$^1$H NMR

Protons (nucleus of a hydrogen atom) also have a net spin and can be observed in the NMR.

- Hydrogen atoms are more than 99% $^1$H.
- Other isotopes have special names:
  - $^2$H = deuterium
  - $^3$H = Tritium (radioactive)
- Remember $^{13}$C is only 1% of carbon; $^1$H NMR is much more sensitive.
  - Practically speaking for a typical lab molecule, you can obtain a $^1$H-NMR with 1-2 mg of compound in a matter of minutes but the same sample may require a few hours to obtain a $^{13}$C spectrum.

![Diagram of energy levels and transitions in magnetic fields.](Diagram)

Protons resonate at a different frequency than $^{13}$C's. Typical compounds lie within a smaller range of frequencies than $^{13}$C.

PROTONS ON TYPICAL ORGANIC COMPOUNDS **1-12 ppm**

Typical locations of $^1$H-NMR resonances.

**Down Field**

![Down field diagram](Diagram)

**Up Field**

![Up field diagram](Diagram)
WHAT IS SO SPECIAL ABOUT PROTON NMR?

• You can accurately integrate your spectra to know how many of each proton type you have.
• Through bond coupling tells us about what is adjacent to the protons of a particular resonance.

¹H-NMR peaks can be integrated!!

Tells you the ratio of the number of protons that compose each resonance. This is particularly helpful when you have symmetry.
Protons can split other protons by through bond J-coupling.

Coupling can be observed between two protons. The coupling originates because in a magnetic field, the nuclear spin will perturb the local distribution of electrons.

Protons on adjacent carbons are said to be **Vicinal** protons.

Are coupled over three bonds.

**Splitting over two bonds is usually not observed.**

Geminal coupling is only observed when the two protons are in different "chemical environments".

Note: there are exceptions when the protons are diastereotopic (more on this later).

Protons on the same carbons are said to be **geminal** protons.

Proton NMR signals are split following the N+1 rule for proton NMR; N typically represents the number of adjacent protons.

N+1 RULE APPLIES

(note: it can get more complicated)

N+1 rule extends beyond quartets
clickers

\[
\begin{align*}
&\text{a. singlet} \\
&\text{b. doublet} \\
&\text{c. triplet} \\
&\text{d. quartet}
\end{align*}
\]

Rules for J-coupling

Nuclei must be chemical shift NON-EQUIVALENT to show (obvious) coupling to each other:

- 1,2-dichloroethane is a singlet

- The coupling is mutual: \( A \) splits \( B \) the same amount as \( B \) splits \( A \)

- Coupling constants are reported in Hz and will have the same value on different instruments.

C\(_2\)H\(_4\)O

CLICKERS

Which is it?

A  

B  

C  

note: 6:4 ratio = 3:2 ratio
Same compound run on a 60 MHz and a 300 MHz spectrum

Coupling constant is measured by taking the difference between peaks (in ppm) within a multiplet and multiplying by the field strength in Hz.
Common Splitting Patterns

Ethyl
- quartet

triplet

Isopropyl
- triplet

doublet

aromatic protons have (almost) the same chemical shift
Protons in different chemical structures have different amounts of splitting or "coupling constants".

- Bad News: Life gets more complicated
- Good News: Splitting tells us more about the chemical structure.
Coupling Constants Depends on Structure and Geometry

Approximate Coupling Constants:

\[
\begin{align*}
7 \text{ Hz (in-plane)} \\
10 \text{ Hz} \\
15 \text{ Hz} \\
2 \text{ Hz} \\
8 \text{ Hz}
\end{align*}
\]

Special Couplings over more than 3 bonds:

\[
\begin{align*}
2 \text{ Hz} \\
0 \text{ Hz} \\
0.3 \text{ Hz, depends on geometry}
\end{align*}
\]

Karplus Equation:

\[
J_{HH} (\text{Hz}) = \frac{1}{2} \left( \frac{\theta}{180} \right)^2
\]

\[
\begin{align*}
J = 2-3 \text{ Hz} \\
J = 8-10 \text{ Hz}
\end{align*}
\]
Why is A a singlet? How do you explain the splitting pattern of B? How do you explain the splitting pattern of C?

Magnet analogy

Observe coupled protons

Lower energy state

High energy state

Two "degenerate" (same energy) states

Spin splitting diagrams
What if we have a strong and weak magnet?

What if the H's are different, and have very different coupling constants??!
Aromatic (o,m,p) coupling constants

Hₘ 7.55 ppm
Hₜ 7.29 ppm
Hₐ 6.92 ppm

JₘHₛ 1.9 Hz
JₜHₛ 8.0 Hz
JₗHₛ 0.3 Hz

3 doublets of doublets

‘Doublets of triplets’ and ‘doublets of quartets’

where JₘHₜ = JₗHₛ
When the going gets really tough...

... we call things a multiplet (m)

situation 1: coupling pattern is very complex

described as: 1.5–1.3 (m, 1H)

situation 2: your peak overlaps with other resonances

14 overlapping H's!

1.31–1.26 (m, 14H)
Diastereotopic Protons

- Some chemical shift
- No coupling

Diastereotopic protons:
- CH$_3$ nearby a chiral center
- Chemical shifts differ (but may overlap in some cases)
- Coupling can often be observed

Diastereotopic Protons: not just in cyclic systems

HH: 3.6 ppm, dd, J = 8.0 Hz, 4.0 Hz
HH: 3.9 ppm, dd, J = 6.8, 4.8 Hz
HH: 4.5 ppm, dd, J = 6.8, 8.0 Hz

Still diastereotopic
3 diastereotopic methylenes

Notice the coupling!

Coupling to Hetero Atoms

Observed Only Sometimes
Depends on Concentration
Solvent used

Rarely Observed

WHY: hydrogen atoms exchange due to hydrogen bonding

Easy Test

The hydrogen isotope deuterium (D) has no spin and cannot couple