

1 | : Measurement, Data Processing and Analysis

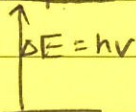
Date

No.

Proton Nuclear Magnetic Resonance Spectroscopy [$^1\text{H-NMR}$]

- protons spin, specifically, H^1 protons
- When in an external magnetic field, the protons will either spin in a direction aligned with the field or will spin anti parallel to the field, which requires more energy
- Hence, 2 energy levels formed

nucleus spins antiparallel

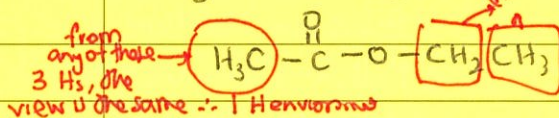


} $\uparrow \Delta E$, stronger field
 $\downarrow \Delta E$, weaker field

nucleus spins parallel

- Electromagnetic waves are used to excite lower energy protons to the higher level
- The point in the spectrum where the absorption occurs is called the chemical shift
- Different chemical environments have different chemical shifts because, for instance, deshielding, when a neighbouring atom holds the e^- in the bond to a greater extent, reduces the shielding from the external magnetic field, \therefore more energy absorbed

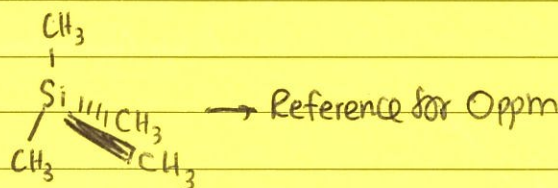
Hydrogen Environments



- 1) Think like a H atom, how many different points are there in terms of perspective?
- 2) Count up - the number of H environments \rightarrow number of peaks on a low-res spectrum

Reference

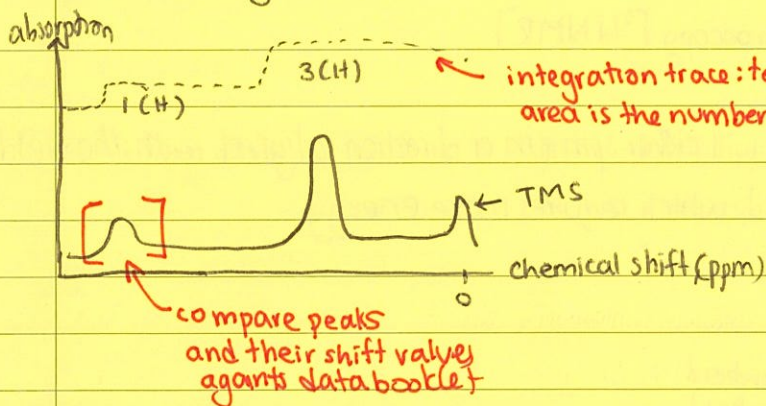
- tetramethylsilane



- Single H environment, only 1 peak
- Unreactive, does not interfere with species under study as strong bonds
- Absorption out of range from most other protons
- Low b.p due to LDFs, easy to remove.
- Soluble in most organic molecules

Understanding the spectra

Date _____ No. _____



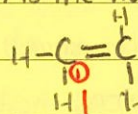
integration trace: tells us the ratio of the areas under the graph, area is the number of H atoms in the ^H environment

[Low Res Spectrum]

High Resolution



→ Allows us to determine splitting pattern
 → Splitting = n+1, where n is the number of Hs on an adjacent Carbon.



for 1, 2 Hs on the next C atom, hence 3 splits ∴ triplet

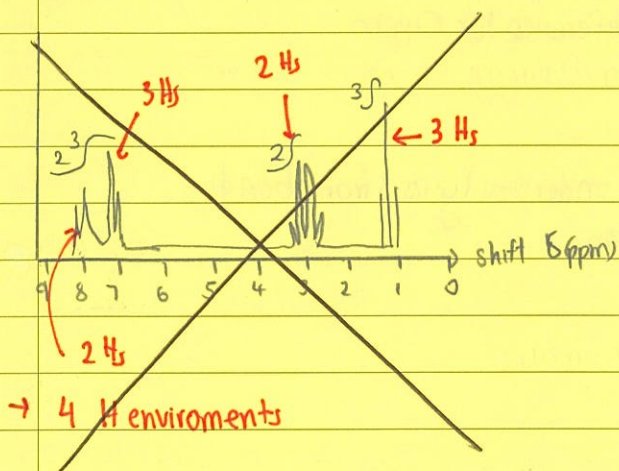
Splitting and Spin-spin Coupling

USES

- Determining structure
 - Medicine → determine extent of damage after heart attacks, check tumours and hydrocephalus
- This variant is MRI

Example Analysis

A Low Res Spectrum is shown

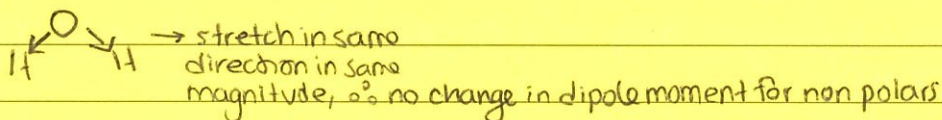


Infrared Spectroscopy

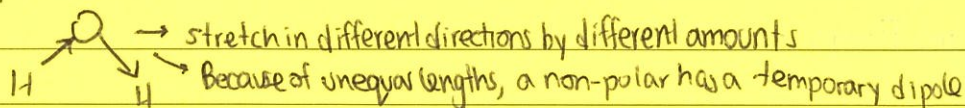
- IR is absorbed by certain bonds, resulting in stretching or bending, giving us information about bonds
- IR absorption is dependent on a change in dipole moment
- If ~~expos~~ the new bent or stretched bonds have new dipoles, then those bonds are infrared active
- The separate δ^+ and δ^- s in a molecule allow the electrical component of IR to increase the vibrational energy of the molecule, producing a corresponding change in the bond's dipole moment. This then affects the polarity of the bond and hence the intensity of absorption
- Why is HI infrared active and I_2 is not? → HI is polar due to the electronegativity difference, hence the electrical component of the IR increases the molecule's vibrational energy, resulting in a change in dipole moment and hence an absorption of IR.
 I_2 is a pure covalent compound and has no partial charges with which the electrical component of IR can interact with \downarrow , \therefore infrared inactive
- Vibrational Frequency and Wavenumber: \uparrow Atomic Mass, ~~down~~ \uparrow wavenumber, as lower energy, \uparrow bond strength, \uparrow wavenumber, \uparrow E

Bending and Stretching

1) Symmetric Stretch



2) Asymmetric Stretch



3) Bending → bending away from geometry → produces change in dipole \therefore IR active

Question: What happens on a molecular level when molecules absorb IR?

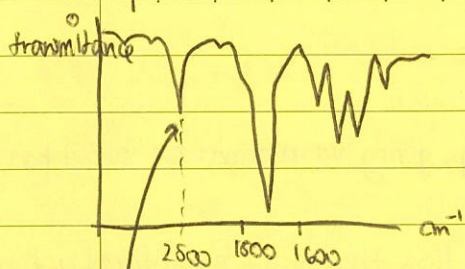
- The separate δ^+ and δ^- allow the electrical component of IR to change the vibrational energy of bonds, stretching or bending them. This changes their polarity, and the energy for this is quantised. The polarity then affects IR absorption

NOTE: The finger print region of an IR spectra is 1400-1800, it peaks here distinguish the compounds as a hydrocarbon

Spectra

Date

No.



Not O-H because it is not strong and broad, see data booklet
indicates that it is a C=O → ∴ either aldehyde or ketone

NOTE: Hydrogen bonds → broadened peak as O-H vibration in hydroxyls change, broader absorption + lower frequency

IR can be used to confirm or eliminate potential functional groups, as only IR of certain wavelengths absorbed and other wavelengths transmitted. Functional groups have characteristic IR absorption

Index of Hydrogen Deficiency (IHD)

- degree of unsaturation
 - number of H₂ molecules needed to fully saturate a molecule [C_xH_{2x+2}]
- Formula = $\frac{2x+2 - [y]}{2}$, where y is number of Hs
- Note; halogens = hydrogens and a nitrogen = 1 C and 1 H and O and S do not affect IHD

Uncertainties and Errors

↳ Uncertainty

- ① Analogue → half of the smallest division
- ② Digital → the smallest division
- ③ Unquantifiable → delay in reaction time, point of indicator colour change

Error

- ① Random → caused by measuring instrument (uncertainties), insufficient data, effect of change in surroundings or misinterpretation of results; reduced by repeats, readings to high balanced by low ones.

- ② Systematic → poor experimental design/procedure, repeating does not help.
 e.g. measuring from top and not bottom of meniscus, using an acid base indicator that is clearly unsuitable. We reduce random error by better experimental design.

Accuracy and precision

- Accuracy - how close observed values are to the true value, small systematic error
- Precision: closer to each other, ∴ low random error and reproducible.

Percentage Error Uncertainty and Error

Uncertainty

$\frac{|\text{uncertainty}|}{\text{measured value}} \times 100\% \rightarrow$ Add all % uncertainties up, this = total random error

Error (Total)

$\frac{\text{True value} - \text{experimental value}}{\text{true value}} \times 100\%$

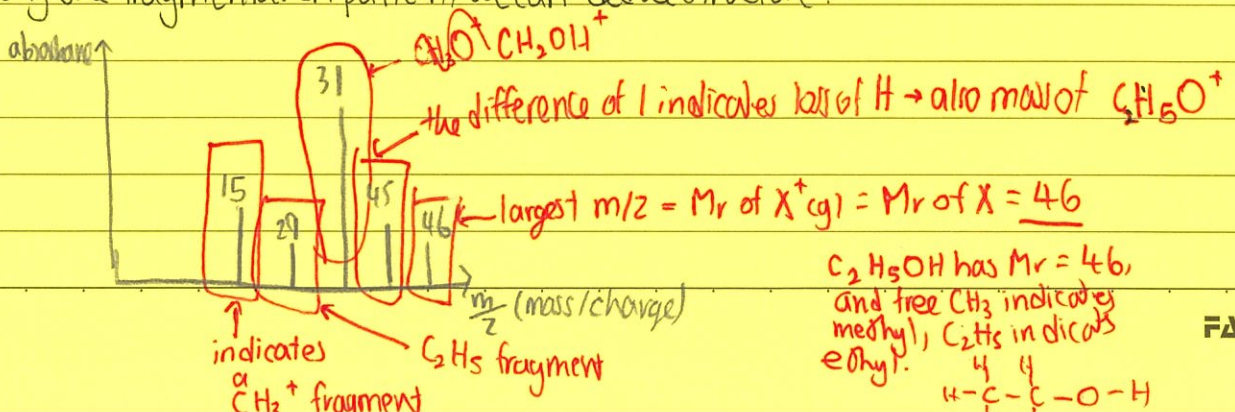
Absolute uncertainty = calc value × % uncertainty

Rounding off answers

- If adding or subtracting → use the d.p given, not s.f. e.g. $5.00\text{g} - 2.83\text{g} = \underline{\underline{2.17\text{g}}}$ (2.d.p)
- If multiplying or dividing, use s.f. of least precise apparatus.
 E.g. heat ^{needed} ~~prod~~ when water heated to 25°C from RTP = $q = mc\Delta T = 0.125\text{kg} \cdot 4.18 \times 10 = 5.225 \approx \underline{\underline{5.2\text{kJ}}}$ (2.s.f)

Mass Spectrometry

- determines Mr of a compound
- Molecule is ionised as followed → $X(\text{g}) + e^- \rightarrow X^+(\text{g}) + 2e^-$, same RMM, corresponds to the largest peak. This X^+ ion is called the parent ion
- However, one ion molecule can be further fragmented, to form different ions that are detected by the mass spectrometer
- Using the fragmentation pattern, we can deduce structure.



When comparing frag patterns, compare why one has a particular peak while another does not, compare overall Mr and any implicit functional groups. Compare peaks, one peak would be larger because of more sites for fragmentation.

Waves

Radiowaves - used in HNMR, ~~are~~ absorbed by nuclei, allow spin reversal

Microwaves - used to increase bond rotational energy \rightarrow for bond length

IR - stretch/bend bonds in IR spectrometry

(UV) / VL - produce electronic transitions \rightarrow e.g Lyman series for H emission spectra

X-Rays - When electrons make transitions between inner energy levels \rightarrow produce diffraction patterns.