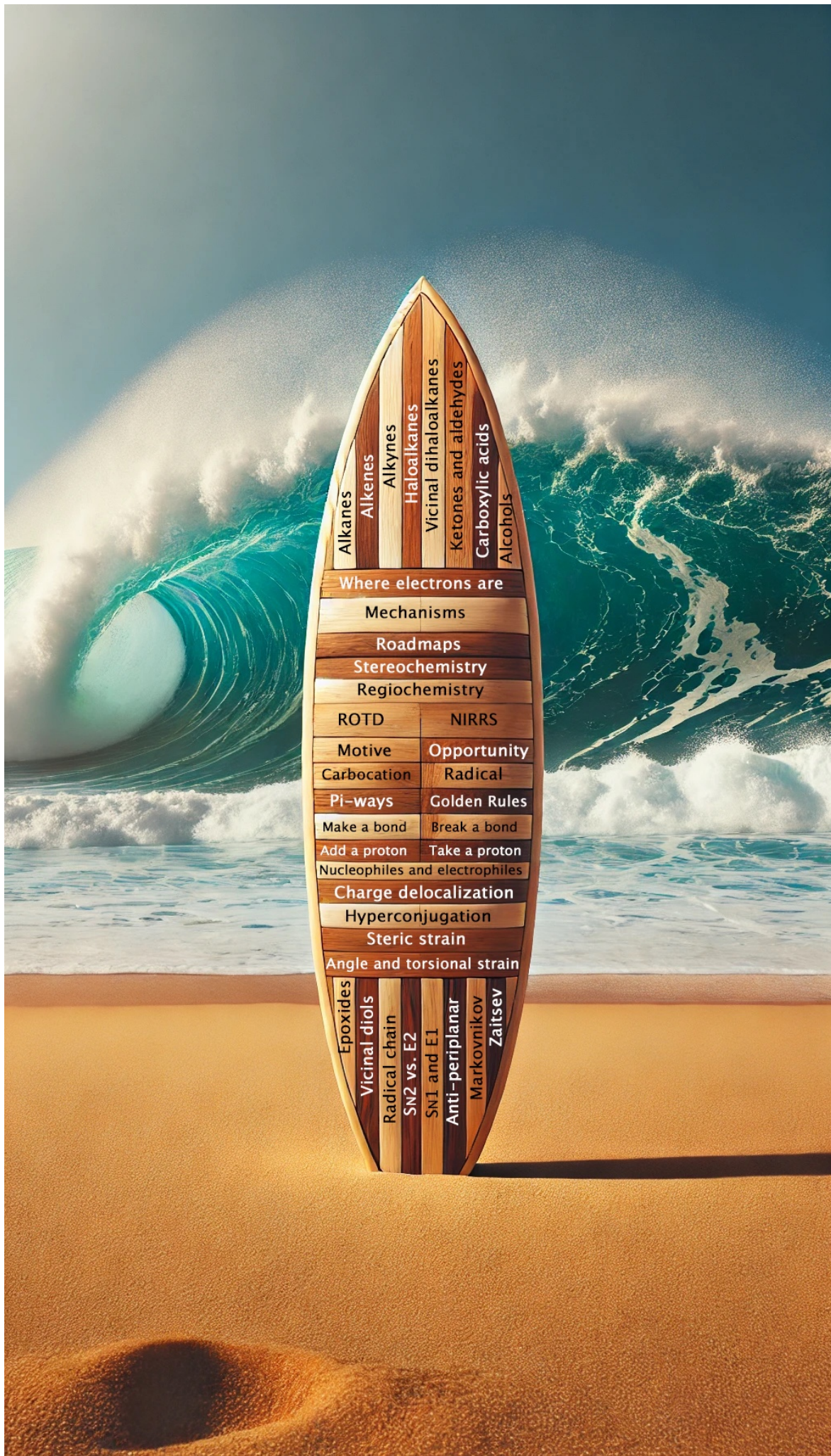




“You can’t stop the waves, but you can learn to surf”

Jon Kabat-Zinn



Described by
Maxwell's Equation

To understand NMR you need to know the following:

A. Physics: Moving charge generates a magnetic field, and a moving magnetic field causes charges to move in a conductor.

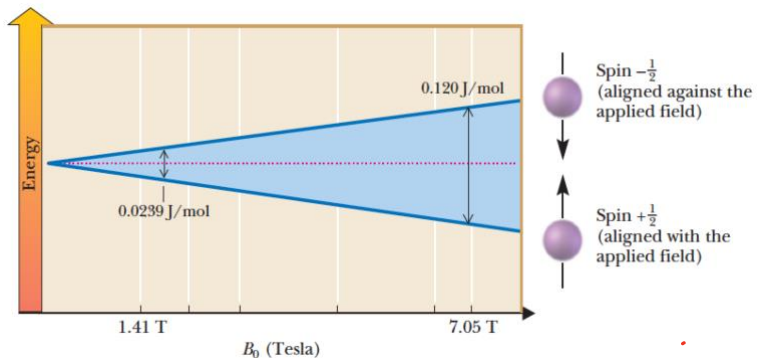
B. Atomic nuclei, like electrons, have a quantum mechanical property of "spin". Spin can be thought of as a small magnetic field around the nucleus created as if the positive charge of the nucleus were circulating.

C. NMR, nuclear magnetic resonance, is used to assign structures of organic molecules.

D. We care about the nuclei ^1H and ^{13}C since these are commonly found in organic molecules and they have spin quantum numbers of 1/2.

E. Nuclei with spin quantum number 1/2 are quantized in one of two orientations, "+1/2" (lower energy) or "-1/2" (higher energy) in the presence of an external magnetic field, that is, with and against the external field, respectively.

F. The difference in energy between the +1/2 and -1/2 nuclear spin states is proportional to the strength of the magnetic field felt by the nucleus.



G. Electron density is induced to circulate in a strong external magnetic field, which in turn produces a magnetic field that opposes the external magnetic field. This **shields** nuclei from the external magnetic field. The greater the electron density around a nucleus, the more shielded it is, and the lower the energy (frequency) of electromagnetic radiation required to flip its nuclear spin.

H. In the classic ^1H -NMR experiment, the molecule of interest is placed in solvent (the solvent has deuterium atoms in place of H atoms so the solvent molecules will not show up in the spectra, see R.) then is put in a spinning tube in a very strong magnetic field. The sample is exposed to radiofrequency irradiation and if it is of exactly the right frequency energy is absorbed and spins flip from +1/2 to -1/2 (come into resonance). The absorbed energy is plotted in the spectra.

I. All ^1H -NMR spectra are recorded as **chemical shift** (δ , **delta**) in the units of **ppm** (parts per million). Shielding magnetic field effects are around 1 millionth as large as the external magnetic field in which the sample is placed. Tetramethylsilane (TMS, $(\text{CH}_3)_4\text{Si}$) is placed in the sample as a standard and assigned the value of 0.0 ppm. **Warning the NMR scale is plotted "backwards", with higher values to the left!!**

Certain nuclei such as ^1H nuclei have a quantum mechanical property called **spin** that comes with an associated **magnetic field**.

^1H nuclei can exist in two different **spin states**, $+\frac{1}{2}$ and $-\frac{1}{2}$.

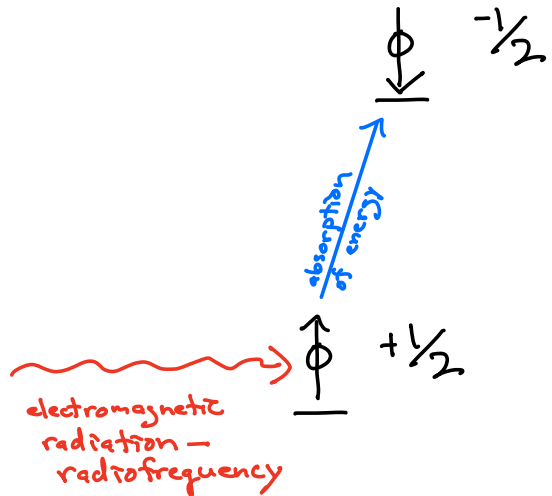
In a **strong magnetic field**, the nuclei with spin line up with $(+\frac{1}{2})$ and against $(-\frac{1}{2})$ the magnetic field.

Nuclei in the $+\frac{1}{2}$ **spin state** are of lower energy and nuclei in the $-\frac{1}{2}$ **spin state** are of higher energy in a magnetic field.

The **difference in energy** between the $+\frac{1}{2}$ and $-\frac{1}{2}$ spin states is directly proportional to the strength of the **magnetic field** experienced by the nuclei

Radiofrequency electromagnetic radiation of exactly the right energy (i.e. frequency) is **absorbed** by $+\frac{1}{2}$ spin state nuclei causing them to "**flip**" to the $-\frac{1}{2}$ spin state. \Rightarrow A process called "**resonance**"

NMR experiment \rightarrow place sample of a molecule in a very strong magnetic field



The energy absorption/nuclear spin flipping phenomenon is called "Resonance"

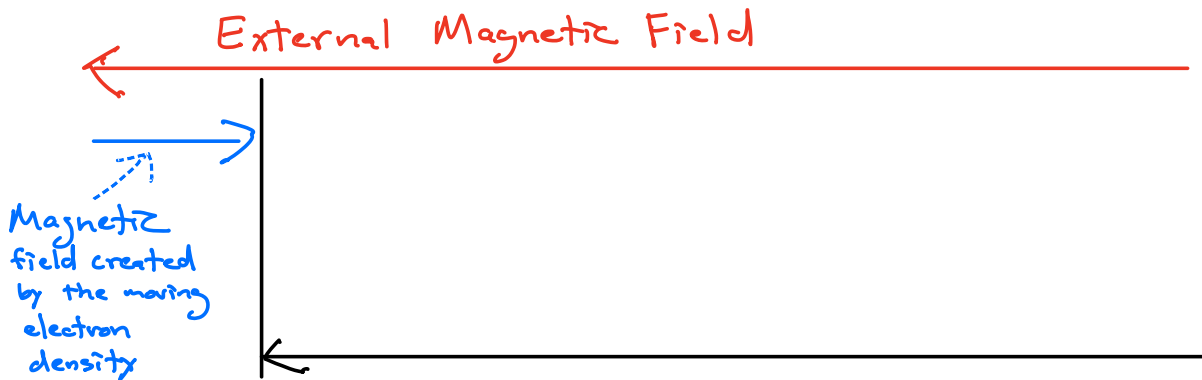
The ^1H nucleus of spin state $+\frac{1}{2}$ absorbs a quanta of energy of precisely the correct frequency and the nucleus is "excited" to the $-\frac{1}{2}$ spin state.

Key Point → The energy of the of electromagnetic energy that is absorbed must match exactly the energy difference between the $+\frac{1}{2}$ and $-\frac{1}{2}$ nuclear spin states for resonance to happen

We monitor the energy that is absorbed by the nuclear spins as they flip

Shielding \rightarrow explanation

The external magnetic field induces electron density to circulate, which creates its own small magnetic field that will always directly oppose the external magnetic field.



The magnitude of the magnetic field experienced by a nucleus under the electron density.

Shielding Bottom Line →

⇒ More electron density generates a larger opposing magnetic field so a nucleus under more electron density experiences a smaller magnetic field.

⇒ More electron density around a nucleus provides more shielding of the external magnetic field

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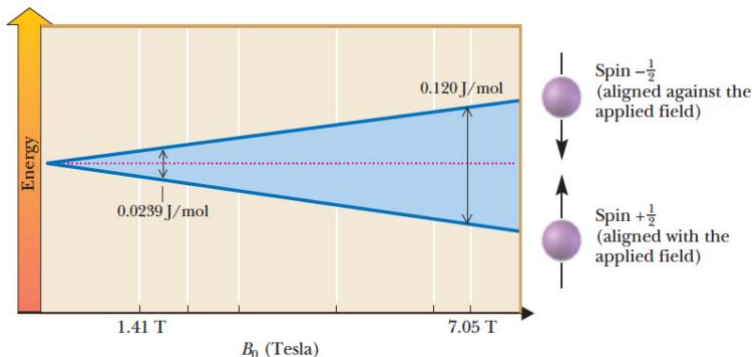
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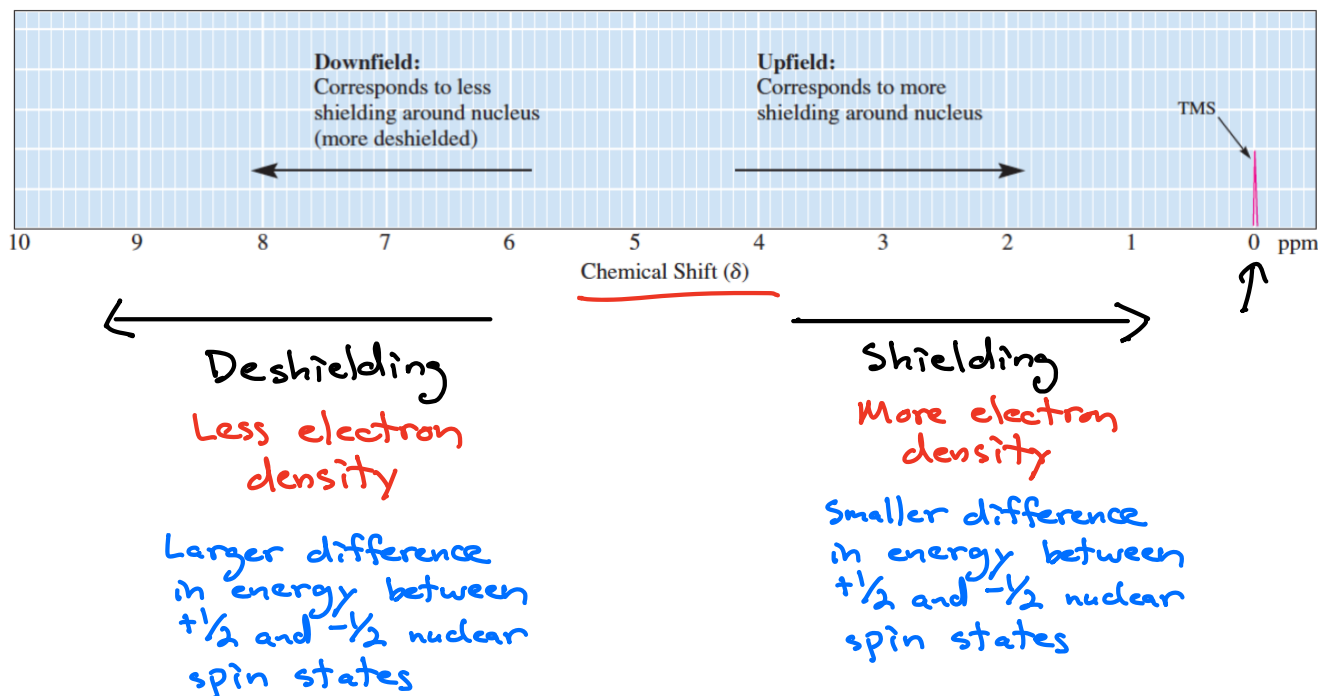


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← Plot is backwards → larger values to the left!



J. The hybridization state of carbon atoms attached to an H atom influences shielding in predictable ways by removing differing amounts of electron density around adjacent nuclei.

K. Electron density in pi bonds also has a large effect on H atom shielding because pi electrons are more free to circulate in an a magnetic field compared to electron density in sigma bonds.
Geometry of the pi bond is important.

Table 13.3 The Effect of Hybridization on Chemical Shift

Type of Hydrogen (R = alkyl)	Name of Hydrogen	Chemical Shift δ
RCH_3 , R_2CH_2 , R_3CH	Alkyl	0.8–1.7
$R_2C=C(R)CHR_2$	Allylic	1.6–2.6
$RC\equiv CH$	Acetylenic	2.0–3.0
$R_2C=CHR$, $R_2C=CH_2$	Vinylic	4.6–5.7
$RCHO$	Aldehydic	9.5–10.1

Type of Hydrogen (R = alkyl, Ar = aryl)	Chemical Shift (δ)*	Type of Hydrogen (R = alkyl, Ar = aryl)	Chemical Shift (δ)*
R_2NH	0.5-5.0	RCH_2OH	3.4-4.0
ROH	0.5-6.0	RCH_2Br	3.4-3.6
RCH_3	0.8-1.0	RCH_2Cl	3.6-3.8
RCH_2R	1.2-1.4	$\begin{array}{c} O \\ \\ RCOCH_3 \end{array}$	3.7-3.9 ✓
R_3CH	1.4-1.7	$\begin{array}{c} O \\ \\ RCOCH_2R \end{array}$	4.1-4.7
$R_2C=CRCHR_2$	1.6-2.6	RCH_2F	4.4-4.5
$RC\equiv CH$	2.0-3.0	$ArOH$	4.5-4.7
$\begin{array}{c} O \\ \\ RCCH_3 \end{array}$	2.1-2.3	$R_2C=CH_2$	4.6-5.0
$\begin{array}{c} O \\ \\ RCCH_2R \end{array}$	2.2-2.6	$R_2C=CHR$	5.0-5.7
$ArCH_3$	2.2-2.5	$\begin{array}{c} O \\ / \backslash \\ H_2C \quad CH_2 \end{array}$	3.3-4.0
RCH_2NR_2	2.3-2.8	$\begin{array}{c} O \\ \\ RCH \end{array}$	9.5-10.1
RCH_2I	3.1-3.3	$\begin{array}{c} O \\ \\ RCOH \end{array}$	10-13
RCH_2OR	3.3-4.0		

* Values are relative to tetramethylsilane. Other atoms within the molecule may cause the signal to appear outside these ranges.

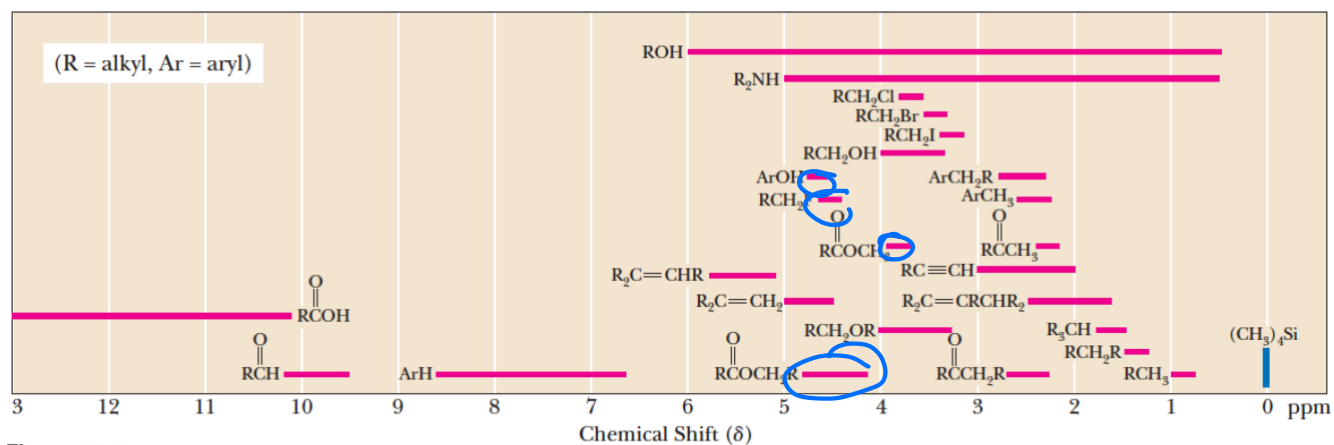
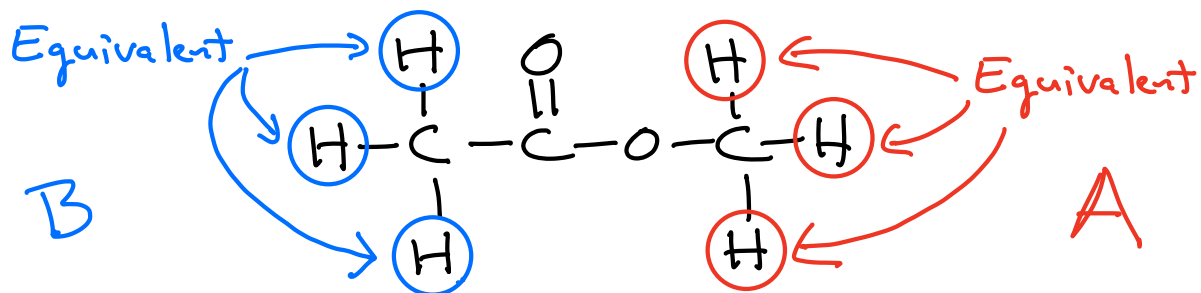


Figure 13.8

Average values of chemical shifts of representative types of hydrogens. These values are approximate. Other atoms or groups in the molecules may cause signals to appear outside of these ranges.

L. Chemically **equivalent** H atoms give rise to the same $^1\text{H-NMR}$ signal. **Equivalent** H atoms have the same chemical environment because they are bonded to the same freely rotating sp^3 C atom (molecular motion, nanosecond, is fast compared the time it takes for a spin to flip, microsecond) OR they are equivalent due to symmetry in the molecule.



← Less Electron Density

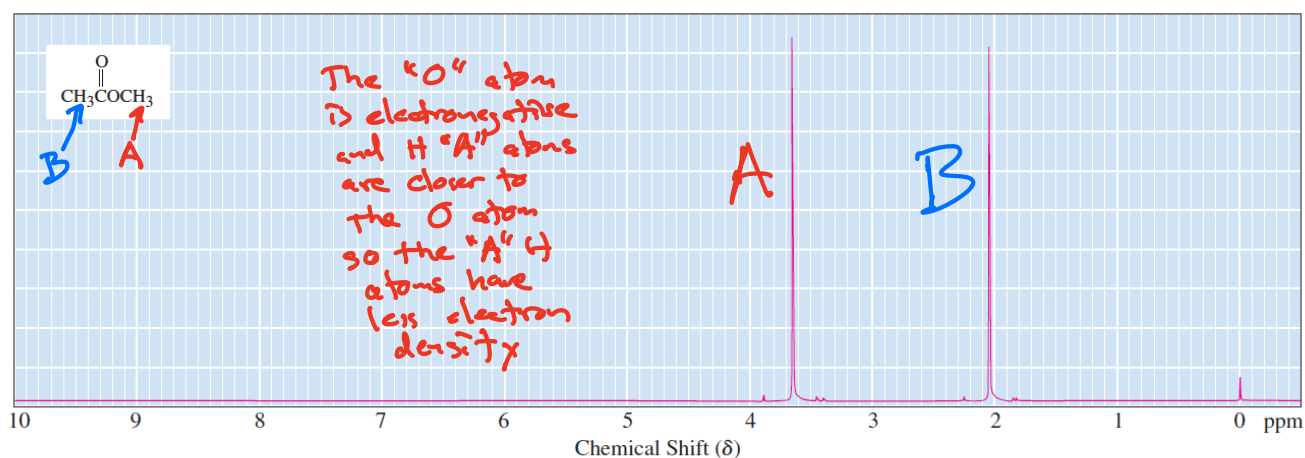


Figure 13.5

$^1\text{H-NMR}$ spectrum of methyl acetate

M. The area of a $^1\text{H-NMR}$ signal is proportional to the number of equivalent H atoms that give rise to that signal.

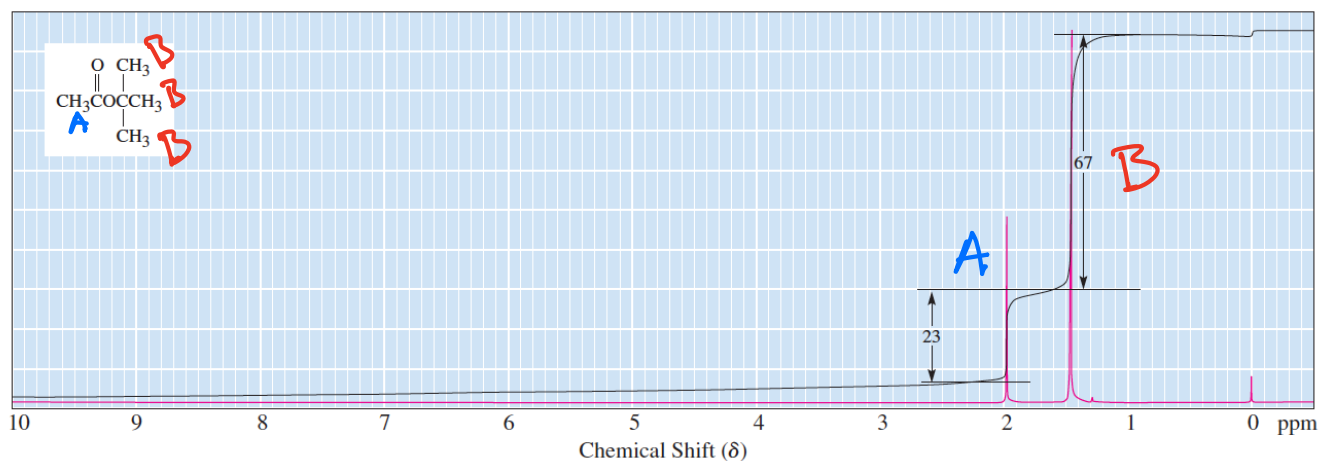
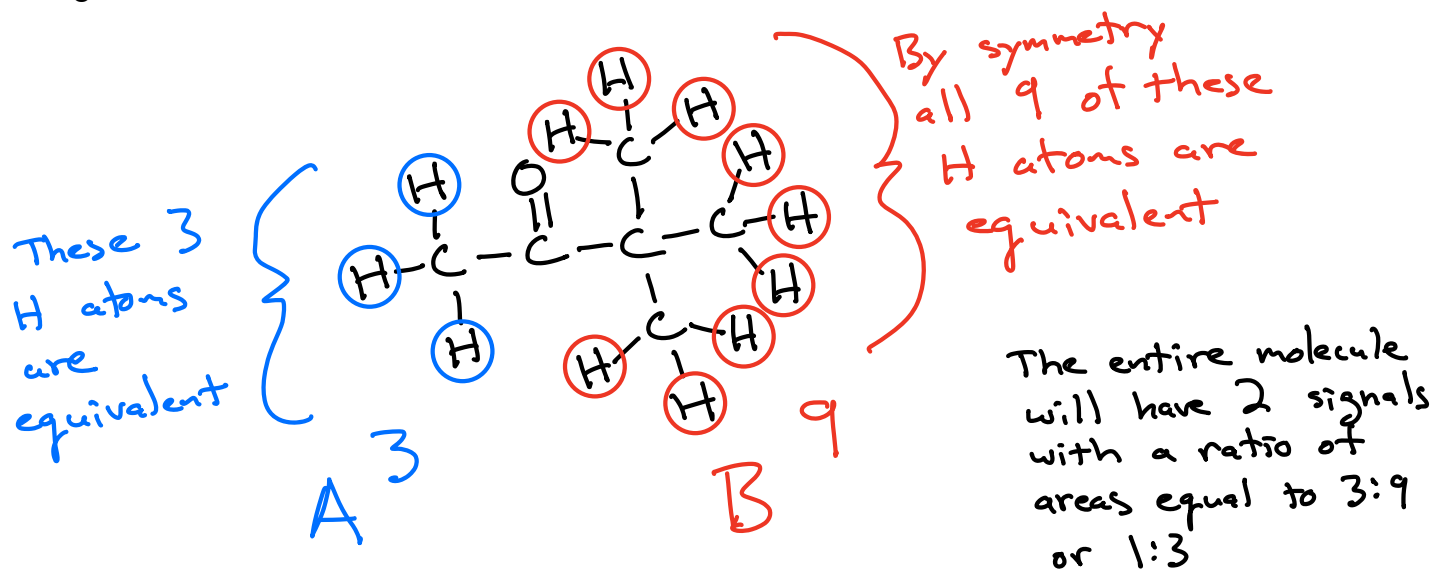


Figure 13.7

$^1\text{H-NMR}$ spectrum of *tert*-butyl acetate showing the integration. The total vertical rise of 90 chart divisions corresponds to 12 hydrogens, 9 in one set and 3 in the other.

Surprising Fact → The absolute energy difference between ^1H nuclei in a $+\frac{1}{2}$ and $-\frac{1}{2}$ spin state is so small → according to the Boltzmann distribution, at any one time there is only a small excess of ^1H nuclear spins in the $+\frac{1}{2}$ spin state.

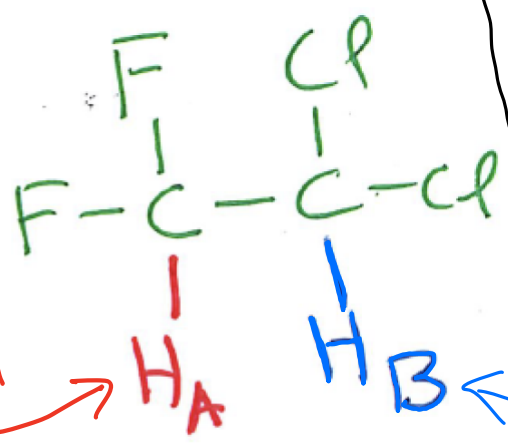
Nearly
1:1

The magnetic field produced by a ^1H nucleus in a $+\frac{1}{2}$ spin state is different than that produced by a ^1H nucleus in a $-\frac{1}{2}$ spin state.

Definition → "Adjacent" means no more than 3 bonds away.

N. Adjacent nuclei have magnetic fields associated with their spins. The spins of equivalent adjacent nuclei can be either $+1/2$ or $-1/2$, and at room temperature they are found in about a 50:50 mixture at any given nucleus (very slight excess of lower energy $+1/2$). These can add to give $n+1$ different spin combinations in the proportions predicted by Pascal's triangle. Each different spin combination produces a different magnetic field, which leads to $n+1$ splittings in the peaks of the NMR spectra of the adjacent (no more than three bonds away) nuclei.

Cl is less electronegative than F, so there will be more electron density around H_B compared to H_A → The H_B signal will be closer to 0 than the signal for H_A



Can be $+1/2$ or $-1/2$ in a $\sim 1:1$ ratio → H_A

Can be $+1/2$ or $-1/2$ in a $\sim 1:1$ ratio ← H_B

