

# Relaxation Process in NMR

## **Spin-Lattice Relaxation, $T_1$**

The absorbed energy is lost through vibrational and rotational motion to the magnetic components of the “lattice” of the sample. Problem: The temperature of the sample can rise over time.

Spin-Lattice relaxation processes cause an exponential decay of the excited state population. The more viscous a sample is, or the more restricted the motion of a molecule is, the longer the  $T_1$ .

Spin-Lattice relaxation is the slowest of the relaxation processes.

## **Spin-Spin Relaxation, $T_2$**

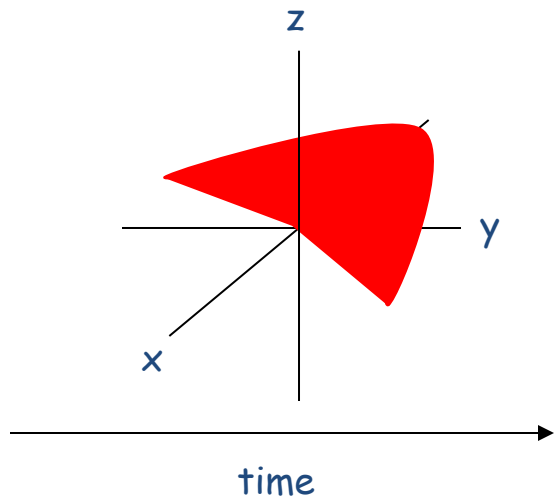
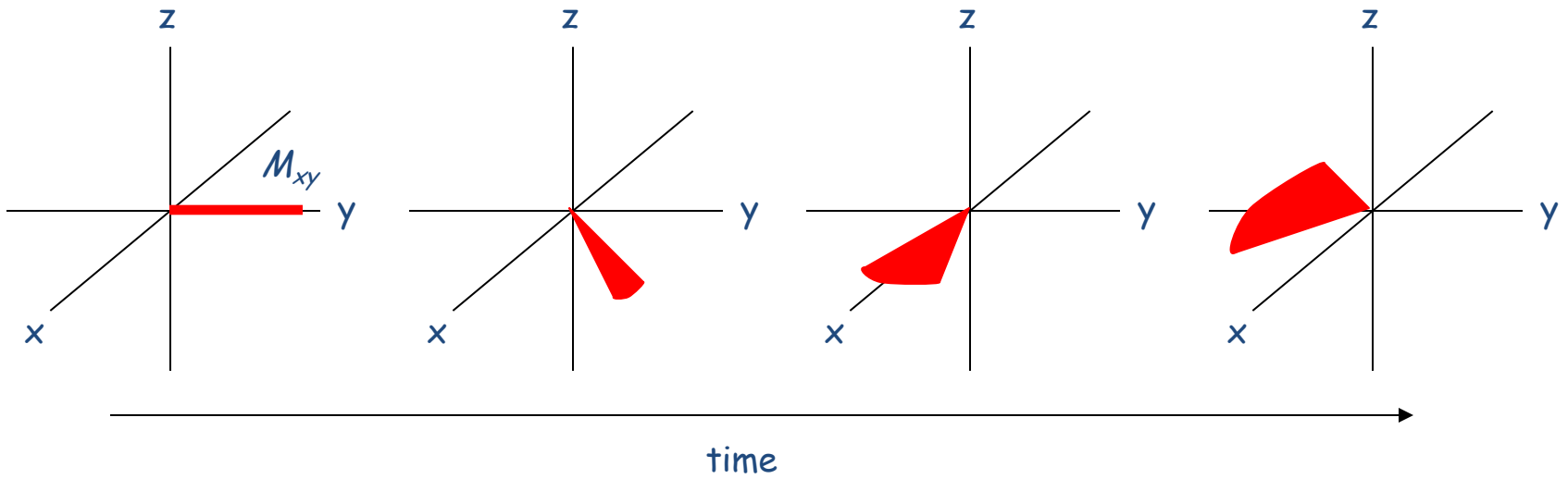
Several processes are “lumped” under this term, but one of the predominant techniques is spin diffusion, a process requiring neighboring nuclei to have the same precession rates, but different magnetic quantum numbers.

Another cause is a disruption in the homogeneity of the magnetic field through the sample caused by the sample itself. (*e.g.* – formation of dimers, trimers, *etc.* that change the relaxation rates of nuclei.)

Spin-Lattice relaxation is the slowest of the relaxation processes ( $T_1 > T_2$ ). Thus,  $T_2$  is the primary influence on line broadening in the spectrum.

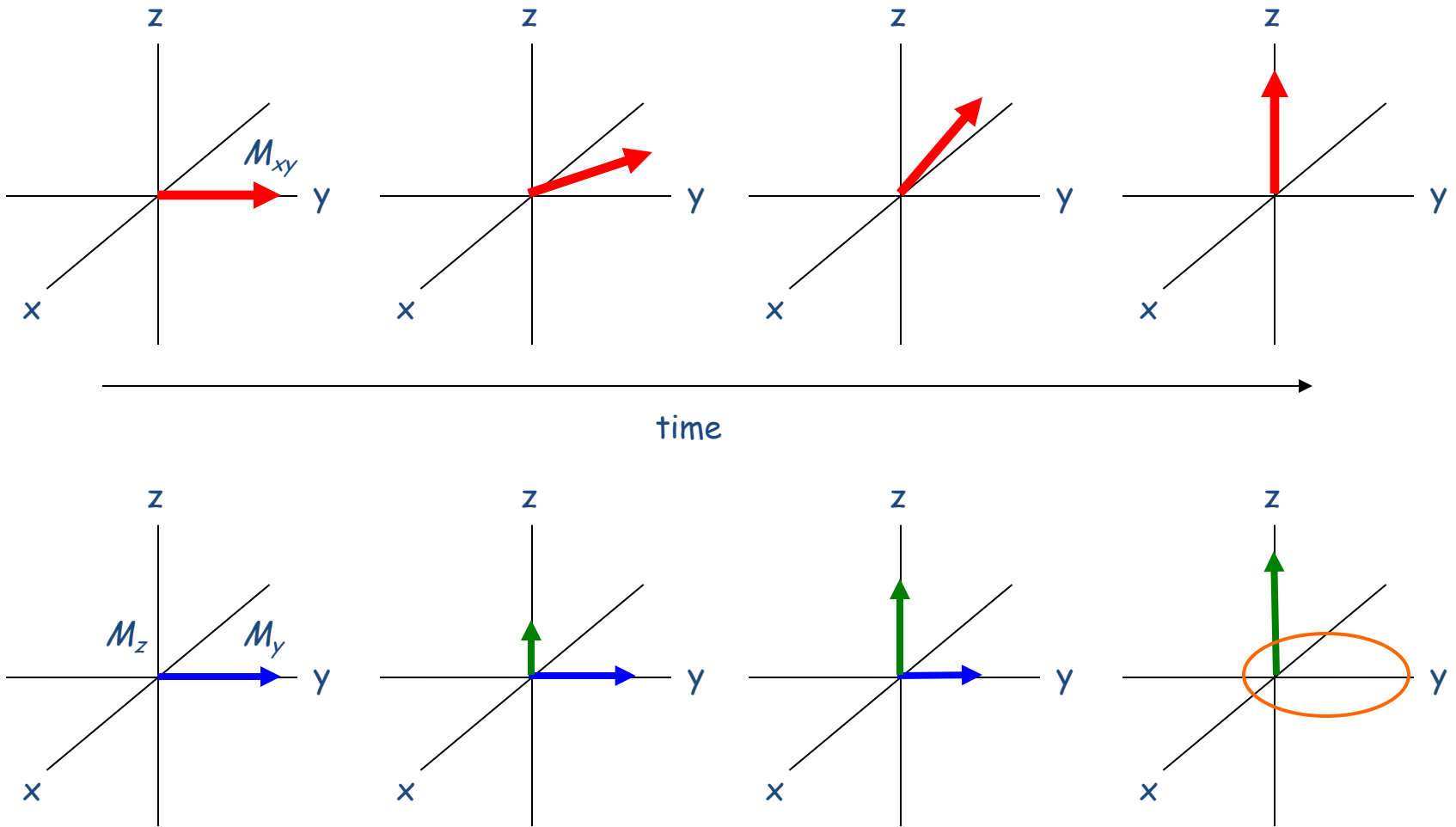
- ◆ **Spin-lattice relaxation** converts the excess energy into translational, rotational, and vibrational energy of the surrounding atoms and molecules (the lattice).
- ◆ **Spin-spin relaxation** transfers the excess energy to other magnetic nuclei in the sample.

# Spin-Spin Relaxation, $T_2$



$$M_{xy} = M_{xy0} \exp\left(\frac{-t}{T_2}\right)$$

# Longitudinal Spin-Lattice Relaxation, $T_1$



# Longitudinal Spin-Lattice Relaxation, $T_1$

The time constant,  $T_1$ , describes how  $M_z$  returns to its equilibrium value. The equation governing this behavior as a function of the time  $t$  after its displacement is:

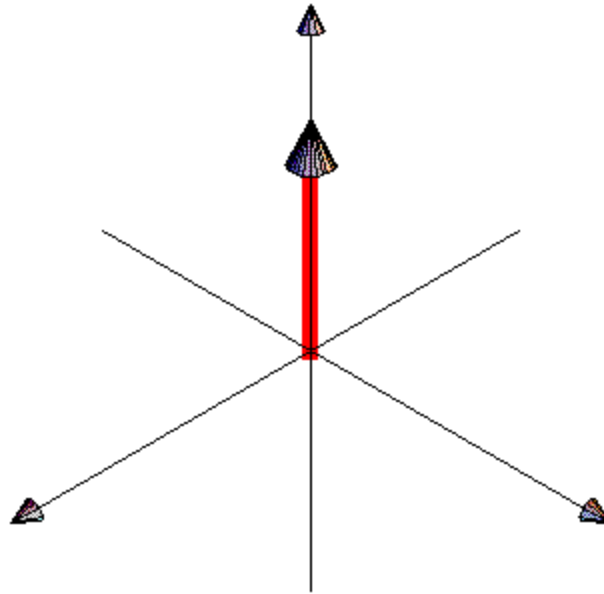
$$M_z = M_0 \left( 1 - \exp\left(\frac{-t}{T_1}\right) \right) \text{ for } \text{pw} \leq 90^\circ$$

$T_1$  is therefore defined as the time required to change the Z component of magnetization by a factor of e.

If the net magnetization is placed along the “-Z” axis (*i.e.* –  $\text{pw} = 180^\circ$ ), it will gradually return to its equilibrium position along the “+Z” axis at a rate governed by  $T_1$ . The equation governing this behavior as a function of the time  $t$  after its displacement is:

$$M_z = M_0 \left( 1 - 2 \exp\left(\frac{-t}{T_1}\right) \right) \text{ for } \text{pw} = 180^\circ$$

# Relaxation of $M_{xy}$ During Fourier Transform NMR

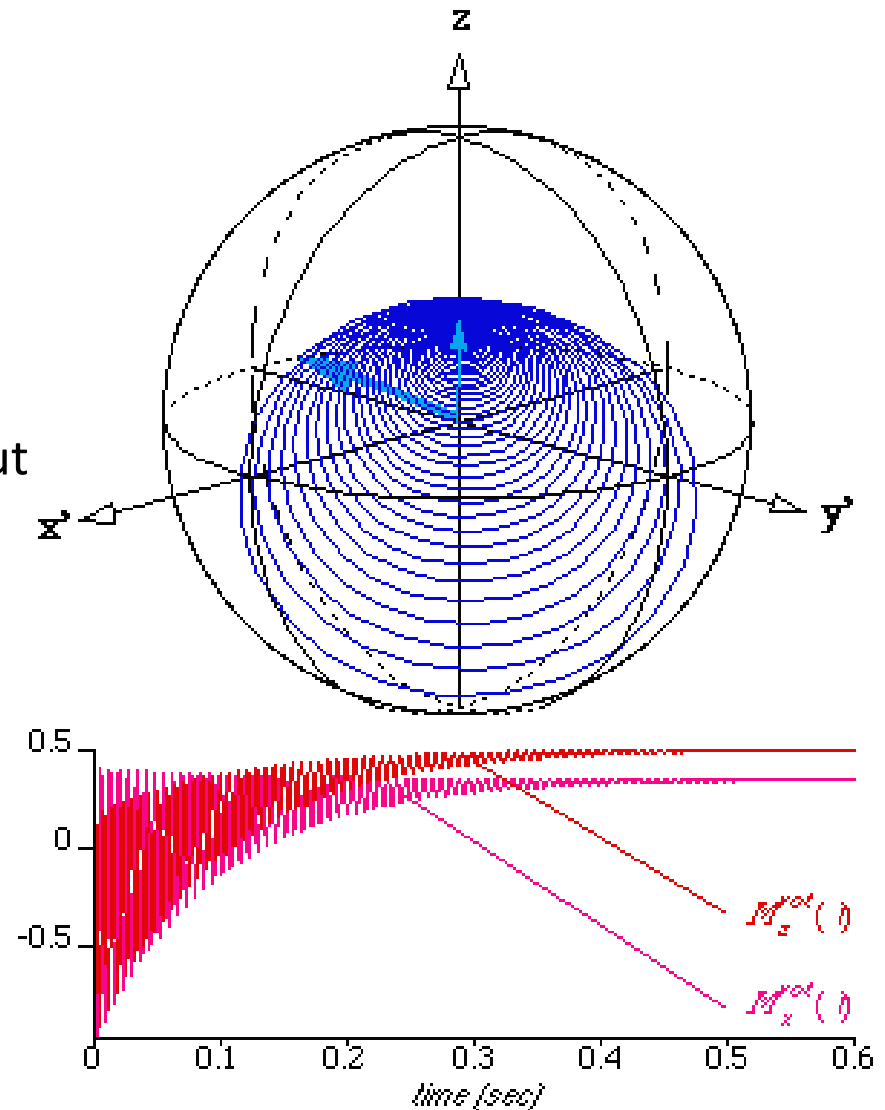


Responses Due to  $T_1$  AND  $T_2$

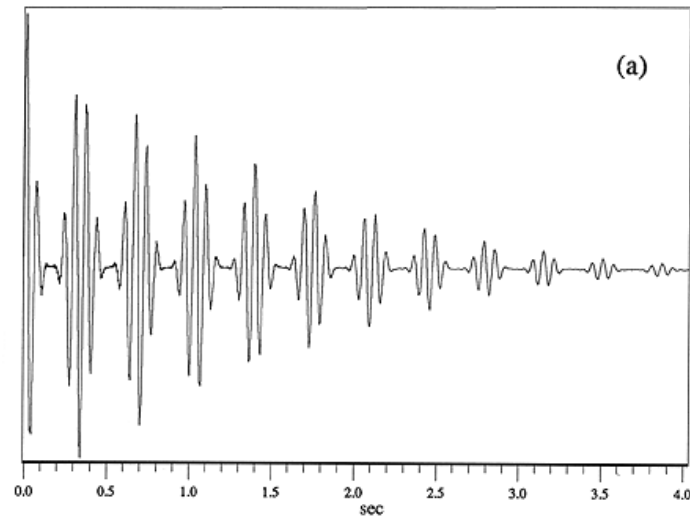
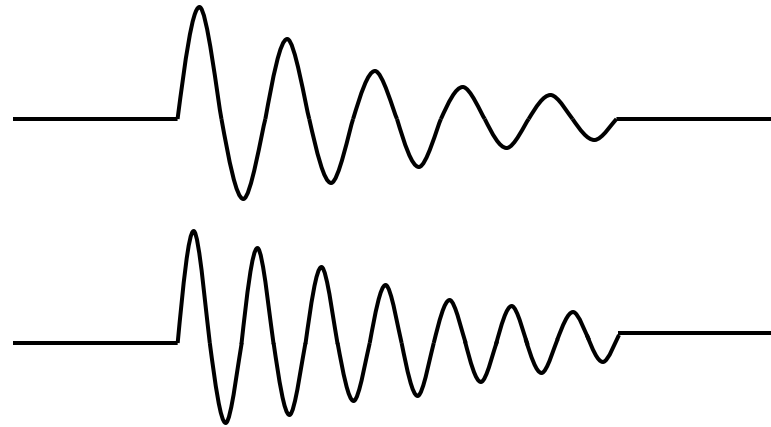
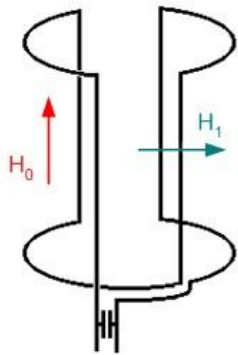
# The Bloch Equations

## magnetization vector's trajectory

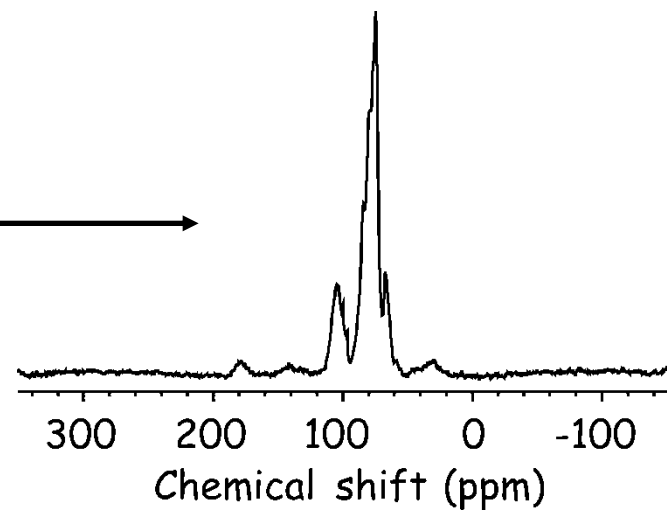
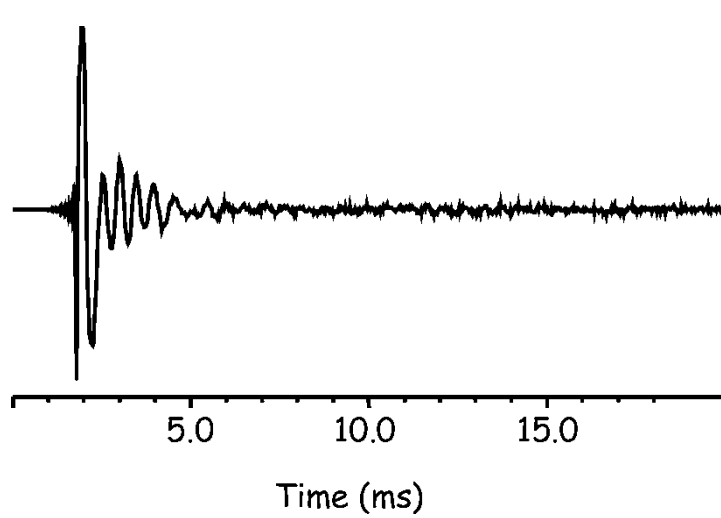
The initial vector,  $\mathbf{M}_0$ , evolves under the effects of  $T_1$  &  $T_2$  relaxation and from the influence of an applied rf-field. Here, the magnetization vector  $\mathbf{M}(t)$  precesses about an effective field axis at a frequency determined by its offset. It ends up at a "steady state" position as depicted in the lower plot of x- and y- magnetizations.

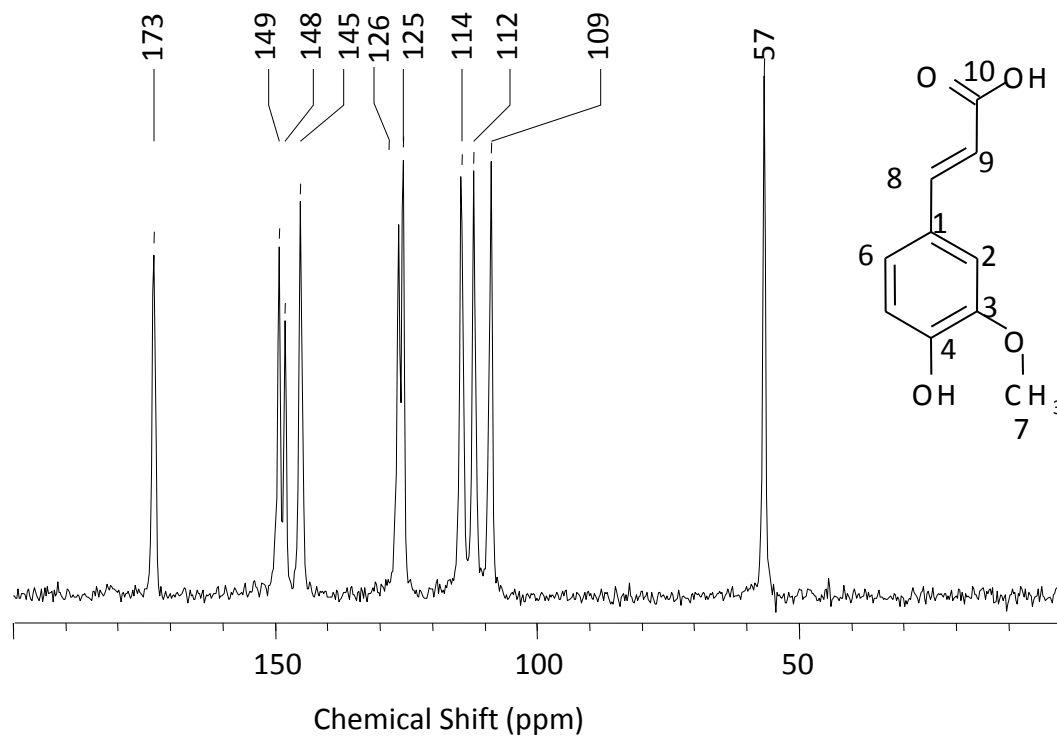


# Basics of Fourier Transform NMR: The Free Induction Decay









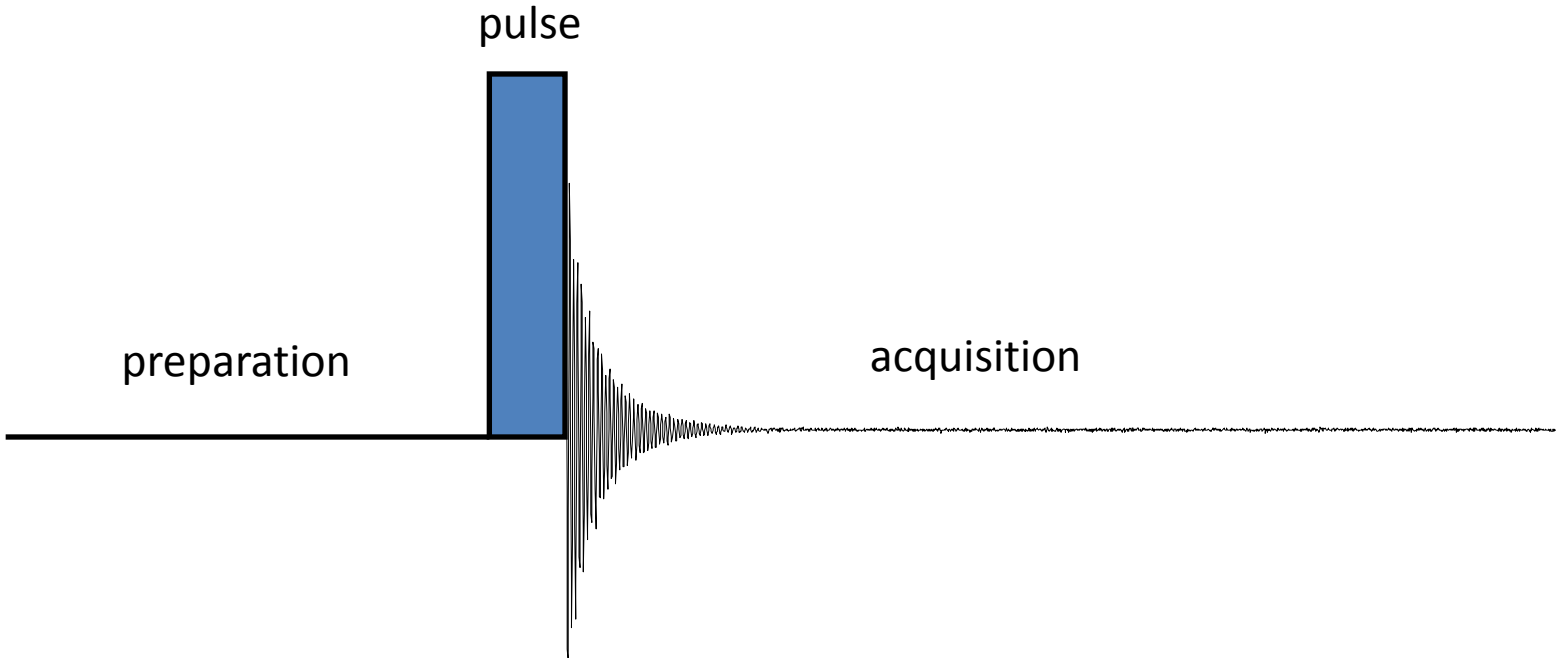
- 1=126 ppm
- 2=125 ppm
- 3=148 ppm
- 4=149 ppm
- 5=114 ppm
- 6=112 ppm
- 7=56 ppm
- 8=145 ppm
- 9=109 ppm
- 10=173 ppm

$$\nu = \frac{\gamma}{2\pi} B_0 (1 - \sigma) \longrightarrow \delta = \frac{\nu_S - \nu_R}{\nu_R} \times 10^6$$

# Basic NMR experiment



Direct detection



# How to measure $T_2$

$$M_{xy}(t) = M_{xy}(0)e^{-t/T_2}$$

At its most fundamental level, spin-spin relaxation corresponds to a decoherence of the transverse nuclear spin magnetization.

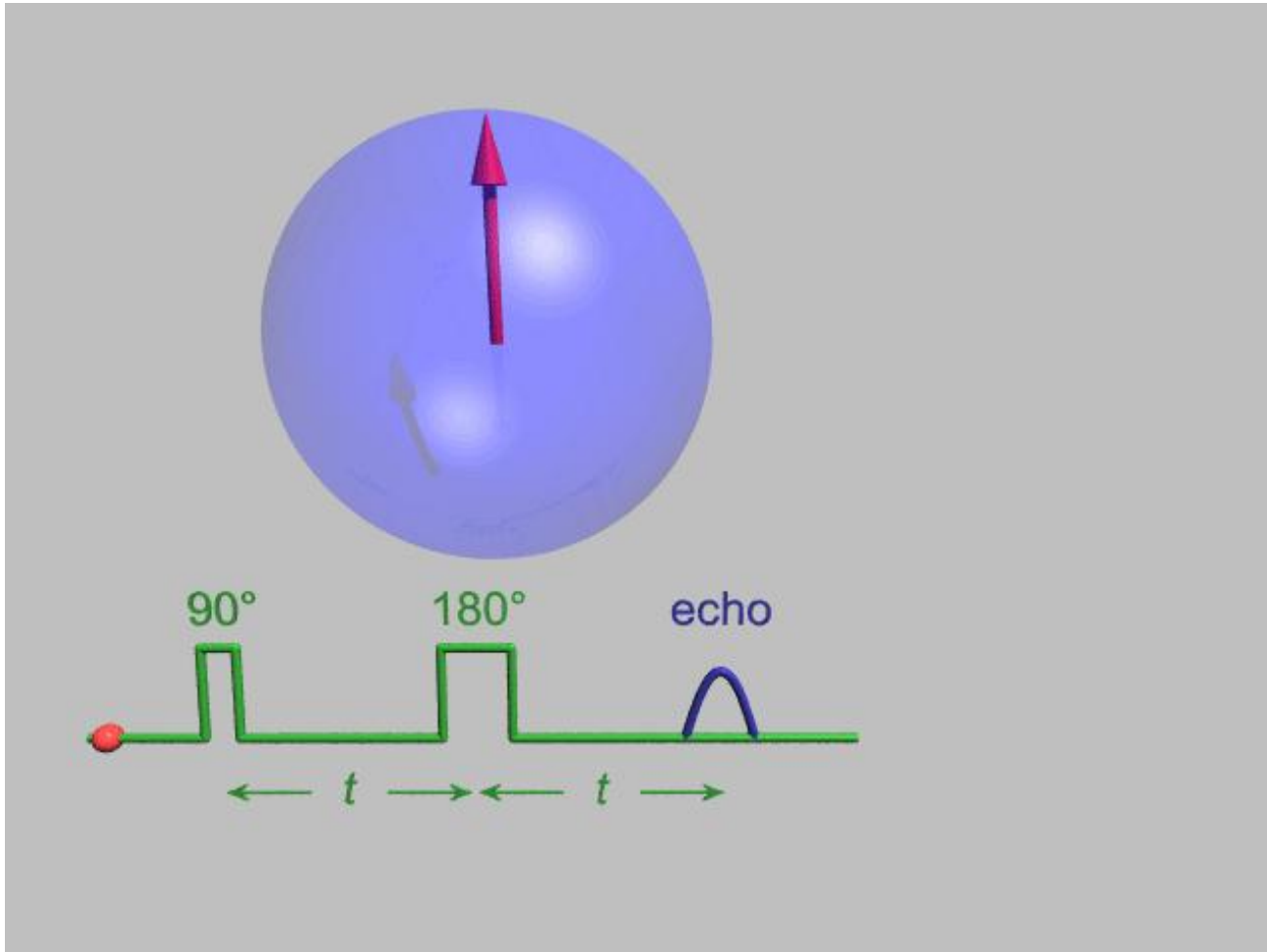
Random fluctuations of the local magnetic field lead to random variations in the instantaneous NMR precession frequency of different spins.

As a result, the initial phase coherence of the nuclear spins is lost, until eventually the phases are disordered and there is no net xy magnetization.

Because  $T_2$  relaxation involves only the phases of other nuclear spins it is often called "spin-spin" relaxation.

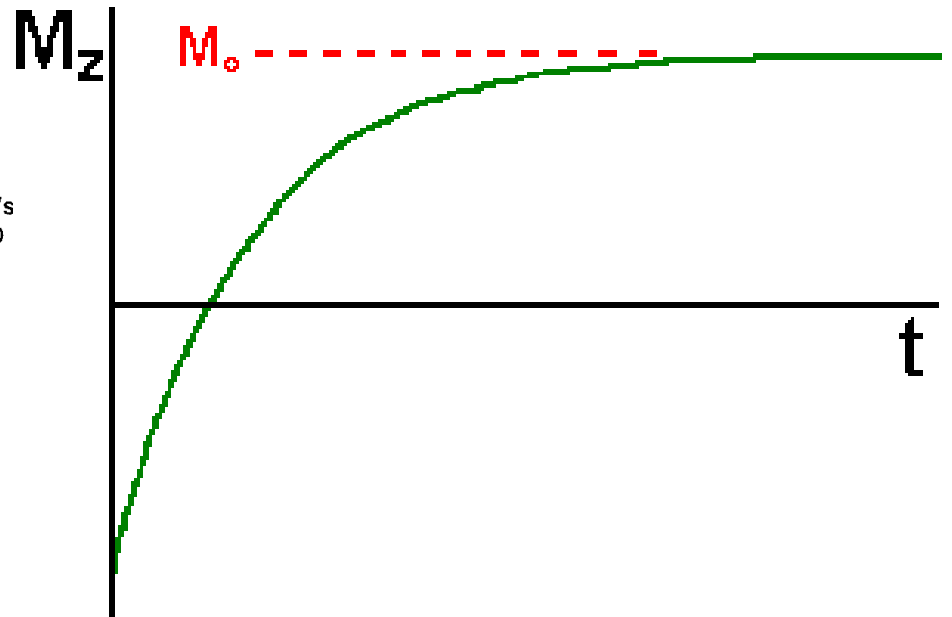
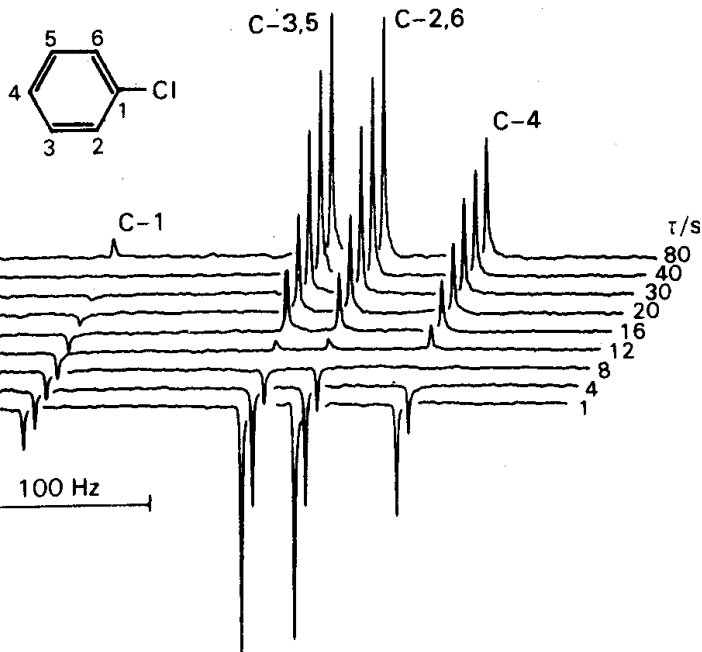
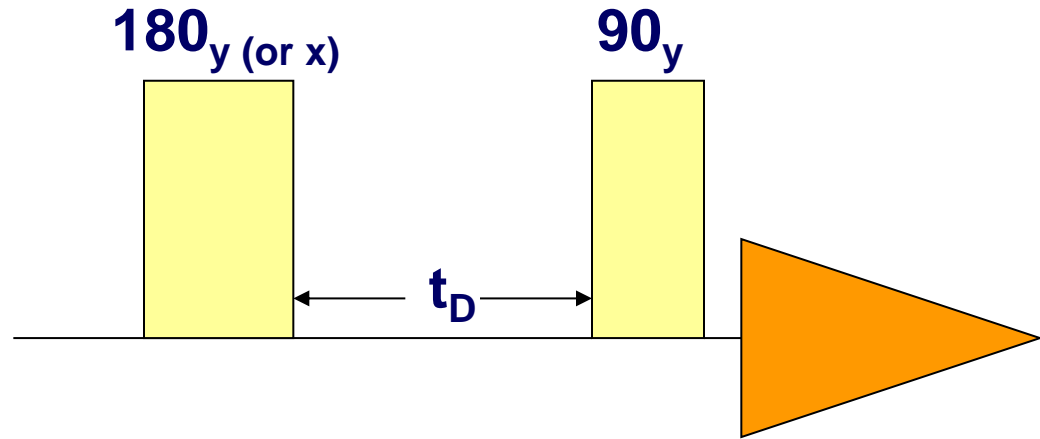
$T_2$  values are generally much less dependent on field strength, B, than  $T_1$  values.

# Spin echo sequence

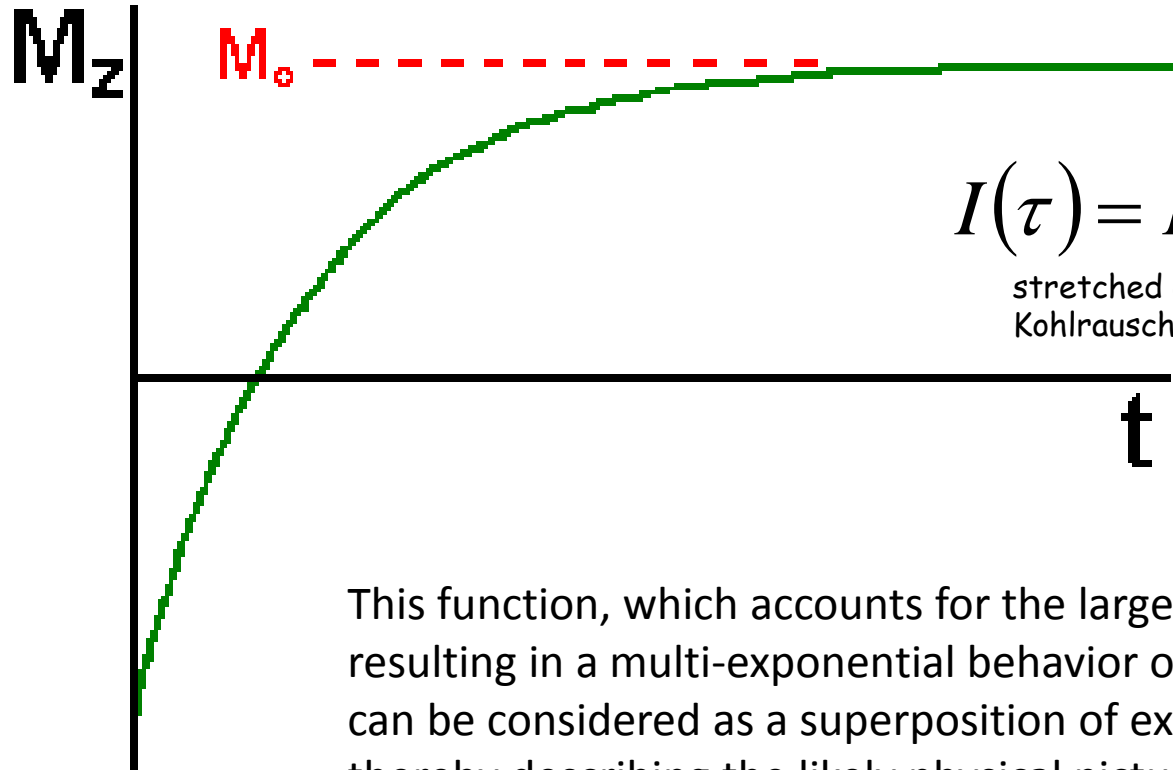


# How to measure $T_1$

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



# How to measure $T_1$



$$I(\tau) = I_0 \exp\left[(-\tau/T_1)^k\right] + y_0$$

stretched exponential function (also known as Kohlrausch-Williams-Watts function)

This function, which accounts for the large sample heterogeneity resulting in a multi-exponential behavior of the decay/recovery curves, can be considered as a superposition of exponential contributions, thereby describing the likely physical picture of some distribution in  $T_1$ .

The equation has the advantage that it is able to handle a wide range of behaviors within a single model. For this reason, assumptions about the number of exponentials to be used in modeling NMRD data are not necessary.

# Relaxation and correlation time

For peptides in aqueous solutions the dipole-dipole spin-lattice and spin-spin relaxation process are mainly mediated by other nearby protons

$$T_1^{-1} = \frac{2}{5} \frac{\gamma^4 \hbar^2}{r^6} \mathbf{I}(\mathbf{I} + 1) \tau_c \left[ \frac{1}{1 + \omega^2 \tau_c^2} + \frac{4}{1 + 4\omega^2 \tau_c^2} \right]$$
$$T_2^{-1} = \frac{1}{5} \frac{\gamma^4 \hbar^2}{r^6} \mathbf{I}(\mathbf{I} + 1) \tau_c \left[ 3 + \frac{5}{1 + \omega^2 \tau_c^2} + \frac{2}{1 + 4\omega^2 \tau_c^2} \right]$$



# Relaxation and correlation time

Model free analysis

$$J(\omega_L) = \frac{\sum c_i \frac{\tau_{Ci}}{1 + (\omega_L \tau_{Ci})^2}}{\sum c_i}$$

$$\langle \tau \rangle = \frac{\sum_i c_i \tau_{Ci}}{\sum_i c_i}$$

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Model free analysis

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$$R_1 = \frac{1}{T_1} = \alpha + \beta [0.2J(\omega_L) + 0.8J(2\omega_L)]$$

**Bloembergen-Purcell-Pound (BPP) model**

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$\alpha$  represents the high-field relaxation rate and  $\beta$  is a constant related to the dipolar interactions. The latter contains the proton quantum-spin number, the proton gyromagnetic ratio, the Planck constant and the electron-nuclear hyperfine coupling constant which describes the interactions between resonant protons and unpaired electrons.

The **correlation time** is roughly defined as the time taken for a molecule to rotate one radian or move a distance of the order of its own dimension. Usually it is assumed that the correlation time depend on temperature according to an Arrhenius type of function;

$$\frac{1}{\tau_c} = \nu_0 \exp\left(-\frac{E}{RT}\right)$$