Class schedule for the next four days

◆ **Today: NMR theory**

    How it works, why it works

◆ **^{1}H NMR**

    Integration

    Spin-spin splitting theory

◆ **^{13}C NMR**

    How it works, what it does

◆ **DEPT and COSY experiments**

    Getting extra information

◆ **Interpretation of NMR spectra**

Nuclear Magnetic Resonance (NMR) spectroscopy

◆ **A spectroscopic technique that gives us information about the number and types of atoms in a molecule:**

    hydrogen using ^{1}H-NMR spectroscopy

    carbon using ^{13}C-NMR spectroscopy

    phosphorus using ^{31}P-NMR spectroscopy

    silicon using ^{29}Si-NMR spectroscopy

    ^{19}F, ^{119}Sn, ^{195}Pt, ...

Nuclear Spin States

◆ **Any atomic nucleus that has an odd mass, 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.**

◆ **A nucleus with spin quantum number I has $2I + 1$ spin states. If $I = 1/2$, there are two allowed spin states.**
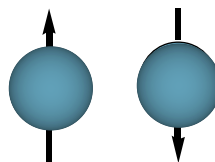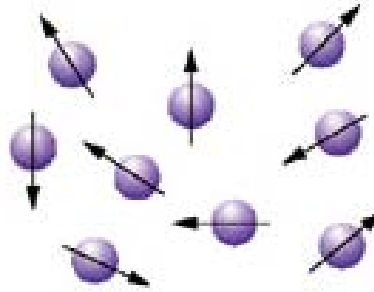

Nuclear Spin States

◆ **Spin quantum numbers and allowed nuclear spin states for selected isotopes of elements common to organic compounds**

| Element	^{1}H	^{2}H	^{12}C	^{13}C	^{14}N	^{16}O	^{31}P	^{32}S
nuclear spin quantum number (I)	1/2	1	0	1/2	1	0	1/2	0
number of spin states	2	3	1	2	3	1	2	1

Nuclear Spins in Zero Field

- ◆ Within a collection of ^1H or ^{13}C atoms, nuclear spins are completely random in *orientation*.
- ◆ The number of allowed nuclear spin *states* does not change.

Nuclear Spins in B_0

- ◆ When placed in an external magnetic field of strength B_0, only certain *orientations* of nuclear magnetic moments are allowed.

B_0
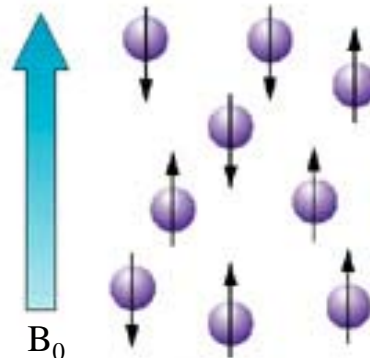
Nuclear Magnetic Resonance

- ◆ **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.**
- ◆ **If a nucleus is irradiated with electromagnetic radiation of the appropriate energy,**
  - **the 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).**

Nuclear Magnetic Resonance

- ◆ **Resonance: the absorption of electromagnetic radiation by a nucleus and the flip of its nuclear spin from a lower energy state to a higher energy state.**

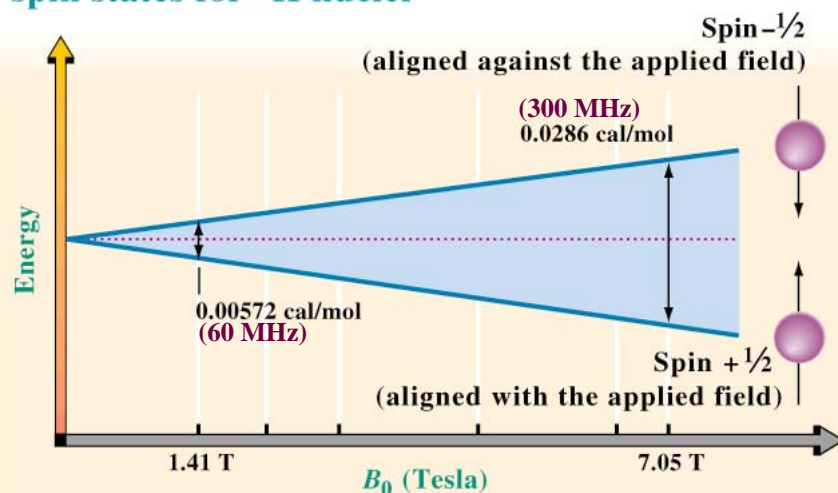- ◆ **The instrument detects this and records it as a signal.**

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.**

◆ **Deuterated solvents are used to eliminate ^{1}H signals from the solvent.**

NMR Spectrometer

5
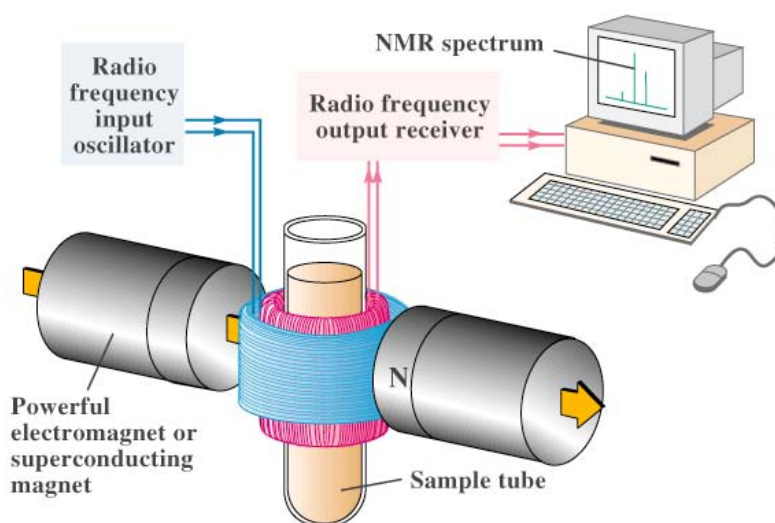
Nuclear Spins in B_0

Energy difference between allowed nuclear spin states for ^1H nuclei

Spin $-\frac{1}{2}$
(aligned against the applied field)

(300 MHz)
0.0286 cal/mol

Energy

0.00572 cal/mol
(60 MHz)

Spin $+\frac{1}{2}$
(aligned with the applied field)

1.41 T   7.05 T

B_0 (Tesla)

Nuclear Spins in B_0

◆ **In an applied field strength of 1.41T, which is the strength of the electromagnet in our NMR spectrometer, the difference in energy between nuclear spin states for**

> ^1H **is approximately 0.00572 cal/mol, which corresponds to electromagnetic radiation of 60 MHz (60,000,000 Hz).**

> ^{13}C **is approximately 0.00143 cal/mol, which corresponds to electromagnetic radiation of 15 MHz (15,000,000 Hz).**

Nuclear Spins in B_0

◆ **In an applied field strength of 7.05T, which is readily available with present-day superconducting electromagnets, the difference in energy between nuclear spin states for**

> **^{1}H is approximately 0.0286 cal/mol, which corresponds to electromagnetic radiation of 300 MHz (300,000,000 Hz).**

> **^{13}C is approximately 0.00715 cal/mol, which corresponds to electromagnetic radiation of 75 MHz (75,000,000 Hz).**
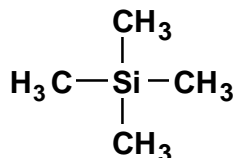
Chemical Shift

◆ **If we were dealing with nuclei isolated from other atoms and electrons, any combination of applied field and radiation that produces a signal for one nucleus would produce a signal for all identical nucleii.**

◆ **Hydrogen or carbon nucleii in organic molecules are not isolated from other atoms; they are surrounded by electrons, which are caused to circulate by the presence of the applied field.**

Chemical Shift

◆ 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.

◆ The difference in resonance frequencies among the various hydrogen or carbon nuclei within a molecule due to shielding or deshielding is generally very small.

Chemical Shift

◆ It is customary to measure the resonance frequency (signal) of individual nuclei relative to the resonance frequency (signal) of a reference compound.

◆ The reference compound now universally accepted is tetramethylsilane (TMS).

$$H_3C - \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}} - CH_3$$

Tetramethylsilane (TMS)

Chemical Shift

- ◆ For a ^{1}H-NMR spectrum, signals are reported by their shift from the 12-H signal in TMS.
- ◆ For a ^{13}C-NMR spectrum, signals are reported by their shift from the 4-C signal in TMS.
- ◆ Chemical shift (δ): the shift of an NMR signal from the signal of TMS. Normally given in parts per million (ppm).

$$\delta = \frac{\text{Shift in frequency from TMS (Hz)}}{\text{Frequency of spectrometer (Hz)}}$$

Chemical Shift

- ◆ The difference in resonance frequencies for hydrogens in CH_3Cl compared to CH_3F under an applied field of 7.05T is 360 Hz, which is 1.2 parts per million (ppm) compared with the irradiating frequency.
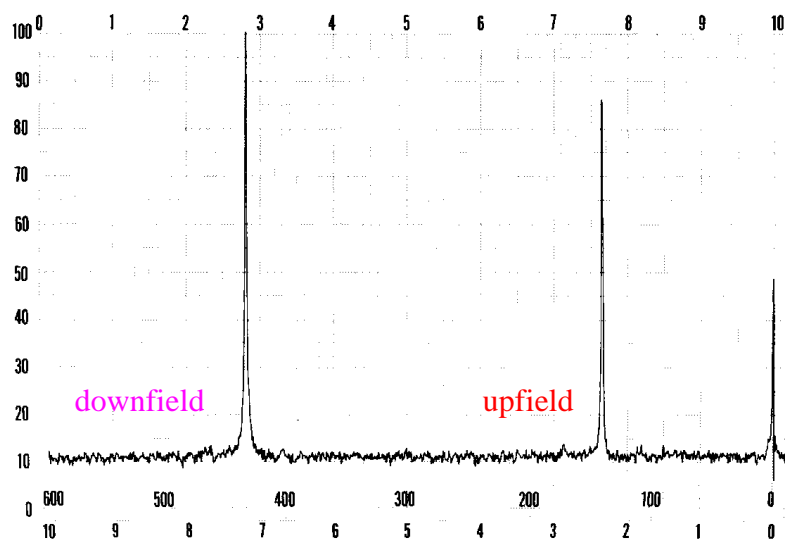
$$\frac{360 \text{ Hz}}{300 \times 10^6 \text{ Hz}} = \frac{1.2}{10^6} = 1.2 \text{ ppm}$$

- ◆ On our 60-MHz spectrometer, the difference is 72 Hz, but it is still 1.2 ppm!

NMR Spectrum

◆ **Downfield:** the shift of an NMR signal to the left on the chart paper.

◆ **Upfield:** the shift of an NMR signal to the right on the chart paper.

A 60-MHz ^{1}H-NMR Spectrum

downfield   upfield
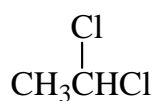
Equivalent Atoms

◆ **Equivalent atoms** have the same chemical environment and may be related by symmetry.

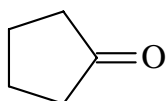◆ **Molecules with**

　　1　set of equivalent atoms give 1 NMR signal.

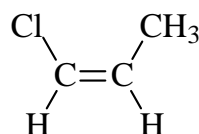　　2 or more sets of equivalent atoms give a different NMR signal for each set.

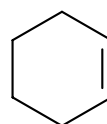Cl
|
CH_3CHCl

2 ^1H signals

2 ^{13}C signals

2 ^1H signals

3 ^{13}C signals

Cl　　　CH$_3$
　\　／
　C=C
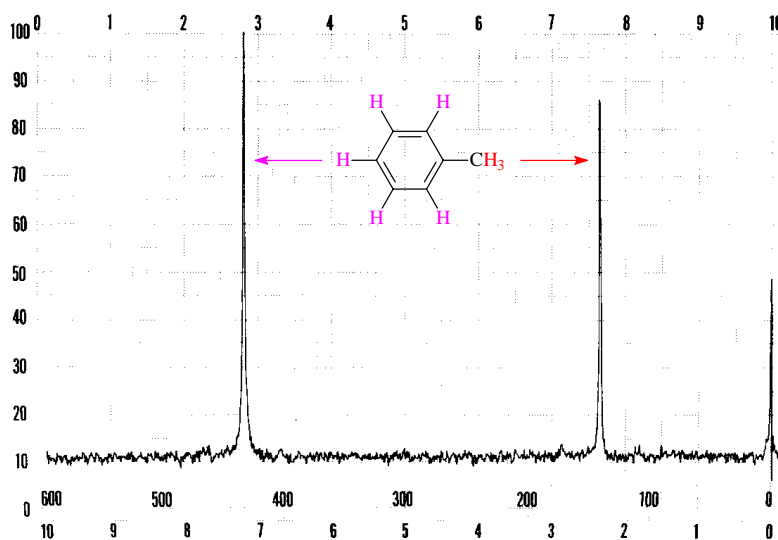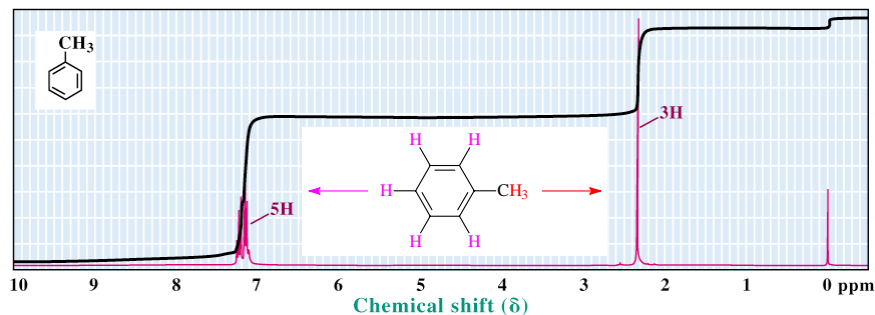　／　\
H　　　H

3 ^1H signals

3 ^{13}C signals

3 ^1H signals

3 ^{13}C signals

Accidental vs. real equivalence:
60-MHz ^1H-NMR Spectrum of toluene

11

Accidental vs. real equivalence:
300-MHz ^{1}H-NMR Spectrum of toluene

Chemical Shift

◆ **Depends on**

  electron density $\rightarrow$ **induced magnetic field**
  $\rightarrow$ shielding **and** deshielding

◆ **Electron density depends on**

  electronegativity of nearby atoms

  hybridization of nearby atoms

  magnetic induction within an adjacent π bond
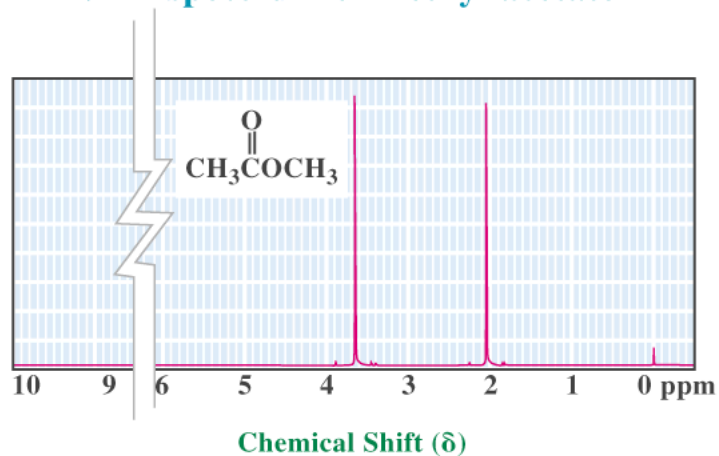
Chemical Shift:
Electronegativity effects

CH_3-X	Electroneg-ativity of X	δ of H
CH_3 F	4.0	4.26
CH_3 OH	3.5	3.47
CH_3 Cl	3.1	3.05
CH_3 Br	2.8	2.68
CH_3 I	2.5	2.16
$(CH_3)_4$ C	2.1	0.86
$(CH_3)_4$ Si	1.8	0.00 (by definition

Chemical Shift:
Hybridization effects

Type of ^{1}H	Name	Chemical shift
R-CH_2–H	methyl	0.8-1 .0
R_2CH–H	methylene	1.2-1.4
R_3C–H	methyne	1.4-1.7
RC≡C–H	acetylenic	2.0-3.0
R_2C=CR–H	vinylic	4.5-6.0
Ar–H	aromatic	6.5-8.0

^{1}H-NMR spectrum of methyl acetate

$$CH_3COCH_3$$

Chemical Shift (δ)

Chemical Shift: adjacent π bonds

CH$_3$-X	^{13}C chemical shift
CH$_3$-C$_6$H$_{13}$	14.0
CH$_3$-Ph	20.9
CH$_3$-CH=CH-Ph	16.6
CH$_3$-C≡N	2.0

Chemical Shift

◆ **Magnetic induction in pi bonds of a**
  carbon-carbon triple bond shields an acetylenic
  hydrogen and shifts its signal upfield (to the
  right) to a smaller δ value.

Magnetic field induced in the pi bonds of
a carbon-carbon triple bond
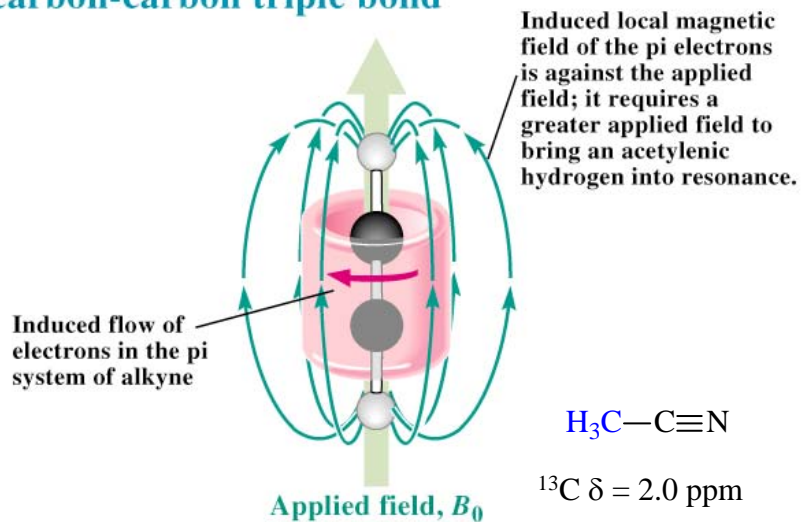
Induced local magnetic
field of the pi electrons
is against the applied
field; it requires a
greater applied field to
bring an acetylenic
hydrogen into resonance.

Induced flow of
electrons in the pi
system of alkyne

H_3C—$C{\equiv}N$

^{13}C δ = 2.0 ppm

Applied field, B_0

Chemical Shift

◆ **Magnetic induction in pi bonds of a**

> carbon-carbon triple bond shields an acetylenic hydrogen and shifts its signal upfield (to the right) to a smaller δ value.

carbon-carbon double bond deshields vinylic hydrogens and shifts their signal downfield (to the left) to a larger δ value.

Magnetic field induced in the pi bond of a carbon-carbon double bond

Induced circulation of pi electrons in the alkene

Induced local magnetic field of the pi electrons reinforces the applied field and provides part of the field necessary to bring a vinyl hydrogen into resonance.

$^{13}C \; \delta = 24.0 \text{ ppm}$

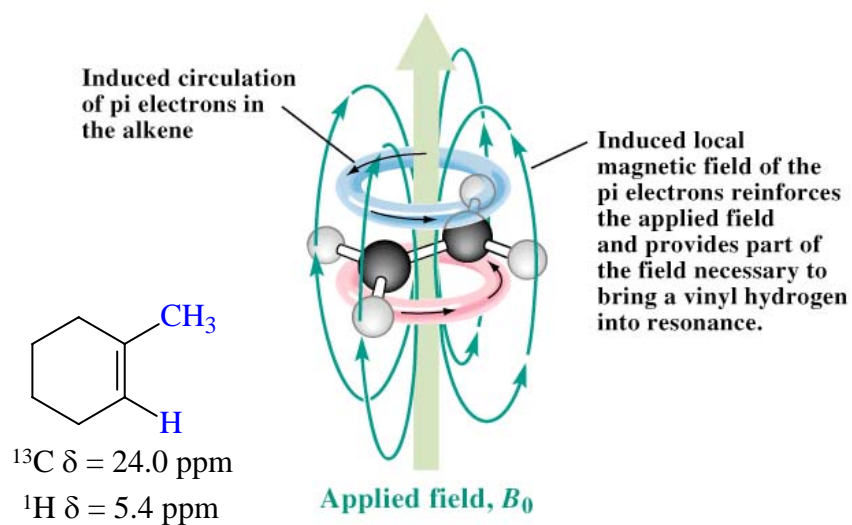$^{1}H \; \delta = 5.4 \text{ ppm}$

Applied field, B_0

Chemical Shift

◆ **Magnetic induction in pi bonds of a(n)**

carbon-carbon triple bond shields an acetylenic hydrogen and shifts its signal upfield (to the right) to a smaller δ value.

carbon-carbon double bond deshields vinylic hydrogens and shifts their signal downfield (to the left) to a larger δ value.

aromatic ring deshields aromatic hydrogens and shifts their signal downfield (to the left) to a yet larger δ value. This extra inductive effect is known as the ring current and is seen in a wide variety of aromatic rings.

Ring Current in aromatics

^{13}C δ = 21.4 ppm

^1H δ = 7.1 ppm