

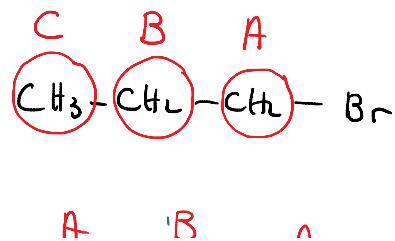
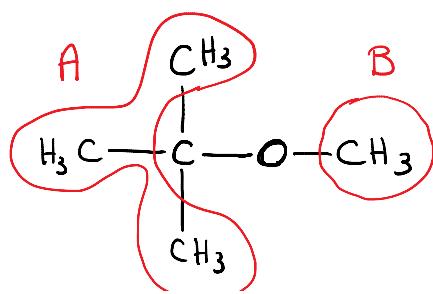
Interpretation of NMR Spectra

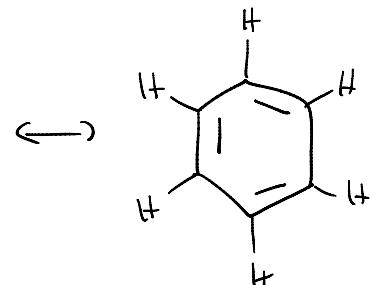
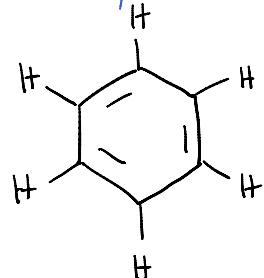
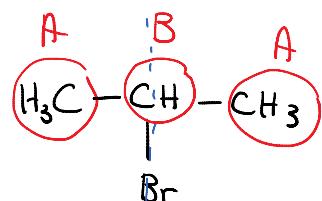
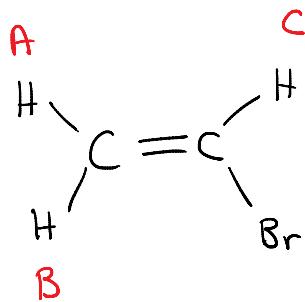
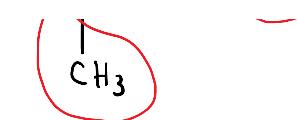
When analyzing an NMR spectrum, we get info from:

- ① # of signals (how many sets of unique H's)
- ② signal area (how many H's represented by each signal)
- ③ chemical shift (chemical structure, environment info)
- ④ signal splitting (how many neighboring nuclei)

① # of signals / Equivalent H's

- equivalent nuclei have the same chemical environment
 - groups related by symmetry (plane, axis, or center) in any conformation have equivalent H's
 - H's that experience same average environment via rotation about a single bond are equivalent (e.g. $-\text{CH}_3$)



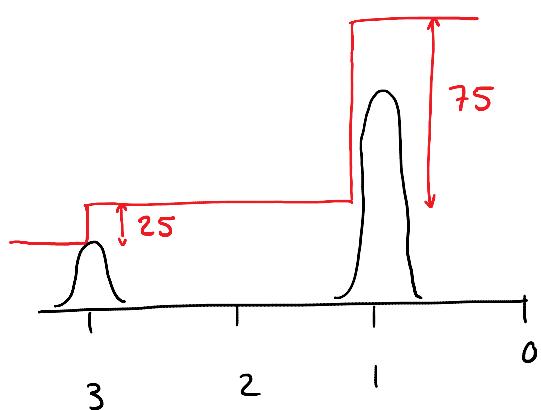


all equivalent
 \Rightarrow 1 peak

(2)

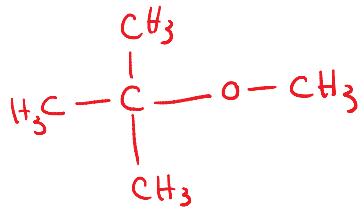
Signal area

- area of each peak is proportional to # of H's



- integral height is proportional to area
- $75 : 25 = 3 : 1$
- really 9 : 3 in this case

$^1\text{H-NMR}$ for



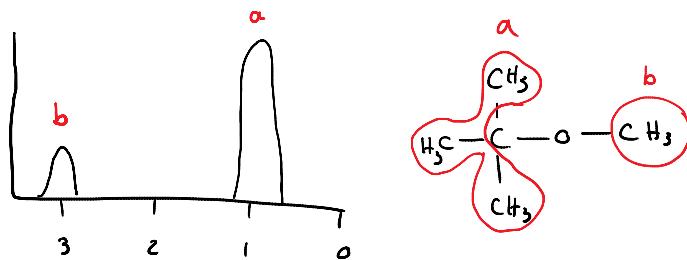
(3) Chemical Shift

- The chemical shift of a nucleus can give you valuable info about its chemical environment.
- Chemical shift depends on 3 factors:

- EN of nearby atoms
- hybridization of adjacent atoms
- magnetic induction within an adjacent π-bond

(A) EN of nearby atoms:

- adjacent EN atom withdraws e^- density and deshields nearby atoms.

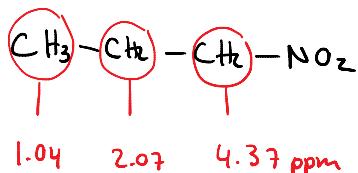


$\text{CH}_3 - X$	EN of X	δ of methyl H's (ppm)
$(\text{CH}_3)_4\text{Si}$ TMS	1.8	0.00 by definition
$(\text{CH}_3)_4\text{C}$	2.1	0.86
CH_3I	2.5	2.16
$\text{H}_3\text{C}-\text{OH}$	3.5	3.47

$\text{H}_3\text{C}-\text{OH}$	3.5	↓	2.16
CH_3F	4.0		3.47

		↓	4.26
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note: this effect is highly distance dependent:

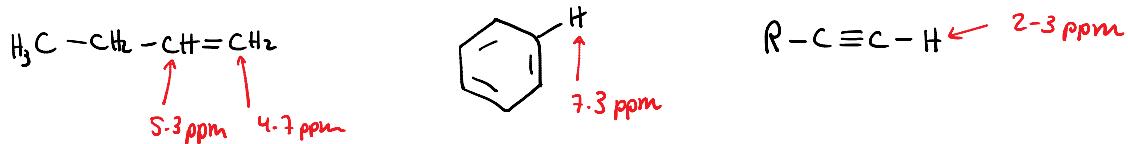


(B) hybridization of adjacent atoms

<u>molecule</u>	<u>hyb.</u>	<u>% s</u>	<u>δ</u>
$\text{H}_3\text{C}-\text{CH}_3$	sp^3	25	0.8 - 1.7
$\begin{array}{c} \text{H} \quad \text{H} \\ \quad / \\ \text{H}-\text{C}=\text{C}-\text{H} \\ \backslash \quad \text{H} \end{array}$	sp^2	33	4.6 - 5.7
$\text{H}-\text{C}\equiv\text{C}-\text{H}$	sp	50	2.0 - 3.0

greater EN of sp^2 C vs sp^3 C appears to explain alkane vs alkene shifts but not alkynes, so there must be another effect operating - see (C)

(C) Effects from π -bonds

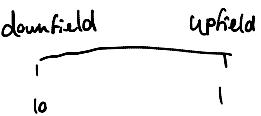


- $\pi - e^-$ are less tightly held by nuclei than $\sigma - e^-$, more free to move in response to the mag. field.
- if mag. field induced by $\pi - e^-$ in the same direction as B_0 , the mag. fields reinforce each other.

$$\nu \sim B_0$$

↗ ↑
higher higher

H^1 's shifted downfield (higher ppm)

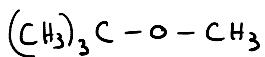
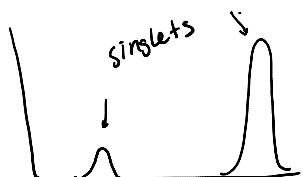


ex: benzene, alkenes

- if the mag. field induced by $\pi - e^-$ opposes B_0 , H^1 's shifted upfield (lower ppm).
- ex: alkynes

(4) splitting of signals

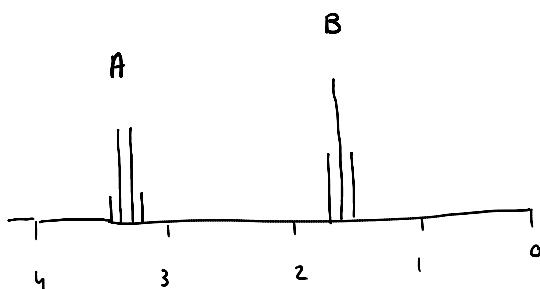
- signal splitting pattern will tell us how many neighboring nuclei are present.



H's attached to C's that are attached to nuclei with no H's → singlets

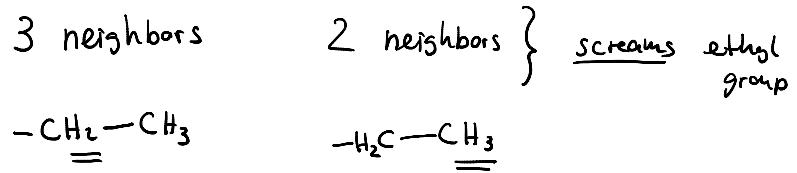
<u># lines in signal</u>	<u>name</u>
1	singlet
2	doublet
3	triplet
4	quartet
5	quintet
6	sixtet
n	multiplet

ex : $\text{H}_3\text{C}-\text{CH}_2-\text{Br}$
1.6 ppm 3.4 ppm



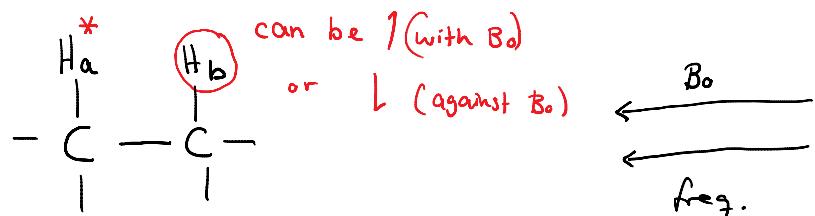
Integration : 2 3

Multiplet : quartet triplet

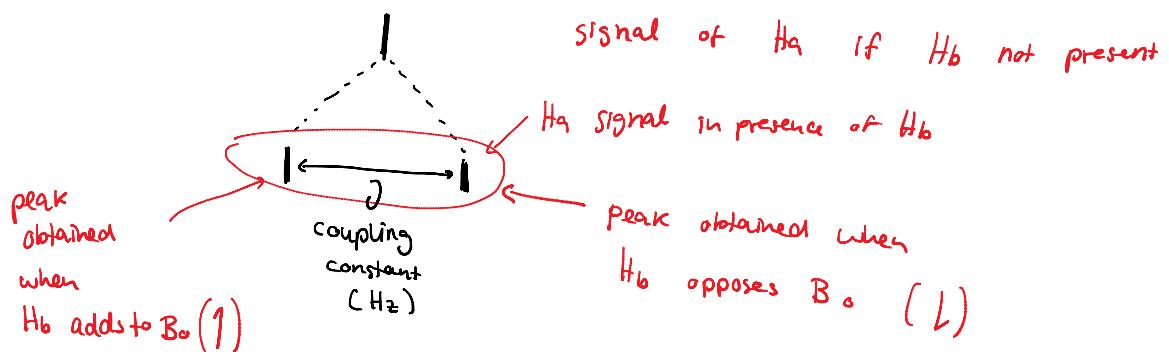


$(n+1)$ -rule : the signal of a hydrogen (or a set of equivalent H's) is split into $n+1$ peaks by non-equivalent set of equivalent neighboring H's.

Why is this true?



H_a signal :

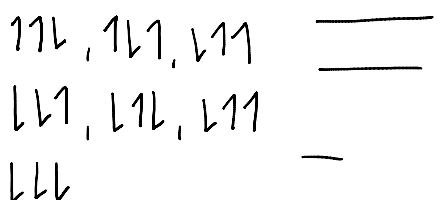


- H_a is coupled to H_b
- H_b " " " H_a

- equivalent sets of nuclei do not split each other by spin-spin coupling.

Back to $\text{CH}_3\text{-CH}_2\text{-Br}$:

- CH_2 next to CH_3 "sees": 111

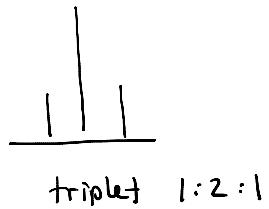
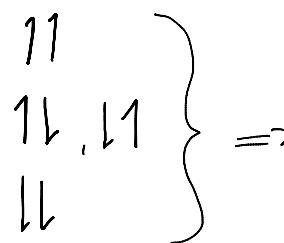


CH_3 signal:



quartet w/ intensities 1 : 3 : 3 : 1

- CH_3 next to CH_2 "sees"



triplet 1:2:1

relative peak intensities obey Pascal's triangle:

Singlet - - - - - |

○ coupling

Doubt - - - - - | |

| coupling

Triplet - - - - - | 2 |

2

Quartet - - - - - | 3 3 |

3

quartet --- 1 3 3 1 3
quintet --- 1 4 6 4 1 4
sixlet --- 1 5 10 10 5 1 5

Coupling constant (J) is the distance between the peaks in the split.

Signal given in Hertz, Hz. typically 0-18 Hz.

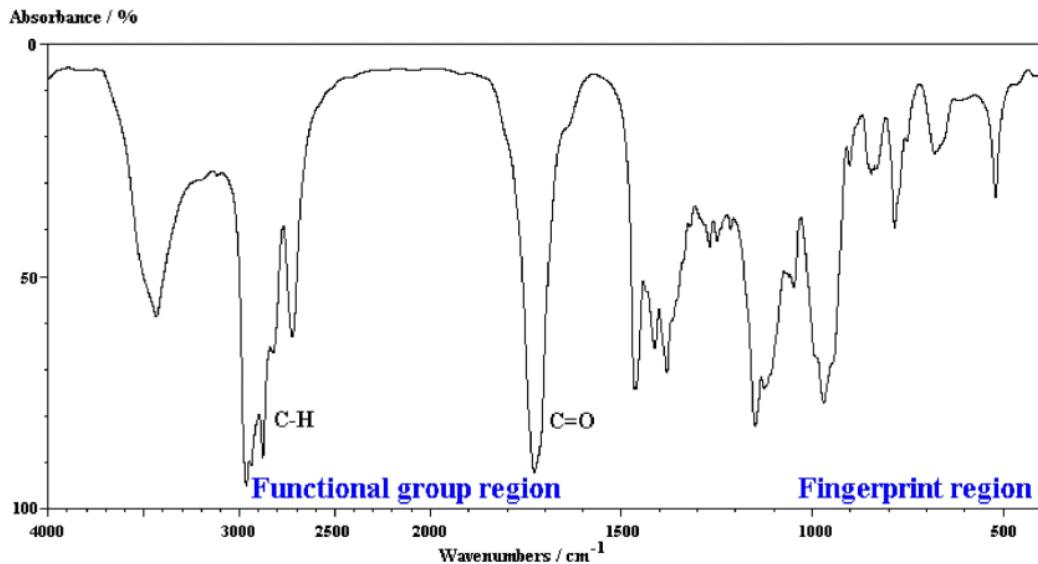
Orgo1 Lab NMR - TEMPLATE handout



Orgo1 Lab ...

Pointers for solving IR (Infrared Spectroscopy) problems:

- Read from left to right
- Do Not try to interpret every little peak



- $3500 - 3200 \text{ cm}^{-1}$ alcohol OH $\text{R}-\text{O}-\text{H}$
very broad
- $3300 - 2500 \text{ cm}^{-1}$ carboxylic acid O-H $\text{R}-\overset{\text{O}}{\underset{\text{H}}{\text{C}}}-\text{O}-\text{H}$
very broad and C=O stretch must also be present
 $(1800 - 1600 \text{ cm}^{-1})$
- $3200 - 3000 \text{ cm}^{-1}$ C-H of alkene
looks like a pointing finger

Orgo1 Lab NMR Page 1

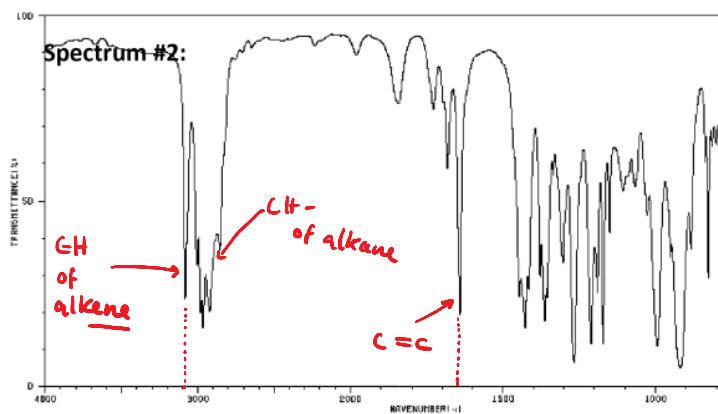
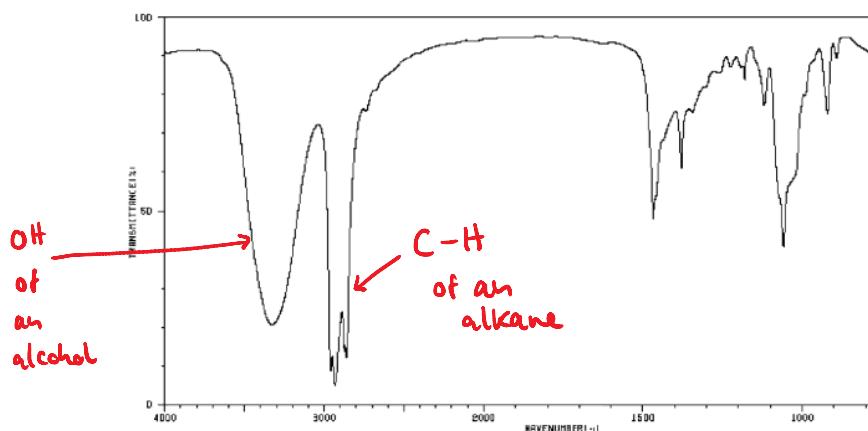
- $3000 - 2800 \text{ cm}^{-1}$ C-H of an alkane
looks like a pointing finger
 - $1800 - 1600 \text{ cm}^{-1}$ carbonyl stretch C=O - Strong
- ketone
- IR Spectra interpretation

IR Spectra interpretation

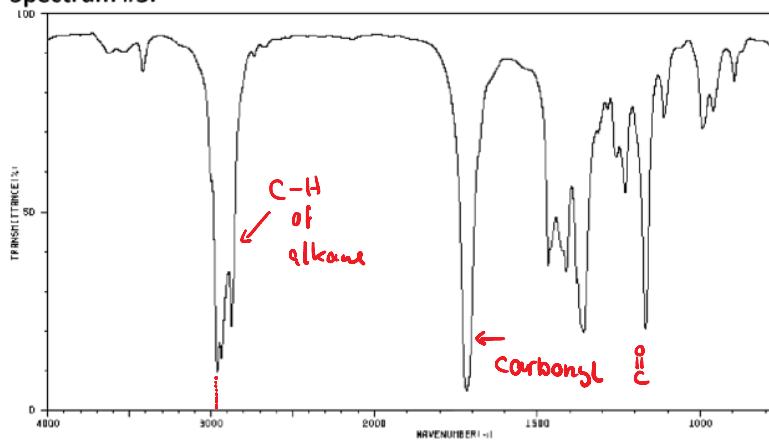
Thursday, August 28, 2014
5:05 PM

$\text{C}=\text{O}$ C=C
- ketone
usually 1715 cm^{-1}

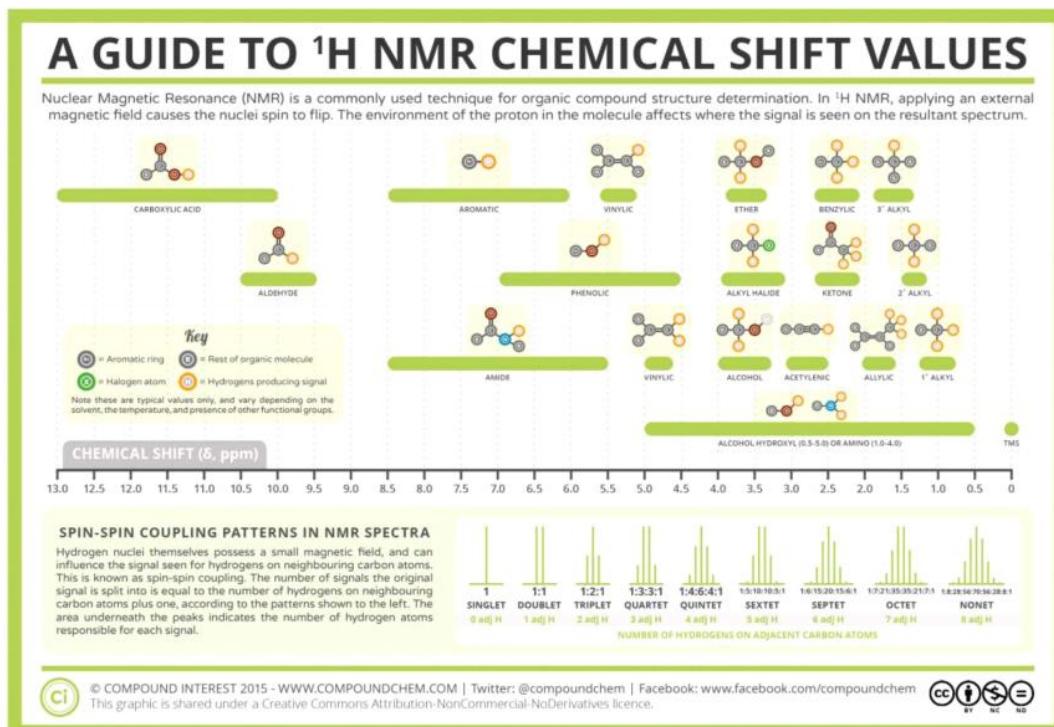
Spectrum #1:



Spectrum #3:



Pointers for Solving NMR-spectra



Pointers for solving NMR problems:

Steps :

- 1) If the chem. formula is given
calculate IHD (index of hydrogen deficiency)
(see your textbook page 193)

The # tells you # of π-bonds or rings present.

2. # of signals in spectrum

tells you how many many inequivalent groups of Hydrogens are present.

3. Integrals / Ratios between the peaks

indicates how many hydrogens each peak represents

4. Chemical shift δ

indicates the electronic environment of Hydrogens

e^- -rich = left of NMR spectrum (downfield)

e^- -poor = right of NMR spectrum (upfield)

Orgo1 Lab NMR Page 6

5. Splitting : indicates the # of neighboring H's
Apply $n+1$ rule

1 neighboring H → $1+1 = \text{doublet}$

2 " " → $2+1 = \text{triplet}$

3 " " → $3+1 = \text{quartet}$

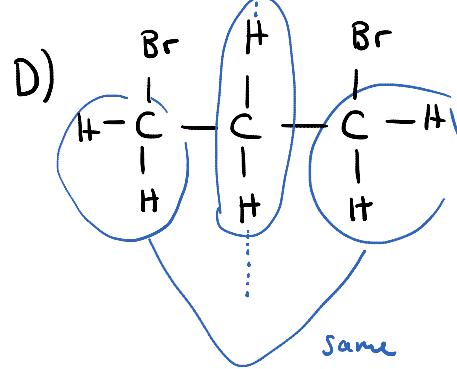
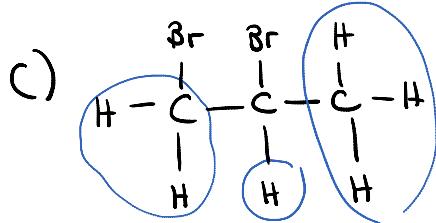
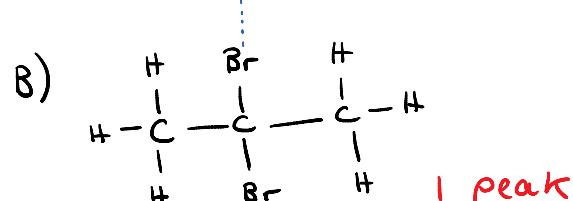
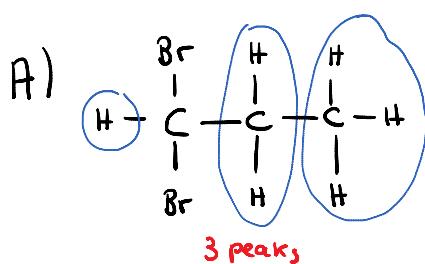
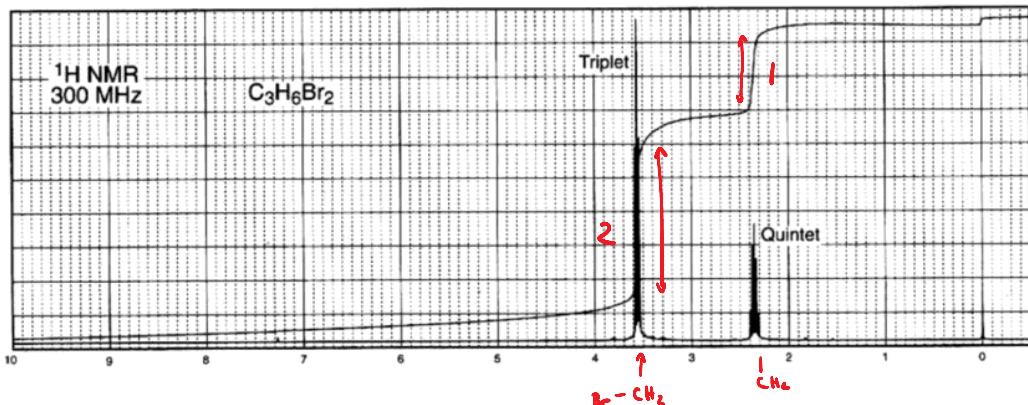
Problem 1: NMR

$$\begin{array}{l}
 \text{1 neighboring H} \longrightarrow 1 + 1 = \text{doublet} \\
 \text{2 " " } \longrightarrow 2 + 1 = \text{triplet} \\
 \text{3 " " } \longrightarrow 3 + 1 = \text{quartet}
 \end{array}$$

Problem 1: NMR

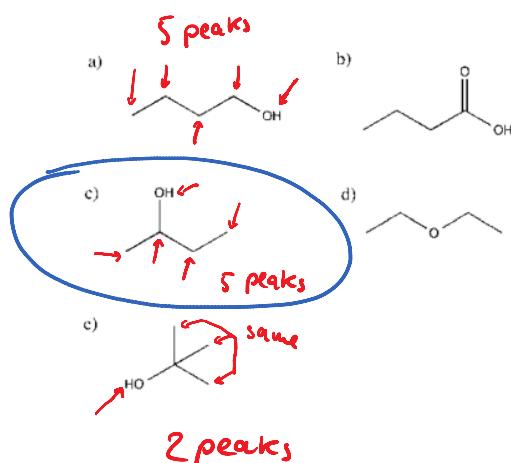
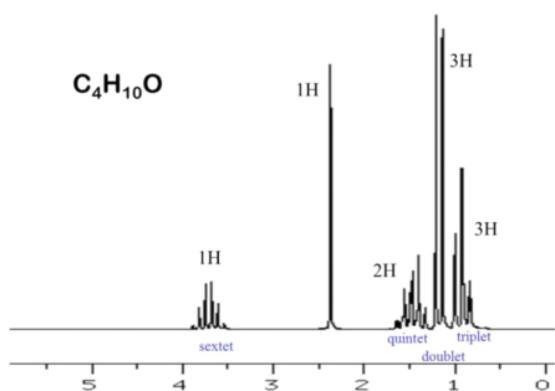
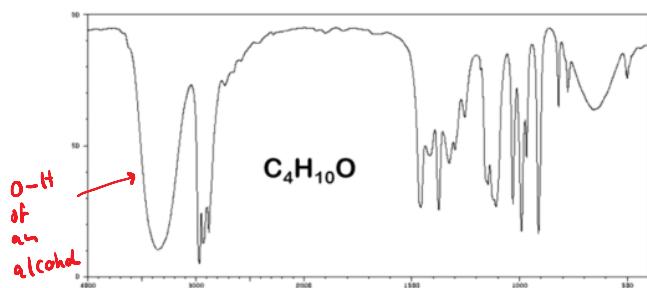
Elucidate the structure of the compound from the proton NMR below.

$2:1 \cong 4:2 \rightarrow \text{accounts for } 6 \text{ H's}$



Problem 2: NMR and IR combo

Elucidate the structure of the compound using the proton NMR and IR spectra below.

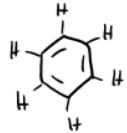


Ratio : 1:1:2:3:3

for c) : 1:1:2:3:3 matches

for a) : 3:2:2:2:1

H-NMR of Benzene derivatives

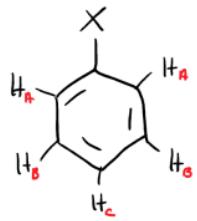


1 peak @ 7.26 ppm

integral = 6

aromatic region 6-8 ppm

Mono-subs. Benzene:



how many peaks?

3

(but sometimes

2

Integral ratios?

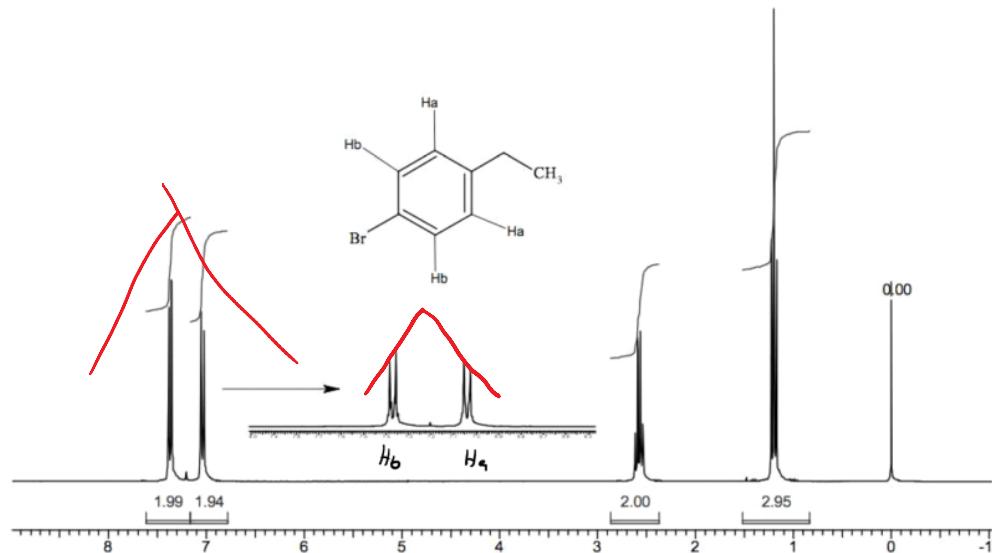
2 : 2 : 1

2 : 3)

Di-subs. Benzene

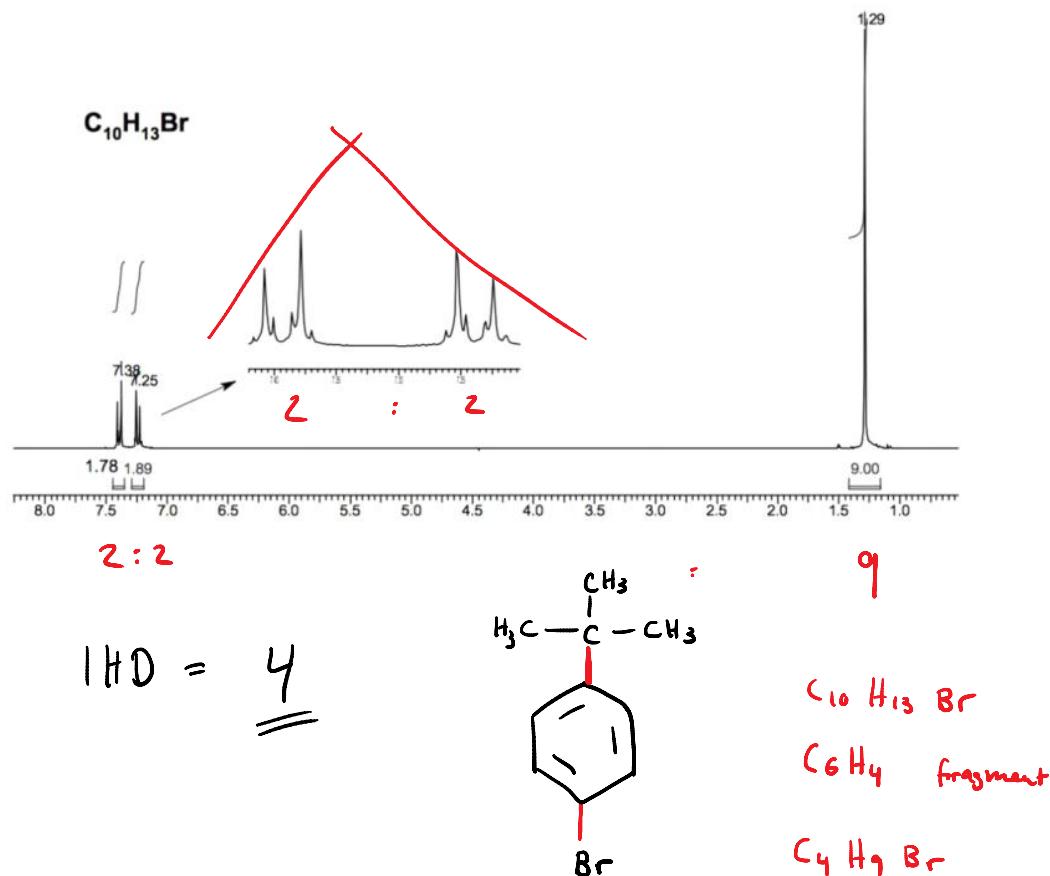
	# of peaks	Integral ratio
	4	1 : 1 : 1 : 1
	4	1 : 1 : 1 : 1
	2	2 : 2

H-NMR of para-substituted Benzene derivatives



2. Propose structures for the compounds that would be expected to generate the following ^1H NMR spectra. Calculate the degree of unsaturation of each compound and assign the protons to their respective peaks.

A.



C.

$$\text{HDO} = 4$$

