29

SPECTROSCOPY–1

Student Learning Outcomes

[C-12-E-03 to C-12-E-18]

- Explain that the degree of unsaturation or index of hydrogen deficiency (IHD) can be used to determine from a molecular formula, the number of rings or multiple bonds in a molecule.
- Explore how Mass spectrometry (MS), proton nuclear magnetic resonance spectroscopy (^1H NMR), infrared spectroscopy (IR) are techniques that can be used to help identify compounds and to determine their structure.
- Interpret an infrared (spectrum of a simple molecule to identify functional groups.
- Deduce possible structures for organic compounds using IR spectrum and molecular formula (Examples: phenol, acetone, ethanol).
- Predict whether a given molecule will absorb in the UV/visible region.
- Predict the colour of a transition metal complex form its UV/visible spectrum.
- Explain atomic emission and atomic absorption spectrum.
- Explain how a mass spectrometer can be used to determine the relative atomic mass of an element from its isotopic composition.
- Perform calculations involving non-integer relative atomic masses and abundance of isotopes from given data, including mass spectra.
- Explain the concept of emission spectra. Use the concept of emission spectra to deduce the electronic configuration of elements.
- Analyze mass spectra in terms of m/e values and isotopic abundances (knowledge of the working of the mass spectrometer is not required).
- Calculate the relative atomic mass of an element given the relative abundances of its isotopes, or its mass spectrum.
- Deduce the molecular mass of an organic molecule from the molecular ion peak in a mass spectrum.
- Suggest the identity of molecules formed by simple fragmentation in a given mass spectrum.
- Deduce the number of carbon atoms, n, in a compound using the M^+ peak and the formula n = 1.1x abundance of M^+.
- Deduce the presence of bromine and chlorine atoms in a compound using the M peak.

Light and other forms of electromagnetic radiation travel in the form of waves, which consist of oscillating electric and magnetic fields. These waves are defined by their wavelength **(λ)** and frequency **(υ)**, and they travel at the speed of light (**$c = 3.0 \times 10^8$ m/s**). The relationship between these is given by:

$$c = \lambda \nu$$

where **λ** is the wavelength (in meters), **ν** is the frequency (in Hertz or s^{-1}), and **c** is the speed of light (in ms^{-1}).

The electromagnetic spectrum comprises of different radiations, including radio waves, microwaves, infrared radiation, visible light, ultraviolet radiation, X-rays, and gamma rays.

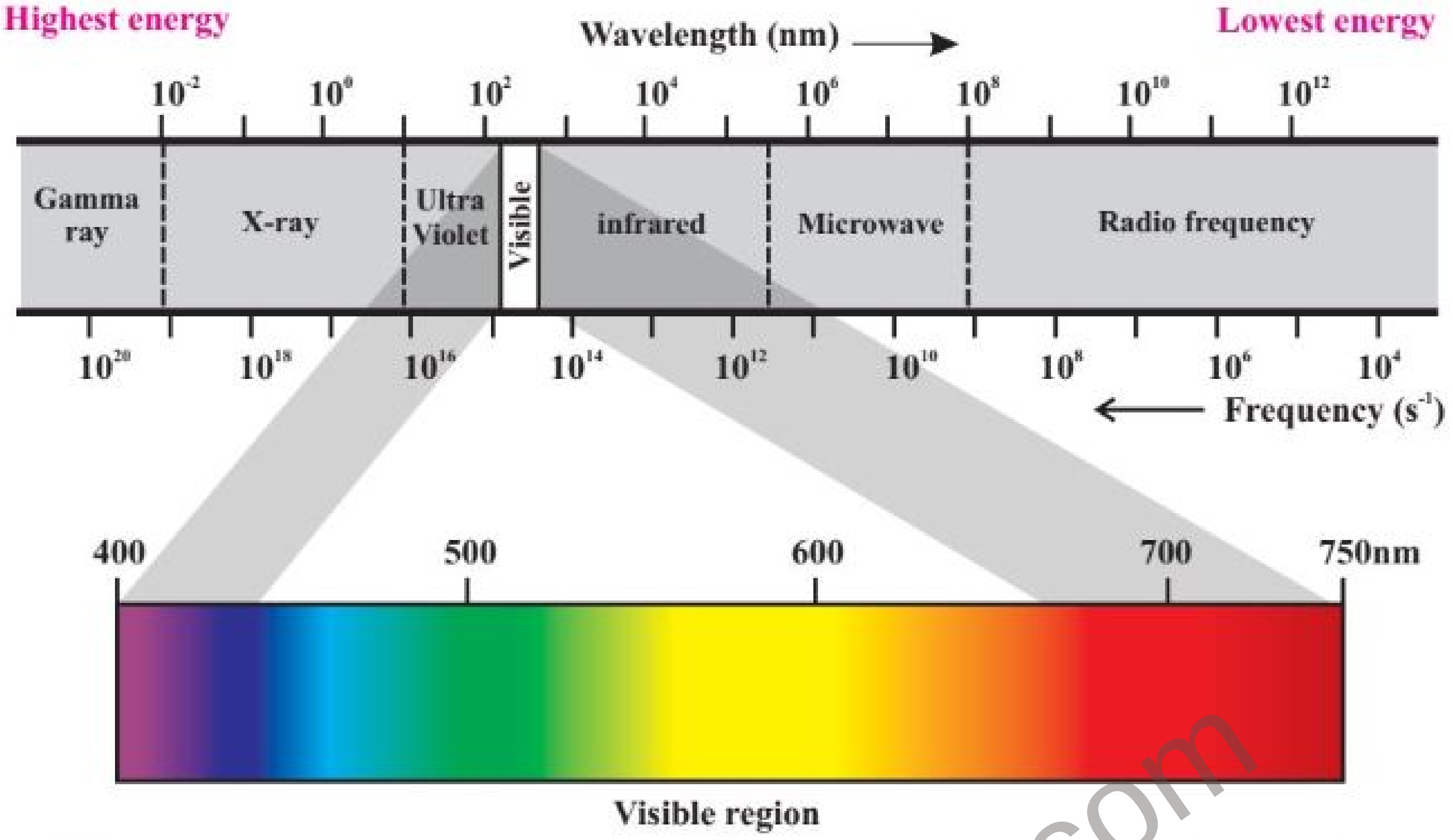


Figure 29.1 **Electromagnetic spectrum showing wavelength, frequency, energy, and the visible light region.**

According to Planck's quantum theory

1. Only discrete amounts of energy may be emitted or absorbed by various atoms and molecules. Quantum energy is the smallest quantity of electromagnetic radiation that can be released or absorbed.
2. The frequency of a radiation and the energy it carries are directly proportional to each other.

The energy of radiation is expressed as,

Where,

E = Energy of the radiation

h = Planck's constant (6.626×10^{-34} J.s)

v= Frequency of radiation

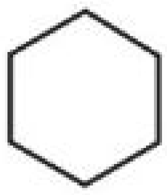
$$E = \frac{\underbrace{\overset{J.s}{h}\,\overset{m/s}{c}}}{\underset{m}{\lambda}}$$

$$J \longrightarrow E = hc\upsilon \longrightarrow cm^{-1}$$

29.1 INDEX OF HYDROGEN DEFICIENCY (IHD)

Consider the given compounds shown here.

1-Hexene
(C_6H_{12})



Cyclohexane
(C_6H_{12})

These compounds have the same molecular formula but different structures, i.e. these are two isomers. However, there is one more similarity between these two compounds. Both these have two hydrogens less than a saturated alkane. It means they have a deficiency of two hydrogen atoms. The deficiency of hydrogen corresponds to the degree of unsaturation of a compound. The index of hydrogen deficiency (IHD) is a measure of the **degrees of unsaturation** in a compound. A compound is said to have one degree of unsaturation for every two hydrogen atoms that are missing.

This is why the above two compounds have an IHD equal to 1. The degree of unsaturation (U), or index of hydrogen deficiency (IHD), is defined as the difference in the number of pairs of hydrogen atoms between the compound and the acyclic alkane with the same number of carbon atoms. Each double bond or ring costs two hydrogen atoms compared to a saturated analog and results in one degree of unsaturation. For example, if a compound has the molecular formula C_4H_6, it has four hydrogen atoms less than the saturated, compound C_4H_{10}. Therefore, this compound has two degrees of unsaturation (IHD=2).

Importance of IHD

Knowing the **IHD** of a molecule gives clues about its composition and structure. For example, if the IHD is **0**, it is certain that the chemical has no rings and no double bonds. This is very helpful because you can find this number easily just by looking at the chemical formula.

Keep in Mind

A double bond and ring each counts as one IHD. A triple bond counts as two IHD.

If the IHD is **1**, the chemical must have either **one ring or one double bond**, but it cannot have both. If the IHD is **2**, there are a few choices: it could have two rings, two double bonds, one of each, or one triple bond. Thus, IHD can give us very useful information about a chemical without using complex analytical techniques. Also, before using an analytical technique IHD will help to assess which technique would be better for the compound under study. The IHD for hydrocarbons can be calculated using the data given in **Table 29.1.**

Table 29.1 Index of hydrogen deficiency

Formula	**Index of Hydrogen Deficiency (IHD)**	**Structure Unit Involved**
C_nH_{2n+2}	0	open chain alkane only
C_nH_{2n}	1	1 double bond **or** 1 ring
C_nH_{2n-2}	2	2 double bonds **or** 2 rings **or** 1 double bond plus 1 ring **or** 1 triple bond

Quick Check 29.1

a) Calculate the IHD for each of the following.
   i) C_6H_6 ii) C_6H_{12} iii) C_4H_4

b) Propose the structure of the above compounds.

c) Hopanes are the waxy solids found in petroleum products as residues after refining the crude oil. A hopane has the formula $C_{30}H_{62}$,
   i) Find its IHD. ii) Predict whether this compound is saturated or not.

29.2 ATOMIC SPECTRUM

Atomic spectra are observed when atoms emit or absorb light of a certain wavelength, known as emission spectra and absorption spectra respectively. Atomic spectra provide evidence that electrons in atoms can only transition between discrete atomic energy levels. When energy is absorbed by electrons of an atom, electrons move from lower energy levels to higher energy levels. These excited electrons radiate energy to return from the excited state to ground states and form emission spectra. Emission spectra can be produced by heating a low-pressure gas. Heating provides energy to excite electrons to higher energy levels.

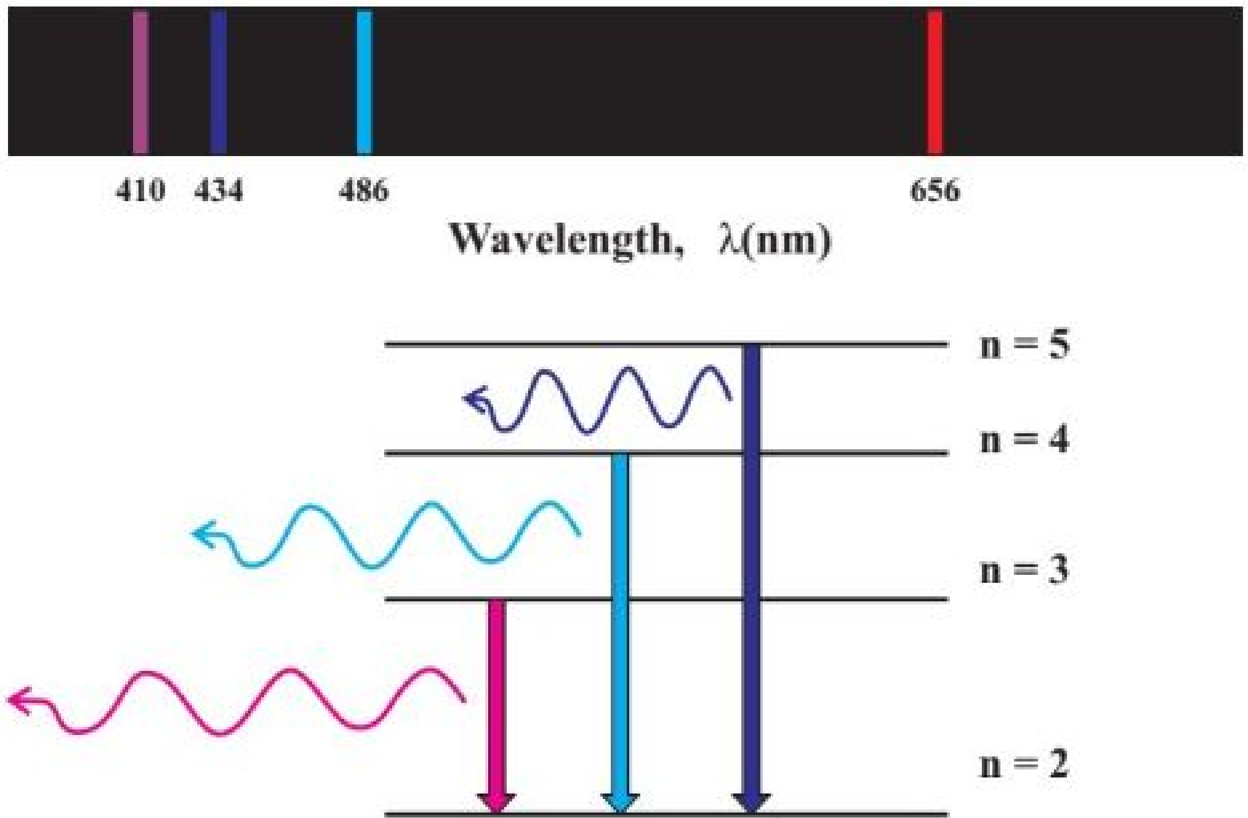


Figure 29.2 Hydrogen emission spectrum

When an electron transitions back to a lower energy level, it emits a photon. Each transition corresponds to a specific wavelength of light which appears as an observable spectral line. The resulting emission spectrum contains a set of distinct wavelengths, represented by coloured lines on a black background.

On the other hand, an absorption spectrum contains the frequencies of light transmitted in the form of dark bands when energy is absorbed by the electrons in the ground state to reach higher energy states. Absorption spectra can be produced by passing white light through a cool, low-pressure gas. Only photons with the exact energy required to excite electrons will be absorbed. Each absorbed photon corresponds to a specific wavelength of light which appears as a dark line on a coloured background. These lines correspond to the same lines observed on an emission spectrum for the same element. An absorption spectrum is like a photographic negative of an emission spectrum.

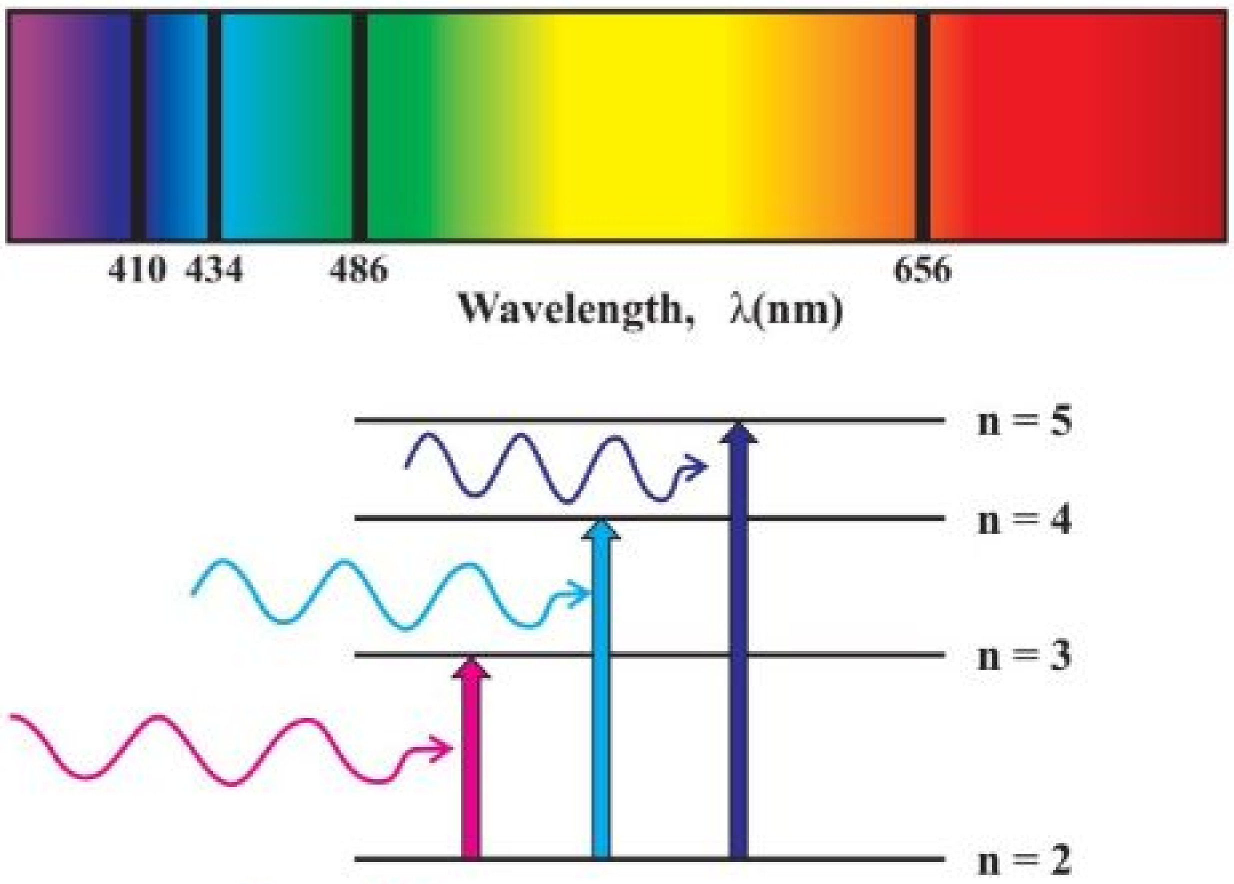


Figure 29.3 Hydrogen absorption spectrum

29.3 SPECTROSCOPY

Spectroscopy deals with the production, measurement, and interpretation of spectra arising from the **interaction of electromagnetic radiation with matter**. A spectrum can be used to obtain information about atomic and molecular energy levels, molecular geometries, interactions of molecules and the nature of chemical bonds. A spectroscopic measurement can also be used for measuring the amount of a specific substance in a sample (quantitative analysis) or even just to identify an unknown sample (qualitative analysis).

The **chemical composition** of a substance can be investigated using emission and absorption spectra. Each element produces a unique pattern of spectral lines. No two elements produce the same set of spectral lines, therefore, elements can be identified by their atomic spectra. Emission line spectra are unique to each element, like a fingerprint.

For example, hydrogen is known to produce strong spectral lines in the red portion of the visible spectrum, at 656 nm. When sodium is burned, a characteristic yellow flame is observed due to the strong spectral lines in the yellow portion of the spectrum, at 589 nm. When mercury is burned, most of the emission lines are below 450 nm, which produce a characteristic blue light.

Did You Know?

Atomic spectra can also help astronomers to determine the chemical composition of stars. By analyzing the light emitted from these celestial bodies, scientists can uncover the mysteries of the universe.

29.4 UV/VISIBLE SPECTROSCOPY

Ultraviolet-visible (UV-Vis) spectroscopy is one of the most popular analytical techniques because it is very versatile and easy to use. In UV-Vis spectroscopy, the UV-Vis light is passed through a sample and the transmittance of light is measured. The absorbance (A) can be determined from the transmittance (T) using the formula A=-log (T). A UV-Vis spectrum displays the absorbance of a substance at various wavelengths. The amount of absorbance at any wavelength is due to the electronic structure of the molecule.

Types of electrons in a compound can be:

- σ electrons (σ-bonds)
- π electrons (in unsaturated compounds only)
- n electrons (non-bonded electrons)

Sigma bonding orbitals are lower in energy than π bonding orbitals, which in turn, are lower in energy than non-bonding orbitals. When electromagnetic radiation of the correct frequency is absorbed, a transition occurs from one of these orbitals (π or n) to an empty orbital, usually an antibonding orbital, σ^* or π^*. UV-Vis spectroscopy uses the wavelengths from 200-800 nm to study the changes in electronic energy levels. These changes are due to the transfer of electrons from π- or non-bonding orbitals as shown in **Figure 29.4**.

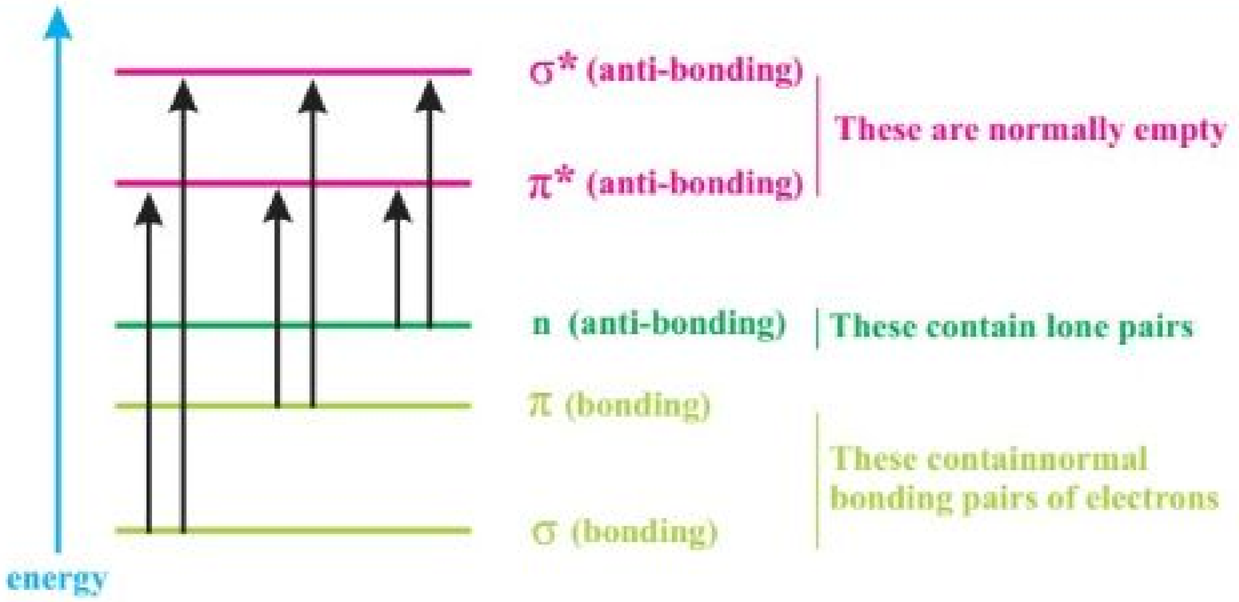


Figure 29.4 Transition of electrons from lower energy to higher energy levels

In each possible case, an electron is excited from a filled orbital into an empty anti-bonding orbital. Each jump takes energy from the light of a specific wavelength will be absorbed.
The important electronic transitions are:

- from pi bonding orbitals to pi anti-bonding orbitals (π to π*)
- from non-bonding orbitals to pi anti-bonding orbitals (n to π*)
- from non-bonding orbitals to sigma anti-bonding orbitals (n to σ*)

The diagram below shows a simple UV-visible absorption spectrum for buta-1,3-diene, $CH_2=CH-CH=CH_2$. Absorption peaks at a value of 217 nm corresponds to the wavelength absorbed maximum and is called λ_{max}. This is in the UV region and so there would be no visible sign of any light being absorbed the compound is colourless. There are no non-bonding electrons so the only electron jumps taking place (within the range that the spectrometer can measure) are from pi bonding to pi anti-bonding orbitals.

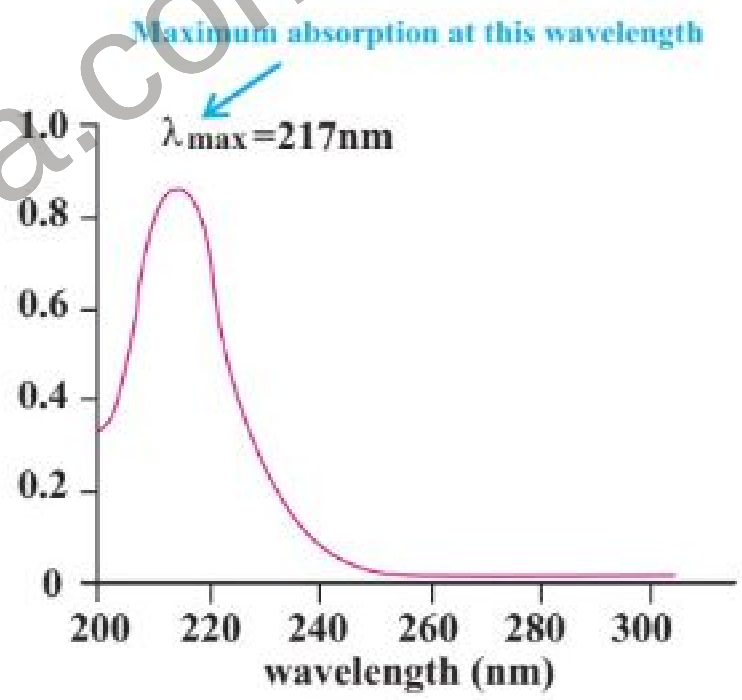
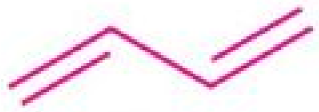


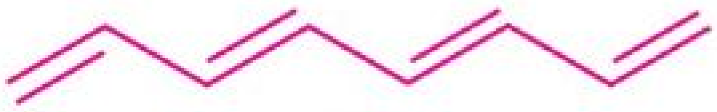
Figure 29.5 Absorption spectrum

The value of λ_{max} for a particular compound is highly dependent on the extent of conjugation. To illustrate this point, compare the MOs of butadiene, hexatriene, and octatetraene.



217 nm

257 nm



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In a conjugated system, atoms share electrons across a long chain. The more "conjugated" a compound is, the more energy levels it has, and the gaps between those levels become smaller. Because these gaps are smaller, it takes less energy to push an electron from a low level to a higher one. Since the energy of light depends on its frequency, these smaller energy gaps allow the compound to absorb light with less energy (lower frequency), which is why highly conjugated compounds often have bright colours. Because longer light waves have less energy, these chemicals absorb light with a longer wavelength, called the λ_{max}. This means that the more double bonds a compound has connected together, the higher its λ_{max} number will be. Usually, every time you add one more double bond to the chain, that number increases by about 30 to 40 nm. By looking at this number, the extent of conjugation in a compound can be determined.

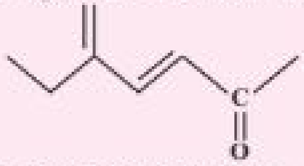
Quick Check 29.2

a) Which type of electronic transitions require least energy in UV/Vis spectroscopy? Explain.

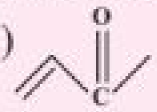
i) $\sigma \rightarrow \sigma^*$ ii) $\pi \rightarrow \pi^*$ iii) $n \rightarrow \sigma^*$ iv) $n \rightarrow \pi^*$

b) Arrange the following in an increasing order of λ_{max}

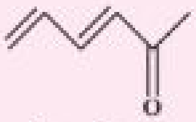
i)



ii)



iii)



c) Will $CH_3CHOHCH_3$ show a significant absorption in the UV-Vis region.

MORE INFO Interesting Information

An Interesting InfoGreen tomato and a red ripen tomato both have different colours. Green tomato has chlorophyll in higher quantities, while red tomato contains lycopene. Both these compounds have different λ_{max} and a specific colour in the visible range.

29.5 INFRARED SPECTROSCOPY

All covalent bonds act rather like springs, the bonds can vibrate in a number of different ways. The frequencies of vibrations occur in the infra-red region of the electromagnetic spectrum. If an organic molecule is irradiated with the infra-red energy that matches the natural vibration frequency of its bonds, it absorbs some of that energy and the amplitude of vibration increases.

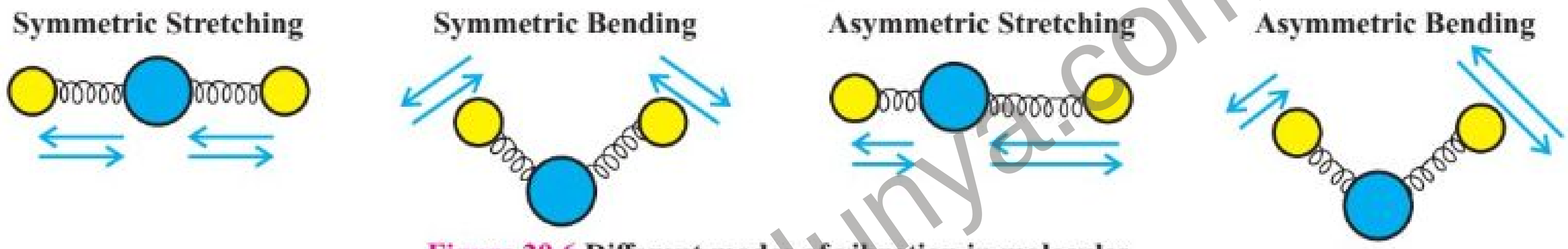


Figure 29.6 Different modes of vibration in molecules

Infrared (IR) spectroscopy is a technique used to identify compounds which is based on changes in vibrations of atoms when they absorb IR of specific frequencies. A spectrophotometer irradiates the sample with IR radiation and then detects the absorption of radiation by the molecule. IR energy is absorbed only if a molecule has a permanent dipole that changes as it vibrates. Symmetrical and nonpolar molecules such as O_2 or H_2, are, therefore, IR inactive. Polar bonds such as O-H, N-H, etc. show absorption at higher wavenumbers. Similarly, bonds with smaller bond length and those with multiple bonds (e.g., HC≡CH also absorb at higher wavenumbers. The reason for these observations is that these bonds are stronger and require higher energy. An IR spectrum consists of two regions. The fingerprint region below 1500 cm^{-1} and the functional group region above 1500 cm^{-1}. Only functional region is discussed here which is enough to interpret the nature of organic compound. The table below gives information about infrared absorption frequencies (wave numbers).

Did You Know?

Infrared spectroscopy can be used to measure alcohol levels using modern roadside breathalyser. A ray of infrared radiation is passed through the breath that is exhaled into the breathalyser chamber. The characteristic bonds of ethanol are detected and measured - the higher the absorbance of infrared radiation, the more ethanol in the person's breathe.

Table 29.2 IR Absorption ranges of functional groups (cm^{-1})

Bond	Functional groups containing the bond	Characteristic infrared absorption range (in wavenumbers)/cm^{-1}
C—O	Alcoholic, ester	1040–1300

C═C	aromatic compound, alkene	1500–1680
C═O	amide carbonyl, carboxyl ester	1640–1690 1670–1740 1710–1750
C≡N	nitrile	2200–2250
C–H	alkane	2850–2950
N–H	amine, amide	3300–3500
O–H	carboxyl hydroxy	2500–3300 3200–3600

29.5.1 Interpreting and Predicting Infrared Spectra

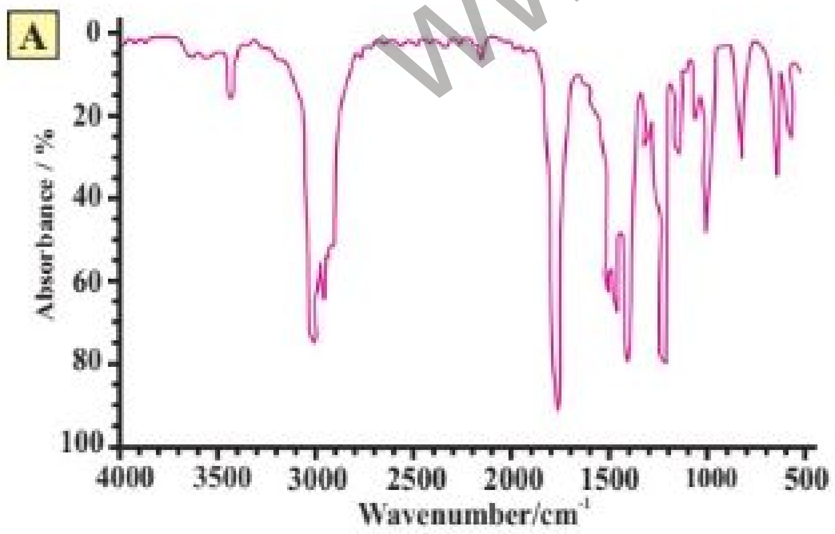
The best way to understand how to interpret an IR spectrum is by looking at solved examples and becoming familiar with the characteristic features of an IR spectrum.

Example 29.1

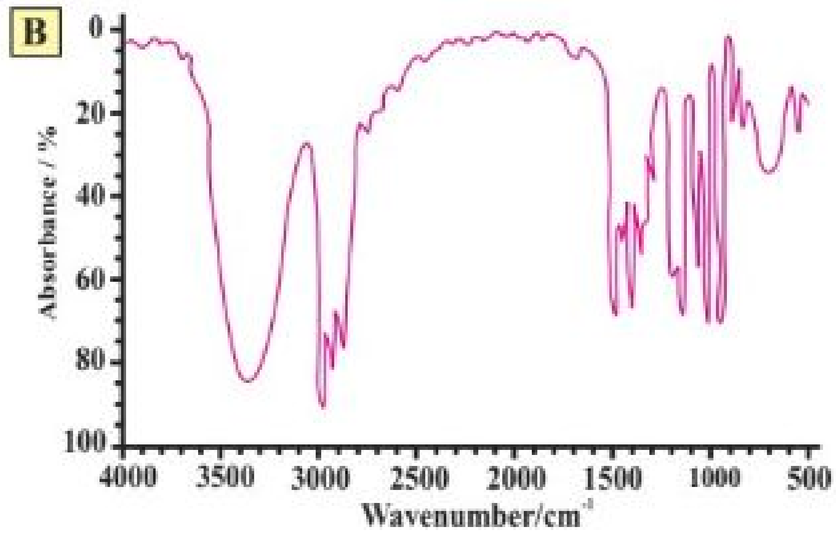
Examine the two spectra shown and determine which one belongs to propan-2-ol and which one belongs to propanone.

Answer

- The presence of a strong, sharp absorption around 1710 cm corresponds to the characteristic C=O, carbonyl, the functional group in a ketone. IR spectrum A is propanone.

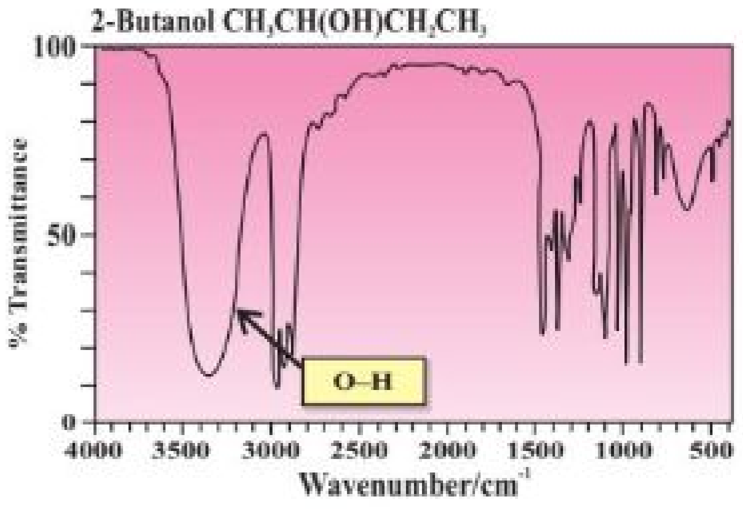


- In spectrum B the presence of a strong, absorption around 3200–3600 cm suggests that there is an alcohol group present, which corresponds to the -OH group in propan-2-ol.

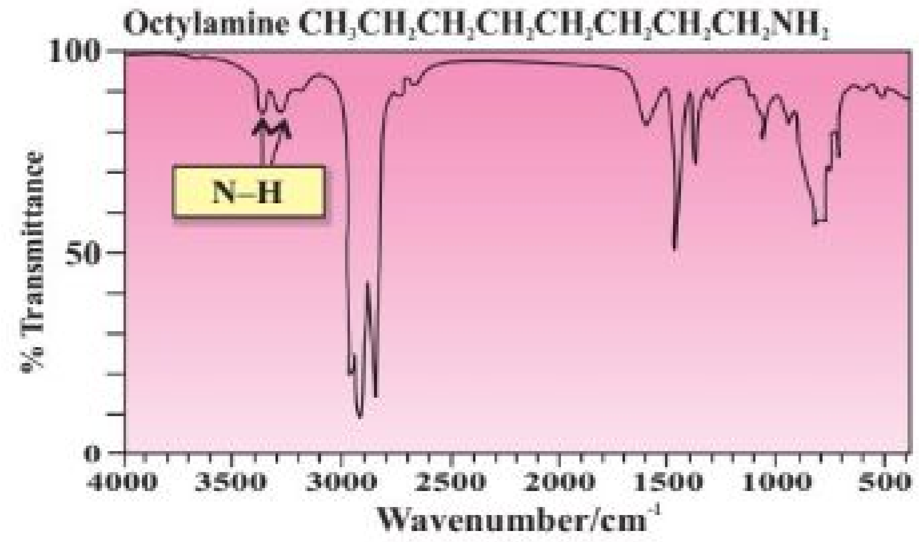


29.5.2 IR Spectra of Important Functional Groups

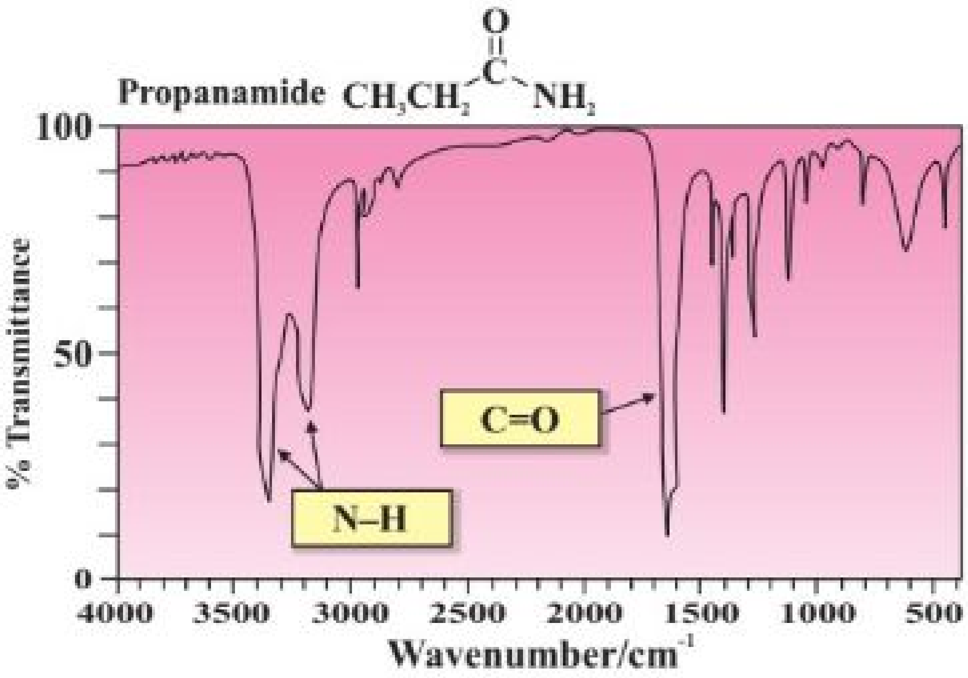
The OH group of the alcohol shows a strong absorption at 3600-3200 cm^{-1}. The peak at 3000 cm^{-1} is due to sp^3 hybridized C−H bonds.


2-Butanol $CH_3CH(OH)CH_2CH_3$

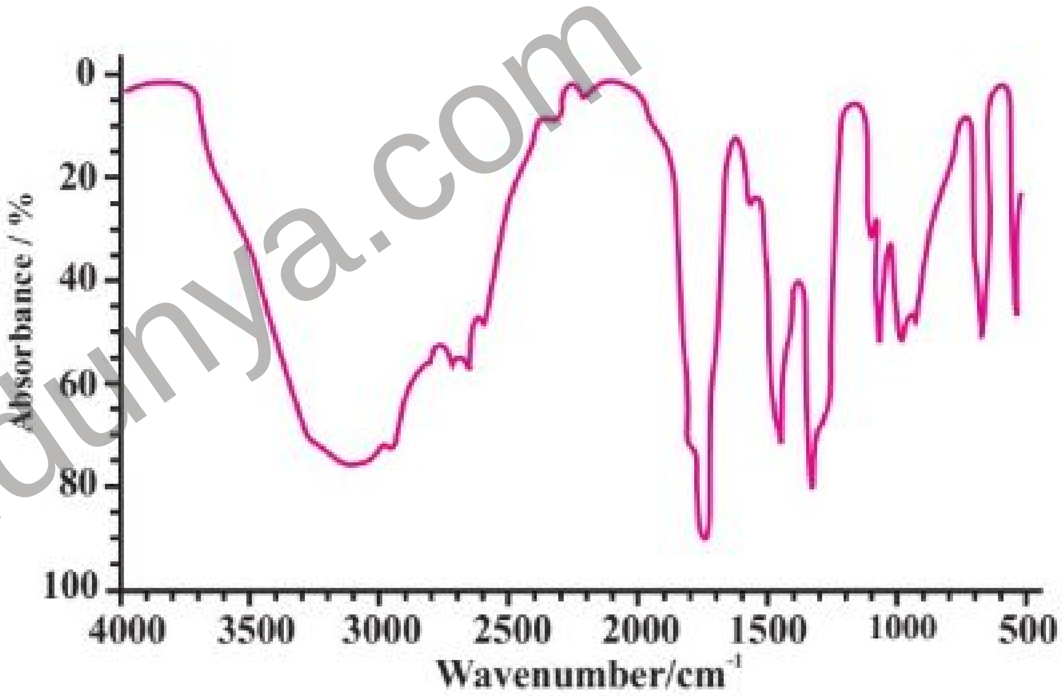
The N−H bond in an amine gives rise to two weak absorptions at 3300 and 3400 cm^{-1}.



An amide exhibits absorptions above 1500 cm^{-1} for both its N−H and C=O groups: N−H (two peaks) at 3200 and 3400 cm^{-1}; C=O at 1660 cm^{-1}.



The C=O group in the carboxylic acids shows a strong absorption at 1700 cm^{-1} along with broad and deep absorption of the O-H bond of a carboxylic acid between 2500 and 3300 cm^{-1}. The broad peak caused by the O-H bond of a carboxylic acid between 2500 and 3300 cm^{-1}. This right hand side of this peak is often distorted by the peaks from C-H bonds.



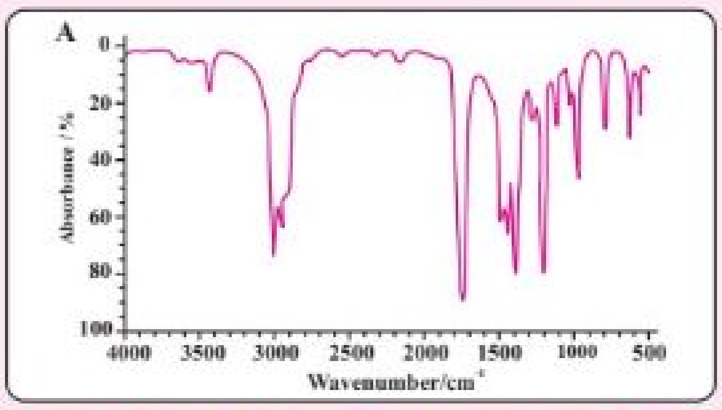
NOTE: N-H signal in amines is broad but it is not broader than O-H signal in alcohols.

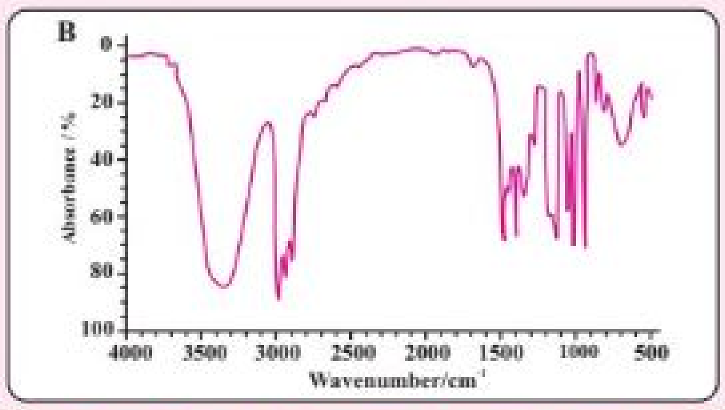
Did You Know?

Infrared spectroscopy is used to identify pollutants in vehicle emissions. The air sensors detect and measure the amount of pollutants such as carbon monoxide, carbon dioxide and unburnt hydrocarbons. This commonly occurs on motorways and in busy town centres to monitor localised pollution.

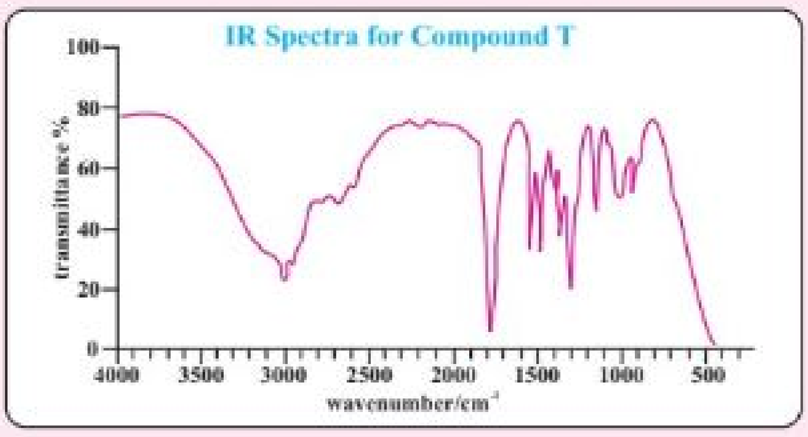
Quick Check 29.2

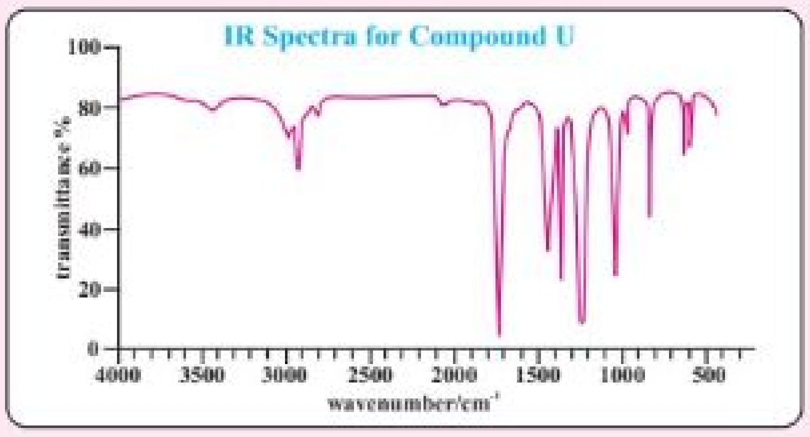
I. Which one of the infra-red spectra is that of butanone and which one is of butan-2-ol?





ii. Compounds T and U are isomers with the molecular formula $C_3H_6O_2$. Suggest their structures based on the spectra shown below:



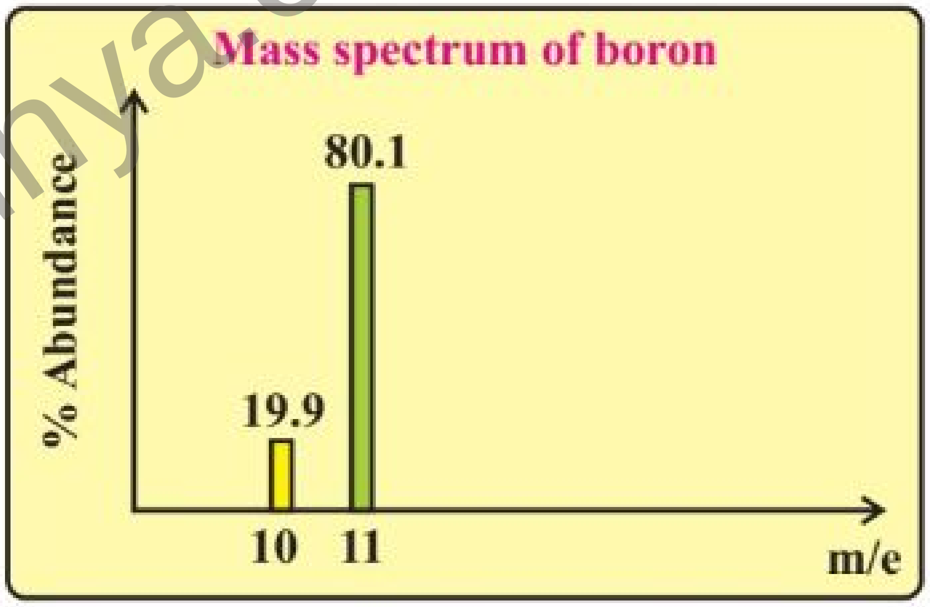


29.6 MASS SPECTROMETRY

Mass spectrometry is an analytical technique used to identify unknown compounds. The molecules/atoms in the small sample are bombarded with high energy electrons which can cause a molecule/atom to lose an electron. As a result, a positive ion is formed which is detected by detector and recorded as m/e (mass to charge ratio of the ion) versus percentage of ion.

29.6.1 Isotopic Mass and Abundance

Mass spectrometry can be used to find the relative abundance of the isotopes experimentally. The relative abundance is the proportion of a particular isotope in a mixture of isotopes found in nature. For example, the relative abundance of Cl-35 and Cl-37 is 75% and 25% respectively. The heights of the peaks in mass spectroscopy show the proportion of each isotope present. For example, in the graph below, the peak heights show the relative abundance of the boron isotopes: boron-10 has a relative abundance of 19.9% and boron-11 has a relative abundance of 80.1%.



Calculating Relative Atomic Mass

The mass of an element is given as relative atomic mass, A_r by using the average mass of the isotopes. The relative atomic mass of an element can be calculated by using the relative abundance and isotopic masses. The relative abundance of an isotope is either given or can be read the mass spectrum.

$$\textbf{Relative Atomic Mass } (A_r) = \Sigma\ \frac{\textbf{(isotopic mass} \times \textbf{isotopic abundance)}}{\textbf{100}}$$

Example 29.2

Calculate the relative atomic mass, A_r, of oxygen to 2 decimal point.

Answer

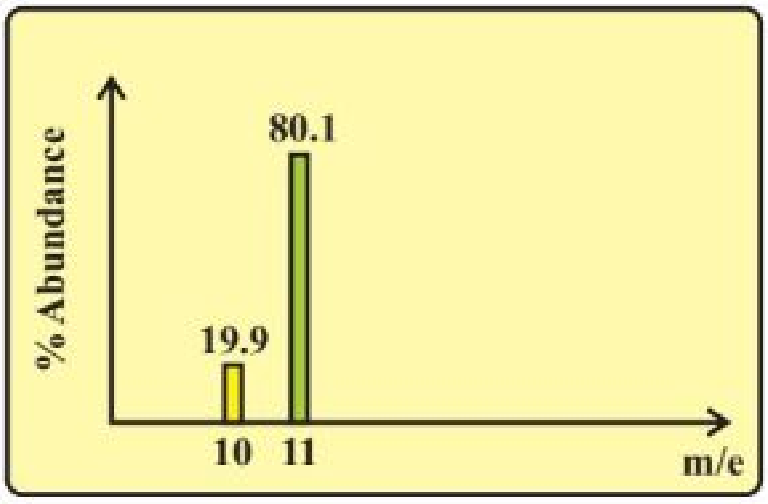
Isotope	Percentage abundance
^{16}O	99.76
^{17}O	0.04
^{18}O	0.20

- $A_r = \dfrac{(99.76 \times 16) + (0.04 \times 17) + (0.20 \times 18)}{100}$
- $A_r = 16.0044$
- $A_r = \mathbf{16.00}$ (to 2 d.p)

Example 29.3

Calculate the relative atomic mass of boron using its mass spectrum, to 2 decimal point.

- $A_r = \dfrac{(19.9 \times 10) + (80.1 \times 11)}{100}$
- $A_r = 10.801$
- $A_r = \mathbf{10.80}$ (to 2 decimal point)



29.6.2 Molecular Ion Peak and Fragmentation

When molecules in a sample compound are bombarded with highly accelerated electrons it causes the molecules to lose electrons. This results in the formation of a positively charged molecular ion with one unpaired electron. One of the electrons in the pair has been removed by the beam of electrons.

$$\textbf{Molecule} \xrightarrow{\text{electron bombardment}} \textbf{Molecule}^{+\bullet} + e^-$$

Molecule$^{+\bullet}$ represents the molecular ion. The molecular ion can further fragment to form new ions, molecules, and free radicals.

a) Deducing Molecular Formula

Each peak in the mass spectrum corresponds to a certain fragment with a particular m/e value. The peak mostly with the highest m/e value is the molecular ion (M^+) peak which gives information about the molecular mass of the compound. The molecular ion is the entire molecule that has lost one electron when bombarded with a beam of electrons.

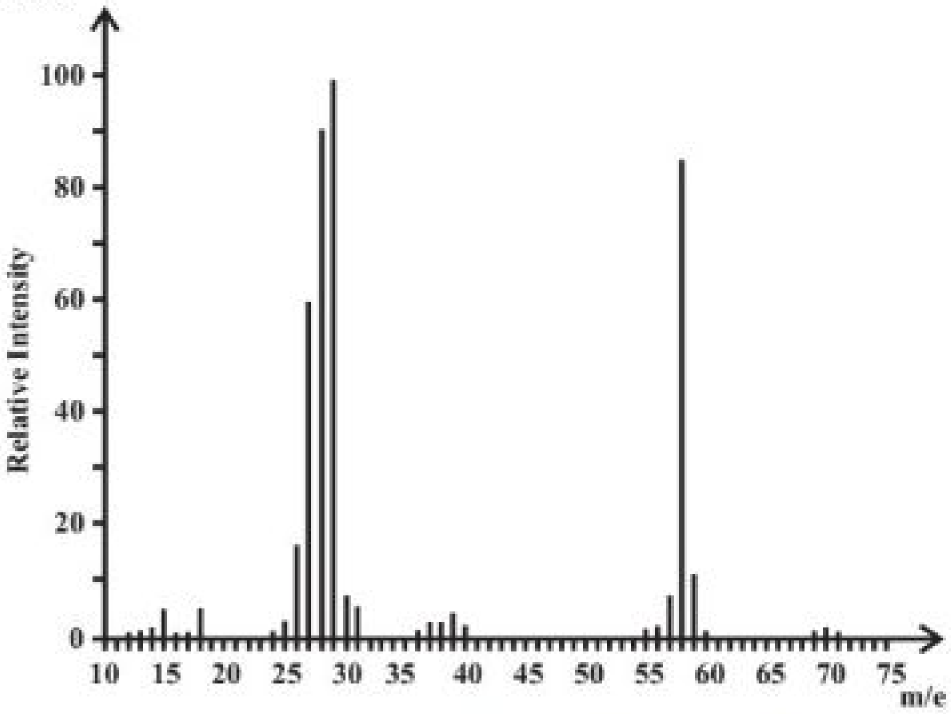
$$\textbf{Molecule} \xrightarrow{\text{electron bombardment}} \textbf{Molecule}^{+\bullet} + e^-$$

The [M+1] peak is a smaller peak which is due to the natural abundance of the isotope carbon-13. The height of the [M+1] peak for a particular ion depends on how many carbon atoms are present in that molecule; the more carbon atoms, the larger the [M+1] peak is. For example, the height of the [M+1] peak for hexane (containing six carbon atoms) ion will be greater than the height of the [M+1] peak of ethane (containing two carbon atoms) ion.

Example 29.4

Determine whether the following mass spectrum corresponds to propanal, CH_3CH_2CHO or butanal, $CH_3CH_2CH_2CHO$.

Answer: The mass spectrum corresponds to propanal as the molecular ion peak is at m/e = 58. The molecular ion mass of $CH_3CH_2CHO^+$ ion is 58 and butanal arises from the $CH_3CH_2CH_2CHO^+$ ion which has a m/e of 72.



b) Identifying Molecules Using Fragmentation

The molecular ion peak can be used to identify a compound by its molecular mass. However, different compounds may have the same molecular mass. To further determine the structure of the unknown compound, fragmentation is used. Fragments may appear due to the formation of characteristic smaller ions or the loss of small molecules. For example, loss of small molecules/fragments give rise to peaks at 18 (H_2O), 29 ($C_2H_5^+$), and 44 (CO_2).

Alkanes

Simple alkanes are fragmented in mass spectroscopy by breaking the C-C bonds. m/e values of some of the common alkane fragments are given in the **Table 29.3**.

Table 29.3 Common fragments of hexane

Fragment	m/e
CH_3^+	15
$C_2H_5^+$	29
$C_3H_7^+$	43
$C_4H_9^+$	57
$C_5H_{11}^+$	71
$C_6H_{13}^+$	85

The fragmentation of the straight chain hexane: 86, 71, 57, 43, 29 and 15, which is due to the fragment at different location.

- $CH_3–CH_2–CH_2–CH_2–CH_2–CH_3$ (Mass:86)
- $CH_3–CH_2–CH_2–CH_2–CH_2^+$ (Mass:71)
- $CH_3–CH_2–CH_2–CH_2^+$ (Mass:57)
- $CH_3–CH_2–CH_2^+$ (Mass:43)
- $CH_3–CH_2^+$ (Mass:29)
- CH_3^+ (Mass:15)

c) The M+1 & M+2 Peaks

i. Determine the Number of Carbon Atoms Using M+1 Peak

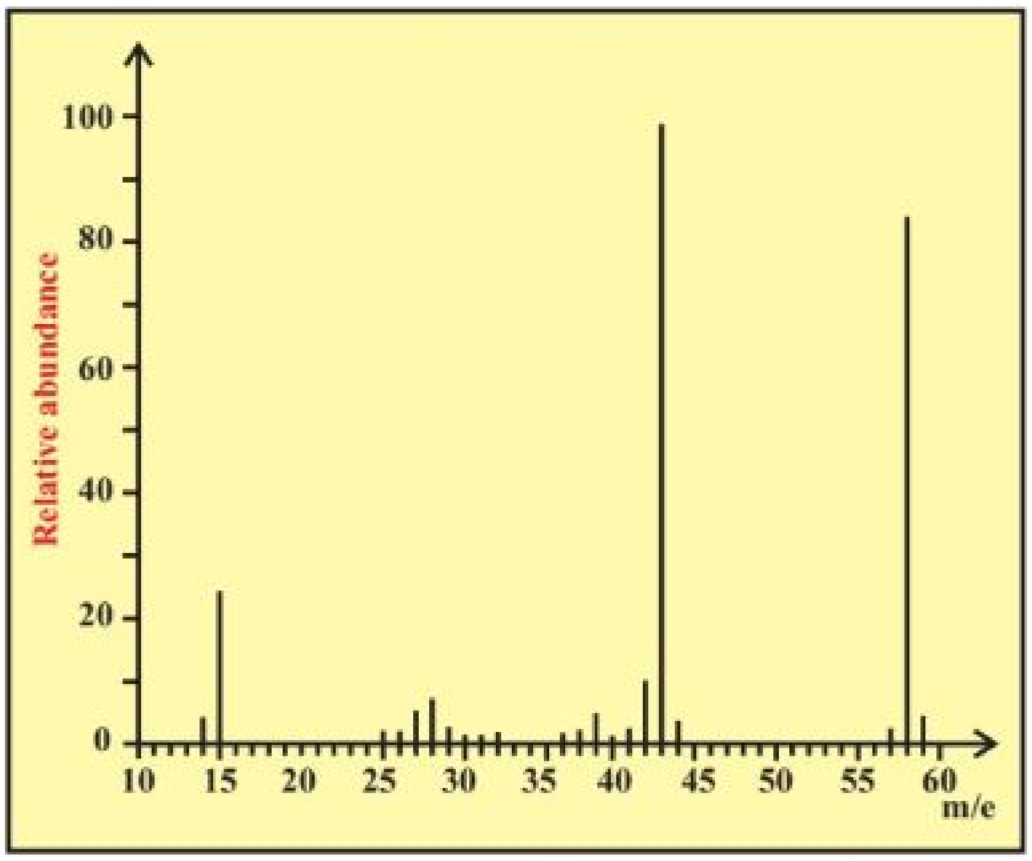
The [M+1] peak is caused by the presence of the carbon-13 (^{13}C) isotope in the molecule. Carbon-13 makes up approximately 1.1% of all carbon atoms. Therefore, the [M+1] peak is much smaller than the M peak as the isotope is less common. The ratio of ^{13}C to ^{12}C is approximately 1:99. Thus, the greater the number of carbon atoms present in a molecule the greater the height of the [M+1] peak.

The number of carbon atoms, n, in a compound can be deduced using the [M+1] peak and the following formula:

$$n = \frac{100 \times \text{abundance of [M+1]}}{1.1 \times \text{abundance of } M^+ \text{ ion}}$$

Example 29.5

Determine the number of carbon atoms of compound X with the following mass spectrum:



Answer

The M ion peak is at m/e 58 with a relative abundance of around 85.

The [M+1] peak is at m/e 59 with a relative abundance of 3.

Therefore, the number of carbon atoms (n) is:

$$n = \frac{100 \times 3}{1.1 \times 85} = 3.21$$

There are, therefore, 3 carbon atoms present in compound X.

ii. Detecting Bromine and Chlorine Atoms Using M+2 Peak

The presence of bromine or chlorine atoms in a compound gives rise to a [M+2] and possibly [M+4] peak

Chlorine

Chlorine exists as two isotopes, ^{35}Cl and ^{37}Cl.

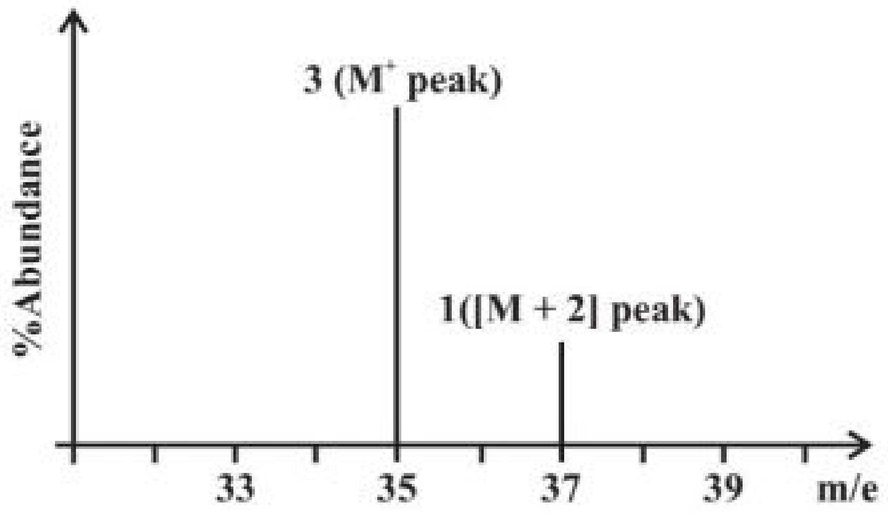
A compound containing one chlorine atom will, therefore, have two molecular ion peaks due to the two different isotopes, it contain,

^{35}Cl = M^+ peak

^{37}Cl = [M+2]peak

The ratio of the peak heights is 3:1 (as the relative abundance of ^{35}Cl is 3× greater than that of ^{37}Cl.

Compounds Containing 1Cl Atom



A compound containing two chlorine atoms will have three molecular ion peaks due to the different combinations of chlorine isotopes they can contain

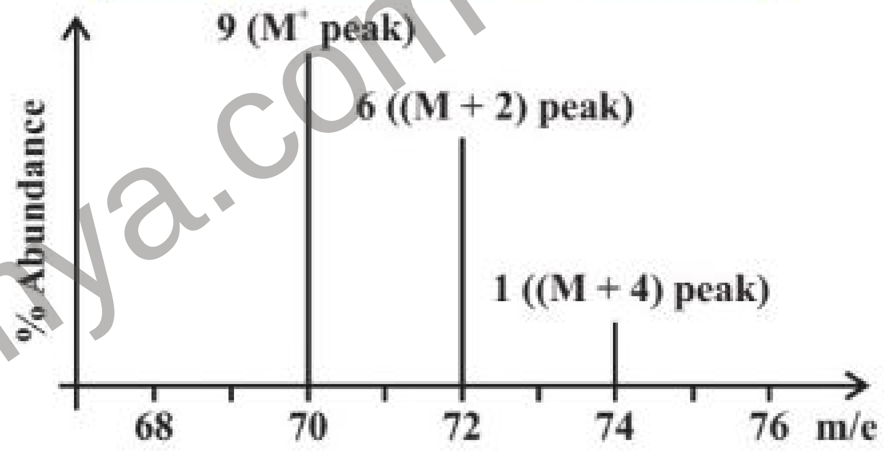
^{35}Cl + ^{35}Cl = M^+ peak

^{35}Cl + ^{37}Cl = [M+2] peak

^{37}Cl + ^{37}Cl = [M+4] peak

The ratio of the peak heights is 9:6:1

Compounds Containing 2Cl Atoms



Bromine

Bromine also exists as two isotopes, ^{79}Br and ^{81}Br.

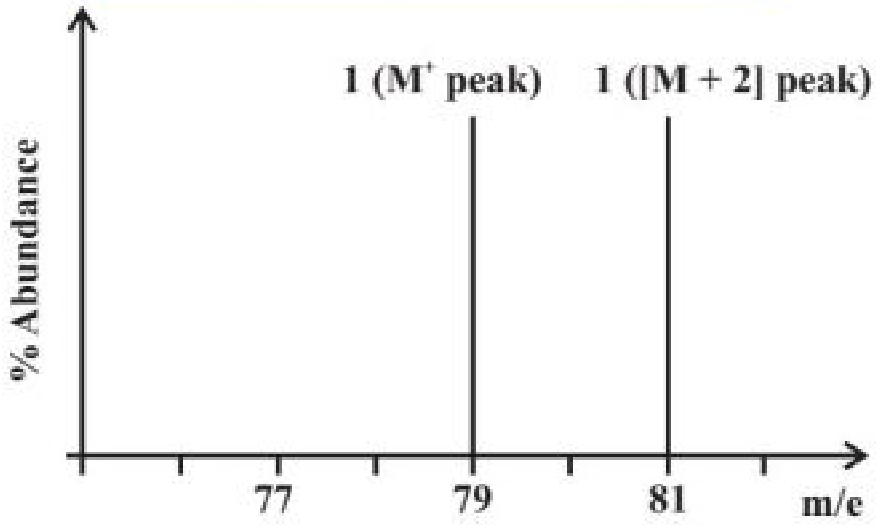
A compound containing one bromine atom will have two molecular ion peaks

^{79}Br = M^+ peak

^{81}Br = [M+2] peak

The ratio of the peak heights is 1:1 (they are of similar heights as their relative abundance is the same).

Compounds Containing 1Br Atoms



A compound containing two bromine atoms will have three molecular ion peaks.

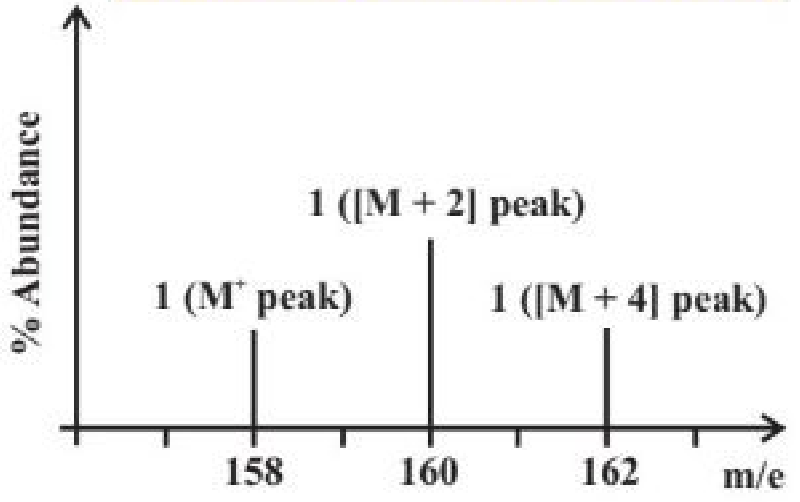
^{79}Br + ^{79}Br = M peak

^{79}Br + ^{81}Br = [M+2] peak

^{81}Br + ^{81}Br = [M+4] peak

The ratio of the peak heights is 1:2:1

Compounds Containing 2Br Atoms



Quick Check 29.3

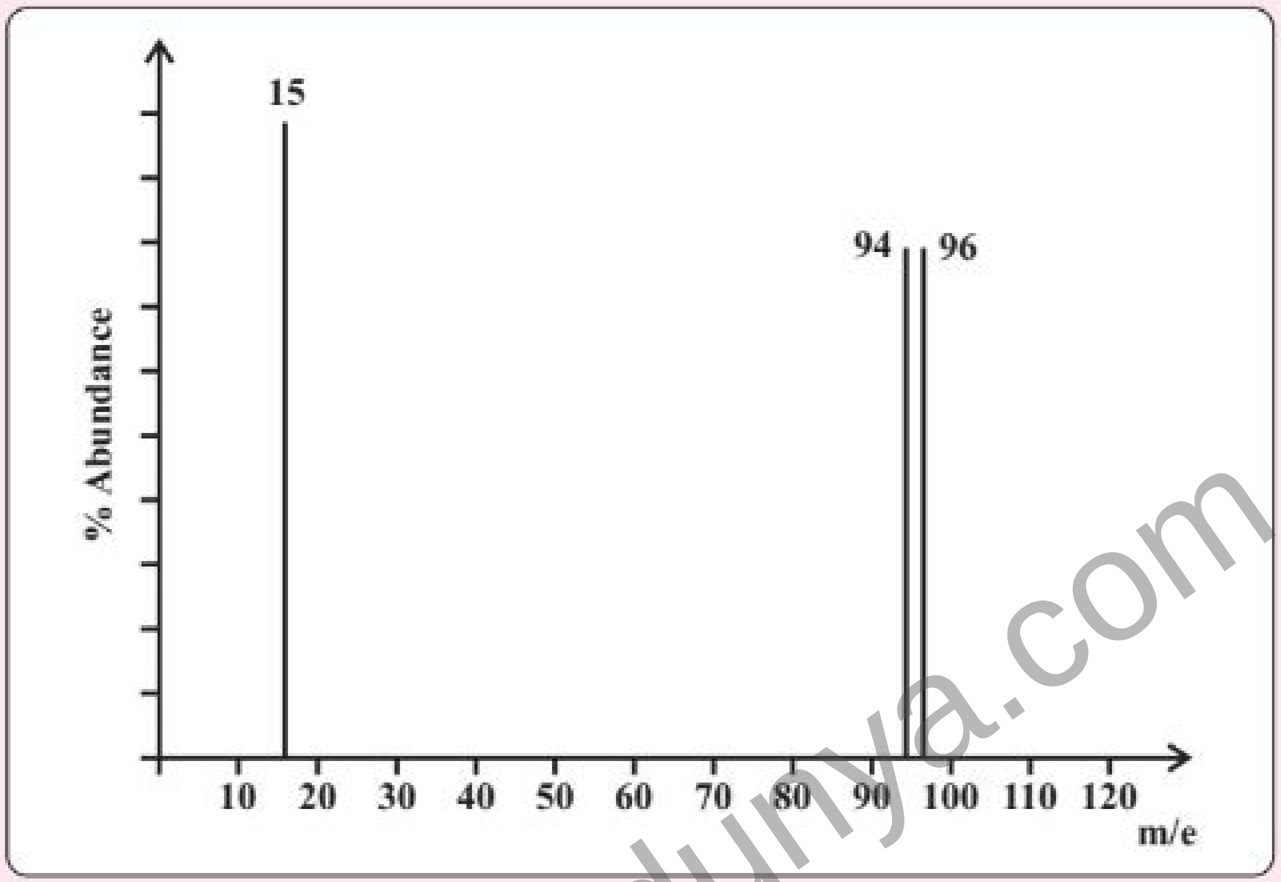
a) Show all the possible fragments of

i) C_4H_{10} ii) C_5H_{12} iii) C_7H_{16}

b) The mass spectrum of CH_3Br is given below.

i) Identify the fragment against each peak.

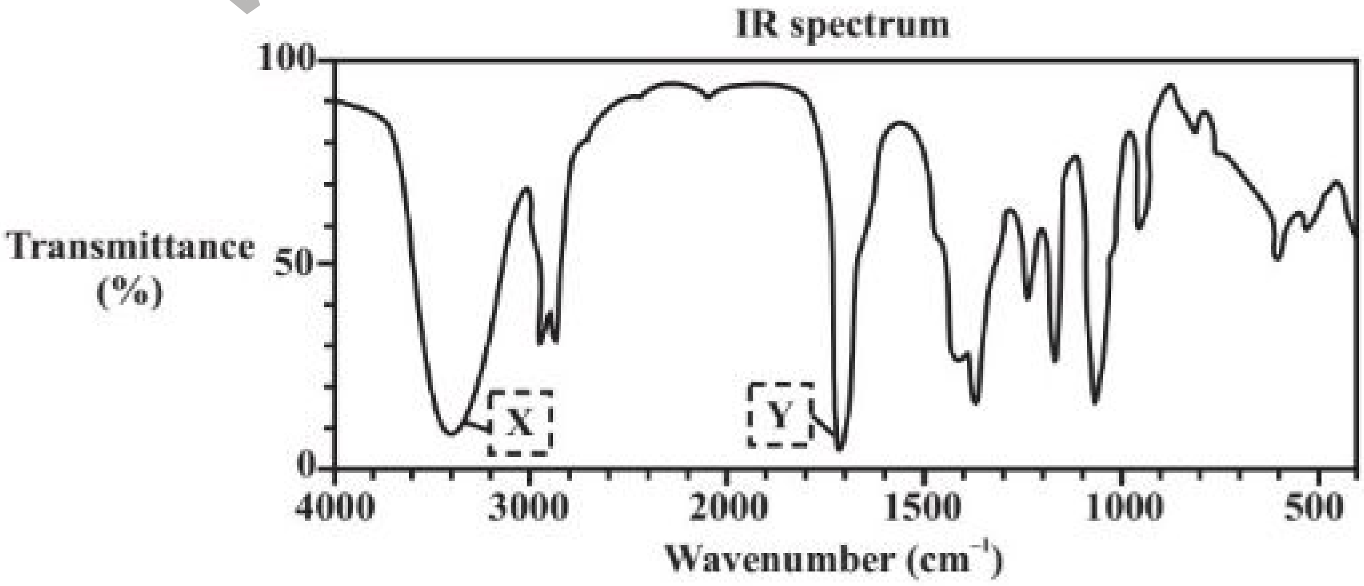
ii) What is the justification of two peaks at 94 and 96?



Exercise

Q1. MULTIPLE CHOICE QUESTIONS :

I) Which of the following compounds could produce the IR spectrum shown below?



a) propanoic acid b) 4-hydroxybutanone

c) pentan-1-ol d) 2-hydroxybut-1-ene

II. What is the wavelength range of the UV spectrum?

a) 100 nm to 500 nm b) 200 nm to 800 nm

c) 300 nm to 1000 nm d) 400 nm to 1600 nm

III. The λ of σ to σ* transitions lies in the

a) IR region b) Visible region

c) UV region d) None of the above

IV. The types of transitions possible in UV-visible region for a compound with molecular formula C_2H_4 are:

a) n→π* b) n→σ*

c) σ→σ* d) π→π*

V. What is index of hydrogen deficiency of C_8H_8?

a) 1 b) 2

c) 3 d) 4

VI. Which of the following statements about the mass spectrum of CH_3Cl is correct?

a) There is one peak for the molecular ion with an m/e value of 45.

b) There is one peak for the molecular ion with an m/e value of 52.

c) The last two peaks have abundances in the ratio 1:1 and occur at m/e values of 50 and 52.

d) The last two peaks are of equal size and occur at m/e values of 50 and 52.

Q2. SHORT ANSWER QUESTIONS

a) Bromobutane, $CH_3CH_2CH_2CH_2Br$, can be reacted with hot aqueous sodium hydroxide to prepare butan-1-ol.

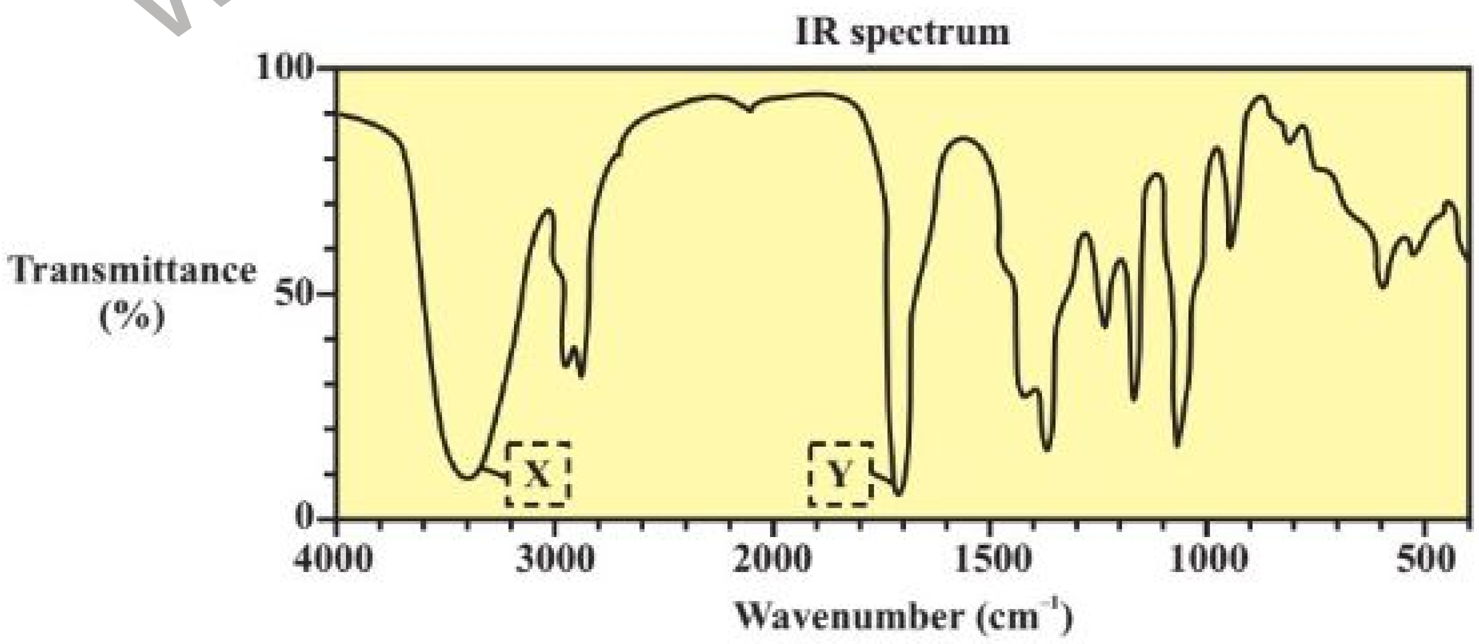
$$CH_3CH_2CH_2CH_2Br + OH^- \rightarrow CH_3CH_2CH_2CH_2OH + Br^-$$

Butan-1-ol produced can be analysed by mass spectrometry.

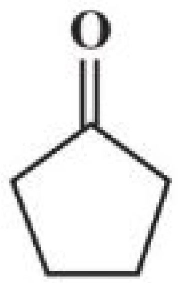
i. Predict the formula of fragment ion which is produced to m/e value of 17.

ii. Predict two other fragment ions that you would expect to see in the mass spectrum of butan-1-ol and state the m/e value of each ion.

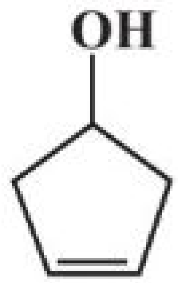
b) Identify the functional groups responsible for the peaks labelled X and Y.



c) Explain how the two isomers shown in the diagram can be distinguished using IR spectroscopy.



A



B

d) The molecular formulas of but-1-ene and but-1,4-diene are given below:

but-1-ene: C_4H_8 but-1,3-diene: C_4H_6

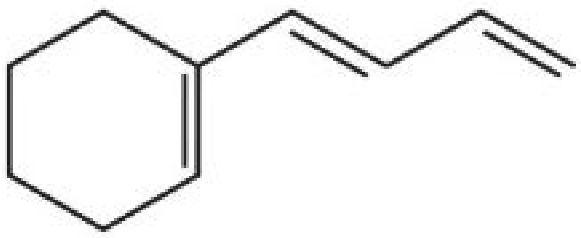
i. Fine out the IHD for both of these compounds.

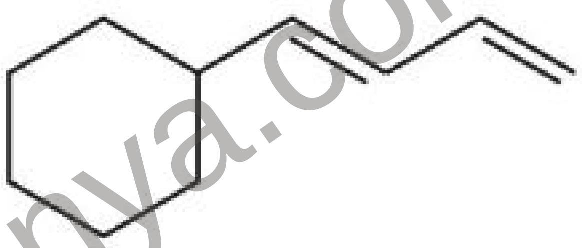
ii. Compare the UV absorption spectrum of but-1-ene to that of but-1,3-diene by stating the difference in their λ_{max} qualitatively.

Q3. CONSTRUCTED RESPONSE QUESTIONS

a) Compound **X** is an atmospheric pollutant emitted from fuel combustion of petrol and diesel vehicles. Compound X is a potent human carcinogen. Analysis of compound X showed the following percentage composition by mass: C, 88.89% and H, 11.1%. Mass spectrometry showed a molecular ion peak at m/e = 54. Compound X reacts with H_2 in the presence of a nickel catalyst in a 1 : 2 molar ratio. Analyse and interpret this information to determine a possible structure for compound X. Show all your working.

b) How will you differentiate between the following using the UV visible spectroscopy.

i) 

ii) 

DESCRIPTIVE QUESTIONS

Q4. Describe various possible electronic transitions in a compound having sigma, pi bonds, and non-bonding electrons.

Q5. Explain two types of atomic spectrum.

Q6. How mass spectrometry is used to determine the isotopic mass and average atomic masses of elements? Explain giving an example.