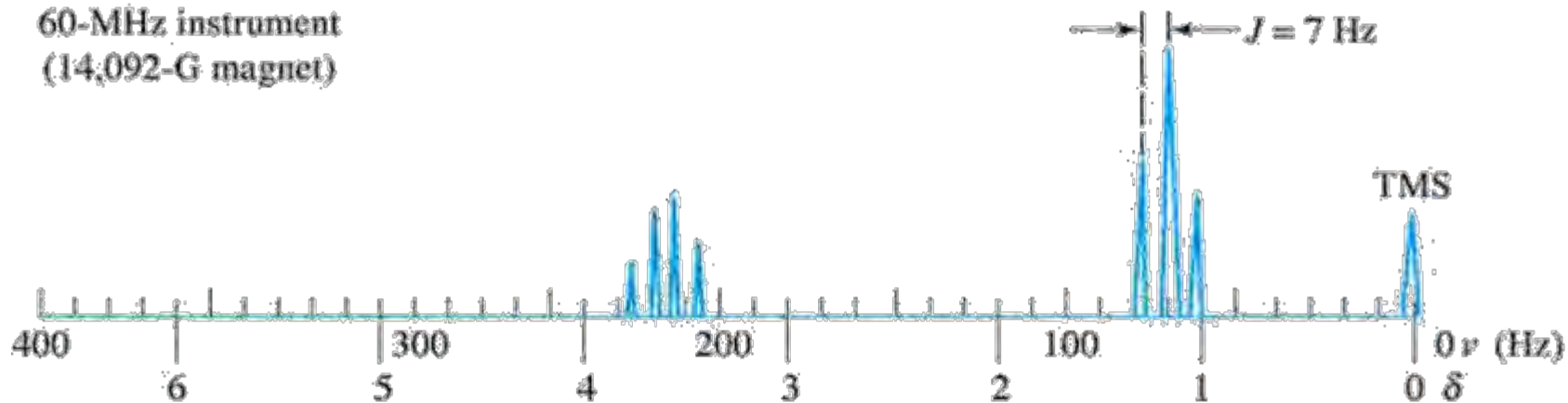
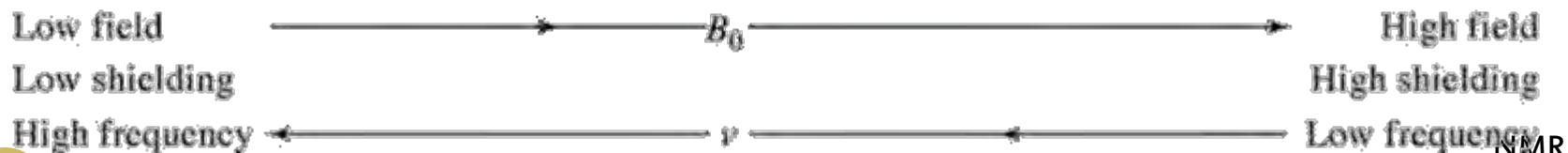
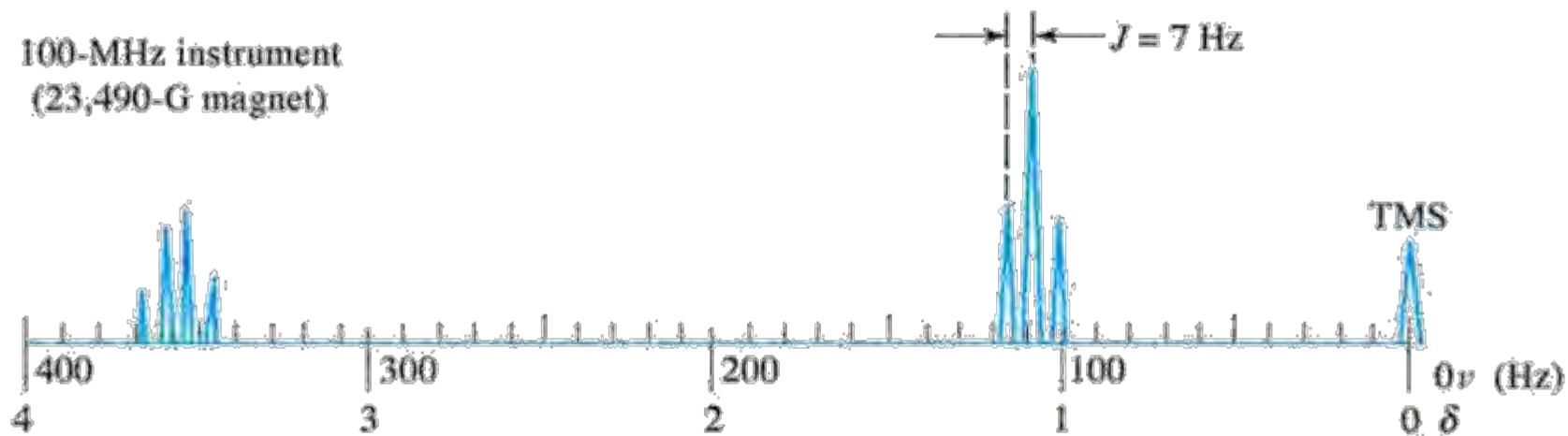


60-MHz instrument
(14,092-G magnet)

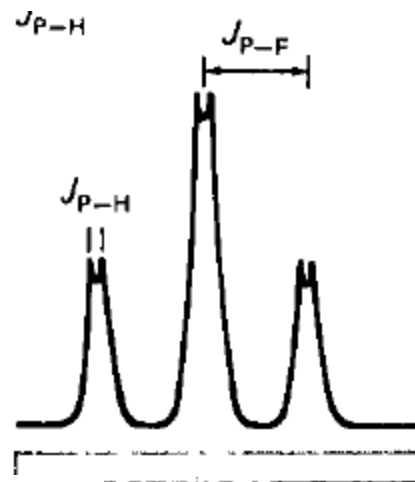
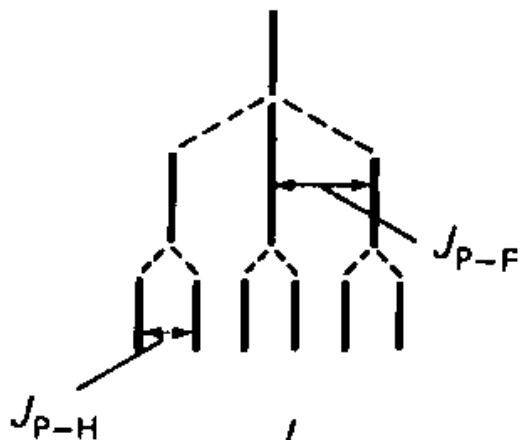


100-MHz instrument
(23,490-G magnet)

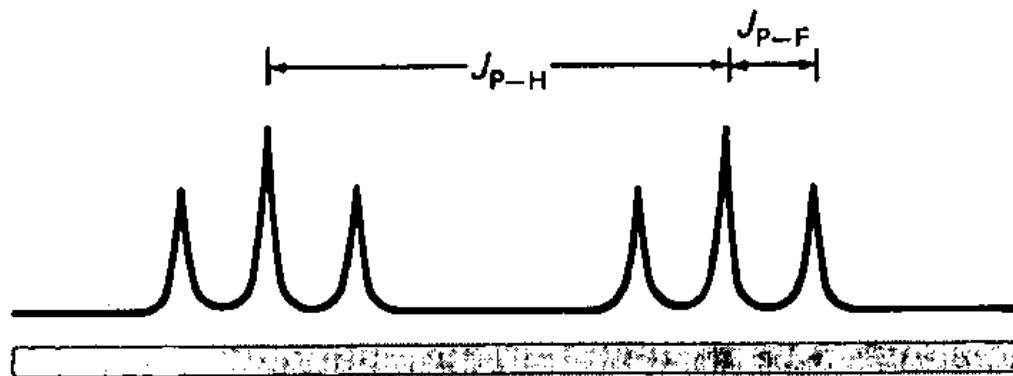
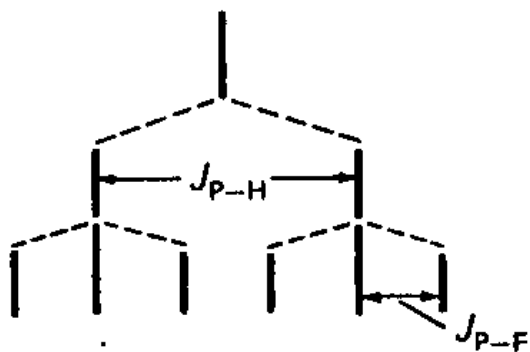


NMR

EFFECT OF THE NUMBER AND NATURE OF THE BONDS ON SPIN-SPIN COUPLING

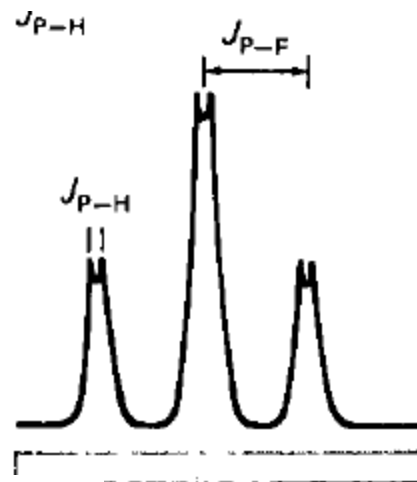
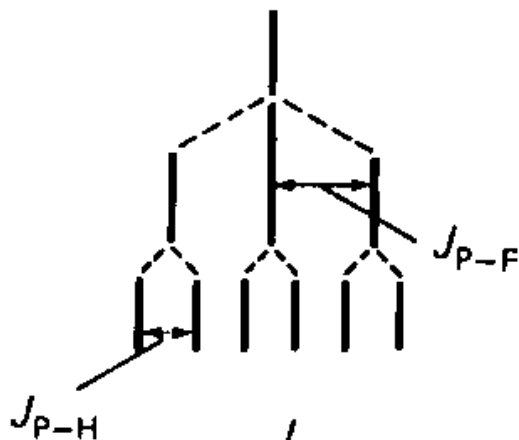


HPF₂ if $^1J_{P-H} < ^1J_{P-F}$.



HPF₂ if $^1J_{P-H} > ^1J_{P-F}$.

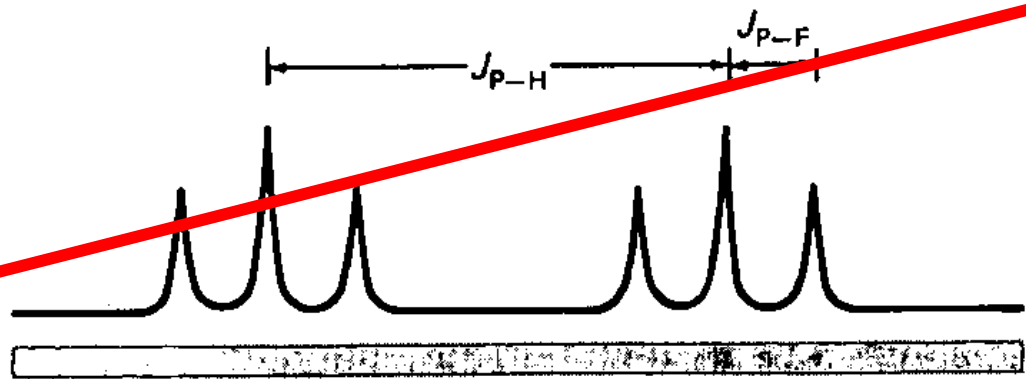
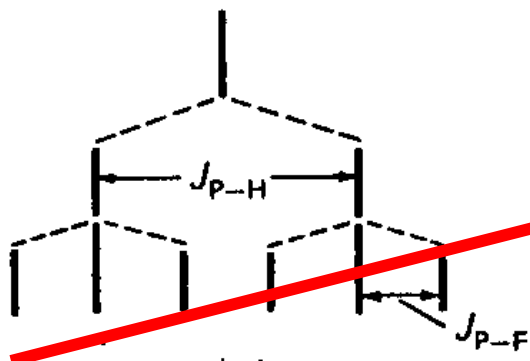
EFFECT OF THE NUMBER AND NATURE OF THE BONDS ON SPIN-SPIN COUPLING



$^1J_{P-F}$
1500 Hz

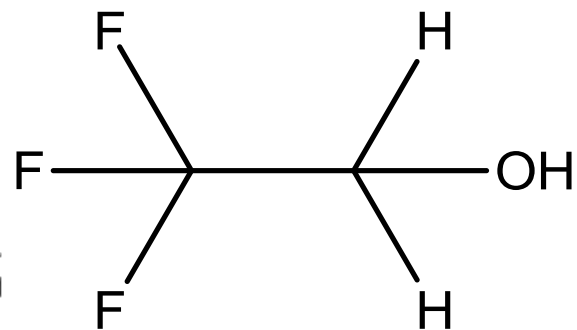
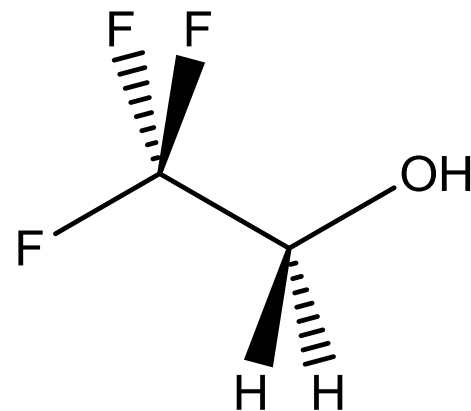
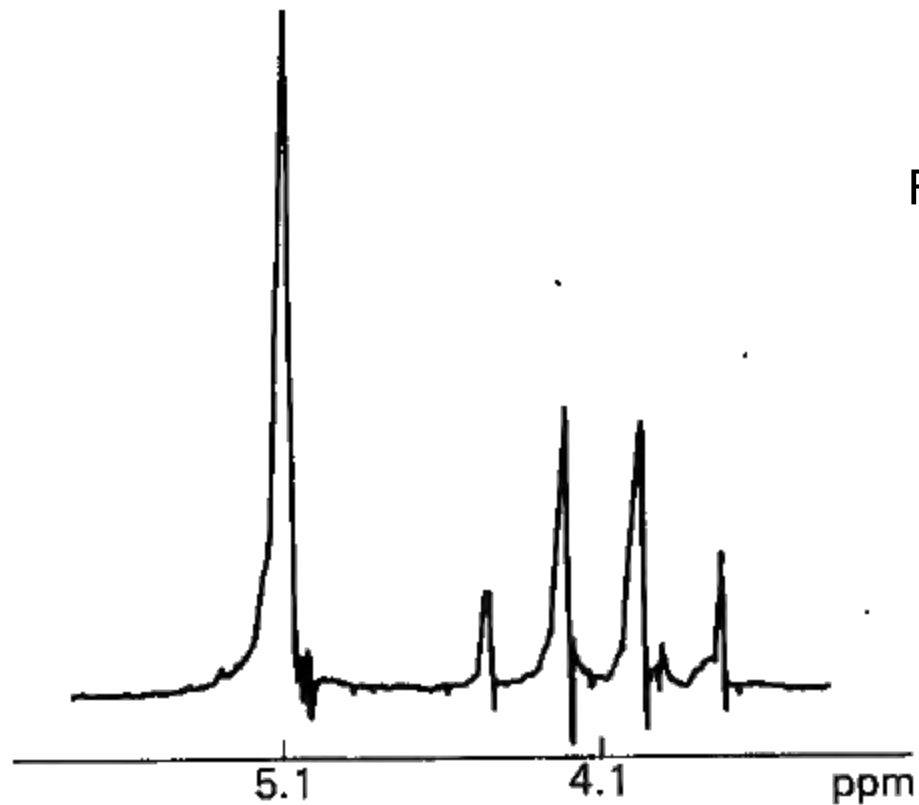
$^1J_{P-H}$
200 Hz

HPF_2 if $^1J_{P-H} < ^1J_{P-F}$.

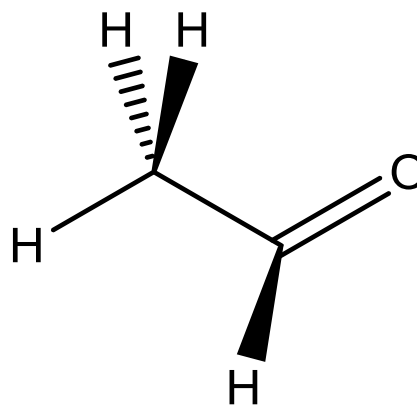


HPF_2 if $^1J_{P-H} > ^1J_{P-F}$.

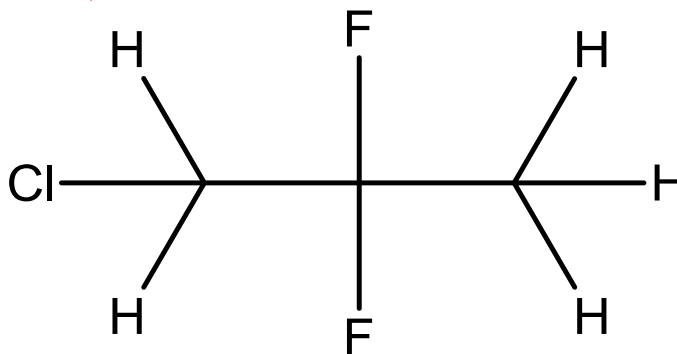
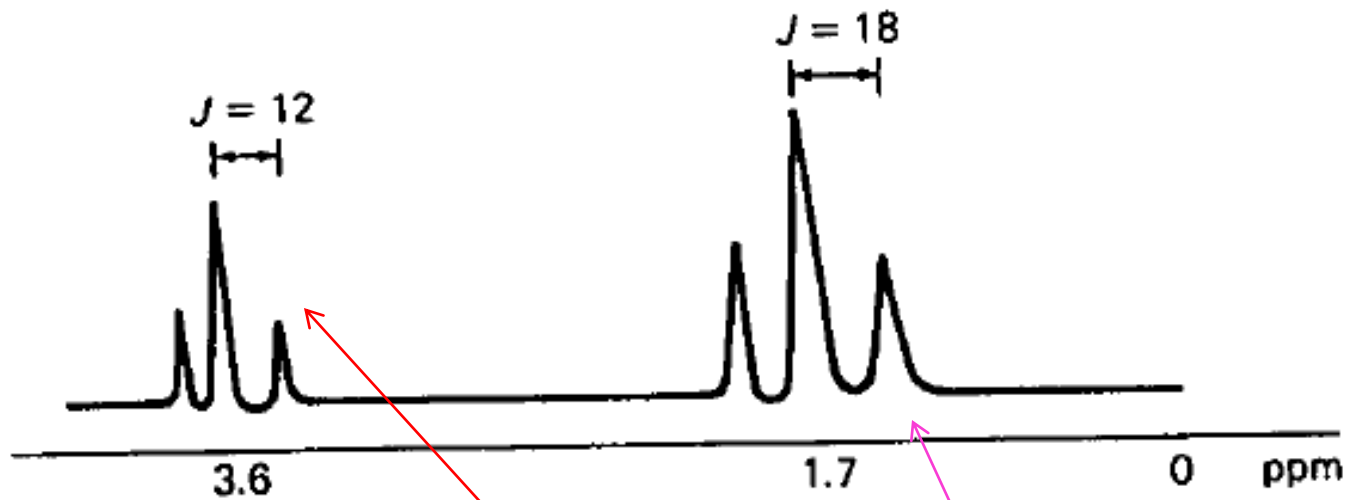
A compound with empirical formula $C_2H_3F_3O$.



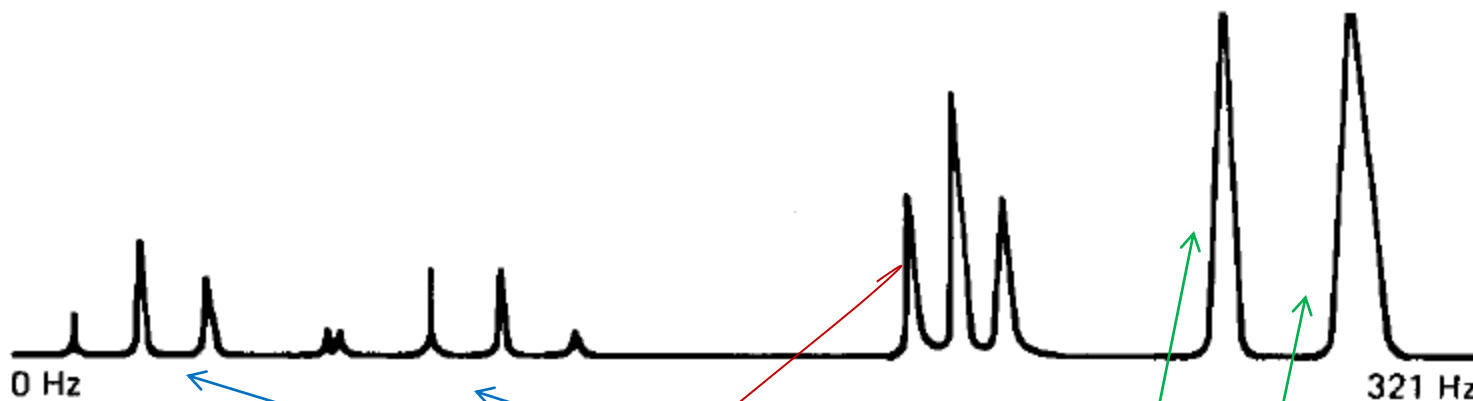
e. A compound with empirical formula C_2H_4O .



A compound with empirical formula $C_3H_5ClF_2$.



A compound with empirical formula $(\text{SiH}_3)_2\text{PSiH}_2\text{CH}_3$.

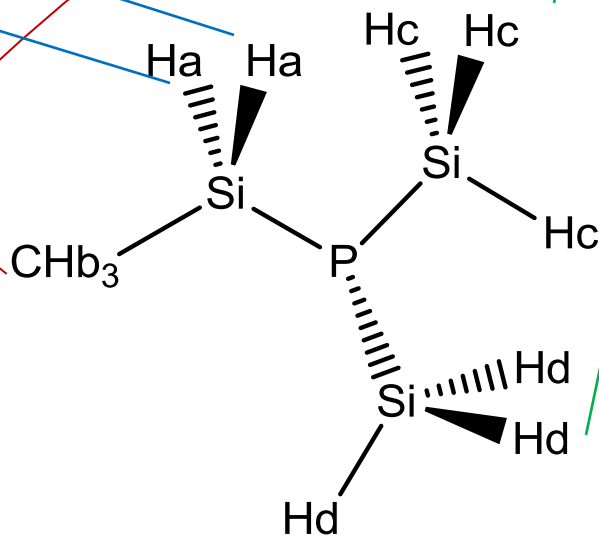


a splitting b \leftrightarrow 3

p splitting c \leftrightarrow 1

p splitting d \leftrightarrow 1

b and P splitting d \leftrightarrow 4



^{13}C NMR

- In a ^{13}C NMR spectrum the area under the signal is not simply proportional to the number of carbons giving rise to the signal because the NOE (**Nuclear Overhauser Effect**) from proton decoupling is not equal for all the carbons.
- In particular, unprotonated carbons receive very little NOE, and their signals are always weak, only about 10% as strong as signals from protonated carbons.

proposed that nuclear spin polarization could be enhanced by the microwave irradiation of the conduction electrons in certain metals

- Because the resolution in ^{13}C NMR is excellent, the number of peaks in the spectrum is a measure of the carbon count adjusted for the symmetry of the molecule. For example, hexane gives three peaks: the two methyls are equivalent as are two sets of methylenes.



The ^{13}C NMR is **directly** about the carbon skeleton not just the proton attached to it.

- The **number of signals** tell us how many different carbons or set of equivalent carbons
- The **splitting of a signal** tells us how many hydrogens are attached to each carbon. (N+1 rule)
- The **chemical shift** tells us the hybridization (sp^3 , sp^2 , sp) of each carbon.
- Integration: Not useful for ^{13}C NMR

Proton –coupled spectrum shows splitting of the carbon signal only by protons attached to *that* carbon *itself*.

^{13}C _H coupling not ^{13}C _ ^{13}C _H or not ^{13}C _ ^{13}C _ ^{13}C _H or not ^{12}C _ ^{13}C

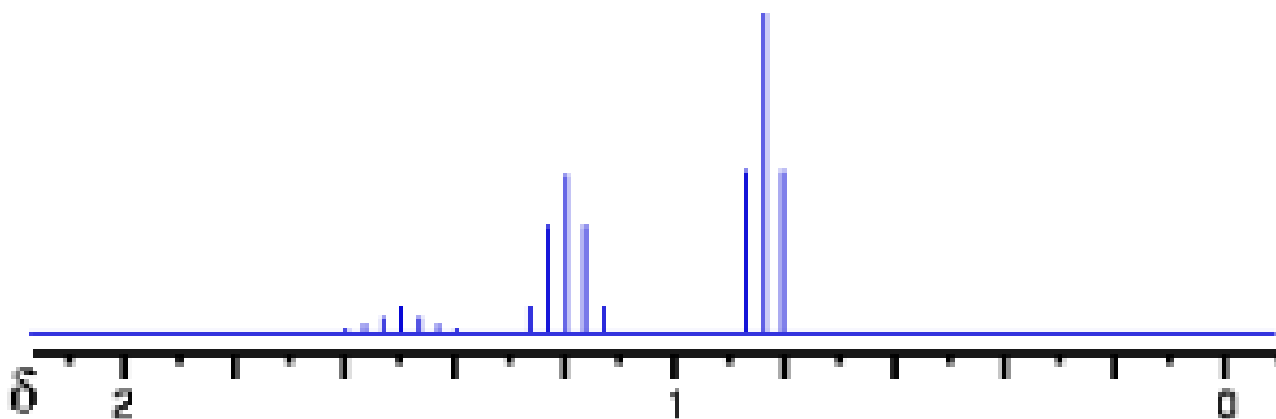
coupling occurs but very low
due to low abundance 1.1 %x1.11%

No coupling
 ^{12}C I=0

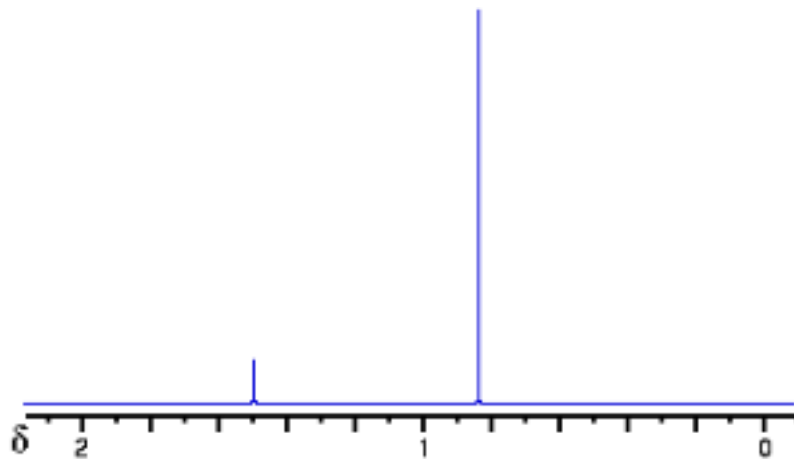
Note: Due to low natural abundance, ^{13}C NMR spectra do not ordinarily show carbon-carbon splitting two ^{13}C being next to other is $1.1\% \times 1.1\% = 0.012\%$ (because ^{12}C does not have a magnetic moment, it cannot split the signal of an adjacent ^{13}C), and are thus enormously simplified.

- The signal-to-noise ratio in an NMR spectrometer is related to the population difference between the lower and upper spin state. The larger this difference the larger the signal.

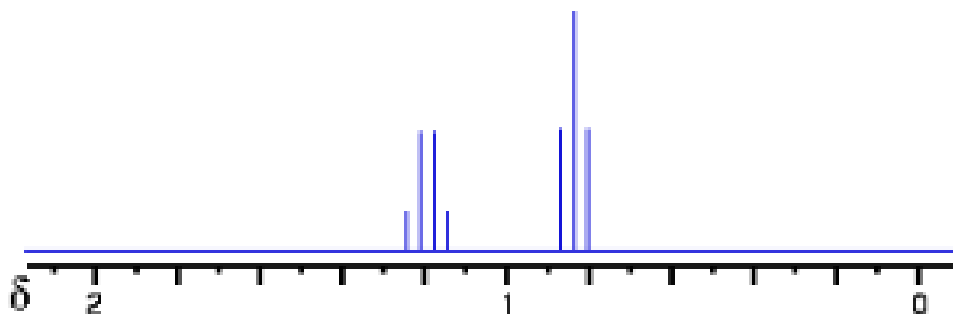
- To understand decoupling, consider the familiar hydrogen NMR spectrum of $\text{HC}-(\text{CH}_2\text{CH}_3)_3$. The HC hydrogen peaks are difficult to see in the spectrum due to the splitting from the 6 $-\text{CH}_2-$ hydrogens.



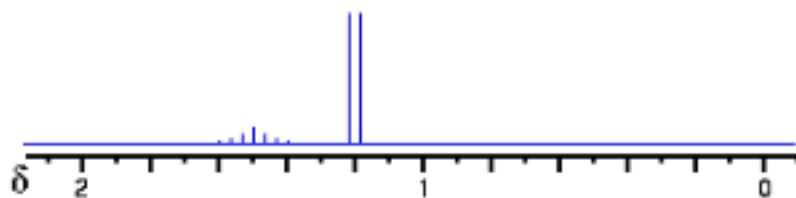
- If the effect of the 6 -CH₂- hydrogens could be removed, we would lose the 1:6:15:20:15:6:1 splitting for the HC hydrogen and get one peak.



- We would also lose the 1:3:1 splitting for the CH₃ hydrogens and get one peak. The process of removing the spin-spin splitting between spins is called decoupling. Decoupling is achieved with the aid of a saturation pulse. If the affect of the HC hydrogen is removed, we see the following spectrum.

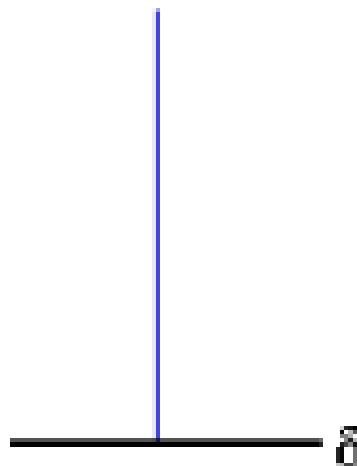


- Similarly, if the affect of the $-CH_3$ hydrogens is removed, we see this spectrum

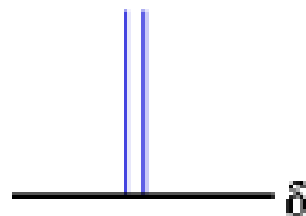


- The NMR spectrum from the carbon-13 nucleus will yield one absorption peak in the spectrum.

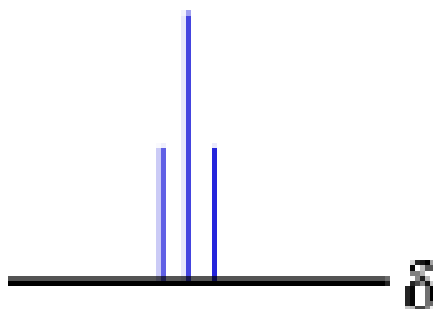
- CH_3I



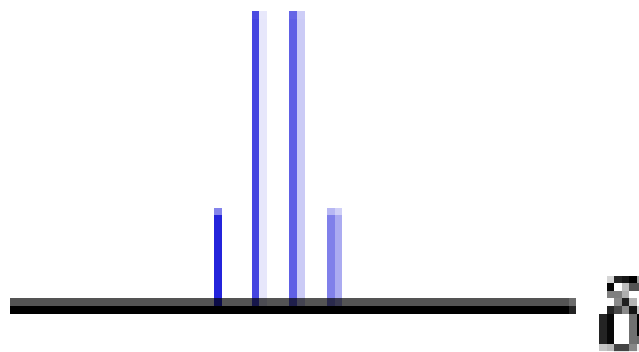
- Adding the nuclear spin from one hydrogen will split the carbon-13 peak into two peaks.



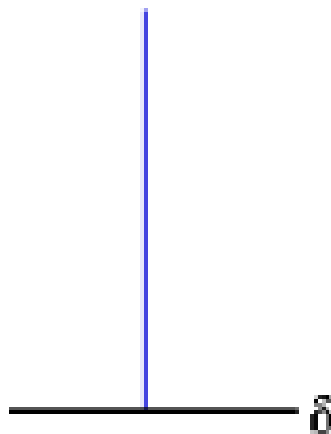
- Adding one more hydrogen will split each of the two carbon-13 peaks into two, giving a 1:2:1 ratio.



- The final hydrogen will split each of the previous peaks, giving a 1:3:3:1 ratio.



- If the hydrogen spin system is **saturated**, the four lines collapse into a single line having an intensity which is eight times greater than the outer peak in the 1:3:3:1 quartet since $1+3+3+1=8$

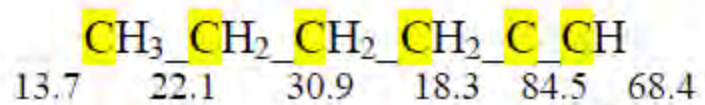
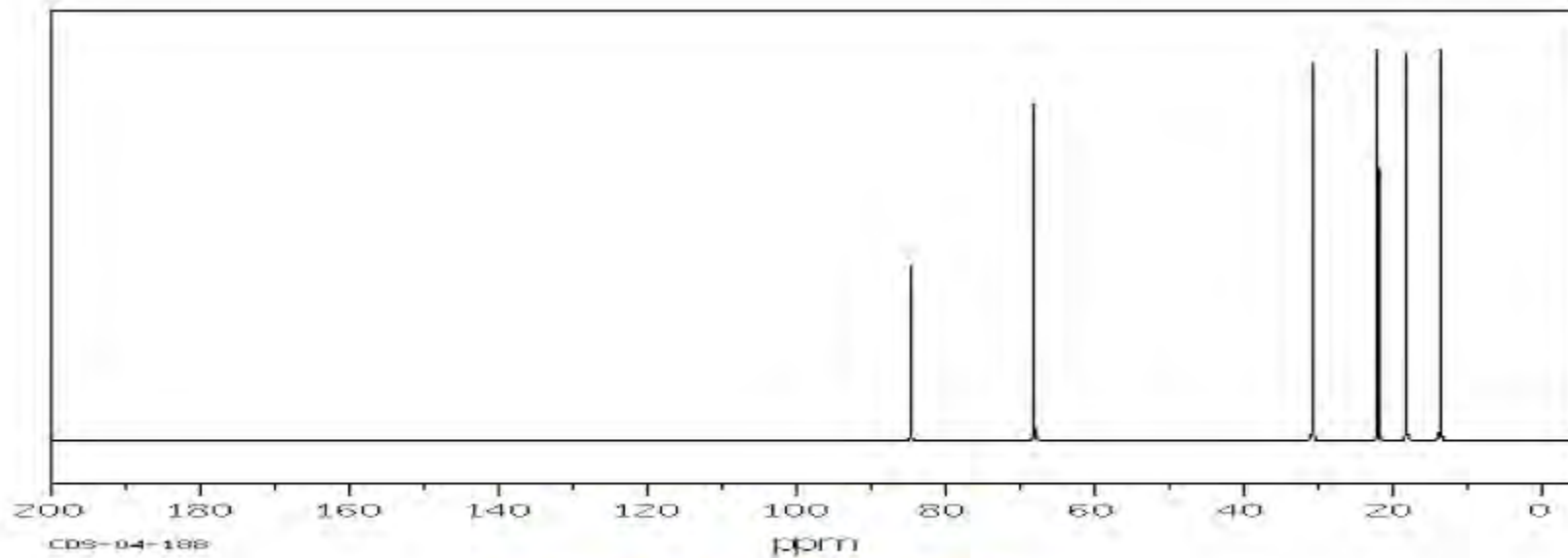


Chemical Shift in ^{13}C NMR spectrum arises in the same way as in the proton NMR spectrum. Each carbon nucleus has its own electronic environment, different from the environment of other, non-equivalent nuclei; it feels a different magnetic field, and absorbs at different applied fields strength.

- ❖ Electronegative atoms and pi bonds cause downfield shifts
- ❖ ^{13}C chemical shift range 0-250 ppm

In ^{13}C NMR spectrum, the more electronegative group bonded to carbon atom \rightarrow deshielding increases. This table demonstrates this effect.

	I	Br	Cl	F
Electronegativity (Pauling Scale)	2.5	2.8	3.0	4.0
Sp^3 hybrid carbon	CH_3I	CH_3Br	CH_3Cl	CH_3F
Chemical shift (ppm)	9.6	25.6	49.9	71.6

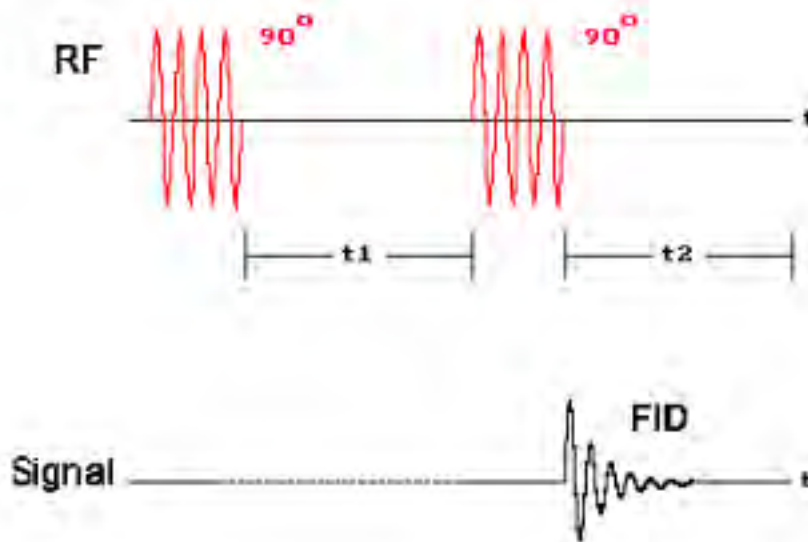


2D- NMR: Interaction of nuclear spins plotted in two dimensions.

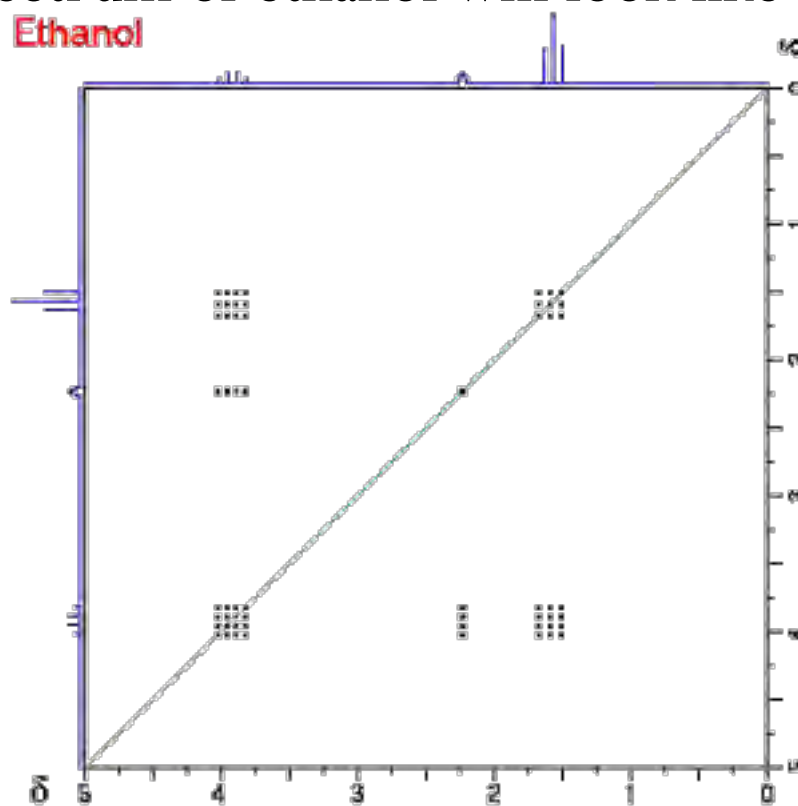
Correlation Spectroscopy (COSY)

- ❖ Two axes correspond to the single isotope
- ❖ The interaction indicates with H's are coupled → gives better understanding of structure.

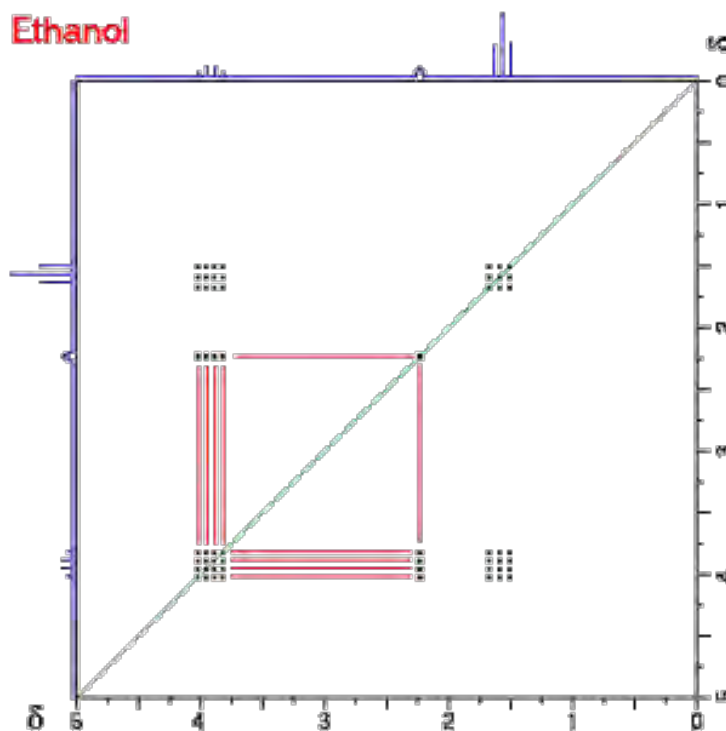
- The application of two 90 degree pulses to a spin system will give a signal which varies with time t_1 where t_1 is the time between the two pulses.



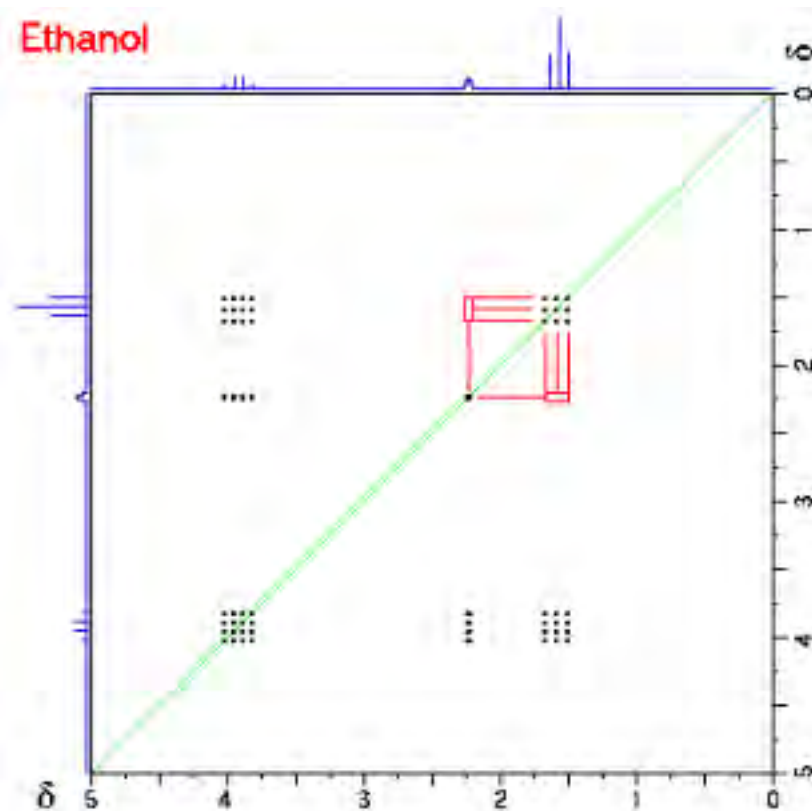
- The Fourier transform of both the t_1 and t_2 dimensions gives us chemical shift information. The 2-D hydrogen correlated chemical shift spectrum of ethanol will look like this.



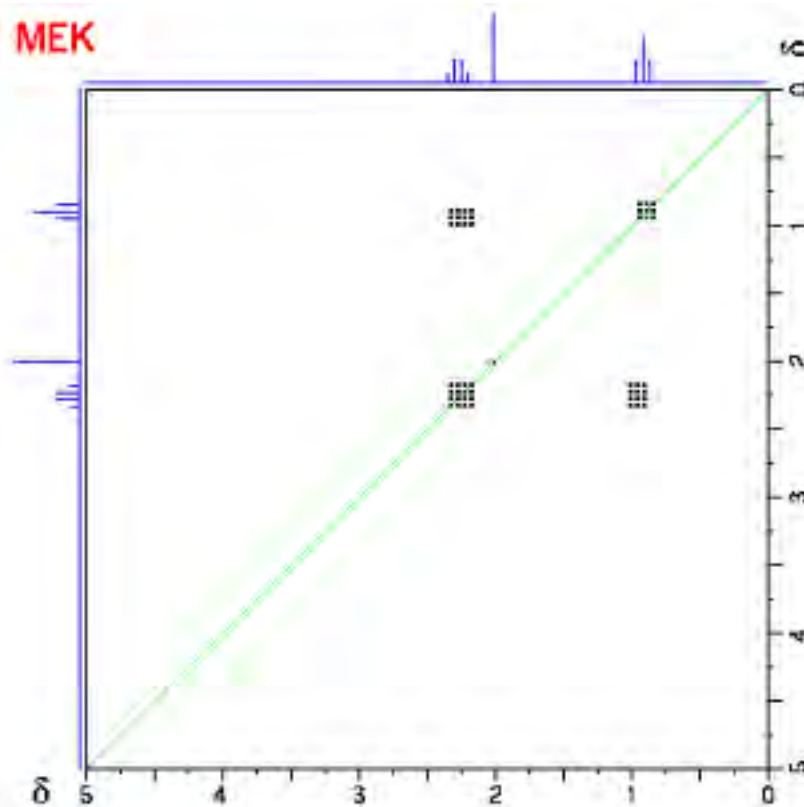
- There is a wealth of information found in a COSY spectrum. A normal (chemical shift) 1-D NMR spectrum can be found along the top and left sides of the 2-D spectrum. Cross peaks exist in the 2-D COSY spectrum where there is spin-spin coupling between hydrogens. There are cross peaks between OH and CH₂ hydrogens, and also between CH₃ and CH₂ hydrogens



- There are no cross peaks between the CH₃ and OH hydrogens because there is no coupling between the CH₃ and OH hydrogens

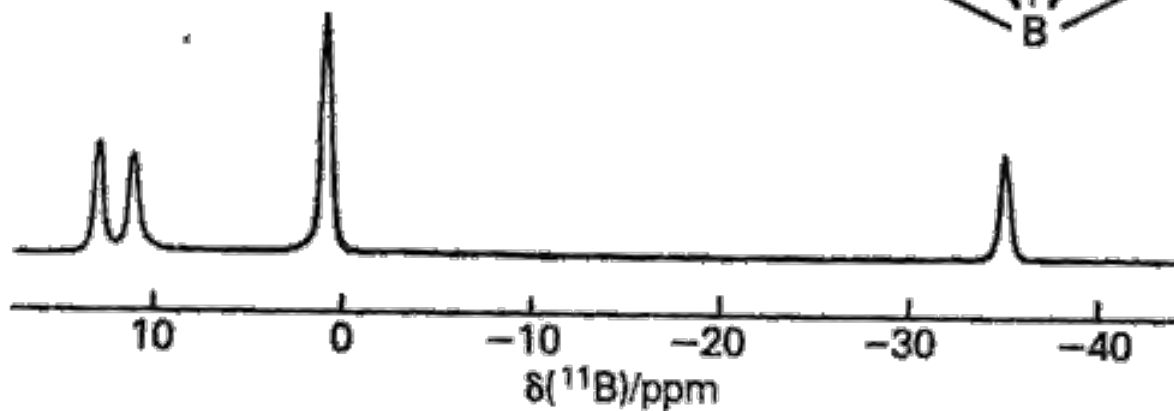
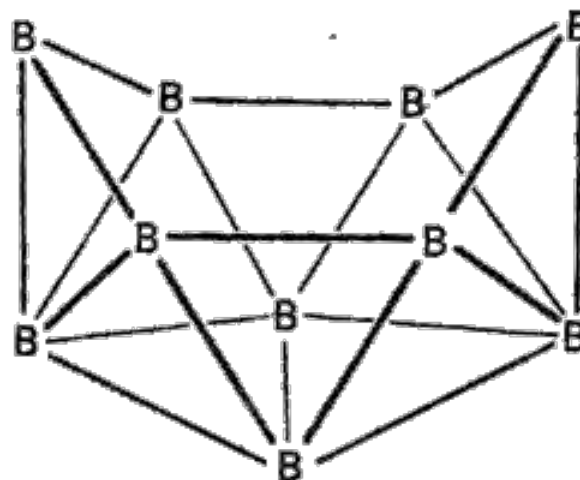


methyl ethyl ketone $\text{CH}_3(\text{C}=\text{O})\text{CH}_2\text{CH}_3$



^{11}B : NMR of $\text{B}_{10}\text{H}_{14}$

4 equivalent Boron give rise to strongest peak
then there are 3 pairs of equivalent signals
giving rise to 3 smaller peaks



H-NMR of Sn compound

3 isotopes with spin $\frac{1}{2}$:

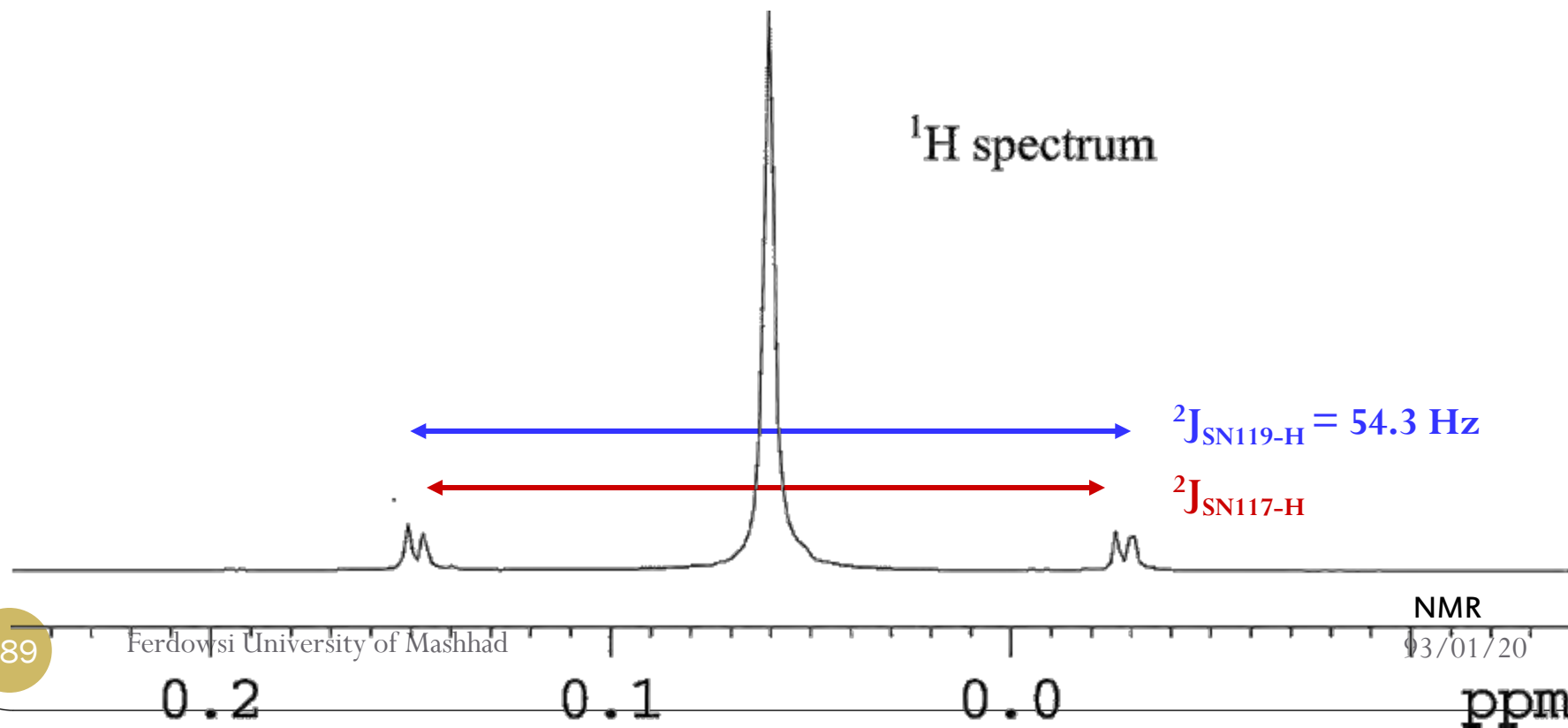
Sn-115 a=0.35%

Sn-117 a=7.61%

Sn-119 a=8.58%

$${}^2J_{\text{Sn119-H}} = 1.046 * {}^2J_{\text{Sn117-H}}$$

(ratio of \blacksquare of the 2 isotopes)



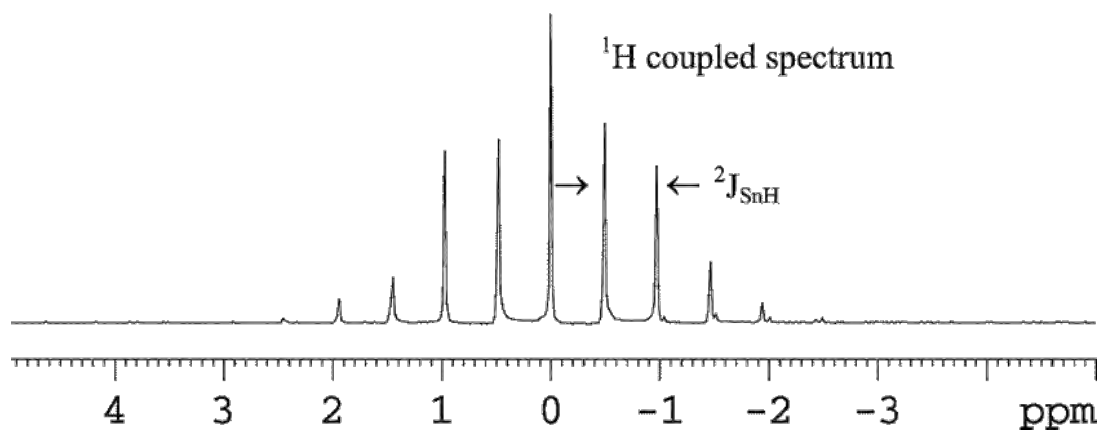
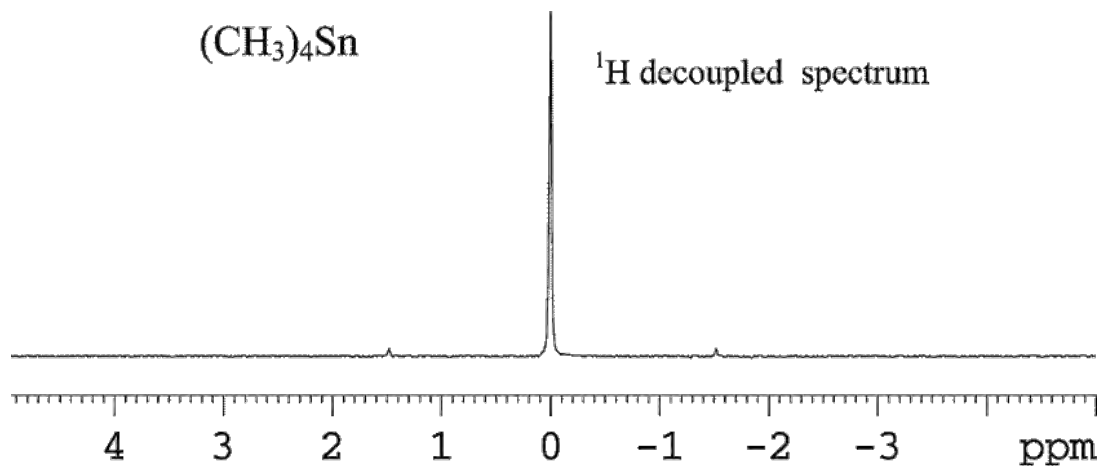
Sn-119

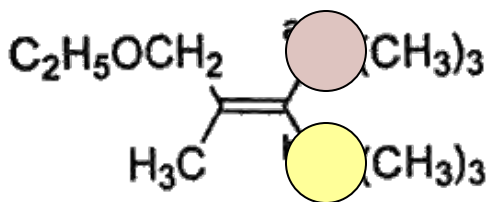
3 isotopes with spin $\frac{1}{2}$:

Sn-115 $a=0.35\%$

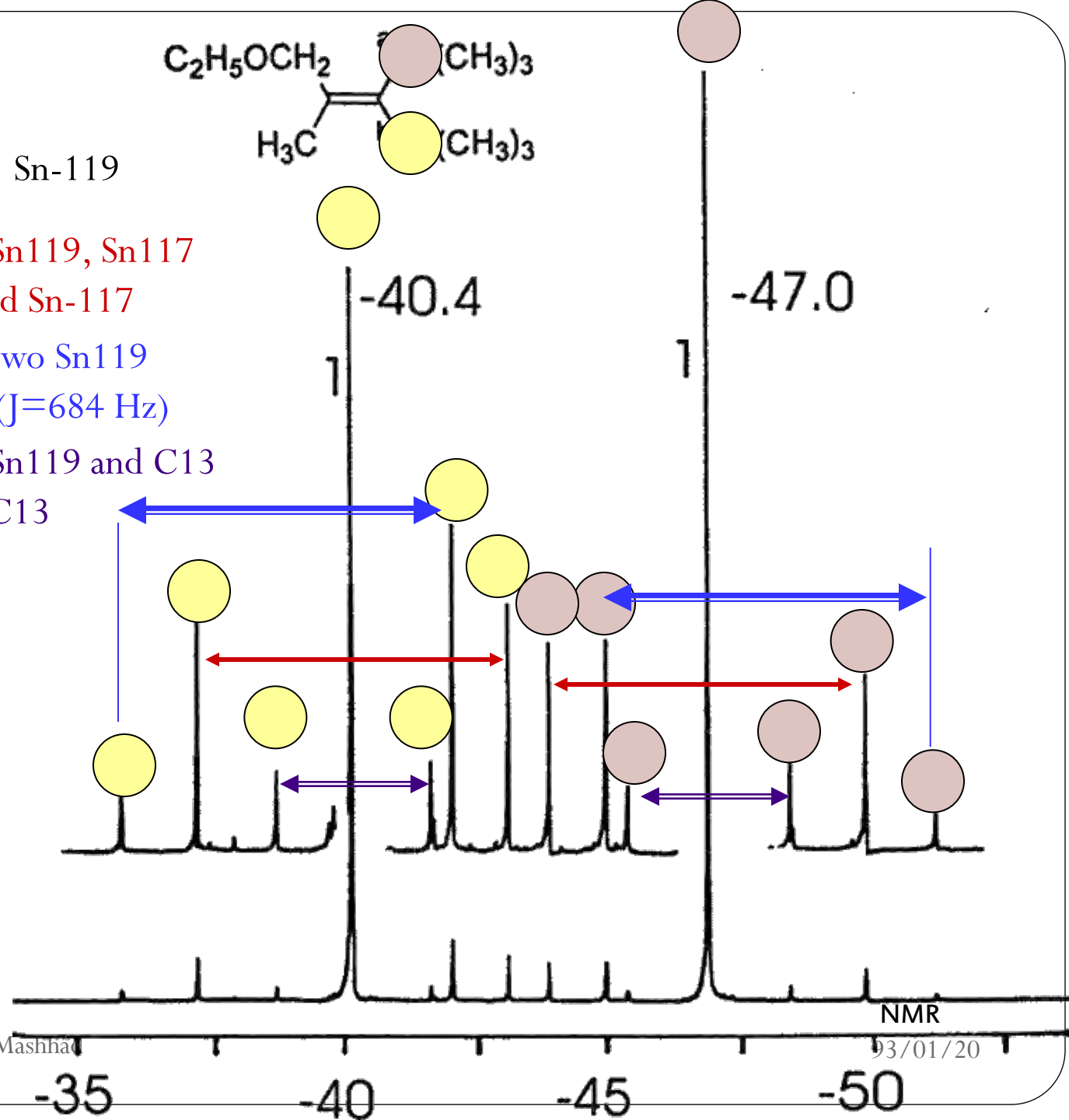
Sn-117 $a=7.61\%$

Sn-119 $a=8.58\%$



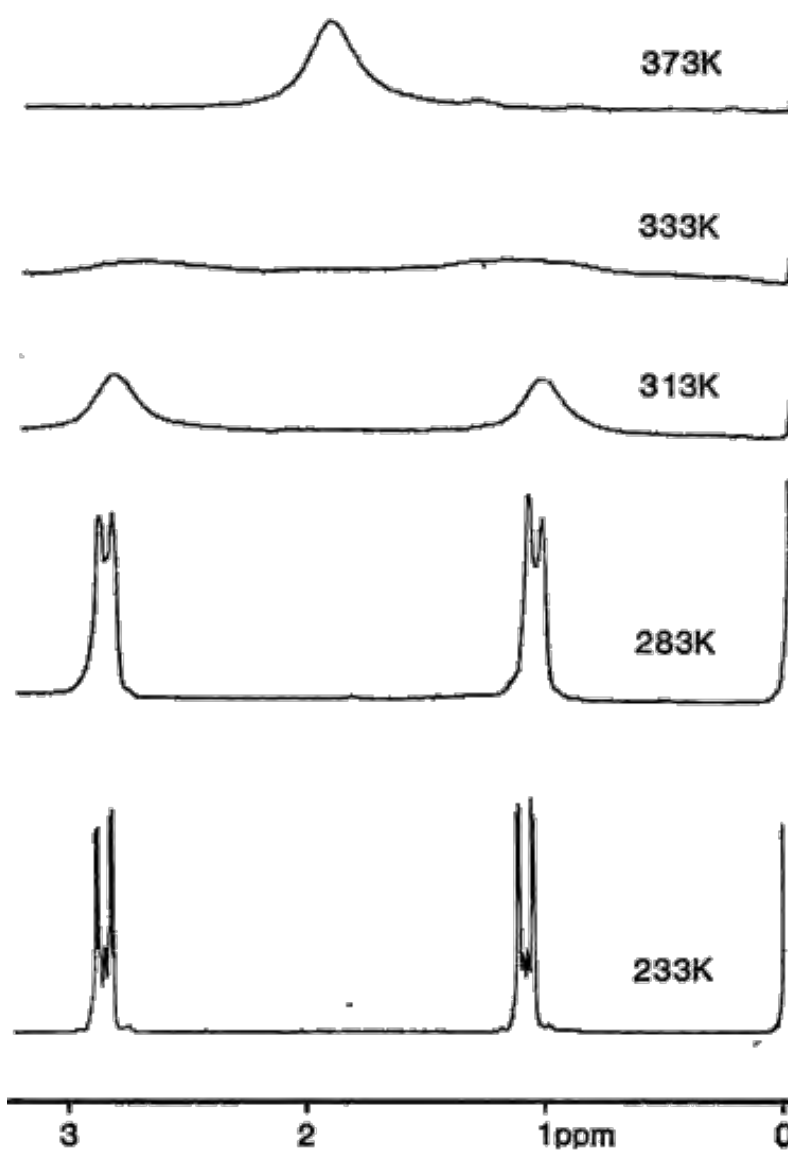


- 1- molecule containing 1 Sn-119
- 2- molecule containing Sn119, Sn117
J between Sn-119 and Sn-117
- 3- molecule containing two Sn119
Form an AB spectra (J=684 Hz)
- 4- molecule containing Sn119 and C13
J between Sn119 and C13



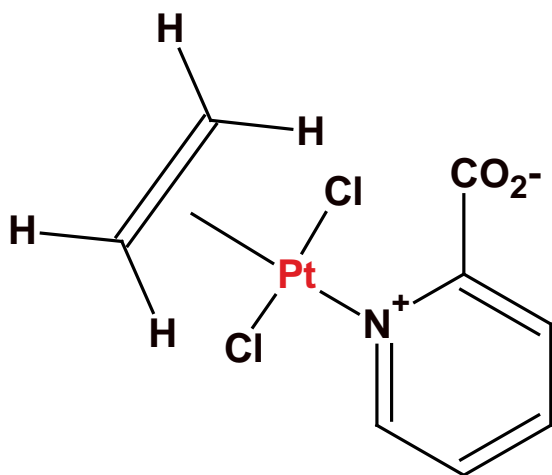
Sn-117 a=7.61%
 Sn-119 a=8.58%

DYNAMIC NMR



$^1\text{H-NMR}$ spectrum of $\text{C}_5\text{H}_5\text{Rh}(\text{C}_2\text{H}_4)_2$ (200 MHz).

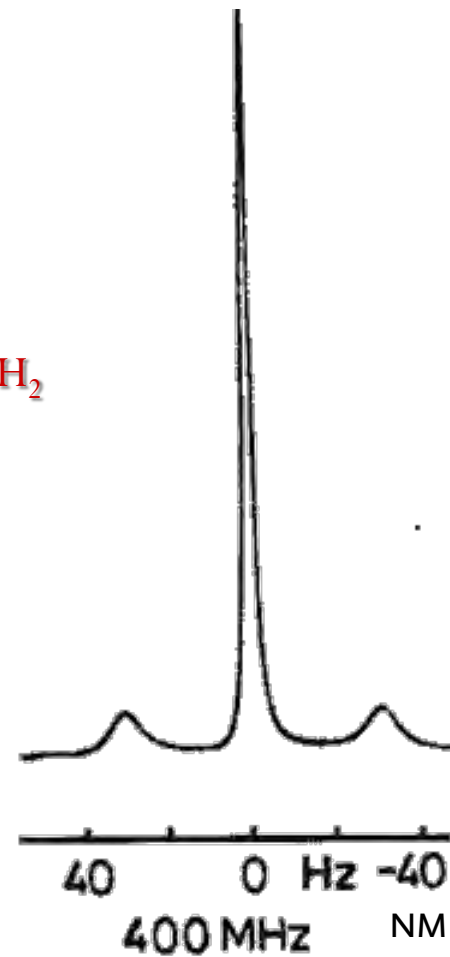
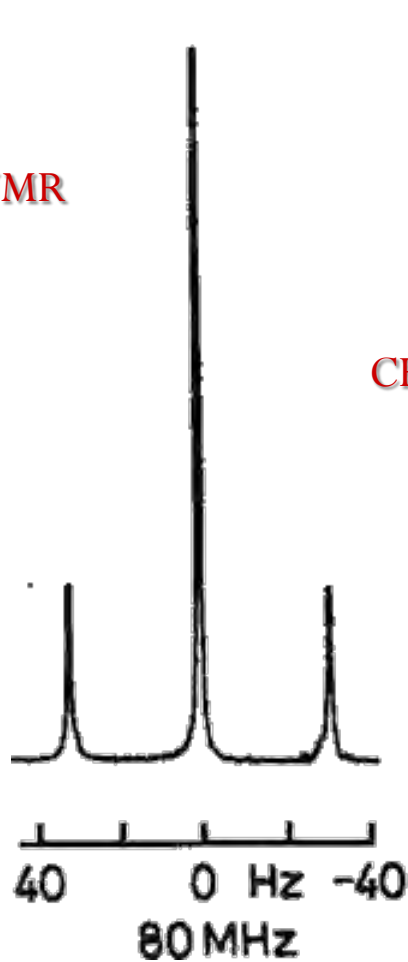
relaxation on ^{195}Pt can have unexpected influence on proton satellites. CSA relaxation increases with the square of the field. If the relaxation (time necessary for the spins to change their spin state) is fast compare to the coupling, the coupling can even disappear!



$a=33.8\%$

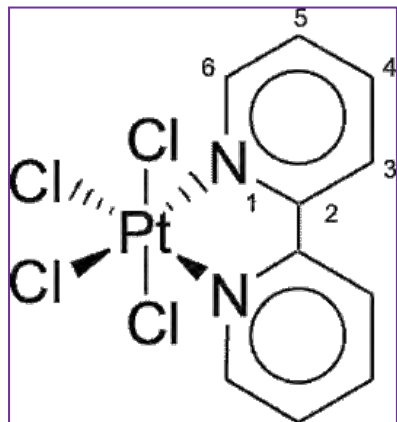
$^1\text{H-NMR}$

$\text{CH}_2=\text{CH}_2$



NMR
93/01/20

$I = \frac{1}{2}$ $a = 33.8\%$



H6 : dd

$$J_{4-6} = 1.3 \text{ Hz}$$

$$J_{5-6} = 6.2 \text{ Hz}$$

$$J_{\text{H6-Pt195}} = 26 \text{ Hz}$$

^{195}Pt satellites

^{195}Pt satellites

P-31 SPECTRUM OF $\text{PF}_2\text{H}(\text{NH}_2)_2$ LABELED WITH ^{15}N

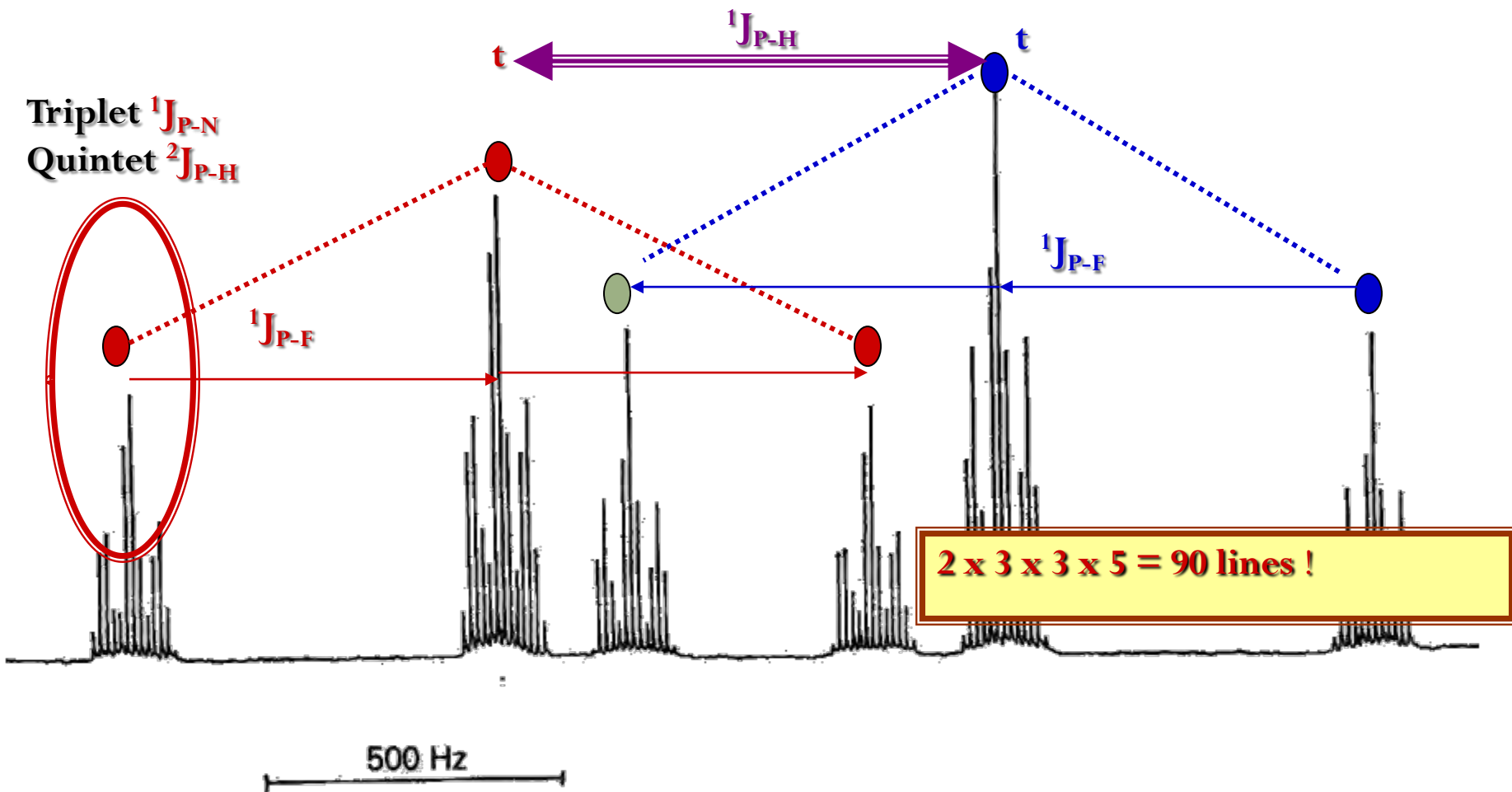


Fig 2.9 ^{31}P NMR spectrum of $\text{PF}_2\text{H}(\text{NH}_2)_2$. It is a doublet (J_{PH}) of triplets (J_{PF}) of triplets (J_{PN}) of quintets (J_{PH}) – 90 lines in all.

SI-29 COUPLING

- ^{29}Si has 5% abundance.
- For $\text{H}_3\text{Si-SiH}_3$, the chance of finding
- $\text{H}_3\text{-}^{28}\text{Si}\text{-}^{29}\text{Si}\text{-H}_3$ is 10%.
Interestingly we can see that the two kind of protons are no longer equivalent so **homonuclear coupling become observable!**
The molecule with 2 Si-29 is present with 0.25% intensity and is difficult to observe.
- The second group gives smaller coupling

