Proton Nuclear Magnetic Resonance Spectroscopy (\(^1\)H NMR)

- Protons spin, specifically, \(^1\)H protons

- 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

\[
\Delta E = h\nu
\]

\[\uparrow \Delta E, \text{ stronger field} \]

\[\downarrow \Delta E, \text{ weaker field} \]

- 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 neighboring atom holds the electron in the bond more strongly, reduces the shielding from the external magnetic field, requiring more energy absorbed.

Hydrogen Environments

\[
\begin{array}{c}
\text{Hydrogen Environments}\\
\text{from atom A}\\
\text{3 Hs, one view is the same}\\
\end{array}
\]

1. Think like a H atom. How many different points are there in terms of perspective?
2. Count up - the number of H environments = number of peaks on a low-resolution spectrum.

Reference

- Tetramethylsilane

\[
\begin{array}{c}
\text{CH}_3 \text{Si}
\end{array}
\]

\[
\text{Reference for ppm}
\]

- A single H environment, only 1 peak
- Unreactive, does not interfere with species under study as strong bond
- Absorption out of range from most other proton
- Low b.p. due to LDFs, easy to remove.
- Soluble in most organic molecules
Understanding the spectra

Integration trace: tells us the ratio of the areas under the graph, and is the number of H atoms in the environment.

Compare peaks and their shift values against a database.

High Resolution

- Allows us to determine splitting pattern
- Splitting: $n+1$, where $n$ is the number of Hs on an adjacent carbon.

\[ \text{H} - \text{C} = \text{C} \]

For 1, 2 Hs on the next C atom, hence 3 splits: triplet.

Splitting and Spin-spin Coupling

Example Analysis

A Low Res Spectrum is shown.

4 H environments
Infra-Red Spectroscopy

1. IR is absorbed by certain bonds, resulting in stretching or bending, giving us information about bonds.
2. IR absorption is dependent on a change in dipole moment.
3. If new bent or stretched bonds have new dipoles, then those bonds are infrared active.
4. The separate $S^+$ and $S^-$ 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.
5. 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 molecular 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 $\downarrow$; $\downarrow$ infrared inactive

- Vibrational Frequency and Wavenumber: $\uparrow$ Atomic Mass, $\downarrow$ Wavenumber, as lower energy, $\uparrow$ bond strength, $\uparrow$ Wavenumber, $\uparrow$ E

Bending and Stretching

1) Symmetric Stretch
   $\uparrow$ Stretch in same direction in same magnitude, $\uparrow$ no change in dipole moment for non-polar

2) Asymmetric Stretch
   $\uparrow$ Stretch in different directions by different amounts
   $\downarrow$ Because of unequal lengths, a non-polar has a temporary dipole

3) Bending $\rightarrow$ bending away from geometry $\rightarrow$ produces change in dipole $\uparrow$ IR active

Question: What happens on a molecular level when a molecule absorbs IR?

- The separate $S^+$ and $S^-$ 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 quantized. The polarity then affects IR absorption.

NOTE: The fingerprint region of an IR spectra is 1400-1800; $\uparrow$ peak here distinguishing the compounds as a hydrocarbon.
Spectra

Not +H because it is not strong

H and broad, see data booklet

NOTE: Hydrogen bond → broadened peak as O−H vibration in hydroxyl. Change, broader absorption → lower frequency

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

**Index of Hydrogen Deficiency (IHD)**

→ degree of unsaturation

→ number of Hs needed to fully saturate a molecule \([C_xH_{2x+2}]\)

Formula: \(\frac{2x+2}{3y}\), where \(y\) is number of Hs

→ Note: halogen = hydrogen and a nitrogen = [CandH] and [OandNS] 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 (uncertainty), insufficient data, effect of change in surroundings or misinterpretation of results; reduced by repeat, 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 a 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

\[
\text{Uncertainty} = \frac{\text{measured value}}{100} \quad \rightarrow \quad \text{Add all } \% \text{ uncertainties up, this } \approx \text{ total random error}
\]

Error (Total)

\[
\text{True value} - \text{experimental value} \times 100\% \quad \rightarrow \quad \text{Absolute uncertainty} = \text{calculated value} \times \% \text{ uncertainty}
\]

Rounding off answers

- If adding or subtracting → use the one given. No! S.F. e.g. 5.00g - 2.83g = 2.17g
- If multiplying or dividing, use S.F. at least precise apparatus.
  E.g. heat released when water heated to 25°C from RTP = q = mc\Delta T = 0.125 \times 4.18 \times 10
  = 5.25 \times 5.2kJ (2 sf)

Mass Spectrometry

- Determines Mr of a compound.
- Molecule is ionised as followed → X(g) + e^- → X^+(g) + 2e^-. Some RM, correspond to the largest peak. This X^+ ion is called the parent ion.
- However, one or more molecules can be further fragmented, to form different ions that are detected by the mass spectrometer.
- Using the fragmentation pattern, we can deduce structure.

\[
\text{C}_3\text{H}_5\text{O}_4^+ \quad \text{C}_2\text{H}_5\text{OH} \quad \text{H} \rightarrow \text{also ions of } \text{C}_3\text{H}_5\text{O}^+ \text{, largest m/z = } \text{Mr of } X^+(g) = \text{Mr of } X = 46
\]

\[
\text{C}_2\text{H}_5\text{OH} \text{ has Mr = 46, and thus } \text{CH}_3 \text{OH indicates methyl, } \text{C}_2\text{H}_5 \text{ indicates ethyl, } \text{e}^{+} \text{ indicates } n + 1, \text{ thus } n = 4 \text{ - } n - e = - e - O - H
\]
When comparing fragment 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, to absorb by nuclei, allow spin reversal
Microwaves - used to increase bond rotational energy → for bond length
IR - stretch/bend bonds in IR spectrometry
(UV/Vis) - produce electronic transitions → e.g., Lyman series; for H emission spectra
X-Rays - when electrons make transitions between inner energy levels → produce diffraction patterns.