HIGH RESOLUTION MASS SPECTROMETRY

- Mass spectrometry is used to find the relative molecular mass (M_r) of compounds.

- Compounds are converted into 1+ ions (often called the molecular ion)

	Electron impact	Electrospray ionisation
What it does	removes one electron to form M+ ion $M(g) \rightarrow M^+(g) + e^-$	Adds one proton to form MH+ ion $M(g) + H^+(g) \rightarrow MH^+(g)$
Which compounds	Compounds with low M_r	Compound with high M_r (e.g. proteins)
How is it done	High energy electrons (from an "electron gun" are fired at the sample).	The compound is dissolved in a volatile solvent and sprayed out into a fine mist via a hypodermic needle whose tip is connected to the positive terminal of a high voltage power supply.

- Note that electron impact often breaks the molecular ion into smaller fragments. In this work we are ignoring (and not showing) any fragments.

The impact of ^{13}C and ^{2}H isotopes on signals for the molecular ion

- Spectra measure the mass of individual ions that hit the detector. Therefore whether an ion contains a ^{13}C rather than a ^{12}C atom, or ^{2}H instead of ^{1}H, affects the mass detected.

- The more C and H atoms there are in an organic molecule, the more chance of there being one ^{13}C (1.1% of C atoms) or one ^{2}H atom (0.015% of H atoms). There is often a small peak with a value that is 1 greater than that for the molecular ion.
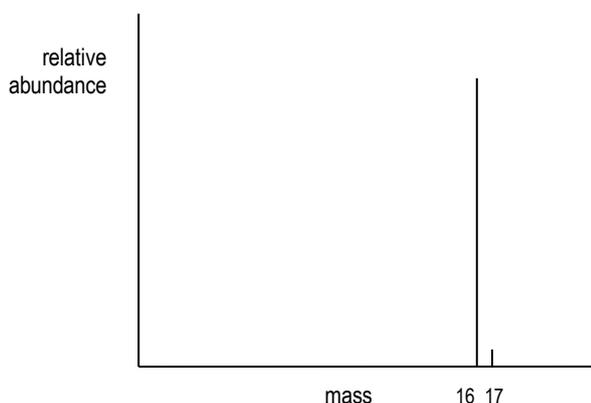
Isotopes of Cl and Br

- Chlorine contains 75% ^{35}Cl and 25% ^{37}Cl (and so ¾ of Cl atoms have mass 35 and ¼ of Cl atoms have mass 37)

- Bromine contains 50% ^{79}Br and 50% ^{81}Br (and so ½ of Br atoms have mass 79 and ½ of Br atoms have mass 81)

- Molecular ions in compounds containing chlorine or bromine are impacted significantly by these isotopes.

Compound	Molecule	Mass	Probability	Mass spectrum peaks
CH_3Cl	$CH_3{}^{35}Cl$	50	$\frac{3}{4}$	2 signals @ 50, 52 in ratio 3:1
	$CH_3{}^{37}Cl$	52	$\frac{3}{4}$	
CH_2Cl_2	$CH_2{}^{35}Cl_2$	84	$\frac{3}{4} \times \frac{3}{4} = \frac{9}{16}$	3 signals @ 84, 86, 88 in ratio 9:6:1
	$CH_2{}^{35}Cl^{37}Cl$	86	$\frac{3}{4} \times \frac{1}{4} = \frac{3}{16}$ ⎱ $\frac{6}{16}$	
	$CH_2{}^{37}Cl^{35}Cl$		$\frac{1}{4} \times \frac{3}{4} = \frac{3}{16}$ ⎰	
	$CH_2{}^{37}Cl_2$	88	$\frac{1}{4} \times \frac{1}{4} = \frac{1}{16}$	

TASK 1 – Molecular ion peaks

- For the compounds shown, determine the mass of each molecular ion and their relative abundance.
- Assume that all C atoms are ^{12}C and all H atoms are ^{1}H
- Bromine atoms are 50% ^{79}Br and 50% ^{81}Br
- Chlorine atoms are 75% ^{35}Cl and 25% ^{37}Cl

1) CH_3Br

2) CH_2Br_2

3) CH_2BrCl

4) CCl_4

- Most mass spectrometers record masses to the nearest 1 or 0.1, but high-resolution mass spectrometers record masses to a much higher resolution (e.g. 0.0001).

- The M_r given by a high-resolution mass spectrometer allows the **molecular formula** of a compound to be determined.

type of mass spectrometer	low-resolution	high-resolution
resolution of M_r	nearest unit (e.g. 60)	0.0001 or better (e.g. 60.0211)
what it tell us	M_r to nearest unit	M_r to to high resolution molecular formula

- High-resolution mass spectrometry does not identify a compound, but it does give the **molecular formula**.

- For example:

  - if a low-resolution mass spectrometer gives M_r = 60, then there are many compounds it could be with several different molecular formulas (e.g. propan-1-ol, propan-2-ol, methoxyethane, ethanoic acid, methyl methanoate, urea)

  - if a high-resolution mass spectrometer gives M_r = 60.0211 then it indicates that the molecular formula mass be $C_2H_4O_2$ narrowing down what the compound could be (ethanoic acid or methyl methanoate)

Low resolution M_r	High resolution M_r	Molecular formula	Possible compounds	
60	60.0211	$C_2H_4O_2$	CH_3COOH	ethanoic acid
			$HCOOCH_3$	methyl methanoate
60	60.0575	C_3H_8O	$CH_3CH_2CH_2OH$	propan-1-ol
			$CH_3CH(OH)CH_3$	propan-1-ol
			$CH_3OCH_2CH_3$	methoxethane
60	60.0324	CH_4N_2O	H_2NCONH_2	urea

TASK 2 – High-resolution mass spectrometry problems

In this task, assume that the H, C, N and O atoms are ^1H, ^{12}C, ^{14}N and ^{16}O

Accurate masses of atoms:

^1H	^{12}C	^{14}N	^{16}O	^{35}Cl	^{37}Cl
1.0078	12.0000	14.0031	15.9949	34.9689	36.9659

1)   How could high-resolution mass spectroscopy be used to distinguish propane and ethenol?

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2) A compound is found to have an accurate relative formula mass of 46.0417. It is thought to be either CH_3CH_2OH or $H_2NCH_2NH_2$. Calculate the M_r of each compound to 4 decimal places to work out which one it is.

CH_3CH_2OH ....

$H_2NCH_2NH_2$ ....

Molecular formula of compound = ……………………………………...

3) High-resolution mass spectroscopy showed the M_r of difluoromethane to be 52.0124. The only stable isotope of fluorine is ^{19}F. Calculate the mass of one atom of ^{19}F to 4 decimal places.

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4) Calculate the accurate mass to 4 decimal places of the two molecular ion peaks in the high-resolution mass spectrum of chloroethane.

peak 1 ....

peak 2 ....

5) Analysis of an organic compound showed that its relative formula mass is 102. High resolution mass spectroscopy showed it to be 102.0678.

a) Calculate the M_r to 4 decimal places of each of these molecular formulas (which have M_r = 102) and then determine the correct molecular formula.

$C_5H_{14}N_2$ ....

$C_5H_{10}O_2$ ....

$C_3H_6N_2O_2$ ....

Molecular formula = ………………………………………….

b) Identify two possible compounds that have M_r = 102.0678

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