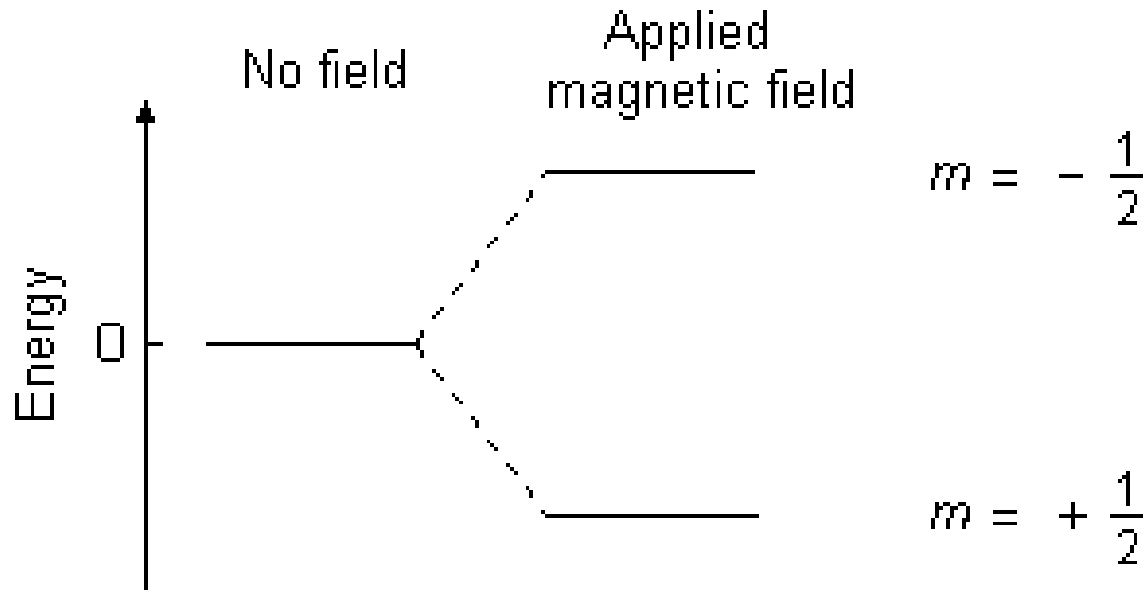# Nuclear spin and the splitting of energy levels in a magnetic field

Energy levels for a nucleus with spin quantum number 1/2

Chemical Shifts

Fortunately for the chemist, all proton resonances do not occur at the same position. The Larmor precession frequency (v_o) varies because the actual magnetic field B at the nucleus is always **less** than the external field B_o. The origin of this effect is the "superconducting" circulation of electrons in the molecule, which occurs in such a way that a local induced magnetic field B_{ind} is created, which opposes B_o (B_{ind} is proportional to B_o).
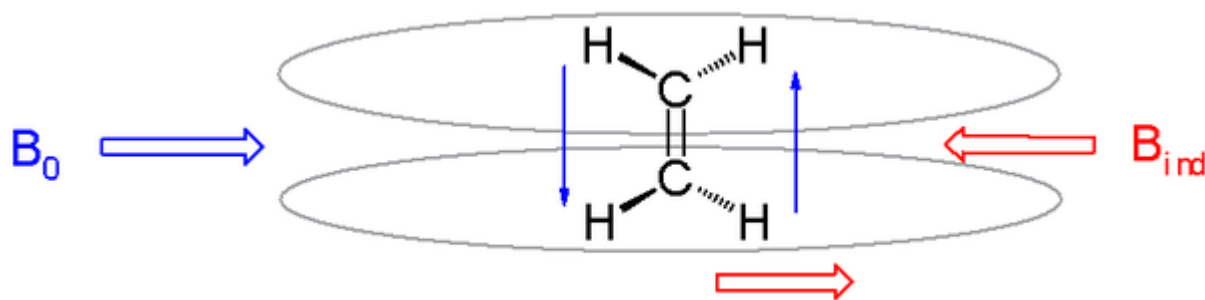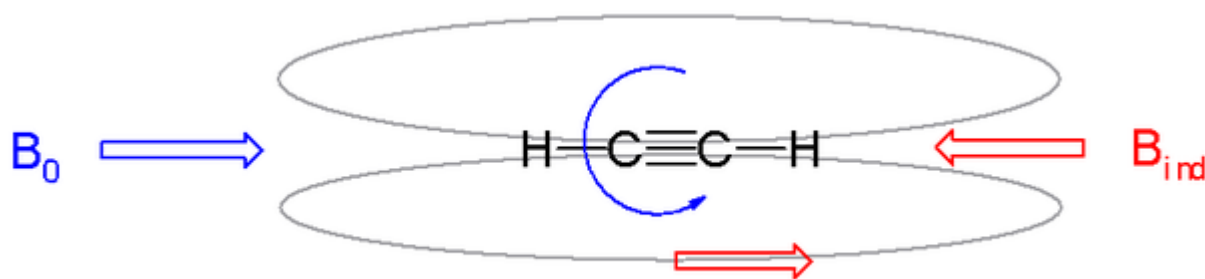
Thus $B = B_o - B_{ind}$. We therefore say that the nucleus is **shielded** from the external magnetic field. The extent of shielding is influenced by many structural features within the molecule such as electron density, electronegativity of neighboring groups and anisotropic induced magnetic field effects, hence the name **chemical shift**. Since the extent of shielding is proportional to the external magnetic field B_o, we use **field independent** units for chemical shifts: δ values, whose units are ppm. Spin-spin splitting is not dependent on the external field, so we use energy units for coupling constants: Hz, or cycles per second.

The Proton Chemical Shift Scale

Experimentally measured proton chemical shifts are referenced to the ^1H signal of tetramethylsilane (Me_4Si). For NMR studies in aqueous solution, where Me_4Si is not sufficiently soluble, an alternative reference standard, DSA ($Me_3Si\text{-}CH_2CH_2\text{-}NH_3^+$ $CF_3CO_2^-$) has been suggested.

Proton chemical shifts cover a range of over 30 ppm, but the vast majority appears in the region δ 0-10 ppm, where the origin is the chemical shift of tetramethylsilane.
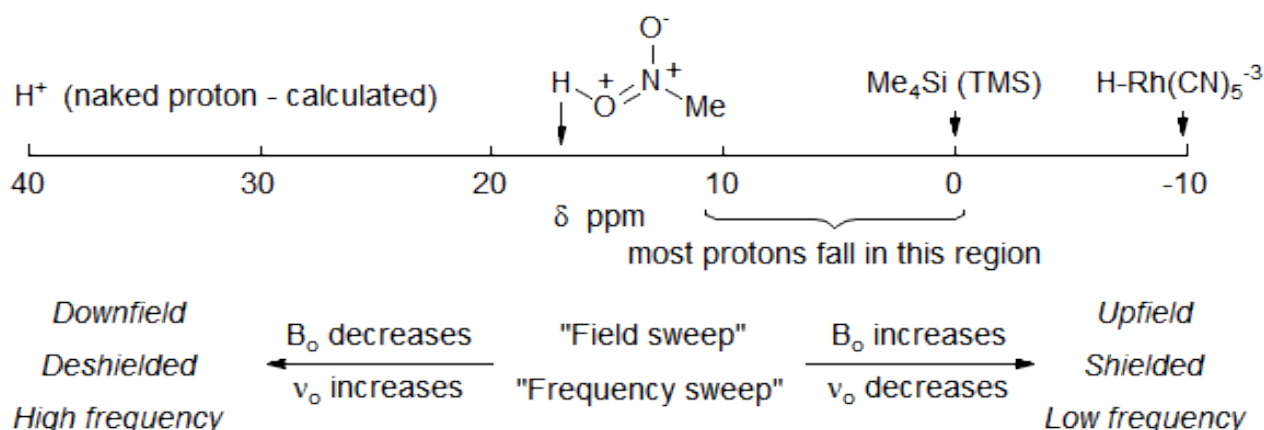
Signals on the right are referred as upfield or shielded and signals to the left as downfield or deshielded. δ units are defined as follows:

$$\delta = \frac{[v_{0(H)} - v_0(TMS)]}{[Spectrometer\ frequency\ in\ MHz]}$$

$$\frac{300\,\text{Hz}}{300 \times 10^6\,\text{Hz}} = 1 \times 10^{-6} = 1\,\text{ppm}$$

Conversion Between tesla and MHz

The tesla (symbol T) is the SI derived unit of magnetic flux density, commonly denoted as B.
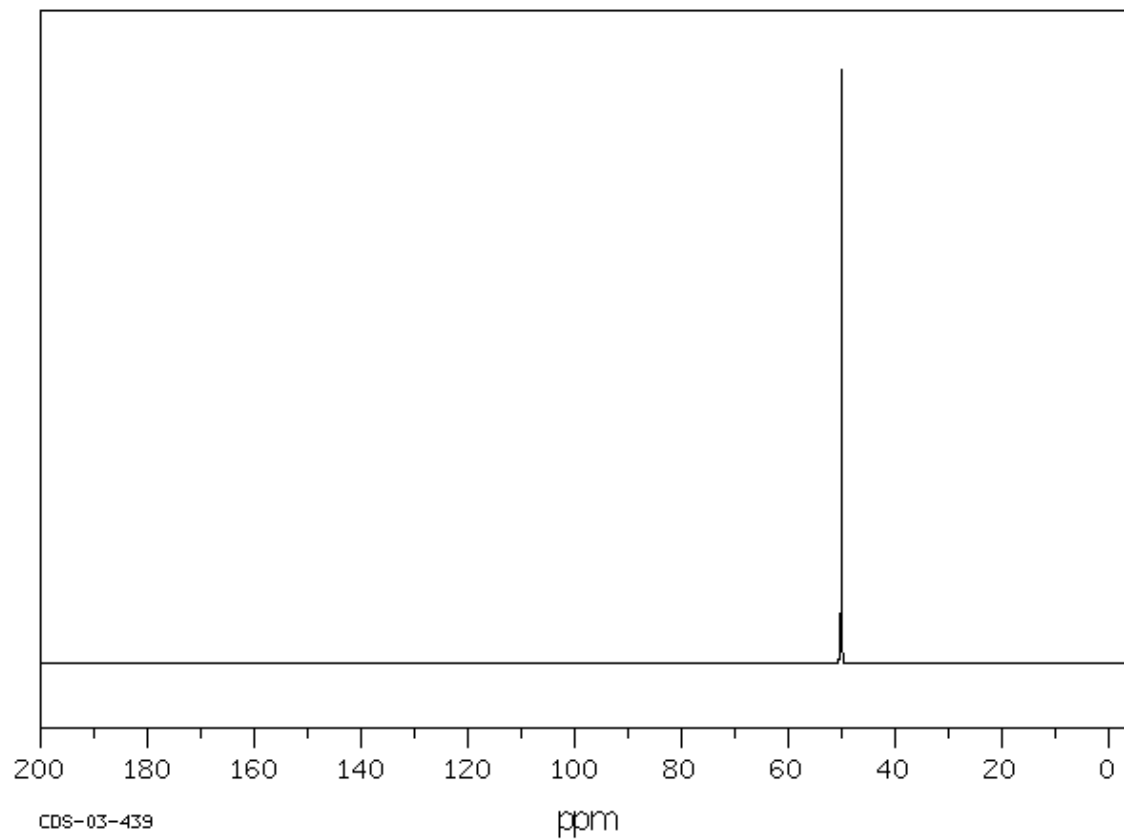
1 tesla is equivalent to:

42.6 MHz of the ^{1}H nucleus frequency, in NMR. Thus a 1 GHz NMR magnetic field is 23.5 tesla.
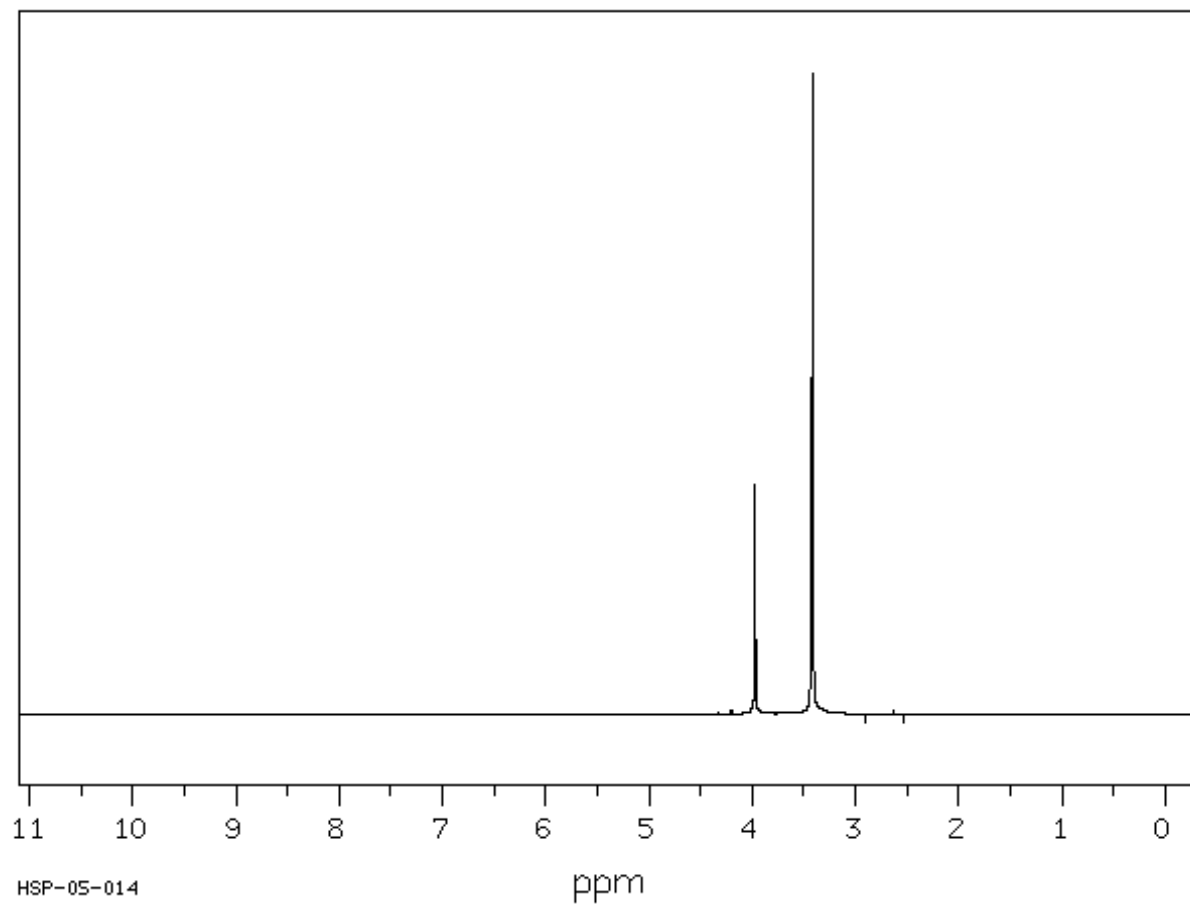
Top 3 list for ^{13}C NMR Interpretation

- 1. Symmetry
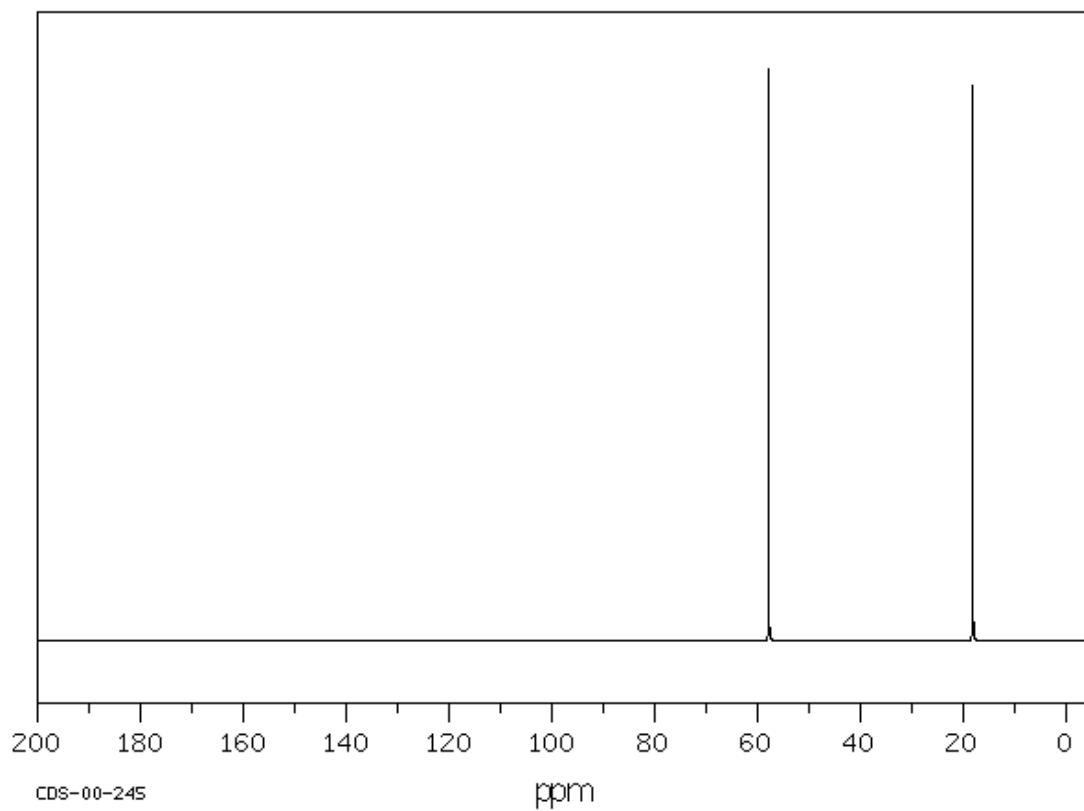- 2. Chemical Shifts
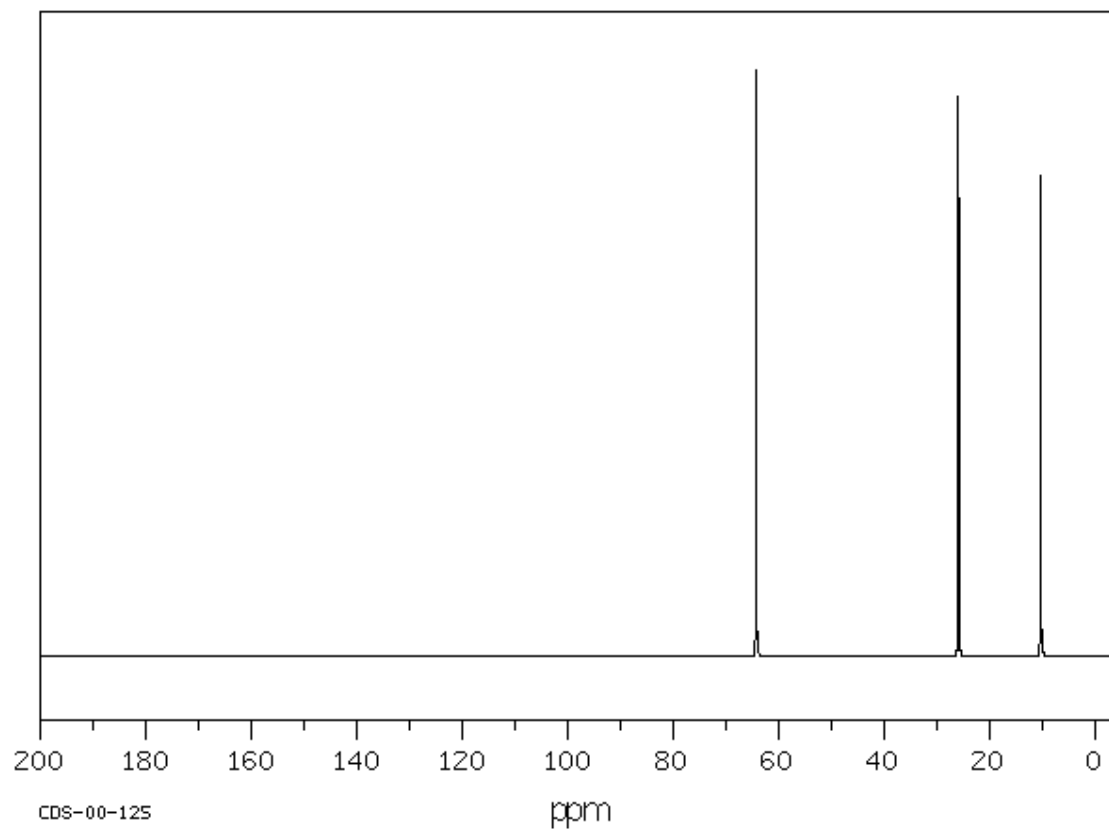- 3. Multiplicity

^{13}C NMR of CH$_3$OH

200   180   160   140   120   100   80   60   40   20   0
ppm

CDS-03-439

^{1}H NMR of CH$_3$OH

HSP-05-014

^{13}C NMR of CH$_3$CH$_2$OH

CDS-00-245

¹³C NMR of 1-Propanol

CDS-00-125

ppm

¹H NMR of 1-Propanol

HSP-03-833

¹³C NMR of 2-Propanol

CDS-00-521
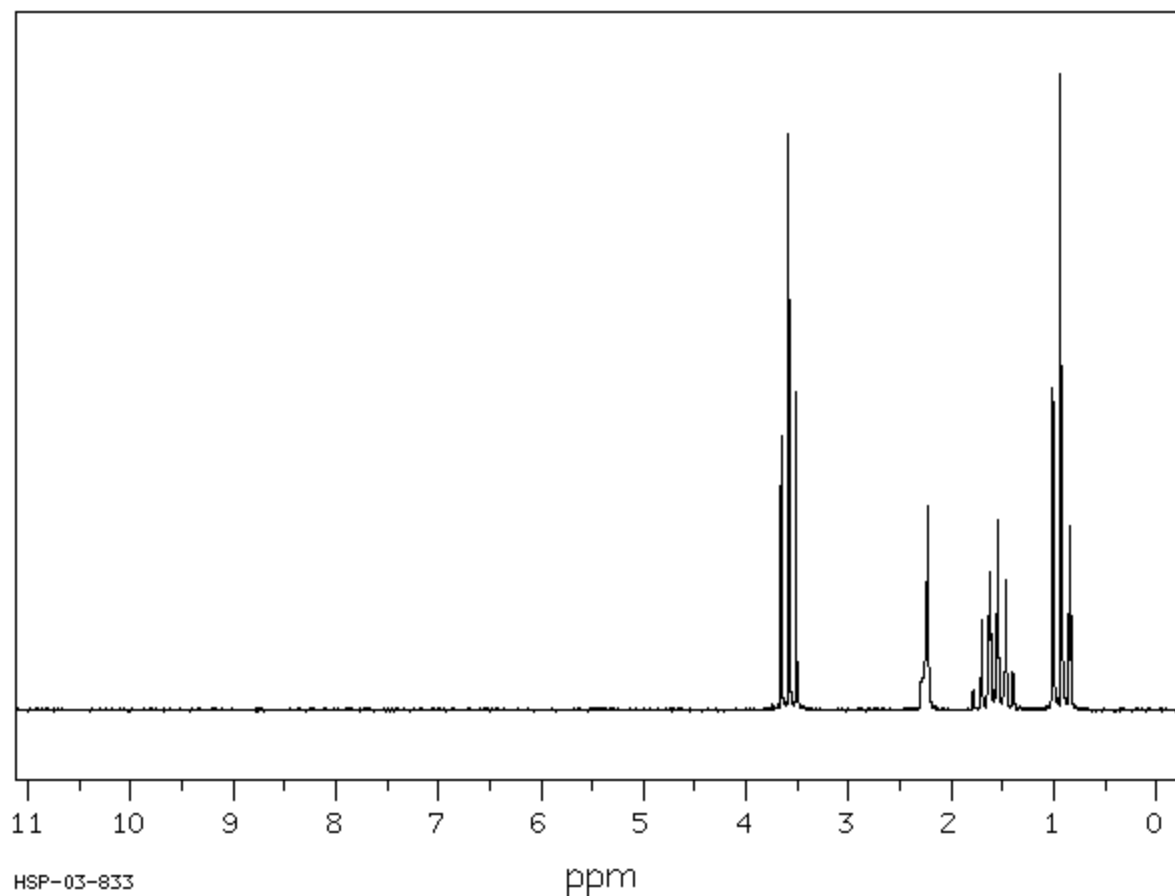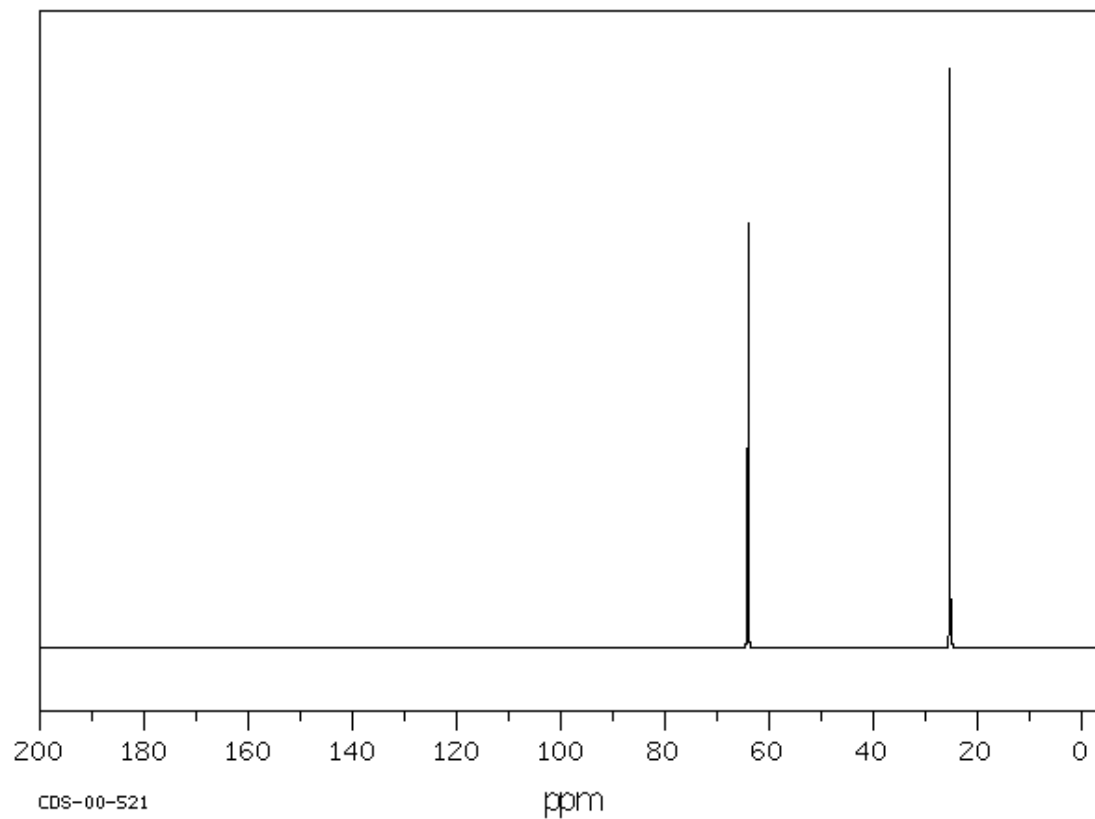
¹H NMR of 2-Propanol

HSP-03-214

¹³C NMR of p-Xylene

CDS-00-328
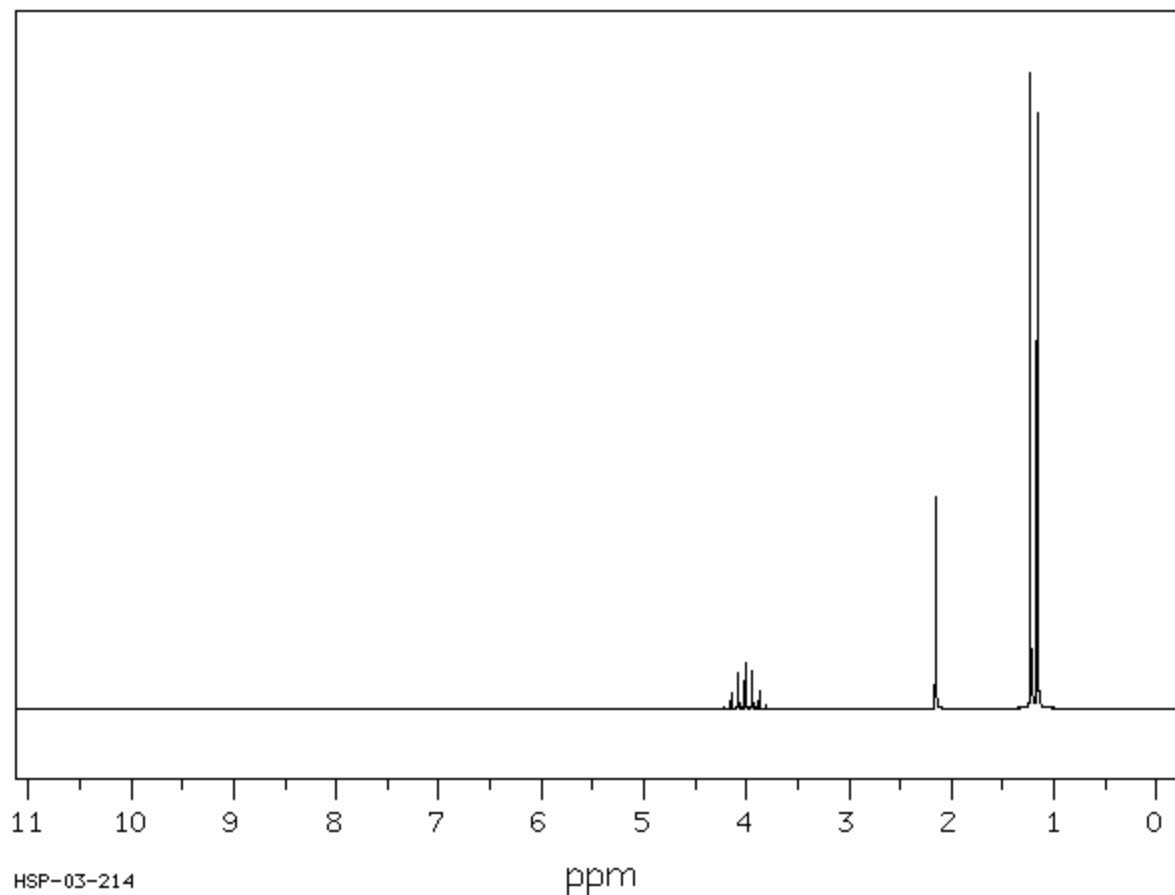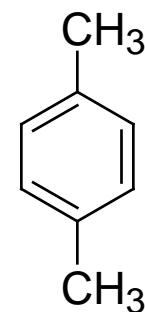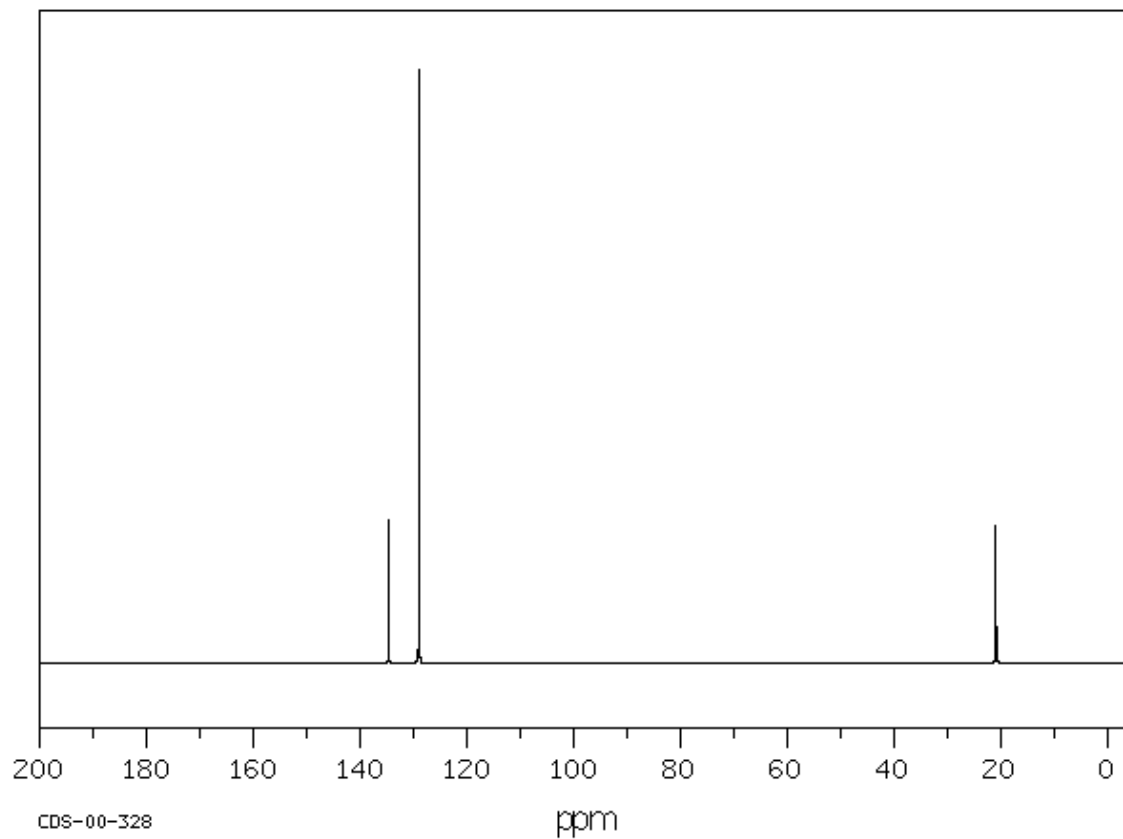
¹³C NMR of o-Xylene

¹³C NMR of m-Xylene

CDS-00-327
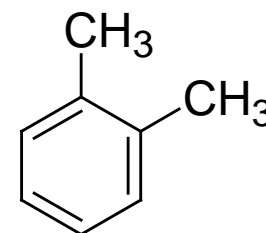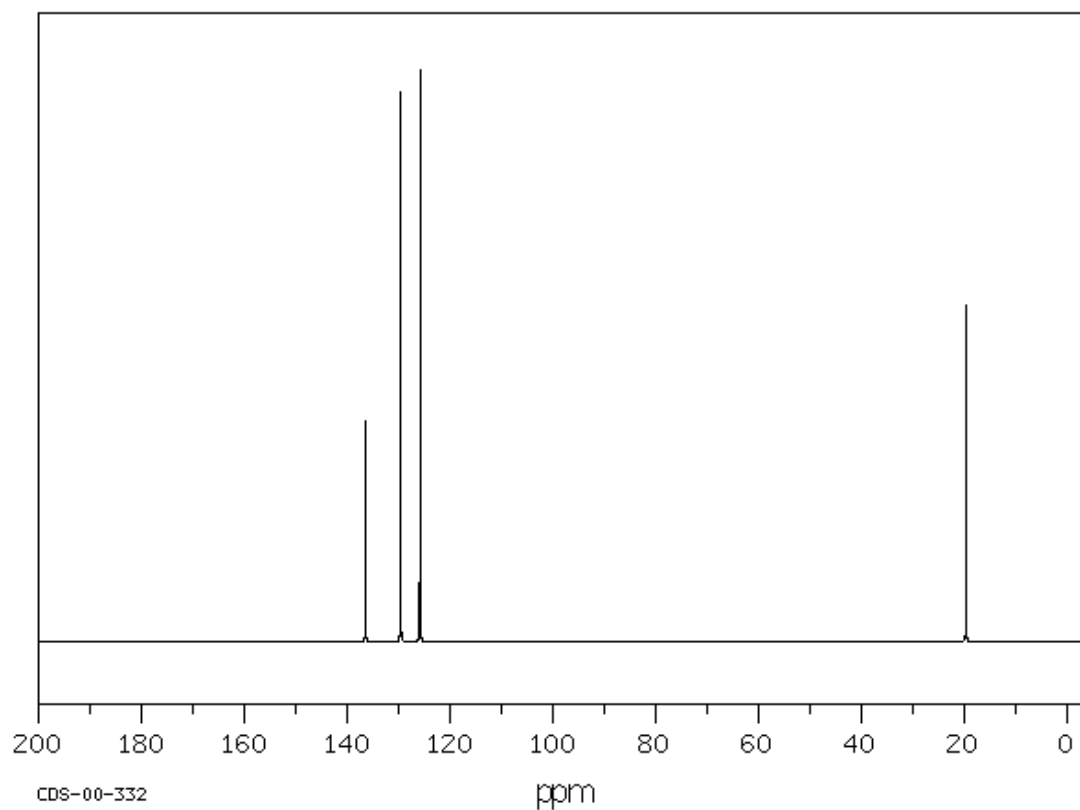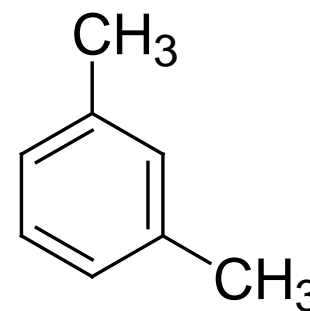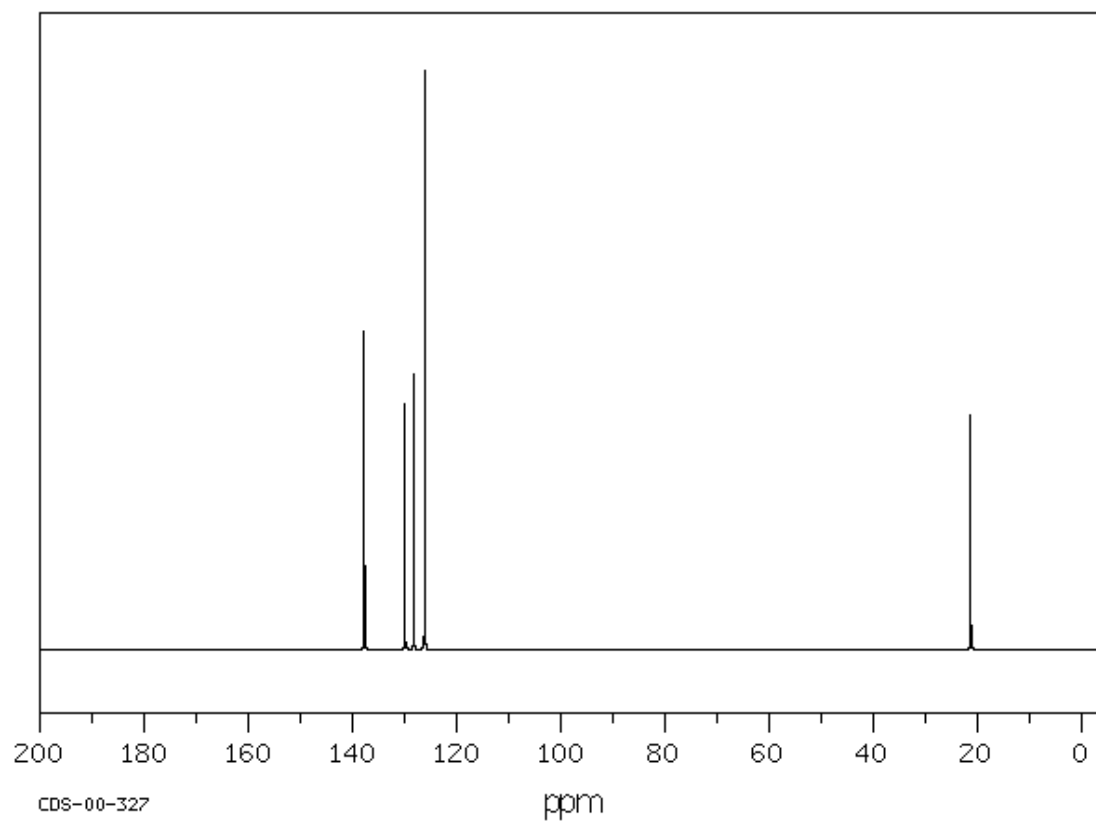
¹³C NMR of o-Tolualdehyde
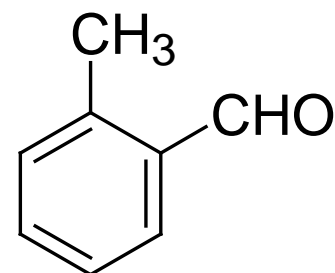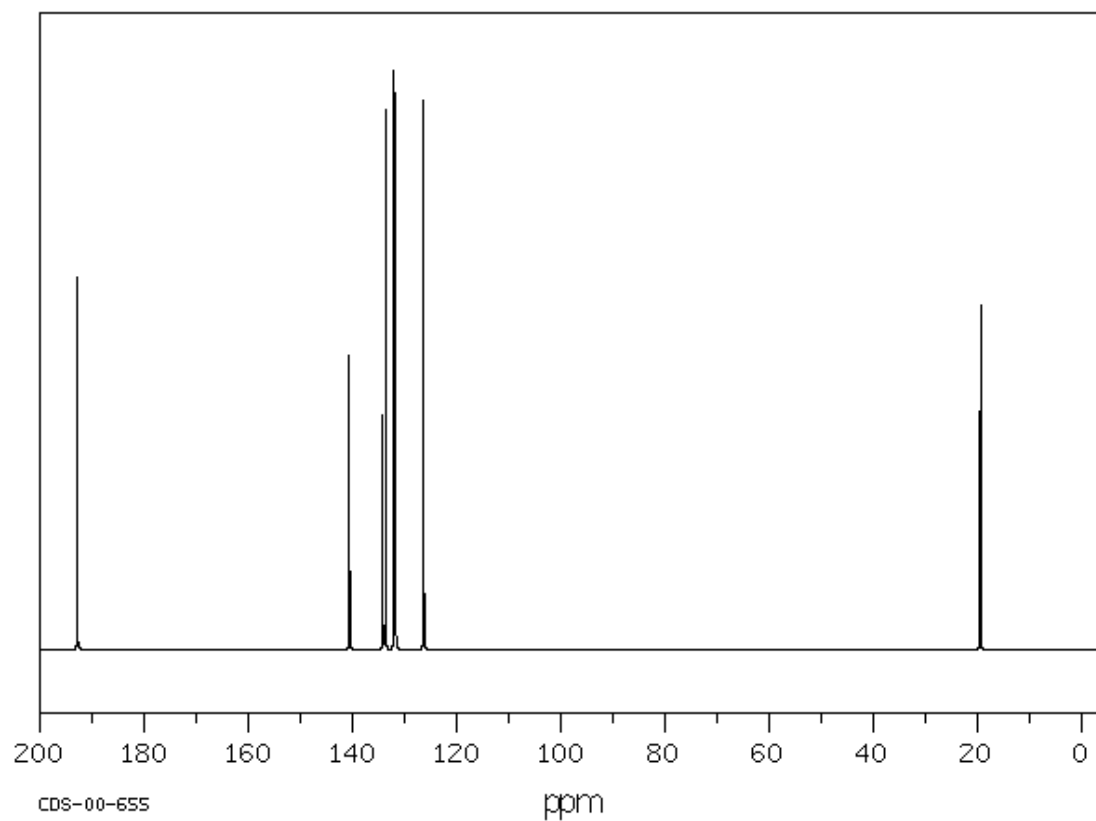
¹³C NMR of Acetophenone
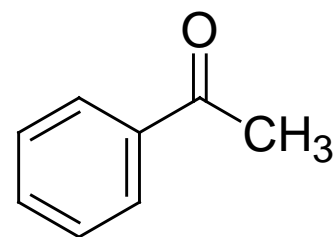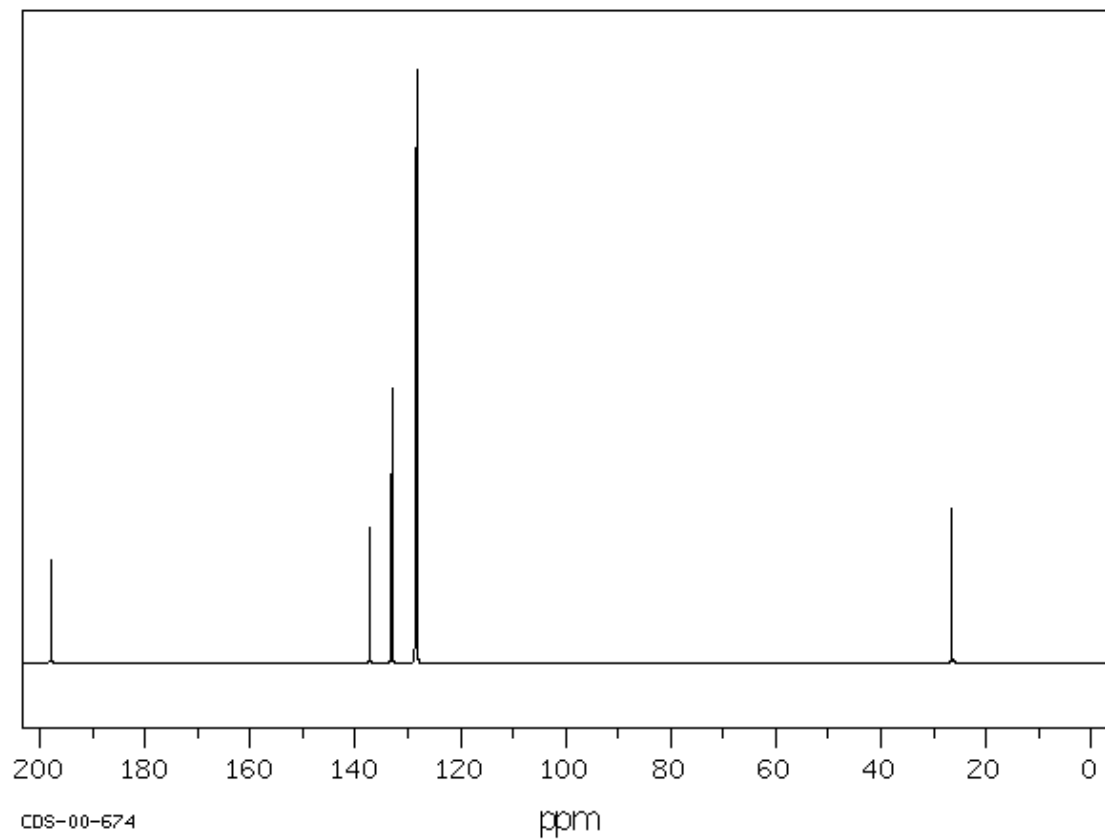
¹³C NMR of n-Butyl Ether

CDS-00-713
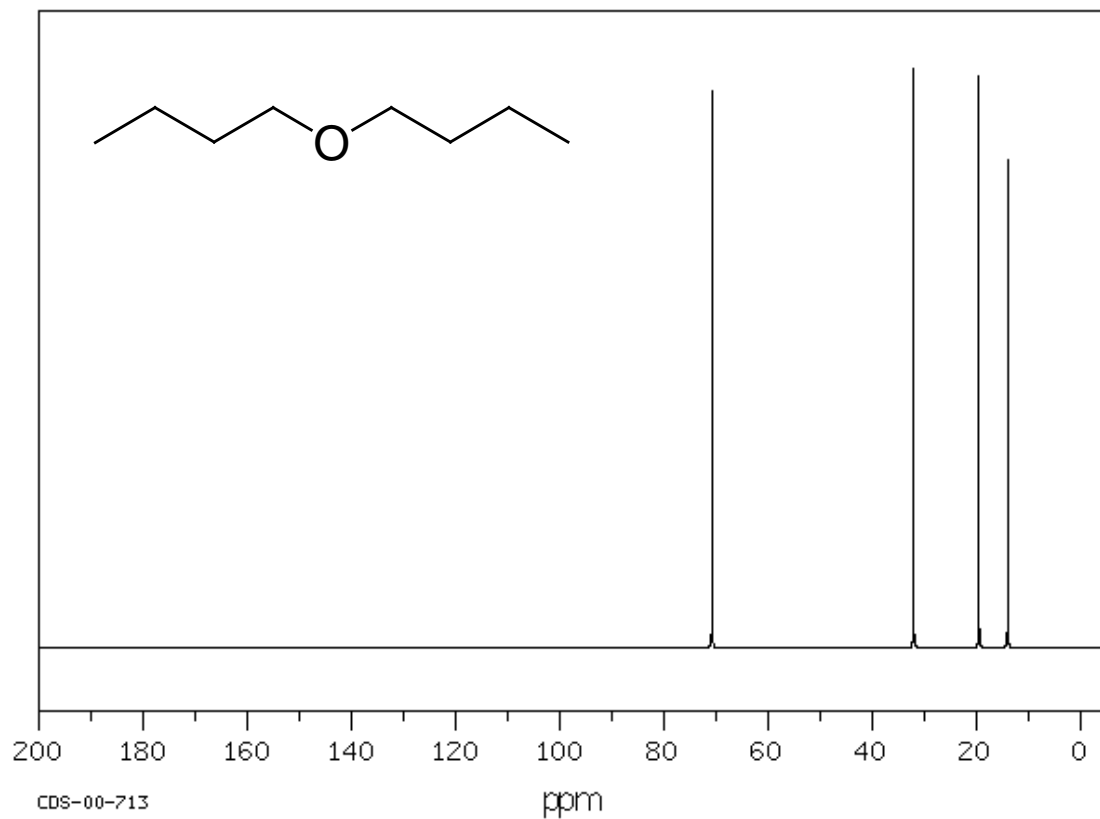
¹³C NMR of 2-furancarboxylic acid octyl ester

CR200300287TS

¹³C NMR Chemical Shifts

Aldehydes, RCH=O

Ketones, R₂C=O

R₂C=CH₂

RHC=CHR

R₂C=CH₂

C–F

C–NO₂

C–Cl

C–Br

C–H Saturated Alkanes

Aromatics

Heteroaromatics

C–NR₂

C–OH

C–SR

Carboxylic Acids R–CO₂H

RC≡N

C–OR

C–Ar

Esters R–CO₂R'

Sulfoxides, Sulfones C–SO₂R

C–C≡C

Amides R–CONR₂

C≡CR

C–C(=O)–R

200   150   100   50   0.0 ppm (δ)
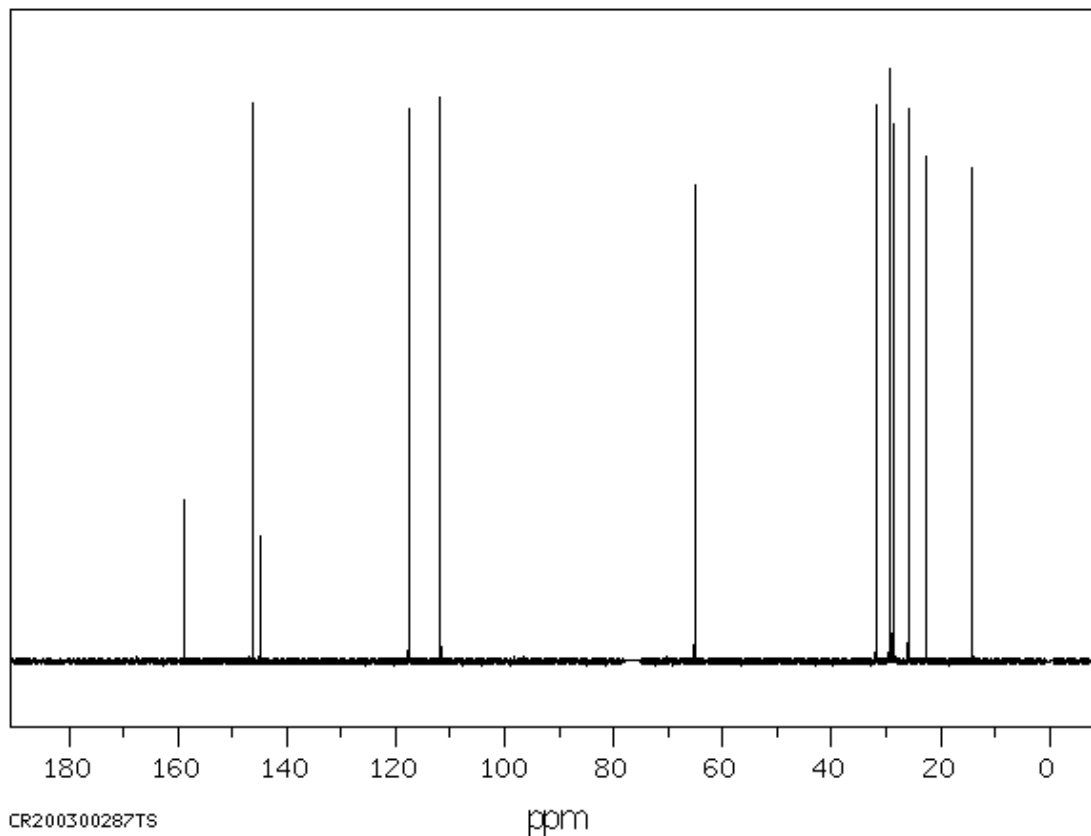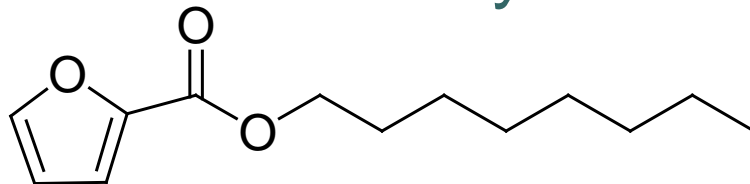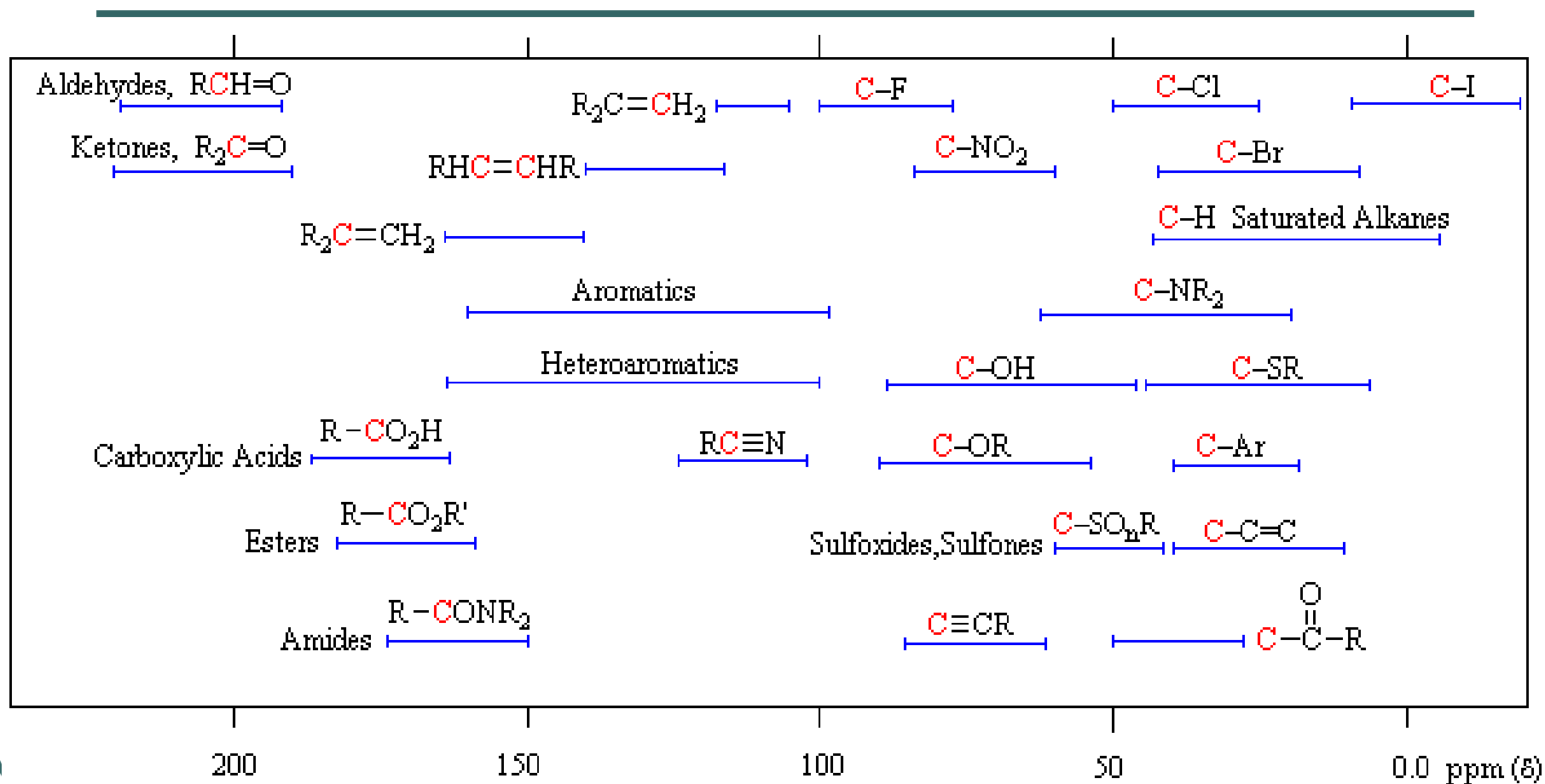
DEPT C-NMR Spectra

Normal 13C spectra are broadband decoupled. With the development of more modern spectroscopic methods it has become possible to use a programed sequences of radio frequency pulses to determine other structural features.

One of these techniques is known as **DEPT** (*distortionless enhancement of polarization transfer*) which can be used to give the number of attached H. DEPT is an NMR technique for distinguishing among ^{13}C signals for CH_3, CH_2, CH, and quaternary carbons.
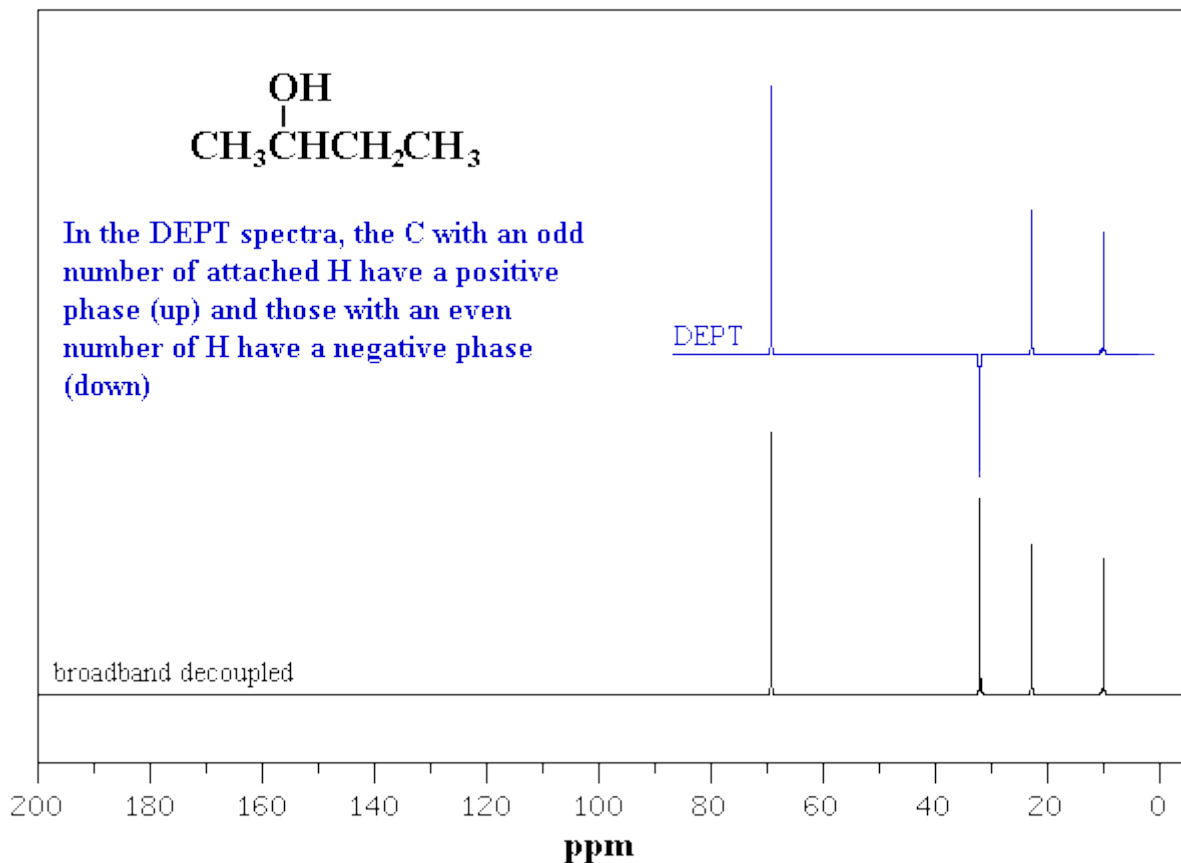
In a DEPT experiment, a sequence of pulses with various delay times are used to create the DEPT spectra where $-CH_3$ and CH peaks appear as normal and $-CH_2-$ peaks appear inverted. Quaternary C are not usually seen. This way the number of H attached to C can usually be deduced. An example of a DEPT is shown below for 2-butanol (notice how the peak for the $-CH_2-$ points down) with the corresponding broadband decoupled spectra.

OH
|
$CH_3CHCH_2CH_3$

In the DEPT spectra, the C with an odd number of attached H have a positive phase (up) and those with an even number of H have a negative phase (down)

DEPT

broadband decoupled

200 180 160 140 120 100 80 60 40 20 0

ppm

The DEPT method

The DEPT methods uses a complex series of pulses in both the ^{1}H and ^{13}C ranges: a 45° pulse, a 90° pulse and a 135° pulse

- quaternary carbons give no signal
- 45° pulse: all H-bearing peaks are positive
- 90° pulse: only CH carbons are seen
- 135° pulse: carbon signals show different phases
- DEPT signals for CH_3 and CH carbons give positive signals
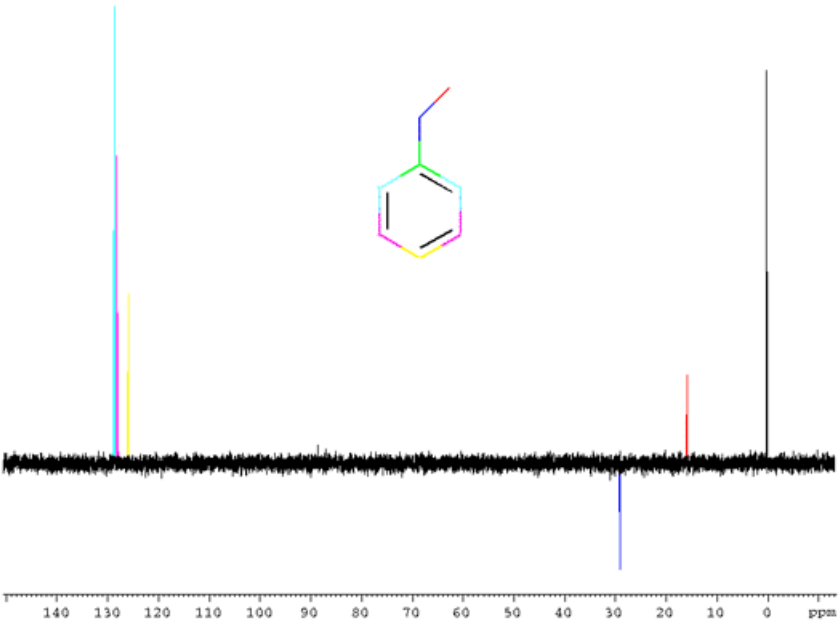- DEPT signals for CH_2 carbons give negative signals
-

13C NMR spectrum for Ethylbenzene
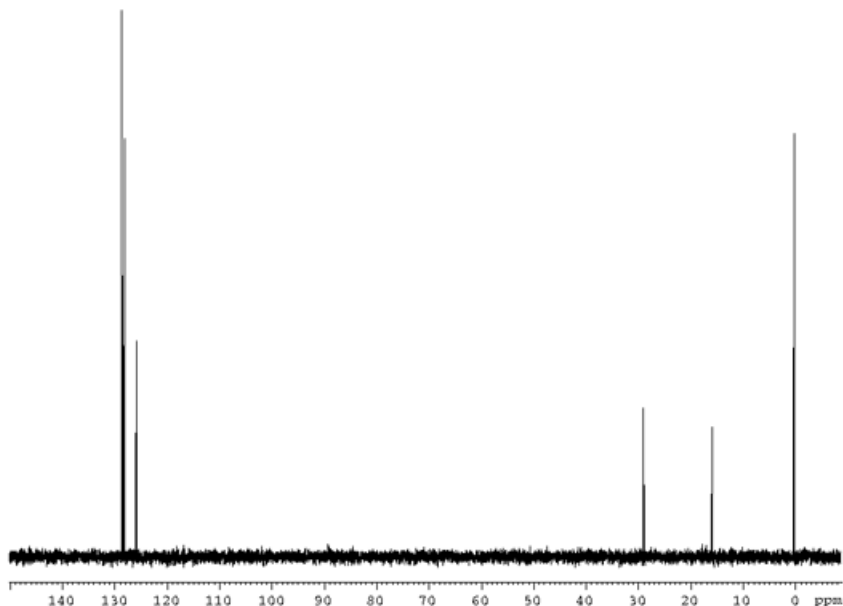
Ethylbenzene: DEPT 90°
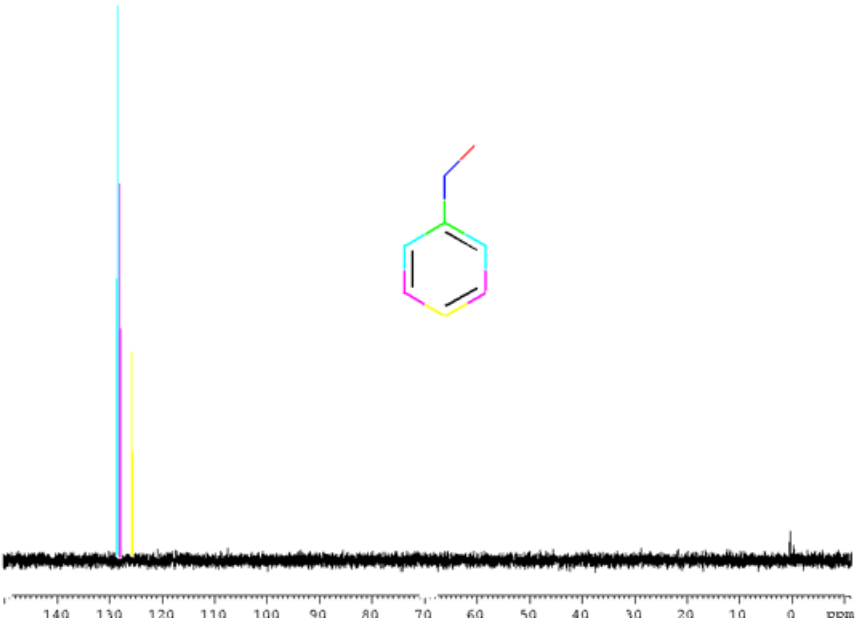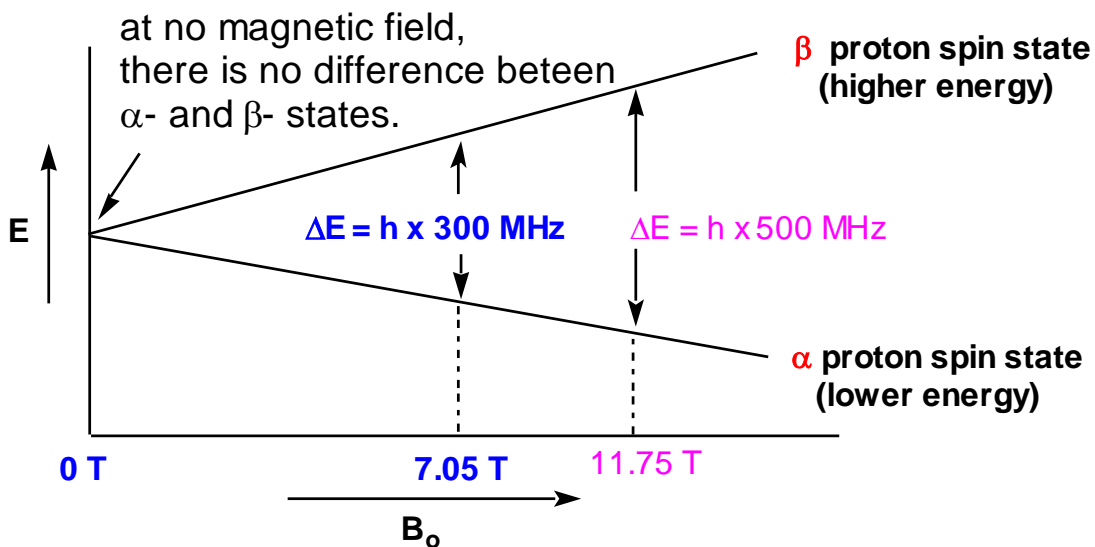

Ethylbenzene: DEPT 135°

Top 5 list for ^{1}H NMR Interpretation

1. Symmetry
2. Chemical Shifts
3. Multiplicity (spin spin coupling)
4. Integration of peak area
5. Protons that exchange with deuterium

^{1}H NMR: Basic Experimental Principles

- Imagine placing a molecule, for example, CH_4, in a magnetic field.
- We can probe the energy difference of the α- and β- state of the protons by irradiating them with EM radiation of just the right energy.

Graphical relationship between

magnetic field (B_o) and frequency (ν)

for ^{1}H NMR absorptions

at no magnetic field,
there is no difference beteen
α- and β- states.

β **proton spin state**
(higher energy)

E

$\Delta E = h \times 300\ MHz$ $\Delta E = h \times 500\ MHz$

α **proton spin state**
(lower energy)

0 T   7.05 T   11.75 T

B_o

The Chemical Shift (Also Called δ) Scale

Here's how it works. We decide on a sample we'll use to standardize our instruments. We take an NMR of that standard and measure its absorbance frequency. We then measure the frequency of our sample and subtract its frequency from that of the standard. We then divide by the frequency of the standard. This gives a number called the "chemical shift,", which does not depend on the magnetic field strength. Why not? Let's look at examples.

Imagine that we have a magnet where our standard absorbs at 300,000,000 Hz (300 megahertz), and our sample absorbs at 300,000,300 Hz. The difference is 300 Hz, so we take 300/300,000,000 = 1/1,000,000 and call that 1 part per million (or 1 PPM). Now lets examine the same sample in a stronger magnetic field where the reference comes at 500,000,000 Hz, or 500 megahertz. The frequency of our sample will increase proportionally, and will come at 500,000,500 Hz. The difference is now 500 Hz, but we divide by 500,000,000 (500/500,000,000 = 1/1,000,000, = 1 PPM).

^{1}H NMR of CH_3CH_2OH

HSP-01-876
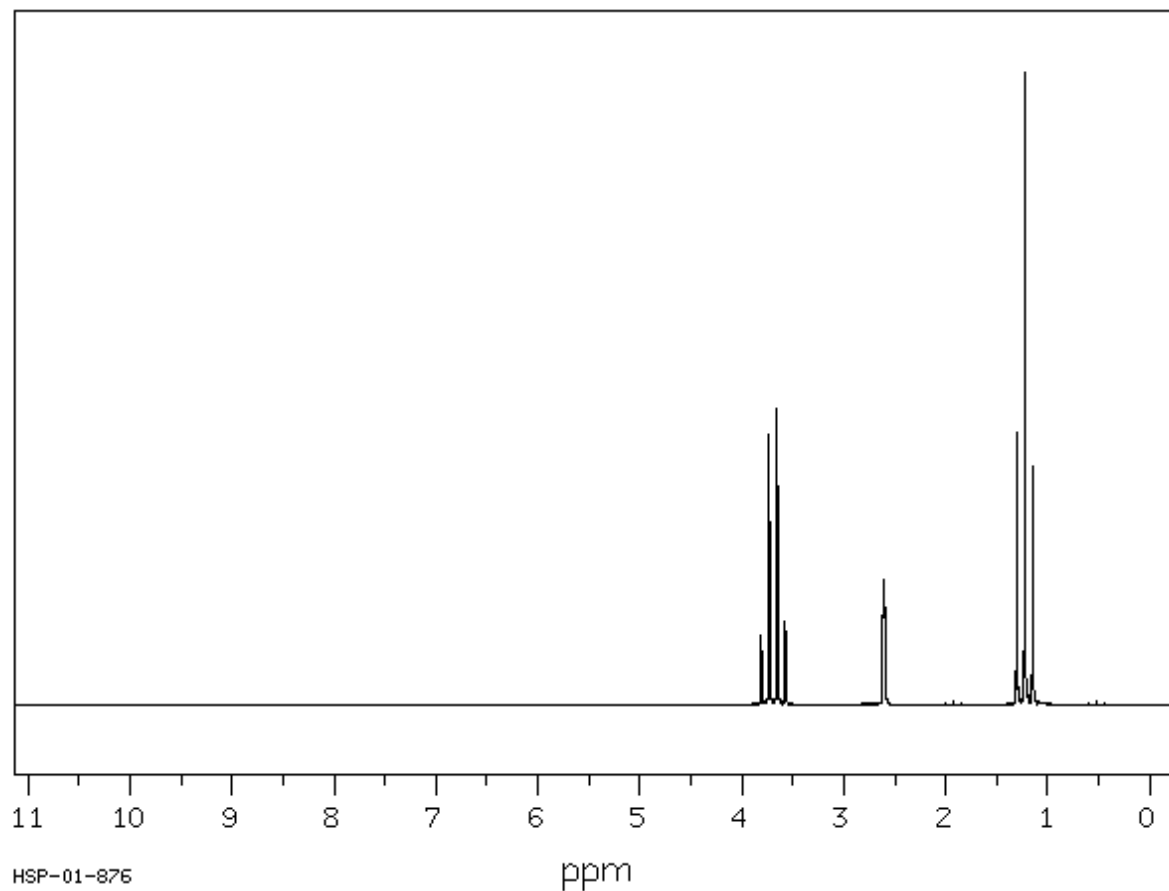
The Chemical Shift of Different Protons

What makes the ^{1}H NMR useful is that different protons usually appear at different chemical shifts. So, we can distinguish one kind of proton from another. Why do different protons appear at different δ? There are several reasons, one of which is shielding. The electrons in a bond shield the nuclei from the magnetic field. So, if there is more electron density around a proton, it sees a slightly lower magnetic field, less electron density means it sees a higher magnetic field:
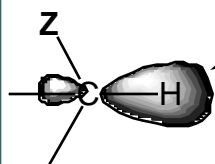
This represents the electron density of a C-H bond. How much electron density is on the proton depends on what else is attached to the carbon. If Z is an elelctronegative atom, the carbon becomes electron deficient and pulls some of the electron density away from the H. if Z is an electron donating group, more electron density ends up on the H.

The Part we are responsible- Interpreting Spectra

The spectrum of ethyl acetate is shown below. For ^{1}H NMR, there are three kinds each of which we will consider each of these separately:

1. Chemical shift data - tells us what kinds of protons we have.
2. Integrals - tells us the ratio of each kind of proton in our sample.
3. [1]H - [1]H coupling - tells us about protons that are near other protons.
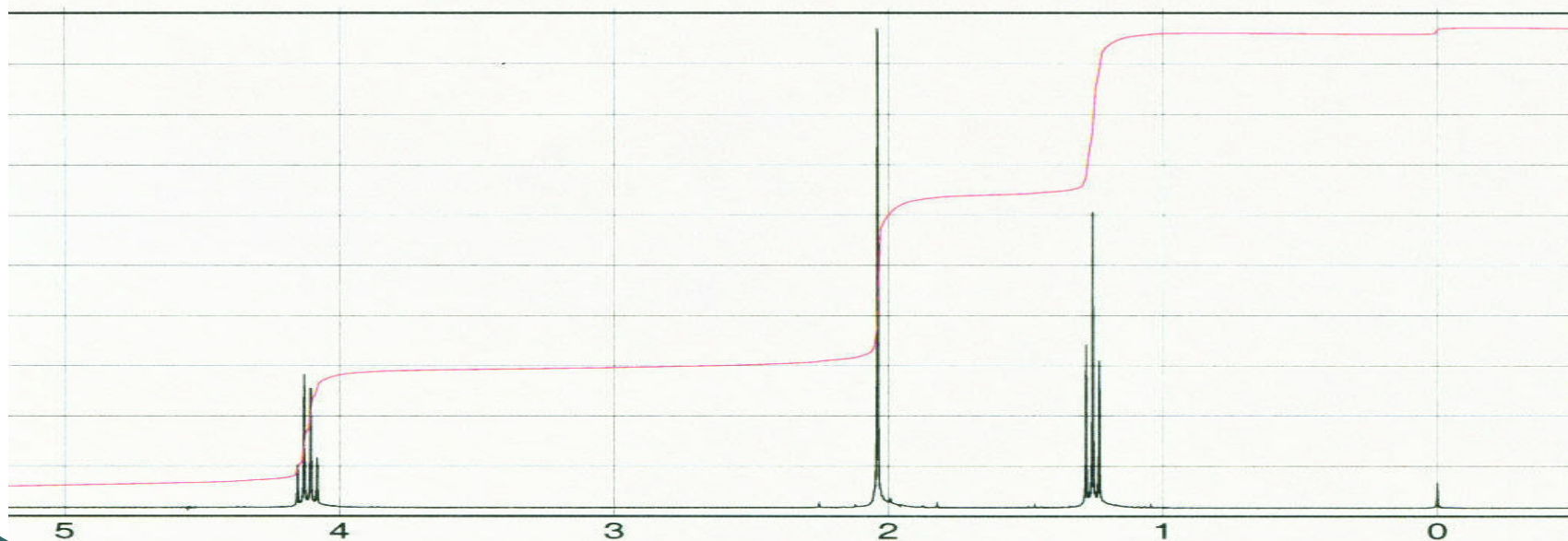
Different kinds of protons typically come at different chemical shifts. Shown below is a chart of where some common kinds of protons appear in the δ scale. Note that most protons appear between 0 and 10 ppm. The reference, tetramethylsilane (TMS) appears at 0 ppm, and aldehydes appear near 10 ppm.

Chemical Shift Data

Downfield region of the spectrum

δ ppm

Upfield region of the spectrum
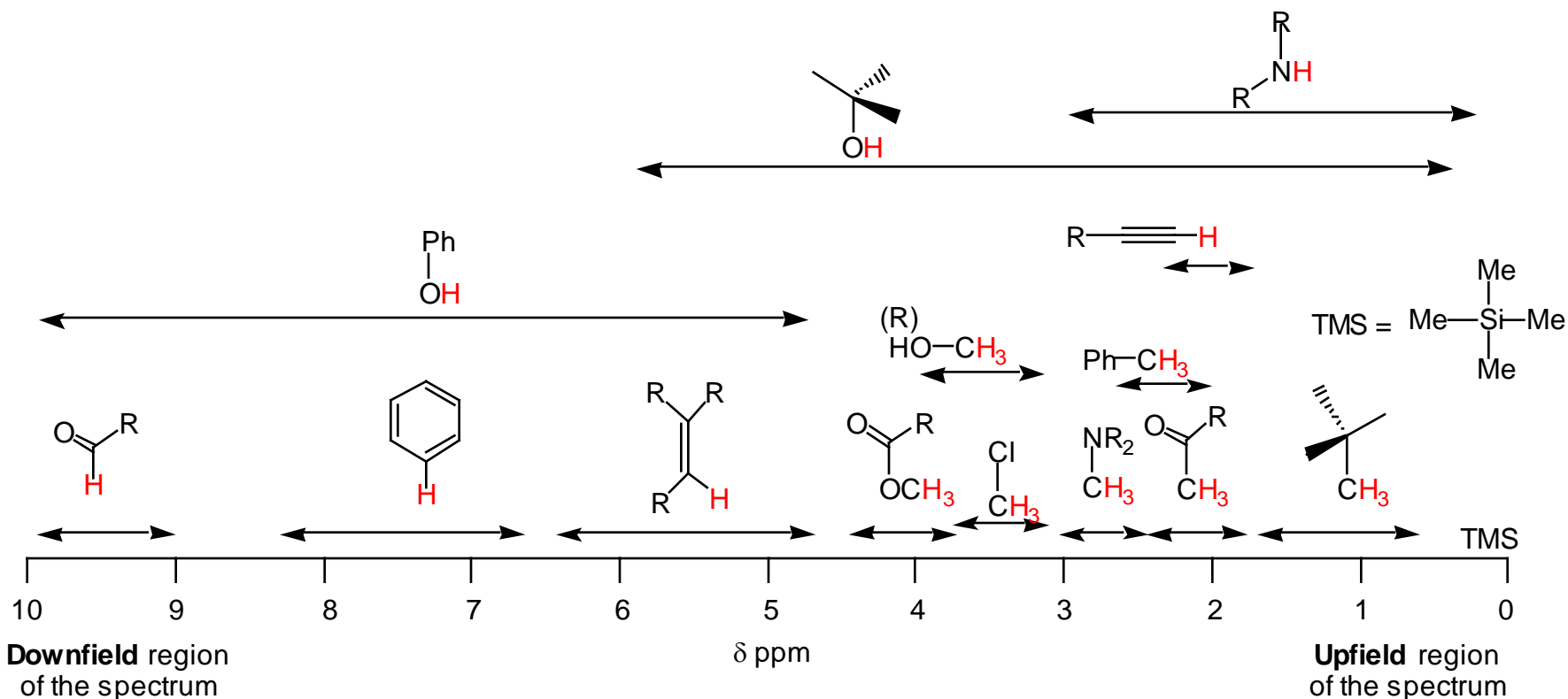
Integrals tell us the ratio of each kind of proton. They are lines, the heights of which are proportional to the intensity of the signal. Consider ethyl acetate. There are three kinds of protons in this molecule, the CH_3 next to the carbonyl, the CH_2 next to the O and the CH_3 next to the CH_2. The ratio of the signals arising from each of these kinds of protons should be 3 to 2 to 3, respectively.

Integrals
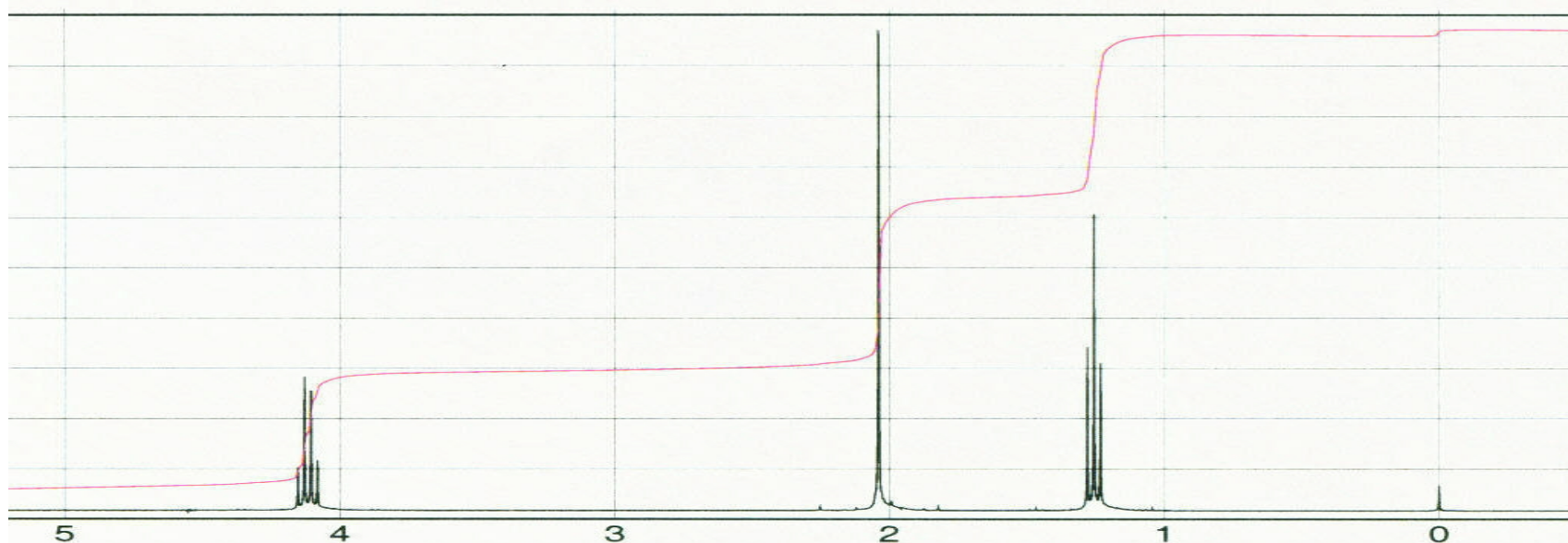
For this line, H_B is lined up **with** the magnetic field (adds to the overall magnetic field, so the line comes at higher frequency)

For this line, H_B is lined up **against** the magnetic field (subtracts from the overall magnetic field, so the line comes at lower frequency)

H_A

H_B

H_A is split into two lines because it feels the magnetic field of H_B.

H_B is split into two lines because it feels the magnetic field of H_A.

$-\overset{\overset{\displaystyle H_A}{|}}{\underset{|}{C}}-\overset{\overset{\displaystyle H_B}{|}}{\underset{|}{C}}-$
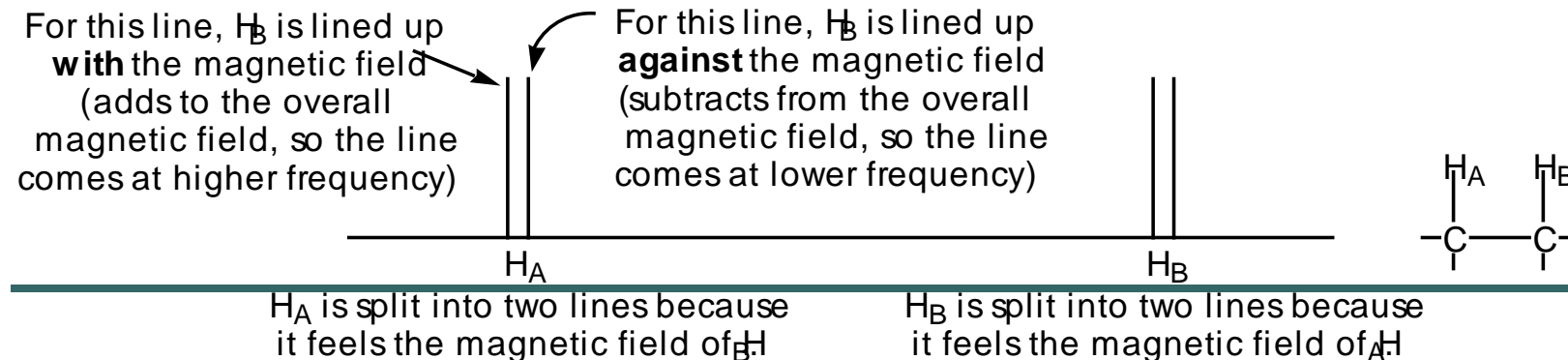
1H - 1H Coupling

the signals don't appear as single lines, sometimes they appear as multiple lines. This is due to ^{1}H-^{1}H coupling (also called spin-spin splitting or J-coupling). these protons are tiny little magnets, that can be oriented either with or against the magnetic field of the NMR machine. When the field created by HB reinforces the magnetic field of the NMR machine HA feels a slightly stronger field, but when the field created by HB opposes B_0, H_A feels a slightly weaker field. So, we see two signals for H_A depending on the alignment of H_B. The same is true for H_B, it can feel either a slightly stronger or weaker field due to H_A's presence. So, rather than see a single line for each of these protons, we see two lines for each.

More ^1H - ^1H Coupling

What happens when there is more than one proton splitting a neighboring proton? We get more lines. Consider the molecule below where we have two protons on one carbon and one proton on another.

Note that the signal produced by H_A + $H_{A'}$ is twice the size of that produced by H_B

H_A + $H_{A'}$

H_B
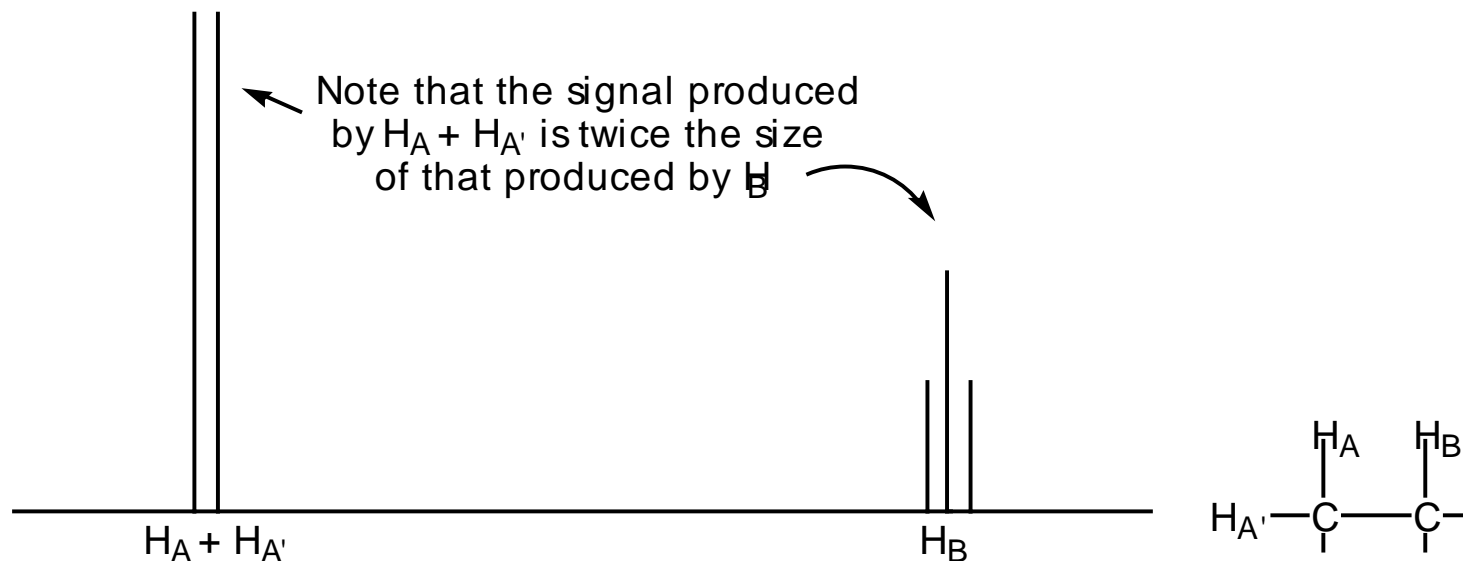
H_A and $H_{A'}$ appear at the same chemical shift because they are in identical environments
They are also split into two lines (called a doublet) because they feel the magnetic field of H_B

H_B is split into three lines because it feels the magnetic field of H_A and $H_{A'}$

Why are There Three Lines for H_B?
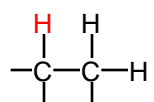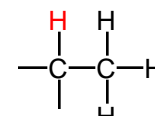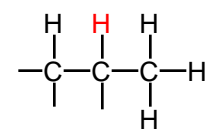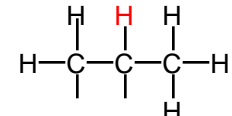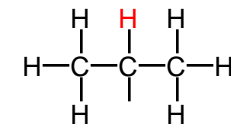
H_B feels the splitting of both H_A and H_A'. So, let's imagine starting with H_B as a single line, then let's "turn on" the coupling from H_A and H_A' one at a time:

H_B If uncoupled, H_B would appear as a singlet where the dashed line indicates the chemical shift of the singlet.

Now, let's "turn on" H_B - H_A coupling. This splits the single line into two lines

Now, let's "turn on" H_B - H_A' coupling. This splits each of the two new lines into two lines, but notice how the two lines in the middle overlap. Overall, we then have three lines.

H_A H_B

$$H_A' - C - C -$$
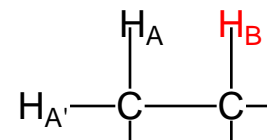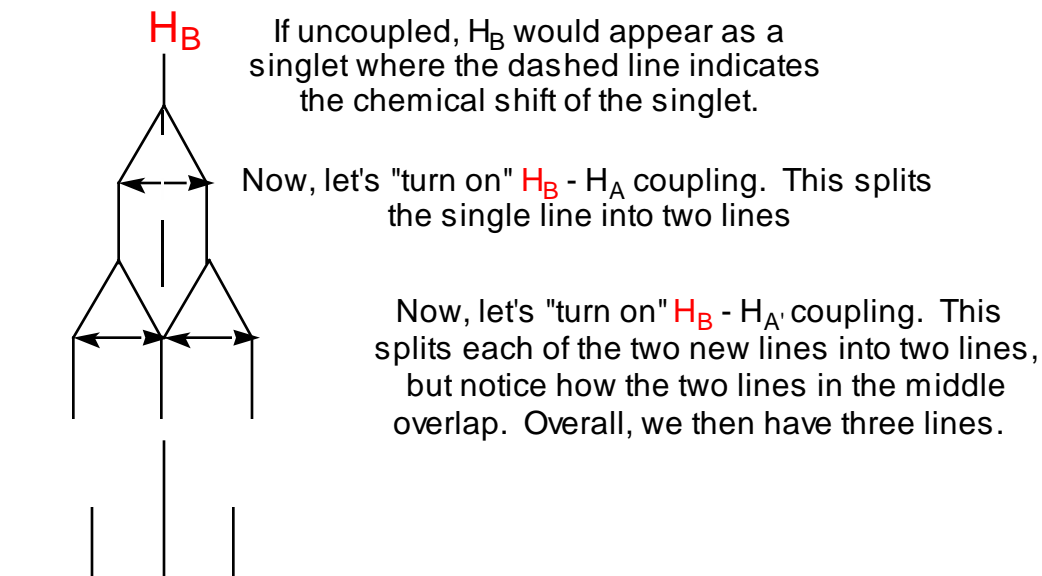
Because the two lines in the middle overlap, that line is twice as big as the lines on the outside. More neighboring protons leads to more lines as shown on the next slide.

If a proton has n neighboring protons *that are equivalent,* that proton will be split into n+1 lines. So, if we have four equivalent neighbors, we will have five lines, six equivalent neighbors… well, you can do the math. The lines will not be of equal intensity, rather their intensity will be given by **Pascal's triangle** as shown below.

Splitting Patterns with Multiple Neighboring Protons

no. of neighbors	relative intensities	pattern	example
0	1	singlet (s)	
1	1 1	doublet (d)	
2	1 2 1	triplet (t)	
3	1 3 3 1	quartet (q)	
4	1 4 6 4 1	pentet	
5	1 5 10 10 5 1	sextet	
6	1 6 15 20 15 6 1	septet	

Chemical Equivalency

All of the protons found in chemically identical environments within a molecule are **chemically equivalent**. They often exhibit the same chemical shift.

The blue protons all come at the same chemical shift and do not split each other

$$H-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-Br$$
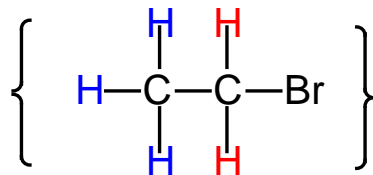
The red protons both come at the same chemical shift and do not split each other
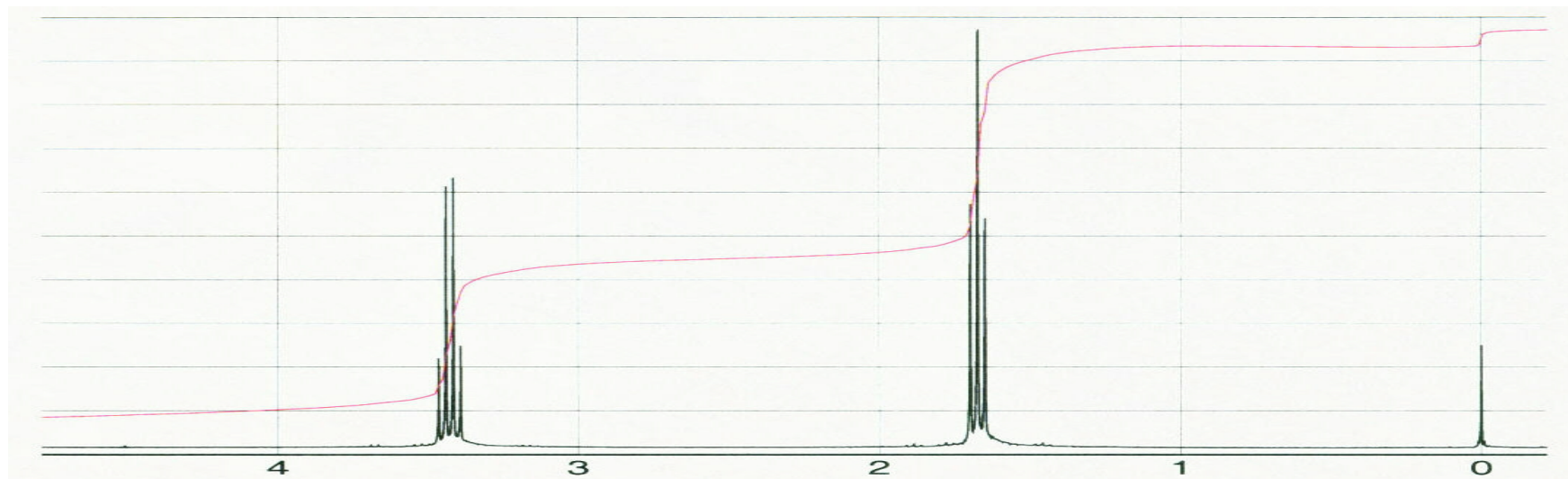
When protons couple to each other, they do so with a certain intensity. This is called the "coupling constant." Coupling constants can vary from 0 Hz (which means that the protons are not coupled, even though they are neighbors) to 16 Hz.

Second Order Coupling

H_M H_A H_X

Coupling constant H_A- H_X = 12
Coupling constant H_A- H_M = 6

H_A If uncoupled, H_A would appear as a singlet where the dashed line indicates

12 Hz   Now, let's "turn on" H_A - H_X coupling. This splits the single line into two lines that are 12 Hz apart

6 Hz   6 Hz   Now, let's "turn on" H_A - H_M coupling. This splits each of the two new lines into two lines that are 6 Hz appart for a total of four lines

If the protons are not equivalent, they can have different coupling constants and the resulting pattern will not be a triplet, but a "doublet of doublets." Sometimes, nonequivalent protons can be on the same carbon as described on the next slide.

The coupling of *trans* protons to each other is typically very large, around 16 Hz, while the coupling of *cis* protons, while still large, is a little smaller, around 12 Hz. This leads to the pattern shown below, and an example of a molecule with this splitting pattern is shown on the next slide.
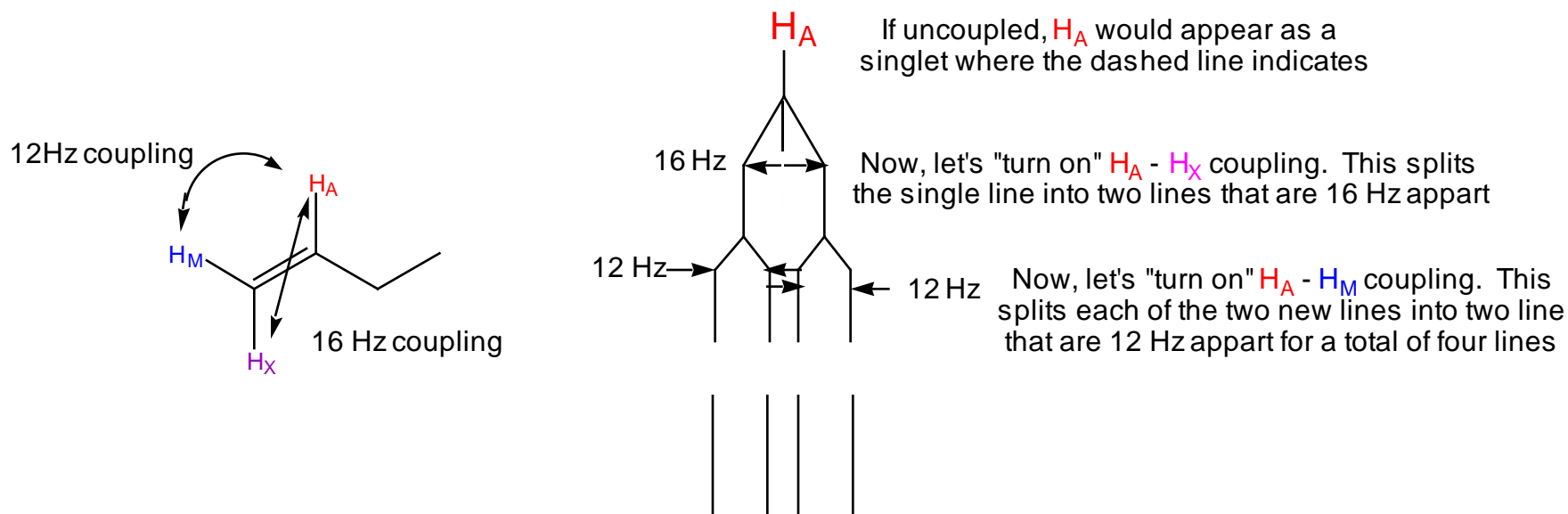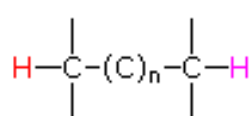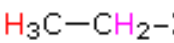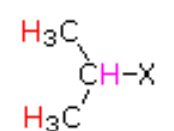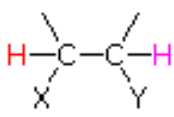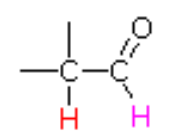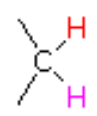
A molecule with a terminal alkene
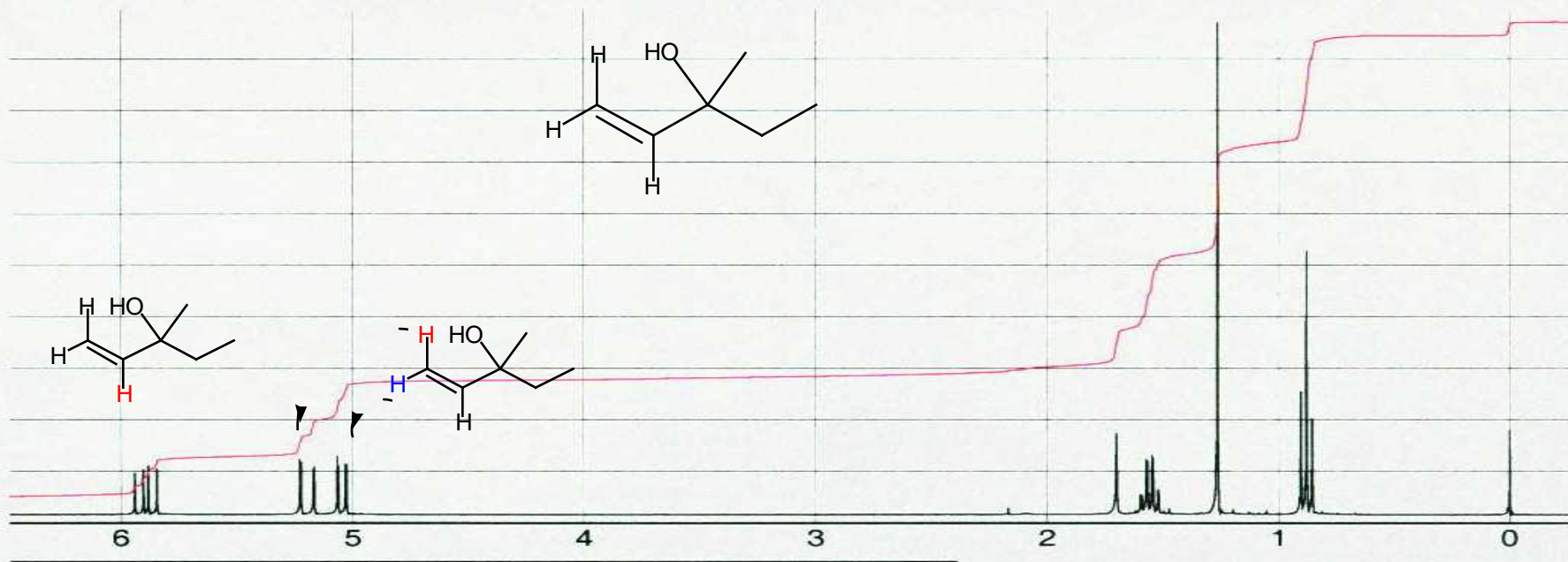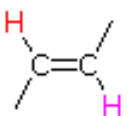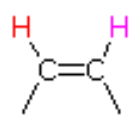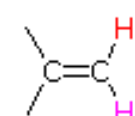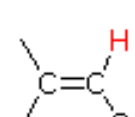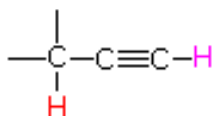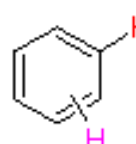
A molecule with a nine line splitting pattern
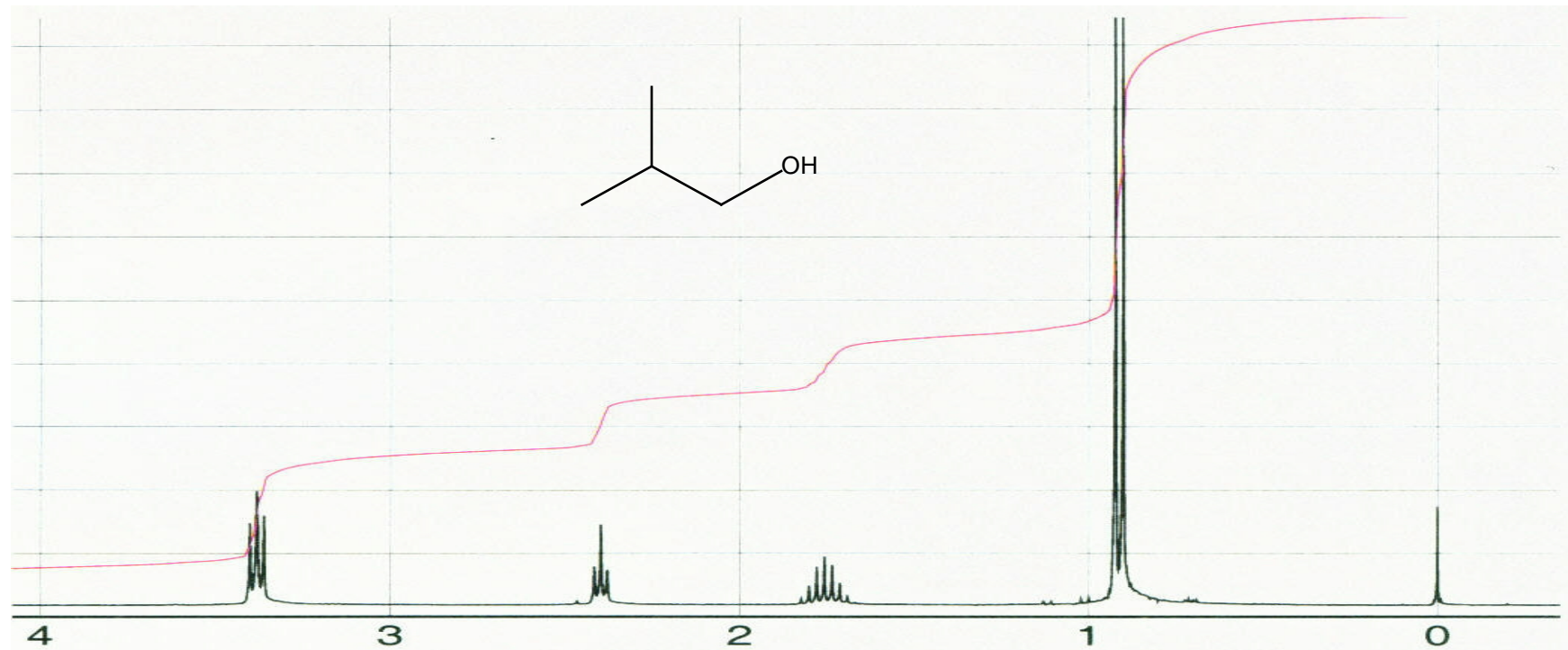
Magnitude of some typical coupling constants

Karplus equation

Application of Karplus equation
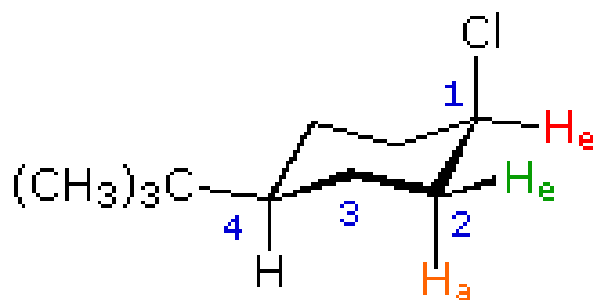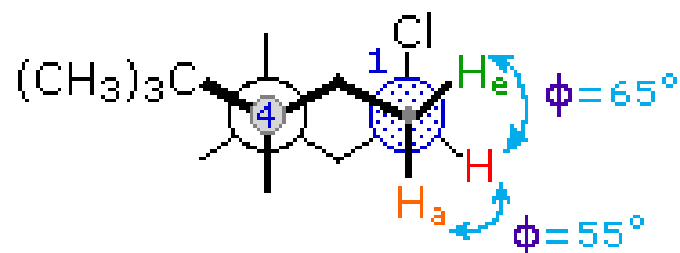
$J_{ee} = 3.5 \text{ Hz}$ $J_{ea} = 4.0 \text{ Hz}$

cis-4-tert-butyl-1-chlorocyclohexane
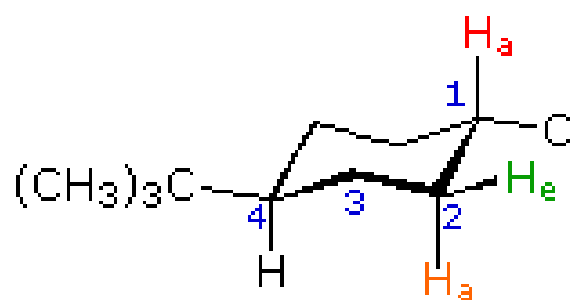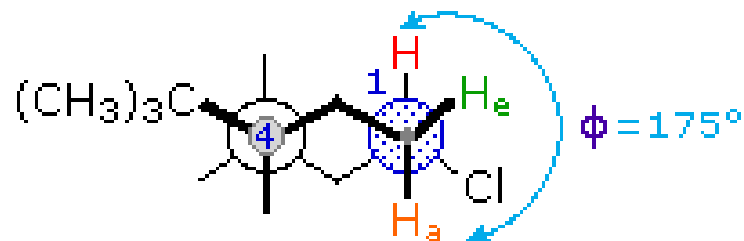
$J_{aa} = 12.0 \text{ Hz}$

trans-4-tert-butyl-1-chlorocyclohexane

Using Vicinal Coupling to establish isomer

Ha

J_{ab}

J_{ad}

J_{ac}

Ha

R   1

OH

Hc

Hd

Hb
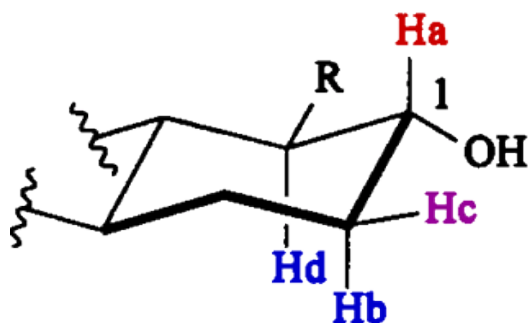
$J_{ab} = J_{ad} = 11$ Hz

$J_{ac} = 4$ Hz
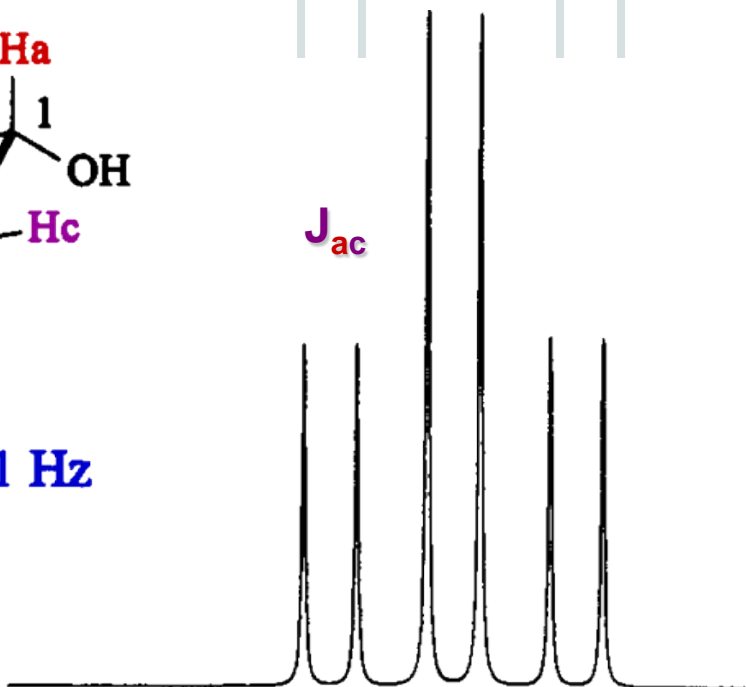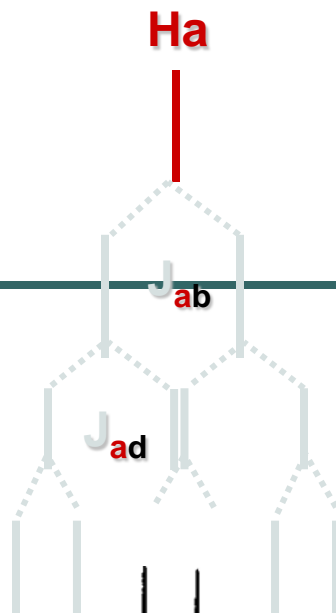
Long Range coupling

$$H-C=C=C-H$$
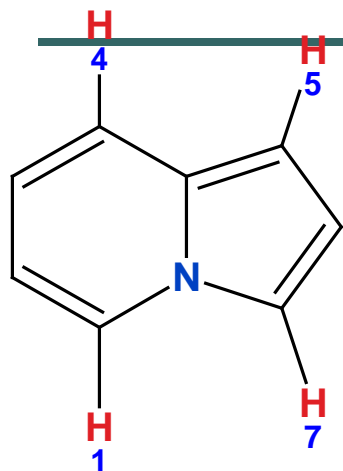
$$^4J_{H-H} = 9 \text{ Hz}$$

$^4J_{H1-H3} = 1.07$ Hz
$^5J_{H1-H4} = 1.21$ Hz
$^5J_{H1-H5} = 0.95$ Hz
$^5J_{H4-H7} = 0.67$ Hz

$$H-C=C=C-C-H$$

$$^5J_{H-H} = 3 \text{ Hz}$$

$$H-C\equiv C-C-H$$

$$^4J_{H-H} = 3 \text{ Hz}$$

$^4J_{H-H} = 1\text{-}2$ Hz

$$H-C-C\equiv C-C-H$$
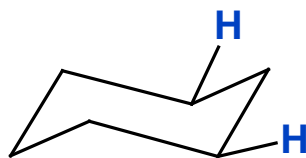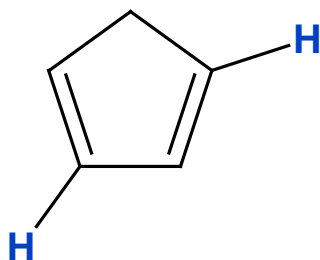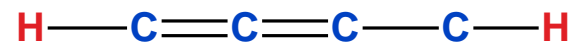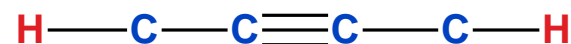
$$^5J_{H-H} = 3 \text{ Hz}$$

$^4J_{H-H} = 1.1$ Hz

Nomenclature of proton spin system

1. **Summary of Pople Notations**

- Coupled two-spin systems: AX and AB patterns

- Analyzable three spin systems: AX_2, AB_2, AMX, ABX systems.

2. **A popular classification system that assigns protons to one of three types**:

- 1. homotopic

- 2. enantiotopic

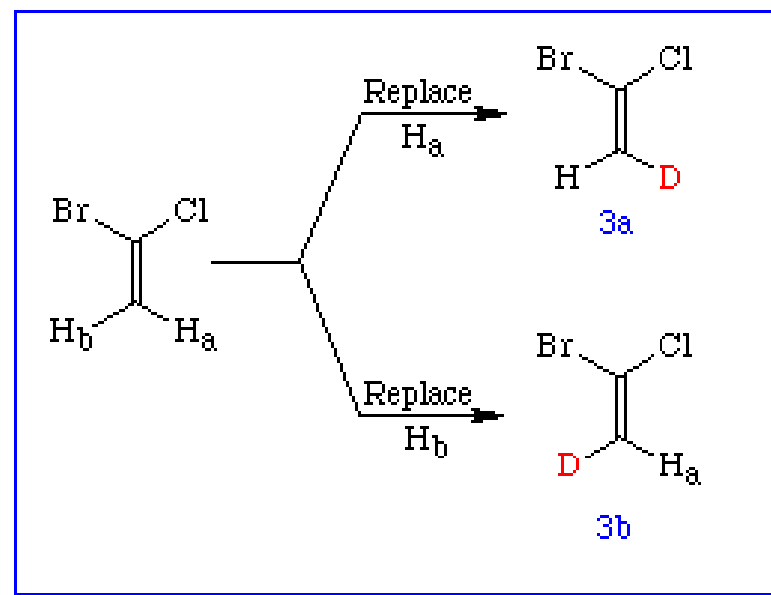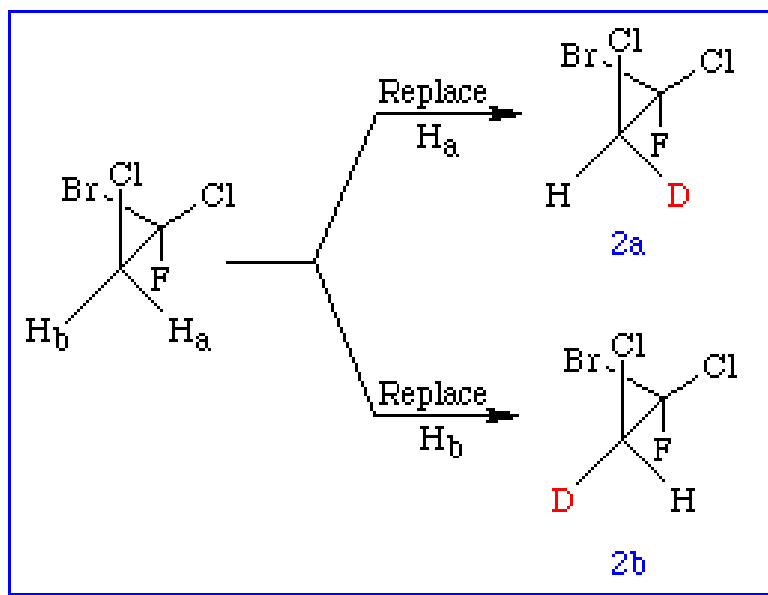- 3. diastereotopic.

Homotopic Hydrogens

- Identical protons
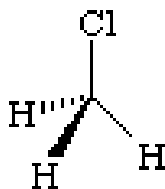
Enantiotopic Hydrogens
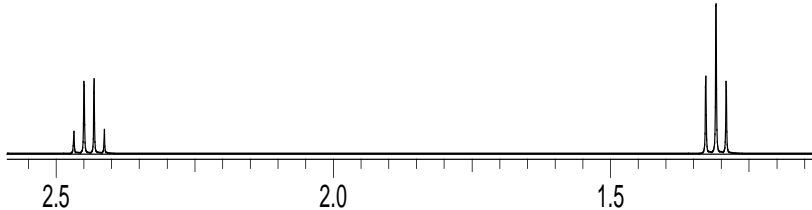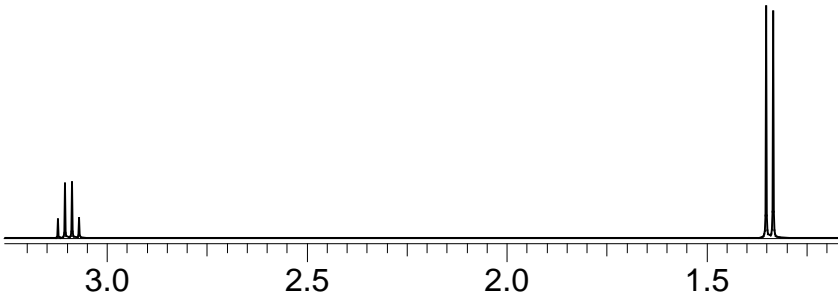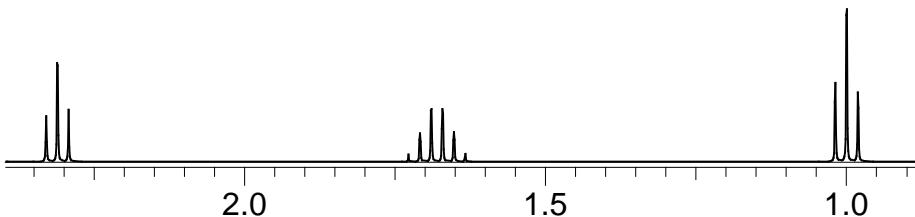
- Not Identical, but have the same chemical shift
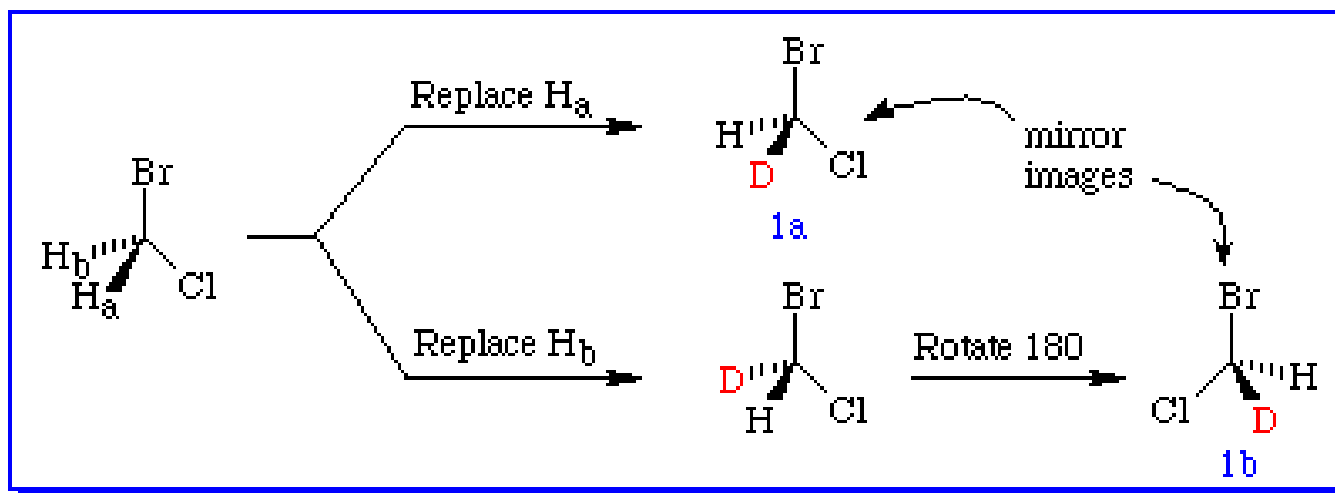
Diasteretopic Hydrogens

- When the replacement procedure described above generates two compounds that are diastereomers, the two hydrogen atoms that were replaced are classified as diastereotopic. They have different chemical shifts.
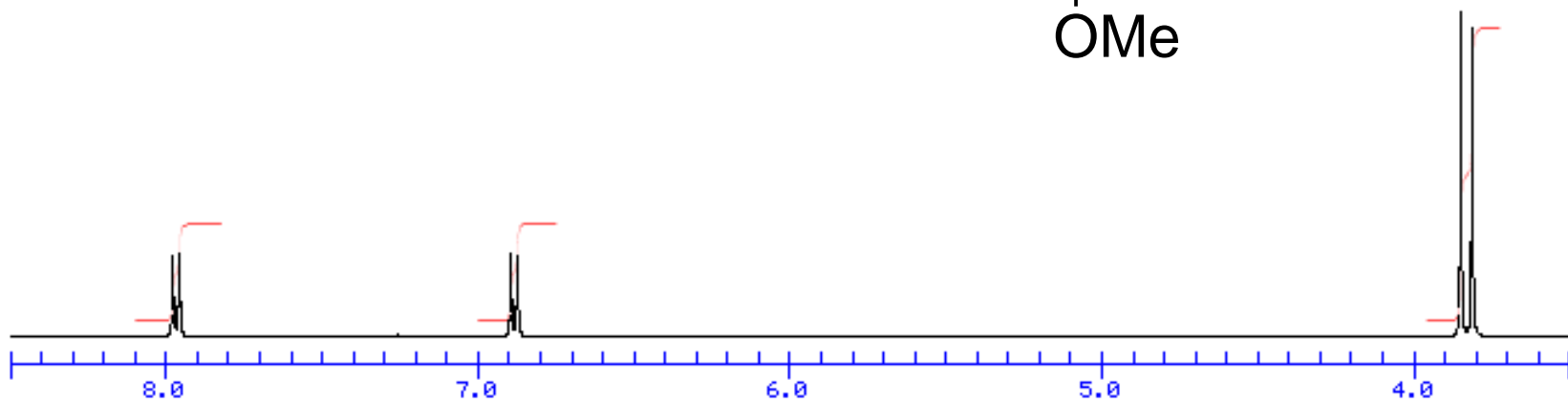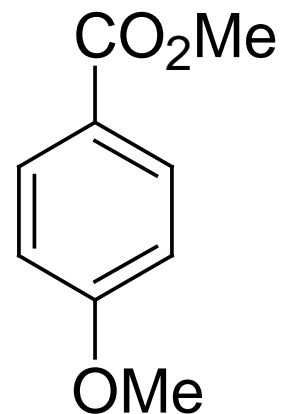
For examples of diastereotopic protons, see Notre Dame problems 8 and 18.

Spin System in Pople notation

Structural Unit	Spin system	Partial spectrum
$-CH_2-CH_3$	A_3X_2	
$-CH-CH_3$	A_3X	
$CH_2-CH_2-CH_3$	$A_3M_2X_2$	

AX spin system

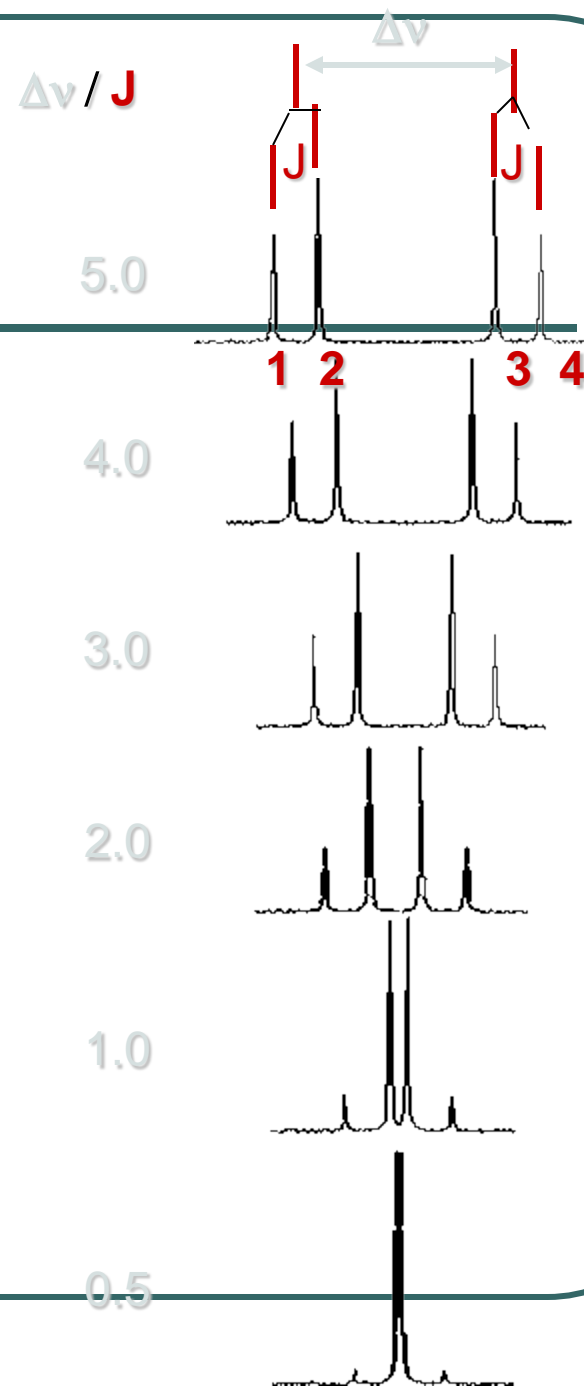- *p*-Meoxy-Methyl benzoate

Second Order spectra: AB instead of AX

As the difference in shift become smaller- compare with the size of the coupling the outer peaks become smaller in intensity

ν_A and ν_B : center of gravity of doublet
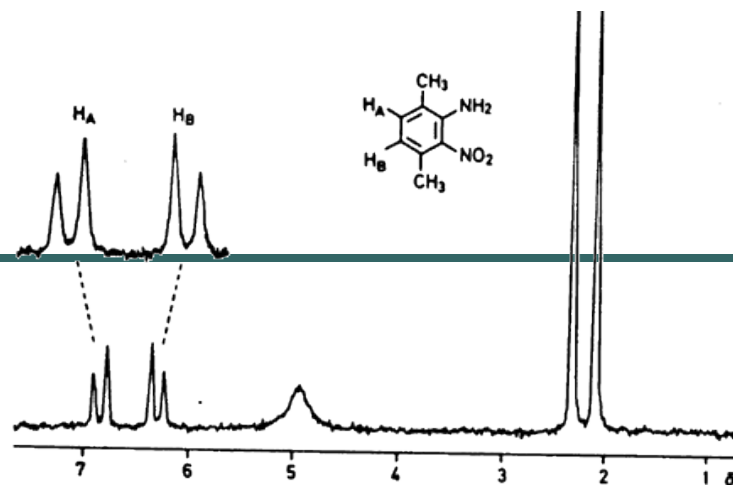Chemical shift

$\Delta\nu = \sqrt{(1\text{-}4) * (2\text{-}3)}$

$\Delta\nu$ / **J**

$\Delta\nu$

5.0

1 2   3 4

4.0

3.0

2.0

1.0

0.5

AB-Spectra

Figure 5.4 ^{1}H n.m.r. spectrum of 1-amino-3,6-dimethyl-2-nitrobenzene at 60 MHz
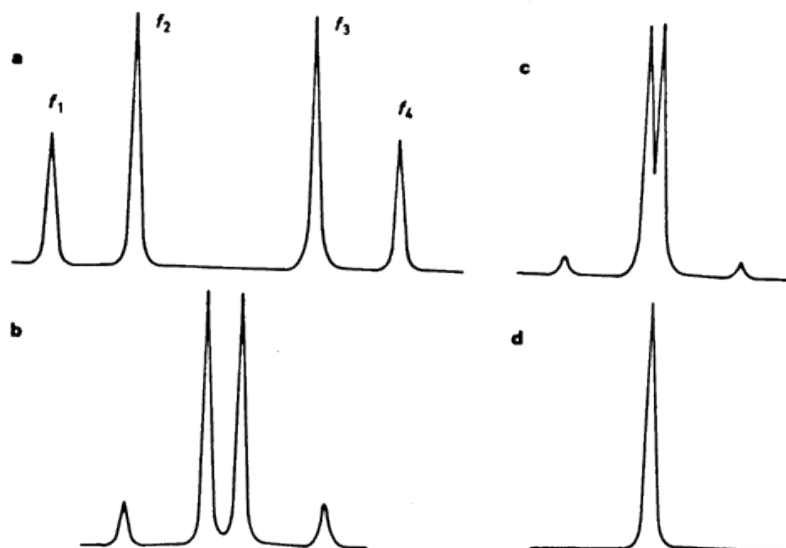

Figure 5.5 Dependence of the AB system on the ratio $J/\nu_0\delta$; spectra illustrated are for values of $J/\nu_0\delta$ of (a) 1:3, (b) 1:1, (c) 5:3, and (d) 5:1.
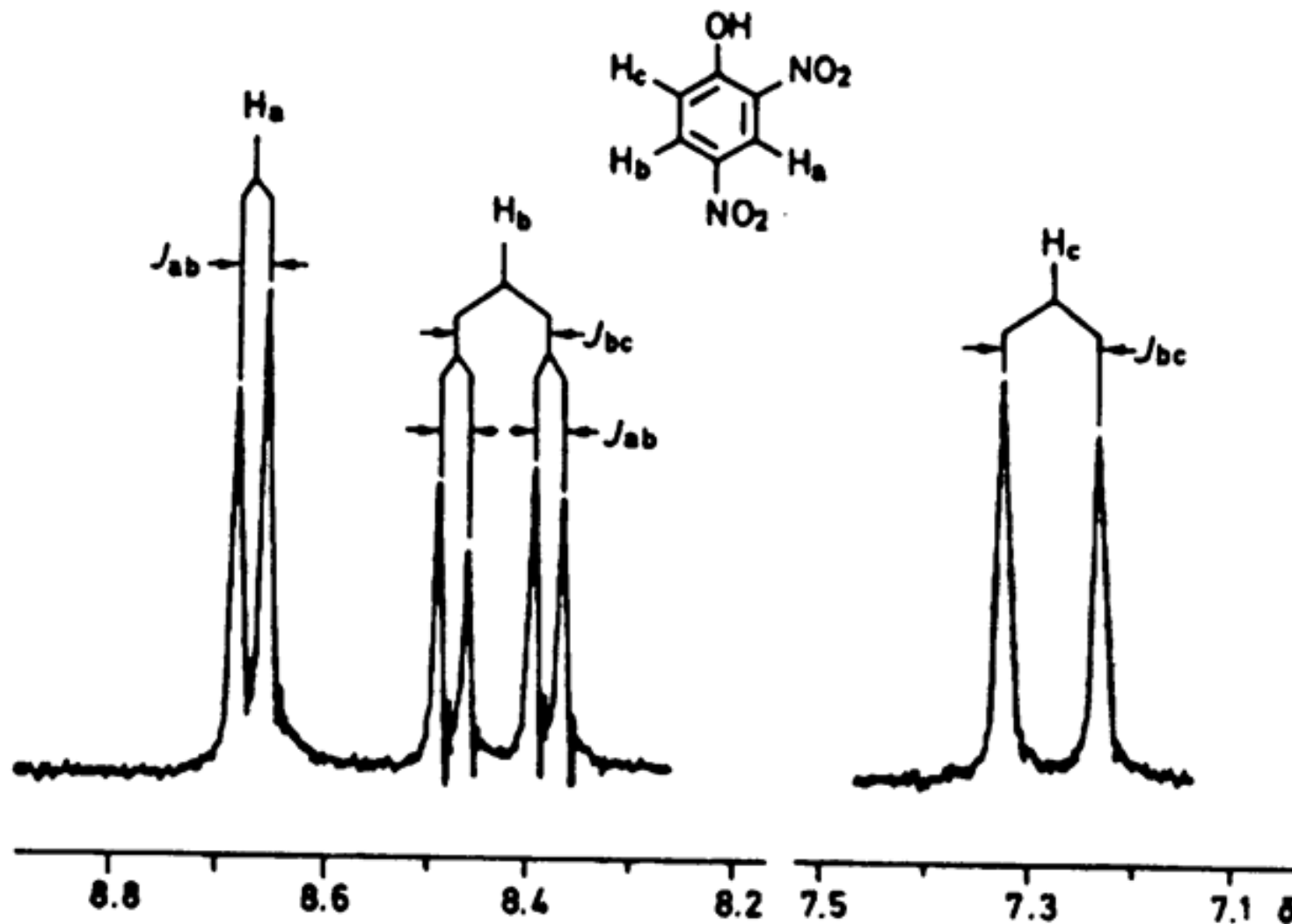
AMX

Figure 2.14 Signal splitting due to spin–spin coupling in the 100 MHz proton magnet resonance spectrum of 2,4-dinitrophenol. One finds $J_{bc} = 9.1$ Hz and $J_{ab} = 2.8$ Hz. J_{ac} is no observed (rule 4)
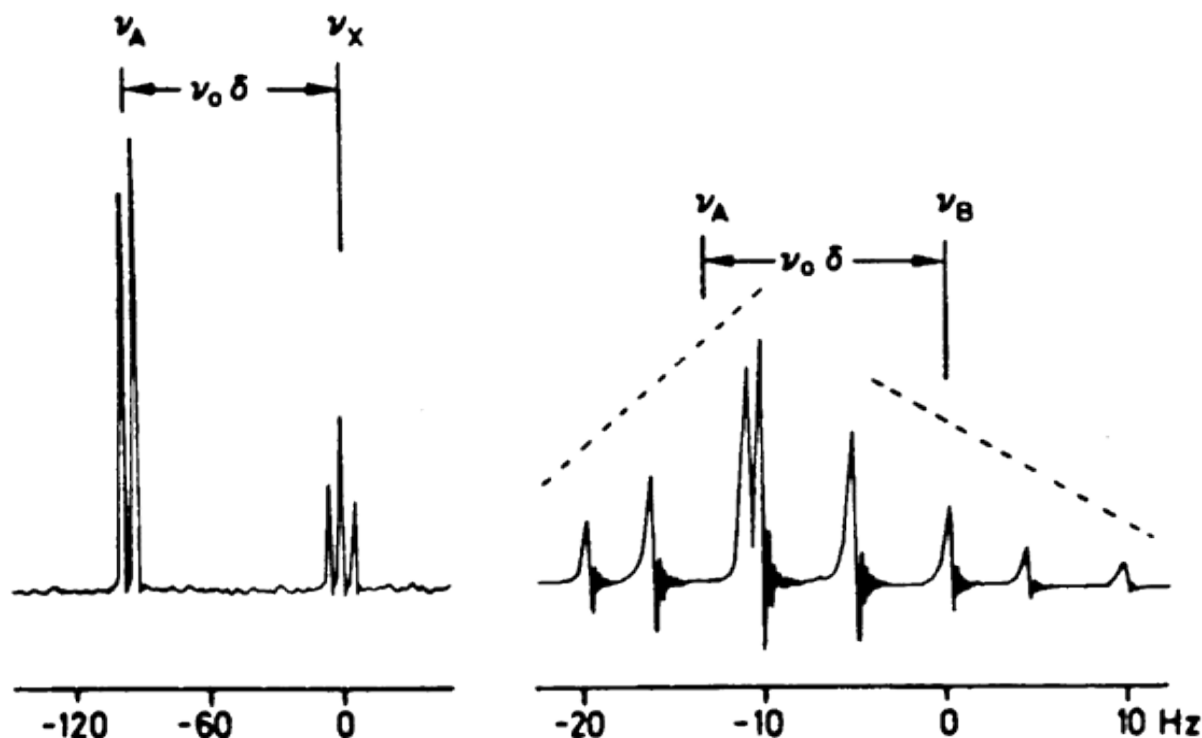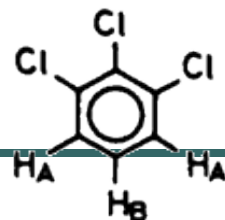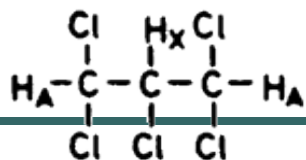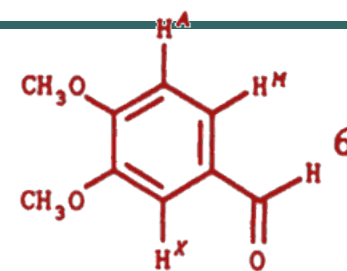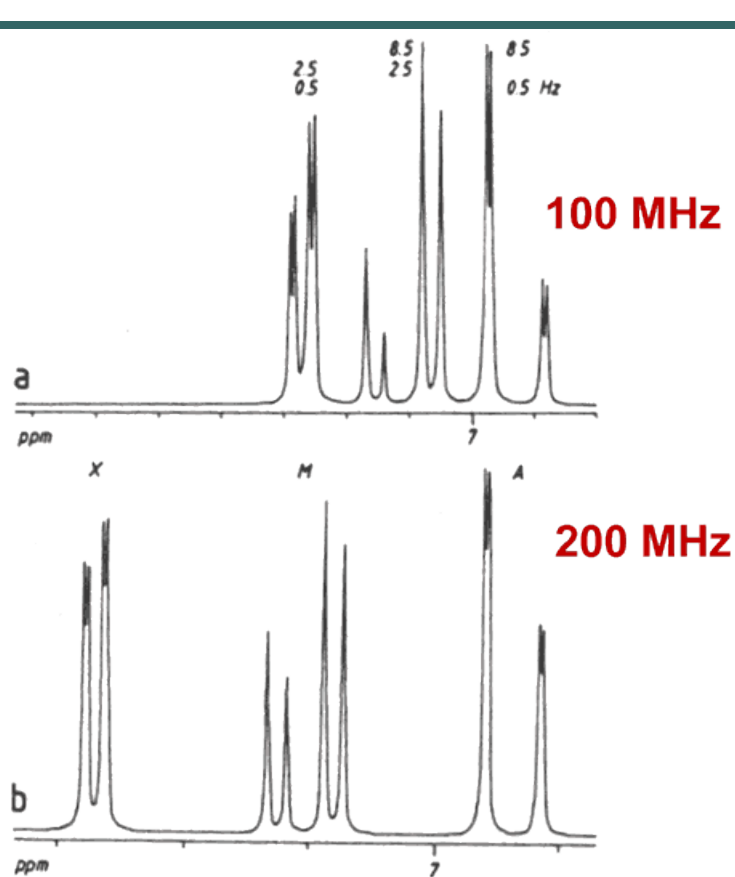
A$_2$X and A$_2$B

Figure 2.22 Proton magnetic resonance spectrum of 1,1,2,3,3-pentachloropropane and 1,2,3-trichlorobenzene. The ratio $J/v_0\delta$ in the first case is 0.06 and in the second it is 0.7; number of lines increases from five to eight

AMX

100 MHz

200 MHz

$^3J_{AM} = 8.5$ (ortho)
$^4J_{MX} = 2.5$ (meta)
$^5J_{AX} = 0.8$ (para)

6

7

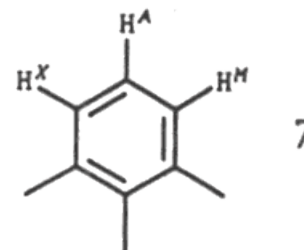Fig. 2.7. ^1H NMR spectrum of 3,4-dimethoxybenzaldehyde (6) [aromatic shift range, CDCl$_3$, 25 °C, (a) 100 MHz (b) 200 MHz]