Chem 263 Outline 1 Start

Light & Energy

$E = h\nu = hc/\lambda$

E = energy

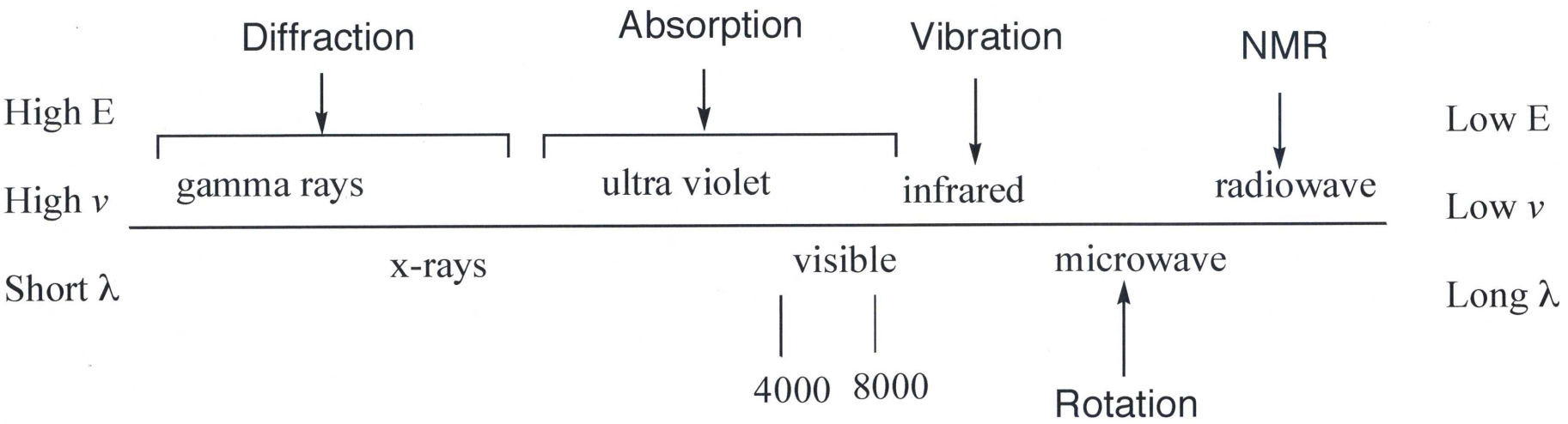
c = speed of light = 3×10^8 m/sec

ν= frequency

λ = wavelength

h = Planck's constant = 6.6×10^{-34} joule sec

Electromagnetic Spectrum



Nuclear Magnetic Resonance (NMR)

If you have an odd # of protons and/or an odd # of neutrons there is a nuclear magnetic moment (i.e. nuclear spin).

Example: ^{1}H has atomic number 1, nuclear spin ½

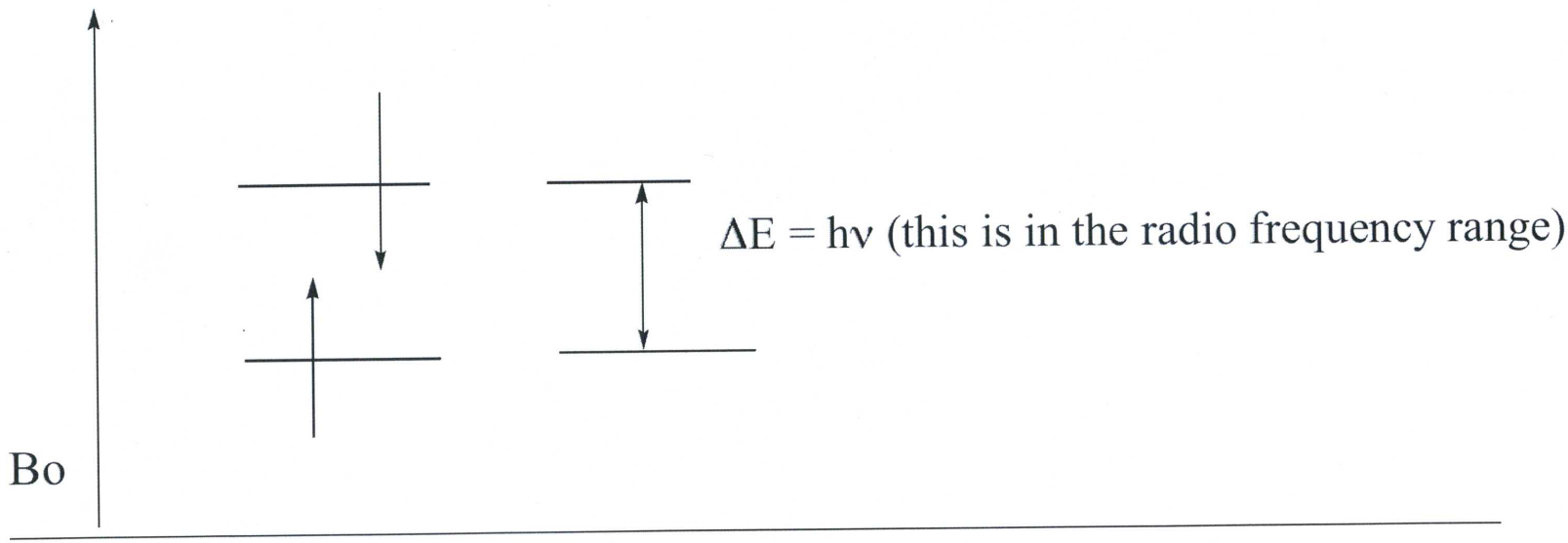
^{12}C has atomic number 6, number of neutrons 6, no nuclear spin

^{13}C (1% of all carbon) has atomic number 6, number of neutrons 7, can be detected by NMR

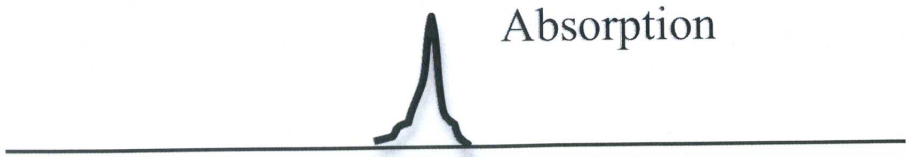
^{14}C has atomic number 6, number of neutrons 8, no nuclear spin, radioactive

NMR Continued (focusing on ^{1}H NMR)

If you apply a magnetic field (B_O) to the nuclei there are two possible energy states, one with the spin aligned with the field and the other opposed.



Absorption from the lower energy state to the higher one becomes possible, which allows a spectrum to be observed:

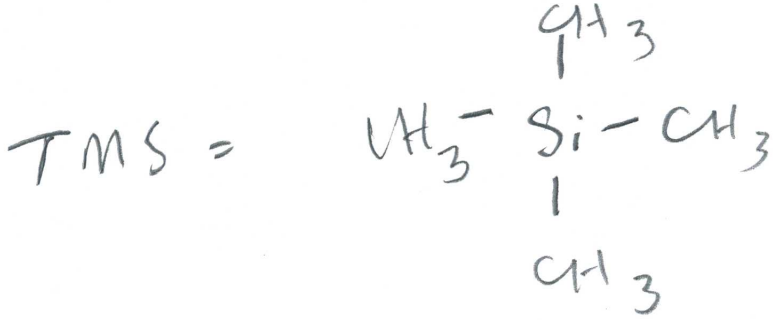


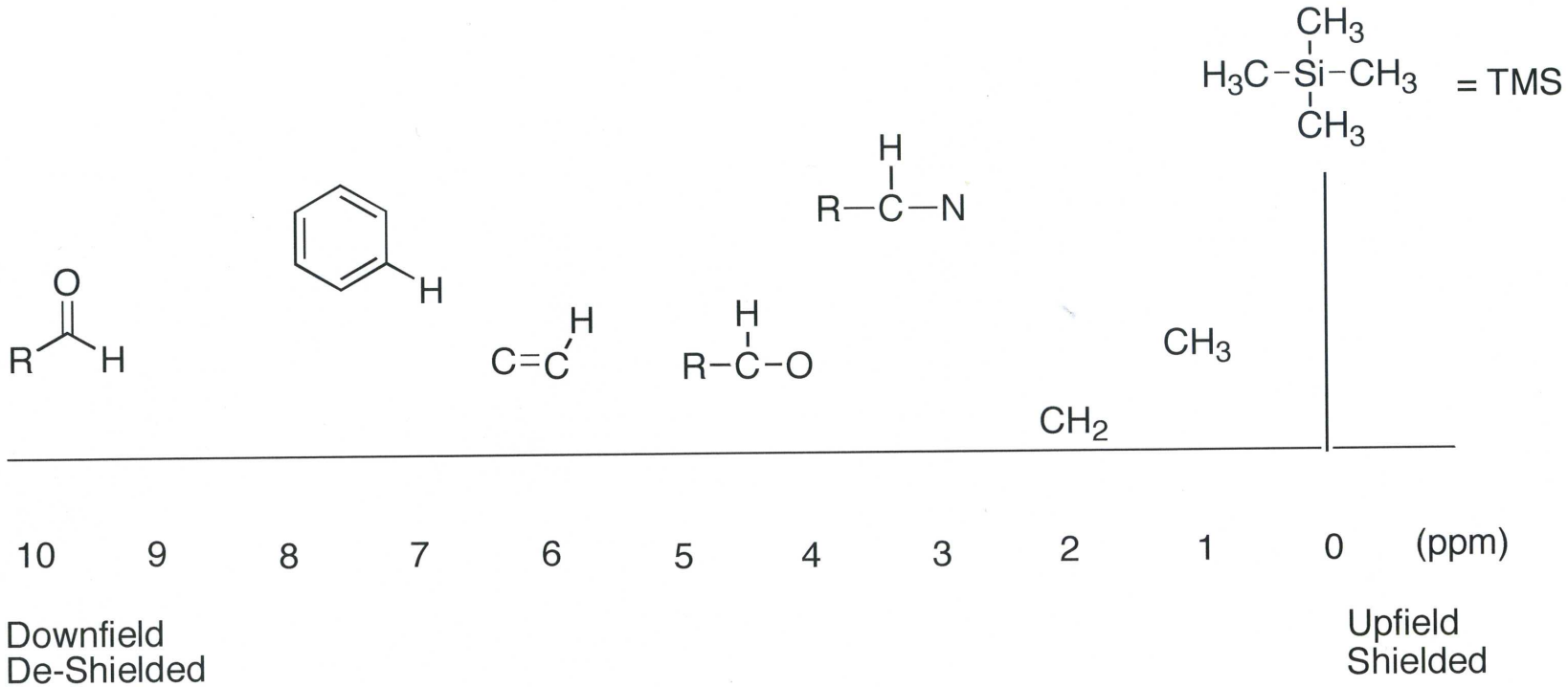
Chemical Shift

Chemical shift is the change in the frequency of absorption. The chemical shift is typically shown in units of parts per million (ppm) and is compared to a reference. For hydrogens this reference is usually tetramethylsilane (TMS).

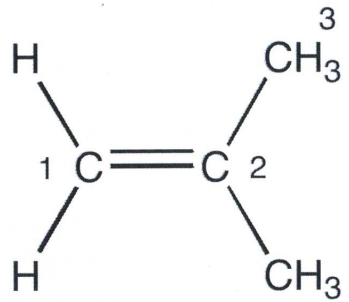
The hydrogen atoms in TMS are highly shielded and the signal for TMS is at 0 ppm.

Deshielding occurs when electrons are pulled away from a hydrogen atom, which can be caused by attaching an electron withdrawing group, such as a carbonyl. When the electrons are pulled away, the nuclei is more exposed to the magnetic field resulting in a downfield chemical shift.

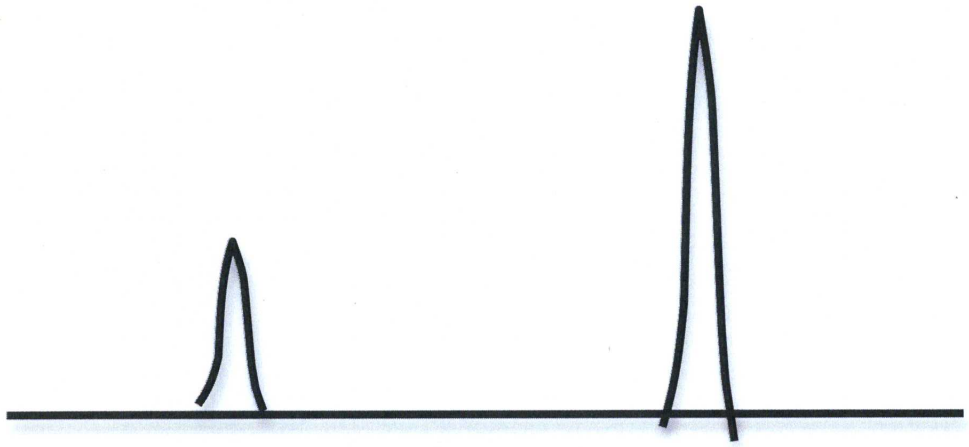



CH3
H3C–Si–CH3
CH3
= TMS
H
R–C–N
O
R
H
H
C=C
H
H
R–C–O
CH3
CH2
10
9
8
7
6
5
4
3
2
1
0
(ppm)
Downfield
De-Shielded
Upfield
Shielded

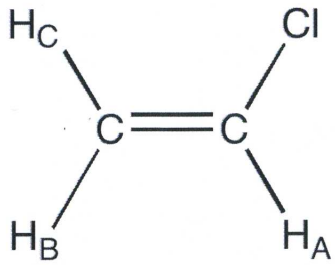
Examples



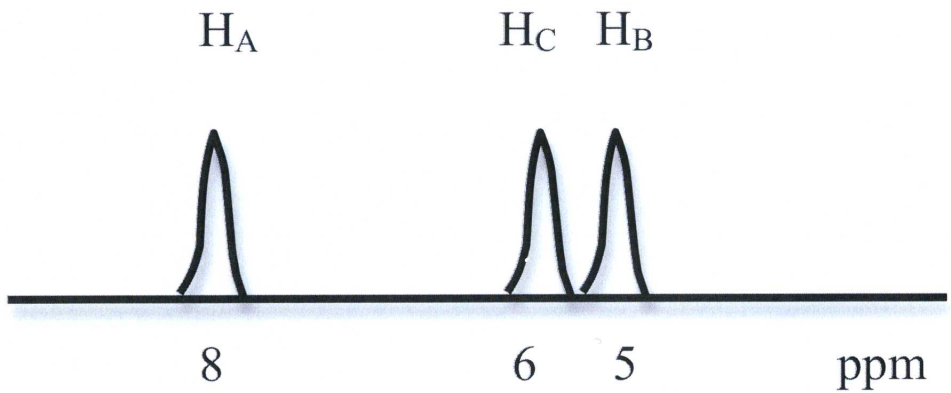
2-methylpropene



The intensity depends on the number of hydrogen atoms, in this case 2:6 which is the same as 1:3

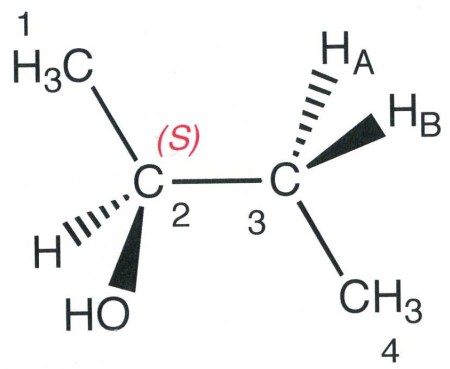


1-chloroethene aka
chloroethylene
vinyl chloride



H_B and H_C are different due to the distance from the Cl;
H_B is trans to the Cl while
H_C is cis to the Cl

Diastereotopic Protons - can have different chemical shifts



(S)-2-butanol

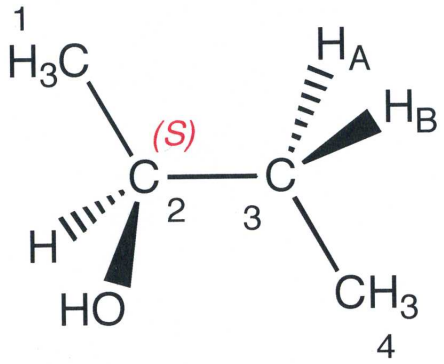
C-2 is a stereogenic centre
no plane of symmetry in molecule
H_A and H_B are in different environments
have different chemical shifts
they are diastereotopic

methyl group is one signal because the C-C bond can freely rotate

barrier to single bond rotation is a few Kcal per mole
about 15-20 kilocalories per mole of energy are available at 20 C

NMR cannot distinguish between the methyl H's.

Diastereotopic Protons - can have different chemical shifts



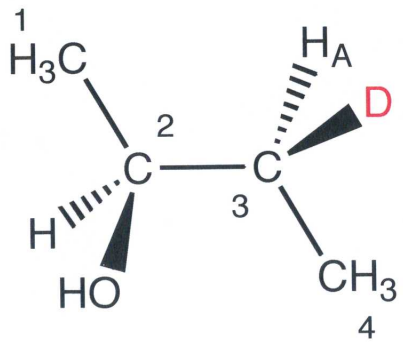
(S)-2-butanol

H_A and H_B are in different environments
have different chemical shifts
they are diastereotopic

How to Tell ?

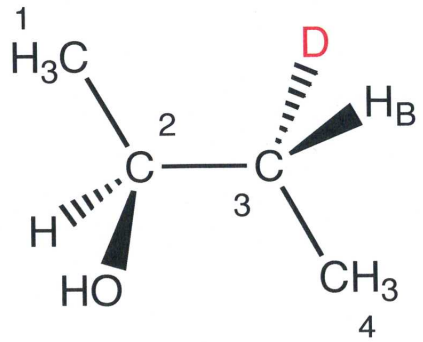
substitute H_A or H_B with deuterium (labeled as D)

if you get diastereomers -> diastereotopic



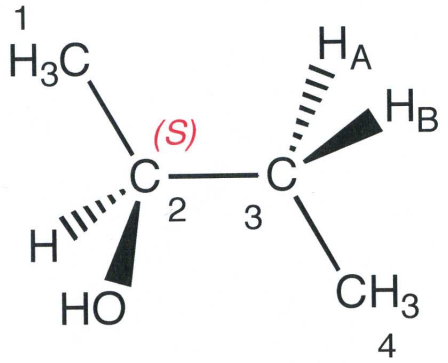
SS isomer

diastereomers



SR isomer

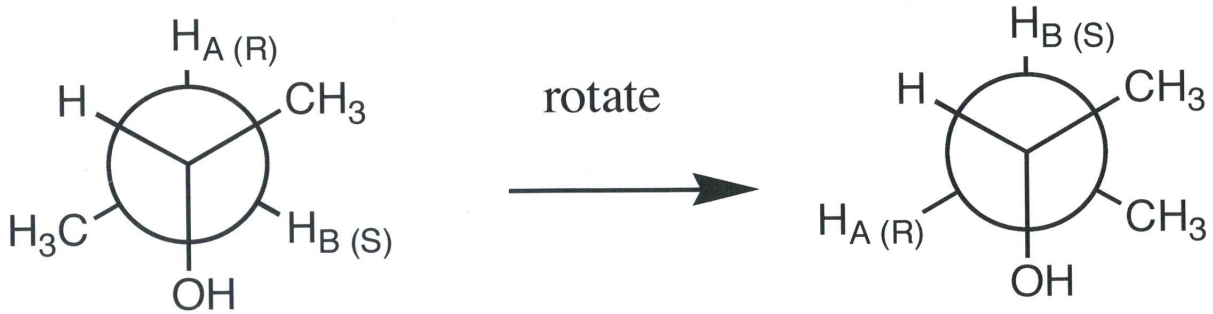
Diastereotopic Protons - can have different chemical shifts



H_A and H_B are in different environments
have different chemical shifts
they are diastereotopic

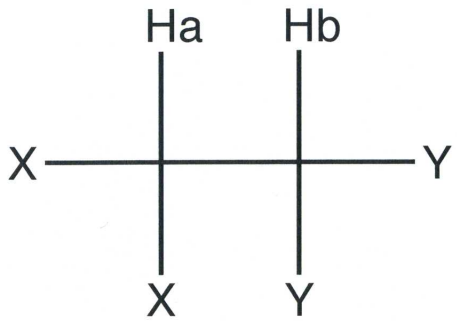
Newman Projection

Round circle in structure below is back carbon (carbon 3 of 2-butanol)
carbon 2 is directly attached to it -> front point where the bonds meet



Bond rotation can bring H_B to the position where H_A was
but not into same environment

Spin-Spin Splitting (Coupling) : J is coupling constant in Hertz

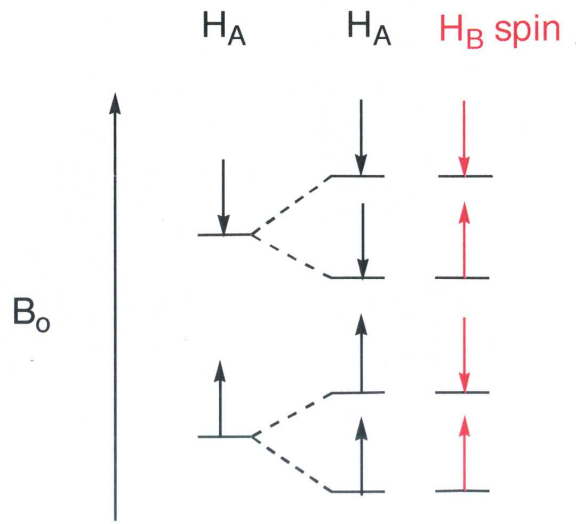


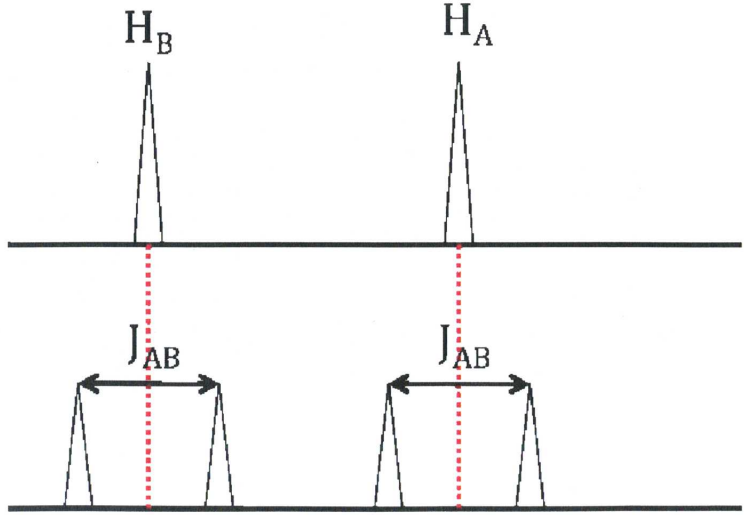
$X \neq Y$

H_A is not a singlet due to the influence of H_B on its spin and vice versa.

The diagram shows the energy for H_A

the spins for H_B are shown in red only to show the effect on H_A





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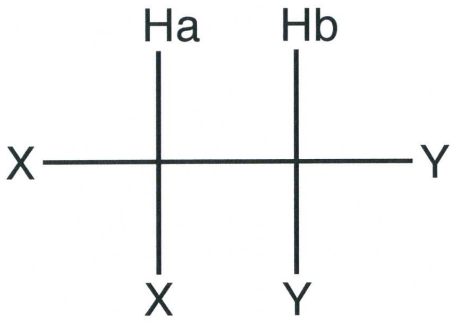

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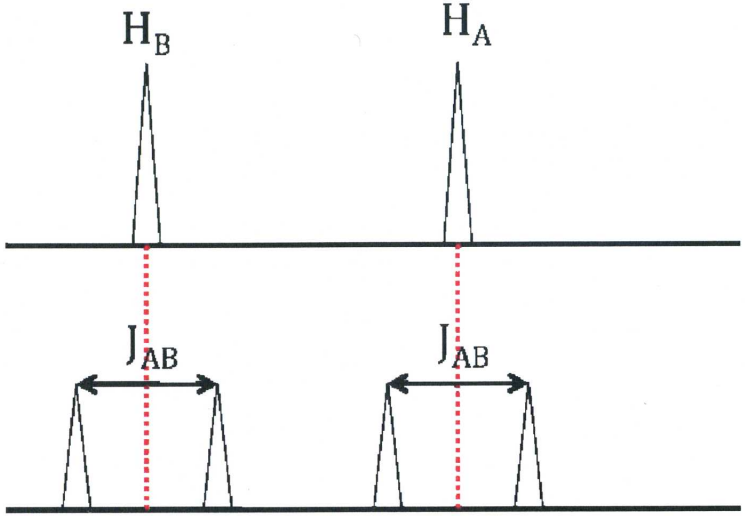

Limitations of Coupling

2 to 3 bonds separating nuclei (typically not seen further than 3 bonds

usually no coupling across O, N, S, C=O

H_A and H_B would not couple due to the oxygen

there are exceptions to these rules