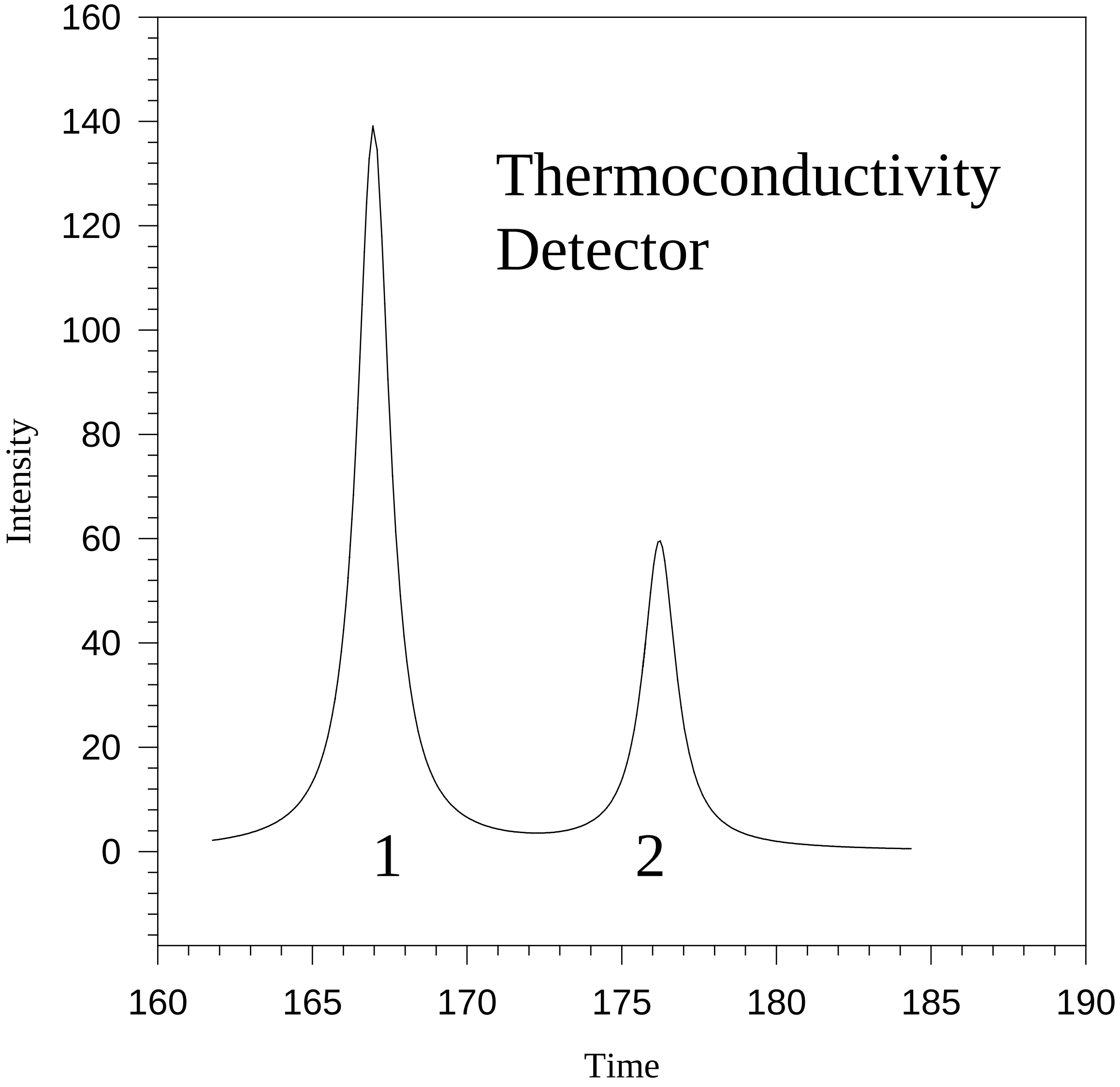
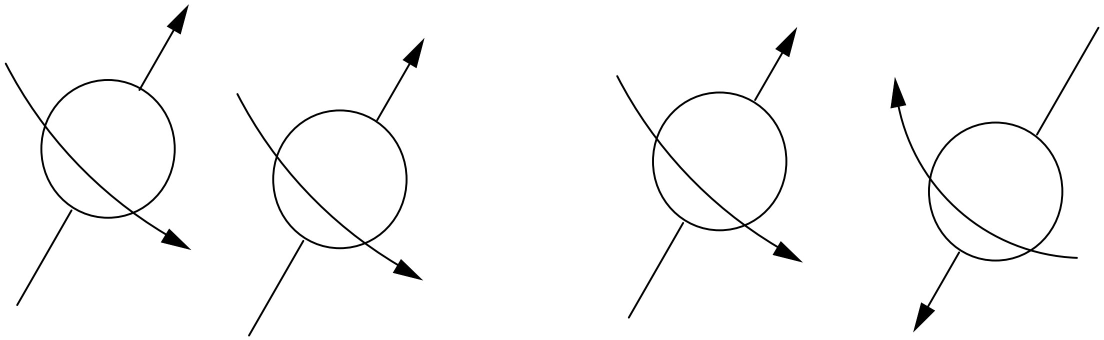
^{1}H Nuclear Magnetic Resonance

Gas Chromatograph of Molecular Hydrogen at –100 °C



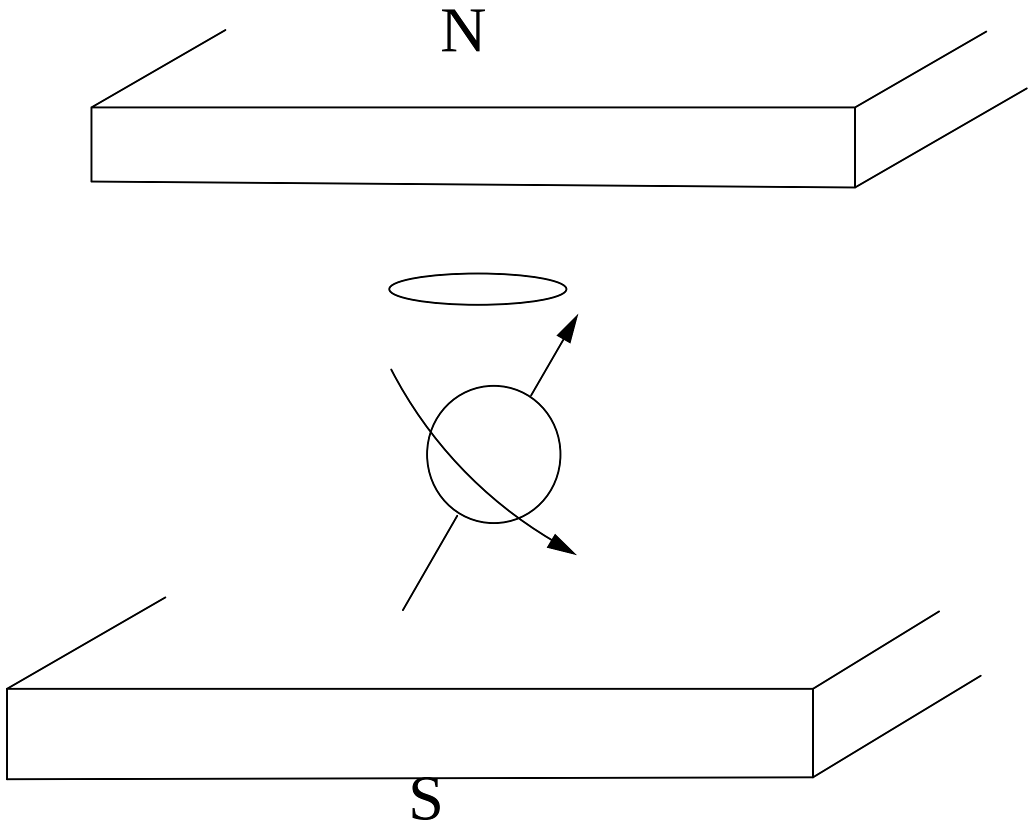
Whats going on?



Ortho Hydrogen Para Hydrogen

O/P = 1:1 at 80 K

The magnetic moment of a spinning nucleus is colinear with the axis of spin



For a nucleus with a spin of ±1/2, only two orientations in a magnetic field are allowed. Regardless of the strength of the magnetic fields currently available, only a very slight difference in population exist between the two orientations

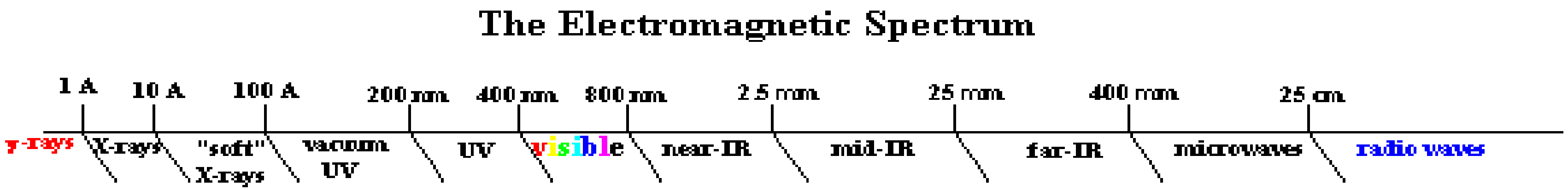
Processional frequency, ν, is proportional to the magnetic field strength, **H**

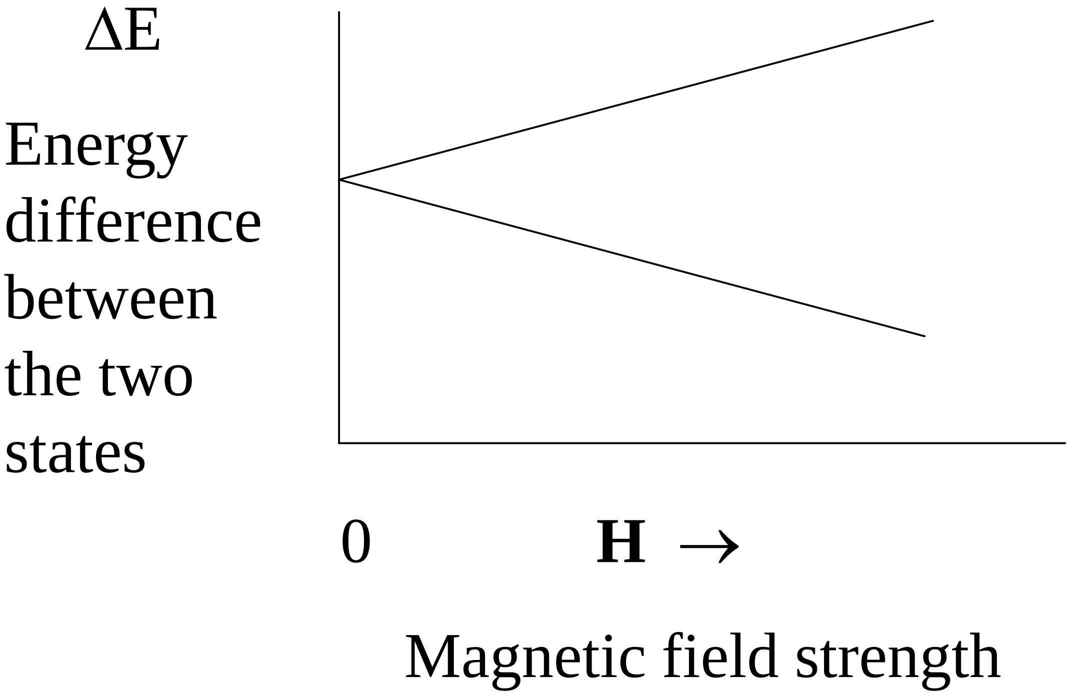
$\nu = \gamma \mathbf{H}$

1 Hz = 1 cycle/second

	For ^{1}H	For ^{13}C
At 14,000 Gauss (1.4Tesla)	ν = 60 MHz	ν = 14 MHz
At 70,500 Gauss (7.05 Tesla)	ν = 300 MHz	ν = 70 MHz
At 141000 Gauss (14.1 Tesla)	ν = 600 MHz	ν = 140 MHz

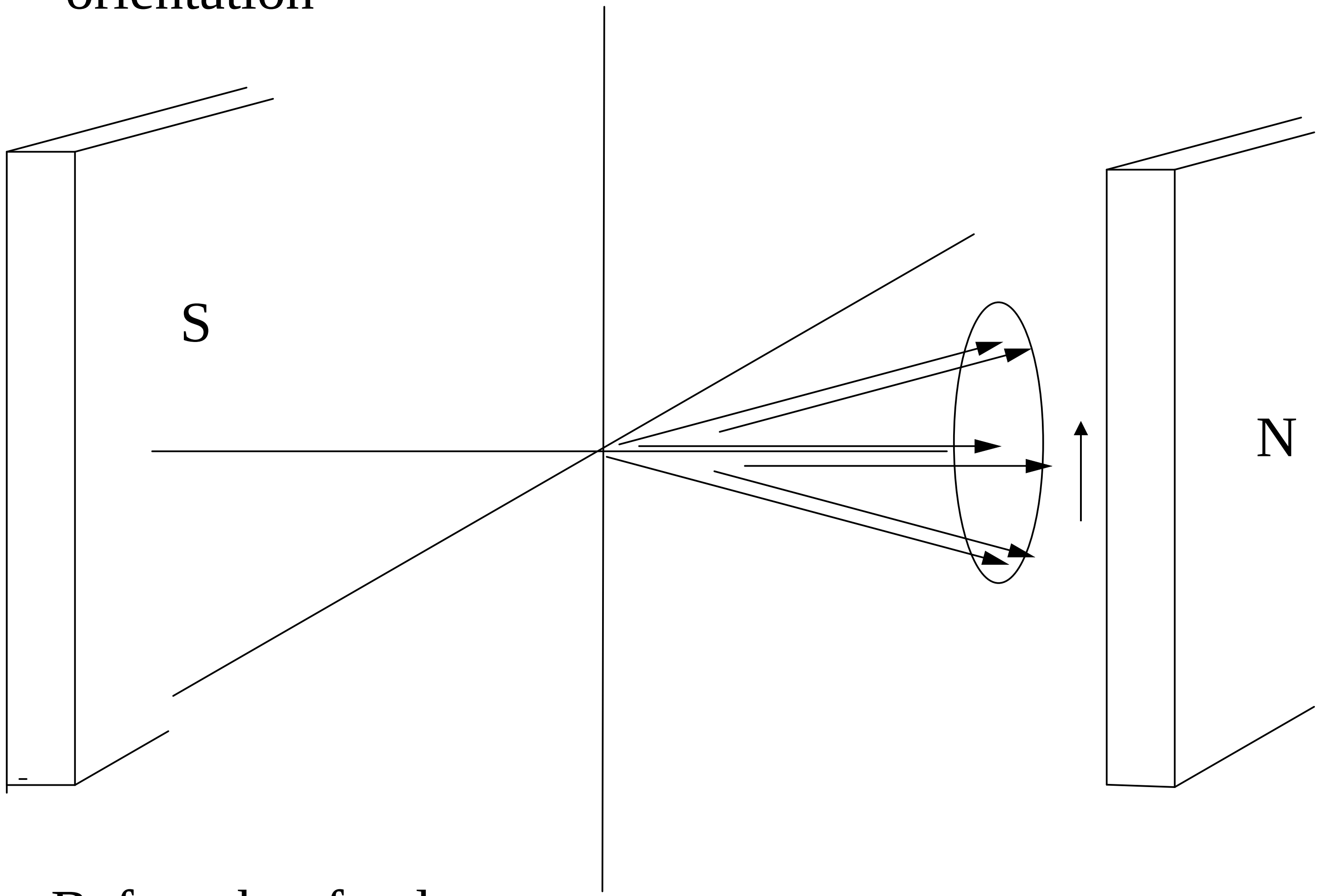
$c = \lambda\nu$; $\lambda = 3*10^{10}$ cm sec^{-1}/600*10^{6} sec^{-1} = 50 cm





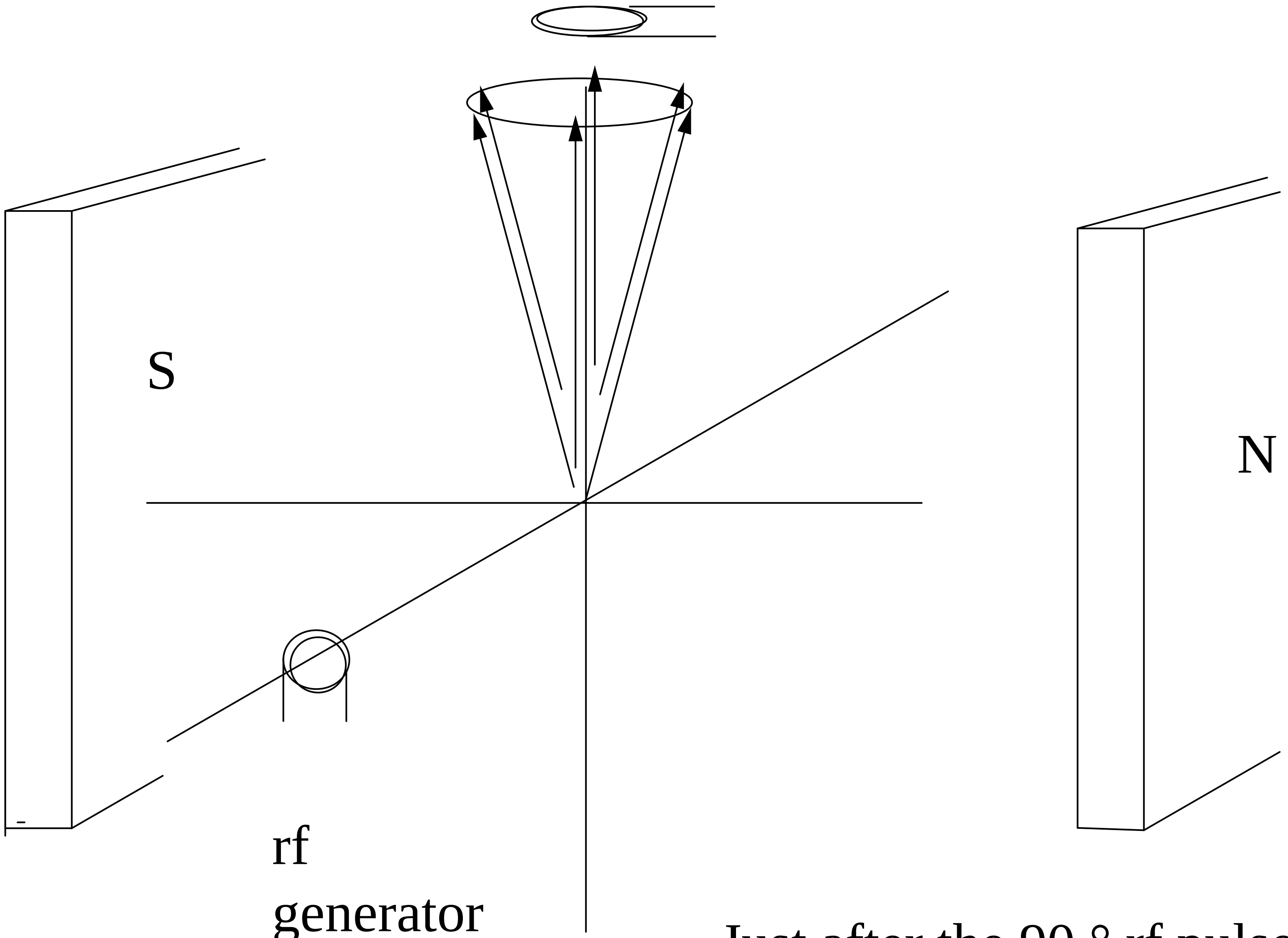
If a nucleus experiences a different magnetic field it will precess at a different frequency and absorb at a different frequency (E = hν)

Consider a set of identical excess nuclei with the following orientation



Before the rf pulse

detector coil

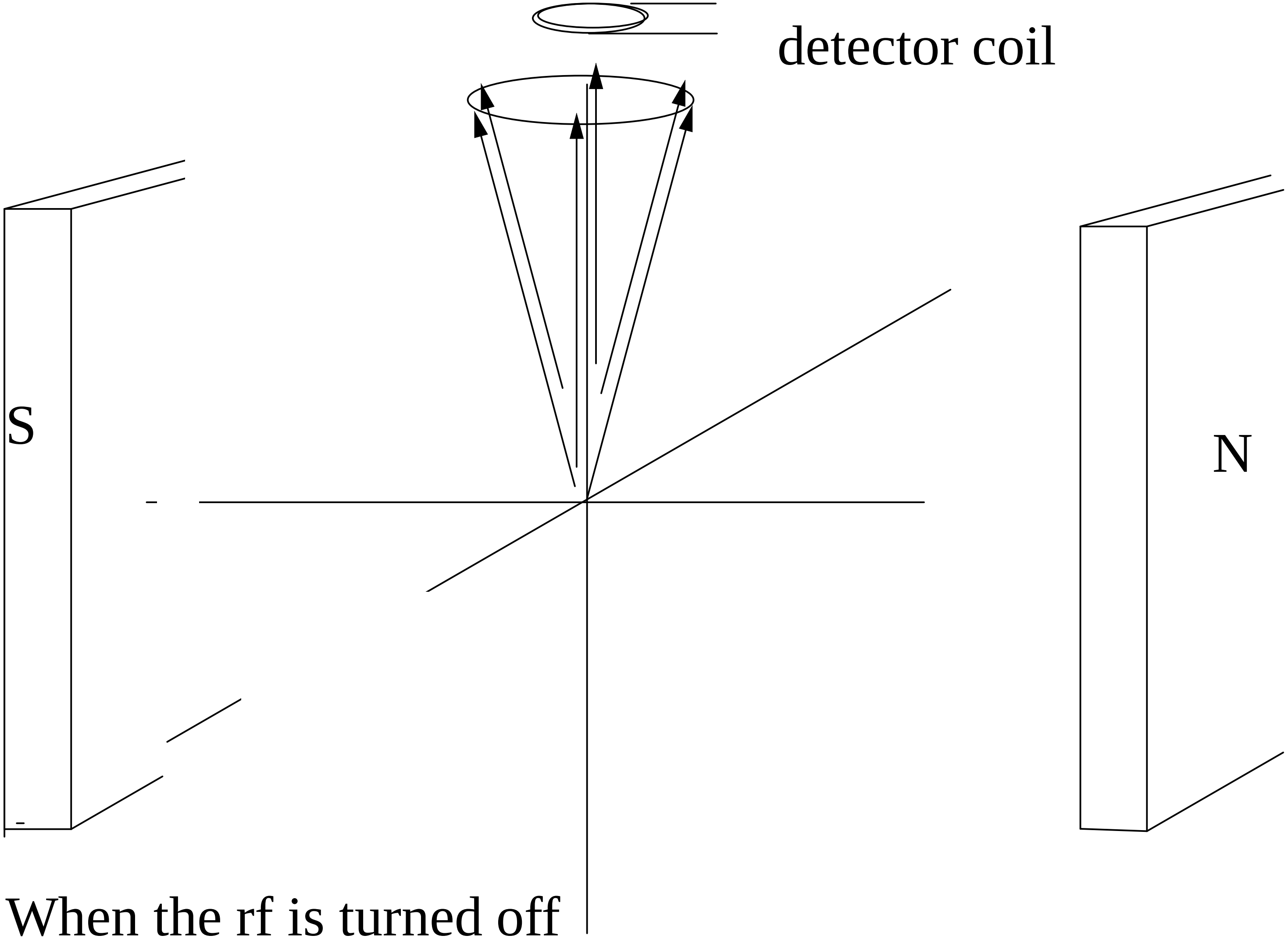


S

N

rf
generator

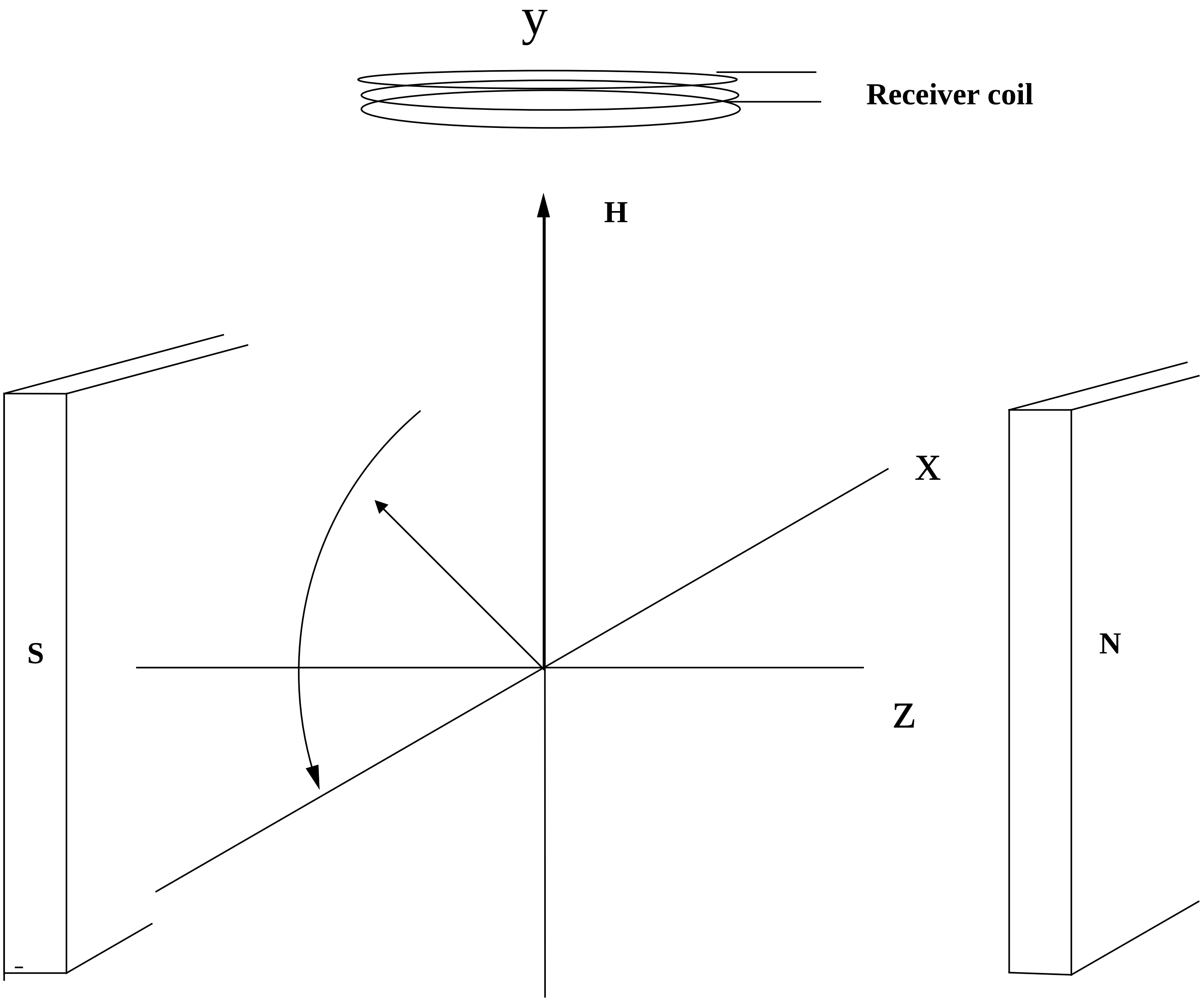
Just after the 90 ° rf pulse



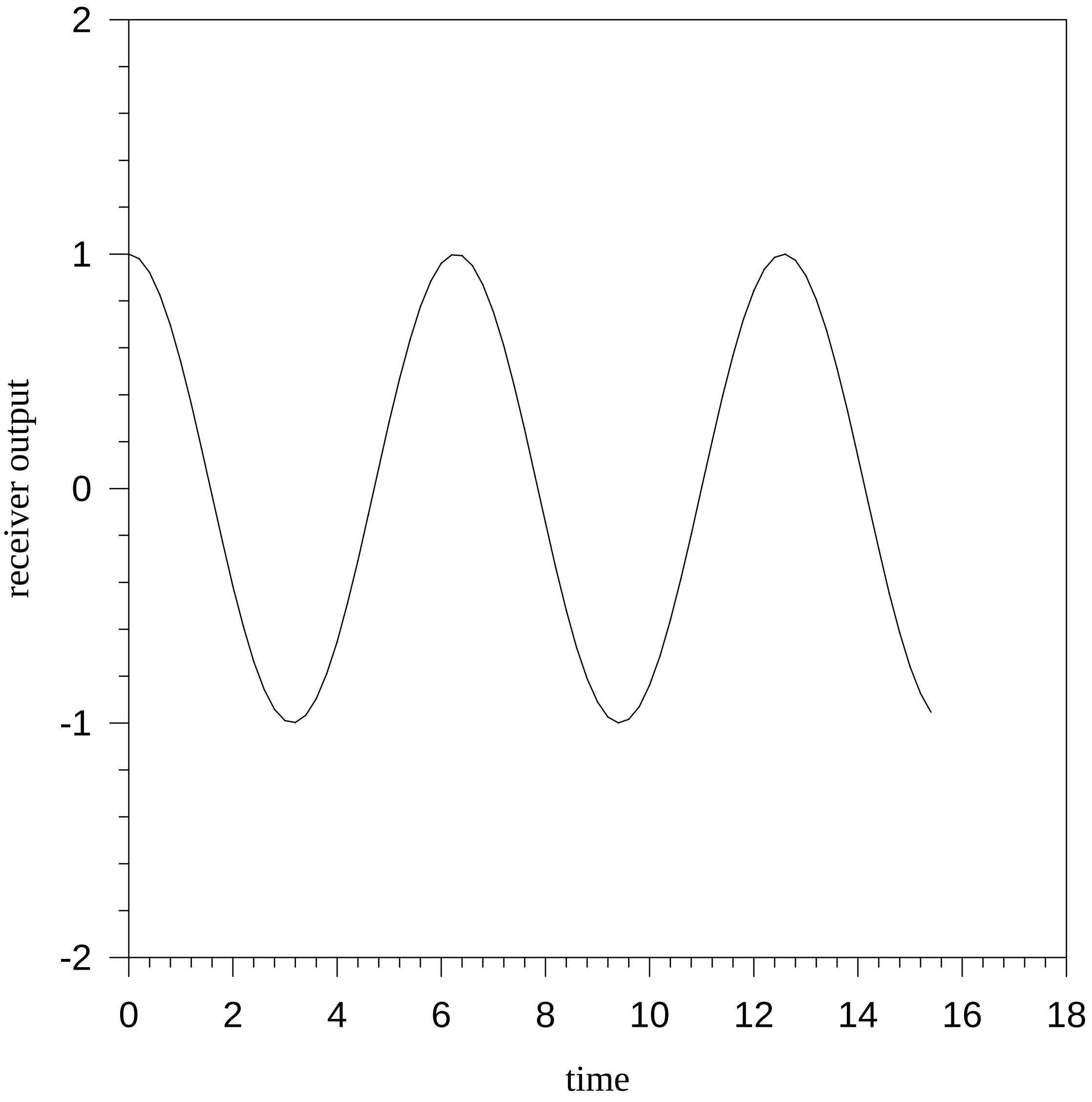
Resultant moment

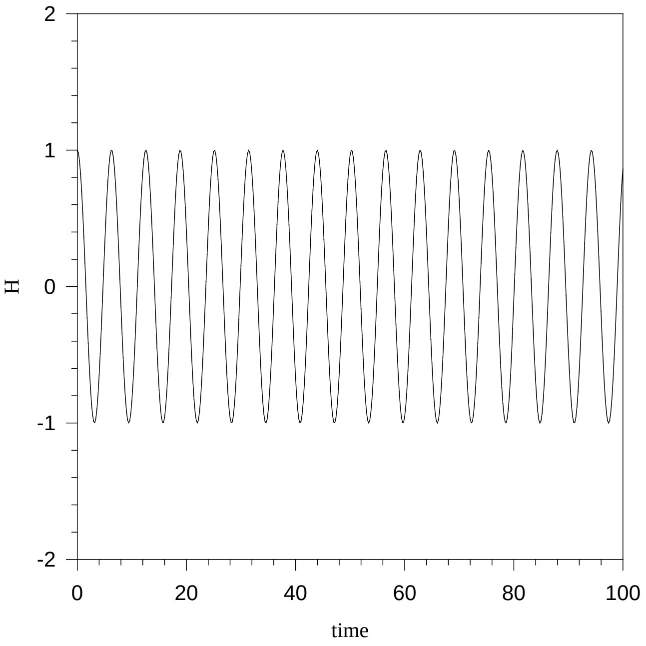
detector coil

When the rf is turned off

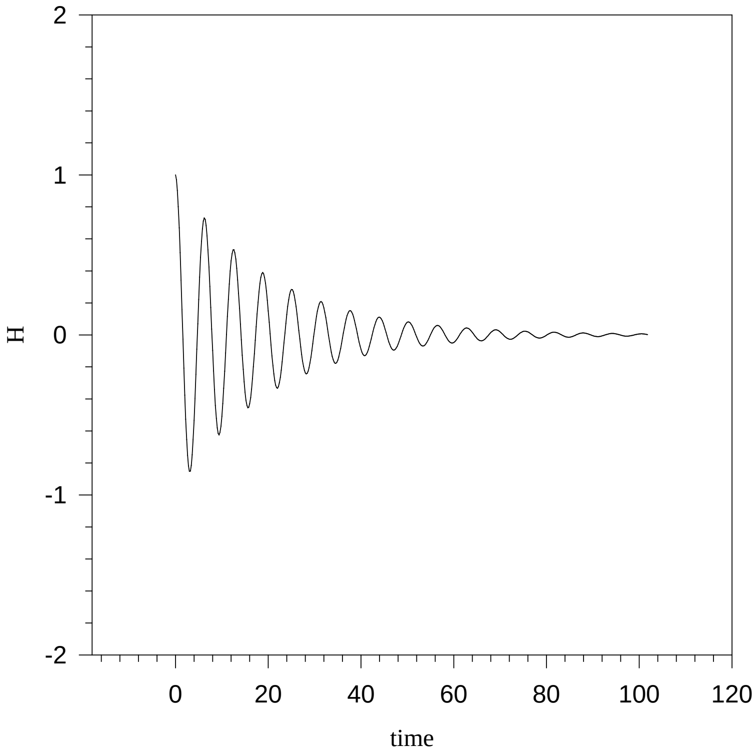

y
Receiver coil
H
X
S
Z
N

Receiver coil output with time



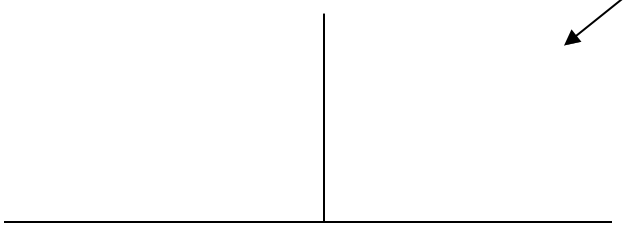


→



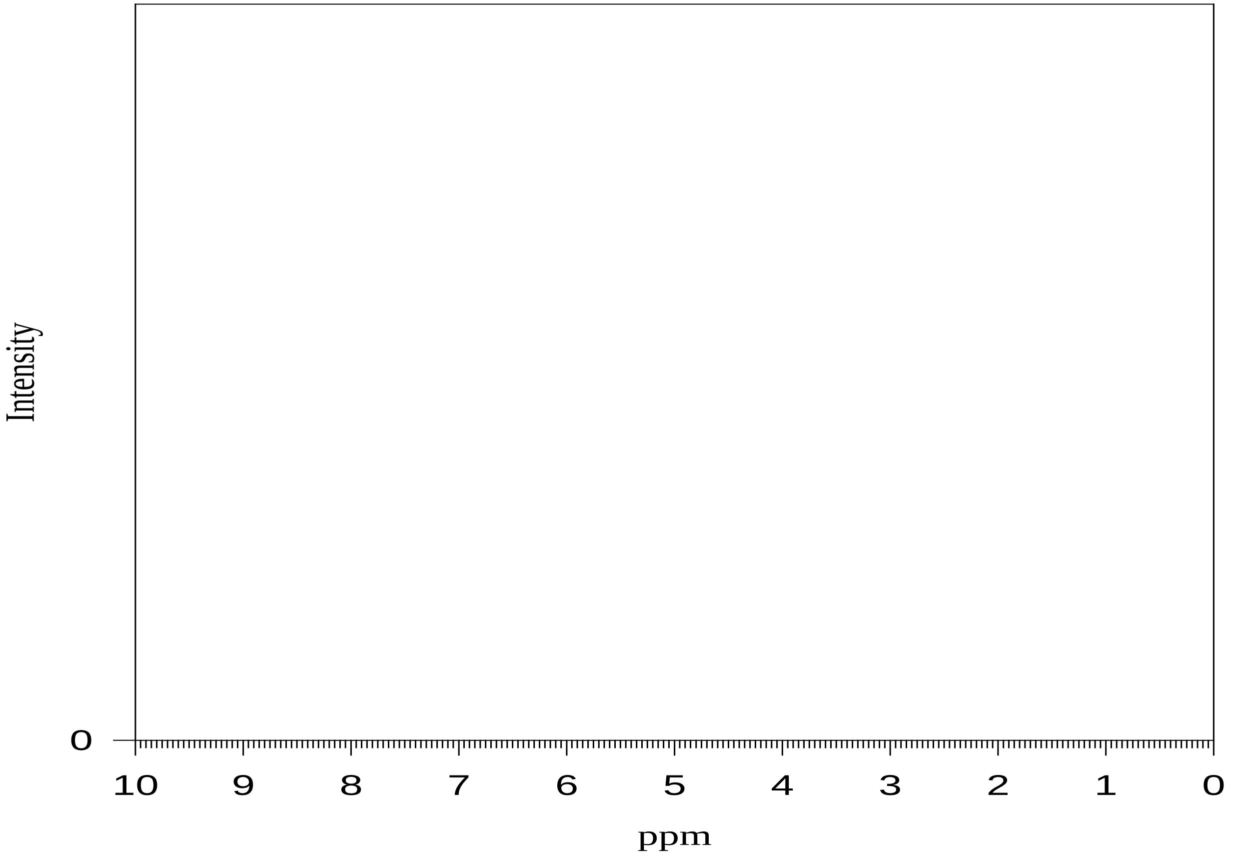
No magnetic inhomogeneity

With magnetic inhomogeneity



Net magnetic moment detected by the detector coil. This signal is converted by the electronics and software to look like an absorption signal via a Fourier transform

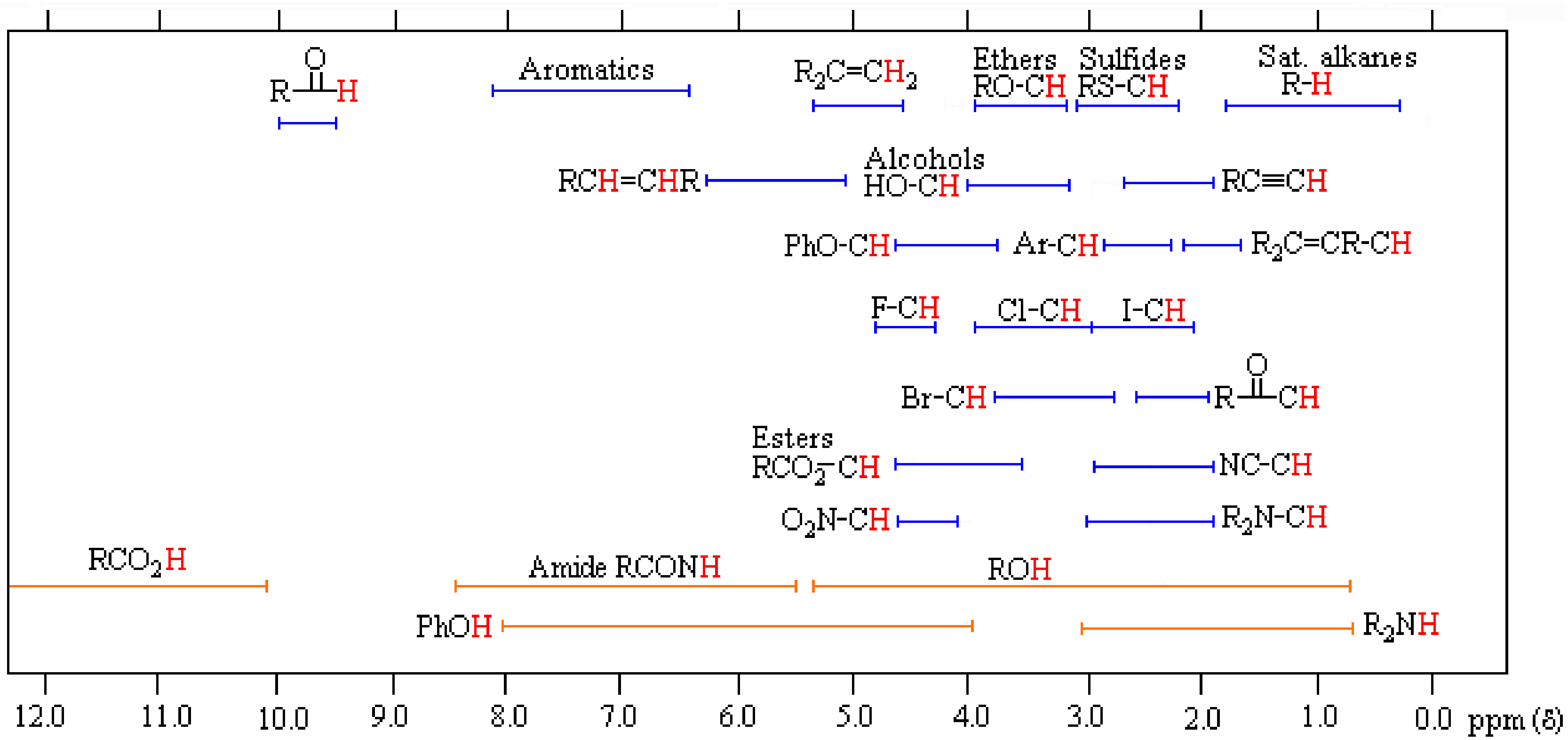
A typical 1H NMR spectrum in frequency reported in parts per million



Since the frequency (cycles/sec) depends on the strength of the magnetic field, chemical shifts are reported relative to a standard, frequently tetramethylsilane (0 ppm). If the spectrum is run at a magnetic field strength that generates precessional frequencies of 300 MHz (300 million cycles per sec, 7.05 Tesla), 1 ppm is equal to 300 Hz (300 cycles per second). At 600MHz, 1 ppm = 600 Hz. Chemical shifts reported in ppm are independent of the field strength (or frequency)

Typical NMR Chemical Shifts

Tetramethylsilane = 0 ppm (standard)



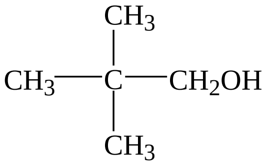
What causes the chemical shift?

The protons are immersed in a sea of electrons which are charged and have both an electric field and a magnetic field associated with their charge.

Information obtained by a NMR spectrum

1. Chemical shift: indicates the type of proton
2. Relative areas: provide a ratio of the number of each type of H nucleus
3. Number of nearest neighbors (first order spectra)

The nmr of 2,2,-dimethylpropanol



$$\mathrm{CH_3}-\overset{\overset{\displaystyle \mathrm{CH_3}}{|}}{\underset{\underset{\displaystyle \mathrm{CH_3}}{|}}{\mathrm{C}}}-\mathrm{CH_2OH}$$

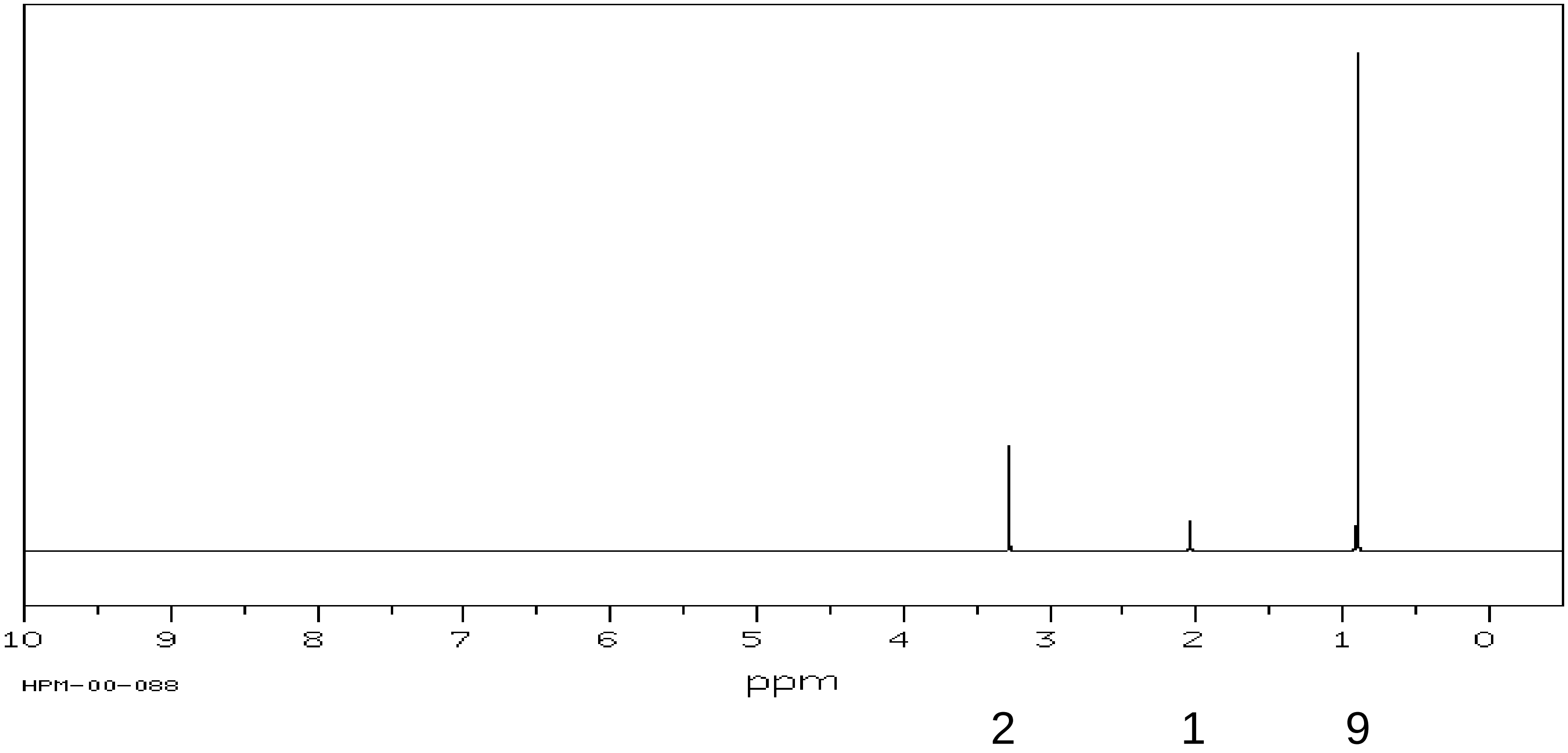
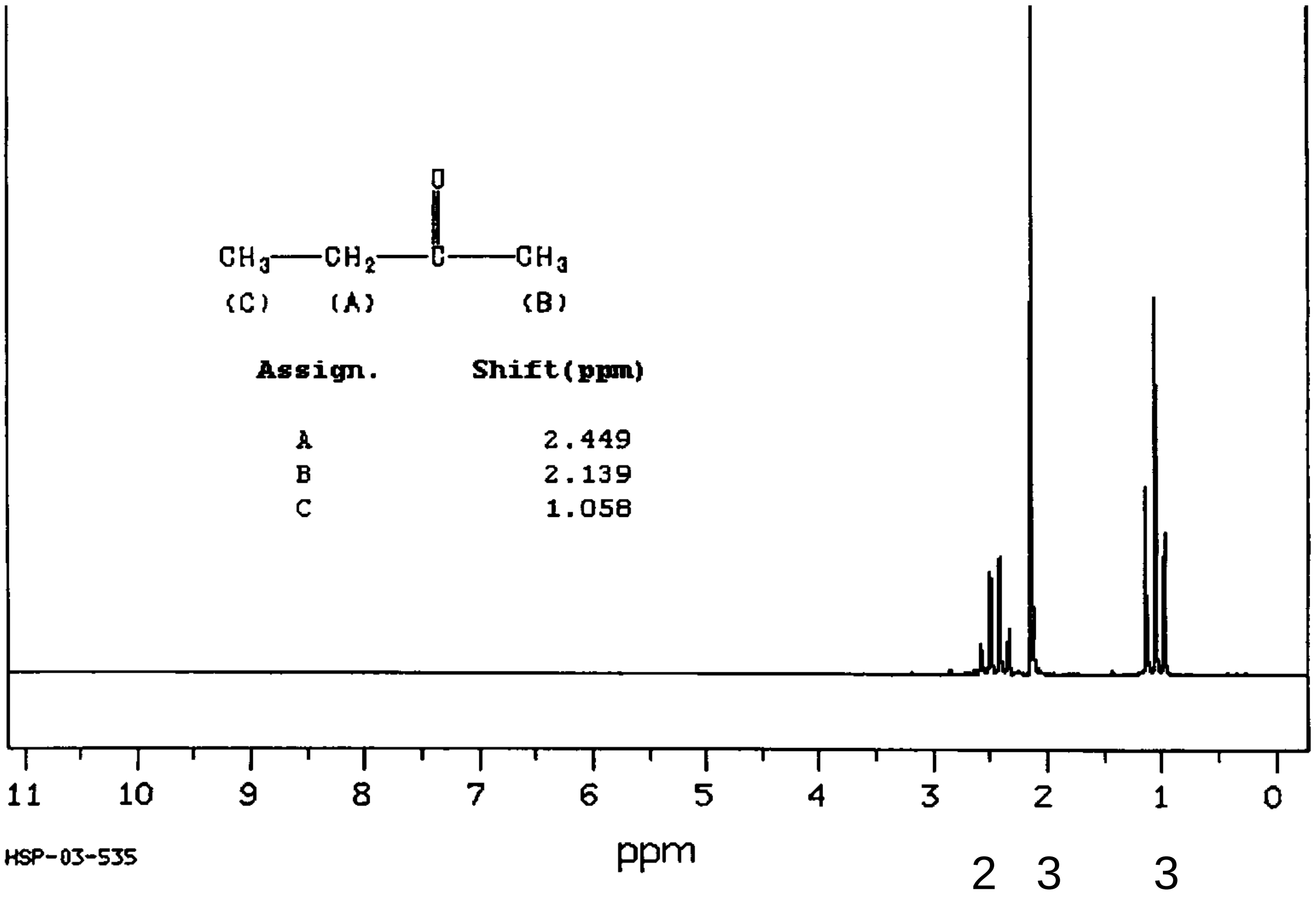
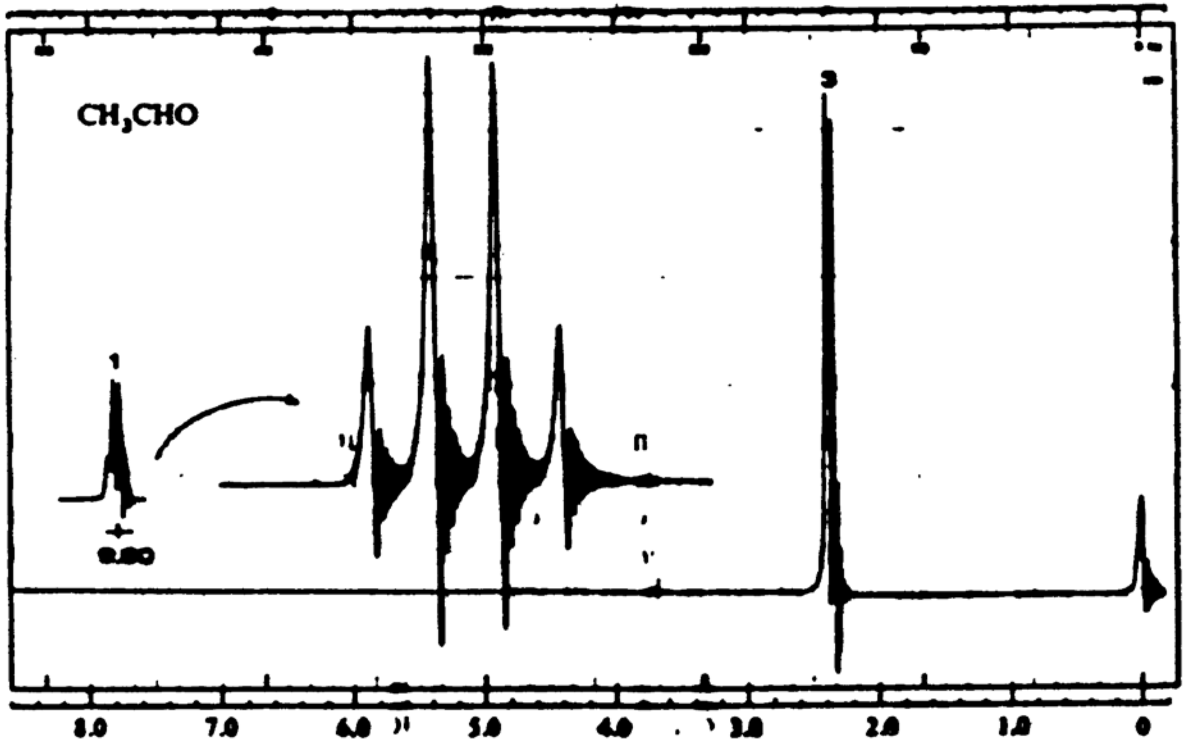


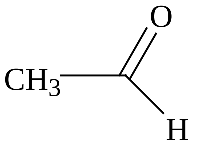
Figure NMR-2. The NMR spectrum of 2,2-dimethylpropanol



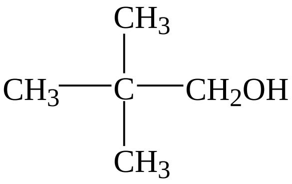
Assign.	Shift(ppm)
A	2.449
B	2.139
C	1.058

Why the multiplicity?





The hydrogens are three bonds removed

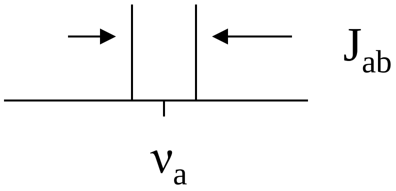


$$CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-CH_2OH$$

The hydrogens are four or more bonds removed

except for the OH

Consider the following:

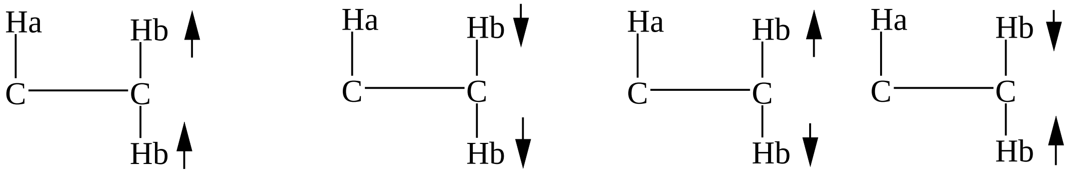


If H_a has a different chemical shift from H_b, roughly 50% of the nuclei of H_b will have one orientation of their magnetic moment and the other will have just the opposite

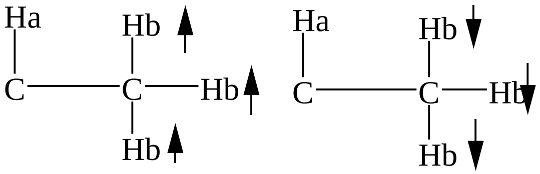
The total field felt by H_a will be due to the external field, the local field due to electronic environment and the field due to the proton(s) three bonds removed. The field due to the local proton will either add or subtract to the total field experience by H_a. Roughly 50% will have a neighbor with a ↑ and 50 % with a neighbor ↓ resulting in two lines observed for H_a

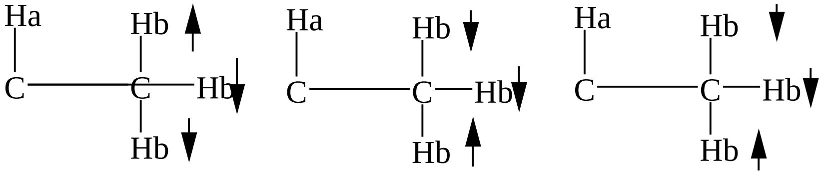
J_{ab} is called the coupling constant

With two identical neighbors:

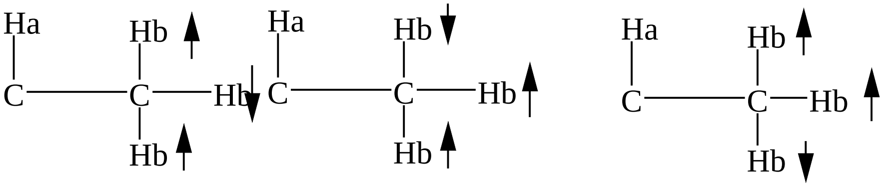


With three identical neighbors:



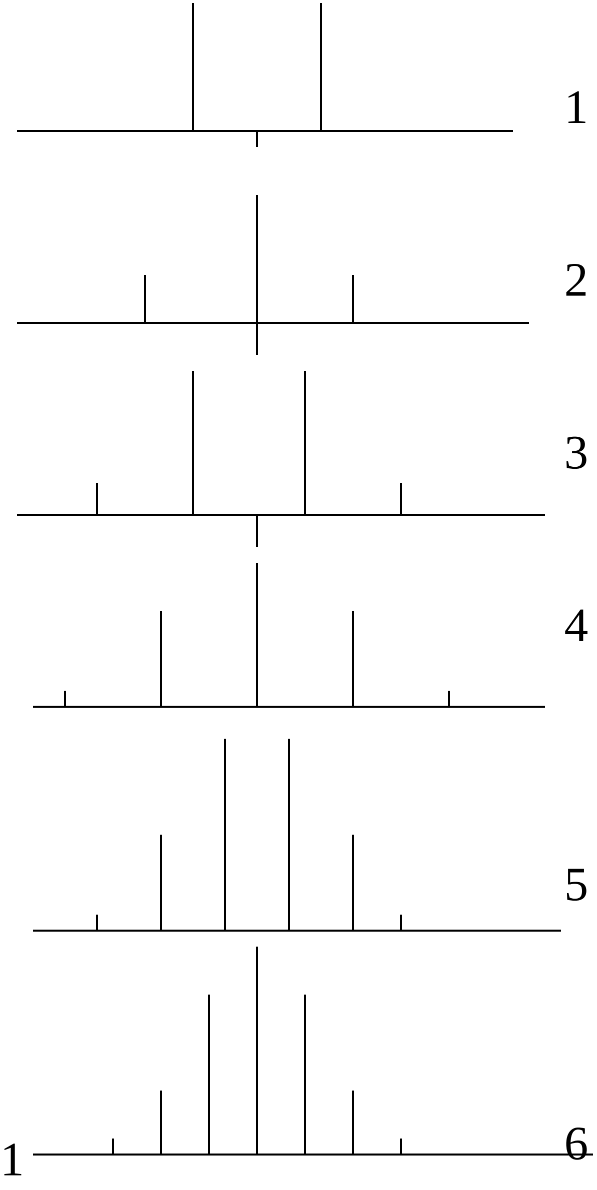


2 down, 1 up



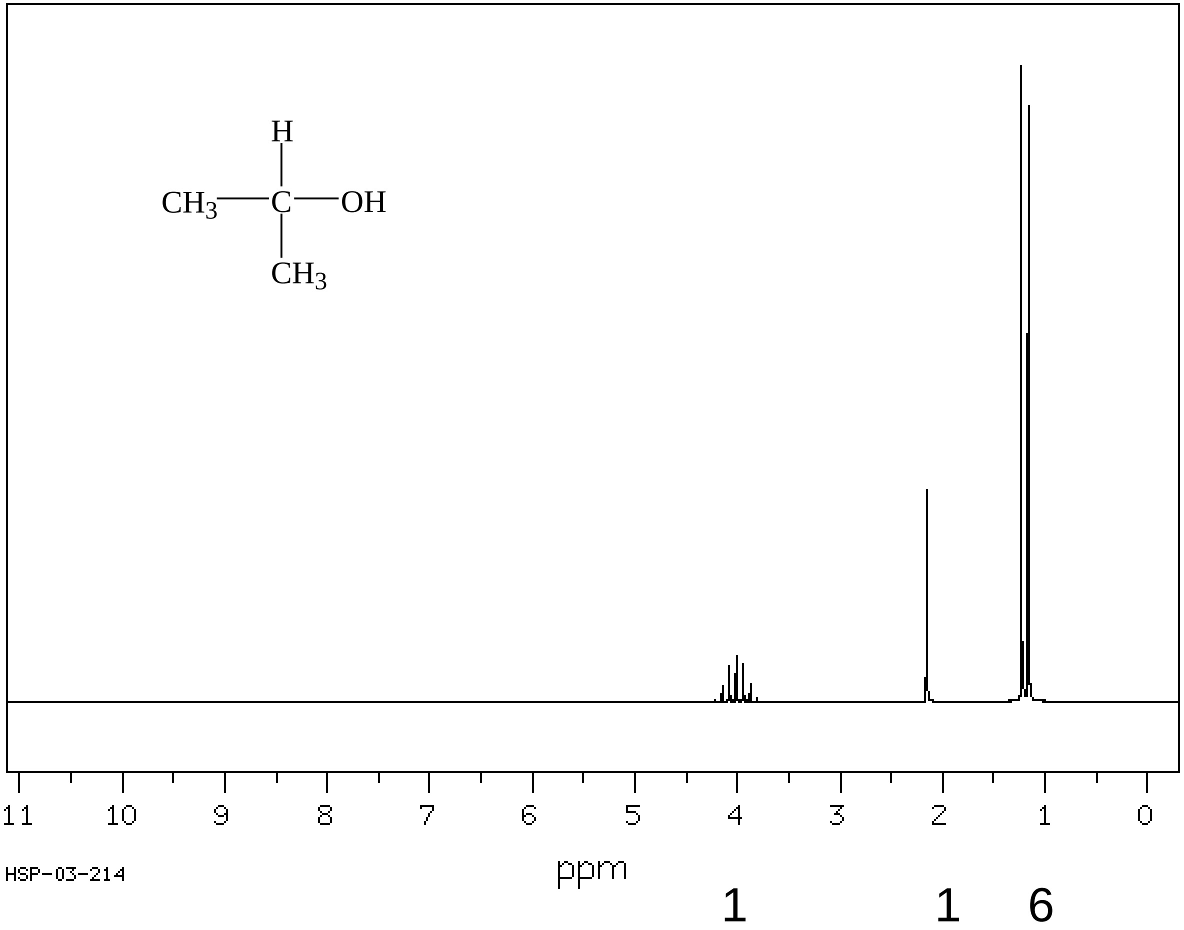
2 up, 1 down

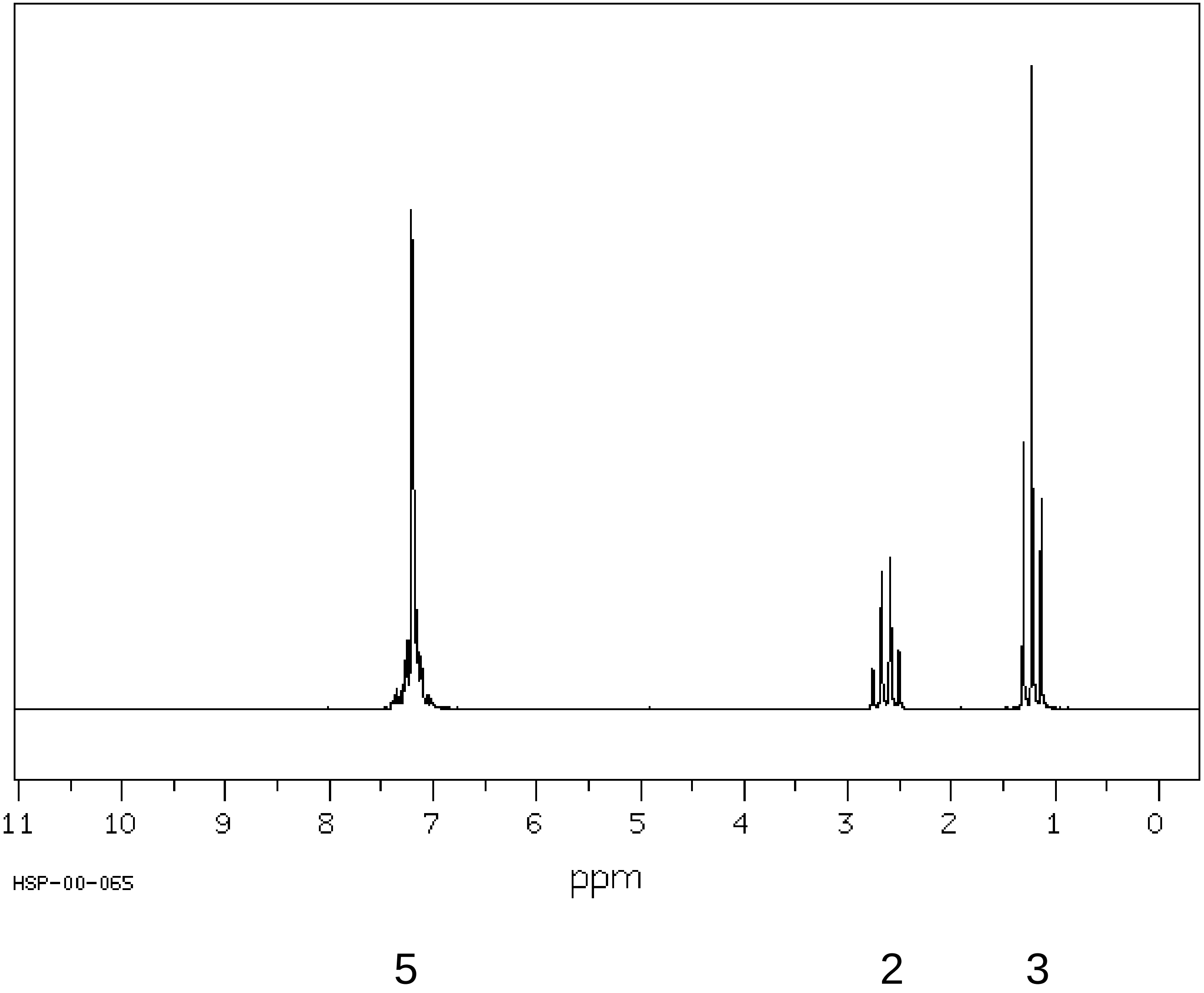
n+1 rule = number of lines observed equals the number of nearest Hb neighbors + 1

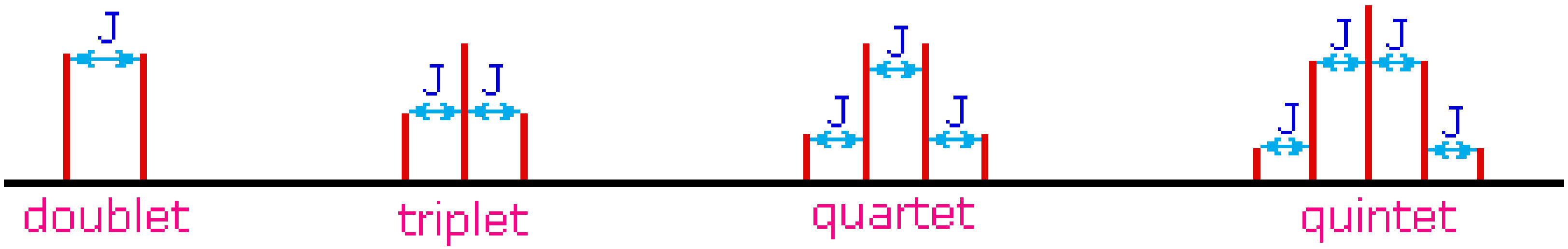


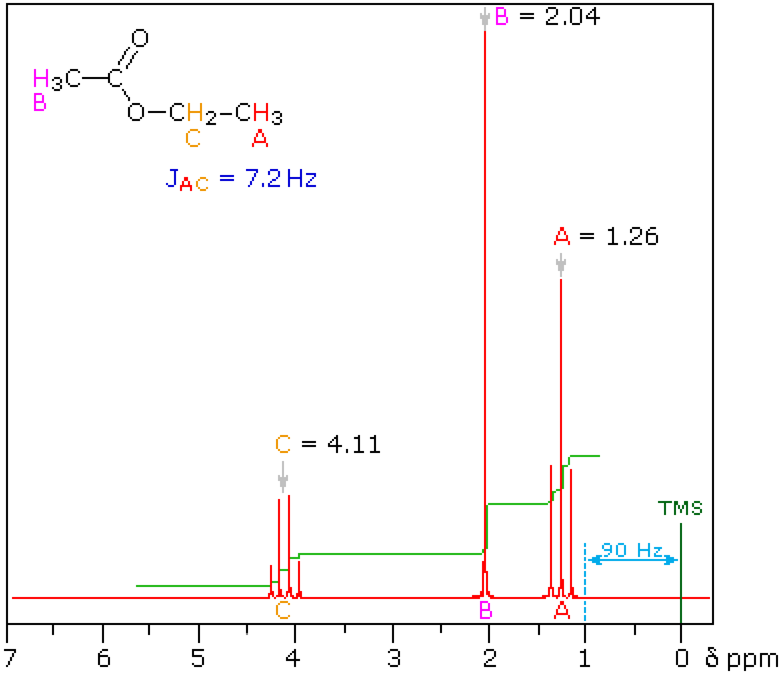
1 1	1 neighbor
1 2 1	2 identical neighbors
1 3 3 1	3 identical neighbors
1 4 6 4 1	4 identical neighbors
1 5 10 10 5 1	5 identical neighbors
1 6 15 20 15 6 1	6 identical neighbors

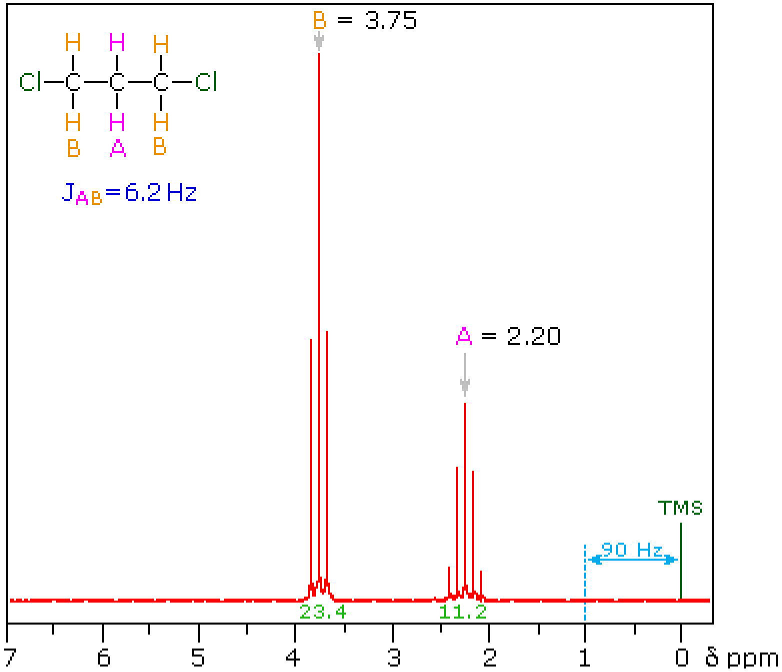
neighbors are identical in the sense that the coupling constants are the same or very similar


H
CH_3
C
OH
CH_3
11
10
9
8
7
6
5
4
3
2
1
0
ppm
HSP-03-214
1
1
6


11
10
9
8
7
6
5
4
3
2
1
0
ppm
HSP-00-065
5
2
3


J
J J
J
J J
J J
J J
doublet
triplet
quartet
quintet


H3C—C(=O)—O—CH2—CH3
B
C
A
JAC = 7.2 Hz
B = 2.04
A = 1.26
C = 4.11
TMS
90 Hz
C
B
A
7
6
5
4
3
2
1
0
δ ppm

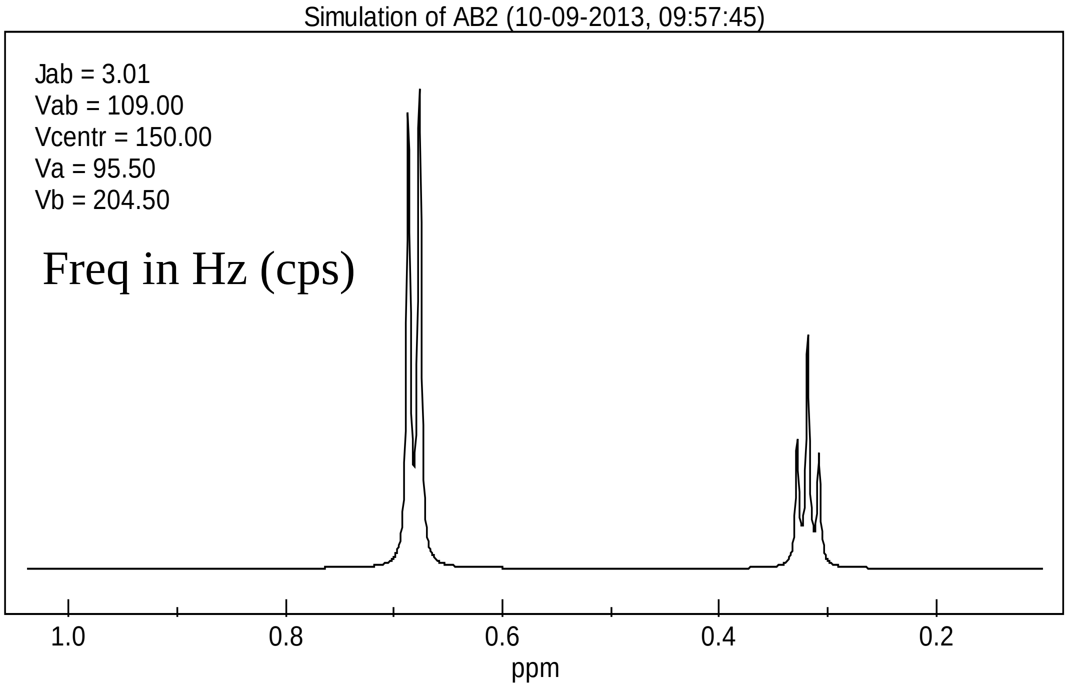

Cl—CH2—CH2—CH2—Cl
H H H
H H H
B A B
JAB=6.2 Hz
B = 3.75
A = 2.20
TMS
90 Hz
23.4
11.2
7
6
5
4
3
2
1
0
δ ppm

2 3 3

2 1

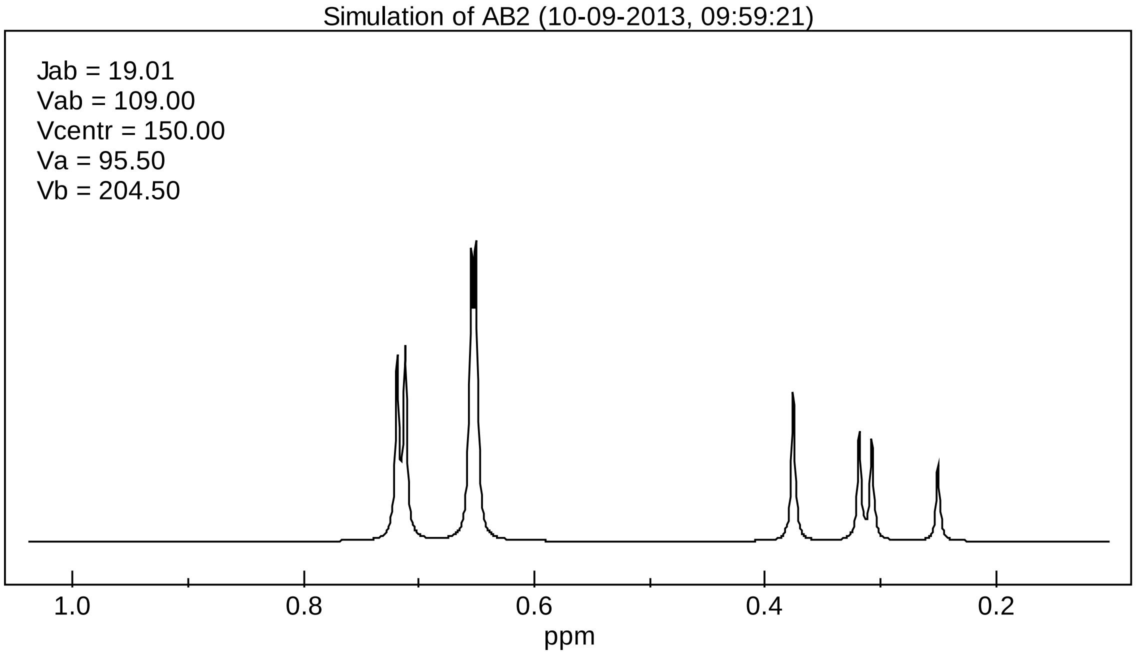
One Criterium for First Order Spectra

The chemical shift difference between the hydrogens that are coupled to each other is greater than 10 times the magnitude of the coupling constant.



Freq in Hz (cps)

$X\text{-}CH_2CHY_2$



^{13} C NMR: natural abundance of 1%, spin of ½ (like hydrogen)

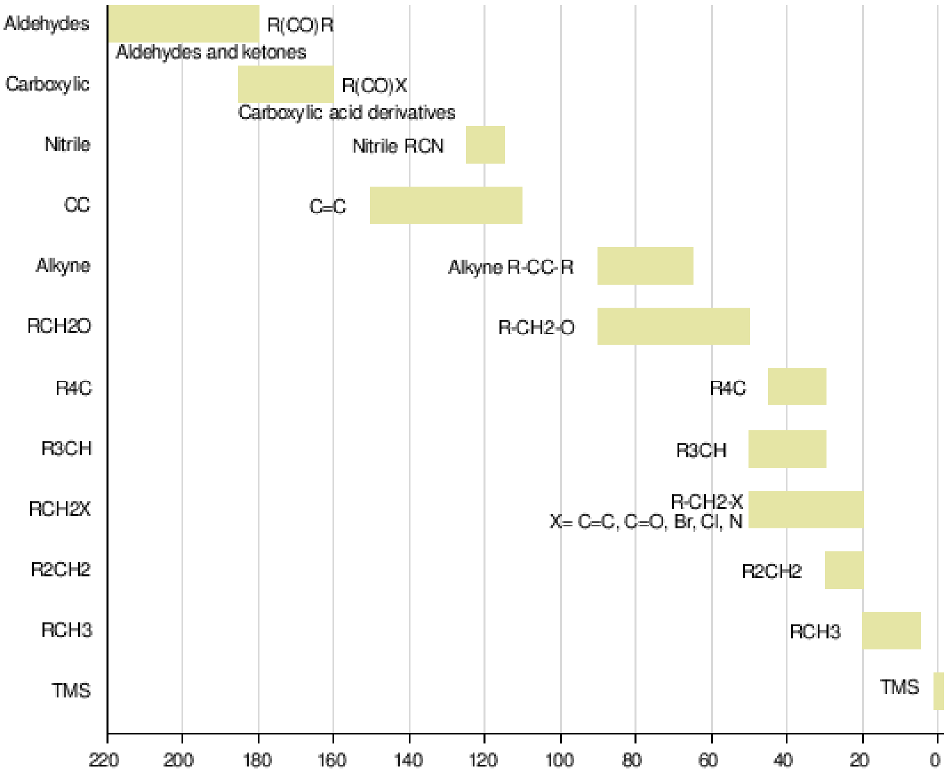
The probability of finding 2 ^{13} C atoms next to each other is 0.01^2 or 10^{-4}

Hydrogen and carbon do couple to each other. However because the amount of ^{13} C is so small, spectra are generally decoupled during aquisition. This is done by irradiating all the hydrogens and causing them to rapidly change their spin orientation. It is somewhat analogous to the decoupling observed in alcohols where the hydrogens three bonds removed are decoupled to an OH hydrogen due to rapid chemical exchange

Information from ^{13}C spectra

1. Number of chemically different carbons
2. Chemical shift information: the chemical environment of the carbon

^{13}C NMR Chemical Shifts

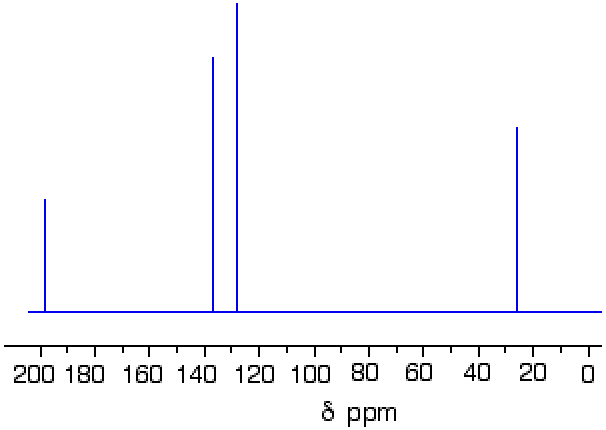


carbon environment	**chemical shift (ppm)**
C=O (in ketones)	205 - 220
C=O (in aldehydes)	190 - 200
C=O (in acids and esters)	170 - 185
C in aromatic rings	125 - 150
C=C (in alkenes)	115 - 140
RCH_2OH	50 - 65
RCH_2Cl	40 - 45
RCH_2NH_2	37 - 45
R_3CH	25 - 35
CH_3CO-	20 - 30
R_2CH_2	16 - 25
RCH_3	1

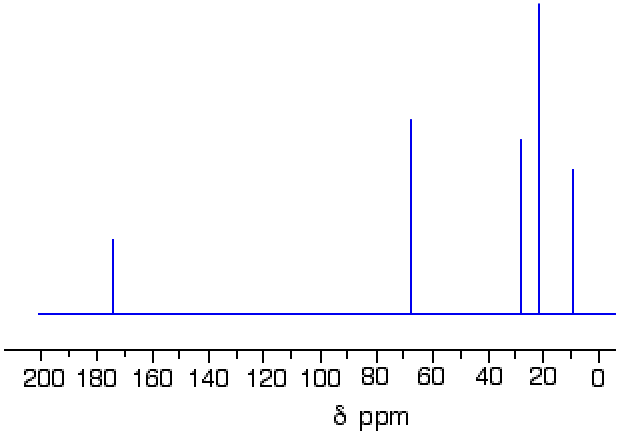
Information from ^{13}C NMR

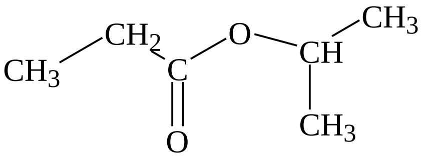
Carbon count

Chemical Shift



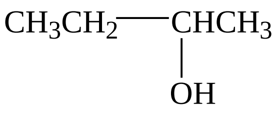
$CH_2{=}CH\text{-}CO\text{-}CH_3$



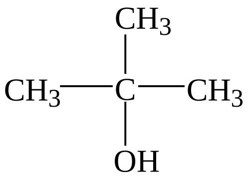


Which of the following alcohols produced the ^{13}C NMR spectrum below?

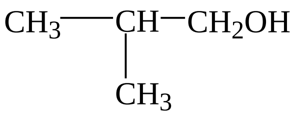
$CH_3CH_2CH_2CH_2OH$



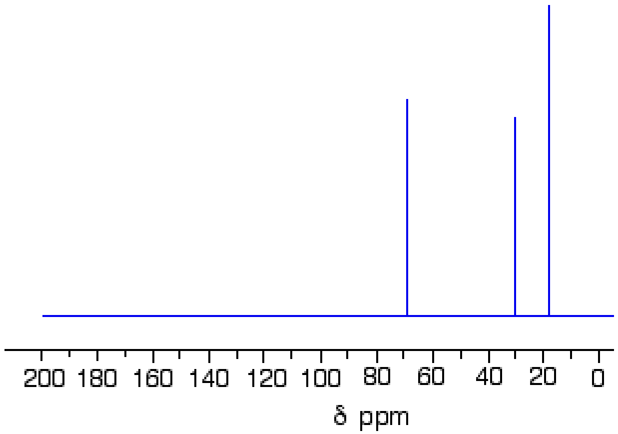
$CH_3CH_2{-}\underset{OH}{CH}CH_3$



$CH_3{-}\overset{CH_3}{\underset{OH}{C}}{-}CH_3$

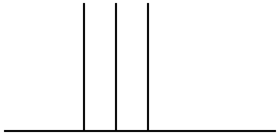


$CH_3{-}\underset{CH_3}{CH}{-}CH_2OH$



Common NMR solvent: $CDCl_3$; CCl_4, CD_3SOCD_3; C_6D_6; $CD_3COCD_{3;\,;}$ D_2O

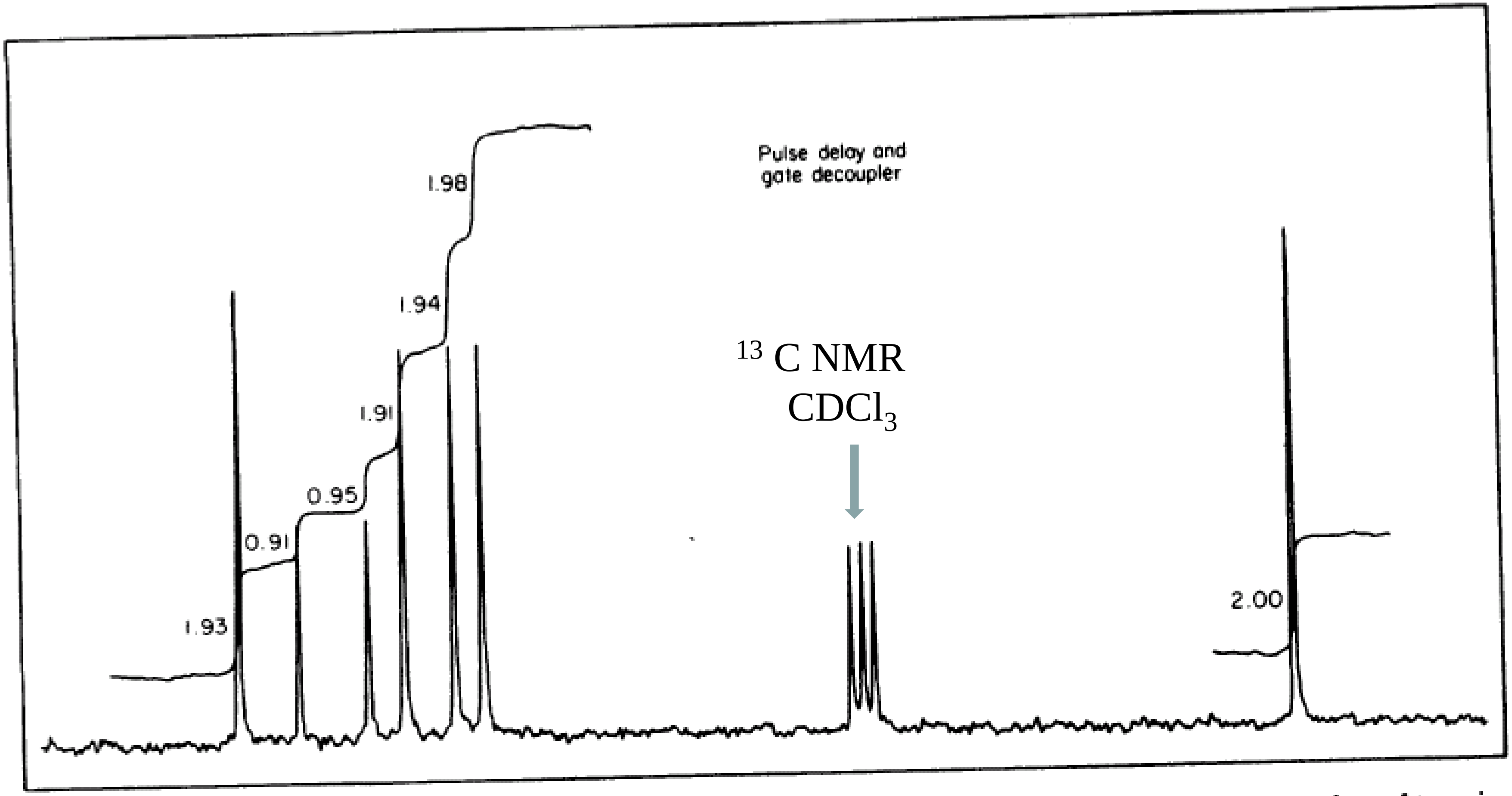
Deuterium ^{2}H also has a spin; it has three orientation in a magnetic field



$CDCl_3$

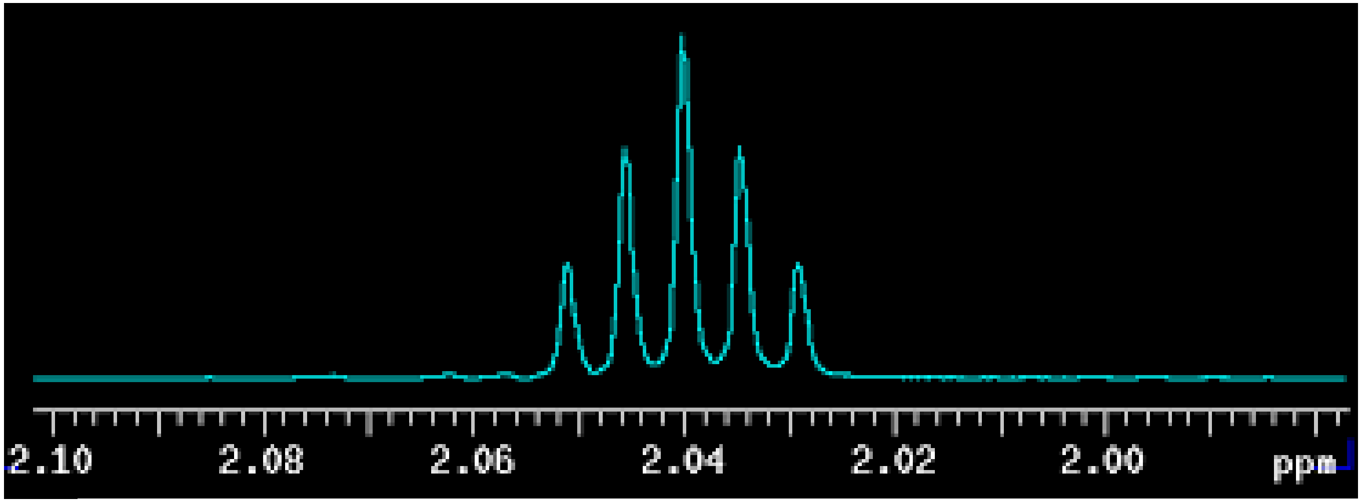
Solvent	**Formula**	**H-NMR shift***	**C-NMR shift**	**multiplet**
Chloroform-d	$CDCl_3$	7.24 (singlet)	77.0	triplet
Carbon tetrachloride	CCl_4		96.7	triplet
Dimethylsulfoxide-d_6	CD_3SOCD_3	2.49 (pentet)	39.7	septet
Benzene-d_6	C_6D_6	7.2 (singlet)	128.0	triplet
Acetone-d_6	CD_3COCD_3	2.04 (pentet)	29.8	septet
Water-d_2	D_2O	4.65 (singlet)		

*The H-NMR peak is due to a residual amount of ^{1}H in the deuterated solvent and is small



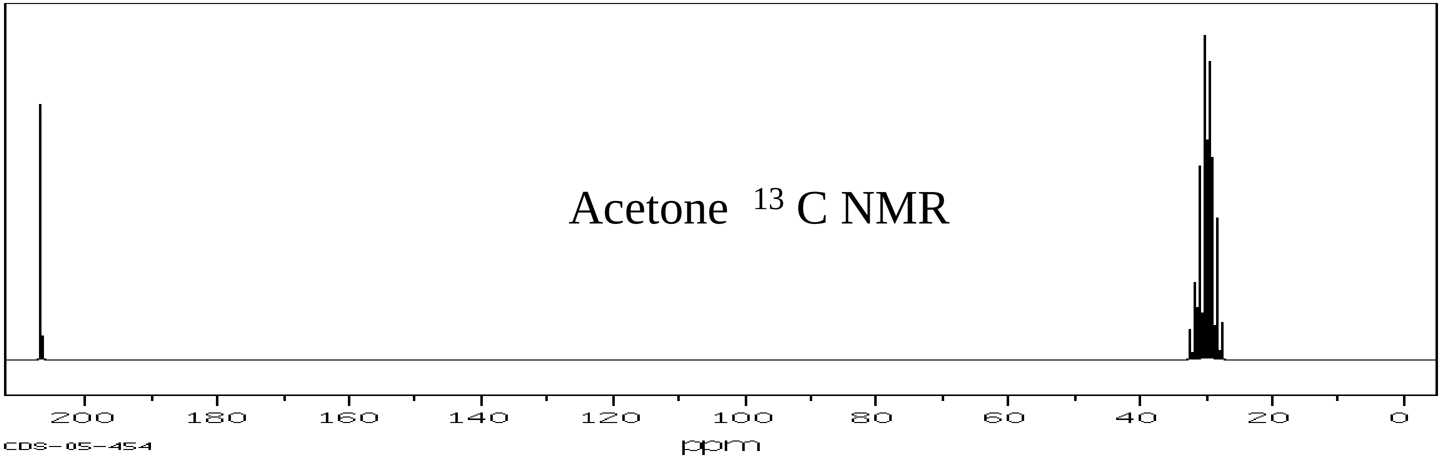
^{13}C NMR
$CDCl_3$

. 7.8 Acenaphthene. Same conditions as Fig. 7.7 but with decoupler ON only during acquisition time; number of transients, 150.

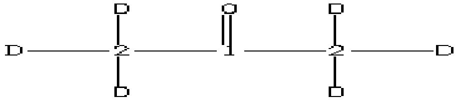


^{1}H NMR

25.16 MHz
0.75 ml : 1.5 ml $CDCl_3$



Acetone ^{13}C NMR



ppm	Int.		标记碳
206.80	787		1
32.29	93	1)	2
31.52	235	1)	2
30.78	596	1)	2
30.00	1000	1)	2
29.22	918	1)	2
28.44	437	1)	2
27.66	115	1)	2