Nuclear Magnetic Resonance

Chapter 13
Nuclear magnetic resonance (NMR) spectroscopy: a spectroscopic technique that gives us information about the number and types of atoms in a molecule, for example, about the number and types of

- hydrogen atoms using $^1$H-NMR spectroscopy
- carbon atoms using $^{13}$C-NMR spectroscopy
- phosphorus atoms using $^{31}$P-NMR spectroscopy
Nuclear Spin States

◆ An electron has a spin quantum number of 1/2 with allowed values of +1/2 and -1/2
  • this spinning charge creates an associated magnetic field
  • in effect, an electron behaves as if it is a tiny bar magnet and has what is called a magnetic moment

◆ The same effect holds for certain atomic nuclei
  • any atomic nucleus that has an odd mass number, an odd atomic number, or both also has a spin and a resulting nuclear magnetic moment
  • the allowed nuclear spin states are determined by the spin quantum number, \( I \), of the nucleus
Nuclear Spin States

- A nucleus with spin quantum number $I$ has $2I + 1$ spin states; if $I = 1/2$, there are two allowed spin states.
- Table 13.1 gives the spin quantum numbers and allowed nuclear spin states for selected isotopes of elements common to organic compounds.

<table>
<thead>
<tr>
<th>Element</th>
<th>$^1$H</th>
<th>$^2$H</th>
<th>$^{12}$C</th>
<th>$^{13}$C</th>
<th>$^{14}$N</th>
<th>$^{16}$O</th>
<th>$^{31}$P</th>
<th>$^{32}$S</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nuclear spin quantum number ($I$)</td>
<td>1/2</td>
<td>1</td>
<td>0</td>
<td>1/2</td>
<td>1</td>
<td>0</td>
<td>1/2</td>
<td>0</td>
</tr>
<tr>
<td>Number of spin states</td>
<td>2</td>
<td>3</td>
<td>1</td>
<td>2</td>
<td>3</td>
<td>1</td>
<td>2</td>
<td>1</td>
</tr>
</tbody>
</table>
Nuclear Spins in $B_0$

- within a collection of $^1$H and $^{13}$C atoms, nuclear spins are completely random in orientation
- when placed in a strong external magnetic field of strength $B_0$, however, interaction between nuclear spins and the applied magnetic field is quantized, with the result that only certain orientations of nuclear magnetic moments are allowed
Nuclear Spins in $B_0$

- for $^1H$ and $^{13}C$, only two orientations are allowed

![Diagram showing energy levels and spin states for nuclear spins in $B_0$]
Nuclear Spins in $B_0$

In an applied field strength of 7.05T, which is readily available with present-day superconducting electromagnets, the difference in energy between nuclear spin states for

- $^1$H is approximately 0.120 J (0.0286 cal)/mol, which corresponds to electromagnetic radiation of 300 MHz (300,000,000 Hz)
- $^{13}$C is approximately 0.030 J (0.00715 cal)/mol, which corresponds to electromagnetic radiation of 75MHz (75,000,000 Hz)
Nuclear Spin in $B_0$

- The energy difference between allowed spin states increases linearly with applied field strength.
- Values shown here are for $^1$H nuclei.
Nuclear Magnetic Resonance

- When nuclei with a spin quantum number of 1/2 are placed in an applied field, a small majority of nuclear spins are aligned with the applied field in the lower energy state.
- The nucleus begins to precess and traces out a cone-shaped surface, in much the same way a spinning top or gyroscope traces out a cone-shaped surface as it precesses in the earth’s gravitational field.
- We express the rate of precession as a frequency in hertz.
If the precessing nucleus is irradiated with electromagnetic radiation of the same frequency as the rate of precession,

- the two frequencies couple,
- energy is absorbed, and
- the nuclear spin is flipped from spin state $+1/2$ (with the applied field) to $-1/2$ (against the applied field)
Nuclear Magnetic Resonance

- Figure 13.3 the origin of nuclear magnetic "resonance"
Nuclear Magnetic Resonance

**Resonance:** in NMR spectroscopy, resonance is the absorption of electromagnetic radiation by a precessing nucleus and the resulting “flip” of its nuclear spin from a lower energy state to a higher energy state.

**The instrument used to detect this coupling of precession frequency and electromagnetic radiation records it as a signal**

- **signal:** a recording in an NMR spectrum of a nuclear magnetic resonance
Nuclear Magnetic Resonance

- if we were dealing with $^1$H nuclei isolated from all other atoms and electrons, any combination of applied field and radiation that produces a signal for one $^1$H would produce a signal for all $^1$H. The same is true of $^{13}$C nuclei
- but hydrogens in organic molecules are not isolated from all other atoms; they are surrounded by electrons, which are caused to circulate by the presence of the applied field
- the circulation of electrons around a nucleus in an applied field is called diamagnetic current and the nuclear shielding resulting from it is called diamagnetic shielding
Nuclear Magnetic Resonance

- the difference in resonance frequencies among the various hydrogen nuclei within a molecule due to shielding/deshielding is generally very small.

- the difference in resonance frequencies for hydrogens in CH$_3$Cl compared to CH$_3$F under an applied field of 7.05T is only 360 Hz, which is 1.2 parts per million (ppm) compared with the irradiating frequency.

\[
\frac{360 \text{ Hz}}{300 \times 10^6 \text{ Hz}} = \frac{1.2}{10^6} = 1.2 \text{ ppm}
\]
Nuclear Magnetic Resonance

- signals are measured relative to the signal of the reference compound tetramethylsilane (TMS)

\[
\begin{align*}
\text{CH}_3 \\
\text{CH}_3 \text{Si} \text{CH}_3 \\
\text{CH}_3
\end{align*}
\]

Tetramethylsilane (TMS)

- for a $^1$H-NMR spectrum, signals are reported by their shift from the 12 H signal in TMS
- for a $^{13}$C-NMR spectrum, signals are reported by their shift from the 4 C signal in TMS

Chemical shift ($\delta$): the shift in ppm of an NMR signal from the signal of TMS
NMR Spectrometer

Radio frequency input oscillator

Radio frequency output receiver

Powerful electromagnet or superconducting magnet

Sample tube

NMR spectrum

16-16
Essentials of an NMR spectrometer are a powerful magnet, a radio-frequency generator, and a radio-frequency detector.

The sample is dissolved in a deuterated solvent, most commonly CDCl₃ or D₂O, and placed in a sample tube which is then suspended in the magnetic field and set spinning.

Using a Fourier transform NMR (FT-NMR) spectrometer, a spectrum can be recorded in about 2 seconds.
What information do we get from NMR?

- First we get different information depending on the nucleus studied (\(^1\)H, \(^{13}\)C, \(^{31}\)P etc)
- We get information about the different types of hydrogens and carbons present in the molecule as well as their numbers and how they “connect” with one another.
- We can visualize an NMR spectrum like a “puzzle formed by different pieces”. Putting it together will help us to identify the structure of molecule. In general we will work with information from NMR and IR and we can also use information from MS spectrometry and reactivity to help us.
NMR Spectrum

- $^1$H-NMR spectrum of methyl acetate

- **Downfield**: the shift of an NMR signal to the left on the chart paper (LARGER CHEMICAL SHIFT; DESHIELDED)
- **Upfield**: the shift of an NMR signal to the right on the chart paper (SMALLER CHEMICAL SHIFT; MORE SHIELDING)
**Equivalent Hydrogens**

**Equivalent hydrogens:** have the same chemical environment

- a molecule with 1 set of equivalent hydrogens gives 1 NMR signal

Propanone (Acetone)  1,2-Dichloroethane  Cyclopentane  2,3-Dimethyl-2-butene

**Conditions:**
- H are bonded to the same sp³ hybridized carbon atom that can rotate freely at RT
- H are related by symmetry (plane or point of symmetry) in the molecule
Equivalent Hydrogens

- A molecule with 2 or more sets of equivalent hydrogens gives a different NMR signal for each set.

1,1-Dichloroethane (2 signals)
Cyclopentanone (2 signals)
(Z)-1-Chloro-3-propene (3 signals)
Cyclohexene (3 signals)
Signal Areas

- Relative areas of signals are proportional to the number of \( H \) giving rise to each signal
- Modern NMR spectrometers electronically integrate and record the relative area of each signal

![Chemical Shift Graph](attachment:image.png)
ChemActivity 16: Spectroscopy

- Split quickly in groups of 4
- Read hand out (Chem Activity 16, Parts B and C)
- Work on the critical thinking questions (10-29)
- You have 35 min
- We will discuss the questions in 10-15 min (first part B and then we will do part C)
### Chemical Shifts

#### $\text{^{1}H-NMR}$

<table>
<thead>
<tr>
<th>Type of Hydrogen</th>
<th>Chemical Shift ($\delta$)</th>
<th>Type of Hydrogen</th>
<th>Chemical Shift ($\delta$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(\text{CH}_3)_4\text{Si}$</td>
<td>0 (by definition)</td>
<td>$\text{O}$</td>
<td>$\text{O}$</td>
</tr>
<tr>
<td>$\text{RCH}_3$</td>
<td>0.8-1.0</td>
<td>$\text{RCOCH}_3$</td>
<td>3.7-3.9</td>
</tr>
<tr>
<td>$\text{RCH}_2\text{R}$</td>
<td>1.2-1.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{R}_3\text{CH}$</td>
<td>1.4-1.7</td>
<td>$\text{RCOCH}_2\text{R}$</td>
<td>4.1-4.7</td>
</tr>
<tr>
<td>$\text{R}_2\text{C}=\text{C}\text{RCH}_2\text{R}_2$</td>
<td>1.6-2.6</td>
<td>$\text{RCH}_2\text{I}$</td>
<td>3.1-3.3</td>
</tr>
<tr>
<td>$\text{RC}≡\text{CH}$</td>
<td>2.0-3.0</td>
<td>$\text{RCH}_2\text{Br}$</td>
<td>3.4-3.6</td>
</tr>
<tr>
<td>$\text{ArCH}_3$</td>
<td>2.2-2.5</td>
<td>$\text{RCH}_2\text{Cl}$</td>
<td>3.6-3.8</td>
</tr>
<tr>
<td>$\text{ArCH}_2\text{R}$</td>
<td>2.3-2.8</td>
<td>$\text{RCH}_2\text{F}$</td>
<td>4.4-4.5</td>
</tr>
<tr>
<td>$\text{ROH}$</td>
<td>0.5-6.0</td>
<td>$\text{ArOH}$</td>
<td>4.5-4.7</td>
</tr>
<tr>
<td>$\text{RCH}_2\text{OH}$</td>
<td>3.4-4.0</td>
<td>$\text{R}_2\text{C}=\text{CH}_2$</td>
<td>4.6-5.0</td>
</tr>
<tr>
<td>$\text{RCH}_2\text{OR}$</td>
<td>3.3-4.0</td>
<td>$\text{R}_2\text{C}=\text{CHR}$</td>
<td>5.0-5.7</td>
</tr>
<tr>
<td>$\text{R}_2\text{NH}$</td>
<td>0.5-5.0</td>
<td>$\text{ArH}$</td>
<td>6.5-8.5</td>
</tr>
<tr>
<td>$\text{RCCH}_3$</td>
<td>2.1-2.3</td>
<td>$\text{RCH}$</td>
<td>9.5-10.1</td>
</tr>
<tr>
<td>$\text{RCCH}_2\text{R}$</td>
<td>2.2-2.6</td>
<td>$\text{RCOCH}$</td>
<td>10-13</td>
</tr>
</tbody>
</table>
Chemical Shift

- Depends on (1) electronegativity of nearby atoms, (2) the hybridization of adjacent atoms, and (3) diamagnetic effects from adjacent pi bonds.

- **Electronegativity**

<table>
<thead>
<tr>
<th>CH$_3$-X</th>
<th>Electronegativity of X</th>
<th>Chemical Shift ($\delta$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$F</td>
<td>4.0</td>
<td>4.26</td>
</tr>
<tr>
<td>CH$_3$OH</td>
<td>3.5</td>
<td>3.47</td>
</tr>
<tr>
<td>CH$_3$Cl</td>
<td>3.1</td>
<td>3.05</td>
</tr>
<tr>
<td>CH$_3$Br</td>
<td>2.8</td>
<td>2.68</td>
</tr>
<tr>
<td>CH$_3$I</td>
<td>2.5</td>
<td>2.16</td>
</tr>
<tr>
<td>(CH$_3$)$_4$C</td>
<td>2.1</td>
<td>0.86</td>
</tr>
<tr>
<td>(CH$_3$)$_4$Si</td>
<td>1.8</td>
<td>0.00</td>
</tr>
</tbody>
</table>

The effect of an electronegative substituent falls off quickly with the distance (2 atoms is 10%, 3 atoms negligible)
Chemical Shift

◆ Hybridization of adjacent atoms

<table>
<thead>
<tr>
<th>Type of Hydrogen (R = alkyl)</th>
<th>Name of Hydrogen</th>
<th>Chemical Shift (δ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RCH₃, R₂CH₂, R₃CH</td>
<td>Alkyl</td>
<td>0.8 - 1.7</td>
</tr>
<tr>
<td>R₂C=C(R)CHR₂</td>
<td>Allylic</td>
<td>1.6 - 2.6</td>
</tr>
<tr>
<td>RC≡CH</td>
<td>Acetylenic</td>
<td>2.0 - 3.0</td>
</tr>
<tr>
<td>R₂C=CHR, R₂C≡CH₂</td>
<td>Vinylic</td>
<td>4.6 - 5.7</td>
</tr>
<tr>
<td>RCHO</td>
<td>Aldehydic</td>
<td>9.5-10.1</td>
</tr>
</tbody>
</table>

sp²-hybridized carbon more EN than sp³ (more s-character)
Diamagnetic effects of pi bonds

- A carbon-carbon triple bond shields an acetylenic hydrogen and shifts its signal upfield (to the right) to a smaller $\delta$ value.
- A carbon-carbon double bond deshields vinylic hydrogens and shifts their signal downfield (to the left) to a larger $\delta$ value.

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</tr>
<tr>
<td>$\text{R}_2\text{C}≡\text{CH}_2$</td>
<td>Vinylic</td>
<td>4.6 - 5.7</td>
</tr>
</tbody>
</table>
Chemical Shift

- Magnetic induction in the pi bonds of a carbon-carbon triple bond (Fig 13.9)

Induced flow of electrons in the pi system of alkyne

Induced local magnetic field of the pi electrons is against the applied field; it requires a greater applied field to bring an acetylenic hydrogen into resonance.

Applied field, $B_0$
Chemical Shift

• magnetic induction in the pi bond of a carbon-carbon double bond (Fig 13.10)

![Diagram of induced circulation of pi electrons in an alkene](image)

Induced local magnetic field of the pi electrons reinforces the applied field and provides part of the field necessary to bring a vinyl hydrogen into resonance.

Presence of pi electrons in the carbonyl group same effect on chemical shift of H in an aldehyde group
Chemical Shift

- magnetic induction of the pi electrons in an aromatic ring (Fig. 13.11)
Signal Splitting; the \((n + 1)\) Rule

- **Peak**: the units into which an NMR signal is split; doublet, triplet, quartet, etc.
- **Signal splitting**: splitting of an NMR signal into a set of peaks by the influence of neighboring nonequivalent hydrogens
- **\((n + 1)\) rule**: if a hydrogen has \(n\) hydrogens nonequivalent to it but equivalent among themselves on the same or adjacent atom(s), its \(^1\text{H}-\text{NMR}\) signal is split into \((n + 1)\) peaks
Signal Splitting (n + 1)

- $^1$H-NMR spectrum of 1,1-dichloroethane

For these hydrogens, $n = 1$; their signal is split into $(1 + 1) = 2$ peaks; a doublet

For this hydrogen, $n = 3$; its signal is split into $(3 + 1) = 4$ peaks; a quartet