NUCLEAR MAGNETIC RESONANCE (NMR)
Nuclear Magnetic Resonance (NMR) Spectroscopy

NMR spectroscopy identifies the carbon–hydrogen framework of an organic compound.

Certain nuclei, such as $^1$H, $^{13}$C, $^{15}$N, $^{19}$F, and $^{31}$P, have a nonzero value for their spin quantum number; this property allows them to be studied by NMR.
Nuclear Magnetic Resonance Spectroscopy

Introduction to NMR Spectroscopy

• Nuclear magnetic resonance spectroscopy is a powerful analytical technique used to characterize organic molecules by identifying carbon-hydrogen frameworks within molecules.

• Two common types of NMR spectroscopy are used to characterize organic structure: $^1$H NMR is used to determine the type and number of H atoms in a molecule; $^{13}$C NMR is used to determine the type of carbon atoms in the molecule.

• The source of energy in NMR is radio waves which have long wavelengths, and thus low energy and frequency.

• When low-energy radio waves interact with a molecule, they can change the nuclear spins of some elements, including $^1$H and $^{13}$C.
Nuclear Magnetic Resonance Spectroscopy

Introduction to NMR Spectroscopy

• When a charged particle such as a proton spins on its axis, it creates a magnetic field. Thus, the nucleus can be considered to be a tiny bar magnet.

• Normally, these tiny bar magnets are randomly oriented in space. However, in the presence of a magnetic field $B_0$, they are oriented with or against this applied field. More nuclei are oriented with the applied field because this arrangement is lower in energy.

• The energy difference between these two states is very small (<0.1 cal).
Nuclear Magnetic Resonance Spectroscopy

Introduction to NMR Spectroscopy

• In a magnetic field, there are now two energy states for a proton: a lower energy state with the nucleus aligned in the same direction as $B_0$, and a higher energy state in which the nucleus aligned against $B_0$.

• When an external energy source ($h\nu$) that matches the energy difference ($\Delta E$) between these two states is applied, energy is absorbed, causing the nucleus to “spin flip” from one orientation to another.

• The energy difference between these two nuclear spin states corresponds to the low frequency RF region of the electromagnetic spectrum.
The Δ Energy Between the Two Spin States Depends on the Strength of the Applied Magnetic Field ($B_0$)
Thus, two variables characterize NMR: an applied magnetic field $B_0$, the strength of which is measured in tesla (T), and the frequency $\nu$ of radiation used for resonance, measured in hertz (Hz), or megahertz (MHz)—(1 MHz = 10^6 Hz).

A nucleus is in resonance when it absorbs RF radiation and “spin flips” to a higher energy state.
Nuclear Magnetic Resonance Spectroscopy

Introduction to NMR Spectroscopy

- The frequency needed for resonance and the applied magnetic field strength are proportionally related:

\[ \nu \propto B_0 \]

- The stronger the magnetic field, the larger the energy difference between the two nuclear spin states, and the higher the \( \nu \) needed for resonance.

- NMR spectrometers are referred to as 300 MHz instruments, 500 MHz instruments, and so forth, depending on the frequency of the RF radiation used for resonance.

- These spectrometers use very powerful magnets to create a small but measurable energy difference between two possible spin states.
All the Hydrogens in a Compound Do Not Experience the Same Magnetic Field

$$B_{\text{effective}} = B_{\text{applied}} - B_{\text{local}}$$

The electrons surrounding the nucleus decrease the effective applied magnetic field sensed by the nucleus.
An NMR spectrometer. The sample is dissolved in a solvent, usually CDCl₃ (deuterochloroform), and placed in a magnetic field. A radiofrequency generator then irradiates the sample with a short pulse of radiation, causing resonance. When the nuclei fall back to their lower energy state, the detector measures the energy released, and a spectrum is recorded. The superconducting magnets in modern NMR spectrometers have coils that are cooled in liquid helium and conduct electricity with essentially no resistance.
Nuclear Magnetic Resonance Spectroscopy

Introduction to NMR Spectroscopy

- Protons in different environments absorb at slightly different frequencies, so they are distinguishable by NMR.
- The frequency at which a particular proton absorbs is determined by its electronic environment.
- The size of the magnetic field generated by the electrons around a proton determines where it absorbs.
- Modern NMR spectrometers use a constant magnetic field strength $B_0$, and then a narrow range of frequencies is applied to achieve the resonance of all protons.
- Only nuclei that contain odd mass numbers (such as $^1$H, $^{13}$C, $^{19}$F and $^{31}$P) or odd atomic numbers (such as $^2$H and $^{14}$N) give rise to NMR signals.
Chemically Equivalent Protons
(protons in the same environment)

\[
\text{CH}_3\text{CH}_2\text{CH}_2\text{Br}
\]
Nuclear Magnetic Resonance Spectroscopy

$^1$H NMR—The Spectrum

- An NMR spectrum is a plot of the intensity of a peak against its chemical shift, measured in *parts per million (ppm)*.
Nuclear Magnetic Resonance Spectroscopy

\(^1\)H NMR—The Spectrum

- NMR absorptions generally appear as sharp peaks.
- Increasing chemical shift is plotted from left to right.
- Most protons absorb between 0-10 ppm.
- The terms “upfield” and “downfield” describe the relative location of peaks. Upfield means to the right. Downfield means to the left.
- NMR absorptions are measured relative to the position of a reference peak at 0 ppm on the \( \delta \) scale due to tetramethylsilane (TMS). TMS is a volatile inert compound that gives a single peak upfield from typical NMR absorptions.
The Reference Compound

TMS is the reference compound (it appears at $= 0$ ppm).
An $^1\text{H}$ NMR Spectrum

The greater the chemical shift, the higher the frequency.
Nuclear Magnetic Resonance Spectroscopy

$^1$H NMR—The Spectrum

• The chemical shift of the $x$ axis gives the position of an NMR signal, measured in ppm, according to the following equation:

$$\text{chemical shift (in ppm on the } \delta \text{ scale)} = \frac{\text{observed chemical shift (in Hz) downfield from TMS}}{\nu \text{ of the NMR spectrometer (in MHz)}}$$

• By reporting the NMR absorption as a fraction of the NMR operating frequency, we get units, ppm, that are independent of the spectrometer.

• Four different features of a $^1$H NMR spectrum provide information about a compound’s structure:
  a. Number of signals
  b. Position of signals
  c. Intensity of signals.
  d. Spin-spin splitting of signals.
Nuclear Magnetic Resonance Spectroscopy

$^1$H NMR—Number of Signals

• The number of NMR signals equals the number of different types of protons in a compound.
• Protons in different environments give different NMR signals.
• Equivalent protons give the same NMR signal.

To determine equivalent protons in cycloalkanes and alkenes, always draw all bonds to hydrogen.
Nuclear Magnetic Resonance Spectroscopy

$^1$H NMR—Number of Signals

The number of $^1$H NMR signals of some representative organic compounds:

- **ClCH$_2$CH$_2$Cl**
  - 1 type of H
  - 1 NMR signal

- **ClCH$_2$CH$_2$CH$_2$Br**
  - 3 types of H’s
  - 3 NMR signals

- **CH$_3$COOCH$_3$**
  - 2 types of H’s
  - 2 NMR signals

- **CH$_3$CH$_2$OH**
  - 3 types of H’s
  - 3 NMR signals
Each set of chemically equivalent protons give a signal in the $^1$H NMR spectrum.
In comparing two H atoms on a ring or double bond, two protons are equivalent only if they are cis (or trans) to the same groups.
Number of Signals

- CH$_3$OCHCl$_2$: two signals
- $\text{C} \equiv \text{C}$: two signals
- $\text{C} \equiv \text{C}$: one signal
- $\text{C} \equiv \text{C}$: one signal
- NO$_2$: three signals
Nuclear Magnetic Resonance Spectroscopy

\(^1\)H NMR—Number of Signals

- Proton equivalency in cycloalkanes can be determined similarly.

![cyclopropane](cyclopropane.png)

- All H’s are equivalent. 1 NMR signal

![chlorocyclopropane](chlorocyclopropane.png)

- 3 types of H’s. 3 NMR signals
Number of Signals

its $^1$H NMR spectrum has three signals

bromoethene
$H_a$ and $H_b$ are not equivalent

its $^1$H NMR spectrum has five signals

chlorocyclobutane
$H_a$ and $H_b$ are not equivalent
$H_c$ and $H_d$ are not equivalent
Enantiotopic Hydrogens

Replacing one of the enantiotopic hydrogens with a deuterium (or any other atom or group other than CH$_3$ or OH) forms an asymmetric center.

Enantiotopic hydrogens are chemically equivalent.
Diastereotopic Hydrogens

Replacing each of the diastereotopic hydrogens in turn by a deuterium forms a pair of diastereomers.

Diastereotopic hydrogens are not chemically equivalent.
Diastereotopic Hydrogens are Not Chemically Equivalent

Diastereotopic hydrogens react with achiral reagents at different rates.
The three methyl hydrogens are in different environments because of rotation about the C—C bond; but on the NMR time scale, they are in the same environment.
Nuclear Magnetic Resonance Spectroscopy

\(^1H\) NMR—Cyclohexane Conformers

- Recall that cyclohexane conformers interconvert by ring flipping.
- Because the ring flipping is very rapid at room temperature, an NMR spectrum records an average of all conformers that interconvert.
- Thus, even though each cyclohexane carbon has two different types of hydrogens—one axial and one equatorial—the two chair forms of cyclohexane rapidly interconvert them, and an NMR spectrum shows a single signal for the average environment that it “sees”.

Axial and equatorial H’s rapidly interconvert. NMR sees an average environment and shows one signal.
The axial and equatorial hydrogens of cyclohexand-$d_{11}$ are equivalent and show one sharp signal.

The rate of chair–chair interconversion is temperature dependent: as the temperature decreases, the signal broadens and eventually two signals are observed.
## Terms to Remember

<table>
<thead>
<tr>
<th>Protons in electron-poor environments</th>
<th>Protons in electron-dense environments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Deshielded protons</td>
<td>Shielded protons</td>
</tr>
<tr>
<td>Downfield</td>
<td>Upfield</td>
</tr>
<tr>
<td>High frequency</td>
<td>Low frequency</td>
</tr>
<tr>
<td>Large $\delta$ values</td>
<td>Small $\delta$ values</td>
</tr>
</tbody>
</table>

![Diagram of NMR spectrum](image.png)

- $\delta$ ppm
- Frequency

![Diagram of NMR spectrum](image.png)

- Downfield (deshielded)
- Upfield (shielded)
- Calibration peak (TMS)
- Direction of field sweep
- Low-field
- High-field

Where Protons Show a Signal

these protons sense a larger effective magnetic field, so come into resonance at a higher frequency

these protons sense a smaller effective magnetic field, so come into resonance at a lower frequency

"downfield"  Frequency  "upfield"

Intensity
Where $^1$H NMR Signals Appear
Nuclear Magnetic Resonance Spectroscopy

$^1$H NMR—Position of Signals

- The less shielded the nucleus becomes, the more of the applied magnetic field ($B_0$) it feels.
- This deshielded nucleus experiences a higher magnetic field strength, so it needs a higher frequency to achieve resonance.
- Higher frequency is to the left in an NMR spectrum, toward higher chemical shift—so deshielding shifts an absorption downfield.
- Protons near electronegative atoms are deshielded, so they absorb downfield.
Relative Positions of the Signals

Protons in electron-poor environments show signals at high frequencies.

Electron withdrawal causes NMR signals to appear at a higher frequency (at a larger $\delta$ value).
Relative Positions of the Signals

The closer the electronegative the atom (or group), the more it deshields the protons.
Table 15.1  Approximate Values of Chemical Shifts for $^1$H NMR $^a$

<table>
<thead>
<tr>
<th>Type of proton</th>
<th>Approximate chemical shift (ppm)</th>
<th>Type of proton</th>
<th>Approximate chemical shift (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$-\text{CH}_3$</td>
<td>0.85</td>
<td>$\text{I} - \text{C} - \text{H}$</td>
<td>2.5–4</td>
</tr>
<tr>
<td>$-\text{CH}_2-$</td>
<td>1.20</td>
<td>$\text{Br} - \text{C} - \text{H}$</td>
<td>2.5–4</td>
</tr>
<tr>
<td>$-\text{CH}$</td>
<td>1.55</td>
<td>$\text{Cl} - \text{C} - \text{H}$</td>
<td>3–4</td>
</tr>
<tr>
<td>$-\text{C} = \text{C} - \text{CH}_3$</td>
<td>1.7</td>
<td>$\text{F} - \text{C} - \text{H}$</td>
<td>4–4.5</td>
</tr>
<tr>
<td>$-\text{C} - \text{CH}_3$</td>
<td>2.1</td>
<td>$\text{R} - \text{NH}_2$</td>
<td>Variable, 1.5–4</td>
</tr>
<tr>
<td>$\text{C} - \text{C} - \text{H}$</td>
<td>2.3</td>
<td>$\text{R} - \text{OH}$</td>
<td>Variable, 2–5</td>
</tr>
<tr>
<td>$\text{C} - \text{C} - \text{H}$</td>
<td>2.4</td>
<td>$\text{R} - \text{OH}$</td>
<td>Variable, 4–7</td>
</tr>
<tr>
<td>$\text{R} - \text{O} - \text{CH}_3$</td>
<td>3.3</td>
<td>$\text{O} - \text{C} - \text{H}$</td>
<td>6.5–8</td>
</tr>
<tr>
<td>$\text{R} - \text{C} = \text{CH}_2$</td>
<td>4.7</td>
<td>$\text{O} - \text{C} - \text{OH}$</td>
<td>Variable, 10–12</td>
</tr>
<tr>
<td>$\text{R} - \text{C} = \text{C} - \text{H}$</td>
<td>5.3</td>
<td>$\text{O} - \text{C} - \text{NH}_2$</td>
<td>Variable, 5–8</td>
</tr>
</tbody>
</table>

$^a$The values are approximate because they are affected by neighboring substituents.
Where They Show a Signal?

Methine protons appear at higher frequency than methylene protons, which appear at a higher frequency than methyl protons.
The Relative Positions of Signals

In the same environment, a methine proton appears at a higher frequency than methylene protons, which appear at a higher frequency than methyl protons.
Protons Attached to $sp^2$ Carbons

The chemical shift of protons attached to $sp^2$ carbons appear at higher frequencies than one would predict.
Nuclear Magnetic Resonance Spectroscopy

$^1$H NMR—Chemical Shift Values

- In a magnetic field, the six $\pi$ electrons in benzene circulate around the ring creating a ring current.
- The magnetic field induced by these moving electrons reinforces the applied magnetic field in the vicinity of the protons.
- The protons thus feel a stronger magnetic field and a higher frequency is needed for resonance. Thus they are deshielded and absorb downfield.
Diamagnetic Anisotropy
(Benzene Ring Protons)

The protons show signals at higher frequencies because they sense a **larger effective magnetic field**.
Nuclear Magnetic Resonance Spectroscopy

$^1$H NMR—Chemical Shift Values

- In a magnetic field, the loosely held $\pi$ electrons of the double bond create a magnetic field that reinforces the applied field in the vicinity of the protons.
- The protons now feel a stronger magnetic field, and require a higher frequency for resonance. Thus the protons are deshielded and the absorption is downfield.

The induced magnetic field reinforces the external field $B_0$ in the vicinity of the protons.

The protons are deshielded. The absorption is downfield at 4.5–6 ppm.
Diamagnetic Anisotropy
(Alkenes and Aldehydes)

The protons show signals at higher frequencies because they sense a larger effective magnetic field.
A Hydrogen Bonded to an $sp$ Carbon

The chemical shift of a hydrogen bonded to an $sp$ carbon appears at a lower frequency than it would if the $\pi$ electrons did not induce a magnetic field.
Nuclear Magnetic Resonance Spectroscopy

$^1$H NMR—Chemical Shift Values

• In a magnetic field, the $\pi$ electrons of a carbon-carbon triple bond are induced to circulate, but in this case the induced magnetic field opposes the applied magnetic field ($B_0$).
• Thus, the proton feels a weaker magnetic field, so a lower frequency is needed for resonance. The nucleus is shielded and the absorption is upfield.
Nuclear Magnetic Resonance Spectroscopy

$^1$H NMR—Position of Signals

Shielding and deshielding effects

- As the electron density around the nucleus increases, the nucleus feels a smaller resultant magnetic field, so a lower frequency is needed to achieve resonance.
- **The absorption shifts upfield.**

- As the electron density around the nucleus decreases, the nucleus feels a larger resultant magnetic field, so a higher frequency is needed to achieve resonance.
- **The absorption shifts downfield.**
Nuclear Magnetic Resonance Spectroscopy

$^1$H NMR—Intensity of Signals

- The area under an NMR signal is proportional to the number of absorbing protons.
- An NMR spectrometer automatically integrates the area under the peaks, and prints out a stepped curve (integral) on the spectrum.
- The height of each step is proportional to the area under the peak, which in turn is proportional to the number of absorbing protons.
- Modern NMR spectrometers automatically calculate and plot the value of each integral in arbitrary units.
- The ratio of integrals to one another gives the ratio of absorbing protons in a spectrum. Note that this gives a ratio, and not the absolute number, of absorbing protons.
INTEGRATION
The Relative Number of Protons

The area under each signal is proportional to the number of protons giving rise to the signal.
Nuclear Magnetic Resonance Spectroscopy

$^1$H NMR—Intensity of Signals

NMR integration

$\text{CH}_3\text{OC(CH}_3)_3$

chemical shift (ppm)
The $^1$H NMR Spectrum of 1,3-Dibromopropane

BrCH$_2$CH$_2$CH$_2$Br

- **Triplet**: two neighboring protons
- **Quintet**: four neighboring protons
An $^1$H NMR Spectrum

\[ \text{CH}_3\text{CH}_2\text{CH}_2\text{C}=\text{OCHCH}_3 \]
An $^1\text{H}$ NMR Spectrum of Allyl Bromide
The signals for the $H_c$, $H_d$, and $H_e$ protons overlap because the electronic effect of an ethyl substituent is similar to that of a hydrogen.
An $^1$H NMR Spectrum of Nitrobenzene

The signals for the $H_a$, $H_b$, and $H_c$ protons do not overlap because the nitro group is strongly electron withdrawing.
Nuclear Magnetic Resonance Spectroscopy

$^1$H NMR—Spin-Spin Splitting

- Spin-spin splitting occurs only between nonequivalent protons on the same carbon or adjacent carbons.

Let us consider how the doublet due to the CH$_2$ group on BrCH$_2$CHBr$_2$ occurs:

- When placed in an applied electric field, (B$_0$), the adjacent proton (CHBr$_2$) can be aligned with (↑) or against (↓) B$_0$.

- Thus, the absorbing CH$_2$ protons feel two slightly different magnetic fields—one slightly larger than B$_0$, and one slightly smaller than B$_0$.

- Since the absorbing protons feel two different magnetic fields, they absorb at two different frequencies in the NMR spectrum, thus splitting a single absorption into a doublet.
SPLITTING \((N + 1)\)

\(N\) is the number of equivalent protons on adjacent carbons that are not equivalent to the protons that produce the signal.
A Splitting Diagram

The number of peaks observed depends on the relative magnitudes of the coupling constants.

CH₃CH₂CH₂Br

The splitting pattern for 1-bromopropane is shown in the diagram with the following conditions:

- $J_{ba} \gg J_{bc}$: 12 peaks
- $J_{ba} = 2J_{bc}$: 9 peaks
- $J_{ba} = J_{bc}$: 6 peaks
Nuclear Magnetic Resonance Spectroscopy

$^1$H NMR—Spin-Spin Splitting

The frequency difference, measured in Hz between two peaks of the doublet is called the coupling constant, $J$.

- One adjacent proton splits an NMR signal into a doublet.
Nuclear Magnetic Resonance Spectroscopy

$^1$H NMR—Spin-Spin Splitting

**With no adjacent H's:**
The absorbing H feels only one magnetic field.

**With two adjacent H's:**
The absorbing H feels three different fields, so it absorbs at three different frequencies.

How a triplet arises

The NMR signal is a single peak.

The NMR signal is split into a triplet.

three different magnetic fields
Nuclear Magnetic Resonance Spectroscopy

$^1\text{H NMR—Spin-Spin Splitting}$

Three general rules describe the splitting patterns commonly seen in the $^1\text{H}$ NMR spectra of organic compounds.

1. Equivalent protons do not split each other’s signals.

2. A set of $n$ nonequivalent protons splits the signal of a nearby proton into $n + 1$ peaks.

3. Splitting is observed for nonequivalent protons on the same carbon or adjacent carbons.

If $H_a$ and $H_b$ are not equivalent, splitting is observed when:

- $H_a$ and $H_b$ are on the same carbon.
- $H_a$ and $H_b$ are on adjacent carbons.
Splitting is Observed if the Protons are Separated by No More Than Three Bonds

$H_a$ and $H_b$ split each other’s signal because they are separated by three $\sigma$ bonds

$H_a$ and $H_b$ do not split each other’s signal because they are separated by four $\sigma$ bonds

$H_a$ and $H_b$ may split each other’s signal because they are separated by four bonds, one of which is a double bond

Splitting may occur through four bonds if one is a double bond.
Nuclear Magnetic Resonance Spectroscopy

\(^1\text{H} \text{NMR—Spin-Spin Splitting}\)

When two sets of adjacent protons are different from each other (\(n\) protons on one adjacent carbon and \(m\) protons on the other), the number of peaks in an NMR signal = \((n + 1)(m + 1)\).

\[
\text{Number of peaks} = (n + 1)(m + 1)
\]

- The \(H_b\) signal is split into 12 peaks, a quartet of triplets. The number of peaks actually seen for the signal depends on the relative size of the coupling constants, \(J_{ab}\) and \(J_{bc}\). When \(J_{ab} \gg J_{bc}\), as drawn in this diagram, all 12 lines of the pattern are visible. When \(J_{ab}\) and \(J_{bc}\) are similar in magnitude, peaks overlap and fewer lines are observed.

\[
CH_3CH_2CH_2\text{Br}
\]

\(H_a\) \(H_b\) \(H_c\)

A splitting diagram for the \(H_b\) protons in 1-bromopropane.
Splitting

\[
\text{CH}_3\text{CH}_2\text{C} = \text{OCH}_3
\]

\(a\) is a triplet
\(b\) is a quartet
\(c\) is a singlet
Splitting

$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{H}$

- $a$ is a triplet
- $b$ is a sextet
- $c$ is a triplet
- $d$ is a singlet
Equivalent Protons Do Not Split Each Other’s Signals

CH₃Br  
**bromomethane**

ClCH₂CH₂Cl  
**1,2-dichloroethane**

each compound shows one singlet in its $^1$H NMR spectrum because equivalent protons do not split each other’s signals.
What Causes Splitting?

- If the magnetic field of the methine proton is in the same direction as the applied magnetic field, it will add to the applied magnetic field, so the adjacent methyl protons will show a signal at a slightly higher frequency.

- If the magnetic field of the methine proton is lined up against the applied magnetic field, it will subtract from the applied magnetic field, so the adjacent methyl protons will show a signal at a slightly lower frequency.

- Chemical shift of the signal for the methyl protons if there were no protons on the adjacent carbon.

- Direction of the applied field.
What Causes Splitting?

- Chemical shift of the methine proton if there were no protons on the adjacent carbon.
- Signal for the methine proton is split into a quartet.
Why a Quartet?
Why 1:3:3:1?

the ways in which the magnetic fields of three protons can be aligned
A Quartet *versus* a Doublet of Doublets

- **A Quartet**
  - Relative intensities: 1 : 3 : 3 : 1

- **A Doublet of Doublets**
  - Relative intensities: 1 : 1 : 1 : 1
Nuclear Magnetic Resonance Spectroscopy

$^1$H NMR—Spin-Spin Splitting

- Protons on carbon-carbon double bonds often give characteristic splitting patterns.
- A disubstituted double bond can have two geminal protons, two cis protons, or two trans protons.
- When these protons are different, each proton splits the NMR signal of the other so that each proton appears as a doublet.
- The magnitude of the coupling constant $J$ for these doublets depends on the arrangement of hydrogen atoms.

![Diagram showing characteristic coupling constants for three types of disubstituted alkenes]

- $J_{\text{geminal}}$ (geminal H’s) $0–3$ Hz
- $J_{\text{cis}}$ (cis H’s) $5–10$ Hz
- $J_{\text{trans}}$ (trans H’s) $11–18$ Hz
The coupling constant \( (J) \) is the distance between two adjacent peaks of a split NMR signal in hertz. **Coupled protons** have the same coupling constant.
# Coupling Constants

<table>
<thead>
<tr>
<th>Types of protons</th>
<th>Approximate value of $J_{ab}$ (Hz)</th>
<th>Types of protons</th>
<th>Approximate value of $J_{ab}$ (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( H_a ) -C- ( H_b )</td>
<td>12</td>
<td>( H_a ) ( C=) ( H_b )</td>
<td>15 (trans)</td>
</tr>
<tr>
<td>( C=) ( H_a ) ( H_b )</td>
<td>2</td>
<td>( H_a ) ( C=) ( H_b )</td>
<td>10 (cis)</td>
</tr>
<tr>
<td>( H_a ) ( H_b ) -C-</td>
<td>7</td>
<td>( H_a ) ( C=) ( H_b ) ( C ) ( H_b )</td>
<td>1 (long-range coupling)</td>
</tr>
<tr>
<td>( H_a ) ( H_b ) -C-</td>
<td>0</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Nuclear Magnetic Resonance Spectroscopy

$^1$H NMR—Spin-Spin Splitting

$^1$H NMR spectra for the alkenyl protons of (E)- and (Z)-3-chloropropenoic acid

- Although both (E)- and (Z)-3-chloropropenoic acid show two doublets in their $^1$H NMR spectra for their alkenyl protons, $J_{\text{trans}} > J_{\text{cis}}$. 

\[ J_{\text{trans}} = 14 \text{ Hz} \quad \text{and} \quad J_{\text{cis}} = 8 \text{ Hz} \]
Nuclear Magnetic Resonance Spectroscopy

$^1H$ NMR—Spin-Spin Splitting

The $^1H$ NMR spectrum of vinyl acetate ($\text{CH}_2=\text{CHOCCOCH}_3$)
Nuclear Magnetic Resonance Spectroscopy

$^1$H NMR—Spin-Spin Splitting

Splitting diagrams for the alkenyl protons in vinyl acetate are shown below. Note that each pattern is different in appearance because the magnitude of the coupling constants forming them is different.

Splitting diagram for the alkenyl protons in vinyl acetate ($\text{CH}_2=\text{CHOCHOCH}_3$)

\[ J_{bc} = 1.2 \text{ Hz (geminal)} \]
\[ J_{cd} = 6.5 \text{ Hz (cis)} \]
\[ J_{bd} = 14 \text{ Hz (trans)} \]
The Coupling Constant is Greater for Trans Protons Than for Cis Protons

trans-3-chloropropenoic acid

\[ J_{ba} = 14 \text{ Hz} \quad J_{ab} = 14 \text{ Hz} \]

cis-3-chloropropenoic acid

\[ J_{ba} = 9 \text{ Hz} \quad J_{ab} = 9 \text{ Hz} \]
Protons Bonded to O or N

a. pure ethanol

b. ethanol with acid
\[ J_{ab} = J_{ac} \]
Nuclear Magnetic Resonance Spectroscopy

$^1$H NMR—OH Protons

- Under usual conditions, an OH proton does not split the NMR signal of adjacent protons.
- The signal due to an OH proton is not split by adjacent protons.

The $^1$H spectrum of ethanol (CH$_3$CH$_2$OH)
Nuclear Magnetic Resonance Spectroscopy

\(^1\)H NMR—OH Protons

- Ethanol (CH\(_3\)CH\(_2\)OH) has three different types of protons, so there are three signals in its NMR spectrum.
- The \(H_a\) signal is split by the two \(H_b\) protons into three peaks (a triplet).
- The \(H_b\) signal is split only by the three \(H_a\) protons into four peaks, a quartet. The adjacent OH proton does not split the signal due to \(H_b\).
- \(H_c\) is a singlet because OH protons are not split by adjacent protons.
- Protons on electronegative atoms rapidly exchange between molecules in the presence of trace amounts of acid or base. Thus, the CH\(_2\) group of ethanol never “feels” the presence of the OH proton, because the OH proton is rapidly moving from one molecule to another.
- This phenomenon usually occurs with NH and OH protons.
Acid-Catalyzed Proton Exchange

The chemical shift depends on the extent of hydrogen bonding.

They generally appear as broad signals.
Deuterium Signals are Not Seen in an $^1$H NMR Spectrum

$\text{R-O-H} + \text{D-O-D} \rightarrow \text{R-O-D} + \text{D-O-H}$

seen in $^1$H NMR  

not seen in $^1$H NMR
Summary

- The **number of signals** tells us the number of sets of equivalent protons in the compound.

- The **value of the chemical shifts** tells us the nature of the chemical environment: alkyl, alkene, benzene, etc.

- The **integration values** tells us the relative number of protons.

- The **splitting** tells us the number of neighboring protons.

- The **coupling constants** identifies coupled protons.
$^{13}$C NMR Spectroscopy

- The number of signals reflects the number of different kinds of carbons in a compound.
- The chemical shift ranges over 220 ppm.
- The reference compound is TMS.
<table>
<thead>
<tr>
<th>Type of carbon</th>
<th>Approximate chemical shift (ppm)</th>
<th>Type of carbon</th>
<th>Approximate chemical shift (ppm)</th>
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<tr>
<td>((\text{CH}_3)_4\text{Si})</td>
<td>0</td>
<td>C—I</td>
<td>−20–10</td>
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<td>R—CH₃</td>
<td>0–35</td>
<td>C—Br</td>
<td>10–40</td>
</tr>
<tr>
<td>R—CH₂—R</td>
<td>15–55</td>
<td>C—Cl</td>
<td>25–50</td>
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<tr>
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<td>C—N</td>
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<tr>
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<td>C—O</td>
<td>50–90</td>
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<td>70–90</td>
<td>(\text{RCH}_2\text{CO})</td>
<td>165–175</td>
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<tr>
<td>C≡N</td>
<td>110–120</td>
<td>(\text{ROCH}_2\text{CO})</td>
<td>175–185</td>
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<tr>
<td>C=(\text{C})</td>
<td>80–145</td>
<td>(\text{RCH}_2\text{HCO})</td>
<td>190–200</td>
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<tr>
<td>C≡N</td>
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<td>(\text{RCH}_2\text{RCO})</td>
<td>205–220</td>
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<tr>
<td>(\text{C})</td>
<td>110–170</td>
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</tbody>
</table>
Where $^{13}$C NMR Signals Appear
Nuclear Magnetic Resonance Spectroscopy

$^{13}\text{C}$ NMR

$^{13}\text{C}$ Spectra are easier to analyze than $^1\text{H}$ spectra because the signals are not split. Each type of carbon atom appears as a single peak.
The $^{13}$C NMR Spectrum of 2-Butanol
Nuclear Magnetic Resonance Spectroscopy

\( ^{13}\text{C} \) NMR

- The lack of splitting in a \( ^{13}\text{C} \) spectrum is a consequence of the low natural abundance of \( ^{13}\text{C} \).

- Recall that splitting occurs when two NMR active nuclei—like two protons—are close to each other. Because of the low natural abundance of \( ^{13}\text{C} \) nuclei (1.1\%), the chance of two \( ^{13}\text{C} \) nuclei being bonded to each other is very small (0.01\%), and so no carbon-carbon splitting is observed.

- A \( ^{13}\text{C} \) NMR signal can also be split by nearby protons. This \( ^{1}\text{H}-^{13}\text{C} \) splitting is usually eliminated from the spectrum by using an instrumental technique that decouples the proton-carbon interactions, so that every peak in a \( ^{13}\text{C} \) NMR spectrum appears as a singlet.

- The two features of a \( ^{13}\text{C} \) NMR spectrum that provide the most structural information are the number of signals observed and the chemical shifts of those signals.
Nuclear Magnetic Resonance Spectroscopy

$^{13}$C NMR—Number of Signals

• The number of signals in a $^{13}$C spectrum gives the number of different types of carbon atoms in a molecule.

• Because $^{13}$C NMR signals are not split, the number of signals equals the number of lines in the $^{13}$C spectrum.

• In contrast to the $^1$H NMR situation, peak intensity is not proportional to the number of absorbing carbons, so $^{13}$C NMR signals are not integrated.

![Spectra Diagrams](Diagram.png)

Both C’s are equivalent.
**Nuclear Magnetic Resonance Spectroscopy**

**$^{13}$C NMR—Number of Signals**

- The three types of C’s in methyl acetate—identified as $C_a$, $C_b$, and $C_c$—give rise to three $^{13}$C NMR signals.
- The carbonyl carbon ($C_b$) is highly deshielded, so it absorbs farthest downfield.
- $C_a$, an $sp^3$ hybridized C that is not bonded to an O atom, is the most shielded, and so it absorbs farthest upfield.
- Thus, in order of increasing chemical shift: $C_a < C_c < C_b$. 

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![Diagram of methyl acetate with NMR spectrum]
Nuclear Magnetic Resonance Spectroscopy

$^{13}$C NMR—Number of Signals

Representative $^{13}$C NMR spectra

- The three types of C’s in 1-propanol—identified as $C_a$, $C_b$, and $C_c$—give rise to three $^{13}$C NMR signals.
- Deshielding increases with increasing proximity to the electronegative O atom, and the absorption shifts downfield; thus, in order of increasing chemical shift: $C_a < C_b < C_c$. 

![Diagram of 1-Propanol C NMR spectrum with labels $C_a$, $C_b$, and $C_c$]