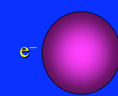
Mass Spectrometry

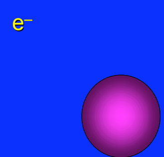
*Principles of Electron-Impact Mass Spectrometry*

Atom or molecule is hit by high-energy electron




*Principles of Electron-Impact Mass Spectrometry*

Atom or molecule is hit by high-energy electron




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

*Principles of Electron-Impact Mass Spectrometry*

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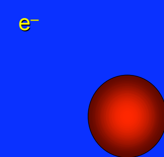
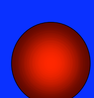



electron is deflected but transfers much of its energy to the molecule

*Principles of Electron-Impact Mass Spectrometry*

This energy-rich species ejects an electron.



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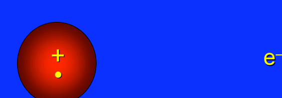



forming a positively charged, odd-electron species called the *molecular ion*

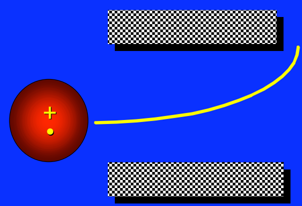
*Principles of Electron-Impact Mass Spectrometry*

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



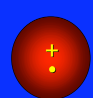

*Principles of Electron-Impact Mass Spectrometry*

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.

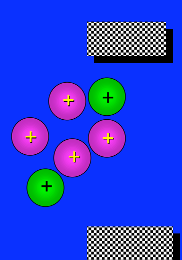

Usually several fragmentation pathways are available and a mixture of ions is produced.

*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*

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

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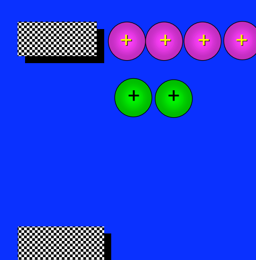
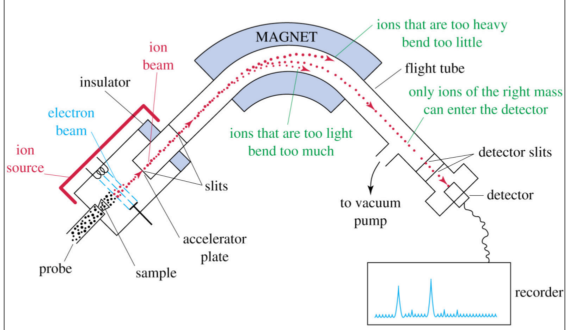
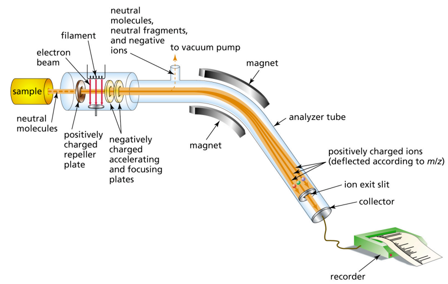
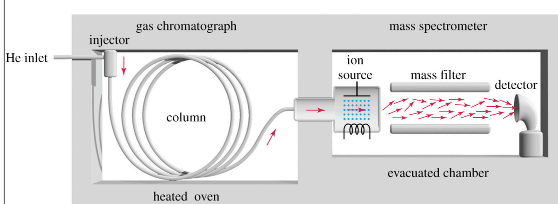


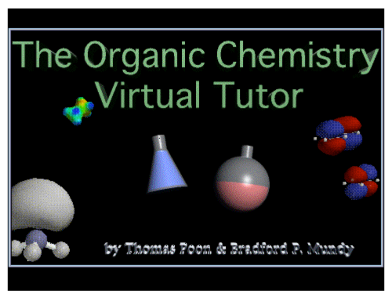



# A Mass Spectrometer

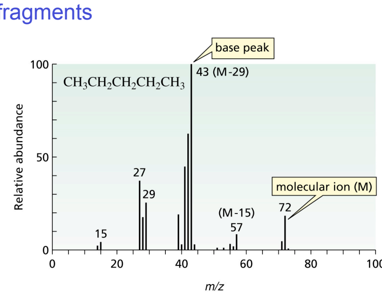
The mass spectrometer records a mass spectrum




A mass spectrum records only positively charged fragments




| m/z | Relative abundance |
|---|---|
| 73 | 0.52 |
| 72 | 18.56 |
| 71 | 4.32 |
| 57 | 11.20 |
| 43 | 100.00 |
| 42 | 55.27 |
| 41 | 37.93 |
| 39 | 12.44 |
| 29 | 26.65 |
| 28 | 17.75 |
| 27 | 31.22 |
| 15 | 4.22 |
| 14 | 2.56 |

*m/z* = mass to charge ratio of the fragment

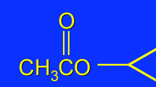
- *Nominal molecular mass*: the molecular mass to the nearest whole number
- Each *m/z* value is the nominal molecular mass of the fragment
- The peak with the highest *m/z* value usually represents the molecular ion (M)

Molecular Formula

as a

Clue to Structure

## *Molecular Weights*

| | $CH_3(CH_2)_5CH_3$ |   |
|---|---|---|
| | Heptane | Cyclopropyl acetate |
| 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 =

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

## *Example 1*

$C_7H_{14}$

index of hydrogen deficiency

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

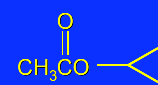
$CH_3(CH_2)_5CH_2OH$ (1-heptanol, $C_7H_{16}O$) has same number of H atoms as heptane

index of hydrogen deficiency =

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

no rings or double bonds

## *Oxygen has no effect*




Cyclopropyl acetate

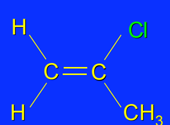
index of hydrogen deficiency =

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

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 $C_3H_6$

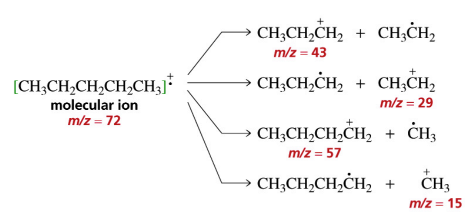
## *Rings versus Multiple Bonds*

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

Catalytic hydrogenation tells us how many multiple bonds there are.

- Peaks other than the molecular ion have smaller *m/z* values—called fragment ion peaks—represent positively charged fragments of the molecule
- The base peak is the peak with the greatest intensity, due to its having the greatest abundance
- Weak bonds break in preference to strong bonds
- Bonds that break to form more stable fragments break in preference to those that form less stable fragments

The base peak of 43 in the mass spectrum of pentane indicates the preference for C-2 to C-3 fragmentation



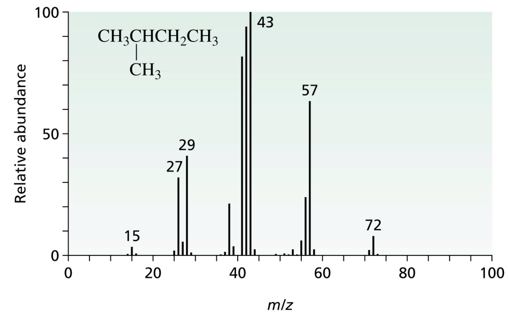

To identify fragment ions in a spectrum, determine the difference between the *m/z* value of a given fragment ion and that of the molecular ion

Carbocations can undergo further fragmentation

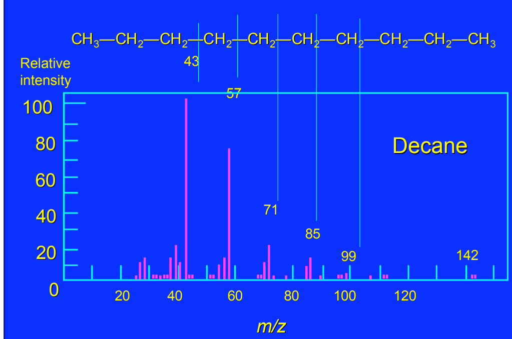
$$\overset{+}{CH_3CH_2CH_2} \;(m/z = 43) \xrightarrow{-H^\bullet} [CH_3CHCH_2]^{+\bullet} \;(m/z = 42) \xrightarrow{-H^\bullet} \overset{+}{CH_2}CH{=}CH_2 \;(m/z = 41)$$

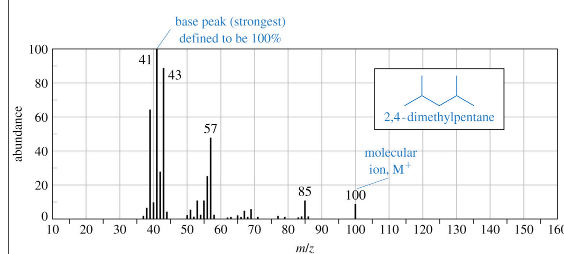
2-methylbutane has the same *m/z* as pentane

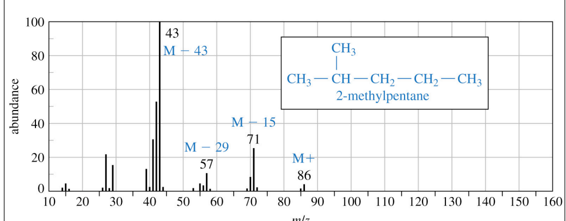
but the peak at *m/z* = 57 (M – 15) is more intense




*Alkanes undergo extensive fragmentation*

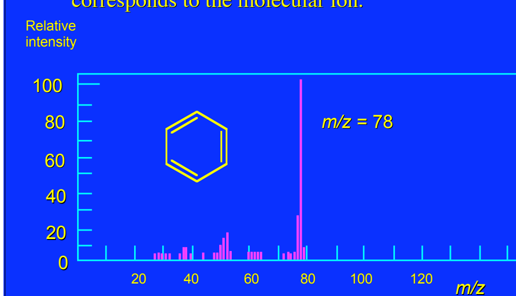


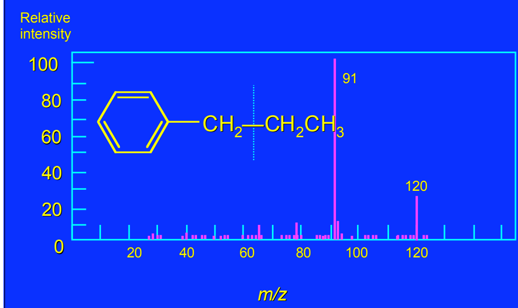




*Some molecules undergo very little fragmentation*

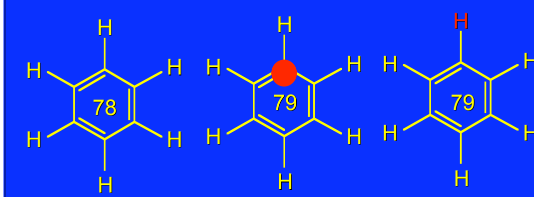
Benzene is an example. The major peak corresponds to the molecular ion.



## *Propylbenzene fragments mostly at the benzylic position*




## *Isotopic Clusters*

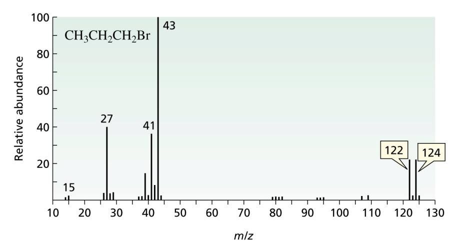



| 93.4% | 6.5% | 0.1% |
|---|---|---|
| all H are $^{1}H$ and all C are $^{12}C$ | one C is $^{13}C$ | one H is $^{2}H$ |

## Isotopes in Mass Spectrometry

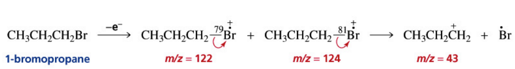
- peaks that are attributable to isotopes can help identify the compound responsible for a mass spectrum
- M + 2 peak: a contribution from $^{18}O$ or from two heavy isotopes in the same molecule
- a large M + 2 peak suggests a compound containing either chlorine or bromine: a Cl if M + 2 is 1/3 the height of M; a Br if M + 2 is the same height as M
- In calculating the molecular masses of molecular ions and fragments, the atom mass of a single isotope of an atom must be used

## The Mass Spectrum of Bromopropane



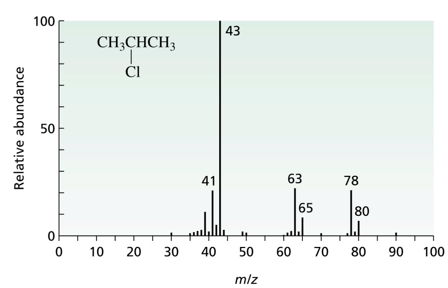

The weakest bond is the C–Br bond

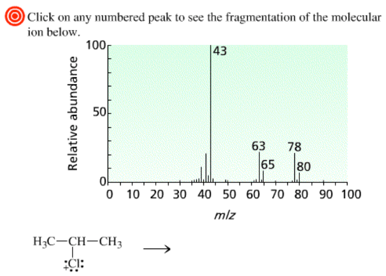
The base peak is at *m/z* = 43 [M – 79, or (M + 2) – 81]




The propyl cation has the same fragmentation pattern it exhibited when it was formed in the cleavage of pentane

## The Mass Spectrum of 2-Chloropropane



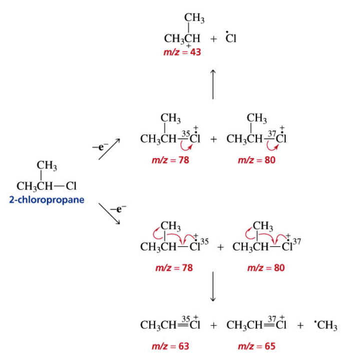


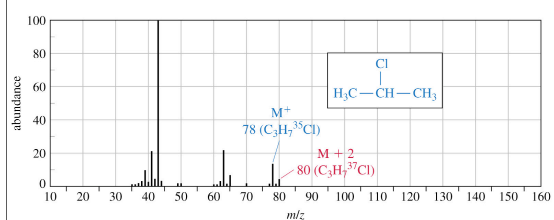

The compound contains a chlorine, because M + 2 peak is 1/3 the height of the molecular ion peak

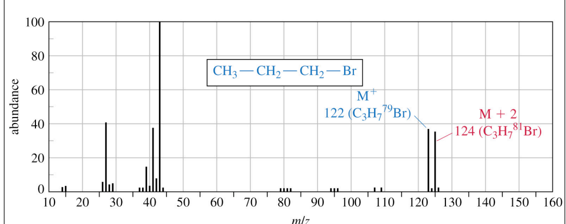
The base peak at $m/z$ = 43 results from heterolytic cleavage of the C–Cl bond

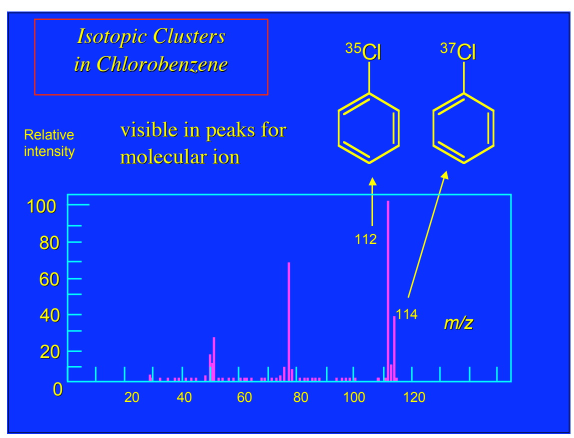
The peaks at $m/z$ = 63 and $m/z$ = 65 have a 3:1 ratio, indicating the presence of a chlorine atom

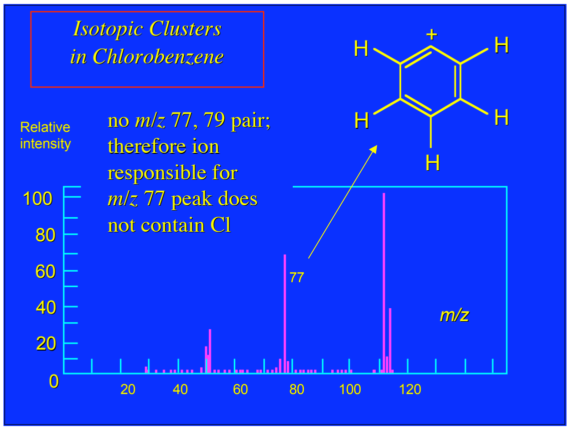
$\alpha$ cleavage results from the homolytic cleavage of a C–C bond at the $\alpha$ carbon



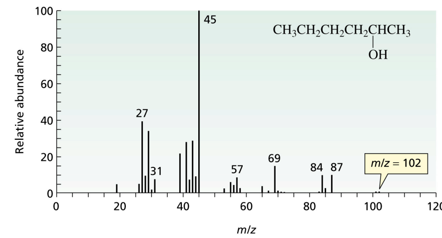



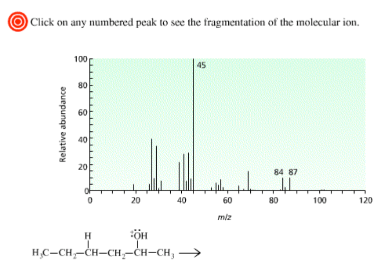



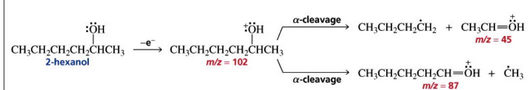



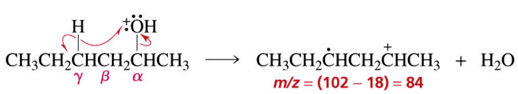


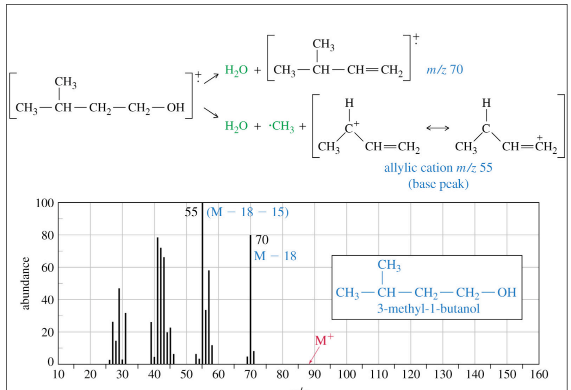

## The Fragmentation of Alcohols



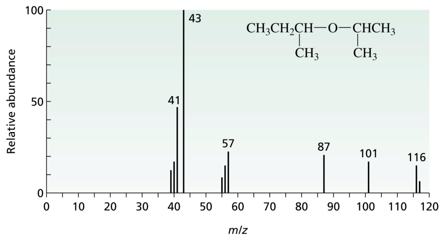



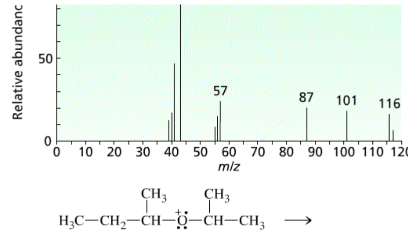



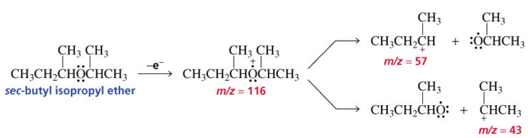



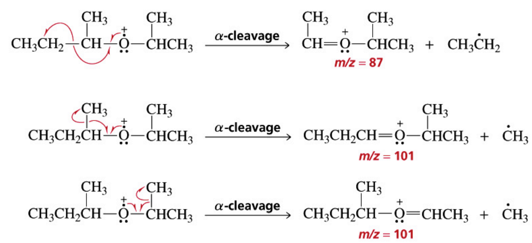



# The Fragmentation Pattern of Ethers



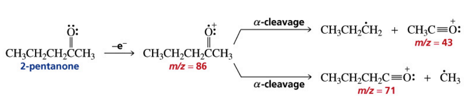



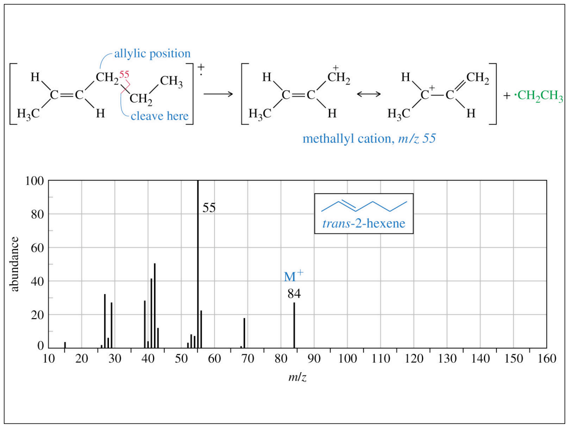




# Fragmentation Pattern of Ketones

An intense molecular ion peak




McLafferty rearrangement may occur


allylic position
cleave here
55
methallyl cation, m/z 55
+ ·CH2CH3
trans-2-hexene
abundance
m/z
M+
84
55