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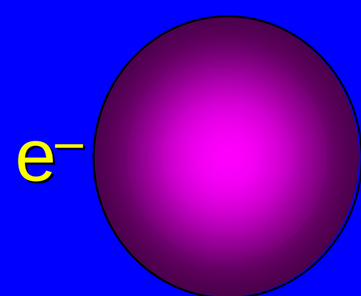
Mass Spectrometry

Principles of Electron-Impact Mass Spectrometry

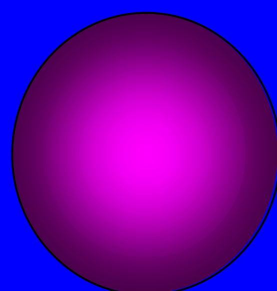
Atom or molecule is hit by high-energy electron



Principles of Electron-Impact Mass Spectrometry

Atom or molecule is hit by high-energy electron

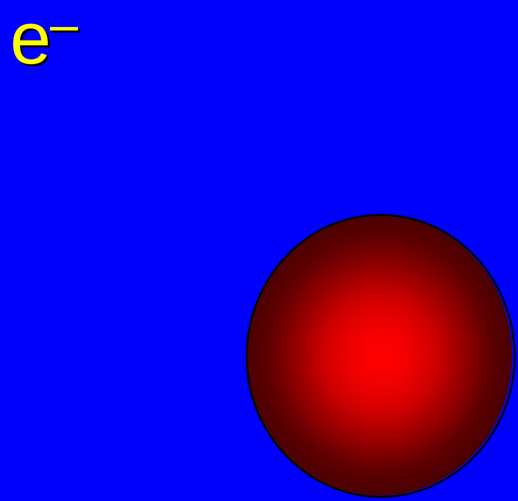
e^{-}



electron is deflected but transfers much of its energy to the molecule

Principles of Electron-Impact Mass Spectrometry

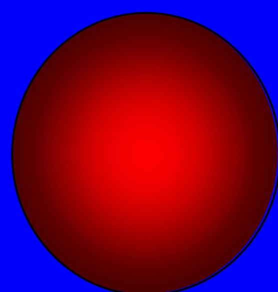
Atom or molecule is hit by high-energy electron



electron is deflected but transfers much of its energy to the molecule

Principles of Electron-Impact Mass Spectrometry

This energy-rich species ejects an electron.



Principles of Electron-Impact Mass Spectrometry

This energy-rich species ejects an electron.

forming a positively charged, odd-electron species called the *molecular ion*

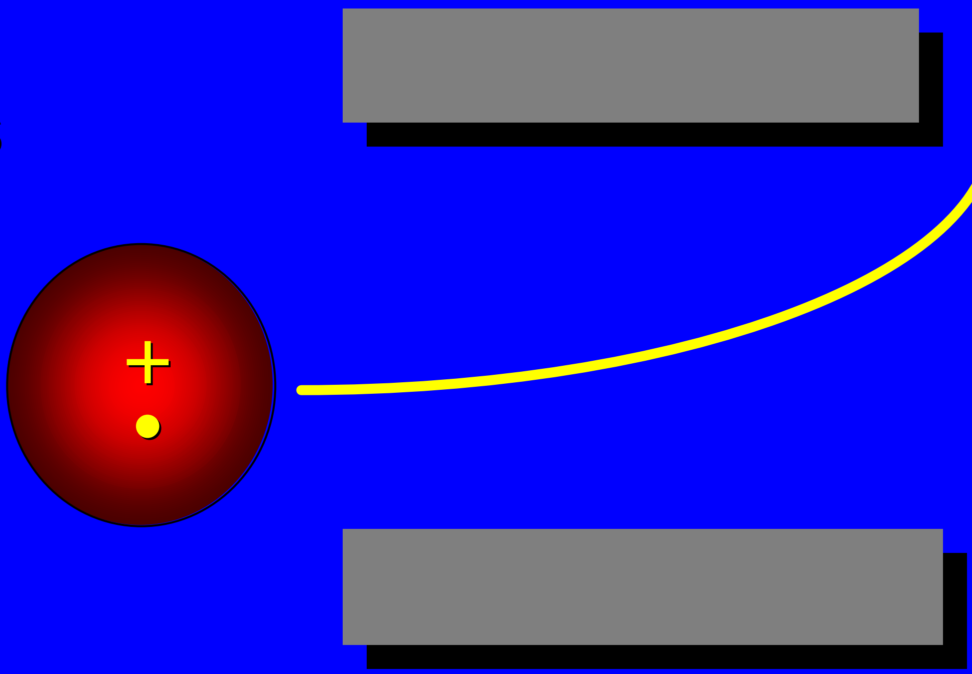
Principles of Electron-Impact Mass Spectrometry

Molecular ion passes between poles of a magnet and is deflected by magnetic field

amount of deflection depends on mass-to-charge ratio

highest m/z deflected least

lowest m/z deflected most



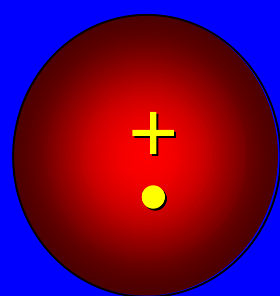
Principles of Electron-Impact Mass Spectrometry

If the only ion that is present is the molecular ion, mass spectrometry provides a way to measure the molecular weight of a compound and is often used for this purpose.

However, the molecular ion often fragments to a mixture of species of lower m/z.

Principles of Electron-Impact Mass Spectrometry

The molecular ion dissociates to a cation and a radical.



Principles of Electron-Impact Mass Spectrometry

The molecular ion dissociates to a cation and a radical.

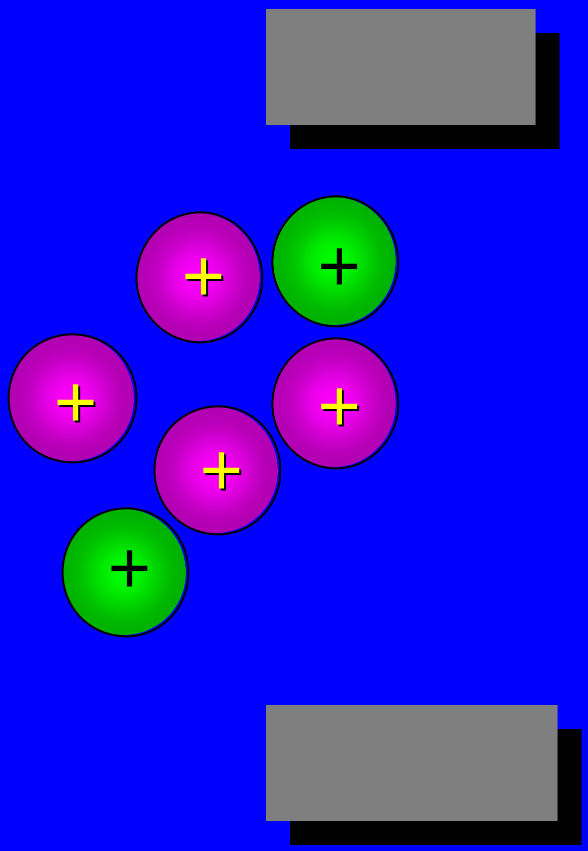
Usually several fragmentation pathways are available and a mixture of ions is produced.

Principles of Electron-Impact Mass Spectrometry

mixture of ions of different mass gives separate peak for each m/z

intensity of peak proportional to percentage of each ion of different mass in mixture

separation of peaks depends on relative mass



Principles of Electron-Impact Mass Spectrometry

mixture of ions of different mass gives separate peak for each m/z

intensity of peak proportional to percentage of each atom of different mass in mixture

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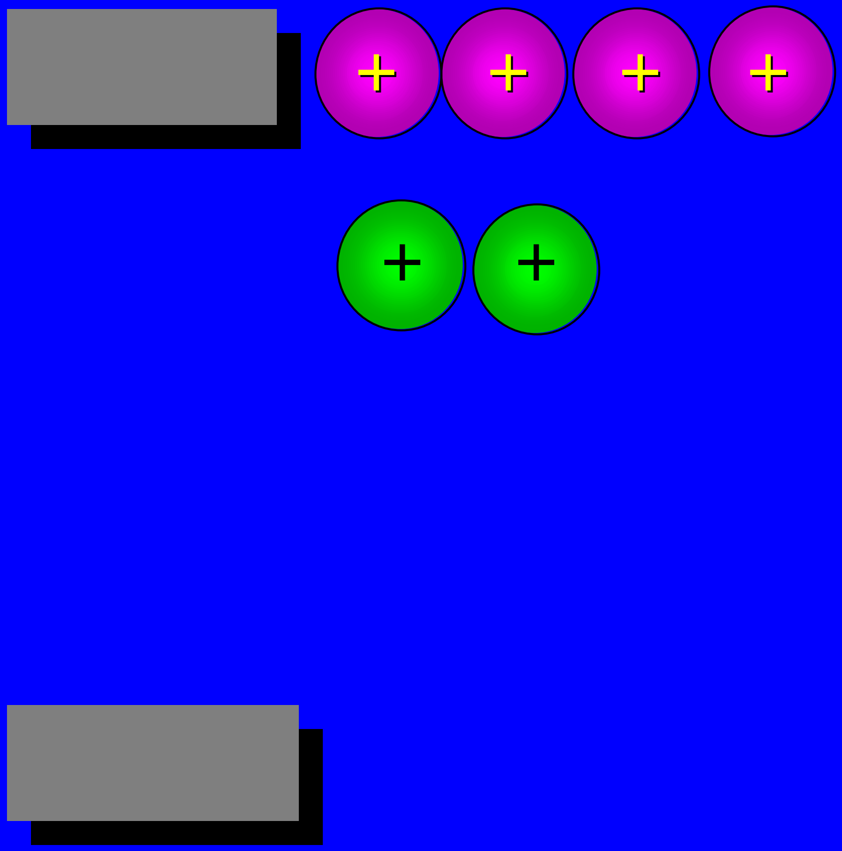
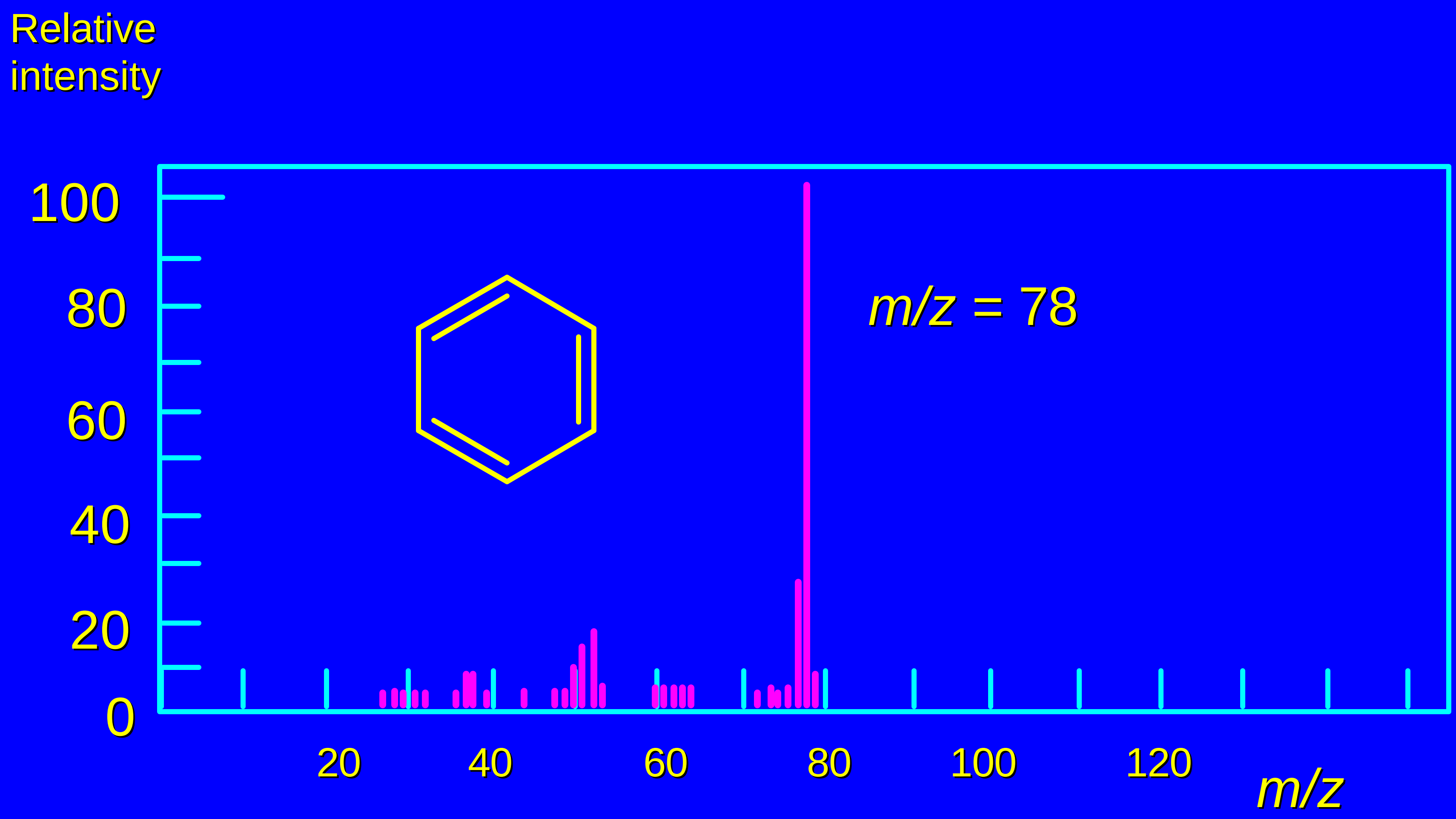
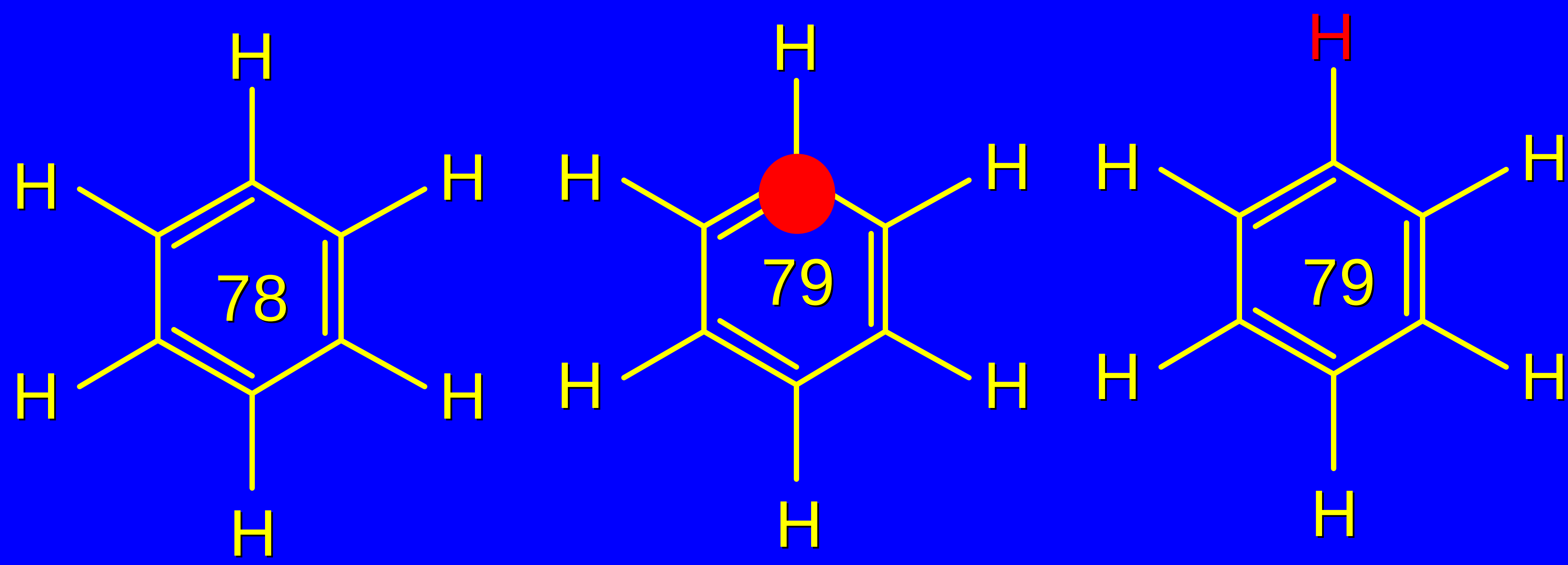


Some molecules undergo very little fragmentation

Benzene is an example. The major peak corresponds to the molecular ion.

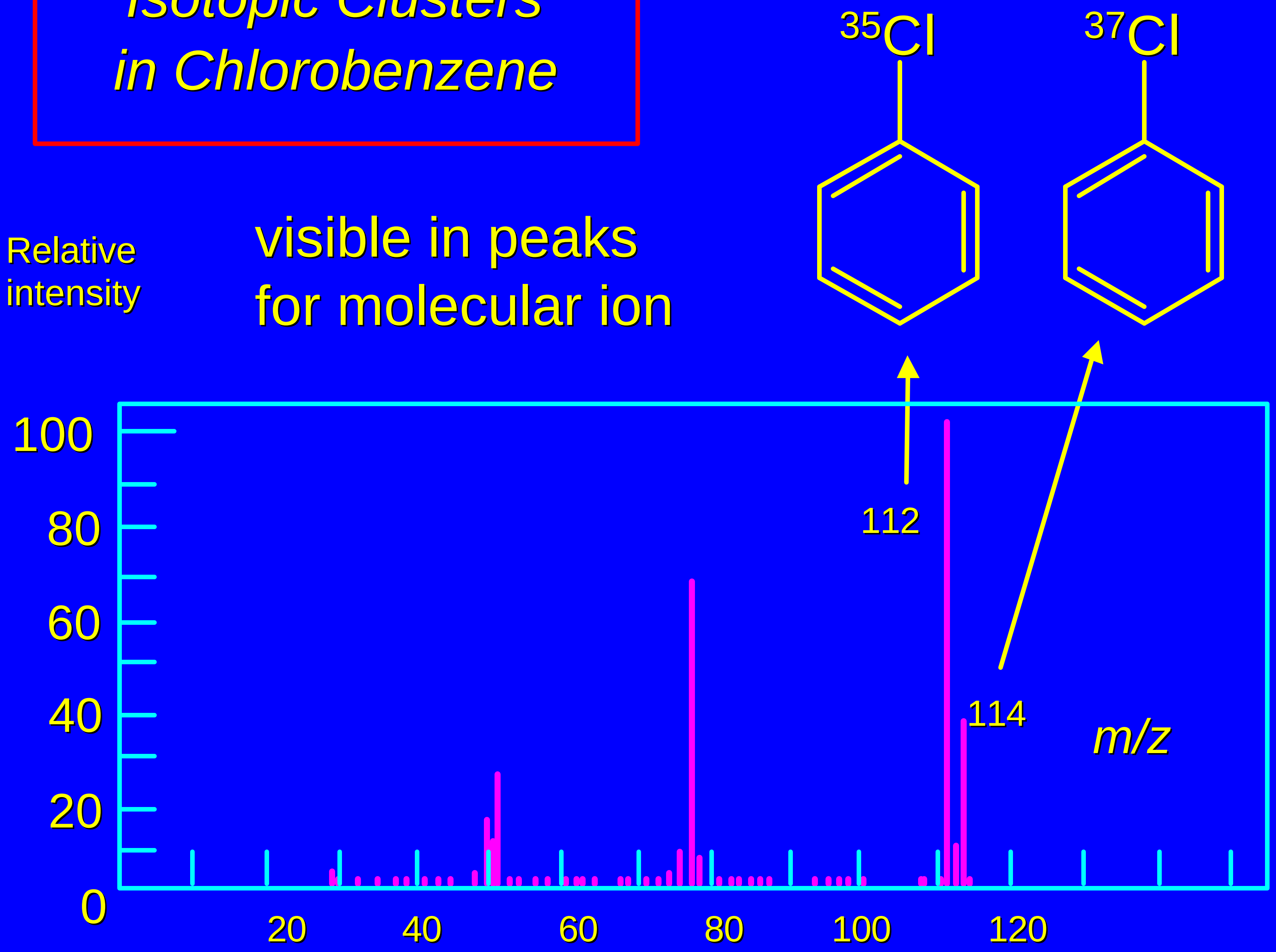


Isotopic Clusters

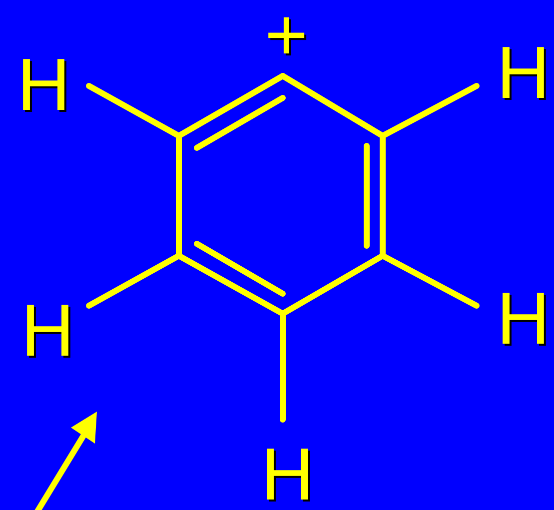


93.4%	6.5%	0.1%
all H are ^{1}H and all C are ^{12}C	one C is ^{13}C	one H is ^{2}H

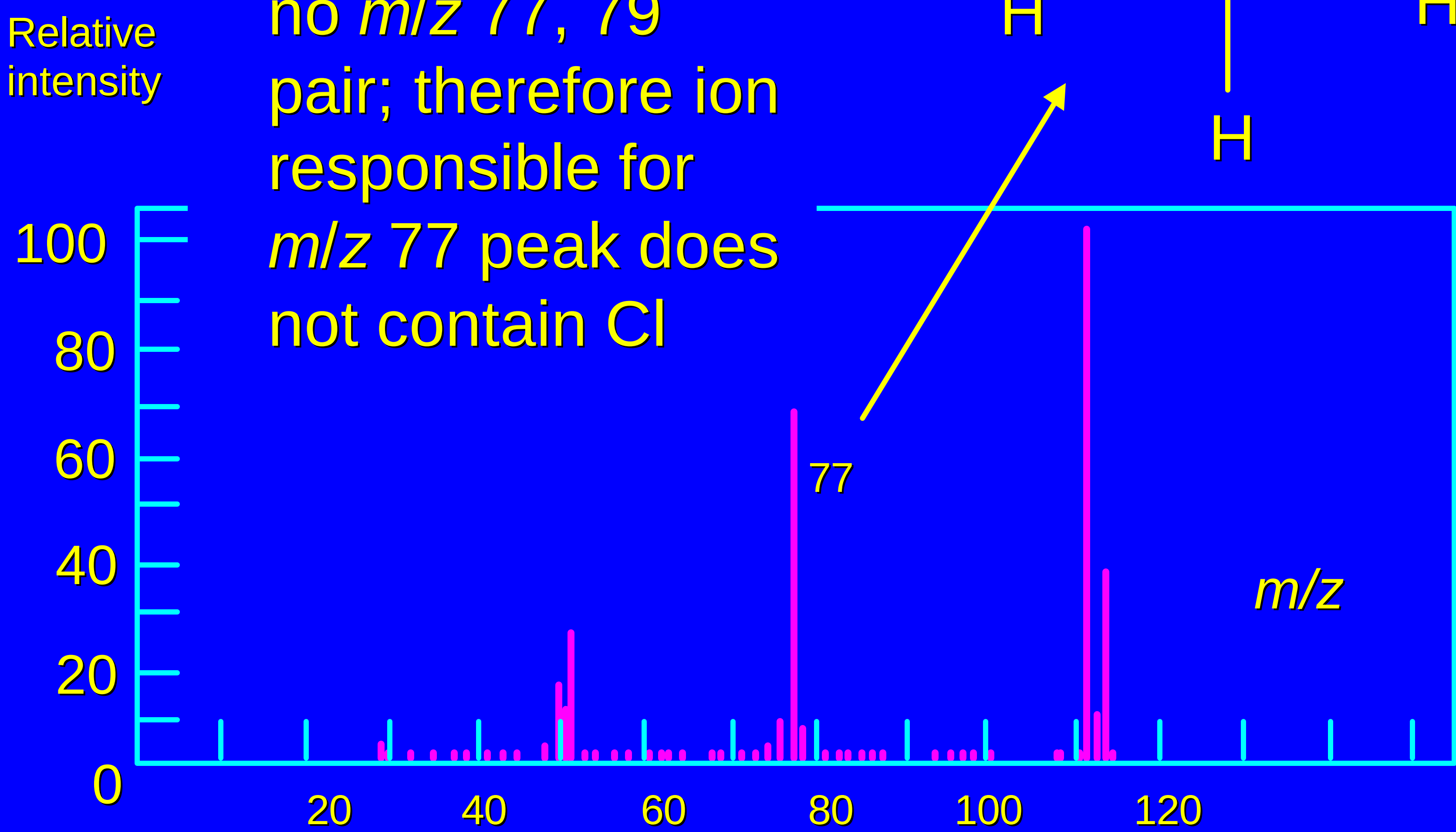
Isotopic Clusters in Chlorobenzene



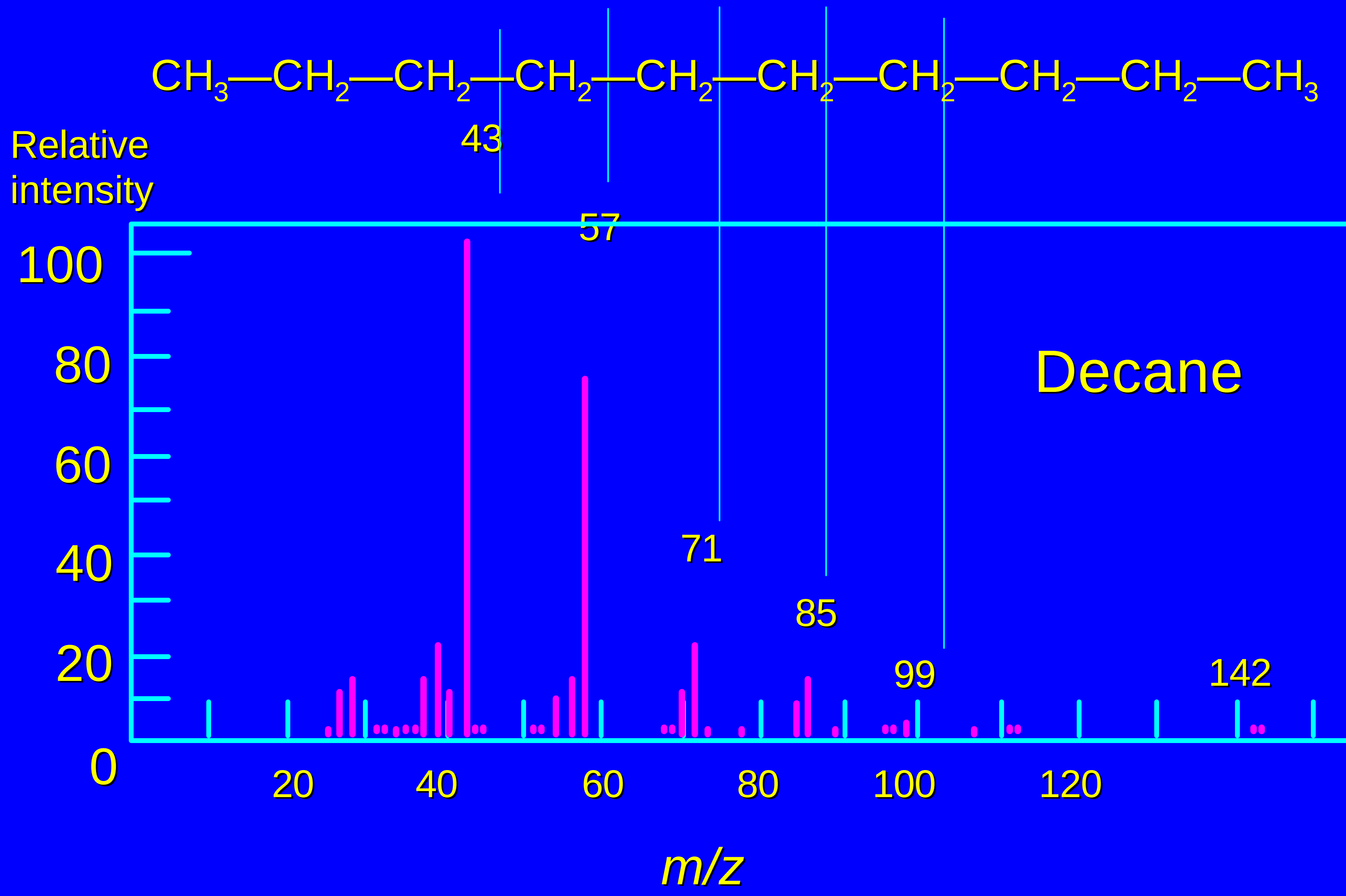
Isotopic Clusters in Chlorobenzene



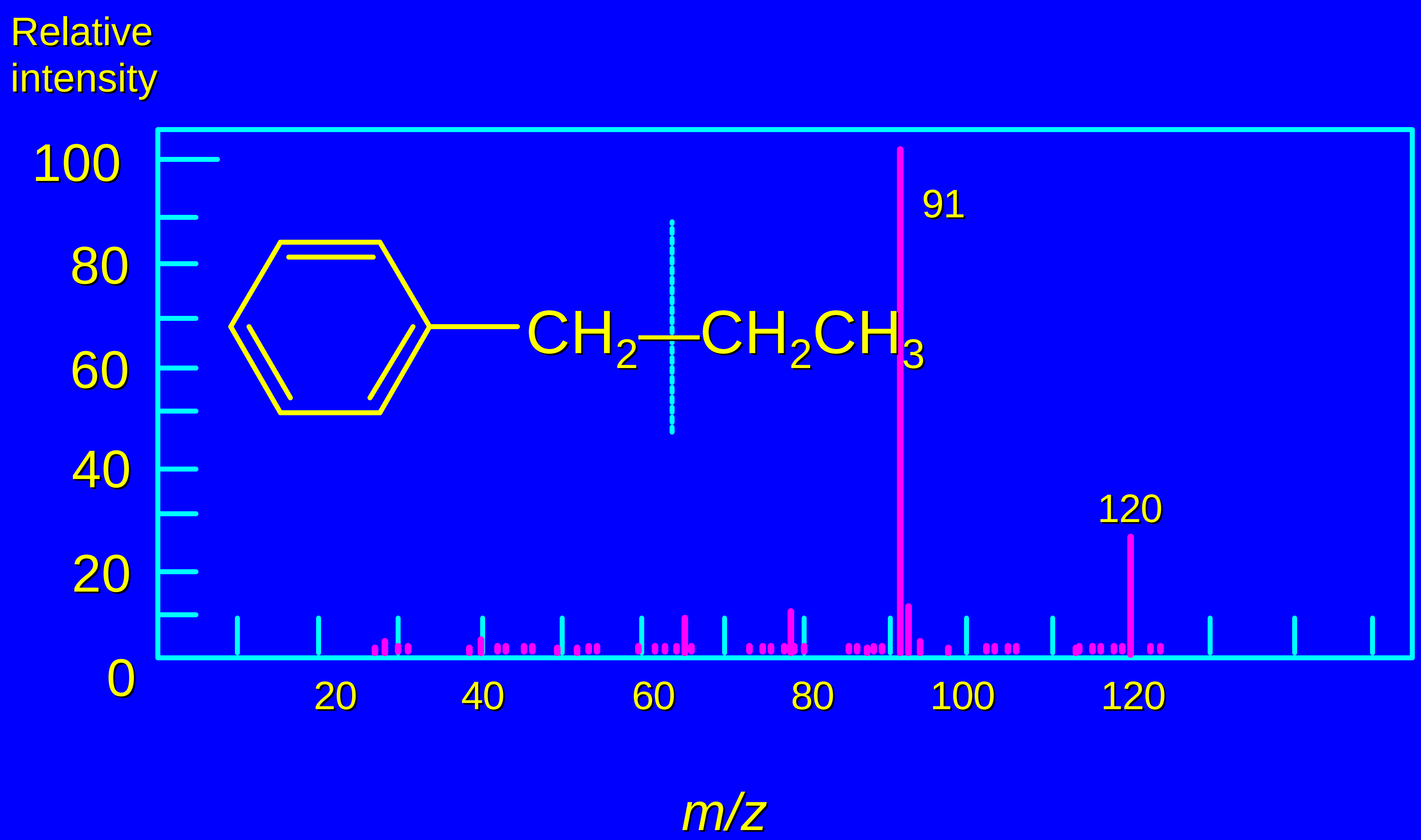
no *m/z* 77, 79 pair; therefore ion responsible for *m/z* 77 peak does not contain Cl



Alkanes undergo extensive fragmentation



Propylbenzene fragments mostly at the benzylic position



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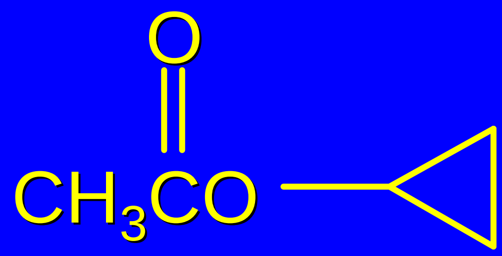
Molecular Formula

as a

Clue to Structure

Molecular Weights

	Heptane	Cyclopropyl acetate
Structure	$CH_3(CH_2)_5CH_3$	
Molecular formula	C_7H_{16}	$C_5H_8O_2$
Molecular weight	100	100
Exact mass	100.1253	100.0524

Mass spectrometry can measure exact masses. Therefore, mass spectrometry can give molecular formulas.

Molecular Formulas

Knowing that the molecular formula of a substance is C_7H_{16} tells us immediately that is an alkane because it corresponds to C_nH_{2n+2}

C_7H_{14} lacks two hydrogens of an alkane, therefore contains either a ring or a double bond

Index of Hydrogen Deficiency

relates molecular formulas to multiple bonds and rings

index of hydrogen deficiency =

$$\frac{1}{2}\text{ (molecular formula of alkane – molecular formula of compound)}$$

Example 1

C_7H_{14}

index of hydrogen deficiency

$$= \frac{1}{2}\text{(molecular formula of alkane – molecular formula of compound)}$$

$$= \frac{1}{2}(C_7H_{16} - C_7H_{14})$$

$$= \frac{1}{2}(2) = 1$$

Therefore, one ring or one double bond.

Example 2

C_7H_{12}

$$= \frac{1}{2}(C_7H_{16} - C_7H_{12})$$

$$= \frac{1}{2}(4) = 2$$

Therefore, two rings, one triple bond, two double bonds, or one double bond + one ring.

Oxygen has no effect

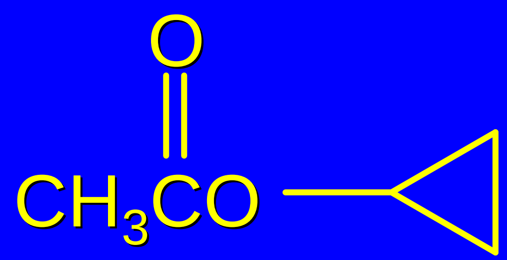
$CH_3(CH_2)_5CH_2OH$ (1-heptanol, $C_7H_{16}O$) has same number of H atoms as heptane

index of hydrogen deficiency =

$$\frac{1}{2}\ (C_7H_{16} - C_7H_{16}O)\ = 0$$

no rings or double bonds

Oxygen has no effect



Cyclopropyl acetate

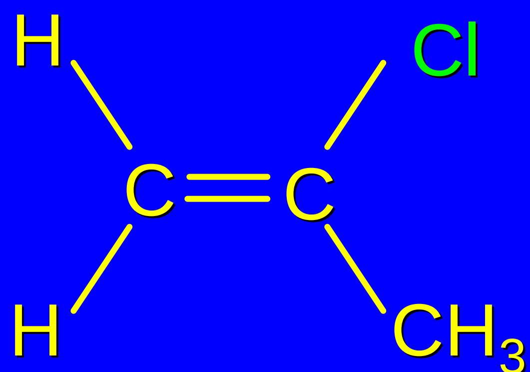
index of hydrogen deficiency =

$$\frac{1}{2}\left(C_5H_{12} - C_5H_8O_2\right) = 2$$

one ring plus one double bond

If halogen is present

Treat a halogen as if it were hydrogen.



C_3H_5Cl

same index of hydrogen deficiency as for C_3H_6

Rings versus Multiple Bonds

Index of hydrogen deficiency tells us the sum of rings plus multiple bonds.

Catalytic hydrogenation tells us how many multiple bonds there are.