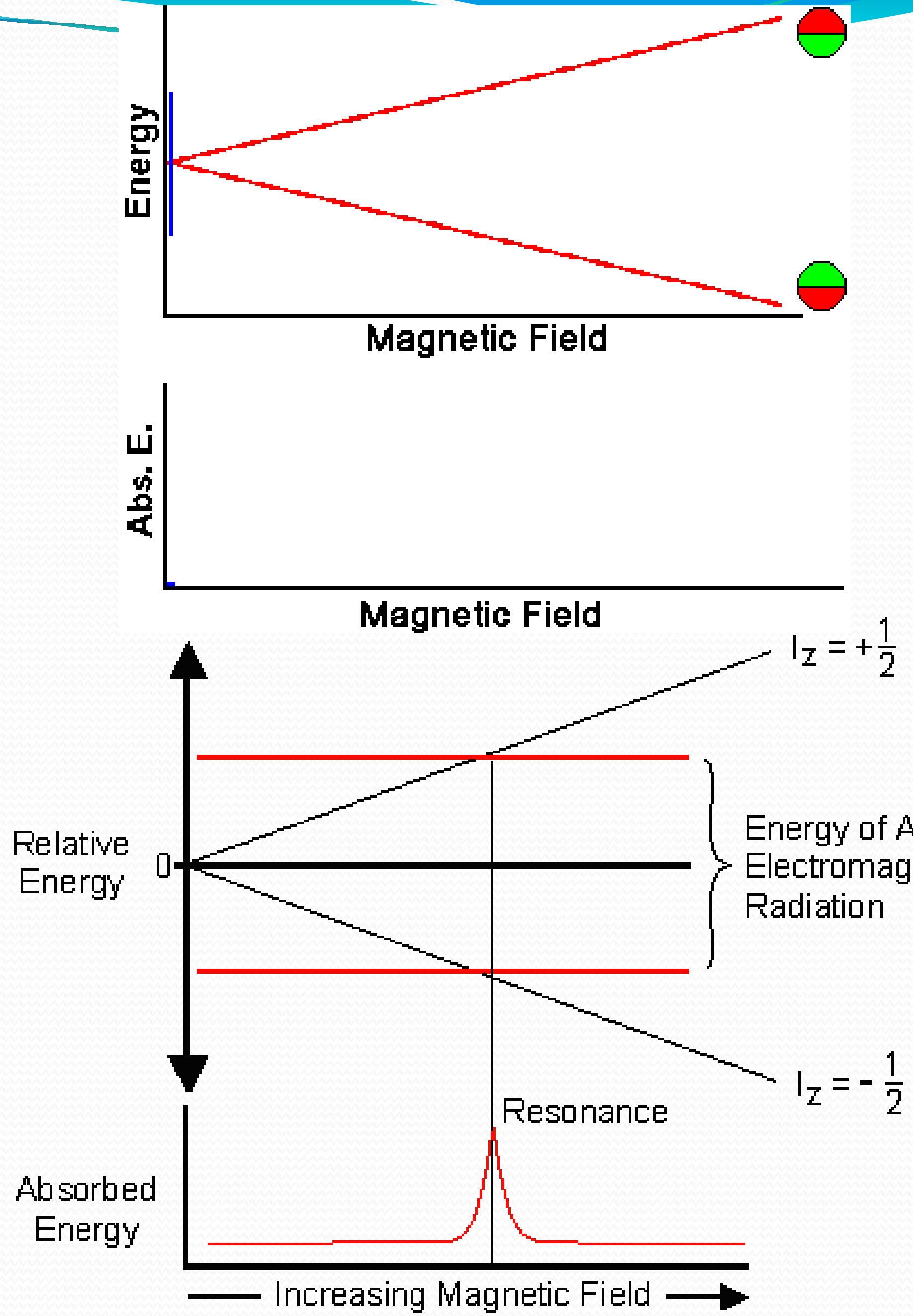
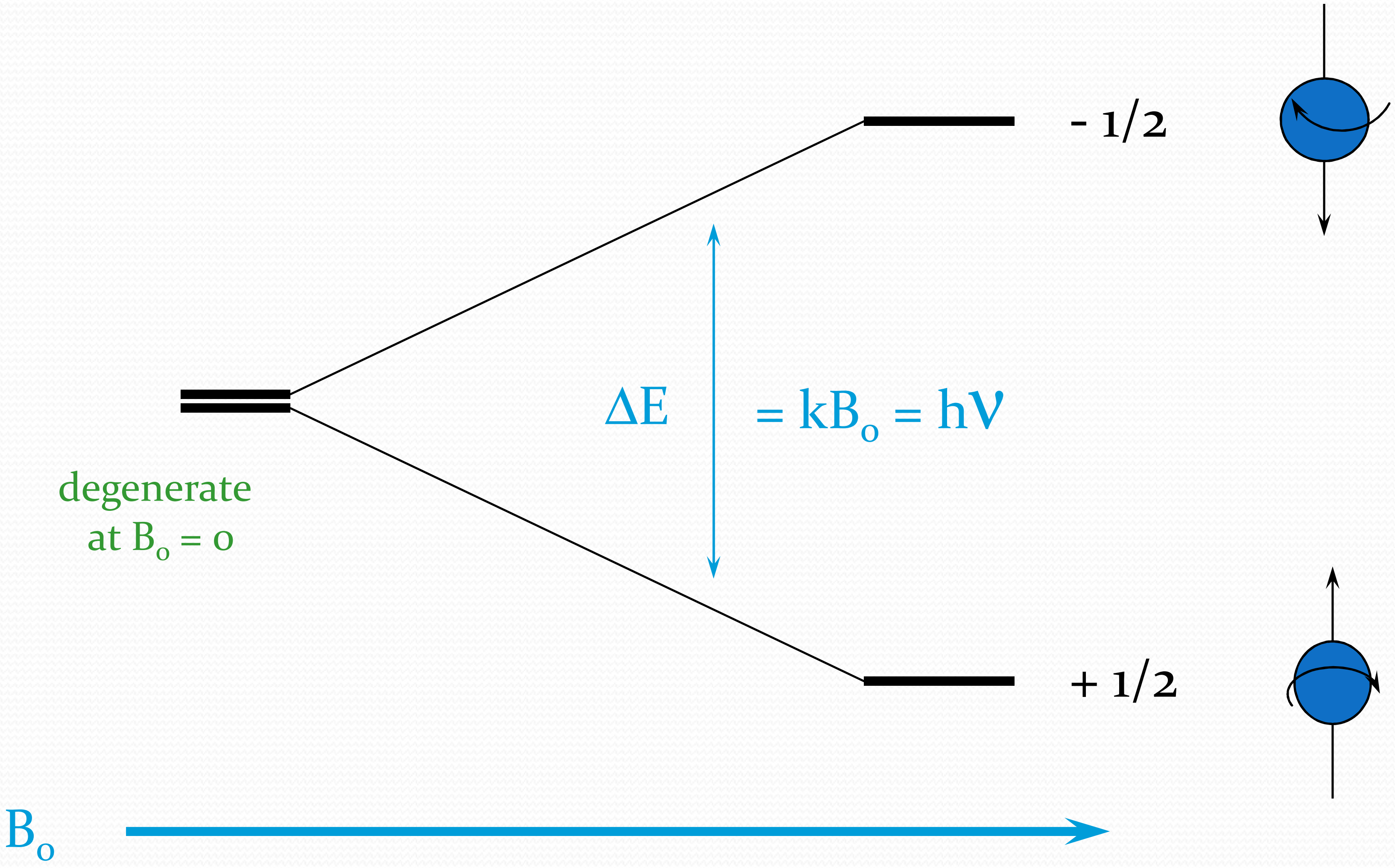
NMR EXPERIMENT

When magnetically active nuclei are placed into an external magnetic field, the magnetic fields align themselves with the external field into two orientations. During the experiment, electromagnetic radiation of a specific frequency is applied. By sweeping the magnetic field, an energy difference between spin states will occur that has the same energy as that f the applied radio frequency and plot of frequency versus energy absorption can be generated. This is the NMR spectrum



The Energy Separation Depends on B_o



- 1/2

ΔE $= kB_o = h\nu$

degenerate
at $B_o = 0$

+ 1/2

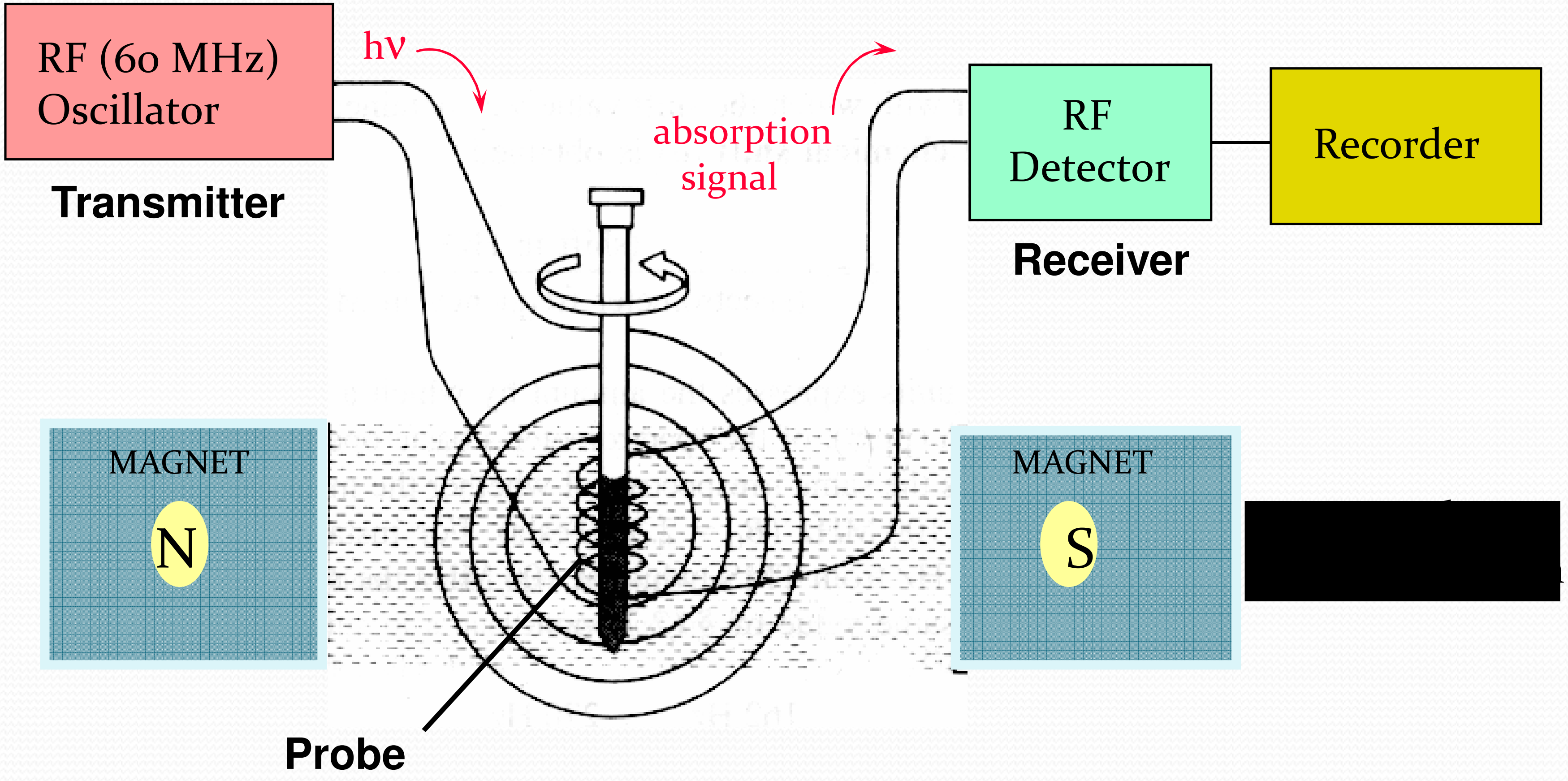
B_o

increasing magnetic field strength

Classical Instrumentation: The Continuous-Wave NMR

typical before 1965;
field is scanned

A Simplified 60 MHz NMR Spectrometer



RF (60 MHz) Oscillator

Transmitter

hν

absorption signal

RF Detector

Recorder

Receiver

MAGNET

N

MAGNET

S

[redacted]

Probe

Modern Instrumentation: the Fourier-Transform NMR

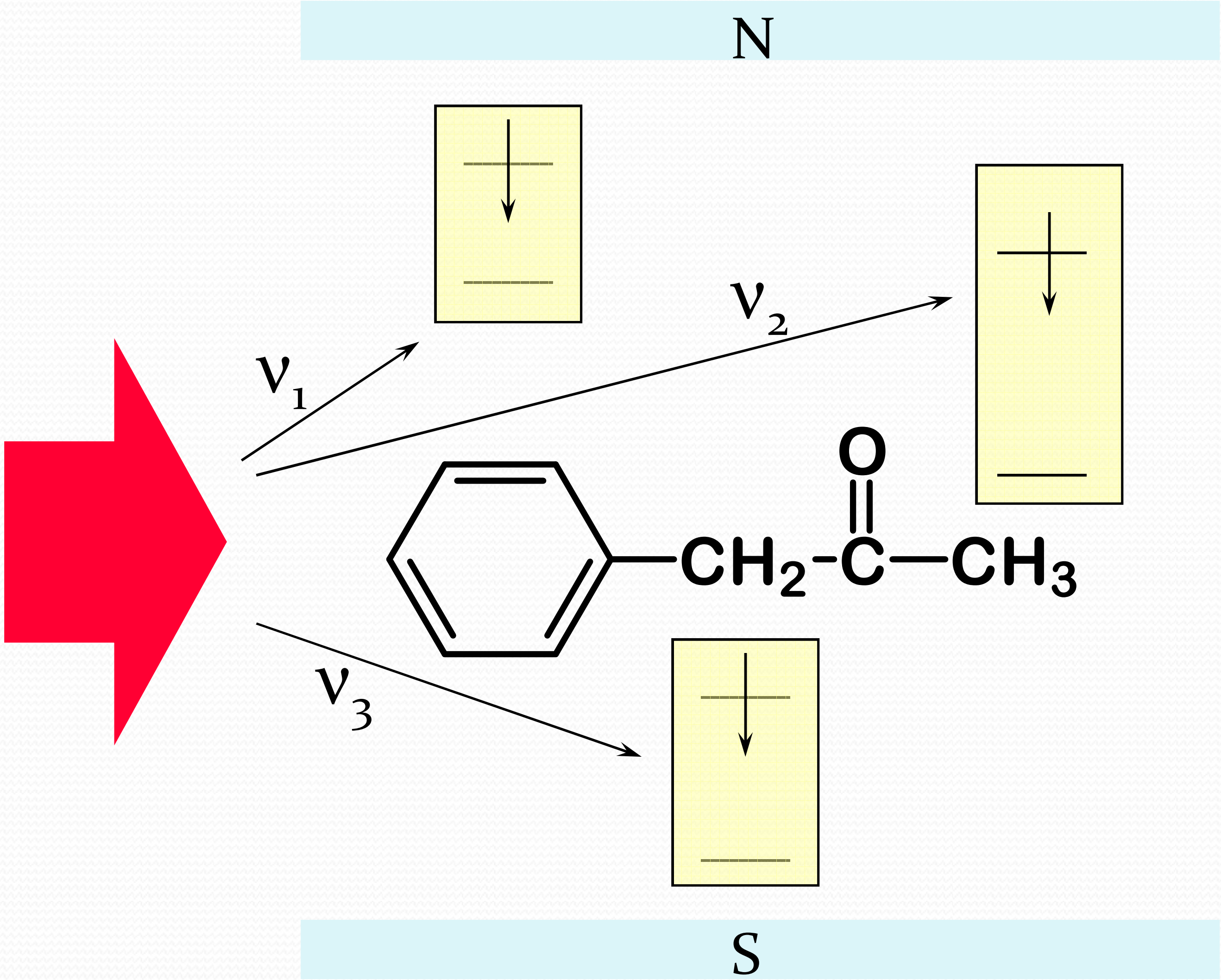
FT-NMR

requires a computer

PULSED EXCITATION

BROADBAND
RF PULSE

contains a range
of frequencies
$(\nu_1 \ldots\ldots \nu_n)$



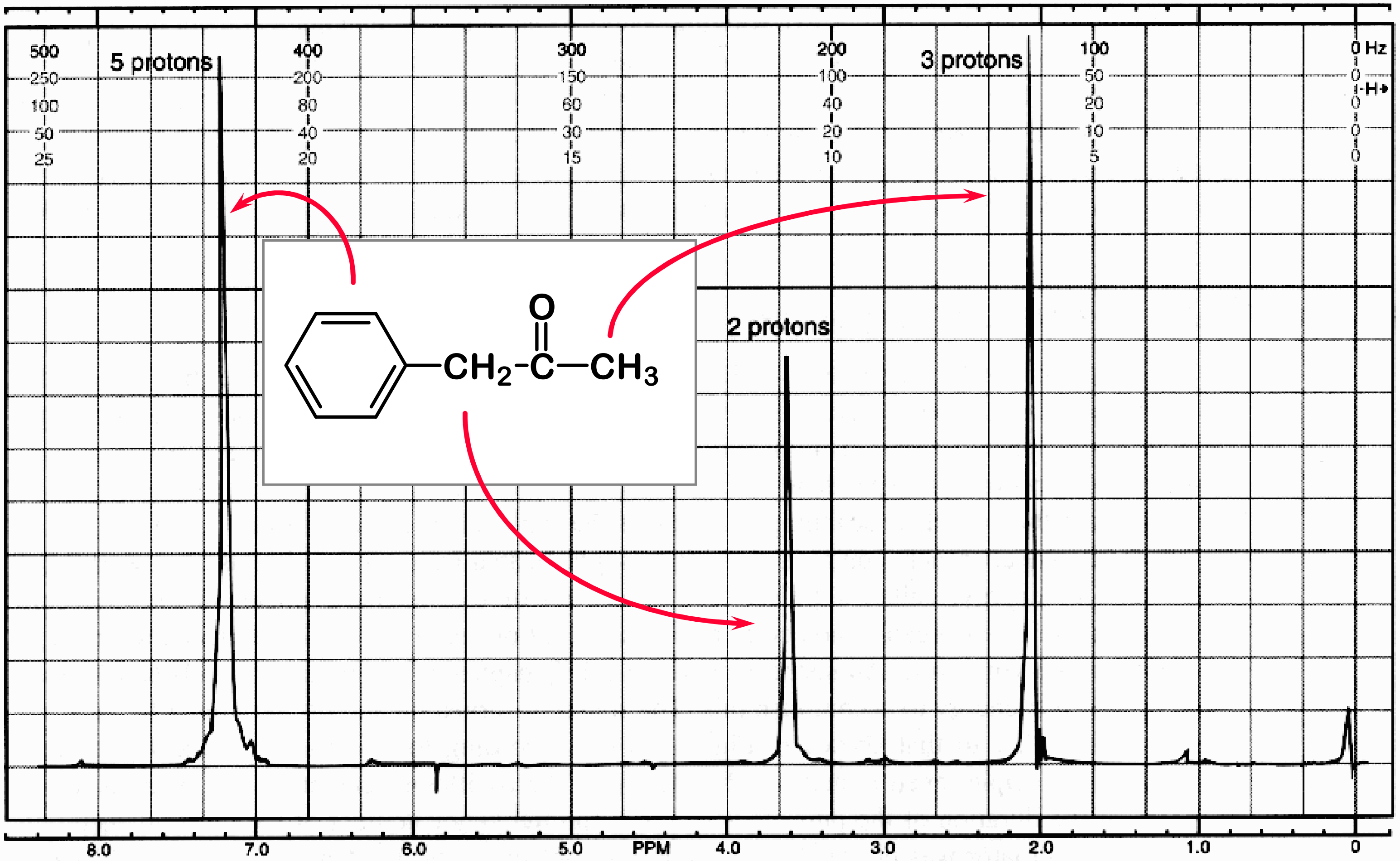
All types of hydrogen are excited
simultaneously with the single RF pulse.

Espectro de RMN de Hidrogênio (Proton NMR Spectrum)

The NMR Spectrum

- The vertical axis shows the intensity of Rf absorption.
- The horizontal axis shows relative energy at which the absorption occurs (in units of parts per million = ppm)
- Tetramethylsilane (TMS) in included as a standard zero point reference (0.00 ppm)
- The area under any peak corresponds to the number of hydrogens represented by that peak.

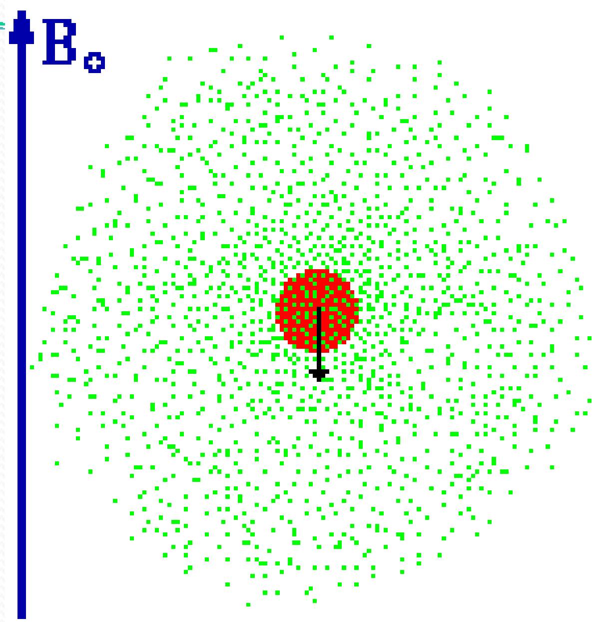
NMR Spectrum of Phenylacetone



EACH DIFFERENT TYPE OF PROTON COMES AT A DIFFERENT PLACE - YOU CAN TELL HOW MANY DIFFERENT TYPES OF PROTONS THERE ARE BY INTEGRATION.

DIAMAGNETIC SHIELDING

Why should the proton nuclei in different compounds behave differently in the nmr experiment? The answer to this question lies with the electron(s) surrounding the proton in covalent compounds and ions. Since electrons are charged particles, they move in response to the external magnetic field (B_o) so as to generate a secondary field that opposes the much stronger applied field. This secondary field shields the nucleus from the applied field, so B_o must be increased in order to achieve resonance (absorption of rf energy). Thus B_o must be increased to compensate for the induced shielding field.



When an atom is placed in a magnetic field, its electrons circulate about the direction of the applied magnetic field. This circulation causes a small magnetic field at the nucleus which opposes the externally applied field. The magnetic field at the nucleus (the effective field) is therefore generally less than the applied field by a fraction σ .

$$B = B_o (1-\sigma)$$

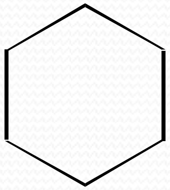
1. Número de sinais: Quantos tipos diferentes de hidrogênios na molécula.

Hidrogênios magneticamente equivalentes ressoam no mesmo campo aplicado.

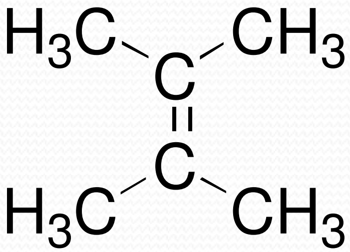
Hidrogênios são magneticamente equivalente também quimicamente equivalente.

de sinais? CH_4 CH_3CH_3

Número de sinais?



um



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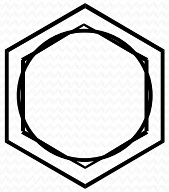

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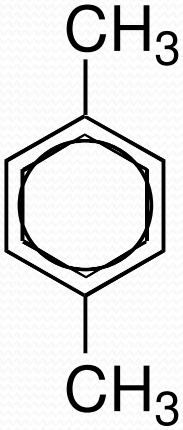
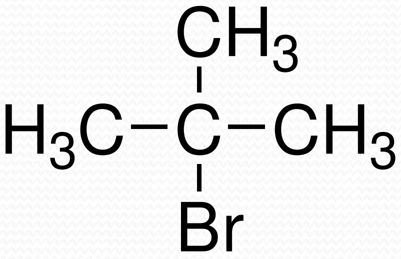


dois



$$\begin{array}{ccccc} & & \mathrm{CH_3} & & \\ & & | & & \\ \mathrm{H_3C} & - & \mathrm{C} & - & \mathrm{CH_3} \\ & & | & & \\ & & \mathrm{Br} & & \end{array}$$

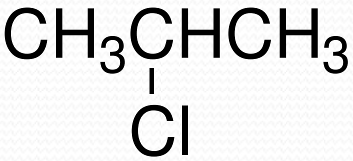
um

$CH_3CH_2\text{-}Br$

dois

$CH_3CH_2CH_2\text{-}Br$

três



$$\begin{array}{c} \mathrm{CH_3CHCH_3} \\ | \\ \mathrm{Cl} \end{array}$$

dois

$$\underset{\displaystyle Br}{CH_3CHCH_2CH_3}$$

quatro

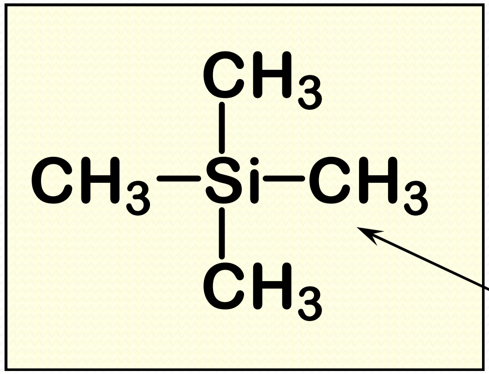
$Cl\text{-}CH_2CH_2CH_2\text{-}Cl$

dois

O Deslocamento Químico
(The Chemical Shift)

PEAKS ARE MEASURED RELATIVE TO TMS

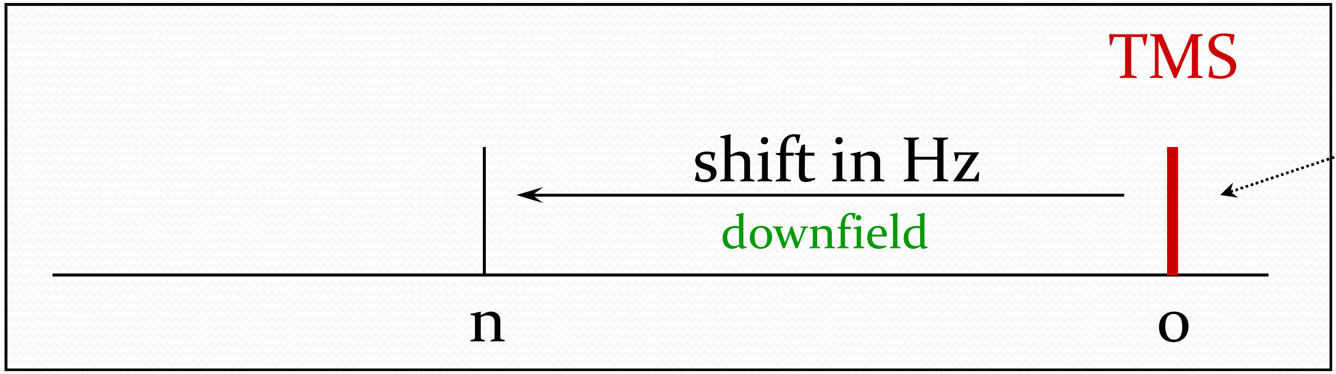
Rather than measure the exact resonance position of a peak, we measure how far downfield it is shifted from TMS.



$$CH_3-\underset{CH_3}{\overset{CH_3}{Si}}-CH_3$$

reference compound
tetramethylsilane
"TMS"

Highly shielded protons appear way upfield.

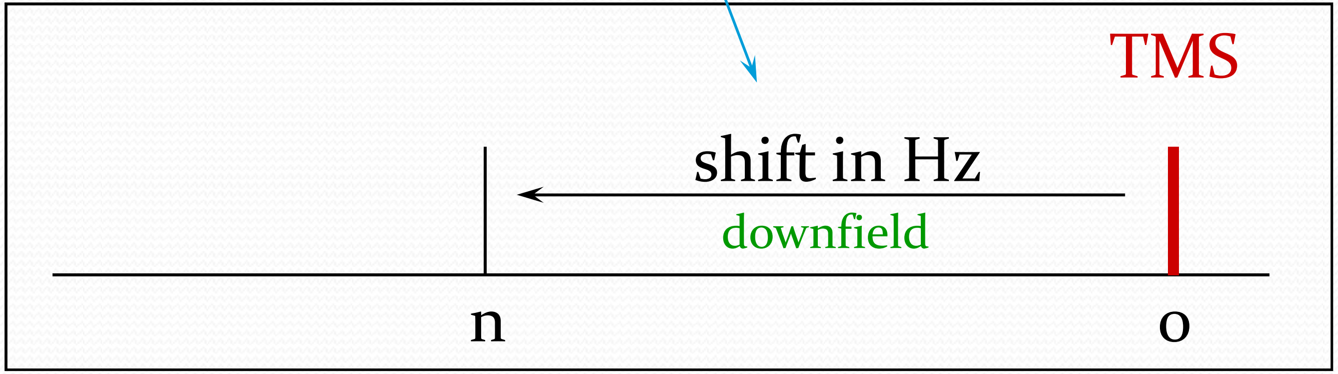


Chemists originally thought no other compound would come at a higher field than TMS.

HIGHER FREQUENCIES GIVE LARGER SHIFTS

The shift observed for a given proton in Hz also depends on the frequency of the instrument used.

Higher frequencies
= larger shifts in Hz.



TMS

shift in Hz

downfield

n

o

THE CHEMICAL SHIFT

The shifts from TMS in Hz are bigger in higher field instruments (300 MHz, 500 MHz) than they are in the lower field instruments (100 MHz, 60 MHz).

We can adjust the shift to a field-independent value, the "chemical shift" in the following way:

parts per million

$$\text{chemical shift} = \delta = \frac{\text{shift in Hz}}{\text{spectrometer frequency in MHz}} = \text{ppm}$$

This division gives a number independent of the instrument used.

A particular proton in a given molecule will always come <u>at the same chemical shift</u> (constant value).

Chemical Shift (δ)

- **The chemical shift (δ) in units of ppm is defined as:**

$$\delta = \frac{\text{distance from TMS (in hz)}}{\text{radio frequency (in Mhz)}}$$

- **A standard notation is used to summarize NMR spectral data. For example *p*-xylene:**

δ 2.3 (6H, singlet)
δ 7.0 (4H, singlet)

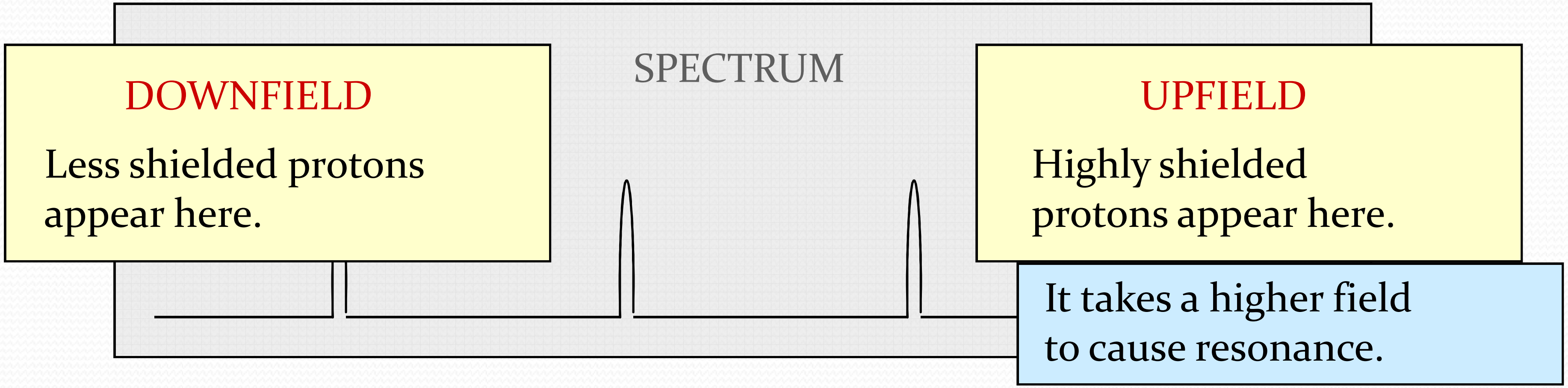
- **Hydrogens in identical chemical environments (equivalent hydrogens) have identical chemical shifts.**

PROTONS DIFFER IN THEIR SHIELDING

All different types of protons in a molecule have a different amounts of shielding.

They all respond differently to the applied magnetic field and appear at different places in the spectrum.

This is why an NMR spectrum contains useful information (different types of protons appear in predictable places).



SPECTRUM

DOWNFIELD

Less shielded protons appear here.

UPFIELD

Highly shielded protons appear here.

It takes a higher field to cause resonance.

Overview of where protons appear in an NMR spectrum

acid COOH	aldehyde CHO	benzene CH	alkene =C-H	C-H where C is attached to an electronega-tive atom X-C-H	CH on C next to pi bonds X=C-C-H	aliphatic C-H

12 10 9 7 6 4 3 2 0

Some Specific Structural Effects on NMR Chemical Shift

Type of Hydrogen	δ (ppm
Alkyl (C – H)	0.8 – 1.7
Alkyl Halide (RCH_2X)	3 - 4
Alkene ($R_2C=CH_2$)	4 - 6
Aromatic (e.g. benzene)	6 - 8
Carboxylic Acid (RCOOH)	10 - 12

Shielding – The Reason for Chemical Shift Differences

- Circulation of electrons within molecular orbitals results in local magnetic fields that oppose the applied magnetic field.

- The greater this “shielding” effect, the greater the applied field needed to achieve resonance, and the further to the right (“upfield”) the NMR signal.

Structure Effects on Shielding

- Electron donating groups increase the electron density around nearby hydrogen atoms resulting in increased shielding, shifting peaks to the right.

- Electron withdrawing groups decrease the electron density around nearby hydrogen atoms resulting in decreased shielding, (deshielding) shifting peaks to the left.

DESHIELDING AND ANISOTROPY

Three major factors account for the resonance positions (on the ppm scale) of most protons.

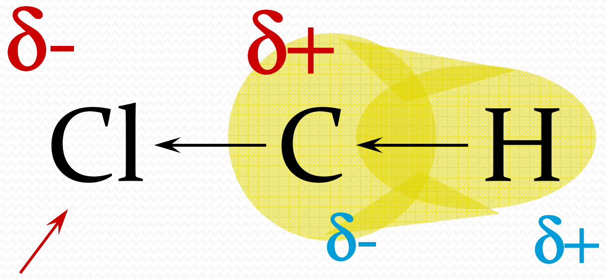
1. Deshielding by electronegative elements.
2. Anisotropic fields usually due to π-bonded electrons in the molecule.
3. Deshielding due to hydrogen bonding.

GENERALIZATIONS

- electrons shield nucleus
- electronegativity: withdraws electrons to deshield nucleus
- downfield (deshielding) = left side of spectrum
- upfield (shielding) = right side of spectrum
- delta values increase from right to left!

DESHIELDING BY ELECTRONEGATIVE ELEMENTS

DESHIELDING BY AN ELECTRONEGATIVE ELEMENT



electronegative
element

Chlorine “deshields” the proton, that is, it takes valence electron density away from carbon, which in turn takes more density from hydrogen deshielding the proton.

NMR CHART

“deshielded“
protons appear
at low field

highly shielded
protons appear
at high field

←

deshielding moves proton
resonance to lower field

Electronegativity Dependence of Chemical Shift

Dependence of the Chemical Shift of CH_3X on the Element X

Compound CH_3X	CH_3F	CH_3OH	CH_3Cl	CH_3Br	CH_3I	CH_4	$(CH_3)_4Si$
Element X	F	O	Cl	Br	I	H	Si
Electronegativity of X	4.0	3.5	3.1	2.8	2.5	2.1	1.8
Chemical shift δ	4.26	3.40	3.05	2.68	2.16	0.23	0

most deshielded

← TMS

deshielding increases with the electronegativity of atom X

Substitution Effects on Chemical Shift

most
deshielded

$CHCl_3$	CH_2Cl_2	CH_3Cl	
7.27	5.30	3.05	ppm

The effect increases with greater numbers of electronegative atoms.

most
deshielded

$-CH_2-Br$	$-CH_2-CH_2Br$	$-CH_2-CH_2CH_2Br$	
3.30	1.69	1.25	ppm

The effect decreases with incresing distance.

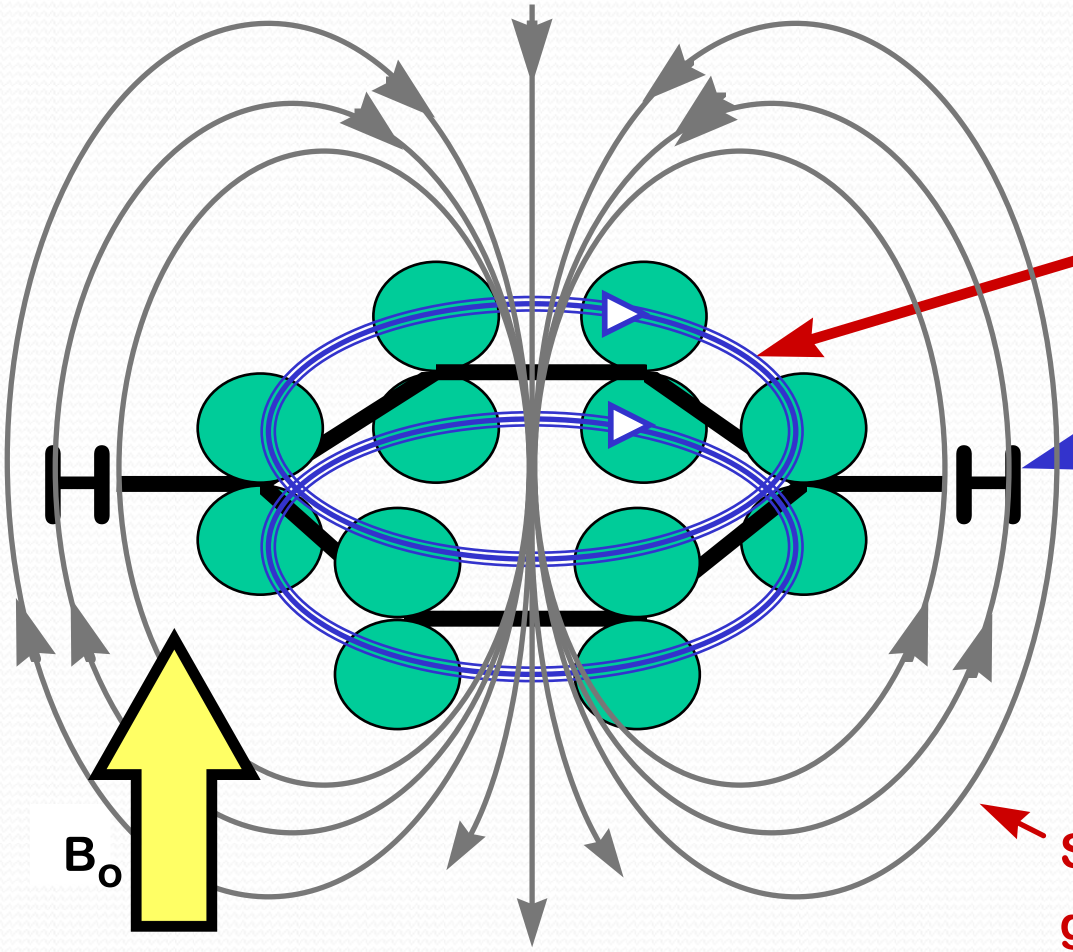
ANISOTROPIC FIELDS

DUE TO THE PRESENCE OF PI BONDS

The presence of a nearby π bond greatly affects the chemical shift.

Benzene rings have the greatest effect.

Ring Current in Benzene



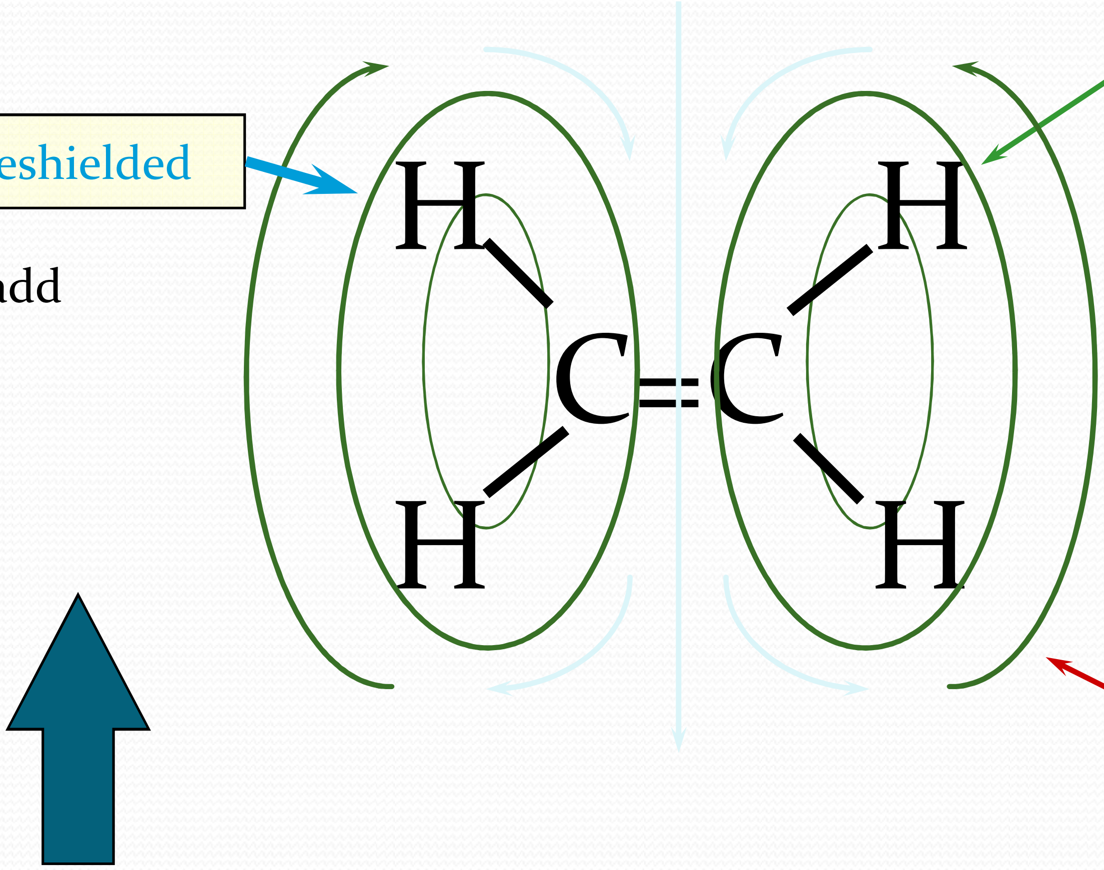
Circulating π electrons

Deshielded

fields add together

Secondary magnetic field generated by circulating π electrons deshields aromatic protons

ANISOTROPIC FIELD IN AN ALKENE



Deshielded

protons are deshielded

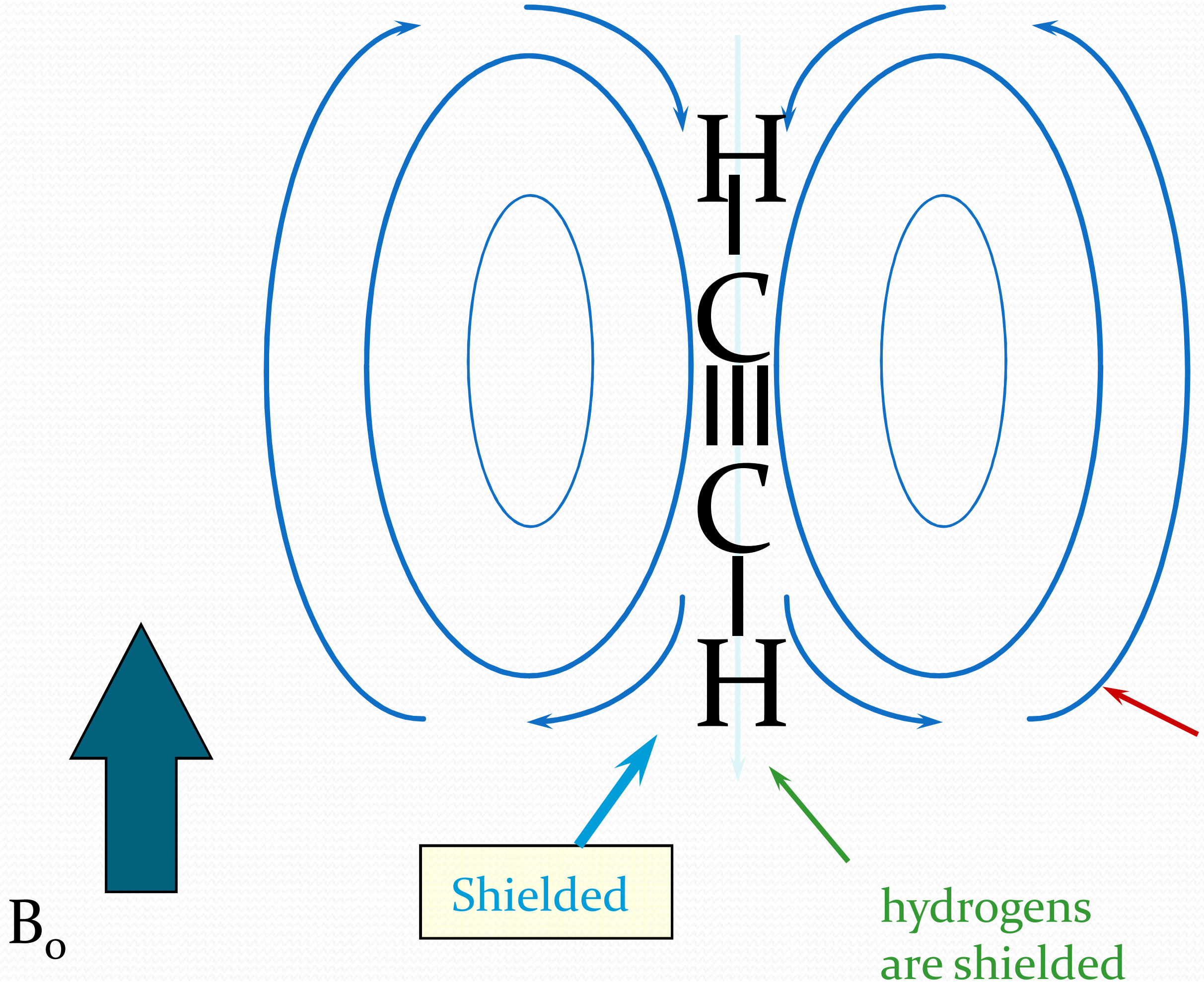
shifted downfield

fields add

secondary magnetic (anisotropic) field lines

B_o

ANISOTROPIC FIELD FOR AN ALKYNE



B_o

Shielded

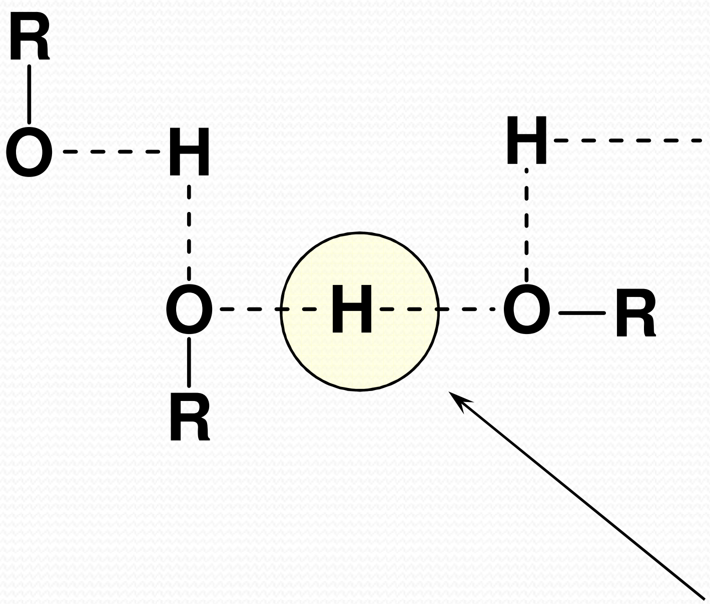
fields subtract

hydrogens
are shielded

secondary
magnetic
(anisotropic)
field

HYDROGEN BONDING

HYDROGEN BONDING DESHIELDS PROTONS

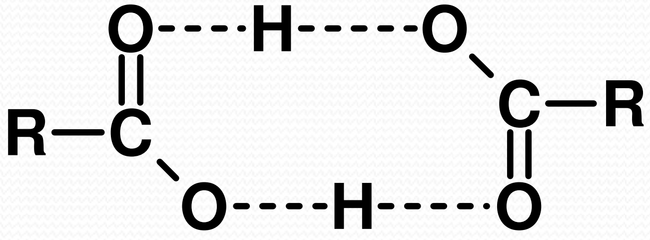


The chemical shift depends
on how much hydrogen bonding
is taking place.

Alcohols vary in chemical shift
from 0.5 ppm (free OH) to about
5.0 ppm (lots of H bonding).

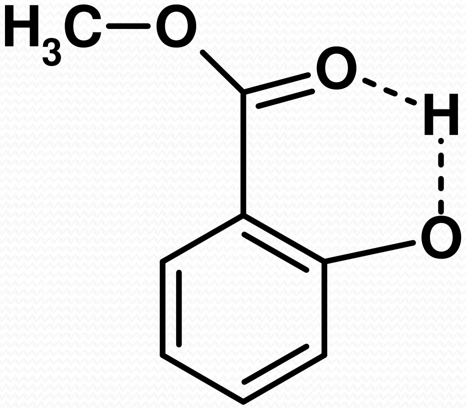
Hydrogen bonding lengthens the
O-H bond and reduces the valence
electron density around the proton
- it is deshielded and shifted
downfield in the NMR spectrum.

SOME MORE EXTREME EXAMPLES



Carboxylic acids have strong hydrogen bonding - they form dimers.

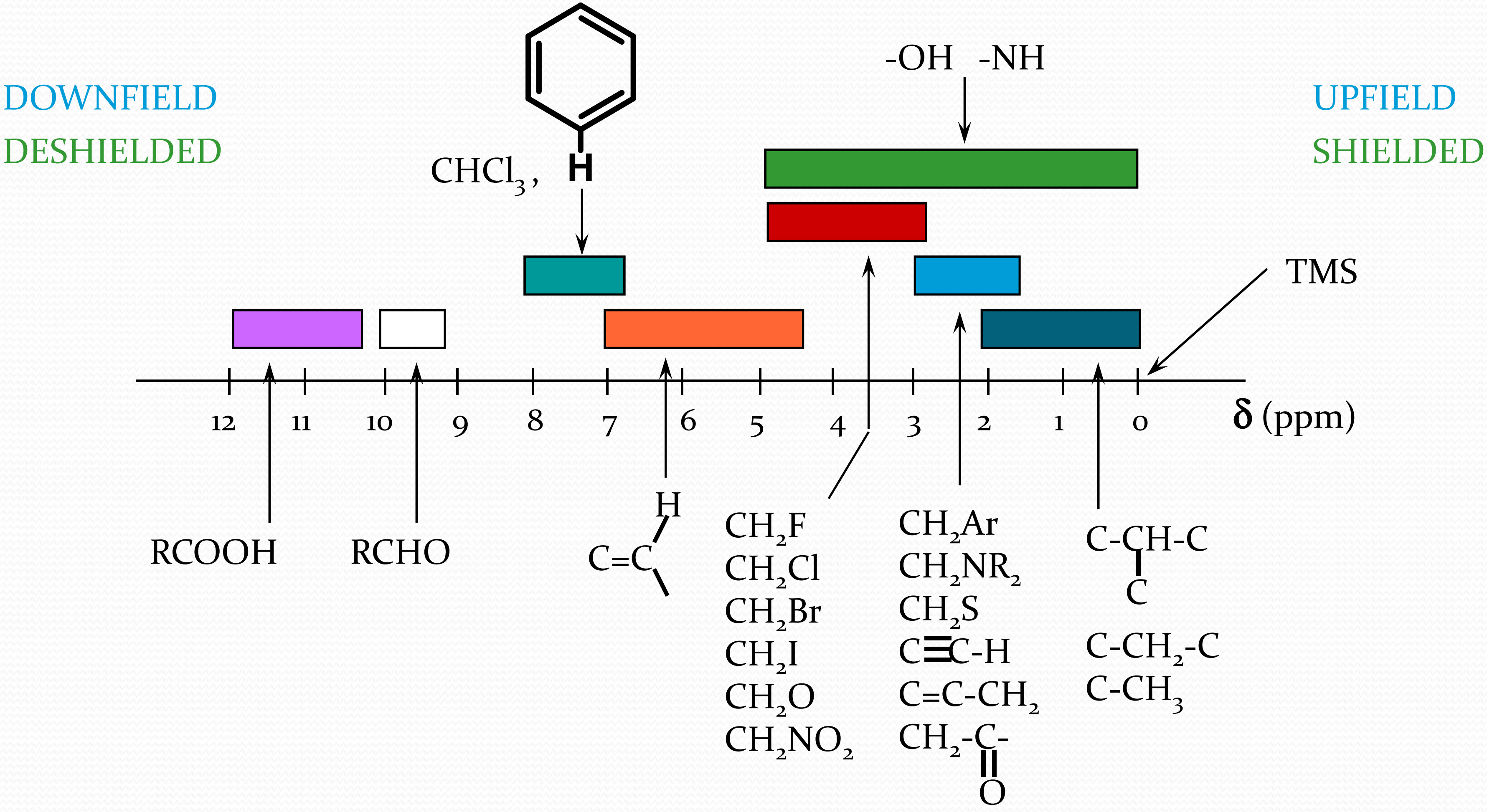
With carboxylic acids the O-H absorptions are found between 10 and 12 ppm very far downfield.



In methyl salicylate, which has strong internal hydrogen bonding, the NMR absorption for O-H is at about 14 ppm, way, way downfield.

Notice that a 6-membered ring is formed.

NMR Correlation Chart



DOWNFIELD
DESHIELDED

UPFIELD
SHIELDED

$CHCl_3$, **H**

-OH -NH

TMS

12 11 10 9 8 7 6 5 4 3 2 1 0 δ (ppm)

RCOOH

RCHO

H
C=C

CH_2F
CH_2Cl
CH_2Br
CH_2I
CH_2O
CH_2NO_2

CH_2Ar
CH_2NR_2
CH_2S
$C\equiv C\text{-}H$
$C{=}C\text{-}CH_2$
$CH_2\text{-}\underset{\displaystyle\overset{\|}{O}}{C}\text{-}$

$C\text{-}\underset{\displaystyle\overset{|}{C}}{CH}\text{-}C$

$C\text{-}CH_2\text{-}C$
$C\text{-}CH_3$