# Chemistry 4631

## Instrumental Analysis

## Lecture 12

# Nuclear Magnetic Resonance Spectroscopy (NMR)

History

W. Pauli – 1924 – atomic nuclei have properties of spin and magnetic moment and exposure to magnetic field would split energy levels.

Bloch and Purcell – 1946 – demonstrated nuclei absorb electromagnetic radiation in a strong magnetic field with energy level splitting. (1952 – Nobel Prize)

1953 – 1st high resolution NMR spectrometer – Varian

Pre 1970’s – continuous wave (CW) NMR

Post 1970’s – fourier transform (FT) NMR

# Nuclear Magnetic Resonance Spectroscopy (NMR)

NMR measures absorption of electromagnetic radiation by atomic nuclei in the radio frequency region of 4 - 900 MHz.

For absorption to occur the analyte is placed in an intense magnetic field.

Nuclei of atoms rather than outer electrons are involved in the absorption process.

# NMR

## Quantum Theory

Nuclei rotate about an axis and have a spin with angular momentum, p.

In many atoms (such as $^{12}C$) these spins are paired against each other, such that the nucleus of the atom has no overall spin. However, in some atoms (such as $^{1}H$ and $^{13}C$) the nucleus does possess an overall spin.

The angular momentum is quantized and must be an integral or half-integral multiple of $h/2\pi$

(h – Planck's constant).

# NMR

## Quantum Theory

The rules for determining the net spin of a nucleus are as follows;

1. If the number of neutrons and the number of protons are both even, then the nucleus has NO spin.
2. If the number of neutrons plus the number of protons is odd, then the nucleus has a half-integer spin (i.e. 1/2, 3/2, 5/2)
3. If the number of neutrons and the number of protons are both odd, then the nucleus has an integer spin (i.e. 1, 2, 3)

# NMR

Quantum Theory

Maximum number of values for p is the spin quantum number, I.

The nucleus has 2I + 1 discrete states.

In absence of an external field, the various states have identical energies.

Each nucleus has 2 spin states:

I = +1/2 and I = -1/2

Magnetic quantum states, m

m = I, I-1, I-2, …, -I

If I = ½, m = -1/2, +1/2 I = 1, m = -1, 0, 1

# NMR

| Mass # | atomic number | spin# |
|---|---|---|
| Odd | even or odd | ½, 3/2, 5/2, … |
| Even | even | 0 |
| Even | odd | 1, 2, 3 |

I = 0 (non-spinning nuclei) $^{12}C$ $^{16}O$

I = ½ (spherical spinning charges) $^{1}H$ $^{13}C$ $^{19}F$ $^{31}P$

I > ½ (nonspherical spinning charges) have both magnetic moment and quadrupole

I = 1 $^{2}H$ $^{14}N$ I = 3/2 $^{11}B$ $^{35}Cl$ $^{37}Cl$ $^{79}Br$

I = 2 $^{36}Cl$ $^{58}Co$ I = 5/2 $^{25}Mg$ $^{27}Al$

# NMR

## Quantum Theory

The nuclei of greatest use in NMR are $^{1}H$, $^{13}C$, $^{19}F$, and $^{31}P$.

A spinning, charged nucleus creates a magnetic field.

$$\mu = \gamma p \qquad \text{(Larmor equation)}$$

$\mu$ – magnetic moment

$p$ – angular moment

$\gamma$ – proportionality constant called the magnetogyric ratio (value differs with type of nucleus)

# NMR

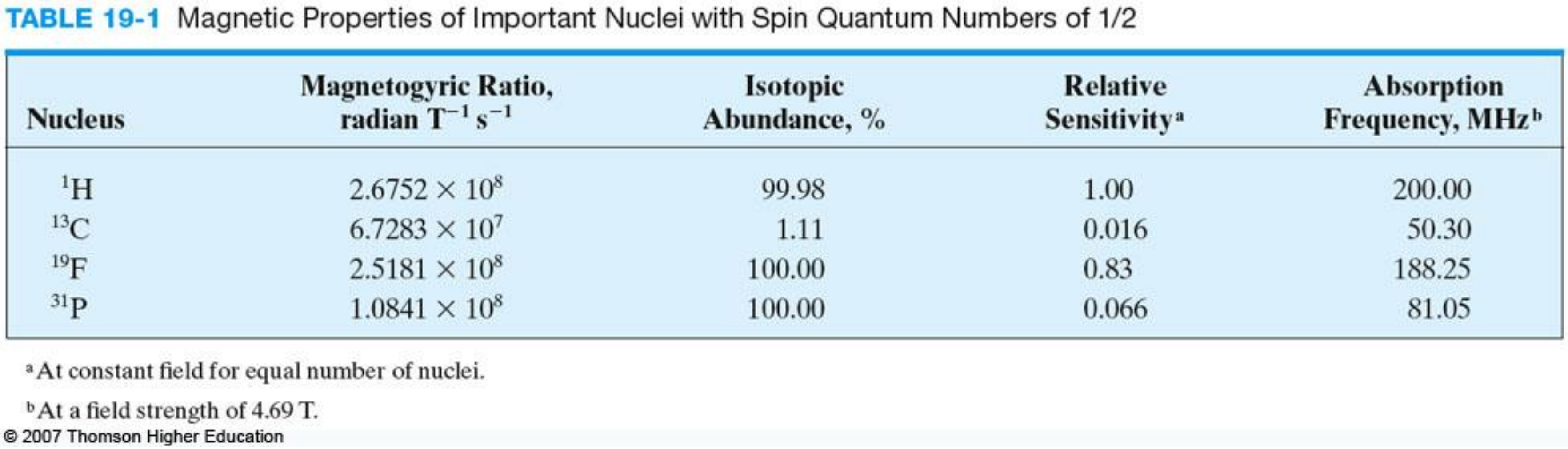


**TABLE 19-1** Magnetic Properties of Important Nuclei with Spin Quantum Numbers of 1/2

| Nucleus | Magnetogyric Ratio, radian $T^{-1}$ $s^{-1}$ | Isotopic Abundance, % | Relative Sensitivity[a] | Absorption Frequency, MHz[b] |
|---|---|---|---|---|
| $^{1}H$ | $2.6752 \times 10^{8}$ | 99.98 | 1.00 | 200.00 |
| $^{13}C$ | $6.7283 \times 10^{7}$ | 1.11 | 0.016 | 50.30 |
| $^{19}F$ | $2.5181 \times 10^{8}$ | 100.00 | 0.83 | 188.25 |
| $^{31}P$ | $1.0841 \times 10^{8}$ | 100.00 | 0.066 | 81.05 |

[a] At constant field for equal number of nuclei.

[b] At a field strength of 4.69 T.

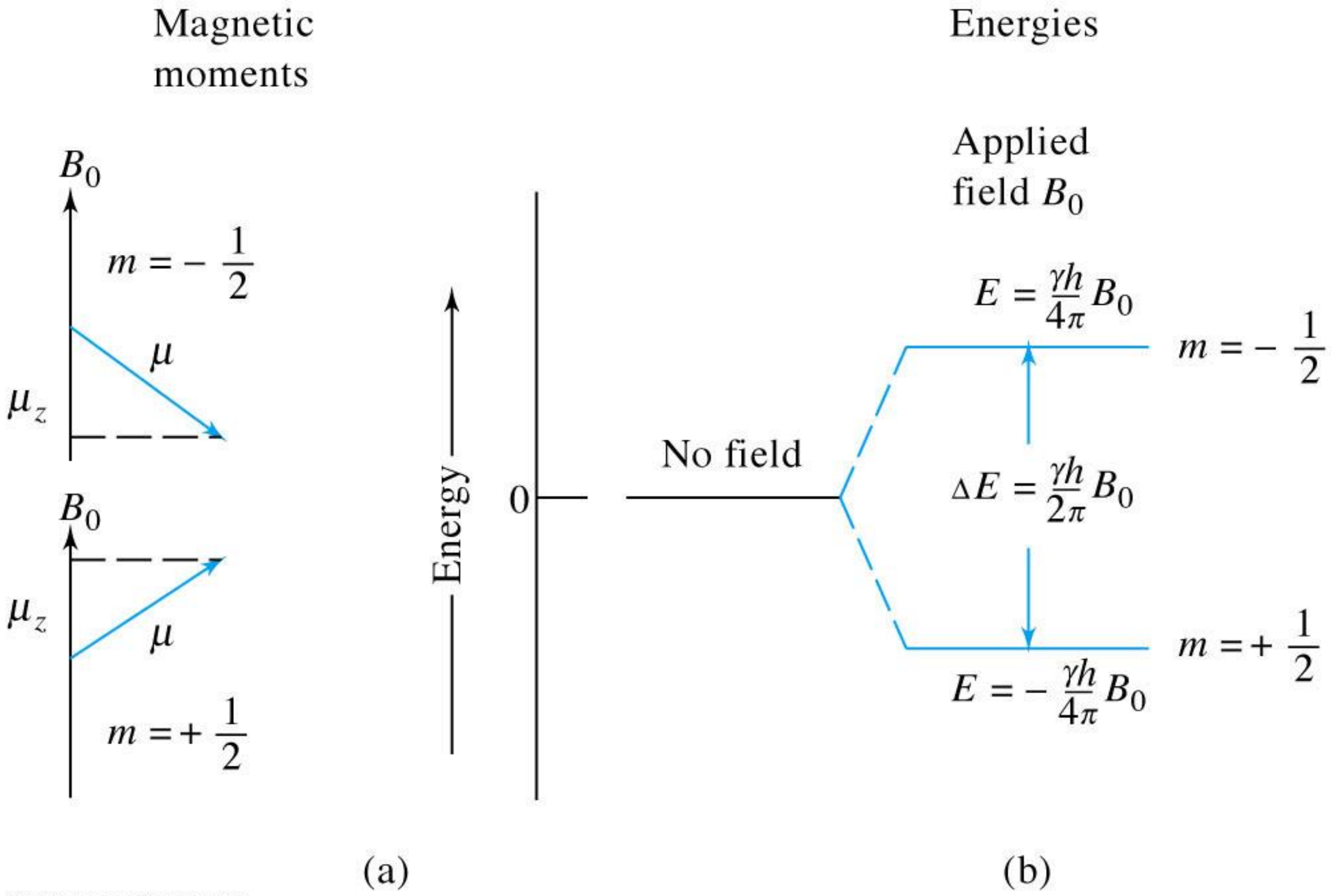
# NMR

## Energy Levels

When a nucleus with a spin of ½ is exposed to a magnetic field, $B_o$, the magnetic moment becomes oriented in one or two directions with respect to the field.

# NMR

## Energy Levels



# NMR

**Energy Levels**

**Potential energy, E, of a nucleus is given by:**

$$E = -(\gamma\ m\ h)\ /\ (2\ \pi)\quad Bo$$

**Transition between energy states can be brought about by absorption or emission of radiation of a frequency, $v_o$.**

$$v_o = (\gamma\ B_o) /\ (2\ \pi)$$

# NMR

## Energy Levels

In the absence of magnetic fields, the energy of the magnetic quantum states of a nucleus are identical.

When placed in a magnetic field, the nuclei tend to orient so that the lower energy state (m = +1/2) predominates.

Just like in optical spectroscopy – transition between energy states can be brought about by absorption or emission of electromagnetic radiation.

For H (proton) absorption to occur need ~ 200 MHz.

# NMR

## Energy Levels

The relative number of excess low energy nuclei is linearly related to the magnetic field strength. (Boltzman equation)

The intensity of an NMR signal increases linearly as the field strength increases.

Therefore manufactures are always trying to produce magnets with higher field strength.

# NMR

**Energy Levels**

**Boltzman equation**

$N_j/N_o = \exp(-\Delta E/kT)$

$N_j$ - # of protons in higher energy state ($m = -1/2$)

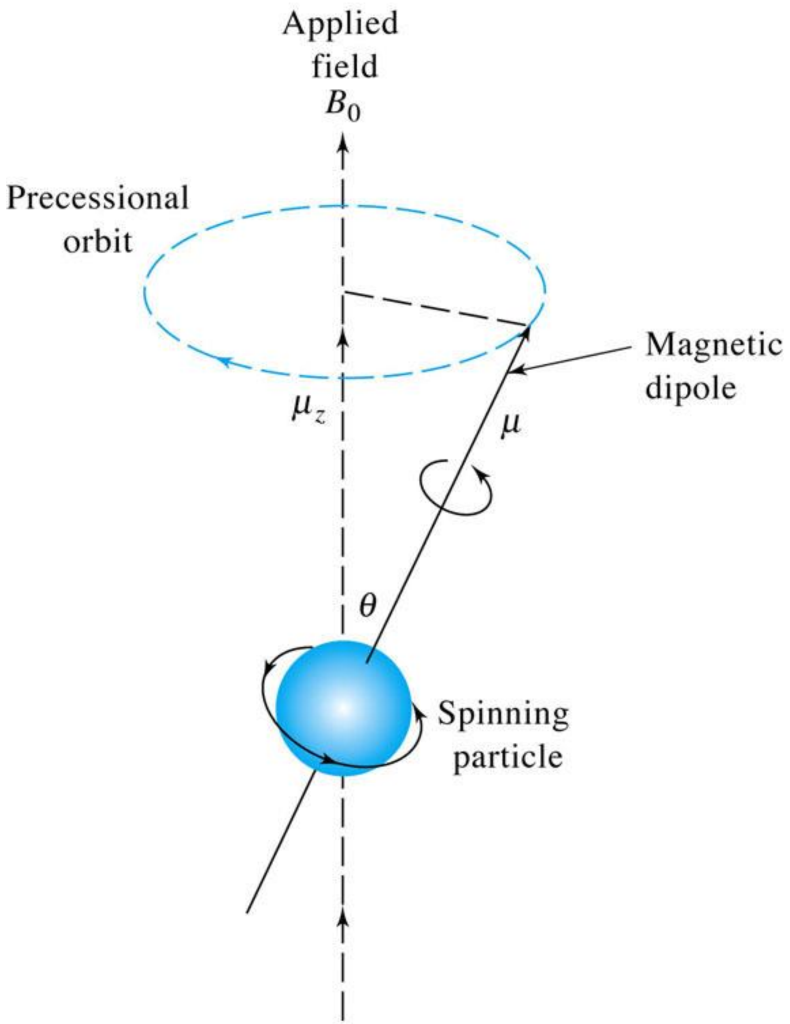
$N_o$ - # in lower energy state

k – Boltzman constant ($1.38 \times 10^{-23}$ J $K^{-1}$)

T – absolute temperature

$\Delta E$ – difference in energy between two states

# NMR


Applied field $B_0$
Precessional orbit
Magnetic dipole
$\mu_z$
$\mu$
$\theta$
Spinning particle

# NMR

Relaxation process in NMR spectrum

- Spin-lattice or longitudinal relaxation

  Energy lost in lattice, gives sharp lines.

- Spin-spin or transverse relaxation

  Energy lost by spin exchange with neighbor.

# NMR

- Relaxation process in NMR spectrum
  - Spin-lattice relaxation
    - Absorbing nuclei in an NMR experiment are part of the larger collection of atoms that make up the sample.
    - The entire collection is called the lattice.
    - The lattice field contains a continuum of magnetic components some which correspond in frequency and phase with the precessional frequency of the magnetic nuclei of interest.

# NMR

## Relaxation process in NMR spectrum

### Spin-spin relaxation

Two neighboring nuclei of identical precession rates, but different magnetic quantum states, can interact with each other to cause interchange of states.

Nucleus in lower spin state is excited while excited nucleus relaxes to lower energy state.

This shortens the average lifetime of the excited nucleus and broadens the line.

# NMR

Relaxation process in NMR spectrum

- Spin-spin relaxation
  - This spin-spin relaxation is small (10$^{-4}$ sec) and not seen except by using special techniques such as $^{13}$C NMR of solids.

# NMR

Techniques of NMR spectra

- Wide-line spectra
- High-resolution spectra

# NMR

## Techniques of NMR spectra

### Wide-line spectra

- Bandwidth is large enough to obscure fine structure due to chemical environment.
- Usually obtained at relatively low magnetic field strength.

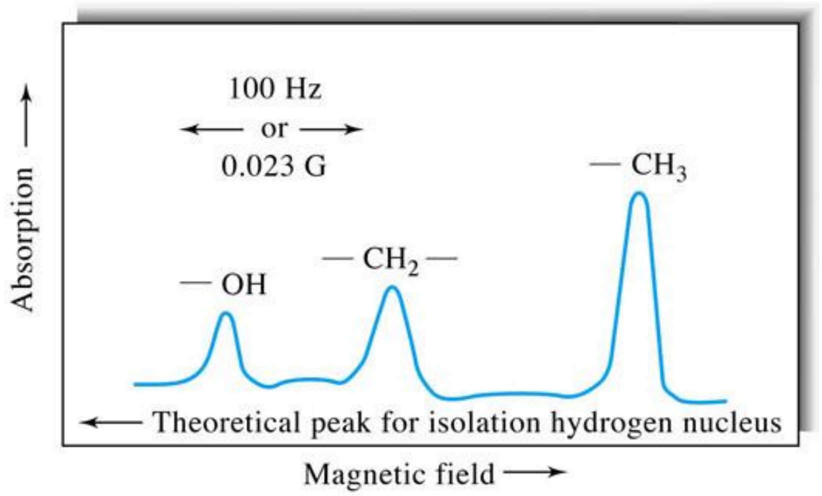
# NMR

Techniques of NMR spectra

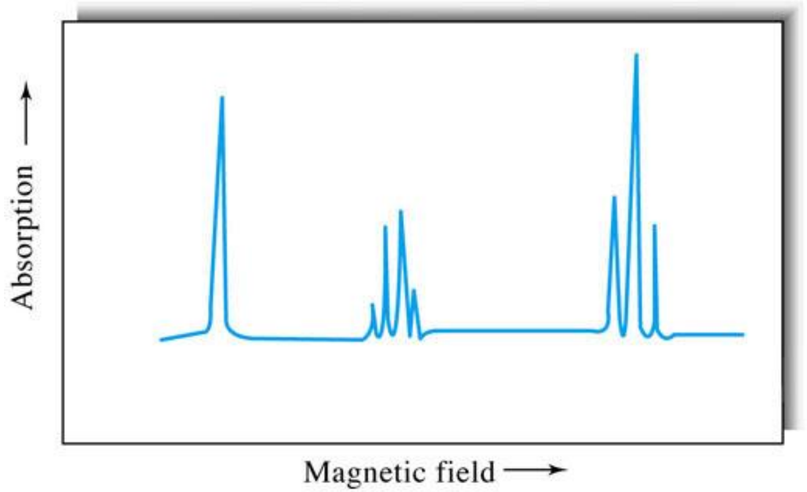
- High-resolution spectra
  - Most common.
  - Instruments can differentiate between small frequencies of 0.01 ppm or less.
  - Shows difference in chemical environments.

# NMR

(a) Low resolution



(b) High resolution



# NMR

## Environmental Effects

- Frequency of RF radiation absorbed by a nucleus is strongly affected by its chemical environment (i.e. nearby electrons and nuclei)
- This can be used to obtain spectral information on molecules.

# NMR

## Environmental effects

### Types of environmental effects

- Chemical shift
- Spin-spin splitting

# NMR

- Environmental effects
  - Chemical shift
    - Protons from different functional groups will have differences in absorption frequencies leading to a shift in the spectrum.
    - Peak separation is proportional to field strength.

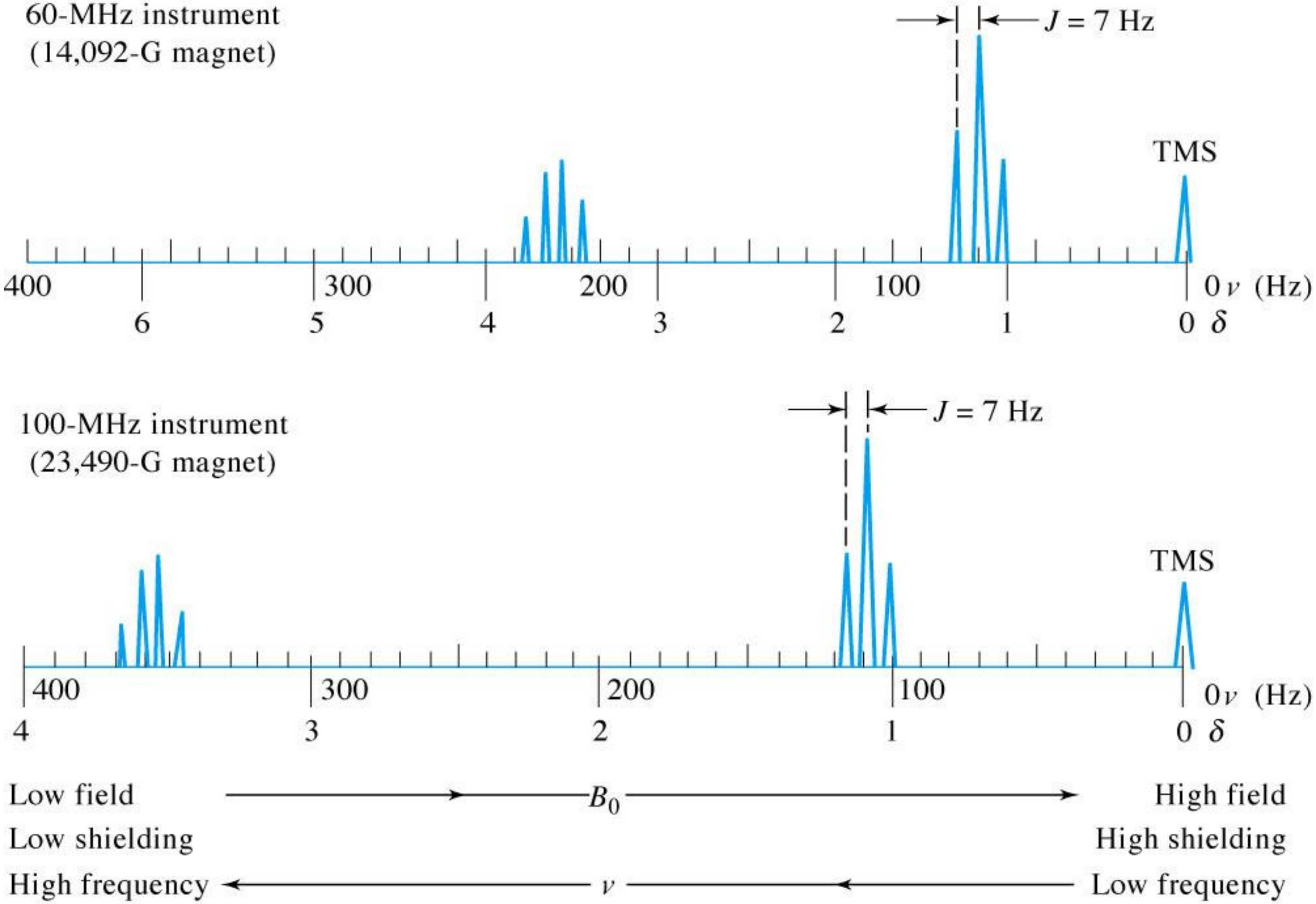
# NMR

Environmental effects

- Spin-spin splitting
  - Splitting of a peak related to the same functional group.
  - Peak separation is independent of field strength.

# NMR

## Environmental effects



# NMR

## Environmental effects

### Chemical shift

Caused by small magnetic fields generated by electrons as they oscillate around nuclei.

Usually oppose the applied field.

# NMR

**Environmental effects**

**Chemical shift**

**Magnitude of field developed internally is proportional to the applied external field.**

$$B_o = B_{appl} - \sigma B_{appl} = B_{appl}(1-\sigma)$$

$B_{appl}$ – **magnitude of applied field**

$B_o$ – **magnitude of resultant field**

$\sigma$ – **screening constant – determined by electron density and spatial distribution around the nucleus.**

# NMR

## Environmental effects

### Chemical shift

Magnitude of field developed internally is proportional to the applied external field.

$$B_o = B_{appl} - \sigma B_{appl} = B_{appl} (1-\sigma)$$

$$v_o = \gamma/2\pi B_o (1-\sigma) = k (1-\sigma)$$

$$k = \gamma B_o/2\pi$$

# NMR

## Environmental effects

### Spin-spin splitting

Splitting of chemical shift peaks occur when magnetic moment of a nucleus interacts with magnetic moment of immediate adjacent nuclei.

# Assignment

- Read Chapter 19
- HW7 Chapter 19: 2, 3, 4, and 31- 37
- HW7 Due 2/26/24
- http://teaching.shu.ac.uk/hwb/chemistry/tutorials/molspec/nmr1.htm
- http://teaching.shu.ac.uk/hwb/chemistry/tutorials/molspec/nmr2.htm
- http://teaching.shu.ac.uk/hwb/chemistry/tutorials/molspec/nmr3.htm
- http://teaching.shu.ac.uk/hwb/chemistry/tutorials/molspec/nmr4.htm