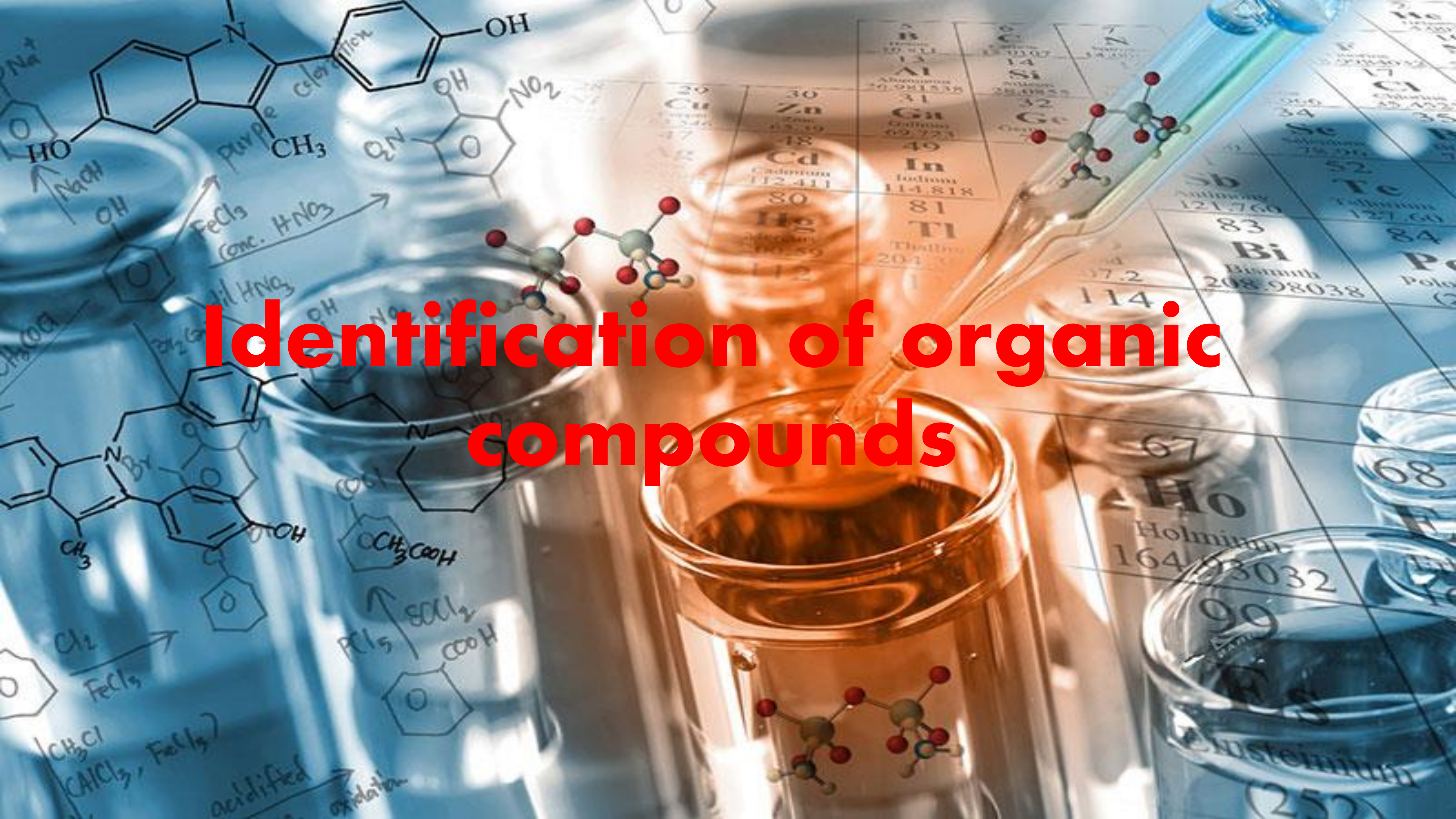
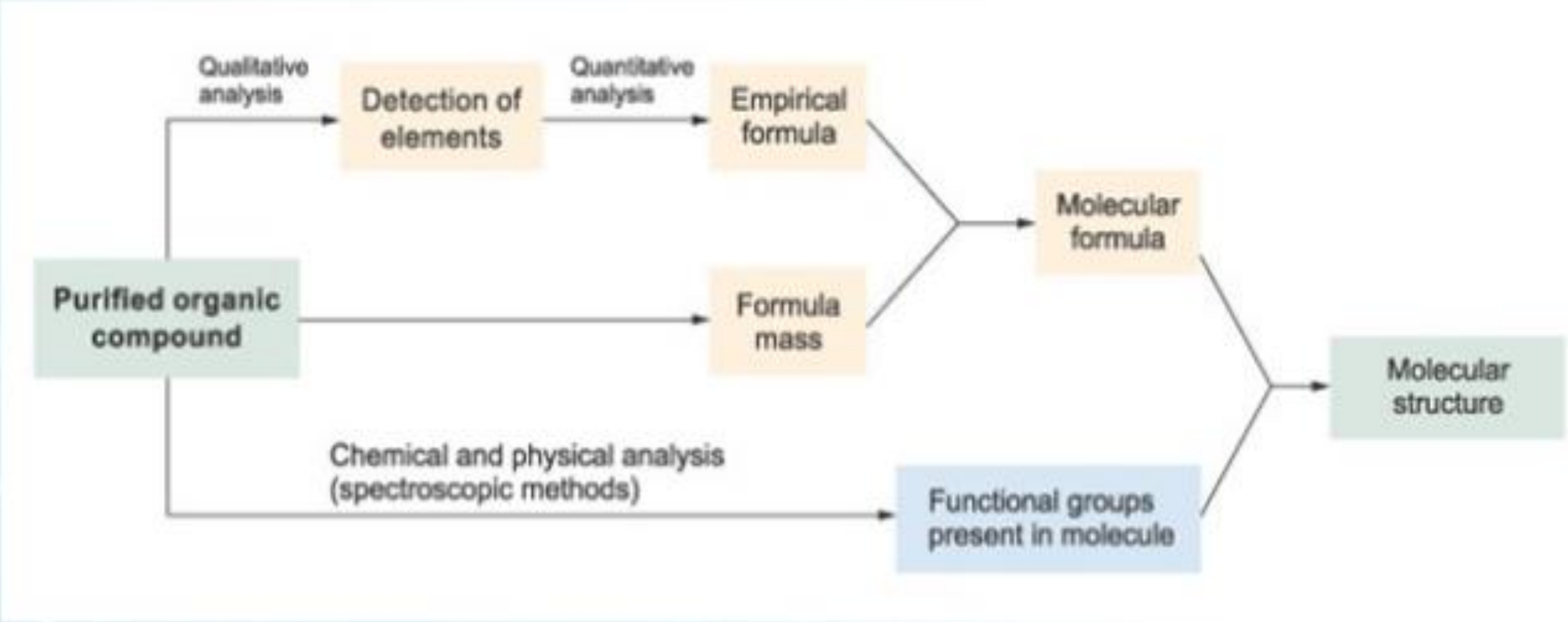


Identification of organic compounds

Introduction

- The determination of the structure of an organic compound involves:
  1. Isolation and purification of the compound
  2. Qualitative analysis of the elements present in the compound
  3. Determination of the molecular formula of the compound
  4. Determination of the functional group present in the compound

Introduction



The general steps to determine the structure of an organic compound

Isolation and Purification of Organic Compounds

- These techniques include:

1. Filtration
2. Centrifugation
3. Crystallization
4. Solvent extraction
5. Distillation

5. Fractional distillation
6. Sublimation
7. Chromatography

Isolation and Purification of Organic Compounds

- The selection of a proper technique

  ➔ depends on the particular differences in physical properties of the substances present in the mixture

A summary of different techniques of isolation and purification

Technique	Aim
(a) Filtration	To separate an insoluble solid from a liquid (slow)
(b) Centrifugation	To separate an insoluble solid from a liquid (fast)
(c) Crystallization	To separate a dissolved solute from its solution
(d) Solvent extraction	To separate a component from a mixture with a suitable solvent
(e) Distillation	To separate a liquid from a solution containing non-volatile solutes

A summary of different techniques of isolation and purification

Technique	Aim
(f) Fractional distillation	To separate miscible liquids with widely different boiling points
(g) Sublimation	To separate a mixture of solids in which only one can sublime
(h) Chromatography	To separate a complex mixture of substances

Tests for Purity

- If the substance is a solid,

  ➔ its purity can be checked by determining its melting point

- If it is a liquid,

  ➔ its purity can be checked by determining its boiling point

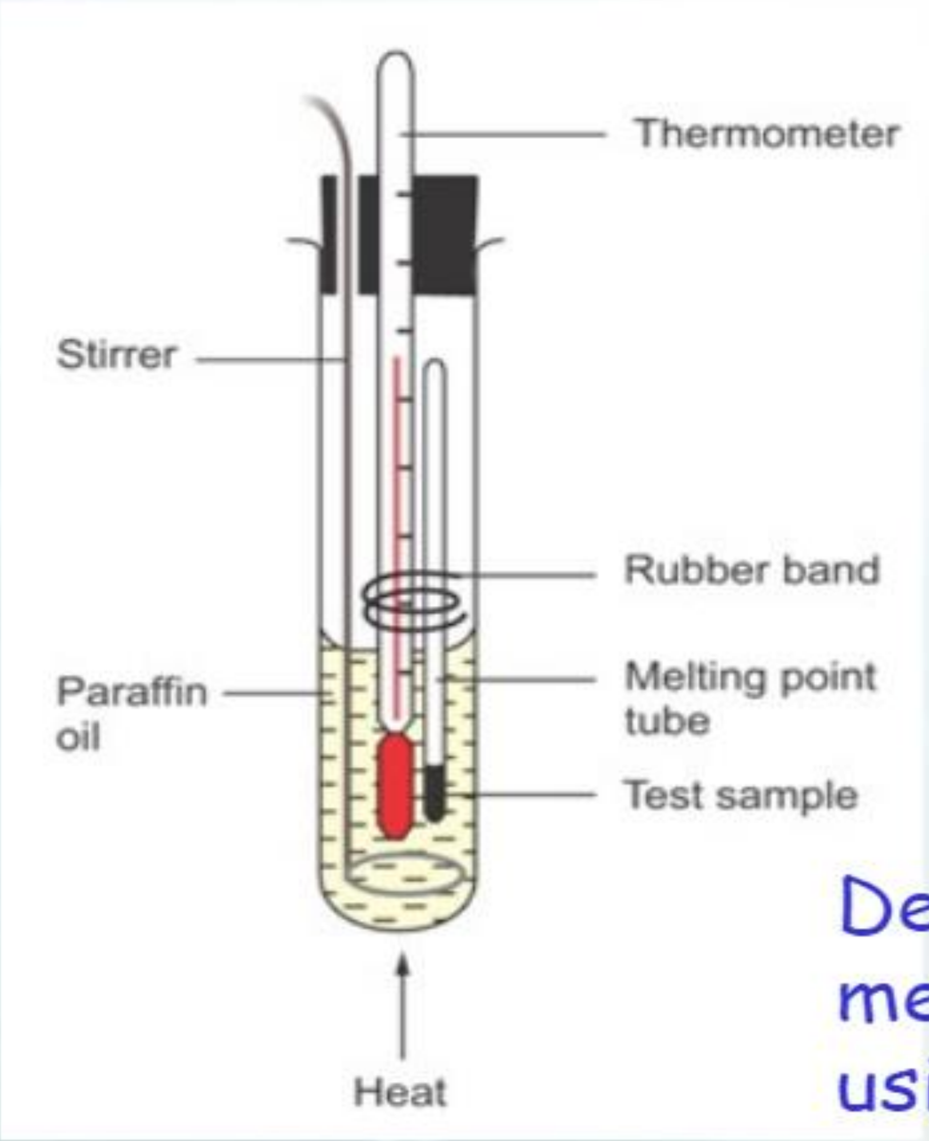
Determination of Melting Point

- To determine the melting point of a solid,

  ➔ some of the dry solid is placed in a thin-walled glass melting point tube

- The tube is attached to a thermometer

Determination of Melting Point



Determination of the melting point of a solid using an oil bath

Determination of Melting Point

- A pure solid has a sharp melting point
  - ➔ melting occurs within a narrow temperature range (usually less than 0.5°C)
- An impure solid does not have a sharp melting point
  - ➔ melts gradually over a wide temperature range

Determination of Melting Point

- The presence of impurities lowers the melting point of a solid
- Melting point is a useful indication of the purity of a substance

Determination of Boiling Point

- The boiling point of a liquid can be determined by using the distillation apparatus
- The temperature at which the liquid boils steadily is its boiling point
- A flammable liquid should be heated in a water bath, instead of heated with a naked flame

Determination of Boiling Point

- The boiling point of a pure liquid is quite sharp
- The presence of non-volatile solutes such as salts raises the boiling point of a liquid

Qualitative Analysis of an Organic Compound

- Qualitative analysis of an organic compound is

  ➔ to determine what elements are present in the compound

Determination of Empirical Formula and Molecular Formula from Analytical Data

Quantitative Analysis of an Organic Compound

- After determining the constituent elements of a particular organic compound

➔ perform quantitative analysis to find the percentage composition by mass of the compound

➔ the masses of different elements in an organic compound are determined

Quantitative Analysis of an Organic Compound

- After determining the percentage composition by mass of a compound,

  ➔ the empirical formula of the compound can be calculated

Quantitative Analysis of an Organic Compound

The empirical formula of a compound is the formula which shows the simplest whole number ratio of the atoms present in the compound

Quantitative Analysis of an Organic Compound

- When the relative molecular mass and the empirical formula of the compound are known,

  ➔ the molecular formula of the compound can be calculated

Quantitative Analysis of an Organic Compound

The molecular formula of a compound is the formula which shows the actual number of each kind of atoms present in a molecule of the compound

Structural Information from Physical Properties

- The physical properties of a compound include its colour, odour, density, solubility, melting point and boiling point
- The physical properties of a compound depend on its molecular structure

Structural Information from Physical Properties

- From the physical properties of a compound,

  ➔ obtain preliminary information about the structure of the compound

Structural Information from Physical Properties

- e.g.

  ➔ Hydrocarbons have low densities, often about 0.8 g cm^{-3}

  ➔ Compounds with functional groups have higher densities

Structural Information from Physical Properties

- The densities of most organic compounds are $< 1.2\ \text{g cm}^{-3}$
- Compounds having densities $> 1.2\ \text{g cm}^{-3}$ must contain multiple halogen atoms

Physical properties of some common organic compounds

Organic compound	Density at 20°C	Melting point and boiling point	Solubility	
			In water or highly polar solvents	In non-polar organic solvents
Hydrocarbons (saturated and unsaturated)	All have densities < 0.8 g cm^{-3}	• Generally low but increases with number of carbon atoms in the molecule • Branched-chain hydrocarbons have lower boiling points but higher melting points than the corresponding straight-chain isomers	Insoluble	Soluble

Physical properties of some common organic compounds

Organic compound	Density at 20°C	Melting point and boiling point	Solubility	
			In water or highly polar solvents	In non-polar organic solvents
Aromatic hydrocarbons	Between 0.8 and 1.0 g cm^{-3}	Generally low	Insoluble	Soluble

Physical properties of some common organic compounds

Organic compound	Density at 20°C	Melting point and boiling point	Solubility	
			In water or highly polar solvents	In non-polar organic solvents
Halo-alkanes	• 0.9 - 1.1 g cm^{-3} for chloro-alkanes • >1.0 g cm^{-3} for bromo-alkanes and iodo-alkanes	• Higher than alkanes of similar relative molecular masses (∵ haloalkane molecules are polar) • All haloalkanes are liquids except halomethanes • Both the m.p. and b.p. increase in the order: $RCH_2F < RCH_2Cl < RCH_2Br < RCH_2I$	Insoluble	Soluble

Physical properties of some common organic compounds

Organic compound	Density at 20°C	Melting point and boiling point	Solubility	
			In water or highly polar solvents	In non-polar organic solvents
Alcohols	• Simple alcohols are liquids and alcohols with > 12 carbons are waxy solids	• Much higher than hydrocarbons of similar relative molecular masses (∵ formation of hydrogen bonds between alcohol molecules)	• Lower members: Completely miscible with water (∵ formation of hydrogen bonds between alcohol molecules and water molecules)	Soluble

Physical properties of some common organic compounds

Organic compound	Density at 20°C	Melting point and boiling point	Solubility	
			In water or highly polar solvents	In non-polar organic solvents
Alcohols	• All simple alcohols have densities < 1.0 g cm^{-3}	• Straight-chain alcohols have higher b.p. than the corresponding branched-chain alcohols	• Solubility decreases gradually as the hydrocarbon chain lengthens	Soluble

Physical properties of some common organic compounds

Organic compound	Density at 20°C	Melting point and boiling point	Solubility	
			In water or highly polar solvents	In non-polar organic solvents
Carbonyl compounds (aldehydes and ketones)	• <1.0 g cm^{-3} for aliphatic carbonyl compounds	Higher than alkanes but lower than alcohols of similar relative molecular masses (Molecules of aldehydes or ketones are held together by strong dipole-dipole interactions but not hydrogen bonds)	• Lower members: Soluble in water (∵ the formation of hydrogen bonds between molecules of aldehydes or ketones and water molecules)	Soluble

Physical properties of some common organic compounds

Organic compound	Density at 20°C	Melting point and boiling point	Solubility	
			In water or highly polar solvents	In non-polar organic solvents
Carbonyl compounds (aldehydes and ketones)	• > 1.0 g cm^{-3} for aromatic carbonyl compounds		• Solubility decreases gradually as the hydrocarbon chain lengthens	Soluble

Physical properties of some common organic compounds

Organic compound	Density at 20°C	Melting point and boiling point	Solubility	
			In water or highly polar solvents	In non-polar organic solvents
Carboxylic acids	• Lower members have densities similar to water • Methanoic acid has a density of 1.22 g cm^{-3}	Higher than alcohols of similar relative molecular masses (∵ the formation of more extensive intermolecular hydrogen bonds)	• First four members are miscible with water in all proportions • Solubility decreases gradually as the hydrocarbon chain lengthens	Soluble

Physical properties of some common organic compounds

Organic compound	Density at 20°C	Melting point and boiling point	Solubility	
			In water or highly polar solvents	In non-polar organic solvents
Esters	Lower members have densities less than water	Slightly higher than hydrocarbons but lower than carbonyl compounds and alcohols of similar relative molecular masses	Insoluble	Soluble

Physical properties of some common organic compounds

Organic compound	Density at 20°C	Melting point and boiling point	Solubility	
			In water or highly polar solvents	In non-polar organic solvents
Amines	Most amines have densities less than water	• Higher than alkanes but lower than alcohols of similar relative molecular masses	• Generally soluble • Solubility decreases in the order: 1° amines > 2° amines > 3° amines	Soluble

Physical properties of some common organic compounds

Organic comp-ound	Density at 20°C	Melting point and boiling point	Solubility	
			In water or highly polar solvents	In non-polar organic solvents
Amines		• 1° and 2° amines are able to form hydrogen bonds with each other but the strength is less than that between alcohol molecules (N—H bond is less polar than O — H bond)		

Physical properties of some common organic compounds

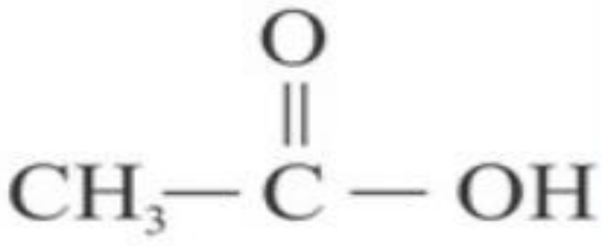
Organic compound	Density at 20°C	Melting point and boiling point	Solubility	
			In water or highly polar solvents	In non-polar organic solvents
Amines		• 3° amines have lower m.p. and b.p. than the isomers of 1° and 2° amines (∵ molecules of 3° amines cannot form intermolecular hydrogen bonds)		

Structural Information from Chemical Properties

- The molecular formula of a compound
  - ➔ does not give enough clue to the structure of the compound
- Compounds having the same molecular formula
  - ➔ may have different arrangements of atoms and even different functional groups

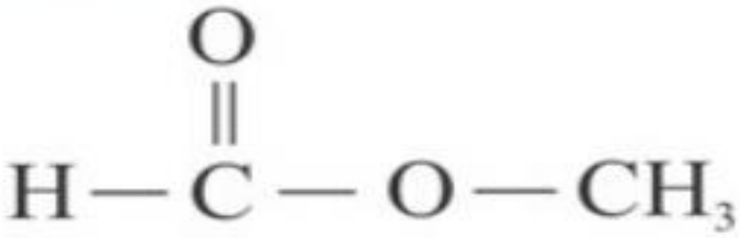
Structural Information from Chemical Properties

- e.g.
  The molecular formula of $C_2H_4O_2$ may represent a carboxylic acid or an ester:



$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-OH$$

Ethanoic acid



$$H-\overset{\overset{\displaystyle O}{\|}}{C}-O-CH_3$$

Methyl methanoate

Structural Information from Chemical Properties

- The next stage is

  ➔ to find out the functional group(s) present

  ➔ to deduce the actual arrangement of atoms in the molecule

Chemical tests for different groups of organic compounds

Organic compound	Test	Observation
Saturated hydrocarbons	• Burn the saturated hydrocarbon in a non-luminous Bunsen flame	• A blue or clear yellow flame is observed

Chemical tests for different groups of organic compounds

Organic compound	Test	Observation
Unsaturated hydrocarbons ($C = C$, $C \equiv C$)	• Burn the unsaturated hydrocarbon in a non-luminous Bunsen flame	• A smoky flame is observed
	• Add bromine in 1,1,1-trichloroethane at room temperature and in the absence of light	• Bromine decolourizes rapidly
	• Add 1% (dilute) acidified potassium manganate(VII) solution	• Potassium manganate(VII) solution decolourizes rapidly

Chemical tests for different groups of organic compounds

Organic compound	Test	Observation
Haloalkanes (1°, 2° or 3°)	• Boil with ethanolic potassium hydroxide solution, then acidify with excess dilute nitric(V) acid and add silver nitrate(V) solution	• For chloroalkanes, a white precipitate is formed • For bromoalkanes, a pale yellow precipitate is formed • For iodoalkanes, a creamy yellow precipitate is formed

Chemical tests for different groups of organic compounds

Organic compound	Test	Observation
Halobenzenes	• Boil with ethanolic potassium hydroxide solution, then acidify with excess dilute nitric(V) acid and add silver nitrate(V) solution	• No precipitate is formed

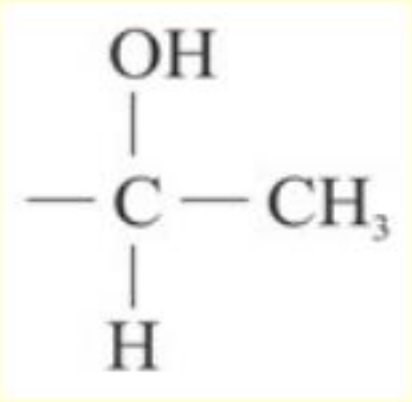
Chemical tests for different groups of organic compounds

Organic compound	Test	Observation
Alcohols (— OH)	• Add a small piece of sodium metal	• A colourless gas is evolved
	• Esterification: Add ethanoyl chloride	• The temperature of the reaction mixture rises • A colourless gas is evolved

Chemical tests for different groups of organic compounds

Organic compound	Test	Observation
Alcohols (— OH)	• Add acidified potassium dichromate(VI) solution	• For 1° and 2° alcohols, the clear orange solution becomes opaque and turns green almost immediately • For 3° alcohols, there are no observable changes

Chemical tests for different groups of organic compounds

Organic compound	Test	Observation
Alcohols (— OH)	• Iodoform test for:  $-\overset{\displaystyle OH}{\underset{\displaystyle H}{C}}-CH_3$ Add iodine in sodium hydroxide solution	• A yellow precipitate is formed

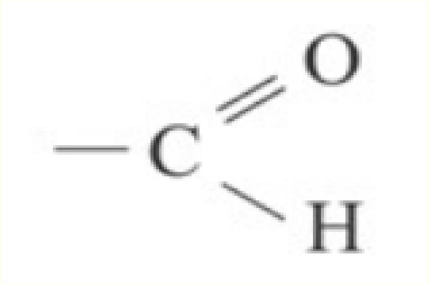
Chemical tests for different groups of organic compounds

Organic compound	Test	Observation
Alcohols (— OH)	• Lucas test: add a solution of zinc chloride in concentrated hydrochloric acid	• For 1° alcohols, the aqueous phase remains clear • For 2° alcohols, the clear solution becomes cloudy within 5 minutes • For 3° alcohols, the aqueous phase appears cloudy immediately

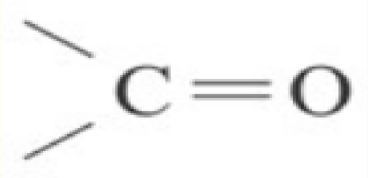
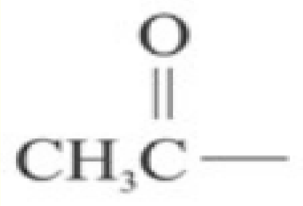
Chemical tests for different groups of organic compounds

Organic compound	Test	Observation
Ethers (— O —)	• No specific test for ethers but they are soluble in concentrated sulphuric(VI) acid	—

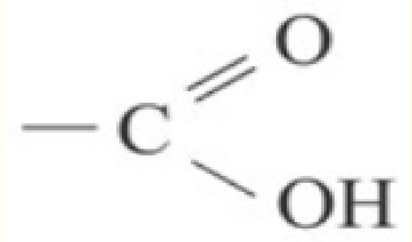
Chemical tests for different groups of organic compounds

Organic compound	Test	Observation
Aldehydes ()	• Add aqueous sodium hydrogensulphate(IV)	• Crystalline salts are formed
	• Add 2,4-dinitrophenylhydrazine	• A yellow, orange or red precipitate is formed
	• Silver mirror test: add Tollens' reagent (a solution of aqueous silver nitrate in aqueous ammonia)	• A silver mirror is deposited on the inner wall of the test tube

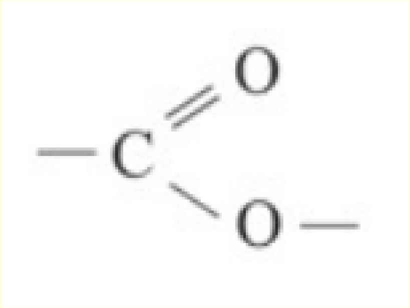
Chemical tests for different groups of organic compounds

Organic compound	Test	Observation
Ketones ()	• Add aqueous sodium hydrogensulphate(IV)	• Crystalline salts are formed (for unhindered ketones only)
	• Add 2,4-dinitrophenylhydrazine	• A yellow, orange or red precipitate is formed
	• Iodoform test for:  $CH_3\overset{\overset{O}{\|}}{C}-$ Add iodine in sodium hydroxide solution	• A yellow precipitate is formed

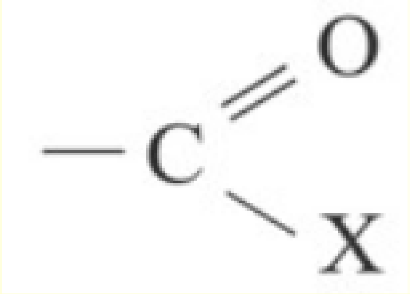
Chemical tests for different groups of organic compounds

Organic compound	Test	Observation
Carboxylic acids ()	- Esterification: warm the carboxylic acid with an alcohol in the presence of concentrated sulphuric(VI) acid, followed by adding sodium carbonate solution	- A sweet and fruity smell is detected
	- Add sodium hydrogencarbonate	- The colourless gas produced turns lime water milky

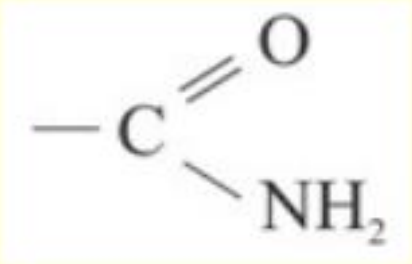
Chemical tests for different groups of organic compounds

Organic compound	Test	Observation
Esters ()	• No specific test for esters but they can be distinguished by its characteristic smell	• A sweet and fruity smell is detected

Chemical tests for different groups of organic compounds

Organic compound	Test	Observation
Acyl halides ()	• Boil with ethanolic potassium hydroxide solution, then acidify with excess dilute nitric(V) acid and add silver nitrate(V) solution	• For acyl chlorides, a white precipitate is formed • For acyl bromides, a pale yellow precipitate is formed • For acyl iodides, a creamy yellow precipitate is formed

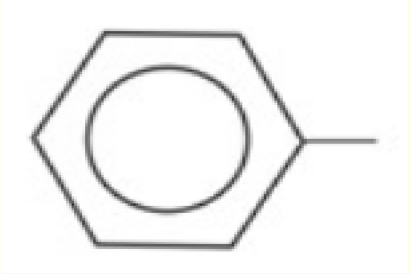
Chemical tests for different groups of organic compounds

Organic compound	Test	Observation
Amides ()	• Boil with sodium hydroxide solution	• The colourless gas produced turns moist red litmus paper or pH paper blue

Chemical tests for different groups of organic compounds

Organic compound	Test	Observation
Amines (—NH_2)	• 1° aliphatic amines: dissolve the amine in dilute hydrochloric acid at 0 – 5 °C, then add cold sodium nitrate(III) solution slowly	• Steady evolution of $N_2(g)$ is observed
	• 1° aromatic amines: add naphthalen-2-ol in dilute sodium hydroxide solution	• An orange or red precipitate is formed

Chemical tests for different groups of organic compounds

Organic compound	Test	Observation
Aromatic compounds ()	• Burn the aromatic compound in a non-luminous Bunsen flame	• A smoky yellow flame with black soot is produced
	• Add fuming sulphuric(VI) acid	• The aromatic compound dissolves • The temperature of the reaction mixture rises

Use of Infra-red Spectrocopy in the Identification of Functional Groups

The Electromagnetic Spectrum

- Electromagnetic radiation has dual property
  - ➔ i.e. the properties of both wave and particle
- Can be described as a wave occurring simultaneously in electrical and magnetic fields
- Can also be described as consisting of particles called quanta or photons

The Electromagnetic Spectrum

- All electromagnetic radiation travels through vacuum at the same velocity, 3×10^8 m s^{-1}
- The relationship between the frequency (ν) of an electromagnetic radiation, its wavelength (λ) and velocity (c) is:

$$\boxed{\nu = \frac{c}{\lambda}}$$

The Electromagnetic Spectrum

- The energy of a quantum of electromagnetic radiation is directly related to its frequency:

$$E = h\nu$$

where *h* is the Planck constant (i.e. 6.626×10^{-34} J s).

The Electromagnetic Spectrum

- $\because \nu = \frac{c}{\lambda}$

➔ the energy of a quantum of electromagnetic radiation is inversely proportional to its wavelength:

$$\boxed{E = \frac{hc}{\lambda}}$$

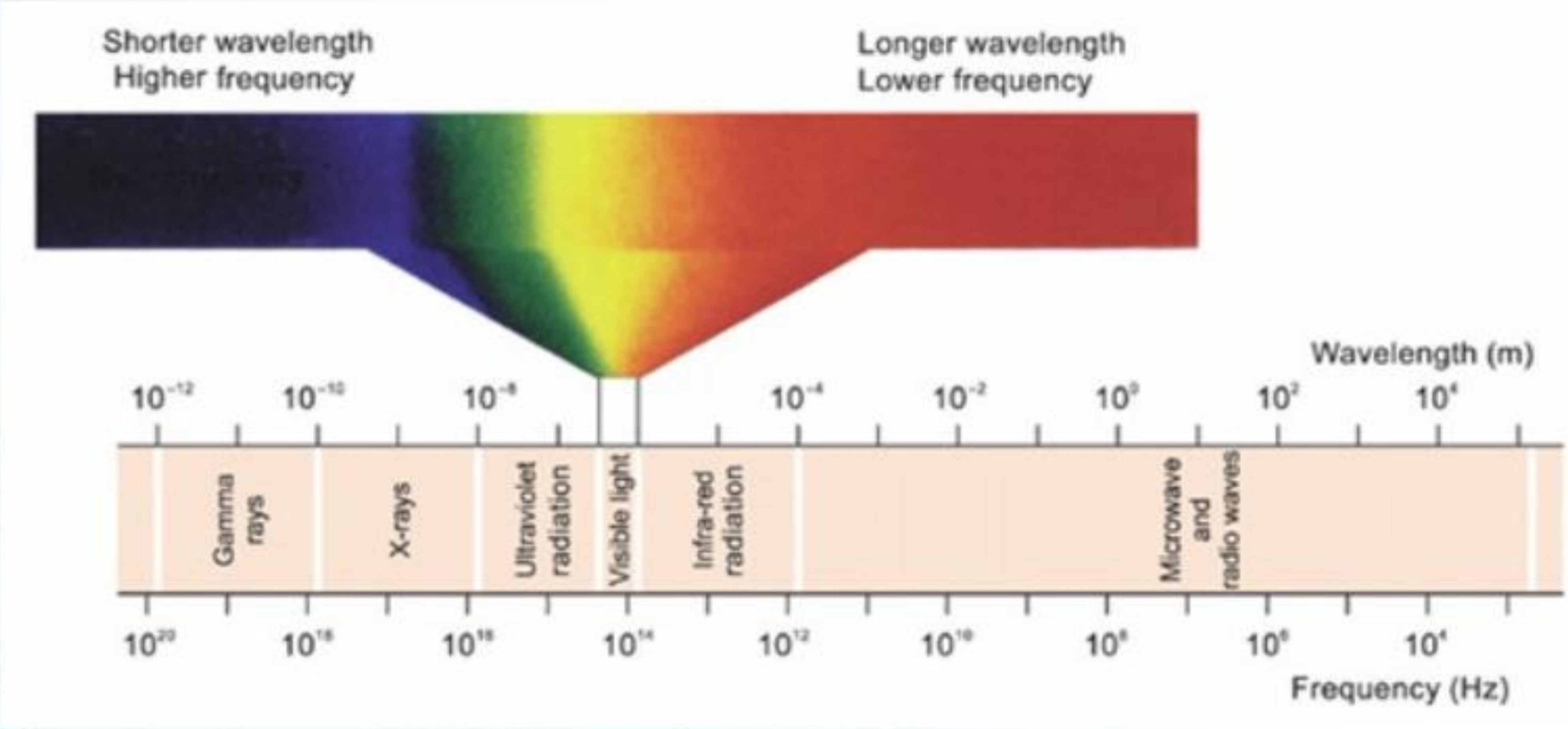
The Electromagnetic Spectrum

- Electromagnetic radiation of long wavelength has low energy
- Electromagnetic radiation of short wavelength has high energy

The Electromagnetic Spectrum

- Electromagnetic radiation of long wavelength has low energy
- Electromagnetic radiation of short wavelength has high energy

The Electromagnetic Spectrum



Regions of the electromagnetic spectrum

The Electromagnetic Spectrum

- When electromagnetic radiation falls onto a hydrogen atom,

  ➔ the electron in the hydrogen atom will absorb a definite amount of energy

- The electron is excited from the ground state to a higher energy level

The Electromagnetic Spectrum

- ∵ The electron is unstable at a higher energy level

  ➔ it will fall back to a lower energy level

- Excess energy is given out in the form of electromagnetic radiation

The Electromagnetic Spectrum

- The radiation emitted has the frequency as shown by the following relationship:

$$\Delta E = E_2 - E_1 = h\nu = \frac{hc}{\lambda}$$

The Electromagnetic Spectrum

- The atomic spectrum of hydrogen is originated from

  ➔ electron transitions between energy levels in a hydrogen atom

The Electromagnetic Spectrum

- In the case of molecules, the absorption of energy can
  - ➔ cause the excitation of electrons
  - ➔ increase the extent of vibration of the bonds and the speed of rotation of the molecule
- This is the basis of infra-red spectroscopy

Infra-red Spectroscopy

- Organic compounds absorb electromagnetic radiation in the IR region of the spectrum

➔ IR radiation does not have sufficient energy to cause the excitation of electrons

Infra-red Spectroscopy

- IR radiation causes

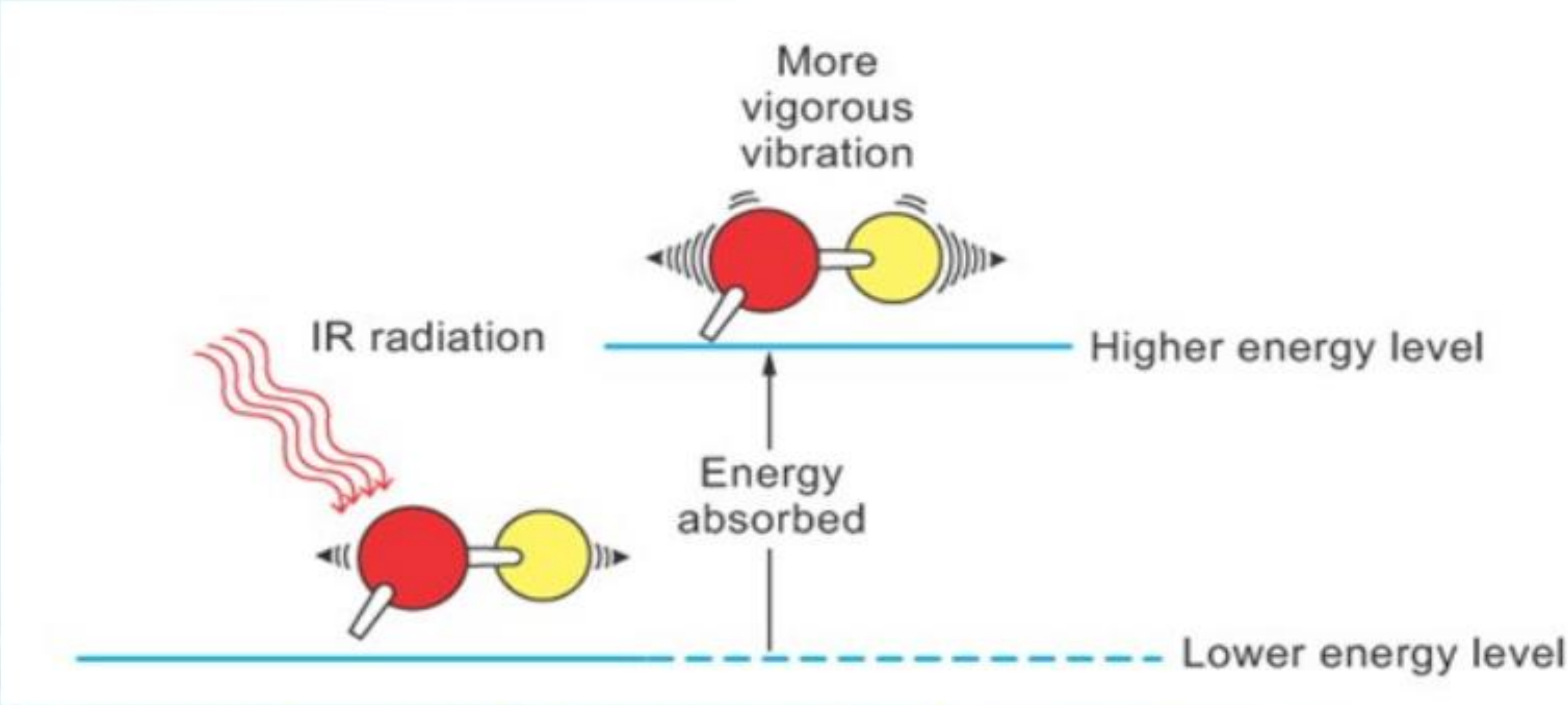
  ➔ atoms and groups of atoms of organic compounds to vibrate with increased amplitude about the covalent bonds that connect them

Infra-red Spectroscopy

- These vibrations are quantized

  ➔ the compounds absorb IR radiation of a particular amount of energy only

Infra-red Spectroscopy



Effect of absorption of IR radiation on vibration of atoms in a molecule

Infra-red Spectroscopy

- Infra-red spectrometer is used to

  ➔ measure the amount of energy absorbed at each wavelength of the IR region

An infra-red spectrometer

Infra-red Spectroscopy

- A beam of IR radiation is passed through the sample

  ➔ the intensity of the emergent radiation is carefully measured

- The spectrometer plots the results as a graph called infra-red spectrum

  ➔ shows the absorption of IR radiation by a sample at different frequencies

Infra-red Spectroscopy

- The IR radiation is usually specified by its wavenumber (unit: cm^{-1})

➔ the reciprocal of wavelength

- ∵ Frequency and wavelength are related by the equation $c = \nu\lambda$

➔ Wavenumber is a direct measure of frequency

Infra-red Spectroscopy

- The IR radiation is usually specified by its wavenumber (unit: cm^{-1})

➔ the reciprocal of wavelength

- ∵ Frequency and wavelength are related by the equation $c = \nu\lambda$

➔ Wavenumber is a direct measure of frequency

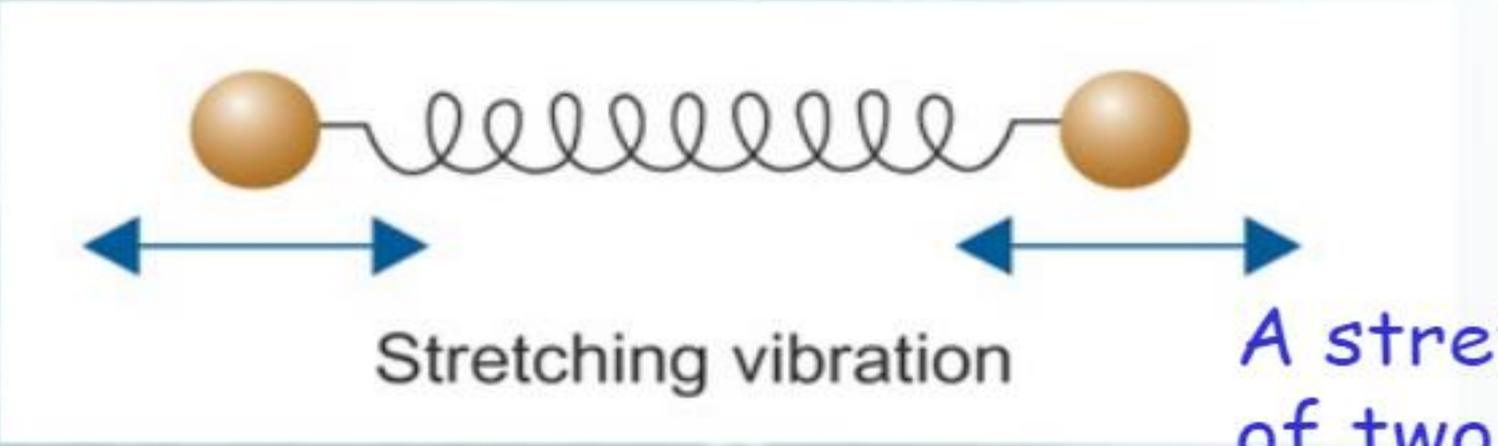
Infra-red Spectroscopy

- When the compound absorbs IR radiation of the exact energy required (or a particular wavelength or a particular frequency)

  ➔ the excitation of a molecule from one vibrational energy level to another occurs only

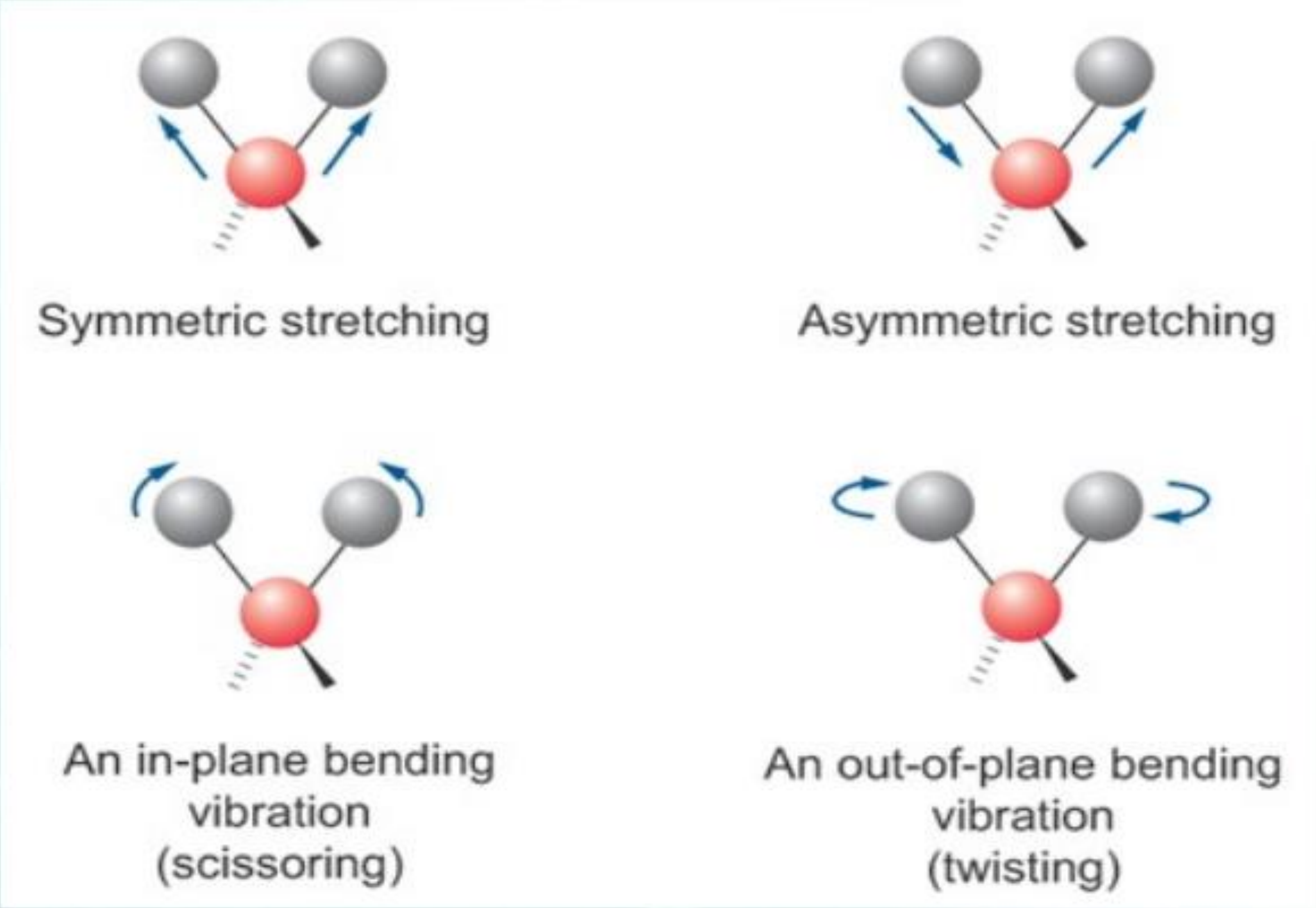
Infra-red Spectroscopy

- Molecules can vibrate in a variety of ways
- Two atoms joined by a covalent bond can undergo a stretching vibration where the atoms move back and forth as if they were joined by a spring



A stretching vibration of two atoms

Infra-red Spectroscopy



Symmetric stretching

Asymmetric stretching

An in-plane bending vibration (scissoring)

An out-of-plane bending vibration (twisting)

A variety of stretching and bending vibrations

Infra-red Spectroscopy

- The frequency of a given stretching vibration of a covalent bond

  ➔ depends on the masses of the bonded atoms and the strength of the bond

- Lighter atoms vibrate at higher frequencies than heavier ones

Infra-red Spectroscopy

Let's Think 3

- The stretching vibrations of single bonds involving hydrogen (C — H, O — H and N — H) occur at relatively high frequencies

Bond	Range of wavenumber (cm^{-1})
C — H	2840 – 3095
O — H	3230 – 3670
N — H	3350 – 3500

Characteristic absorption wavenumbers of some single bonds in infra-red spectra

Infra-red Spectroscopy

- Triple bonds are stronger and vibrate at higher frequencies than double bonds

Bond	Range of wavenumber (cm^{-1})
$C \equiv C$	2070 – 2250
$C \equiv N$	2200 – 2280
$C = C$	1610 – 1680
$C = O$	1680 – 1750

Characteristic absorption wavenumbers of some double bonds and triple bonds in infra-red spectra

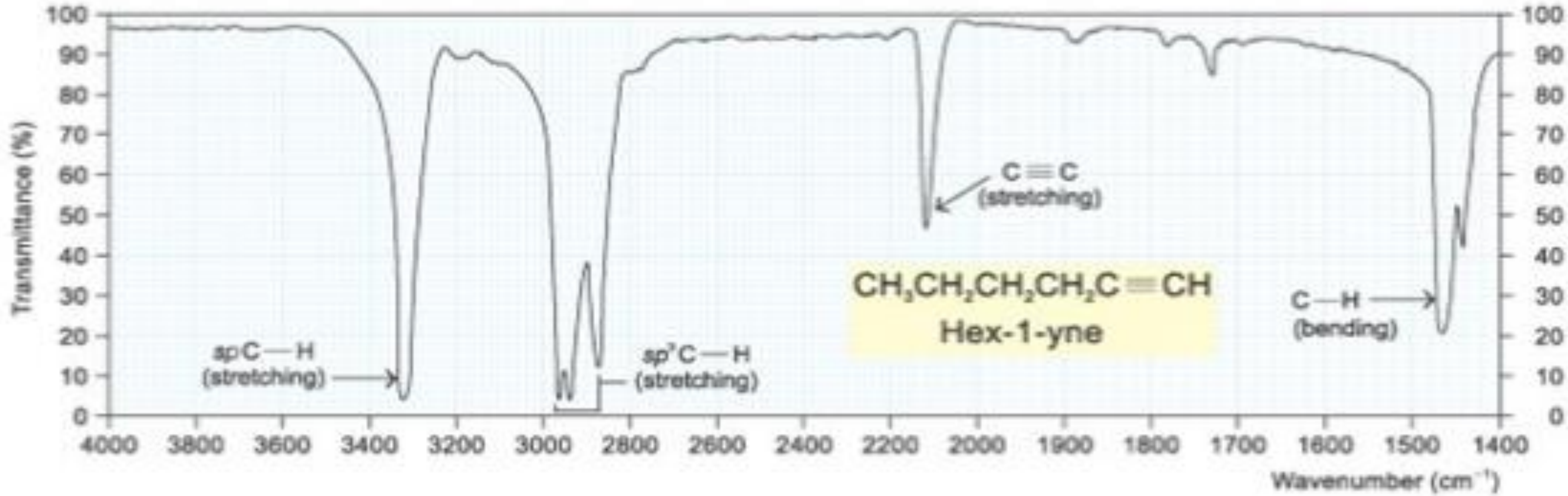
Infra-red Spectroscopy

- The IR spectra of even relatively simple compounds contain many absorption peaks
- The possibility of two different compounds having the same IR spectrum is very small
- An IR spectrum has been called the “fingerprint” of a compound

Use of IR Spectrum in the Identification of Functional Groups

- An IR spectrum is a plot of percentage of transmittance against wavenumber of IR radiation

Use of IR Spectrum in the Identification of Functional Groups



The IR spectrum of hex-1-yne

Use of IR Spectrum in the Identification of Functional Groups

- 100% transmittance in the spectrum

  ➔ implies no absorption of IR radiation

Use of IR Spectrum in the Identification of Functional Groups

- When a compound absorbs IR radiation,
  - ➔ the intensity of transmitted radiation decreases
  - ➔ results in a decrease in percentage of transmittance
  - ➔ a dip in the spectrum
  - ➔ often called an absorption peak or absorption band

Use of IR Spectrum in the Identification of Functional Groups

- In general, an IR spectrum can be split into four regions for interpretation purpose

The four regions of an IR spectrum

Range of wavenumber (cm^{-1})	Interpretation
400 – 1500	• Often consists of many complicated bands • Unique to each compound • Often called the fingerprint region • Not used for identification of particular functional groups
1500 – 2000	Absorption of double bonds, e.g. $C = C$, $C = O$
2000 – 2500	Absorption of triple bonds, e.g. $C \equiv C$, $C \equiv N$
2500 – 4000	Absorption of single bonds involving hydrogen, e.g. $C — H$, $O — H$, $N — H$

Use of IR Spectrum in the Identification of Functional Groups

- The region between 4 000 cm^{-1} and 1 500 cm^{-1} is often used for

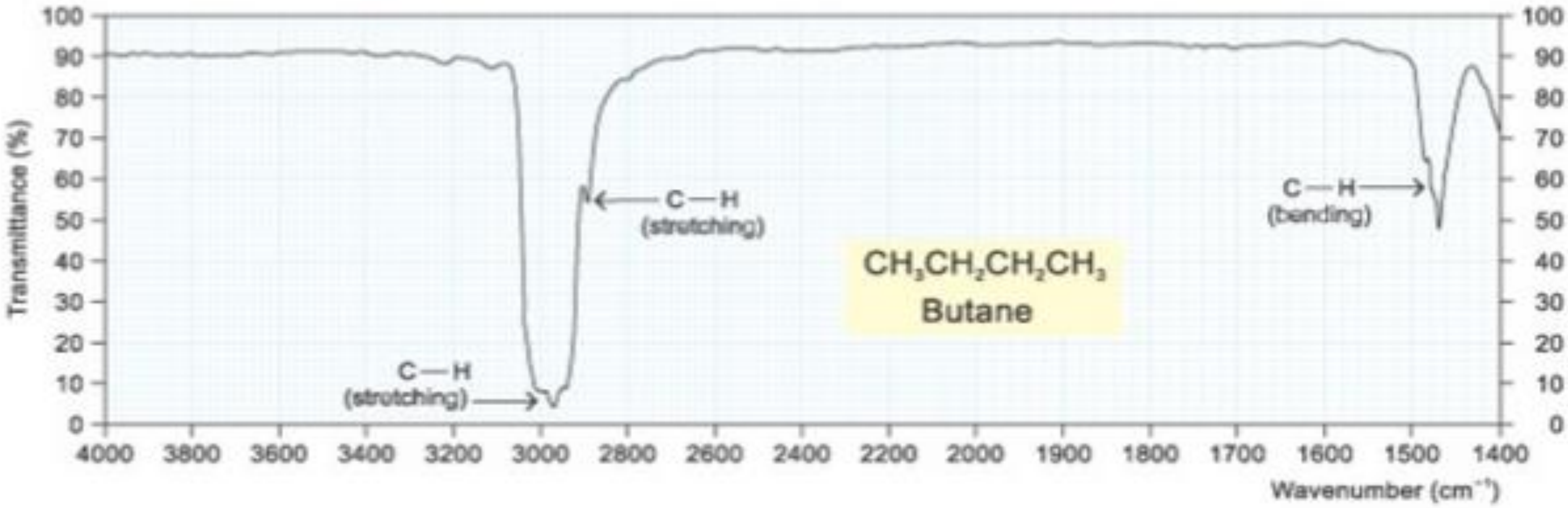
  ➔ identification of functional groups from their characteristic absorption wavenumbers

Characteristic range of wavenumbers of covalent bonds in IR spectra

Compound	Bond	Characteristic range of wavenumber (cm^{-1})
Alkenes	$C=C$	1610 – 1680
Aldehydes, ketones, acids, esters	$C=O$	1680 – 1750
Alkynes	$C\equiv C$	2070 – 2250
Nitriles	$C\equiv N$	2200 – 2280
Acids (hydrogen-bonded)	$O-H$	2500 – 3300
Alkanes, alkenes, arenes	$C-H$	2840 – 3095
Alcohols, phenols (hydrogen-bonded)	$O-H$	3230 – 3670
Primary amines	$N-H$	3350 – 3500

Interpretation of IR Spectra

1. Butane



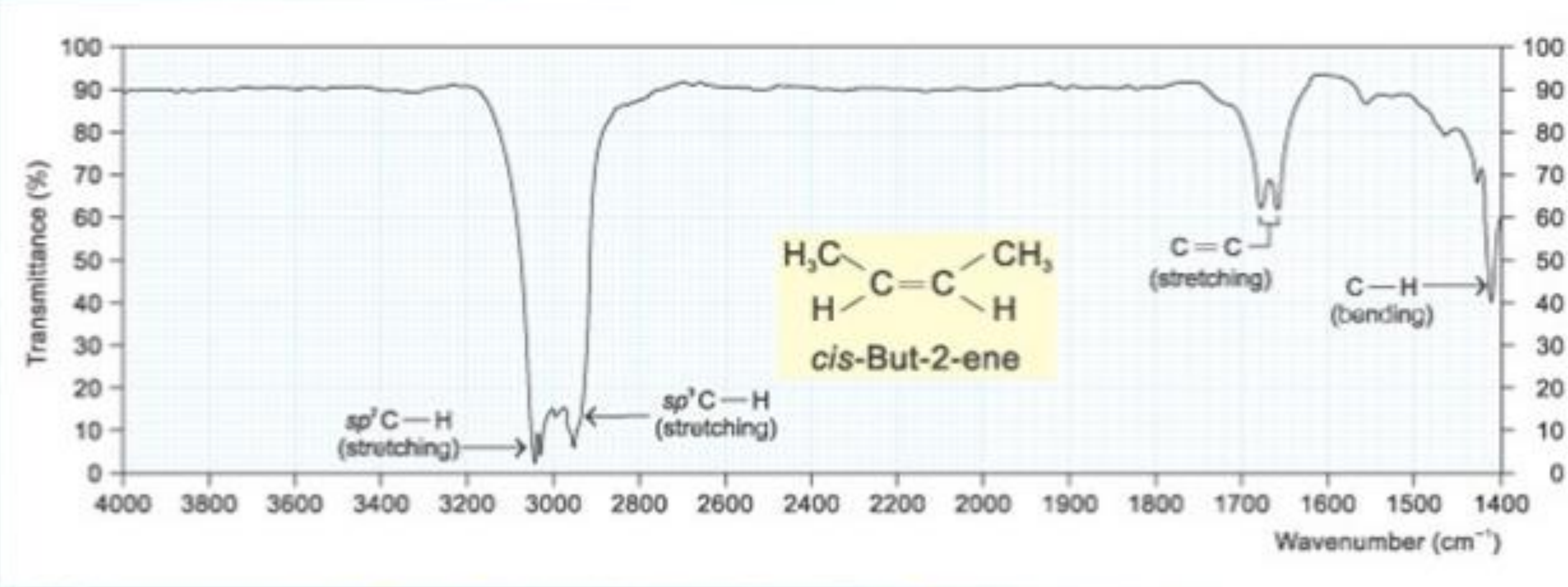
The IR spectrum of butane

1. Butane

Wavenumber (cm^{-1})	Intensity	Indication
2968	Very strong	C — H stretching
2890	Medium	
1468	Strong	C — H bending

Interpretation of the IR spectrum of butane

2. *cis*-But-2-ene



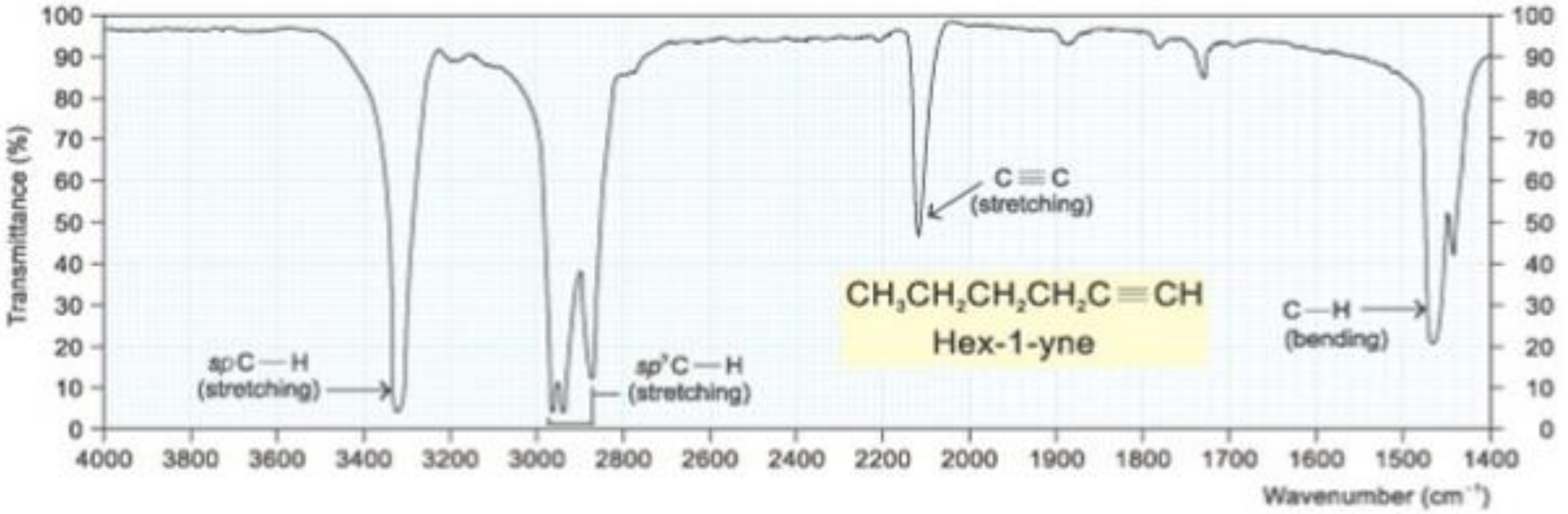
The IR spectrum of *cis*-but-2-ene

2. *cis*-But-2-ene

Wavenumber (cm $^{-1}$)	Intensity	Indication
3044	Very strong	C — H stretching (sp^2 C — H)
3028	Very strong	
2952	Very strong	C — H stretching (sp^3 C — H)
1677	Medium	C = C stretchinh
1657	Medium	
1411	Strong	C — H bending

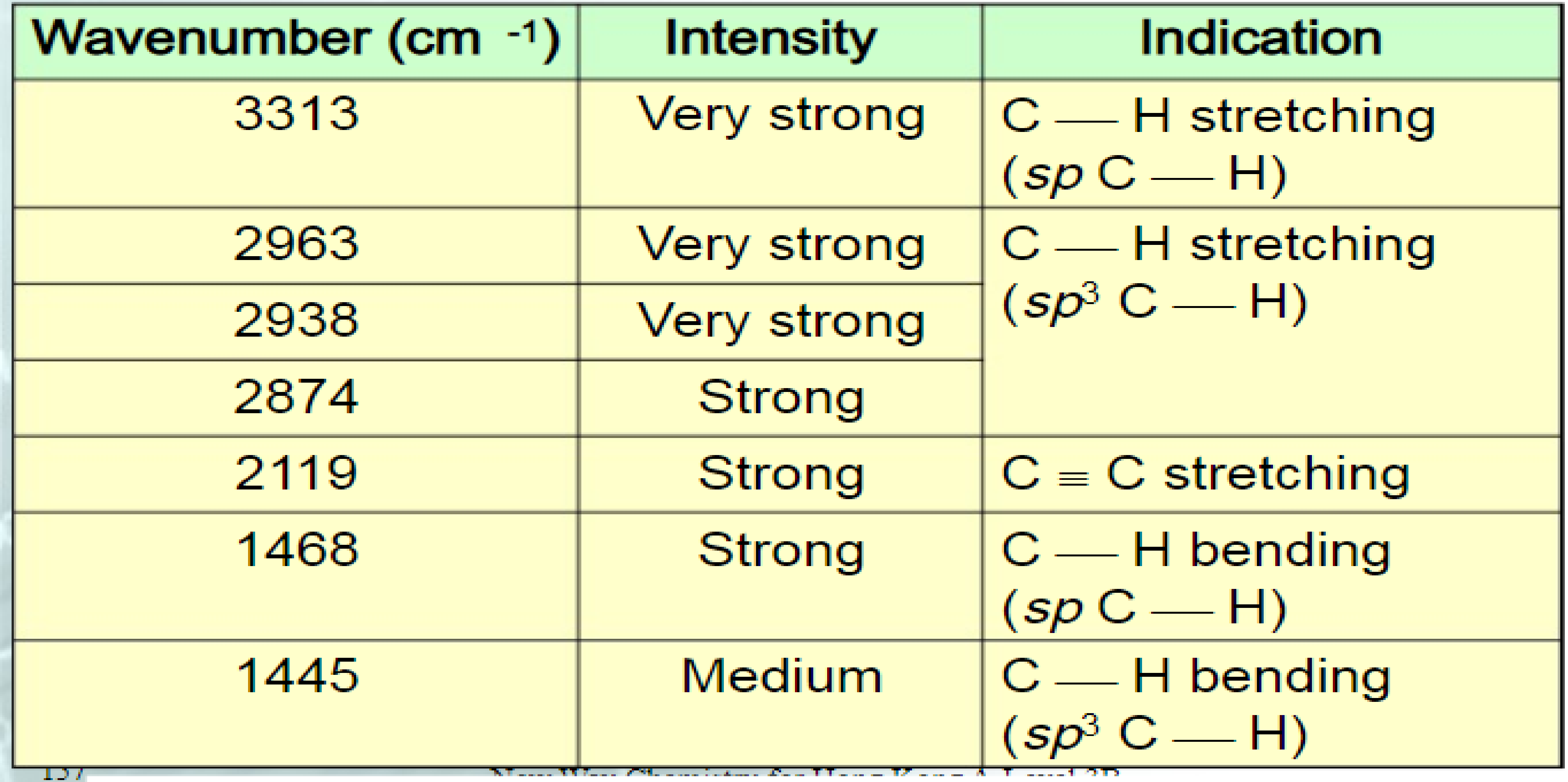
Interpretation of the IR spectrum of *cis*-but-2-ene

3. Hex-1-yne



The IR spectrum of hex-1-yne

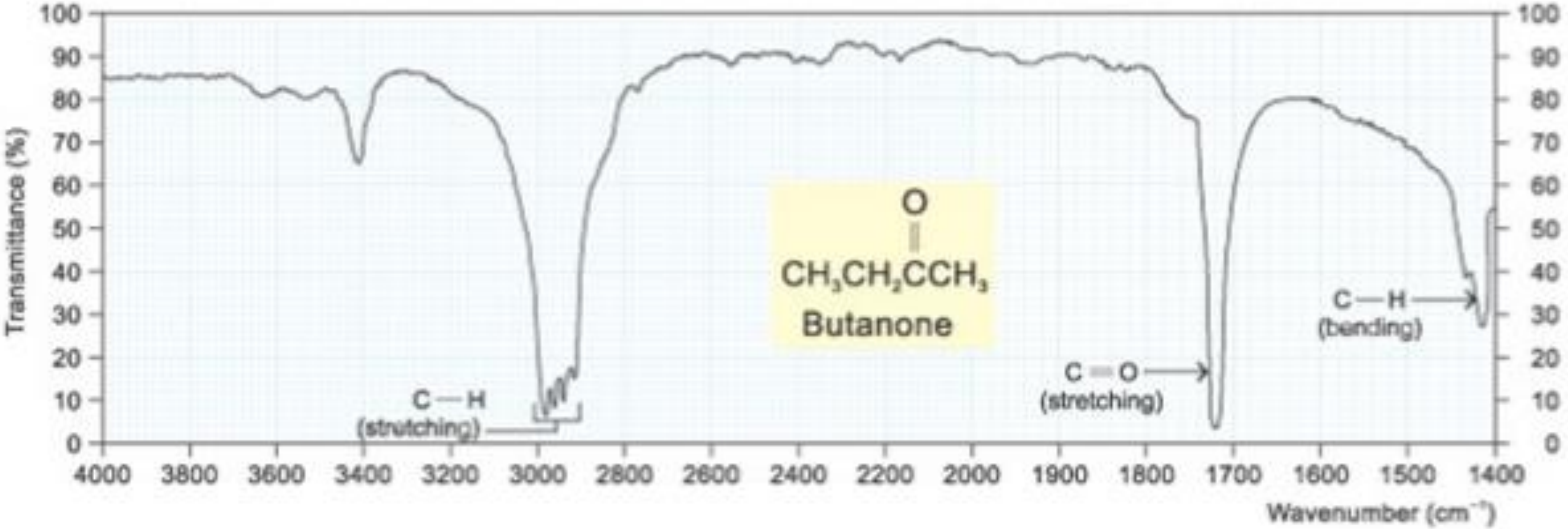
3. Hex-1-yne



Wavenumber (cm $^{-1}$)	Intensity	Indication
3313	Very strong	C — H stretching (*sp* C — H)
2963	Very strong	C — H stretching (sp^3 C — H)
2938	Very strong	
2874	Strong	
2119	Strong	C ≡ C stretching
1468	Strong	C — H bending (*sp* C — H)
1445	Medium	C — H bending (sp^3 C — H)

Interpretation of the IR spectrum of hex-1-yne

4. Butanone



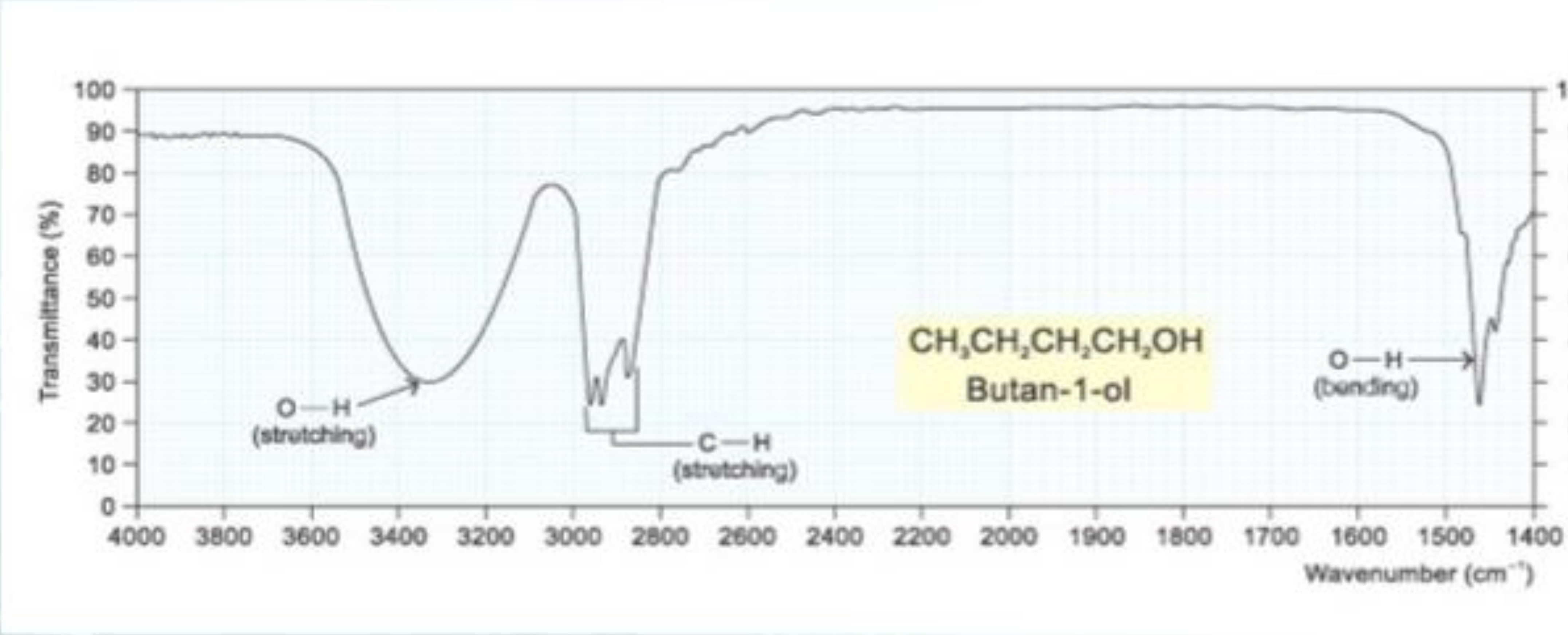
The IR spectrum of butanone

4. Butanone

Wavenumber (cm $^{-1}$)	Intensity	Indication
2983	Strong	C — H stretching
2925	Strong	
1720	Very strong	C = O stretching
1416	Medium	C — H bending (shifted as adjacent to C = O)

Interpretation of the IR spectrum of butanone

5. Butan-1-ol



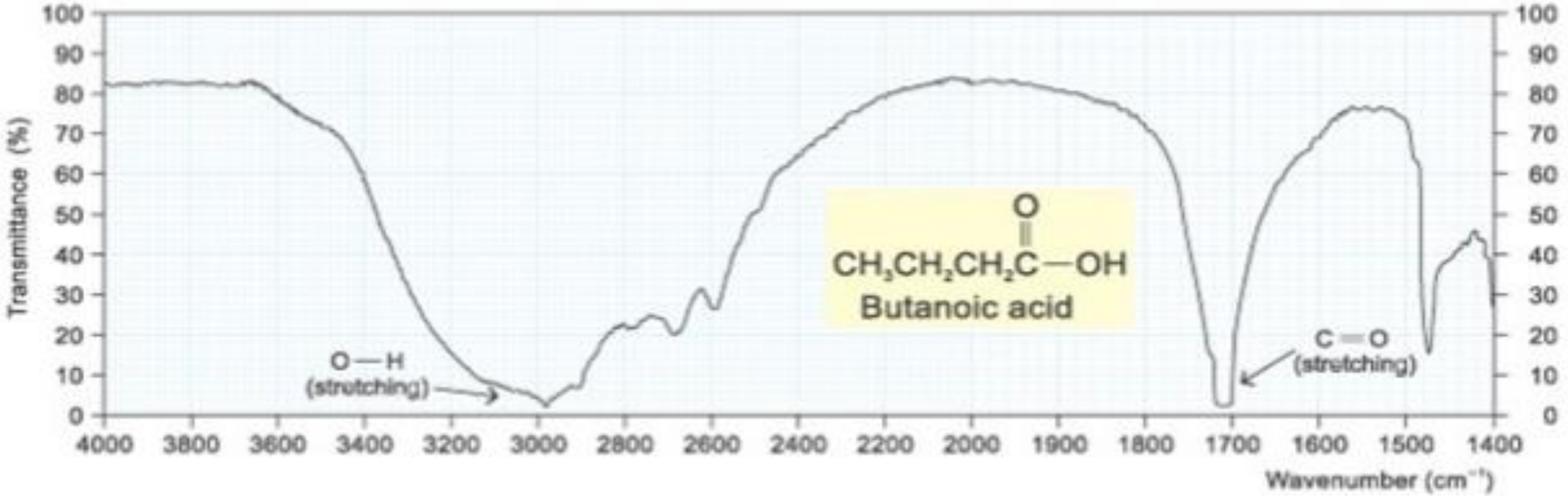
The IR spectrum of butan-1-ol

5. Butan-1-ol

Wavenumber (cm^{-1})	Intensity	Indication
3330	Broad band	O — H stretching
2960	Medium	C — H stretching
2935	Medium	
2875	Medium	

Interpretation of the IR spectrum of butan-1-ol

6. Butanoic Acid



The IR spectrum of butanoic acid

6. Butanoic Acid

Wavenumber (cm^{-1})	Intensity	Indication
3100	Broad band	O — H stretching
1708	Strong	C = O stretching

Interpretation of the IR spectrum of butanoic acid

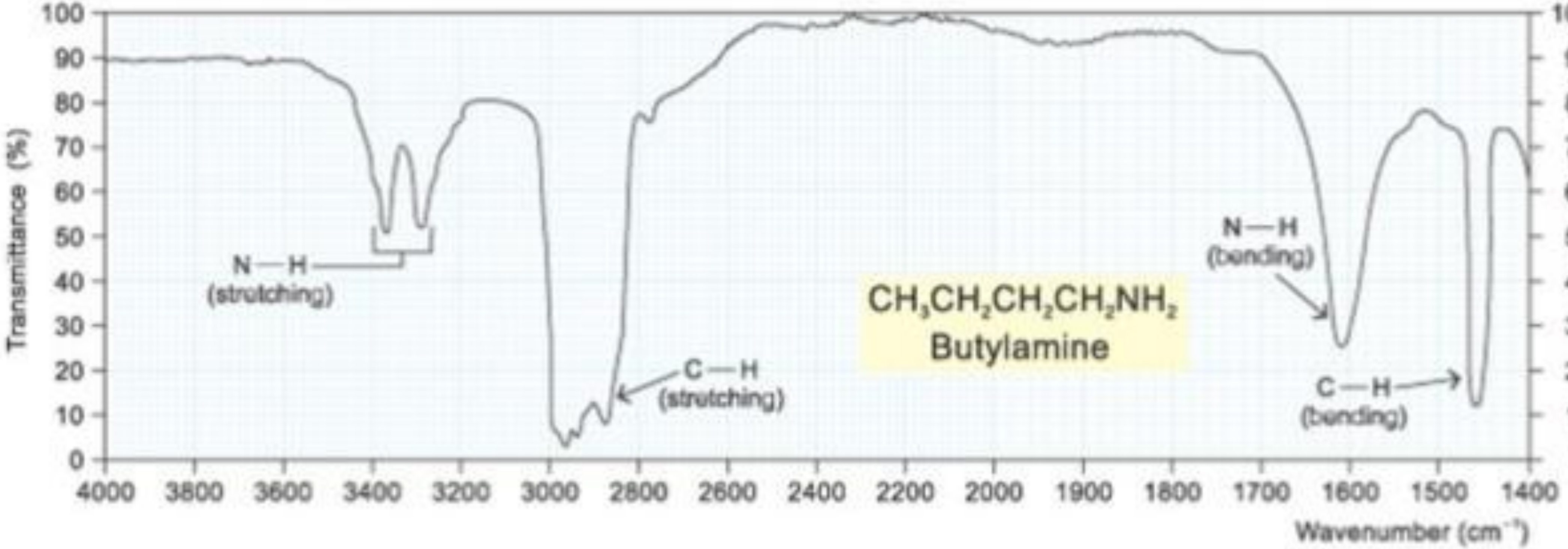
6. Butanoic Acid

- The absorption of the O — H group in alcohols and carboxylic acids does not usually appear as a sharp peak

➔ a broad band is observed

➔ the vibration of the O — H group is complicated by the hydrogen bonding formed between the molecules

7. Butylamine



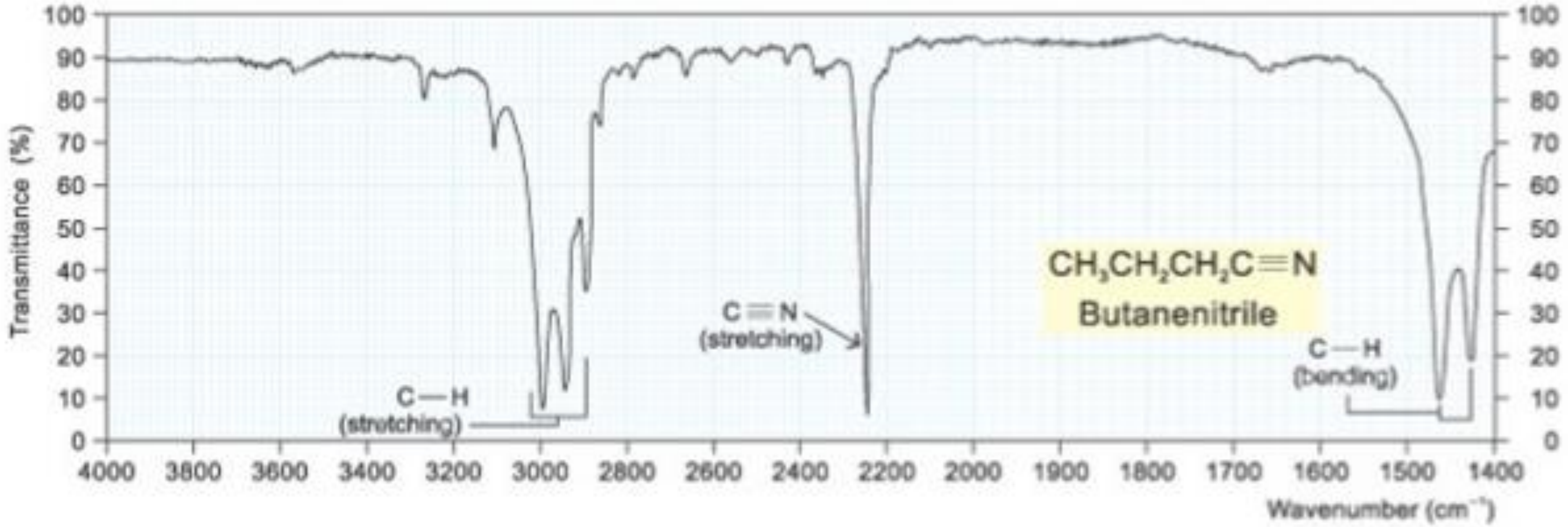
The IR spectrum of butylamine

7. Butylamine

Wavenumber (cm $^{-1}$)	Intensity	Indication
3371	Strong	N — H stretching
3280	Strong	
2960 – 2875	Weak	C — H stretching
1610	Medium	N — H bending
1475	Medium	C — H bending

Interpretation of the IR spectrum of butylamine

8. Butanenitrile



The IR spectrum of butanenitrile

8. Butanenitrile

Wavenumber (cm^{-1})	Intensity	Indication
2990 – 2895	Strong	C — H stretching
2246	Very strong	$C \equiv N$ stretching
1420	Strong	C — H bending
1480	Strong	

Interpretation of the IR spectrum of butanenitrile

Strategies for the Use of IR Spectra in the Identification of Functional Groups

1. Focus at the IR absorption peak at or above 1500 cm^{-1}

   ➔ Concentrate initially on the major absorption peaks

Strategies for the Use of IR Spectra in the Identification of Functional Groups

2. For each absorption peak, try to list out all the possibilities using a table or chart

   ➔ Not all absorption peaks in the spectrum can be assigned

Strategies for the Use of IR Spectra in the Identification of Functional Groups

3. The absence and presence of absorption peaks at some characteristic ranges of wavenumbers are equally important

   ➔ the absence of particular absorption peaks can be used to eliminate the presence of certain functional groups or bonds in the molecule

Limitation of the Use of IR Spectroscopy in the Identification of Organic Compounds

1. Some IR absorption peaks have very close wavenumbers and the peaks always coalesce
2. Not all vibrations give rise to strong absorption peaks

Limitation of the Use of IR Spectroscopy in the Identification of Organic Compounds

3. Not all absorption peaks in a spectrum can be associated with a particular bond or part of the molecule

4. Intermolecular interactions in molecules can result in complicated infra-red spectra

Use of Mass Spectra to Obtain Structural Information

Mass Spectrometry

- One of the most sensitive and versatile analytical tools
- More sensitive than other spectroscopic methods (e.g. IR spectroscopy)
- Only a microgram or less of materials is required for the analysis

Mass Spectrometry

In a mass spectrometric analysis, it involves:

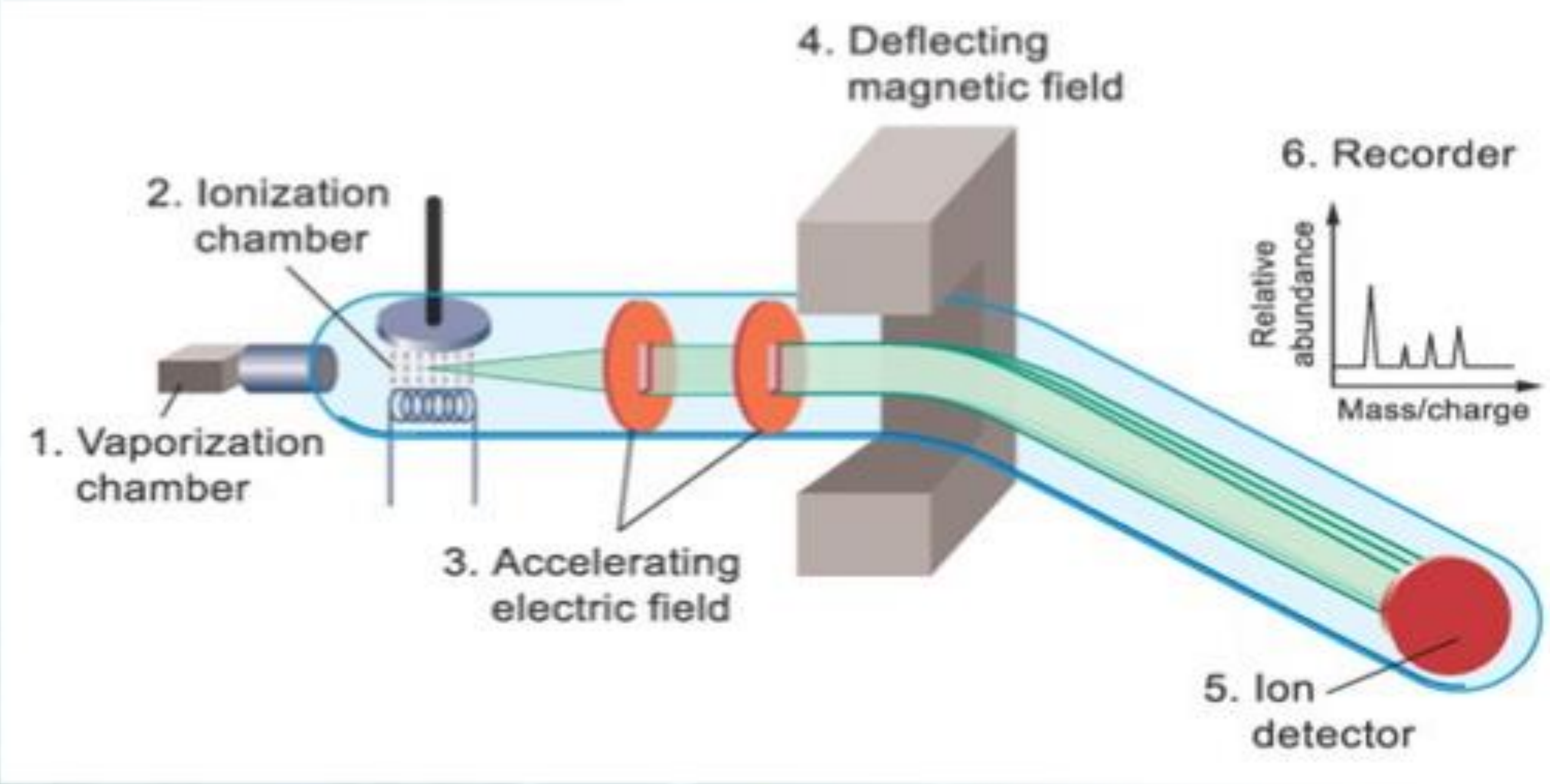
1. the conversion of molecules to ions
2. separation of the ions formed according to their mass-to-charge (m/e) ratio

➔ m is the mass of the ion in atomic mass units and e is its charge

Mass Spectrometry

- Finally, the number of ions of each type (i.e. the relative abundance of ions of each type) is determined
- The analysis is carried out using a mass spectrometer

Mass Spectrometry



Components of a mass spectrometer

Mass Spectrometry

In the vaporization chamber,

- the sample is heated until it vaporizes

  ➔ changes to the gaseous state

Mass Spectrometry

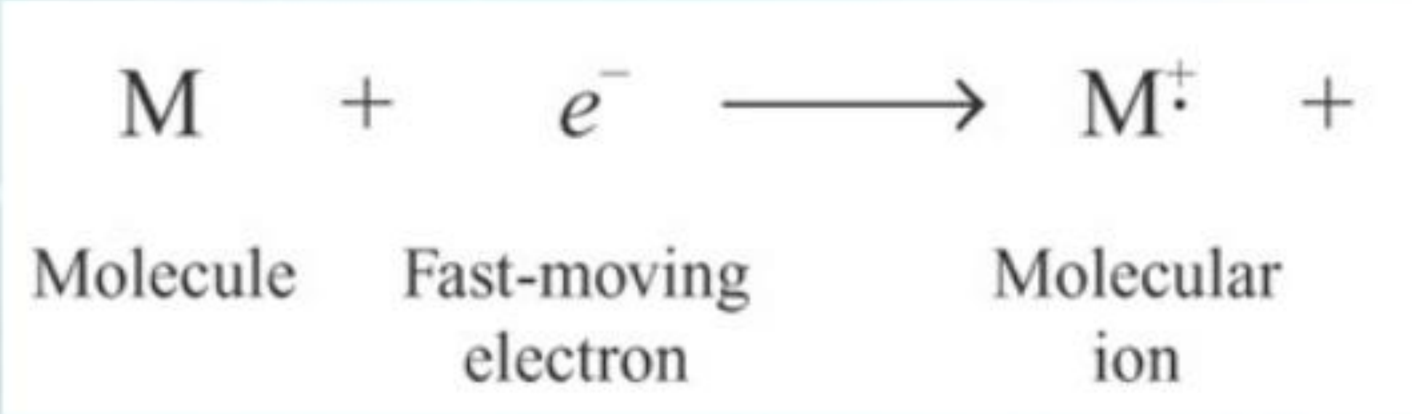
- The molecules in the gaseous state are bombarded with a beam of fast-moving electrons

➔ Positively-charged ions called the molecular ions are formed

➔ One of the electrons of the molecule is knocked off

Mass Spectrometry

- Molecular ions are sometimes referred to as the parent ion



$$\underset{\text{Molecule}}{M} + \underset{\substack{\text{Fast-moving}\\ \text{electron}}}{e^-} \longrightarrow \underset{\substack{\text{Molecular}\\ \text{ion}}}{M^{+\cdot}} + 2e^-$$

Mass Spectrometry

- ∵ one of the electrons is removed from the molecules during the ionization process

➔ the molecular ion contains a single unpaired electron

➔ the molecular ion is not only a cation, it is also a free radical

Mass Spectrometry

- e.g.

  if a molecule of methanol (CH_3OH) is bombarded with a beam of fast-moving electrons

  ➔ the following reaction will take place:

$$\mathrm{CH_3}\underset{\cdot\cdot}{\ddot{\mathrm{O}}}\mathrm{H} + e^- \longrightarrow \left[\mathrm{CH_3}\underset{\cdot\cdot}{\dot{\mathrm{O}}}\mathrm{H}\right]^{+} + 2e^-$$

Molecular ion
of methanol
($m/e = 32$)

Mass Spectrometry

- The molecular ions formed in the ionization chamber are energetically unstable

  ➔ undergo fragmentation

- Fragmentation can take place in a variety of ways

  ➔ depend on the nature of the particular molecular ion

Mass Spectrometry

- The way that a molecular ion fragments

➔ give us highly useful information about the structure of a complex molecule

Mass Spectrometry

- The positively charged ions formed are then accelerated by electric field and deflected by magnetic field

  ➔ causes the ions to arrive the ion detector

- The lighter the ions, the greater the deflection

Mass Spectrometry

- Positively charged ions of higher charge have greater deflection
- Ions with a high *m*/*e* ratio are deflected to smaller extent than ions with a low *m*/*e* ratio

Mass Spectrometry

- In the ion detector,

  ➔ the number of ions collected is measured electronically

- The intensity of the signal is

  ➔ a measure of the relative abundance of the ions with a particular *m*/*e* ratio

Mass Spectrometry

- In the ion detector,

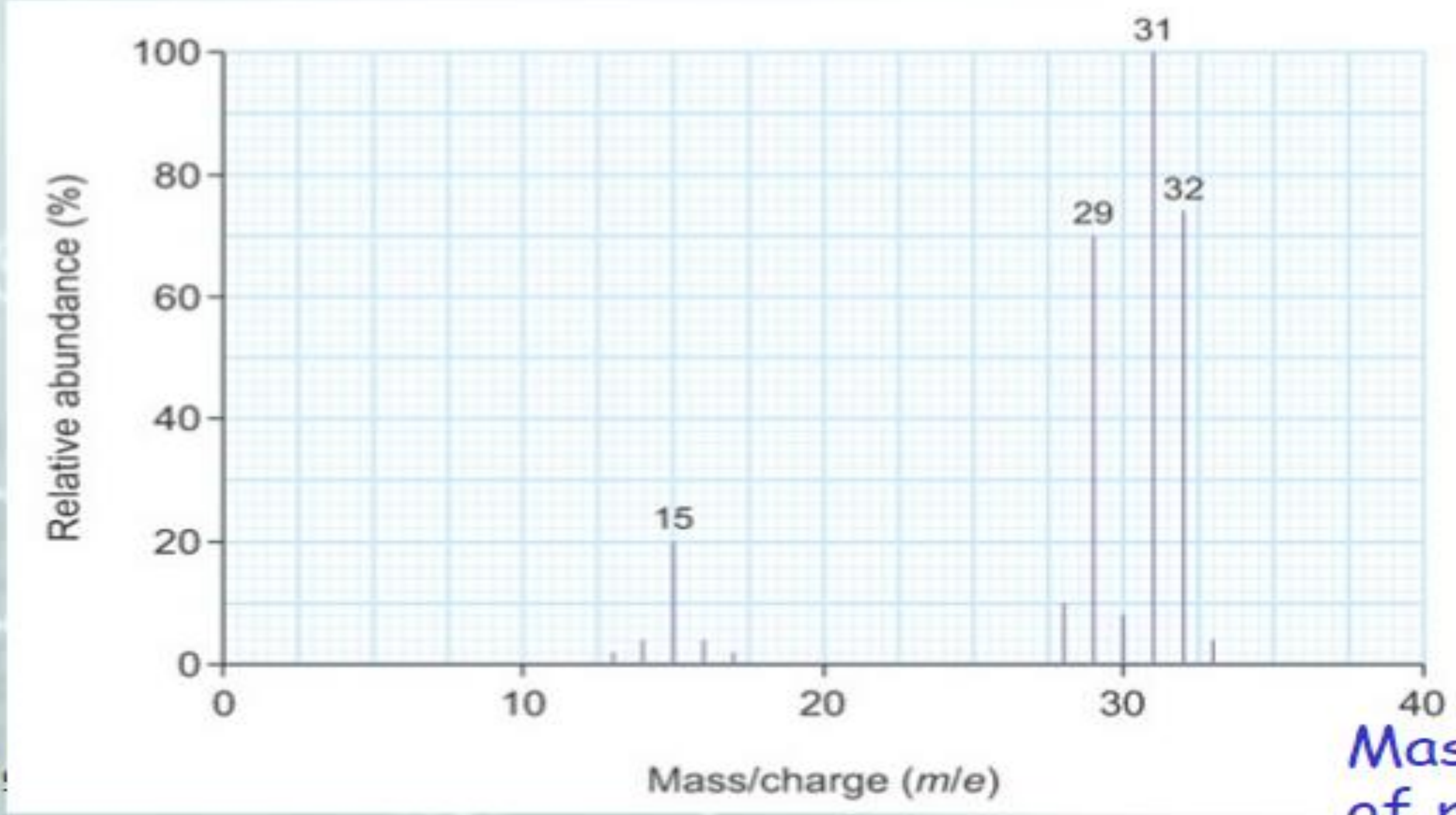
  ➔ the number of ions collected is measured electronically

- The intensity of the signal is

  ➔ a measure of the relative abundance of the ions with a particular *m*/*e* ratio

Mass Spectrum

- Generally published as bar graphs.



Mass spectrum of methanol

Mass Spectrum

Corresponding ion	m/e ratio
H_3C^+	15
$H \equiv CO^+$	29
$H_2C = OH^+$	31
$CH_3OH^{\overset{+}{\bullet}}$	32

Interpretation of the mass spectrum of methanol

Formation of Fragments

- The molecular ions formed in the ionization chamber are energetically unstable
  - ➔ Some of them may break up into smaller fragments
  - ➔ Called the daughter ions

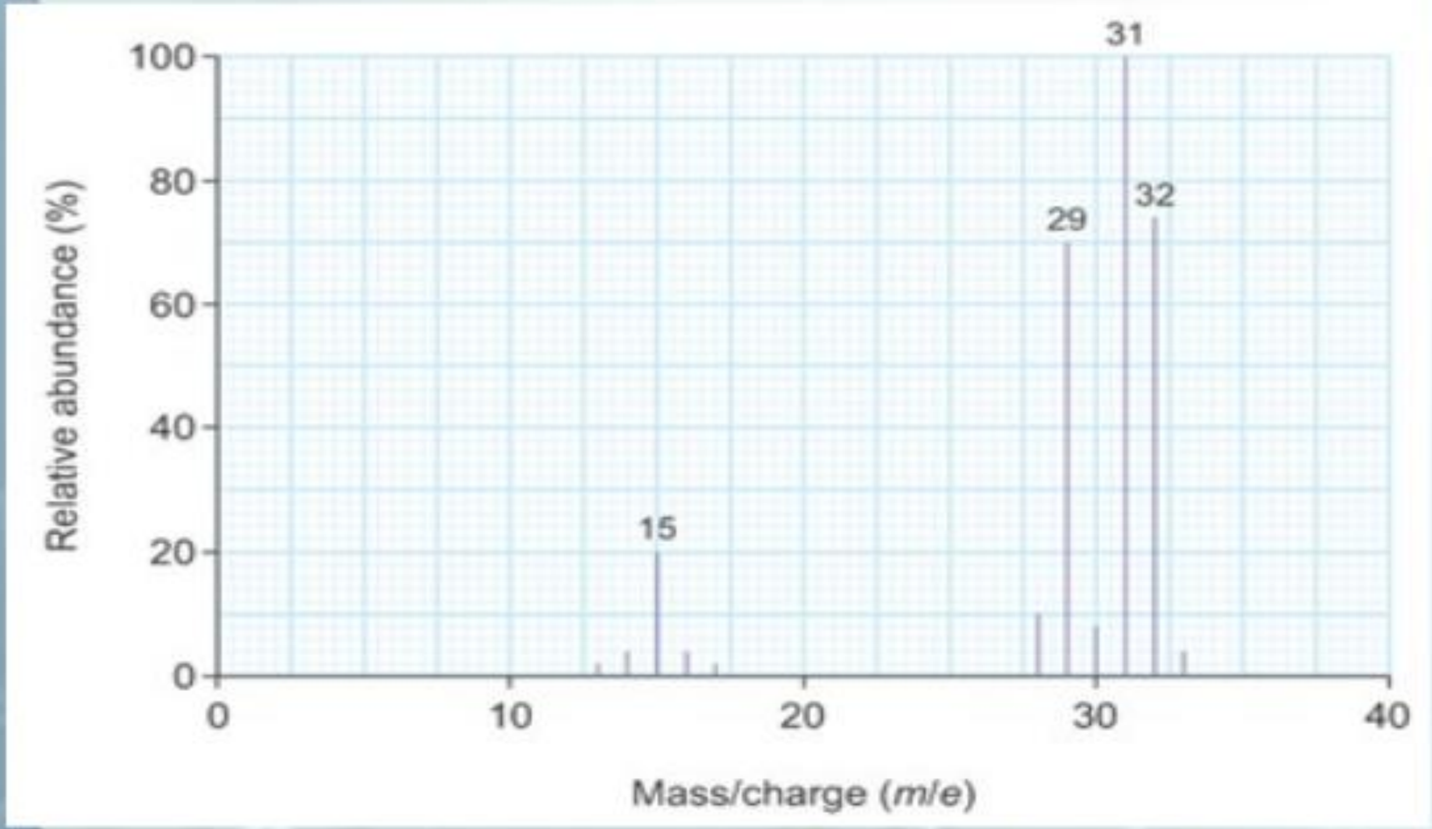
Formation of Fragments

- These ionized fragments are accelerated and deflected by the electric field and magnetic field
- Finally, they are detected by the ion detector and

  ➔ their *m/e* ratios are measured

  ➔ explains why there are so many peaks appeared in mass spectra

Formation of Fragments



Mass spectrum of methanol

- The peak at *m/e* 31

  ➔ the most intense peak

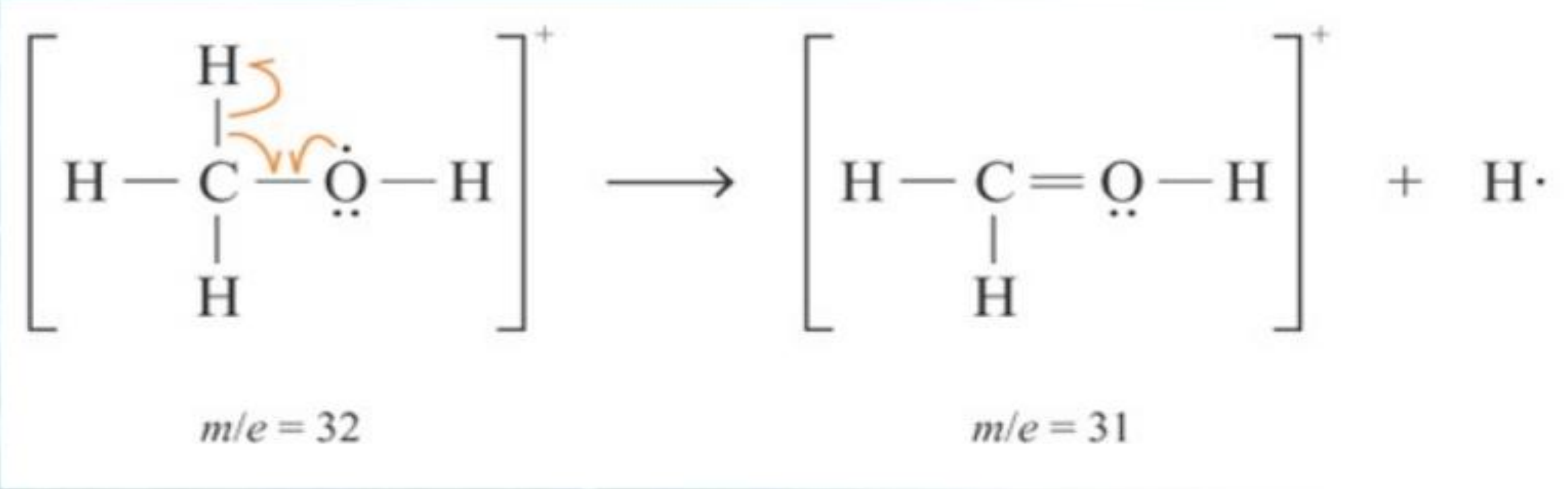
- Arbitrarily assigned an intensity of 100%

  ➔ Called the base peak

  ➔ Corresponds to the most common ion formed

Formation of Fragments

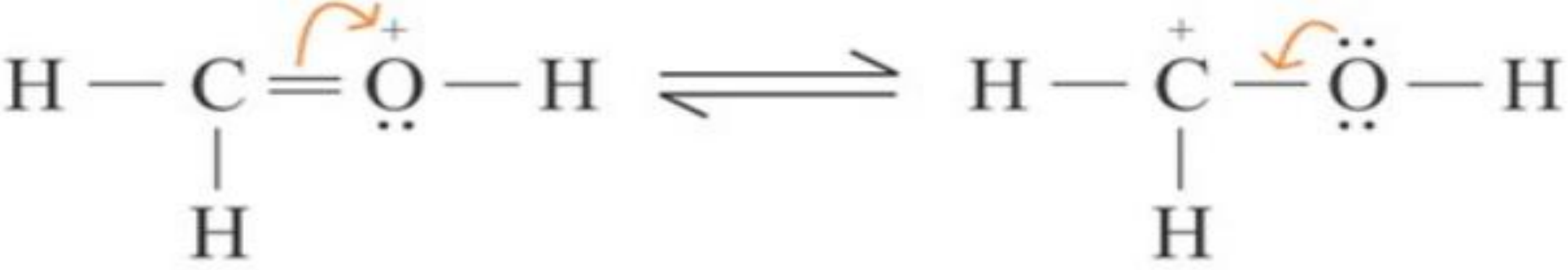
- The peak at *m/e* 31
  - ➔ corresponds to the ion $H_2C = OH^+$
  - ➔ formed by losing one hydrogen atom from the molecular ion



$$\left[H-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-\dot{\ddot{O}}-H\right]^{+} \longrightarrow \left[H-\underset{\underset{\displaystyle H}{|}}{C}=\ddot{O}-H\right]^{+} + H\cdot$$

Formation of Fragments

- The ion $H_2C = OH^+$ is a relatively stable ion
  - ➔ ∵ the positive charge is not localized on a particular atom
  - ➔ it spreads around the carbon and the oxygen atoms to form a delocalized system

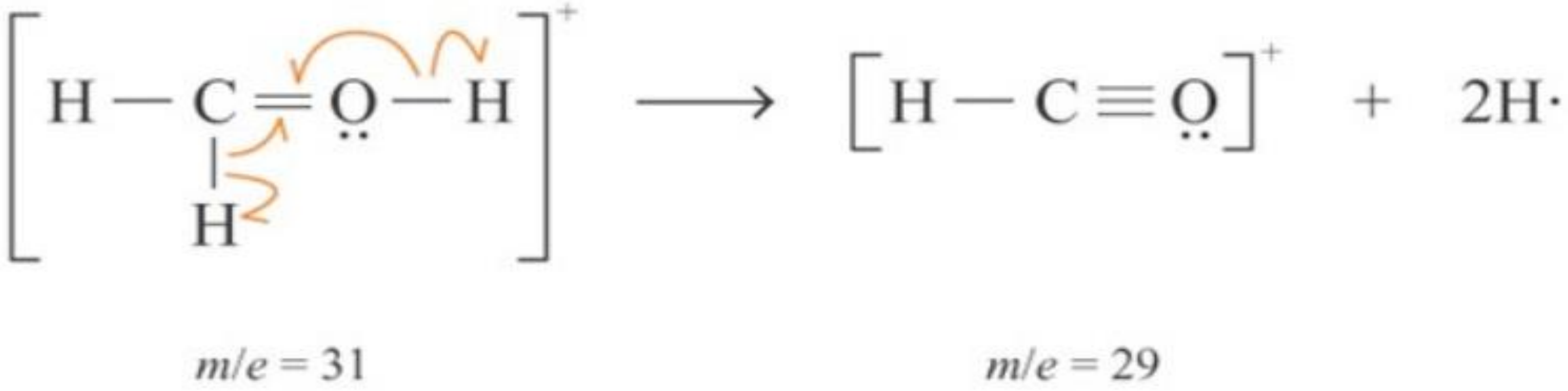


$m/e = 31$

Formation of Fragments

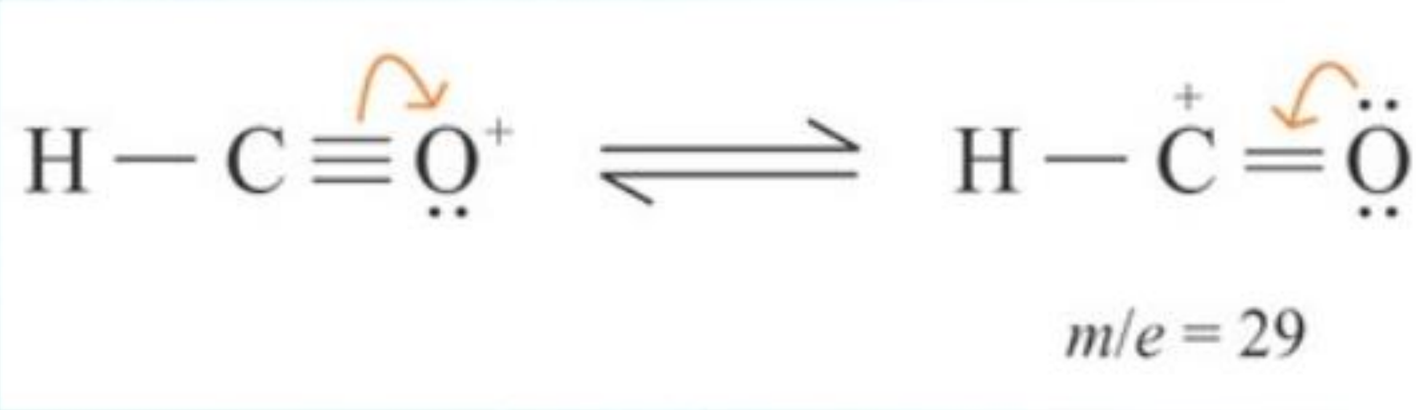
- The peak at *m*/*e* 29 corresponds to the ion $HC \equiv O^+$

➔ formed by losing two hydrogen atoms from the ion $H_2C = OH^+$



Formation of Fragments

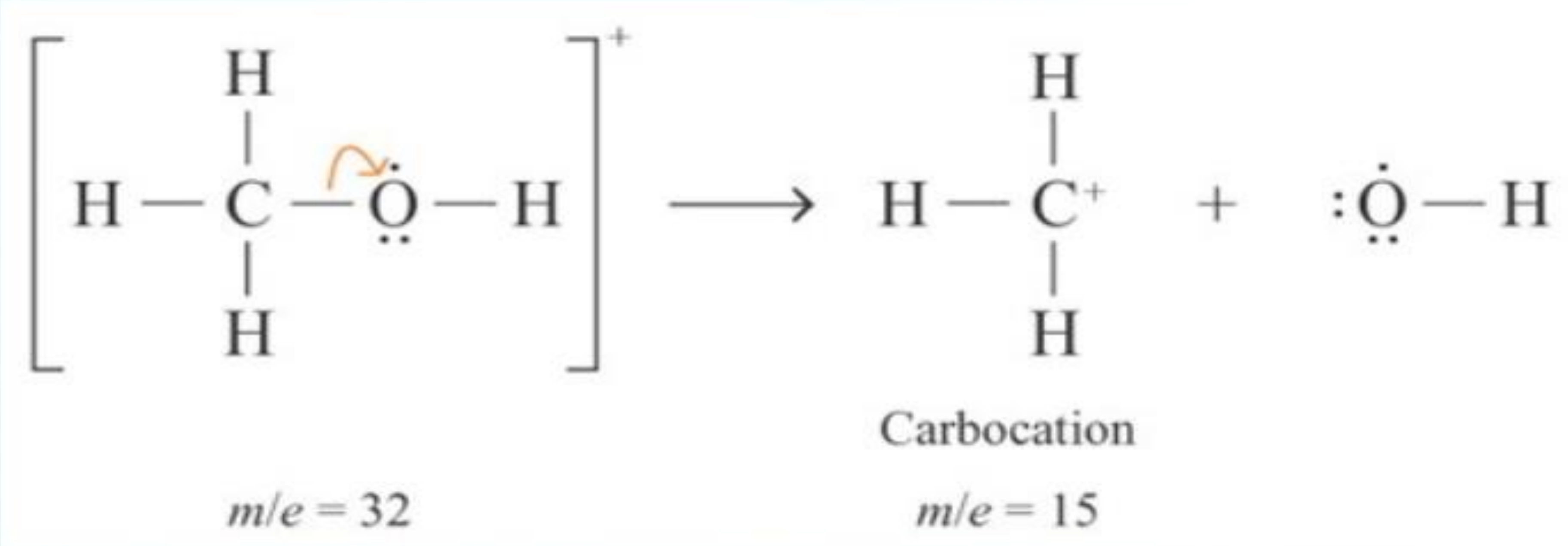
- The ion $HC \equiv O^+$ has two resonance structures:



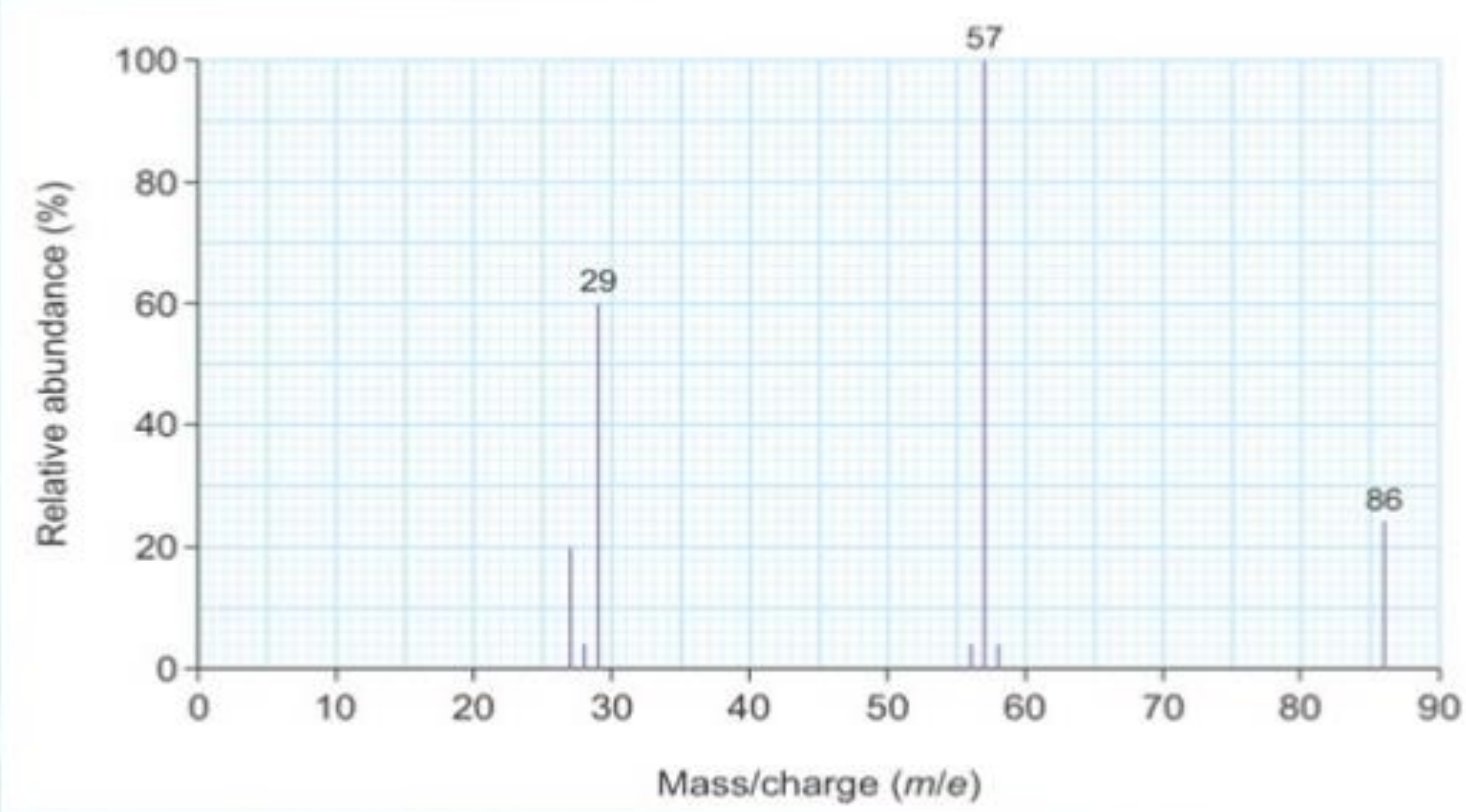
Formation of Fragments

- The peak at *m/e* 15 corresponds to the ion H_3C^+

➔ formed by the breaking of the C — O bond in the molecular ion



Formation of Fragments



Mass spectrum of pentan-3-one

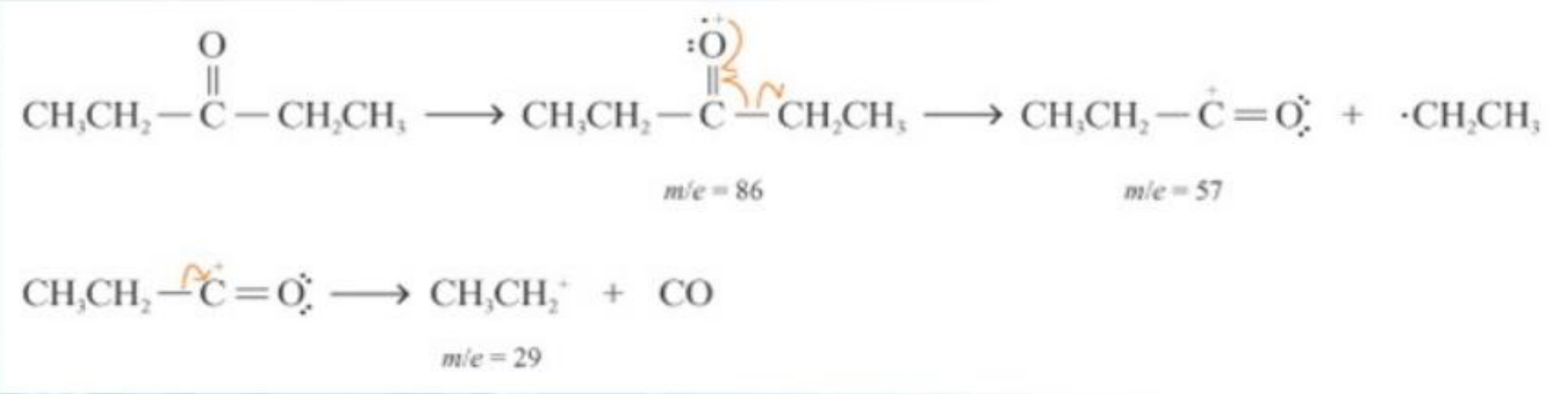
Formation of Fragments

Corresponding ion	*m*/*e* ratio
$CH_3CH_2^+$	29
$CH_3CH_2CO^+$	57
$CH_3CH_2COCH_2CH_3^{+\bullet}$	86

Interpretation of the mass spectrum of pentan-3-one

Formation of Fragments

- The fragmentation pattern of pentan-3-one is summarized below:



$$CH_3CH_2-\overset{O}{\overset{\|}{C}}-CH_2CH_3 \longrightarrow \underset{m/e\,=\,86}{CH_3CH_2-\overset{:\ddot{O}^{\cdot+}}{\overset{\|}{C}}-CH_2CH_3} \longrightarrow \underset{m/e\,=\,57}{CH_3CH_2-\overset{+}{C}=\ddot{O}:} + \cdot CH_2CH_3$$

$$CH_3CH_2-\overset{+}{C}=\ddot{O}: \longrightarrow \underset{m/e\,=\,29}{CH_3CH_2^{+}} + CO$$

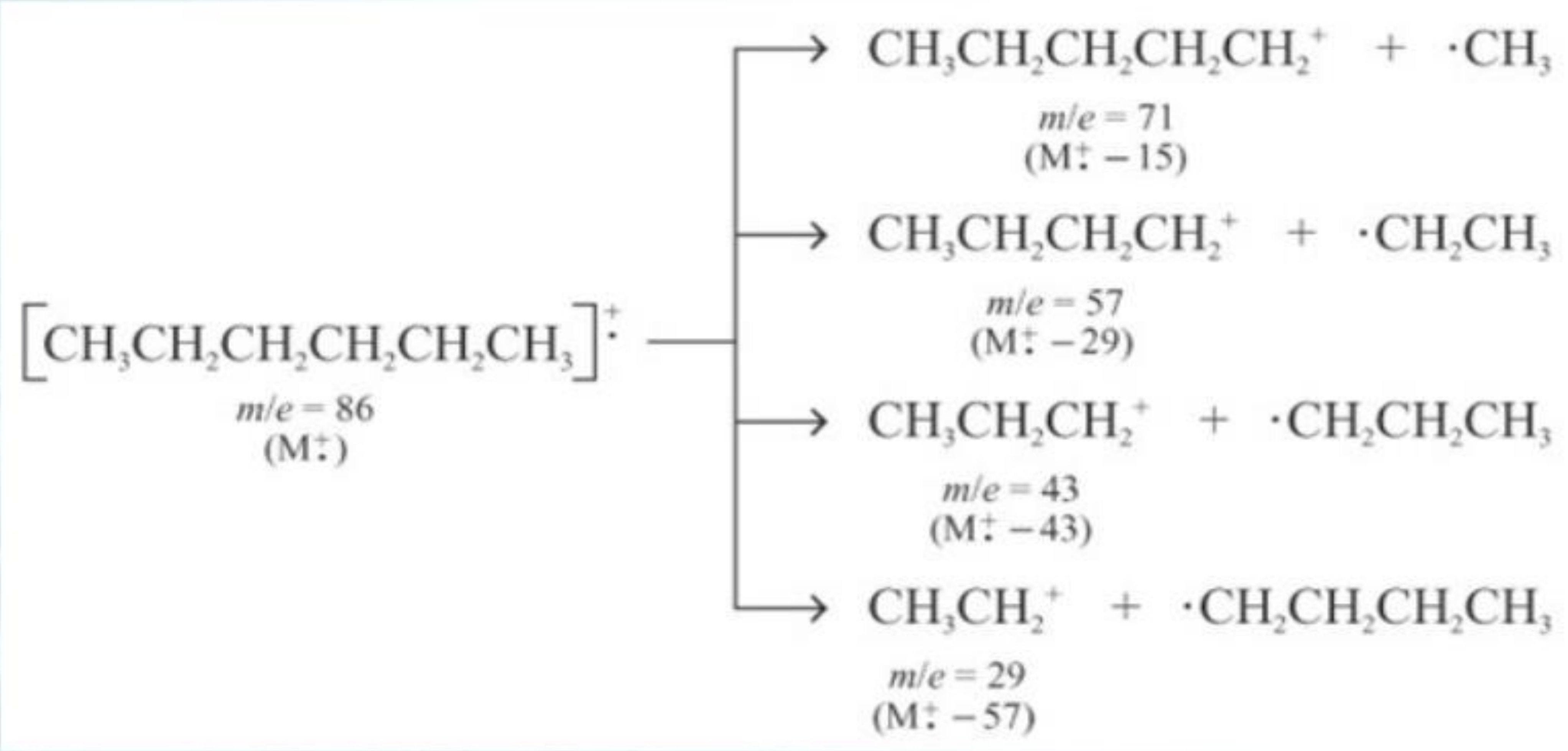
Fragmentation Pattern

1. Straight-chain Alkanes

- Simple alkanes tend to undergo fragmentation by
  - ➔ the initial loss of a $\cdot CH_3$ to give a peak at $M^{\overset{+}{\cdot}} - 15$
  - ➔ This carbocation can then undergo stepwise cleavage down the alkyl chain

1. Straight-chain Alkanes

- Take hexane as an example:



$[CH_3CH_2CH_2CH_2CH_2CH_3]^{+\cdot}$

$m/e = 86$ $(M^{+\cdot})$

$\rightarrow CH_3CH_2CH_2CH_2CH_2^{+} + \cdot CH_3$

$m/e = 71$ $(M^{+\cdot} - 15)$

$\rightarrow CH_3CH_2CH_2CH_2^{+} + \cdot CH_2CH_3$

$m/e = 57$ $(M^{+\cdot} - 29)$

$\rightarrow CH_3CH_2CH_2^{+} + \cdot CH_2CH_2CH_3$

$m/e = 43$ $(M^{+\cdot} - 43)$

$\rightarrow CH_3CH_2^{+} + \cdot CH_2CH_2CH_2CH_3$

$m/e = 29$ $(M^{+\cdot} - 57)$

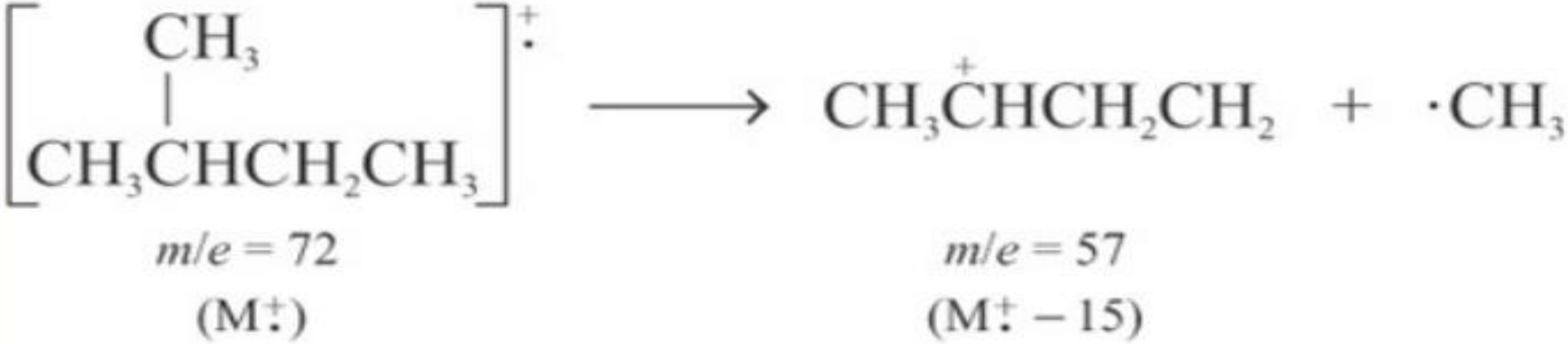
2. Branched-chain Alkanes

- Tend to cleave at the “branch point”

  ➔ more stable carbocations are formed

2. Branched-chain Alkanes

- e.g.



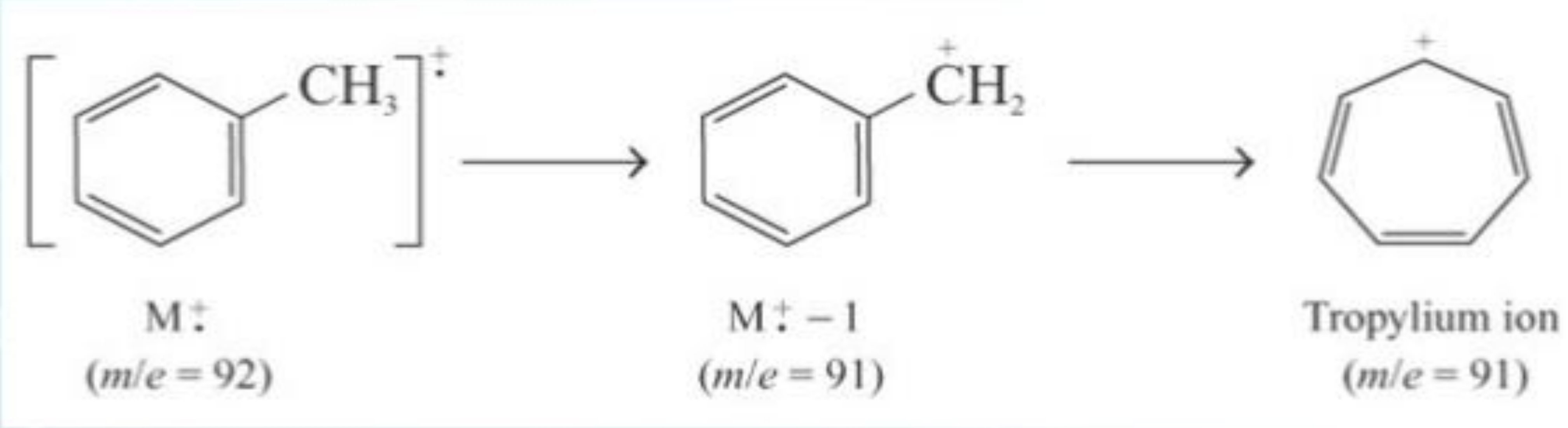
$$\left[\begin{array}{c}CH_3\\|\\CH_3CHCH_2CH_3\end{array}\right]^{\overset{+}{\cdot}} \longrightarrow CH_3\overset{+}{C}HCH_2CH_2 + \cdot CH_3$$

$m/e = 72$ ($M^{\overset{+}{\cdot}}$)

$m/e = 57$ ($M^{\overset{+}{\cdot}} - 15$)

3. Alkyl-substituted Aromatic Hydrocarbons

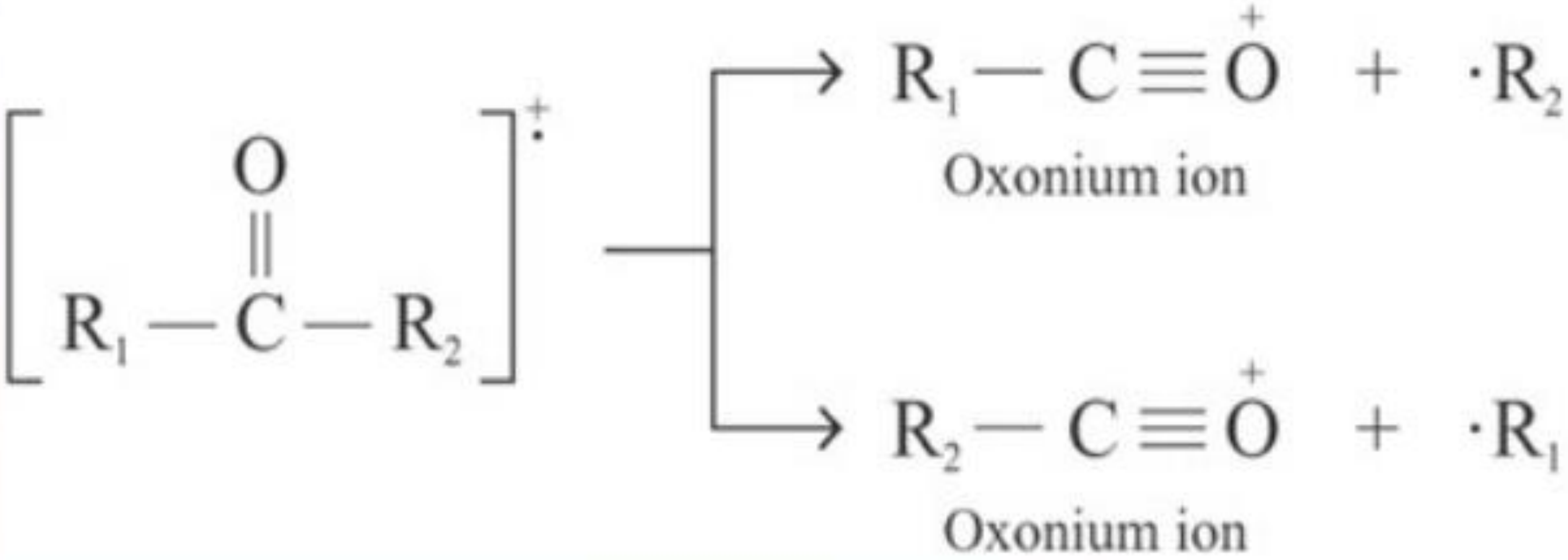
- e.g.



4. Aldehydes and Ketones

- Frequently undergo fragmentation by losing one of the side chains
  - ➔ generate the substituted oxonium ion
  - ➔ often represents the base peak in the mass spectra

4. Aldehydes and Ketones



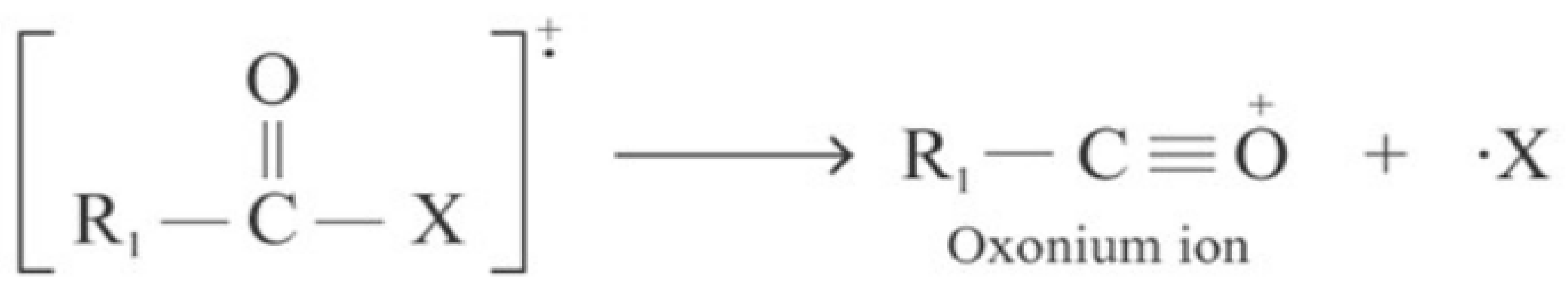
$$\left[R_1-\overset{\overset{\displaystyle O}{\|}}{C}-R_2\right]^{+\cdot} \longrightarrow R_1-C\equiv\overset{+}{O} + \cdot R_2$$

$$\left[R_1-\overset{\overset{\displaystyle O}{\|}}{C}-R_2\right]^{+\cdot} \longrightarrow R_2-C\equiv\overset{+}{O} + \cdot R_1$$

5. Esters, Carboxylic Acids and Amides

- Often undergo cleavage that involves the breaking of the C —X bond

➔ form substituted oxonium ions as shown below:



$$\left[R_1-\overset{\overset{\displaystyle O}{\|}}{C}-X \right]^{+\cdot} \longrightarrow R_1-C\equiv\overset{+}{O} + \cdot X$$

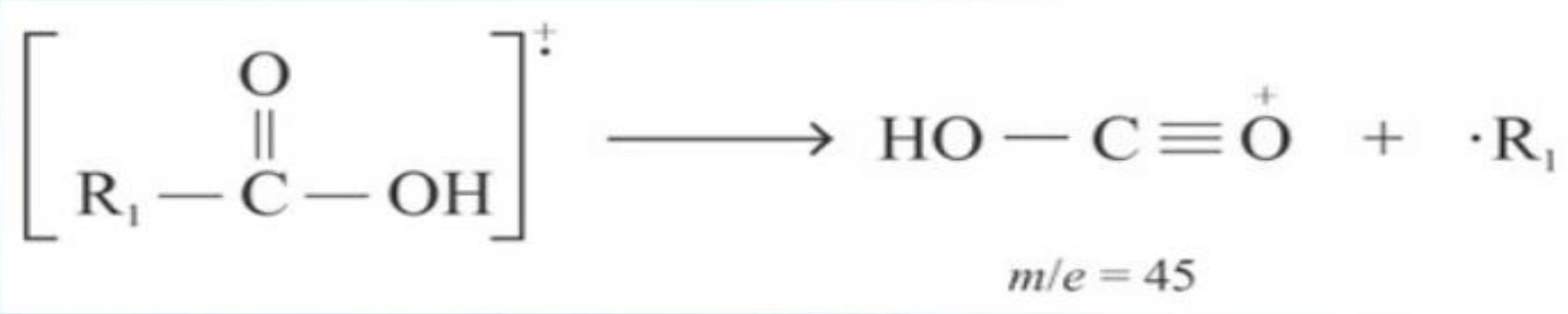
Oxonium ion

(where X = OH, OR, NH_2, NHR, NR_2)

5. Esters, Carboxylic Acids and Amides

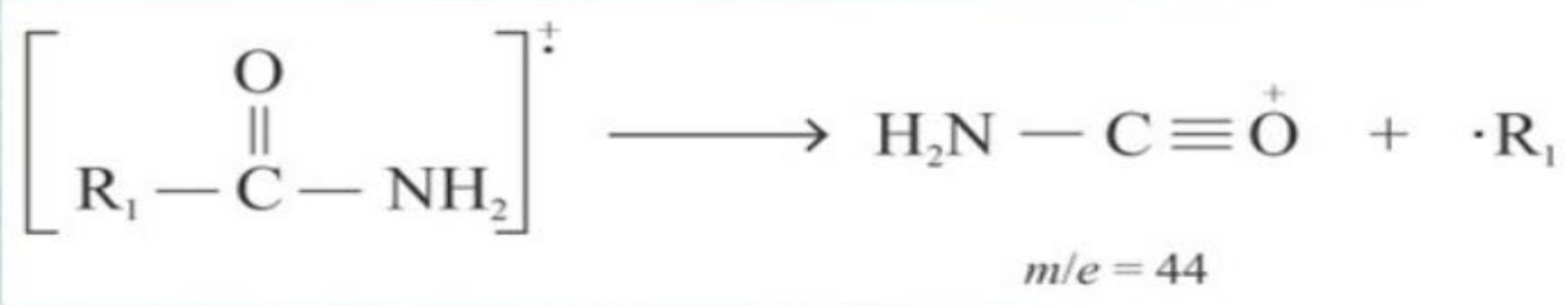
- For carboxylic acids and unsubstituted amides,

  ➔ characteristic peaks at *m*/*e* 45 and 44 are observed respectively



$$\left[R_1-\overset{\overset{\displaystyle O}{\|}}{C}-OH \right]^{+\cdot} \longrightarrow HO-C\equiv\overset{+}{O} \;+\; \cdot R_1$$

$m/e = 45$



$$\left[R_1-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2 \right]^{+\cdot} \longrightarrow H_2N-C\equiv\overset{+}{O} \;+\; \cdot R_1$$

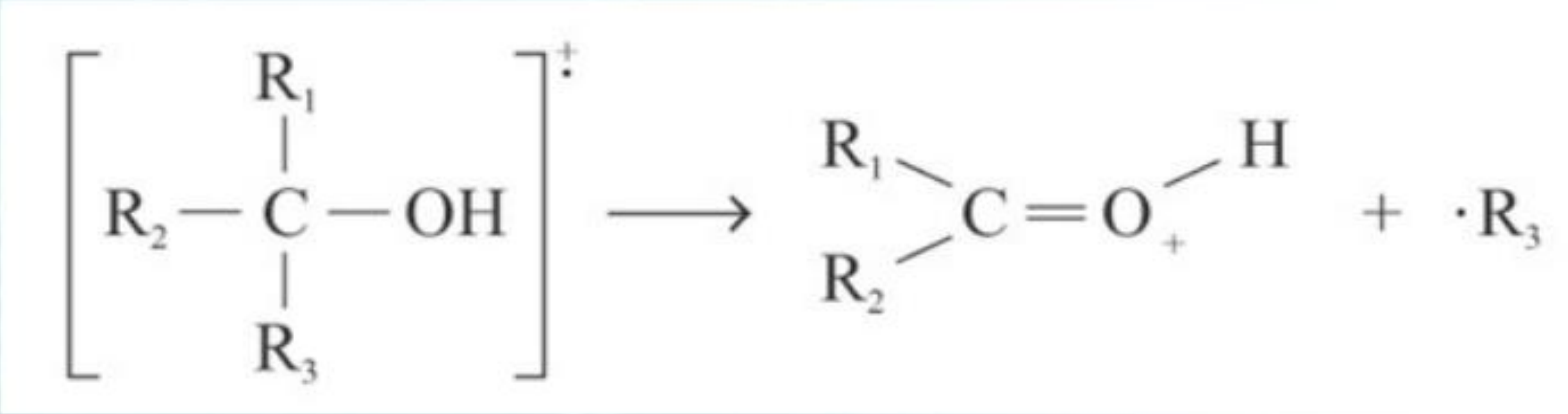
$m/e = 44$

6. Alcohols

- In addition to the loss of a proton and the hydroxyl radical,

  ➔ alcohols tend to lose one of the α alkyl groups (or α hydrogen atoms)

  ➔ form oxonium ions

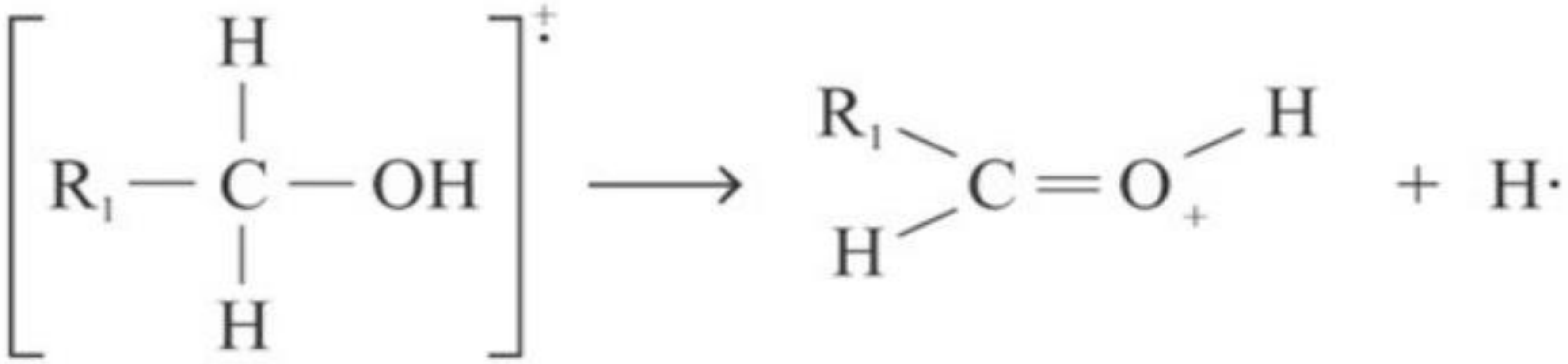


6. Alcohols

- For primary alcohols,

→ the peak at *m/e* 31, 45, 59 or 73 often appears

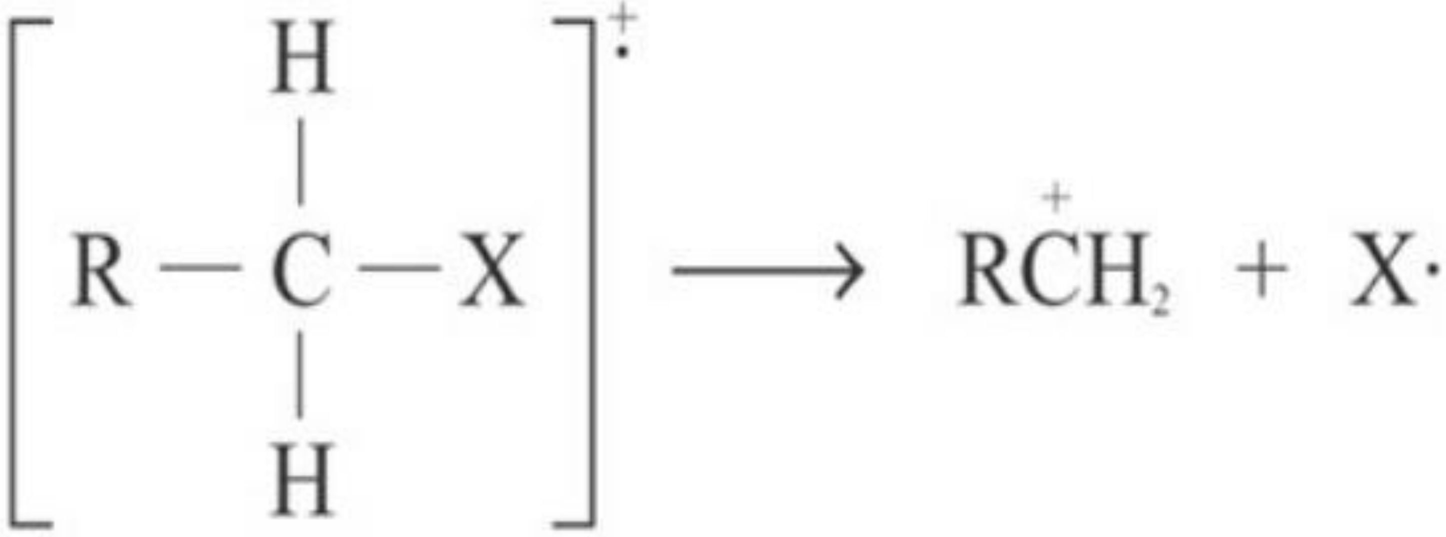
→ depends on what the R_1 group is



m/e = 31, 45, 59, 73, etc.

7. Haloalkanes

- Haloalkanes simply break at the C — X bond



$$\left[R-\overset{\displaystyle H \atop |}{\underset{| \atop \displaystyle H}{C}}-X \right]^{+\cdot} \longrightarrow R\overset{+}{C}H_2 + X\cdot$$

7. Haloalkanes

- In the mass spectra of chloroalkanes,

  ➔ two peaks, separated by two mass units, in the ratio 3 : 1 will be appeared

7. Haloalkanes

- In the mass spectra of bromoalkanes,

  ➔ two peaks, separated by two mass units, having approximately equal intensities will be appeared