

Instrumental Lab

Nuclear Magnetic Resonance

Dr Alex J. Roche

Nuclear Magnetic Resonance (NMR) Spectroscopy

NMR is the most powerful analytical tool currently available to an organic chemist.

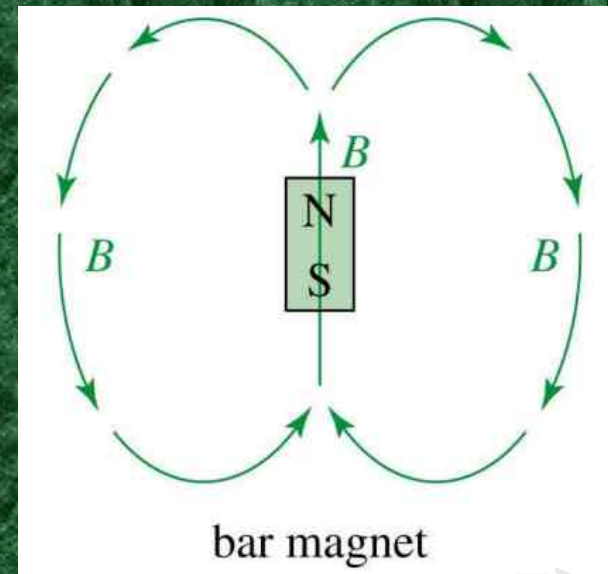
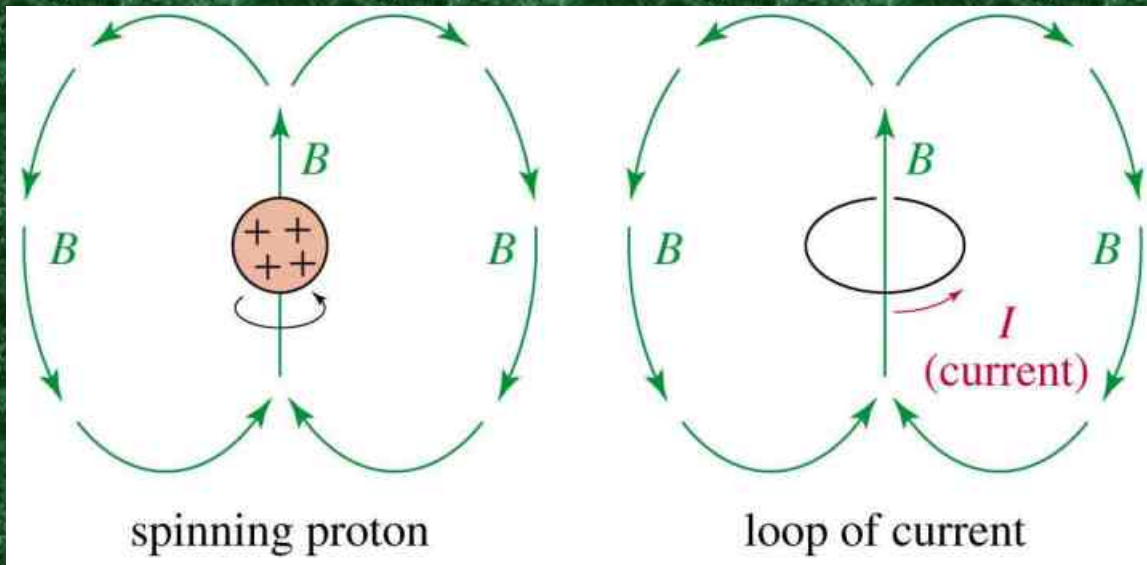
NMR allows characterization of a very small amount of sample (10mg), and does not destroy the sample (non-destructive technique).

Typically NMR is used in conjunction with other types of spectroscopy and chemical analysis to fully confirm a complicated molecule's structure.

NMR Theory

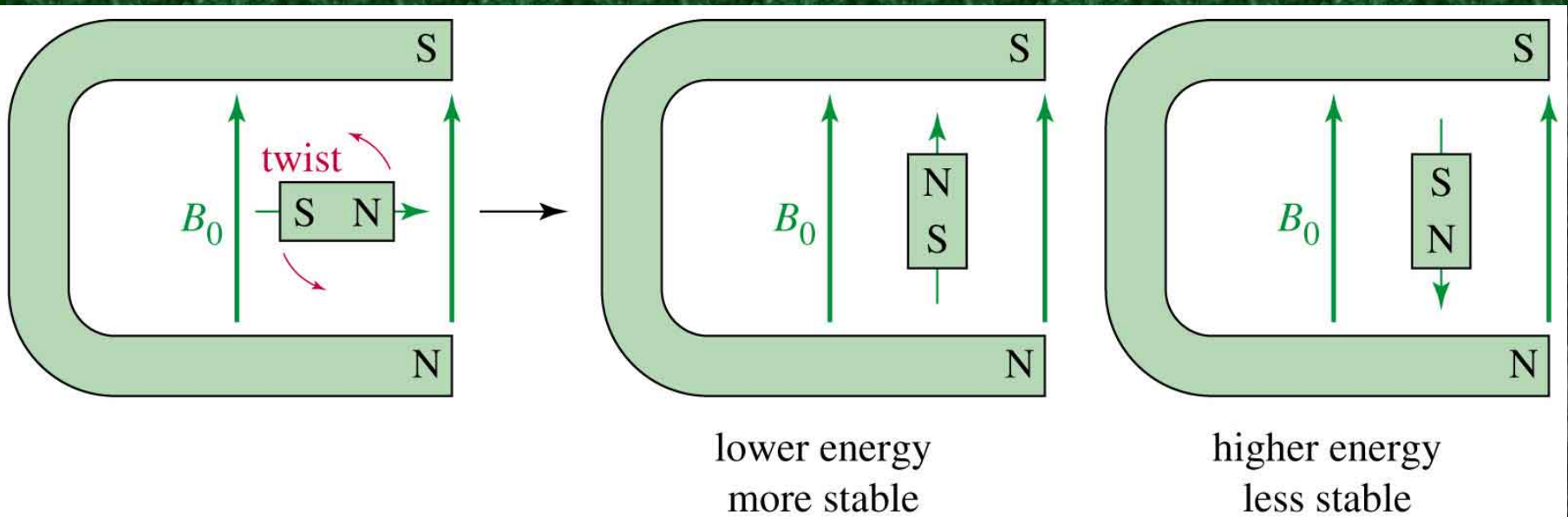
A nucleus with an odd atomic number or an odd mass Number has a nuclear spin. (e.g. ^1H , ^{13}C , ^{19}F , ...etc)

The spinning charged nucleus generates a magnetic field.



NMR Theory cont

When placed in an external field, spinning protons act like bar magnets.



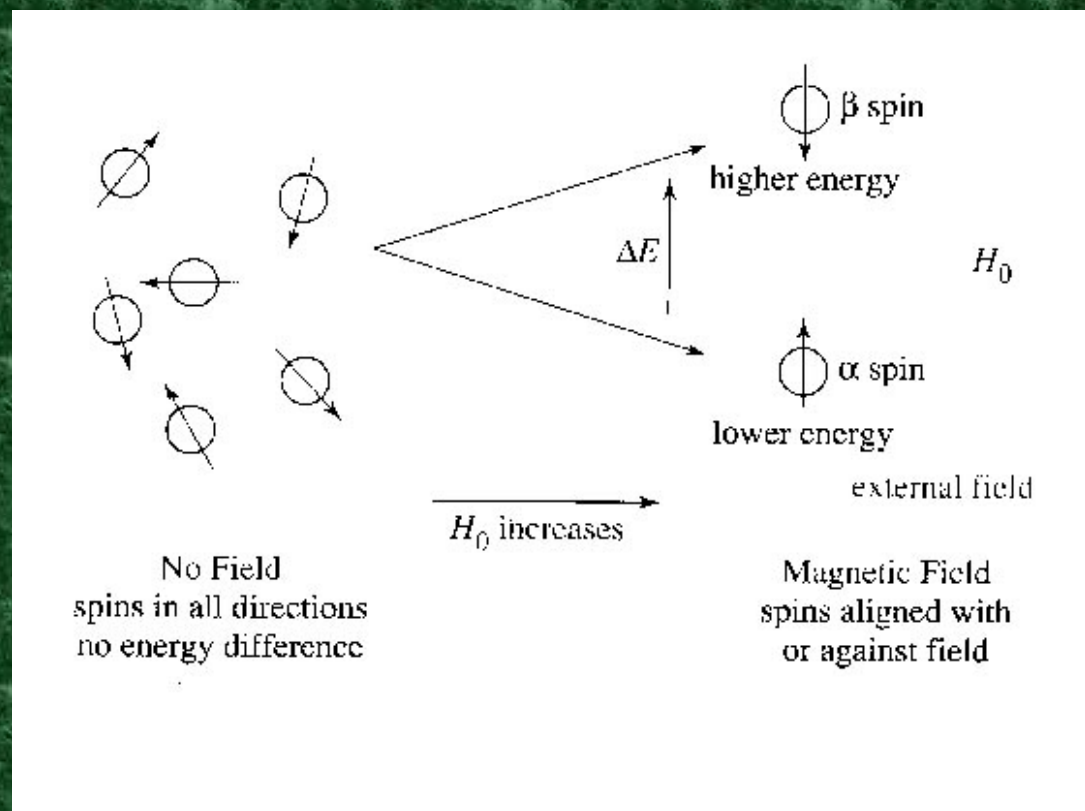
NMR Theory cont

When NMR active nuclei are subjected to a powerful magnetic field (H_0), they have a tendency to align their spins with the external field.

Either :
parallel / α state
(lower energy)

or

antiparallel / β state
(higher energy).



NMR Physics

The difference in energy between the α and β states depends on the applied field. (Typically 10^{-5} kcal/mol).

$$\Delta E = h\nu = \gamma H_0 \frac{h}{2\pi} \quad h = \text{Planck's constant}$$

ν = frequency of radiowaves

H_0 = External magnetic field

γ = gyromagnetic constant

Radiowaves ($\nu \sim 10^{10}$ Hz) can thus flip / excite spin states of atomic nuclei.

It is this interplay of magnetic field, RF waves and nuclear spin states that is the key to observing NMR.

(Excite all nuclei with RF, observe their decay)

A Simple NMR Machine

An NMR machine consists of:

- (1) A powerful, supercooled magnet (stable, with sensitive control, producing a precise magnetic field).
- (2) A radio-frequency transmitter (emitting a very precise frequency).
- (3) A detector to measure the emission of radiofrequency by the sample.
- (4) A recorder (to plot the output).

NMR System



Use of the NMR Machine

Put sample in magnet

Tell computer what experiment you desire (e.g. $^1\text{H} / \text{CDCl}_3$)

Lock and Shim (Establish magnetic field homogeneity)

Acquire (Zap it with an all-exciting pulse of RF; Delay;

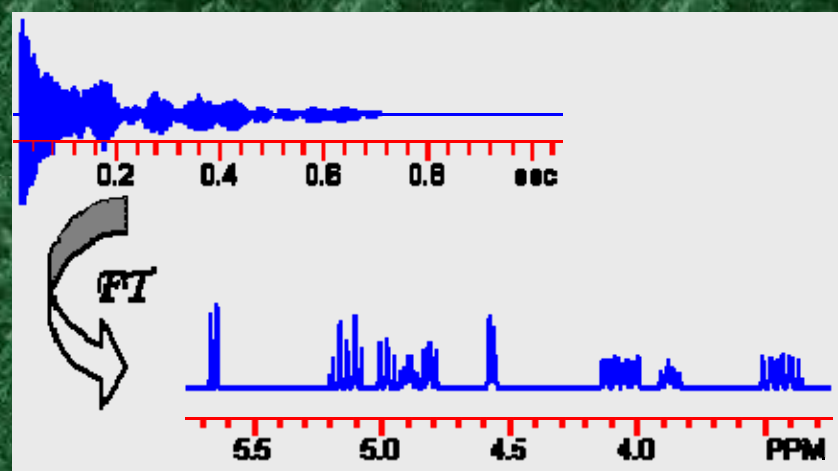
Observe relaxation decay = FID.)

Repeat “excitation - delay – decay” 2^n times.

Fourier Transform combined FID's into an NMR spectrum.

(From time domain
into frequency domain)

Manipulate and print Spectrum.

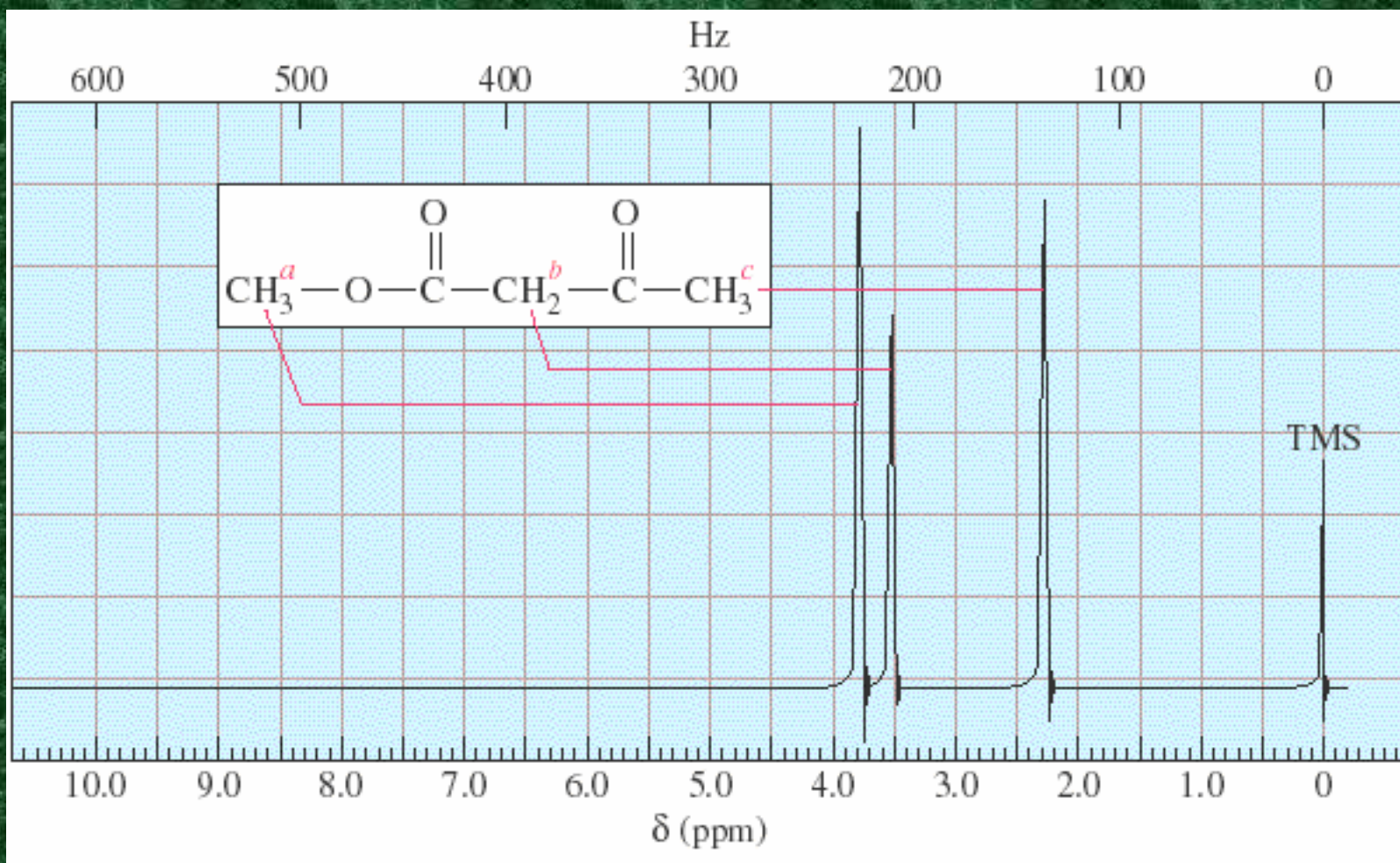


^1H NMR Tells Us...

- (1) The number of different absorptions implies how many different types of hydrogens are present.
- (2) The amount of shielding (chemical shift) is determined by each hydrogen's environment, and so we get information about the local electronic surroundings for each hydrogen.
- (3) The intensities of the signals tell us the number of identical hydrogens.
- (4) The splittings of each signal tells us about the other groups proximate to the hydrogens in question.

Number of Signals

Equivalent hydrogens have the same chemical shift.

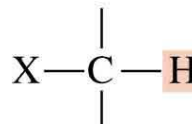
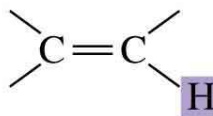
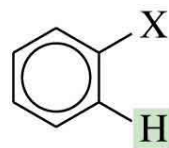
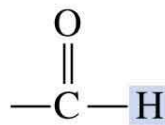


Typical Values

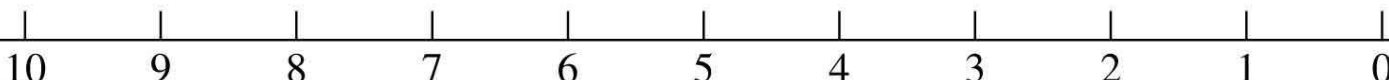
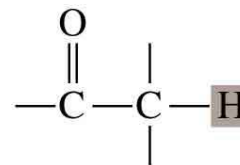
Type of Proton	Approximate δ	Type of Proton	Approximate δ
alkane ($-\text{CH}_3$)	0.9	>C=C< CH_3	1.7
alkane ($-\text{CH}_2-$)	1.3	Ph—H	7.2
alkane ($-\text{CH}-$)	1.4	Ph— CH_3	2.3
$\text{—}\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_3$	2.1	R—CHO	9–10
$-\text{C}\equiv\text{C}-\text{H}$	2.5	R—COOH	10–12
R— CH_2 —X (X = halogen, O)	3–4	R—OH	variable, about 2–5
>C=C< H	5–6	Ar—OH	variable, about 4–7
		R— NH_2	variable, about 1.5–4

—COOH

δ 11- δ 12

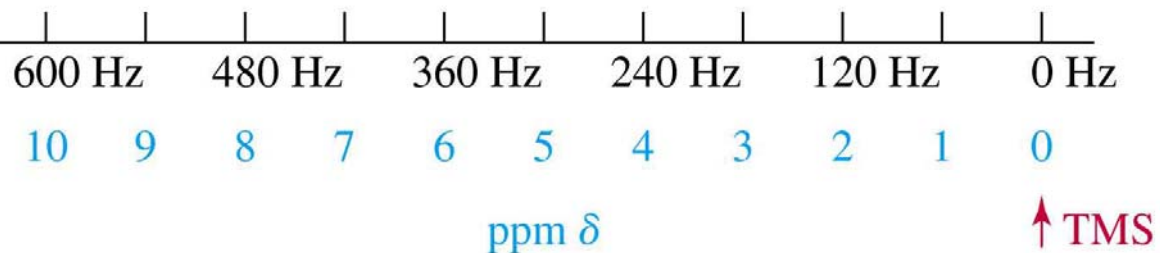


X = O, hal

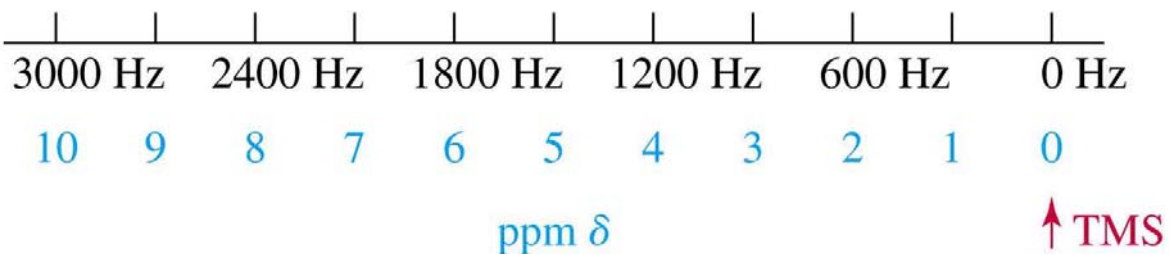


Delta Scale

$$\text{chemical shift, ppm } \delta = \frac{\text{shift downfield from TMS (in Hz)}}{\text{spectrometer frequency (in MHz)}}$$



60 MHz

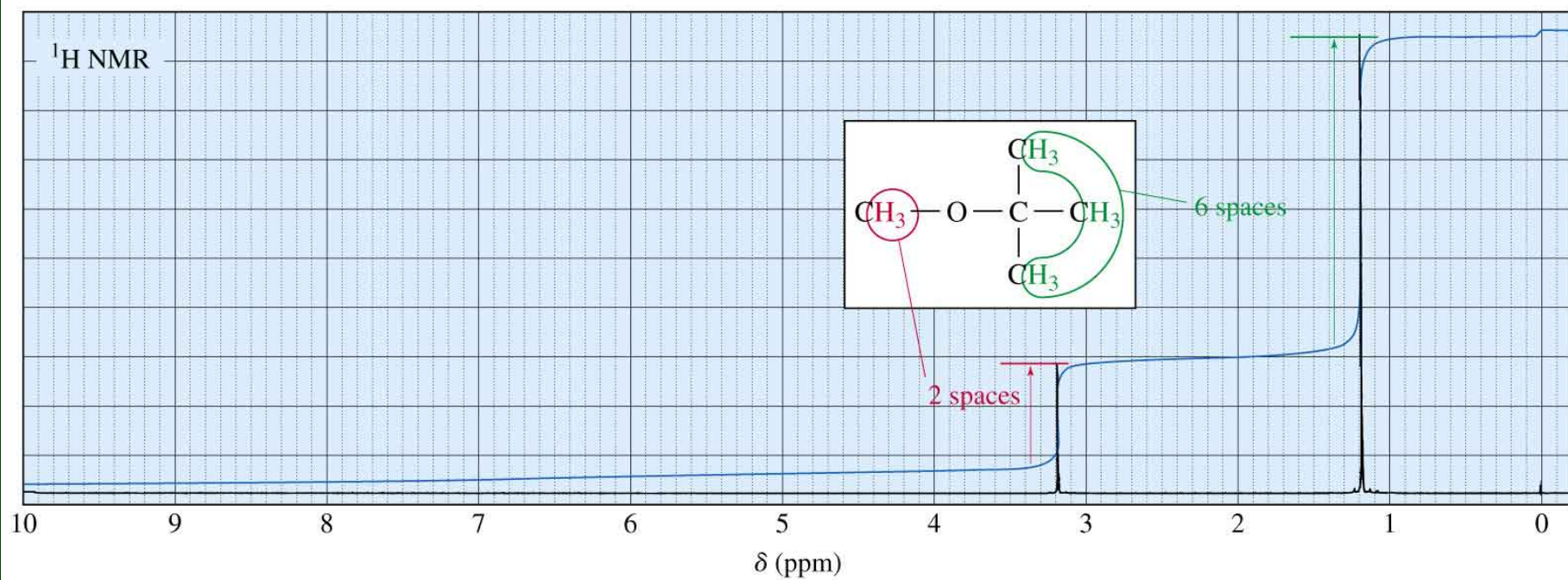


300 MHz

Intensity of Signals

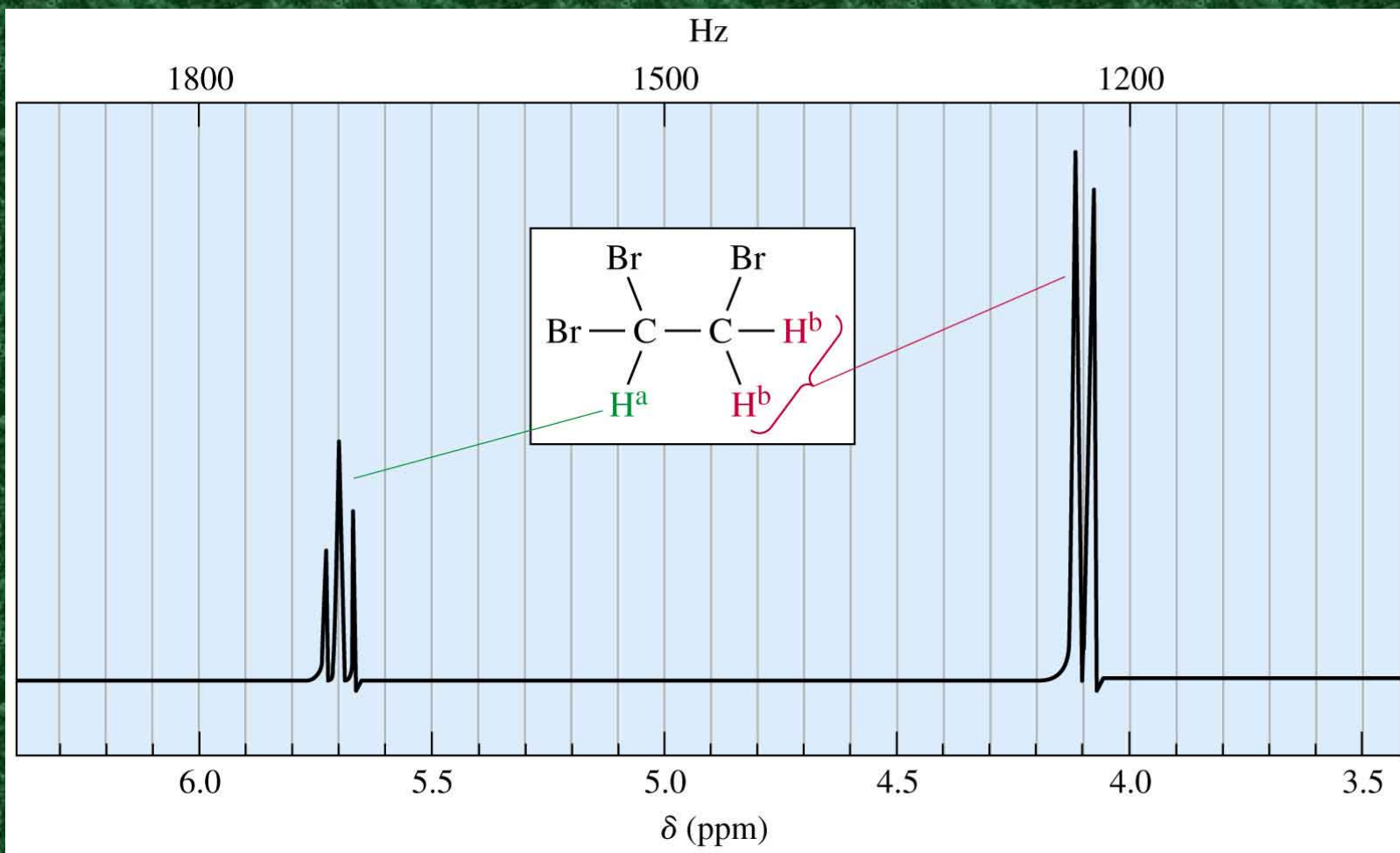
The area under each peak is proportional to the number of protons. (The Integral Trace)

It is just a RATIO.

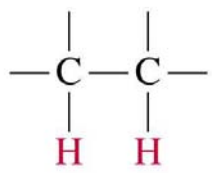
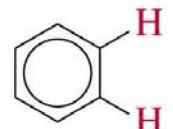
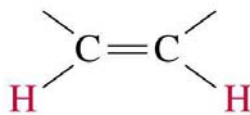
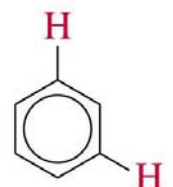
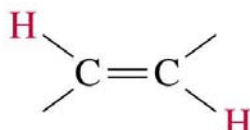
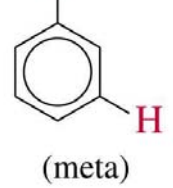
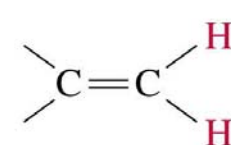
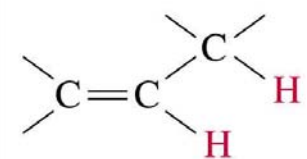


The $N + 1$ Rule

If a signal is split by N equivalent protons, it is split into $N + 1$ peaks.



Values for Coupling Constants

		<u>Approx. J</u>		<u>Approx. J</u>
	(free rotation)	7 Hz ^a		8 Hz
	(cis)	10 Hz		(ortho)
	(trans)	15 Hz		2 Hz
	(geminal)	2 Hz		6 Hz
			(allylic)	

^aThe value of 7 Hz in an alkyl group is averaged for rapid rotation about the carbon-carbon bond. If rotation is hindered by a ring or bulky groups, other splitting constants may be observed.

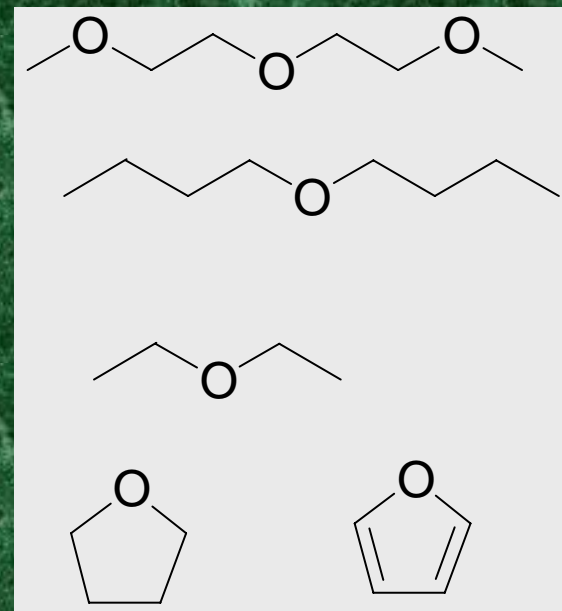
^1H NMR Information

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^{13}C NMR

Can also observe other NMR active nuclei
Common others are ^{19}F , ^{13}C and ^{32}P .

^{13}C is extremely useful for organic molecules!

However:

^{13}C only 1% of naturally occurring carbon atoms.

^{13}C has 60 times less NMR sensitivity than ^1H .

⇒ Effectively 6000 times harder to observe ^{13}C than ^1H !

Modern ^{13}C NMR

To achieve detectable ^{13}C NMR signals:

Concentrated samples (of high purity)

Higher number of scans

Remove H couplings (“broad band decoupling”)

⇒ Signals are singlets

^{13}C NMR not quantitative. (No integrations)

^{13}C NMR tells you

Number of Different Carbons

Chemical Type of Carbons

¹³C NMR Shifts

Appendix C The ¹³C Correlation Chart for Chemical Classes

R = H or alkyl substituents

Y = polar substituents

Acyclic hydrocarbons

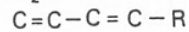
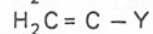
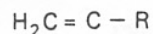


Alicyclic hydrocarbons



C_4H_8 to $\text{C}_{10}\text{H}_{20}$

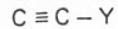
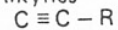
Alkenes



Allenes



Alkynes



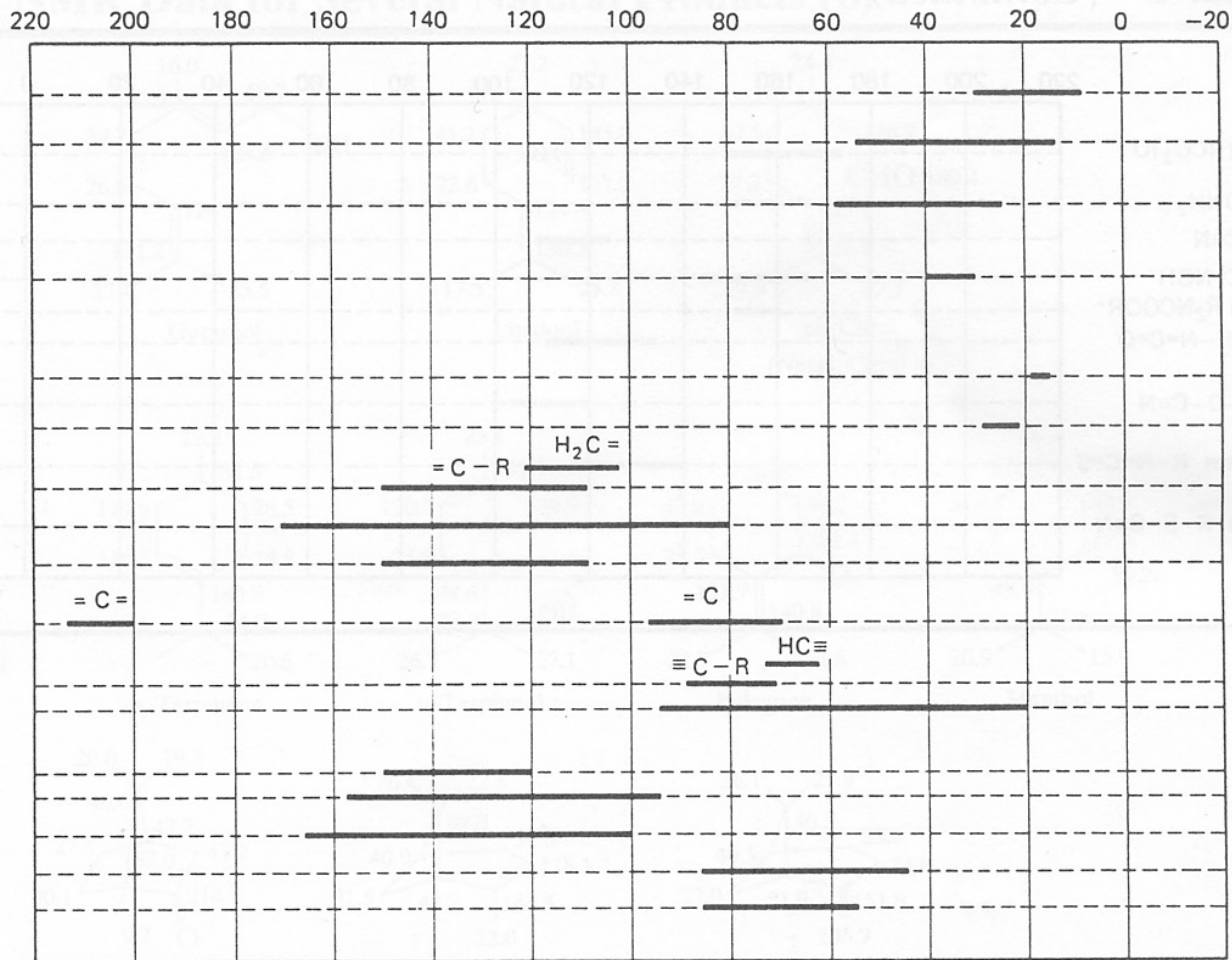
Aromatics



Heteroaromatics

Alcohols $\text{C}-\text{OH}$

Ethers $\text{C}-\text{O}-\text{C}$



Typical ^{13}C NMR

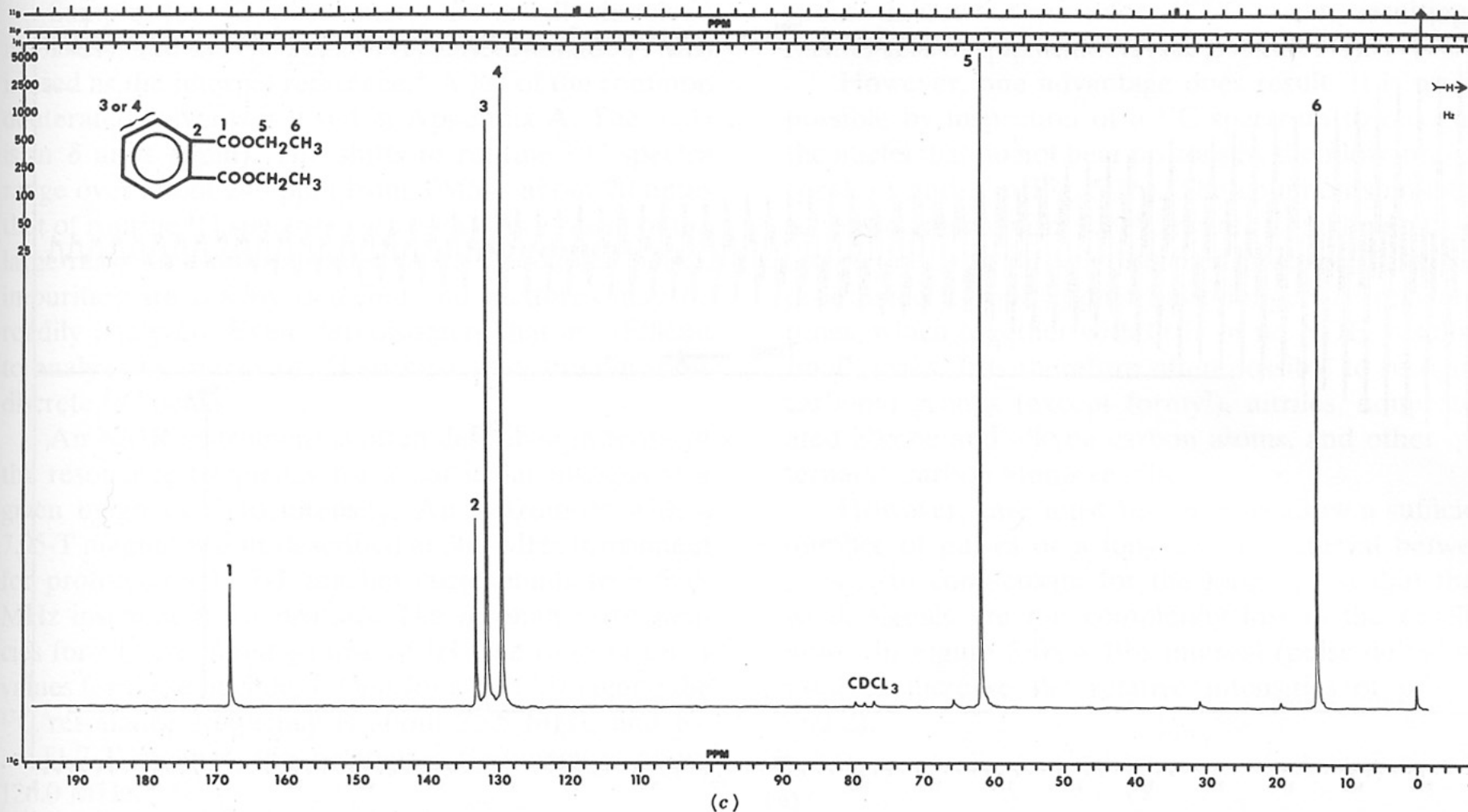
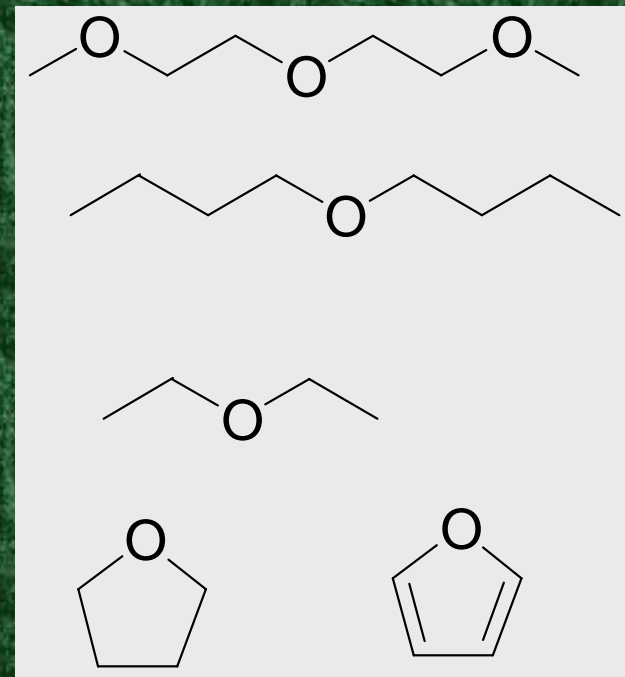


FIGURE 5.1(c). The ^{13}C -NMR spectrum of diethyl phthalate with the protons completely decoupled and a 10-s delay between pulses. The solvent used was CDCl_3 at 25.2 MHz.

^{13}C NMR Peaks and Shifts

^{13}C will differentiate these ethers.

^{13}C and ^1H are almost always used in conjunction with one another.



Your Work / Problems

- Match the five Ethers with their ^1H NMRs
- Identify the two Ethers and their ratio in the mixture samples
- Identify an Ether from its ^{13}C NMR

