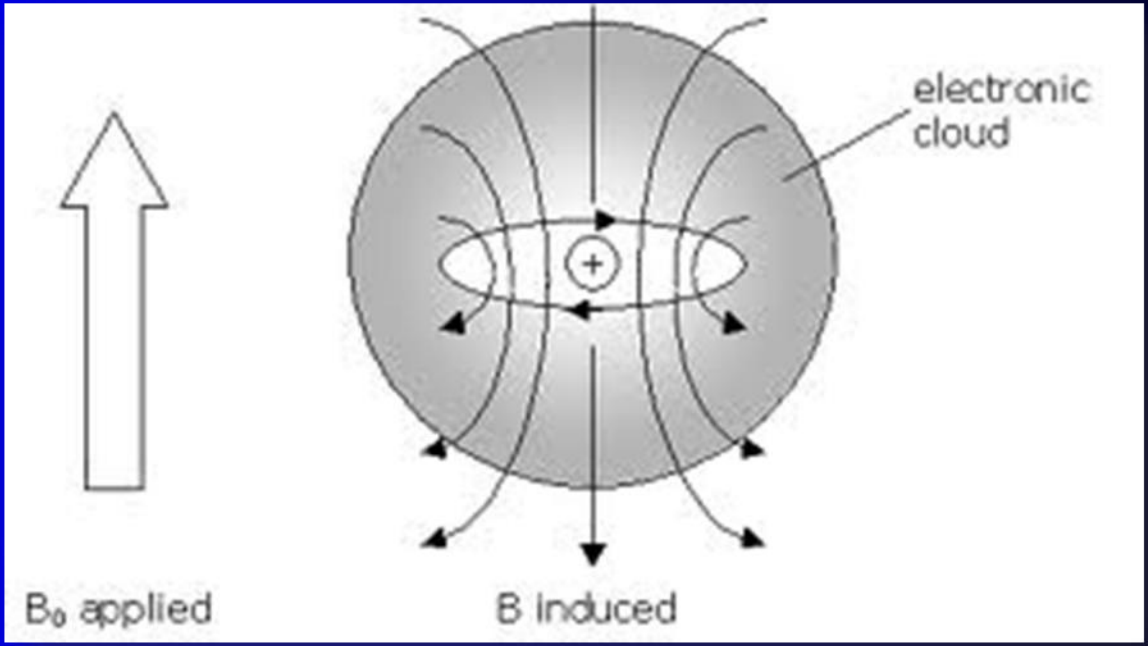
Lecture 4

Some More nmr

Heinrich Lenz

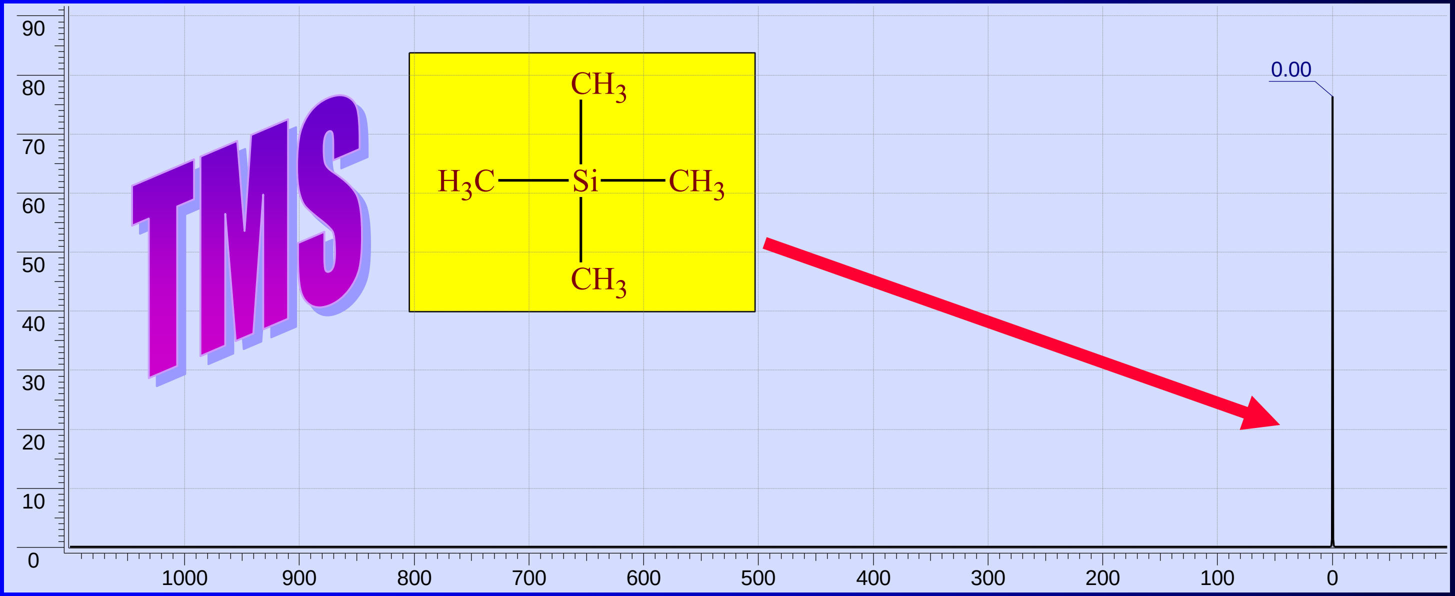
1804-1865

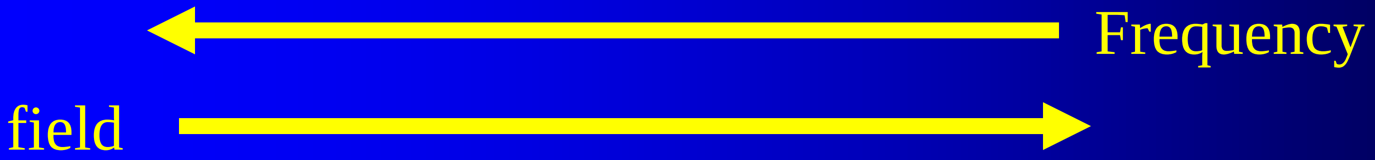


January 31, 2019

Chemistry 328N

The 100MHz nmr Chart



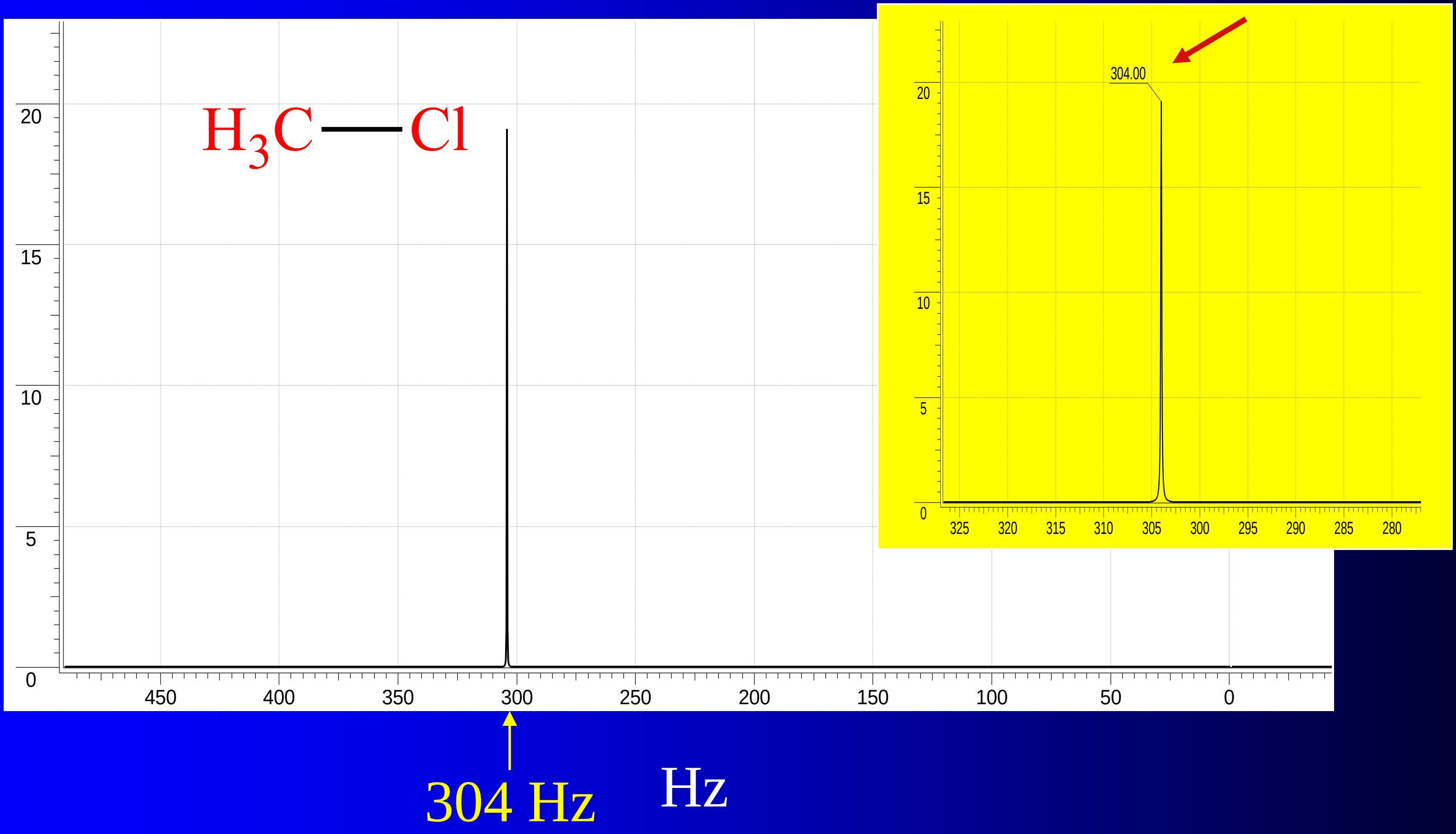


Frequency

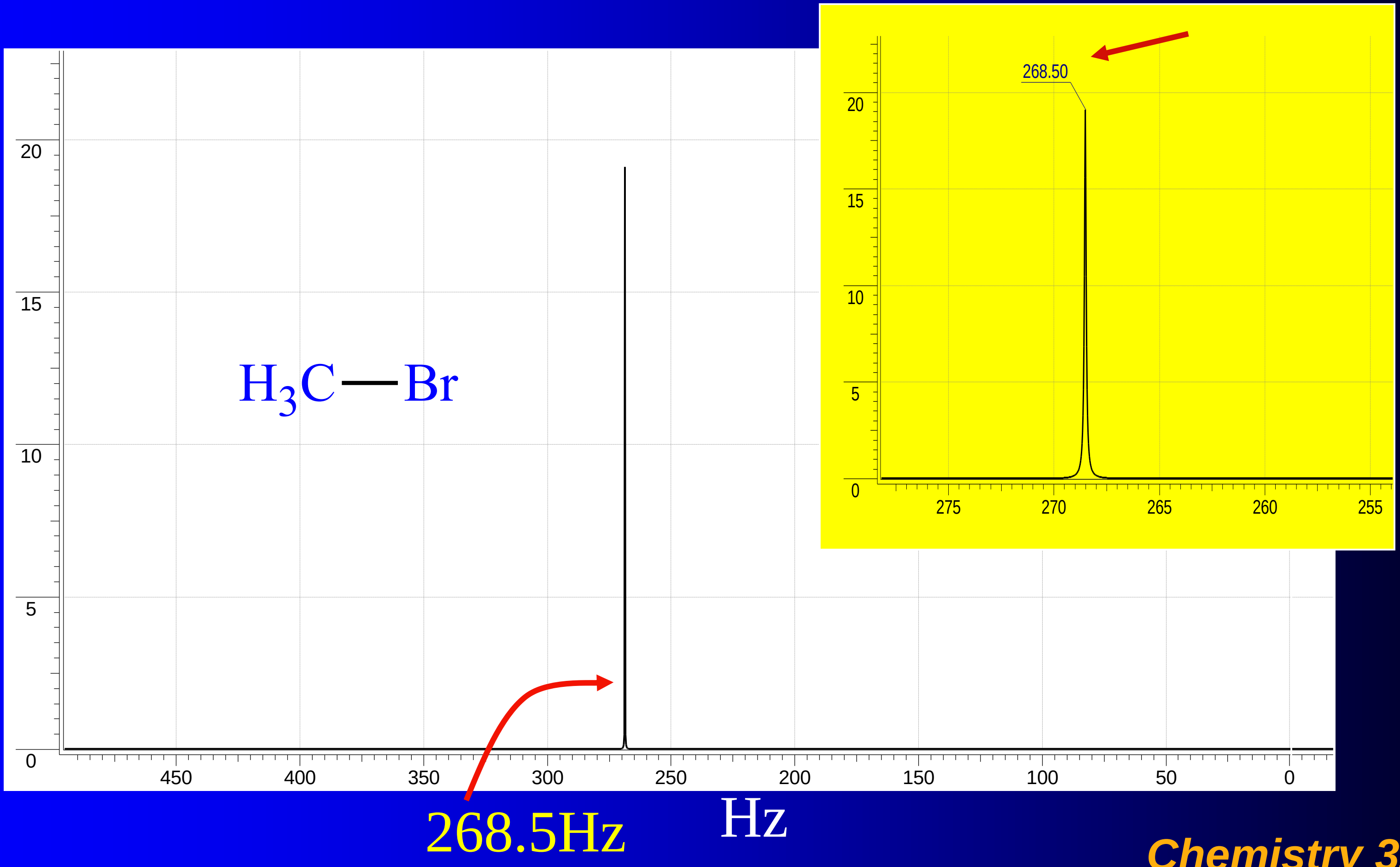
field

The TMS resonance is defined as having “0” frequency

100MHz Spectrum



100MHz nmr Spectrum



$H_3C—Br$

Why are these spectra different?

- If we were dealing with ^1H nuclei isolated from all other atoms and electrons, any combination of applied field and radiation that produces a signal for one ^1H would produce a signal for all ^1H. The same for ^{13}C nuclei

- But ….hydrogens in organic molecules are <u>not</u> isolated from all other atoms; they are surrounded by electrons, which are caused to circulate by the presence of the applied field

Why are these spectra different??

- The circulation of electrons around a nucleus in an applied field is called diamagnetic current.
- This current generates a field that opposes the applied field ...diamagnetic nuclear shielding results. Lenz's Law??
- The difference in resonance frequencies between the various hydrogen nuclei within a molecule is due to shielding/deshielding is very small but very important

Conditions for Resonance

- It is the frequency of the radiation and the NET field at the nucleus that matters.
- The NET field is the sum of all incident magnetic fields including those from:
  - The Giant Magnet (applied field)
  - Diamagnetic Shielding field (electrons)
  - Coupling (spin fields of adjacent nuclei)
  - credit card strips, earth’s field, etc…..

Calculating Chemical Shift in ppm

At 7.05 T, a resonance is at 715 Hz (from TMS)

1. What is the spectrometer frequency?

$\nu = \gamma B = (42.5\text{MHz/T})(7.05\text{T}) = 300\text{MHz}$

2. What is the “chemical shift” in ppm or δ compared to TMS ???

$$\frac{715 \text{ Hz}}{300 \times 10^{6} \text{ Hz}} = \frac{2.38}{10^{6}} = 2.38 \text{ ppm}$$

Chemical Shift

- The difference in resonance frequencies for hydrogens in CH_3Cl compared to CH_3Br under an applied field of 2.34T is only 35.5Hz, which is 0.35 parts per million (ppm, "δ") compared with the irradiating frequency

$$\frac{35\ \text{Hz}}{100 \times 10^6\,\text{Hz}} = \frac{0.35}{10^6} = 0.35\ \text{ppm} = 0.35\ \delta$$

Here, 35Hz is the difference in resonance frequency and 100MHz is the ^1H resonance frequency for B=2.34T and γ = 42.58 MHz / Tesla

The Power of δ

Chemical shift expressed in ppm or δ is normalized to the spectrometer frequency and therefore independent of the size of the magnet! This makes it possible to produce tables of cemical shifts that are valid for all spectrometers.

Changing Spectrometers

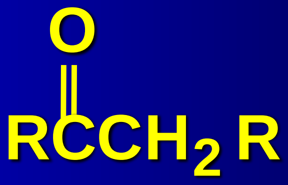
- If the resonance of the peak on a 7.05 T instrument is 715 Hz, what will the resonance frequency be at 23.5 T
- What is the resonance in ppm at 7.05 T ?
- What is the resonance in ppm at 23.5 T?

Chemical Shift

- Depends on several things (1) electronegativity of nearby atoms, (2) the hybridization of adjacent atoms, and (3) magnetic induction within an adjacent pi bond
- (1) Electronegativity

CH_3-X	Electroneg-ativity of X	δ of H
CH_3F	4.0	4.26
CH_3OH	3.5	3.47
CH_3Cl	3.1	3.05
CH_3Br	2.8	2.68
CH_3I	2.5	2.16
$(CH_3)_4C$	2.1	0.86
$(CH_3)_4Si$	1.8	0.00 (by definition

Chemical Shift - ^{1}H-NMR

Type of H	δ	Type of H	δ
$(CH_3)_4Si$	0	ROH	0.5-6.0
RCH_3	0.9	RCH_2OR	3.3-4.0
RCH_2R	1.2-1.4	R_2NH	0.5-5.0
R_3CH	1.4-1.7		
$R_2C{=}CRCHR_2$	1.6-2.6	 $R\overset{\overset{O}{\Vert}}{C}CH_3$	2.1-2.3
$RC{\equiv}CH$	2.0-3.0	 $R\overset{\overset{O}{\Vert}}{C}CH_2R$	2.2-2.6
$ArCH_3$	2.2-2.5		

Chemical Shift - ^{1}H-NMR

Type of H	δ	Type of H	δ
 $R\overset{O}{\overset{\Vert}{C}}OCH_3$	3.5-3.9	$R_2C{=}CH_2$	4.6-5.0
 $R\overset{O}{\overset{\Vert}{C}}OCH_2R$	4.1-4.7	$R_2C{=}CHR$	5.0-5.7
RCH_2I	3.1-3.3	ArH	6.5-8.5
RCH_2Br	3.4-3.6	 $R\overset{O}{\overset{\Vert}{C}}H$	9.5-10.1
RCH_2Cl	3.6-3.8		
RCH_2F	4.4-4.5	 $R\overset{O}{\overset{\Vert}{C}}OH$	10-13

Chemical Shift

- (2) The Hybridization of C Effects ^1H chemical Shift

Hybrid	Type of H	Name	δ
sp^3	RCH_3	alkyl	0.8- 1.0
sp	$RC\equiv CH$	acetylenic	2.0 - 3.0
sp^2	$R_2C=CH_2$	vinylic	4.6 - 5.7

?

This seems like a Mystery!!

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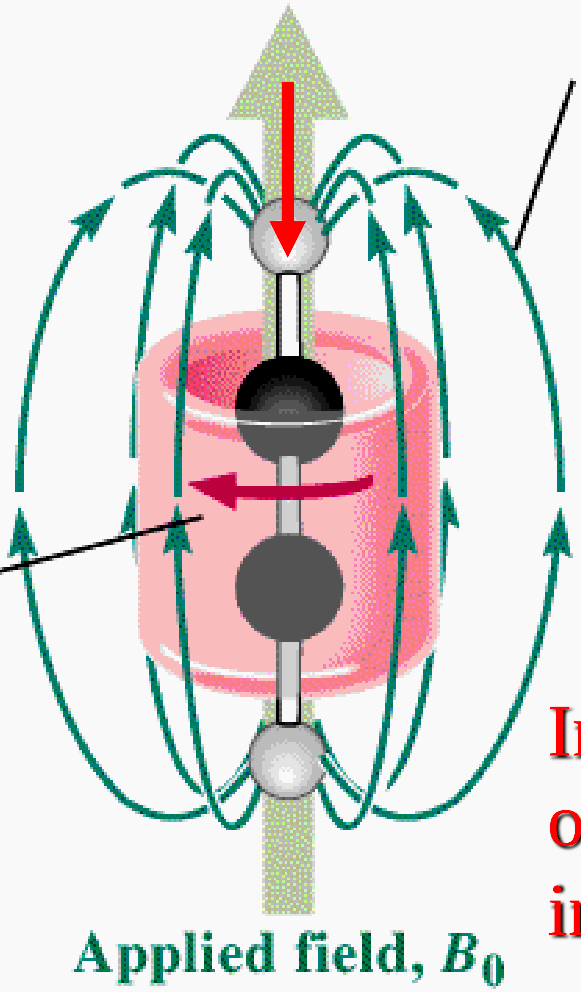
Chemical Shift

- Magnetic induction in pi bonds of a….
  - a carbon-carbon triple bond shields an acetylenic hydrogen and shifts its signal upfield (to the right) to a smaller δ value
  - carbon-carbon double bond deshields vinylic a hydrogens and shifts their signal downfield (to the left) to a larger δ value

Magnetic field induced in the pi bonds if a carbon-carbon triple bond

is this arrow correct for electron flow???

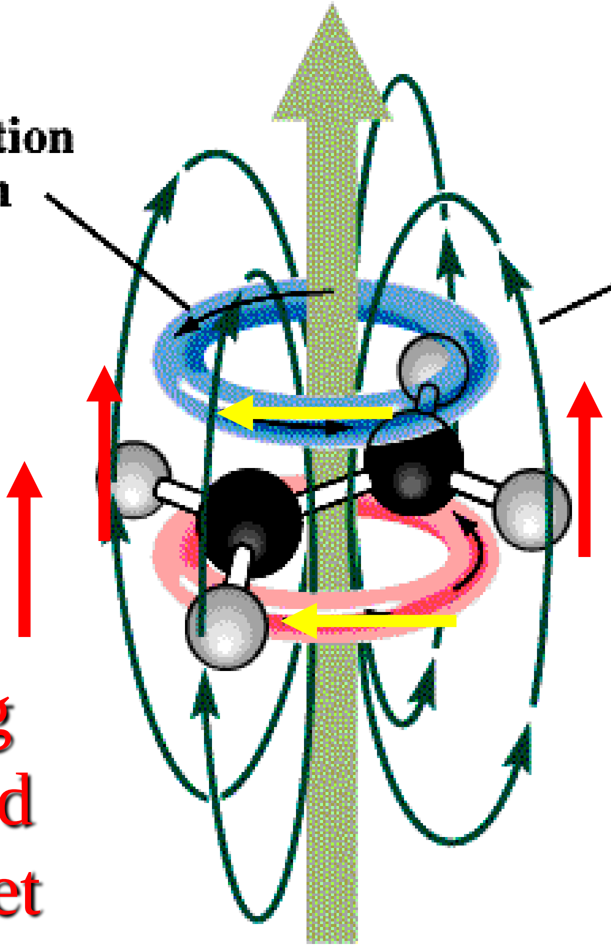


Induced local magnetic field of the pi electrons is against the applied field; it requires a greater applied field to bring an acetylenic hydrogen into resonance.

Induced flow of electrons in the pi system of alkyne

Induced field ↓ opposes big magnet inside the ring

Magnetic field induced in the pi bond of a carbon-carbon double bond



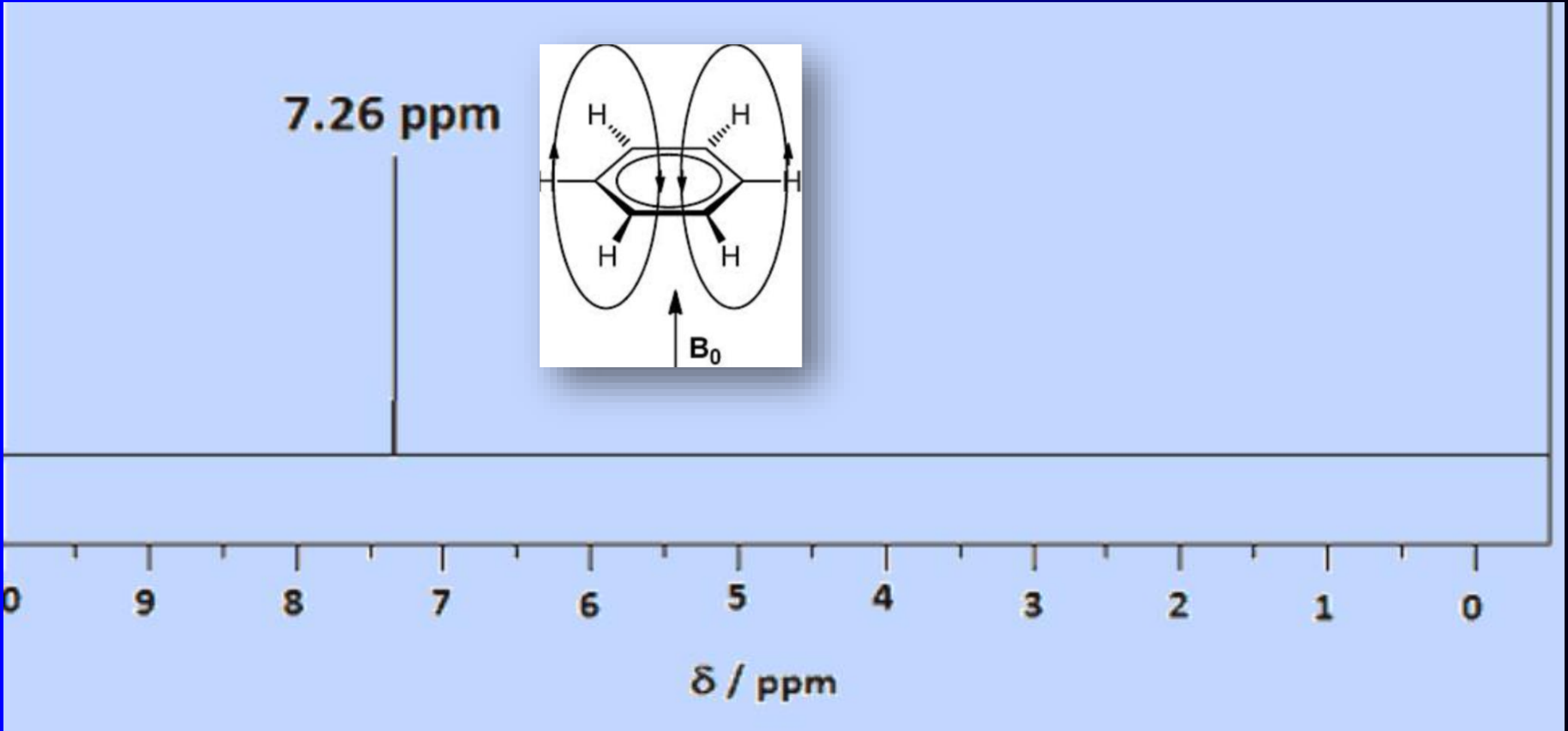
Induced circulation of pi electrons in the alkene

Induced local magnetic field of the pi electrons reinforces the applied field and provides part of the field necessary to bring a vinyl hydrogen into resonance.

Applied field, B_0

Outside the ring the induced field helps big magnet

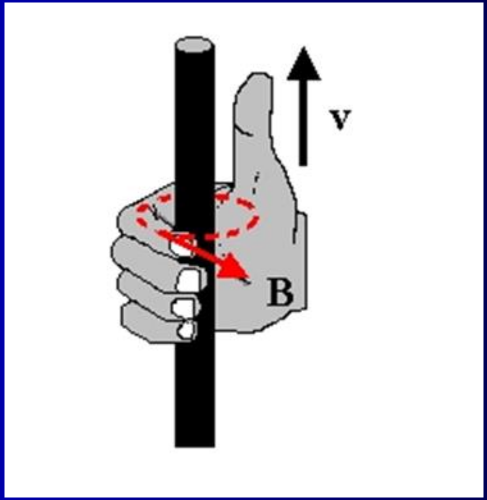
^{1}H-nmr spectrum of benzene



Some Confusing Definitions

http://www.mi.mun.ca/users/cchaulk/eltk1100/ivse/ivse.htm

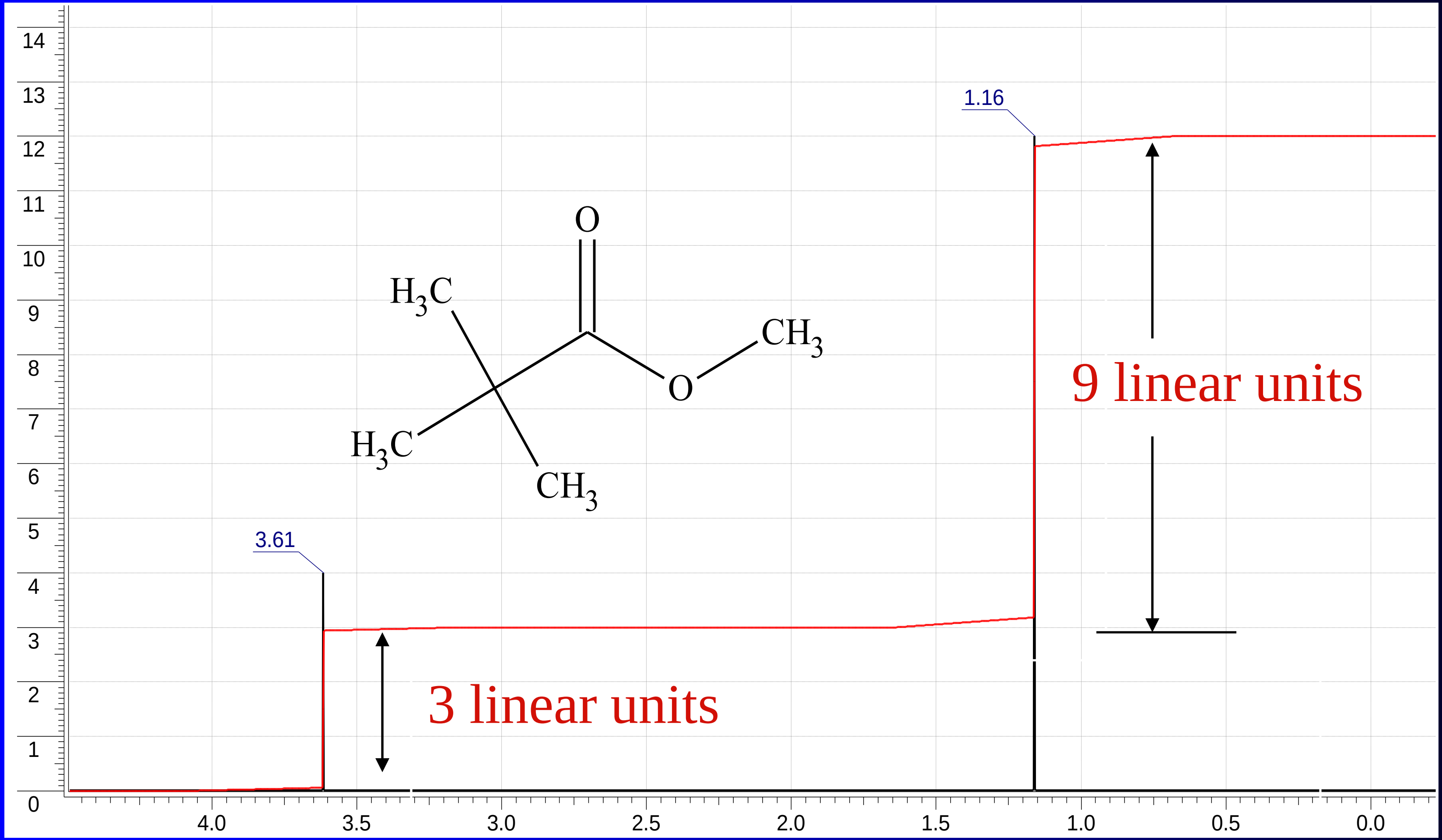
The Right-Hand Rule #2 determines the direction of the magnetic field aroud a current-carrying wire and vice-versa



BUT………………..

When using the Right-Hand Rules, it is important to remember that the rules assume charges move in a conventional current (the hypthetical flow of positive charges). In order to apply the Right-Hand Rule to a moving negative charge, the direction of charge flow must be reversed--….or use your LEFT hand.

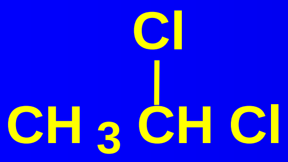
Integration



“up field”

Equivalent Hydrogens

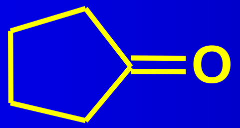
- Have exactly the same chemical environment



$$CH_3\overset{\overset{Cl}{|}}{C}HCl$$

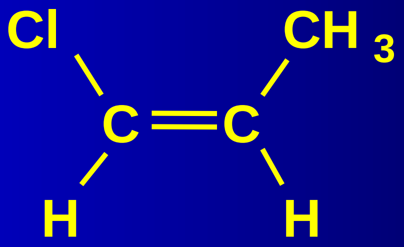
1,1-Dichloro-ethane

2 signals



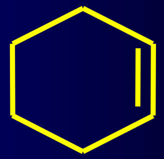
Cyclopentanone

2 signals



(Z)-1-Chloropropene

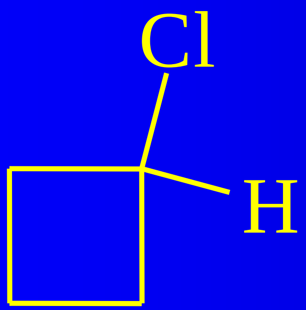
3 signals

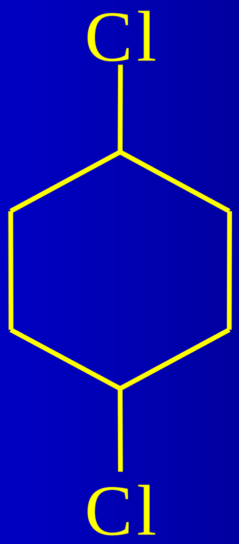


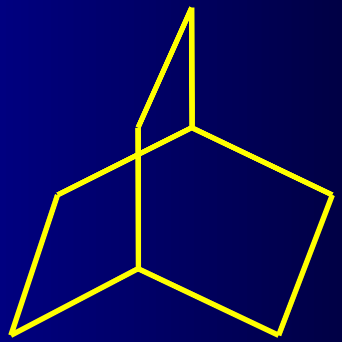
Cyclohexene

3 signals

How many equivalent hydrogens??

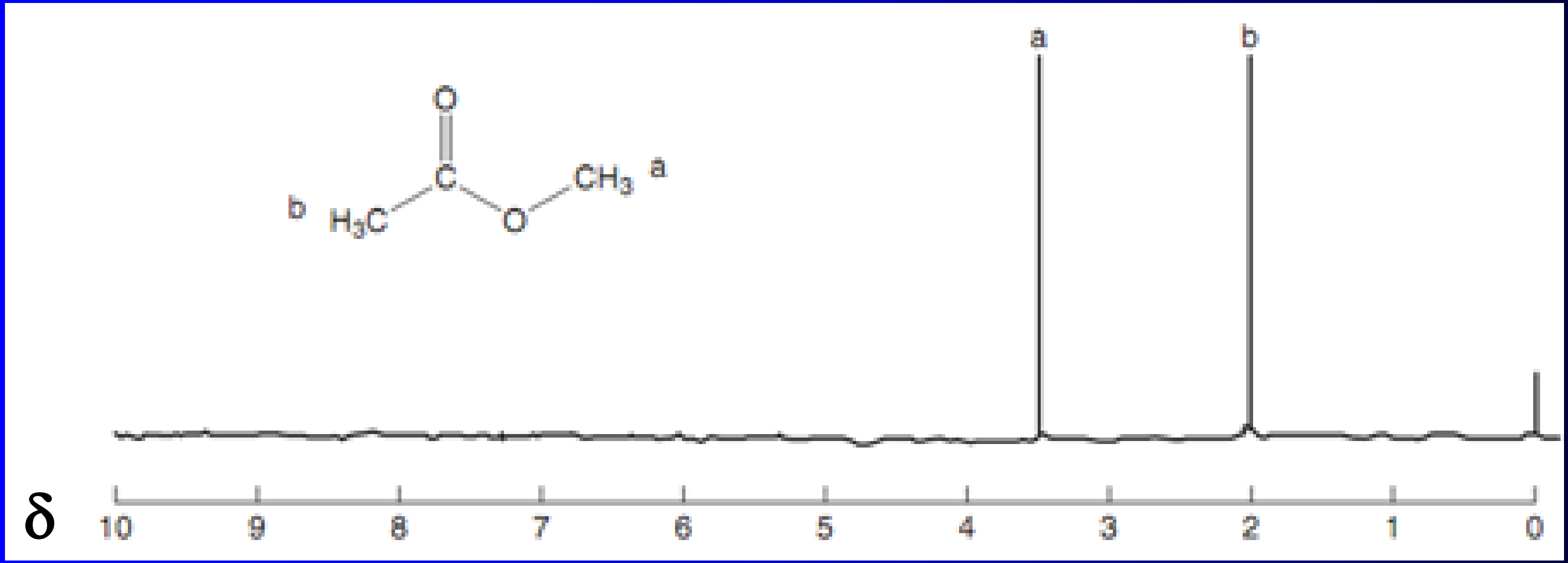






This looks “easy” but it is not!!

Chemical shift in ppm (δ) is independent of the size of the magnet.!



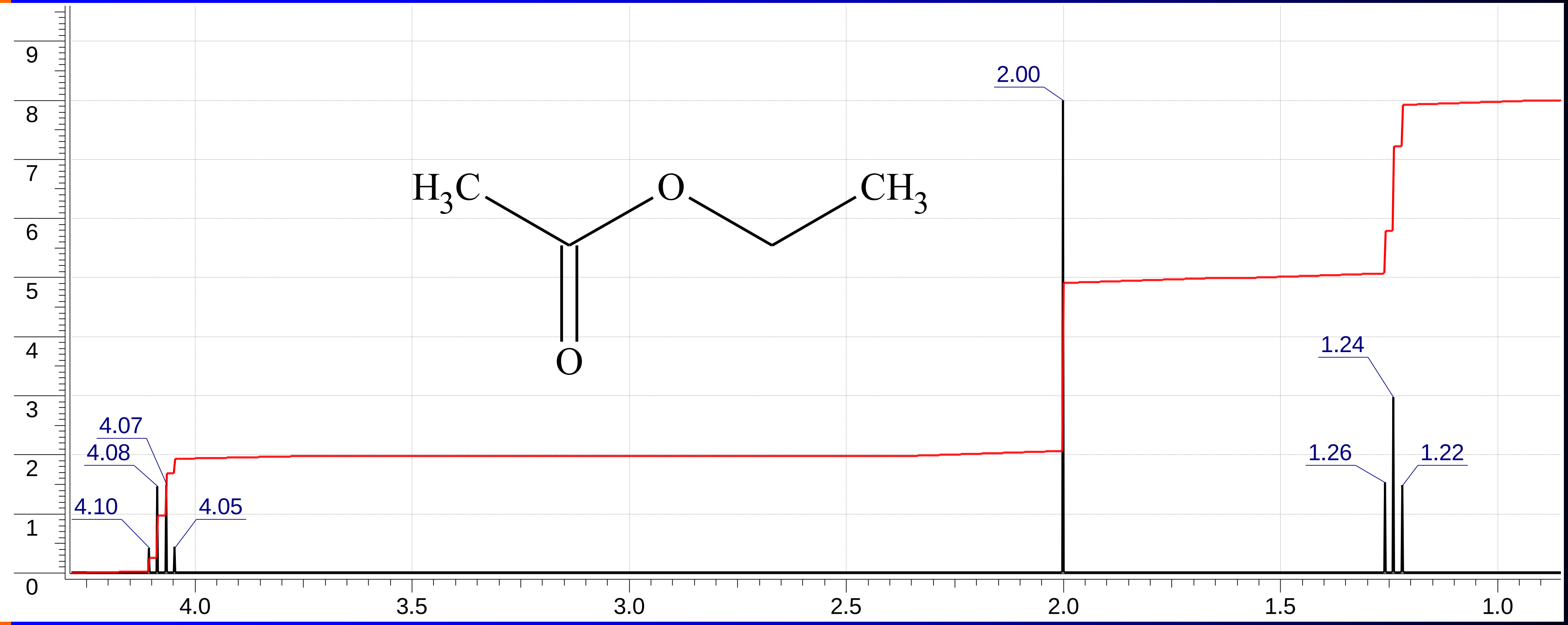
Frequency

Field

Up Field

Down Field

Ethyl Acetate



Signal Splitting

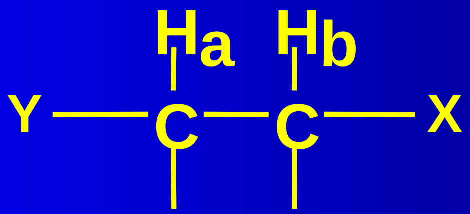
Huh?? Why??? What is going on here??

What a mess!!

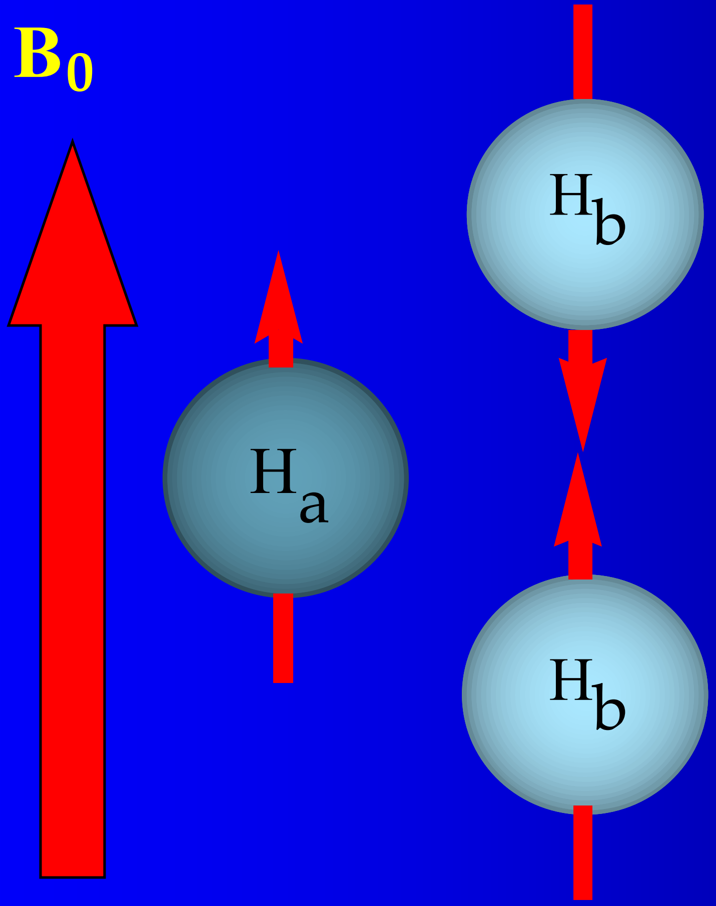
- Signal splitting: splitting of an NMR signal into a set of peaks by the influence of neighboring nonequivalent hydrogens
- This splitting business is actually rich in information…it is a wonderful thing!

Origins of Signal Splitting

- When the chemical shift of one nucleus is influenced by the spin of another, the two are said to be *coupled*
- Consider nonequivalent hydrogens H_a and H_b on adjacent carbons
  - the chemical shift of H_a is influenced by whether the spin of H_b is aligned with or against the applied field



Origins of Signal Splitting

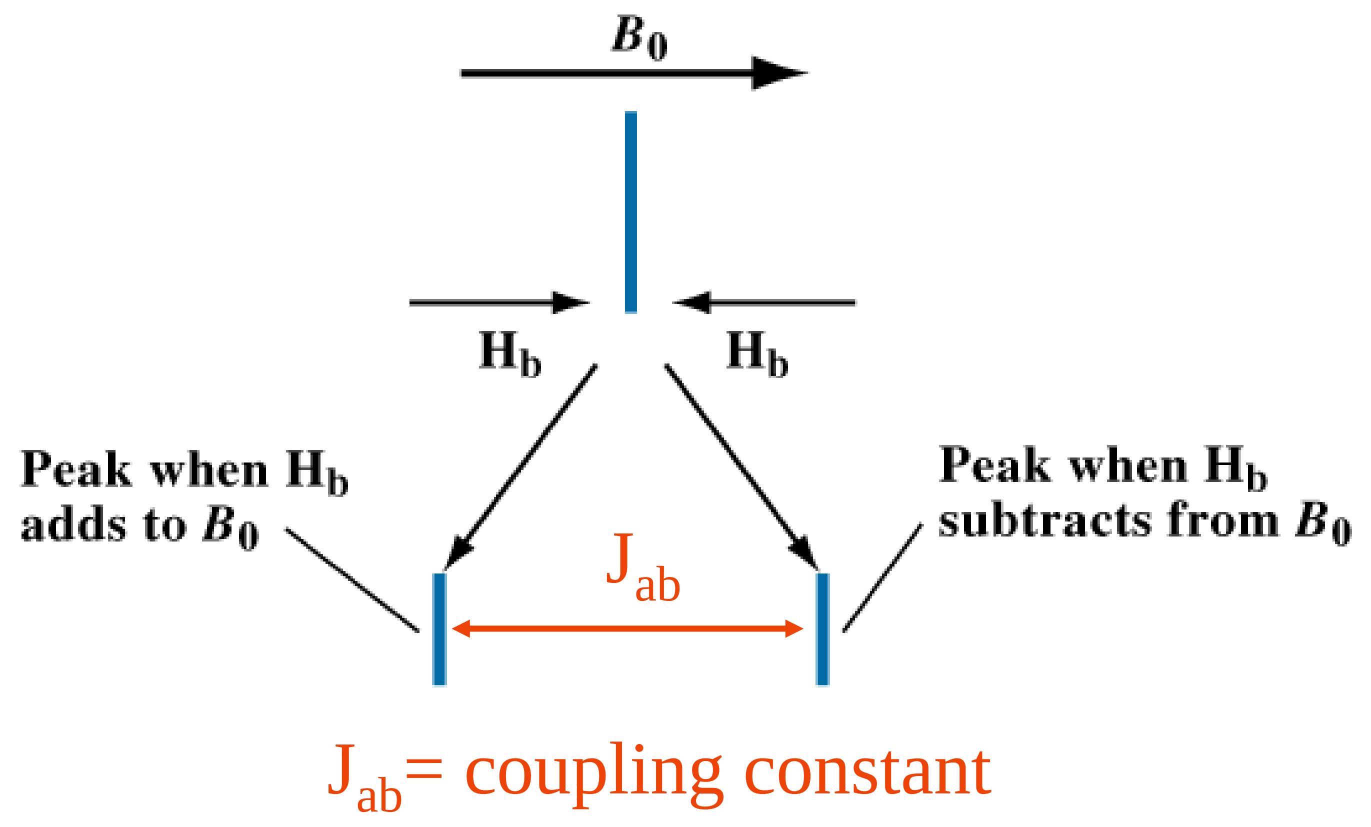


Magnetic field of H_b subtracts from the applied field; H_b signal appears at a higher applied field

Magnetic field of H_b adds to the applied field; H_a signal appears at a lower applied field

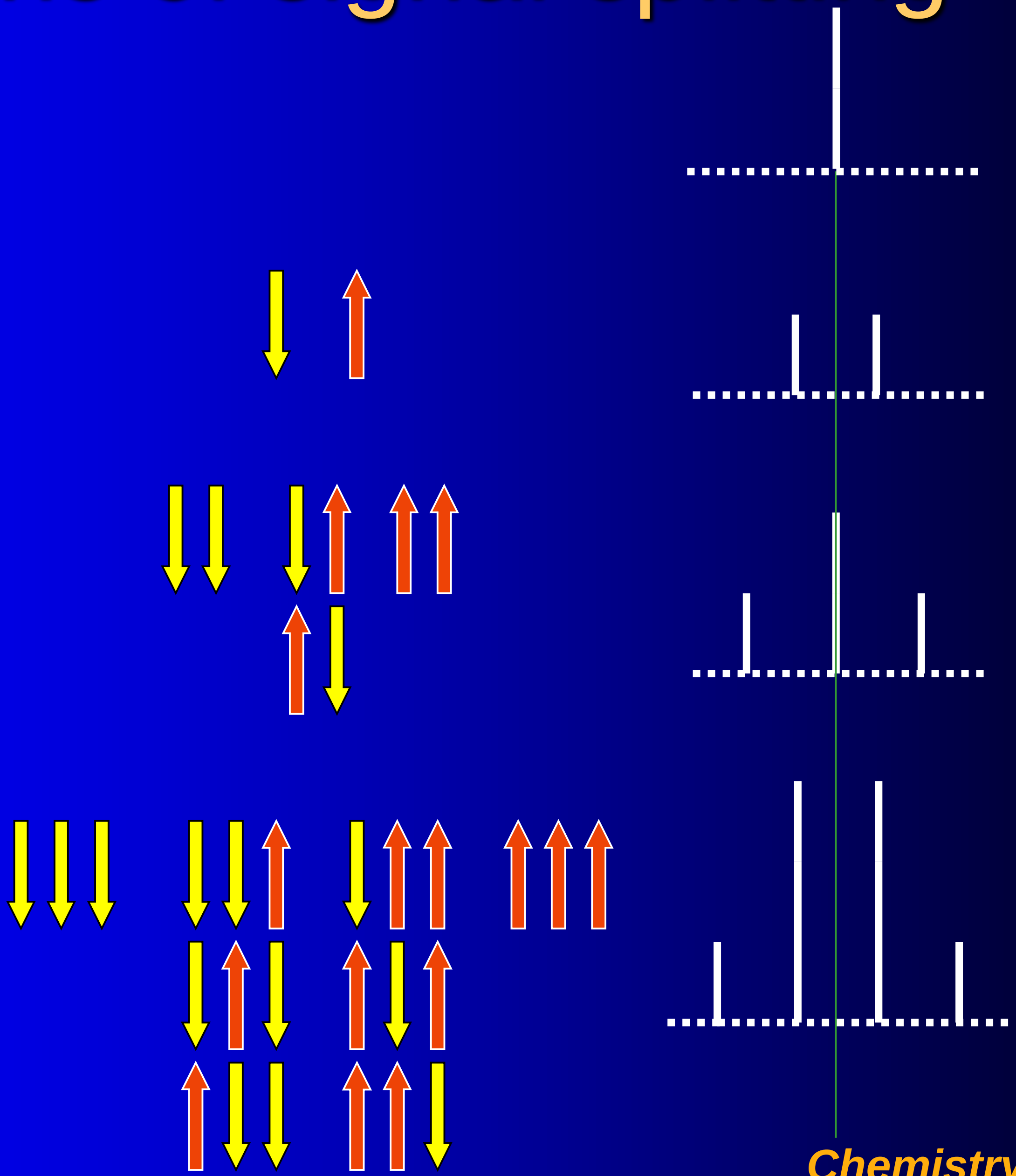
Remember…it is the NET field that counts

The signal of Ha is split into two peaks of equal area (a doublet)



J_{ab}= coupling constant

Origins of signal splitting



no neighbors

one spin

two spins

three spins