**Spectroscopy I**

**Master of Science (M.Sc.)**
**Semester - 1**
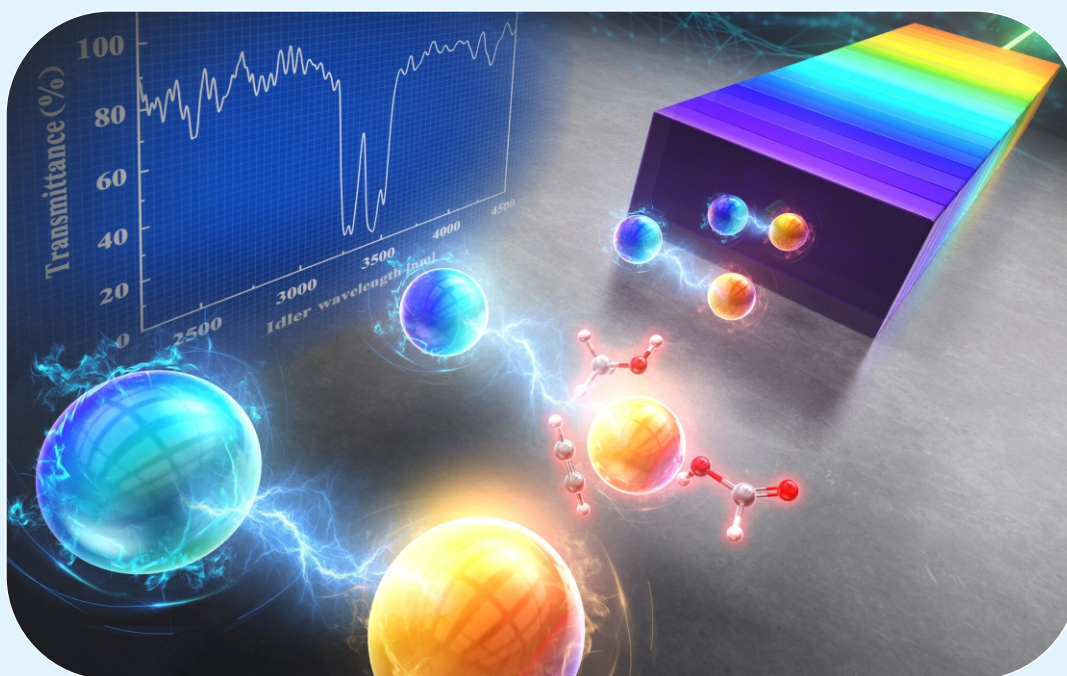


**SELF LEARNING MATERIAL**

# MASTER OF SCIENCE
# (M.Sc.)

## SPECTROSCOPY I
### CODE: ODL/MSS/MSCCH/104

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## Acknowledgement

**Block 1**
**UNIFYING PRINCIPLES AND MICROWAVE SPECTROSCOPY**

**Unit 1: Introduction to Spectroscopy**

Structure

1.1 Introduction
1.2 Objectives
1.3 Electromagnetic Radiation and Its Properties
1.4. Adsorption, Emission and Transmission
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**1.1 Introduction**

The spectrum of light is nothing bridging to the revolutions in the historical science, becoming the most sophisticated scientific method of enlightening a different world of matter and energy by looking deep into the fundamentals of chemical and physical nature and their interaction with space or electromagnetic radiations. Fundamentally, it is an analytical methodology that examines the interaction of various types of materials when exposed to electromagnetic radiation, enabling

scientists to gain unparalleled access to the structural, compositional, and energetic properties of atoms, molecules, and complex systems that span several scientific fields. The early beginnings of spectroscopy as an area of research stem from the 19th century explorations of the interaction between light and matter and has included many iconic contributions from pioneering researchers aiming to decode the astrophysical landscape of electromagnetic interactions. The stages through which light passes first among mystics and the faithful, later with the experiments, and eventually the speck of the atom, the bearded face, the prism, and the them as it disperses, and then nothing, just your efforts are still, at quantum level, just the dissimilarities in the spirit that are used to represent the different types of psychedelic crystals in the Bowie and Williams of your choosing. In the years that followed, scientists such as Joseph von Fraunhofer built on those discoveries, carefully studying the dark lines in solar spectra and demonstrating that different materials have unique spectral signatures that can be used to identify and characterize their essential properties. Spectroscopy is a

## 1.2 Objectives

1. To develop a strong conceptual foundation of the unifying principles of spectroscopy, including the uncertainty principle, selection rules, energy quantization, and molecular transitions.

2. To understand the theory, instrumentation, and applications of microwave spectroscopy in studying rotational energy levels of molecules.

3. To analyze how the Born-Oppenheimer approximation and molecular energy levels serve as a basis for interpreting microwave spectra.

4. To provide skills to interpret rotational spectra, derive molecular parameters (bond length, moment of inertia, dipole moment), and distinguish isotopic effects.

5. To familiarize students with instrumentation and techniques (cavity resonators, waveguides, Fourier-transform microwave spectroscopy).

## 1.3 Electromagnetic Radiation and Its Properties

Spectroscopy is a scientific field that is defined by the interaction between electromagnetic radiation and matter. This definition is more than just a measurement technique; it is a powerful analytical framework that enables researchers to examine the quantum-mechanical traits of everything from individual subatomic particles to entire astronomical objects.

They provide scientists the ability to obtain rich information on a material's composition, structure, energy states, and dynamics by measuring electromagnetic radiation absorption, emission, and scattering as a function of wavelength. Why so, Well, Spectroscopy is based on Quantum Mechanical Model, which states that energy exchange takes place between matter and radiation quantized in separate packets. Electromagnetic radiation can be absorbed by a material in which case the energy is transferred to the material emitted from a material (the material done it to transfer energy to the radiation)

or scattered (the radiation is redirected by the material with little or no energy lost to the material). These interactions yield distinct spectral fingerprints, providing a powerful window into the quantum mechanical activity underlying the system under investigation. Electromagnetic radiation, in many respects, is the foundation of spectroscopic analysis, acting as both the probing medium and source of information about material properties. This extraordinary type of energy moves across the cosmos in the form of oscillating electric and magnetic fields, propagating at the speed of light and described by their own unique properties of wavelength, frequency and energy. The wide range of types of physical processes that can be monitored spectroscopic ally can be achieved only through the vast diversity of radiation types offered by the electromagnetic spectrum. Electromagnetic radiation is fundamentally quantum mechanical in nature, best understood through the concept of wave-particle duality. This groundbreaking realization indicates that electromagnetic radiation can demonstrate dual natures, possessing wave-like and particle-like properties, contingent upon the experimental conditions. The double-slit experiment Daniel P. Hines, "Interference and diffraction" image–source peratt.com Electromagnetic radiation carries with it energy proportional to its frequency and inversely proportional to its wavelength as elegantly expressed by the Planck-Einstein equation.

$$E = h\nu,$$

where 'E' is energy, 'h' is Planck's constant and 'ν' frequency.

The diverse regions of the electromagnetic spectrum offer complementary spectroscopic investigation opportunities with varying advantages and intellectual input into material property. The longest

wavelength radio waves of the lowest energy are used in nuclear magnetic resonance spectroscopy. Rotational spectroscopy is made possible by microwave radiation, while molecular vibrations can be studied by infrared radiation. Visible light spectroscopy enables the analysis of color, ultraviolet radiation probes electronic transition, while high-energy X-rays and gamma rays shed light on atomic and nuclear processes (Anderson et al., 2017). Although spectroscopic techniques can achieve such an extraordinary level of detail and precision, this comes as no surprise from the quantum mechanical nature of electromagnetic radiation.
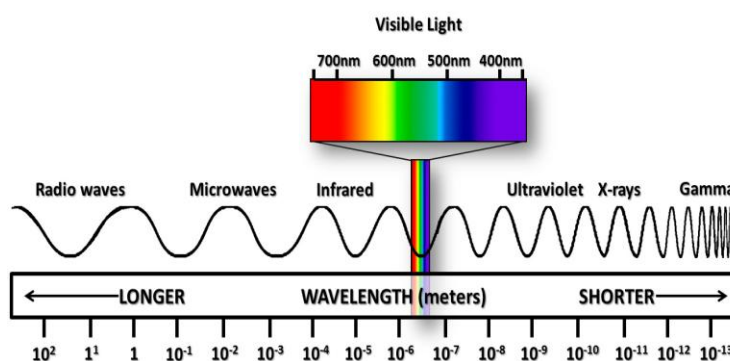


**Figure 1.1 Electromagnetic radiation**

Wavelengths vary from the thousands of kilometers-long radio waves to the pedometer-long gamma rays. This enables scientists to investigate phenomena along multiple scales/energy ranges as each wavelength region allows us view different properties of matter with different insight. Frequency is another central characteristic of electromagnetic radiation that is critical to spectroscopic studies. Frequency is directly related to wavelength via the speed of light and describes how many wave oscillations occur in a second. The higher the frequency, the higher the energy radiation, which allows for more energetic interactions with matter, accesses different quantum mechanical transitions. Spectroscopic observations can be accurately predicted and understood by researchers using the relationship between frequency and energy. Electromagnetic radiation has an

energy associated with it, which is a defining factor for how the radiation will interact with matter. Using the Planck-Einstein equation where energy is linear to frequency and inverse to wavelength. This mapping allows researchers to predict and comprehend the quantum mechanical transitions facilitated by spectroscopic measurements, providing a theoretical basis for the interpretation of complex spectral data.

## 1.4 Absorption, Emission, and Transmission

Absorption is one of the most significant and instructive reactions between electromagnetic energy and matter. Absorption is the transfer of energy from electromagnetic waves to material electrons when they shift between different quantum mechanical energy states. This process is very selective and dictated by the electronic arrangement of atoms or molecules, resulting in specific absorption spectra that serve as unique identifiers of material composition. This indicates that each distinct material absorbs radiation at certain wavelengths, corresponding to transitions in the atomic and molecular energy levels inside the material, so offering researchers an effective method to identify and analyze various compounds. This absorption process is a complex interaction dictated by quantum mechanics, wherein photons are absorbed by electrons, elevating them to a higher energy state.

## 1.5 Reflection, Dispersion, and Polarization

Reflection happens when some electromagnetic radiation interacts and a boundary between two different media and is returned into media. This phenomenon is governed by the optical properties of the materials, such as their refractive indices and surface features. It is thus said that reflection can be secular, when the radiation in response is reflected according to the angles mentioned (according to incidence angle), or diffuse, when the radiation is emitted into various directions. The ability of materials to reflect light has important relevance to optical

devices, telecommunications, and the study of the surface of materials. Dispersion is the separation of electromagnetic wave(s) into its component wavelength(s) because they travel through a material at different speeds. This process explains why rainbows are formed and gives a basic mechanism for spectroscopic analysis. The degree to which this radiation separates, varies with the material's optical properties and the wavelength of the radiation, allowing researchers to analyze the composition and electronic structure of materials via accurate measurements of the wavelengths over which the radiation is dispersed. Polarization describes how the oscillating electric and magnetic fields of electromagnetic radiation are oriented. The polarization of radiation can change when it interacts with matter, which allows more information about the electronic and molecular structure of the material. The role of polarization effects in light-matter interactions also underpins a range of applications, from optical communications, through materials characterization, to advanced imaging methods.
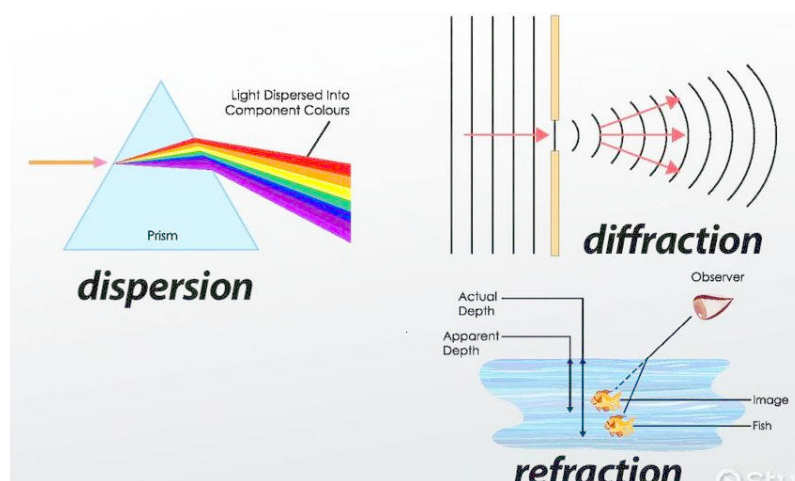


**Figure 1.2 Diffraction and refraction of light**

### 1.6 Scattering Mechanisms

Scattering mechanisms are a heterogeneous and complex variety of interactions wherein EMR is re-routed through the transmission of energy through particles or structural in homogeneities in the material.

There are several scattering mechanisms, and each reveals information about the material properties in its own context. Rayleigh scattering, which is to do with particles far less than the wavelengths of radiation in question, explains things like the blue color of the sky. Raman scattering also produces very specific information about molecular vibrations and rotational states, and Mie scattering is relevant to interactions with particles of comparable radius to the radiation wavelength. This redirection of radiation without change in energy is called elastic scattering and preserves the original wavelength and frequency. Inelastic scattering, on the other hand, means that some energy is exchanged between the radiation and the scattering medium, leading to shifts in wavelengths. For example, this inelastic scattering is especially important, as it gives us detailed information about molecular vibrations, which allows it to be used as an instrumental analytical technique in chemistry and materials science, which we call Raman scattering.

**Check Your Progress**

Q1. Define electromagnetic radiation and desribe its characteristics .

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Q2. Discuss the interaction of electromagnetic radiation with matter, including absorption, , emission, and scattering mechanism.

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## 1.7 Summary

Electromagnetic radiation refers to the energy transmitted through space in the form of oscillating electric and magnetic fields. It travels at the speed of light and exhibits both wave-like and particle-like properties, known as wave-particle duality. The electromagnetic spectrum covers a wide range of wavelengths and frequencies, including radio waves, microwaves, infrared, visible light, ultraviolet, X-rays, and gamma rays. Each region of the spectrum has unique applications, such as communication, medical imaging, and energy transfer. The wavelength is inversely proportional to frequency, and together they determine the energy of radiation, with higher frequency waves like gamma rays being more energetic and potentially harmful. Electromagnetic radiation does not require a medium and can propagate through a vacuum, making it essential for transmitting signals across space.

# 1.8: Exercises

## 1.7.1 Multiple Choice Questions

1. Which of the following is *not* a form of electromagnetic radiation?

a) Radio waves

b) Sound waves

c) Microwaves

d) Gamma rays

**Answer:** b) Sound waves

2. Which electromagnetic radiation has the *longest wavelength*?

a) Radio waves

b) Infrared rays

c) Ultraviolet rays

d) X-rays

Answer: a) Radio waves

3. Electromagnetic radiation consists of:

a) Only electric fields

b) Only magnetic fields

c) Both electric and magnetic fields oscillating perpendicular to each other

d) Neither electric nor magnetic fields

Answer: c) Both electric and magnetic fields oscillating perpendicular to each other

4. Which electromagnetic radiation is mainly responsible for causing

sunburn?

a) Infrared rays

b) Ultraviolet rays

c) Visible light

d) Radio waves

Answer: b) Ultraviolet rays

5. **Which of the following has the *shortest wavelength*?**

a) Radio waves

b) Gamma rays

c) Microwaves

d) Ultraviolet rays

**Answer:** b) Gamma rays

### 1.7.2 Short answer type Questions

1. Define spectroscopy and explain its importance in chemistry.
2. What are the key properties of electromagnetic radiation?
3. Differentiate between absorption, emission, and transmission of radiation.

### 1.7.3 Long answer type Questions

1. Describe the properties of electromagnetic radiation with a proper diagram.
2. Explain Reflection, Dispersion, and Polarization with suitable examples.
3. Explain the concept of natural line width and broadening in spectroscopy.

### 1.9 References and Suggested Reading

1. Banwell, C. N., & McCash, E. M. (1994). Fundamentals of Molecular Spectroscopy (4th ed.). McGraw-Hill Education (India) Private Limited Chennai.
2. Atkins, P., & Friedman, R. (2011). Molecular Quantum Mechanics (5th ed.). Oxford University Press, London, UK.
3. Hollas, J. M. (2004). Modern Spectroscopy (4th ed.). John Wiley & Sons, Hoboken, New Jersey, USA

SPECTROSCOPY - I

### 2.1 Introduction

The Heisenberg uncertainty principle, often known as the uncertainty relation, is a fundamental tenet of quantum physics. It articulates a fundamental impossibility regarding the precision of specific pairings of physical attributes, namely location and momentum, that can be simultaneously known or measured. The product of the errors in the measurements of location ($\Delta x$) and momentum ($\Delta p$) is theoretically described as being at least a constant value of two:

$$\Delta x \cdot \Delta p \geq \frac{\hbar}{2}$$

where $\hbar/2$ represents the reduced Planck constant. First stated by Werner Heisenberg in 1927, this principle follows directly from the wave-particle of duality of matter — a hallmark of the quantum mechanics. In the classical mechanics, we can know with arbitrary precision the position and momentum of a particle. But the uncertainty principle in quantum mechanics imposes a fundamental limit to the knowledge of these quantities.

### 2.2  Objectives

- To understand the Heisenberg Uncertainty Principle and its implications in spectroscopy.

- To study natural line width and factors causing broadening of spectral lines.
- To explain transition probabilities and selection rules in molecular transitions.

- To apply time-dependent perturbation theory in quantum systems.

- To understand the Born–Oppenheimer approximation in separating nuclear and electronic motion.

- To explore molecular energy levels: rotational, vibrational, and electronic.

- To analyze how these energy levels determine molecular spectra.

## 2.3 Natural Line Width and Broadening

Atomic and molecular spectroscopy YAG laser parametric accelerator. The interaction between an atom or molecule and radiation, characterized by the absorption or emission of radiation, establishes the relationship between the energy of the photon and the energy difference between two quantum states. However, those changes are not distinctly delineated. The intrinsic line width arises from the finite lifetime of the excited state of the atom or molecule. Due to the limited duration of the state's existence, the energy-time uncertainty principle indicates an uncertainty in the state's energy.

Lifetime of an excited state and the natural line width are related through:

$$\Delta E \cdot \Delta t \geq \hbar$$

where $\Delta E$ is the uncertainty associated with the energy of the state and $\tau$\tau is the lifetime of the excited state. The wider the spectral line, the shorter the lifetime, and vice versa; the longer the lifetime of the excited state, the narrower will be the spectral line.

In quantum physics, transition probabilities quantify the likelihood of shifting from one state to another as a result of external influences, such

as electromagnetic radiation. The absorption or emission of a photon by an atom or molecule corresponds to a transition between two energy states. The transition is feasible if all conditions are met, including the type of interaction, the energy difference between the states, and the symmetry features of the states.

For electric dipole transitions, for example, the transition probability takes the form:

$$P_{i \to f} = \frac{2\pi}{\hbar} \left| \langle f | H_{\text{int}} | i \rangle \right|^2 \rho(E)$$

where $P_{\{i \text{ to } f\}}$ is the transition probability from the initial state $|i\rangle|i\rangle$ to the final state $|f\rangle|f\rangle$, $H_{\{int\}}H_{int}$ is the interaction Hamiltonian, and $\rho(E)$ is the density of states (at the energy corresponding to the transition).

Certain transitions are permitted while others are prohibited, and selection criteria assist in assessing the phase of that process. These laws arise from the symmetries of the quantum states pertinent to the transition, including the characteristics of atomic orbitals and the parabolic nature of the electromagnetic field. The selection rules for electric dipole transitions stipulate that the orbital angular momentum quantum number must vary by $\pm 1$ (i.e., $\Delta l = \pm 1$), while the total angular momentum quantum number $j$ may vary by 0 or $\pm 1$, except that $j = 0$ is prohibited from changing by 0.

## 2.4 Time-Dependent Perturbation Theory

The time-dependent perturbation theory is a mathematical approach to a perturbation of a quantum system by using the time evolution of a quantum particle in the presence of a time-varying external perturbation (e.g. electromagnetic field). This is especially applicable to the situation where the system is not at its ground state and that small perturbations may occur to also excite the system to other energy levels. In its most basic form, one writes down the Hamiltonian of a given system as per

the Lorentz an details (unperturbed part, $H_0$) and perturbed part due to interaction outside the system ($H'(t)H'(t)$) that is dependent on time. H = H $_1$ + H $_2$ + H e (28) The net Hamiltonian can now be expressed as:

$$H(t)=H0+H'(t)$$

The time evolution of this system is governed by the time-dependent Schrödinger equation:

$$i\hbar\frac{\partial}{\partial t}|\psi(t)\rangle = H(t)|\psi(t)\rangle$$

We then proceed to make several assumptions about the perturbative regime we are in, in order to be able to clean up the equation and express a series in perturbation theory of the solution. For instance, the first-order correction to wave function describes the amplitude for the system to evolve from an initial state to a final state due to action of the perturbation. This is a common approach in studying atomic and molecular transitions driven by electromagnetic radiation, where the perturbing potential is usually the interaction between the system and radiation field. These transition probabilities are calculated charges using time-dependent perturbation theory: they provide information on rates for absorption/emission processes, something you have looked into in the context of spectra (at a high level).

## 2.5 Approximation of Born and Oppenheimer

The Born-Oppenheimer approximation is a method that simplifies the analysis of molecular systems by separating the movements of nuclei and electrons. This approximation relies on the principle that the nuclei of a molecule possess significantly greater mass than the electrons, resulting in their comparatively slower motion. The objective is to decouple nuclear motion from electrical motion, rendering the problem manageable. The Born-Oppenheimer approximation is employed to express the electronic wave function, wherein the locations of the

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nuclei are fixed, and the nuclei are regarded as classical particles traveling inside the potential created by the electrons. This results in an effective potential energy surface for nuclear motion, which can be utilized to characterize the vibrations and rotations of the molecule. This outcome can serve as a foundation for addressing the time-dependent Schrödinger equation utilizing two distinct coordinates, electronic and nuclear, which culminated in the Born-Oppenheimer approximation, extensively employed in molecular spectroscopy and dynamics. While it significantly simplifies calculations, it is not devoid of limitations.
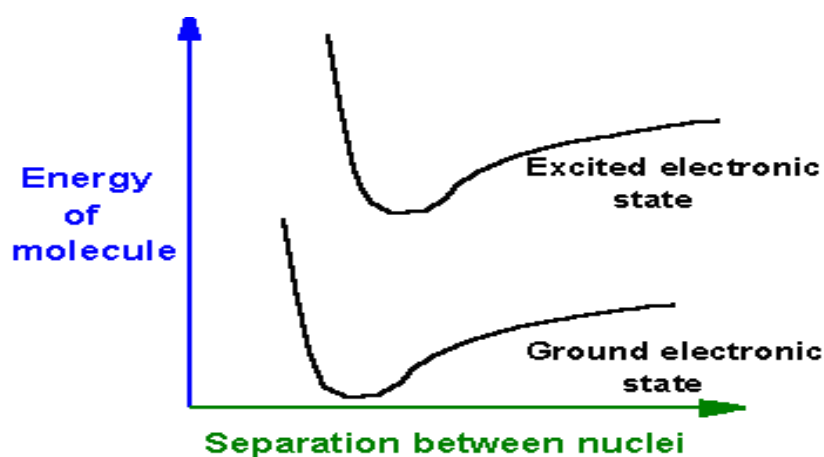


**Figure 1.3 Energy state of Molecules**

**2.6 Molecular Energy Levels**

Molecular energy levels are central to the interaction of molecules with electromagnetic radiation, reactivity in chemical transformations, and the behavior of matter as a function of temperature, as well as physical properties measured by spectroscopy. In a molecule, energy could be stored in different degrees of freedom, i.e. translational, rotational, vibration and electronic degrees of freedom, resulting into quantization of energy levels.

## 2.7 Rotational Energy Levels

Rotational: Rotational energy levels are the energy levels associated with the rotation of a molecule as a whole. In quantum mechanics, the rotational motion of molecules of the molecule is considered as a rigid body system, where the molecule rotates around its center of mass. Such motion is quantized, that is, only certain discrete energy levels are permitted. Molecular rotations can be approximately described by the rigid rotor model, where a molecule is imagined to consist of two vibrating masses, which represent atoms or groups of atoms, and rotate about an axis.

A diatomic molecule can only rotate at specific, quantized rotational energy levels, which are given by:

$$E_J = \frac{J(J+1)\hbar^2}{2I}$$

where:

• $E_J$ is the energy of the rotational level with quantum number J,

• J is the rotational quantum number (where J=0,1,2)

• $\hbar$ bar the reduced Planck constant,

• I is the moment of inertia of the molecule and depends on the masses of the atoms and the bond length between them.

For linear molecules the moment of inertia is given by:

$I=\mu r^2$

Here, $\mu$ represents the decreased mass of the molecule, defined as $\mu$ = (m1m2) / (m1 + m2), and r denotes the bond length between the two atoms. Nonetheless, regarding nonlinear molecules, the last statement

is not entirely accurate, as the moment of inertia is determined by various bond lengths and the angles between them; still, the underlying concepts remain unchanged! The rotational energy levels, expressed as $\hbar^2/2I$ in increments of $\hbar^2/2I$, indicate that adjacent levels diverge as the quantum number J escalates. The ground state occurs at J=0, representing the lowest accessible energy level. The rotational energy levels are pertinent in the microwave area of the electromagnetic spectrum, where molecular rotation can be stimulated by the absorption or emission of microwave radiation.

## 2.8 Vibrational Energy Levels

Vibrational energy levels relate to the periodic motion of atoms within a molecule, wherein the atoms oscillate about their equilibrium positions. Vibrational energy, like rotational energy, is quantized, allowing only specific discrete energy levels. The vibration of a diatomic molecule can fundamentally be described using the harmonic oscillator approximation, wherein the potential energy as a function of atomic displacement from equilibrium is presumed to be quadratic, much to a spring.
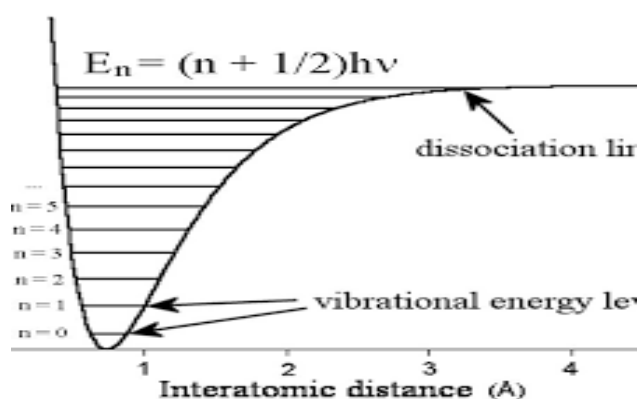


**Figure 1.4 Interatomic distance**

The vibrational energy levels are quantized for a harmonic oscillator:

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

where:

• Ev is the energy of the vibrational state with the quantum number vv,

• v is the vibration quantum number (v=0,1,2,…),

• h is Planck's constant, and

• ν is the frequency of the vibration, a function of both the mass of the atoms and the strength of the atomic bonds.

For neighboring vibration levels, the energy separation remains constant and is equivalent to hvh nu. The zero-point energy (the energy at v=0) of 12hv represents the system's minimal energy, as dictated by the Heisenberg uncertainty principle: atoms cannot stay stationary even at absolute zero temperature. However, the harmonic oscillator serves as an approximation that fails to adequately represent real molecule vibrations at elevated energy levels, where anharmonic effects become significant. The energy is represented as an enharmonic oscillator, with parameters accounting for the non-ideal nature of the bond, resulting in energy levels converging as vv grows. In the enharmonic oscillator model, the energy levels may be expressed as:

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

where ωe is a parameter which sets the magnitude of the non-harmonics. Infrared (IR) is the part of the electromagnetic spectrum where vibrational transitions take place, and IR radiation may be absorbed or emitted in the same frequency as the molecular vibration. Thus, the strength of the bond between atoms and the molecular

symmetry can affect the intensity of such vibrational transitions. For adjusted vibration, a substance with a dipole moment that changes during vibration interacts strongly with IR radiation than one that does not react with IR radiation when vibration occurs, so due to this, we see stronger vibrational absorption spectra of the molecule.

## 2.9 Electronic Energy Levels

Electronic energy levels refer to atomic and molecular configurations and their corresponding electronic states. Regulating Electron Exchange Between Molecules – The electronic structure of a molecule refers to the arrangement of its electrons into different molecular orbitals (MOs), quantized energy levels associated with the MOs. They are usually far higher than rotational or vibration levels and correspond to electronic transitions among various electronic states. The state of the molecule can simply be described as its electronic configuration based on the concept of polymer-orbital theory. The electronic energy levels can be conveniently described by this equation:

$$E_{\text{elec}} = E_{\text{HOMO}} - E_{\text{LUMO}}$$

where: • $E_{\text{elec}}$ is the electronic energy of the molecule,

• $E_{\text{HOMO}}$ The energy of the highest occupied molecular orbital (HOMO), and

• $E_{\text{LUMO}}$ is the energy of the lowest unoccupied molecular orbital (LUMO).

Molecular electrons can absorb or emit energy during transitions between electronic states, typically within the ultraviolet (UV) or visible parts of the electromagnetic spectrum. These transitions occur when the energy disparity between electronic states corresponds to the energy of the entering or exiting photon. In systems characterized by conjugation, particularly those exhibiting aromatic or prolonged pi-bonding, the electronic transitions are pronounced, yielding distinct UV-Visible absorption spectra. Nonetheless, the arrangement of electronic states in

**Check Your Progress**

Q1. With suitable diagrams,explain the regions of the electro

magnetic spectrum associated with different molecular transitions.

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Q2. Describe the Approximation of Born and Oppenheimer.

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## 2.10 Summary

The Heisenberg Uncertainty Principle relates the uncertainty in energy and time, leading to the concept of natural line width in spectral transitions. Spectral lines are further broadened due to Doppler, collisional, and instrumental effects. Transition probability, governed by quantum mechanics, determines the intensity of spectral lines, while selection rules restrict allowed transitions. Time-dependent perturbation theory provides a framework to calculate transition rates under external fields. The Born–Oppenheimer approximation simplifies molecular quantum mechanics by treating nuclei and electrons separately. Molecular spectra arise from quantized rotational, vibrational, and electronic energy levels. Rotational transitions lie in the microwave region, vibrational in infrared, and electronic in UV–visible spectra. Understanding these principles is crucial for interpreting molecular spectroscopy.

## 2.11 Exercises

### 2.11.1 Multy Choice Questions

1. The uncertainty principle is expressed as:

a) $\Delta E \cdot \Delta t \geq \hbar/2$

b) $\Delta p \cdot \Delta x = 0$

c) $E = mc^2$

d) $\Delta E \cdot \Delta t = 0$

Answer: a)

2. Natural line width arises due to:

a) Instrumental error

b) Finite lifetime of excited state

c) Collisions between molecules

d) Doppler effect

Answer: b)

**3.** The Born–Oppenheimer approximation assumes:

a) Electrons and nuclei move with the same speed

b) Nuclear motion is negligible compared to electronic motion

c) Electrons are stationary

d) Vibrations are ignored

Answer: b)

4. Rotational spectra generally fall in:

a) Infrared region

b) Microwave region

c) UV–visible region

d) X-ray region

Answer: b)

5. A selection rule for rotational transitions is:

a) $\Delta J = 0$

b) $\Delta J = \pm 1$

c) $\Delta J = \pm 2$

d) $\Delta J =$ any integer

Answer: b)

**2.11.2 Short answer type Questions**

1. State the Heisenberg uncertainty principle and explain its significance in spectroscopy.

2. Differentiate between natural line width and Doppler broadening.

3. What is the physical meaning of transition probability?

4. Write one important selection rule for electronic transitions.

5. Define the Born–Oppenheimer approximation.

**2.11.3 Long answer type Questions**

1. Derive the relation between energy uncertainty and natural line width. Discuss factors contributing to line broadening.

2. Explain time-dependent perturbation theory and its application in transition probability calculations.

3. Discuss the Born–Oppenheimer approximation in detail. Why is it important in molecular spectroscopy?

4. Describe molecular energy levels and explain differences among rotational, vibrational, and electronic transitions.

**2.13 References and Suggested reading**

1. Banwell, C. & McCash, E. (1994) Fundamentals of Molecular Spectroscopy, 4rth Ed., McGraw-Hill Higher Education, Chennai

2. B. K. Sharma (2023) Instrumental Methods of Chemical Analysis Vol-1: Spectroscopy Krishna Prakashan Media Ltd, Meerut.

## Unit 3
## Microwave Spectroscopy

Structure

## 3.1 Introduction

Microwave spectroscopy examines the molecular structure, energy levels, and transitions of molecules, with a particular focus on rotational transitions within the microwave region of the electromagnetic spectrum. This type of spectroscopy offers essential information about the physical properties of molecules, such as the distance between atoms, the moment of inertia, and symmetries. Rotational transitions are only significantly affected by both the moment of inertia and the symmetry, which is why microwave spectroscopy is well-suited for analyzing both gas-phase and lighter species. The microwave spectroscopy field is important in numerous sciences, including chemistry, physics, and environmental sciences. It offers insights into molecular structural properties, the nature of molecular interactions, and even for the identification of molecular species within complex mixtures.

### 3.2 Objectives

- To understand the principle and theory behind microwave spectroscopy.
- To study the interaction of molecules with microwave radiation.
- To analyze rotational transitions in molecules.
- To learn about the selection rules for rotational spectra.
- To distinguish between diatomic, polyatomic, and symmetric/asymmetric top molecules in microwave spectra.
- To understand applications of microwave spectroscopy in molecular structure determination.

**Microwave Spectroscopy: Linear Molecules**

Subsets of molecules in which all atoms are lined up linearly are also referred to as linear molecules. They usually have only one degree of freedom regarding the rotational motion around the axial line of the atoms. Linear molecules may be made up of two or more atoms, chalking the way for diatomic molecules (e.g., oxygen ($O_2$), nitrogen ($N_2$), carbon monoxide (CO)) as classic examples. Linear molecules have a permanent dipole moment, allowing them to engage with microwave radiation, which is a key signature of linear molecules. In microwave spectroscopy, the transitions that are observed in linear molecules occur when the molecule absorbs or emits radiation that is equivalent to a change between the rotational energy states of the molecule.

The motion of the Symmetric top molecules is more complex. This kind of molecular symmetry gives rise to more complex rotational energy levels than with spherical molecules but is still simpler than the analysis of asymmetric top molecules. Symmetric top (last book table) are molecules like ammonia ($NH_3$) or methyl fluoride ($CH_3F$) there are two equivalent of the rotational axes and one differences. This symmetry leads to the splitting of the rotational energy levels into separate components detectable in the microwave spectrum. The microwave spectrum of symmetric top molecules is also consist of series of lines, with each line corresponding to the transition of the rotational energy levels of a molecule.

### 3.3 Spherical Molecules

Spherical molecules are those that are spherical symmetric. In microwave spectroscopy, these molecules are relatively simple to analyze because they are uniform in all directions. Methane ($CH_4$) is an example of a spherical molecule high symmetry. Methane is a symmetric tetrahedral molecule in which the hydrogen atoms are

arranged symmetrically around a central carbon atom. This symmetry creates an isotropic distribution of mass, which means the rotational properties of the molecule are identical in all directions. The rotational states of spherical molecules are degenerate (the molecule can rotate freely without changing the energy). This symmetry makes the analysis of the microwave spectrum easier, as often only one rotational constant need be considered. For spherical molecules, the rotational transitions black and the spectral lines correspond to transitions between quantized rotational levels representative of (j = 0, 1, 2, 3… (where j = total momentum quantum number). Hello everyone, I have worked out the rotational spectrum of spherical molecules (typical example: Methane) and it is quite easy to diffuse and hence features will not be complex splitting and other things related to the higher energy level spin states of the molecules.

### 3.3.2 Symmetric Top Molecules

The motion of the Symmetric top molecules is more complex. This kind of molecular symmetry gives rise to more complex rotational energy levels than with spherical molecules but is still simpler than the analysis of asymmetric top molecules. Symmetric top (last book table) are molecules like ammonia ($NH_3$) or methyl fluoride ($CH_3F$) there are two equivalent of the rotational axes and one differences. This symmetry leads to the splitting of the rotational energy levels into separate components detectable in the microwave spectrum. The microwave spectrum of symmetric top molecules is also consist of series of lines, with each line corresponding to the transition of the rotational energy levels of a molecule.

### 3.3.3 Asymmetric Top Molecules

Asymmetric top molecules: The most complicated molecules in aspects of rotational spectroscopy These are unsymmetrical molecules with respect to the following rotational axes; hence the length of all three rotational axes is different and the rotational constants are also

different for this kind of molecule. Asymmetric top molecules are those which have three axes of rotation of which one is more easily rotated than the other two (see image), such as water ($H_2O$), hydrogen sulfide ($H_2S$) and some large organic molecules. Gunned and his colleagues found that in these molecules, the lack of symmetry makes their microwave spectra more complex and difficult to interpret. Asymmetric top microwave spectra consist of a series of rotational transitions which are more complicated than linear, non-linear or symmetric top molecules. The energy level spectrum for rotations of these molecules is not degenerate, and the transitions between them give rise to uniquely shaped spectra, with lines spread out in frequency and having different intensity and spacing.
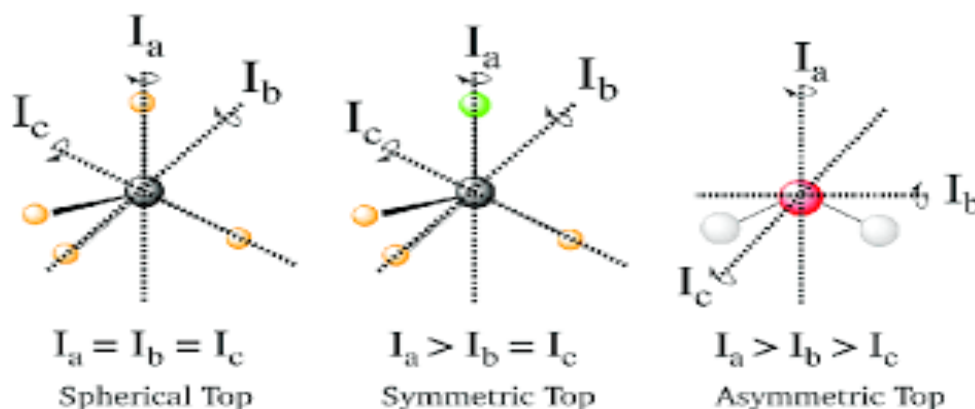


**Figure 1.5 Non-Rigid Rotor and Rigid Rotor Model**

The simplest molecular model can be perfectly represented in microwave spectroscopy by a rigid rotor model. This means that, for this model, a molecule is simply a rigid rotor, no molecules bend or vibrate back and forth as atoms move around with respect to the center of mass of the molecule. The rigid rotor approximation is most frequently used for diatomic molecules, though it can also be applied to some polyatomic molecules with certain constraints.

In the rigid rotor model, the energy conditions associated with rotational motion are described by the relation:

$$E_J = \frac{J(J+1)\hbar^2}{2I}$$

where:

• $E_J$ is the energy of the J rotational state,

• J= rotational quantum number (an integer value such as 0, 1, 2,...)

• $\hbar^2$ is the reduced Planck constant, where

• I, the moment of inertia of the molecule.

However, real molecules are not perfectly rigid objects: they can vibrate and rotate, and these types of motion influence each other. Therefore, the non-rigid rotor model is commonly used to take into account these interactions. The non-rigid rotor model considers that molecules may slightly deform as they rotate and vibrate. At higher rotational quantum numbers, centrifugal forces come into play leading to some deformations in their structures and breaking the assumption of rigid rotors.

This is based on the modifications of the energy levels due to moving rotors that carry a non-rigid rotor model of centrifugal distortion which adds further corrections to the energy equation. These corrections may be accounted for by the introduction of a centrifugal distortion constant, resulting in energy shifts of the rotational levels. For a non-rigid rotor, the energy equation becomes adjusted:

$$E_J = \frac{J(J+1)\hbar^2}{2I} - D_J(J+1)^2$$

$D_J$ is the centrifugal distortion constant. This correction takes into consideration the fact that the moment of inertia increases slightly at the time of rotation of the molecule due to the centrifugal forces experienced by the atoms. For high rotational quantum numbers and for

large molecules, the rigid rotor model breaks down, and the non-rigid rotor model becomes crucial. This model takes into account centrifugal distortion effects and gives a better description of rotational energy levels for complex molecules in gas phase.

### 3.3.4 Isotopic Substitution Effects

It is the fact that microwave spectroscopy allows one to study the effects of isotopic substitution on molecular spectra. This is when isotopic substitution takes place, that is, one atom is replaced in a given molecule with its isomer, resulting in a change in the mass of the atom without affecting its chemical reactivity. In microwave spectroscopy, isotope substitution primarily influences the moment of inertia, hence affecting the rotational energy levels of the molecule. The moment of inertia of a molecule is dictated by the masses of its constituent atoms and the distances between them. Substituting an atom with one of its isotopes alters the moment of inertia, thereby affecting the rotational energy levels. For example, substituting a hydrogen atom (mass $m\_H$) in a diatomic molecule like HCl with its isotope deuterium (mass $m\_D$) will result in a distinct moment of inertia due to the greater mass of the deuterium atom. The moment of inertia is defined as follows:

$I = \mu r^2$

where $\mu$ is the reduced mass, defined as $\mu = \dfrac{m_1 m_2}{m_1 + m_2}$ and r is the bond length.

Once again, since the moment of inertia is proportional to the mass of the atom, the rotational energy levels will be driven to lower frequencies (longer wavelengths) when the lighter isotope gets substituted by its heavier counterpart. The difference is especially apparent for isotopic substitutions based on hydrogen ones, where the hydrogen atom is replaced with either deuterium atom (H to D) or tritium atom (H to T), which have much greater difference in the mass

between its isotopes. Microwave techniques are used extensively to determine bond lengths by using isotopic substitution, in reaction dynamics and to identify various isotopes in the sample. All types of isotopic substitution are important for probing the physical properties of molecules; this is critical in studies of molecular interactions or in investigations of molecular vibrations in addition to rotational transitions.

### 3.3.5 The Stark Effect and Interaction with an External Field

This phenomenon is termed the Stark effect, when the introduction of an external electric field induces the splitting or shifting of a molecule's energy levels. This effect results from the interaction between the molecule's dipole moment and the external electric field. The Stark effect can provide insights about the dipole moment of the molecule, its symmetry, and the impact of external perturbations. The "Stark" effect in microwave spectroscopy is best observed for molecules with a finite permanent dipole moment. The energy levels related to the rotational transitions split or shift when a molecule is introduced to an electric field. The size of the reaction depends on how strong the electric field is and how the dipole moment are oriented to the field. Using perturbation theory, we can calculate the energy shift due to the Stark effect, yielding the following follow expression for energy shift:

$$\Delta E = -\vec{\mu} \cdot \vec{E}$$

where:

• $\Delta E$ the energy shift,

• $\vec{\mu}$ the dipole moment of the molecule, and

• $\vec{E}$ the external electric field.

Molecular properties like dipole moments and polarizabilities can be analyzed with the Stark effect. It is frequently applied for determining

dipole moments of gas-phase molecules, for which the field can cause charge separation across the molecule. In addition, the Stark splitting on the rotational spectra can be used to evaluate the distribution of charge in the molecule as well as the geometry of its electronic structure.

## Check Your Progress

Q 1. What is the principle of microwave spectroscopy?

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Q2.List some applications of microwave spectroscopy in scientificresearch.

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## 3.4 Summary

Microwave spectroscopy is a branch of rotational spectroscopy that deals with the absorption of microwave radiation by molecules, leading to transitions between quantized rotational energy levels. It is particularly useful for studying polar molecules, as a permanent dipole moment is required for microwave activity. The rotational constant BBB, related to the moment of inertia of a molecule, plays a key role in determining spectral lines. The selection rule for pure rotational transitions in diatomic molecules is $\Delta J = \pm 1$\Delta J = \pm 1$\Delta J = \pm 1$. Microwave spectra provide valuable information about bond lengths, bond angles, and molecular geometry. This technique finds applications in structural determination, isotopic substitution studies, and analysis of interstellar molecules.

### 3.5 Exercises

### 3.4.1 Multipe choice Questions

1. Which region of the electromagnetic spectrum does microwave spectroscopy primarily involve?

A. Infrared B. Visible C. Microwave D. Ultraviolet

**Answer: C. Microwave**

**2**. Microwave spectroscopy is mainly used to study:

A. Vibrational transitions B. Rotational transitions C. Electronic transitions D. Nuclear transitions

**Answer: B. Rotational transitions**

**3.** The energy of a photon is given by which of the following equations?

A. E=mc2$E = mc^2$E=mc2

B. E=hcλ$E = \frac{hc}{\lambda}$E=λhc

C. E=12mv2$E = \frac{1}{2}mv^2$E=21mv2

D. E=Fd$E = F \cdot d$E=F ·d

Answer: B. E=hcλ$E = \frac{hc}{\lambda}$E=λhc

4. Which of the following molecules is/are microwave active?

[Consider rigid model] $H_2$, HCl, $CO_2$, OCS

A. $H_2$ and OCS

B. HCl and OCS

C. HCl and $CO_2$

d. Only OCS

Answer: B. HCl and OCS

5. In rotational spectroscopy, the selection rule for transitions is: A. ΔJ=±2$\Delta J = \pm 2$ΔJ=±2 B. ΔJ=0$\Delta J = 0$ΔJ=0

C. ΔJ=±1$\Delta J = \pm 1$ΔJ=±1 D. ΔJ=±3$\Delta J = \pm 3$ΔJ=±3 Answer: C. ΔJ=±1$\Delta J = \pm 1$ΔJ=±1

6. What is the unit of frequency commonly used in microwave spectroscopy?

A. $cm^{-1}$

B. Hz

C. GHz

D. nm

Answer: C. GHz

7. The rotational constant BBB is related to:

A. Dipole moment

B. Moment of inertia

C. Bond energy

D. Temperature

Answer: B. Moment of inertia

8. Which of the following is not typically considered a unifying principle in spectroscopy?

A. Energy quantization

B. Transition probability

C. Classical mechanics

D. Electromagnetic radiation interaction

Answer: C. Classical mechanics

9. What is the primary cause of nuclear spin-spin coupling?

A. The magnetic interaction between electron spins and nuclear spins.

B. The direct magnetic interaction between two nearby nuclear spins.

C. The electrostatic repulsion between two nuclei.

D. The exchange interaction between nucleons.

Answer: B. The direct magnetic interaction between two nearby nuclear spins.

10. Which of the following nuclei are most likely to exhibit strong spin-spin coupling with a nearby proton ($^1H$)?

A. $^{12}C$

B. $^{13}C$

C. $^{16}O$

D. $^{14}N$

Answer: D. $^{14}N$

### 3.5.2 Short answers type Questions

- Define spectroscopy and explain its importance in chemistry.
- What are the key properties of electromagnetic radiation?
- Differentiate between absorption, emission, and transmission of radiation.
- Explain the concept of natural line width and broadening in spectroscopy.
- What is the Born-Oppenheimer approximation? Why is it important?
- Describe the different types of molecular energy levels.
- Explain the rigid rotor model and its assumptions in microwave spectroscopy.
- How does isotopic substitution affect the rotational spectrum of a molecule?
- What is the Stark effect, and how does it influence microwave spectra?

### 3.5.3 Long answers type Questions

1. Discuss the interaction of electromagnetic radiation with matter, including absorption, emission, and scattering mechanisms.
2. Explain the fundamental theoretical concepts of spectroscopy, including the uncertainty principle, transition probability, and selection rules.
3. Describe the different molecular energy levels (rotational, vibrational, and electronic) and their corresponding spectroscopic techniques.
4. Explain the principles of microwave spectroscopy and its application in determining molecular structure.
5. Discuss the rigid rotor model and non-rigid rotor model in

microwave spectroscopy.

6. Explain the effects of isotopic substitution on rotational spectra and molecular moment of inertia.

7. Describe the Stark effect and its significance in external field interactions.

8. How does nuclear and electron spin interaction influence microwave spectra?

9. Compare and contrast rotational, vibrational, and electronic spectroscopy in terms of energy transitions.

10. Discuss the major applications of microwave spectroscopy in chemistry, physics, and environmental science.

## 3.6 References and Suggested readings

1. Banwell, C. N., & McCash, E. M. (1994). Fundamentals of molecular spectroscopy (4th ed.).McGraw-Hill Education Pvt. Ltd. Chennai

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# BLOCK 2
# ATOMIC, MOLECULAR, AND PHOTOELECTRON SPECTROSCOPY

## Unit 4: The Atomic Spectroscopy and Molecular Spectroscopy

### Structure

## 4.1 Introduction

Atomic spectroscopy examines the fundamental interactions between atoms and electromagnetic radiation, elucidating the discrete energy transitions that occur when atoms absorb or emit photons of specific wavelengths, thus offering essential insights into atomic structure, electronic configurations, and quantum mechanical behavior. The fundamental premise involves atomic orbital energy levels—quantized states where electrons are positioned based on quantum mechanics—where transitions between these levels generate distinct spectral lines that act as unique identifiers for each element. The vector representation of angular momentum offers a mathematical framework for comprehending the contributions of orbital angular momentum (L) and spin angular momentum (S) to atomic properties, as these vectors possess both magnitude and direction in three-dimensional space, facilitating accurate descriptions of electron behavior. Vector coupling schemes, specifically Russell-Saunders (LS) coupling for lighter elements and j-j coupling for heavier elements, elucidate the combination of angular momenta to ascertain the total angular momentum (J) of an atom, which directly affects spectral patterns via selection rules and fine structure splitting. Term symbols, shown as $^{2S+1}L_J$, succinctly convey an atom's electronic configuration by indicating multiplicity ($^{2}S+1$), orbital angular momentum (L, denoted by S, P, D, F), and total angular momentum (J), thereby allowing spectroscopists to systematically identify and anticipate spectrum transitions.

## 4.2 Objectives

1. To understand the fundamental principles of atomic absorption, emission, and fluorescence spectroscopy.

2. To study the origin of atomic spectra based on electronic transitions.

## 4.3 Atomic Orbitals and Their Energy Levels

Atomic orbital's, spectroscopy, energy levels They correspond to quantized states that the electrons occupy in an atom. Energy levels arise because the electron's energy in the atom is quantized, an effect that occurs due to quantum mechanics. A particle is comparable to the motion of an electron within an atom, where the energy levels of the electron are contingent upon the attraction to the nucleus and the electron's mobility.

$$E_n = -\frac{13.6\,\text{eV}}{n^2}$$

In a hydrogen atom, the most fundamental atom, the energy levels are delineated by the Bohr model and can be articulated by the equation:

where:

• $E_n$ is the energy of the electron at the principal quantum number n.

• n is the main quantum number (where n=1,2,3,…).

• 13.6eV is the energy at the lowest quantum-state of hydrogen.

This means that when n decreases the energy of an electron becomes more negative and when n increases the energy levels become more close together. The movement of electrons between these energy levels reflects the emission or absorption of some specific wavelengths of electromagnetic radiation, and form the hydrogen atomic spectrum. In

many-electron systems, such as multi-electron atoms, energy levels are influenced by both the nucleus and the electron-electron repulsion. It introduces additional complexity to the configuration of the energy levels. In atoms possessing multiple electrons, energy levels can be characterized by: The primary quantum number (n), orbital angular momentum quantum number (l), magnetic quantum number (m_l), and spin quantum number (m_s) are essential for comprehending the attributes and behaviors of electrons in atoms. These quantum numbers emerge from the resolution of the Schrödinger equation for an atom, specifying the quantized energy levels, orbital forms, their orientations, and the intrinsic spin of electrons within the atom. Each quantum number fulfills a distinct role in delineating the features and behavior of the electron, thus establishing a comprehensive characterization of the electron's state in quantum mechanics.

### 4.4 Introducing the Principal Quantum Number (n)

The first quantum number the principal quantum number (n) It indicates the total amount of energy that the electron carries and is crucial for determining the electron's orbital size and energy. It can take on the positive integer values only (n = 1, 2, 3,... ) which correspond to the distance of the electron from the nucleus. The orbital's that are interacting from the nucleus increase up to n. The principal quantum number is connected with the energy of the electron in the atom. For instance, the energy of an electron in a hydrogen atom is inversely proportional to the square of the principal quantum number (n), according to the energy formula:

$$E_n = -\frac{13.6 \text{ eV}}{n^2}$$

where $E_n$ is the energy of the electron at the $n^{th}$ energy level (and 13.6eV= $E_0(01)$ Thus, as you increase the value of nnn, the electron is less tightly bound as the energy becomes less negative, and we say that the electron occupies a higher energy level.

## Orbital angular momentum quantum number l

The second quantum number is the orbital angular momentum quantum number (l) that describes the shape of an electron's orbital. The value of l can take any integer value between 0 to $n^{-1}$, where n stands for the principal quantum number. For a given value of n, l specifies the type of orbital the electron occupies. For every value of l, we have a different type of orbital:

• l=0: s orbital (spherical symmetry)

• l=1: p-orbital (dumbell shaped)

• l=2: d orbital (cloverleaf-shaped)

•l=3: f orbital (complex shapes)

Different amplitude electron density distribution around nucleus is found by these orbital's.

The angular momentum of the electron is also determined by the orbital angular momentum quantum number. |L|=mvr | L | = mvr

$$L = \hbar\sqrt{l(l+1)}$$

where L denotes the magnitude of the orbital angular momentum and $\hbar^2$ represents the decreased Planck constant. l specifies the angular characteristics of the wave function, dictating the spatial distribution of the electron's probability density. The l quantum number defines the angular momentum of a particle in the plane and the intricacy of the related orbital's structure; hence, higher l values indicate greater angular momentum and more complex interactions with external fields. The value of l also dictates the different potential orientations of the orbital. For any l value, there are $2l + 1$ distinct spatial orientations of the orbital, as indicated by the magnetic quantum number ml.

The magnetic quantum number (ml) delineates the spatial orientation of the orbital in relation to the applied magnetic field. For a constant value of the orbital angular momentum quantum number l, ml will assume integer values ranging from -l to +l, inclusive of zero. For each value of \ell, the magnetic quantum number possesses $2\ell + 1$ possibilities. These represent the distinct orientations that an orbital can assume in space. The permissible values of ml can be ascertained from the aforementioned expression; for instance, when l=1 (a p orbital), ml can assume the values -1, 0, and +1, signifying three potential orientations of a p orbital, as illustrated in the image. For l=2 (a d orbital), the values of ml can range from −2 to +2, yielding five potential orientations of the d orbital. Comprehending the magnetic quantum number is essential for grasping the behavior of electrons in magnetic fields. The energy levels of atoms are divided in an external magnetic field based on their magnetic quantum number, a phenomenon referred to as the Zeeman effect. The orbitals, characterized by the ml quantum numbers, react variably to the magnetic field, resulting in distinct energy shifts. The effect is often utilized in spectroscopy to analyze the characteristics of atoms and molecules in the presence of a magnetic field. The magnetic quantum number also delineates the degeneracy of energy levels. For instance, orbitals with identical l values but differing ml values exhibit identical behavior (they are degenerate) in the absence of an external magnetic field. The presence of a magnetic field disrupts this degeneracy, eliminating the equivalence of orbitals with differing ml eigenvalues at varying energy levels.

### 4.5 The Spin Quantum Number (ms)

The inherent quantum number of spin is referred to as the spin quantum number (ms). The other three quantum numbers define the spatial aspect of the electron's wave function, however the electron spin quantum number pertains to an inherent characteristic of the electron. Electrons are fundamental particles possessing intrinsic spin. Spin does

not represent a physical rotation and does not equate to the actual spinning of an electron; rather, it constitutes a form of angular momentum that contributes to the electron's overall angular momentum. The spin quantum number of an electron possesses two potential values, $+1/2$ or $-1/2$, reflecting the two distinct states of an electron's spin. The spin alignment of these values is commonly designated as "spin-up" and "spin-down," respectively. Identical: The spin quantum number is crucial for defining the magnetic characteristics of electrons and their interactions with particles and fields. Electrons may possess varying spin quantum numbers and interact to create distinct chemical bonds, hence determining the overall atomic or molecule spin state. The spin quantum number is an essential element of the Pauli Exclusion Principle, which asserts that no two electrons in an atom may possess identical sets of four quantum numbers.

## 4.6 The Quantum Numbers that Describe the Electron Configuration

The four quantum numbers (n, l, ml, ms) collectively delineate the quantum state of the electron within the atom. These quantum numbers delineate the electron arrangement of an atom, specifically its electron configuration within the orbitals. You possess expertise in a certain sequence of electron configuration, progressing from the lowest energy orbital to the highest energy level. The primary quantum number n defines the overall energy level, whereas the orbital angular momentum quantum number l specifies the orbital's structure. The magnetic quantum number m delineates the orientation of the orbital, while the spin quantum number m_s specifies the direction of the spin. Chemists can forecast an atom's binding energy, reactivity, and other qualities that characterize its behavior in chemical processes by evaluating its electron configuration. The valence electrons in the outermost energy levels participate in chemical bonding, affecting the atom's reactivity and the types of bonds it can establish. You study the four quantum

numbers: primary quantum number (n), orbital angular momentum quantum number (l), magnetic quantum number ($m_l$), and spin quantum number ($m_s$), which characterize the quantum state of an electron within an atom. Collectively, these quantum numbers provide a comprehensive and precise characterization of the electron, encompassing its behavior, orbital form, orbital orientation, and spin. Quantum numbers are essential components of atomic structure, spectroscopy, and quantum mechanics. In many-electron atoms, the electron's behavior is influenced not just by the nucleus but also by interactions with other electrons, necessitating the employment of more complex methods such as the Hartree-Fock technique or configuration interaction to approximate the true energy levels. The fine structure arises from relativistic effects, while the hyperfine structure results from the interaction between nuclear spin and electron spin.

This renders their motion a vector representation of moments in atomic spectroscopy. Quantum mechanics posits that moments are vectors, and the overall momentum of a system can be seen as a vector that can be decomposed into components along various spatial directions. The overall momentum of an electron in an atom is represented by the vector sum of its linear and rotational momentum contributions. The angular momentum of an electron orbiting an atom is quantized by quantum numbers, with the orbital angular momentum quantum number denoted as l. Magnitude of the orbital angular momentum:

$$L = l(l+1)\hbar$$

where $\hbar^2$ represents the decreased Planck constant. The angular momentum vector lacks a definite direction, and quantum mechanics integrates the uncertainty principles along with the intrinsic probabilistic characterization of the electron's position and velocity. This picture omits the fact that, alongside orbital angular momentum, there exists the electron's spin angular momentum, represented by the spin quantum number ss. Here, j is the total angular momentum quantum number, representing the total angular momentum of the

electron, which is the vector sum of its orbital angular momentum and spin angular momentum. The total angular momentum vector is defined by its magnitude:

$$J=j(j+1)\hbar^2$$

j takes values between $|l-s|$ and $l+s$ inclusive and integer steps between. But we will use this in Next sub-section, to calculate the magnetic properties of the atoms, splitting of the energy levels, when an atom is put on an external field.

## 4.7 Vector Coupling and Term Symbols

Methods for Incorporating Angular Momenta   Vector Coupling Computation of Orbital and Spin Angular Momentum   Orbital Angular Momentum   Spin Angular Momentum   Vector Coupling in Quantum Mechanics   Vector coupling is a mathematical technique used to amalgamate angular momenta originating from many sources, such as the orbital and spin angular momenta of an electron or the angular momenta of two electrons. Vector coupling principles are employed to ascertain the overall angular momentum of a system and the corresponding term symbols that characterize the electronic state of an atom. In atomic systems, the total angular momentum is the vector sum of the individual angular momenta. The individual angular momenta of electrons in a multi-electron atom are combined to form the total orbital angular momentum L and total spin angular momentum S. The total angular momentum J is derived from the coupling of L and S. The permissible values of J are established through the vector addition of the individual angular momenta:

$$J = L + S, \quad J = |L - S|, \quad J = |L - S| + 1, \quad \ldots, \quad J = (L \pm 1)L/2(2 - L)$$

When the total angular momentum has been established, the atomic electronic configuration can be expressed in terms of a so-called term

symbol. For all energy levels we can use the symbolic representation which describes them as such; the all S, L, J. The following expression represents the term symbol:

$$^{2S+1}L_J^{2S+1}L_J$$

where:

• $2^{S+1}$ is the multiplicity (the number of possible spin states),

• Spectroscopic letter (S, P, D, F, etc.) representing L

• J is the total angular momentum quantum number.

For instance, the term symbol 2P$_{3/2}$ indicates an atom with $S=\frac{1}{2}$ (a multiplicity of 2), a L=1 (the letter P) and a $J=\frac{3}{2}$.

Vector coupling and term symbols characterize atomic states and provide understanding of the energy configuration of atoms. These notions are particularly pertinent when examining the fine structure of atomic spectra, which refers to the splitting of energy levels due to spin-orbit coupling and similar interactions.

## 4.8  Spectra of Hydrogen and Alkali Metals

Notable and significant instances in atomic spectroscopy include the spectra of hydrogen and alkali metals. These atoms possess electronic configurations that may be succinctly characterized, featuring multiple energy levels and transitions amenable to detailed analysis. The hydrogen atom possesses a single electron, resulting in a spectrum that is less complex than that of multi-electron atoms. The energy levels of hydrogen are quantized and expressed as:

$$E = -\frac{13.6 \text{ eV}}{n^2}$$

For n=1,2,3,4, the energy levels are:

$$E_1 = -13.6 \text{ eV}, \quad E_2 = -3.4 \text{ eV}, \quad E_3 = -1.51 \text{ eV}, \quad E_4 = -0.85 \text{ eV}, \ldots$$

Thus, the rewritten form is:

$$E_n = -\frac{13.6 \text{ eV}}{n^2}, \quad \text{for } n = 1, 2, 3, 4, \ldots$$

The emission or absorption of electromagnetic radiation corresponds to transitions between energy levels. The Ryder formula elucidates the wavelengths of transitions that generate the spectral lines observed in the hydrogen spectrum. The hydrogen atom's spectrum has multiple series, including the Lyman series (ultraviolet), the Balmer series (visible), and the Paschen series (infrared), among others. Each series denotes transitions among different energy levels of the hydrogen atom, with the resultant spectral lines produced by electron transitions between these levels.
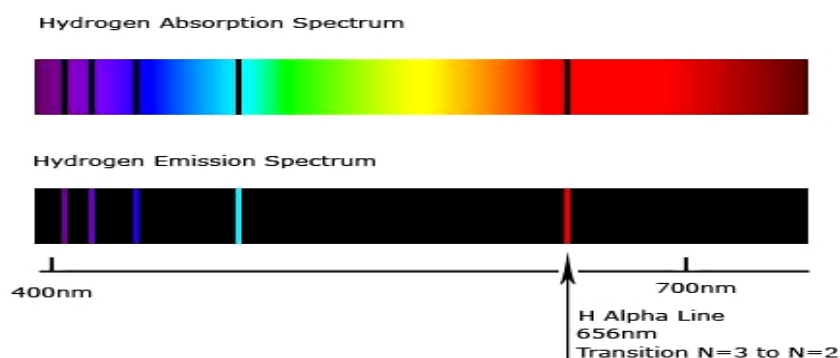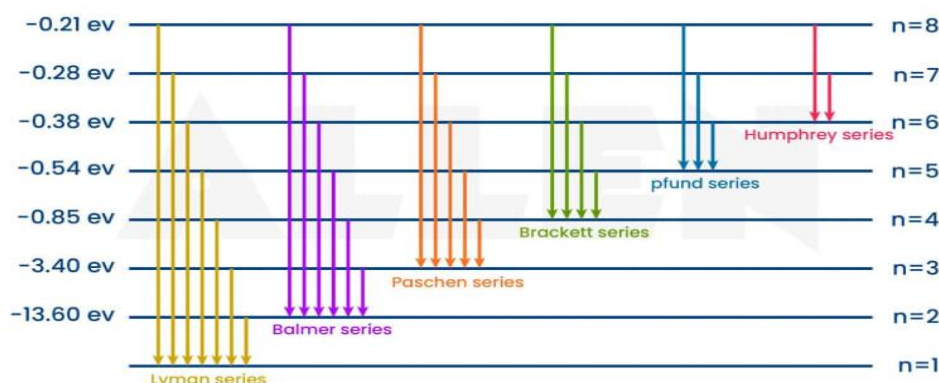


**Figure 2.1 The hydrogen atom's spectrum**

**Check Your Progress**

Q1. Differenciate between molecular spectroscpy and atomic spectroscopy.

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Q2. Explain the advantages of Atomic Absorption Spectroscopy.

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### 4.9 : Summary

Atomic spectroscopy is the study of electromagnetic radiation absorbed and emitted by atoms. It is based on electronic transitions between discrete energy levels of atoms. The main branches are Atomic Absorption Spectroscopy (AAS), Atomic Emission Spectroscopy (AES), and Atomic Fluorescence Spectroscopy (AFS). AAS measures absorbed light when atoms in the ground state absorb radiation, while AES measures light emitted by excited atoms. Each element has a unique line spectrum, making atomic spectroscopy highly sensitive and selective for elemental analysis. Line broadening (natural, pressure, and Doppler broadening) and selection rules influence spectral features. Applications include environmental monitoring, clinical analysis, metallurgy, and chemical research.

### 4.10 Exercises
### 4.10.1 Multiple Choice Questions

1. Atomic spectroscopy is primarily based on:
   a) Nuclear transitions
   b) Electronic transitions
   c) Vibrational transitions
   d) Rotational transitions
   **Answer:** b) Electronic transitions

2. Which type of atomic spectroscopy measures the absorption of light by ground-state atoms?
   a) AAS
   b) AES
   c) AFS
   d) NMR
   **Answer:** a) AAS

3. The line spectrum of hydrogen was first explained by:
   a) Bohr's theory
   b) Rutherford's theory
   c) Planck's theory

d) Einstein's theory
**Answer:** a) Bohr's theory

4. Which broadening effect is due to random motion of atoms?
   a) Natural broadening
   b) Pressure broadening
   c) Doppler broadening
   d) Collisional broadening
   **Answer:** c) Doppler broadening

5. In atomic emission spectroscopy, atoms are excited by:
   a) Absorbing photons
   b) External energy sources (flame, plasma, arc, spark)
   c) Vibrational resonance
   d) Nuclear decay
   **Answer:** b) External energy sources

## 4.10.2 Short answer type Questions

1. Define atomic spectroscopy.

2. Differentiate between atomic absorption and atomic emission spectroscopy.

3. What are selection rules in atomic spectroscopy?

4. Write a short note on line broadening.

5. State two applications of atomic spectroscopy in industry.

## 4.10.3 Long answer type Questions

1. Explain the principle, instrumentation, and applications of Atomic Absorption Spectroscopy (AAS).

2. Discuss different types of broadening mechanisms in atomic spectra.

3. Describe the difference between Atomic Absorption, Emission, and Fluorescence Spectroscopy with examples.

4. Explain the quantum mechanical basis of atomic spectra and selection rules.

5. Describe the role of atomic spectroscopy in environmental and clinical analysis with examples.

## 4.11 References and Suggested Reading

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# Unit 5
# Molecular Spectroscopy Fundamentals of Infrared Spectroscopy

## Structure

5.1 Introduction
5.2 Objectives
5.3 Vibrational Progressions in Excited States
5.4 Frank-Condon Principle
5.5 Charge Transfer Spectra of Transition Metal Complexes
5.6 Summary
5.7 Exercises
5.8 References and Suggested Reading

## 5.1 Introduction

Molecular spectroscopy is the study of how electromagnetic radiation interacts with matter, primarily by analysis of the electromagnetic spectrum electromagnetic radiation interacts with atoms, molecular molecular. This area of study investigates the ways that molecules interact with radiation within various parts of the electromagnetic spectrum, offering important information on molecular structure, dynamics and interactions. Schematic representation of different types of molecular spectroscopy. In this section we will touch upon molecular energy levels, vibronic transitions, vibrational progressions, Frank-Condon principle, emission spectra and charge transfer spectra and applications.

Vibronic transitions occur when both electronic and vibrational levels of a molecule are concurrently engaged. This is characteristic of molecular spectroscopy in general, and specifically in UV-Vis spectroscopy. Vibronic transitions occur when an electrical transition coincides with a change in the vibrational state of the molecule. molecule can be activated by the absorption of light, which is the principle of UV-Vis absorption spectroscopy, wherein an electron absorbs a photon and transitions to a higher electronic state. In actual molecules, vibronic modes interconnect electronic transitions with the vibrational modes of the molecule. Consequently, during an electrical transition, the molecule may concurrently alter its vibrational state.

## 5.2 Objectives

1. To understand the fundamental principles of infrared (IR) spectroscopy.

2. To learn how molecular vibrations interact with IR radiation.

3. To study vibrational modes (stretching and bending) in molecules.

## 5.3 Vibrational Progressions in Excited States

Energy absorption induces excitation, transitioning molecules from a ground electronic state to an excited electronic state. In addition to this electronic excitation, there may also be a modification in the vibrational state of the molecule, resulting in vibrational progressions detected in the excited states. These, frequently referred to as vibrational progressions, are collections of vibrational transitions originating from the excited electronic state of the molecule. Each electronic state of a molecule comprises many vibrational energy levels. The straightforward photon transition to a singular excitation vibrational level is frequently inaccurate, as the molecule is subsequently excited to several vibrational levels. The transitions between vibrational levels generate a vibrational series.

## 5.4 Frank-Condon Principle

The v-distribution of vibronic transitions is characterized by the Frank-Condon principle. It signifies that electronic transitions occur almost instantaneously in relation to nuclear action. This indicates that the locations of the nuclei in the molecule remain relatively unchanged during an electronic transition. Consequently, the likelihood of a vibronic transition between two electronic states is dictated by the characteristics of the vibrational wavefunctions of both

states. According to the Franck-Condon principle, the strength of a vibronic transition is proportional to the square of the vibrational overlap integral between the beginning and final vibrational wavefunctions. This overlap is dictated by the spatial arrangement of nuclei in the ground and excited electronic states. This results in transitions between the two states that include minor displacements of the nuclei being far more probable. Consequently, the Frank-Condon principle produces a characteristic pattern in molecular spectra. In the excited state, transitions to higher vibrational levels often exhibit lesser strength than those to lower vibrational levels, resulting in a succession of spectral peaks corresponding to various vibrational excitations. This notion is crucial for elucidating the intensity distribution of peaks in molecular spectra and serves as the foundation for absorption and emission spectra.
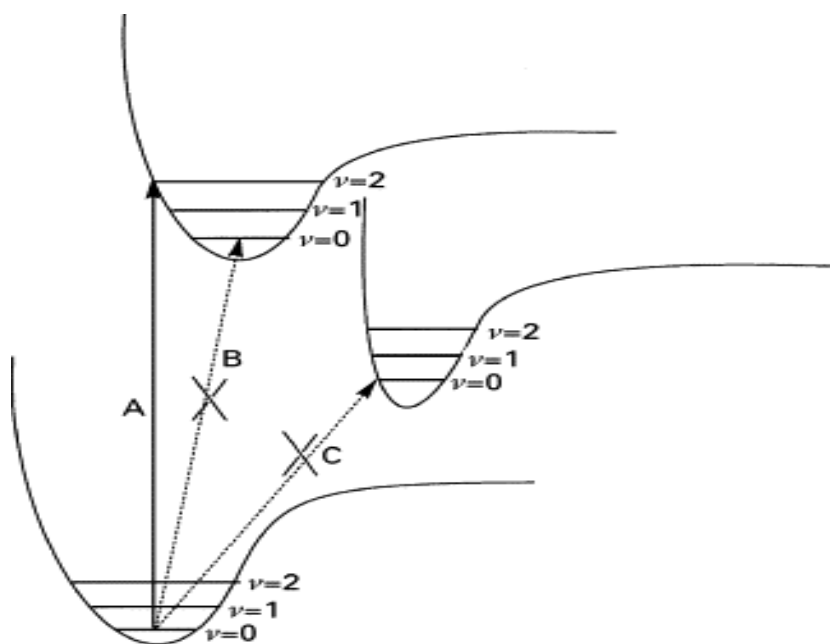


**Figure 2.3 Vibrational Progressions in Excited States**

**Emission Spectra: Radiative and Non-Radiative Decay**

Radiative decay is an essential mechanism in molecular spectroscopy. The radiation emitted by the emission spectrum provides insights on

the electronic and vibrational characteristics of molecules, including their chemical composition, molecular structure, and molecular dynamics. The particulars of radioactive decay depend on the energy levels involved, the electronic states of the molecule, and whether the molecule exists in an isolated or organized environment. The two primary forms of radioactive decay processes are fluorescence and phosphorescence. Both represent kinds of electronic relaxation resulting in light emission; yet, they significantly differ in their specific characteristics concerning excited states and emission kinetics.

**Fluorescence**

Fluorescence is a type of photoluminescence in which a molecule or atom absorbs light (usually UV or visible**)** and then reemits light at a longer wavelength (lower energy). The process occurs very rapidly-typically within nanoseconds ($10^{-9}$ seconds**)**-and stops almost immediately when the excitation source is removed. It is commonly observed in fluorescent dyes, minerals, biological tissues, and in many analytical and medical techniques.

**Phosphorescence**

Phosphorescence **is a** type of photoluminescence that occurs when a substance absorbs energy (usually from UV or visible light) and emits it slowly over time as visible light. Unlike fluorescence, which ceases almost immediately after excitation stops, phosphorescence can persist from microseconds to minutes or even hours after the excitation source has been removed.

**Emission spectra arise from radiative decay**

The emission spectrum resulting from radioactive decay typicall produces multiple lines or bands. These denote numerous transition between the vibrational or rotational levels of elevated electronic state and the molecule's ground state. Our emphasis was on electronic

transitions; nevertheless, the energy levels involved are contingent upon the electronic state of the molecule as well as its vibrational and rotational states. Emission spectra are typically analyzed based on the energy differential between the molecule's beginning and final states. The emission spectrum of molecules transiting between electronic states reveals details on the molecule's electronic structure, the energy necessary to elevate the molecule to a higher energy state, and the energy emitted when it reverts to the ground state.

### Non-Radiative Decay

This energy can be released non-radiatively, wherein the molecule in an excited state (S1 for singlet or T1 for triplet) dissipates its energy without photon emission. The molecule does not emit energy in the form of light; instead of radiating energy as light, it discharges surplus heat through several methods that do not generate electromagnetic radiation. Non-radiative processes are essential for understanding energy loss pathways and the overall efficiency of energy transfer; thus, they are significant in any system that aims to avoid light production. The primary mechanisms of non-radiative decay encompass various processes, notably internal conversion (IC) and vibrational relaxation (VR). Radiative decay entails the conversion of electronic energy into light, whereas these processes require the transformation of electronic energy into thermal energy or the redistribution of vibrational energy among molecular degrees of freedom.

### Internal Conversion (IC)

Internal Conversion (IC) is a radiationless process in which a molecule in an excited electronic state transitions to a lower electronic state of the same spin multiplicity (e.g., from $S_1$ to $S_0$) without emitting a photon. The energy is released as thermal (vibrational) energy, which is dissipated to the surroundings. Example: A molecule in the $S_1$ (first singlet excited state) can undergo internal

conversion to $S_0$ (ground state), converting the excess energy into vibrational energy, which is eventually released as heat.

**Vibrational Relaxation (VR)**

Vibrational Relaxation (VR) **is a** non-radiative process by which an excited molecule or atom dissipates excess vibrational energy and returns to the **lowest vibrational level** of a given electronic state. This happens very rapidly, typically in the time range of $10^{-12}$ to $10^{-14}$ seconds (picoseconds to femtoseconds).

It is one of the fastest energy dissipation processes and usually precedes radiative transitions **like** fluorescence or phosphorescence.

**Comparison between Radiative and Non-Radiative decay**

Radiative and non-radiative decay are fundamental mechanisms that facilitate the relaxation of agitated molecules. Radiative decay refers to the emission of photons and underpins the phenomena of fluorescence and phosphorescence, while non-radiative decay entails the dissipation of excess energy as heat, exemplified by internal conversion and vibrational relaxation. The processes of interest in this example are dictated by the molecular type, the energy levels engaged, and the environmental variables. Radiative decay process when the emitted light type is noteworthy.

**5.5 Charge Transfer Spectra of Transition Metal Complexes**

In transition metal complexes, **electronic transitions** can occur not only within the metal ion's d-orbitals (**d–d transitions**) but also between the **metal and the ligands**. These latter transitions are known as **charge transfer (CT) transitions**. When a transition involves the transfer of electron density from a ligand to the metal or vice versa, the resulting absorption spectrum is called a **Charge Transfer Spectrum**. Charge transfer bands are usually **intense** and occur at **higher energies**

**(shorter wavelengths)** compared to d–d transitions, making them highly useful in characterizing coordination compounds.

**Applications of Molecular Spectroscopy**

Molecular spectroscopy is a potent analytical method employed in diverse scientific and industrial fields to examine molecular structures, interactions, and compositions. A vital application is in chemical analysis and identification, where techniques like Infrared (IR) and Raman spectroscopy facilitate the determination of functional groups in organic and inorganic molecules. This is crucial in medicines, forensic science, and quality assurance in chemical manufacture. Molecular spectroscopy serves a crucial role in environmental monitoring by facilitating the identification of pollutants, including greenhouse gases, volatile organic compounds, and heavy metal contaminants in air, water, and soil. Methods such as UV-Vis and fluorescence spectroscopy are extensively utilized in the examination of environmental contaminants and their impacts on ecosystems. In the medical and biomedical domains, spectroscopy is essential for disease diagnosis and pharmaceutical development. Near-infrared spectroscopy (NIRS) is employed in non-invasive medical imaging, whereas nuclear magnetic resonance (NMR) spectroscopy is crucial for metabolic profile and biomarker identification in illnesses including cancer and neurological diseases.

**Check Your Progress**

Q1. Explain the Principle of IR Spectroscopy.
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Q2. Describe the instrumentation of IR based spectrophotometer
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## 5.6: Summary

Infrared (IR) spectroscopy is a technique based on the absorption of infrared radiation by molecules, leading to vibrational transitions. Molecules absorb IR radiation when the vibration causes a change in dipole moment. The IR region is divided into near (14000–4000 $cm^{-1}$), mid (4000–400 $cm^{-1}$), and far IR (400–10 $cm^{-1}$). Each molecule exhibits characteristic vibrational frequencies that serve as a "fingerprint" for structural identification. The two main vibrational modes are stretching (symmetric and asymmetric) and bending (scissoring, rocking, wagging, twisting). The selection rule states that only vibrations producing a dipole moment change are IR active. IR spectroscopy finds applications in identifying functional groups, structural elucidation, monitoring chemical reactions, and material characterization.

## 5.7: Exercises

### 5.7.1 Multiple Choice Questions (MCQ)

1. The IR region used for structural studies is:
   a) Near IR
   b) Mid IR
   c) Far IR
   d) Visible region
   Answer: b) Mid IR

2. IR spectroscopy is based on:
   a) Rotational transitions
   b) Vibrational transitions
   c) Electronic transitions
   d) Nuclear transitions
   Answer: b) Vibrational transitions

3. Which vibration is *not* IR active?
   a) Symmetric stretch in $CO_2$
   b) Asymmetric stretch in $CO_2$
   c) Bending vibration in $H_2O$
   d) Stretching in HCl
   Answer: a) Symmetric stretch in $CO_2$

4. The IR absorption frequency is expressed in:
   a) Hertz (Hz)
   b) Wavelength (nm)
   c) Wavenumber ($cm^{-1}$)
   d) Joule (J)
   Answer: c) Wavenumber ($cm^{-1}$)

5. Fingerprint region of IR spectrum lies in:
   a) 5000–4000 $cm^{-1}$
   b) 2000–1500 $cm^{-1}$
   c) 1500–400 $cm^{-1}$
   d) 4000–2500 $cm^{-1}$
   Answer: c) 1500–400 $cm^{-1}$

### 5.7.2 Short Questions

1. Define infrared spectroscopy and its principle.

2. What are stretching and bending vibrations? Give examples.

3. Explain the selection rule for IR absorption.

4. What is the fingerprint region in IR spectroscopy? Why is it important?

5. Differentiate between near, mid, and far IR regions.

### 5.7.3 Long Questions

1. Discuss the principle, theory, and applications of IR spectroscopy in detail.

2. Explain different types of molecular vibrations with suitable diagrams.

3. Describe the construction and working of an IR spectrometer.

4. Write notes on applications of IR spectroscopy in chemical and pharmaceutical analysis.

5. Derive the relation between vibrational frequency and force constant of a diatomic molecule (Hooke's law approximation).

### 5.8 References and Suggested Reading

1.Banwell, C. & McCash, E. (1994) Fundamentals of Molecular Spectroscopy, 4th Ed., McGraw-Hill Higher Education, London, UK.
2.B. K. Sharma (2023) Instrumental Methods of Chemical Analysis-Vol-1: Spectroscopy Krishna Prakashan Media Ltd Meerut

# Unit 6

## Photoelectron Spectroscopy (PES) Fundamentals of Infrared Spectroscopy

## Structure

6.1 Introduction: Basics of the Photoelectric effect
6.2 Objectives
6.3 Koopman's Theorem and the Ionization Process
6.4 Electron Spectroscopy for Chemical Analysis
6.5 Summary
6.6 Exercises
6.7 References and Suggested Reading

## 6.1   Introduction: The Basics  of the Photoelectric Effect

Nonetheless, you remain uninformed about Photoelectron Spectroscopy (PES), a remarkable scientific technique that enables the measurement of binding energies of electrons in atoms and molecules. PES is employed to irradiate a sample with photons and quantify the energy of individual electrons upon their ejection from the sample, providing critical insights into the electronic structure, chemical content, and bonding characteristics of the material.  It is highly beneficial in fields such as surface science, materials science, and chemistry, which necessitate an understanding of the electronic states of atoms and molecules.

The photoelectric phenomenon is A phenomenon when electrons are emitted from a substance following exposure to electromagnetic radiation.    Photoelectron Spectroscopy (PES) necessitates comprehension of the fundamental principles of the photoelectric effect.  The phenomenon was initially observed by Heinrich Hertz in 1887, but it gained widespread recognition following Albert Einstein's explanation in 1905, for which he was awarded the Nobel Prize in Physics in 1921.  PES operates by hitting a sample with high-energy photons, often X-rays or ultraviolet light.  The energy of a photon must exceed a threshold known as the work function to dislodge electrons

from it. The energy of the expelled electron is measured, which correlates with the binding energy of the electron within the material. The kinetic energy Ekin of the released electron is articulated by Einstein's photoelectric equation:

$$E_{\text{kin}} = h\nu - \phi$$

Where:

• $E_{\text{kin}}$: kinetic energy of the emitted electron;

• h is Planck's constant,

• $\nu$ = frequency of the incident photon,

• $\phi$\phi the work function, the minimum energy needed to leave an electron on the surface of the material.

By measuring the kinetic energy of electrons released upon the absorption of incident photons with known energy, one can compute the binding energy of each electron within the atom or molecule, therefore elucidating the electronic structure. The energy of the ejected electron signifies the amount of energy required to extricate it from the binding condition. The binding energies correlate to certain electron orbitals, facilitating the identification of chemical elements and the examination of their electronic states.

### 6.2 Objectives

1. To understand the basic principles and instrumentation of Photoelectron Spectroscopy (PES).

2. To study the interaction of high-energy photons with matter and the resulting photoemission of electrons.

3. To learn how PES is used to determine ionization energies, electronic structures, and chemical bonding.

## 6.3 Koopman's Theorem and the Ionization Process

In photoelectron spectroscopy, a photon irradiates the sample, resulting in the absorption of energy that causes the ionization of the target atom or molecule, specifically the ejection of an electron. This pertains to quantum physics, and the ionization energy corresponds to the energy required to ionize a bound electron. To an occupied molecular orbital (MO). One example of a fundamental component of PES is Koopman's theorem, which provides an initial approximation of a molecule's ionization energy. Koopman's theorem, developed by B. Koopmans in 1933, posits that the configurations of the remaining electrons remain identical when an electron is removed from a molecule. The theorem states that for a molecular Hamiltonian, the ionization energy of an electron corresponds to the negative value of the energy of that electron's orbital within the molecule, as described by Hartree-Fock theory.

Koopman's theorem mathematically suggests that the binding energy $E_{\text{binding}}$ of an electron in a specific orbital will be approximately:

$$E_{\text{binding}} = -\epsilon_i i$$

**Where:**

• $\epsilon_i$ is the energy of the molecular orbital of the removed electron, is obtained from quantum mechanical calculations.

Koopmans's theorem serves as a valuable framework for comprehending potential energy surface (PES) spectra, especially for simple molecules or atoms with established electron configurations. Nonetheless, for intricate compounds where electron correlation effects are significant, the theorem's accuracy may be limited, as the loss of a single electron can affect the distribution of the remaining electrons.

Koopman's theorem, despite its limitations, is essential for interpreting the results of PES and serves as a valuable first-order basis for theoretical analyses of ionization energies.

**Structural Interpretation of PES of Simple Molecules**

In particular, the interpretation of PES spectra entails inferring the binding energy of electrons in specific chemical orbitals from the position and intensity of each peak in the spectrum. In PES studies, the energy of incident photons is often established far beyond the threshold required to ionize core-level electrons that are firmly bound by the nucleus. The PES spectra of simple molecules are very straightforward to interpret. The peaks signify electrons from various orbitals, with the binding energy of each peak corresponding to the energy required to ionize an electron in each orbital. The peaks in the PES spectrum are generally categorized based on the type of orbital from which the electron emanates (i.e., s-orbitals, p-orbitals, or d-orbitals).
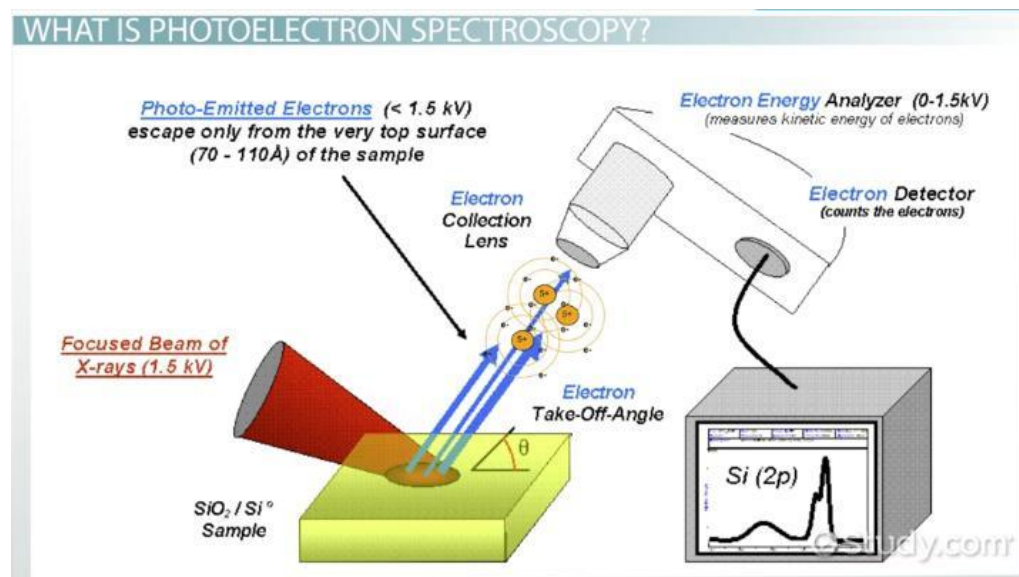


**Figure 2.3 Photoelectron Spectroscopy**

**6.4 Electron Spectroscopy for Chemical Analysis (ESCA)**

ESCA, also known as X-ray Photoelectron Spectroscopy (XPS), is prevalent surface analysis approach grounded in photoelectron

spectroscopy. X-ray photoelectron spectroscopy (ESCA) offers comprehensive insights into surface composition, chemical bonding, and electronic states by analyzing the kinetic energy of electrons ejected from the sample's surface during X-ray exposure. In ESCA, a sample is subjected to X-ray radiation, and the emitted photoelectrons are collected and evaluated. By quantifying the energies of the photoelectrons, one can ascertain their binding energies and get insights into the oxidation states of the chemical elements. ESCA is particularly effective for surface analysis as the emitted photoelectrons predominantly originate from the uppermost layers of the material, typically within the top 1-10 nm. ESCA offers a significant advantage by delivering chemical information regarding the material's surface.

### Auger electron spectroscopy(AES)

Auger electron spectroscopy (AES) is an additional surface analysis technique associated with photoelectron spectroscopy (PES) and electron spectroscopy for chemical analysis (ESCA). This method entails the identification of expelled electrons from the material resulting from the Auger effect during the de-excitation of the atom following the ejection of a core-level electron. The Auger effect involves the ejection of an inner-shell electron from an atom, resulting in the atom being in an excited state. This additional energy is transferred to another electron within the atom, compelling its expulsion. The energy of released Auger electrons is characteristic of the element and its chemical state. AES is frequently employed to investigate the surface chemistry of samples, particularly when the analytical surface is susceptible to sputtering from surface contaminants. PES and ESCA focus on the binding energies of core-level electrons, while Auger electron spectroscopy (AES) provides complementary information by examining the energies of Auger electrons emitted from the material during the Auger process.

**Check Your Progress**

Q1. What kind of chemical information can be obtained from ESCA?

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Q2. How does charge transfer spectroscopy apply to transition metal complexes?

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### 6.5 Summary

This Block examines the electromagnetic radiation absorbed and emitted by atoms. Techniques such as Flame Emission Spectroscopy (FES), Atomic Absorption Spectroscopy (AAS), and Atomic Emission Spectroscopy (AES) are described with schematic diagrams. Their analytical applications in chemistry, medicine, and environmental science are highlighted.

Molecular Spectroscopy explores the interaction of electromagnetic radiation with molecules, involving changes in rotational, vibrational, or electronic states. The Spectrum regions include: Infrared (IR): studies vibrational transitions, Ultraviolet-Visible (UV-Vis): studies electronic transitions, and Raman Spectroscopy, which is based on light scattering, are discussed with key concepts.

Molecular Energy Levels include vibrational, rotational, and electronic states. Selection Rules determine allowed transitions. In Photoelectron Spectroscopy (PES), the energies of electrons ejected from atoms or molecules when exposed to UV or X-ray photons are measured. This technique also covers the determination of ionization energies, analysis of electronic structure, and surface composition analysis in materials science.

**6.6 Exercises**

6.6.1  Multiple Choice Questions

1.  Which of the following transitions in atomic spectroscopy involves the emission of light?

    A. Electron absorbs energy and jumps to a higher level

    B. Electron drops from a higher to a lower energy level

    C. Electron remains in the same energy level

    D. Nucleus absorbs energy

Answer: B

2.  The Balmer series in atomic spectroscopy appears in which region of the electromagnetic spectrum?

    A. Ultraviolet

    B. Infrared

    C. Visible

    D. Microwave

Answer: C

3.  Which of the following elements is most commonly analyzed using atomic absorption spectroscopy (AAS)?

6.  Which of the following transitions is responsible for the UV-Vis absorption spectrum of molecules?

    A. Rotational transitions

    B. Vibrational transitions

    C. Electronic transitions

    D. Nuclear transitions

Answer: C

7. Photoelectron spectroscopy is primarily used to measure:

A. Molecular rotation

B. Atomic masses

C. Ionization energy

D. Molecular weight

Answer: C

8. In PES, when photons strike an atom, electrons are ejected. What property of the photon determines whether ejection occurs?

A. Wavelength

B. Energy

C. Velocity

D. Amplitude

Answer: B

9. What type of radiation is commonly used in ultraviolet photoelectron spectroscopy (UPS)?

A. Microwave

B. X-ray

C. UV

D. Infrared

Answer: C

10. Which of the following is not a direct output of a photoelectron spectroscopy experiment?

A. Ionization energy

B. Electron binding energy

C. Number of electrons emitted

D. Electron spin

Answer: D

### 6.6.2 Short Answer Questions

1. What are atomic orbitals, and how do they relate to atomic energy levels?
2. Explain the concept of vector coupling in atomic spectroscopy.
3. What are term symbols, and how are they derived?
4. Describe the significance of vibrational progressions in molecular spectra.
5. How does the Frank-Condon principle influence molecular electronic transitions?

6. What is the primary difference between emission and absorption spectroscopy?
7. Define Koopman's theorem and its application in photoelectron spectroscopy.
8. What kind of chemical information can be obtained from ESCA?
9. How does charge transfer spectroscopy apply to transition metal complexes?
10. What is the basic principle of Auger Electron Spectroscopy?

### 6.6.3 Long Answer Questions

1. Explain the energy level structure of atomic orbitals and its significance in atomic spectroscopy.
2. Discuss the vector representation of momenta in atomic spectroscopy and its role in determining atomic properties.
3. Describe in detail the electronic spectra of hydrogen and alkali metals and compare their spectral features.
4. Explain the molecular orbital theory and how it helps understand molecular spectroscopy.

5. Describe the principles of vibronic transitions and their role in molecular electronic spectra.

6. Discuss the Frank-Condon principle and its implications in molecular spectroscopy.

7. Explain the process of radiative and non-radiative decay and their significance in emission spectroscopy.

8. Describe the principles of photoelectron spectroscopy and its applications in chemical analysis.

9. Discuss Electron Spectroscopy for Chemical Analysis (ESCA) and the types of chemical information it provides.

10. Explain Auger Electron Spectroscopy (AES), its working principle, and its applications in material science.

## 6.7 References and Suggested Reading

1. Banwell, C. & McCash, E. (1994) Fundamentals of Molecular Spectroscopy, 4th Ed., McGraw-Hill Higher Education: England.

2. B. K. Sharma (2023) Instrumental Methods of Chemical Analysis-Vol-1: SpectroscopyKrishna Prakashan Media Ltd

## Structure

## 7.1 Introduction

Infrared Spectroscopy (IR) is a technique for measuring the vibrational mass of molecules when they absorbs infrared. Useful insights on a substance's molecular structure, functional groups, and bonding can be gleaned from this. Applications of Infrared Spectroscopy IR spectroscopy provides useful data about molecular vibrations and chemical compounds in chemistry, biochemistry and materials science. The underlying principles of IR spectroscopy is among the most important but also less understood topics in chemistry because molecular vibrations, energy quantization, and the potential energy surfaces that characterize these vibrations are all involved. The main theoretical background, which is critical to understand IR spectroscopy, including the linear harmonic oscillator model, zero-point energy, force constants, anharmonicity, and Morse potential diagram, will be described in this section.

This is called the Linear Harmonic Oscillator (LHO) Model– a simple model of a vibrating molecule. In IR spectroscopy, the model describes how the atoms in a molecule move relative to one another as they vibrate. In the LHO model, the restoring force on a vibrating molecule is based on the idea that the displacement of the atoms from the equilibrium position is directly related to the force acting on them. It is similar to the action of a mass attached to a spring, which is pushed or pulled, the spring providing a restoring force. The LHO model has a special role in elucidating the foundation physics of molecular vibrations.

## 7.2 Objectives

1. To understand the instrumentation and application of IR Spectroscopy
2. To analyse the advantages of IR spectroscopy

### Model of a LinearHarmonic Oscillator

The potential energy VV for a harmonic oscillator according to classical mechanics is given by:

$$V(x) = \frac{1}{2}kx^2$$

Where:

• V(x) is a potential energy as a function of the displacement xx,

• k is the force constant, which shows the stiffness of the bond between atoms,

• x is the displacement of the atoms from their equilibrium position.

In our model, the atoms vibrates about some equilibrium position based on a fixed frequency determined by the mass of the atom and the force of attraction or side of the bond between them. The pitch ν\nu of the vibration can be derived through the relation:

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

Where:

• μ is the reduced mass of the two atoms which are vibrating, where μ= $\frac{m_1 m_2}{m_1+m_2}$ and $\frac{m_1 m_2}{m_1+m_2}$ are the masses of the atoms.

The low frequency behavior is that of the linear harmonic oscillator, which predicts that the frequency of vibration is independent of the amplitude of vibration, so the bond vibrates at a fixed frequency regardless of the amount that it is stretched or compressed. This models provide the basis for interpreting molecular vibrations, and it will enable to predict the vibrational frequencies that can be seen in the IR spectra. However, the vibrations of real molecules are imperfectly harmonic. When we talk about the harmonic model of the vibrations of

a molecule, we have to also take into account that the molecules deviate from the harmonic form due to anharmonicity (something we will discuss here soon). For most vibrational modes, the harmonic oscillator model is a reasonable approximation, particularly at small displacements around the equilibrium position.

## 7.3 Force Constant and Zero-Point Energy

So when we talk about zero-point energy (ZPE), we are referring to the minimum amount of energy a molecule can have, even at 0 K temperatures. This is a quantum mechanical phenomenon coming from the fact that the particle (either an atom or a bunch of atoms) cannot have a completely rest state at its ground state. In quantum mechanics, the energy of a harmonic oscillator is quantized so that the molecule can only have certain energy levels. Then, the energy of these levels is:

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

Where:

• Ev is the energy of the v-[th] vibrational level,

• v is the vibrational quantum number (with v=0 being the ground state),

• h is Planck's constant,

• $\nu$ is the frequency of the vibration.

The background energy associated with zero-point energy is the energy for the ground state (v=0):

$E_0 = 12h\nu$

This implies that even at the lowest vibrational state of a molecule, it still has some energy left over. This energy is there to stay and is a pure consequence of quantum mechanical fluctuations present in every system with a nonzero temperature. One consequence of the existence of zero-point energy is that it has ramifications for the IR spectra of molecules. In a normal gas even with zero thermal excitation, molecules still occupy a finite amount of ground state energy, that translates in their vibrational modes and the IR absorption. The force constant k describes the stiffness of a bond between two atoms in a molecule, which in turn determines the vibrational frequency of the molecule. Higher force constant means a stronger bond and higher frequency vibration. The stronger the restoring force is, the larger the value of the force constant.

That is, the force constant of vibration is related to the frequency of vibration:

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

Where:

• $\nu$ is the frequency of the vibration,

• k is the force constant,

• $\mu$ is the reduced mass.

In IR spectroscopy, the vibrational frequency of a molecule plays a major role in its absorbance properties. Generally, stronger bonds (higher force constants) vibrate at a higher frequency, corresponding to IR absorption peaks at higher wave numbers.

**Harmonicity / Harmonic Potential / Harmonic Oscillator**

The linear harmonic oscillator model describes molecular vibrations well, but assumes a restoring force exactly proportional to displacement. In reality, the vibrations of molecules behave differently from this idealized picture at larger displacements. This is what is called anharmonicity. In large vibrational amplitude, the potential energy curve is nonlinear and thus leads the harmonic approximation to fail. An alternative to the harmonic oscillator model is the Morse potential, which is a more accurate description of the potential energy curve that incorporates anharmonicity. The math for the Morse potential is described by the equation:

Based on the previous equations, we know that the potential is given by :

$$V(x) = D_e \left(1 - e^{-\alpha(x-x_e)}\right)^2.$$

Where:

• V(x): Potential energy as a function of displacement xx,

• De is the energy needed to break the bond (the dissociation energy),

α is a constant that defines the potential well width,

• xe is the equilibrium bond length (the minimum of the potential position).

Due to the fact that the bond weakens further apart the restoring force does too, the Morse potential usually provides a much better representative of molecular vibrations. This creates a steeper line

around the equilibrium bond length and a more horizontal line for larger displacements, which indicates that the bond is more strained as the atoms are pulled apart. More importantly, the Morse potential provides a more accurate representation of the vibrational energy levels. The harmonic oscillator model assumes that the energy levels are equally spaced, while the Morse potential predicts that the spacing between the energy levels decreases as the vibrational quantum number increases. This is because the molecule becomes less stiff when the bond is stretched, which lowers the vibrational frequency. The vibration levels in a Morse potential diagram are not equidistant. Unlike the harmonic oscillator model where the energy levels are equally spaced, the energy levels become increasingly closer together as the vibration progresses to higher quantum states.
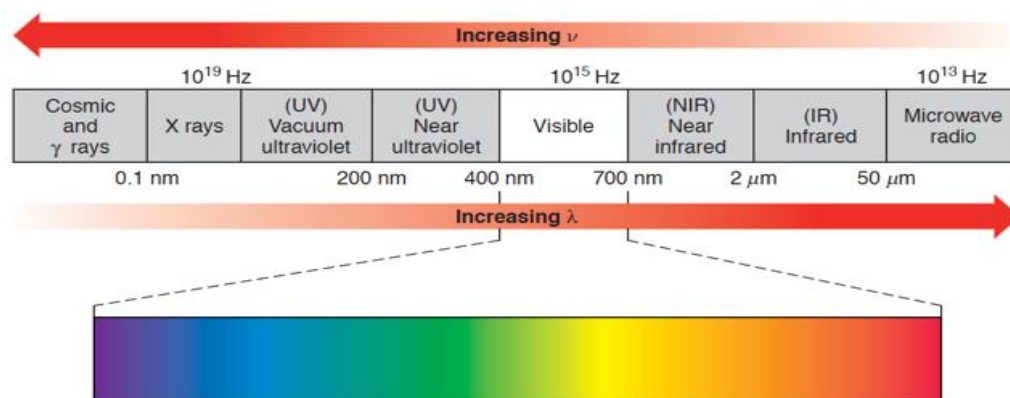


**Figure 3.1 Energy level of electromagnetic radiation**

**7.4 Vibration-Rotational Spectroscopy**

We also consider several applications which combine the infrared an microwave regions in vibration-rotational spectroscopy. This is due t molecular energy states that are determined by vibration and rotatio of the molecule. The two motions are typically coupled, and their ne impact on the energy levels is observable in the infrared part of th electromagnetic spectrum. Unlike many other techniques, whic enhance only specific molecular arrangements, vibration-rotationa spectra convey information about molecular structure, bond lengths,

and elemental masses. The energy levels for this type of molecule are allowed and play a major role in the analytics of this type of molecule as the energy carrying units in this type of molecule are both vibrational and rotational in nature. This will include understanding the basic principles of rotational and vibrational energy levels, the coupling of these motions, and the interpretation of the spectra in terms of more useful structure data characterizations.

### Branches of Spectra: P, Q, and R

The absorption spectrum in vibration-rotational spectroscopy entails of a chain of absorption lines, that Transitions between the energy levels of molecules are the basic block of the understanding of molecular spectroscopy. (Transitions happen when a molecule absorbs or emits energy associated with the difference in energy between two quantum states.) Usually, these transitions fall into one of three categories, known as the P branch, Q branch, and R branch. The branches account for various kinds of transitions in the rotational-vibrational energy levels of a molecule. They are, in fact, closely connected to the changes in the rotational quantum number, which occurs during a vibrational transition as we have discussed previously in context of the P, Q and R branches. These branches represent vital sections of molecular diagrams critical for understanding molecular behavior and energy interactions, at the crux of molecular spectral analysis.

### P Branch

Transitions in which one takes a single step down in rotational quantum number are called the P branch. That is to say, the transition goes from a higher rotational state (labeled by the quantum number J) to a lower one (labeled by J-1). From a molecular energy level perspective, this is an absorption process in which an energy transition occurs from a higher rotational level to a lower one, and therefore there is also a transition in the vibrational state of the molecule. The P part is

normally seen at lower frequencies or low wave number in the spectrum. Vibrational-rotational spectrum In a vibrational-rotational spectrum, transits will usually be represented as a series of lines. The P branch lines are located at lower wave numbers than the R branch. For the P branch, the corresponding energy differences between rotational levels can be shown. With successive values of rotational quantum number, energy levels approach closer. Thus the energy difference between adjacent rotational levels decreases. This means that the energy separation between the P branch adjacent lines actually decreases as the rotational quantum number increases, resulting in a narrower spacing because going from high-energy end to low-energy end of the P branch. This behavior reflects the fact that for rotational energy levels, increasing quantum number gives rise to ever closer energy levels. For molecular systems, this is an important phenomenon which makes it possible for determining the rotational constants and other similar properties of the molecule The rotational structure of the molecule has particular value in the P branch, and you can use equations to derive structures such as moment of inertia from this branch. As a last point regarding the application of lucy and Frankie, the appearance and distension of the lines in the P branch provides information about the physical nature of the molecule being analyzed. Finally, the P branch may have characteristic appearance of closely spaced lines, whose positions depend on the isotopic composition of the molecule, changing the distribution of mass segments and the respective rotational constants.

**Q Branch**

The Q branch is more similar to the P and R branches when transitions do not change the rotational quantum number. These are the transitions where the rotational state of the molecule does not change in the course of a vibrational transition ($J \rightarrow J$) Unlike in rotational transitions, in vibrational transitions the absorbed or emitted energy reflects just the change in the vibrational state of the molecule. Thus, the Q branch

generally is manifests as a single, narrow line within the vibrational-rotational spectrum. This result reflects the fact that the line position is generally very close to the zero-point of the vibrational mode; the transition involves no change in rotational energy. Many molecular spectra lack a Q branch or show it only as a weak line because selection rules for rotational transitions favor transitions where the rotational quantum number changes (the P and R branches). On the other hand, according to the selection rules a change in the rotational quantum number is usually needed for a transition. Hence, both the P and R branches represent transitions that involve considerable shifts in the rotational and vibrational states, while the Q branch represents the transition that is purely vibrational without any change in the rotational symmetries. A defining characteristic of the Q branch is of its location along the entire spectrum. As there is no change in the rotational quantum number, the Q branch frequently appears as a single peak in the spectrum and can sometimes overlap with the zero point of the vibrational transition. The intensity of the Q branch is generally lower than that of the P and R branches due to the fewer transitions which fulfill the selection rules for such transitions. The Q branch can, though, be informative in regimes where the vibrational transition is much stronger than the rotation from continuum states or in symmetric species, allowing for transitions with no change in the rotational quantum number.

**R Branch**

R branch: transitions for which the rotational quantum number increases by one During these transitions, the molecule obtains energy in both vibrational and rotation modes, thus, the shift form lower rotation state (J) to upper rotation state (J+1). Consequently R branch is usually seen at the high frequency or higher crowd Block than P branch. This increase in frequency reflects the energy carried by the increase in the rotational quantum number. Inequity, the rotational lines within the R branch additionally form a sure pattern—this can be seen

in the spacing of the trace in Fig. a. The pattern occurs because the energy accumulations of rotational lines become increasingly crowded with each upward change in the quantum number, thus the difference between the energies of higher rotational levels is diminished. So the separation between the lines in the R branch is reduced upon increasing the rotational quantum number. R branch transitions are basically transitions represented on the high energy side of the transitions spectrum with each transition corresponding to an increase in the rotational quantum number by one unit and a change in the vibrational state. The R branch, much like the P branch, contains important information regarding the rotational structure of the molecule. They give a lot of information about the rotational constants and the moments of inertia of the molecule through the spacing and the pattern of the lines in the R branch. In contrast, the R branch is often more vivid than the Q branch because the molecule has a high dipole moment. Moreover, the R branch is an important aspect of the molecular spectrum during transitions when the molecule is entering the higher vibrational states and the rotational and vibrational states are highly coupled.

## 7.5 Born-Oppenheimer Approximation

The Born-Oppenheimer approximation is a common assumption in quantum chemistry that simplifies the treatment of molecular systems by assuming that the motion of nuclei and the electrons in a molecule can be considered separately. The approximation assumes that the nuclear motion (nuclei are much heavier than electrons) could be treated in a way separate from electron motion. This means that the electronic wave function can be solved completely separately from the nuclear motion, treating the electronic energy as a potential energy that drives the nuclear motion. In reality, the Born-Oppenheimer approximation has its limits; there are situations where breaking down into nuclear and electronic motions simply does not work anymore. Under certain conditions, however, this approximation can break

down, resulting in those idealized results deviating from reality. The relationship is much tighter for the quadratic term in vibration-rotational spectroscopy, where the nuclei and electron motion are coupled more closely.

**Large Atomic Mass Differences**

We make the Born-Oppenheimer approximation, which is valid because nuclei are much heavier than electrons. In fact, a proton (the nucleus of hydrogen) has a mass about 1836 times larger than an electron, and the ratio between the nucleus's mass and that of the electrons only increases for heavier elements. So large is the mass difference that the approximation holds that the nuclei and electrons do not move together, but rather that the electrons respond instantaneously to changes in the positions of the nuclei. This assumption works well for most molecules, because the electrons usually react much faster than the nuclei. However, this approximation can break down if atoms in a molecule have large differences in atomic mass. And in particular, the case when molecules contain light atoms (hydrogen's) and much heavier ones (chlorine, iodine and other heavier elements) the motion of the nuclei can no longer be neglected. Hydrogen atoms, for instance, are relatively light, so they can wiggle quite well in particular vibrational modes. As the hydrogen nuclei motion becomes significant compared to the electron motion, one can expect deviations from the normal vibrational energy levels. For some molecules, the nuclei move enough to induce changes in the potential energy surface of the molecule, which then must be treated by coupling nuclear and electronic motion in a more involved way. For example, in molecules with heavier atoms bonded to hydrogen, such as hydrogen halides (HCl, HF, etc.), the large contrast in atomic masses between the hydrogen nucleus and the halogen can yield strong nuclear motion, especially in vibrational modes. Such nuclear motion allows for breakdown of the Born–Oppenheimer approximation, and non-adiabatic effects must be used to describe the system accurately. In

such cases the electron wave function may no longer be able to respond instantaneously to the motion of the nuclei as is assumed in the Born-Oppenheimer approximation. This means that for cases in which the mass difference between the atoms is large, the approximation breaks down, and more advanced models that take into account the coupling of nuclear and electronic motions are needed.

**Large Nuclear Displacements**

The Born-Oppenheimer approximation also fails in systems of widely displaced nuclei, namely systems with large amplitude vibrations. This approximation relies on the fact that nuclei vibrate around their equilibrium positions with small amplitudes, displacing the nuclei from their equilibrium positions small enough to not perturb the electronic wave function away from adiabatic separation from the nuclear motion. In certain cases, however, the displacement is large enough that the wave function, which reflects the distribution of charge about the nuclei, begins to depend on the position of the nuclei, nuclear motion. The potential energy surface of the molecule may change considerably when the displacements of the nuclei become large enough. As a result the electronic levels can intermingle, and the electronic wave function can no longer be considered a mere trial function of the nuclear positions. In these situations, the nuclear motion can no longer be separated from the electronic motion, and as a result, non-adiabatic effects need to be incorporated. This leads to complication of the nuclear and electronic motions, which can give rise to signs of non-adiabatic transitions between electronic states. In more practical terms, this can be seen in the case of molecules with large vibrational motions, or in the excited states, where we can have significant displacements from equilibrium positions. Thus, especially in large amplitude vibrational modes in molecules (which is the case for large molecular clusters or large polyatomic molecules), the assumption of small nuclear displacements is lost. The electronic wave function may not be able to instantaneously rearrange itself to these large

displacements, leading to the breaking of the Born-Oppenheimer approximation.

**An Electron-Nuclear Coupling  Stronger than Typical**

The Born-Oppenheimer approximation becomes especially useful when the coupling between the nuclear and electronic motions  is weak. However, this approximation may fail  in some systems, particularly those which are highly excited states or have strongly interacted with electron−nuclear bodies. Some molecular systems  including transition metal complexes, molecules having large dipole moments, or systems with strong spin-orbit coupling that show strong coupling between electronic and nuclear motions. This  breaks the adiabatic separation in the Born-Oppenheimer approximation and makes non-adiabatic effects quite significant in the treatment of the system. For example, a major case where this breakdown happens are molecules with strong electron-nuclear interactions (like transition metal complexes). This sometimes results in cases where excited electronic states of these  molecules lie close in energy such that nuclear motions couple strongly to them so their electronic wave function cannot be considered adiabatically separated from nuclear positions. In these systems, the electronic structure of a molecule can  change rapidly with nuclear motion, and so the assumption that electrons adjust instantaneously to nuclear configuration changes breaks down. One well-known example of these systems is the transition metal complex, where the interactions of the d-electrons of the metal with the legends  resolving the nucleus-clutch of the motions with strong coupling. By contrast, these types of systems are especially susceptible to non-adiabatic effects, as the electronic state energy levels can depend very sensitively on the nuclear positions. For examples in the case of molecules possessing large dipole moments or systems with spin-orbit coupling the electron-nuclear coupling is strong enough to lead to deviations from Born-Oppenheimer approximation. These phenomena can be attributed to the breakdown of the Born-Oppenheimer approximation in such cases,

leading to modifications of the expected energy levels, which could become evident as shifts in vibrational frequencies, modified rotational constants, or even the involvement of non-adiabatic transitions between states of different electronic lifetimes. The other is due to systems that have conical intersections, which is the scenario where two or more electronic potential energy surfaces approach each other very closely, which is also a case where the Born-Oppenheimer approximation fails. Similar conical intersections exist also in excited states, and these are seen to facilitate non-adiabatic transitions that can result in strong coupling between electronic and nuclear motions. This interaction is especially prevalent in the fields of photochemistry and photo physics, where the dynamics of the excited state are important to molecular evolution.

This is noteworthy because one of the Han and Yang's findings is the preferred decomposition of the mass of the difference between the Born-Oppenheimer approximation, which also decouples electrons and nuclei in certain situations. If a molecule gets excited from one electronic level to another because of light absorbed, this does not mean that a molecule was excited by an electronic jump from its ground to an excited state. The assumption that the nuclei can be treated as fixed while the electrons respond instantaneously to the change in electronic state becomes invalid. In systems exhibiting ultrafast dynamics, processes that happen on femtosecond timescales, electronic and nuclear motion are no longer separated by orders of magnitude in energy. During such rapid processes, the electronic and nuclear motions can become coupled and push the system out of the Born-Oppenheimer approximation. This is mostly the case for systems that are engaged in photochemical reactions, in which energy contained in the excited electronic state can couple to nuclear motion on a timescale for the system to flip between electronic states. Such processes demand a more detailed description, involving the coupling between nuclear and electronic degrees of freedom, which the Born-Oppenheimer approximation cannot sufficiently account for. Non-Adiabatic

Transitions; The transitions that a molecule can get between the electronic states which are near energy, it is said that non-adiabatic transitions take place. The Born-Oppenheimer approximation breaks down in these instances because the molecule cannot stay in a single electronic state while moving like that of nucleus. The molecule can, instead of just having the electrons moving, it can actually change electronic states as the nuclei move and that will change the vibrational and rotational spectra.

Those transitions where the electronic and vibrational motions are coupled, i.e not satisfying the parameters of Born-Oppenheimer approximation, but still possible are commonly referred to as vibronic transitions and they represent one of the most known fashion of breakdown of Born-Oppenheimer approximation. The transition is called vibronic when the molecule undergoes a simultaneous application of an electronic and vibrational transition. In these situations, the motion of the nuclei affects the electronic state of the molecule and the reverse holds true as well, resulting in a more coupled interaction that predicted by the Born–Oppenheimer approximation. The failure of the Born-Oppenheimer approximation manifests in phenomena such as avoided crossings (often seen as the splitting of levels that did not split in the simplified model), rotational anomalies and the emergence of additional vibrational modes not predicted by the simplified model. This would give further information of the coupling between the electronic and nuclear motions, giving deeper insight into the electronic structure and dynamics of the molecule. This means that the Born-Oppenheimer approximation is no longer valid, and this breakdown has important consequences in terms of the properties of the vibration-rotational spectra. There may be irregularities in the spacing of the P, Q, and R branches for example, or their respective intensities might be affected. The effects make it necessary to understand subtle details of the dynamics of the molecule and may also need sophisticated theoretical treatment to calculate the spectra.

## Vibrations of Polyatomic Molecules

Vibrational spectroscopy is of fundamental importance for molecular structure and dynamic properties, particularly for polyatomic molecules, which are molecules that contain more than two atoms. In polyatomic molecules, vibrational modes become more complicated because they contain more degrees of freedom and thus more vibrational modes, each with their own frequencies. Chemists and spectroscopists can derive information about molecular geometry, bonding, and atom-atom interactions through the study of the vibrational modes of these molecules. When the bond between two molecules stretches and bends, they produce multiple frequencies that characterize the polyatomic molecules. These modes are affected by molecular mass, bond strength, and the symmetry of the molecule. Vibrational spectra thus obtained contain abundant information on molecular structure and dynamics. Here we discuss the key points of polyatomic molecular vibrations which will include selection rules for vibrations, normal modes of vibration, group frequencies and overtones, hot bands and Fermi resonance. All of these facets are crucial to understand the meaning attributions of vibrational spectra and provide a comprehensible apprehension of molecular vibrations.

### Vibration Selection Rules

Selection rules in molecular spectroscopy determine the allowed transitions between different vibrational energy states. These criteria follow from the symmetry of the molecule and the way in which the molecule interacts with electromagnetic radiation. Selection rules for polyatomic molecules are more complicated compared with how they are for diatomic molecules as there are more vibrational modes and more complicated interactions possible. One of the main guidelines for a molecule undergoing a vibrational transition is that there must be a change in the dipole moment of the molecule. This is because the

molecular state must couple to the electric field of the infrared radiation for absorption to take place. Consequently, for a transition to be infrared active, there must be a change of dipole moment through the vibration.

A vibration to be infrared active also has a selection rule, as follows:

$\Delta q \neq 0$

where q is the dipole moment and $\Delta q$ is the change in the dipole moment once the vibrational motion happens. However, if a vibration does not cause a change in the dipole moment, it will not absorb infrared radiation and will be termed IR inactive.

Check Your Progress

Q1. What is vibrational frequency?

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Q2. Discuss the selection rules for vibrational energy state in molecular spectroscopy.

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## 7.6 Summary

Vibration–rotational spectroscopy deals with molecules in which both vibrational and rotational motions occur simultaneously. When a molecule vibrates (like two atoms connected by a spring), it changes the distribution of mass, which in turn affects its moment of inertia. Since rotational energy depends on moment of inertia, vibrational and rotational motions are coupled. These combined transitions typically fall in the infrared region of the electromagnetic spectrum. In an infrared spectrum, this coupling gives rise to characteristic P-branch and R-branch patterns, representing transitions to higher or lower rotational levels while a vibrational transition occurs. Quantum mechanics tells us that molecular vibrations are quantized; they can only exist in specific energy levels. Importantly, the lowest vibrational state is not zero energy, but instead has a small finite value. This is the Zero-Point Energy (ZPE

The Born–Oppenheimer Approximation (BOA) helps simplify molecular calculations by recognizing the enormous difference in mass between electrons and nuclei. Electrons are much lighter and move much faster, while the nuclei are heavier and move slowly. Using BOA, the electronic motion is solved first (assuming nuclei are fixed), and the nuclear motion (vibration and rotation) is calculated relative to that electronic distribution. This separation allows the molecular Schrödinger equation to be broken into simpler parts. Without BOA, solving molecular energy levels would be extremely complex.

vibration–rotational spectroscopy provides insight into both bond strength and molecular geometry. The force constant reflects how strong the bond is, zero-point energy shows the quantum nature of molecular motion, and the Born–Oppenheimer Approximation allows these properties to be examined through manageable mathematical models.

## 7.7 Exercises

### 7.7.1 MULTIPLE CHOICE QUESTIONS (MCQs)

1. The force constant of a bond is directly proportional to:
a) Vibrational frequency
b) Rotational energy
c) Molecular mass
d) Zero point energy

Answer: a) Vibrational frequency

2. Zero Point Energy is present in a molecule because:
a) Molecules rotate continuously
b) Heisenberg uncertainty principle
c) Bonds are not perfectly rigid
d) Temperature cannot reach zero

Answer: b) Heisenberg uncertainty principle

3. The Born-Oppenheimer approximation separates:
a) Rotational and translational energies
b) Electronic and nuclear motions
c) Vibrational and electronic energies
d) Nuclear and rotational levels

Answer: b) Electronic and nuclear motions

4. Vibration-rotational spectra are mainly observed in:
a) UV region
b) IR region
c) X-ray region
d) Microwave region

Answer: b) IR region

5. A higher force constant indicates:
a) Weaker bond
b) Stronger bond
c) No bond
d) Larger atomic radius

Answer: b) Stronger bond

### 7.7.2 SHORT ANSWER QUESTIONS

1. Define force constant and explain its significance.

2. What is Zero Point Energy? Why does it exist?

### 7.7.3 LONG ANSWER QUESTIONS

1. Describe the relationship between vibrational frequency, force constant, and reduced mass. How does this help determine bond strength?

2. Explain Zero Point Energy with the help of the quantum harmonic oscillator model. Why can it not be zero?

## 7.8 References and suggested Reading

1. Atkins, P., & Friedman, R. (2011). Molecular Quantum Mechanics (5th ed.). Oxford University Press, London, UK

2. Hollas, J. M. (2004). Modern Spectroscopy (4th ed.). John Wiley & Sons, New Jersey, USA

# Unit 8

## Stretching Modes

Structure

## 8.1 Introduction

These are referred to as stretching modes, as can be seen from the slight alteration to the positions of the atoms along the bond axis of a molecule. The bond length toggles between compressed states and extended states as the atoms are pulled close and pushed away from one another in these modes. Pulsatory patterns are fundamental to comprehend how the bond strength and the bond length between two atoms affect those molecules physical properties and their reactivity. Stretching modes are divided into two sub-subcategories (that is, they're a subcategory of a subcategory) symmetric stretching and asymmetric stretching.

## 8.2 Objectives

1. To understand the quantum mechanical model of a linear harmonic oscillator.

2. To explain the significance of force constant and zero-point energy in molecular vibrations.

3. To study harmonicity, anharmonicity, and their effects on vibrational spectra.

4. To analyze the principles of vibration–rotational spectroscopy in diatomic molecules.

## 8.3 Symmetric Stretching

Symmetric stretching is a bond stretching mode that does not vary in width with respect to the center of a molecule. In this mode, all the atoms involved in the stretching motion, move in the same direction simultaneously, and interatomic distances are symmetrically displaced. Symmetric stretching is common in molecules where multiple identical bonds exist, such as in diatomic molecules, or in molecules with symmetric arrangements of atoms. In this mode, the bonds are expanding and contracting evenly, resulting in an even distribution of energy through the molecule. As an example, consider a simple linear molecule such as carbon dioxide ($CO_2$); due to symmetric stretching, both C=O bonds are extended together, thus making the molecule longer or shorter along the bond axis. This symmetric stretching mode is generally lower-frequency than other vibrational modes, as the change in bond length is distributed over the entire molecule. Symmetric stretching modes are usually associated with the most intense peaks in infrared absorption spectra resulting from the high activity of the corresponding electric dipole moment change throughout the vibration. Molecules that exhibit so are undergo symmetric stretching where they exist in a more symmetrical state like $O_2$ or $N_2$. The symmetric stretching modes are the simplest to find and describe in spectroscopic studies. Symmetric stretching modes, such as }, indicate infinitesimal shifts in molecular bonds that may contribute to the strength and nature of interactions in the molecular species. The strength of these vibrational modes can also provide insight into the polarizability of the molecule, as well as the molecular architecture.

### Asymmetric Stretching

This mode is called asymmetric stretching where the atoms are moving in opposite direction causing an uncoordinated change in the bond length. For each bond length, one length rises while the other falls, and the atoms pull apart and go toward each other out of sync with each other, like a slowly spiraling lotus. Asymmetric Stretching is especially

significant in molecules which have multiple bonds, whereas polyatomic molecules vibrate such different atoms do not shift in and out to the same extent. In a species such as carbon dioxide ($CO_2$), asymmetric stretching refers to the lengthening of one of the C=O bonds while the other bond shorten and the central carbon remains roughly stationary. Asymmetric stretching, the atoms change its movement along the bonding axis is different, so it does more complex motion than symmetric stretching. Again, this mode is characterized by higher frequencies than symmetric stretching, because this involves a much greater change in the bond length. An example of asymmetric stretching can be seen in molecules consisting of dissimilar atoms bonded with covalent bonds, where bond length is altered unequally, such $H_2O$ or $CH_3OH$. Asymmetric stretching in molecular spectroscopy is significant as it reflects the differential forces acting on the atoms, thus providing insight into the different interactions. Asymmetric stretch modes are usually found in the higher energy states for vibrational analysis as the vibrational motion in this type is more complex. Since these modes are very active and contribute significantly to the vibrational absorption of molecules, they manifest as large peaks in infrared absorption spectra. Paralleling asymmetric stretching is an important mode in the research of polyatomic molecules and the information it contains regarding the molecular structure and couplings of the various bonds.

**Bending Modes**

In contrast, bending modes are vibrational motions in which the angle between two bonds is changing, as opposed to the bond length itself. (9) These modes refer to a variation in the bond angle rather than the bond length, resulting in a different kind of atomic displacement. In bending motions, atoms can also be displaced in a molecule plane (in-plane bending), or can be moved toward or away the plane (out-of-plane bending) and numerous bending subtypes can be defined according to the atoms direction of the displacement. The modifications

in geometries become vital because of their impact on most of the physical properties or reactivity of the molecules.

**In-plane Bending (Scissoring)**

In-plane bending (Scissoring); The angle between two bonds of the same plane of the molecule over changes In this mode, the atoms belted by the bonds slide toward and away from each other, but stay in the plane of the molecule. The resulting motion is reminiscent of the scissoring motion, with the bonds "opening" or "closing," in synchronicity. Modes related to in-plane bending are changes in bond angles in the plane of the molecule and are seen most often in non-linear or bent molecules.

An example of in-plane bending mode is that of water ($H_2O$), in which the two hydrogen atoms move towards each other or away from each other, changing the angle between two O-H bonds. Movement in water occurs via bending, a process during which the bond angle between the oxygen and hydrogen atoms changes, which in turn affects the molecular geometry and, in turn, the physical properties of the molecules, the part of the molecule's dipole moment and intermolecular interactions. The frequency of the in-plane bending motion is usually in the infrared region of the spectrum, and this mode is often intense in the vibrational spectra of bent molecules. Scissoring modes are particularly important in angular or bent molecules as they inform on the vitamin of the bond angles in the molecule. In general, the bending modes in plane have higher frequency compared to the stretching modes, since bending motions usually needs more energy to enable because of bond angle distortions.

**8.4 Bending (Rocking, Wagging, Twisting) Out-of-plane**

Out-of-plane bending refers to changes in bond angles in directions orthogonal to the molecule plane. These bending motions represent movements such as rocking, wagging, or twisting, where the atoms

participating in the bond move in a direction perpendicular to the plane of the given molecule. Out-of-plane bending modes can also be more detailed than in-plane bending modes and the types of out-of-plane bending modes will be determined by the molecular geometry and relative displacement of the moving atoms.

The out-of-plane bending modes can be classified into the following types:

- Rocking: In rocking, the bonds move in opposite directions, and the atoms "rock" back and forth around an axis. Such motion is seen most often in linear or almost linear molecules, where the atoms rotate around a central atom in such a way that the bond angles are perturbed.

- Wagging: Wagging is a bending motion in which atoms move in and out of the molecular plane, similar to the motion of a wagging. This does occur more common for most asymmetrical atoms in which the atoms are shifted in opposite directions but only about a plane.

- Twist: Twist is a way of rotation where atoms of a molecule rotate through an axle resulting in change in bond angle and causing non planar geometry of the molecule. Twisting modes often appear in large molecules with flexible structures that are capable of undergoing large change in orientation.
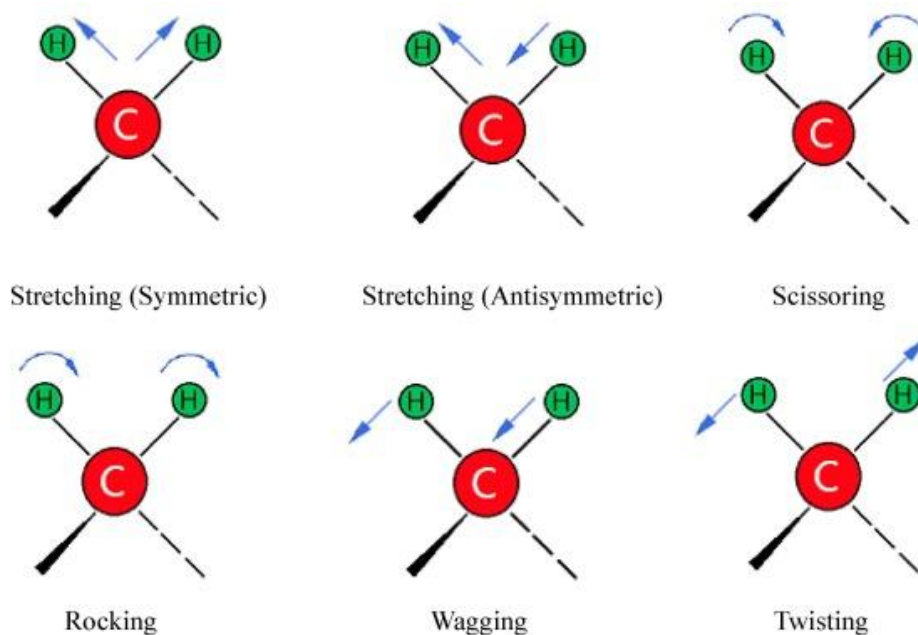
**Figure : 3.4 plane bending modes**

Molecules with more complicated structures, like polyatomic species that have multiple bonds in separate planes, tend to show out-of-plane bending motions. The bending modes are particularly critical in the analysis of large organic molecules and biological macromolecules since bending motions affect the global conformation of the molecule as in its interaction with other molecules. The frequency of the out-of-plane bending modes varies significantly based on molecular architecture and bending motions. For example, the twisting motion usually happens at lower frequencies than rocking or wagging motions. Out-of-plane bending modes may sometimes be more challenging to interpret, as they represent more complicated deformations of the molecular geometry; however, they still provide important information about molecular flexibility and the capacity for alteration and/or conformational change within a previously static molecule.

### Echo Harmonics, Frequency Groups

But in molecular vibrational spectroscopy, group frequencies are the characteristic vibrational frequencies associated with specific functional groups within a molecule. These frequencies depend on the

bonding context and the species of atoms involved. In fact, group frequencies are especially useful for detecting specific functional groups, since they are more consistent for a certain kind of bond.

For example:

• The C-H stretch of hydrocarbons usually shows up near 2900 cm$^{-1}$.

• The carbonyl C=O stretch normally occurs in the 1700 cm$^{-1}$ region.

• The O-H stretch from alcohols and phenols typically occurs in the range of about 3200-3600 cm$^{-1}$.

These group frequencies are affected by the atom masses, strength of bonds, and any activity with adjacent atoms or groups/g0 Polyatomic IR spectra contains overlapping bands due to various functional groups vibrations at individual group frequencies. Harmonics are higher frequencies of vibrations at integral multiples of the base vibrational frequency. These overtones can be seen in the IR spectrum at about two, three, or four times the frequency of the fundamental mode. Overtones, however, are usually very weak in intensity compared to the fundamental bands because the transition probability for overtone absorptions is orders of magnitude lower than for fundamental transitions. So, while overtones generally don't amount to much in most isolated molecules, they're still relevant in cases of large amplitude vibrations or highly excited vibrational states. Overtone bands not only provide information about the mechanics of the matrix element for the molecular vibration, but, through the intensity and position of a series of overtone bands, can also give an indication of the anharmonicity of the molecular vibration, as enharmonic potentials must lead to overtone bands.

## Hot Bands and Fermi Resonance

Hot bands are vibrational transitions that take place when a molecule is in an excited vibrational state at temperatures above absolute zero. Generating vibrations through thermal energy at very high temperatures Most of the molecules will be in excited states in terms of vibration at high temperatures Unlike transition from ground state to excited state, these molecules transition from and excited state to a higher vibrational state when absorbing infrared radiation. These transitions are called "hot bands." The hot bands are usually seen at higher wave numbers as compared to the principle vibrational transitions. They are generally less intense than fundamental bands because fewer molecules occupy an excited vibrational state at a given temperature. But the intensity of hot bands is temperature dependent, since more molecules can occupy higher vibrational levels. Hot bands are indeed an important part of most IR spectra, whilst providing key insights into the temperature dependent distributions of molecules in each vibrational state; as such, they can also be used to study the thermodynamics of molecular vibrations. Fermi resonance occurs when two of such vibrational modes of similar frequency are involved, which causes an alteration of the frequencies of both modes. This interaction causes the two vibrations to couple, producing a phenomenon where the two modes affect each other and their energy levels are mixed. Fermi resonance commonly takes place when the energy separation between the two modes is small ($200$ cm$^{-1}$) and can have the effect of splitting or shifting bands in the vibrational spectrum.

## Metal-Ligand Vibrations

Metal-Ligand Vibrations the vibrational modes of a metal complex where a metal ion is coordinated to one or more legends. The information regarding the bonding, structure, and geometry of the metal complex is available from these vibrations, which can be studied by infrared (IR) spectroscopy. In particular, this vibration can be studied by examining the frequencies of the metal-ligand bonds, which shows

how different metal-ligand interactions the metal and legends have. Vibrational modes typically fall into the far infrared (Far IR) region of the spectrum, but other regions can be observed in accordance with the type of bond. High-frequencies for metal-ligand vibrations enlighten the nature of the metal-ligand bond, its strength, the floridity of the complex, and eventually even with the electronic structure of the metal center. Normal coordinate analysis and other sophisticated methods in handling these vibrations are prominently studied and employed in polyatomic molecules. Together this can help chemists determine the identity of the complex, based on the presence of specific functional groups (fingerprints) and/or overall group frequency.

### Far IR Region Spectroscopy

Typically defined as wavelengths between 15 to 1000 micrometers (or frequencies between 30–200 $cm^{-1}$), the Far IR Region of the electromagnetic spectrum is crucial for the study of low-energy vibrations, including metal-ligand complexes. The connections being referred to in-between the metal-ligand bond is responsible for the stretching and bending modes of these two electrons, as seen in the Far IR area. In contrast to the mid-IR region, where standard organic molecule vibrational modes are observed, the Far IR region is defined by reduced energy. Since heavier elements, such as metals, have much lower frequencies for metal-ligand vibrations than lighter elements, this region is very relevant for getting insight into the vibrational profiles of heavier atoms. For instance, the stretching frequencies of metal-ligand bonds typically fall in this region, which is well-suited for discerning the bonding environment surrounding a metal center. For complexes of this type, the Far IR spectra can even give information on the metal-ligand bond force constants. The stiffer the bond (larger force constant) the higher the frequency of the vibration. In contrast, weaker bonds vibrate at lower frequencies. As an example, stretching vibrations of metal-oxygen (M-O) bonds in transition metal oxide complexes are usually seen in the Far IR region. Far IR spectroscopy essentially

focuses on the identification of the metal-ligand stretching vibration appearing in the spectrum as rising peaks. The peaks can give insights about the coordination number, geometry, and type of metal ligand interaction.

**Normal Coordinate Analysis**

Normal Coordinate Analysis is a Mathematical function which is used to study the vibrational modes of polyatomic molecules such as metal-ligand complexes. Normal coordinate analysis seeks a transformation of the coordinates where the vibrations of a molecule decouple into a set of independent vibrations called normal modes. Each normal mode is a specific vibration, like a bond stretching or bending motion, that has its own frequency. Normal coordinate analysis is fundamental for describing how the metal and ligand moves with respect to each other in a vibration in metal-ligand complexes. This approach sums the energies of the various normal modes to give the total vibrational energy of the system, providing a mathematical route to solve it based on quantum mechanical principles. The description of the system starts by the generation of the potential energy surface for a system, which describes the energy of a system as a function of atoms positions. From this PES, the system's force constants can be extracted. Force constants give valuable insight in the strength of the bonds and the stiffness of the metal-ligand interaction. The frequencies of the normal modes can be determined by solving the equations of motion for the system. Normal coordinate analysis makes possible the extraction of metal–ligand vibrational coupling.

**8.6 Understanding group frequencies using fingerprints**

The concept of fingerprints and group frequency interpretation are th most important used in the interpretation of IR spectra including that o metal-ligand complexes. In IR spectroscopy, a fingerprint is a uniqu set of vibrational frequencies that can be used to identify a specifi molecule or complex. The fingerprint regions can be located in the mid-

IR region but also have the opportunity to exist as vibrational states within certain metal-ligand vibrations in the Far IR region. So the fingerprint region can be critical for determining what kind of metal-ligand bond we're looking at, since each complex will yield a fingerprints of vibrational frequencies for the given metal-ligand bond. The nature of the metal center, legends, geometry and oxidation state of the metal will dictate these frequencies. Researchers can identify the metal-ligand complex by comparing the observed frequencies to standard reference spectra. As an illustration, in the case of a metal-carbonyl complex, the stretching frequencies corresponding to M-C bonds in the Far IR region can serve as an identifying feature of the complex and can thus differentiate it from other compounds. Likewise, CO ligand bending vibrations can also be classified as a feature that offers identity in the fingerprint region, separating the complex from other metal-ligand species. Group frequency interpretation 215 involves the evaluation of modes consistent with certain functional groups or coordination environments. It has been reported that a bundle of metal-ligand complexes can give rise to vibrational frequencies characteristic of the metal-ligand bond formation. Group frequencies (see IR spectrum section, above) can be helpful for the identification of legends or specific bonding motifs in metal complexes.
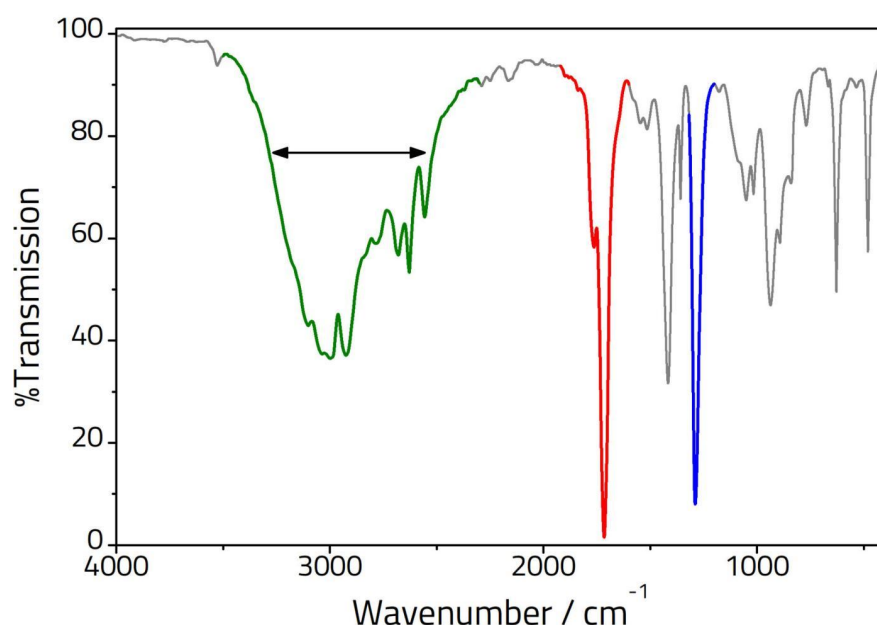


**Figure Graph between % Transmission and Wavenumber/cm**

**Check Your Progress**

Q1. What is vibrational frequency?

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Q2. Discuss the selection rules for vibrational energy state in molecular spectroscopy.

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## 8.5 Summary

The linear harmonic oscillator model approximates the vibrational motion of a diatomic molecule where the atoms oscillate about an equilibrium position under the restoring force proportional to displacement. The force constant (k) determines bond strength, while the zero-point energy is the minimum vibrational energy a molecule possesses even at absolute zero. Real molecules deviate from ideal$^{-1}$ harmonic motion, leading to anharmonicity, which allows overtones and combination bands in spectra.

In vibration-rotational spectroscopy, transitions involve simultaneou changes in vibrational and rotational levels, producing a band structure. These transitions are classified into P-branch ($\Delta J = -1$), Q-branch ($\Delta = 0$), and R-branch ($\Delta J = +1$). The Born–Oppenheimer approximatio separates electronic, vibrational, and rotational motions, simplifying

spectroscopic analysis. For polyatomic molecules, vibrations are more complex and include normal modes such as symmetric stretching, asymmetric stretching, scissoring, rocking, wagging, and twisting

**8.7 Exercises**

**8.7.1 Multiple Choice Questions MCQs**

1. The energy levels of a harmonic oscillator are:
   a) $E_v = h\nu(v+1)$
   b) $E_v = h\nu(v+1/2)$
   c) $E_v = h\nu v^2$
   d) $E_v = h\nu v$
   **Answer: b**

2. Zero-point energy corresponds to:
   a) The minimum possible vibrational energy of a molecule
   b) The energy at absolute zero temperature
   c) The absence of vibrational motion
   d) The difference between two energy levels
   **Answer: a**

3. In vibration–rotational spectra, the P-branch corresponds to:
   a) $\Delta J = +1$
   b) $\Delta J = 0$
   c) $\Delta J = -1$
   d) $\Delta J = +2$
   **Answer: c**

4. The Born–Oppenheimer approximation separates:
   a) Vibrational and nuclear motion
   b) Vibrational and electronic motion
   c) Electronic, vibrational, and rotational motion
   d) Nuclear and electronic spins
   **Answer: c**

5. The number of normal modes of vibration for a nonlinear triatomic molecule is:
   a) 3
   b) 6
   c) 4
   d) 9
   **Answer: b ($3N - 6 = 3 \times 3 - 6 = 3$)**

**8.7.2 Short Answer Questions**

1. Define zero-point energy. Why does it arise in quantum mechanics?

2. Differentiate between harmonic and anharmonic oscillators.

3. What is the significance of the force constant in vibrational spectroscopy?

4. Explain the origin of the P, Q, and R branches in a vibration–rotational spectrum.

5. State the Born–Oppenheimer approximation and its importance.

### 8.7.3 Long Answer Questions

1. Derive the energy expression for a quantum harmonic oscillator and explain the concept of zero-point energy.

2. Discuss anharmonicity in molecular vibrations. How does it affect vibrational spectra?

3. Explain the structure of vibration–rotational spectra of diatomic molecules with suitable diagrams.

4. Describe the branches of vibration–rotational spectra (P, Q, and R). Give examples.

5. Discuss the Born–Oppenheimer approximation and its limitations in molecular spectroscopy.

6. Explain vibrational modes of polyatomic molecules with examples of stretching and bending vibrations

### 8.8 References and Suggested Reading

1. Atkins, P., & Friedman, R. (2011). Molecular Quantum Mechanics (5th ed.). Oxford University Press, London, UK
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**Structure**

**9.1 Introduction**

Fourier Transform Infrared Spectroscopy (FT-IR) is one of the most popular analytical techniques for sampling the vibrational modes of molecules and retrieving information about its molecular structure. FT-IR works on the premise that bonds in a molecule have distinct absorption frequencies in the infrared region of the electromagnetic spectrum, thus, it provides chemical information at the molecular level. FT-IR differs from classical dispersive infrared spectroscopy as instead of directly converting raw data into a readable spectrum, raw data is first collected and then transformed into a readable spectrum through the use of Fourier transformation. This groundbreaking approach led to a transformative improvement in infrared spectroscopy, offering enhanced specificity, resolution, and rapid acquisition of high-quality spectra with less effort.

FT-IR spectroscopy is based on the basic principles of infrared absorption spectroscopy. Infrared radiation interacts with molecules in

**9.2 Objectives**

1. To understand the principle and working of Fourier Transform Infrared Spectroscopy (FT-IR).

2. To differentiate between conventional dispersive IR spectroscopy and FT-IR.

3. To study the instrumentation of FT-IR, including interferometer, laser, detector, and computer system.

Instrumentation and FT-IR

a way that causes their bonds to vibrate. Unique bonds in a molecule absorb infrared radiation at different fingerprints matching the vibrational frequencies of the specific bonds (C-H, N-H, O-H stretching etc.). The absorption spectrum obtained gives a molecular fingerprint of the sample analyzed. Unlike conventional IR spectroscopy, FT-IR collects data over a wide frequency range simultaneously. In conventional IR spectroscopy, the sample is illuminated with a monochromatic beam of infrared radiation, and the transmitted light is detected at various wave numbers or frequencies in order to generate a spectrum. This technique, called dispersive infrared spectroscopy, works by dispersing light into constituent wavelengths. FT-IR spectroscopy is based on a Michelson interferometer; this is essentially the key to its functioning, and it is different from the older technique. Their interferometer consists of two beams of light of different optical path lengths interfering with one another and the resulting pattern is subjected to a mathematical transform known as a Fourier transform to yield a spectrum. It had some advantages including but not limited to better signal-to-noise and resolution improvement and faster data acquision. The FT-IR spectrometer generates a wide range of infrared light at multiple wave numbers. This light is focused at the sample, where it interacts with the sample and excites different bonds in the molecules to vibrate. Vibrational transitions occur when the frequency of the incident infrared light is equal to the same frequency of vibration of a particular bond in the sample. The light that comes out of the sample is then routed through the interferometer, generating an interference pattern.

**Speed and Efficiency**

One major advantage of FT-IR (Fourier Transform Infrared) relative to more traditional dispersive IR methods is the ease and speed at which spectra can be collected. In a traditional IR system, the spectrometer is required to step over various wavelengths one at a time. Scanning individual samples can take a long time; seconds to minutes for each

spectrum to be collected. It typically employs a moving monochromatic or a diffraction grating to select single wavelengths of infrared light, thus it needs to scan over a wide spectral range. FT-IR spectroscopy, on the contrary, relies on a different technique. FT-IR works differently, instead of scanning a single wavelength at a time, FT-IR uses an interferometer to acquire all wavelengths at once in an interferogram. Following this, the interferogram is run through a Fourier transform algorithm to produce the spectrum. FT-IR spectrometers can then record the full spectrum within seconds or less. FT-IR is a much faster process than traditional methods since it collects data across a wide range of frequencies at the same time. Advantages of using the BioID for application high throughput In pursuit of high throughput in which many samples need to be analyzed at once, this speed is extremely beneficial. Moreover, it enhances the throughput in experiments and analytical pipelines, enabling scientists and technicians to generate more data in shorter periods of time.

## High Sensitivity

FT-IR spectroscopy is very sensitive, which is one of its main benefits. Sensitivity in the context of a spectrometer is linked to the low concentration of the sample and the precise determination of infrared absorption. The sensitivity enhancement of FT-IR systems is primarily attributed to the higher signal-to-noise ratio, which is further improved through mathematical processing of the interferogram. For FT-IR spectrometers, it is common to average multiple scans to enhance the data quality. This common technique is called signal averaging, which will be used to reduce random noise in the spectrum and improve signal clarity. The outcome is a better description of the vibrational modes that the sample exhibits, even if the material being measured is present only at trace amounts. Consequently, FT-IR is well-suited to applications in which the detection of minimal volumes of substances is paramount. In the case of environmental monitoring, FT-IR can detect and quantify the pollutants at very low concentration. FT-IR is

equally employed in the pharmaceutical sector, one addition is drug molecular characterization, and the other isotyping routes to identify for trace components in complex chemical mixtures.

### Improved Resolution

FT-IR Spectroscopy: FT-IR spectroscopy offers higher resolution than traditional dispersive IR systems. In infrared spectroscopy, resolution is the separation between adjacent bands that still can be used to distinguish them in a spectrum. Higher resolution makes it possible to resolve individual vibrational modes of a molecule more clearly, thus informing our understanding of the sample's structure and behavior at the molecular level. In FT-IR the resolution depends both on the maximum optical path difference (OPD) in the interferometer and the number of data points collected. FT-IR instruments manipulate the interferogram mathematically and thus can extract higher-resolution spectral information. Higher precision and more detailed spectrum than when using more traditional methods based on scanning over the individual wavelengths are achieved with the Fourier transform algorithm; this allows the interferogram to be converted into spectrum.

### No Scanning Monochromatic Required

The primary and perhaps, most definitive part of a traditiona dispersive IR system is its scanning monochromatic which isolate individual wavelengths of light for detection. This necessitate mechanical moving parts, like mirrors or gratings, which can wear ou over time and need regular maintenance. And also, these moving part could lower the overall reliability and steadiness of the instrument. FT-IR spectroscopy, on the other hand, allows using an FTIR system, which does not require a scanning monochromatic. Instead, FT-IR use an interferometer, which splits the incoming light into two beams an recombines them to form an interference pattern. This produces a interferogram that contains information on all the wavelengths of th infrared light in parallel. Therefore, the FT-IR system is able to output

the sample spectrum directly from the Fourier transform algorithm in the time domain in which the interferogram is processed without mechanical scanning. All this means the absence of moving parts and improved stability and reliability of FT-IR spectrometers. FT-IR systems have lower maintenance costs and longer lifetimes due to fewer wear-and-tear mechanical parts. Additionally, eliminating the need for a monochromatic speed up data collection by avoiding time-intensive scans across the different wavelengths.

### Quantitative Analysis

Qualitative analysis: FT-IR spectroscopy is not only more useful for qualitative analysis; it is highly efficient for quantitative analysis. FT-IR is employed in qualitative analysis to identify functional groups, chemical bonds, and molecular structures based on characteristic infrared absorption patterns. FT-IR can be used in quantitative analysis to measure the concentration of specific components within a mixture. Its high resolution combined with sensitivity is especially beneficial in quantification of substances, even in complicated mixtures such as biological samples. The intensity of absorption of a particular vibrational mode is proportional to the concentration of the associated component, and hence Beer's law is established; that is, the intensity of an absorption band can be used to quantify concentration of a particular compound. The repeated scans increase the reproducibility and precision of FT-IR measurements which is one of the advantages for quantitative analysis. FT-IR instruments offer high-quality spectra with minimal noise, allowing for accurate and reliable data in the industries like pharmaceuticals, food and beverage, and environmental monitoring. FT-IR is often used in the pharmaceutical industry to monitor the required amounts of active ingredients in drugs.

## 9.3 Improved Accuracy, Precision and Reproducibility

A critical aspect of FT-IR spectroscopy is its highly reproducible results, a fact that is a prerequisite in various industries that depend upon routine analysis and quality control. High sensitivity combined with low sample preparation and the ability to average multiple scans leads to spectra that are accurate and reproducible. More frequent in quality control environments like pharma and chemicals industries, consistency and reliability of data is of utmost importance. FTIR allows the identification of compounds to be done in a repeatable manner and ensuring the specifications of products and preventing contamination. The high reproducibility of FT-IR measurements is a factor that minimizes the error possibilities as well as assures that the data collected over a period of time are consistent and serves long-term monitoring and routine testing approaches excellently.
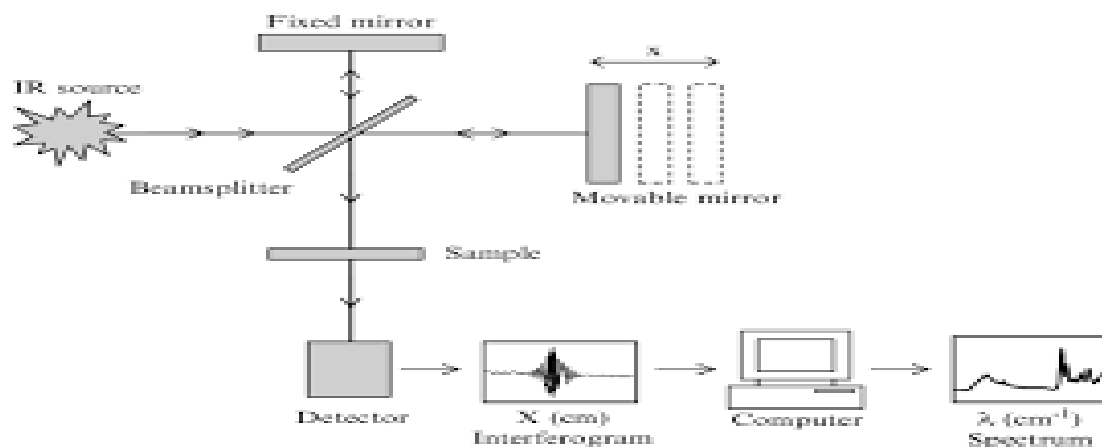


**Figure 3.5 FT-IR measurements technique**

## 9.4 FT-IR Spectroscopy Uses

The introduction of FT-IR (Fourier-transform infrared) spectroscopy changed the landscape of analytical chemistry due to its fast, nondestructive, and sensitive capabilities in the identification and characterization of chemical substances. FT-IR spectrometers are

employed in a variety of industries and areas of research, such as environmental analysis, material science, foodstuffs, environmental science, chemical analysis, pharmaceuticals, forensic science, etc. Tapping into the molecular vibrations of different bonds, this method provides rich information on molecular structure, chemical makeup, and functional groups. FT-IR spectroscopy has some of the main applications given below:

**Analysis and Identification of Chemicals**

FT-IR Spectroscopy is a potent analytical method for the quantification and identification of chemicals in the target of analyze samples. The methodology used is capable of identifying organic and inorganic functional groups and bonding types. FT-IR imaging creates unique molecular fingerprints in the infrared spectrum, which can be used for the identification of unknown compounds by comparing them to known spectra.

**Environmental Monitoring**

Environmental monitoring using FT-IR Spectroscopy; FTIR Spectroscopy is an important tool for environmental monitoring, which involves the analysis of air, water, and soil samples for pollutants. It is capable of sensing various environmental pollutants including volatile organic compounds (VOCs), greenhouse gases ($CO_2$, $CH_4$), industrial effluent, and particulate matter. The sensitivity and ability of FT-IR to rapidly analyze complex samples make the technique a mainstay of environmental monitoring, particularly outdoors.

## 9.5 Applications in the Pharmaceutical and Biomedical Industries

FT-IR spectroscopy is commonly used in pharmaceutical and biomedical industries. One important application is to confirm raw

materials, intermediates, and finished products purity and quality. FT-IR is used by pharmaceutical companies to verify that drug APIs comply with specific purity requirements. To investigate recipients (inactive ingredients) and discover possible impurities in pharmaceutical formulation, FTIR can also be employed.

Polymer and Materials Science

FT-IR is widely applied in materials science field such as polymers and materials characterization, chemical composition, and molecular structure. FT-IR can identify functional groups and bonding configurations in long chains of repeating units, which make up polymers. This makes FT-IR, therefore, absolutely indispensable in polymer synthesis, analysis and characterization. Polymer degradation; One of the leading applications of FT-IR in polymer science. "Polymers can degrade if they're exposed to heat, light, oxygen, or when they undergo chemical reactions. Through the chemical structural alterations, researchers and manufacturers assess the stability of materials and their longevity, which can be detected using FT-IR. FT-IR is also useful for investigating curing processes in thermosetting polymers.

Food and Agriculture

Many applications have been developed to use FT-IR spectroscopy in the food industry. It is employed to study the makeup of food products, track quality, and enforce safety regulations. Moisture, fat, and protein are important factors that will affect the nutritional value and quality of food products. FT-IR is widely used for the determination of food moisture, fat content, and protein content.

Forensic Science

FT-IR spectroscopy is also a useful analytical technique in forensic science for examination of trace evidence that may lead to the evidence

on the case in criminal investigation. FT-IR is known for its role in forensic analysis of society wherein forensic scientists identify substances present at crime scenes such as fibers, paints, drugs, explosives, and materials. This is especially important doing  fibers and paints, as FT-IR shows what chemicals are in the fibers they will identify what kind of molecules.

Materials Characterization

FT-IR spectroscopy has been used extensively in materials characterization, such as thin films, coatings,  and composite materials. The lab will use a powerful new technique to help tell them the detailed composition and molecular structure of materials — a key tool for anyone developing new materials with certain properties. In FT-IR analysis  of thin films and coatings, the molecular structure, thickness, and uniformity can be analyzed. These insights are important for the design of high-efficiency coatings for electronics, optics and other applications. Composite materials with components from polymeric elastomers,  polyethylene, etc. have been studied as well using FT-IR spectrometry.

## 9.6 Summary

Photoacoustic spectroscopy (PAS) is a sensitive analytical technique based on the photoacoustic effect, where absorbed modulated light causes localized heating and generates acoustic waves due to thermal expansion.

These sound waves are detected using microphones or piezoelectric sensors. PAS is especially useful for studying opaque, solid, or highly scattering samples, and it enables depth profiling and detection of trace gases.

It offers advantages such as minimal sample preparation, non-destructive analysis, and applicability to condensed phases. Raman spectroscopy, on the other hand, is based on the inelastic scattering of

monochromatic light, typically from a laser, where the scattered light exhibits energy shifts corresponding to vibrational, rotational, or other low-frequency transitions in molecules. This technique provides a molecular fingerprint of the sample and is widely used for both qualitative and quantitative analysis. Unlike infrared (IR) spectroscopy, Raman is effective for symmetric molecular vibrations and is ideal for aqueous samples since water produces a weak Raman signal. Raman spectroscopy can be enhanced using techniques like Surface-Enhanced Raman Spectroscopy (SERS) or Resonance Raman Spectroscopy to improve sensitivity.

## 9.7 Exercises

### 9.7.1 Multiple Choice Questions

Which region of the electromagnetic spectrum does infrared spectroscopy utilize?

A) Ultraviolet
B) Visible
C) Infrared
D) Microwave
Answer: C) Infrared

2. What is the primary purpose of infrared spectroscopy?

A) Determine atomic mass
B) Identify functional groups in molecules
C) Measure magnetic fields
D) Detect nuclear spin
Answer: B) Identify functional groups in molecules

3. Which molecular movements are studied in IR spectroscopy?

A) Electronic transitions
B) Nuclear spin flips
C) Vibrational and rotational motions

D) Ionization of atoms

Answer: C) Vibrational and rotational motions

4. In IR spectroscopy, a molecule must _____ to absorb IR radiation.

A) Have a permanent dipole moment

B) Be symmetrical

C) Be ionized

D) Be radioactive

Answer: A) Have a permanent dipole moment

5. The typical range for mid-infrared spectroscopy is:

A) 0.1 – 10 nm

B) 4000 – 400 cm$^{-1}$

C) $10^6$ – $10^9$ Hz

D) 1 – 10 Å

Answer: B) 4000 – 400 cm$^{-1}$

6. What component in FT-IR replaces the monochromator used in dispersive IR instruments?

A) Quartz window

B) Grating

C) Interferometer

D) Detector

Answer: C) Interferometer

7. The major advantage of FT-IR over dispersive IR is:

A) Lower resolution

B) Faster analysis and better signal-to-noise ratio

C) Uses visible light

D) Requires no sample

Answer: B) Faster analysis and better signal-to-noise ratio

8. What mathematical tool is used to convert interferogram data in FT-IR?

A) Sine transform

B) Matrix multiplication

C) Fourier Transform

D) Differential equation

Answer: C) Fourier Transform

9. Which detector is commonly used in modern FT-IR instruments?

A) Photomultiplier tube

B) Thermocouple

C) Deuterated triglycine sulfate (DTGS)

D) Flame ionization detector

Answer: C) Deuterated triglycine sulfate (DTGS)

10. What is the function of the beam splitter in an FT-IR instrument?

A) Focus the light beam

B) Separate the IR spectrum into wavelengths

C) Split the IR beam into two paths

D) Absorb excess radiation

Answer: C) Split the IR beam into two paths

### 9.7.2 Short Answer Questions

1. What is the significance of the harmonic oscillator model in IR spectroscopy?

2. Explain the concept of anharmonicity and its effect on vibrational energy levels.

3. How does the Born-Oppenheimer approximation simplify molecular spectroscopy?

4. What is the difference between P, Q, and R branches in vibration-rotational spectroscopy?

5. Why are selection rules important in infrared spectroscopy?

6. What are normal modes of vibration, and how are they determined for polyatomic molecules?

7. How does the presence of overtones affect IR spectra?

8. What is the purpose of normal coordinate analysis in metal-

ligand vibrations?

9. How does FT-IR differ from conventional IR spectroscopy?

10. List three major applications of infrared spectroscopy in chemical analysis.

### 9.7.3 Long Answer Questions

1. Describe the linear harmonic oscillator model and its limitations in infrared spectroscopy.

2. Explain zero-point energy and discuss its role in vibrational spectroscopy.

3. Discuss anharmonicity and how the Morse potential diagram improves the understanding of molecular vibrations.

4. Explain the formation of P, Q, and R branches in vibration-rotational spectroscopy with an example.

5. Describe the selection rules for vibrational transitions and their effect on IR spectra.

6. Explain the concept of normal modes of vibration and their determination using group theory.

7. Discuss the significance of metal-ligand vibrations and their study in the far-infrared region.

8. What is the fingerprint region in infrared spectroscopy, and why is it important?

9. Explain the working principle of Fourier Transform Infrared Spectroscopy (FT-IR) and its advantages over traditional methods.

10. Discuss the applications of infrared spectroscopy in environmental, pharmaceutical, and forensic analysis.

### 9.8 References and Suggested Reading

1. Banwell, C. N., & McCash, E. M. (1994). Fundamentals of Molecular Spectroscopy (4th ed.). McGraw-Hill, Oxford UK.

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**Unit 10: Photoacoustic Spectroscopy**

Structure

10.0 Objectives
10.1 Introduction
10.2 Basic Principles of PAS
10.3 Pros of Photoacoustic Spectroscopy
10.4 Condensed Systems
10.5 Summary
10.6 Exercises
10.7 References and Suggested Reading

### 10.0 Objectives

1. To understand the fundamental principles of Photoacoustic Spectroscopy and its relation to absorption phenomena.

2. To explore the instrumentation, working mechanism, and detection techniques used in PAS.

3. To analyze the advantages of PAS over conventional spectroscopic methods.

### 10.1  Photoacoustic Spectroscopy (PAS)

Photoacoustic Spectroscopy (PAS) is a powerful new analytical technique combining the principles of optical and acoustic spectroscopy. The process of PAS involves having a modulated light (not a continuous wave) source absorbed by a sample, which generates thermal energy that subsequently produces sound49. By analyzing these sound waves, one can obtain information regarding the sample's absorption characteristics, chemical composition, and structural properties. Overall, the advantage of PAS is its capability of yielding ultrasensitive measurements with nearly no treatment of the sample and hence it is widely used in many applications, such as pollution detection, chemical sensing, material sciences and so on. The core concept behind PAS is the photoacoustic effect, which describes light absorption by a material that rapidly heats the material and induces pressure wave traversing (acoustic wave) (Fig. 1). This is especially

true for energies that are not efficiently dissipated as heat, which instead manifest as an acoustic signature that can be measured.

## 10.2 Basic Principles of PAS

Photoacoustic Spectroscopy (PAS) is based on the interaction between modulated light (usually from a laser) and the sample, resulting in the production of an acoustic signal. The process starts with modulated beam of light, usually a laser, that hits the surface of the sample. The sample absorbs light, and it converts its absorbed energy to heat, according to the material. If the absorption is strong enough, it can lead to a rapid increase in temperature in the material, which when the sample expands brings a pressure wave. The pressure wave is what PAS detects/analyzes.

Modulated Light Source: A light source commonly, a pulsed or modulated laser shines onto the specimen. The light source can be adjusted to certain wavelengths depending on the material one wants to study. The power of the light is modulated, typically a square wave or sinusoidal modulation, often a periodic signal. The modulation enables the examination of the absorption characteristics of the sample across various frequencies. Light Absorption; Once the light comes into contact with the sample, sample absorbs energy. The degree of absorption is governed by materiality and absorption spectra. In the case of organic materials, the absorption can be because of electronic transitions, however, in other materials it may be because of vibrational or rotational transitions.

1. Absorption of Light: The incoming light energy is absorbed by the sample which gets heated up. Depending on the sample itself and its absorption properties, it can heat uniformly or in localized spots. The material will then expand due to heating.

2. Sound Wave Generation: With the ultra-fast heating, the material expands and contracts, producing a pressure wave, or

sound wave. This is the photoacoustic effect, and the frequency and amplitude of the sound wave depend on the amount of absorbed light and the thermal properties of the sample.

3. Acoustic Signal Detection: The pressure wave or acoustic signature is subsequently detected by a highly sensitive microphone or piezoelectric transducer positioned in close proximity to the sample. A specific acoustic phenomenon is observed as a result of light being absorbed in various samples, allowing for spectrometry and other analyses based on the association between the intensity of the absorbed light and the detected signal.

4. Filters: Different types of filters may be applied to concentrate on specific frequency ranges. For example, low-pass filters can enhance sensitivity by removing high-frequency noise, while band-pass filters can isolate features of interest. The accuracy and quality of the spectral data can be determined from the filter settings. Reconstructions; Using known data about the medium characteristics and the signal, reconstructions can be made to obtain images with multi-dimensional data (3D or 2D) using reconstruction algorithms. The Fourier transform is one way of converting the time-domain signal (the captured acoustic wave) into the frequency-domain, which can be compared with the known absorption spectra's of materials.

One of the most prominent features of PAS is its capability to achieve both bulk and surface sensitivity. The penetration depth of light varies with both the wavelength used and the optical properties of the material. Longer wavelengths, for example, may penetrate deeper into opaque or scattering materials, while shorter wavelengths are more surface sensitive. Additionally, PAS can be used in conjunction with other techniques, like ultraviolet-visible (UV-Vis) absorption spectroscopy, to obtain additional insights into a material's properties.

## 10. 3 Pros of Photoacoustic Spectroscopy

**High Sensitivity:** High sensitivity is one of the most important reasons for using PAS. Because little material is needed to generate a measurable acoustic signal from the absorbed light, the technique can detect very low quantities of material. This characteristic makes PAS highly advantageous for trace analysis, which focuses on low concentration species. Non-destructive Non-destructive Technique; One of the key advantages of PAS is that it is a non-destructive technique, which means that the sample is not damaged or altered during the analysis. This is especially crucial in the investigation of fragile materials or when the sample needs to stay whole for subsequent examinations. Results are not dependent on the transparency of samples; PAS can be performed on opaque or scattering samples which is not the case with traditional absorption spectroscopy where samples must be transparent to the light. In addition, PAS can be employed to analyze a variety of sample types (powders, liquids, solids) that are often difficult or impossible to analyze using traditional absorption spectroscopy.

1. Bulk vs Surface Sensitivity: PAS can access both the bulk and the surface region of materials, depending on light wavelength. This is especially advantageous when investigating heterogenous materials, such as composites, coatings, or multi-layered system.

2. High resolution: PAS works on the principle of modulation of the light source and the analysis of resulting acoustic signal which leads to high spectral resolution. It enables investigation of high-resolution vibrational modes and electronic transitions for materials having more insight into the properties of materials.

3. Broad Applicability: PAS can be used in a wide variety of environments, including gases, liquids, and solids. It that is appropriate for studying complex systems including biological tissues, environmental samples, and materials science.

### Gaseous and condensed system applications

In the case of photoacoustic spectroscopy, it has been elegantly been used for gaseous as well as condensed systems, thus making it a versatile tool for numerous scientific and industrial applications.

### Gaseous Systems

In case of gaseous systems, PAS is commonly deployed for the absorption spectra studies in the infrared range. When modulated light passes through a sample of gas, each gas molecule absorbs specific wavelengths of light that match the energy and frequency of the molecules' vibrational transitions. The presence of these absorption features may be monitored through the detection of induced photoacoustic signals, and analysis of these signals yields key details about gas molecular structure, concentration, and identity. Detection of trace gases in atmospheric studies is one of the significant applications of PAS in gaseous systems. The method used can detect gases at very low concentrations, often at parts per billion (ppb) levels. This sensitivity is what makes PAS particularly appealing for application in environmental monitoring (detecting pollutants/greenhouse gases like $CO_2$, $CH_4$, or $NO_2$). Another application of PAS is in pollutants monitoring, where it can detect harmful gases that are released in the atmosphere from industrial processes, transportation, and burning. The real-time monitoring provided by PAS is a valuable asset for compliance to environmental regulations and reduced impact of air pollution. PAS has an application not only in environmental monitoring but in chemical analysis of gases. In the example of a gas-phase reaction study, PAS can monitor the concentration of reactants and products involved in a chemical reaction. This ease to various reaction kinetics and mechanism comprehension.

## 10.4 Condensed Systems

PAS has been used to study absorption and thermal properties of condensed systems (liquids and solids). Because condensed materials typically have different light absorption wavelengths compared to gases, PAS is especially useful in studying solids and liquids' electronic and vibrational spectra. For instance, employing this technique in solid materials (semiconductors, metals and insulators) it allows to investigate the vibrational modes of the atoms in the material. This gives useful insight of the crystal structure, bonding and defects in the material. PAS can also be employed in liquid systems to investigate the molecular vibrations of liquids and solutions. This method is useful for the study of solvation effects, solvent-solute interactions, and chemical reaction dynamics in solution. Notably PAS has been widely used in studying biological systems (for example protein-ligand interactions, and the pharmaceutical industry, where it can aid understanding of drug solubility as well as formulation properties. PAS is also applied to material characterization. By analyzing PAS data, researchers can gain valuable insights into processes related to the molecular structure and degradation of polymeric materials, guiding the design and optimization of materials used in various industrial applications.

### Formulations for Chemical and Surface Applications

Photoacoustic spectroscopy is especially good for a wide range of chemical properties and surface properties of materials. PAS is also a powerful technique to investigate heterogeneous system, because it can yield information about both bulk and surface properties.

Check Your Progress

Q1. What is the principle of Photoacoustic Spectroscopy?

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Q2. Discuss the applications of Photoacoustic Spectroscopy

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## 10.5 Summary

Photoacoustic Spectroscopy (PAS) is an analytical technique based on the photoacoustic effect, where absorbed modulated light by a sample produces acoustic waves due to periodic heating and expansion. A microphone or piezoelectric detector converts these pressure waves into measurable signals. PAS is highly sensitive, non-destructive, and capable of analyzing solids, liquids, and gases, even in opaque or highly scattering media where conventional transmission spectroscopy fails.

Its instrumentation typically includes a modulated light source (laser or monochromator), a sample chamber, and an acoustic detector. PAS finds wide applications in trace gas analysis, pollution monitoring, biomedical diagnostics (e.g., blood glucose detection, tumor imaging), and characterization of semiconductors and nanomaterials. The technique combines high sensitivity with versatility, making it a valuable tool in modern spectroscopy.

## 10.6  Exercises

### 10.6.1 Multiple Choice Questions

1. The principle of Photoacoustic Spectroscopy is based on:
   a) Raman scattering
   b) Fluorescence emission
   c) Photoacoustic effect
   d) Nuclear spin resonance
   Answer: c) Photoacoustic effect

2. In PAS, absorbed light is converted into:
   a) Electric current
   b) Sound waves
   c) Magnetic field
   d) Emission spectra
   Answer: b) Sound waves

3. The detector most commonly used in PAS is:
   a) Photomultiplier tube
   b) Microphone
   c) Bolometer
   d) Photodiode
   Answer: b) Microphone

4. Which of the following is an advantage of PAS?
   a) Requires transparent samples
   b) Can analyze opaque and scattering samples
   c) Works only for gaseous samples
   d) Produces high background noise
   Answer: b) Can analyze opaque and scattering samples

5. A major application of PAS is:
   a) Protein sequencing
   b) Trace gas detection
   c) X-ray crystallography
   d) Electron spin resonance
   Answer: b) Trace gas detection

## 10.6.2 Short Answer Questions

1. Define Photoacoustic Spectroscopy.

2. Explain the photoacoustic effect in simple terms.

3. List two main advantages of PAS over conventional absorption spectroscopy.

4. Name two types of detectors used in PAS.

5. Mention any two applications of PAS in environmental science.

## 10.6.3 Long Answer Questions

1. Describe the principle and working mechanism of Photoacoustic Spectroscopy with the help of a labeled diagram.

2. Explain the instrumentation of PAS and discuss the function of each component.

3. Discuss the advantages, limitations, and applications of PAS compared to conventional IR spectroscopy.

4. How is PAS applied in trace gas monitoring? Explain with suitable examples.

5. Write a detailed note on biomedical applications of PAS.

### 10.7 References and suggested Reading

1. Hollas, J. M. (2004). Modern Spectroscopy (4th ed.). John Wiley& Sons, New York, USA
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## Unit 11

## Raman Spectroscopy

SPECTROSCOPY - I

### 11.0: Objectives

1. To understand the principle and theory of Raman Effect.

2. To differentiate between Raman Spectroscopy and Infrared Spectroscopy.

3. To study instrumentation, including light sources, sample handling, and detectors.

4. To analyze vibrational, rotational, and vibrational–rotational Raman spectra.

### 11.1 Quantum and Classical Theories of the Raman Effect

Raman Spectroscopy, a fundamental technique widely employed in the fields of analytical chemistry, physics, and material science, offers molecular level information about vibrational, rotational, and other low-frequency modes of a system. Raman spectroscopy, unlike infrared spectroscopy, measures the scattering of light so it gives complementary information on the molecular composition of a sample. The technique is named for the Indian physicist C.V. Raman, who first described the phenomenon in 1928 and won a Nobel Prize in Physics in 1930 for it.

Before diving into the basic principle of Raman Spectroscopy, it is crucial to gain insight into the Raman Effect, which underpins this phenomenon, as well as its theoretical underpinnings; classical and quantum. Jayesh Kumar, Waste Management Division, UCLA Department of Civil and Environmental Engineering. Electromagnetic radiation and interaction of light with matter are at the base of classical theory of Raman effect (Figure 2). According to this theory, when

mono-chromatic light (most commonly laser light) is scattered by a molecule, there will be a shift of the frequency of the scattered light based on the vibrational or rotational modes of the molecule. It is these frequency shifts that we see as the Raman effect. When light falls on a molecule, it interacts with the electrons of the molecule. If the frequency of the light is equal to one of the vibrational modes of the molecule, some of the energy is absorbed and the molecule moves to a higher vibrational state.

**Quantum Theory of the Raman Effect**

Though the Raman effect is explainable through classical theory, the use of quantum theory offers a more comprehensive and precise framework to understand it. Based on quantum mechanics, molecules are made of discrete energy states, including rotational and vibrational energy levels. When light hits a molecule, it can cause transitions between these levels, but this interaction always involves the absorption or emission of quanta of light, the photons, and is thus governed by the rules of quantum mechanics. Beginning with the concept of virtual states, one can describe a quantum explanation for this phenomenon known as Raman scattering. In quantum language, when a photon meets a molecule, it excites the molecule to a virtual, transient state that doesn't correspond to any real energy level of the molecule. The molecule then relaxes from this virtual state by either emitting or absorbing a photon. The frequency shift of the scattered light is determined by the energy difference between the initial and final states (the vibrational states of the molecule). The electromagnetic field of the incident photon interacts with the polarizability of the molecule and produces Raman scattering. This interaction is quantified in quantum terms and corresponds to the change in energy states of the molecule, resulting in a shift of the frequency of the diffused photon. Additionally, the quantum theory includes selection rules, rules that state which transitions are permitted and how likely they are to occur.

## 11.2 Inherent Rotational, Vibrational, and Vibro-Rotational Spectra

Raman is especially good for vibrational and rotational states of moleculeses. These correspond to different classes of molecular motion, each producing distinctive features in the spectrum. In order to understand the spectra obtained in Raman spectroscopy, it is essential to understand the three types of spectra that can be generated as pure spectra which are pure rotational spectra, vibrational spectra, and vibro-rotational spectra.

### Pure Rotational Spectra:

Pure rotational Raman spectra are transitions between rotational energy levels of molecules. Such transitions are hence common in gaseous molecules possessing well-described  ghf states corresponding to molecular rotation. The lower rotational states are populated  at room temperature, so rotational transitions are highly sensitive probes of molecular interactions and can be detected on a short time scale (ns) due to the energy difference between rotational states corresponding to a shift in scattering frequency. Generally, the rotational Raman spectra are shown for top in linear or symmetric shape molecules. Low-temperature spectra are the most common since rotations need  less energy than vibrations, so that the population of excited rotational states is low at high temperatures. Hence from the rotational Raman spectra, one may extract the moment of inertia and symmetry of the molecule. In order for rotational Raman scattering to occur, the molecule must have a permanent dipole moment which facilitates  the interaction with the incident light's electromagnetic field. The changes in frequencies seen in the spectra are related to the rotational constants of the molecule and give bond lengths and other structural information.

## Vibrational Spectra:

The public domain Vibrational Raman spectra come from the transitions between various vibrational energy levels within the molecule. If the interaction leads to dipoled electronic transitions, it is possible for the energy quantum of the incident light to be equal to the energy difference between two vibrational states, which often results in the scattering of the light (Raman spectroscopy), which occurs in the mid-infrared spectrum. Molecules can stretch, bend, and rotate in multiple ways, but each type of vibrational motion has a frequency that is determined by the mass of the atoms involved and the bond strength between them. Stokes and anti-Stokes bands are usually observed in Raman spectroscopy due to vibrational transitions. Stokes bands are produced when the molecule gains the energy of the incident photons and goes to a higher vibrational state. Anti-Stokes bands, on the other hand, happen when the molecule starts in an excited vibrational state, and the vibrational energy is transferred to the scattering photon, giving a higher frequency of the scattered light. We consider the final result as the reference where we can obtain comprehensive information about the vibrational modes of the molecule including the frequency of each mode and the coupling of different modes are represented from the Raman spectrum. Useful for understanding molecular structure, bond strength, and chemical reactivity. Moreover, Raman spectroscopy is able to what is known as segmental substitution of the same molecule, ultimately providing information regarding isotopic substitution and examining molecular dynamics.

## Vibro-Rotational Spectra:

Raman spectroscopy detects vibro-rotational spectra besides pure rotational and vibrational spectra as they are simultaneous transitions that helps to study the vibrational and rotational energy states of molecules. As such, vibro-rotational transitions are of particular importance for the study of polyatomic molecules, for which

considerable coupling between the rotational and vibrational motions takes place. The reason these spectra appear is that the rotation and the vibration of the molecule are coupled. Because spectra are influenced by both the molecular rotation and vibration, vibro-rotational spectra have more complicated shapes than vibrational spectra. These transitions usually involve a change in both the rotational quantum number and vibrational quantum number, allowing probing of the coupled dynamics of the molecule. The vibro-rotational raman spectra also give us in-depth information about the rotational-vibrational coupling, the geometry of the molecules, the interaction of various vibrational modes with each other etc. So this spectroscopy is generally used in complex molecules studies including biological systems, complex organic molecules, and molecular assemblies.

## 11.3 Dependent Selection Rules and Mutual Exclusion Principle

It is called selection rules in Raman spectroscopy referring to the rules which govern the allowed vibrational or rotational transition. They are derived from the symmetry of the molecule and its interaction with the electromagnetic field of the incident light. The selection rules provide vital information about possible transitions in a scattering process and for understanding the Raman spectrum. Raman spectroscopy is an important and widely used technique to explore vibrational, rotational and other low-frequency modes in molecules. Raman spectrocopy definition revolves around the selection rules: understanding what vibrational or rotational transitions are observable in the Raman spectra. These selection rules determine when a molecule will scatter light through the process of Raman scattering. Specifically, three general selection rules identify Raman active vibrational modes: the change in polarizability of the molecule, vibrational symmetry of the normal mode, and conservation of energy. The interaction of all of these factors plays an important role in dictating whether or not this type of molecular vibration will result in observable Raman scattering and, subsequently, if it can be detected by Raman spectroscopy. In this post,

we shall delve into these selection rules in more detail and explain their importance and role in the Raman scattering process.

**Change in Polarizability**

First and foremost requirement for the selection rule in Raman scattering is that the polarizability of the molecule must change as it goes through vibrational or rotational motion. Polarizability of a molecule describes how readily its electron cloud will be distorted by an external stimulus like an electric field, for instance, that introduced by the process of light impinging on the molecule. Raman scattering is thus possible because the polarizability of the molecule changes during its vibrational motion. In other words, Raman active means the oscillation of the atoms when vibrating causes a change in the electron cloud of the molecule. If the vibration causes a temporary distortion of the electron cloud, which changes the polarizability, then the molecule can interact with incident light. This interaction results in the scattering of the photon, and the energy dispersion of this scattering process contributes to the formation of what we call the Raman spectrum. This rule means that only those vibrational modes that change the polarizability will cause Raman scattering. Some vibrational modes, for example those involved in bond stretching and bending, will induce an electron cloud displacement with bond compression or elongation. These modes are Raman active as they result in a change in the polarizability of the molecule. Conversely, vibrational modes that lead to no change in the electron cloud or the molecular polarizability are Raman inactive. For example, symmetric stretching or bending motions in which the overall electron distribution remains invariant would have no observable Raman scattering.

## 11.4 Symmetry of Vibrational Modes

Another important selection rule for Raman scattering is the symmetry of the molecular vibrations. Whether a vibration can induce change of

the polarizability detectable by the incident light is determined by the symmetry with respect to the vibrational modes of the molecule. To determine whether a vibration will be Raman active, you need to analyze the molecular symmetry. Symmetry analysis is a method used, passed on the group theory (branch of mathematics) around the symmetry analysis of molecules. Group theory assists in classifying the symmetry properties of different molecular vibrations, including how they behave for rotations and reflections. For a molecule, by applying group theory to its vibrational modes, one can ascertain which modes will give rise to a change in polarizability and which will not. To be Raman active, then, the vibrational mode must belong to a specific symmetry species that permits it to couple with the incident light. So the vibration has to produce a change in polarisability that can couple with the electric field of the incoming light. Whether this interaction can happen, depends on the symmetry of the vibration. A particular example of this arise when a certain symmetry species within a molecule's vibrational modes are Raman active, as the change in polarizability they induce is symmetry allowed. Take any simple molecule, for example carbon dioxide ($CO_2$), a linear molecule which possesses high symmetry. Vibrational modes of the molecule can be grouped based on their symmetry properties. $CO_2$ bending modes are Raman active, as they involve change in the polarizability of the molecule. On the other hand, some modes e.g. symmetric stretching mode does not change polarizability and would be Raman inactive.

## 11.5 Energy Conservation

As with all spectroscopic techniques, Raman scattering adheres to the law of conservation of energy, which dictates that the sum of energy in the system before and after a scattering event must remain constant. As a result, the energy difference between the starting and ending slots of the molecule is preserved throughout the scattering process. For example, in Raman scattering, energy conservation means that the energy difference between the incoming photon and the outgoing

photon must equal the energy of the molecular vibration This is both Stokes and anti-Stokes scattering events.

## Stokes Scattering

Raman scattering in the form of Stokes scattering is one of the two main processes of Raman spectroscopy. That's when the incident photon interacts with the molecule and passes on part of its energy, making the molecule move to a higher vibrational state. Consequently, the scattered photon leaving the molecule will have lower energy than the incoming photon. This energy loss of the photon matches the energy difference between the initial and final vibrational states of the molecule, representing the signature of Stokes scattering. Stokes scattering proceeds as follows:

Molecule sits in its ground vibrational state. When one of the laser photons hits the molecule, the photon transfers some of its energy to the molecule, exciting it to a higher vibrational state.

1. Energy Transfer: The energy gap between the ground state and excited vibrational state, is transferred from the photon to the molecule. Because of this interaction, the photon loses energy.
2. The Scattered Photon: After this interaction, the photon leaving the molecule as a scattered photon has lower energy than the incoming photon. The difference in energy between the incident and scattered photons is associated with the vibrational transition in the molecule.
3. Stokes Shift: The difference in energy between the scattered and incident photon leads a shift toward longer wavelength (lower frequency) in the Raman spectrum. This characteristic is known as the "Stokes shift," and it is a hallmark of Stokes scattering.

That gives the Stokes shift information on the vibrational modes of the molecule. Scientists analyze the wavelength or frequency of the Stokes-

scattered light, it gives them information on molecular structure and the chemical composition of the sample and which types of molecular vibrations are taking place in the sample. Moreover, temperature, concentration, and the type of molecular interactions also determine the magnitude of Stokes peaks in the corresponding Raman spectrum.

**Anti-Stokes Scattering**

Anti-Stokes scattering, the opposite of Stokes scattering, takes place when the photon emitted has more energy than the incoming one. This is when the molecule is first in an excited vibrational state. In this case, the molecule loses energy to the incident photon, so the photon scatters at a higher energy than it originally had. The increase in energy of the emitted photon corresponds to the energy difference between the vibrational ground state and the excited vibrational state of the molecule, and appears as an anti-Stokes shift in the Raman spectrum.

Anti-Stokes scattering process can be explained as follows:

Excitation of the molecule: Not in its ground vibrational state. In contrast, it is already in an excited vibrational state (above the ground state). This happens because of former thermal excitation, in which the molecule has absorbed from the environment energy and in a higher vibrational state.

1. Photon to Energy Transfer: When photon hits the molecule, energy from the molecule is transferred to the photon The reason is that the scattered photon has a greater energy than the incoming photon.
2. The scattered photon: as a consequence of scattering, it has more energy than the incident photon, and the energy difference between the incident photon and the scattered photon corresponds to the energy difference between the initial and final vibrational states of the molecule.

3. Anti-Stokes Shift: The subsequent increase in energy of the scattered photon causes a shift in the Raman spectrum towards shorter wavelengths (higher frequency), known as the "anti-Stokes shift."

Anti-Stokes scattered light is less intense than Stokes scattered light in general. This is because at room temperature, there are fewer molecules in higher vibrational states than in the ground state, so there are less chances for anti-Stokes scattering to happen. For example, the relative intensities of the Stokes and anti-Stokes peaks can reveal the sample temperature, since the population of molecules in excited vibrational states is a function of the temperature.

## 11.6 Raman Spectroscopy: Stokes and Anti-Stokes Scattering

Stokes and Anti-Stokes scattering are central to the Raman effect, which is utilized in Raman spectroscopy to ultimately deduce vibrational information about the molecule. Raman spectrum generally has Stokes and anti-Stokes components, with Stokes scattering is usually the larger component of this spectrum due to the larger number of molecules in the vibrational ground state.

**Related effects of temperature and the Stokes/Anti-Stokes Intensity Ratio**

Thermodynamic information can be gleaned from the ratio of the intensities of the Stokes vs. anti-Stokes peaks. The distribution of molecules in various vibrational states (anti Stokes and Stokes scattering) follows a Boltzmann distribution, and there is always a population in an excited vibrational state, but it decreases with temperature. As a result, at higher temperatures, the intensity of anti-Stokes peaks increases as a larger fraction of molecules reside in excited states. At lower temperatures, more molecules can be found in the ground vibrational state, giving rise to Stokes peaks. Depending on the energy levels of the vibrational states and the temperature of the

system, the ratio of the Stokes to anti-Stokes peak intensity can be related to the temperature of the sample and, therefore, the relative intensities may be used for such a measurement.

**Stokes and Anti-Stokes Scattering Applicability**

Molecular Identification: The detailed vibrational spectra acquired from both the Stokes and anti-Stokes scattering are utilized in molecular identification. This result in peaks that represent the absorbance of the various bonds within a compound, and, by studying the displacements and strengths of these peaks, scientists can identify the chemical bonds and functional groups within a sample.

1. Material identification: The Stokes and anti-Stokes shifts present in the Raman spectra are extremely helpful in identifying the materials whether polymers, nanomaterials, thin film, etc. The spectral characteristics help to probe into the molecular structures, chemical compositions as well as mechanical properties of the materials.

2. Thermal Analysis: As indicated previously, the relative intensities of the Stokes and anti-Stokes peaks are temperature sensitive. By well understanding these intensities, scientists can learn about the thermal properties of materials and study the thermally induced molecular vibrations.

3. Pharmaceutical and biomedical applications: Raman spectroscopy, especially the usages of Stokes and anti-Stokes scattering, finds potential application in the pharmaceutical industry for the analysis of drugs, monitoring of purity of the pharmaceutical products, and studies of drug–biomolecule interactions. At the same time, within biomedical research, Raman spectroscopy benefits tissue and cell studies, offering precise chemical profiles that improve disease detection or biological processes monitoring.

Environmental sensing: Raman spectroscopy, owing to the Stokes and anti-Stokes scattering, is also employed for environmental monitoring, such as the identification of pollutants and greenhouse gases. Both scattering techniques allow for the sensitive detection of numerous chemical compounds in air, water, and soil matrices,

Check Your Progress

Q1. What is the principle of Raman Spectroscopy?

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Q2. Discuss the advantages of Raman Spectroscopy .

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## 11.7 Summary

Raman Spectroscopy is a vibrational spectroscopic technique based on inelastic scattering of monochromatic light (usually from a laser). When light interacts with a molecule, most photons undergo Rayleigh scattering (elastic), but a small fraction undergoes Raman scattering (inelastic), leading to frequency shifts corresponding to molecular vibrational energies. Raman active vibrations occur when there is a change in polarizability of the molecule.

The technique complements infrared spectroscopy since some vibrational modes that are IR-inactive can be Raman-active. The Raman spectrum provides information about molecular structure, chemical bonding, and symmetry. Modern Raman instruments use lasers, monochromators, and sensitive detectors (CCD). Raman spectroscopy finds applications in chemistry, physics, biology, pharmaceuticals, materials science, and forensic analysis.

## 11.8 Exercises

### 11.8.1 Multiple Choice Questions

1. The Raman Effect is based on:
   a) Absorption of light
   b) Inelastic scattering of light
   c) Elastic scattering of light
   d) Emission of radiation
   Answer: b) Inelastic scattering of light

2. Raman lines appear due to:
   a) Change in dipole moment
   b) Change in polarizability
   c) Change in magnetic moment
   d) Change in electron spin
   Answer: b) Change in polarizability

3. Which of the following is NOT true about Raman spectroscopy?
   a) It uses monochromatic light source
   b) Raman scattering is weaker than Rayleigh scattering
   c) Water is a strong Raman scatterer
   d) It detects changes in dipole moment
   Answer: d) It detects changes in dipole moment

4. The central line in a Raman spectrum corresponds to:
   a) Stokes line
   b) Anti-Stokes line
   c) Rayleigh scattering
   d) Resonance Raman scattering
   Answer: c) Rayleigh scattering

5. The selection rule for rotational Raman spectra is:
   a) $\Delta J = \pm 1$
   b) $\Delta J = \pm 2$
   c) $\Delta J = 0$
   d) $\Delta J = \pm 3$
   Answer: b) $\Delta J = \pm 2$

### 11.8.2 Short Answer Questions

1. Define Raman Effect.

2. Differentiate between Stokes and Anti-Stokes lines.

3. What is the selection rule for Raman rotational spectra?

4. Why is Raman Spectroscopy considered complementary to IR spectroscopy?

5. State one major application of Raman Spectroscopy in material science.

### 11.8.3 Long Answer Questions

1. Explain the principle of Raman Spectroscopy and distinguish it from Infrared Spectroscopy.

2. Discuss the instrumentation of Raman Spectroscopy with a neat labeled diagram.

3. Derive the selection rules for rotational Raman spectra of diatomic molecules.

4. Explain Stokes and Anti-Stokes Raman scattering with energy level diagrams.

5. Describe the applications of Raman Spectroscopy in chemistry, biology, and material sciences.

### 11.9 References and Suggested Reading

1. Atkins, P., & Friedman, R. (2011). Molecular Quantum Mechanics (5th ed.). Oxford University Press, Oxford, UK
2. Hollas, J. M. (2004). Modern Spectroscopy (4th ed.). John Wiley & Sons.
3. Housecroft, C. E., & Sharpe, A. G. (2012). Inorganic Chemistry (4th ed.). Pearson Education Limited, London, UK.

## Unit 12 : Advanced Raman Techniques

**Structure**

### 12.0 Objectives

1. To understand the fundamental principles and quantum theory underlying Raman scattering.

2. To explore advanced instrumentation techniques such as Fourier Transform Raman, Surface-Enhanced Raman Spectroscopy (SERS), and Resonance Raman Spectroscopy.

3. To analyze Raman selection rules, polarization effects, and intensity distributions in detail.

4. To develop the ability to apply Raman spectroscopy in advanced fields such as nanomaterials, catalysis, biological systems, and surface science.

### 12.1 Introduction

Raman Spectroscopy, a  technique that measures the scattering of light from gas molecules (due to molecular vibrations), is now an invaluable tool in a multitude of different fields from material science and chemistry to biology. Conventional Raman spectroscopy offers a deep insight into molecular vibrations and interactions, whereas advanced Raman techniques improve the sensitivity, resolution, and scope of applications of this technique. These advanced techniques include Resonance Raman Spectroscopy and Coherent Anti-Stokes Raman Spectroscopy (CARS), both of which provide unique advantages for probing molecular structures and dynamics. These  approaches extend the limits of conventional Raman spectroscopy, giving investigators the ability to see fine details in materials that might be difficult to analyze otherwise.

**Resonance Raman Spectroscopy**

Resonance Raman Spectroscopy (RRS) - RRS is an advanced Raman technique where the Raman scattering signal is amplified using the resonance effect between the moratilar laser light and target molecule cide transition or vibrations. In fact, the major concept of resonance Raman spectroscopy is that when the frequency of incident light coincides with a molecular electronic transition, the scattering efficiency is significantly enhanced. This resonance effect enhances the intensity of the corresponding spectral features, significantly improving the sensitivity of the detection of those specific vibrational modes, which is the reason why resonance Raman spectroscopy is such a powerful tool, particularly in the analysis of systems that possess any suitably weak or poorly detectable vibrational modes in comparison to other modes, which can hamper study using general Raman techniques. The resonance effect is when the frequency of the incident laser light closely matches an electronic transition of the molecule, causing the system to "resonate." Now when the molecule is placed in the vicinity of the nano-material, the energy of the incoming photon is selectively absorbed and scattered by this molecule, leading to an enhancement of the Raman signal.

**Resonance Raman Spectroscopy and Its Applications**

It is also very important in the study of chromophores, which are molecules that absorb light at specific wavelengths and are accountable for the coloration of biological as well as chemical systems (Raman spectroscopy and its applications). Resonance Raman spectroscopy yields high sensitivity and selectivity because their high-power laser light resonantly excites the electronic transitions of these molecules and allows them to detect even the weak chromophore vibrational modes which are hard to observe by usual Raman spectroscopy. Biological and Biochemical Research: RRS is often used to probe biological systems, such as proteins, nucleic acids, and

metalloenzymes. Many of these biomolecules harbored chromophores or metal centers that can be excited with resonance light, producing enhanced Raman signals that elucidate molecular structure, dynamics, and interactions.

### Benefits of Using Resonance Raman Spectroscopy

Resonance Raman spectroscopy (RRS) is a very powerful and highly labeling free vibrational spectroscopic tool that is based on the enhancement of the Raman scattering cross-section by exciting the system close to an electronic absorption band. This improvement significantly increases the sensitivity and power of Raman spectroscopy and allows it to examine a wider variety of samples from low concentration species to complex biological systems. RRS offers all the access to subtle vibrational features necessary for understanding molecules' complexities on the electronic and dynamical scales by analysing the inelastic scattering of monochromatic light by molecules. Resonance Raman spectroscopy has a number of key benefits, which makes this technique highly relevant both in terms of fundamental research and applied sciences.

### Enhanced Sensitivity

This resonance effect leads to one of the biggest advantages of resonance Raman spectroscopy, an increase in sensitivity. In standard Raman spectroscopy, as scattered light is normally weak, background noise can dominate the Raman scattering signal. However, when we choose an excitation wavelength in resonance with a certain electronic transition of that molecule, the intensity of the Raman scattering increases in orders of magnitude. This improvement is due to the effective coupling of the incident light with the electronic states of the molecule, resulting in an enhanced probability of the Raman scattering from selective vibrational modes. Raman signal enhancement using resonance enables exclusive enhancement of certain vibrational modes, making weak vibrational features detectable that would be

otherwise unobservable in non-resonance Raman spectroscopy. This is especially advantageous when analyzing molecules found in low concentrations, like trace analyses in complex matrices.

## Selective Probing

Resonance Raman has another important advantage that is selective enhancement of the vibrations, which gives to opportunity to probe specific molecular components in multicomponent systems. Since Raman's scattering is weak, the scattering from certain vibrational modes, and be selective and is often used in RRS to identify specific chemical bonds, functional groups, or molecular conformations allowing RRS to be a strong tool for differentiating between components in mixtures or complex biological samples. In case of complex mixtures, we can identify and examine the individual components based on their characteristic vibrational signatures using the technique of resonance Raman spectroscopy. This enables chemists to amplify certain resonances of interest while suppressing others, facilitating the study of the modes of interest relevant to functional groups, e.g., aromatic rings, double bonds (C=C, N=N), or metal-ligand bonds

## Non-destructive Analysis

As with conventional Raman spectroscopy, one of the main advantages of resonance Raman spectroscopy is its non-destructive character. Because resonance Raman spectroscopy is based on scattering of the light from the sample rather than the absorption or emission of photons by the sample, it does not necessitate any chemical alteration or destruction of the sample. Its label-free nature makes RRS extremely useful for studying sensitive or expensive samples such as rare biological specimens, historical artworks, and thin films of modern materials.

In biological applications, resonance Raman spectroscopy minimizes changes to the sample itself, enabling repeated measurements to be made without altering its structure or properties. This is especially crucial in live-cell, tissue or organism studies where the impacts of sample preparation or invasive methods (such as labeling) may alter the native system activity. One those methods, resonance Raman spectroscopy has been widely used to investigate protein-ligand interactions, enzyme catalysis, and even cell biology without perturbing the tested biological system. Because it is non-destructive, resonance Raman spectroscopy can be used for real-time probing of chemical reactions or molecular interactions. The direct observation of a particularly sensitive vibrational transition can yield information about the kinetics of reactions or other critical processes on the fly, opening a door to applications in areas such as drug screening to monitor how a candidate drug scaffold interacts with a biological system without alteration.

**More Spectral Information**

Resonance Raman spectroscopy allows for significantly more spectral detail than traditional Raman spectroscopy. If the excitation wavelength is tuned into resonance with an electronic transition of the molecule, the Raman scattering intensity for this mode is enhanced, as is the resolution of less intense or even hidden modes in ordinary Raman spectra. Such additional modes can yield important information about the molecular structure, electronic properties and dynamics of the system being studied. GaN) to further investigate excited-state dynamics, charge transfer, and electron-phonon coupling within molecular systems. Researchers can gain insights into the electronic structure, including energy levels, electron density distributions, and electronic-vibrational coupling, by examining shifts in spectral wavelengths and reversible or irreversible changes in the intensity of specific vibrational hot spots. This supplementary spectral information is particularly useful in analyzing conjugated systems (e.g., polyenes,

proteins, and nucleic acids) and metalloproteins in which coupling between electronic structure and vibrational characteristics is pronounced.

### Applications in Biological and Medicinal Chemistry

Another area where resonance Raman spectroscopy has shown great potential is in the study of biological and medicinal chemistry, with applications ranging from the study of individual biomolecules to complex biological processes. The unique capability of this technique to selectively enhance certain vibrational modes and to probe molecular structure in multi-component, complex biological systems has made this an invaluable technique for studying proteins, nucleic acids (DNA and RNA), lipids, and drug interactions. The role of resonance Raman spectroscopy in protein studies is very important, given that it is frequently employed at the level of secondary and tertiary structures to assess biologically relevant structural variations, either induced by binding events or enzymatic activity. Additionally, in the field of drug design and pharmacology, resonance Raman spectroscopy has been employed to investigate the binding of small molecules to their targets, including binding to receptors, enzymes, or membrane proteins. Indeed, by selectively enhancing the vibrational modes that are related to either the drug or to the target, researchers can achieve detailed information about the binding site, the binding affinity, and even the conformational changes that drug binding induces. It plays an essential role in modulating the pharmacological properties of drug candidates and elucidating the molecular mechanisms of action of existing therapeutics.

### Applications in the field of materials science

In the field of materials science, resonance Raman spectroscopy is used to investigate semiconductors, nanomaterials, and carbon-based materials, including graphene and carbon nanotubes. The technique

provides valuable insights into the electronic structure and vibrational dynamics of these materials, making it a powerful tool for the characterisation of advanced materials at the molecular level. For instance, in the research of graphene and other carbon nanomaterials, we could study the D-band and the G-band vibrations by employing resonance Raman spectroscopy, which are sensitive to the defects, dopants, and local ordering of the carbon atoms in the specimen. Such tools and techniques provide researchers with detailed information regarding the quality, functionality, and electronic properties of material, all of which is essential for applications in electronics, energy storage, and nanotechnology. In a similar vein, phonon modes and exciton behavior in semiconductors can be probed by resonance Raman spectroscopy, unlocking information about the optical properties of the material, the band structure, and charge transport characteristics. Such information is hugely important for the design of new materials for solar cell, light-emitting diodes (LEDs) and other optoelectronic materials. Resonance Raman spectroscopy (RRS), a well-established technique to study molecular vibrations, provides a significantly improved signal-to-noise ratio by utilizing the resonance between the incident light and the electronic transition of the molecule being monitored . RRS has many advantages when compared to traditional spectroscopic techniques, including greater sensitivity and selectivity of probing but also limitations, including the inability to efficiently study complex molecular systems. These restrictions may lead to reduced applicability of the technique and prevent it from providing adequate and precise structural information in some cases. Importantly, those employing resonance Raman spectroscopy should understand the limitations of the technique and should consider when and how to best apply it, and when other techniques may be better suited for the question at hand.

**Resonance Conditions**

One key drawback of resonance Raman spectroscopy is that the incident light must resonate with the electronic transition of the molecule being studied. The incident photons be absorbed by the molecule through resonance, in which case their energy is close to the energy difference between the ground state and the excited electronic state of the molecule, for this to take place. When the energy of the incident light is not required to resonate with the electronic transition or close to it, the Raman scattering will not be enhanced (no resonance effect will occur), and the collected scattering signal will always be small (or even undetectable). While specificity in term of resonance conditions can be a serious stumbling block, especially for those molecules for which the electronic transitions of interest do not match with the excitation wave-lengths available in laboratory. In these cases, obtainment of improved Raman signals are very hard or even impossible, resulting in weak or insufficient spectral details. Additionally, the resonance conditions can be hard to satisfy, since an experimental step may deal with a complex molecule or a system with many overlapping electronic transitions, which yield ambiguities in spectral interpretation and lower specificity when trying to probe certain vibrational modes. If these means are not available, then we can revert to normal Raman spectroscopy or other spectroscopic techniques that do not provide the same level of sensitivity or specificity as resonance Raman does. Consequently, this hampers the general applicability of RRS for all the molecules or systems, particularly when the resonance conditions are challenging to satisfied.

## Overlapping Signals

Resonance raman spectroscopy can show some overlapping signals limitations, especially when the peaks related to the enhanced electronic transition show such an intense dominance on the spectrum. This effect is known as resonance Raman scattering and it dramatically increases the intensity of the scattered radiation from particular bonding modes close to the electronic transition of the molecule. This is a useful improvement, but it can lead to the situation where certain vibrational modes are dominating over others, which can happen if the studied molecule has several vibrational modes with close in energy. This creates challenges particularly in cases where the vibrational modes are closely spaced or when the signal from the primary electronic transition drowns out the vibronic transitions.

### Bioreactor Equipment at Commercial  Scale

Although resonance Raman spectroscopy is more sensitive than normal Raman  spectroscopy in many cases, the resonance effect is also very sensitive to temperature, solvent effects, and impurities. Variations in these  parameters can alter both the energy of the electronic transitions, which may result in changes to whether the resonance conditions are satisfied. Such dependence on the experimental environment can lead to difficulty in obtaining reproducible results in different conditions, particularly in heterogeneous or dynamic materials. This would change the resonance conditions if the solvent environment is influencing the electronic transition of the molecule, that would not be in conformance with the intensity and profile of the Raman peaks. Likewise, temperature changes can affect the vibrational frequencies and electronic states of the molecule, and therefore the resonance Raman spectrum. In the presence of biological or complex materials, movement and fluctuations in the surrounding environment can lead to spectral features to shift or broaden, thus making it difficult to interpret what is actually  being probed in the measurement. In order to minimize these challenges, researchers usually go to painstaking lengths to

control the experimental conditions temperature, choice of solvent, sample purity, etc. Nonetheless, the environmental sensitivity of resonance Raman spectroscopy finally presents an important caveat in systems facing dynamic or intermittent conditions and to the best of our knowledge all this has not been addressed so far.

## Instrumentation and Cost

Resonance Raman spectroscopy necessitates specialized instrumentation to facilitate the appropriate resonance conditions, such as tunable lasers with specific excitation wavelengths that correspond to the electronic transitions of the molecular species being studied. Typically, this specialized equipment is costly and may not be present in common laboratory provisions. So the lack of such instruments may restrict the widespread application of the technique, for example in labs with limited resources or that do not often require high-resolution vibrational spectroscopy. Resonance Raman spectroscopy often demands elaborate experimental setups beyond just the price of the laser systems and detectors, in order to obtain the desired excitation wavelengths and preserve stable experimental circumstances. This could involve highly controlled conditions for the sample, such as stabilizing at a specific temperature or ensuring proper alignment of the sample with the laser beam. The extra demands of resonance Raman experiments could add complexity and expense, limiting its adoption in not so reasonable disciplines or some exploration. Furthermore, resonance Raman spectroscopy can depend on knowledge of how to obtain specialized instrumentation, interpretation of complex spectra, and the expertise of resonance enhancement. This specialized knowledge and skill set not only require thorough training but also may pose challenges for researchers who are not experienced with the technique, restricting its use in various research domains.

## Restricted to Molecular Systems with Available Electronic Transitions

Resonance Raman spectroscopy works best on molecules that have electronic transitions accessible to the excitation light. Not all molecules do, however, or have such fast and well-defined electronic transitions within reach of the excitation laser. For instance, larger, more complex molecules or molecules that do not have a clear absorption characteristic in the visible or ultraviolet (UV) spectral region may not lead to resonance enhancement and thus make RRS less effective for such systems. For a molecule with electronic transitions that are not rendered in the range of available lasers for excitation or with low energy transitions (instead of a high-energy former resonance Raman spectroscopy could not be used or can provide very little information. For example, small or non-aromatic molecules, in addition to having weak electronic transitions, may not experience enough resonance enhancements to be useful as spectral data.

While it allows for significant visualizations of the vibrational modes of small and medium-sized molecules, resonance Raman spectroscopy is less suited to study large or highly complex systems, such as large proteins, nucleic acids, or supermolecular assemblies. This limitation can primarily be attributed to the complexity of the spectra produced by large molecules, which can have an extensive number of overlapping vibrational modes. Under such resonant conditions, the spectrum can become quite complex, with many enhanced and challenging-to-assign peaks, particularly when the sample contains clinically novel combinations of interacting components. The ER peaks in large bimolecular-like proteins can correlate with contributions of individual parts of the molecule, making it difficult to separate

individual vibrational modes. Despite resonance Raman spectroscopy yielding some useful structural information on certain aspects of large molecules (such as metal coordination or specific functional groups), it is not adequate for obtaining a global structural view of the entire macromolecule. To paint a more complete picture of the molecule's structural and dynamic character, researchers typically combine resonance Raman spectroscopy with numerous other techniques, including nuclear magnetic resonance (NMR) spectroscopy, X-ray crystallography or cryo-electron microscopy (cryo-EM).

**Challenges in Identifying Enumerated  Vibrational Modes**

One more drawback of resonance Raman spectroscopy remains the difficulty in assigning the vibrational modes to specific molecular features or  functional groups, especially under resonance conditions in the presence of many overlapping transitions. For resonance condition, the enhanced Raman peaks give rise to a congested spectrum, resulting in difficulties in resolving and identifying individual vibrational modes to bonds or molecular features. This is especially the case for molecules with  complicated electronic structure or multiple functional groups. Since vibrational peaks sometimes overlap and provide complicated signals, researchers can be going for advanced computational methods, like density functional theory (DFT),  to help in making assignments. Even so, assigning vibrational  modes remains a laborious process, especially for larger molecules or systems with complex electronic spectra, even with these powerful techniques.

**12.2 CARS Coherent Anti Stokes Raman Spectroscopy**

Micro-Raman or Coherent Anti-Stokes  Raman Spectroscopy (CARS) is another advanced technique, which offers high spatial resolution and high: Coherent Anti-Stokes Raman Spectroscopy. CARS utilizes two laser fields, commonly called the pump and Stokes beams, to drive non-linear Raman  scattering. The unique factor of CARS is that it produces

an anti-Stokes signa- was a coherent photon released at a frequency higher than that of both pump and Stokes photons.

## Principle of CARS

[CARS] During CARS, multiple radio-electromagnetic fields are non-linearly interacting with a molecule, causing non-linear bi-Ramane scattering. These laser frequencies can be adjusted, such that the difference between pump and Stokes lasers makes up a specific fundamental vibrational frequency of the molecule. This condition causes a coherent coupling between the fields and the molecule, leading to the emission of an anti-Stokes signal which encodes information on the vibrational modes of the molecule. The anti-Stokes generated in CARS is, of course, much stronger than in conventional Stokes Raman scattering because the CARS generation comes from coherent rather than incoherent processes. This results in a great improvement on the signal-to-noise ratio and makes CARS especially suitable to study low-concentration samples or weak Raman scattering materials. Unlike traditional Raman spectroscopy, CARS does not rely on the detection of the scattered photons from the incident light. The anti-Stokes signal may, however, be directly accessed, allowing for a wider and enhanced intensity for the spectral assessment. This also enables CARS to be applied for time-resolved experiments, where the pump and Stokes pulses are temporally aligned to investigate dynamic phenomena.

## Applications of CARS

Biological and cellular imaging One of the most potent applications of CARS is certainly detailed biological imaging. Because of the large amplification of the anti-Stokes signal, CARS is particularly well suited for imaging biological tissues and cells without fluorescent labels. The technique, which does not rely on contrast agents, enables the visualization of biological structures such as lipid droplets or protein assemblies through their unique vibrational signatures. Furthermore, the use of CARS to probe the localization of lipid

molecules and other biomolecules has advanced our understanding of cellular processes including lipid metabolism, membrane dynamics, and protein-lipid interactions. Chemical and Material Characterization: CARS is extensively used to characterize nanomaterials, polymers, and nanostructures. The improved Raman signal means that tiny amounts of material are necessary, enabling researchers to investigate the molecular structure, chemical makeup and surface characteristics of nanomaterials with an unparalleled level of accuracy. Environmental and surface studies CARS is also important in the study of surfaces and interfaces. The technique is sensitive to surface vibrational modes, making it a powerful probe of surface chemistry, thin films, and coatings. For such low concentration of detection, when environmental monitoring is concerned to detect trace gases or other pollutants, also SBT–CARS can play this role. Time-Resolved CARS (TR-CARS); One of the powerful advantages of CARS lies in its capacity for real-time observation of dynamic processes.

**Enhanced Signal Strength**

This provides the most important benefit of Coherent Anti-Stokes Raman Spectroscopy (CARS); the ability to produce an anti-Stokes signal which is orders of magnitude stronger than the regular Raman scattering signal. In normal Raman spectroscopy, the obtained Raman scattering signal is a combination of Stokes and anti-Stokes component, however the Stokes signal is significantly stronger because in the populations of the molecules the energy is statistically distributed. In contrast, when the incident photons interact with the molecules to reach a virtual energy state before decaying to the high energy anti-Stokes photon. In CARS, the generation of the anti-Stokes signal can be phase-matched and coherent between the incident laser fields resulting in a much higher intensity of the anti-Stokes signal compared to normal Raman scattering (3). This increase happens because CARS is a four-wave mixing process that involves the interaction of three laser

light beams: a pump beam, a Stokes beam, and a probe beam. When these different beams struck the sample, they interfere coherently and generate the anti-Stokes signal. This enhancement of the signal enables the detection of low concentration species or weak vibrational modes, which would be hard to detect in traditional Raman spectroscopy. Such increased signal in CARS allows to enhance the sensitivity of the technique and render the CARS approach feasible for studies of low-molarity Raman active species. This signal enhancement and detection capability make CARS a highly sensitive technique for molecular identification, particularly in biological and chemical systems with potentially low target molecule concentration. This advantage is especially useful in applications where the samples are dilute, such as in analyzing small amounts of compounds in biological tissues, environmental samples or chemical processes.

**Non-linear Process**

CARS is based on a non-linear optical process, which accounts for several advantages regarding sensitivity and signal-to-noise ratio. CARS is a non-linear process, unlike linear Raman scattering, where signals are generated in proportion to the intensity of incoming light. This nonlinear behaviour leads to a signal generation that is more efficient, producing a stronger anti-Stokes signal than Raman scattering. This increased efficiency is especially useful in studies of weak Raman-active modes or low amounts of analytes. The ultra-sensitive and non-linear nature of CARS also indicates a considerably higher sensitivity compared to conventional Raman spectroscopy. The nonlinear character of this process leads to the brightness of the signal being proportional to the intensity of the laser fields being used, resulting in a signal that can be much weaker and still detectable than would be possible in standard Raman experiments, where all transmitted intensity is assumed lost to noise.

**Label-free Imaging**

A crucial benefit of CARS is that it can perform label-free imaging of biological tissues and cells, thus, it is an important technique for medical and biological investigations. Label-free imaging allows you to obtain detailed information directly from the sample without the need for fluorescent/covalent markers, which are so widely used in another imaging technique like fluorescence microscopy. The unique property of imaging without any extrinsic labels is especially powerful in studies of biology, where fluorescent dyes or chemical probes can sometimes perturb the biological system being studied. In biological tissues, CARS can selectively image specific molecular vibrations, such as those in lipids, proteins, and nucleic acids, and does not have any need for labeling or staining beforehand. CARS microscopy has been applied to study the dynamics of membrane lipids and the localization of proteins and other biomolecules. Thus, this capability for label-free imaging delivers a more accurate depiction of the native condition of the sample, as well as circumventing potential influence from the labels themselves. Furthermore, CARS allows the study of dynamic processes in living cells and tissues in real time. Now, CARS, unlike other imaging technologies, does not need to label or dye a biological system, which can disrupt the biological system; instead, it can take images of the cellular structures and molecular dynamics in their natural environment.

## 12.3 High Spatial and Temporal Resolution

CARS additionally shows high temporal and spatial resolution that allows it to excel as an imaging tool at the microscale and to carry out real-time analyses of dynamic processes. The spatial resolution of CARS is maximally comparable to other advanced imaging approaches, including fluorescence microscopy, and can be tuned so that detailed cellular or subcellular images can be acquired. What makes CARS particularly powerful is its high spatial resolution, which

is a result of the finely focused nature of the laser beams used and the coherence of the CARS process itself. High spatial resolution is especially advantageous in biological studies, where the structure and arrangement of cells or tissues are of great interest. CARS can generate high-resolution images of cellular organelles (membranes, mitochondria, and lipid droplets) and track dynamic molecular changes at higher spatiotemporal scales, during several biological phenomena, including cell division, migration, and differentiation. It allows researchers to observe the molecular dynamics of live cells in real-time without the use of exogenous labeling or staining, making it an ideal experimental tool for cell biology and biochemistry. CARS provides not only a high spatial resolution, but also a great temporal resolution (Jansen et al., 2009) that allows monitoring dynamical processes in situ. Such time-resolved ability is essential for the investigation of ultrafast molecular dynamical events, e.g., conformational changes of proteins, or chemical reactions in which the temporal evolution of the system is central to dissect the microscopic mechanism.

**Complex Setup**

CARS is a powerful technique, but one of its biggest challenges is the complexity of the experiment. While Raman spectroscopy generally has only one laser source with a simple configuration to detect the scattered light, CARS depends on a more complex system with multiple laser beams. CARS in particular requires two synchronized sources of lasers, known as the pump and the Stokes lasers. Specifically, this requires careful alignment and maintenance of these lasers to ensure their frequencies are appropriate for obtaining the necessary resonance conditions for producing anti-Stokes signals. The need for two precisely synchronized lasers makes the experimental setup much more difficult. It requires both lasers to be meticulously tuned to the right frequencies and their temporal and spatial overlap controlled in order to produce the coherent anti-Stokes signal. It can be technically challenging to synchronize this accurately, and high-

precision equipment and laser optics knowledge is needed to do so. Moreover, the anti-Stokes signal intensity greatly depends on the timing and phase of the pump and Stokes pulses relative to each other. Such a discrepancy in the timing leads to ineffective signal production, or worse, no anti-Stokes signal at all.

Another limitation to the CARS methodology is the limited spectral range available which, due to the inherent properties of the laser sources, it can not be extended to any wavelength. In reality, the pump and Stokes lasers need to be tuned to certain frequencies to meet the resonance condition for the respective non-linear process, resulting in limited vibrational modes to study effectively. In order for CARS to work the energy gap between the pump and Stokes lasers must correspond to the vibrational frequencies of the molecule being studied, and this criteria can limit the types of molecules, or materials to be studied. Nevertheless, and although CARS is also a powerful technique for probing specific vibrational modes, particularly those located in the fingerprint region (e.g., C-H, O-H, and N-H bending modes in biological systems), the range of sequences or available vibrational modes remains more limited than those possible using standard Raman spectroscopy. Unlike resonance techniques, Raman spectroscopy can interrogate a wider range of vibrational modes in a single experiment. However, the absorption region of CARS is constrained by the laser sources used to generate it, making it less ideal for probing the entire spectrum of vibrational modes in any sample. Furthermore, since the pump and Stokes wavelengths must be chosen and optimized specifically for the sample being studied, CARS often requires different laser setups in order to analyze different molecule types. Reducing these effects reduces the ranges of vibrational modes that can be studied using the same laser source, forcing researchers to either manipulate or switch laser sources depending on the modes that they are interested in studying. Although, the commercial Raman spectroscopy has high versatility because it can access a large number

of molecular vibrations without the excitation light being in resonance and can cover a wide range of vibrational frequencies simply by changing the laser source. Similarly, in biological and chemical samples the selected laser wavelengths may in some instances overlap with the intrinsic absorption features of the sample which can result in interference.

**Interference due to Signal Overlap**

Another important limitation of CARS consists in signal overlap and interference with other non-linear processes. CARS is an extremely sensitive technique that produces very intense anti-Stokes signals, but the nonlinear nature of the technique can also lead to contamination from unwanted signals. CARS spectra, in particular, can become contaminated by other nonlinear processes that occur, such as four-wave mixing (FWM). FWM is an interacting with four laser beams process, through which new signals are generated and may compete with the CARS signal. This ring can impede the reading of the spectra and hamper the isolation of the CARS signal to other background contributions. In some cases, these unwanted signals can overwhelm the CARS spectra and mask the vibrational information of interest. In spectra, the affected (composed of other peaks in addition to those from the nonlinear processes e.g., shown for FWM, but that can also proceed via scattering of the pump and/or Stokes beams itself), making it quite difficult to obtain bona fide molecular information. This is often an issue in coarse-grained models of complex systems with many vibrational modes or samples that strongly scatter laser beams. (exact figure depends on experimental conditions) to alleviate signal overlap and interference. This may require researchers to employ advanced optical filtering techniques to discriminate the CARS signal from background noise. Moreover, depending on the molecules and their concentrations, applying some spectral analysis methods could also be necessary in order to deconvolve the spectra and separate the signals of interest.

**Check Your Progress**

Q1. What is phtoacoustic spectroscopy?

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Q2. Discuss the advantages of Raman Spectroscopy.

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## 12.4 Summary

Photoacoustic spectroscopy (PAS) is a sensitive analytical technique based on the photoacoustic effect, where absorbed modulated light causes localized heating and generates acoustic waves due to thermal expansion.

These sound waves are detected using microphones or piezoelectric sensors. PAS is especially useful for studying opaque, solid, or highly scattering samples, and it enables depth profiling and detection of trace gases.

It offers advantages such as minimal sample preparation, non-destructive analysis, and applicability to condensed phases. Raman spectroscopy, on the other hand, is based on the inelastic scattering of monochromatic light, typically from a laser, where the scattered light exhibits energy shifts corresponding to vibrational, rotational, or other low-frequency transitions in molecules. This technique provides a molecular fingerprint of the sample and is widely used for both qualitative and quantitative analysis. Unlike infrared (IR) spectroscopy, Raman is effective for symmetric molecular vibrations and is ideal for aqueous samples since water produces a weak Raman signal. Raman spectroscopy can be enhanced using techniques like Surface-Enhanced Raman Spectroscopy (SERS) or Resonance Raman Spectroscopy to improve sensitivity. Both PAS and Raman are complementary

spectroscopic tools used in chemical, biological, environmental, and materials research, offering non-invasive and highly specific molecular information.

## 12.5 Exercises

### 12.5.1 Multiple Choice Questions

1. Photoacoustic Spectroscopy (PAS) is based on which of the following principles?

a) Absorption of light and emission of fluorescence.
b) Absorption of light and conversion to heat, leading to pressure fluctuations.
c) Scattering of light and detection of reflected radiation.
d) Emission of light from excited molecules.

Answer: b) Absorption of light and conversion to heat, leading to pressure fluctuations.

2. In PAS, the acoustic signal is typically detected using:

a) A photomultiplier tube.
b) A microphone or piezoelectric transducer.
c) An electron multiplier.
d) A photodiode.

Answer: b) A microphone or piezoelectric transducer.

3. What is the Raman effect?

a) The absorption of light by a molecule.
b) The scattering of light by a molecule, where the scattered light has a different frequency than the incident light.
c) The emission of light by a molecule.
d) The reflection of light by a molecule.

Answer: b) The scattering of light by a molecule, where the scattered light has a different frequency than the incident light.

4. Raman scattering is typically observed when using:

a) Microwave radiation

b) Infrared radiation

c) Visible or near-infrared radiation

d) X-ray radiation

Answer: c) Visible or near-infrared radiation

5. Raman spectroscopy is used to study:

a) Electronic transitions

b) Nuclear magnetic resonance

c) Molecular vibrations and rotations

d) Atomic energy levels

Answer: c) Molecular vibrations and rotations

6. What is the degree of freedom for a molecule with N atoms?

a) 2N

b) 2N + 1

c) 3N

d) 3N + 1

Answer: c) 3N

7. In Raman scattering, what is not conserved?

a) Total energy

b) Momentum

c) Kinetic energy

d) Electronic energy

Answer: c) Kinetic energy

8. Which of the following is NOT a component of a typical Raman spectrometer?

a) Laser source

b) Monochromator

c) Detector

d) Electromagnet

Answer: d) Electromagnet

### 12.5.2 Short Answer Questions

1. What is the basic principle of Photoacoustic Spectroscopy (PAS)?

2. How does PAS help in chemical and surface analysis?

3. Explain the difference between Stokes and anti-Stokes Raman scattering.

4. What are the selection rules for Raman spectroscopy?

5. How does the mutual exclusion principle apply to molecules with a center of symmetry?

6. What is the advantage of Resonance Raman Spectroscopy over conventional Raman techniques?

7. How does Coherent Anti-Stokes Raman Spectroscopy (CARS) enhance spectral resolution?

8. Why is Raman spectroscopy often used for studying inorganic compounds?

9. How does the Raman effect differ from Rayleigh scattering?

10. What are the main advantages of Raman spectroscopy over infrared spectroscopy?

### 12.5.3 Long Answer Questions

1. Explain the working principle of Photoacoustic Spectroscopy (PAS) and its key applications.

2. Discuss the role of PAS in analyzing condensed and gaseous systems.

3. Compare the classical and quantum mechanical explanations of the Raman effect.

4. Explain in detail the selection rules for Raman spectroscopy and their significance.

5. Describe how the mutual exclusion principle affects vibrational spectra in centrosymmetric molecules.

6. What are the different types of Raman spectra, and how do they arise from molecular vibrations?

7. Explain the principles of Resonance Raman Spectroscopy and how it enhances spectral sensitivity.

8. Describe the mechanism of Coherent Anti-Stokes Raman Spectroscopy (CARS) and its advantages.

9. Compare the instrumentation of Raman and infrared spectroscopy.

10. Discuss the applications of Raman spectroscopy in pharmaceutical, material science, and biological research.

## 12.6 References and Suggested reading

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3. Housecroft, C. E., & Sharpe, A. G. (2012). Inorganic Chemistry (4th ed.). Pearson Education Limited, London, UK.

## Unit 13    Fundamentals of NMR Spectroscopy

13.1 Introduction - Nuclear Spin and Magnetic Resonance
13.2 Objectives
13.3 Chemical Shifts and- Spin Spin Coupling
13.4 Summary
13.5 Exercises
13.6 References and Suggested Reading

### 13.1  Nuclear Spin and Magnetic  Resonance

Nuclear Magnetic Resonance (NMR) spectroscopy is one of the most powerful and commonly used methods in analytical chemistry and biochemistry. It covers the molecular structure, dynamics, and interactions of molecules. NMR spectroscopy is based on the interaction of certain atomic nuclei with an externally applied magnetic field, and the two most commonly observed nuclei are 1H and 13C, which both have a nuclear property known as spin. Nuclear magnetic resonance (NMR) derives from the unique properties of atomic nuclei and their behaviors in the presence of external magnetic fields and radiofrequency (RF) radiation. The following sections will introduce the core of NMR spectroscopy, covering nuclear spin and magnetic resonance before transitioning towards saturation and relaxation, the two mechanisms at the heart of NMR signal generation and information processing.

Nuclear spin is an essential feature  behind NMR spectroscopy. Spin is an inherent property of all atomic nuclei, and is related to their angular momentum. Nuclei with an uneven number of  protons and/or neutrons have a net nuclear spin and thus a magnetic moment. Nuclei  that are used most commonly in NMR spectroscopy, such as hydrogen ($^1$H) and carbon-13 ($^{13}$C), have a nonzero nuclear spin. The spin quantum number (I) determines the magnitude of the nuclear spin, and it can have quantized values that govern how the nuclei respond in a magnetic field. The hydrogen nucleus (proton), as an example, has a spin quantum number I = ½, which  means that it acts like a tiny magnet,

and can take on one of two possible spin states, spin-up ($+\frac{1}{2}$) or spin-down ($-\frac{1}{2}$). These two states correspond to different energy levels when exposed to an external magnetic field on the nucleus. The energy difference across these spin states is small but significant, and it is this difference that is exploited by NMR spectroscopy to produce signals. Nuclei with even numbers of protons and even numbers of neutrons (e.g., carbon-12, oxygen-16) have no nuclear spin- their total spin cancels, giving them no net magnetic moment, which makes them invisible to NMR spectroscopy. In contrast, nuclei with an odd atomic number like $^1$H and $^{13}$C exhibit non-zero spins and can therefore be detected with NMR.

### 13.2 Objectives

1. To understand the fundamental principles of Nuclear Magnetic Resonance (NMR) spectroscopy.

2. To study nuclear spin, magnetic properties, and resonance conditions.

3. To explain the concept of chemical shift and its applications in structural determination.

4. To analyze spin-spin coupling and multiplicity in NMR spectra.

### Magnetic Resonance

The word magnetic resonance describes the property of certain atomi nuclei to absorb and re-emit electromagnetic radiation in a magnetic field. This happens when the energy difference between the nuclea spin states is resonant with the applied radiofrequency (RF) radiation. This means that, when the external magnetic field is applied to sample, the individual nuclear spins interact with the field, and the align themselves to the magnetic field with two possible orientations: parallel (lower energy) or ant parallel (higher energy) to the field. Mor

specifically, this energy difference varies with the strength of the external magnetic field and the nucleus' magnetic moment. In the presence of suitable RF radiation, the nuclei would transition from lower energy to the higher energy state (spin-up to spin-down). Such interaction is very selective. The Larmor frequency is defined by the strength of the magnetic field and the gyro magnetic ratio ($\gamma$), which is a constant that characterizes the correlation between the magnetic moment and the angular momentum of the nucleus. A RF pulse perturbs the equilibrium spin population population from lower energy state to the higher energy state. Once the RF pulse is turned off, these nuclei return to their lower energy state, during which they re-emit RF energy. The emitted RF signal is detected and captured to reveal the chemical environment and interactions of the nuclei.

### Mechanisms of Saturation and Relaxation

At the same time, NMR spectroscopy is based not only on the interaction of nuclear spins with RF radiation but also the saturation and relaxation mechanisms. These processes are important to know in detail to understand how NMR signals are generated and how the system comes back to equilibrium after perturbation.

### Relaxation Mechanisms

This is followed by the relaxation of the excited nuclei back into equilibrium, following the RF pulse is switched off. This process (relaxation) can take place via two basic phenomenon, spin-lattice relaxation ($T_1$), spin–spin relaxation($T_2$).

### Spin-Lattice Relaxation ($T_1$)

Relaxation of spins in a lattice means that in order to achieve thermal equilibrium, the nuclear spins give energy to the neighbor atoms (the lattice) and that is explained. This relaxation process has a time constant $T_1$, known as the longitudinal relaxation time. $T_1$ is the time

constant determining the time taken for the system to return to equilibrium after the RF pulse is applied. $T_1$ relaxation is the process of energy transfer from the spins to the surrounding environment. The rate of this transfer of energy depends on things like the local molecular environment and temperature. Nuclei in more rigid environments usually have longer $T_1$ relaxation times while nuclei in more fluid or less ordered environments typically have faster relaxation times. $T_1$ relaxation time $T_1$ is significant in practice because it determines how long one has to wait between consecutive RF pulses allowing the system to relax back to equilibrium. Shaw et al., 2008During the creation of spectrum in pulsed NMR, in general, waiting times are selected in such a way to guarantee complete recovery of the spin system, which ensures the maximum possible signal-to-noise ratio in the created spectrum.

### Spin-Spin Relaxation ($T_2$)

Spin-spin relaxation describes the decay of phase coherence between nuclear spins in the transverse plane (the plane perpendicular to the magnetic field). This process has a time constant $T_2$, known as the transverse relaxation time. $T_2$ relaxation happens when the individual nuclear spins interact with one another such that the coherence between their magnetic moments decays. While $T_1$ relaxation is associated with the transfer of energy to the surrounding lattice, $T_2$ relaxation arises from interactions between the spins themselves. $T_2$ Relaxation Rates The rate of $T_2$ relaxation is dependent on the molecular environment and, in particular, molecular motion and the interactions amongst neighboring nuclei. Stronger motion of the molecules, on the other hand, leads to faster dephasing of the spins due to random collisions. For stiff systems, we generally observe $T_2$ relaxation is slow. The second important factor is $T_2$ which is crucial in determining the line width of the NMR peaks. Shorter $T_2$ relaxation times imply broader NMR peaks, which degrades the NMR spectral resolution. Thus, in high-resolution NMR experiments, longer $T_2$ times are preferred.

Furthermore, $T_2$ relaxation gives us insight into the molecular dynamics of our sample including diffusion and rotational motion.

### 13.3 : Chemical Shifts and Spin Spin Coupling

The technique Nuclear Magnetic Resonance (NMR) spectroscopy has become an essential tool for the identification and structural elucidation of organic compounds. Two key measurements are chemical shifts and spin-spin coupling among its parameters. These parameters give some insight into the electronic environment around nuclei, especially those of hydrogen and carbon, in a molecule. They enable chemists to identify distinct functional groups, comprehend molecular environments, and ascertain the relative placement of atoms in a molecule. Here, we will discuss the principles of chemical shifts and spin-spin coupling. We will delve into shielding and deshielding and their effects, how chemical shifts are measured and factors affecting chemical shifts. Next, we will find out what spin-spin coupling tell us about the number and nearest-neighboring of the nuclei of the molecule.

**Effects of Shielding and Deshielding**

It is a fundamental concept of shielding and deshielding related to NMR spectroscopy and chemical shifts. Chemical shift is the difference in the resonance frequency of a nucleus compared to a standard reference. This variation is due to the local electronic environment surrounding the nucleus. Electrons around a nucleus can shield a nucleus from the external magnetic field, which lowers the energy to flip the nuclear spin and vice versa. This is related to the shielding effect and hence affects the observed chemical shift.

**Shielding**

When the nucleus is shielded, the electron cloud around the nucleus influences its ability to be penetrated by the external magnetic field.

Electrons themselves generate a weak magnetic field, which opposes the supplied external magnetic field. This causes a reduction in the effective magnetic field experienced by the nucleus, leading to a smaller energy gap between the nuclear spin states. Specifically, over the same energy states, whereas a nucleus with a larger energy gap needs a higher frequency of radiofrequency (RF) radiation to flip between spin states, which results in a downfield shift or a shift toward both higher $\delta$ values (i.e., chemical shift values). The degree of shielding is influenced by multiple factors, including but not limited to the surrounding electron cloud of the nucleus, chemical bonding characteristics and electronegativity of adjacent elements. For example, a proton ($^1H$) attached to a carbon-carbon single bond is more shielded than a proton attached to a highly electronegative atom like oxygen or nitrogen, as the electron density around the proton is pulled towards the electronegative atom in the latter case.

**Deshielding**

On the other hand, in cases where a nucleus is deshielded, the electron cloud surrounding the nucleus is sparse or disrupted through proximity of electronegative atoms (or functional groups). Deshielding is when electron-withdrawing groups (eg, halogens, carbonyl groups or nitrides) remove electron density from the nucleus, making it feel the full effect of the external magnetic field. This increases the energy gap between the nuclear spin states making a transition require a higher frequency of RF radiation. For this reason, deshielded nuclei resonate downfield in the NMR spectrum, at larger $\delta$ values. We commonly see deshielding effects in nuclei that are attached to electronegative atoms or groups. For example, protons on a carbon next to a carbonyl group (C=O) will be deshielded, as the carbonyl is electron-withdrawing, pulling electron density away from the proton, causing it to feel a stronger external magnetic field.

**Measuring chemical shifts**

Chemical shifts are per million (ppm) in practice, which makes it comparable with chemical shifts in other substances because this unit tends to avoid difference in magnetic field and frequency. Tetramethylsilane (TMS) was chosen as the standard reference compound in proton NMR ($^1$H NMR) and assigned a chemical shift of 0 ppm. In the case of carbon-13 NMR ($^{13}$C NMR), the reference is typically $CDCl_3$ (deuterated chloroform), which is assigned an arbitrary shift of 0 ppm for the central carbon atom.
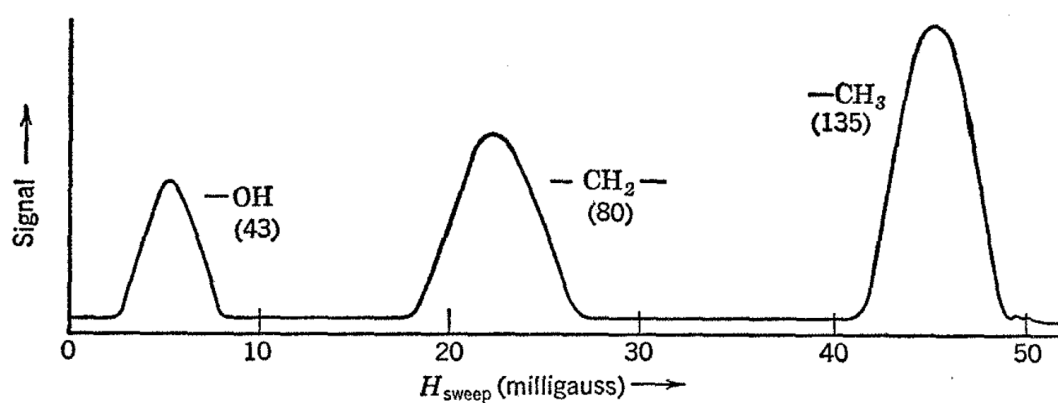


**Fig. 2-1.** Low-resolution NMR spectogram of ethanol protons at 40 Mc and 9,400 gauss. Numbers in parentheses adjacent to each peak are experimental figures for peak areas in arbitrary units.

**Check Your Progress**

Q1. What is NMR Spectroscopy?

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Q2. Discuss the chemical shift.

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## 13.4 Summary

Nuclear Magnetic Resonance (NMR) spectroscopy is a powerful analytical technique based on the magnetic properties of nuclei. Certain nuclei with a non-zero spin, such as $^1H$ and $^{13}C$, absorb radiofrequency radiation when placed in a strong magnetic field, leading to resonance. The resulting signals provide information about the chemical environment of the nuclei.

Key concepts include chemical shift, which reflects electronic shielding around nuclei, and spin-spin coupling, which reveals connectivity and neighboring protons. Relaxation times ($T_1$ and $T_2$) explain the return of nuclei to equilibrium states. NMR spectroscopy is widely applied in structural elucidation, conformational analysis, and studying molecular dynamics. Advanced techniques like 2D-NMR, DEPT, and NOESY enhance resolution and provide deeper structural insights.

## 13.5 Exercises

### 13.5.1 Multipel Choice Question

1. The basic principle of NMR spectroscopy is based on:
   a) Electronic transitions
   b) Nuclear spin transitions
   c) Vibrational transitions
   d) Rotational transitions
   Answer: b) Nuclear spin transitions

2. The most commonly studied nucleus in NMR spectroscopy is:
   a) $^{13}C$
   b) $^{15}N$
   c) $^1H$
   d) $^{31}P$
   Answer: c) $^1H$

3. The unit of chemical shift in NMR is:
   a) ppm
   b) $cm^{-1}$
   c) Hz
   d) Tesla
   Answer: a) ppm

4. Spin-spin splitting in NMR provides information about:
   a) Electronic shielding
   b) Neighboring nuclei
   c) Functional groups

d) Relaxation times

Answer: b) Neighboring nuclei

5. The resonance condition in NMR is satisfied when:
a) Radiofrequency matches the energy difference between nuclear spin states
b) Infrared radiation is absorbed
c) The nucleus relaxes to the ground state
d) Magnetic shielding is removed

Answer: a) Radiofrequency matches the energy difference between nuclear spin states

**13.5.2 Short Answer Questions**

1. Define chemical shift and explain its significance in NMR.

2. What is nuclear spin, and why is it important in NMR spectroscopy?

3. Explain the difference between shielding and deshielding effects.

4. What are relaxation processes ($T_1$ and $T_2$) in NMR?

5. State two main applications of NMR spectroscopy in chemistry.

**13.5.3 Long Answer Questions**

1. Explain the principle of NMR spectroscopy and derive the resonance condition.

2. Discuss chemical shift in detail. How does it help in identifying functional groups?

3. Describe spin-spin coupling and explain how multiplicity patterns are determined using the (n+1) rule.

4. Explain the working of an NMR spectrometer with a neat block diagram.

5. Discuss the applications of NMR spectroscopy in structural elucidation of organic molecules with examples.

## 13.6 References and Suggested Reading

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2. Hollas, J. M. (2004). Modern Spectroscopy (4th ed.). John Wiley& Sons, Hoboken, New Jersey, USA

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**Structure**

SPECTROSCOPY - I

## 14.1 Introduction

The chemical shift scale is normalized to TMS (or other reference compounds) and is in parts per million (ppm) scale. Since the scale is independent of the operating frequency of the NMR at which measurements are being made, the ppm scale allows for the comparison of chemical shifts from different NMR instruments.

The chemical shift ($\delta$) is defined as:

$$\delta = \frac{\text{Frequency of sample signal} - \text{Frequency of reference signal}}{\text{Operating frequency of the spectrometer}} \times 10^6 \text{ ppm}$$

Using this formula, the value of chemical shift is not dependent on the operating frequency of the spectrometer, allowing spectra from different machines to be compared.

### Types of NMR Spectra

Chemical shifts can be used in a wide range of NMR spectra, such as proton NMR ($^1$H NMR), carbon-13 NMR ($^{13}$C NMR), and more specialized forms of spectroscopy such as nitrogen-15 NMR ($^{15}$N NMR) and phosphorus-31 NMR ($^{31}$P NMR). Chemical shifts: Each type of NMR spectrum possesses a specific range of chemical shifts. In proton NMR ($^1$H NMR), the chemical shifts have a range from 0 to 12 ppm, with alkyl group signals (e.g. $-CH_3$) appeared in the region of around 0.5–2 ppm, and electronegative groups (i.e. $-OH$, $-NH_2$) at higher shifts (5–12 ppm). In carbon-13 NMR ($^{13}$C NMR), chemical

shifts are typically 0–220 ppm, with signals due to carbon atoms in alkyl groups appearing at 0–40 ppm and downfield in more deshielded environments (e.g. carbonyl groups) 160–220 ppm.

## 14.2 Course Objectives

To understand the concept of chemical shift in NMR spectroscopy.

1. To learn the reference standards used in chemical shift measurement (e.g., TMS).

2. To study the factors influencing chemical shift values such as shielding, deshielding, electronegativity, hybridization, anisotropy, and hydrogen bonding.

## 14.3 Factors Determining the Chemical Shift

In NMR spectroscopy, a myriad of factors control the chemical shifts of nuclei. These factors encompass the electronic environment, functional moieties, molecular symmetry, and even solvent effects. The knowledge of these influences is essential for knowing how to interpret NMR spectra and what structural information could be extracted from those spectra.

**Electronegative Substituents**

Electronegative atoms or groups (halogens (Cl, Br, I, F), O, N, S) will deshield neighboring nuclei substantially. As an example, a proton connected to a carbon that is directly connected to a fluorine atom will be quite deshielded since fluorine is highly electronegative and, thus, extracts electron density from the proton, pushing it downfield in the spectrum.

**Hydrogen Bonding**

Hydrogen bonding has also a strong influence on the chemical shifts. For example, protons participating in hydrogen bonding (such as in alcohols or amides) typically have broadened peaks and appear at downfield shifts on the chemical shift scale compared to protons not involved in hydrogen bonding. The hydrogen bond also decreases the magnetic shielding around the proton, eventually shifting it further downfield.

## Inductive Effects

The first one is known as inductive effect, which is the electron movement effect of electronegative atoms or groups on neighboring atoms through sigma bonds. Substituents that are electronegative, like fluorine or chlorine, are able to withdraw electron density through bonds, deshielding the protons that are attached to carbons on adjacent carbons. This may result in a downfield shift in the proton NMR spectrum, with the protons on the carbons adjacent to the electronegative substituents showing higher ppm values.

## Resonance Effects

Chemical shifts can also be influenced by the presence of resonance capable functional groups. The protons on a benzene ring undergo deshielding due to resonance with the pi electrons of the aromatic ring. In much the same way, protons attached to carbon atoms in close proximity to a double bond (e.g. alkenes) will show shifts downfield as a result of conjugative (i.e. resonance based) shifts between the pi-electrons of the double bond and the hydrogen atoms bonded to the neighboring carbons.

## Solvent Effects

The solvent also influences the observed chemical shifts in an NMR experiment. Many solvents, particularly polar ones, have hydrogen bond donor and acceptor sites, and they can interact with solute molecules via hydrogen bonding or dipole-dipole interactions, ultimately shielding or deshielding certain nuclei. For example, deuterated chloroform ($CDCl_3$) is the most common solvent for proton NMR spectra. This is, however, a minor effect as solvent molecules do mix and interact with solute molecules but only up to certain degree so they can somewhat shift the values of chemical shift but these effects are far less than other forces.

## Molecular Symmetry

Another factor is that a molecule can has some symmetry and the chemical shift of nuclei in symmetrical molecule are affected by the symmetry. Symmetry can make nuclei equivalent, thus equivalently giving rise to similar chemical shifts for the protons or carbons themselves that are chemically equivalent. For symmetrical molecules (like benzene or toluene) the protons in equivalent positions (ortho, meta, para) will have the same chemical shift and thus provide this simplification of the NMR spectrum.

## Spin-Spin Coupling

Chemical shifts give insight into the local electronic environment of nuclei, while spin-spin coupling (or J-coupling) offers some additional information on the number of neighbouring nuclei and their interactions. If two nuclei are close enough together, their magnetic fields interact, leading to an effect known as spin-spin coupling. If two or more nuclei are coupling, their NMR signals will splita multiplet depending on the number of neighboring nuclei. This splitting gives us information of the number of neighbouring nuclei and their orientations or proximity to the surrounding molecule. The coupling constant (J), defined in Hertz (Hz), measures the strength of the coupling between coupled nuclei and can provide information about bond angles and bond type.

## Coupling Between Protons

In proton NMR ($^1$H NMR), spin-spin coupling generally takes between protons in close proximity, at a distance of 2–3 bonds. For instance, when coupled with one or more neighboring protons, the proton signal is split into a doublet, triplet, quartet, etc., depending on the number of neighboring protons. The splitting pattern and coupling constants can be used to deduce the relative locations of the protons in the molecule.

### 14.3 Spin-Spin Interaction and Coupling Constant (J)

### Classification of Coupling Patterns (ABX, AMX, ABC, A2B2)

With this basic knowledge I want to delve into something that might be more of interest to NMR practitioners: Spin-spin coupling (J-coupling) This is a phenomenon that happens when neighboring nuclei magnetic fields have the interaction with each other and result in splitting NMR signals to peaks. Such interactions yield essential information regarding the local chemical environment and spatial arrangement of atoms in a molecule. Spin-Spin Coupling – J Coupling, ABX, AMX, ABC, A2B2. In addition, we will study how and why the coupling constants we have just discussed affect the size of the J-couplings and, concomitantly, the final NMR spectra. (For example, $^1$H or $^{13}$C)In NMR spectroscopy, nuclei that have a non-zero magnetic moment (such as $^1$H or $^{13}$C) show spin-spin interactions with neighboring nuclei. These interactions occur because of the magnetic fields produced by the nuclear spins of neighboring nuclei. If two or more nuclei come close enough, usually within 2–3 bonds, their magnetic fields interfere with one another, resulting in a splitting of the NMR signals. This is called spin-spin coupling.

### Spin of nuclei and the mechanism of coupling

A molecule consists of multiple nuclei, and nuclear spin is a quantum property which means every nucleus acts as a tiny magnet. Under the influence of an external magnetic field, these atomic nuclei adopt it parallel or antiparallel to the field resulting in discrete energy states. When two nuclei are close to each other, their spins interact via chemical bonds, through the electrons, modifying each other's energy levels. These splits manifest as peaks (sometimes referred to as multiplets).

The extent of this splitting is determined by the strength of the spin-spin interaction, represented by the coupling constant (J). The coupling

constant is related to the interaction strength between the spins of two nuclei and is expressed in Hertz (Hz). The J-coupling constant is not dependent on the magnetic state of the atoms nor the applied magnetic field strength, and is usually constant for any given system under the same experimental conditions. Since the parameter was experimentally different at Solvent 2 and 3, even though slightly reflected by both Solvent 1 and 4, it can be said that Tip-A also explains different between Solvent 1 and 4, which distance of nuclei involved and type of bonding environment are the primary factor to get reference of splitting in tip based parameter, even though this is in contact, and quite reflected by the charge solvation energy.

## 14.4 Multiplet Formation

The coupling of nuclei belonging to the same molecule leads to splitting in the NMR signal, the pattern of which is determined by the number and relative orientations of the neighbouring coupled nuclei. For one proton (or other nucleus), the splitting pattern will appear as multiple peaks separated by the coupling constant. Please note that these peaks would be the parts of a multiplet, and the exact pattern of the multiplet will tell you about the number and type of neighboring nuclei. The coupling constant (J) is an important quantity that determines the splitting of NMR signals. This is directly measurable from the distance between the peaks in the multiplet. The fact that the size and shape of the multiplet is also affected by the spin multiplicity, follows from the fact that the number of neighbors that are coupled with the observed nucleus determines the spin multiplicity. In Nuclear Magnetic Resonance (NMR) spectroscopy, the coupling constant (J) is key to understand the interactions between nuclei in a molecule. The coupling constant corresponds to the difference in frequency between adjacent peaks in an NMR signal, and arises because when two or more nuclei are chemically coupled (bonded together with chemical bonds), their NMR signals split into multiple peaks. The degree of this splitting is

represented by the so-called coupling constant, which is represented by the symbol J, and is measured in herts (Hz).

## 14.5 Effect of Bonding Type on Coupling Constants

The coupling constant (J) is primarily dependent on the type of bonding between the coupled nuclei. Different types of bonds (i.e., single bonds, double bonds, and triple bonds) lead to different coupling constants due to differences in the strengths of the bonds, the distributions of electron density, and the geometry of the atoms involved.

### $^1H–^1H$ Coupling

A common example of J-coupling is that with hydrogen nuclei (protons). J-coupling between two protons, known as spin-spin coupling, can cause the NMR signal to split into multiple peaks, with the splitting pattern oftentimes correlating with the number of protons coupled to the observed proton. There are generally observed when hydrogen's are next to each other in a molecule, like in alkyl groups or aromatic systems. J-coupling constants, particularly for $^1H–^1H$ interactions, are greater than other couplings, such as between proton and carbon ($^1H–^{13}C$), as the interaction between protons is relatively very strong. The value of J for these types of interactions is typically between 5 and 15 Hz, depending on the specific molecular environment and amount of interaction between the two coupled protons. One such example is the cis-trans isomerism in alkenes: here we highlight how the spatial arrangement of protons affects coupling between them, and therefore affects the coupling constant. In cis-alkenes, because the protons are closer to each other, the J-coupling constant is usually greater, however in trans-alkenes, the protons are farther away, leading to a smaller J-coupling value.

¹H–¹³C, ¹H–¹⁹F, ¹H–¹⁷O: Coupling Between Protons and Other Nuclei

1H–nucleus (e.g. 1H–13C, 1H–19F or 1H–17O) coupling constants are frequently of smaller magnitude than 1H–1H coupling^3. The strength of the coupling constant is determined by the electron affinity of the atoms involved and by the interactions at play. The coupling constant between ¹H and ¹³C, however, is typically lower (1 to 10 Hz) because the ¹H–¹C interaction is weaker than a ¹H–¹H interaction. Nevertheless, ¹H–¹³C coupling remains vital in carbon-13 NMR spectroscopy, giving information about the connectivity of carbon atoms in organic compounds. Likewise, the couplings between protons and fluorine (¹H–¹⁹F) vary with molecular environment. Since fluorine atoms are strongly electronegative, coupling constants will be considerably affected by the presence of such atoms in the surrounding of the coupled nuclei. Fluorine has a greater effect than carbon on the electron density of nearby nuclei, so coupling constants between protons and fluorine atoms are more significant than those between protons and carbon.

## 14.6 Parity Violation: Symmetry Considerations for Coupling Constants

Although the nature of the bond between the coupled nuclei is the primary factor in the couplings constant, the bond angles and the geometries of the molecule are significant factors in the magnitude of the J-coupling. As such, the proximity within space of coupled nuclei dictates the extent of direct coupling, along with the chance of spin-spin interactions between the nuclei.

### Cis-Trans Isomerism & Coupling Constants

However, in the case of alkenes, the CIS-TRANS isomerism can greatly affect the J-coupling values between neighboring protons. However, in the case of cis-isomers with protons positioned on the same side of the double bond, the proximity of the protons in 3D space

yields a larger coupling constant. With trans-isomers, where the protons are on the opposite of the double bond, the distance between protons is larger so the coupling constant is smaller. This difference in J-coupling for cis and trans isomeric forms of the same molecule is one of the fundamental concepts for the distinction of isomers using NMR spectroscopy. Splitting patterns and coupling constants can provide insight into how closely packed the atoms are relative to each other in the structure, and ultimately may explain if a compound is in a molecular cis or trans formation.

**Cyclic and Ring Structures**

The shape of the cyclic structures can also have an important impact on the NMR coupling constant measurement as well. In the case of cycloalkanes, there will be different coupling constants for protons on adjacent carbons due to the effect of ring size and ring stereochemistry. In small rings, like cyclopropane or cyclobutane, the bond angle is significantly smaller than tetrahedral, giving rise to atypical coupling constants. In larger rings, such as cyclohexane, the coupling constants of the protons can be influenced by the conformational freedom of the ring. Also heterocyclic compounds which have atoms besides carbon (like O, N & S) can show different coupling constants due to heteroatoms affecting electronic environment and spatial configuration of the compound.

**14.7 Effect of electron density on coupling constants**

The electron density in the vicinity of each of the coupled nuclei primarily determines how large the J-coupling constant will be. For example, the presence of electronegative atoms, such as fluorine, oxygen, or nitrogen, can substantially modify the spin-spin interactions between nuclei by changing the electron density throughout the bonds.

## Electronegative Atoms and the Coupling Constants

Electronegative atoms withdraw electron density from adjacent atoms, and this can affect the coupling constants between nuclei directly. For example, attachment of a fluorine atom causes a decrease in the electron density at a carbon, which in turn affects the spin-spin coupling between the bonded carbon atom and surrounding protons. This frequently leads to greater coupling constants (J values) between protons and fluorine than between protons and other constituents. Coupling constants are also affected by the presence of oxygen or nitrogen atoms since these atoms can interact with the hydrogen nuclei by changing the electronic environment surrounding them. In some cases, this results in long-range couplings, where nuclei that do not share bonding electrons still show appreciable J-coupling efficiencies owing to their exposure to electronegative atoms attached to other positions of the same monomer.

## Role of J-Coupling in Structural Identification

J-coupling constants have a pivotal role in molecular structure determination, and their measurement and analysis are widely used in practice. J-coupling constants can give detailed information on the connectivity and spatial arrangement of atoms in a molecule. The rules for splitting patterns and for relative coupling constants enable chemists to identify relative positions of atoms and build the 3D structure of a compound. J-coupling constants are commonly employed in organic chemistry to verify the positions of functional groups and determine isomeric forms of the compounds. For instance, the magnetic shielding can be applied to aromatic compounds to identify the relative positioning of substituents to the benzene. In a similar manner to aliphatic compounds, the presence of coupling can be utilized to determine neighboring atom interactions and differentiate between stereoisomers or conformers.

## J-Coupling: Applications in Biological Systems

For example, J-coupling constants are widely used in biological chemistry, structural biology, and the study of various biomolecules including proteins, nucleic acids, and carbohydrates. Due to the size and heterogeneity of these biomolecules, traditional 1D NMR spectroscopy is rarely capable of providing full characterization. Conformational J-coupling allows for three-dimensional structure determination in solution, relevant to the study of large proteins and nucleic acids.

### Protein NMR

A J-coupling constant, $J_{NM}$ is measured in protein NMR and analyzed to provide information about the tertiary structure of proteins. By measuring the coupling constants among the different protons and other nuclei, scientists can deduce how the different parts of the protein interact with and fold into its functional structure. However, as proteins are getting bigger, multidimensional NMR measurements becomes essential in resolving complicated coupling patterns in order to assemble a detailed structural representation.

### RNA and DNA NMR

Analogously, J-coupling is important for interpretation of the secondary and tertiary structures of nucleic acids in RNA and DNA NMR. The interactions between the protons for the backbone and bases of RNA or DNA can be used to determine the 3-D folding and study their functional roles in biological processes like transcription and replication.

## 14.8 Effect of Various Factors on Coupling Constant

The coupling constant (J) may be affected by a number of factors, its magnitude being determined by the spin-spin interaction strength between the coupled nuclei. These factors include:

### Bond Length and Geometry

The most influential element on J-coupling is the distance between the coupled nuclei. The closer the nuclei, the greater the coupling constant. For example, vicinal couplings (coupling between the nuclei that are separated by two bonds) are greater than long-range couplings (coupling between the nuclei separated by more than three bonds). Coupling also depends on the bond angle, with nuclei exhibiting optimal angular spatial alignment between bonds giving rise to greater coupling.

### Type of Bond (Single, Double, and Triple Bonds)

Furthermore, the specific nature of the chemical bond that connects the coupled nuclei plays an important role in determining the coupling constant. Therefore, single bonds have lower J-coupling constants than double or triple bonds because the delocalization of electron density in double and triple bonds increases the spin-spin interaction. A simple example is that of cis/trans isomerism in alkenes, where different spatial arrangements of the coupled protons result in different coupling constants.

### Hypercoupling and Through-Bond Effects

In some situations, non-bonded nuclei may still interact via a process referred to as hypercoupling. As an example, the electronic effects in aromatic rings or conjugated systems contribute to the spin-spin interactions between non-bonded nuclei, which interact through conjugation or resonance. Such through-bond interactions can influence the coupled constants actually observed and create more complex splitting patterns.

**Check Your Progress**

Q1. Compare the NMR with IR Spectroscopy.

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Q2. Discuss the medical application of NMR.

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## 14.9 Summary

The chemical shift scale is a fundamental concept in Nuclear Magnetic Resonance (NMR) spectroscopy, representing the resonance frequency of nuclei relative to a reference standard, usually Tetramethylsilane (TMS, $\delta = 0$ ppm). Chemical shift ($\delta$) values are expressed in parts per million (ppm) to eliminate dependence on the spectrometer frequency. It arises from differences in electronic environments around nuclei, influenced by factors like electronegativity, hybridization, anisotropic effects of $\pi$-bonds, and hydrogen bonding. For example, alkane protons appear around 0.5–2 ppm, aromatic protons at 6–8 ppm, and aldehydic protons around 9–10 ppm. Thus, the chemical shift scale provides critical information about the structural and electronic environment in a molecule, making it essential for molecular identification and structural elucidation.

## 14.10 Exercises

### 14.10.1 Multiple Choice Questions

1. The reference compound used in proton NMR spectroscopy is:

   a) Benzene

   b) Chloroform

c) Tetramethylsilane (TMS)

d) Acetone

Answer: c) Tetramethylsilane (TMS)

2. Chemical shift ($\delta$) is expressed in which unit?

a) Hertz (Hz)

b) Tesla (T)

c) Parts per million (ppm)

d) Gauss (G)

Answer: c) Parts per million (ppm)

3. Which factor causes downfield shift (higher $\delta$ value)?

a) Shielding

b) Increased electron density

c) Deshielding by electronegative atoms

d) Magnetic shielding by aromatic ring currents

Answer: c) Deshielding by electronegative atoms

4. Aromatic protons usually appear in the NMR spectrum at:

a) 0–1 ppm

b) 1–2 ppm

c) 6–8 ppm

d) 9–10 ppm

Answer: c) 6–8 ppm

5. The chemical shift of aldehyde protons generally lies at:

a) 1–2 ppm

b) 2–4 ppm

c) 6–8 ppm

d) 9–10 ppm

Answer: d) 9–10 ppm

## 14.10.2 Short Answer Questions

1. Define chemical shift and state its unit.
2. Why is TMS used as a standard reference in NMR spectroscopy?
3. Differentiate between upfield and downfield shifts.
4. List the approximate δ values for alkane, alkene, and aromatic protons.
5. Explain the effect of electronegativity on chemical shift.

## 14.10.3 Long Answer Questions

1. Explain the principle of chemical shift in NMR spectroscopy. Discuss how TMS is used as a reference compound.
2. Describe in detail the factors affecting chemical shift (electronegativity, hybridization, anisotropy, hydrogen bonding).
3. With suitable examples, discuss the approximate chemical shift ranges for different functional groups.
4. Explain the concept of shielding and deshielding in NMR with diagrams.
5. How does the chemical shift scale help in structural elucidation of organic compounds?

## 14.11  References and Suggested Reading

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2. Hollas, J. M. (2004). Modern Spectroscopy (4th ed.). John Wiley & Sons, Housecroft, Hoboken, New Jersey, USA
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# Unit 15: Advanced NMR Techniques

## Structure

## 15.1 Introduction

Particularly when intricate multiplet patterns emerge due to spin-spi coupling. NMR methods are vital for determining the characteristi chemical environments and structural information, advanced NM methods allow in-depth molecular characterization of comple mixtures, higher molecular resolution in terms of molecula interactions and dynamics insight compared to classical NM approaches. Several advanced techniques such as Spin Decoupling an Double Resonance and the Nuclear Overhauser Effect (NOE) ar critical genres of methods aimed at enhancing the quality of NMR data, establishing the structure of molecules. Although standard Nuclea Magnetic Resonance (NMR) spectroscopy is among the most powerfu tools available for bimolecular, complex organic matter, and molecule in hybrid environments. role, we will dissect Spin Decoupling an Double Resonance and Nuclear Overhauser Effect (NOE), covering the

theory, applications, and ways both techniques can serve to reduce confusion in NMR spectra. These advanced techniques are crucial for the analysis of complex molecular systems, especially large  In this

**Spin decoupling**

Spectra. can oftentimes be a wide variety of broad and complex multiplet patterns. The sequences for simplifying these patterns are known as spin decoupling and double resonance sequences, interrupting or minimizing the coupling interactions present in the With these complex spin spin couplings, there

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## 15.2 Objectives

1. Understand the theoretical foundations of advanced NMR spectroscopy.

2. Differentiate between 1D and multidimensional NMR techniques.

3. Apply 2D NMR methods (COSY, HSQC, HMBC, NOESY, TOCSY) for structural elucidation.

4. Interpret chemical shift, coupling constant, and relaxation parameters for molecular analysis.

## 15.3 Principles of Spin Decoupling

The multiple peaks in the NMR signal. Nucleus. Spin decoupling is used to simplify the multiple splitting by removing the interaction from the molecules that give rise to leaving the remaining coupling interactions intact. This is usually performed by irradiating a given the Nucleus, at the resonant frequency, decoupling the Nucleus from its coupled neighboring To achieve this, a process known as spin decoupling sheds the effects of specific spin-spin couplings, and to better understand the environment of the nucleus underlie. Therefore the signal presents as a singlet or a lower complexity multiple. Which make it easier to read In a decoupled spectrum, the nuclei that are coupled no longer split the signal of the observed nucleus, and
(i) broadband decoupling (ii) selective decoupling.

**Double Resonance Techniques**

Nuclei interact with one other yielding detail on the molecular architecture and dynamics. Distinct nuclei are selectively excited. That is to investigate how the two exciting two or more nuclei. In an experiment, double resonance means that two spin decoupling seeks to simplify the spectrum by decoupling between spins, while double

resonance can provide higher resolution by simultaneously nuclei can be beneficial for gaining sensitivity. Excited and the cross peaks in the 2D spectrum show which protons are attached to which carbons. This value is particularly useful in carbon-13 NMR, where, due to lower natural abundance, carbon-13 signals tend to be weak, where coupling with hydrogen experiment, the (proton)-(C nucleus) interaction is used. In this experiment the proton and carbon nuclei are mutually although 1H-13C heteronuclear correlation (HETCOR) is the most popular application of a double resonance can be employed in proteins where many nuclei via their interactions with hydrogen, nitrogen, and carbon nuclei give a more detailed picture of the structure. techniques can be used not only for the coupling of 1H and 13C, but also for the coupling of other nuclei in 1H-15N or 1H-31P pairs according to the system being studied.

## 15.4 Overhauser Effect (NOE) Nuclear

of molecules which is particularly useful in structural biology where such data is used to determine the arrangement of atoms within macromolecul contrast to spin-spin coupling, which requires interaction between spins linked by a chemical bond, the NOE arises from magnetic interactions between nuclei that are close in space, specifically within 5 Å of one another. The NOE contains information about the three-dimensional structure NMR spectroscopy that it can give useful information about the spatial proximity of nuclei within a molecule is the NOE (Nuclear Overhauled Effect). In One more advanced method ines like proteins and nucleic acids.

**Principles of the NOE**

Stronger NOE. to a modification of the intensity of the NMR signal o the neighboring nucleus. The strength of the NOE effect is als dependent on the distance between the two nuclei, with closer nucle yielding to it. This interaction leads in space. If one nucleus get

excited by an NMR pulse, it can transfer its magnetization to a nearby nucleus that is physically close NOE is a result of the dipole-dipole interaction between nuclear spins that are close to each other Overhauled Effect Spectroscopy) or 3D NOESY spectra giving a much broader view on the spatial relationships between nuclei. Suppression of the signal of a nearby nucleus following irradiation of the nucleus of interest. More commonly the NOE is seen in 2D NOESY (Nuclear In 1D NMR the NOE can be detected as either an enhancement or a

**Types of NOE**

**Two flavors:  NOE comes mainly in**

are close enough (usually  of its own intensity and the intensity of a neighboring nucleus, if the intensity of the NMR signal of a neighboring nucleus increases when a particular nucleus is excited, that's called a positive NOE. This is usually seen in cases when those two nuclei Positive NOE; Since the NMR signal of any nucleus is some combination < 3 Å) and the NOE effect is strong. detailed interpretation for the experiments in which they are used. of a neighboring nucleus decreases after a nucleus has been excited. Under some conditions and in some systems negative NOEs can sometimes be observed and require a  Negative NOE: This is the case when the NMR signal intensity conformational dynamics of molecules, revealing the positioning of atoms within a single molecule.  the same molecule). Intermolecular NOEs are especially valuable for studies on the Intermolecular NOE (NOE between different molecules) and intramolecular NOE (NOE within

**15.5  Information and Binding Analysis Using NOE  Structure**

Complex systems.  to capture the non-bonded interaction through time makes NOE an important asset in structural biology, molecular dynamics, drug design, and multidimensional NMR spectroscopy. NOE data can provide insights into molecular structure, dynamics, and interactions in  much about distance or proximity between nuclei other

than bonded ones (the NOE indicates proximity). The ability denaturation of osmotes provides valuable insights concerning the three-dimensional structure of moleculus such as proteins, nucleic acids, and other macromolecules, specifically those that are large and complex in nature. 1D NMR spectra, although containing chemical environment information on different types of protons, do not inform Overhauser Effect, which is a phenomenon that is observed in nuclear magnetic resonance (NMR) spectroscopy, where the magnetization of one nucleus affects the relaxation of a nearby nucleus. The NOE is an acronym of Nuclear

**Structural Biology:**

Structure Determination Separation of Proteins, protein conformation. non-bonded atoms closest to each other in the folded protein. This means that in principle, the NOE can expose how dispersed atoms in the sequence are brought closer together in the folded their 3D conformation is critical for understanding their biological functions. This NOE gives spatial information between tertiary structure.) Proteins are complex macromolecules made of long chains of amino acids, and knowledge about Nuclear Overhauled effect (NOE, in protein NMR NOE is vital to determine protein folded protein structure in solution can then be achieved through the establishment of observable distance restraints using NOE, as well as chemical shift analysis. shape can be known. Coverage of the most crucial part is related to the backbone assignment which is basically to identify where the main chain atoms are located in the protein. Based on NOE interactions, the folding of the protein into its functional 3D In the case of NMR-based protein structure determination one of the (as we will see below), where one needs to describe drug–target protein interactions at the atomic scale. provides information on the active sites of enzymes.

## 15.6 Determination of nucleic acids (DNA and RNA) structure

This research field. Structures required for their biological function which makes them excellent subjects of study using NMR in solution. RNA, because of its inherent flexibility and dynamism is often poorly characterized by static structural methods and therefore the NOE has proven vital in dynamics determination of these macromolecules. Nucleic acids adopt complex secondary and tertiary NOE is also commonly used for nucleic acids like DNA and RNA for tertiary structure and and diffusion measurements, to study the structure and flexibility of RNA molecules and how they relate to function and stability. and translation processes. NOE data can be paired with other NMR strategies, such as chemical shift study the double helix structure for DNA, as well as to examine the binding of DNA-binding proteins to specific sequences in DNA. Likewise, for RNA the NOE spectroscopy provides an insight in its folding and conformational changes that are essential for transcription

### Molecular Dynamics:

NOE helps resolve the flexibility and conformational alteration of macromolecules, which are important for studying biological functions, e.g., enzyme catalysis, molecular recognition, and molecular transportation. molecule. More specifically, the An NOE is in fact both a practical means of structural determination as well as a means of probing the dynamic forces of a Proteins Flexibility and Dynamics of molecule's flexibility. can exame small ones by showing brief interactions between distant atoms in the protein. This NOE signal (weak) is dependent on the proximity in space of the interacting nuclei and can be modulated by the conformational changes as it performs its biological function. These conformational changes can be slow and the NOE A protein moves constantly, undergoing table to measure the dynamic behavior of proteins is essential for the understanding of processes such as end some atoms may remain constant, whereas a flexible or dynamic protein would present more variation in the intensities. Being For instance, in case of a rigid protein structure, the

NOE intensities between me substrate binding, protein folding and protein protein interactions. a molecule's binding to one site can influence the structure and function of a non-adjacent site on the target protein. NOE provides a means of observing the equilibrium distribution of conformations and characterizes their interconversion. Such a technique is especially valuable in studying the allosteric regulation of proteins, in which dynamics of protein conformations. For systems where multiple conformations are equilibrated, the The NOE can additionally be applied to monitor exchange

## 15.7 Drug Design:

is often a protein, and how this affinity can be optimized and improved for therapeutic effect. NOE is useful in drug design, as it can aid in determining how potential drug candidates interact with their molecular targets. The key to finding a new drug is to understand how the drug molecule attaches to its target, which The with Substance-Target Interactions Interacting  drug molecule versus target protein. drug candidates)-target protein interactions. The scientists can deduce the binding site, mode of interaction and etc., based on NOE between nuclei in The NOE is frequently used in drug design to investigate small molecule (i.e., can indicate whether the binding is specific or the drug molecule binds to multiple sites in the protein. concerning binding site topology and have proven useful for identification of critical residues that contribute to the binding interaction.

## Multidimensional NMR:

Very well looked at at conventional 1D NMR. in more detail. These methods are very useful for analyzing macromolecules containing proteins, nucleic acids and big organic compounds that cannot be  Even the explosion of multidimensional NMR techniques, like NOESY (Nuclear Overhauled Effect Spectroscopy) and ROESY (Rotating Frame Overhauled Effect Spectroscopy), made the NOE a powerful tool for larger the organization of molecules.

## 15.8 NOESY and ROESY Techniques

In building three-dimensional structures of molecules. may or may not be covalently linked. This experiment gives detailed data about non-bonded atoms and their distance which is essential the NOE to determine the spatial proximity of nuclei in large molecules. In a NOESY, the NOE is detected between nuclei which are close in space but NOESY and ROESY are two-dimensional NMR experiments that use used in determining the three-dimensional structures of proteins, nucleic acids, and other large bimolecular. Effects and yielding clearer signals for specific types of molecules. NOESY and ROESY are widely The NOE in ROESY experiments is observed in the rotating frame of reference, thereby reducing spin-spin relaxation.

## 3D and 4D NMR

High-resolution models of large bimolecular through the management of a greater number of spatial constraints. Greater resolution of molecular interactions and structures. NOE makes these types of experiments possible and enables the development of systems such as three-dimensional (3D) and four-dimensional (4D) NMR experiments; however for large systems, the sheer data acquisition time and computation of processing can be daunting. These techniques provide an even Multidimensional NMR can be further extended to reconstruct more complex derived, resultingantly aiding drug design, protein engineering and structural biology. Using multidimensional NOEs (from multidimensional NMR experiments), high-quality structural information regarding the dynamics, folding, and intermolecular interactions of complex molecules can be.

Nuclear Magnetic Resonance (NMR) spectroscopy is among the tmost potent analytical techniques in chemistry and biochemistry, enabling the study of structure, dynamics, and interactions of molecules. The introduction of Fourier Transform NMR (FT-NMR) is one of the major advances which has significantly enhanced NMR utility. FT-NMR has transformed the way that NMR spectra are recorded and interpreted, resulting in more rapid, sensitive and accurate measurements. FT-NMR has found numerous applications in various fields, especially in the medical diagnostics domain where it allows non-invasive imaging of the inner body and the analysis of biological systems. We will learn about the fundamentals of Fourier Transform NMR, instrumentation, many benefits an d medical diagnostic applications facilitated by NMR technology. In this blog post, we will explore the technical details and practical implications of FT-NMR, providing a deeper understanding of this powerful tool in modern science and medicine.

## 15.9 FT-NMR: The Fourier Transform Advantage

**Fourier Transform NMR (FT-NMR)**

FT-NMR: It is a method based on Fourier transformation that converts raw data which can be collected in the time domain (free induction decay or FID) to a spectrum in the frequency domain. The revolutionized data processing is greatly advancing the capability of NMR spectroscopy, marking one of the most significant developments in NMR history. Normally, in a ground state NMR experiment (aka continuous wave or CW-NMR), one frequency is used to excite the nuclei, then as the signal decays, it is analyzed. But FT-NMR utilizes many different frequencies to excite all nuclei in a sample. More information is obtained in less time using this approach, and higher quality spectra can be acquired. The Fourier Transform converts a parameter that varies with time, the signal, into one that varies with frequency, the spectrum, with the signal maxima corresponding to the resonances of the nuclei in the sample. Evidently, the FID itself is the

uncooked signal, and this decaying signal, when passed through Fourier transformation (standard NMR practice), reveals the corresponding spectrum (which in general is more acknowledged, where one can watch up for chemical shifts and couplings)! FT-NMR offers the ability to gather data over a wider range of frequencies at once, which is the key reason FT-NMR is preferred over traditional ones. As a result, it accelerates data generation, enhances sensitivity, and provides superior peak resolution, rendering it an indispensable asset in chemical analysis.

**Fourier Transform Principles in  NMR**

To have the complete grasp of FT-NMR, its indispensable we understand the significance of Fourier Transform in this whole process. The main application of NMR spectroscopy in this country was in traditional mode, where each signal at  a specific frequency was detected and analyzed one by one. In FT-NMR, instead, a broadband pulse is applied, exciting all the resonating nuclei in the sample simultaneously. This produces a strong signal over which decays over time as the nuclei lose energy. This decaying signal is called free induction decay (FID). The free induction decay (FID) encompasses all of the information about the resonant frequencies  of the nuclei within the sample.

**15.10  Advantages of FT-NMR**

There are some main advantages of FT-NMR over traditional NMR where FT-NMR is being widely used in several scientific areas. Advantages of FT-NMR: Some  of the important advantages of FT-NMR are:

1. Increased Sensitivity: The FT-NMR is much more sensitive to NMR signals.    Since    FT-NMR excites    all    nuclei simultaneously with a broadband pulse, it enables the more efficient collection of more signal in a shorter period of time.

FT-NMR's ability to detect even low-concentration species with high precision is especially beneficial when working with small amounts of sample.

2. Faster Data Collection: FT-NMR can collect all the data for an NMR spectrum at once. In conventional CW-NMR, one frequency is measured at a time, which increases acquisition times. FT-NMR collects data orders of magnitude quicker enabling the rapidly available analysis of samples. This is particularly valuable in high-throughput genomics research and clinical settings where speed of results is paramount.

3. Improved Resolution and Accuracy: Fourier Transform improves the resolution of the NMR spectrum considerably. FT-NMR is only dependent on analyzing data in the frequency domain so the resulting noise is much less distorted, and overlap peaks are more easily separated. This leads to clearer, more accurate spectra that enable a better understanding of the molecular structure of the sample.

Additionally, FT-NMR reduces artifacts due to signal averaging that result in improved signal-to-noise ratio. A reduction in noise leads to more accurate chemical shift assignments and allows for the observation of small features in the spectrum like coexisting structural variations or impurities in a sample.

1. Multi-dimensional NMR : FT-NMR not only allows us to record one-dimensional spectra. It may be extended into multi-dimensional NMR techniques (2D, 3D, or even 4D NMR). These 2D and 3D techniques contribute to obtaining more in-depth structural and dynamic details of large and complex biological molecules such as proteins and nucleic acids. The pioneering use of FT−NMR coupled with multidimensional techniques, however, allowed researchers to progressively unpick interactions between nuclei that would be otherwise indiscernible in one-dimensional spectra.

2. Non-Destructive Analysis: Since FT-NMR is a non-destructive technique, it does not otherwise change the sample being examined. This means that repeated measurements can be performed on the same samples, without damaging the valuable or sensitive samples, something that is particularly important for restorative samples that cannot be easily duplicated.

This enables FT-NMR to be employed in a variety of settings, from academic laboratories to clinical diagnostics.

## 15.11 Fourier Transform NMR: Applications in Medical Diagnostics

FT-NMR has been tremendously influential in the the applications of medical diagnostics, especially in the field of magnetic resonance imaging (MRI) and metabolomics. Such applications draw upon the physical principles behind NMR spectroscopy to give non-invasive ways through which the human body can be investigated and a multitude of diseases could potentially be diagnosed. Here, we will look into a few key areas of FT-NMR applications in medicine. While the primary application of FT-NMR has been in chemical analysis, its relative, magnetic resonance imaging (MRI), has become widely used in medicine. The same basic principles of NMR are applied in MRI to image the internal structures of the body. MRI uses a strong magnet and radiofrequency pulses to excite the hydrogen nuclei in the body (mostly in water molecules). Detection is performed, and these signals are positioned on a grid to produce detailed scans of soft tissues within our body. FT-NMR is at the heart of MRI, as it enables us to convert the time-domain data (the FID) into high quality frequency-domain images. This conversion is critical to generating high-resolution images that allow physicians to see organs, tissues and growths, such as tumors. MRI's non-invasive and high-resolution imaging capabilities

have made it one of the most potent diagnostic tools available in medicine today.

One potential application of FT-NMR is in the multidisciplinary field of metabolomics, which deals with the identification and quantification of small molecules (metabolites) present in biological material. FT-NMR also has potential for use in metabolic profiling of body fluids like urine, blood, and cerebrospinal fluid, revealing important information about metabolic status, and allowing for the early detection of diseases. FT-NMR, for instance, is utilized for metabolite identification and quantification in the blood of individuals afflicted with diseases such as diabetes, cancer, cardiovascular disease, and neurodegenerative disease. Often, diseases will have significant change in the metabolic profile before the disease itself becomes clinically apparent. FT-NMR can distinguish metabolites between healthy individuals and patients, and aid in the diagnoses of diseases, tracking disease progression over time, and determining treatment efficacy.

**Diagnosis and Monitoring of Cancer**

The cancer diagnosis potential of FT-NMR has also been very promising. Metabolomic profile is often changed due to the metabolic alterations in cancerous tissues. Non-invasive tumor detection and monitoring of tumor progression using FT-NMR spectroscopy FT-NMR spectroscopy detects such variations. FT-NMR can enable the analysis of tissue biopsies and blood samples or cancer biomarkers, providing vital insight of what type of cancer, the current stage, and the aggressiveness of the cancer. This will help inform treatment choices, resulting in better patient outcomes. FT-NMR applications are not limited to diagnosis they can also be used in monitoring cancer therapies (e.g., chemotherapy and radiation) by using the metabolic profile of the patient.

**Check Your Progress**

Q1. List three key applications of NMR spectroscopy in medical diagnostics.

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Q2. Compare 1H-NMR and 13C-NMR in terms of chemical shifts,relaxation times, and sensitivity.

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## 15.12 Summary

Nuclear Magnetic Resonance (NMR) Spectroscopy is a powerfu analytical technique used to determine the structure of organi compounds by examining the environment of atomic nuclei. The mos commonly studied nucleus in NMR is the hydrogen nucleus ($^1$H), though others like $^{13}$C, $^{19}$F, and $^{31}$P are also used. NMR operates on th principle that nuclei with a non-zero spin can absorb radiofrequenc radiation in the presence of an external magnetic field, causin transitions between nuclear spin states. The absorbed frequenc depends on the magnetic environment of the nucleus, which i influenced by surrounding electrons. This leads to variations i absorption frequencies known as chemical shifts. The chemical shift i measured in parts per million (ppm) relative to a reference compound, typically tetramethylsilane (TMS), which is assigned a value of 0 ppm. The chemical shift scale is crucial because it provides a standardize way to compare data from different instruments. Chemical shifts giv valuable information about the electronic structure and environment o nuclei, allowing chemists to deduce the nature of functional groups, types of hydrogen or carbon atoms, and their connectivity. Th shielding or deshielding of a nucleus due to the electron cloud and

nearby electronegative atoms determines whether the shift appears upfield (lower ppm) or downfield (higher ppm). NMR spectra consist of peaks corresponding to different types of nuclei in a molecule, with splitting patterns caused by spin-spin coupling further providing insight into the number of neighboring nuclei. The area under each peak is proportional to the number of equivalent nuclei represented by that peak. Overall, NMR is indispensable in organic and inorganic chemistry for structure elucidation, identification, and dynamic studies of molecules.

## 15.13 Exercises

### 15.13.1 Multiple Choice Questions

1. What is the unit of chemical shift in NMR spectroscopy?

A. Hz

B. ppm

C. T

D. m/s

Answer: B. ppm

2. Which nucleus is most commonly studied in NMR spectroscopy?

A. $^{14}N$

B. $^{16}O$

C. $^{13}C$

D. $^{1}H$

Answer: D. $^{1}H$

3. Chemical shift depends on which of the following factors?

A. External magnetic field only

B. Electron density around the nucleus

C. Temperature only

D. Sample mass

Answer: B. Electron density around the nucleus

4. Shielding in NMR refers to:

A. Increase in nuclear spin

B. Effect of the applied magnetic field on the solvent

C. Reduction of effective magnetic field at the nucleus due to surrounding electrons

D. Reflection of radio waves by the nucleus

Answer: C. Reduction of effective magnetic field at the nucleus due to surrounding electrons

5. A nucleus is said to be deshielded when:

A. It has more surrounding electrons

B. It absorbs at a higher field

C. It experiences a stronger external magnetic field

D. It absorbs at a lower field (downfield shift)

Answer: D. It absorbs at a lower field (downfield shift)

6. In $^1$H NMR, the typical chemical shift range is:

A. 0 to 10 ppm

B. 0 to 100 ppm

C. 0 to 200 ppm

D. 0 to 1000 ppm

Answer: A. 0 to 10 ppm

7. Which solvent is commonly used in proton NMR spectroscopy due to its lack of $^1$H signal?

A. Water

B. Methanol

C. Deuterated chloroform ($CDCl_3$)

D. Ethanol

Answer: C. Deuterated chloroform ($CDCl_3$)

8. Tetramethylsilane (TMS) is used in NMR as:

A. Internal standard

B. Solvent

C. Magnetic field stabilizer

D. Radiofrequency source

Answer: A. Internal standard

9. Downfield shift in chemical shift means the signal appears:

A. At a higher ppm value

B. At a lower ppm value

C. At zero ppm

D. At negative ppm

Answer: A. At a higher ppm value

10. Which of the following would appear farthest downfield in $^1$H NMR?

A. Methyl protons

B. Aromatic protons

C. Aliphatic protons

D. Shielded methylene protons

Answer: B. Aromatic protons

## 15.13.2 Short Answer Questions

1. What is the fundamental principle of NMR spectroscopy?
2. Define chemical shift and explain its significance in NMR.
3. What is shielding and deshielding in NMR?
4. How does spin-spin coupling lead to peak splitting in an NMR spectrum?
5. What are the different types of coupling patterns observed in NMR?
6. Explain the role of the Fourier Transform (FT-NMR) technique in modern NMR spectroscopy.
7. What factors influence the chemical shift of a nucleus in NMR?
8. How does spin decoupling help simplify NMR spectra?
9. What is the importance of relaxation mechanisms in NMR?

## 15.13.3 Long Answer Questions

1. Explain nuclear spin and magnetic resonance in detail. How

does an external magnetic field affect nuclear spins?

2. Describe the mechanism of chemical shifts and the factors affecting them in NMR spectroscopy.

3. What is spin-spin coupling, and how is the coupling constant (J-value) determined?

4. Discuss the different coupling patterns (ABX, AMX, ABC, A2B2) observed in NMR. Provide examples.

5. Explain shielding and deshielding effects and how they influence the chemical shift in an NMR spectrum.

6. How does spin decoupling work in NMR, and why is it useful?

7. What is the Nuclear Overhauser Effect (NOE), and how is it applied in structural determination?

8. Describe the working principle and advantages of Fourier Transform NMR (FT-NMR).

9. Compare 1H-NMR and 13C-NMR in terms of chemical shifts, relaxation times, and sensitivity.

10. Discuss the major applications of NMR spectroscopy in medical diagnostics, pharmaceuticals, and structural biology.

## 15.14 References and Suggested Readings

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**Glossary of Spectroscopy Terms**

| Term | Definition |
|---|---|
| **Spectroscopy** | The study of interaction between matter and electromagnetic radiation. |
| **Spectrum** | A display of the intensity of radiation as a function of wavelength or frequency. |
| **Electromagnetic Radiation (EMR)** | Energy that travels in waves and spans a spectrum from radio waves to gamma rays. |
| **Wavelength ($\lambda$)** | The distance between two consecutive peaks of a wave, usually measured in nanometres (nm) or meters (m). |
| **Frequency ($\nu$)** | The number of wave cycles passing a point per second, measured in Hertz (Hz). |
| **Wavenumber ($\bar{\nu}$)** | The number of wave cycles per unit distance, measured in $cm^{-1}$; commonly used in IR spectroscopy. |
| **Energy Levels** | Discrete levels of energy that electrons, atoms, or molecules can occupy. |
| **Absorption** | The process where matter absorbs energy from radiation, causing transitions to higher energy levels. |
| **Emission** | The process where energized matter releases energy in the form of radiation. |
| **Ground State** | The lowest possible energy state of an atom or molecule. |
| **Excited State** | A higher-energy state reached when energy is absorbed. |
| **Transition** | Movement of particles (electrons or nuclei) from one energy level to another. |
| **Quantum Number** | A number describing the energy or angular momentum of particles in atoms or molecules. |
| **UV-Visible Spectroscopy** | Technique used to study electronic transitions in atoms and molecules using UV and visible light. |

| Term | Definition |
|---|---|
| **Infrared (IR) Spectroscopy** | Technique used to study molecular vibrations; used to identify functional groups. |
| **Raman Spectroscopy** | Technique based on scattering of light due to molecular vibrations; complementary to IR. |
| **NMR (Nuclear Magnetic Resonance) Spectroscopy** | Technique that studies the magnetic properties of atomic nuclei to determine molecular structure. |
| **Mass Spectrometry (MS)** | Technique used to determine molecular mass and molecular formula by ionizing and fragmenting molecules. |
| **Monochromatic Light** | Light consisting of a single wavelength or frequency. |
| **Polychromatic Light** | Light containing multiple wavelengths or frequencies (e.g., sunlight). |
| **Bandwidth** | The range of wavelengths transmitted by an instrument. |
| **Detector** | Device that measures the intensity of transmitted or emitted radiation. |
| **Baseline** | Reference level of signal intensity on a spectrum. |
| **Resolution** | Ability of an instrument to distinguish between two closely spaced spectral features. |
| **Calibration** | The process of adjusting instruments to ensure accurate measurements. |
| **Beer–Lambert Law** | Relationship between absorbance, concentration, and path length: $A = \varepsilon bc$. |
| **Chromophore** | Part of a molecule responsible for absorbing UV/Visible light. |
| **Fluorescence** | Emission of light by a substance after absorbing radiation, usually with short lifetime. |
| **Phosphorescence** | Similar to fluorescence but with delayed emission (longer lifetime). |

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