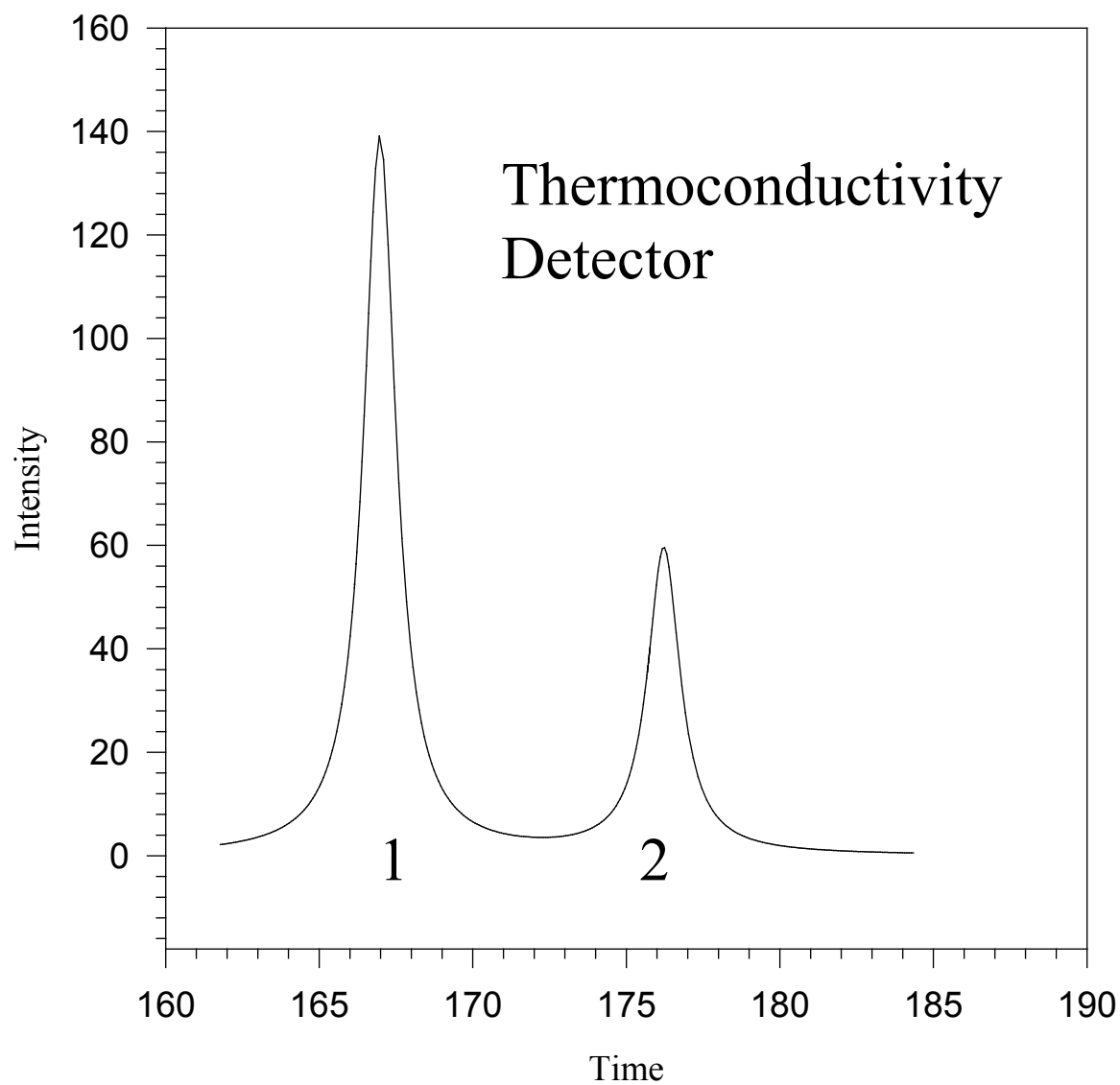
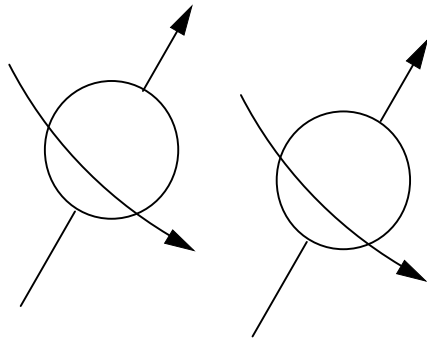


^1H Nuclear Magnetic Resonance

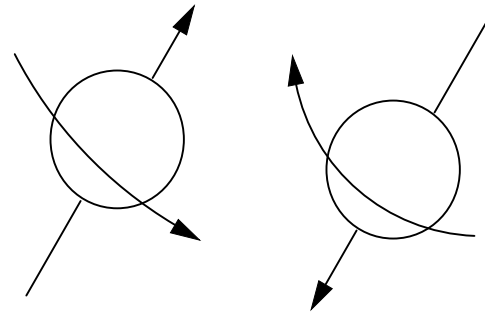
Gas Chromatograph of Molecular Hydrogen at $-100\text{ }^{\circ}\text{C}$



Whats going on?



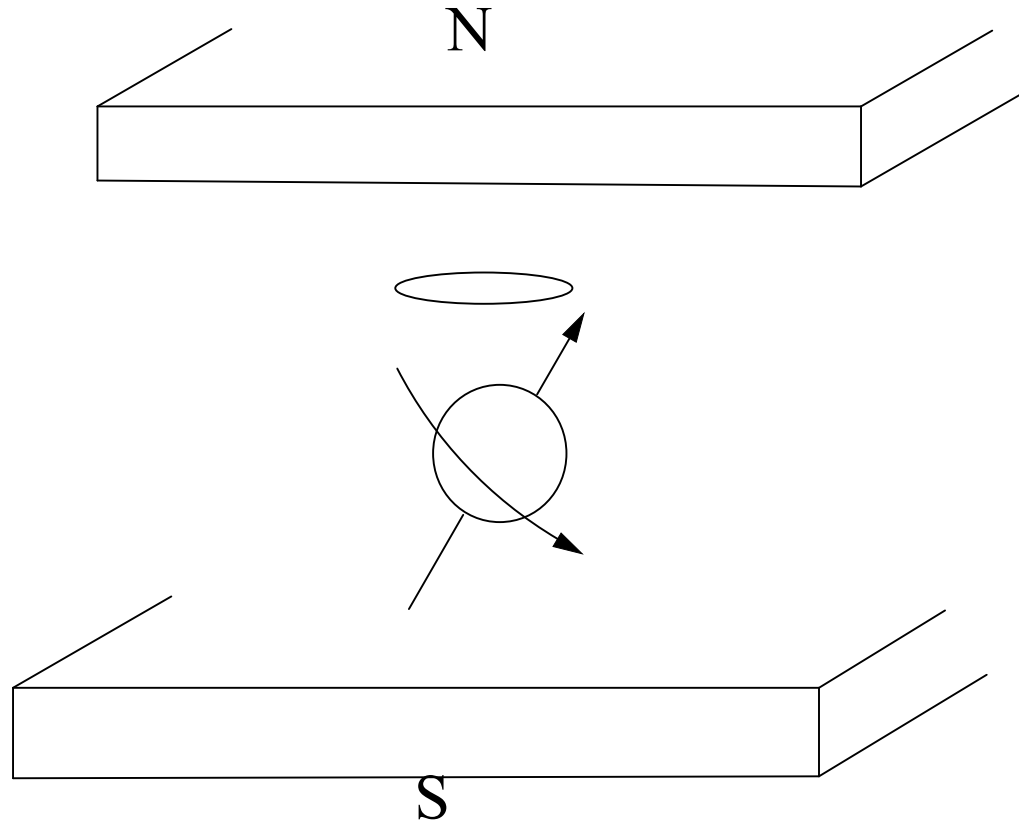
Ortho Hydrogen



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 $\pm 1/2$, 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

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

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

$$1 \text{ Hz} = 1 \text{ cycle/second}$$

For ^1H

For ^{13}C

At 14,000 Gauss (1.4 Tesla)

$$\nu = 60 \text{ MHz}$$

$$\nu = 14 \text{ MHz}$$

At 70,500 Gauss (7.05 Tesla)

$$\nu = 300 \text{ MHz}$$

$$\nu = 70 \text{ MHz}$$

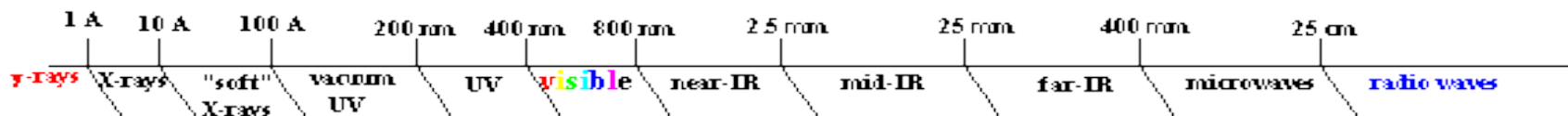
At 141000 Gauss (14.1 Tesla)

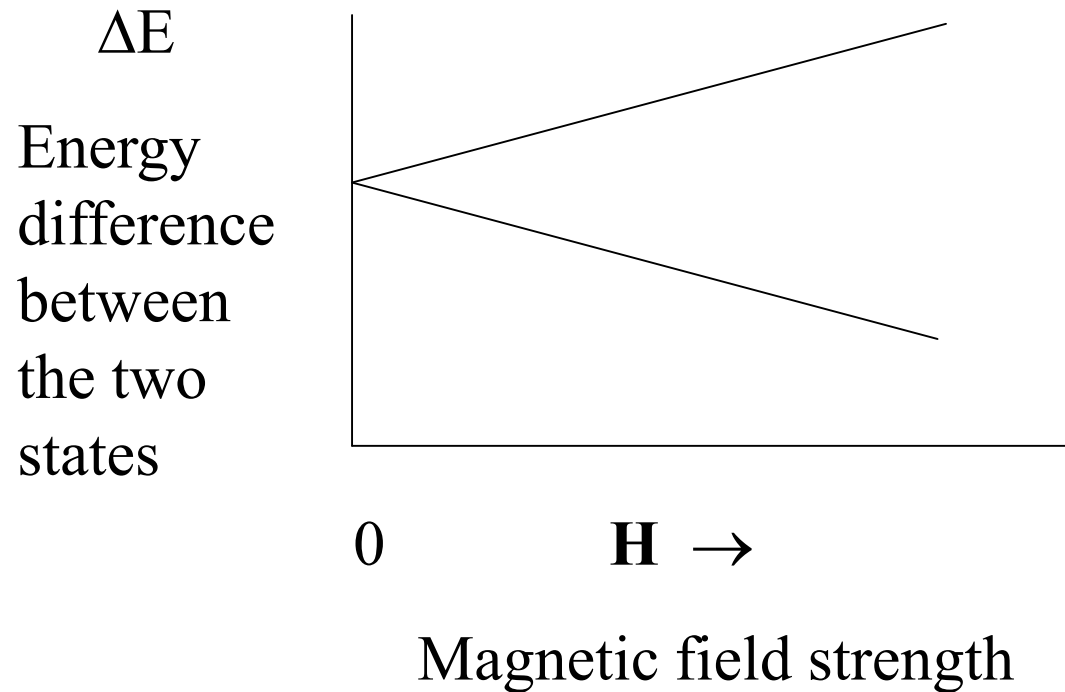
$$\nu = 600 \text{ MHz}$$

$$\nu = 140 \text{ MHz}$$

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

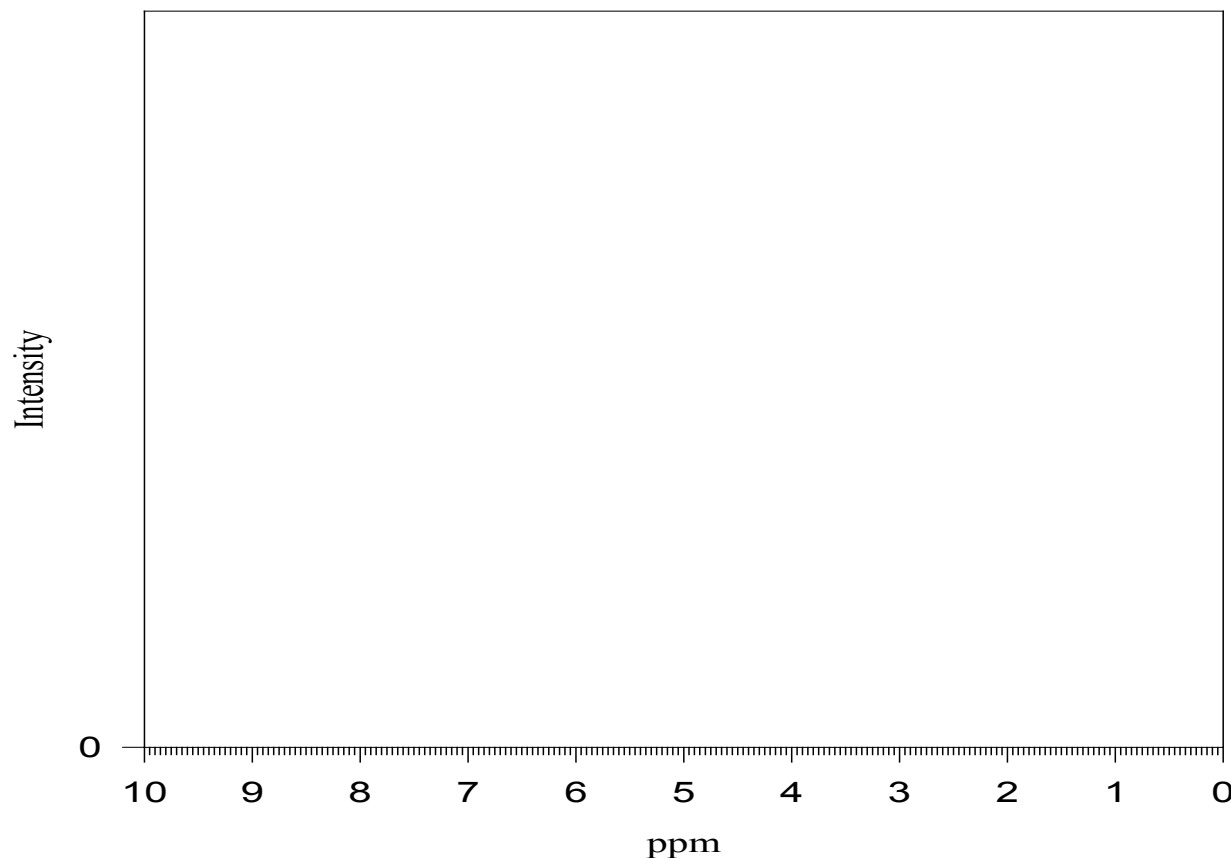
The Electromagnetic Spectrum





If a nucleus experiences a different magnetic field it will precess at a different frequency and absorb at a different frequency ($E = h\nu$)

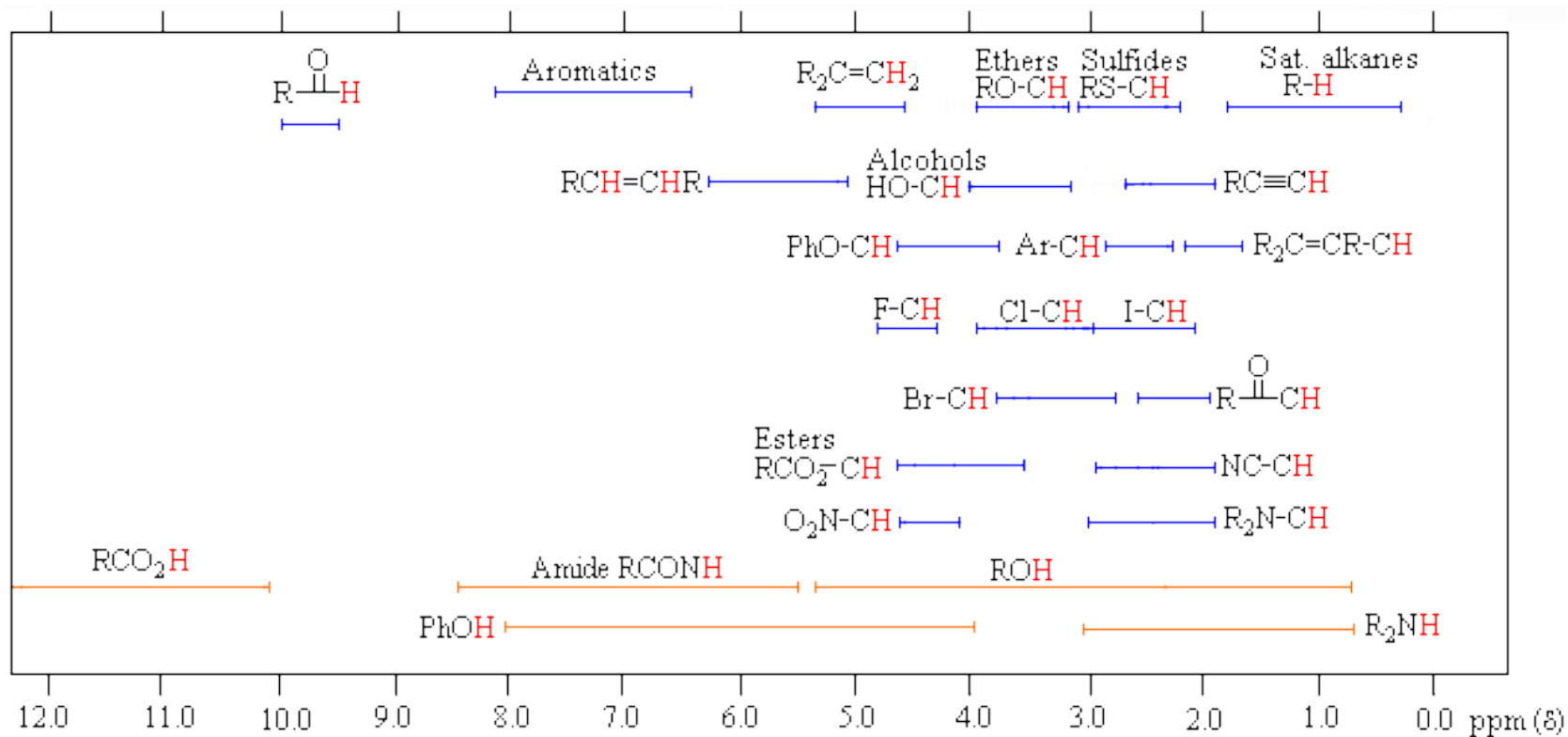
A typical ^1H NMR spectrum in frequency reported in parts per million



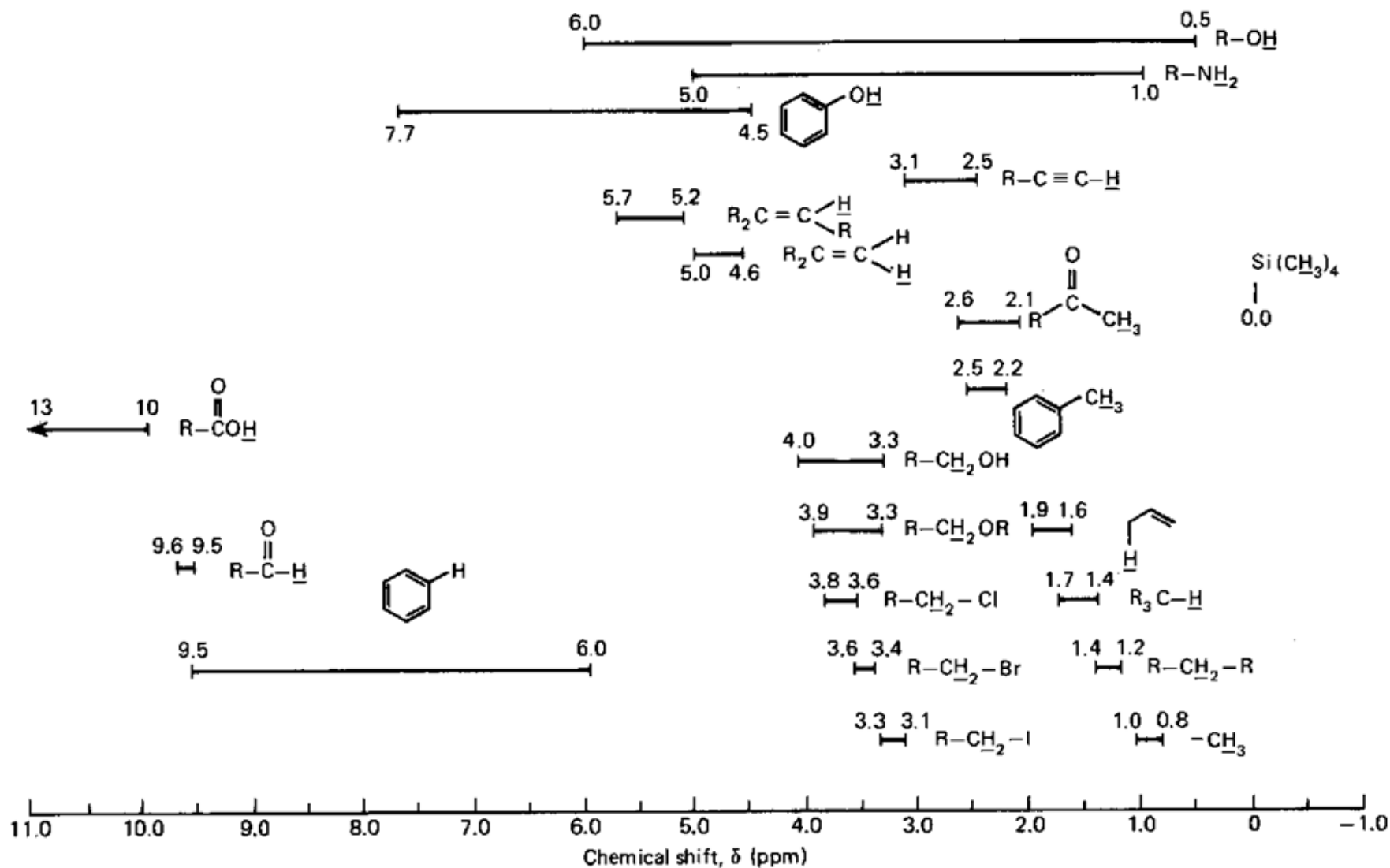
Since the frequency (cycles/sec) depends on the strength of the magnetic field, chemical shifts are reported relative to a standard, frequently tetramethylsilane (0 ppm). If the spectrum is run at a magnetic field strength that generates precessional frequencies of 300 MHz (300 million cycles per sec, 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)



Typical NMR Chemical Shifts



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.

The nmr of 2,2,-dimethylpropanol

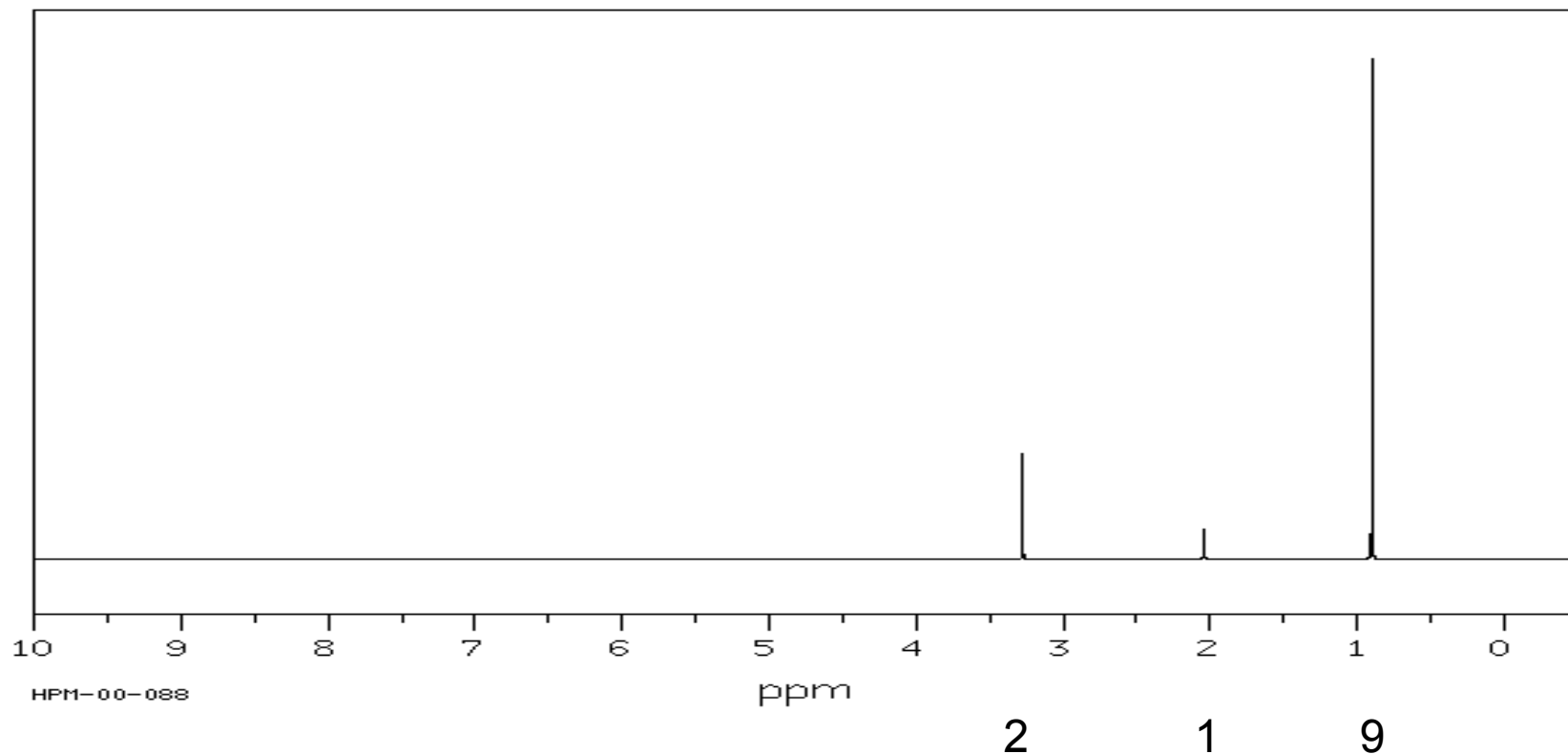
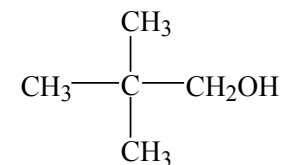
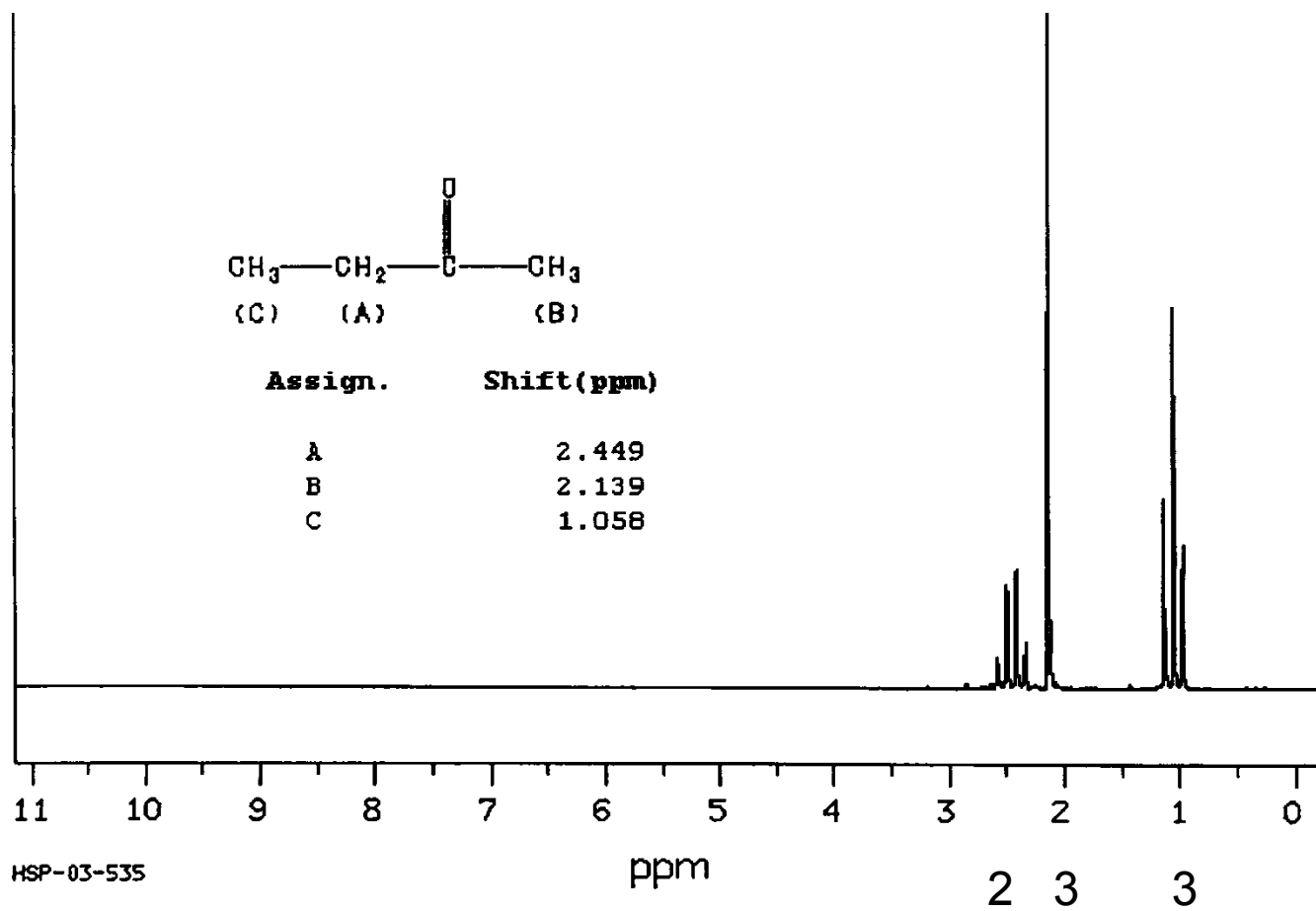
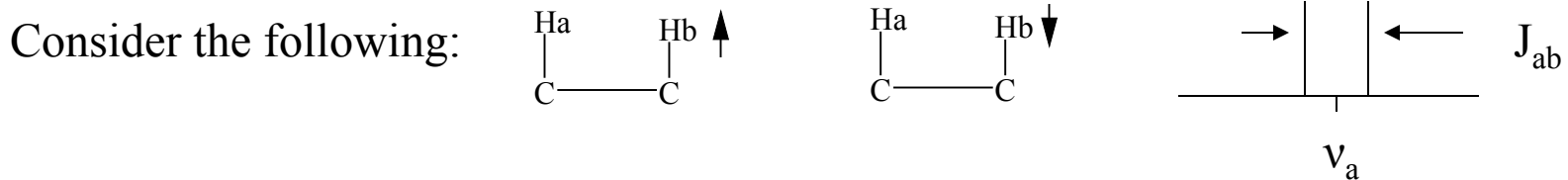


Figure NMR-2. The NMR spectrum of 2,2-dimethylpropanol



Why the multiplicity?

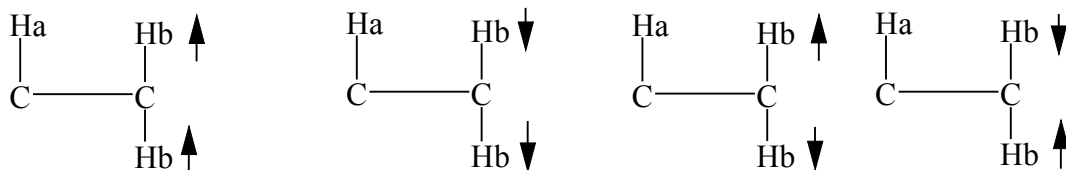


If H_a has a different chemical shift from H_b , roughly 50% of the nuclei of H_b will have one orientation of their magnetic moment and the other will have just the opposite

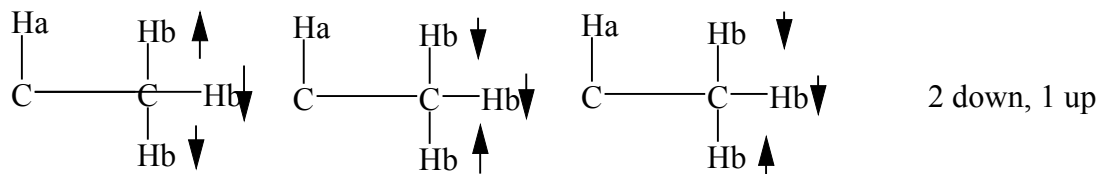
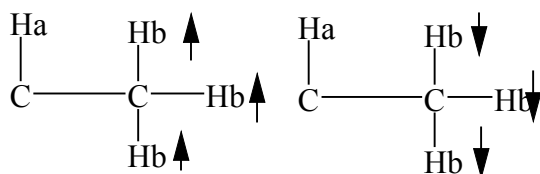
The total field felt by H_a will be due to the external field, the local field due to electronic environment and the field due to the proton(s) three bonds removed. The field due to the local proton will either add or subtract to the total field experienced by H_a . Roughly 50% will have a neighbor with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

J_{ab} is called the coupling constant

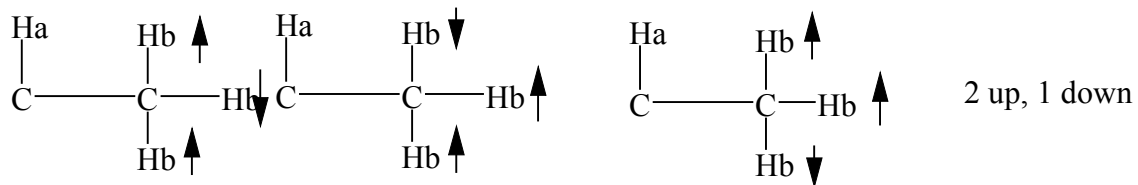
With two identical neighbors:



With three identical neighbors:

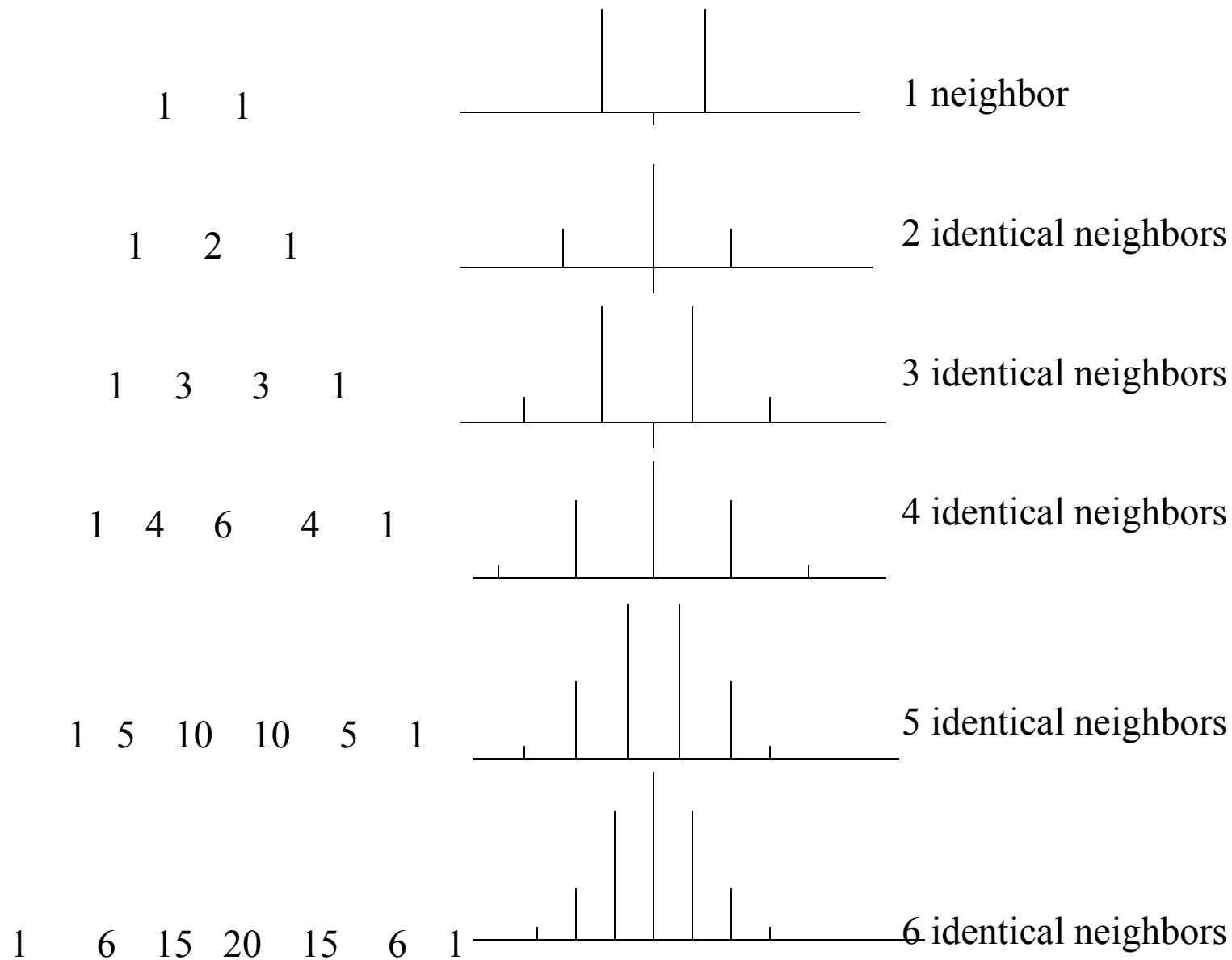


2 down, 1 up



2 up, 1 down

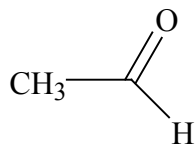
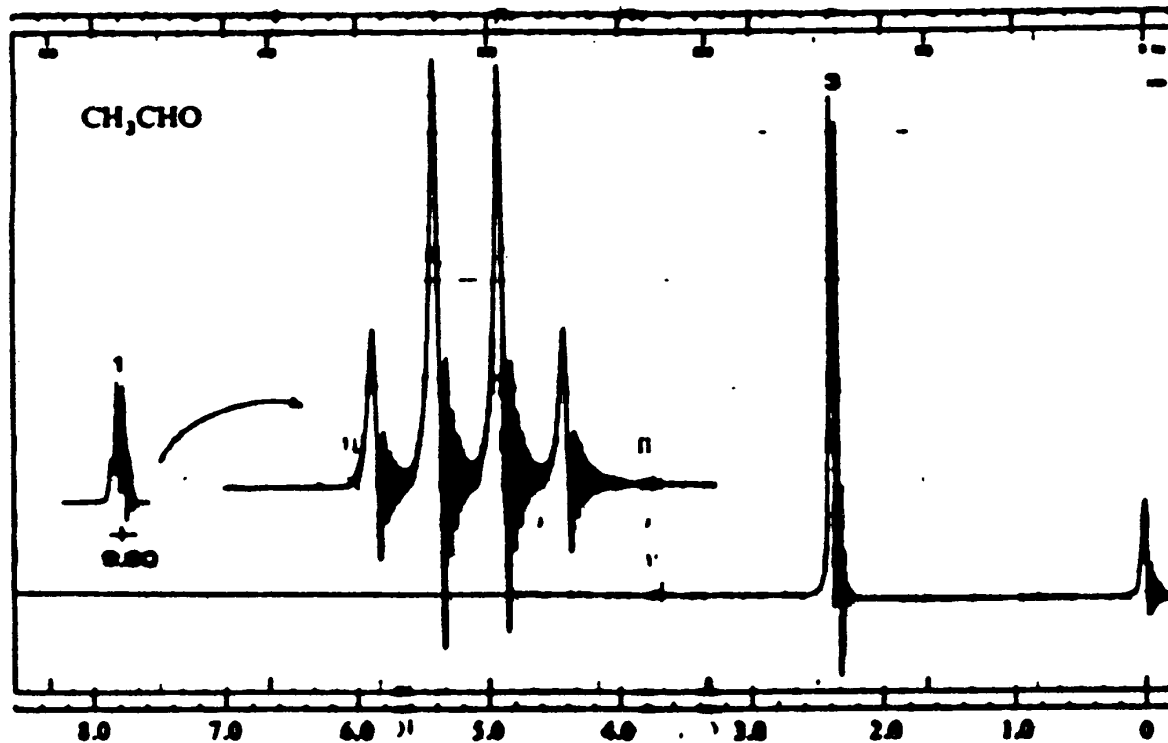
$n+1$ rule = number of lines observed equals the number of nearest Hb neighbors + 1



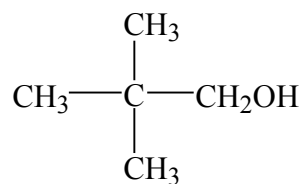
neighbors are identical in the sense that the coupling constants are the same or very similar

Information obtained by a NMR spectrum

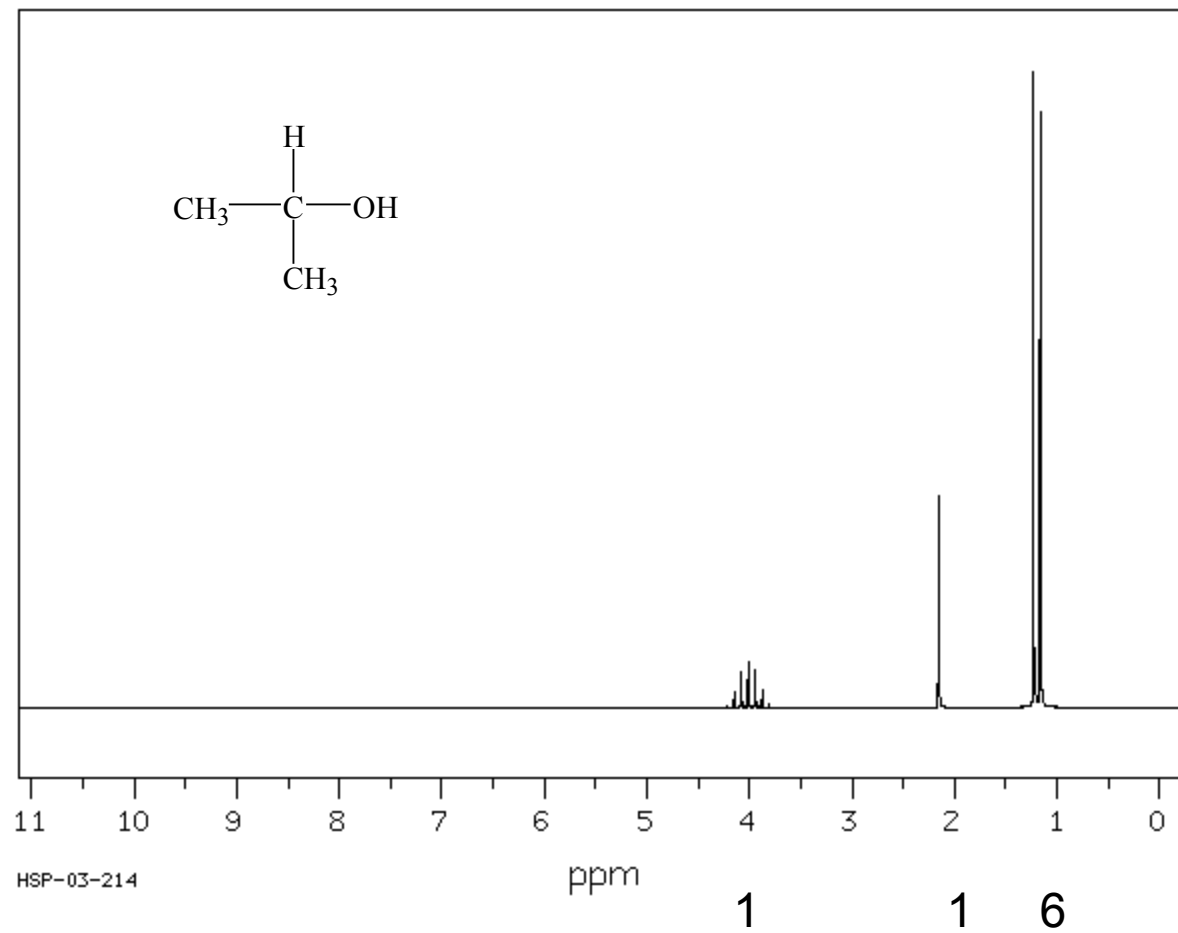
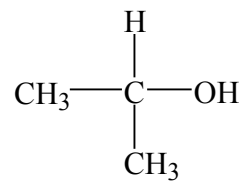
1. Chemical shift: indicates the type of proton
2. Relative areas: provide a ratio of the number of each type of H nucleus
3. Number of nearest neighbors (first order spectra)

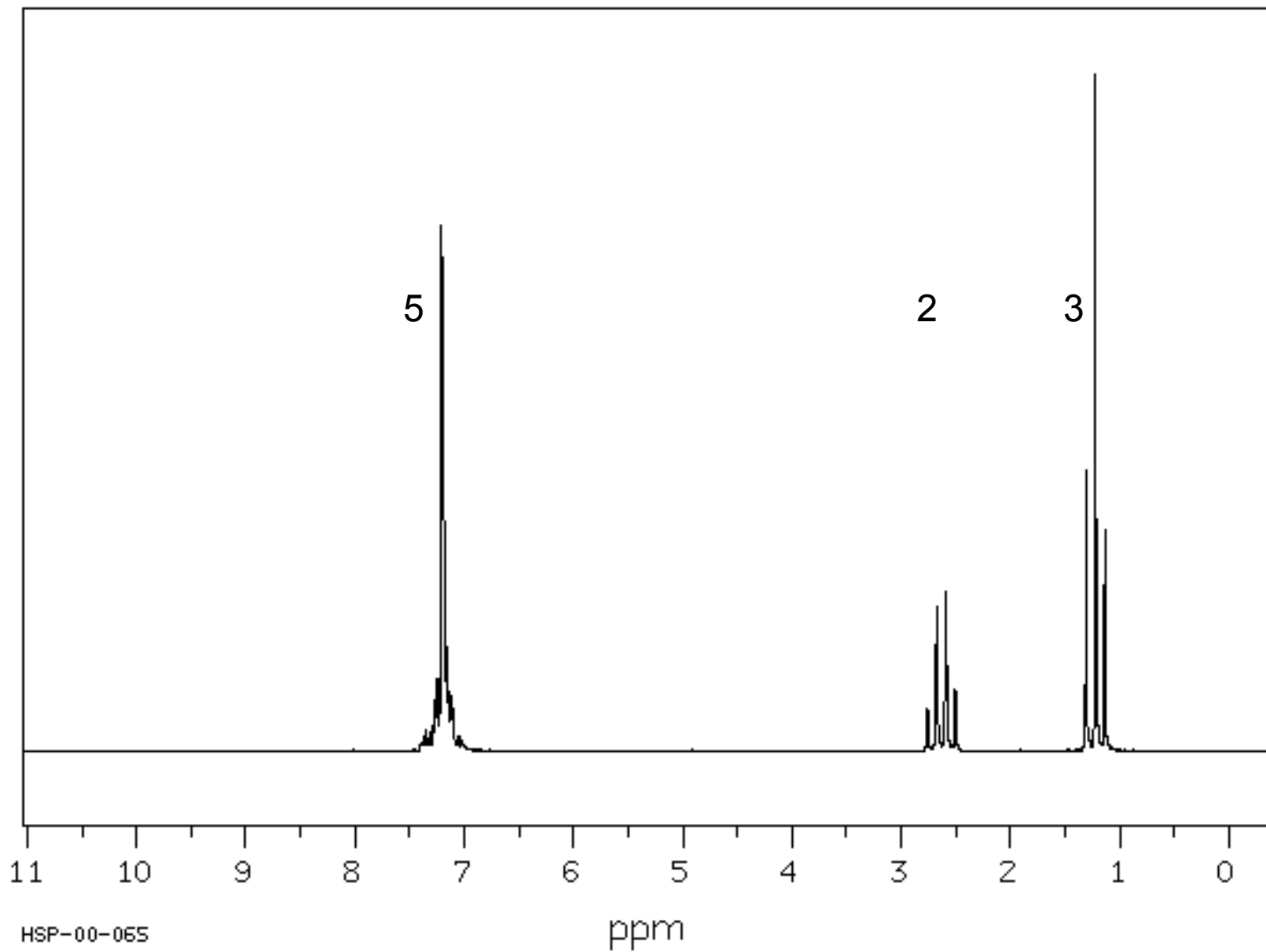


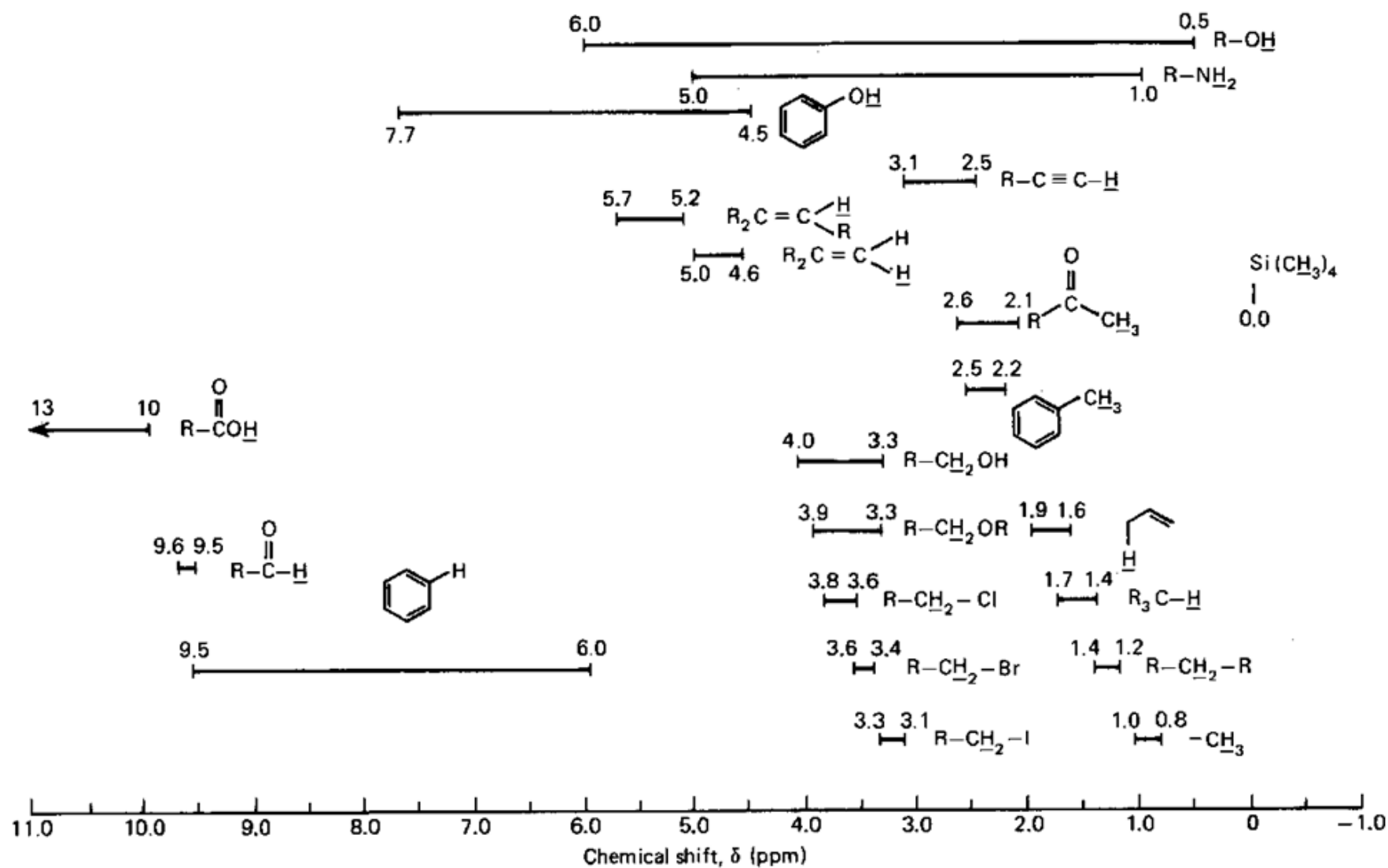
The hydrogens are three bonds removed

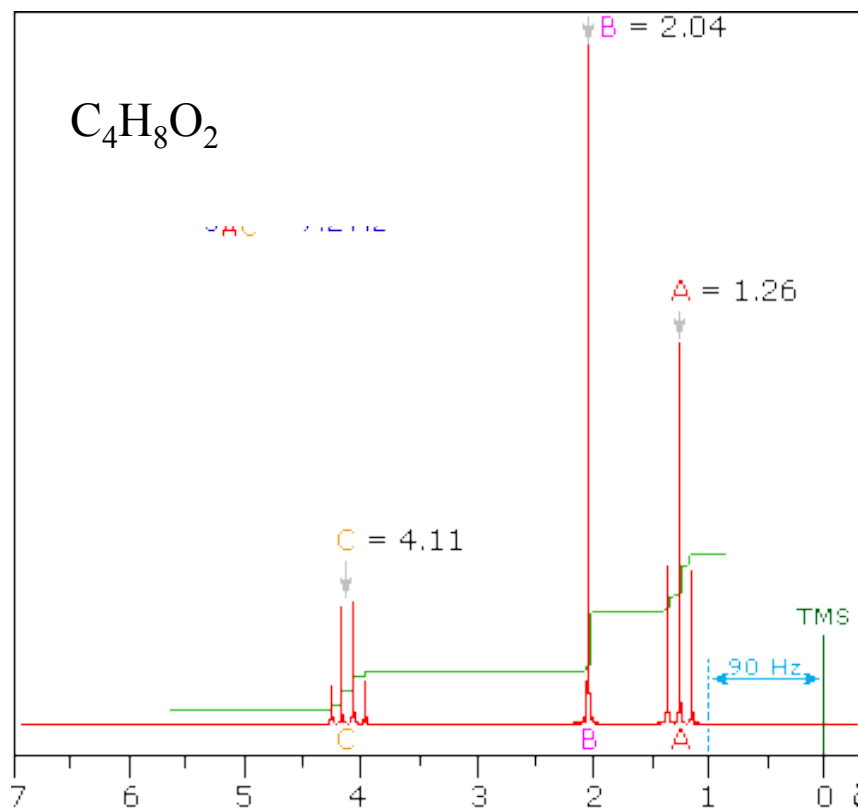
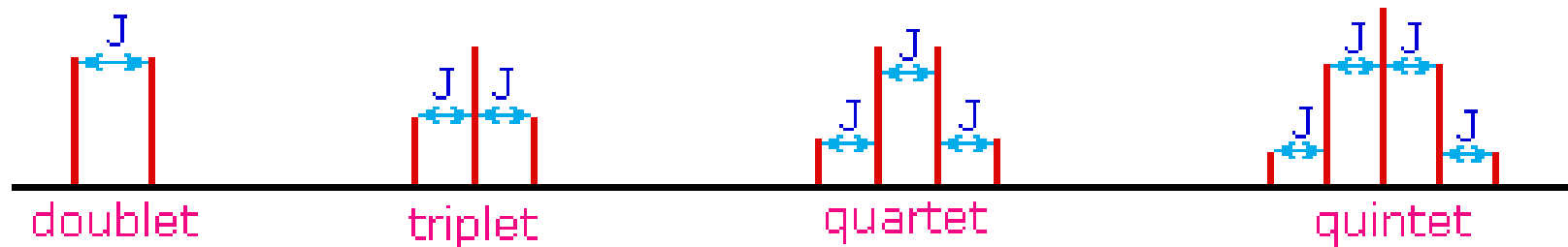


The hydrogens are four or more bonds removed
except for the OH





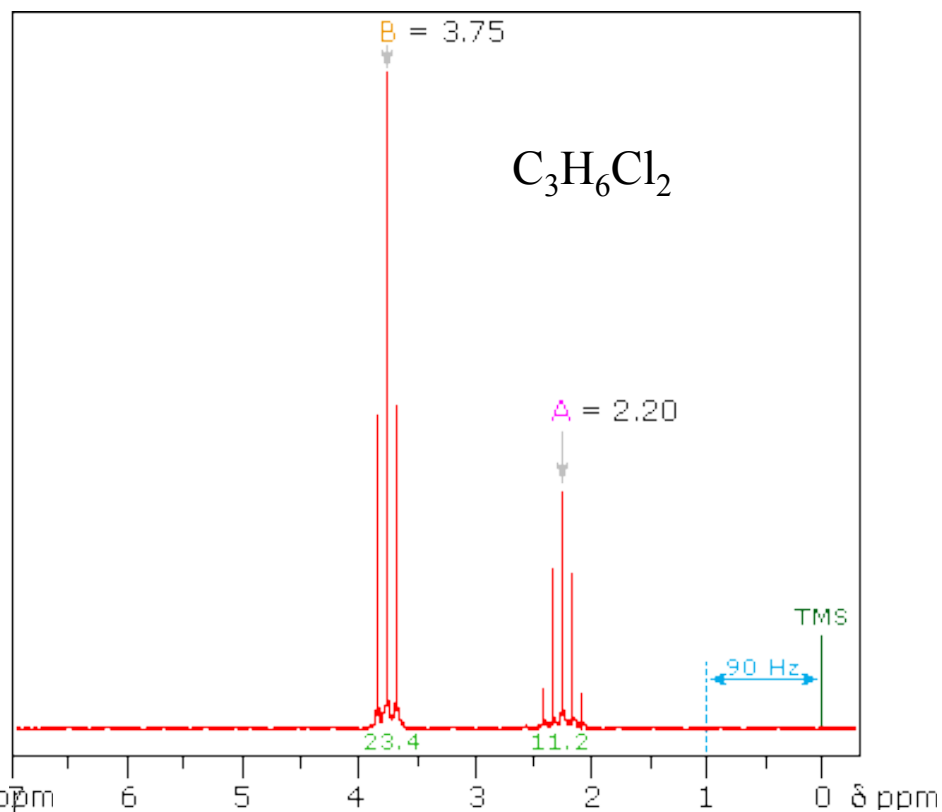




2

3

3



2

1

The nmr of 2,2,-dimethylpropanol

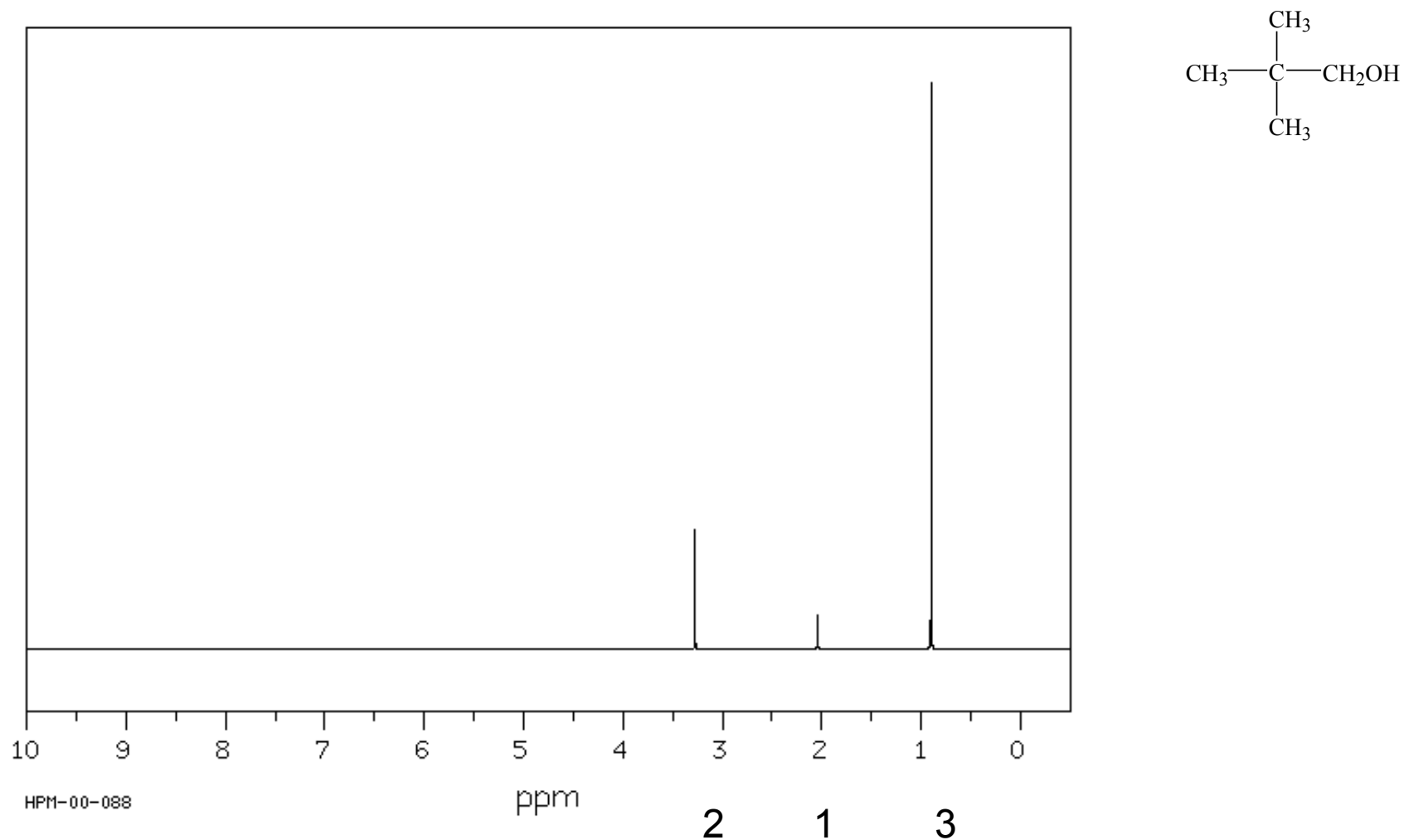
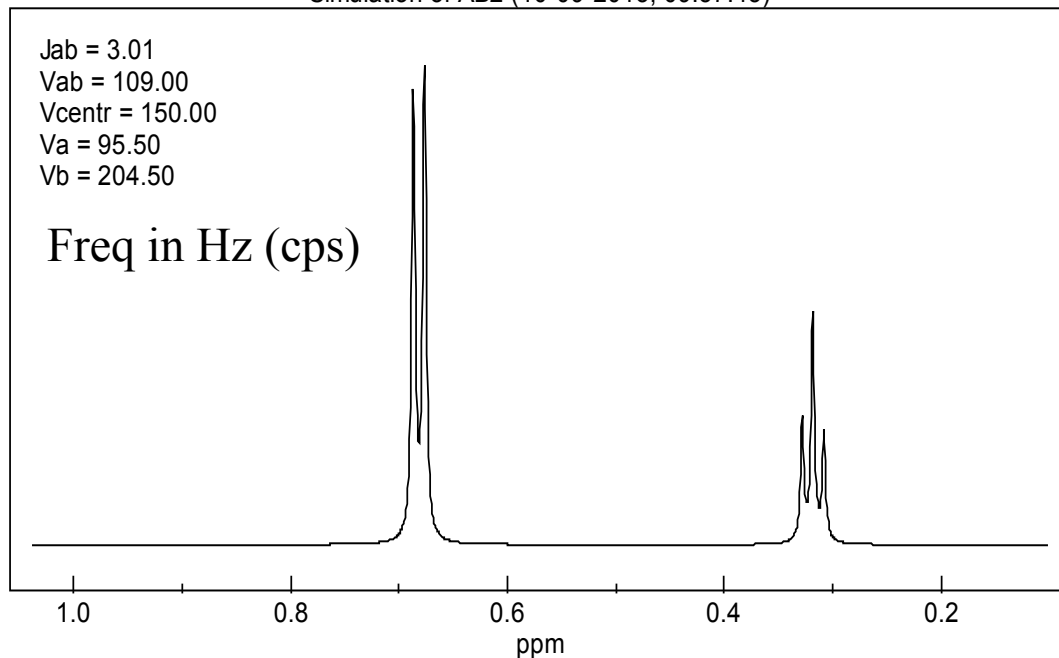


Figure NMR-2. The NMR spectrum of 2,2-dimethylpropanol

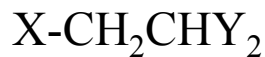
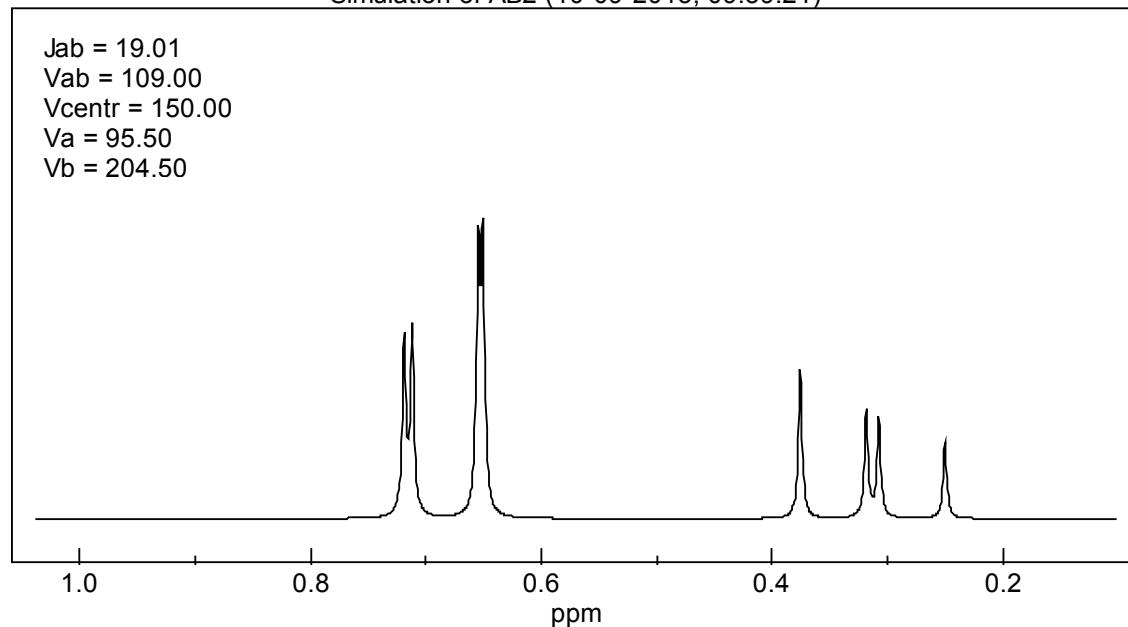
One Criterium for First Order Spectra

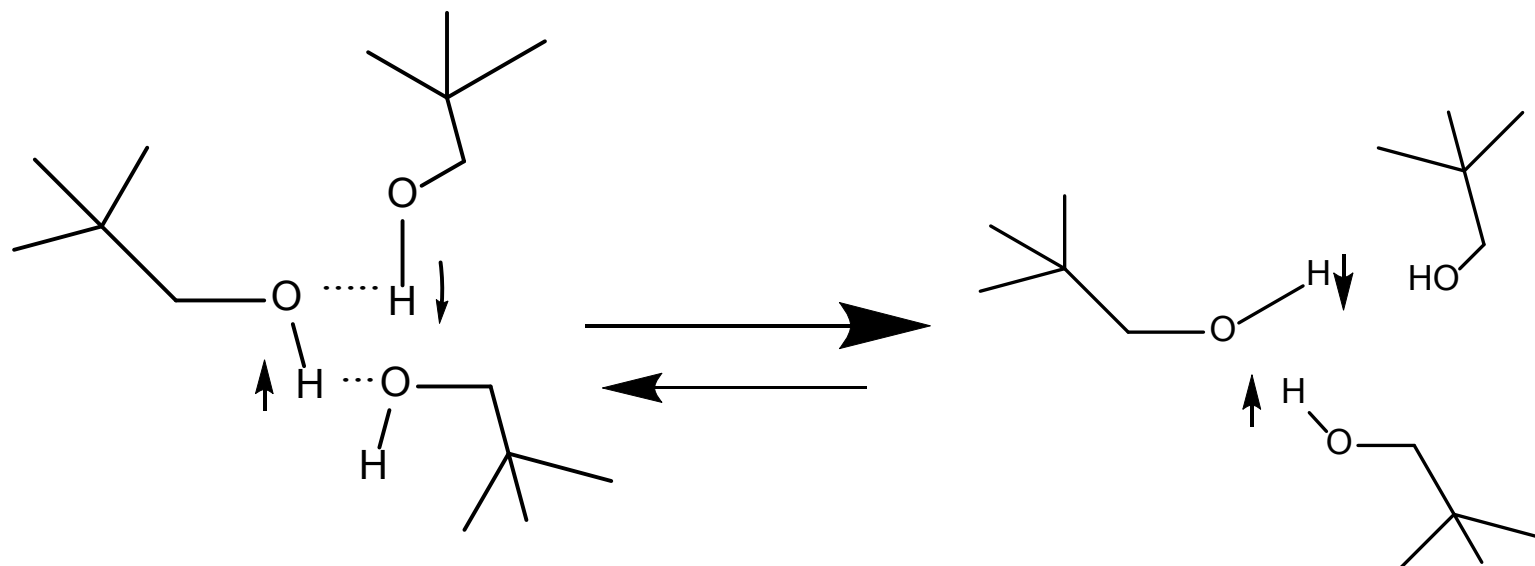
The chemical shift difference between the hydrogens that are coupled to each other is greater than 10 times the magnitude of the coupling constant.

Simulation of AB2 (10-09-2013, 09:57:45)



Simulation of AB2 (10-09-2013, 09:59:21)





^{13}C NMR: natural abundance of 1%, spin of $\frac{1}{2}$ (like hydrogen)

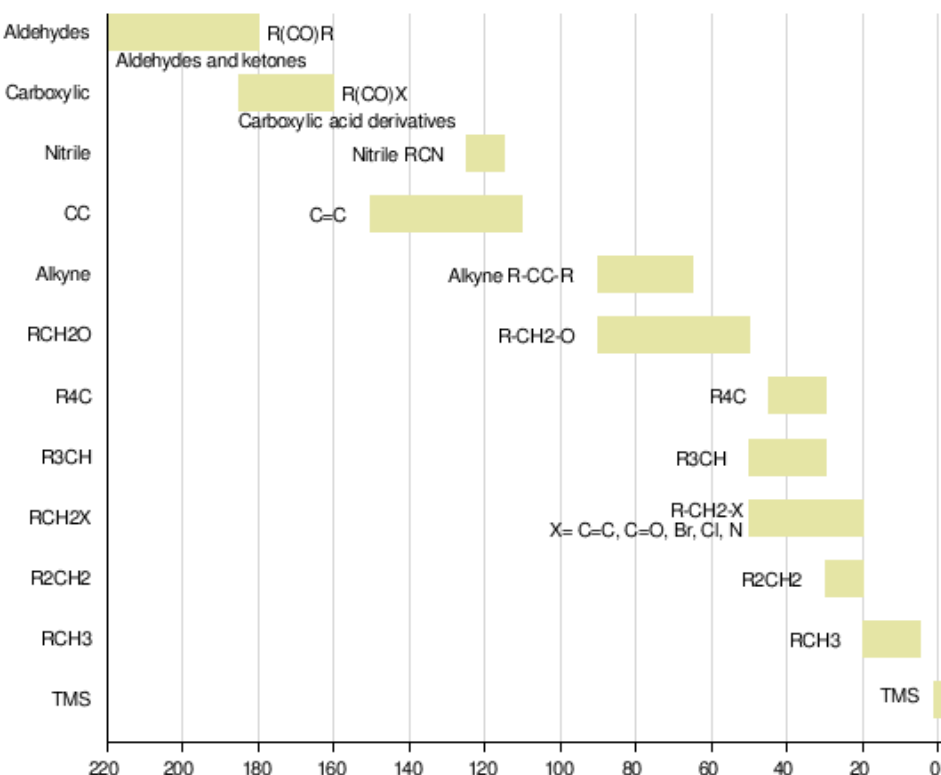
The probability of finding 2 ^{13}C atoms next to each other is 0.01^2 or 10^{-4}

Hydrogen and carbon do couple to each other. However because the amount of ^{13}C is so small, spectra are generally decoupled during acquisition. 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

RCH₂OH 50 - 65

RCH₂Cl 40 - 45

RCH₂NH₂ 37 - 45

R₃CH 25 - 35

CH₃CO- 20 - 30

R₂CH₂ 16 - 25

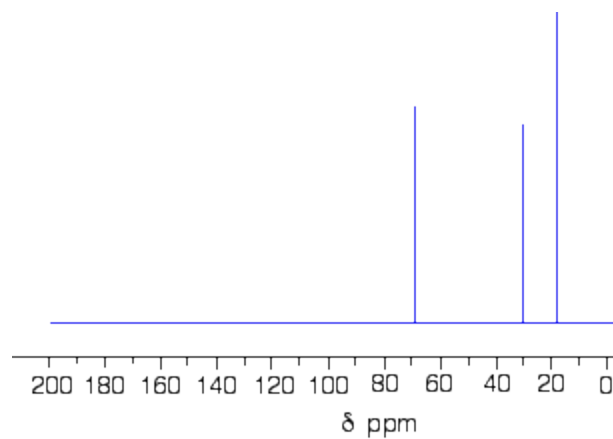
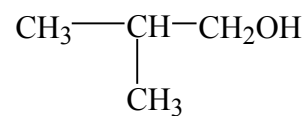
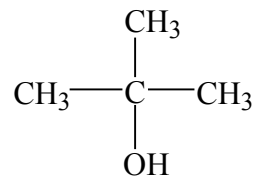
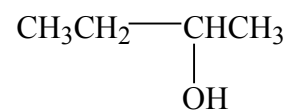
RCH₃ 1

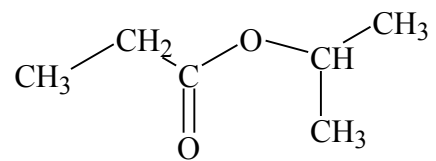
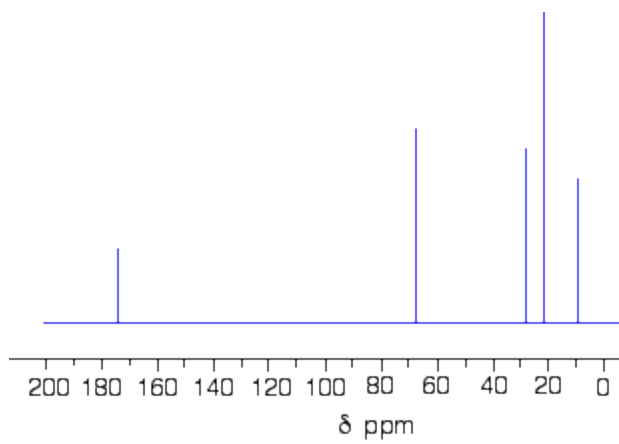
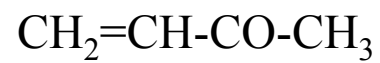
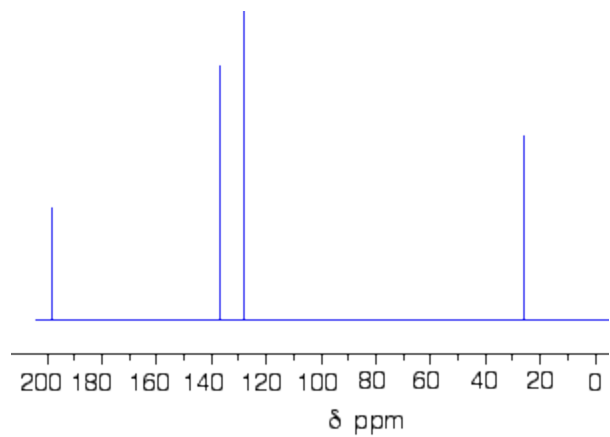
Information from ¹³ C NMR

Carbon count

Chemical Shift

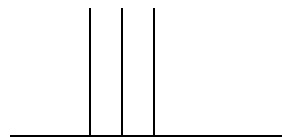
Which of the following alcohols produced the ^{13}C NMR spectrum below?





Common NMR solvent: CDCl_3 ; CCl_4 , CD_3SOCD_3 ; C_6D_6 ; CD_3COCD_3 ; D_2O

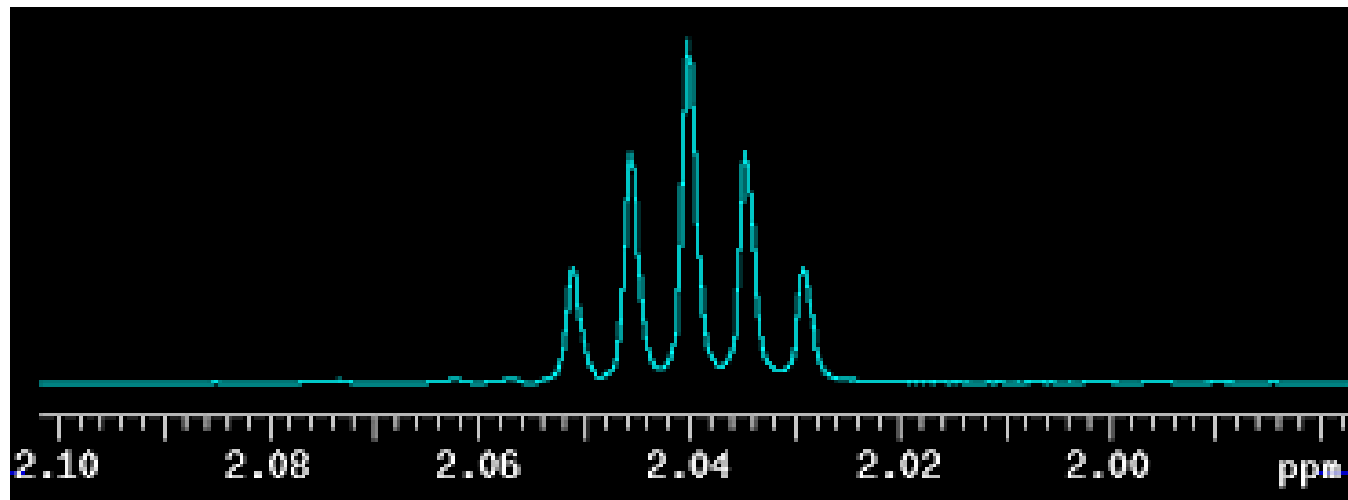
Deuterium ^2H also has a spin; it has three orientation in a magnetic field



CDCl_3

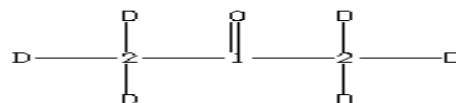
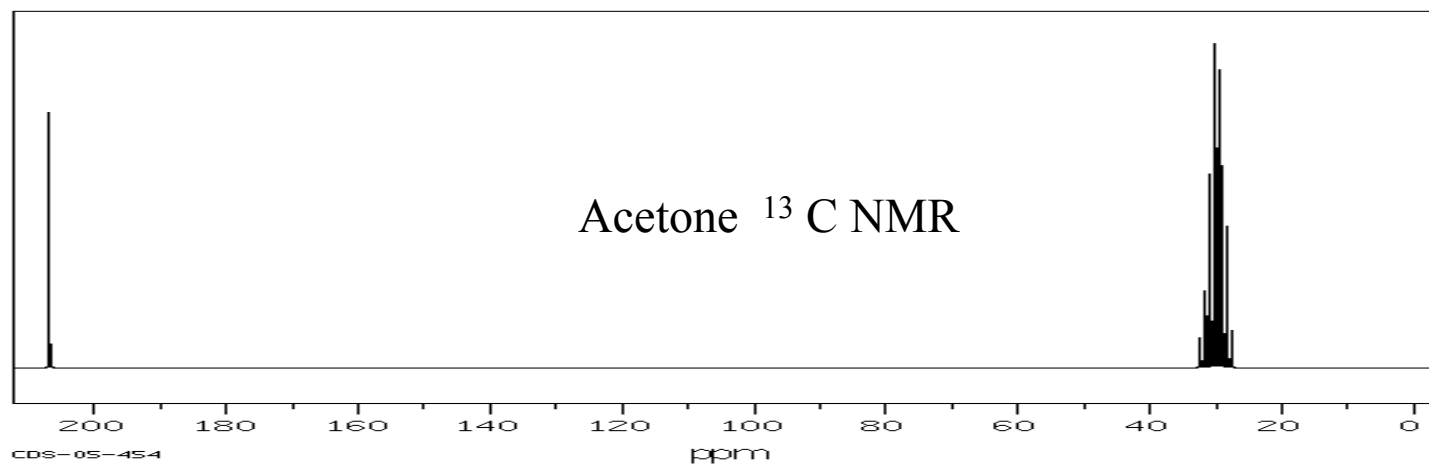
Solvent	Formula	H-NMR shift*	C-NMR shift	multiplet
Chloroform-d	CDCl_3	7.24 (singlet)	77.0	triplet
Carbon tetrachloride	CCl_4		96.7	singlet
Dimethylsulfoxide-d ₆	CD_3SOCD_3	2.49 (pentet)	39.7	septet
Benzene-d ₆	C_6D_6	7.2 (singlet)	128.0	triplet
Acetone-d ₆	CD_3COCD_3	2.04 (pentet)	29.8	septet
Water-d ₂	D_2O	4.65 (singlet)		

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



25.16 MHz

0.75 ml : 1.5 ml CDCl_3



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

<http://www.orgchemboulder.com/Spectroscopy/Problems/index.shtml>

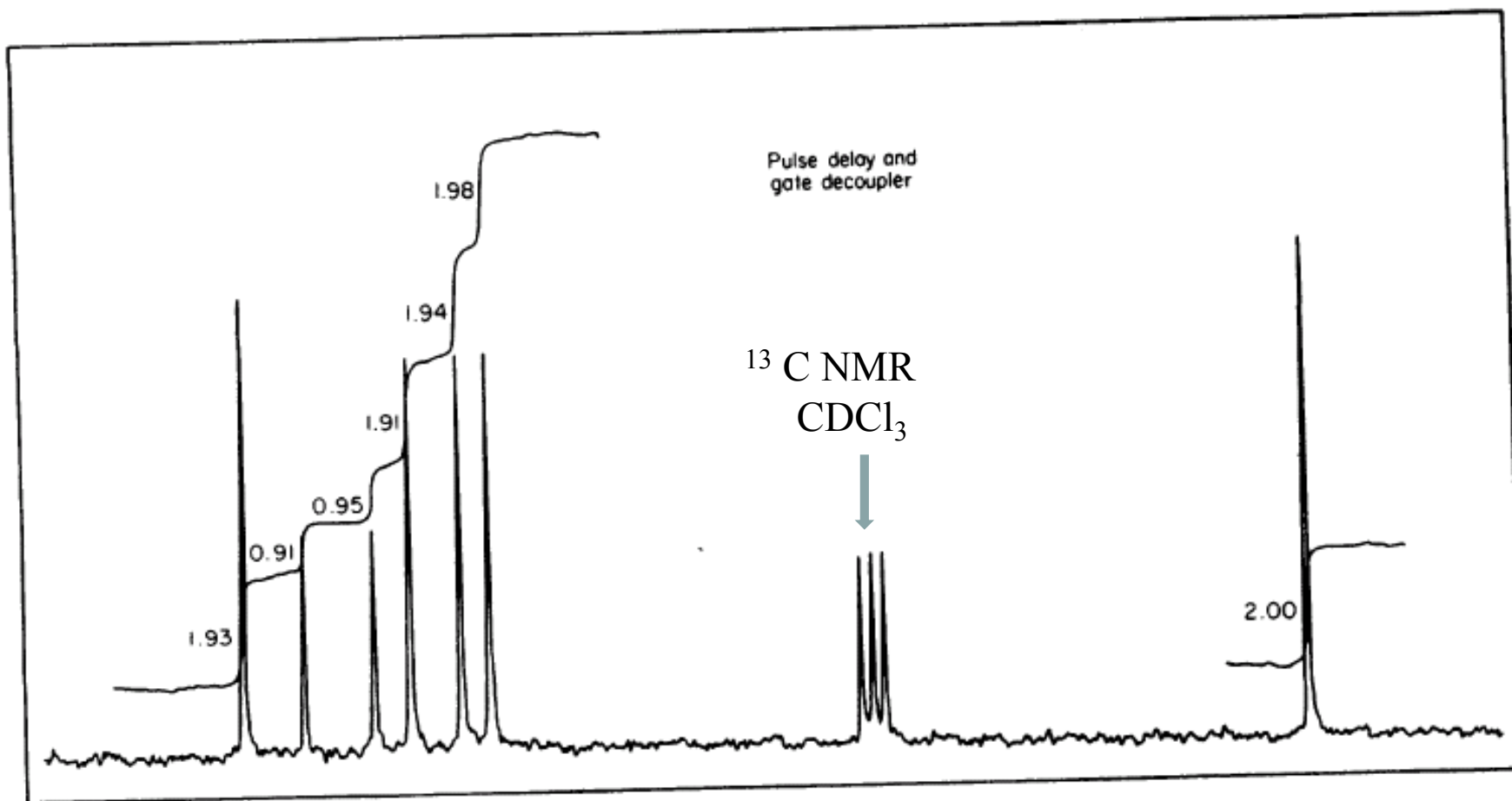


Fig. 7.8 Acenaphthene. Same conditions as Fig. 7.7 but with decoupler ON only during acquisition time; number of transients, 150.