

Today

Section 14.10 - 17
Splitting and Multiplicity

Section 14.20
 ^{13}C $\{^1\text{H}\}$ NMR

Practice Determining Structure Based on
Spectroscopic Data

Second Class from Today

Chapter 15
Carbonyl Chemistry

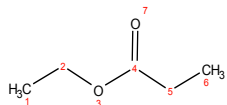
Next Class

Chapter 15
Carbonyl Chemistry

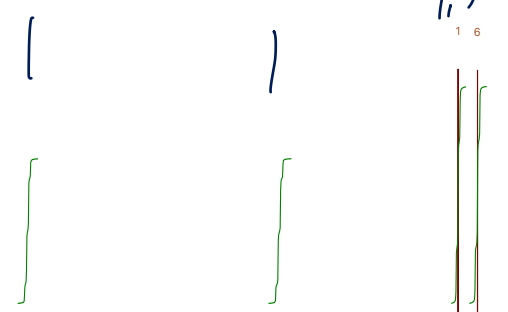
Third Class from Today

The NMR Spectrum

Predicted ¹H NMR Spectrum



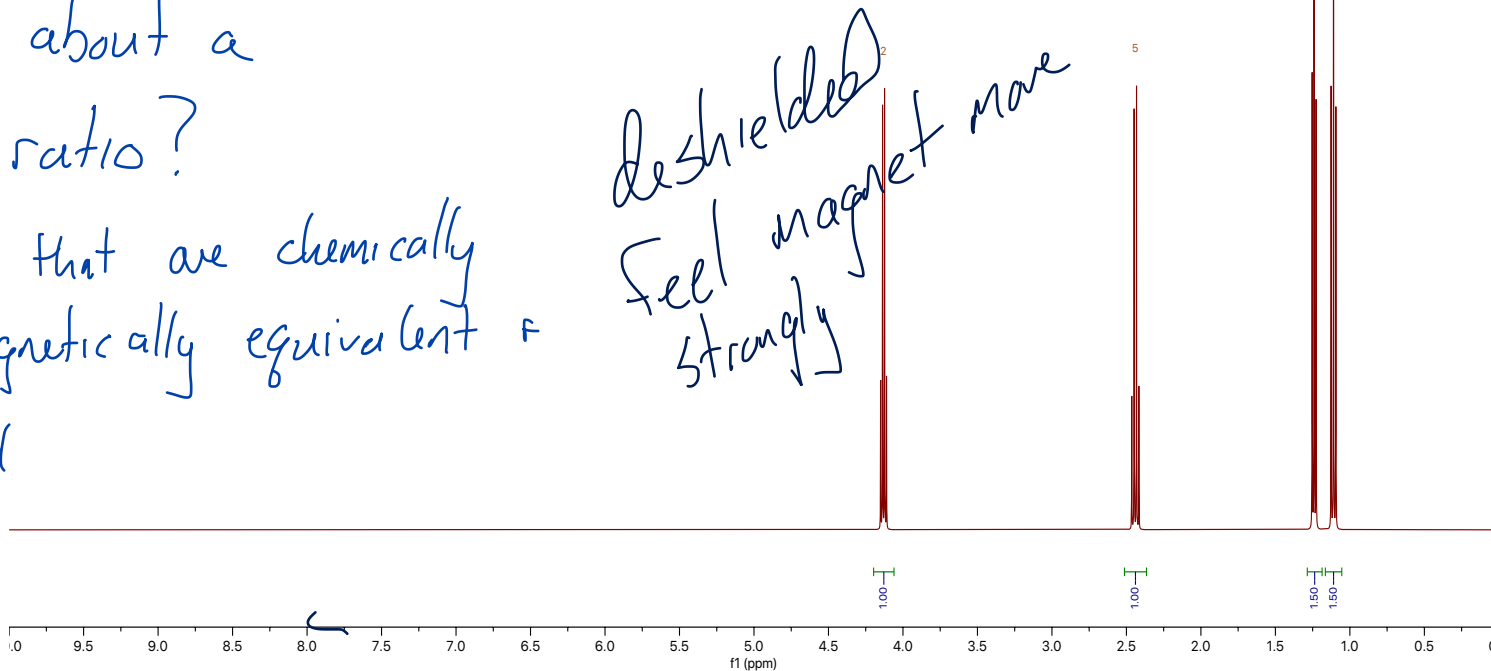
CH₂ 2 CH₂ 2 CH₃ 3 CH₃ 3
1.5 1.5
1 6



What about a 6:1 ratio?

2 CH₃ that are chemically + magnetically equivalent + a CH

deshielded
Feel magnet more strongly

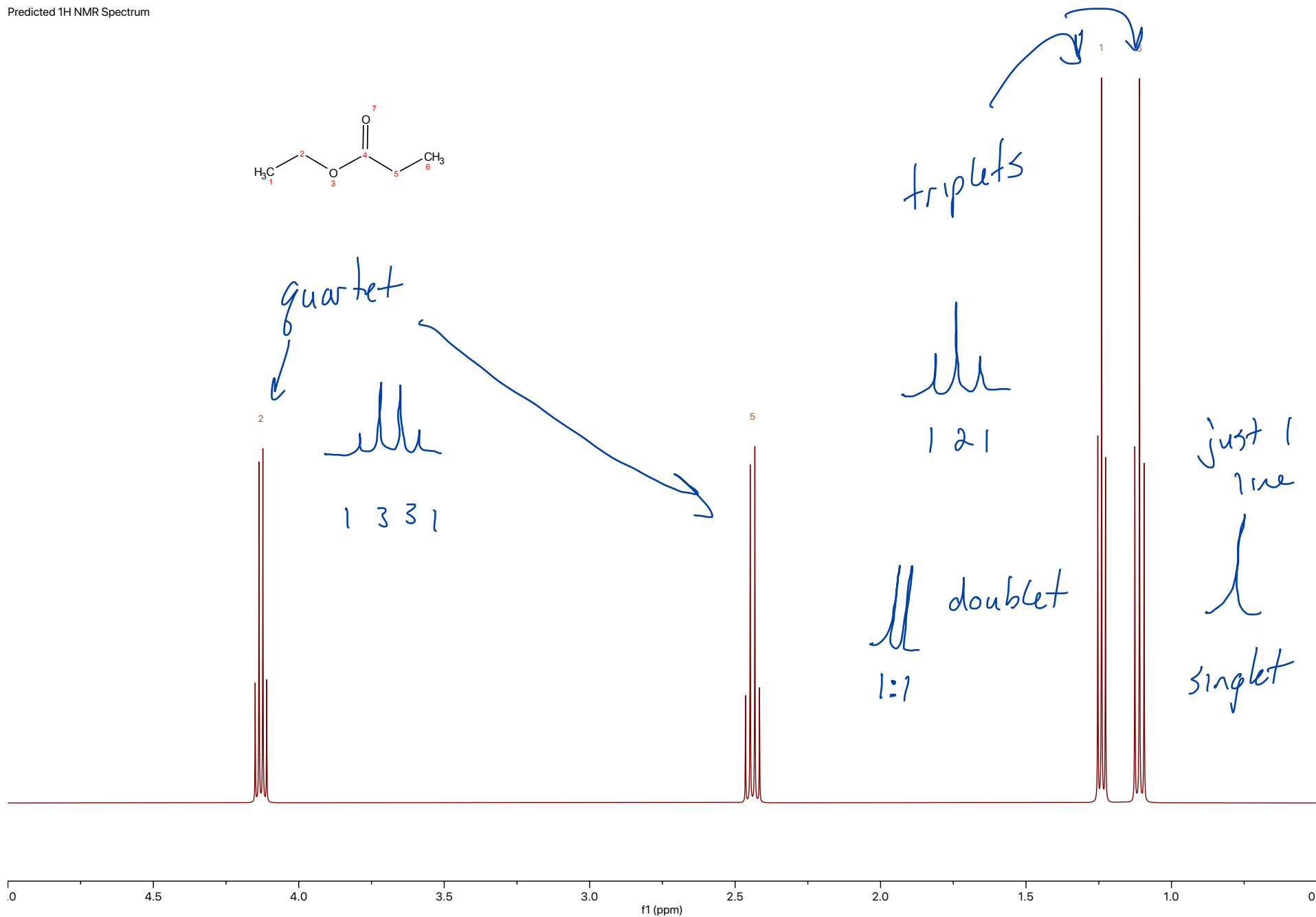
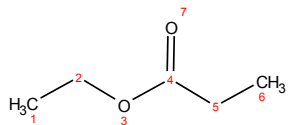


# of different types of H atoms	Chemical environments of the H atoms	How many of each type of H atom	# of H atom neighbors
3	3	3	3

Multiplicity: Why are there several lines in some peaks?

Section 14.11 – 14.14

Predicted ¹H NMR Spectrum



Multiplicity: Why are there several lines in some peaks?

Scalar or First Order Coupling

H_c exists next to the H_a

The H_c 's on the these 3 molecules exist in a different environment

1 H_c next to $\uparrow\uparrow$ resonate at higher freq

H_c next to $\downarrow\uparrow$ resonates at

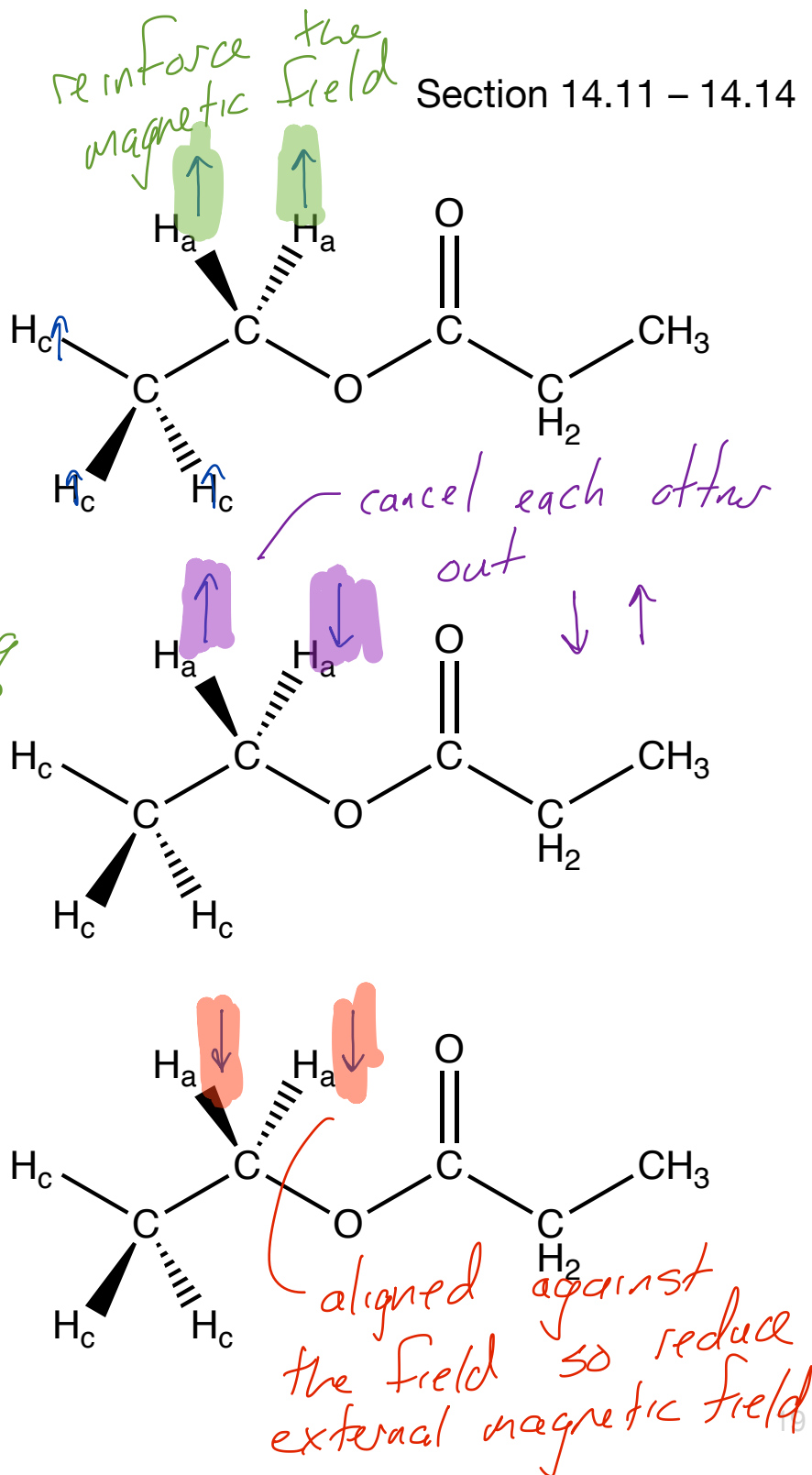
expected frequency

two ways to do this one so...

H_c next to $\downarrow\downarrow$ resonate at

lower frequency

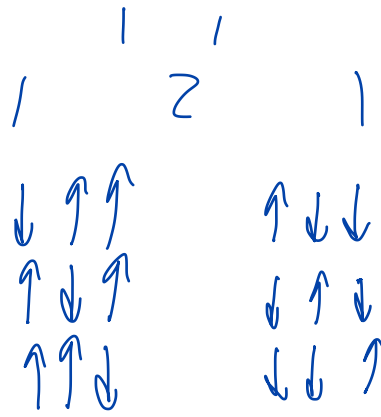
Section 14.11 - 14.14



3 neighbors

↑ ↑ ↑

1



3

3

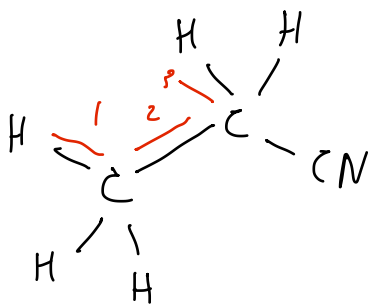
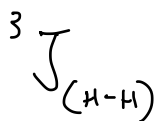
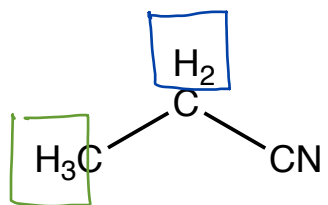
↓ ↓ ↓

1

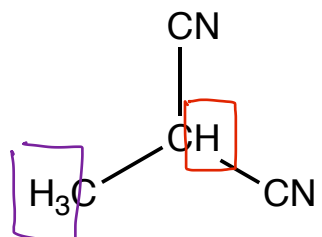
Multiplicity: $n + 1$ rule

Section 14.11 – 14.14

For H to H coupling, the pattern of lines in a peak is $n + 1$, where n is the number of magnetically equivalent H atoms 3 bonds away from and magnetically inequivalent to the H atoms causing the resonance peak.



There are 3 H's 3 bonds away. So we get $n+1$ lines or 4 lines a quartet

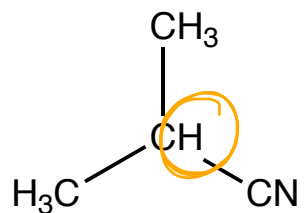


There are 3 H's ... quartet

There is one neighbor... doublet

There are 2 H's 3 bonds away... $n+1 = 3$ triplet

a singlet has...



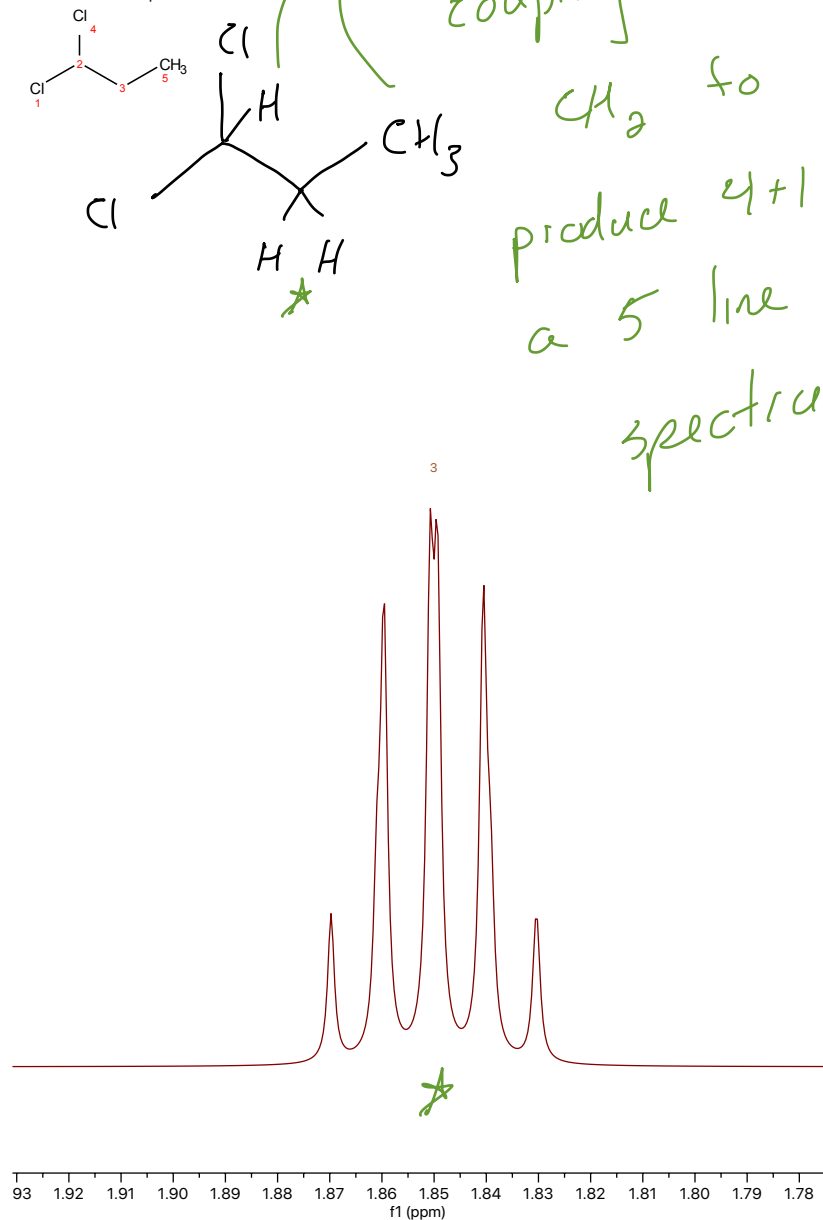
There are 6 chemically + magnetically equivalent neighbors ...

$6+1 \Rightarrow$ septet often called a multiplet

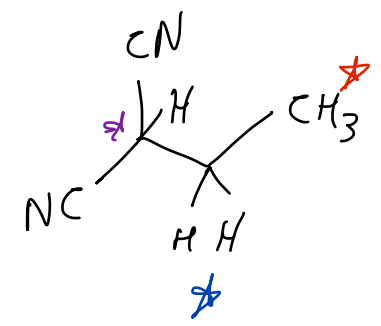
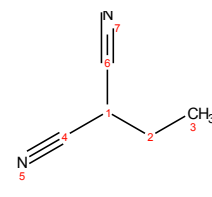
$n+1 = 1$ singlet
 $n=0$

Multiplicity: more than one set of magnetically inequivalent H atoms 3 bonds away

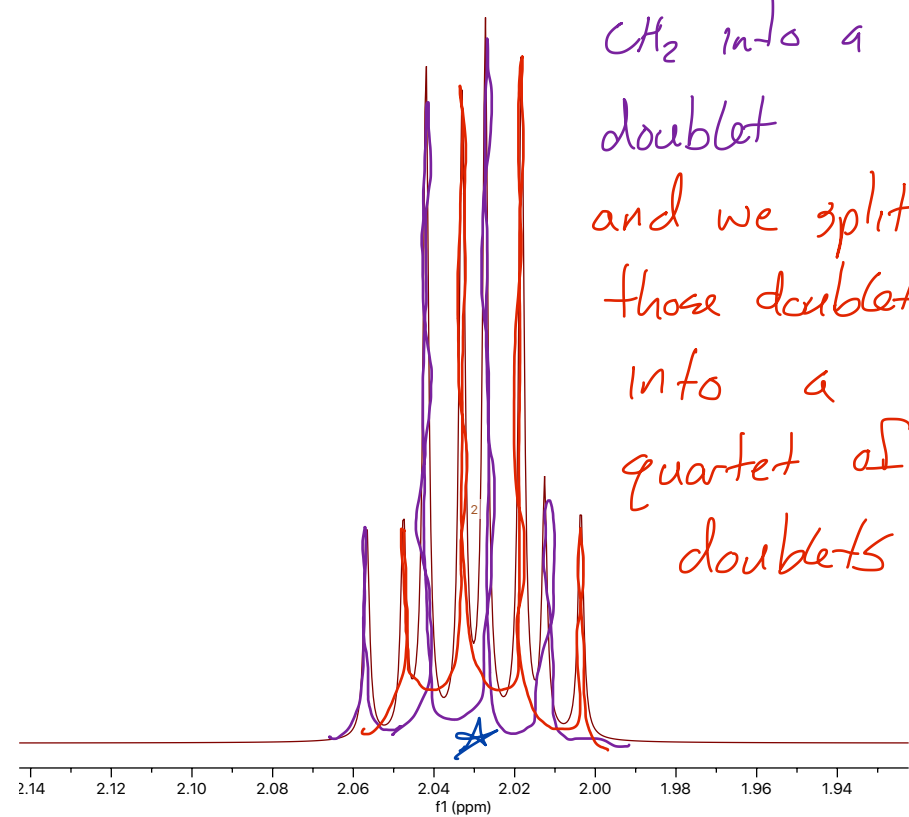
Predicted ¹H NMR Spectrum



similar enough coupling to CH₂ to produce 4+1 = 5 a 5 line spectrum

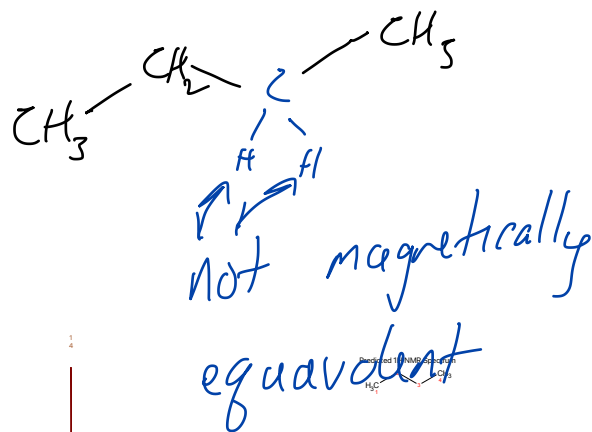


I turn the CH₂ into a doublet and we split those doublets into a quartet of doublets

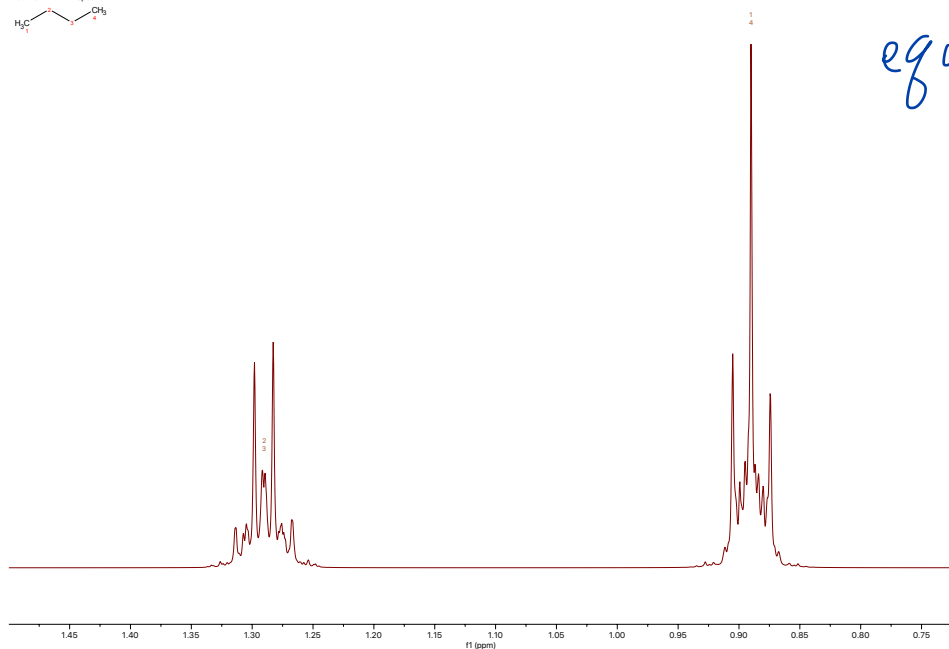


Multiplicity: more than one set of magnetically inequivalent H atoms 3 bonds away

Section 14.11 - 14.14

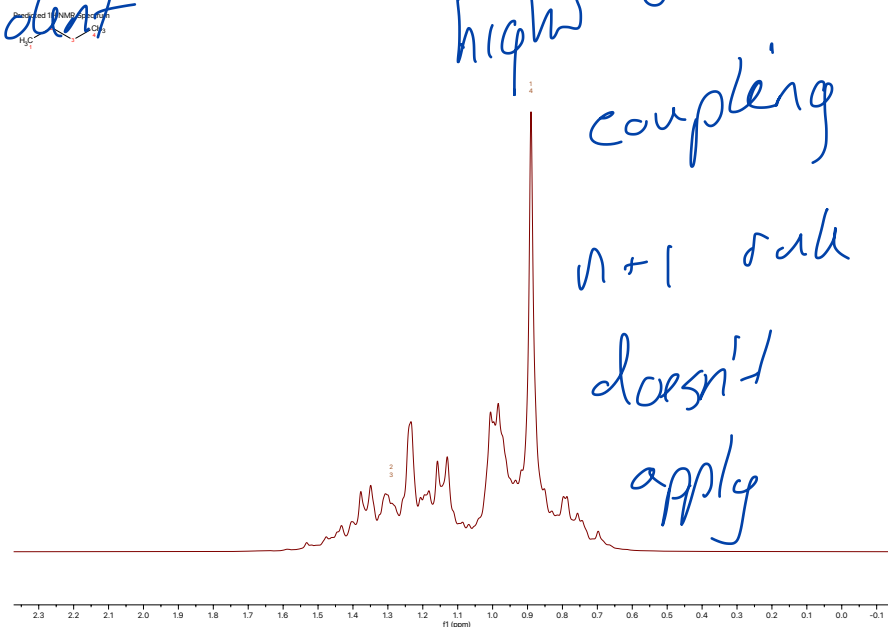


Predicted ¹H NMR Spectrum



high magnetic field (500 MHz)

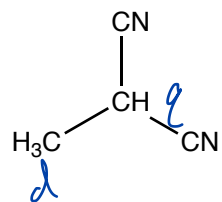
Predicted ¹H NMR Spectrum



low magnetic field (60 MHz)

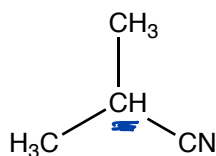
Multiplicity Summary

1 set of chemically and magnetically inequivalent neighbors



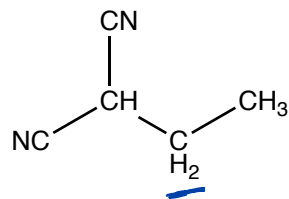
$n+1$ rule ✓

2 sets of chemically and magnetically inequivalent neighbors that are equivalent to each other

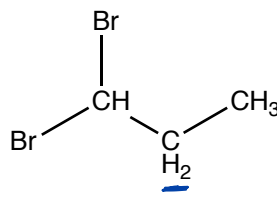


add up the # of H's and use the $n+1$ rule

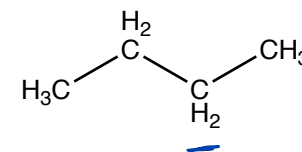
2 sets of chemically and magnetically inequivalent neighbors that are inequivalent to each other



can form
 $(n+n+1)$ lines

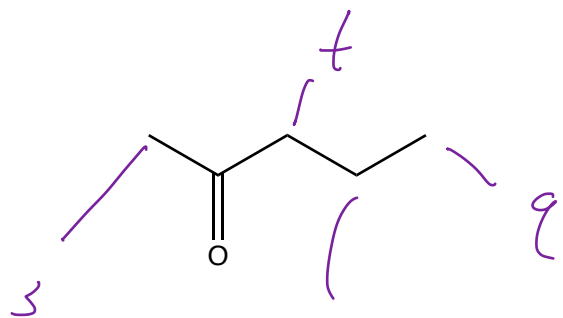


$(n+1)$ of $(n+1)$ peaks
2 of 4 peaks
doublet of quartets

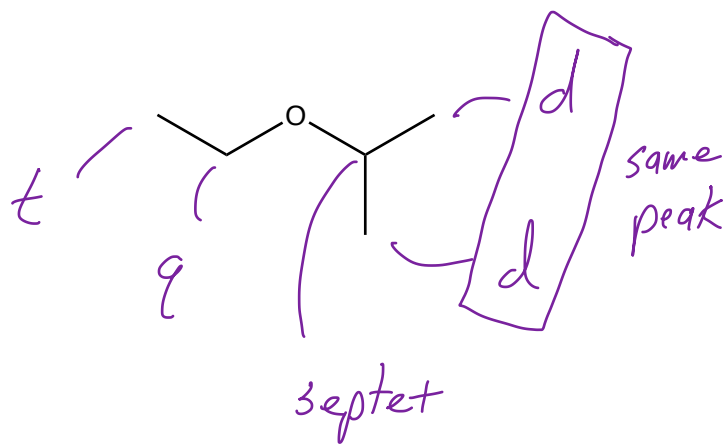


mess

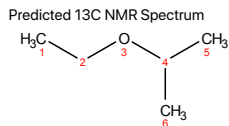
Predict Multiplicity



possible
t of q,
6 line peak,
or
complicated
pattern



^{13}C $\{^1\text{H}\}$ NMR

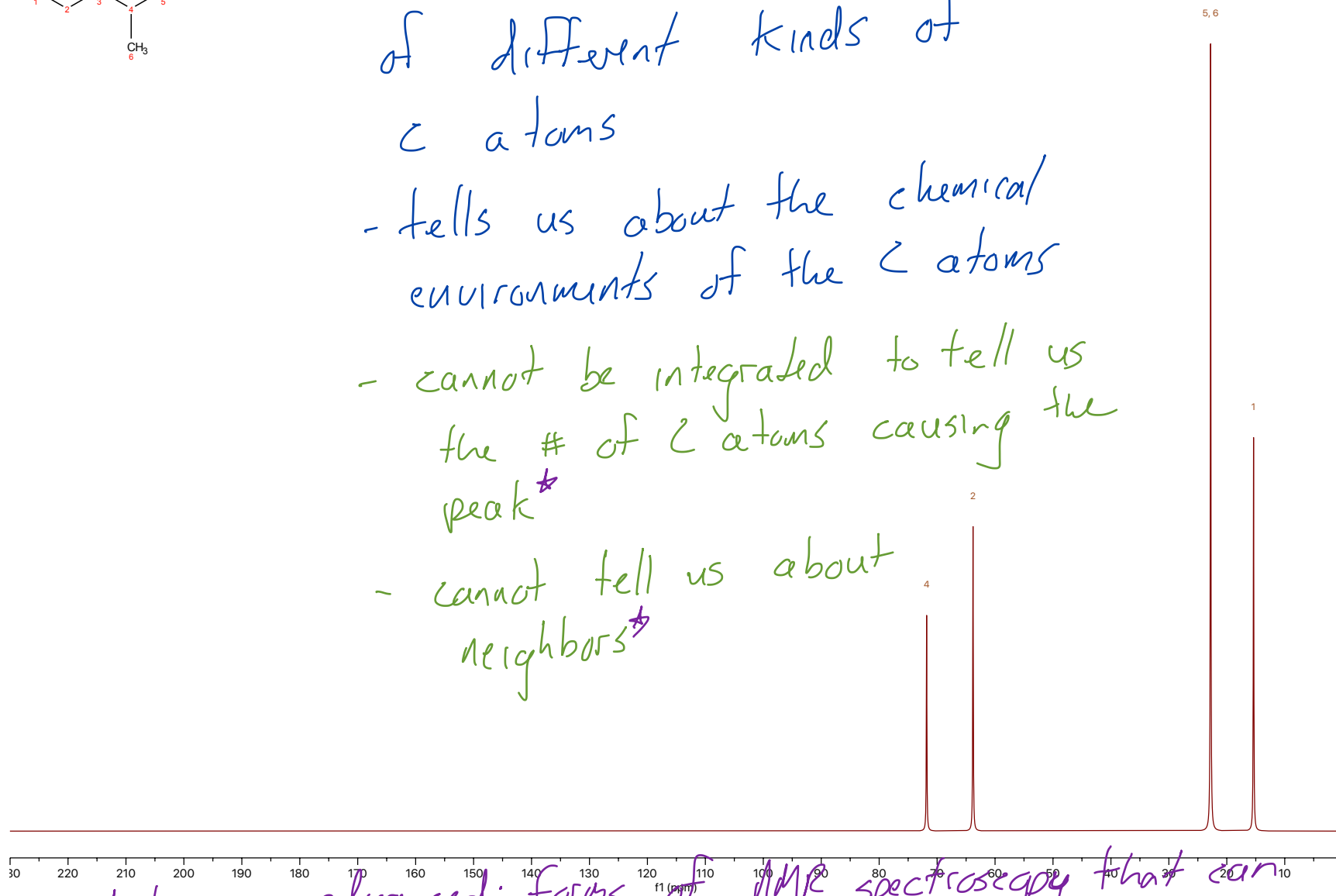


^{13}C - tells us about the # of different kinds of C atoms

- tells us about the chemical environments of the C atoms

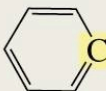
- cannot be integrated to tell us the # of C atoms causing the peak*

- cannot tell us about neighbors*



* there are advanced forms of NMR spectroscopy that can give us more information

^{13}C $\{^1\text{H}\}$ NMRTable 14.4 Approximate Values of Chemical Shifts for ^{13}C NMR

Type of carbon	Approximate chemical shift (ppm)	Type of carbon	Approximate chemical shift (ppm)
$(\text{CH}_3)_4\text{Si}$	0	$\text{C}-\text{I}$	0–40
$\text{R}-\text{CH}_3$	8–35	$\text{C}-\text{Br}$	25–65
$\text{R}-\text{CH}_2-\text{R}$	15–50	$\text{C}-\text{Cl}$	35–80
$\begin{array}{c} \text{R} \\ \\ \text{R}-\text{CH}-\text{R} \end{array}$	20–60	$\text{C}-\text{N}$	40–60
$\begin{array}{c} \text{R} \\ \\ \text{R}-\text{C}-\text{R} \\ \\ \text{R} \end{array}$	30–40	$\text{C}-\text{O}$	50–80
$\equiv\text{C}$	65–85	$\begin{array}{c} \text{R} \\ \diagdown \\ \text{C}=\text{O} \\ \diagup \\ -\text{N} \end{array}$	165–175
$=\text{C}$	100–150	$\begin{array}{c} \text{R} \\ \diagdown \\ \text{C}=\text{O} \\ \diagup \\ \text{RO} \end{array}$	165–175
	110–170	$\begin{array}{c} \text{R} \\ \diagdown \\ \text{C}=\text{O} \\ \diagup \\ \text{HO} \end{array}$	175–185
		$\begin{array}{c} \text{R} \\ \diagdown \\ \text{C}=\text{O} \\ \diagup \\ \text{H} \end{array}$	190–200
		$\begin{array}{c} \text{R} \\ \diagdown \\ \text{C}=\text{O} \\ \diagup \\ \text{R} \end{array}$	205–220