Magnets placed in a magnetic field align with the magnetic field.

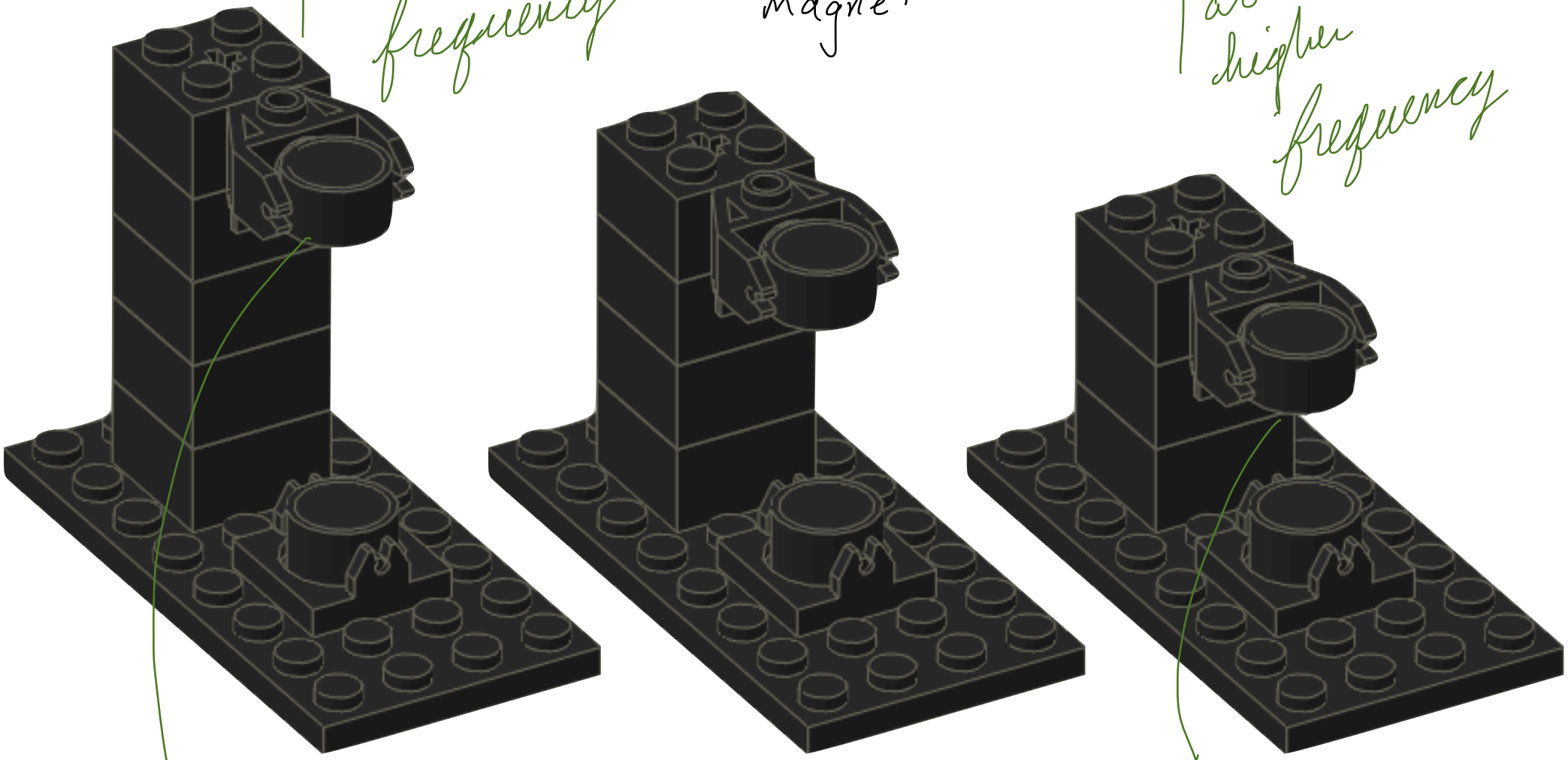
When perturbed the magnets will "resonate".

The frequency of the resonance depends on the strength of the magnetic fields

resonates at lower frequency

^1H is a magnet

resonates at higher frequency



weaker field

stronger field

^3H & ^2H not magnets

spin $\frac{1}{2}$

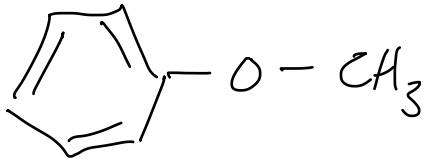
a super conducting wire with e^- going round and round

~1.4 T magnet will cause ^1H to align & resonate at ~60,000,000 Hz

900 MHz, (21.2 T) NMR Magnet at HWB-NMR, Birmingham, UK

https://en.wikipedia.org/wiki/Nuclear_magnetic_resonance#/media/File:HWB-NMR_-_900MHz_-_21.2_Tesla.jpg

sample experiences a uniform magnetic field

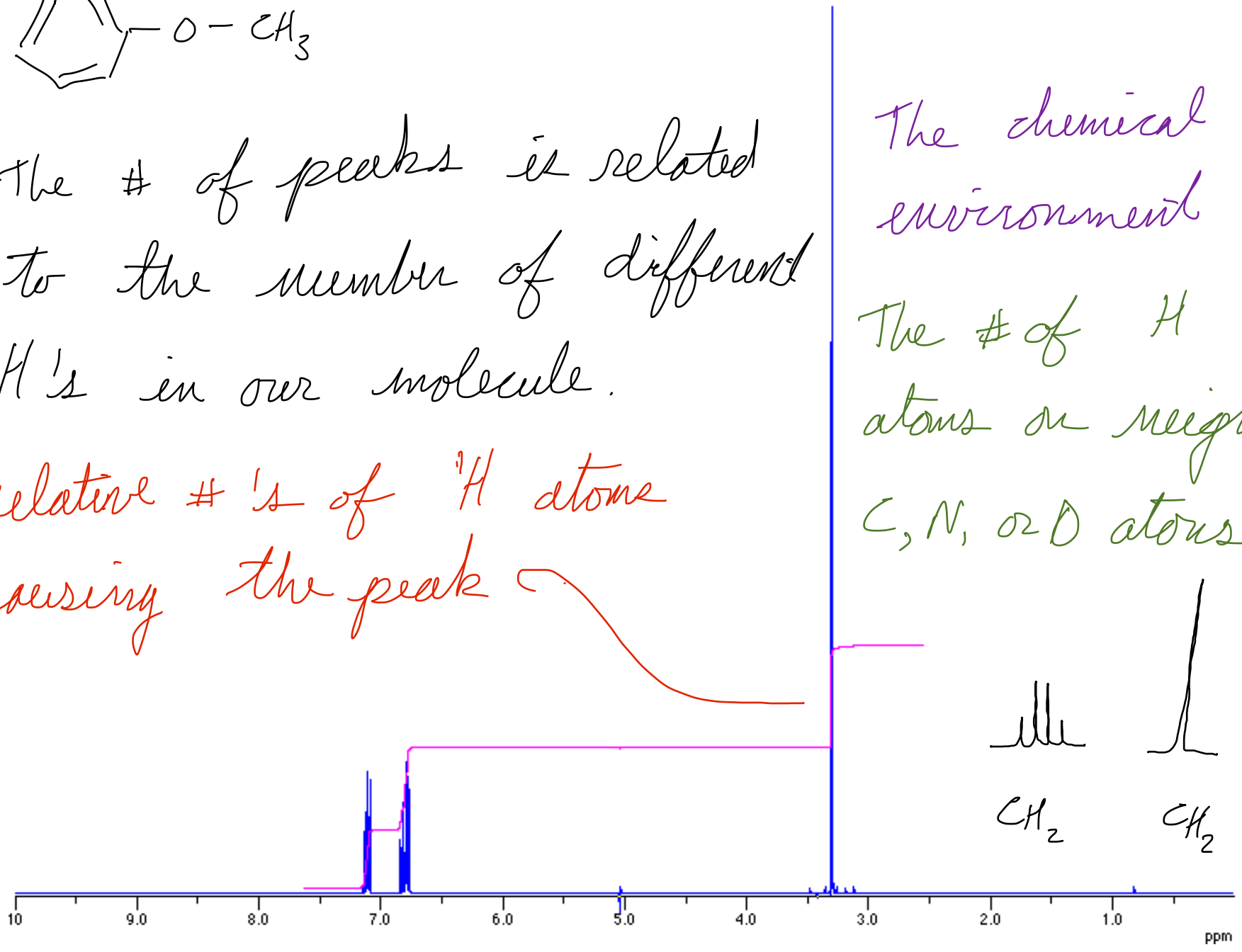


The # of peaks is related to the number of different H's in our molecule.

The chemical environment

The # of H atoms on neighboring C, N, or O atoms

relative #'s of ^1H atoms causing the peak



magnetic field varies based on position

www.radiologyinfo.org

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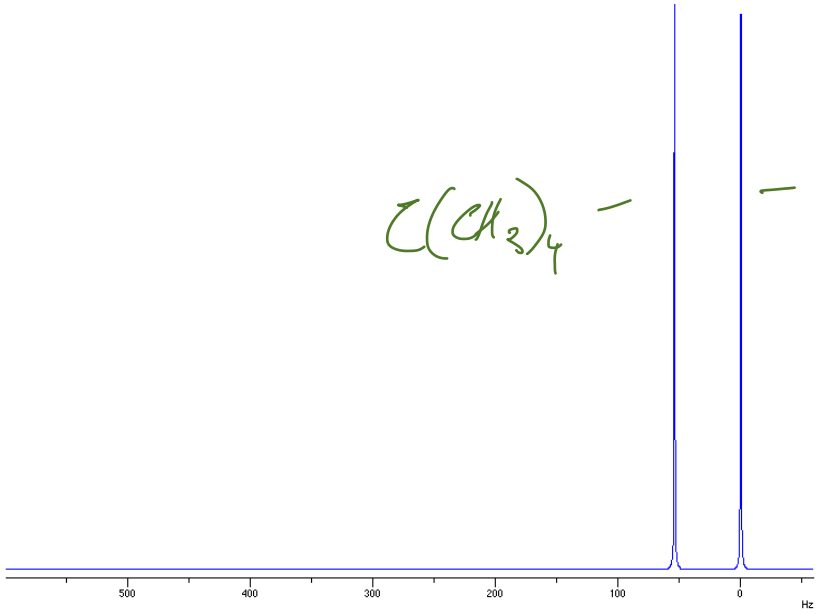
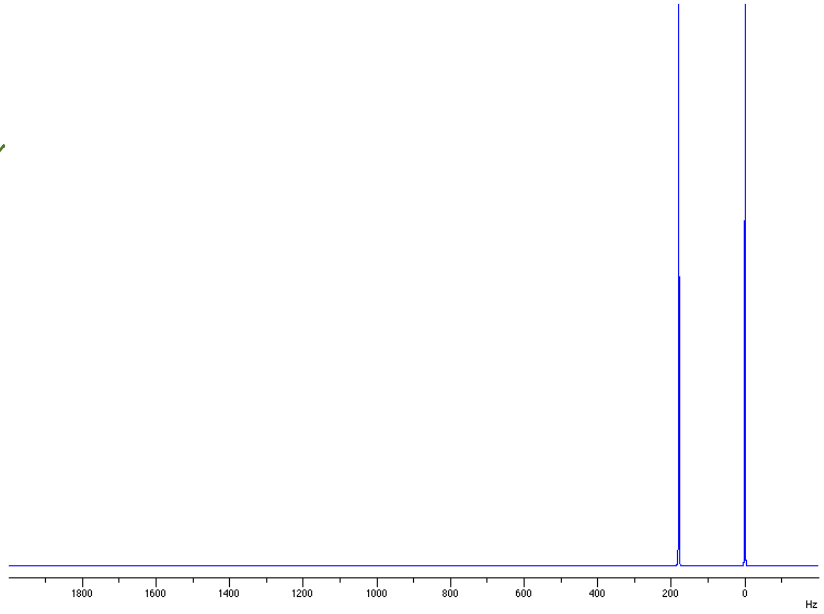
Magnetic Resonance Imaging H_2O



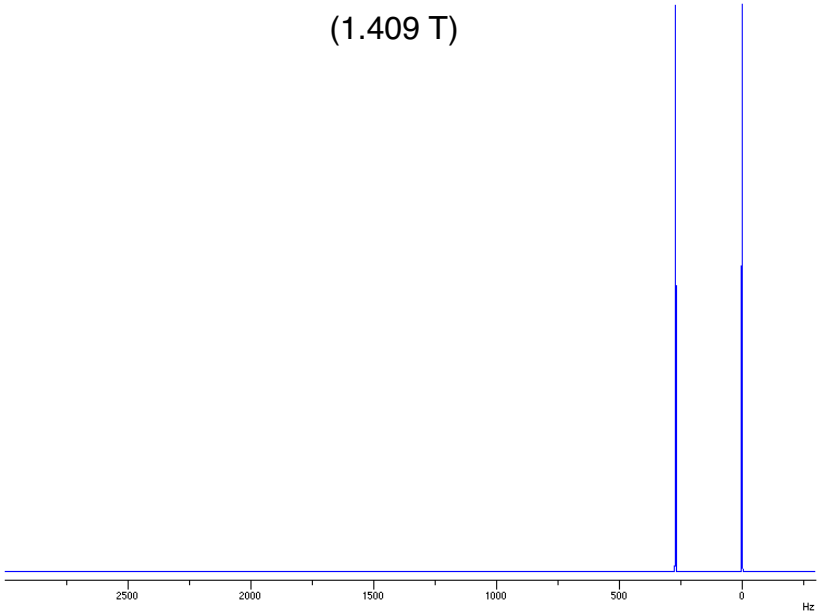
+ 60,000,000 Hz (60 MHz)

(1.409 T)



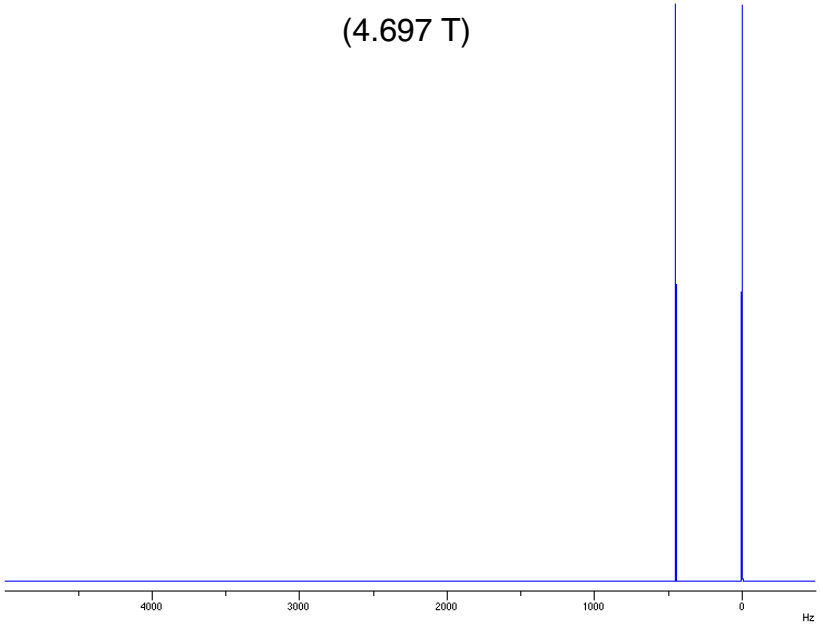
+ 200,000,000 (200 MHz)

(4.697 T)



+300,000,000 Hz (300 MHz)

(7.046 T)



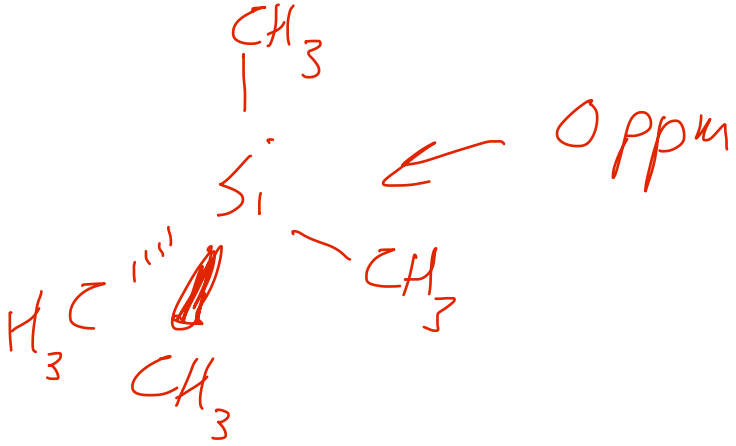
+ 500,000,000 Hz (500 MHz)

(11.743 T)

$$\delta \text{ ppm} = \frac{\nu_{(peak)}\text{Hz} - \nu_{(TMS)}\text{Hz}}{\nu_{(TMS)}\text{MHz}}$$

← reference molecule

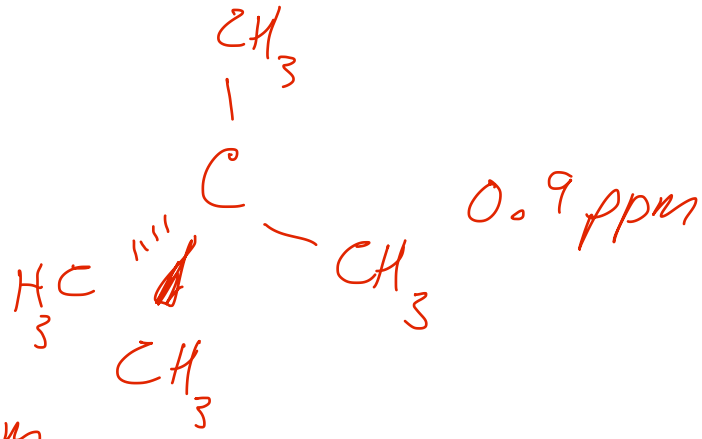
TMS = tetramethyl silane



← 0 ppm

1.409 T magnet TMS resonates at 60,000,000 Hz

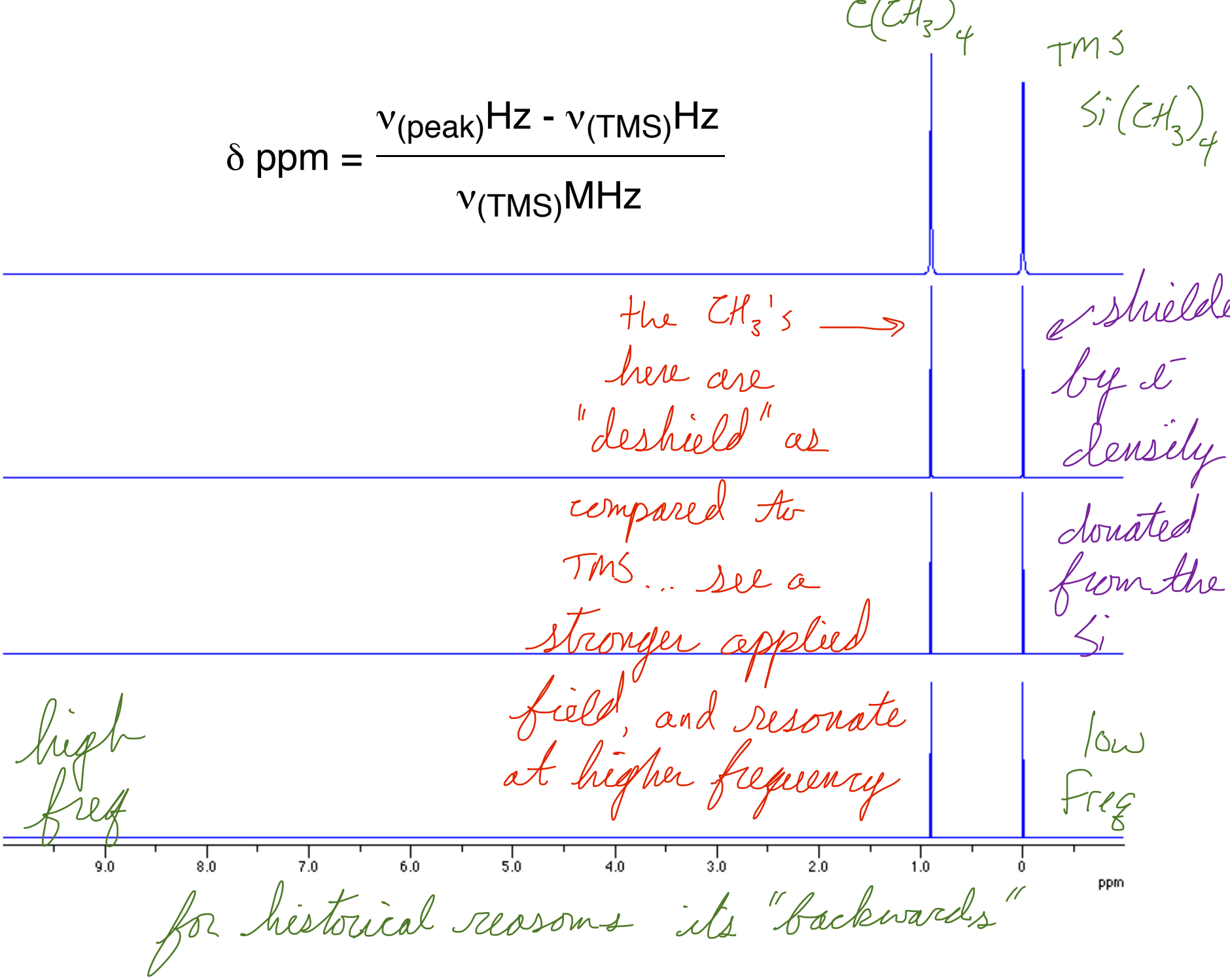
neopentane resonates at 60,000,054 Hz



0.9 ppm

$$\frac{(60,000,054 - 60,000,000)\text{Hz}}{60\ \text{MHz}} = 0.9\ \text{ppm}$$

$$\delta \text{ ppm} = \frac{\nu_{(peak)}\text{Hz} - \nu_{(TMS)}\text{Hz}}{\nu_{(TMS)}\text{MHz}}$$

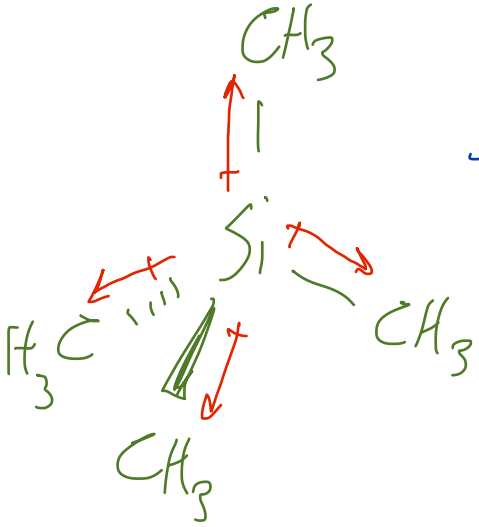


for historical reasons its "backwards"

shielding causes these H's to "see" a weaker field & thus resonate at a lower freq

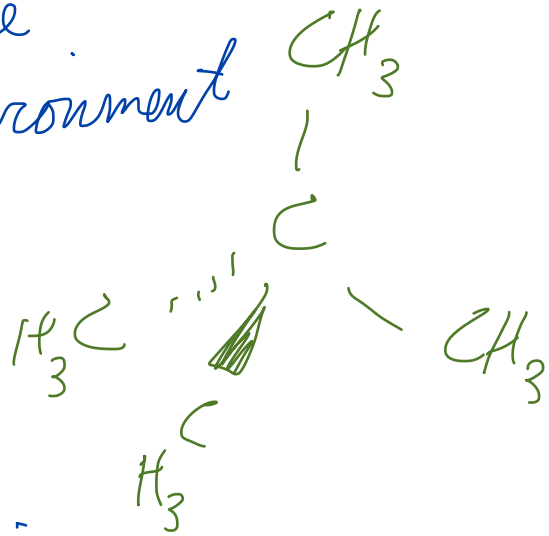
What gives rise to differences in chemical shift?

Why do the H's of tetramethylsilane resonate at a different frequency than 2,2-dimethylpropane?



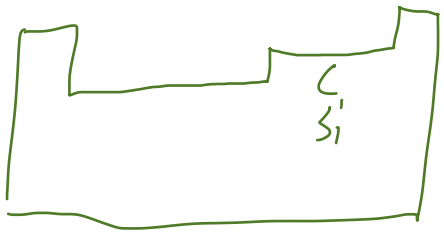
these H are in a more e⁻ rich environment

vs



position in NMR spectrum

these moving e⁻'s are creating a magnetic field which shields the H's from the applied field



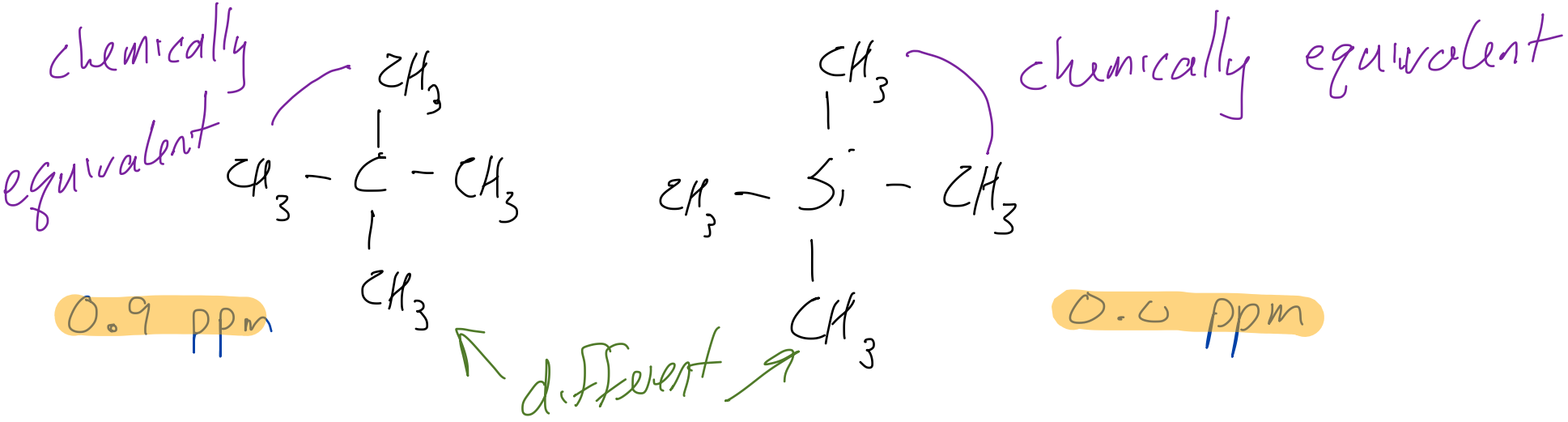
When placed in a magnetic field magnets will align with the applied field.

When perturbed magnets will resonate until they return to their equilibrium position.

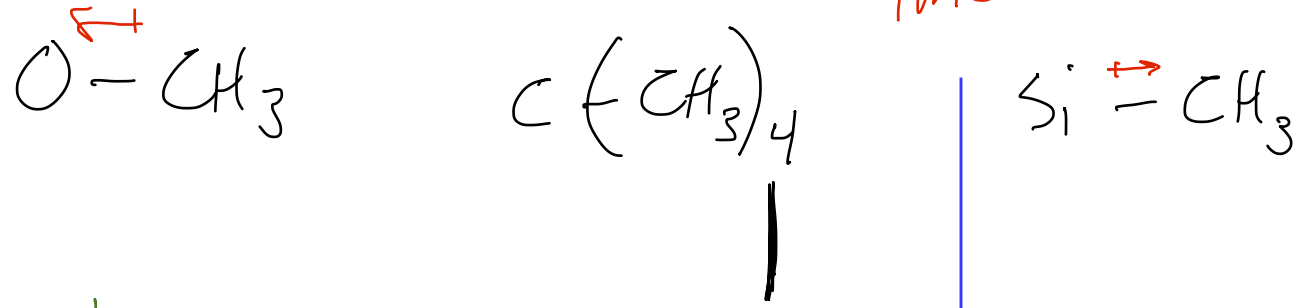
The frequency of the resonance is determined by the strength of the magnetic field.

Chemically inequivalent H atoms will usually exist in different magnetic environments and will, thus, be magnetically inequivalent and resonate at different frequencies. The position of the peaks relative to the position of a reference peak is referred to as their chemical shift.

Electronegative atoms deshield ^{1}H atoms. Deshielded ^{1}H atoms close to electronegative atoms experience a stronger applied field and resonate at higher frequencies as compared to well shielded ^{1}H atoms like those of tetramethylsilane.



TMS



'H's resonating over here would be "deshielded" by electro-negative atoms pulling the e⁻'s away

most organic 'H's are over here

'H's resonating over here would be strongly shielded by e⁻ density donated from neighbor-ing atoms

metal-H compounds

ethyl propionate

4 peaks means

4 sets of inequivalent H's

chemically inequivalent

magnetically inequivalent

higher freq deshielded

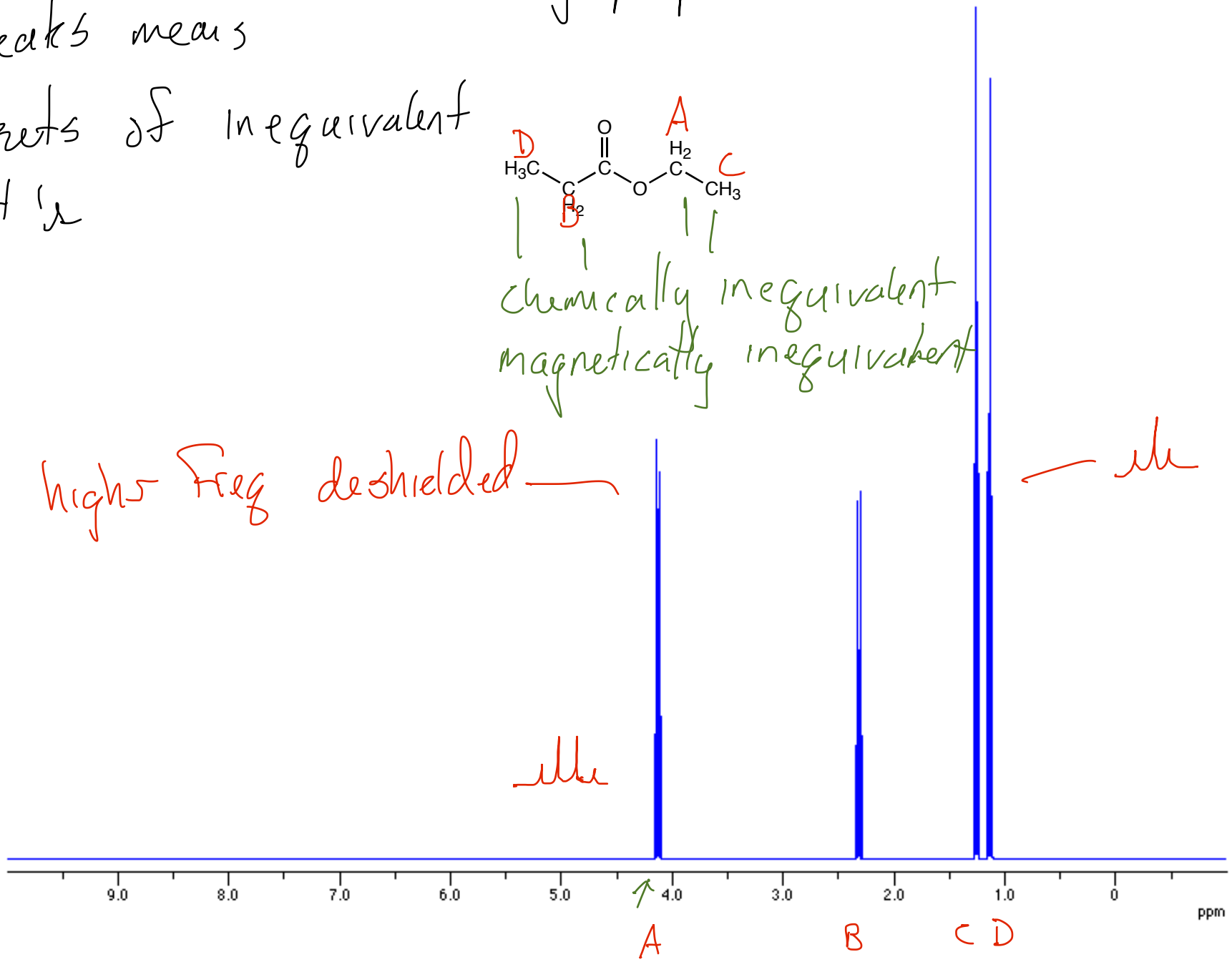
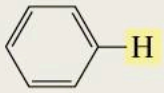
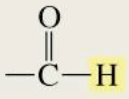
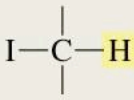
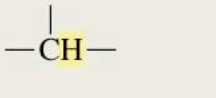
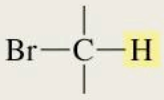
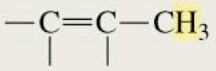
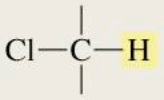
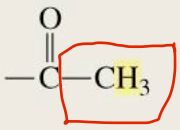
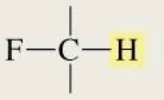
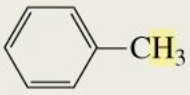
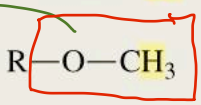
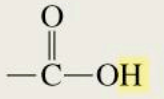
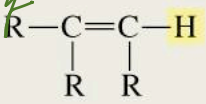
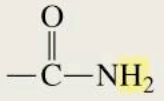


Table 14.1 Approximate Values of Chemical Shifts for ^{1}H NMR[a]

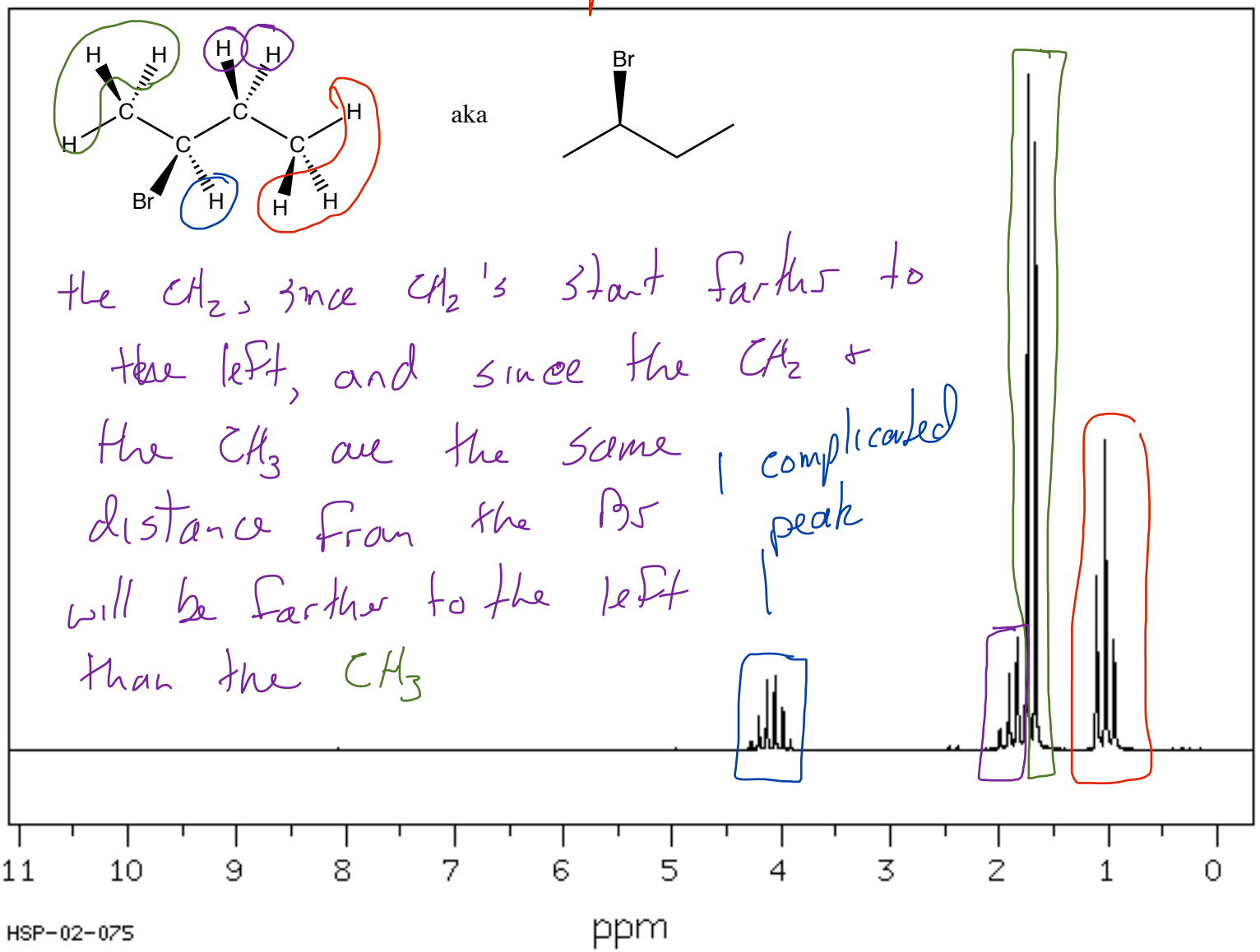
Type of proton	Approximate chemical shift (ppm)	Type of proton	Approximate chemical shift (ppm)
$(CH_3)_4Si$	0		6.5–8
$-CH_3$	0.9		9.0–10
$-CH_2-$	1.3		2.5–4
	1.4		2.5–4
	1.7		3–4
	2.1		4–4.5
	2.3	RNH_2	Variable, 1.5–4
$-C\equiv C-H$	2.4	ROH	Variable, 2–5
	3.3	ArOH	Variable, 4–7
	4.7		Variable, 10–12
	5.3		Variable, 5–8

[a]The values are approximate because they are affected by neighboring substituents.

π bonds create a magnetic field that reinforces the external field

O is deshielding CH_3 so CH_3 resonates at higher frequency

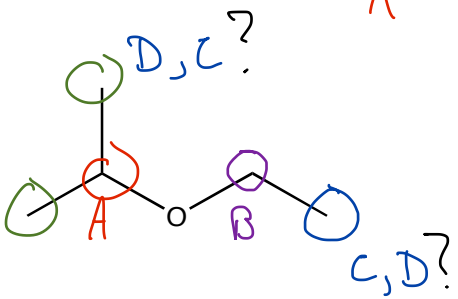
4 peaks



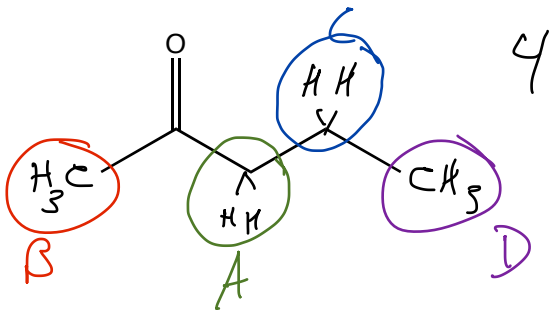
https://sdbs.db.aist.go.jp/sdbs/cgi-bin/landingpage?sdbsno=500

chemically inequivalent = magnetically inequivalent
most of the time

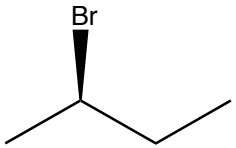
peaks

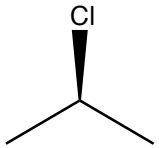


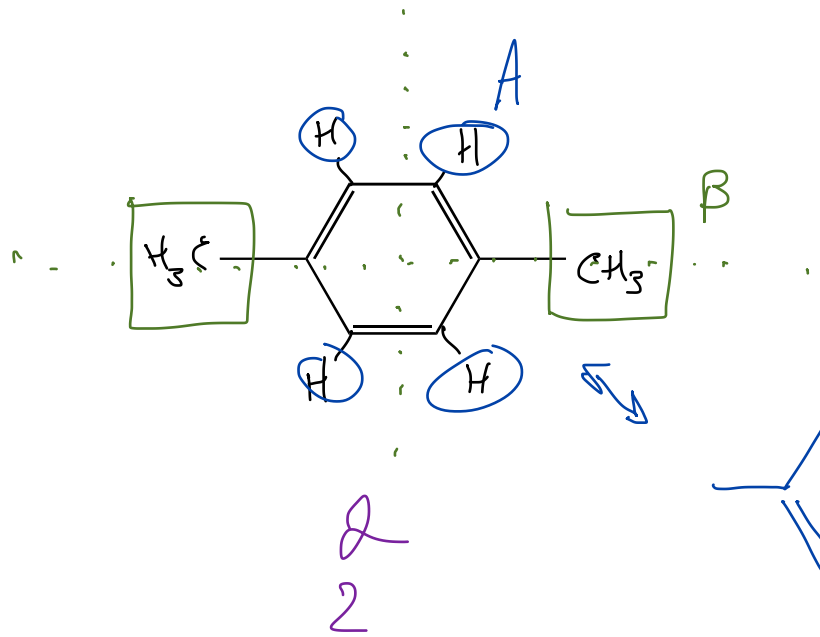
3 4



4 5

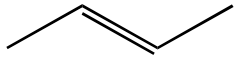






2

2



Number of different types of H atoms

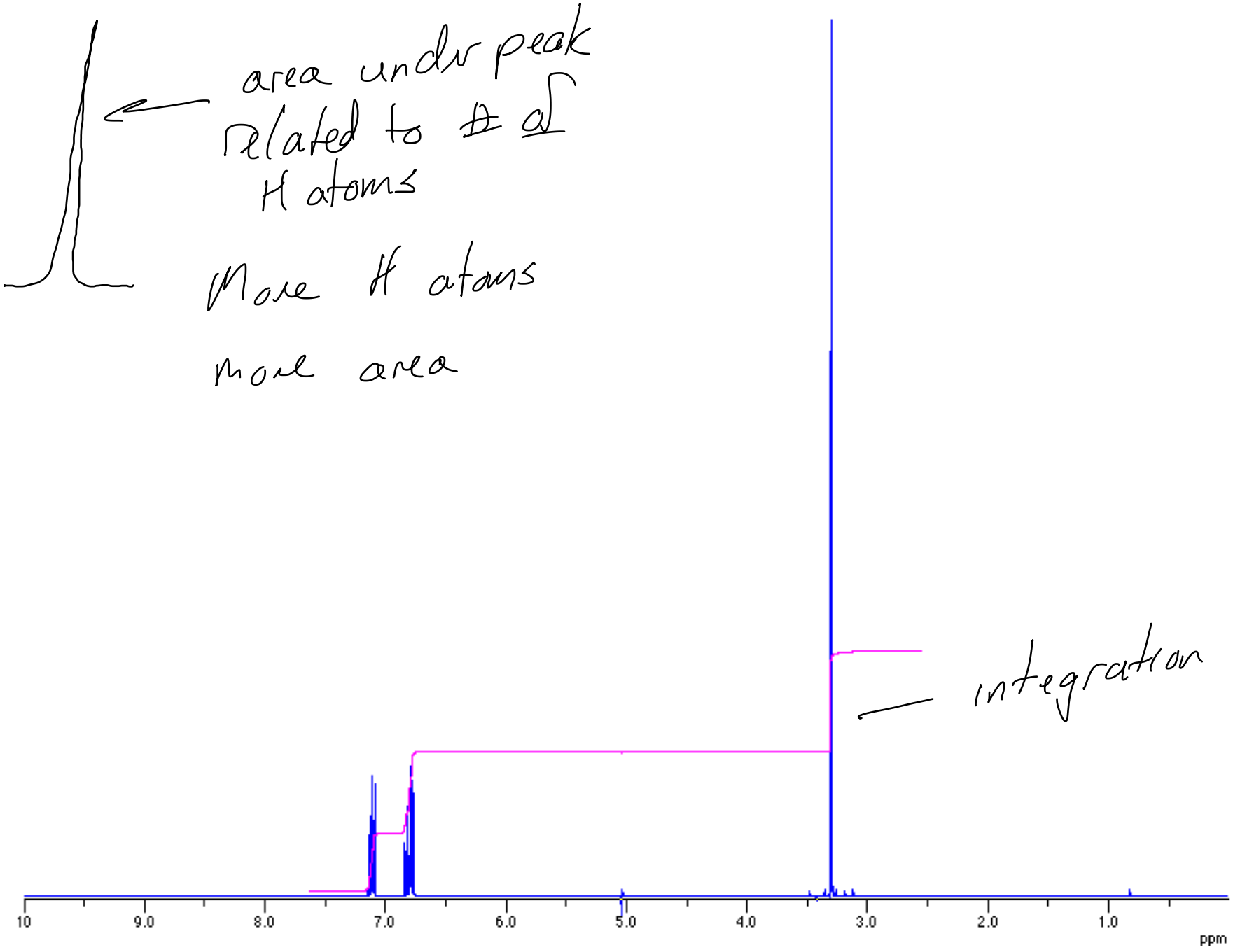
# of peaks

Chemical environments of the H atoms

will determine their chemical shift

to the left ... near enrg atoms

to the left near = bonds


area under peak
related to # of
H atoms
More H atoms
more area
integration
10
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm

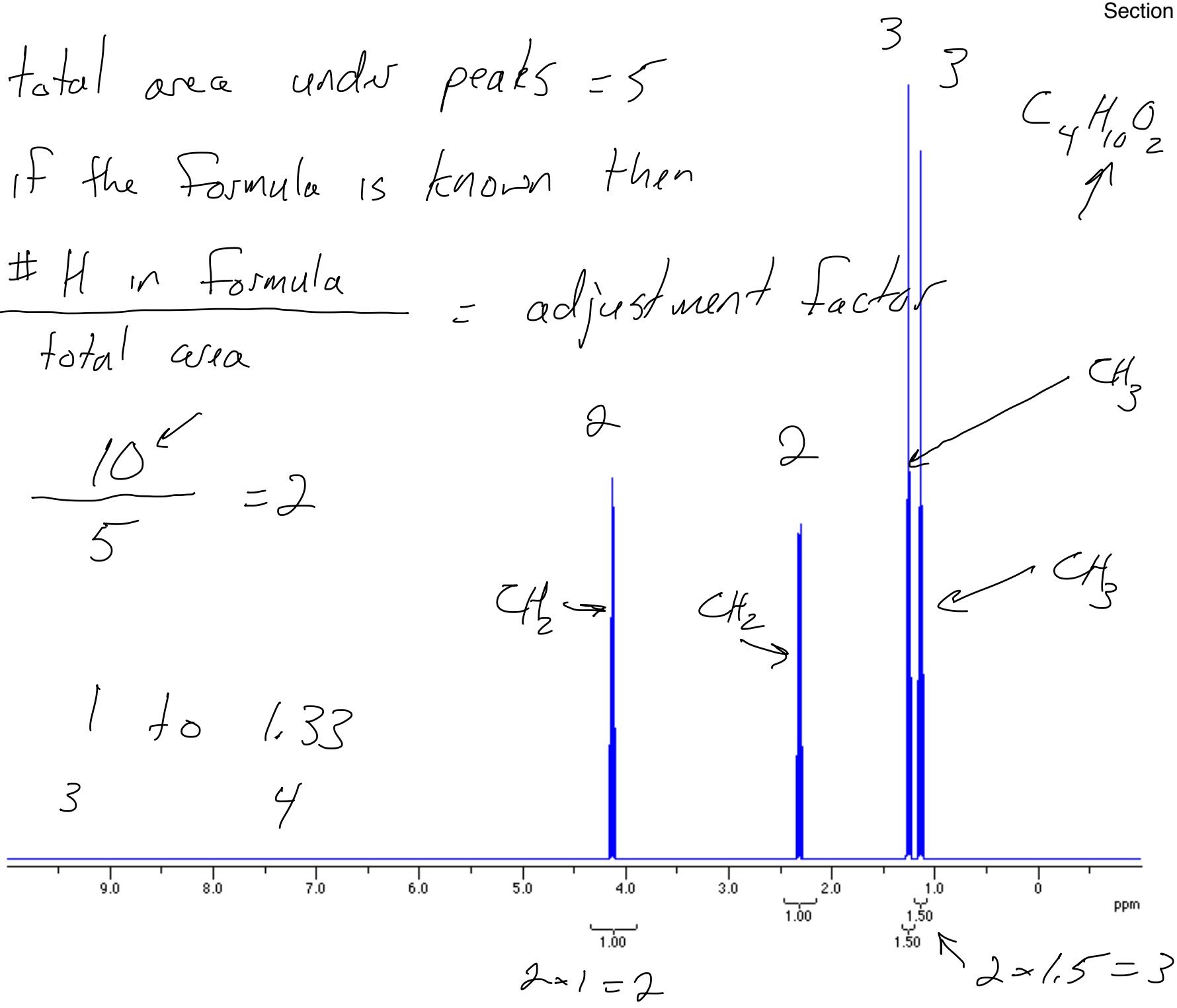
total area under peaks = 5

if the formula is known then

$$\frac{\#\ H\ \text{in formula}}{\text{total area}} = \text{adjustment factor}$$

$$\frac{10}{5} = 2$$

$C_4H_{10}O_2$



1 to 1.33

3 4

$2 \times 1 = 2$

$2 \times 1.5 = 3$

Number of different types of H atoms

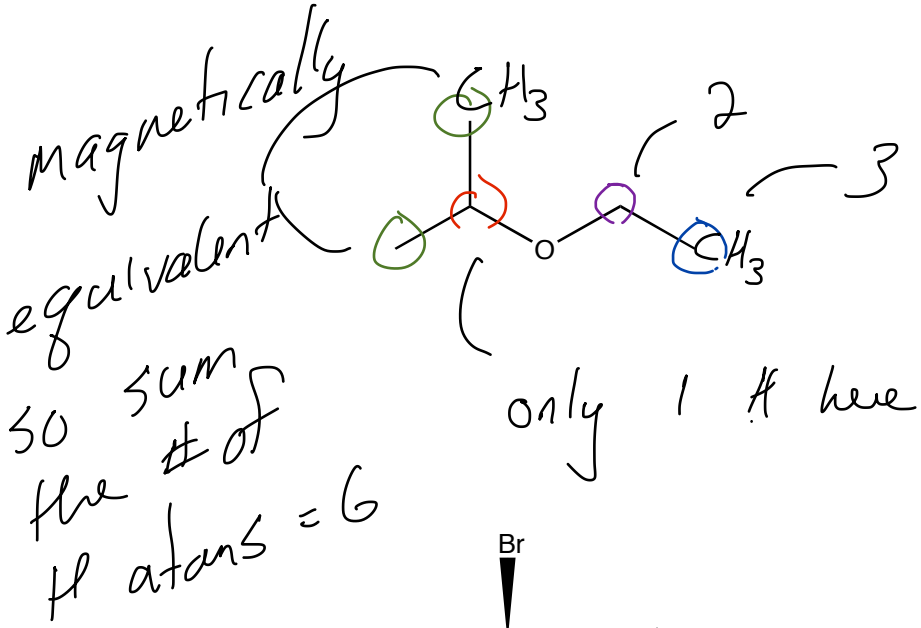
Number of different peaks in the spectrum tells us about the number of chemically distinct kinds of H atoms present

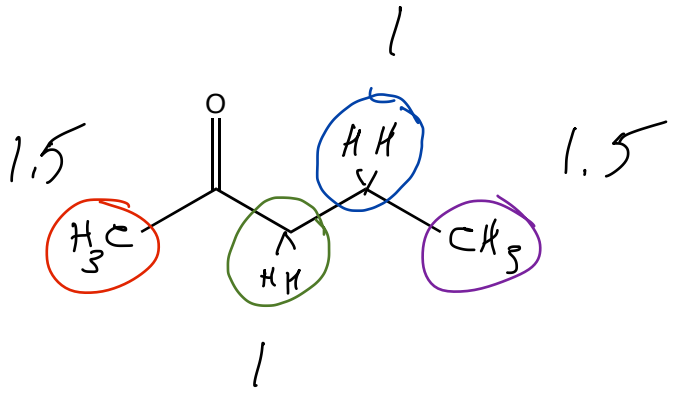
Chemical environments of the H atoms

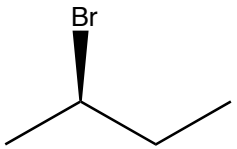
The position of the peak in the spectrum tells us about the chemical environment of the H atoms; e.g., whether the H atoms are near a π bond, an electronegative atom, or other alkyl groups.

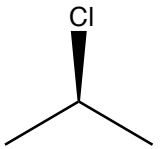
How many of each type of H atom

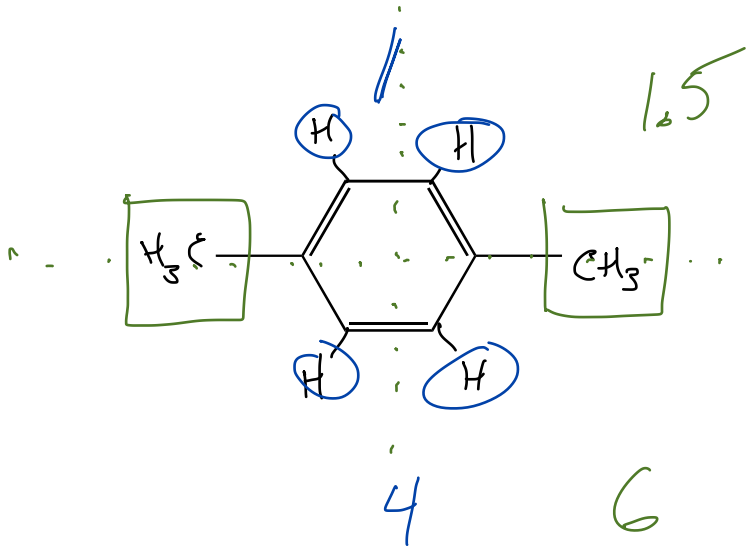
The area under the peaks tells us about relative number of H atoms giving rise to the peak, and can be used to determine the number of H atoms giving rise the the peak.

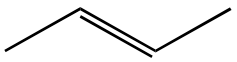












If the integration of the smallest peak is set to 1 the areas of the other peaks would be….

Multiplicity pattern

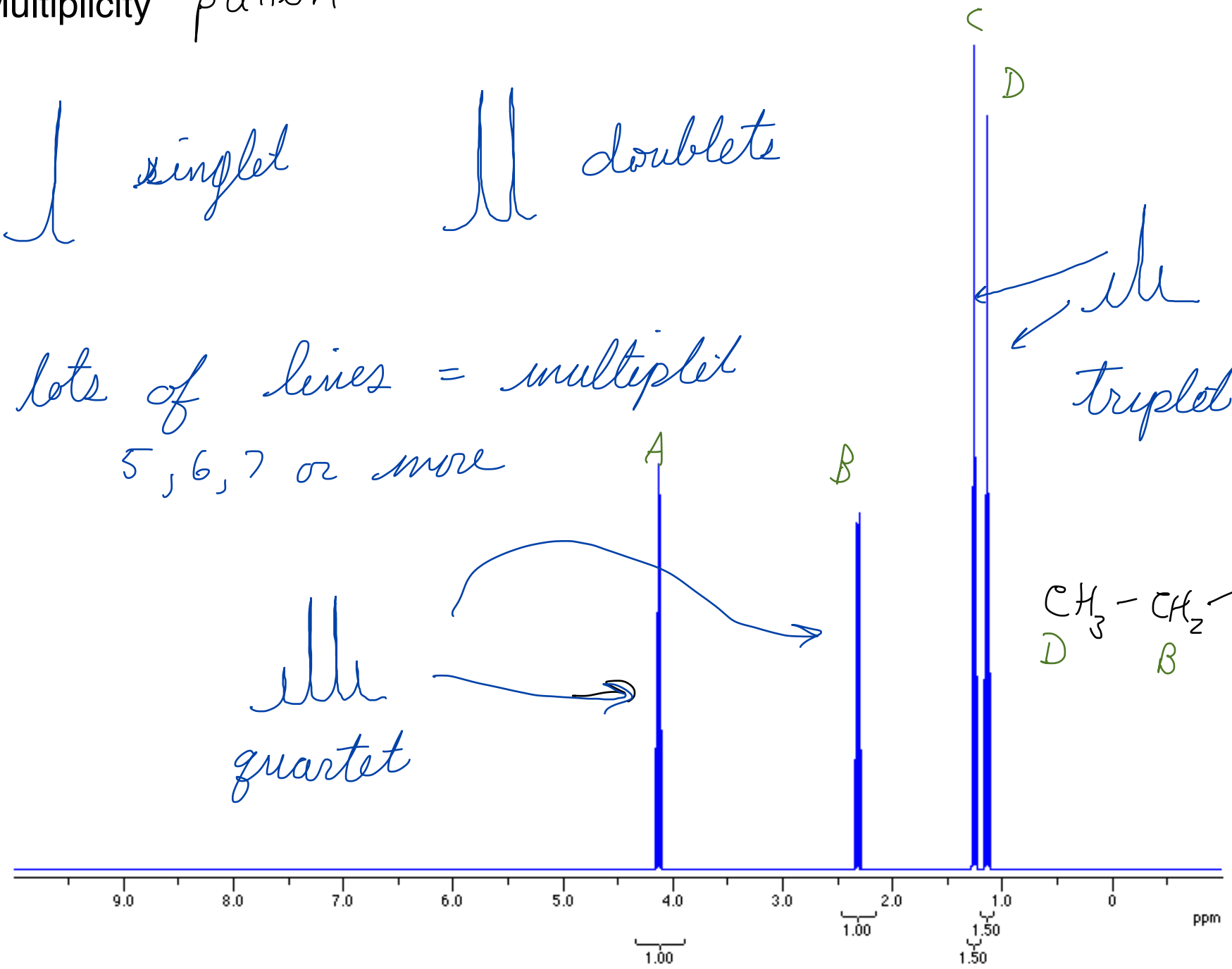
singlet

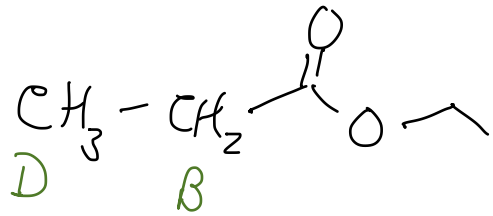
doublete

lots of lines = multiplet
5, 6, 7 or more

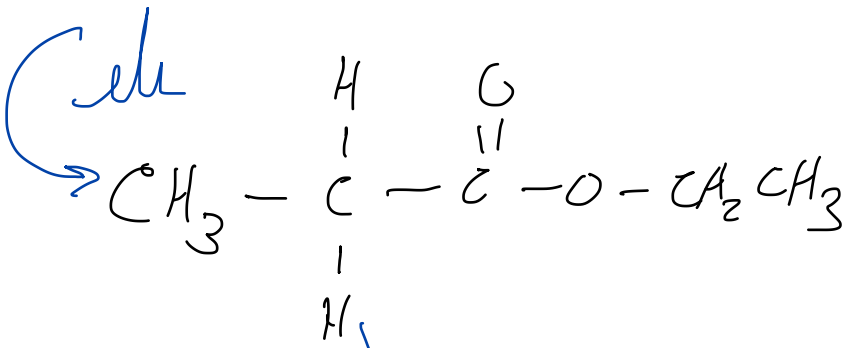
triplet

quartet





Multiplicity: The Triplet

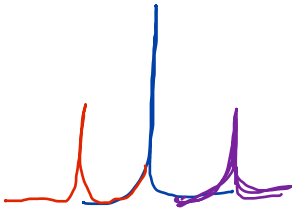


these little magnets can align with the applied field

field looks stronger ↑ ↑ both H's of CH_2 align with the field

no effect { ↑ ↓ one of the CH_2's H's aligns with and one aligns against
↓ ↑ one of the CH_2's H's aligns with and one aligns against

field looks weaker ↓ ↓ both aligned against



Multiplicity: The Quartet

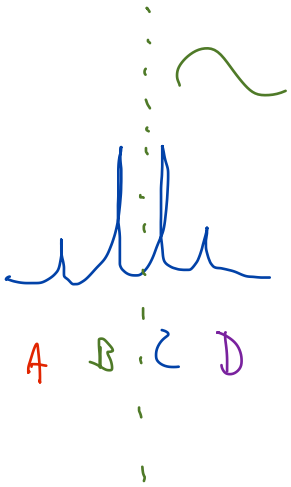
CH_3-CH_2-

A ↑ ↑ ↑

B ↑ ↑ ↓ ↑ ↓ ↑ ↓ ↑ ↑ slightly reinforced

C ↑ ↓ ↓ ↓ ↑ ↓ ↓ ↓ ↑ slightly decrease

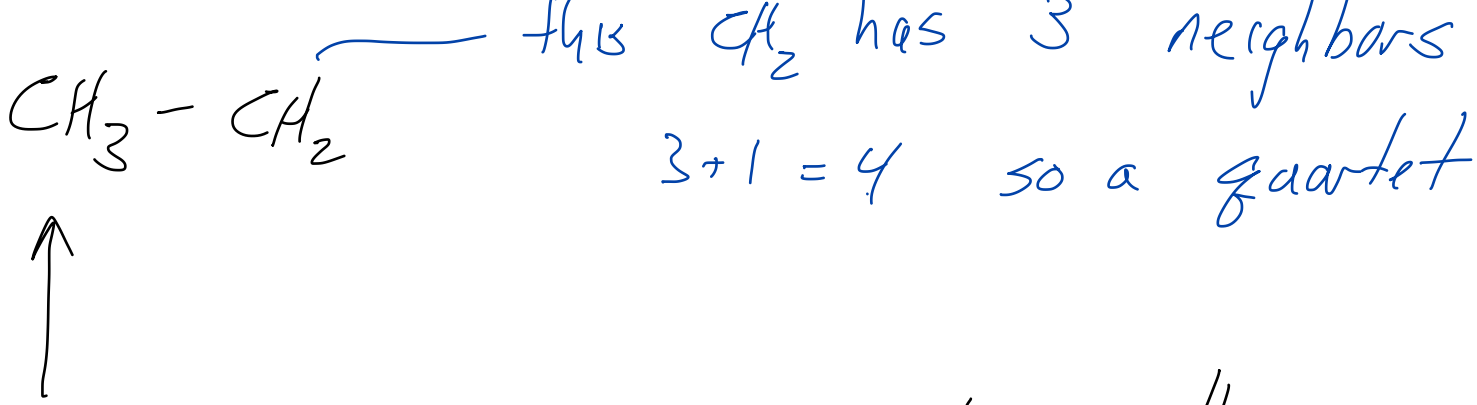
D ↓ ↓ ↓



if there was no spin coupling the peak would be in the middle, and that is the chemical shift that is reported

Multiplicity: The n + 1 rule

The multiplicity of a peak is determined by the number of H atoms on neighboring C atoms

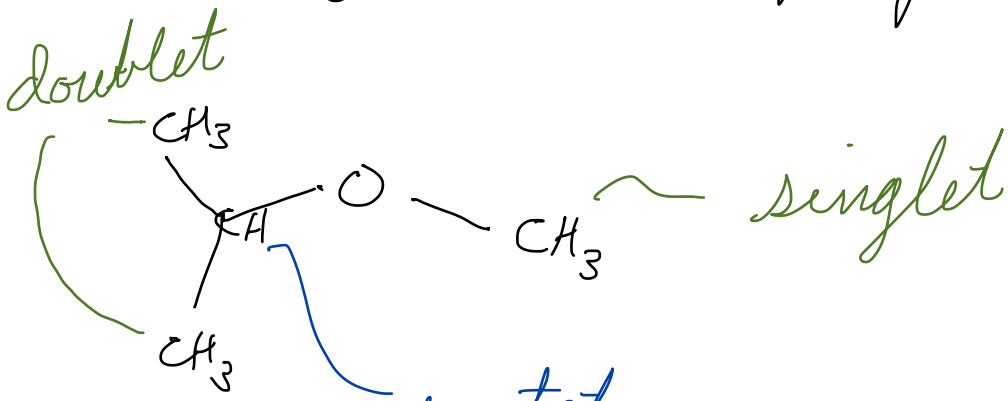


neighbor has 2 H's so the pattern is

2 + 1 = 3 triplet

Multiplicity: More than one set of neighbors

$CH_3 - CH_3$ coupling not observed



when magnetically equivalent H atoms from more than 1 C couple add up all of the H's first

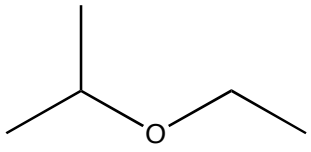
the tiny peaks at the end of the septet may be buried in the noise

1

1 1

1 2 1

1 3 3 1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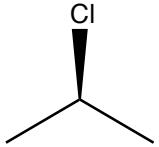
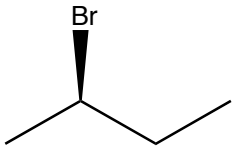
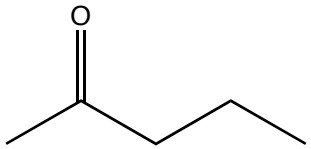

Cl


Br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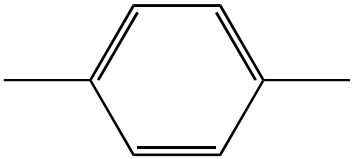

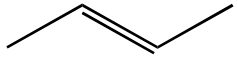

Number of different types of H atoms

Chemical environments of the H atoms

How many of each type of H atom

How many H atoms neighbor each different type of H atom