

## CHM 422 Organic Synthesis, Dr. Laurie S. Starkey

### Interpretation of Infrared Spectra: a Basic Approach

"Read" the spectrum from left to right and pick out any of the following obvious bands. Next, look to the weaker bands for additional evidence of the FG's you suspect are present.

Obvious bands (cm <sup>-1</sup> )	Functional Group	Notes/Add'l evidence
3500–3200 (m)	O–H N–H	<u>broad</u> signal (water?!)
3200–3000 (m-s)	C–H, sp <sup>2</sup> (aromatic, alkene)	substitution patterns <1000
3000–2800 (s)	C–H, sp <sup>3</sup> (alkane)	C–H bend at 1460, 1380
2250–2000 (m-w)	C≡N C≡C	often weak
1800–1600 (s)	C=O	see table, lowered by conjugation

(s) = strong, (m) = medium, (w) = weak, (v) = variable

#### Other peaks to look for:

$\equiv\text{C}-\text{H}$  sp C–H stretch is sharp peak around 3300 (s)

$\begin{array}{c} \text{O} \\ || \\ -\text{C}-\text{H} \end{array}$  aldehyde C–H stretch appears as two sharp peaks 2900–2800 and 2800–2700 (w)

C=C stretches occur 1680–1630 with variable intensity (v) and will disappear if symmetrical.

C–O stretches occur 1150–1050 and are typically sharp (s)

$\begin{array}{c} \text{O} \\ || \\ -\text{C}-\text{OH} \end{array}$  Carboxylic acids should be obvious because the H-bonded dimer has a HUGE O–H stretch (3400–2400) that overlaps with the C–H stretch bands. Acids will also have a C=O stretch (1725–1700) and a C–O stretch (1320–1210).

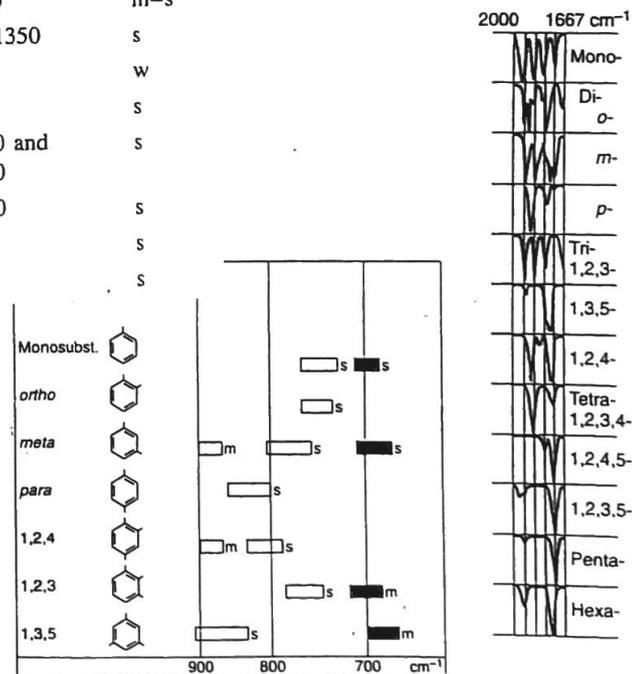
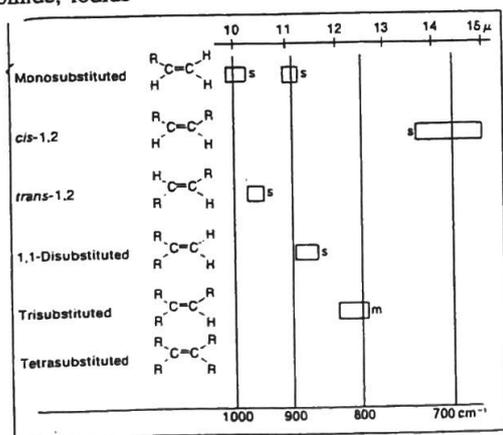
$\begin{array}{c} \text{O} \\ || \\ -\text{C}-\text{OR} \end{array}$  Since esters have two C–O bonds, they typically have two C–O stretches. Together with the C=O stretch, it's known as the "rule of 3" (~1700, 1200, 1100).

alkene C–H bend	1000–700	} gives excellent information on substitution patterns (o,m,p, etc)
benzene C–H bend	850–700 (+ overtone 2000–1700)	

C=N is not a common FG and C–N stretches are typically not useful.

**DO NOT try to interpret every little peak in the spectrum but DO recognize which ones are significant and are giving you clues to the sample's structure. It takes practice!**

	Type of Vibration	Frequency (cm <sup>-1</sup> )	Intensity	
C—H	Alkanes (stretch)	3000–2850	s	
	—CH <sub>3</sub> (bend)	1450 and 1375	m	
	—CH <sub>2</sub> — (bend)	1465	m	
	Alkenes	(stretch)	3100–3000	m
		(out-of-plane bend)	1000–650	s
	Aromatics	(stretch)	3150–3050	s
		(out-of-plane bend)	900–690	s
	Alkyne	(stretch)	ca. 3300	s
	Aldehyde		2900–2800	w
			2800–2700	w
C—C	Alkane	Not interpretatively useful		
C=C	Alkene	1680–1600	m–w	
	Aromatic	1600 and 1475	m–w	
C≡C	Alkyne	2250–2100	m–w	
C=O	Aldehyde	1740–1720	s	
	Ketone	1725–1705	s	
	Carboxylic acid	1725–1700	s	
	Ester	1750–1730	s	
	Amide	1680–1630	s	
	Anhydride	1810 and 1760	s	
	Acid chloride	1800	s	
	C—O	Alcohols, ethers, esters, carboxylic acids, anhydrides	1300–1000	s
O—H	Alcohols, phenols			
	Free	3650–3600	m	
	H-bonded	3400–3200	m	
	Carboxylic acids	3400–2400	m	
N—H	Primary and secondary amines and amides			
	(stretch)	3500–3100	m	
	(bend)	1640–1550	m–s	
C—N	Amines	1350–1000	m–s	
C=N	Imines and oximes	1690–1640	w–s	
C≡N	Nitriles	2260–2240	m	
X=C=Y	Allenes, ketenes, isocyanates, isothiocyanates	2270–1940	m–s	
N=O	Nitro (R—NO <sub>2</sub> )	1550 and 1350	s	
S—H	Mercaptans	2550	w	
S=O	Sulfoxides	1050	s	
	Sulfones, sulfonyl chlorides, sulfates, sulfonamides	1375–1300 and 1350–1140	s	
C—X	Fluoride	1400–1000	s	
	Chloride	785–540	s	
	Bromide, iodide	< 667	s	

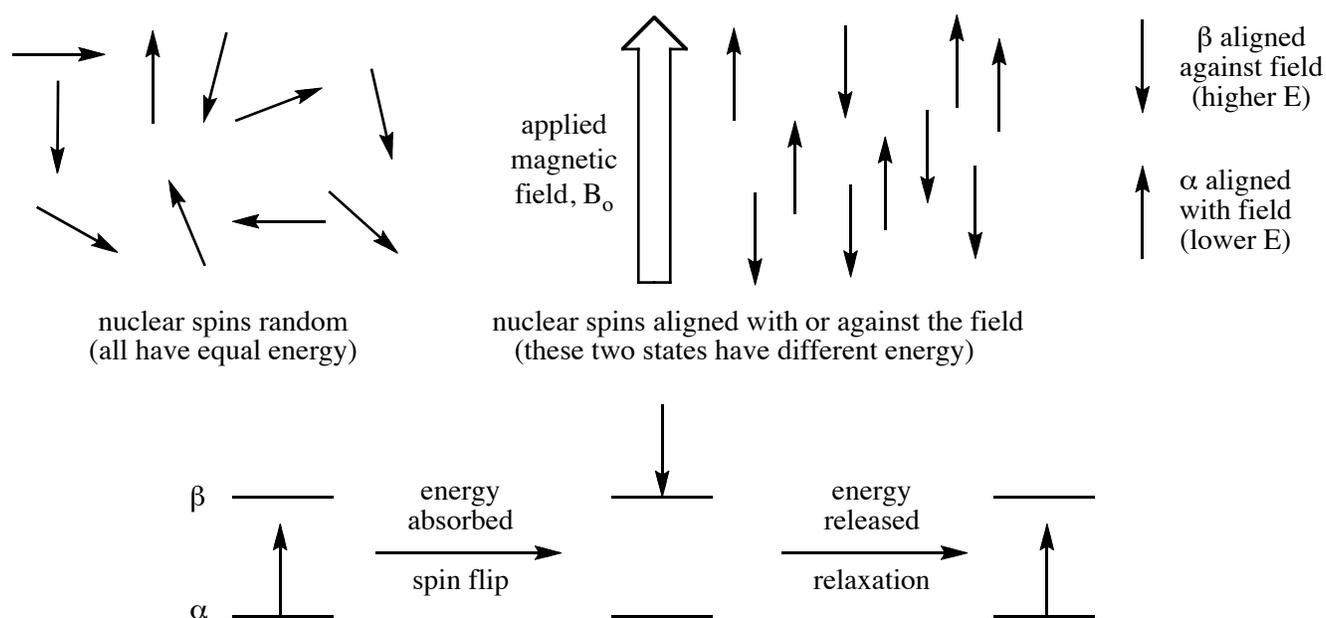


▶ FIGURE 2.28 (a) The C—H out-of-plane bending vibrations for substituted benzenoid compounds. (b) The 2000-to-1667-cm<sup>-1</sup> region for substituted benzenoid compounds (from Dy John R., *Applications of Absorption Spectroscopy of Organic Compounds*, Prentice-Hall.

# Introduction to Nuclear Magnetic Resonance (NMR) Spectroscopy

## Dr. Laurie S. Starkey, Cal Poly Pomona

Like all spectroscopic methods, NMR involves the use of energy to excite a sample. By observing this interaction, we can learn something about the structure of the sample. In IR spectroscopy, absorption of IR light leads to bond vibrations (stretching and bending). In NMR, radio frequency waves are used (60,000,000 Hz or 60 MHz, also 200, 360, 500, etc.) and the resulting motion is a change in the spin of the nucleus. The nuclei which can be observed include  $^1\text{H}$  (proton),  $^{13}\text{C}$  (C-13),  $^{15}\text{N}$ ,  $^{19}\text{F}$ ,  $^{31}\text{P}$ . These all have magnetic moments (like tiny magnets) and will interact with an applied magnetic field. Each of these nuclei has a spin quantum number  $I=1/2$  and has **two** spin states of equal energy. When a magnetic field is applied, these spin states will align **with** or **against** the field. Those aligned with the field ( $\alpha$ ) are lower in energy than those aligned against the field ( $\beta$ ); the difference in energy between  $\alpha$  and  $\beta$  is proportional to the strength of the magnet used. Application of radio waves (energy) at just the right frequency will cause certain nuclei to absorb energy and "flip" from the  $\alpha$  to the  $\beta$  spin state. As the excited nucleus relaxes back to the ground state, a signal is recorded and an NMR spectrum can be obtained. The frequency of this energy transition depends on the electronic environment of the nucleus.



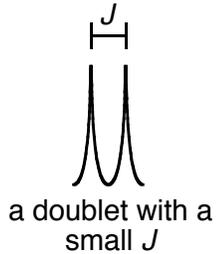
### Information obtained from a $^1\text{H}$ NMR spectrum:

- 1) **# of signals** indicates the number of different types of hydrogens (consider chemical equivalence).
- 2) **Integration** or peak area indicates how many hydrogens are in each signal. It is given as a ratio.
- 3) **Chemical shifts** are given as  $\delta$  (delta) values, in ppm. The chemical shift indicates the electronic environment of the hydrogens (electron-rich/shielded or electron-poor/deshielded).
- 4) **Splitting patterns** indicate the # of *neighboring* hydrogens. The magnitude of the coupling constants (given as  $J$  values) depend on the spatial relationship (dihedral angle) of the two hydrogens.

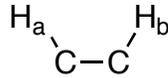
# Dr. Laurie S. Starkey, Cal Poly Pomona - NMR Spectroscopy: Spin-Spin Coupling

The magnitude of the coupling between two neighboring protons is determined by their spatial relationship. When considering the dihedral angle between hydrogens (as observed via a Newman projection), the maximum coupling constant ( $J$ ) occurs at  $0^\circ$  and  $180^\circ$  (eclipsed and anti protons, respectively), and is at a minimum when they are at  $90^\circ$  (orthogonal protons). Spin-spin coupling can occur through 2, 3 or even 4 bonds and can be generally classified as small ( $<3$  Hz), medium ( $\sim 7$  Hz) or large ( $>10$  Hz). Not all protons are split by neighboring protons. Protons on N or O are acidic and are exchangeable. As a result, these signals usually do not couple with neighboring protons (**OH and NH are typically broad singlets**). Also, since protons on carbonyls have very small coupling constants, **aldehyde H's typically appear as singlets**.

## General coupling constants (called "J values")



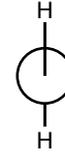
vicinal (3-bond)



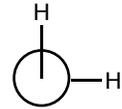
$J_{ab} \sim 7$  Hz  
(freely rotating, so no fixed dihedral angle)



$0^\circ$  dihedral angle  
large coupling  
 $J_{ab} \sim 2-14$  Hz

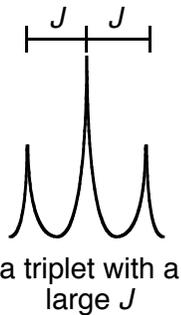


$180^\circ$  dihedral  
large coupling  
 $J_{ab} \sim 4-16$  Hz

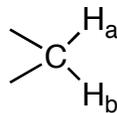


$90^\circ$  dihedral  
small coupling  
 $J_{ab} \sim 0-2$  Hz

(for fixed dihedral angles - no free rotation)



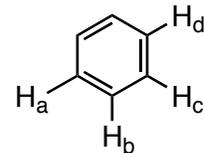
geminal (2-bond)



$J_{ab} \sim 10-15$  Hz

*note: only nonequivalent hydrogens will experience splitting, so this geminal coupling is for diastereotopic H's only (i.e., those near a chiral center).*

longer-range coupling is also possible (very small)



ortho  $J_{ab} \sim 7-10$  Hz  
meta  $J_{ac} \sim 2-3$  Hz  
para  $J_{ad} \sim 0-1$  Hz

geminal (alkene)

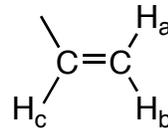
$J_{ab} \sim 1-2$  Hz

trans (alkene)

$J_{ac} \sim 11-18$  Hz

cis (alkene)

$J_{bc} \sim 6-15$  Hz



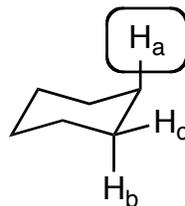
*note: gem coupling in an alkene ( $sp^2$   $CH_2$ ) is **much** smaller than for an alkane ( $sp^3$   $CH_2$ ):  $\sim 1$  vs.  $\sim 12$  Hz!*

cyclohexane (ax-ax)

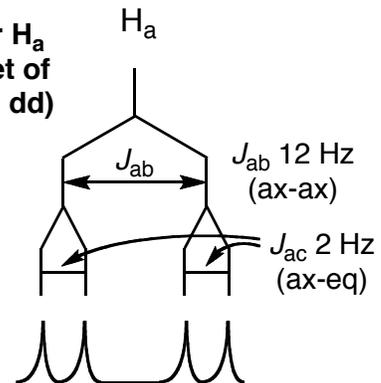
$J_{ab} \sim 10-13$  Hz  
( $180^\circ$  dihedral)

cyclohexane (ax-eq) or (eq-eq)

$J_{ac} \sim 2-5$  Hz  
( $60^\circ$  dihedral)



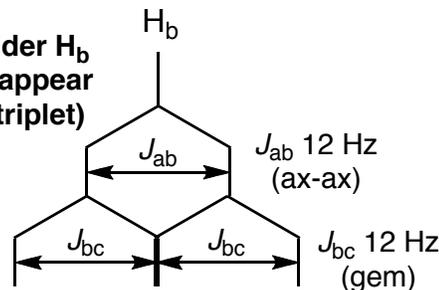
consider  $H_a$   
(a doublet of doublets, dd)



a doublet of doublets, dd  
(four peaks but not a quartet - all equal heights/integration, and not even spacing between peaks)

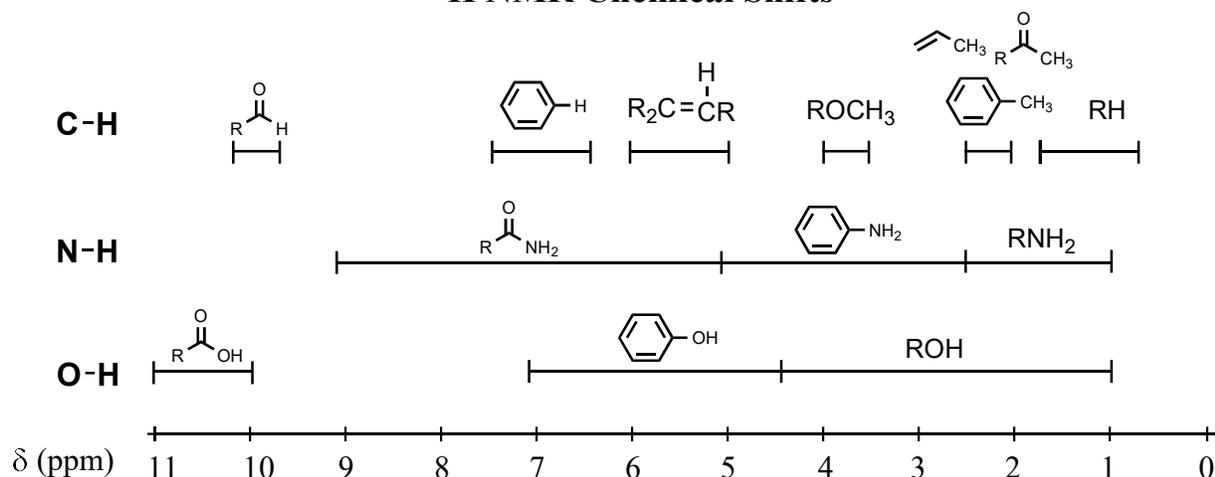
*note:  $H_b$  (a doublet of doublets, dd) may appear as an apparent triplet if the large gem coupling ( $J_{bc}$ ) is about the same as the large ax-ax coupling ( $J_{ab}$ ). i.e., if J values are equal, then two neighbors result in a triplet ( $n+1$  rule).*

consider  $H_b$   
(may appear as a triplet)



this dd appears as an apparent triplet, t (three peaks with even spacing and 1:2:1 peak height ratio)

## <sup>1</sup>H NMR Chemical Shifts



### Protons on Carbon

Type of C-H	$\delta$ (ppm)	Description of Proton
R-CH <sub>3</sub>	0.9	alkyl (methyl)
R-CH <sub>2</sub> -R	1.3	alkyl (methylene)
R <sub>3</sub> C-H	1.5-2	alkyl (methine)
	1.8	allylic (C is next to a pi bond)
	2-2.3	$\alpha$ to carbonyl (C is next to C=O)
Ar-CH <sub>3</sub>	2.3	benzylic (C is next to Ph)
RC $\equiv$ C-H	2.5	alkynyl
R <sub>2</sub> N-CH <sub>3</sub>	2-3	$\alpha$ to nitrogen (C is attached to N)
R-CH <sub>2</sub> -X	2-4	$\alpha$ to halogen (C is attached to Cl, Br, I)
RO-CH <sub>3</sub>	3.8	$\alpha$ to oxygen (C is attached to O)
R-CH <sub>2</sub> -F	4.5	$\alpha$ to fluorine (C is attached to F)
	5-5.3	vinylic (H is attached to alkene C)
Ar-H	7.3	aromatic (H is on phenyl ring)
	9.7	aldehyde (H is on C=O)

Note: aldehyde (-CHO) proton usually does not couple with neighboring H's so appears as a singlet

### Protons on Oxygen/Nitrogen\*

Type of H	$\delta$ (ppm)	Description
ROH	0.5-5	alcohol
ArOH	4-7	phenol
	10-13	carb. acid
RNH <sub>2</sub>	0.5-5	amine
ArNH <sub>2</sub>	3-5	aniline
	5-9	amide

\*Protons on N or O typically have wide ranges of expected chemical shifts; the actual  $\delta$  value depends on the solvent used, the concentration, temp., etc. Because these protons are acidic and, therefore, exchangeable, they may be broad peaks and usually do not couple with neighboring protons (typically they are broad singlets). If a protic deuterated solvent is used (e.g., D<sub>2</sub>O or CD<sub>3</sub>OD), then the NH and OH protons will exchange with the deuterium and the peaks will shrink or disappear entirely, since D (<sup>2</sup>H) does not show up in the <sup>1</sup>H NMR spectrum.

R = alkyl group

Ar = aromatic ring, such as phenyl (Ph)

**California State Polytechnic University, Pomona, Dr. Laurie S. Starkey**  
**Calculating <sup>1</sup>H NMR Chemical Shifts**

If a carbon has more than one functional group directly attached to it, the following table can be used to estimate the chemical shift of an attached hydrogen.

$$\text{—CH}_2\text{—} \quad \text{Calculation} \quad \delta \text{ (ppm)} \quad \text{R}_1\text{—CH}_2\text{—R}_2 = 1.2 + \Delta_{\text{R}_1} + \Delta_{\text{R}_2}$$

Methylenes (CH<sub>2</sub>) have two groups attached, so the starting chemical shift (1.2 ppm) will be adjusted using two values from the table (Δ values).

$$\begin{array}{c} | \\ \text{—CH} \\ | \end{array} \quad \text{Calculation} \quad \delta \text{ (ppm)} \quad \begin{array}{c} \text{R}_1 \\ | \\ \text{R}_2\text{—}\dot{\text{C}}\text{—H} \\ | \\ \text{R}_3 \end{array} = 1.5 + \Delta_{\text{R}_1} + \Delta_{\text{R}_2} + \Delta_{\text{R}_3}$$

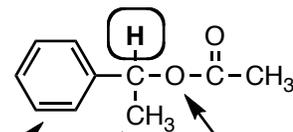
Methines (CH) have three groups attached, so the starting chemical shift (1.5 ppm) will be adjusted using three values from the table (Δ values).

**Protons on sp<sup>3</sup> Carbons: Chemical Shift Calculation Table**

—R	Δ	Description	—R	Δ	Description
—CH <sub>2</sub> R	0.0	alkyl	—OH	2.3	α to alcohol O
—CR=CR <sub>2</sub>	0.8	allylic (next to alkene)	—OR	2.1	α to ether O
—C≡CR	0.9	propargylic (next to alkyne)	—OAr	2.8	α to O of aromatic ether
—C≡N	1.2	α to cyano	$\text{—O—}\overset{\text{O}}{\parallel}{\text{C}}\text{—R}$	2.8	α to O of ester
—Ar	1.4	benzylic	$\text{—O—}\overset{\text{O}}{\parallel}{\text{C}}\text{—Ar}$	3.1	α to O of aromatic ester
$\text{—}\overset{\text{O}}{\parallel}{\text{C}}\text{—R}$	1.2	α to ketone or aldehyde C=O	—NR <sub>2</sub>	1.5	α to amine
$\text{—}\overset{\text{O}}{\parallel}{\text{C}}\text{—OR}$	1.1	α to ester or carb. acid C=O	—NO <sub>2</sub>	3.2	α to nitro
$\text{—}\overset{\text{O}}{\parallel}{\text{C}}\text{—Ar}$	1.7	α to C=O of aromatic ketone	—SR	1.3	α to thiol or thioether
—F	3.2	α to fluorine			
—Cl	2.2	α to fluorine			
—Br	2.1	α to bromine			
—I	2.0	α to iodine			

**Example:**

estimate the chemical shift of the selected proton

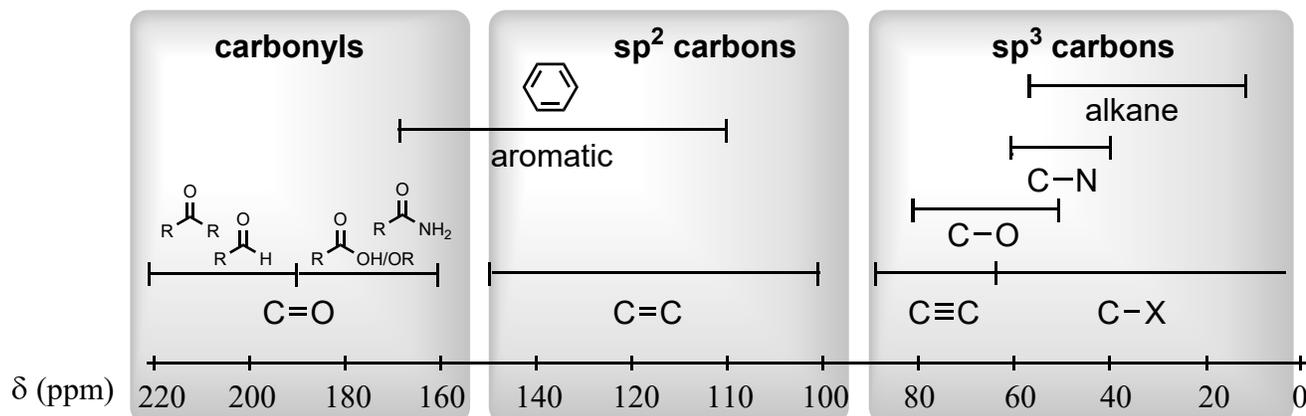


$$\begin{aligned} \delta &= 1.5 + \Delta(-\text{Ar}) + \Delta(-\text{R}) + \Delta(-\text{OCOR}) \\ \delta &= 1.5 + 1.4 + 0.0 + 2.8 \\ \delta &= 5.7 \text{ ppm (actual 5.4 ppm)} \end{aligned}$$

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## <sup>13</sup>C NMR Chemical Shifts



Type of carbon	$\delta$ (ppm)	Description of carbon
R-CH <sub>3</sub>	10-30	primary alkyl (methyl)
R-CH <sub>2</sub> -R	15-55	secondary alkyl (methylene)
R <sub>3</sub> C-H $\begin{array}{c} \text{R} \\   \\ \text{R}-\text{C}-\text{R} \\   \\ \text{R} \end{array}$	20-60	tertiary or quaternary alkyl
C-I	0-40	attached to iodine
C-Br	25-65	attached to bromine
C-N	40-60	attached to nitrogen
C-Cl	35-80	attached to chlorine
C-O	40-80	attached to oxygen
RC≡CR	65-90	alkynyl
R <sub>2</sub> C=CR <sub>2</sub>	100-150	alkenyl
	110-170	aromatic (phenyl ring C)
$\begin{array}{ccc} \text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{OH} & \text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{OR} & \text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{NH}_2 \end{array}$	165-185	C=O, carboxylic acid, ester, amide
$\begin{array}{cc} \text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{R} & \text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{H} \end{array}$	185-220	C=O, ketone or aldehyde

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## **$^1\text{H}$ NMR Problem-Solving Strategies**

The goal of solving a  $^1\text{H}$  NMR spectrum is to determine the structure that is consistent with ALL the NMR data. Since the NMR provides a lot of data, we must develop a systematic approach. First, we must determine what pieces are present. Next, we figure out how those pieces fit together. Finally, we check our structure to see if it matches the spectral data given.

- 1) If given an IR spectrum: what functional groups (FG) are present? These are pieces to your puzzle.
- 2) If given molecular formula: check for sites/degrees of unsaturation (DU).
  - If saturated, formula fits  $\text{C}_n\text{H}_{2n+2+\#N}$ .
  - every 2 missing H's = 1 DU
  - each DU = a  $\pi$  bond or a ring
  - 4 DU = a possible benzene ring (3  $\pi$  bonds, plus 1 ring)
- 3) Using the peak integration, determine the pieces of your molecule.
  - 3 H signal =  $\text{CH}_3$
  - 2 H signal =  $\text{CH}_2$
  - 1 H signal = CH or OH or NH
  
  - 6 H signal = 2 equivalent  $\text{CH}_3$  groups
  - 4 H signal = 2  $\text{CH}_2$ 's or a  $\text{CH}_3 + \text{CH}$  (overlapping signals?)
  
  - peaks around 7 ppm = aromatic H's (indicates presence of a benzene ring)
    - may be a single peak (singlet) or may be several signals in the region
    - a total of 5 H's around 7 ppm = monosubstituted benzene ring
    - a total of 4 H's around 7 ppm = disubstituted benzene ring (groups can be *ortho*, *meta* or *para*)
- 4) Do you have all your pieces? "Add up" your pieces and compare to your molecular formula
  - have you accounted for the calculated DU?
  - have you accounted for the functional groups in the IR?
- 5) Put the pieces together! Start with an end piece, such as a methyl ( $\text{CH}_3$ ).
  - consider chemical shift
    - is it next to an oxygen? ( $\sim 3.8$  ppm)
    - is it next to a  $\text{C}=\text{O}$  or a benzene ring? ( $\sim 2.2$  ppm)
  - consider splitting patterns (n+1 rule, where n = # of nonequivalent neighbors)
    - is it a triplet? It must be attached to a  $\text{CH}_2$  (2 neighbors = 3 peaks)
    - is it a singlet? There must be no protons on neighboring carbon atoms (0 neighbors = 1 peak).
- 6) Check your answer! Final structure must match molecular formula, and IR and NMR spectra.
  - Look for symmetry. How many peaks should be in the NMR? What would integration be?
  - Calculate chemical shifts, predict splitting patterns, and compare to NMR spectrum.