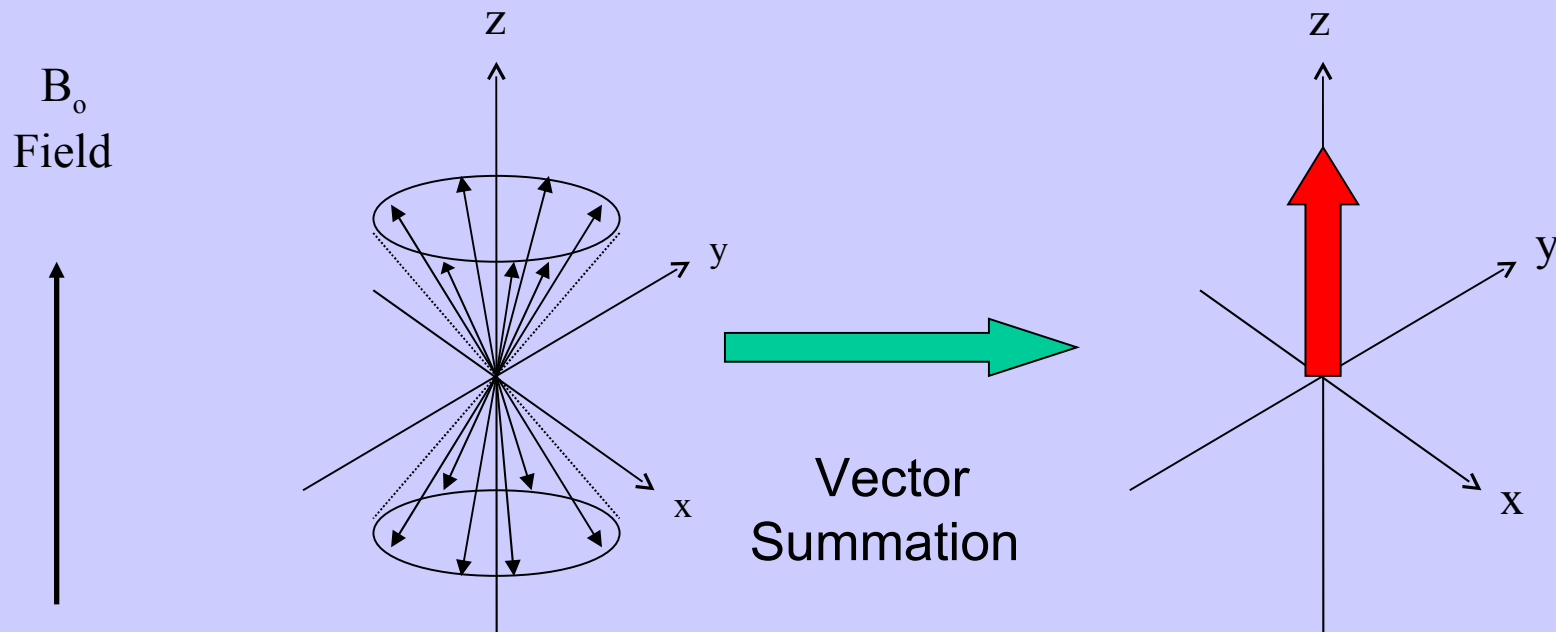


Pulsed NMR Spectroscopy

R. V. Hosur

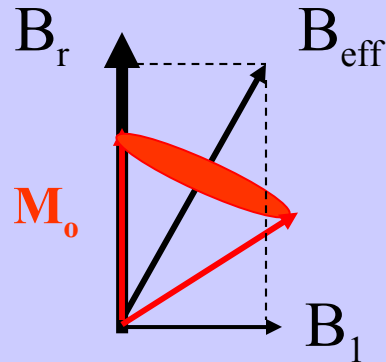
**Department of Chemical Sciences
Tata Institute of Fundamental Research
Homi Bhabha Road, Mumbai**

Fourier Transform (FT) NMR



Fourier transform NMR

Rotating frame

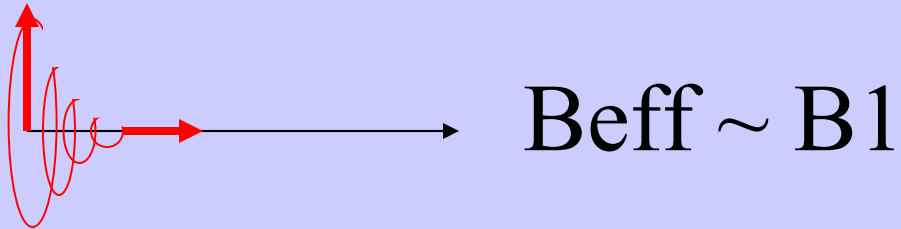


$$\omega_{\text{eff}} = \gamma B_{\text{eff}}$$

$$\omega_{\text{ri}} = \omega_i - \omega_{\text{RF}}$$

$$B_{\text{ri}} = B_i - \omega_{\text{RF}} / \gamma$$

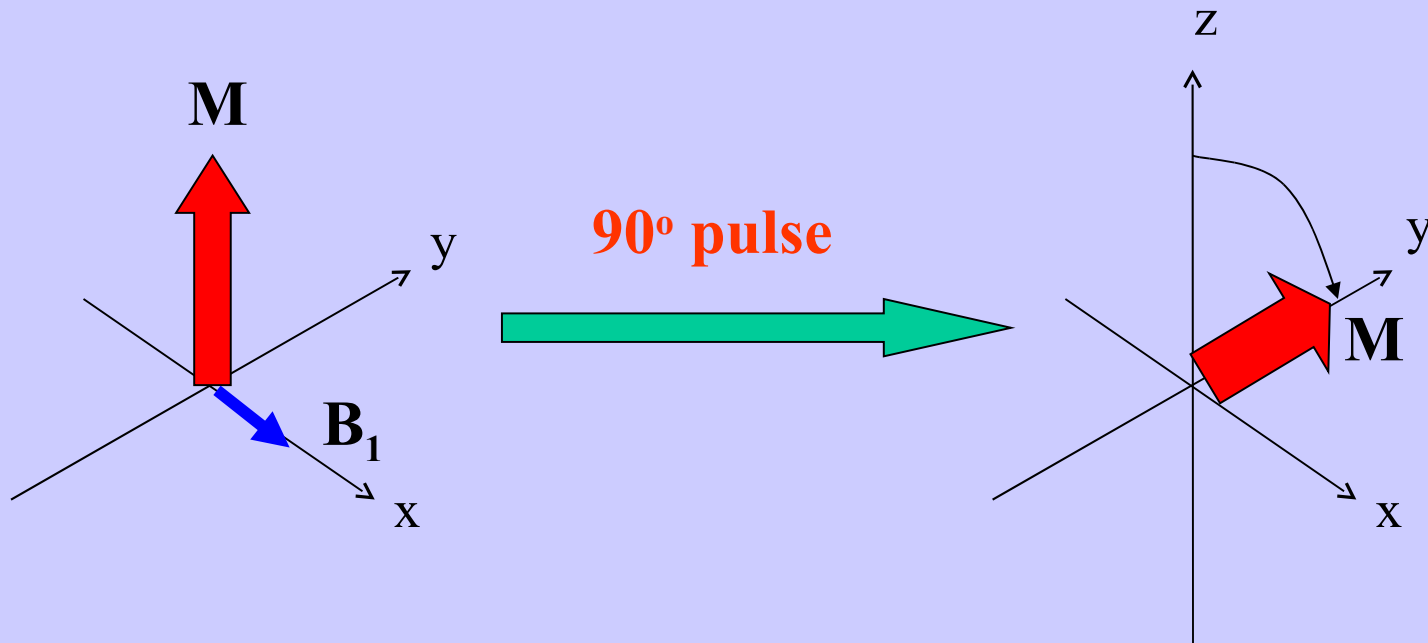
If $B_1 \gg B_{\text{ri}}$, then $B_{\text{eff}} \sim B_1$ for all i .



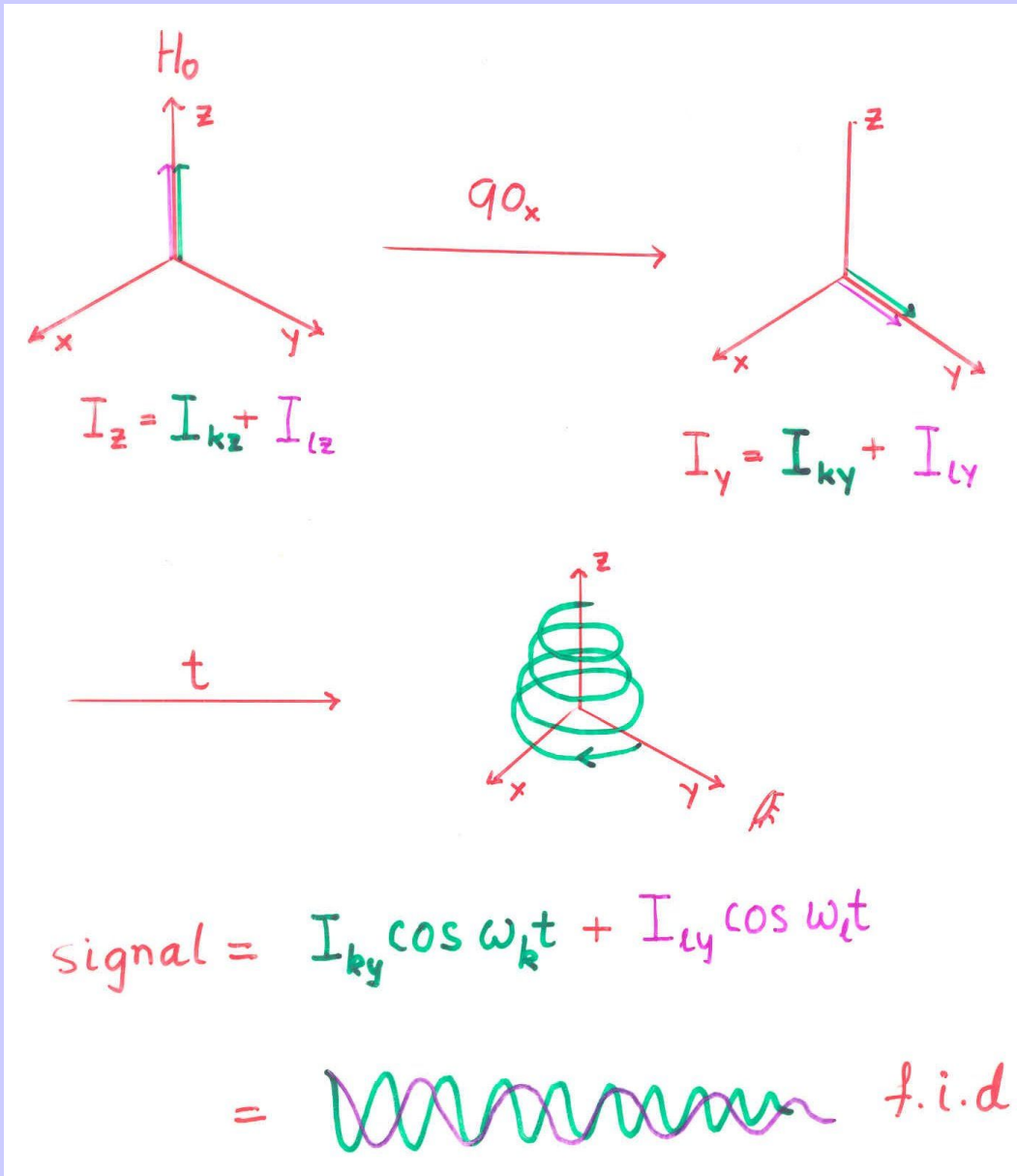
Pulse width (τ) = time for which B_1 is applied

Flip angle (θ) = $\gamma B_1 \tau$

Application of RF rotates the magnetisation



Fourier Transform NMR



$$f(t) \xrightarrow{\text{FT}} F(\omega)$$

Fourier Transform NMR

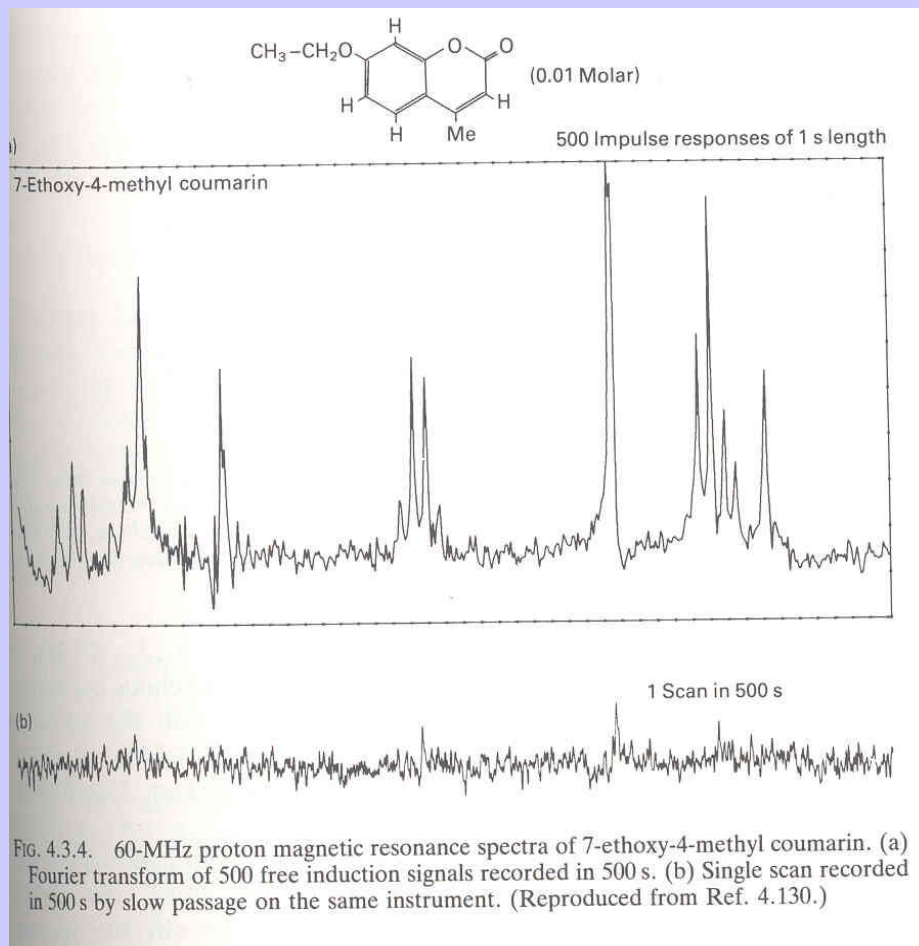
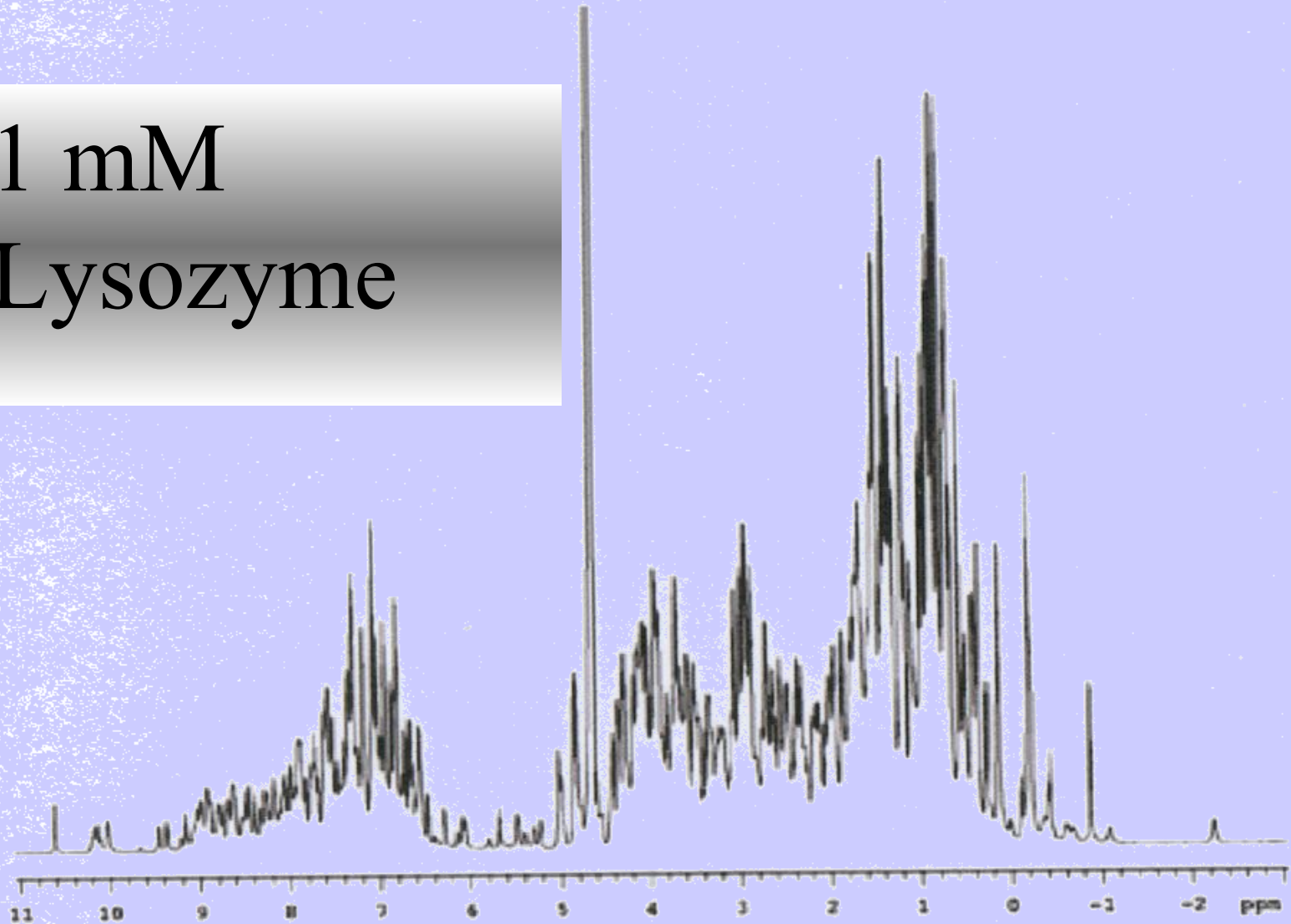


FIG. 4.3.4. 60-MHz proton magnetic resonance spectra of 7-ethoxy-4-methyl coumarin. (a) Fourier transform of 500 free induction signals recorded in 500 s. (b) Single scan recorded in 500 s by slow passage on the same instrument. (Reproduced from Ref. 4.130.)

R. R. Ernst and W. A. Anderson
Rev. Scientific Instrum. 37, 93 (1966)

Resolution

1 mM
Lysozyme



Water suppression

H₂O : 110 M in protons

Protein : 1 mM

Dynamic range problem

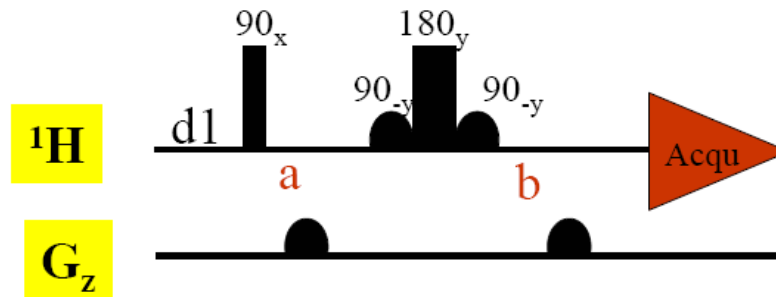
Presaturation

Jump and return

Flipback

Watergate....Excitation sculpting

WATERGATE



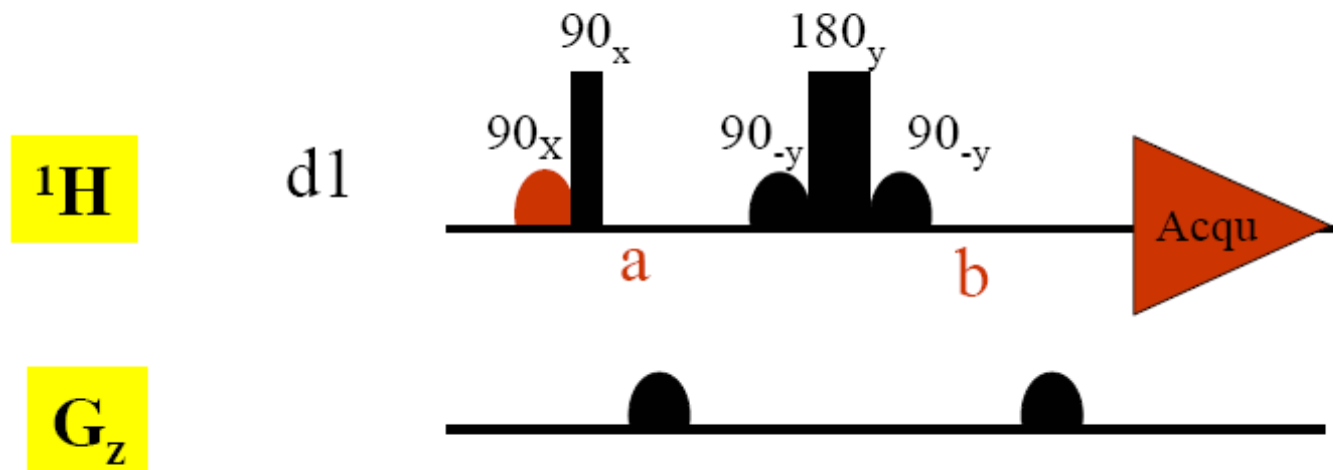
•A strong Z-gradient pulse can be used to destroy transverse magnetization.

•A destroyed (dephased) magnetization can be refocused by another z-gradient pulse of the same amplitude but of opposite phase. (or use a 180 pulse in between the two identical z-gradient pulse).

•**H₂O**: the two extra selective 90 pulse on water makes the 2nd z-gradient pulse act as another defocus gradient pulse.

•**Protein signals**: the 180 pulse makes the 2nd Z-gradient act as a refocus gradient.

Water Flip-back WATERGATE



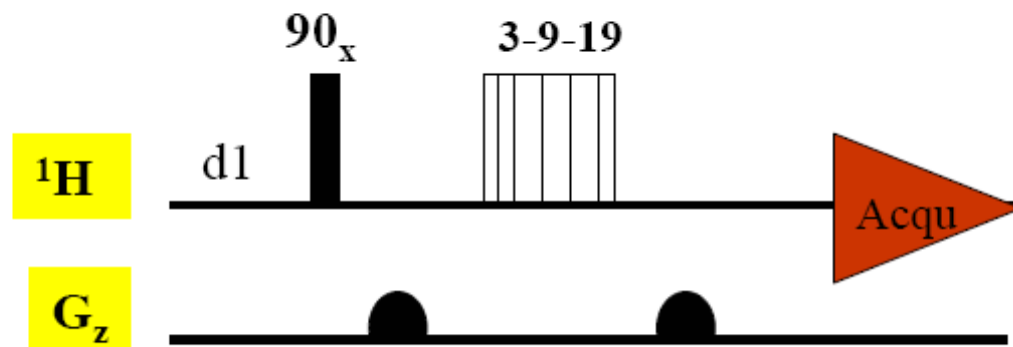
S. Grzesiek and A. Bax, J. Am. Chem. Soc., 115, 12593-12594 (1993)

- Water is aligned along the z axis before any z-gradient pulse (point “a”). So, it is not destroyed by the z-gradient pulse.
- This reduces the signal loss of exchangeable protons due to attenuation of water signal (saturation transfer).

Parameter adjustment:

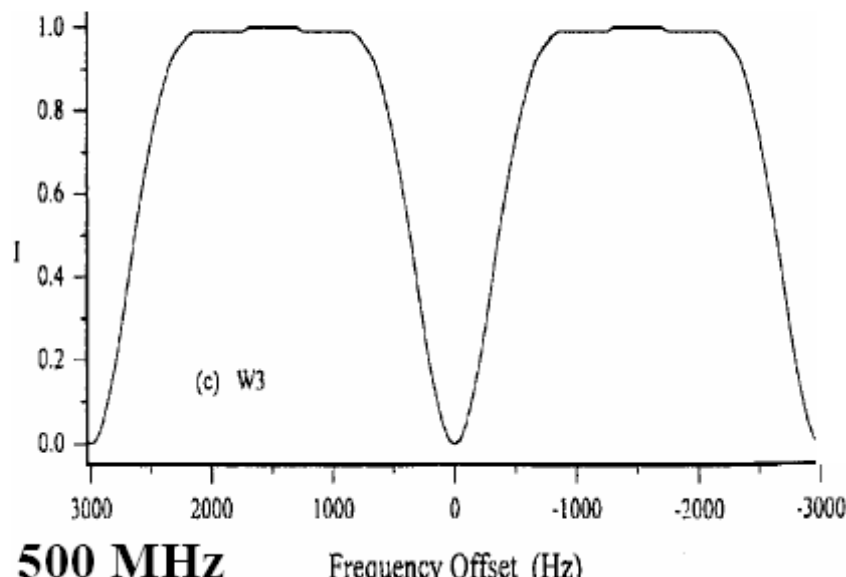
Pulprog=fp*, i.e. “hsqcetfpf3gp” calibrate the shaped pulse as describe in WATERGATE.

3-9-19 WATERGATE



Sklenar et al., J. Magn. Reson., A102, 241-245 (1993)

- Off resonance DANTE excitation technique.
- **3-9-19: $3\alpha-\tau-9\alpha-\tau-19\alpha-\tau-19\alpha-\tau-3\alpha$** , where $26\alpha=180$, τ =delay.
(This is also referred as “W3”.)



Delay $\tau = 1/(4 \Delta\nu_{\max})$,
where $2\Delta\nu_{\max}$ = distance of next null (Hz)
(The delay τ is field-dependent !!)

Excitation Sculpting

$\pi/2 - G1 - R - G1 - G2 - R - G2 - \text{acquire}$

$$R = (\pi_{\text{sel}} - \pi)$$

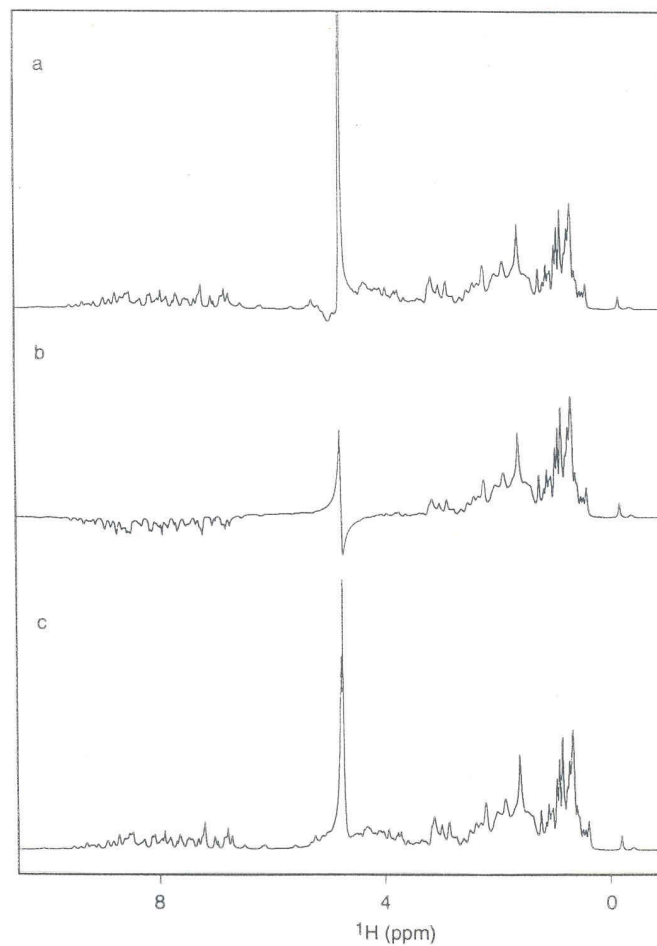
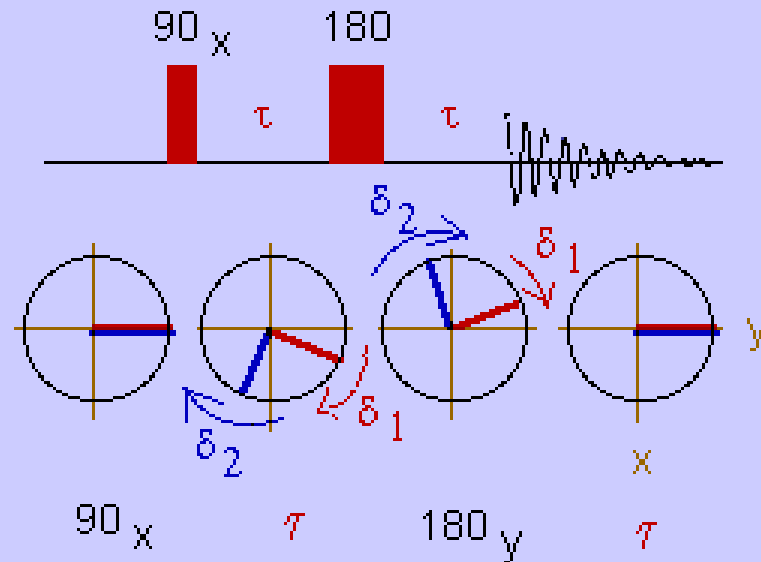


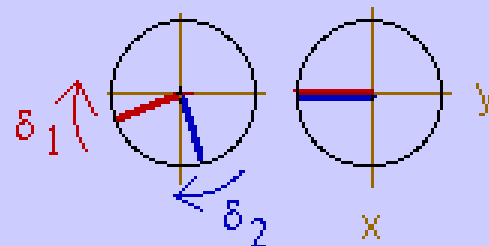
FIGURE 3.29 Water suppression using (a) presaturation, (b) jump-return, and (c) spin-lock purge pulses. Additional postacquisition water suppression can be obtained using a digital low-pass filter as illustrated in Fig. 3.30.

Spin Echo

Refocuses chemical shift evolution



or:

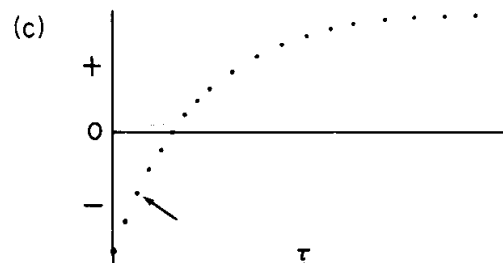
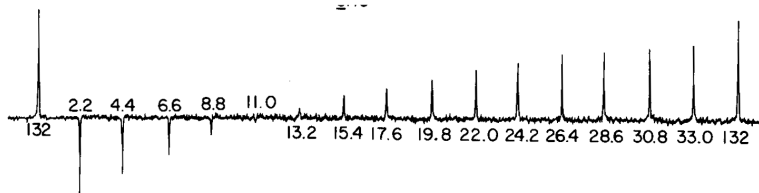
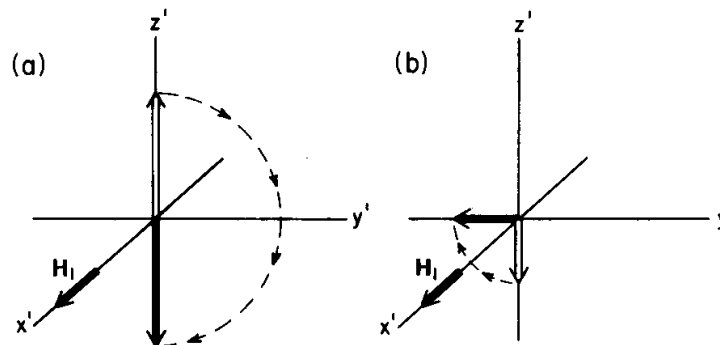
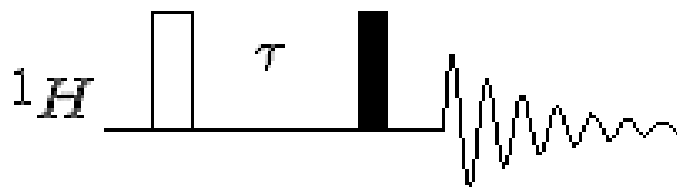


Method for T2 measurements: SE amplitude is dictated by T2 relaxation

Inversion recovery T1 measurement

2.2 Measurement of T_1

21



$$y = 1 - p_1 e^{-\frac{x}{p_2}}$$

Figure 2.3. Determination of T_1 by 180° , τ , 90° sequences. (a) \mathbf{M} is inverted by a 180° pulse at time 0. (b) After a time τ a 90° pulse rotates \mathbf{M} to the y' (or $-y'$) axis. (c) The initial amplitude of the FID after the 90° pulse, which is proportional to the value of \mathbf{M} at time τ , is plotted as a function of τ . Note that each point results from a separate 180° , τ , 90° sequence. The point corresponding to (b) is indicated by the arrow.