SECTION 12 – NMR SPECTROSCOPY

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- $^1$H NMR and $^{13}$C NMR

12-1 -- $^1$H NMR
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• Off-Resonance Decoupling (“Spin-Coupled Mode”)
• Singlet, Doublet, Triplet, Quartet
Section 12: NMR Spectroscopy.

-> "Nuclear Magnetic Resonance":
   - a spectroscopic technique that provides information about the carbon-hydrogen framework (structural info) of a molecule.

* we will study two types of NMR spectroscopy:

1. $^1H\text{ NMR} = "\text{proton NMR}"$.
   - begins on this page.

2. $^{13}C\text{ NMR} = "\text{Carbon-13 NMR}"$.
   - begins on page 12-16

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* $^1H\text{ NMR} \Rightarrow \text{most important to us in finding structural info of a molecule.}$

- Protons ($^1H$ nuclei) and some other nuclei have spin.
  - there are 2 spin states.
    - $+\frac{1}{2}$, or $\alpha$
    - $-\frac{1}{2}$, or $\beta$
  - "spin quantum #’s"

* these 2 spin states have magnetic moments.

* in a magnetic field, these spin states have different energies...
Illustration of how/why these 2 spin states have different energies:

In a magnetic field $H_0$, we have:

- The electromagnetic radiation of this energy difference ($\Delta E$) gets absorbed and causes a spin flip ($\alpha \rightarrow \beta$).
- Radio frequency electromagnetic radiation is required to do a spin flip.
- The energy difference ($\Delta E$) is proportional to the magnetic field that's actually "felt" by the proton, $H_p$ (as opposed to $H_0$).

* For a "bare" proton ($H^+$), $H_p \approx H_0$, but protons in molecules are shielded to various extents by surrounding $e^-$ clouds and thus "feel" slightly less than the full applied field.
different "types" of protons, i.e. protons in different molecular environments, are shielded to different extents.

There are 2 ways to do these experiments:

1. **Hold magnetic field constant and vary the frequency.** Each type of proton has a different $\Delta E$ for $\alpha \rightarrow \beta$ spin flip and absorbs at a different frequency.

2. **Hold frequency constant and vary $H_0$.** Each type of proton requires a different field strength to attain the correct $\Delta E$ for absorbance.

   outdated; used with older instruments.

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**A Sample $^1H$ NMR Spectrum.**

ex: $\text{Cl-CH}_2\text{-C}^\text{\textbullet}_{\text{Cl}}\text{-CH}_3$

added $(\text{CH}_3)_4\text{Si}$ (tetramethyl silane, or TMS) to define zero point = 0 ppm.

"downfield" — increasing $H_0$ — "upfield"

ppm scale (or $\delta$ scale)
the absorption peak, or "resonance," of the CH₃ protons is said to be 2.2 ppm downfield of TMS, or at δ 2.2.

the CH₂ protons appear 4.0 ppm downfield of TMS, or at δ 4.0.

* δ-values are "chemical shifts" of the protons (independent of spectrometer field strength).

* chemical shifts depend on the environment of the protons.

Characteristic Chemical Shifts:

- Electronegative atoms withdraw e⁻ density, and this will cause nearby protons (H's) to be deshiledled.

→ this deshielding will cause H's to appear at a lower field strength.

→ higher δ-value = higher ppm.

→ "further downfield"
\[ \text{ex: } X - \overset{\text{1}}{\text{C}} - \overset{\text{1}}{\text{H}} \quad \delta 2.5-4.0 \]
(usually at \( \delta 3.5 \))
\[ X = -\text{Cl}, -\text{Br}, -\text{O} \]

- **Alkyl groups** can have an effect on the chemical shift.
  
  \[ \text{R-CH}_3 \quad \delta 0.9 \]
  \[ \text{R}_2\text{CH} \quad \delta 1.2 \]
  \[ \text{R}_3\text{CH} \quad \delta 1.5 \]

- **Electronegative atoms in the \( \beta \)-position.**
  
  If there are H's \( \beta \) to \(-X\) (\( \text{H-}\overset{\text{1}}{\text{C}}-\overset{\text{1}}{\text{C}}-X\)), you will see shifts downfield slightly ("to the left") from their normal \( \delta \)-value (\( \sim 0.1-0.7 \) ppm).

\[ \text{ex: } \overset{\text{1}}{\text{CH}}_3 - \overset{\text{1}}{\text{CH}}_2 - \overset{\text{1}}{\text{CH}}_2 - \text{Cl} \]
\[ \delta 0.9 \quad \delta 1.3 \quad \delta 3.44 \]

\[ \text{ex: } \begin{array}{l}
\overset{\text{1}}{\text{Cl}} - \overset{\text{1}}{\text{CH}}_2 - \overset{\text{1}}{\text{C}} - \overset{\text{1}}{\text{CH}}_3 \\
\end{array} \]
\[ \delta 4.0 \quad \delta 2.2 \]

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- **6 Factors that Allow us to understand 'H NMR.**

- **addressed on next page...**

  "proton NMR"
Relative Areas Under Peaks are proportional to the numbers of H's that represent the peaks. These areas are determined by "electronic integration."

\[ \text{Cl} - \text{CH}_2 - \text{C} - \text{CH}_3 \]

\[ \text{integration} \]

\[ \text{7.5 mm} \]

\[ \Rightarrow \]

You can see we have measured the integral step heights (in mm).

* Ratio of above areas: \( 2H : 3H \)

Spin-Spin Splitting (Coupling) tells us how things are connected in the organic compound. Protons (H's) "feel" spins of protons (H's) on adjacent carbons:

\[ \text{Cl} - \text{C} - \text{C} - \text{H}_b \]

\[ \text{H}_b \]

\[ \text{Ha} \]

\[ \text{ex: Cl} - \text{C} - \text{C} - \text{H}_b \]

\[ \text{H}_b \]

\[ \text{H}_a \]

Ratio: \( 1H : 2H \)
... in the previous example:

**Consider the H_b absorption = why 2 peaks?**

- in ≈ 50% of the molecules, H_a has α spin, and in the other ≈ 50%, H_a has β spin.

- the neighboring α-spin adds to the field felt by H_b.

- the neighboring β-spin adds to the field felt by H_b

* therefore H_b appears as a "doublet".

**Consider the H_a absorption = why 3 peaks?**

- similar to the reasoning above.

- H_a is "next to" 2 equivalent neighboring protons, H_b

- each H_b can have α or β spin possible combinations:

- 25% 25% 25%

- 1H:2H:1H peak ratio (of intensities)

- H_a appears as a "triplet".
SECTION 12 – NMR SPECTROSCOPY

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