

CHEM / BCMB 4190/6190/8189

Introductory NMR

Lecture 8

Relaxation:

Applying an rf pulse:

- alters the population ratios
- produces transverse magnetic field components (M_x and M_y)

The system returns to equilibrium via two relaxation processes:

T_1 Relaxation: in the static field direction, spin-lattice or longitudinal.

T_2 Relaxation: perpendicular to the static field, spin-spin or transverse.

Spin-Lattice Relaxation:

Energy absorbed from the rf pulse is transferred to the surroundings, lattice and neighboring molecules.

^1H : order of seconds.

^{13}C : vary from milliseconds (large molecules) to hundreds of seconds.

Factors contributing to T_1 relaxation:

- dipole-dipole relaxation (ie NOE).
- spin-rotation relaxation
- chemical shift anisotropy.
- scalar coupling.
- electric quadrupolar relaxation
- unpaired electrons in paramagnetic compounds.

$$\tau_c = \text{Correlation time} \propto 1/T_1$$

- interval between two successive rotations.
- the faster a molecule moves the greater the T_1

Relaxation:

T_1 : spin-lattice relaxation time (longitudinal)

T_2 : spin-spin relation time (transverse)

After we remove the pulse, the magnetization vector returns to equilibrium.

Bloch assumed that the processes were first-order and defined them by T_1 and T_2 .

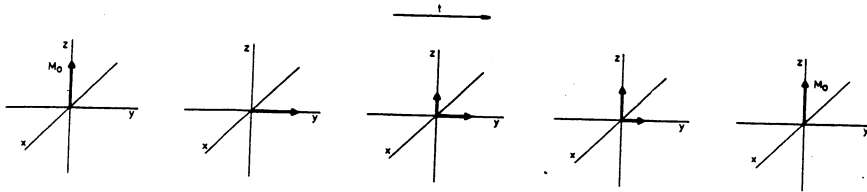
$$dM_z/dt = - (M_z - M_0)/T_1$$

so

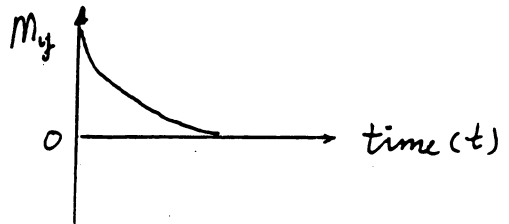
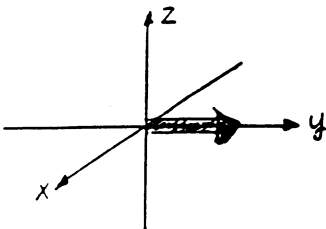
$$M_z = M_0(1 - e^{-t/T_1})$$

$$dM_x/dt = -M_x/T_2$$

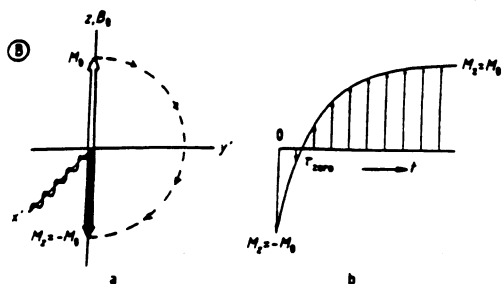
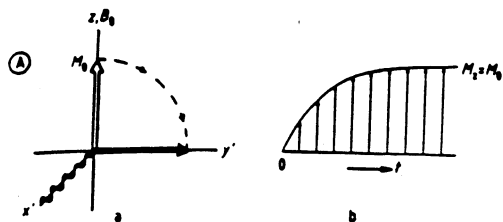
$$dM_y/dt = -M_y/T_2$$



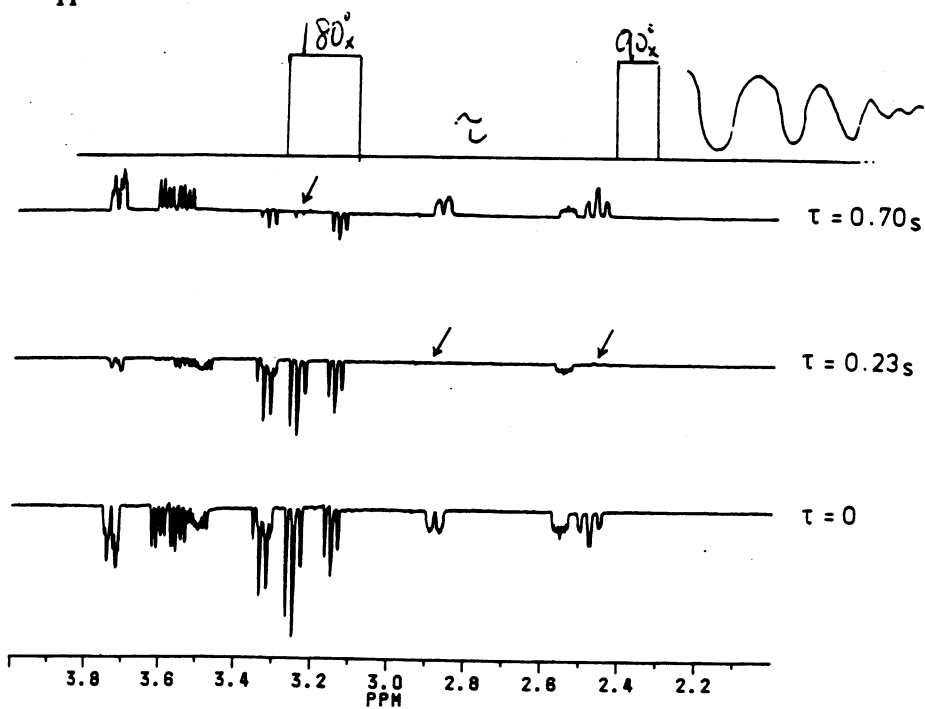
On-resonance



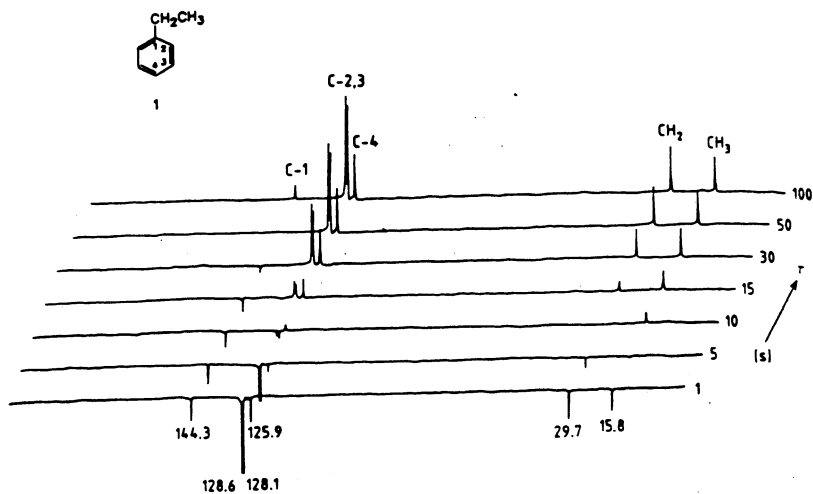
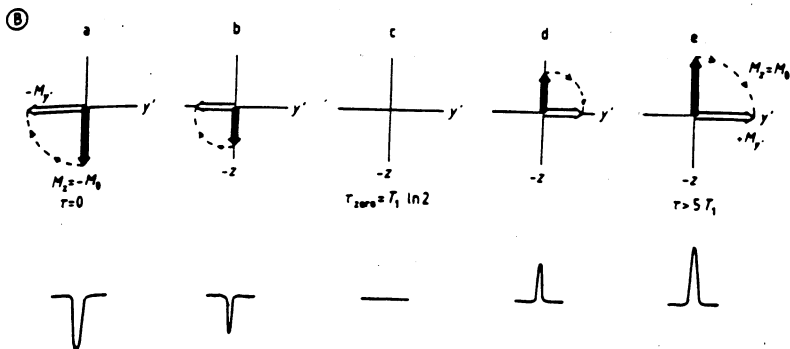
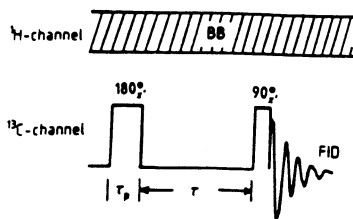
Experimental Determination of T_1 :



^1H



¹³C:



How do we determine the T_1 value?

$$M_0 - M_z = Ae^{-\tau/T_1}$$

After a 180° pulse during the inversion recovery experiment $M_0 = -M_z$
so $A = 2M_0$:

$$M_0 - M_z = 2M_0e^{-\tau/T_1}$$

$$\ln(M_0 - M_z) = \ln 2M_0 - \tau/T_1$$

Substituting I for M where I is intensity of signal:

$$\ln(I_0 - I_z) = \ln 2I_0 - \tau/T_1$$

$$T_{\text{zero}} = T_1 \ln 2$$

T_1 values can vary greatly from one nuclei to the next in the same molecule.

Need to wait $5T_1$ periods for system to return to equilibrium so:

$$(5 T_1 - 180^\circ_x - \tau - 90^\circ_x - \text{FID})_n$$

Why measure T_1 ?

- $\pi/2$ pulse elicits maximal NMR signal at thermal equilibrium.
- for repetitive signal averaging this is not always the best pulse angle.
- need to wait about $5T_1$ for z-magnetization to return to equilibrium.
- more efficient to repeat sooner.

Ernst Angle:

$$\cos\alpha_E = e^{-T_r/T_1}$$

T_r = the delay between pulses.

- best value of α actually depends on offsets of signals in spectrum but this is an average value.

If stick with $\pi/2$ pulses then:

the optimum repetition rate is $T_r = 1.27 T_1$

- in this case you are about 80% efficient.

Influence of protons on ^{13}C T_1 values:

- main contribution is via dipole-dipole interactions, so directly bonded protons can have large effects.

- increasing the number of protons shortens the T_1 although the correlation is not always direct.

Influence of molecular size on T_1 :

- T_1 values decrease as the size of the molecules

Suppression of Water Signal:

$$(\text{180}^\circ_{x'} - \tau - \text{90}^\circ_{x'} - \text{FID})_n$$

T_1 for H_2O is $\sim 3\text{sec}$ and thus is greater than T_1 of most organic molecules so one can chose τ to minimize solvent signal.

Spin-Spin Relaxation: (T_2)

After 90°_x pulse $M_z = 0$ and net magnetization is along the y-axis. The population of N_α and N_β are equal .

Phase Coherence: a small proportion of nuclear dipoles are bunched along the y-axis.

T_2 - determines how fast M_x and M_y return to zero.

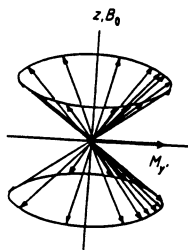


Figure 1-12.
Pictorial representation of phase coherence: after a 90°_x pulse a fraction of the nuclear spins (not all!) are bunched together in phase as they precess about the field direction z .

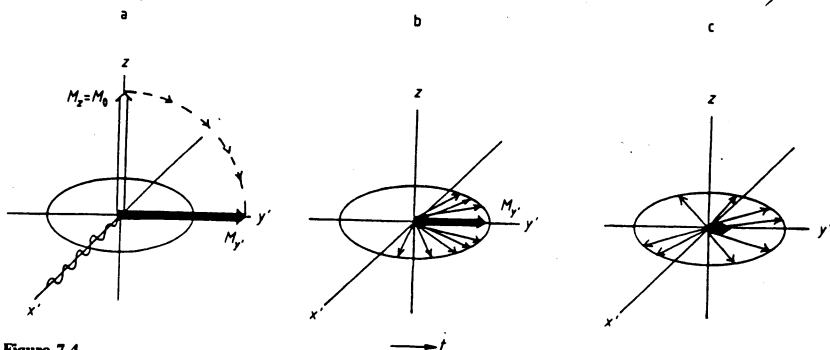


Figure 7-4.

Decay of the transverse magnetization M_y (in the rotating coordinate system x', y', z) after a 90°_x pulse, as the precessing bunched spins fan out as a result of magnetic field inhomogeneities.

How do we view this?:

Nuclei change from one energy state to the other and we lose the phase coherence.

- this is not the main contribution.

Magnetic Field inhomogeneities: there is a small ΔB_0 throughout the sample which leads to fanning out of signals.

-fanning out process causes signals that are chemically equivalent to precess with slightly different Larmor frequencies.

- the net result is an increase in the line width of the various signals.

By definition though $T_1 \geq T_2$

Experimental Determination of T_2 :

Want to measure a true value which is independent of the ΔB_0 fanning out process.

Spin-echo experiment:

After initial 90°_x pulse you apply a 180°_x pulse at set interval τ .

At 2τ - resultant transverse magnetization is $-y'$ direction.

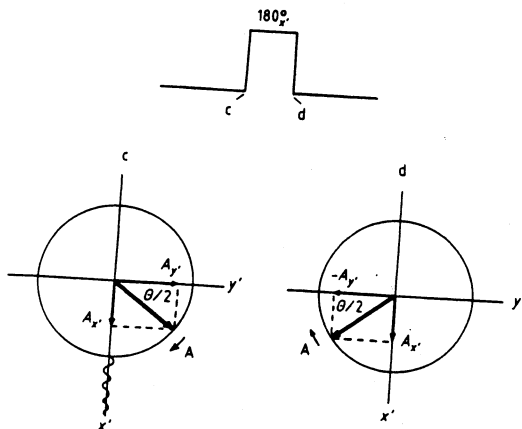
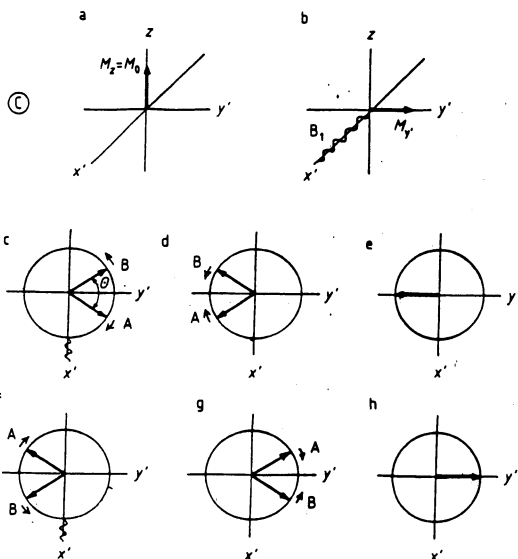
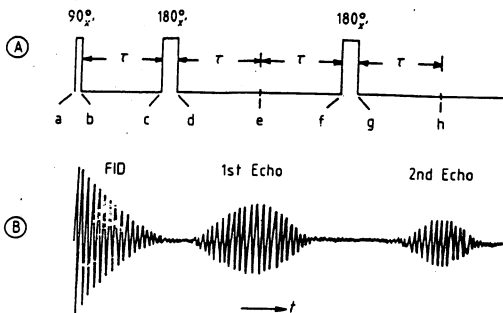
4τ - magnetization is y' direction.

6τ - magnetization is $-y'$ direction.

Etc.....we get an echo with alternating phase at intervals of 2τ .

However, the net magnetization is decreasing with each echo due to true spin-spin relaxation.

$$90^\circ_{x'} - \tau - 180^\circ_{x'} - \tau (1\text{st echo}) - \tau - 180^\circ_{x'} - \tau (2\text{nd echo}) \dots$$



- the $180^\circ_{x'}$ pulse turns the $A_{y'}$ component into the $(-y')$ direction but has not effect on the $A_{x'}$. The angle between vector A and the y' -axis is unchanged if we disregard sign
- the effect of a $180^\circ_{x'}$ pulse is that vectors A and B undergo reflections in the x', z' plane.

Quantitatively:

$$M_y = A e^{-t/T_2}$$

At $t=0$, $A=M_0$

$$\ln M_y = \ln M_0 - t/T_2$$

since $I \propto M_y$,

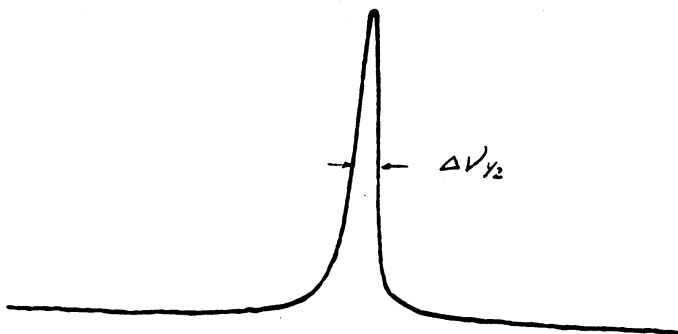
$$\ln I(t) = \ln I_0 - t/T_2$$

plot $I(t)$ vs t where $I(t)$ is intensities at each echo. Slope of line is $-1/T_2$.

For the most part we do not concern ourselves with T_2 measurement.

Of more consequence is T_2^* which takes into account the inhomogeneity of the magnetic field.

Line Widths of NMR Signals



$$\Delta\nu_{1/2} = \frac{1}{\pi T_2^*}$$

$$\frac{1}{T_2^*} = \frac{\gamma \Delta B_0}{2} + \frac{1}{T_2}$$