
Unit 2: Spectroscopic Techniques and Applications & Stereochemistry

1. Introduction to Spectroscopy

Spectroscopy is defined as the study of the **interaction of matter with electromagnetic radiation**. It is a powerful analytical tool that provides information about the electronic, vibrational, and rotational energy levels of atoms and molecules.

There are two main types of spectra:

- **Absorption Spectrum:** Obtained when a molecule is excited from a lower energy level to a higher energy level by the **absorption of energy**.
- **Emission Spectrum:** Obtained when a molecule falls from a higher energy level to a lower energy level by the **emission of energy**.

Atoms give rise to atomic spectra, while molecules give rise to molecular spectra, with transitions occurring between their respective energy levels.

Molecular Energy Levels: Molecules possess different quantum mechanical energy states:

- **Electronic Energy Level:** Associated with electrons in bonding or anti-bonding molecular orbitals. The energy gap falls in the **UV-Visible region** of the electromagnetic spectrum.
- **Vibrational Energy Level:** Associated with atoms vibrating within the molecule. The energy gap falls in the **infrared (IR) region**.
- **Rotational Energy Level:** Associated with the molecule rotating in space about an axis. The energy gap falls in the **microwave region**.
- **Translational Energy Level:** Associated with the change in position of the center of mass. This energy is generally **not quantized** and is considered negligible.

The **total energy** of a molecule is approximately the sum of its electronic, vibrational, and rotational energies: $E_{\text{total}} = E_{\text{el}} + E_{\text{vib}} + E_{\text{rot}}$.

2. UV-Visible Spectroscopy

UV-Visible Spectroscopy (typically 200-800 nm) involves the excitation of electrons from lower to higher energy levels within a molecule by absorbing UV or visible light. Unlike atomic spectra, electronic transitions in molecules are observed as broad "bands" rather than discrete lines because they are accompanied by significant changes in vibrational and rotational energies.

2.1 Beer-Lambert's Law

This law is fundamental to quantitative UV-Vis spectroscopy and describes the relationship between the absorbance of a solution and the concentration of the absorbing substance.

Statement: When a parallel beam of monochromatic electromagnetic radiation passes through a solution of an absorbing substance, the rate of decrease in intensity of radiation with the thickness of the absorbing medium is proportional to the intensity of radiation at that point and also to the concentration of the solution. **Formula:** $A = \epsilon cl$ Where:

- **A = Absorbance** (dimensionless)
- **ϵ = Molar extinction coefficient or molar absorptivity** ($\text{L mol}^{-1} \text{cm}^{-1}$)
- **c = Concentration** of the absorbing substance (mol L^{-1})
- **l = Path length** of the absorbing medium (cm)

Transmittance (T) is defined as the ratio of the intensity of the transmitted light (I) to the intensity of the incident light (I_0): $T = I / I_0$. Absorbance (A) can also be expressed in terms of transmittance: $A = \log_{10}(I_0/I)$.

Applications of Beer-Lambert's Law:

- **Identification of a substance.**
- **Determination of the concentration of a solution.**
- **Study of kinetics of chemical reactions.**
- **Detection of impurities** (e.g., benzene in cyclohexane).
- **Quantitative estimation** of substances like blood sugar or cholesterol.

Limitations of Beer-Lambert's Law:

- Only valid in **dilute solutions** (electrostatic interactions cause deviations in concentrated solutions).
- Cannot be used for **turbid solutions** due to light scattering.
- Requires **monochromatic light**.
- Deviations occur if the absorbing species undergo **association, dissociation, or reaction with the solvent**.
- Invalid if there is **fluorescence or phosphorescence** in the sample.

Numerical Problems (Examples from Source):

- **Problem 1:** A dye solution of concentration 0.04 M shows absorbance of 0.045 at 530 nm. A test solution of the same dye shows absorbance 0.022 under the same conditions. Find the concentration of the test solution.
 - **Given:** $A_1 = 0.045$, $c_1 = 0.04 \text{ M}$, $A_2 = 0.022$. Path length (l) is constant.
 - **Solution:** Since $A = \epsilon cl$, and ϵ and l are constant for both solutions:
 - $A_1 / c_1 = A_2 / c_2$
 - $0.045 / 0.04 = 0.022 / c_2$
 - **$c_2 = 0.0195 \text{ M}$**
- **Problem 2:** A solution of thickness 2 cm transmits 40% incident light. Calculate the concentration if $\epsilon = 6000 \text{ L mol}^{-1} \text{cm}^{-1}$.

- **Given:** $l = 2 \text{ cm}$, %Transmittance = 40% ($I/I_0 = 0.40$).
- **Solution:** $A = \log(I_0/I) = \log(100/40) = \log(2.5) \approx 0.3979$.
 - $A = \epsilon cl$
 - $0.3979 = 6000 \times c \times 2$
 - $c = 3.316 \times 10^{-5} \text{ mol L}^{-1}$
- **Problem 3:** A monochromatic radiation is incident on a 0.05 M solution. Intensity is reduced to one fourth (25%) after passing through 10 cm. Calculate the molar absorption coefficient.
 - **Given:** $c = 0.05 \text{ M}$, $I/I_0 = 0.25$ (1/4), $l = 10 \text{ cm}$.
 - **Solution:** $A = \log(I_0/I) = \log(1/0.25) = \log(4) \approx 0.602$.
 - $A = \epsilon cl$
 - $0.602 = \epsilon \times 0.05 \times 10$
 - $\epsilon = 1.204 \text{ L mol}^{-1} \text{ cm}^{-1}$ (Calculation derived from values; original source provides only the problem without full solution steps)
- **Problem 4:** A 0.01 M solution absorbs 10% of incident light in a path of 1 cm. What would be the concentration if it is to absorb 90% of the same radiation, with the same path length?
 - **Given:** $c_1 = 0.01 \text{ M}$, $l = 1 \text{ cm}$. For 1st case: $I_1/I_0 = (100-10)/100 = 0.90$. For 2nd case: $I_2/I_0 = (100-90)/100 = 0.10$.
 - **Solution:**
 - $A_1 = \log(100/90) = 0.0457$.
 - $A_2 = \log(100/10) = 1$.
 - Since $A = \epsilon cl$ and ϵ , l are constant: $A_1/c_1 = A_2/c_2$
 - $0.0457 / 0.01 = 1 / c_2$
 - $c_2 \approx 0.222 \text{ M}$

2.2 Types of Electronic Transitions

Major electronic transitions observed in UV-Vis spectroscopy include:

- **$\sigma \rightarrow \sigma^*$ Transitions:**
 - Occur in **saturated hydrocarbons** (C-C and C-H σ bonds).
 - Require **high energy**.
 - Typically occur **below 150 nm**, which is outside the range of ordinary UV machines (200-700 nm), so saturated hydrocarbons are generally not detected by standard UV-Vis.
- **$\pi \rightarrow \pi^*$ Transitions:**
 - Occur in **unsaturated centers** (e.g., double bonds, triple bonds, aromatic systems).
 - Examples include alkenes, alkynes, carbonyl compounds, cyanides, azo compounds.
 - Example: Ethylene (169 nm), conjugated alkenes (170-190 nm), 1,3-butadiene (213 nm).
 - The transition takes place from the **Highest Occupied Molecular Orbital (HOMO)** to the **Lowest Unoccupied Molecular Orbital (LUMO)**.

- **$n \rightarrow \pi^*$ Transitions:**
 - Observed in compounds with **carbonyl groups** (e.g., aldehydes, ketones) which possess both π electrons and non-bonding (n) electrons.
 - Require the **least amount of energy** and are observed with **least intensity**.
- **$n \rightarrow \sigma^*$ Transitions:**
 - Occur in **saturated compounds containing at least one heteroatom** (e.g., S, N, O) with unshared electron pairs (e.g., saturated halides, alcohols, ethers, amines).
 - These transitions are generally **forbidden** and occur with **low intensity**.
 - Examples: Water (167 nm), methanol (174 nm), CH_3Cl (169 nm).

2.3 Key Terms in UV-Vis Spectroscopy

- **Chromophore:** Any **isolated covalently bonded group** that shows characteristic absorption in the UV-Vis region. These groups typically contain double or triple bonds or lone pairs of electrons that can be excited by absorbing energy in the visible or near UV region.
- **Auxochrome:** A group that **cannot act as a chromophore itself** but, when present, causes a **shift of the absorption band towards longer wavelengths** (a bathochromic or red shift). Auxochromes achieve this by extending the conjugation of the chromophore through the sharing of non-bonding electrons. Examples include $-\text{OH}$, $-\text{NH}_2$, $-\text{NHR}$, $-\text{NR}_2$, $-\text{SH}$, $-\text{X}$ (halogens). For instance, benzene absorbs at 250 nm, while aniline (with an $-\text{NH}_2$ auxochrome) absorbs at 280 nm.

2.4 Instrumentation of UV-Vis Spectrophotometer

A typical UV-Vis spectrophotometer consists of the following components:

- **Light Sources:**
 - **Deuterium or hydrogen discharge tube:** Used for the UV region (200-370 nm).
 - **Tungsten filament lamp:** Used for the visible region (325-750 nm).
- **Monochromator:** A **quartz prism or diffraction grating** used to disperse light from the source and select a monochromatic beam through slits.
- **Sample and Reference Cells:** Most instruments are **double-beam**, dividing the monochromatic beam into two equal intensity beams. One passes through the sample cell, and the other through a reference cell containing only the solvent.
- **Detector System:** Receives the beams from the sample and reference cells and transmits a signal.
- **Recorder:** Converts the signal into an absorption spectrum (a plot of absorbance vs. wavelength).
- **Diagram Description** (based on): A colorimeter instrument typically features a **wavelength selection knob** (1), a **printer button** (2), a **concentration factor adjustment** (3), a **UV mode selector** (4) (for deuterium lamp), a **readout display** (5), a **sample compartment** (6) where cuvettes are placed, a **zero control (100% T) knob** (7), and a **sensitivity switch** (8).

3. Infrared (IR) Spectroscopy

Infrared (IR) Spectroscopy involves transitions between the **vibrational energy levels** of a molecule. These transitions are induced by absorbing IR radiation, typically in the range of **500-4000 cm⁻¹**.

3.1 Vibrations

Molecular vibrations are of two main types:

- **Stretching Vibration:** A vibration along the bond axis that results in a change (increase or decrease) in the distance between two atoms.
- **Bending Vibration (Deformation):** A vibration that causes a change in bond angles.

3.2 Conditions for IR Activity

For a molecule's vibration to interact with IR radiation and result in absorption, two conditions must be met:

1. The **dipole moment of the bond must vary** during the vibration.
 2. The **frequency of the incident IR radiation must exactly correspond** to the frequency of the specific vibrational mode of the molecule.
- For example, stretching vibrations in homonuclear diatomic molecules (e.g., O₂, N₂) are IR inactive because there is no change in dipole moment. However, in heteronuclear diatomic molecules like HCl, stretching is IR active due to a change in dipole moment with internuclear distance.

3.3 Number of Vibrational Modes (Degrees of Freedom)

The number of vibrational modes for a molecule depends on its geometry and the number of atoms (n):

- For a **Non-linear molecule:** The number of vibrational degrees of freedom is **(3n-6)**.
 - Example: Water (H₂O) is a non-linear triatomic molecule (n=3). Number of modes = (3×3) - 6 = **3 vibrational modes** (symmetric stretching, asymmetric stretching, and bending), all of which are IR active.
- For a **Linear molecule:** The number of vibrational degrees of freedom is **(3n-5)**.
 - Example: Carbon dioxide (CO₂) is a linear triatomic molecule (n=3). Number of modes = (3×3) - 5 = **4 vibrational modes**. However, symmetric stretching is IR inactive, while asymmetric stretching (2349 cm⁻¹) and the two degenerate bending modes (667 cm⁻¹) are IR active, leading to **only two observed absorption frequencies**.

3.4 Simple Harmonic Oscillator Model

A vibrating diatomic molecule can be modeled as a simple harmonic oscillator.

- The energy difference (ΔE) between vibrational states is given by **$\Delta E = h\nu$** .
- For absorption spectroscopy, the change in vibrational quantum number (ΔV) must be **+1**, meaning the frequency of absorbed IR radiation (ν) must equal the fundamental vibrational frequency of the molecule (ν_0): **$\nu = \nu_0$** .
- While theory predicts a single line, **a band is observed** in practice due to anharmonicity at high quantum levels.

3.5 Applications of IR Spectroscopy

- **Determination of force constant of diatomic molecules.**
- **Identification of functional groups in organic molecules:** Specific functional groups absorb IR radiation at characteristic frequency ranges (e.g., C=O in saturated ketones at 1700-1725 cm^{-1} , O-H in alcohols at 3300-3500 cm^{-1} , C=C in alkenes at 1620-1650 cm^{-1}).
- **Determination of purity:** Impurities introduce extra absorption bands.
- **Distinguishing between inter- and intramolecular hydrogen bonding:** The O-H stretching frequency for intramolecular H-bonding (e.g., o-hydroxyphenol) does not change upon dilution, whereas for intermolecular H-bonding (e.g., p-hydroxyphenol), the O-H absorption frequency shifts upon dilution as molecules separate.

Numerical Problems (Examples from Source):

- **Formula for Force Constant (K):** $K = 4\pi^2\nu^2\mu$, where ν is the frequency and μ is the reduced mass.
 - Reduced mass (μ) = $(m_1 \times m_2) / (m_1 + m_2)$.
- **Problem 1:** The CO molecule absorbs IR frequency of 2140 cm^{-1} . Calculate the force constant of the chemical bond (C = 12 amu, O = 16 amu).
 - **Given:** $\nu = 2140 \text{ cm}^{-1} = 2140 \times 3 \times 10^{10} \text{ s}^{-1} = 6.42 \times 10^{13} \text{ s}^{-1}$ (speed of light used for conversion from cm^{-1} to Hz). $m_{\text{C}} = 12 \text{ amu}$, $m_{\text{O}} = 16 \text{ amu}$. $1 \text{ amu} \approx 1.66 \times 10^{-27} \text{ kg}$.
 - **Solution:**
 - $\mu = (12 \times 16) / (12 + 16) = 192 / 28 = 6.857 \text{ amu} = 6.857 \times 1.66 \times 10^{-27} \text{ kg} = 1.138 \times 10^{-26} \text{ kg}$.
 - $K = 4 \times (3.14159)^2 \times (6.42 \times 10^{13} \text{ s}^{-1})^2 \times (1.138 \times 10^{-26} \text{ kg}) \approx \mathbf{1858.9 \text{ N m}^{-1}}$ (Calculations derived from values, original source provides only the problem without full solution steps but includes the formula).
- **Problem 2:** If the fundamental vibrational frequency of HCl is $8.667 \times 10^{13} \text{ s}^{-1}$, calculate the force constant of HCl bond [H = 1.008; Cl = 35.45].
 - **Given:** $\nu = 8.667 \times 10^{13} \text{ s}^{-1}$. $m_{\text{H}} = 1.008 \text{ amu}$, $m_{\text{Cl}} = 35.45 \text{ amu}$.
 - **Solution:**
 - $\mu = (1.008 \times 35.45) / (1.008 + 35.45) = 35.736 / 36.458 = 0.980 \text{ amu} = 0.980 \times 1.66 \times 10^{-27} \text{ kg} = 1.627 \times 10^{-27} \text{ kg}$.
 - $K = 4 \times (3.14159)^2 \times (8.667 \times 10^{13} \text{ s}^{-1})^2 \times (1.627 \times 10^{-27} \text{ kg}) \approx \mathbf{482.086 \text{ N m}^{-1}}$.

4. Nuclear Magnetic Resonance (NMR) Spectroscopy

NMR Spectroscopy involves the interaction of the **spin of certain atomic nuclei with an external magnetic field**. It provides detailed information about the structure and environment of atoms within a molecule.

4.1 Nuclear Spin (I)

Not all nuclei exhibit spin. The nuclear spin quantum number (I) can take values of 0, 1/2, 1, 3/2, etc..

- **Nuclei with I = 0:** Possess **zero spin**. These include nuclei with an even number of both protons and neutrons (e.g., $^2\text{He}^4$, $^{12}\text{C}^6$, $^{16}\text{O}^8$).
- **Nuclei with Integral Spin (I = 1, 2, ...):** Possess an **integral spin**. These include nuclei with an odd number of both protons and neutrons (e.g., $^2\text{H}^1$, $^{14}\text{N}^7$).
- **Nuclei with Half-Integral Spin (I = 1/2, 3/2, ...):** Possess a **half-integral spin**. These include nuclei with an odd mass number (e.g., $^1\text{H}^1$, $^{15}\text{N}^7$, $^{19}\text{F}^9$, $^{31}\text{P}^{15}$, $^{17}\text{O}^8$, $^{13}\text{C}^6$).
 - For a proton, $I = 1/2$.

In the presence of an external magnetic field, the degeneracy of nuclear spin orientations is destroyed, leading to **(2I+1) different energy orientations**. For a proton ($I=1/2$), there are two orientations: alignment with the field (+1/2) and alignment against the field (-1/2). The +1/2 orientation is lower in energy.

4.2 Larmour Frequency

When a spinning charged particle (like a proton) is placed in an external magnetic field, its spin axis precesses around the magnetic field, similar to a spinning top in a gravitational field. The **frequency of this precession is called the Larmour frequency (ν)**.

- **Formula: $\nu = \gamma B_0 / 2\pi$**
 - **ν :** Larmour frequency (frequency of radiation that comes into resonance).
 - **γ :** Gyromagnetic ratio (a fundamental nuclear constant unique to each nucleus).
 - **B_0 :** Strength of the external magnetic field.
 - **Resonance** occurs when the Larmour frequency matches the radiofrequency of the incident radiation, causing the proton spin to "flip" and absorb energy.

4.3 Chemical Shift

Chemical shift (δ) refers to the **shift in the resonance position of a nucleus** that results from its unique electronic environment within a molecule. The energy required for resonance is dependent on the local electronic environment around the nucleus.

- **Shielding:** When a molecule is placed in an external magnetic field, its electrons circulate, producing a **secondary magnetic field that opposes the applied field**. This causes the **net field felt by the proton to be less** than the applied field. Such a proton is said to be **shielded**. Shielded protons require a **greater strength of the applied field** to achieve resonance and absorb at **higher field strengths (upfield)**.

- **Deshielding:** If the secondary magnetic field produced by the electrons **reinforces the applied field**, the **net field felt by the proton is greater** than the applied field. Such a proton is said to be **deshielded**. Deshielded protons absorb at a **lower field strength (downfield)** (e.g., protons in an aromatic ring).

Reference Standard:

- **Tetramethylsilane (TMS), $\text{Si}(\text{CH}_3)_4$** , is used as the standard for ^1H and ^{13}C NMR.
- **Reasons for using TMS:**
 - Silicon is more electropositive than carbon, causing electron density to be pushed towards the methyl protons, making them **more shielded** than most organic compounds' protons. Thus, the TMS signal appears at the **extreme right (0 ppm on the δ scale)**.
 - All **12 hydrogen nuclei in TMS are chemically equivalent**, producing a single, sharp, and intense resonance.
 - It is a **low boiling point substance**, easily removable from the sample.

Calculation of Chemical Shift (δ scale): $\delta \text{ (ppm)} = (\nu_{\text{sample}} - \nu_{\text{TMS}}) / \text{Operating frequency (MHz)}$ Where ν_{sample} is the frequency of the sample signal and ν_{TMS} is the frequency of the TMS signal.

Factors Influencing Chemical Shift:

1. **Electron Density:** As electron density around a proton decreases, shielding decreases, and the δ value increases (moves downfield).
 - Example: CH_3F (4.3 ppm) > CH_3Cl (3.1 ppm) > CH_3Br (2.6 ppm) > CH_3I (2.2 ppm).
2. **Cumulative Effect of Electronegative Substituents:** The more electronegative substituents present on a carbon, the more deshielded the protons on that carbon.
 - Example: CHCl_3 (7.3 ppm) > CH_2Cl_2 (5.3 ppm) > CH_3Cl (3.1 ppm).
3. **Distance from Electronegative Atom:** The deshielding effect decreases with increasing distance from the electronegative atom.
 - Example: $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{Cl}$ (δ values: 1.0, 1.4, 3.4 respectively).
4. **Magnetic Anisotropy of π -system:** Electrons in π systems (aromatic compounds, alkenes, alkynes) interact with the applied magnetic field, creating localized magnetic fields that can cause both shielding and deshielding depending on the proton's position relative to the induced field. This effect leads to significant deshielding for aromatic protons.

Interpretation of NMR Spectra (for ^1H NMR):

1. **Number of Signals:** Indicates the **number of different kinds (chemically non-equivalent) of protons** present in the molecule.
2. **Position of Signal (δ value):** Provides information about the **electronic environment** of the protons.

3. **Intensity of Signals (Area under each peak):** Directly proportional to the **relative ratio of different kinds of protons**.

4.4 Spin-Spin Coupling (Splitting)

Spin-spin coupling is the phenomenon where the magnetic fields of neighboring protons interact with the external magnetic field, leading to the **splitting of NMR signals**. This fine structure provides information about the number of equivalent protons on adjacent carbon atoms.

- **Multiplicity (n+1 Rule):** The signal for a particular proton is split into **(n+1) peaks**, where **n is the number of equivalent protons on adjacent carbon atoms** (vicinal protons).
 - Singlet (n=0), Doublet (n=1), Triplet (n=2), Quartet (n=3), Pentet (n=4), Sextet (n=5), Septet (n=6), Octet (n=7).
- **Coupling Constant (J):** The **distance between the peaks in a multiplet** is called the coupling constant (J) and is a measure of the effectiveness of spin-spin coupling.

Examples of Splitting Patterns:

- **Ethyl Bromide (CH₃-CH₂-Br):**
 - The **CH₂ signal** (a) is more deshielded due to the electronegative Br. It is split into a **quartet** (n=3 for CH₃) with an intensity ratio of 1:3:3:1.
 - The **CH₃ signal** (b) is less deshielded. It is split into a **triplet** (n=2 for CH₂) with an intensity ratio of 1:2:1.
- **1,1-Dichloroethane (CH₃-CHCl₂):**
 - The **CH₃ signal** is split into a **doublet** (n=1 for CH) with an intensity ratio of 1:1.
 - The **CH signal** is split into a **quartet** (n=3 for CH₃) with an intensity ratio of 1:3:3:1.
- **Ethanol (CH₃-CH₂-OH):**
 - **OH proton:** Most deshielded. Gives a **singlet** if there is rapid proton exchange (e.g., with water traces). In a very pure sample, it can split into a triplet due to coupling with CH₂ protons.
 - **CH₂ protons:** Next most deshielded. Split into a **quartet** by the CH₃ protons (intensity 1:3:3:1). In pure ethanol, it would be a complex multiplet (double quartet) due to coupling with both CH₃ and OH protons.
 - **CH₃ protons:** Least deshielded. Split into a **triplet** by the CH₂ protons (intensity 1:2:1).
 - **Area ratio CH₃:CH₂:OH is 3:2:1.**
- **Cl-CH₂-CH₂-Cl:** There is **only one peak (a singlet)** as the two CH₂ groups are equivalent, and there are no vicinal protons to cause splitting.

4.5 Applications of NMR Spectroscopy

- **Magnetic Resonance Imaging (MRI):** A diagnostic procedure that visualizes internal body structures. It is based on the alignment and relaxation of protons (primarily from water) in a strong magnetic field after being excited by radiofrequency pulses.
- **Structural Elucidation:** Used for determining the detailed structure of many inorganic and organic compounds.
- **Quantitative Analysis:** The **areas under the peaks are directly proportional to the number of protons** causing those peaks, forming the basis for quantitative analysis.
- **Detection of Hydrogen Bonding:** Both intermolecular and intramolecular hydrogen bonding cause a downfield shift in the absorption position of the H-bonded proton. Intermolecular H-bonding is concentration-dependent, while intramolecular H-bonding is not.

5. Stereochemistry

Stereochemistry deals with the three-dimensional arrangement of atoms within molecules and their effects on chemical properties. Unit 2 specifically mentions "Optical isomerism in compounds without chiral carbon," "Geometrical isomerism," and "Chiral Drugs".

5.1 Isomerism

Isomers are different compounds that have the same molecular formula but different arrangements of atoms.

5.2 Optical Isomerism in Compounds without Chiral Carbon

Optical isomerism typically arises from the presence of a chiral carbon (a carbon atom bonded to four different groups). However, some compounds can exhibit optical isomerism even without a chiral carbon. This occurs in molecules with structural features that prevent planarity and generate non-superimposable mirror images.

- The source mentions that asymmetrically substituted compounds with an **even number of cumulative double bonds** (like allenes or spiranes) can exhibit optical isomerism. These molecules are chiral due to their inherent three-dimensional arrangement, even if no single carbon atom fits the traditional chiral center definition.

5.3 Geometrical Isomerism (Cis-Trans and E-Z Isomerism)

Geometrical isomerism (also known as cis-trans isomerism or E-Z isomerism) arises in compounds where there is restricted rotation around a bond (e.g., double bonds or cyclic structures), leading to different spatial arrangements of substituents that cannot interconvert without breaking bonds.

- The source notes that compounds with an **odd number of cumulative double bonds** (like some cumulenes) can exhibit geometrical isomerism.
- **Cis-Trans Isomerism:** Used for disubstituted alkenes where two identical groups are either on the same side (cis) or opposite sides (trans) of the double bond.

- **E-Z Nomenclature:** A more general system used when there are more than two different substituents on the double bond. It assigns priorities to the groups based on atomic number (Cahn-Ingold-Prelog rules). If high-priority groups are on the same side, it's **Z** (Zusammen - together); if on opposite sides, it's **E** (Entgegen - opposite).

5.4 Chiral Drugs

Chiral drugs are pharmaceutical compounds that exist as enantiomers (non-superimposable mirror images). The biological activity of enantiomers can differ significantly, with one enantiomer often being therapeutically active and the other inactive or even toxic. This makes stereochemistry critically important in drug design and manufacturing.

Note: While the provided sources mention other types of isomerism (structural, conformational, enantiomers, diastereomers) and their explanations within question banks, the detailed syllabus for Unit 2 specifically highlights "Optical isomerism in compounds without chiral carbon" and "Geometrical isomerism." Therefore, the notes focus on these specified topics.

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