Chapter 14 Nuclear Magnetic Resonance Spectroscopy

Nuclear Magnetic Resonance (NMR) spectroscopy uses energy in the radiowave portion of the electromagnetic spectrum. The nuclei of atoms such as hydrogen and carbon absorb radio-frequency radiation when placed in a magnetic field.

Principle: Nuclei of atoms with an odd mass number such as ^{13}C and ^{1}H (which have a spin number of $^{1}/_{2}$) have nuclear spin. Consider a proton, for example:

| spinning proton | loop of current | bar magnet |
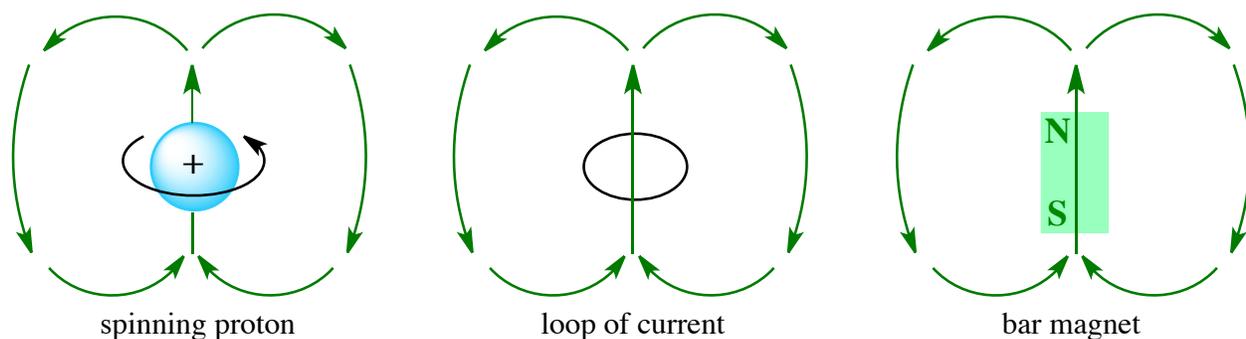
The movement of charge is like an electric current in a loop of wire. It generates a magnetic field, and resembles a small bar magnet. When placed in a magnetic field, the nuclei align themselves either *with* or *against* an applied magnetic field, **H$_o$**.

no external field

H_o *increases*

ΔE

higher energy

lower energy

H$_o$ *(applied magnetic field)*
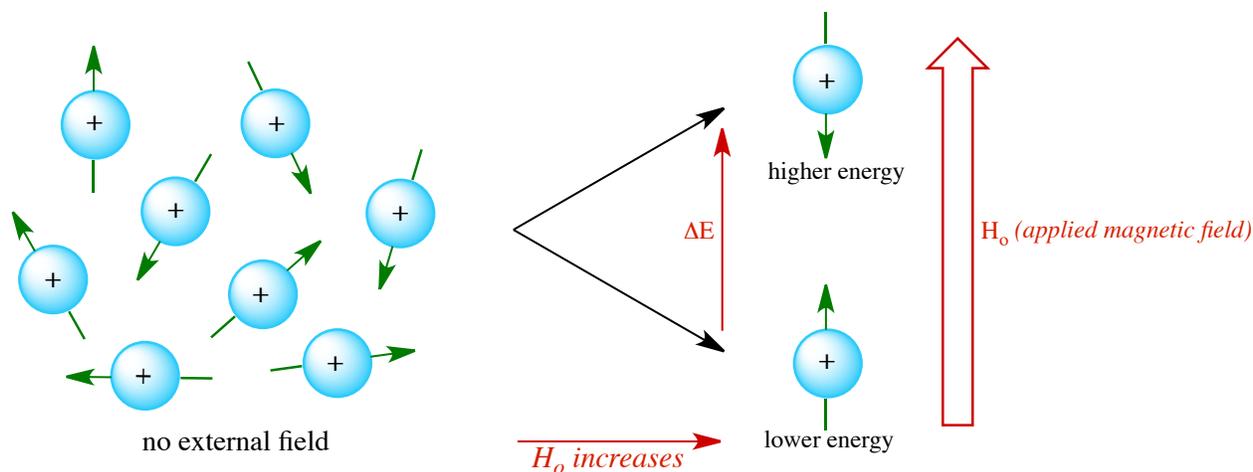
Slightly more align themselves *with* (lower energy) than *against* the magnetic field. Absorption of energy (radio frequency pulse, ν) causes more nuclei to align against the magnetic field, a higher energy state.

☞   Once the radiofrequency pulse is discontinued, the nuclei relax back to the ground state, releasing energy. The energy released is quantized, and is dependent on the environment of the nuclei.

The environment of a proton is critical in determining how it will react to an applied magnetic field. A typical proton is surrounded by electrons that partially **shield** it from the external magnetic field. This **shielding** results from the electron's ability to circulate and generate a small "induced" magnetic field that opposes the externally applied field.

An example of a ^{1}HNMR Spectrum:

H_3C—CH_2—Br

4.0	3.5	3.0	2.5	2.0	1.5	1.0	0.5	0.0 pp
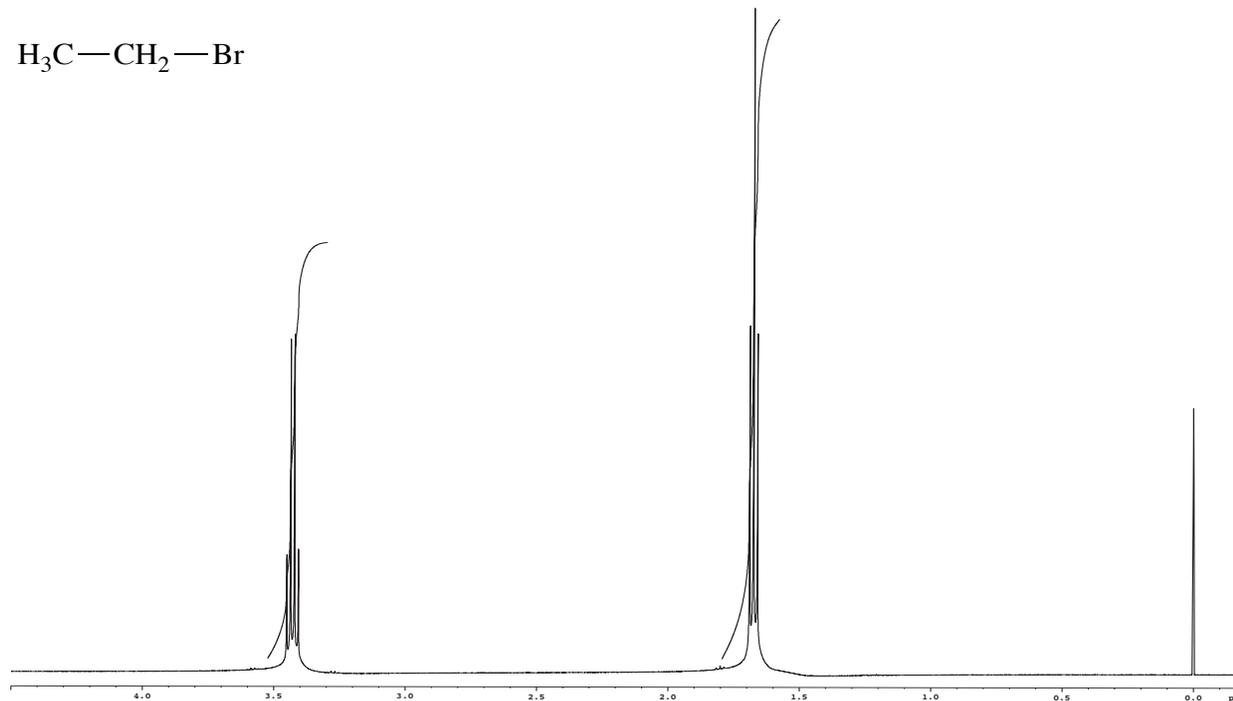
Important points:

1) The signals are called **chemical shifts** and are reported in ppm (δ). The signals are referenced to **TMS** (tetramethylsilane) which is set at 0 ppm.

$$\delta = \text{chemical shift (ppm)} = \frac{\text{distance downfield from TMS (Hz)}}{\text{operating frequency of spectrometer (MHz)}}$$

2) The protons of **TMS** are more shielded than most organic compounds, because they have a higher electron density around them.
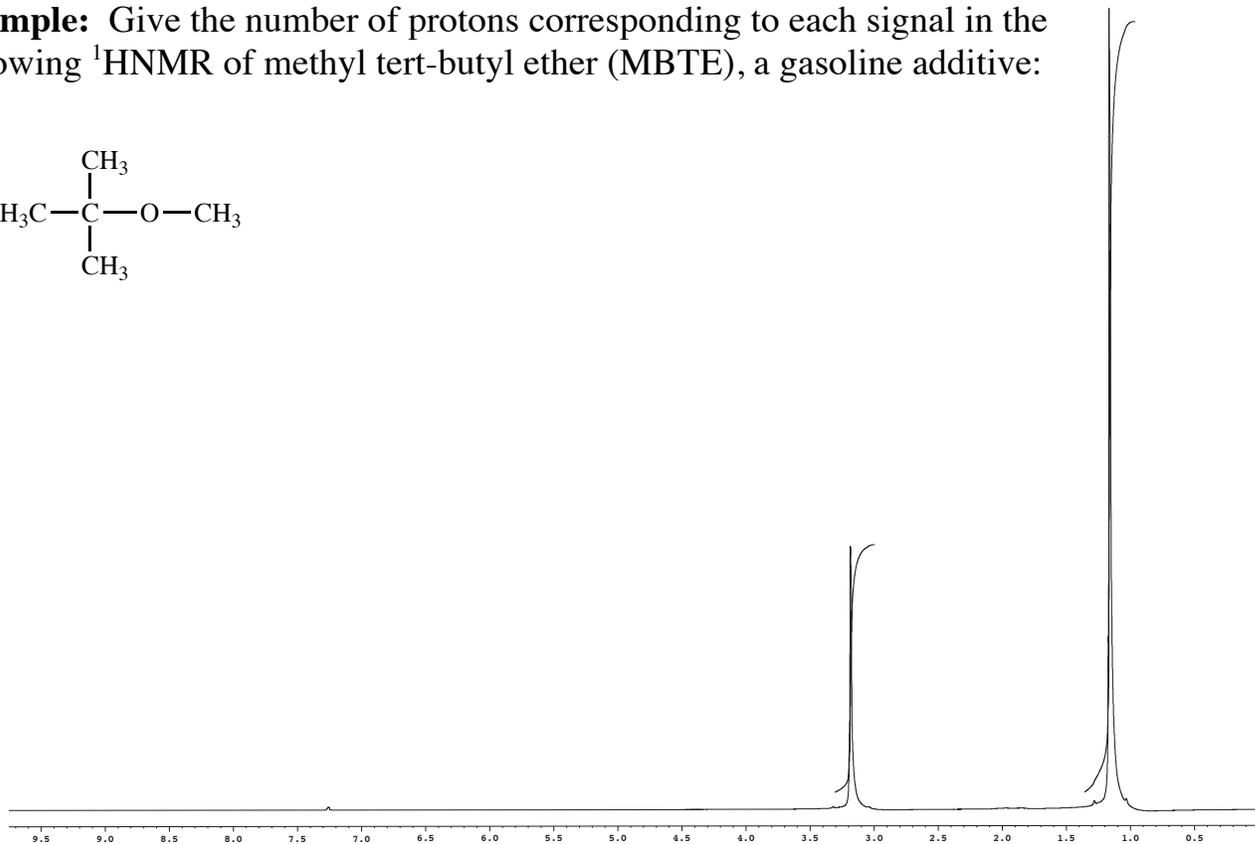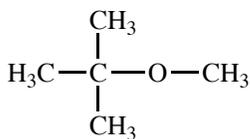
$$\text{Si}\text{—}\text{CH}_3 \qquad\qquad \textit{compare with:} \qquad\qquad \text{C}\text{—}\text{CH}_3$$
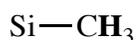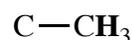
3) The terms **upfield** and **downfield** describe the relative locations of signals, Upfield means *to the right* (towards TMS), and downfield means *to the left* (away from TMS). Protons that are *shielded* are moved towards TMS (upfield), and protons that are *deshielded* are moved away from TMS.

4) The area underneath each signal is displayed in the form of a line of integration superimposed on the original spectrum. The vertical rise of the integration line over each signal is proportional to the area under that signal, which, in turn, is proportional to the number of H's giving rise to that signal. Newer NMR spectrometers automatically calculate and plot the value of each integral in arbitrary units.

Example: Give the number of protons corresponding to each signal in the following ¹HNMR of methyl tert-butyl ether (MBTE), a gasoline additive:

CH₃
|
H₃C—C—O—CH₃
|
CH₃

| 9.5 | 9.0 | 8.5 | 8.0 | 7.5 | 7.0 | 6.5 | 6.0 | 5.5 | 5.0 | 4.5 | 4.0 | 3.5 | 3.0 | 2.5 | 2.0 | 1.5 | 1.0 | 0.5 |

5) Hydrogens in identical environments *(aka: equivalent hydrogens)* give the same ¹HNMR signal.

Examples:

CH₃
|
H₃C—C—CH₂—CH₃
|
H

Cl   H
  \\   /
   C=C
  /   \\
 H   H

H   Cl
| H |
⌐◢◣⌐
| ◥◤ |
H | H
   H

174
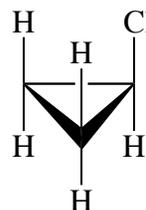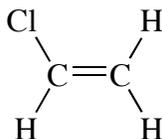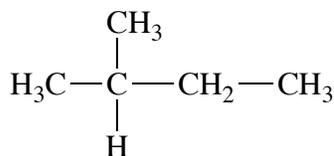
Q. **How does the structure of a compound affect peak position (*chemical shift*)?**

$$\overset{\displaystyle O}{\underset{\displaystyle |}{\overset{\displaystyle \|}{C}}} - \overset{|}{C} - \mathbf{H} \quad \blacksquare$$
2.1–2.6

$$Ph - \overset{|}{C} - \mathbf{H}$$
2.3–2.9

$$\underset{}{\overset{}{C}} = \overset{}{C} \quad \mathbf{H} \ \blacksquare\!\!\!\blacksquare$$
4.5–6.0

$$\overset{O}{\overset{\|}{C}} - \mathbf{H} \ \blacksquare\!\!\!\blacksquare$$
9–10

$$C = \overset{|}{C} - \mathbf{H} \quad \blacksquare$$
1.6–2.8

$$Ph - \mathbf{H} \quad \blacksquare\!\!\!\blacksquare$$
6.5–8.0

$$-O - \overset{|}{C} - \mathbf{H} \quad \blacksquare$$
3.2–4.2

$$-\overset{|}{C} - \mathbf{H} \quad \blacksquare$$
0.7–1.7

$$-C \equiv C - \mathbf{H} \quad \blacksquare$$
2.5

$$\delta \ (\text{ppm})$$

| 11 | 10 | 9 | 8 | 7 | 6 | 5 | 4 | 3 | 2 | 1 | 0 |

Protons bonded to oxygen:

$$\overset{O}{\overset{\|}{C}} - O - \mathbf{H} \ \approx 10 - 13$$

$$R - O - \mathbf{H} \ \approx 1 - 4$$
$$\approx 4 - 6 \text{ in DMSO}$$

$$Ph - O - \mathbf{H} \ \approx 4 - 8$$

$$\approx 5 - 12 \text{ (w/ intramolecular hydrogen bond)}$$

$$I - \overset{|}{C} - \mathbf{H} \quad \blacksquare\!\!\!\blacksquare$$
2.2–4.2

$$Br - \overset{|}{C} - \mathbf{H} \quad \blacksquare$$
2.7–4.2

$$Cl - \overset{|}{C} - \mathbf{H} \quad \blacksquare$$
3.3–4.2

$$-N - \overset{|}{C} - \mathbf{H} \quad \blacksquare$$
2.3–3.0
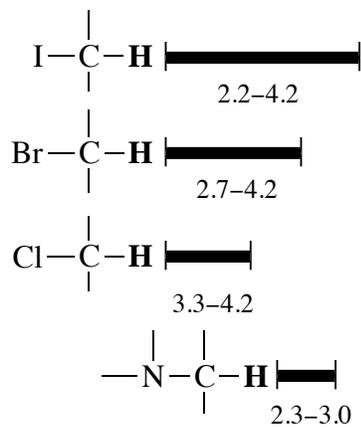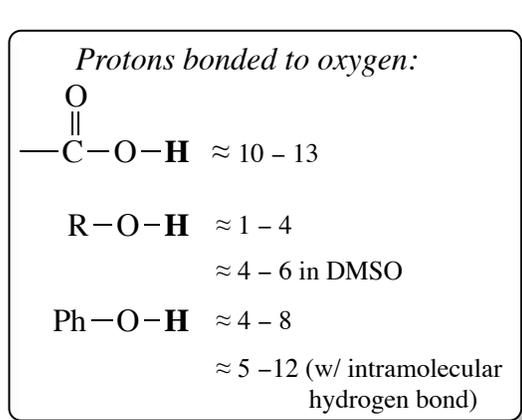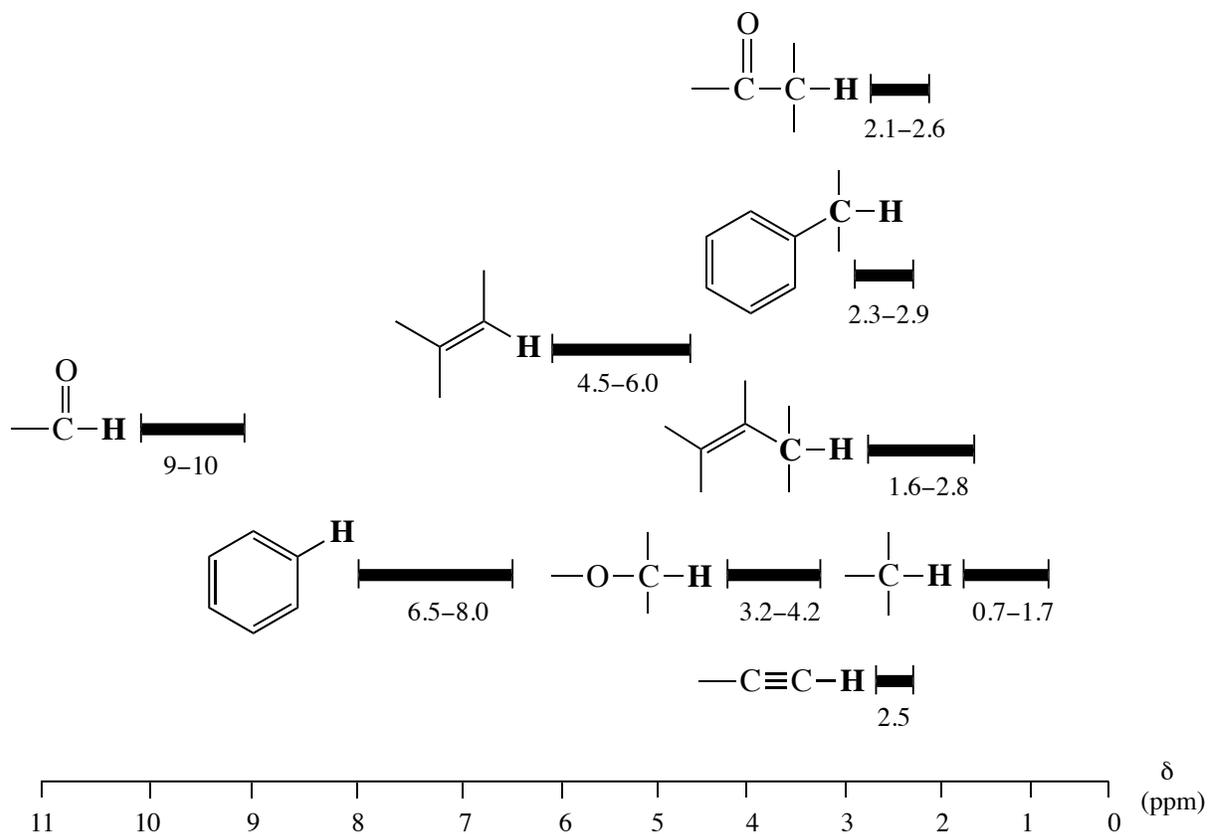
1. The electron density of substituents in a compound affects peak position.

a) Electronegative substituents shift things **downfield**. They are **deshielding**.

CH_3I	CH_3Br	CH_3Cl	CH_3F
δ 2.16	δ 2.68	δ 3.05	δ 4.26

b) There is a rapid falloff with distance *(as the electronegative group gets farther away, the deshielding affect rapidly decreases.)*

$$RO-CH_3 \qquad\qquad RO-CH_2CH_3$$

$$\text{δ 3.3} \qquad\qquad\qquad \text{δ 1.58}$$

c) Each additional electronegative group increases the chemical shift by a predictable increment:

CH_3Cl	CH_2Cl_2	$CHCl_3$
δ 3.1	δ 5.3	δ 7.3

d) In a similar environment, the signal for methyl protons (–CH_3) occurs at a lower frequency than the signal for methylene protons (–CH_2–), which in turn occurs at a lower frequency than the signal for a methine proton (–CH–):

$$\begin{array}{c} CH_3 \\ | \\ H_3C-C-CH_2-CH_3 \\ | \\ H \end{array}$$