NMR Proton Spectroscopy

Muthana University Science Faculty
/Chemistry department 4th (2020-2021)
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Chemical Shift

- Measured in parts per million.
- Ratio of shift downfield from TMS (Hz) to total spectrometer frequency (Hz).
- Same value for 60, 100, or 300 MHz machine.
- Called the delta scale.

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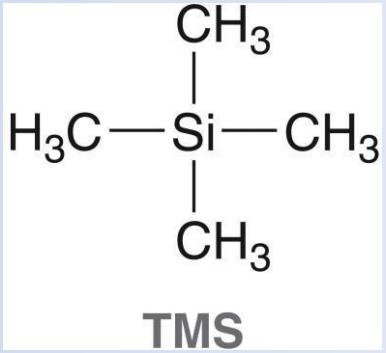
Chemical Shift

- In many NMR solvents, 1% TMS is added as an internal standard. The frequency of the protons in TMS is lower than that observed for most organic compounds



- The shift for a proton signal is calculated as a comparison to TMS

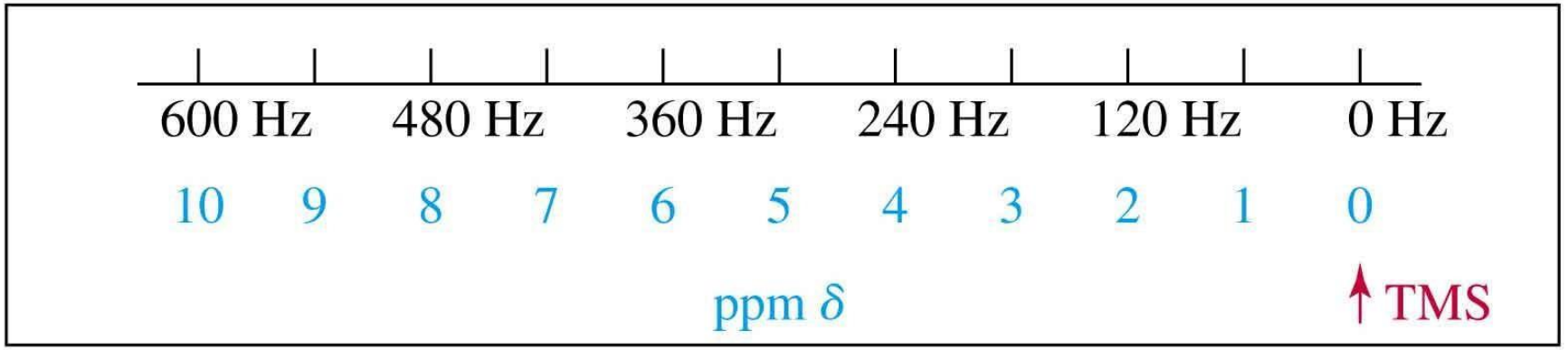
$$\delta = \frac{\text{observed Shift from TMS in hertz}}{\text{operating frequency of the instrument in hertz}}$$

- For benzene on a 300 MHz instrument

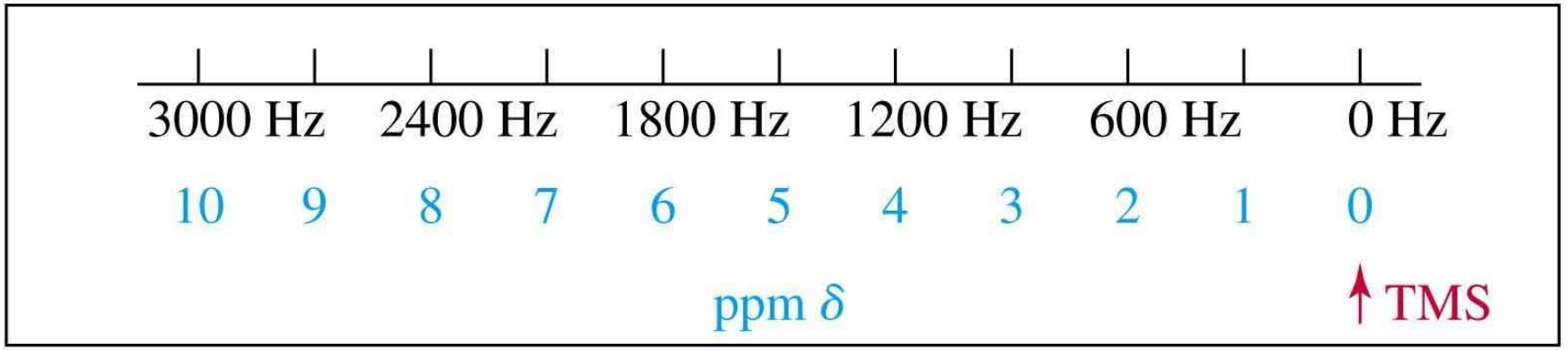
$$\delta = \frac{2181\ \text{Hz}}{300 \times 10^6\ \text{Hz}} = 7.27 \times 10^{-6}$$

Delta Scale

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



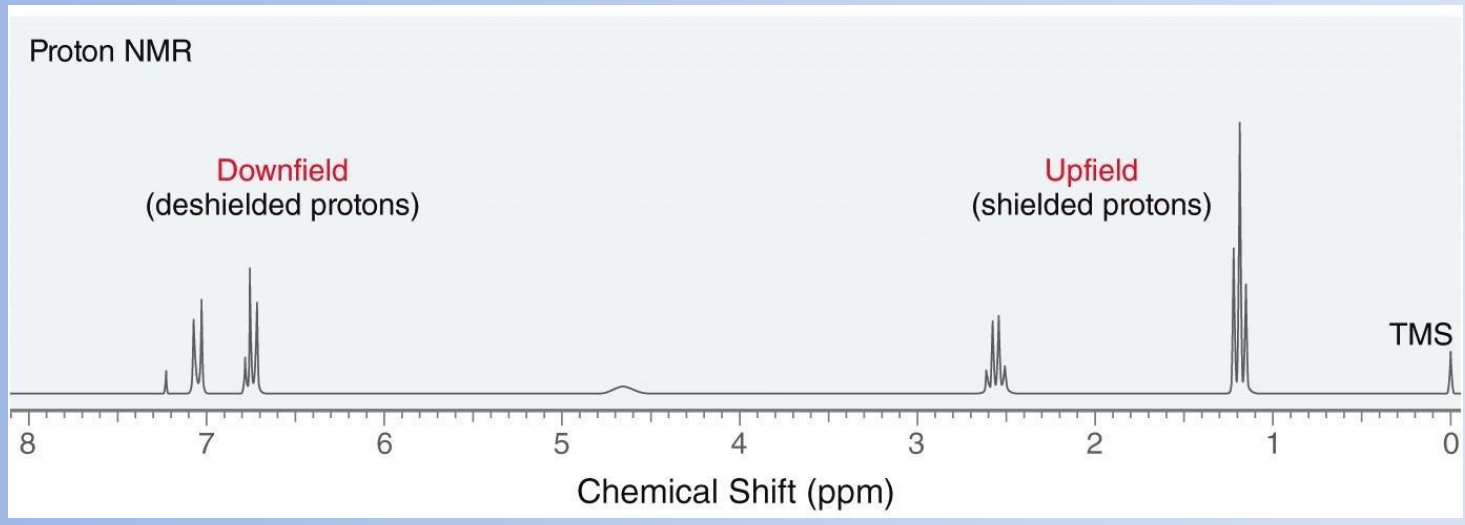
60 MHz



300 MHz

Chemical Shift

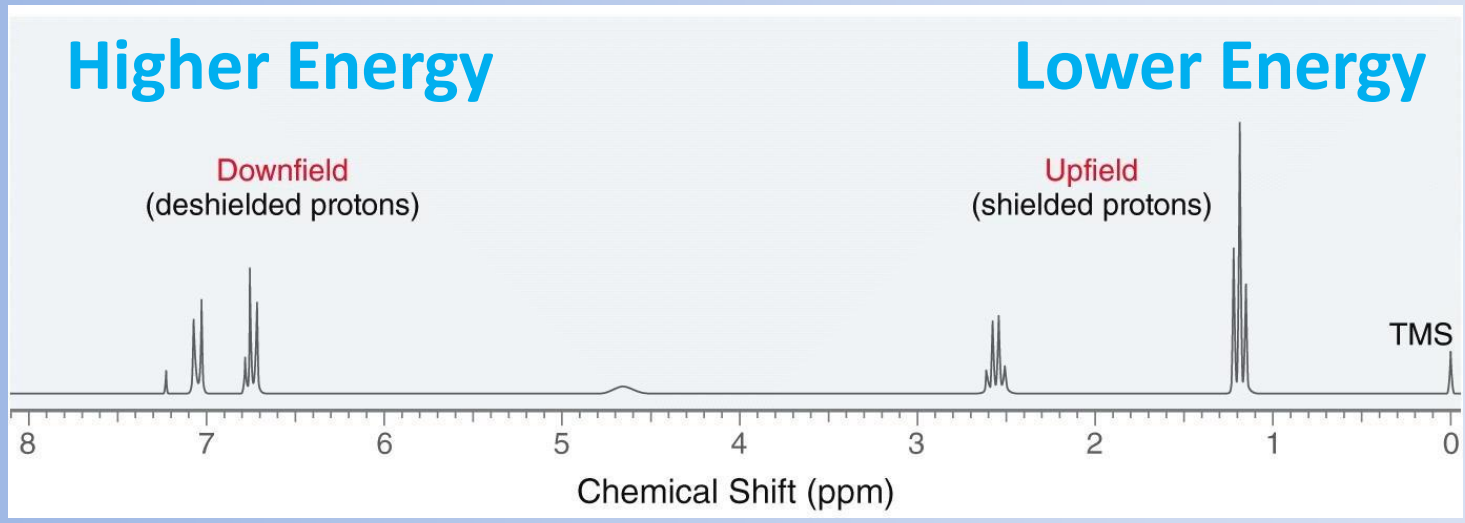
- Early NMRs analyzed samples at a constant energy over a range of magnetic field strengths
- low field strength = **downfield**
- high field strength = **upfield**
- Shielded protons required a stronger external magnetic field to be excited at the same energy as deshielded protons.



`Chemical Shift

- Current NMRs analyze samples at a constant field strength over a range of energies

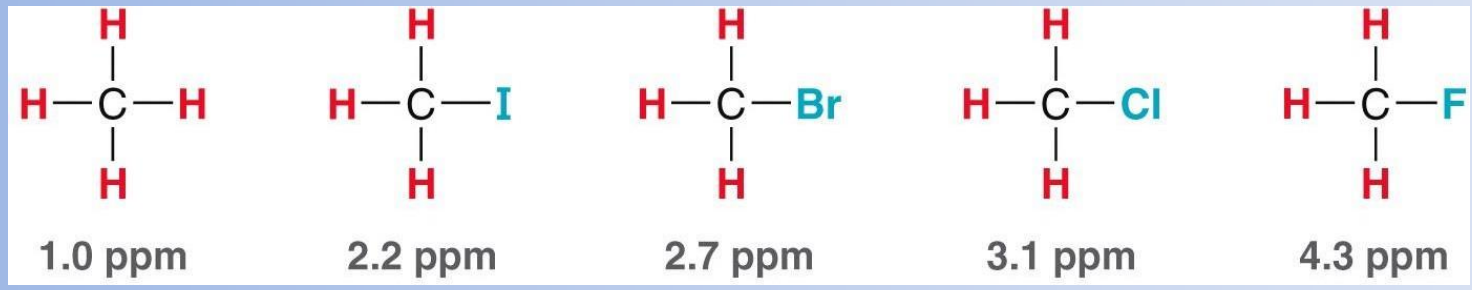
- Shielded protons have a smaller magnetic force acting on them, so they have smaller energy gaps and absorb lower energy radio waves

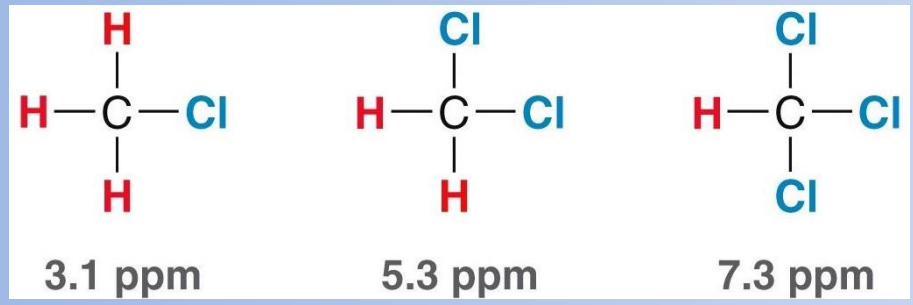


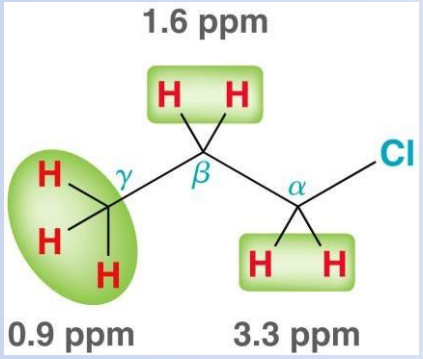
Chemical Shift

- Alkane protons generally give signals around 1-2 ppm

- Protons can be shifted downfield when nearby electronegative atoms cause deshielding.

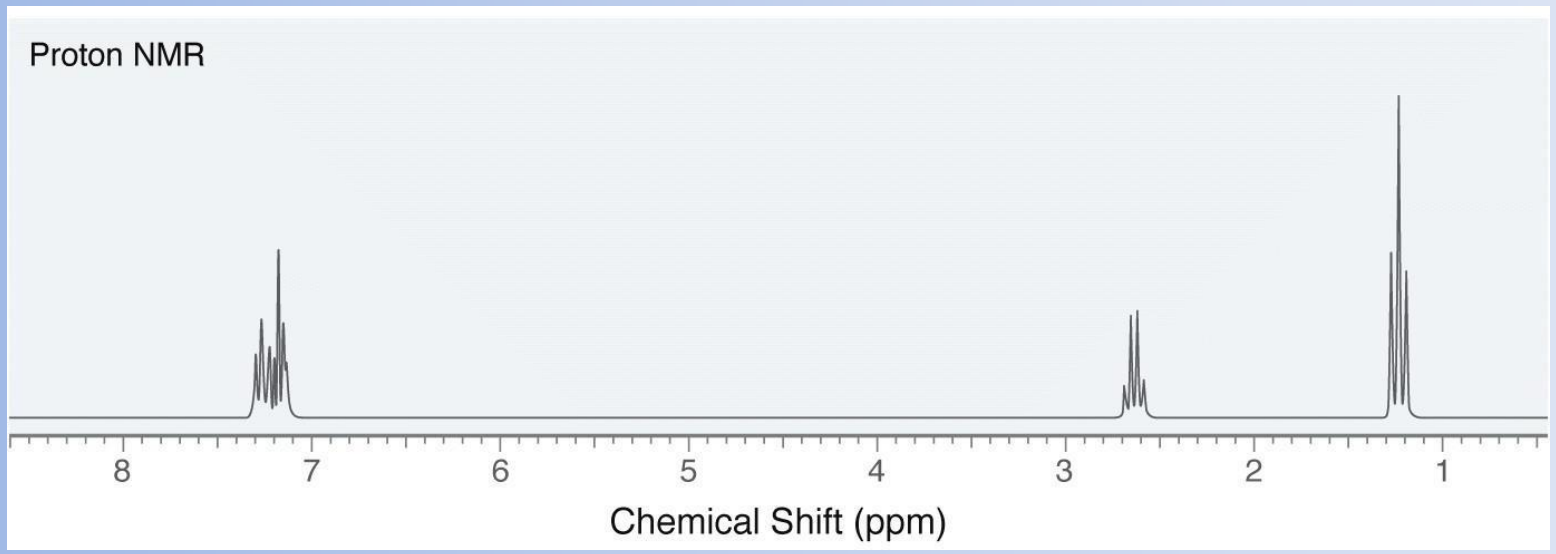




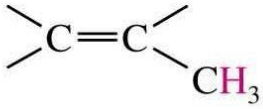
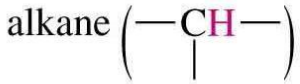
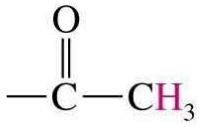
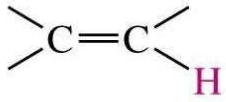


Characteristics of a ^{1}H NMR Spectrum

- NMR spectra contain a lot of structural information
  - Number of signals
  - Signal location (chemical shift(
  - Signal intensity (area under the signal(
  - Signal shape (splitting pattern(

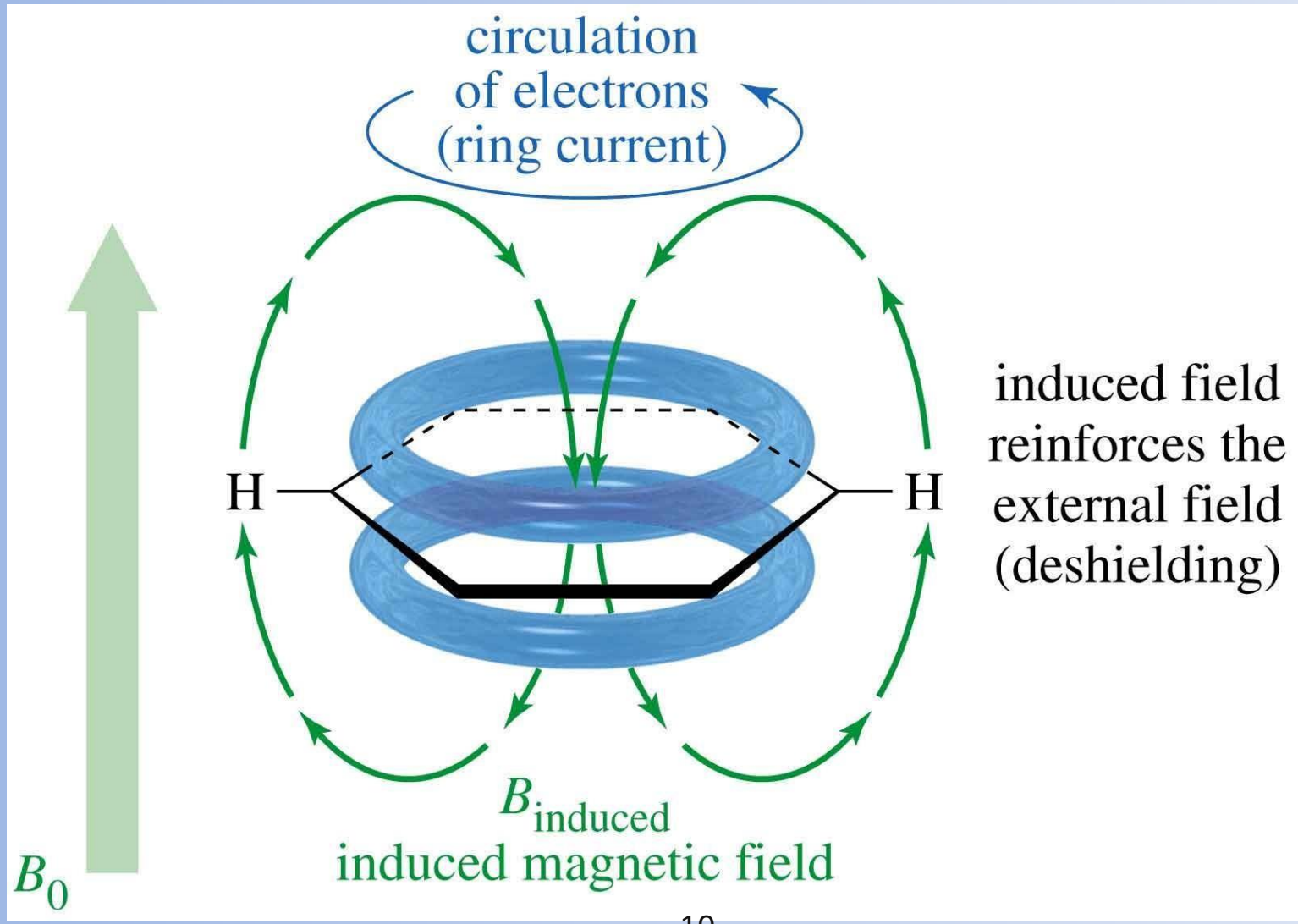


Typical Values

Type of Proton	Approximate δ	Type of Proton	Approximate δ
alkane ($-CH_3$)	0.9		1.7
alkane ($-CH_2-$)	1.3	Ph—H	7.2
alkane 	1.4	Ph—CH_3	2.3
	2.1	R—CHO	9–10
—C≡C—H	2.5	R—COOH	10–12
R—CH_2—X (X = halogen, O)	3–4	R—OH	variable, about 2–5
		Ar—OH	variable, about 4–7
	5–6	R—NH_2	variable, about 1.5–4

Note: These values are approximate, as all chemical shifts are affected by neighboring substituents. The numbers given here assume that alkyl groups are the only other substituents present. A more complete table of chemical shifts appears in Appendix 1.

Aromatic Protons, δ7-δ8



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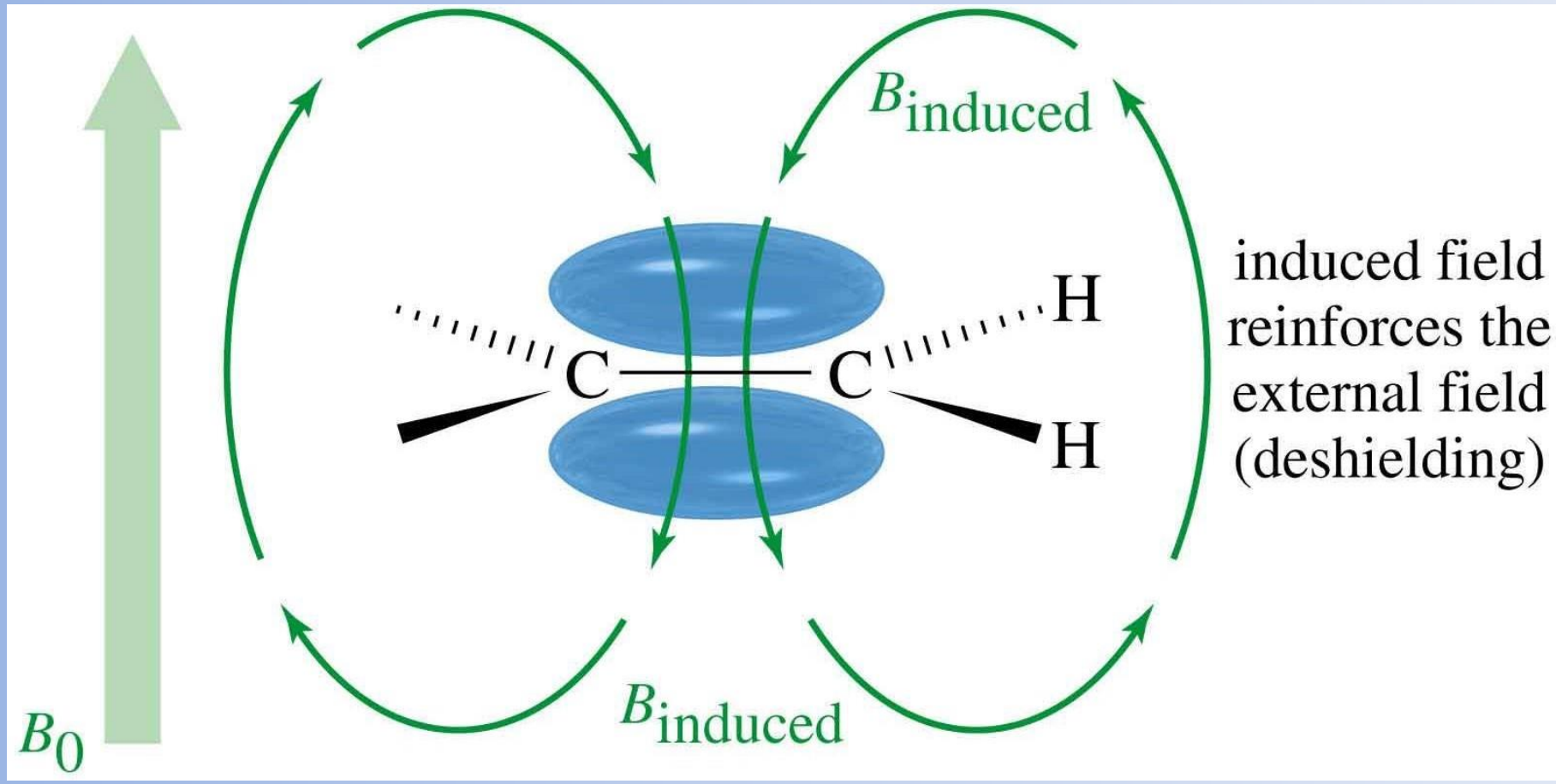
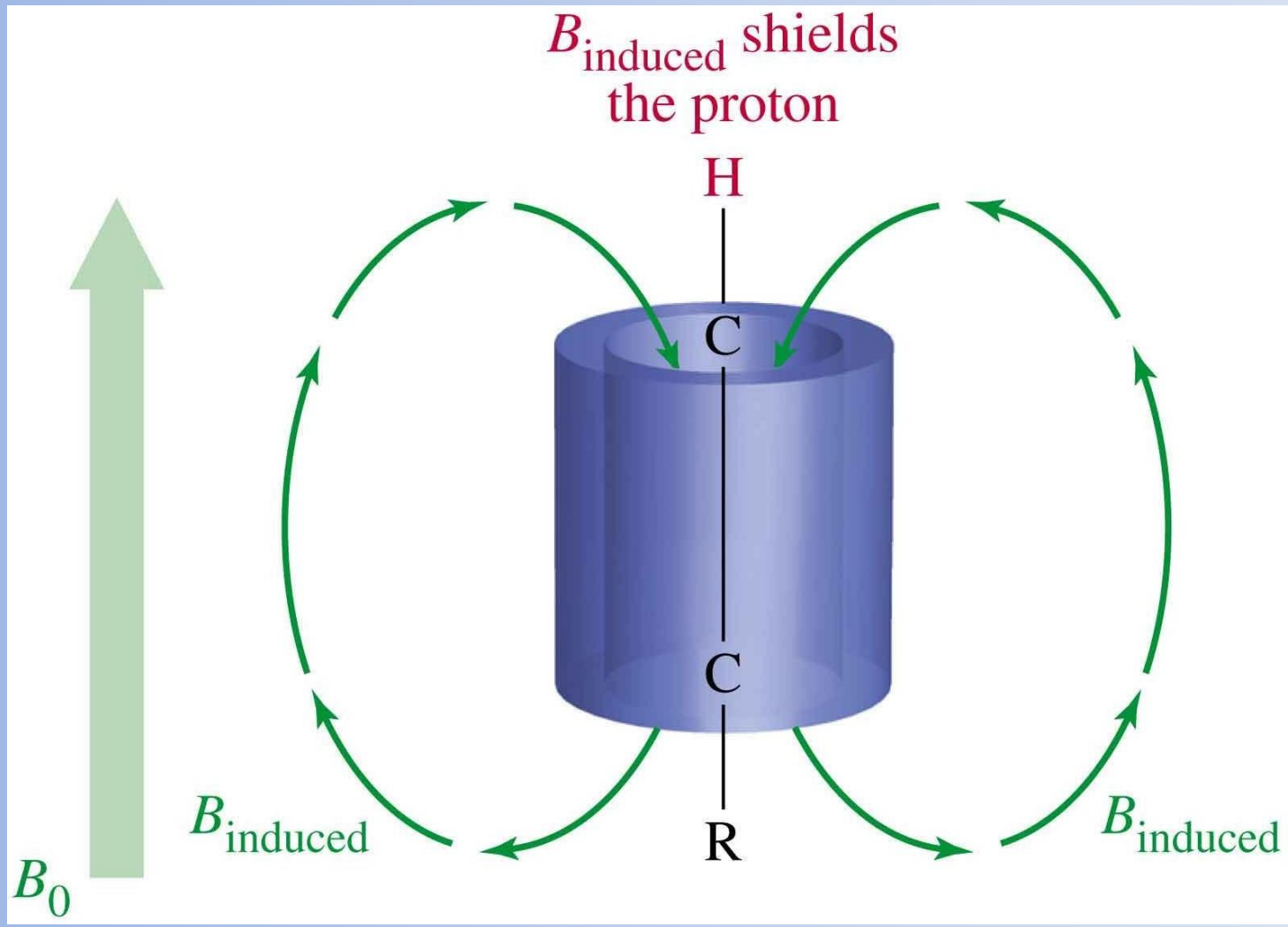
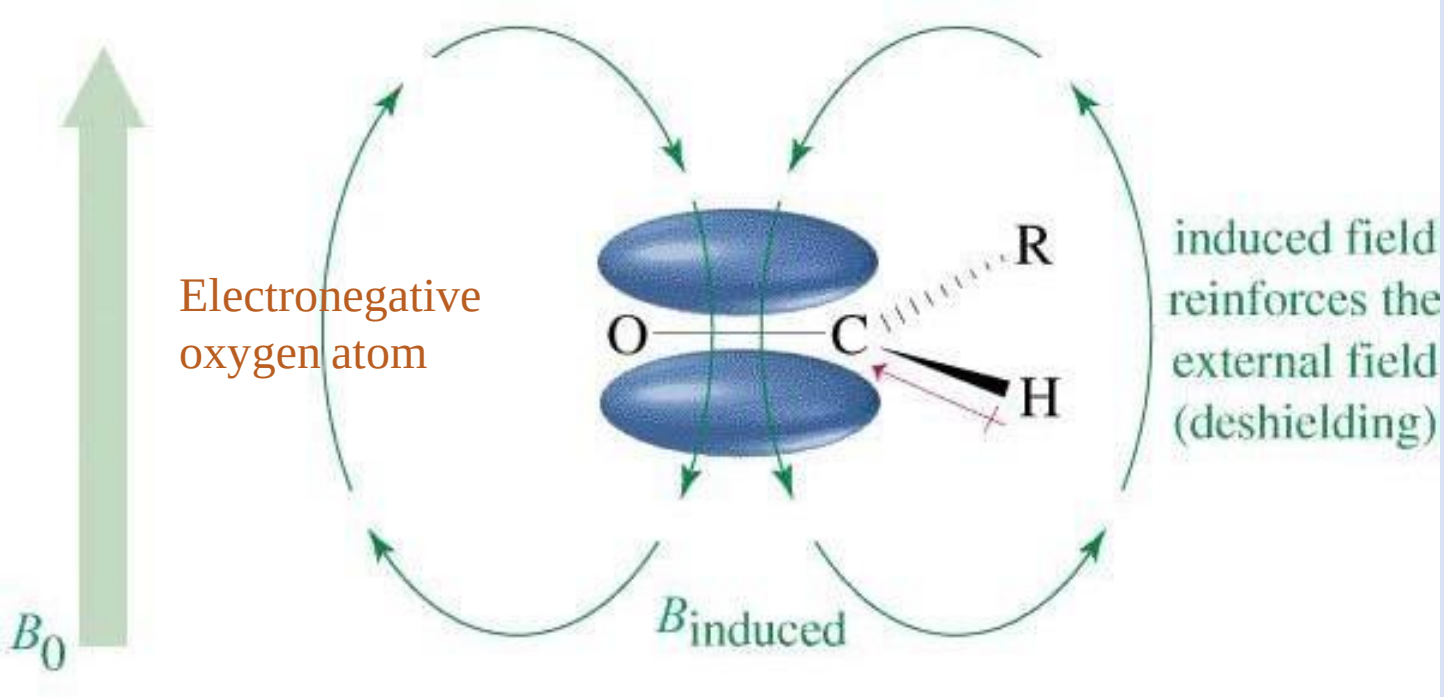
Vinyl Protons, δ5-δ6



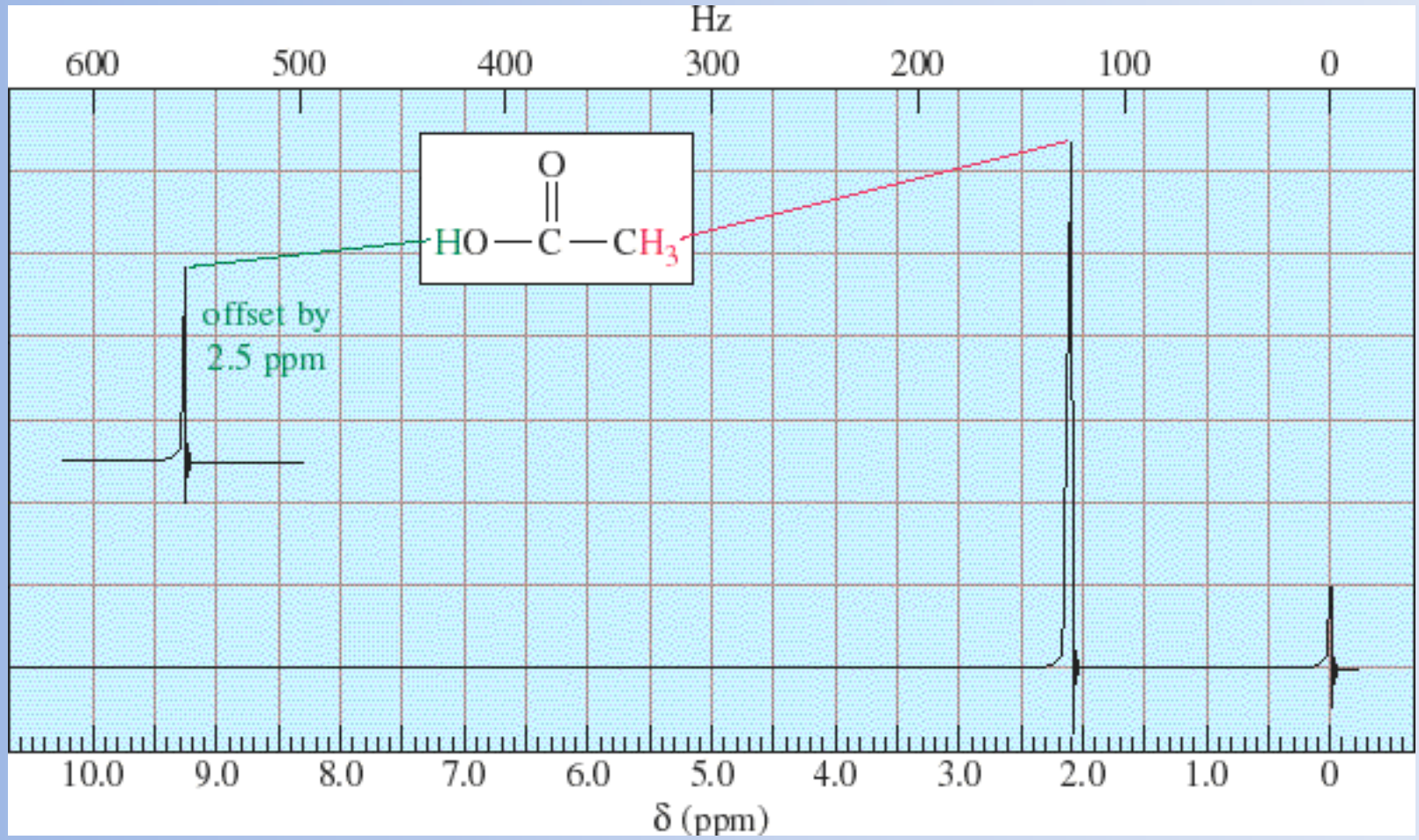
Acetylenic Protons, δ2.5



Aldehyde Proton, δ9-δ10

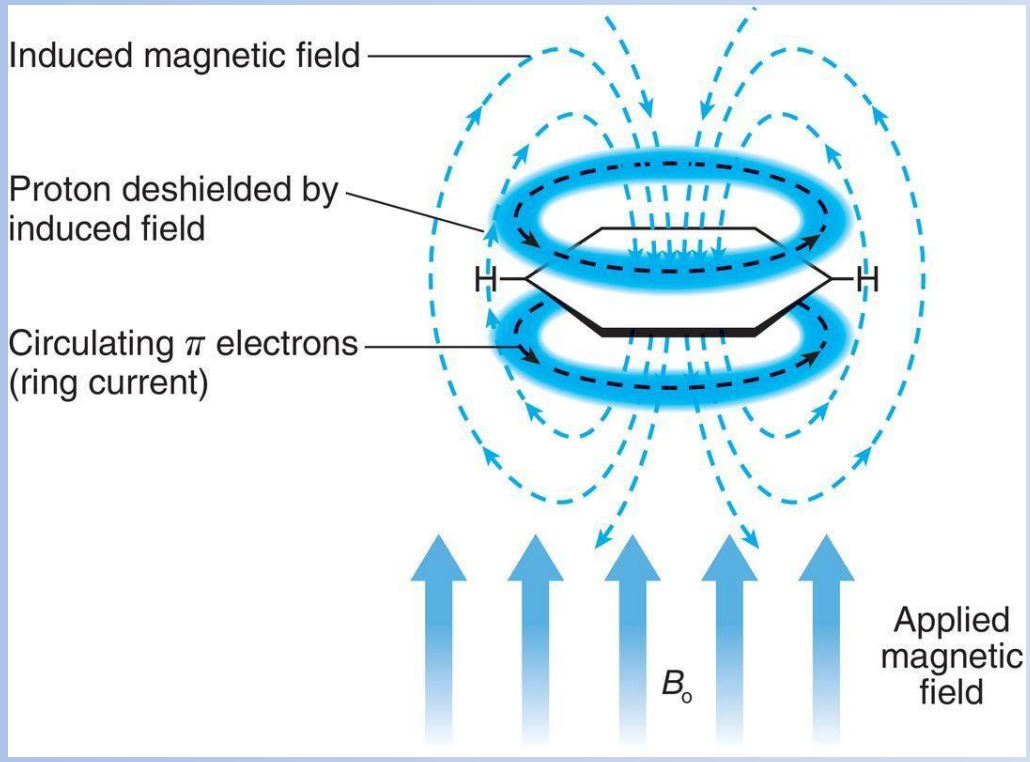


Carboxylic Acid Proton, δ+10



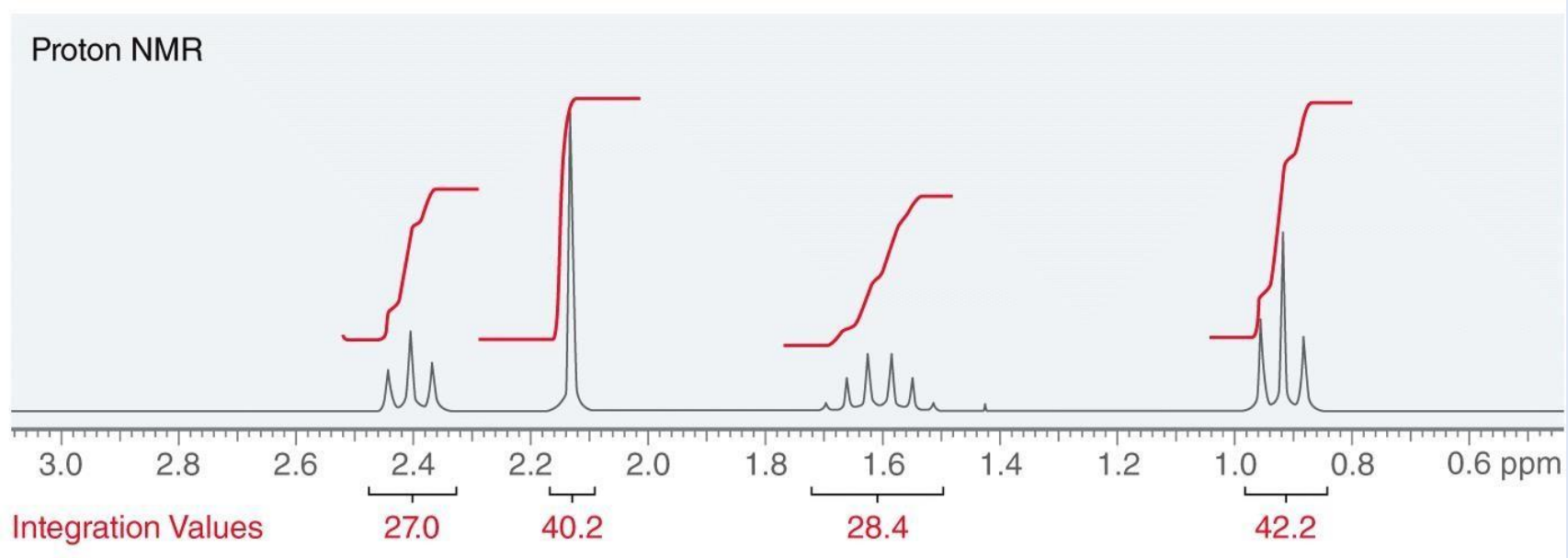
Chemical Shift – Anisotropic Effects

- When the electrons in a pi system are subjected to an external magnetic field, they circulate and produce a magnetic field, causing **diamagnetic anisotropy**



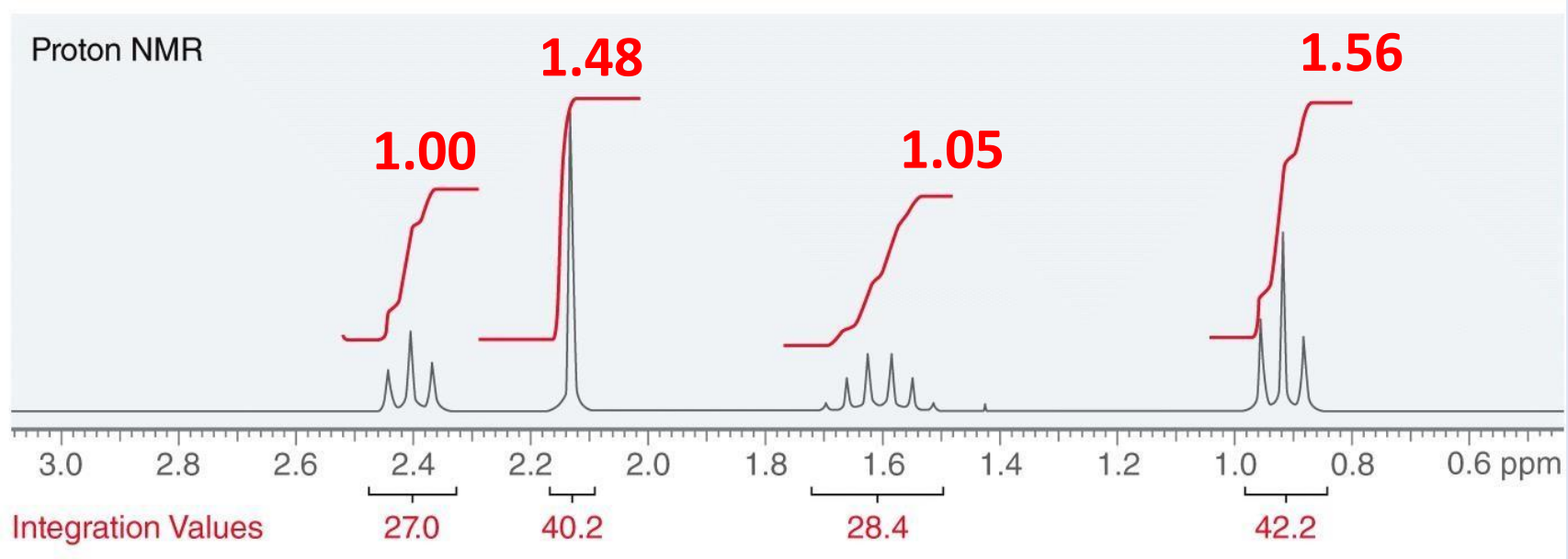
Integration

- The **integration** (area) under the peak quantifies the relative number of protons giving rise to a signal
- A computer will calculate the area of each peak representing that area with a **step-curve**
-



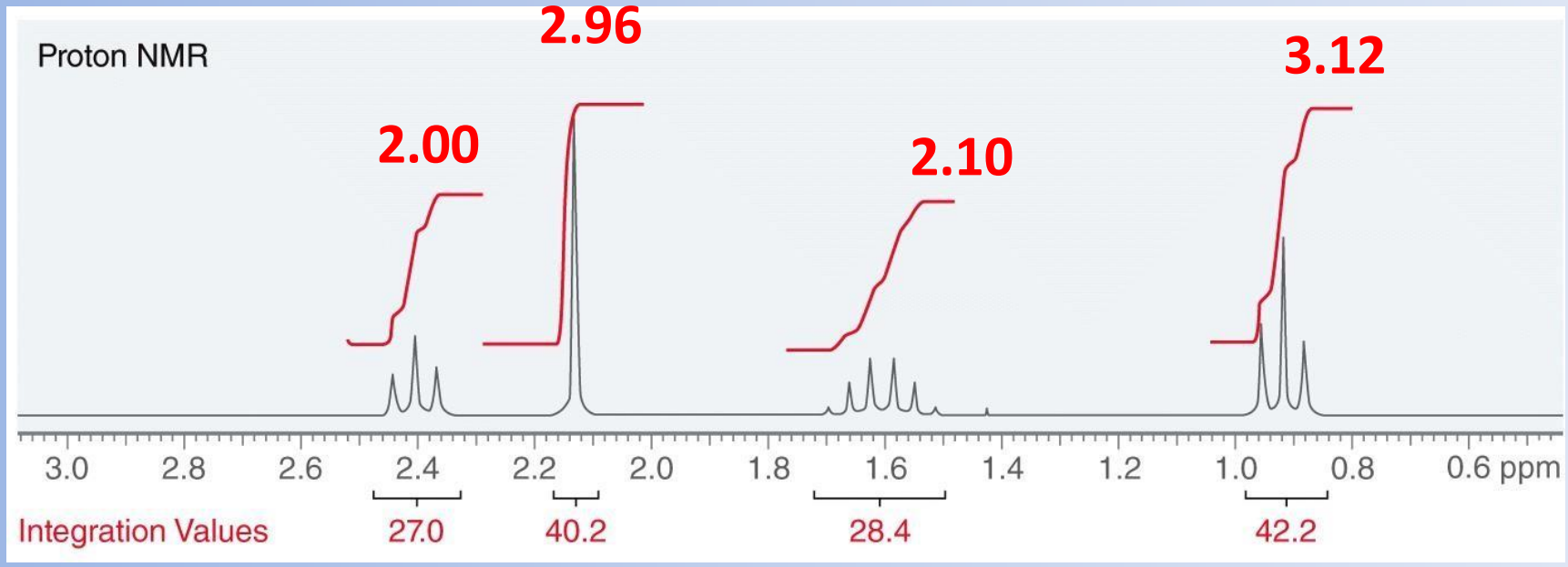
Integration

- The computer operator sets one of the peaks to a whole number to let it represent a number of protons
- The computer uses the integration ratios to set the values for the other peaks



Integration

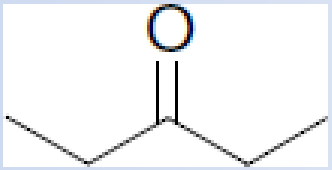
- Integrations represent numbers of protons, so you must adjust the values to whole numbers
- If the integration of the first peak is doubled, the computer will adjust the others according to the ratio



Integration

- The **integrations** are relative quantities rather than an absolute count of the number of protons

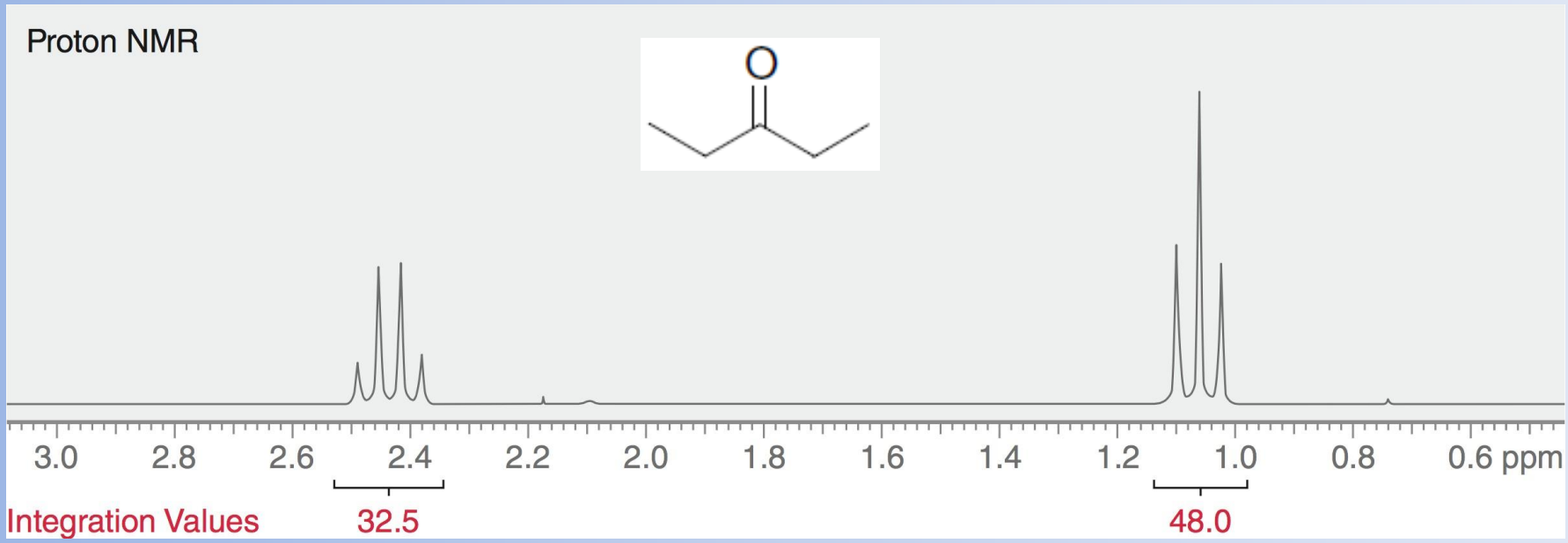
- Symmetry can also affect integrations



- -3pentanone has two kinds of protons. The relative integration value of the two signals would be 2:3

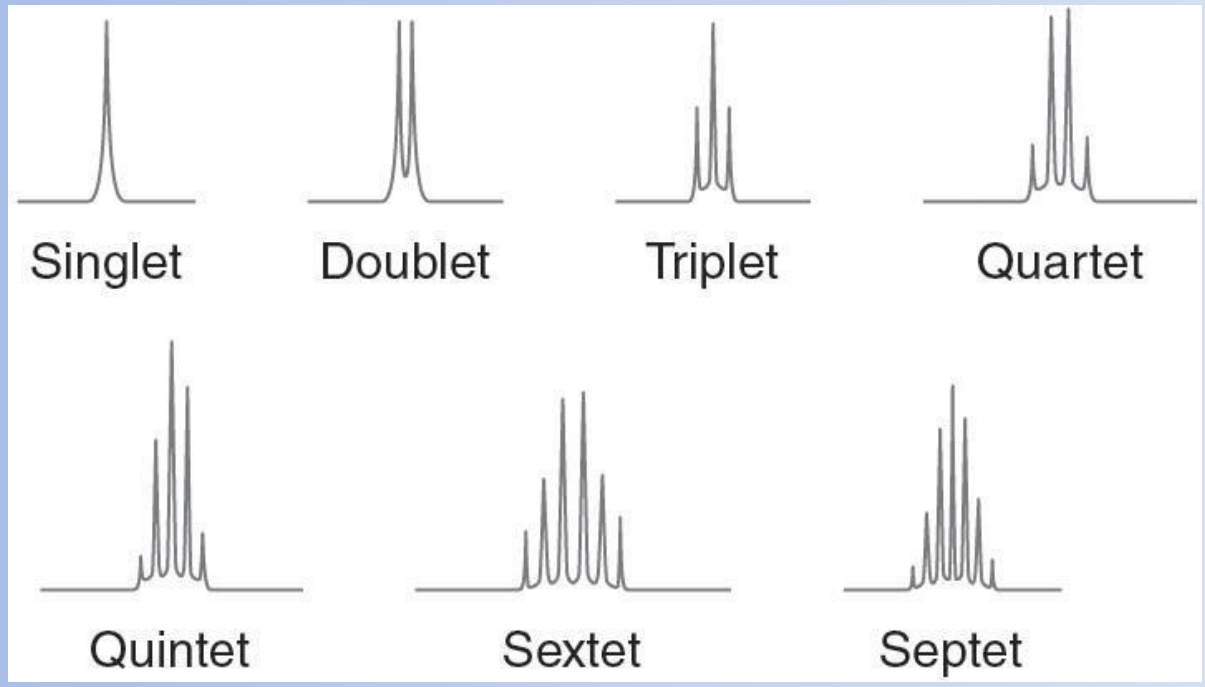
Integration

- The molecular formula ($C_5H_{10}O$) must be known in order to know that the **absolute ratio is actually 4:6**, and not 2:3



Multiplicity

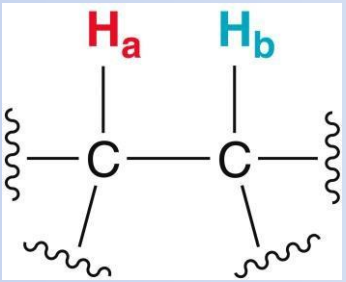
- **Multiplicity (splitting pattern):** the number of peaks in a given signal



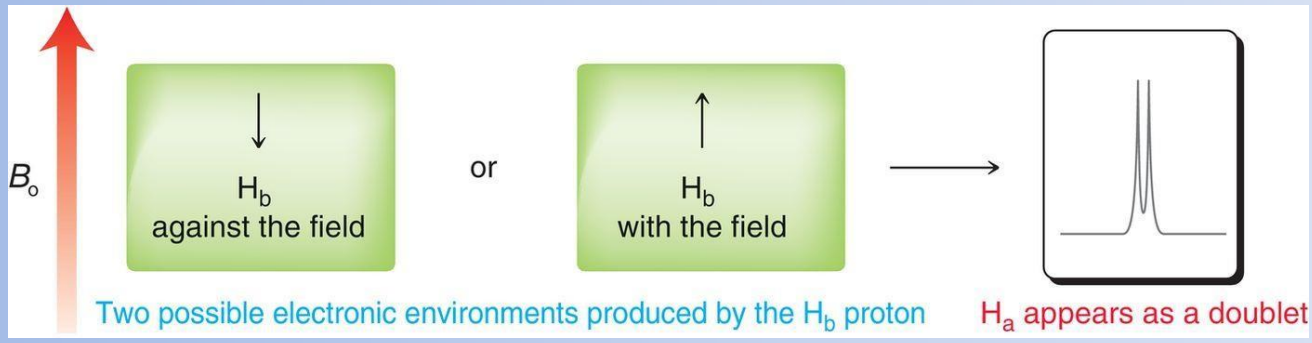
Multiplicity

- Multiplicity results from magnetic affects that protons have on each other

- Consider protons H_a and H_b

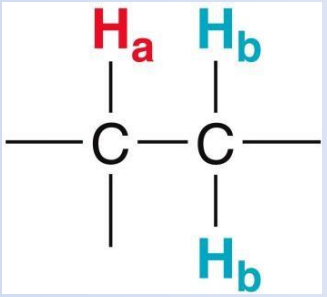


- Since protons align with or against the external magnetic field, so there will be two different magnetic environments for H_a:

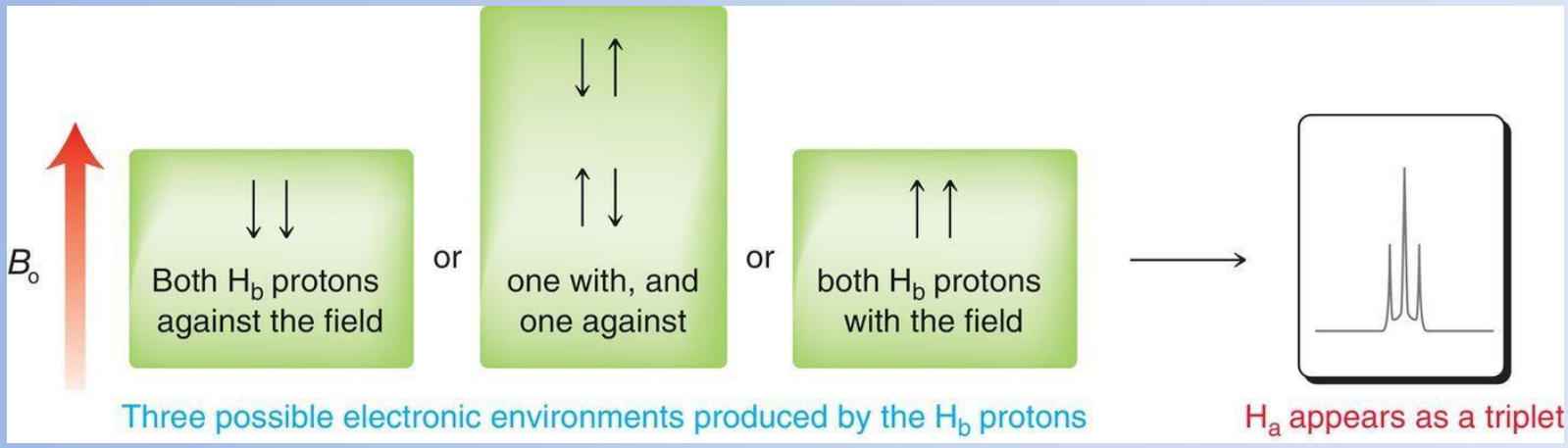


Multiplicity

- Consider an example where there are two protons on the adjacent carbon

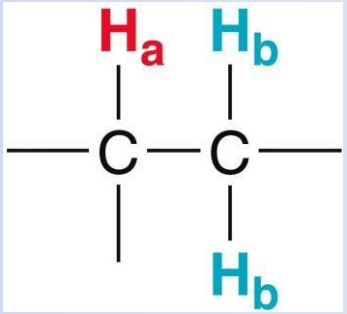


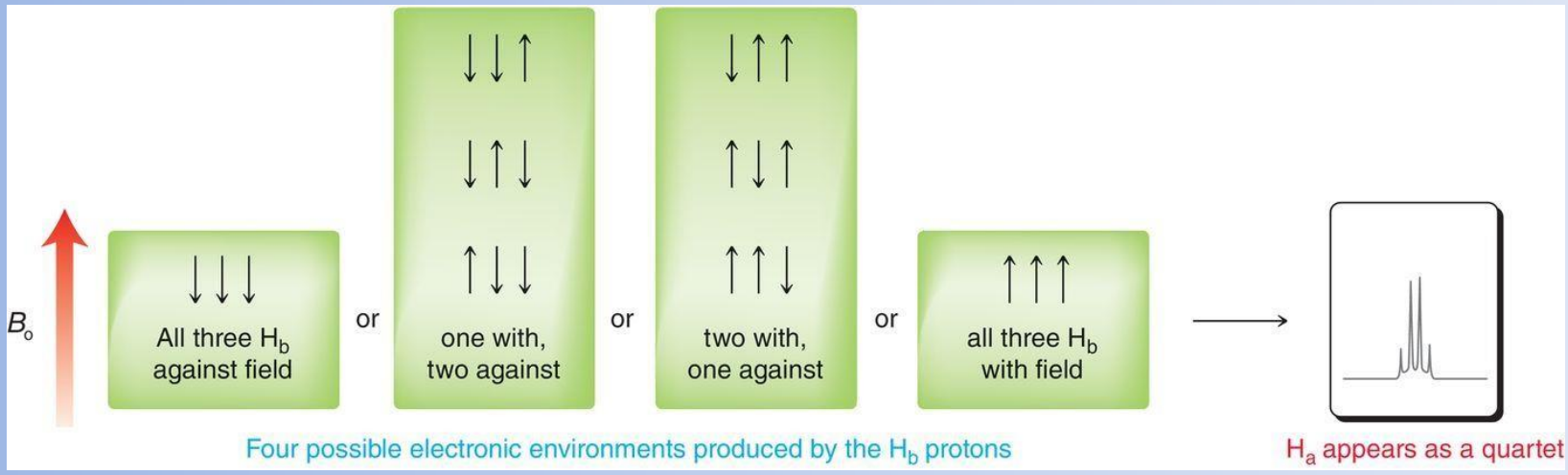
- Here, there are three possible environments for H_a



Multiplicity

- Now, consider a scenario where H_a is split by three neighboring H_b atoms:





The N + 1 Rule

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

Relative Peak Intensities of Symmetric Multiplets		
Number of Equivalent Protons Causing Splitting	*Number of Peaks (multiplicity)*	*Area Ratios (Pascal's triangle)*
0	1 (singlet)	1
1	2(doublet)	1 1
2	3 (triplet)	1 2 1
3	4 (quartet)	1 3 3 1
4	5 (quintet)	1 4 6 4 1
5	6 (sextet)	1 5 10 10 5 1
6	7 (septet)	1 6 15 20 15 6 1

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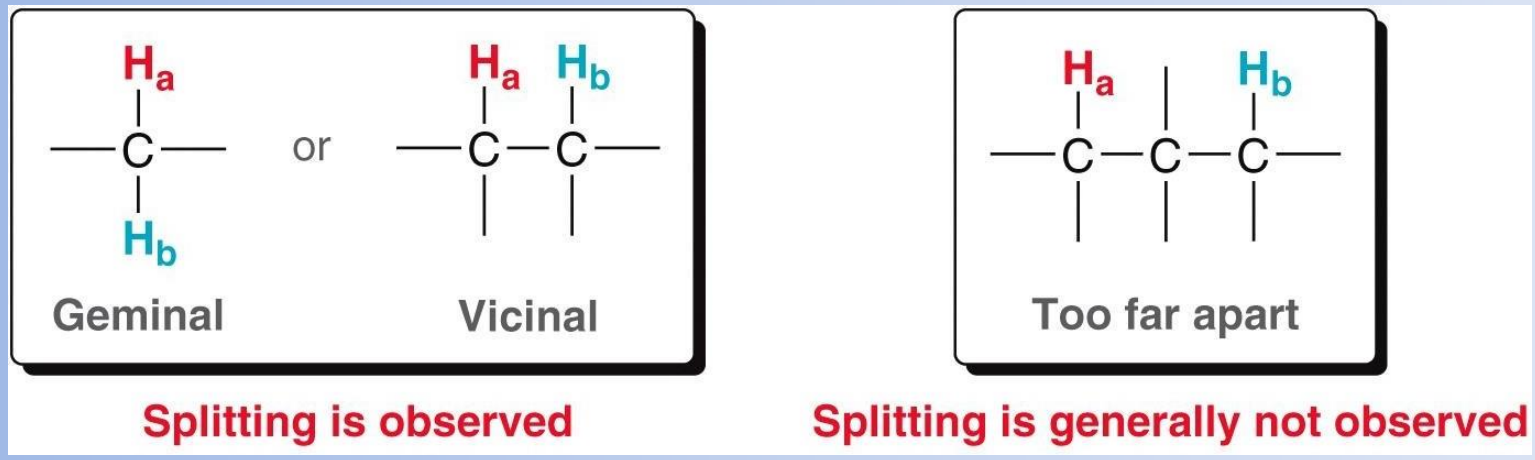
Multiplicity

- Remember **three key rules** for splitting:

1. Equivalent protons can not split one another because they resonate together
2. To split each other, protons must be within a 2 or 3 bond distance

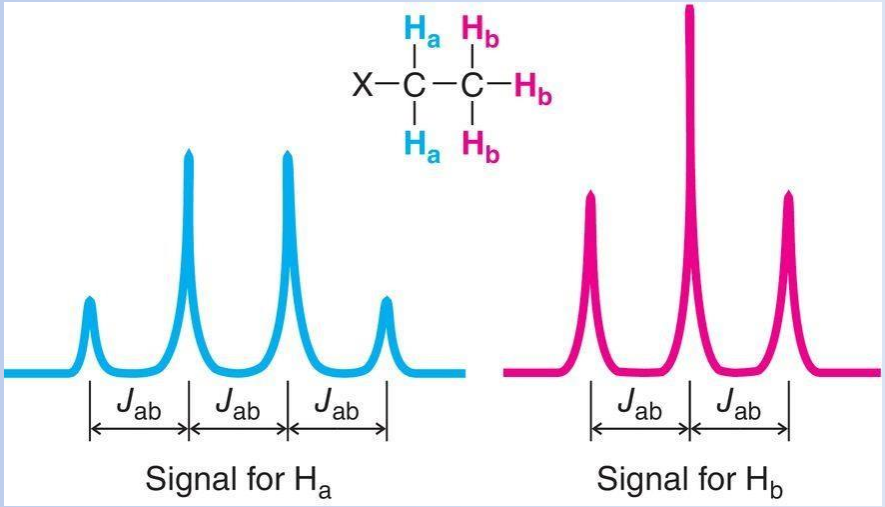


Multiplicity

- The degree to which a neighboring proton will couple to its neighbor is called a **coupling constant**, or ***J* value**
- The ***J* value** is the distance between peaks of a splitting pattern measured in units of Hz

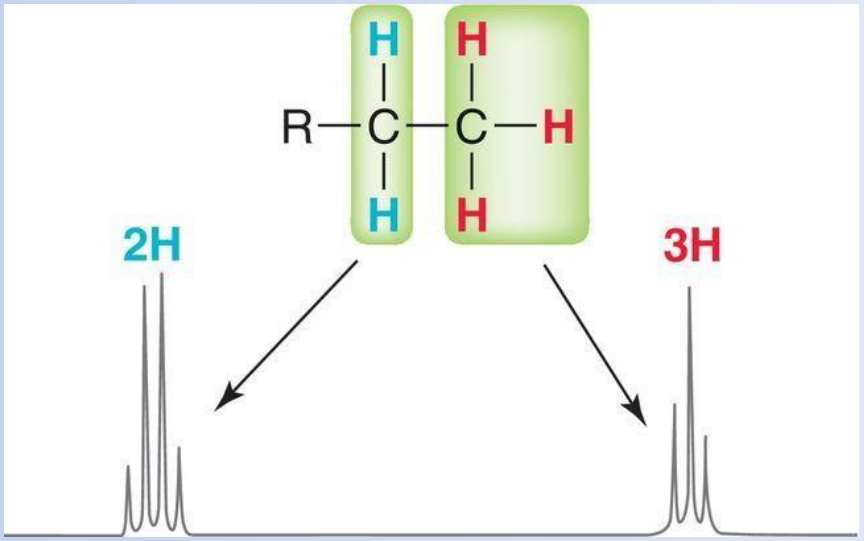
- protons splitting each other will have the same coupling constant

- $J_{ab} = J_{ba}$



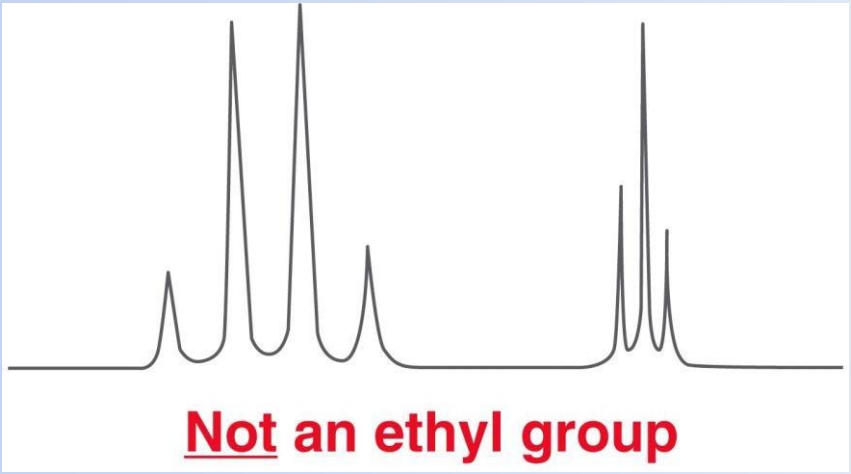
Multiplicity

- Sometimes recognizable splitting patterns will stand out in a spectrum



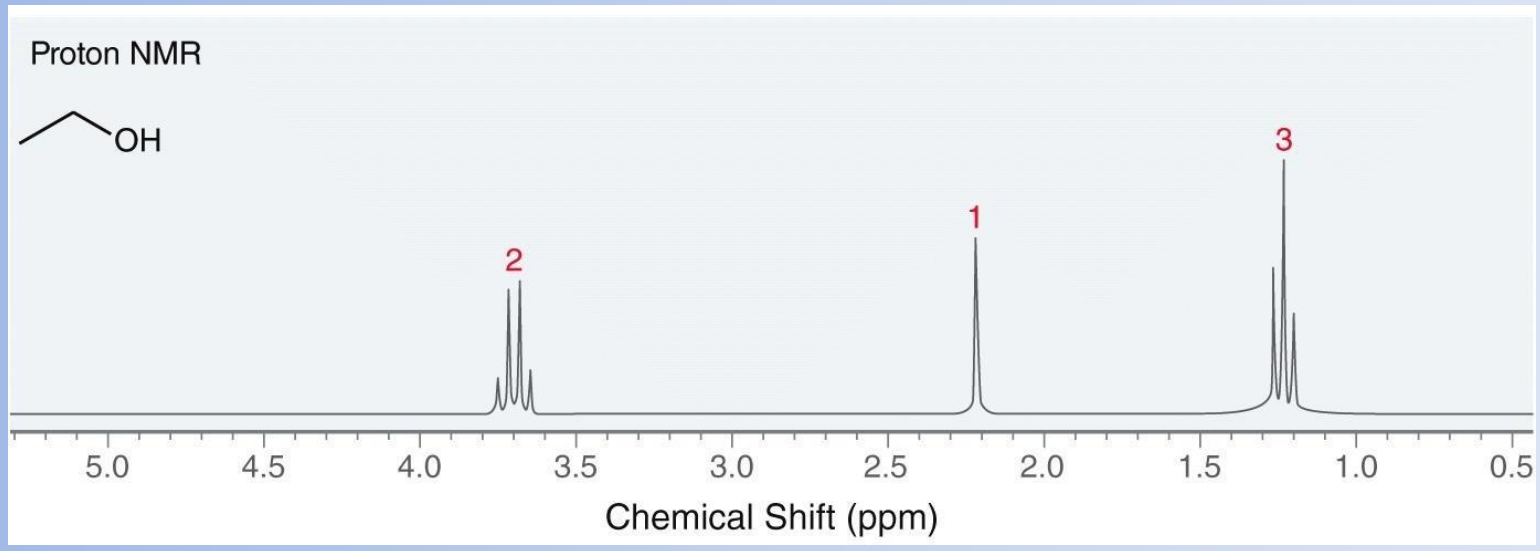
- An isolated ethyl group gives a triplet and a quartet

- The triplet and quartet must have the same coupling constant if they are splitting each other



Multiplicity

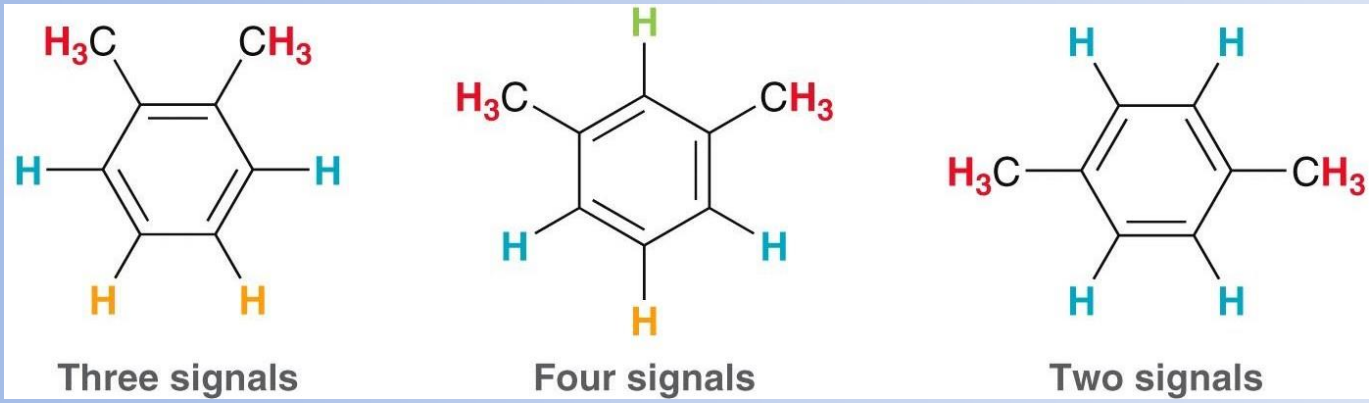
- Splitting is not observed for some protons. Consider ethanol



- The protons bonded to carbon split each other, but the hydroxyl proton is not split

Using 1H NMR to Distinguish between Compounds

- The three molecules below might be difficult to distinguish by IR of MS.



- They are easily distinguished with ^{1}H NMR because they do not have the same # of protons.

Range of Magnetic Coupling

- Equivalent protons do not split each other.
- Protons bonded to the same carbon will split each other only if they are not equivalent.
- Protons on adjacent carbons normally will couple.
- Protons separated by four or more bonds will not couple.

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Coupling Constants

- Distance between the peaks of multiplet
- Measured in Hz
- Not dependent on strength of the external field
- Multiplets with the same coupling constants may come from adjacent groups of protons that split each other.

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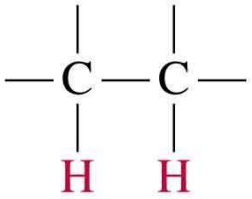
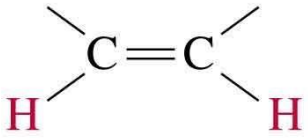
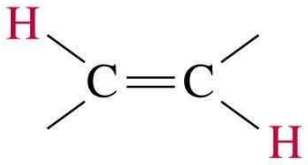
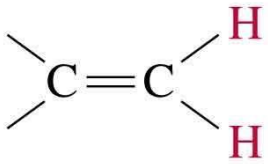
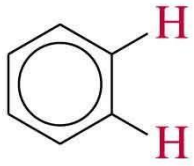
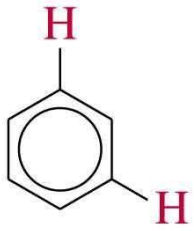
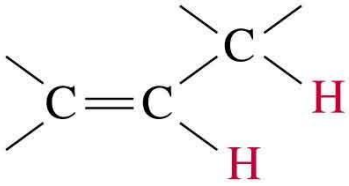
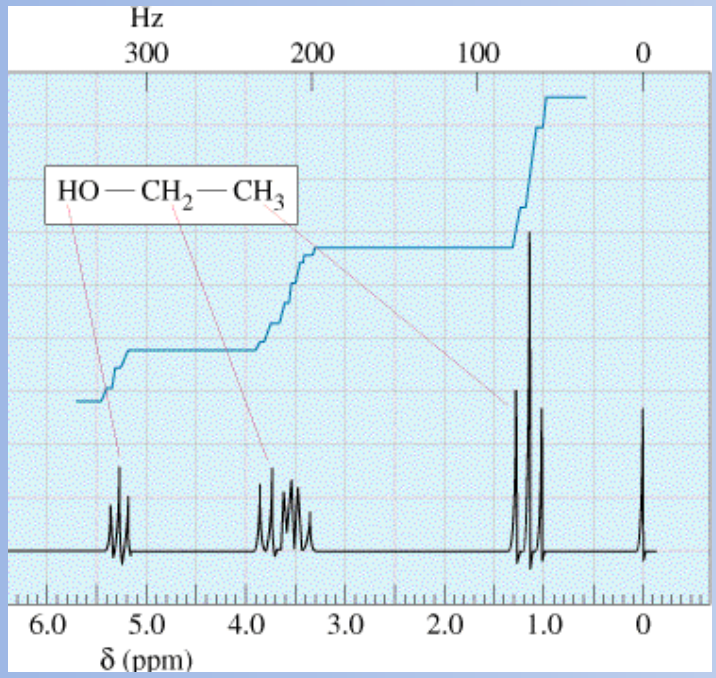
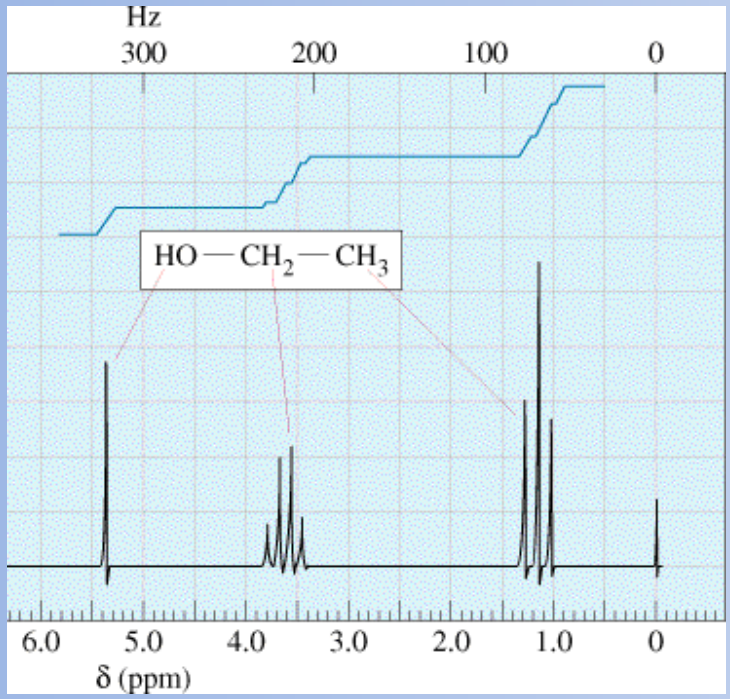
Values for Coupling Constants

		Approx. J
	(free rotation)	7 Hz[a]
	(cis)	10 Hz
	(trans)	15 Hz
	(geminal)	2 Hz

		Approx. J
	(ortho)	8 Hz
	(meta)	2 Hz
	(allylic)	6 Hz

[a]The 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.



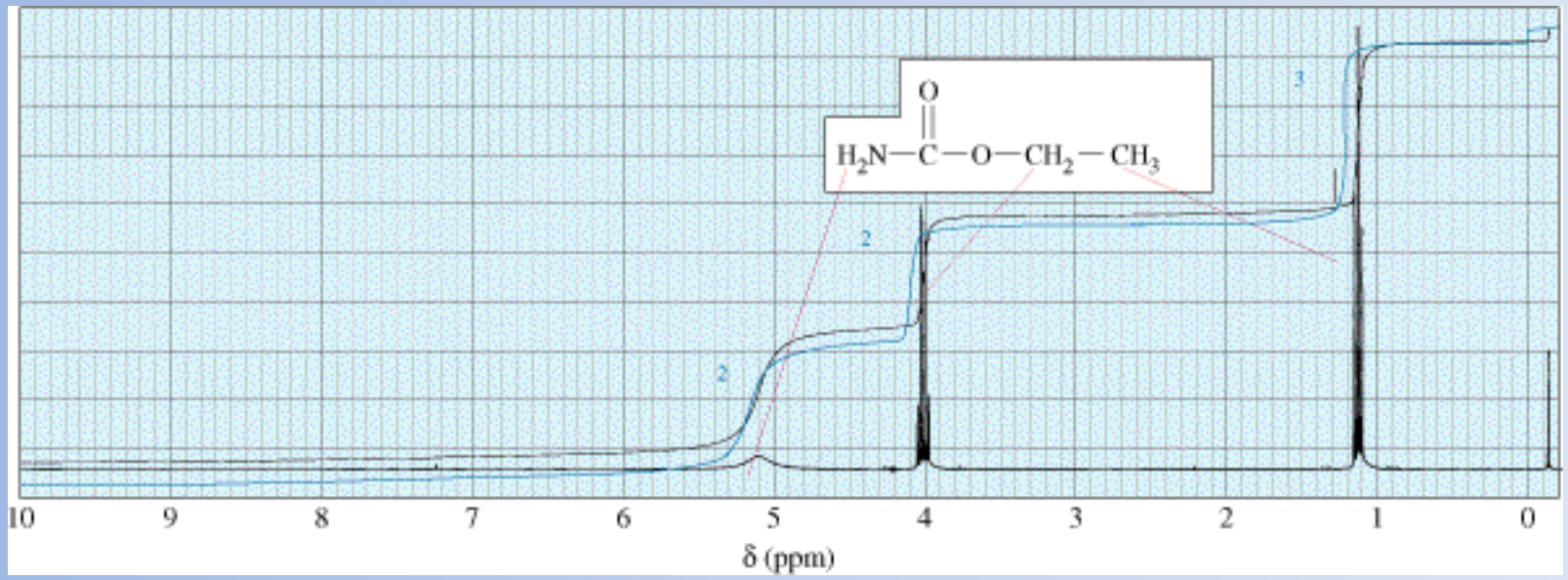


Hydroxyl Proton

- Ultrapure samples of ethanol show splitting.
- Ethanol with a small amount of acidic or basic impurities will not show splitting.

N-H Proton

- Moderate rate of exchange.
- Peak may be broad.



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