

## REVISION AID

# Spectroscopy



## Physical Constants

Name	Common Symbol	Value
Avogadro constant	$N_A$	$6.0221 \times 10^{23} \text{ mol}^{-1}$
Boltzmann constant	$k$	$1.3807 \times 10^{-23} \text{ J K}^{-1}$
Elementary charge	$e$	$1.6022 \times 10^{-19} \text{ C}$
Faraday constant	$F$	$9.6485 \times 10^4 \text{ C mol}^{-1}$
Gas constant	$R$	$8.3145 \text{ J K}^{-1} \text{ mol}^{-1}$
Mass of an electron	$m_e$	$9.1094 \times 10^{-31} \text{ kg}$
Planck constant	$h$	$6.6261 \times 10^{-34} \text{ J s}$
Speed of light	$c$	$2.9979 \times 10^8 \text{ m s}^{-1}$
Vacuum permittivity	$\epsilon_0$	$8.8542 \times 10^{-12} \text{ C}^2 \text{ J}^{-1} \text{ m}^{-1}$

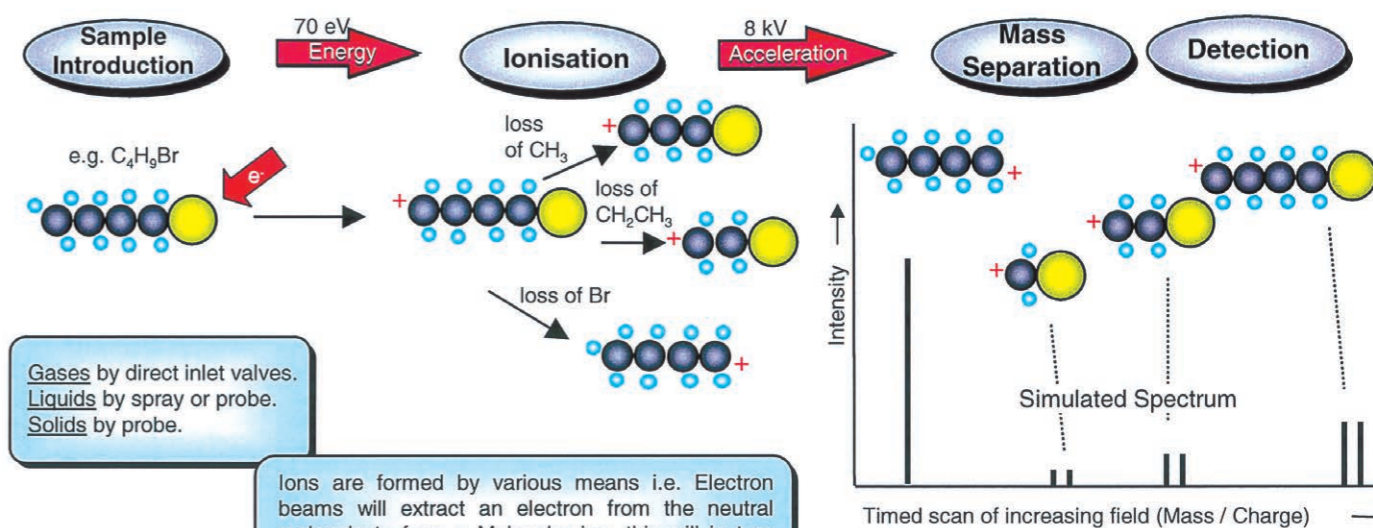
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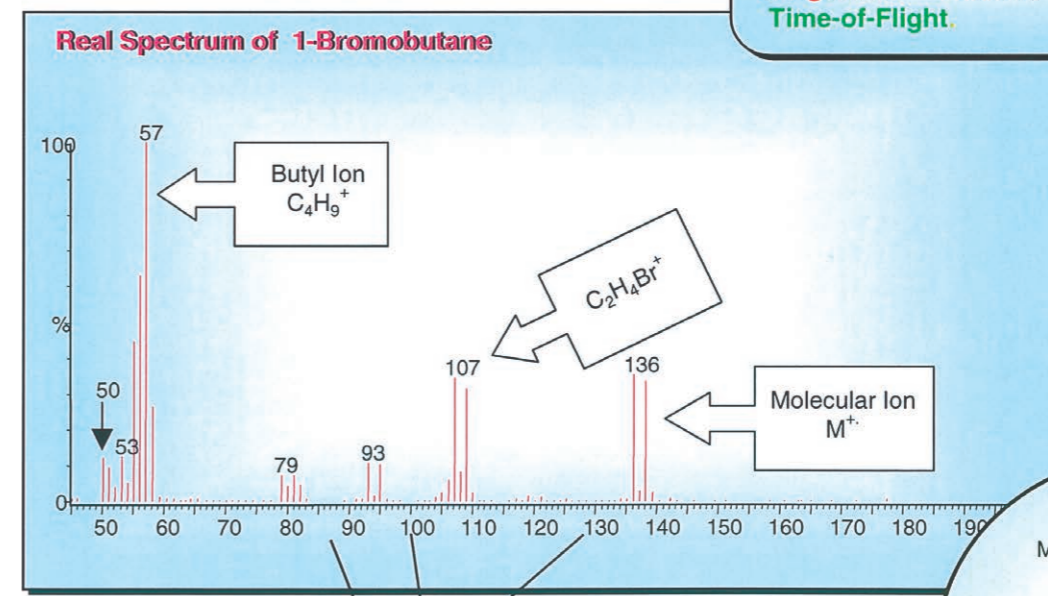
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## MASS SPECTROMETRY

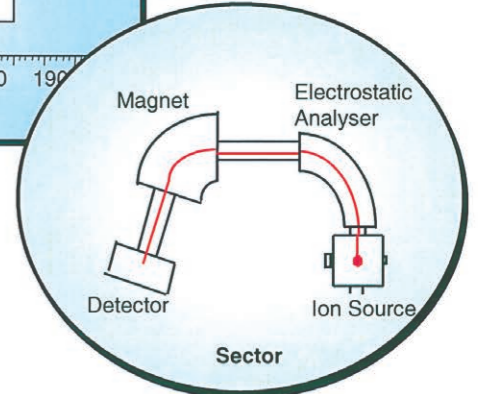


Ions are formed by various means i.e. Electron beams will extract an electron from the neutral molecule to form a **Molecular ion**, this will in turn break up to form fragment ions and neutral radicals/molecules.

Only charged species (i.e. Ions) will be detected by the instrument. In order for mass separation to occur the ions are usually deflected from their path of travel by magnetic or electric fields. The instruments are usually named after the means of ion separation, i.e. **Magnetic Sector**, **Quadrupole** or **Time-of-Flight**.



All ions containing Br will show the characteristic pattern of **isotopes**, in this case two main lines of equal intensity.



Type		Chemical Shift / ppm
Primary	RCH <sub>3</sub>	0.9
Secondary	R <sub>2</sub> CH <sub>2</sub>	1.3
Tertiary	R <sub>3</sub> CH	1.5
Vinyl	C=C-H	4.6-5.9
Acetylenic	C≡C-H	2-3
Aromatic	Ar-H	6-8.5
Benzylic	Ar-C-H	2.2-3
Allylic	C=C-CH <sub>3</sub>	1.7
Fluorides	F-C-H	4-4.5
Chlorides	Cl-C-H	3-4
Bromides	Br-C-H	2.5-4
Iodides	I-C-H	2-4
Alcohols	HO-C-H	3.4-4
Ethers	RO-C-H	3.3-4
Esters	RCOO-C-H	3.7-4.1
Acids	HCOO-C-H	2-2.6
Carbonyl compounds	O=C-C-H	2-2.7
Aldehydic	R-(C=O)-H	9-10
Hydroxylic	RO-H	1-5.5
Phenilic	ArO-H	4-12
Enolic	C=C-O-H	15-17
Carboxylic	RCOOH	10.5-12
Amino	RNH <sub>2</sub>	1-5

<sup>1</sup>H NMR ASSIGNMENTS

Compound type	Bond	Frequency Range /cm <sup>-1</sup>
Alkanes	C-H	2850-2960
		1350-1470
Alkenes	C-H	3020-3080
		675-1000
Aromatic rings	C-H	3000-3100
		675-870
Alkynes	C-H	3300
Alkenes	C=C	1640-1680
Alkynes	C≡C	2100-2260
Aromatic rings	C=C	1500-1600
Alcohols, esters, ethers, acids	C-O	1080-1300
Aldehydes, ketones, acids, ethers	C=O	1690-1760
Alcohols	OH	3610-3640 monomeric 3200-3600 hydrogen bonded (broad)
Amines	N-H	3300-3500
Amines	N-C	1180-1360
Nitriles	N≡C	2210-2260
Nitro compounds	NO <sub>2</sub>	1515-1560 1345-1385

INFRA RED ASSIGNMENTS

# INFRARED SPECTROSCOPY

## INFRARED SOURCE



Example: Nichrome wire or coiled rod of silicon carbide



Placed in instrument using a variety of sample holders (see below)



Compares currents generated by sample and reference beams



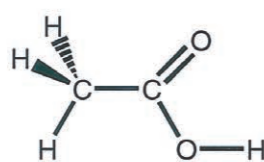
Plot of absorbance against wavenumber



Frequency =  $1.2 \times 10^{13}$  -  $1.2 \times 10^{14}$  Hz



Wavenumber =  $4000 - 400 \text{ cm}^{-1}$



Ethanoic Acid



Some radiation absorbed by sample



Frequency absorbed ( $\nu$ )

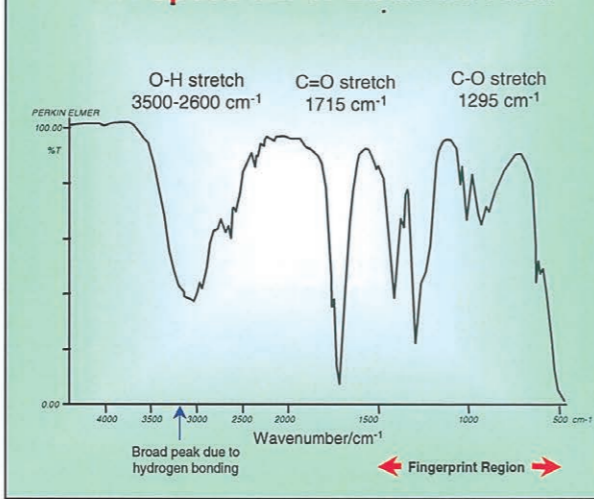
Example: C=O stretch wavenumber =  $1700 \text{ cm}^{-1}$

### Relationship between frequency and wavenumber

$$\text{wavenumber} = \frac{1}{\text{wavelength } (\lambda)}$$

$$\text{wavelength } (\lambda) = \frac{\text{speed of light } (c)}{\text{frequency } (\nu)}$$

### IR Spectrum of Ethanoic Acid



### FINGERPRINT REGION

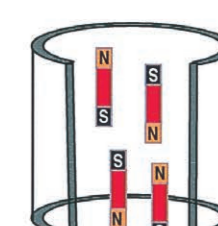
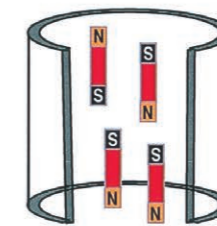
Below  $1500 \text{ cm}^{-1}$  the overall pattern of absorption is unique for different molecules and therefore acts as a chemical fingerprint

# NMR SPECTROSCOPY

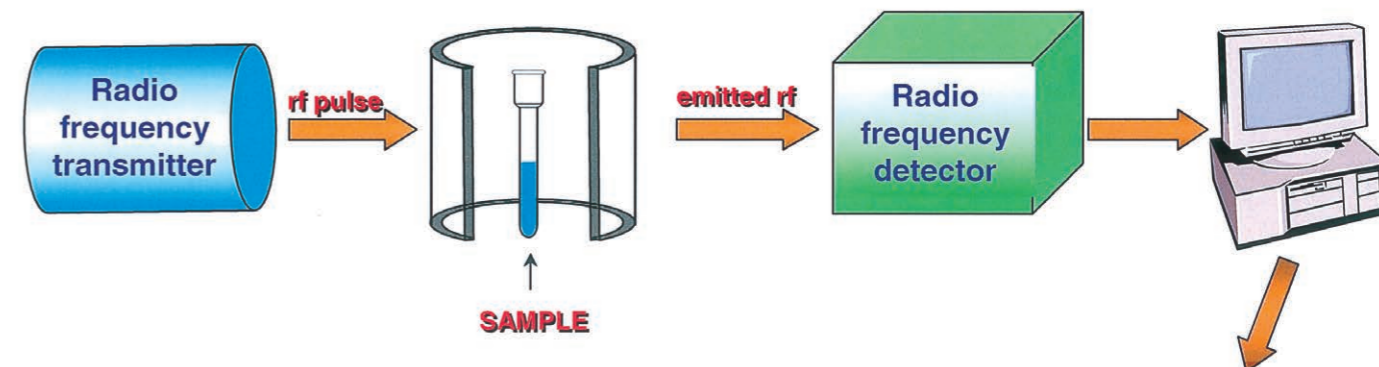
Nuclei of atoms possess a property called spin - which makes the nuclei behave like tiny bar magnets

When placed inside a very strong magnetic field, the spins line up with the field - just like a compass needle pointing to magnetic north - either parallel (*low energy*) or anti-parallel (*high energy*) to the field

If a radio frequency (rf) pulse is now applied, the spins can be made to go into a high energy spin state.



When the rf pulse is switched off the spins return to a low energy spin state and emit radio frequencies - the frequency emitted depends upon the nucleus ( $^1\text{H}$  frequencies are different from  $^{13}\text{C}$  frequencies). The NMR spectrometer is like a tunable radio - you can select the nucleus (station) you wish to observe (listen to).



The proton ( $^1\text{H}$ ) frequencies detected will be slightly different for protons from different groups within a molecule. Thus the NMR spectrum can be regarded as a 'fingerprint' of the observed compound.

Tetramethylsilane (TMS) is added as a standard zero point for  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra.

