Origins of Signal Splitting

$^1$H-NMR signals are split into multiple peaks when molecules containing nonequivalent hydrogen atoms that are separated by no more than three bonds.

- **Signal coupling:** an interaction in which the nuclear spins of adjacent atoms influence each other and lead to the splitting of NMR signals.
- **Coupling constant (J):** the separation on an NMR spectrum (in hertz) between adjacent peaks in a multiplet;
  - a quantitative measure of the influence of the spin-spin coupling with adjacent nuclei.
Origins of Signal Splitting

\[ H_a \quad H_b \]

- Spin-spin coupling

\[ H_a \quad H_b \quad +\frac{1}{2} = H_b \text{ spin} \]

\[ H_a \quad H_b \quad -\frac{1}{2} = H_b \text{ spin} \]

\[ J_{ab} \]

\[ H_a \text{ signal} \]

\[ H_b \text{ signal} \]
Origins of Signal Splitting

- because splitting patterns from spectra taken at 300 MHz and higher are often difficult to see, it is common to retrace certain signals in expanded form
- $^1$H-NMR spectrum of 3-pentanone; scale expansion shows the triplet quartet pattern more clearly
**Coupling Constants**

- **Coupling constant (J):** the distance between peaks in a split signal, expressed in hertz
  - the value is a quantitative measure of the magnetic interaction of nuclei whose spins are coupled

<table>
<thead>
<tr>
<th>Structure</th>
<th>Coupling Constant (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{H}_a \text{H}_b )</td>
<td>6-8 Hz</td>
</tr>
<tr>
<td>( \text{H}_a \text{H}_b )</td>
<td>8-14 Hz</td>
</tr>
<tr>
<td>( \text{H}_a \text{H}_b )</td>
<td>0-5 Hz</td>
</tr>
<tr>
<td>( \text{H}_a \text{H}_b )</td>
<td>0-5 Hz</td>
</tr>
<tr>
<td>( \text{H}_a \text{H}_b )</td>
<td>11-18 Hz</td>
</tr>
<tr>
<td>( \text{H}_a \text{H}_b )</td>
<td>5-10 Hz</td>
</tr>
<tr>
<td>( \text{H}_a \text{H}_b )</td>
<td>0-5 Hz</td>
</tr>
<tr>
<td>( \text{H}_a \text{H}_b )</td>
<td>8-11 Hz</td>
</tr>
</tbody>
</table>
Origins of Signal Splitting

- C — C —
  \( H_a \quad H_b \)
  Spin-spin coupling
  One \( H_b \) atom

- C — C —
  \( H_a \quad H_b \)
  Spin-spin coupling
  Two equivalent \( H_b \) atoms

- C — C —
  \( H_b \quad H_a \)
  Spin-spin coupling
  Three equivalent \( H_b \) atoms

\[
\begin{align*}
\text{1 : 1} & \quad \text{1 : 2 : 1} & \quad \text{1 : 3 : 3 : 1}
\end{align*}
\]

Observed splitting in signal of \( H_a \)
**Signal Splitting**

- **Pascal’s Triangle**
  - as illustrated by the highlighted entries, each entry is the sum of the values immediately above it to the left and the right

Careful with electronic noise that prevents distinguishing the smaller side peaks for a particular H with a signal of low intensity.
Physical Basis for \((n + 1)\) Rule

- Coupling of nuclear spins is mediated through intervening bonds
  - H atoms with more than three bonds between them generally do not exhibit noticeable coupling
  - for H atoms three bonds apart, the coupling is referred to as vicinal coupling
Coupling Constants

- an important factor in vicinal coupling is the angle $\alpha$ between the C-H sigma bonds and whether or not it is fixed
- coupling is a maximum when $\alpha$ is 0° and 180°; it is a minimum when $\alpha$ is 90°

Bonds that rotate rapidly at RT do not have a fixed angle between adjacent C-H bonds: average angle and average coupling are observed
More Complex Splitting Patterns

- thus far, we have concentrated on spin-spin coupling with only one other nonequivalent set of H atoms
- more complex splittings arise when a set of H atoms couples to more than one set H atoms
- a tree diagram shows that when $H_b$ is adjacent to nonequivalent $H_a$ on one side and $H_c$ on the other, the resulting coupling gives rise to a doublet of doublets
More Complex Splitting Patterns

- If $H_c$ is a set of two equivalent $H$, then the observed splitting is a doublet of triplets.

In the general case, a signal will be split into $(n + 1) \times (m + 1)$ peaks for an $H$ atom coupled to a set of $n$ $H$ atoms with one coupling constant, and to a set of $m$ $H$ atoms with another coupling constant.
More Complex Splitting Patterns

- because the angle between C-H bond determines the extent of coupling, bond rotation is a key parameter.
- in molecules with relatively free rotation about C-C sigma bonds, H atoms bonded to the same carbon in CH₃ and CH₂ groups generally are equivalent.
- if there is restricted rotation, as in alkenes and cyclic structures, H atoms bonded to the same carbon may not be equivalent.
- nonequivalent H on the same carbon will couple and cause signal splitting.
- this type of coupling is called geminal coupling (*J* = 0-5 Hz).
More Complex Splitting Patterns

- in ethyl propenoate, an unsymmetrical terminal alkene, the three vinylic hydrogens are nonequivalent.
More Complex Splitting Patterns

- A tree diagram for the complex coupling of the three vinylic hydrogens in ethyl propenoate.
More Complex Splitting Patterns

- cyclic structures often have restricted rotation about their C-C bonds and have constrained conformations
- as a result, two H atoms on a CH$_2$ group can be nonequivalent, leading to complex splitting

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More Complex Splitting Patterns

- a tree diagram for the complex coupling in 2-methyl-2-vinyloxirane
More Complex Splitting Patterns

- Complex coupling in flexible molecules
  - coupling in molecules with unrestricted bond rotation often gives only $m + n + l$ peaks
  - that is, the number of peaks for a signal is the number of adjacent hydrogens + 1, no matter how many different sets of equivalent H atoms that represents
  - the explanation is that bond rotation averages the coupling constants throughout molecules with freely rotating bonds and tends to make them similar; for example in the 6- to 8-Hz range for H atoms on freely rotating $sp^3$ hybridized C atoms
More Complex Splitting Patterns

- simplification of signal splitting occurs when coupling constants are the same
More Complex Splitting Patterns

- an example of peak overlap occurs in the spectrum of 1-chloro-3-iodopropane
- the central CH₂ has the possibility for 9 peaks (a triplet of triplets) but because J_{ab} and J_{bc} are so similar, only 4 + 1 = 5 peaks are distinguishable
Fast exchange:

- Hydrogen atoms bonded to oxygen or nitrogen atoms can exchange with each other faster than the time it takes to acquire a $^1$H-NMR spectrum
- Process facilitated by traces of acid or base
- Consequences:
  a) Broad signals
  b) Signals will disappear when $D_2$O or deuterated alcohol is added

Important affected functional groups: carboxylic acids, alcohols, amines, and amides
Stereochemistry & Topicity

- Depending on the symmetry of a molecule, otherwise equivalent hydrogens may be:
  - homotopic
  - enantiotopic
  - diastereotopic

- The simplest way to visualize topicity is to substitute an atom or group by an isotope; is the resulting compound:
  - the same as its mirror image
  - different from its mirror image
  - are diastereomers possible
Homotopic atoms or groups

Dichloromethane (achiral)

Substitution does not produce a stereocenter; therefore hydrogens are homotopic.

- homotopic atoms or groups have identical chemical shifts under all conditions
Enantiotopic groups

Substitution produces a stereocenter; therefore, hydrogens are enantiotopic. Both hydrogens are prochiral; one is pro-R-chiral, the other is pro-S-chiral.

- Enantiotopic atoms or groups have identical chemical shifts in achiral environments.
- They have different chemical shifts in chiral environments (e.g. chiral solvents).
Diastereotopic groups

- H atoms on C-3 of 2-butanol are diastereotopic
- substitution by deuterium creates a chiral center
- because there is already a chiral center in the molecule, diastereomers are now possible

- diastereotopic hydrogens have different chemical shifts under all conditions (can lead to unexpected complexity in spectra of simple compounds)
The methyl groups on carbon 3 of 3-methyl-2-butanol are diastereotopic

- if a methyl hydrogen of carbon 4 is substituted by deuterium, a new chiral center is created
- because there is already one chiral center, diastereomers are now possible

\[
\begin{array}{c}
\text{OH} \\
\text{3-Methyl-2-butanol}
\end{array}
\]

- protons of the methyl groups on carbon 3 have different chemical shifts
1H-NMR spectrum of 3-methyl-2-butanol

- the methyl groups on carbon 3 are diastereotopic and appear as two doublets
Low abundance of $^{13}\text{C}$ (1.1%) results in weak signals

Magnetic moment of $^{13}\text{C}$ is much smaller than that of $^1\text{H}$

Each nonequivalent $^{13}\text{C}$ gives a different signal
  - a $^{13}\text{C}$ signal is split by the $^1\text{H}$ bonded to it according to the $(n + 1)$ rule
  - coupling constants of 100-250 Hz are common, which means that there is often significant overlap between signals, and splitting patterns can be very difficult to determine

The most common mode of operation of a $^{13}\text{C}$-NMR spectrometer is a hydrogen-decoupled mode
In a hydrogen-decoupled mode, a sample is irradiated with two different radio frequencies:

- one to excite all $^{13}\text{C}$ nuclei
- a second broad spectrum of frequencies to cause all hydrogens in the molecule to undergo rapid transitions between their nuclear spin states

On the time scale of a $^{13}\text{C}$-NMR spectrum, each hydrogen is in an average or effectively constant nuclear spin state, with the result that $^{1}\text{H}$-$^{13}\text{C}$ spin-spin interactions are not observed; they are decoupled


• hydrogen-decoupled $^{13}$C-NMR spectrum of 1-bromobutane

**Caution:** integration of signals is not reliable in $^{13}$C NMR spectroscopy (long relaxation times)
## Chemical Shift - $^{13}$C-NMR

<table>
<thead>
<tr>
<th>Type of Carbon</th>
<th>Chemical Shift (δ)</th>
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<th>Chemical Shift (δ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RCH$_3$</td>
<td>10-40</td>
<td></td>
<td></td>
</tr>
<tr>
<td>RCH$_2$R</td>
<td>15-55</td>
<td>C-R</td>
<td>110-160</td>
</tr>
<tr>
<td>R$_3$CH</td>
<td>20-60</td>
<td></td>
<td></td>
</tr>
<tr>
<td>RCH$_2$I</td>
<td>0-40</td>
<td>RCO$_3$</td>
<td>160 - 180</td>
</tr>
<tr>
<td>RCH$_2$Br</td>
<td>25-65</td>
<td>O</td>
<td></td>
</tr>
<tr>
<td>RCH$_2$Cl</td>
<td>35-80</td>
<td>RC$_2$</td>
<td>165 - 180</td>
</tr>
<tr>
<td>R$_3$COH</td>
<td>40-80</td>
<td>O</td>
<td></td>
</tr>
<tr>
<td>R$_3$COR</td>
<td>40-80</td>
<td>RCCO$_3$</td>
<td>165 - 185</td>
</tr>
<tr>
<td>RC≡CR</td>
<td>65-85</td>
<td>O</td>
<td></td>
</tr>
<tr>
<td>R$_2$C=CR$_2$</td>
<td>100-150</td>
<td>RCH, RCR</td>
<td>180 - 215</td>
</tr>
</tbody>
</table>
Chemical Shift - $^{13}$C-NMR
The DEPT Method

- In the hydrogen-decoupled mode, information on spin-spin coupling between $^{13}\text{C}$ and hydrogens bonded to it is lost.

- The DEPT method is an instrumental mode that provides a way to acquire this information.
  - **Distortionless Enhancement by Polarization Transfer (DEPT):** an NMR technique for distinguishing among $^{13}\text{C}$ signals for CH$_3$, CH$_2$, CH, and quaternary carbons.
The DEPT Method

- The DEPT method uses a complex series of pulses in both the $^1$H and $^{13}$C ranges, with the result that CH$_3$, CH$_2$, and CH signals exhibit different phases;
  - signals for CH$_3$ and CH carbons are recorded as positive signals
  - signals for CH$_2$ carbons are recorded as negative signals
  - quaternary carbons give no signal in the DEPT method
Isopentyl acetate

- $^{13}$C-NMR: (a) proton decoupled and (b) DEPT
Interpreting NMR Spectra

◆ Alkanes
  • $^1$H-NMR signals appear in the range of $\delta$ 0.8-1.7
  • $^{13}$C-NMR signals appear in the considerably wider range of $\delta$ 10-60

◆ Alkenes
  • $^1$H-NMR signals appear in the range $\delta$ 4.6-5.7
  • $^1$H-NMR coupling constants are generally larger for *trans* vinylic hydrogens ($J = 11-18$ Hz) compared with *cis* vinylic hydrogens ($J = 5-10$ Hz)
  • $^{13}$C-NMR signals for $sp^2$ hybridized carbons appear in the range $\delta$ 100-160, which is downfield from the signals of $sp^3$ hybridized carbons
Interpreting NMR Spectra

- $^1$H-NMR spectrum of vinyl acetate (Fig 13.31)
Interpreting NMR Spectra

◆ Alcohols
  ◆ $^1$H-NMR O-H chemical shifts often appears in the range $\delta$ 3.0-4.0, but may be as low as $\delta$ 0.5.
    • $^1$H-NMR chemical shifts of hydrogens on the carbon bearing the -OH group are deshielded by the electron-withdrawing inductive effect of the oxygen and appear in the range $\delta$ 3.0-4.0

◆ Ethers
  • a distinctive feature in the $^1$H-MNR spectra of ethers is the chemical shift, $\delta$ 3.3-4.0, of hydrogens on carbon attached to the ether oxygen
Interpreting NMR Spectra

- $^1$H-NMR spectrum of 1-propanol (Fig. 13.32)
Interpreting NMR Spectra

◆ Aldehydes and ketones
  • $^1$H-NMR: aldehyde hydrogens appear at $\delta$ 9.5-10.1
  • $^1$H-NMR: $\alpha$-hydrogens of aldehydes and ketones appear at $\delta$ 2.2-2.6
  • $^{13}$C-NMR: carbonyl carbons appear at $\delta$ 180-215

◆ Amines
  • $^1$H-NMR: amine hydrogens appear at $\delta$ 0.5-5.0 depending on conditions
Interpreting NMR Spectra

- Carboxylic acids
  - $^1H$-NMR: carboxyl hydrogens appear at $\delta$ 10-13, lower than most any other hydrogens
  - $^{13}C$-NMR: carboxyl carbons in acids and esters appear at $\delta$ 160-180
Interpreting NMR Spectra

- **Spectral Problem 1; molecular formula** $\text{C}_5\text{H}_{10}\text{O}$
Interpreting NMR Spectra

- **Spectral Problem 2; molecular formula** $\text{C}_7\text{H}_{14}\text{O}$