^{13}C-NMR

We can examine the nuclear magnetic properties of carbon atoms in a molecule to learn about a molecules structure.

Most carbons are ^{12}C; ^{12}C has an even number of protons and neutrons and cannot be observed by NMR techniques.

Only 1% of carbons are ^{13}C, and these we can see in the NMR.

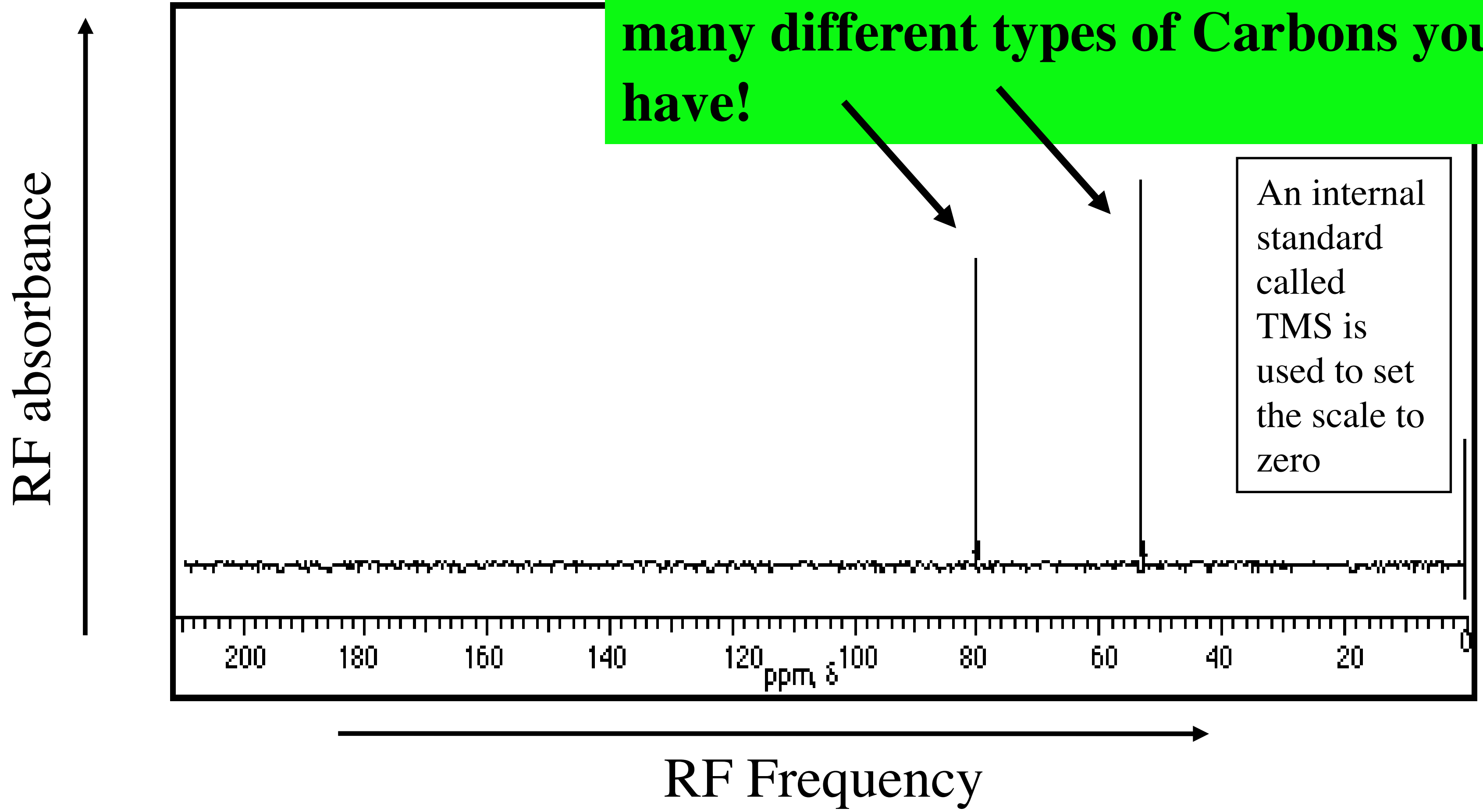
This makes ^{13}C-NMR much less senstive than carbon NMR.

This affects the how we see splitting patterns.

A ^{13}C-NMR spectrum.

Here is what's cool about ^{13}C-NMR:

Different carbons appear at different frequencies! - Now you know how many different types of Carbons you have!

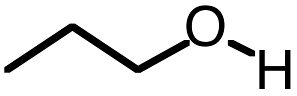


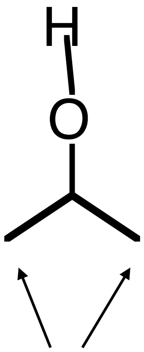
An internal standard called TMS is used to set the scale to zero

The intensity of the peak doesn't does not necessarily correlate to the number of carbons.

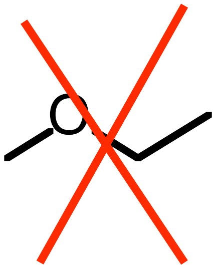
Example: Two alcohols (-OH compound) with formula C_3H_8O

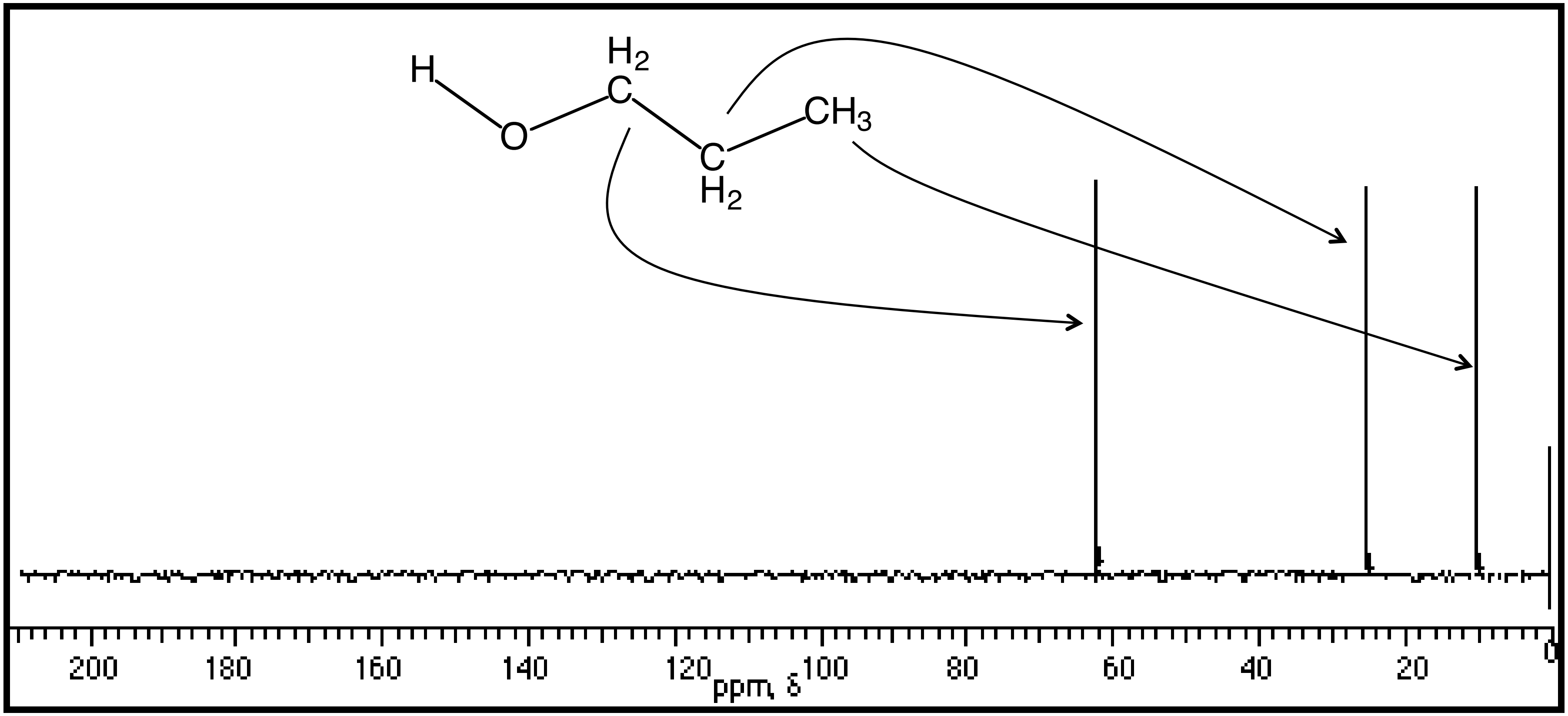
1. IHD = 0
2. Possible structures:



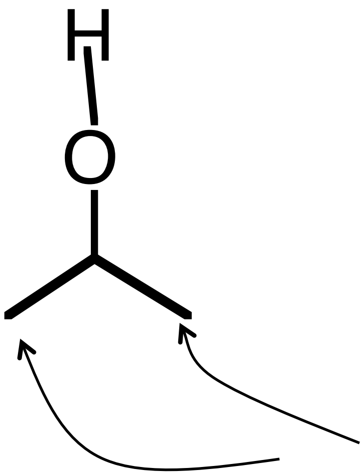


Same!

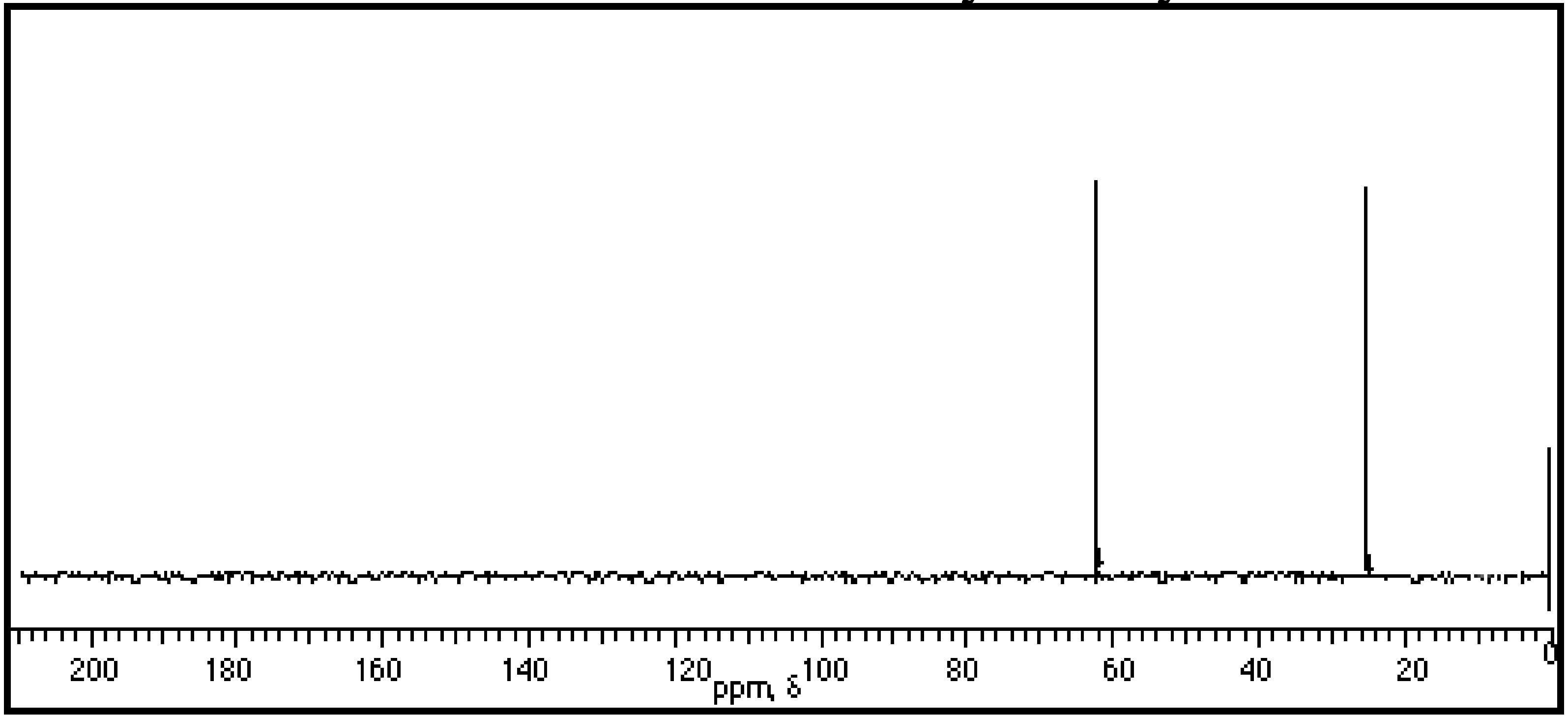




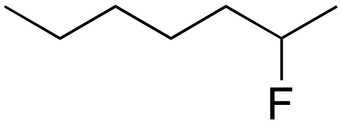
The C-NMR spectrum of isopropanol only shows two different carbons!

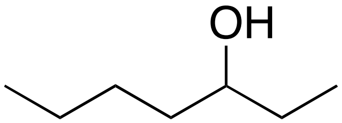


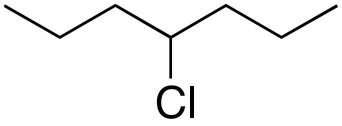
These two carbons are identical by symmetry:

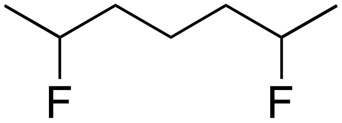


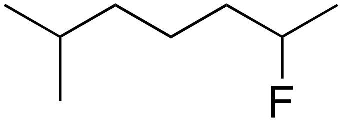
How Many ^{13}C NMR resonances?

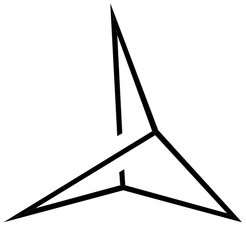


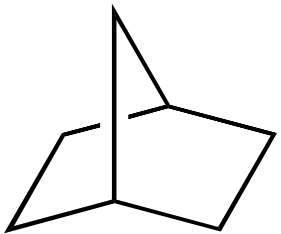


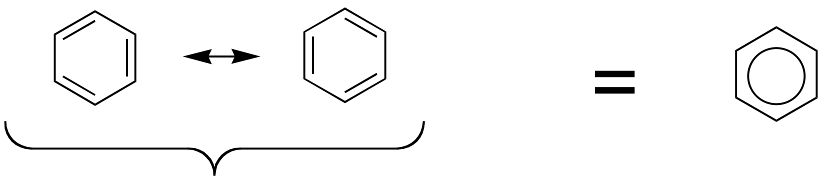






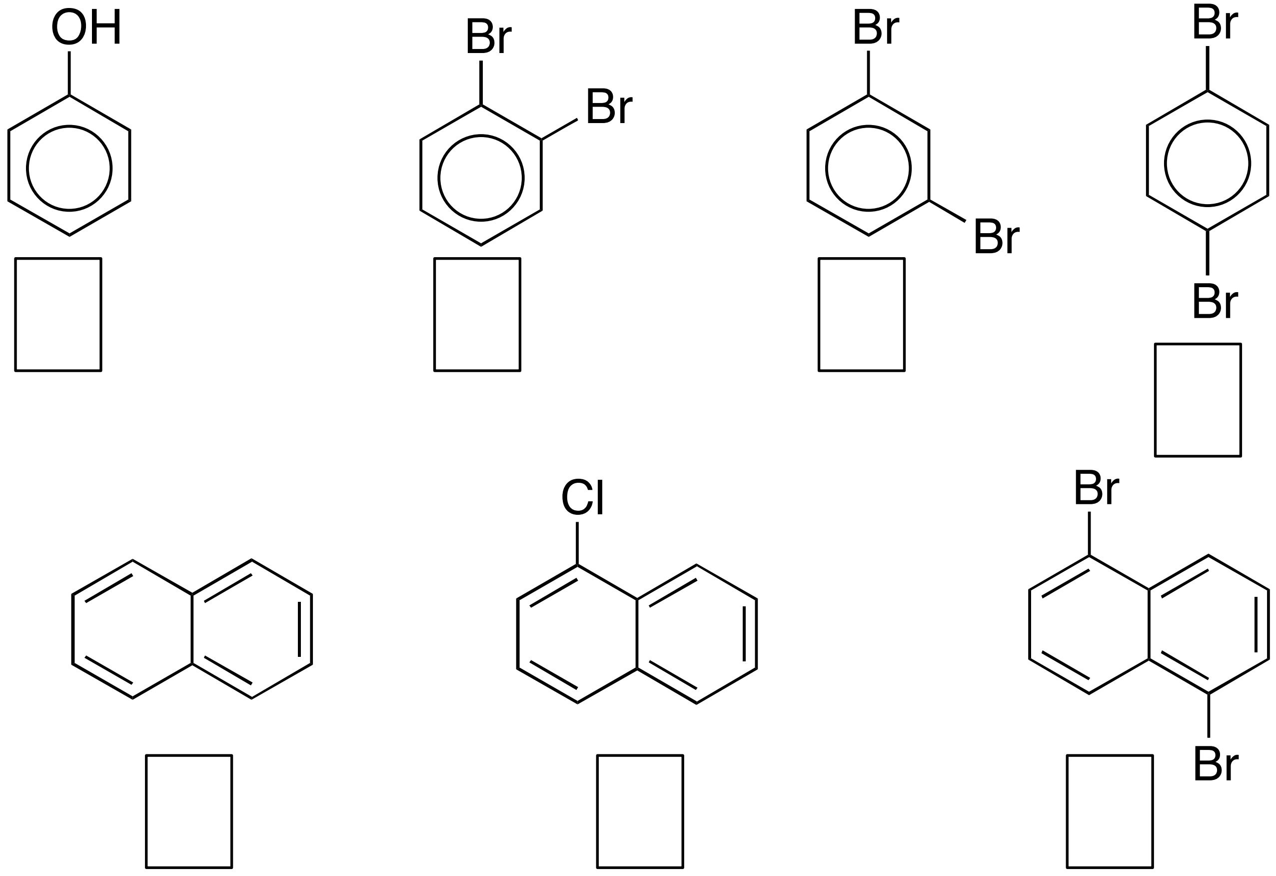




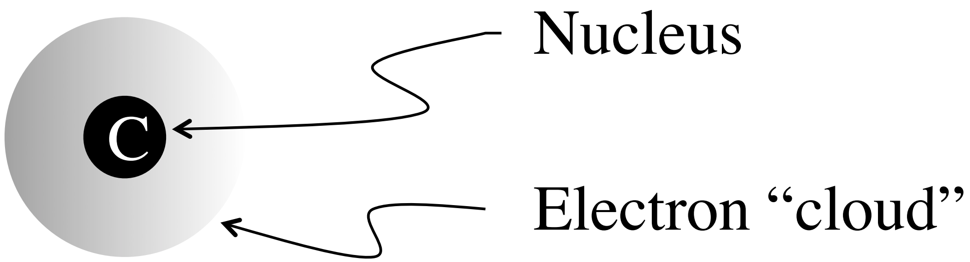


equivalent resonance structures

1

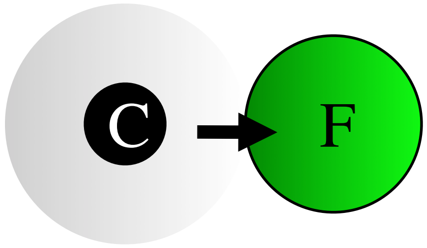


An isolated ^{13}C atoms have the same chemical shift. (resonate at the same frequency)



The electron cloud of the atom partially shields the nucleus from the surrounding magnetic field

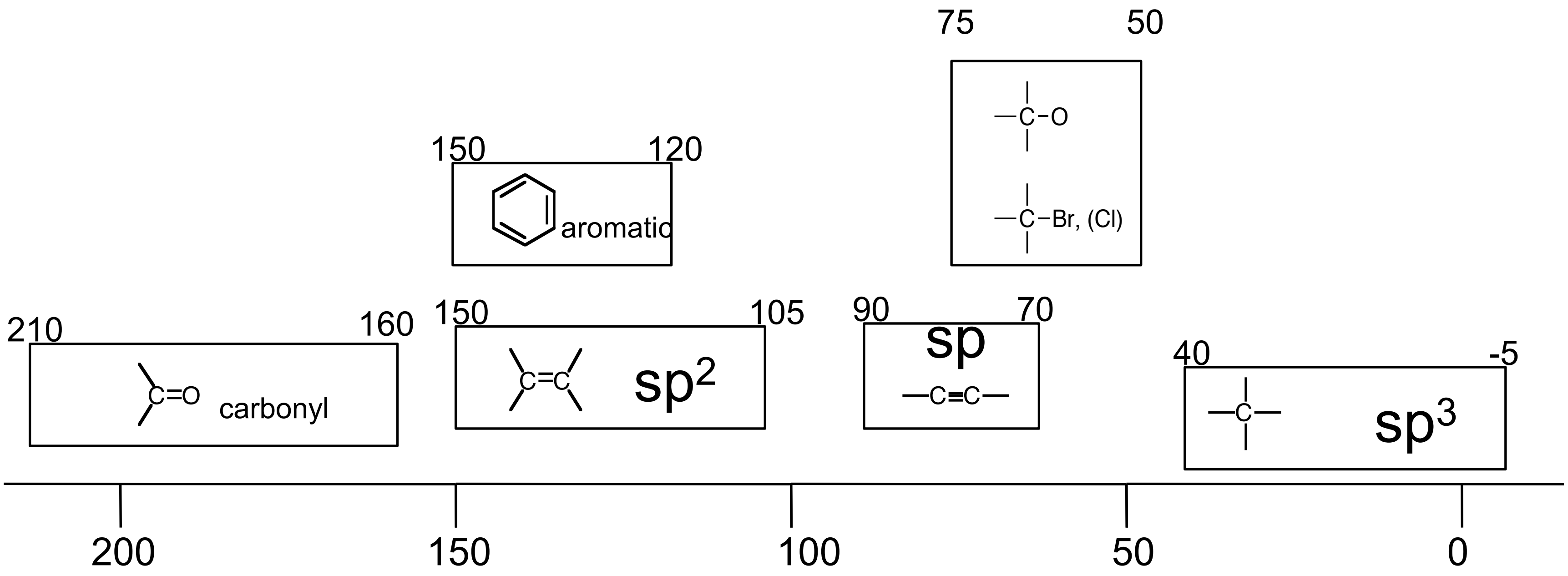
When the carbon nucleus is adjacent to an electronegative atom, the carbon nuclei has fewer Electrons around it.



Nuclei with less electron density around them will resonate at a different frequency: It requires shorter wavelength radio waves (or a weaker magnetic field) to cause a carbon nuclei to resonate if it has less electron density around it.

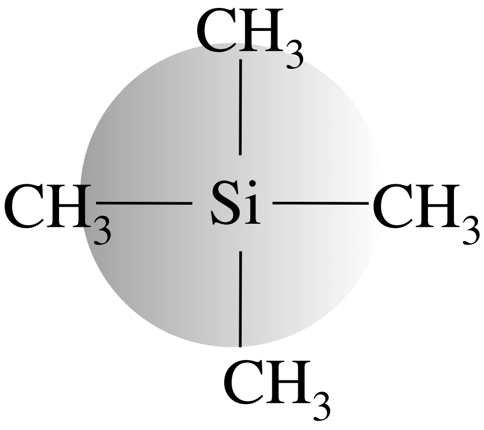
Typical Values of Chemical shift depend on the

1. Hybridization
2. Electronegativity of attached atom(s).



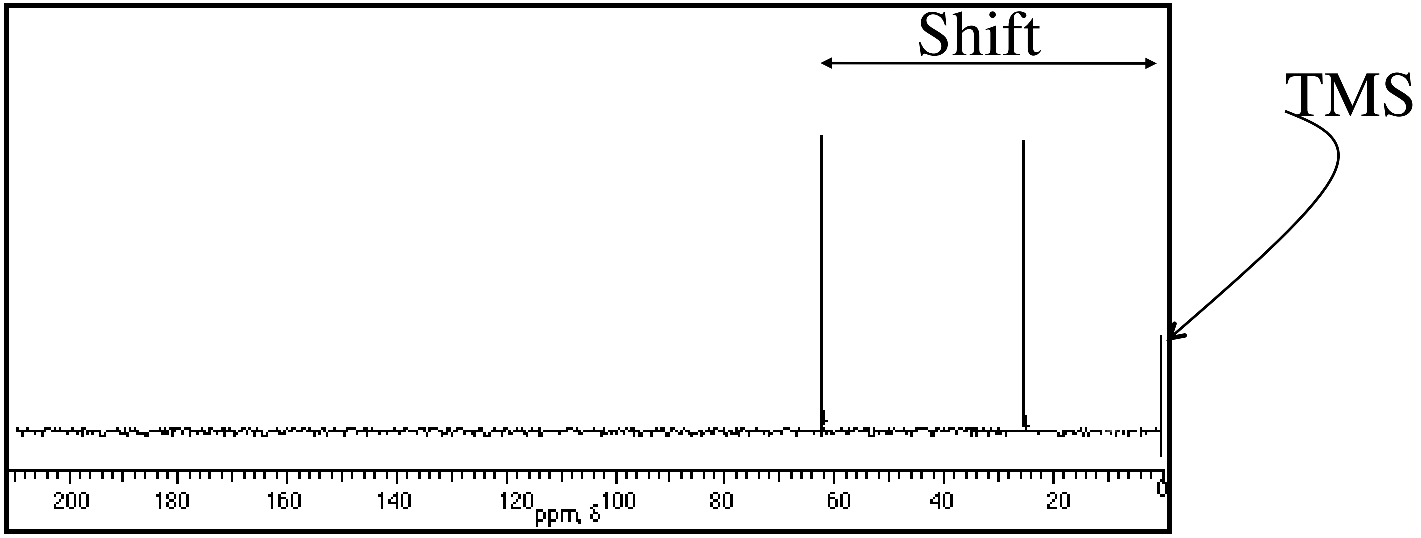
Some specific values are included in tables Section IV your text book!

Conversely atoms that donate electron density cause nuclei to resonate at lower frequencies (higher field strengths).



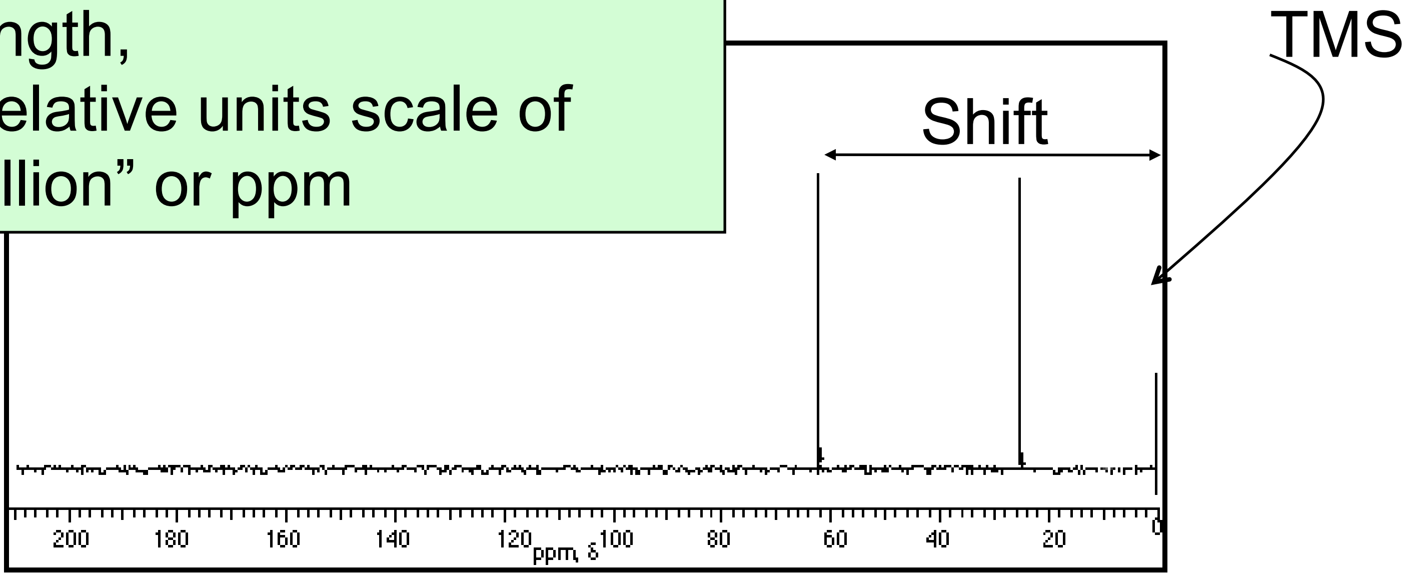
The silicon in tetramethylsilane (TMS) shields the carbon nuclei and makes them appear “up-field”

The chemical shift spectrum is measured relative to TMS.



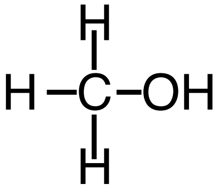
THE δ SCALE IS USED TO MEASURE CHEMICAL SHIFT

δ= is used to signify chemical shift.
Because the frequency depends on the field strength,
one uses a relative units scale of "parts per million" or ppm



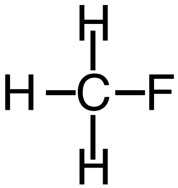
Chemical shifts reported as ppm units give the same values for the same compound regardless of the instrument used!

$$\boxed{\delta = (\nu_{(\text{compound})} - \nu_{(\text{TMS})}) / \nu_{(\text{TMS})}}$$



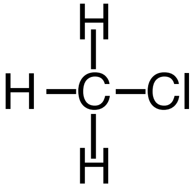
$\mathrm{CH_3OH}$

50.2 ppm



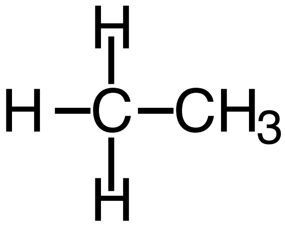
$\mathrm{CH_3F}$

71.6 ppm



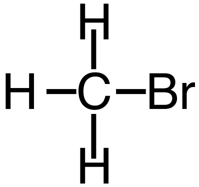
$\mathrm{CH_3Cl}$

25.6 ppm



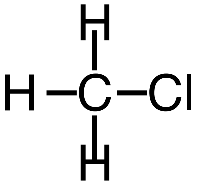
$\mathrm{CH_3CH_3}$

7.3 ppm



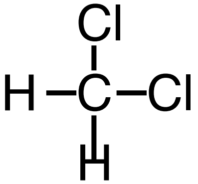
$\mathrm{CH_3Br}$

9.6 ppm



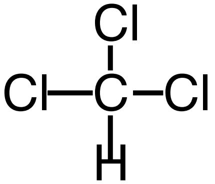
$\mathrm{CH_3Cl}$

25.6



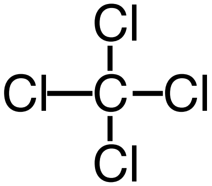
$\mathrm{CH_2Cl_2}$

54.0



$\mathrm{CHCl_3}$

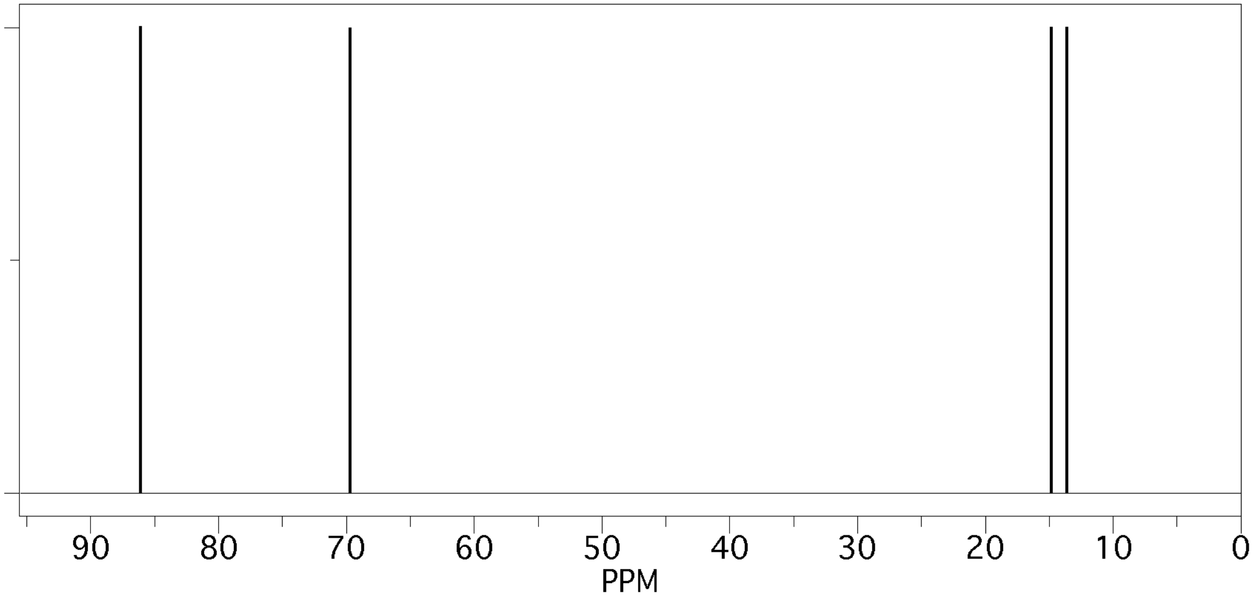
77.2

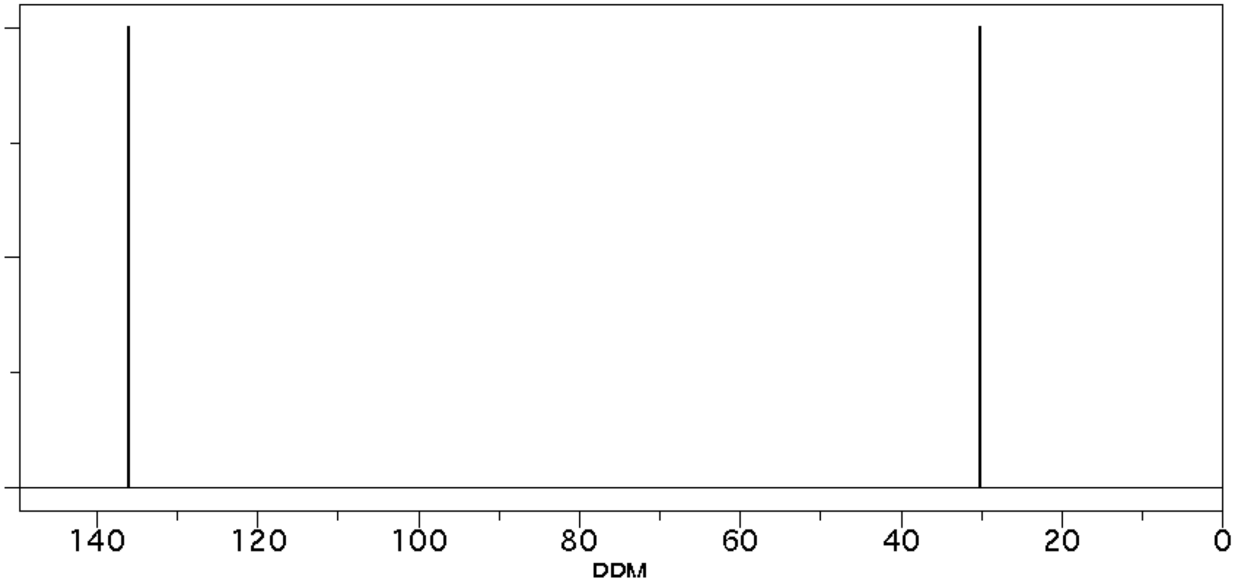


$\mathrm{CCl_4}$

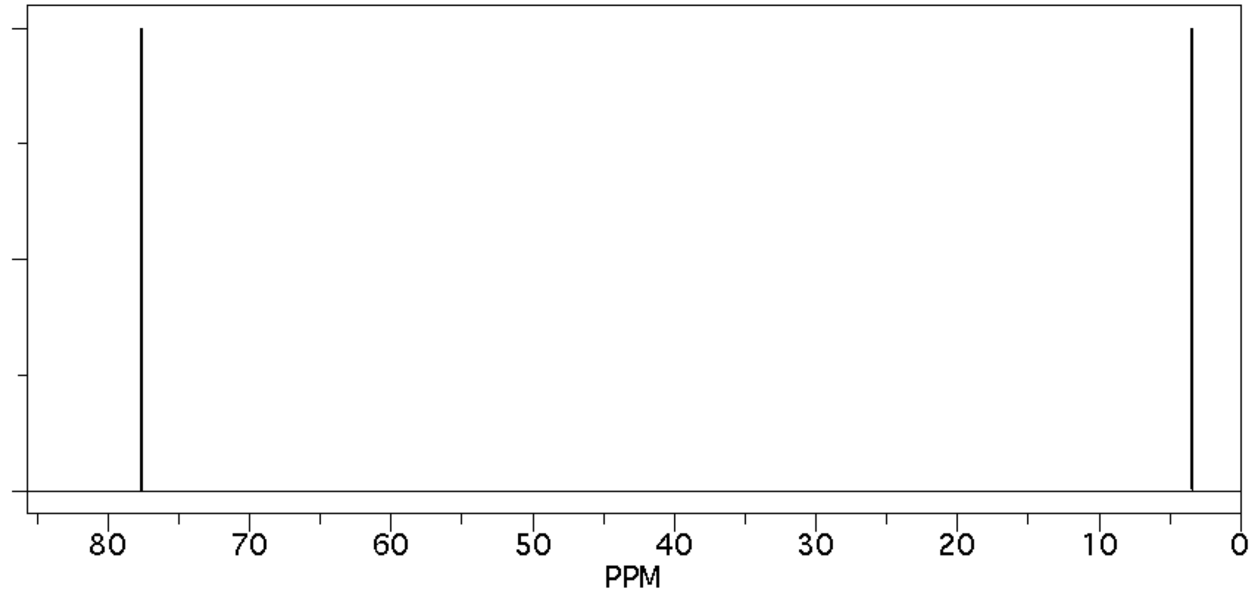
96.1

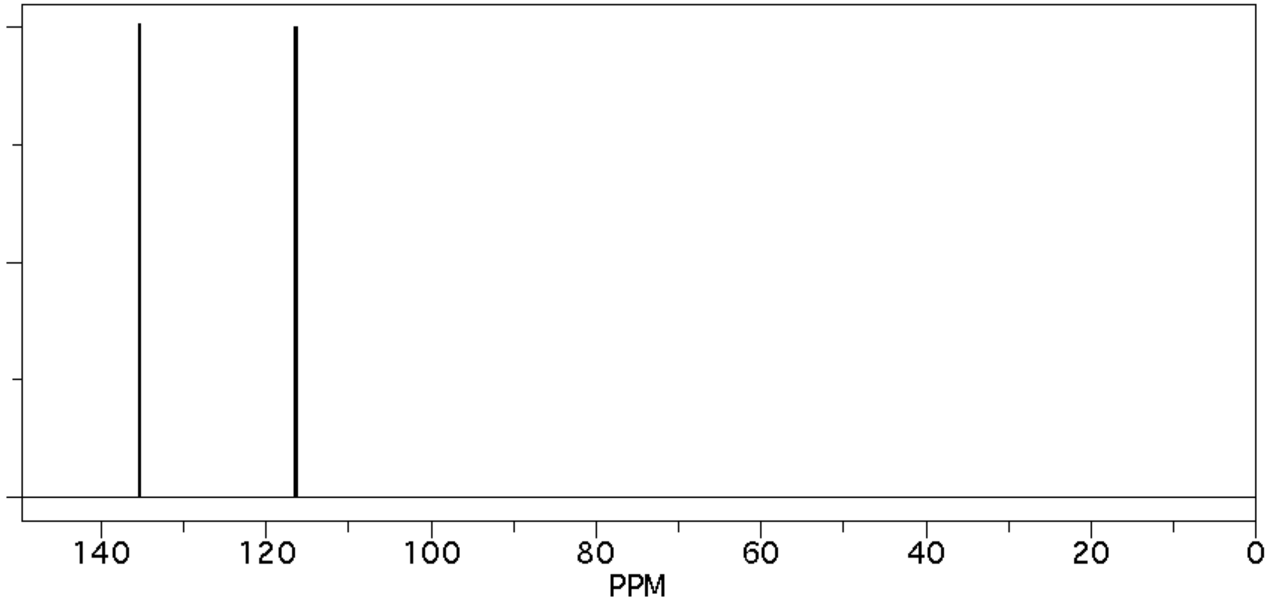
C_4H_6



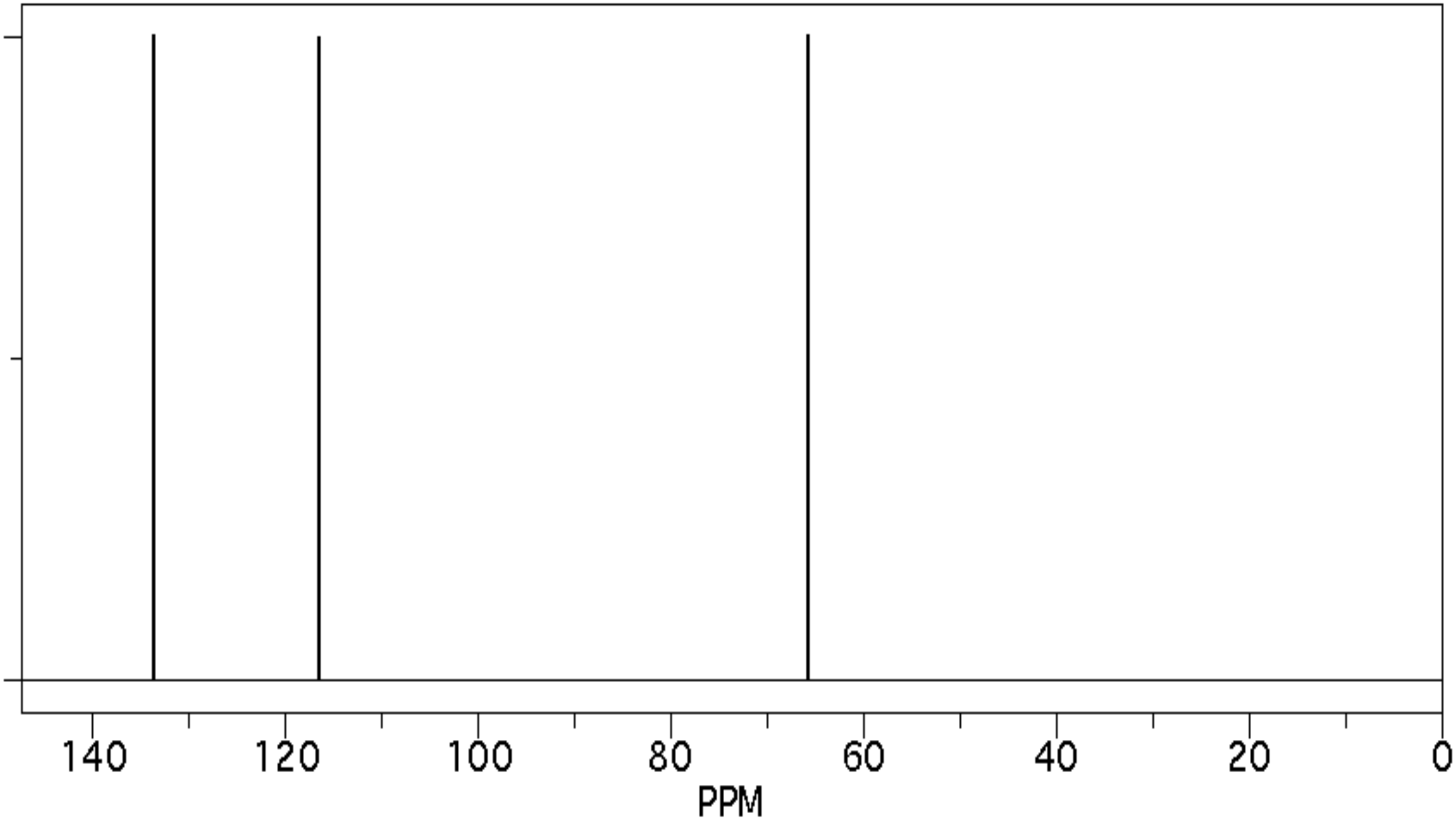


C_4H_6

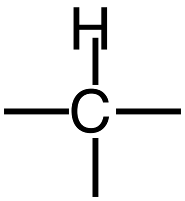




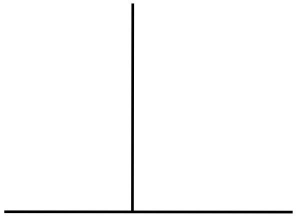
C_3H_6O



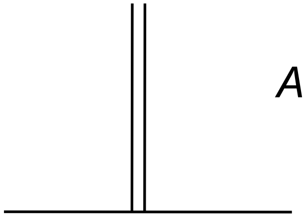
^{13}C peaks are in reality split by bonded protons.



Generally
shown like this:

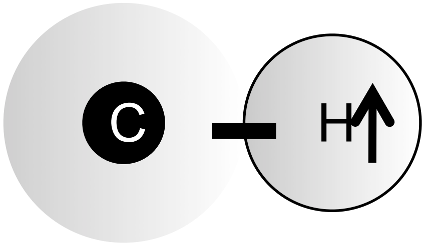


Actually looks
like this:

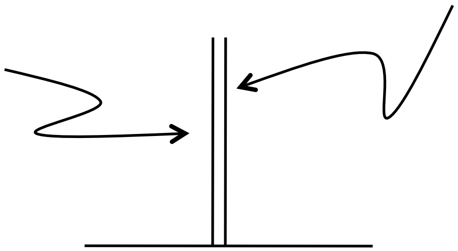


A "doublet"

Why??



Adjacent nuclear spin of the proton <u>locally</u> increases magnetic field felt by carbon nuclei.

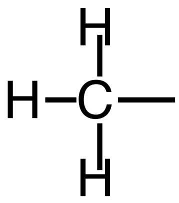


Carbons next to down proton spin

Carbons next to up proton spin

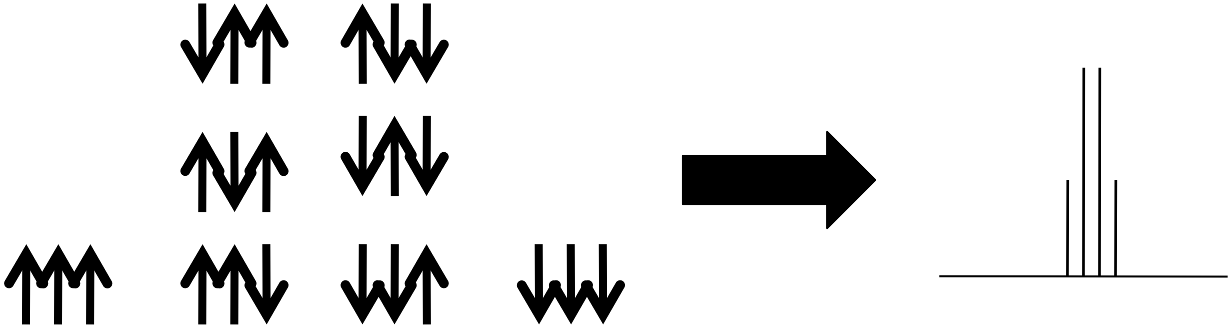
NOTE: There are only two possible peaks for C's having one adjacent proton.

↑ or ↓



Appears as **quartet.**

There are eight possibilities:



The general rule is:

The number of peaks observed is equal to the number of attached protons, (N), plus one.

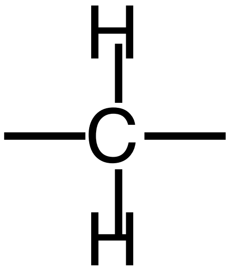
Splitting = N+1

FOR ^{13}C it is the number of protons directly attached to the carbon that cause splitting.

PAY ATTENTION!:

^{13}C-NMR

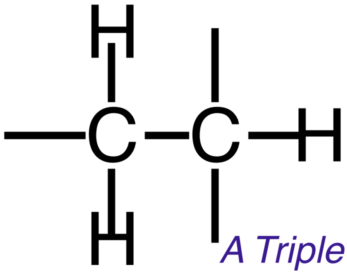
Splitting pattern reflects how many protons are directly attached to the carbon atom



A Triplett

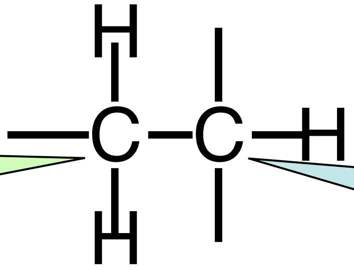
^{1}H-NMR

Splitting pattern reflects how many protons are connected to adjacent carbon atom(s)



A Triplett

A doublet

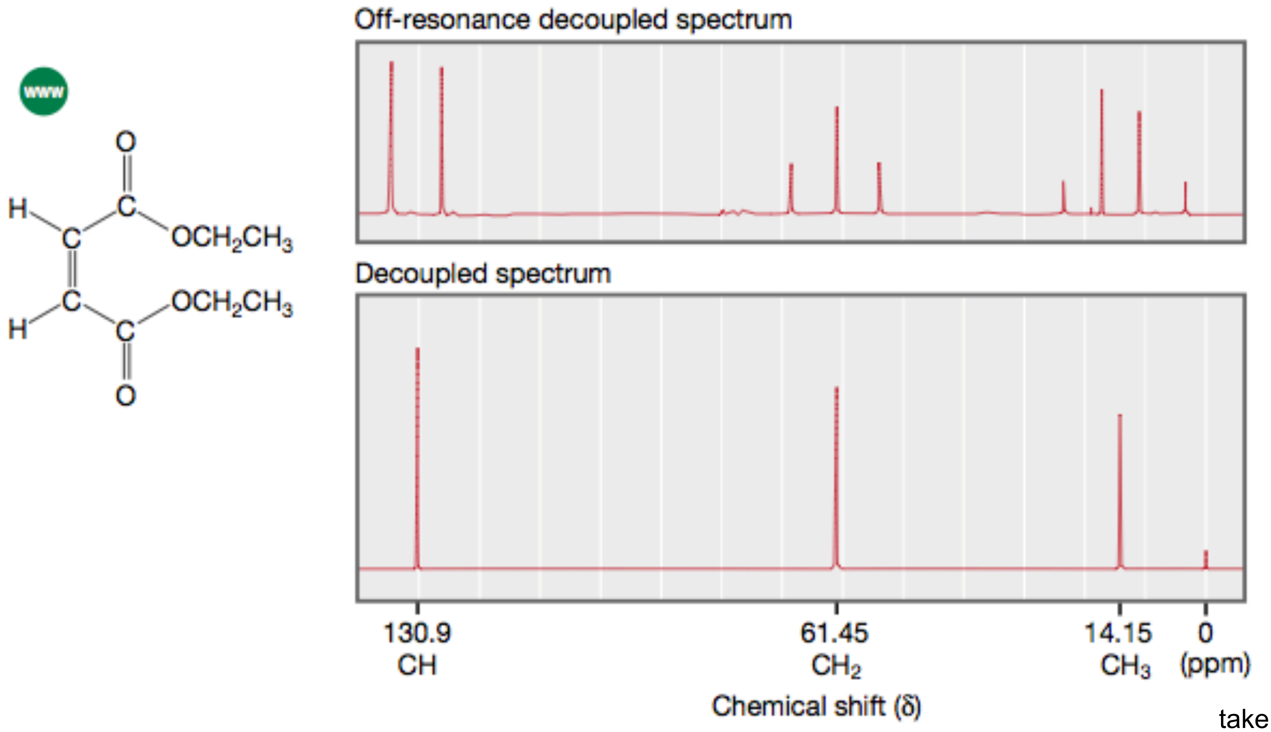


The chances that my neighbor is also a C-13 is 1/100

there is a 99% chance that the attached “H” has a spin

We typically observe decoupled Spectra

Decoupled and off-resonance decoupled ^{13}C NMR spectra of



taken from Maitland Jones 3rd Ed.

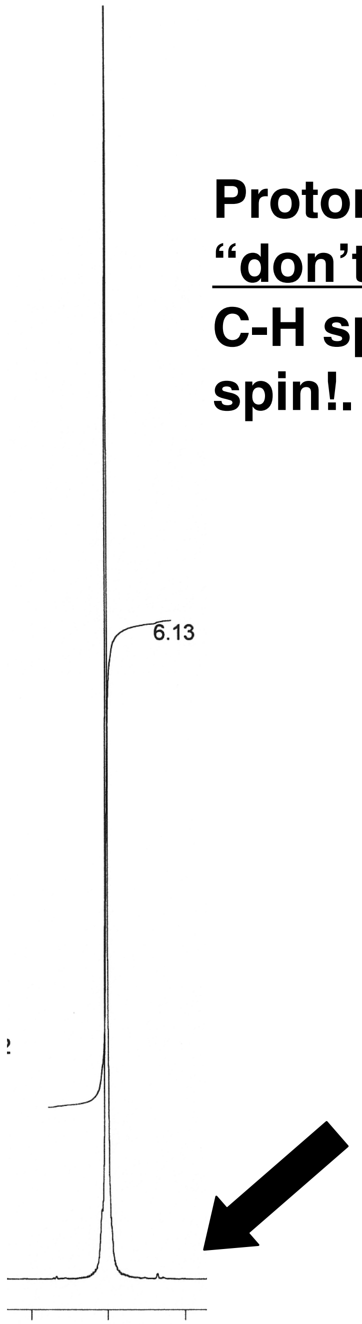
- More sensitive!
- less confusing.

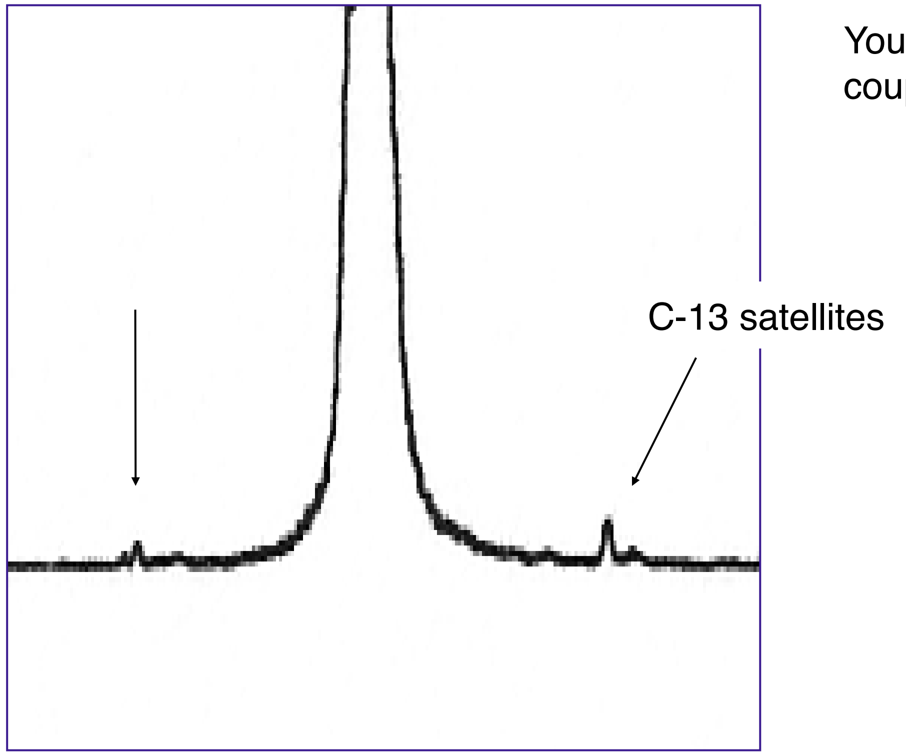
Why don’t the spins on adjacent Carbons split each

C–C

Only 1% of Carbons have a spin! (Most are ^{12}C and are NMR inactive).
Therefore only 1 in ten thousand pairs of Cs have both have spin and are coupled. That’s too small to detect!

Protons can couple (cause splitting) of C-13 peaks but <u>we "don't see" splitting of proton peaks by carbon!!</u>
C-H splitting is very small because only 1% of Carbon has a spin!.



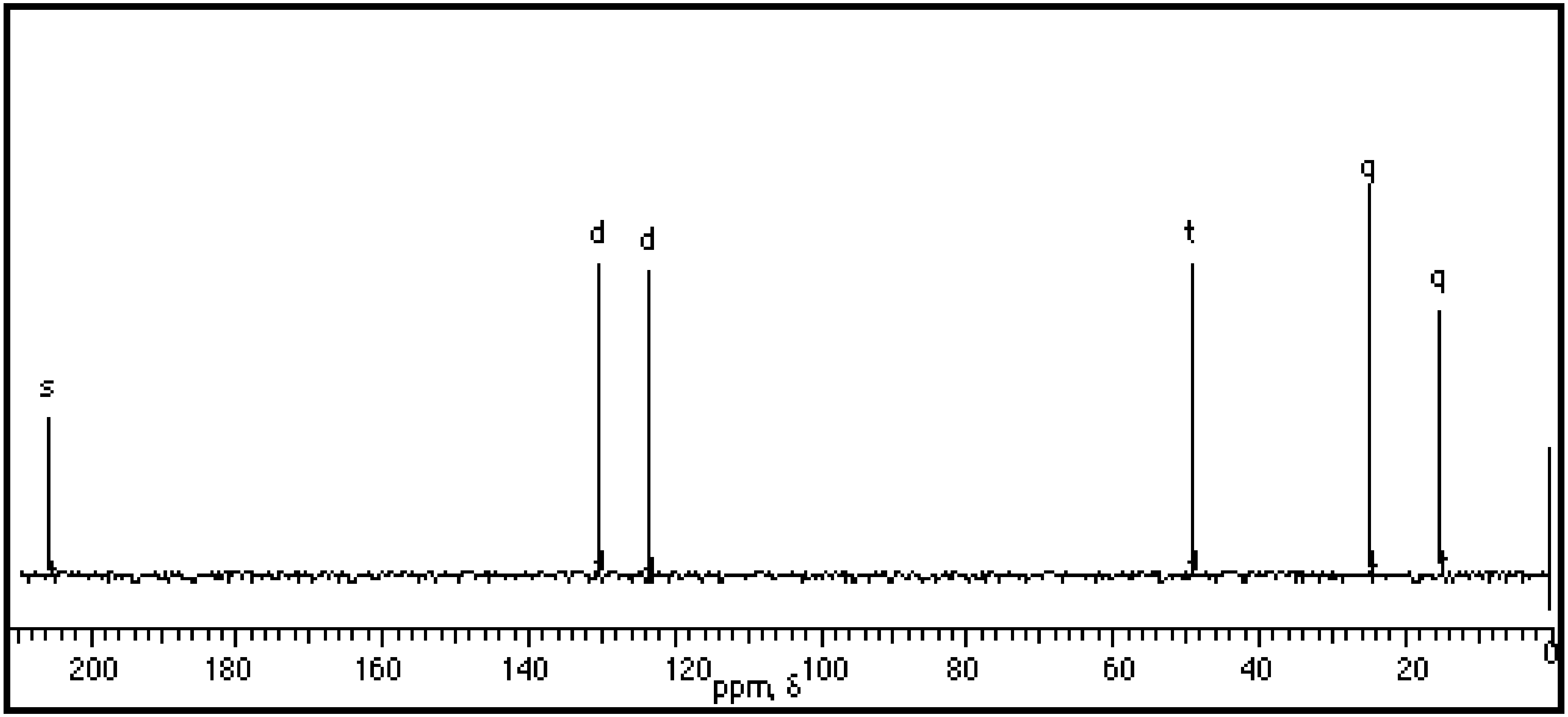


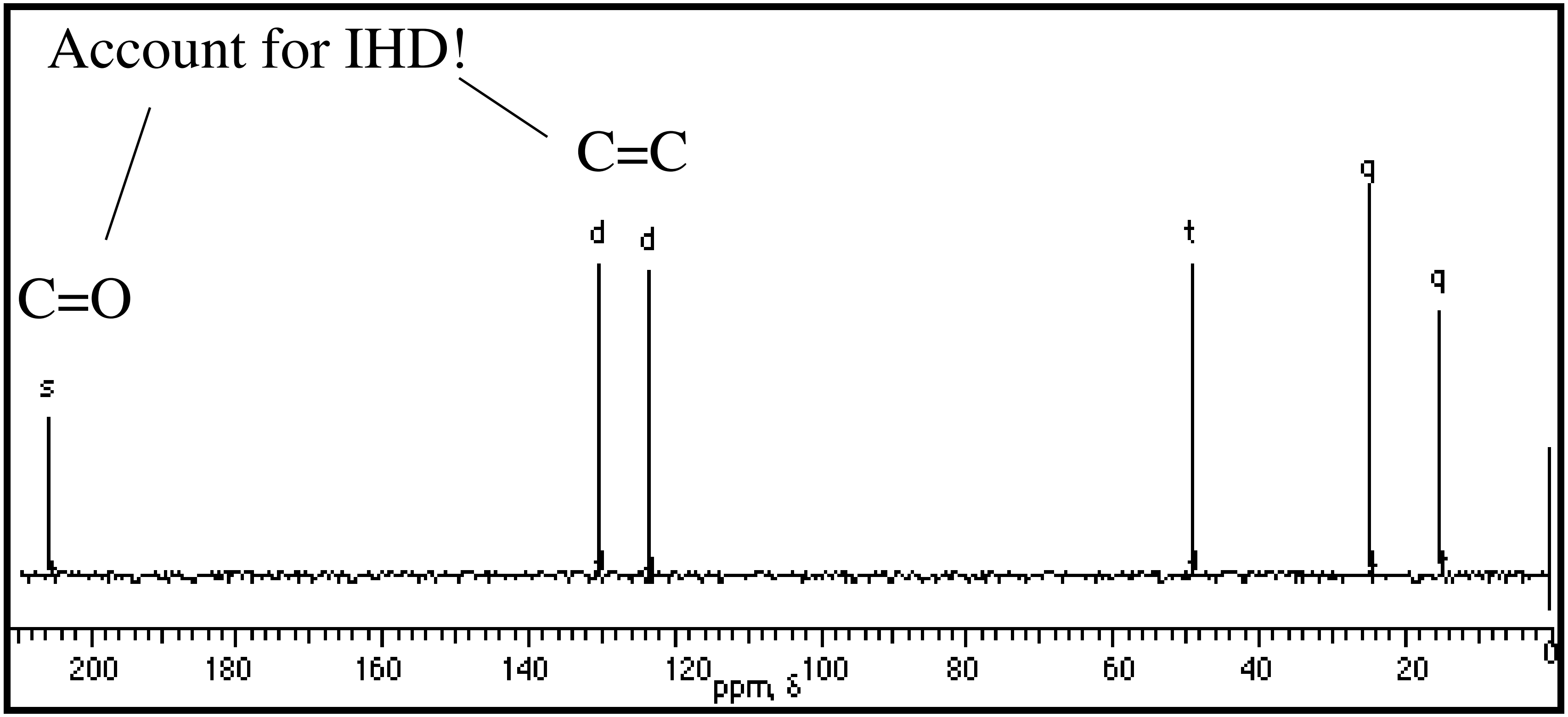
You can see carbon-proton coupling if you look very closely!

Note all of these split peaks can quickly get confusing:

Am I looking at two different carbon resonances or a single doublet?

For this reason we show our spectra without splitting. But we often see the splitting indicated over the peak:




Account for IHD!

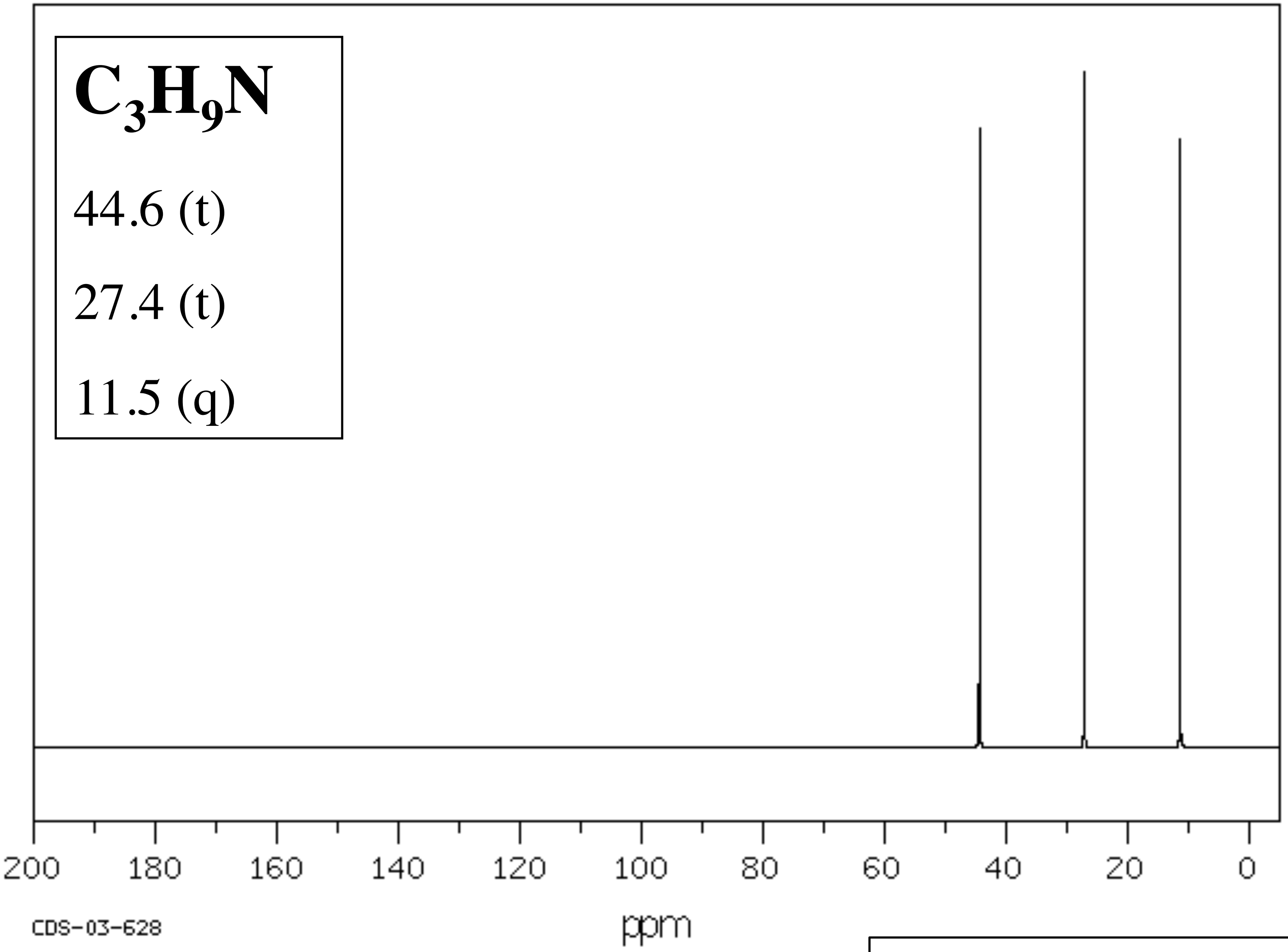
C=O

C=C

$C_6H_{10}O$

IHD = 2

SYMMETRY No, same number of resonances as formula



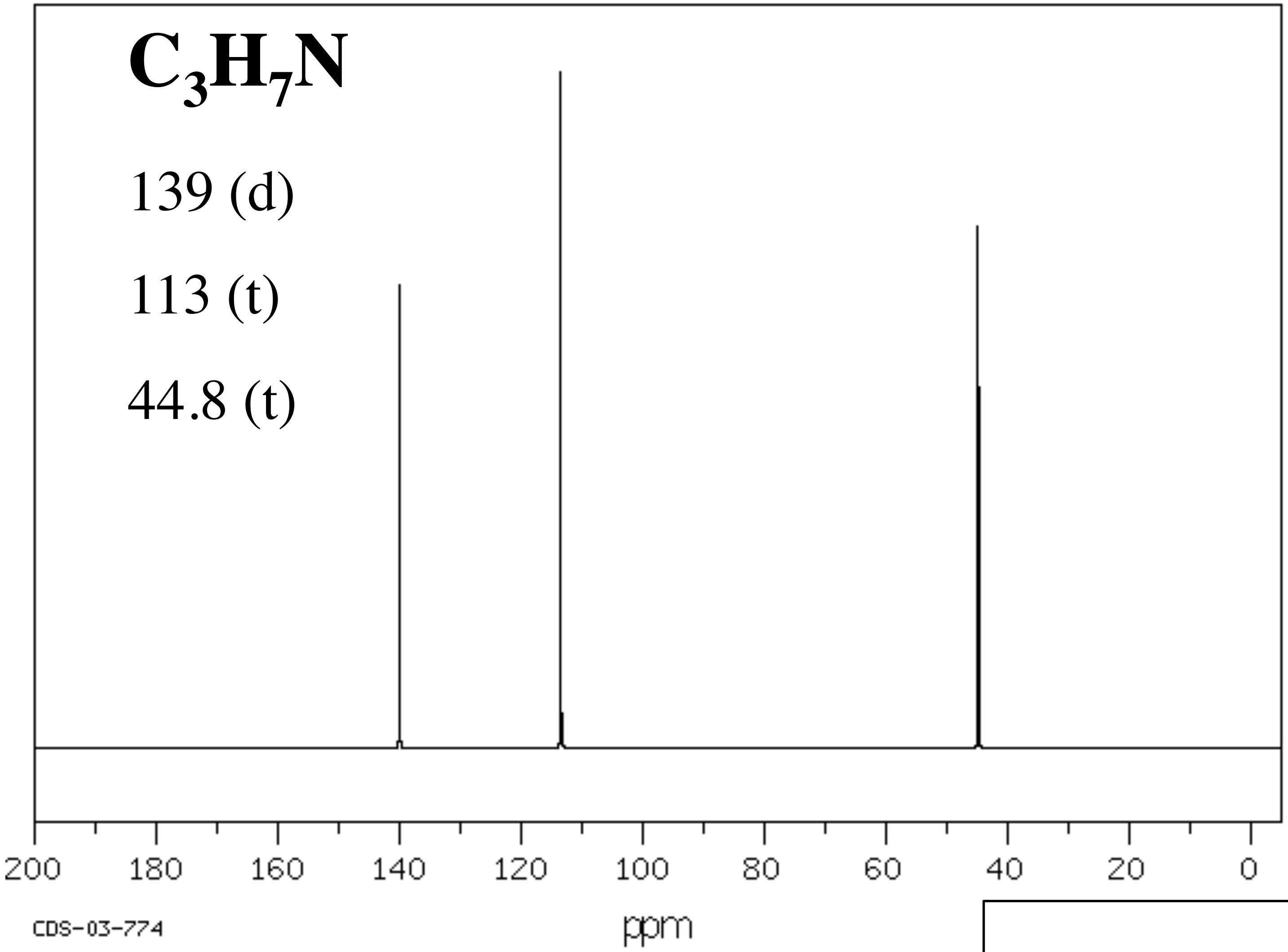
C_3H_9N

44.6 (t)

27.4 (t)

11.5 (q)

CDS-03-628



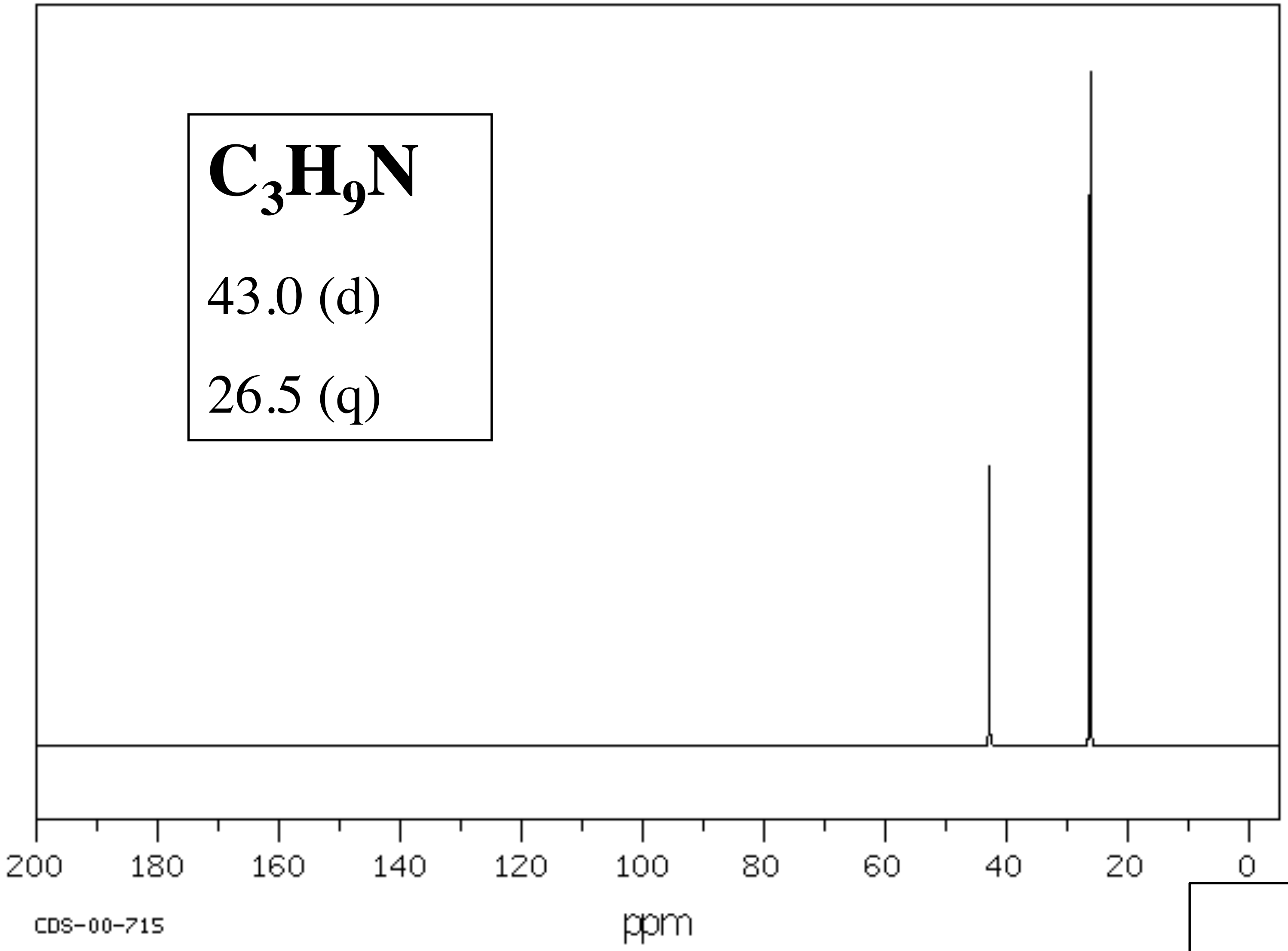
C_3H_7N

139 (d)

113 (t)

44.8 (t)

CDS-03-774



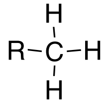
C_3H_9N

43.0 (d)

26.5 (q)

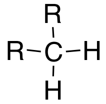
It is helpful to know what typical values of unfunctinalized C’s

Approximate Chemical Shifts ranges for unsubstituted Alkanes



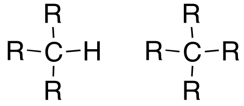
$\mathrm{R{-}CH_3}$

5-22 ppm



$\mathrm{R_2CH_2}$

15-33 ppm



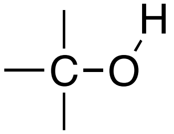
$\mathrm{R_3CH}$ $\mathrm{R_4C}$

25-35ppm

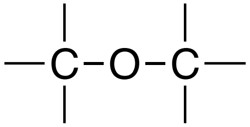
C=C 110-150ppm

—C≡C— 66-90ppm

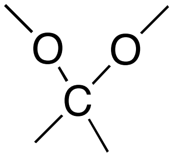
If your molecules containing Oxygen:



50 - 75 ppm



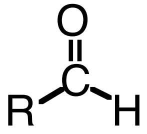
50 - 75ppm
(Similar to alcohol
but two of them!)



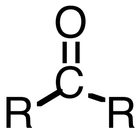
90 - 100 ppm

R = alkyl

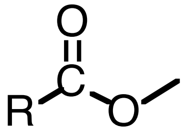
X = Cl, Br, I



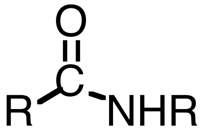
195 - 220
doublet



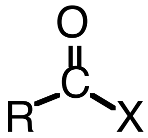
195 - 220
but singlet!



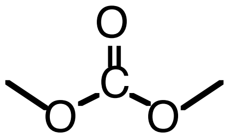
165-180



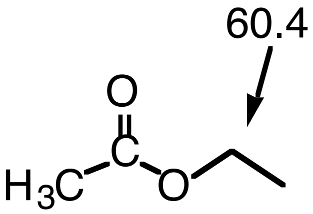
165-180

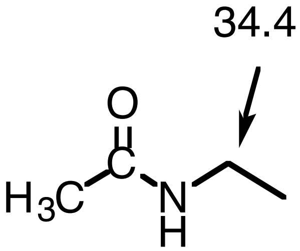


165-180



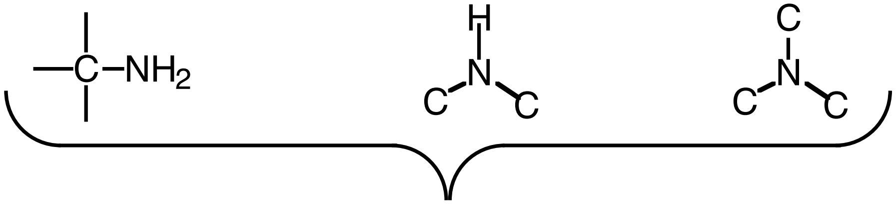
~155





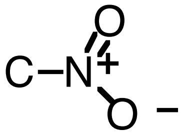
If your molecule contains Nitrogen:

Amines:



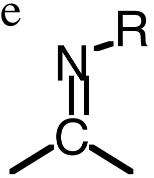
28-47 ppm

Nitro-

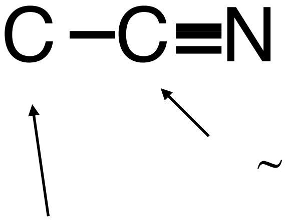


61 - 85 ppm

Imine

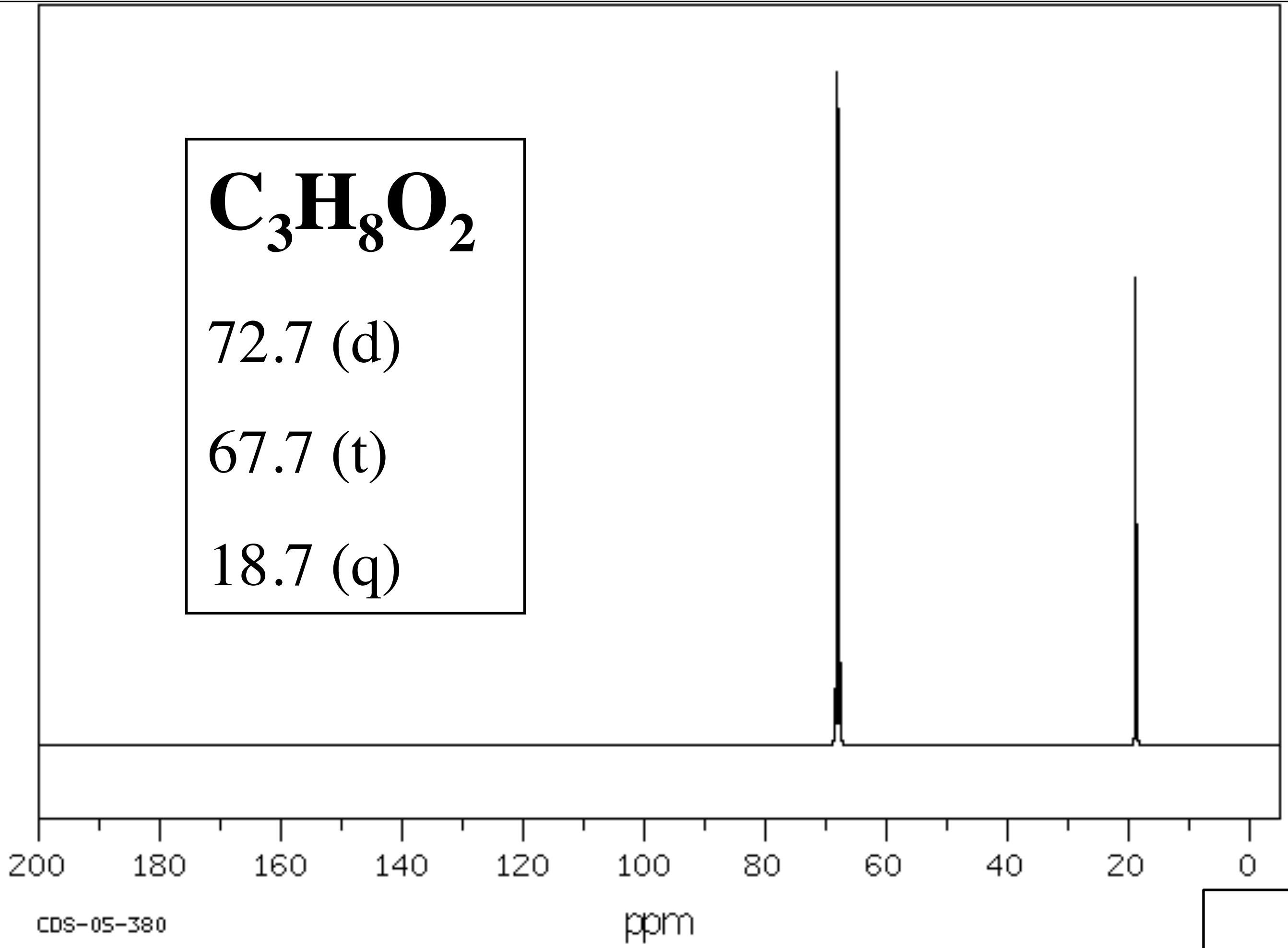


~155 ppm



~120

14-30

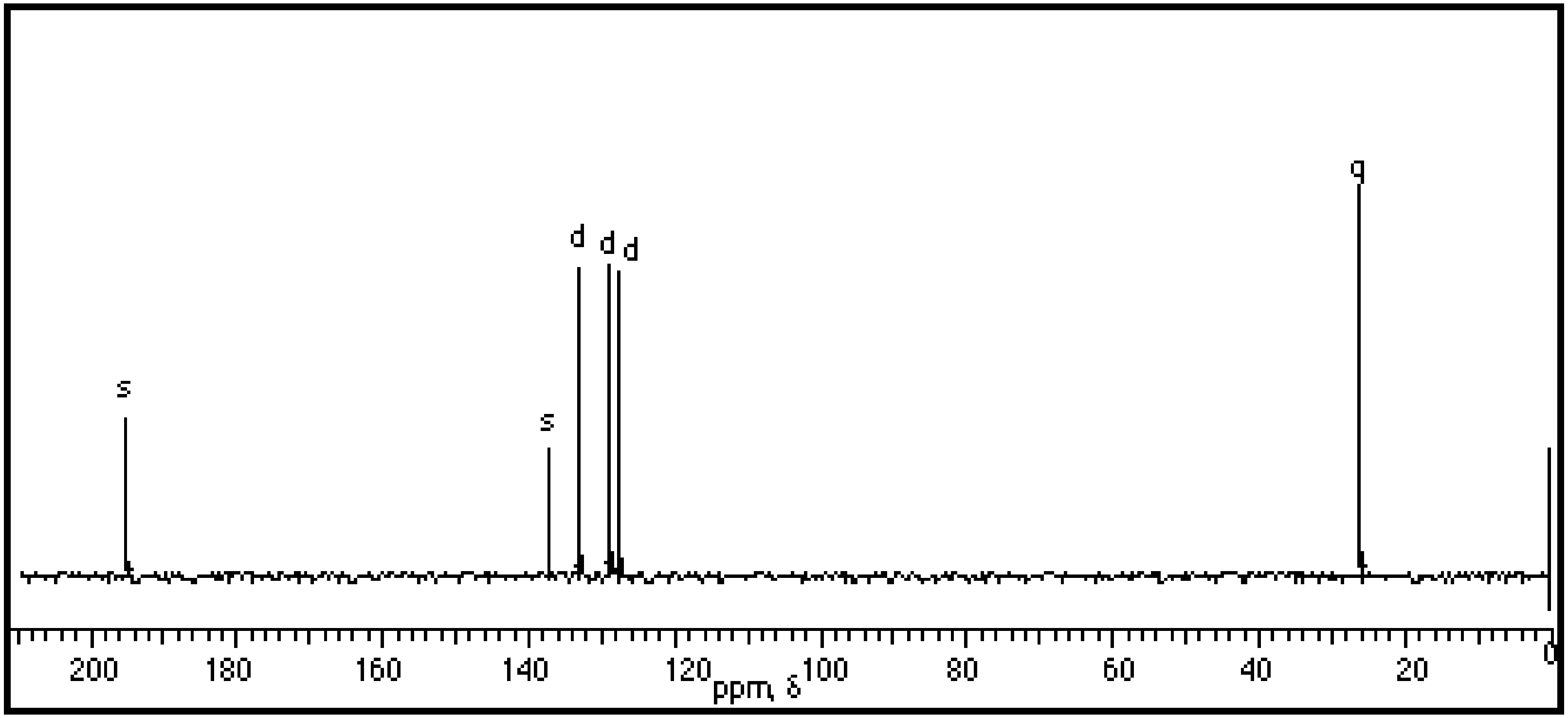


$C_3H_8O_2$

72.7 (d)

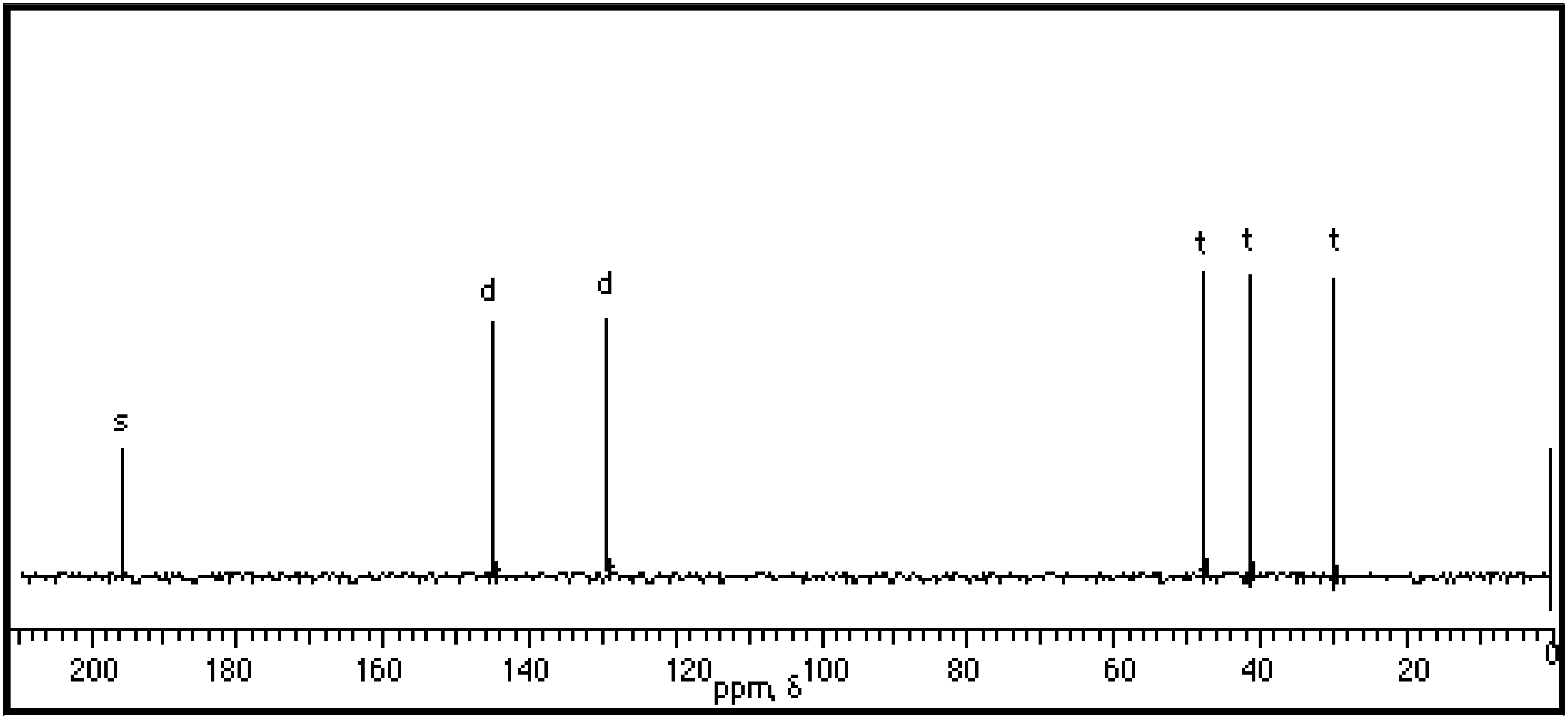
67.7 (t)

18.7 (q)



C_8H_8O

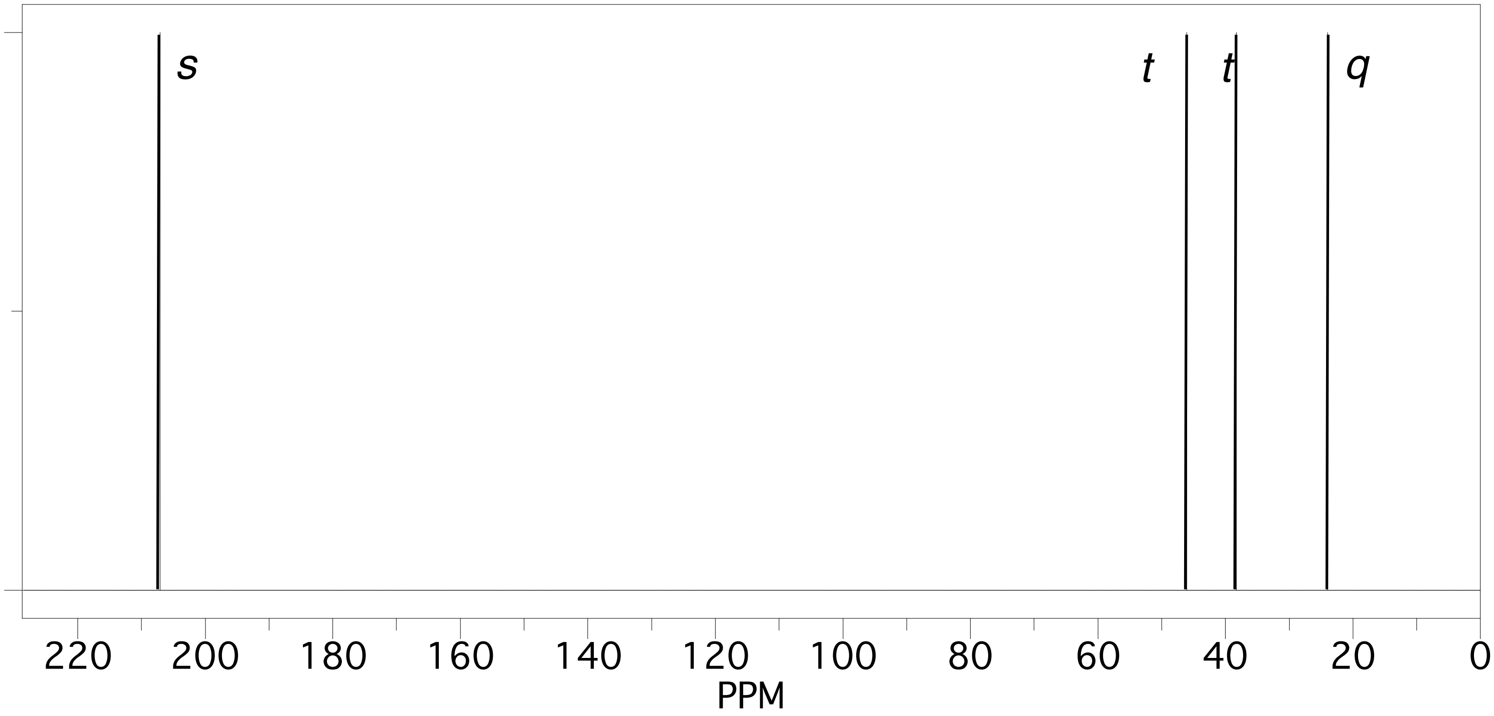
IHD
Symmetry
What is the O doing?
What other groups can you identify?

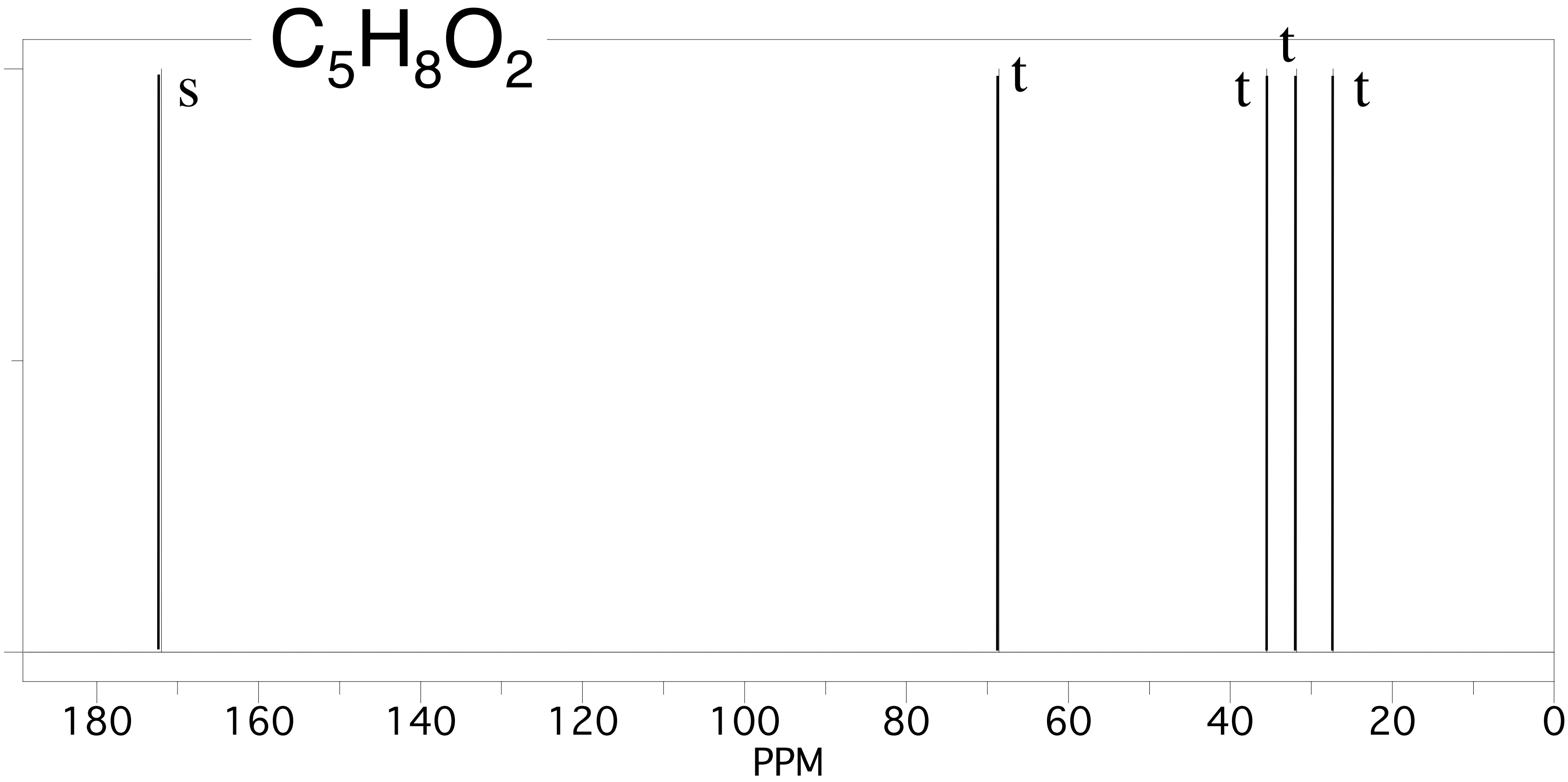


C6H8O

IHD
Symmetry
What is the O doing?
What other groups can you identify?
Can you account for the IHD?

C_4H_7ClO



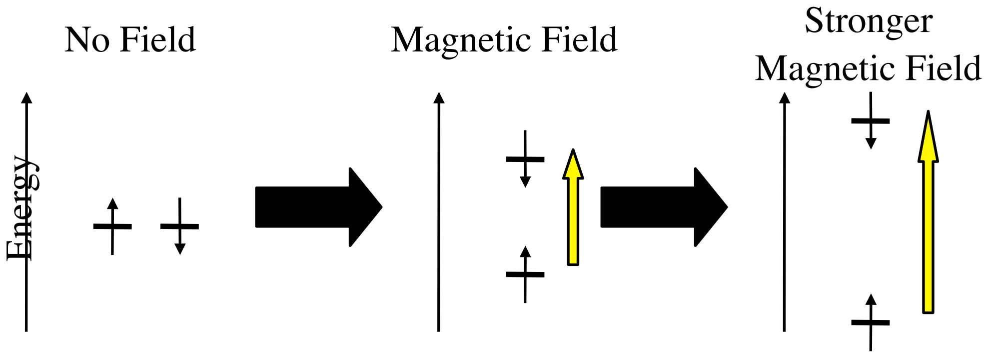

$C_5H_8O_2$
s
t
t
t
t
180
160
140
120
100
80
60
40
20
0
PPM

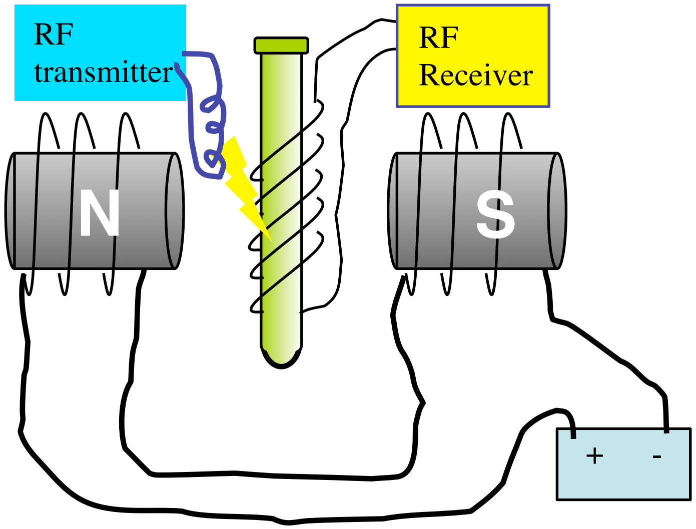
How do you take an NMR??

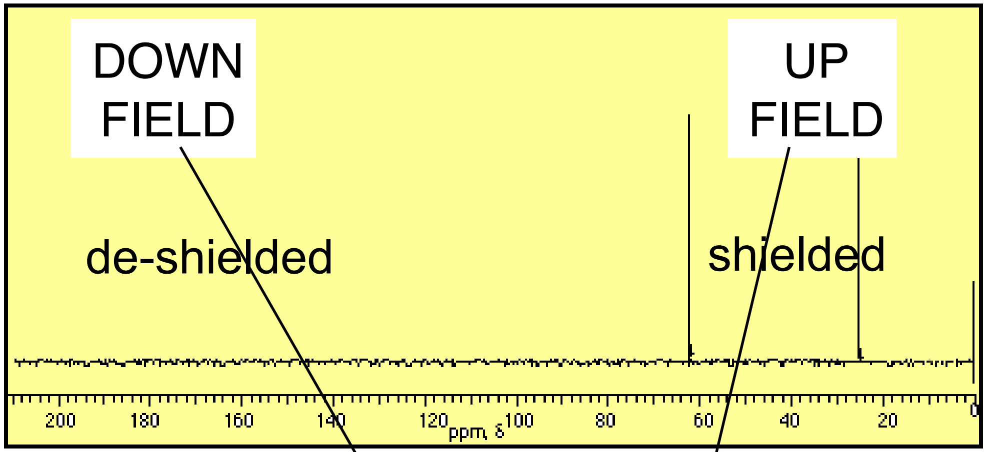
Max Tofield Rogers 1956

I. Constant Radio frequency but change magnetic field

OLD TRADITIONAL WAY!

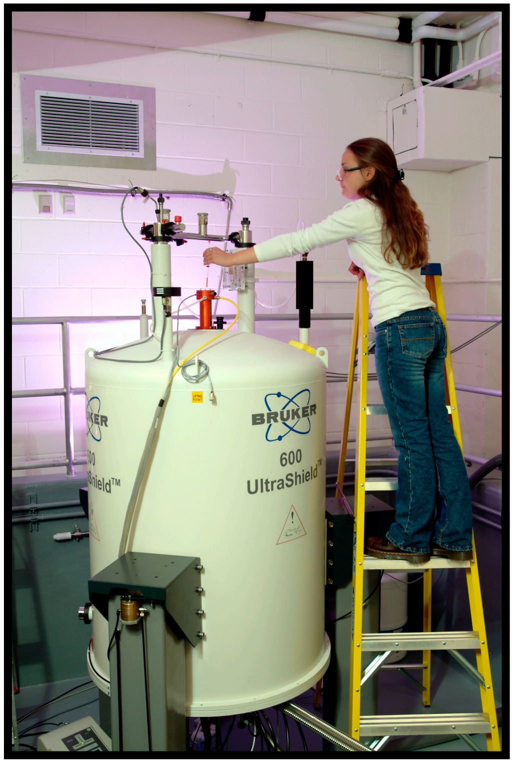




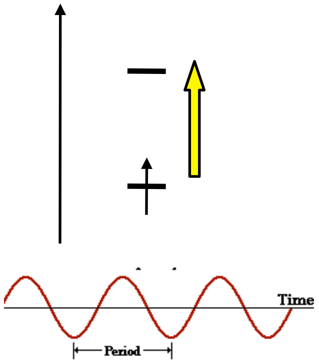


Know these terms!!

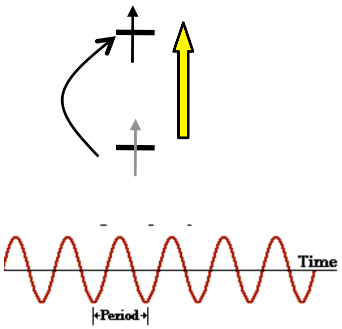
Modern NMR spectra are obtained at constant field strength



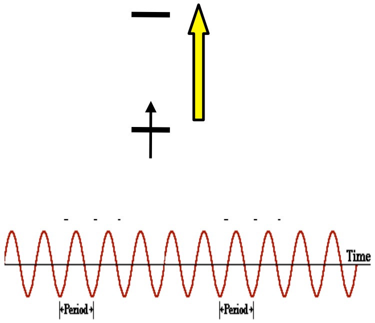
CONSTANT MAGNETIC FIELD!--Change Frequency



No Absorbtion
not enough
energy



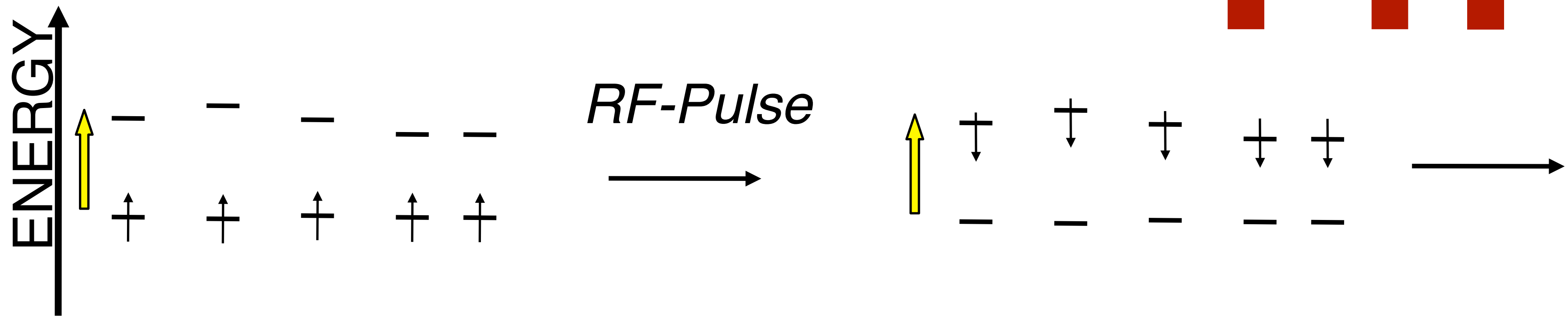
Absorbtion
Energies Match!



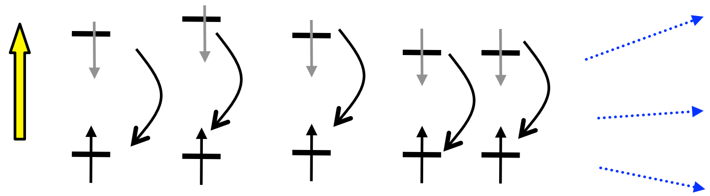
No Absorbtion
Energy too high

FT-NMR

FYI

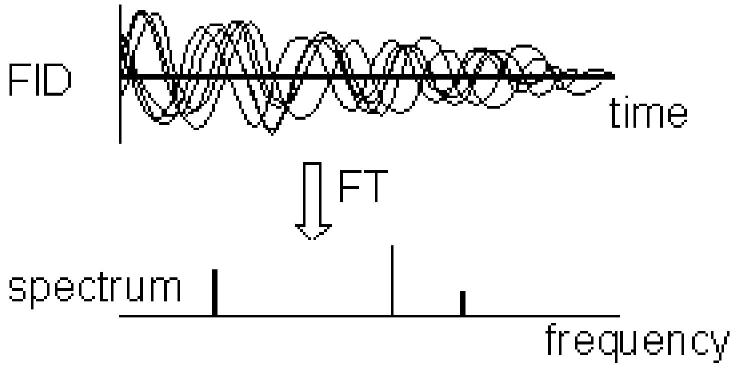


RF-Pulse



different RF frequencies

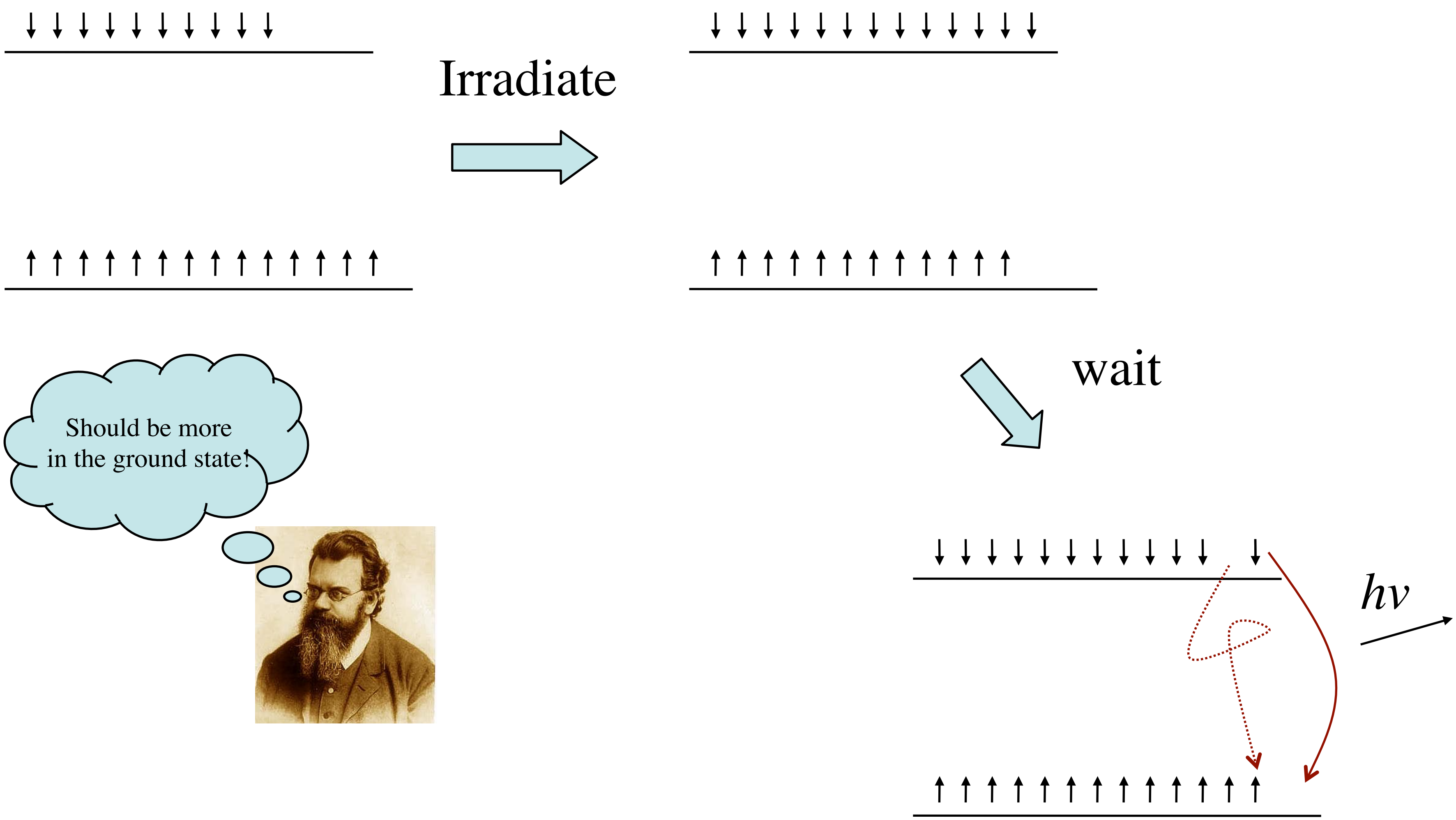
^{13}C



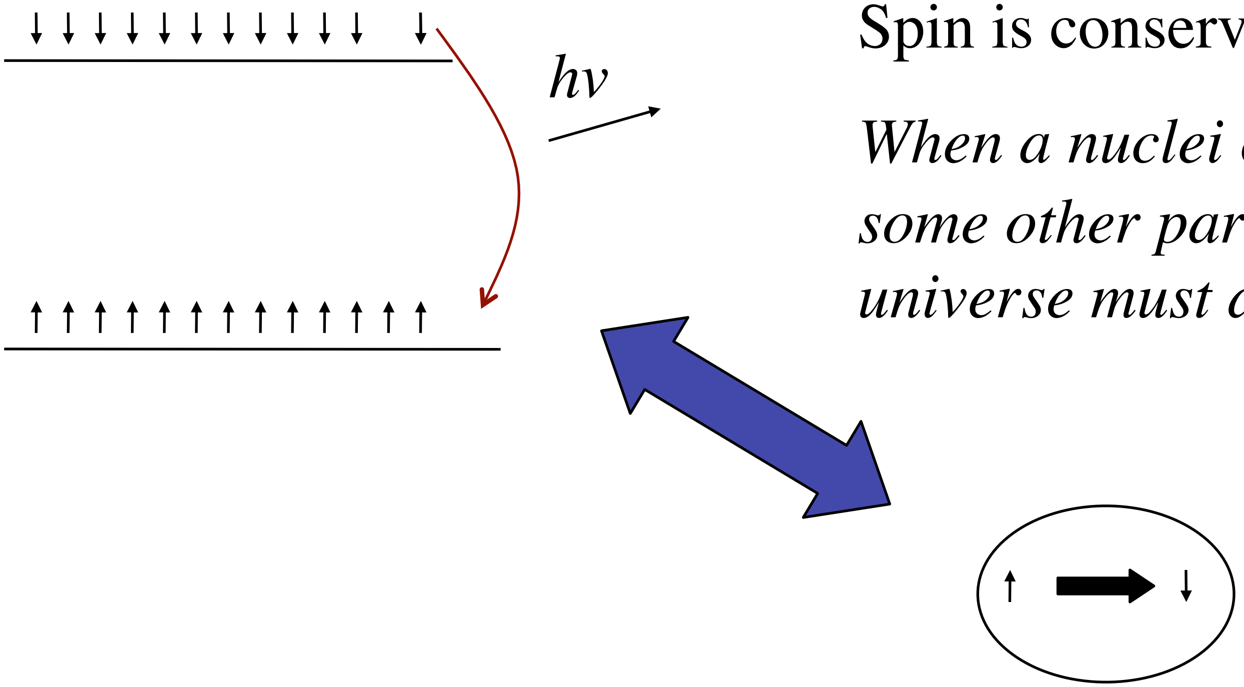
Technically speaking: you don't selectively excite all the nuclei but rather you saturate the exchange of nuclei between the upper an lower energy states. At equilibrium (in the absence of the RF energy) there are slightly more nuclei in the lower energy state than in the upper energy state based on the normal Boltzman distributions.

Consider the population of like-nuclei in a sample:

FYI



FYI



Spin is conserved:

When a nuclei changes spin, some other particle in the universe must also change spin.

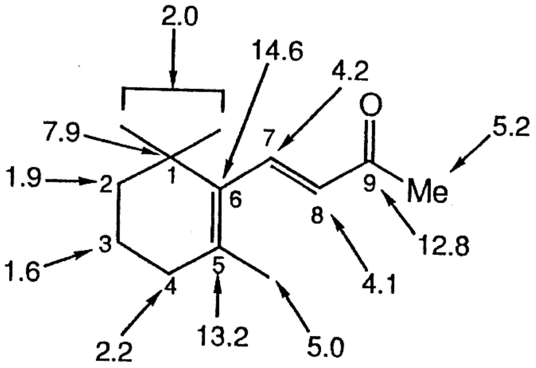
The coupling of spin is more efficient the closer the two particles are and if they are connected by bonds.

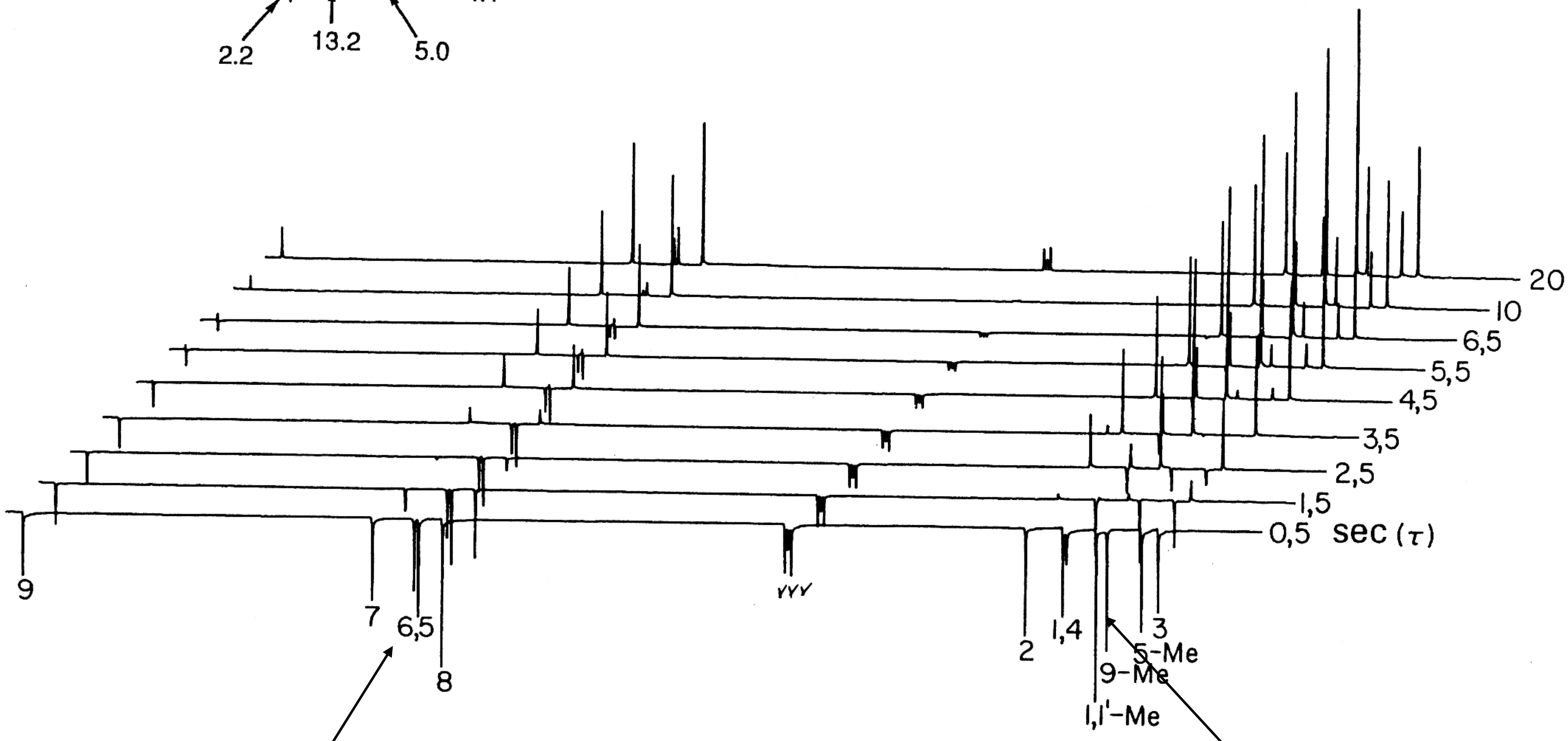
FYI

Different nuclei require different amounts of time to relax.

WHY???

T_1 value (sec)





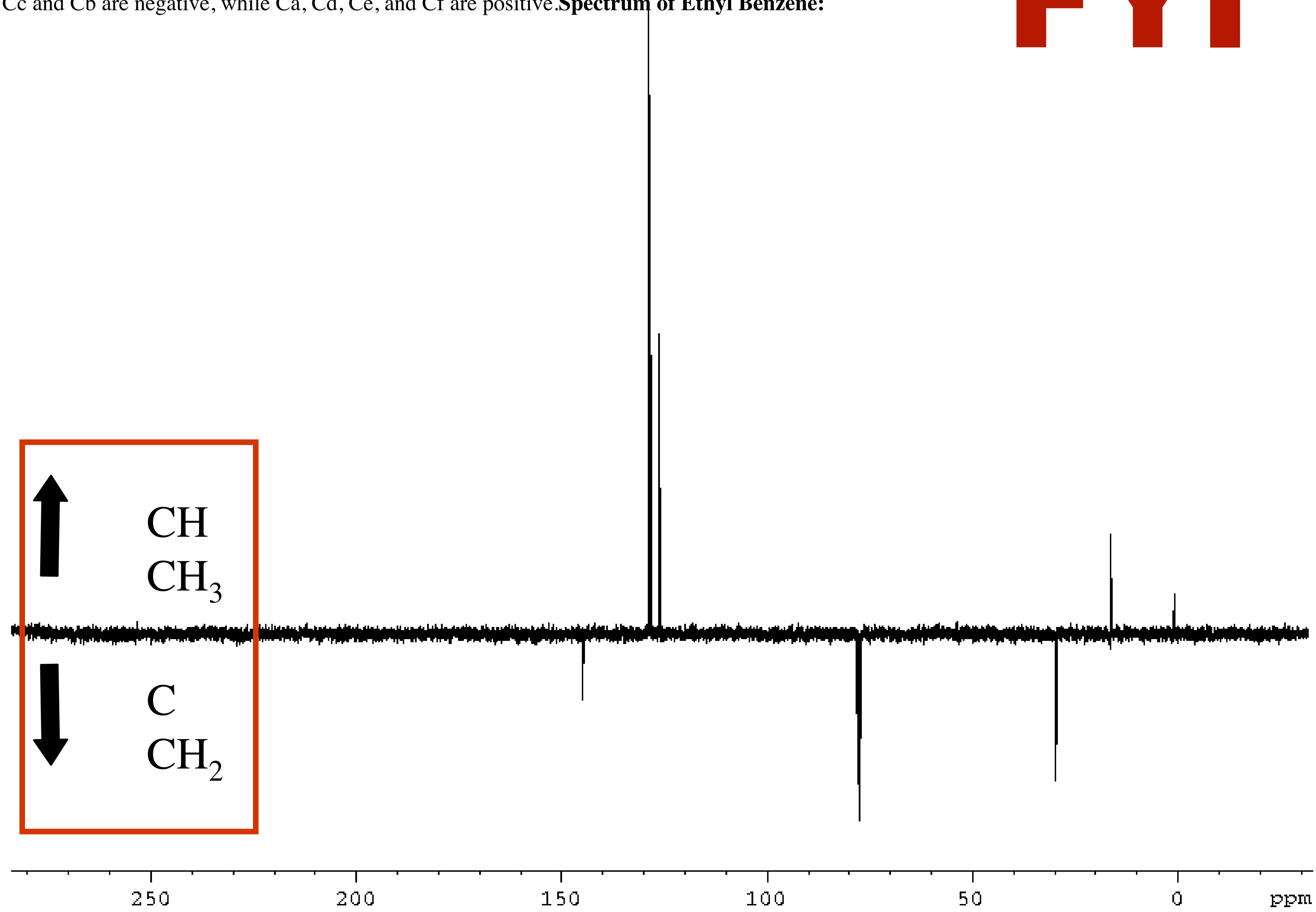
slowest

62.5 MHz ^{13}C-NMR (CDCl$_3$)$^{2)}$

fastest

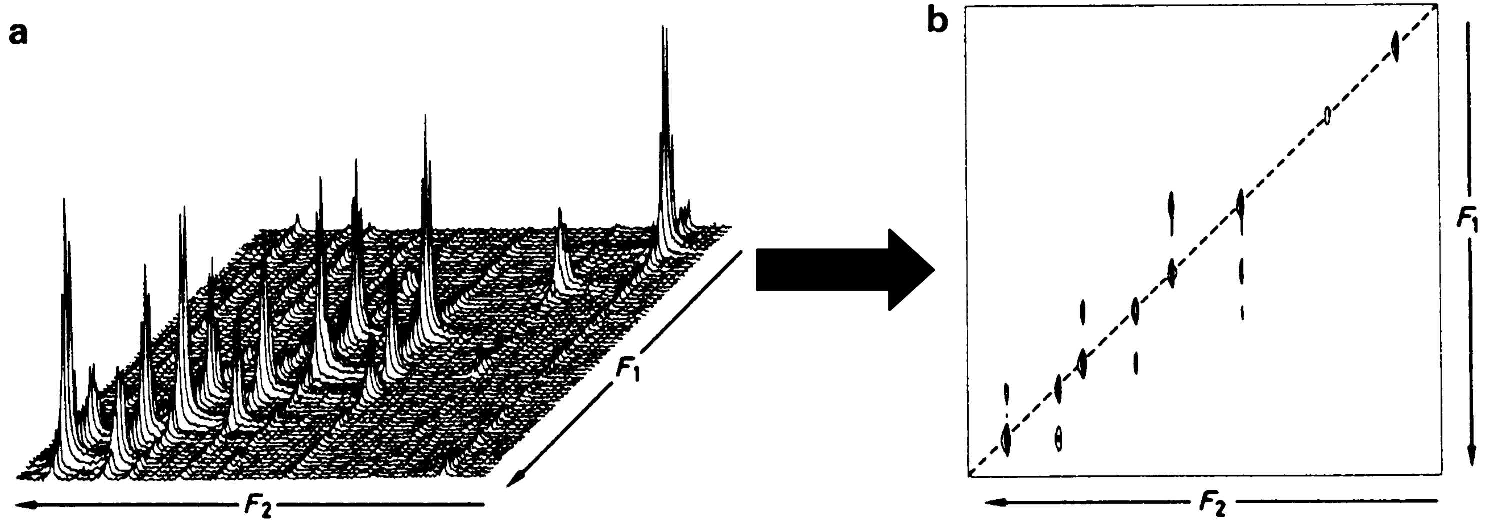
DEPT (JVERT): APT (Attached Proton Test) experiment is not as sensitive as a DEPT experiment, the APT has the advantage of seeing all carbons present: CH0 at 145 ppm and CH2 at 29 ppm are negative, while CH3 at 16 ppm and CH in the range of 1[illegible]-129 ppm are positive. Thus Cc and Cb are negative, while Ca, Cd, Ce, and Cf are positive.**Spectrum of Ethyl Benzene:**

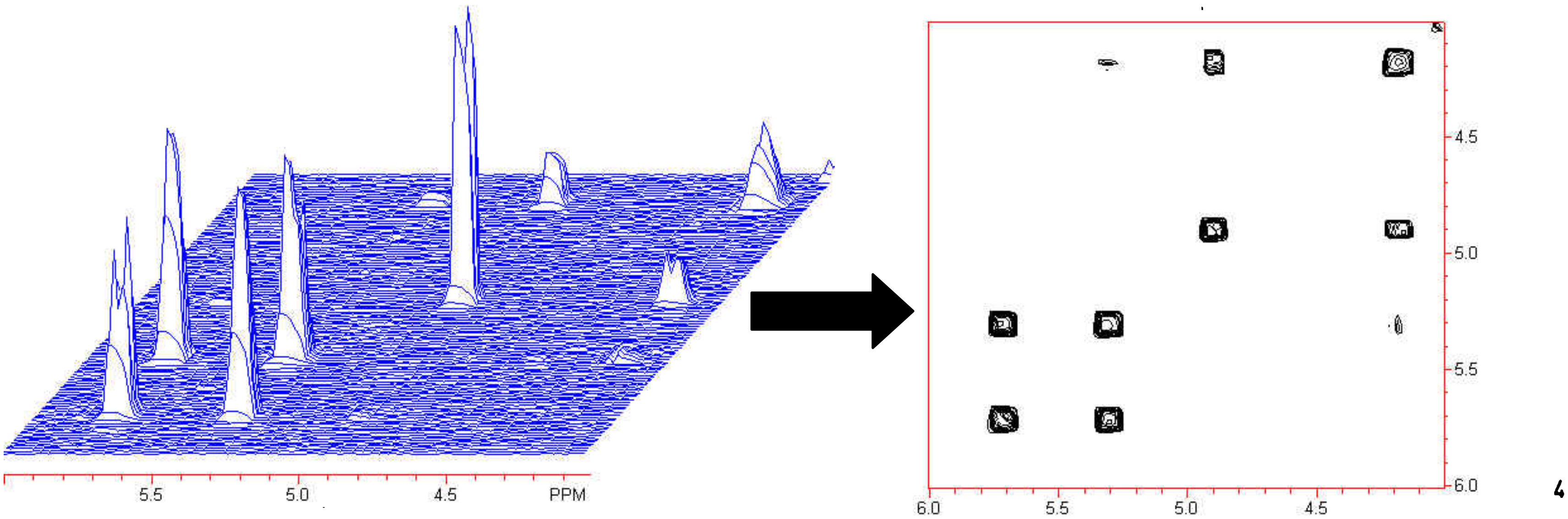
FYI



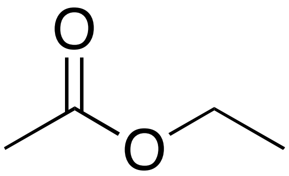
Presentation of Two Dimensional NMR

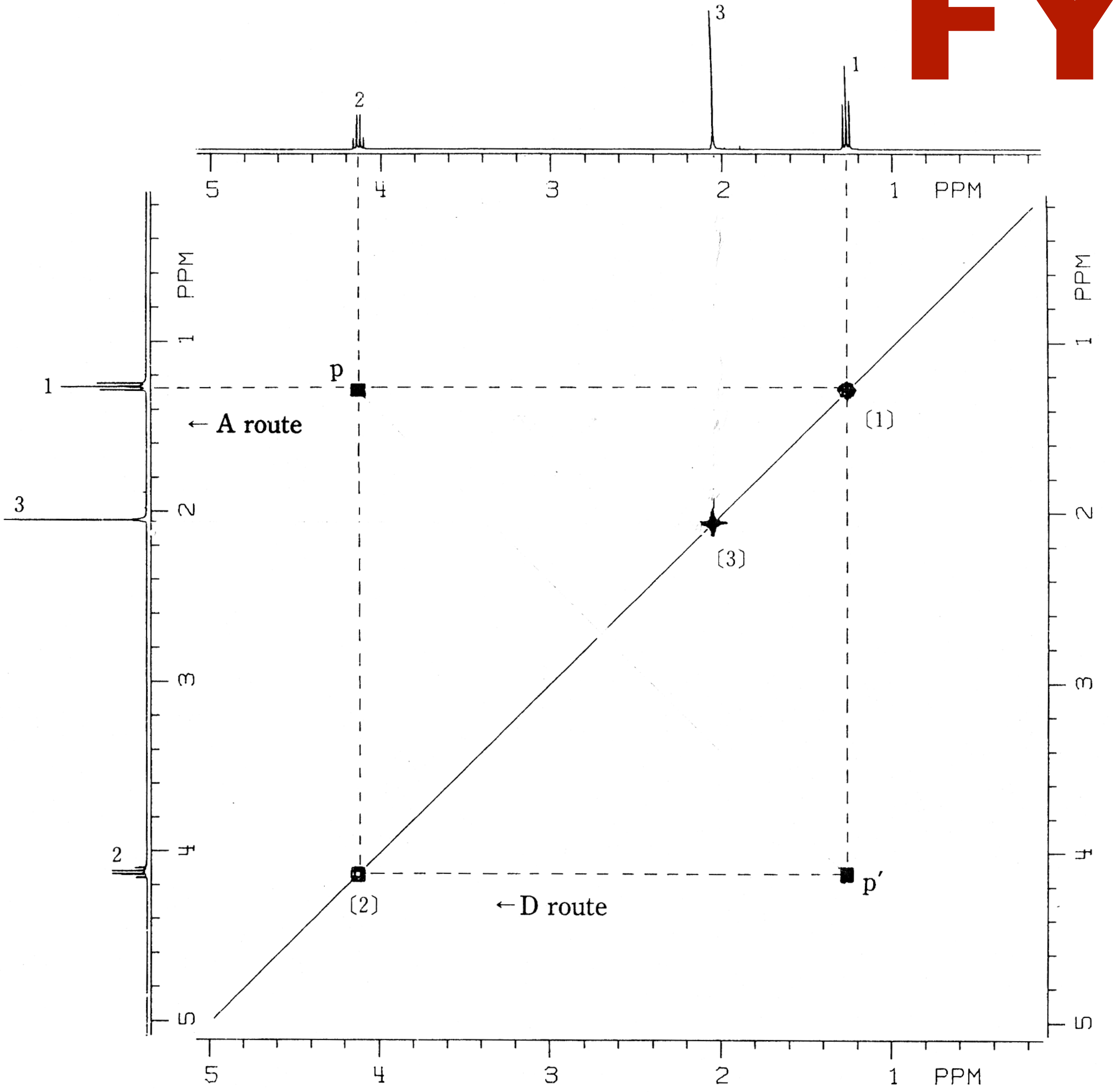
FYI



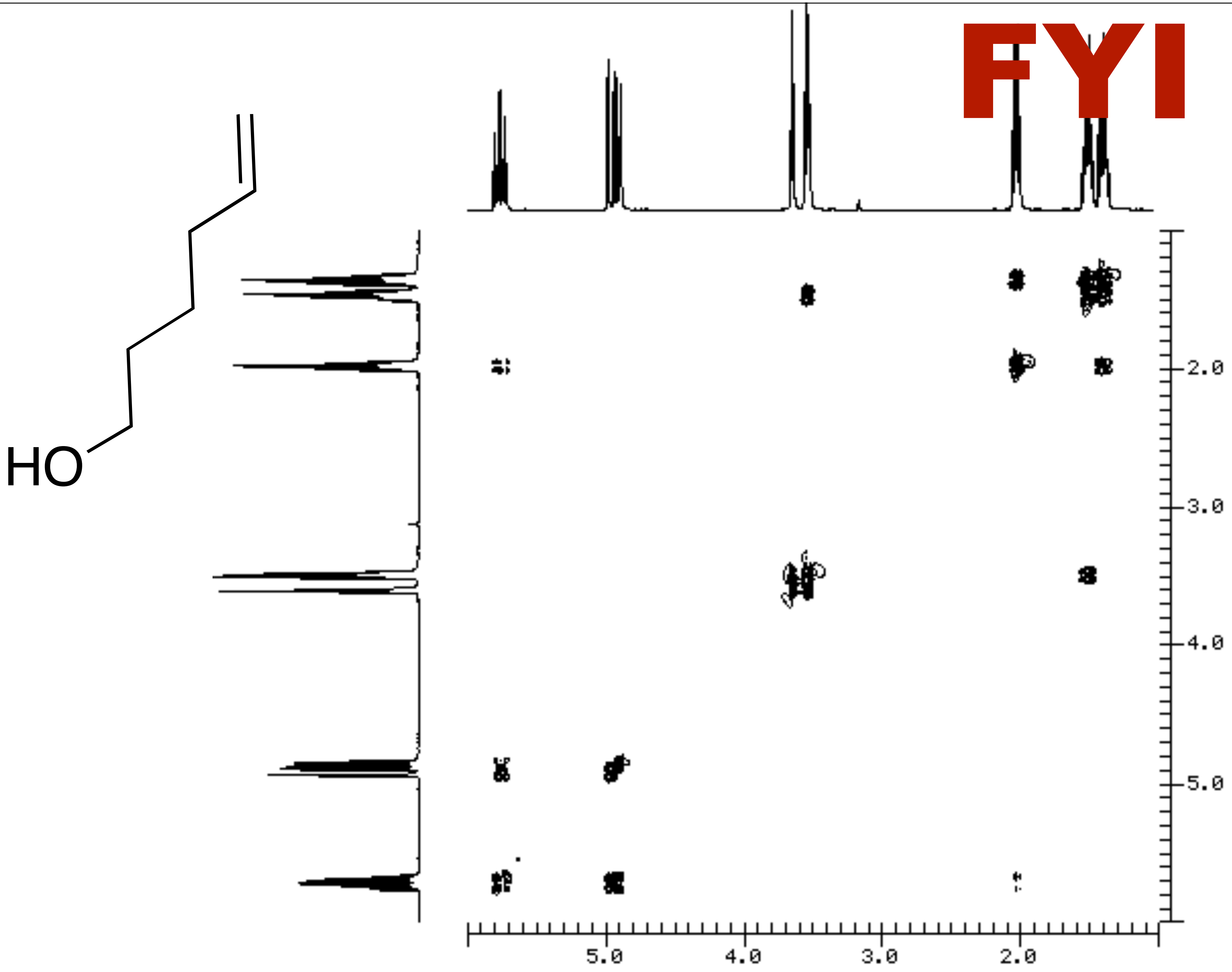


FYI

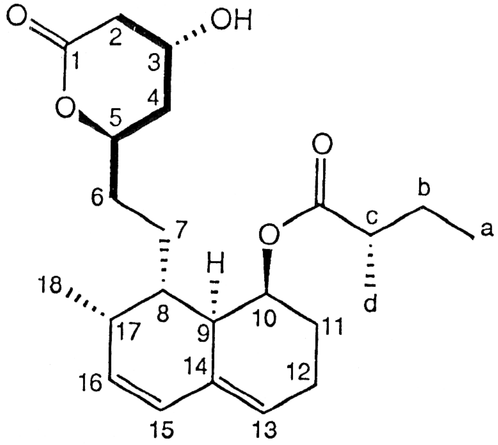




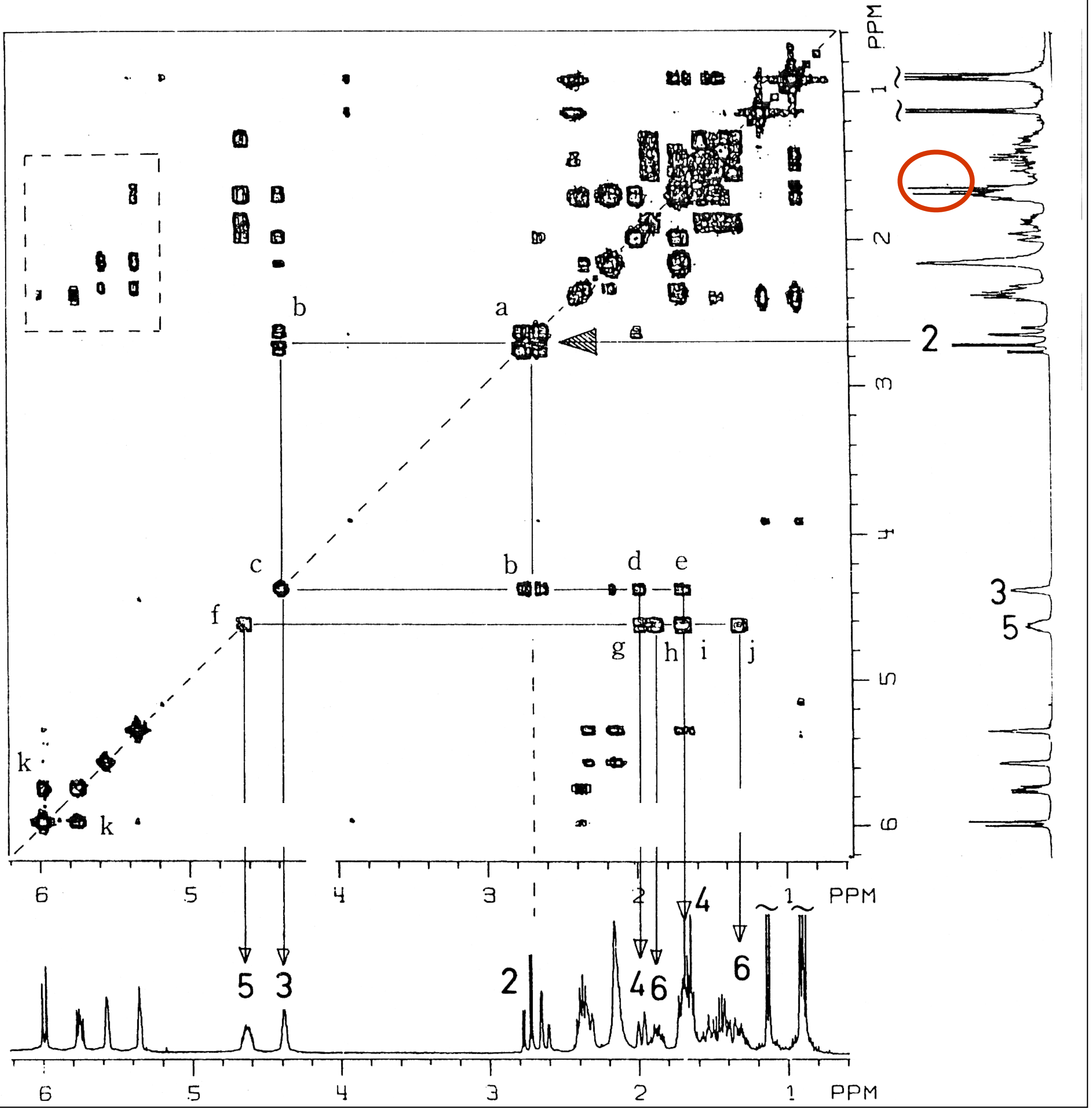
FYI



FYI



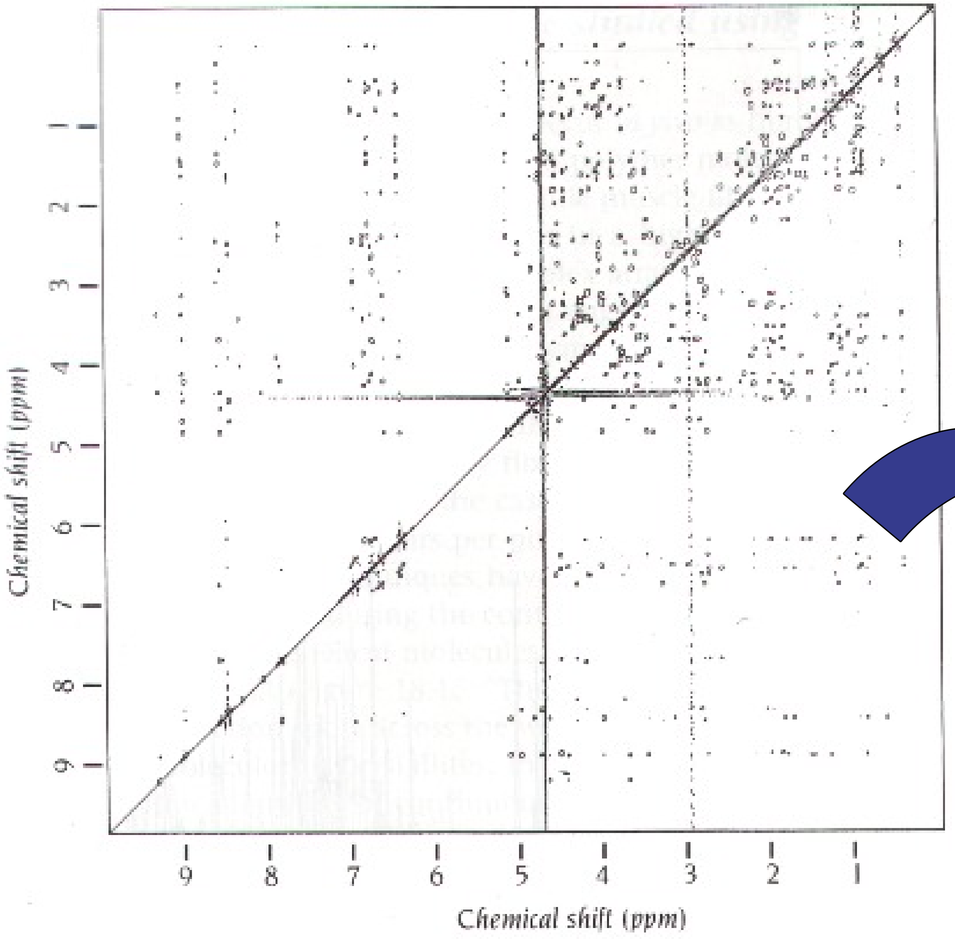
O
OH
1
2
3
4
5
O
6
7
O
b
a
c
d
O
H
18
8
9
10
11
17
14
12
16
15
13

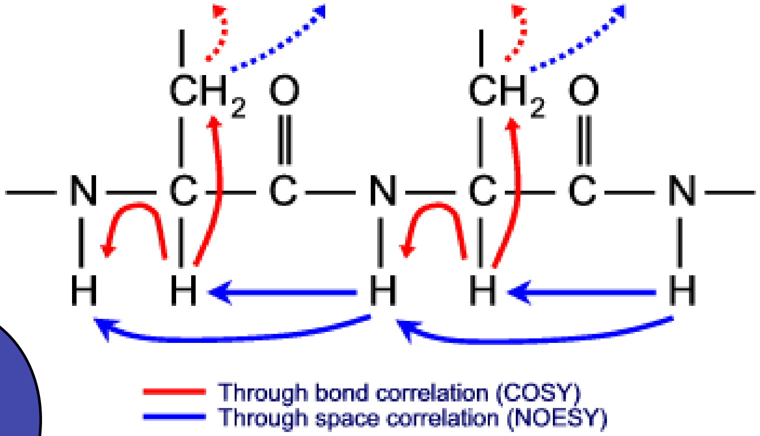


PPM
1
2
3
4
5
6
a
b
2
c
b
d
e
f
g
h
i
j
3
5
k
k
6
5
4
3
2
1
PPM
5
3
2
4
6
4
6

FYI

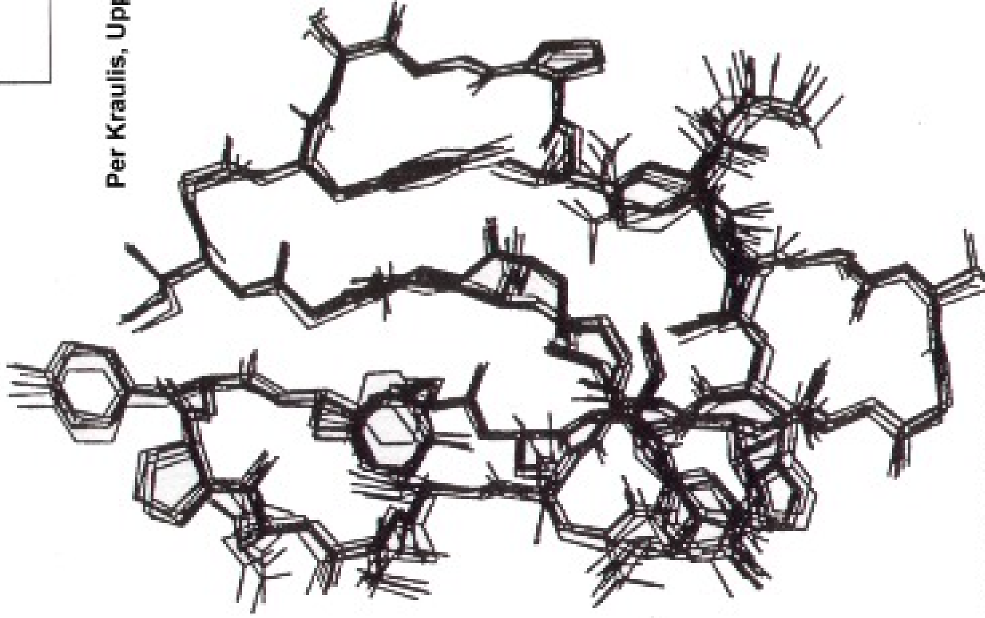
2D-NOESY spectrum of the C-terminal domain of a cellulase





The C-terminal domain of a cellulase

Per Kraulis, Uppsala



Per Kraulis, Uppsala

NMR is being used to determine the structure of small proteins.