

## Today

Section 14.1 - 14.9  
Introduction to Nuclear Magnetic Resonance,  
Shielding, Chemical Shift, and Integration

Section 14.10 - 17  
Splitting and Multiplicity

## Second Class from Today

Chapter 15  
Carbonyl Chemistry

## Next Class

Section 14.10 - 17  
Splitting and Multiplicity

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

Practice Determining Structure Based on  
Spectroscopic Data

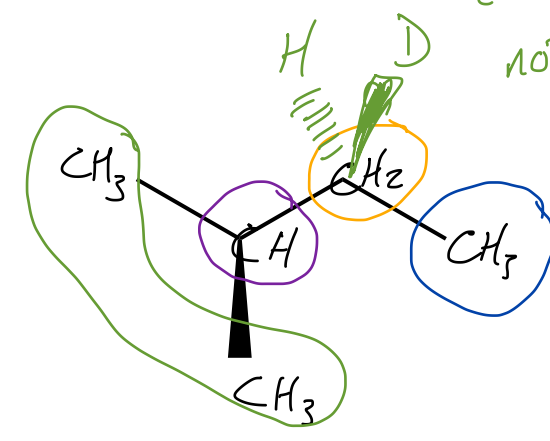
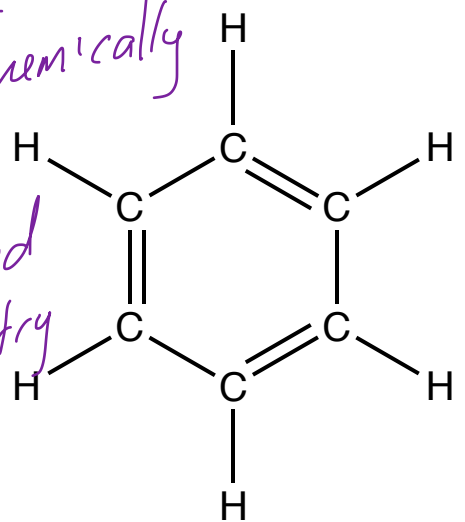
## Third Class from Today

Chapter 15  
Carbonyl Chemistry

# What makes $^1\text{H}$ 's Different or the Same

Section 14.3 – 14.7

just one peak  
these are chemically  
the same  
all are related  
by symmetry



enantiomers  
not diastereomers

enantiomers  
not diastereomers



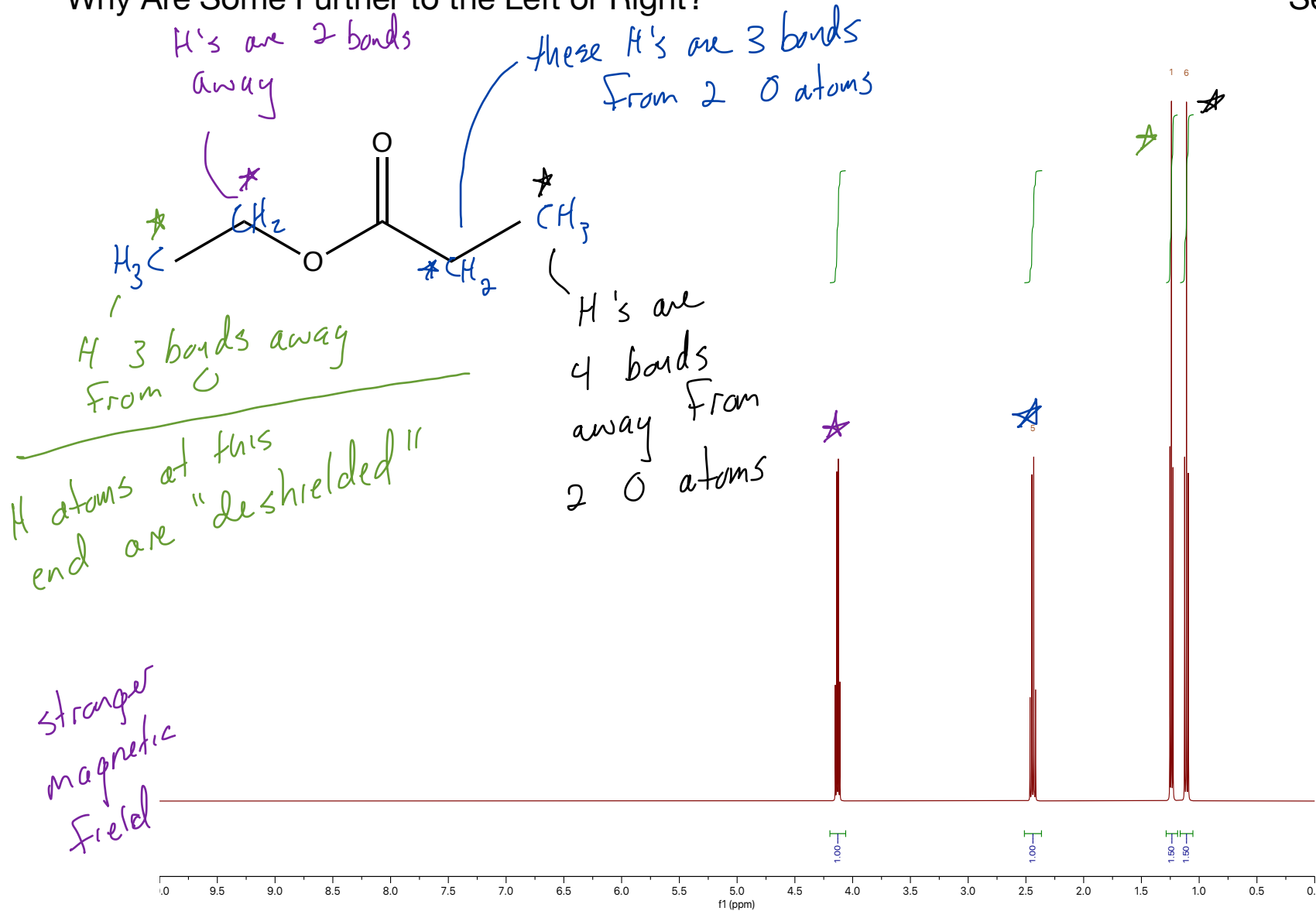
Look for different chemical environments to make them different.

Look for symmetry to make them the same

Double check for diastereotopic  $\text{H}$ 's when 2 groups or  $\text{H}$  atoms are "equivalent"

to form diastereomers 2 stereogenic centers are needed  
 $\text{CH}_2$   $\text{H}$ 's not diastereotopic  $\text{CH}_3$   $\text{H}$ 's are not diastereotopic

# Why Are Some Further to the Left or Right?



H atoms at this end are "deshielded"

stronger magnetic field

these H's are 3 bonds from 2 O atoms

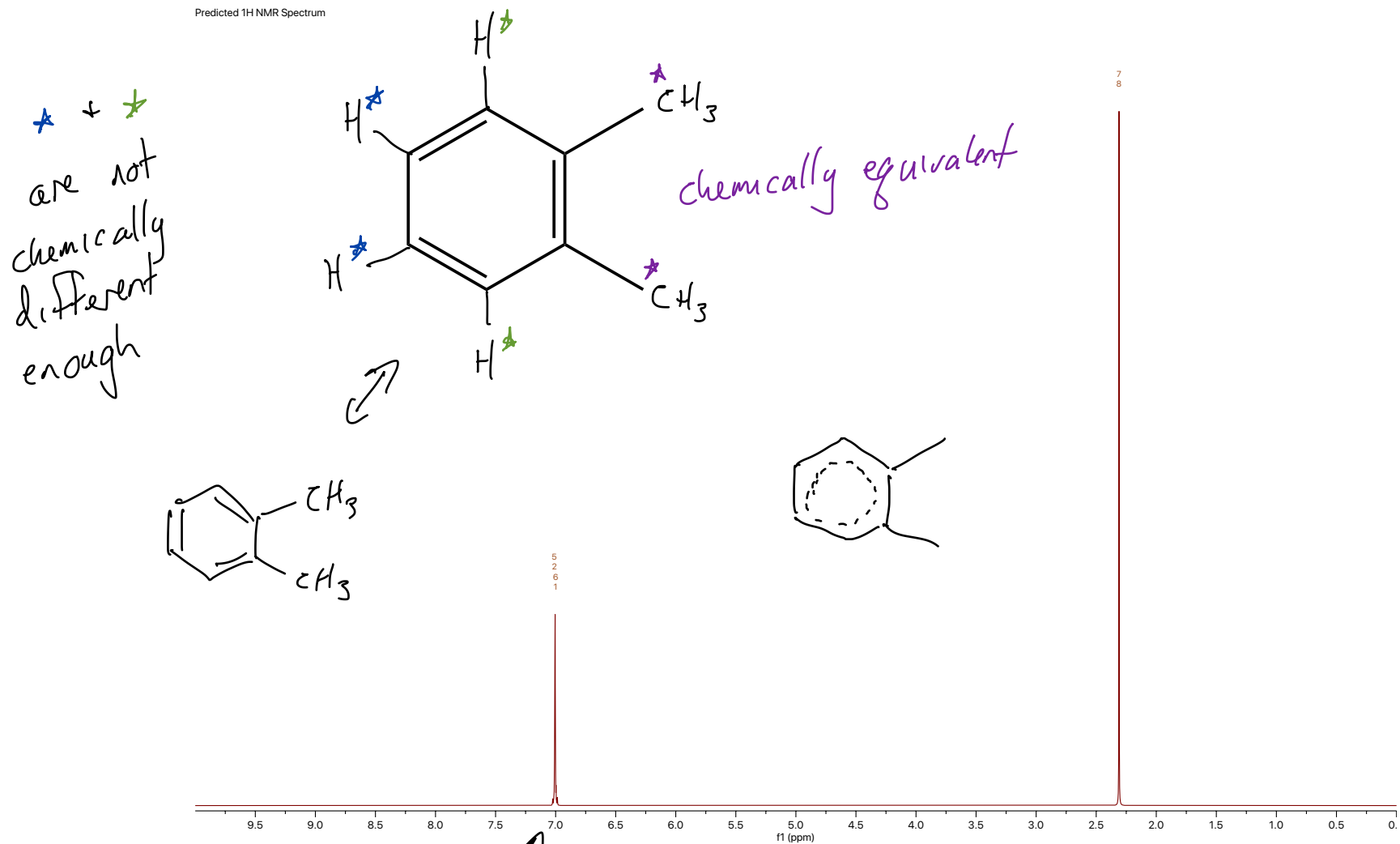
H's are 4 bonds away from 2 O atoms

H atoms are "shielded" from the magnetic field weaker magnetic field

H atoms close to electronegative elements have their e-'s drawn away and are deshielded

H atoms further from electronegative atoms maintain their shielding

# Why Are Some Further to the Left or Right?

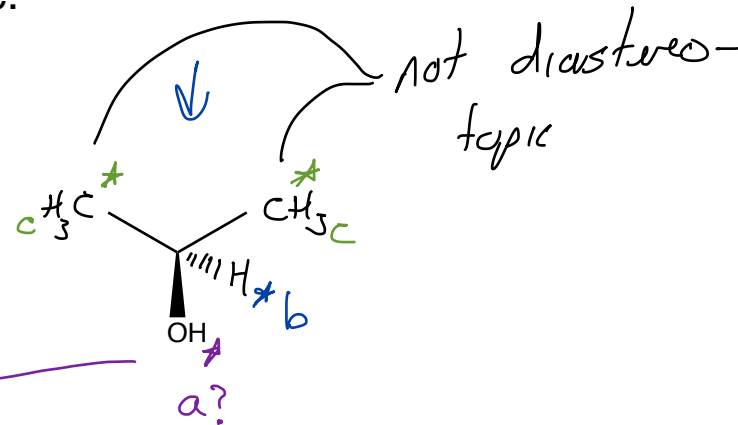
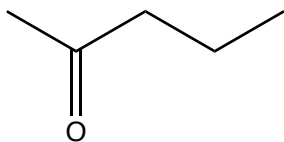


ring currents in  $\pi$  bonds of benzene  
"deshield" the H's and they resonate at  
higher frequency

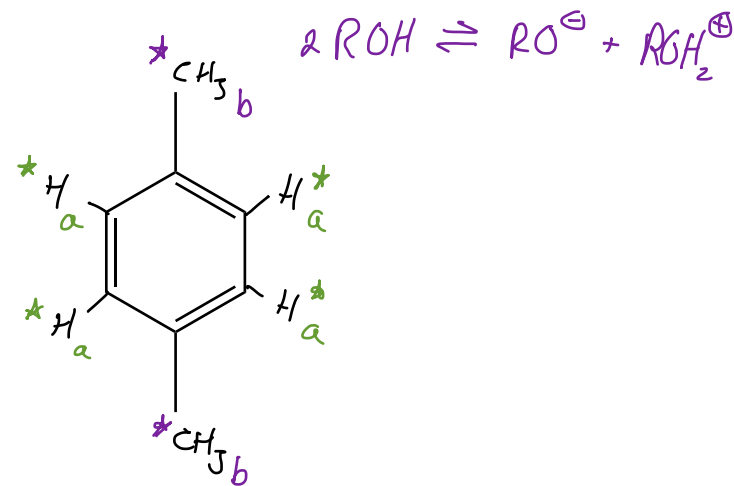
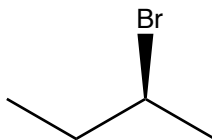
# Why Some Further to the Left or Right?

## Section 14.3 - 14.7

Practice: How many peaks? Assign letters alphabetically based on expected position in the NMR spectrum: A farthest to the left, B first peak to the right of A, etc.



OH's are very strange...  
the H-bond with other OH's, and  
they can exchange

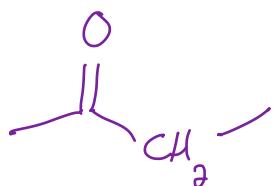


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# Characteristic Chemical Shifts

# Section 14.3 - 14.7

lines mean just more  
 $sp^3$  C-H stuff



$CH_3$  to  $CH_2$  is +.4

$CH_3$  bonded to a carbonyl carbon is 2.1  
 2.5

Table 14.1 Approximate Values of Chemical Shifts for  $^1H$  NMR<sup>a</sup>

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
$-CH-$	1.4		2.5-4
$-C=C-CH_3$	1.7		3-4
	2.1		4-4.5
	2.3	$R-O-CH_3$	Variable, 1.5-4
$-C\equiv C-H$	2.4	$R-C=CH_2$	Variable, 2-5
$R-O-CH_3$	3.3	$ArOH$	Variable, 4-7
$R-C=CH_2$	4.7		Variable, 10-12
$R-C=C-H$	5.3		Variable, 5-8

<sup>a</sup>The values are approximate because they are affected by neighboring substituents.

# What Does the Integration Tell Us?

The size signal is proportional to the H's that are resonating.

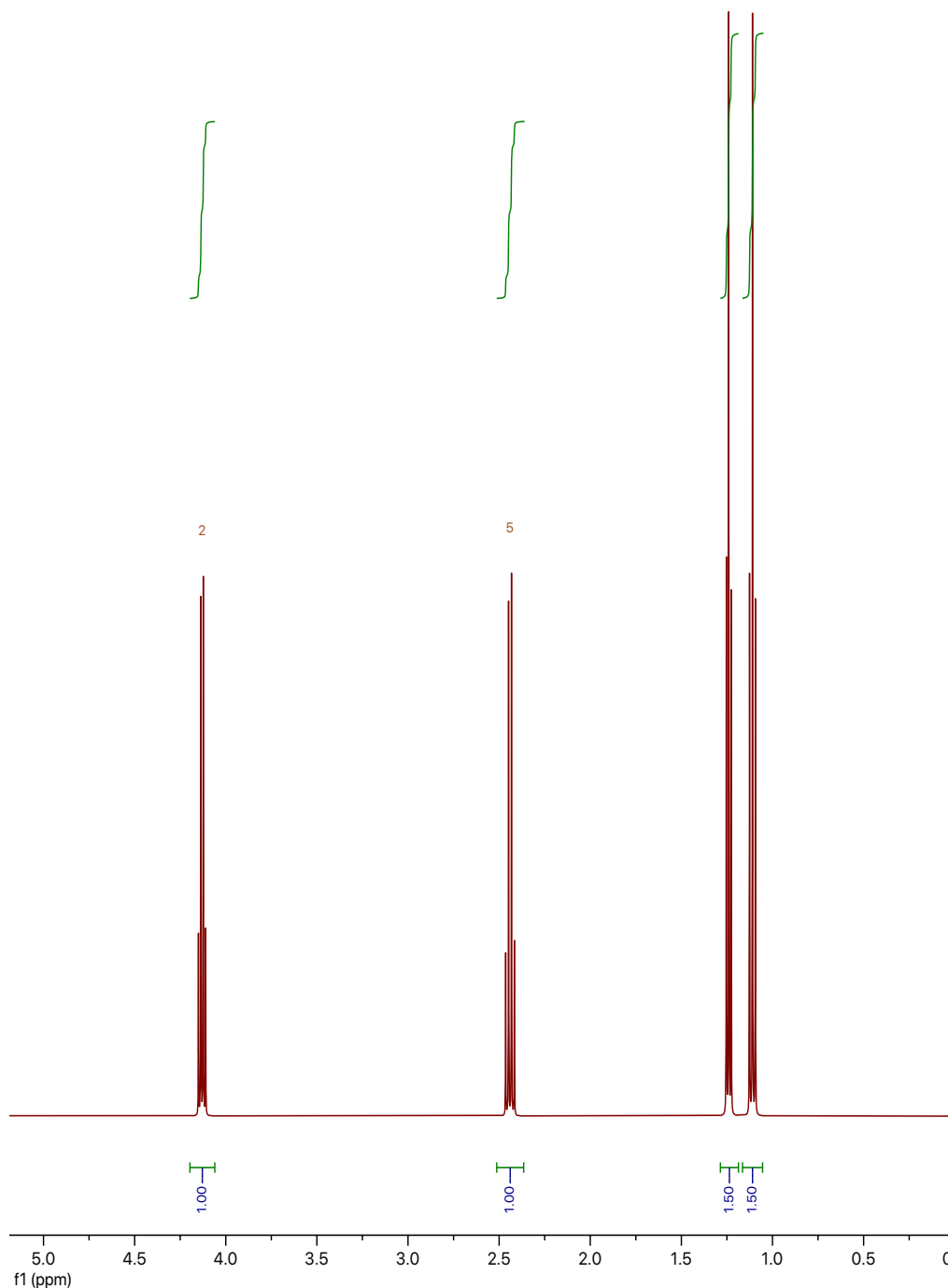
Instruments set one peak to 1 and determine the relative area of the other peaks.

Then we need to find the lowest whole # ratio

$$1 : 1 : 1.5 : 1.5$$

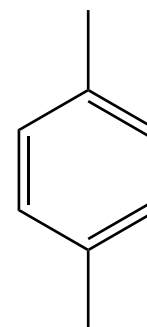
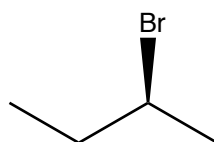
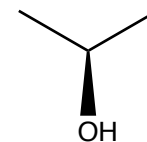
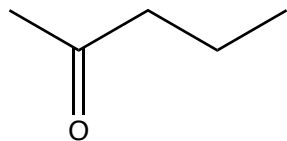
$$\times 2$$

$$2 : 2 : 3 : 3$$



Integration: What ratios will the computer give us if the smaller peak is assign and area of 1?

Section 14.9

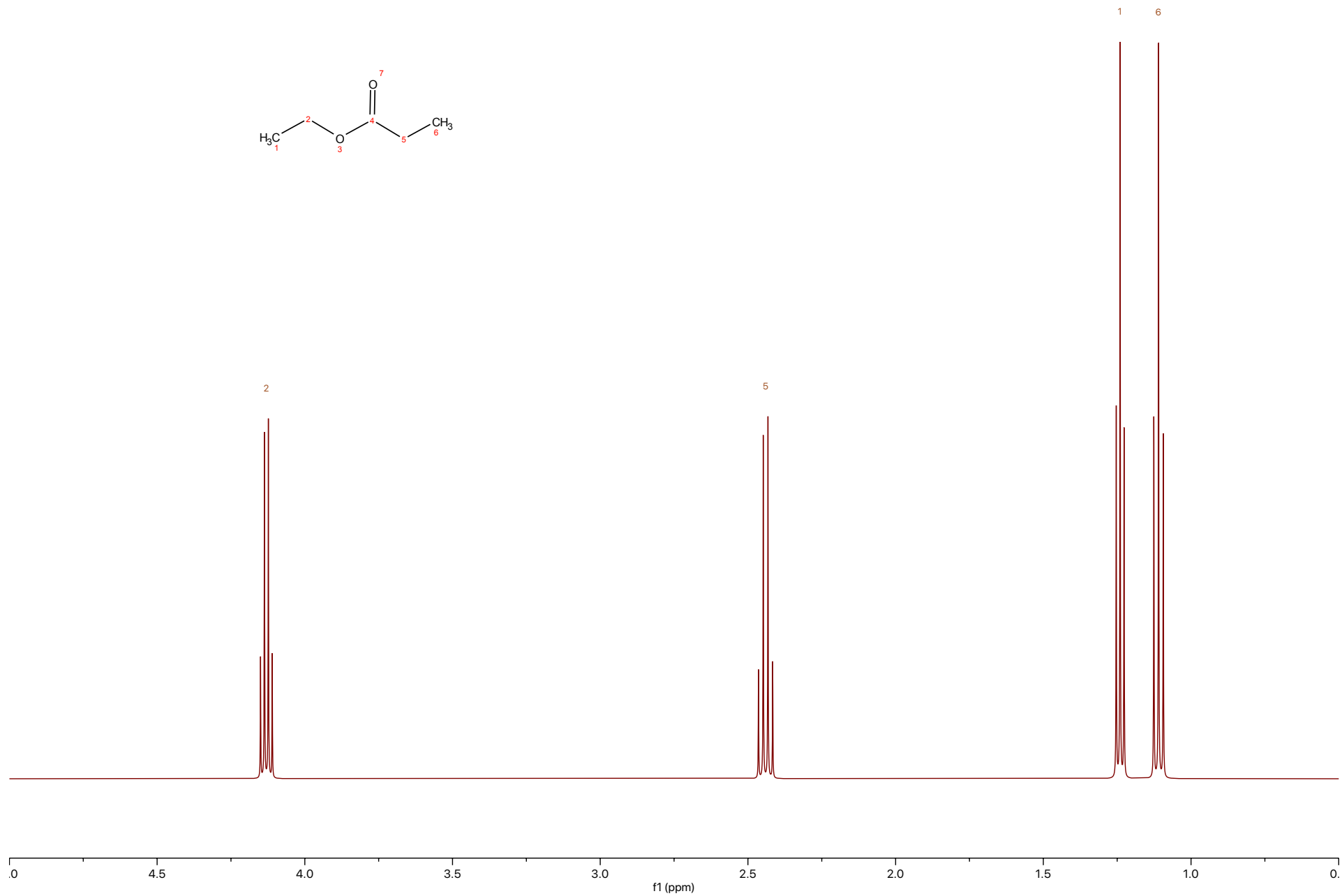
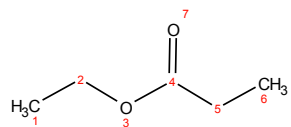




# Multiplicity: Why are there several lines in some peaks?

## Section 14.11 – 14.14

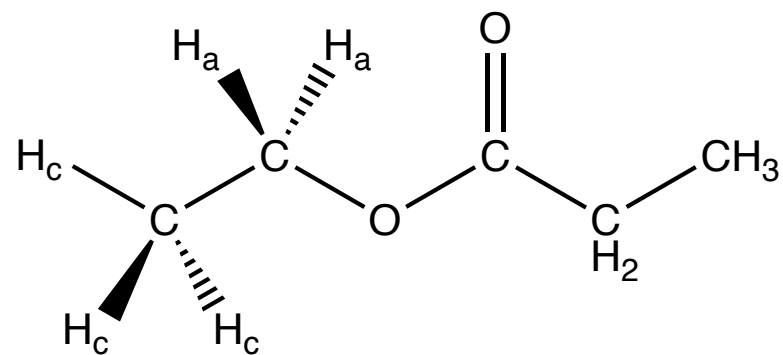
Predicted  $^1\text{H}$  NMR Spectrum



Multiplicity: Why are there several lines in some peaks?

Section 14.11 – 14.14

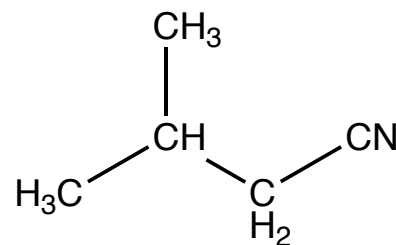
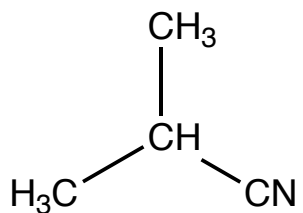
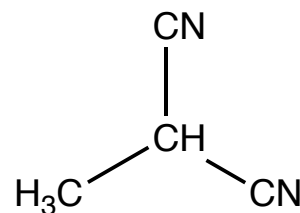
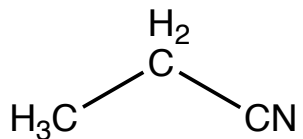
Scalar or First Order Coupling



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 inequivalent H atoms 3 bonds away from the H atoms causing the resonance peak.



Topic

Section

