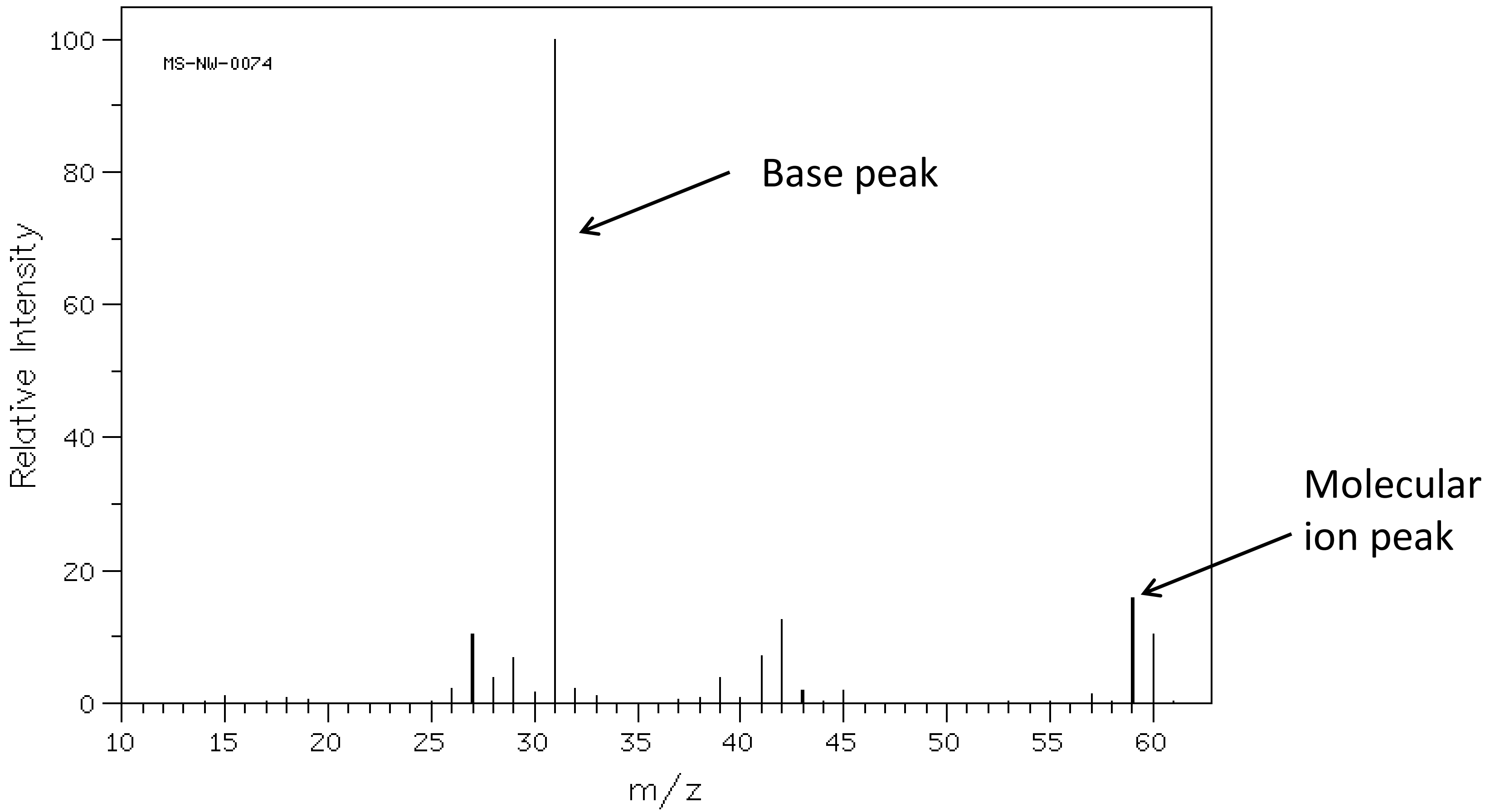
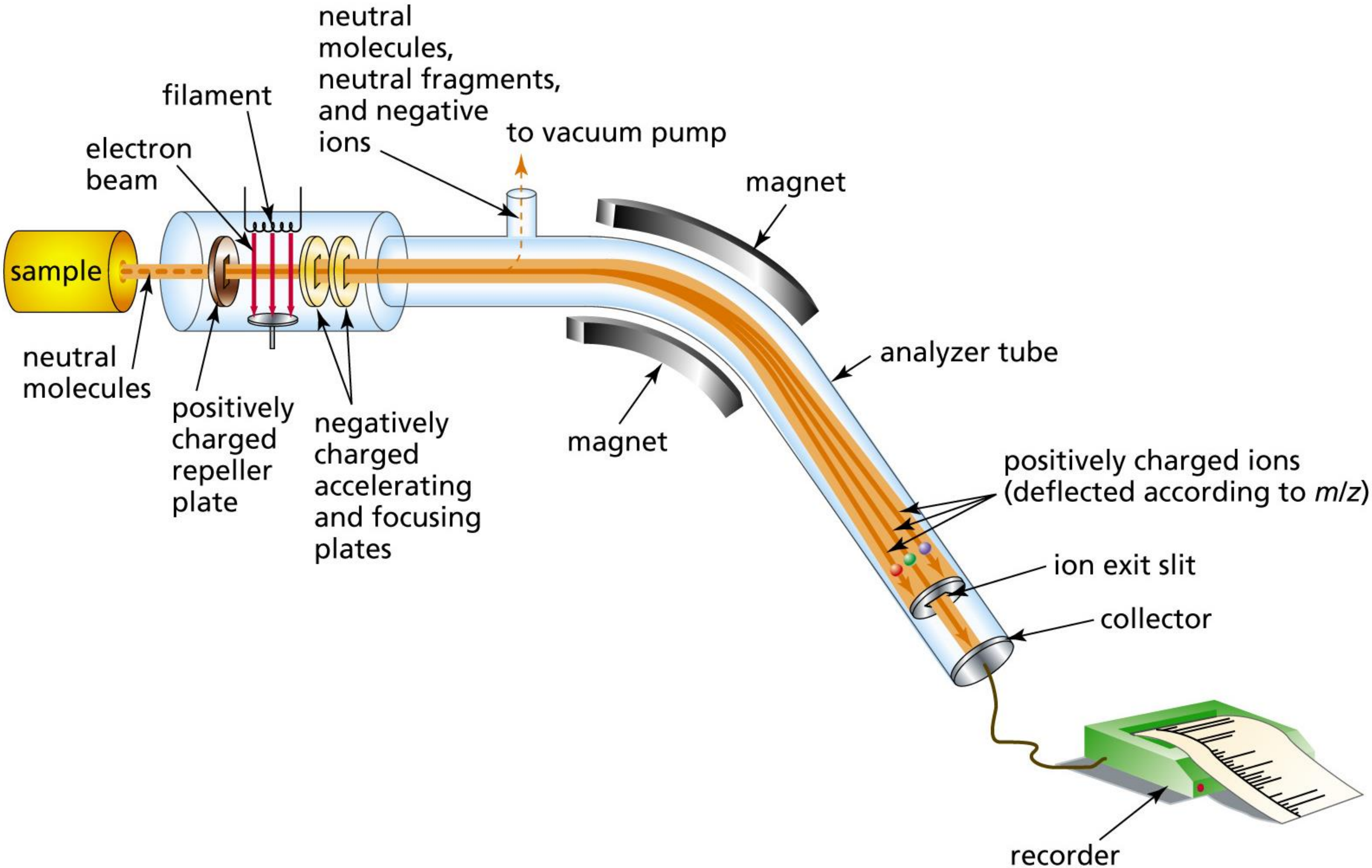
Mass spectrometry

- Measures the mass to charge ratio of molecules
- Gives structural (fragmentation) information about a compound
- Give the molecular mass of the compound



Mass spectrometry



Mass spectrometry

The mass spectrometer bombards the sample with electrons this knocks one electron off the molecule and forms a cation with the same mass as the molecular mass.

This cation is measured as the molecular peak and is often noted as [M^+]. M for molecular mass and $^+$ indicating a $^+$ charge.

Other peaks are also present in the mass spectrum, they are a result of fragmentation and atomic isotopes. We will look at how to interpret these later.

Only positively charged compounds (cations) will be detected by mass spectrometry.

Mass spectrometry

Firstly: Mass spectrometry usually tells us the **molecular mass** of the compound

Secondly: The molecular mass of a compound can inform us about the presence of nitrogen atoms in a compound. If the molecular mass is odd there will be an odd number of nitrogen atoms. If the molecular mass is even there will be either no nitrogen atoms or an even number of nitrogen atoms. This is the nitrogen rule.

eg. CH_3CH_3 m/z = 30, $CH_3CH_2NH_2$ m/z = 45, $H_2NCH_2CH_2NH_2$ m/z = 60

Do now:

Where would the molecular ion peak be in the mass spectrum for the following compounds?

$C_4H_{10}O$

$CH_3CH_2CONH_2$

2-methylbutanoic acid

but-1-ene

Isotope analysis

The m/z value measured depends on the isotopes of the atoms present in the particular compound being measured.

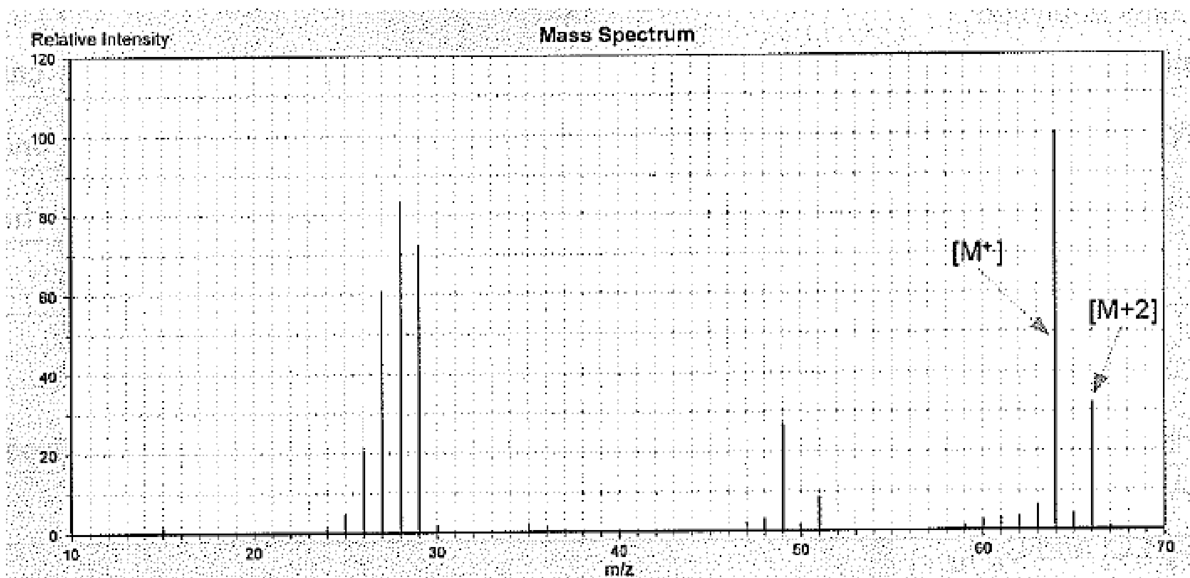
In most mass spectra you will find a small peak at $M^+ + 1$ on the spectra to the right of the molecular ion peak. This corresponds to the ^{13}C isotope present in a compound whose mass was measured.

Mass spectra are particularly useful for identifying the presence of halogens in a compound because their isotopes have different masses.

Chlorine isotopes

<u>Chlorine</u> has two isotopes ^{35}C and ^{37}C. They are naturally present in a 3:1 ratio (ie 75% abundance ^{35}C and 25% abundance ^{37}C). This shows up in the mass spec in the molecular ion peak (and any other fragment peak with Cl in it).

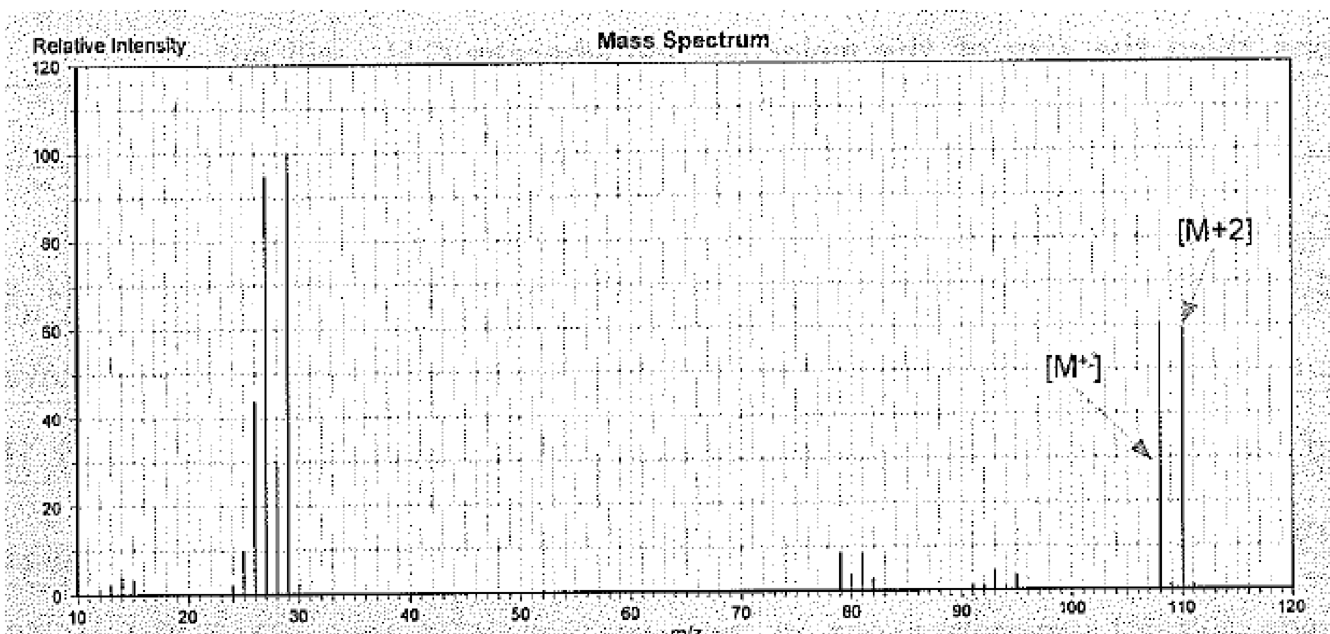
The mass spectrum will have a characteristic M^+ peak and a $M^+ + 2$ peak **1/3** of the size.



Isotope analysis

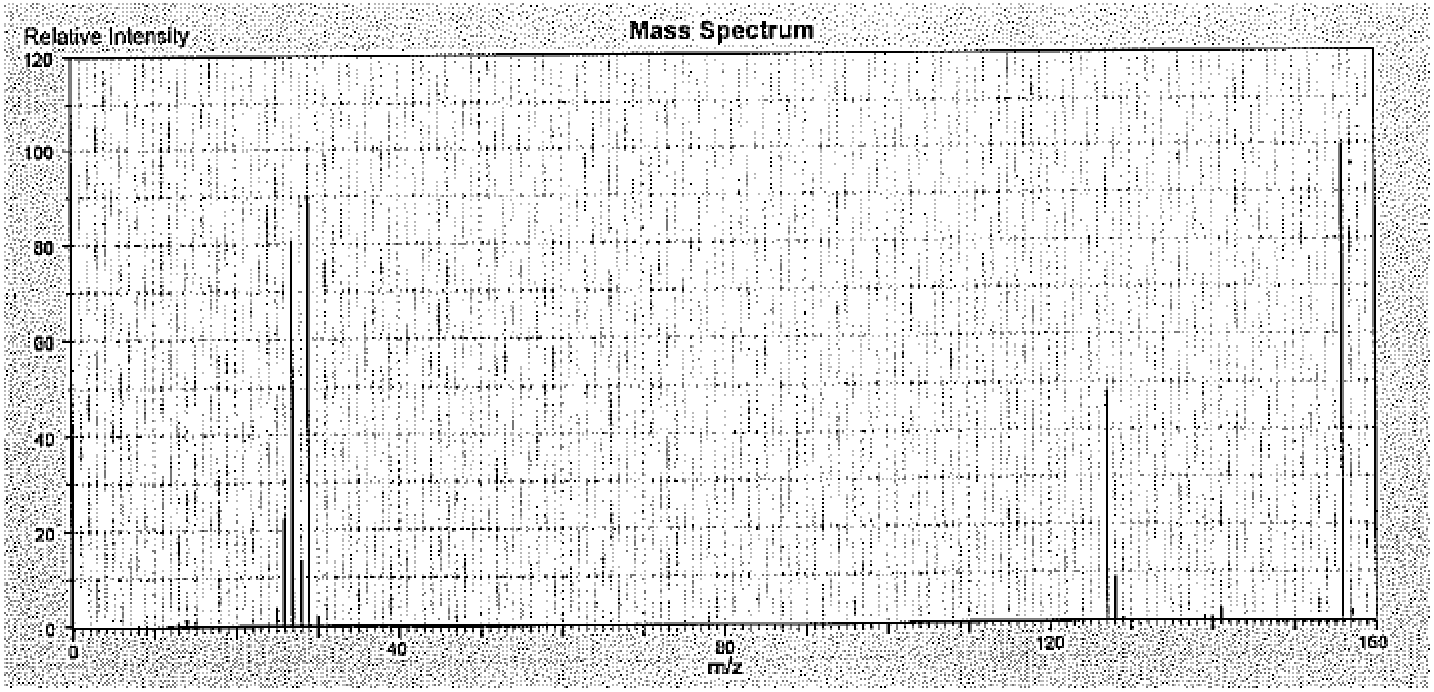
Bromine has two isotopes ^{79}Br and ^{81}Br. They are naturally present in a 1:1 ratio (ie 50% abundance ^{79}Br and 50% abundance ^{81}Br). This shows up in the mass spec in the molecular ion peak (and any other fragment peak with Br in it).

The mass spectrum will have a characteristic M^+ peak and a $M^+ + 2$ peak the **same** size.



Isotope Analysis

Iodine does not have multiple isotopes. But its large mass (127) makes it very distinctive.
The molecular ion will usually be well separated from other fragmentation peaks (there will be a peak for loss of I, and sometimes a I^+ (127) or HI^+ (128) peak.



Do now:

What would expect the molecular ion peak to look like for the following compounds?

C_4H_9Cl $4 \times 12 + 9 + 35 = 92$

Molecular ion peak would be at 92, with a peak 1/3 the size at 94 for ^{37}Cl isotope

C_2H_5Br $2 \times 12 + 5 + 79 = 108$

Molecular ion peak would be at 108, with a peak the same size at 110 for ^{81}Br isotope

propanoic acid $3 \times 12 + 6 + 2 \times 16 = 74$

Molecular ion peak would be at 74, with a small peak at 75 for ^{13}C isotope

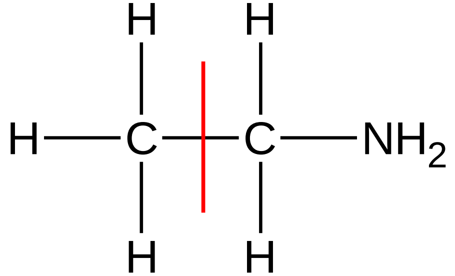
2-chloropropanal $3 \times 12 + 7 + 35 = 78$

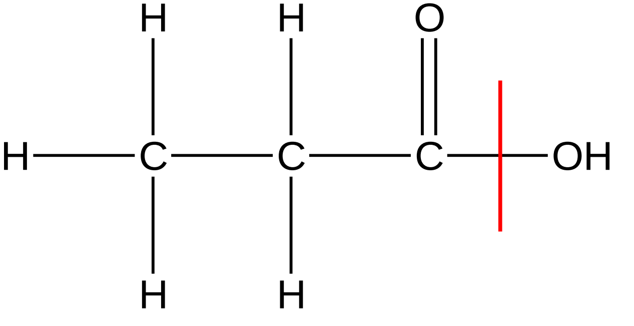
Molecular ion peak would be at 78, with a peak 1/3 the size at 80 for ^{37}Cl isotope

Fragmentation analysis

Because the molecules are bombarded with electrons during the process of collecting the mass spectrum they are exposed to a lot of energy. One way to dissipate this energy is by breaking bonds. This is called fragmentation and these fragments are also measured in the mass spectrum.

Weak bonds in the compound usually break and we see peaks for them or the molecule that is left behind without them.





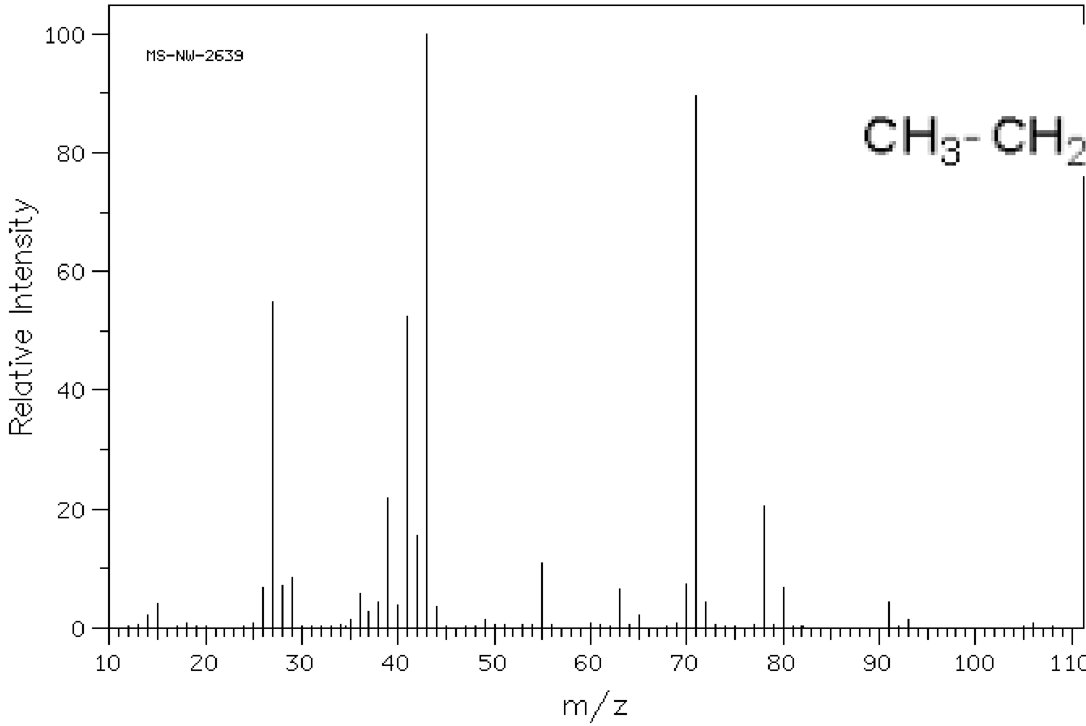
Do now:

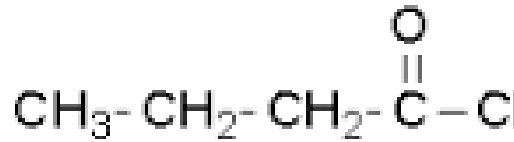
What is a fragment in mass spectroscopy?

Why do molecules form fragments in mass spectroscopy?

Butanoyl chloride has a molecular ion peak at 106 ppm, what would you expect the molecular ion peak to look like in the mass spectrum?

Fragmentation analysis





What bonds do you think might break to form fragments in the mass spectrum?

Butanoyl chloride has a fragment in its mass spectrum at 71 m/z. What is this fragment a result of?

What is the fragment at 43 m/z a result of?

Fragmentation analysis

Fragments that are likely to break off a molecule:

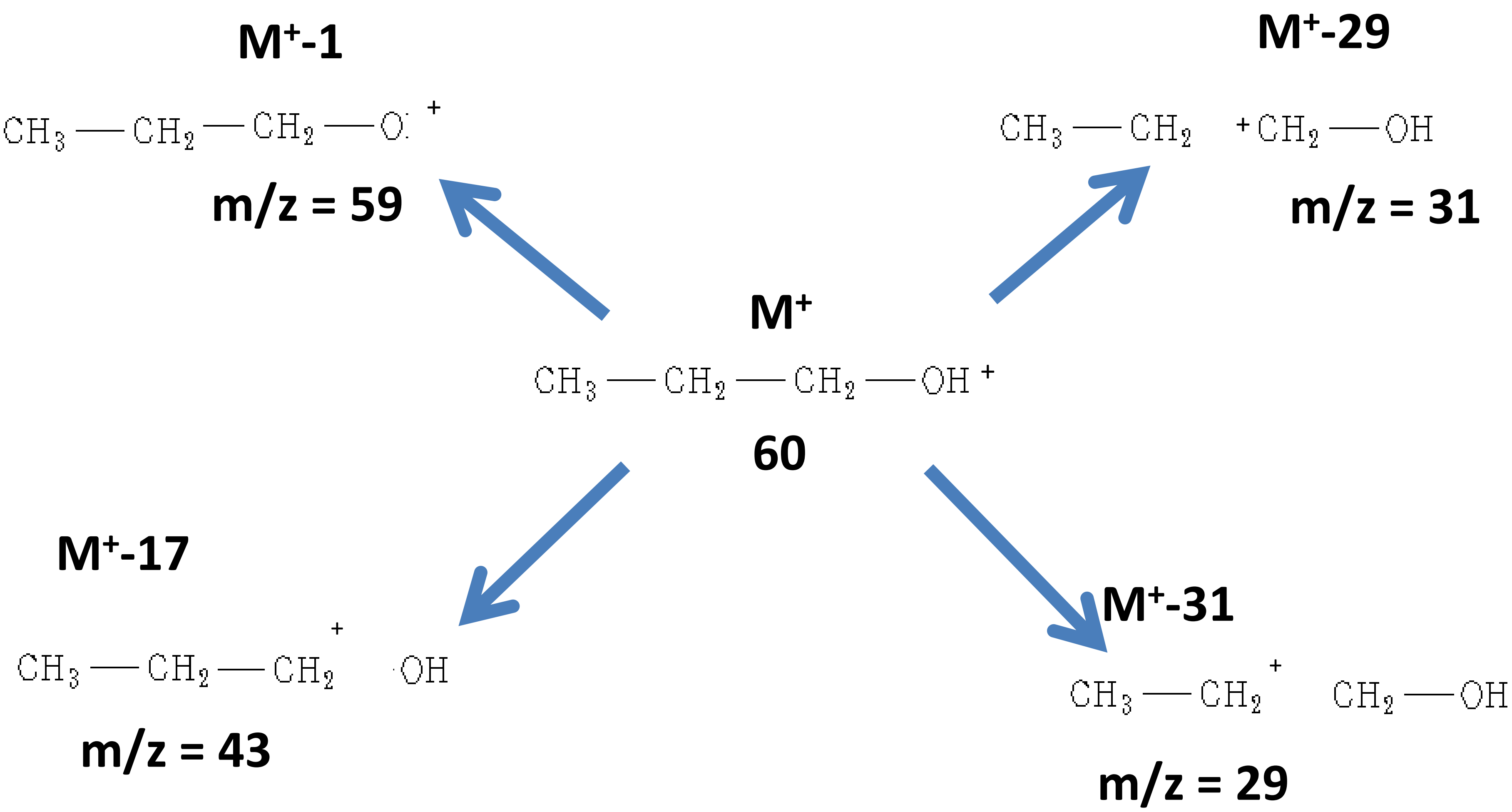
- H bonded to O or N
- OH
- OH_2
- COOH

Bonds that are likely to break

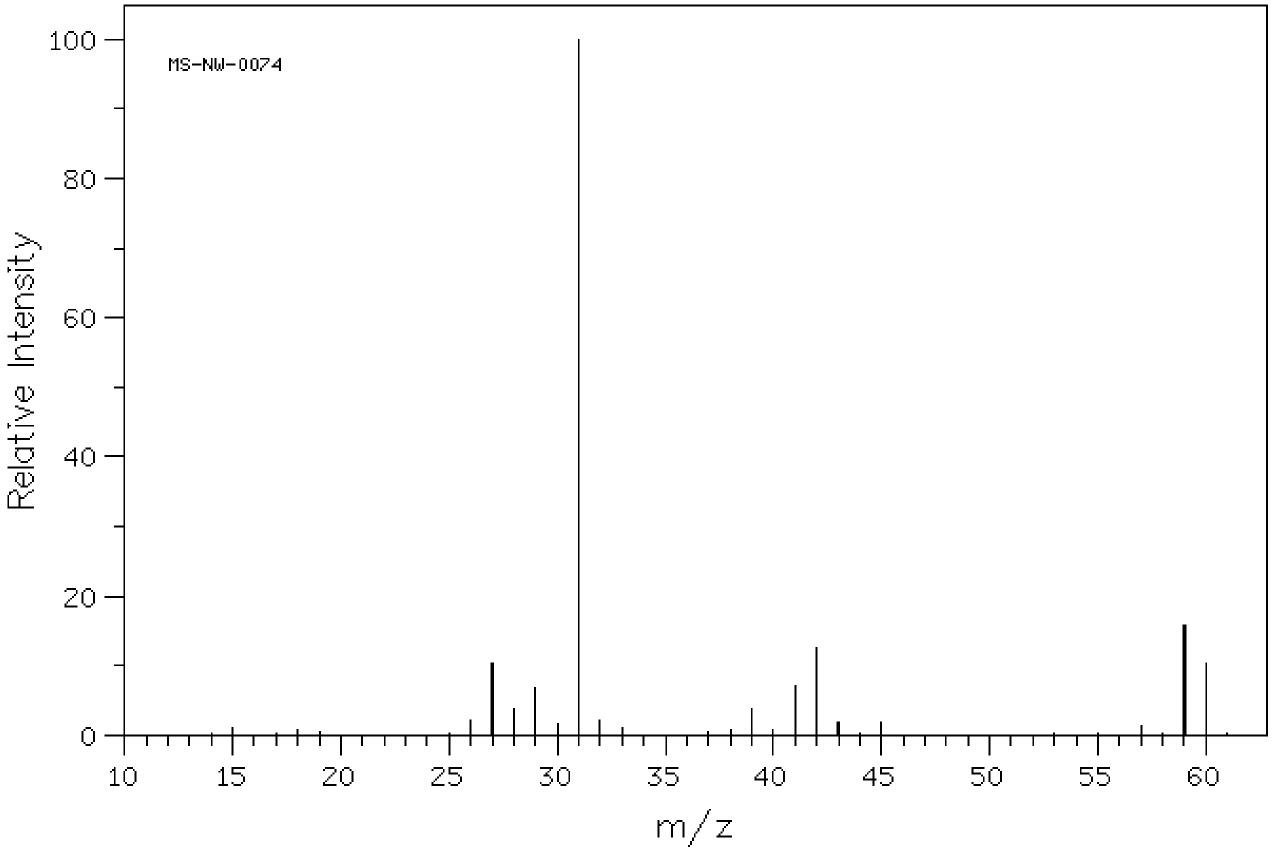
- Ester bonds
- Amide bonds
- Bonds connected to a carbonyl (C=O) group

- Carbon carbon bonds where one carbon is bonded to an O or N

Fragmentation analysis

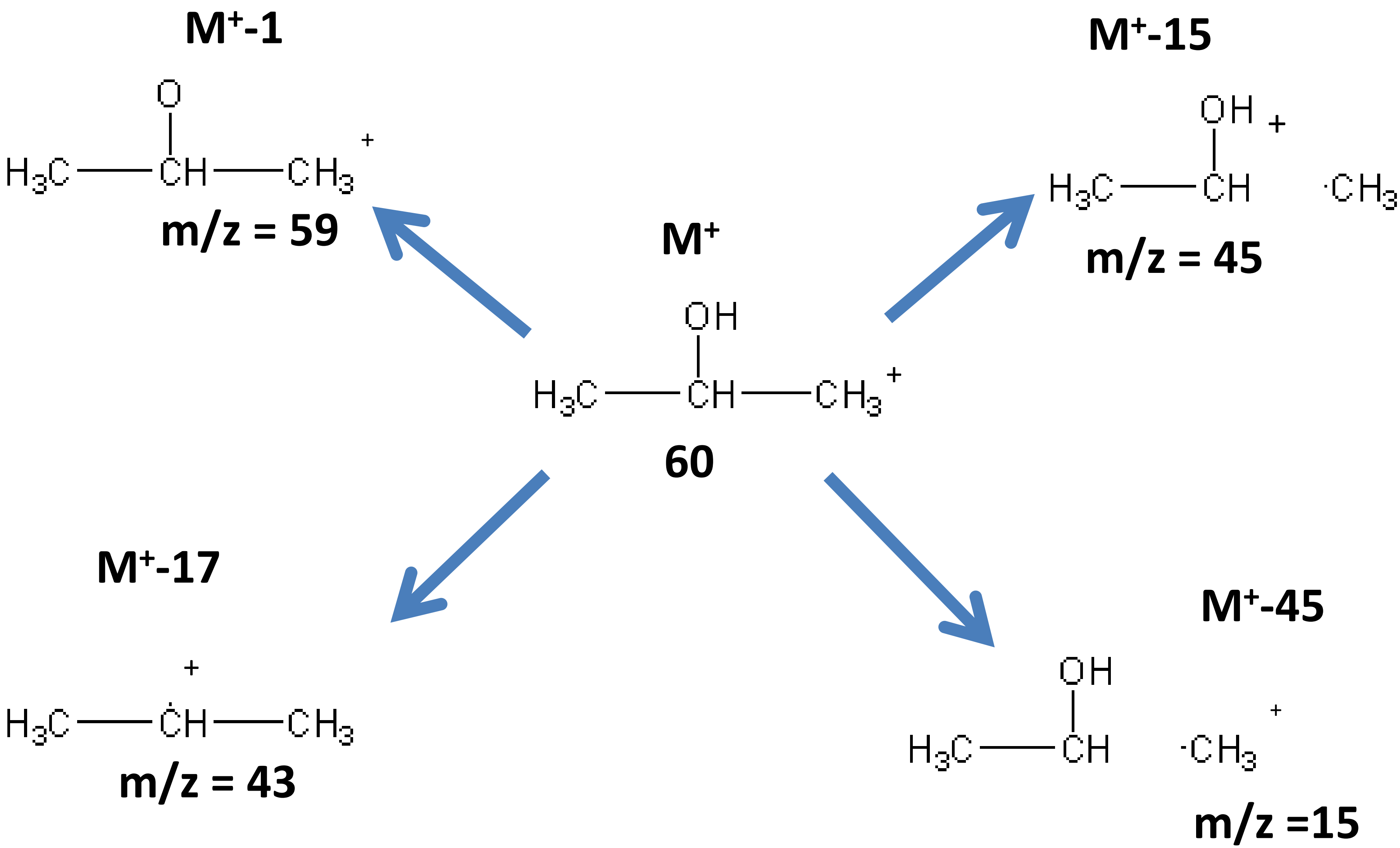


Fragmentation analysis

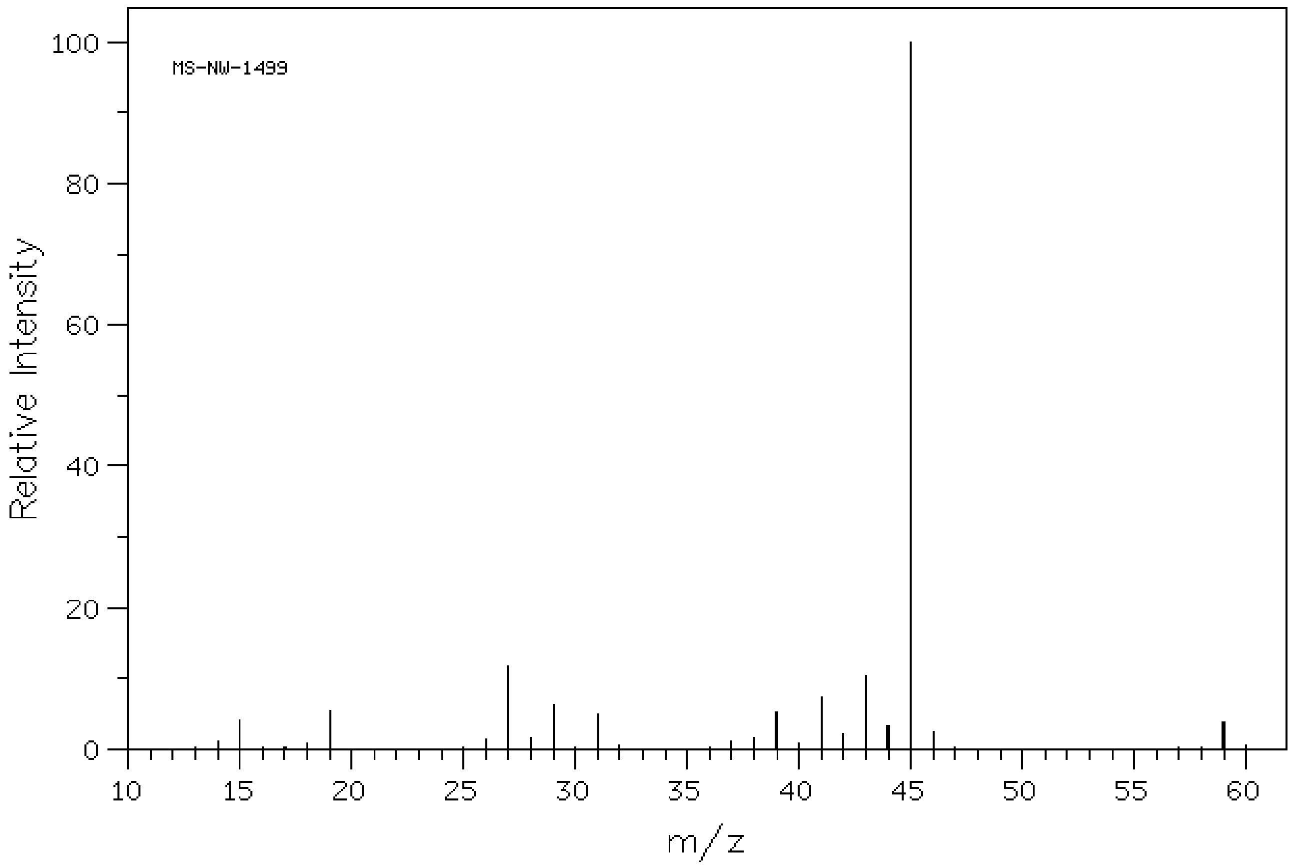


Peaks	Peaks
60	M+
59	M+ -1
43	M+ -17
31	**M+ - 29**
29	M+ - 31

Fragmentation analysis

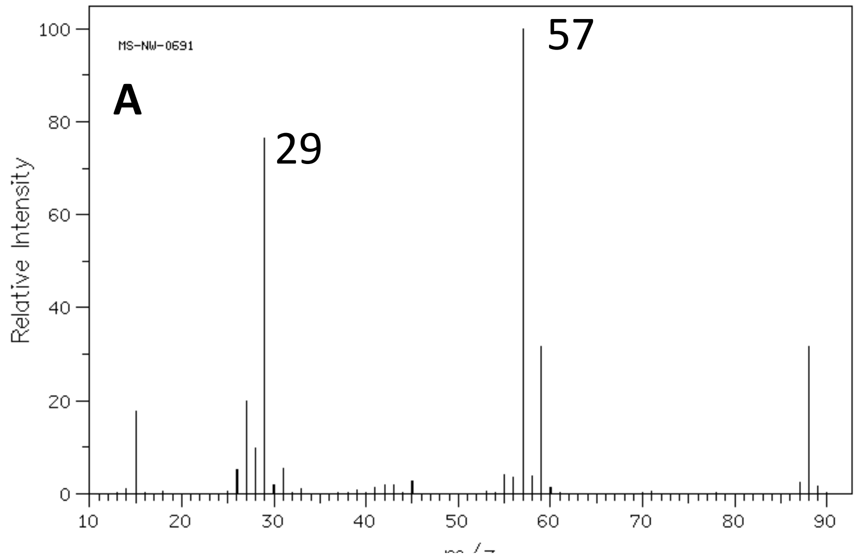


Fragmentation analysis

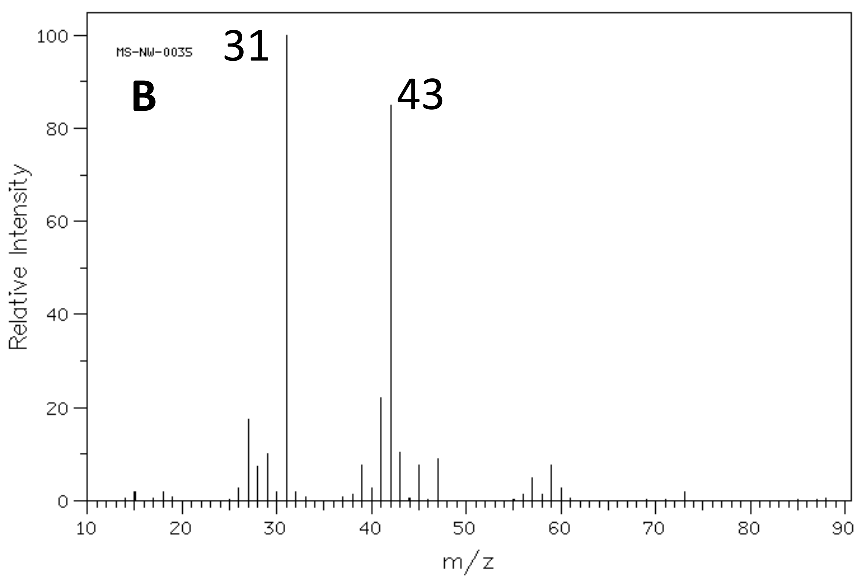


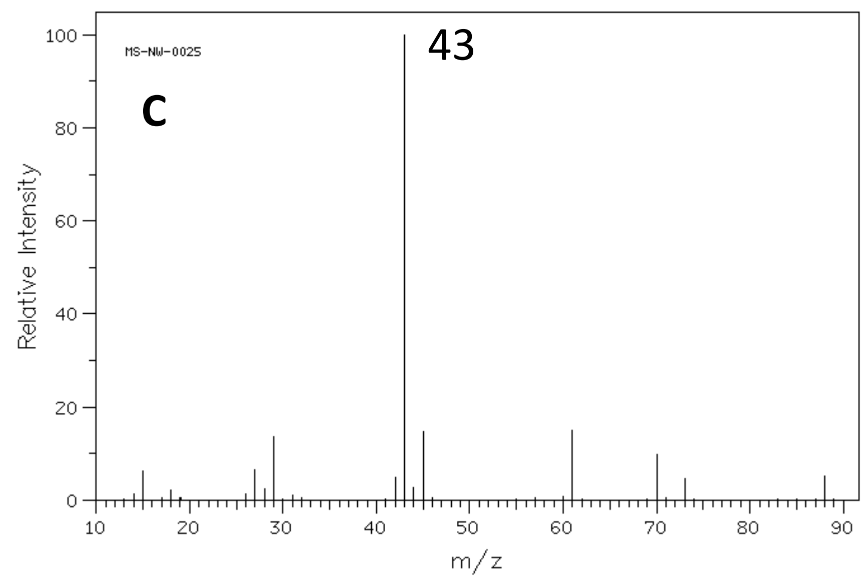
Peaks	Peaks
60	M+
59	M+ -1
45	**M+ -15**
43	**M+ -17**
15	**M+ -45**

Fragmentation analysis

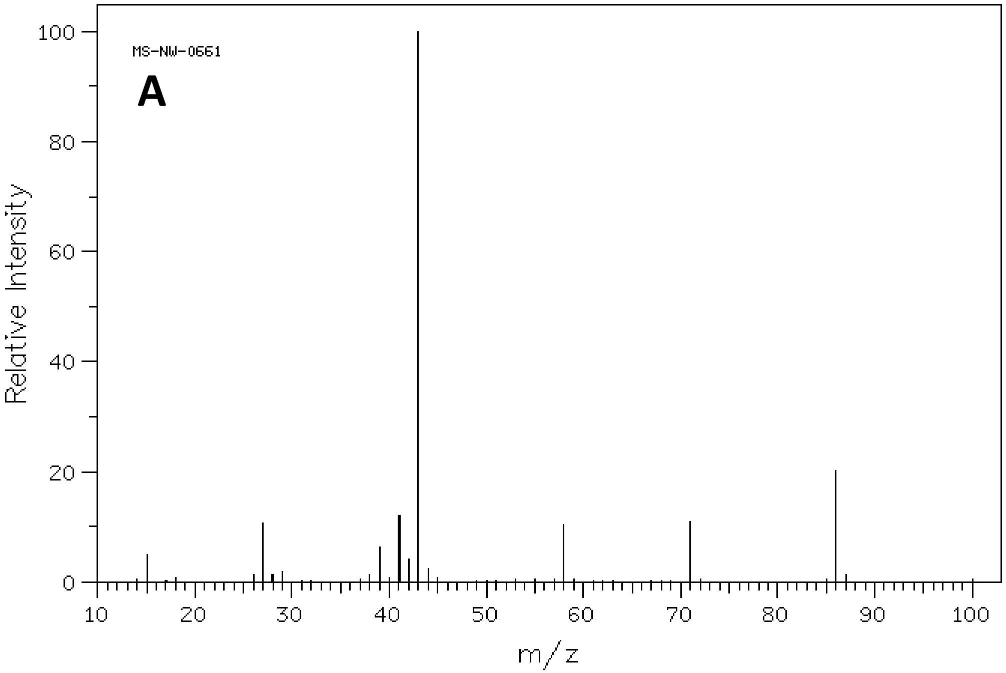


These three mass spec are from three different esters with the formula $C_4H_8O_2$. Can we decide which ester belongs to which mass spec?

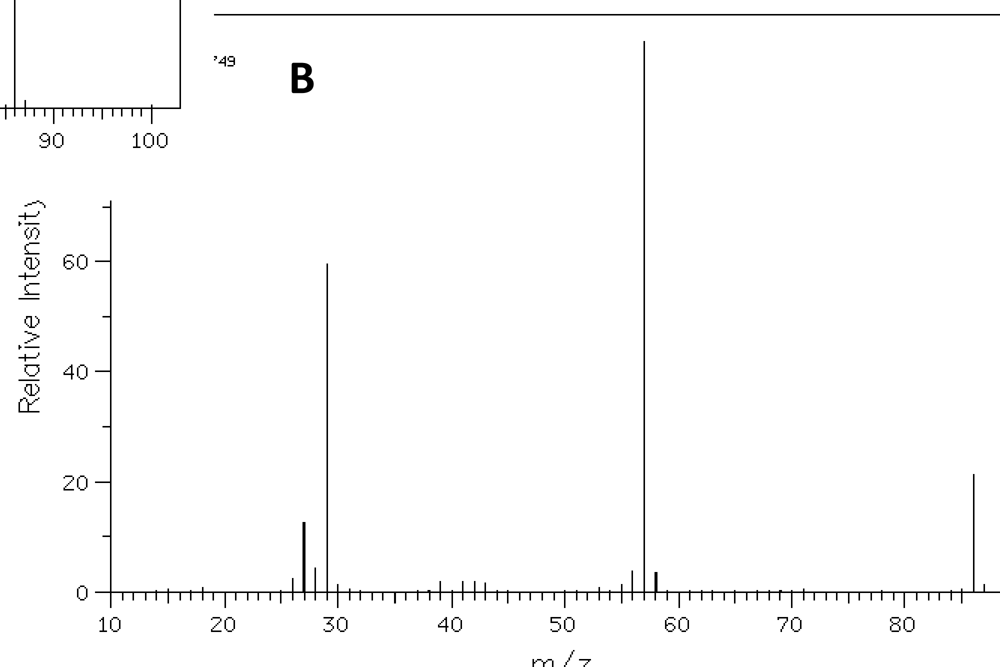




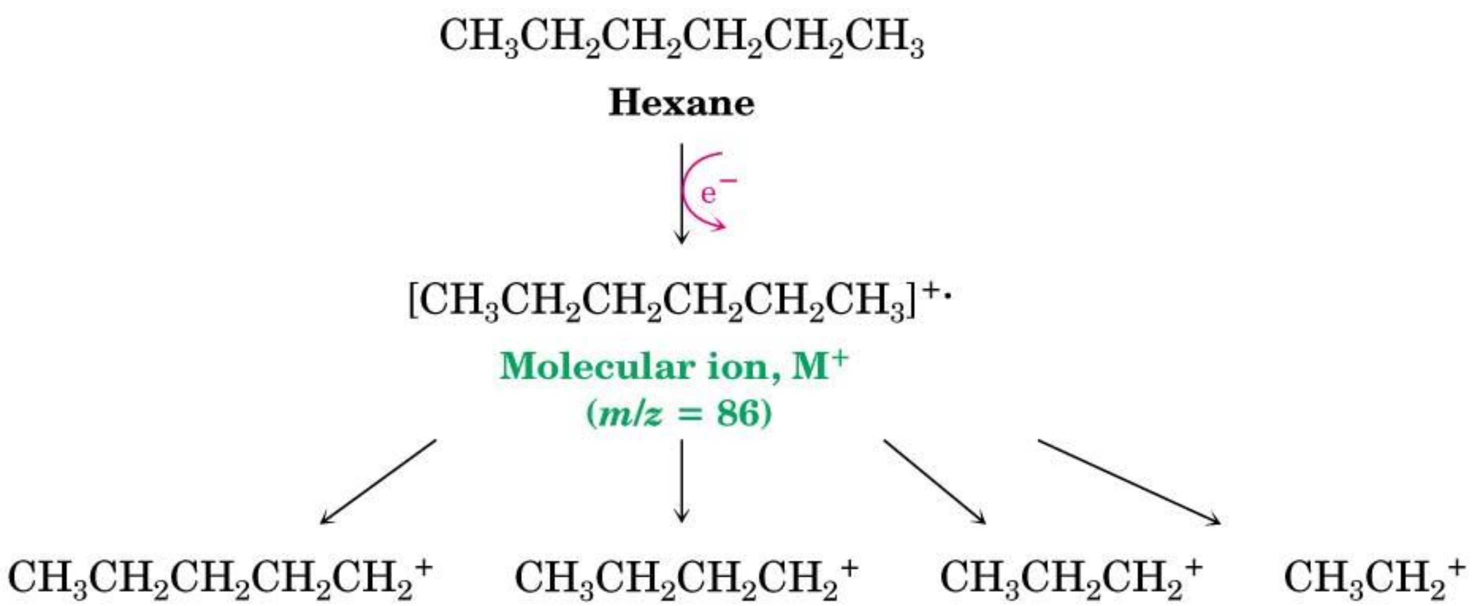
Fragmentation analysis



These two mass spec are from two ketones with the formula $C_5H_{10}O$. Can we decide which ketone belongs to which mass spec?



Fragmentation analysis



m/z:	71	57	43	29
Relative abundance (%):	10	100 (base peak)	75	40

Fragmentation analysis

How to look at a mass spectrum and decide what bonds have broken and what fragments are present.

Firstly: Fragments that you expect may not always be present, fragments you do not expect might not be present.

Secondly: Your fragmentation analysis only supports structural decisions about unknown molecules, ^{13}C NMR and IR provide more definitive answers about structures and functional groups.

Thirdly: Common fragments are given to you

Solving spectroscopy problems

1. Try and identify functional group from IR and ^{13}C
2. Try and identify the molecular formula from mass spec and information given

3. Use ^{13}C NMR to identify compound
    - Symmetry (# of C environments v # of C environments in NMR)
    - Chemical shifts of carbon atoms

4. Look at the fragmentation in mass spec to confirm parts of molecule

Achievement Requirements

For A:

Use IR to identify <u>parts</u> of a molecule

Use ^{13}C NMR to identify <u>parts</u> of a molecule

Use mass spec to identify <u>parts</u> of a molecule

For M:

Identify the molecule

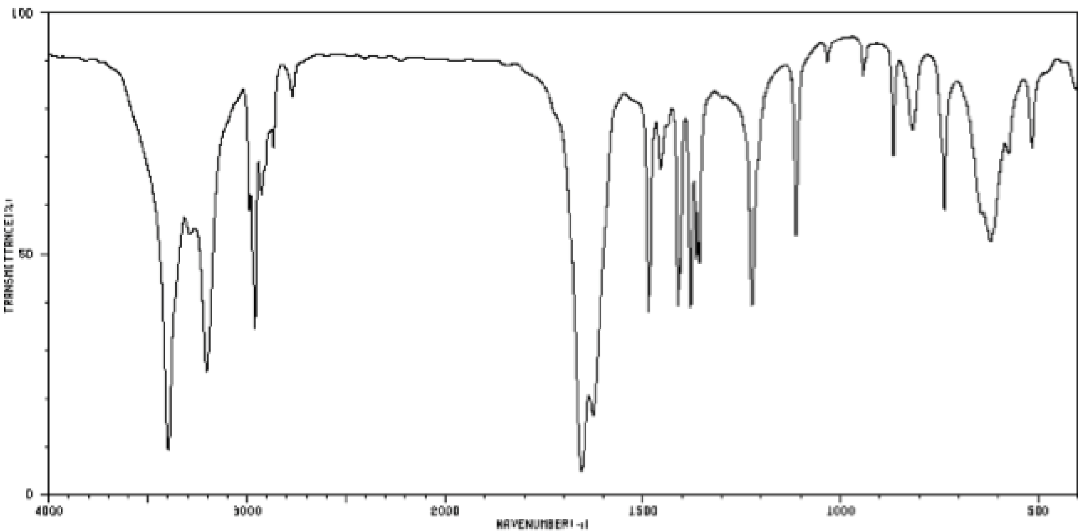
Use 2 or 3 spectra to <u>explain identification</u> of the molecule

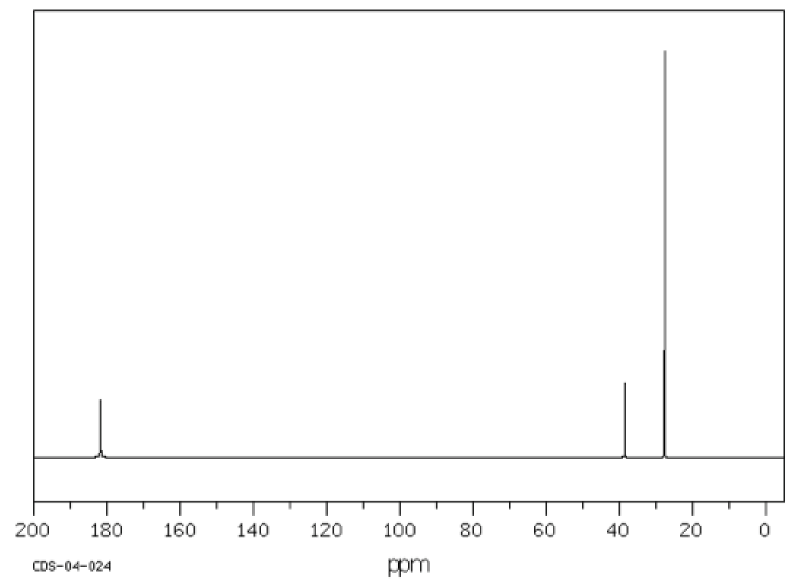
For E:

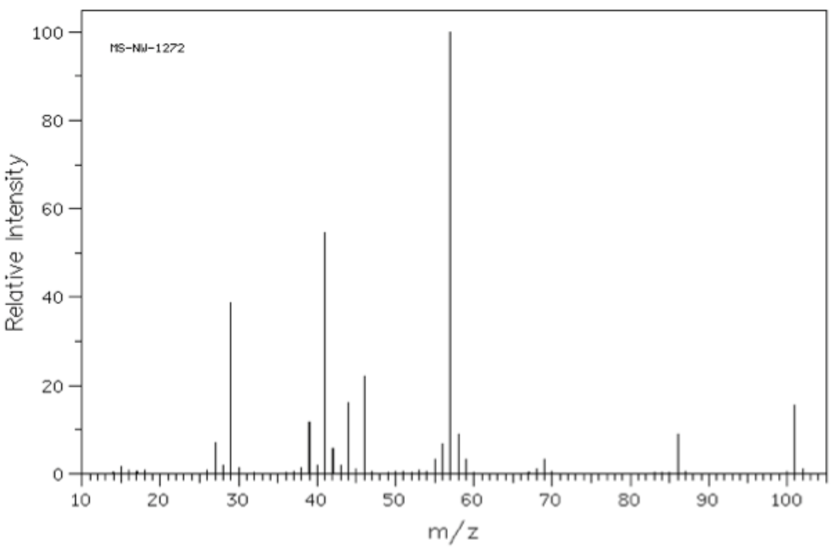
Identify the molecule

Use all 3 spectra to <u>comprehensively explain</u> identification of the molecule

A model answer







Molecular formula is $C_5 H_{11}ON$