SPECTROSCOPY

What is spectroscopy?

Spectroscopy is the branch of science which deals with the study of the interaction of electromagnetic radiation with matter.

It is the most powerful tool available for the study of structures of atoms and molecules.

There are several spectroscopic techniques that help in investigating various aspects of atomic and molecular structure.

What are electromagnetic radiations?

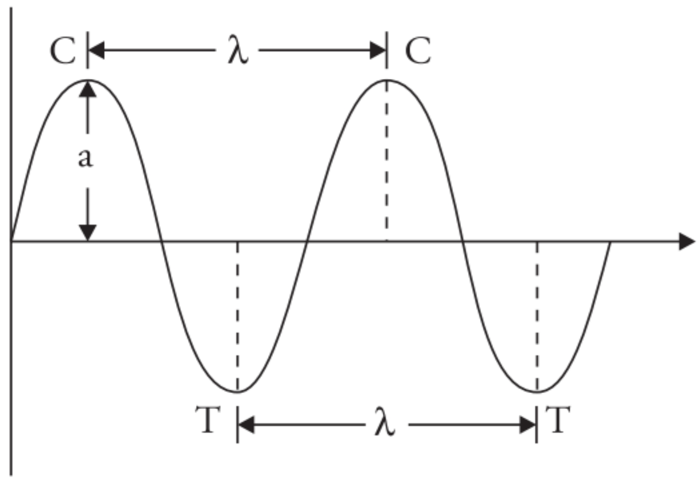
Electromagnetic radiation is a form of radiant energy which has both particle as well as wave nature.

In vacuum, it normally travels in a straight line with the speed of light (3×108 m/s).

It has both electric and magnetic field components, which are coplanar and oscillate perpendicular to each other and perpendicular to the direction of wave propagation

What are the properties of electromagnetic radiations?

1. Wavelength- It is the distance between two adjacent crests and troughs in a wave. It is denoted by lambda.



Read the conversions(micron, angstrom, nm to cm) from class notes given by me.

2. Frequency- It is the number of waves which can pass through a point in one second.

It is denoted by nu

Frequency is expressed in cycles per second or Hertz (Hz) where 1 Hz = 1 cycle/s.

Nu = c/lambda, where c is speed of light

3. Velocity- It is the distance travelled by a wave in one second.

It is denoted by c.

Electromagnetic radiations travel with the speed of light, hence the value of c is 18600 miles per second or 2.98 x 10^8 m/s

4. Wave number- It is the total number of waves in a length of one centimetre.

It is denoted by nu bar.

Wave number is the reciprocal of wavelength and is expressed in per centimetre or cm−1

Nu bar = 1/lambda(in cm)

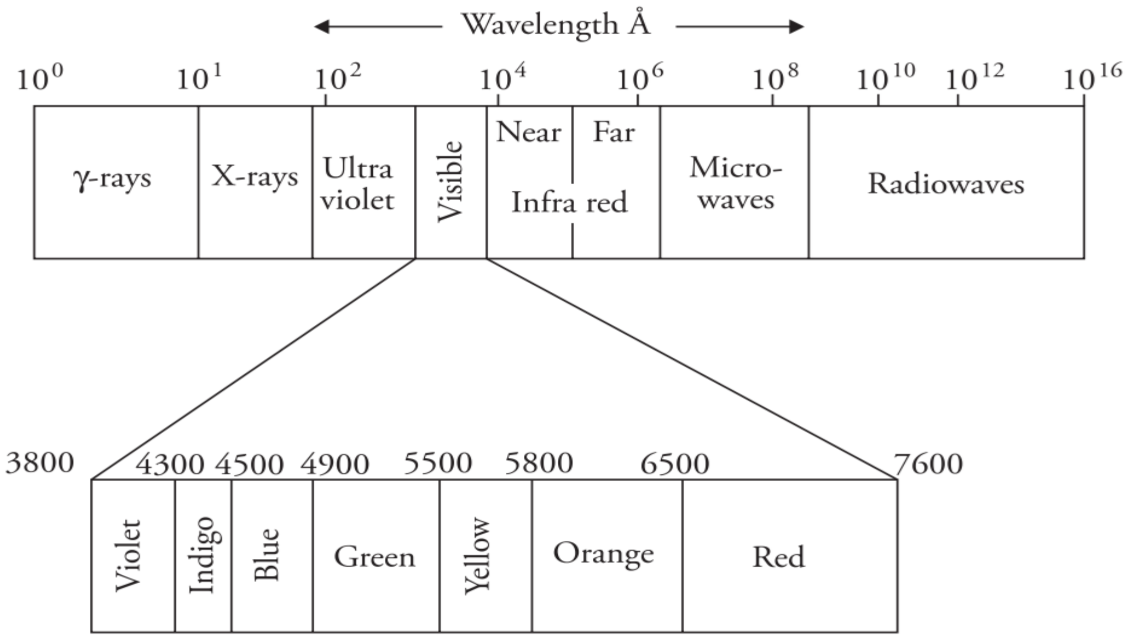
5. Energy- It represents the energy that a wave possesses.

It is denoted by E.

E = h nu = hc/lambda

where h = Planck's constant = 6.626 x 10^(-34) Joules seconds

What is Electromagnetic spectrum?



1\. The electromagnetic spectrum is a range of all types of electromagnetic radiation arranged by wavelength and frequency.

2\. It includes visible light which we can see but also extends beyond what our eyes can detect including radio waves, microwaves, infrared, ultraviolet, X rays and gamma rays.

3\. Each type of radiation has a different wavelength. Radio waves have long wavelengths while gamma rays have very short wavelengths.

4\. Wavelength and frequency are inversely proportional and so shorter wavelengths correspond to higher frequencies, and vice versa.

5. The energy of electromagnetic radiation increases as frequency increases. Gamma rays, with their high frequency, carry the most energy, while radio waves carry the least.

6. Different parts of the spectrum are used for various communication technologies.

Ex- radio waves are used for broadcasting and microwaves for cell phones and cooking and infrared for remote controls in tv

7. Infrared radiation is responsible for heat which we feel as warmth from the sun or a fire.

Visible light is also part of the spectrum and allows us to see objects around us.

8. Radiation at the higher energy end of the spectrum, such as X rays and gamma rays is ionizing which means that it can remove electrons from atoms. Lower energy radiation like radio waves and microwaves are non ionizing and generally considered less harmful.

9. Different types of electromagnetic radiation interact with matter in various ways. Ex- X rays can penetrate soft tissues but are absorbed by denser materials like bones.

There are many types of spectra-

1. Continuous Spectrum: When white light passes through a prism, it splits into different colors, merging seamlessly without discontinuity.

It's obtained from light emitted by certain incandescent substances.

2. Emission Spectrum: It occurs when there's a transition from a higher energy level to a lower one, resulting in emitted energy.
It is obtained by heating a substance and passing the emitted radiation through a prism.

3. Absorption Spectrum: This arises from transitions from lower to higher energy states, with absorbed energy equal to the energy difference.

Dark lines appear indicating absorbed wavelengths.

4. Atomic Spectra: Results from the interaction of atoms with electromagnetic radiation, showing sharp lines corresponding to electron transitions between electronic energy levels. These lines serve as characteristic fingerprints of atoms.

5. Molecular Spectra: It deals with electromagnetic radiation interacting with molecules, involving transitions not only between electronic levels but also rotational and vibrational levels.

Read the born oppenheimer approximation relation

UV VISIBLE SPECTROSCOPY/ ELECTRONIC SPECTROSCOPY/ PHOTOMETRY

It focuses on electron transitions between energy levels within molecules.

UV Visible Spectroscopy: Falls within the UV visible region **200-760 nm** of the electromagnetic spectrum, also known as electronic spectroscopy.

It is used to analyze molecules, especially to determine the number of conjugated double bonds and differentiate between conjugated and non conjugated systems.

When molecules absorb radiation of a specific frequency, electrons move to higher energy states, resulting in decreased light intensity passing through the sample.
It records the amount of light absorbed by the sample at different wavelengths, typically represented by absorption bands.

Read the answer from organizer too.

Laws of absorption

1. **Beer’s Law -** It states that when a parallel beam of monochromatic light enters perpendicularly into a homogenous absorbing medium, the absorbance is directly proportional to the length of the path traversed by the beam

Study the equation from the class notes I shared.

2. **Lambert’s Law-** It states that when a parallel beam of monochromatic light enters perpendicularly into a dilute solution, the absorbance is directly proportional to the concentration of the solution.

Equation is in the class notes

Beer Lambert Law- It is the combined form of Beer’s law and Lambert’s law. According to this law when a beam of monochromatic light is passed through a solution, the decrease in intensity of radiation with thickness of the absorbing material is directly proportional to the intensity of incident radiation as well as to the concentration of the solution

Equation is in class notes

Learn about transmittance too from the notes

What is a spectrophotometer?

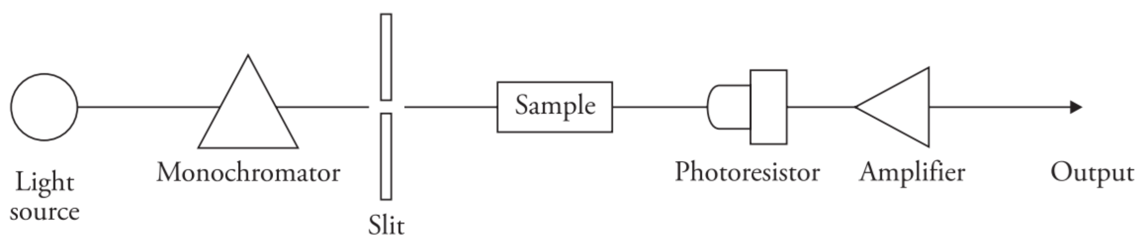
A spectrophotometer (a combination of a spectrometer and a photometer) is used to detect the percentage transmittance or absorbance of light radiation when light of a certain intensity or frequency range is passed through the sample.

The instrument compares the intensity of the transmitted light with that of the incident light.

Types-

1. Single Beam Spectrophotometer: It utilizes a single beam of light that passes through the sample.

Sample and reference solutions need to be manually interchanged for each wavelength measurement.

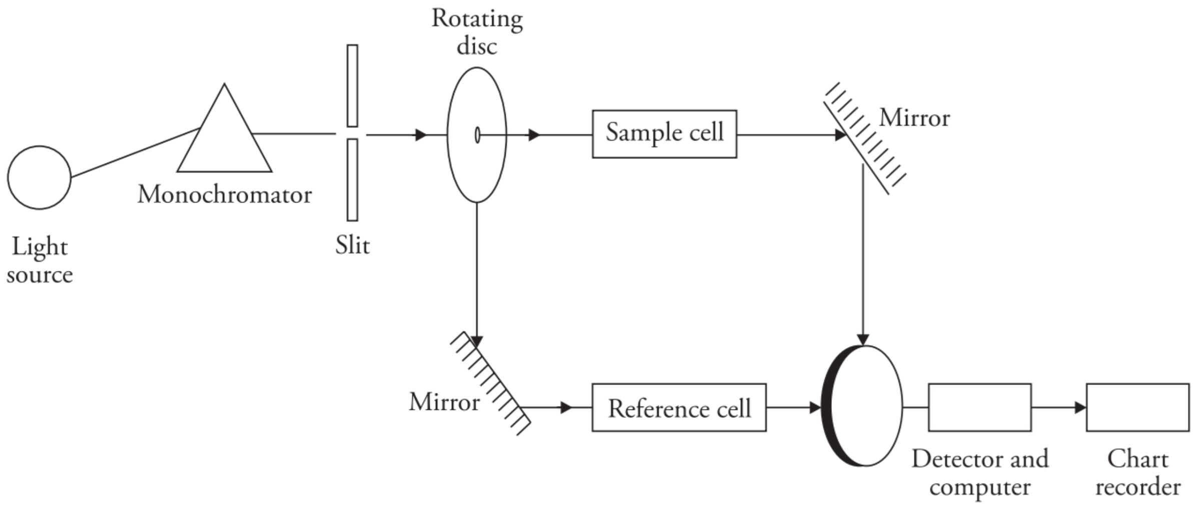


2. Double Beam Spectrophotometer: Splits the light beam into two equal intensity beams.

One beam passes through the reference solvent, while the other goes through the sample solution.

The instrument measures the absorbance of both simultaneously, subtracting the solvent absorption electronically to isolate the compound's absorbance or transmittance characteristics.

The resulting spectrum is automatically recorded, often represented as absorbance against wavelength.



What are electronic transitions?

When a molecule absorbs UV or visible light, its electrons move from bonding orbitals (like s or p orbitals) to anti bonding orbitals (denoted by *) at higher energy levels.

Types of Transitions-

1. s → s* Transitions: These occur when electrons in bonding orbitals are promoted to anti bonding orbitals, require high energy, found in the far UV region (~150 nm), common in hydrocarbons like methane and propane.

2. n → s* Transitions: These involve electrons from unshared pairs on heteroatoms moving to anti bonding orbitals, requiring less energy and found in saturated compound with heteroatoms carrying unshared electron pairs. Ex- alcohols, ethers, and amines.

3. p → p* Transitions: Occur in compounds with double and triple bonds, needing less energy, thus appearing at longer wavelengths.
4. n → p* Transitions: Electrons from unshared pairs on heteroatoms are excited to p* orbitals, requiring the least energy and occurring at larger wavelengths.

Ex- Saturated aldehydes exhibit both n → p* transitions around 280 nm and p → p* transitions around 180 nm.

Here s is the sigma and p is the pi.

Study the order of energy of all the transitions from class notes shared by me.

Allowed Transitions:

Allowed transitions have extinction coefficient values (emax) greater than 10^4 and commonly result from p → p* transitions.

They occur when electrons transition from bonding to anti bonding molecular orbitals, often in compounds with double or triple bonds, and are more energetically favorable, leading to higher absorption intensity.

Forbidden Transitions:

Forbidden transitions have extinction coefficient values below 10^4 and primarily arise from n → p* transitions.

These transitions involve electrons from unshared pairs on heteroatoms moving to anti bonding orbitals, which typically require lower energy, resulting in lower absorption intensity compared to allowed transitions.

What are chromophore and auxochromes?

Chromophore-

Any system causing color in a compound was termed as a chromophore but now it refers to a covalently bonded group exhibiting characteristic UV or visible absorption.

Two types include those with π electrons undergoing $\pi \rightarrow \pi^*$ transitions (Ex- C=C, -C=C-) and those with both π and non bonding electrons undergoing both $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions (Ex- C=O, -C≡N, -N=N-).

Responsible for imparting color through electronic transitions within a molecule.

Auxochrome-

Auxochromes are color enhancers that don't cause color themselves but shift absorption bands towards the red end of the spectrum.

Saturated groups like OH, NH2, and Cl, they change intensity and wavelength of maximum absorption when attached to a chromophore.

Enhances the color intensity and shifts the absorption spectrum towards longer wavelengths.

Write about the various shifts in absorption spectra?

1. **Bathochromic Shift (Red Shift):** Absorption maximum shifts to longer wavelengths due to auxochromes or solvent polarity decrease.

2. **Hypsochromic Shift (Blue Shift):** Absorption maximum shifts to shorter wavelengths, often due to removal of conjugation or changes in solvent.

3. **Hyperchromic Shift:** Intensity of absorption maximum increases, often caused by the introduction of auxochromes.

4. **Hypochromic Shift:** Intensity of absorption maximum decreases, typically due to geometric distortions induced by certain groups.

What are the applications of UV visible spectroscopy?

1. UV visible spectroscopy is widely used for quantitative analysis of compounds by measuring the absorbance of known concentrations, enabling determination of concentrations in unknown samples.

2. It helps in identifying molecular structures based on characteristic absorption patterns, aiding in the analysis of complex organic molecules.

3. UV visible spectroscopy is crucial in pharmaceutical industries for assessing drug purity, identifying active ingredients, and monitoring reaction kinetics during drug development.

4. It plays a vital role in environmental monitoring by detecting and quantifying pollutants in air, water, and soil, contributing to efforts in pollution control and management.

5. UV visible spectroscopy is extensively used in biochemical research for studying protein structure, enzyme kinetics, and DNA interactions, providing insights into biological processes and mechanisms.

IR SPECTROSCOPY/VIBRATIONAL SPECTROSCOPY

What is IR spectroscopy?

1. Infrared (IR) spectroscopy involves the study of molecular vibrations induced by infrared radiation, where covalent bonds between atoms act as tiny springs, causing molecular atoms to vibrate.

2. An IR spectrophotometer consists of a light source (such as a Globar or Nernst filament), a filter or monochromator for obtaining monochromatic light, sample holders made of materials like NaCl, and detectors like thermocouples.

3. Samples are typically prepared in cells made of NaCl or alkali metal halides, with solid samples often ground with KBr into discs.

It's crucial to ensure the samples are completely dry, as water absorbs strongly in the IR region.

4. In IR spectroscopy, a beam of IR radiation is passed through the sample.

The molecules absorb radiation of appropriate energy, transitioning to higher vibrational levels.

The difference in intensity between the beam passing through the sample and the reference is recorded to obtain the IR spectrum.

5. The IR region extends from 0.8 μm to 200 μm, but the most relevant region for analysis is 2.5 μm to 15 μm. This range is divided into three regions: near IR, mid IR (the most significant for absorptions), and far IR (dealing with pure rotational motion).

6. IR light is absorbed only when there's a difference in the dipole moment between two vibrational levels of a molecule.

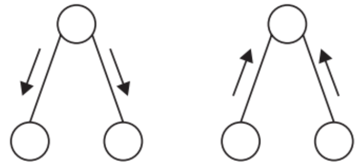
This interaction between the oscillating dipole moment due to molecular vibrations and the electric vector of the IR beam leads to absorption bands in the spectrum.

What are the various types of vibrations?

Broadly two types-

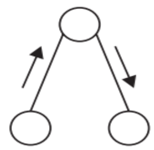
Stretching vibrations- In this type of vibrations, the distance between the atoms increases or decreases but the atoms remain in the same bond axis. Stretching can be of two types-

1. Symmetric stretching- In symmetric stretching, the movement of the atoms with respect to a particular atom is in the same direction



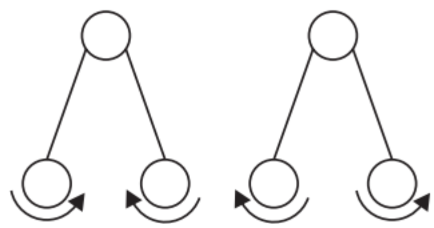
2. Asymmetric stretching- In these vibrations, one atom approaches the central atom and the other departs from it

Bending vibrations-The position of the atom changes with respect to the original bond axis but the distance between the atoms remains constant. It is of two types:

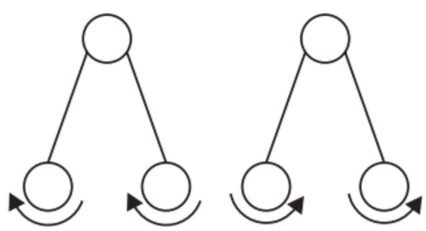


1. In plane bending- The atoms remain in the same plane as the nodal plane of the system. These are of two types-

A. Scissoring- The two atoms approach each other and move away like the two arms of a scissors

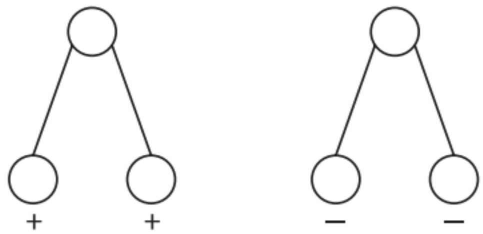


B. Rocking- Both the atoms move in the same direction

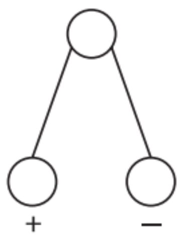


2. Out of plane bending- The atoms move out of the nodal plane with respect to the central atom. These are of two types-

A. Wagging- Both the atoms swing up and down with respect to the central atom

B. 

Twisting- One atom moves up the plane and the other moves down the plane with respect to the central atom



What is degrees of freedom?

Degrees of freedom refer to the number of independent ways a system can move or vary without violating any constraints or conditions.
It's like counting the number of different things that can change without breaking any rules.

	Types of degree of freedom	**Total degree of freedom**
Isolated atom	Only translational degree of freedom (it does not have rotational and vibrational degree of freedom)	3
Molecule	Translational + rotational + vibrational degree of freedom	$3n$ where n is the number of atoms in a molecule

For linear molecules of n atoms

Total degrees of freedom = 3n

Translational degree of freedom = 3

Rotational degree of freedom = 2

Vibrational degree of freedom = 3n – 3 – 2 = 3n – 5

Number of fundamental bands for a linear molecule = 3n – 5.

For non linear molecules of n atoms

Total degrees of freedom = 3n

Translational degree of freedom = 3

Rotational degree of freedom = 3

Vibrational degree of freedom = 3n – 3 – 3 = 3n – 6
Hence, number of fundamental bands = 3n – 6
Describe the fingerprint region of IR spectroscopy

The fingerprint region in IR spectroscopy refers to the spectral range between 1500 cm^-1 and 667 cm^-1.

1. This region contains absorption bands resulting from bending vibrations and stretching vibrations of various bonds like C-C, C-O, and C-N bonds

2. The bands in the fingerprint region are unique to each organic compound, akin to fingerprints being unique to individuals.

3. By comparing the fingerprint region of an unknown compound with reference spectra, chemists can identify and characterize organic compounds accurately.

4. While the functional group region (4000-1500 cm^-1) provides information about specific functional groups, the fingerprint region offers a broader and more complex spectrum that aids in comprehensive compound identification.

What are the applications of IR spectroscopy?

1. Analyzing characteristic absorption frequencies of functional groups aids in determining the structures of organic compounds.

2. Used to ensure the purity and composition of drugs, supporting quality control processes in pharmaceutical manufacturing.

3. Helps forensic scientists identify unknown substances found at crime scenes by comparing their IR spectra with reference databases.

4. Contributes to monitoring environmental pollutants in air, water, and soil, supporting efforts in environmental protection and management.

5. Crucial in characterizing polymers to understand their molecular structure, composition, and properties, aiding in various industrial applications.

NMR SPECTROSCOPY(NUCLEAR MAGNETIC RESONANCE)/ PROTON MAGNETIC RESONANCE SPECTROSCOPY

1. NMR spectroscopy involves the absorption of electromagnetic radiation in the radiofrequency region by nuclei in a sample.

2. Nuclei possess magnetic moments, behaving as tiny bar magnets due to their spinning charge, which can align with or against an external magnetic field.

3. Nuclei undergo precessional motion akin to spinning tops when placed in an external magnetic field, resulting in alignment either parallel or anti-parallel to the field.

4. Transition between these orientations occurs when the nucleus absorbs energy, termed flipping, with the frequency matching that of the radiofrequency beam, leading to resonance.

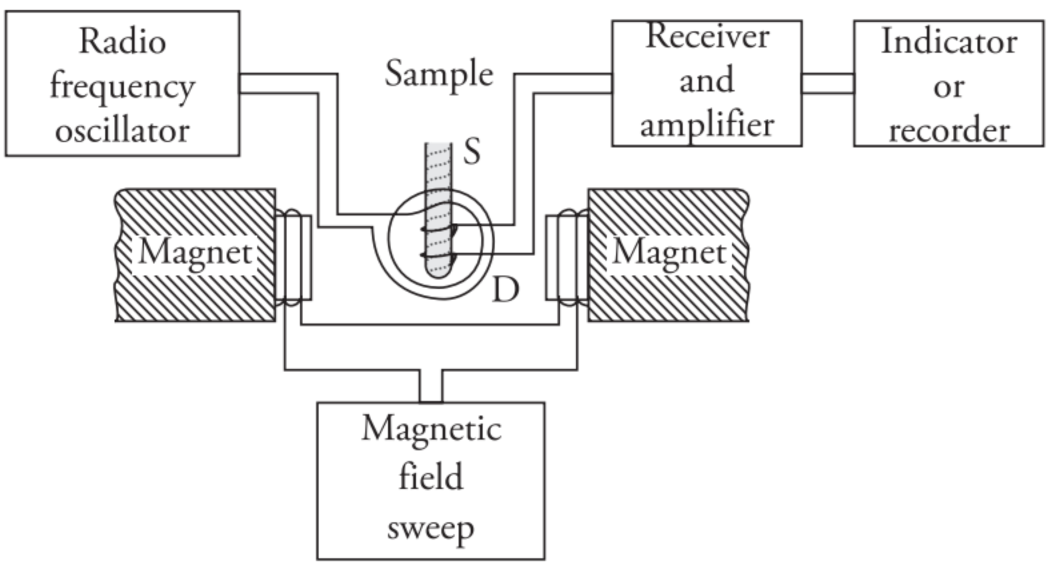
5. Only nuclei with spin quantum number (1) greater than zero exhibit NMR, with the spin quantum number determined by the mass and atomic numbers of the nucleus.

6. NMR spectrophotometers consist of a magnet to supply the magnetic field, a radiofrequency source, a sample holder, and

a signal detector and recording system to observe the resonance signals.

Read this answer from organizer too

NMR SPECTROMETER



What is chemical shift and how is it measured?

1. Chemical shift refers to the shift in the position of NMR spectrum signals caused by shielding or deshielding of protons by surrounding electrons.

2. The chemical shift depends on the electron density around the proton, the presence of nearby protons, and other environmental factors.

3. Protons experiencing shielding are shifted upfield, indicating higher effective magnetic field strength, while deshielded protons are shifted downfield, suggesting lower effective field strength.

4. Chemical shift is measured relative to a standard reference compound, commonly **tetramethylsilane (TMS)**, which has a sharp single signal due to its 12 equivalent protons and high shielding.

5. The difference in the absorption position of protons compared to the TMS signal is quantified as the chemical shift, providing valuable information about the molecular environment and structure.

Measurement of Chemical Shift:

1. Chemical shift is measured by comparing the absorption frequencies of protons in a sample to those of TMS, which is

arbitrarily assigned a chemical shift value of 0 ppm (parts per million).

2. NMR spectrometers record the relative absorption frequencies of protons in the sample compared to TMS, allowing researchers to determine the chemical shift values accurately.

3. The sharp, well defined signal of TMS serves as a reliable reference point for measuring chemical shifts, facilitating precise analysis of NMR spectra.

Chemical shift positions are usually expressed in delta units and it is dimensionless.

$$\delta = \frac{\nu_{\text{sample}} - \nu_{\text{TMS}}}{\text{operating frequency in megacycles}} = \frac{\Delta\nu}{\text{operating frequency in megacycles}}$$

$\Delta\nu$ = frequency shift

What are the applications of NMR?

1. NMR spectroscopy is crucial for predicting the structures of organic compounds by analyzing the number of signals, splitting patterns, and signal positions, providing info about molecular composition and bonding.

2. It can distinguish between isomeric compounds based on the distinct number of signals and splitting patterns in their NMR spectra, helping in compound identification and characterization.

3. NMR spectra show chemical shifts, indicating the shielding or deshielding of protons by surrounding electrons, which helps in determining the molecular environment, functional groups, and hydrogen bonding within compounds.

4. NMR spectroscopy can quantitatively analyze the concentration of compounds in mixtures, making it valuable for quality control in industries such as pharmaceuticals.

5. NMR spectroscopy has found applications in medical imaging techniques like magnetic resonance imaging (MRI),

allowing non invasive visualization of internal body structures and abnormalities.

What is MRI and its applications?

MRI STANDS FOR MAGNETIC RESONANCE IMAGING

1. MRI utilizes strong magnetic fields and radiofrequency pulses to detect abnormalities in tissue molecules, particularly relying on the magnetic properties of hydrogen atoms in water molecules.

2. It consists of-

Primary Magnet: Generates the static magnetic field (B0) aligning protons along the z-axis.

Gradient Magnets: Create variable magnetic fields for spatial encoding of MRI images.

Radiofrequency Coils (RF Coils): Produce RF pulses to excite protons and induce resonance.

Computer System: Processes RF signals, performs mathematical calculations, and generates images.

Appliactions of MRI-

1. MRI is widely used for diagnosing various medical conditions, including cancer, soft tissue injuries, and neurological disorders, providing detailed anatomical images for accurate diagnosis and treatment planning.

2. MRI enables precise visualization of brain structures, aiding in the diagnosis and monitoring of neurological diseases such as stroke, Alzheimer's, and multiple sclerosis.

3. MRI is valuable for evaluating musculoskeletal injuries, assessing joint integrity, and detecting conditions like ligament tears, osteoarthritis, guiding orthopedic treatments.

What is mass spectrometry?

1. Mass spectrometry analyzes molecules based on their mass to charge ratio (m/z), separating ions by mass and detecting them to generate a mass spectrum, helping in compound identification and structural information

2. Samples are ionized using techniques like electron impact or electrospray ionization, converting molecules into charged ions for analysis,

3. Ions are separated based on their mass to chargeratio as they travel through an electric or magnetic field, allowing for the differentiation of compounds in the sample and providing info into their molecular weight and structure.

Applications of Mass Spectrometry:

1. It is widely used in forensic analysis, drug discovery, and environmental monitoring for accurate identification of unknown compounds, ensuring product safety and regulatory compliance in various industries.

2. Essential tool in studying proteins and metabolites in biological samples, enabling biomarker discovery, disease

diagnosis, and understanding metabolic pathways for advancements in healthcare and biotechnology.

3. Used in pharmaceuticals, food, and environmental testing for quality assurance, detecting contaminants, verifying product integrity, and ensuring compliance with regulatory standards, contributing to consumer safety and product reliability.