


Intro to NMR for CHEM 645

we also visited the website:
[The Basics of NMR](#) by Joseph P. Hornak, Ph.D.

<http://www.cis.rit.edu/htbooks/nmr/>

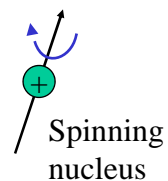
Brian Bahnson
Department of Chemistry & Biochemistry
University of Delaware

A Spinning Nucleus Gives a Magnetic Moment


 unpaired
electron spin

$$\nu = \gamma B$$

photo frequency \uparrow \downarrow gyromagnetic ratio
 applied magnetic field \uparrow

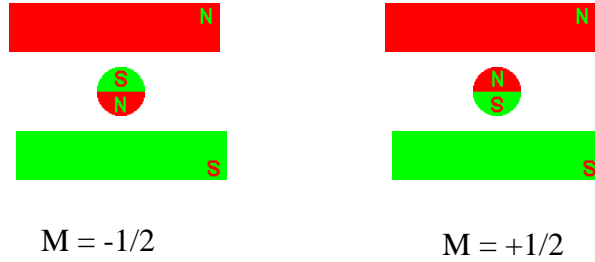


Natural abundance

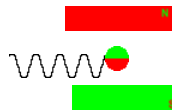
	Nuclei	Unpaired Protons	Unpaired Neutrons	Net Spin	γ (MHz/T)
99.98 →	¹ H	1	0	1/2	42.6
	² H	1	1	1	6.5
	³¹ P	1	0	1/2	17.3
0.36 →	²³ Na	1	2	3/2	11.3
	¹⁵ N	0	1	1/2	4.3
1.11 →	¹³ C	0	1	1/2	10.7
	¹⁹ F	1	0	1/2	40.1

Tesla
↓

For $I = 1/2$ nuclei have two spin states

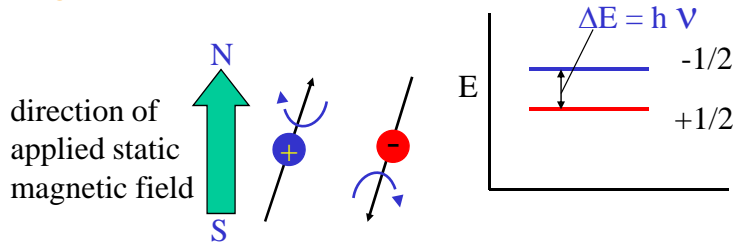


$E = h \nu$
 ↑
 Planck's constant



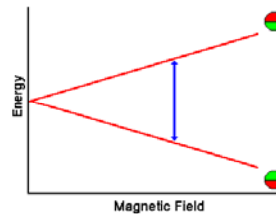
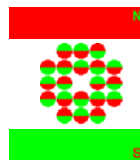
The energy gap between states is small and corresponds to radio frequency waves

The energy gap gives rise to a slight excess of the +1/2 state

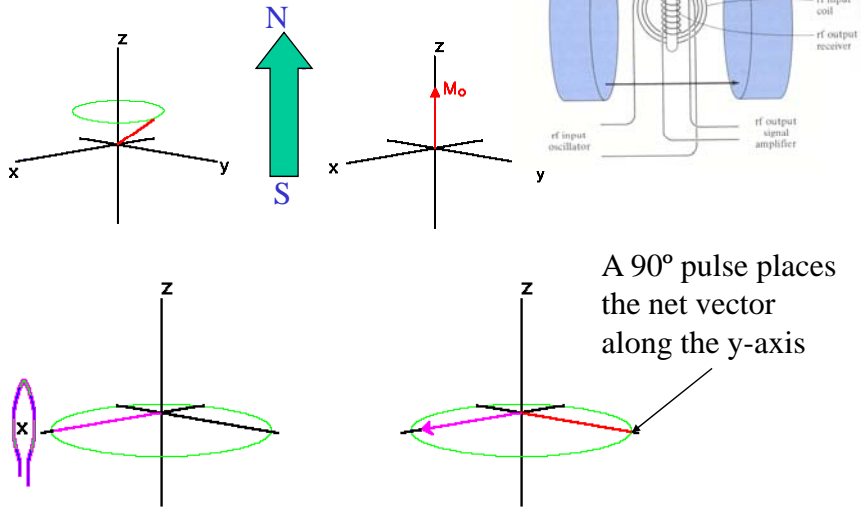


Boltzmann Distribution

$$N_{\text{upper}}^- / N_{\text{lower}}^+ = e^{-E/kT}$$



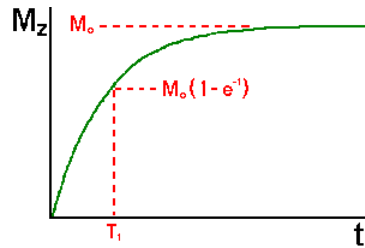
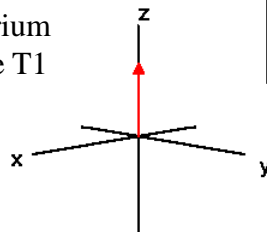
The Net Magnetization Vector



The spin-lattice relaxation time – T1

For a clearer description click: [The Basics of NMR](#) and follow the links – spin physics – T1 processes

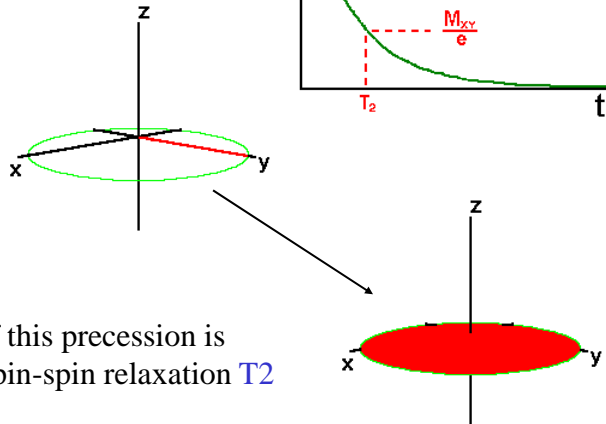
The return to equilibrium along the z-axis is the T1



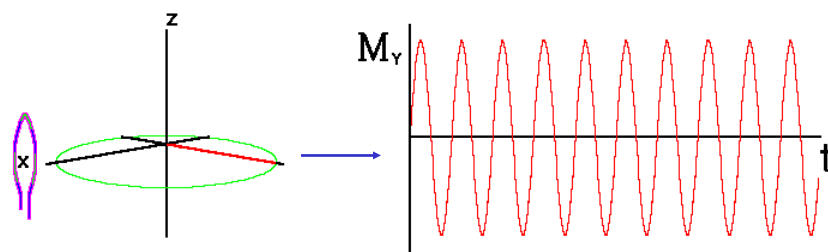
The spin-spin relaxation time – T2

For a clearer description click: [The Basics of NMR](#)
and follow the links – spin physics – T2 processes

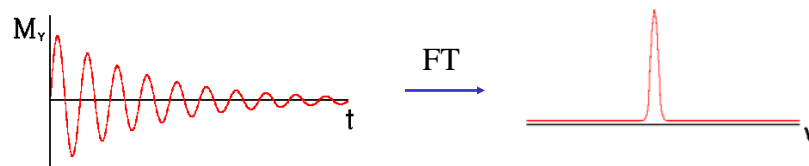
Following a 90° pulse



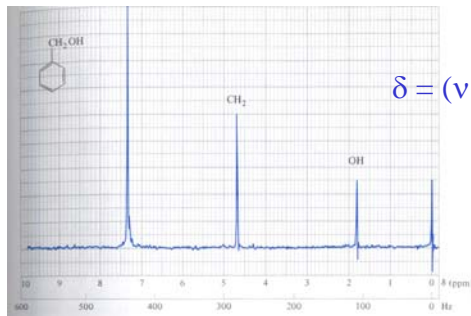
What is actually measured in NMR experiment?



But due to the T1 relaxation:

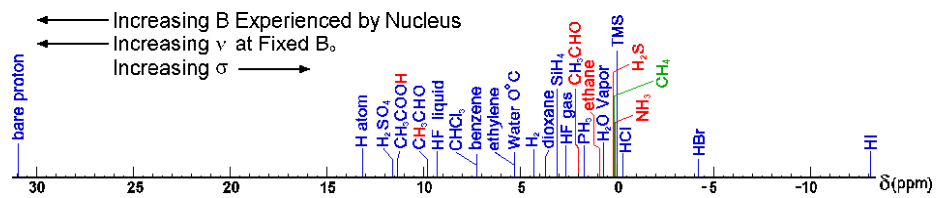


Definition of Chemical Shift



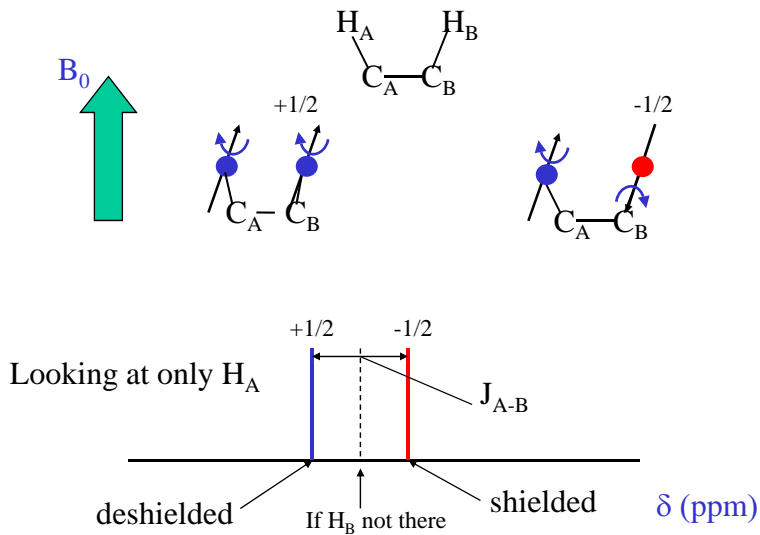
$$\delta = (\nu - \nu_{\text{REF}}) \times 10^6 / \nu_{\text{REF}}$$

units of ppm

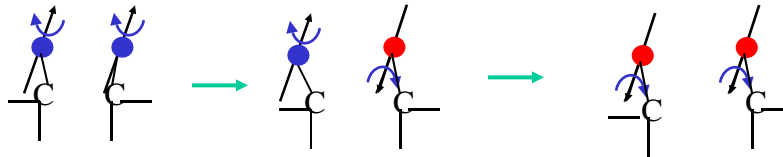


Spin-Spin Coupling is Through Bonds

a.k.a. scalar-coupling or J-coupling



NOE Effects are Through Space

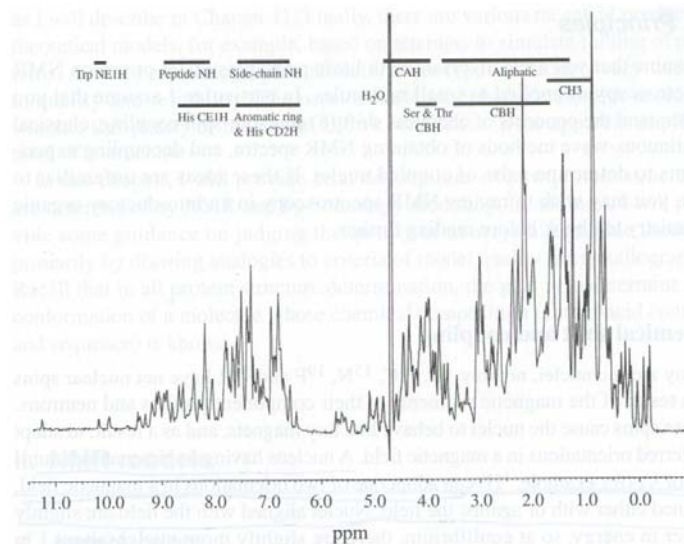


$$\text{NOE} \propto 1/r^6 \cdot f(\tau_c)$$

NOEs are highly distant dependent, seen from 2-5Å

Correlation time is a combination of rotational motions, molecule size + shape dependent, and intra-molecular motions

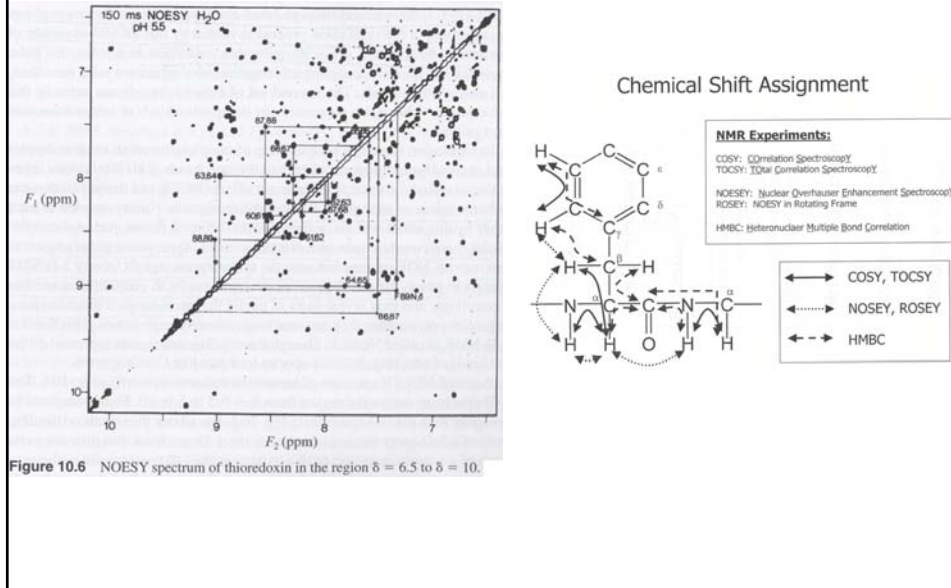
A Protein's $^1\text{H-NMR}$ Spectra is Complex



To assign peaks of proteins, this needs to be spread into a 2nd or 3rd dimension.

Figure 10.1 $^1\text{H-NMR}$ spectrum of thioredoxin, reduced form.

2-D and 3-D Separates Out Spectra



Two Papers to Read for next Thursday's Class

[Wuthrich](#), (1989) "Protein Structure Determination in Solution by Nuclear Magnetic Resonance Spectroscopy" *Science* 243, 45-50.

[Ikura et al.](#), (1989) "A Novel Approach for Sequential Assignment of ¹H, ¹³C, and ¹⁵N Spectra of Larger Proteins: Heteronuclear Triple-Resonance Three-Dimensional NMR Spectroscopy. Application to Calmodulin" *Biochemistry* 29, 4659-4667.