Bloch Equations

Description of the evolution of the macroscopic magnetic vector by the phenomenological Bloch equations

R.F. Magnetic Field

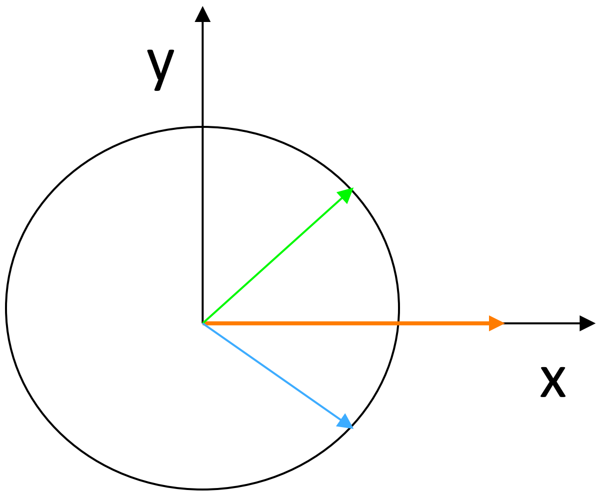
- Nuclear magnetic resonance is obtained by applying an electromagnetic radiation in the radiofrequency range
- The radiofrequence, owing to the way it is originated, is coherent and linearly polarized

Rotating Magnetic Field B_1

A linearly polarized magnetic field can be represented as the sum of two counterotating circularly polarized fields

Mazinga ed il pugno atomico rotante

http://animeoltre.altervista.org/robot/grandemazinga.html



The xy plane is perpendicular to z axis, which is coincident with the directionof the static magnetic field $\mathbf{B_0}$

B_{rf} is the linearly polarized r.f. magnetic field

$$B_{rf}(t)=2B_1\cos(\omega_{rf}t+\phi)\mathbf{e_x}$$

$$B_{rf}(t)= B_1\cos(\omega_{rf}t+\phi)\mathbf{e_x} + i\ B_1\sin(\omega_{rf}t+\phi)\mathbf{e_y}$$
$$+\ B_1\cos(\omega_{rf}t+\phi)\mathbf{e_x} - i\ B_1\sin(\omega_{rf}t+\phi)\mathbf{e_y}$$

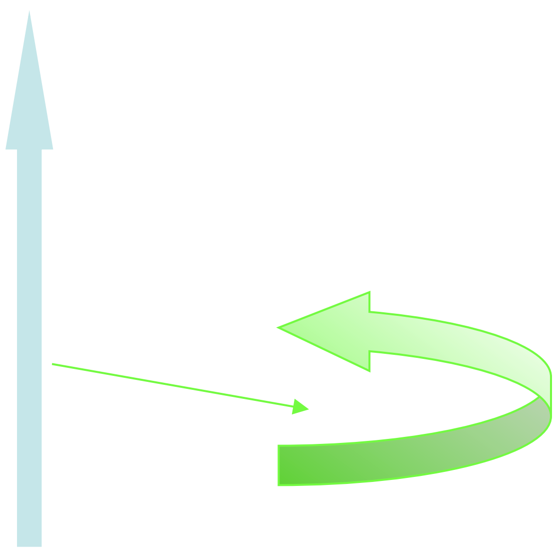
recalling the Euler formula:

$$e^{i\alpha}=\cos\alpha+i\ \mathrm{sen}\alpha$$

$$B_{rf}(t)=B_1\exp[i(\omega_{rf}t+\phi)] + B_1\exp[-i(\omega_{rf}t+\phi)]$$

The effect is exclusively due to the rotating field with the same sense as Larmor precession of the examined nucleus (which depends on the sign of γ_N), the latter field is disregarded

$B_{rf}(t)$ can be represented by $B_1\exp[i(\omega_{rf}t+\phi)]$



The ensamble of nuclei is affected both by the permanent static magnetic field, B_0, and by the r.f. field, $B_{rf}(t)$. The latter may be applied just during certain times, with the aid of the gates of radiofrequency.

Motion of a Magnetic Moment in the presence of a Mgnetic Field

It is described by the following equation

$$\frac{d\vec{M}(t)}{dt} = \gamma \vec{M}(t) \wedge \vec{B}(t)$$

Actually, they are 3 coupled differintial equations.

it can be checked by expliciting the vector product.

This equation is based on:

A magnetic moment in the presence of a magnetic field is affected by a torque

$$\vec{\Gamma} = \vec{M} \wedge \vec{B}$$

that acts to bring it to the position of minimum energy, i.e. parallel to the magnetic field

$$E = -\vec{M} \cdot \vec{B}$$

A well known example is the compass needle, which aligns with the earth magnetic field

since $\vec{M} = \gamma \vec{l}$ e $\dfrac{d\vec{l}}{dt} = \vec{\Gamma}$

$$\frac{d\vec{M}}{dt} = \gamma \frac{d\vec{l}}{dt} = \gamma\vec{\Gamma} = \gamma\vec{M} \wedge \vec{B}$$

<u>vector product by use of the determinant</u>

$$\left| \begin{array}{ccc|cc} i & j & k & i & j \\ M_x & M_y & M_z & M_x & M_y \\ B_x & B_y & B_z & B_x & B_y \end{array} \right.$$

i, **j** and **k** are unit vectors

$$i(M_y B_z - M_z B_y)$$

$$j(M_z B_x - M_x B_z)$$

$$k(M_x B_y - M_y B_x)$$

equations to be solved:

$$\frac{dM_x(t)}{dt} = \gamma\left[M_y(t)B_z - M_z(t)B_y(t)\right]$$

$$\frac{dM_y(t)}{dt} = \gamma\left[M_z(t)B_x(t) - M_x(t)B_z\right]$$

$$\frac{dM_z(t)}{dt} = \gamma\left[M_x(t)B_y(t) - M_y(t)B_x(t)\right]$$

The method to solve these equations is to employ a **rotating frame**, where the r.f. magnetic field is static. In this way the **coefficients** are time **independent**.

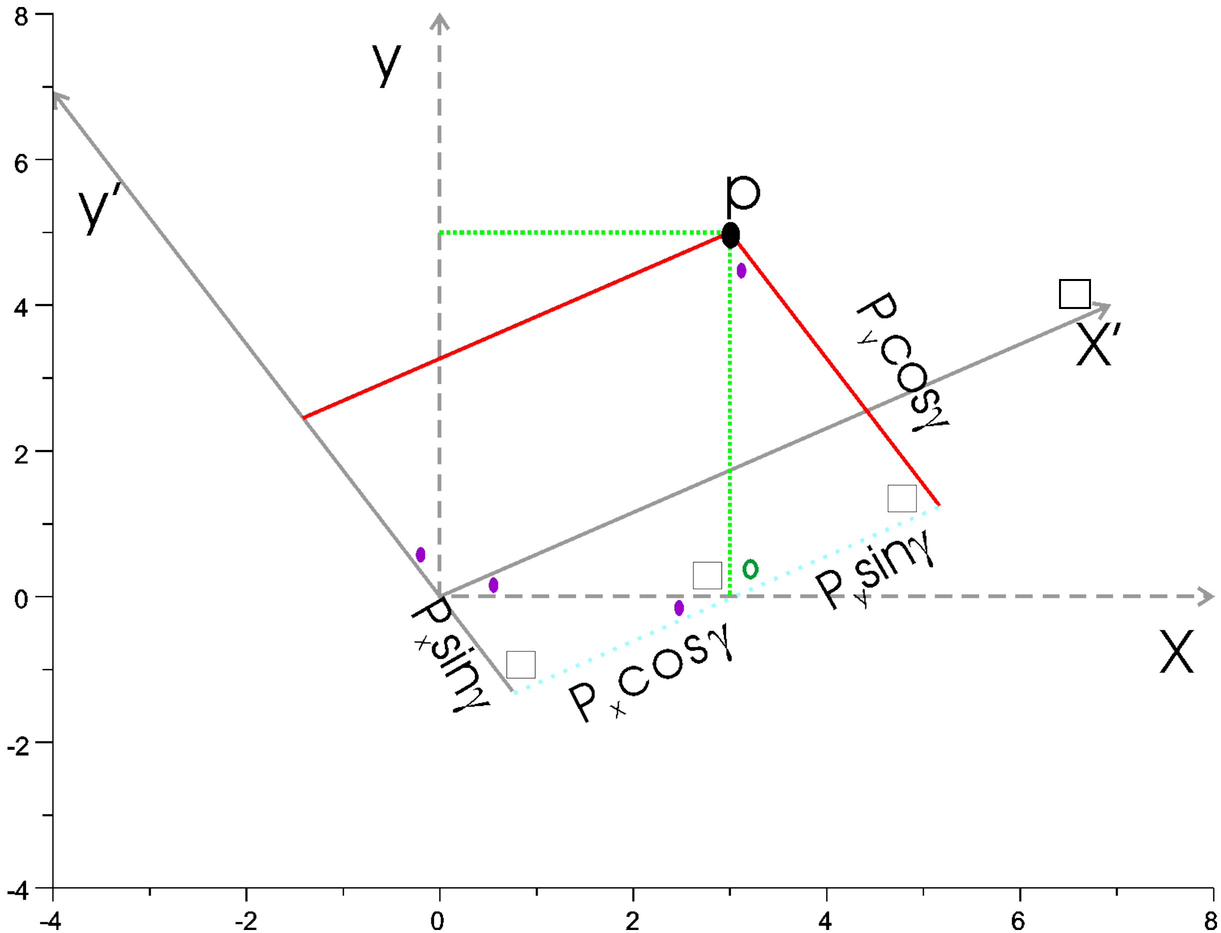
$$\frac{dM_x^r(t)}{dt} = \gamma\left[M_y^r(t)B_z^{eff} - M_z^r(t)B_y^{eff}\right]$$

$$\frac{dM_y^r(t)}{dt} = \gamma\left[M_z^r(t)B_x^{eff} - M_x^r(t)B_z^{eff}\right]$$

$$\frac{dM_z^r(t)}{dt} = \gamma\left[M_x^r(t)B_y^{eff} - M_y^r(t)B_x^{eff}\right]$$

Axes Rotations

- γ rotation angle about z axis



$y' = y\cos\gamma - x\,\mathrm{sen}\gamma$

$x' = x\cos\gamma + y\,\mathrm{sen}\gamma$

e.g.. P(x=3, y=5) γ= 30° y’ =? x’ =?

$$x' = x\cos\gamma + y\sin\gamma = 3\frac{\sqrt{3}}{2} + 5\frac{1}{2} = 5.098$$

$$y' = -x\sin\gamma + y\cos\gamma = -3\frac{1}{2} + 5\frac{\sqrt{3}}{2} = 2.83$$

The point P position can be represented by the vector r_P

with components x and y in the former frame

and x’ and y’ in the new axes system

Transform Matrix for Axes Rotation

Vector components: column matrix

2D

$$\begin{vmatrix} x \\ y \end{vmatrix}$$

3D

$$\begin{vmatrix} x \\ y \\ z \end{vmatrix}$$

The transform matrix is a square matrix of the suited coefficients 2x2 in the former case and 3x3 in the latter

Transform by rotating of a γ angle about z

$$\bar{r}'_P = \bar{\bar{T}}(\gamma) r_P$$

$$\begin{vmatrix} x' \\ y' \end{vmatrix} = \begin{vmatrix} \cos\gamma & \sin\gamma \\ -\sin\gamma & \cos\gamma \end{vmatrix} \begin{vmatrix} x \\ y \end{vmatrix} = \begin{vmatrix} x\cos\gamma + y\sin\gamma \\ -x\sin\gamma + y\cos\gamma \end{vmatrix}$$

trsform matrix

Trasform matrix for rotation of a γ about z in 3 D

$$\overline{\overline{T}}_z(\gamma) = \begin{vmatrix} \cos\gamma & \sin\gamma & 0 \\ -\sin\gamma & \cos\gamma & 0 \\ 0 & 0 & 1 \end{vmatrix}$$

NB to transform from the lab frame to the rotating frame

$\gamma = \omega_{RF} t$

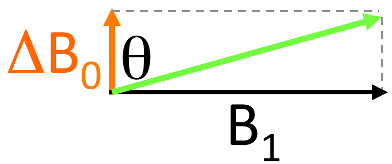
Magnetization Evolution in the Rotating Frame

$$\frac{d\vec{M}^r(t)}{dt} = \gamma \vec{M}^r(t) \wedge \vec{B}^r_{eff}$$

$$\vec{B}^r_{eff} = \begin{vmatrix} B^r_x \\ B^r_y \\ B_0 + \dfrac{\omega_{RF}}{\gamma} \end{vmatrix}$$

efficient magnetic field
in the rotating frame

Efficient Magnetic Field B_{eff}



$$\vec{B}^{r}_{eff} = \begin{vmatrix} 0 \\ B_1 \\ \Delta B_0 \end{vmatrix}$$

the rotating frame is such that B_1 lies on y' axis

modulus of B_{eff}

$$B^{r}_{eff} = \sqrt{B_1^2 + \Delta B_0^2}$$

Larmor frequency

$\omega_0 = -\gamma B_0$

$$\Delta B_0 = B_0 + \frac{\omega_{RF}}{\gamma} = -\frac{\omega_0}{\gamma} + \frac{\omega_{RF}}{\gamma} =$$

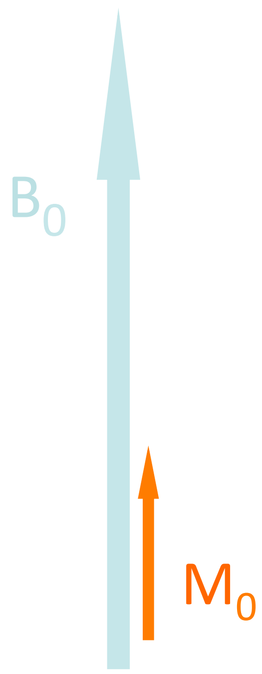
$$= -\frac{\Omega_0}{\gamma}$$

with $\Omega_0 = \omega_0 - \omega_{RF}$

For the isofrequency case $\omega_{RF} = \omega_0$, $\Omega_0 = 0$, $\Delta B_0 = 0$

thus B_{eff} coincides with B_1

Pulsed Experiment in the Isofrequency Case



- At equilibrium M is aligned with the z axis (M_0)
- the e.m. radiation of $\nu_{RF}=\nu_0$ is applied
- The motion of the M vector is described in a frame with y' axis coinciding with the r.f. rotating magnetic field, B_1

Magnetic Field B in the Rotating Frame

$$\vec{B}_1^r = \overline{\overline{T}}\vec{B}_1^{LAB}$$

The most general B^{LAB} corresponds to

$$\vec{B}^{LAB} = \begin{vmatrix} B_1\cos(\omega_{RF}t+\phi) \\ B_1\sin(\omega_{RF}t+\phi) \\ B_0 \end{vmatrix}$$

$$\vec{B}^r = \begin{vmatrix} \cos\omega_{RF}t & \sin\omega_{RF}t & 0 \\ -\sin\omega_{RF}t & \cos\omega_{RF}t & 0 \\ 0 & 0 & 1 \end{vmatrix} \begin{vmatrix} B_1\left[\cos\omega_{RF}t\cos\phi - \sin\omega_{RF}t\sin\phi)\right] \\ B_1\left[\sin\omega_{RF}t\cos\phi + \cos\omega_{RF}t\sin\phi)\right] \\ B_0 \end{vmatrix}$$

Magnetic Field B_1 in the Rotating Frame

$$\vec{B}_1^r = \begin{vmatrix} B_1 \cos\phi \\ B_1 \sin\phi \\ 0 \end{vmatrix}$$

Choosing sensitively the phase angle (ϕ) B_1 may lie

on either axis x' or y' or –x' or –y' (phase shift by 90° and multiples)

or at intermediate positions for phase shifts lower than 90° (not implemented in the oldest spectrometers)

Differential Equations for the Motion of M in the Rotating Frame: Isofrequency

$$\frac{d\vec{M}^r(t)}{dt} = \gamma \vec{M}^r(t) \wedge \vec{B}^r_{eff}$$

$$B^r_{eff} = \begin{vmatrix} 0 \\ B_1 \\ 0 \end{vmatrix}$$

$$\frac{dM^r_x(t)}{dt} = -\gamma M^r_z(t) B_1$$

$$\frac{dM^r_y(t)}{dt} = 0$$

$$\frac{dM^r_z(t)}{dt} = \gamma M^r_x(t) B_1$$

the systems of to coupled differential equations has to be solved

- The forme is derived again with respect to t

$$\frac{d^2 M_x^r}{dt^2} = -\gamma B_1 \frac{dM_z^r}{dt}$$

- then it is sustituted for the third

$$\frac{d^2 M_x^r}{dt^2} = -\gamma^2 B_1^2 M_x^r$$

The so obtained equation is very common, e.g. in the classical harmonic oscillator

$$\frac{d^2 y}{dt^2} + \omega^2 y = 0$$

Its general solution is:

$$M_x^r = C_1 \cos(-\gamma B_1 t) + C_2 \mathrm{sen}(-\gamma B_1 t)$$

C_1 and C_2 are two constants that must be determined on the basis of the initial conditions:

- t=0 $M_x^r(0) = 0$, therefore $C_1 = 0$
- Max is M_0 (when il sin=1), thus $C_2 = M_0$

$$M_x^r(t) = M_0 \sin(-\gamma B_1 t)$$

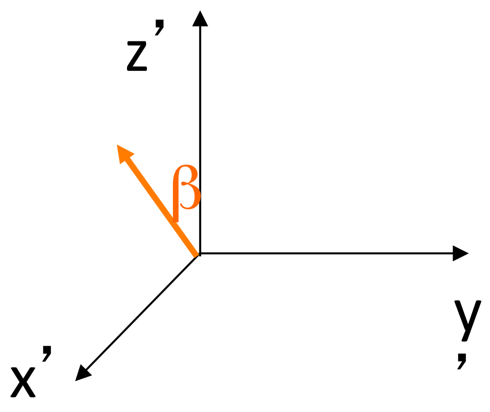
sometimes $-\gamma B_1$ is written as ω_1 and called Rabi frequency

The espression found for M_x^r is substituted in the differential equation for M_z^r:

$$\frac{dM_z^r}{dt} = \gamma B_1 M_0 \sin(-\gamma B_1 t)$$

$$M_z^r(t) = M_0 \cos(-\gamma B_1 t)$$

- The applicaton of an oscillating magnetic field, in the plane perpendicular to the intrumental static field, with frequency equal to the Larmor fequency induces M rotation about the axis on which B_1 in lying.
- In the present case its rotation takes place in the zx plane
- The rotation angle $\beta = -\gamma B_1 t$



If B_1, lies along another axis:

B_1	M* rotates in the plane
x	z(-y)
-x	zy
-y	z(-x)

Measurement of the $\pi/2$ Pulse Length

- The NMR signal is proprotional to the component of magnetization in the plane perpendicular to B_0
- Acquiring various signaks obtained upon incresing the r.f. pulse length a sine dependence on time must be observed
- The first maximum of the sinus curve occurs at $-\gamma B_1 t = \pi/2$

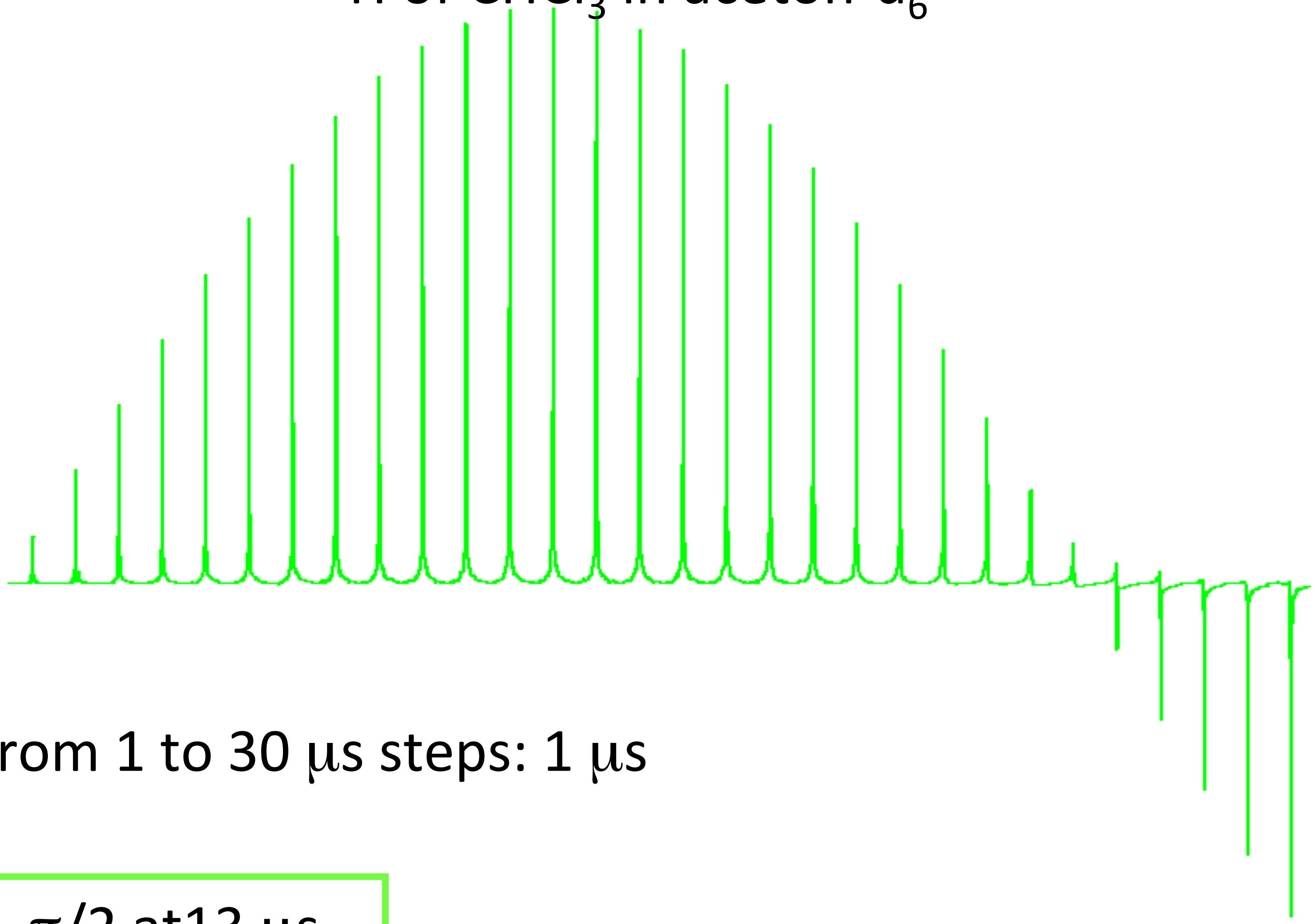
Measurement of $\pi/2$ Pulse Length

- γ depends on the nucleus
- B_1 depends on the instrument, usually is such to have $t_{\pi/2}$ on the order of 10 μs
- if $\pi/2$= 10 μs for ^{1}H (γ_H=26.75·10^7 radT^{-1}s^{-1})

B_1= 5.84·10^{-4} T

- The trasmitter for the heternuclei is more powerful, e.g. if $\pi/2$ = 10 μs for ^{13}C (γ_C= 6.73·10^7 radT^{-1}s^{-1}) B_1= 23.3 ·10^{-4} T
- if $\pi/2$ for ^{15}N (γ_N= -2.71 · 10^7 radT^{-1}s^{-1}) is 52 μs: B_1=11.15 ·10^{-4} T

^1H of $CHCl_3$ in aceton-d_6

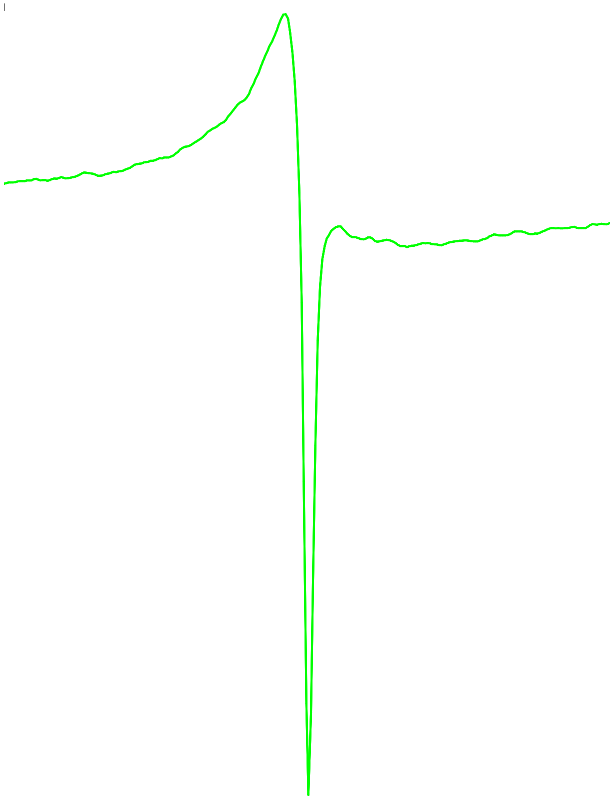


t from 1 to 30 μs steps: 1 μs

π/2 at13 μs

Inhomogeneity of B_1

B_1 may slightly differ over the sample



the signal should be zero for a π pulse