

Bibliography: - Harris, Ch 7.3
 - Slichter, Ch. 7.18-7.21, 7.25
 - Ernst, Ch. 2.1, 4.5.4, 4.5.5
 - Abragam, Ch XII-7.D

World of
 coupled spin
 A1 & A2 NOT AB5
 (10)

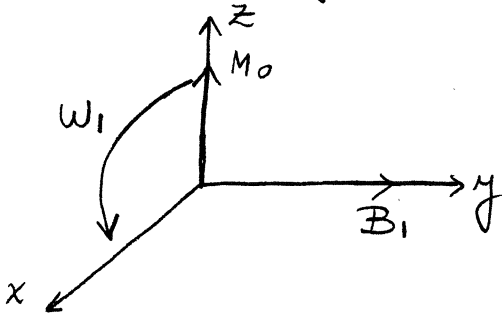
V: MANIPULATING SPIN COHERENCES: DECOUPLING, SPECTRAL EDITING AND COHERENCE TRANSFER

V.1 J-COUPPLINGS: IN-PHASE AND ANTI-PHASE COHERENCES

Some time ago (Section I.10) we showed that for an ensemble of isolated spin 1/2 nuclei, the classical magnetization picture and the exact density matrix analysis afforded identical results:

Classical

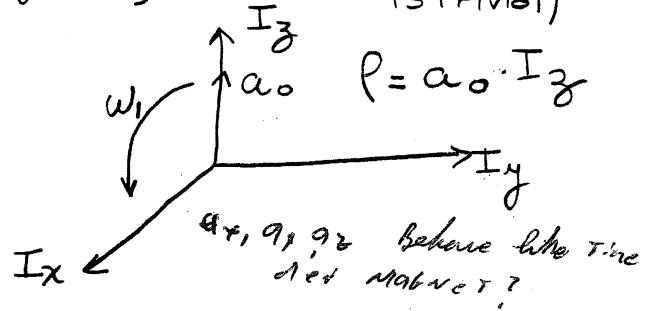
$\{x, y, z\}$ rotating frame



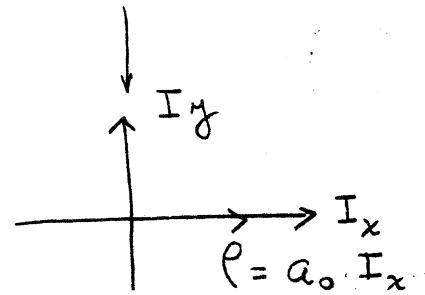
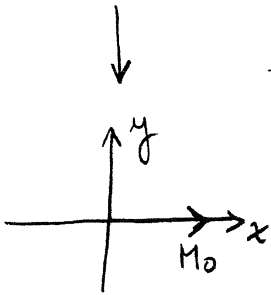
Quantum-mechanical

$\{I_x, I_y, I_z\}$ basis set (plus $\mathbb{1}$ which is trivial)

Initial



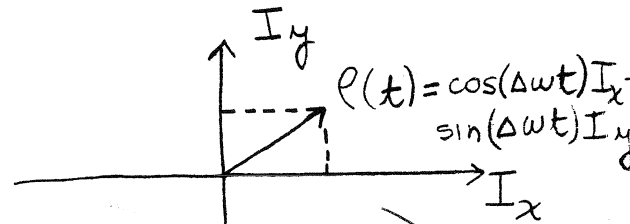
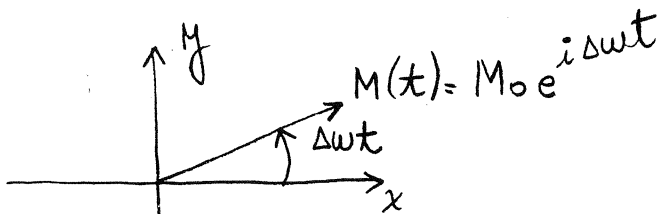
$\pi/2$ pulse



chemical shift evolution

Phase = $\Delta\omega t$

$\mathcal{H}_0 = -\Delta\omega I_z$



One of
 m.f.

IN class, Real w/ vectors, which Mess by C.S
 Imaginer Desc to M_x, M_y, M_z
 # INO.M dens. matrix, can describe all that happens

Thus, both B_1 and $\Delta\omega$ produce the following rotations of the spin operators:

PULSE ROTATIONS

For rf pulses $\beta = \omega_1 \cdot \tau$ along the y-axis:

$$I_z \xrightarrow{\beta I_y} I_z \cos \beta + I_x \sin \beta$$

$$I_y \xrightarrow{\beta I_y} I_y$$

$$I_x \xrightarrow{\beta I_y} \cos \beta I_x - \sin \beta I_z$$

} i.e. can fit
out dens.
matrix.

For rf pulses along the x-axis:

$$I_z \xrightarrow{\beta I_x} \dots I_z \cos(\beta) - I_y \sin(\beta)$$

$$I_y \xrightarrow{\beta I_x} \dots I_y \cos(\beta) + I_z \sin(\beta)$$

$$I_x \xrightarrow{\beta I_x} I_x$$

Due to chemical shift evolution:

Chemical shift rotates

Coherent state

$$I_z \xrightarrow{\Delta\omega t I_z} I_z$$

$x \rightarrow y \rightarrow z \rightarrow x$

$$I_x \xrightarrow{\Delta\omega t I_z} I_x \cos(\Delta\omega t) + I_y \sin(\Delta\omega t) = \frac{I_+ e^{-i\Delta\omega t} + I_- e^{+i\Delta\omega t}}{2}$$

rotates a DIFF
direction

$$I_y \xrightarrow{\Delta\omega t I_z} I_y \cos(\Delta\omega t) - I_x \sin(\Delta\omega t) = \dots$$

Just a vector rotating in x-y

only works for $2H^1$'s at high B_0 's ;
 For f^{15} ... or C-H's

Note that I_x is the sum of 2 coherences rotating in opposite directions, which can be distinguished if I_y is also detected.

EVOLUTIONS OF COUPLED SPINS

Consider now an ensemble composed by pairs of weakly coupled inequivalent spins. We try to extend this analogy between classical and quantum-mechanical pictures to include these cases.

With respect to pulses and chemical shift, the operators still behave in the same way: Chem Shift

$$I_{1z} + I_{2z} \xrightarrow{(\pi/2)_y} I_{1x} + I_{2x}$$

$$I_{1x} + I_{2x} \xrightarrow{\Delta\omega_1 t I_{1z} + \Delta\omega_2 t I_{2z}} I_{1x} \cos(\Delta\omega_1 t) + I_{1y} \sin(\Delta\omega_1 t) + I_{2x} \cos(\Delta\omega_2 t) + I_{2y} \sin(\Delta\omega_2 t)$$

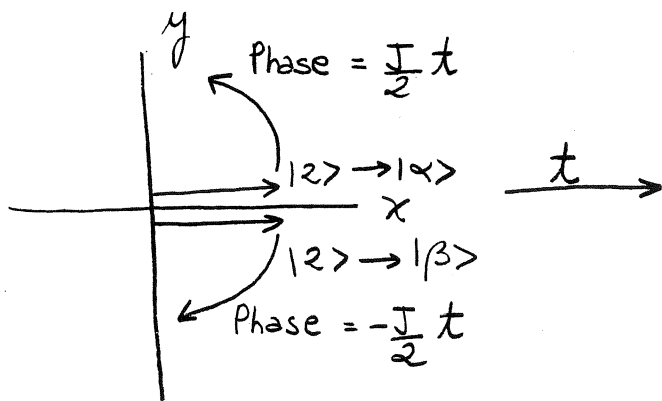
rotate at DIFF Freqs $\Delta\omega_1, \Delta\omega_2, \dots$

J-Coupling

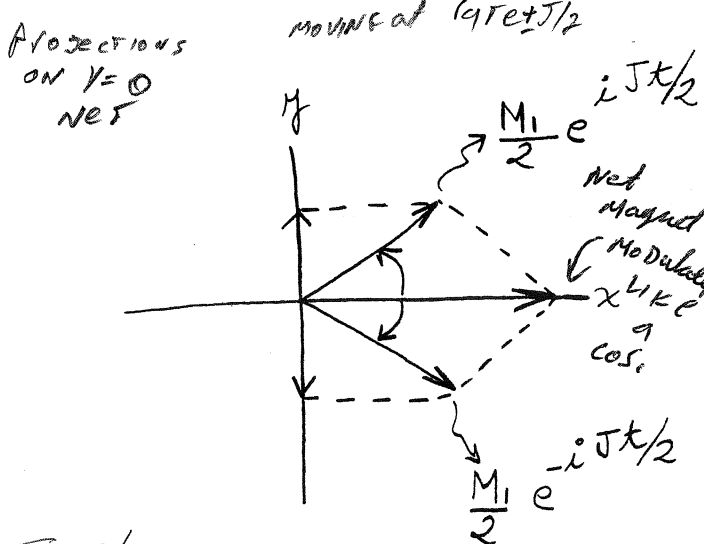
What about the J-coupling? According to the classical picture:

Spin 1 immediately after the pulse

J-



Spin 1 after evolving for a time t



Hamilton

$$J_{12} I_{1z} I_{2z}$$

$$\langle \alpha_2 | J_{12} I_{1z} I_{2z} | \alpha_2 \rangle = \frac{J}{2} I_{1z}$$

$$\langle \beta | J_{12} I_{1z} I_{2z} | \beta \rangle = -\frac{J}{2} I_{1z}$$

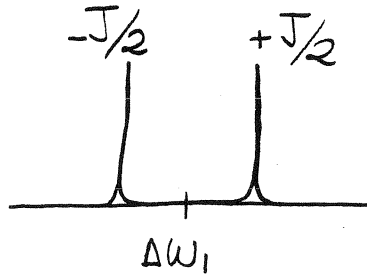
Chem. Shifts affected? \downarrow FT

The projection along x is the only net observable signal:

Pr of thing
no mod →

$$M_{x1}(t) = M_1 \cos(Jt/2)$$

1/2 BRINGS INTENSITY



The projection along y is constantly zero ($M_y(t) = 0$), but only because the number of $|\alpha\rangle$ and $|\beta\rangle$ states of spin 2 throughout the sample are essentially identical.

M_y should actually be described as:

$$M_{y1}(t) = M_1 \left[(\text{pop } \alpha_2 \cdot \sin(Jt/2) + \text{pop } \beta_2 \cdot \sin(-Jt/2)) \right]$$

Factor out

Or, since $(\text{pop } \alpha_2 - \text{pop } \beta_2) \propto M_{2z}$:

10^{-5} very small

∴ cosine signal 5X'S THAT OF sine's

$$M_{y1}(t) \propto M_1 \cdot M_{2z} \cdot \sin(Jt/2)$$

IF QUANTUM WILL SHOW LATER THE SAME

Classical M_x & M_y

So Far

Becomes NON NEG.

Very small ∴ No signal BUT still there $\sim 10^{-5}$

Dens. Matrix INTERPRET.

The full density matrix analysis of this problem gives a very similar answer.

Using the operator formalism, we know that after the pulse:

Now Q.M.

$$\rho_0 = I_{1z} + I_{2z} \xrightarrow{(\pi/2) I_{1y}} I_{1x} + I_{2z}$$

↑
pulse on

Reduced Dens. Mat. ρ

The subsequent time evolution of spin 1 will then be given by

$$\rho_1(t) = e^{-i\mathcal{H}_J t} I_{1x} e^{i\mathcal{H}_J t}, \quad \mathcal{H}_J = J \cdot I_{1z} \cdot I_{2z}$$

1st order J-coupling
Hamiltonian, this
is how ρ_1 evolves

$$= e^{-i(JI_{2z})t} I_{1z} I_{1x} e^{i(JI_{2z})t}$$

~~J's behave~~ I_{2z} behaves like \hbar , \therefore () similar
to C.S. behavior

This is equivalent to a chemical shift evolution of spin 1 with an offset
 $\Delta\omega_1 = J I_{2z}$

$$\Rightarrow \rho_1(t) = I_{1x} \cos(JI_{2z}t) + I_{1y} \sin(JI_{2z}t) \quad (*)$$

(really) offset \hbar though

recall $I_z^2 = 1$
 $I_z^{\text{odd}} = I_z$

We can evaluate the trigonometric functions by expanding them in power series:

$$\cos(JI_{2z}t) = 1 - (JI_{2z}t)^2/2 + (JI_{2z}t)^4/4! - \dots = \cos(Jt/2)$$

$$\sin(JI_{2z}t) = JI_{2z}t - (JI_{2z}t)^3/3! + (JI_{2z}t)^5/5! - \dots$$

Factor of 4

and recalling that since

$$I_{2z} \cdot I_{2z} = \frac{1}{4} \cdot \sigma_{2z}^2 = \frac{1}{4} \cdot 1$$

it follows that

$$\begin{aligned} \cos(JI_{2z}t) &= \cos(Jt/2) \cdot 1 \\ \sin(JI_{2z}t) &= \sigma_{2z} \cdot \sin(Jt/2) = 2 I_{2z} \sin(Jt/2) \end{aligned}$$

I_{xy} ∇

New For us, use direct products

Finally, inserting this into (*)

look like for rot.

Now get same as in classical case ∇ New

$$I_{1x} \xrightarrow{J I_{1z} I_{2z} t} I_{1x} \cos(Jt/2) + 2 I_{1y} I_{2z} \sin(Jt/2)$$

in-phase coherences
anti-phase coherences

I_{1y} I_{2z}

Still, the signal $S(t)$ that we detect from spins 1 in the experiment cannot directly detect the antiphase term:

no need to write D, M,

spin coh, i see signal
spin coh, i no see
cant see sig just like in class case

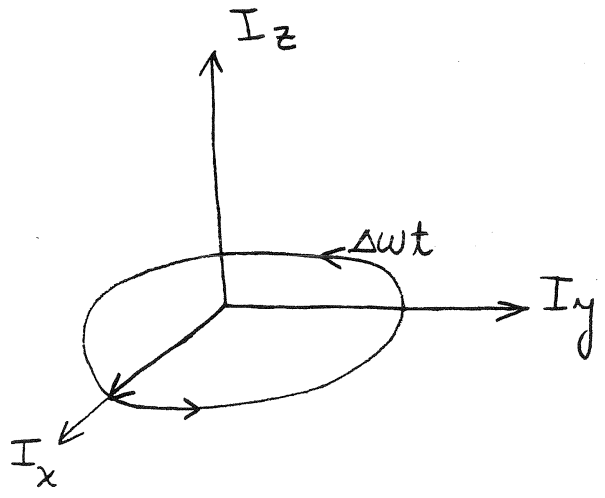
$$S(t) = \text{Tr} [\rho(t) \cdot I_{1+}] \propto a_0 \cos(Jt/2) \text{Tr} (I_{1x} I_{1+}) + \neq 0$$

$$\sin(Jt/2) \text{Tr} (2 I_{1y} I_{2z} I_{1+}) = a_0 \cos(Jt/2)$$

$\text{Tr}(I_{2z}) \rightarrow 0$

single Linear Rotations

In the same way as we talked about rotations around the I_z axis due to chemical shift in the x, y, z-space



$$[I_x, I_y] = i I_z (\hbar)$$

* This defines a 3D non-commut. space
∴ Real Reason for rotation, underlying reason why $I_y \rightarrow I_x$ & $I_x \rightarrow I_y$.

* for rot, time evol of under effect of J_{eff}

* C.S. effects on anti-phase

We analyze now the evolution of anti-phase coherences under the effect of chemical shifts:

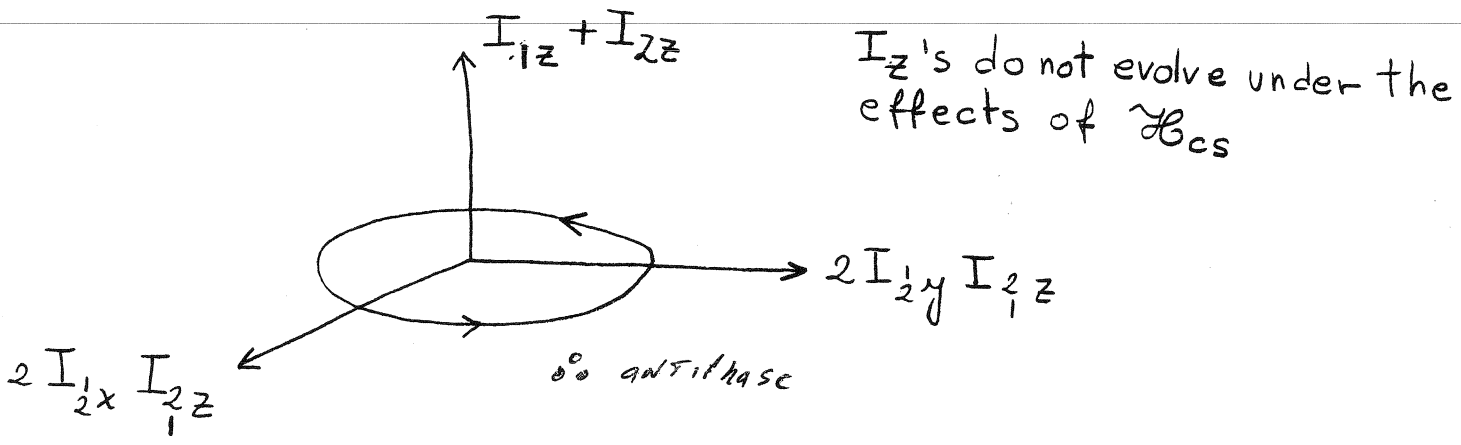
How do these evolve under C.S. diff. now

$$\mathcal{H}_{cs} = -\Delta\omega_1 I_{z1} - \Delta\omega_2 I_{z2}$$

$$\Rightarrow \rho(t) = e^{i\Delta\omega_1 I_{z1} t} e^{i\Delta\omega_2 I_{z2} t} 2 I_{1x} I_{2z} e^{-i\Delta\omega_1 I_{z1} t} e^{-i\Delta\omega_2 I_{z2} t}$$

$$= 2 I_{1x} I_{2z} \cos(\Delta\omega_1 t) + 2 I_{1y} I_{2z} \sin(\Delta\omega_1 t)$$

$[I_{1?}, I_{2?}] = 0$



In the presence of both J- and chemical shift- evolution we can use the fact that to first order $[\mathcal{H}_{cs}, \mathcal{H}_J] = 0 \Rightarrow$

$$e^{-i\mathcal{H}_{cs} t} e^{-i\mathcal{H}_J t} = e^{-i\mathcal{H}_J t} e^{-i\mathcal{H}_{cs} t} \Rightarrow$$

remember I_{1z} / rf

$$\left[I_{1x} \xrightarrow{\Delta\omega_1 I_{1z} t} \xrightarrow{J I_{1z} I_{2z} t} \right] = \left[I_{1x} \xrightarrow{J I_{1z} I_{2z} t} \xrightarrow{\Delta\omega_1 I_{1z} t} \right] \dots$$

under CSA $I_{1x} \rightarrow I_{1z} C(\omega_1 t) + I_{1y} S(\omega_1 t)$ under J-coupling $\rightarrow I_{1y} C(\frac{Jt}{2}) + 2I_{1x} I_{2z} S(\frac{Jt}{2})$

$$I_{1x} C(\frac{Jt}{2}) + I_{2x} I_{2z} S(\frac{Jt}{2})$$

V.2 THE EFFECTS OF A SECOND PULSE: ZERO- AND DOUBLE-QUANTUM COHERENCES

Given a system composed by two spins, we have that before the first pulse

$$\rho = I_{1z} + I_{2z}$$

\swarrow \swarrow
 populations, diagonal elements of ρ

After the first pulse and in the presence of couplings and chemical shifts, ρ evolves as a linear combination of

$I_{1z}, I_{2z}, I_{1x}, I_{2x}, I_{1y}, I_{2y}, I_{1z}I_{2x}, I_{1x}I_{2z}, I_{1y}I_{2z}, I_{1z}I_{2y}$

transverse basis set
rewrite in I_z & I_{\pm}
single-quantum coherences; operators proportional to $I_{1\pm}, I_{2\pm}, I_{1\pm}I_{2z}, I_{1z}I_{2\pm}$
only contain one of that looks like a single q. coh's
look at mat. elems of Diags have this connection

We investigate now what happens with these 2-spin operators if a second pulse is applied. The evolution of the pulse can be

Rotates in spin space
Matrices

$$R = e^{i\beta I_{1x}} \text{ or } e^{i\beta I_{2x}} \quad ; \quad R = e^{i\beta I_x} \text{ or } e^{i\beta I_y}$$

selective *DIFF HARD easy hetero* *non-selective REV*

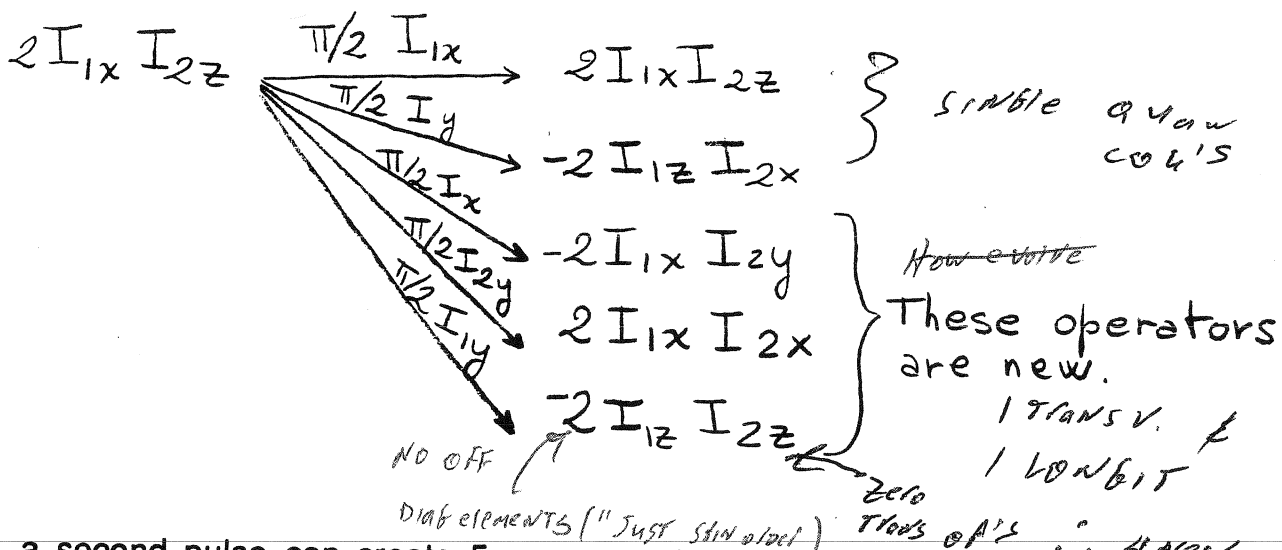
The effect of R on an anti-phase operator of the form $I_{1x}I_{2z}$:

$$2 I_{1x} I_{2z} \xrightarrow{R} 2 \underbrace{R I_{1x} R^{-1}}_{\text{ROTATIONS}} \underbrace{R I_{2z} R^{-1}}_{\text{1 = a click}}$$

rotate INDEP of one another

These products of operators evolve independently, like single spin operators. *consider INDEP*

Thus for instance



Overall, a second pulse can create 5 new operators

$$\underbrace{2I_{1x}I_{2x}, 2I_{1y}I_{2y}, 2I_{1x}I_{2y}, 2I_{1y}I_{2x}}_{\text{Double-quantum coherences}} \quad \underbrace{2I_{1z}I_{2z}}_{\text{zero-quantum coherences}}$$

Double-quantum coherences zero-quantum coherences
 Come from 2 pulses & J-coups & 5 new state → 15 new states + zero? → 16 states
 In total we have these 5 operators, 2 populations (I_{1z}, I_{2z}) and 8 single-quantum operators = 15 operators. If we add the identity operator we have a total of 16 operators O_1, O_2, \dots, O_{16} ; which form a basis set for the 2-spin space. Thus, any $1/2$ state ρ representing a two-spin system can be written as:

$2I_{1z}I_{2z} \neq$ a coh

$$\rho = \sum_{i=1}^{16} c_i \cdot O_i$$

Behav. in spin order

$$2I_{1x}I_{2x} = 2(I_{1+} + I_{1-})(I_{2+} + I_{2-})$$

$$= I_{1+}I_{2+} + I_{1-}I_{2+} + I_{1+}I_{2-} + I_{1-}I_{2-}$$

Interactions other than RF now and any full density matrix calculation can be carried out using this product operator formalism.
 Note now have 2 prod ops together.

We investigate how the new product operator terms behave under different interactions.

The zero-quantum coherence does not evolve with \mathcal{H}_{CS} or \mathcal{H}_J :
 spin operator

$$[I_{1z}I_{2z}, \mathcal{H}_{CS}] = [I_{1z}I_{2z}, \mathcal{H}_J] = 0 : \text{it behaves like populations}$$

our basis set (16 terms) allows for easy det. of these

Under the effects of chemical shift, each spin operator in a double-quantum coherence evolves independently:

$$\underbrace{e^{-i\Delta\omega_1 t I_{1z}} e^{-i\Delta\omega_2 t I_{2z}}}_{R^{-1}} \underbrace{2 I_{1x} I_{2x}}_{R \cdot R^{-1}} \underbrace{e^{i\Delta\omega_1 t I_{1z}} e^{i\Delta\omega_2 t I_{2z}}}_{R} \longrightarrow$$

$$\longrightarrow 2 \left[I_{1x} \cos(\Delta\omega_1 t) + I_{1y} \sin(\Delta\omega_1 t) \right] \left[I_{2x} \cos(\Delta\omega_2 t) + I_{2y} \sin(\Delta\omega_2 t) \right]$$

4 ops
4 e/e
all M, Q.

all the resulting coherences are double-quantum operators
* now have chem. shifts by M, Q for

By contrast, the evolution with respect to \mathcal{H}_J ,

$$\underbrace{e^{iJ I_{1z} I_{2z} t} I_{1x} e^{-iJ I_{1z} I_{2z} t}}_{I_{1x} \cos(Jt/2) + 2 I_{1y} I_{2z} \sin(Jt/2)} \underbrace{e^{iJ I_{1z} I_{2z} t} I_{2x} e^{-iJ I_{1z} I_{2z} t}}_{I_{2x} \cos(Jt/2) + 2 I_{1z} I_{2y} \sin(Jt/2)} =$$

$$= I_{1x} I_{2x} \cos^2(\dots) + 4 \underbrace{I_{1y} I_{1z}}_{\frac{-i I_{1x}}{2}} \underbrace{I_{2z} I_{2y}}_{\frac{i I_{2x}}{2}} \sin^2(\dots) + \cos(\dots) \sin(\dots) \left[\underbrace{2 I_{1x} I_{1z} I_{2y}}_{\frac{-i I_{1y}}{2}} + \underbrace{2 I_{1y} I_{2z} I_{2x}}_{\frac{i I_{2y}}{2}} \right]$$

$$\Rightarrow I_{1x} I_{2x} \xrightarrow{J I_{1z} I_{2z} t} I_{1x} I_{2x}$$

* NOT intuitive
* DOESN'T GO ANYWHERE
EJ + E-J in them

Neither zero nor double-quantum operators evolve due to J-couplings

In an NMR experiment the observed signal S is proportional to $T_r(e \cdot I_+)$ \Rightarrow only states which have one transverse operator can be detected

$$T_r(I_{1y} I_+), T_r(I_{2y} I_+) \neq 0$$

$$T_r(I_{1y} I_{2z} I_+) = T_r(I_{1z} I_{2y} I_+) = T_r(I_{1z} I_{2z} I_+) = T_r(I_{1y} I_{2y} I_+) = 0$$

None are visible, $\gamma = 0$

However, if the spins are coupled, all single-quantum operators can give origin to observable signals:

$$I_{1x} \xrightarrow{J I_{1z} I_{2z}} I_{1x} \cos(Jt/2) + 2 I_{1y} I_{2z} \sin(Jt/2)$$

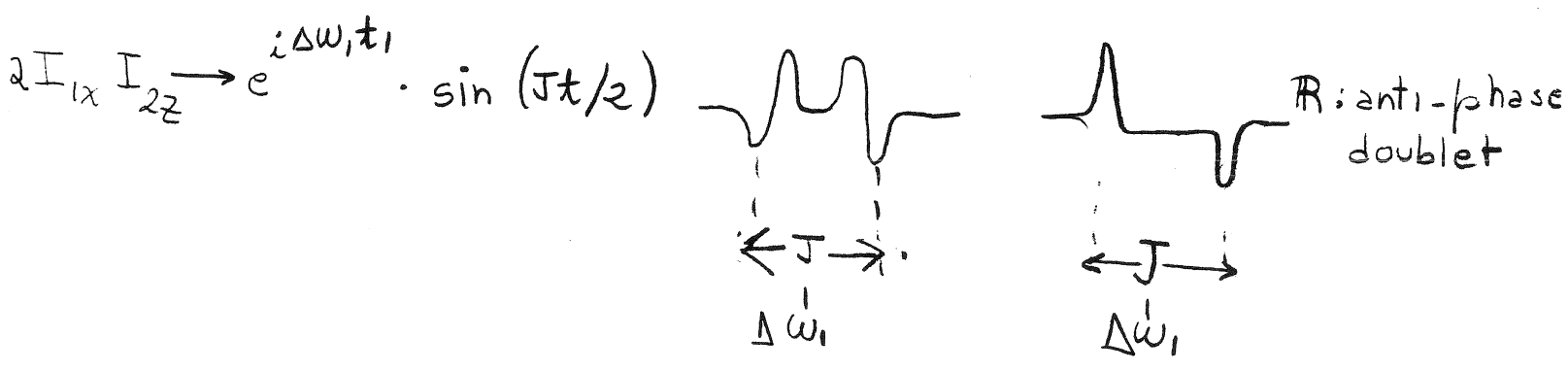
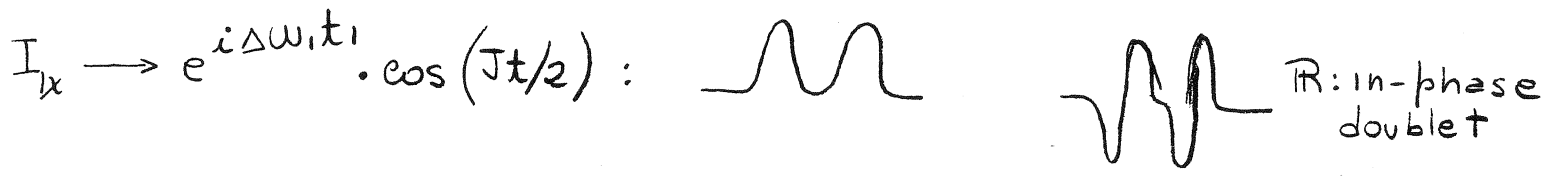
observable

$$2 I_{1x} I_{2z} \xrightarrow{J I_{1z} I_{2z}} 2 I_{1x} I_{2z} \cos(Jt/2) + I_{1y} \sin(Jt/2)$$


NOT observable *J-coupling makes it observable now* *observable*


The shape of the signals originated by these coherences:

R: absorptive I: dispersive



That's why these operators are called in-phase and anti-phase coherences.

(recall) $\cos \rightarrow \frac{e^{iJt/2} + e^{-iJt/2}}{2} \Rightarrow$  *in phase*

$\sin \rightarrow \frac{e^{iJt/2} - e^{-iJt/2}}{2i} \Rightarrow$  *anti phase doublet*

V.3 DOUBLE RESONANCE_PART 1: π -PULSES AND DECOUPLING

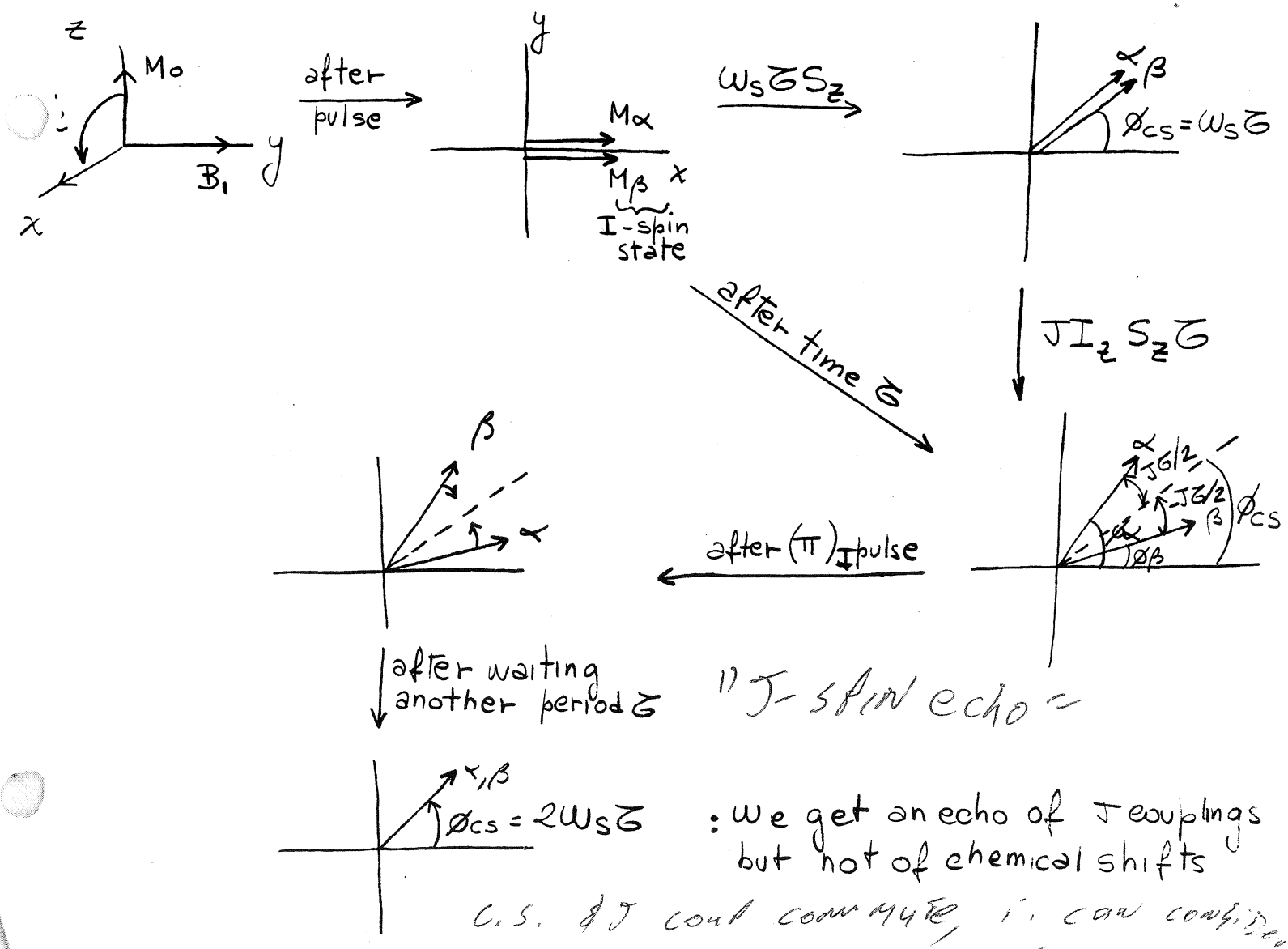
Let's consider a two-spin system I-S composed by a pair of nuclei with widely different chemical shifts (e.g., a spin I = ^1H and a spin S = ^{13}C) which are coupled among them. The Hamiltonian in the doubly rotating frame (i.e., rotating frame for I and S) is given by:

chem shift NOT LAMARSH / / ADIATE
(OFFSETS IN DBL ROT PLANE) ON DOF4

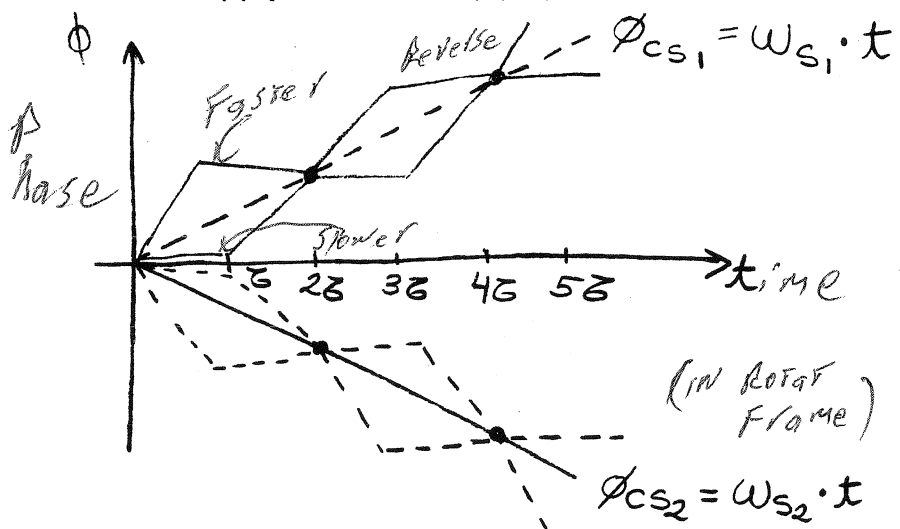
$$\mathcal{H} = -\omega_I I_z - \omega_S S_z + J I_z S_z$$

I = PROTON
S = N, C, ...
 $\omega_I = I$ COMPS
lev change with
J-coupl Hetero $\pi/2 =$

We focus on the signal arising from the S-spins after a $(\pi/2)_S$ pulse using a classical picture, assuming a π -pulse on the I-spins at time τ



Consider now a system composed by 2 S spins, each one coupled to its I spin, on which we apply a train of $(\pi)_I$ pulses:



$0, 3T, 5T$: pulse
 $2T, 4T, \dots$: J-echo
 calc spect:
 $S_+ \rightarrow (S_+)^2$

If T is short enough, the signal that can be detected corresponds to an **I-decoupled S-spectrum**. The limit of this sequence is a CW irradiation of the I spins with a B_2 field; in this case the I-S Hamiltonian, is

Full Hamil
 For carbon
 516.491

$$\mathcal{H}_{IS} = -\omega_S S_z - \omega_I I_z + J I_z S_z + \omega_2 \cdot I_x$$

offset btw H_{CS} & RF
 δB_2 of term on all time
 IN THE ROTATING FRAME
 decoupling rf field B_2 oscillating close to the Larmor frequency of I-spins.
 2-3 KHz

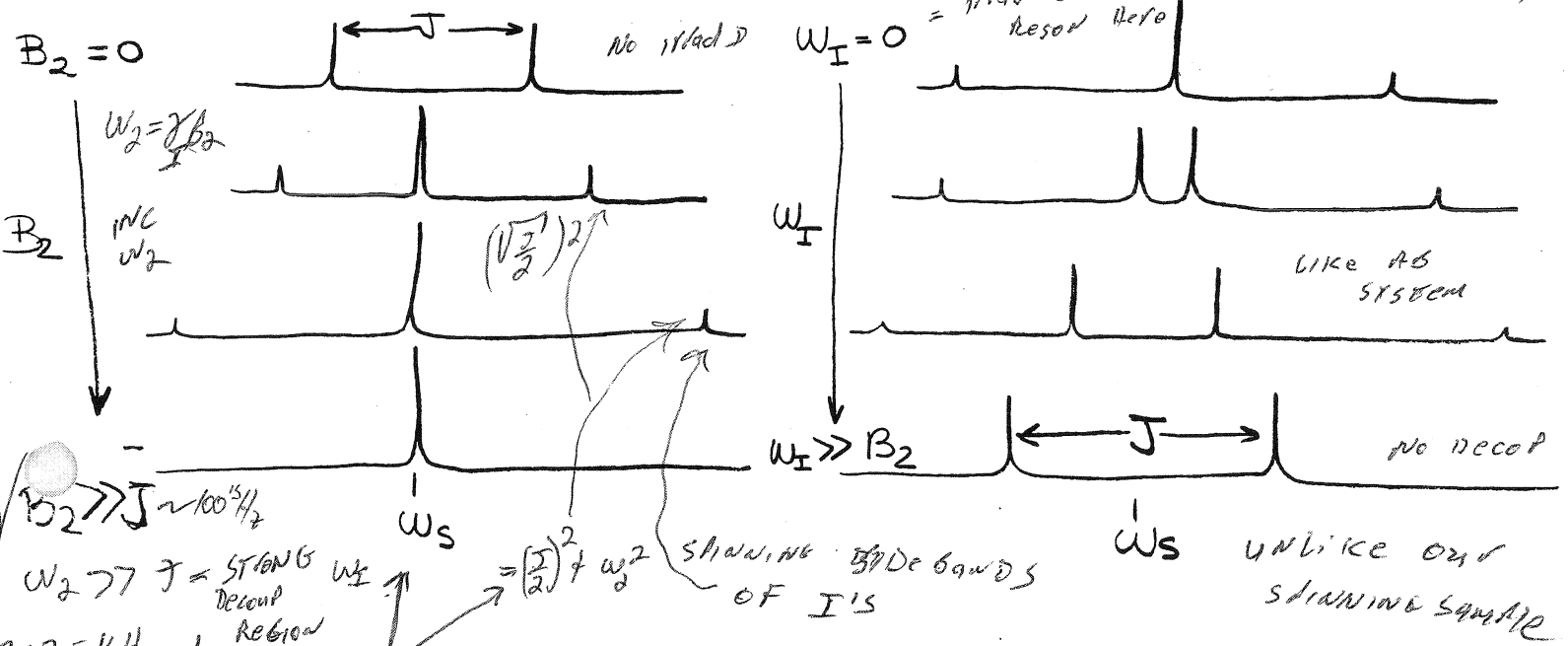
TIME INDEP

\mathcal{H}_{IS} can be diagonalized; the resulting S spectrum behaves as follows:

$\omega_I = 0$: on resonance decoupling

$B_2 \approx J$

solve anal. 4x4 Hamil



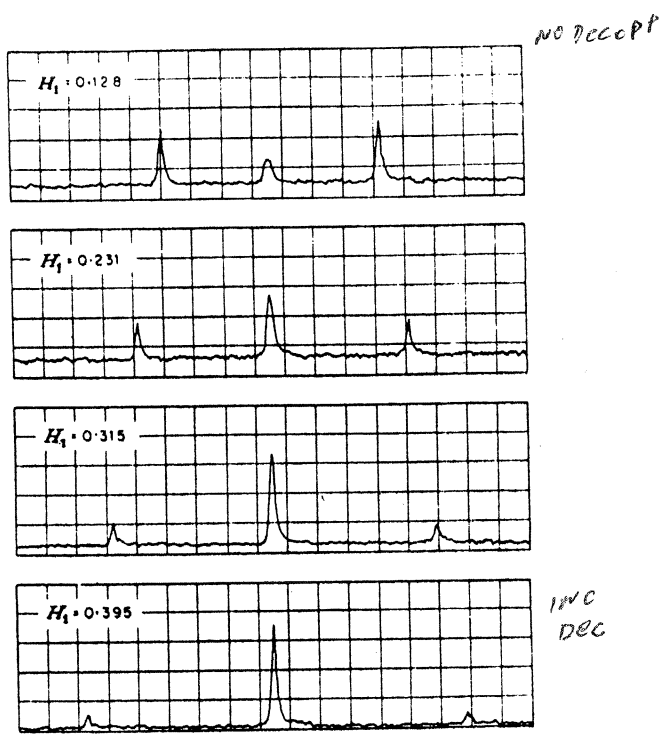


Fig. XII, 3. Effect on the fluorine spectrum of stirring the phosphorus at exact resonance with an r.f. field H_1 of varying magnitude. The top and bottom traces of Fig. XII, 4 are also part of this series.

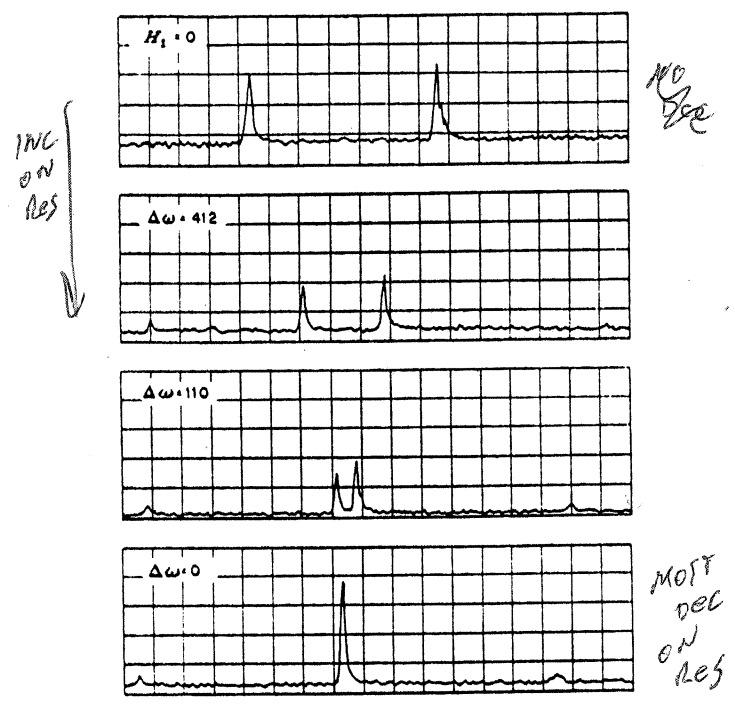
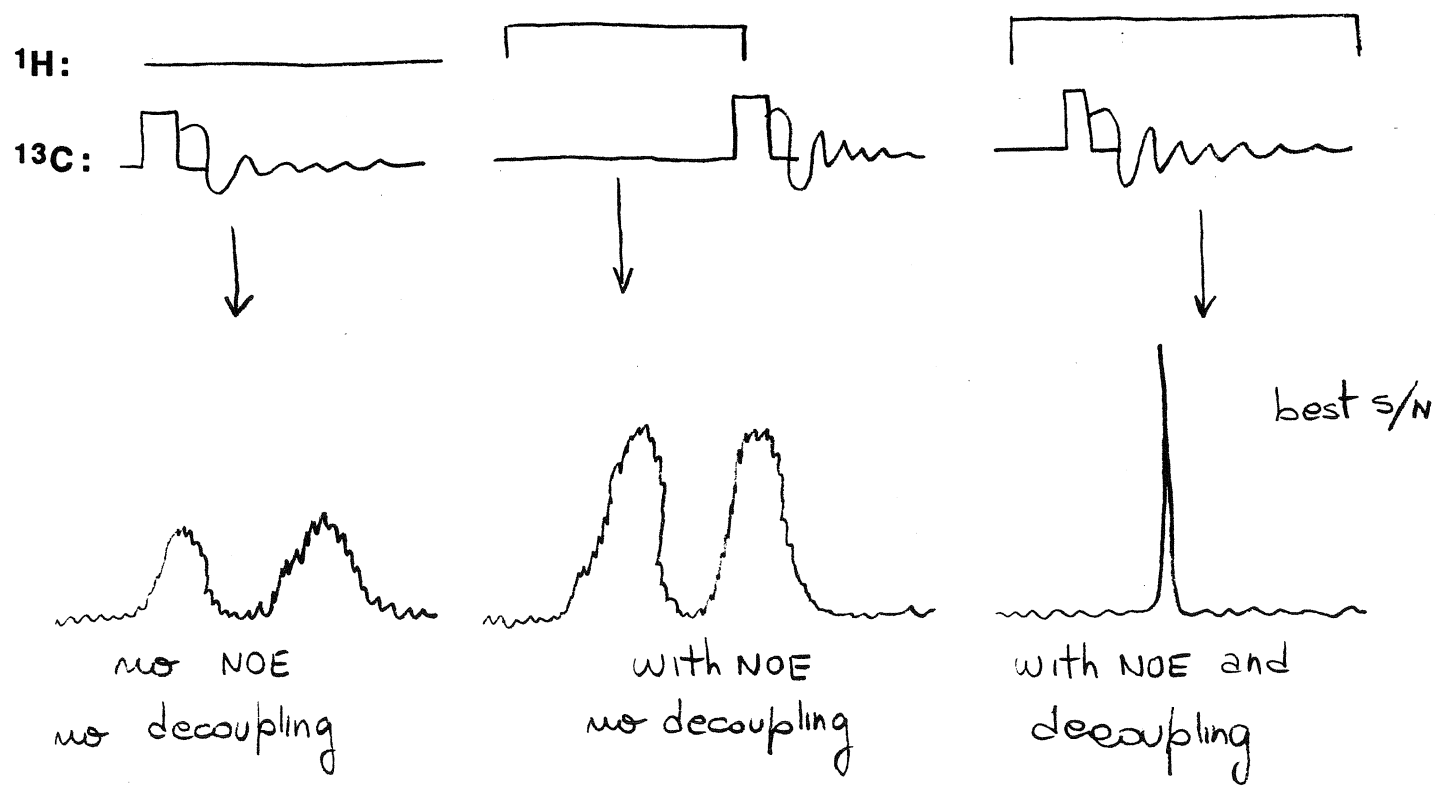


Fig. XII, 4. Effect on the fluorine spectrum of stirring the phosphorus with an r.f. field $H_1 = 0.464$ at a frequency ω near the phosphorus frequency $\omega_P = |\frac{1}{2}\gamma_P H_0/\pi|$. We define $\Delta\omega = \omega_P - \omega$.

In the case of ^{13}C NMR, we thus have the following alternatives:

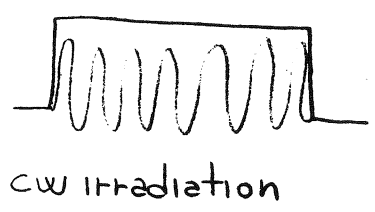
Summary



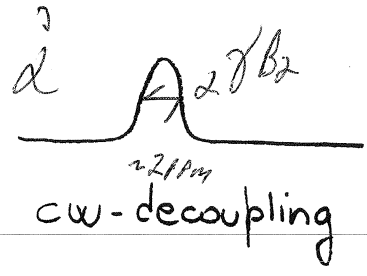
small offset \rightarrow $\downarrow \rightarrow \uparrow$

eg) 2W bulb hot
 160 mW For cool coil
 * Power Boil sample
 $\delta B_2 \ll 2 \text{ kHz}$
 noisy

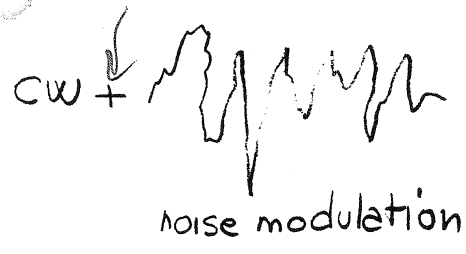
Decoupling is very sensitive to the I-spin offset. If $I = 1H$, at 500 MHz, the 1H dispersion is ca 5000 Hz. The B_2 in CW decoupling has to be very large to cover such a frequency range; this is impractical due to probe and sample heating problems. Instead, efficiency can be improved by superimposing on the CW irradiation an rf modulation. Two common choices are **noise and square-wave decoupling**



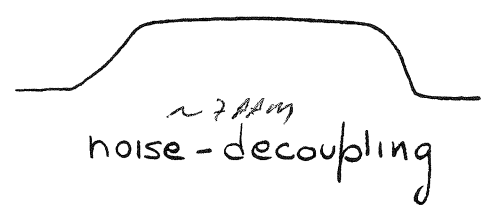
FT \rightarrow



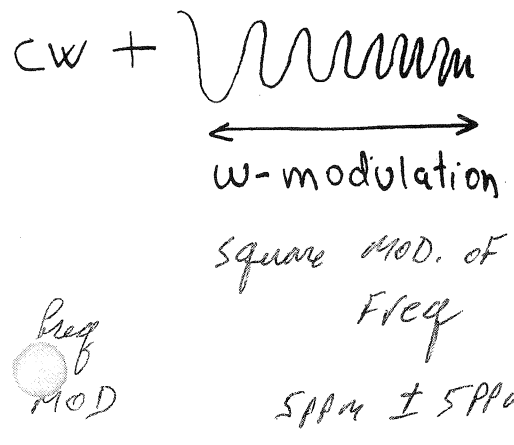
ERMST says do this



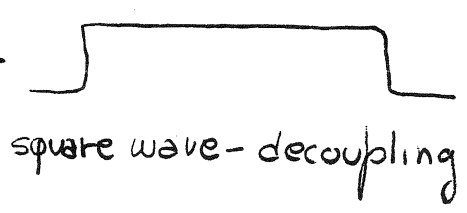
FT \rightarrow



GLUTZNER



FT \rightarrow



regions of decoupling

Too LITTLE range now days

The most efficient way of doing heteronuclear decoupling is using trains of π -pulses, where each π -pulse is a composite pulse: **composite pulse decoupling**

Malcolm LEVY
Say? DO this

MLEV 3
4
16
64 - Best
128

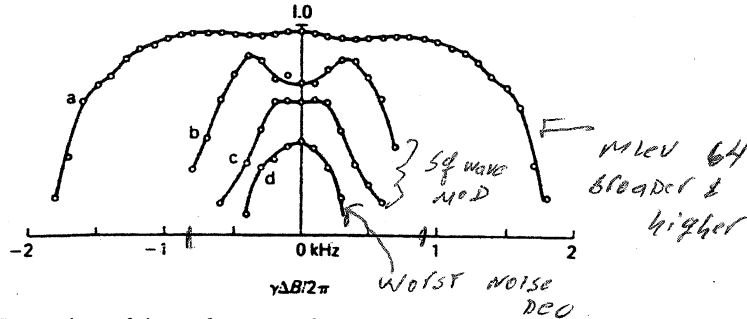
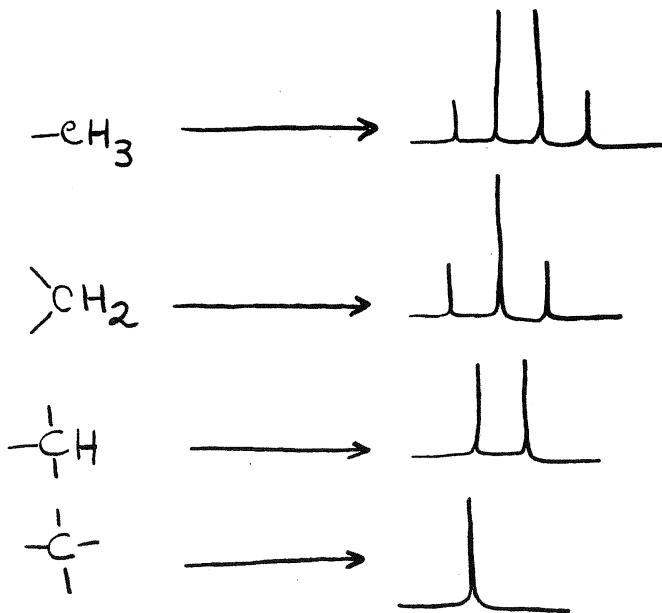


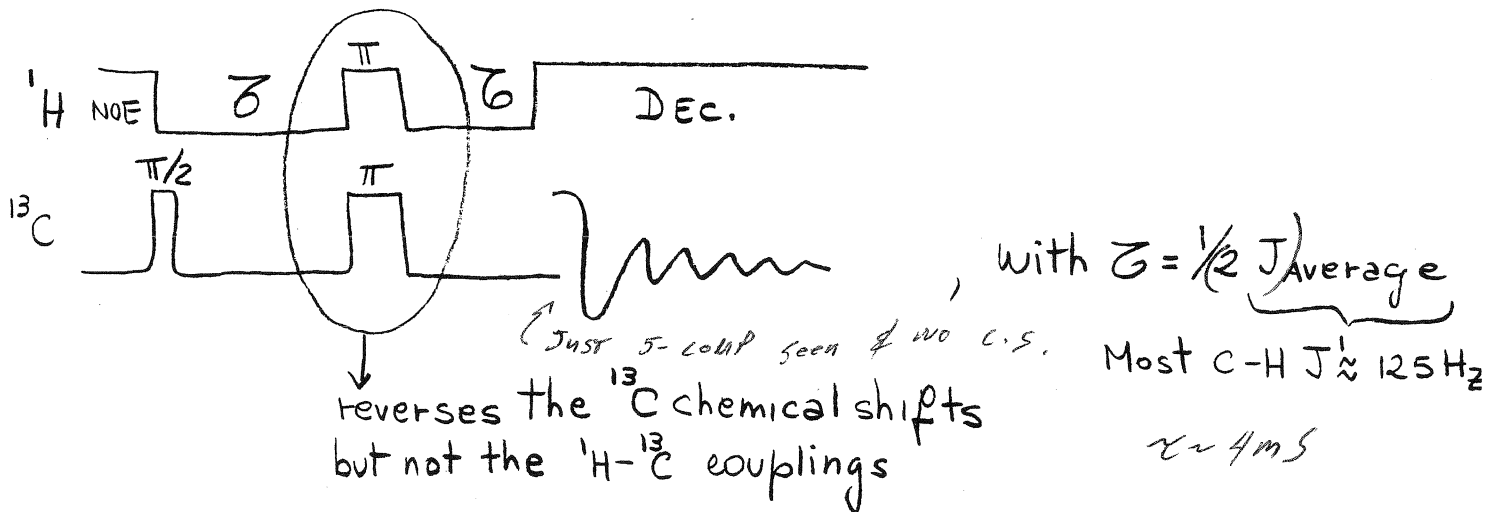
FIG. 4.7.7. Comparison of the performance of various decoupling schemes as a function of the offset of the decoupled nuclei. The experimental points indicate the height of the proton-decoupled carbon-13 signal of formic acid, which gives a measure of the line-narrowing efficiency. The amplitude of the decoupling field is $\gamma B_2/(2\pi) = 1.5$ kHz throughout. (a) MLEV-64 sequence with the composite inversion sequence $R = (\pi/2)_0(\pi)_{\pi/2}(\pi/2)_0$ of eqn (4.2.55). (b) Frequency-swept square-wave phase modulation. (c) 100-Hz square-wave phase modulation. (d) Noise decoupling with 1-kHz clock rate.

$\gamma B_2 = 1.5$ kHz

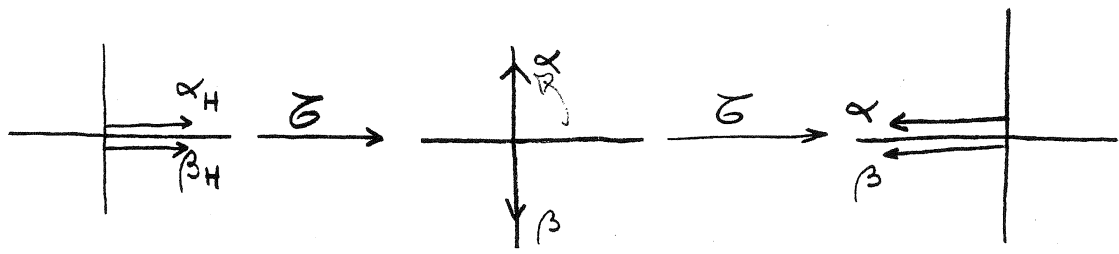
In ^{13}C NMR however, J couplings may be useful because they contain structural information:



This information can be partially preserved in decoupled spectra using the attached proton test (APT) experiment. Its pulse sequence:

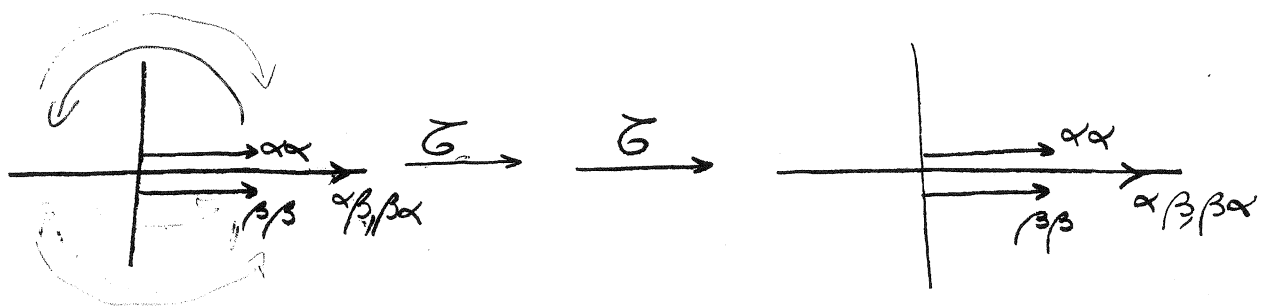


^1H :



$\frac{\partial \tau}{\partial J} \therefore$ need $t = 2J$ for full recovery

CH_2 :

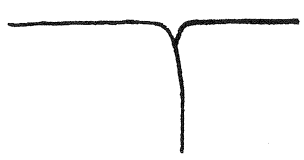


The different phases:

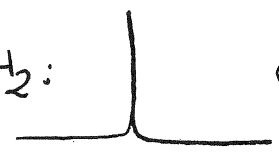
C:



CH:



CH_2 :



CH_3 :



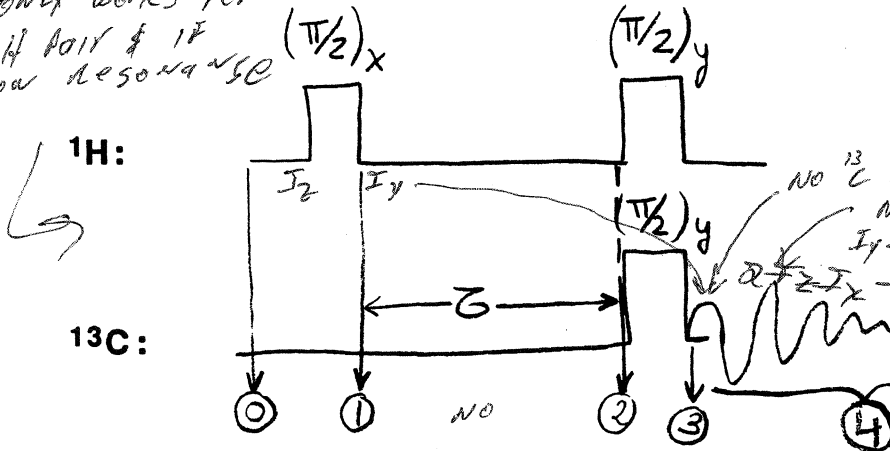
V.4 DOUBLE RESONANCE PART 2: HETERONUCLEAR COHERENCE TRANSFER AND THE INEPT EXPERIMENTS

¹H clean shift give peaks

NOE can be used to transfer populations incoherently from ¹H to ¹³C via relaxation. Coherences can also be transferred from protons to carbons if the ¹H-¹³C pair is spin-coupled. The simplest pulse sequence capable of achieving this:

only works for CH pair & if on resonance

single QUANT. ANTIPHASE terms can be used to inv. S/N (DON'T usually observe these)



NO ¹³C singlet
New IT blows Iy -> Sy
Iy -> Sy (takes phi = pi/2)
* TRANSFER H magnet INTO ¹³C
* DENS. MAT ONLY H¹⁵ I_z
* FORGET ABOUT C

Assume no ¹H (I-spin) or ¹³C (S-spin) offset, and no initial ¹³C magnetization. The evolution of rho in this sequence

single QUANT. ANTIPHASE H VS C

$$\rho_0 = I_z \xrightarrow{\pi/2 I_x} I_y \xrightarrow{J I_z S_z \tau} I_y \cos(J\tau/2) - 2 I_x S_z \sin(J\tau/2) \xrightarrow{\pi/2 I_y}$$

rho = gamma I I_z
Lagrange
rho = gamma S I_z

2 pi -> I_z

$$I_y \cos(J\tau/2) - 2 I_x S_z \sin(J\tau/2) \xrightarrow{\pi/2 S_y}$$

single QUANT. ANTIPHASE C VS H

$$I_y \cos(J\tau/2) + 2 I_z S_x \sin(J\tau/2)$$

INTERCH. gamma_I FOR I_S

but tau = 1/2J

$$2 \sin(J\tau/2) [I_z S_x \cos(J\tau/2) + S_y \sin(J\tau/2)]$$

less gamma_I in phase gamma_S

observable ¹³C signal

If we tune tau = 1/2J
=> at 2 : I_y -> 0
2 I_x S_z -> maximum

* also now DON'T have to wait for protons to relax now

$S_y \xrightarrow{J} S_y S_x \xrightarrow{J} 2S_y I_x \xrightarrow{J} 2S_y I_x S_x$

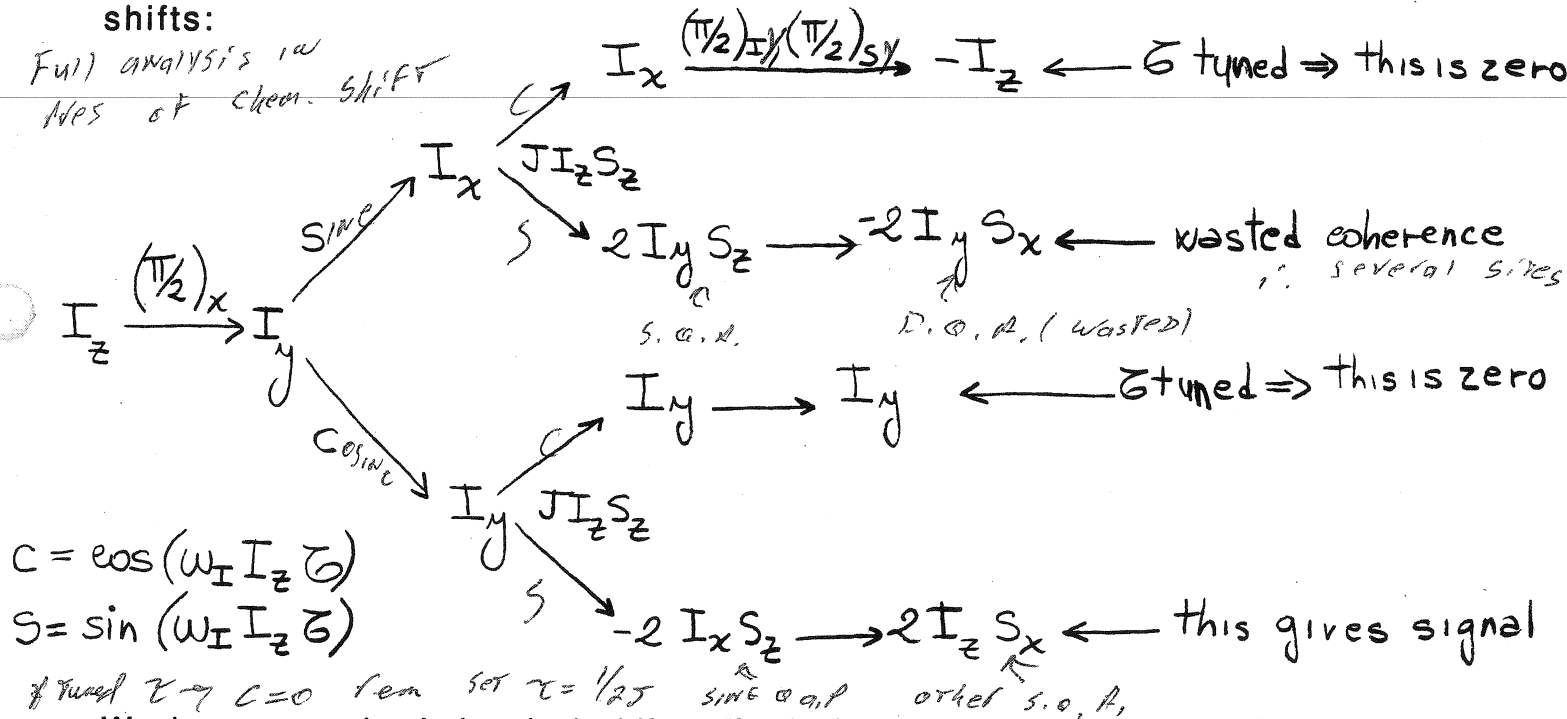
Notice that since we started from I_z , there is an enhancement in the ^{13}C signal arising from this sequence = γ_I / γ_S . So

Coherence transfer: signal enhancement $\propto \gamma_I / \gamma_S$ For $^{13}C \approx 4$; $^{15}N \approx 10$

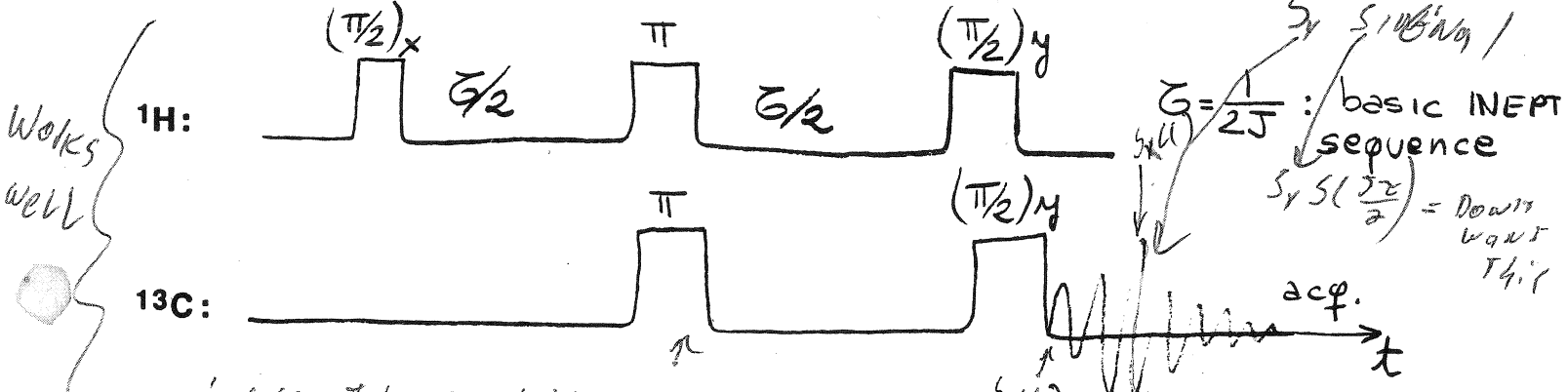
NOE: signal enhancement $\propto 1 + \gamma_I / 2\gamma_S$ For $^{13}C \approx 3$; $^{15}N \approx 4$

This simple sequence however has its problems. In the presence of chemical shifts:

Full analysis in terms of Chem. Shift

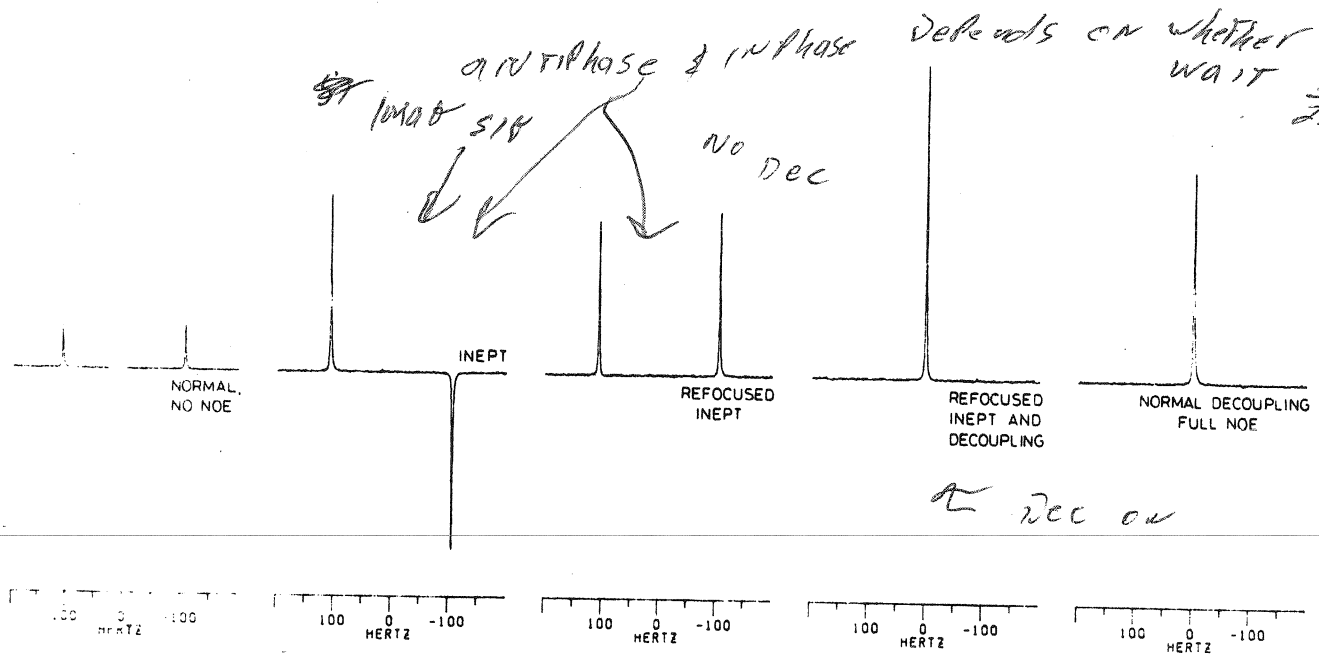


We have to make I-chemical shifts effectively zero to maximize the S signal, but without affecting the I,S J-coupling. This can be achieved by putting simultaneous I and S π -pulses in the middle of τ



use two π pulses to elim (retocus) $S_x S_x$ & keep J-coupling

Overall, we have the following alternatives for recording a ¹³C NMR spectrum (so far!)



antiphase
DO48

Figure 6.9 Permutations on the spectrum of chloroform. It can be seen that the refocused INEPT spectrum shows some loss of intensity as compared with simple INEPT; this is partly due to transverse relaxation during the refocusing period, and partly to imperfections in pulses.

- 1) refoc INEPT
- 2) " " dec " " "
- 3) NO H'S splitting
- 4) faster pulses

V.5 MULTISPIN SYSTEMS: INEPT SPECTRAL EDITING AND THE DEPT EXPERIMENT

Let's consider now a system composed by 3 weakly coupled spins $\{I_1, I_2, I_3\}$. We have new operators of the type:

$$2 I_{1x} I_{2z} \xrightarrow{J I_{1z} I_{3z} t} ?$$

The result could be *for J-coupl I1 & I3, doesn't evolve*

3 SPINS YIELD all these.

$2 I_{1z} I_{3z}, 4 I_{1z} I_{2z} I_{3z}$: zero-quantum coherences

$2 I_{1x} I_{2z}, 4 I_{1x} I_{2z} I_{3z}$: single-quantum coherences

$2 I_{1x} I_{2y}, 4 I_{1x} I_{2y} I_{3z}$: double-quantum coherences

$4 I_{1x} I_{2x} I_{3x}, 4 I_{1x} I_{2x} I_{3y}$: triple-quantum coherences

Just look at SING. Q. pairs, o/s
 $I_{1+} I_{2+} I_{3+} \rightarrow \text{sing. Q.}$
 $I_{1+} I_{2+} I_{3-} \rightarrow \text{S.Q.}$
Total z-angmom = ± 1

Evolution of $I_j I_k$ operators under the effects of $\omega_j I_{zj}$ or $J I_{zj} I_{zk}$ remain as in the case of 2 spins. We have to deal now however with new situations, like for instance

$$2 I_{1x} I_{2z} \xrightarrow{J_{13} I_{1z} I_{3z} t} ?$$

** J-coupl can only give single quat,*



The result

$$\rho(t) = 2e^{-iJ_{13}I_{1z}I_{3z}t} I_{1x} e^{iJ_{13}I_{1z}I_{3z}t} I_{2z} \quad : \text{only spin 1 evolves}$$

$$\downarrow$$

$$2 \left[I_{1x} \cos\left(\frac{J_{13}t}{2}\right) + 2 I_{1y} I_{3z} \sin\left(\frac{J_{13}t}{2}\right) \right] I_{2z} \Rightarrow$$

$$\Rightarrow 2 I_{1x} I_{2z} \xrightarrow{J I_{1z} I_{3z} t} 2 I_{1x} I_{2z} \cos\left(\frac{J_{13}t}{2}\right) + 4 I_{1y} I_{2z} I_{3z} \sin\left(\frac{J_{13}t}{2}\right)$$

S. Q. A. P.

A. P.

Compare with our previous situation

$$2 I_{1x} I_{2z} \xrightarrow{J_{12} I_{1z} I_{2z} t} 2 I_{1x} I_{2z} \cos\left(\frac{J_{12}t}{2}\right) + I_{1y} \sin\left(\frac{J_{12}t}{2}\right)$$

S. Q. A. P.

or with the remaining possibility

$$2 I_{1x} I_{2z} \xrightarrow[\text{evolves}]{J I_{2z} I_{3z} t} 2 I_{1x} I_{2z}$$

easy to understand w/out

recall D. Q. evolves at sum of C.S
 "DIF" " " " "

Moreover there is an additional complication. Recall that although in systems composed by pairs of spins double-quantum states did not evolve:

$$2 I_{1x} I_{2y} \xrightarrow{J I_{1z} I_{2z}} 2 I_{1x} I_{2y}$$

these states **do evolve** in the presence of coupling to a third spin ($J_{13} \neq 0$ for instance):

$$2 I_{1x} I_{2y} \xrightarrow{J I_{1z} I_{3z}} 2 I_{1x} I_{2y} \cos\left(\frac{J_{13} t}{2}\right) + 4 I_{1y} I_{2y} I_{3z} \sin\left(\frac{J_{13} t}{2}\right)$$

*D.O. S.O. D.O. S.O. * Just evolves.*

Consider the INEPT experiment on a 3 spin system CH₂ with $J_{CH^1} = J_{CH^2} = J$. We focus on the evolution after the second pair of ($\pi/2$) pulses:

Sign missed

$$I_{z1} + I_{z2} \xrightarrow{(\pi/2)_x} I_{y1} + I_{y2} \xrightarrow{\tau/2} \xrightarrow{(\pi)_{I_3}} \xrightarrow{\tau/2} 2(I_{x1} + I_{x2}) S_z$$

NO C.S. # J.C.O.Y.

$$\xrightarrow{[(\pi/2)_y]_{I_3}} 2(I_{z1} + I_{z2}) S_x \xrightarrow{J I_{z1} S_z t'} 2 I_{z1} S_x \cos\left(\frac{J t'}{2}\right) + S_y \sin\left(\frac{J t'}{2}\right)$$

J I_{z2} S_z t' → 2 more terms missing

$$2 I_{z1} S_x \cos^2\left(\frac{J t'}{2}\right) + 4 I_{z1} I_{z2} S_y \cos\left(\frac{J t'}{2}\right) \sin\left(\frac{J t'}{2}\right)$$

NOT observables

$$S_y \sin\left(\frac{J t'}{2}\right) \cos\left(\frac{J t'}{2}\right) - 2 I_{z2} S_x \sin^2\left(\frac{J t'}{2}\right)$$

Observable?

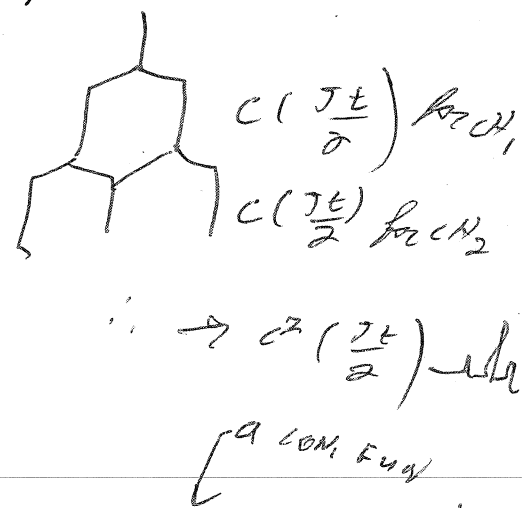
Out of all these operators, only the term proportional to S_y is observable!
 Overall, the observable part of the S-spin density matrix arising from CH_n groups in an INEPT experiment (with β tuned to $\sin(\frac{J\beta}{2}) = 1$) is given by:

each has DIFF coeffs \therefore can get pure spectra for each (COULDN'T DO FOR APT)

CH: $\rho \propto S_y \sin \frac{J\beta}{2}$

CH₂: $\rho \propto -2S_y \sin \frac{J\beta}{2} \cos \frac{J\beta}{2}$

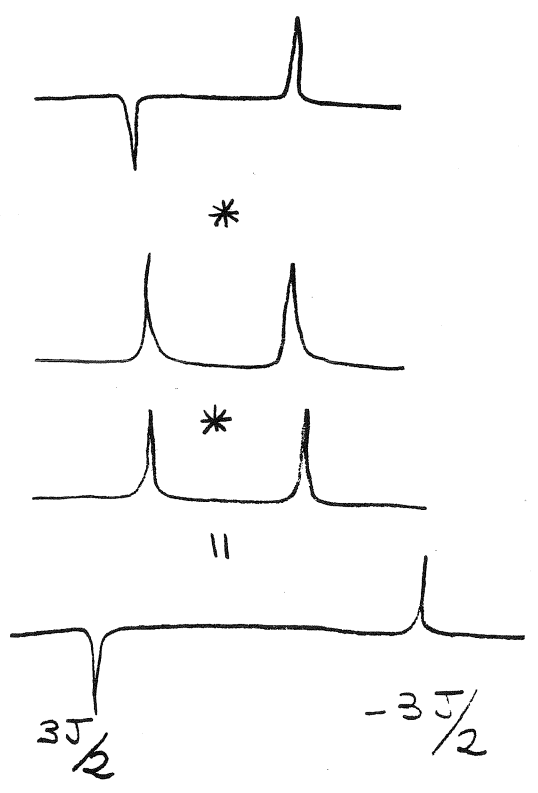
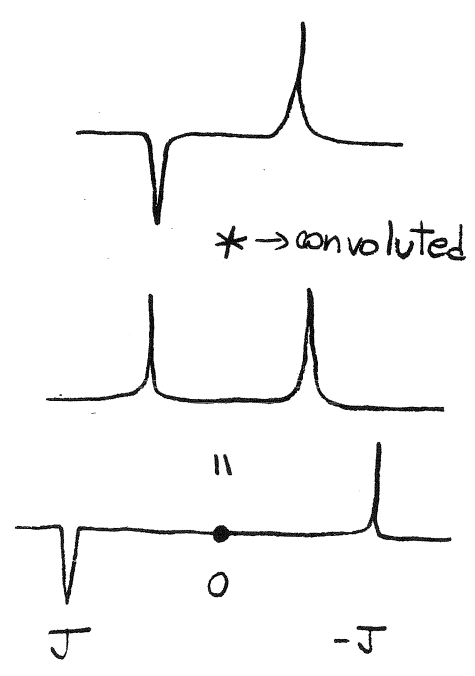
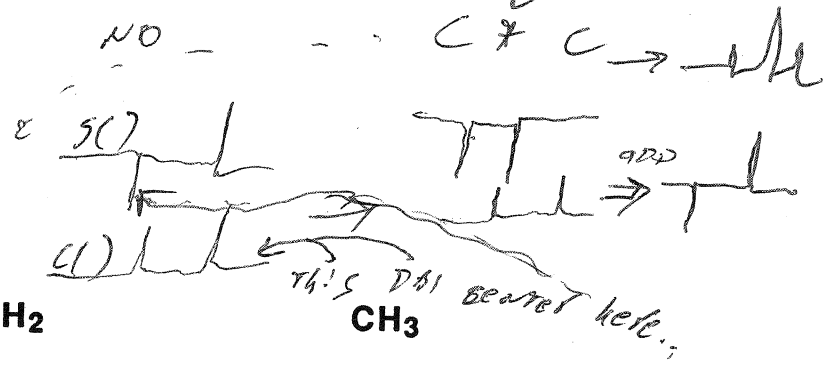
CH₃: $\rho \propto 3S_y \sin \frac{J\beta}{2} \cos^2 \frac{J\beta}{2}$



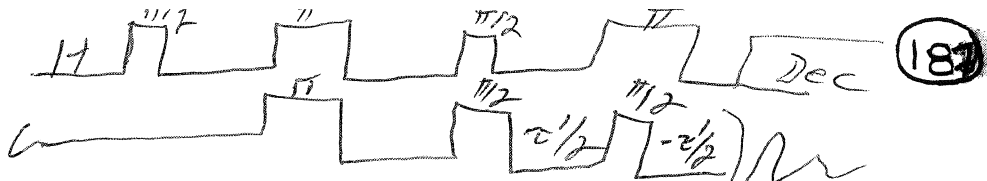
The line shapes:

ambiphase
CH

$S(\rho)$ \xrightarrow{FT}
CH₂



How do this ext



The factors multiplying S_y can be used to edit the intensity of the different carbons. To do so, one carries out a number of experiments for different J_C^1 values; for instance,

	$\frac{J_C^1}{2} = 1/8 \text{ cyc}$	$\frac{J_C^1}{2} = 1/4 \text{ cyc}$	$\frac{J_C^1}{2} = 3/8 \text{ cyc}$
CH:	$1/\sqrt{2}$	1	$1/\sqrt{2}$
CH ₂ :	1	0	-1
CH ₃ :	$1.5/\sqrt{2}$	0	$1.5/\sqrt{2}$

~~These~~ can use via combos of this to get purely CH ext.

and obtains the subspectra according to

CH: spectrum $(\frac{J_C^1}{2} = 1/4)$

CH₂: spectrum $(\frac{J_C^1}{2} = 1/8) - \text{spectrum}(\frac{J_C^1}{2} = 3/8)$

CH₃: spectrum $(\frac{J_C^1}{2} = 1/8) + \text{spectrum}(\frac{J_C^1}{2} = 3/8) - \sqrt{2} \cdot \text{spectrum}(\frac{J_C^1}{2} = 1/4)$

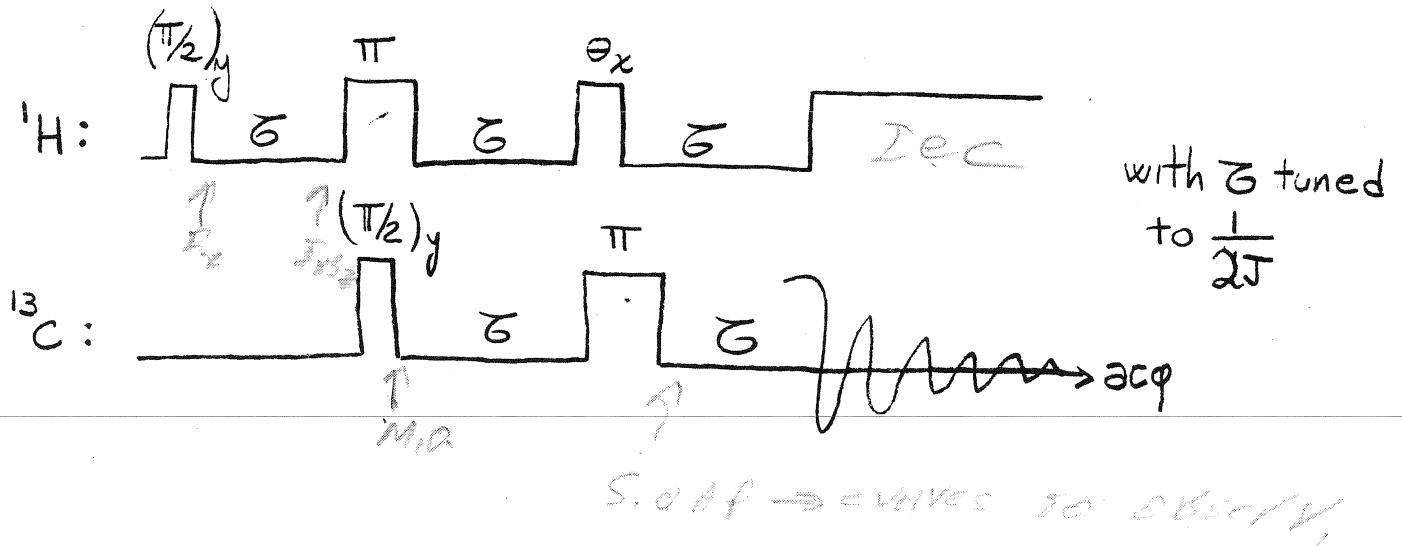
The main problem of INEPT is that it works based on the assumption that all $J_{C,H}$ are equal. This is only partly true, but relatively small dispersions in $J_{C,H}$ can ruin an INEPT

* albumin CH & C¹³ & CH₃ , cant get

$\frac{J_C^1}{2} = 1/8$ for all C¹³ eq) ~ 100%

* have problem w/ long range etc
eg δ -C-H will have an δ (large)

There is a second polarization transfer procedure whose efficiency is independent of the strength of J couplings, and which therefore affords a much better quality in the subspectral editing: Distortionless Enhancement by Polarization Transfer (DEPT). The pulse sequence of DEPT:



Let's analyze the evolution of ρ for an SI_n group (CH_3 , etc.). Since the only effect of the π pulses is to refocus the chemical shifts (which we ignore anyway); we have that

$$m \gamma_I I_z \xrightarrow{\pi/2 I_y} m \gamma_I I_x \xrightarrow{J I_z S_z \tau} m 2 \gamma_I I_y S_z$$

$$\xrightarrow{\pi/2 S_y} m 2 \gamma_I I_y S_x$$

πI multiple-quantum coherence

* DEPT gets rid of odd J-coupling problems

* still some left

To analyze the evolution of this last term, we analyze the fate of each one of its components:

$$2 I_y S_x = 2 I_{y_1} S_x + 2 I_{y_2} S_x + \dots \xrightarrow{J I_z S_z \tau} J I_{z_1} S_z \tau + J I_{z_2} S_z \tau + J I_{z_3} S_z \tau$$

M.R.C., t... I_y S_x

they all commute

$$2 I_{y_1} S_x \xrightarrow{J I_{z_2} S_z \tau} 2 I_{y_1} S_x \cos\left(\frac{J \tau}{2}\right) + 4 I_{y_1} I_{z_2} S_y \sin\left(\frac{J \tau}{2}\right)$$

↑ of $J \tau = 1/2$

H.D.O.C (for I & S) does not evolve under J-coupling $I_{y_1} = \text{const}$

$$4 I_{y_1} I_{z_2} S_y \sin \cdot \cos$$

$$J I_{z_3} S_z \tau$$

$$8 I_{y_1} I_{z_2} I_{z_3} S_x \sin^2\left(\frac{J \tau}{2}\right)$$

Note started with $I_{y_1} S_x \rightarrow I_{y_1} S_x$

=> before the θ_x -pulse:

$$\rho \propto \text{something} + m \gamma_I 2^m S_x (I_{y_1} I_{z_2} I_{z_3} \dots + I_{z_1} I_{y_2} I_{z_3} \dots + \dots)$$

After the θ_x -pulse: (Rf total)

$$I_{y_1} \xrightarrow{\theta} I_{y_1} \cos \theta + I_{z_1} \sin \theta$$

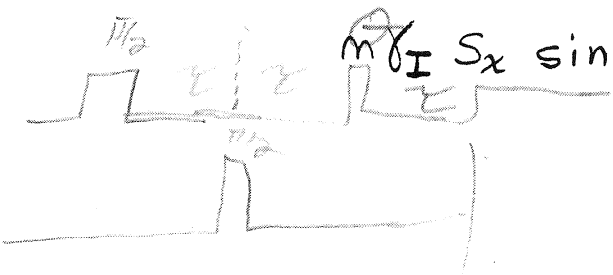
$$\underbrace{I_{z_2} I_{z_3} \dots}_{m-1 \text{ terms}} \xrightarrow{\theta} I_{z_2} I_{z_3} \dots \cos^{m-1} \theta \dots$$

LOW BIT'S & NONE ARE OBS YET

$$\Rightarrow \rho = m \gamma_I 2^m S_x I_{z_1} I_{z_2} \dots \sin \theta \cos^{m-1} \theta$$

(or S_{y_1} depends on $J I_z S_z \tau$)

* ONE PLANT I LOW BIT pulse $\rightarrow S_x \neq S_y$



$$m \gamma_I S_x \sin \theta \cos^{m-1} \theta : \text{observable}$$

* NOW S_x DEPEND ON PULSE * ANGLES & NOT J-COUP

w

Let's compare INEPT with DEPT:

$$\text{INEPT}(I_m S): m \gamma_I I_z \xrightarrow{\text{both } S, Q} m \gamma_I I_x \xrightarrow{\text{both } S, Q} m \gamma_I^2 I_y S_z \xrightarrow{\text{both } S, Q} m \gamma_I^2 I_z S_x$$

$m \gamma_I S_y \sin \frac{J \tau}{2} \cos^{m-1} \frac{J \tau}{2}$
 $\uparrow J \tau$

$$\text{DEPT}(I_m S): m \gamma_I I_z \xrightarrow{\text{both } S, Q} m \gamma_I I_x \xrightarrow{\text{both } S, Q} m \gamma_I^2 I_y S_z$$

$m \gamma_I S_x \sin \theta \cos^{m-1} \theta$
 \uparrow

$m \gamma_I^2 I_y: S_y I_{zj} I_{zk} \xrightarrow{\text{both } S, Q} m \gamma_I^2 I_z S_y \sin \theta \cos^{m-1} \theta$

The "transfer functions" of both experiments are very similar, but in INEPT the tuning depends on J whereas in DEPT it is a function of a pulse angle.

Editing can then be carried out like in INEPT, with θ 's = $\frac{\pi}{4}, \frac{\pi}{2}, \frac{3\pi}{4}$

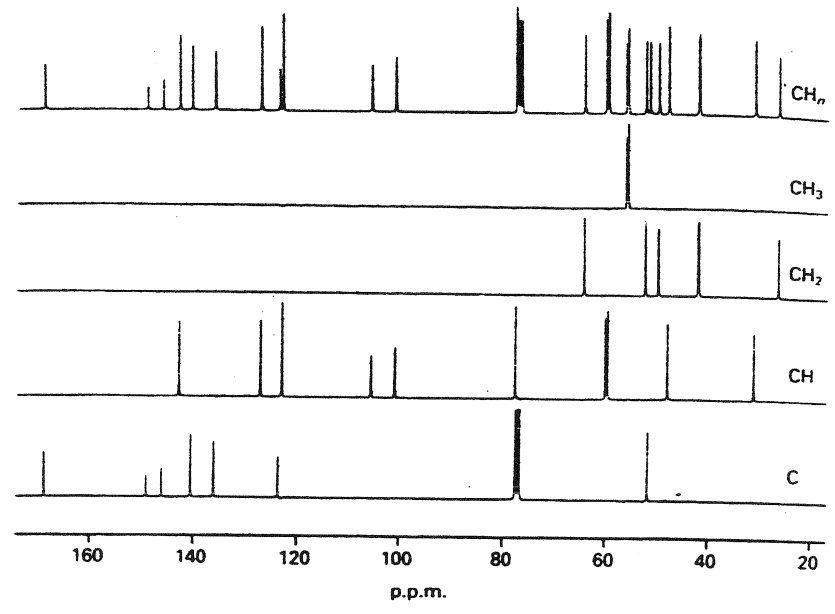


FIG. 4.5.6. Editing of proton-decoupled carbon-13 spectra of a mixture of brucine and 2-bromothiazole, which has a spread of J-couplings from ca. 125 to 192 Hz. Note the clean separation of the signals associated with CH_n groups and the absence of cross-talk.

* use this for spectra editing (DEPT)
 * false seq.

V.6 PROBLEMS

1) Using the full 4 x 4 density matrixes representing the space of a pair of spins, demonstrate the following evolutions:

a) $I_{1z} + I_{2z} = F_z \xrightarrow{(\pi/2)_y} F_x = I_{1x} + I_{2x}$

b) $F_x \xrightarrow{\Delta\omega_1 I_{1z} t + \Delta\omega_2 I_{2z} t} I_{1x} \cos(\Delta\omega_1 t) + I_{1y} \sin(\Delta\omega_1 t) + I_{2x} \cos(\Delta\omega_2 t) + I_{2y} \sin(\Delta\omega_2 t)$

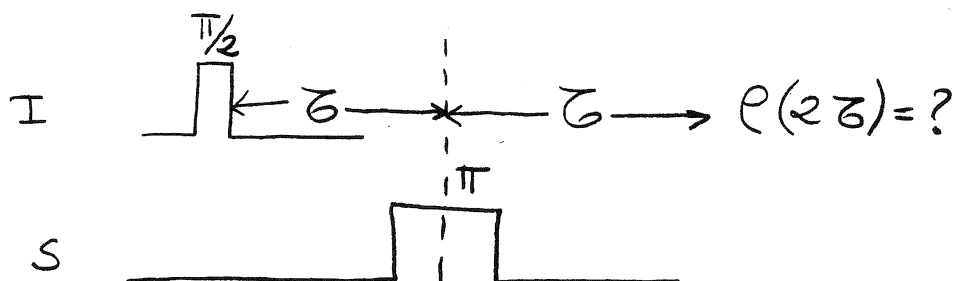
c) $I_{1x} \xrightarrow{J I_{1z} I_{2z} t} I_{1x} \cos(Jt/2) + 2 I_{1y} I_{2z} \sin(Jt/2)$

d) $2 I_{1y} I_{2z} \xrightarrow{J I_{1z} I_{2z} t} 2 I_{1y} I_{2z} \cos(Jt/2) - I_{1x} \sin(Jt/2)$

2) Complete the following rotation table

I_{1z}	$\xrightarrow{J I_{1z} I_{2z} t}$	
I_{1y}	$\xrightarrow{J I_{1z} I_{2z} t}$	
$2 I_{1y} I_{2z}$	$\xrightarrow{J I_{1z} I_{2z} t}$	
$2 I_{1x} I_{2z}$	$\xrightarrow{J I_{1z} I_{2z} t}$	
I_{1x}	$\xrightarrow{J I_{1z} I_{2z} t}$	$\xrightarrow{\Delta\omega_1 I_{1z} t}$
I_{1x}	$\xrightarrow{\Delta\omega_1 I_{1z} t}$	$\xrightarrow{J I_{1z} I_{2z} t}$

- 3) Write the matrix expression for the 16 elements of the two-spin product operator base.
- 4) Write the product operator base of a system composed by 3 spins 1/2.
- 5) Using the product operator formalism, calculate $\rho(2\tau)$ for the following pulse sequence



- 6) Calculate the frequency and intensities of the S-spin transitions in the I-decoupled Hamiltonian

$$\mathcal{H}_{IS} = -\omega_S S_z - \omega_I I_z + J I_z S_z + \omega_2 I_x$$

Demonstrate that for $\omega_I = 0$ (on-resonance I irradiation), $\omega_2 \gg J$, the S signal is decoupled from the I spins

- 7) Calculate the classical ^{13}C magnetizations of $-\text{CH}_3$, $-\text{CH}_2-$, $-\overset{|}{\text{C}}\text{H}-$ and $-\overset{|}{\text{C}}-$ groups at time 2τ in the APT pulse sequence.

- 8) Calculate $\rho_{^{13}\text{C}}$ at the beginning of the acquisition period in the refocused INEPT sequence for a C-H pair.

- 9) Calculate the signals arising from the ^{13}C spins of $-\overset{|}{\text{C}}-$, $-\overset{|}{\text{C}}\text{H}-$, $-\text{CH}_2-$, and $-\text{CH}_3$ groups in an INEPT experiment.