Introduction to Nuclear Magnetic Resonance (NMR) Spectroscopy

Chapter 4 Spin-Spin Interactions

Types of interaction between spins:

1. Dipolar Coupling
2. Scalar Coupling

^{1}H NMR spectrum of Ethyl acetate

2nI + 1 Rule for prediction of spin-spin splitting

Pascal's triangle

Transition and Spin Orientation of CH_3 on to CH_2

Common splitting patterns in ^{1}H NMR spectra

^{1}H NMR spectrum of 1, 2-Dichloroethane

^{1}H NMR spectrum of styrene

Coupling Constant

The most common coupling constants are ^{2}J, ^{3}J, & ^{4}J

Second Order Couplings

The higher field instruments.

^{31}P Nucleus NMR Properties

^{1}H NMR Spectrum of Di-t-butylphosphite

^{31}P & ^{195}Pt Nuclei NMR Interactions to ^{1}H

^{195}Pt nucleus NMR Properties

^{1}H NMR Spectrum of BistriphenylphosphinePlatinumHydrochloride

^{10}B & ^{11}B Nuclei NMR Interactions to ^{1}H

^{10}B & ^{11}B Nuclei NMR Properties

^{1}H NMR Spectrum of Sodium Borohydride $NaBH_4$ in D_2O

^{19}F NMR Spectrum of Sodium tetrafluoroborate $NaBF_4$

^{73}Ge nucleus NMR Interactions to ^{1}H

^{73}Ge nucleus NMR Properties

^{1}H NMR Spectrum of Germanium hydride GeH_4

Chapter 8 Two-Dimensional NMR Spectroscopy

Typical 2D NMR Pulse Sequence

The Preparation Time:

The Evolution Time:

The Mixing Time:

The Detection Time:

COSY: **Correlation Spectroscopy**

COSY Pulse Sequence

2D COSY ^{1}H NMR Spectrum of
$CH_3(CH_2)_3$-C_6H_4-N=N-C_6H_4-O-$(CH_2)_2CH_3$
4-n-Butyl, 4'-n-Propoxy Diazobenzene

2D ^{1}H COSY NMR of codeine $C_{18}H_{21}NO_3$ in $CDCl_3$

HETCOR: Heteronuclear Correlated Spectroscopy

The XHCORR pulse Sequence

2D XHCORR NMR Spectrum of n-Butyl Salicylate

2D HHCOSY NMR Spectrum of n-Butyl Salicylate

INADEQUATE: Incredible Natural Abundance Double Quantum Transfer Experiment

2D-Inadequate: Nuclear connectivity of low abundance nuclei (^{13}C, ^{15}N, ^{183}W)

2D INADEQUATE Pulse Sequence

^{13}C NMR Spectrum of Sucrose $C_{12}H_{22}O_{11}$

2D INADEQUATE ^{13}C NMR Spectrum of Sucrose $C_{12}H_{22}O_{11}$

2D INADEQUATE ^{13}C NMR Spectrum of Geraniol $C_{10}H_{18}O$

2D INADEQUATE ^{13}C NMR Spectrum of Menthol $C_{10}H_{20}O$

Introduction to Nuclear Magnetic Resonance (NMR) Spectroscopy

Chapter 1 Basic theory

Spectroscopy is the study of the interactions between light and matter. Light refers to any sort of Electromagnetic Radiation such as Gamma Rays (γ-rays) X- Rays (x-rays) Ultraviolet Rays (UV), Infrared Rays (IR), Microwave (MW), Nuclear Magnetic Resonance Wave (NMR), and Radio Wave (RW). Matter refers to molecules.

Click S1

The Wavelength equals to the speed of light divided by the frequency.

Lambda $\lambda = c / \upsilon$ (nu)

The Energy equals to the Plank's constant times frequency

$E = h \times \upsilon$

The speed of light is equal to 299,792,458 m/s (meters per second) and equal to (186,212 miles/second). Planck's constant is equal to 6.626×10^{-27} erg-seconds. or 6.626×10^{-34} J S^{-1}.

Wavelength and frequency are inversely proportional hence higher the frequency (υ) means shorter the wavelength (λ)

Click S2

In the most of spectroscopy the molecules have a set of energy levels which generate the lines in the energy spectrum are due to the transitions of these energy levels. The difference between two energy levels $\Delta E = E2 - E1$ is fundamentally related to the frequency by quantum mechanics as follows

$$E = h \upsilon$$

Click S3

In IR and UV spectroscopy the absorption or emission detects the absorption of frequencies in the electromagnetic spectrum by certain nuclei in the molecule.
To understand the Nuclear Magnetic Resonance (NMR) spectroscopy we must understand the quantum mechanics of single spin and multiple spins.
As opposed to the atomic mass and charge, the spin has no macroscopic equivalent. The spin exits as a period. Think about the point (air valve) on a car wheel which is rotating about its centre. If the car is moving at a constant speed, the point is returned to the same position at regular intervals each time it has completed the 360^0 of rotation. The time taken for the point to return to its original position is called the period. τ
Frequencies are most commonly quoted in Hertz (Hz) which relates to number of cycles per second. Ten times per second mean frequency $\upsilon = 10$ Hz.

The frequency υ equals to the inverse of the period τ.

$$\upsilon = 1 / \tau$$

If the period is 0.01 second then frequency $\upsilon = 1/0.01 = 100$ Hz

Angular frequency ω

The rotation of 360^0 equals to the 2π Radians. The angular frequency ω equals to the rotation through 2π over the period τ

$$\omega = 2\pi / \tau$$

The angular frequency unit is Radians per Second.
Now substitute $1/\tau$

$$\omega = 2\pi \upsilon$$

Click S4

Energies

The photon of a frequency υ has energy E is given by the equation.

$$E = h \upsilon \quad \upsilon = \omega / 2\pi \quad E = h \omega / 2\pi \quad E = \hbar \omega$$

Where h = Plank's constant joules per second $J S^{-1}$ ($6.626 \times 10^{-34} J S^{-1}$)

$\hbar$ = Plank's constant divided by 2π (Pronounced h bar or h cross)

Quantum Mechanical Treatment of The Atomic Nucleus

The dipole moment μ is related to the angular momentum J as below,
$\mu = \gamma J$ Where γ is the gyro magnetic ratio of the nucleus.

According to the quantum theory, the dipole moment and angular momentum are quantized. The maximum components of the angular momentum J in the Z direction are measured in the unit of $h/2\pi$. ($\hbar$) and are defined by the equation.

$$J_z = \hbar m_I$$

Where m_I is the magnetic quantum number. As per quantum condition these magnetic quantum numbers are related to the spin quantum number I of the respective nucleus.

$m_I = -I , -I + 1, \ldots.,0, \ldots..I - 1, I.$

This leads to Energy Levels = 2I + 1

Energy Levels and Spin States Table

	Spin Number(I)	Energy Levels	Spin States(m)	Orbital
1.	0	1	0	s
2.	1/2	2	-1/2 +1/2	
3.	1	3	-1 0 +1	p
4.	3/2	4	-3/2 -1/2 +1/2 +3/2	
5.	2	5	-2 -1 0 +1 +2	d

6. 3 7 -3 -2 -1 0 +1 +2 +3 f

For ^{1}H, ^{13}C, ^{15}N, ^{19}F, ^{29}Si & ^{31}P $I = ½$ $m_I = +1/2$ & $m_I = -1/2$

Click S5

For ^{2}H, ^{7}Li, and ^{14}N $I = 1$ $m_I = +1,\ 0,\ -1$

Click S6

Only nuclei with spin number $I \neq 0$ can absorb or emit in electromagnetic spectrum. To observe NMR signal for various nuclei the following table is useful.

Click S7

Nucleus	I_N	γ $[10^8\ T^{-1}s^{-1}]$	Srel	Nat. Abd.
^{1}H	½	2.675	1.00	99.98
^{13}C	½	0.673	1.76×10^{-4}	1.11
^{19}F	½	2.518	0.834	100.00
^{15}N	½	-0.2712	3.85×10^{-6}	0.37
^{29}Si	½	-0.5319	3.68×10^{-4}	4.70
^{31}P	½	1.083	0.0665	100.00
^{2}H	1	0.411	1.11×10^{-6}	0.0115
^{6}Li	1	0.3937	6.45×10^{-4}	7.59

^{14}N	1	0.193	0.001	99.635

I_N = Nuclear Spin Number

γ = Nuclear gyromagnetic Ratio

S_{rel} = Nuclear relative signal strength (sensitivity)

$N_{at.\ Abd}$ = Nuclear isotopic natural abundance

The Macroscopic View of Spins

In macroscopic behavior, the sum of the dipole moments of all nuclei is called Magnetization. The NMR sample of spin I= ½ nuclei precess about the static magnetic field has the equilibrium between α and β states. Their phases are not correlated. For each vector pointing in one direction of the transverse plane a corresponding vector can be found which point into the opposite direction. Therefore, the vector sum of the transverse components is vanishing as far as the phases of the spins are not correlated.

Click S8 & Click S9

In practice the coherence can be achieved by applying the radio frequency (RF) field B_1 perpendicular to the static magnetic field H_o or B_o i.e., along the x-axis or y-axis. This creates the state in which the phases of the spins are partially correlated. The vector sum of the transverse components is non-vanishing and this can be detected in the receiver coil. This is known as NMR signal which is normally amplified and recorded as NMR Spectrum.

Click S10

Boltzmann Distribution

The energy difference of α and β levels is

$$\Delta E = \gamma \, h \, H_o / 2\pi$$

The Ratio of $\frac{N_\alpha}{N_\beta} = e^{\frac{E_\beta - E_\alpha}{KT}} = e^{\frac{\Delta E}{KT}}$

Where :-
K = Boltzmann Constant = 1.3805×10^{-23} J / Kelvin
T = Temperature in Kelvin (273.15 + Celsius)

For ^1H at Radio Frequency (RF= ω) 400 MHz @ 9.4 T (Tesla) applied field Ho or Bo, the energy difference ΔE = 4×10^{-5} Kcal / Mole .

The ratio of spins $\frac{N_\alpha}{N_\beta} = 1.000064$

This means there are only 64 spins NMR active out of one million spins hence the NMR Spectroscopy method is not very sensitive in comparison to Infrared (IR) and Ultraviolet (UV) Spectroscopy methods.

The Radio Frequency υ (= Larmor Frequency ω) range is
60 MHz to 900 MHz.

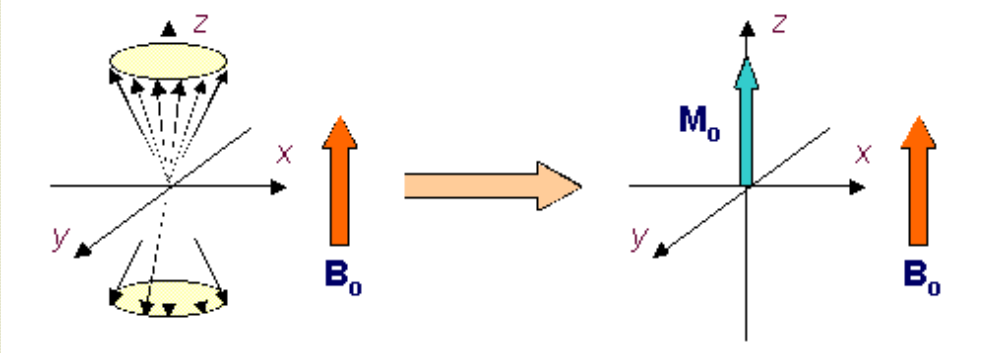
The Precession Frequency ω_o range is 1 Hz to 20 KHz

Click S11

Laboratory and Rotating Frames

Click S12

In conventional coordinate system, the applied magnetic field H_o or B_o and the net magnetisation vector M_o at equilibrium are both along the Z-axis.



The system is in equilibrium hence the energy difference ΔE = Zero.

Click S13

In reality the whole system is spinning.

Click S14

Magnetic field along the x – axis

When a direct current is passed through the coil of wire will produce the magnetic field along the x – axis. An alternating current will produce the alternating field along the x – axis.

Click S15

In magnetic resonance condition, the frequency of the alternate current is same as the frequency of the right vector of the field B_1. In other words, the magnetic field created by the coil passing the alternate current at the Larmor frequency is called the B_1 magnetic field. The alternating current through the coil when it is turned on and off, it generates a pulsed B_1 magnetic field along the x – axis.

The relative orientation of B_1 vectors in the x-y plane can be controlled by changing the relative phase of the irradiating Radio frequency (RF). The irradiation of RF (υ) corresponding to the Larmor frequency(ω) of a given nucleus (^{1}H , ^{13}C , ^{19}F, & ^{31}P) for a short time induces a complicated spiral movement of macroscopic magnetization M_o away from the Z axis towards the x-y plane.

$\upsilon = \omega / 2\pi$ Duration τ

In the rotating coordinate frame this process is called nutation which is a simple rotation of macroscopic magnetization M_o around the axis of the field B_1. The nutation angle θ is a function of the magnitude of B_1 and its duration τ.

$$\theta = -\gamma B_1 \tau$$

Click S16

It is usual to use a coordinate frame which rotates around the B_o or H_o = Z axis with the circular frequency ω_o. The resulting stroboscope effect allows it to describe the precession ω in terms of frequency difference.

$$\Omega = \omega - \omega_o$$

In the following examples we will use the rotating frame for all vector diagrams.

Only the transverse magnetization in $x - y$ plane is observed of correlated states. This leads to the detectable signal in the receiver coil as NMR signal. This is achieved by applying the 90^0 ($\pi / 2$) pulse as shown below.

Click S17 & Click S18

Chapter 2 Chemical Shifts

When an NMR sample is placed in the magnetic field B_o or H_o, the local field generated by each nucleus generally will oppose the magnetic field. The effective field at the nucleus can be given by the following equation.

$$B_{eff.} = B_o (1 - \sigma)$$

σ is the magnetic shielding constant of the nucleus.

Click S19

The effective field at each nucleus (^1H , ^{13}C , ^{19}F, & ^{31}P) will vary depending on the chemical structure of the molecule. This is called the chemical shift phenomenon. Let us look at the ^1H NMR spectrum of the Nitromethane CH_3NO_2.

Click S20 & Click S21

In NMR spectroscopy we use the relative scale referring the all-NMR signals to the reference NMR signal (Normally a singlet). It is denoted by δ and reported in PPM (parts per million).

$$\delta = \frac{\omega - \omega_{ref}}{\omega_{ref}} \text{ PPM}$$

$$\delta = \frac{\text{Difference in precession frequency between two nuclei (Hz)}}{\text{Operating frequency of the magnet (MHz)}}$$

Since the numerator is usually in hertz, and the denominator in megahertz, delta is expressed in PPM.

The detected frequencies (in Hz) for ^{1}H, ^{13}C, and ^{29}Si nuclei are usually referenced against TMS (TetraMethylSilane), which is assigned the chemical shift of zero. Other standard materials are used for setting the chemical shift for other nuclei.

Click22 & Click S23

Thus, an NMR signal at 300 Hz from TMS at an applied frequency of 300MHz has a chemical shift of:

$$\delta = \frac{300 \text{ Hz}}{300 \times 10^{6} \text{ Hz}} = \frac{1}{1 \times 10^{6}} = 1 \times 10^{-6} = 1 \text{ PPM}$$

An NMR signal at 450 Hz from TMS at an applied frequency of 300MHz has a chemical shift of:

$$\delta = \frac{450 \text{ Hz}}{300 \times 10^{6} \text{ Hz}} = \frac{1.5}{1 \times 10^{6}} = 1.5 \times 10^{-6} = 1.5 \text{ PPM}$$

The variations of nuclear magnetic resonance frequencies of the same kind of nucleus, due to variations in the electron distribution, are called the chemical shifts.

Click S24

Chemical shifts are used for distinguishing one nucleus from another. It can in fact reveal the information regarding the chemical surroundings of the nucleus (structural information).

Click S25

The NMR chemical shift is a tensor quantity. The observed quantity depends on the relative orientation of the molecule with respect to the axis of the applied magnetic field.

For example, take the fluorobenzene molecule. The ^{19}F NMR chemical shift will vary with the orientation of the fluorobenzene molecule inside the magnet. The least shielded (highest chemical shift) is called the 11 components while the most shielded (lowest chemical shift) is called the 33 components. In the solid state, this can be measured if one works with a single crystal of fluorobenzene.

With a powder sample, one observes a broad signal which shows all the possible orientations and the chemical shift that corresponds to each of these orientations. This powder patter will have singularities which give rise to the three principal components 11, 22, and 33.
11 and 33 will be at the wings while 22 will be the most probable and therefore most intense portion of the powder pattern.

In solution, liquid, or gas, the molecules are freely tumbling so one does not observe the tensor but an average chemical shift (isotropic chemical shift) which is equal to the average of the 11, 22, 33 components.

Click S26

In liquid phase the splitting of NMR signals is caused by Zeeman interaction and by the scalar spin spin couplings.

Factors affecting the chemical shifts ^{1}H NMR Spectroscopy.

Many different factors are known that may influence the exact field strength at the nucleus.

$$B_{eff.} = B_o (1 - \sigma)$$

σ is the magnetic shielding factor at the nucleus

Three major factors affect ^{1}H NMR chemical shifts are:

1. Deshielding by electronegative elements
2. Deshielding due to hydrogen bonding
3. Anisotropic effect due to double and triple bonds

The stronger the electronegative element causes the greater the deshielding hence ^{1}H chemical shifts shift towards the lower field or away from TMS.

Click S27 & Click S28

More number of the electronegative element is attached to the same atom causes more deshielding effect at ^{1}H nucleus.

Deshielding effects decreases as the substitution chain increases.
As the distance from the electronegative element increases the deshielding effect at ^{1}H nucleus proportionally decreases to the lesser degree.

Click S29

The same is true for the H bonding. The stronger the H bonding causes the greater the deshielding hence ^{1}H chemical shifts shift towards the lower field or away from TMS.

Click S30

In anisotropic effects the secondary field generated by the electron circulation either it opposes the applied static field, or it gets added to the applied static field depending on the geometry of the ^{1}H.

If the secondary field at the nucleus ^{1}H opposes to the applied static field, then it causes the deshielding hence ^{1}H chemical shifts shift to the lower field or away from TMS.

Click S31 & Click S32

If the secondary field at the nucleus ^{1}H gets added to the applied static field, then it causes the shielding hence ^{1}H chemical shifts shift to higher field or towards TMS.

Click S33 & Click S34

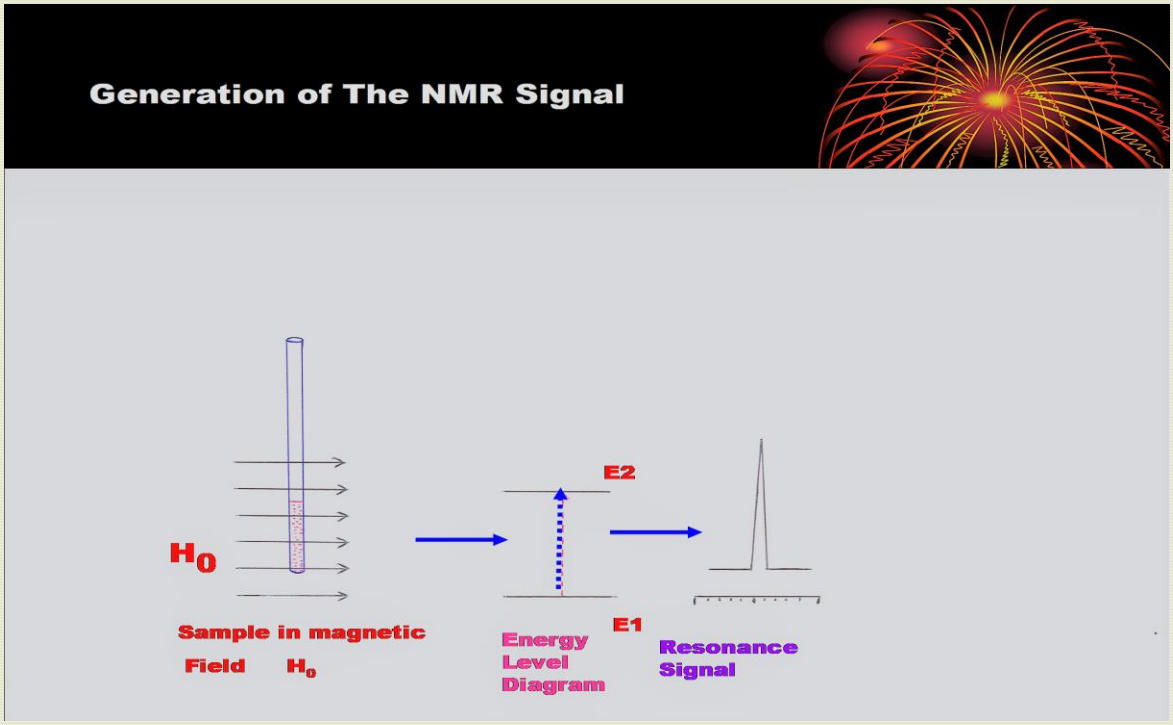
Depending on the local chemical environment, different protons in a molecule resonate at slightly different frequencies. This is the effectively the NMR spectrum of the given molecule and it is the unique fingerprint of that molecule.

Click S35 & Click S36

When certain Nuclei are placed in a strong magnetic field, ^{1}H, ^{10}B, ^{11}B, ^{13}C, ^{14}N, ^{15}N, ^{19}F, & ^{31}P These nuclei can absorb electromagnetic radiation in the radio frequency (R.F.) range.

The absorption of energy can be detected, amplified, and recorded as NMR signal. This phenomenon is known as NMR spectroscopy.

Click S37



How NMR Signals are generated

In Ethyl benzene molecule there are three kinds of ^{1}H groups. These ^{1}H precess at different frequency at a constant magnetic field. The radio frequency of 250 MHz would require the magnetic field of 5.88 Tesla for the NMR spectrometer.

Click S38 & Click S39 & Click S40

Introduction To NMR Spectroscopy Part 1(Link)

Chapter 3 Integration of ^{1}H NMR Spectra

There are two ways used in measuring the integration of NMR spectrum.

1. Manual measurement

In manual measurement the height of the different peaks areas are measured using the ruler and then all the areas are divided by the smallest area of the peak to get the relative areas ratio of the rest of peaks. The areas are rounded to the whole number.

2. Electronic (computer) measurement

In electronic measurement the relative areas are integrated and under the each peak the integral number is printed. Then the integral number is rounded to the whole number. All the areas are divided by the smallest area of the peak to get the relative areas ratio of the rest of peaks.

Analysis of ^{1}H NMR Spectrum of Ethyl Acetate

$CH_3—CO—O—CH_2–CH_3$

Click S41 & Click S42 & Click S43 & Click S44 & Click S45

Chapter 4 Spin-Spin Interactions

There are two types of interaction between spins:

1. Dipolar Coupling
2. Scalar Coupling

The dipolar coupling depends on the orientation of the connecting vector to the static field. In isotropic (liquid) phase the orientation rapidly changes due to molecular tumbling and the dipolar coupling cannot be observed due to coupling averages to zero value. However, this can be observed in solid state and in liquid crystals.

For example, take the fluorobenzene molecule. The ^{19}F NMR chemical shift will vary with the orientation of the fluorobenzene molecule inside the magnet. The least shielded (highest chemical shift) is called the 11 components while the most shielded (lowest chemical shift) is called the 33 components. In the solid state, this can be measured if one works with a single crystal of fluorobenzene.

Click S26

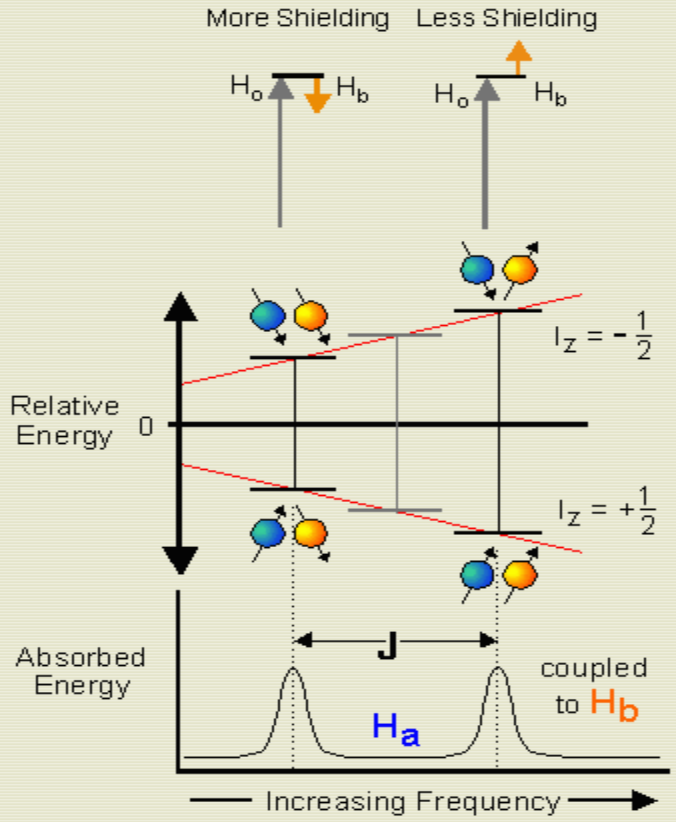
The scalar coupling leads to a splitting of resonance lines. The effect is mediated via the electrons and its magnitude therefore rapidly decreases when the number of intervening bonds increases.

Nuclei which are close to one another exert an influence on each other's effective magnetic field. This effect shows up in the NMR spectrum when the nuclei are nonequivalent. If the distance between non-equivalent nuclei is less than or equal to three bond lengths, this effect is observable. This effect is called spin-spin coupling or J coupling.

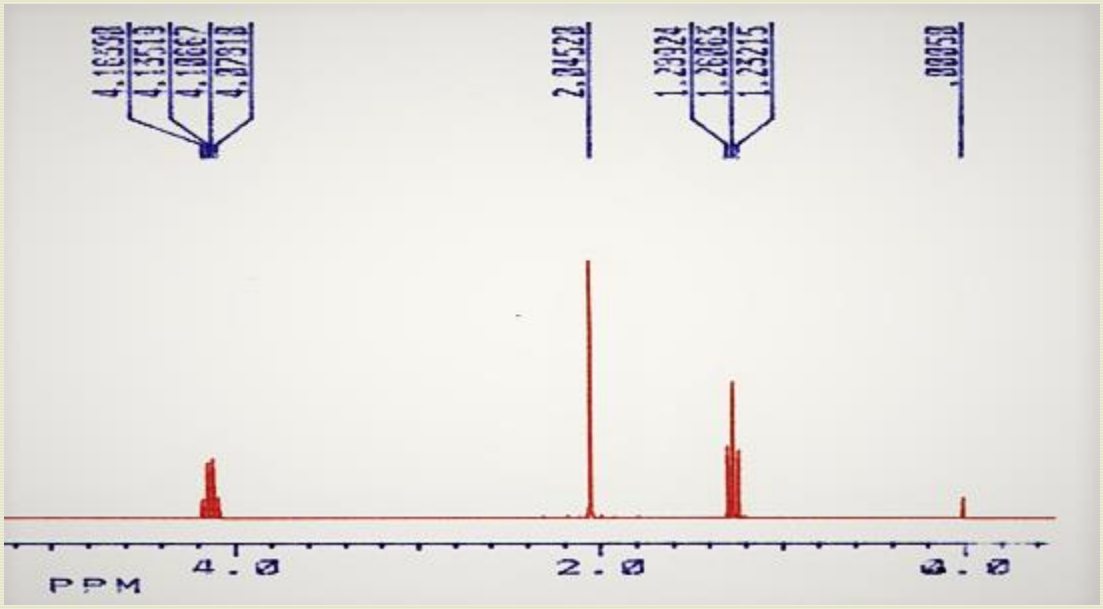
Click S46

To understand this effect, imagine a sample of molecules having two suitably close hydrogen atoms, A and B, which have different chemical shifts. This last condition (different chemical shifts) turns out to be rather important. Hydrogen A has two spin states, I_Z=+1/2 and I_Z= -1/2 and in the absence of hydrogen B, it will give a single NMR peak. It's neighbors, hydrogen B, has a small magnetic field, however, which is either aligned with or against the external field. We know that the two orientations have about the same probability. When hydrogen B's field is aligned with H_o, hydrogen A will be **deshielded** and H_{eff} will become slighter larger. When hydrogen B's field is aligned against H_o, hydrogen A will be **shielded** and H_{eff} will become slightly smaller. In our sample, half of the molecules will have hydrogen B's magnetic field aligned with H_o. Hydrogen A in these molecules will resonate at a higher frequency (Down field). The other half of the molecules will have hydrogen B's magnetic field aligned against H_o and hydrogen A will resonate at a lower frequency (up field). The presence of hydrogen B, therefore, causes the single peak for hydrogen A to split into a doublet (two peaks).
The frequency separation between these two peaks is called **J**, the **coupling constant**, and typically is between 0 and 15 Hz. whereas the chemical shift is dependent on the strength of H_o and is reported in PPM, the coupling constant is **independent** of H_o and is reported in Hz.

An important point to note is that if hydrogen B splits the peak for hydrogen A by J Hz, the reverse is true too. Hydrogen A will split the peak for hydrogen B by J Hz as well. This fact is very useful for identifying which hydrogens are coupled to each other.



^{1}H NMR spectrum of Ethyl acetate



CH_3 CO OCH_2 CH_3 Ethyl acetate

- **CH_3** Singlet @ 2.05 PPM
- **CH_2** Quartet @ 4.12 PPM
- **CH_3** Triplet @ 1.26 PPM
- CO no NMR signal.
- O no NMR signal.

2nI + 1 Rule for prediction of spin-spin splitting

Where I = Spin number of the observed spin active nucleus
n = Number of spin active neighbouring nuclei

Click S7

Number of Peaks = 2nI + 1 for Ethyl acetate

CH_3 CO OCH_2 CH_3

For CH_3

n = zero (no neighbouring ^1H)

I = ½ for ^1H

Number of peaks = 2 x n x I + 1
= 2 x 0 x ½ + 1
= 0 + 1
= 1 (Singlet @ 2.05 PPM)

For CH_2

n = Three (neighbouring ^1H from CH_3)

I = ½ for ^1H

Number of peaks = 2 x n x I + 1
= 2 x 3 x ½ + 1
= 3 + 1
= 4 (Quartet @ 4.12 PPM)

For CH_3

n = Two (neighbouring ^1H from CH_2)

I = ½ for ^1H

Number of peaks = 2 x n x I + 1
= 2 x 2 x ½ + 1
= 2 + 1
= 3 (Triplet @ 1.26 PPM)

Click S41

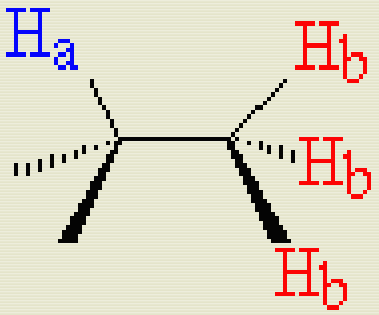
Pascal's triangle for ^{1}H, ^{13}C, ^{19}F Where I = ½

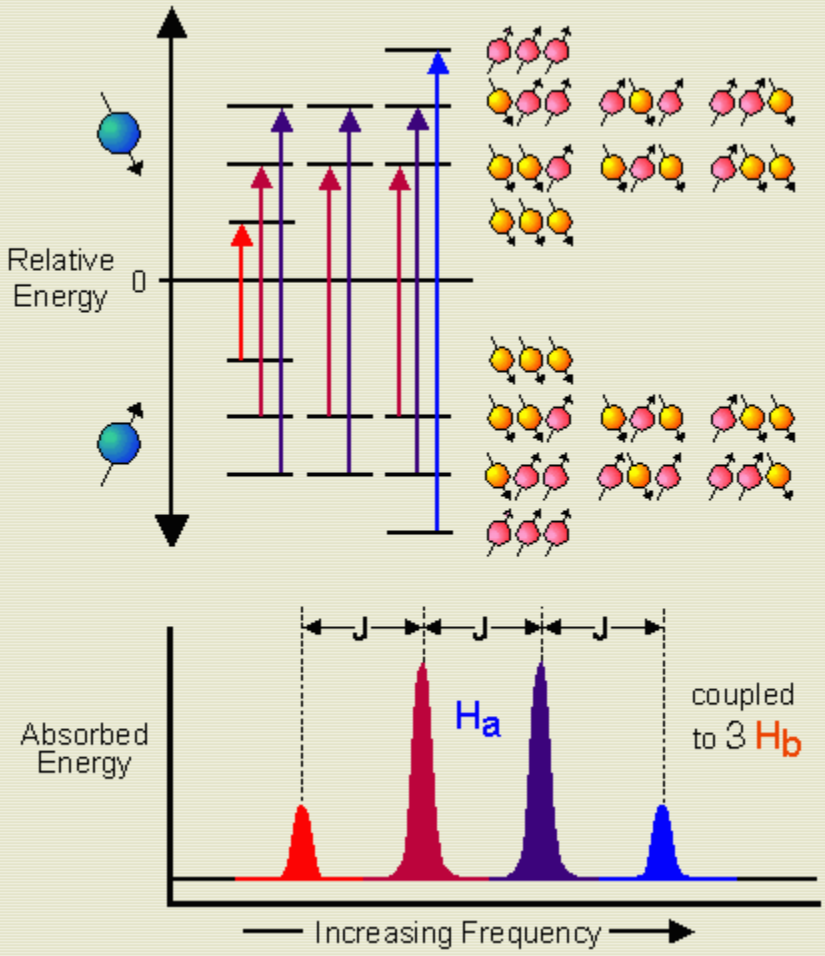
	No. of Peaks	Terminology	Intensity Ratio
n=0	One Peak	Singlet	1
n=1	Two Peaks	Doublet	1 1
n=2	Three Peaks	Triplet	1 2 1
n=3	Four Peaks	Quartet	1 3 3 1
n=4	Five Peaks	Quintet	1 4 6 4 1
n=5	Six Peaks	Sextet	1 5 10 10 5 1
n=6	Seven Peaks	Septet	1 6 15 20 15 6 1
n=7	Eight Peaks	Octet	1 7 21 35 35 21 7 1

Click S47

How **CH_2** and **CH_3** in Ethyl acetate split into quartet and triplet, respectively.

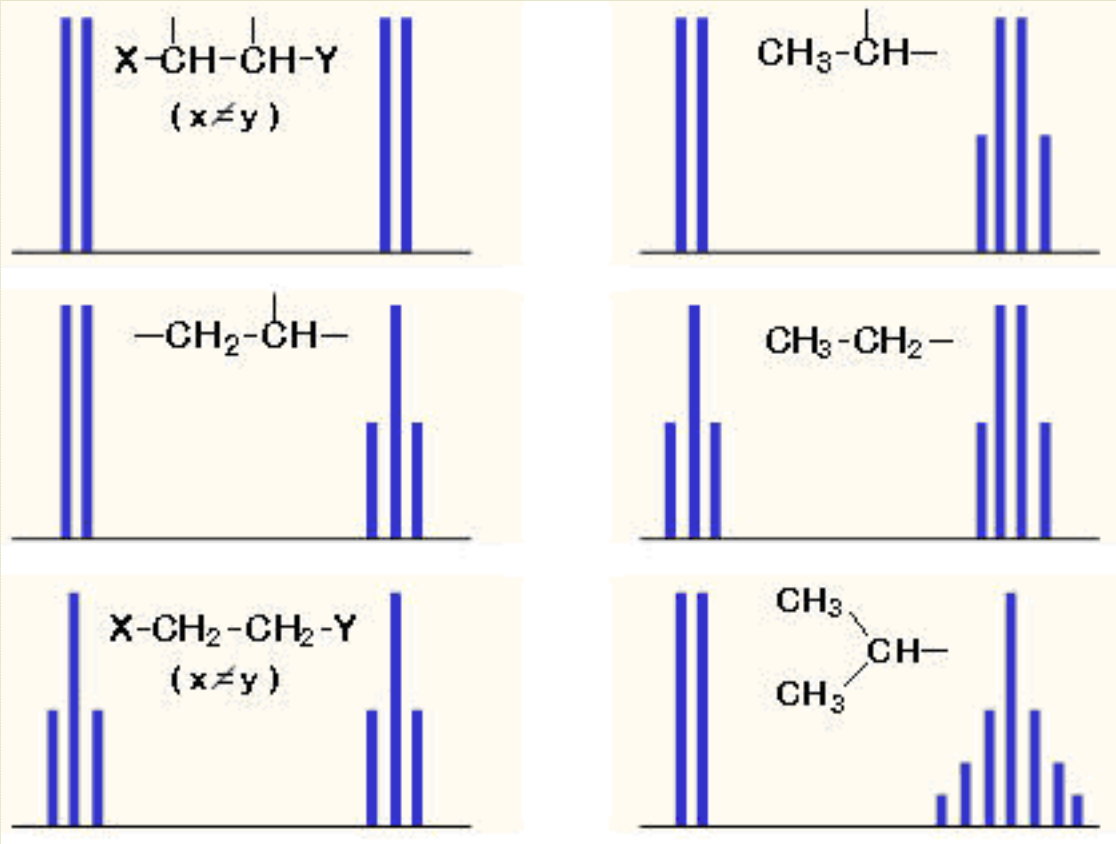
Transition and Spin Orientation of CH_3 on to CH_2





Click S48 & Click S49 & Click S50

Common splitting patterns in ^{1}H NMR spectra



Protons that are chemically and magnetically equivalent and usually they are symmetrical; do not interact with each other (no splitting of NMR signal).

X—CH_2—CH_2—Y if X = Y No Splitting (singlet only)

^{1}H NMR spectrum of 1, 2-Dichloroethane

Click S51 & Click S52

Protons that are attached to same atom with sigma bond do not split the NMR signal.

CH_3—X X—C H_2—Y

Click S53 & Click S54

Protons that are attached to double and π (pi) bonds; each proton will interact with each other and give rise to more complex NMR spectrum.

^{1}H NMR spectrum of styrene

Click S55

Coupling Constant

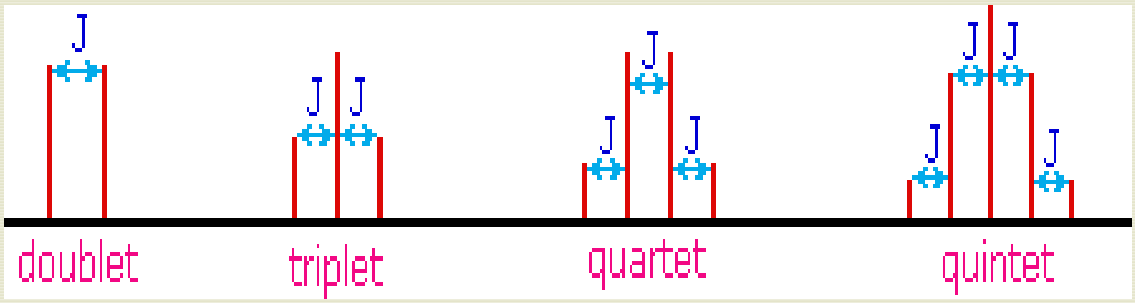
The most commonly observed patterns have been given descriptive names, such as
Doublet (two equal intensity signals 1:1),

Triplet (three signals with an intensities ratio of 1:2:1)

Quartet (a set of four signals with intensities ratio of 1:3:3:1)

Quintet (a set of five signals with intensities ratio of 1:4:6:4:1)

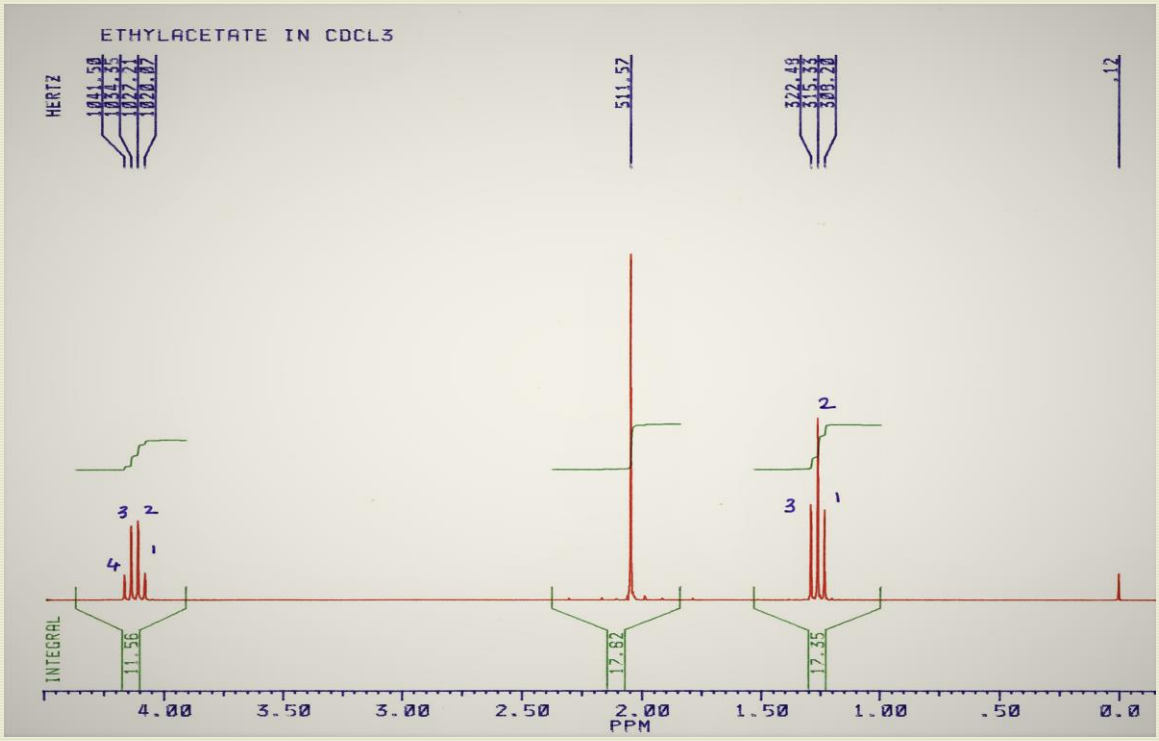
Four such patterns are displayed in the following illustration. The line separation is always constant within a given multiplet and is called the **coupling constant (J)**. The magnitude of J is given in units of Hz. It is independent of magnetic field H_o or B_o.



1:1 1:2:1 1:3:3:1 1:4:6:4:1

Intensities ratio can be predicted using Pascal's triangle.

Measurement of coupling constant in Ethyl acetate

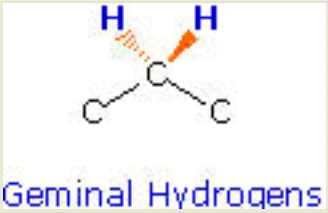


Click S56 & Click S57 & Click S58

The most common coupling constants are ^{2}J, ^{3}J, & ^{4}J

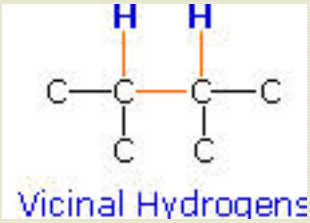
The spacing (Gaps) between each adjacent peak in Triplet and Quartet are equal and constant. This spacing is known as Coupling constant and it is denoted by letter J. It is also denoted as ^{3}J indicating the coupling constant of the nuclei separated by three bonds. The most common coupling constants are ^{2}J, ^{3}J, & ^{4}J but longer-range coupling constants are also observed.

^{2}J is also called geminal coupling constant. The geminal coupling does not occur when the two protons are equivalents due the rotations around the other two bonds (mostly $^{2}J = 0$).



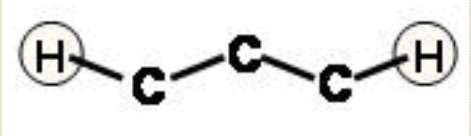
Geminal Hydrogens

^{3}J is also called vicinal coupling constant.

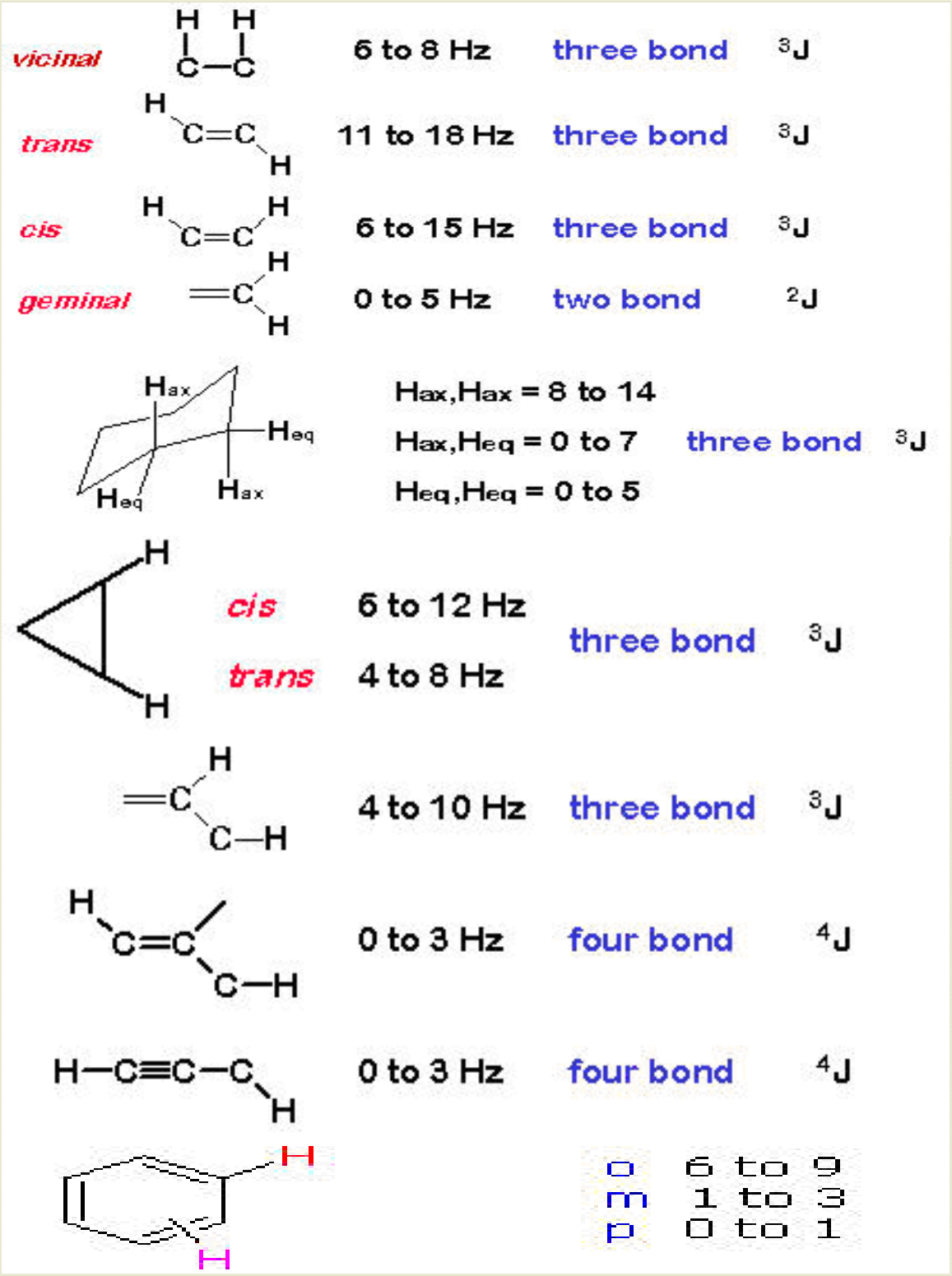


Vicinal Hydrogens

^{4}J is observed in bicyclic compounds where the molecule is forced to adapt the " W " conformation.



Magnitudes of Some typical examples of ^{1}H ^{2}J, ^{3}J, & ^{4}J coupling constants.

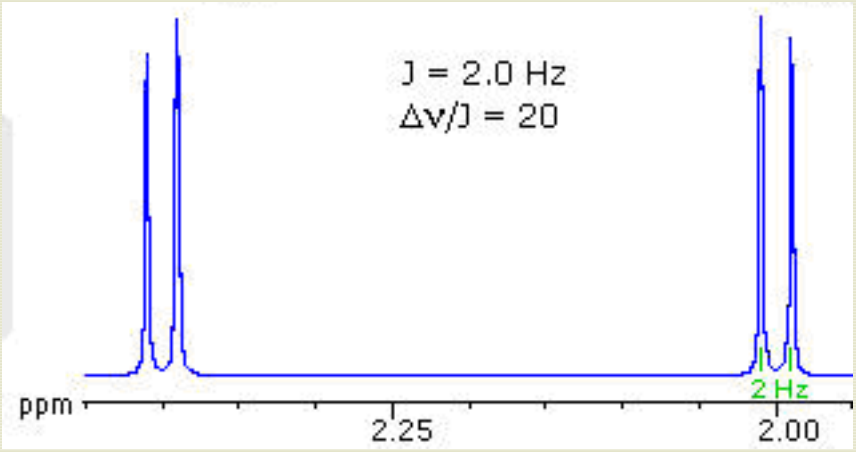


Couplings that occur at distances greater than three bonds are called long range couplings. They are usually smaller than 3Hz and mostly nonexistent (= zero Hz).

Second Order Couplings

The rules for line multiplicities and intensities described by Pascal's Triangle are only valid in the case of weak coupling.

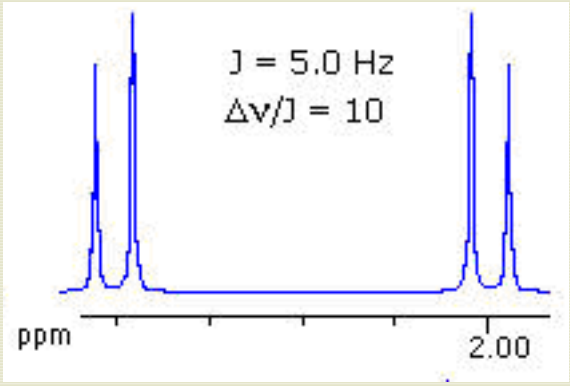
We would expect the NMR spectrum of two spin-coupled protons, A & B, to display a pair of doublets first order NMR spectrum.

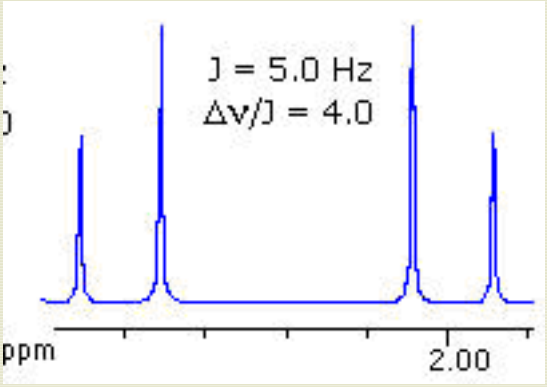


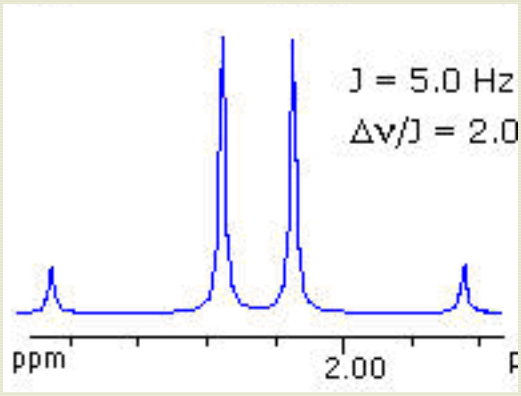
However, if the ratio of the chemical shift difference $\Delta\nu$ to the scalar coupling constant J (both in Hz) decreases to less than 10 then a significant distortion of this expected pattern will take place, as shown in the following diagram. The intensity ratio rules do not apply anymore.

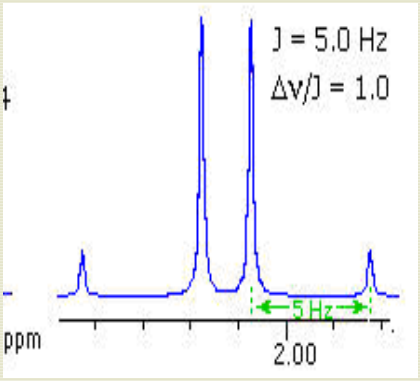
In the strong-coupling case spin properties are mixed. A practical consequence is that a resonance line cannot be referred to belong to a spin A or B. whereas in the limit of weak coupling a spin-flip of spin A does not cause spin B to flip there is a probability to do so in the strong coupling case. In order to derive coupling constants or chemical shifts from strongly coupled spins these parameters may not be extracted from the spectrum but must be derived from a simulation and comparison to the measured spectrum.

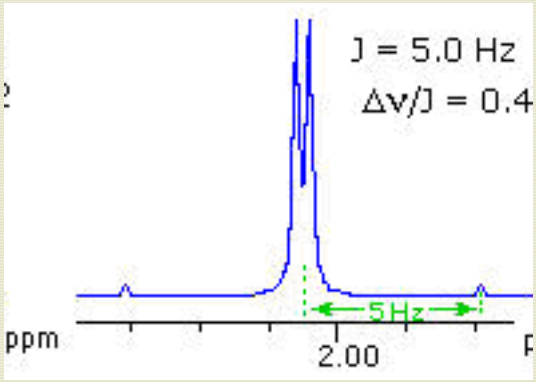
For the case of two doublets due to two strongly coupled protons the inner lines are larger than the outer ones ("roof effect"). Thereby it is possible to decide which signals are coupled with each other.

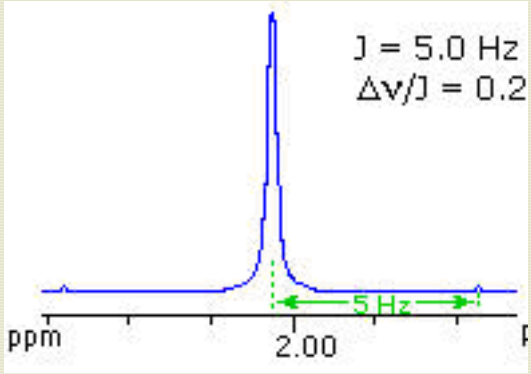





J = 5.0 Hz
Δν/J = 2.0
ppm
2.00


J = 5.0 Hz
Δν/J = 1.0
5 Hz
ppm
2.00


J = 5.0 Hz
Δν/J = 0.4
5 Hz
ppm
2.00

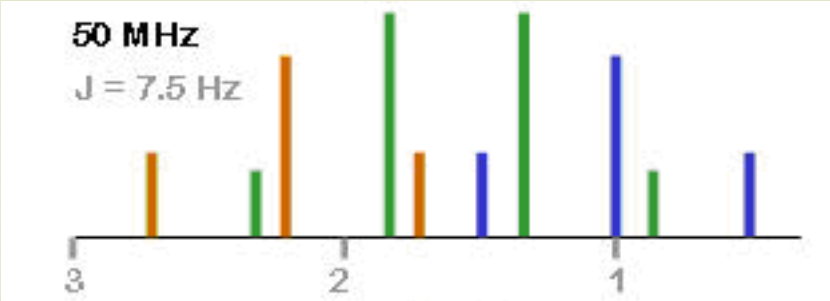

J = 5.0 Hz
Δν/J = 0.2
5 Hz
ppm
2.00

- When A & B become more similar then
- All NMR Peaks move closer hence,
- Outer peaks get smaller and finally disappear but
- Inner peaks get taller and finally merge into single peak.

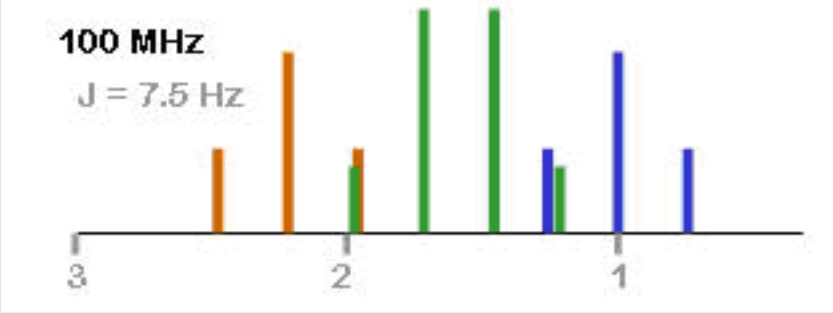
Second-order effects decrease as the frequency difference between multiplets increases, so that high-field (i.e., high-frequency) NMR spectra display less distortion than lower frequency spectra. Early spectra at 50 MHz were more prone to distortion than spectra from later machines typically operating at frequencies at 200 MHz or above.

What are the advantages of the higher field instruments?

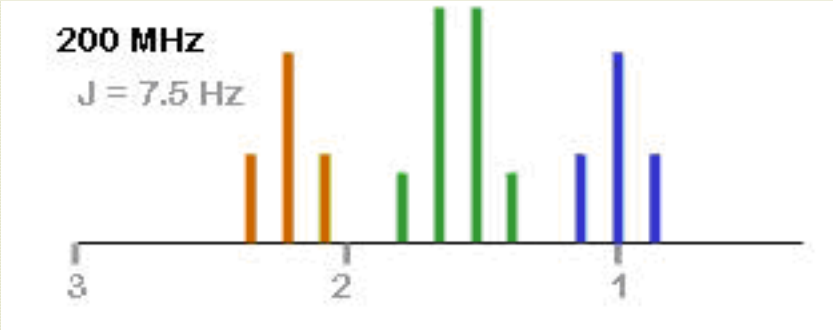
As the coupling constants are constant. They do not alter with field strengths of the instruments. NMR spectra are simplified at higher field.



Over lapping multiplets are separated and simplified to first order.



The second order effects are minimized to lesser degree.



Chapter 5 ^{13}C NMR Spectroscopy

^{13}C NMR Spectroscopy is the application of nuclear magnetic resonance study with respect to carbon atom. It is very similar to ^{1}H NMR Spectroscopy and very important technique in structure elucidation in Chemistry and Biology.

However, carbon NMR spectroscopy has a number of complications that are not encountered in proton NMR spectroscopy. Carbon NMR spectroscopy is much less sensitive than ^{1}H NMR spectroscopy since the major isotope of carbon, the ^{12}C isotope, has a spin quantum number of zero and so is not magnetically active. Only the much less common ^{13}C isotope, present naturally at 1.1% abundance, is

magnetically active with a spin quantum number of 1/2 (like ^{1}H). Therefore, only the few carbon-13 nuclei present resonate in the magnetic field, though this can be overcome by isotopic enrichment of e.g., Protein samples. In addition, the gyromagnetic ratio (6.728284 10^{7} rad T^{-1} s^{-1}) is only 1/4 that of ^{1}H, further reducing the sensitivity. The overall receptivity of ^{13}C is about 6 x 10^{4} orders of magnitude worse than ^{1}H.

Facts about Carbon Atom:

- Carbon ^{12}C is in most abundance 98.89 %
- Carbon ^{12}C is non-NMR active as spin number I = 0
- Carbon ^{13}C is in less abundance 1.108 %
- Carbon ^{13}C is NMR active as spin number I = ½
- ^{13}C NMR signal is 6000 times weaker than ^{1}H NMR signal.
- To see ^{13}C NMR signals Pulsed FT NMR is required
- Chemical Shift Range
- ^{1}H 0 to 12.00 PPM
- ^{13}C 0 to 220.00 PPM

- Resonance Frequency and Applied Field Strength

Applied Field	^{1}H RF	^{13}C RF
1.41 Tesla	60.00 MHz	15.10 MHz
2.35 T	100.00 MHz	25.00 MHz
5.88 T	250.00 MHz	62.90 MHz
7.05 T	300.00 MHz	75.00 MHz

Spin Spin Coupling In ^{13}C NMR Spectroscopy

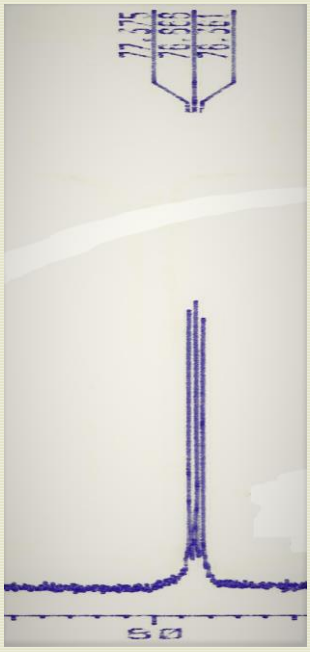
$^{13}C—^{13}C$ is not seen because the probability of two ^{13}C nuclei being in the same molecule is very small.

$^{13}C—^{1}H$ splitting is not seen in normal ^{13}C NMR Spectra because they are measured under broad band decoupling conditions which suppress these splitting.

Click S59

Normally ^{13}C NMR signal is a singlet but if ^{13}C is attached to spin active nuclei like ^{2}H (D), ^{19}F, ^{31}P then coupling are present from these nuclei. $CDCl_3$ solvent gives triplet in NMR spectrum due to ^{2}H coupling to ^{13}C. (^{2}H, I = 1)

Click S60



^{13}C NMR spectrum of $CDCl_3$ 90.00 to 70.00 PPM

Distortion less Enhancement of Polarization Transfer

DEPT is useful technique to differentiate how many ^{1}H attached to ^{13}C atom (C, CH, CH_2 & CH_3).

DEPT 45 gives positive signals from all carbon attached to protons

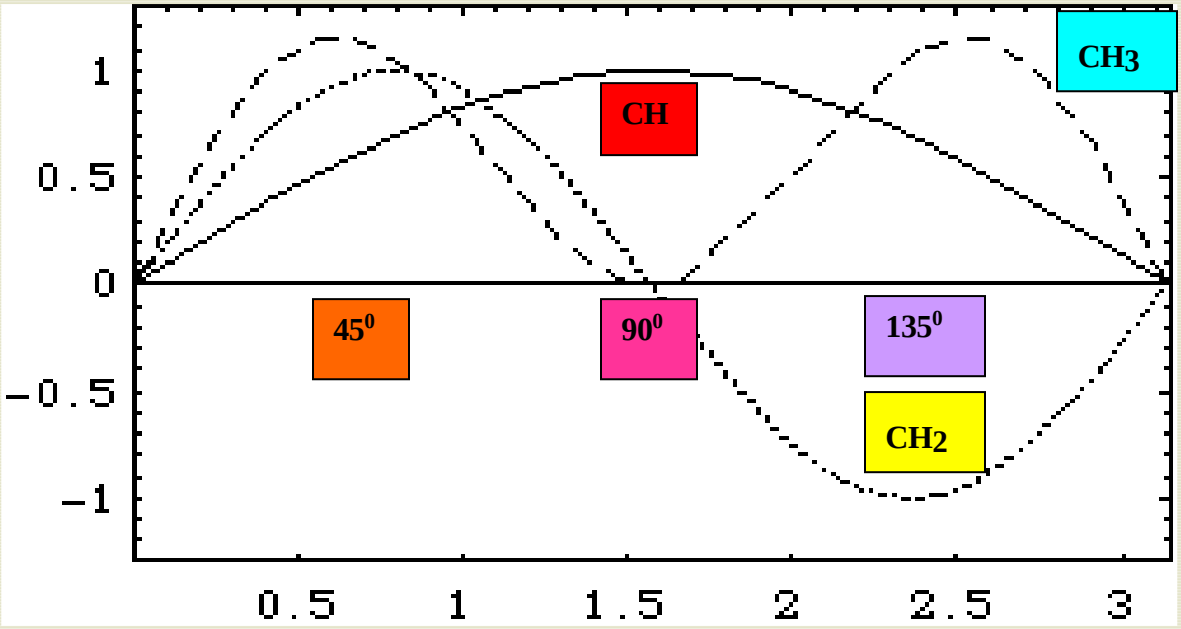
DEPT 90 gives positive signals of CH groups only.

DEPT 135 gives CH_3 & CH as positive signals.

CH_2 as negative signal

C (Quaternary) as null signal

The effect of the flip angle pulse on DEPT sequences



Click S61 & Click S62 & Click S63

Signals from quaternary carbons and other carbons without attached protons are always absent.

The polarization transfer from ^{1}H to ^{13}C has the secondary advantage of increasing the sensitivity over the normal ^{13}C spectrum (which has a modest enhancement from the NOE (Nuclear Overhauser Effect) due to the ^{1}H decoupling).

- Due to the low abundance, we do not usually see ^{13}C-^{13}C coupling.
- Chemical shift range is normally 0 to 220 ppm.
- Chemical shifts are also measured with respect to TetraMethylSilane, $(CH_3)_4Si$ (TMS)
- Similar factors affect the chemical shifts in ^{13}C as seen for ^{1}H-NMR.
- Long relaxation times (excited state to ground state) mean no integrations.
- "Normal" ^{13}C spectra are "broadband, proton decoupled" so the Peaks show as single lines.
- Number of peaks indicates the number of types of Carbons.

Introduction To NMR Spectroscopy Part2 (Link)

Chapter 6 Relaxation Processes T1 & T2

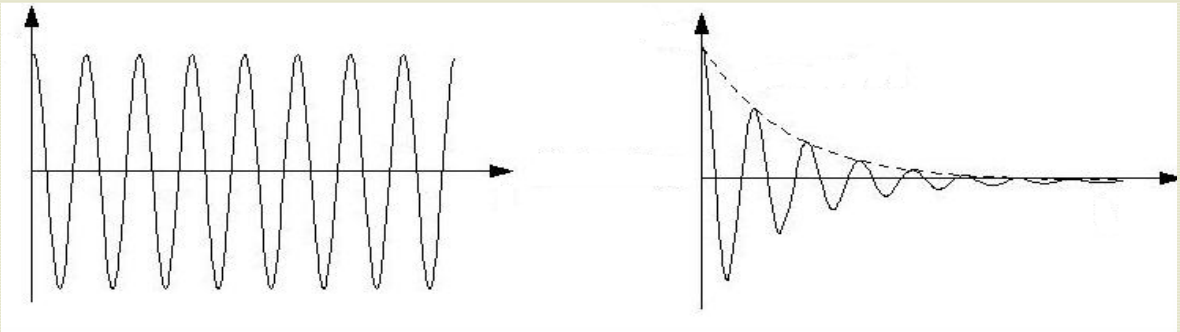
The magnetization does not precess infinitely in the transverse plane but turns back to the equilibrium state. This process is called relaxation. Two different time-constants describe this behaviour:

1. The re-establishment of the equilibrium α / β state distribution (T1)

2. Dephasing of the transverse component (destruction of the coherent state, T2). The T2 constant characterizes the exponential decay of the signal in the receiver coil.

The precessing spins slowly return to the z-axis. Instead of moving circularly in the transverse plane they slowly follow a spiral trajectory until they have reached their initial position aligned with the +/- Z-axis:

- T1 is called Longitudinal Relaxation Time
- T2 is called Transverse Relaxation Time



Signal without relaxation Real signal FID with relaxation

- T1 relaxation is an enthalpic process where the energy is taken from or transferred to

neighbouring spins. The surrounding of the spins is called lattice hence T1 is also known as spin lattice relaxation. In this process the Z – Component of the magnetization is return back to its equilibrium state. T1 values are useful information for NMR experiment what to set up as repetition time between each NMR scan. For ^{1}H T1 values are from 0.5 Seconds to few seconds.

Click S64 & Click S65 & Click S66

- T2 relaxation is an entropic process and does not affect the population of spins hence there is no change in the energy. T2 is also known as spin spin relaxation. In this process the decay of the transverse (X , Y) components of the magnetization is described.

Click S67 & Click S68

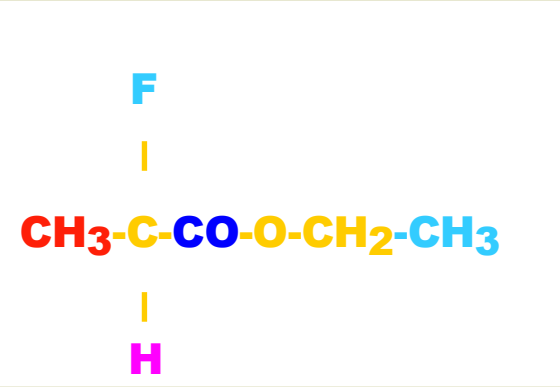
Chapter 7 Interactions of other Nuclei To ^{1}H & ^{13}C

^{19}F Nucleus

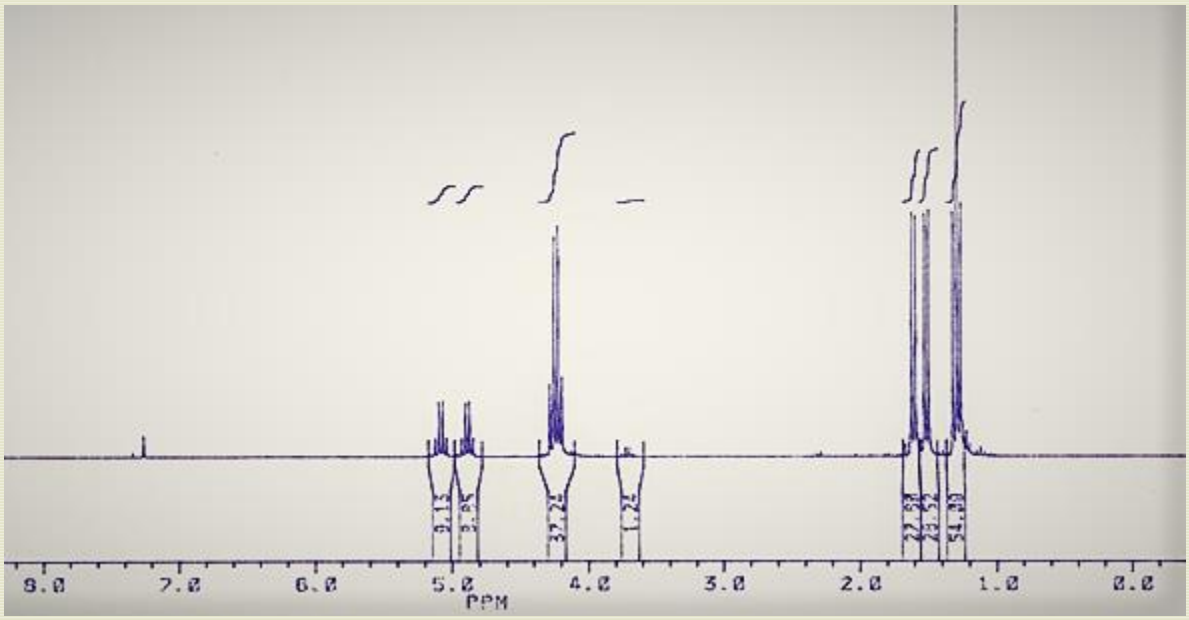
Facts about ^{19}F nucleus

Isotope	^{19}F
Natural abundance	100 %
Spin number	½
Spectral Frequency (relative to ^{1}H =100MHz)	94.094 MHz
Nuclear gyromagnetic ratio γ (10^{7} rad T^{-1} S^{-1})	25.182
Sensitivity (Relative to ^{1}H = 1.00)	0.834

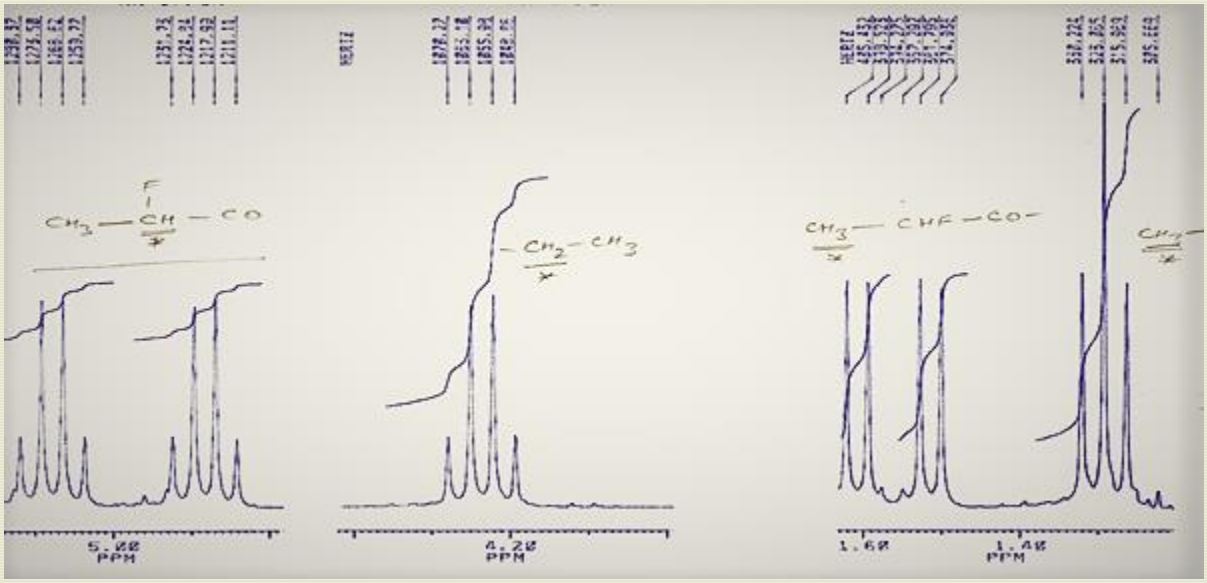
^{1}H NMR Spectrum of Ethyl-2-Fluoropropionate



^{1}H NMR Spectrum 0.0 to 10.00 PPM range



Expansion of various parts of the spectrum at 5.00, 4.00 & 1.5 PPM



CH **CH_2** **CH_3** **CH_3**

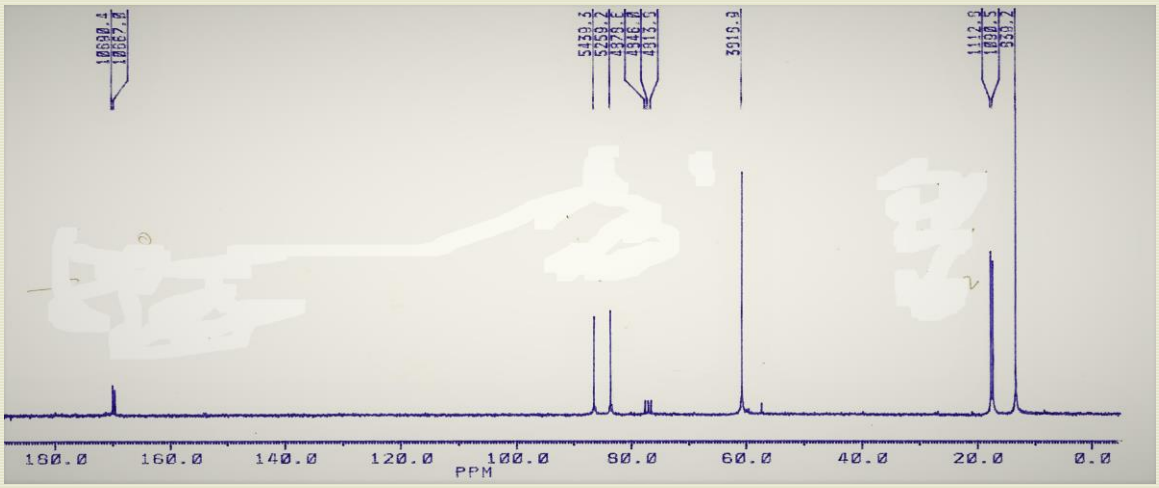
Doublet of Quartet Quartet Doublet of Doublet Triplet

Click S69

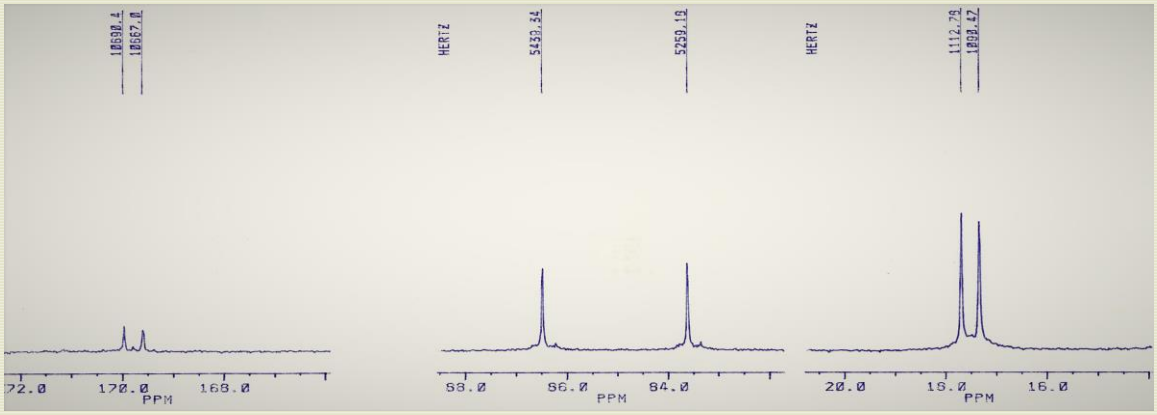
^{19}F to ^{1}H Coupling constants are ^{2}J = 48.66 Hz (**CHF**) and ^{3}J = 22.31 Hz (**CH_3—CHF**)

^{13}C NMR Spectrum of Ethyl-2-Fluoropropionate

CH_3—CHF—CO—O—CH_2—CH_3



Expansion of various parts of the spectrum at 170, 85 & 18 PPM

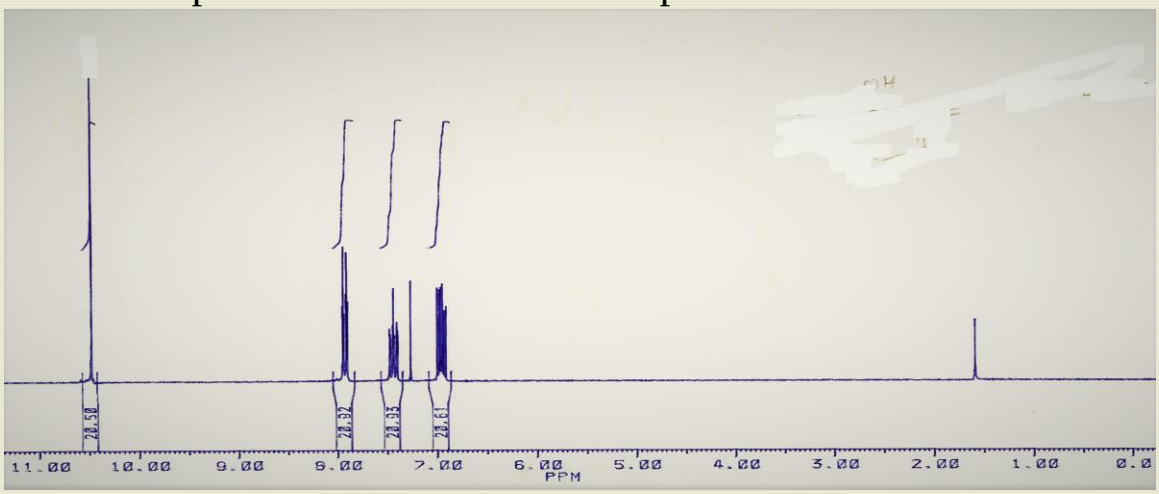


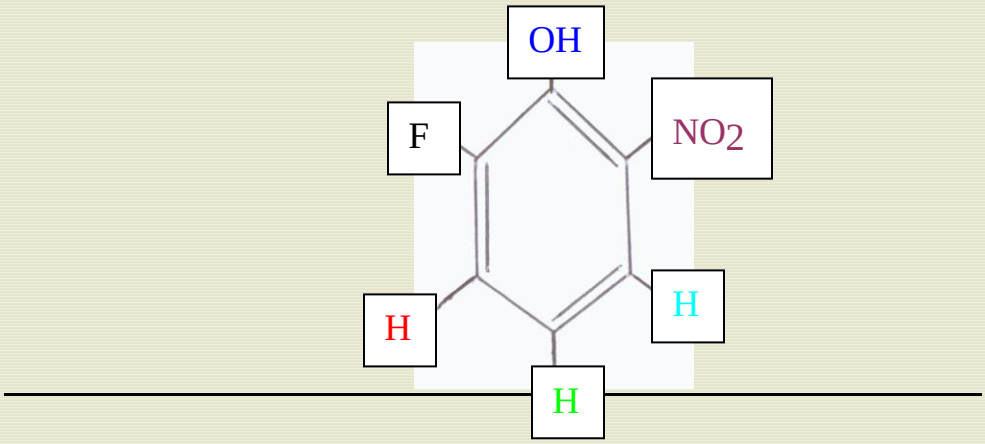
CO **CHF** **CH_3**

Click S70 & Click S71

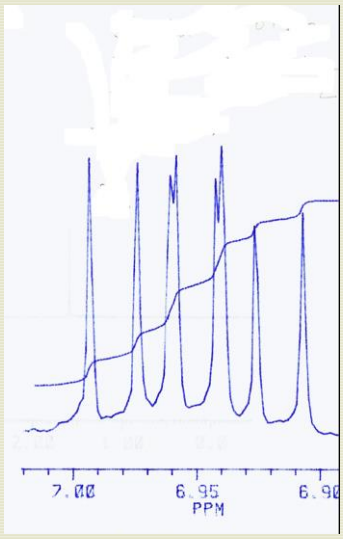
^{19}F to ^{13}C Coupling constants are ^{1}J = 180.10 Hz (**CHF**), ^{2}J = 23.40 Hz (**CHF—CO**) and 22.31 Hz (**CH_3—CHF**).

^{1}H NMR Spectrum of 2-Fluoro-6-Nitrophenol

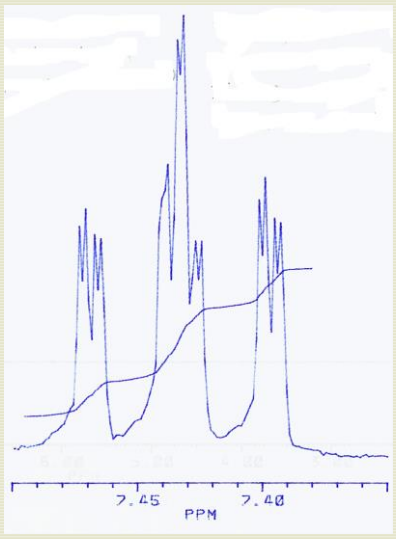




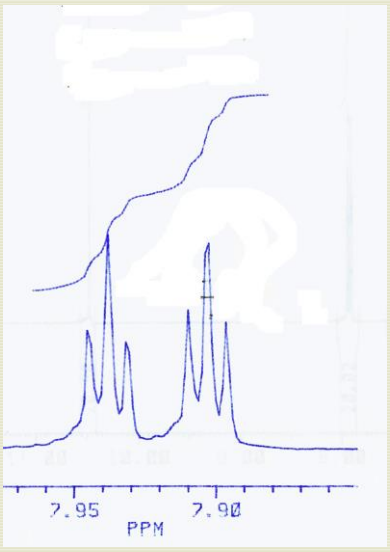
Expansion of Aromatic region 7.00 to 8.00 PPM



3 H



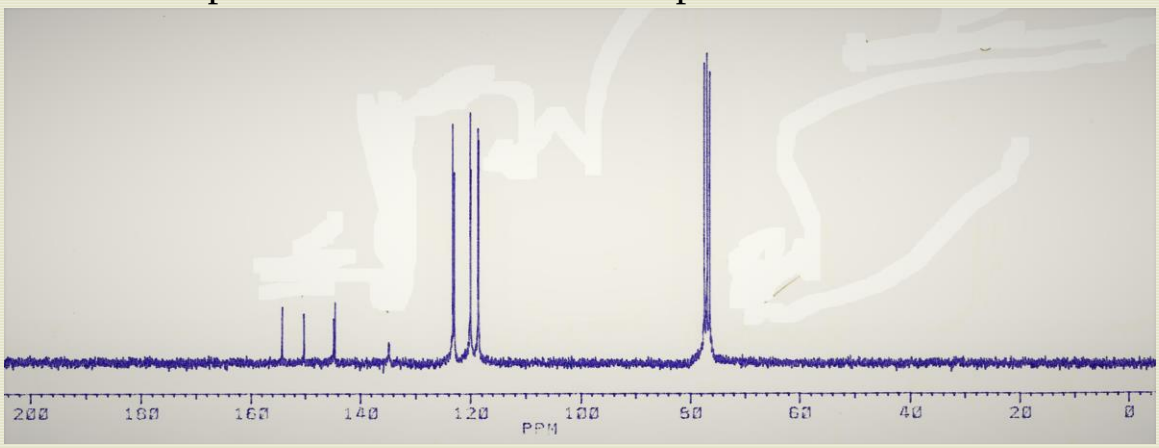
4 H



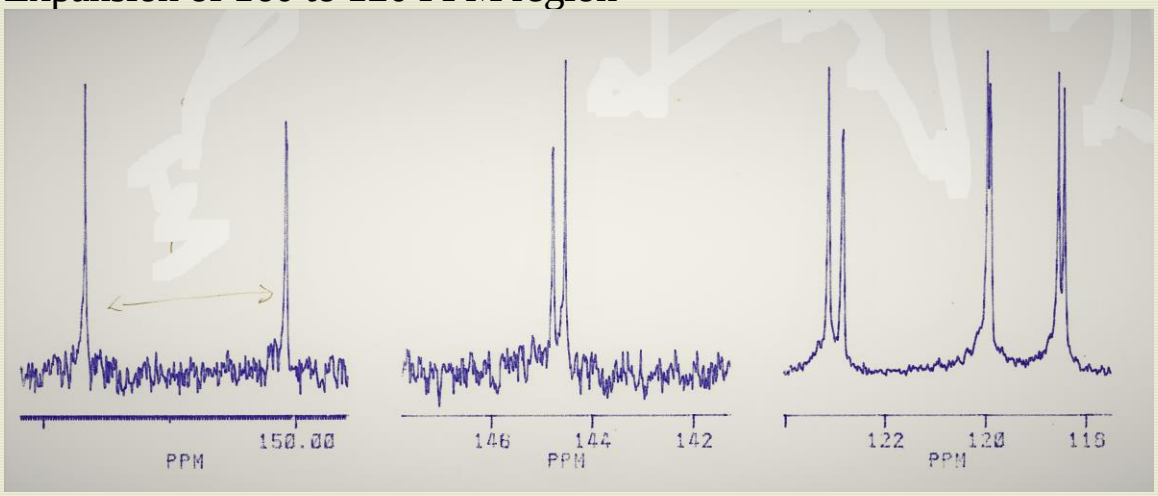
5 H

Click S72

^{13}C NMR Spectrum of 2-Fluoro-6-Nitrophenol



Expansion of 160 to 120 PPM region



C2 C1 C3 C5 C4

All carbon signals are doublet and coupling constant as below:

C2—F	= 250.60 Hz	^{1}J
C1—C2—F	= 15.15 Hz	^{2}J
C3—C2—F	= 15.15 Hz	^{2}J
C4—C3—C2—F	= 7.22 Hz	^{3}J
C5—C4—C3—C2—F	= 3.65 Hz	^{4}J

Click S73 & Click S74

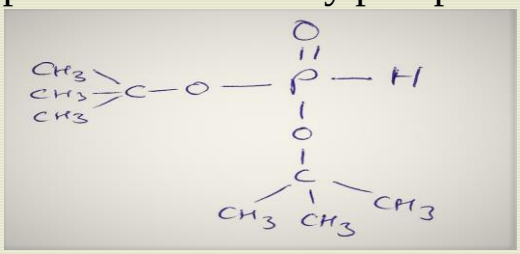
^{31}P NMR Interactions to ^{1}H

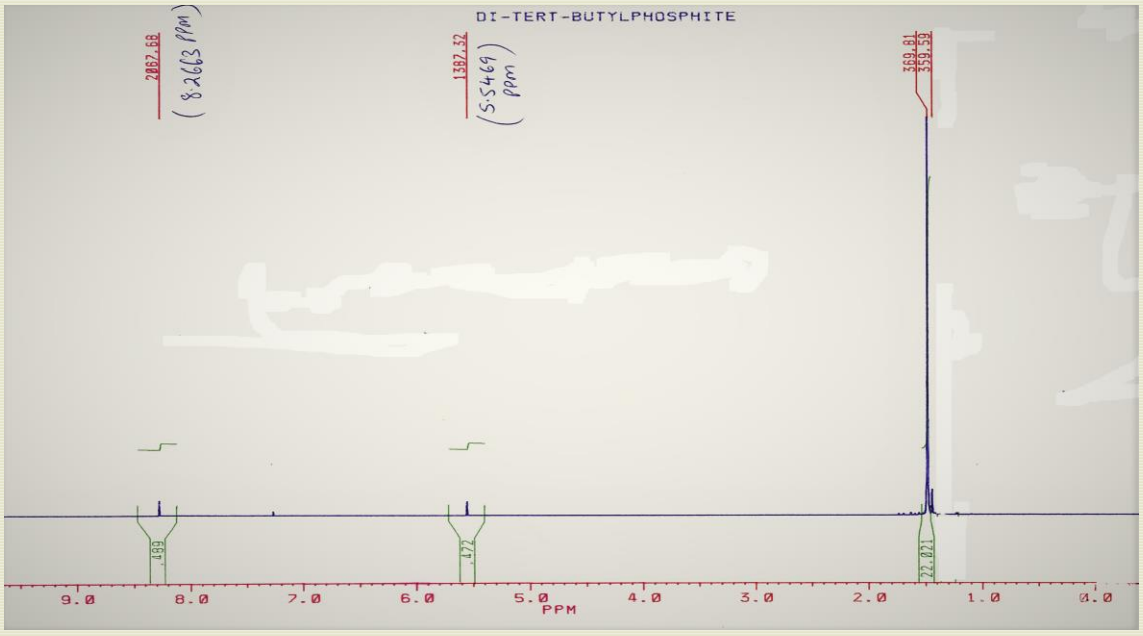
^{31}P Nucleus

Facts about ^{31}P nucleus

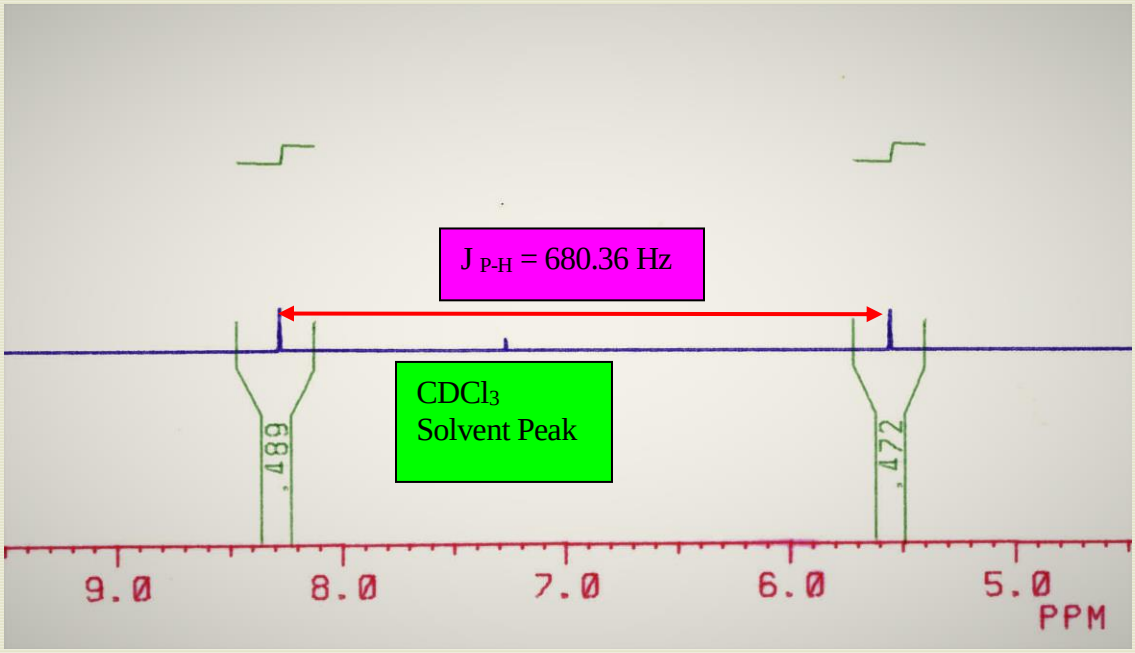
Isotope	^{31}P
Natural abundance	100 %
Spin number	½
Spectral Frequency (relative to ^{1}H =100MHz)	40.048 MHz
Nuclear gyromagnetic ratio γ (10^{7} rad T^{-1} S^{-1})	10.839
Sensitivity (Relative to ^{1}H = 1.00)	0.067

^{1}H NMR Spectrum of Di-t-butylphosphite





Expansion of 9.50 to 4.50 PPM Region



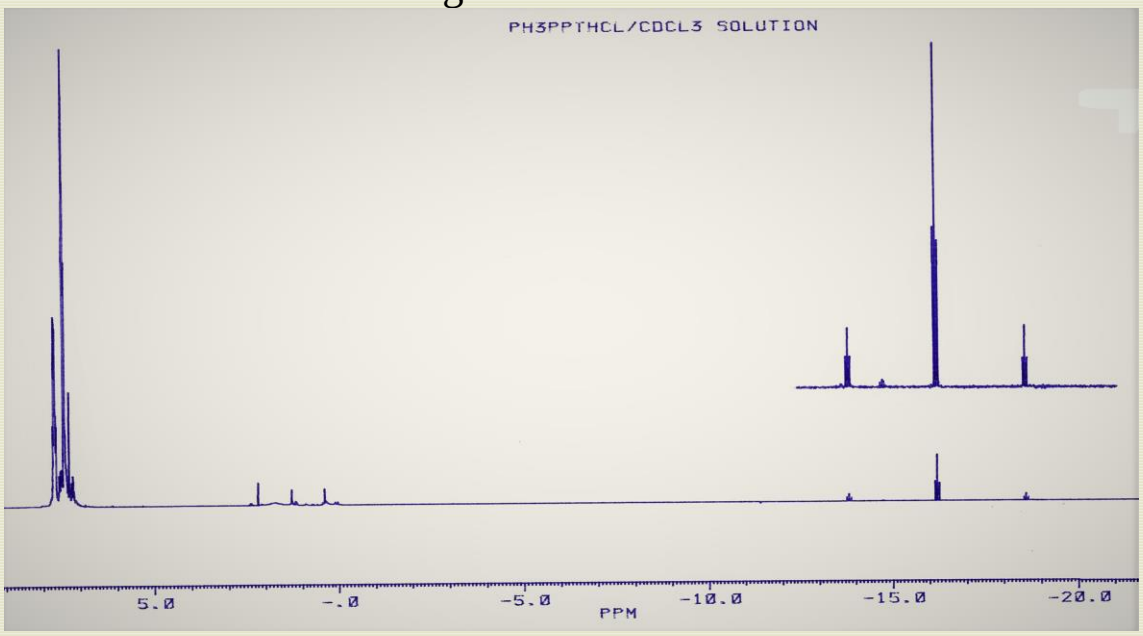
Doublet @ 6.91 PPM. P—H & Singlet@ 1.48 PPM t-Butyl
Coupling Constant $^{1}J\ ^{31}P—^{1}H$ = 680.36 Hz

^{31}P & ^{195}Pt Nuclei NMR Interactions to ^{1}H

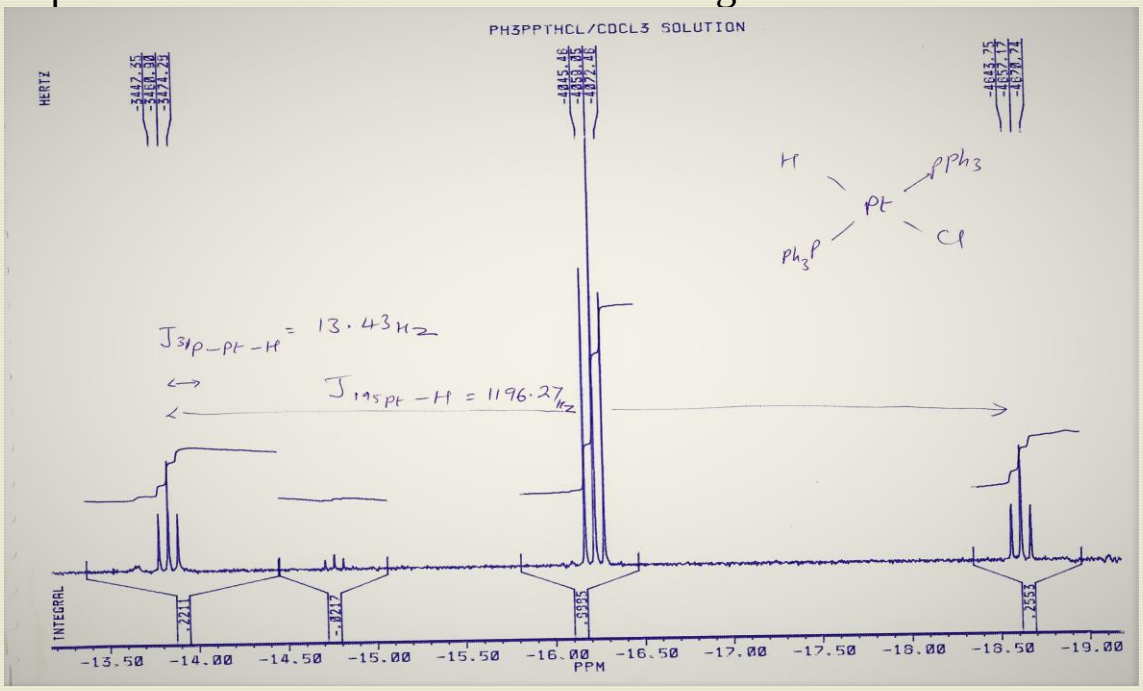
Facts about ^{195}Pt nucleus

Isotope	^{195}Pt
Natural abundance	33.8 %
Spin number	½
Spectral Frequency (relative to ^{1}H =100MHz)	21.414 MHz
Nuclear gyromagnetic ratio γ (10^{7} rad T^{-1} S^{-1})	5.8385
Sensitivity (Relative to ^{1}H = 1.00)	0.0035

^{1}H NMR Spectrum of BistriphenylphosphinePlatinumHydrochloride
10.00 To – 22.00 PPM range



Expansion of – 13.00 To – 19.00 PPM Range



Analysis of coupling constant of Pt—H signal.

Interaction to ^{195}Pt

Doublet from ^{195}Pt—H & 1/3 intensity (further splitting to triplet by two equivalents ^{31}P).

^{195}Pt—H Coupling Constant = 1196.27 Hz

Interaction to ^{31}P

Doublet of triplet from two equivalents ^{31}P & 1/3 intensity

Triplet from ^{31}P—H (two equivalents ^{31}P) & 3 times Intensity

^{31}P—H Coupling Constant = 13.43 Hz

Intensity of the signal will always be proportional to isotopic ratio.

^{31}P isotopic abundance = 100 %

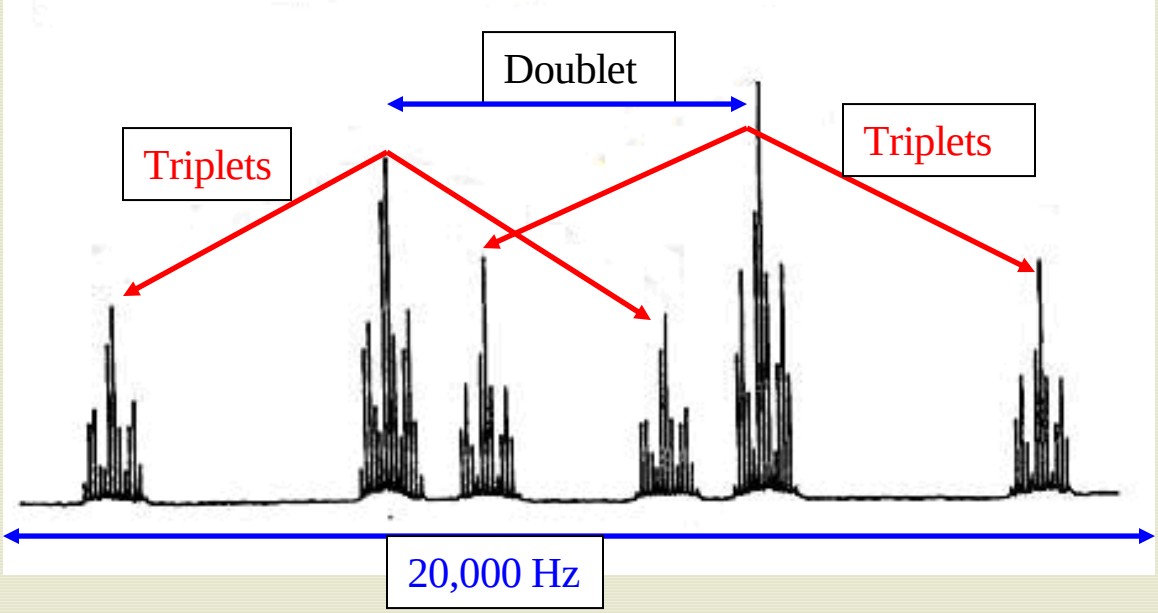
^{195}Pt isotopic abundance = 33.80 % (about 1/3 of ^{31}P)

The center of both isotopic peaks is the same hence there is no isotopic shift present in this case. (- 16.23 PPM or 4059.05 Hz).

^{1}H, ^{15}N (Labelled), & ^{19}F Nuclei NMR Interactions to ^{31}P

For all above nuclei I = 1/2 & Isotopic abundance = 100 %

^{31}P NMR Spectrum of $PF_2H(NH_2)_2$



^{31}P NMR Spectrum of $PF_2H(NH_2)_2$

It looks very complex NMR Spectrum but on analysis with little care and understanding of the theory principles would make it a simple example of four different interactions to ^{31}P Nucleus.

$PF_2H(NH_2)_2$

^{1}H (one) Interactions to ^{31}P Nucleus gives doublet (2 lines)

^{19}F (two) Interaction to ^{31}P Nucleus gives doublet of triplets (6 lines)

^{15}N (two labelled) Interaction to ^{31}P Nucleus gives,
Doublet of triplets of triplets (2x3x3= 18 lines)

^{1}H (four) Interaction to ^{31}P Nucleus gives,
Doublet of triplets of triplets of quintets (2x3x3x5= 90lines)

Analysis of Interactions To ^{31}P Nucleus in order of coupling constant

J_{P-H}	Doublet
J_{P-F}	Doublet of Triplets
J_{P-N}	Doublet of Triplets of Triplets
J_{P-H}	Doublet of Triplets of Triplets of Quintets

There are no different heights of triplets because the isotopic ratio of all nuclei is equal to 100 %.

Click S100

^{10}B & ^{11}B Nuclei NMR Interactions to ^{1}H

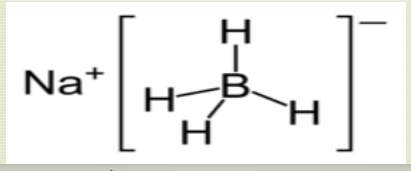
Facts about Boron ^{10}B & ^{11}B nuclei

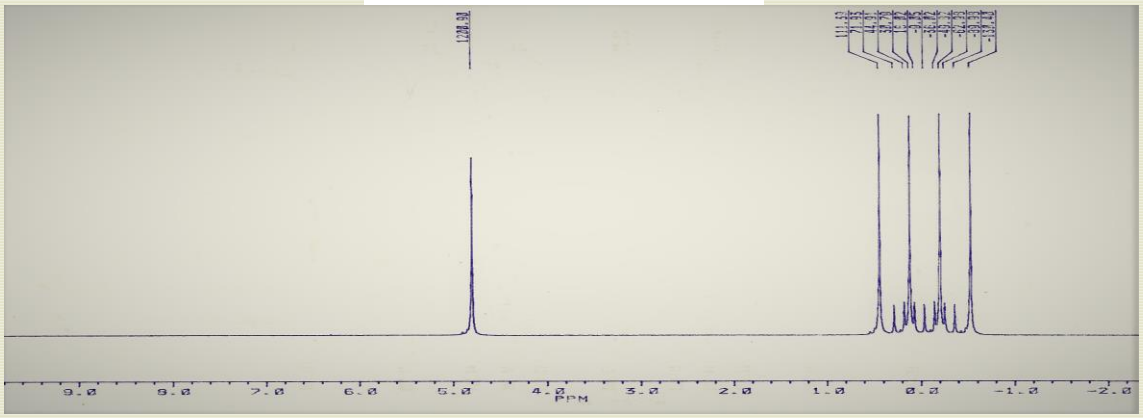
Isotope	^{10}B	^{11}B
Natural abundance	19.90	80.10 %
Spin number	3	3/2
Spectral Frequency (relative to ^{1}H =100MHz)	10.74	32.08 MHz
Nuclear gyromagnetic ratio γ (10^{7} rad T^{-1} S^{-1})	2.875	8.585
Sensitivity (Relative to ^{1}H = 1.00)	0.004	0.132

^{1}H NMR Spectrum of Sodium Borohydride $NaBH_4$ in D_2O

In solution the ratio of molecules from $Na^{11}BH_4$ 80.10 %

and $Na^{10}BH_4$ 19.90 %





Why is there Quartet and Septet in the ^{1}H NMR Spectrum?

No. of peaks = 2nI + 1 where n = spin active nucleus, I = spin No.

For ^{10}B Interaction to ^{1}H

n = 1 (^{11}B) I = 3

No. of peaks = 2 x 1 x 3 + 1 = 6 +1 = 7 (Septet of equal intensity)

For ^{11}B Interaction to ^{1}H

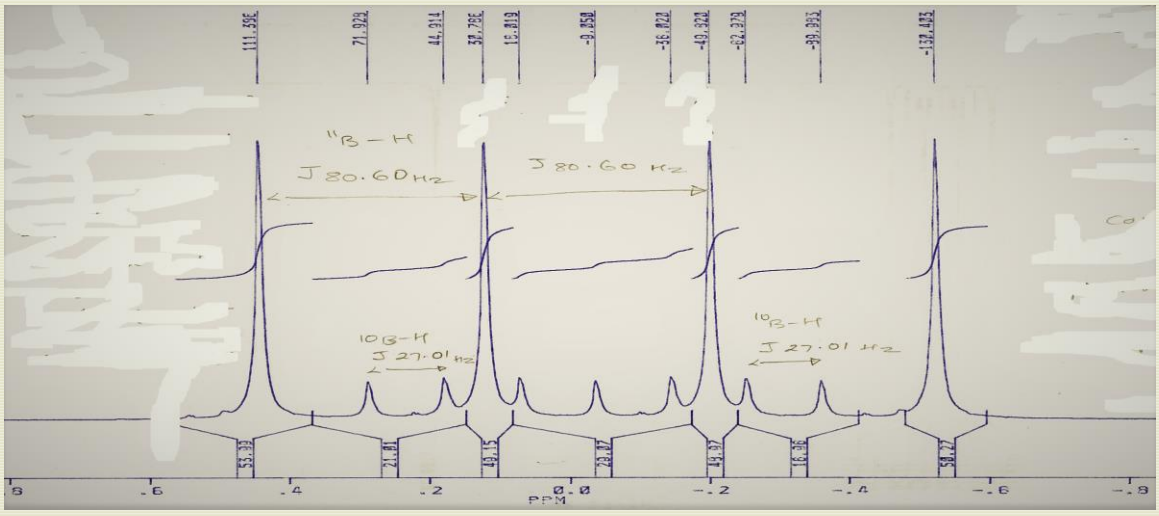
n = 1 (^{10}B) I = 3/2

No. of peaks = 2 x 1 x 3/2 + 1 = 3 +1 = 4 (Quartet of equal intensity)

Why is the Quartet 4 time taller than Septet?

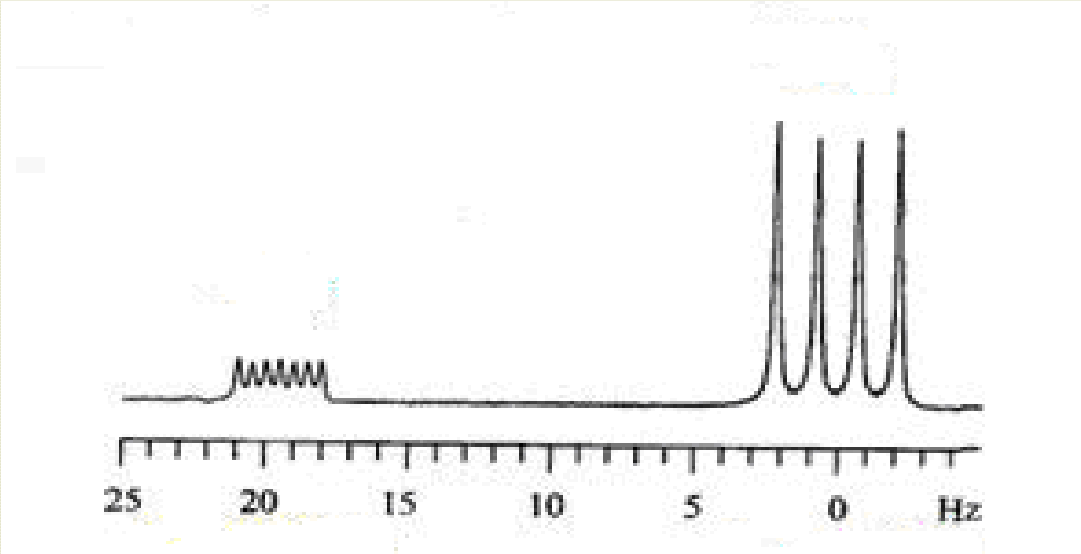
The isotopic ratio of ^{11}B To ^{10}B is 80.10 / 19.90 = 4 : 1

Hence the signal from ^{11}B is 4 times greater in intensity.



Click S75 & Click S76 & Click S77

^{19}F NMR Spectrum of Sodium tetrafluoroborate $NaBF_4$



Septet $J_{10B—F4}$ = 0.5 Hz and Quartet $J_{11B—F4}$ = 1.5 Hz

Click S78

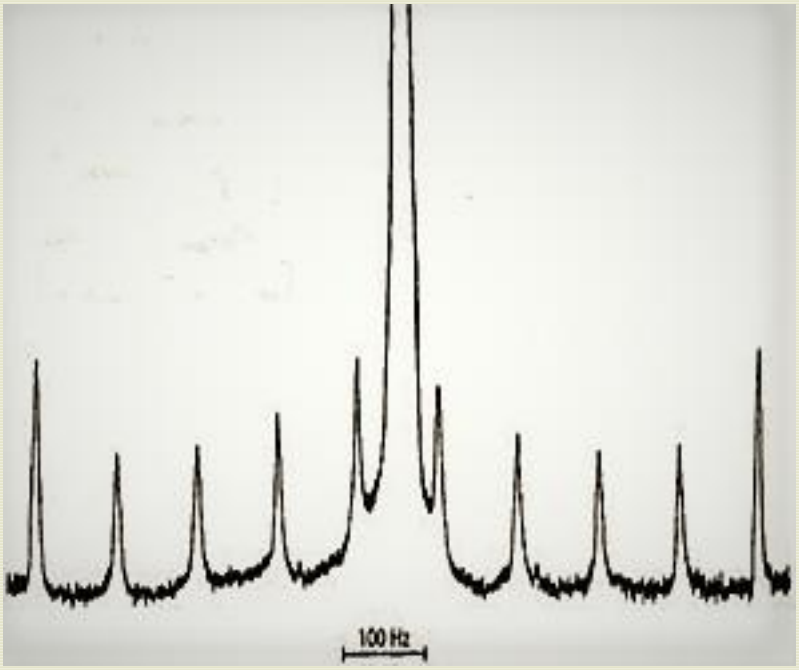
^{73}Ge nucleus NMR Interactions to ^{1}H

^{73}Ge nucleus

Facts about ^{73}Ge nucleus

Isotope	^{73}Ge
Natural abundance	7.73 %
Spin number	9/2
Spectral Frequency (relative to ^{1}H =100MHz)	3.488 MHz
Nuclear gyromagnetic ratio γ (10^7 rad T^{-1} S^{-1})	0.9360
Sensitivity (Relative to ^{1}H = 1.00)	0.0001

^{1}H NMR Spectrum of Germanium hydride GeH_4



No. of peaks = 2 n I + 1 n = 1 (^{73}Ge) I = 9/2

= 2 x 1 x 9/2 + 1

= 9 + 1

= 10

In the above spectrum there are 10 lines (peaks) are evenly spaced due to the interaction of 7.73 % ^{73}Ge isotope to ^{1}H. The intense central line is from other isotopic hydrides ($^{70}GeH_4$, $^{72}GeH_4$, $^{74}GeH_4$ & $^{76}GeH_4$). The other isotopes of Germanium are not NMR active as the spin no. I = 0 hence singlet.

The coupling constant $^{1}J_{^{73}Ge—H}$ = 100 Hz

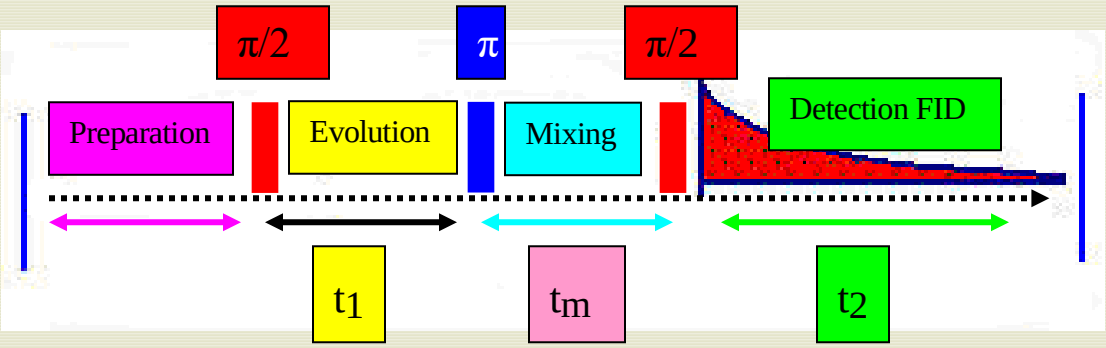
Chapter 8 Two-Dimensional NMR Spectroscopy

The 2-dimensional NMR experiment is characterized by the introduction of a second frequency axis, which allows to *correlate* frequencies. The two frequency domains are called the *direct* (F2) and the *indirect* (F1) frequency domains. Frequencies of signals in the direct dimension have been directly detected in the receiver coil; those of the indirect dimension were derived from the second Fourier transform of the amplitude modulated signals.

Homonuclear 2D spectra are usually symmetric about the diagonal. The diagonal contains the one-dimensional spectrum. Off-diagonal peaks at the frequency F2=ΩA, F1=ΩB are called *cross-peaks*, and they indicate the spins with frequencies ΩA and ΩB are correlated

Typical 2D NMR Pulse Sequence

Each pulse-sequence for a 2D experiment contains the basic elements of various time periods and RF pulses (45, 90, 180, & 270).



Click S83

The Preparation Time:

The spin system under the study is firstly prepared by application of 90^0 pulse ($\pi/2$) which may cause decoupling or a transverse magnetization. This allows the excited nuclei to get back to their equilibrium state between two successively executed pulse sequences.

The Evolution Time:

The spin system during the evolution time t_1 is evolving under the effect of different factors. Each coherence evolves at its own characteristic frequency as a function of the chemical shift (δ) and of the scalar coupling (J) of the respective nucleus.
The evolution time is characterized by a variable time delay. In 2-D NMR experiment this time delay is increased in equal increments. The coherences present during this period will be revealed during the acquisition period.

The Mixing Time:

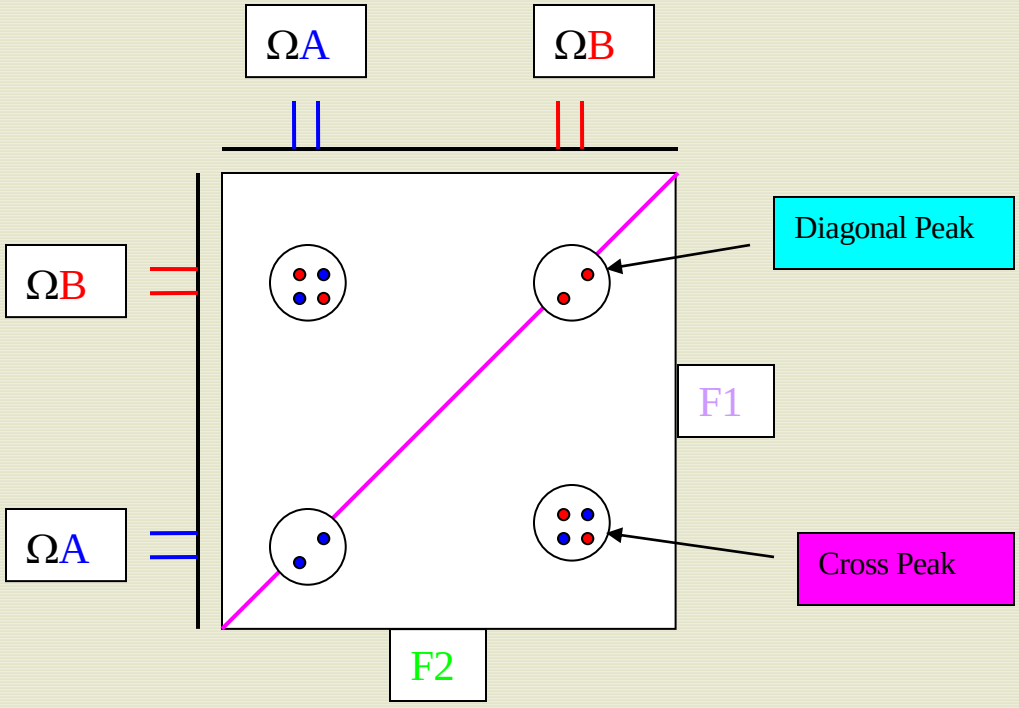
The coherence transfer from spin A to spin B is achieved during the mixing time. The mixing time is characterized by RF pulse or pulses if the coherence is being transferred via chemical bonds. Similarly, the mixing time can be of fixed period for dipolar relaxation to occur and to achieve the coherence transfer via space.

The Detection Time:

The acquisition of the modulated signal takes place during the detection period t_2.

For the example of the F1=ΩA, F2=ΩB cross peak, the spin A is excited in the preparation period, then chemical shift labelled during the evolution period. Subsequently, magnetization is transferred from spin A to spin B in the mixing period. Finally, magnetization is detected on the spin B.

Appearance of homonuclear COSY 2D NMR Spectrum.



The most common and widely useful techniques are: -

1. COSY: **Correlation Spectroscopy**
2. HETCOR: Heteronuclear Correlated Spectroscopy
3. 2D-Inadequate: Nuclear connectivity

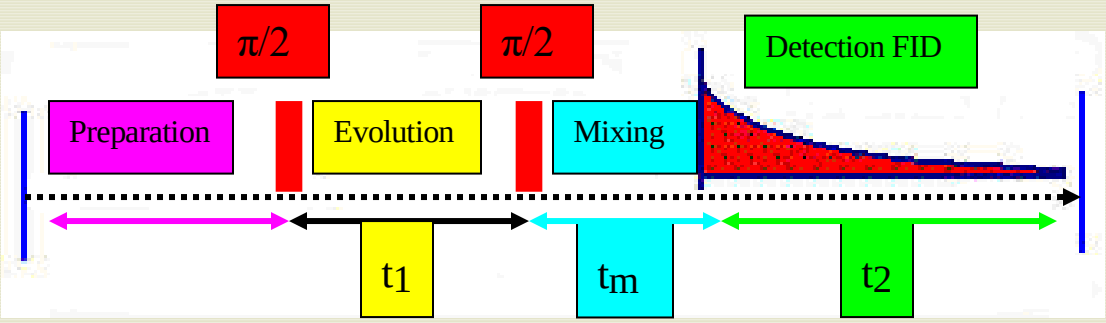
Many of the two-dimensional techniques are easy to set up and use on modern NMR Spectrometers and they provide a wealth of information that is not available using one dimensional technique. The coherence transfer can occur as follow:

1. Through chemical bond (scalar coupling)
2. Through space (dipolar coupling)
3. Through physical or chemical exchange process.

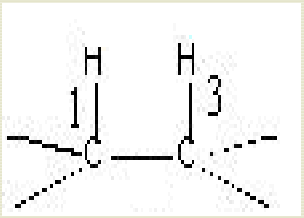
COSY: **Correlation Spectroscopy**

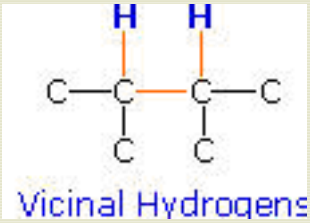
Correlation experiments reveal connections between the atoms in a molecule. This is deduced from observations of the coupling between the nuclear spins. Spin coupling is typically observed between nuclei that are separated by one to three bonds, and most correlation experiments are designed to emphasize these short-range couplings. Experiments designed to emphasize long-range coupling can also be useful. By observing several sets of overlapping correlations, it is possible to establish the chemical structure with great certainty. In a one-dimensional spectrum, spin coupling is observed as multiplet structure in the peaks. In a two-dimensional spectrum, spin coupling causes the appearance of cross peaks, or peaks off the diagonal.

COSY Pulse Sequence



Click S83





F1 Dimension gives info about δ_H and J_{HH}

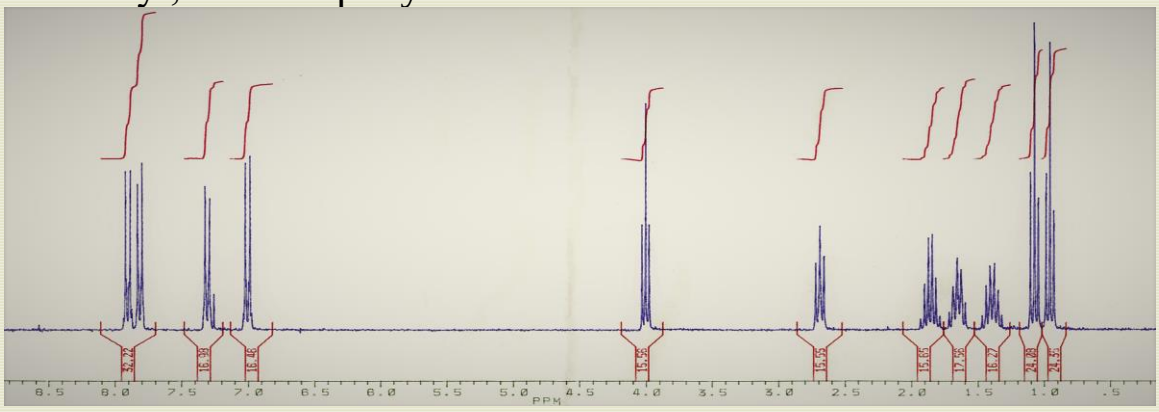
F2 Dimension gives info about δ_H and J_{HH}

Click S79 & Click 80

One dimension ^1H NMR Spectrum of

$CH_3(CH_2)_3$-C_6H_4-N=N-C_6H_4-O-$(CH_2)_2CH_3$

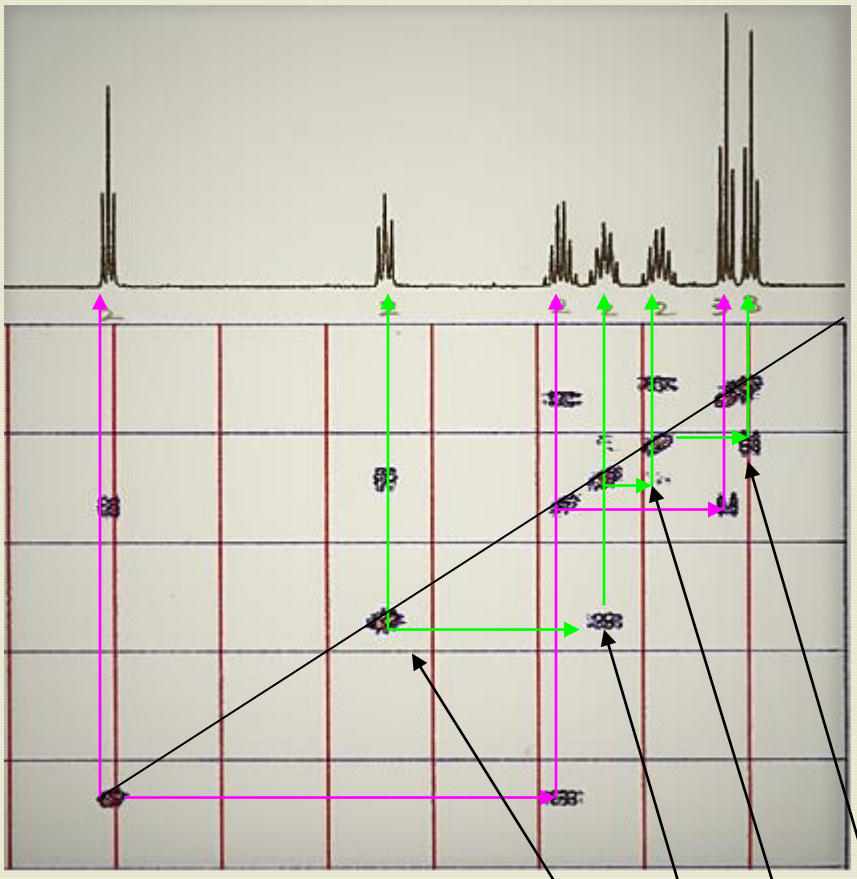
4-n-Butyl, 4'-n-Propoxy Diazobenzene



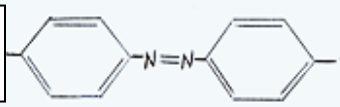
2D COSY ^{1}H NMR Spectrum of

$CH_3(CH_2)_3$-C_6H_4-N=N-C_6H_4-O-$(CH_2)_2CH_3$

4-n-Butyl, 4'-n-Propoxy Diazobenzene



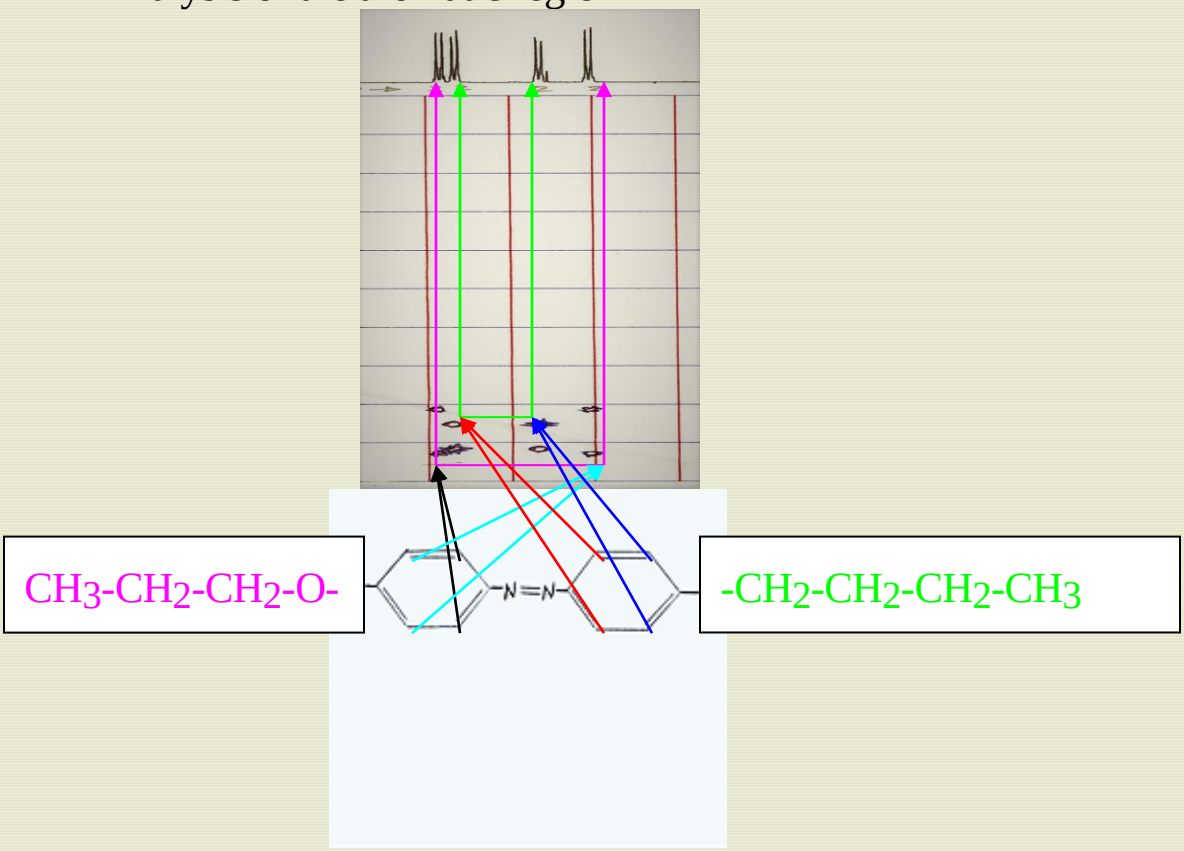
CH_3-CH_2-CH_2-O-



-CH_2-CH_2-CH_2-CH_3

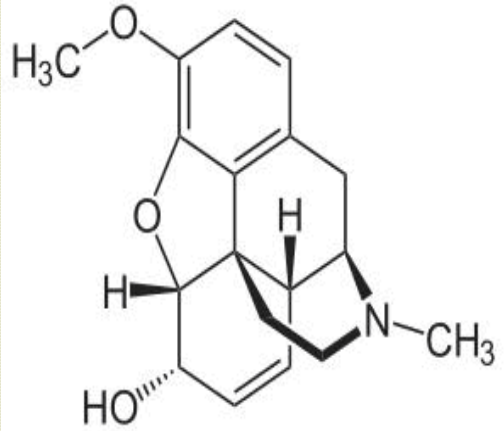
The complexity of the n-butyl and n-propoxy chains can easily be sorted out that which peak is coupled to which one as indicated by green and magenta colour arrows.

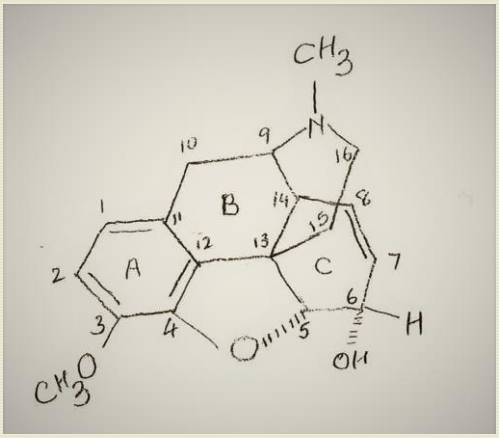
Analysis of the aromatic region

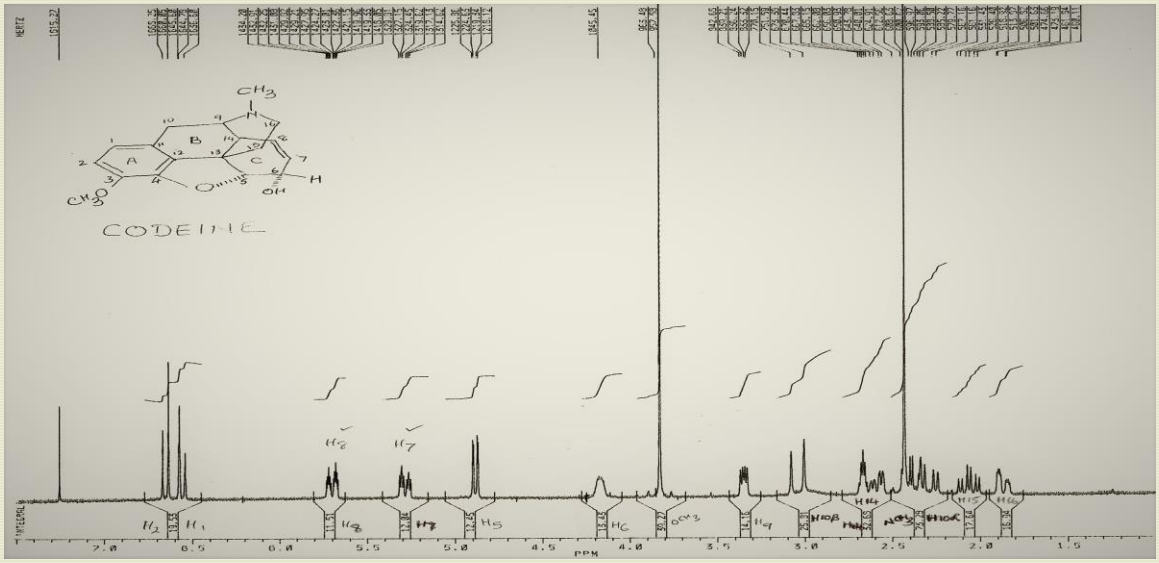


One dimension ^{1}H NMR Spectrum of Codeine $C_{18}H_{21}NO_3$

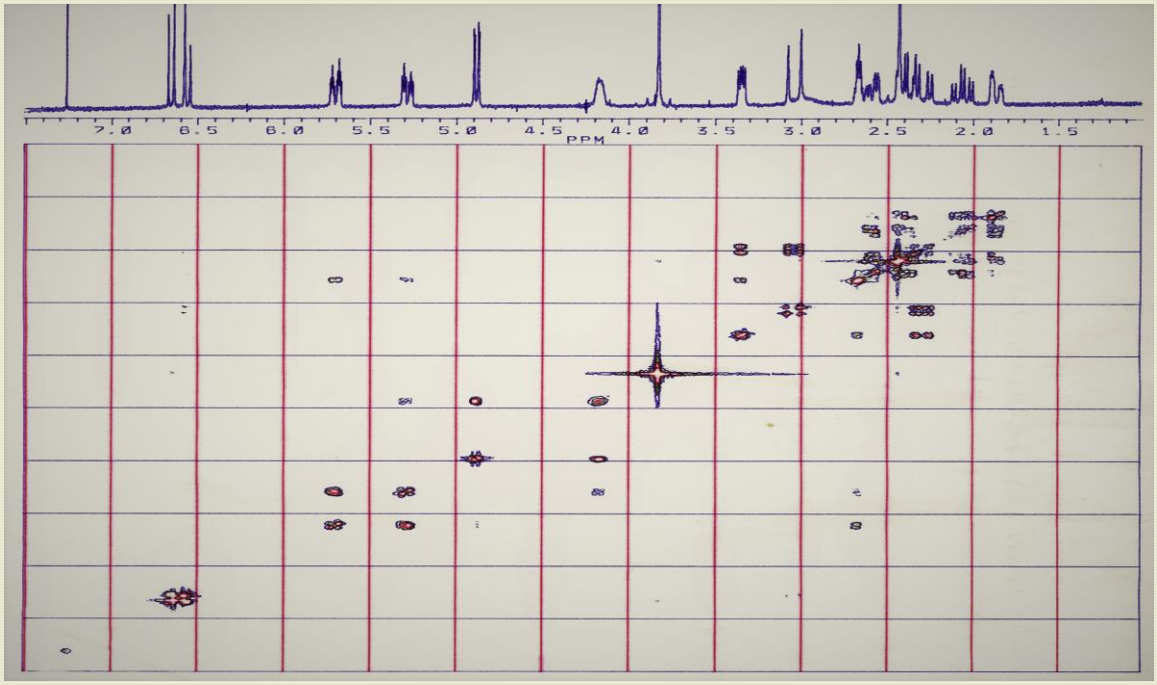
(5α,6α)-7,8-didehydro-4,5-epoxy-3-methoxy-17-methylmorphinan-6-ol







2D ^{1}H COSY NMR of codeine $C_{18}H_{21}NO_3$ in $CDCl_3$



2D COSY NMR of codeine in $CDCl_3$ is very complex but made it easier to identify the coupled hydrogen.

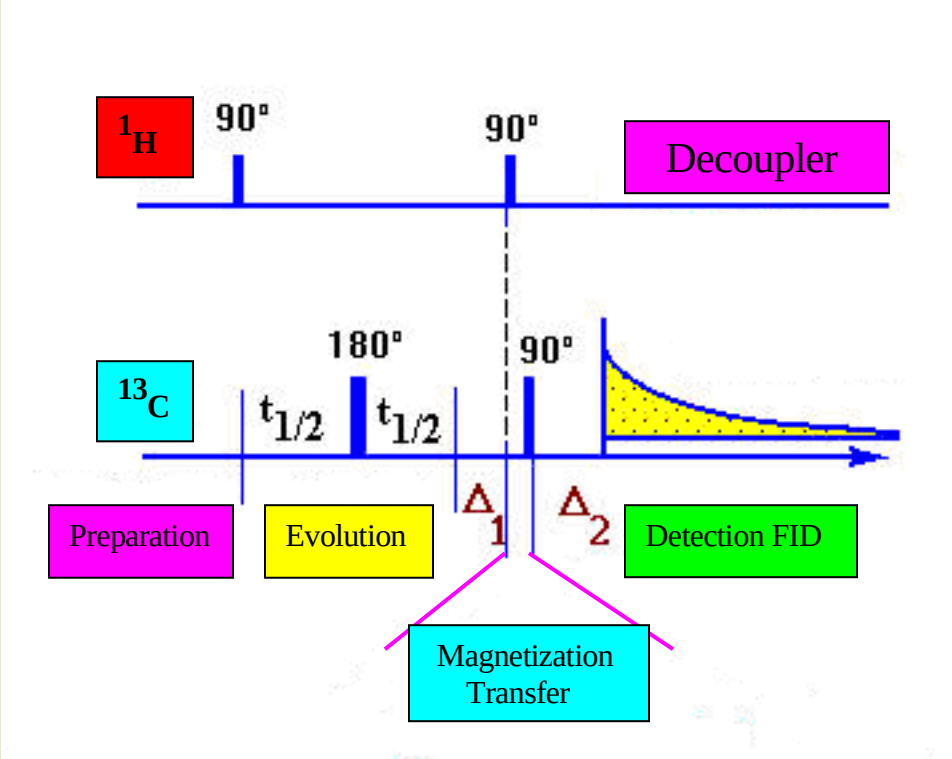
Click S81 & Click S82

HETCOR: Heteronuclear Correlated Spectroscopy

The heteronuclear correlation of chemical shifts by scalar coupling derives from the existence of the heteronuclear scalar coupling allowing the magnetization transfer from the more sensitive nucleus (^{1}H) to the less sensitive nucleus (^{13}C, or ^{15}N, or ^{31}P).

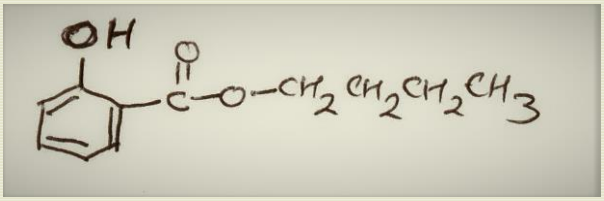
Click S83

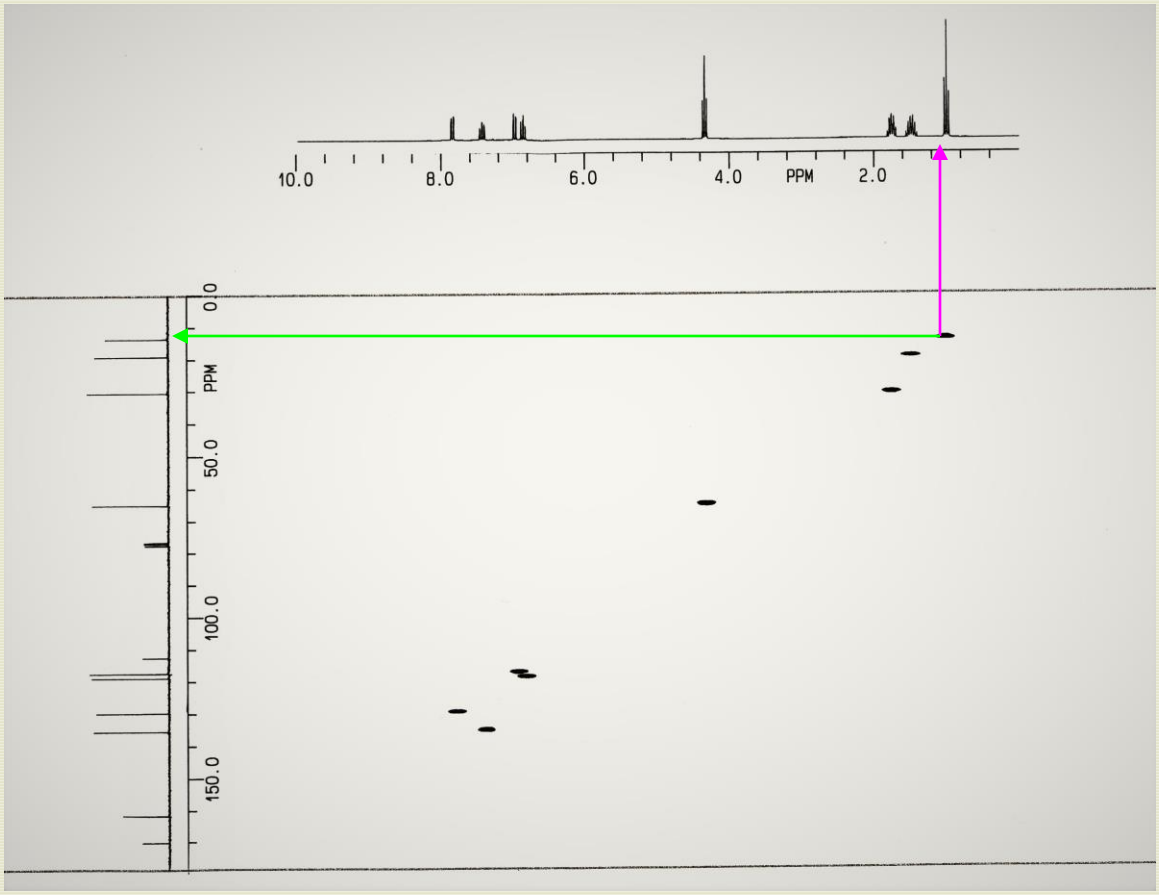
The XHCORR pulse Sequence



This sequence allows to correlate the signals of ^{1}H nucleus to that of ^{13}C nucleus to which ^{1}H is bound.

2D XHCORR NMR Spectrum of n-Butyl Salicylate



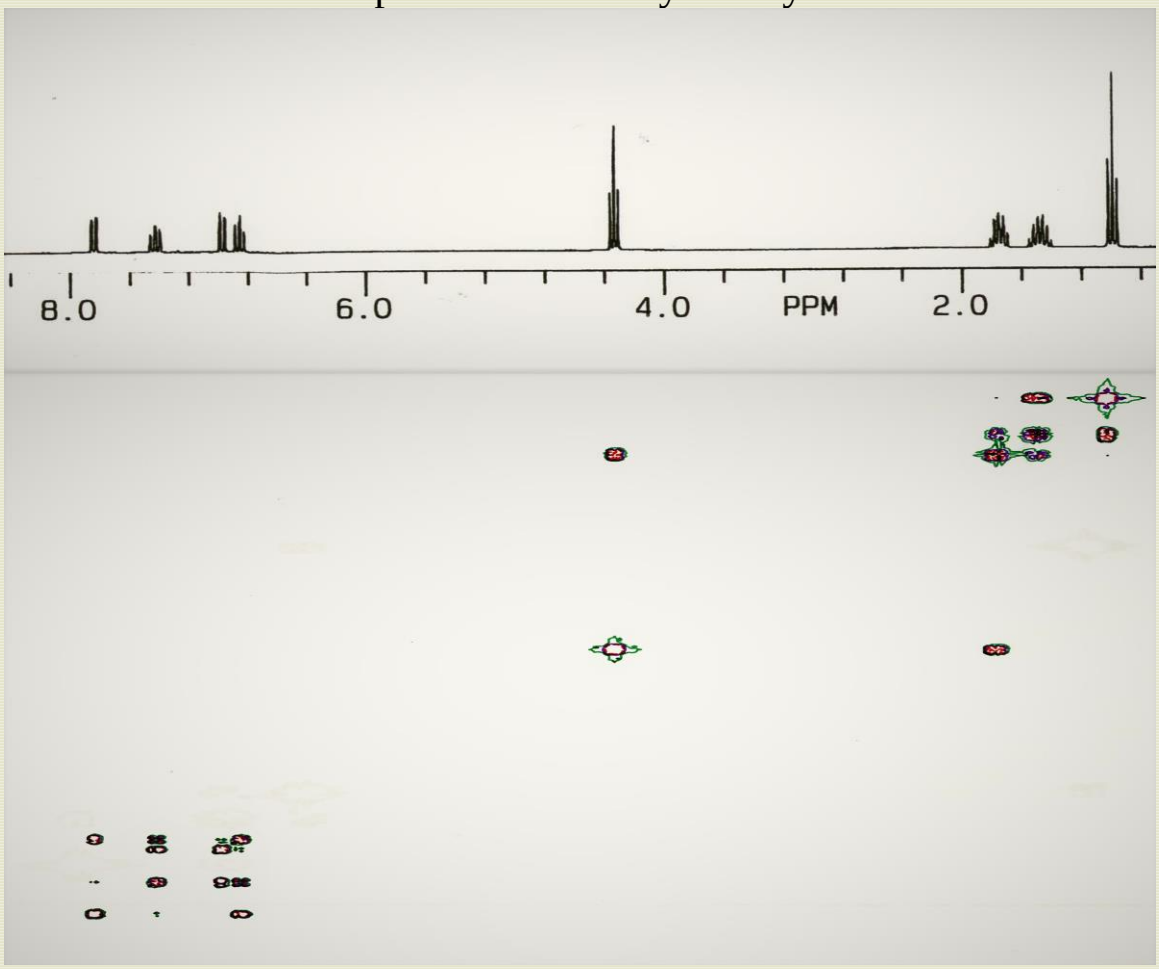


On X-axis ^{1}H NMR and on Y-axis ^{13}C NMR Spectrum. To correlate the peak, you have to just trace the X-axis contour to Y-axis.

CH_3 group peaks for ^{1}H (Pink Arrow) and ^{13}C (Green Arrow) contour is traced in the above example. There are no diagonal contours and no contour for quaternary ^{13}C.

Click S84 & Click S85

2D HHCOSY NMR Spectrum of n-Butyl Salicylate



Click S86

INADEQUATE: Incredible Natural Abundance Double Quantum Transfer Experiment

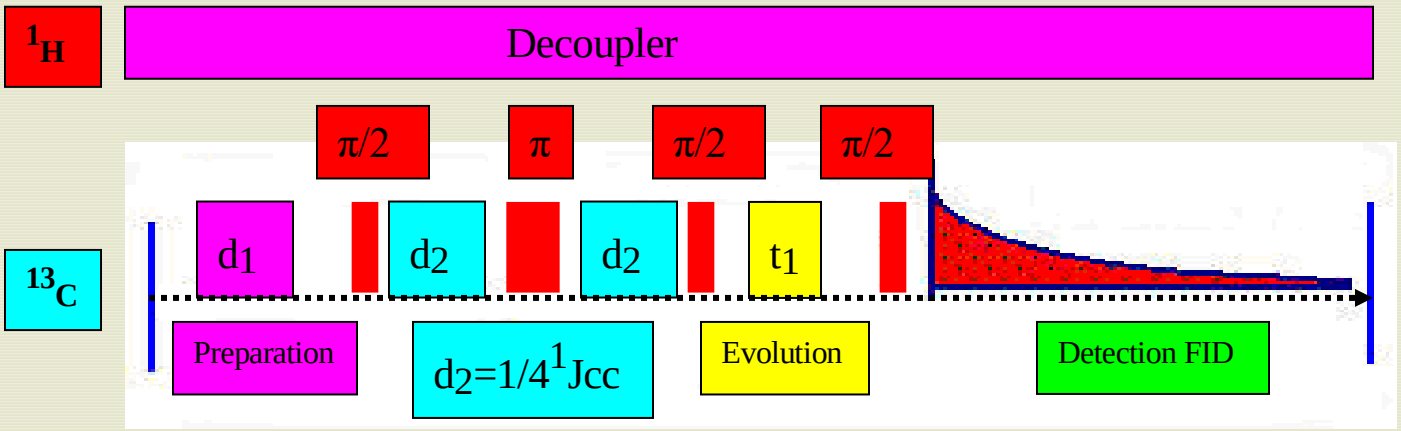
2D-Inadequate: Nuclear connectivity of low abundance nuclei (^{13}C, ^{15}N, ^{183}W)

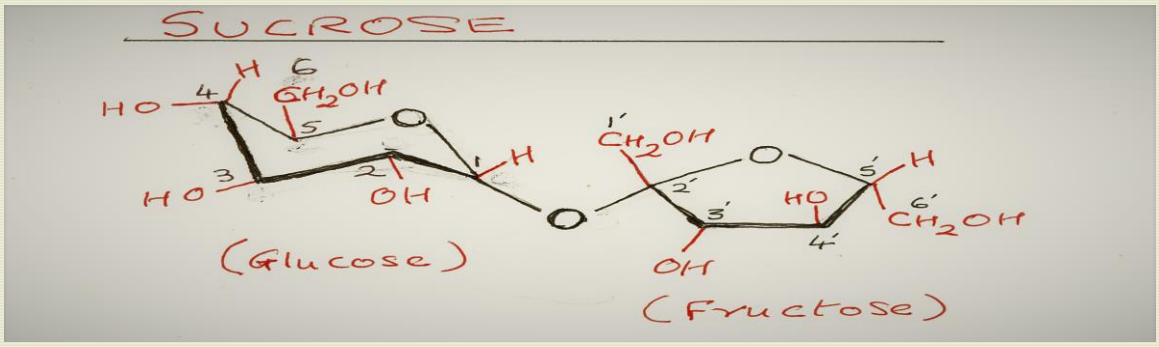
INADEQUATE mostly used for carbon, carbon correlation experiments for natural abundance samples.

It is the ultimate experiment to determine the connectivity in the carbon skeleton of a molecule. It uses the ^{1}J ^{13}C—^{13}C coupling to map out which carbon atoms are attached to each other. It is insensitive due to the fact that ^{13}C is only 1.1% at natural abundance. Hence the concentrated sample is required for the experiment and may require the over night or weekend collection of data for the spectrum.

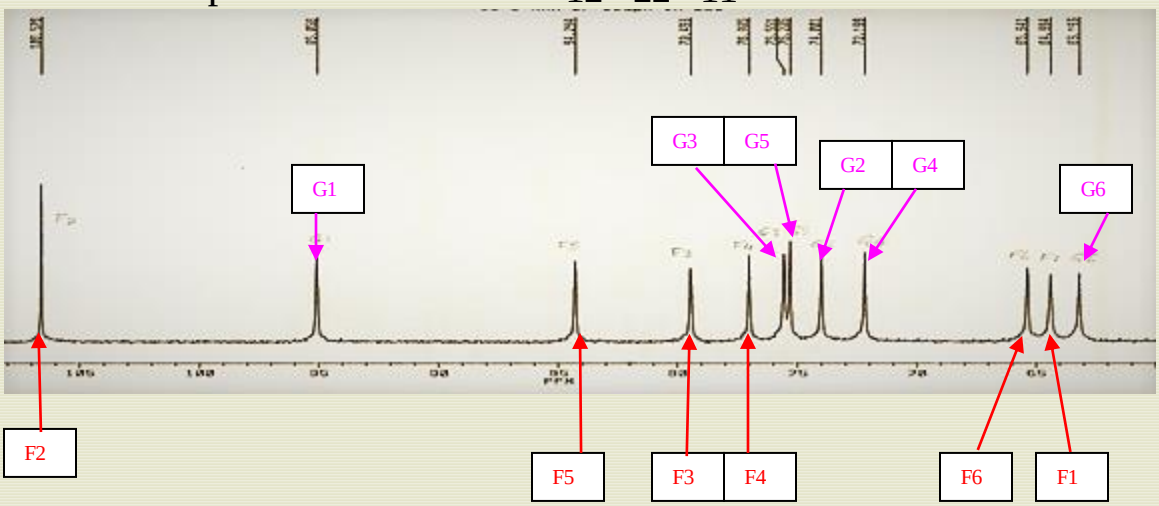
A 2D Inadequate spectrum yields one bond correlations *via* spin-spin coupling. The spectrum does not appear in the same form as a COSY spectrum but rather the f_2 axis is the carbon chemical shift and the f_1 axis is the double quantum frequency, *i.e.*, the sum of the two correlating frequencies. There are no diagonal signals. Signals with similar chemical shifts loose sensitivity due to second order coupling

2D INADEQUATE Pulse Sequence



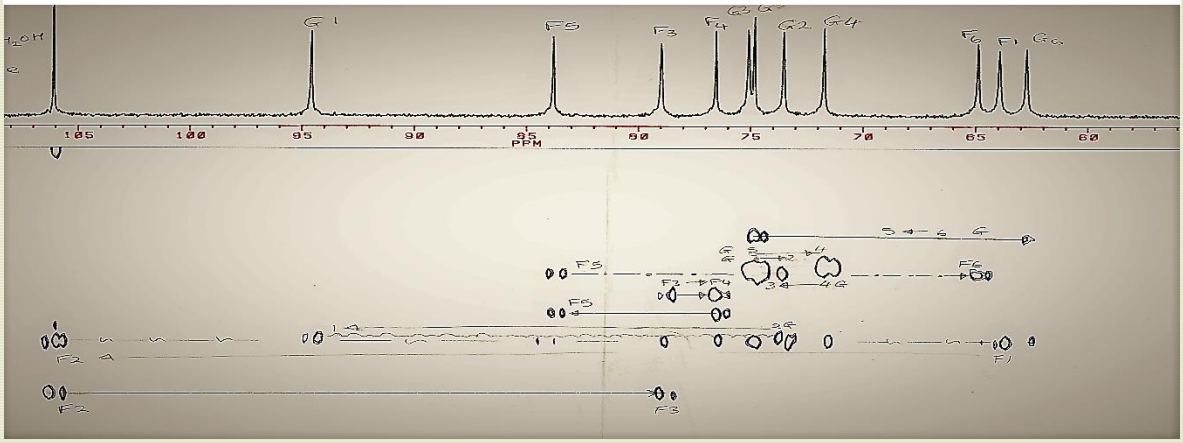


^{13}C NMR Spectrum of Sucrose $C_{12}H_{22}O_{11}$



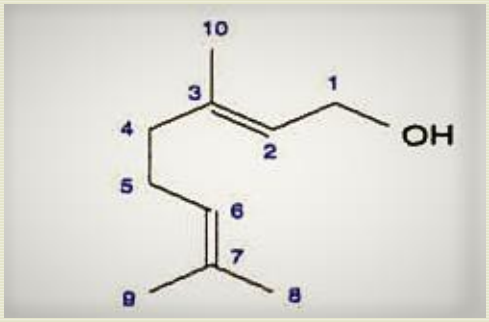
2D INADEQUATE ^{13}C NMR Spectrum of Sucrose $C_{12}H_{22}O_{11}$

F2 G1 F5 F3 F4 G3G5 G2 G4 F6 F1 G6



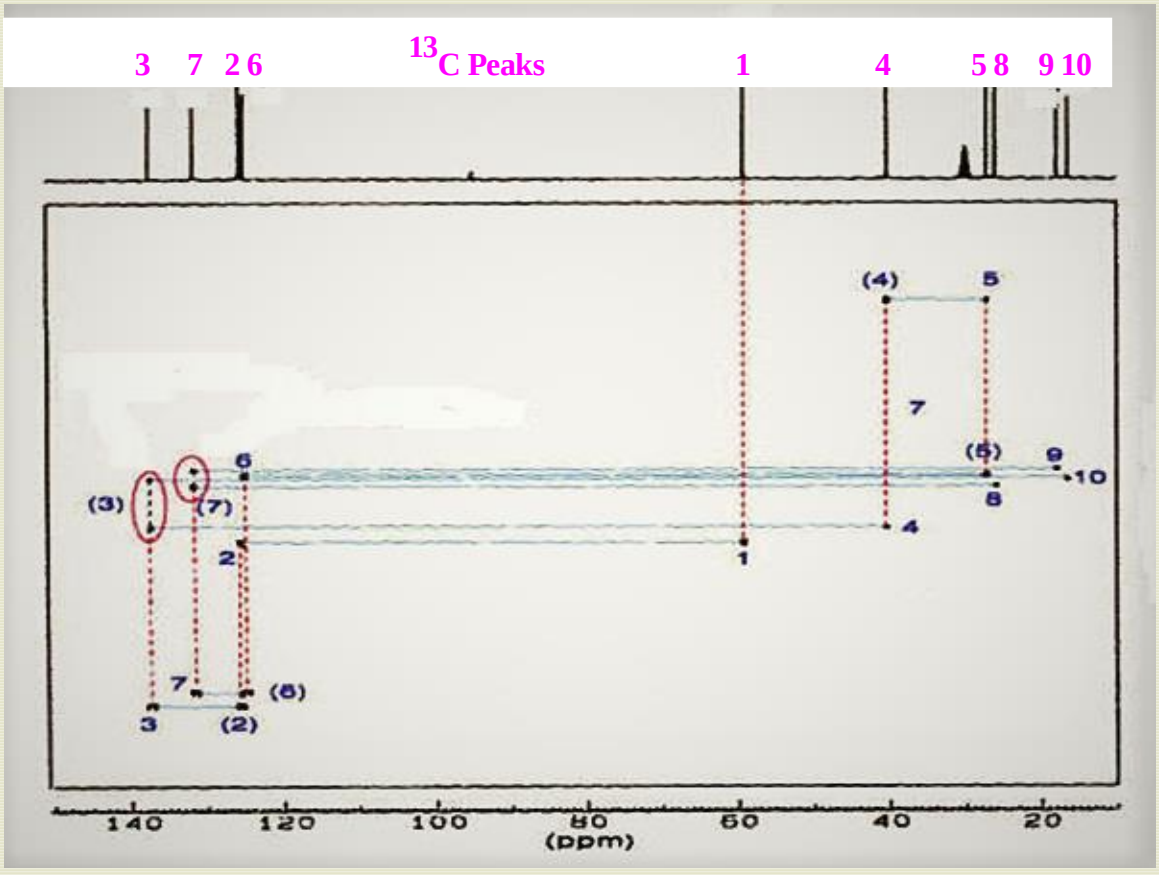
Click S87 & Click S88 & Click S89

Geraniol $C_{10}H_{18}O$

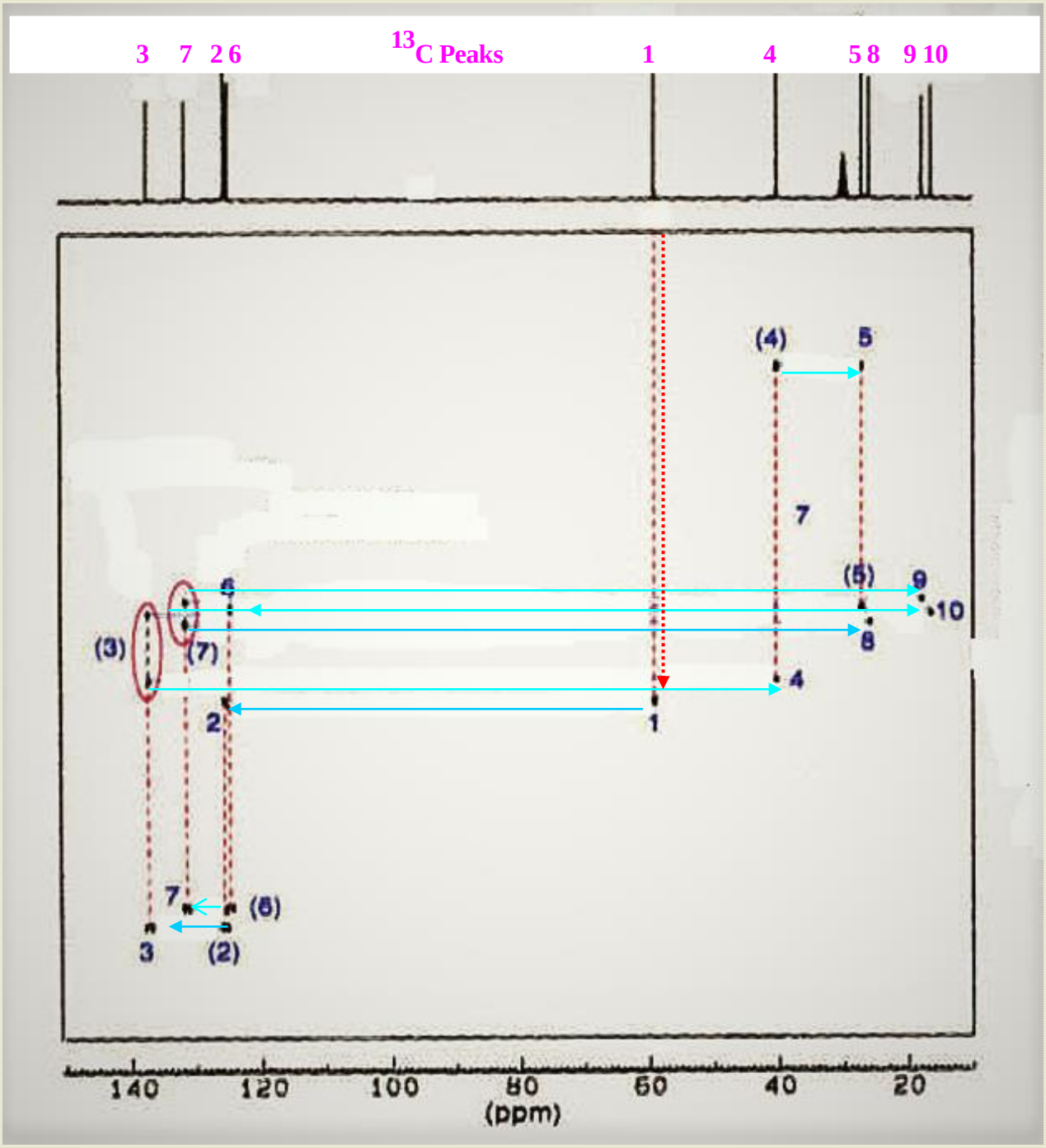


2D INADEQUATE ^{13}C NMR Spectrum of Geraniol $C_{10}H_{18}O$

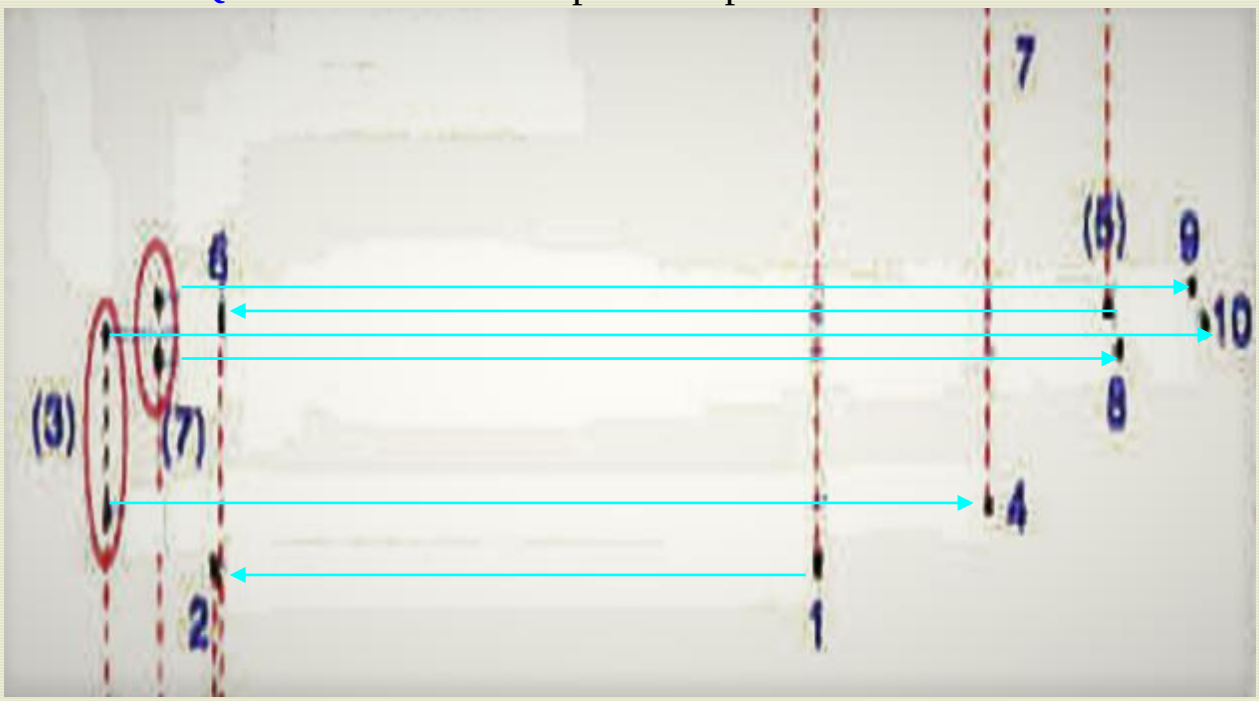
Links are C1—C2—C3—(C10)—C4—C5—C6—C7—(C9)—C8

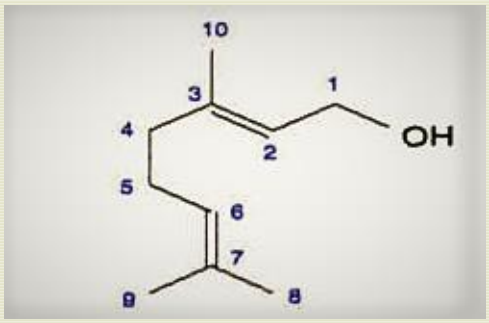


2D INADEQUATE ^{13}C NMR Spectrum of Geraniol

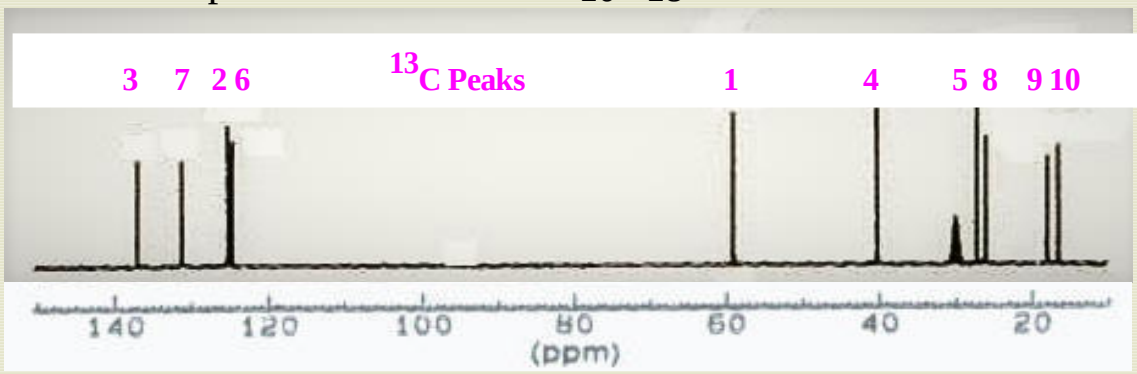


2D INADEQUATE ^{13}C NMR Expanded Spectrum of Geraniol



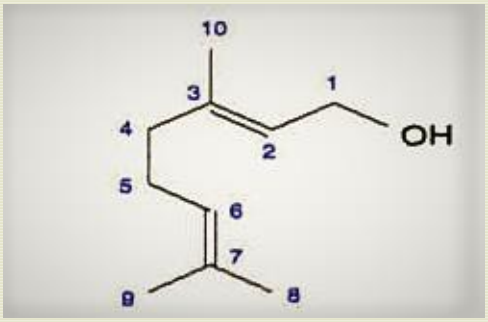


^{13}C NMR Spectrum of Geraniol $C_{10}H_{18}O$



Analysis of the 2D INADEQUATE ^{13}C NMR Spectrum of Geraniol

$C_{10}H_{18}O$ $(CH_3)_2C{=}CH{-}CH_2{-}CH_2{-}C(CH_3){=}CH{-}CH_2OH$



C1 has only 1 connection to C2 → 2 Contours

C2 has 2 connections to C1 & C3 → 4 Contours

C3 has 3 connections to C2, C4 & C10 → 6 Contours

C4 has 2 connections to C3 & C5 → 4 Contours

C5 has 2 connections to C4 & C6 → 4 Contours

C6 has 2 connections to C5 & C7 → 4 Contours

C7 has 3 connections to C6, C8 & C9 → 6 Contours

Basically, you should look under the peak along the vertical f_1 axis (the f_1 axis is the double quantum frequency, *i.e.*, the sum of the two correlating frequencies) and the number of contours will reveal the how many connecting atoms are attached to that atom. To reveal the connecting atom you should trace horizontally on f_2 axis (the f_2 axis is the carbon chemical shift) on either side from the vertical axis contour to opposite contour.

C3 has three contours. The horizontal traces reveal the following connections.

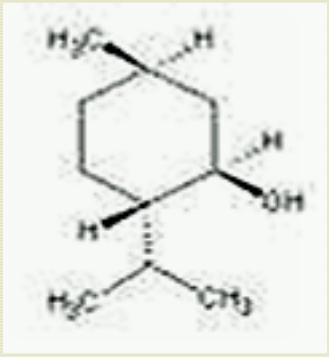
The top contour C3 to C10
The middle contour C3 to C4
The bottom contour C3 to C2

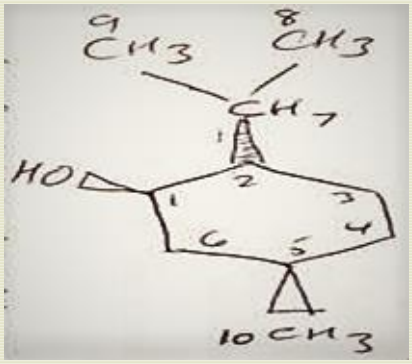
.

There will be no opposite contour for the dead end atom.
C1, C8, C9, & C10 contours.

Click S90

2D INADEQUATE ^{13}C NMR Spectrum of Menthol $C_{10}H_{20}O$





Analysis of the 2D INADEQUATE ^{13}C NMR Spectrum of Menthol

C1 has 2 connections to C2 & C6 → 4 Contours

C2 has 3 connections to C1, C3 & C7 → 6 Contours

C3 has 2 connections to C2 & C4 → 4 Contours

C4 has 2 connections to C3 & C5 → 4 Contours

C5 has 3 connections to C4, C6 & C10 → 6 Contours

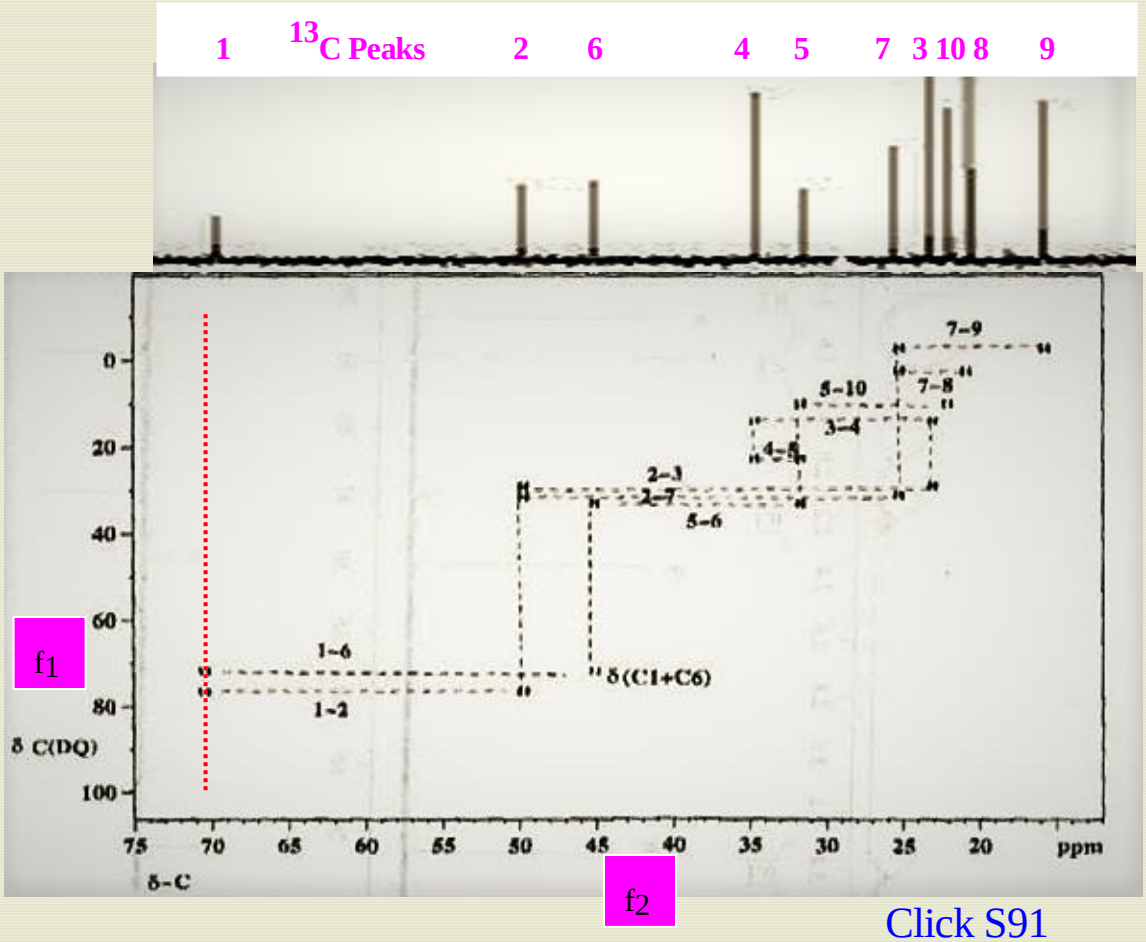
C6 has 2 connections to C1 & C5 → 4 Contours

C7 has 3 connections to C2, C8 & C9 → 6 Contours

C8 has only 1 connection to C7 → 2 Contours

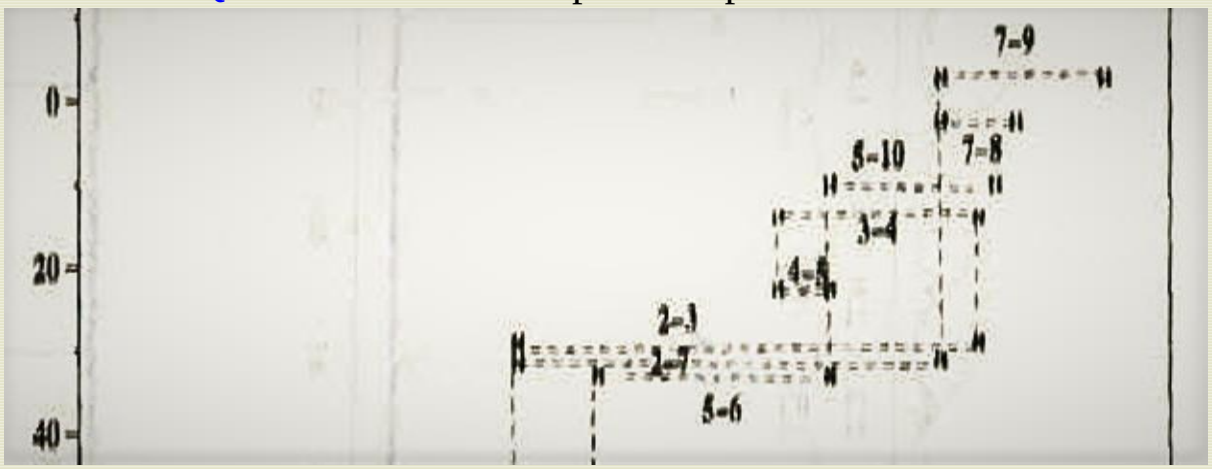
C9 has only 1 connection to C7 → 2 Contours

C10 has only 1 connection to C5 → 2 Contours



Click S91

2D INADEQUATE ^{13}C NMR Expanded Spectrum of Menthol



Introduction To NMR Spectroscopy Part 3 (Link)