nk}t}\right)$$

$$\frac{\partial c_n(t)}{\partial t} = \frac{1}{i\hbar}\left(\mathcal{V}_{ni}(t)e^{i\omega_{ni}t} + \sum_{k\neq i}\mathcal{V}_{nk}(t)\frac{1}{i\hbar}e^{i\omega_{nk}t}\int_0^t e^{i\omega_{ki}t'}\mathcal{V}_{ki}(t')dt'\right)$$

$$c_n^{(2)}(l) = \frac{-1}{\hbar^2}\sum_{k\neq i}\int_0^t dl''\mathcal{V}_{nk}(l'')e^{i\omega_{nk}t''}\int_0^{t''} dl' e^{i\omega_{ki}t'}\mathcal{V}_{ki}(l')$$

$$c_n^{(2)}(t) = \frac{-1}{\hbar^2}\sum_{k\neq i}\int_0^t dt''\mathcal{V}_{nk}(t'')e^{i\omega_{nk}t''}\int_0^{t''} dt' e^{i\omega_{ki}t'}\mathcal{V}_{ki}(t')$$

The Golden Rule and its Applications

In quantum physics, Fermi's golden rule is a formula that describes the transition rate (probability of transition per unit time) from one energy eigenstate of a quantum system to a group of energy eigenstates in a continuum, as a result of a weak perturbation. This transition rate is effectively independent of time (so long as the strength of the perturbation is independent of time) and is proportional to the strength of the coupling between the initial and final states of the system, typically described by the square of the matrix element of the perturbation, along with the density of states. It is also applicable when the final state is not part of a continuum if there is some de-coherence in the process, like relaxation of the atoms or like noise in the perturbation, in which case the density of states is replaced by the reciprocal of de-coherence bandwidth.

Fermi's Golden Rule, also referred to as, the Golden Rule of time dependent perturbation theory, is an equation for calculating transition rates. The result is obtained by applying the time dependent perturbation theory to a system that undergoes a transition from an initial state $|i\rangle$ to a final state $|f\rangle$ that is part of a continuum of states.

Fermi's golden rule describes a system which begins in an eigenstate, $|i\rangle$, of an unperturbed Hamiltonian, H_0 and considers the effect of a perturbing Hamiltonian, H' applied to the system. If H' is considered time independent, then the system goes only into those states in the continuum that have the same energy as the initial state. If H' is oscillating sinusoidally as a function of time, i.e., it is a harmonic perturbation, with an angular frequency É, then the transition is into states with energies that differ by ‘É from the energy of the initial state.

In both cases, the transition probability per unit of time from the initial state $|i\rangle$ to a set of final states $|f\rangle$ is essentially constant. It is given, to first order approximation, by,

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$$\Gamma_{i\to f} = \frac{2\pi}{\hbar} |\langle f | H' | i\rangle|^2 \rho(E_f)$$

Where $\langle f|H'|i\rangle$ is the matrix element (in bra–ket notation) of the perturbation H' between the final and initial states and $\rho(E_f)$ is the density of states (number of continuum states in an infinitesimally small energy interval $E + dE$ at the energy E_f of the final states. This transition probability is also called 'Decay Probability' and is related to the inverse of the mean lifetime. Thus, the probability of finding the system in state $|f\rangle$ is proportional to $e^{-\Gamma_{i\to f}t}$.

The standard way to derive the equation is to start with time dependent perturbation theory and to take the limit for absorption under the assumption that the time of the measurement is much larger than the time needed for the transition.

1.3.10 Selection Rules

Selection Rules

A Raman transition from one state to another is allowed only if the molecular polarizability of those states is different. For a vibration, this means that the derivative of the polarizability with respect to the normal coordinate associated to the vibration is non-zero:

$$\frac{\partial \alpha}{\partial Q} \neq 0 .$$

In general, a normal mode is Raman active if it transforms with the same symmetry of the quadratic forms, ($x^2, y^2, z^2, xy, xz, yz$) which can be verified from the character table of the molecule's symmetry group.

The specific selection rules state that the allowed rotational transitions are $\Delta J = \pm 2$, where 'J' is the rotational state.

The allowed vibrational transitions are $\Delta v = \pm 1$, where 'u' is the vibrational state.

1.3.11 Intensity of Spectral Lines

A spectral line is a dim or bright line in a generally uniform and constant spectrum, coming about because of emission or absorption of light in a narrow recurrence range, contrasted and the close by frequencies. Spectral lines are regularly used to recognize atoms and particles. A spectral line might be noticed either as an emission line or an absorption line.

Spectral lines are the consequence of a connection between a quantum framework (normally atoms, yet in some cases particles or nuclear cores) and a solitary photon. Whenever a photon has about the perfect proportion of energy (which is associated with its frequency) to permit an adjustment of the energy condition of the framework (on account of a molecule this is generally an electron evolving orbitals), the photon is ingested.

The force of otherworldly still up in the air by the overall probabilities advances between different energy levels. The intensity of a spectral line at a given frequency is related to the net rate of absorption (or emission) at that frequency.

Check Your Progress

8. What is an electromagnetic radiation?
9. Define diffraction.
10. Define refraction.
11. What do you understand by dispersion?
12. Define polarization.
13. What do you understand by transition probability?

1.4 BORN-OPPENHEIMER (B-O) APPROXIMATION

The Born–Oppenheimer (B-O) approximation is the best known mathematical approximation in molecular dynamics. Specifically, it is the assumption that the motion of atomic nuclei and electrons in a molecule can be treated separately, based on the fact that the nuclei are much heavier than the electrons. The approach is named after Max Born and J. Robert Oppenheimer who proposed it in 1927, in the early period of quantum mechanics.

The approximation is widely used in quantum chemistry to speed up the computation of molecular wave functions and other properties for large molecules. There are cases where the assumption of separable motion no longer holds, which make the approximation lose validity, it is said to ‘break down’, but is then often used as a starting point for more refined methods.

In molecular spectroscopy, using the BO approximation means considering molecular energy as a sum of independent terms, for example:

$$\mathbf{E}_{\mathbf{Total}} = \mathbf{E}_{\mathbf{Electronic}} + \mathbf{E}_{\mathbf{Vibrational}} + \mathbf{E}_{\mathbf{Rotational}} + \mathbf{E}_{\mathbf{Nuclear\ Spin}}$$

These terms are of different orders of magnitude and the nuclear spin energy is so small that it is often omitted. The electronic energies $\mathbf{E}_{\mathbf{Electronic}}$ consist of kinetic energies, interelectronic repulsions, internuclear repulsions, and electron–nuclear attractions, which are the terms typically included when computing the electronic structure of molecules.

The benzene molecule consists of 12 nuclei and 42 electrons. The Schrödinger equation, which must be solved to obtain the energy levels and wave function of this molecule, is a partial differential eigenvalue equation in the three-dimensional coordinates of the nuclei and electrons, giving $3 \times 12 + 3 \times 42 = 36$ Nuclear + 126 Electronic = 162 Variables for the wave function. The computational complexity, i.e., the computational power required to solve an eigenvalue equation, increases faster than the square of the number of coordinates.

When applying the Born–Oppenheimer (B-O) approximation, the following two consecutive steps are significant:

For a given position of the nuclei, the electronic Schrödinger equation is solved, while treating the nuclei as stationary (not "coupled" with the dynamics of the electrons). This corresponding eigenvalue problem then consists only of the 126 electronic coordinates. This electronic computation is then repeated for other possible positions of the nuclei, i.e. deformations of the molecule. For benzene, this could be done using a grid of 36 possible nuclear position coordinates. The electronic energies on this grid are then connected to give a potential energy surface for the nuclei. This potential is then used for a second Schrödinger equation containing only the 36 coordinates of the nuclei.

The slope of the potential energy surface can be used to simulate molecular dynamics, using it to express the mean force on the nuclei caused by the electrons and thereby skipping the calculation of the nuclear Schrödinger equation.

Principally, the Born-Oppenheimer (B-O) approximation is the assumption that the electronic motion and the nuclear motion in molecules can be separated. It leads to a molecular wave function in terms of electron positions and nuclear positions. Following are the assumptions:

1. The electronic wavefunction depends upon the nuclear positions but not upon their velocities, i.e., the nuclear motion is so much slower than electron motion that they can be considered to be fixed.
2. The nuclear motion, for example rotation, vibration, observes a smeared out potential from the speedy electrons.

If a Hamiltonian is separable into two or more terms, then the total eigenfunctions are products of the individual eigenfunctions of the separated Hamiltonian terms, and the total eigenvalues are sums of individual eigenvalues of the separated Hamiltonian terms.

Consider, for example, a Hamiltonian which is separable into two terms, one involving coordinate q_1 and the other involving coordinate q_2.

$$H = H_1(q_1) + H_2(q_2)$$

With the overall Schrödinger equation being,

$$H\psi(q_1, q_2) = E\psi(q_1, q_2)$$

If we assume that the total wavefunction can be written in the form $\psi(q_1, q_2) = \psi_1(q_1)\psi_2(q_2)$, where $\psi_1(q_1)$ and $\psi_2(q_2)$ are eigenfunctions of H_1 and H_2 with eigenvalues E_1 and E_2, then,

$$\begin{aligned}
H\psi(q_1, q_2) &\underline{=} (H_1 + H_2)\psi_1(q_1)\psi_2(q_2) \\
&\underline{=} H_1\psi_1(q_1)\psi_2(q_2) + H_2\psi_1(q_1)\psi_2(q_2) \\
&\underline{=} E_1\psi_1(q_1)\psi_2(q_2) + E_2\psi_1(q_1)\psi_2(q_2) \\
&\underline{=} (E_1 + E_2)\psi_1(q_1)\psi_2(q_2) \\
&\underline{=} E\psi(q_1, q_2)
\end{aligned}$$

Thus the eigenfunctions of H are products of the eigenfunctions of H_1 and H_2, and the eigenvalues are the sums of eigenvalues of H_1 and H_2.

The eigenfunctions and eigenvalues of this Hamiltonian can be given by solution of the time-independent Schrödinger equation of the form,

$$[T_N + T_e + V_{ee}(\mathbf{r}) + V_{NN}(\mathbf{R}) + V_{eN}(\mathbf{r}, \mathbf{R})]\,\Psi(\mathbf{r}, \mathbf{R}) = E\Psi(\mathbf{r}, \mathbf{R}).$$

Using the Born-Oppenheimer approximation considering that there is a strong separation of time scales between the electronic and nuclear motion, since the electrons are lighter than the nuclei by three orders of magnitude. This can be broken by assuming a quasi-separable form,

$$\Psi(\mathbf{x}, \mathbf{R}) = \phi_e(\mathbf{x}, \mathbf{R})\phi_N(\mathbf{R})$$

Where $\phi_N(\mathbf{R})$ is a nuclear wave function and $\phi_e(\mathbf{x}, \mathbf{R})$ is an electronic wave function that depends parametrically on the nuclear positions.

Fundamentally, the Born-Oppenheimer (B-O) approximation is based on the fact that nuclei are several thousand times heavier than electrons. The proton, itself, is approximately 2000 times more massive than an electron. The electrons can be regarded as particles that follow the nuclear motion adiabatically, meaning that they are 'dragged' along with the nuclei without requiring a finite relaxation time. This, certainly, is an approximation, since there could be non-adiabatic effects that do not allow the electrons to follow in this 'instantaneous' method, however, in many systems, the adiabatic separation between electrons and nuclei is an excellent approximation. Another consequence of the mass difference between electrons and nuclei is that the nuclear components of the wave function are spatially more localized than the electronic component of the wave function. In the classical limit, the nuclear are fully localized about single points representing classical point particles.

The B-O approximation recognizes the large difference between the electron mass and the masses of atomic nuclei, and correspondingly the time scales of their motion. Given the same amount of kinetic energy, the nuclei move much more slowly than the electrons. In mathematical terms, the BO approximation consists of expressing the wavefunction of a molecule as the product of an electronic wavefunction and a nuclear (vibrational, rotational) wavefunction. This enables a separation of the Hamiltonian operator into electronic and nuclear terms, where cross-terms between electrons and nuclei are neglected, so that the two smaller and decoupled systems can be solved more efficiently.

Check Your Progress

14. What is Born-Oppenheimer Approximation?
15. What is the main use of Born-Oppenheimer approximation in quantum chemistry?

1.5 ROTATIONAL, VIBRATIONAL, AND ELECTRONIC ENERGY LEVELS

NOTES

Rotational spectroscopy is concerned with the measurement of the energies of transitions between quantized rotational states of molecules in the gas phase. The spectra of polar molecules can be measured in absorption or emission by microwave spectroscopy or by far infrared spectroscopy. The rotational spectra of non-polar molecules cannot be observed by those methods, but can be observed and measured by Raman spectroscopy. Rotational spectroscopy is sometimes referred to as pure rotational spectroscopy to distinguish it from rotational-vibrational spectroscopy where changes in rotational energy occur together with changes in vibrational energy, and also from ro-vibronic spectroscopy (or just vibronic spectroscopy) where rotational, vibrational and electronic energy changes occur simultaneously.

For rotational spectroscopy, molecules are classified according to symmetry into spherical top, linear and symmetric top; analytical expressions can be derived for the rotational energy terms of these molecules. Analytical expressions can be derived for the fourth category, asymmetric top, for rotational levels up to J=3, but higher energy levels need to be determined using numerical methods. The rotational energies are derived theoretically by considering the molecules to be rigid rotors and then applying extra terms to account for centrifugal distortion, fine structure, hyperfine structure and Coriolis coupling. Fitting the spectra to the theoretical expressions gives numerical values of the angular moments of inertia from which very precise values of molecular bond lengths and angles can be derived in favourable cases. In the presence of an electrostatic field there is Stark splitting which allows molecular electric dipole moments to be determined.

A molecule in the gas phase is free to rotate relative to a set of mutually orthogonal axes of fixed orientation in space, cantered on the center of mass of the molecule. Free rotation is not possible for molecules in liquid or solid phases due to the presence of intermolecular forces. Rotation about each unique axis is associated with a set of quantized energy levels dependent on the moment of inertia about that axis and a quantum number. Thus, for linear molecules the energy levels are described by a single moment of inertia and a single quantum number, **J**, which defines the magnitude of the rotational angular momentum.

For nonlinear molecules which are symmetric rotors, there are two moments of inertia and the energy also depends on a second rotational quantum number, **K**, which defines the vector component of rotational angular momentum along the principal symmetry axis.

Analysis of spectroscopic data with the expressions results in quantitative determination of the value(s) of the moment(s) of inertia. From these precise values of the molecular structure and dimensions may be obtained.

For a **linear molecule**, analysis of the rotational spectrum provides values for the rotational constant and the moment of inertia of the molecule, and, knowing the atomic masses, can be used to determine the **bond length** directly.

For **diatomic molecules** this process is straightforward.

For linear molecules with more than two atoms it is necessary to measure the spectra of two or more isotopologues, such as $^{16}O^{12}C^{32}S$ and $^{16}O^{12}C^{34}S$. This allows a set of simultaneous equations to be set up and solved for the bond lengths.

A bond length obtained in this way is slightly different from the equilibrium bond length. This is because there is zero-point energy in the vibrational ground state, to which the rotational states refer, whereas the equilibrium bond length is at the minimum in the potential energy curve. The relation between the rotational constants is given by,

$$B_v = B - \alpha(v + \frac{1}{2})$$

Where v is a vibrational quantum number and α is a vibration-rotation interaction constant which can be calculated if the B values for two different vibrational states can be found.

For other molecules, if the spectra can be resolved and individual transitions assigned both bond lengths and bond angles can be deduced. When this is not possible, as with most asymmetric tops, all that can be done is to fit the spectra to three moments of inertia calculated from an assumed molecular structure. By varying the molecular structure the fit can be improved, giving a qualitative estimate of the structure. Isotopic substitution is invaluable when using this approach to the determination of molecular structure.

Classification of Molecular Rotors

The free rotation of a molecule is quantized, so that the rotational energy and the angular momentum can take only certain fixed values, which are related simply to the moment of inertia, **I**, of the molecule. For any molecule, there are three moments of inertia, $\mathbf{I_A}$, $\mathbf{I_B}$ and $\mathbf{I_C}$ about the three mutually orthogonal axes A, B, and C with the origin at the center of mass of the system. The general convention is to define the axes such that $\mathbf{I_A} \leq \mathbf{I_B} \leq \mathbf{I_C}$ corresponding to the smallest moment of inertia. Some authors, however, define the **A** axis as the molecular rotation axis of highest order.

The particular pattern of energy levels and, hence, of transitions in the rotational spectrum for a molecule is determined by its symmetry. A convenient way to look at the molecules is to divide them into four different classes, based on the symmetry of their structure. These are,

Spherical Tops (Spherical Rotors): All three moments of inertia are equal to each other: $\mathbf{I_A} = \mathbf{I_B} = \mathbf{I_C}$. Examples of spherical tops include phosphorus tetramer (P_4), carbon tetrachloride (CCl_4) and other tetrahalides, methane (CH_4), silane, (SiH_4), sulfur hexafluoride (SF_6) and other hexahalides. The molecules all belong to the cubic point groups T_d or O_h.

Linear Molecules: For a linear molecule the moments of inertia are related by, $\mathbf{I_A} << \mathbf{I_B} = \mathbf{I_C}$. For most purposes, $\mathbf{I_A}$ can be taken to be zero. Examples of linear molecules include dioxygen (O_2), dinitrogen (N_2), carbon monoxide (CO), hydroxy radical (OH), carbon dioxide (CO_2), hydrogen cyanide (HCN), carbonyl sulphide (OCS), acetylene (ethyne, HCa≡CH) and dihaloethynes. These molecules belong to the point groups $C_{\infty v}$ or $D_{\infty h}$.

Symmetric Tops (Symmetric Rotors): A symmetric top is a molecule in which two moments of inertia are the same, $\mathbf{I_A = I_B}$ or $\mathbf{I_B = I_C}$. By definition a symmetric top must have a 3-fold or higher order rotation axis. As a matter of convenience, spectroscopists divide molecules into two classes of symmetric tops, Oblate symmetric tops (saucer or disc shaped) with $\mathbf{I_A = I_B < I_C}$ and Prolate symmetric tops (rugby football, or cigar shaped) with $\mathbf{I_A < I_B = I_C}$. The spectra look rather different, and are instantly recognizable. Examples of symmetric tops include,

Oblate: Benzene (C_6H_6), Ammonia (NH_3)

Prolate: Chloromethane (CH_3Cl), Propyne (CH_3Ca"CH)

As a detailed example, ammonia has a moment of inertia $\mathbf{I_C} = 4.4128 \times 10^{-47}$ kg m^2 about the 3-fold rotation axis, and moments $\mathbf{I_A = I_B} = 2.8059 \times$ 10"47 kg m^2 about any axis perpendicular to the C_3 axis. Since the unique moment of inertia is larger than the other two, the molecule is an oblate symmetric top.

Asymmetric Tops (Asymmetric Rotors): The three moments of inertia have different values. Examples of small molecules that are asymmetric tops include water, H_2O and nitrogen dioxide, NO_2 whose symmetry axis of highest order is a 2-fold rotation axis. Most large molecules are asymmetric tops.

Effect of Vibration on Rotation

The population of vibrationally excited states follows a Boltzmann distribution, so low-frequency vibrational states are appreciably populated even at room temperatures. As the moment of inertia is higher when a vibration is excited, the rotational constants (B) decrease. Consequently, the rotation frequencies in each vibration state are different from each other. This can give rise to 'Satellite' lines in the rotational spectrum, for example cyanodiacetylene, $H-C\equiv C-C\equiv C-C\equiv N$.

Further, there is a fictitious force, Coriolis coupling, between the vibrational motion of the nuclei in the rotating (non-inertial) frame. However, as long as the vibrational quantum number does not change, i.e., the molecule is in only one state of vibration), the effect of vibration on rotation is not important, because the time for vibration is much shorter than the time required for rotation. The Coriolis coupling is often negligible, too, if one is interested in low vibrational and rotational quantum numbers only.

Maxwell-Boltzmann Distribution

Maxwell–Boltzmann distribution is a particular probability distribution named after James Clerk Maxwell and Ludwig Boltzmann. It was first defined and used for describing particle speeds in idealized gases, where the particles move freely inside a stationary container without interacting with one another, except for very brief collisions in which they exchange energy and momentum with each other or with their thermal environment. The term 'particle' in this context refers to gaseous particles only (atoms or molecules), and the system of particles is assumed to have reached thermodynamic equilibrium. The energies of such particles follow what is known as Maxwell–Boltzmann statistics, and the statistical distribution of speeds is derived by equating particle energies with kinetic energy.

Mathematically, the Maxwell–Boltzmann distribution is the **Chi distribution** with **three degrees of freedom** (the components of the velocity vector in Euclidean space), with a scale parameter measuring speeds in units proportional to the square root of **T/m** (the ratio of temperature and particle mass).

The Maxwell–Boltzmann distribution is a result of the kinetic theory of gases, which provides a simplified explanation of many fundamental gaseous properties, including pressure and diffusion. The Maxwell–Boltzmann distribution applies fundamentally to particle velocities in three dimensions, but turns out to depend only on the speed (the magnitude of the velocity) of the particles. A particle speed probability distribution indicates which speeds are more likely: a particle will have a speed selected randomly from the distribution, and is more likely to be within one range of speeds than another. The kinetic theory of gases applies to the classical ideal gas, which is an idealization of real gases. In real gases, there are various effects, for example van der Waals interactions, vertical flow, relativistic speed limits, and quantum exchange interactions, that can make their speed distribution different from the Maxwell–Boltzmann form. However, rarefied gases at ordinary temperatures behave very nearly like an ideal gas and the Maxwell speed distribution is an excellent approximation for such gases. Ideal plasmas, which are ionized gases of sufficiently low density, frequently also have particle distributions that are partially or entirely Maxwellian.

The distribution was first derived by Maxwell in 1860 on heuristic grounds. Boltzmann later, in the 1870s, carried out significant investigations into the physical origins of this distribution.

For particles confined to move in a plane, the speed distribution is given by

$$P(s < |\vec{v}| < s + ds) = \frac{ms}{kT} \exp\left(- \frac{ms^2}{2kT} \right) ds$$

This distribution is used for describing systems in equilibrium. However, most systems do not start out in their equilibrium state. The evolution of a system towards its equilibrium state is governed by the Boltzmann equation. The equation predicts that for short range interactions, the equilibrium velocity distribution will follow a Maxwell–Boltzmann distribution.

Vibrational Spectrum

InfraRed spectroscopy (IR spectroscopy or Vibrational Spectroscopy) is the spectroscopy that deals with the infrared region of the electromagnetic spectrum, i.e., light with a longer wavelength and lower frequency than visible light. It covers a range of techniques, mostly based on absorption spectroscopy.

Infrared spectroscopy or IR spectroscopy or vibrational spectroscopy is the measurement of the interaction of infrared radiation with matter by absorption, emission, or reflection. It is used to study and identify chemical substances or functional groups in solid, liquid, or gaseous forms. The method or technique of infrared spectroscopy is conducted with an instrument called an infrared spectrometer (or spectrophotometer) which produces an infrared spectrum. An IR spectrum can be visualized in a graph of infrared light absorbance or transmittance on the vertical axis vs. frequency or wavelength on the horizontal axis. Typical units of frequency used in IR spectra are reciprocal centimetres (sometimes called wave numbers), with the symbol cmd1. Units of IR wavelength are commonly given in micrometres (formerly called 'microns'), symbol μm, which are related to wave numbers in a reciprocal way. A common laboratory instrument that uses this technique is a Fourier Transform InfraRed (FTIR) spectrometer.

The infrared portion of the electromagnetic spectrum is usually divided into three regions; the near-infrared, mid-infrared and far-infrared, named for their relation to the visible spectrum. The higher-energy near-IR, approximately 14000–4000 cm^{d1} (0.7–2.5 μm wavelength) can excite overtone or combination modes of molecular vibrations. The mid-infrared, approximately 4000–400 cm^{d1} (2.5–25 μm) is generally used to study the fundamental vibrations and associated rotational–vibrational structure. The far-infrared, approximately 400–10 cm^{d1} (25–1000 μm) has low energy and may be used for rotational spectroscopy and low frequency vibrations. The region from 2–130 cm^{d1}, bordering the microwave region, is considered the terahertz region and may probe intermolecular vibrations. The names and classifications of these subregions are conventions, and are only loosely based on the relative molecular or electromagnetic properties.

Infrared spectroscopy exploits the fact that molecules absorb frequencies that are characteristic of their structure. These absorptions occur at resonant frequencies, i.e. the frequency of the absorbed radiation matches the vibrational frequency. The energies are affected by the shape of the molecular potential energy surfaces, the masses of the atoms, and the associated vibronic coupling.

In particular, in the **Born–Oppenheimer** and **harmonic approximations**, i.e., when the molecular Hamiltonian corresponding to the electronic ground state can be approximated by a harmonic oscillator in the neighbourhood of the equilibrium molecular geometry, the resonant frequencies are associated with the normal modes of vibration corresponding to the molecular electronic ground state potential energy surface. The resonant frequencies are also related to the strength of the bond and the mass of the atoms at either end of it. Thus, the frequency of the vibrations are associated with a particular normal mode of motion and a particular bond type.

Check Your Progress

16. State the significance of rotational spectroscopy.
17. How molecules are classified in rotational spectroscopy?
18. Define vibrational spectroscopy.

1.6 ANSWERS TO 'CHECK YOUR PROGRESS'

1. Group Theory is a mathematical method by which aspects of a molecule's symmetry can be determined.
2. 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.

3. Symmetry elements are the geometrical elements like line, plane with respect to which one or more symmetric operations are carried out.
4. Plane of symmetry is a plane of reflection through which an identical copy of the original molecule is given. This is also called a mirror plane and abbreviated as σ.
5. An n-fold rotation followed by reflection through mirror plane perpendicular to rotation axis also known as rotation reflection axis.
6. A group 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.
7. The operation with respect to which a group is defined is often called the group operation.
8. Electromagnetic radiation (often abbreviated E-M radiation or EMR) is a form of energy exhibiting wave-like behaviour as it travels through space.
9. 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.
10. 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.
11. The variation of the refractive index with the frequency is called as dispersion.
12. 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.
13. The transition probability is defined as the probability of particular spectroscopic transition to take place.
14. The Born-Oppenheimer (B-O) approximation is the best known mathematical approximation in molecular dynamics.
15. The approximation is widely used in quantum chemistry to speed up the computation of molecular wave functions and other properties for large molecules.
16. Rotational spectroscopy is concerned with the measurement of the energies of transitions between quantized rotational states of molecules in the gas phase.
17. For rotational spectroscopy, molecules are classified according to their symmetry.
18. Vibrational Spectroscopy is the spectroscopy that deals with the infrared region of the electromagnetic spectrum, i.e., light with a longer wavelength and lower frequency than visible light.

1.7 SUMMARY

NOTES

- Group theory is a mathematical method by which aspects of a molecule's symmetry can be determined.
- Group theory can be considered the study of symmetry: the collection of symmetries of some object preserving some of its structure forms a group
- 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.
- These are the geometrical elements like line, plane with respect to which one or more symmetric operations are carried out.
- A molecule or object is said to possess a particular operation if that operation when applied leaves the molecule unchanged.
- n-fold rotation followed by reflection through mirror plane perpendicular to rotation axis also known as Rotation Reflection axis.
- A group 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.
- Any subset of element which form a group is called as subgroup.
- Symmetry operations which commute with all symmetry operations forms a class.
- 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.
- 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.
- The Schoenflies notation or Schoenflies notation, named after the German mathematician Arthur Moritz Schoenflies, is one of two conventions commonly used to describe crystallographic point groups.
- Group actions, and in particular representations, are very important in group theory and also to physics and chemistry.
- 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 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.
- A representation of higher dimension which can be reduced to representation of lower dimension is called reducible representation.

- The great orthogonality theorem is concerned with the elements of matrices constituting irreducible representation of a point group.
- For each point group, a character table summarizes information on its symmetry operations and on its irreducible representations.
- 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.

NOTES

1.8 KEY TERMS

- **Group Theory:** It is a mathematical method by which aspects of a molecule's symmetry can be determined.
- **Electromagnetic Radiations:** These are the radiations having electric field as well as magnetic field both are perpendicular to each other & are also perpendicular to the line of propagation.
- **Symmetry:** 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.
- **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.
- **Centre of Symmetry:** A molecule has a centre of symmetry when, for any atom in the molecule, an identical atom exists diametrically opposite this centre an equal distance from it.
- **Group:** A group 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.
- **Cyclic Group:** In cyclic group all the elements of a group can be generated from one element.
- **Monoid:** A group is a monoid each of whose elements is invertible.
- **Finite Group:** If there are a finite number of elements, the group is called a finite group.
- **Character of a Representation:** The set of matrices for the various symmetry operations of a point group forms a representation.
- **Reducible Representation:** A representation of higher dimension which can be reduced to representation of lower dimension is called reducible representation.
- **Irreducible representation:** Those representations which cannot be further reduced to representations of lower dimension are called irreducible representation.

1.9 SELF-ASSESSMENT QUESTIONS AND EXERCISES

NOTES

Short-Answer Questions

1. State the types of symmetry operations.
2. What do you understand by reflection?
3. What do you understand by groups and sub groups?
4. How can the groups be classified on the basis of elements?
5. What do you understand by conjugacy relation and class?
6. Define Schoenflies symbols.
7. What do you understand by character representation?

Long-Answers Questions

1. Describe the symmetry operations of elements.
2. Differentiate between finite and infinite groups.
3. Describe the relation between orders of a finite group and its sub group.
4. Explain point groups.
5. Describe the representation of group by matrices.
6. Explain the uses of character tables.

1.10 FURTHER READING

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UNIT 2 VIBRATIONAL SPECTROSCOPY

NOTES

Structure

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 spectroscopies. For most electromagnetic radiation, wavelengths are too small to be 45 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.

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. Raman spectroscopy is the measurement of the wavelength and intensity of inelastically scattered light from molecules.

2.1 OBJECTIVES

After going through this unit, you will be able to:

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

2.2 MICROWAVE SPECTROSCOPY

A technique for chemical investigation and the determination of sub-atomic structure (bond lengths, bond angles, and dipole moments), and relative atomic masses. It depends on the rule that microwave radiation (see microwaves) causes changes in the rotational energy levels of atoms and their absorption thus occurs at characteristic wavelengths. In a microwave spectrometer a microwave source, normally a klystron valve, delivers a beam that passes through a gaseous sample. The beam then, encroaches on the locator, typically a crystal detector, and the signal (wavelength against intensity) is shown, either as a printed plot or on an oscilloscope. Microwave spectroscopy is the spectroscopy strategy that utilizes microwaves, i.e., electromagnetic radiation at GHz frequencies, for the analysis of the matter.

2.2.1 Classification of Molecule and Intensities

Microwave spectroscopy utilizes photons in the microwave range to cause transitions between the quantum rotational energy levels of a gas molecule. For microwave spectroscopy, molecules can be broken down into 5 categories based on their shape and the inertia around their 3 orthogonal rotational axes. These 5 categories include:

- **Diatomic Molecules:** Molecules composed of only two atoms of some or different chemical element
- **Linear Molecules:** All the atoms are arranged in a straight line.
- **Spherical Tops:** When a molecule has all the three moment of inertia identical.
- **Symmetric Tops:** When the two moment of inertia are identical and third is different.
- **Asymmetric Tops:** When all the three moment of inertia are different from each other.

The reason why the sample must be in the gas phase is due to intermolecular interactions hindering rotations in the liquid and solid phases of the molecule.

The ***intensity*** of a spectral line at a given frequency is related to the net rate of absorption (or emission) at that frequency.

2.2.2 Rigid Rotor and Non-Rigid Rotor Model

The rigid rotor is a mechanical model of rotating systems. A self-assertive rigid rotor is a 3-D rigid object, like a top. To situate such an item in space requires three angles, which are called the Euler angles. An exceptional rigid rotor is a straight, linear rotor requiring just two angles to portray, for instance of a diatomic molecule.

In typical diatomic molecule the rotational levels are separated by 1–10 cm^{-1} while the vibrational level are separated by nearly 3000 cm^{-}1. Therefore, to a first approximation rotational and vibrational motions can be considered independently. The rotational and vibrational energy is the sum of the separate energies, i.e., $E_{total} = E_{rot} + E_{vib}$ (Joules).

The rigid rotor is commonly used to describe the rotational energy of diatomic molecules but it is not a completely accurate description of such molecules. This is because molecular bonds (and therefore the interatomic distance are not completely fixed; the bond between the atoms stretches out as the molecule rotates faster (higher values of the rotational quantum number. This effect can be accounted for by introducing a correction factor known as the centrifugal distortion constant D (bars on top of various quantities indicate that these quantities are expressed in cm^{-1})

$$\bar{E}_l = \frac{E_l}{hc} = \bar{B}l\,(l+1) - \bar{D}l^2\,(l+1)^2$$

Where,

$$\bar{D} = \frac{4\bar{B}^3}{\bar{\omega}^2}$$

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$\bar{\omega}$ is the fundamental vibrational frequency of the bond (in cm^{-1}). This frequency is related to the reduced mass and the force constant (bond strength) of the molecule according to

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

The non-rigid rotor is an acceptably accurate model for diatomic molecules but is still somewhat imperfect. This is because, although the model does account for bond stretching due to rotation, it ignores any bond stretching due to vibrational energy in the bond (anharmonicity in the potential).

2.2.3 Effects of Isotopic Substitution on the Transition Frequencies

Isotopic substitution is a valuable procedure because of the fact that the ordinary methods of an isotopically substituted particle are not quite the same as the typical methods of an unsubstituted molecule, prompting different comparing vibrational frequencies for the substituted atoms. Isotopes are particles that share a similar number of protons, however, contrast in the number of neutrons contained in the nucleus, hence, giving these atoms different mass numbers. The particular mass of every atom will influence the reduced mass of the entire molecule, hence, changing the vibrational frequencies of that atom.

The wavelengths of the spectral lines in the visible spectra of hydrogen can be calculated by the Balmer series formula which describes the energy change accompanying the jump of an electron from the nth orbit to the 2nd

$$\frac{1}{\lambda_H} = R\left(\frac{1}{2^2} - \frac{1}{n^2}\right), \quad (n > 2)$$

Where λ_H is the wavelength of a spectral line, R is the Rydberg constant which depends on the mass of the nucleus.

2.2.4 Stark Effect

The Stark Effect is the moving and splitting of spectral lines of molecules and atoms because of the presence of an externally applied electric field. The Stark effect can be noticed both for emission and absorption spectra.

Specifically, the Stark effect is responsible for the pressure broadening (Stark expanding) of spectral lines by charged particles in the plasma. For most of the spectral lines, the Stark effect is either linear (corresponding to the applied electric field) or quadratic with high accuracy.

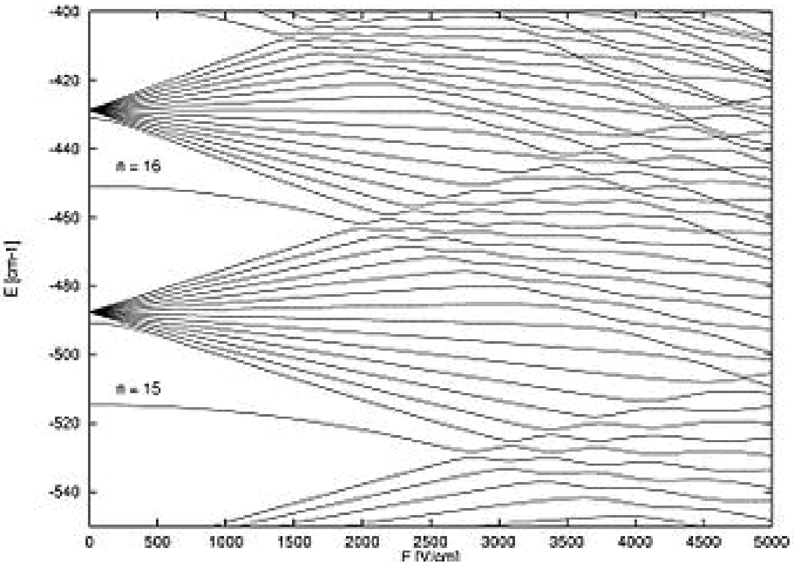


Fig 2.1: *Stark Effect (Computed Energy Level Spectrum of Hydrogen as a Function of the Electric Field near n = 15 for Magnetic Quantum Number m = 0. Each n Level Consists of n –1 Degenerate Sublevels)*

This effect is named after the German physicist Johannes Stark, who discovered it in 1913. The disclosure of this effect contributed critically to the advancement of the quantum hypothesis and Stark won the Nobel Prize in Physics in the year 1919.

2.2.5 Nuclear and Electron Spin Interactions

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.

$\sqrt{I (I+1)}\ h/2\pi$ where $I = 0, ½, 1, 3/2, \ldots\ldots\ldots\ldots$

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, ……. 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)

2.2.6 Applications of Microwave Spectroscopy

Some important applications of microwave spectroscopy are discussed below:

- **Determination of Molecular Structure:** Microwave spectroscopy yields structures undistorted by intermolecular interactions in the crystalline state. Bond lengths can be measured up to 0.1 ppm (10-3A°).
- **Determination of Bond Angles and Bond Lengths:** A microwave spectrum can provide up to three moments of inertia, I for the molecule. Employing I's an appropriate 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 + 3% and C^{13} in the range of 1.1 to 10% within + 2%.
- **Inversion Spectrum of Ammonia:** It was the first molecule to be studied 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 oxy-fluoride is characteristic 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

1. What is microwave spectroscopy?
2. What do you understand by linear molecules?
3. What do you understand by symmetric top molecules?
4. Define spherical top molecules.
5. What do you understand by asymmetric top molecules?
6. State the Stark effect.

2.3 INFRARED SPECTROSCOPY

NOTES

Infrared spectroscopy is the measurement of the interaction of infrared radiation with matter by absorption, emission, or reflection. It is used to study and identify chemical substances or functional groups in solid, liquid, or gaseous forms. It can be used to characterize new materials or identify and verify known and unknown samples. The method or technique of infrared spectroscopy is conducted with an instrument called an infrared spectrometer (or spectrophotometer) which produces an infrared spectrum. An IR spectrum can be visualized in a graph of infrared light absorbance (or transmittance) on the vertical axis vs. frequency or wavelength on the horizontal axis. Typical units of frequency used in IR spectra are reciprocal centimeters (sometimes called wave numbers), with the symbol cm^{-1}. Units of IR wavelength are commonly given in micrometers (formerly called "microns"), symbol μm, which are related to wave numbers in a reciprocal way. A common laboratory instrument that uses this technique is a Fourier transform infrared (FTIR) spectrometer. Two-dimensional IR is also possible as discussed below.

The infrared portion of the electromagnetic spectrum is usually divided into three regions; the near-, mid- and far- infrared, named for their relation to the visible spectrum. The higher-energy near-IR, approximately 14,000–4,000 cm^{-1} (0.7–2.5 μm wavelength) can excite overtone or combination modes of molecular vibrations. The mid-infrared, approximately 4,000–400 cm^{-1} (2.5–25 μm) is generally used to study the fundamental vibrations and associated rotational–vibrational structure. The far-infrared, approximately 400–10 cm^{-1} (25–1,000 μm) has low energy and may be used for rotational spectroscopy and low frequency vibrations. The region from 2–130 cm^{-1}, bordering the microwave region, is considered the terahertz region and may probe intermolecular vibrations. The names and classifications of these subregions are conventions, and are only loosely based on the relative molecular or electromagnetic properties.

Infrared (IR) absorption spectrum of a compound is its energy absorption pattern in infrared region. Due to comparatively lower amounts of energy associated with infrared radiations, they are not capable of electronic excitations in a molecule as is observed in ultraviolet and visible region. Infrared radiations, therefore, cause vibrational and rotational energy changes in the molecule which are also quantised.

The ordinary infrared region varies from 2.5 to 15 μ (4,000 to 667 cm^{-1}) and is the common infrared region, the region from 0.8 to 2.5 μ (12,500 to 4,000 cm^{-1}) is called the near infrared region and the region from 15 to 200 μ (667 to 50 cm^{-1}) is called the far infrared region.

2.3.1 Linear Harmonic Oscillator

The linear harmonic oscillator describes vibrations in molecules and their counterparts in solids, the phonons. Many more physical systems can, at least approximately, be described in terms of linear harmonic oscillator models. The linear harmonic oscillator, even though it may represent rather non-elementary objects like a solid and a molecule, provides a window into the most elementary structure of the physical world. The most likely reason for this connection with fundamental properties of matter is that the harmonic oscillator Hamiltonian is symmetric in momentum and position, both operators appearing as quadratic terms.

The important role of the harmonic oscillator certainly justifies an approach from two perspectives, i.e., from the path integral (propagotor) perspective and from the Schr¨odinger equation perspective. The path integral approach gave us a direct route to study time-dependent properties, the Schrödinger equation approach is suited particularly for stationary state properties.

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,

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

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. 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,

$$dE = -\,Fdx \qquad \ldots(2)$$

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

$$dE = kx\,d \qquad \ldots(3)$$

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

$$E = \ldots - F\,kx\,d \qquad \ldots(4)$$

The potential energy curve for a simple harmonic oscillator derived from equation (4). 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,

$$F = ma \qquad \ldots(5)$$

Where ***m*** is the mass and ***a*** is 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 with respect to time.

Assuming the behavior of a molecular vibration analogous to the mechanical model just described, the frequency of the molecular vibration can be calculated where k becomes the force constant for the chemical bond containing two atoms of masses m1 and m2. 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.

2.3.2 Vibrational Energies of Diatomic Molecules

Atoms within molecules may vibrate about their average positions undergoing periodic displacements from positions. The vibration of an atom with respect to other atoms in a molecule involves bending or stretching of the valence bonds which hold it. Vibrational spectra result from the changes in vibrational energy levels the vibrational energy levels of a molecule are given by:

$$E = \left(v + \frac{1}{2}\right)hv_0 \qquad \text{...(1)}$$

Where v is the vibrational quantum number.

The vibrational frequency ν of a diatomic molecule is given by Hook's law. The two atoms and their connecting bond are treated as a simple harmonic oscillator composed of two masses M_x and M_y connected by a spring.

$$\bar{v} = \frac{1}{2\pi c}\left(\frac{\frac{f}{M_x M_y}}{M_x + M_y}\right)^{1/2} \qquad \text{...(2)}$$

Where $\bar{v}$ = Vibrational Frequency (cm^{-1})

c = Velocity of Light

f = Force Constant of the Bond

The value of f is approximate 5×10^5 dynes per cm for single bonds and approximately 2 and 3 times this value for double bonds and triple bonds respectively. The frequency of infra-red absorption is commonly used to calculate the force constants of bonds. In the IR studies the wave number ($\bar{v}$) are often called frequencies though it is not rigorously correct. B and intensities are expressed either as transmittance (T) or absorbance (A).

A molecule has many degrees of freedom as the total degrees of freedom of its individual atom. Each atom has 3 degrees of the vibrational energies which are quantised and for a simple harmonic oscillator it is given by,

$$E_v = \left(v + \frac{1}{2}\right)h\bar{w}_{oSc}\text{Joules}$$

where v is called vibrational quantum number and have values, $v = 0, 1, 2,...$ In spectroscopic units $\in_v$ (cm^{-1}) we have,

$$\in_v = \frac{E_v}{hc} = \left(v + \frac{1}{2}\right)\bar{w}_{osc}cm^{-1}$$

For $v = 0$

$$\in_0 = \frac{1}{2}\bar{w}_{osc}cm^{-1}$$

2.3.3 Zero Point Energy

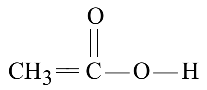
Zero-point energy (ZPE) is the most reduced conceivable energy that a quantum mechanical system might possess. Unlike in traditional mechanics, quantum mechanics continually vacillate in their lowest energy state as depicted by the Heisenberg uncertainty principle.

In classical mechanics, every particle can be considered possessing some energy comprised of their potential energy and kinetic energy. Temperature, for instance, emerges from the intensity of a random molecular movement brought about by the kinetic energy (known as Brownian movement). As the temperature is diminished to absolute zero, it very well may be felt that all the movement stops and particles come totally to rest. Indeed, the kinetic energy is held by particles even at the lowest possible temperature. The arbitrary movement relating to this zero-point energy never vanishes as a result of the uncertainty principle of quantum mechanics.

2.3.4 Bond Strength and Force Constant

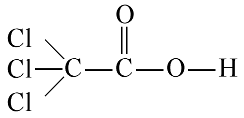
Strength of Bond. The greater the strength of bond greater will be its stretching frequency. Any factor that weakens the bond lowers its stretching frequency. Thus O—H bond in alcohols is stronger than the O—H bond in acetic acid which in turn is stronger than O—H bond in trichloroacetic acid (due to –I effect of — Cl).

CH_3—CH_2—OH ν (O — H) 3640 cm^{-1}



$CH_3=\overset{\overset{O}{\|}}{C}—O—H$ ν (O — H) 3500 cm^{-1}

(—O—H bond is weaker due to resonance effect)



ν (O — H) 3400 cm^{-1}

(—O —H bond is weaker due to strong –I effect of —Cl)

Force Constants: Force constant for a diatomic molecule can be calculated by the equation

$$f = 4\pi^2 \mu c^2 (\bar{\nu})^2 \frac{1}{N_0}$$

Where f = force constant, N_0 = Avogadro number

μ = reduced mass

c = velocity of light

$\bar{\nu}$ = wave number of radiation.

Thus, H—Cl absorbs at 2890 cm^{-1} and hence its force constant can be calculated by above equation as

$$f = 4\pi^2 \frac{(1.008)(35.5)}{(1.008 + 35.5)} (3 \times 10^{10})^2 (2890)^2 \frac{1}{6.023 \times 10^{23}}$$

$$= 4.84 \times 10^5 \text{ dynes/cm}$$

Calculation of force constants for polyatomic molecules can be done if the interatomic distances and angles are known.

2.3.5 Anharmonicity

Real molecules do not obey exactly the laws of simple harmonic oscillator, the real bonds though elastic so as to obey Hooke's law. This is due to anharmonicity in the vibrational motion, and in such case $\bar{w}_e$ is the oscillation frequency and x_e is the anharmonicity constant. One can introduce y_e, z_e, etc.

$$\in_M = \left(v+\frac{1}{2}\right)\bar{w}_e - \left(v+\frac{1}{2}\right)^2 \bar{w}_e x_e cm^{-1}$$

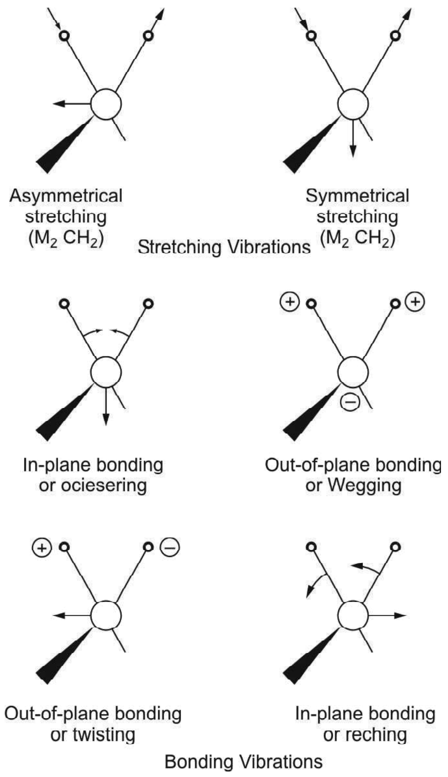


Fig. 2.2 *Vibrational Modes for a CH_2 Group (+ and – Indicate Movement Perpendicular to the Plane of the Page)*

In order to account for higher order corrections freedom corresponding to the cartesian coordinates (x, y, z) needed to define its position relative to other atoms in the molecule. A molecule of n atoms therefore has $3n$ degrees of freedom. For non-linear molecules 3 degrees of freedom describe rotation and 3 describe translation motion. Hence there will be $3n-6$ vibrational degrees or fundamental vibrations. Linear molecules will have $3n-5$ vibrational degrees of freedom. Since two degrees of freedom are required to describe its rotations motion. There are two types of vibrations; stretching vibrations and bending vibrations. A stretching vibration is a rhythmical movement along and bond axis such that the interatomic distances are increasing or decreasing. On the other hand, a bending vibration may consist of a change in bond angle between bonds with a common atom or the movement of a group of atoms in the group with respect to one another. The various stretching and bending modes for CH_2 group in a hydrocarbon molecule are shown in Figure 2.2 CH_2 being a portion of a molecule $3n-6$ rule does not apply in this case.

The theoretical number of fundamental vibrations are seldom observed because overtones (multiples of a given frequency) and combination tones (sum of two other vibrations increase the number of bands whereas the other factors reduce the number of bands.

(i) Fundamental frequencies that fall outside the 4000–666 cm^{-1} region.
(ii) Fundamentals that are too weak to be observed.
(iii) Fundamental vibrations which absorb at the same frequencies.
(iv) Fundamental vibrations that do not cause a change in the dipole moment.

2.3.6 Morse Potential Energy Diagram

The Morse potential, named after physicist Philip M. Morse, is a reliable interatomic structural model for the potential energy of a diatomic molecule. It is a more reliable approach to analyse the vibrational structure of the atom than the quantum harmonic oscillator since it conventionally incorporates the impacts of bond breaking, like the presence of unbound states. It likewise represents the anharmonicity of real bonds and the non-zero transition probability for overtone and combination bands. The Morse potential can likewise be utilized to demonstrate different interactions like the one between an atom and a surface. Because of its simple structure (just three fitting parametrs), it isn't utilized in modern day spectroscopy.

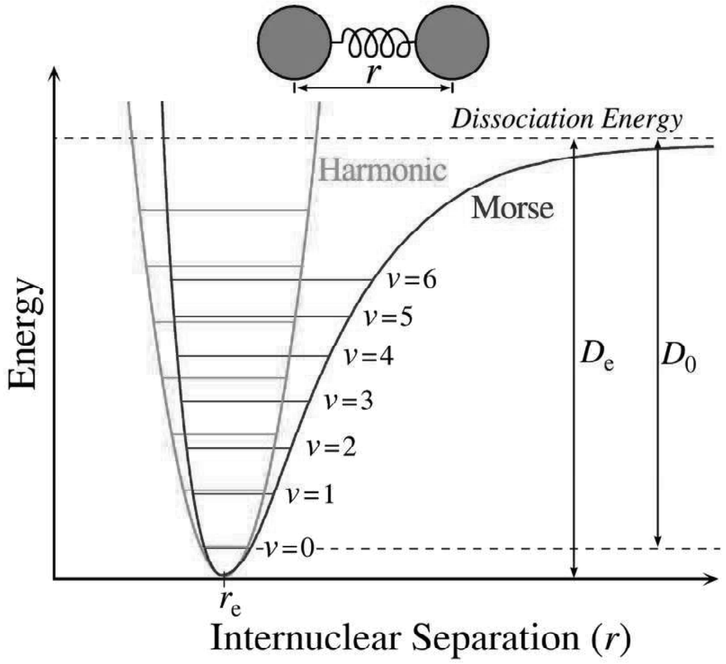


Fig 2.3 *Moarse Potential Energy Diagram*

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 α controls the 'width' of the potential (the smaller a is, 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 (stiffness) 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, α, is

NOTES

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

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

2.3.7 Vibration Rotation Spectroscopy

Vibration-Rotation Spectra: Vibration-rotation spectra are exhibited by diatomic molecules with permanent dipole moments, Homonuclear diatomic molecules with permanent dipole moments, Homonuclear diatomic molecules, such as O_2, Cl_2 of H_2, do not show vibration-rotation spectra since they do not have permanent dipoles.

In typical diatomic molecule the rotational levels are separated by 1–10 cm^{-1} while the vibrational level are separated by nearly 3000 cm^{-1}. Therefore, to a first approximation rotational and vibrational motions can be considered independently. The rotational and vibrational energy is the sum of the separate energies, i.e.,

$$E_{\text{total}} = E_{\text{rot}} + E_{\text{vib}} \text{ (Joules)}$$

$$\in_{\text{total}} = \in_{\text{rot}} + \in_{\text{vib}} \text{ (cm}^{-1}\text{)}$$

$$\in_{J,v} = \in_J + \in_v$$

$$\in_{J,v} = \text{BJ } (J+1) - DJ^2(\text{J}+1)^2 + \ldots + \left(v+\frac{1}{2}\right)\overline{w}_e - x_e\left(v+\frac{1}{2}\right)^2 \overline{w}_e \quad \ldots(1)$$

Ignoring D the non-rigidity constant in (Equation 11), we get,

$$\in_{J,v} = \text{BJ (J + 1)} + \left(v+\frac{1}{2}\right)\overline{w}_e - x_e\left(v+\frac{1}{2}\right)^2 \overline{w}_e$$

$$\in_{J,v} = \text{BJ } (J+1) + \left(v+\frac{1}{2}\right)\overline{w}_e - x_e\left(v+\frac{1}{2}\right)^2 \overline{w}_e$$

The selection rules are

$$\Delta v = \pm 1, \pm 2, \text{ etc.}, \Delta J = \pm 1 \quad \ldots(2)$$

It is the convention in spectroscopy to use single prime for the upper state and double prime for the lower state.

Let us consider the transition from $v = \text{o} \rightarrow v = 1$

$$\Delta \in_{Jv} = \in_{\text{J}',\text{v}} = 1 - \in_{\text{J}'',\text{v}=0}$$

$$\Delta\in_{J,v} = \left\{BJ'(J'+1) + 1\frac{1}{2}\overline{w}_e - 2\frac{1}{4}x_e\overline{w}_e\right\} - \left\{BJ''(J''+1) + \frac{1}{2}\overline{w}_e - \frac{1}{4}\overline{w}_e x_e\right\} \quad \ldots(3)$$

$$\Delta\in_{J,v} = \bar{w}_e\left(1-2x_e\right) + B\left(J'-J''\right)\left(J'+J''+1\right)cm^{-1} \qquad ...(4)$$

Where $\bar{w}_0 = \bar{w}_e(1-2x_e)$

$$\Delta\in_{J,v} = \overline{w}_0 + B(J'-J'') + (J'+J''+1) \qquad ...(5)$$

Here two cases arise

Case I$\Delta J + 1$ $J' = J'' + 1;\ J' = J'' = 1$

$$\Delta\in_{J,v} = \overline{w}_0 + 2B(J''+1)\ \text{cm}^{-1} \qquad ...(6)$$

Case II$\Delta J = -1$ $J'' = 0\ 1, 2, ...$

$J'' = J' + 1 \quad J' - J'' = -1$

$$\Delta\in_{J,v} = \overline{w}_0 - 2B(J'+1)\ \text{cm}^{-1} \qquad ...(7)$$

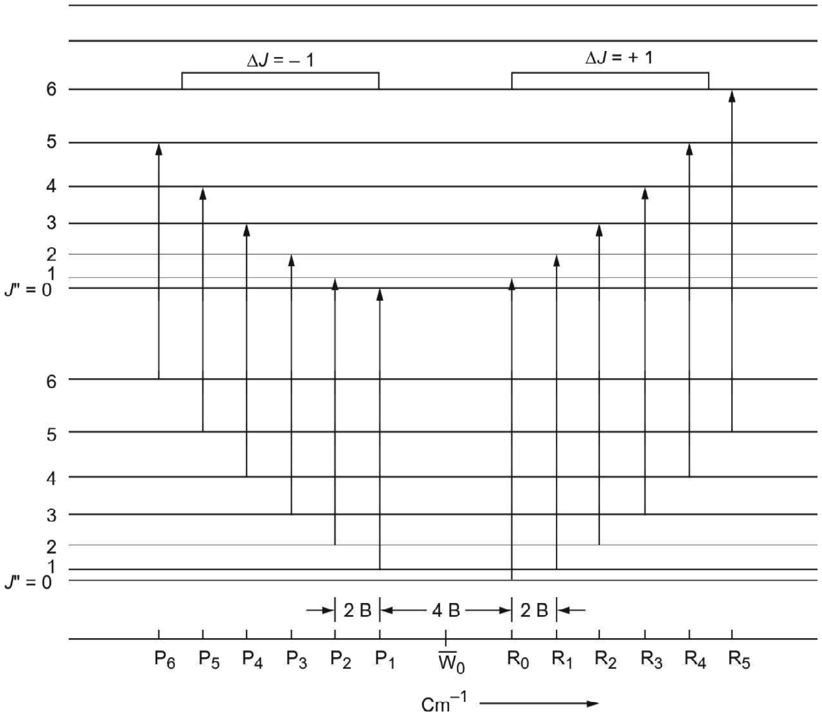


Fig. 2.4 *Vibration-Rotation Spectrum of HBr for Transition from* v = *0 to* v = *1*

These two expressions may be conveniently combined to

$$\Delta \in_{J,v} = \bar{w}_0 - 2Bm \quad \text{cm}^{-1}; \quad m = 1, 2, ... \qquad ...(8)$$

$\bar{w}_0$ is called the band origin or centre lines corresponding to the low frequency side of $\bar{w}_0$ corresponding m negative ($\Delta I = -1$) are called P branch and those corresponding to m positive ($\Delta J = -1$) are called R branch

lines arising from ΔJ=	-2	-1	0	$+1$	$+2$
	O	P	Q	R	S

Figure 2.4 shows the vibrational levels of a diatomic molecule

2.3.8 P-Q-R Branches

Each of the normal modes of vibration of heteronuclear diatomic molecules in the gas phase also contains closely-spaced (1-10 cm-1 difference) energy states attributable to rotational transitions that accompany the vibrational transitions. A molecule's rotation can be affected by its vibrational transition because there is a change in bond length, so these rotational transitions are expected to occur. Since vibrational energy states are on the order of 1000 cm-1, the rotational energy states can be superimposed upon the vibrational energy states.

We treat the molecule's vibrations as those of a harmonic oscillator (ignoring anharmonicity). The energy of a vibration is quantized in discrete levels and given by

$$E_v = h\nu\left(v + \frac{1}{2}\right)$$

Where v is the vibrational quantum number and can have integer values 0, 1, 2..., and ν is the frequency of the vibration given by:

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

Where k is the force constant and μ is the reduced mass of a diatomic molecule with atom masses m_1 and m_2, given by

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

We treat the molecule's rotations as those of a rigid rotor (ignoring centrifugal distortion). The energy of a rotation is also quantized in discrete levels given by

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

In which ***I*** is the moment of inertia, given by

$I=\mu r^2$

where μ is the reduced mass from above and r is the equilibrium bond length.

Experimentally, frequencies or wavenumbers are measured rather than energies, and dividing by h or hc gives more commonly seen term symbols, F(J) using the rotational quantum number J and the rotational constant B in either frequency

$$F(J) = \frac{E_r}{h} = \frac{h}{8\pi^2 I}J(J+1) = BJ(J+1)$$

or wavenumbers,

$$F(J) = \frac{E_r}{hc} = \frac{h}{8\pi^2 cI}J(J+1) = BJ(J+1)$$

The transition ΔJ = 0 (i.e. $J'' = 0$ and $J' = 0$), but where $v_0 = 0$ and Δv = +1, is forbidden and the pure vibrational transition is not observed in most cases. The rotational selection rule gives rise to an R-branch (when ΔJ = +1) and a P-branch (when ΔJ = –1). Each line of the branch is labeled R(J) or P(J), where J represents the value of the lower state.

R-Branch: When $\Delta J = +1$, i.e., the rotational quantum number in the ground state is one more than the rotational quantum number in the excited state – R branch (in French, riche or rich). To find the energy of a line of the R-branch:

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$$\begin{aligned}\Delta E &= h\nu_0 + hB\,[J(J+1) - J'(J'+1)] \\ &= h\nu_0 + hB\,[(J+1)(J+2) - J(J+1)] \\ &= h\nu_0 + 2hB(J+1)\end{aligned}$$

P-Branch: When $\Delta J = -1$, i.e., the rotational quantum number in the ground state is one less than the rotational quantum number in the excited state – P branch (in French, pauvre or poor). To find the energy of a line of the P-branch:

$$\begin{aligned}\Delta E &= h\nu_0 + hB\,[J(J+1) - J'(J'+1)] \\ &= h\nu_0 + hB\,[J(J-1) - J(J+1)] \\ &= h\nu_0 - 2hBJ\end{aligned}$$

Q-Branch: At the point when $\Delta J = 0$, i.e., the rotational quantum number in the ground state is equivalent to the rotational quantum number in the energized state - Q branch (basic, the letter among P and R). To find the energy of a line of the Q-branch:

$$\begin{aligned}\Delta E &= h\nu_0 + hB[J(J+1) - J'(J'+1)] \\ &= h\nu_0\end{aligned}$$

The Q-branch can be seen in polyatomic atoms and diatomic molecules with electronic angular momentum in the ground electronic state, e.g., nitric oxide, (NO). Most diatomic molecules, like O_2, have a little snapshot of inactivity and along these lines smaller angular momentum and yield no Q-branch.

2.3.9 Breakdown of Oppenheimer Approximation:

The Born–Oppenheimer (B-O) approximation is the best known mathematical approximation in molecular dynamics. Specifically, it is the assumption that the motion of atomic nuclei and electrons in a molecule can be treated separately, based on the fact that the nuclei are much heavier than the electrons. The approach is named after Max Born and J. Robert Oppenheimer who proposed it in 1927, in the early period of quantum mechanics.

The approximation is widely used in quantum chemistry to speed up the computation of molecular wave functions and other properties for large molecules. There are cases where the assumption of separable motion no longer holds, which make the approximation lose validity, it is said to 'break down', but is then often used as a starting point for more refined methods.

In molecular spectroscopy, using the BO approximation means considering molecular energy as a sum of independent terms, for example:

$$\mathbf{E}_{\text{Total}} = \mathbf{E}_{\text{Electronic}} + \mathbf{E}_{\text{Vibrational}} + \mathbf{E}_{\text{Rotational}} + \mathbf{E}_{\text{Nuclear Spin}}$$

These terms are of different orders of magnitude and the nuclear spin energy is so small that it is often omitted. The electronic energies $\mathbf{E}_{\text{Electronic}}$ consist of kinetic energies, interelectronic repulsions, internuclear repulsions, and electron–nuclear attractions, which are the terms typically included when computing the electronic structure of molecules.

The benzene molecule consists of 12 nuclei and 42 electrons. The Schrödinger equation, which must be solved to obtain the energy levels and wave function of this molecule, is a partial differential eigenvalue equation in the three-dimensional coordinates of the nuclei and electrons, giving 3 × 12 + 3 × 42 = 36 Nuclear + 126 Electronic = 162 Variables for the wave function. The computational complexity, i.e., the computational power required to solve an eigenvalue equation, increases faster than the square of the number of coordinates.

When applying the Born–Oppenheimer (B-O) approximation, the following two consecutive steps are significant:

For a given position of the nuclei, the electronic Schrödinger equation is solved, while treating the nuclei as stationary (not "coupled" with the dynamics of the electrons). This corresponding eigenvalue problem then consists only of the 126 electronic coordinates. This electronic computation is then repeated for other possible positions of the nuclei, i.e. deformations of the molecule. For benzene, this could be done using a grid of 36 possible nuclear position coordinates. The electronic energies on this grid are then connected to give a potential energy surface for the nuclei. This potential is then used for a second Schrödinger equation containing only the 36 coordinates of the nuclei.

The slope of the potential energy surface can be used to simulate molecular dynamics, using it to express the mean force on the nuclei caused by the electrons and thereby skipping the calculation of the nuclear Schrödinger equation.

Principally, the Born-Oppenheimer (B-O) approximation is the assumption that the electronic motion and the nuclear motion in molecules can be separated. It leads to a molecular wave function in terms of electron positions and nuclear positions. Following are the assumptions:

1. The electronic wavefunction depends upon the nuclear positions but not upon their velocities, i.e., the nuclear motion is so much slower than electron motion that they can be considered to be fixed.
2. The nuclear motion, for example rotation, vibration, observes a smeared out potential from the speedy electrons.

If a Hamiltonian is separable into two or more terms, then the total eigenfunctions are products of the individual eigenfunctions of the separated Hamiltonian terms, and the total eigenvalues are sums of individual eigenvalues of the separated Hamiltonian terms.

Consider, for example, a Hamiltonian which is separable into two terms, one involving coordinate q_1 and the other involving coordinate q_2.

$$H = H_1(q_1) + H_2(q_2)$$

With the overall Schrödinger equation being,

$$H\psi(q_1, q_2) = E\psi(q_1, q_2)$$

If we assume that the total wavefunction can be written in the form $\psi(q_1, q_2) = \psi_1(q_1)\psi_2(q_2)$, where $\psi_1(q_1)$ and $\psi_2(q_2)$ are eigenfunctions of H_1 and H_2 with eigenvalues E_1 and E_2, then,

$$\begin{aligned} H\psi(q_1, q_2) &= (H_1 + H_2)\psi_1(q_1)\psi_2(q_2) \\ &= H_1\psi_1(q_1)\psi_2(q_2) + H_2\psi_1(q_1)\psi_2(q_2) \\ &= E_1\psi_1(q_1)\psi_2(q_2) + E_2\psi_1(q_1)\psi_2(q_2) \\ &= (E_1 + E_2)\psi_1(q_1)\psi_2(q_2) \\ &= E\psi(q_1, q_2) \end{aligned}$$

Thus the eigenfunctions of H are products of the eigenfunctions of H_1 and H_2, and the eigenvalues are the sums of eigenvalues of H_1 and H_2.

The eigenfunctions and eigenvalues of this Hamiltonian can be given by solution of the time-independent Schrödinger equation of the form,

$$[T_N + T_e + V_{ee}(\mathbf{r}) + V_{NN}(\mathbf{R}) + V_{eN}(\mathbf{r}, \mathbf{R})]\,\Psi(\mathbf{r}, \mathbf{R}) = E\Psi(\mathbf{r}, \mathbf{R}).$$

Using the Born-Oppenheimer approximation considering that there is a strong separation of time scales between the electronic and nuclear motion, since the electrons are lighter than the nuclei by three orders of magnitude. This can be broken by assuming a quasi-separable form,

$$\Psi(\mathbf{x}, \mathbf{R}) = \phi_e(\mathbf{x}, \mathbf{R})\phi_N(\mathbf{R})$$

Where $\phi_N(\mathbf{R})$ is a nuclear wave function and $\phi_e(\mathbf{x}, \mathbf{R})$ is an electronic wave function that depends parametrically on the nuclear positions.

Fundamentally, the Born-Oppenheimer (B-O) approximation is based on the fact that nuclei are several thousand times heavier than electrons. The proton, itself, is approximately 2000 times more massive than an electron. The electrons can be regarded as particles that follow the nuclear motion adiabatically, meaning that they are 'dragged' along with the nuclei without requiring a finite relaxation time. This, certainly, is an approximation, since there could be non-adiabatic effects that do not allow the electrons to follow in this 'instantaneous' method, however, in many systems, the adiabatic separation between electrons and nuclei is an excellent approximation. Another consequence of the mass difference between electrons and nuclei is that the nuclear components of the wave function are spatially more localized than the electronic component of the wave function. In the classical limit, the nuclear are fully localized about single points representing classical point particles.

The B-O approximation recognizes the large difference between the electron mass and the masses of atomic nuclei, and correspondingly the time scales of their motion. Given the same amount of kinetic energy, the nuclei move much more slowly than the electrons. In mathematical terms, the BO approximation consists of expressing the wavefunction of a molecule as the product of an electronic wavefunction and a nuclear (vibrational, rotational) wavefunction. This enables a separation of the Hamiltonian operator into electronic and nuclear terms, where cross-terms between electrons and nuclei are neglected, so that the two smaller and decoupled systems can be solved more efficiently.

2.3.10 Vibrations of Polyatomic Molecules

NOTES

In a polyatomic molecule each atom is having three degrees of freedom in three directions which are at right angle 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.

These vibration are generally of two types:

1. **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.
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:
   - **(i) 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).
   - **(ii) Rocking:** In rocking, the structural unit swings back and forth in the plane of the molecule (in plane bending).
   - **(iii) Wagging:** In wagging, the structural unit swings back and forth out of the plane of the molecule (out of plane bending).
   - **(iv) 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.

2.3.11 Selection Rules

Infrared radiation can induce transition among the vibrational energy levels only when the vibration of molecule leads to an oscillating dipole moment. If this happens then vibrational absorption spectrun is observed. This means that symmetrical molecules like H_2, N_2, O_2 etc. will not show any absoption in infrared region while unsymmetrical molecules like HCl, CO, NO_2, etc. will give infrared absorption spectra.

Absorption of infrared radiations causes significant change in the existing molecular vibrations and during transition change in vibrational quantum number can only be ± 1.

Different types of bonds absorb different infrared radiations as the absorption frequency or wave number of radiation is related to the mass of atoms involved as well as the strength of bond connecting them.

Also the different chemical bonds in a molecule involve different values of force constant and reduced masses hence absorption of radiations will occur over a wide range of frequencies. Thus in infrared spectrum of even a simple compound a series of absorption bands are observed due to stretching and bending vibrations.

A polyatomic non-linear molecule having n number of atoms has a total of $3n$ degrees of freedom and since 3 of these are transitional degrees of freedom and 3 are rotational degree of freedom, there will be $3n - 6$ vibrational degree of freedom. For a linear molecule the figure is reduced to $3n - 5$. Hence, if vibrations corresponding to all these degrees of freedom are associated with oscillating dipole moments, there will be as many absorption bands.

Additional non-fundamental absorption bands may be observed due to presence of overtones or harmonics that occur with reduced intensity, *i.e.*, half or one third of wavelength of fundamental vibrations. Combination bands (sum of two or more bands) and difference bands (difference of two or more bands) may also appear in IR absorption spectra.

2.3.12 Normal Modes of Vibration

Vibrations in the molecules can be of two types:

(*i*) **Stretching** in which the distance between two atoms increases or decreases but the atoms remain in the same bond axis; and

(*ii*) **Bending** (or deformation), in which the position of atoms, relative to the original bond axis, changes. These stretching and bending vibrational modes are shown in the Figure 2.5 below:

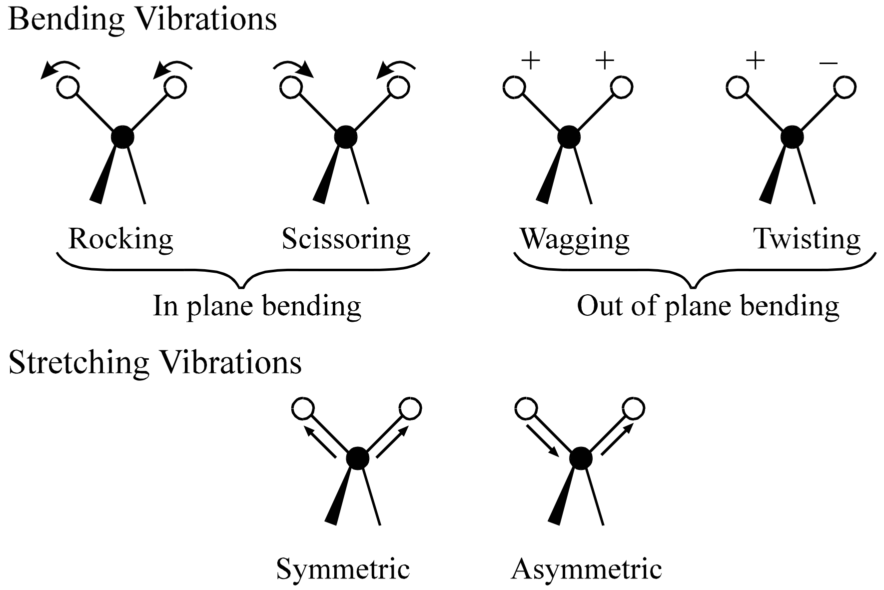


Fig. 2.5 *Stretching and bending vibrations.*

These stretching and bending vibrations of a bond are quantized and when infrared radiations of matching frequency are incident upon the molecule energy is absorbed and the amplitude of the vibration increases. The absorbed energy is finally released as heat.

The energy required for bending vibrations is much less than that required for stretching vibration. Consequently the bending vibrations occur at lower frequency.

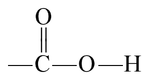
Stretching vibrations are denoted by ν while bending vibrations are denoted by δ.

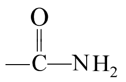
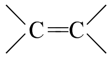
In addition to these, stretching and bending vibrational energy changes, absorption of lower frequency radiations in IR region also causes rotational motion. The region between 7–11 μ (1430–910 cm^{-1}) shows a number of absorption bands corresponding to vibrational and rotational motion which are characteristic of a particular molecule. Hence this region is regarded as the *fingerprint* region in IR spectra because no two compounds can have identical spectra in this region.

It may be noted that actual number of absorption bands observed for a polyatomic molecule are far less than expected theoretically. This may be due to weak vibrational bands, degeneration of bands or absent due to no change in dipole moment.

Table 2.1 lists the characteristic absorption frequencies of principal groups and bonds in IR region, based on the data available in the literature.

Table 2.1 *Characteristic absorption frequencies in IR*

Group	*Class of Compound*	*Type of Vibration*	*Wave number range cm^{-1}*
	Pr. Alcohol	ν (O—H)	3630
—O— H	Sec. Alcohol	δ (O—H)	3620
	Alcohols	ν (O—H)	1350–1260
	Phenol	ν (O—H)	3600
		δ (O—H)	1410
	Alcohols	ν (C—O)	1080–1010
	Phenols	ν (C—O)	1230–1140
C—O	Ethers	ν (C—O)	1150–1080
	Esters	ν (C—O)	1200
	Aldehyde	ν (C═O)	1730–1700
	Ketones	ν (C═O)	1720–1660
	Esters	ν (C═O)	1735
 $\overset{\overset{\displaystyle O}{\|}}{—C}—O—H$	Acids	ν (C═O)	1725
		ν (O—H)	3500
		ν (C—O)	1320–1210
—NH$_2$	Amines	ν (N—H)	3450–3400
		ν (C—N)	1340–1250
		δ (N—H)	1650

 $-\overset{\overset{\displaystyle O}{\parallel}}{C}-NH_2$	Amides	ν (N—H)	3500
		ν (C═O)	1690
		δ (N—H)	1600
—C≡N	Cyanides	ν (C≡N)	2250–2225
	Aromatic Nitro	ν (N═O)	1550–1510 1365–1335
	Aliphatic Nitro	ν (N═O)	1565–1510 1385–1360
	Alkene	ν (C═C)	1680–1600
		ν (C—H)	3090–3040
		δ (C—H)	1420, 995–915
—C≡C—	Alkyne	ν (C≡C)	2250–2100
		ν (C—H)	3200
		δ (C—H)	650
R—X	Alkyl halide	ν (C—F)	1400–1000
		ν (C—Cl)	800–600
		ν (C—Br)	600–500
		ν (C—I)	500
	Alkane	ν (C—H)	3000–2850
	Alkene	ν (C—H)	3100–3000
	Alkyne	ν (C—H)	3300

2.3.13 Group Frequencies

The approximate frequency (or wave number) at which an organic functional group 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*. The group 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.

Hooke's Law

For stretching vibrations the bond between two atoms may be considered to be similar to the vibration of two balls at the end of a spring a situation to which **Hooke's law** applies. It states "Tension in a spring is proportional to extension from its natural length."

Tension (T) = ($I - I_0$) and hence frequency of vibration $\nu = K\sqrt{f/\mu}$

where K = Stiffness constant, I_0 = Original length of spring, I = Extended length of spring, f = Force constant and μ = Reduced mass.

Thus the vibration frequency (ν) is directly related to force constant (f) of the bond and inversely related to reduced mass (μ) of the vibrating atoms. Therefore the force constant is a measure of the resistance to vibration which in turn is related to bond energy. It is therefore to be expected that stronger bonds among atoms of comparable mass will absorb at higher frequency which is in accordance with bond strength. The strength of bond and absorption frequencies for C—C bonds are in the order triple > double > single.

NOTES

2.3.14 Hot Bands and Overtones

A hot band is a band centered on a hot transition, which is a change between two excited vibrational states, i.e., neither of them is the general ground state. In infrared or Raman spectroscopy, hot bands allude to the transitions for a specific vibrational mode that emerges from a state containing the thermal population of the other vibrational mode.

Hot bands are unmistakable from the combination bands, which include concurrent excitation of multiple normal modes with a solitary photon, and overtones, which are the transitions that include changing the vibrational quantum number for a typical mode by more than 1.

- **Vibrational Hot Bands:** In the harmonic oscillations, the normal modes of an atom are not coupled, and all vibrational quantum levels are spaced equally, so the hot bands would not be discernable from so-called basic transitions emerging from the overall vibrational ground state. In any case, vibrations of real molecules normally have some anharmonicity, which causes coupling between various vibrational modes that move the observed frequencies of hot bands in the vibrational spectra. Since anharmonicity diminishes the spacing between the nearby vibrational levels, hot bands exhibit the redshift (show up at lower frequencies than the relating fundamental transitions). The magnitude of the observed shift is related to the level of anharmonicity in comparing normal modes.
- **Combination Bands:** As referenced above, combination bands include changes in vibrational quantum quantities of more than one normal mode. These changes are prohibited by consonant oscillator selection rules, yet are seen in vibrational spectra of real systems due to anharmonic couplings of normal modes. Combination bands regularly have weak spectral intensities, yet can turn out to be very intense in situations where the anharmonicity of the vibrational potential is large.

2.3.15 Factors Affecting the Band Intensities and Positions

There are many factors that affect the band positions and intensities in a spectra. Some of them are as follows:

(i) **Electronegativity of Bonded Atoms**. The stretching frequency of bonds joining atoms increases with increase in electronegativity of constituent atoms. The electronegativity of $O > N > C$ and consequently.

O—H	N—H	C—H
$\nu = 3600\ \text{cm}^{-1}$	$\nu = 3500\text{–}3300\ \text{cm}^{-1}$	$\nu = 3000\text{–}2850\ \text{cm}^{-1}$

The greater the electronegativity of X in RCOX higher is the frequency of absorption.

The N—H bond stretching frequency are lowered to a lesser extent than O—H bond stretching due to H-bonding.

(ii) Atomic Weight of Bonded Atoms: the greater the atomic weight of involved atoms, lower is the stretching frequency. Thus,

O — H	O — D	C — H	C — D
ν=3600 cm^{-1}	ν=2600 cm^{-1}	ν=3000–2850 cm^{-1}	ν=2200 cm^{-1}

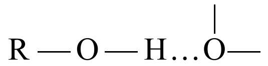
(iii) Hydrogen Bonding: Hydrogen bonding generally lowers the stretching frequency but increases the bending frequency.

R — O — H

Isolated in very dilute solution

ν (O—H) = 3600 cm^{-1}

δ(O—H)= 1350 cm^{-1}



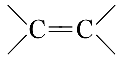
$$R — O — H \ldots \overset{|}{O} —$$

Alcocol (hydrogen bonded)

ν (O—H) = 3500 cm^{-1}

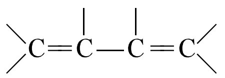
δ(O—H)= 1430 cm^{-1}

(iv) Conjugation. The stretching frequency of multiple bonds is decreased due to conjugations as it increases the bond length by resonance.



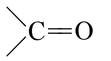
Isolated

ν = 1680 cm^{-1}



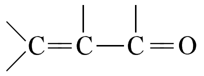
Conjugated

ν = 1600 cm^{-1}



Isolated

ν = 1720 cm^{-1}



Conjugated

ν = 1675 cm^{-1}

2.3.16 Far IR Region, Metal Ligand Vibrations and Normal Co-ordinate Analysis

Far infrared (FIR) is a region in the infrared spectrum of electromagnetic radiation. Far infrared is often defined as any radiation with a wavelength of 15 micrometers (μm) to 1 mm (corresponding to a range of about 20 THz to 300 GHz), which places far infrared radiation within the CIE IR-B and IR-C bands. The long-wave side of the FIR spectrum overlaps with so named terahertz radiation. Different sources use different boundaries for the far infrared; for example, astronomers sometimes define far infrared as wavelengths between 25 μm and 350 μm.

Metal Ligand Vibrations

The tendency to form predominantly covalent bonds between metals and donor atoms of ligands is greatest when the donor atom is a nonmetal from Group V through VII in the periodic table. The recent interest in the far-infrared region has centered on the search for vibrations involving metal-ligand donor atoms. It is difficult to prepare compounds in which the donor atom is replaced by an atom of the same group in the periodic table but of heavier mass and observe the shift of the metal-ligand vibration toward lower frequency as has been done with the metal-halide vibrations.

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 a basis to calculate fundamental frequencies of larger polyatomic molecules. The intramolecular force constants are associated to the electronic structure and these can be correlated with bond nature, interatomic repulsion and electron delocalization.

Check Your Progress

7. What is the range of the far IR region?
8. What do you understand by symmetric stretching?
9. What do you understand by asymmetric stretching?
10. Define bending vibrations.
11. What is Rayleigh scattering?
12. State the mutual exclusion principle.

2.4 RAMAN SPECTROSCOPY

When a beam of monochromatic visible or ultraviolet light is passed through a homogeneous medium, some light may be absorbed, some will be transmitted and some of it will be scattered. The scattered energy will consist almost entirely of radiation of the incident frequency. This is known as Rayleigh scattering, but in addition, certain, discrete frequencies above and below that of the incident beam will be scattered; this is referred to as Raman scattering.

The schematic arrangement for recording Raman spectrum is shown in Figure 2.6

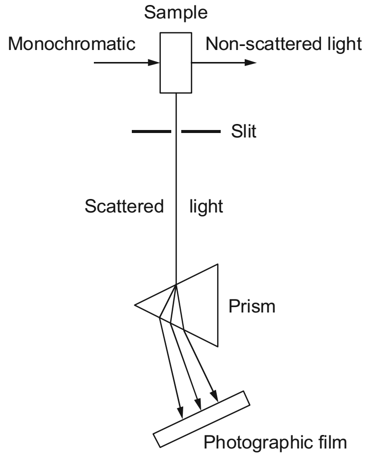


Fig. 2.6 Schematic Diagram for Raman Spectroscopy

Raman found that the difference, Δv, between the incident and scattered radiation is constant, characteristic of the substance irradiated and is completely independent of the frequency of the incident radiation. In the Raman spectrum, the radiation scattered with a frequency lower than that of the incident beam is known as stokes radiation while that of the higher frequency is called antistokes radiation. Stokes radiation is generally more intense than anti-stokes. The Raman spectra can be used to study the vibration energy levels of molecules.

The differences between the frequencies of the scattered light and the frequency of the incident light correspond to transition between vibrational and rotational energy levels in the molecule. Thus, Raman spectroscopy essentially provides the same kind of information as infrared spectroscopy with one important difference, i.e., a given molecular vibration will be Raman active only if there is a change in the polarizability of the molecule during the vibration. Qualitatively, it is associated with the deformation of electron cloud surrounding a molecule. The polarizability of a molecule will change during vibration if during vibration, the electron cloud become compact or diffuse in going from one extreme vibrational configuration to another. The numbers of fundamental molecular vibrations which are infrared active or Raman active can be predicted for any molecular geometry. The proposed geometry of a molecule is confirmed by the agreement of its observed spectrum with the predicted spectrum.

2.4.1 Classical and Quantum Theories of Raman Effect

1. Classical Theory: : The classical hypothesis of the Raman Effect depends on the polarizability of atoms and molecules, which reflects how simple an electron haze of a molecule can be mutilated by an electric field (light). The technique depends on the molecular distortions in electric field E determined by molecular polarizability α. The laser beam can be considered as a wavering electromagnetic wave with electrical vector E. On interacting with the sample it actuates electric dipole moment $P = \alpha E$ which deforms molecules. Due to the periodical deformity, particles begin vibrating with a specific frequency (McCreery, 2000).

The dissipated light can have a frequency equivalent to the incident light (Rayleigh), equivalent to the incident light excluding the vibrational frequency (Stokes) and equivalent to the occurrence light in addition to the vibrational frequency (anti-Stokes).

2. Quantum Theory of Raman Effect: At the point when light collaborates with the matter, the photons which make up the light might be retained or scattered, or they may directly pass through the material (Smith and Dent, 2005). Whenever monochromatic light interacts with molecules, a large portion of the photons are scattered with no adjustment of energy. This interaction is called versatile or Rayleigh scattering, and it happens when the electrons in an atom sway in resonance with the applied electric field of the incident light. However, few photons (1 out of 106 to 109) are inelastically scattered and go through an adjustment of energy.

The relationships between energy, frequency, wave number and the wavelength are as follows:

E = hv (h is Planck's constant, and v is frequency in sec-1)

E = hcν (c is the speed of light in cm/sec, and ν is wave number in cm-1)

N = 1/λ (λ is wavelength in nm)

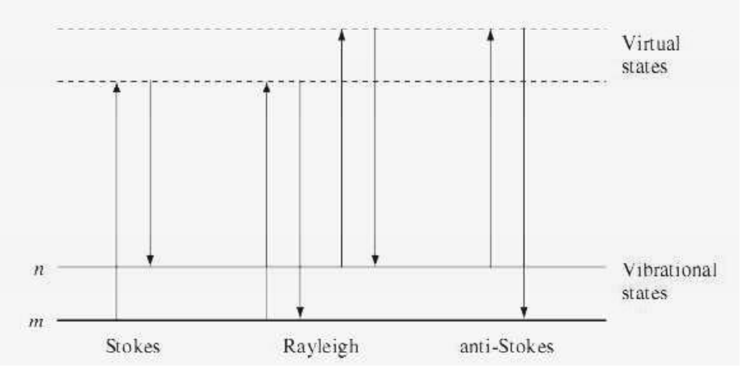


Fig 2.7 *Diagram of Rayleigh and Raman Scattering Processes*

The inelastic scattering process is called Raman scattering (Raman Effect). The change in photon energy occurs because a molecule may vibrate during the time the electrons oscillate in resonance with the applied electric field. A vibrational mode that changes molecular polarizability (dipole moment induced by electric field) results in a change of incident photon energy. The difference in energy between the incident photons and in-elastically scattered photons is called Raman shift. A plot of the intensity of the in-elastically scattered light as a function of the energy change is called Raman Spectrum.

2.4.2 Rotational, Vibrational, and Vibrational-Rotational Raman Spectra

(i) Rotational Absorption Spectra: Pure rotational absorption spectra are observed in the far infrared and microwave regions of the electromagnetic spectrum. The molecule must have a permanent dipole moment, before it can produce the rotational absorption spectra. Rotational energy levels are spaced close together with separations of ~300 cal. The energies of the rotational levels of a diatomic molecule AB is given by

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

Where J is the rotational quantum number and I is the moment of inertia given by,

$$I = \left(\frac{m_A m_B}{m_A + m_B}\right) r_{AB}^2 \qquad ...(2)$$

Where m_A and m_B are the respective masses of the atoms and r_{AB} is the bond length. The term inside the brackets is called the reduced mass of the molecule and is denoted by μ. Transitions occur only between adjacent quantum levels, that is the permitted transitions according to the selection rule is,

$$\Delta J = \pm 1$$

When a molecule is raised form one rotation level to another, i.e., from quantum number $J-1$ to the level J, the energy emitted is given by,

$$h\nu = E_J - E_{J-1}$$

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

$$\nu = \frac{h^2}{4\pi^2 I}J$$

Or $$\nu = \frac{h}{4\pi^2 I}J \quad ...(3)$$

From Equation (2), it is clear that the spacing between the lines is equal to $\frac{h}{4\pi^2 I}$. In terms of wave number, we have

Or $$\bar{\nu} = \frac{1}{\lambda} = \frac{\upsilon}{c} = \frac{h}{4\pi^2 cI} \quad ...(4)$$

The moment of inertial is obtained from the measured spacing between the lines in the rotational spectrum. The bond length r_{AB} can thus, be determined for heteronuclear diatomic molecule from the knowledge of I and μ.

(ii) Vibrational Spectra: Atoms within molecules may vibrate about their average positions undergoing periodic displacements from positions. The vibration of an atom with respect to other atoms in a molecule involves bending or stretching of the valence bonds which hold it. Vibrational spectra result from the changes in vibrational energy levels. All the vibrations of a molecule can be described as one or a combination of a certain number of fundamental modes of vibration. Consider a molecule containing n atoms. The position of each atom can be defined by specifying the three coordinates, i.e., x, y and z Cartesian coordinates. This will give rise to $3n$ number of coordinates. Since each coordinate value may be specified independently, a molecule of n atoms has $3n$ degrees of freedom. Once all $3n$ coordinates have been fixed, the bond distances and bond angles of the molecule are all fixed.

When a molecule is free to move in three dimensional space as a whole without change of shape, we can refer to such movement by noting the position of its centre of gravity at any instant and the position can be described if the values of its three coordinates is known. This translational motion use 3 degrees of freedom and hence the remaining degrees of freedom will be $3n-3$. Similarly, the rotation of a non-linear molecule can be resolved into components about three perpendicular axes and this will require three degree of freedom. The molecule will now be left with $3n-6$ degrees of freedom.

Therefore, for a non-linear molecule, the number of fundamental vibrations $= 3n - 6$.

If the molecule is linear, there is no rotation about the bond axis, hence only two degrees of rotational freedom are required leaving $3n-5$ degrees of vibrational freedom. It can be shown from quantum mechanical considerations that the vibrational energy levels of a molecule are given by:

$$E = \left(v + \frac{1}{2}\right) h v_0 \qquad ...(5)$$

Where v is the vibrational quantum number.

The vibrational frequency ν of a diatomic molecule is given by Hook's law. The two atoms and their connecting bond are treated as a simple harmonic oscillator composed of two masses M_x and M_y connected by a spring.

$$\bar{v} = \frac{1}{2\pi c}\left(\frac{\dfrac{f}{M_x M_y}}{M_x + M_y}\right)^{1/2} \qquad ...(6)$$

Where $\bar{v}$ = Vibrational Frequency (cm^{-1})

c = Velocity of Light

f = Force Constant of the Bond

The value of f is approximate 5×10^5 dynes per cm for single bonds and approximately 2 and 3 times this value for double bonds and triple bonds respectively. The frequency of infra-red absorption is commonly used to calculate the force constants of bonds. In the IR studies the wave number ($\bar{v}$) are often called frequencies though it is not rigorously correct. B and intensities are expressed either as transmittance (T) or absorbance (A).

(iii) Vibration-Rotation Spectra: Vibration-rotation spectra is exhibited by diatomic molecules with permanent dipole moments. Homonuclear diatomic molecules, such as O_2, Cl_2 of H_2, do not show vibration-rotation spectra since they do not have permanent dipoles.

In typical diatomic molecule the rotational levels are separated by 1–10 cm^{-1} while the vibrational level are separated by nearly 3000 cm^{-1}. Therefore, to a first approximation rotational and vibrational motions can be considered independently.

2.4.3 Selection Rules

For Raman spectra the molecules undergo transitions in which an **incident** photon is absorbed and another **scattered** photon is emitted. The general selection rule for such a transition to be allowed is that the molecular polarizability must be anisotropic, which means that it is not the same in all directions. Polarizability is a 3-dimensional tensor that can be represented as an ellipsoid. The polarizability ellipsoid of spherical top molecules is in fact spherical so those molecules show no rotational Raman spectrum. For all other molecules both Stokes and anti-Stokes lines can be observed and they have similar intensities due to the fact that many rotational states are thermally populated. The selection rule for linear molecules is **$\Delta J = 0, \pm 2$**. The reason for the values **±2** is that the polarizability returns to the same value twice during a rotation. The value **$\Delta J = 0$** does not correspond to a molecular transition but rather to Rayleigh scattering in which the incident photon merely changes direction.

The selection rule for symmetric top molecules is,

ΔK = 0

If **K = 0,** then **ΔJ** = **±2**

If **K ‘d 0**, then **ΔJ = 0, ±1, ±2**

Transitions with **ΔJ = +1** are said to belong to the **R** series, whereas transitions with **ΔJ = +2** belong to an **S** series. Since Raman transitions involve two photons, it is possible for the molecular angular momentum to change by two units.

2.4.4 Mutual Exclusion Principle

Rule of Mutual Exclusion: It is a general rule which provides extremely useful information about the molecular structure. It states the following.

If a molecule has a centre of symmetry then Raman active vibrations are infrared inactive and *vice versa*. If there is no center of symmetry then some (note necessarily all) vibrations may be both Raman and infrared active.

The converse of this rule also holds, i.e., In case there are no common lines in the Raman and infrared spectra of a molecule, it implies that the molecule has a center of symmetry. Here a word of caution is necessary since sometimes the Raman spectra may be too weak to be detected. This may lead to wrong conclusion. But if some of the vibrational modes are both Raman and infrared active it is certain that the molecule does not have a center of symmetry.

Raman spectra and infrared spectra of a molecule help in the structure determination. Let us consider an example of a simple triatomic molecule of AB, type. Here it is to be decided whether the molecule is linear or not, and if linear whether it is symmetrical (B–A–B) or a symmetrical (B–B–A). In case of carbon dioxide CO_2 and nitrous oxide N_2O, both molecules give infrared bonds with PR contours they must therefore be linear. The mutual exclusion rule shows that CO_2 has a center of symmetry (O–C–O) while N_2O has not (N–N–O).

In case of a non-linear molecule the PR contours are absent and the rotational fine spectra is complicated.

We can study the rotations and vibrations of molecules such as O_2 or H_2 which are in accessible to infrared or microwave techniques. We can also observe the symmetric vibrations of CO_2 which produces no dipole change and therefore no infra-red spectrum. For center of symmetric molecules Raman and infra-red studies are exactly complementary. For other molecules too Raman technique yields data which can not be obtained otherwise.

Example 1: A molecule A_2B_2 has infrared absorptions and Raman spectral lines as in the following table.

cm^{-1}	*Infrared*	*Raman*
3374	—	Strong
3287	Very strong, PR contour	—
1973	—	Very strong
729	Very strong PQR contour	—
612	—	Weak

Deduce what you can regarding the structure of the molecule and assign the observed vibrations to particular molecular modes as far as possible.

Solution. The molecule is liner (PR contour of an infra-red band) and has a center of symmetry hence, is A–B–B–A. 3374 cm^{-1} and 3287 cm^{-1} are close to the ≡ C–H stretching frequency. So the molecule is acetylene HC≡CH.

3374 cm^{-1}; Symmetric C–H Stretch

3287 cm^{-1} Asymmetric C–H Stretch.

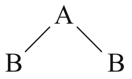
1973 cm^{-1}; a ≡ C Stretch

729 and 612 cm^{-1}; Bending Vibrations

Example 2 A molecule AB_2 has the following infrared and Raman spectra

cm^{-1}	Infrared	Raman
3756	Very strong Perpendicular	—
3652	Strong, Parallel	Strong, Polarised
1595	Very strong, Parallel	—

The rotational fine structure of the infrared bands is complex and does not show PR or PQR characteristics. Comment on the molecular structure and assign the observed lines to specific molecular vibrations as far as possible.

Solution: The molecule is non-linear and does not have an center of symmetry, hence  3756 cm and 3652 cm^{-1} are in the region of OH stretching frequency, so the molecule is H_2O Assignments:

3756 m^{-1} : Asymmetric Stretch

3652 cm^{-1} : Symmetric Stretch

1595 cm^{-1} : Bend

2.4.5 Resonance Raman Spectroscopy

Resonance Raman Spectroscopy (RR Spectroscopy) is a Raman spectroscopy procedure wherein the incident photon energy is close in energy to the electronic progress of a compound or material under assessment. The frequency coincidence event (or resonance) can prompt the incredibly upgraded intensity of the Raman scattering, which works with the analysis of substances present at low concentrations.

Raman spectroscopy and RR spectroscopy give data about the vibrations of molecules, and can likewise be utilized for distinguishing unknown substances. RR spectroscopy has tracked down wide applications to the investigation of bioinorganic molecules. The method estimates the energy expected to change the vibrational condition of an atom as the infrared (IR) spectroscopy. The mechanism and selection rules are different in every procedure, however, band positions are indistinguishable and thus the two strategies give correlative data.

RR spectroscopy is an augmentation of regular Raman spectroscopy that can give expanded aversion to specific (coloured) intensifies that are available at low concentrations (micro to millimolar) in a generally perplexing combination of compounds. A benefit of resonance Raman spectroscopy over (ordinary) Raman spectroscopy is that the intensity of bands can be expanded by a few significant degrees.

In resonance Raman spectroscopy, the frequency of the approaching photons harmonizes with the electronic transitions of the atom or molecule. Electronic excitation of a molecule brings about primary changes which are reflected in the improvement of Raman scattering of specific vibrational modes. Vibrational modes that go through an adjustment of bond length or potentially constant during the electronic excitation can show a huge expansion in polarizability and thus Raman intensity.

This is known as Tsuboi's rule, which gives a subjective connection between the idea of an electronic transition and the upgrade pattern in resonance Raman spectroscopy. The enhancement factor can be by a component of 10 to > 100,000 and is most evident on account of π-π* advances and least for metal focused (d-d) transitions.

Sample handling in Raman spectroscopy offers extensive benefits over FTIR spectroscopy in that glass can be utilized for windows, focal points, and other optical parts. A further benefit is that while water assimilates unequivocally in the infrared region, which restricts the path lengths that can be utilized and covering huge area of the range, the power of Raman dissipating from water is typically frail and direct absorption interferes just when close infrared lasers (e.g., 1064 nm) are utilized. Accordingly, water is an ideal solvent. Nonetheless, since the laser is engaged to a relatively smaller spot size, quick heating of tests can happen. Whenever resonance Raman spectra are recorded, nonetheless, sample heating and photo-bleaching can harm and change the Raman spectra that were obtained. Besides, on the off chance that the absorbance of the example is high (> OD 2) over the wavelength range in which the Raman spectra is recorded then inward channel impacts (reabsorption of the Raman scattering by the example) can decrease signal power drastically. Regularly, the example is set into a cylinder, which can then be turned to reduce the exposure of the sample to the laser light, and decrease the impacts of photo degradation. Gaseous, liquid and solid samples can be generally examined utilizing RR spectroscopy.

2.4.6 Coherent Anti Stokes Raman Spectroscopy

Coherent anti-Stokes Raman spectroscopy, likewise called Coherent anti-Stokes Raman scattering spectroscopy (CARS), is a type of spectroscopy utilized essentially in chemical science, physical science and related fields. It is sensitive to similar vibrational marks of molecules as seen in Raman spectroscopy, ordinarily the atomic vibrations of chemical bonds. Unlike Raman spectroscopy, CARS utilizes different photons to address the atomic vibrations and produces a coherent signal. Thus, CARS is significantly more grounded than spontaneous Raman emission. CARS is a third-order nonlinear optical interaction including three laser radiations: a pump beam of frequency ωp, a Stokes beam of frequency ωS and a probe beam frequency ωpr. These beams interact with the sample and create a coherent optical signal at the anti-Stokes frequency (ωpr+ωp-ωS). The last option is enhanced when the frequency distinction between the pump and the Stokes beams (ωp-ωS) corresponds with the frequency of a Raman resonance, which is the basis of this technique's natural vibrational contrast instrumentation.

The CARS can be described by utilizing either a traditional oscillator model or by utilizing a quantum mechanical model that fuses the energy levels of the atom. Conventionally, the Raman active vibrator is displayed as a (damped) harmonic oscillator with a characteristic frequency of ωv. In CARS, this oscillator isn't driven by a solitary optical wave, however, the distinct frequency (ωp-ωS) between the pump and the Stokes beams instead of it. This driving component is like hearing the low combination tone while striking out two different high vibe piano keys: your ear is delicate to the distinct frequency of the higher tones. Also, the Raman oscillator is susceptible to the distinct frequency of two optical waves. Whenever the distinct frequency ωp-ωS approaches ωv, the oscillator is driven effectively. On a molecular level, this infers that the electron cloud encompassing the substance bond is overwhelmingly wavering with the recurrence ωp-ωS. These electron movements adjust the optical properties of the example, for example, there is an occasional regulation of the refractive index of the material. This periodic modulation can be tested by a third laser beam, the probe beam. At the point when the probe beam is spreading through an intermittently altered medium, it secures a similar modulation. Part of the probe, initially at ωpr will currently get adjusted to ωpr+ωp-ωS, which is anti-Stokes emission. Under specific bar calculations, the counter Stokes discharge might diffract away from the probe beam and can be recognized in a different direction.

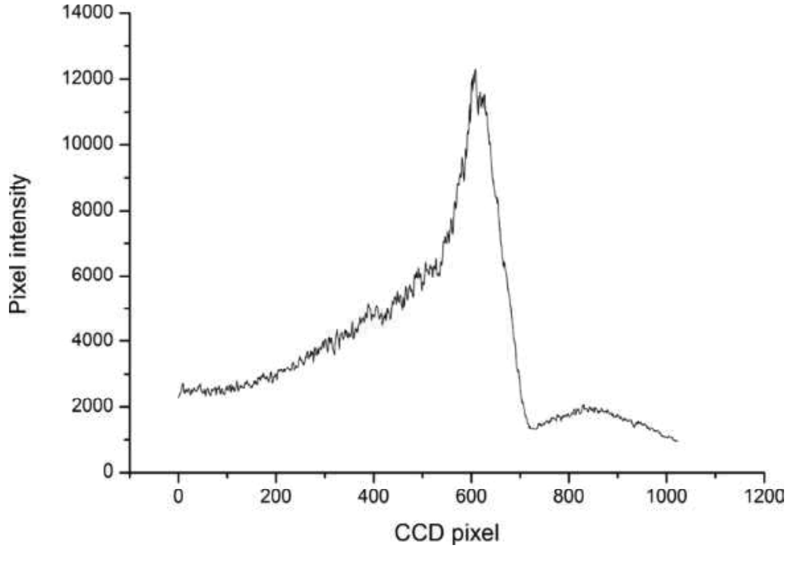


Fig 2.8 *Coherent Anti-Stokes Raman Spectrum of Microscopy Oil*

CARS is frequently compared with Raman spectroscopy as the two strategies test similar Raman dynamic modes. Raman spectroscopy should be possible utilizing a solitary consistent wave (CW) laser but CARS requires (normally) two pulsed laser sources. The Raman signal is distinguished on the red side of the approaching

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radiation where it may need to contend with other fluorescent processes. The CARS signal is identified on the blue side, which is liberated from fluorescence, however, it accompanies a non-resonant contribution. The distinctions between the signals from Raman and CARS (there are numerous variations of the two techniques) stems generally from the way that Raman depends on unconstrained transition while CARS depends on a coherently driven transition. The overall Raman signal gathered from a sample is emitted in every direction. The overall CARS signal comes from a coherent expansion of the signal from individual atoms. For the intelligible expansion, phase matching should be fulfilled. For tightly focused conditions, this is not a limitation. When phase matching is satisfied the signal amplitude increases directly with distance so the power increases quadratically. This sign structures a collimated beam that is easy to handle. The way that the CARS signal is quadratic somewhere far off makes it quadratic as for the fixation and consequently sensitive to the majority of constituents. The net CARS signal likewise contains an intrinsic non-resonant background. This non-resonant signal can be considered as the consequence of (a few) distant resonance transitions that additionally add coherently. To think about the spectra from multiple-components compounds, the (resonant) CARS spectrum amplitude significantly ought to be contrasted with the Raman spectral intensity.

Check Your Progress

13. Define Rayleigh scattering.
14. Define selection rule.
15. State the rule of mutual exclusion.
16. What do you understand by Resonance Raman spectroscopy?

2.5 ANSWERS TO 'CHECK YOUR PROGRESS'

1. Microwave spectroscopy deals with the part of electromagnetic spectrum which extends from 100 µm (3x1013 Hz) to 1 cm. (3x1010 Hz). This region of electromagnetic spectrum is known as microwave 46 region which lies between far infrared and radiofrequency region.
2. In these molecules all the atoms are arranged in straight line.
3. In these molecules two moment of inertia are equal and the third being different from these two.
4. When a molecule has all the three moments of inertia identical, are called spherical top molecules.
5. The molecules that have all the three moments of inertia different, are called asymmetric top molecules.
6. 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.
7. The range of the far IR region is 15-200 µ.
8. In this type of stretching with respect to a particular atom, other two atoms in a molecule move in the same direction.

9. In this type of stretching one atom moves away from the central atom, while the other atom moves towards the central atom.
10. 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.
11. The photon energy of this scattered light is equal to that of the incoming light. This process is called Rayleigh scattering.
12. 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.
13. When a beam of monochromatic visible or ultraviolet light is passed through a homogeneous medium, some light may be absorbed, some will be transmitted and some of it will be scattered. The scattered energy will consist almost entirely of radiation of the incident frequency.
14. The selection rule states that for Raman spectra the molecules undergo transitions in which an incident photon is absorbed and another scattered photon is emitted.
15. If a molecule has a centre of symmetry then Raman active vibrations are infrared inactive and vice versa. If there is no center of symmetry then some (note necessarily all) vibrations may be both Raman and infrared active.
16. Resonance Raman spectroscopy (RR spectroscopy) is a Raman spectroscopy technique in which the incident photon energy is close in energy to an electronic transition of a compound or material under examination.

2.6 SUMMARY

- 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.
- 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 spectroscopies.
- 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).
- Frequency is directly proportional to energy but as energy increases the wave length decreases.
- 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.
- Microwave spectroscopy deals with the part of electromagnetic spectrum

which extends from 100 µm (3x1013 Hz) to 1 cm. (3x1010 Hz). This region of electromagnetic spectrum is known as microwave 46 region which lies between far infrared and radiofrequency region.

- 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.
- Rotating molecules having a permanent dipole or magnetic moment generate an electric field which can interact with the electric component of the microwave region.
- 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.
- 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.
- 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/2π, and the spin angular momentum of a particular nucleus has one of the values.
- Vibrational spectra are given by diatomic molecule with permanent dipole moment and polyatomic molecule with and without permanent dipole moment.
- In a molecule in the gas phase, there will however be a simultaneous change in its rotational energy also.
- The infrared radiation lies between visible & microwave region.
- 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.
- 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.
- In a polyatomic molecule each atom is having three degrees of freedom in three directions which are at right angle to one another. Thus, a polyatomic molecule of N atoms is said to have 3N degree of freedom.

- 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.
- 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.
- 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.
- 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.
- The energy of a vibration and thus the wavelength of its absorption peak may be influenced by other vibration in the molecule.
- 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$^{-1.}$
- 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.
- 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.
- The Raman Effect, named after Noble prize winner Chandrasekhar Venkat 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.
- Raman scattering is due to the oscillation of the induced electronic dipole moment when the molecules are put into an oscillating electric field.
- 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.
- 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 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.

- 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.

2.7 KEY TERMS

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- **Microwave Spectroscopy:** Microwave spectroscopy deals with the part of electromagnetic spectrum which extends from 100 μm (3x1013 Hz) to 1 cm. (3x1010 Hz).
- **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.
- **Vibrational Motion:** 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.
- **Morse Potential:** The Morse potential, named after physicist Philip M. Morse, is a convenient model for the potential energy of a diatomic molecule.
- **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.
- **Symmetric Stretching:** In this type of stretching with respect to a particular atom, other two atoms in a molecule move in the same direction.
- **Asymmetric Stretching:** In this type of stretching one atom moves away from the central atom, while the other atom moves towards the central atom.
- **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).
- **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.
- **Mesomeric Effect:** It causes lengthening or the weakening of a bond leading to the lowering of absorption frequency.
- **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.

- **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.
- **Vibrational Coupling:** The energy of a vibration and thus the wavelength of its absorption peak may be influenced by other vibration in the molecule.
- **Normal Coordinate 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.

2.8 SELF-ASSESSMENT QUESTIONS AND EXERCISES

Short-Answer Questions

1. State the principle of microwave spectroscopy.
2. What do you understand by the classification of molecules?
3. Define rigid rotor.
4. Define non-rigid rotor.
5. What do you understand by the frequency of rotational spectral lines?
6. State the selection rule for rotational spectra.
7. State the Stark effect.
8. State the principle of IR spectroscopy.
9. Define Anharmonicity.

Long-Answer Questions

1. Describe linear harmonic oscillator.
2. Explain the vibrational energies in a diatomic molecule.
3. Explain the selection rule for the vibrational transitions.
4. Describe the bond strength and the force constant.
5. Explain the Moarse potential energy diagram.
6. Describe the P, Q, R branches.
7. Explain the vibrations in a polyatomoic molecule.
8. What do you understand by Raman effect? Explain the classical and the quantum theories of Raman effect.
9. Explain the coherent anti stokes Raman spectroscopy.

2.9 FURTHER READING

NOTES

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UNIT 3 ELECTRONIC SPECTROSCOPY

NOTES

Structure

3.0 INTRODUCTION

When a beam of polychromatic light is passed through a prism or grating, it is broken up into its constituent colours. This array of colours 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 OBJECTIVES

After going through this unit, you will be able to:

- Measure the wavelength of visible light emitted by atomic hydrogen.
- Verify the measured wavelengths against those predicted by quantum theory.
- Identify elements through their emission spectra.
- Examine an absorption spectrum.
- Learn about the Bohr's model of the atom.
- Use atomic spectroscopy to verify some predictions of Bohr's model and measure the Rydberg constant. Understand relationship between energy levels and spectroscopy.
- Sketch absorption, emission and ionization processes on energy diagrams.

3.2 ATOMIC SPECTROSCOPY

Atomic spectroscopy is the investigation of the electromagnetic radiation absorbed and transmitted by particles. Since interesting components have trademark (signature) spectra, nuclear spectroscopy, explicitly the electromagnetic range or mass range, is applied for assurance of natural elemental composition.

Atomic spectroscopy is additionally separated into atomic absorption spectroscopy and atomic emission spectroscopy. In atomic absorption spectroscopy, the light of a foreordained wavelength is gone through an assortment of atoms. In the event that the wavelength of the source light has energy relating to the energy distinction between two energy levels in the atoms, a part of the light will be retained. The contrast between the power of the light transmitted from the source (e.g., light) and the light emitted by the source yields an absorbance value. This absorbance value can then be utilized to decide the concentration of atoms (or molecules) inside the example. The connection between the centralization of molecules, the distance the light goes through the assortment of particles, and the piece of the light absorbed is given by the Beer-Lambert law. In atomic emission spectroscopy, the force of the transmitted light is straightforwardly related to the concentration of atoms.

3.2.1 Energies of Atomic Orbitals

The relative energies of molecular orbitals depends upon:

(*i*) The energies of atomic orbitals used in the formation of molecular orbitals.

(*ii*) The extent of overlapping between the atomic orbitals. The greater the overlap, the more the bonding orbital lowered and antibonding orbital is raised in energy relative to AOs. For example, the extent of over- lapping in case of σ orbital is more than the π-orbital. Consequently, the energy of $\sigma 2p_z$ is lower than that of $\pi 2p_x$ or $\pi 2p_y$ MOs.

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2*s* atomic orbitals have higher energies than 1*s* atomic orbitals and the MOs obtained from 2*s* AOs have higher energy than molecular orbital obtained from 1*s* atomic orbitals. Again, within the same pair of molecular orbitals, antibonding molecular orbitals have higher energy than the bonding molecular orbitals. Similarly 2*p* orbitals will have higher energy of its molecular orbitals compared to that of the molecular orbitals obtained from the 2*s* atomic orbitals.

Of the six molecular orbitals generated from combination of *p* atomic orbitals, σ_{2p_z} has the lowest energy and $\sigma^*_{2p_z}$ has highest energy. π_{2p_x} and π_{2p_y} are degenerate (equal energies), so as $\pi^*_{2p_x}$ and $\pi^*_{2p_y}$. π_{2p_x} and π_{2p_y} have lower energy compared to $\pi^*_{2p_x}$ and $\pi^*_{2p_y}$. The order of energy of molecular orbitals has been determined experimentally by spectroscopic methods. The sequence of energies (in the increasing order) of MOs may be written as

$$\sigma_{1s}, \sigma^*_{1s}, \sigma_{2s}, \sigma^*_{2s}, \sigma_{2p_z}, \begin{cases} \pi_{2p_x} \\ \pi_{2p_y} \end{cases} \begin{cases} \pi^*_{2p_x}, \sigma^*_{2p_z} \\ \pi^*_{2p_y} \end{cases}$$

increasing energy

The bonding π_{2Px} and π_{2Py} as well as antibonding $\pi^*_{2P_x}$ and $\pi^*_{2P_y}$ molecular orbitals are doubly degenerate.

The energy level of the above order is followed by molecules such as O_2, F_2 and Ne_2 and is represented diagrammatically as follows:

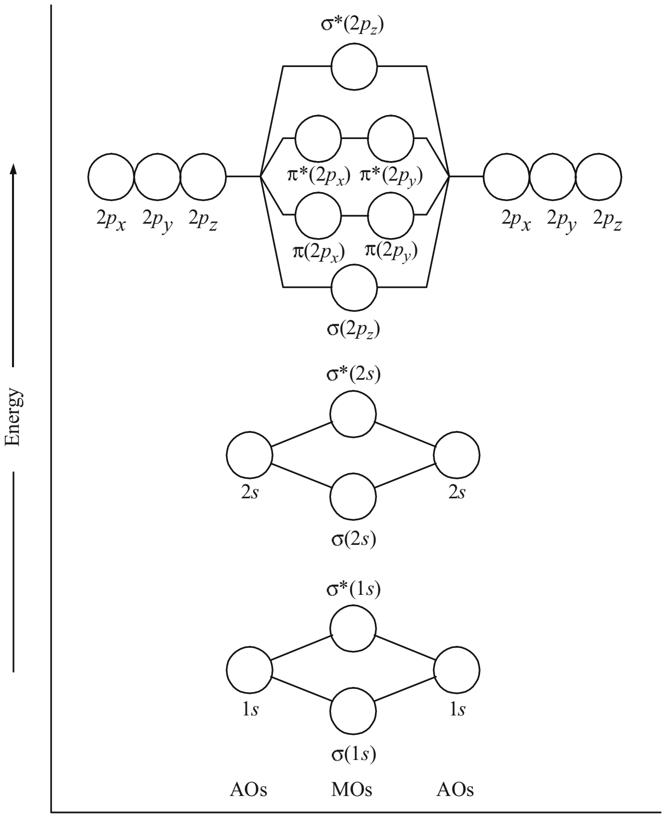

Fig. 3.1 Energy level diagram of molecular orbitals of O_2, F_2 and Ne_2.

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The order of energy of molecular orbitals of molecules such as Li_2, Be_2, B_2, C_2 and N_2, however, does not follow the above sequence and the order in such molecules is

$$\underset{\text{increasing energy}}{\xrightarrow{\sigma_{1S}, \overset{*}{\sigma}_{1S}, \sigma_{2S}, \overset{*}{\sigma}_{2S}, \begin{cases} \pi_{2P_x} \\ \pi_{2P_y} \end{cases} \sigma_{2P_z}, \begin{cases} \overset{*}{\pi}_{2P_x}, \overset{*}{\sigma}_{2P_z} \\ \overset{*}{\pi}_{2P_y} \end{cases}}}$$

Diagrammatically it is represented as

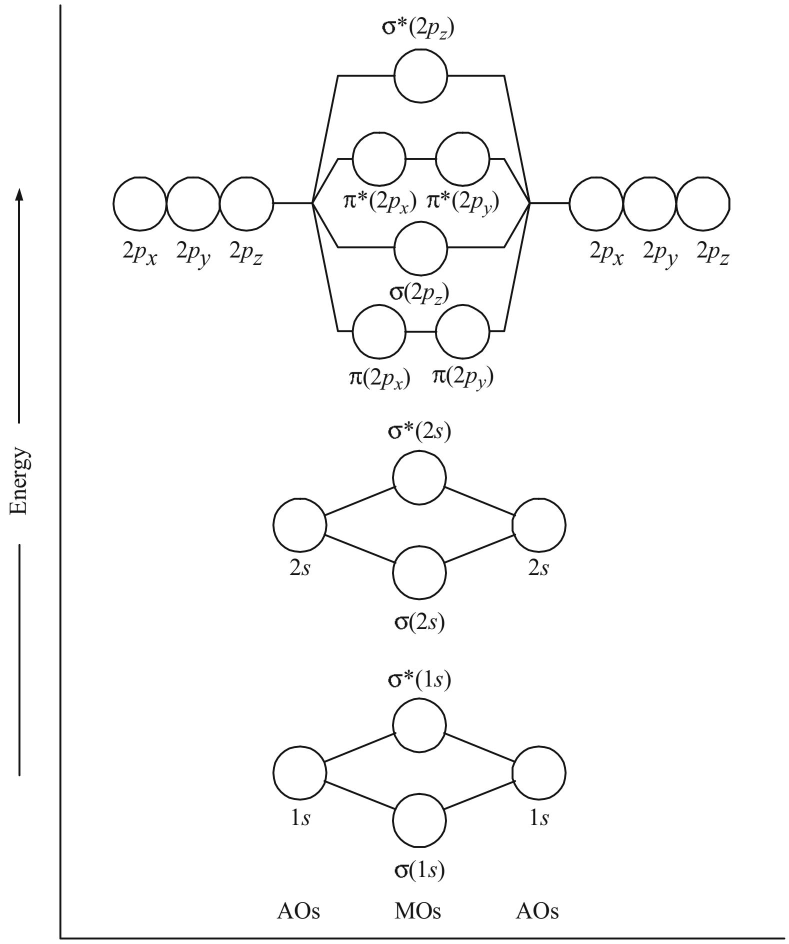

Fig. 3.2 Energy level diagram of molecular orbitals of Li_2, Be_2, B_2, C_2 and N_2.

The main reason for this difference is due to interaction of 2*s* and 2p_z atomic orbitals. In case of Li_2, Be_2, B_2, C_2 and N_2 the energy difference between 2*s* and 2p_z atomic orbitals is small and thus they easily interact with each other. But in the case of O_2, F_2 and Ne_2 this difference is large and thus no interaction takes place.

3.2.2 Vector Representation of Momenta and Vector Coupling

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 momentum of 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 gives rise to vector model of the atom.

Orbital Angular Momentum: The orbital angular momentum for an atomic electron is a vector model where the precise force vector is processed about a course in space. Since there is a magnetic moment connected with the orbital angular momentum, the precession can measure up to the precession of a traditional magnetic moment brought about by the force applied by a magnetic field. This precession is called Larmor precession and has a characteristic frequency called the Larmor frequency.

Total Angular Momentum: It is the vector total of orbital angular moment and spin angular moment. The magnitude and Z component are determined by 2 quantum numbers j and mj.

$$\mathbf{J_z = m_j\ h/2\pi}$$

Where, j is inner quantum number mj is mafntic quantum number j is half integral since quantum quantum number s is half integral for one electron atom.

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 momenta are seen as precessing about the direction of the total angular momentum J. Given two angular momenta (of any kind) L1 and L2, when one generates states that are eigenstates of their vector sum L=L1+L2, one can obtain L values of

L1+L2, L1+L2?1,...|L1?L2|

It applies to two electrons for which the complete twist S can be 1 or 0 as delineated exhaustively above, or to a p and a d orbital for which the absolute orbital angular momentum L can be 3, 2, or 1.

The basic "vector coupling" technique applies to any angular momentum. Nonetheless, if the angular momentum is "same" as in they include indistinguishable particles that possess a similar orbital shell (e.g., 2p3 includes 3 identical electrons; 2p13p14p1 includes 3 non-comparable electrons; 2p23p1 includes 2 identical electrons and one non-identical electron), the Pauli guideline takes out a portion of the normal term images (i.e., while the relating wave-functions are framed, some evaporate in light of the fact that their Slater determinants disappear). Later in this part, strategies for managing the comparable rakish momenta case are presented. These strategies include utilizing the above devices to acquire a rundown of competitor term images after which Pauli-violating term images are wiped out.

3.2.3 Spectra of Hydrogen Atom and Alkali Metal Atom

The least difficult atomic orbitals are those that are found in a molecule with a solitary electron, like the hydrogen atom. For this situation, the atomic orbitals are the eigenstates of the hydrogen Hamiltonian. An atom of some other element ionized down to a solitary electron is the same as hydrogen, and the orbitals take a similar structure.

A (hydrogen-like) atomic orbital is recognized by one of a kind upsides of three quantum numbers: n, l, and ml. The fixed states (quantum conditions) of the hydrogen-like molecules are their atomic orbital. Electron states are best addressed by time-depending "blends" (direct mixes) of numerous orbitals.

In present-day quantum mechanics, n decides the mean distance of the electron from the core; all electrons with a similar worth of n lie at a similar normal distance. Thus, orbitals with a similar worth of n are said to contain a shell. Orbitals with a similar worth of n and a similar worth of l are significantly more firmly related and are said to include a subshell. The nuclear range of hydrogen has assumed a critical part in the improvement of nuclear design.

In the outflow range of hydrogen, when an electric release is gone through hydrogen gas, the particles of hydrogen break into iotas. The hydrogen iotas get invigorated and go into an energized state. The energized particles then, at that point, return to the ground state by producing light. Hydrogen particles produce pale blue light. Ongoing this light through a crystal, a broken line range comprising of a few sharp lines is acquired. This is the line range of hydrogen.

Four sharp hued lines were seen in the noticeable district of this range by Balmer, in the bright area by Lyman, in the infrared locale by Paschen, Brackett and Pfund. These series of lines are named after these researchers who found them. Balmer communicated these lines as far as opposite of their wavelength (ν) by a numerical connection, which was subsequently changed by Rydberg.

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

Where RH is the Rydberg's constant and 'n1', 'n2' are integers with values equal to or greater than 3 and 'l' is the wavelength.

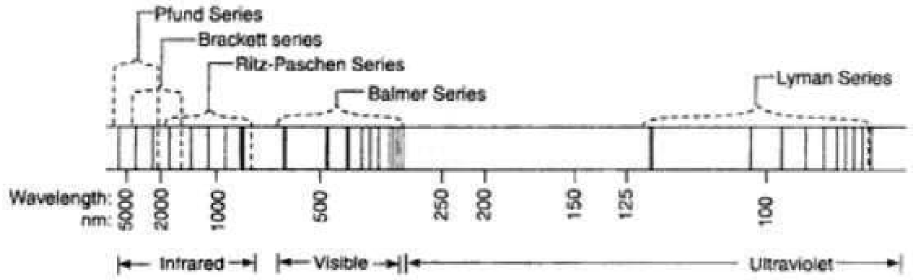

Fig 3.3: *Line Spectrum of Hydrogen Atom*

Transitions Between Orbitals: Under quantum mechanics, every quantum state has an obvious energy. When applied to nuclear orbitals, this implies that each state has a particular energy and that assuming an electron is to move between states, the energy distinction is likewise exceptionally fixed. Consider two states of the Hydrogen atom:

- State 1) n=1, l=0, ml=0 and s= +1/2
- State 2) n=2, l=0, ml=0 and s= +1/2

By quantum hypothesis, state 1 has decent energy of E1, and state 2 has proper energy of E2. The electron needs to acquire an energy of precisely E2 - E1 to bounce from E1 to E2. Assuming the electron gets energy that is not exactly or more noteworthy than this worth, it can't jump from state 1 to state 2.

Presently, assume we illuminate the atom with a wide spectrum of light. Photons that arrive at the atoms that have an energy of precisely E2 - E1 will be absorbed by the electron in state 1, and that electron will leap to state 2. Notwithstanding, photons that are more noteworthy or lower in energy can't be absorbed by the electron, on the grounds that the electron can leap to one of the orbitals, it can't leap to a state between orbitals. The outcome is that the main photons of a particular recurrence will be consumed by the particle. This makes a line in the range, known as an absorption line, which compares to the energy contrast between states 1 and 2.

Alkali Metal Spectra: 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. However, the electrostatic interactions of this electron with the core electrons and with the nucleus yield a strong l-dependence of the energy levels.

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.

For Example, Li – 1s2 ,2s1

Na – 1s2 ,2s2 2p6 3s1

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.

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. What do you mean by spectrum?
2. What do you understand by emission spectrum?
3. Define continuous spectrum.
4. Define line spectrum.
5. What do you understand by band spectrum?
6. What do you understand by absorption spectrum?
7. State if the angular momentum is a scalar quantity or a vector quantity.

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 is 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.

3.3.1 Energy Levels and Molecular Orbitals

A molecule is portrayed by the complete energy coming about because of these connecting or interacting forces. Similar to the case with atoms, the permitted energy conditions of an atom are quantized.

Sub-atomic spectra result from either the absorption or the emission of electromagnetic radeiation as particles go through changes starting with one quantized energy state then onto the next. To examine the sub-atomic or molecular spectra, it is important to think about all the while the impacts of the multitude of commitments from the various sorts of sub-atomic movements and energies.

Types of Energies Possessed by the Molecule: Different types of energies are possessed by a molecule and they are as follows:

Electronic Energy: The molecule is portrayed by the complete energy coming about because of these connecting or interacting forces. Similar to the case with atoms, the permitted energy conditions of an atom are quantized.

Sub-atomic spectra result from either the absorption or the emission of electromagnetic radiation as particles go through changes starting with one quantized energy state then onto the next. To examine the sub-atomic or molecular spectra, it is important to think about all the while the impacts of the multitude of commitments from the various sorts of sub-atomic movements and energies.

Types of Energies Possessed by the Molecule: Different types of energies are possessed by a molecule and they are as follows:

Electronic Energy: The electrons in an atom have dynamic energy because of their movements and potential energy emerging from their fascination with the positive nuclei and their mutual repulsion. These two energy factors, alongside the likely energy because of the common electrostatic repulsion of the positive nuclei, comprise the electronic energy of a molecule.

Vibrational Energy: Atoms are not unbending designs, and the movement of the nuclei inside the sub-atomic system leads to vibrational energy levels.

Rotational Energy: In the gas stage, where they are generally isolated compared with their size, atoms can go through free pivot and subsequently have quantized measures of rotational energy.

Translational Energy: Principally, the translational energy of particles through space is additionally quantized, however, practically speaking the quantum impacts are tiny that they are not recognizable, and the movement seems persistent.

Molecular spectra are seen when a particle goes through the absorption or emission of electromagnetic radiation with a subsequent increment or decline in energy. The principal condition for the assimilation of electromagnetic radiation by an atom going through progress from a lower energy state, E_{lo}, to a higher energy state, Ehi, is that the recurrence of the consumed radiation should be connected with the adjustment of energy by E_{hi} “ E_{lo} = hν, where ν is radiation recurrence and h is Planck’s consistent.

The term energy level is normally utilized for the energy levels of electrons in particles or atoms, which are limited by the electric field of the core, yet can likewise allude to energy levels of cores or vibrational or rotational energy levels in particles.

The energy spectrum of a framework with such discrete energy levels is supposed to be quantized. Assuming the potential energy is set to zero at endless separation from the nuclear core or particle, the typical show, then, at that point, bound electron states have negative likely energy. Assuming more than one quantum mechanical state is at similar energy, the energy levels are degenerate. They are then called degenerate energy levels.

Quantized energy levels result from the connection between a molecule's energy and its frequency. For a restricted molecule, for example, an electron is a particle, the wave work has the type of standing waves. Just fixed states with energies relating to essential quantities of frequencies can exist; for different states the waves meddle disastrously, bringing about zero probability density.

As discrete atoms approach each other to covalently bond, their orbitals influence each other's energy levels to shape holding and hostile to holding sub-atomic orbitals. The energy level of the holding orbitals is lower, and the energy level of the counter holding orbitals is higher. For the bond in the particle to be steady, the covalent holding electrons involve the lower energy holding orbital, which might be connoted by such images as ζ or π relying upon the circumstance.

Relating against holding orbitals can be implied by adding a bullet to get ζ* or π* orbitals. In polyatomic atoms, different vibrational and rotational energy levels are additionally involved. A sub-atomic energy state, i.e., an eigenstate of the sub-atomic Hamiltonian, is the amount of the electronic, vibrational, rotational, atomic, and translational parts, with the end goal that:

$$E = E_{\text{electronic}} + E_{\text{vibrational}} + E_{\text{rotational}} + E_{\text{nuclear}} + E_{\text{translational}}$$

Where Electronic is an eigenvalue of the electronic atomic Hamiltonian (the worth of the potential energy surface) at the balance calculation of the particle. The atomic energy levels are named by the sub-atomic term images.

The particular energies of these parts differ with the particular energy state of the substance. Particles can go through advances in their vibrational or rotational energy levels. Energy level advances can likewise be non-radiative, meaning outflow or ingestion of a photon isn't involved.

If an atom, ion, or molecule is at the most minimal conceivable energy level, it and its electrons are supposed to be in the ground state. Assuming it is at a higher energy level, it is supposed to be energized, or any electrons that have higher energy than the ground state are excited.

3.3.2 Vibrionic Transition and Vibrational Progression: Geometry of Excited States

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. TThe word vibronic is the blend of the words vibrational and electronic. Vibrational and rotational progress might be joined by vibrational coupling. In vibronic coupling, electron advances are all the while joined with both vibrational and rotational advances. Photons associated with transitions might have energy of different reaches in the electromagnetic range, contingent upon the sort of progress.

In an extremely broad manner, energy level contrasts between electronic states are bigger, contrasts between vibrational levels are transitional, and contrasts between rotational levels are more modest, even though there can be cross-over. Translational energy levels are essentially persistent and can be determined as dynamic energy utilizing old style mechanics.

3.3.3 Franck-Condon Principle

According to **Franck-Condon** principle during electronic transitions electrons move and rearrange much faster than the nuclei of the molecules. Thus the electronic configuration changes without altering the position of nuclei during excitation of electrons in ultraviolet or visible regions. Whereas an electron takes about 10^{-16} s to circle an atom (calculated from Bohr's model), the typical period of vibration of a molecule is around 10^{-13} s, *i.e.*, about a thousand times greater. Hence electronic transitions take place without any change in the position of nuclei.

Molar extinction coefficient (ε) is related to the probability of electronic transition (p) as

$$\varepsilon = 0.87 \times 10^{20}\, p.a$$

Where a = target area of absorbing system which is generally the chromophore.

The value of p, the transition probability is generally 1 or less and if the target area *i.e.* chromophore has a size of 1 nm by 1 nm, the value of ε (molar extinction coefficient) will be of the order of 1000. The highest observed value is close to 10^5. For fully allowed transition ε values are about 10,000 while for low transition probability the ε values are 1000 or less. Thus the area of a particular chromophore is related to its absorption intensity. A typical UV spectrum is shown in Figure 3.4

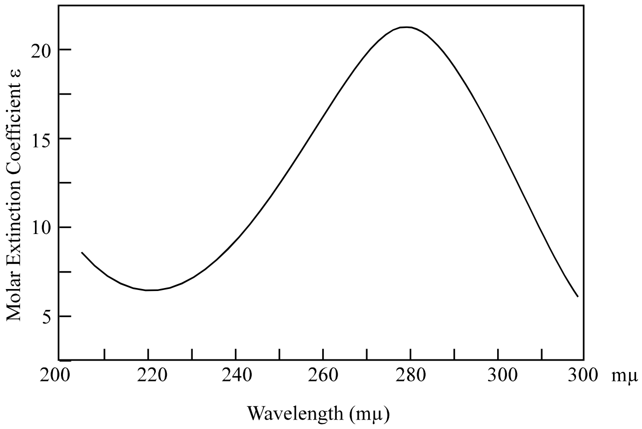

Fig. 3.4 *UV Spectrum of Acetone*

3.3.4 Electronic Spectra of Polyatomic Molecule

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 does not 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 states. The absorption bands because of electronic transition, which usually occur in the ultraviolet or visible regions, play an 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 coloured, 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 this co-ordination.

3.3.5 Emission Spectra

Emission is the process by which a higher energy quantum mechanical condition of a molecule becomes changed over to a lower one through the outflow of a photon, bringing about the formation of light. The recurrence of light discharged is a component of the energy of the change. Since energy should be saved, the energy distinction between the two states approaches the energy taken away by the photon. The energy conditions of the changes can prompt discharges over an exceptionally vast range of frequencies.

The discharge range of a substance component or synthetic compound is the range of frequencies of electromagnetic radiation produced by the component's iotas or the compound's particles when they are gotten back to a lower energy state. Every component's outflow range is remarkable. Hence, spectroscopy can be utilized to distinguish the components in a matter of obscure composition. Also, the outflow spectra of atoms can be utilized in the compound examination of substances.

At the point when the electrons in the molecule are invigorated, for instance by being warm, the extra energy pushes the electrons to higher energy orbitals. Whenever the electrons fall and leave the energized state, energy is re-transmitted as a photon. The frequency (or equally, recurrence) of the not entirely settled by the distinction in energy between the two states. These produced photons structure the element's emission spectrum.

The way that main certain shadings show up in a discharge range implies that main certain frequencies of light are emitted. Each of these frequencies are related to energy by the formula:

$$\mathbf{E_{photon} = h\,\nu}$$

Where, E is the energy of the photon, ν is its frequency, and h is Planck's constant.

The standard of the atomic emission spectrum clarifies the changed tones in neon signs, as well as synthetic fire test. The frequencies of light that a molecule can emanate are subject to states the electrons can be in. Whenever energized, an electron moves to a higher energy level/orbital. At the point when the electron falls back to its ground level the light is emitted.

3.3.6 Radiative and Non Radiative Decay

In the rate-equation above, it is assumed that decay of the number of excited states N only occurs under emission of light. In this case one speaks of full radiative decay and this means that the quantum efficiency is 100%. Besides radiative decay, which occurs under the emission of light, there is a second decay mechanism; non-radiative decay. To determine the total decay rate radiative and non-radiative rates should be summed as:

$$\Gamma_{tot} = \Gamma_{rad} + \Gamma_{nrad}$$

Where, Γ_{tot} is the total decay rate, Γ_{rad} is the radiative decay rate and Γ_{nrad} is the non-radiative decay rate. The quantum efficiency (QE) is defined as the fraction of emission processes in which emission of light is involved:

$$QE = \frac{\Gamma_{rad}}{\Gamma_{nrad} + \Gamma_{rad}}.$$

In non-radiative relaxation, the energy is released as phonons, more commonly known as heat. Non-radiative relaxation 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 non-radiative 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 band gap in semiconductors. Large non-radiative transitions do not occur frequently because the crystal structure generally cannot support large vibrations without destroying bonds (which generally doesn't happen for relaxation). Meta-stable states form a very important feature that is exploited in the construction of lasers. Specifically, since electrons decay slowly from them, they can be deliberately piled up in this state without too much loss and then stimulated emission can be used to boost an optical signal.

3.3.7 Internal Conversion and Spectra of Transition Metal Complexes

The radioactive process, where an energized nucleus interfaces with an electron in one of the lower nuclear orbitals, makes the electron to be transmitted from the molecule. In an interchange process, a high-energy electron is radiated from the radioactive atom, without the beta decay.

Thus, the fast electrons from the internal conversion are not beta particles (β particles), since the last option comes from beta decay. Since no beta decay happens in internal conversion, the element atomic number doesn't change, and consequently, no change of one element to another is seen. Likewise, no neutron is transmitted in internal conversion.

Internally converted electrons don't have the characteristic highly energized spread range of β particles, which comes about because of shifting measures of rot energy being taken away by the neutrino (or antineutrino) in beta decay. Internally converted electrons, which carry a specific proportion of the characteristic decay energy, have an all-around determined discrete energy. The energy spectrum of a β molecule is subsequently a wide protuberance, reaching out to the maximum decay energy value, while the range of inside changed over electrons is a sharp peak.

In the inside transformation process, the wave capacity of an inward shell electron infiltrates the nucleus (i.e., there is a limited likelihood of the electron in a 's' nuclear orbital being found in the nucleus) and when this is the situation, the electron might couple to the energized state and take the energy of the atomic change straightforwardly, without a transitional gamma beam being delivered first.

As an electromagnetic quantum process, the most common way of conferring energy to the electron might be viewed as occurring through a virtual photon, yet in that sense, the photon included can be considered as a virtual gamma beam, which never shows up beside as an equation, rather than a straightforwardly quantifiable molecule. The active energy of the emitted electron is equivalent to the transition energy in the nucleus, minus the binding energy of the electron.

Most internally converted electrons come from the K shell, as these two electrons have the most noteworthy probability of being found inside the nucleus. After the electron has been produced, the atom is left with an opening in one of the internal electron shells. This opening will be loaded up with an electron from one of the greater shells and thus, the characteristic X-beam or Auger electron will be radiated.

Spectra of Transition Metal Complexes: The d-orbitals of free transition metal atoms or particles are degenerative (all have similar energy.) However, when progress metals structure coordination buildings, the d-orbitals of the metal are connected with the electron haze of the ligands in such a way that the d-orbitals become non-degenerate (not all having similar energy.) How the orbitals are parted into various energy levels is subject to the calculation of the complex. The precious stone field hypothesis can be utilized to anticipate the energies of the different d-orbitals, and how the d electrons of a changing metal are conveyed among them. Whenever the d-level isn't filled, it is feasible to advance an electron from a lower energy d-orbital to a higher energy d-orbital by retention of a photon of electromagnetic radiation having proper energy. Electromagnetic radiations in the apparent area of the range regularly have the transition energy for such advances.

3.3.8 Charge Transfer Spectra

A charge-move complex (CT complex) or electron donor-acceptor complex is a relationship of at least two atoms, or various pieces of one extremely huge particle, in which a small amount of electronic charge is moved between the molecular levels. The subsequent electrostatic attraction gives a balancing out power to the atomic complex. The source atom from which the charge is moved is known as the electron donor and the receiving species is known as the electron acceptor.

The attraction in a charge-move complex is certainly not a steady chemical bond and is a lot more fragile than covalent bonds. The attraction is made by electronic progress into an excited electronic state and is best portrayed as a feeble electron resonance. The excitation energy of this resonance occurs as often as possible in the noticeable region of the electromagnetic spectrum, which creates the generally serious colour characteristic for these complexes.

These optical absorption bands are frequently alluded to as charge-transfer bands (CT bands). Optical spectroscopy is a strong method to portray charge-transfer bands. Charge-transfer complexes exist in many types of molecules, inorganic as well as natural, and in all states of matter.

Charge transfer spectra are of two types:

- **Ligand-to-Metal Charge-Transfer (LMCT) Complex:** In this type, the electron moves from the MO with ligand like character to the metal.
- **Metal-to-Ligand Charge-Transfer (MLCT) Complex:** In this type, the electron moves from the MO with a metal-like character to the ligand.

The intensity of the charge-transfer bands in the absorbance range is emphatically reliant upon the degree (balance consistent) of this affiliation reaction. Techniques have been created to decide the harmony consistent for these complexes in the arrangement by estimating the force of absorption bands as a function of the concentration of the donor and acceptor parts in the provided solution.

Check Your Progress

8. What do you understand by molecular spectroscopy?
9. What do you understand by vibronic transition?
10. Define emission spectrum.
11. What do you understand by emission spectroscopy?
12. What do understand by charge transfer spectra?

3.4 PHOTOELECTRON SPECTROSCOPY

Photoelectron spectroscopy involves the measurement of kinetic energy of photoelectrons to determine the binding energy, intensity and angular distributions of these electrons and use the information obtained to examine the electronic structure of molecules. It differs from the conventional methods of spectroscopy in that it detects electrons rather than photons to study electronic structures of a material.

3.4.1 Basic Principle of Photoelectron Spectroscopy

Photoelectron spectroscopy depends on the photoelectric effect, a phenomenon originally described by Albert Einstein in 1905. The photoelectric effect states: when electrons in a metal are exposed to light of adequate radiation, the electrons are ejected from the metal surface. Assuming that we know the active energy of the ejected electrons (known as photoelectrons) and the energy of the radiation, we can ascertain the energy of the electrons in the strong metal.

Photoelectron spectroscopy just applies the photoelectric effect to free atoms or molecules rather than metals. In PES, an example is assaulted with high-energy radiation, typically UV or X-ray beam, which makes electrons be ejected out from the sample. The ejected electrons go from the sample to an energy analyzer, where their active energies are recorded, and afterward to a detector, which counts the quantity of photoelectrons at different kinetic energies.

The energy expected to discharge an electron from the sample is known as the electron's ionization energy or binding energy. We know the energy of the radiation (h\ν) is used to launch the electron. Thus, by estimating the binding energy of the photoelectron (K Eelectron) we can compute the binding energy (BE) of the electron in the sample:

$$\text{BE} = h\nu \text{ “ } \text{KE}_{\text{electron}}$$

The binding energy of an electron in an atom relies upon its area around the nucleus. Electrons in the peripheral shell (valence electrons) are more shielded and farther from the nucleus, so they have the most minimalbinding energies of each of the electrons in an atom. Conversely, electrons in internal shells (center electrons) are less shielded and nearer to the nucleus, so they have higher binding energies.

3.4.2 Photoelectric Effect

Photoelectric effect was another phenomena accounted for by the hypothesis of quantization. When light falls on a freshly cleaned metallic surface like zinc, caesium, etc., electrons are emitted. Photoelectrons are produced when light of frequency higher than some threshold value strikes the metallic surface. The threshold frequency is a characteristic property of the substance and sometimes the condition of its surface. The alkali metals yield photo-electrons with visible light, but for most substances the threshold lies in the ultraviolet.

The rate of electron emission can be determined by measuring the current through a collector plate, the electron's kinetic energy is measured by the voltage required to prevent them from reaching the collector. Below the threshold frequency v_0 no electrons are at all emitted. Above v_0, electrons with different energies are obtained; the energy distribution is independent of the light intensity but varies with frequency. The maximum electron energy for a frequency v obeys the equation,

$$E_{\max} = hv - hv_0 \qquad ...(2)$$

Where h is Planck's constant; hv_0 is known as work function. For a given frequency, the rate of electron emission is proportional to the light intensity.

However, if the energy were distributed uniformly, it would take rather a longer time for any one electron to obtain the observed energy, but no such tag is observed. This can be explained, if we assume that light can behave both as a stream of particles and as wave. This explanation was given by Einstein in 1905. He assumed that the striking photoelectric surface consists of discrete particles $E = hv$.

Each electron emitted from the surface then corresponds to the absorption of a single quantum of light. It must take a certain minimum energy, the work function hv_0 to remove an electron from a solid surface; 'Quanta' with less energy have no effect. If the quantum absorbed has more than the requisite amount of energy, then the extra energy is retained by the emitted electrons as kinetic energy. The more quanta of a given frequency strike the surface, the more electrons of the corresponding energy distribution are emitted, thus giving the observed dependance on light intensity.

3.4.3 Ionization Process

The most basic level ionization energies are obvious thermodynamic amounts connected with the heat of protonation, oxidation/reduction chemistry, and ionic and covalent bond energies. Ionization energies are firmly connected with the ideas of electronegativity, electron-richness, and the overall reactivity of atoms.

Ionization is expressly characterized as far as advances between the ground condition of an atom and its ionic states. Ionization of electrons results from the bonding of sub-atomic orbitals, lone pairs of electrons, anti-bonding sub-atomic orbitals, or nucleus. These depictions mirrors the relationship of ionization energies to the atomic orbital model of electronic structure.

The chances of ionization is subjected to the energy of the ionizing photon, the atomic properties of the orbitals ionized, the place where photoelectrons are gathered, and the polarized idea of the photons. These probabilities of photoionization are perceived as far as photoionization cross-sections. The reliance of photoionization cross-sections upon the energy of the ionization photon and the personality of the sub-atomic orbital has been especially helpful in the tasks of the spectra of multi-atomic molecules.

3.4.4 Koopman's Theorem

The basic rule that the ionization energy of an atom is equivalent to the orbital energy of the ejected electron. It is the premise of the interpretation of spectra in photoelectron spectroscopy. Koopmans' hypothesis is an estimate in that it disregards any redesign of electrons in the particle framed. It is named after the Dutch mathematician and economist Charles Koopman.

Speculations of Koopmans' Theorem: While Koopmans' hypothesis was initially expressed for working out ionization energies from confined (closed shell) Hartree-Fock wave functions, the term has since taken on a more summed up significance as an approach to utilizing orbital energies to compute energy changes because of changes in the quantity of electrons in a framework.

Koopman's hypothesis applies to the expulsion of an electron from any involved atomic orbital to shape a positive particle. Expulsion of the electron from various involved sub-atomic orbitals prompts the particle in various electronic states. The most minimal of these states is the ground state and this frequently, yet not generally, emerges from expulsion of the electron from the HOMO. Different states are energized electronic states.

3.4.5 Photoelectron Spectra of Simple Molecule

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.

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.

3.4.6 Electron Spectroscopy for Chemical Analysis (ESCA)

It is 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, fibres, metals, semi-conductors, paper, etc.) and to identify surface constituents as well as their chemical state.

Chemical Information from ESCA

Using ESCA, one can be able to evaluate the:

- 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.

Also, 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.

3.4.7 Auger Electron Spectroscopy

Auger Electron Spectroscopy (Auger spectroscopy or AES) was developed in the late 1960's by Pierre Auger, a French Physicist. 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.

Until the early 1950s Auger transitions were considered nuisance effects by spectroscopists, not containing much relevant material information, but studied so as to explain anomalies in X-ray spectroscopy data. Since 1953 however, AES has become a practical and straightforward characterization technique for probing chemical and compositional surface environments and has found applications in metallurgy, gas-phase chemistry, and throughout the microelectronics industry.

Instrumentation: Surface sensitivity in AES arises from the fact that emitted electrons usually have energies ranging from 50 eV to 3 keV and at these values, electrons have a short mean free path in a solid. The escape depth of electrons is therefore localized to within a few nanometers of the target surface, giving AES an extreme sensitivity to surface species. Because of the low energy of Auger electrons, most AES setups are run under ultra-high vacuum (UHV) conditions. Such measures prevent electron scattering off of residual gas atoms as well as the formation of a thin "gas (adsorbate) layer" on the surface of the specimen, which degrades analytical performance.

In this configuration, focused electrons are incident on a sample and emitted electrons are deflected into a cylindrical mirror analyzer (CMA). In the detection unit, Auger electrons are multiplied and the signal sent to data processing electronics. Collected Auger electrons are plotted as a function of energy against the broad secondary electron background spectrum. The detection unit and data processing electronics are collectively referred to as the electron energy analyzer.

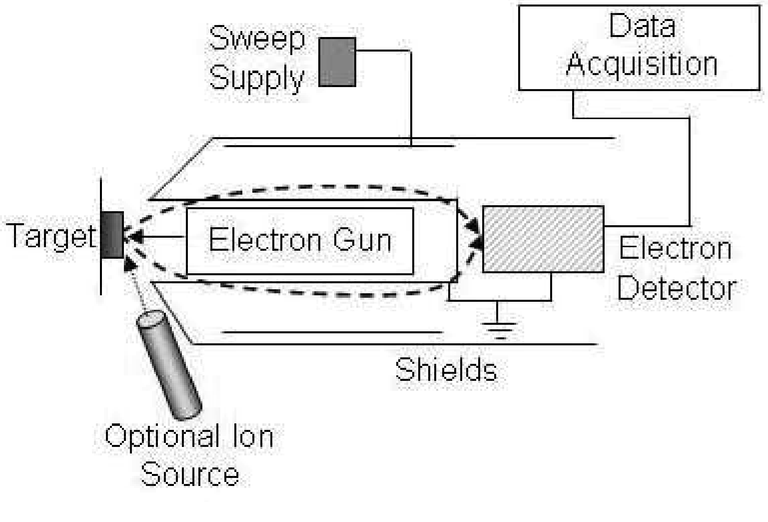

Fig 3.5 *Auger Electron Spectroscopy*

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.

Quantitative Analysis: Semi-quantitative compositional and element analysis of a sample using AES is dependent on measuring the yield of Auger electrons during a probing event. Electron yield, in turn, depends on several critical parameters such as electron-impact cross-section and fluorescence yield. Since the Auger effect is not the only mechanism available for atomic relaxation, there is a competition between radiative and non-radiative decay processes to be the primary de-excitation pathway.

Uses: 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

13. Define ionization energy.
14. Define photoelectric effect.
15. What kind of radiation is used in a photoelectron spectroscopy?
16. What do you understand by auger electron spectroscopy?

3.5 PHOTOACOUSTIC SPECTROSCOPY

Photoacoustic spectroscopy is the measurement of the effect of absorbed electromagnetic energy (particularly of light) on matter by means of acoustic detection. 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 causes local heating, generating a thermal expansion which creates 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 of the light. 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 photoacoustic spectroscopy is as much a type of calorimetry as it is spectroscopy.

3.5.2 Photoacoustic Spectroscopy: Gas and Condensed System

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 deexcitation is intermolecular colliding, which ultimately leads to increases in translation energy of the gas particles, i.e., 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.

The mechanism of the photoacoustic effect in condensed samples is not as straightforward as it is for gas samples. 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 non-dissipative (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.

3.5.3 Chemical and Surface Applications

PAS has been used successfully as a spectroscopic tool for:

- Investigating and characterizing coloured 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 colouring agents such as cytochrome and haemoglobin 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.

Check Your Progress

17. What do you understand by photoacoustic spectroscopy?
18. Mention the significance of photoacoustic spectroscopy

3.6 ANSWERS TO 'CHECK YOUR PROGRESS'

1. When a beam of polychromatic light is passed through a prism or grating, it is broken up into its constituent colours. This array of colours is known as spectrum.
2. Spectrum which is obtained when the light coming after passing through a prism or a grating, is examined directly with a spectroscope is alled an emission spectrum.
3. When the source emitting light is an incandescent solid, liquid, or gas at a high temperature, the spectrum so obtained is called continuous spectrum.
4. When the light emitting substance is in the atomic state, the spectrum so obtained is called line spectrum.

5. Band 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.
6. When the light from a source emitting a continuous spectrum is first passed through an absorbing substance and then observed through a spectroscope, it will be found that certain colours (or wavelength) are missing which leave dark lines or bands at their places. The observed spectrum is called absorption spectrum.
7. Angular momentum is a vector quantity because it has both magnitude and direction.
8. 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 is called molecular spectroscopy.
9. A transition in an energy level of an electron in a molecule may be combined with a vibrational transition and are called as vibronic transition.
10. 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.
11. 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.
12. 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.
13. The difference between the photon energy, which is known, and the electron kinetic energy which is measured, is known as the ionization energy.
14. 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.
15. Monochromatic radiation is used in a photoelectron spectroscopy.
16. Auger electron spectroscopy is a surface analytical technique, used for determining the composition of the surface layers of a sample.
17. Photoacoustic spectroscopy is the measurement of the effect of absorbed electromagnetic energy (particularly of light) on matter by means of acoustic detection.
18. 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.

3.7 SUMMARY

NOTES

- When a beam of polychromatic light is passed through a prism or grating, it is broken up into its constituent colours. This array of colours 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.
- Atomic spectroscopy is the study of the electromagnetic radiation absorbed and emitted by atoms. Since unique elements have characteristic (signature) spectra, atomic spectroscopy, specifically the electromagnetic spectrum or mass spectrum, is applied for determination of elemental compositions.
- Atomic spectroscopy is divided into atomic absorption spectroscopy and atomic emission spectroscopy.
- Molecular spectroscopy 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.
- A molecular spectrum is observed when a molecule undergoes the absorption or emission of electromagnetic radiation with a resulting increase or decrease in energy.
- 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.
- 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.
- 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.
- 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.

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- 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.
- Translational energy levels are practically continuous and can be calculated as kinetic energy using classical mechanics.
- 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.
- The absorption bands because of electronic transition, which usually occur in the ultraviolet or visible regions, play an important role in the analysis and characterization of organic and inorganic compounds.
- 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.
- 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.
- Through an absorbing substance, & then observed through a spectroscope, it will be found that certain colours (or wavelength) are missing which leave dark lines or bands at their places. The observed spectrum is called absorption spectrum.
- 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.
- 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.
- Angular momentum is a vector quantity, i.e., it has magnitude as well as direction, therefore total angular momentum is also a vector quantity.
- The orbital angular momentum for an atomic electron is a vector model where the angular momentum vector is precessing about a direction in space.
- Molecular spectra are observed when a molecule undergoes the absorption or emission of electromagnetic radiation with a resulting increase or decrease in energy.

- 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.
- The difference between the photon energy (hν), which is known, and the electron kinetic energy (K.E.), which is measured, is the ionization energy.
- 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.
- Koopmans' theorem is an approximation in that it ignores any reorganization of electrons in the ion formed. It is named after the Dutch mathematician and economist Charles Koopmans.
- 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.
- Auger process and is one of the most commonly employed surface analytical techniques for determining the composition of the surface layers of a sample.
- Photoacoustic spectroscopy is the measurement of the effect of absorbed electromagnetic energy (particularly of light) on matter by means of acoustic detection.
- 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.

3.8 KEY TERMS

- **Spectrum:** When a beam of polychromatic light is passed through a prism or grating, it is broken up into its constituent colours. This array of colours is known as spectrum.
- **Molecular Spectrum:** When the emitter in the molecular state is excited, each molecule emits bands which are characteristic of molecules then it is called molecular spectrum.
- **Atomic Spectrum:** When the light emitting substance is in the atomic state, atomic spectrum is obtained.
- **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.
- **Continuous Spectrum:** When the source emitting light is an incandescent solid, liquid or gas at a high temperature, the spectrum so obtained is continuous.
- **Line Spectrum:** This is obtained when the light emitting substance is in the atomic state. Therefore, it is also called Atomic Spectrum.
- **Angular Momentum:** Angular momentum is something that has both magnitudes, as well as a direction.
- **Subshells:** 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".

- **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.
- **Vibronic State:** A transition in an energy level of an electron in a molecule may be combined with a vibrational transition and called a vibronic transition.
- **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.
- **Photoelectric Effect:** The photoelectric effect is a process whereby light falling on a surface knocks electrons out of the surface.
- **Photoacoustic Spectroscopy:** Photoacoustic spectroscopy is the measurement of the effect of absorbed electromagnetic energy (particularly of light) on matter by means of acoustic detection.

NOTES

3.9 SELF-ASSESSMENT QUESTIONS AND EXERCISES

Short-Answer Questions

1. Why non radiative transitions do not occur frequently?
2. What are vibrionic transitions?
3. State the Plank's constant.
4. What do you understand by the ionization process?
5. State the basic principle of photoelectric spectroscopy.
6. State the Koopman's theorem.
7. What do you understand by photoacoustic spectroscopy?
8. State the basic principle of photoacoustic spectroscopy.

Long-Answer Questions

1. What do you by atomic spectroscopy? Explain various types of spectrums found in atomic spectroscopy.
2. Explain the energies of the atomic orbital.
3. Describe the vector representation of momenta and vector coupling.
4. Explain the spectra of hydrogen atoms and alkali metal atoms.
5. Describe various types of energies possessed by a molecule.
6. Explain in detail the Franck's-Condon Principle.
7. Describe the Auger Photoelectron Spectroscopy.
8. What do you understand by the photoacoustic spectroscopy? State its chemical and surface applications.

3.10 FURTHER READING

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UNIT 4 MAGNETIC RESONANCE SPECTROSCOPY

NOTES

Structure

4.0 INTRODUCTION

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.

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NMR can detect very fine structural components, works for organic and inorganic, qualitative and quantitative, versatile, and 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

After going through this unit, you will be able to:

- Explain nuclear & electronic spin.
- State the number & type of protons in a molecule.
- Describe the proton – electron interaction.
- Define molecular geometries.
- Explain the nature & number of chemical bonds.
- Define the interactions & processes related to molecules.
- Describe the components of a sample (qualitative analysis).
- State the amount of material in a sample (quantitative analysis).

4.2 NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

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 is called Nuclear Magnetic Resonance (NMR) spectroscopy. It utilizes the magnetic properties of specific nuclei's to decide physical and synthetic properties of atoms or the molecules in which they are present. It gives point by point details about the constitution, elements, reaction state, and chemical environment of the molecules.

Atomic nuclei of many atoms have a spin magnetic moment associated with the spinning of a charged nucleus on its axis. The mechanical spin or angular momentum of nuclei depends on the nuclear spin or *spin quantum number* I, which may have values of 0, $\frac{1}{2}$, 1, $\frac{3}{2}$ etc. .... depending on the nucleus. Magnetic properties are observed in nuclei of odd mass number and nuclei of even mass number but odd atomic number. Thus nuclei like ^{12}C, ^{16}O, ^{32}S etc. with even mass number and even atomic number have no magnetic properties and are insensitive to NMR method. Nuclei with spin quantum number of $\frac{1}{2}$ *e.g.* ^{1}H, ^{19}F,

^{31}P are most useful for NMR studies. Nuclei with spin quantum number 1 (*e.g.* ^{2}H, ^{14}N) or $\frac{3}{2}$ (*e.g.* ^{11}B, ^{35}Cl) possess an electric quadruple moment in addition to spin magnetic moment and are studied by *nuclear quadruple resonance* (NQR) method.

However, the main application of NMR spectroscopy in organic chemistry is confined to hydrogen nuclei or proton since they are present in almost all organic compounds and also because they are highly sensitive to the method. The study of hydrogen nuclei by nuclear magnetic resonance method is commonly referred to as *proton magnetic resonance* (PMR) spectroscopy.

As explained earlier, the spinning nucleus gives rise to a magnetic field whose axis is coincident with the axis of spin. Such a nucleus behaves as a tiny magnet of magnetic moment μ. If such a nucleus is placed in an external magnetic field of H° gauss, then according to quantum mechanics, it may assume any of (2I + 1) orientations with respect to the direction of the applied magnetic field. Thus for proton ($I = \frac{1}{2}$), there is a possibility of two orientations only—aligned with the direction of external field (parallel orientation), $m = +\frac{1}{2}$ or aligned against the direction of external field (antiparallel orientation), $m = -\frac{1}{2}$ which correspond to energy levels of $+\mu H°$ and $-\mu H°$ respectively. The parallel orientation of the tiny nuclear magnet is more stable and favourable. Hence under ordinary conditions there is a slight excess of nuclei in lower spin state which are responsible for absorption of discrete amount of energy (ΔE) such that $\Delta E = 2\mu H° = h\nu$. For protons in a magnetic field of 14,000 gauss the frequency of such energy is in the radio frequency regions of about 60 mega cycles per second.

4.2.1 Nuclear Spin, Nuclear Resonance and Saturation

Nuclear spin is a method to represent the total angular momentum of a nucleus by the symbol *I*. For electrons in molecules we make a reasonable differentiation between electron spin and electron orbital angular momentum, and afterward join them to give the total angular momentum. Yet, the nucleus behaves as though they are a solitary entity with intrinsic angular momentum I. Related with each nuclear spin is a nuclear magnetic moment which produces magnetic interactions with its current environment.

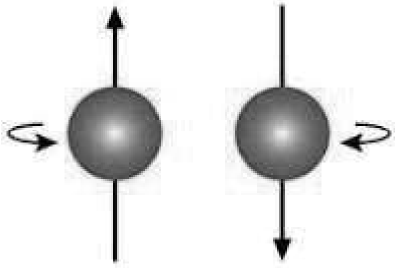


Fig 4.1 *Nuclear Spin*

The nuclear spins for individual protons and neutrons matches the treatment of electron spin, with spin 1/2 and a related magnetic moment. The magnetic moment is a lot more modest than that of the electron. For the mix neutrons and protons in the nucleus, the circumstance is more confounded.

4.2.2 Nuclear Resonance

In an applied external magnetic field the *processional frequency* of the spinning nucleus must be exactly equal to the frequency of electromagnetic radiations (radio frequency)

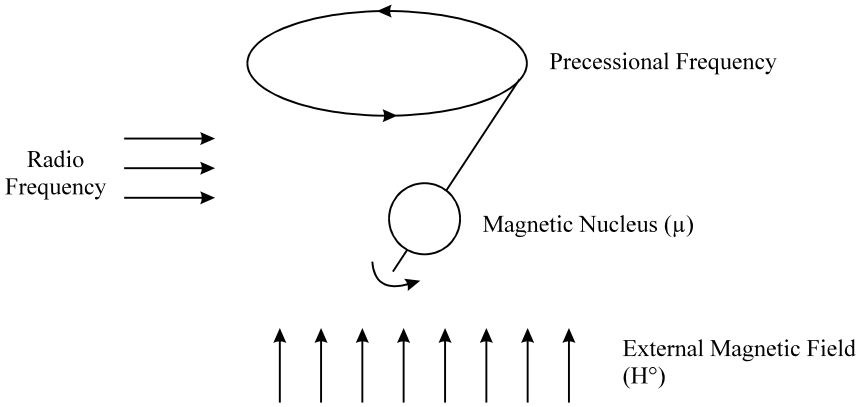


Fig. 4.2 *Schematic description of precessional frequency.*

necessary to induce transition from one nuclear spin state to another. When the precessional frequency of spinning nucleus coincides with the frequency of rotating magnetic field, they are in *resonance* and then and only then the absorption or emission of energy by the nucleus can occur.

In this respect NMR spectroscopy is different from UV, visible and infrared spectroscopy as here in NMR different energy states between which transition may occur are not pre-existent but created as a result of application of external magnetic field and resonance is essential for absorption or emission of energy.

The transition of nucleus from one spin state to another corresponds to change in angle that the axis of nuclear magnet makes with respect to applied magnetic field. The nucleus in higher energy state reverts back to lower energy state through spin-spin relaxations and spin-lattice relaxations.

It is also important to note that resonance frequencies for different types of nuclei differ considerably from each other and their NMR spectra do not overlap.

4.2.3 Saturation

The saturation in the NMR experiment is another spectroscopic method to study the interactions, in solution, between a large molecule (receptor) and a medium-small sized molecule (ligand), and, alike tr-NOESY, it is based on the Nuclear Overhauser Effect and the observation and analysis of the resonances of the ligand protons.

STD (Saturation Transfer Difference) NMR is a strong ligand-based apparatus for evaluating relatively smaller molecules with low molecular weight parts for their collaboration with a given macromolecule.

STD NMR is a ligand based NMR strategy that is utilized in the binding of ligands to proteins because of its appropriateness across the wide scope of noticed dissociation constants in the range 100 nM—10 nM. STD NMR has been used to track spatial proximities of ligand/s with protein of interest under the condition that ligand undergoing fast exchange.

The Saturation Transfer Difference (STD) is performed by securing two one-dimensional (1D) NMR spectra that are then deducted to make the STD spectrum, along these lines the distinction for the sake of the analysis. The protein is saturated by an underlying train of 90° Gaussian pulses that substitute on progressive outputs between on-resonance (specifically immersing protein resonances) and off-resonance spectra.

Resonances will be noticed distinctly in the STD range for those compounds that lose a portion of their signal intensity in the on-resonance spectrum due to the saturation of the protein.

4.2.4 Shielding of Magnetic Nuclei and Deshielding

The chemical shift values of different nuclei in a molecule arise due to differences in the local magnetic field felt by nuclei in different parts of the molecule. Due to the effects like inductive effect, resonance effect, anisotropic effect and ring currents effects the electron density surrounding the differential nuclei in a molecule may result in shielding or deshielding of these nuclei.

When a bond and its electron density are subjected to an external magnetic field, there is an induced magnetic field which is anisotropic (anisotropy is the property of being directionally dependent). Chemical shift anisotropy is generally caused by the pi electrons which is predictable in most simple organic compounds and loads to shielding or deshielding.

Electronegativities of carbon atoms in some common hydrocarbons is in the order $C_2H_2 > C_2H_4 > C_2H_6$. Therefore the expected chemical shifts for the protons in these molecules should also be in the same order but experimentally found order is $C_6H_6(\delta \sim 8$ p.p.m.$) > C_2H_4(\delta \sim 5$ p.p.m.$) > C_2H_2$ $(\delta \sim 2.5$ p.p.m.$) > C_2H_6$ $(\delta \sim 0.9$ p.p.m.$)$.

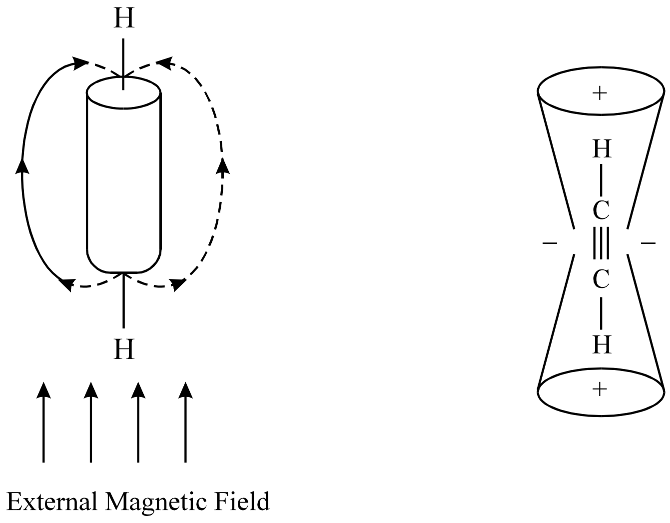


Fig. 4.3 *Showing shielded and deshielded areas in acetylene.*

NOTES

To explain this anomalous behaviour it has been assumed that some kind of shielding- deshielding effect is operative in acetylene and aromatic rings which is much smaller in ethylene. Suppose acetylene is orientated in such a manner that its molecular axis is parallel to applied field, then the induced circulation of electrons in π orbitals produces an induced magnetic field in a direction opposite to that of applied field, resulting in *shielding* of protons in line with triple bond from applied magnetic field. This results in decreased chemical shift and higher τ values. At the same time protons which happen to lie above or below the shielded area are *deshielded*. The net result of this induced magnetic field is that there are areas within which shielding is experienced (shown with +ve sign in figure below) and outside these areas deshielding is experienced (shown by –ve sign) by the protons.

In case of double bond of ethylene or carbonyl compounds shielding and deshielding is much weaker and induced currents are produced only when molecular axis is perpendicular to applied magnetic field.

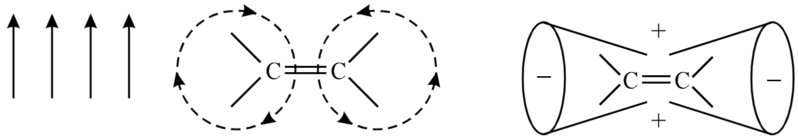


Fig. 4.4 *Shielding and deshielding in ethylene.*

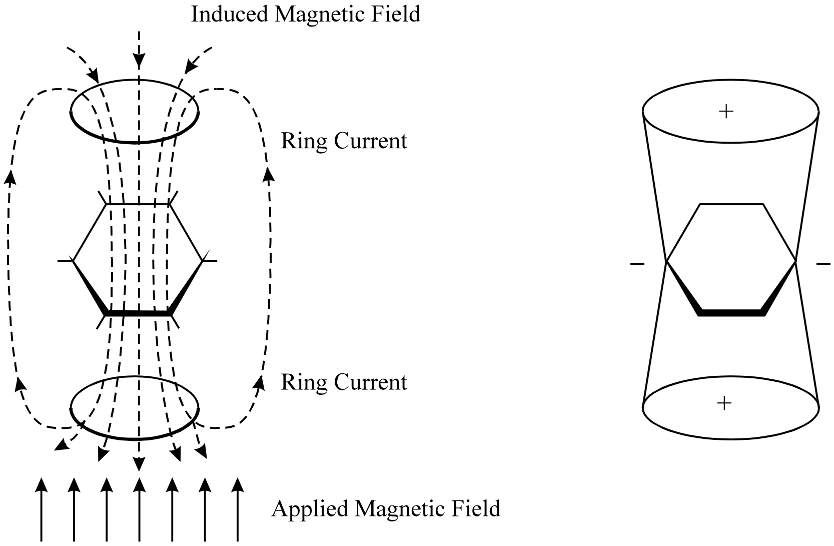


Fig. 4.5 *Shielding and deshielding in aromatic systems.*

In case of aromatic systems, normally the delocalised π electrons can circulate in either direction but when orientated perpendicular to applied magnetic field circulation of π electrons occur only in one direction producing ring currents which induces a magnetic field perpendicular to molecular plane. This induces magnetic field is aligned to external magnetic field outside the ring causing deshielding but opposed to it above and below the area of the ring causing shielding (Fig. 4.5) The protons attached to benzene are in the plane of ring and in the deshielded area and hence their chemical shifts occur at much lower field (τ for aromatic proton of benzene is 2.73).

4.2.5 Chemical Shift and its Measurement and Factors Influencing Chemical Shift

It might be expected that different protons in a molecule will absorb the same frequency (as H_0, μ and *h* all are constant) and if it were so the PMR spectra of a compound will be of little use to organic chemists. The protons in molecules are surrounded by electrons which shield them from the applied magnetic field H° to different extent. Hence, the magnetic field experienced by different protons in different environments in a molecule is somewhat lower or

$$H_{\text{effective}} = (1-\sigma)H^\circ$$

where σ is known as *shielding constant*. The protons in different environment in same molecule are shielded by the circulation of surrounding electrons to different extent. Thus the electron withdrawing groups or atoms *e.g.* —F, —Cl, —NO_2, —OH, —COOR etc. adjacent to the proton reduce the density of electron cloud and the shielding constant (σ) and the resonance therefore, occurs at a lower magnetic field while the electron releasing groups *e.g.* —R etc. have the reverse effect. This separation of resonance frequencies of protons in different structural environments from some arbitrary standard is termed as *chemical shift.*

The shielding effect is proportional to the magnitude of the applied magnetic strength and therefore the magnitude of chemical shifts is also dependent on the strength of applied magnetic field. Different kind of protons in organic compounds absorb at frequencies spread over 700 cycles per second at a magnetic field of 14,000 gauss. The absorption of protons at this magnetic field is at a frequency of about 60×10^6 cycles per sec. which makes it difficult to measure the position of absorption of protons with accuracy. Therefore absolute absorption frequencies cannot be observed directly and relative proton resonance frequencies are determined. It is also desirable that chemical shift values be expressed in some form independent of field strength and hence these are recorded as fraction of the field strength or frequency.

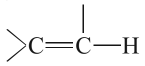
$$\delta = \frac{(H_r - H_s)}{H_r} = \frac{\Delta\nu \times 10^6}{\text{Oscillator frequency in c.p.s.}}$$

where H_r and H_s are field strengths corresponding to resonance for proton in reference compound (H_r) and sample (H_s) respectively and Δν is the difference in absorption frequencies of sample and reference. The delta (δ) values so obtained are dimensionless and are expressed as ppm (parts per million).

Alternatively tetramethyl silane (TMS) is taken as a reference because it is chemically inert, volatile, miscible with most solvents and gives only one resonance absorption at higher frequency than most common organic protons. When TMS is used as a reference the chemical shift values are expressed in tau (τ) where $\tau = 10 - \delta$ and it is also expressed in ppm. Thus PMR values can be expressed either as δ (reference compound must be mentioned) or τ (TMS is assumed as reference).

Chemical shift value for protons in different environment are tabulated below:

***Table 4.1** Typical chemical shift values for protons*

Type of proton		δ *ppm*	τ *ppm*
Alkanes			
	$R{-}CH_3$	0.86	9.14
	 $R_2{>}CH_2$	1.3	8.7
	R_3CH	1.45	8.55
Adjacent to sp² carbon			
	$>C{=}CH{-}CH_3$	1.6–2.7	8.4–7.3
	 $>C{=}\overset{\mid}{C}{-}H$	4.5–6.5	5.5–3.5
Terminal alkynes $R{-}C{\equiv}CH$		2.5	7.5
Aromatic		6.5–8.5	3.5–1.5
Adjacent to electronegative atom			
	$R{-}CH_2{-}Cl$	3.7	6.3
	$R{-}CH_2{-}Br$	3.5	6.5
	$R{-}CH_2{-}I$	3.0	7.0
	$R{-}OH$	5.0	5.0
Aldehydes CH_3CHO			
	Alkyl proton	2.17	7.83
	Aldehydic proton	9.5	0.5
Acids	RCOOH	9.7	0.3
Esters	CH_3COOR	2.0	8.0
Amines	$R{-}NH_2$	1.8	8.2

Chemical shift values are also dependent on the nature of solvent, temperature and concentration.

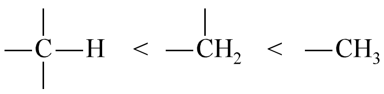
The area under the absorption peak curve in PMR spectrum is proportional to the number of protons of a given type which may be calculated either graphically or with the help of electronic integrator.

Some generalizations may be made regarding the chemical shift values of protons:

(*i*) All hydrogens with identical environment have the same chemical shift even though they may be on different carbon atoms in the molecule.

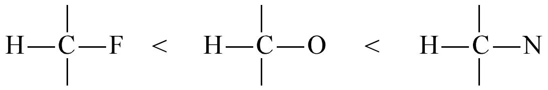
(*ii*) The hydrogens of methylene group may not be equivalent in (*a*) rigid cyclic system (remember *axial* and *equatorial* hydrogen in cyclo-hexane), and (*b*) hindered rotation.

(*iii*) In identical circumstances greater the number of hydrogen on one carbon, greater is the shielding and thus greater τ value.



$$-\underset{\mid}{\overset{\mid}{C}}-H \;<\; -\overset{\mid}{C}H_2 \;<\; -CH_3$$

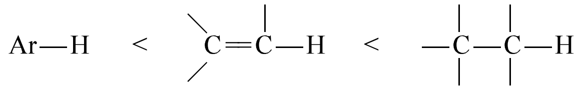
(*iv*) When an electronegative atom is attached to carbon of C—H bond, it causes deshielding, greater the electronegativity, greater is the deshielding and lower the τ values.



$$H-\underset{\mid}{\overset{\mid}{C}}-F \;<\; H-\underset{\mid}{\overset{\mid}{C}}-O \;<\; H-\underset{\mid}{\overset{\mid}{C}}-N$$

(*v*) The greater the ring size in alicyclic compounds lower is shielding and lower τ values.

(*vi*) Unsaturation generally lowers τ values



$$\mathrm{Ar{-}H} < \mathrm{>C{=}C{-}H} < \mathrm{{-}C{-}C{-}H}$$

(*vii*) Protons on heteroatoms (*e.g*. H—O, H—N etc.) show variable chemical shifts.

4.2.6 Spin Spin Interactions

Consider the PMR spectrum of ethyl bromide. It exhibits two peaks, one corresponding to three protons of methyl group and the other corresponding to two protons of methylene group (Fig. 4.6). Now observe the high resolution PMR spectrum of pure ethyl bromide (Fig. 4.7). It can be seen that PMR signal for —CH_3 group has split into a triplet while that for —CH_2— group has split into a quartet. In contrast to the chemical shift the line spacing for these splittings are independent of the applied magnetic field or radio frequency.

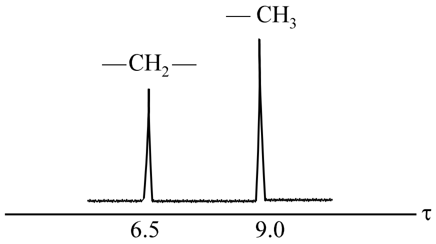


Fig. 4.6 *PMR spectrum of ethyl bromide.*

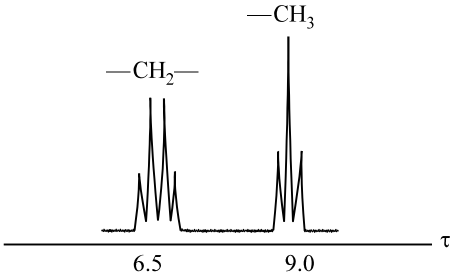


Fig. 4.7 *High resolution PMR spectrum of pure ethyl bromide.*

In the case of ethyl bromide it can be seen that the multiplicity of lines is $(n + 1)$ where 'n' is number of protons on adjacent carbon atom. Thus it is clear that protons on adjacent atoms are able to split the chemical shift absorption peaks by modifying the effective magnetic field at a proton or group of protons, so that it is not the same as the applied field. One adjacent proton may have two orientations ↑ and ↓ leading to a symmetrical doublet, two adjacent protons may have three orientations shown below:

↑↑

↑↓ ↓↑

↓↓

Leading to a 1 : 2 : 1 triplet, three adjacent protons may lead to a 1 : 3 : 3 : 1 quartet due to four orientations and so on.

↑↑↑

↑↑↓ ↑↓↑ ↓↑↑

↓↓↑ ↓↑↓ ↑↓↓

↓↓↓

The distance between multiple peaks in spin-spin splitting is a measure of the extent of effectiveness of spin-spin coupling and is known as coupling constant ‘J’. The magnitude of ‘J’ is expressed in cycles per second and is independent of applied field strength but depends on number and kind of intervening chemical bonds and on the spatial relationship between the groups. It is important to note that spin-spin splitting is not observed in case of identical protons. Thus there is no spin-spin splitting of proton signals in $Cl.CH_2.CH_2.Cl$ or $Cl.CH{=}CH.Cl$ or cyclobutane etc.

4.2.7 Classification Spin Decoupling and Factors Influencing Coupling Constant ‘J’

Spin decoupling is the act of illuminating one set of NMR-active spins to alter and improving the quality of the NMR signal received from a second set of spins. Decoupling a specific set of NMR-active spins brings about saturation of these spins. Saturation is the process to even out the entities of non-degenerate spin states. Decoupling can be either homonuclear or heteronuclear, implying that the nuclide we notice might be something similar or it could be unique in relation to the nuclide being seriously lighted. Heteronuclear decoupling is most commonly found.

Decoupling works by prompting changes between the spin state of one nuclide (e.g., 1H) to keep those nuclei from persevering in a specific spin state to the point of influencing the recurrence of the nuclide being noticed.

Homonuclear decoupling is utilized when the nucleus being (rf) illuminated are similar isotope as the nucleus noticed in the spectrum. Heteronuclear decoupling is utilized when the nuclei being (rf) illuminated are of an unexpected isotope in comparison to the nuclei being seen in the range. For a given isotope, the whole range for all nuclei of that isotope can be illuminated in extensive band decoupling, or just a specific range for selected nuclei of that isotope can be illuminated.

Factors Influencing Coupling Constants

Some important factors that influence the coupling constant in the NMR spectra are:

- **Adjacent π-Bonds**: The 2J coupling constants for a basic hydrocarbon like methane is - 12 Hz. At the point when the C-H bond can overlap with an adjoining π bond, the coupling constant is found to be more negative or you van say slightly bigger. The impact is more prominent when the hyper conjugation is with the π-bond of a carbonyl group than when it is essentially with a C=C bond. In this manner in acetone, the coupling constant is - 14.9 Hz and in toluene it is - 14.3 Hz.

- **Angle Strain**: Increasing the H-C-H bond, makes 2J more positive, or you can say comparatively smaller than before. This impact is most observable in the methylene groups of alkenes, where the angle has reached close to 120° and the coupling constant is near about zero. This coupling is exceptionally subjected to the idea of substituents at the opposite end of the π-bond, electronegative elements, for example, fluorine, making them more negative and electropositive elements, e.g., lithium, really making the coupling positive and larger.

- **Bond Length Dependence:** Aromatic carbon-carbon bonds have bond lengths lying in middle between ordinary single and double bonds. As a result, ortho coupling constants are normally around 8 Hz, maybe lower over cisolefinic coupling constants in cyclohexenes (8.8-10.5 Hz).

4.2.8 Bascic Ideas about Instruments

The substance is taken in a cylindrical sample tube placed between the poles of an electromagnet producing a uniform constant high strength field. Radio frequency field is applied at right angles to the magnetic field by passing an alternating current through a coil wound around the sample tube. The sample tube is spun several hundred times per minute to let the sample experience homogeneous magnetic field. Theoretically it is immaterial if external magnetic field is kept constant and radio frequency is varied or radio frequency is kept constant and external magnetic field is varied. Practically it is more convenient to keep radio frequency constant and vary external magnetic field, when at a certain value the sample absorbs the energy and the current flow in the coil falls off. This variation is amplified and transmitted to recorder through oscillograph.

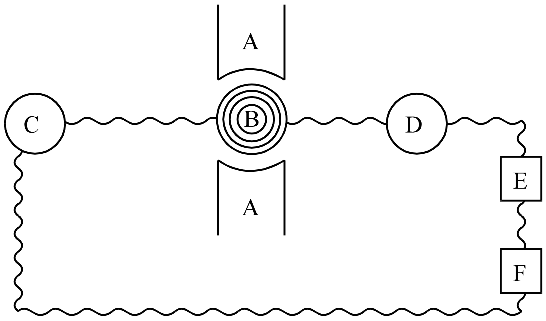


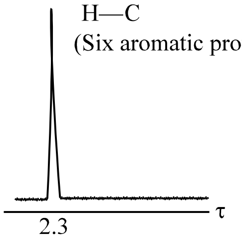
Fig. 4.8 *Schematic representation of NMR instrument (A = External magnetic field, B = Sample tube with sample, C = Radio frequency generator, D = Amplifier, E = Oscillograph, F = Recorder).*

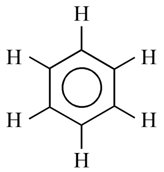
Usually the sample is taken in liquid or solution form and the solvent must be liquid which does not give PMR spectra *e.g.* CCl_4, CS_2 etc.

4.2.9 NMR Studies of Nuclei Other than Proton ^{13}C, ^{19}F and ^{31}P

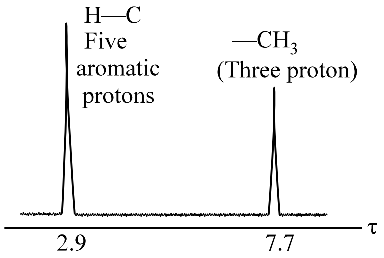
Schematic representation of PMR spectra of some organic compounds are given below with peak assignments which are self-explanatory.

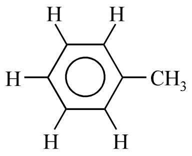
1. Benzene



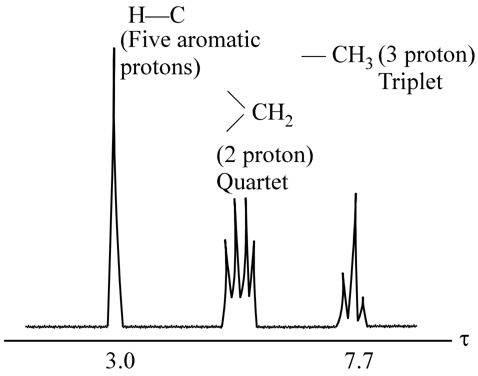


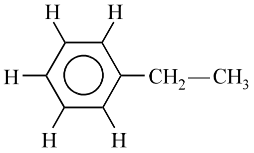
2. Toluene



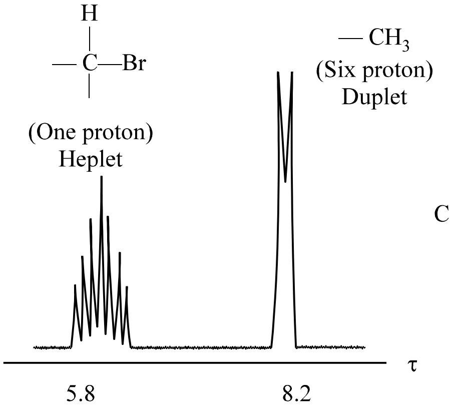


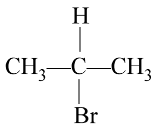
3. Ethyl benzene





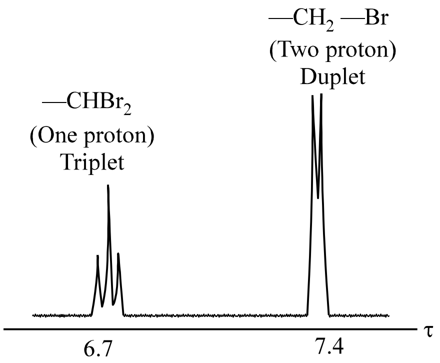
4. Isopropylbromide





$CH_3-\underset{Br}{\overset{H}{C}}-CH_3$

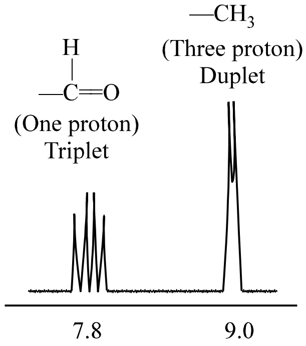
5. 1,1,2-Tribromoethane



Br—CH_2—$CHBr_2$

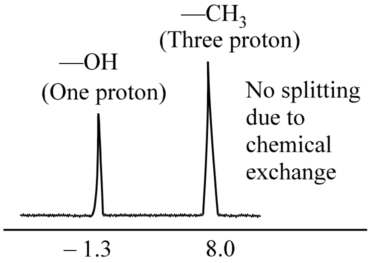
NOTES

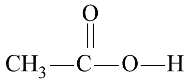
6. Acetaldehyde



$CH_3—CH=O$

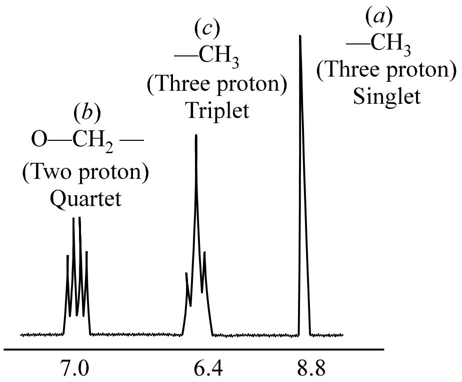
7. Acetic acid

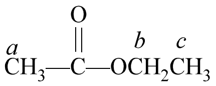




$$CH_3—\overset{\overset{\large O}{||}}{C}—O—H$$

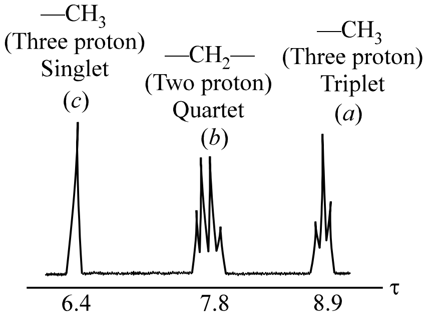
8. Ethyl acetate

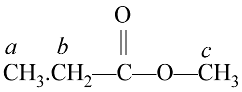




$$\overset{a}{CH_3}—\overset{\overset{\large O}{||}}{C}—O\overset{b}{CH_2}\overset{c}{CH_3}$$

9. Methyl propionate

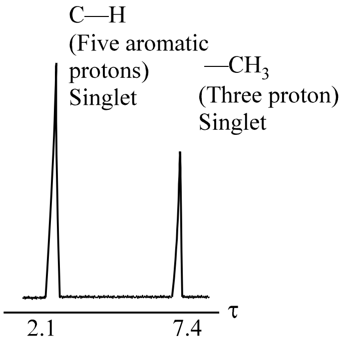


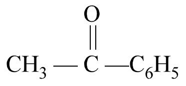


$$\overset{a}{CH_3}.\overset{b}{CH_2}—\overset{\overset{\large O}{||}}{C}—O—\overset{c}{CH_3}$$

NOTES

10. Acetophenone





$$CH_3 - \overset{\overset{\displaystyle O}{\|}}{C} - C_6H_5$$

4.2.10 Fourier Transform Nuclear Magnetic Resonance (FT-NMR)

A revolution in NMR occurred when short radio-frequency pulses began to be used, with a frequency centered at the middle of the NMR spectrum. Fourier Transform Nuclear Magnetic Resonance (FT-NMR) is an analytical technique used to analyze the structure of molecules range from a small organic molecule or metabolite, to a mid-sized peptide or a natural/synthetic product based on the magnetic property of certain nuclei (e.g., 1H, 13C etc.).

Basically, a short pulse of a given carrier frequency contains a scope of frequencies focused with regards to the carrier frequency, with the scope of excitation (bandwidth) being conversely corresponding to the pulse span, i.e., the Fourier change of a short pulse includes all the frequencies in the neighbourhood of the principal frequency. The confined scope of the NMR frequencies made it somewhat simple to utilize short (1-100 microsecond) radio frequency pulses to excite the whole NMR spectrum.

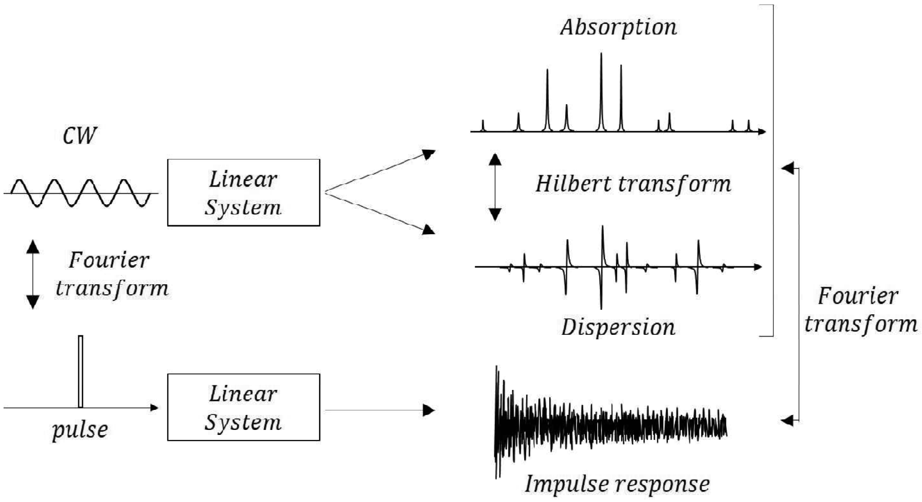


Fig 4.9 *FT- NMR*

Applying these pulses to a specific set of nuclear spins all the while energizes all the single-quantum NMR transitions. As far as the net magnetization vector is concerned, this compares to shifting the magnetization vector away from its balanced (equilibrium) position (adjusted along the external magnetic field). The out-of-equilibrium magnetization vector then, at that point, processes the outside magnetic field vector at the NMR frequency of the spins. This oscillating magnetization vector initiates a voltage in a close-by pickup coil, making an electrical signal oscillate at the NMR frequency. This sign is known as the Free Induction Decay (FID), and it contains the amount of the NMR reactions from each and every excited spin. To acquire the frequency domain NMR spectra (NMR absorption intensity versus NMR frequency) this time-domain signal (force versus time) should be Fourier transformed. Luckily, the advancement of Fourier Transformation (FT) NMR in coordination with the improvement of digital computers and the advanced Fast Fourier Transform. Fourier strategies can be applied to many kinds of spectroscopy.

Richard R. Ernst was one of the trailblazers of pulse NMR and won a Nobel Prize for it in 1991 for his work on Fourier Transform NMR and his advancement of complex NMR spectroscopy.

4.2.11 Advantages of FT-NMR

FT NMR has many advantages over the conventional spectroscopic techniques. Few advantages of FT_NMR are listed below:

1. **Time-Saving:** NMR active nuclei present in the molecules are analyzed at the same time resulting in more noteworthy helpful structural analysis from samples containing nuclei other than 1H.
2. **Higher Sensitivity:** Co-expansion of spectral response throughout a given time span works on signal-to-noise proportions and this prompts further developed sensitivity. In contrast to CW - NMR which is utilized principally for 1H examinations NMR data on different nuclei like ^{13}C, ^{31}P, ^{19}F give a poor response because of their lower isotopic numbers. FT-NMR bears the cost of more prominent awareness for studies on such nuclei because of signal averaging. Exceptional expansion in sensitivity regularly brings about helpful data from the restricted accessible sample amounts.
3. **Multiple Scans:** The benefit of the Fourier Transform NMR (FT-NMR), over Continuous Wave NMR, is the capacity to gather multiple scans that are on average, expanding the sign to-noise proportion. This is especially significant for C-13 NMR where the regular wealth of the isotope is so little.

4.2.12 Use of NMR in Medical Diagnostics

In the field of diagnostic medicine, Nuclear Magnetic Resonance (NMR) spectroscopy has found wide applications. Simplicity of sample preparation, biological safety, non-invasiveness, and non-destructiveness are the advantages of NMR based metabolic studies. Few advantages can be listed as:

1. Neuropsychiatric problems like schizophrenia, panic issues, significant gloom, bipolar issues and mental imbalance issues like autism etc. have been researched methodically utilizing NMR spectroscopy.

2. NMR metabolomics is utilized in the quest for biomarkers of infections like tuberculosis, malaria and pneumonia, neurological problems and Parkinson's disease.
3. NMR metabolomics has been utilized in the recognizable proof of biomarker for cardiovascular illnesses and hazard stratification.
4. It has also been used in cancer diagnosis and therapy. NMR metabolomics has been used to investigate processes like transformation, progression, proliferation and metastasis in cancer cell lines.
5. Other examples for applications of NMR metabolomics include gastro-intestinal disorders, endocrine and nutritional disorders, disorders of the nervous system and respiratory system disorders.

Check Your Progress

1. Define NMR.
2. What do you understand by nuclear spin?
3. What do you understand by resonance?
4. Define nuclear shielding.
5. What do you understand by chemical shift?

4.3 ELECTRON SPIN RESONANCE SPECTROSCOPY

Electron Spin Resonance (ESR) otherwise called Electron Magnetic Resonance (EMR) or Electron Paramagnetic Resonance (EPR) is a part of absorption spectroscopy where radiations having a frequency in the microwave region (0.04 - 25 cm) is consumed by paramagnetic substances to prompt changes between magnetic energy levels of electrons with unpaired spins. ESR depends on the way that atoms, molecules, ions or sub-atomic fragments which have an odd number of electrons display specific magnetic properties. An electron has a spin and because of that spin, there is a magnetic moment. Since its revelation in 1944 by E.K. Zavoisky, EPR spectroscopy has been taken advantage of as an exceptionally sensitive and enlightening method for the examination of various types of paramagnetic species in strong or fluid states.

An electron possesses spin angular momentum and because of this momentum a spin magnetic moment. The spin may take two orientations denoted as α or β with respect to some selected direction.

$$E_{ms} = 2\mu_B,\, m_s B, \qquad m_s = \pm\,\frac{1}{2}$$

where B is the applied magnetic field, μ_B is the Bohr magneton. It shows that the electron with a spin ($m_s = +1/2$) rise while that of the β-spin electron talls as the magnetic field is raised. The energy of separation of the two spin states is shown in Figure 4.10.

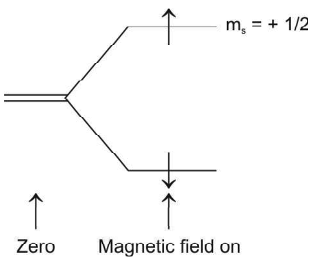


Fig. 4.10 Electron Spin Energy Levels in a Magnetic Field

$$\Delta E = E_{1/2} - E_{-1/2} = 2\mu_B B$$

The sample is bathed in a radiation of frequency v. The unpaired electron spins of the sample have energy levels that come into resonance with the radiation when the magnetic field has been adjusted so that

$$hv = 2\mu_B B$$

When this condition is satisfied the energy levels are in resonance with the surrounding radiation. The resonance condition is satisfied and strong energy absorption takes place. The electron spin resonance spectroscopy technique is also called electron paramagnetic resonance is the study of the properties of molecules containing unpaired electrons by observing the magnetic fields at which they produce resonance with the applied field of define frequency.

4.3.1 Basic Principle

The peculiarity of Electron Spin Resonance (ESR) depends on the fact that an electron is a charged molecule. It twirls around its axis and this makes it behave like a minuscule bar magnet. At the point when a particle or compound with an unpaired electron is set in a solid magnetic field, the spin of the unpaired electron can adjust in two distinct ways making two spin states ms = ± ½.

The arrangement can either be along the course (parallel) to the magnetic field which relates to the lower energy state ms = - ½, i.e., opposite (antiparallel) to the heading of the applied magnetic field ms = + ½

The two arrangements have various energies and this distinction in energy lifts the decadence of the electron spin states.

The energy difference is given by:

Δ E = E+ – E- = hv = gmßB

Where,

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

v = the frequency of radiation

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

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

NOTES

An unpaired electron can move between the two energy levels by either absorbing or emitting a photon of energy, such that the resonance condition, hv = Δ E, is obeyed.

The block diagram of a simple esr spectrometer is shown is Figure 4.11. As in NMR spectrometer the frequency is kept constant and the magnetic field is swept through resonance. Microwave radiation from a klystron passes down a waveguide to a resonant cavity containing the sample. When there are transitions between electron spin levels containing the sample. When there are transitions between electron spin levels in the sample, energy is absorbed from the microwave radiation and less microwave energy is received at the crystal detector. By using a field modulator and a phase sensitive detector the derivative of the absorption line is recorded on the oscilloscope or on a phase sensitive detector. The sample may be a gas liquid or solid but the gas phase involves complications. The only requirement is that the molecules of sample must possess unpaired spins. Therefore ESR may be used for studying free radicals formed during chemical reactions or on photolysis, from transition metal complexes and the molecules in the triplet state. However, it is insensitive to normal spin paired molecules.

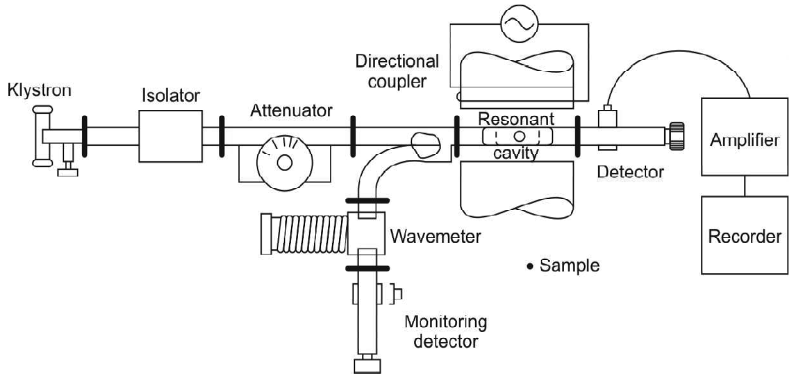


Fig. 4.11 *A Electron Spin Resonance Spectrometer*

4.3.2 Zero Field Splitting and Kramer's Degeneracy

Zero Field Splitting (ZFS) depicts different connections of the energy levels of an atom or ion coming about because of the presence of more than one unpaired electron. In quantum mechanics, an energy level is called degenerate, assuming it relates to at least two different quantifiable conditions of a quantum system. Within a magnetic field, the Zeeman Effect is noticeable to divide the degenerate states. In quantum mechanics phrasing, the decadence is supposed to be "lifted" by the presence of the magnetic field. Within the sight of more than one unpaired electron, the electrons commonly connect to lead to at least two energy states. Zero field splitting alludes to this lifting of degeneracy even without a magnetic field. ZFS is answerable for some, impacts connected with the magnetic properties of materials, as appeared in their electron spin resonance spectra and magnetism.

Kramer's Degeneracy: Kramer's degeneracy hypothesis expresses that for each energy Eigen state of a period inversion symmetric system with a half-integer absolute spin, there is another Eigen state with similar energy. In short, each energy level is in some measure doubly degenerate assuming it has a half-integer spin. The law is named for the Dutch physicist H. A. Kramer.

4.3.3 Factors Affecting 'G' Value

Electron g-factor is the ratio of magnetic moment of the electron to the total spin angular momentum of the electron. For a free electron the value of g is 2.0023. In many free radicals, the value of the odd electron is close to that of a free electron, but in metal ions g values are often quite different from the free electron value.

In general, the magnitude of g depends upon the orientation of the molecule/ ion containing the unpaired electron with respect to the magnetic field applied. In a solution, or in the gas phase, g is averaged over all orientations because of the free motion of the molecules/ ions. However, in a crystal, the movement of molecules/ions is restricted. If the paramagnetic radical or ion is located in a perfectly cubic crystal site, i.e., an octahedral or tetrahedral site, the g-value is independent of the orientation of the crystal and is said to be isotropic. In a crystal site of lower symmetry, the value of g depends upon the orientation of the crystal and is said to be anisotropic.

4.3.4 Isotropic and Anisotropic Hyperfine Coupling Constants

Two normal components by which electrons and nuclei communicate are the Fermi contact cooperation and by dipolar connection. The previous applies generally to the instance of isotropic interactions (free of test direction in a magnetic field) and the last option to the instance of anisotropic communications (spectra reliant upon test direction in a magnetic field). Spin polarization is a third instrument for communications between an unpaired electron and an atomic spin, being particularly significant for ?-electron organic radicals, like the benzene radical anion. The symbol "a" or "A" are utilized for isotropic hyperfine coupling constants while "B" is generally utilized for anisotropic hyperfine coupling constants.

Much of the time, the isotropic hyperfine parting design for a radical uninhibitedly tumbling in a solution (isotropic framework) can be anticipated. 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 ßa

a. **Isotropic hyperfine splitting constant** is the measure of separation between two ESR signals.

   Its value is same in all directions $A = [\{g\beta H + \frac{1}{2} A\} - \{g\beta H - \frac{1}{2} A\}]$. It occurs in the case where rotation of spinning species are free.

b. **Anisotropic hyperfine splitting constant** – B or A_{iso} or A_o 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, $\|$ 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.

4.3.5 Spin Hamiltonian and Spin Densities

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. The spin Hamiltonian equation consists of magnetic field–dependent interaction and magnetic field–independent interaction.

The Spin Hamiltonian interacts in a straight manner (e.g., a collaboration of the electron spin with the static field B0) or bilinear terms (e.g., coupling among electron and atomic spins) of spin angular momentum administrators and contains a couple of phenomenological constants which can be connected with the properties of the spin system (e.g., atomic gn factors). The finite dimension of the Hilbert space for an electron spin *S* coupled to *n* nuclear spins $I_1, I_2, ..., I_n$ is given by:

$$d_{HS} = (2S+1)\prod_{k=1}^{n}(2I_k+1)$$

The spin quantum number S reflects either the genuine electron spin for a system where the contribution of orbital angular momentum to the ground state are little (for example organic radicals) or an effective spin of a subsystem with 2S+1 states (e.g., ground condition of rare earth elements with enormous spin-orbit coupling).

Spin Densities: The density applies to the free radicals is called spin density. It can further be described as the overall density of the electron in a single spin minus the overall density of electron in the remaining spins.

4.3.6 McConnel 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 and is proportional to unpaired π spin density ρ, on the adjacent carbon atom. Q is constant. For 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.

4.3.7 Applications of ESR Spectroscopy

All applications of ESR are based on three aspects, which are:

- Study of free radicals.
- Investigation of molecules in the triplet state.
- Study of inorganic compounds.

NOTES

a. **Study of Free Radicals:** Indeed, even in an extremely low concentration of sample ESR can review utilizing free radicals. It is additionally applied in the structural determination of organic and inorganic free radicals. The power of the ESR signal is straightforwardly corresponding to the no. of free radicals present. Subsequently utilizing ESR we can gauge the relative concentration of free radicals.

b. **Investigation of Molecules in the Triplet State**: A triplet atom has a complete spin S=1 so that, its multiples can be given as 2S+1=3. While free radicals with S=½ has an odd no. of unpaired electrons. A triplet atom has an even no. of electrons and two of them are unpaired. In a triplet atom, the unpaired electrons should connect though, in diradical, the unpaired electrons don't interact as they are at a significant distance apart.

c. **Study of Inorganic Compounds:** ESR is extremely effective in the investigation of inorganic mixtures. The ESR studies might be utilized in knowing the specific structures of solvated metal particles, in the investigation of catalysts, in the assurance of oxidation condition of metal, e.g., Copper is found as divalent in copper protein complexes though it is viewed as monovalent in some biologically active copper complexes. The information of unpaired electrons is exceptionally valuable in different viewpoints in the uses of ESR. Like, spin labels, structural analysis, rate of reaction and reaction mechanism.

   1. **Spin Labels:** Groups with unpaired electrons can be easily attracted to the macromolecules, for example, protein and membranes to acquire a lot of data to analyse their structure. The nitroxide molecules bound to macromolecules are called spin labels. These spin labels are steady particles that have unpaired 2p electrons. A regularly utilized TEMPOL (2,2,6,6-tetramethyl piperidinol-n-oxyl). The hyperfine design of an ESR spectrum is a sort of unique finger impression that assists with recognizing the free radicals present in the sample. Spin labels give extremely helpful data about the molecules to which they are bound. Likewise, we get data like the rate of motion of macromolecules to which they are bound, or how much thermal motion in a membrane is observed to which they have been embedded. The spin labels can give data about the polarity of its surroundings.

   2. **Structural Determination:** It doesn't enlighten us regarding the structural arrangement of the atoms in a molecule. However, the symmetry of the atom can be in some cases found from the arrangements of equivalent nuclei. In specific cases, ESR can give helpful data about the structure of the radicals.

d. **Protein Structure and Dynamics:** ESR assists with finding the interactions among ligands and target protein model in the review on the ion siderophore complex and it's limiting to site coordinated spin labelled ferric enterobactin receptor answerable for iron take-up by enterobacteria.

e. **Biological Systems:** From the ESR investigations of the organic system, for example, leaves, seeds, and tissue culture, it is seen that a clear, relationship exists between the grouping of free radicals and the metabolic action of the plant material. ESR has concentrated on the presence of free radicals in healthy and sick tissues. The greater part of the oxidative compounds works employing a one-electron redox reaction including the development of either protein-bound free radicals or by an adjustment of the valence state of transition metal ions. This has been affirmed by ESR studies. A large part of the ESR work on photosynthesis has been completed with photosynthetic microscopic organisms. The oxidation of bacterio-chlorophyll in vitro delivers an ESR signal.

f. **Reaction Velocities and Reaction Mechanisms:** A huge number of natural responses is realized which continue by an extreme radical mechanism. The greater part of the radicals is shaped during organic reactions that are not steady yet are exceptionally reactive. The ESR spectroscopy can be utilized to concentrate on extremely fast electron trade responses.

Check Your Progress

5. What do you mean by ESR?
6. State the basic principle of ESR.
7. Define zero field splitting.
8. State the basic concept of Kramer's degeneracy.
9. What do you understand by spin Hamiltonian?

4.4 NUCLEAR QUADRUPOLE RESONANCE SPECTROSCOPY

Nuclear Quadrupole Resonance Spectroscopy or NQR is a compound investigation method connected with Nuclear Magnetic Resonance (NMR). Dissimilar to NMR, NQR advances of nuclei can be distinguished without any magnetic field, and thus NQR spectroscopy is alluded to as "zero-field NMR". The NQR resonance is intervened by the connection of the electric field gradient (EFG) with the quadrupole moment of the nuclear charge distribution. Unlike NMR, NQR is pertinent just to solids and not fluids, on the grounds that in fluids the quadrupole moment averages out. Since the EFG at the nucleus in a given substance is resolved basically by the valence electrons associated with the specific bond with other nearby nuclei, the NQR recurrence at which advances happen is one of a kind for a given substance. A specific NQR frequency in a compound or crystal is relative to the result of the atomic quadrupole second, a property of the core, and the EFG in the neighbourhood of the nuclei. It is this item that is named the nuclear quadrupole coupling consistent for a given isotope in any material and can be found in tables of known NQR transitions. In NMR, a practically equivalent and not indistinguishable peculiarity is the coupling constant, which is likewise the consequence of an inter-nuclear association between nuclei in the analyte.

Any nucleus with more than one unpaired atomic molecule (protons or neutrons) will have a charge dispersion which brings about an electric quadrupole moment. Permitted thermal energy levels are moved inconsistently because of the collaboration of the nuclear charge of an electric field slope provided by the non-uniform distribution of electron density (for example from bonding electrons) and additionally encompassing ions. As on account of NMR, the illumination of the nucleus with an explosion of RF electromagnetic radiation might bring about absorption of some energy by the core which can be seen as a perturbation of the quadrupole energy level. Not at all like the NMR case, the NQR absorption taken place without a trace of an outside magnetic field. Utilization of an outside static field to a quadrupolar nucleus splits the quadrupole levels by the energy anticipated from the Zeeman interaction. The procedure is extremely delicate to the nature and symmetry of the bonding around the nucleus. It can portray phase transitions in solids when performed at different temperatures. Because of symmetry, the shifts are equal to zero in the fluid stage, so NQR spectra can only be estimated for solids.

NOTES

4.4.1 Quadrupole Nuclei, Quadrupole Moment, and Electric Field Gradient

Quadrupole Nuclei: A quadrupole nucleus is one having a quantum spin number more prominent than ½. Such nuclei have comparatively lower symmetry than spin -½ nuclei. The quadrupole moment that changes between nuclei is a proportion of this deviation.

Quadrupole Moment: The nuclear electric quadrupole moment is a standard that depicts the shape of the ellipsoid of nuclear charge distribution. A non-zero quadrupole moment Q demonstrates that the charge distribution isn't spherically symmetric. Somehow, the value of Q is taken to be positive on the off chance that the ellipsoid is prolate and negative assuming it to be oblate.

Electric Field Gradient (EFG): The Electric Field Gradient (EFG) measures the pace of progress of the electric field at a nucleus produced by the electronic charge distribution with different nuclei. The EFG couples with the nuclear electric quadrupole moment of quadrupolar nuclei (those with a spin quantum number more prominent than one-half) to create an impact which can be estimated utilizing a few spectroscopic strategies, like Nuclear Magnetic Resonance (NMR), microwave spectroscopy, Electron Paramagnetic Resonance (EPR, ESR), Nuclear Quadrupole Resonance (NQR). The EFG is non-zero provided that the charges encompassing the nuclei violates the cubic symmetry and along these lines create an inhomogeneous electric field at the nucleus. EFGs are profoundly touchy to the electronic density in the vicinity of a nucleus.

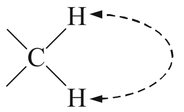
4.4.2 Coupling Constant

The distance between the peaks in a given multiplet (fine structures) is a measure of magnitude of splitting effect. This is known as coupling constant and is designated by the symbol J, which is expressed in cycle per second or Hertz (Hz). Whereas chemical shift is dependent on applied field, the coupling constant is independent of the applied field but depends on the structure of a molecule.

In case of mutually coupled protons the magnitude of splitting of signal of one proton by the other is the same. The coupling constant is determined by the nature of the bond and the spatial relations between the protons.

(*a*) For protons attached to the same carbon atom (i.e., geminal protons), the value of J varies from 0–20 Hz depending on bond angle and overall structure of the molecule.

NOTES



$J = 0 - 20$ Hz

(*b*) For protons attached to adjacent carbon atoms (i.e., vicinal protons), the value of J depends on the dihedral angle.

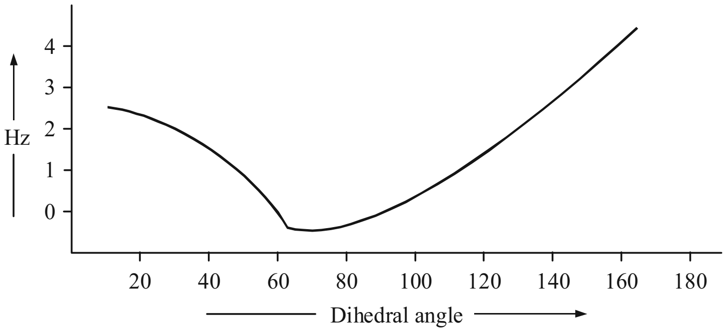
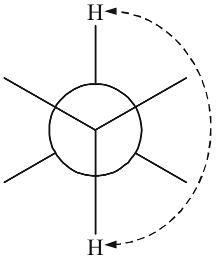


Fig. 4.12 *Variation of J with dihedral angle*

For 0º and 180º, coupling constants is higher. At 90º 'J' is slightly negative.

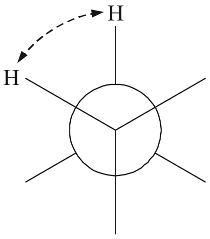
In case of ethane (C_2H_6), which has freely rotating groups, protons with anti conformation have 'J' value 5–12 Hz while protons with gauche conformation have $J = 2 - 4$ Hz.

J = 5 – 12 Hz



Anti

J = 5 – 14 Hz



Gauche

Coupling constants are a measure of the effectiveness of spin-spin coupling and are helpful in determining complex molecular structures.

4.4.3 Splittings

Consider the PMR spectrum of ethyl bromide. It exhibits two peaks, one corresponding to three protons of methyl group and the other corresponding to two protons of methylene group (Fig. 4.13). Now observe the high resolution PMR spectrum of pure ethyl bromide (Fig. 4.14). It can be seen that PMR signal for —CH_3 group has split into a triplet while that for —CH_2— group has split into a quartet. In contrast to the chemical shift the line spacing for these splittings are independent of the applied magnetic field or radio frequency.

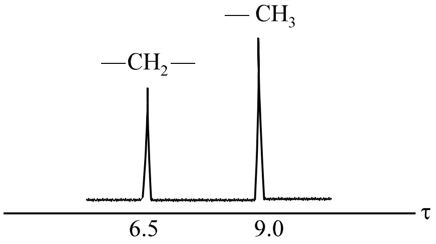


Fig. 4.13 *PMR Spectrum of Ethyl Bromide.*

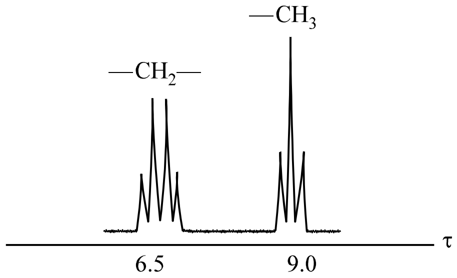


Fig. 4.14 *High resolution PMR Spectrum of Pure Ethyl Bromide.*

In the case of ethyl bromide it can be seen that the multiplicity of lines is $(n + 1)$ where 'n' is number of protons on adjacent carbon atom. Thus it is clear that protons on adjacent atoms are able to split the chemical shift absorption peaks by modifying the effective magnetic field at a proton or group of protons, so that it is not the same as the applied field. One adjacent proton may have two orientations ↑ and ↓ leading to a symmetrical doublet, two adjacent protons may have three orientations shown below:

↑↑

↑↓ ↓↑

↓↓

Leading to a 1 : 2 : 1 triplet, three adjacent protons may lead to a 1 : 3 : 3 : 1 quartet due to four orientations and so on.

↑↑↑

↑↑↓ ↑↓↑ ↓↑↑

↓↓↑ ↓↑↓ ↑↓↓

↓↓↓

The distance between multiple peaks in spin-spin splitting is a measure of the extent of effectiveness of spin-spin coupling and is known as *coupling constant* 'J'. The magnitude of 'J' is expressed in cycles per second and is independent of applied field strength but depends on number and kind of intervening chemical bonds and on the spatial relationship between the groups. It is important to note that spin-spin splitting is not observed in case of identical protons. Thus there is no spin-spin splitting of proton signals in $Cl.CH_2.CH_2.Cl$ or $Cl.CH{=}CH.Cl$ or cyclobutane etc.

4.4.4 Applications of Nuclear Quadrupole Resonance Spectroscopy

Nuclear quadrupole resonance spectroscopy is used for:

1. Identification of isomers and conformers
2. Identification of double bond character
3. Detection of aromaticity in aromatic compound
4. Detection of hydrogen bonding
5. Detection of electronegative atom or group

Check Your Progress

10. What do you understand by quadrupole nuclei?
11. Define quadrupole moment.
12. Define electric field gradient.
13. What is the measurement factor of intrinsic magnetic moment of an electron?

4.5 ANSWERS TO 'CHECK YOUR PROGRESS'

NOTES

1. 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 is called Nuclear Magnetic Resonance (NMR) spectroscopy.
2. It is a method to represent the total angular momentum of a nucleus by the symbol I.
3. When the precessional frequency of the spinning nucleus coincides with the frequency of rotating magnetic field, they are said to be in resonance.
4. 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.
5. 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.
6. ESR is a branch of absorption spectroscopy in which radiations having frequency in the microwave region (0.04 – 25 cm) is absorbed by paramagnetic substances to induce transitions between magnetic energy levels of electrons with unpaired spins.
7. The phenomenon of electron spin resonance (ESR) is based on the fact that an electron is a charged particle. It spins around its axis and this causes it to act like a tiny bar magnet.
8. Zero Field Splitting (ZFS) describes various interactions of the energy levels of a molecule or ion resulting from the presence of more than one unpaired electron.
9. The Kramer's degeneracy theorem states that for every energy Eigen state of a time-reversal symmetric system with half-integer total spin, there is at least one more Eigen state with the same energy.
10. 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.
11. A quadrupole nucleus is one that has a quantum spin number greater than ½. Such nuclei have a lower symmetry than spin-½ nuclei.
12. The nuclear electric quadrupole moment is a parameter which describes the effective shape of the ellipsoid of nuclear charge distribution.
13. 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.
14. G value is the measurement factor of intrinsic magnetic moment of an electron.

4.6 SUMMARY

- Nuclear Spin is a method to represent the total angular momentum of a nucleus by the symbol *I*.
- The nuclear spins for individual protons and neutrons parallels the treatment of electron spin, with spin 1/2 and an associated magnetic moment.
- The saturation in the NMR experiment is another spectroscopic method to study the interactions, in solution, between a large molecule (receptor) and a medium-small sized molecule (ligand), and, alike tr-NOESY, it is based on the Nuclear Overhauser effect and the observation and analysis of the resonances of the ligand protons.
- STD (Saturation Transfer Difference) NMR is a powerful ligand-based tool for screening small molecules and low molecular weight fragments for their interaction with a given macromolecule.
- Resonances will be observed only in the STD spectrum for those compounds that lose some of their signal intensity in the on-resonance spectrum due to receiving saturation from the protein.
- The chemical shift values of different nuclei in a molecule arise due to differences in the local magnetic field, felt by the nuclei in different parts of the molecule.
- Chemical shift values are also dependent on the nature of solvent, temperature, and concentration as well.
- The distance between the multiple peaks in spin-spin splitting is a measure of effectiveness of coupling and is called as the coupling constant.
- 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.
- Fourier Transform Nuclear Magnetic Resonance (FT-NMR) is an analytical technique used to analyze the structure of molecules range from a small organic molecule or metabolite, to a mid-sized peptide or a natural/synthetic product based on the magnetic property of certain nuclei.
- The restricted range of the NMR frequencies made it relatively easy to use short (1-100 microsecond) radio frequency pulses to excite the entire NMR spectrum.
- Richard R. Ernst was one of the pioneers of pulsed NMR and won a Nobel Prize in chemistry in 1991 for his work on Fourier Transform NMR and his development of multi-dimensional NMR spectroscopy.
- NMR metabolomics has been used in the identification of biomarker for cardiovascular diseases and risk stratification.
- 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.

NOTES

- Microwave absorption is measured as a function of the magnetic field by ESR spectroscopy.
- 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.
- *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.
- The g-factor is a unit less measurement of the intrinsic magnetic moment of the electron. It is a tensor quantity.
- 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.
- EPR spectrometers work by generating microwaves from a source like klystron. A Klystron oscillator is generally operated at 9500 Mc/sec.
- Two common mechanisms by which electrons and nuclei interact are the Fermi contact interaction and by dipolar interaction.
- The hyperfine splitting constant, known as a, can be determined by measuring the distance between each of the hyperfine lines.
- Isotropic hyperfine splitting constant is the measure of separation between two ESR signals. Its value is same in all directions.
- In the absence of magnetic field the three values of Ms are degenerated but when the magnetic field is applied to it then it get splits up into three energy levels.
- 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.
- 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.
- Nuclear quadrupole resonance spectroscopy or NQR is a chemical analysis technique related to nuclear magnetic resonance (NMR).
- A particular NQR frequency in a compound or crystal is proportional to the product of the nuclear quadrupole moment, a property of the nucleus, and the EFG in the neighborhood of the nucleus.
- Unlike the NMR case, NQR absorption takes place in the absence of an external magnetic field.
- A quadrupole 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.
- The nuclear electric quadrupole moment is a parameter which describes the effective shape of the ellipsoid of nuclear charge distribution.

- 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.

4.7 KEY TERMS

- **Nuclear Spin:** It is a method to represent the total angular momentum of a nucleus by the symbol *I*.
- **Saturation:** The saturation in the NMR experiment is another spectroscopic method to study the interactions, in solution, between a large molecule (receptor) and a medium-small sized molecule (ligand), and, alike tr-NOESY, it is based on the Nuclear Overhauser effect and the observation and analysis of the resonances of the ligand protons.
- **FT NMR:** Fourier Transform Nuclear Magnetic Resonance (FT-NMR) is an analytical technique used to analyze the structure of molecules range from a small organic molecule or metabolite, to a mid-sized peptide or a natural/synthetic product based on the magnetic property of certain nuclei (e.g., ^1H, ^{13}C etc.).
- **Electron Spin Resonance (ESR):** It is a branch of absorption spectroscopy in which radiations having frequency in the microwave region (0.04 – 25 cm) is absorbed by paramagnetic substances to induce transitions between magnetic energy levels of electrons with unpaired spins.
- **Zero Field Splitting:** Zero Field Splitting (ZFS) describes various interactions of the energy levels of a molecule or ion resulting from the presence of more than one unpaired electron.
- **Kramer's Degeneracy:** The Kramer's degeneracy theorem states that for every energy Eigen state of a time-reversal symmetric system with half-integer total spin, there is at least one more Eigen state with the same energy.
- **Spin Hamiltonian:** The spin Hamiltonian equation consists of magnetic field–dependent interaction and magnetic field–independent interaction.
- **Quadrupole Nuclei:** A quadrupole 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.
- **Quadrupole Moments:** The nuclear electric quadrupole moment is a parameter which describes the effective shape of the ellipsoid of nuclear charge distribution.
- **Electric Field Gradient:** 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.

4.8 SELF-ASSESSMENT QUESTIONS AND EXERCISES

Short-Answer Questions

1. State the basic principle of NMR.
2. Define resonance.
3. What do you understand by transition energy?
4. What do you understand by spin spin relaxation?
5. State shielding and de shielding effects.
6. Define anisotropic effect.
7. Define spin spin interaction.
8. What do you understand by g value?
9. Define Kramer's degeneracy.
10. What do you understand by quadrupole nuclei?
11. Define electric field gradient.
12. Define coupling constant.

Long-Answer Questions

1. Describe the instrumentation of NMR.
2. Explain in detail the various aspects of NMR system.
3. What do you understand by chemical shift? Explain in detail the measurement of chemical shift.
4. Describe the factors affecting chemical shift.
5. Explain spin decoupling in detail.
6. Describe the factors affecting G value
7. Discuss the instrumentation of ESR.
8. Mention the applications of ESR.
9. Discuss in detail the basic principle and components of nuclear quadrupole resonance spectroscopy.

4.9 FURTHER READING

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UNIT 5 DIFFRACTION

NOTES

Structure

5.0 INTRODUCTION

Electromagnetic radiation, X-ray beams might be explained concerning their electric and magnetic properties and components. These components are considered to oscillate transitionally and sinusoidally in the direction of the movement of the photon and are normal to one another. Whenever X-ray photons collide with the sample, the oscillating electric field of the radiation makes the charged parts of the atoms sway with a similar frequency as the episodic radiation and give structural details of the atoms in a wide scope of materials.

Electron diffraction is the electron microscopy strategy. In contrast to other different kinds of radiation utilized in diffraction investigations of materials, for example, X-ray, neutrons, electrons are charged particles and interact with the surrounding matter through the Coulomb forces. This implies that the incident electrons feel the impact of both the positively charged nuclei and the encompassing electrons. Electron diffraction is an aggregate dissipating peculiarity with electrons being (almost elastic) dispersed by molecules in a regular array (crystal).

Neutron diffraction or elastic neutron scattering is the utilization of neutron dispersing to the determination of the nuclear as well as magnetic structure of a material. Neutrons are neutral particles and interact mainly with the nuclei in a sample. Their scattering properties rely on the perplexing neutron-nucleus connection; as a result, isotopes of similar elements can have different neutron scattering properties.

5.1 OBJECTIVES

After going through this unit, you will be able to:

- Understand the basics of various diffraction techniques.
- Describe the procedure of X-ray structure analysis.
- Highlight modern advances in XRD instrumentation and techniques.
- Explain the phase identification problem.
- Conceptualize the phenomenon of X-ray, electron, and neutron diffraction methods.

5.2 X-RAY DIFFRACTION

X-rays are electromagnetic radiation with normal photon energies varying from 100 eV - 100 keV. They were invented by Wilhelm Conrad Röntgen in 1895. For diffraction applications, just short frequency X-rays (hard X-rays) in the range of a couple of angstroms to 0.1 angstroms (1 keV - 120 keV) are utilized. Since the frequency of X-rays is practically identical to the size of atoms, they are appropriate for analysing the structure of atoms and molecules in a wide variety of materials. The vivacious X-rays can enter profound into the materials and give data about the bulk structure.

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.

5.2.1 Bragg's Condition and Bragg's Method

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 $2d\sin\theta$, where θ is the scattering angle.

$$2d\sin\theta = n\lambda$$

Where, n is an integer determined by the order given, and λ is the wavelength. A diffraction pattern is acquired by estimating the intensity of scattered waves as an element of scattering angle. Sharp intensities known as Bragg peaks can be found in the diffraction pattern when scattered waves fulfil the Bragg condition.

Bragg diffraction was first proposed by William Lawrence Bragg and William Henry Bragg in 1913 because of their revelation that crystalline solids create astonishing patterns of reflection. They tracked down that these crystals, at specific wavelength and incident angles, delivered intense pinnacles of reflected radiation (known as Bragg peaks).

W. L. Bragg and his father, Sir W. H. Bragg, received the Nobel Prize in physics in 1915 for their work in determining the crystal structures starting with NaCl, ZnS, and crystals. X-ray essentially interacts with electrons present in the atoms. Whenever X-ray photons collide with the electrons, a few photons from the incident beam will be diverted away from their source and in this situation, two things can occur:

1. If the wavelength of these scattered X-rays didn't change (implying that X-ray photons didn't lose any energy), the cycle is called Rayleigh scattering or Elastic scattering (Thompson Scattering). Momentum is carried away in the scattering system. X-rays provide information about the electron appropriation in the atoms.
2. Similarly, in the inelastic scattering process (Compton Scattering), X-rays donate a portion of their energy to the electrons and the scattered X-rays will have an unexpected wavelength in comparison to the incident X-rays.

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 the molecules can disrupt one another and the resultant intensity distribution is emphatically tweaked by this connection.

Assuming the atoms are organized periodically, as in crystals, the diffracted waves will comprise of sharp interference maxima (peaks) with a similar symmetry as in the distribution of atoms. Estimating the diffraction pattern in this manner permits us to conclude the distribution of atoms in a material.

Bragg contemplated that constructive interference would happen just when the path length distinction between rays scattered from parallel crystal planes would be a fundamental number of wavelengths of the radiation. At the point when the crystal planes are separated by a distance d, the path length difference would be $2d\sin\theta$. Similarly, for the constructive interference to take place the accompanying connection should remain constant.

$$n\lambda = GY + YH$$

$GY = YH = XY \sin\theta$

$n\lambda = 2\, d \sin\theta \; (XY = d)$

NOTES

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.

5.2.2 Miller Indices

Miller indices record structure determination system in crystallography for lattice planes in crystal lattices. Miller indices are utilized to indicate direction and planes. These directions and planes could be in lattices or crystals. The number of indices will coordinate with the lattices' dimension or the crystal, e.g., in 1D there will be 1 index and 2D there will be two indices and so on.

Miller indices, a group of three numbers that demonstrate the direction of a plane or a set of parallel planes of atoms in a crystal. If each and every atom in the crystal is denoted by a point and these points are associated by the lines, the subsequent lattice might be partitioned into various indistinguishable blocks or unit cells; the intersecting edges of one of the unit cells characterize a bunch of crystallographic axes, and the Miller indices are determined by the intersection of the plane with these axes.

This theory, provided by British mineralogist and crystallographer William Hallowes Miller, in 1839, has the perk of eliminating the fragments from the notation for a plane. In the hexagonal system, having four crystallographic axes, a comparable plan of four Bravais-Miller indices is utilized.

There are two identical ways of characterizing the significance of the Miller indices: [1] through a point in the reciprocal lattice, or as the backwards blocks along the lattice vectors. The two definitions are given below. Regardless, one necessity to pick the three lattice vectors a1, a2, and a3 that characterize the unit cell (note that the conventional unit cell might be bigger than the crude cell of the Bravais lattice, as the models beneath show). Given these, the three primitive primitive reciprocal lattice vectors are also mentioned (signified b1, b2, and b3).

Then, given the three Miller indices h, k, ℓ, (hkℓ) denotes planes orthogonal to the reciprocal lattice vector:

$$\mathbf{g_{hkl} = hb_1 + kb_2 + lb_3}$$

That is, (hkℓ) essentially demonstrates a typical to the planes on the basis of the primitive reciprocal lattice vectors. Since the coordinates are integers, this normal is generally a reciprocal lattice vector. The prerequisite of least terms implies that it is the briefest corresponding grid vector in the provided direction.

Identically, (hkℓ) indicates a plane that intercepts the three focuses a1/h, a2/k, and a3/ℓ, or some numerous thereof. That is, the Miller indices are relative to the inverses of the captures of the plane, in the premise of the lattice vectors. Assuming one of the files is zero, it implies that the planes don't intersect that axis (the intercept is "at infinity").

Thinking about just ($hk\ell$) planes converging at least one grid focuses (the lattices planes), the perpendicular distance d between neighbouring lattices planes is connected with the (most limited) reciprocal lattice vector symmetrical to the planes by the equation

$$d = 2\pi / |g_{hk\ell}|$$

The related notation [$hk\ell$] denotes the direction.

Apparently,

$ha_1 + ka_2 + la_3$

That is, it uses the direct lattice basis instead of the reciprocal lattice.

5.2.3 Laue Method

Laue diffraction, in X-ray, a normal cluster of spots on a photo emulsion coming about because of X-ray dissipated by specific groups of parallel atomic planes inside a crystal. When a dainty, pencil-like light emission beams is permitted to encroach on a crystal, those of specific wavelength will be arranged at only the appropriate point to a group of atomic planes so they will consolidate in a phase to create exceptional, consistently dispersed spots on a film or plate based on the focal picture from the shaft, which goes through un-strayed. Laue diffraction, first distinguished by Max von Laue, a German physicist, is priceless for crystals.

Max von Laue utilized consistent radiation (with every conceivable wavelength) to effect on a fixed crystals. With this methodology the crystals creates a bunch of diffracted radiates that show the internal symmetry of the crystal. In these conditions, and considering Bragg's Law, the exploratory constants are inter-planar dispersing *d* and the gem position alluded to the incident beam. The variables are the wavelength λ and the integer number n:

$$n\lambda = 2\ d_{hkl}\ \sin\ \theta_{nh,nk,nl}$$

Consequently, the diffraction pattern will contain (for a similar spacing d) the diffracted radiates comparing to the main order of diffraction (n=1) of a specific wavelength, the subsequent order (n=2) of the wavelength reduced to half (λ/2), the third order (n=3) with wavelength λ/3, and so on. Thus, the Laue chart is essentially a stereographic projection of the crystal.

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 un-deviated. 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.

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5.2.4 Debye-Scherrer Method of Crystal Analysis

A technique for X-ray diffraction in which a light emission beams is diffracted by material as powder. Since the powder comprises of tiny precious stones of the material in every possible direction, the diffraction pattern is a progression of concentric circles. This kind of example permits the unit cell to be found with incredible accuracy. This technique was first utilized by Peter Debye and Paul Scherrer in 1916 and later by Albert Hull in 1917.

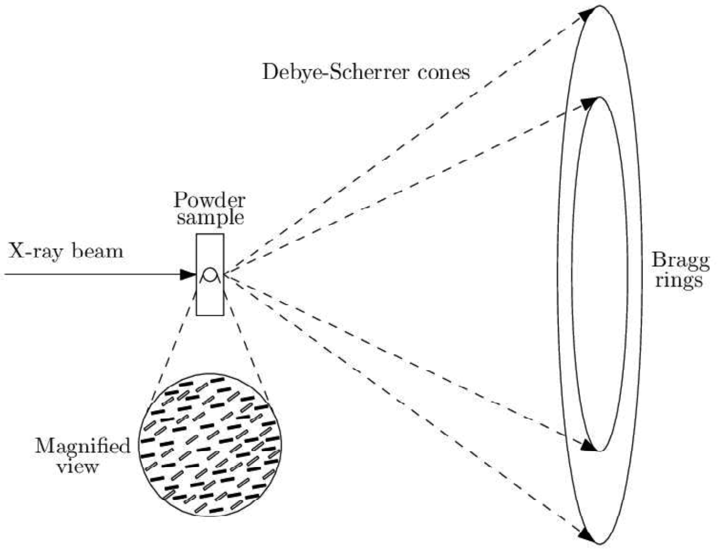

Fig 5.1 *Debye-Scherrer Method*

A thin parallel light beam of monochromatic X-rays, after falling onto a polycrystalline sample and being reflected back by the crystallites making up the sample, creates various coaxial, i.e., having one normal pivot, diffraction cones.

The direction of the primary X-ray serves as the axis of the cones and their vertices lie within the object under study and the apex angles are determined as per to the Bragg condition,

$n\lambda = 2d \sin \theta$

Where, n is a positive integer, λ is the wavelength of the X rays, d is the distance between the parallel planes of the points of the space crystal lattice, and θ is the angle between the reflecting plane and the incident beam.

The cone's apex angle is equivalent to four times the worth of the point of reflection ø. The force and position of the diffraction cones is recorded on a photographic film or by one of the ionization strategies.

The Debye-Scherrer strategy is of specific significance for the arrangement of different technical issues. For instance, it could be utilized for the investigation of underlying changes emerging during different treatments of metals and alloys. On account of plastically disfigured crystals, this strategy makes it conceivable to decide the presence of the surface in the sample and during thermal treatment to notice the phase transitions.

The Debye-Scherrer strategy is likewise broadly utilized in mineralogy and science for the recognizable proof of different minerals and synthetic compounds.

5.2.5 Index Reflections and Unit Cell Identification

X-Ray Diffraction (XRD) is one of various experimental instruments that are utilized to distinguish the structure of crystals. Indexing is the interaction by which reflection indices are alloted to the peaks in the diffraction process. When an adequate number of reflection records have been doled out to specific peaks, then, at that point, the unit cell can be determined.

The tiniest group of particles in the material that establishes this repeating pattern is the unit cell of the structure. The unit cell totally mirrors the symmetry and structure of the whole crystal, which is developed by the interpretation of the unit cell along its principle axes. The interpretation vectors characterize the nodes of the Bravais lattice.

Crystal construction is depicted as per the calculation of course of action of particles in the unit cell. The unit cell is characterized as the smallest repeating unit having the full symmetry of the crystal structure. The calculation of the unit cell is characterized as a parallelepiped, giving six lattice parameters taken as the lengths of the cell edges (a, b, c) and their respective angles (α, β, γ).

The respective positions of the particles inside the unit cell are portrayed by the fractional coordinates (xi, yi, zi) along the cell edges, estimated from a reference point. It is simply important to mention the coordinates of a smallest asymmetrical subset of particles. This group of particles might be picked up so it consumes the smallest of the actual physical space, and it implies that not all the particles should be genuinely situated inside the limits given by the lattice parameters. Any remaining particles of the unit cell are produced by the symmetry operations that describe the symmetry of the unit cell. The assortment of symmetry tasks of the unit cell is communicated officially as the space group of the gem structure.

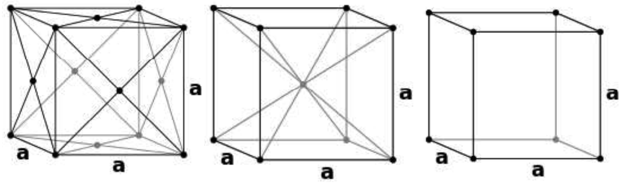

Fig 5.2 *From Left to Right (a) Simple Cubic, (b) Body-Centred Cubic, (c) Face-Centred Cubic*

Simple Cubic Unit Cell: It is the least complex repeating unit in a basic cubical design. Each side of the unit cell is characterized by a lattice point where an ion, atom, or molecule can be found in the crystal. Conventionally, the edge of a unit cell generally associates equivalent points. Every eight corners of the unit cell should contain an indistinguishable molecule. Different particles can be available on the edges or faces of the unit cell, or inside the unit cell structure. In either case, the base that should be available for the unit cell to be named as simple cubic is eight identical particles on the eight corners.

Body-Centred Cubic Unit Cell: It is the simplest repeating unit in a body-centred cubic structure. Once again, there are eight identical particles on the eight corners of the unit cell. However, this time there is a ninth identical particle in the centre of the body of the unit cell.

Face Centred Cubic Unit Cell: The face-focused cubic unit cell is the easiest repeating unit in a cubic closest-packed construction. Basically, the presence of face-focused cubic unit cells in this structure clarifies why the structure is known as cubic closet-packed.

The lengths of the principal axes, or edges, of the unit cell and the points between them are the grid constants, additionally called lattice parameters or cell parameters. The symmetry properties of the crystal are depicted by the idea of space groups. All conceivable symmetric plans of particles in three-dimensional space might be portrayed by the 230 space groups.

The gem design and evenness assume a basic part in deciding numerous actual properties, for example, cleavage, electronic band structure, and optical transparency.

5.2.6 Structure of Simple Lattices and X-Ray Intensities

Suppose, all the charges are continuously distributed over a region in space. It will be very difficult to consider the positions of the charges separately to find $\vec{r}_1$. Hence, for continuous distribution of charges for the electric field as given below

$$\vec{E}(\vec{r}) = \frac{1}{4\pi \in_0}\int \frac{dq}{|\vec{r}-\vec{r}'|^3}(\vec{r}-\vec{r}')$$

where, $\vec{r}$ is position vector of observation point and $\vec{r}'$ is the same of source point.

If the source charges are continuously distributed over a line with linear charge density λ, $dq = \lambda dl'$ (where, dl' is elementary part of the line); if the source charges are continuously distributed over a surface with surface charge density σ, $dq = \sigma dS'$ (dS' is elemental portion of the surface); similarly, if the charges are continuously distributed over a volume with volume charge density ρ, $dq = \rho dv'$ (dv' is an elemental portion of the volume), so

$$dq \Rightarrow \lambda dl' \sim \sigma dS' \sim \rho dv'$$

Hence, the expression for the electric field should be modified as

$$\vec{E}(\vec{r}) = \frac{1}{4\pi \in_0}\int \frac{\lambda dl'}{|\vec{r}-\vec{r}'|^3}(\vec{r}-\vec{r}')$$

[For a linear distribution]

$$\vec{E}(\vec{r}) = \frac{1}{4\pi \in_0}\int \frac{\sigma ds'}{|\vec{r}-\vec{r}'|^3}(\vec{r}-\vec{r}')$$

[For a surface distribution]

and
$$\vec{E}(\vec{r}) = \frac{1}{4\pi \in_0}\int \frac{\rho\, dv'}{|\vec{r}-\vec{r}'|^3}(\vec{r}-\vec{r}')$$

[For a volume distribution]

In each of the above integrals, the primed quantities are associated with source position.

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5.2.7 Structure Factor and its Relation to Electron Density

The structure factors, are the essential quantities on which the function of electron density depends. These are vital magnitude, since the maxima of the electron density function, ρ, shows the area of the molecules, that is, the internal structure of the crystals.

The structural factors address the diffracted waves, which while crashing into a photographic plate, or a detector, make some meaningful difference as distinct spots that structure the diffraction design. In this way, according to an exploratory perspective, a precious stone design is characterized by as many construction factors as spots contained in the diffraction pattern.

The atomic scattering factor is free of the place of the molecule in the unit cell. It relies just upon the sort of particle and the course of scattering, with the goal of arriving a maximum in similar direction of the incident X-ray, and diminishes as a component of the angle of departure. The variety of the scattering factor of the carbon atom is displayed in the left drawing. At the angular value comparing to $(\sin\theta)/\lambda = 0$, the extent of the atomic scattering factor is equivalent 100% of the absolute number of electrons in the molecule, yet diminishes firmly as the angular value increases.

5.2.8 Phase Problem and Procedure of X-ray structure Analysis

Whenever X-ray are bombarded on a sample, the resultant waves (with characteristic wavelength, amplitude, and phase) are because of the association between the incident beam and the crystal structure. X-ray diffraction results when there is constructive impedance between scattered rays. This can happen due to the intermittent nature of the crystal lattice. The information gathered is alluded to as the reciprocal lattice and can be connected with the electron density by Fourier transformation of the amplitudes and phases of the diffracted rays.

How to Solve the Phase Problem: As of now, structures are generally addressed either utilizing an ab initio approach (direct techniques) or the Patterson strategy, which depends on having a few unmistakable heavy molecules in the structure. The phase problem can in any case be an issue during structural arrangement and refinement today, particularly with huge, non-centro symmetric structures with no heavy elements.

Crystals are the regular array of molecules, while X-rays can be considered as influxes of electromagnetic radiation. Crystal scatters X-rays, principally through connection with the electrons. This peculiarity is known as elastic scattering; the electron is known as the scatterer. The regular array of scatterers delivers a regular cluster of spherical waves.

In the majority of directions, these waves cancel each other out through destructive interference, however, they add constructively in a few specific directions, as determined by Bragg's law:

$$2d\sin\theta = n\lambda$$

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Where d is the spacing between diffracting planes, θ is the incident angle, n is an integer, and λ is the beam wavelength. The specific directions appear as spots on the diffraction pattern called reflections. Consequently, X-ray diffraction patterns result from electromagnetic waves impinging on a regular array of scatterers.

Highly intense X-rays are now a days produced with synchrotrons. In a material, the X-rays might experience a loss of energy contrasted with the incident beam. This energy loss of the reappearing beam mirrors an interior excitation of the atomic structure, a X-ray sample to the notable Raman spectroscopy that is broadly utilized in the optical region.

In the X-ray region there is adequate energy to test the changes in the electronic state (advances between orbitals; this is interestingly, with the optical region, where the loss of energy is on a regular basis because of changes in the state of the rotational or vibrational degree of freedom). For example, in the ultra soft X-ray region (underneath around 1 keV), crystal field excitations lead to the loss of energy.

The photon-in-photon-out interaction might be considered as a scattering event. At the point when the X-ray energy interacts with the binding energy of a core level electron, this scattering is thunderously improved by many significant degrees. This kind of X-ray emission spectroscopy is frequently called as Resonant Inelastic X-Ream Scattering (RIXS).

Because of the wide detachment of orbital energies of the core, it is feasible to choose a specific atom of interest. The little spatial degree of core level orbitals powers the RIXS cycle to mirror the electronic construction in close area of the picked iota. Hence, RIXS tests give significant data about the neighbourhood electronic structure of perplexing systems, and hypothetical computations are somewhat easy to perform.

5.2.9 Absolute Configuration of Molecules

Absolute configuration alludes to the spatial arrangements of atoms and molecules inside a chiral molecular entity (or group) and its resultant sound sterio-chemical depiction. Absolute configuration is majorly significant in organic molecules, where carbon is attached to four distinct substituents.

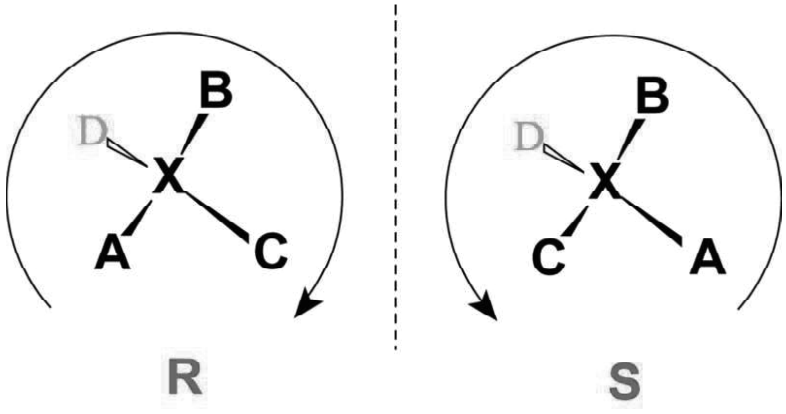

Fig 5.3: *Absolute Configuration of Molecules*

This sort of development makes two potential enantiomers. Absolute configuration utilizes certain specific set rules to portray the overall positions of each bond around the chiral central atom. The most well-known marking strategy utilizes the descriptors R or S depends on the Cahn-Ingold-Prelog priority rules. R and S allude to Rectus and Sinister, separately, which are Latin for right and left.

5.2.10 Ramchandran Plot

The tasks of describing and understanding structure of large macromolecules such as proteins are approached at several levels of complexity which are therefore set in a category of theoretical chain of command. The four levels of protein structure were first defined by Linderstrom and Lang which includes primary structure, secondary structure, tertiary structure and quaternary structure. In mathematical term, these are also depicted as 1º, 2º, 3º and 4º respectively.

Primary Structure of Protein

The linking of different amino acid residues in a polypeptide chain by covalent bonds mainly peptide bonds and disulfide bonds constitute the primary structure of protein**.** The fundamental primary structure of a protein is relatively simple and consists of one or more linear chains of a number of amino acid units (Figure 5.4). An example of primary structure is angiotensin II, which is the hypertensive octapeptide and has the sequence Asp-Arg-Val-Tyr-Ile-His-Pro-Phe. The peptide bond links α -carboxyl group of one amino acid residue to the α -amino group of the other amino acid is the major type of linkage of the amino acids found in proteins . The proteins may consist either of one or of more peptide chains.

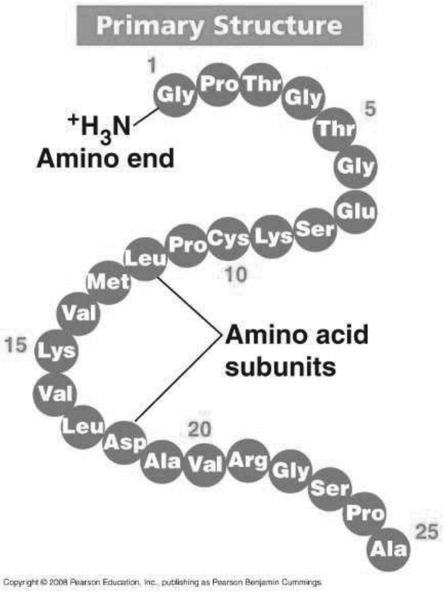

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Fig. 5.4 Showing the Primary Structure of Protein

Linus Pauling and Robert Corey in 1930, confirmed that α -carbons of adjacent amino acids are separated by three covalent bonds, arranged in **C_α–C-N- C_α form**. The studies of crystals of amino acids, simple dipeptides and tripeptides by X-ray diffraction studies confirmed that C-N bond present in the peptide is

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somewhat shorter than the C-N bond present in a simple amine. With this intention, they confirmed that the atoms associated with the peptide bond are coplanar due to a resonance or partial sharing of two pairs of electrons between the carbonyl oxygen and the amide nitrogen (Figure 5.4). The nitrogen atom has a partial positive charge and the oxygen has a partial negative charge, providing setting up a small electric dipole. The six atoms of the peptide group be positioned in a single plane, with the oxygen atom of the carbonyl group and the hydrogen atom of the amide nitrogen remaining trans to each other. Pauling and Corey from these findings concluded that the peptide C-N bonds are unable to rotate freely for the reason that of their partial double-bond nature, whereas rotation is allowed only about the **N-** $\mathbf{C}_\alpha$ and the **C-** $\mathbf{C}_\alpha$ bonds. The backbone of a polypeptide chain can be thus pictured as a sequence of rigid planes with consecutive planes sharing a common point of rotation at $\mathbf{C}_\alpha$. The rigid peptide bonds limit the range of conformations that can be assumed by a polypeptide chain.

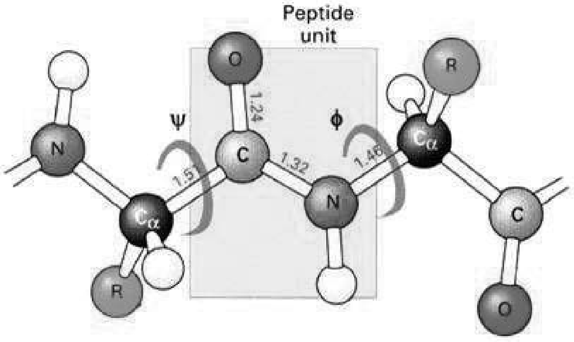

Fig. 5.5 Showing Rigid and Planar Peptide Bond

In 1963, G. N. Ramachandran recognized that an amino acid residue in a polypeptide chain cannot have just any pair of values of ϕ and ψ. The bond angles resulting from rotations at $\mathbf{C}_\alpha$ are labeled by convention as ϕ (phi) for the N- $\mathbf{C}_\alpha$ bond and ψ (psi) for the C-$\mathbf{C}_\alpha$ bond. When the polypeptide is in its fully extended conformation and all peptide groups are in the same plane, both ϕ and ψ are defined as 180° again by convention. In principle, the values of ϕ (phi) and ψ (psi) can lies between -180° and +180°. Many values are prohibited by steric interference between atoms in the polypeptide backbone and amino acid side chains. The conformation of the main polypeptide chain can be completely determined if the values ϕ and ψ for each amino acid residue in the chain are known.

By assuming that atoms behave as hard spheres, allowed ranges of ϕ and ψ can be predicted and visualized in steric contour diagram called **Ramachandran plots** (Figure 5.6). The values for ϕ and ψ are graphically revealed when ψ is plotted versus ϕ**.** One of them contains ϕ–ψ values that generate the antiparallel α sheet, the parallel Beet and the collagen helix. A second region has ϕ–ψ values that produce the right-handed α helix, the left-handed α helix. Left-handed helices are not found in proteins because they are much less favored energetically.

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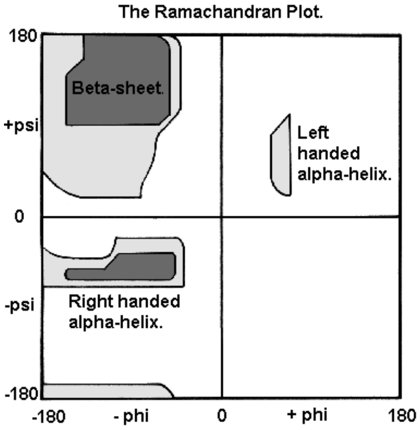

Fig. 5.6 Showing Ramachandran Plot

Secondary Structure of Protein

The term **secondary structure** refers to the local conformation of some part of a polypeptide (Figure 5.7). The discussion of secondary structure most beneficially focuses on common regular folding patterns of the polypeptide backbone. The most prominent secondary structure includes **α-helix** and **α-pleated sheets** as described below. In 1951, Pauling and Corey predicted the existence of these secondary structures by using fundamental chemical principles and a few experimental observations. A few types of secondary structure are predominantly stable and occur widely in proteins. In addition, the α- helix and α-pleated sheet structures of proteins, which were discovered by Pauling and Corey in 1950s, there is also an existence of a third type of secondary structure in proteins known as random coil. When a polypeptide contains neighboring immense amino acid residues such as isoleucine or charged residues such as aspartic acid and glutamic acid, repulsion involving these groups creates the polypeptide to suppose a random coil arrangement which lack well- defined structure (Figure 5.7). Therefore, we observe that the R groups dispersed all along the polypeptide backbone establish the secondary structure of protein implemented by diverse portions of the polypeptide.

Fig. 5.7 Showing Secondary Structure of Protein

Check Your Progress

1. Define X-rays.
2. What happens when X-ray photons collide with matter?
3. What is the Bragg's condition of X-ray diffraction?
4. State the Laue's method of X-ray diffraction.
5. State the Debye Scherrer Method of X-ray diffraction.

5.3 ELECTRON DIFFRACTION

Electron diffraction is a procedure that permits the assurance of the crystal structure of materials. At the point when the electron beam is projected on a sample, its crystal lattice goes about as a diffraction grating, scattering the electrons in an anticipated way, and bringing about a specific diffraction pattern.

Electron diffraction alludes to the wave nature of electrons. In any case, from a specialized or pragmatic perspective, it could be viewed as a strategy used to concentrate on issue by terminating electrons at a specific sample and noticing the subsequent interference pattern. This peculiarity is usually known as wave-particle duality, which expresses that a particle matter (for this situation the incident electron) can be depicted as a wave. Consequently, an electron can be viewed as a wave similar as sound or water waves. This method is like X-ray and neutron diffraction.

In an electron microscope, the diffraction design shows up either on a fluorescent screen or is recorded on a photographic film or identified by a sensor like a CCD (charge-coupled device) camera. From the diffraction pattern, the arrangement of the molecules in a material can easily be analysed. Electron diffraction can be obtained with either TEM or SEM (electron backscattered diffraction).

Electron diffraction is most often utilized in strong state physical science and chemical science studies to concentrate on the crystalline structure of solids. Tests are typically performed in a Transmission Electron Microscope (TEM), or a Scanning Electron Microscope (SEM) as electron backscatter diffraction. In these instruments, electrons are speed up by an electrostatic potential to acquire the ideal energy and their wavelength before they interface with the sample to be contemplated.

The periodic structure of a crystalline solid goes about as a diffraction grating, scattering the electrons in an anticipated way.

5.3.1 Scattering Intensity and Scattering Angle

The scattering intensity is the amount of radiation (e.g., x-ray or neutron) scattered at any particular angle. This quantity is usually given by $I_{(q)}$, where q is the momentum transfer (a vector in reciprocal-space).

The angle between the initial and final directions of motion of a scattered particle is known as *scattering angle*.

5.3.2 Wierl Equation

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 may be regarded as made up of different components:

- Atomic coherent scattering
- Molecular coherent scattering

The coherent or elastic scattering is represented by an equation devised by Mark and Wierl. The Wierl equation expresses the diffracted intensity in terms of the separation of nuclei (Rij), the scattering angle and the electronic scattering factors f:

NOTES

Wierl Equation: $I(\theta) = \sum f_i . f_j (\sin sR_{ij}) / sR_{ij}$

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 " has been carried out over all pairs of atoms in the molecule, irrespective of whether the atoms have been linked or not.

5.3.3 Measurement Techniques

Electrons are boiled off from the hot filament made up of tungsten and accelerated through a potential difference of 40,000 V /cm (which produces a wavelength of about 0.06 angstrom) which is then allowed to pass through the stream of gaseous sample and on to a fluorescent screen.

The sample being gaseous, presents all possible orientations of the scattering atom–atom separations to the beam and the diffraction pattern is the superimposition of the scattering due to entire range of orientation. This appears in the diffraction picture as a series of concentric undulations on a decreasing background. The undulation can be ascribed to the sharply defined scattering from the nuclear positions and the background ascribed to contributions from the continuous distribution of electron density in the molecule. One way of eliminating the unwanted background is to insert a rotating heart shaped disc in front of the screen, this exposes the outer parts more than the inner and helps to emphasize the undulations.

5.3.4 Elucidation of Structure of Simple Gas Phase Molecules

Gas Electron Diffraction (GED) is one of the utilizations of electron diffraction techniques. The objective of this technique is to analyse the structure of gaseous molecules for example the geometrical arrangement of the atoms from which a molecule is formed. GED is one of the two experimental techniques (other than microwave spectroscopy) for the structural determination of the free molecules, undistorted by intermolecular forces, which are ubiquitous in the solid as well as in the liquid state.

Diffraction occurs because the wavelength of electrons accelerated by a potential of a few thousand volts is of the same order of magnitude as inter-nuclear distances in molecules. The principle is the same as that of other electron diffraction methods such as LEED (Low Energy Electron Diffraction) and RHEED (Reflection High Energy Electron Diffraction), but the obtainable diffraction pattern is considerably weaker than those of LEED and RHEED because the density of the target is about one thousand times smaller. Since the orientation of the target molecules relative to the electron beams is random, the inter-nuclear distance information obtained is one-dimensional. Thus only relatively simple molecules can be completely structurally characterized by electron diffraction in the gas phase.

The total scattering intensity in GED (Gas Electron Diffraction) is given as a function of the momentum transfer, which is defined as the difference between the wave vector of the incident electron beam and that of the scattered electron beam and has the reciprocal dimension of length. The total scattering intensity is composed of two parts: the atomic scattering intensity and the molecular scattering intensity. The former decreases monotonically and contains no information about the molecular structure. The latter has sinusoidal modulations as a result of the interference of the scattering spherical waves generated by the scattering from the atoms included in the target molecule.

5.3.5 Low Energy Electron Diffraction (LEED)

Low-Energy Electron Diffraction (LEED) is a procedure for the analysis of the surface structure of single-crystalline materials by barrage with a collimated beam of low energy electrons (30-200 eV) and perception of diffracted electrons as spots on a fluorescent screen. LEED might be utilized in either of two ways:

1. Qualitatively, where the diffraction pattern is recorded and investigation of the spot positions gives information on the symmetry of the surface structure. Within the sight of an adsorbate, the subjective investigation might uncover information about the size and rotational arrangement of the adsorbate unit cell regarding the substrate unit cell.
2. Quantitatively, where the forces of diffracted beams are recorded as a function of incident electron beam energy to produce the purported I-V curves. By correlation with hypothetical bends, these may give exact information on nuclear situations on a superficial level nearby.

5.3.6 Structure of Surface

Low Energy Electron Diffraction (LEED) has ended up being the most dependable quantitative strategy for surface structure determination. Reportedly, ongoing advancements connected with the hypothesis that gives backing to LEED structural determination are being discussed as a crucial analysis of hypothetical approximation; the muffin-tin computation.

The determination of the structure of a surface utilizing LEED is an interaction with two phases. To start with setting up the sample and putting it in laboratory conditions, the scattered beams are gathered and mathematically treated as an element of energy of the incident beam, in different directions. These curves are normally called LEED-IV curves since the incident electron energy is a component of the voltage applied to the electron gun. Second, one should figure out models for the surface and performs a hypothetical computation of the scattered intensity as a function of voltage, expecting the presence of long-range order on a superficial level. This is then trailed by a quantitative examination of the two sets of curves, exploratory and hypothetical.

To perform out the estimations, it is important to expect values for a set of structural and non-structural parameters, each altogether influencing the computation yield. A coincidence among hypothetical and analytical curves upholds the conviction that the set of parameters utilized in the hypothesis relates to the real surface. In this way, underlying the structural determination includes a quest interaction of a satisfactory set of parameters for which the degree of coincidence between the two sets of curves is boosted. LEED based structural analysis requires an estimation cycle to computationally mirrors the design of the genuine surface. A model for the surface design, having as an underlying theory the mass structure and other data of trial or hypothetical nature, is imagined and a set of hypothetically determined LEED-IV curves are processed.

The surface determination is undeniably accomplished when it becomes conceivable to fit, up satisfactorily, the two sets of curves, analytical and hypothetical. These curves are contrasted with one another utilizing a reliability factor (R factor) which establishes a quantitative proportion of the degree of arrangement between them.

Check Your Progress

6. What is electron diffraction?
7. State the Wierl law of electron diffraction.

5.4 NEUTRON DIFFRACTION

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. A sample to be examined is placed in a beam of thermal or cold neutrons to obtain a diffraction pattern that provides information of the structure of the material. The technique is similar to X-ray diffraction but due to their different scattering properties, neutrons and X-rays provide complementary information: X-Rays are suited for superficial analysis, strong x-rays from synchrotron radiation are suited for shallow depths or thin specimens, while neutrons having high penetration depth are suited for bulk samples.

The technique requires a source of neutrons. Neutrons are usually produced in a nuclear reactor or spallation source. At a research reactor, other components are needed, including a crystal monochromator, as well as filters to select the desired neutron wavelength. Some parts of the setup may also be movable. At a spallation source, the time of flight technique is used to sort the energies of the incident neutrons (higher energy neutrons are faster), so no monochromator is needed, but rather a series of aperture elements synchronized to filter neutron pulses with the desired wavelength.

The technique is most commonly performed as powder diffraction, which only requires a polycrystalline powder. Single crystal work is also possible, but the crystals must be much larger than those that are used in single-crystal X-ray crystallography. It is common to use crystals that are about 1 mm3.

The main disadvantage to neutron diffraction is the requirement for a nuclear reactor. For single crystal work, the technique requires relatively large crystals, which are usually challenging to grow. The advantages to the technique are many - sensitivity to light atoms, ability to distinguish isotopes, absence of radiation damage, as well as a penetration depth of several cm.

5.4.1 Scattering of Neutrons by Solids and Liquids

Neutron scattering, the sporadic dispersal of free neutrons by matter, can allude to either the normally occurring physical interaction itself or to the man-made exploratory strategies that utilize the natural process for examining materials. The regular/actual peculiarity is of the basic significance in nuclear engineering and the atomic sciences.

Fast neutrons have kinetic energy above 1 MeV. They can be dissipated by condensed matter-nuclei having kinetic energies far under 1 eV as a substantial experimental approximation of an elastic collision with a molecule at rest. With every collision, the fast neutron transfers a critical portion of its kinetic energy to the scattering nuclei (consolidated matter), the more so the lighter the nucleus. Furthermore, with every collision, the fast neutron is eased back until it arrives at thermal equilibrium with the material in which it is scattered.

Since neutrons are electrically neutral, they enter more profoundly into matter than electrically charged particles of similar kinetic energy, and thus, are significant as probes of bulk properties.

Neutrons associate with nuclei and with magnetic fields from unpaired electrons, causing articulated interference and energy transfer impacts in neutron scattering tests. Not at all like an X-ray photon with a comparable wavelength, which cooperates with the electron cloud encompassing the nucleus, neutrons collaborate principally with the nucleus itself, as portrayed by Fermi's pseudopotential. Neutron scattering and absorption cross-section change broadly from one isotope to another.

Neutron scattering can be unintelligible or lucid, likewise relying upon isotope. Among all isotopes, hydrogen has the most elevated scattering cross-segments. Significant components like carbon and oxygen are very apparent in neutron scattering and this is in checked differentiation to X-ray scattering where cross-sections increase deliberately with atomic number. Accordingly, neutrons can be utilized to investigate materials with lower atomic numbers, including proteins and surfactants. This should be possible at synchrotron sources, however, extreme intensities are required, which might make the structural change. The nucleus gives an extremely short range, as isotropic potential differs haphazardly from one isotope to another, which makes it conceivable to tune the (scattering) contrast to suit the test.

Dispersing quite often presents both elastic and inelastic components. The portion of elastic scattering is demonstrated by the Debye-Waller factor or the Mössbauer-Lamb factor. Contingent upon the research methodologies, most estimations focus on one or the other elastic or inelastic scattering.

5.4.2 Magnetic Scattering and Measurement Techniques

The neutron has a net electric charge of zero, yet it has a critical magnetic moment, however, just around 0.1% of that of the electron. In either case, it is sufficiently enormous to scatter from nearby magnetic fields inside the condensed matter, giving pitiful interfacing and thus penetrating probes of ordered magnetic structures and electron spin fluctuations.

The neutron diffraction technique is the same as the X-ray technique as it depends on flexible distortions that cause changes in the dispersing of the lattice planes from the stress-free condition. With high spatial resolution, the neutron diffraction technique can give a total of three-dimensional maps of the leftover stresses in the material.

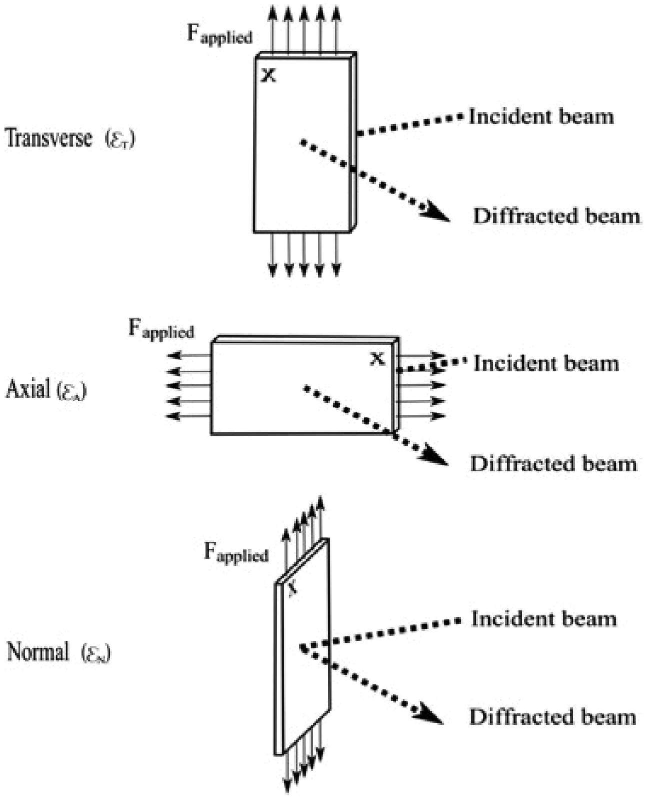

Fig 5.8 *Neutron Diffraction*

With the higher spatial resolution, the neutron diffraction strategy can give a total of three-dimensional maps of the residual stress in the material. At every estimation point, the strain was estimated in three orthogonal directions: along with the sample axis (pivotal strain εA), transverse to it (transverse strain εT), and through the wall (ordinary strain εN). This was accomplished by mounting each example in three distinct directions.

The benefit of the neutron diffraction strategies in correlation with the X-ray procedure is its bigger penetration profundity. Indeed, the X-ray diffraction strategy has limitations in estimating lingering stresses through the thickness of a welded structure. Then again, a neutron can infiltrate a couple of centimetres within a material, in this way it may be generally applied to assess the internal residual stress of materials.

When contrasted with other diffraction strategies, for example, X-ray diffraction, the general expense of utilization of the neutron diffraction strategy, is a lot higher. It is too costly to be in any way utilized for routine process quality control in engineering applications.

5.4.3 Elucidation of Structure of Magnetically Ordered Unit Cell

The most widespread use of neutron diffraction is of course the determination of magnetic structures, i.e., the determination of the directions in which moments point in a magnetically ordered material. To describe magnetic structures, it is intuitive and convenient to relate them to the underlying crystal structures, and therefore to use unit cells.

Let us consider a single crystal containing several atoms per unit cell. Such a crystal is called a non-Bravais crystal (by opposition, a Bravais crystal contains only one atom per unit cell). Let $R_{n\nu}$ be the position of atom number ν in the cell number n[1]:

$$R_{n\nu} = R_n + r_\nu$$

Where, $R_n = n_a a + n_b b + n_c c$ (n_a, n_b, n_c integers) is the position of cell number n compared to an arbitrary origin in the crystal, $r_\nu = x_\nu a + y_\nu b + z_\nu c$ (x_ν, y_ν, z_ν are the atomic positions defined in the International Tables) is the position of atom ν in this cell and a, b, c are the unit cell vectors.

From the unit cell, one can define a reciprocal lattice by three vectors (V is the volume of the unit cell)[2]:

$$a'' = 2\ b \times c\ V$$

$$b'' = 2\ c \times a\ V$$

$$c'' = 2\ a \times b\ V$$

The volume of the reciprocal unit cell is $(2\pi)^3/V$. A reciprocal lattice vector is thus defined as;

$$Q = h\,a'' + k\,b'' + l\,c''.$$

For an unpolarized neutron beam, there is no interference between the nuclear and the magnetic scattering, and the differential elastic cross section for such a crystal is:

$$\frac{d\sigma}{d\Omega}(\boldsymbol{Q}) = \frac{d\sigma_N}{d\Omega}(\boldsymbol{Q}) + \frac{d\sigma_M}{d\Omega}(\boldsymbol{Q}).$$

The nuclear interaction potential in the crystal is:

NOTES

$$V_N(\boldsymbol{r}) = \frac{2\pi\hbar^2}{m}\sum_{n,v} b_v\, \delta(\boldsymbol{r} - \boldsymbol{R}_{nv})$$

and

$$\begin{aligned}\frac{d\sigma_N}{d\Omega}(\boldsymbol{Q}) &= \left| < \boldsymbol{k}_f\, \boldsymbol{\sigma}_f | \sum_{n,v} b_v\, \delta(\boldsymbol{r} - \boldsymbol{R}_{nv}) | \boldsymbol{k}_i\, \boldsymbol{\sigma}_i > \right|^2 \\ &= \left| \sum_{n,v} b_v\, e^{i\boldsymbol{Q}\cdot\boldsymbol{R}_{nv}} \right|^2 \\ &= \frac{(2\pi)^3}{V}\mathcal{N}\sum_{\boldsymbol{H}} |F_N(\boldsymbol{Q})|^2\, \delta(\boldsymbol{Q} - \boldsymbol{H})\end{aligned}$$

Where N is the number of unit cells contained in the crystal. In this expression, FN (Q) is the unit cell nuclear structure factor, defined as:

$$F_N(\boldsymbol{Q}) = \sum_{v} b_v\, e^{i\boldsymbol{Q}\cdot\boldsymbol{r}_v}.$$

The sum $\sum_{v}$ is taken over the atoms of the unit cell. The relation Q = H arising from the function is nothing but the Bragg condition of reflection. It demonstrates that a coherent elastic scattering occurs in a perfect crystal only for scattering vectors that coincide with a reciprocal lattice vector. This result is purely a consequence of the symmetry of the crystal lattice and does not depend upon the nature of the neutron-lattice interaction. This last result, derived in the case of nuclear scattering, can be extended to the magnetic scattering.

Check Your Progress

8. What do you understand by neutron diffraction?
9. What is coherent scattering?
10. State the basic nature of neutrons.

5.5 ANSWERS TO 'CHECK YOUR PROGRESS'

1. X-rays are electromagnetic radiation with typical photon energies in the range of 100 eV - 100 keV.
2. 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.
3. Two beams with identical wavelength and phase approach a crystalline solid and are scattered off two different atoms within it.

4. According to the Laue's law, a 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.
5. When the 2-D diffraction pattern is recorded, it shows concentric rings of scattering peaks corresponding to the various d spacings in the crystal lattice. The positions and the intensities of the peaks are used for identifying the underlying structure (or phase) of the material.
6. Electron diffraction is a collective scattering phenomenon with electrons being (nearly elastically) scattered by atoms in a regular array (crystal).
7. The Wierl equation expresses the diffracted intensity in terms of the separation of nuclei (Rij), the scattering angle and the electronic scattering factors f.
8. 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.
9. Scattering associated with Bragg's reflections is called coherent scattering.
10. Neutrons are electrically neutral; they penetrate matter more deeply than electrically charged particles of comparable kinetic energy; therefore, they are valuable probes of bulk properties.

5.6 SUMMARY

- Electromagnetic radiation, X-ray may be described in terms of their electric and magnetic components.
- 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.
- 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
- 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.
- 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.

- 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.
- Diffracted waves from different atoms can interfere with each other and the resultant intensity distribution is strongly modulated by this interaction.
- 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
- 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 scattering of radiation and interference between scattered photons produces a resulting pattern called a diffraction.
- In crystallography, the static structure factor (or structure factor) is a mathematical description of how a material scatters incident radiation.
- X-ray diffraction is based on constructive interference of monochromatic X-rays and a crystalline sample.
- According to Ramachandran & Sasisekharan (1968). The fully allowed regions are shaded; the partially allowed regions are enclosed by a solid line
- 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 Wierl equation expresses the diffracted intensity in terms of the separation of nuclei (Rij), the scattering angle and the electronic scattering factors f.
- LEED is the principal technique for the determination of surface structures.
- LEED is used mainly for the study of the structure of single-crystal surfaces and of processes on such surfaces that are associated with changes in the lateral periodicity of the surface.
- 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 particles found in the atomic nucleus of almost all atoms, but they are bound. The technique requires free neutrons and these normally do not occur in nature, because they have limited life-time. In a nuclear reactor, however, neutrons can be set free through nuclear decay particularly when fission occurs.
- Neutron diffraction is a technique which is more similar to x-ray diffraction and applicable particularly to biopolymers and particulate structure.

- One major advantage of neutron diffraction over X-ray diffraction is that the latter is rather insensitive to the presence of hydrogen in the structure whereas, the nuclei ^{1}H and ^{2}H are strong scatterer for neutrons.

5.7 KEY TERMS

- **X-ray:** X-rays are electromagnetic radiation with typical photon energies in the range of 100 eV - 100 keV.
- **Bragg's Condition:** Two beams with identical wavelength and phase approach a crystalline solid and are scattered off two different atoms within it.
- **Laue's Law:** 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.
- **Crystals:** Crystals are solids that often have well-defined, smooth faces and straight edges. The angles between similar faces of different samples of a crystalline substance are always constant.
- **Unit Cells:** Each unique piece of the 3-dimensional array of crystals is called a unit cell.
- **Electron Diffraction:** Electron diffraction is a collective scattering phenomenon with electrons being (nearly elastically) scattered by atoms in a regular array (crystal).
- **Wierl Equation:** The Wierl equation expresses the diffracted intensity in terms of the separation of nuclei (Rij), the scattering angle and the electronic scattering factors f.
- **Neutron Diffraction:** 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.

5.8 SELF-ASSESSMENT QUESTIONS AND EXERCISES

Short-Answers Questions

1. What do you understand by X-ray diffraction techniques?
2. State the Bragg's law of X-ray diffraction.
3. What is the Laue's method of X-ray diffraction?
4. State Miller Indices.
5. What do you understand by the structural analysis of crystals?
6. What do you understand by the absolute configuration of molecules?
7. Define Phase problem.

Long-Answer Questions

1. Describe the instrumentation of X-ray spectroscopy.
2. Explain the Bragg's condition and Bragg's law of X-ray diffraction techniques.
3. Describe the method of unit cell identification.
4. Define structure factor. State its relation to intensity abd electron density.
5. Explain the measurement techniques of electron diffraction.
6. Describe the applications of electron diffraction spectroscopy.
7. What do you mean by neutron diffraction? Describe its measurement techniques.

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