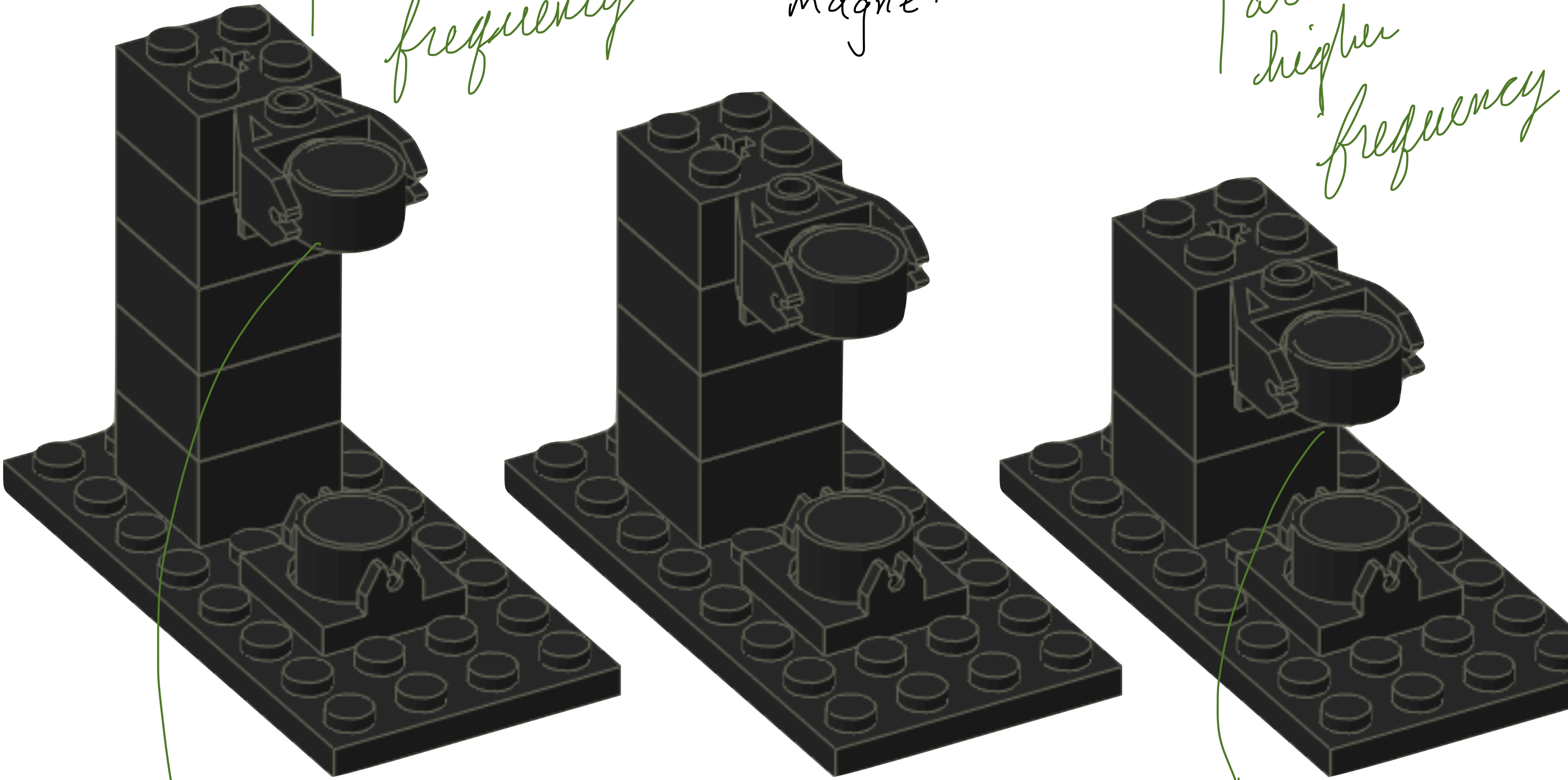
Magnets placed in a magnetic field align with the magnetic field.

When perturbed the magnets will "resonate".

The frequency of the resonance depends on the strength of the magnetic fields resonates a lower frequency

^1H is a magnet

resonates at higher frequency



weaker field

stronger field

^3H & ^2H not magnets

spin $\frac{1}{2}$

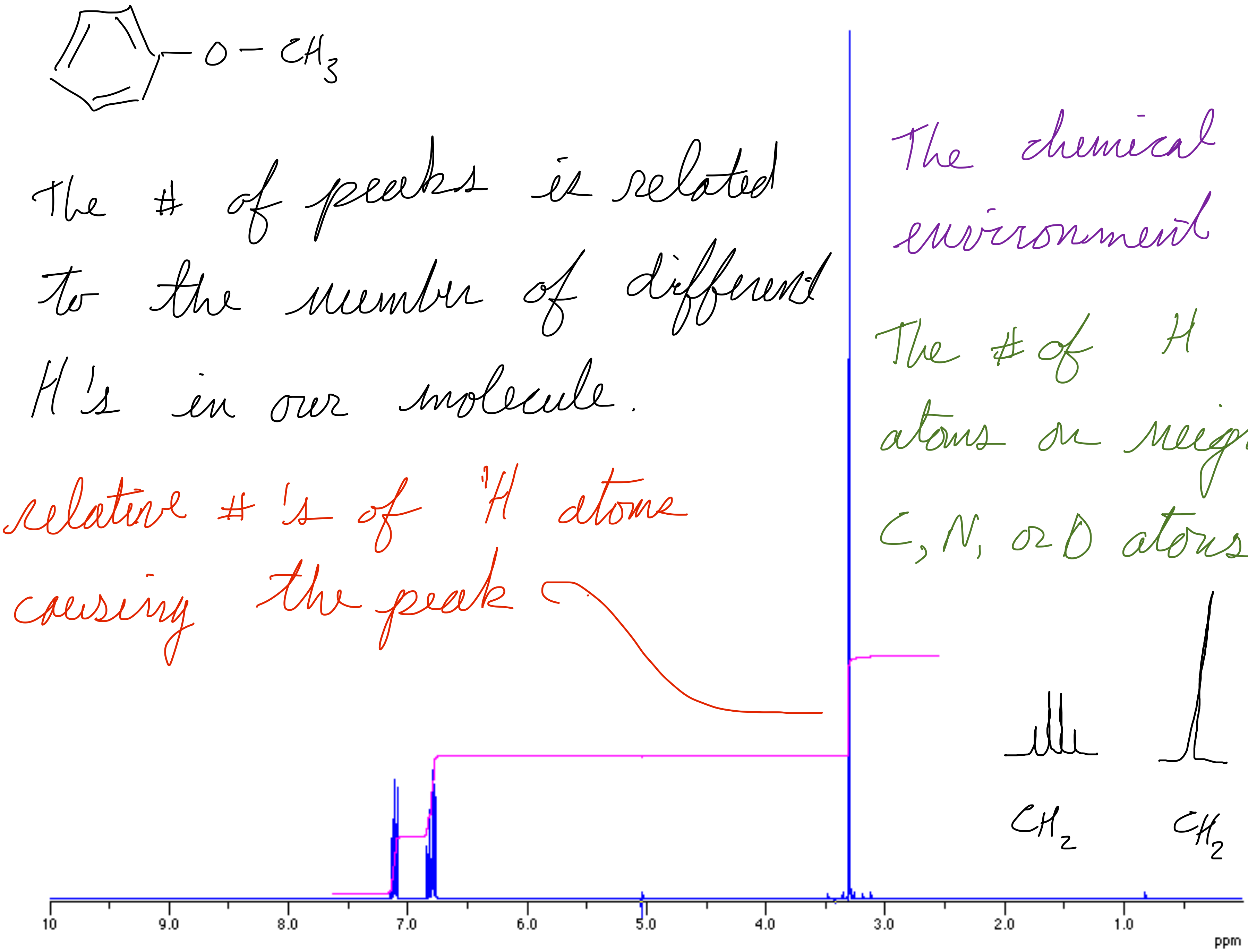
a super conducting wire with e^- going round and round

~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.

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

The chemical environment

The # of H atoms on neighboring C, N, or O atoms magnetic field varies based on position

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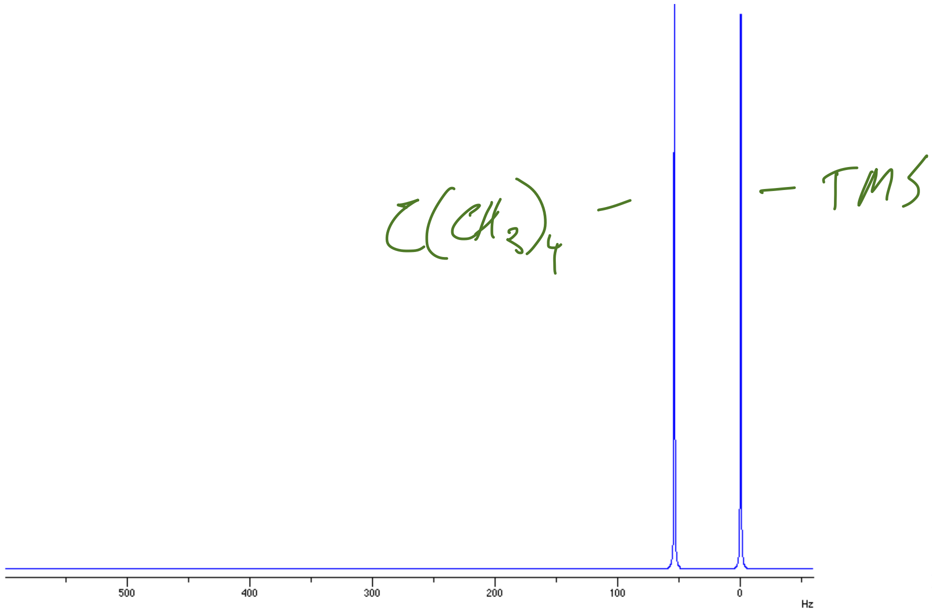
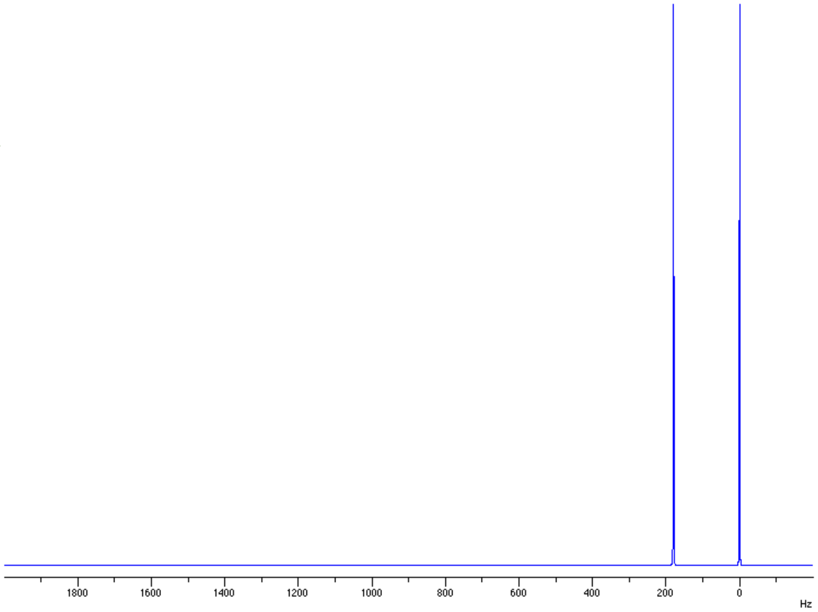
Magnetic Resonance Imaging H_2O



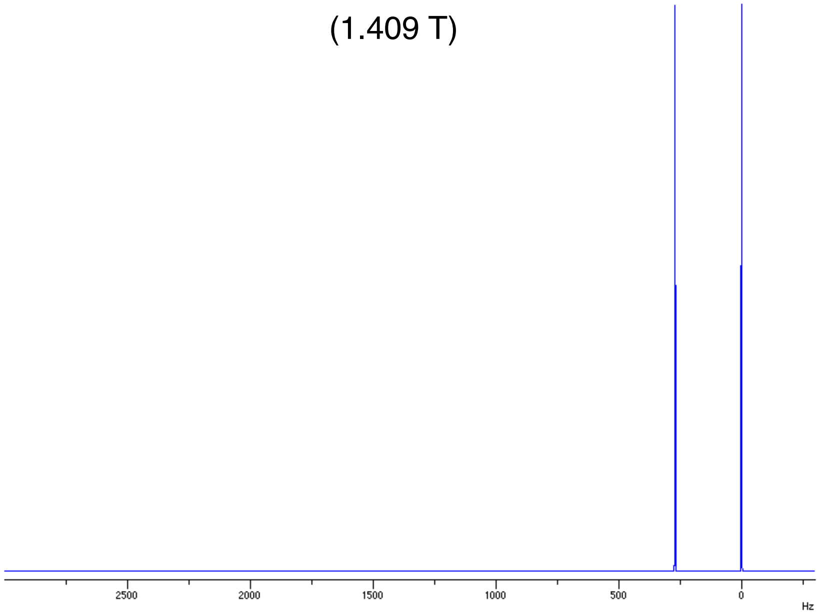
+ 60,000,000 Hz (60 MHz)

(1.409 T)



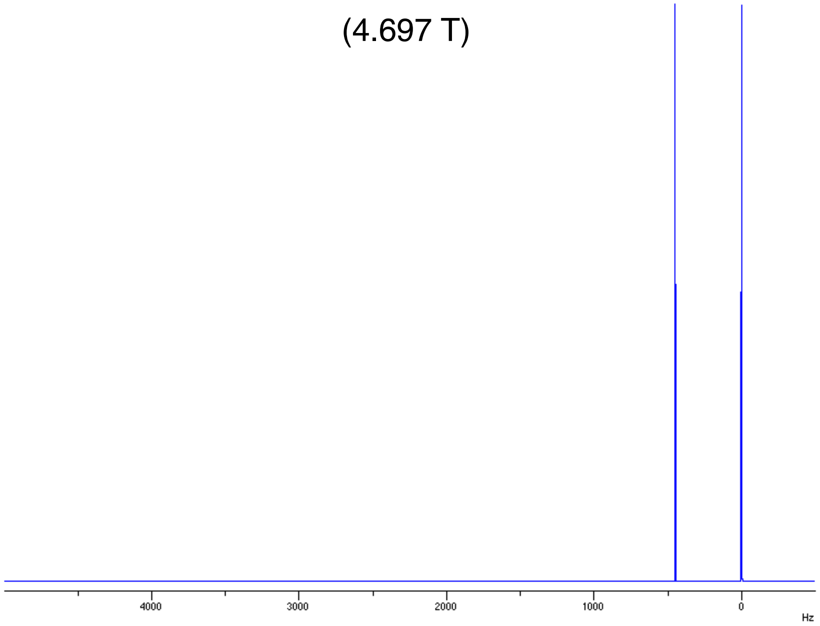
+ 200,000,000 (200 MHz)

(4.697 T)



+300,000,000 Hz (300 MHz)

(7.046 T)



+ 500,000,000 Hz (500 MHz)

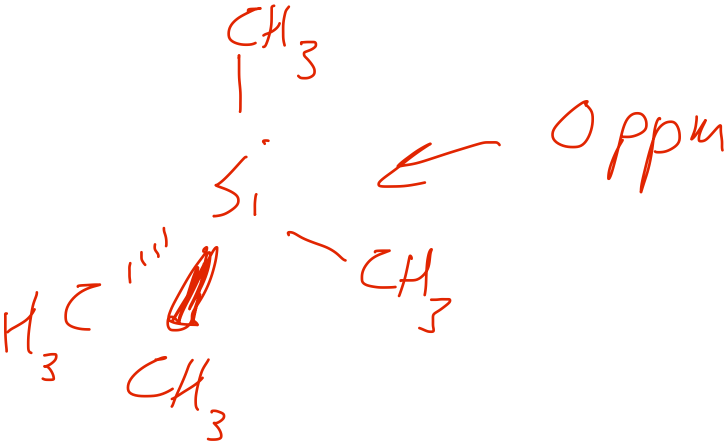
(11.743 T)

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

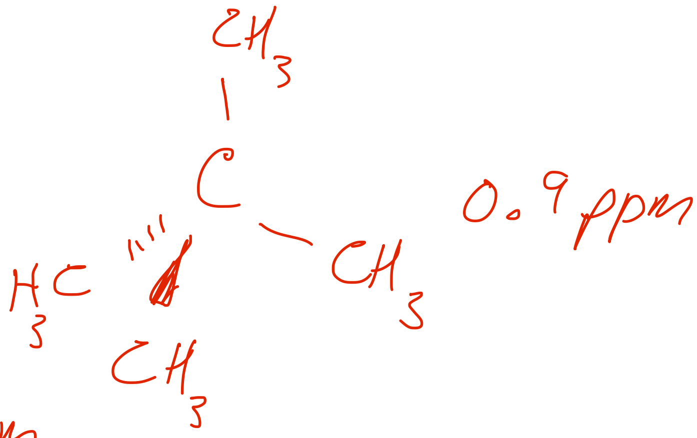
← reference molecule

TMS = tetramethyl silane

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

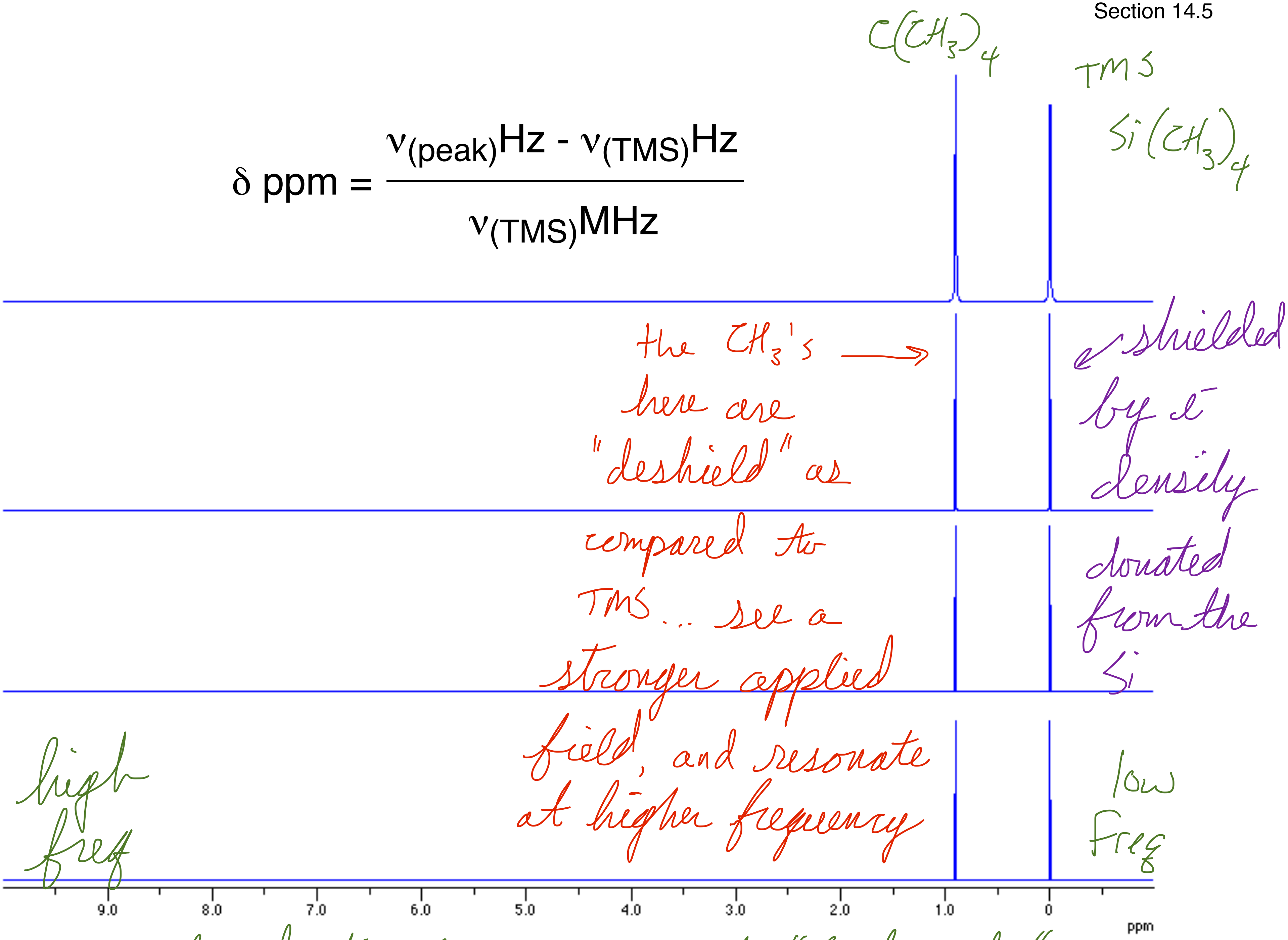


neopentane resonates at 60,000,054 Hz



$$\frac{(66{,}000{,}054 - 60{,}000{,}000)\text{Hz}}{60 \text{ MHz}} = 0.9 \text{ ppm}$$

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



the CH$_3$'s → here are "deshield" as compared to TMS... see a stronger applied field, and resonate at higher frequency

← shielded by e⁻ density donated from the Si

for historical reasons its "backwards"

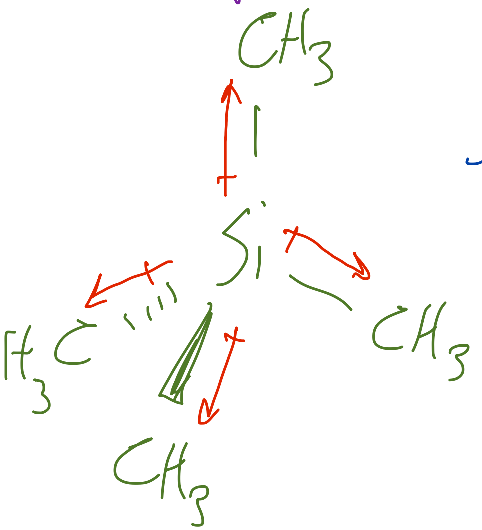
shielding causes these H's to "see" a weaker field & thus resonate at a lower freq

What gives rise to differences in chemical shift?

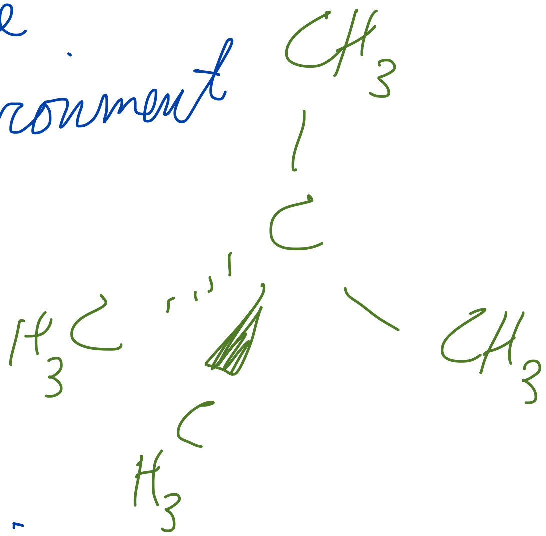
position in NMR spectrum

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

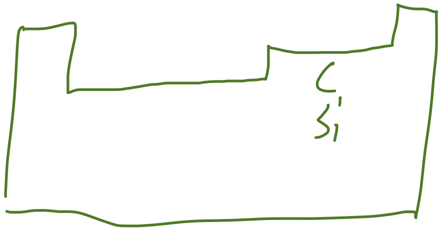
these ^1H are in a more e^- rich environment



vs



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



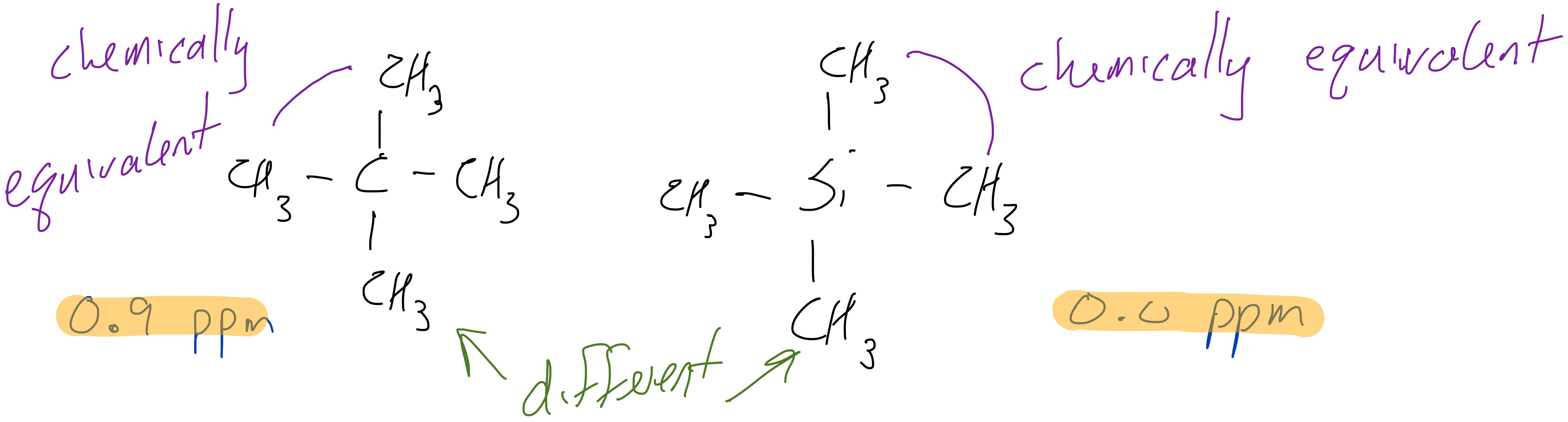
When placed in a magnetic field magnets will align with the applied field.

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.

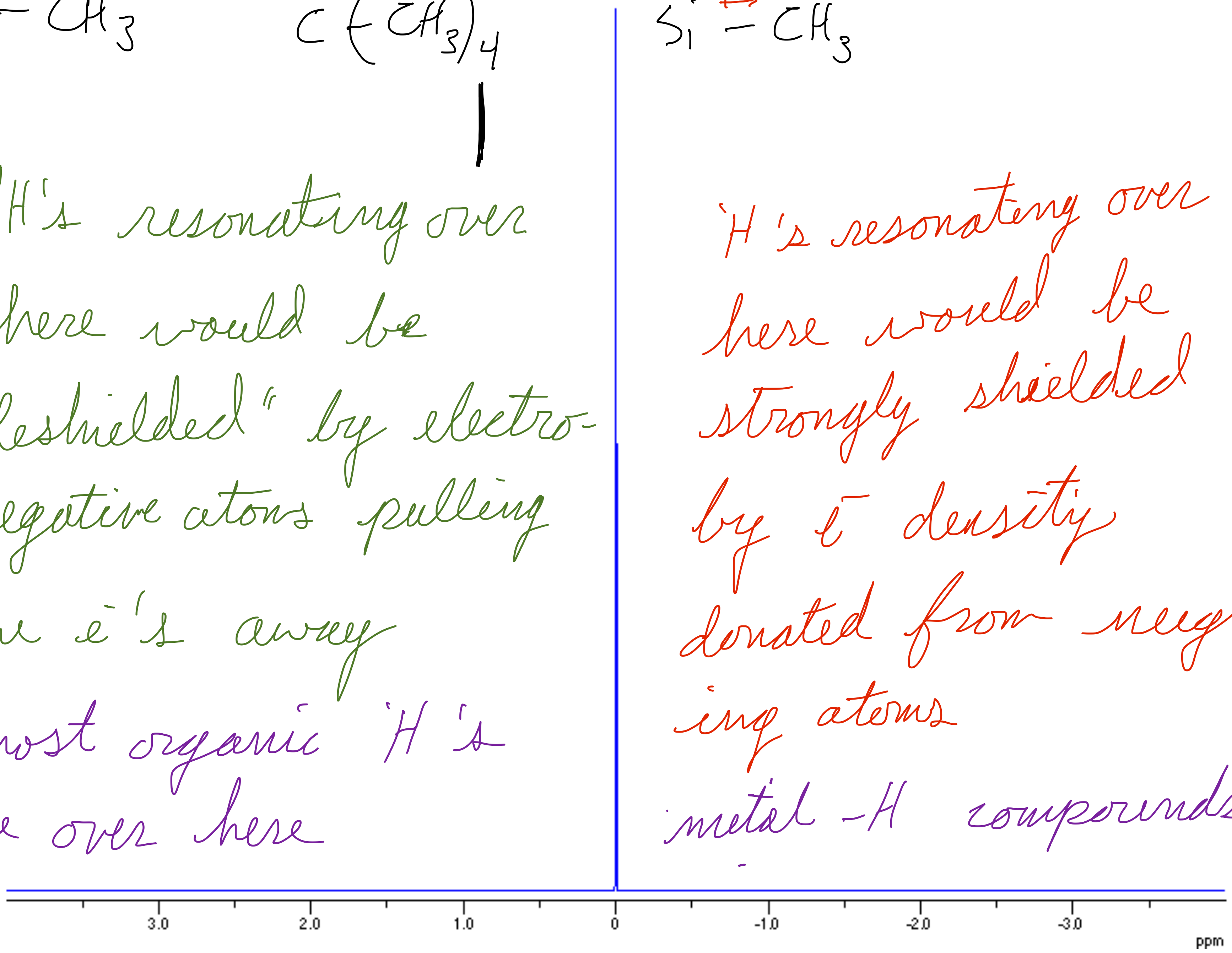


TMS

$O \overset{\leftarrow}{-} CH_3$

$C(CH_3)_4$

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



^1H's resonating over here would be "deshielded" by electronegative atoms pulling the e^-'s away

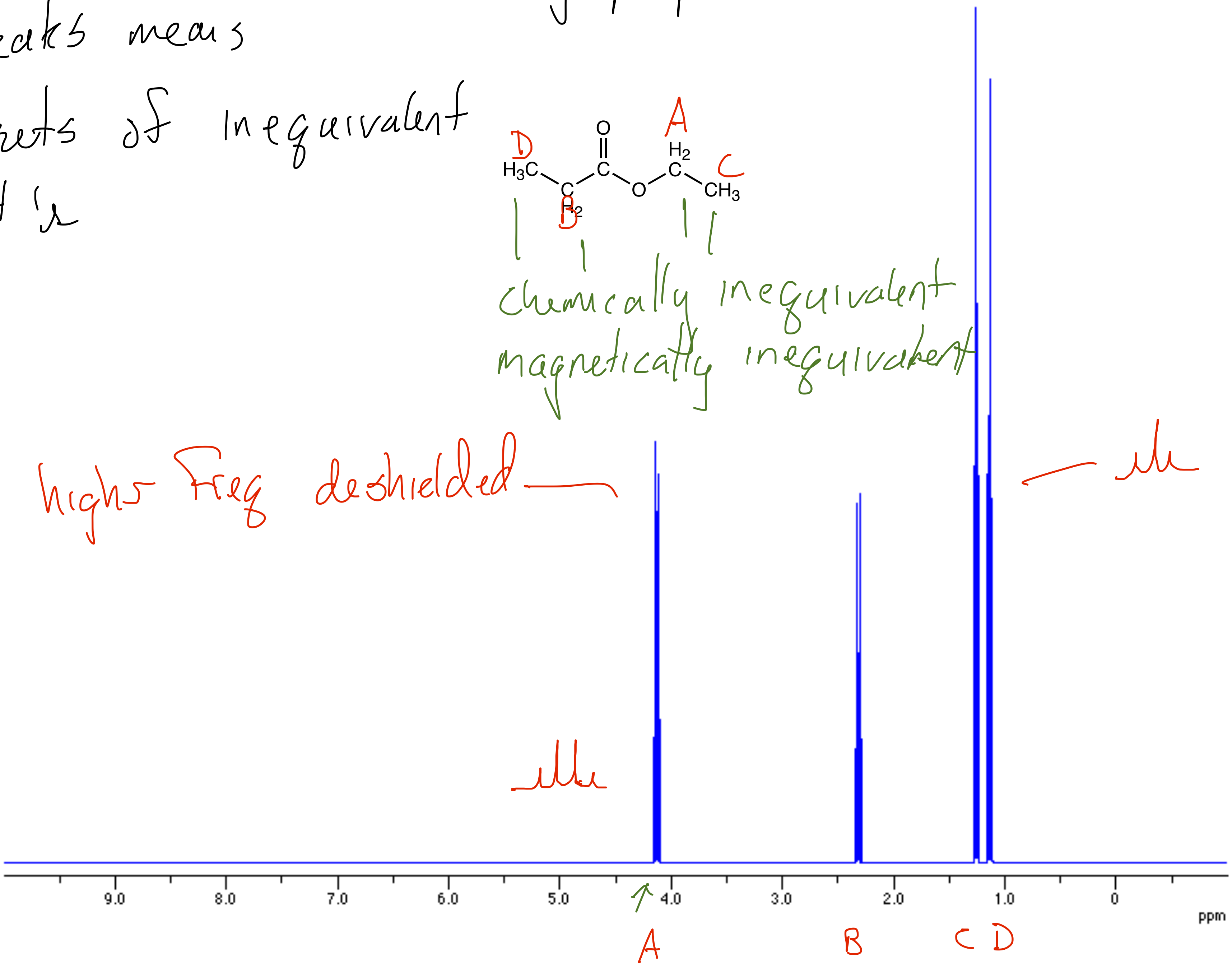
most organic ^1H's are over here

^1H's resonating over here would be strongly shielded by e^- density donated from neighboring atoms

metal-H compounds

ethyl propionate

4 peaks means
4 sets of inequivalent
^1H's



chemically inequivalent
magnetically inequivalent

high freq deshielded

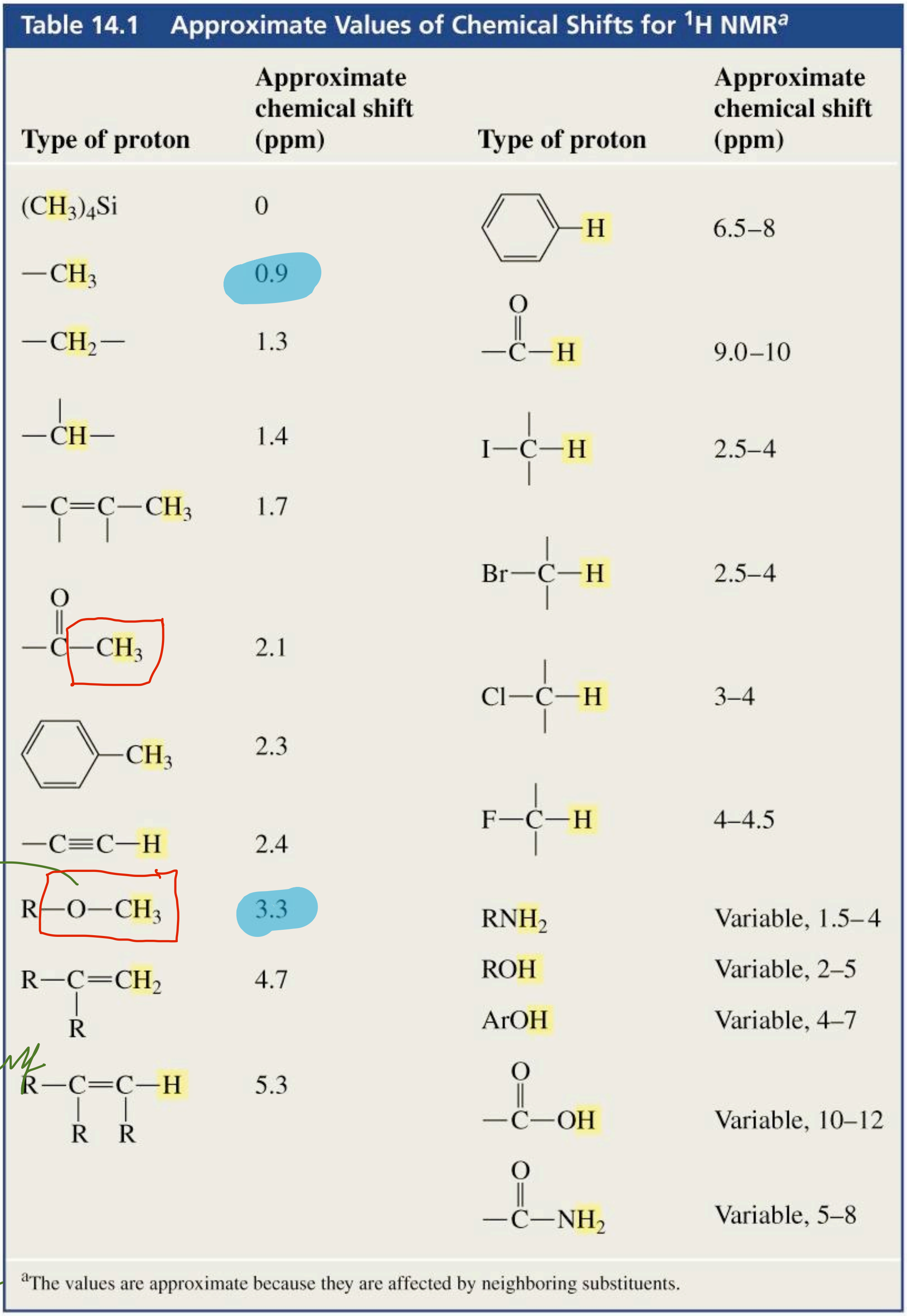


Table 14.1 Approximate Values of Chemical Shifts for ^{1}H NMR[a]

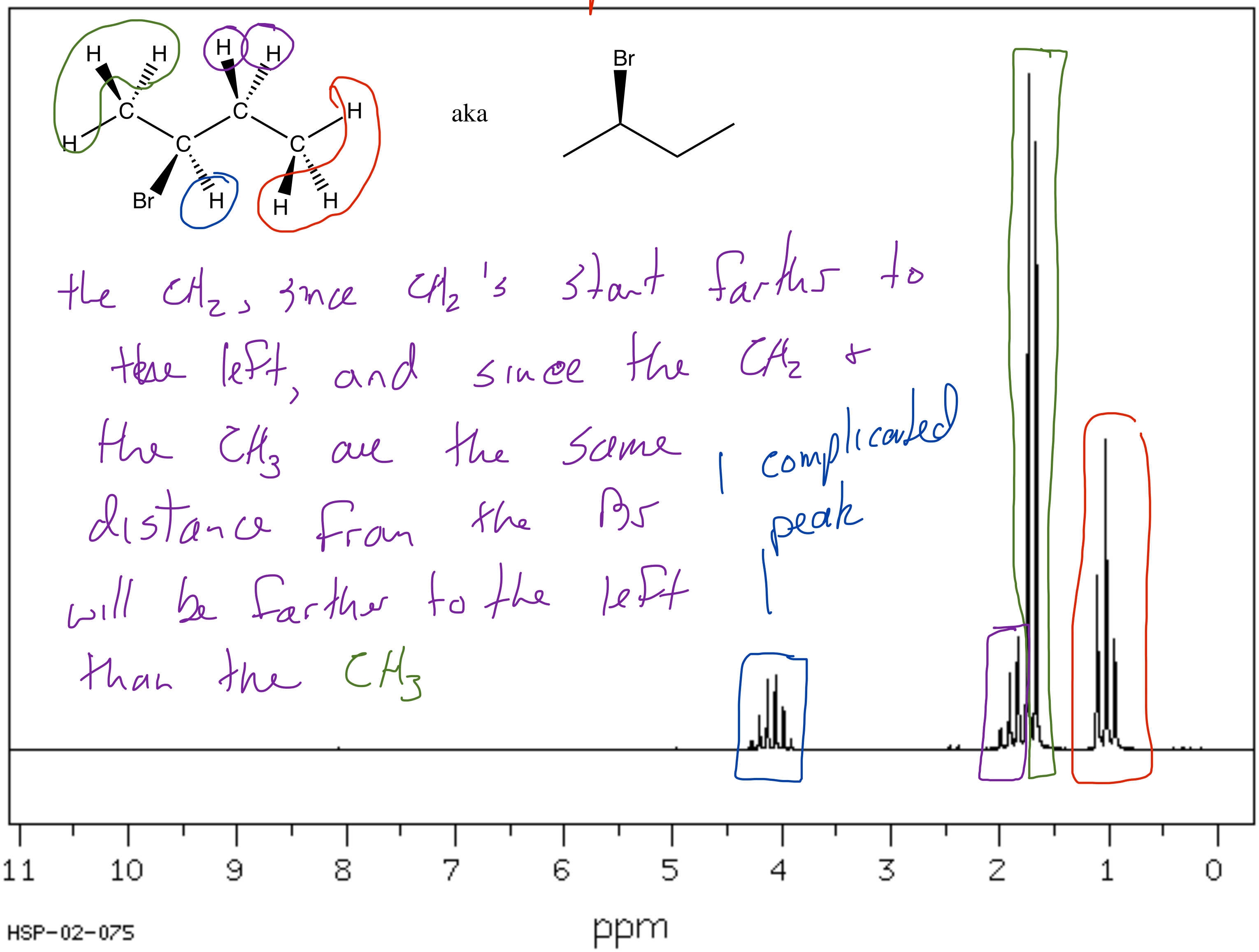
Type of proton	Approximate chemical shift (ppm)	Type of proton	Approximate chemical shift (ppm)
$(CH_3)_4Si$	0	⌬—H	6.5–8
$-CH_3$	0.9	$-\overset{O}{\overset{\|}{C}}-H$	9.0–10
$-CH_2-$	1.3	$I-\overset{\|}{\underset{\|}{C}}-H$	2.5–4
$-\overset{\|}{C}H-$	1.4	$Br-\overset{\|}{\underset{\|}{C}}-H$	2.5–4
$-\underset{\|}{C}=\underset{\|}{C}-CH_3$	1.7	$Cl-\overset{\|}{\underset{\|}{C}}-H$	3–4
$-\overset{O}{\overset{\|}{C}}-CH_3$	2.1	$F-\overset{\|}{\underset{\|}{C}}-H$	4–4.5
⌬—CH_3	2.3	RNH_2	Variable, 1.5–4
$-C\equiv C-H$	2.4	ROH	Variable, 2–5
$R-O-CH_3$	3.3	ArOH	Variable, 4–7
$R-\underset{\underset{R}{\|}}{C}=CH_2$	4.7	$-\overset{O}{\overset{\|}{C}}-OH$	Variable, 10–12
$R-\underset{\underset{R}{\|}}{C}=\underset{\underset{R}{\|}}{C}-H$	5.3	$-\overset{O}{\overset{\|}{C}}-NH_2$	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



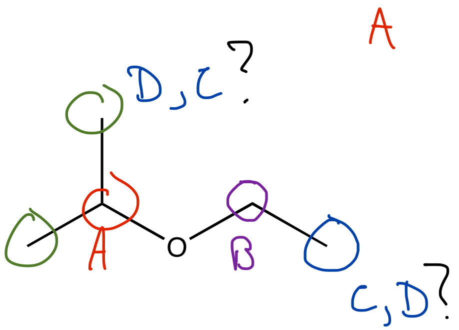
the CH_2, since CH_2's start farther to the left, and since the CH_2 & the CH_3 are the same distance from the Br will be farther to the left than the CH_3

complicated peak

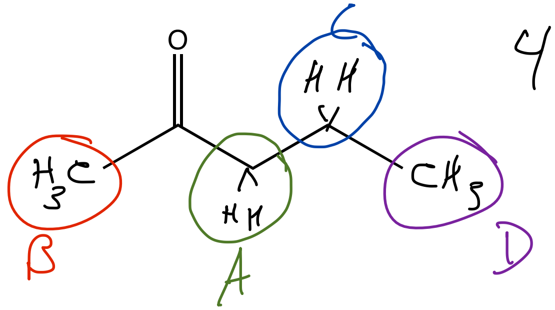
https://sdbs.db.aist.go.jp/sdbs/cgi-bin/landingpage?sdbsno=500

chemically inequivalent = magnetically inequivalent most of the time

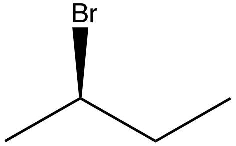
peaks

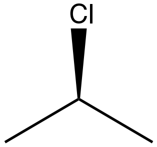


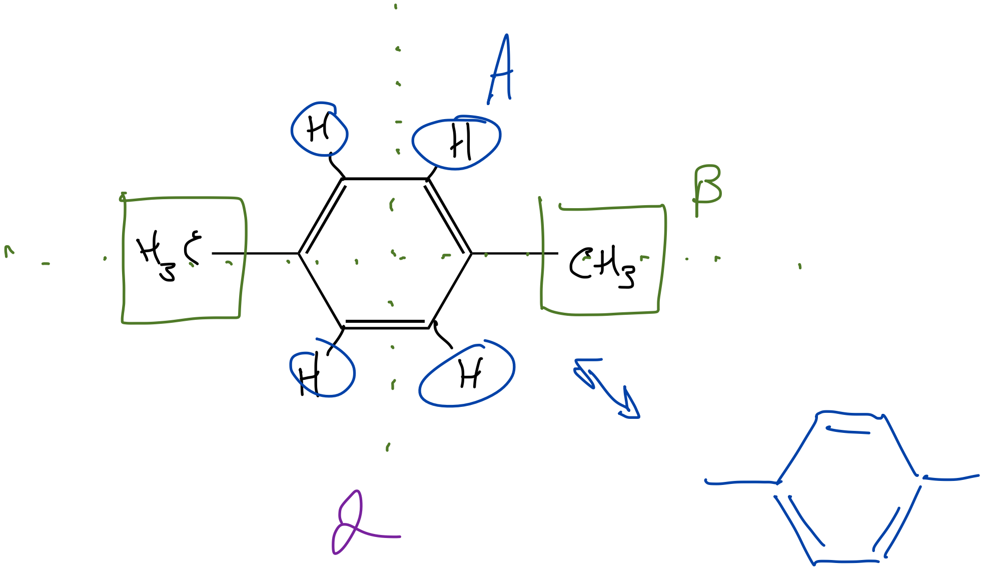
3 [✓ 4]

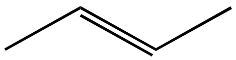


4 5









2

Number of different types of H atoms

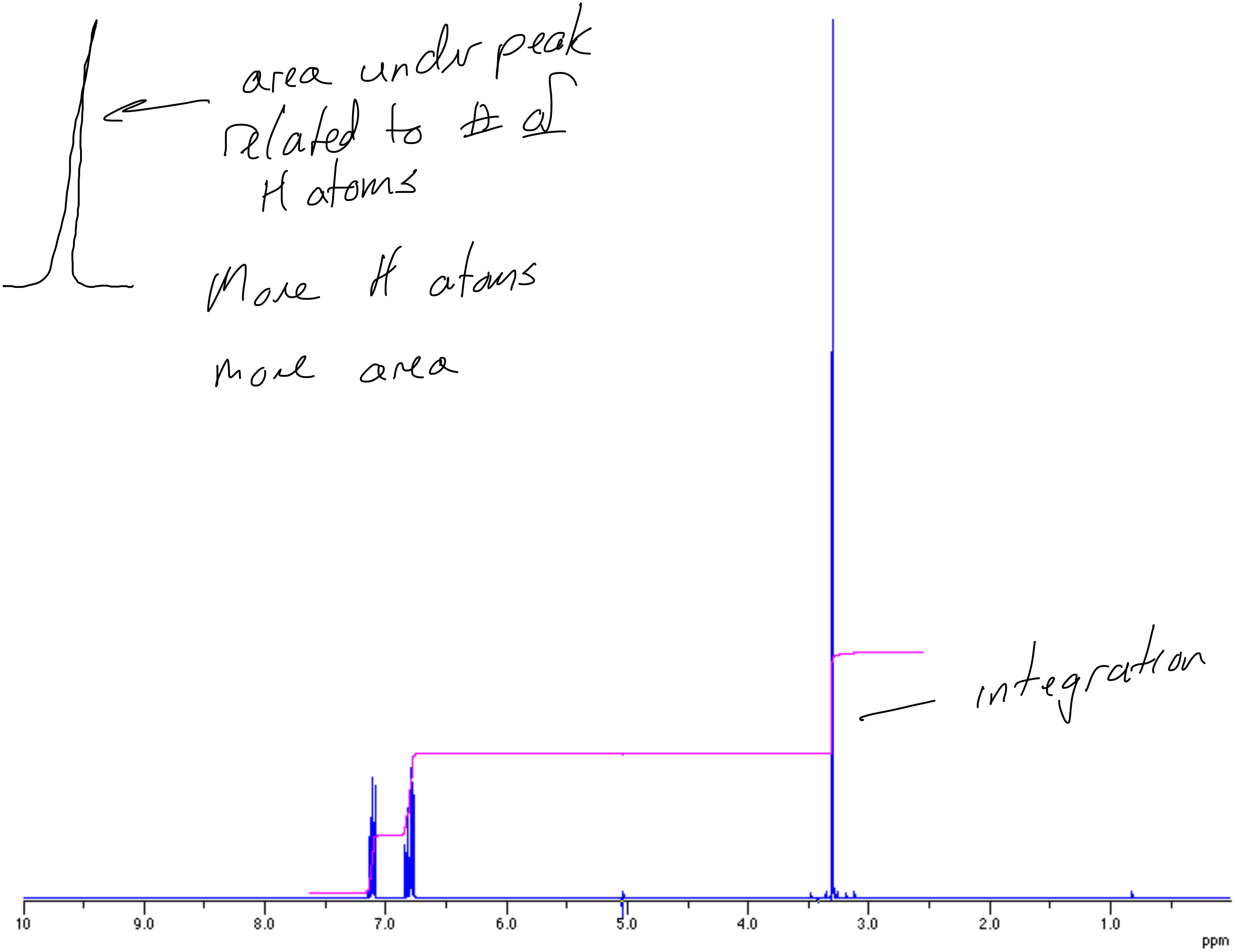
of peaks

Chemical environments of the H atoms

will determine their chemical shift

to the left ... near eneg atoms

to the left near = bonds



area undr peak related to # of H atoms

More H atoms more area

integration

total area under peaks = 5

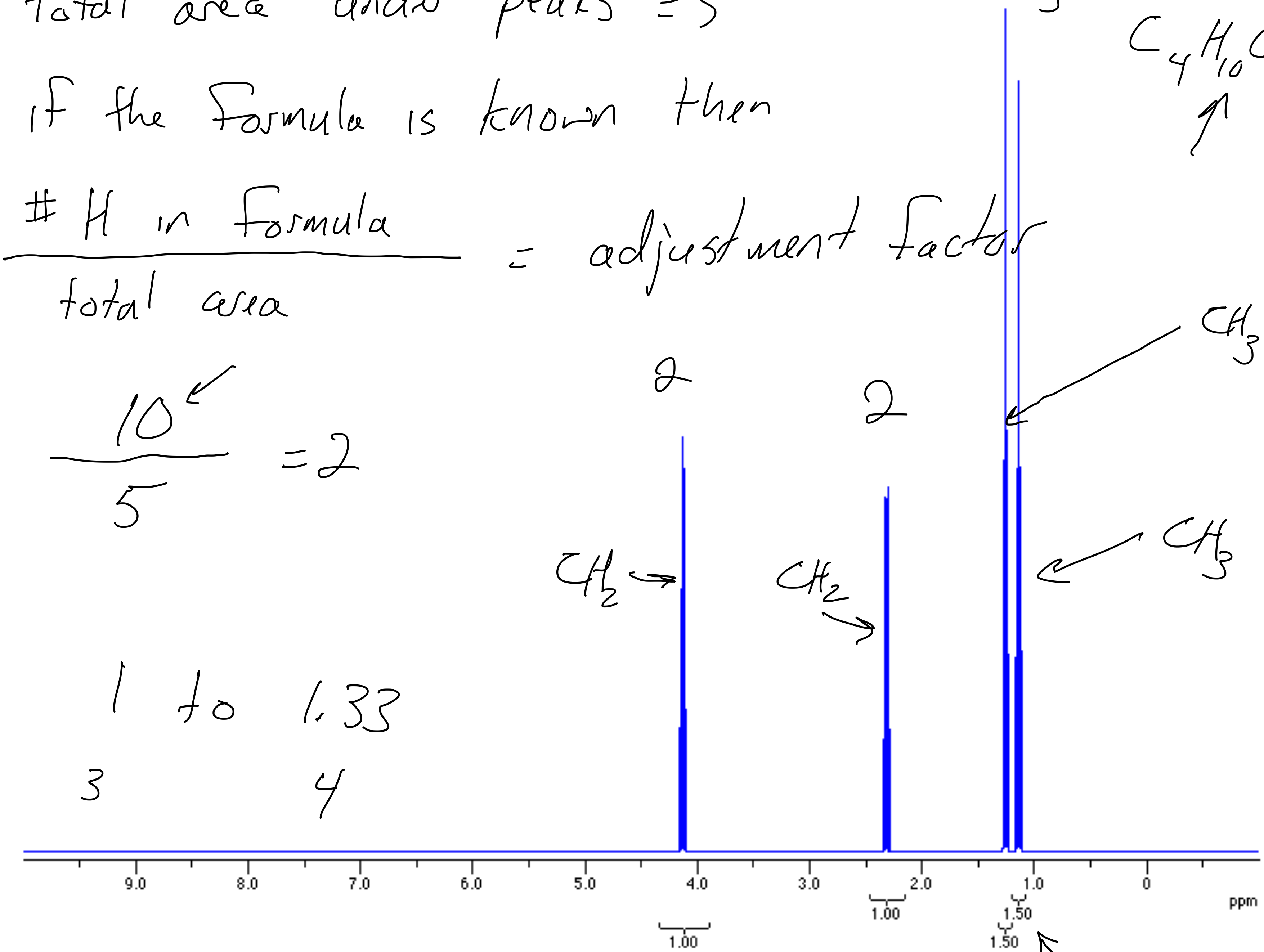
if the Formula is known then

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

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

1 to 1.33

3 4



2×1 = 2

2×1.5 = 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

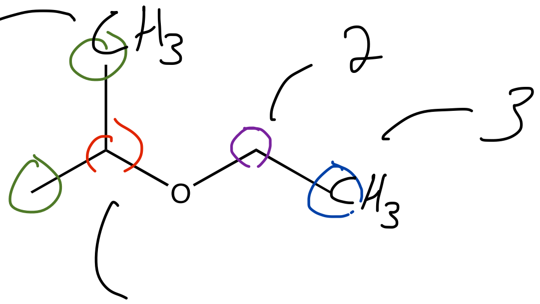
The position of the peak in the spectrum tells us about the chemical environment of the H atoms; e.g., whether the H atoms are near a π bond, an electronegative atom, or other alkyl groups.

How many of each type of H atom

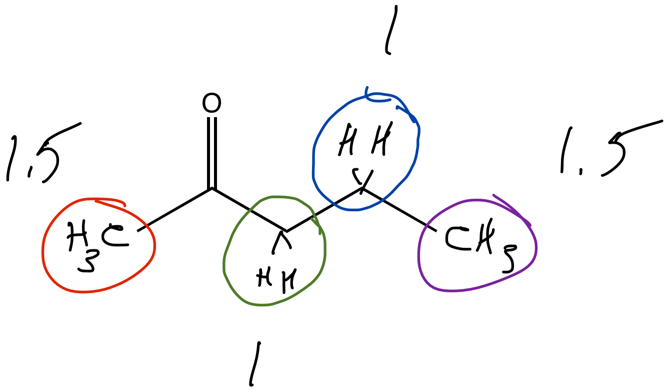
The area under the peaks tells us about relative number of H atoms giving rise to the peak, and can be used to determine the number of H atoms giving rise the the peak.

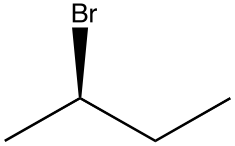
magnetically equivalent

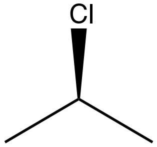
so sum the # of H atoms = 6

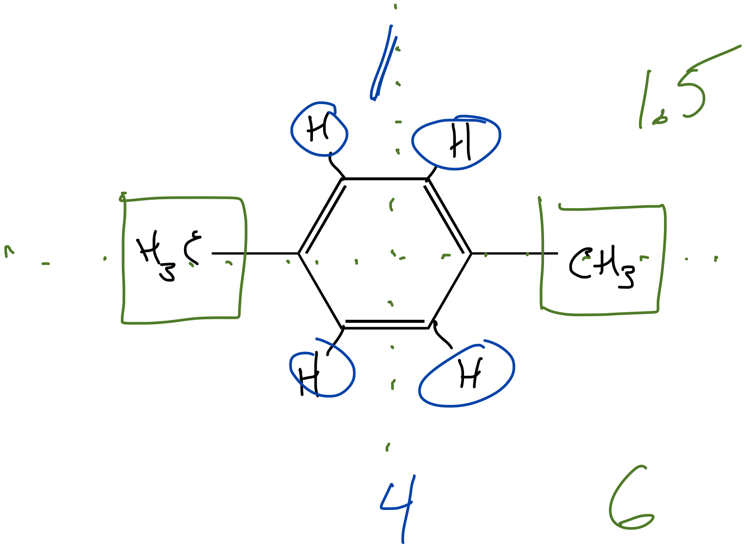


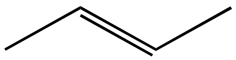
only 1 H here







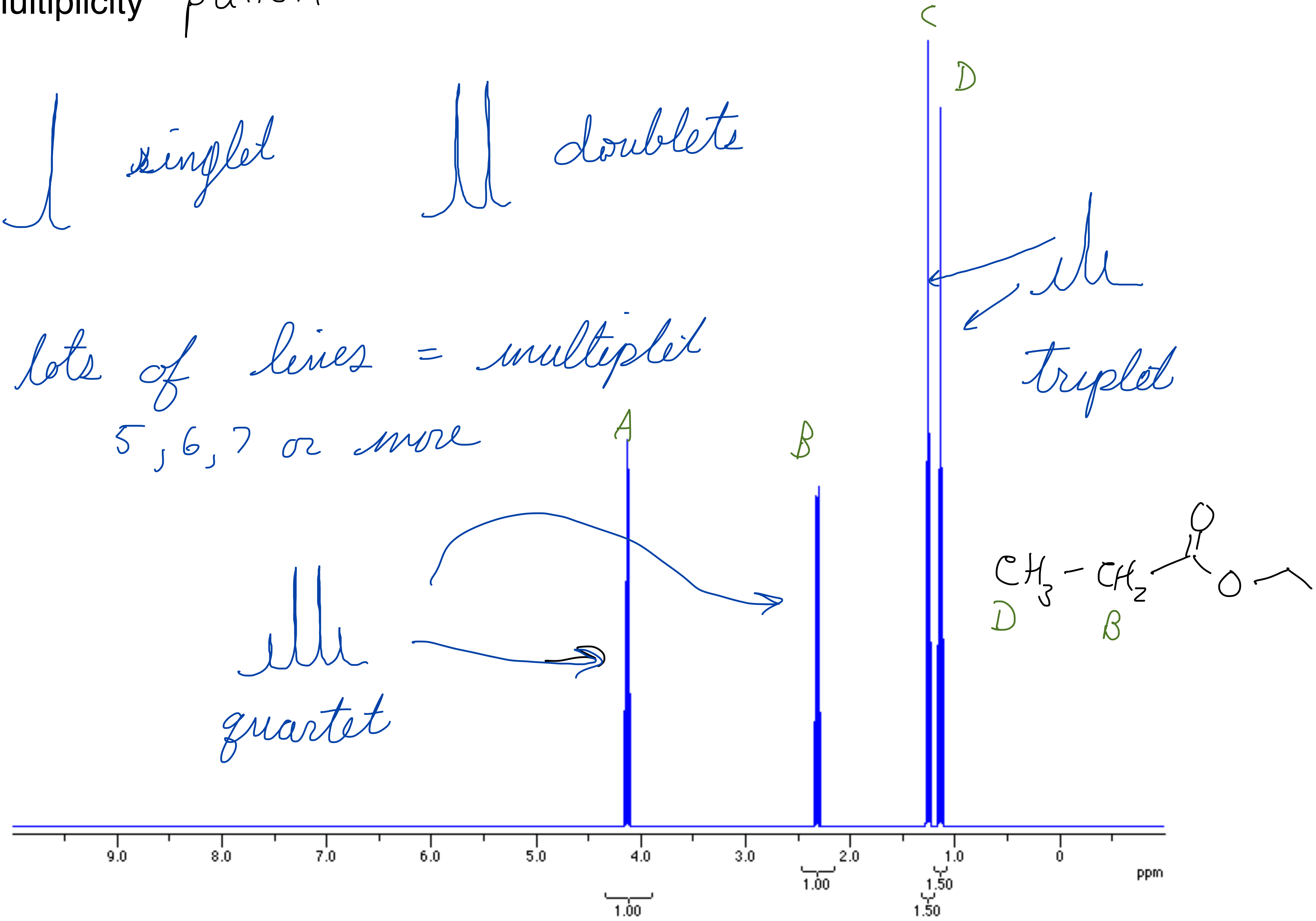




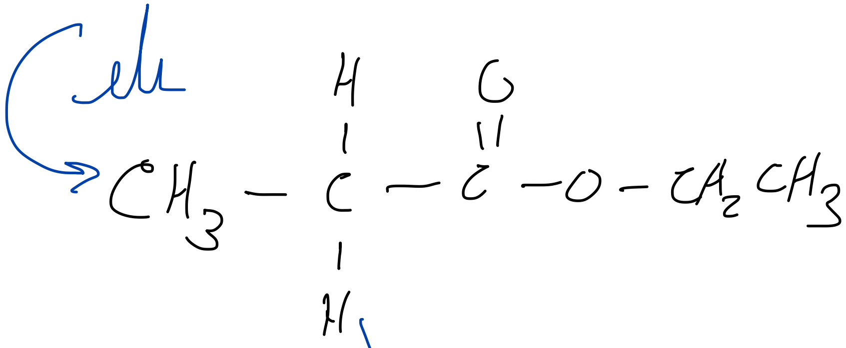
If the integration of the smallest peak is set to 1 the areas of the other peaks would be….

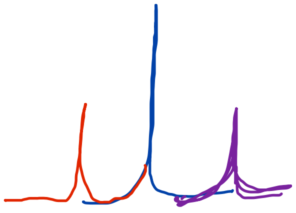
Multiplicity pattern

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



Multiplicity: The Triplet


$CH_3-CH_2-C(=O)-O-CH_2CH_3$



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

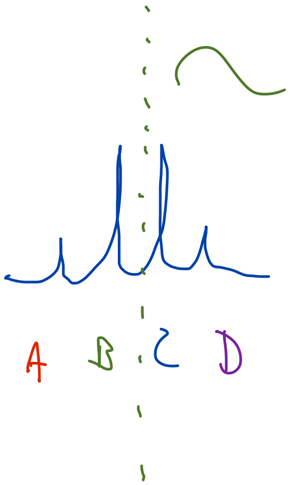
$CH_3-\overset{\downarrow}{CH_2}-$

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

each peak can be a series of lines

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

$CH_3 - CH_2$

this CH_2 has 3 neighbors

3+1 = 4 so a quartet

neighbor has 2 H's so the pattern is

2+1 = 3 triplet

this 2 comes from the CH_2 so the CH_3 is a

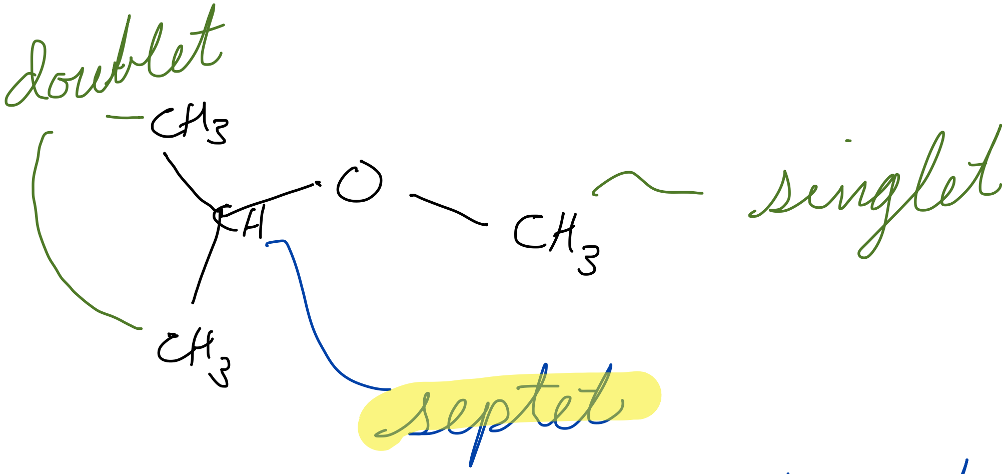
Coupling between chemically and magnetically equivalent H atoms

$CH_3 - CH_3$

↑

these three H atoms have neighbors, the other 3 H atoms. Since the H atoms are chemically & magnetically equivalent, the coupling is not observed.

Multiplicity: More than one set of neighbors



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

J^3 coupling to H atoms 3 bonds away

sometimes it is hard to see the ends

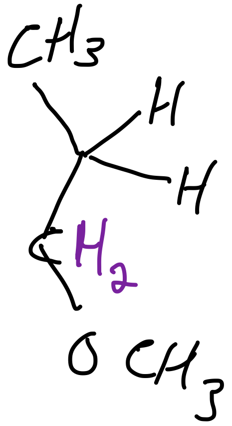
1

1 1

1 2 1

1 3 3 1

Magnetically unequivalent + chemical shift is very different



the multiplicity of this CH_2 ...

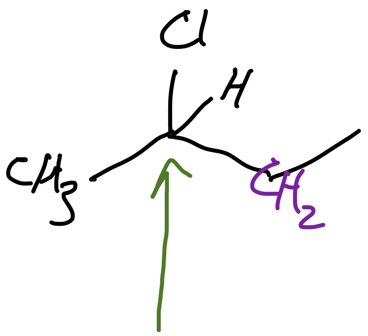
CH_3 and CH_2 H's are chemically + magnetically very different, so we have to count them separately.

CH_3 splits the signal into a quartet

CH_2 splits the quartet into triplets

quartet of triplets or a triplet of quartets

Multiple not so different neighbors



special...
chiral

CH_3 + CH_2 are not very different ... higher order coupling occurs. This turns into a mess that you use software to untangle

if equiv

3+2=5

sextet

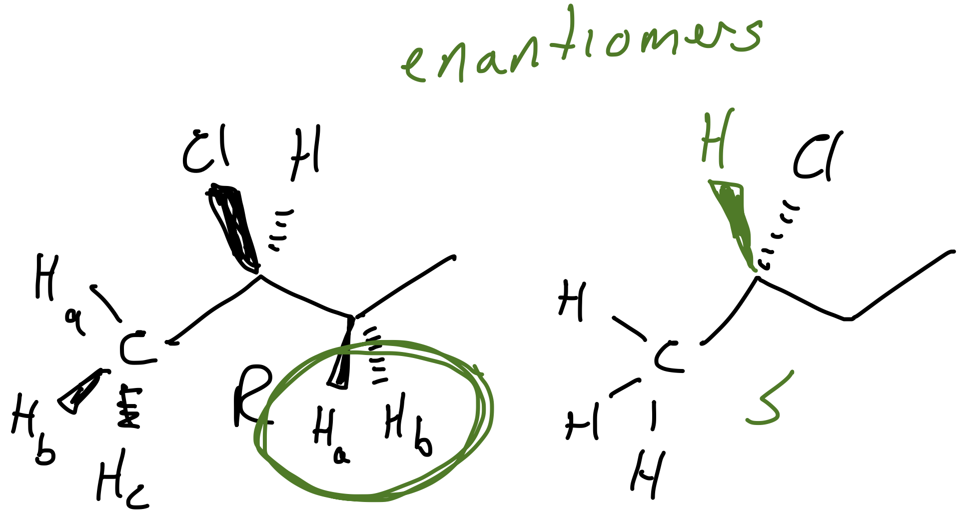
look for

6 to 12 lines

if inequiv

3 => quartet

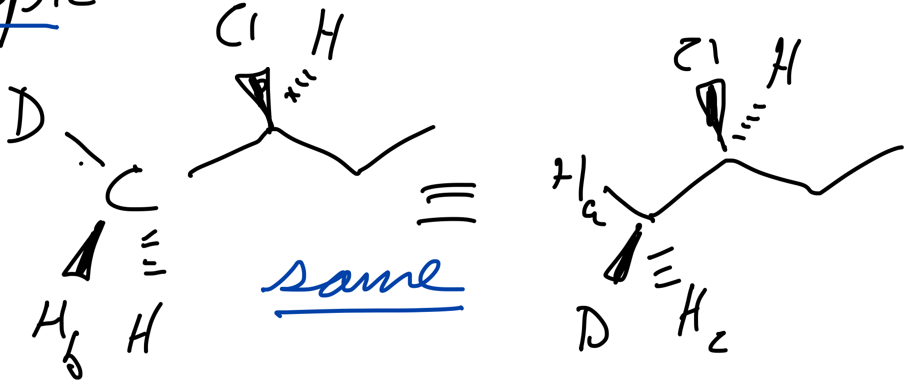
2 => triplet of quartets



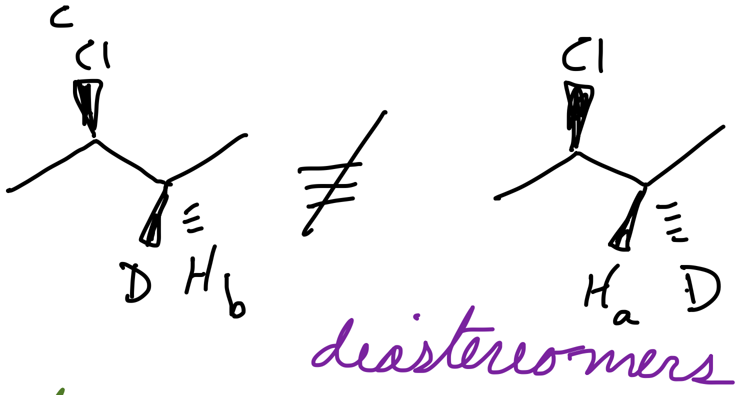
R and S H atoms are chemically equivalent and "enantiotopic" H's are chemically equiv.

CH$_3$ H atoms are "homotopic"

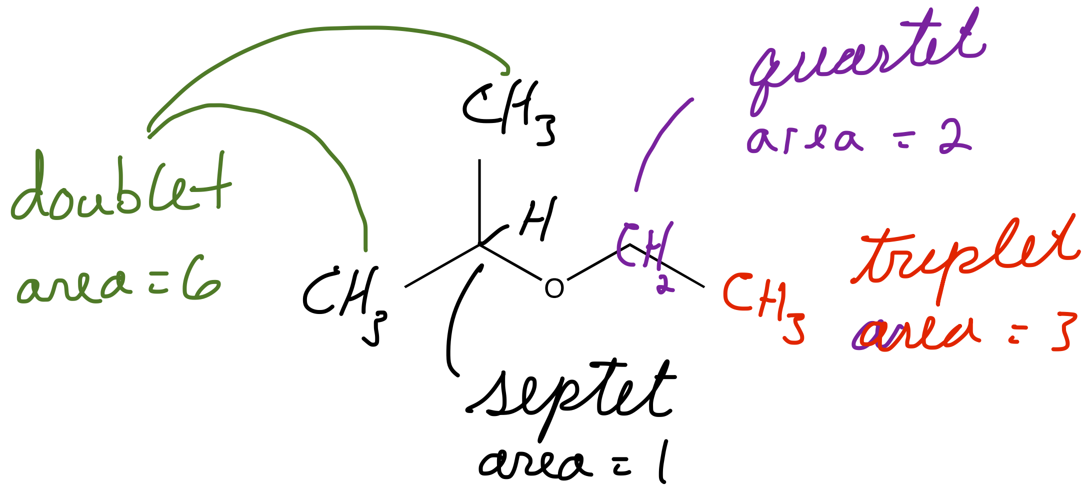
replace the H with D



CH$_2$'s H atoms are "diastereotopic" because replacing one H creates one of a pair of diastereomers



Not chemically equivalent

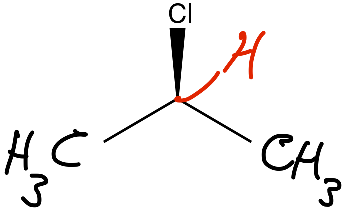


doublet
area = 6

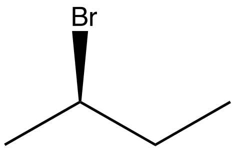
quartet
area = 2

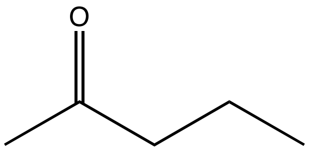
triplet
area = 3

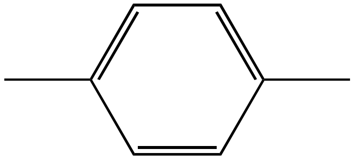
septet
area = 1

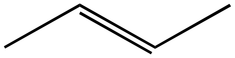


area 1









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