CHEM 222 section 01

Crash course in interpretting NMR spectra – for lab

NMR = the workhorse of characterization tools
reveals connectivity & alkyl chains

For a basic overview of NMR (to help interpret spectra):

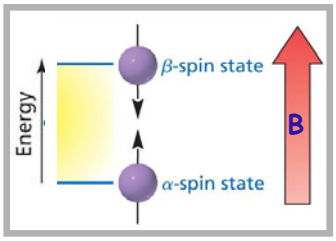
- **read these summary slides**
- **read Ch.13 sections 1 (superficially) + 7 & 10 (details)**

(details & explanations later in class)

(1) **Helpful website for spectroscopy topics: Michigan State University**
http://www.cem.msu.edu/~reusch/VirtualText/Spectrpy/spectro.htm#contnt

Nuclear magnetic resonance (NMR) spectroscopy - the basic principles

- Many **nuclei spin** about their axis, like e⁻s
  ^{1}H ^{13}C ^{31}P ^{19}F
  ⇨ generate own tiny magnetic field
- If place **sample in magnetic field**, B
  ⇨ nuclei's field can (α) line up with field
  OR (β) align opposite



- Radio waves (low freq. radiation) = sufficient energy to excite nuclei to higher E spin state (β)

⇨ NMR = another type of absorption spectroscopy

^{1}H NMR spectrum:
- x-axis = ***relative*** freq. of radio wave absorbed: ***chemical shift "δ"***
- y-axis = absorption ***intensity***, *which scales with # Hs absorbing*

(2) *δ = relative to what?! More in class later…*

Information provided by a ^{1}H NMR spectrum

1) Chemical shift (δ) = peak position: *e⁻-richness of H's environment*

- neighbouring groups' electrons *shield* nearby H nuclei (make $\Delta E_{\alpha\text{-}\beta}$ lower)
- H near EWG ⇨ *deshielded* ⇨ H's peak appears at higher δ (ppm)

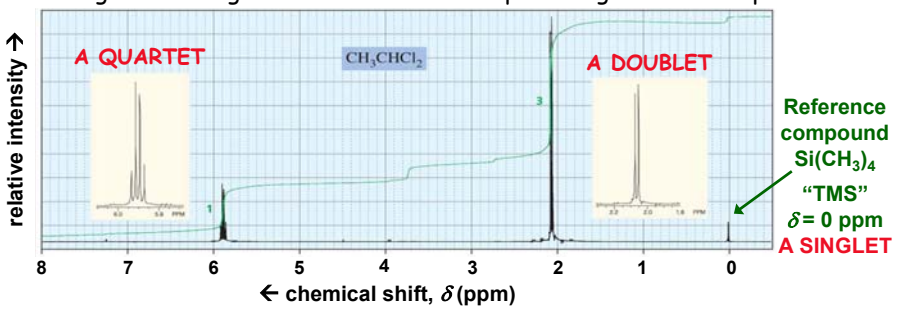
2) Multiplicity = peak shape: indicates # of H's on adjacent C atom(s)

- Hs feel presence of *Hs on next-door C atom:* H-C-*C*-H_n...
- Effect of *coupling*:

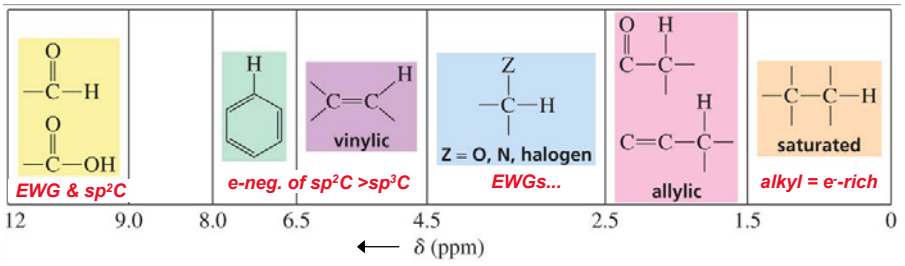
H sees 0H ⇨ peak not split	= singlet	1	*s*
H sees 1H ⇨ peak split into 2	= doublet	1:1	*d*
H sees 2H ⇨ peak split into 3	= triplet	1:2:1	*t*
H sees 3H ⇨ peak split into 4	= quartet	1:3:3:1	*q*

3) Intensity = peak area: scales with # Hs causing the peak

- Heights of integration trace ⇨ relative peak heights ⇨ # Hs/peak



Characteristic chemical shifts for ^{1}H NMR spectra



- If know potential structure: look for key features in NMR (CH_3, Ph, *etc*)
- Alkyl region (δ = 0-3 ppm): most cluttered, but yields most information
- Complex peaks = multiplets: can be due to overlapping *d*, *t* or *q* peaks

STRATEGY FOR INTERPRETTING SPECTRA: ***steps 1&2 together...***

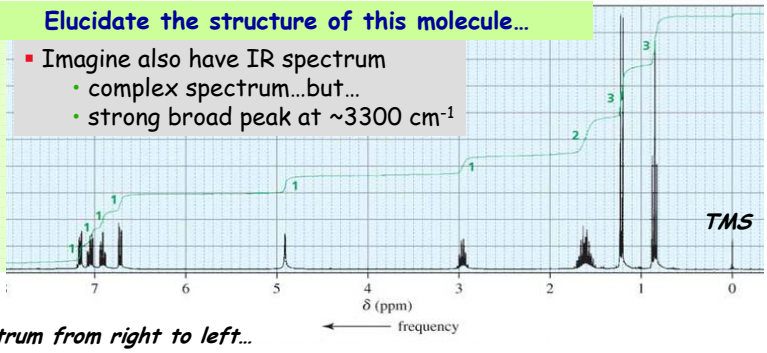
1) Chemical shifts: 1st identify well-resolved peaks, then overlapping peaks
2) Multiplicity: identify isolated Hs (singlets)
   use multiplicity to identify neighbours on alkyl chain
3) Integration: determine #Hs per peak & correlate with proposed IDs
4) Combine everything: propose a structure ⇨ would it give observed spectrum?

Don't forget other tools: anything learned from UV/Vis, IR, MS ?

Example: **Elucidate the structure of this molecule…**

For maximum learning, follow/work alongside WITHOUT skipping ahead to see answer

- Imagine also have IR spectrum
  - complex spectrum…but…
  - strong broad peak at ~3300 cm^{-1}

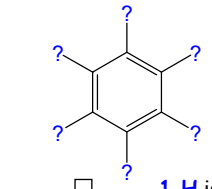


Reading spectrum from right to left…

Region	δ (ppm)	Mult.	Tells us…	# Hs	Ideas? (colour coded…)
alkyl	0.85	*t*	coupled to 2 H	3 H	CH_3-CH_2-
alkyl	1.2	*d*	coupled to 1 H	3 H	CH_3-CH-
alkyl	1.6	*mult*	coupled to MANY	2 H	R-CH_2-R' …nearer EWG
alkyl	2.95	*mult*	coupled to many	1 H	R-CH-R' very near EWG
C=C? ROH?	4.9	*s*	isolated, 4°C-X-H	1 H	-OH ! *(suggested by IR!!)*
phenyl	6.7	*d*	coupled to 1 H	1 H	On phenyl ring, seeing 1H
phenyl	6.9	*t*	coupled to 2 H	1 H	On Ph ring, H on each side?
phenyl	7.05	*t*	coupled to 2 H	1 H	On Ph ring, H on each side?
phenyl	7.15	*d*	coupled to 1 H	1 H	On phenyl ring, seeing 1H

Space for you to work…

Try to piece this into a structure: start with Ph ring (arbitrary…)

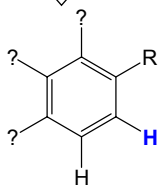


1ST

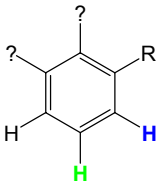
- follow connectivity suggested by multiplicities

δ (ppm)	Mult.	# Hs	Ideas? (colour coded…)
6.7	*d*	1 H	On phenyl ring, beside 1H
6.9	*t*	1 H	On Ph ring, H on each side?
7.05	*t*	1 H	On Ph ring, H on each side?
7.15	*d*	1 H	On phenyl ring, beside 1H

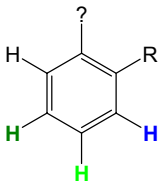
2ND ⇩ 1 H is beside 1 H & no other Hs



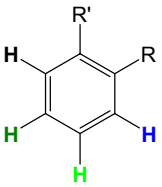
3RD 1 H beside this H ⇨ + 1 H on other side



4TH another 1 H ⇨ should have 1H on each side



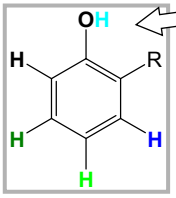
5TH ⇩ our last 1 H should have an H on only one side



6TH ⇦ **What do we know about substituents R *vs* R'?**
- look at 2 Hs beside Rs
- H more deshielded than H

⇨ **R' = a heteroatom? ⇨ OH?**

conclude…



Try to piece this into a structure: continue with R group on Ph ring

1ST

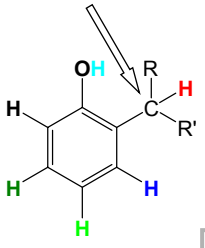
- Follow connectivity suggested by mult. & positions

WE KNOW:
R = alkyl chain on Ph ring
PLACE TO START:
Find atom attached to Ph

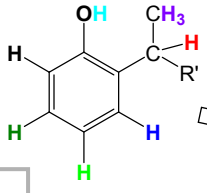
2ND ⇩

Ph attachment = sp^2 C like an EWG
⇨ -CH (δ 2.95) is on Ph !

δ (ppm)	Mult.	Tells us…	#Hs	Ideas? (colour coded…)
0.85	*t*	sees 2 H	3 H	CH_3-CH_2-
1.2	*d*	sees 1 H	3 H	CH_3-CH-
1.6	*mult*	sees many	2 H	R-CH_2-R' …near EWG
2.95	*mult*	sees many	1 H	R-CH-R' NEAR EWG
4.9	*s*	isolated	1 H	-OH ?

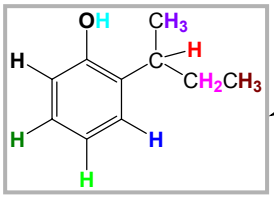


3RD CH_3 is coupled to this H ⇨ = R or R'…



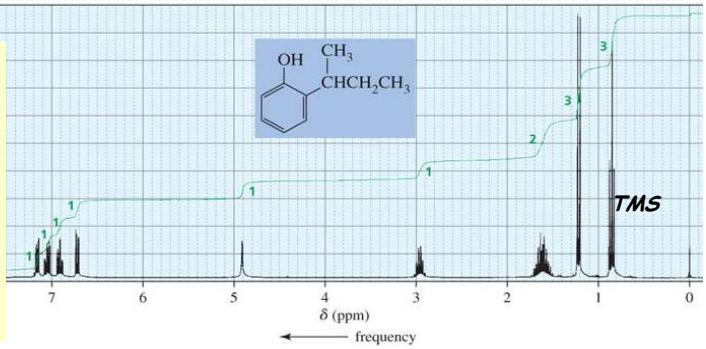
4TH Still missing CH_2 & CH_3… But…

5TH CH_3 is coupled to a CH_2… …and the only one not accounted for yet is CH_2



Answer: correct!

It takes practice:
- start with simple examples in text (simpler than this)
- be organized
- be logical
- draw possibilities
- test hypotheses
  ⇨ get right peaks?
- be patient.



Region	δ (ppm)	Mult.	Tells us…	# Hs	Idea?
alkyl	0.85	*t*	coupled to 2 H	3 H	CH_3-CH_2-
alkyl	1.2	*d*	coupled to 1 H	3 H	CH_3-CH-
alkyl	1.6	*mult*	coupled to MANY	2 H	R-CH_2-R' …nearer EWG
alkyl	2.95	*mult*	coupled to many	1 H	R-CH-R' very near EWG
C=C? ROH?	4.9	*s*	isolated, 4°C-X-H	1 H	-OH ?
phenyl	6.7	*d*	coupled to 1 H	1 H	On phenyl ring, beside R= ?
phenyl	6.9	*t*	coupled to 2 H	1 H	On Ph ring, H on each side
phenyl	7.05	*t*	coupled to 2 H	1 H	On Ph ring, H on each side
phenyl	7.15	*d*	coupled to 1 H	1 H	On phenyl ring, beside R= ?