

Nuclear Magnetic Resonance Principles

Nagarajan Murali

Rutgers, The State University of
New Jersey

References

Understanding NMR Spectroscopy

James Keeler

John Wiley & Sons (2006,2007)

Spin Dynamics Basics of Nuclear
Magnetic Resonance

Malcolm H. Levitt

John Wiley & Sons (2007)

Overview

- **Larmor Precession**
- **Bulk Magnetization**
- **Rotating Frame**
- **RF Pulse in Rotating Frame**
- **FID**
- **Product Operators – Foundation for Future Lectures**
- **pw calibration, pw calibration by Nutation**
- **Simple 1D**
- **Spin Echo**
- **T2 – Relaxation**
- **T1 - Relaxation**
- **Spin Lock**
- **2D Correlation Spectroscopy (COSY)**
- **2D NOESY**
- **2D ROESY**
- **pw_x calibration**
- **HMQC and HSQC**

Nuclear Magnetic Moment

- The nucleus of many atoms behaves like a tiny bar magnet – we say the nucleus possesses a ***magnetic moment*** μ .
- The magnetic moments arise from a fundamental property of the nucleus known as ***Spin*** which gives rise to an angular momentum \mathbf{I} and given as

$$\mu = \gamma \mathbf{I}$$

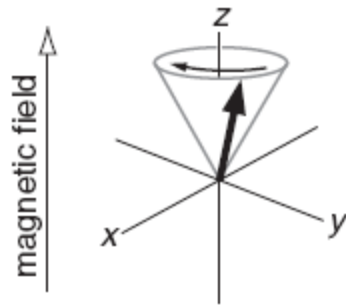
γ – gyromagnetic ratio specific for a nucleus and can be positive (μ and \mathbf{I} are parallel) or negative (μ and \mathbf{I} are anti-parallel) .

Larmor Precession

The magnetic moment μ in a magnetic field \mathbf{B}_0 experiences a torque

$$\frac{d\mu}{dt} = \mu \times \gamma \mathbf{B}_0$$

The size of the magnetic moment μ is fixed - the effect of the torque is to rotate the magnetic moment around the magnetic field. This rotation is called **Larmor precession** and the frequency is **Larmor frequency**.



$$\gamma > 0$$

Larmor frequency

$$\omega_0 = -\gamma B_0 \quad \text{rad s}^{-1}$$

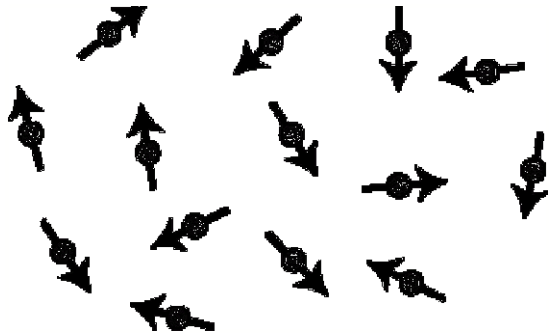
$$\nu_0 = -\frac{1}{2\pi} \gamma B_0 \quad \text{Hz}$$

Bulk Magnetization

- In NMR experiments we observe a large number of such nuclear *magnetic moments*.
- When an external magnetic field is applied to a sample the magnetic moments give a net contribution – called a *magnetization* along the direction of the applied magnetic field.
- At equilibrium the individual magnetic moments are predominantly oriented at an angle and precess on the surface of a cone at the Larmor frequency with no net magnetization perpendicular to the field.

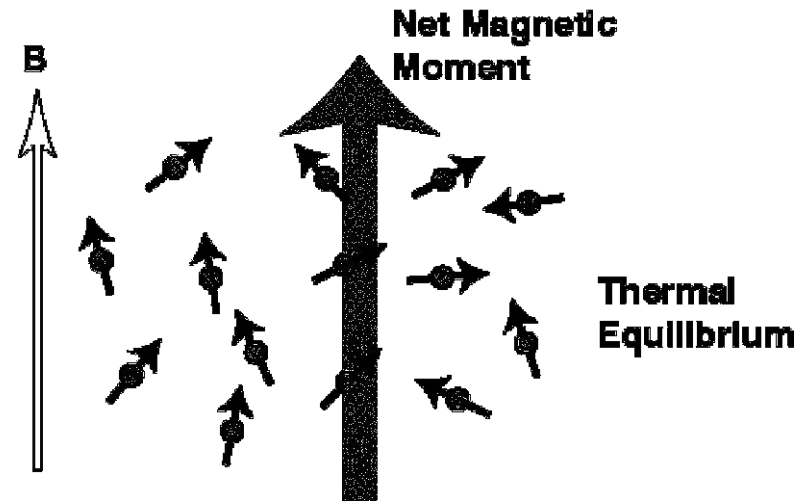
Alignment of Nuclear Magnetic Moments

No external magnetic field



Net magnetization is 'zero'

External Field induces net magnetization

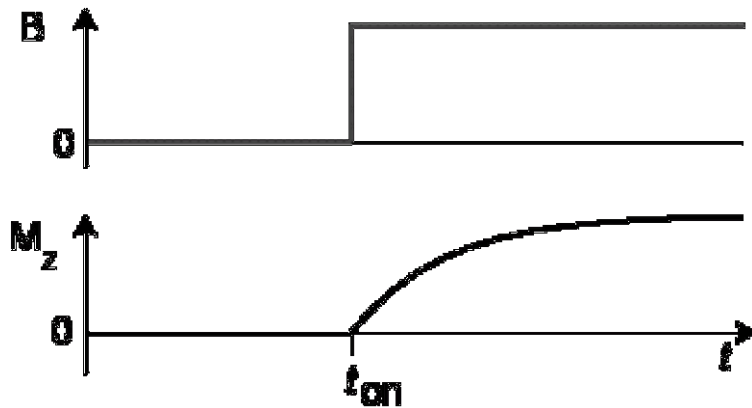


$$M_0 = \mu_0 \frac{N\gamma^2 \hbar^2 I(I+1)B_0}{3kT}$$

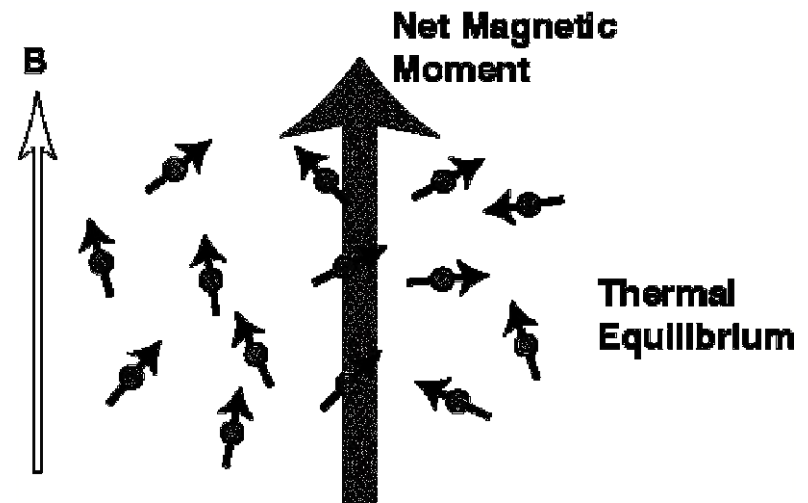
N – number of spins, γ – gyromagnetic ratio, \hbar – Planks constant, I – spin quntum number, μ_0 – permeability of free space, B_0 – Applied magnetic field strength (induction), K - Boltzman constant, T – temperature.

Alignment of Nuclear Magnetic Moments

It takes a finite time to induce the magnetization by the external field and the time constant T_1 is known as longitudinal relaxation time.



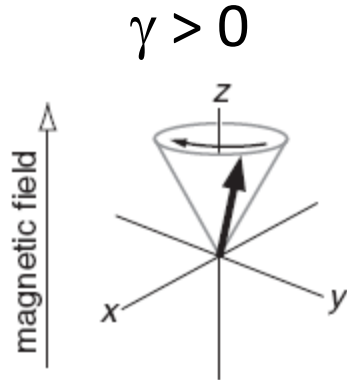
External Field induces net magnetization



$$M_0 = \mu_0 \frac{N\gamma^2 \hbar^2 I(I+1)B_0}{3kT}$$

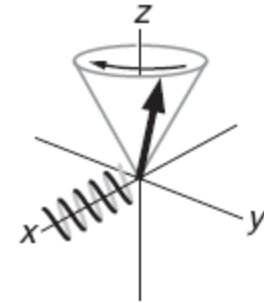
N – number of spins, γ – gyromagnetic ratio, \hbar – Planks constant, I – spin quntum number, μ_0 – permeability of free space, B_0 – Applied magnetic field strength (induction), K - Boltzman constant, T – temperature.

Signal



$$\omega_0 = -\gamma B_0 \quad \text{rad s}^{-1}$$

$$\nu_0 = -\frac{1}{2\pi} \gamma B_0 \quad \text{Hz}$$

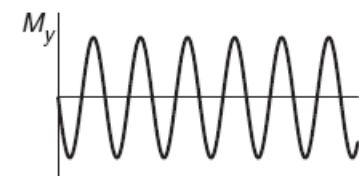
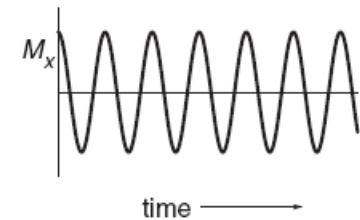


If by some means the bulk magnetization is tilted, all individual magnetic moments are also tilted and as the moments precess around the field the bulk magnetization also precesses and induces a **signal** in a coil placed perpendicular to the applied field. Suppose the vector is tilted by an angle β from z axis towards the x axis then the observed signal will be along x axis

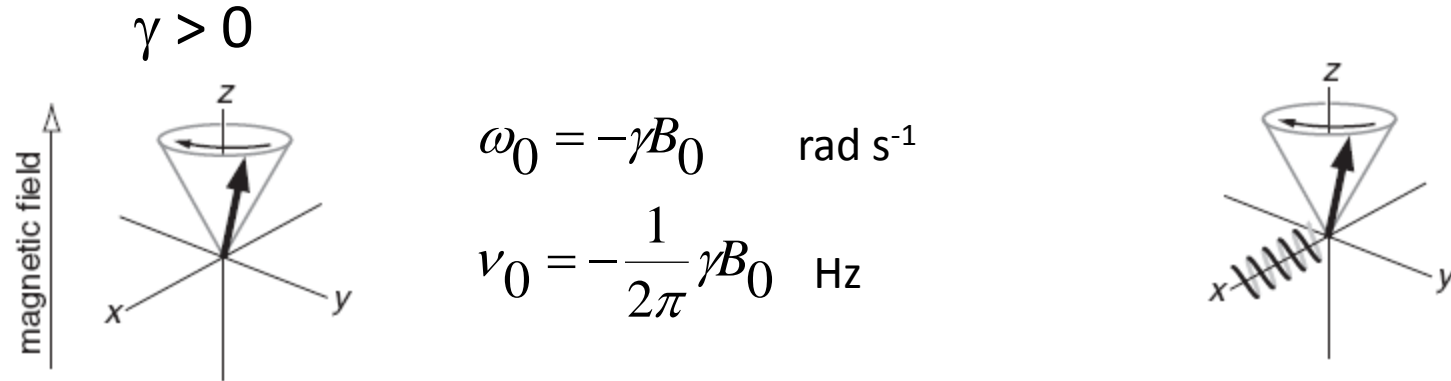
$$M_x = M_0 \sin \beta \cos(\omega_0 t)$$

Along a coil in y axis, it would be

$$M_y = -M_0 \sin \beta \sin(\omega_0 t)$$



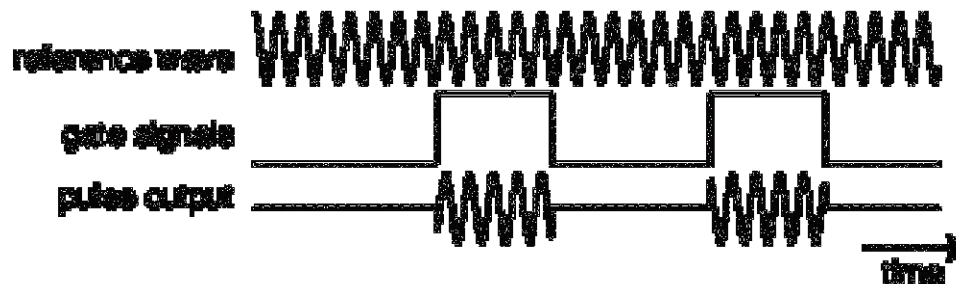
Radio Frequency Pulse



A radio frequency (RF) pulse at or near (**resonance**) the Larmor frequency applied along the x-axis can tilt the magnetization and is represented as

$$B_1 \cos(\omega t) \quad \omega \cong \omega_0$$

B_1 is the amplitude of rf field and ω is the frequency and t is the duration of the pulse.



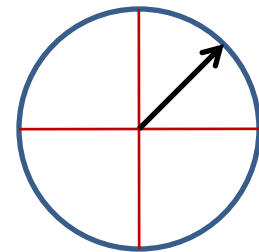
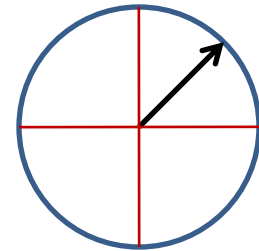
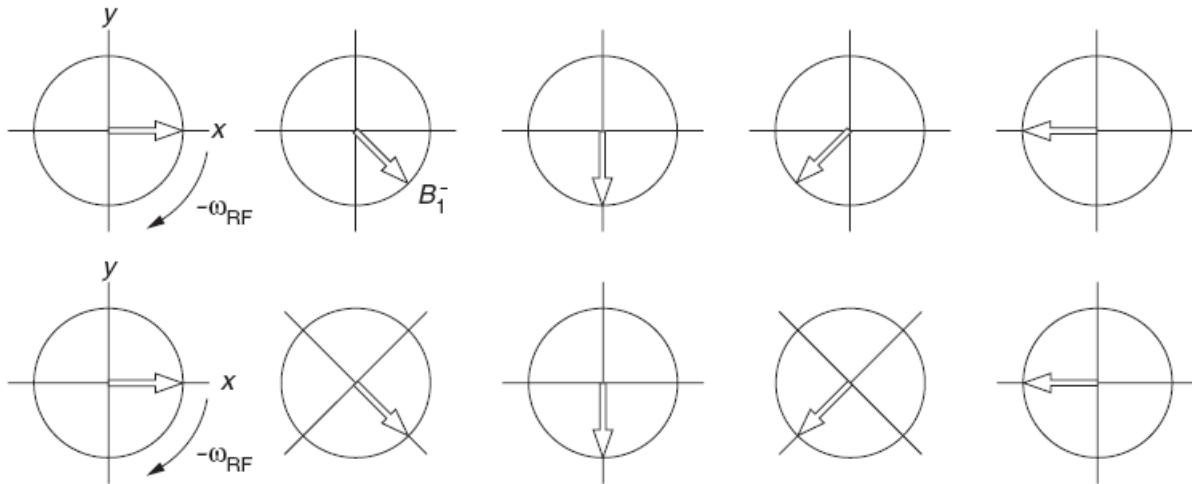
Motion in the presence of RF

$$\frac{d\boldsymbol{\mu}}{dt} = \boldsymbol{\mu} \times \gamma(\mathbf{B}_0 + \mathbf{B}_1(t))$$

The motion of the magnetic moments is now complicated as the field is time-dependant due to the RF.

The dynamics can be simplified in a *rotating frame* where the field appears static.

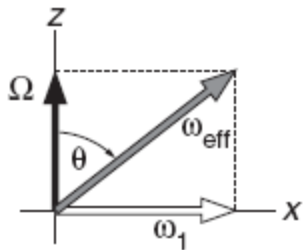
Rotating Frame



In the top figure a vector rotates in x-y plane, in bottom figure the x-y axes system is rotating and the vector is always along x-axis

Rotating Frame

Let's use the rotating frame to understand the effect of RF pulses. Say the applied field B_0 is along Z-axis and an RF field $B_1 \cos(\omega t)$ applied along the X-axis of the laboratory frame. Then the figures below show the fields in the rotating frame rotating at a frequency ω given by the axes system (xyz).



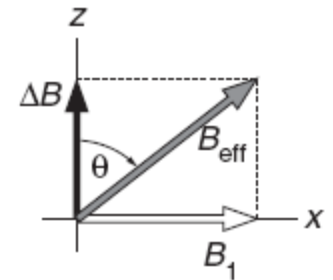
$$\omega_0 = -\gamma B_0$$

$$\omega = -\gamma B$$

$$\Omega = \omega_0 - \omega = -\gamma(B_0 - B) = -\gamma \Delta B$$

$$B_{eff} = \sqrt{\Delta B^2 + B_1^2}$$

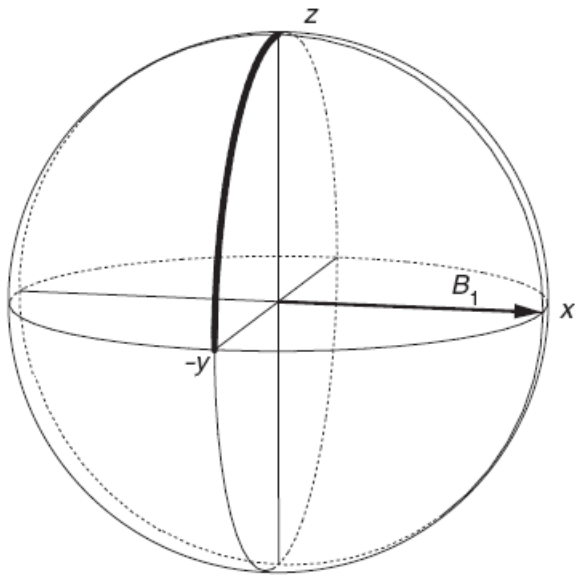
$$\omega_{eff} = -\gamma B_{eff}$$



If $B_1 \gg \Delta B$ then the effective field is along B_1 and the magnetization vector will rotate about the x-axis.

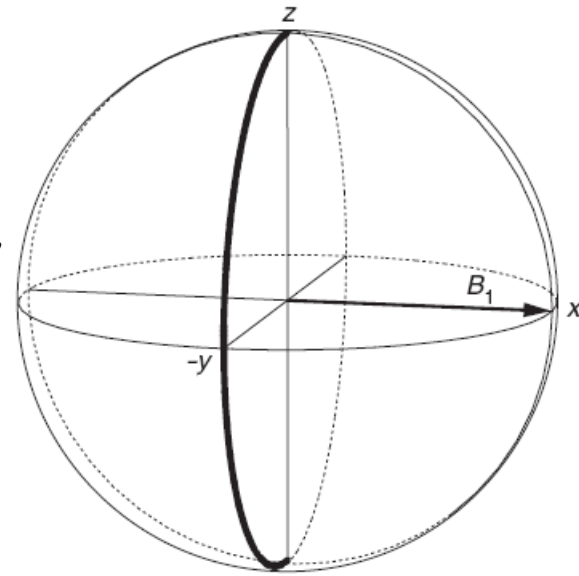
Effect of Radio Frequency Pulse

Radio Frequency (RF) pulses at a frequency ω_0 and strength B_1 rotates the magnetization.



90° rotation

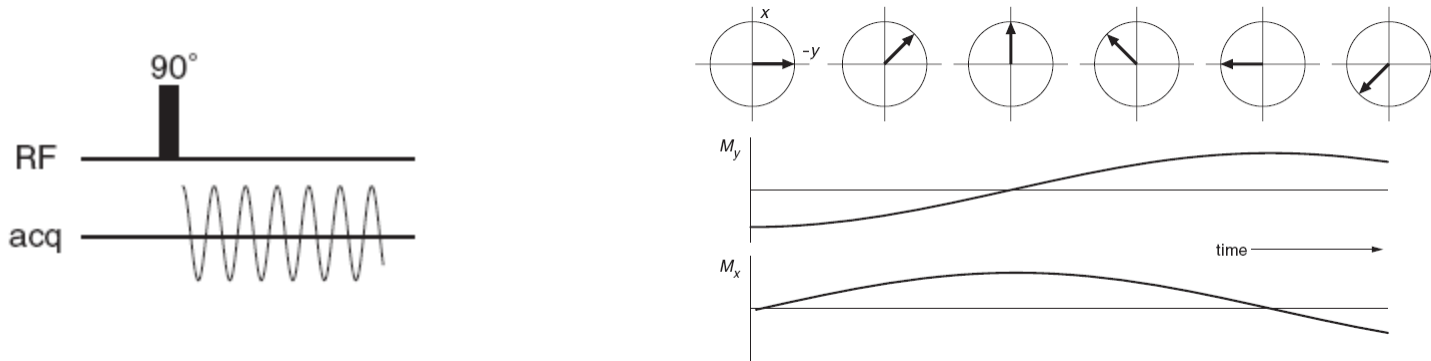
$$\beta = -\gamma B_1 t_{pw} = \omega_1 t_{pw}$$



180° rotation

In the rotating frame, the static field along z-direction is zero on-resonance. The RF field appears static along x-axis. The rotation angle β increases with increasing pulse width for a given RF strength.

One Pulse Experiment



With a 90° pulse along x axis, the magnetization vector rotated from z to $-y$ and evolves with a precession frequency $\Omega = \omega_0 - \omega_{rot}$

$$M_y = -M_0 \cos(\Omega t)$$

$$M_x = M_0 \sin(\Omega t)$$

Free Induction Decay - FID

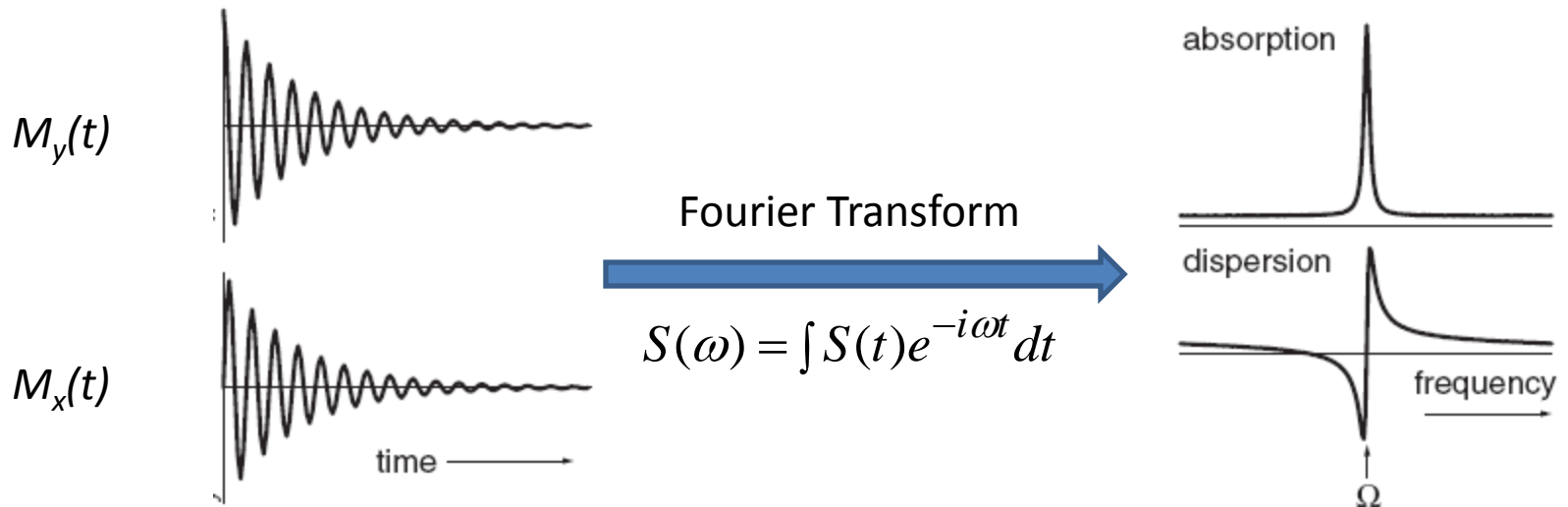
With a 90° pulse along x axis, the magnetization vector rotated from z to $-y$ then the observed FID is

$$S(t) = (M_y(t) - iM_x(t))e^{-t/T_2}$$

$$S(t) = -M_0(\cos(\Omega t) + i \sin(\Omega t))e^{-t/T_2}$$

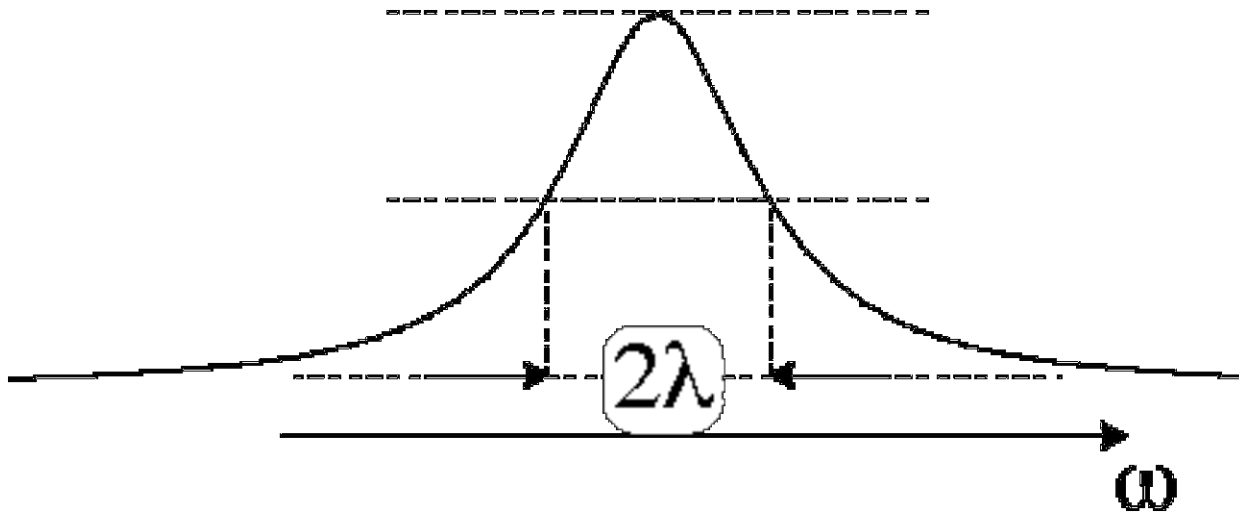
$$S(t) = -M_0 e^{i\Omega t} e^{-t/T_2}$$

T_2 is the decay constant of the signal in the xy plane or the transverse relaxation time constant.



Transverse relaxation – T_2

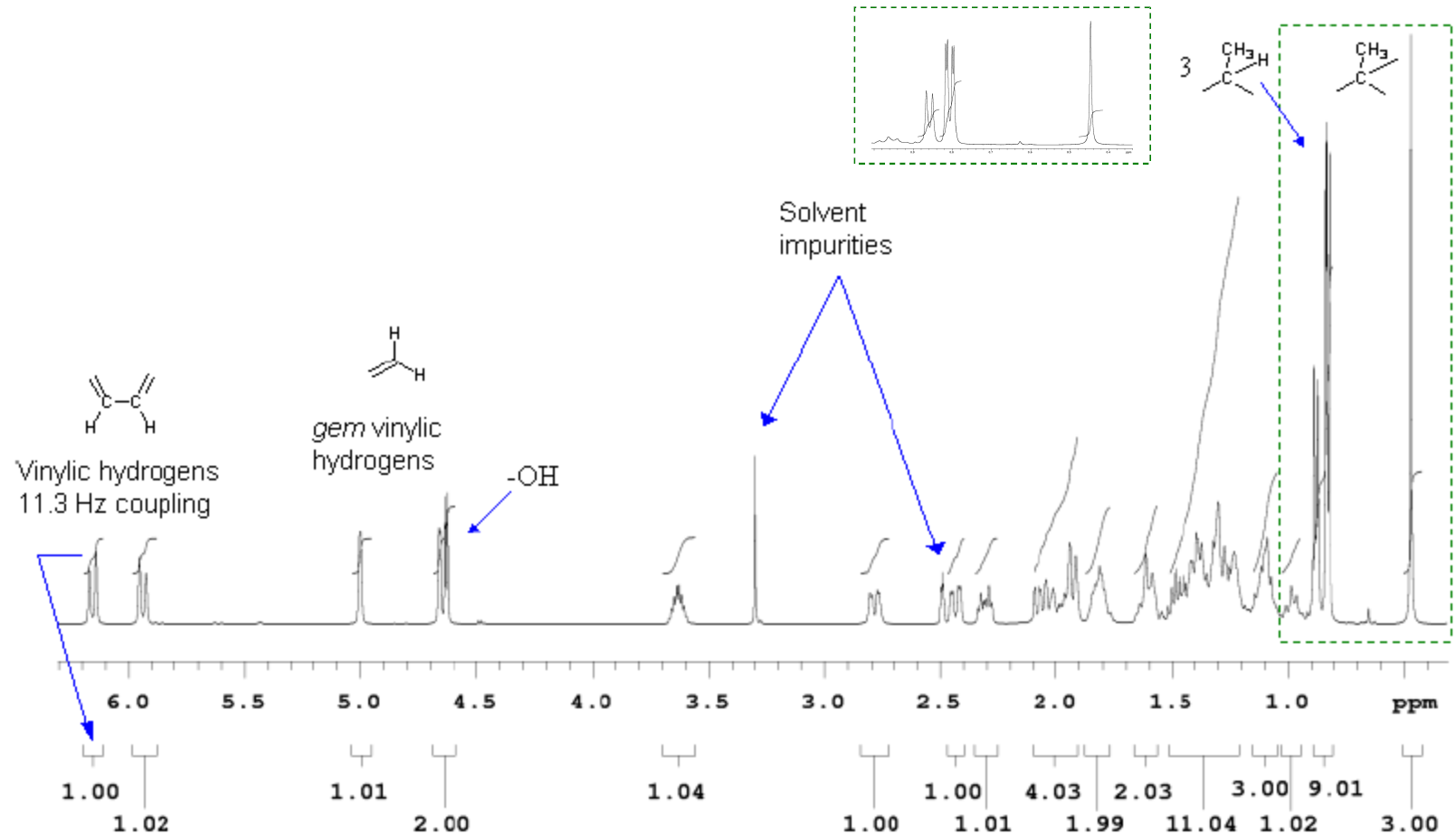
The relaxation rate constant in terms of half the line width at half maximum $T_2 = \frac{1}{\lambda}$



Line width ($LW=2\delta$) is usually measured in units of Hz, therefore

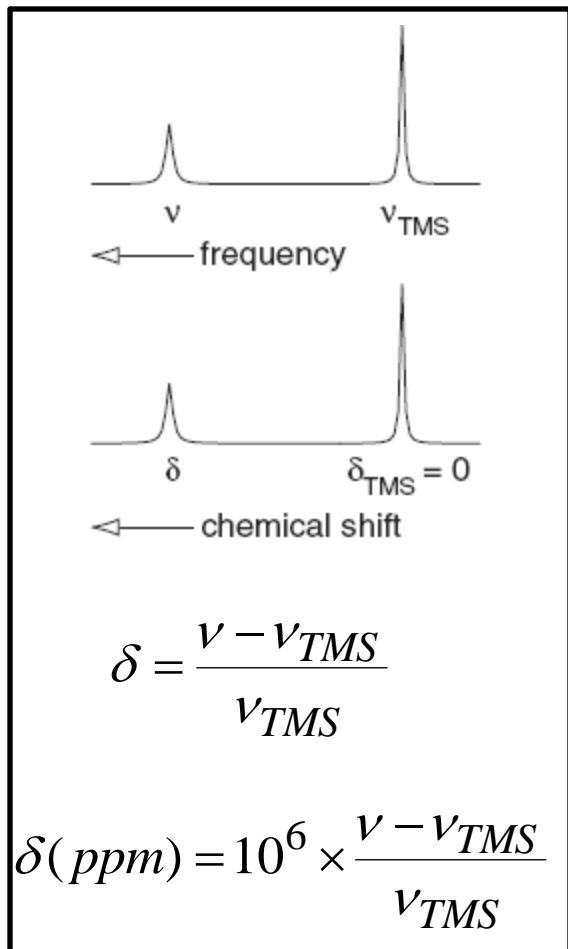
$$T_2 = \frac{1}{2\pi\delta} = \frac{1}{\pi * LW(\text{Hz})}$$

Proton NMR Spectrum



Proton NMR spectrum illustrating major functional groups. The solvent is deuterated dimethylsulfoxide.

Chemical Shift



$$\delta_1(ppm) - \delta_2(ppm) = 10^6 \times \frac{\nu_1 - \nu_{TMS}}{\nu_{TMS}} - 10^6 \times \frac{\nu_2 - \nu_{TMS}}{\nu_{TMS}}$$

$$\Delta\delta(ppm) = 10^6 \times \frac{(\nu_1 - \nu_2)}{\nu_{TMS}}$$

$$(\nu_1 - \nu_2) = \Delta\delta(ppm) \times 10^{-6} \times \nu_{TMS}$$

$$(\nu_1 - \nu_2) = \Delta\delta(ppm) \times 10^{-6} \times \nu_0$$

Since the frequency increases with the field strength the chemical shift difference between two peaks is larger in frequency units. 1ppm at 400MHz = 400Hz; 1ppm at 500MHz = 500Hz.

Tools for Understanding NMR Experiments

To understand NMR experiments with more than one type of spins and many pulses we need more sophisticated tools developed based on quantum mechanics and is popularly known as ***Product Operator Formalism*** (POF).

The state of the magnetizations (spin states) of different species are represented by operators and their products to describe the time evolution of the spin states.

Operators Approach

Operators for two species I and S

I_z	Longitudinal Magnetization	Multiple Quantum Coherence (MQC)
I_x	Single Quantum Coherence X Magnetization	$2 I_x S_x, 2 I_y S_y, 2 I_x S_y, 2 I_y S_x$
I_y	Single Quantum Coherence Y Magnetization	Longitudinal 2- Spin Order $2 I_z S_z$
$2 I_x S_z$	Anti-phase X Coherence	Zero Quantum Coherence (ZQC)
$2 I_y S_z$	Anti-phase Y Coherence	
E	Identity operator	$2 I_x S_x - 2 I_y S_y$ Double Quantum Coherence (DQC)
		$2 I_x S_y - 2 I_y S_x$ ZQC
		$2 I_x S_y + 2 I_y S_x$ DQC

Hamiltonian Parts

$$\omega_I I_z$$

I – Spin Chemical Shift

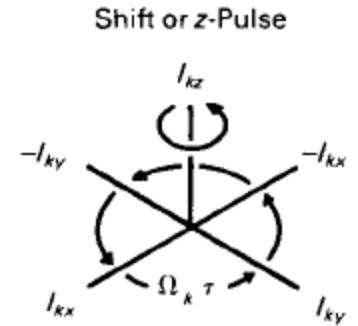
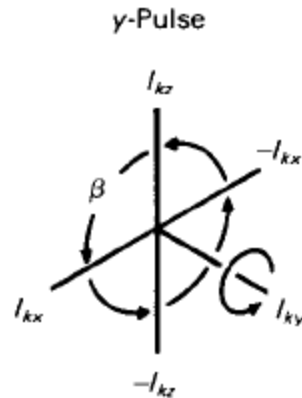
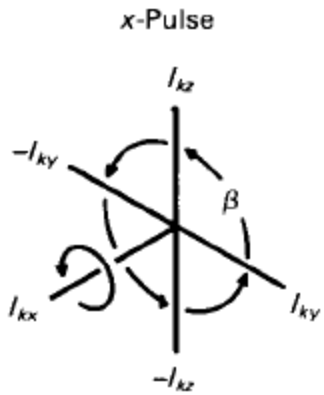
$$\omega_S S_z$$

S – Spin Chemical Shift

$$\pi J_{IS} 2 I_z S_z$$

J – Coupling between Spins I & S

Operators Approach



$$I_x \xrightarrow{\beta_x} I_x$$

$$I_y \xrightarrow{\beta_x} I_y \cos \beta + I_z \sin \beta$$

$$I_z \xrightarrow{\beta_x} I_z \cos \beta - I_y \sin \beta$$

$$I_x \xrightarrow{\beta_y} I_x \cos \beta - I_z \sin \beta$$

$$I_y \xrightarrow{\beta_y} I_y$$

$$I_z \xrightarrow{\beta_y} I_z \cos \beta + I_x \sin \beta$$

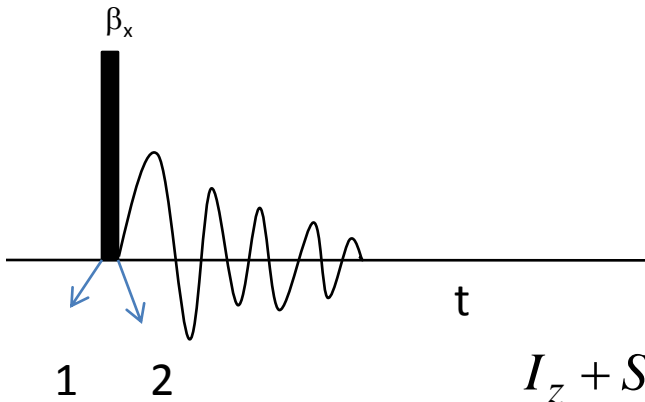
$$I_x \xrightarrow{\beta_z} I_x \cos \beta + I_y \sin \beta$$

$$I_y \xrightarrow{\beta_z} I_y \cos \beta - I_x \sin \beta$$

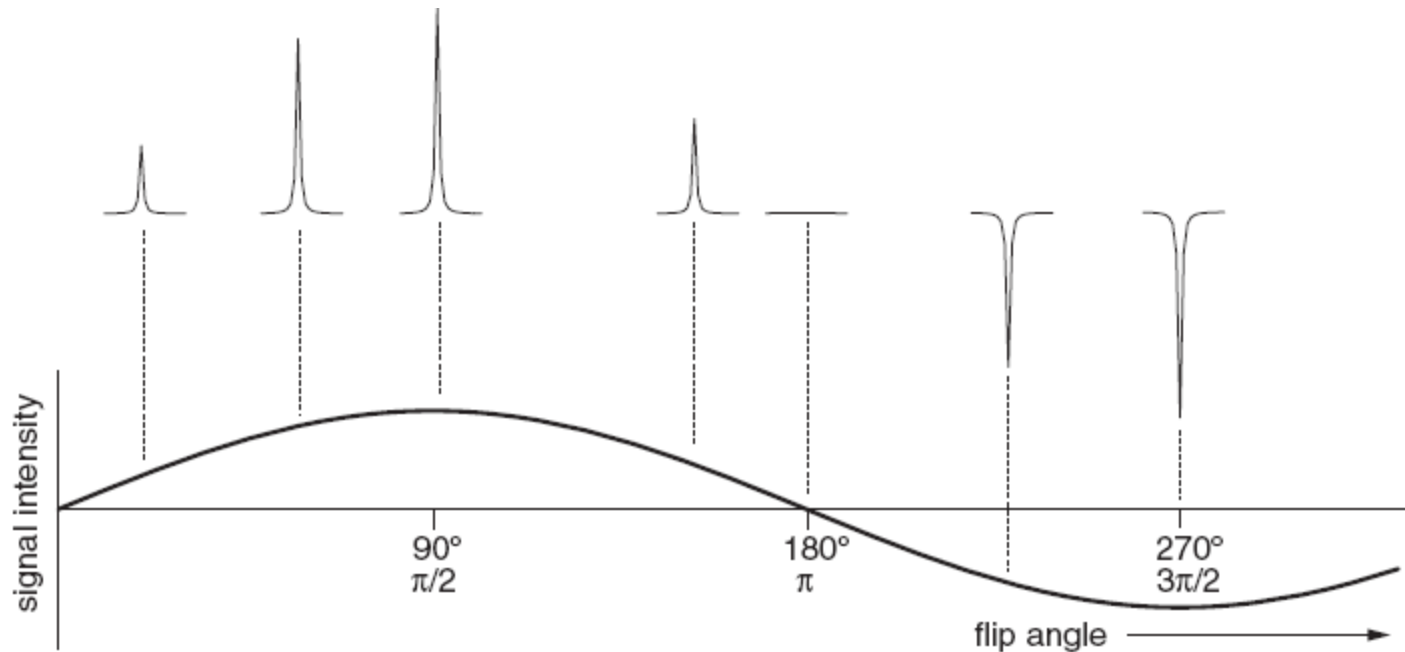
$$I_z \xrightarrow{\beta_z} I_z$$

NMR Experiments can be understood by following the evolution of operators.

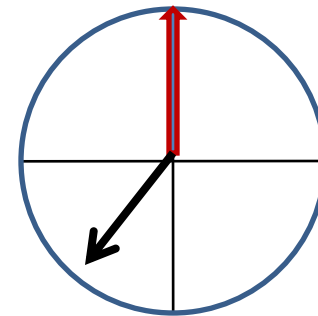
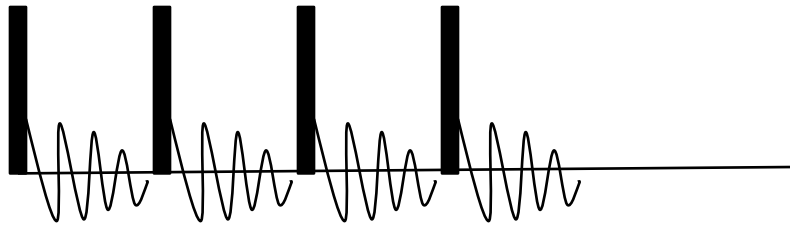
Pulse Calibration



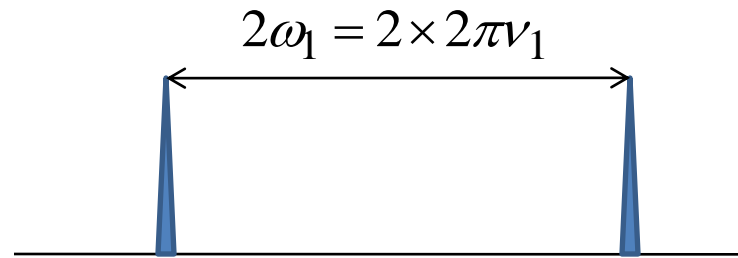
$$I_z + S_z \xrightarrow{\beta_x} I_z \cos \beta - I_y \sin \beta + S_z \cos \beta - S_y \sin \beta$$



PW-Calibration by Nutation



$$\omega_1 = -\gamma B_1$$

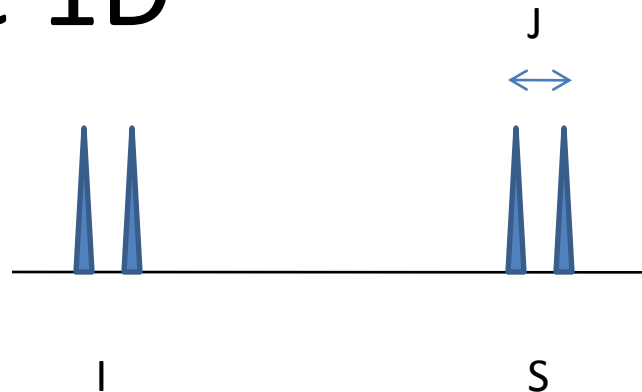
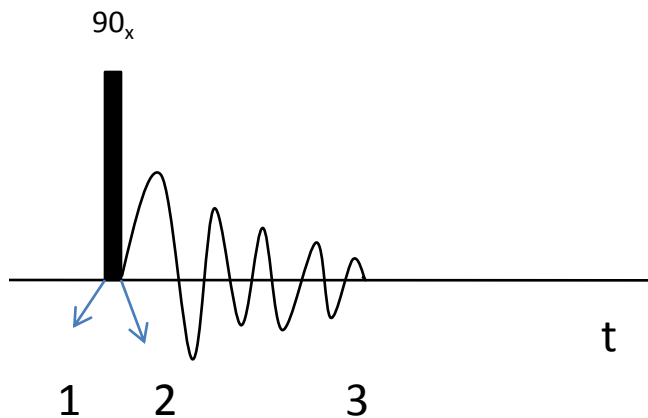


$$\omega_1 \tau_p = \frac{\pi}{2}$$

$$\tau_p = \frac{\pi}{2} \times \frac{1}{\omega_1} = \frac{1}{4\nu_1 (\text{Hz})}$$

Ref: Rapid pulse length determination in high-resolution NMR
Peter S.C. Wu, Gottfried Otting, J. Magn. Reson 176(1), 115, 2005

Simple 1D



1 $I_z + S_z$

↓ 90_x

2 $-I_y - S_y$

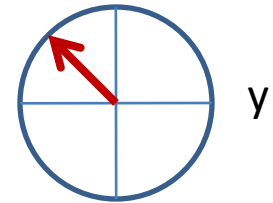
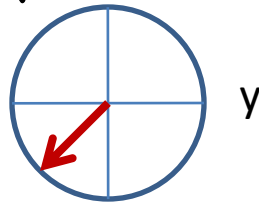
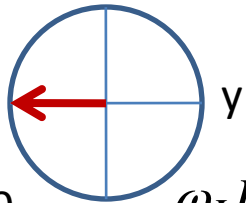
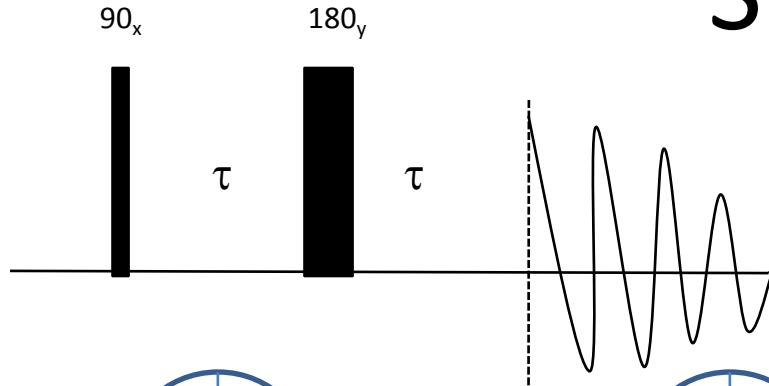
↓ $(\omega_I I_z + \omega_S S_z)t$

3 $-I_y \cos(\omega_I t) + I_x \sin(\omega_I t)$
 $-S_y \cos(\omega_S t) + S_x \sin(\omega_S t)$

$(\pi J_{IS} 2I_z S_z)t$

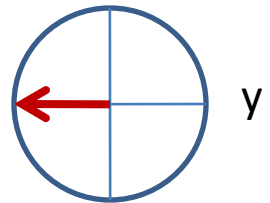
$$\begin{aligned}
 & -I_y \cos(\omega_I t) \cos(\pi J_{IS} t) + 2I_x S_z \cos(\omega_I t) \sin(\pi J_{IS} t) \\
 & + I_x \sin(\omega_I t) \cos(\pi J_{IS} t) + 2I_y S_z \sin(\omega_I t) \sin(\pi J_{IS} t) \\
 & -S_y \cos(\omega_S t) \cos(\pi J_{IS} t) + 2S_x I_z \cos(\omega_S t) \sin(\pi J_{IS} t) \\
 & + S_x \sin(\omega_S t) \cos(\pi J_{IS} t) + 2S_y I_z \sin(\omega_S t) \sin(\pi J_{IS} t)
 \end{aligned}$$

Spin Echo



$$I_z \xrightarrow{90_x} -I_y \xrightarrow{\omega_I I_z \tau} -I_y \cos(\omega_I \tau) + I_x \sin(\omega_I \tau) \xrightarrow{180_y} -I_y \cos(\omega_I \tau) - I_x \sin(\omega_I \tau)$$

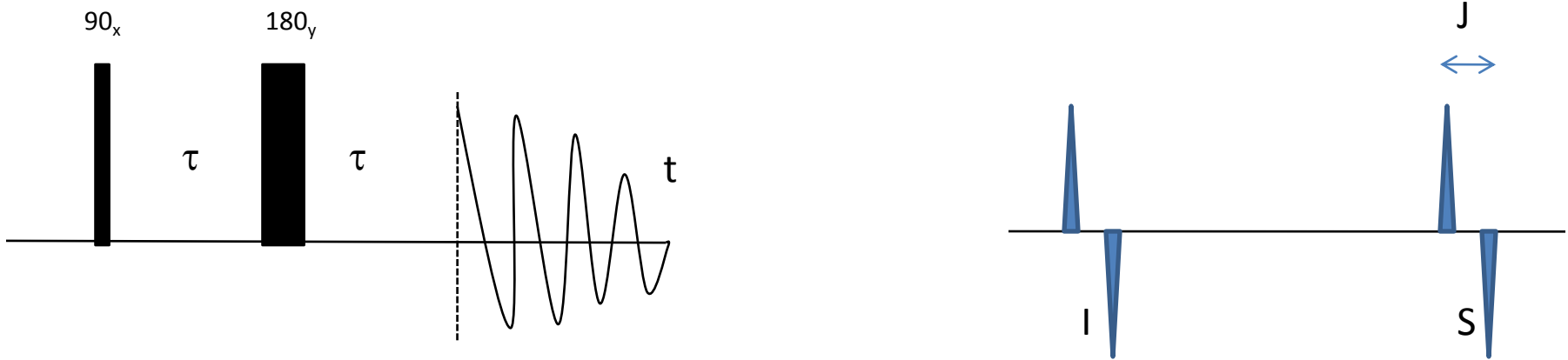
$$\omega_I I_z \tau \left[\begin{array}{l} -I_y \cos(\omega_I \tau) \cos(\omega_I \tau) + I_x \cos(\omega_I \tau) \sin(\omega_I \tau) \\ -I_x \sin(\omega_I \tau) \cos(\omega_I \tau) - I_y \sin(\omega_I \tau) \sin(\omega_I \tau) \end{array} \right] = -I_y (\cos^2(\omega_I \tau) + \sin^2(\omega_I \tau))$$



$$= -I_y$$

At the end of 2τ period chemical shift evolution is refocused.

Spin Echo –J Evolution



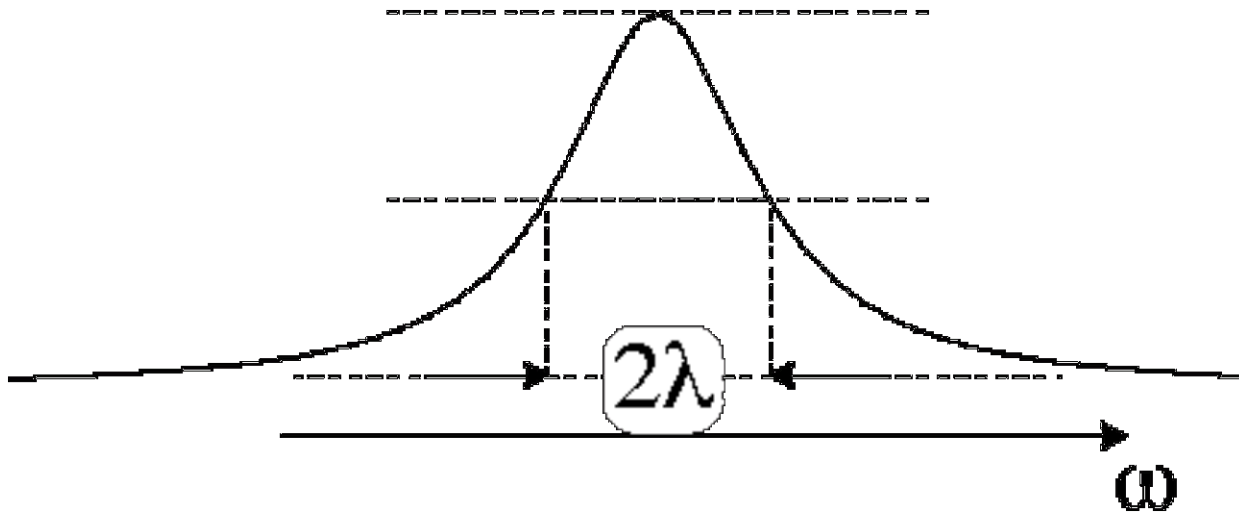
$$-I_y \xrightarrow{(\pi J_{IS} 2\tau) 2I_z S_z} -I_y \cos(\pi J_{IS} 2\tau) + 2I_x S_z \sin(\pi J_{IS} 2\tau)$$

$$\tau = \frac{1}{4J} : 2I_x S_z \xrightarrow{\text{FID}} 2I_x S_z \cos(\omega_I t) \cos(\pi J t) + I_y \cos(\omega_I t) \sin(\pi J t) + 2I_y S_z \sin(\omega_I t) \cos(\pi J t) - I_x \sin(\omega_I t) \sin(\pi J t)$$

At the end of 2τ period the anti-phase coherence is generated.

Transverse relaxation – T_2

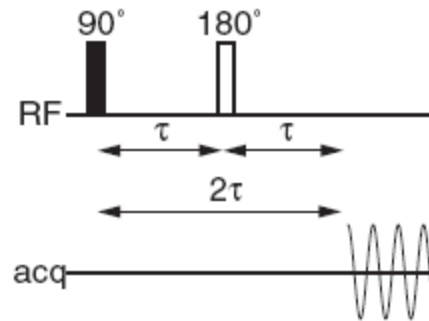
The relaxation rate constant in terms of half the line width at half maximum $T_2 = \frac{1}{\lambda}$



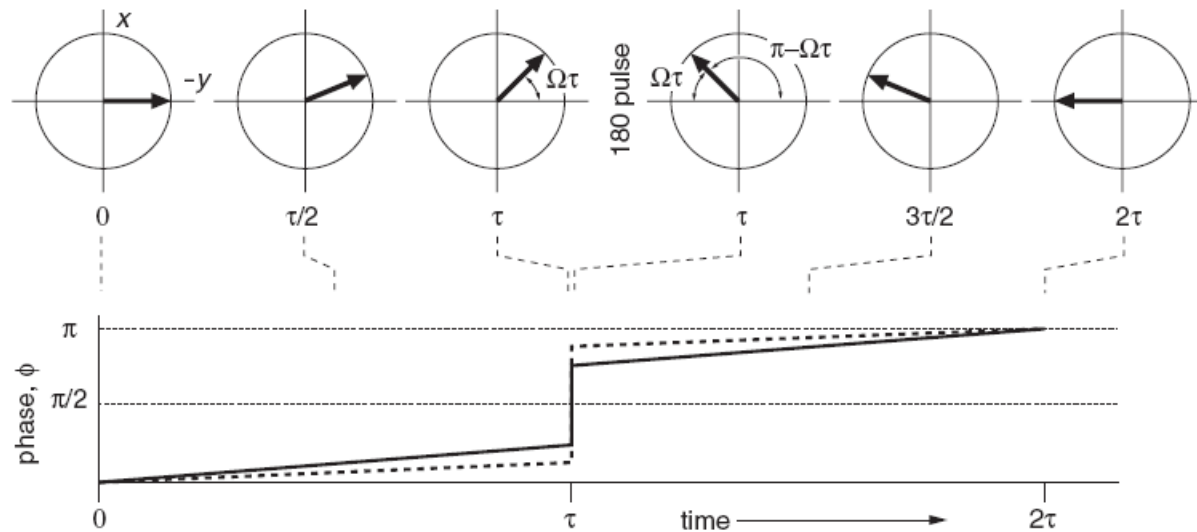
Line width ($LW=2\delta$) is usually measured in units of Hz, therefore

$$T_2 = \frac{1}{2\pi\delta} = \frac{1}{\pi * LW(Hz)}$$

T₂ By Spin Echo Method



$$M(2\tau) = M_0 e^{-2t/T_2}$$



Spin Echo principle is used to measure the transverse relaxation time T₂

T₂ Relaxation

index freq(ppm) intensity
 1 9.42982 66.7623
 2 9.39694 62.1995
 Exponential data analysis:

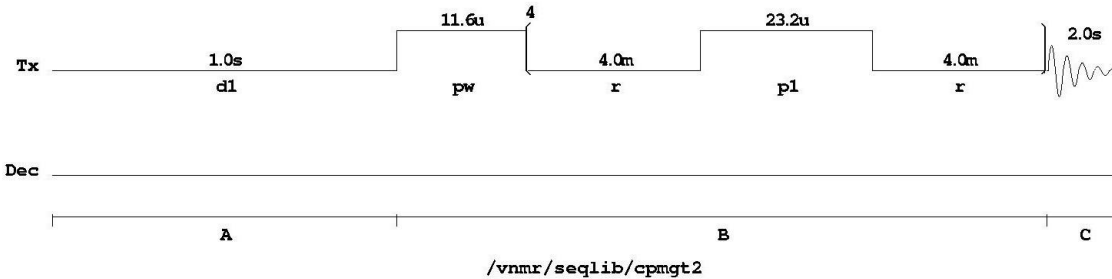
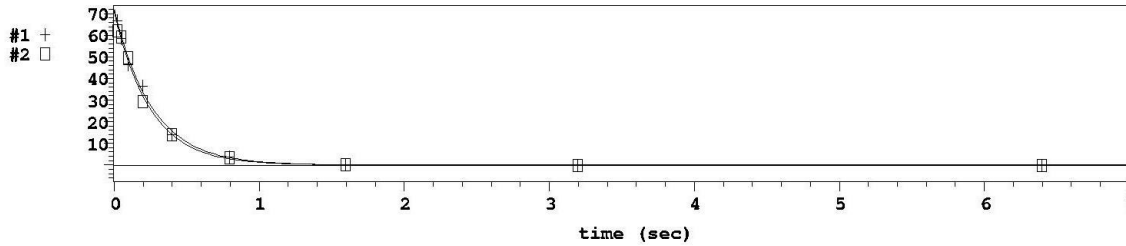
peak	T2	error
1	0.2626	0.01905
2	0.2472	0.01599

peak number 1
 T2 = 0.263 error = 0.019

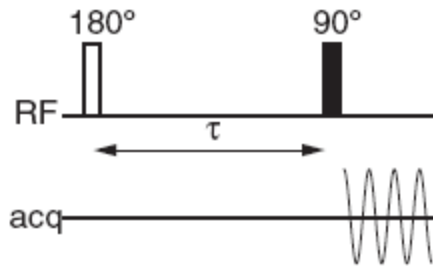
time	observed	calculated	difference
0.025	66.8	65.3	1.43
0.05	58.7	59.4	-0.756
0.1	46.5	49.1	-2.58
0.2	36.7	33.6	3.11
0.4	14.2	15.8	-1.52
0.8	3.81	3.53	0.284
1.6	0.41	0.279	0.131
3.2	-0.01	0.117	-0.127
6.4	0.02	0.117	-0.0969

peak number 2
 T2 = 0.247 error = 0.016

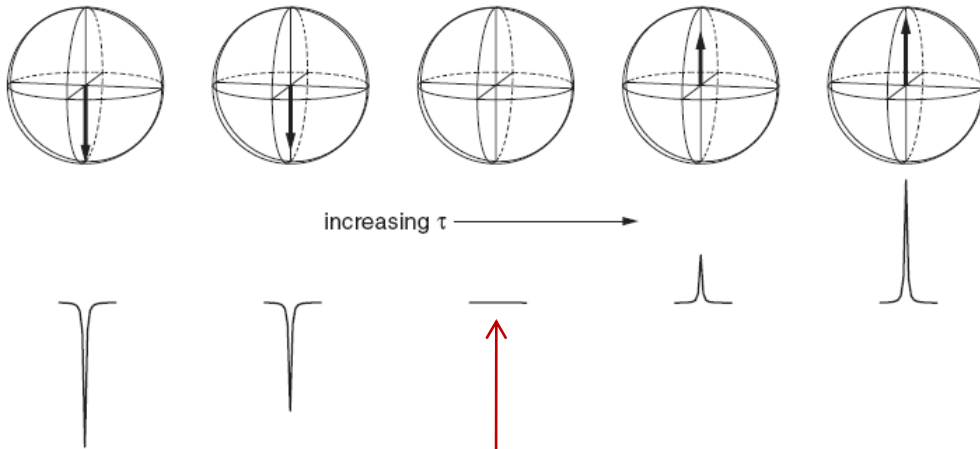
time	observed	calculated	difference
0.025	62.2	64.1	-1.94
0.05	59.5	58	1.47
0.1	49.7	47.4	2.3
0.2	29.5	31.7	-2.17
0.4	14.2	14.2	0.0361
0.8	3.62	2.96	0.655
1.6	0.29	0.292	-0.00242
3.2	-0.02	0.183	-0.203
6.4	0.02	0.183	-0.163



T₁ Relaxation – Inversion Recovery



$$M(\tau) = M_0(1 - 2e^{-\tau/T_1})$$



$$M(\tau_{null}) = 0 = M_0(1 - 2e^{-\tau_{null}/T_1})$$

$$2M_0e^{-\tau_{null}/T_1} = M_0$$

$$e^{-\tau_{null}/T_1} = \frac{1}{2}$$

$$\frac{\tau_{null}}{T_1} = \ln 2$$

$$T_1 = \frac{\tau_{null}}{\ln 2} \approx 1.44\tau_{null}$$

T₁ Relaxation

index freq(ppm) intensity
 1 7.75198 50.4851
 2 7.73657 54.2945
 Exponential data analysis:

peak T1 error
 1 19.67 0.5721
 2 19.75 0.4794

peak number 1

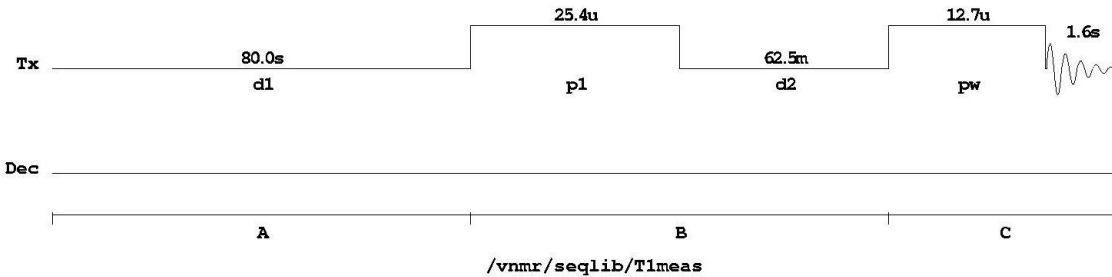
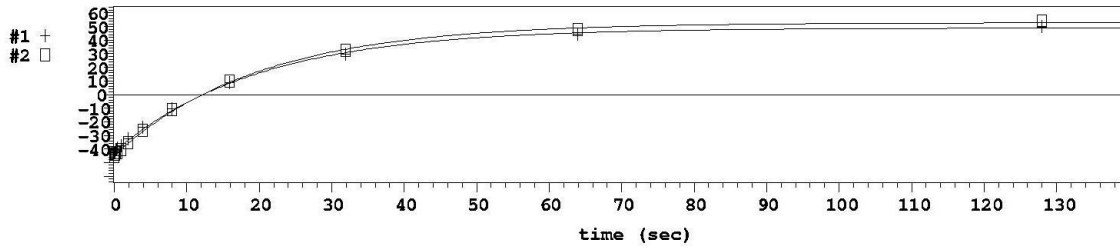
T1 = 19.7 error = 0.572

time	observed	calculated	difference
0.0625	-42.2	-41.3	-0.859
0.125	-42.2	-41	-1.2
0.25	-40.4	-40.5	0.0324
0.5	-39.1	-39.3	0.28
1	-37.1	-37.1	0.0173
2	-32.3	-32.8	0.498
4	-23.9	-24.9	1.01
8	-10.2	-11.3	1.05
16	9.19	8.94	0.248
32	30	31.4	-1.38
64	44.7	45.7	-1.02
128	50.5	49.1	1.41

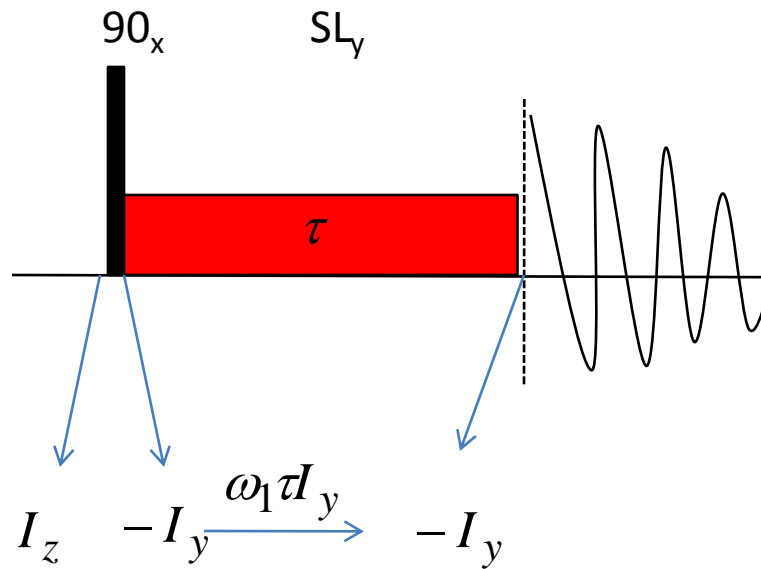
peak number 2

T1 = 19.8 error = 0.479

time	observed	calculated	difference
0.0625	-45	-44.1	-0.918
0.125	-43.7	-43.8	0.155
0.25	-42.5	-43.2	0.683
0.5	-42.6	-42	-0.558
1	-40.1	-39.6	-0.456
2	-35.1	-35	-0.0456
4	-25.9	-26.6	0.643
8	-10.9	-11.9	1.04
16	10.2	9.73	0.451
32	32.7	33.8	-1.15
64	48.2	49.3	-1.06
128	54.3	53	1.31



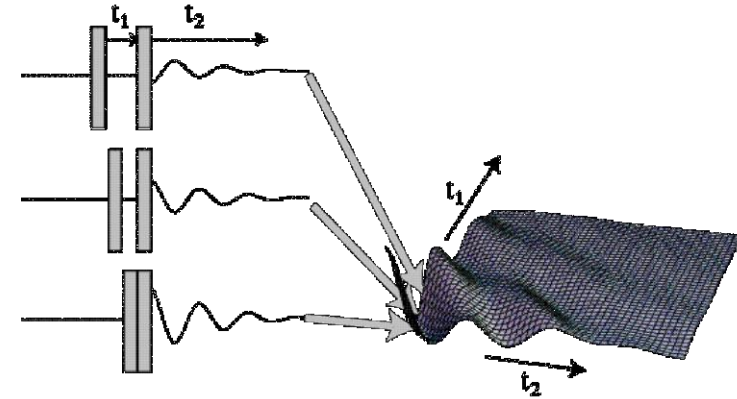
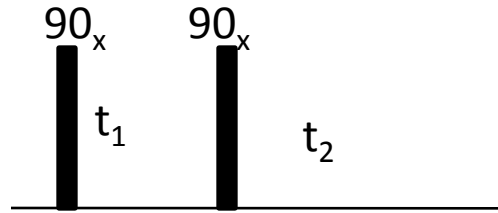
Spin Lock



During the delay τ the I_y coherences of the spins are locked along the y axis along which RF is applied. Other components rotate about y -axis (nutations) and decay.

2D Correlated Spectroscopy - COSY

$$\begin{array}{l}
 I_z \\
 \downarrow 90_x \\
 -I_y \\
 \downarrow (\omega_I I_z)t_1
 \end{array}$$



$$-I_y \cos(\omega_I t_1) + I_x \sin(\omega_I t_1)$$

$$\downarrow (\pi J_{IS} 2I_z S_z)t_1$$

$$-I_y \cos(\omega_I t_1) \cos(\pi J_{IS} t_1) + 2I_x S_z \cos(\omega_I t_1) \sin(\pi J_{IS} t_1)$$

$$+ I_x \sin(\omega_I t_1) \cos(\pi J_{IS} t_1) + 2I_y S_z \sin(\omega_I t_1) \sin(\pi J_{IS} t_1)$$

$$\downarrow 90_x$$

Diagonal Peak

Cross Peak

$$-I_z \cos(\omega_I t_1) \cos(\pi J_{IS} t_1) - 2I_x S_y \cos(\omega_I t_1) \sin(\pi J_{IS} t_1)$$

$$+ I_x \sin(\omega_I t_1) \cos(\pi J_{IS} t_1) - 2I_z S_y \sin(\omega_I t_1) \sin(\pi J_{IS} t_1)$$

2D Spectrum

Cross Peaks

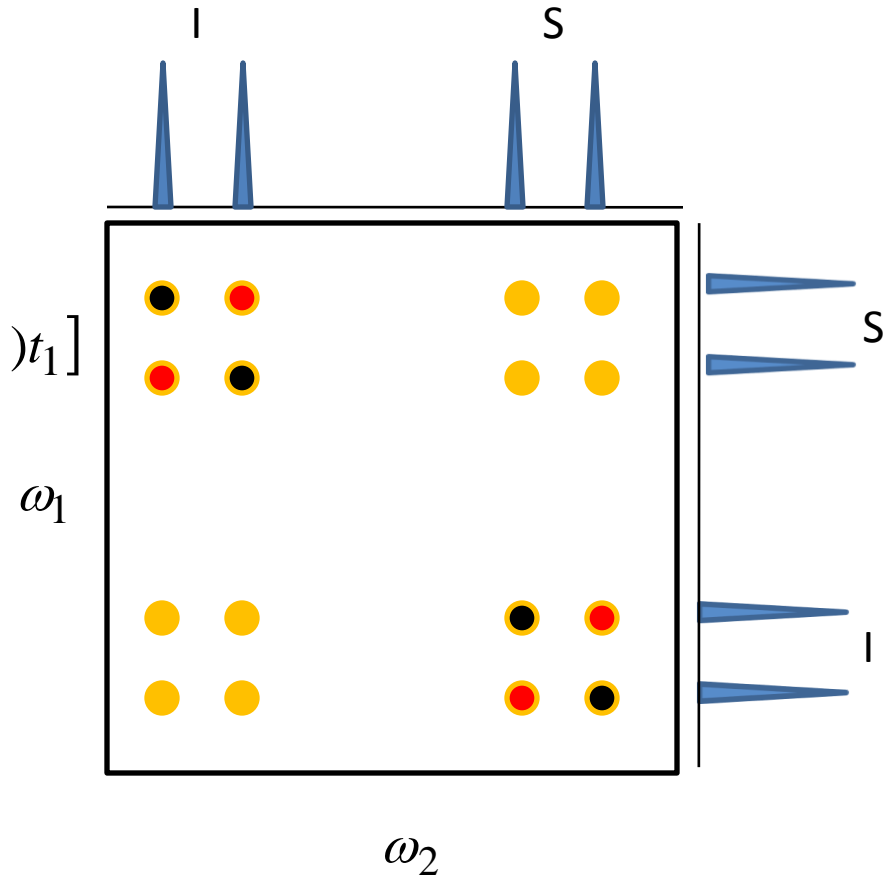
$$-2I_z S_y \sin(\omega_I t_1) \sin(\pi J_{IS} t_1)$$

$$= 2I_z S_y \times \frac{1}{2} [\cos(\omega_I + \pi J_{IS}) t_1 - \cos(\omega_I - \pi J_{IS}) t_1]$$

Diagonal Peaks

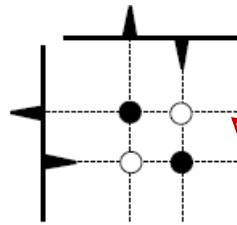
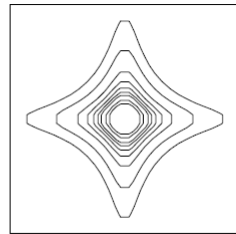
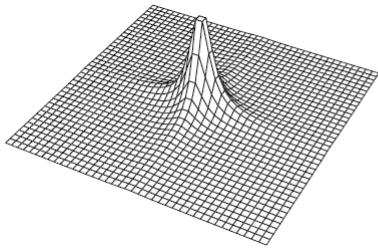
$$I_x \sin(\omega_I t_1) \cos(\pi J_{IS} t_1)$$

$$= I_x \times \frac{1}{2} [\sin(\omega_I + \pi J_{IS}) t_1 + \sin(\omega_I - \pi J_{IS}) t_1]$$

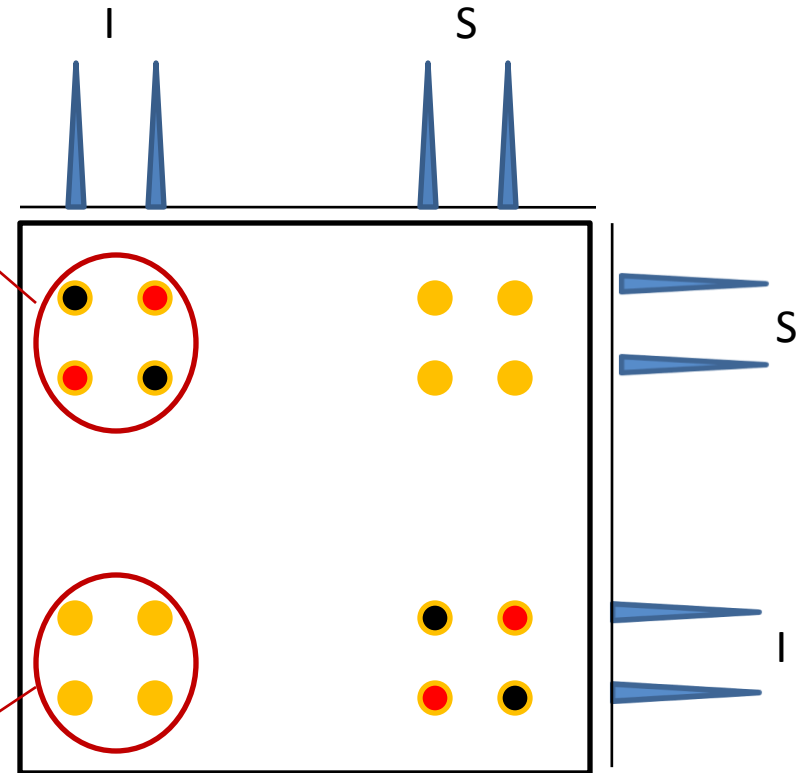
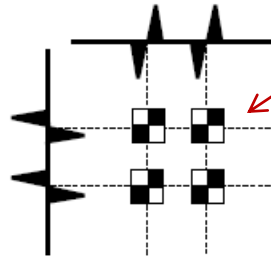
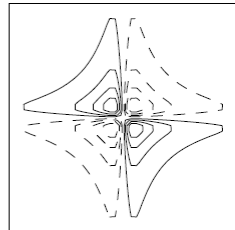
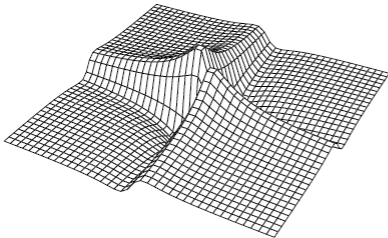


2D COSY Spectrum Line Shape

Cross Peaks



Diagonal Peaks



2D Nuclear Overhauser Spectroscopy - NOESY

$$\begin{array}{l}
 I_z \\
 \downarrow 90_x \\
 -I_y \\
 \downarrow (\omega_I I_z)t_1
 \end{array}$$

$$-I_y \cos(\omega_I t_1) + I_x \sin(\omega_I t_1)$$

$$\downarrow (\pi J_{IS} 2I_z S_z)t_1$$

$$-I_y \cos(\omega_I t_1) \cos(\pi J_{IS} t_1) + 2I_x S_z \cos(\omega_I t_1) \sin(\pi J_{IS} t_1)$$

$$+ I_x \sin(\omega_I t_1) \cos(\pi J_{IS} t_1) + 2I_y S_z \sin(\omega_I t_1) \sin(\pi J_{IS} t_1)$$

$$\downarrow 90_x$$

$$-I_z \cos(\omega_I t_1) \cos(\pi J_{IS} t_1) - 2I_x S_y \cos(\omega_I t_1) \sin(\pi J_{IS} t_1)$$

$$+ I_x \sin(\omega_I t_1) \cos(\pi J_{IS} t_1) - 2I_z S_y \sin(\omega_I t_1) \sin(\pi J_{IS} t_1)$$

$$\downarrow \text{Relaxation in } \tau_m$$

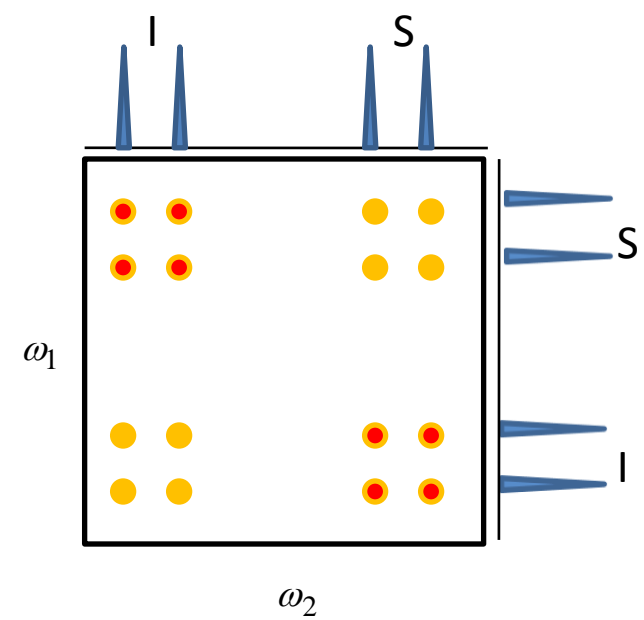
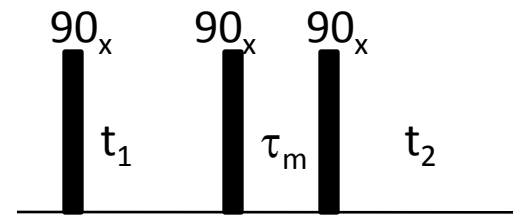
$$-I_z \cos(\omega_I t_1) \cos(\pi J_{IS} t_1) a_{II}(\tau_m)$$

$$-S_z \cos(\omega_I t_1) \cos(\pi J_{IS} t_1) a_{IS}(\tau_m)$$

$$\xrightarrow{90_x}$$

$$I_y \cos(\omega_I t_1) \cos(\pi J_{IS} t_1) a_{II}(\tau_m)$$

$$+ S_y \cos(\omega_I t_1) \cos(\pi J_{IS} t_1) a_{IS}(\tau_m)$$



2D Rotating Frame Overhauser Spectroscopy - ROESY

$$\begin{array}{l}
 I_z \\
 \downarrow 90_x \\
 -I_y \\
 \downarrow (\omega_I I_z)t_1
 \end{array}$$



$$-I_y \cos(\omega_I t_1) + I_x \sin(\omega_I t_1)$$

$$\downarrow (\pi J_{IS} 2I_z S_z)t_1$$

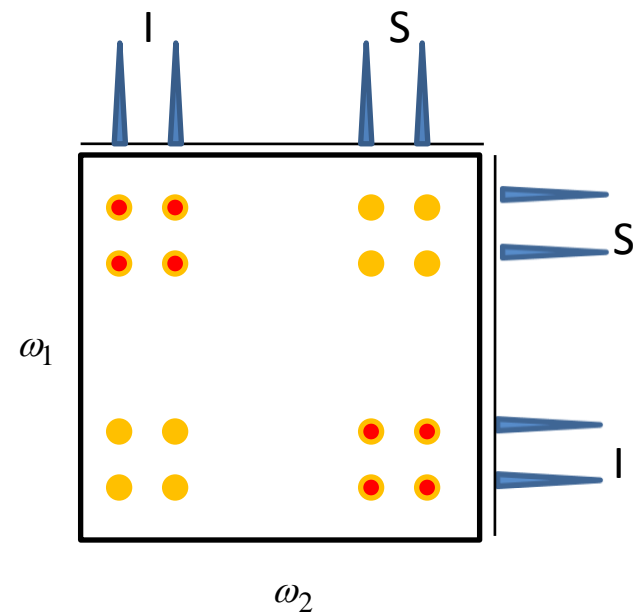
$$-I_y \cos(\omega_I t_1) \cos(\pi J_{IS} t_1) + 2I_x S_z \cos(\omega_I t_1) \sin(\pi J_{IS} t_1)$$

$$+ I_x \sin(\omega_I t_1) \cos(\pi J_{IS} t_1) + 2I_y S_z \sin(\omega_I t_1) \sin(\pi J_{IS} t_1)$$

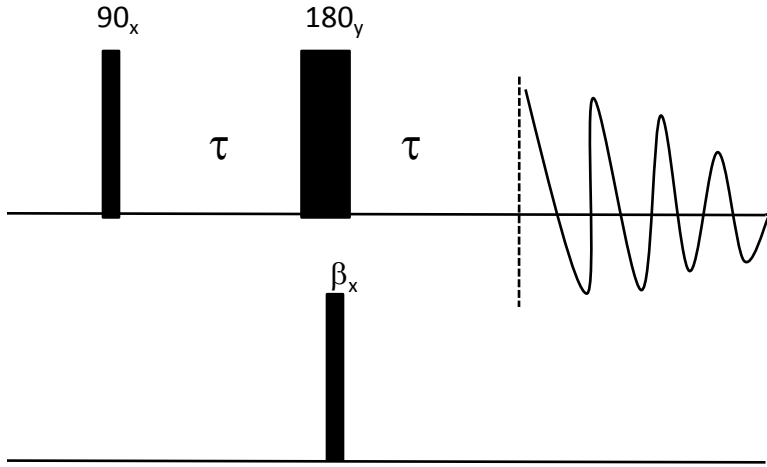
$$\downarrow S_{L_y} \text{ Relaxation in } \tau_m$$

$$-I_y \cos(\omega_I t_1) \cos(\pi J_{IS} t_1) a_{II}^r(\tau_m)$$

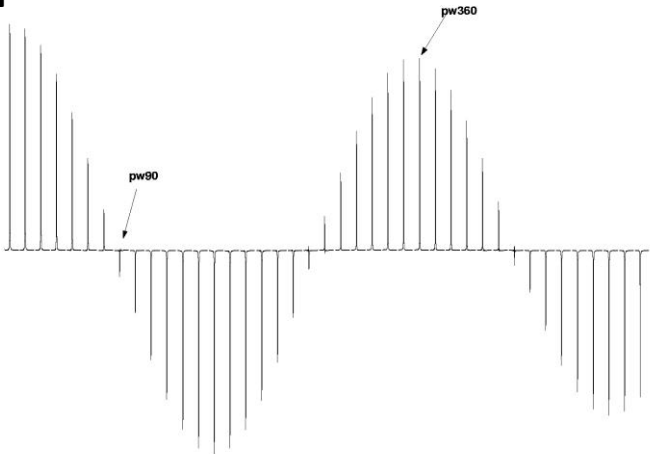
$$-S_y \cos(\omega_I t_1) \cos(\pi J_{IS} t_1) a_{IS}^r(\tau_m)$$



X-Nucleus PW Calibration



$\beta=0$ the signal is maximum.
 $\beta=90^\circ$ there is no signal as the multiple quantum coherence is unobservable.



$$\tau = \frac{1}{2J}$$

$$-I_y$$



$$(\pi J_{IS}\tau)2I_zS_z$$

$$-I_y \cos(\pi J_{IS}\tau) + 2I_xS_z \sin(\pi J_{IS}\tau)$$

$$= 2I_xS_z$$



$$\beta S_x + \pi I_y$$

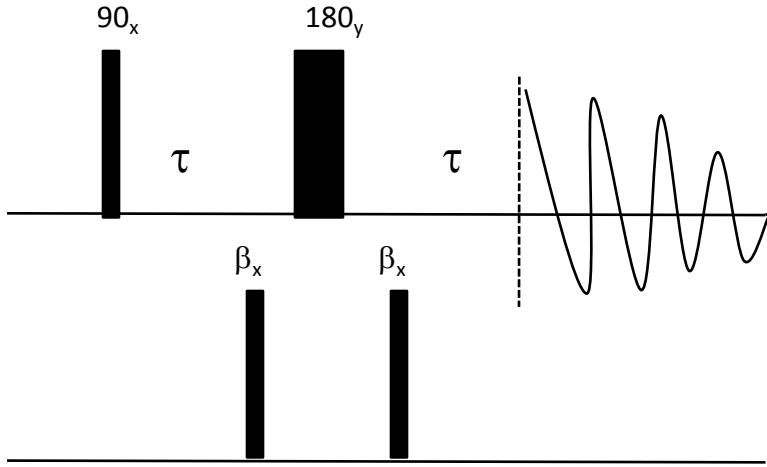
$$-2I_xS_z \cos \beta + 2I_xS_y \sin \beta$$



$$(\pi J_{IS}\tau)2I_zS_z$$

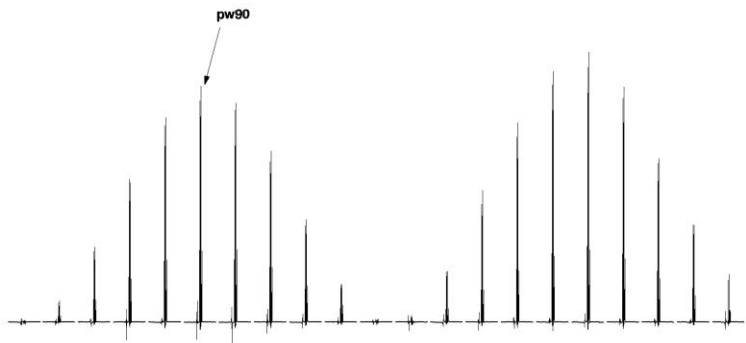
$$-I_y \cos \beta + 2I_xS_y \sin \beta$$

HMQC - type



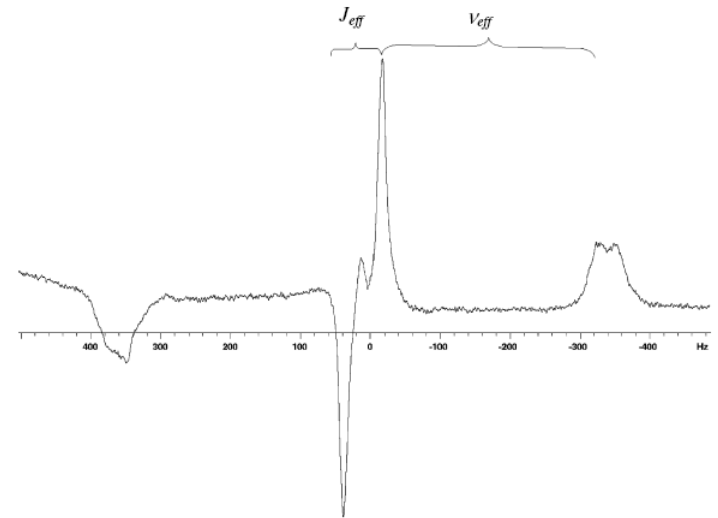
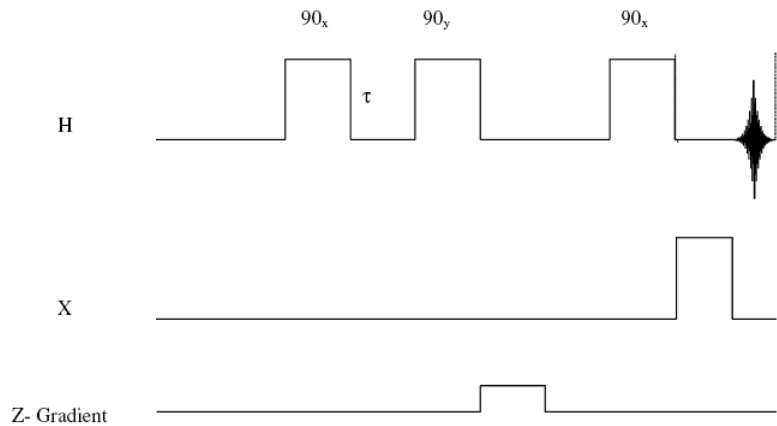
$$\tau = \frac{1}{2J}$$

$\beta=0$ the signal is maximum.
 $\beta=90^\circ$ the signal is maximum.



$$\begin{aligned}
 & -I_y \quad \downarrow \quad (\pi J_{IS}\tau)2I_zS_z \\
 & -I_y \cos(\pi J_{IS}\tau) + 2I_xS_z \sin(\pi J_{IS}\tau) \\
 & = 2I_xS_z \\
 & \quad \downarrow \quad \beta S_x + \pi I_y \\
 & -2I_xS_z \cos \beta + 2I_xS_y \sin \beta \\
 & \quad \downarrow \quad \beta S_x \\
 & 2I_xS_y \sin \beta \cos \beta + 2I_xS_z \sin^2 \beta \\
 & \quad \downarrow \quad (\pi J_{IS}\tau)2I_zS_z \\
 & 2I_xS_y \sin \beta \cos \beta + I_y \sin^2 \beta
 \end{aligned}$$

PWX-Calibration by Nutation



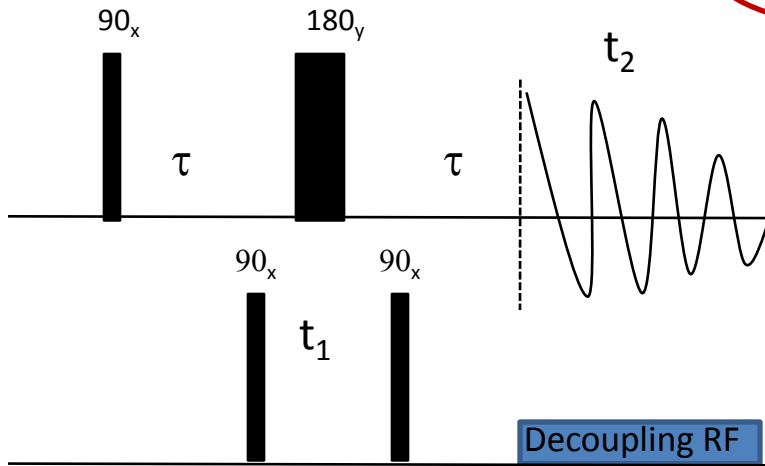
$$\omega_1 \tau_p = \frac{\pi}{2}$$

$$\tau_p = \frac{\pi}{2} \times \frac{1}{\omega_1} = \frac{1}{4\nu_1 (\text{Hz})}$$

Ref: IDEAL- A fast single scan method for X pulse width calibration
 Nagarajan Murali, J. Magn. Reson 183, 142, 2006

2D-HMQC

$$\tau = \frac{1}{2J_{IS}}$$



$$-I_y$$



$$(\pi J_{IS}\tau)2I_zS_z$$

$$-I_y \cos(\pi J_{IS}\tau) + 2I_xS_z \sin(\pi J_{IS}\tau)$$

$$= 2I_xS_z$$



$$\frac{\pi}{2}S_x$$

$$2I_xS_y$$



$$\pi I_y, (\omega_s S_z)t_1$$

$$2I_xS_y \cos(\omega_s t_1) - 2I_xS_x \sin(\omega_s t_1)$$



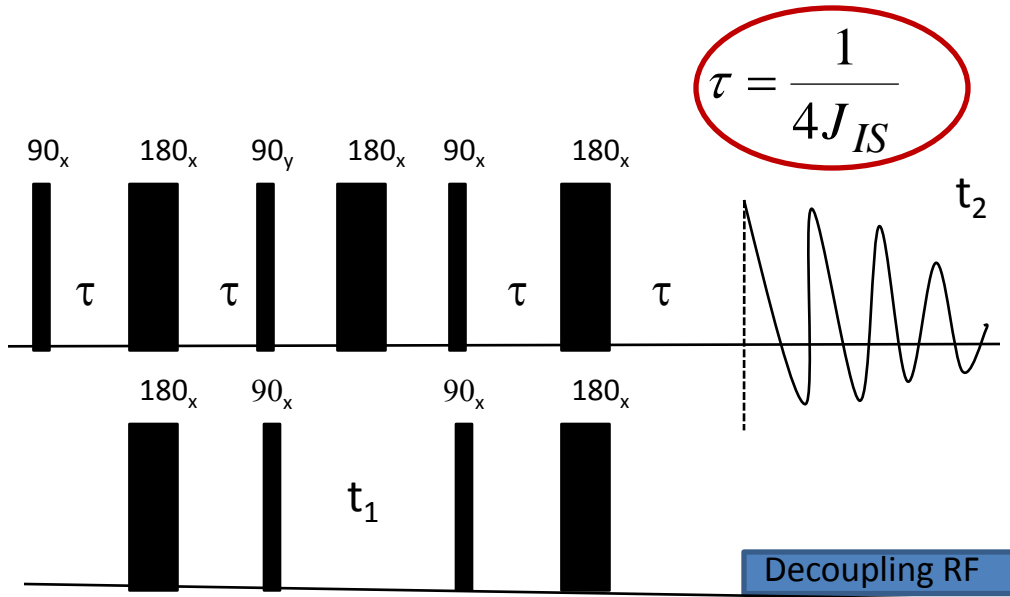
$$\frac{\pi}{2}S_x$$

$$(\pi J_{IS}\tau)2I_zS_z$$

$$I_y$$

$$\leftarrow 2I_xS_z \cos(\omega_s t_1) + 2I_xS_x \sin(\omega_s t_1)$$

2D-HSQC



$$\tau = \frac{1}{4J_{IS}}$$

$$\begin{aligned}
 & -I_y \\
 & \pi I_x + \pi S_x \downarrow (\pi J_{IS} 2\tau) 2I_z S_z \\
 & I_y \cos(\pi J_{IS} 2\tau) - 2I_x S_z \sin(\pi J_{IS} 2\tau) \\
 & = -2I_x S_z
 \end{aligned}$$

$$\begin{aligned}
 & \downarrow \frac{\pi}{2} I_y + \frac{\pi}{2} S_x \\
 & -2I_z S_y
 \end{aligned}$$

$$\begin{aligned}
 & \downarrow \pi I_x, (\omega_s S_z) t_1 \\
 & -2I_z S_y \cos(\omega_s t_1) + 2I_z S_x \sin(\omega_s t_1)
 \end{aligned}$$

$$\downarrow \frac{\pi}{2} I_x + \frac{\pi}{2} S_x$$

$$\begin{aligned}
 & \left(\frac{\pi J_{IS} 2\tau}{\pi I_x + \pi S_x} \right) 2I_z S_z - 2I_y S_z \cos(\omega_s t_1) - 2I_y S_x \sin(\omega_s t_1) \\
 & \left(\frac{\pi J_{IS} 2\tau}{\pi I_x + \pi S_x} \right) 2I_z S_z
 \end{aligned}$$

$$I_x$$

2D-HSQC/HMQC

For each IS pair there will be one peak.

If there are homonuclear coupling that will split the lines along the Proton (I) dimension.

