

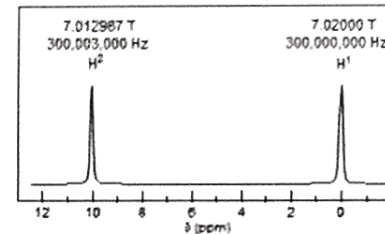
4/2/15 For next week: Keeler Ch 3  
 \* Stopped at Processing \*

## CW NMR

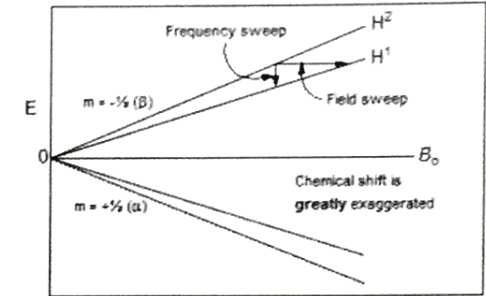
## 1D NMR

Chris Waudby

[c.waudby@ucl.ac.uk](mailto:c.waudby@ucl.ac.uk)



Proton NMR spectrum at 7.02 T (300 MHz)



low field → high field  
 high frequency ← low frequency  
 decreased shielding by electrons → increased shielding by electrons

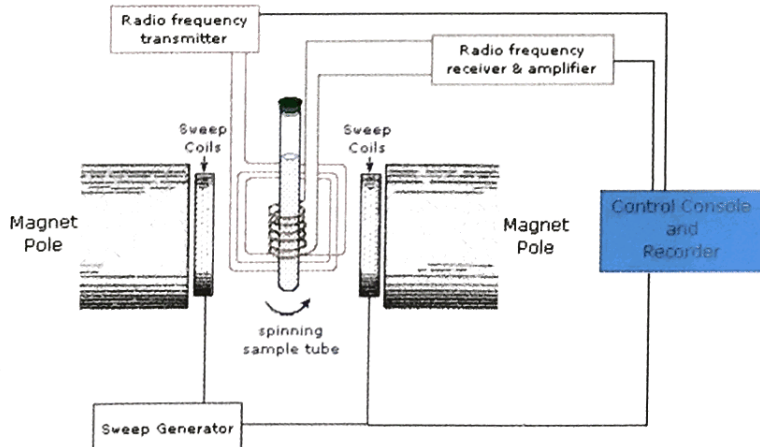
$$\Delta E = \gamma \hbar B (1 - \sigma) = \hbar \omega$$

$$\Rightarrow \omega = \gamma B (1 - \sigma)$$

<http://www.chem.wisc.edu/areas/rech/omr/OS-hmr/CO.cmu.htm>

## CW NMR

- Constant frequency, vary magnetic field to detect resonances



<http://www2.chemistry.msu.edu/faculty/reusch/VirtTxtJml/Spectry/nmr/nmr1.htm>

PHYSICAL REVIEW VOLUME 70, NUMBERS 7 AND 8 OCTOBER 1 AND 15, 1946

### The Nuclear Induction Experiment

F. BLOCH, W. W. HANSEN, AND M. PACKARD  
 Stanford University, California  
 (Received July 19, 1946)

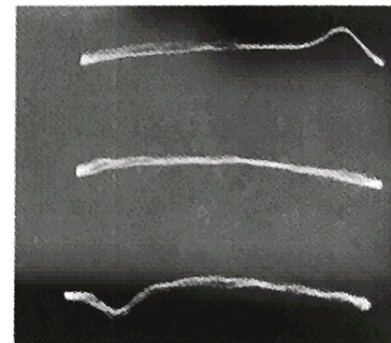


FIG. 8. Photographic record of the proton signal from water. The three traces from top to bottom correspond to the situation a, b, c of Fig. 7.

### The Nobel Prize in Physics 1952



Felix Bloch  
 Prize share: 1/2



Edward Mills Purcell  
 Prize share: 1/2

The Nobel Prize in Physics 1952 was awarded jointly to Felix Bloch and Edward Mills Purcell "for their development of new methods for nuclear magnetic precision measurements and discoveries in connection therewith".

## Chemical Effects on Nuclear Induction Signals from Organic Compounds\*

J. T. ARNOLD, S. S. DHARMATTI, AND M. E. PACKARD  
 Department of Physics, Stanford University, Stanford, California  
 (Received February 5, 1951)

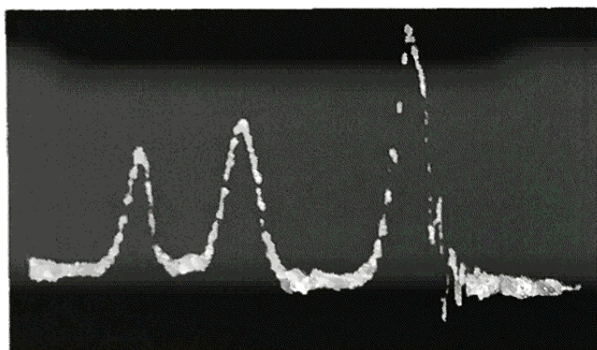
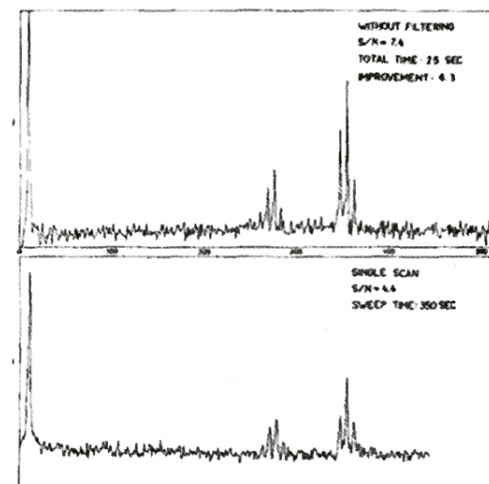


FIG. 1. Oscillograph trace of the nuclear induction signal from ethyl alcohol. The total trace is 75 milligauss wide and was traversed in 2 seconds. The peaks from left to right represent OH, CH<sub>2</sub>, CH<sub>3</sub>.

## Application of Fourier Transform Spectroscopy to Magnetic Resonance

R. R. ERNST AND W. A. ANDERSON  
 Analytical Instrument Division, Varian Associates, Palo Alto, California 94303  
 (Received 9 July 1965; and in final form, 16 September 1965)



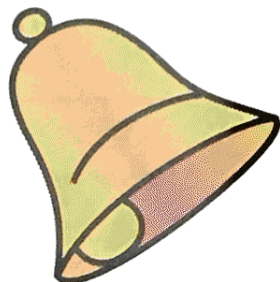
## The Nobel Prize in Chemistry 1991



Richard R. Ernst  
 Prize share: 1/1

The Nobel Prize in Chemistry 1991 was awarded to Richard R. Ernst  
 "for his contributions to the development of the methodology of high resolution nuclear magnetic resonance (NMR) spectroscopy"

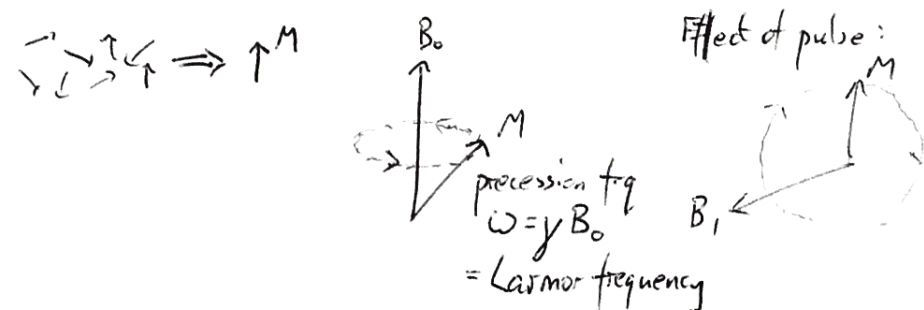
## Principle of FT NMR



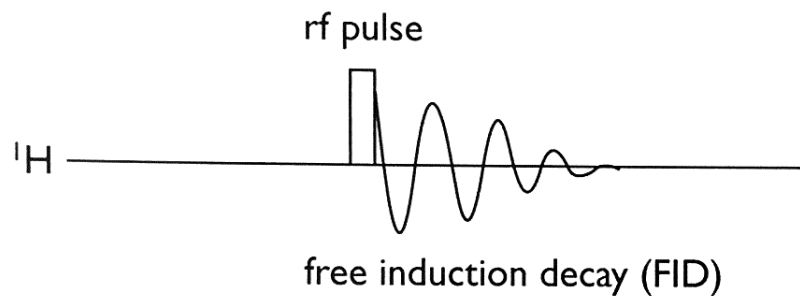
- How do you find out the frequencies of a bell?
- CW approach – scan wide range of frequencies looking for resonances
- FT approach – hit it with a hammer and listen!
- Analysis of frequencies present = 'Fourier transform'
- Relaxation – energy has been put into molecules to set them vibrating, where does it go?

## The vector model

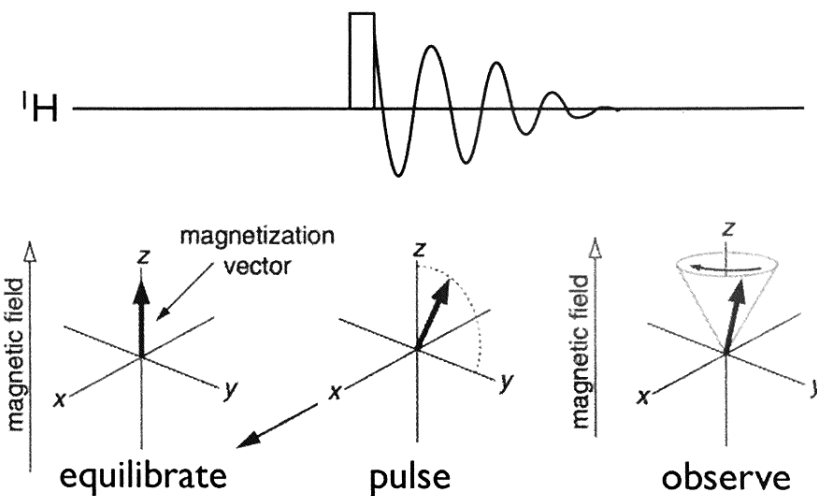
- sum up microscopic spins into a macroscopic magnetic moment / magnetisation vector
- can treat the evolution of this vector using classical physics
- the only bit of classical physics you need – precession of magnetic moments around a field



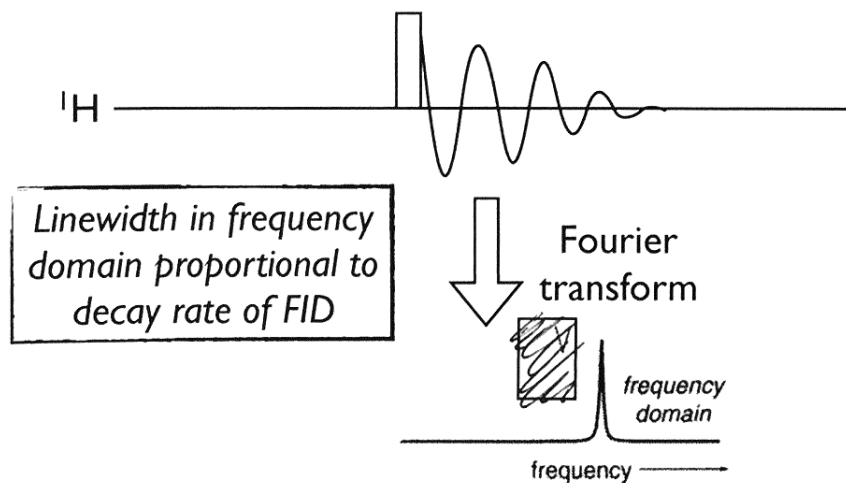
# Pulse-acquire: the simplest NMR experiment



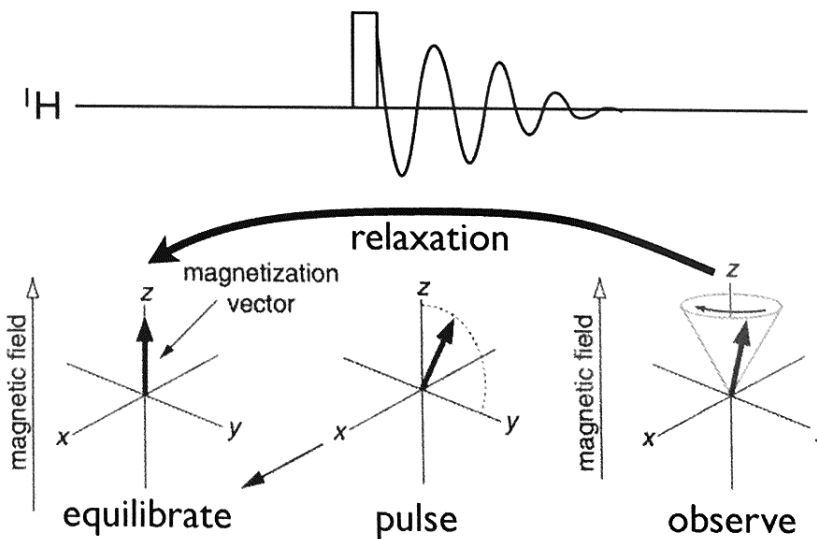
# Pulse-acquire: vector model description



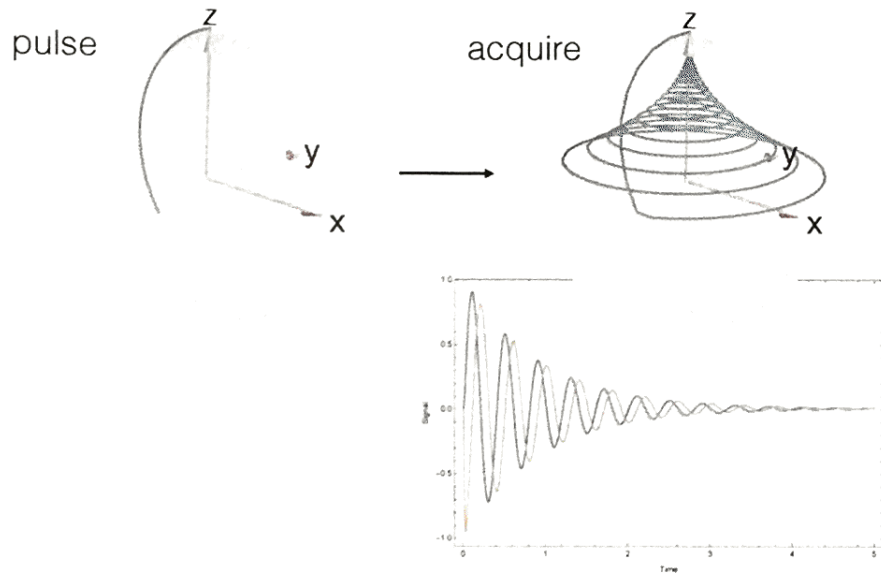
# Pulse-acquire: vector model description



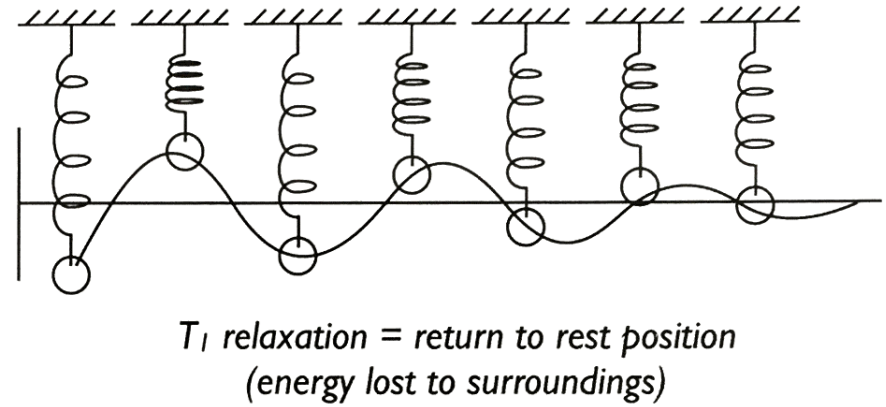
# Pulse-acquire: vector model description



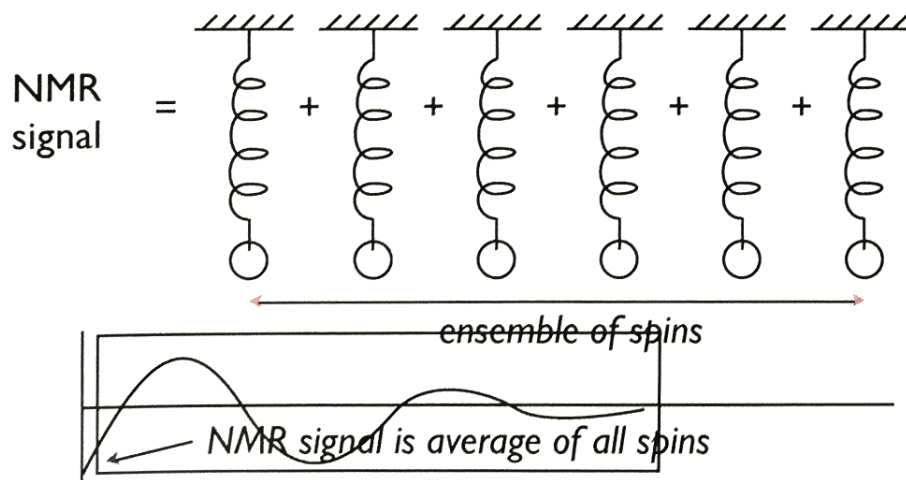
# The Bloch sphere



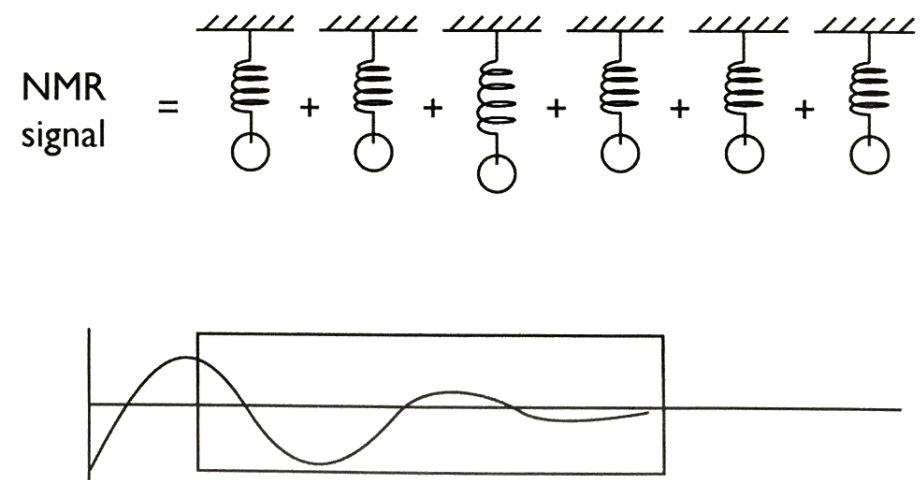
# $T_1$ (longitudinal) relaxation



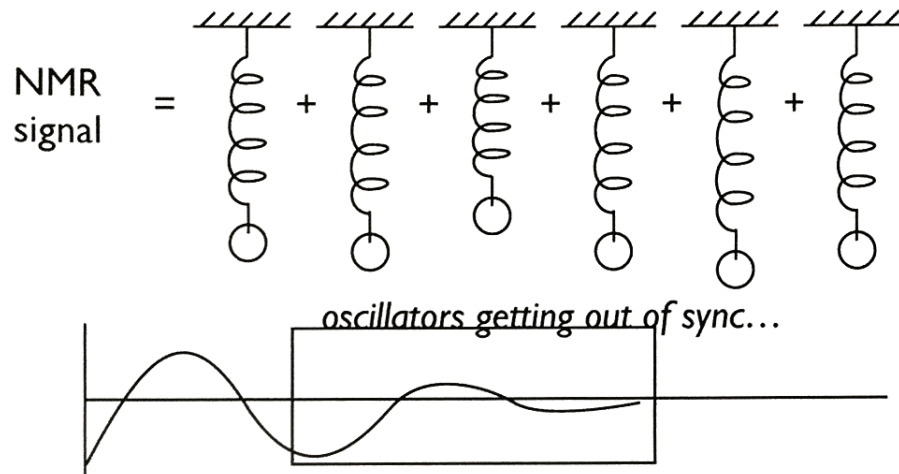
# $T_2$ (transverse) relaxation



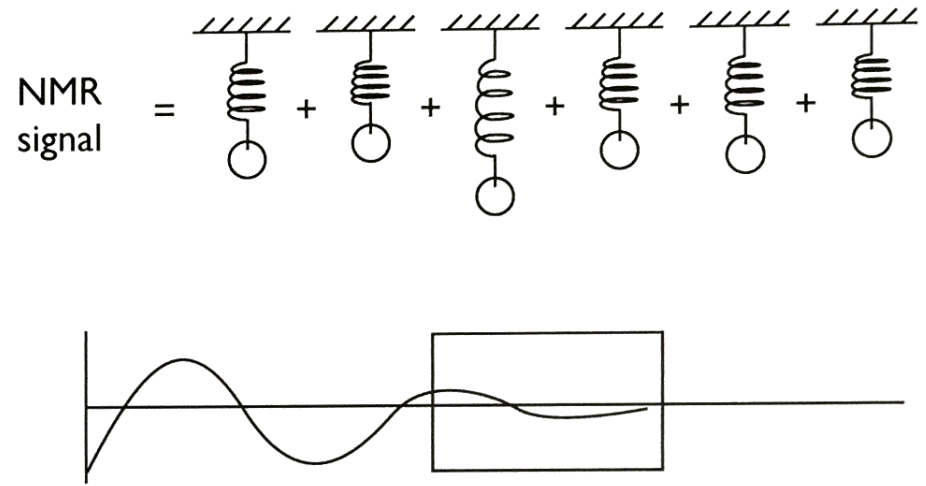
# $T_2$ (transverse) relaxation



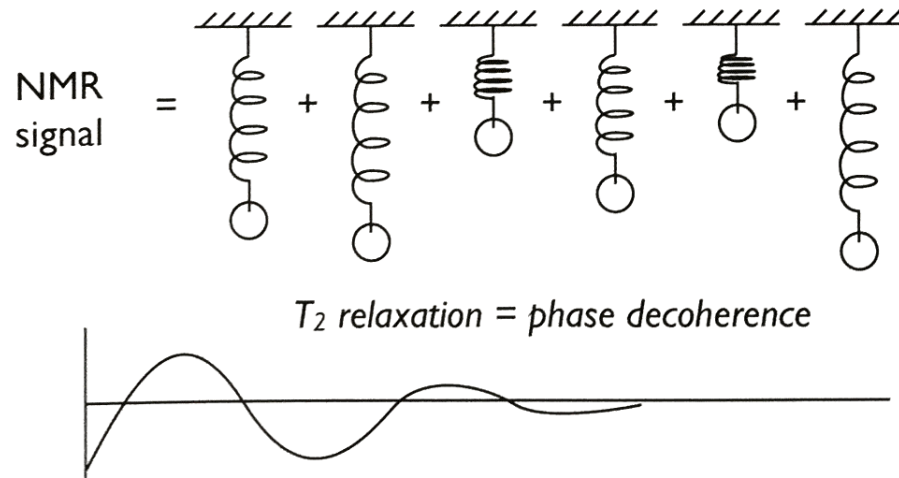
### $T_2$ (transverse) relaxation



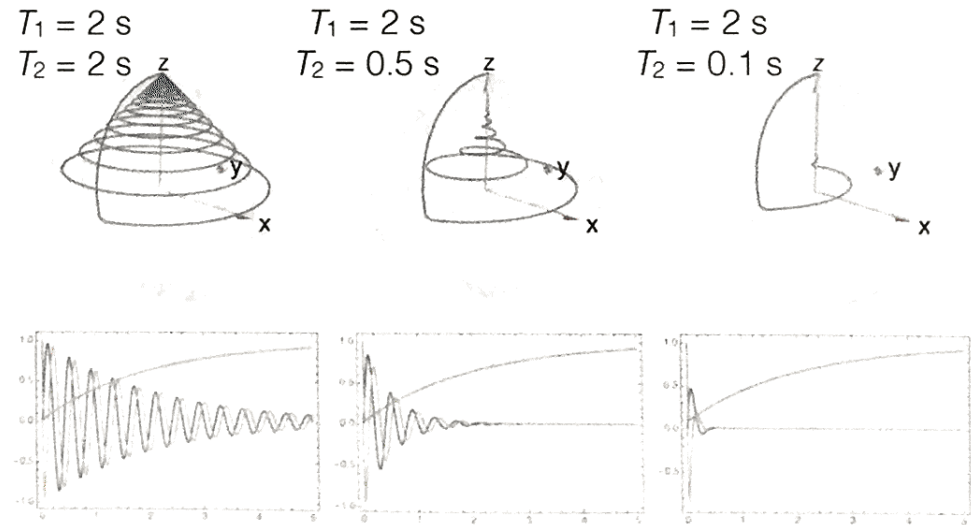
### $T_2$ (transverse) relaxation



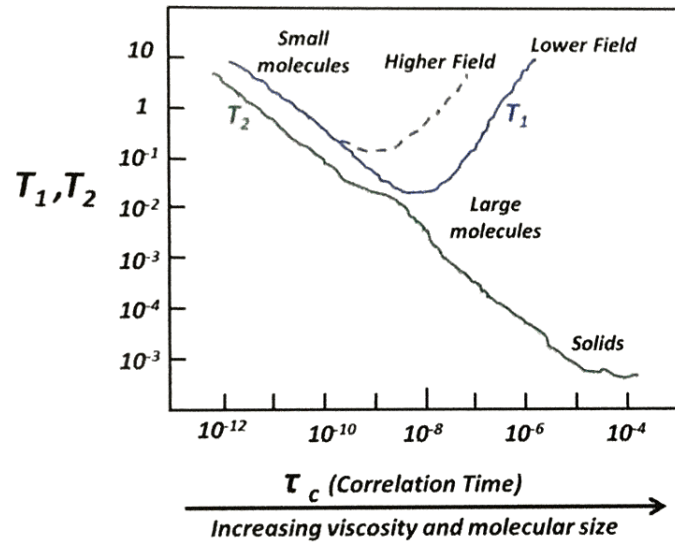
### $T_2$ (transverse) relaxation



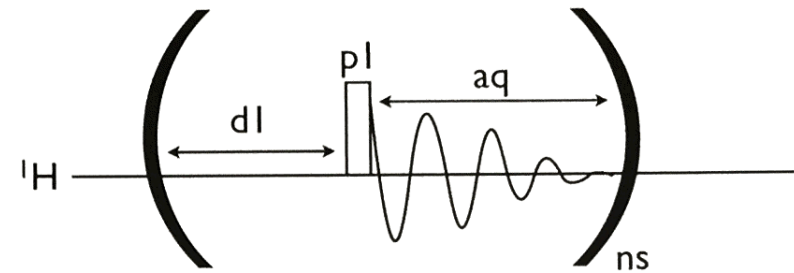
### Relaxation pictured on the Bloch sphere



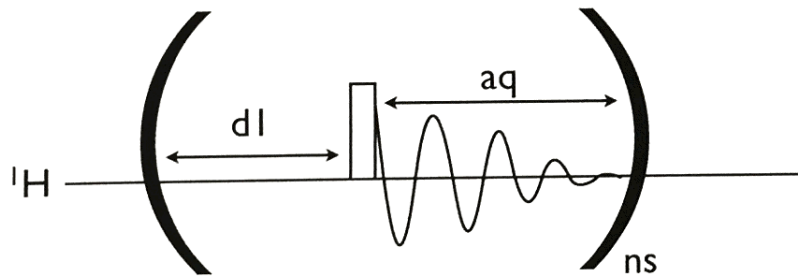
# Relaxation rates and molecular size



# Parameters in the pulse-acquire experiment



## ns and sensitivity

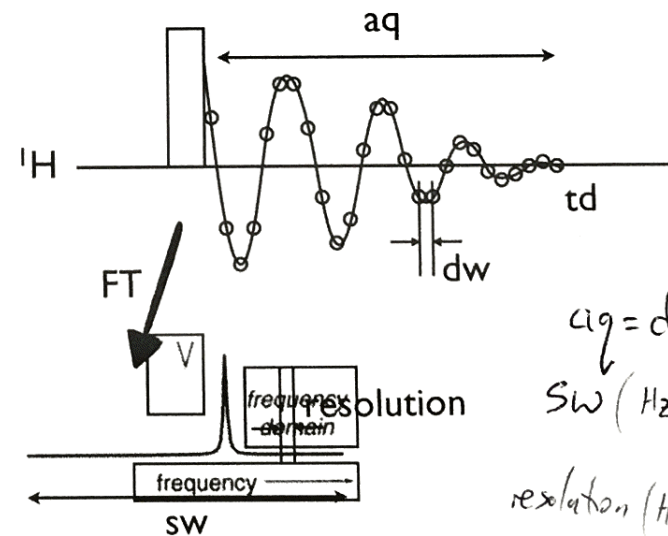


signal  $\sim ns$   
 noise  $\sim ns^{1/2}$

$$\text{SNR} \sim ns^{1/2}$$

$$\text{SNR} \sim ns^{1/2} \cdot \text{conc} \cdot B_0^{3/2} \cdot \gamma_{\text{ex}} \cdot \gamma_{\text{obs}}^{3/2}$$

## aq, td, dw, sw and spectrum resolution



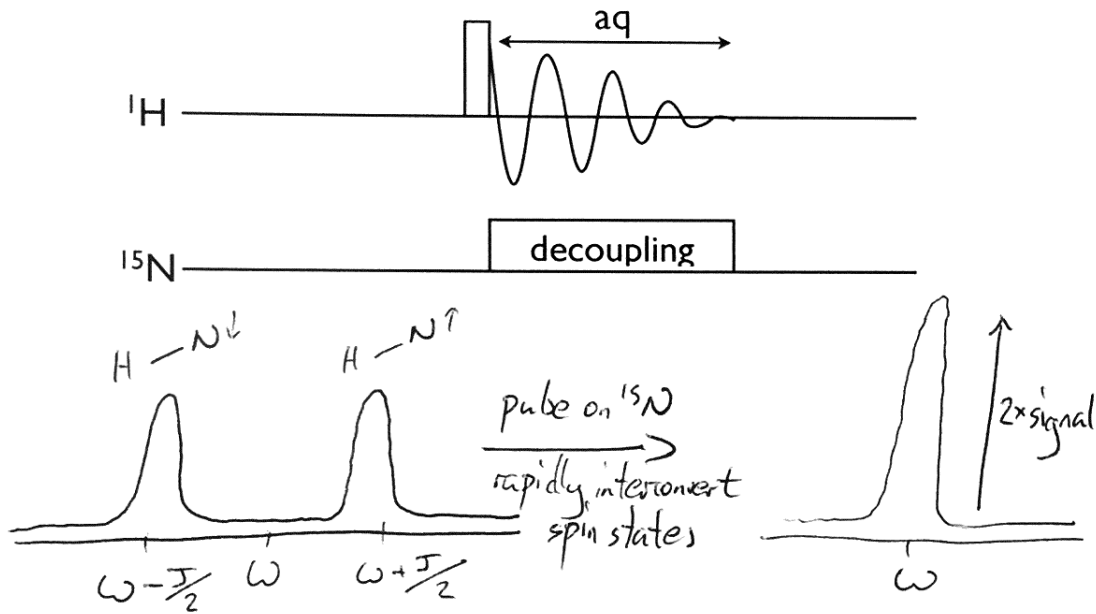
$$aq = dw \times td$$

$$sw \text{ (Hz)} = \frac{1}{dw} = \frac{td}{aq}$$

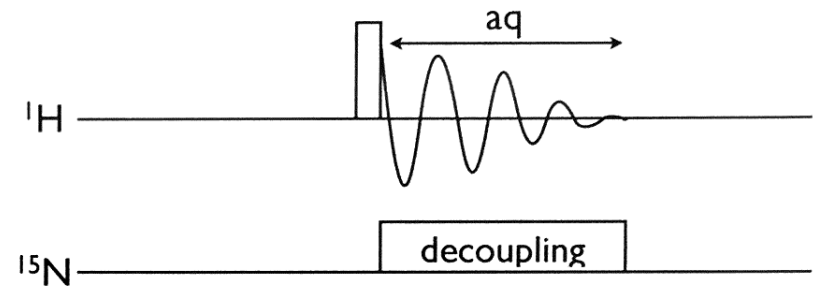
$$\text{resolution (Hz)} = \frac{1}{aq}$$



### decoupling

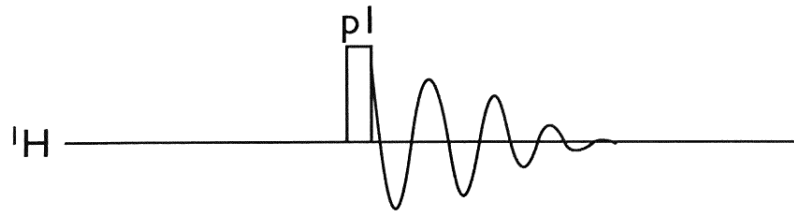


### decoupling – power limits



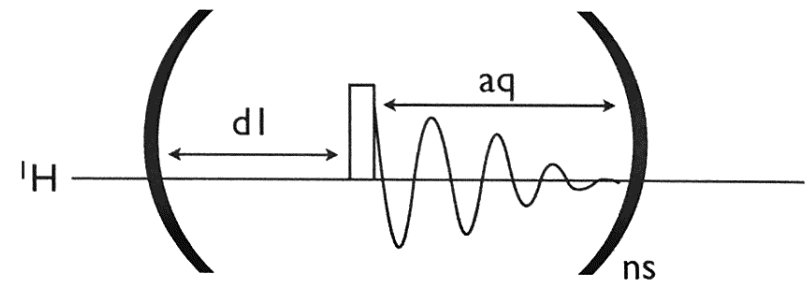
- If decoupling:  $aq$  MUST be less than 100 ms
- Risk of probe damage!

### pulse length / flip angle



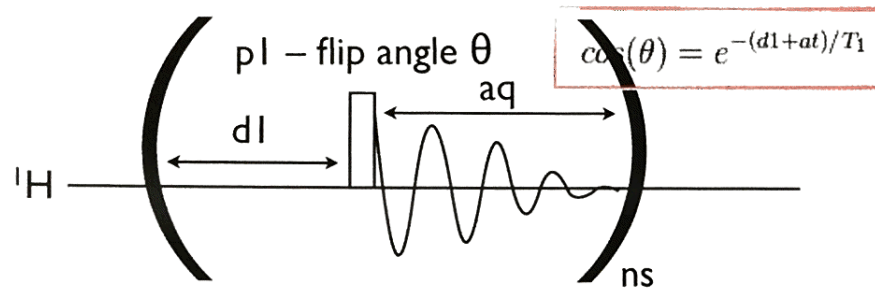
- pulse power vs pulse length
- calibration
- optimum flip angle?

### Recycle delay

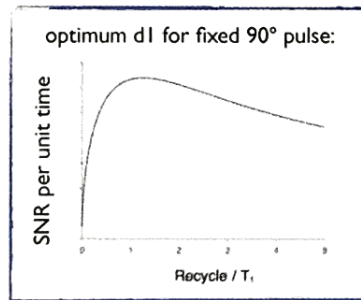


- Must wait for signal to relax ( $T_1$  relaxation)
- Hardware considerations: duty cycle limits
- Optimum combination of  $p1$  and  $d1$ ?

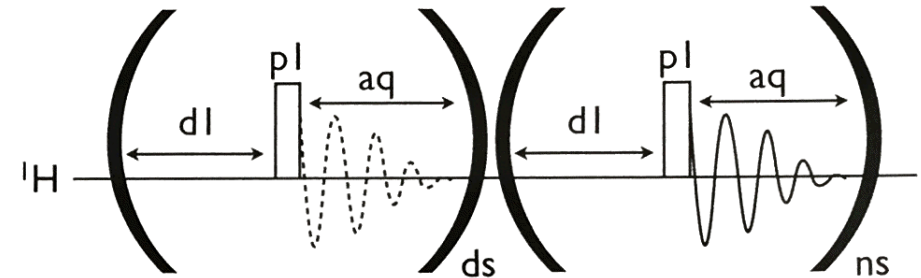
## Ernst angle excitation



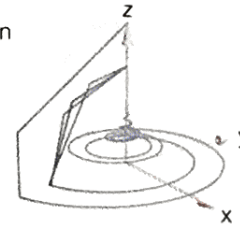
- Small flip angle, small recycle delay
- Large flip angle, large recycle delay
- Optimum delay for 90° pulse  
 $d1 + aq \approx 1.2 T_1$



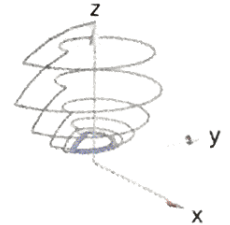
## Practical aspects: dummy scans



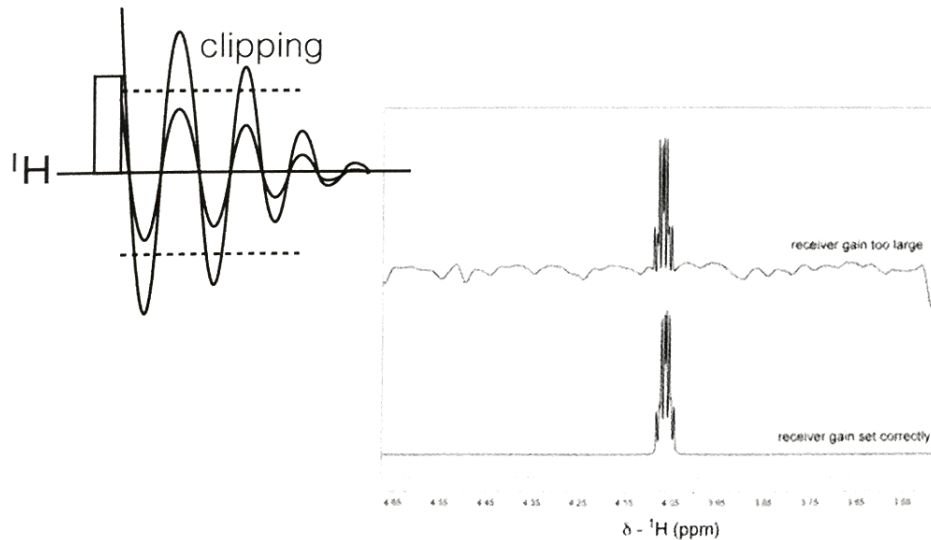
90° excitation  
 $T_1 = 1$  s  
 $d1 = 1.2$  s



36° excitation  
 $T_1 = 1$  s  
 $d1 = 0.1$  s

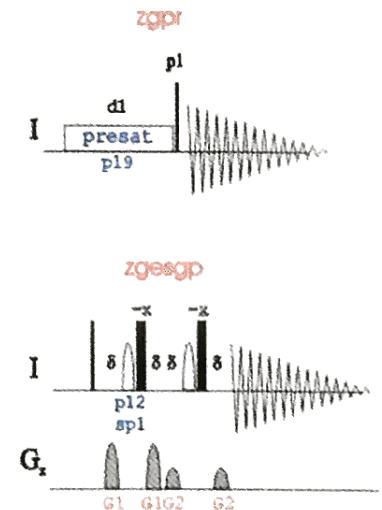


## Practical aspects: receiver gain



## Solvent suppression

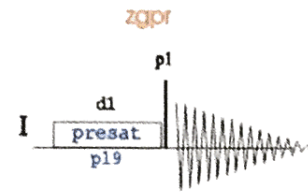
- Proton concentration in  $\text{H}_2\text{O}$  is 110 M!
- Two basic approaches:
  - presaturation
  - frequency selective methods





# Solvent suppression: presaturation

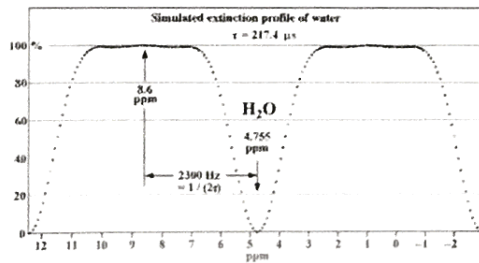
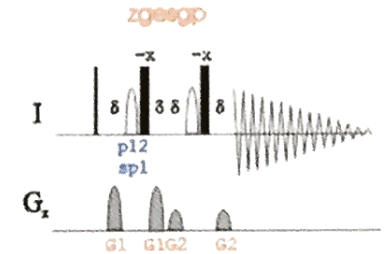
- Low power, very long selective pulse
- Need to calibrate frequency precisely ( $\omega_1$ )
- Simple
- Saturation of labile protons
- Transferred saturation from Ha in big molecules
- No delay between pulse and acquisition:
  - Quantitative
  - No J-coupling evolution



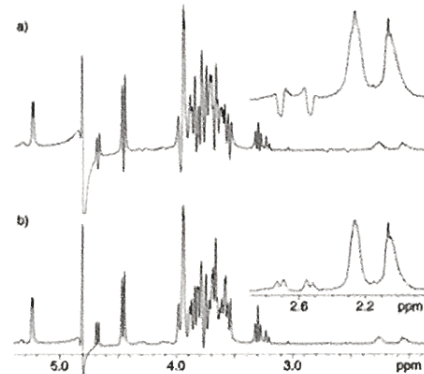
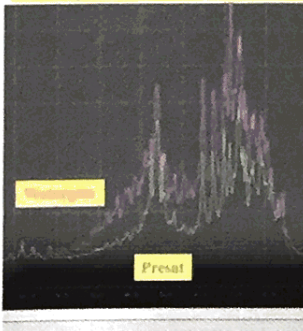
irradiate solvent resonance  
equalise population of spin states

# Solvent suppression: watergate, excitation sculpting

- Avoid disturbing water / return it to +z equilibrium before starting
- Doesn't wipe out labile protons
- No transferred saturation
- Better quality water suppression (particularly if shimming is poor)
- Delay between pulse and acquisition
  - Signal lost (relaxation)
  - Signal lost (diffusion)
  - Homonuclear J-coupling evolution (lineshape distortion)



1D <sup>1</sup>H spectra of TEP-I, pH 6, 290 K.



Processing