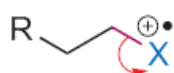


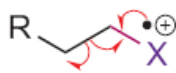
Molecular characterization

13.1 Mass spectrometry

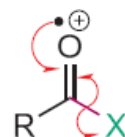
- Mass spectrometry (MS) gives information on the relative molecular mass of compounds by measuring the mass-to-charge ratios (m/z) of ions produced on ionization.
- In electron impact (EI) mass spectrometry, a sample is ionized by bombardment with high-energy electrons to form a radical cation (M^+), called the molecular ion.
- To calculate the number of carbon atoms in the molecule, divide the relative abundance of the $M+1$ peak, expressed as a percentage of the molecular ion peak, by 1.1.
- To identify the presence of a chlorine or bromine atom in the compound, look at the relative abundancies of the $M + 2$ and the M peaks.
- If m/z for the molecular ion is even, the molecule contains an even number of nitrogen atoms or none at all. If m/z for the molecular ion is odd, the molecule contains an odd number of nitrogen atoms.
- The weakest bonds in a molecular ion are often selectively broken to form the most stable fragment cations (which are detected by the spectrometer). Compounds containing functional groups fragment in predictable ways.



$X = \text{Cl, Br, I}$



$X = \text{Cl, Br, I, OH, OR, NHR}$



$X = \text{H, alkyl, OH, OR}$

- Information on partial structures can be deduced by looking at mass differences between the molecular ion (M) and fragment cations (Table 13.1).
- High-resolution spectrometers can distinguish compounds that have different compositions of elements so they can be used to determine the molecular formula of an unknown compound.

Table 13.1 Common fragmentations of molecular ions

Fragment cation	Typical group that is lost	Possible partial structure
M – 1	H	Aldehyde
M – 15	CH ₃	Methyl group
M – 18	H ₂ O	Alcohol
M – 29	CH ₂ CH ₃	Ethyl group
M – 31	CH ₃ O	Methyl ester
	CH ₂ OH	Primary alcohol
M – 35/37	Cl	Chloroalkane
M – 43	CH ₃ CO	Methyl ketone
M – 77	C ₆ H ₅	Phenyl group
M – 79/81	Br	Bromoalkane
M – 91	C ₆ H ₅ CH ₂	Benzyl group

13.2 Infrared spectroscopy

- General trends in the position of absorption bands in an IR spectrum.
 - (i) Absorption bands due to stretching vibrations have higher wavenumbers than the corresponding bending vibrations; for example, for a C–H bond, the stretching vibration has a higher wavenumber than the bending vibration.
 - (ii) Bonds to hydrogen vibrate at a higher wavenumber than those involving heavier atoms; for example, the stretching vibration of a C–H bond has a higher wavenumber than those for C–C, C–O, or C–N bonds.
 - (iii) A triple bond vibrates at a higher wavenumber than a corresponding double bond, which, in turn, vibrates at a higher wavenumber than a single bond (except for bonds to hydrogen).

- In an IR spectrum, the position, relative intensity, and shape of an absorption band are all helpful in structure identification.
- Characteristic group wavenumbers (in cm^{-1}) are due to stretching vibrations of bonds and they provide useful information on functional groups—they are normally found between 4000 cm^{-1} and 1400 cm^{-1} , which is called the functional group region. For example:

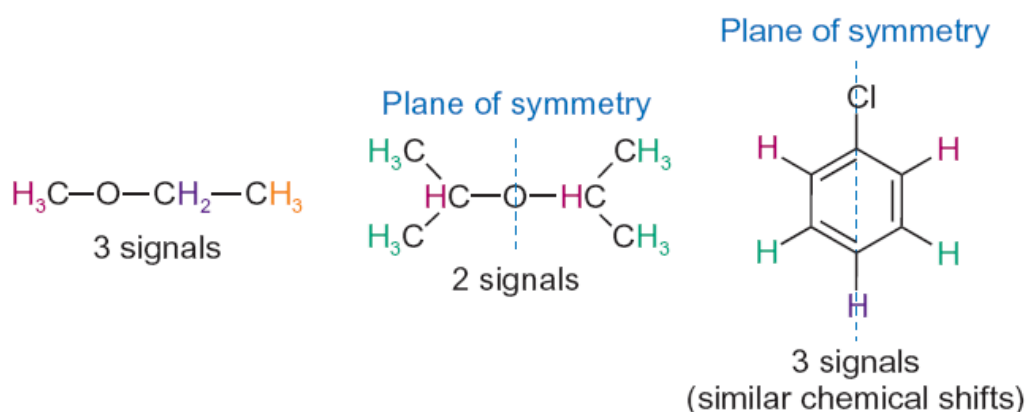
$3600\text{--}2500\text{ cm}^{-1}$ (broad)	O–H	alcohols, carboxylic acids, amines, amides
$3000\text{--}2850\text{ cm}^{-1}$	C–H	
$1820\text{--}1650\text{ cm}^{-1}$	C=O	carbonyls
$1680\text{--}1620\text{ cm}^{-1}$	C=C	alkenes

- Carbonyl functional groups can be identified by the wavenumber of the C=O stretching vibration.
- The area between 1400 cm^{-1} and 600 cm^{-1} in the IR spectrum is called the fingerprint region. Analysis of this region is helpful to confirm structures.

13.3 Nuclear magnetic resonance spectroscopy

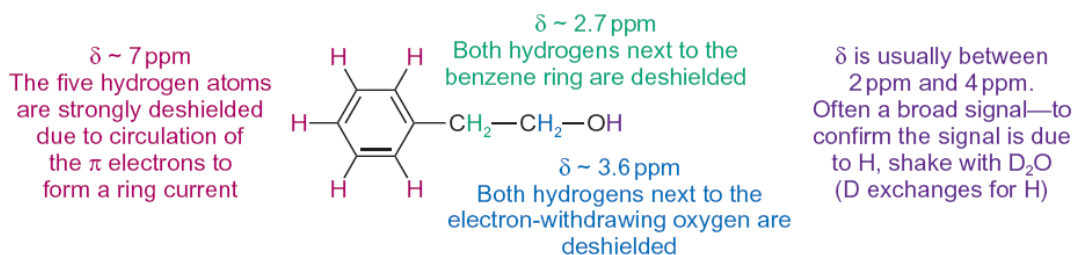
- An FT-NMR spectrum is a plot of intensity of the resonance signal against chemical shift. The frequency (and energy) of the radiofrequency radiation responsible for the signal increases from right to left across the spectrum.
- In a ^1H NMR spectrum, the number, position (chemical shift), area, and appearance of each resonance signal are all helpful in structure identification.

- 1 The number of resonance signals tells you the number of hydrogen atoms in different electronic environments.

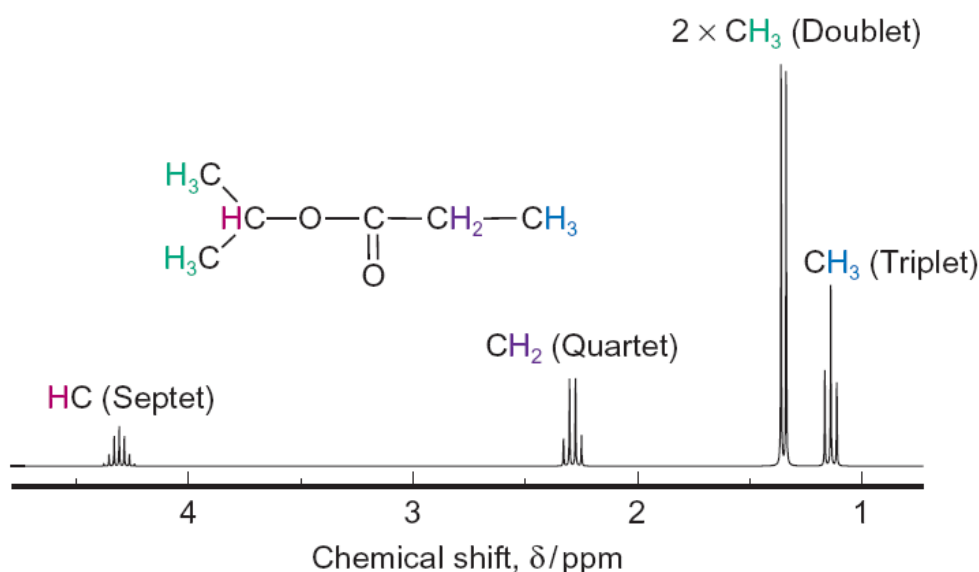


- 2 The chemical shifts give you important information about the electronic environment the hydrogen atoms are in. Resonance signals

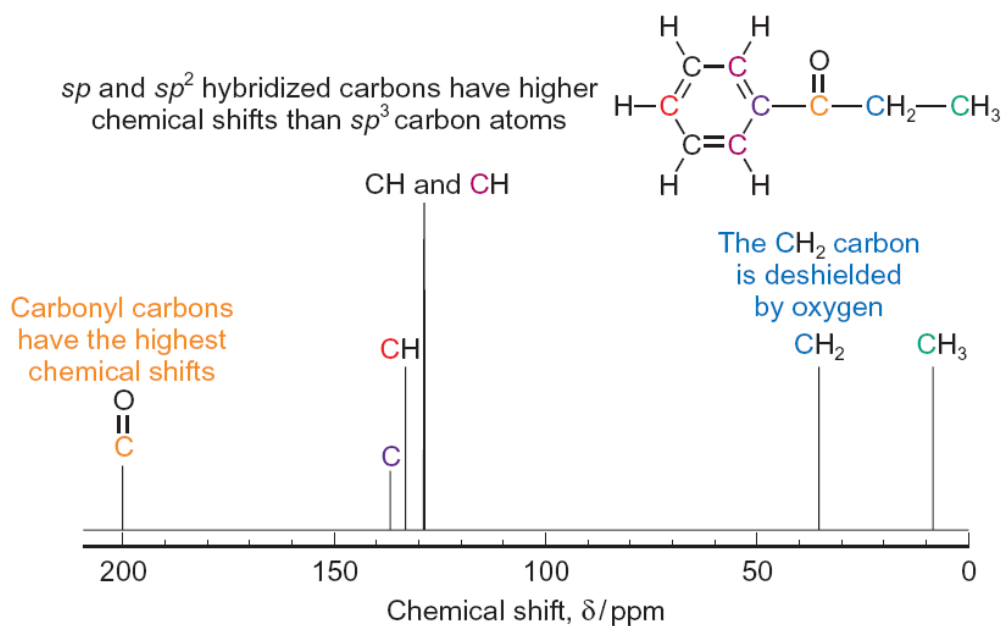
with high chemical shifts (the left-hand side of the spectrum) are from hydrogens atoms that are close to electron-withdrawing groups.



- 3 The ratio of the areas under the peaks tells you the ratio of the numbers of hydrogen atoms in each of these environments.
- 4 The splitting of the signals indicates the number of hydrogen atoms on the carbon atom adjacent to an observed hydrogen atom. The multiplicity of an NMR signal is calculated by the $N + 1$ rule, which states that, if a signal is split by N equivalent hydrogens, it is split into $N + 1$ peaks.



- In a ^{13}C NMR spectrum, the number of different signals indicates the number of carbon atoms in different electronic environments. The chemical shift of a signal indicates the type of carbon atom.



Learning outcomes

By the end of this chapter you should be able to do the following.

- Describe how an EI mass spectrum is produced.
- Understand that the molecular ion ($M^{+\bullet}$) gives the relative molecular mass of a molecule and that high-resolution mass spectrometers can determine the molecular formula of a molecule.
- Use $M + 1$ and $M + 2$ isotope peaks to calculate the number of carbon atoms and/or detect a chlorine or bromine atom(s) in a molecule.
- Identify and predict characteristic fragmentation patterns of molecular ions from compounds containing groups such as alkyl, halogenoalkyl, ether, amine, and carbonyl.
- Suggest partial structures for an unknown molecule, using the differences in mass between the molecular ion and various fragment cations.
- Understand the factors that influence the position of absorption bands in an IR spectrum.
- Use characteristic group wavenumbers to identify functional groups.

- Understand the factors that influence the number of resonance signals in a ^1H or a ^{13}C NMR spectrum.
- Describe the factors that affect the position of a resonance signal (recorded as a chemical shift) in a ^1H or a ^{13}C NMR spectrum.
- Use typical ^1H or ^{13}C chemical shift values (Fig. 13.20) to predict types of CH_3 , CH_2 , and CH groups in an unknown molecule.

Typical ^1H chemical shifts (ppm)			$\text{HC}=\text{C}$	$\text{HC}-\text{Br}$ $\text{HC}-\text{N}$ $\text{HC}-\text{O}$	$\text{HC}-\text{COR}$ $\text{HC}-\text{C}=\text{C}$	$\text{HC}-\text{C}$
	10.0–9.0	8.0–6.5	6.5–4.5	4.5–2.5	2.7–1.7	1.6–0.7
Typical ^{13}C chemical shifts (ppm)	$\text{O}=\text{C}$		$\text{C}=\text{C}$	$\text{N}-\text{C}$ $\text{O}-\text{C}$	$\text{C}-\text{Br}$ $\text{C}-\text{Cl}$	$\text{C}-\text{C}$
	220–165	170–110	150–110	80–40	75–25	50–5

Figure 13.20 Summary of typical ^1H and ^{13}C chemical shifts.

- For a ^1H NMR spectrum, use an integration curve to calculate the relative number of hydrogen atoms that give rise to each signal.
- For a ^1H NMR spectrum, use the splitting pattern of a signal to determine the number of hydrogen atoms bonded to an adjacent carbon.

