

REVISION NOTES: TOPIC 11 & 21 - SPECTROSCOPIC TECHNIQUES

11.3 organic compounds (identification)

degree of UNSATURATION (C=C) of a compound can be called index of hydrogen deficiency (IHD)

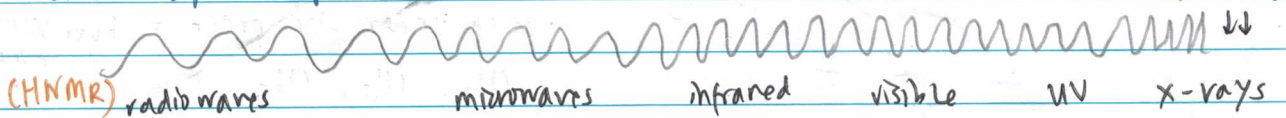
- used to determine no. of rings / multiple bonds in a molecule
- measure how many H's needed to saturate hydrocarbon.

formula: $\frac{1}{2} [(2C+2) + N - X - H]$ or (max no. H - H already present) $\times \frac{1}{2}$

- (ring counts as 1 IHD)
- ↳ O/S do not affect IHD
- ↳ halogens = H atoms
- ↳ N is considered as a carbon.

electromagnetic spectrum

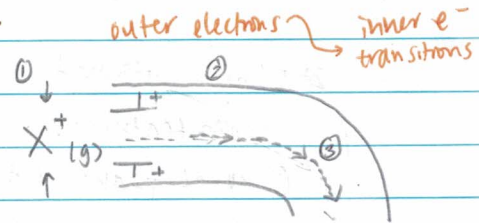
(more energy) ↓↓



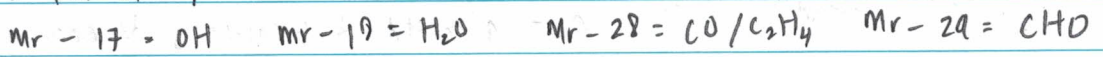
transition:

mass spectrometry

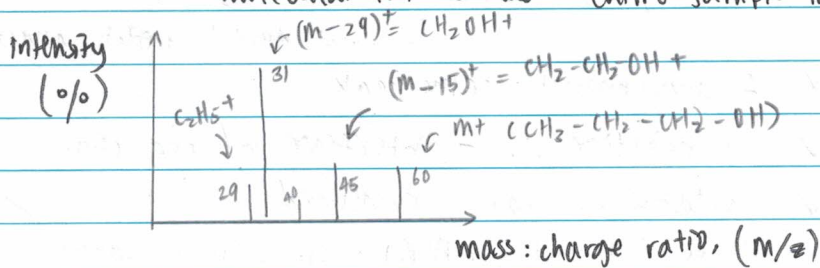
- vapourised sample is ionised $\rightarrow M^+(g)$
 - accelerates inside a magnetic field
 - deflected according to mass:charge ratio
- * fragments also produced - shows up! - the heavier, the less deflection



a few examples:



molecular ion is the entire sample ionised ($M^+(g)$)



isotopes: e.g.
25% ^{37}Cl , 75% ^{35}Cl
will appear at 2 molecular ion peaks in ratio 3:1

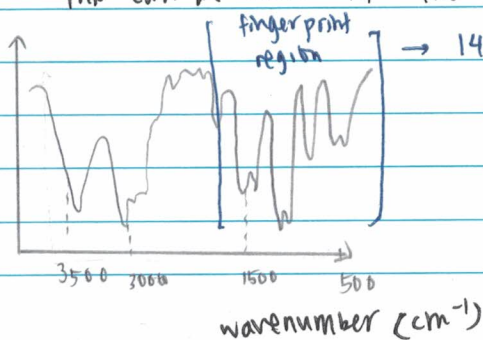
IR & 1H NMR

infrared spectroscopy

nm? depends on bond / other atoms

- when molecules absorb energy from infrared region - they vibrate
- this can be seen in the infrared spectrum

% transmittance



$1400\text{cm}^{-1} \leftrightarrow 400\text{cm}^{-1}$

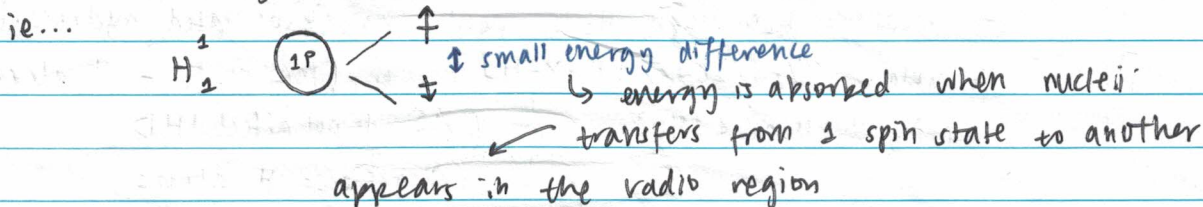
↳ unique to every compound

- ① symmetrical stretch: $x \leftarrow y \rightarrow x$
- ② asym. stretch: $x \leftarrow y \rightarrow x$
- ③ bend:

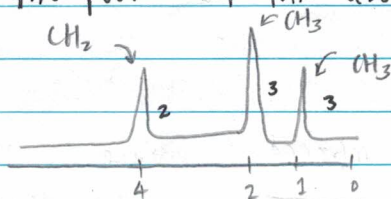
only motions which cause change in dipole moment will absorb IR!

proton nuclear magnetic resonance spectroscopy ($^1\text{H NMR}$)

- info about the chemical environments of all H atoms in a molecule.
- nuclei of ^1H atoms have certain spin
- if strong magnetic field is present \Rightarrow ^1H may align or clash



- the position of this absorption is the **chemical shift**



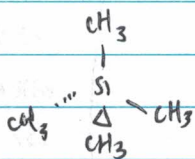
- area under the graph = how many Hs in that environment
 $\text{CH}_2, \text{CH}_3, \text{CH}_3$

21.1 $^1\text{H NMR}$ continued

main features:

- ① no. of peaks (diff chemical environments) e.g. $\text{H}-\text{C}-\text{H}$ vs $\text{H}-\text{C}-\text{OH}$
- ② area under each peak (no. of H atoms) - integration
- ③ chemical shift: spinning electrons - shield effect of magnetic field
 ↓ standard = TMS! \therefore changes the resonance / absorption of energy
 $\uparrow e^- \uparrow$ shield \downarrow frequency \downarrow energy for resonance
- ④ splitting pattern - no. of adjacent equivalent protons (n+1 rule)

use of TMS:



✓ 1 environment: same peak

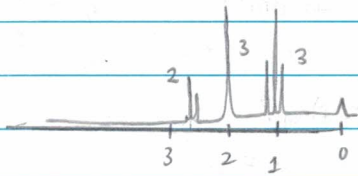
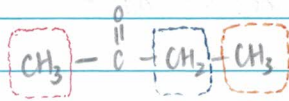
✓ unreactive \therefore \nrightarrow interfere w/ org. com.

✓ volatile \therefore easily removed

↳ all organs have diff water: lip

- protons in H_2O molecules can be detected by NMR: 3D view of organs
- all techniques can be used to test for drug abuse / identify compounds / crime
- crystallography can be used to identify BOND LENGTHS & ANGLES & STRUCTURES

applications of HNMR



no of peaks tells you... no. of diff H environments
 chemical shift tells you... the diff H environments present
 ratio of peak areas/int'g trace... no. of H attached in EACH ENVIRONMENT
 splitting pattern: no. of neighbouring H atoms.

- 3 different H environments
 - 3:2:3 area ratio under graph
 - ↳ has 3 adjacent protons → quartet
 - ↳ has two → triplet...
 - ↳ has 0 → singlet
- shifts: $\text{R}-\text{CH}_3$ is 0.9 ppm
 $\text{CH}_3-\text{C}(=\text{O})$ is 2.0 ppm
 $\text{R}-\text{CH}_2-\text{C}(=\text{O})$ is 2.3 ppm

ask pg 2, 23

HARD QUESTIONS

- HNMR: nuclear spin: radio (Electromagnetic spectrum)
- IR: change in bond polarity/vibrations: Infrared
- predict m/z values of peaks of $\text{C}_2\text{H}_5\text{Br}$: C_2H_5^+ / Br^+ / $\text{C}_2\text{H}_5\text{Br}^+$
- why would peak X have an extremely high abundance? TWO species have this mass.
- dichloromethane: 3 molecular ions if Cl^{37} or Cl^{35} : $74+14$, $70+14$, $72+14$
- explain what happens with IR absorption of CH bonds...
 - asymmetrical stretch → change in bond length = dipole moment
- explain why N_2 does not absorb IR info
 - non-polar bond ∴ no dipole moment even when bending occurs
- why does IR happen at a higher λ than HNMR?
 - IR is vibration of bonds whereas HNMR is transition between energy states
- explain how you could distinguish E/F
 - HNMR → mass spec will give... → list out split, peaks shift! → print region!
- one of the alkanes from which $\text{C}_4\text{H}_9\text{Br}$ can be formed has 9:1 ratio
 - $\text{H}_3\text{C}-\underset{\text{H}_3\text{C}}{\text{C}}-\text{CH}_3$ NOT $\text{C}_4\text{H}_9\text{Br}$
- explain the benefit of MRI > X-ray medical imaging
 - radio-waves safer than X-ray as lower frequency.
- MRI procedure
 - each organ has different water: lipid
 - diff ^1H absorption → 3D-image produced
- structure of ethyl propanoate structure of propanal
 - $\text{CH}_3-\text{CH}_2-\text{O}-\text{C}(=\text{O})-\text{CH}_2\text{CH}_3$
 - $\text{CH}_3-\text{CH}_2-\text{C}(=\text{O})-\text{H}$ (CHO!)
- 44 m/z value.. CH_3CH_3^+ (from 74) → 30 m/z

state what info can be introduced from 3 diff split patterns

→ singlet: no adj H, → doublet: — → triplet: two adj H.

functional group of COO is ester!

tetramethylsilane - advantages

→ protons in same chemical environment → unreactive

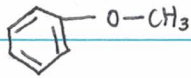
→ does not absorb energy in same region as other protons.

} USED AS A Reference!!!

what can be determined by x-ray crystallography?

→ bond length → bond angle → bond structure

structure of $C_6H_5OCH_3$



benzene = ONE H environment

COCH₃ = ONE H environment