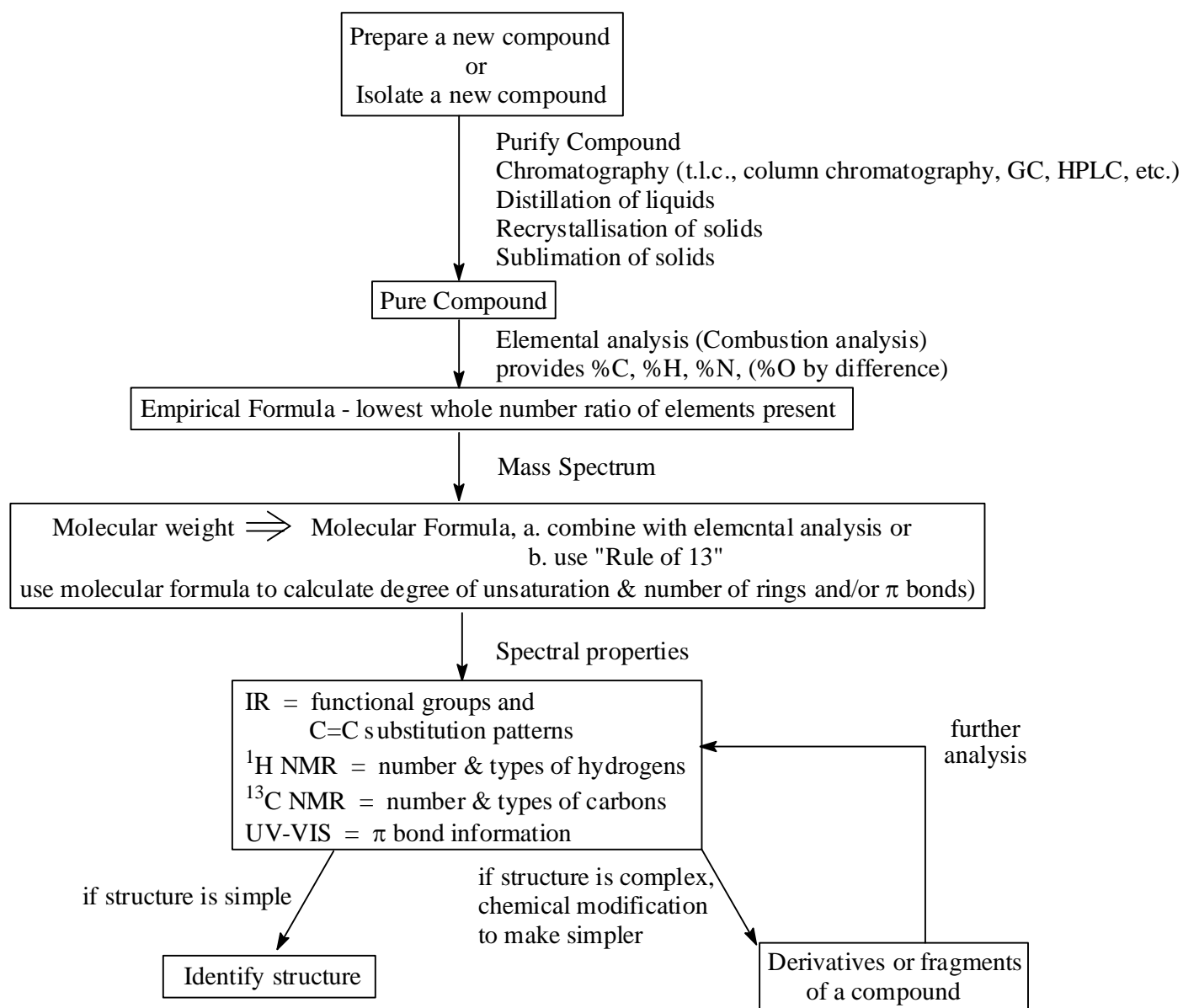


IR Material

(Chem 317, 318, 319, 422, 424)

Beauchamp

General Procedure For Structure Identification Acceptable For Publication

Elemental Analysis Problems

1. Only carbon (93.71%) and hydrogen (6.29%) are present. The molecular weight is 128.16. Calculate the molecular formula. Calculate the degree of unsaturation. Draw one possible structure.
2. The percent carbon is found to be 66.66% and the hydrogen percent is 6.70%. The molecular weight is 180.18. Calculate the molecular formula. Calculate the degree of unsaturation. Draw one possible structure.
3. The percent carbon is found to be 67.02%, the hydrogen percent is 7.30% and the nitrogen percent is 7.82%. The molecular weight is 179.20. Calculate the molecular formula. Calculate the degree of unsaturation. Draw one possible structure.

Rule of 13 Problems

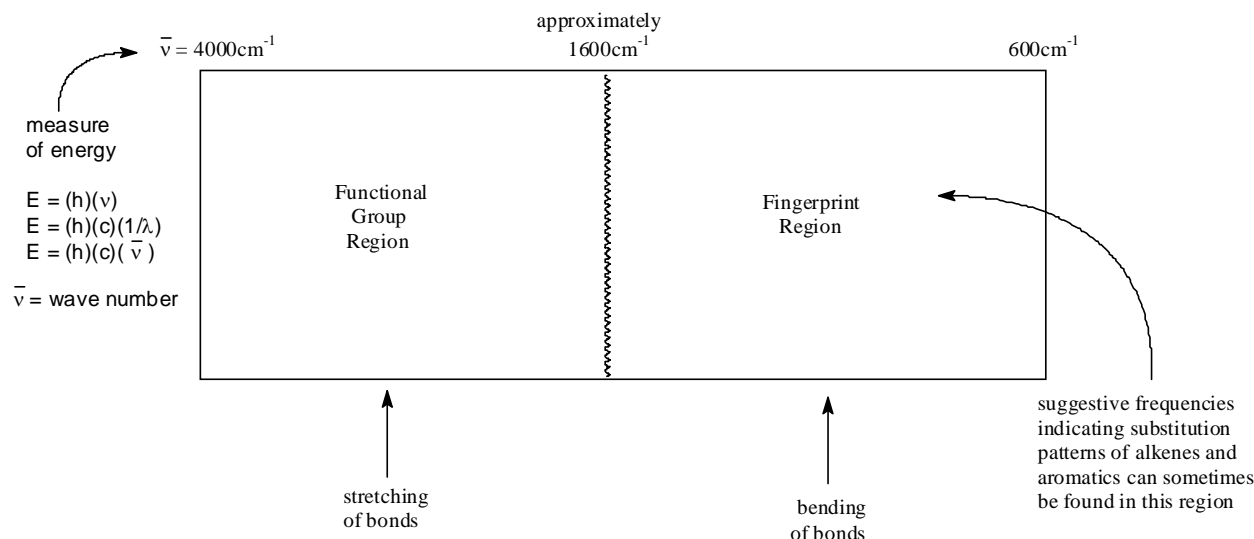
1. Calculate possible formulas for a molecular weight of 180 assuming:
 - a. only carbon and hydrogen present
 - b. carbon, hydrogen and one oxygen present
 - c. carbon, hydrogen and two oxygen atoms present
 - d. carbon, hydrogen and two nitrogen atoms present
 - e. carbon, hydrogen, two nitrogen atoms and one oxygen present

Calculate possible formulas for a molecular weight of 181 assuming:

- a. carbon, hydrogen and some nitrogen present

IR Overview

1. IR peaks can provide functional group information
2. The fingerprint region is frequently unique for each compound, though very similar compounds can have similar looking IRs. IRs of known compounds can sometimes be used to ID known compounds.
3. Substitution patterns of alkenes and aromatics can sometimes be determined from the C-H bending peaks in the Fingerprint region (and their overtones).



Functional Groups: types of bonding patterns giving rise to characteristics absorbing frequencies in the IR region specifics are provided in the table (on the next page).

sp^3 C—H ↑					
sp^2 C—H ↑		amines amides	alcohols ethers esters (acyl & alkoxy)	acids alcohols	
alkenes aromatics					
sp C—H ↑	alkenes aromatics	imines	acids aldehydes ketones esters amides acid chlorides anhydrides		
	alkynes	nitriles		1° and 2° amines amides	halogens
aldehydes					

Typical methods of running a sample

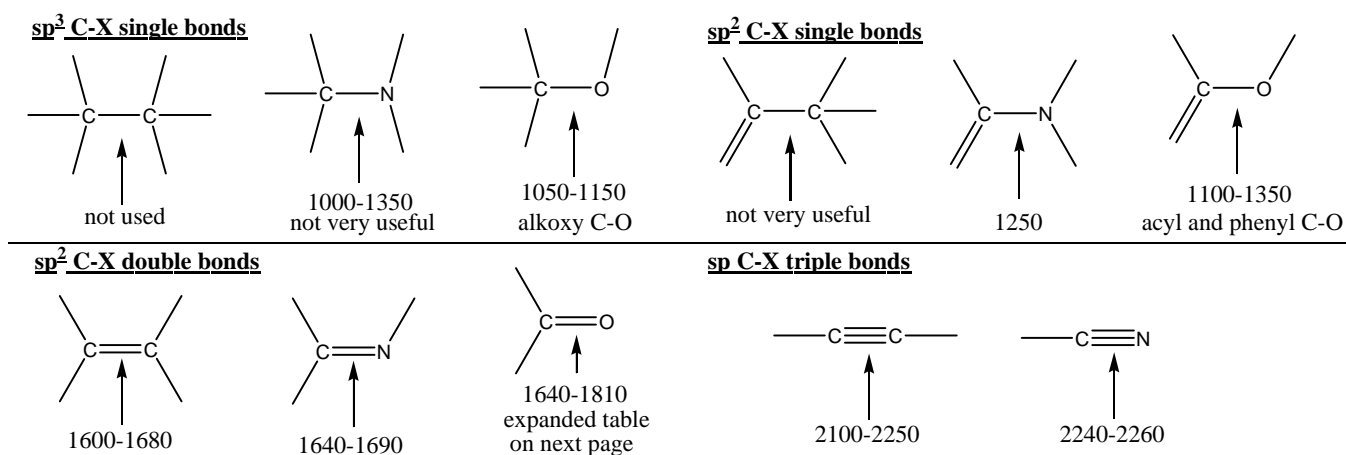
1. Neat - pure liquid is placed between salt plates (NaCl does not absorb IR)
2. Solution cell - sample is dissolved in a relatively transparent solvent and a matching cell is used containing just the solvent or background subtraction is used to cancel the solvent
3. Nujol mull - sample is mixed in a waxy hydrocarbon (alkane) paste which makes the alkane regions of the IR useless since the nujol strongly absorbs there.
4. KBr pellet - a small amount (~0.5%) solid sample is ground up in dry KBr (~99.5%) and pressed into a clear pellet under high pressure (KBr does not absorb IR unless it is wet)

Infrared Tables (short summary of common absorption frequencies)

The values given in the tables that follow are typical values. Specific bands may fall over a range of wavenumbers, cm^{-1} . Specific substituents may cause variations in absorption frequencies. Absorption intensities may be stronger or weaker than expected, often depending on dipole moments. Additional bands may confuse the interpretation. In very symmetrical compounds there may be fewer than the expected number of absorption bands (it is even possible that all bands of a functional group may disappear, i.e. a symmetrically substituted alkyne!). Infrared spectra are generally informative about what functional groups are present, but not always. The ^1H and ^{13}C NMR's are often just as informative about functional groups, and sometimes even more so in this regard. Information obtained from one spectroscopic technique should be verified or expanded by consulting the other spectroscopic techniques.

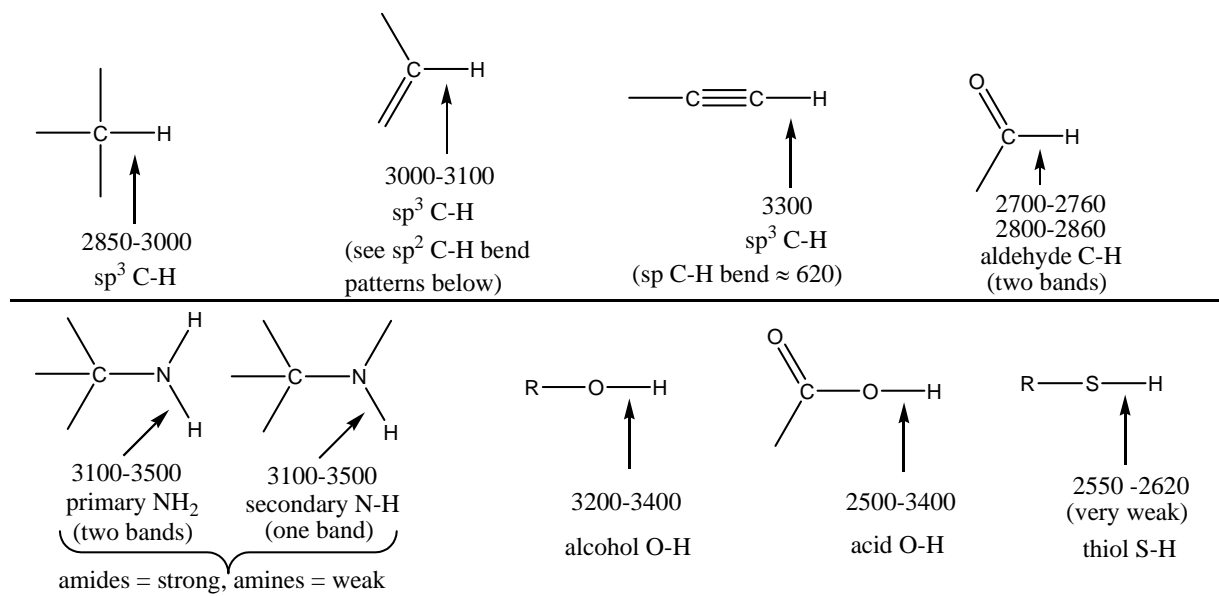
IR Summary - All numerical values in the tables below are given in wavenumbers, cm^{-1}

Bonds to Carbon (stretching wave numbers)



Stronger dipoles produce more intense IR bands and weaker dipoles produce less intense IR bands (sometimes none).

Bonds to Hydrogen (stretching wave numbers)



Carbonyl Highlights (stretching wave numbers)














Aldehydes	Ketones	Esters	Acids
saturated = 1725 conjugated = 1690 aromatic = 1700	saturated = 1715 conjugated = 1680 aromatic = 1690 6 atom ring = 1715 5 atom ring = 1745 4 atom ring = 1780 3 atom ring = 1850	saturated = 1735 conjugated = 1720 aromatic = 1720 6 atom ring = 1735 5 atom ring = 1775 4 atom ring = 1840	saturated = 1715 conjugated = 1690 aromatic = 1690
Amides	Anhydrides	Acid Chlorides	nitro
saturated = 1650 conjugated = 1660 aromatic = 1660 6 atom ring = 1670 5 atom ring = 1700 4 atom ring = 1745 3 atom ring = 1850	saturated = 1760, 1820 conjugated = 1725, 1785 aromatic = 1725, 1785 6 atom ring = 1750, 1800 5 atom ring = 1785, 1865	saturated = 1800 conjugated = 1770 aromatic = 1770	asymmetric = 1500-1600 symmetric = 1300-1390
Very often there is a very weak C=O overtone at approximately $2 \times \bar{\nu}$ ($\approx 3400 \text{ cm}^{-1}$). Sometimes this is mistaken for an OH or NH peak.			

sp² C-H bend patterns for alkenes**sp² C-H bend patterns for aromatics**

alkene substitution pattern	descriptive alkene term	absorption frequencies (cm ⁻¹) due to sp ² CH bend	aromatic substitution pattern	descriptive aromatic term	absorption frequencies (cm ⁻¹) due to sp ² CH bend
	monosubstituted alkene	985-1000 900-920		monosubstituted aromatic	690-710 730-770
	cis disubstituted alkene	675-730 (broad)		ortho disubstituted aromatic	735-770
	trans disubstituted alkene	960-990		meta disubstituted aromatic	680-725 750-810 880-900 (sometimes)
	geminal disubstituted alkene	880-900		para disubstituted aromatic	790-840
	trisubstituted alkene	790-840			
	tetrasubstituted alkene	none			

Aromatic compounds have characteristic weak overtone bands that show up between 1650-2000 cm⁻¹. Some books provide pictures for comparison (not here). A strong C=O peak will cover up most of this region.

IR Flowchart to determine functional groups in a compound (all values in cm^{-1}).

IR Spectrum		IR Spectrum	
has C=O band (1650-1800 cm^{-1}) very strong		does not have C=O band	
<p>aldehydes</p>  <p>1725-1740 (saturated) 1660-1700 (unsaturated)</p> <p>aldehyde C-H 2860-2800 (both weak) ← sometimes lost in sp^3 CH peaks</p> <hr/> <p>ketones</p>  <p>1710-1720 (saturated) 1680-1700 (unsaturated) 1715-1810 (rings: higher in small rings)</p> <hr/> <p>esters - rule of 3</p>  <p>1735-1750 (saturated) 1715-1740 (unsaturated) 1735-1820 (higher in small rings)</p> <p>acyl C—O 1150-1350 (acyl, strong) alkoxy C—O (1000-1150, alkoxy, medium)</p> <hr/> <p>acids</p>  <p>1700-1730 (saturated) 1715-1740 (unsaturated) 1680-1700 (higher in small rings)</p> <p>acyl C—O 1210-1320 (acyl, strong)</p> <p>acid O—H 2400-3400, very broad (overlaps C-H stretch)</p> <hr/> <p>amides</p>  <p>1630-1680 (saturated) 1745 (in 4 atom ring)</p>  <p>3350 & 3180, two bands for 1° amides, one band for 2° amides, stronger than in amines, extra overtone sometimes at 3100</p>  <p>N—H N-H bend, 1550-1640, stronger in amides than amines</p> <hr/> <p>acid chlorides</p>  <p>1800 (saturated) 1770 (unsaturated)</p> <p>Inductive pull of Cl increases the electron density between C and O.</p> <hr/> <p>anhydrides</p>  <p>1760 & 1820 (saturated) 1725-1785 (unsaturated) two strong bands</p> <p>acyl C—O 1150-1350 (acyl, strong)</p>		<p>nitriles</p> <p>$\text{C}\equiv\text{N}$</p> <p>≈ 2250 sharp, stronger than alkynes, a little lower when conjugated</p> <hr/> <p>alkynes</p> <p>$\text{C}\equiv\text{C}$ 2150 (variable intensity)</p> <p>not present or weak when symmetrically substituted, a little lower when conjugated</p> <p>sp C-H stretch 3300 sharp, strong</p> <p>sp C-H bend 620</p> <hr/> <p>All IR values are approximate and have a range of possibilities depending on the molecular environment in which the functional group resides. Resonance often modifies a peak's position because of electron delocalization ($\text{C}=\text{O}$ lower, acyl $\text{C}-\text{O}$ higher, etc.). IR peaks are not 100% reliable. Peaks tend to be stronger (more intense) when there is a large dipole associated with a vibration in the functional group and weaker in less polar bonds (to the point of disappearing in some completely symmetrical bonds).</p> <hr/> <p>Alkene sp^2 C-H bending patterns</p> <p>monosubstituted (985-1000, 900-920) geminal disubstituted (960-990) cis disubstituted (675-730) trans disubstituted (880-900) trisubstituted (790-840) tetrasubstituted (none, no sp^2 C-H)</p> <hr/> <p>Aromatic sp^2 C-H bending patterns</p> <p>monosubstituted (730-770, 690-710) ortho disubstituted (735-770) meta disubstituted (880-900, sometimes, 750-810, 680-725) para disubstituted (790-840)</p> <hr/> <p>There are also weak overtone bands between 1660 and 2000, but are not shown here. You can consult pictures of typical patterns in other reference books. If there is a strong $\text{C}=\text{O}$ band, they may be partially covered up.</p>	
		<p>alkanes</p> <p>sp^3 C-H stretch 2850-3000</p> <p>sp^3 C-H bend 1460 & 1380</p> <p>C—C not useful</p> <hr/> <p>alkenes</p> <p>sp^2 C-H stretch 3000-3100</p> <p>sp^2 C-H bend 650-1000 (see table for spectral patterns)</p> <p>C=C 1600-1660 weak or not present</p> <hr/> <p>aromatics</p> <p>sp^2 C-H stretch 3050-3150</p> <p>sp^2 C-H bend 690-900 (see table), overtone patterns between 1660-2000</p> <p>C=C 1600 & 1480 can be weak</p> <hr/> <p>alcohols</p> <p>alcohol O—H 3600-3500</p> <p>alkoxy C—O 1000-1260 ($3^\circ > 2^\circ > 1^\circ$)</p> <hr/> <p>thiols</p> <p>thiol S—H ≈ 2550 (weak) (easy to overlook)</p> <hr/> <p>amines</p>  <p>1°</p>  <p>2°</p> <p>3300 - 3500, two bands for 1° amines, one band for 2° amines, weaker than in amides,</p> <p>N—H N-H bend, 1550-1640, stronger in amides than amines</p> <p>N—C 1000-1350 (uncertain)</p> <hr/> <p>ethers</p> <p>alkoxy C—O 1120 (aliphatic) 1040 & 1250 (aromatic)</p> <hr/> <p>nitro compounds</p>  <p>1500-1600, asymmetric (strong) 1300-1390, symmetric (medium)</p> <hr/> <p>carbon-halogen bonds</p>  <p>usually not very useful</p> <p>X = F, Cl, Br, I</p>	

1. Explain how IR can distinguish between or among each group below. Use as many distinguishing wave numbers ($\nu = \text{cm}^{-1}$) as possible and identify what feature gives rise to that wave number. Features that are common to all members of a group need not be mentioned (e.g. sp^3 C-H stretch and bend).

