Energy levels in a molecule

A molecule has 4 types of energy levels

1. **Electronic Energy levels.** The energy associated with distribution of electrons in a molecule (bonding and antibonding orbitals). It is quantized, means it can have only certain discrete values. The energy gap between these levels falls in UV-visible region.

2. **Vibrational Energy levels.** The bonds in a molecule always vibrate (stretch or bend). Here during vibration the centre of gravity remains constant while the position of atoms changes. The energy associated with vibrational motion is vibrational energy. It is also quantized. The energy gap between two adjacent vibrational energy levels falls in IR region.

3. **Rotational Energy levels.** Gaseous molecule will always rotate in space about an axis passing through the centre of mass. The energy associated with rotation is called rotational energy levels. This is also quantized. Therefore it can be represented as levels. The energy gap between rotational energy levels corresponds to microwave region.

4. **Translational energy levels.** Energy associated with translational motion. During the translational motion the position of centre of mass changes. The difference between the energy levels is too small (almost zero). Therefore it appears as continuous.

\[ E_{\text{tot}} = E_{\text{trans}} + E_{\text{rot}} + E_{\text{vib}} + E_{\text{elec}} \]

\[ E_{\text{trans}} \ll E_{\text{rot}} \ll E_{\text{vib}} \ll E_{\text{elec}} \]

Therefore the spectroscopic transitions possible in a molecule are rotational, vibrational and electronic.

**Absorption Spectrum:**

When a continuous range of radiation is directed to a molecule, certain frequencies are absorbed by the molecule. The spectrum obtained is called absorption spectrum. Example (UV/Visible (electronic)spectroscopy, Vibrational (IR)spectroscopy)

**Emission Spectrum:**

The molecules get excited by irradiating with electromagnetic radiation. At a later time the molecules will relax back to the initial low energy state. During this process light is emitted. The spectrum obtained is called emission spectrum. Fluorescence spectroscopy, Phosphorescence spectroscopy
Beer Lamberts Law

When a monochromatic light is passed through a dye solution, the absorbance is proportional to product of concentration and thickness of solution. \[ A = \varepsilon \cdot c \cdot t \] \[ \varepsilon \] is molar absorptivity, \( c \) is concentration and \( t \) is thickness of solution.

Derivation:
Consider a parallel beam of monochromatic electromagnetic radiation of intensity \( I_o \) is passed through an absorbing solution of thickness \( x \) and concentration \( c \).

The rate of decrease in intensity \( -dI \) of radiation with thickness of solution \( dx \) is proportional to intensity of incident light \( I \) at that point, concentration of solution and \( dx \).

\[ -dI = k \cdot I \cdot c \cdot dx \]

k constant

On rearranging \[ \frac{-dI}{I} = k \cdot c \cdot dx \]

On integrating \[ -\int_{I_o}^{I} \frac{dI}{I} = k \cdot c \int_{0}^{x} dx \]

\[ \ln \frac{I_o}{I} = k \cdot c \cdot x \]

\[ \log \frac{I_o}{I} = \varepsilon \cdot c \cdot x \]

\( \varepsilon \) is molar absorption coefficient \( (k/2.303) \) \( \text{[unit = M}^{-1}\text{cm}^{-1}] \)

\( \log \frac{I_o}{I} \) is absorbance \( A \)
Facts about Beer-Lamberts law

According to beer lamberts law absorbance increases when one increases concentrations and/or path length (solution thickness).

In order to verify Beer-lamberts law, one has to measure absorbance (a) of a particular dye solution at different concentrations (c). All measurement should be made in the same sample holder (ie path length is constant). A plot of A vs c is a straight line passing through the origin. Colorimetric analysis of quantity of chemicals is possible with Beer_lambers law.

If a non-linear plot is obtained it means there is deviation from Beer-lamberts law.

Beer-lamberts law is applicable only to dilute solution, hence it is a limiting law.

Few cases of deviation of Beer-lamberts law

At higher concentrations the average distance between absorbing species diminishes. Here each absorbing species perturbs the charge distribution of nearby absorbing species. This interaction alters their ability of to absorb a given wavelength of radiation.

According to Kortum and Seiller Molar extinction coefficient depends on refractive index of absorbing solution. At low concentration refractive index is practically constant, hence Beer-lamberts law is obeyed. At high concentration refractive index may vary appreciably, and system deviates from beer-lamberts law.
Electronic spectroscopy or UV/Visible spectroscopy (Module 1 Lecture 2 N 3)

It is an absorption spectroscopy.

A molecule has quantized electronic energy levels. Energy gap between these levels corresponds to the energy of UV/Visible Photons. Therefore one can use UV/visible light to study electronic spectroscopy.

In electronic spectroscopy, transition between electronic energy levels takes place. Absorption of UV/visible radiations results in the transition between electronic energy levels (electronic excitation). That is promotion of an electron from lower energy level to higher energy level. Thus molecular energy increases.

Instrumentation (Schematic representation of double beam UV-Visible spectroscope)

Types of electronic transitions

Three types of electrons are involved in organic molecules

a) $\sigma$ - electrons: Electrons forming sigma bond.

b) $\pi$ – electrons: Electrons responsible for double and triple bond.

c) $n$-electrons: These are unshared or non-bonded electrons.

Four types of transitions are possible in an organic molecule.
n-π* transitions: These types of transitions are related to the promotion of an electron from a non-bonding orbital to π* antibonding orbital. These transitions are shown by unsaturated molecules which contain hetero atoms like N, O, Cl, Br, S etc. These transitions are weak. Example, in aliphatic aldehydes and ketones n-π* transitions generally occurs in the wavelength range 270 to 300 nm.

π-π* transitions: These types of transitions are related to the promotion of an electron from a π-bonding orbital to π* antibonding orbital. These are allowed transitions and therefore are very intense. The unsaturated organic molecules like alkenes have π-bonding orbital as HOMO and π* antibonding orbital as LUMO shows this type of transitions. For example ethylene molecule gives an absorption maximum at 169nm (which is not scanned by commercial spectrometer). Extending the conjugation, further red-shift the absorption maximum.

n-σ* transitions: These types of transitions are related to the promotion of an electron from a non-bonding orbital to σ* antibonding orbital. These are forbidden transitions and therefore are weak intense. The saturated organic molecules with hetero atoms like N, O, S, Cl etc shows this type of transitions. Example ethers, chloroform etc. Usually absorption takes place below 200nm, therefore commercial spectrometers does not scan this.

σ-σ* transitions: These types of transitions are related to the promotion of an electron from a σ-bonding orbital to σ* antibonding orbital. This type of transitions is common for saturated organic molecules without hetero-atoms. These are allowed transitions. Usually this transition occurs below 150 nm. These transitions cannot be observed in commercial spectrometers (200 nm – 750 nm).

**Reason for Broadening of spectra (instead of a single line)**

Each electronic energy levels have vibrational sub levels and each vibrational levels have rotational sub-levels. Each peak represents group of transition from a particular combination of vibrational and rotational level of ground state to the corresponding one in the excited state.
Applications of UV-Visible spectroscopy

1). Qualitative analysis: For characterizing aromatic compound, conjugated dienes and dyes by comparing the spectra (Hartley’s Rule).

2). Detection of impurities: It is one of the best methods for detecting impurities in organic solvents. Example benzene is the most common impurity in cyclohexane. Benzene can be detected by its absorption band at 255 nm.

3). Quantitative analysis: Determination of unknown concentrations. Basis is Beer-Lamberts law.

4). Study kinetics of chemical reaction: Fix the wavelength of ether reactant or product and measure absorbance at different time intervals. Plot absorbance vs time. Slope contains information about rate constant.

Reading Assignments

Correlation of Molecular Structure and Spectra Conjugation

π to π * transitions, when occurring in isolated groups in a molecule, give rise to absorptions of fairly low intensity. However, conjugation of unsaturated groups in a molecule produces a remarkable effect upon the absorption spectrum. The wavelength of maximum absorption moves to a longer wavelength and the absorption intensity may often increase.
It is useful to remember that

\[ 0\%T = \infty A \]
\[ 0.1\% = 3.0A \]
\[ 1.0\%T = 2.0A \]
\[ 10\%T = 1.0A \]
\[ 100\% = 0A \]

Figure 11 (a) %T vs concentration (b) Absorbance vs concentration
Q1. What are the commonly encountered electronic transitions in an organic molecule?

Q2. Arrange the following molecules in the increasing order of $\lambda_{\text{max}}$.

\begin{align*}
(a) & \quad \text{ molecule } \\
(b) & \quad \text{ molecule } \\
(c) & \quad \text{ molecule }
\end{align*}

Q3. Less energy is only required for a $\pi \rightarrow \pi^*$ of 1,3-butadiene than similar transition in ethene. Comment on the statement.

Q4. Predict the electronic transitions involved in the following compounds. (a) Methyl chloride  (b) Methyl alcohol (c) triethylamine.

Q5. Predict the electronic transitions involved in the following compounds. (a) Alkenes  (b) Alkynes  (c) aldehydes (d) ketones (e) carboxylic acids (f) esters (g) amides and (i) haloalkanes

Q6. Name a compound which contains sigma, pi and n-electrons.

Q7. Predict the electronic transitions observable for a saturated aldehydes and ketones.

Q8. List the electronic transitions possible when UV/Visible light is absorbed by the following molecule. (a) $\text{CH}_4$ (b) $\text{CH}_3\text{Cl}$ and (c) $\text{HCHO}$

Q9. The UV spectrum of acetone shows two peaks at $\lambda_{\text{max}} = 189 \text{ nm}$ and $\lambda_{\text{max}} = 273$. Identify the electronic transitions for each peak.

Q10. Which molecule absorbs at the longest wavelength, Cyclo-1,3-hexadiene or Cyclo-1,4-hexadiene?

\begin{align*}
1,3 \text{ hexadiene} & \quad \text{ and } \\
1,4 \text{ hexadiene} & \quad \text{ }
\end{align*}
**Vibrational spectroscopy / IR spectroscopy** *(Module 1 Lecture 4 and 5)*

IR spectroscopy or vibrational spectroscopy is an absorption spectroscopy (Absorption of IR radiations)

Molecules have quantized vibrational energy levels. The energy gap between vibrational levels is in IR region. Therefore absorption of IR photons results in vibrational excitations.

Absorption of IR radiations (wave number 500 cm\(^{-1}\) to 4000 cm\(^{-1}\)) by molecule results in transitions between two vibrational energy levels.

**Plotting the spectra:**

![IR Spectra Graph](mcalt-review.org)

**Modes of vibrations (in a molecule)**

A linear molecule with \( n \) number of atoms will have \( 3n-5 \) types of vibrations are possible. For non-linear molecules \( 3n-6 \) types of vibrations are possible.

**Stretching**

i. Symmetric Stretching

\[
\begin{array}{c}
\text{O} \equiv \text{C} \equiv \text{O} \\
\text{O} \equiv \text{C} \equiv \text{O} \\
\text{O} \equiv \text{C} \equiv \text{O} \\
\text{H} \equiv \text{O} \equiv \text{H} \\
\text{H} \equiv \text{O} \equiv \text{H}
\end{array}
\]

ii. Asymmetric Stretching

\[
\begin{array}{c}
\text{O} \equiv \text{C} \equiv \text{O} \\
\text{O} \equiv \text{C} \equiv \text{O} \\
\text{O} \equiv \text{C} \equiv \text{O} \\
\text{H} \equiv \text{O} \equiv \text{H} \\
\text{H} \equiv \text{O} \equiv \text{H}
\end{array}
\]

**Bending**

i. in-plane bending

\[
\begin{array}{c}
\text{O} \equiv \text{C} \equiv \text{O} \\
\text{O} \equiv \text{C} \equiv \text{O} \\
\text{O} \equiv \text{C} \equiv \text{O} \\
\text{O} \equiv \text{C} \equiv \text{O} \\
\text{O} \equiv \text{C} \equiv \text{O} \\
\text{O} \equiv \text{C} \equiv \text{O} \\
\text{O} \equiv \text{C} \equiv \text{O} \\
\text{O} \equiv \text{C} \equiv \text{O}
\end{array}
\]

ii. out-plane bending

\[
\begin{array}{c}
\text{O} \equiv \text{C} \equiv \text{O} \\
\text{O} \equiv \text{C} \equiv \text{O} \\
\text{O} \equiv \text{C} \equiv \text{O} \\
\text{O} \equiv \text{C} \equiv \text{O} \\
\text{O} \equiv \text{C} \equiv \text{O} \\
\text{O} \equiv \text{C} \equiv \text{O} \\
\text{O} \equiv \text{C} \equiv \text{O} \\
\text{O} \equiv \text{C} \equiv \text{O}
\end{array}
\]

- Scissoring
- Rocking
- Wagging
- Twisting
**Mechanism of interaction of IR light with oscillating dipole moment**

During vibration, if there occurs a change in dipole moment. It will lead to the generation of an oscillating electric field. Consider the asymmetric stretching vibration of carbon dioxide.

Oscillating dipole is called electric field.

When a photon of frequency comes in resonance with the frequency of vibration of molecule, absorption of a photon takes place and molecule will be vibrating in next higher vibrational level.

For a molecular vibrations to be IR active a change in dipole moment is must during vibrations.

**Vibrational energy states:**

The energies of Quantum mechanical simple harmonic oscillator are quantized and the permitted energy levels are

\[ E_v = \left( v + \frac{1}{2} \right) \hbar \omega_0 \]

\[ \omega_0 = \frac{1}{2\pi} \sqrt{\frac{k_f}{\mu}} \]

\( \nu = 0, 1, 2, 3, \ldots \ldots \)  
\( \omega_0 \) is the fundamental frequency of vibration.  
\( \mu \) is the reduced mass = \( m_1.m_2/(m_1+m_2) \)

**Selection rule:**

Gross selection rule: A change in dipole moment is must during vibrations.

Specific selection rule: \( \Delta \nu = \pm 1 \) (A transition to next higher is only possible during absorption)

**Reason for broadening of vibrational spectrum**

Since vibrational levels are quantized and equally spaced, we expect the spectrum to be a discrete line instead we obtain a narrow peak. This is due to anharmonicity effect. In reality the molecule deviates from parabolic expressions and spacing between vibrational levels decreases as vibrational quantum number increases.
Prove that frequency of absorbed IR radiation ($\nu$) is equal to fundamental frequency of molecular vibrations ($V_0$).

Vibrational energy level of a molecule is,

$$E_v = \left( v + \frac{1}{2} \right) \hbar \theta_0$$  \hspace{2cm} v = 0, 1, 2, 3, \ldots \ldots \text{(vibrational energy levels)}

$\theta_0$ is the fundamental frequency of vibration.

Consider a molecule undergoing a vibrational transition from lower vibrational level $v$ to upper vibrational level $v'$ by absorbing an IR radiation energy $h \nu = \Delta E$

$$\nu' - \nu = 1$$  \hspace{2cm} \text{Selection rule:} \quad \Delta \nu = \pm 1$$

$$E_v = \left( v + \frac{1}{2} \right) \hbar \theta_0$$

$$E_{v'} = \left( v' + \frac{1}{2} \right) \hbar \theta_0$$

$$\Delta E = \Delta \nu \hbar \theta_0 = h \theta_0$$

Thus $\nu = \theta_0$ (frequency of absorbed IR radiation ($\nu$) is equal to fundamental frequency of molecular vibrations ($V_0$)).

Applications of IR spectroscopy:

1). Determination of force constant of diatomic molecule.

$$\theta_0 = \frac{1}{2\pi} \sqrt{\frac{K_f}{\mu}} \quad K_f \text{ is the force constant: } \mu \text{ is the reduced mass = } m_1.m_2/(m_1+m_2) \quad \theta_0 \text{ is the fundamental frequency of vibration = frequency of IR radiation absorbed.}$$
2. Identification of functional group.
   The presence of functional group can readily detect from their stretching vibrations.

3. Identification of unknown compound. (Qualitative analysis)
   This is generally done by comparison of IR spectrum of unknown compound with that of known compound. This comparison is especially made at the fingerprint region (700 to 1500 cm\(^{-1}\)). The spectrum in the fingerprint region is unique for each molecule.

4. To distinguish between intermolecular and intramolecular hydrogen bonding.
   The OH (Hydrogen bonding) stretching frequency does not change on dilution in the case of intramolecular hydrogen bonding. While the intermolecular H-bonding weakens on dilution and there is change in absorption frequency.

5. To study the progress of a chemical reaction (Functional group interconversion).
   As the reaction proceeds the OH stretching band of secondary alcohols slowly disappears and the carbonyl stretching band appear as ketone is formed.
Q. Sketch the normal modes of vibrations of a) H\textsubscript{2}O and CO\textsubscript{2} and determine which of them are IR-active/IR-inactive and why?

\begin{itemize}
    \item \textbf{CO\textsubscript{2} is a linear molecule} \( - \text{O} = \text{C} = \text{O} - \)
    \begin{itemize}
        \item Symmetric Stretching - No change in dipole during vibrations, therefore IR inactive
        \begin{itemize}
            \item \( \text{O} = \text{C} = \text{O} \) 0D
            \item \( \text{O} = \text{C} = \text{O} \) 0D
        \end{itemize}
        \begin{itemize}
            \item Asymmetric Stretching - change in dipole during vibrations, therefore IR active
            \begin{itemize}
                \item \( \text{O} = \text{C} = \text{O} \) 0D
                \item \( \text{O} = \text{C} = \text{O} \) 0D
            \end{itemize}
            \begin{itemize}
                \item In-plane bending - change in dipole during vibrations, therefore IR active
                \begin{itemize}
                    \item \( \text{O} = \text{C} = \text{O} \) 0D
                    \item \( \text{O} = \text{C} = \text{O} \) 0D
                \end{itemize}
                \begin{itemize}
                    \item Out-of-plane bending - change in dipole during vibrations, therefore IR active
                    \begin{itemize}
                        \item \( \text{O} = \text{C} = \text{O} \) 0D
                        \item \( \text{O} = \text{C} = \text{O} \) 0D
                    \end{itemize}
                \end{itemize}
            \end{itemize}
        \end{itemize}
    \end{itemize}
    \item \textbf{H\textsubscript{2}Ois a nonlinear molecule} \( - \text{H} - \text{O} - \text{H} - \)
    \begin{itemize}
        \item Symmetric Stretching - There is change in dipole during vibrations, therefore IR active
        \begin{itemize}
            \item \( \text{H} - \text{O} - \text{H} \) 0D
            \item \( \text{H} - \text{O} - \text{H} \) 0D
        \end{itemize}
        \begin{itemize}
            \item Asymmetric Stretching - There is change in dipole during vibrations, therefore IR active
            \begin{itemize}
                \item \( \text{H} - \text{O} - \text{H} \) 0D
                \item \( \text{H} - \text{O} - \text{H} \) 0D
            \end{itemize}
            \begin{itemize}
                \item In-plane bending - change in dipole during vibrations, therefore IR active
                \begin{itemize}
                    \item \( \text{H} - \text{O} - \text{H} \) 0D
                    \item \( \text{H} - \text{O} - \text{H} \) 0D
                \end{itemize}
            \end{itemize}
        \end{itemize}
    \end{itemize}
\end{itemize}
**Chemical Shift**

When a molecule is placed in a magnetic field, the electronic orbital angular momentum can give rise to an additional magnetic field. This secondary field may oppose or reinforce the applied field.

**Shielding:** If the additional magnetic field oppose the applied field, the net field felt by an NMR active nuclei (proton $^1\text{H}$) in a molecule will be less than the applied field, and the NMR active nuclei (proton $^1\text{H}$) is said to be shielded. The more shielded a proton is greater must be the strength of applied field in order to achieve resonance with the RF to produce an absorption signal. Ie a more shielded proton absorbs RF radiation at higher field strength—up field.

**Deshielding:** If the additional magnetic field due to electrons reinforce the applied field, the net field felt by an NMR active nuclei (proton $^1\text{H}$) in a molecule will be greater than the applied field, and the NMR active nuclei (proton $^1\text{H}$) is said to be deshielded. In order to bring resonance for deshielded proton one has to decrease the applied field strength. A more deshielded proton absorbs RF radiation at lower field strength—down field.

Due to shielding and deshielding chemically different protons in a molecule give NMR signal at different field strength. The position of NMR signals depends on the local electronic arrangement. This positional dependence is called chemical shift.

Chemical shift is usually measured relative to a reference compound. For proton ($^1\text{H}$)-NMR the standard reference is tetramethyl silane (TMS) – Si(CH$_3$)$_4$. TMS is chemically inert and has a low boiling point. In TMS all the 12 protons are identical therefore gives one sharp signal. Si is more electropositive than C. Hence the protons in TMS are more shielded than most of the organic compounds (upfield). Therefore the $^1\text{H}$-NMR signals of most of the organic compounds appear down field to TMS.

One of the scale for representing chemical shift is δ scale. For TMS δ value is assigned zero.

$$\delta (\text{scale}) = \frac{\delta_{\text{sample}} - \delta_{\text{TMS}}}{\text{Operating Freq in MHz}} \text{ ppm}$$
**Factors that affect Chemical Shift**

1). **Electro-negativity:**

Electro-negative elements pull the electron density away from the NMR active nuclei (proton). Removal of electron density away from the NMR active nuclei reduces the magnitude of shielding effect (i.e., deshielded). Therefore, the signals will appear more and more down field depending on electronegativity.

![Diagram showing deshielding effect due to electronegativity](image)

The deshielding effect of electronegative atom is cumulative.

![Diagram showing cumulative deshielding effect](image)

The deshielding effect of electronegative atom decreases as the distance is increased from electronegative atom.

![Diagram showing distance effect on deshielding](image)

2). **Magnetic Anisotropy:**

![Diagram showing magnetic anisotropy](image)

The aromatic protons are deshielded due to magnetic anisotropy. Hence signals appear at down field.

![Diagram showing shielding due to magnetic anisotropy](image)

Acetylenic protons are shielded due to magnetic anisotropy. Hence signals appear at up field.
Interpretation of Chemical shift NMR spectrum (low resolution NMR spectrum)

- Number of signals = Number of kinds (chemically different) of hydrogens.
- Position of signals = relative shielding and de-shielding (local electronic arrangements)
- Intensity ratio of signals = ratio of number of protons ($^1$H) of each kind.

Q3. How many kinds of protons are there in (i) CH$_3$-CH$_3$. (ii) CH$_3$-CH$_2$-CH$_3$, (iii) C$_6$H$_5$-CH$_3$ (iv) (CH$_3$)$_2$CHCH$_2$CH$_3$ (v) ClCH$_2$CH$_2$Cl

Ans:

(i) Only one kind of proton
(ii) Two kinds of protons
(iii) Two kinds of protons
(iv) Four kinds of proton.
(v) Only one kind of proton.
**Interpretation of Chemical shift NMR spectrum (low resolution NMR spectrum)**

Consider the chemical shift low resolution spectrum of Methanol (CH$_3$OH)

In methanol we have two different kinds of Hydrogens (Chemically different), 3 Ha protons and 1 Hb proton. Therefore we will get two NMR absorption signals at two different field strengths.

Hb protons are directly connected to electronegative atom whereas Ha protons are not. Therefore signal for Hb protons will be relatively de-shielded with respect to Ha.

The intensity (height) of signal for Ha is greater than the intensity (height) of signal for Hb. The ratio of intensity of heights is the relative ratio of number of protons of each kind (n(Hb): n(Ha) = 1:3).

Consider the chemical shift low resolution spectrum of Ethanol (CH$_3$-CH$_2$-OH)

In ethanol we have three kinds of chemically different protons (3 Ha type, 2 Hb type and 1 Hc type. Therefore we will get three NMR absorption signals at three different field strengths.

Hc protons are directly connected to electronegative O atom therefore the signal for Hc proton will be relatively de-shielded with respect to signal for Ha and Hb. Ha protons are far away from electronegative O atom therefore signal for Ha will be relatively shielded.

( n(Hc) : n(Hb) : n(Hc) = 1 : 2 : 3) Is the relative
Information from a low resolution chemical shift NMR spectrum

>> Number of signals (Peaks) = Number of kinds (chemically different) of hydrogens it has.
   For example, If an NMR spectrum contains 3 signals means it has 3 chemically different kinds of protons.

>> Position of signals = relative shielding and de-shielding (local electronic arrangements close to each kind of proton)

>> Intensity ratio of signals = ratio of number of protons \((^1H)\) of each kind (How many protons of each type are present)

**High Resolution NMR spectrum (Spin-Spin splitting)**

Consider the H-NMR spectrum of 1,1,2-trichloroethane.

There are two types of protons \((1H_a\text{ and } 2H_b)\). Therefore you get two signals in the NMR spectrum.

Ha is connected to a carbon atom that contains 2 electronegative Cl atoms whereas Hb is connected to a carbon atom that contains only one Cl atom. Therefore the NMR absorption signal for Ha will be relatively downfield with respect to signal for Hb.

Intensity of heights \(n(Ha) : n(Hb) = 1 : 2\)
In the high resolution spectra, the signal for Ha is split into triplet (three peaks) whereas signal for Hb is split into a doublet (two peaks). This phenomenon of splitting of signals into multiplets is called spin-spin splitting.

The signal for Hb is split into a doublet means magnetic resonance for Ha protons happens at two different field strengths that vary slightly. We know that, hydrogen nuclei produces a magnetic field due to its spin. Some of the Hydrogen nuclei in the neighbouring Carbon atom will be in $+\frac{1}{2}$ orientation and others will be $-\frac{1}{2}$ orientation. Therefore the one Hydrogen nuclei in the neighbouring Carbon produces two different magnetic field.

Ha protons have one neighbouring vicinal (Separated by 3 bonds) proton (Hb). Ha can orient up-spin or down-spin. Then the signal for Hb proton will split into a doublet.

Hb protons have two neighbouring vicinal (Separated by 3 bonds) proton (Hb). Two Hb can orient in $2+1=3$ ways. Then the signal for Hb proton will split into a triplet.
This is a result of interaction between spins of hydrogen atoms of interest with the spins of neighbouring chemically different vicinal hydrogen atoms (separated by three bonds). Spins of Ha and Hb protons are coupled.

1 Ha proton will split the signal for Hb proton into 1 + 1 (doublet peak)
2 Hb protons will split the signal for Ha proton into 2+1 (triplet peak)

In general the multiplicity (number of peaks) of an NMR signal is given by N+1 rule

N+1 RULE
The (n+1) Rule, For a particular set chemically identical Hydrogens have N number of Vicinal non-equivalent vicinal neighbouring Hydrogens then the multiplicity of the peak is N+1.

Pascal’s Triangle: It predicts the ratio of heights of signals in multiplets.

Coupling Constant, J: The spacing between the lines of a doublet, triplet or quartet (Multiplet) is called the coupling constant.
Q. Predict the High resolution NMR spectrum of 1,1-dichloroethane CH$_3$-CHCl$_2$ (High resolution means spin-spin splitting).

Applications of NMR
1. Structural elucidation of organic molecules. [Mapping C-H frame work] [$^1$H-NMR and $^{13}$C-NMR]
2. $^1$H-NMR is basic principle of MRI of soft tissues.
3. $^{31}$P-NMR can be used for imaging bones.
4. To study dynamics of biomacromolecules (like protein folding).
5. Structure of inorganic molecules
Schematic diagram of NMR spectrometer:

1. A strong magnet to provide the main magnetic field.
2. A sweep circuit consisting of Helmholtz coil super imposing the main magnet to provide additional field required to bring resonance condition.
3. A transmitter to supply the desired RF frequency.
4. A detector and amplifier circuit to pick up and amplify resonance signal.
5. A sample holder between two magnetic poles.
6. A device to receive and record signal.

MRI technique

MRI is magnetic resonance imaging. It is also called nuclear magnetic resonance imaging (NMRI) or magnetic resonance tomography (MRT).

It is an imaging technique used in medical settings to produce images of inside of human body.

It is based on the principle of nuclear magnetic resonance.

Biological tissues consist predominantly of water and fat. Both contain NMR active hydrogen nuclei. (Huge concentration of hydrogen.)

The Hydrogen nuclei has a spin \( I = \frac{1}{2} \). It has two possible orientations \( (2I + 1) \) of equal energy. \( +\frac{1}{2} \) and \( -\frac{1}{2} \)

When the patient is placed in a magnetic field (0.3 T to 1.5 T), these energy levels splits. The difference in energy between the two spin states increases as the magnetic field strength increases.

\( ^{19}F \) is NMR active. \(^{19}F\)-NMR spectra of bromo pentafluoride consists of two peaks with intensity ratio 4:1. More intense peak is split into doublet and less intense peak is split into quintet (5 peaks).

Hint, structure of bromo pentafluoride contains 4 identical fluorine and the fifth fluorine is chemically different in nature. The possible structure is given above.
According to Boltzman distribution more nuclei will be in lower energy state than higher energy state.

By using RF pulse excite the nuclei in lower energy state to higher energy state. At a later time after excitation, spins slowly return to the initial state of equilibrium. The energy is reradiated. This reradiated energy is observed as an **MRI signal** (called Free Induction Decay FID signal) and is processed to construct the image with the help of computer.

**MRI advantages:**
1. MRI is suited for examining soft tissues. – Tendon injuries, ligament injuries, spinal cord injuries, brain tumour.
   - Not suited for imaging of chest and lungs, bone injuries.
2. RF pulse used in MRI does not cause Ionization. No biological health hazards have been reported with the use of MRI.
3. Unlike techniques that examine small part of body (ultra sound scan and mammography) MRI can cover large portion of body. It also image at any angle.

**MRI Application**
1) Identify soft tissue injuries (Like ligament injuries, cartilage injuries, tendon injuries, tennis elbow etc.)
2) Clinical Neurology ( Stroke, multiple sclerosis etc)
3) Can map brain functions (emotional responses)
4) MRI angiogram (image arteries)
5) Detect cancer (brain tumour, breast cancer, prostate, liver etc)

**Compare UV/Visible (electronic); IR (Vibrational) and NMR spectroscopy.**

>> All the three methods are non-destructive detecting methods.
>> All the three are absorption spectroscopy.
>> In UV/Visible spectroscopy electronic excitation takes place.
   In IR spectroscopy, vibrational excitation takes place
   In NMR spectroscopy, nuclear excitation takes (Nuclear Spin Flips)
>> The radiation absorbed in Electronic spectroscopy is UV/Visible light.
   The radiation absorbed in vibrational spectroscopy is IR light
   For NMR its RF light.
>> For taking NMR we have to keep the sample in a strong magnetic field, where as to take electronic and vibrational spectrum, no need to keep the molecule in a magnetic field.
>> Uv/Visible spectrum can be used to characterize pi-conjugated systems, aromatics and coloured compounds.
IR spectroscopy is used to identify the functional group present in a molecule.

NMR spectroscopy can be used to map the C-H frameworks in a molecule.

In Vibrational and electronic spectroscopy a continuous beam of electromagnetic radiation is irradiated to the sample, where as in NMR monochromatic RF light is used (usually in NMR we vary the magnetic field)
Q. Find the absorbance of the dye solution whose transmittance at 600 nm is 20%.

Soln: \[ A = \log \left( \frac{I_o}{I} \right) \]
\[ \text{I}_o \text{ is the intensity of incident light.} \]
\[ I \text{ is the intensity of transmitted light.} \]
\[ \% \text{ Transmittance} \% T = \frac{I}{I_o} \times 100 = 20 \text{ then } I_o/I = 5 \]
\[ A = \log (5) = 0.6989 \]

Q. The percentage transmittance of a 0.01 M dye solution in ethanol is 20 % in a 2cm cell for light of wavelength 5000Å. Find the absorbance A and molar absorption coefficient?

Soln: \[ A = \log \left( \frac{I_o}{I} \right) \]
\[ \text{I}_o \text{ is the intensity of incident light.} \]
\[ I \text{ is the intensity of transmitted light.} \]
\[ \% \text{ Transmittance} \% T = \frac{I}{I_o} \times 100 = 20 \text{ then } I_o/I = 5 \]
\[ A = \log (5) = 0.6989 \]
Beer Lambertz law \[ A = \varepsilon \cdot c \cdot t \]
\[ \varepsilon \text{ molar absorption coefficient} \]
\[ c \text{ concentration (0.01 M)} \]
\[ t \text{ solution thickness (2 cm)} \]
\[ \varepsilon = A/(c \cdot t) = \frac{0.6989}{(0.01 \text{ M} \times 2 \text{ cm})} \]
\[ = 34.9 \text{ M}^{-1} \text{ cm}^{-1} \]

Q. The absorbance of a 0.01 M dye solution in ethanol is 0.6989 in a 2cm cell for light of wavelength 5000Å. Find the molar absorption coefficient and percentage transmittance?

Soln: \[ \log \left( \frac{I_o}{I} \right) = 0.6989 \]
\[ I_o/I = \text{antilog} (0.6989) = 5 \]
\[ \% \text{ Transmittance} \% T = \frac{I}{I_o} \times 100 = \frac{1}{5} \times 100 = 20\% \]
Beer Lambertz law \[ A = \varepsilon \cdot c \cdot t \]
\[ \varepsilon \text{ molar absorption coefficient} \]
\[ c \text{ concentration (0.01 M)} \]
\[ t \text{ solution thickness (2 cm)} \]
\[ 2 \text{ cm} = 0.2 \text{ dm} \quad \text{and} \quad 0.01 \text{ M} = 0.01 \text{ mol/dm}^3 \]
\[ \varepsilon = A/(c \cdot t) = \frac{0.6989}{(0.01 \text{ M} \times 0.2 \text{ dm})} \]
\[ = 349 \text{ dm}^{-2} \text{mol}^{-1} \]

Q. A dye solution of concentration 0.04 M shows absorbance of 0.045 at 530 nm; while a solution of same dye shows absorbance of 0.022 under same conditions. Find the concentration of the test solution?

Soln: \[ A = \varepsilon \cdot c \cdot t \quad \text{Here } \varepsilon \text{ and } t \text{ are constants, therefore} \]
\[ \frac{A_1}{A_2} = \frac{C_1}{C_2} \]
\[ 0.045 = \frac{0.04}{C_2} \]
\[ 0.022 = \frac{0.045}{C_2} \]
\[ c_2 = 0.0195 \text{ M} \]
Q. A 50 ppm std solution of Fe$^{3+}$ after developing red colour with excess ammonium thiocyanate shows a transmittance of 0.2 at 620 nm. While an unknown solution of Fe$^{3+}$ after developing red colour with same amount of ammonium thiocyanate gives a transmittance of 0.4. Find the concentration of Fe$^{3+}$ solution?

**Soln:**

\[
\frac{-\log T_1}{\log T_2} = \frac{C_1}{C_2} = \frac{50}{50} = 1
\]

\[
\log 0.2 = \frac{50}{C_2}
\]

\[
c_2 = 28.4 \text{ ppm}
\]

Q. The absorbance of a 0.01 M dye solution in ethanol is 0.62 in a 2 cm cell for light of wave length 5000 Å. If the path length of light through the sample is doubled and the concentration is made half, what will be the value of absorbance?

**Soln**

\[
A_1 = \varepsilon c_1 l_1
\]

\[
A_2 = \varepsilon \frac{c_1}{2} 2l_1 = \varepsilon c_1 l_1 = A_1 = 0.62
\]

Q. A solution shows a transmittance of 20 % when taken in a cell of 2.5 cm thickness. Calculate its concentration if the molar absorption coefficient is 12000 dm$^2$mol$^{-1}$.

**Soln**

\[
A = \log \left(\frac{I_o}{I}\right) \quad I_o \text{ is the intensity of incident light.}
\]

\[
L \text{ is the intensity of transmitted light.}
\]

\[
\% \text{ Transmittance } %T = \frac{I}{I_o} \times 100 = 20 \quad \text{then } I_o/I = 5
\]

\[
A = \log (5) = 0.6989
\]

Beer Lambertz law \( A = \varepsilon c t \)

\[
\varepsilon \text{ molar absorption coefficient}
\]

\[
c \text{ concentration (0.01 M)}
\]

\[
t \text{ solution thickness (2 cm)}
\]

\[2.5 \text{ cm} = 0.25 \text{ dm}
\]

\[
c = \frac{A}{(\varepsilon t)} = \frac{0.6989}{(12000 \text{ dm}^2\text{mol}^{-1} \times 0.25 \text{ dm})} = \frac{2.32 \times 10^{-4} \text{mol} / \text{dm}^3}{2.32 \times 10^{-4} \text{M}}
\]

Q. A dye solution of concentration of 0.05 M shows an absorbance of 0.055 at 540 nm, while a test solution of the same dye has an absorbance of 0.25 under same conditions. Calculate the concentration of test solution.

**Soln**

\[
A = \varepsilon c t \quad \text{Here } \varepsilon \text{ and } t \text{ are constants, therefore}
\]

\[
\frac{A_1}{A_2} = \frac{C_1}{C_2} = \frac{0.055}{0.25} = \frac{0.05}{C_2}
\]

\[
c_2 = 0.23 \text{ M}
\]
Q1. Give two examples of molecules that will give n → π* transition.

Hint: For a molecule to give n → π* transition the molecule should contain at least a heteroatom like O, S, N, Cl etc and a π bond.

Ans:

Q2. Give two examples of molecules that will give π → π* transition.

Hint: For a molecule to give π → π* transition the molecule should contain a π bond.

Ans:

Q3. Which of the following molecules will give UV/visible absorption spectrum in a commonly used commercial spectrophotometer (Scanning range 200 to 750 nm).


Hint: σ → σ* and n → σ* transition will fall below 200 nm therefore one cannot see these transitions in a spectrophotometer. n → π* and π → π* transitions are can only be recorded.

Ethene has π → π* but it wavelength of maximum absorption is only 169 nm.

Ans: Benzene (π → π*)
Butadiene (n → π*)
Formaldehyde (n → π*)

Q4. What are the type of electronic transitions possible for,

a. Benzene  b. Cyclohexane  c. Acetone  d. CCl₄

Hint: Look for the type of electrons in the molecule

Ans:

a) Benzene has σ-electrons and π-electrons (does not have non bonding electrons)
So the electronic transitions possible are σ → σ* and π → π* transitions.

b) Cyclohexane has only σ-electrons. Therefore σ → σ* is only possible.

c) Acetone has σ-electrons, π-electrons and non-bonding electrons. So four types of transitions are possible here, σ → σ*, π → π*, n → σ* and n → π*.

d) CCl₄ has σ-electrons and non-bonding electrons (no π electrons). The transitions possible are σ → σ* and n → σ*. 
Q5. Suggest a simple spectroscopic method to differentiate the isomeric dienes: 2,4-hexadiene and 2,5-hexadiene.

Hint: Look for conjugation. Conjugated system will give a absorption signal greater than 200 nm.
Non-conjugated π bond, wavelength of maximum absorption of π → π* is only 169 nm.

Ans:

\[
\begin{array}{cccccc}
1 & 2 & 3 & 4 & 5 & 6 \\
H_3C & \equiv & CH & \equiv & CH & \equiv & CH_3 \\
\text{2,4-hexadiene} \\
\end{array}
\]

\[
\begin{array}{cccccc}
1 & 2 & 3 & 4 & 5 & 6 \\
H_3C & \equiv & CH & \equiv & CH_2 & \equiv & CH_2 \\
\text{2,5-hexadiene} \\
\end{array}
\]

By using UV-Visible spectroscopy one can differentiate the isomeric dienes, 2,4-hexadiene and 2,5-hexadiene.
2,4-hexadiene has a conjugated π bond therefore will give an π → π* absorption signal (>200 nm)
2,5-hexadiene is non-conjugated system therefore the π → π* absorption signal will fall below 200nm. It cannot be observed in a commercial spectrophotometer.

Q5. Is it possible to differentiate α-β unsaturated aldehydes and ketones with β-γ isomers using the electronic spectroscopy. If yes, explain.

\[\begin{array}{c}
\beta \\
\alpha \\
\alpha-\beta \text{ Unsaturated aldehyde/ketone} \\
\end{array}\]

\[\begin{array}{c}
\beta \\
\gamma \\
\beta-\gamma \text{ Unsaturated aldehyde/ketone} \\
\end{array}\]

α–β Unsaturated aldehydes and ketones are conjugated systems therefore the wavelength of maximum electronic absorption (λ.max) will greater (red shifted) than non-conjugated β-γ isomer.

Q6. Cyclohexane is an important solvent used in organic chemistry. Benzene is a common impurity present in cyclohexane. How can you identify the presence of benzene in cyclohexane using electronic spectroscopy?

Ans

The electronic transition possible for cyclohexane is σ– σ transition. λ.max value of σ–σ transition is less than 200 nm. Therefore in ordinary electronic spectrophotometer there will not be any UV-Visible absorption signal for cyclohexane.

But for benzene there is π–π transition at 269 nm (λ.max).

When you take electronic spectrum of cyclohexane solvent if there is an absorption signal at 269 nm, then the solvent is contaminated with benzene.
Q7. How 1,3-pentadiene and 1,4-pentadiene can be distinguished by UV-Visible spectroscopy?
Ans:

<table>
<thead>
<tr>
<th>1,3-pentadiene</th>
<th>1,4-pentadiene</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂C═CH—CH═CH—CH₃</td>
<td>H₂C═CH—CH₂—CH═CH₂</td>
</tr>
<tr>
<td>Conjugated double bond</td>
<td>non-Conjugated double bond</td>
</tr>
<tr>
<td>A signal π-π* at around 217 nm is observed in common UV/Visible Spectrophotometer</td>
<td>No signal above 200 nm is observed in common UV/Visible Spectrophotometer</td>
</tr>
</tbody>
</table>

Q8. List the electronic transitions possible when UV light is absorbed by the following molecules. i) CH₄ ii) CH₃Cl iii) HCHO
Ans

\[
\text{i) CH}_4 \quad \text{\textsigma-\textsigma*transition} \quad \text{ii) CH}_3\text{Cl} \quad \text{\textsigma-\textsigma* and n- \textsigma*} \quad \text{iii) HCHO} \quad \text{\textsigma-\textsigma*, n- \textsigma*, \pi-\pi* and n-\pi* transition}
\]

Q9. List all the electronic transitions possible for CH₃Cl and HCHO. (Answer Refer Q8)

Q10. Which among the following molecules will give n→π* transition. C₂H₆, CH₃CHO, C₆H₅CONH₂, C₂H₅OH, C₂H₄. Rationalize your answer.
Ans

C₂H₆ (CₙH₂ₙ₊₂) therefore alkane. No heteroatom (non-bonding electrons)
CH₃CHO Aldehyde — Have heteroatom(non-bonding electrons) + π-bond (C=O)
C₆H₅CONH₂ Amide - Have heteroatom(non-bonding electrons) + π-bond (C=O)
C₂H₅OH Alcohol - Have heteroatom(non-bonding electrons) but no π-bond.
C₂H₄ (CₙH₂ₙ) Therefore an alkene or cycloalkane (but with two carbon atom there is no possibility for cyclic system). No heteroatom only π-bond.
n- π* transition is possible for CH₃CHO and C₆H₅CONH₂.
Q11. Discuss the possible electronic transitions in acetaldehyde.

Ans

\[ \begin{align*}
\text{Has } \sigma, \pi \text{ and } n \text{ orbitals therefore all four } \\
\sigma-\sigma^*, \ n-\sigma^*, \ \pi-\pi^* \text{ and } n-\pi^* \text{ transitions are possible for acetaldehyde.}
\end{align*} \]

Q12. Predict the kind of electronic transitions in a) \( \text{Cl}_2 \) and CO molecule.

Ans

\[ \begin{align*}
\text{\( \text{Cl}-\text{Cl} \): } \sigma-\sigma^* \text{ and } n-\sigma^* \text{ transitions.} \\
\text{\( \text{C}=\text{O} \): Has } \sigma, \pi \text{ and } n \text{ orbitals therefore all four } \\
\sigma-\sigma^*, \ n-\sigma^*, \ \pi-\pi^* \text{ and } n-\pi^* \text{ transitions are possible.}
\end{align*} \]

Q13. Which of the following molecules show UV visible Spectrum. Ethane, Ethene, Butadiene, Benzene, Phenol, Acetamide Acetic acid, Ethyl acetate, aniline, Azo dye. (Conjugated dienes, aromatic compounds and coloured compounds give UV-Visible spectrum)

Ans

Butadiene, Benzene, Phenol, Acetamide Acetic acid, Ethyl acetate, aniline, Azo dye. Can give UV-Visible spectrum

AQ1. Schematically represent and discuss the types of electronic transitions possible for a molecule and arrange them in the increasing order of energy.

AQ2. Draw the block diagram of a typical double beam UV-Visible Spectrophotometer instrument. Briefly describe the various components of the instrument.

\[ \text{Prism/Monochromator} \rightarrow \text{Wavelength Selector} \rightarrow \text{Sample} \rightarrow \text{Relative Reference} \rightarrow \text{Detector (Photovoltaic Effect)} \rightarrow \text{Amplifier and Recorder} \]

After selecting the monochromatic light the light beam is split into two equal intensity beams, one is directed through the sample and the other beam through the reference.

Recorder will give the spectrum, a plot of molar absorptivity Vs wave length.

AQ3. Write the mathematical representation of the law governing the light absorption by molecules in solution.

\[ \text{Hint Beer-Lamberts law.} \]

AQ4. Most absorption bands in the electronic spectra are very broad. Give reason.

AQ5. Write two important applications of electronic spectroscopy.


AQ7. What is a spectrometer? Write the principle components of UV-visible spectrometer.
AQ8. What are the various transitions possible in a molecule? Why does electronic spectrum appear broad?

AQ7. Give a neat labelled sketch of instrumentation of UV-visible spectrometer.

AQ8. Discuss the effect of conjugation in electronic (UV-Visible) spectrum.

AQ9. What are the different kinds of electronic transitions possible in organic molecules? Give two applications of UV-Visible spectroscopy.

AQ10. Explain why the electronic absorption spectra are observed in UV-Visible region?

AQ11. Discuss the factor which determine the broadening of electronic spectrum.

MCQ1. Which of the following statements is consistent with an electronic absorption being broad?

a> An electronic absorption includes vibrational and rotational structure. ☑

b> The absorption of a photon is slower than the timescale of molecular vibrations.

c> Hydrogen bonding causes an electronic absorption to be broad.

d> Electronic transitions are always localized on a single atomic centre.

**Limitations of the Beer-Lambert law**

- deviations in absorptivity coefficients at high concentrations (>0.01M) due to electrostatic interactions between molecules in close proximity
- scattering of light due to particulates in the sample
- fluorescent or phosphorescence of the sample
Q1. Which of the two indicated bonds has a high stretching Frequency?

**HINT:** Fundamental stretching Frequency (in Hertz) \( v_o = \frac{1}{2\pi} \sqrt{\frac{K}{\mu}} \) Where \( K \) is the force constant and \( \mu \) is reduced mass.

Ans: The indicated bonds are \( \text{C} = \text{C} \) & \( \text{C} = \text{C} \)

Stretching frequency is directly proportional to Force constant and inversely proportional to reduced mass.

Here force constant of double bond is less than triple bond, therefore, stretching freq of “a” bond is higher than “b” bond.

Q2. Sort each set of bonds in order of increasing stretching frequency.

\[ \text{C}=\text{N} ; \ \text{C}-\text{N} ; \text{C}=\text{N} \]

**HINT:** Fundamental stretching Frequency (in Hertz) \( v_o = \frac{1}{2\pi} \sqrt{\frac{K}{\mu}} \) Where \( K \) is the force constant and \( \mu \) is reduced mass.

Ans: Stretching frequency is directly proportional to Force constant and inversely proportional to reduced mass.

Here force constant of single bond is less than double bond which is less than triple bond.

\[ \text{V}_{\text{C}=\text{N}} > \text{V}_{\text{C}-\text{N}} > \text{V}_{\text{C}=\text{N}} \]

Q3. The Carbon-Oxygen stretching frequencies of formaldehyde and carbon monoxide are 1746 cm\(^{-1}\) and 2150 cm\(^{-1}\) respectively. Explain this difference based on bond order.

In formaldehyde the Carbon-Oxygen bond is C=O (bond order 2) and in carbon monoxide Carbon-Oxygen bond is C≡O (bond order 3)

Fundamental stretching Frequency (in Hertz) \( v_o = \frac{1}{2\pi} \sqrt{\frac{K}{\mu}} \) Where \( K \) is the force constant and \( \mu \) is reduced mass.

Hence \( \text{V}_{\text{C}=\text{O}} \) > \( \text{V}_{\text{C}=\text{O}} \)

Therefore Carbon-Oxygen stretching frequencies of formaldehyde and carbon monoxide are 1746 cm\(^{-1}\) and 2150 cm\(^{-1}\) respectively.
Q4. Assign these stretching frequencies to the corresponding bonds in methanol. \(1030 \text{ cm}^{-1} ; 2945 \text{ cm}^{-1} \) and \(3340 \text{ cm}^{-1}\)

\[\text{Ans}\]

\[\text{The Stretching frequencies possible for methanol are O-H; C-O and C-H}\]

Fundamental stretching Frequency (in Hertz) \(v = \frac{1}{2 \pi} \sqrt{\frac{K}{\mu}}\) Where \(K\) is the force constant and \(\mu\) is reduced mass.

Stretching frequency is directly proportional to Force constant and inversely proportional to reduced mass.

Reduced mass is very low for O-H and C-H than for C-O, therefore the stretching frequency at \(1030 \text{ cm}^{-1}\).

Usually \(v_{\text{O-H}} > v_{\text{C-H}}\)

Therefore \(2945 \text{ cm}^{-1}\) corresponds to C-H stretching and \(3340 \text{ cm}^{-1}\) corresponds to O-H stretching.

Q5. Which of the following molecules are IR active?

\(\text{H-Br, H-Cl, H-C=N, H}_2, \text{O}_2, \text{O}_3, \text{CO}_2, \text{H}_2\text{O}, \text{Benzene}\)

\[\text{Ans}\]

\(>>\) A molecule is IR active if any of its vibration accompany with a change in dipole moment.

\(>>\) A molecule with more than two atoms will have some asymmetric vibrations which generally changes the dipole moment. All molecules with atom number \(>2\) will be IR active.

\(>>\) Diatomic molecules have only one type of vibration. If it is homo-nuclear diatomic molecule the symmetric stretching will not change the dipole moment, but hetero-nuclear diatomic shows an oscillating dipole moment during asymmetric stretching.

IR active molecules are H-Br, H-Cl, H-C=N, O_3, CO_2, H_2O, Benzene.

IR inactive molecules are H_2, O_2

Q6. How can you distinguish between intermolecular and intramolecular Hydrogen bonding on the basis of IR spectrum?

\[\text{Ans}\]

Intermolecular hydrogen bonding weakens on dilution where as intra-molecular hydrogen bonding is not affected. A change in stretching frequency of hydrogen bond can be observed upon dilution for intermolecular hydrogen bonded molecules.
Q7. How will you distinguish the following pair of compounds by IR spectroscopy? Trans-butene and cis-butene
Ans: For the Trans-2-pentene, there was no C=C reading, at about 1600 cm$^{-1}$ because during symmetric stretching there is no change in dipole moment. For the cis-2-pentene, there is a C=C stretching IR Spectrum reading, here the stretching changes the dipole moment.

Q8. How will you distinguish the following pair of molecules using IR spectroscopy?
$\text{H}_3\text{C--C=CCCC} - \text{CH}_3$ and $\text{H}_3\text{C--C=CCCC} - \text{CF}_3$
Ans

Q9. Sketch the normal modes of vibrations of HCN and which of them are IR active.
Q10. How many number of modes of vibrations are possible for acetylene, benzene and cyclohexane.

Ans

Acetylene \( \text{H} = \text{C} = \text{C} = \text{H} \) is linear molecule. Therefore number of modes of vibrations \( 3N - 5 \) (and \( N = 4 \)) = 12 - 5 = 7 nos.

Benzene \( \text{C}_6\text{H}_6 \) is non-linear molecule. Therefore number of modes of vibrations \( 3N - 6 \) (and \( N = 12 \)) = 36 - 6 = 30 nos.

Cyclohexane \( \text{C}_6\text{H}_{12} \) is non-linear molecule. Therefore number of modes of vibrations \( 3N - 6 \) (and \( N = 18 \)) = 54 - 6 = 48 nos.

Q11. Define IR spectrum. Why HCl is IR active, but hydrogen molecule is not. Write the reason for the statement.

Ans. In order for a vibrational mode in a sample to be "IR active", it must be associated with changes in the dipole moment during vibrations. A permanent dipole is not necessary, as the rule requires only a change in dipole moment. A molecule can vibrate in many ways, and each way is called a vibrational mode.

Hydrogen and hydrogen chloride molecule are both diatomic linear molecules. Therefore \( 3N - 5 = 6 - 5 = 1 \) vibration (\( N = 2 \)) is only possible (stretching).

Q12 Compare IR (or vibrational) spectroscopy and UV-Visible (or electronic) spectroscopy.

Ans

a. Both are absorption spectroscopy.

b. In vibrational spectroscopy vibrational excitation takes place by absorbing IR light, but in electronic spectroscopy electronic excitation takes place by absorbing UV/Visible light.

c. Vibrational spectroscopy is useful for determining the functional group present in a molecule, whereas electronic spectroscopy is useful for finding \( \pi \)-conjugations.

d. Plotting spectra: In electronic spectroscopy Absorbance \( A \) (or molar absorptivity \( \varepsilon \)) vs wave length \( \lambda \) is plotted, whereas in vibrational spectroscopy percentage transmittance %T vs wave number \( \tilde{\nu} \) is plotted.

e. Both are non-destructible detecting systems.

f. Both are non-destructible detecting devices.
Q13 Explain why some characteristic peaks are usually strong or weak and why some may be absent in an IR spectrum.

Ans
http://epgp.inflibnet.ac.in/epgpdata/uploads/epgp_content/S000005CH/P000667/M009109/ET/1459227637CHE_P12_M8_e-Text.pdf

Q14 Define and give an example of each term in the context of IR spectroscopy
(a) Fingerprint region  (b) an IR active vibration

Ans
https://scilearn.sydney.edu.au/organicspectroscopy/?type=Infrared&page=Fingerprint%20Region
The absorption bands in the 4000 – 1500 cm\(^{-1}\) region allows identification of functional groups; this region therefore is also termed the functional group region of the IR spectrum. The lower energy portion of the mid-IR region (1500 – 400 cm\(^{-1}\)) usually contains a very complicated set of peaks arising due to complex vibrations involving several atoms. This region is unique to a particular compound and therefore is known as the fingerprint region of the IR spectrum. Though it is difficult to assign the vibrational modes to these peaks, these are useful to identify a compound if the spectrum of the compound is already known. (https://nptel.ac.in/courses/102103044/module2/lec10/6.html)

Q15 Discuss the strength and limitations of IR spectroscopy

Ans
The most useful aspect of IR spectroscopy is its ability to identify the functional groups, but IR does not provide much information about the carbon-hydrogen framework of a molecule.

Q16 Which of the bonds shown in red are expected to have IR active stretching frequency.

\[
\begin{align*}
\text{H}_3\text{C} & \equiv \text{C} \equiv \text{C} \equiv \text{CH}_3 \\
\text{H}_3\text{C} & \equiv \text{C} \equiv \text{C} \equiv \text{CH}_3 \\
\text{H}_3\text{C} & \equiv \text{C} \equiv \text{C} \equiv \text{CH}_3 \\
\text{H}_3\text{C} & \equiv \text{C} \equiv \text{C} \equiv \text{CH}_3
\end{align*}
\]

Ans

\[
\begin{align*}
\text{H}_3\text{C} & \equiv \text{C} \equiv \text{C} \equiv \text{CH}_3 \\
\text{H}_3\text{C} & \equiv \text{C} \equiv \text{C} \equiv \text{CH}_3
\end{align*}
\]
Q17. Which of the following compound has a vibration that is IR inactive a) 1-butyne b) 2-butyne c) H₂ d) H₂O e) Cl₂ f) ethene.

*Hint: Symmetric molecules symmetric stretching is IR inactive.*

**Ans:**

\[
\begin{align*}
a) & \quad \text{Asymmetric} \\
b) & \quad \text{Symmetric} \quad \text{Has IR Inactive Vibrations} \\
c) & \quad \text{Symmetric} \quad \text{Has IR Inactive Vibration} \\
d) & \quad \text{Asymmetric} \\
e) & \quad \text{Symmetric} \quad \text{Has IR Inactive Vibration} \\
f) & \quad \text{Symmetric} \quad \text{Has IR Inactive Vibrations}
\end{align*}
\]

Q18. How could you use IR spectroscopy to determine whether the following reaction has occurred?

![Reaction Image]

**Ans:** If the reaction has occurred the intensity of IR absorption band at 1700 cm⁻¹ (carbonyl stretching) of the reactant would have decreased.

Q19. Assume that the force constant is approximately same for C-C, C-N and C-O bonds. Predict the relative positions of their stretching vibrations in an IR spectrum.

**Ans:**

If the forces constant are approximately the same, the lighter atom will absorb at higher frequency.

\[\text{C-C} > \text{C-N} > \text{C-O}\]
Q20. For each of the following pairs of compounds, name one absorption band that could be used to distinguish between them.

A) \( \text{H}_3\text{C} \text{--CH}_2 \text{--CH} \text{--CH}_3 \) \text{H}_3\text{C} \text{--CH}_2 \text{--O} \text{--CH}_3 \\
C-O \text{ (stretching at 1200 cm}^{-1}) \text{ Absent} \quad \text{Present} \\

B) \text{OCH}_3 \text{CH}_3 \text{CH} \text{O} \text{CH}_3 \text{OH} \text{OCH}_3 \text{CH} \text{O} \text{CH}_3 \text{OH} \\
O-H \text{ (stretching at 3300 cm}^{-1}) \text{ Absent} \quad \text{Present} \\
(\text{Heary Beard Like peak for carboxylic OH}) \\

C) \text{CH}_3 \text{CH}_2 \text{OH} \text{CH}_3 \text{CH}_2 \text{OH} \\
C=O \text{ (stretching at 1700 cm}^{-1}) \text{ Present} \quad \text{Absent} \\
\text{Carbonyl stretching} \\

Q21. Why do \text{CO}_2 \text{ and } \text{SO}_2 \text{ have a different number of degrees of vibrational freedom?} \\
\text{Ans,} \\
\text{Ans,} \\
\text{CO}_2 \text{ is linear molecule, } 3N-5 = 4, \text{ Vibrations possible and } \text{SO}_2 \text{ is a non-linear molecule } 3N-6 = 3, \text{ vibrations possible.}
Q1. Calculate the reduced mass of $^1\text{H}--^{35.5}\text{Cl}$?

**Soln:** Reduced mass $\mu = \frac{M_1 \cdot M_2}{M_1 + M_2}$ (M1 mass of first atom in Kg, M2 Mass of second atom in Kg).

M1 = 1 amu = $1 \times 1.66 \times 10^{-27}$ Kg

M2 = 35.5 amu = $35.5 \times 1.66 \times 10^{-27}$ Kg

$$\mu = \frac{(1 \times 1.66 \times 10^{-27}\text{ Kg}) \cdot (35.5 \times 1.66 \times 10^{-27}\text{ Kg})}{(1+35.5) \times 1.66 \times 10^{-27}\text{ Kg}}$$

$$= 1.61 \times 10^{-27}\text{ Kg}$$

Q2. $^1\text{H}--^{35.5}\text{Cl}$ has a force constant (k) value of 480 Nm$^{-1}$. Calculate the fundamental frequency in terms of wave numbers?

**Soln:** Fundamental Frequency (in Hertz) $\nu_0 = \frac{1}{2 \pi} \sqrt{\frac{K}{\mu}}$, K is the force constant.

Reduced mass $\mu = \frac{M_1 \cdot M_2}{M_1 + M_2}$ (M1 mass of first atom in Kg, M2 Mass of second atom in Kg).

M1 = 1 amu = $1 \times 1.66 \times 10^{-27}$ Kg

M2 = 35.5 amu = $35.5 \times 1.66 \times 10^{-27}$ Kg

$$\mu = \frac{(1 \times 1.66 \times 10^{-27}\text{ Kg}) \cdot (35.5 \times 1.66 \times 10^{-27}\text{ Kg})}{(1+35.5) \times 1.66 \times 10^{-27}\text{ Kg}}$$

$$= 1.61 \times 10^{-27}\text{ Kg}$$

$$K = 480 \text{ Nm}^{-1}.$$

$$\nu_0 = \frac{1}{2 \pi} \sqrt{\frac{K}{\mu}} = \frac{1}{2 \pi} \sqrt{\frac{480}{1.61 \times 10^{-27}}}$$

$$= 8.69 \times 10^{13}\text{ Hz}$$

$$\nu = \frac{\nu_0}{c} = \frac{(8.69 \times 10^{13}/\text{s})}{3 \times 10^8 \text{m/s}}$$

$$= 2.89 \times 10^5 \text{ m}^{-1}$$

$$= 2.89 \times 10^3 \text{ cm}^{-1}$$

Q3. The fundamental frequency of $^1\text{H}--^{35.5}\text{Cl}$ is $8.69 \times 10^{13}$ Hz. Calculate the force constant?

**Soln:** Fundamental Frequency (in Hertz) $\nu_0 = \frac{1}{2 \pi} \sqrt{\frac{K}{\mu}}$, K is the force constant. On re-arranging $K = 4 \pi^2 \frac{\nu_0^2}{\mu}$

Reduced mass $\mu = \frac{M_1 \cdot M_2}{M_1 + M_2}$ (M1 mass of first atom in Kg, M2 Mass of second atom in Kg).

M1 = 1 amu = $1 \times 1.66 \times 10^{-27}$ Kg

M2 = 35.5 amu = $35.5 \times 1.66 \times 10^{-27}$ Kg

$$\mu = \frac{(1 \times 1.66 \times 10^{-27}\text{ Kg}) \cdot (35.5 \times 1.66 \times 10^{-27}\text{ Kg})}{(1+35.5) \times 1.66 \times 10^{-27}\text{ Kg}}$$

$$= 1.61 \times 10^{-27}\text{ Kg}$$

$$K = 4 \times 3.14^2 \left( 8.69 \times 10^{13} \right)^2 \times 1.61 \times 10^{-27}\text{ Kg}$$

$$= 479.4 \text{ Nm}^{-1}$$
Q4. The IR stretching frequency of $^1\text{H}^{35.5}\text{Cl}$ is 2890 cm$^{-1}$. Calculate the force constant?

**Soln:** Fundamental Frequency (in Hertz) \[ \nu_0 = \frac{1}{2 \pi} \sqrt{\frac{K}{\mu}} \] K is the force constant. On re-arranging \[ K = 4 \pi^2 \nu_0^2 \mu = 4 \pi^2 c^2 \nu^2 \mu \] Reduced mass \[ \mu = \frac{M_1 M_2}{M_1 + M_2} \] (M1 mass of first atom in Kg, M2 Mass of second atom in Kg).

M1 = 1 amu = 1 x 1.66 x 10$^{-27}$ Kg

M2 = 35.5 amu = 35.5 x 1.66 x 10$^{-27}$ Kg

\[ \mu = \frac{(1 \times 1.66 \times 10^{-27} \text{ Kg}) \cdot (35.5 \times 1.66 \times 10^{-27} \text{ Kg})}{(1+35.5) 1.66 \times 10^{-27} \text{ Kg}} \]

\[ = 1.61 \times 10^{-27} \text{ Kg} \]

C = 3 * 10$^8$ m/s

\[ \nu = 2890 \text{ cm}^{-1} = 289000 \text{ m}^{-1} \]

\[ K = 4 \times 3.14^2 \left( 3 \times 10^8 \right)^2 \times \left(289000\right)^2 \times 1.61 \times 10^{-27} \text{ Kg} \]

\[ = 477 \text{ Nm}^{-1} \]

Q5. Calculate the force constant of the CO molecule, if its fundamental vibrational frequency is 2140 cm$^{-1}$.

**Fundamental Frequency (in Hertz)** \[ \nu_0 = \frac{1}{2 \pi} \sqrt{\frac{K}{\mu}} \] K is the force constant. On re-arranging \[ K = 4 \pi^2 \nu_0^2 \mu = 4 \pi^2 c^2 \nu^2 \mu \] [fundamental frequency is given in wavenumber unit]

Reduced mass \[ \mu = \frac{M_1 M_2}{M_1 + M_2} \] (M1 mass of first atom in Kg, M2 Mass of second atom in Kg).

M1 = 12 amu = 12 x 1.66 x 10$^{-27}$ Kg

M2 = 16 amu = 16 x 1.66 x 10$^{-27}$ Kg

\[ \mu = \frac{(12 \times 1.66 \times 10^{-27} \text{ Kg}) \cdot (16 \times 1.66 \times 10^{-27} \text{ Kg})}{(12+16) 1.66 \times 10^{-27} \text{ Kg}} \]

\[ = 11.4 \times 10^{-27} \text{ Kg} \]

c = 3 * 10$^8$ m/s

\[ \nu = 2890 \text{ cm}^{-1} = 214000 \text{ m}^{-1} \] (Converting wave number in cm$^{-1}$ to SI unit m$^{-1}$)

\[ K = 4 \times 3.14^2 \left( 3 \times 10^8 \right)^2 \times \left(214000\right)^2 \times 11.4 \times 10^{-27} \text{ Kg} \]

\[ = 1853 \text{ Nm}^{-1} \]
Q6. Calculate the fundamental vibrational frequency HCl molecule, if the value of force constant of the molecule is \( 483 \text{ Nm}^{-1} \). The atomic masses are \(^1\text{H} = 1.673 \times 10^{-27} \text{ kg} \) and \(^{35}\text{Cl} = 58.06 \times 10^{-27} \text{ kg} \).

Ans

Fundamental Frequency (in Hertz) \( v_0 = \frac{1}{2 \pi} \sqrt{\frac{K}{\mu}} \) K is the force constant and \( \mu \) is reduced mass.

\[
\mu = \frac{M_1 M_2}{M_1 + M_2} \quad (\text{M1 mass of first atom in Kg, M2 Mass of second atom in Kg}).
\]

\[
= \frac{(1.673 \times 10^{-27} \text{ Kg})(58.06 \times 10^{-27} \text{ Kg})}{(1.673 \times 10^{-27} \text{ Kg} + 58.06 \times 10^{-27} \text{ Kg})} = 1.63 \times 10^{-27} \text{ Kg}
\]

Fundamental Frequency (in Hertz) \( v_0 = \frac{1}{2 \pi} \sqrt{\frac{K}{\mu}} = \frac{1}{2 \pi} \sqrt{\frac{483}{1.63 \times 10^{-27}}} = 8.66 \times 10^{13} \text{ Hz} \).

Fundamental Frequency (in wave number cm\(^{-1}\)) \( \bar{v} = \frac{v_0}{c} = \frac{8.66 \times 10^{13}}{3 \times 10^{8}} = 2.89 \times 10^{5} \text{ m}^{-1} = 2.89 \times 10^{3} \text{ cm}^{-1} \).

Q7. The fundamental vibrational frequency of CO is 2140 cm\(^{-1}\). Calculate force constant of the bonds if reduced mass of CO is 1.14 \( \times 10^{-26} \text{ Kg} \).

Ans

Fundamental Frequency (in Hertz) \( v_0 = \frac{1}{2 \pi} \sqrt{\frac{K}{\mu}} \) K is the force constant and \( \mu \) is reduced mass On re-arranging

\[
k = 4 \pi^2 \frac{v_0^2}{c^2} \mu = 4 \pi^2 \frac{1}{c^2} \bar{v}^2 \mu \quad [\text{fundamental frequency is given in wavenumber unit}] \quad \bar{v} = 2140 \text{ cm}^{-1} = 214000 \text{ m}^{-1}.
\]

\[
k = 4 \times 3.14 \times 3.14 \times 3 \times 10^8 \text{ m/s} \times 3 \times 10^8 \text{ m/s} \times 214000 \text{ m}^{-1} \times 214000 \text{ m}^{-1} \times 1.14 \times 10^{-26} \text{ Kg}
\]

\[
= 1853 \text{ Nm}^{-1}.
\]

Q8. The fundamental vibrational frequency of carbon monoxide \(^{12}\text{C}^{16}\text{O}\) is 2140 cm\(^{-1}\). Without calculating force constant, find the fundamental frequency of \(^{13}\text{C}^{17}\text{O}\) in cm\(^{-1}\).

Ans

Assume that the force constant remains same for isotope substitution.

\[
\frac{v_0(1)}{v_0(2)} = \sqrt{\frac{\mu_2}{\mu_1}}
\]

Squaring on both sides \( \left( \frac{v_0(1)}{v_0(2)} \right)^2 = \frac{\mu_2}{\mu_1} \)

Therefore \( [\bar{v}_0(2)]^2 = \frac{\mu_1}{\mu_2} [\bar{v}_0(1)]^2 \)

Then \( \bar{v}_0(2) = \sqrt{\frac{\mu_1}{\mu_2}} [\bar{v}_0(1)]^2 \mu_2 = \frac{13 \times 17}{13 + 17} = 7.37 \text{ amu} \quad \mu_1 = \frac{12 \times 16}{12 + 16} = 6.86 \text{ amu} \)

\[
= \sqrt{\frac{6.86}{7.37}} \times 2140 \times 2140 = 2064 \text{ cm}^{-1}
\]
Q9. The hydrogen fluoride have the following fundamental frequencies $^1$H$^{19}$F(4141.3 cm$^{-1}$). Predict the fundamental vibrational frequency of deuterium fluoride. 967 Nm$^{-1}$ and 3002 cm$^{-1}$.

Ans

Assume that the force constant remains same for isotope substitution.

\[ \frac{\tilde{v}_0(1)}{\tilde{v}_0(2)} = \sqrt{\frac{\mu_1}{\mu_2}} \]

Squaring on both sides \(\left(\frac{\tilde{v}_0(1)}{\tilde{v}_0(2)}\right)^2 = \frac{\mu_2}{\mu_1}\)

Therefore \(\frac{\tilde{v}_0(2)}{\tilde{v}_0(1)} = \frac{\sqrt{\mu_1}}{\sqrt{\mu_2}} \left[\tilde{v}_0(1)\right]^2\)

Then \(\tilde{v}_0(2) = \frac{\mu_1}{\sqrt{\mu_2}} \left[\tilde{v}_0(1)\right]^2\)

\[ \mu_1 = \frac{1 \times 19}{1 + 19} = 0.95 \text{ amu} \]

\[ \mu_2 = \frac{2 \times 19}{2 + 19} = 1.81 \text{ amu} \]

\[ \sqrt{0.95} \times 144141.3 \times 4141.3 = 3000 \text{ cm}^{-1} \]

---

Q10. The fundamental vibration frequency of gaseous $^{14}$N$^{16}$O is 1904 cm$^{-1}$. Calculate the force constant using formula for a simple harmonic oscillator.

Ans

Fundamental Frequency (in Hertz)

\[ \nu_0 = \frac{1}{\pi^2} \sqrt{\frac{K}{\mu}} \]

K is the force constant. On re-arranging

\[ K = 4 \times \pi^2 \times \nu_0^2 \times \mu = 4 \times \pi^2 \times c^2 \times \tilde{\nu}^2 \times \mu \]

[fundamental frequency is given in wavenumber unit]

Reduced mass \(\mu = \frac{M_1 \times M_2}{M_1 + M_2}\) (M1 mass of first atom in Kg, M2 Mass of second atom in Kg).

\[ M_1 = 14 \text{ amu} = 14 \times 1.66 \times 10^{-27} \text{ Kg} \]

\[ M_2 = 16 \text{ amu} = 16 \times 1.66 \times 10^{-27} \text{ Kg} \]

\[ \mu = \frac{(14 \times 1.66 \times 10^{-27} \text{ Kg}) \times (16 \times 1.66 \times 10^{-27} \text{ Kg})}{(14+16) \times 1.66 \times 10^{-27} \text{ Kg}} \]

\[ = 12.4 \times 10^{-27} \text{ Kg} \]

\[ c = 3 \times 10^8 \text{ m/s} \]

\[ \tilde{\nu} = 1904 \text{ cm}^{-1} = 190400 \text{ m}^{-1} \] (Converting wave number in cm$^{-1}$ to SI unit m$^{-1}$)

\[ K = 4 \times 3.14^2 \left(3 \times 10^8\right)^2 \times \left(190400\right)^2 \times 12.4 \times 10^{-27} \text{ Kg} \]

\[ = 1595 \text{ Nm}^{-1} \]
Q11. The fundamental vibration frequency of gaseous $^{14}\text{N}^{16}\text{O}$ is 1904 cm$^{-1}$. Calculate the fundamental vibration frequency of $^{15}\text{N}^{16}\text{O}$.

Ans
Assume that the force constant remains same for isotope substitution.

$$\frac{\bar{V}_0(1)}{\bar{V}_0(2)} = \frac{\sqrt{k}}{\sqrt{\mu_1}}$$

Squaring on both sides

$$(\frac{\bar{V}_0(1)}{\bar{V}_0(2)})^2 = \frac{\mu_2}{\mu_1}$$

Therefore

$$[\bar{V}_0(2)]^2 = \frac{\mu_1}{\mu_2} [\bar{V}_0(1)]^2$$

Then

$$\bar{V}_0(1) = \sqrt[\mu_2]{[\bar{V}_0(2)]^2}$$

$$\mu_1 = \frac{14 \times 16}{14 + 16} = 7.47 \text{ amu}$$

$$\mu_2 = \frac{15 \times 16}{15 + 16} = 7.74 \text{ amu}$$

Therefore

$$\bar{V}_0(1) = \sqrt[\mu_2]{7.47 \times 1904 \times 1904} = 1870 \text{ cm}^{-1}$$

Q12. A carbon deuterium C-D bond is electronically much like a C-H bond and it has similar stiffness, measured by spring constant, k. The deuterium isotope has twice the mass of hydrogen atom. Calculate the IR absorption frequency of a typical C-D bond. Given that IR absorption frequency of C-H is 3000 cm$^{-1}$.

Ans: $v \propto \frac{k}{\sqrt{\mu}}$

$$\mu(\text{Deut}) = \frac{m_1m_2}{m_1+m_2} = \frac{12 \times 2}{12 + 2} = 1.714$$

$$\mu(\text{Hydr}) = \frac{m_1m_2}{m_1+m_2} = \frac{12 \times 1}{12 + 1} = 0.923$$

$$\frac{\bar{V}_D}{\bar{V}_H} = \sqrt{\frac{k}{\mu(\text{Deut})}}$$

$$\frac{\bar{V}_D}{3000 \text{ cm}^{-1}} = \sqrt{\frac{k}{0.923}} = 0.734$$

Therefore

$$\bar{V}_D = 0.734 \times 3000 \text{ cm}^{-1} = 2202 \text{ cm}^{-1}$$
Q13. The molecule $^{12}$C$^{16}$O has a bond force constant of 1860 Nm$^{-1}$. Calculate the vibrational zero point energy of this molecule. Reduced mass of CO is $1.14 \times 10^{-26}$ Kg.

Ans

Fundamental Frequency (in Hertz) \[ \nu_0 = \frac{1}{2} \pi \sqrt{\frac{K}{\mu}} \] K is the force constant and \( \mu \) is reduced mass.

\[ \mu = 1.14 \times 10^{-26} \text{ Kg} \]

Fundamental Frequency (in Hertz) \[ \nu_0 = \frac{1}{2} \pi \sqrt{\frac{K}{\mu}} = \frac{1}{2} \pi \sqrt{\frac{1860}{1.14 \times 10^{-26}}} = 6.43 \times 10^{13} \text{ Hz.} \]

Zero point energy \[ E_0 = \frac{1}{2} \hbar \nu_0 = \frac{1}{2} \times 6.626 \times 10^{-34} \times 6.43 \times 10^{13} = 21.30 \times 10^{-23} \]

Solution: the zero point energy is \[ E_{n=0} = \hbar \omega \left( 0 + \frac{1}{2} \right) = \frac{\hbar \omega}{2} \]

We need \( \omega \), which is given by \[ \omega = \sqrt{\frac{K}{\mu}} = \sqrt{\frac{1860 \text{ Nm}^{-1}}{1.14 \times 10^{-26} \text{ Kg}}} = 4.04 \times 10^{14} \text{ s}^{-1} \]

where the reduced mass for CO was obtained from problem 6a.

\[ \therefore E_{n=0} = \frac{\hbar \omega}{2} = \frac{(1.06 \times 10^{-34} \text{ Js})(4.04 \times 10^{14} \text{ s}^{-1})}{2} = 2.14 \times 10^{-20} \text{ J} \]
Q1. Which of the following nuclei shows NMR activity? H\(^1\), H\(^2\), He\(^4\), C\(^{12}\), C\(^{13}\), O\(^{18}\)

Ans

A nuclei is NMR active when the nuclei have non-zero spin I.

Rules to determine I

If a nuclei has Proton number and Neutron number are both even, then I will be 0.NMR inactive.

If a nuclei has Proton number and Neutron number are both odd, then I will be 1,2,3,...(NMR active)

If a nuclei has odd Proton number and even Neutron number or even Proton number and odd Neutron number (that is mass number is odd) then I will be 1/2 , 3/2 ,5/2 ...

All Nuclei with odd mass number are NMR active

Hydrogen has 1 Proton then H\(^1\), H\(^2\) are both NMR active

Carbon has 6 Proton then C\(^{12}\) is NMR inactive C\(^{13}\) is NMR active

Oxygen has 8 protons and 18-8 = 10 neutrons, both are even so NMR inactive.

Q2. Which of the following nuclei do not show nuclear magnetic resonance? ¹H, ²H, ¹²C, ¹³C, ¹⁴N, ¹⁵N, ¹⁶O, ¹⁹F, ³¹P, ³²S.

Ans

Nuclei with a non-zero I value are NMR active. All nuclei with odd mass number are NMR active. also

Nuclei with even mass number having odd number of protons and neutrons are also NMR active.

Nuclei having even mass number with even number of protons as well as even number of neutrons are NMR inactive.

¹²C, ¹⁶O and ³²S are NMR inactive

Q3. How many kinds of protons are there in (i) CH₃-CH₃. (ii) CH₃-CH₂-CH₃, (iii) C₆H₅-CH₃ (iv) (CH₃)₂CHCH₂CH₃ (v) ClCH₂CH₂Cl

Ans:

(i) Only one kind of proton

(ii) Two kinds of protons

(iii)

(iv) Four kinds of proton.
Q4. Determine which of the following molecules will show spin-spin coupling in their NMR spectra. If splitting is observed, give the multiplicity of each kind of proton.

(a) CICH₂CH₂Cl,  (b) CICH₂CH₂I,  (c) CH₃CHO  (d) CH₃CO CH₃  (e) CH₃CCl₂CH₃

Ans

(a) Same kind of protons cannot give spin-spin splitting

(b) Will give spin-spin splitting. Signal for Hₐ protons are split into triplet by 2 Hₐ neighbours and signal for Hₐ is also a triplet because of 2 Hₐ neighbours.

(c) Will give spin spin splitting. Signal for Hₐ protons are split into doublet by 1 Hₐ neighbour and signal for Hₐ will be a quartet due to 3 Hₐ neighbours.

(d) No vicinal hydrogens. No spin-spin splitting

(e) No vicinal hydrogens. Therefore no spin-spin splitting
Q5. Predict the low resolution NMR spectrum and high resolution NMR spectrum of acetone.

Ans:

All six hydrogens are chemically equivalent. Therefore we get a singlet in low resolution spectrum. Also there are no vicinal non-equivalent neighbouring protons. Therefore high resolution spectrum and low resolution spectrum both look same.

Q6. Predict the low resolution NMR spectrum and high resolution NMR spectrum of propanal.

Ans

Q7. An organic compound C3H6O contains a carbonyl group. How will its NMR spectrum decide whether it is an aldehyde or a ketone.

CH₃CO CH₃  CH₃-CH₂-CHO

Ans: The propanone would only give one peak in its NMR spectrum because both CH₃ groups are in an identical environment - both are attached to -COCH₃. The propanal would give three peaks with the areas underneath in the ratio 3:2:1.
Q8 Predict the NMR spectrum of the compound CH$_3$CO CH$_2$C≡CCH$_3$. 

![NMR spectrum diagram]

The NMR spectrum shows the following splittings:

- **H$_a$** (Ha): 3 peaks (triplet)
- **H$_b$** (Hb): 2 vicinal peaks (quintet), 1 vicinal peak (triplet)
- **H$_c$** (Hc): 3 vicinal peaks

The chemical shift (δ) for TMS is 0.
Q9. How can the NMR spectrum distinguish between the isomers para-Xylene and ethyl-benzene.

![Diagram of para-Xylene and ethyl-benzene]

Q10. Predict the proton NMR spectrum of $H_2$, $CH_4$, $C_2H_6$ and $C_6H_6$.

a) $H_2$

Only one kind of Hydrogen. Which do not show spin-spin interaction, hence a singlet.

b) $CH_4$

All four Hydrogens are identical—Singlet

c) $C_2H_6$

All 6 Hydrogens are chemically equivalent. Therefore no splitting. (Singlet)
d) \( \text{C}_6\text{H}_6 \) 
all six hydrogens are identical. Therefore no spin-spin splitting.

Q11. Below are given the molecular formula of some organic compounds that have only one NMR signal. Draw the structural formula for each of them.

a) \( \text{C}_5\text{H}_{12} \)  
Double bond Index or ring \( = \frac{C - H}{2} + 1 = 5 - \frac{12}{2} + 1 = 5-6+1 = 0 \) 

The compound is alkane.

b) \( \text{C}_3\text{H}_6 \)  
Double bond Index or ring \( = \frac{C - H}{2} + 1 = 3 - \frac{6}{2} + 1 = 1 \) (a ring or 1 DB)

All six hydrogens are identical, Hence a singlet

There are non equivalent Hydrogens. Therefore not a singlet.

c) \( \text{C}_3\text{H}_4 \)  
Double bond Index or ring \( = \frac{C - H}{2} + 1 = 3 - \frac{4}{2} + 1 = 2 \) (2DB or 1 ring+1DB)

There are non equivalent Hydrogens. Therefore not a singlet.

All four hydrogens are identical, Hence a singlet

d) \( \text{C}_4\text{H}_6 \)  
Double bond Index or ring \( = \frac{C - H}{2} + 1 = 4 - \frac{6}{2} + 1 = 2 \) (2DB or 1 ring+1DB)

All six hydrogens are equivalent, hence a singlet.

e) \( \text{C}_8\text{H}_{18} \)  
Double bond Index or ring \( = \frac{C - H}{2} + 1 = 8 - \frac{18}{2} + 1 = 0 \)
Q12. Below are given the molecular formula of some organic compounds that give 2 singlets in their proton NMR spectra. Draw the structural formula for each of them.

h) $\text{C}_2\text{H}_5\text{O}_2$ Double bond Index or ring $= C - H/2 + 1 = 3 - (6/2) + 1 = 1$

\[
\begin{array}{c}
\text{CH}_3 \text{ fragment} + \text{ another CH}_3 \text{ fragment}. \text{ Remaining COO} (\quad \text{o} \quad)
\end{array}
\]

i) $\text{C}_3\text{H}_6\text{O}_2$ Double bond Index or ring $= C - H/2 + 1 = 3 - (8/2) + 1 = 0$

\[
\begin{array}{c}
\text{CH}_3 \text{ fragment} + \text{ another CH}_3 \text{ fragment} + \text{ a CH}_2 \text{ fragment}. \text{ Remaining 2 O}.
\end{array}
\]

j) $\text{C}_2\text{H}_5\text{OCl}$ Double bond Index or ring $= C - H/2 + 1 = 2 - (6/2) + 1 = 0$

\[
\begin{array}{c}
\text{CH}_3 \text{ fragment} + \text{ a CH}_2 \text{ fragment}. \text{ Remaining O and Cl}
\end{array}
\]

k) $\text{C}_3\text{H}_5\text{Cl}_3$ Double bond Index or ring $= C - H/2 + 1 = 3 - (8/2) + 1 = 0$

\[
\begin{array}{c}
\text{CH}_3 \text{ fragment} + \text{ a CH}_2 \text{ fragment} + \text{ 3 Cl and a C}
\end{array}
\]
**Q13. Predict the number of signals, their relative positions and their multiplicities for ethyl acetate.**

There are three types of protons marked a, b and c

“a” protons is attached to electron withdrawing acetate group
“b” protons is attached to electronegative (electron withdrawing) O atom.
“c” protons does not have an electron withdrawing group attached.

Electron withdrawing ability of O > -COO- therefore “b” protons are more deshielded.

“a” protons have no neighbouring Hydrogens. Therefore the signal will be a singlet.
“b” protons have 3 neighbouring Hydrogens. Therefore the NMR signal will split into (3+1 = 4) quartet.
“c” protons have 2 neighbouring Hydrogens. Therefore the NMR signal will split into (2+1 = 3) triplet.
Q14. Predict the number of signals, their relative positions and their multiplicities for 2-bromopropane.

There are two types of protons marked a and b

- “b” protons is attached to electronegative (electron withdrawing) Br atom.
- “a” protons does not have an electron withdrawing group attached.

Signal for “b” protons are more deshielded (left side).

- “a” protons have one neighbouring Hydrogen. Therefore the signal will be a doublet.
- “b” protons have $3+3 = 6$ neighbouring equivalent Hydrogens. Therefore the NMR signal will split into $(6+1 = 7)$ septet.
Q15. Predict the number of signals, their relative positions and their multiplicities for ultra-pure Ethanol.

Least Deshielded. O is far away

\[ \text{CH}_3 - \text{CH}_2 \longrightarrow \text{O} - \text{H} \]

Most deshielded due to direct connection to O

\[ N+1 = 2+1 = 3 \quad \text{Triplet} \]

\[ \text{CH}_2 \]

Has two H neighbour

\[ \text{CH}_3 \] \& \[ \text{OH} \]

Splitting Rule \((N+1)(M+1)\)

\[ = (3+1)(1+1) \]

\[ = 4 \times 2 = 8 \]

= Double quartet

Signal for OH proton \(\text{c}\)  
Signal for \(\text{CH}_2\) \(\text{b}\)  
Signal for \(\text{CH}_3\) \(\text{c}\)

4 8 0
Q16. Predict the High resolution NMR spectrum of CH$_3$-CH$_2$-CHCl$_2$ (High resolution means spin-spin splitting).

Q17. What is meant by spin active nuclei? Give 4 examples of spin active nuclei.
Ans: Spin active nuclei is nuclei having non-zero Spin value. They will show NMR phenomenon. Examples are $^1$H, $^2$H, $^{13}$C and $^{31}$P.

Q18. Explain the term spin-spin splitting. Why does a peak for a particular set of proton split into a multiplet?
Ans.

Q19. “NMR spectroscopy is the most important tool compared to UV-Visible and IR spectroscopy for the structural determination of an unknown organic compound” Justify the statements.
Ans:
- Number of signals in NMR spectrum gives the number of chemically different types of hydrogens present.
- The intensity ratio is the relative ratio of number of hydrogens.
- Position of signals gives an indication about its local electronic arrangement.
- Spin-Spin splitting gives information on number of hydrogen atoms attached to neighbouring atoms.

Ultimately one can logically deduct the structure of molecule.

By UV visible spectroscopy one can find only the conjugation. By IR spectroscopy one can find only the functional groups present.

Q20. Why TMS is used a standard reference in proton NMR spectroscopy?
Ans: TMS $\text{Si(CH}_3\text{)}_4$. All 12 Hydrogens are equivalent therefore one NMR signal. Since Si is electropositive than C, Cl, F, O. The Hydrogens of TMS are highly shielded. The NMR signals of Hydrogens in all organic compounds will be deshielded with respect to TMS hydrogens.
Q21. Give the mechanism of absorption of RF pulse by NMR active nuclei kept in a magnetic field.

Q22. What are the factors affecting Chemical shift?

Q23. Predict the NMR spectrum of CH$_3$-O-C$_2$H$_5$ (Chemical shift and Spin-Spin splitting).

Q24. Match the chemical shift data with the proton environment

Q25. What are equivalent and non-equivalent protons?

Q26. State the significance of peak area in NMR spectrum?
Q27. In which of the following systems energy level separation is largest? (a) a proton in 600 MHz instrument, (b) proton in 300 MHz instrument.
Splitting of energy level is proportional to magnetic field. Therefore splitting will be maximum in 600 MHz instrument.

Q28. Give the applications of NMR spectroscopy.
1. Structural elucidation of organic molecules.
2. $^1$H-NMR is basic principle of MRI of soft tissues.
3. $^{31}$P-NMR can be used for imaging bones.
4. To study dynamics of biomacromolecules (like protein folding).

Q29. What is the use of N+1 rule, Pascal triangle in NMR spectral analysis?

N+1 RULE: The (n+1) Rule, an empirical rule used to predict the multiplicity of each H-NMR signal. It states that if a $^1$H nucleus has n number of vicinal non-equivalent $^1$H, then the multiplicity of the peak is n+1.

Pascal’s Triangle: It predicts the ratio of heights of signals in a split NMR peak.

Coupling Constant, J: The spacing between the lines of a doublet, triplet or quartet (Multiplet) is called the coupling constant.

Home Work Questions

HWQ1. Predict the NMR spectrum
a. CH$_3$-CH$_3$
b. CH$_3$-CH$_2$-CH$_3$
c. CH$_3$-O-CH$_3$
d. CH$_3$-CO-CH$_3$
e. CH$_3$-COO-CH$_3$
f. Propanaldehyde
g. 1-chloropropane
Tutorial 6 NMR related Numericals

Q1. Calculate the frequency of operation of NMR instrument if a particular proton of δ value 4.2 shows a difference in frequency 1260 Hz from TMS?

Soln: Chemical Shift
\[ \delta = \frac{(v_{sample} - v_{TMS}) \times 10^6}{\text{Opp Freq in Hz}} \]

\[ \text{Opp Freq in Hz} = \frac{(v_{sample} - v_{TMS}) \times 10^6}{\delta} = \frac{1260}{4.2} \times 10^6 = 300\text{MHz} \]

Q2. When measured using 300 MHz instrument the signal for proton in CHCl₃ appears 1260 Hz downfield from TMS signal. Calculate chemical shift.

Soln: Chemical Shift
\[ \delta = \frac{(v_{sample} - v_{TMS}) \times 10^6}{\text{Opp Freq in Hz}} \]

\[ = \frac{1260 \times 10^6}{300 \times 10^6} = 4.2 \text{ ppm} \]

Q3. A 300-MHz spectrometer records a proton that absorbs at a frequency 2130 Hz downfield from TMS.
(a) Determine its chemical shift.
(b) Predict this proton's chemical shift at 60 MHz. In a 60-MHz spectrometer, how far downfield (in hertz) from TMS would this proton absorb?

Soln.
(a) Chemical Shift
\[ \delta = \frac{\text{shift downfield (Hz)}}{\text{spectrometer frequency (MHz)}} = \frac{2130}{300} = 7.10 \text{ ppm} \]

(b) The chemical shift is unchanged 7.10 ppm when we change the operating frequency.

\[ \text{Frequency Shift} = \text{Chemical Shift} \times \text{Spectrometer Frequency} \]
\[ = 7.1 \times 60 = 426 \text{ Hz} \]

Q4. A signal has been reported to occur at 600Hz downfield from TMS in an NMR spectrometer with a 300-MHzZ operating frequency.
(a) What is the chemical shift of the signal?
(b) What would its chemical shift be in an instrument operating at 500 MHz?
(c) How many hertz downfield from TMS would the signal be in a 500 MHz NMR spectrometer?
Q5. If two signals differ by 1.5 ppm in a 300 MHZ spectrometer, by how much do they differ in a 100 MHZ spectrometer.

Ans

The chemical shift is independent of the operating frequency. Therefore if the two signals differ by 1.5 ppm in a 300 MHz instrument, they will still differ by 1.5 ppm in a 100 MHz instrument.

Q6. If two signals differ by 90 Hz in a 300 MHZ spectrometer, by how much do they differ in a 100 MHZ Instrument.

\[
\text{b. } \frac{\text{Hz}}{\text{MHz}} = \text{ppm} \\
\frac{90 \text{ Hz}}{300 \text{ MHz}} = 0.3 \text{ ppm} \\
\frac{x \text{ Hz}}{500 \text{ MHz}} = 0.3 \text{ ppm} \\
x = 150 \text{ Hz} \\
\]

They differ by 150 Hz.

Q6. If gyromagnetic ratio of $^{13}$C is $\frac{1}{4}$th of that of $^1$H. What is the frequency that must be irradiated to take $^{13}$C NMR spectrum if the same instrument take $^1$H-NMR spectra at 300 MHZ.

\[
hv = \Delta E = \frac{\gamma_h}{2\pi} B \\
\nu = \frac{\gamma}{2\pi} B \\
B \text{ is constant in both cases}
\]

We can write

\[
\frac{\nu_h}{\nu_C} = \frac{\gamma_h}{\gamma_C}
\]
\[ \frac{v_H}{v_c} = \frac{4 \gamma_H}{\gamma_H} \]

That is
\[ v_c = \frac{v_H}{4} = \frac{300}{4} = 75 \text{MHz} \]

Q1. How many kinds of proton are there in, a) Prop-1-ene  b) (Z)-1,2-dibromoethene  c) (E)-1-bromo-2-chloroethene  d) 1-chloro-1-iodoethene.

Hint

prop-1-ene
\[
\begin{array}{c}
\text{H}_3\text{C} \\
\text{H} \\
\text{C} = \text{C} \\
\text{H} \\
\text{H}
\end{array}
\]

(Z)-1,2-dibromoethene
\[
\begin{array}{c}
\text{H} \\
\text{C} = \text{C} \\
\text{Br} \\
\text{Br} \\
\text{H}
\end{array}
\]

(E)-1-bromo-2-chloroethene
\[
\begin{array}{c}
\text{H} \\
\text{C} = \text{C} \\
\text{Cl} \\
\text{H} \\
\text{H}
\end{array}
\]

1-chloro-1-iodoethene
\[
\begin{array}{c}
\text{H} \\
\text{C} = \text{C} \\
\text{I} \\
\text{Cl} \\
\text{H}
\end{array}
\]

Ans

3 Ha Type

1 Hd type

Total 4 kinds of protons

1 Ha type

1 Hb type

1 Hc type

(Both are identical protons)

(Z)-1,2-dibromoethene

Only One kind of protons

1 Ha type

1 Hb type

Total 2 Kinds of Protons

1 Ha type

1 Hb type

(\(E\))-1-bromo-2-chloroethene

1-chloro-1-iodoethene

Total 2 Kinds of Protons
Q1. Determine which of the following molecules will show spin-spin coupling in their proton-NMR spectra. If the coupling or splitting is observed give the multiplicity of the signal, a) Prop-1-ene  b) (Z)-1,2-dibromoethene  c) (E)-1-bromo-2-chloroethene  d) 1-chloro-1-iodoethene.

Ans

a) 

\[
\begin{align*}
\text{H}_3\text{C} & \quad \text{H} \\
\text{C} & \quad \text{C} \\
\text{H} & \quad \text{H} \\
\end{align*}
\]

prop-1-ene

b) 

\[
\begin{align*}
\text{Br} & \quad \text{Br} \\
\text{C} & \quad \text{C} \\
\text{H} & \quad \text{H} \\
\end{align*}
\]

(Z)-1,2-dibromoethene

Both protons are identical, therefore spin-spin splitting is not observed.

c) 

\[
\begin{align*}
\text{H} & \quad \text{Br} \\
\text{Cl} & \quad \text{C} \\
& \quad \text{H} \\
\end{align*}
\]

(E)-1-bromo-2-chloroethene

The two protons are not equivalent and each is split into a doublet.

d) 

\[
\begin{align*}
\text{H} & \quad \text{I} \\
\text{C} & \quad \text{C} \\
\text{H} & \quad \text{Cl} \\
\end{align*}
\]

1-chloro-1-iodoethene

The two protons are not equivalent (one cis to Cl and other is trans to Cl) so that each is split into doublet.