

Bibliography: Slichter; Par. 5.10, 5.11, 8.2, 8.3  
 - Harris; Par. 3.12-3.17, 4.9-4.11  
 - Abragam, Ch. VIII

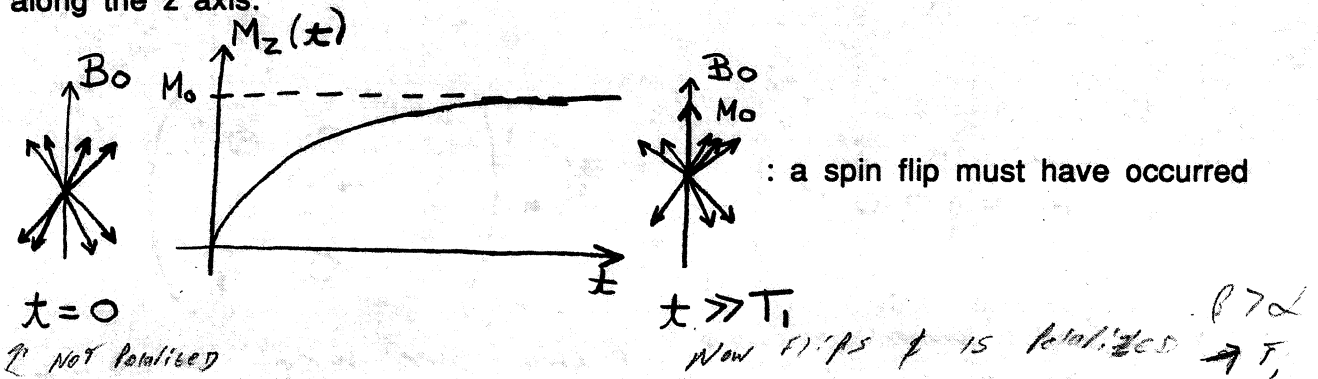
Classes (13)  
 Fri → Tues @ 4  
 Now

## IV: DYNAMIC EFFECTS IN NMR

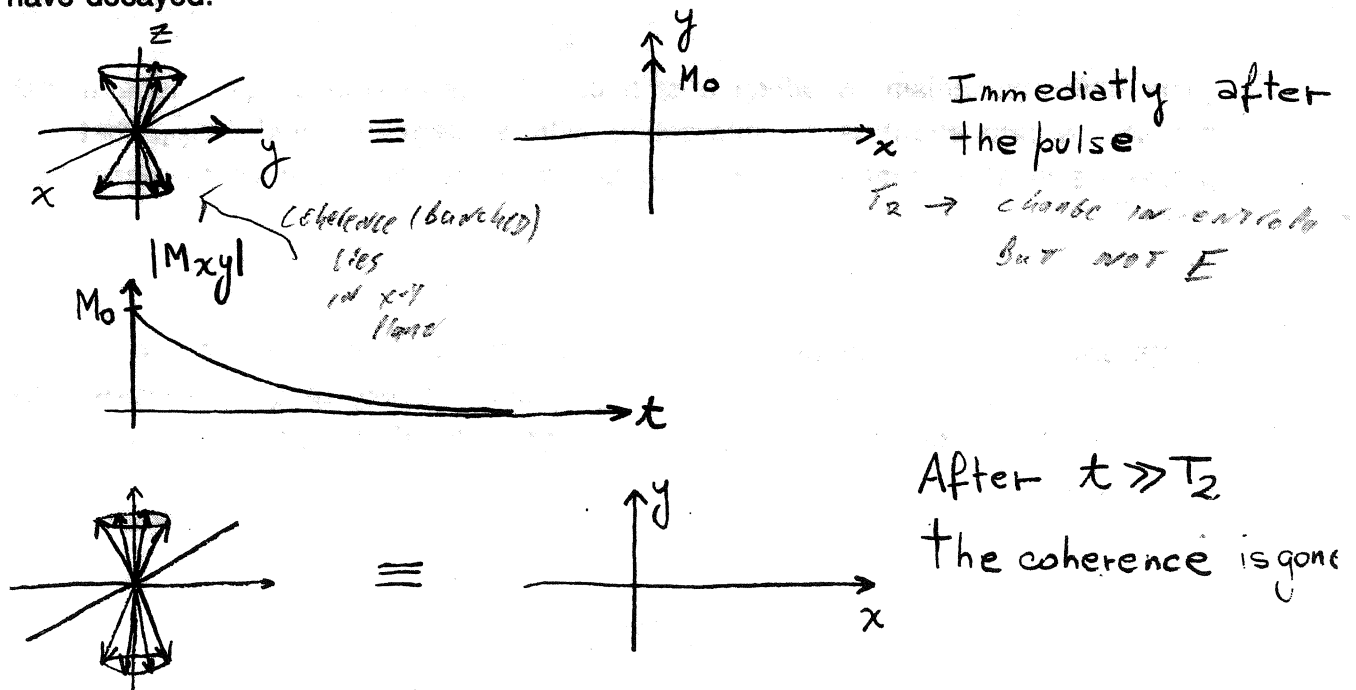
### IVA: SPIN RELAXATION

#### IVA.1 A SEMI-CLASSICAL DESCRIPTION

Although when spins are initially introduced in a magnetic field their orientations are random, if one waits long enough a net magnetization develops along the z axis:



Moreover, even if spins are placed on a perfectly homogeneous  $B_0$ , if we apply a  $\pi/2$  pulse on  $M_0$  and wait long enough the magnetization in the x-y plane will have decayed:



If a system of "non-interacting" spins is considered, these processes are described by the Bloch equations:

$$\dot{\vec{M}}(t) = \gamma \vec{M}(t) \times \vec{B}(t) - \bar{R} \{ \vec{M}(t) - \vec{M}_0 \},$$

Where

$$\vec{M}(t) = \{ M_x(t), M_y(t), M_z(t) \}; \quad \vec{B}(t) = \{ B_{1x}(t), B_{1y}(t), B_0 \}$$

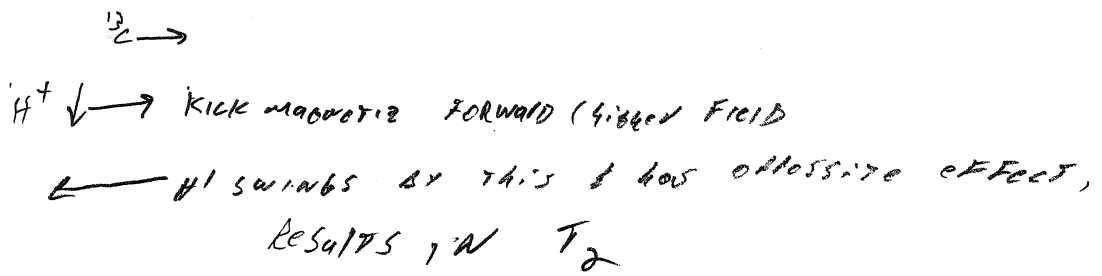
$$\vec{M}_0 = \{ 0, 0, M_0 \} \quad \bar{R} = \begin{pmatrix} T_2^{-1} & 0 & 0 \\ 0 & T_2^{-1} & 0 \\ 0 & 0 & T_1^{-1} \end{pmatrix}$$

CAN'T create magnetiz, BECAUSE we need to communicate to each spin INDIV to do so.

The processes behind relaxation:

\_The only mechanism by which a spin can flip its orientation (T<sub>1</sub>- longitudinal or spin-lattice relaxation) is by interacting with a magnetic field B<sub>local</sub> that precesses at its Larmor frequency and has a component somewhere along the x-y plane.

\_Dephasing in the x-y plane (T<sub>2</sub>-, transverse or spin-spin relaxation) occurs due to the fact that the coherences of individual spins in the sample dephase. Static z-components or oscillating transverse components of random fields can produce these effects.

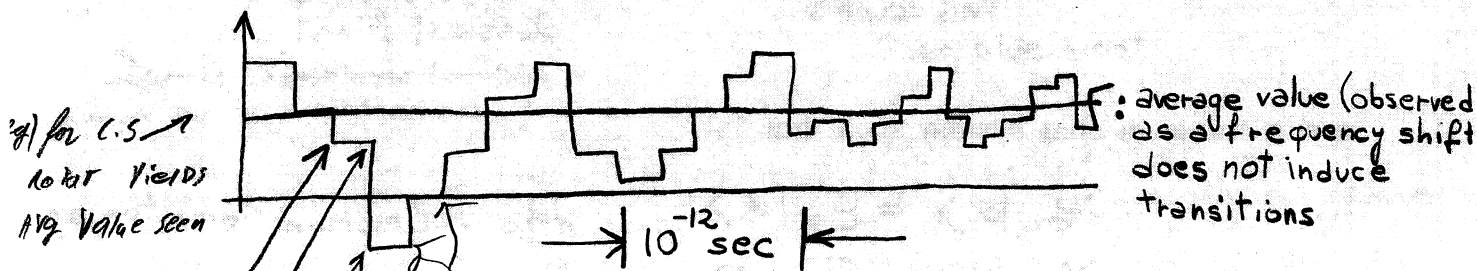


all goes forw. don't lose phase  
 however for back i, dephases

The random fields that produce these relaxation process usually originate in the modulation of the NMR interactions by random molecular reorientations, bond rotations, etc. These changes can be viewed as :

$1 - 3C^2(\theta) \rightarrow$  + intramolec. Modulations  
 0  
 - inter " " " "  
 also causes Relax.

$\vec{B}_{local}$  (produced by internal NMR interactions)



collisions that produce a time dependent field  $\vec{B}_{local}$

\* want to view the oscil.

\* Dip-coupl main Factors For relaxation ~ 90% even thoat avg's  
 to zero

## IVA.2 THE RELAXATION OF POPULATIONS (T1) Slichter, 5.10

To visualize the mechanism involved in longitudinal relaxation let's assume for instance, that we have a field of the form

The field, represented by operators, couples to spin part  
 \* FOR DIP-COUP ASSUMING ONLY ONE SPIN FOR SIMPLICITY

$$\vec{B}_{local}(t) = A \cdot f(t)$$

this couples to the spin part

time dependent classical function  
 \* assume completely random  
 \* DON'T MOVE IN TIME = 0

and a two-level spin system such that

$$\mathcal{H}_0 |\alpha\rangle = E_\alpha |\alpha\rangle$$

$$\mathcal{H}_0 |\beta\rangle = E_\beta |\beta\rangle$$

$\langle \alpha | A | \beta \rangle \neq 0$

$|\mathcal{H}_0| \gg |A|$  (A may be for instance the non-diagonal terms in the dipole-dipole Hamiltonian)

$\mathcal{H}_0$ : Zeeman Hamiltonian  
 USED TO GET SPINS GOING

NON FIELD 1st order A, B, C.

If  $A = 0$ , the time dependence of a general spin system  $|\psi\rangle$  EXACT IF  $A=0$

$$|\psi\rangle = c_\alpha e^{-iE_\alpha t/\hbar} |\alpha\rangle + c_\beta e^{-iE_\beta t/\hbar} |\beta\rangle$$

$A=0$ : NO INTERACTION, WHAT IS TIME DEP NOW? USE TIME DEP.  $P_i, t$   
 IF NOT MUST MAKE  $c_\alpha \neq c_\beta$   
 becomes TIME  
 TAKE IT DERIV

Since  $A \neq 0$  however,  $c_\alpha, c_\beta$  will be "somewhat" time-dependent. From the def. Schrodinger equation it follows that: IF  $E_\alpha \neq E_\beta = \text{both } E \neq 0$   
 THEN  $c_\alpha$  OSCILLATES  $\therefore \neq 0$  THEN  $c_\alpha$  GROWS w/ TIME

$$i \dot{c}_\alpha = f(t) \langle \alpha | A | \beta \rangle \cdot e^{i(E_\alpha - E_\beta)t/\hbar} c_\beta$$

$I_{1z} I_{2z} = c$  term dip. int.  $\rightarrow \langle 1 | I_{1z} I_{2z} | 1 \rangle =$  DOESN'T COMMUTE  $\therefore$  NO CHANGE IN SPECTRUM

1st order  $P_i, t$   
 $f(t) =$  STRENGTH OF COUP IN  $\alpha, \beta$   
 $\langle \alpha | A | \beta \rangle =$  COUPLING OF  $\alpha, \beta$

let  $c_\beta = 1$   
 @  $t=0$   
 $\therefore$  all  $\beta$  at 1st

The relaxation time  $T_1$  is then the rate of population build up; i.e., the rate at which  $|c_\alpha(t)|^2$  grows assuming that at  $t=0$   $c_\alpha(0)=0$  ;  $c_\beta(0)=1$ . To get this, rate we have to integrate the last equation:

relieve  $c_\alpha$  by  $\int$

$$c_\alpha(t) = \frac{1}{i} \int_0^t f(t') \langle \alpha | A | \beta \rangle e^{i\omega_\alpha t'} dt'$$

Population DIFF  $\therefore c_\alpha^2(t)$

and calculate  $\frac{d}{dt} (c_\alpha \cdot c_\alpha^*) =$

$$\frac{d}{dt} (|c_\alpha(t)|^2) = \dot{c}_\alpha(t) \cdot (c_\alpha(t))^* + (\dot{c}_\alpha(t))^* \cdot c_\alpha(t)$$

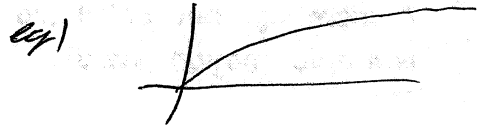
↑ Populations

$$= \left[ \int_0^t f(t) \cdot f^*(t') |\langle \alpha | A | \beta \rangle|^2 e^{i\omega(t-t')} dt' \right] + [ \quad ]^*$$

Time relax. depend on square of interact

Now  $f(t)$  is a random function; therefore, the bulk  $T_1$  comes from carrying out an average over the whole ensemble of spins:

rate @ which populat. changes only  
 BUT NO INFO ON FINAL  $\psi$  LEVELING THOUGH



$$\frac{d}{dt} (|c_\alpha(t)|^2) = \frac{1}{T_1} = \overline{\left[ \int_0^t f(t) f^*(t') |\langle \alpha | A | \beta \rangle|^2 e^{i\omega(t-t')} dt' \right] + [ \quad ]^*}$$

Auto-correl. Func (how time del. Func. correlates w/ itself)

Rate of change of  $c_\alpha^2$  is  $T_1$  ? @  $t=0$  &  $t=t'$

\* need ensemble avg though

IN ensemble MOLEC. DON'T MOVE IN NET, STADY STATE  
 at  $t=0$   $f(t) f^*(t') = 1 =$  set 34's w/

@  $t = \text{long time}$   $= 0 =$  COMPLETELY LOST MEMOY

*Handwritten scribble*

similar to a FFCO which can provide E TRANSIT  
eg 127 → 187

Moreover, since the system under consideration is assumed to be in a steady state, the average

$\overline{f(t)f^*(t')}$  =  $\overline{f(t)f^*(t-\tau)}$  : autocorrelation function of  $f$   
For ensemble as whole

$\tau$  = pos:ve time past & hence correl.

should be independent of the particular  $t$  and only a function of  $\tau > 0$  :  $G(\tau)$

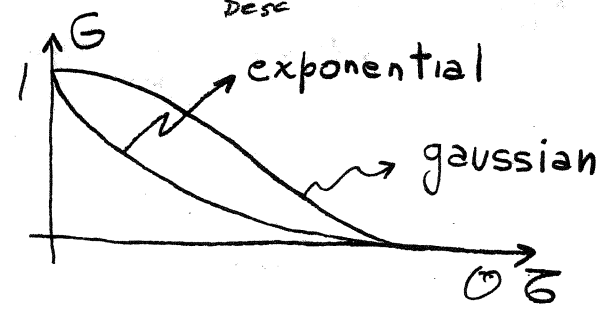
d.c. func

When  $\tau = 0$  :  $\overline{f(t)f^*(t)} = 1$  : Perfect correlation

When  $\tau \rightarrow \infty$  :  $\overline{f(t)f^*(t-\tau)} = 0$  : No one remembers what it was a time  $\tau$  before

A more rigorous calculation of  $G(\tau)$  for random translational or rotational isotropic motion yields:

$G(\tau) = e^{-\tau/\tau_c}$  or  $G(\tau) = e^{-(\tau/\tau_c)^2}$   
isotropic only one time func desc



For benzene → not isot. spins in plane easier

$\tau_c$  is the **correlation time** of the process; a constant that defines the time it takes the system to lose its memory =>

If the system undergoes a  $\left\{ \begin{matrix} \text{large} \\ \text{small} \end{matrix} \right\}$  # of strong collisions per sec =>  $\left\{ \begin{matrix} \text{short} \\ \text{long} \end{matrix} \right\} \tau_c$

how quickly does this random Func. change w/ time =  $\tau_c$

Inverse = Relax rate  $f(t) \cdot f^*(t)$

Then:

$$\frac{1}{T_1} = \left[ \int_0^t G(\tau) |\langle \alpha | A | \beta \rangle|^2 e^{-i\omega_0 \tau} d\tau \right] + \left[ \int_{-t}^0 \dots \right]^* = K |\langle \alpha | A | \beta \rangle|^2 \int_{-t}^t G(\tau) e^{-i\omega_0 \tau} d\tau$$

a # spin of  $\omega$

$\frac{E_k - E_b}{h} = \text{label Fred}$

$$\approx |\langle \alpha | A | \beta \rangle|^2 \int_{-\infty}^{\infty} G(\tau) e^{-i\omega_0 \tau} d\tau$$

$J(\omega_0)$ : spectral density = Fourier transform of correlation function

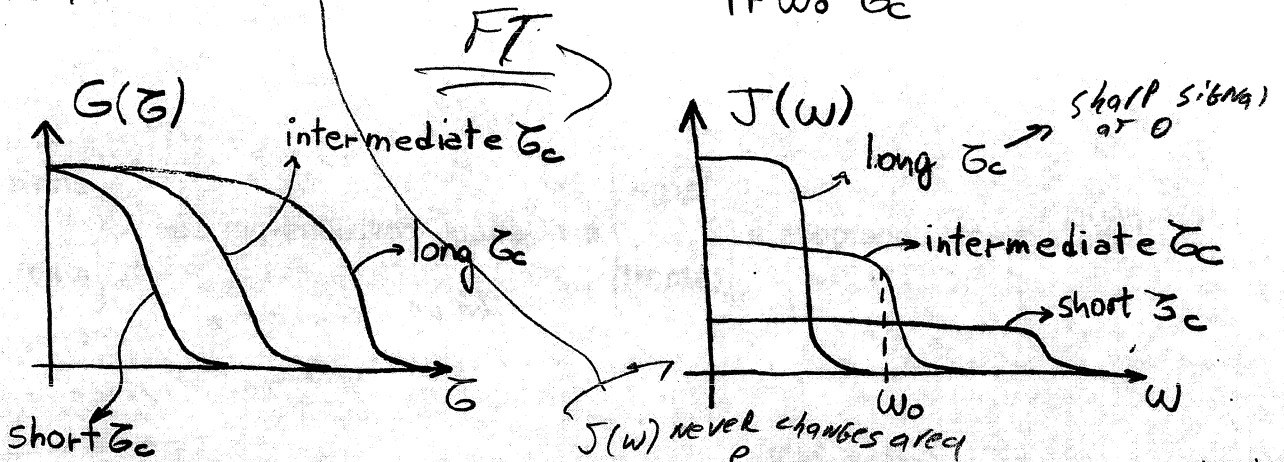
$G(\tau) = e^{-\tau/\tau_c}$  depends only on  $\tau_c$  (want this at  $\omega_0$ )

$$I(\omega) = \int s(t) e^{-i\omega t} dt \quad \text{FT} \quad (30)$$

Then  $\Rightarrow \int I(\omega) d\omega = S(0)$

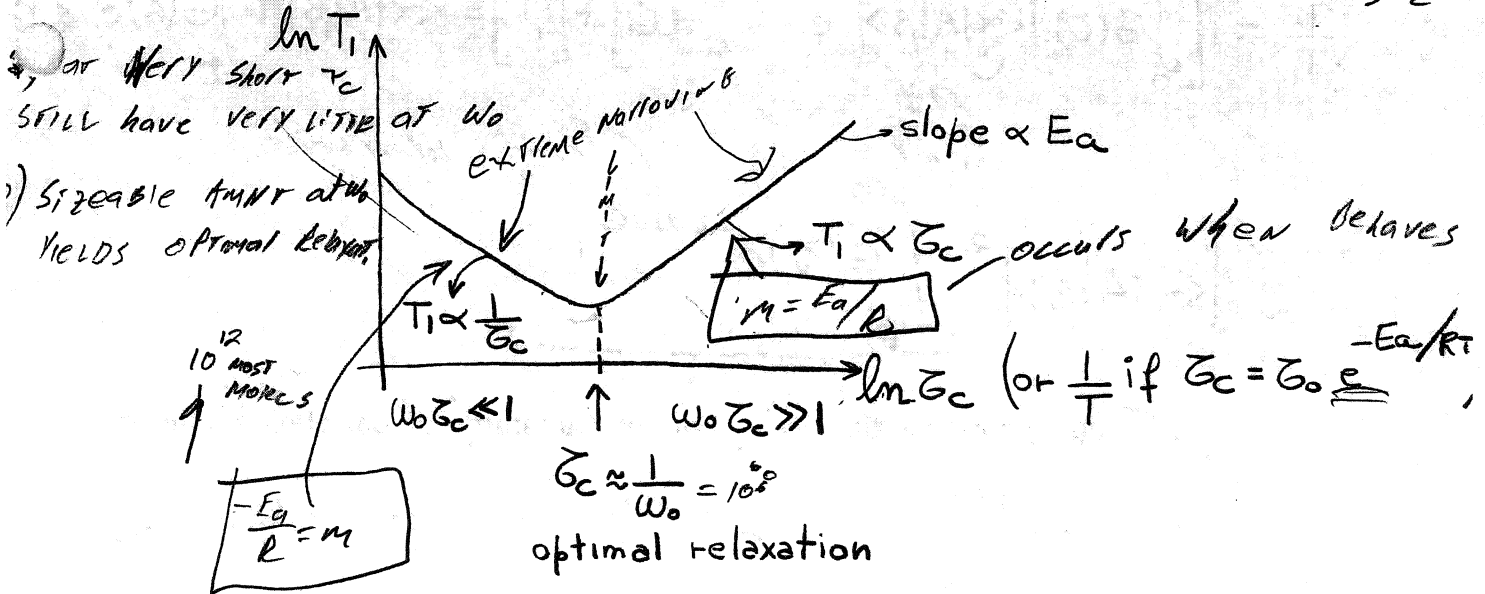
For a decaying exponential  $G(\tau)$ ;  $J(\omega_0) = \frac{S_c}{1 + \omega_0^2 \tau_c^2}$

Let  $s(t) = e^{-t/\tau_c}$   
NOTE



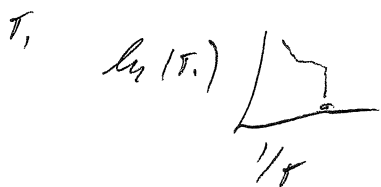
A) independent of short  $\tau_c$   
 $\rightarrow$  inefficient relaxation, ~~fast~~ because NO FIELDS AT  $\omega_0$

$\int J(\omega) d\omega \propto G(0) = \text{constant}$   
 $\neq$  For T, want  $|B\rangle \rightarrow |A\rangle$   
 $\neq$  NEED LATTICE TO PROVIDE THIS E



Most small molecules reorient at  $\tau_c < 10^{-10} \Rightarrow \omega_0 \tau_c \ll 1$  : this is called the extreme narrowing regime.

$\neq$  Non-Arrhenius behavior (or non-VT behavior, if have molec which translates eq)



Difference more than one motion FOR eq) benzene

∴ b/c sum of 2  $\tau_c$  is faster or slower



### IVA.3 FORMAL THEORY OF RELAXATION

A complete analysis of relaxation starts with the Schrodinger equation for the density matrix

$$\frac{\hbar}{i} \dot{\rho} = [\rho(t), \mathcal{H}]$$

coupled spins, AB<sub>2</sub>

IN relax. want to know how  $\rho$  changes w/ t

where  $\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_1(t)$  ;  $\|\mathcal{H}_0\| \gg \|\mathcal{H}_1\|$

e.g. Zeeman

random ;  $\langle \mathcal{H}_1 \rangle = 0$

can use bit.

keep part of it that commutes to  $\mathcal{H}_0$

in rotating frame

In the rotating frame  $\rho_r = e^{i\mathcal{H}_0 t} \rho e^{-i\mathcal{H}_0 t}$  ;

$$\mathcal{H}_{1,r}(t) = e^{i\mathcal{H}_0 t} \mathcal{H}_1(t) e^{-i\mathcal{H}_0 t} ; \frac{\hbar}{i} \dot{\rho}_r = [\rho_r(t), \mathcal{H}_{1,r}(t)]$$

We can integrate this equation by successive approximations:

assuming  $\rho_r(t)$  doesn't change over time.

similar but in rotating frame.

$$\frac{\hbar}{i} [\rho_r(t) - \rho_r(0)] = \int_0^t [\rho_r(0), \mathcal{H}_{1,r}(t')] dt'$$

$$\Leftrightarrow \frac{\hbar}{i} \rho_r(t) = \frac{\hbar}{i} \rho_r(0) + \int_0^t [\rho_r(0), \mathcal{H}_{1,r}(t')] dt' : 2^{nd} \text{ order perturbation theory}$$

a bit correct.  $\therefore$  bis  $\rho$   
square in  $\mathcal{H}$

assume a steady state  
 \* then  $\rho$  doesn't change (132)

Now replacing this back into (1):

$$\dot{\rho}_r(t) = \frac{i}{\hbar} [\rho_r(0), \mathcal{H}_{1r}(t)] + \left(\frac{i}{\hbar}\right)^2 \int_0^t [\rho_r(0), \mathcal{H}_{1r}(t'), \mathcal{H}_{1r}(t)] dt'$$

$\nearrow$  motion that this imparts in  $\rho$ , (assume  $F$ 's to be zero)  
 $\nwarrow$  part  $\nwarrow$  platelet DBI commut.

Now the ensemble average has to be calculated. To carry out this, an additional number of assumptions have to be made:

i) Since  $\mathcal{H}_1$  is random,  $\mathcal{H}_{1r}(t)$  has to be random. Thus, at any given time  $t$ , its ensemble average over the entire system vanishes;  $[\rho_r(0), \mathcal{H}_{1r}(t)] = 0$ : the first term on the right of this equation goes to zero.

ii) Since  $\rho_r$  and  $\mathcal{H}_{1r}$  are uncorrelated (assumption i),  $\rho_r(0)$  is like  $\rho_r$  at any other time  $t \Rightarrow$  replace in  $[\rho_r(0), \mathcal{H}_{1r}(t)]$  by  $[\rho_r(t), \mathcal{H}_{1r}(t)]$

iii) Since it is observed by experiment that the equilibrium state of is not 0 but  $\rho_r^0 \propto I_z$ ,  $\rho_r(t)$  has to be replaced by  $\rho_r(t) - \rho_r^0$ . The ensemble average can therefore be expressed as

$$\dot{c} = -c\hbar^2 \xrightarrow{\text{solve}} = k^2(c - c_0)$$

$$\dot{\rho}_r(t) = -\frac{1}{\hbar^2} \int_0^t [(\rho_r(t) - \rho_r^0), \mathcal{H}_{1r}(t-\tau), \mathcal{H}_{1r}(t)] d\tau$$

$t' = t - \tau$   
 16 #'s

"RedFields eqn", a matrix eqn  
 \* need to calc 16 #'s

$\therefore$  each term has 16 terms which depend on  $H_1$

In matrix representation:

$$(\dot{\rho}_r(t))_{\alpha\alpha'} = -\frac{1}{\hbar^2} \sum_{\beta\beta'} \exp\left\{-i \frac{[(E_{\beta'} - E_{\beta}) - (E_{\alpha'} - E_{\alpha})]t}{\hbar}\right\} R_{\alpha\alpha'\beta\beta'} ((\rho_r(t))_{\beta\beta'} - (\rho_r^0)_{\beta\beta'})$$

$\nwarrow$  4 pairs  
 \* for each pair here

RF Hamiltonian =  $B_1 \cos(\omega t + \phi) I_x = H_{rf}$

(133)

$R_{\alpha\alpha'\beta\beta'}$  : Elements of the Redfield relaxation superoperator, depending on spectral densities and NMR interactions.

$$\begin{pmatrix} (\dot{\rho}_n)_{\alpha\alpha} \\ (\dot{\rho}_n)_{\alpha\beta} \\ \vdots \end{pmatrix} = \begin{pmatrix} R_{\alpha\alpha'\beta\beta'} \end{pmatrix} \begin{pmatrix} (\rho_n)_{\alpha\alpha} \\ (\rho_n)_{\alpha\beta} \\ \vdots \end{pmatrix}$$

vector                      MATRIX                      vector

$\rho_{12}$  &  $\rho_{21}$   
off diag element  
= coherences

This theory also allows one to calculate the relaxation of coherences, affording the expression of  $T_2$ . classical interaction static component Not on hamil.

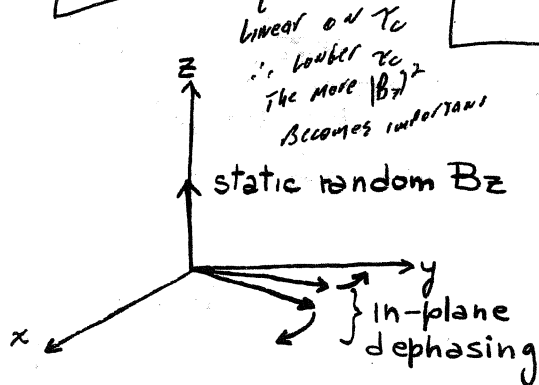
For  $\mathcal{H}_1(t) = B_x(t) I_x + B_y(t) I_y + B_z(t) I_z$

$B_x, B_y$  &  $B_z$   
comes from random motions.

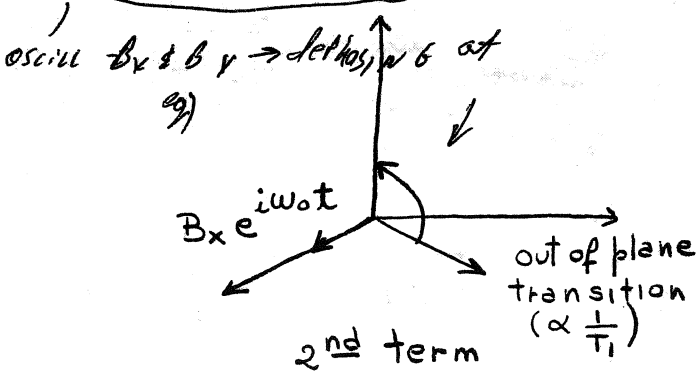
with  $\langle B_{x,y,z}(t) \cdot B_{x,y,z}(t+\tau) \rangle = |B_{x,y,z}|^2 e^{-\tau/\tau_c}$

$$\Rightarrow \frac{1}{T_2} = |B_z|^2 \cdot \tau_c + \frac{(|B_x|^2 + |B_y|^2)}{2} \cdot \frac{\tau_c}{1 + \omega_0^2 \tau_c^2}$$

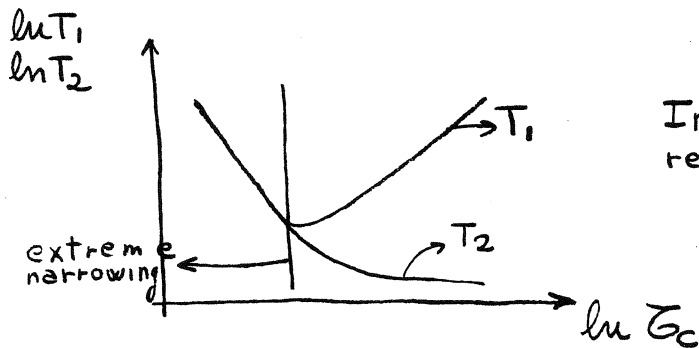
\* both shrink x-y magnetization



1st term.



2nd term

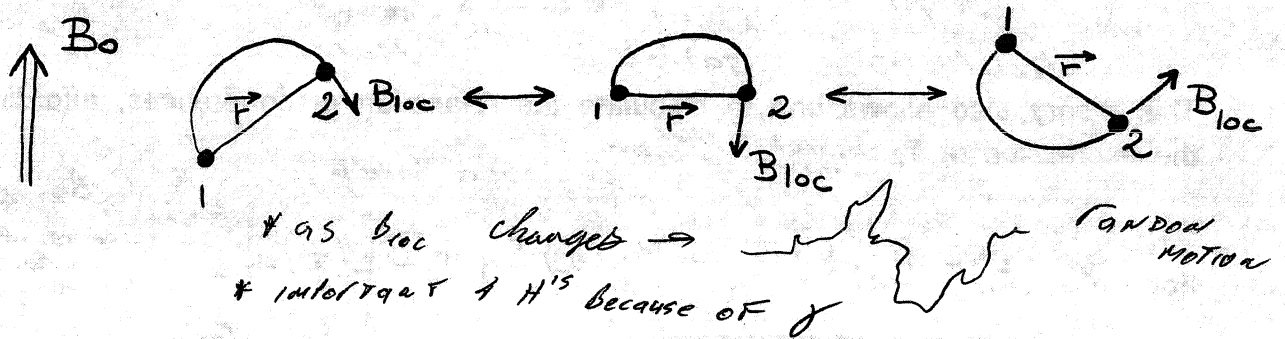


In the extreme narrowing regime,  $T_1 = T_2$

### IVA.4 RELAXATION MECHANISMS FOR SPIN 1/2

harris 3.12-3.17  
Abramson → ch 8

Relaxation is produced by random fluctuations of the NMR or of other microscopic magnetic interactions. In diamagnetic systems, wherever protons are nearby, the most important relaxation mechanism is via **dipole-dipole couplings** to the magnetic moment of the <sup>1</sup>H.



For a homonuclear pair:

But 1/r<sup>6</sup> because of strength of interaction squared.

$\therefore$  small  $\gamma$  not important  
 $\delta_H$  very important

$$T_{1dd}^{-1} = \frac{3\gamma^4 \hbar^2}{10 r^6} \left\{ \frac{\bar{G}_c}{1 + \omega_0^2 \bar{G}_c^2} + \frac{4\bar{G}_c}{1 + 4\omega_0^2 \bar{G}_c^2} \right\}$$

$\frac{1}{\omega_0}$                        $\frac{1}{2\omega_0}$

$$T_{2dd}^{-1} = \frac{3\gamma^4 \hbar^2}{20 r^6} \left\{ 3\bar{G}_c + \frac{5\bar{G}_c}{1 + \omega_0^2 \bar{G}_c^2} + \frac{2\bar{G}_c}{1 + 4\omega_0^2 \bar{G}_c^2} \right\}$$

DIP HAMIL

E.g. <sup>1</sup>H...<sup>1</sup>H, <sup>13</sup>C-<sup>1</sup>H, <sup>15</sup>N-<sup>1</sup>H

A → doesn't matter  
 3 change one spin at a time 1/w  
 e } "ch two" ∴ 1/2w  
 F }

The anisotropy  $\Delta\omega$  of the chemical shift will also be modulated by motions, and induce relaxation of the spin. Note that the resulting rates are proportional to  $B_0^2$ .

$T_1 \neq T_2$  even in the extreme narrowing regime

$$T_{1\text{CSA}}^{-1} = \frac{6}{40} \gamma^2 B_0^2 \Delta\omega^2 \cdot \frac{\zeta_c}{1 + \omega_0^2 \zeta_c^2}$$

*CSA (also a mech. For relaxation)*

$$T_{2\text{CSA}}^{-1} = \frac{\gamma^2 B_0^2 \Delta\omega^2}{40} \left[ 4\zeta_c + \frac{3\zeta_c}{1 + \omega_0^2 \zeta_c^2} \right]$$

*CSA HAMIL only Flips one spin @ a time*

E.g.: Non-protonated spins 1/2 with large  $\Delta\omega$ :  $^{13}\text{C}\text{O}_2\text{H}$ ; c1ccccc1[N+](=O)[O-]  
*& high  $B_0$ 's this becomes important*

A scalar coupling  $J \vec{I}_1 \cdot \vec{I}_2$  will also be instrumental in relaxing spin 1 if spin 2 has a short relaxation time:  
*(relaxation = changing spin state)*

$$T_{1\text{SC}}^{-1} = 2\pi^2 J^2 \frac{T_1'}{1 + (\omega_0 - \omega_0')^2 (T_1')^2}$$

*$T_1' = T_1$  of spin 2  
 \* keep changing coupling due to flips  
 \* DIFF because*

$$T_{2\text{SC}}^{-1} = \pi^2 J^2 \left[ T_1' + \frac{T_1^2}{1 + (\omega_0 - \omega_0')^2 (T_1')^2} \right]$$

E.g.: a spin 1/2 nucleus bonded to nuclei with spin > 1/2:  $^{13}\text{C}-^{14}\text{N}$

A similar situation occurs if spin 2 is an electron spin. The resulting **paramagnetic relaxation** happens in paramagnetic systems and when present is usually the dominant relaxation mechanism.

coupling =  $(A) \bar{I} \cdot \bar{S}$

hyperfine coupling constant

$\Rightarrow T_{1par}^{-1} = \frac{A^2}{2} \frac{\tau_{el}}{1 + \omega_s^2 \tau_{el}^2}$

*Handwritten notes:*  
 Hube A = hyperfine coupling = MHz hube  
 & because  $\tau_{el}$  is huge  
 $\omega_s = \text{spin Larmor freq}$

$T_{2par}^{-1} = \frac{A^2}{4} \left( \tau_{el} + \frac{\tau_{el}}{1 + \omega_s^2 \tau_{el}^2} \right)$

$\tau_{1H} = 15$     $\tau_{1H.e} = 1 \times 10^{-8} s!!$

Coherent molecular rotations (e.g. of a -CH<sub>3</sub> group along its C-C bond) can also generate magnetic fields. Collisions make this fields time-dependent and provide an additional mechanism for relaxation: **spin-rotation**

$T_{1SR}^{-1} = 2\pi I kT c^2 \frac{\tau_j}{1 + \omega_0^2 \tau_j^2}$

I: moment of inertia of the group

$\tau_j$ : spin-rotation correlation time

C: spin-rotation coupling constant

\* coupling btw nucleus & M caused by molec rotat, eg)  $H \frac{1}{C} \rightarrow$

$\therefore$  yields small coupling & only  $T_1$  relaxation

The total relaxation rate that is measured:

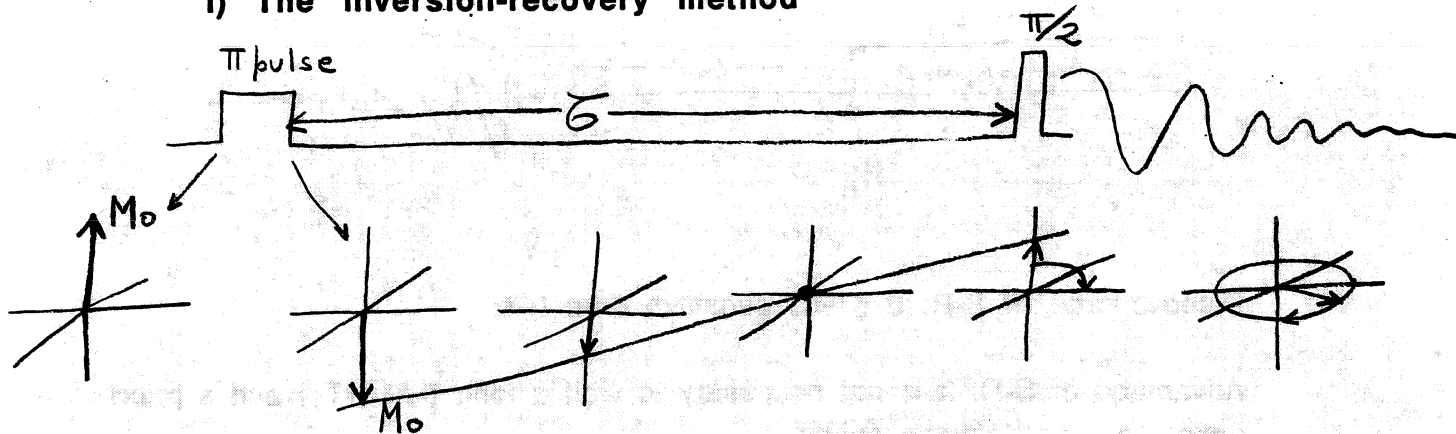
$T_{1/2}^{-1} \approx \sum_i T_{1/2i}^{-1}$

Total Relax = Some of the rates.

### IVA.5 MEASURING T<sub>1</sub> AND T<sub>2</sub>

— There are several pulse sequences for measuring T<sub>1</sub>. The most popular ones are:

#### i) The inversion-recovery method



This sequence measures S as a function of  $\tau$ . Since this signal is proportional to  $M_z(t)$ :

$$\frac{dM_z}{dt} = -\frac{M_z - M_0}{T_1}$$

$$\int_{t=0}^{t=\tau} \frac{dM_z}{M_z - M_0} = -\int_{t=0}^{t=\tau} \frac{dt}{T_1} \Rightarrow \ln(M_z - M_0) \Big|_{t=0}^{t=\tau} = -\frac{\tau}{T_1}$$

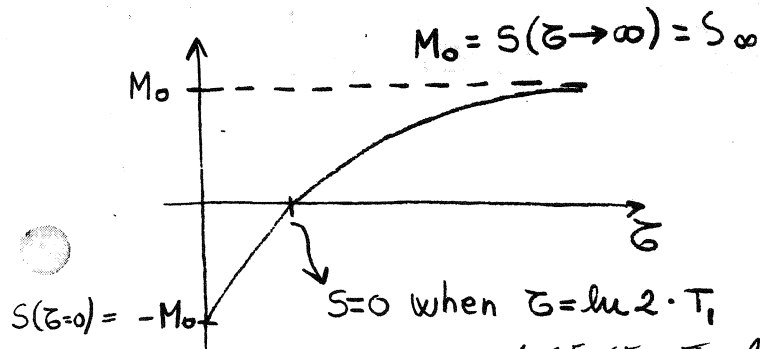
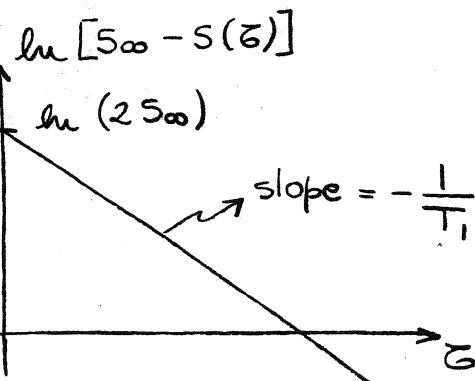
$\nu = 0 \rightarrow -M_0$   
 $\nu = \omega \rightarrow M_0$

$$-\frac{\tau}{T_1} = \ln \left[ \frac{M_z(\tau) - M_0}{-2M_0} \right]$$

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

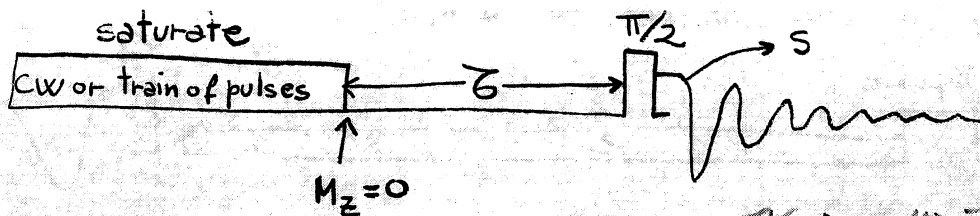
*dependence*

$$\ln[M_0 - M_z(\tau)] = \ln(2M_0) - \frac{\tau}{T_1}$$



\* assume not perfect π pulses  
 then  $M_0 \neq -M_0$   
 # 3 parameters fit  
 $T_1, M_0, \gamma$

ii) Saturation-recovery:



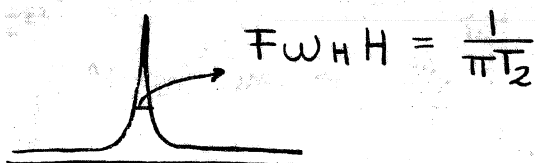
$\tau = 0 \rightarrow M_z = 0$

$\tau = \infty \rightarrow M_z = M_0$

Disadvantage of S-R: It is less sensitive than I-R

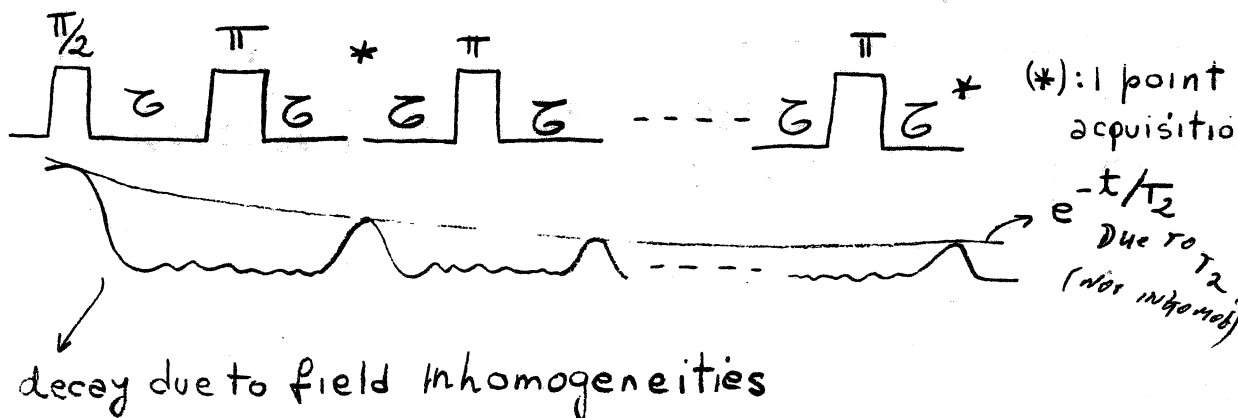
Advantage of S-R: It is not necessary to wait a long ( $\approx 10 \cdot T_1$ ) and a priori unknown time between scans

In principle,  $T_2$  should become available from the line width of a lorentzian NMR peak:



However, could be  $T_2^*$  (to 1st approx.)

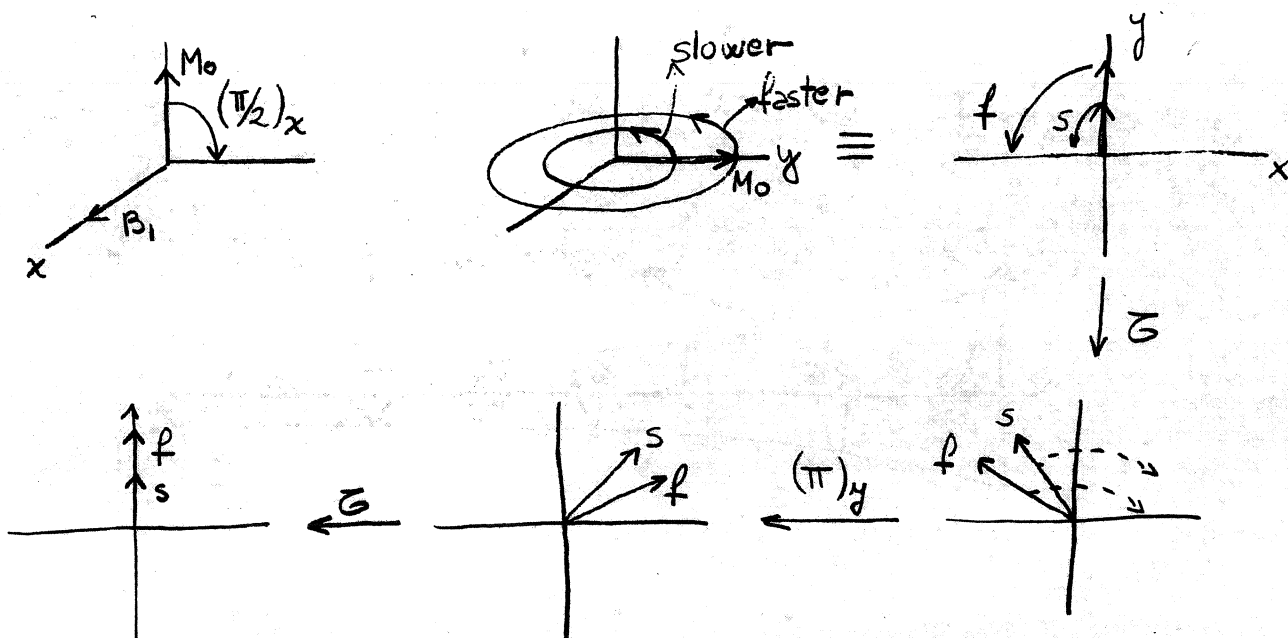
In practice, this doesn't work because the line width is determined mainly by field inhomogeneities. Instead, one uses a "spin-echo" sequence to measure  $T_2$ :



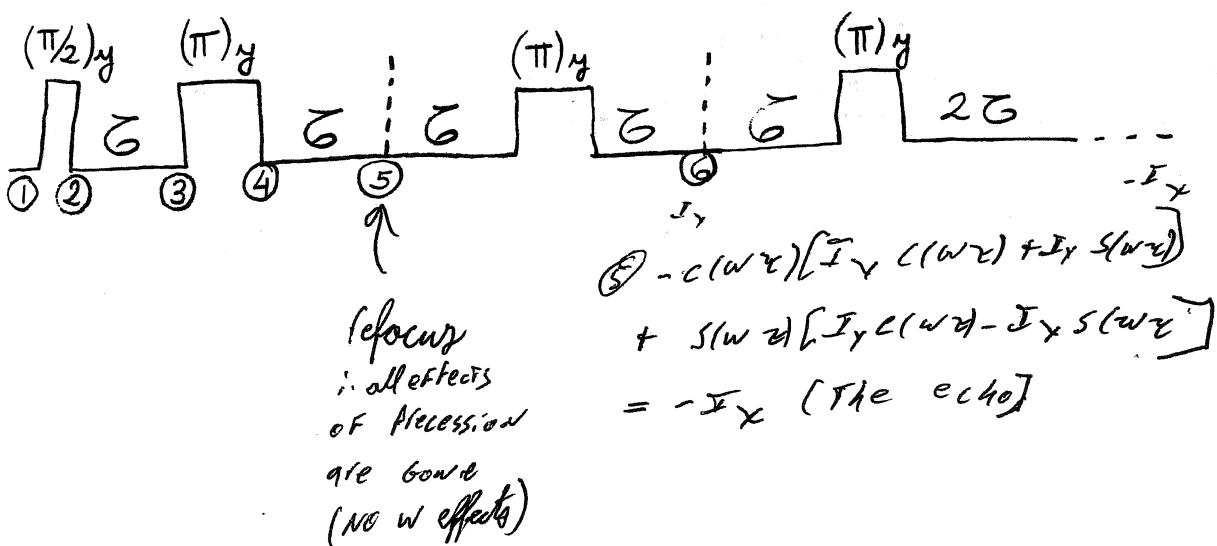
(\*): 1 point acquisition



A classical vector analysis of the spin echo:



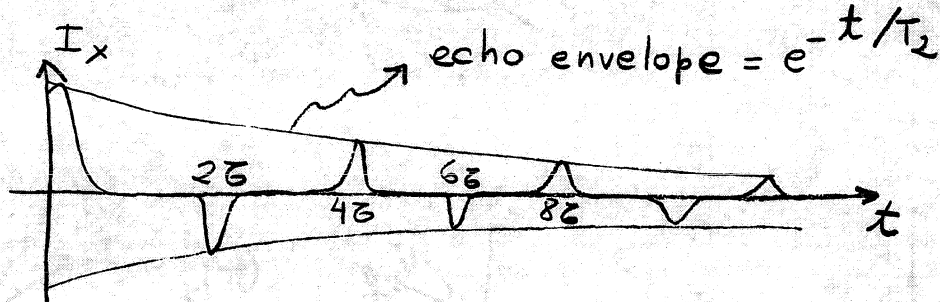
The first spin-echo sequence was proposed by Carr and Purcell



elementary  
of Dewar, 1971  
1955, 1974

Assuming that the only interaction is chemical shift, one has that

- ①  $\rightarrow I_z$
- ②  $\rightarrow I_x$
- ③  $\rightarrow I_x \cos(\Delta\omega\tau) + I_y \sin(\Delta\omega\tau)$
- ④  $\rightarrow -I_x \cos(\Delta\omega\tau) + I_y \sin(\Delta\omega\tau)$
- ⑤  $\rightarrow -I_x$
- ⑥  $\rightarrow +I_x$



It is however difficult (and many times impossible) to give a perfect  $\pi$ -pulse over the whole sample. Small errors in the pulse, for instance using a  $\pi + \epsilon$  pulse, propagate in each cycle. Meiboom and Gill found that these cumulative errors can be largely avoided using the sequence

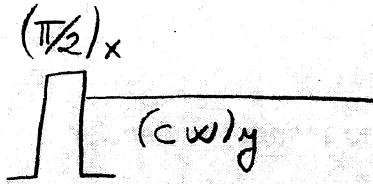


\* cancels out error in  $\pi$

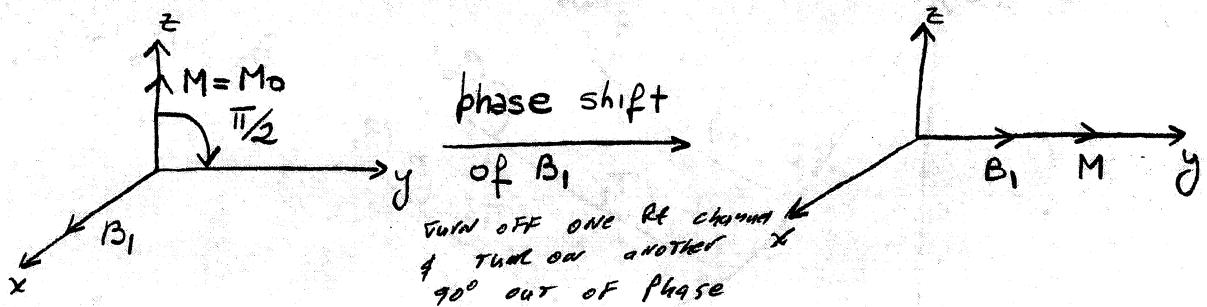
### IVA.6 SPIN-LATTICE RELAXATION IN THE ROTATING FRAME

Consider the following experiment

Redd Field  $\downarrow D$



In the rotating frame



This is called a **spin-lock** experiment. Since  $M \perp B_0$  one would expect the magnetization to decay with a time constant  $\approx T_2$ . Instead

$$M_y(t) = M_0 e^{-t/T_{1e}}, \text{ with } T_{1e} \approx T_1, \text{ not } T_2$$

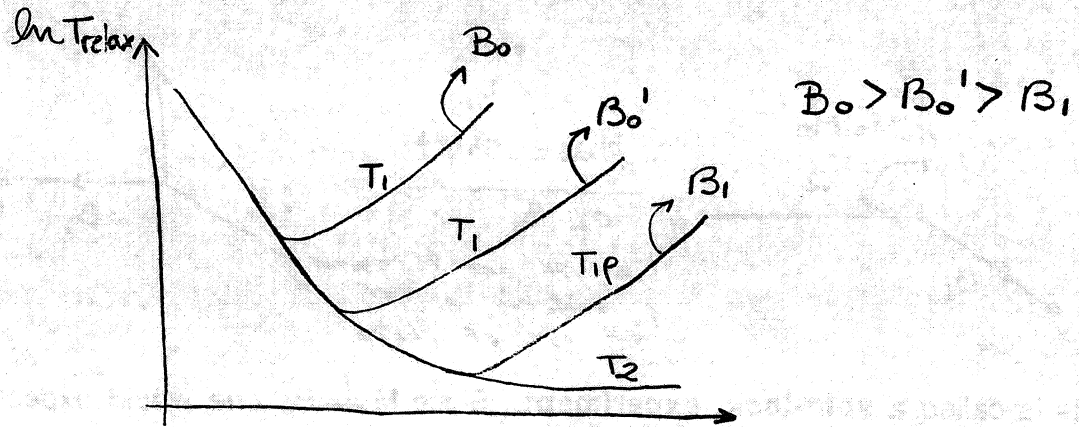
$T_1$  in rotating frame  $(T_1 - \rho_0)$

Moreover,

$$T_{1e}^{-1} \approx (|B_{local}^x|^2 + |B_{local}^z|^2) \cdot \frac{\gamma_c}{1 + \omega_1^2 \gamma_c^2}, \quad \omega_1 = \gamma B_1$$

It is as if  $B_0$  would not exist. This experiment shows that the rotating frame has a true meaning for the spins, and it's not simply a mathematical transformation.

When used together,  $T_{1\rho}$ ,  $T_1$ , and  $T_2$  can be used to monitor molecular reorientations over several orders of magnitude:



$$\frac{1}{\omega_1} \text{ NOT } \frac{1}{\omega_0}$$

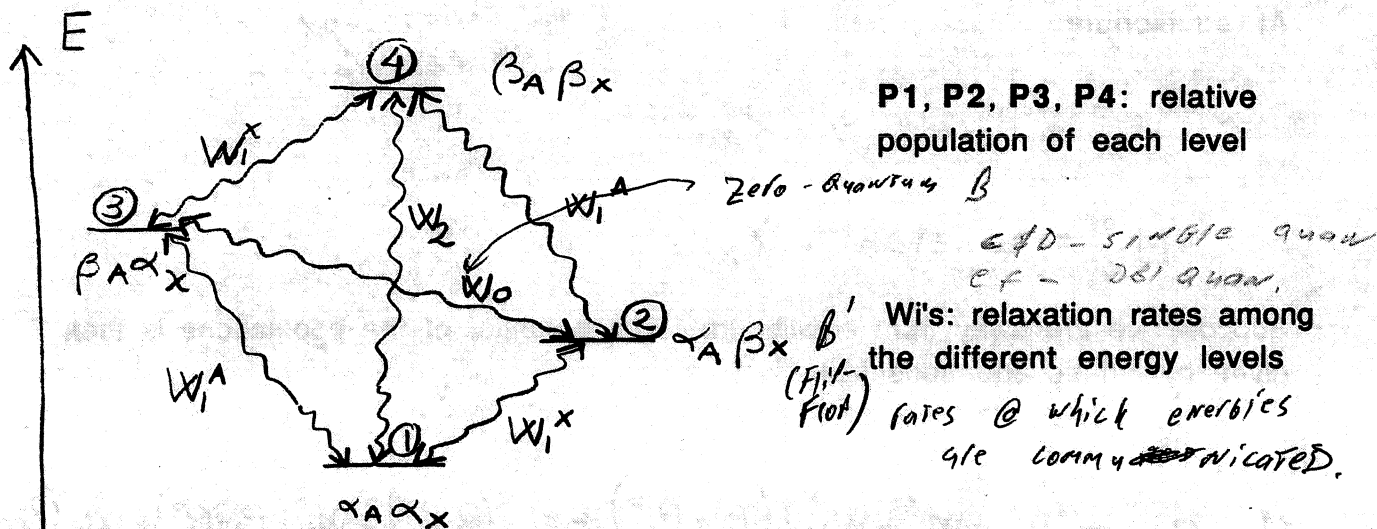
$$\ln \tau_c \propto \frac{1}{\text{Temp}}$$

$\therefore$  SEVERAL ORDERS OF MAGNITUDE LONGER

### IVA.7 THE NUCLEAR OVERHAUSER EFFECT (NOE)

Consider a system of 2 dipole-coupled (i.e., nearby) spins (A,X) tumbling together in solution:

*cross relaxing i.e. dipolar coupled*



\*  $3 - 1 = 4 - 2 =$  DETERMINES INTENSITY OF SIGNAL.  
 \* SATURATE X-SPINS

Among the various terms in the dipolar Hamiltonian: B contributes to  $W_0$   
 C, D contribute to  $W_1$   
 E, F contribute to  $W_2$

A rigorous analysis shows that

$$W_0 = \frac{1}{10} \omega_D^2 \cdot \frac{\gamma_c}{1 + (\omega_A - \omega_X)^2 \tau_c^2}$$

$$\omega_D^2 = \frac{\gamma_A^2 \gamma_X^2 \hbar^2}{r^6}$$

$$W_1^{A,X} = \frac{3}{20} \omega_D^2 \cdot \frac{\gamma_c}{1 + \omega_{A,X}^2 \tau_c^2}$$

$$W_2 = \frac{3}{5} \omega_D^2 \cdot \frac{\gamma_c}{1 + (\omega_A + \omega_X)^2 \tau_c^2}$$

We focus on the intensity of the signal arising from spins A. Its †

$$M_A \propto (P_1 - P_3) + (P_2 - P_4)$$

At equilibrium:

$$M_A^0 = \text{constant} \cdot \gamma_A$$

$$M_X^0 = \text{constant} \cdot \gamma_X$$

Recall curves eqn  $M_0 = \dots$   
@ equilibrium

Saturate X then pop in  
 $\lambda - 1 = 0$   
 $\lambda - 3 = 0$

Suppose we are away from equilibrium. The behavior of the populations is then given by kinetic equations like:

$$\frac{d}{dt} P_1 = -(W_2 + W_1^A + W_1^X)(P_1 - P_1^0) + W_1^X(P_2 - P_2^0) + W_1^A(P_3 - P_3^0) + W_2(P_4 - P_4^0)$$

⋮

It can then be shown that  
*Pop in Popul*

\* also depends on how far X is from equil. also  
↓

$$\frac{dM_A}{dt} = - \underbrace{(W_0 + 2W_1^A + W_2)}_{R_A} (M_A - M_A^0) - \underbrace{(W_2 - W_0)}_{R_{AX}} (M_X - M_X^0)$$

↙ SELF RELAX      ↘ CROSS RELAX

$$\frac{dM_X}{dt} = - \underbrace{(W_2 - W_0)}_{R_{AX}} (M_A - M_A^0) - \underbrace{(W_0 + 2W_1^X + W_2)}_{R_X} (M_X - M_X^0)$$

if irradiate  $M_X$  (saturate)  
then  $M_X = 0$

The relaxation of the populations is coupled!

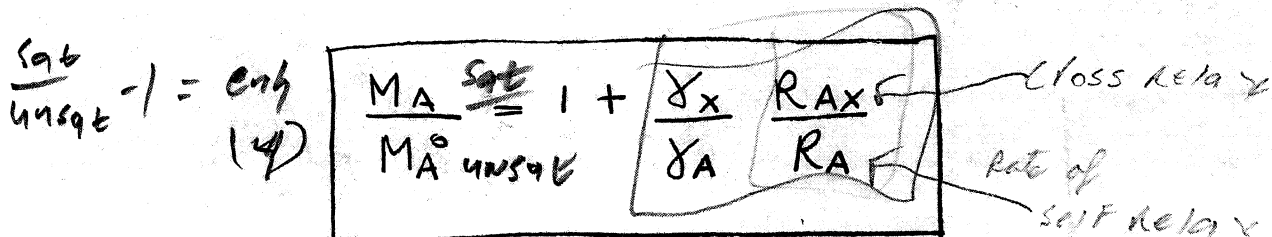
\* Note, DON'T confuse from say CSA, since there aren't any flip flop terms as in DIP-DIP

Assume now that we irradiate the X system until saturation:  $M_x = 0$

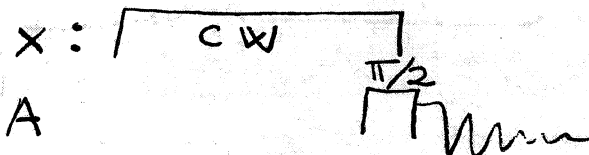
Then, once the system reaches equilibrium (set  $\frac{dM_x}{dt} = 0$  for steady state)

$$0 = -R_A (M_A - M_A^0) - R_{AX} M_x^0 \iff \frac{M_A}{M_A^0} = 1 + \frac{R_{AX}}{R_A} \cdot \frac{M_x^0}{M_A^0}$$

or, since  $M_x^0 / M_A^0 = \gamma_X / \gamma_A$



The signal observed in



is enhanced by  $\eta = 1 + \frac{\gamma_X}{\gamma_A} \frac{R_{AX}}{R_A}$  in the extreme narrowing regime

$$= 1 + \frac{1}{2} \frac{\gamma_X}{\gamma_A}$$

Then  $^1\text{H} \cdots ^1\text{H} : \eta = 1.5$ ;  $^{13}\text{C} \cdots ^1\text{H} : \eta = 2.99$ ;  $^{15}\text{N} \cdots ^1\text{H} : \eta = -3.93$

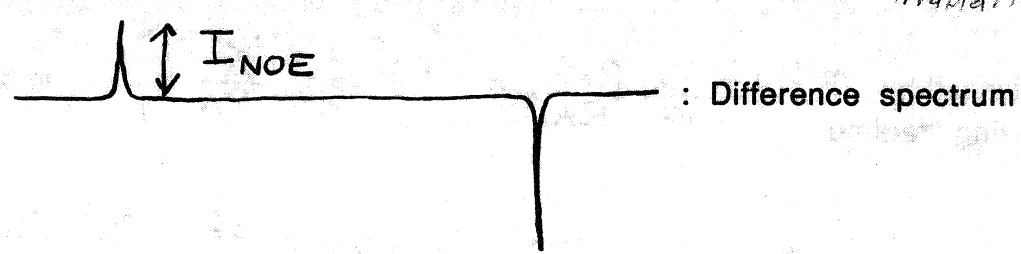
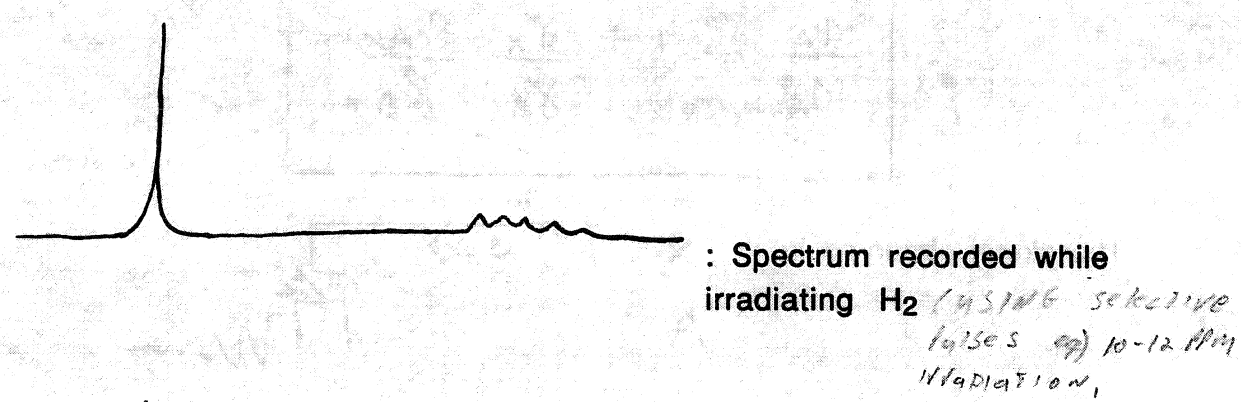
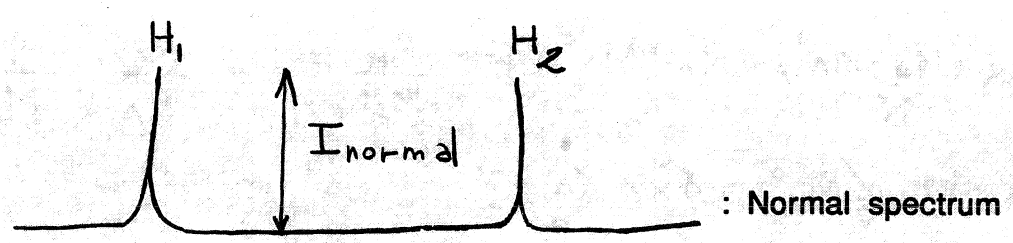
This enhancement is called Nuclear Overhauser Effect (NOE), and is induced by dipolar relaxation. If other relaxation mechanisms are present,  $\eta$  decreases because only dipole-dipole has the  $W_0, W_2$  contributions.

Since  $\eta$  depends on the # of  $^1\text{H}$  attached,  $^{13}\text{C}$ -NMR spectra recorded using  $^{13}\text{C}$ - $^1\text{H}$  NOE are not quantitative.

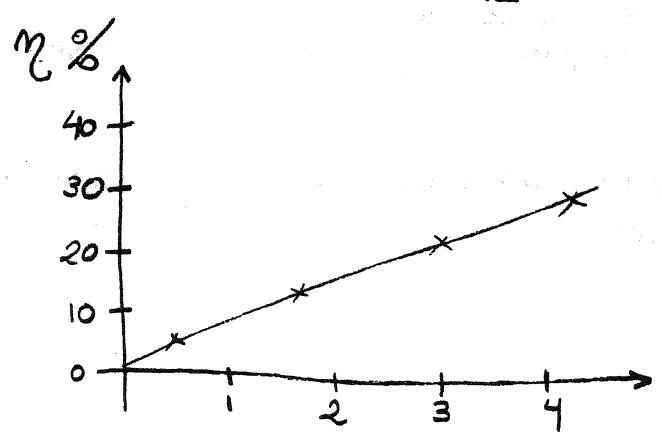


Irradiate with proton and other C-H signal is 750% ... all close

NOE's can be used to measure internuclear distances, mainly in homonuclear systems. For instance, given a 2 proton system



The NOE enhancement  $\eta = \frac{I_{NOE}}{I_{NORMAL}}$  is proportional to  $r_{12}^{-6}$  :



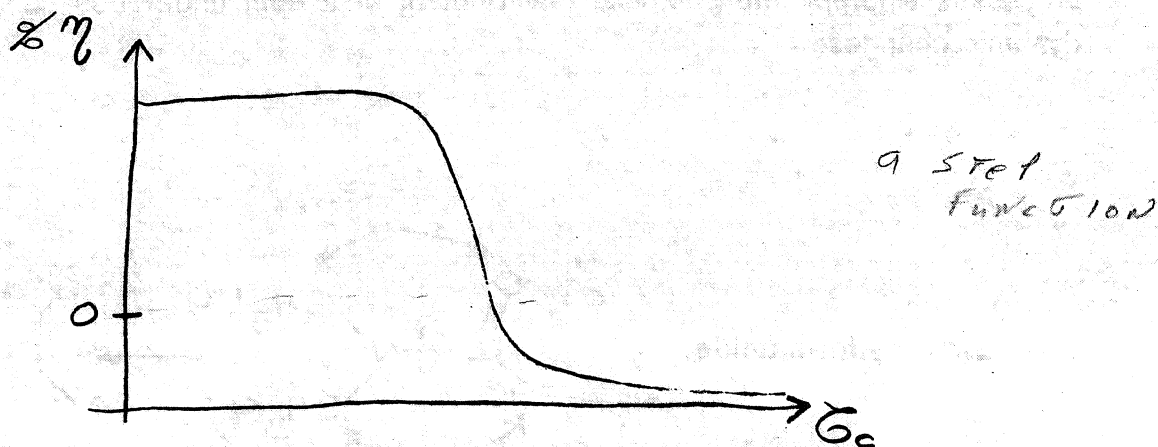
RELAXATION PROCESSES  
 $(\frac{1}{r_{12}})^2$  USE SINGLE

\* Don't need to know correlation  
\* Need to know distance eg) in aromatics  
can calibrate test



Given one pair of spins whose internuclear distance is known, other internuclear distances in the molecule can be obtained by NOE measurements.

NOE's are also dependent on the correlation time of the spin pair:



- NOE's are dependent on the correlation time of the spin pair:
- \* NOE's can fall below 0, give NO! signal!
  - \* NOE's: need model & correl. times

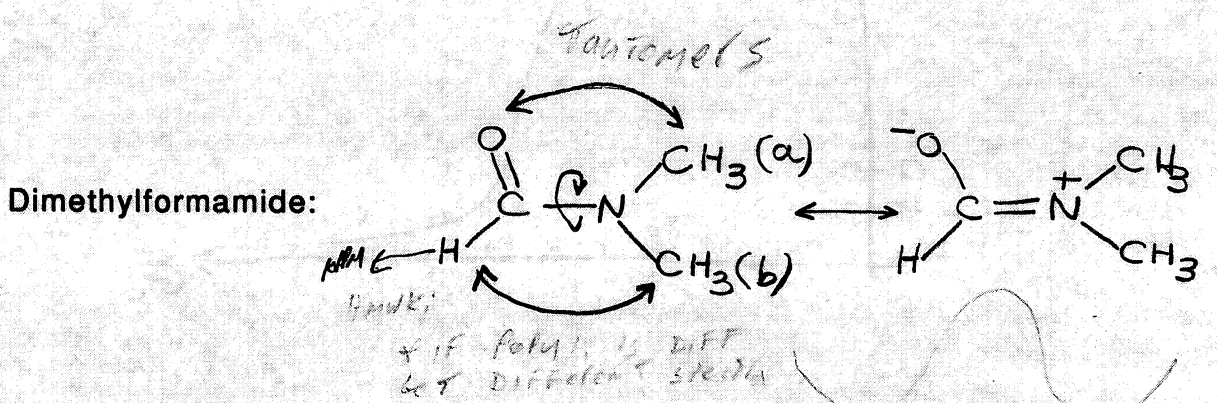
Since  $\eta$  changes sign, for certain heteronuclear cases the intensity of a signal  $(1 + \eta)$  may become zero!

Bibliography: - Harris, Ch 5A  
 - Slichter, Ap. E  
 - Abragam, Ch. X. II

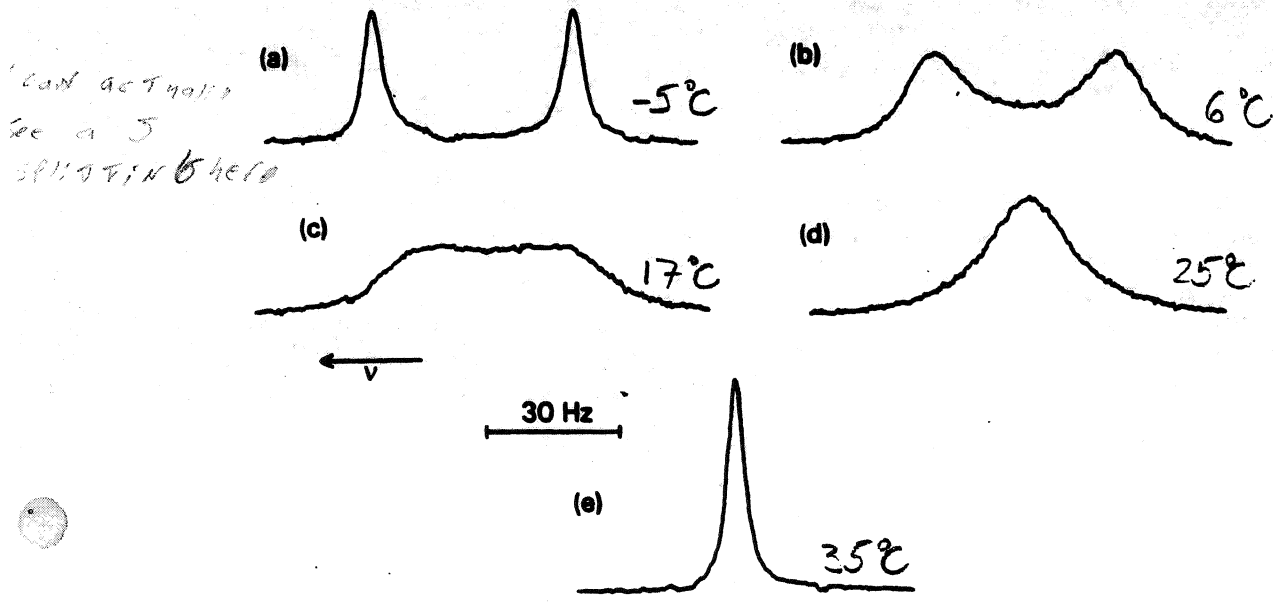
**IVB: NMR AND CHEMICAL EXCHANGE**

**IVB.1 TWO-SITES EXCHANGE PROCESS**

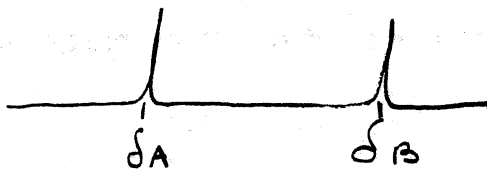
NMR can be particularly useful to analyze chemical exchange processes; i.e., processes whereby the chemical environment of a spin undergoes constant dynamic changes:



The C-N bond rotation is slow; each time the bond rotates, protons in groups **a** and **b** exchange their isotropic chemical shifts. Dynamic NMR relies on measuring the spectra of such systems as a function of temperatures:

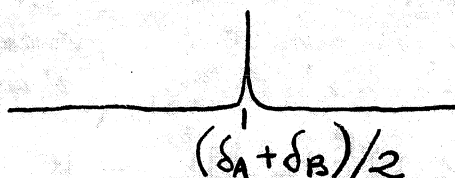


At low temperatures:



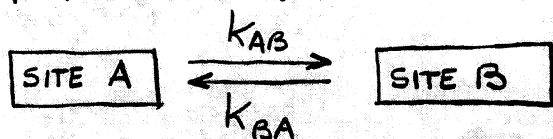
For an  
single  
NMR  
with 2 chem  
environments

At high temperatures:



\* Use magnet model (of matrices)

To see how to extract information (rates, populations, etc.) from these lineshapes, consider a system whose spins can adopt 2 chemical shift values:



k's: rates of the processes (Hz)

$\nu_A$

$\nu_B$

: rotating-frame chemical shift (in Hz)

$T_{2A}$

$T_{2B}$

: natural linewidths (in sec)

$$P_A = \frac{k_{BA}}{k_{AB} + k_{BA}}$$

$$P_B = \frac{k_{AB}}{k_{AB} + k_{BA}} \quad \text{: relative populations}$$

Since no spin-spin couplings are assumed, the system can be treated classically (i.e. avoid density matrix)

The equation of motion for the in-plane magnetizations (page 44):

$$\frac{dM_{\pm}^A}{dt} = i \underbrace{\nu_A}_{\text{rotates at } \nu_A} M_{\pm}^A - \underbrace{\frac{M_{\pm}^A}{T_{2A}}}_{\text{relax}}$$

$$\frac{d[A]}{dt} = -k[A] \rightarrow e^{-kt} = \frac{[A(t)]}{[A(0)]} \quad (50)$$

We take into account the effects of exchange assuming a first-order kinetics:

When you swap from one site to the other, it takes its magnetic w/f.

$$\frac{dM_+^A}{dt} = i\nu_A M_+^A - \frac{M_+^A}{T_{2A}} - \underset{\substack{\uparrow \\ \text{leaving A} \\ \text{at rate } k_{AB}}}{k_{AB}} M_+^A + \underset{\substack{\uparrow \\ \text{leaving B} \\ \text{at rate } k_{BA}}}{k_{BA}} M_+^B$$

$$\frac{dM_+^B}{dt} = i\nu_B M_+^B - \frac{M_+^B}{T_{2B}} - k_{BA} M_+^B + k_{AB} M_+^A$$

Coupled behavior  
∴ put in matrix

In matrix form:

$$\frac{d\vec{M}_+}{dt} = \vec{A} \vec{M}_+$$

$$\frac{d\vec{M}_+}{dt} = \vec{A} \cdot \vec{M}_+ \quad \text{IF } k_{AB}=0 \rightarrow \text{diag}$$

$$\vec{M}_+ = \begin{pmatrix} M_+^A \\ M_+^B \end{pmatrix}$$

↑ as k ↑

\* Small k's have no ESR still but peaks broaden still,

$$\vec{A} = \begin{pmatrix} -\frac{1}{T_{2A}} - k_{AB} + i\nu_A & k_{BA} \\ k_{AB} & -\frac{1}{T_{2B}} - k_{BA} + i\nu_B \end{pmatrix}$$

\* 2x2 exchange matrix  
\* can get 10x10 matrix for 10 diff pos. 5

This equation has a simple formal solution:

$$M_+(t) = e^{\vec{A}t} \cdot M_+(0)$$

assuming steady state at equl

$$M_+(0) \propto \text{populations} : \begin{pmatrix} P_A \\ P_B \end{pmatrix}$$

$e^{\nu t} \cdot M_+ \rightarrow$  steady precess plus 2 site  
\* can't get out of site

$$\int_0^{\infty} e^{-\omega t} dt = \frac{e^{-\omega t}}{-\omega} \Big|_0^{\infty} = 0 - \frac{e^0}{-\omega} = \frac{1}{\omega} \quad (15b)$$

Now there are 2 possible ways to continue:

because it doesn't  $\rightarrow \infty$   
 because of the  
 terms

i) If spectra will be calculated by computer programming, it is convenient to evaluate the time-domain signal and then use standard FFT to get the spectrum.

To calculate  $e^{At}$ , one has to find D such that A is diagonal:

$$D^{-1} \cdot A \cdot D = \lambda \cdot \delta_{ij}$$

$\lambda \in \mathbb{C}$ : real part  $\rightarrow$  line widths  
 imaginary part  $\rightarrow$  frequencies

Diagonalization of A

Then,

$$e^{At} = D \begin{pmatrix} e^{\lambda_1 t} & 0 \\ 0 & e^{\lambda_2 t} \end{pmatrix} D^{-1}$$

and the signal is calculated as

$$S(t) = M_+^A(t) + M_+^B(t) \quad \text{Put in computer}$$

$M_{2 \times 2}$ : can solve anal  $a \rightarrow b \rightarrow a$   
 cannot " eq.  $a \rightarrow b \rightarrow c \rightarrow a$

$M_{5 \times 7}$  ii) To get an analytical expression for the spectrum  $I(\nu)$ , it is necessary to calculate  $(1, 1)$  horiz vector

$$I(\nu) = \text{Re} \left[ \int_0^{\infty} S(t) e^{-i\nu t 2\pi} dt \right] = \text{Re} \left[ \int_0^{\infty} \vec{1} \cdot e^{At} \cdot \overline{M_+(0)} \cdot e^{-i\nu t 2\pi} dt \right]$$

$\left( \begin{matrix} M_+^A(0) \\ M_+^B(0) \end{matrix} \right) \rightarrow \left( \begin{matrix} M_A \\ M_B \end{matrix} \right)$

$$= \text{Re} \left[ \vec{1} \cdot W^{-1} \cdot \overline{M_+(0)} \right]; \text{ Where } \vec{1} = (1, 1) \text{ and}$$

Need to fig out how to invert W.

$$W = A - i2\pi\nu \cdot I$$

$\uparrow$   
 UNITY MATRIX

assume same  $\delta$  equal pops

For the case  $\frac{1}{T_{2A}} = \frac{1}{T_{2B}} = 0$ ;  $k_{AB} = k_{BA} = k$ ,  $\nu_A = -\nu_B = \delta$

variable  $\delta$  or  $1/2$

$$I(\nu) = \frac{4\delta^2 k}{\nu^4 + 2\nu^2(2k^2 - \delta^2) + \delta^4}$$

center of mass  
 fixed set:  $k$   
 change:  $\nu$   
 $a = \frac{\pi \cdot \delta}{k}$   
 $k: 5-1 k$

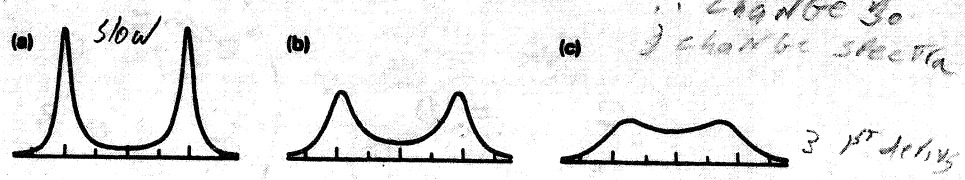
The spectra  $I(\nu)$  as a function of the parameter  $a = \frac{\pi \cdot \delta}{k}$

eg) ON 400MHz spectrum,

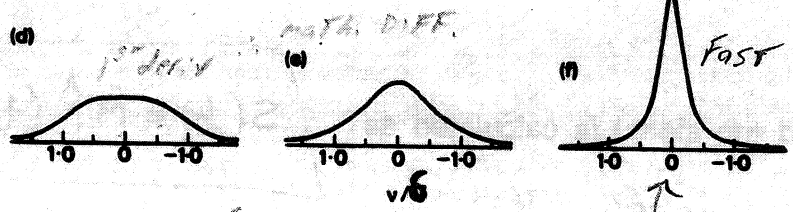
We had to raise the temp 50°C to get the same results, i.e. 400MHz rxn independent

$\delta =$  separation of sites

$\frac{k}{\delta} \rightarrow$  important  
 $\therefore$  change to  $I$  change spectra



(a)  $a = 4$ ;  
 (b)  $a = 2$ ; (c)  $a = 1$ ; (d)  $a = 1/\sqrt{2}$  (coalescence); (e)  $a = 0.5$ ;  
 (f)  $a = 0.2$ . Spectra (a) and (f) are near the slow- and fast-exchange limits respectively.



$\uparrow \uparrow k$  is  $\uparrow$

Shows at c.o.m

Palans The time-scale of dynamic NMR is given by the ratio

DIFF IN Hz  $\rightarrow$

$$\frac{|\nu_I - \nu_{II}|}{k}$$

$f \rightarrow$  set of peaks (in Hz)  
 $k \rightarrow$  rate of change (in Hz)  $\downarrow$  MUST BE SAME UNITS

+  $f - f$  shows at zero for (f) equal pops

$q = \frac{1}{\sqrt{2}}$  have (d) coalesced

In the slow exchange, when  $|\nu_I - \nu_{II}| > k$ ,

\* GET

$$A \approx \begin{pmatrix} -i\delta - (\frac{1}{T_2} + k) & 0 \\ 0 & i\delta - (\frac{1}{T_2} + k) \end{pmatrix}$$

Spectra consists of two lorentzian lines centered at  $\pm\delta$  with line widths proportional to  $(\frac{1}{T_2} + k)$

At coalescence the 2 peaks meet

Beyond coalescence, in the fast exchange regime, the degenerate eigenvalues:

$$P_A \delta_A + P_B \delta_B : \text{II} \leftrightarrow \text{position (avg pos)}$$

$$\frac{1}{T_2} + \frac{|\delta_A - \delta_B|}{K_{AB} + K_{BA}} : \text{IR} \leftrightarrow \text{linewidth}$$

NAT L.W.

$$\rightarrow \frac{1}{T_2}$$

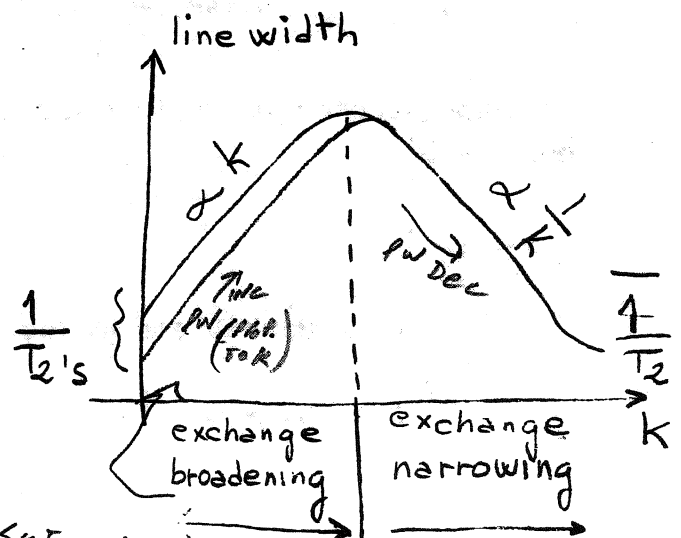
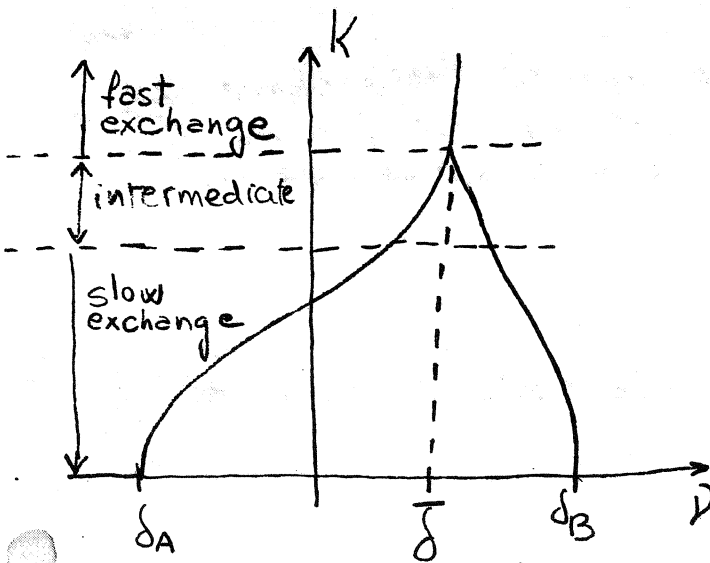
Total Rate

$$K_{AB} = K_{BA} \therefore \uparrow \delta$$

no change

Overall, the peak position and width as a function of rates:

$\uparrow k, \uparrow T$  at  $T=D$  pos become



low k  $\therefore$  peaks don't change but L.W.'s still change

\* ONLY works FOR ISOLATED SYSTEMS

\* DOES NOT WORK FOR J-COUPL SYSTEMS THOUGH

$\frac{(\sigma_1 - \sigma_2)}{J}$

### IVB.2 THE EXCHANGE SUPEROPERATOR

The formalism described above is only suitable if the spin system can be represented by magnetization vectors. Nevertheless in some systems like strongly coupled pairs of spins, the complete Schroedinger equation

~~\* AB strongly coupled system can't be described~~

$$\frac{\hbar}{i} \frac{d\rho}{dt} = [\rho, \mathcal{H}]$$

has to be the starting point for evaluating the effects of chemical exchange. Exchange is taken into account via the exchange superoperator  $\Xi$ , defined by the equation

$$\frac{\hbar}{i} \dot{\rho} = [\rho, \mathcal{H}] + \sum_{\text{\# of processes}} k_i (R \cdot \rho \cdot R^{-1} - \rho)$$

LINEAR ON  $\rho$   
 $\therefore$  can write as sum of ops

rotation around  $\hat{I}$

ELEMENTS IN DENS. MATRIX CHANGE

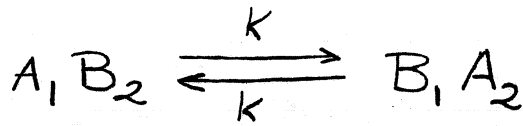
R - describes what exchange does to basis set (ACTUALLY a MATRIX)

For each process i taking place at a rate  $k_i$ , the elements of the exchange operator R

$$R_{ij} = \begin{cases} 1, & \text{if state } |i\rangle \text{ and } |j\rangle \text{ are interconnected by the dynamic process} \\ 0, & \text{otherwise} \end{cases}$$

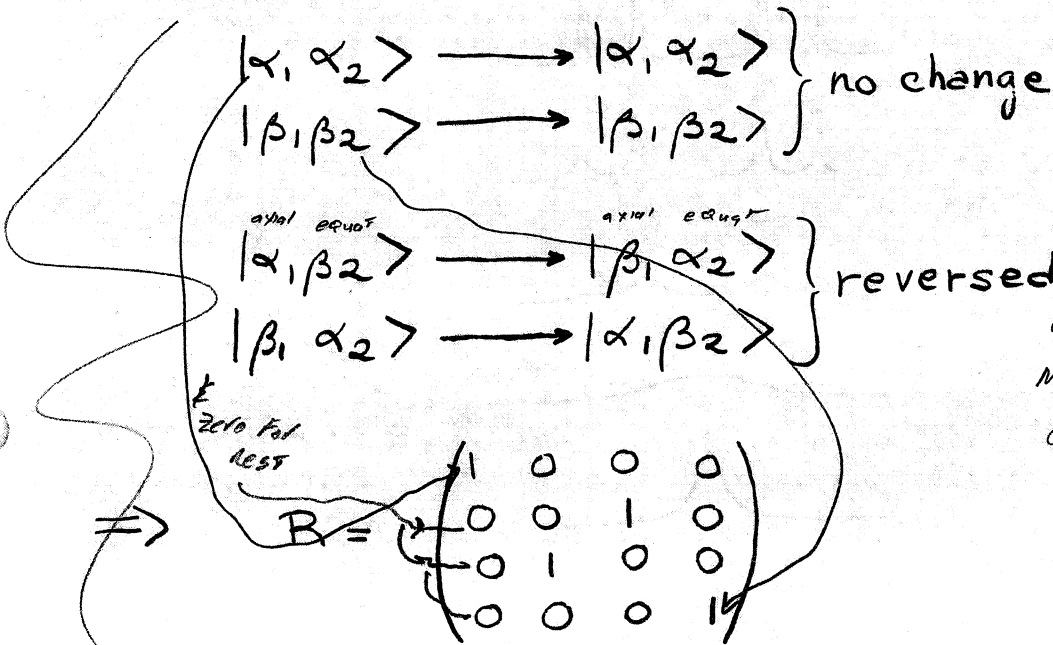


As an example, consider a strongly coupled system undergoing mutual exchange:



a def. exchange  
exchange is mutual w/ same K

The effects of R:



at higher fields  
need higher temps to  
get A2 single peak

$$R = R^{-1}$$

Note that since the exchange is mutual  $R = R^{-1}$

The Liouville equation is then

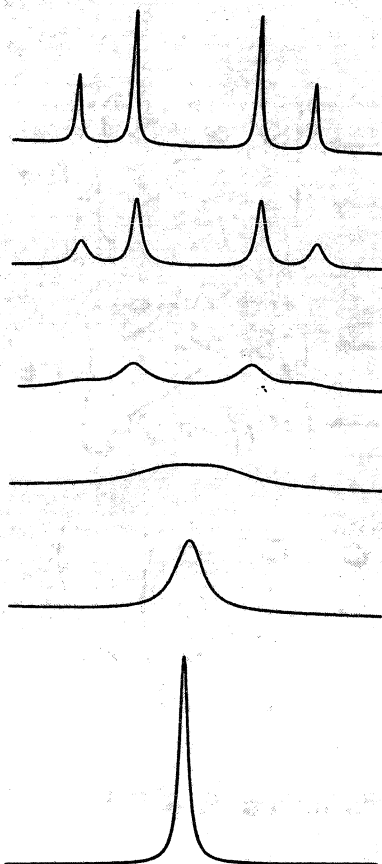
$$\dot{\rho} = i[\rho, \mathcal{H}] + [R \cdot \rho \cdot R - \rho] \cdot K$$

with

$$\mathcal{H} = \begin{pmatrix} -\Sigma + J_{AB}/4 & 0 & 0 & 0 \\ 0 & \Delta - J_{AB}/4 & J_{AB}/2 & 0 \\ 0 & J_{AB}/2 & -\Delta - J_{AB}/4 & 0 \\ 0 & 0 & 0 & \Sigma + J_{AB}/4 \end{pmatrix}$$

$\Sigma = \frac{\omega_A + \omega_B}{2}$   
 $\Delta = \frac{\omega_A - \omega_B}{2}$

The line shapes as a function of k:



A set of AB spectra as a function of the rate of the  $A \rightleftharpoons B$  exchange.  $\delta\nu = 20.0$  Hz,  $J_{AB} = 6.5$  Hz,  $T_2 = 0.5 \cdot s$ ,  $k$  from top to bottom: 0.0, 3.0, 15.0, 57.0 (coalescence), 200.0, 1000.0  $s^{-1}$ .

Time scales &  $\Delta f$  & J-coupl defined

### IVB.3 PROBLEMS

1) Show that a random field of the form

$$\mathcal{H}_1(t) = \sum_{\alpha=x,y,z} B_{\alpha}(t) \cdot I_{\alpha}$$

leads to a  $T_2$  relaxation time

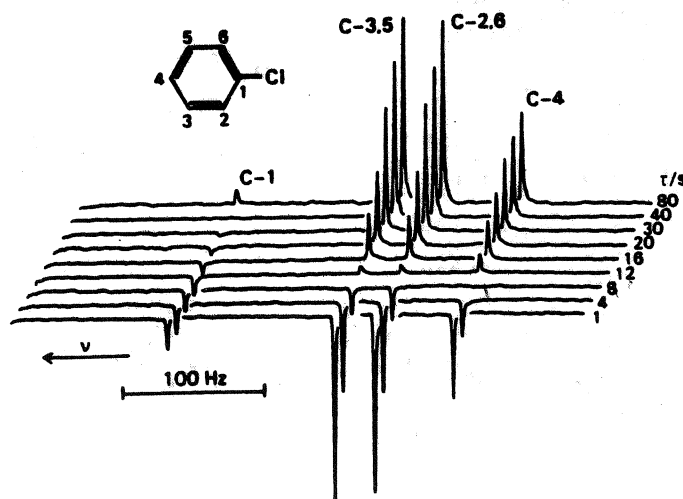
$$\frac{1}{T_2} = \gamma^2 \left[ |B_z|^2 \tau_0 + \frac{(|B_x|^2 + |B_y|^2)}{2} \cdot \frac{\tau_0}{1 + \omega_0^2 \tau_0^2} \right]$$

(See Slichter, Ch. 5.12)

2) Explain the following trend observed for the  $^{13}\text{C}$   $T_1$  times of n-decanol

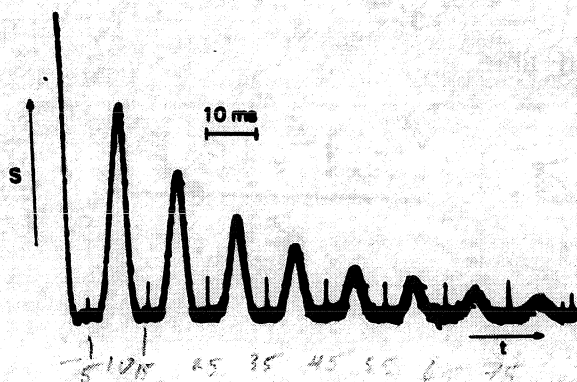
$\text{C}_1$	$\text{C}_3$	$\text{C}_5$	$\text{C}_7$	$\text{C}_9$
0.65 sec	0.77 sec	0.84 sec	1.1 sec	2.2 sec

3) Estimate the  $T_1$  relaxation times of individual carbon sites from the following  $^{13}\text{C}$ NMR inversion recovery data set of chlorobenzene:



4) Calculate the  $\tau$ -dependence of the signals in a saturation-recovery experiment.

5) Estimate the  $T_2$  relaxation time of the spin system giving origin to the following spin-echo FID. What is the  $T_2^*$ ?



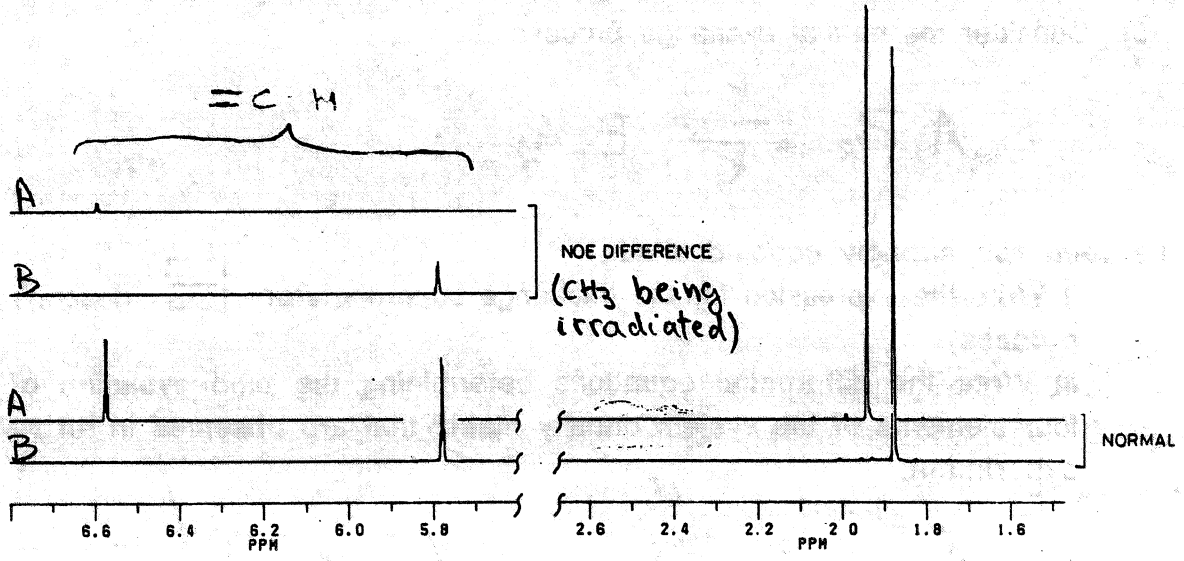
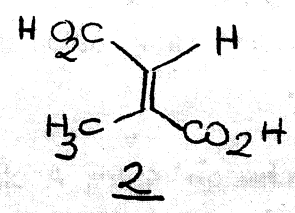
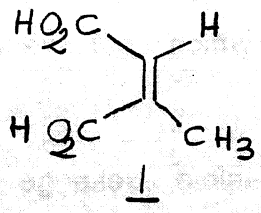
6) Calculate the expression for the density matrix at the top of the n-th spin echo in the Carr-Purcell and in the Meiboom-Gill sequences.

7) Demonstrate the equations for longitudinal relaxation of a dipole-coupled spin pair A,X in solution:

$$\frac{dM_A}{dt} = -R_A (M_A - M_A^0) - R_{AX} (M_X - M_X^0)$$

$$\frac{dM_X}{dt} = -R_{AX} (M_A - M_A^0) - R_X (M_X - M_X^0)$$

8) Assign each spectrum to its corresponding compound on the basis of the following NOE experiments:



9) Demonstrate that given a matrix A that can be diagonalized as

$$[D^{-1} \cdot A \cdot D]_{ij} = \lambda_i \cdot \delta_{ij}$$

then

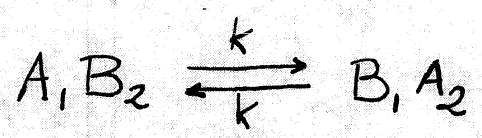
$$e^{At} = D \cdot \begin{pmatrix} e^{\lambda_1 t} & & \\ & \ddots & \\ & & e^{\lambda_n t} \end{pmatrix} \cdot D^{-1}$$

10) Calculate the FID arising from two mutually exchanging sites A,B, assuming  $k_{AB} = k_{BA} = k$ ;  $\frac{1}{T_{2A}} = \frac{1}{T_{2B}} = 0$ ;  $\nu_A = -\nu_B = \nu$

11) For the preceding case, calculate the ratio  $\nu/k$  at which coalescence takes place.

12) Write the exchange matrix A characterizing all possible exchange processes among four uncoupled sites.

13) Consider the mutual exchange process



between two strongly coupled sites.

i) Write the expression for the exchange superoperator  $\mathcal{E}$  describing the process

ii) Write the differential equations determining the time evolution of the four elements of the system density matrix that are observed in an NMR experiment.

$$F^\dagger = \begin{pmatrix} \alpha & 0 \\ 0 & \beta \end{pmatrix}, \quad F = \begin{pmatrix} \alpha & 0 \\ 0 & \beta \end{pmatrix}$$

$$S(t) = \langle M^\dagger \rangle = \text{Tr} (e^{-Ft})$$

$\begin{pmatrix} 1 & 2 & 3 & 4 \\ \dots & \dots & \dots & \dots \\ \dots & \dots & \dots & \dots \\ \dots & \dots & \dots & \dots \end{pmatrix}$

$F^\dagger = \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix} \otimes \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} + \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \otimes \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix}$

For  $S_1$       For  $S_{21}$

$\rho_{11} + \rho_{33} + \rho_{42} + \rho_{43}$