Chemistry 4631

Instrumental Analysis

Lecture 13

NMR

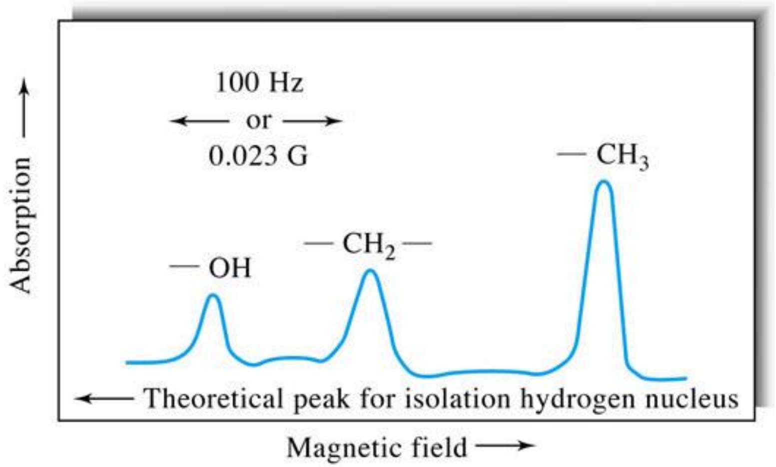
Environmental effects

Types of environmental effects

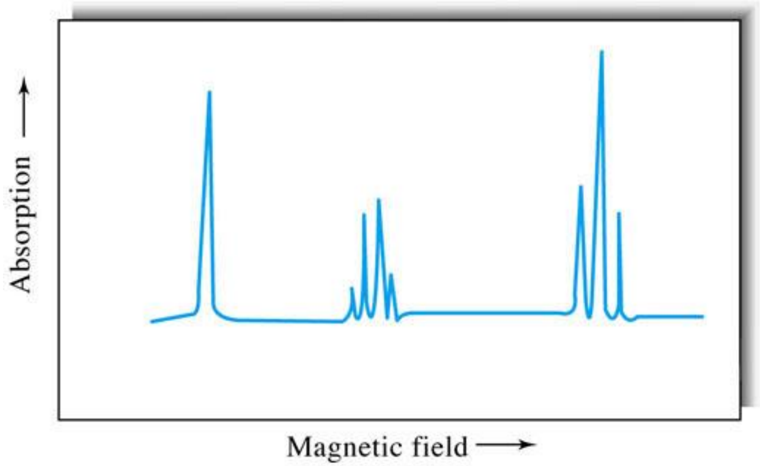
- Chemical shift
  - Differences in the absorption frequency for a proton depend on the group to which the hydrogen atom is bonded. (Ex. Ethanol – three sets of peaks)
  - Chemical shifts can be split by:
- Spin-spin splitting
  - Magnetic moment of nucleus interacts with the magnetic moment of adjacent nuclei. Gives fine structure. (Ex. Ethanol – methylene and methyl peaks split)

NMR

(a) Low resolution



(b) High resolution



NMR

Environmental effects

Chemical shift and Spin-spin splitting can be distinguished from each other since peak separations resulting from chemical shift are directly proportional to field strength or oscillator frequency, while fine-structure peaks within a group, caused by spin-spin coupling are not altered by a frequency change.

NMR

Chemical Shift parameter, δ

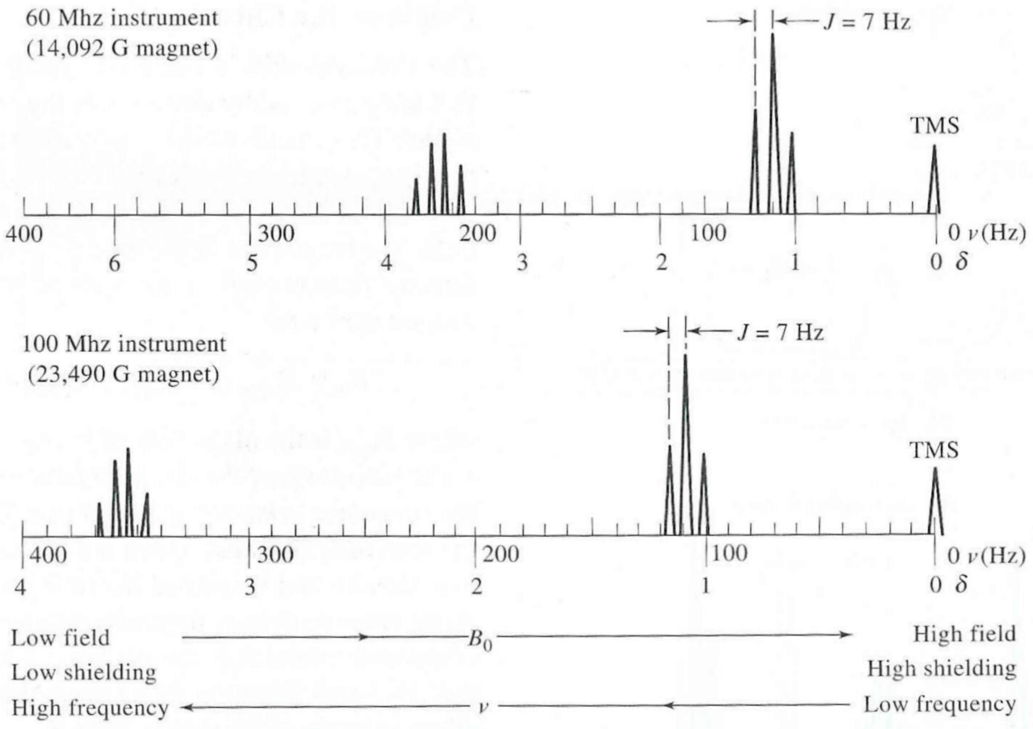


Figure 19-13 Abscissa scales for NMR spectra.

Notice δ is independent of instrumental field

NMR

- NMR plots
  - Cannot determine the absolute magnetic field strength with accuracy but can determine the magnitude of a change in field strength.
  - To do this need internal standards.
  - Most common standards
    - Tetramethysilane (TMS), $(CH_3)_4Si$
    - 2,2-dimethyl-2-silapentane-5-sulfonic acid (DSS)

      $(CH_3)_3SiCH_2CH_2CH_2SO_3Na$

      Used for aqueous solutions

NMR

- NMR plots
  - Tetramethysilane (TMS), $(CH_3)_4Si$
    - All protons are identical giving a single sharp peak in the spectrum and usually isolated from other peaks of interest.
    - Inert, soluble in most organic liquids, and can be removed by distillation.

NMR

Chemical Shift parameter, δ

$$\delta = (\sigma_{ref} - \sigma_{sample}) \times 10^{6} \text{ ppm}$$

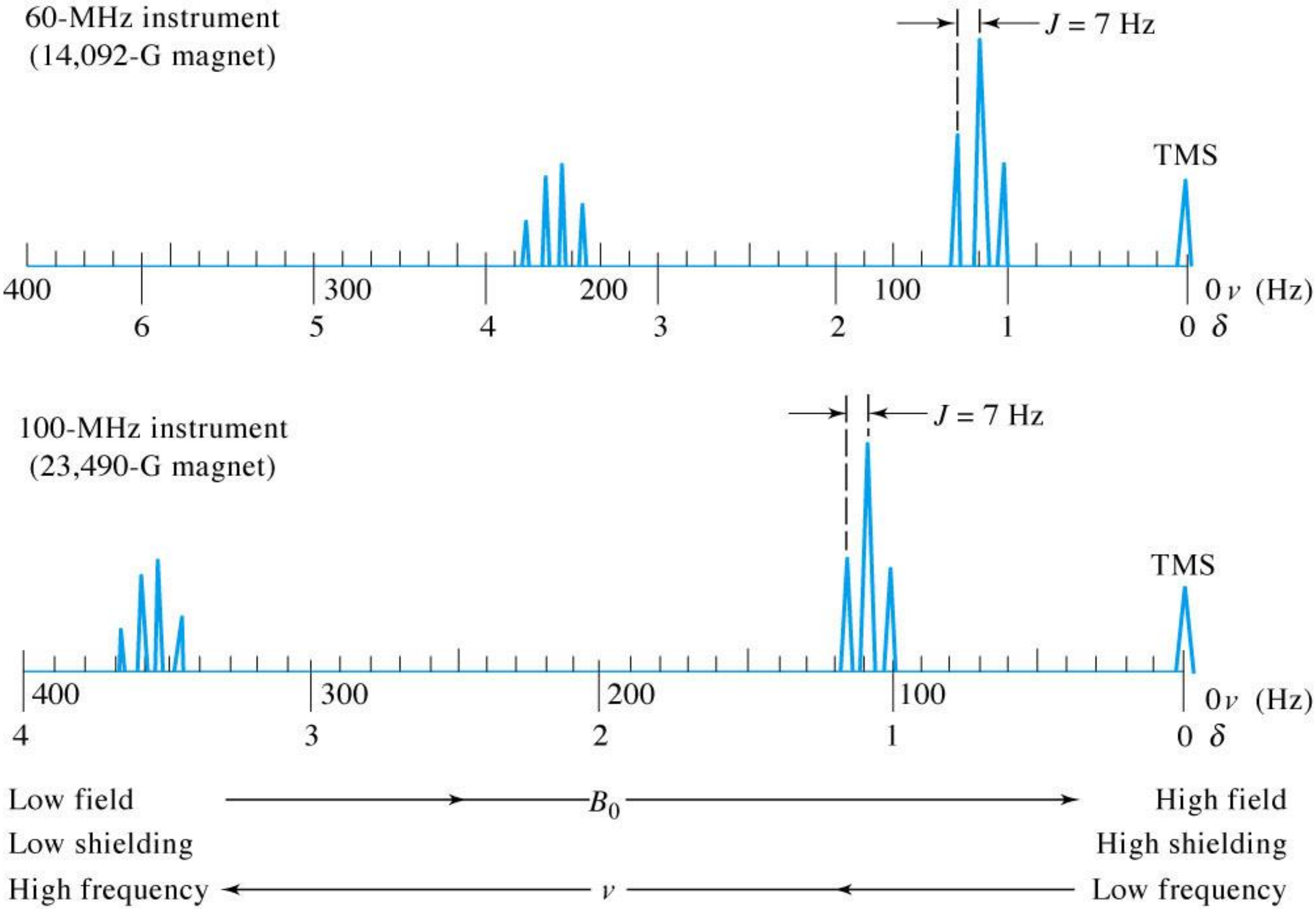
(σ – screening constant)

Most proton peaks are in the δ range of 1 -13.

Chemical shifts for 13C are in the range of 0 - 220 ppm.

(Screening constant is determined by the electron density and spatial distribution around the nucleus)

NMR


60-MHz instrument
(14,092-G magnet)
J = 7 Hz
TMS
400
300
200
100
0 ν (Hz)
6
5
4
3
2
1
0 δ
100-MHz instrument
(23,490-G magnet)
J = 7 Hz
TMS
400
300
200
100
0 ν (Hz)
4
3
2
1
0 δ
Low field
B_0
High field
Low shielding
High shielding
High frequency
ν
Low frequency

NMR

Theory of Chemical Shift

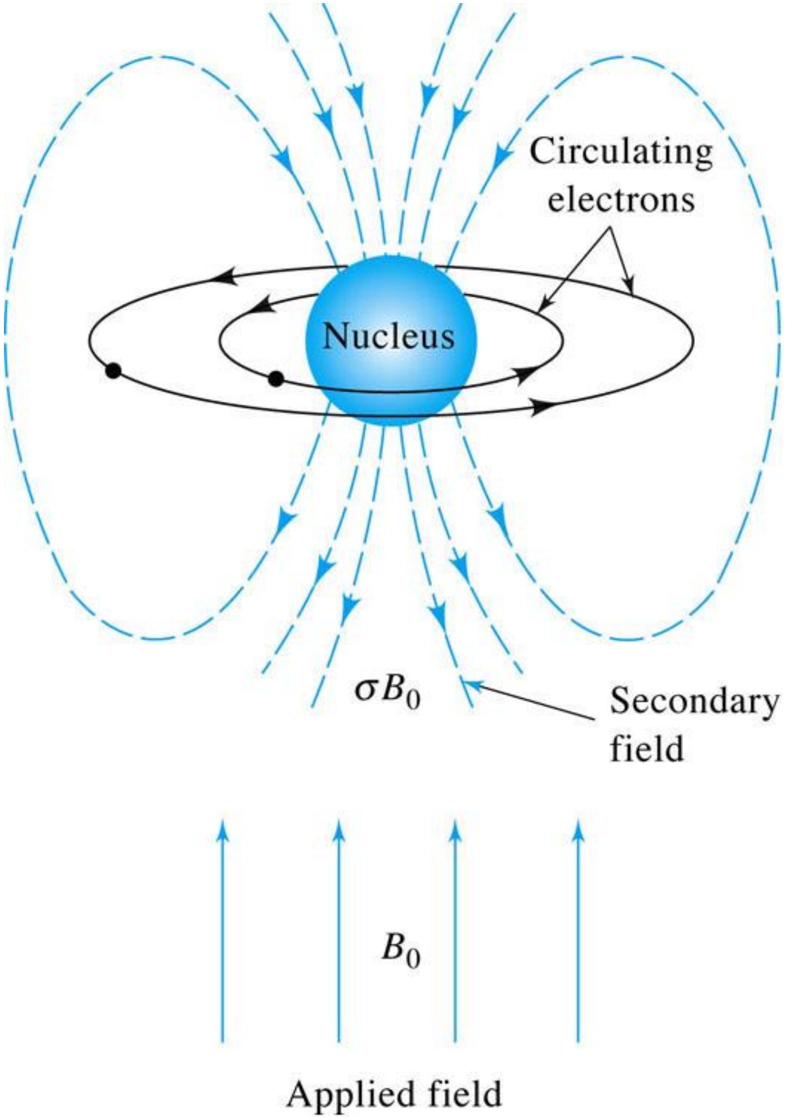
Chemical shift is used to identify functional groups by correlating structure and shift.

NMR

Theory of Chemical Shift

- Under influence of magnetic field, electrons bonding the proton tend to precess around the nucleus in a plane perpendicular to the magnetic field.
- This motion develops a secondary field, which opposes the primary field.
- Thus the external field must be increased to cause nuclear resonance.
- The shielding effect is directly related to electron density around nucleus.

NMR


Circulating electrons
Nucleus
σB_0
Secondary field
B_0
Applied field

NMR

Theory of Chemical Shift

Example CH_3X – δ values depend on shielding effect of halogen.

I - most amount of shielding (least electronegative, does not withdraw electrons from methyl protons as well).

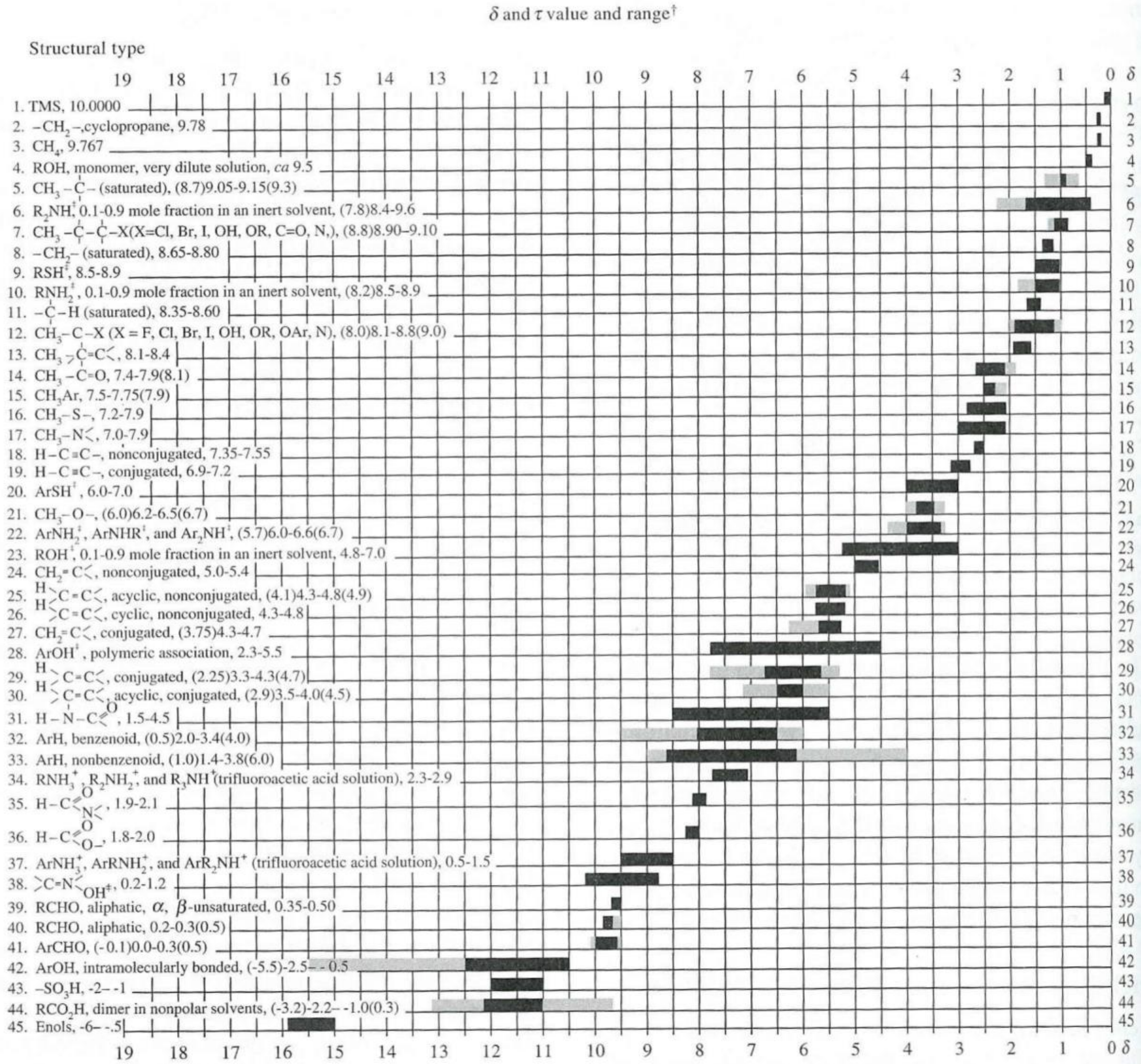
F – least amount of shielding, most electronegative.

δ = I	(2.16)
Br	(2.68)
Cl	(3.05)
F	(4.26)

NMR

Theory of Chemical Shift

Chemical shift is used to identify functional groups and help determine structure. Interpretation of NMR spectra becomes important for chemist. Many charts and tables have been published to aid in interpretation.



†Normally, absorptions for the functional groups indicated will be found within the range shown. Occasionally, a functional group will absorb outside this range. Approximate limits for this are indicated by absorption values in parentheses and by shading in the figure.

‡The absorption positions of these groups are concentration-dependent and are shifted to higher τ values in more dilute solutions.

Figure 19-17 Absorption positions of protons in various structural environments. *(Table taken from J. R. Dyer,* Applications of Absorption Spectroscopy by Organic Compounds, *p. 85. Englewood Cliffs, NJ: Prentice-Hall, 1965. With permission.)*

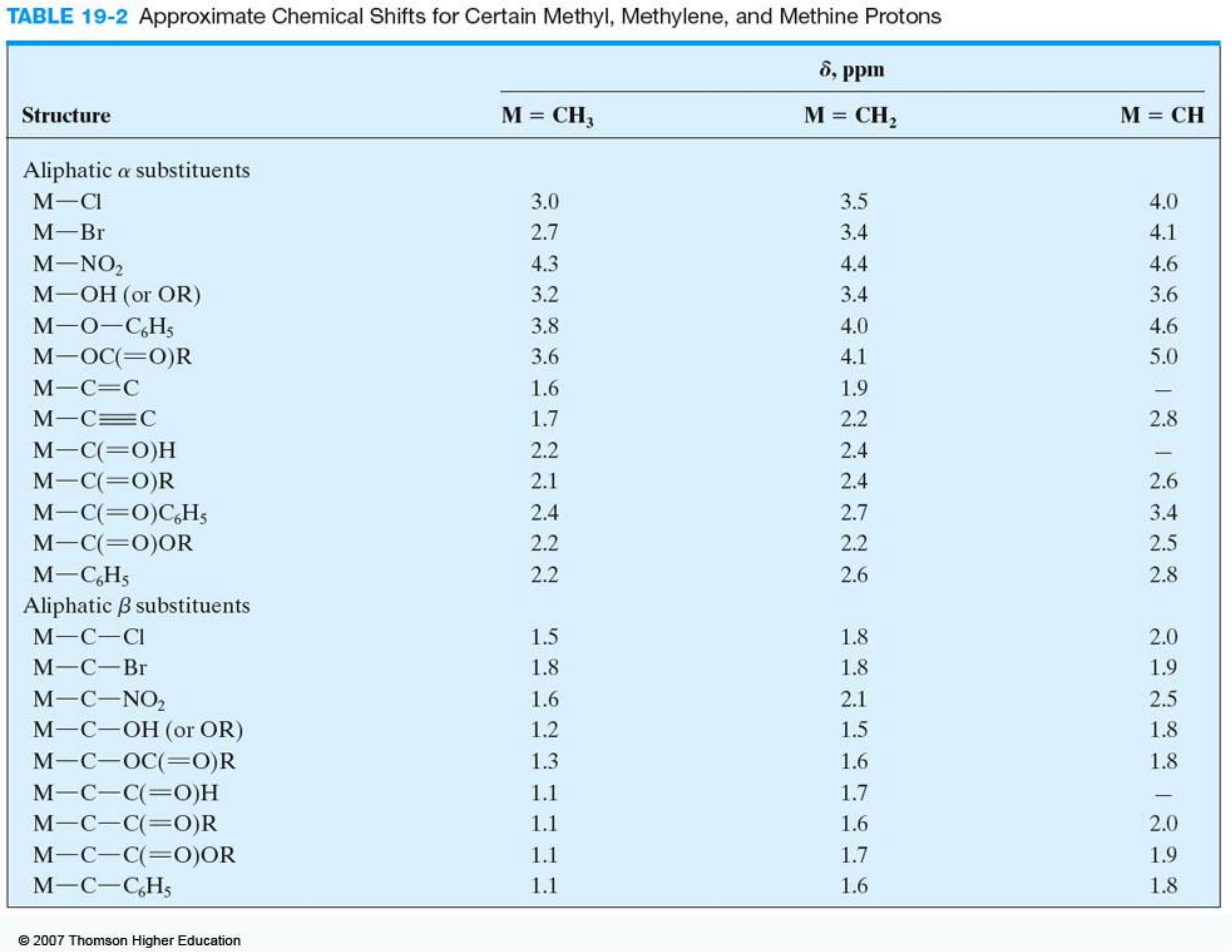


TABLE 19-2 Approximate Chemical Shifts for Certain Methyl, Methylene, and Methine Protons

Structure	δ, ppm M = CH_3	M = CH_2	M = CH
Aliphatic α substituents			
M—Cl	3.0	3.5	4.0
M—Br	2.7	3.4	4.1
M—NO_2	4.3	4.4	4.6
M—OH (or OR)	3.2	3.4	3.6
M—O—C_6H_5	3.8	4.0	4.6
M—OC(=O)R	3.6	4.1	5.0
M—C=C	1.6	1.9	—
M—C≡C	1.7	2.2	2.8
M—C(=O)H	2.2	2.4	—
M—C(=O)R	2.1	2.4	2.6
M—C(=O)C_6H_5	2.4	2.7	3.4
M—C(=O)OR	2.2	2.2	2.5
M—C_6H_5	2.2	2.6	2.8
Aliphatic β substituents			
M—C—Cl	1.5	1.8	2.0
M—C—Br	1.8	1.8	1.9
M—C—NO_2	1.6	2.1	2.5
M—C—OH (or OR)	1.2	1.5	1.8
M—C—OC(=O)R	1.3	1.6	1.8
M—C—C(=O)H	1.1	1.7	—
M—C—C(=O)R	1.1	1.6	2.0
M—C—C(=O)OR	1.1	1.7	1.9
M—C—C_6H_5	1.1	1.6	1.8

NMR

Theory of Chemical Shift

Spin-spin splitting

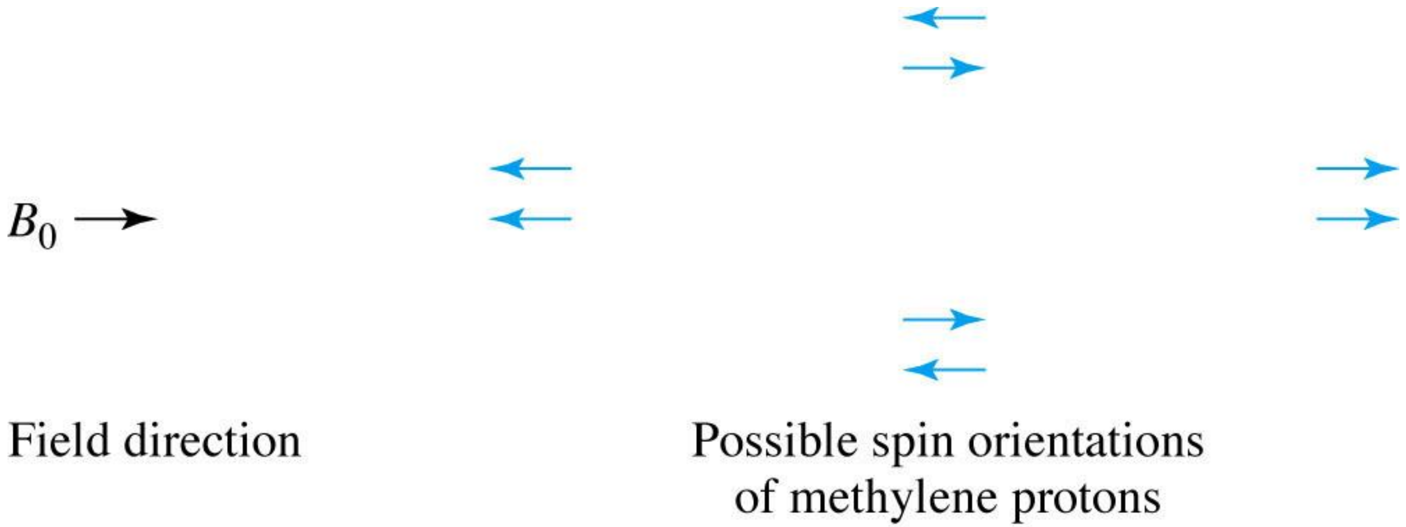
The spacing of the spin-spin splitting peaks is called the coupling constant, J, and is given in hertz. The areas of the lines for each multiplet are an integer ratio of each other.

NMR

Theory of Chemical Shift

Spin-spin splitting

Example: methylene protons in ethanol there are four possible spin orientations which affect the methyl protons to split into a triplet with the center peak twice the area of the other two.

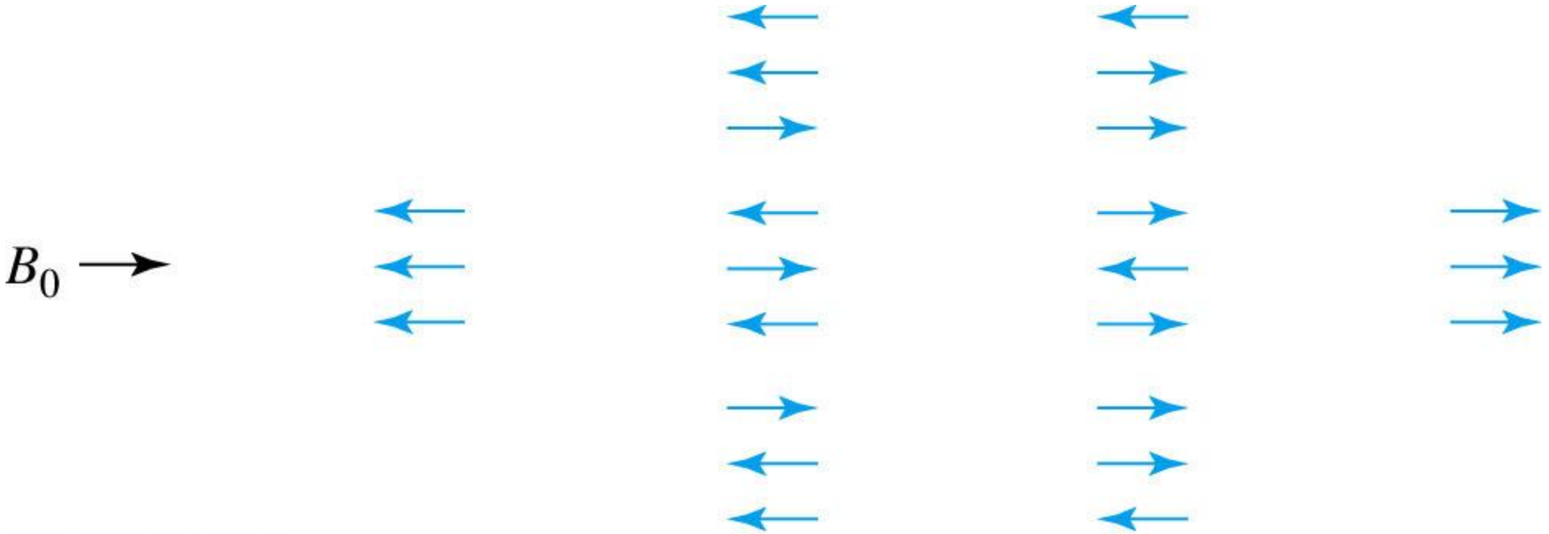


NMR

Theory of Chemical Shift

Spin-spin splitting

Example: methyl protons in ethanol there are eight possible spin orientations which affect the methylene protons to split into a quartet with the ratio of 1:3:3:1.



NMR

Theory of Chemical Shift

Spin-spin splitting

There are general rules that the number of peaks in a split band is equal to the number n of magnetically equivalent protons on adjacent atoms plus one. The number of such peaks is called multiplicity.

NMR

Theory of Chemical Shift

Spin-spin splitting

Rules for interpretation

- Coupling constants decrease with group separation and coupling is rarely observed at distances greater than four bond lengths.
- Coupling constants are independent of the applied field, can distinguish multiplets from chemical shifts by obtaining spectra at two different field strengths.

NMR

Theory of Chemical Shift

Spin-spin splitting

Rules for interpretation

- Equivalent nuclei do not interact with one another i.e. 3 protons on a methyl group do not split themselves.
- Multiplicity of bands is determined by the number, n, of magnetically equivalent protons on the neighboring atoms and given by n + 1.
- Splitting is symmetrical around the midpoint of a band.

NMR

Theory of Chemical Shift

Spin-spin splitting

Rules for interpretation

- If protons on atom B are affected by protons on atoms A and C that are nonequivalent, the multiplicity of B is $(n_A + 1)(n_C + 1)$.
- The relative areas of a multiplet are symmetrical around the midpoint. See table 19-3.

NMR

Theory of Chemical Shift

Spin-spin splitting

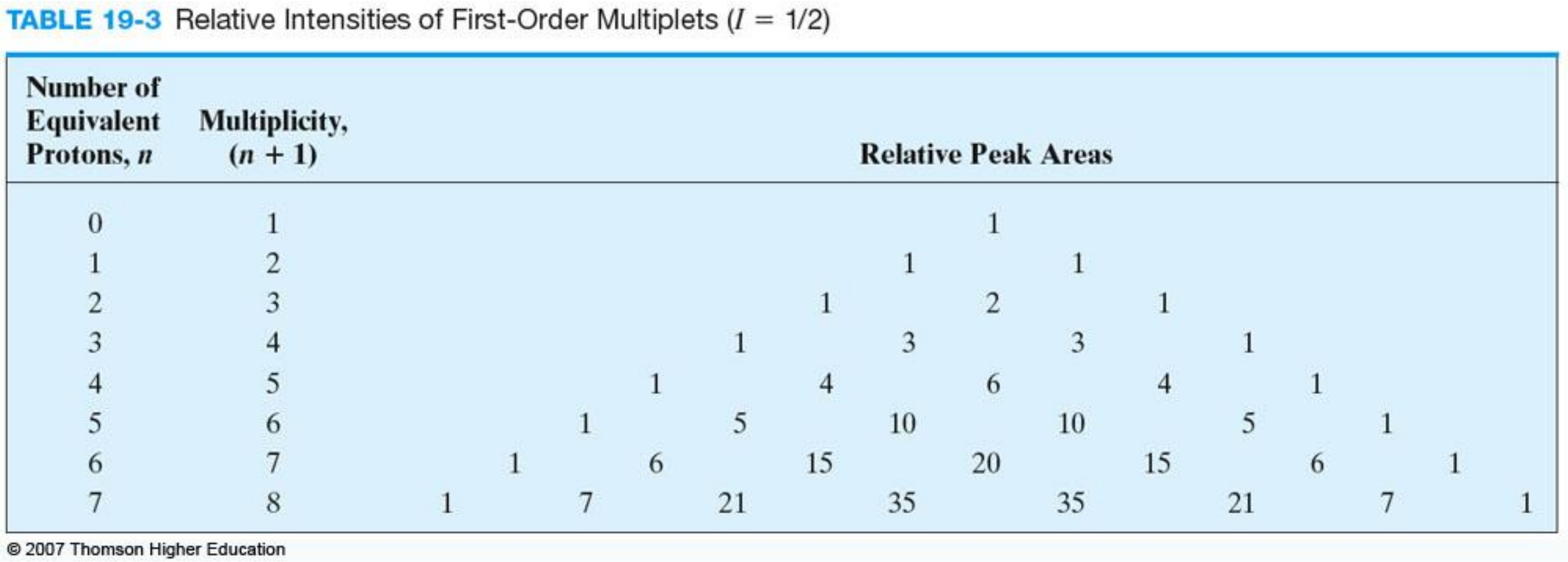


TABLE 19-3 Relative Intensities of First-Order Multiplets ($I = 1/2$)

Number of Equivalent Protons, *n*	Multiplicity, $(n + 1)$	Relative Peak Areas														
0	1								1							
1	2							1		1						
2	3						1		2		1					
3	4					1		3		3		1				
4	5				1		4		6		4		1			
5	6			1		5		10		10		5		1		
6	7		1		6		15		20		15		6		1	
7	8	1		7		21		35		35		21		7		1

NMR

Theory of Chemical Shift

Spin-spin splitting

Examples:

Cl	CH_2	CH_2	CH_2	Cl
	n+1	n+1	n+1	
	2+1=3	4+1=5	2+1=3	
	1:2:1	1:4:6:4:1	1:2:1	

CH_3	CH	Br	CH_3
1+1=2	6+1=7		1+1=2
1:1	1:6:15:20:15:6:1		1:1

NMR

Theory of Chemical Shift

Spin-spin splitting

Examples:

CH_3	CH_2	O	CH_3
n+1	n+1		no splitting
2+1=3	3+1=4		
1:2:1	1:3:3:1		1 peak

NMR

NMR Spectrometers

Two types:

- Wide-line spectrometers
- High-resolution spectrometers

Wide-line

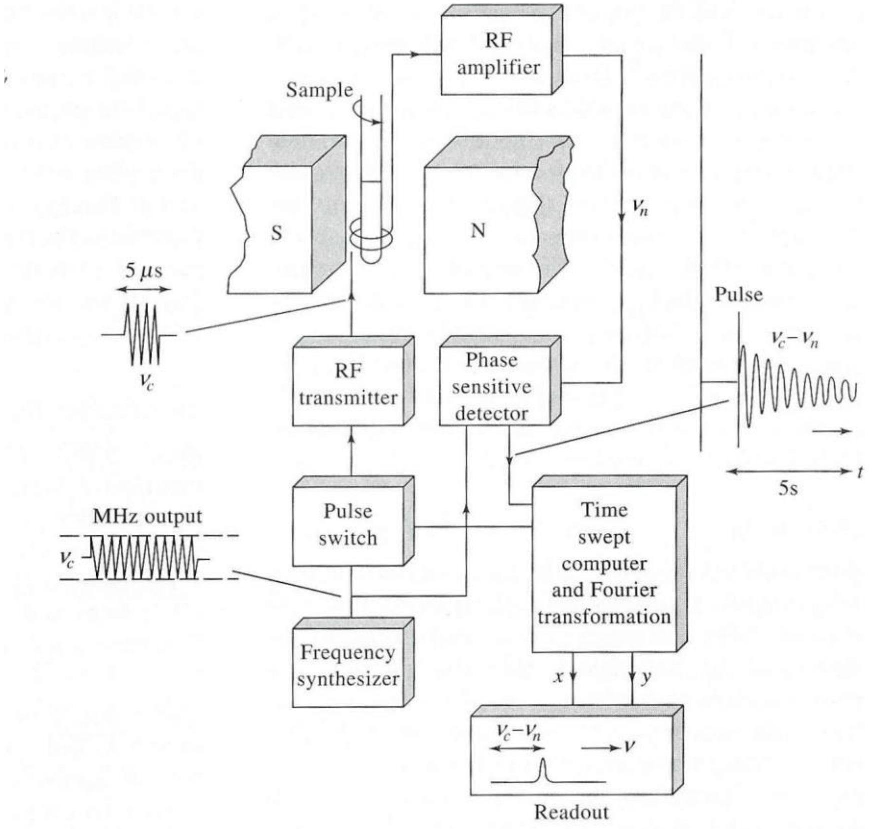
- Magnet strengths ~ 0.1 – 1.0 tesla
- Simple
- Less expensive ~under 100,000

High resolution

- Magnet strengths 1.4 – 23 T
- Proton frequencies 60-1000 MHz
- More expensive ~ ½ to 1 million

NMR

NMR Spectrometers



NMR

NMR Spectrometers

Radio-frequency radiation is produced by a crystal controlled frequency synthesizer having output frequency of v_c.

Signal passes into a pulse switch and power amplifier to create an intense and reproducible pulse of radio-frequency current in the transmitter coil.

Resulting rf radiation impinges on the sample inside the coil.

NMR

NMR Spectrometers

The length, amplitude, shape, and phase of the pulse are selected by the operator.

The resulting signal is picked up by the same coil acting now as a receiver.

The signal is amplified and transmitted to a phase sensitive detector which transforms the time-domain signal to frequency-domain signal (NMR spectra).

NMR

- NMR Spectrometers
  - Components of FTNMRs
    - Magnets
    - Sensitivity and resolution of spectrometer is dependent on strength and quality of magnet.
    - Goal is to increase field strength and produce highly homogeneous, reproducible field.
    - Magnet most expensive component of instrument.

NMR

- NMR Spectrometers
  - Components of FTNMRs
    - Magnets
    - Three types:
- Permanent magnet
- Conventional electromagnet (not used much anymore)
- Superconductivity solenoids

NMR

NMR Spectrometers

Magnets

- Permanent magnets – used in CW
- Field strength 0.7, 1.4 and 2.1 T for 30, 60, and 90 MHz.
- Temperature sensitivity – require extensive thermostating and shielding.
- Field drift problems – not ideal for extended periods.

NMR

NMR Spectrometers

Magnets

Superconductivity magnets

Field strengths up to 23 T for 1 GHz

The solenoid is bathed in liquid He at 4K, superconducting niobium/tin or niobium/titanium wire is wound around the solenoid.

He dewer is bathed with liquid N_2.

Filled w/ liquid N_2 once a week and liquid He every few months.

- High field strength
- High stability
- Low operating cost
- Simple
- Small size

NMR

NMR Spectrometers

Magnets

Superconductivity magnets

Field strengths up to 23 T for 1 GHz

Typically made of Nb-Ti

Critical temperature of 10 kelvins and can superconduct at up to about 15 teslas.

More expensive magnets can be made of niobium-tin (Nb3Sn). These have a Tc of 18 K. When operating at 4.2 K they are able to withstand a much higher magnetic field intensity, up to 25 to 30 teslas.

NMR

NMR Spectrometers

Magnets

Superconductivity magnets

Magnet quenching

A quench is an abnormal termination of magnet operation that occurs when part of the superconducting coil enters the normal (resistive) state.

Due to:

-field inside the magnet is too large,

-rate of change of field is too large (causing eddy currents and resultant heating in the copper support matrix),

-combination of the two

-a defect in the magnet

NMR

NMR Spectrometers

Magnets

Magnets still not stable or homogeneous in of themselves and need methods to compensate for drift and field inhomogeneity.

NMR

NMR Spectrometers

- **Magnets**
  - **Locking magnetic field**
  - **Offsets field fluctuations by using a reference nucleus.**
  - **The reference is continuously irradiated and monitored at a frequency corresponding to its resonance maximum.**
  - **Most modern instruments are stable for 1-20 minutes.**

NMR

NMR Spectrometers

Magnets

Shimming

Shim coils – pair of wire loops with a set current flowing through them to produce small magnetic fields.

Used to compensate for inhomogeneties in primary magnet field.

NMR

NMR Spectrometers

Magnets

Sample spinning

Spin sample to compensate for field inhomogeneity.

NMR

Analytical Applications

Nmr is nondestructive

Possible to carry out analysis in one step

Not great sensitivity but tends to a positive result

Fast

Integrated intensities give only relative abundance of nuclei

With internal standards it is possible to determine the total weight of hydrogen in a known weight of a pure compound.

NMR

Applications

- Define environment of functional groups
- Quantitative determination of compounds in mixtures and can following progress of reactions
- Can yield kinetic and thermodynamic parameters for certain types of chemical reactions
- Give accurate information about the relative position of groups of magnetic nuclei within the molecule.

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