

Chem 564

NOTES 16

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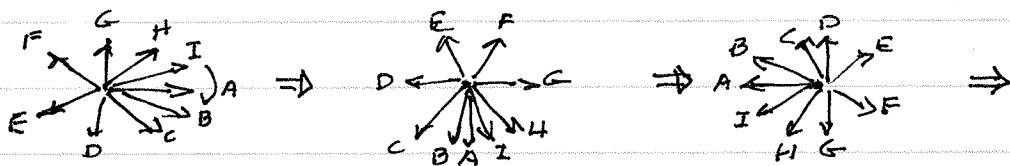
DEPHASING, RELAXATION AND ECHOES

A. DEPHASING (LOSS OF COHERENCE)

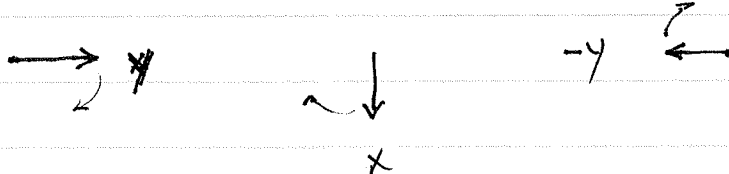
We saw on p. 8 of Notes 15 how  $\langle \vec{E} \rangle$  precesses during the absence of coupling,  $H_{12} = 0$ . The frequency was  $\omega_0 = \frac{H_{22} - H_{11}}{\hbar}$ , the Larmor frequency

If  $H_{22} - H_{11}$  was absolutely constant and the same for every system in the ensemble, the precession and coherence would last indefinitely. This sounds a little like perpetual motion, and indeed the signals  $S(t)$  due to the coherence do die away (usually exponentially),  $S = S_0 e^{-t/T}$  where  $T =$  the "relaxation time".

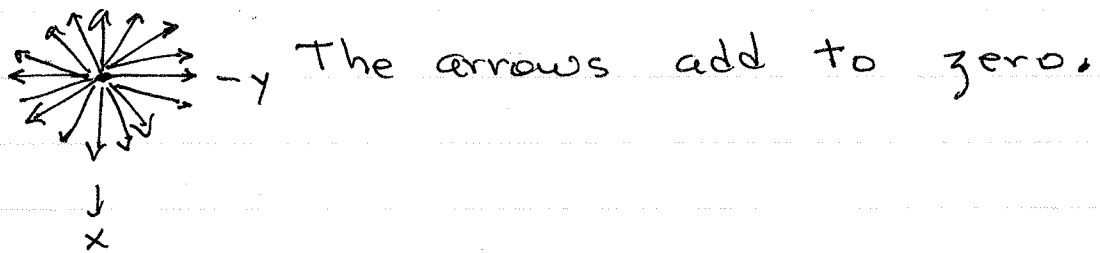
First, visualize the coherence as a slight non-cancellation of many individual density vectors of individual systems.



NET:  $\langle \vec{E} \rangle$



Loss of coherence (dephasing) comes from the loss of the slight bunching of the density vectors — a loss of definite phase relations between the systems — so that the density of vectors is uniform.



The relaxation of  $\langle e_x \rangle$  &  $\langle e_y \rangle \rightarrow 0$  is known as transverse relaxation ( $T_2$ ). This can happen while  $e_z$  remains constant, i.e., no changes in population.

(In magnetic resonance this is known as spin-spin relaxation)

### Mechanisms for transverse relaxation:

One source of transverse relaxation is caused by inhomogeneity in  $H_{11} - H_{22}$ , meaning that different systems of the ensemble have different Larmor frequencies. Thus, the individual  $\vec{e}$  vectors rotate at different rates and their relative phases

will change in time. When dealing with large numbers of systems the relative phases become random. This is dephasing.

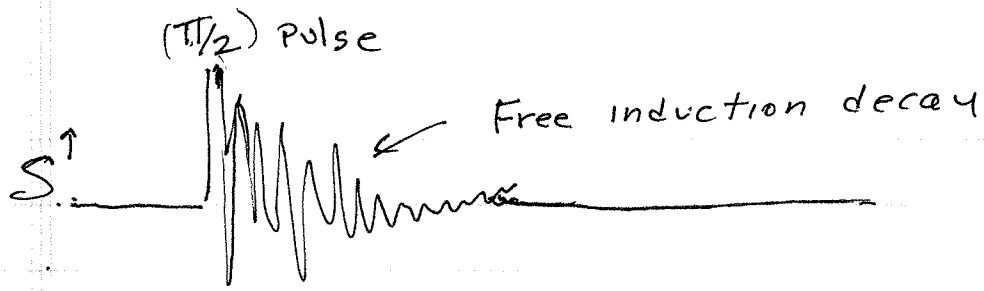
### Two Reasons for a distribution of $H_{11} - H_{22}$ :

- In NMR, if the magnetic field is inhomogeneous (varies across the sample) different systems will have different  $H_{11} - H_{22}$  (different Zeeman splitting)
- the local environment around each system is different during the measuring time (called inhomogeneous broadening)

### B. MEASURING $T_2$ : PHOTON ECHOES

TRUE inhomogeneous broadening — wherein each system has its own characteristic  $H_{11} - H_{22}$  that is constant in time — gives rise to a spectacular phenomenon known as the photon echo (spin echo for spin systems).

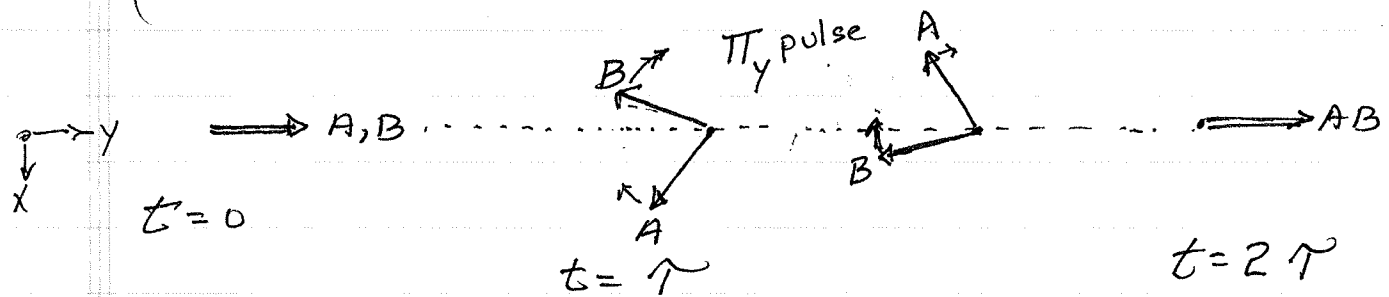
If there is a signal  $S_0$  measured due to the coherence that decays due to dephasing as  $S = S_0 e^{-t/T_2}$ , the experimental result looks like:



The loss of signal does not mean the ensemble has returned to equilibrium. Recall, the  $\pi/2$  pulse makes  $\langle P_{11} \rangle = \langle P_{22} \rangle$ , i.e.,  $\langle P_z \rangle = 0$ . Often the  $T_2$  decay is fast enough that  $\langle P_{11} \rangle = \langle P_{22} \rangle$  after the signal has decayed. All that decayed was the coherence. The ensemble still has hidden order because there still exist definite phase relations between the systems whose  $\vec{P}$  vectors were brought into phase by the  $\pi/2$  pulse. That phase information can be reversed and ultimately refocussed by a  $\pi$  pulse.

Consider first just two systems (or subensembles) A & B with  $\frac{(H_{11} - H_{22})_A}{\hbar} = \omega_{0A}$  and

$$\frac{(H_{11} - H_{22})_B}{\hbar} = \omega_{0B}, \text{ with } \omega_{0A} < \omega_{0B}$$

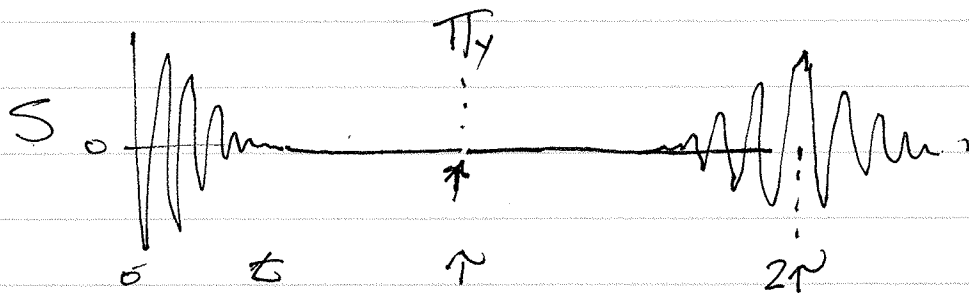


where  $\uparrow$  is an arbitrary time interval.

After time interval  $\tau$  the A vector lags behind the B vector by the amount of angle  $= (\omega_2 - \omega_1)\tau$

The  $\pi_y$  pulse precesses the vectors by  $180^\circ$  about y, putting A ahead of B by the amount  $(\omega_2 - \omega_1)\tau$ . Thus, after another  $\tau$  of time interval, B just catches up to A as they both point in the  $+y$  direction again!

This happens for all pairs of systems and the signal is completely regenerated, only to decay again.



The following two pages show actual photon echoes recorded by the early pioneers of NMR.

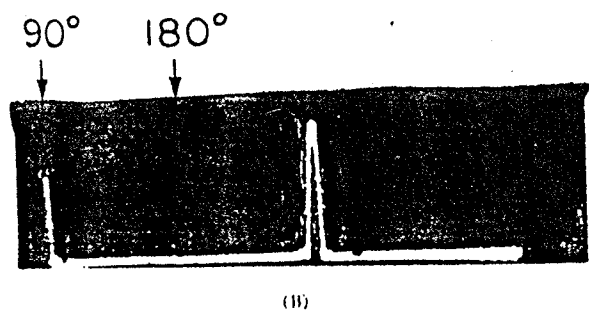
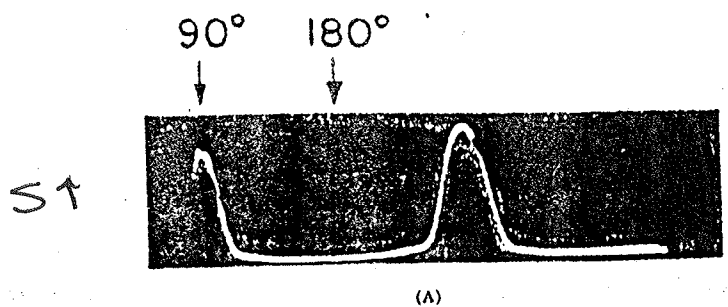


FIG. 4. Effect of the homogeneity of the field on the widths of tails and echoes. The tails and echoes associated with a sample (A) in a very homogeneous field are wide compared to those associated with a sample (B) in a less homogeneous field.

\* Bloembergen, Purcell, and Pound, Phys. Rev. 73, 679 (1948).

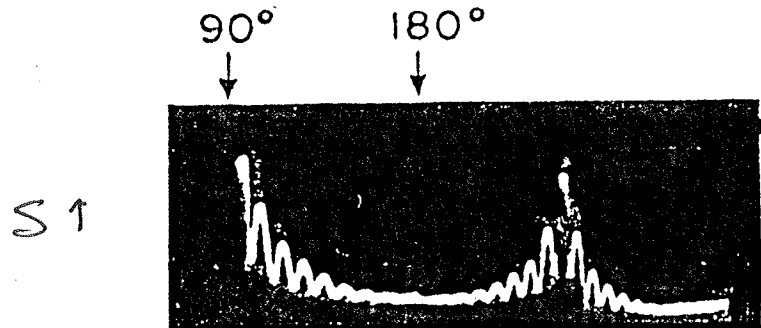


FIG. 5. A tail and echo associated with an acetic acid ( $\text{CH}_3\text{COOH}$ ) sample in a very homogeneous field. The nuclear signal displays modulation typical of the beating of two signals of nearly equal frequencies, the magnitude of one being three times that of the other. The beat frequency shown, corresponding to room temperature and 7000 gauss, is approximately 220 cps.

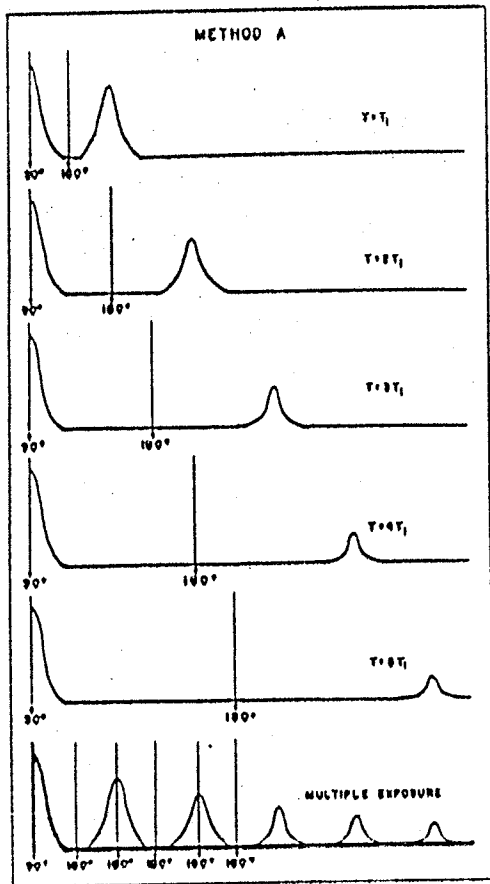
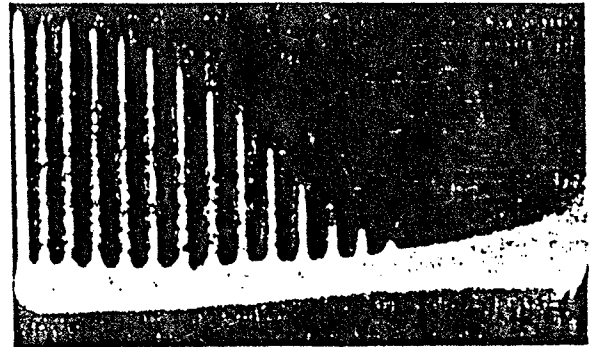
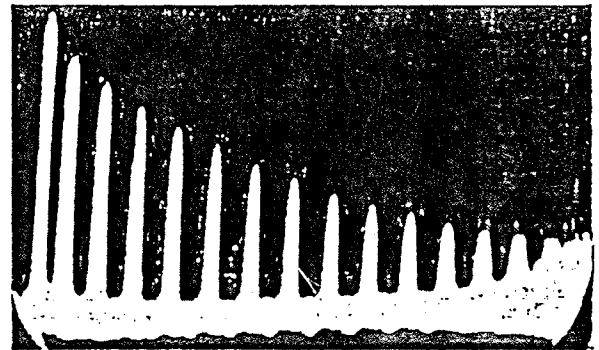


FIG. 6. Comparison of the two free precession methods for observing the decay time of the horizontal component of nuclear magnetic polarization. In "Method A" the sample must return to its equilibrium condition each time an additional echo is to be observed. In "Method B" the sample need only start from equilibrium once. The separate oscilloscope traces of "Method A" are usually displayed superimposed in a multiple exposure picture. Only a single trace and hence a single exposure picture is required in "Method B." However this latter method requires more than one 180° pulse.



(A)



(B)

FIG. 7. (A) A "Method A" decay associated with water at 25°C. The time constant is approximately 0.2 sec. The decay is largely determined by the molecular diffusion through the 0.28 gauss/cm gradient. The decay is dominated by the factor  $\exp(-kt)$ . (B) A "Method B" decay associated with water at 25°C. The time constant of the decay is approximately 2.0 sec. The effect of diffusion has been largely circumvented.

## LONGITUDINAL RELAXATION ( $T_1$ )

On the previous page it is seen that for longer  $\tau$ , less signal is recovered by the  $\pi$  pulse. This decay is caused primarily by decay to the system back to thermal equilibrium, i.e.,  $\langle \rho_z \rangle$  decaying from 0 to  $\langle \rho_z \rangle_{eq}$ . For this to happen

there must be some  $H'_{12}$  coupling the states  $|1\rangle$  and  $|2\rangle$ . This is often a fluctuating interaction provided by the thermal motion of the environment. It can differ from the effects that created the inhomogeneous broadening, discussed above, only by the property that a given system has  $H_{11} - H_{22}$  changing in time randomly. Each system experiences exactly the same random fluctuations over the time scale of the observation, giving what is called homogeneous broadening.

Viewed another way, if the  $H_{11} - H_{22}$  values change on a time scale similar to  $\frac{H_{11} - H_{22}}{h}$  the  $H'_{12}$  interaction could be thought of as an internal driving force, similar to electromagnetic radiation.



"PURE DEPHASING TIME"  $T_2^*$

Usually both homogeneous and inhomogeneous mechanisms are present, giving another term to the observed transverse decay time.  $\frac{1}{T_2^*}$

$$\frac{1}{T_2} = \frac{1}{2T_1} + \frac{1}{T_2^*}$$

$T_2^*$  is called the "pure dephasing time".

This includes both molecular and magnet effects.  
(PAC 21 Apr 13)

Typically, homogeneous broadening gives Lorentzian line shapes  $\frac{A}{\omega_0^2 - \omega^2}$

whereas inhomogeneous broadening gives Gaussian shapes  $e^{-\frac{(\omega_0 - \omega)^2}{\text{width}}}$ .

An ensemble exhibiting only homogeneous broadening will not give an echo following a  $\pi/2 \dots \pi \dots \pi$  sequence.

Why?

## APPENDIX: The "Signal".

Consider an observable  $A$  whose quantum operator is  $\hat{A}$ .

Suppose  $A_{11} = A_{22} = 0$  and  $A_{12} = A_{21} \neq 0$   
For a single system:

$$\langle A \rangle = \langle \psi | A | \psi \rangle = \text{tr}(\hat{\rho} \hat{A})$$

$$= \text{tr} \begin{pmatrix} \rho_{11} & \rho_{12} \\ \rho_{21} & \rho_{22} \end{pmatrix} \begin{pmatrix} A_{11} & A_{12} \\ A_{21} & A_{22} \end{pmatrix}$$

$$= \text{tr} \begin{pmatrix} \rho_{11} & \rho_{12} \\ \rho_{21} & \rho_{22} \end{pmatrix} \begin{pmatrix} 0 & A_{12} \\ A_{21} & 0 \end{pmatrix}$$

$$= \rho_{12} A_{21} + \rho_{21} A_{12} = (\rho_{12} + \rho_{21}) A_{12}$$

$$= \rho_x A_{12}$$

After a  $(\pi/2)_x$  pulse

$$\langle \rho_x(t) \rangle = \langle \rho_{11} - \rho_{22} \rangle_{eq} \sin(\omega_0 t)$$

$$\langle \langle A(t) \rangle \rangle = A_{12} \langle \rho_{11} - \rho_{22} \rangle_{eq} \sin \omega_0 t$$

If  $\hat{A} =$  dipole operator, the ensemble dipole will oscillate in time. This is the signal in many cases, e.g. NMR, lasers, etc.