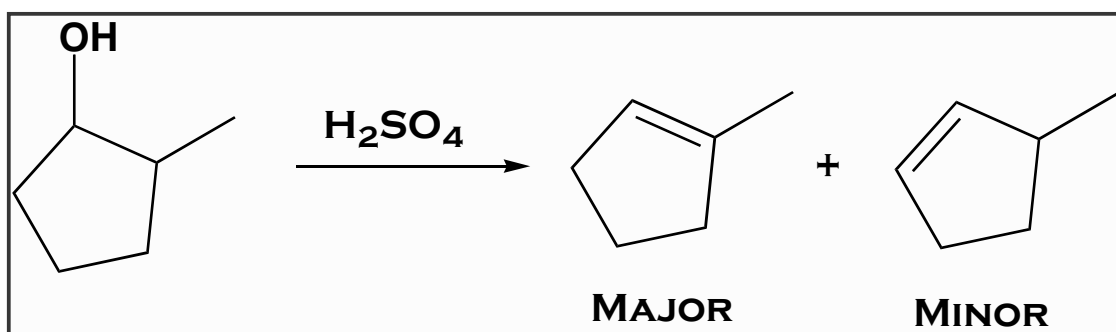


Nuclear Magnetic Resonance

Chapter 13

1

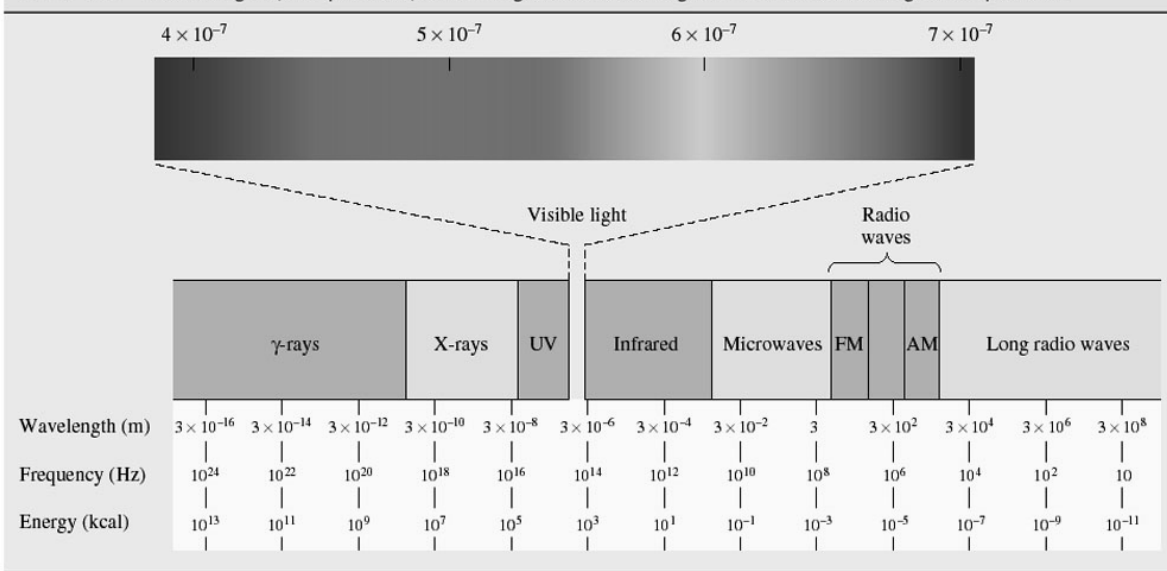
Reactions will often give a mixture of products:



How would the chemist determine which product was formed?
Both are cyclopentenes; they are isomers.
Spectroscopy will provide the solution.

2

Table 12.1 Wavelengths, Frequencies, and Energies of Some Regions of the Electromagnetic Spectrum



Molecular and atomic transitions occur & are frequency dependent.

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Molecular Spectroscopy

- **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 ^1H -NMR spectroscopy
 - carbon atoms using ^{13}C -NMR spectroscopy
 - phosphorus atoms using ^{31}P -NMR spectroscopy

4

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

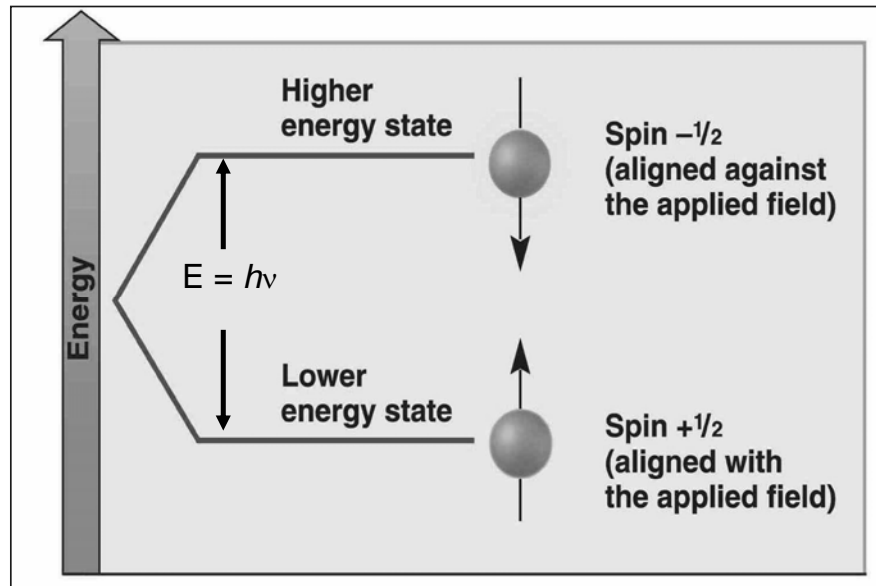
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Nuclear Spins in B_0

- within a collection of ^1H 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** (can occur)

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



7

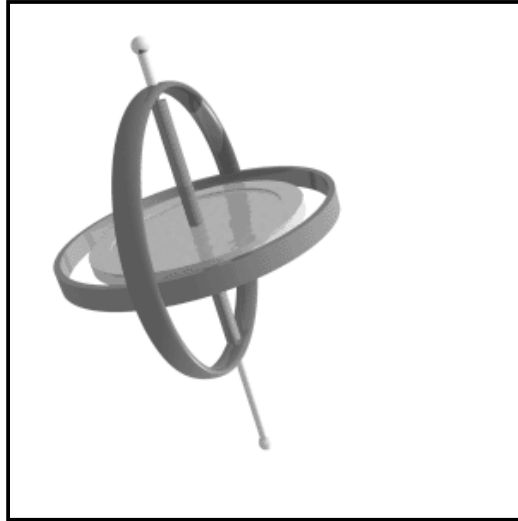
Nuclear Magnetic Resonance

- 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

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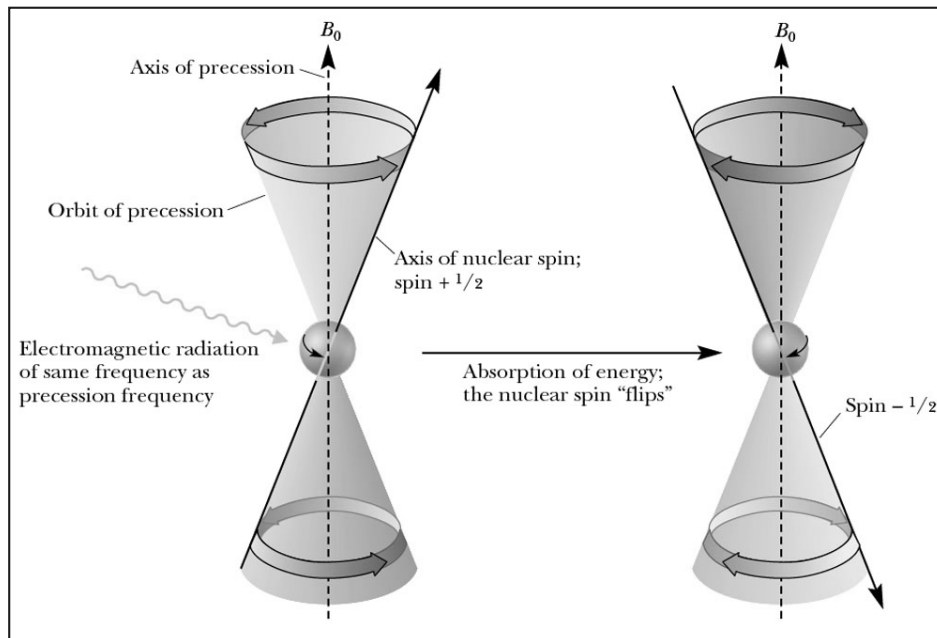
For example-a spinning top or gyroscope traces out a cone-shaped surface as it precesses in the earth's gravitational field

For a nucleus- the rate of precession is expressed as a frequency in hertz (Hz)



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-Figure 13.3 the origin of nuclear magnetic "resonance"



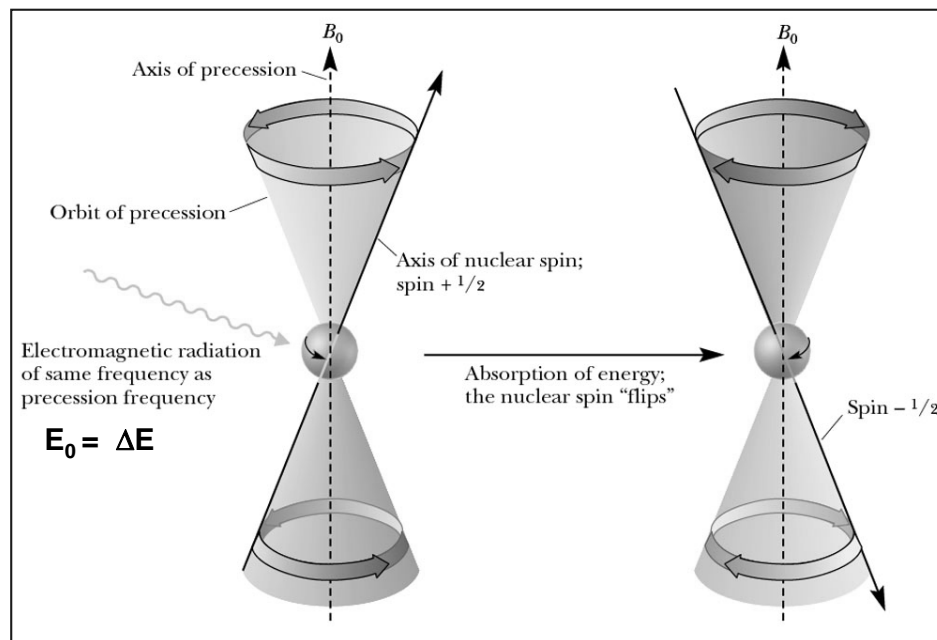
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Nuclear Magnetic Resonance

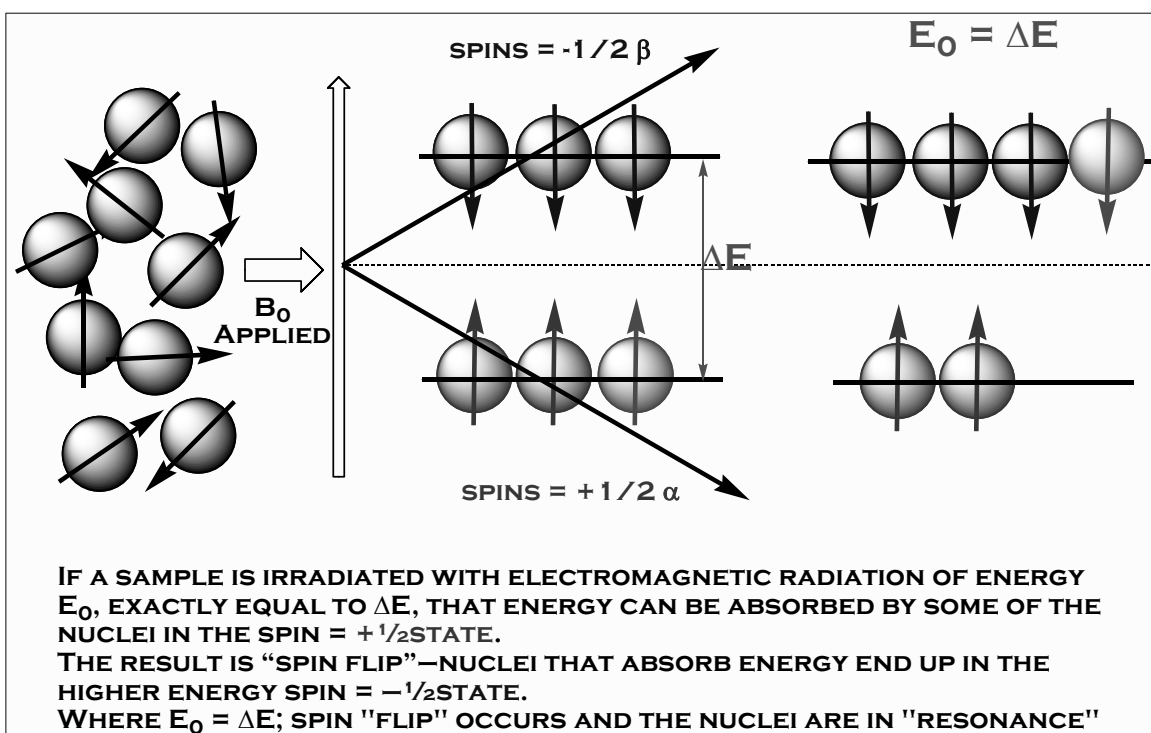
- If the precessing nucleus is irradiated with electromagnetic radiation of the same frequency as the rate of precession,
 - the two frequencies **couple**,
 - energy is **absorbed**, and
 - the **nuclear spin is flipped** from spin state $+1/2$ (with the applied field) to $-1/2$ (against the applied field)
 - This transition occurs when: $E_0 = \Delta E$

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–Figure 13.3 the origin of nuclear magnetic “resonance”



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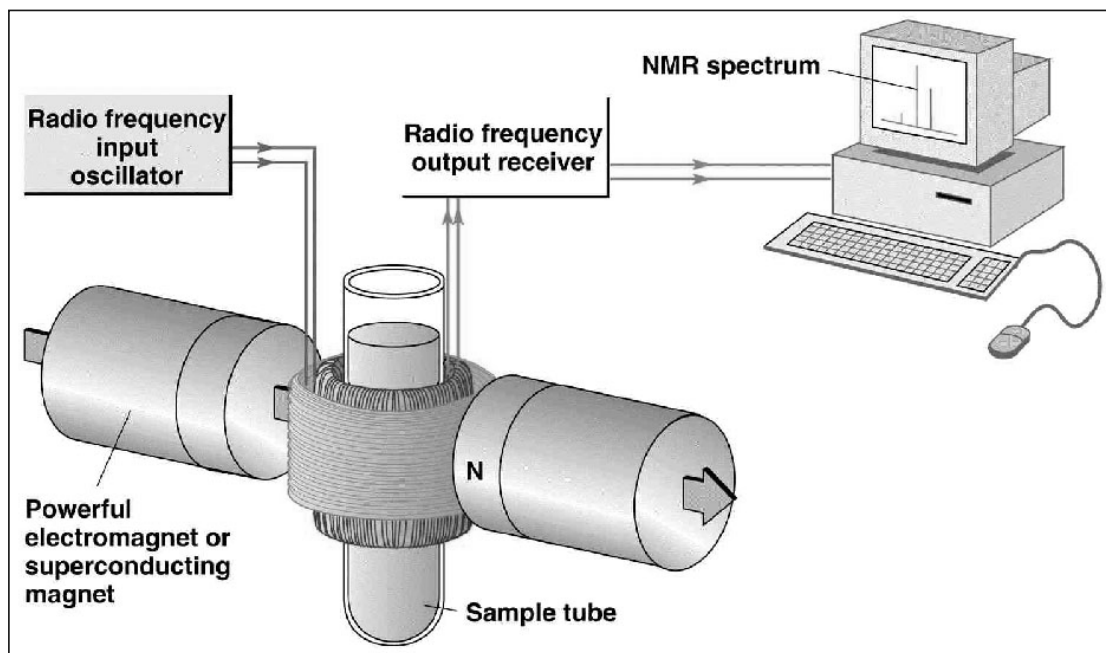
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NMR Spectrometer

- Essentials of an NMR spectrometer are a powerful magnet, a radio-frequency generator, and a radio-frequency detector
- The sample is dissolved in a solvent, most commonly CDCl_3 or D_2O , 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

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NMR Spectrometer



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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 (spectrometer) is used to detect this coupling of precession frequency and electromagnetic radiation records it as a signal: $E_0 = \Delta E$
 - signal: a recording in an NMR spectrum of a nuclear magnetic resonance

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Shielding

- if we were dealing with ^1H nuclei isolated from all other atoms and electrons, any combination of applied field and radiation that produces a signal for one ^1H would produce a signal for all ^1H .
- **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**

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Shielding

All nuclei in molecules are surrounded by electrons. Application of an external magnetic field causes these electrons to circulate, which sets up a local magnetic field ($\mathbf{B}_{\text{local}}$) of their own.

$\mathbf{B}_{\text{local}}$ opposes the applied field (\mathbf{B}_0).

The effective magnetic field (\mathbf{B}_{eff}) experienced by a particular nucleus is somewhat smaller than the applied field (\mathbf{B}_0):

$$\mathbf{B}_{\text{eff}} = \mathbf{B}_0 - \mathbf{B}_{\text{local}}$$

Nuclei in a molecule are shielded from the full effect of \mathbf{B}_0 by the presence of nearby circulating electrons. Since each nucleus exists in a slightly different **electronic environment**, each nucleus will be shielded to a slightly different extent, and \mathbf{B}_{eff} will be slightly different for each nucleus within the molecule, as such:

NOT ALL PROTONS ARE EQUIVALENT

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Shielding

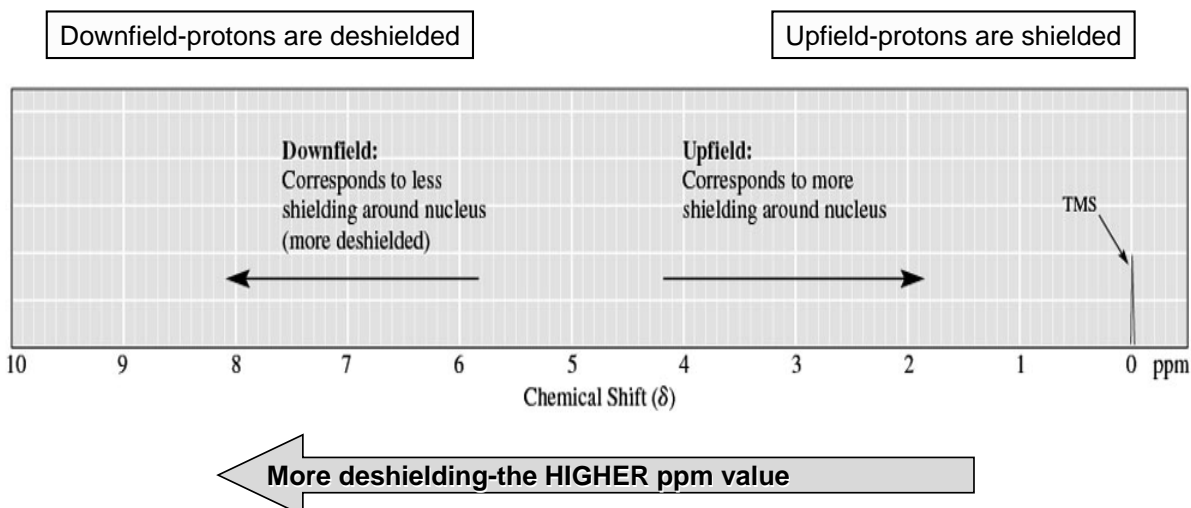
Nuclei surrounded by greater amounts of electron density will be more **shielded** from the external magnetic field, so they will absorb electromagnetic radiation of lower energy, that is, lower frequency.

The converse is also true, namely that nuclei surrounded by lesser amounts of electron density will be less shielded (*referred to as being "deshielded"*) from the external magnetic field, so they will absorb electromagnetic radiation of higher energy, that is, higher frequency.

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Chemical Shift

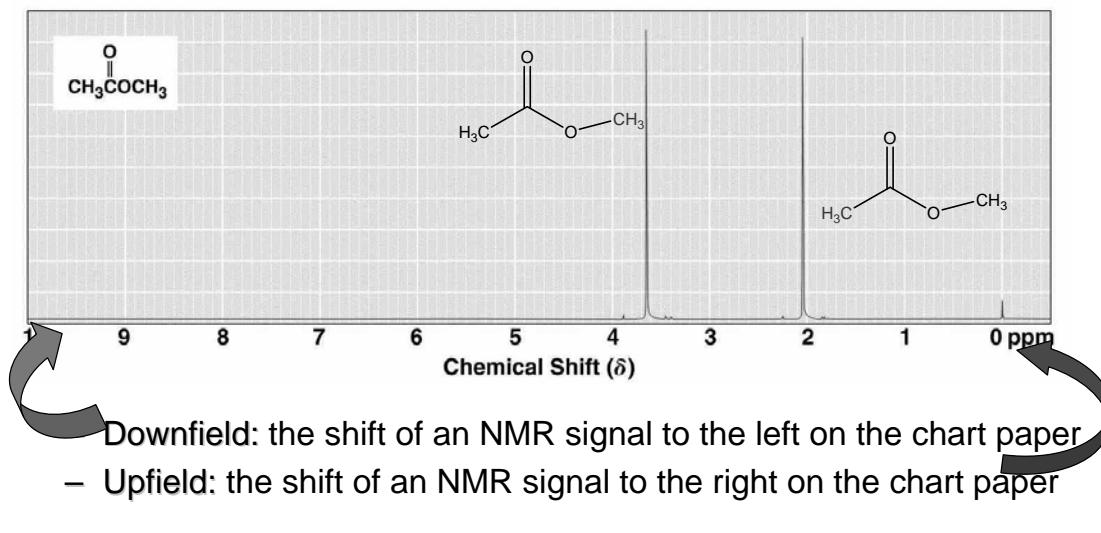
The more deshielded the nucleus, the higher the frequency of resonance, the higher the ppm value in the spectrum.



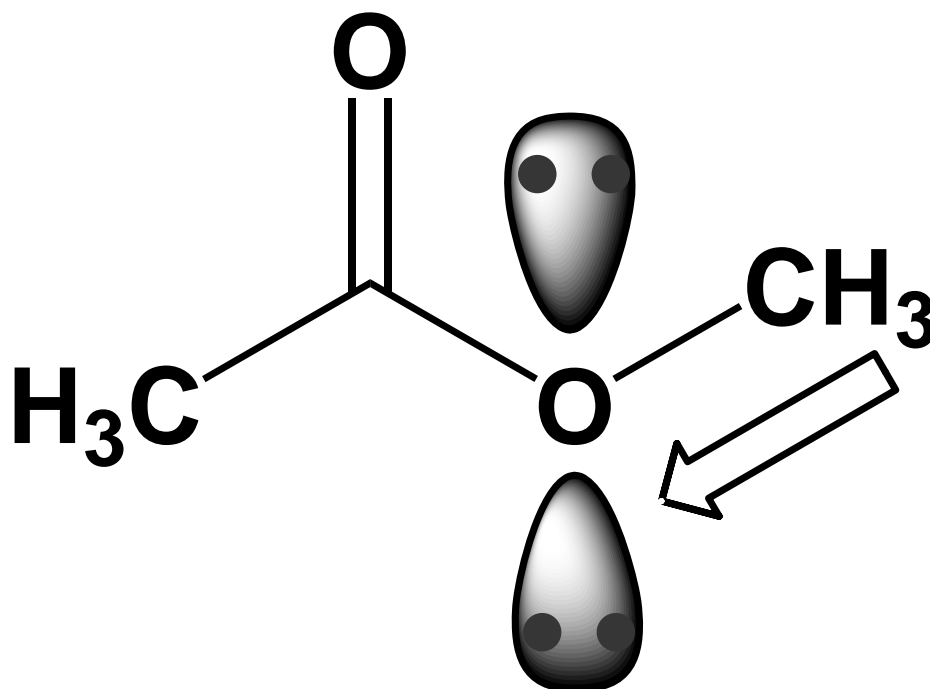
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NMR Spectrum

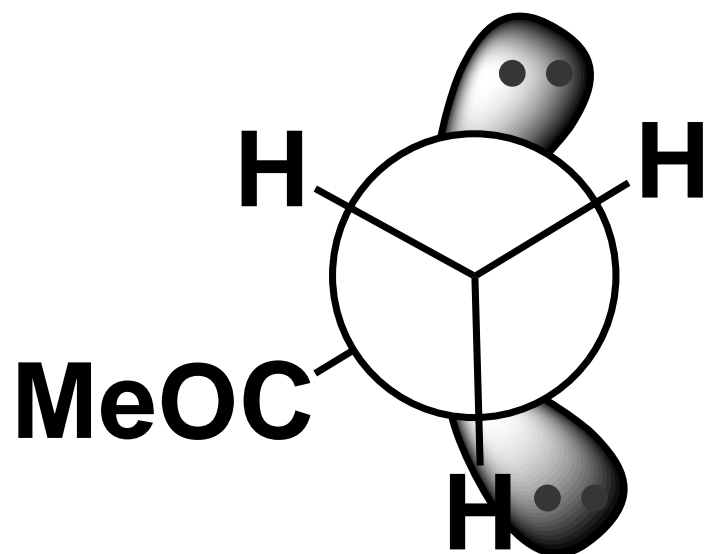
- ^1H -NMR spectrum of methyl acetate



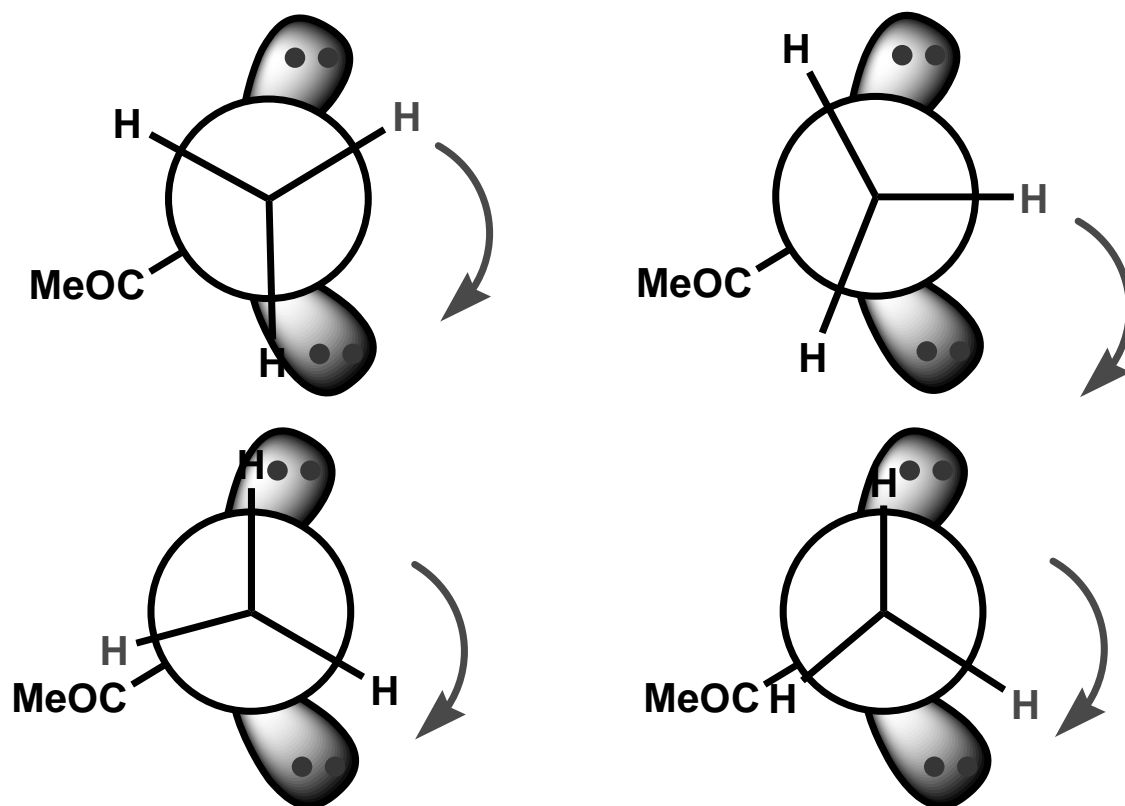
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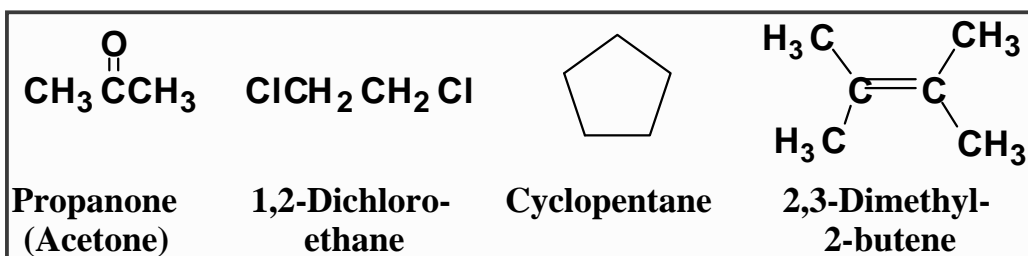
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Equivalent Hydrogens

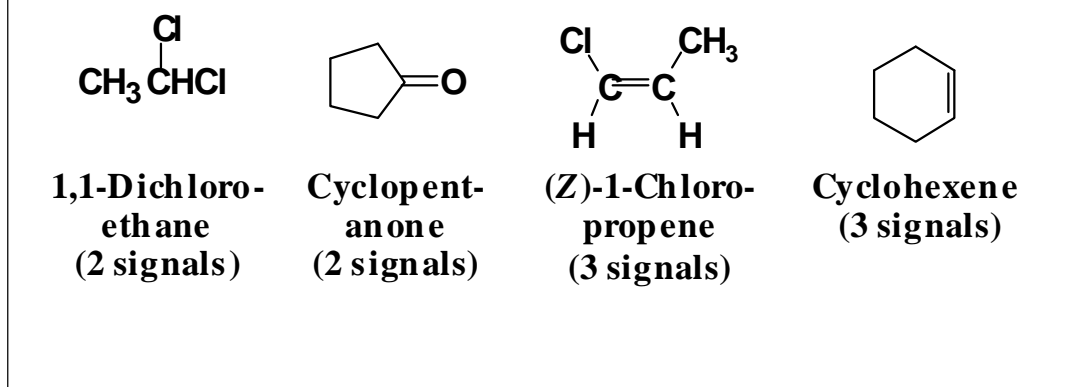
- Equivalent hydrogens: have the same chemical environment
 - a molecule with 1 set of equivalent hydrogens gives 1 NMR signal



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Equivalent Hydrogens

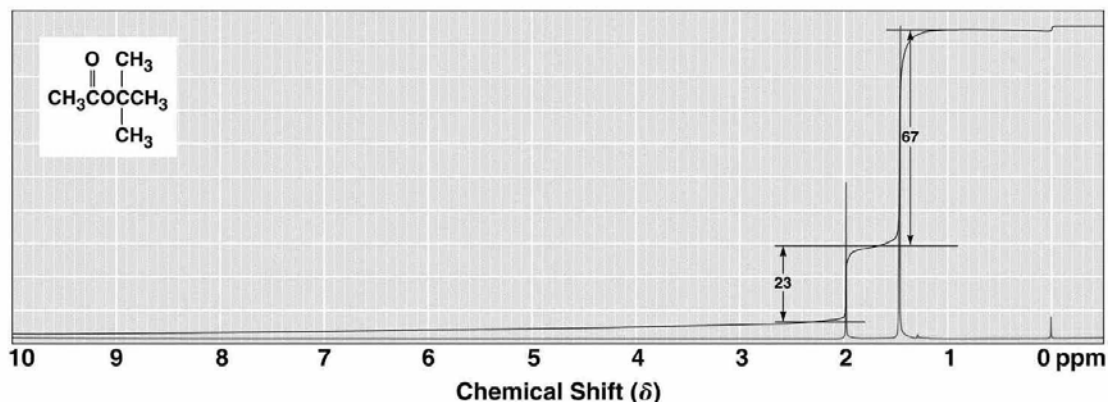
- a molecule with 2 or more sets of equivalent hydrogens gives a different NMR signal for each set



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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



-7

Chemical Shifts
¹H-NMR

Type of Hydrogen	Chemical Shift (δ)	Type of Hydrogen	Chemical Shift (δ)
$(\text{CH}_3)_4\text{Si}$	0 (by definition)	$\begin{array}{c} \text{O} \\ \parallel \\ \text{RCH}_3 \end{array}$	3.7-3.9
RCH_3	0.8-1.0	$\begin{array}{c} \text{O} \\ \parallel \\ \text{RCOCH}_2\text{R} \end{array}$	4.1-4.7
RCH_2R	1.2-1.4	RCH_2I	3.1-3.3
R_3CH	1.4-1.7	RCH_2Br	3.4-3.6
$\text{R}_2\text{C}=\text{CRCHR}_2$	1.6-2.6	RCH_2Cl	3.6-3.8
$\text{RC}\equiv\text{CH}$	2.0-3.0	RCH_2F	4.4-4.5
ArCH_3	2.2-2.5	ArOH	4.5-4.7
ArCH_2R	2.3-2.8	$\text{R}_2\text{C}=\text{CH}_2$	4.6-5.0
ROH	0.5-6.0	$\text{R}_2\text{C}=\text{CHR}$	5.0-5.7
RCH_2OH	3.4-4.0	ArH	6.5-8.5
RCH_2OR	3.3-4.0	$\begin{array}{c} \text{O} \\ \parallel \\ \text{RCH} \end{array}$	9.5-10.1
R_2NH	0.5-5.0	$\begin{array}{c} \text{O} \\ \parallel \\ \text{RCOCH}_3 \end{array}$	2.1-2.3
$\begin{array}{c} \text{O} \\ \parallel \\ \text{RCCH}_3 \end{array}$	2.1-2.3	$\begin{array}{c} \text{O} \\ \parallel \\ \text{RCOCH}_2\text{R} \end{array}$	2.2-2.6
$\begin{array}{c} \text{O} \\ \parallel \\ \text{RCCH}_2\text{R} \end{array}$	2.2-2.6	$\begin{array}{c} \text{O} \\ \parallel \\ \text{RCOH} \end{array}$	10-13

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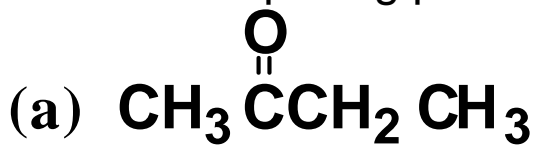
Signal Splitting & the ($n + 1$) Rule

- **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 ^1H -NMR signal is split into ($n + 1$) peaks

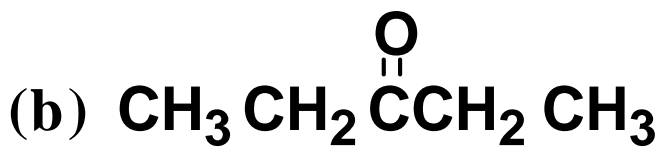
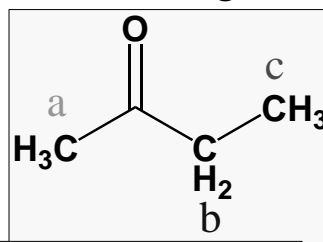
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Signal Splitting ($n + 1$)

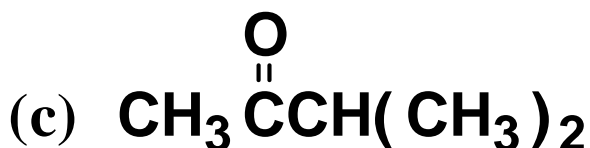
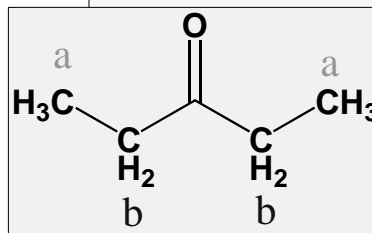
Problem: predict the number of ^1H -NMR signals and the splitting pattern of each



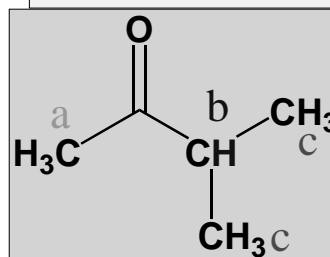
NMR



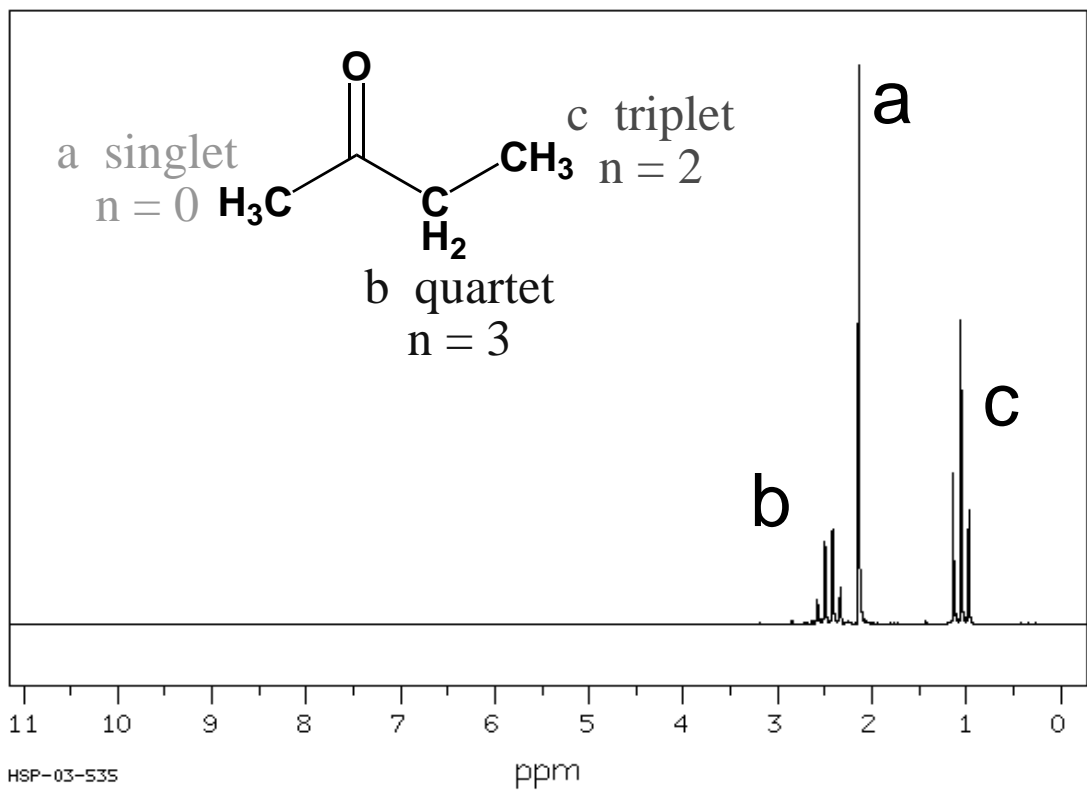
NMR



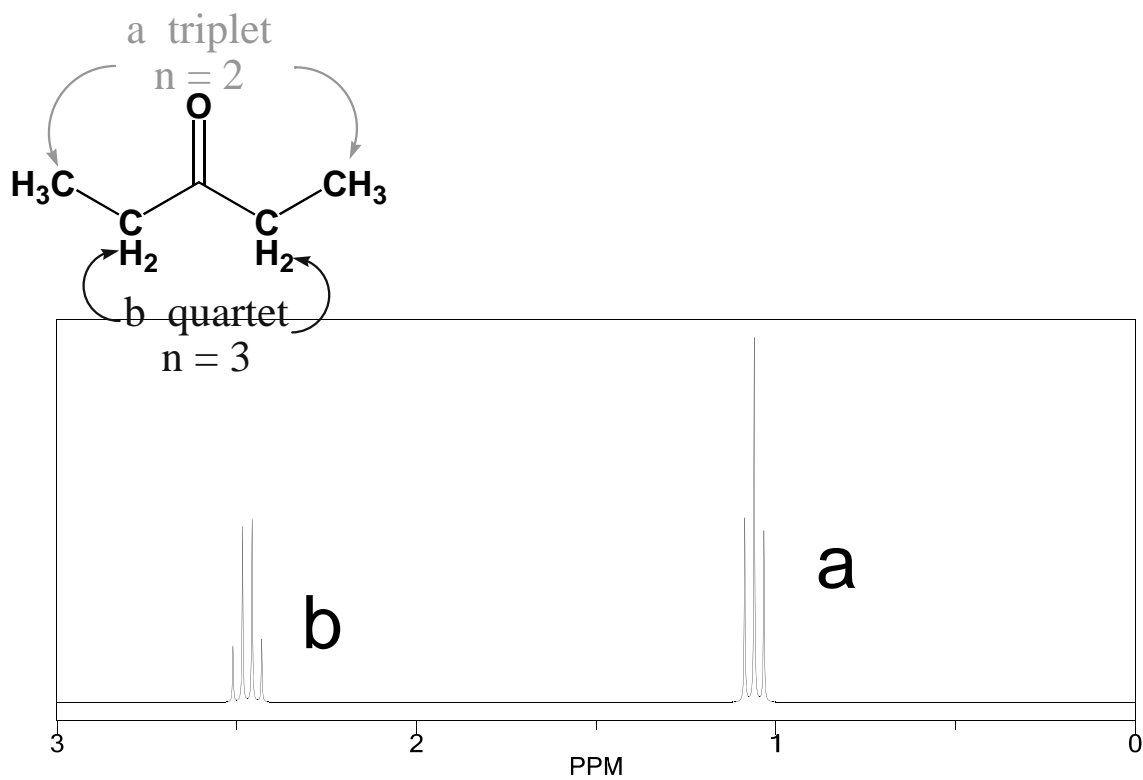
NMR



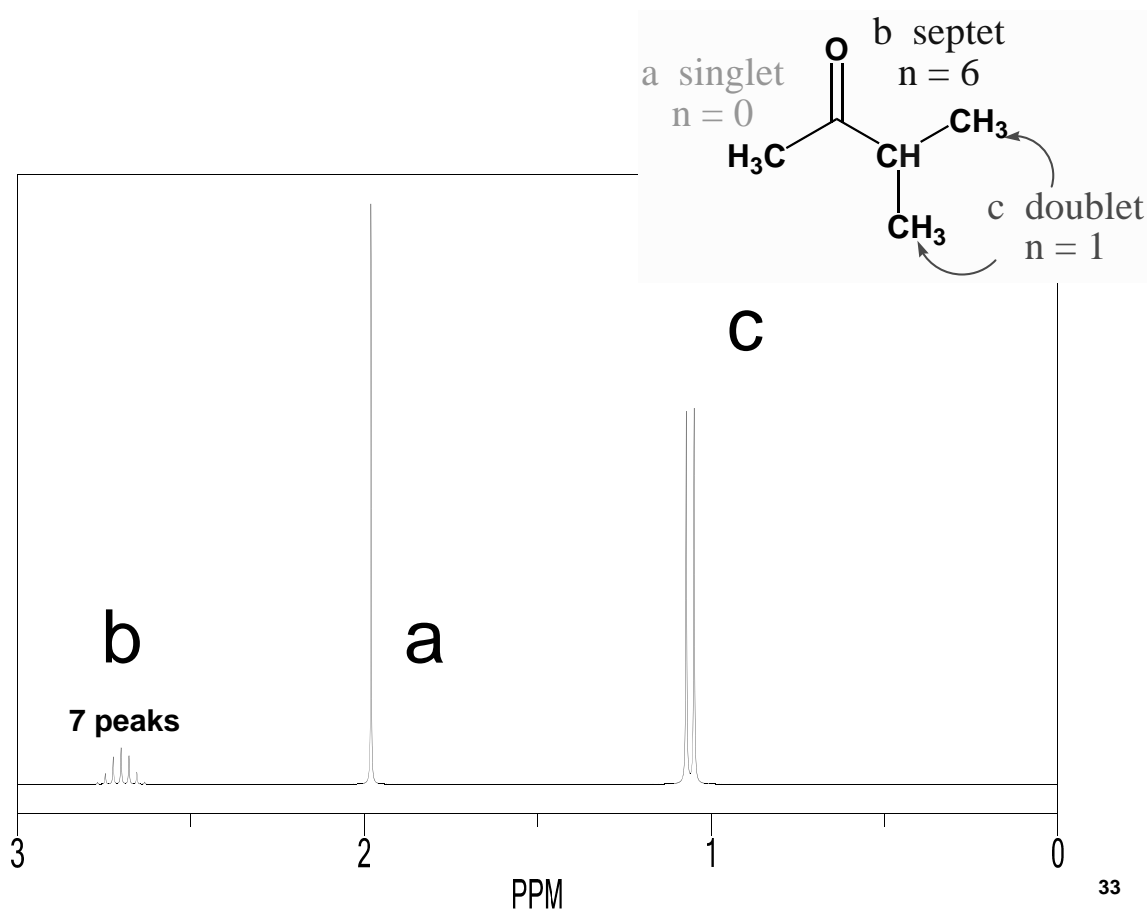
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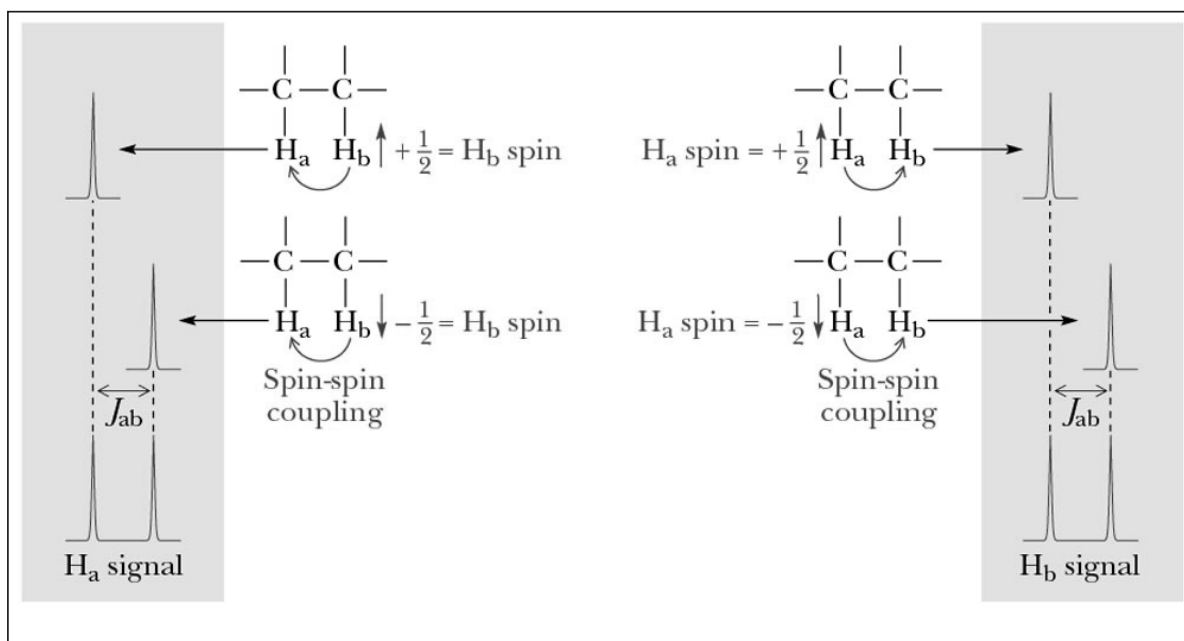
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Origins of Signal Splitting

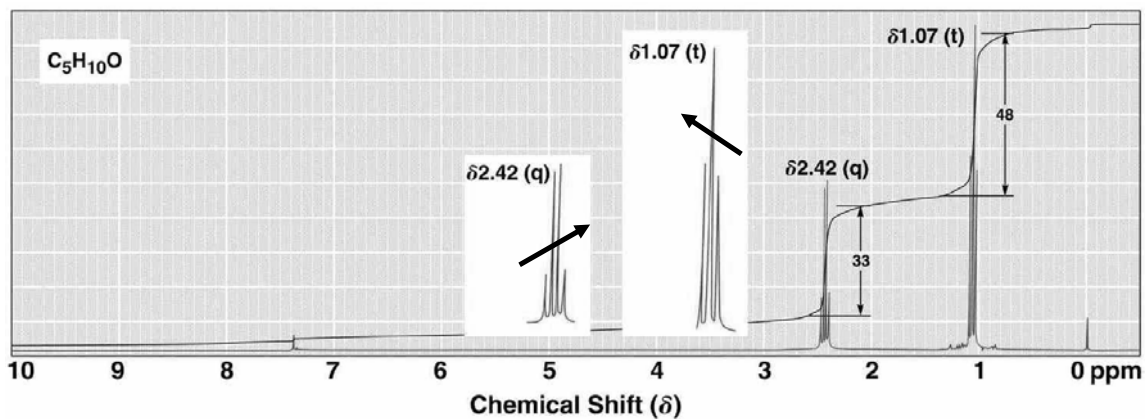
- **Signal coupling:** an interaction in which the nuclear spins of adjacent atoms influence each other and lead to the splitting of NMR signals
- **Coupling constant (J):** the separation on an NMR spectrum (in hertz) between adjacent peaks in a multiplet;
 - a quantitative measure of the influence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

Origins of Signal Splitting



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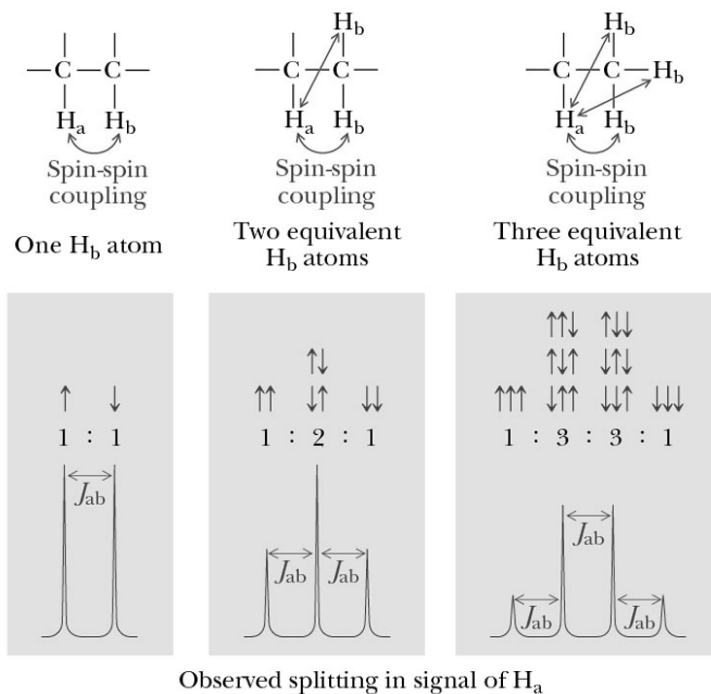
- because splitting patterns from spectra taken at 300 MHz and higher are often difficult to see, it is common to retrace certain signals in expanded form
- ^1H -NMR spectrum of **3-pentanone**; scale expansion shows the triplet quartet pattern more clearly



Note: Integration is ~ 2:3

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Origins of Signal Splitting



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• 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

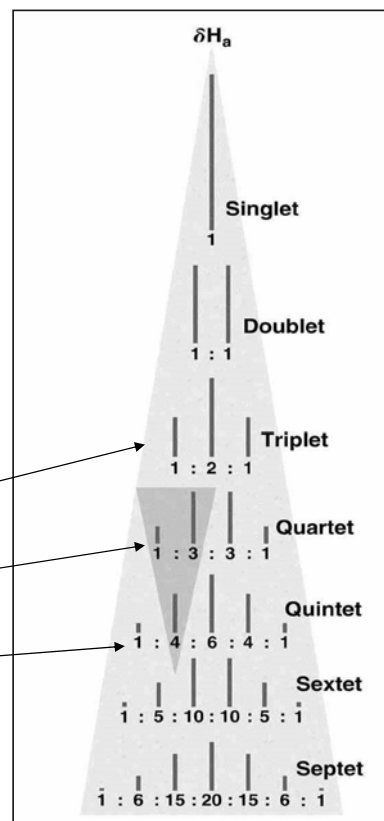
$$(x + y)^n = \sum_{k=0}^n \binom{n}{k} x^{n-k} y^k \quad (1)$$

$$(x + y)^2 = x^2 + 2xy + y^2$$

$$(x + y)^3 = x^3 + 3x^2y + 3xy^2 + y^3$$

$$(x + y)^4 = x^4 + 4x^3y + 6x^2y^2 + 4xy^3 + y^4$$

$$(x + y)^5 = x^5 + 5x^4y + 10x^3y^2 + 10x^2y^3 + 5xy^4 + y^5$$

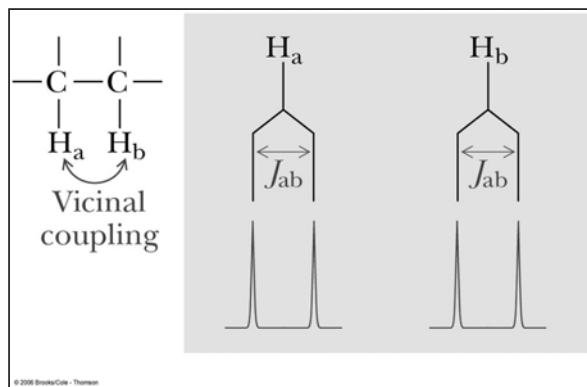


Not exam material

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Physical Basis for $(n + 1)$ Rule

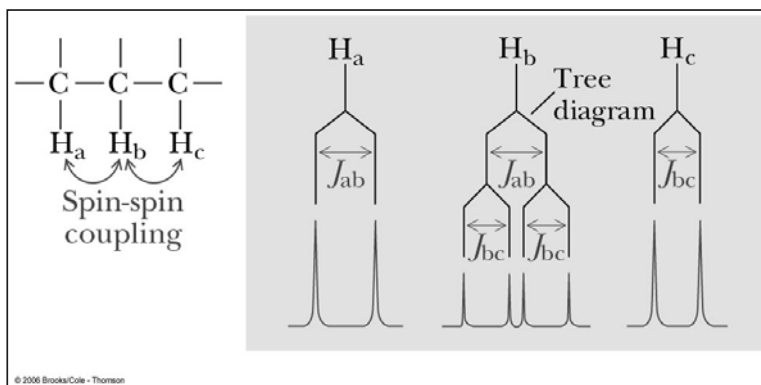
- Coupling of nuclear spins is mediated through intervening bonds
 - H atoms with more than three bonds between them generally do not exhibit noticeable coupling
 - for H atoms three bonds apart, the coupling is referred to as vicinal coupling



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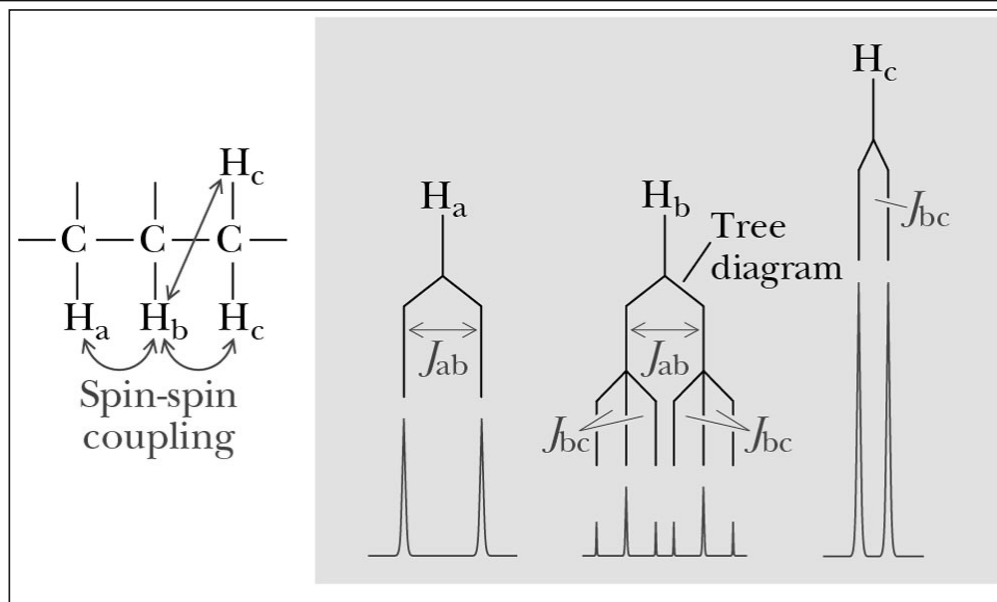
More Complex Splitting Patterns

- 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**



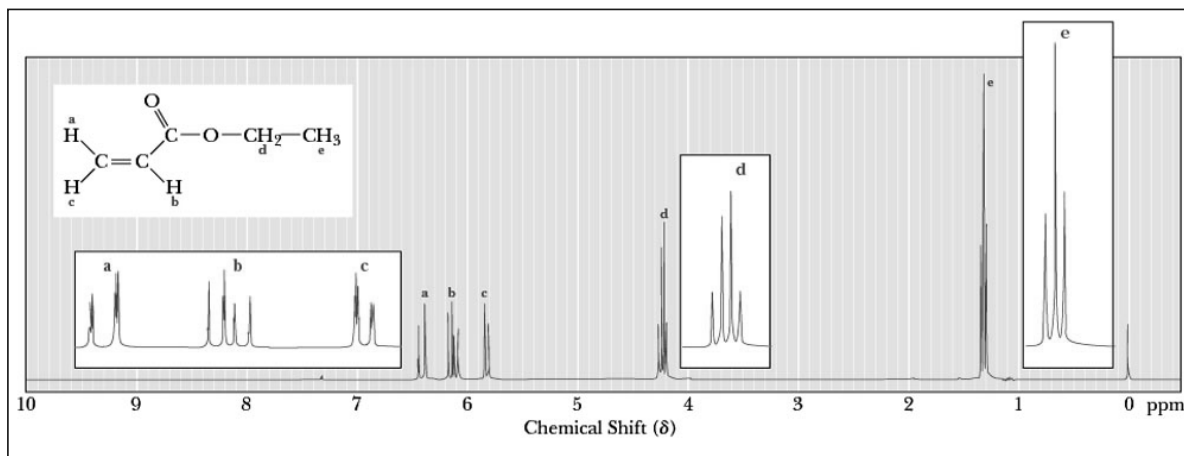
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– if H_c is a set of two equivalent H, then the observed splitting is a **doublet of triplets**



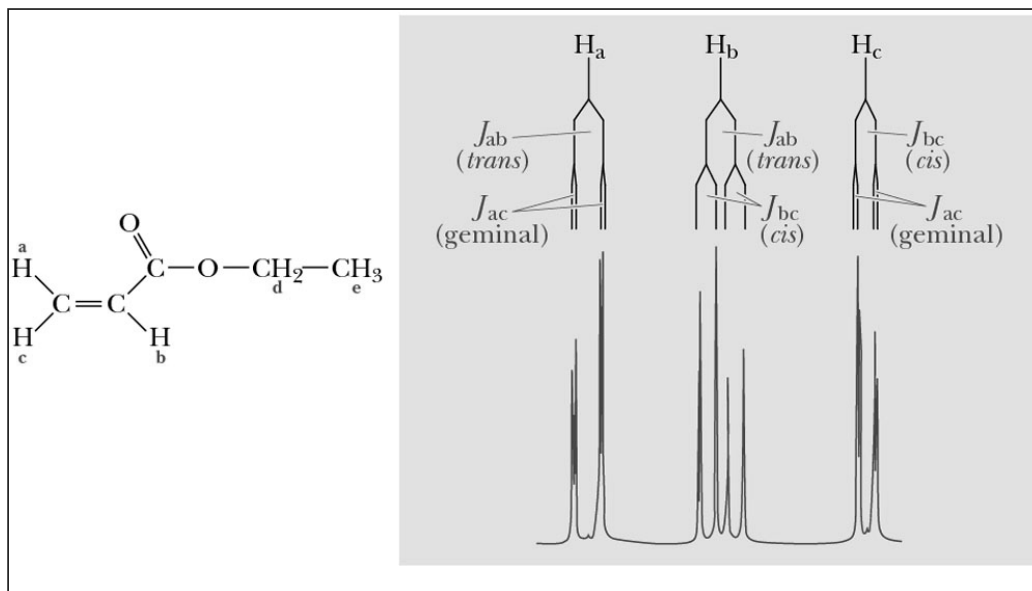
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– in **ethyl propenoate**, an unsymmetrical terminal alkene, the three vinylic hydrogens are nonequivalent



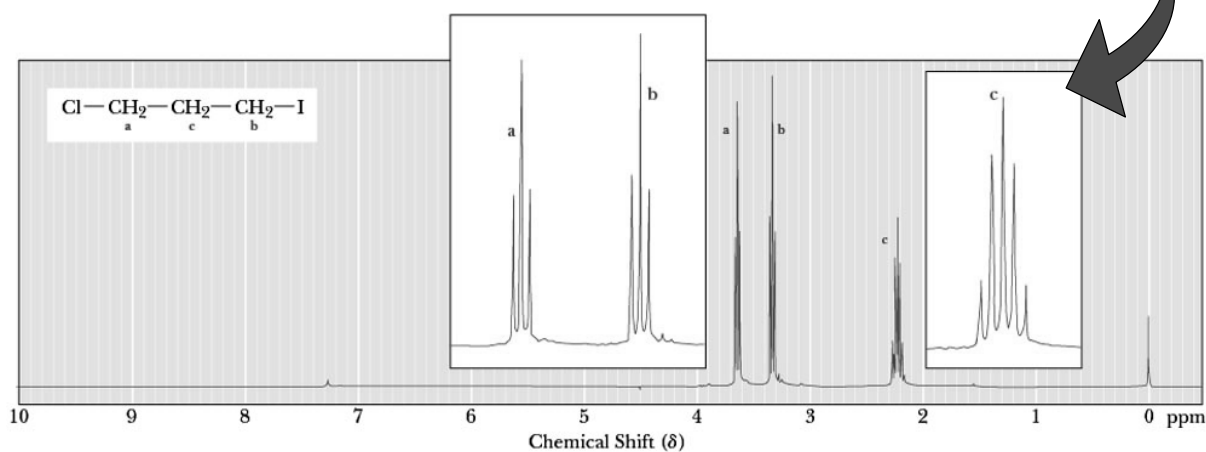
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- a tree diagram for the complex coupling of the three vinylic hydrogens in ethyl propenoate



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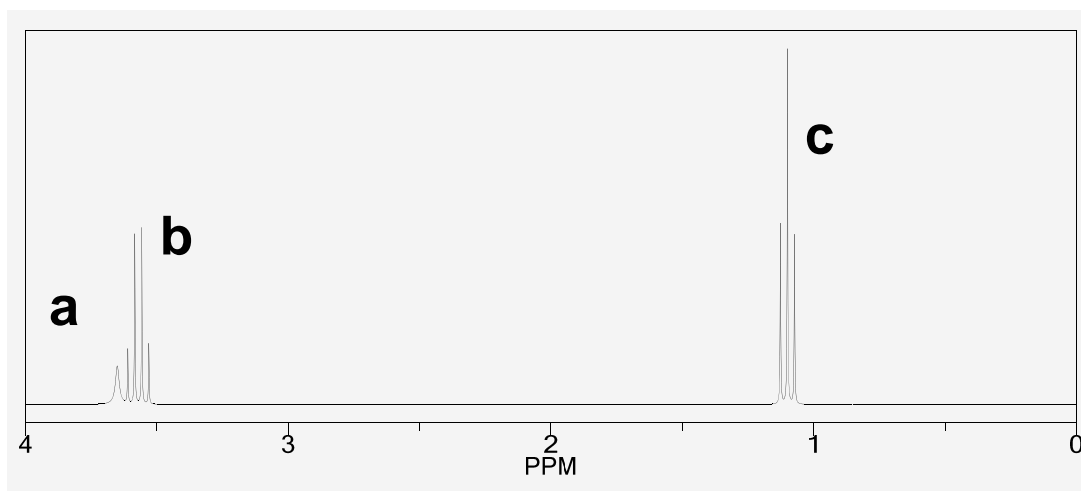
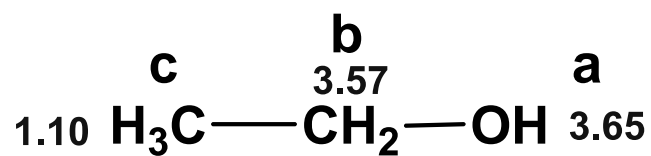
- an example of **peak overlap** occurs in the spectrum of 1-chloro-3-iodopropane
- the central CH_2 has the possibility for 9 peaks (a triplet of triplets) but because J_{ab} and J_{bc} are so similar, only $4 + 1 = 5$ peaks are distinguishable



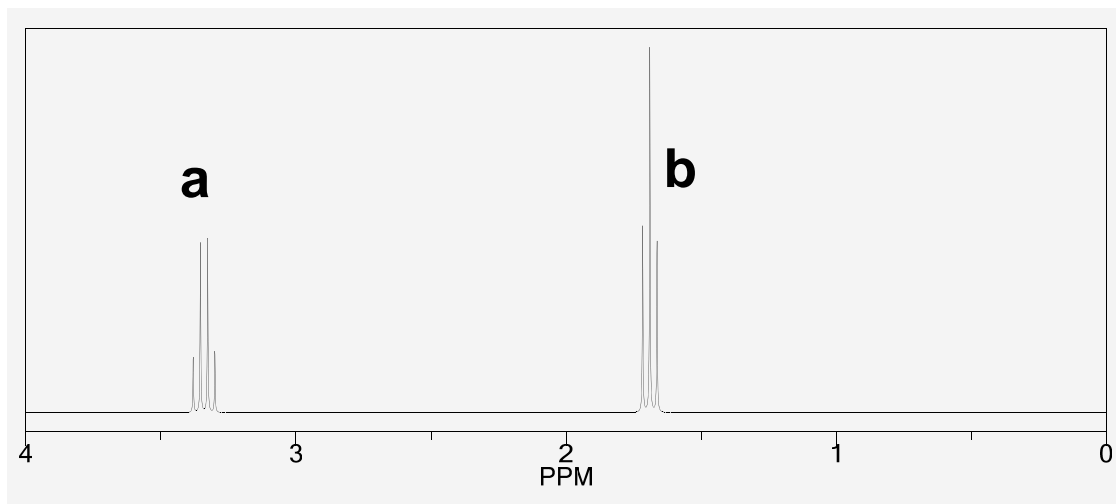
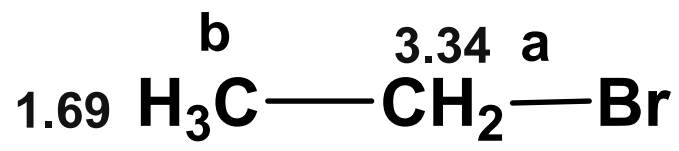
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Refer to NMR Handout

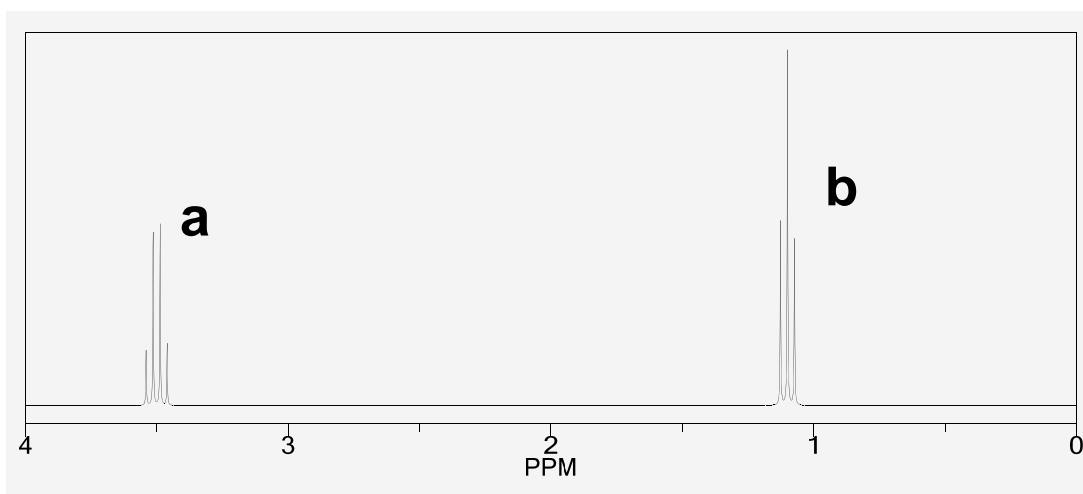
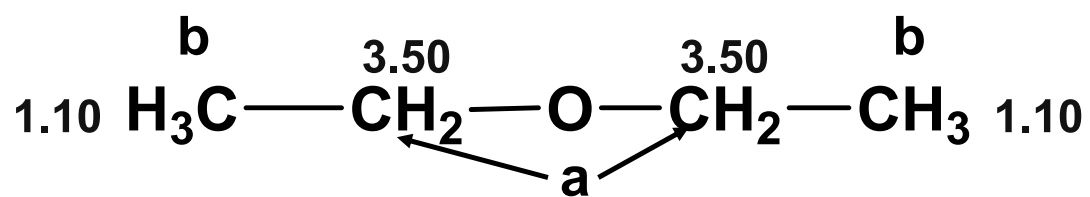
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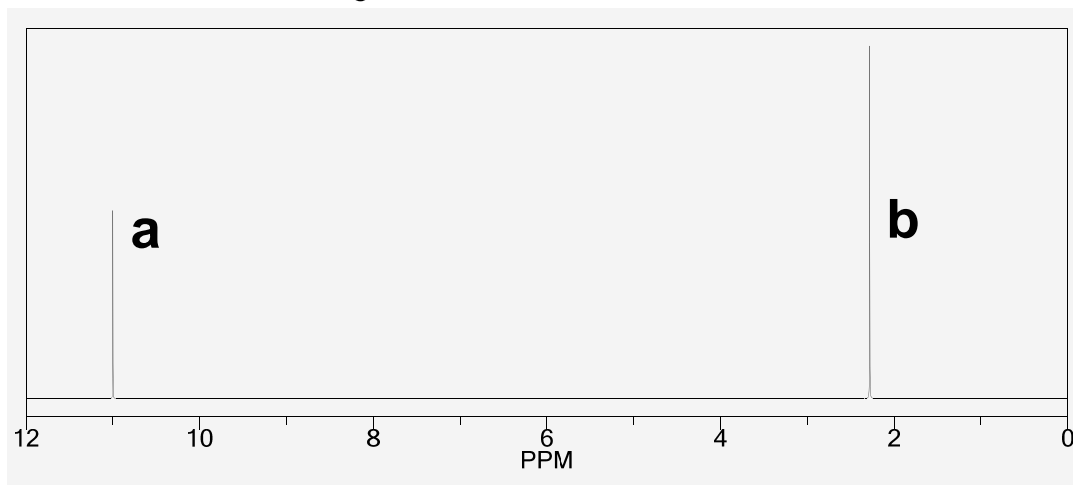
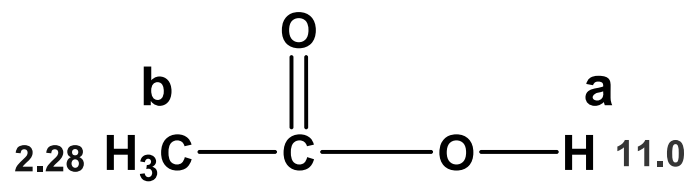
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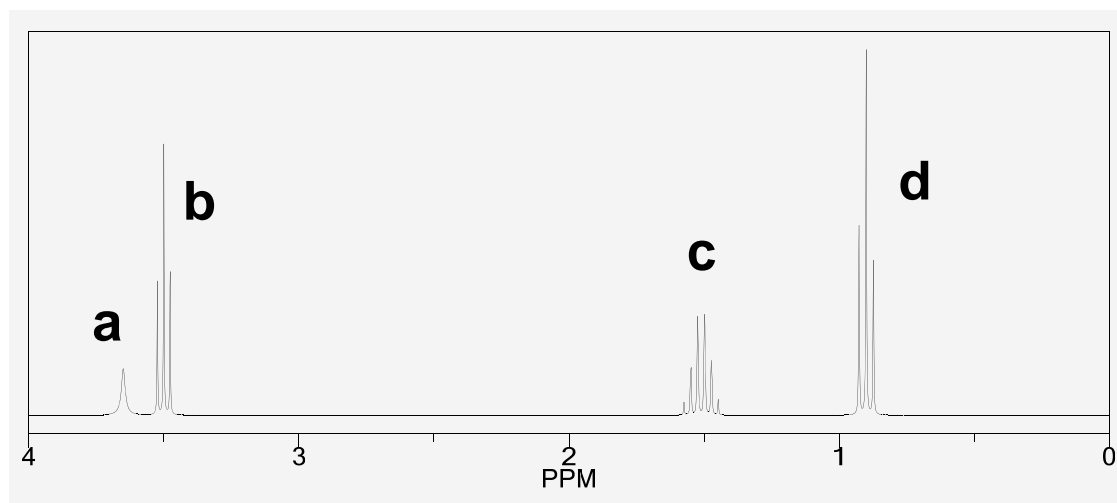
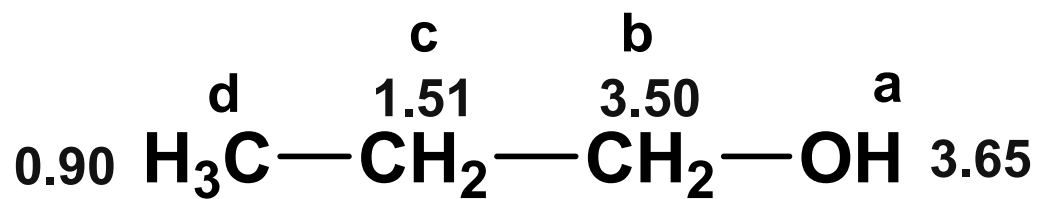
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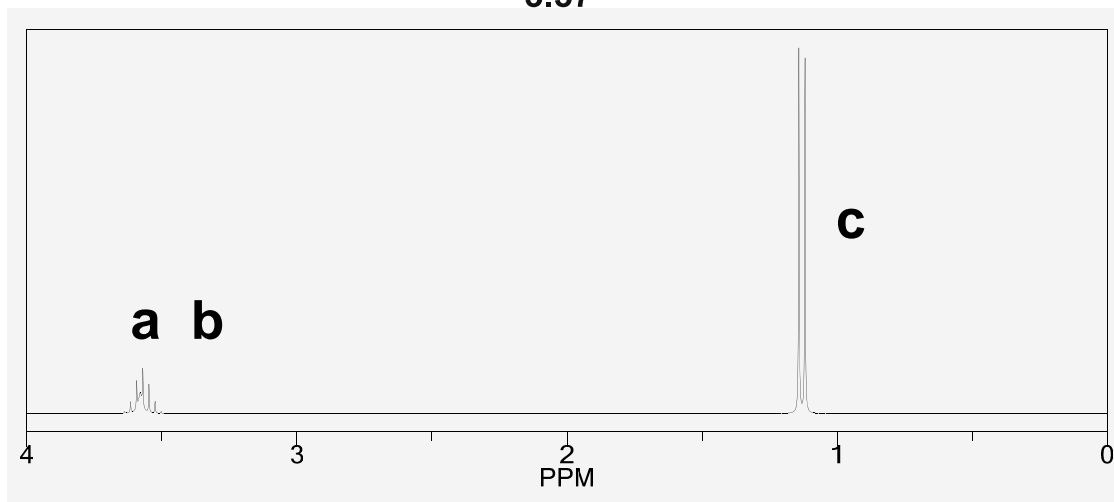
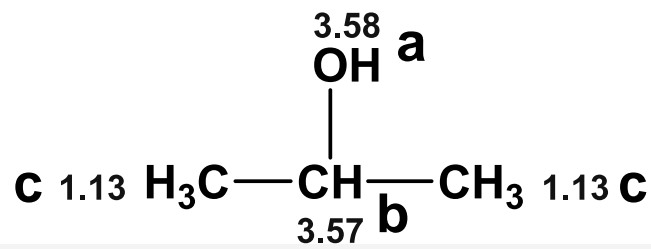
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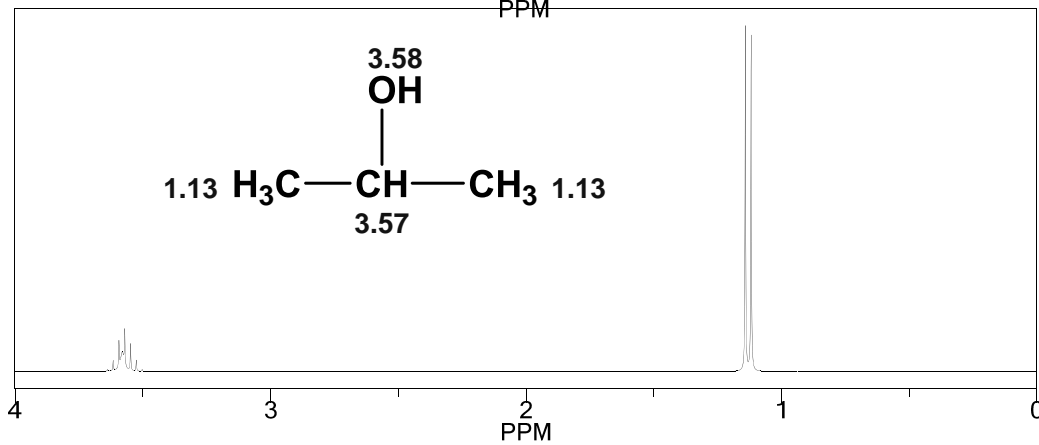
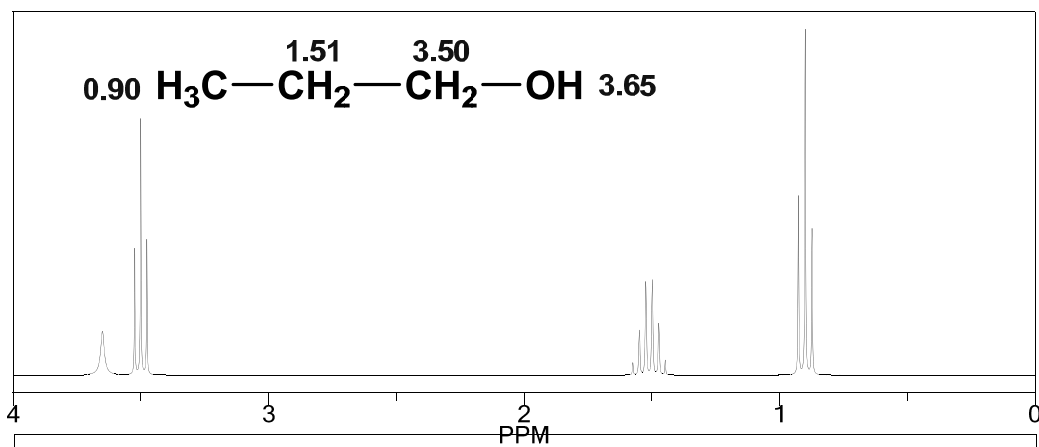
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