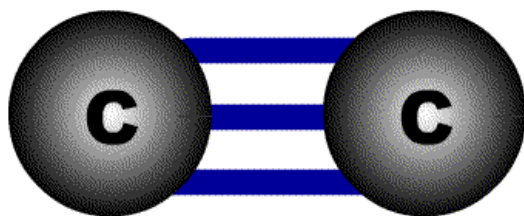




CHEM 210

Infrared Spectroscopy

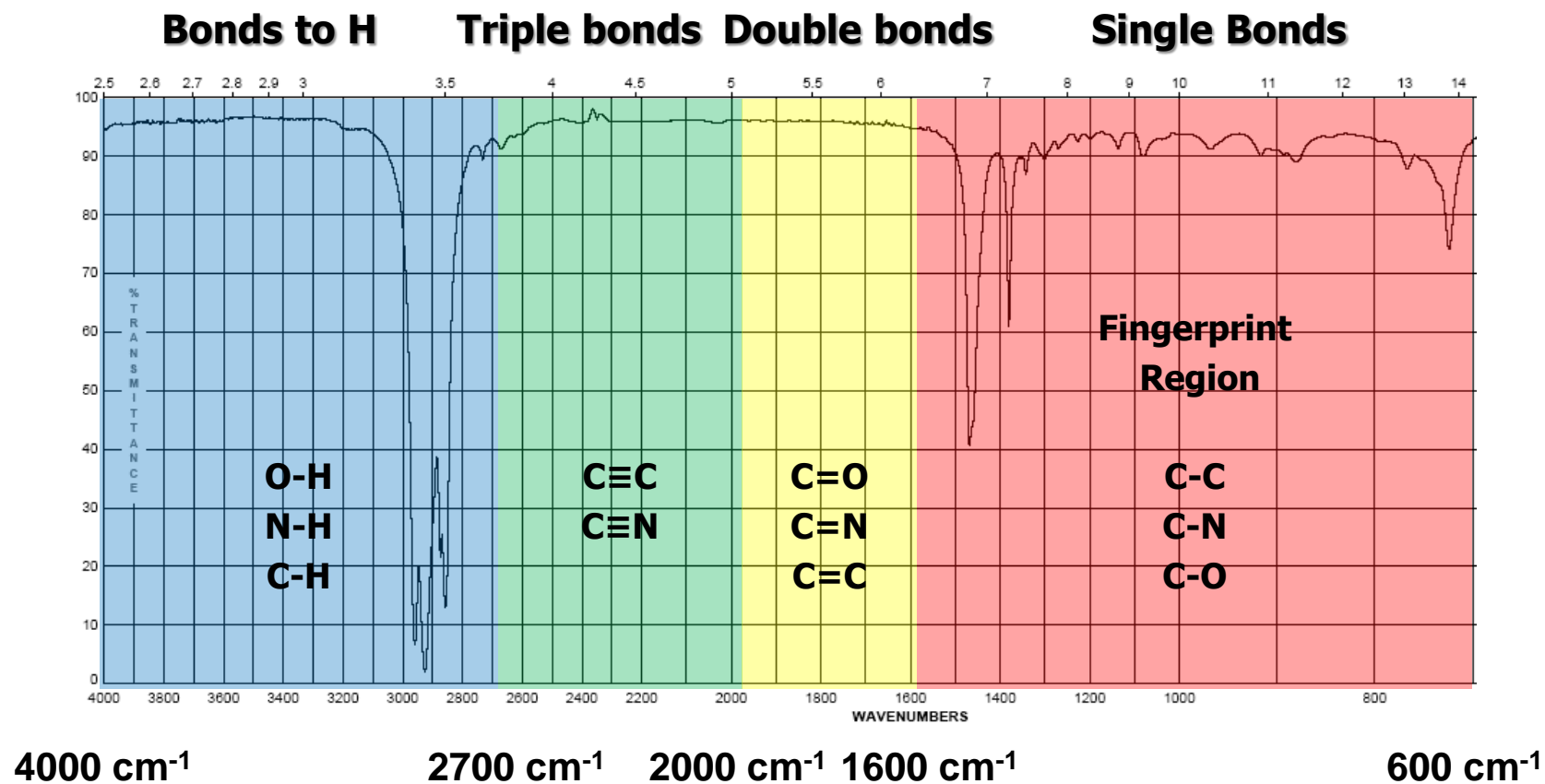


Infrared Spectroscopy

II. Infrared Group Analysis

A. General

5. The four primary regions of the IR spectrum

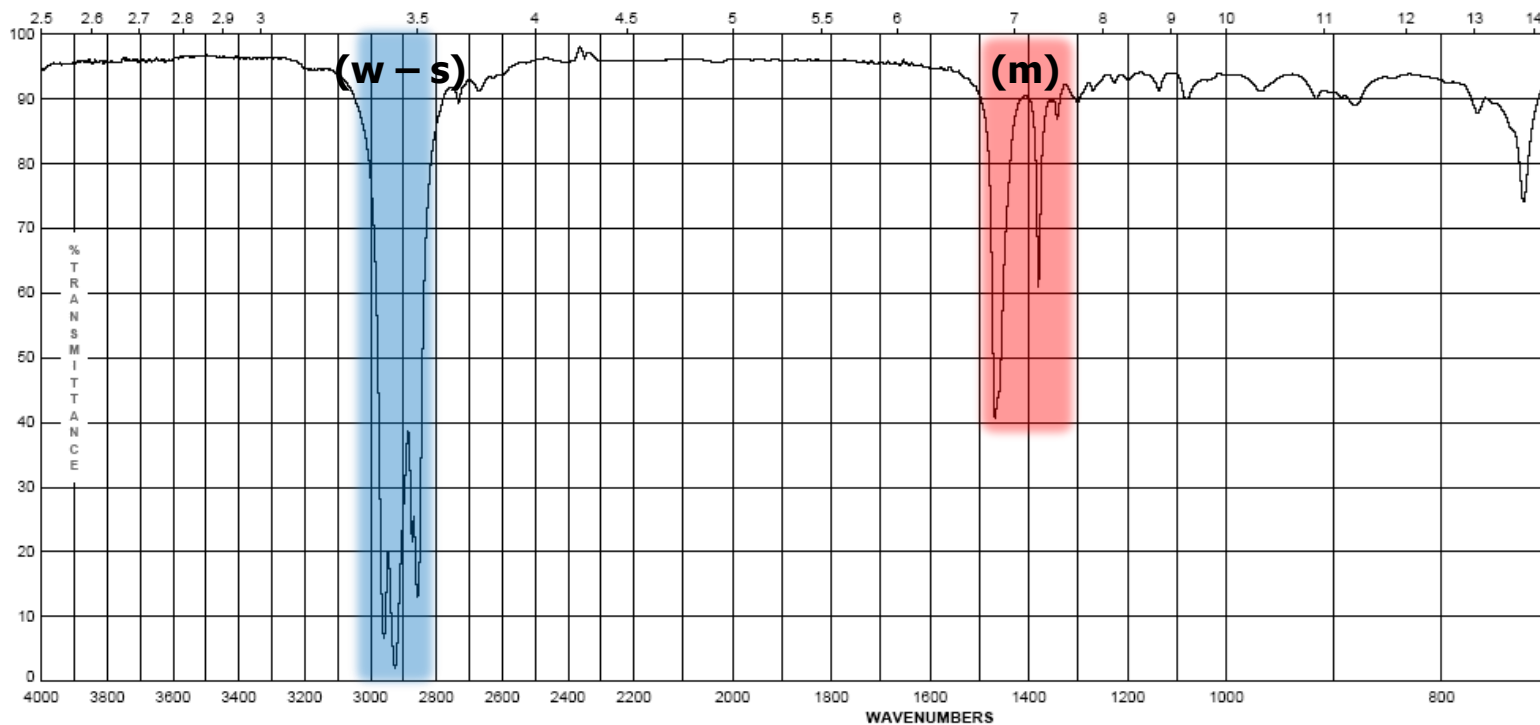
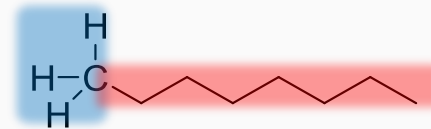


Infrared Spectroscopy

1. Alkanes – combination of C-C and C-H bonds

- C-C stretches and bends 1360-1470 cm^{-1}
- $\text{CH}_2\text{-CH}_2$ bond 1450-1470 cm^{-1}
- $\text{CH}_2\text{-CH}_3$ bond 1360-1390 cm^{-1}
- sp^3 C-H between 2800-3000 cm^{-1}

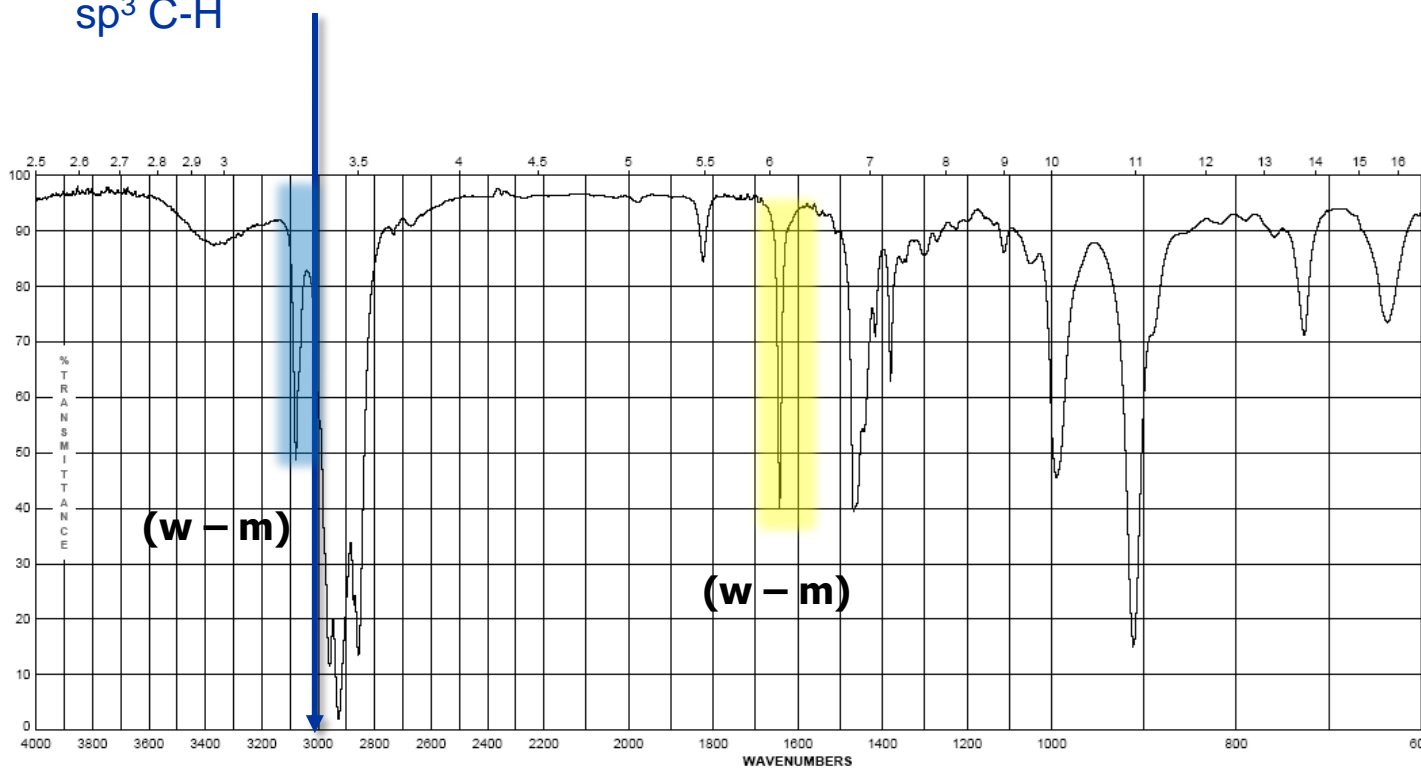
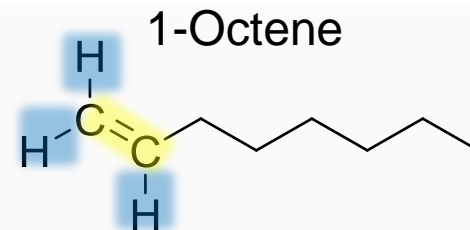
Octane



Infrared Spectroscopy

2. Alkenes – addition of the C=C and vinyl C-H bonds

- C=C stretch at 1620-1680 cm^{-1} weaker as substitution increases
- vinyl C-H stretch occurs at 3000-3100 cm^{-1}
- The difference between alkane, alkene or alkyne C-H is important! If the band is slightly above 3000 it is vinyl sp^2 C-H or alkynyl sp C-H if it is below it is alkyl sp^3 C-H

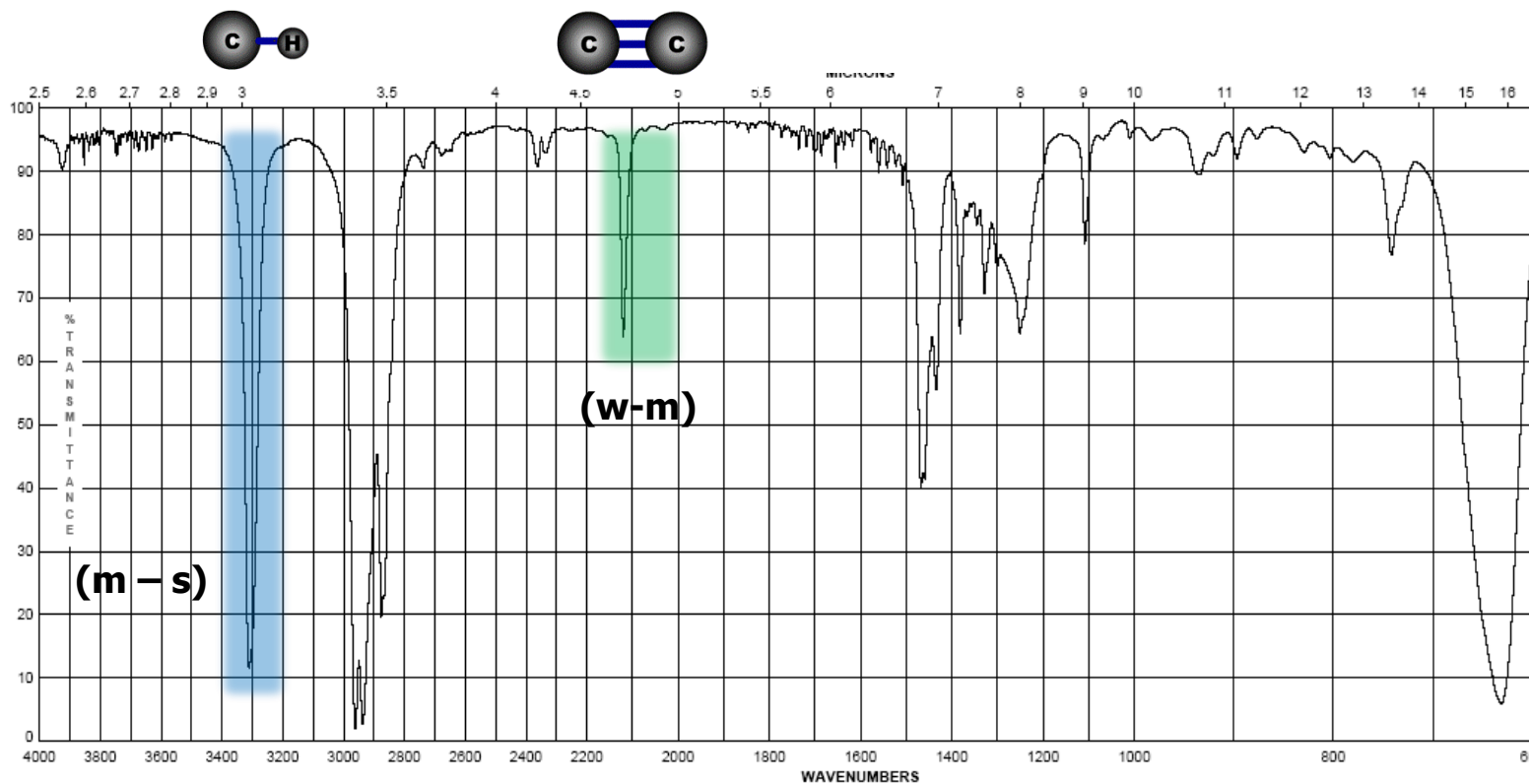
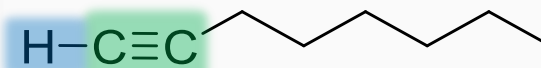


Infrared Spectroscopy

3. Alkynes – addition of the C=C and vinyl C-H bonds

- C≡C stretch 2100-2260 cm^{-1} ; strength depends on asymmetry of bond, strongest for terminal alkynes, weakest for symmetrical internal alkynes
- C-H for *terminal* alkynes occurs at 3200-3300 cm^{-1}
- Internal alkynes (R-C≡C-R) would not have this band!

1-Octyne

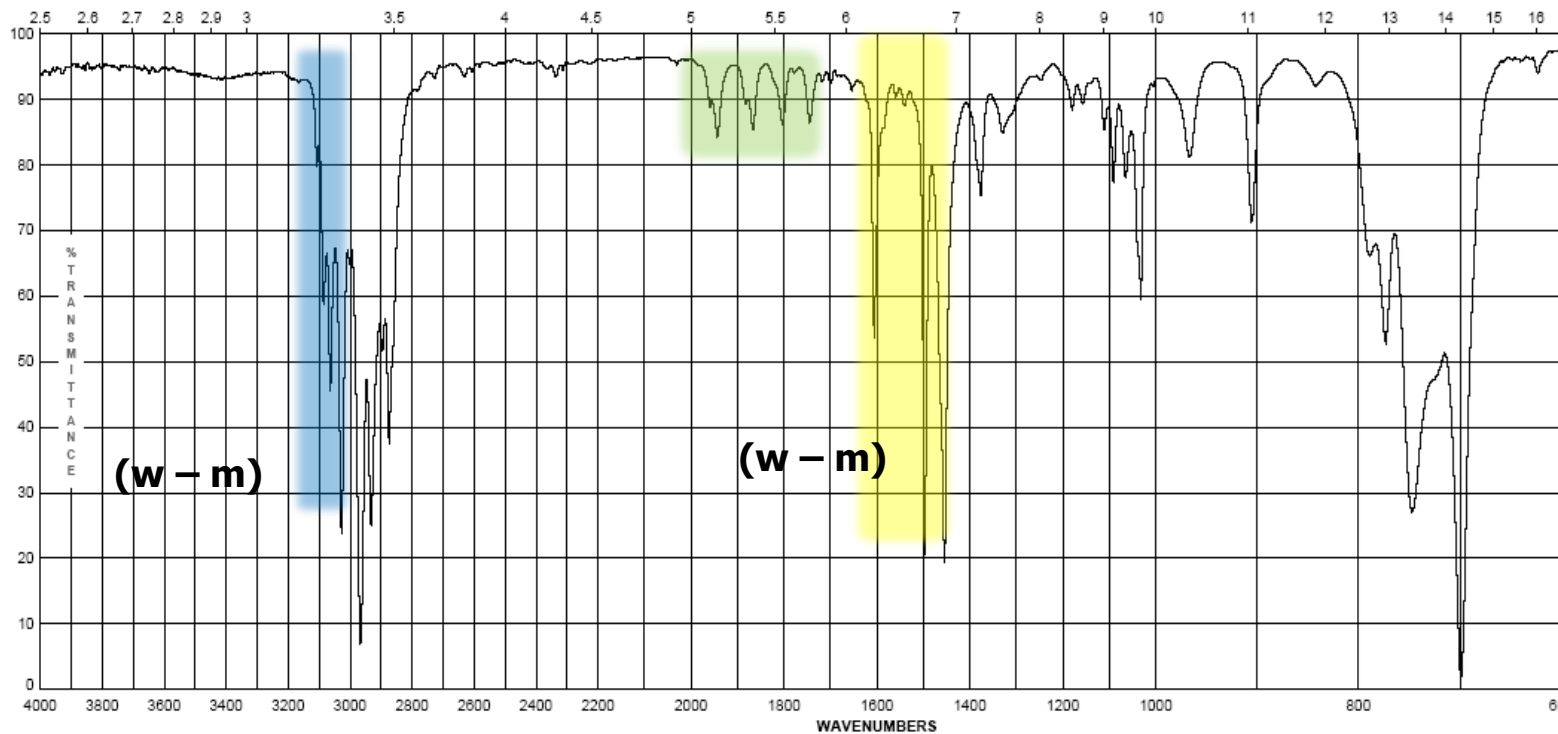
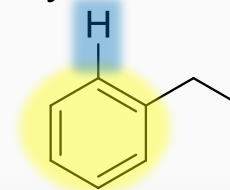


Infrared Spectroscopy

4. Aromatics

- Due to the delocalization of e^- in the ring, C-C bond order is 1.5, the stretching frequency for these bonds is slightly lower in energy than normal C=C
- These show up as a *pair* of sharp bands, 1500 & 1600 cm^{-1} , (lower frequency band is stronger)
- C-H bonds off the ring show up similar to vinyl C-H at 3000-3100 cm^{-1}

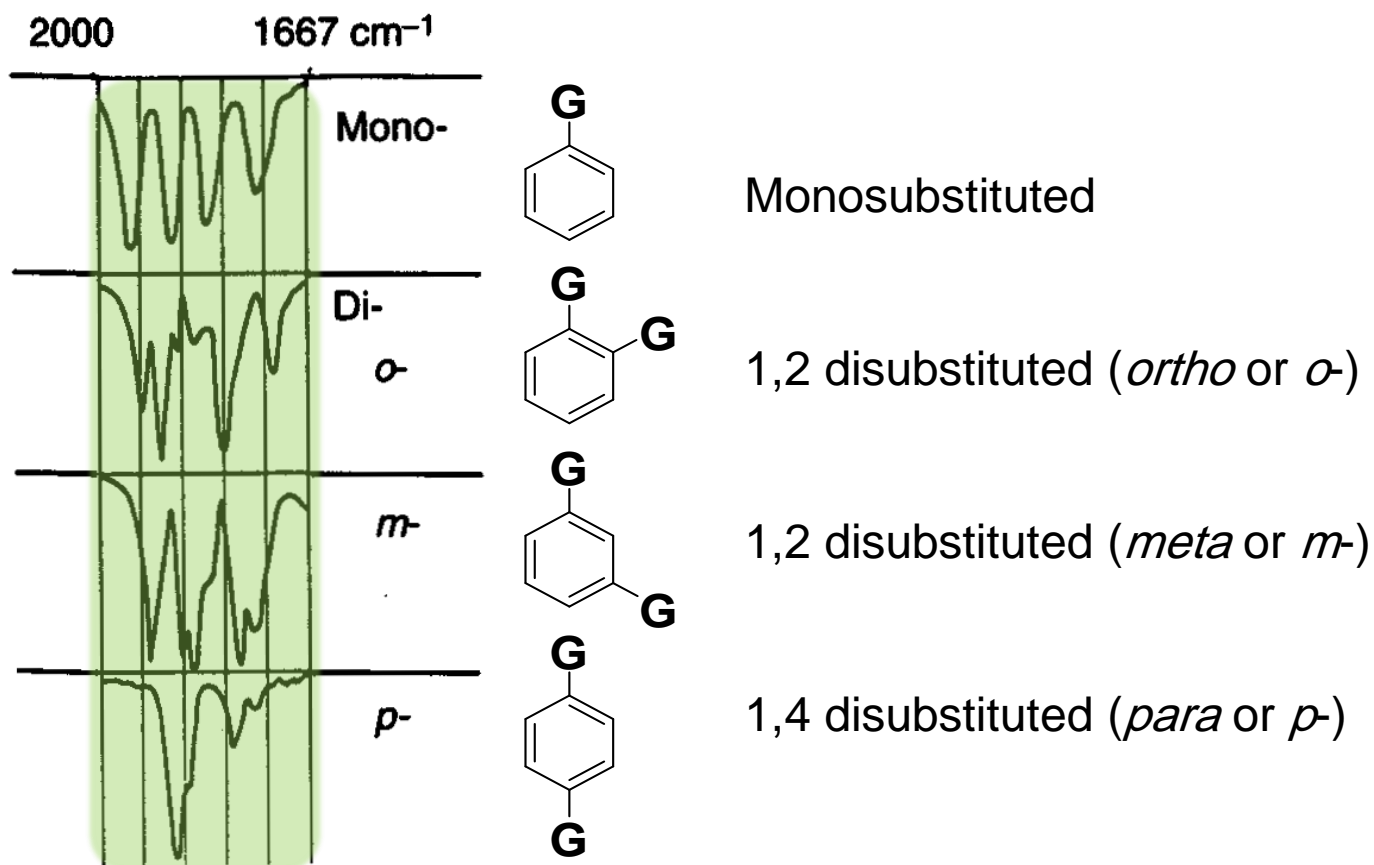
Ethyl benzene



Infrared Spectroscopy

4. Aromatics

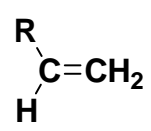
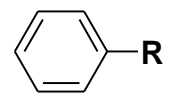
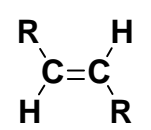
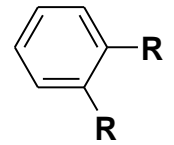
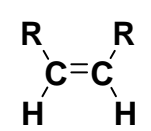
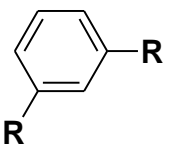
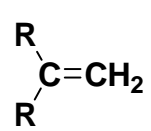
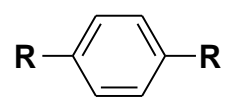
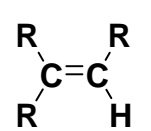
- If the region between $1667\text{-}2000\text{ cm}^{-1}$ (w) is free of interference (C=O stretching frequency is in this region) a weak grouping of peaks is observed for aromatic systems
- Analysis of this region, called the *overtone of bending* region, can lead to a determination of the substitution pattern on the aromatic ring



Infrared Spectroscopy

5. Unsaturated Systems – substitution patterns

- The substitution of aromatics and alkenes can also be discerned through the **out-of-plane bending vibration region**
- However, other peaks often are apparent in this region. *These peaks should only be used for reinforcement of what is known or for hypothesizing as to the functional pattern.*

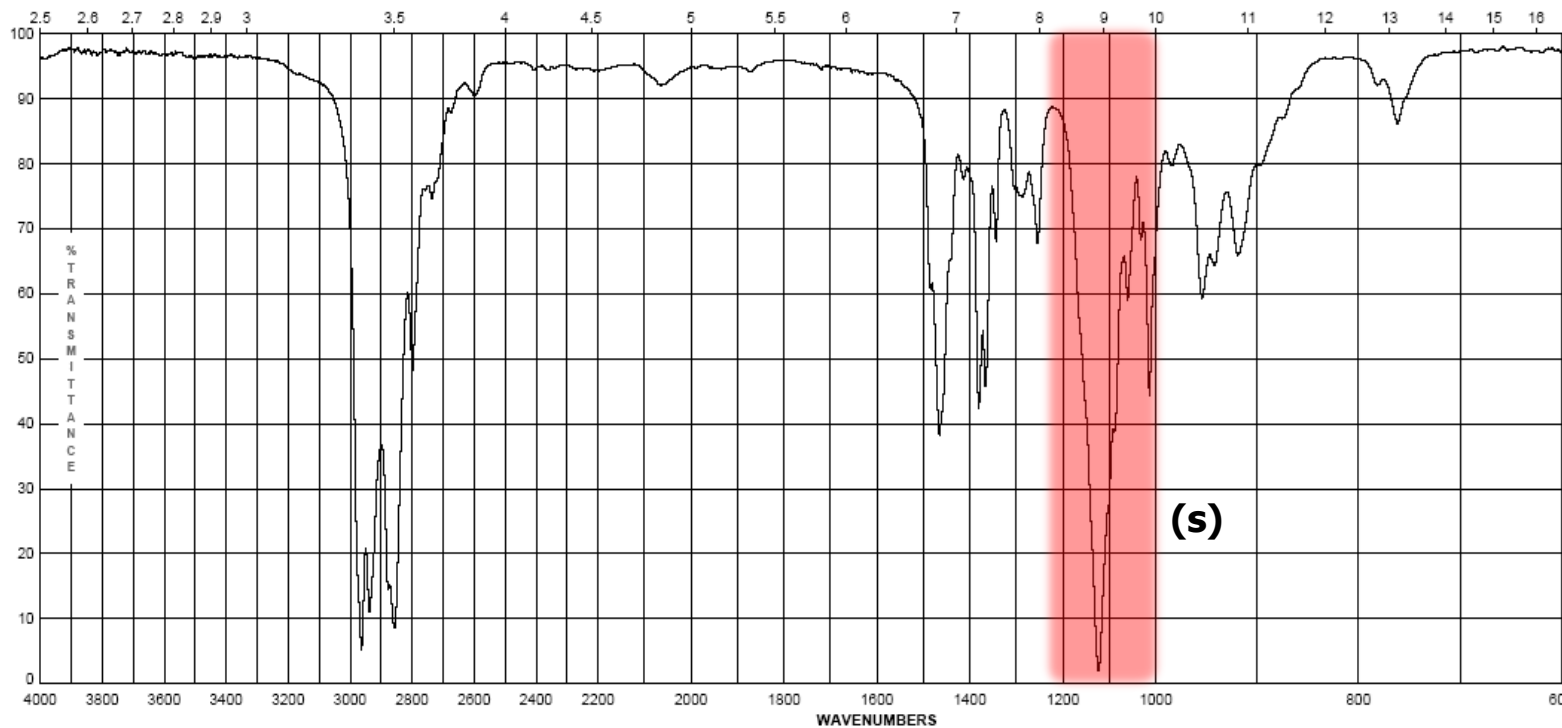
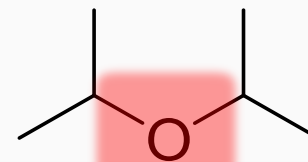
	<u>cm⁻¹</u>		<u>cm⁻¹</u>
	985-997 905-915		730-770 690-710
	960-980		735-770
	665-730		860-900 750-810 680-725
	885-895		800-860
	790-840		

Infrared Spectroscopy

6. Ethers – addition of the C-O-C asymmetric band and vinyl C-H bonds

- Show a strong band for the antisymmetric C-O-C stretch at 1050-1150 cm^{-1}
- Otherwise, dominated by the hydrocarbon component of the rest of the molecule

Diisopropyl ether

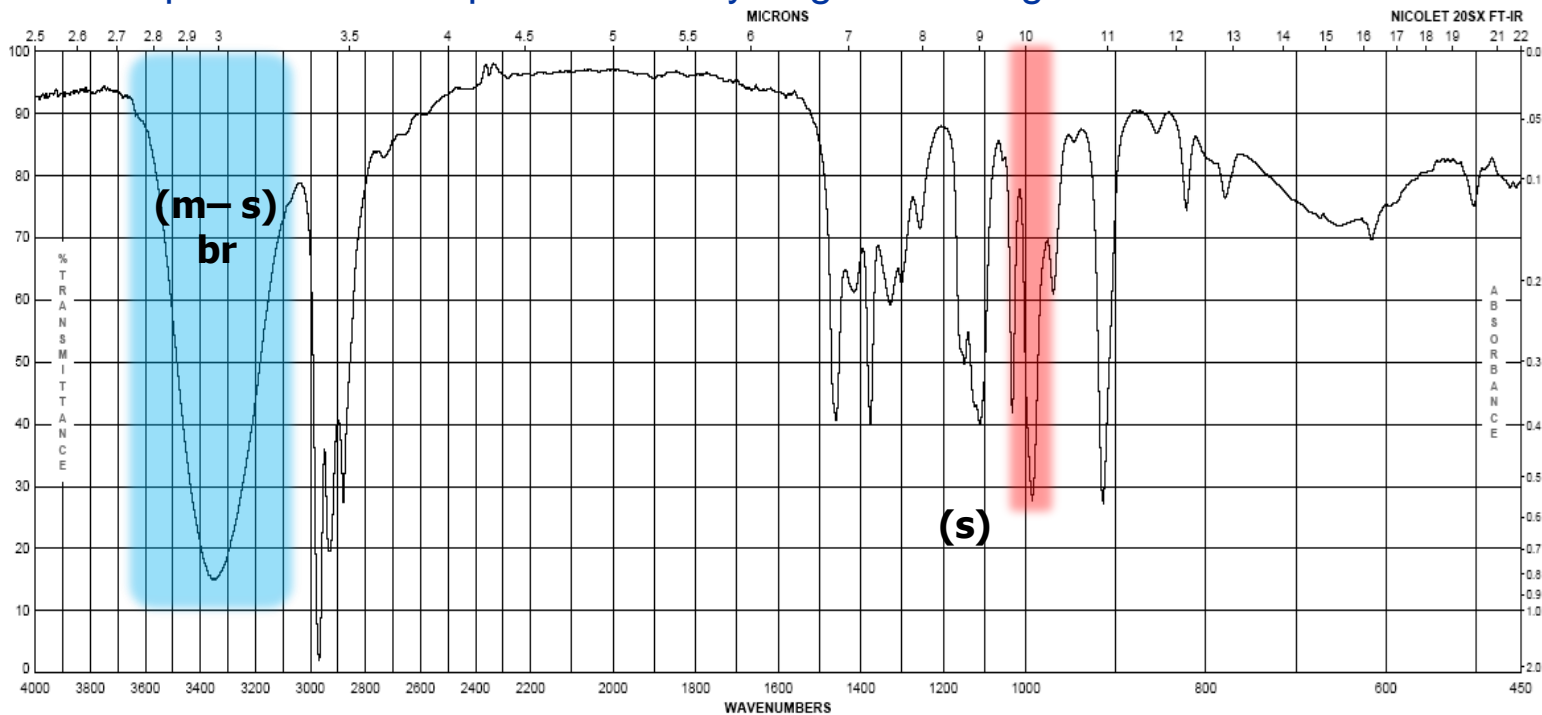
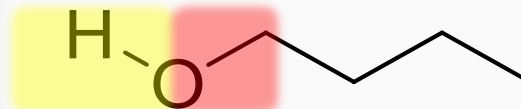


Infrared Spectroscopy

7. Alcohols

- Strong, broad O-H stretch from 3200-3400 cm^{-1}
- Like ethers, C-O stretch from 1050-1260 cm^{-1}
- Band position changes depending on the alcohols substitution: 1° 1075-1000; 2° 1075-1150; 3° 1100-1200; phenol 1180-1260
- The shape is due to the presence of hydrogen bonding

1-butanol

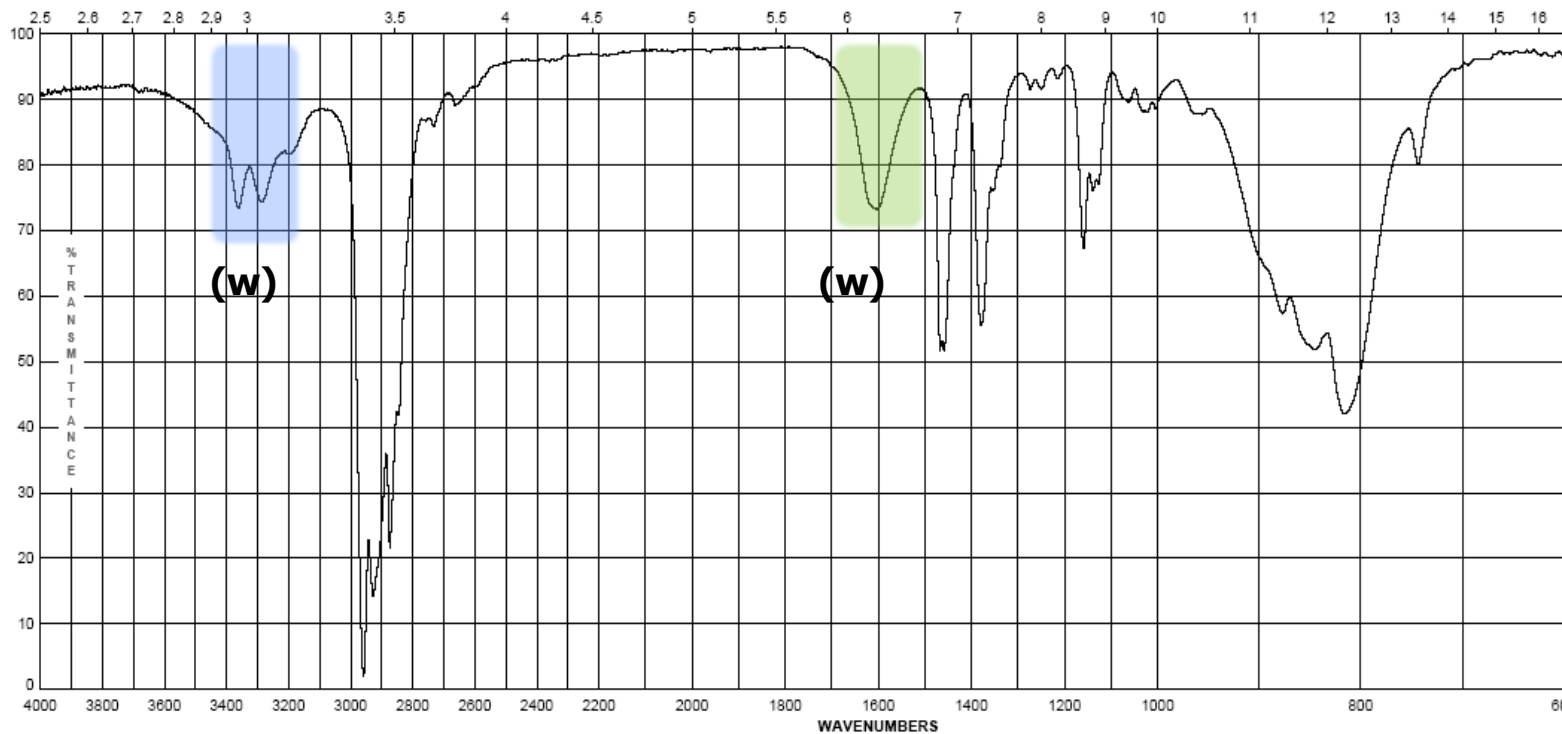
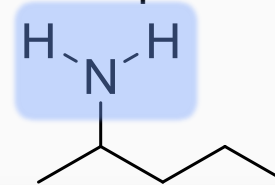


Infrared Spectroscopy

8. Amines - Primary

- Shows the -N-H stretch for NH_2 as a *doublet* between $3200\text{-}3500\text{ cm}^{-1}$ (symmetric and anti-symmetric modes)
- -NH_2 has deformation band from $1590\text{-}1650\text{ cm}^{-1}$
- Additionally there is a “wag” band at $780\text{-}820\text{ cm}^{-1}$ that is not diagnostic

2-aminopentane

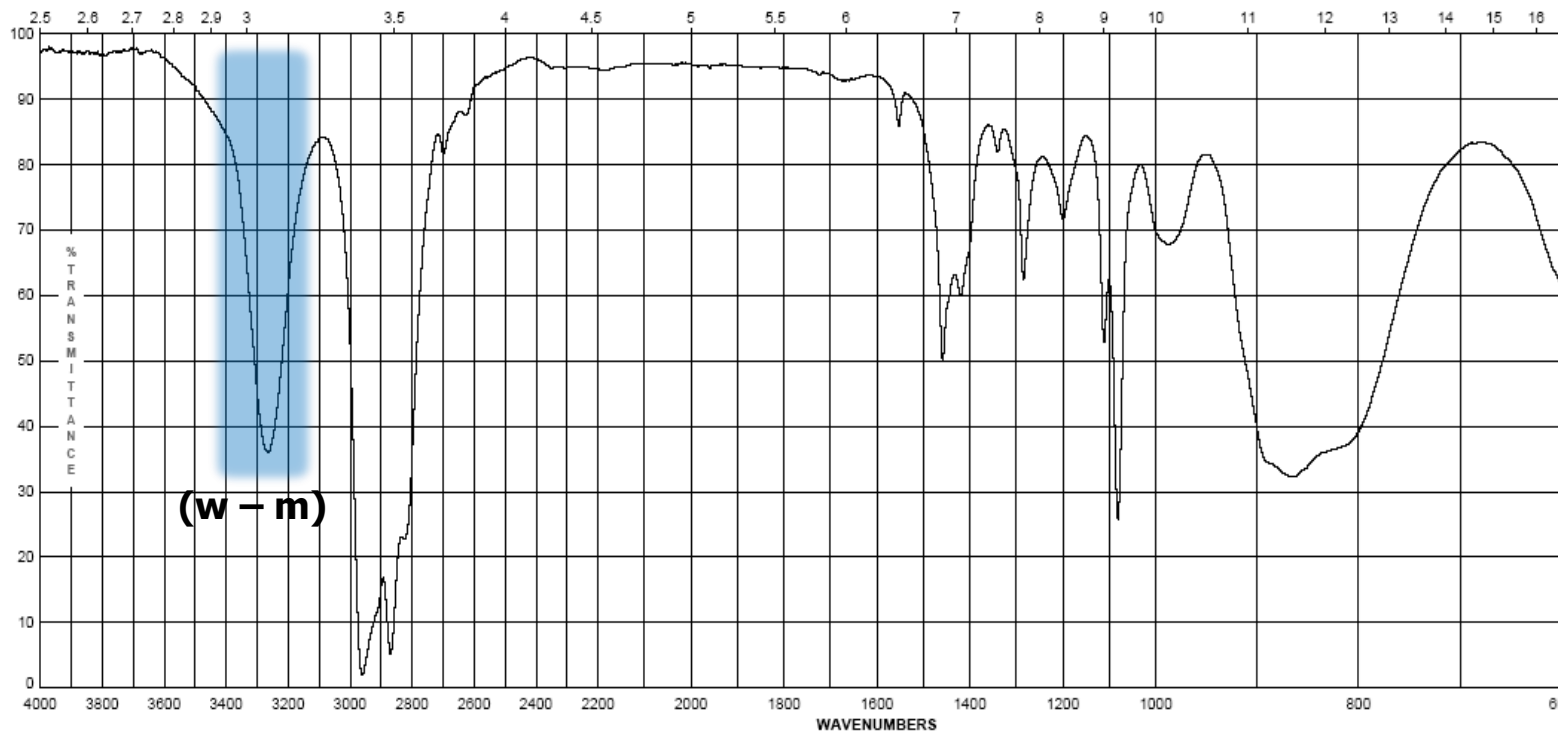
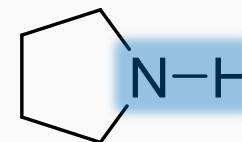


Infrared Spectroscopy

9. Amines – Secondary

- N-H band for R_2N-H occurs at $3200-3500\text{ cm}^{-1}$ as a single sharp peak weaker than $-O-H$
- Tertiary amines (R_3N) have no N-H bond and *will not* have a band in this region

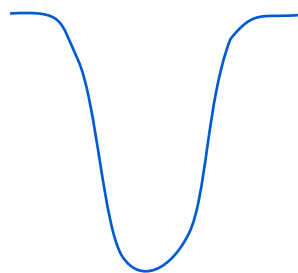
pyrrolidine



Infrared Spectroscopy

Pause and Review

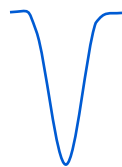
- Inspect the bonds to H region (2700 – 4000 cm^{-1})
- Peaks from 2850-3000 are simply sp^3 C-H in most organic molecules
- Above 3000 cm^{-1} *Learn shapes, not wavenumbers!:*



Broad U-shape peak
-O—H bond



Sharp spike
-C≡C—H bond

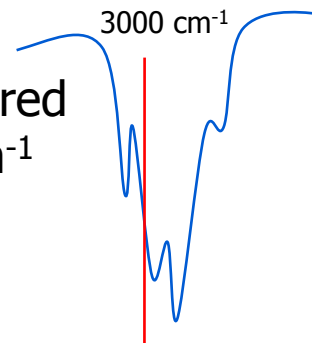


V-shape peak
-N—H bond for 2°
amine (**R₂N—H**)



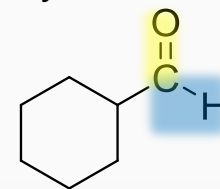
W-shape peak
-N—H bond for 1°
amine (**RNH₂**)

Small peak shouldered
just above 3000 cm^{-1}
C=C—H or **Ph—H**



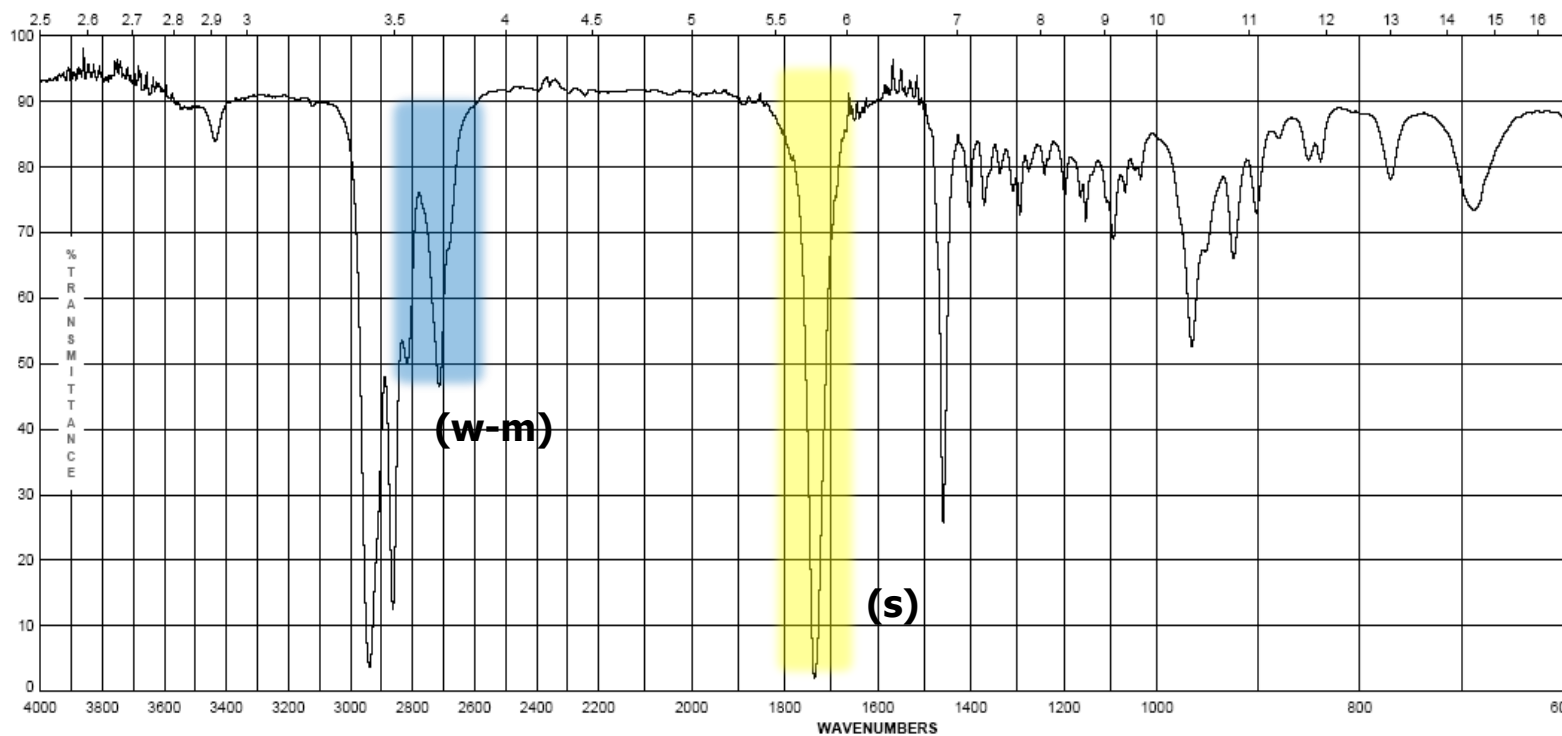
Infrared Spectroscopy

Cyclohexyl carboxaldehyde



10. Aldehydes

- C=O (carbonyl) stretch from 1720-1740 cm^{-1}
- Band is sensitive to conjugation, as are all carbonyls (upcoming slide)
- A highly unique sp^2 C-H stretch appears as a doublet, 2720 & 2820 cm^{-1} called a "*Fermi doublet*"

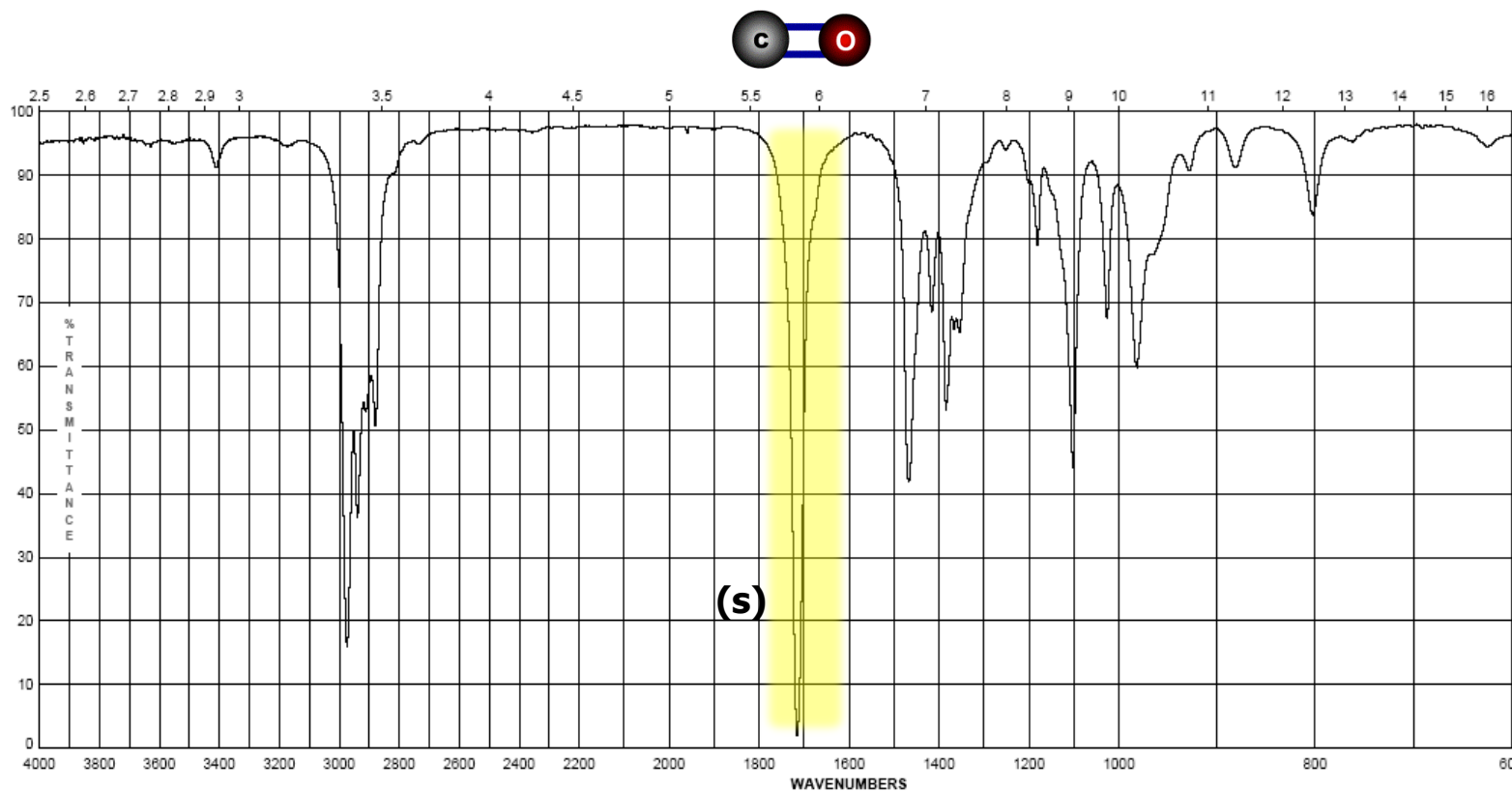
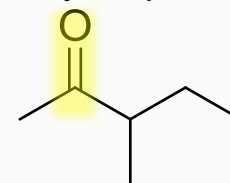


Infrared Spectroscopy

11. Ketones

- Simplest of the carbonyl compounds as far as IR spectrum – carbonyl only
- C=O stretch occurs at 1705-1725 cm^{-1}

3-methyl-2-pentanone

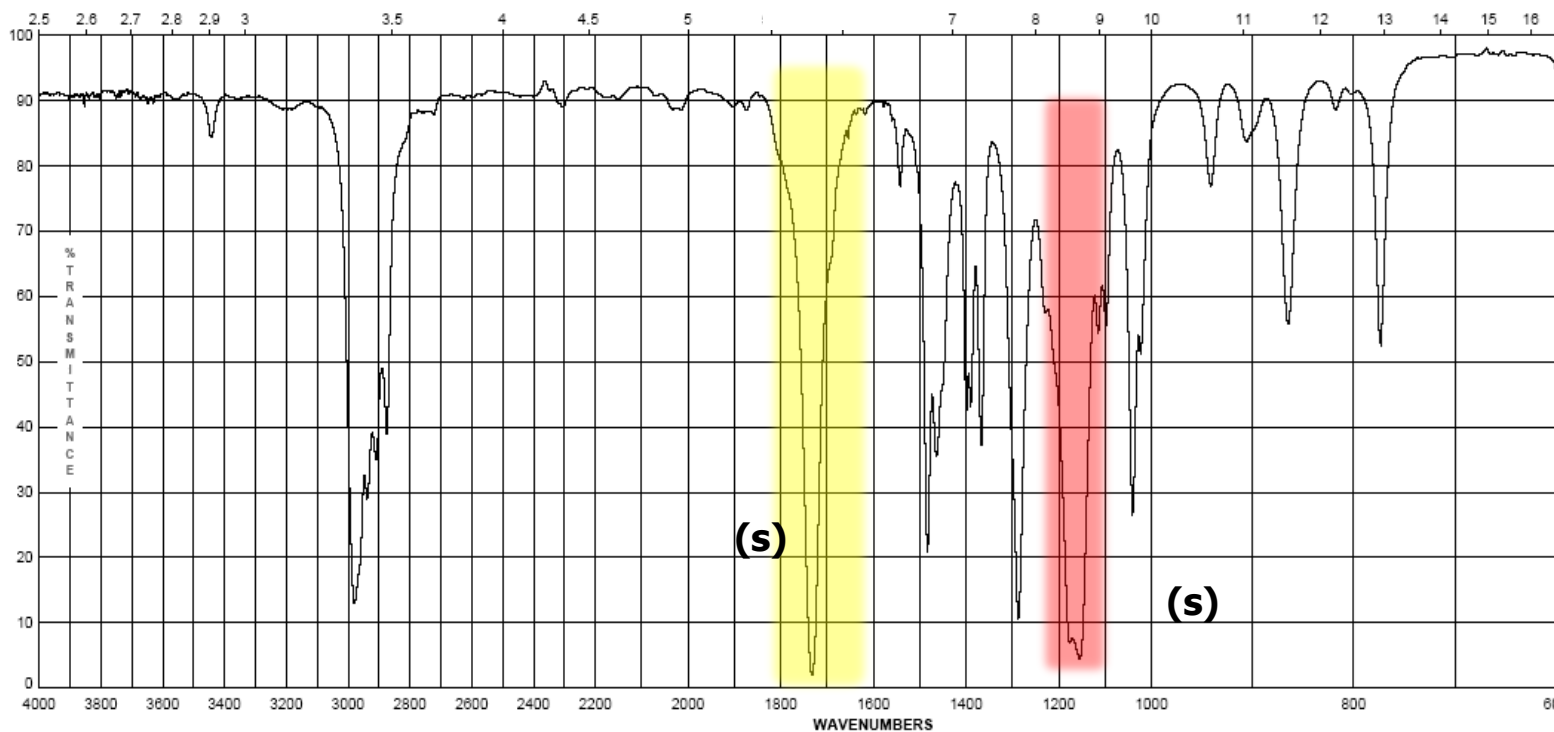
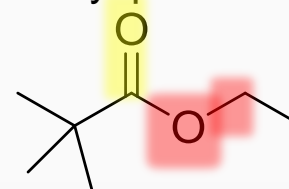


Infrared Spectroscopy

12. Esters

- C=O stretch at 1735-1750 cm^{-1}
- Strong band for C-O at a higher frequency than ethers or alcohols at 1150-1250 cm^{-1}

Ethyl pivalate

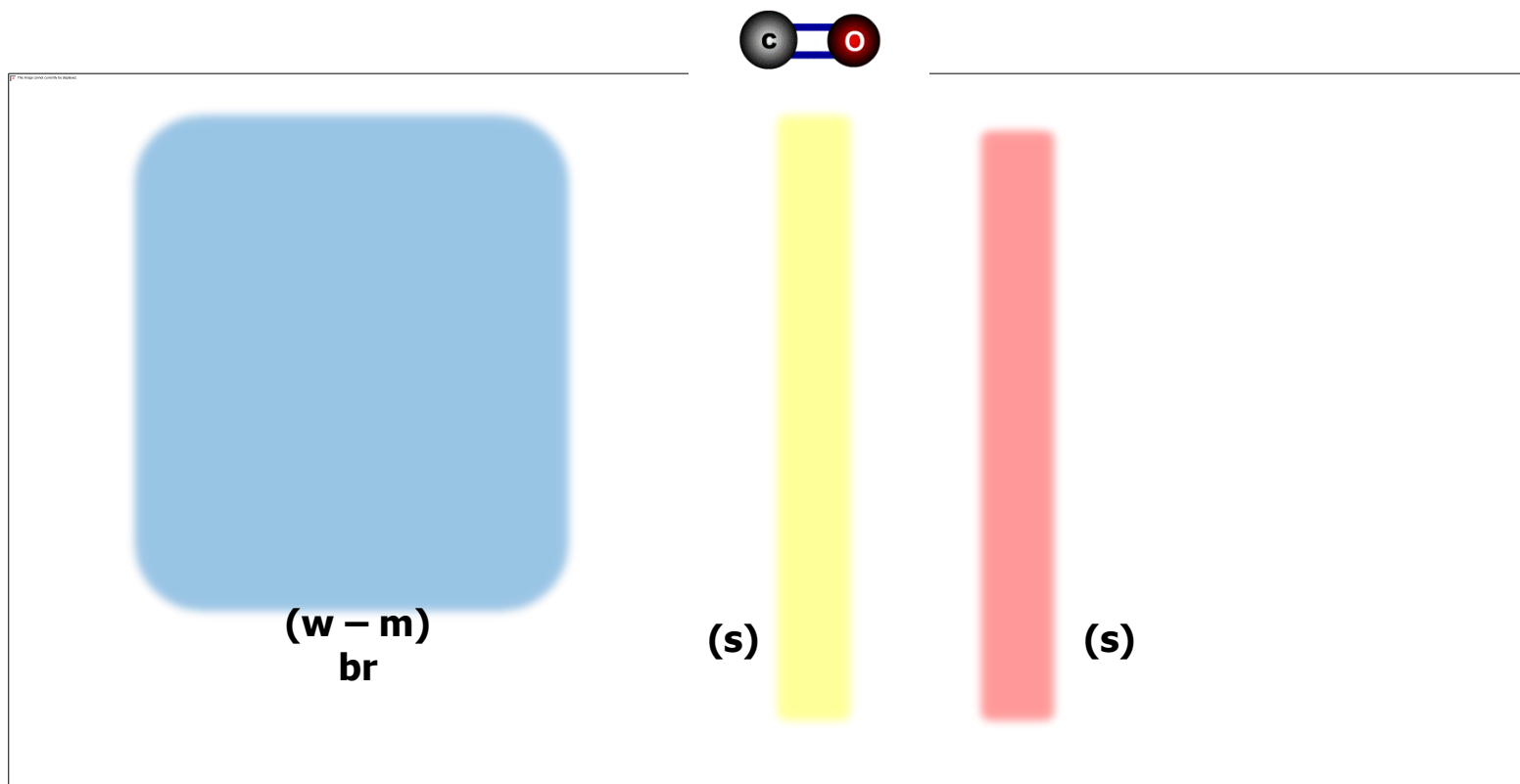
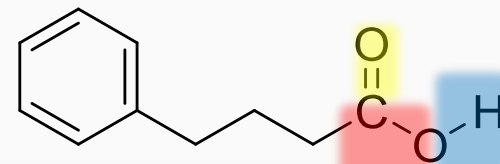


Infrared Spectroscopy

13. Carboxylic Acids:

- Gives the messiest of IR spectra
- C=O band occurs between 1700-1725 cm^{-1}
- The highly dissociated O-H bond has a broad band from 2400-3500 cm^{-1} covering up to half the IR spectrum in some cases

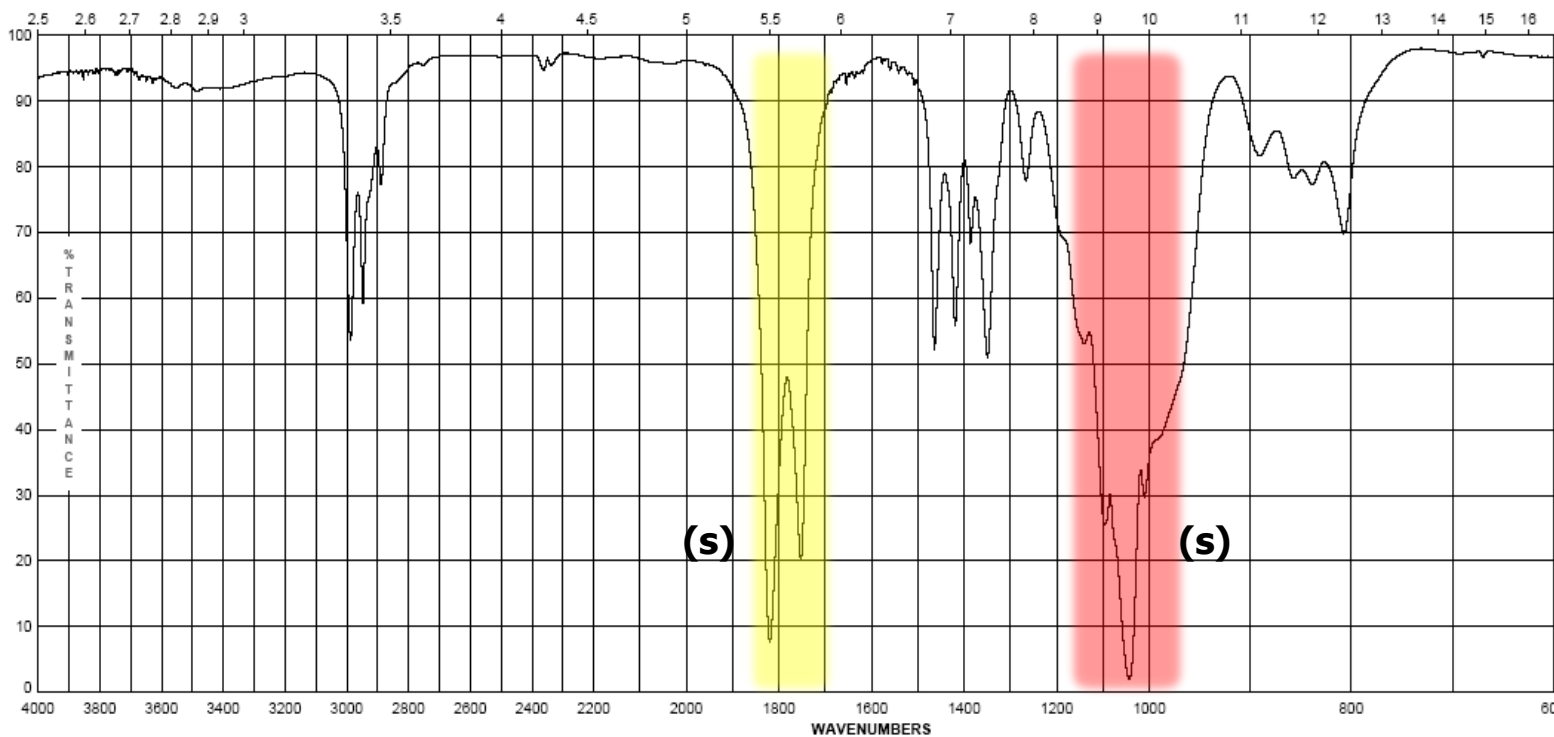
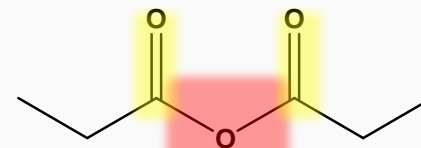
4-phenylbutyric acid



14. Acid anhydrides

- Coupling of the anhydride through the ether oxygen splits the carbonyl band into two with a separation of 70 cm^{-1}
- Bands are at $1740\text{-}1770\text{ cm}^{-1}$ and $1810\text{-}1840\text{ cm}^{-1}$
- Mixed mode C-O stretch at $1000\text{-}1100\text{ cm}^{-1}$

Propionic anhydride



Infrared Spectroscopy

15. Acid halides

- Clefted band at 1770-1820 cm^{-1} for C=O
- Bonds to halogens, due to their size (see Hooke's Law derivation) occur at low frequencies, only Cl is light enough to have a band on IR, C-Cl is at 600-800 cm^{-1}

Propionyl chloride

