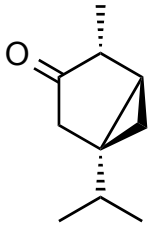
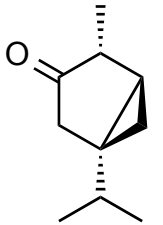


Chemistry 2600

Chapter 14

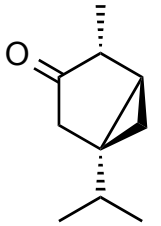
Mass Spectrometry

Mass Spectrometry



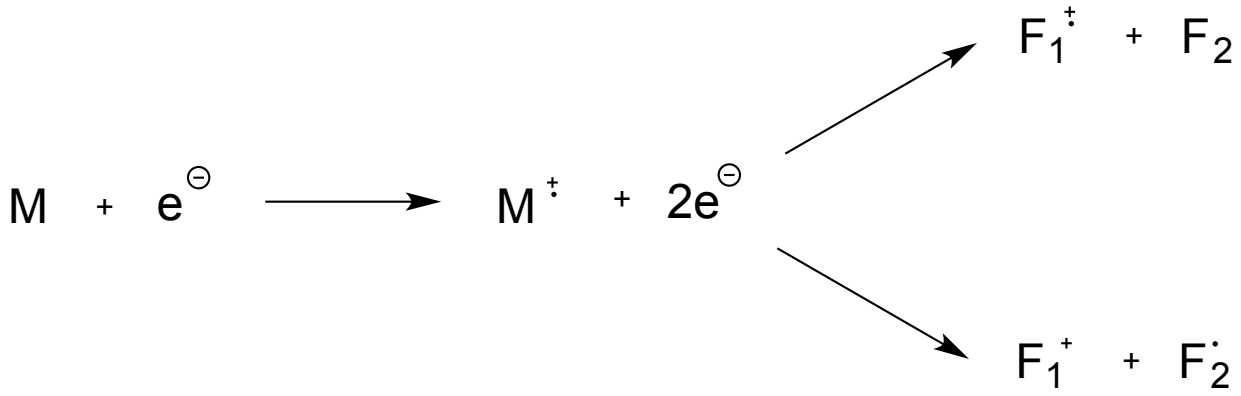
- Mass spectrometry is a technique that gives information on the mass of a compound and the mass of its fragments.
- A ***mass spectrometer*** is used to measure the masses of individual molecules and to break the molecule into fragments.
- The patterns of these fragments (masses and relative abundances) can be used to identify the compound's structure.

Mass Spectrometry

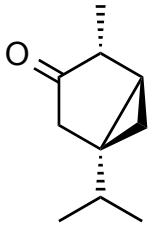


- The Experiment:
  - The vaporized samples are ionized (lose an electron) creating ***molecular ions***.

  - Although ionization can be accomplished in a number of ways, electron impact is the most common method used.



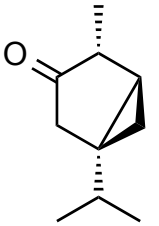
Mass Spectrometry



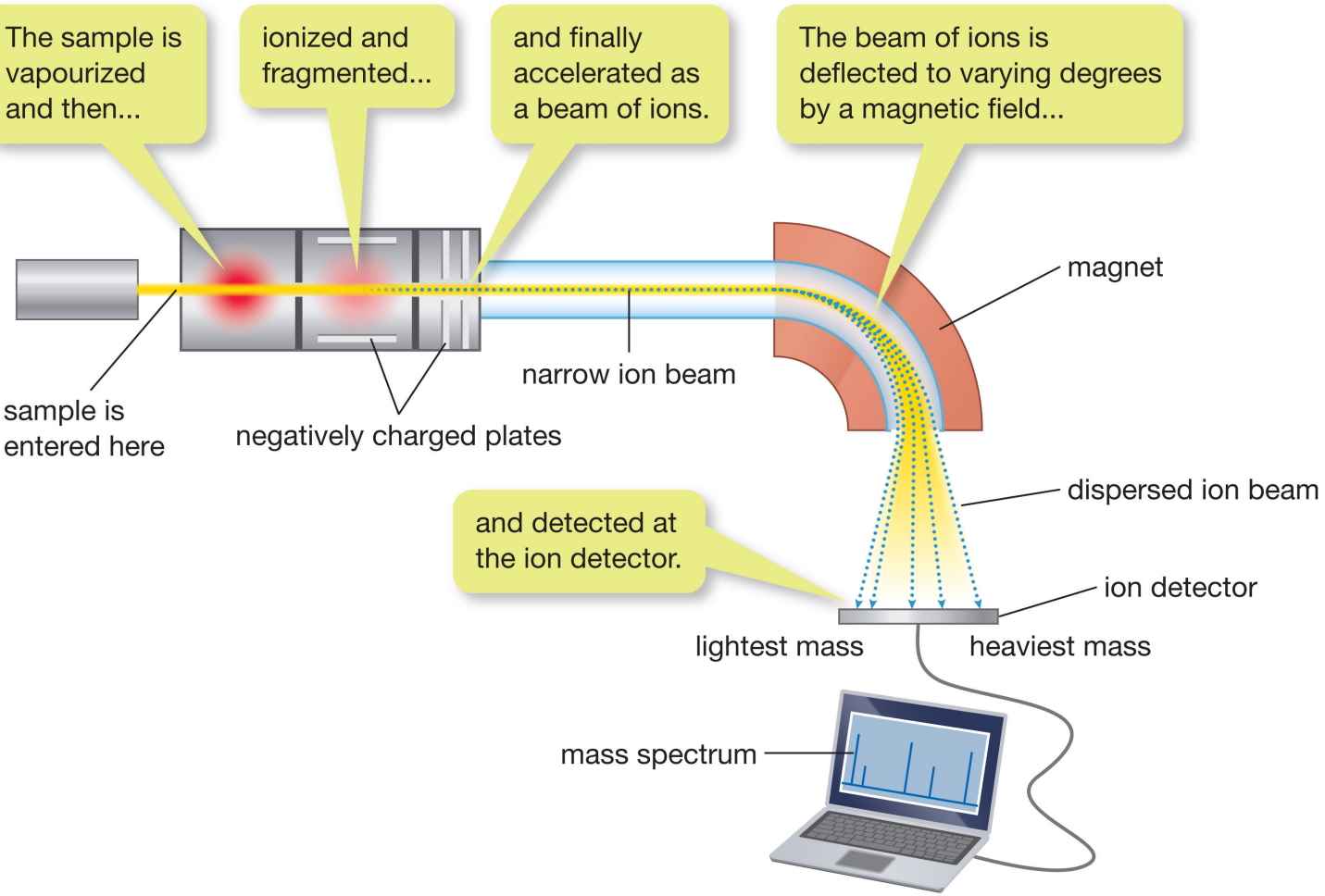
- The Experiment:

- The ions are accelerated then deflected by a magnetic field, separating the ions by size and charge expressed as a ***mass-to-charge*** ratio (*m*/*z*).
- Since the charge of the ions are almost always +1, the m/z is effectively a measure of the mass of the ions.
- The different fragments hit a detector and the results are recorded.

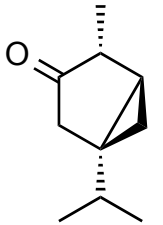
Mass Spectrometry



- The Experiment:

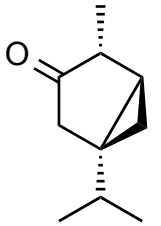


Mass Spectrometry

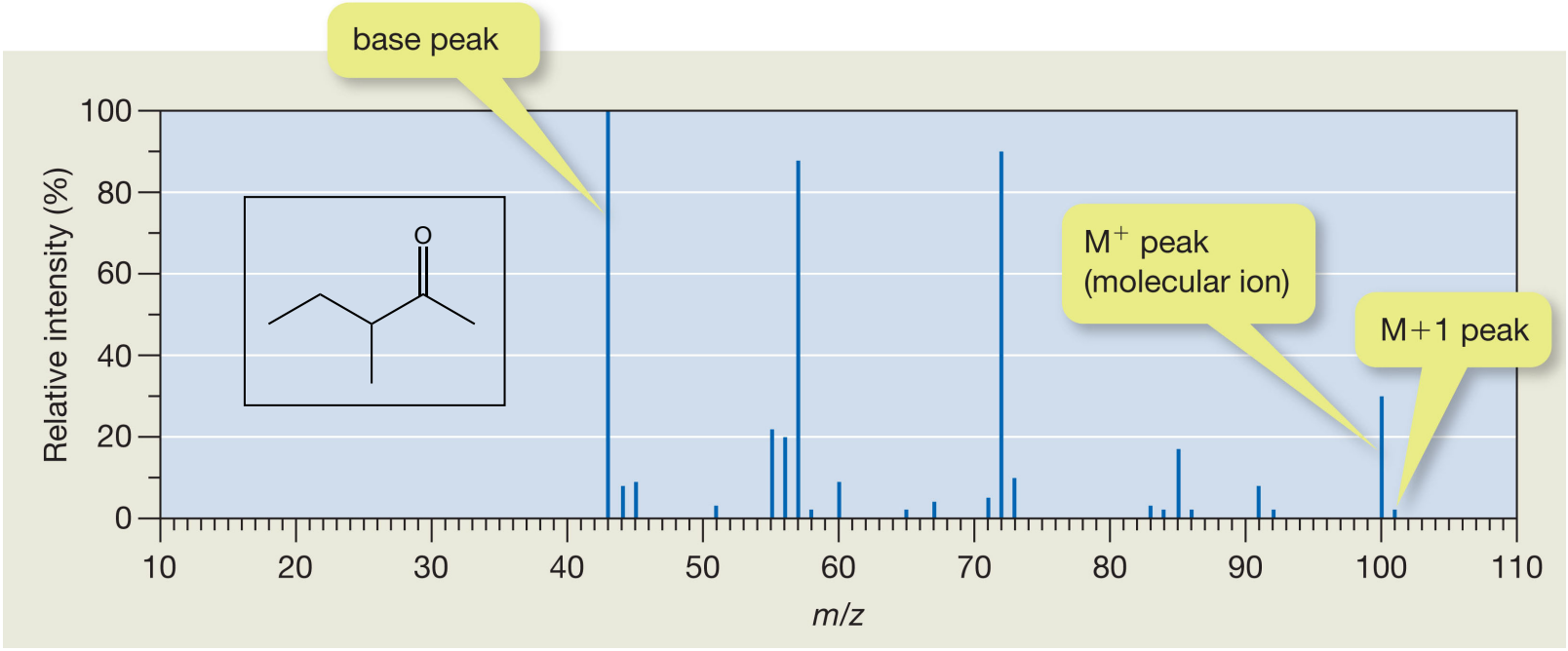


- 5 Important Characteristics of a Mass Spectrum:
  1. Mass of the Molecular ion
  2. Mass of the Base peak
  3. Presence or absence of heavy isotopes
  4. Presence of odd number of N atoms
  5. Fragments formed from the molecular ion

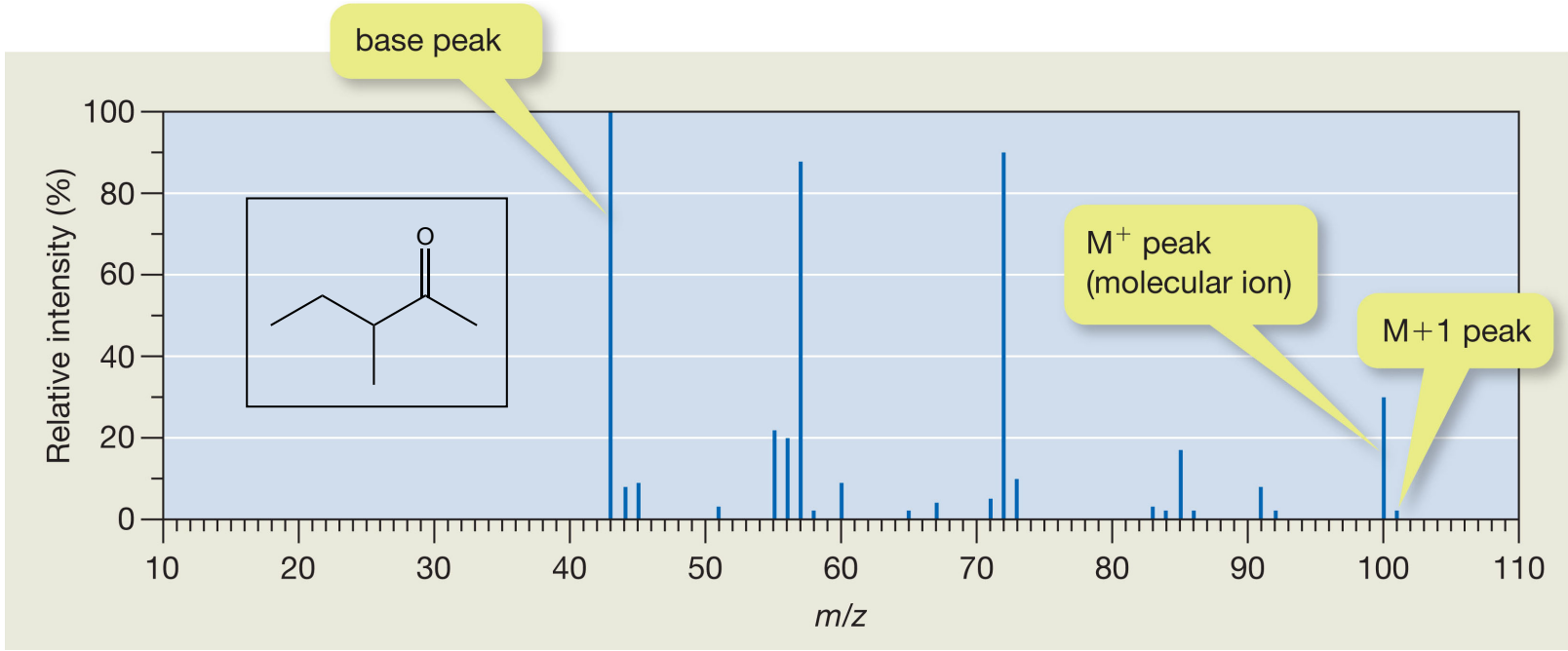
The Mass Spectrum



- A ***low-resolution*** mass spectrum reports the detected ion masses to the nearest amu.
- The ***base peak*** is the tallest peak (assigned an abundance of 100%). All other peaks are relative to the base peak.

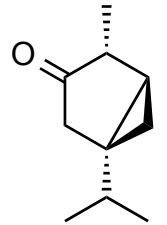


The Mass Spectrum



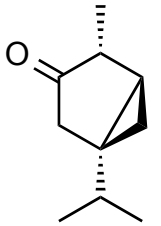
- The M^+ peak is typically the one with the highest mass, however the presence of different isotopes can lead to peaks of higher mass; the M+1 peak in this case.

Isotope Peaks



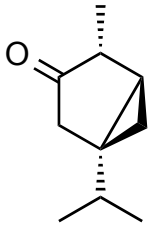
- The height of an isotope peak reflects the percentage of the heavier isotopes in the compound.
- For atoms with isotopes of high natural abundance (Cl and Br), the molecular ion (M^+ and M + 2) peak patterns are very diagnostic.

Isotope Peaks



Element	Isotope	Mass (amu)	Natural Abundance (%)
Hydrogen	^{1}H	1.007825	99.9885
	^{2}H	2.014102	0.0115
Carbon	^{12}C	12.000000	98.93
	^{13}C	13.0033355	1.07
Nitrogen	^{14}N	14.003074	99.632
	^{15}N	15.000109	0.368
Oxygen	^{16}O	15.994915	99.575
	^{18}O	17.999160	0.205
Fluorine	^{19}F	18.998403	100.00
Chlorine	^{35}Cl	34.968853	75.78
	^{37}Cl	36.965903	24.22
Bromine	^{79}Br	78.918338	50.69
	^{81}Br	80.916291	49.31

Isotope Peaks



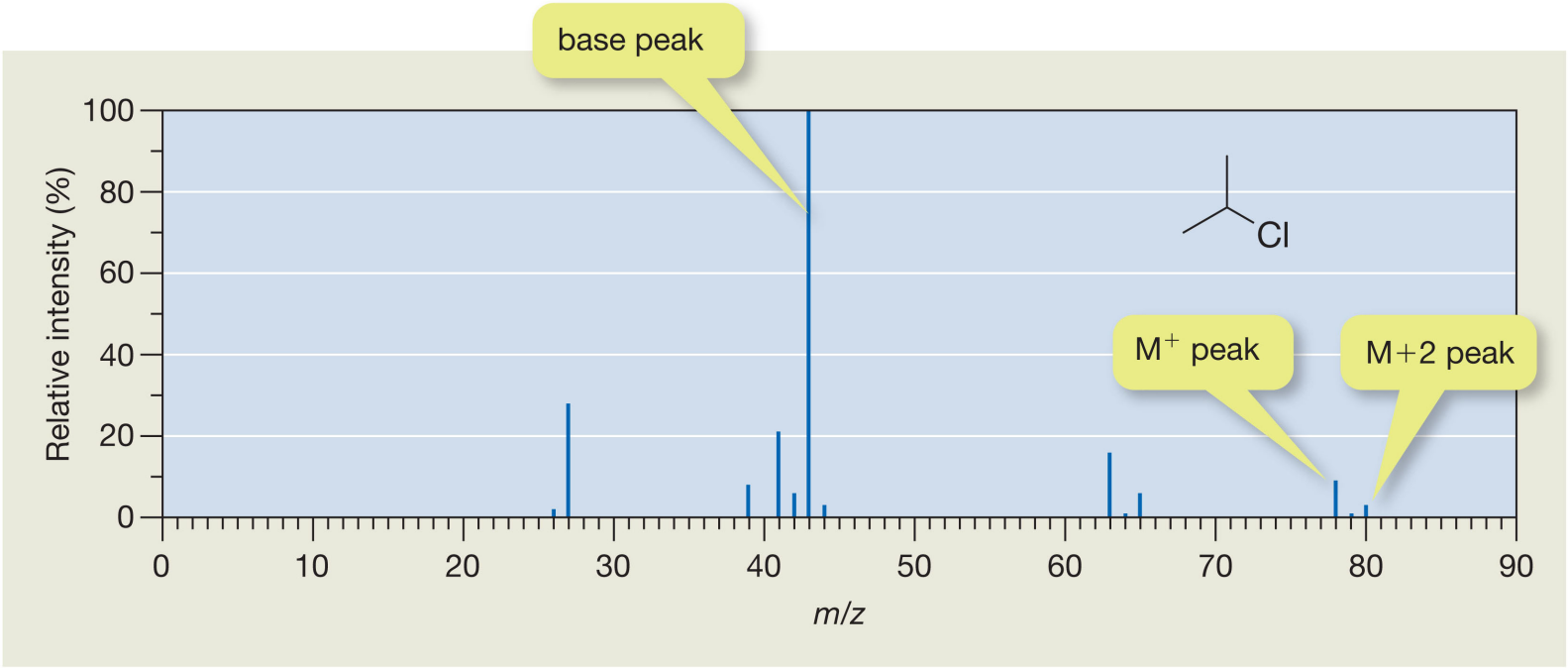
- For the mass spectrum of 2-chloropropane, the M^+ and M + 2 peaks are in ~3:1 ratio as dictated by the isotope abundances.

$^{12}C_3{}^{1}H_7{}^{35}Cl$ (M^+)

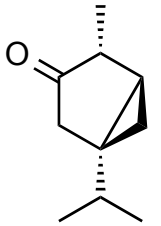
1×34.968853 amu
7×1.007825 amu
3×12.000000 amu
78.023628 amu
78 amu (to the nearest amu)

$^{12}C_3{}^{1}H_7{}^{37}Cl$ $(M+2)$

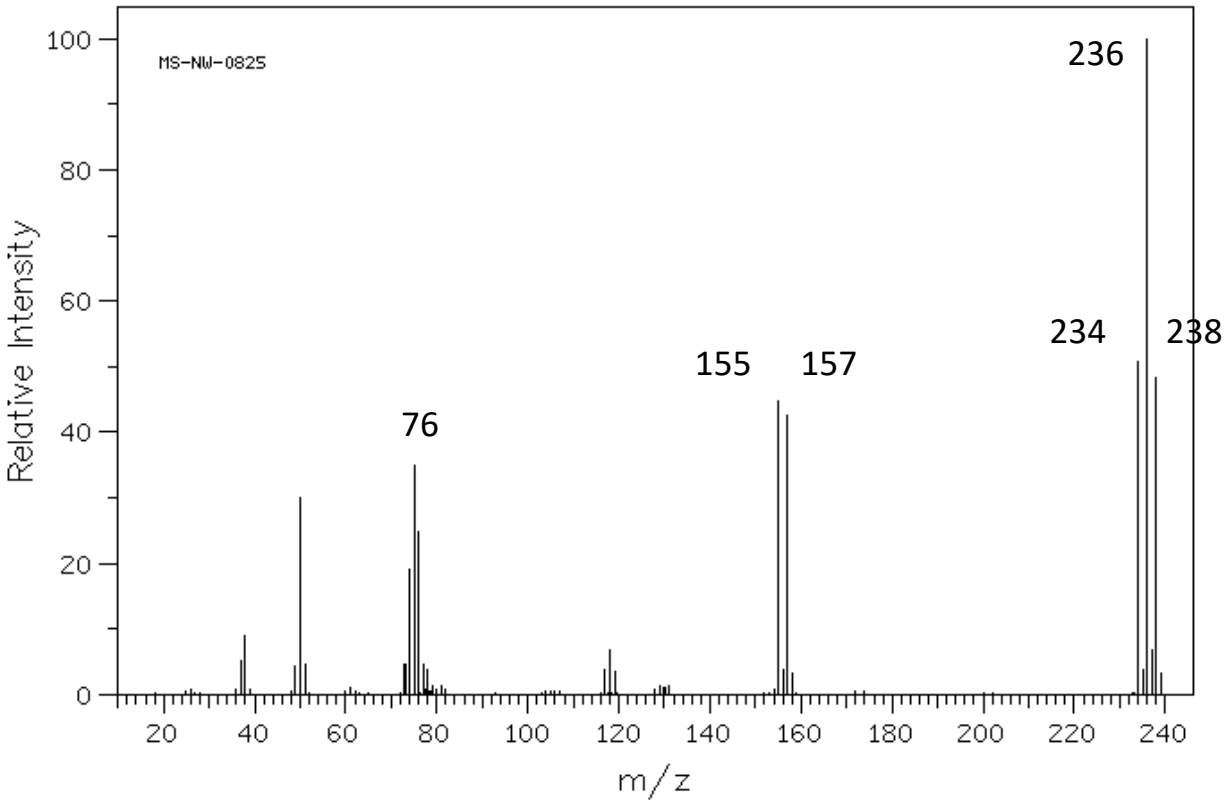
1×36.965903 amu
7×1.007825 amu
3×12.000000 amu
80.020678 amu
80 amu (to the nearest amu)

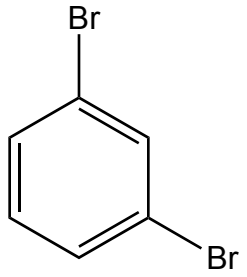


Isotope Peaks



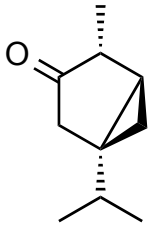
- Heavy isotopes also form diagnostic peak patterns when multiple heave isotopes are present.
- Why is the M+ peak in a 1:2:1 ratio?



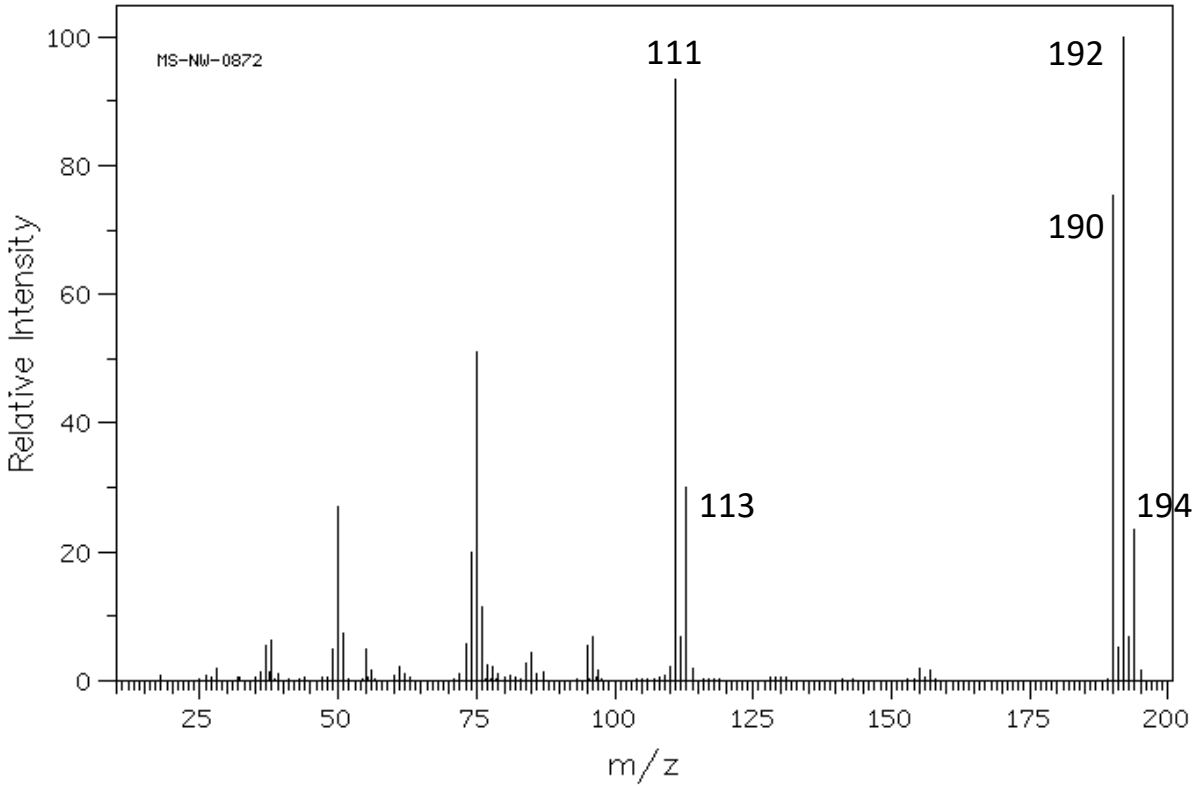


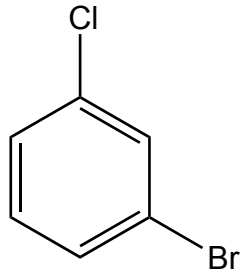
SDBS (https://sdbs.db.aist.go.jp/sdbs/cgi-bin/direct_frame_top.cgi)

Isotope Peaks



- The ratio of peaks is also predictable for mixed isotope systems.





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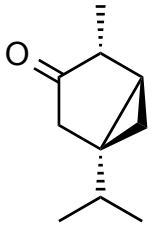
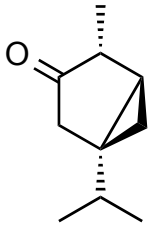
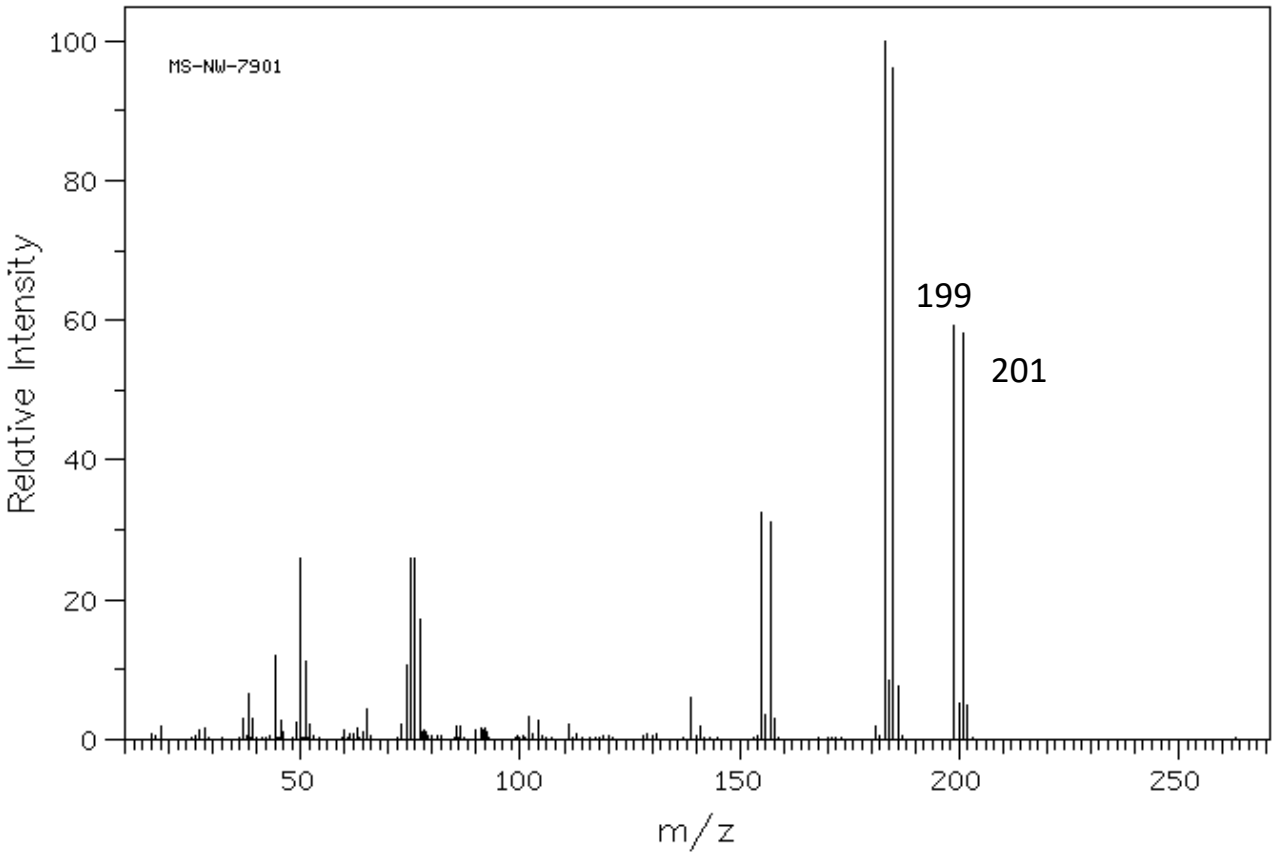
Number of Nitrogen Atoms

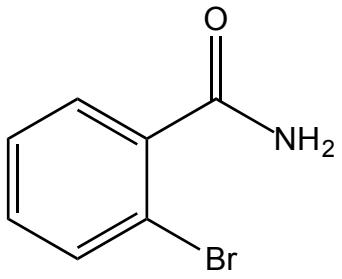


- Because most of the major atoms that make up organic molecules have even masses and form even number of bonds, most molecular ions have an even mass.
- Since nitrogen typically forms an odd number of bonds, molecules with an odd number of nitrogen atoms will have an odd number mass.

Number of Nitrogen Atoms







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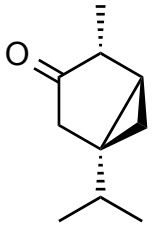
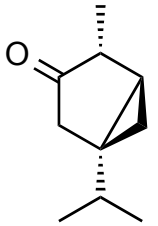
Fragmentation Patterns



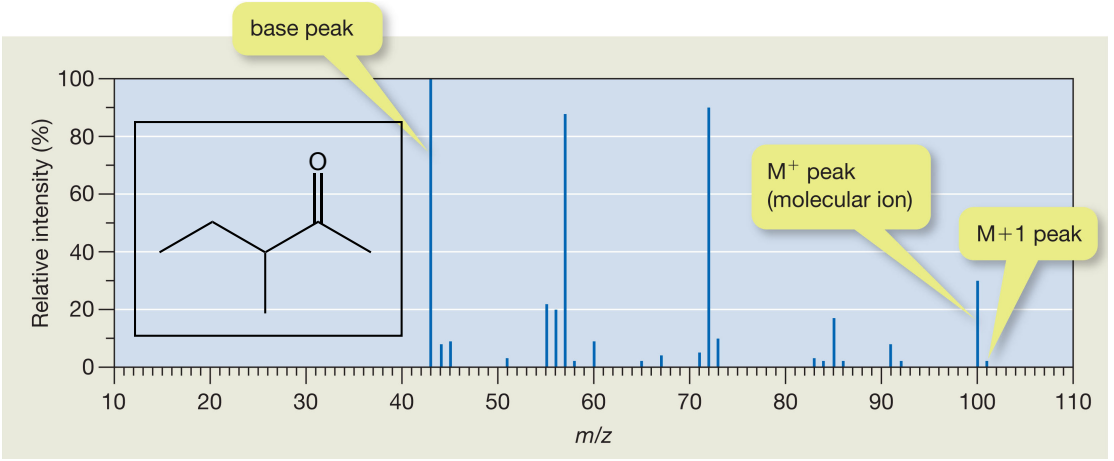
- Most peaks in a mass spectrum result from the fragmentation of the molecular ions.
- These fragmentation peaks and their relative abundances serve as a 'fingerprint' for the molecule.
- Not all fragments are charged and only the charged ones will be detected (recall that mass spectrometry only detects charged species).

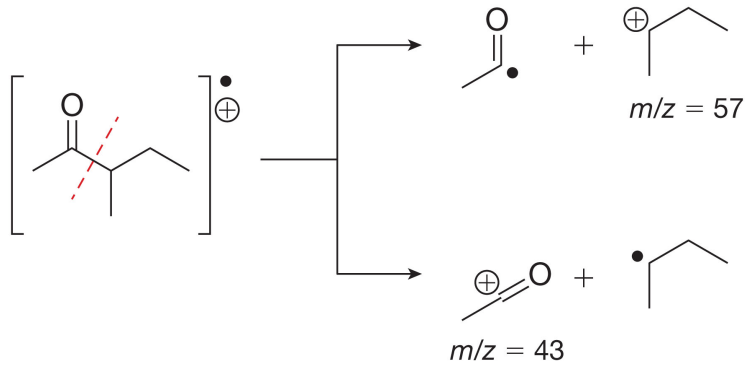
- Sometimes fragmentation is so severe that the M^+ peak is weak or even missing.

Fragmentation Patterns

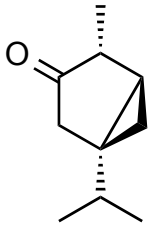


- Typically many, but not all, the other peaks can be linked to relatively stable fragmentation pieces.
- One common pattern is to break bonds on either side of a carbonyl or alcohol group.

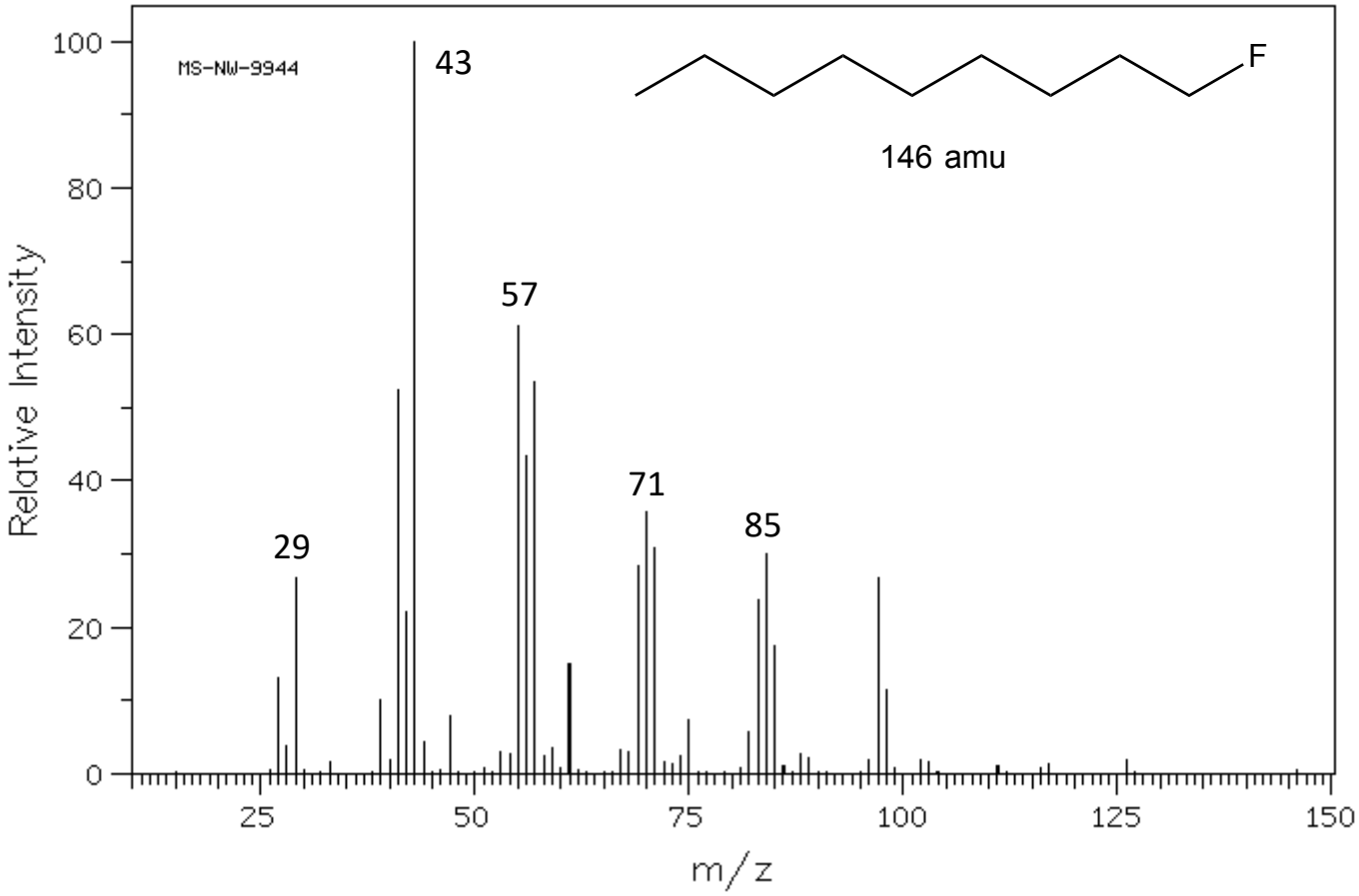




Fragmentation Patterns

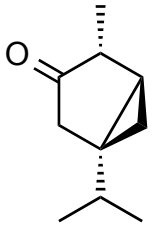


- Molecules with long alkyl chains tend to split apart in 14 *m/z* units, CH_2 groups.

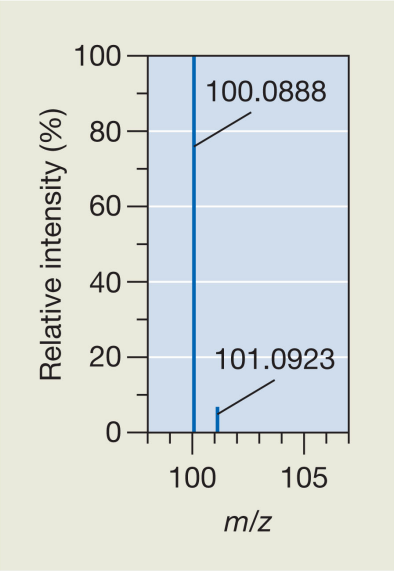


SDBS (https://sdbs.db.aist.go.jp/sdbs/cgi-bin/direct_frame_top.cgi)

High-Resolution Mass Spectrometry



- High-Resolution Mass Spectrometry (HRMS) is used to accurately determine the molecular formula of organic molecules.
- HRMS measures the molecular mass to a very high degree of precision (4 decimal places).



$^{12}C_7{}^{1}H_{16}$ (M^+)

16 × 1.007825 amu
7 × 12.000000 amu
100.125200 amu
100 amu (to the nearest amu)

$^{12}C_6{}^{1}H_{12}{}^{16}O$ (M^+)

1 × 15.994915 amu
12 × 1.007825 amu
6 × 12.000000 amu
100.088815 amu
100 amu (to the nearest amu)

$^{12}C_5{}^{1}H_8{}^{16}O_2$ (M^+)

2 × 15.994915 amu
8 × 1.007825 amu
5 × 12.000000 amu
100.052430 amu
100 amu (to the nearest amu)

$^{12}C_5{}^{1}H_{12}{}^{14}N_2$ (M^+)

2 × 14.003074 amu
12 × 1.007825 amu
5 × 12.000000 amu
100.100048 amu
100 amu (to the nearest amu)