



**“TOPIC”**

# Infrared Spectroscopy

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**➡ DETECTION OF FUNCTIONAL GROUPS**

**➡ IR ABSORPTION FREQUENCY REGION**

**➡ REFERENCES**

# IR Spectroscopy

## I. Introduction

**A. Spectroscopy** is the study of the interaction of matter with the electromagnetic spectrum

1. Electromagnetic radiation displays the properties of both particles and waves
2. The particle component is called a *photon*
3. The energy (**E**) component of a photon is proportional to the frequency. Where **h** is Planck's constant and  $\nu$  is the frequency in Hertz (cycles per second)

$$\mathbf{E = h\nu}$$

4. The term "photon" is implied to mean a small, massless particle that contains a small wave-packet of EM radiation/light – we will use this terminology in the course

# IR Spectroscopy

## I. Introduction

5. Because the speed of light, **c**, is constant, the **frequency**,  $\nu$ , (number of cycles of the wave per second) can complete in the same time, must be inversely proportional to how long the oscillation is, or **wavelength**:

$$\nu = \frac{c}{\lambda} \qquad \therefore E = h\nu = \frac{hc}{\lambda}$$

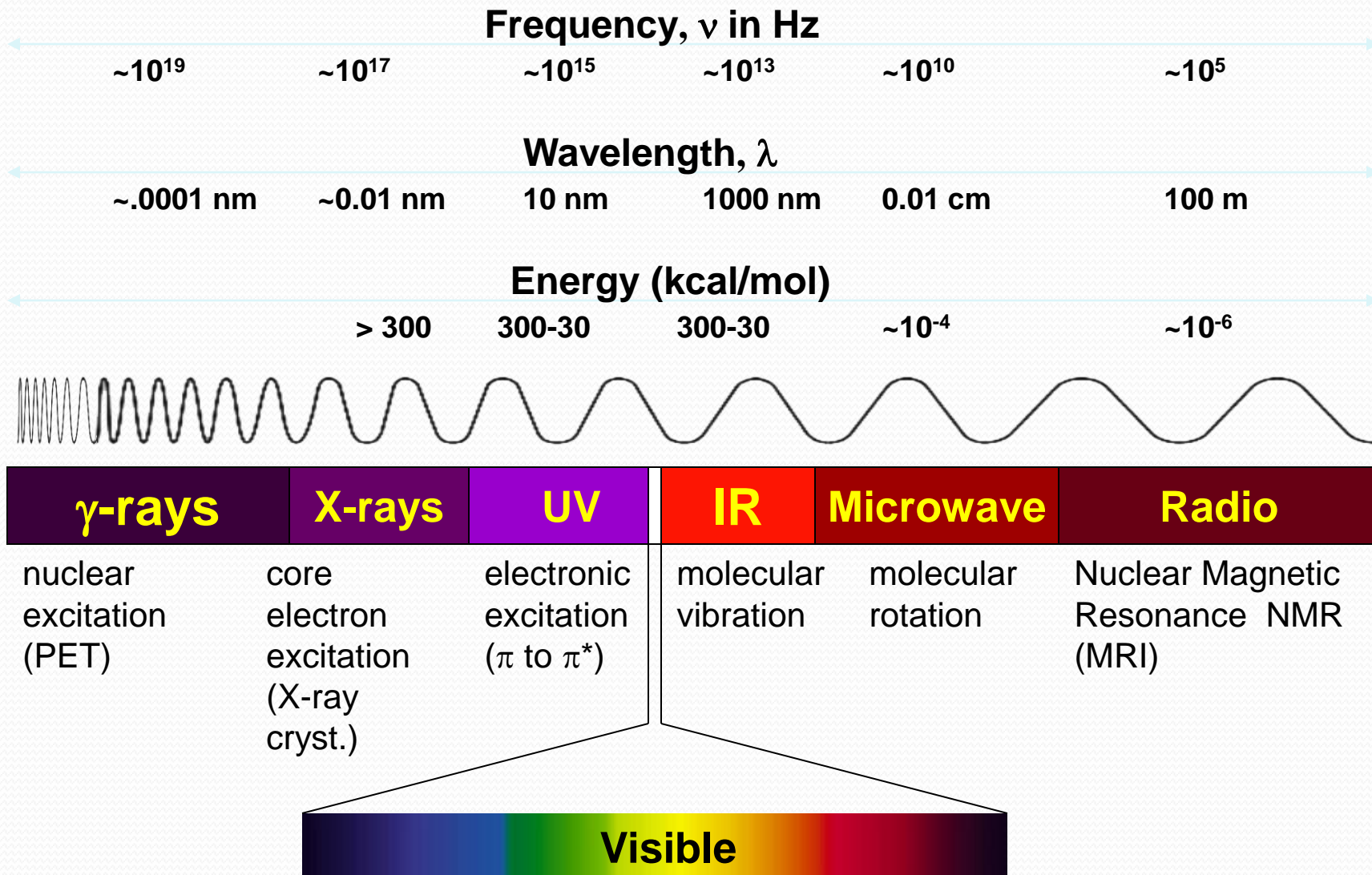
$$c = 3 \times 10^{10} \text{ cm/s}$$

6. Amplitude, **A**, describes the wave height, or strength of the oscillation
7. Because the atomic particles in matter also exhibit wave and particle properties (though opposite in how much) EM radiation can interact with matter in two ways:
- Collision – particle-to-particle – energy is lost as heat and movement
  - Coupling – the wave property of the radiation matches the wave property of the particle and “couple” to the next higher quantum mechanical energy level

# IR Spectroscopy

## I. Introduction

8. The entire electromagnetic spectrum is used by chemists:

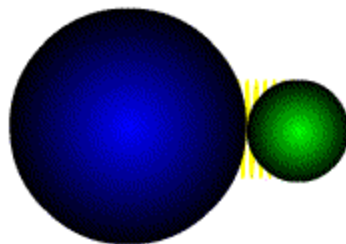


# IR Spectroscopy

## I. Introduction

### C. The IR Spectroscopic Process

1. The quantum mechanical energy levels observed in IR spectroscopy are those of *molecular vibration*
2. We perceive this vibration as heat
3. When we say a *covalent bond* between two atoms is of a certain length, we are citing an average because the bond behaves as if it were a vibrating spring connecting the two atoms
4. For a simple diatomic molecule, this model is easy to visualize:



Vibration of a Diatomic Molecule  
Approximates an Oscillating Spring

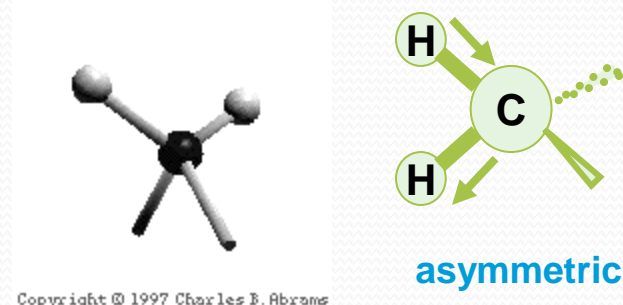
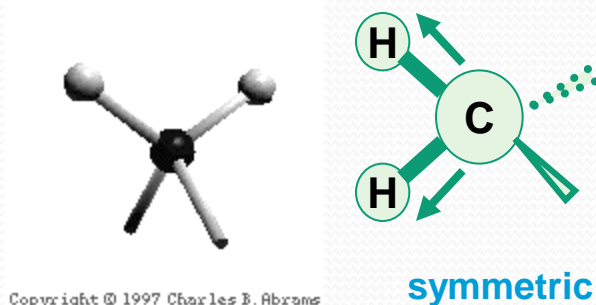
# IR Spectroscopy

## I. Introduction

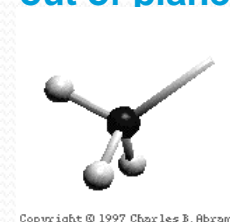
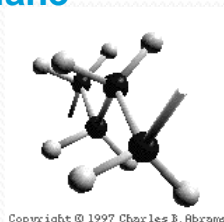
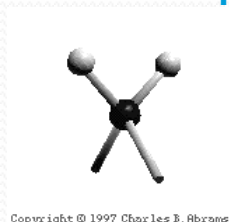
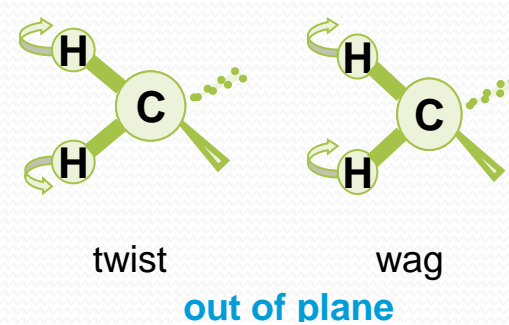
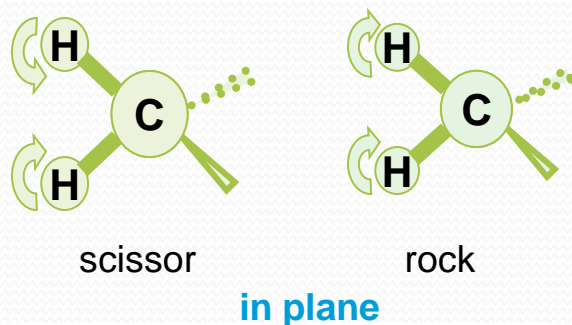
### C. The IR Spectroscopic Process

#### 5. There are two types of bond vibration:

- **Stretch** – Vibration or oscillation along the line of the bond



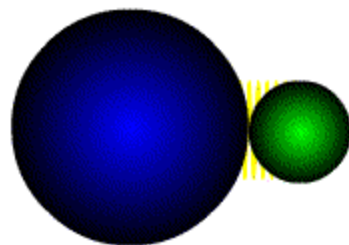
- **Bend** – Vibration or oscillation not along the line of the bond



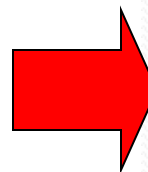
# Infrared Spectroscopy

## C. The IR Spectroscopic Process

6. As a covalent bond oscillates – due to the oscillation of the dipole of the molecule – a varying electromagnetic field is produced



Vibration of a Diatomic Molecule  
Approximates an Oscillating Spring



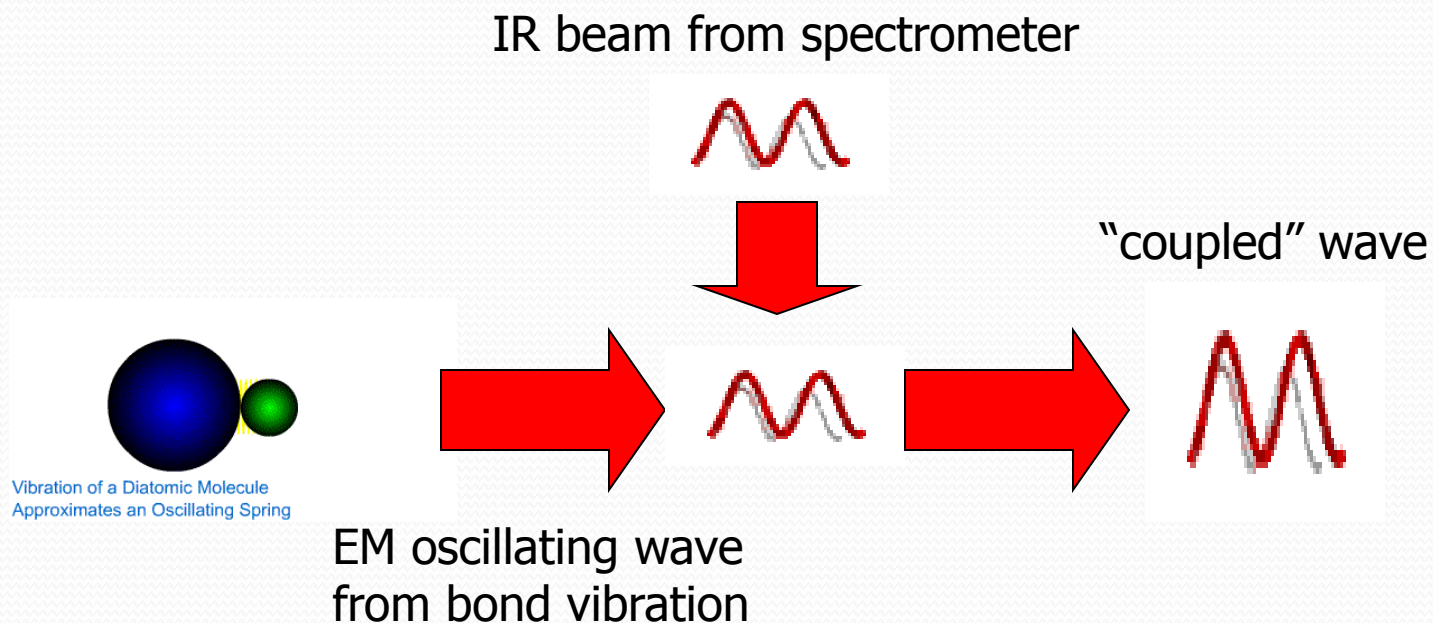
7. The greater the dipole moment change through the vibration, the more intense the EM field that is generated



# Infrared Spectroscopy

## C. The IR Spectroscopic Process

8. When a wave of infrared light encounters this oscillating EM field generated by the oscillating dipole of the same frequency, the two waves couple, and IR light is absorbed
9. The coupled wave now vibrates with twice the amplitude



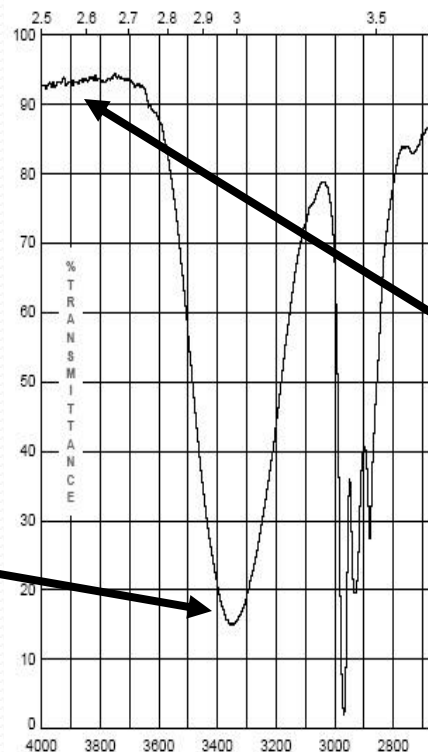
# Infrared Spectroscopy

## D. The IR Spectrum

1. Each stretching and bending vibration occurs with a characteristic frequency as the atoms and charges involved are different for different bonds

The y-axis on an IR spectrum is in units of % transmittance

In regions where the EM field of an osc. bond interacts with IR light of the same  $\nu$  – transmittance is low (light is absorbed)

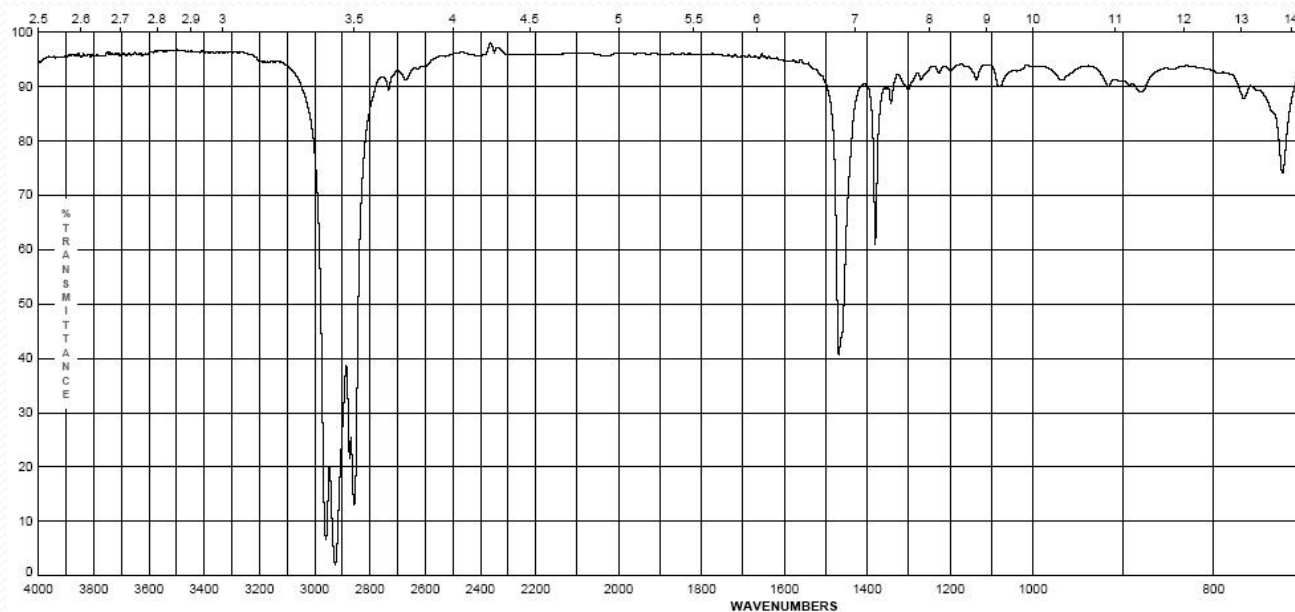


In regions where no osc. bond is interacting with IR light, transmittance nears 100%

# IR Spectroscopy

## D. The IR Spectrum

2. The x-axis of the IR spectrum is in units of wavenumbers,  $\bar{\nu}$ , which is the number of waves per centimeter in units of  $\text{cm}^{-1}$  (Remember  $E = h\nu$  or  $E = hc/\lambda$ )



# IR Spectroscopy

## D. The IR Spectrum

3. This unit is used rather than wavelength (microns) because wavenumbers are directly proportional to the energy of transition being observed – ***chemists like this, physicists hate it***

*High frequencies and high wavenumbers equate higher energy  
is quicker to understand than  
Short wavelengths equate higher energy*

4. This unit is used rather than frequency as the numbers are more “real” than the exponential units of frequency
5. IR spectra are observed for the mid-infrared:  $600\text{-}4000\text{ cm}^{-1}$
6. The peaks are Gaussian distributions of the average energy of a transition

# IR Spectroscopy

## D. The IR Spectrum

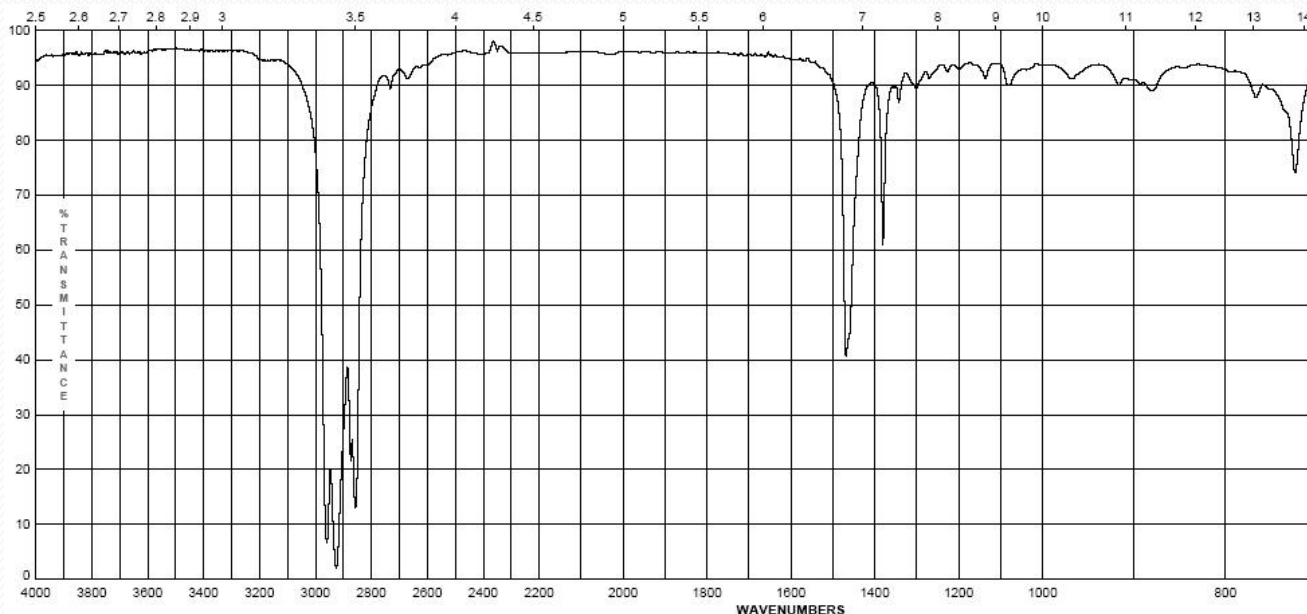
### 7. In general:

Lighter atoms will allow the oscillation to be faster – *higher energy*

This is especially true of bonds to hydrogen – C-H, N-H and O-H

Stronger bonds will have higher energy oscillations

Triple bonds > double bonds > single bonds in energy



← Energy/ $\nu$  of oscillation →

# Infrared Spectroscopy

## E. The IR Spectrum – The detection of different bonds

7. As opposed to chromatography or other spectroscopic methods, the area of a IR band (or peak) is not **directly** proportional to concentration of the functional group producing the peak

8. The intensity of an IR band is affected by two primary factors:

*Whether the vibration is one of stretching or bending*

*Electronegativity difference of the atoms involved in the bond*

- For both effects, the greater the change in dipole moment in a given vibration or bend, the larger the peak.
- The greater the difference in electronegativity between the atoms involved in bonding, the larger the dipole moment
- Typically, stretching will change dipole moment more than bending

# Infrared Spectroscopy

## E. The IR Spectrum – The detection of different bonds

9. It is important to make note of peak intensities to show the effect of these factors:

- **Strong (s)** – peak is tall, transmittance is low (0-35 %)
- **Medium (m)** – peak is mid-height (75-35%)
- **Weak (w)** – peak is short, transmittance is high (90-75%)
- \* **Broad (br)** – if the Gaussian distribution is abnormally broad (*\*this is more for describing a bond that spans many energies*)

*Exact transmittance values are rarely recorded*

# Infrared Spectroscopy

## II. Infrared Group Analysis

### A. General

1. The primary use of the IR is to *detect functional groups*
2. Because the IR looks at the interaction of the EM spectrum with actual bonds, it provides a unique qualitative probe into the functionality of a molecule, as functional groups are merely different configurations of different types of bonds
3. Since most “types” of bonds in covalent molecules have roughly the same energy, i.e., C=C and C=O bonds, C-H and N-H bonds they show up in similar regions of the IR spectrum
4. Remember all organic functional groups are made of multiple bonds and therefore show up as multiple IR bands (peaks)

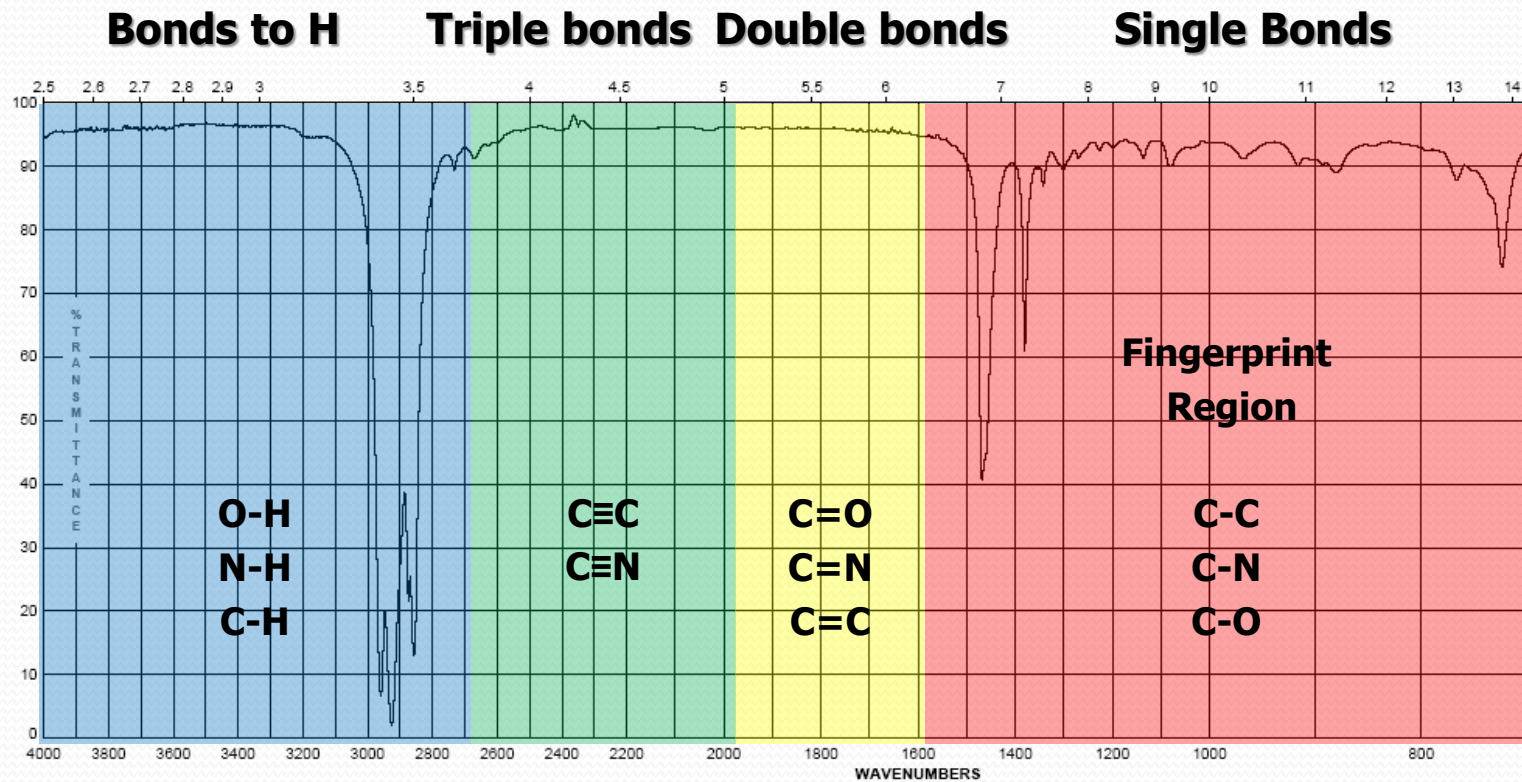


# Infrared Spectroscopy

## II. Infrared Group Analysis

### A. General

5. The four primary regions of the IR spectrum



4000 cm<sup>-1</sup>

2700 cm<sup>-1</sup>

2000 cm<sup>-1</sup>

1600 cm<sup>-1</sup>

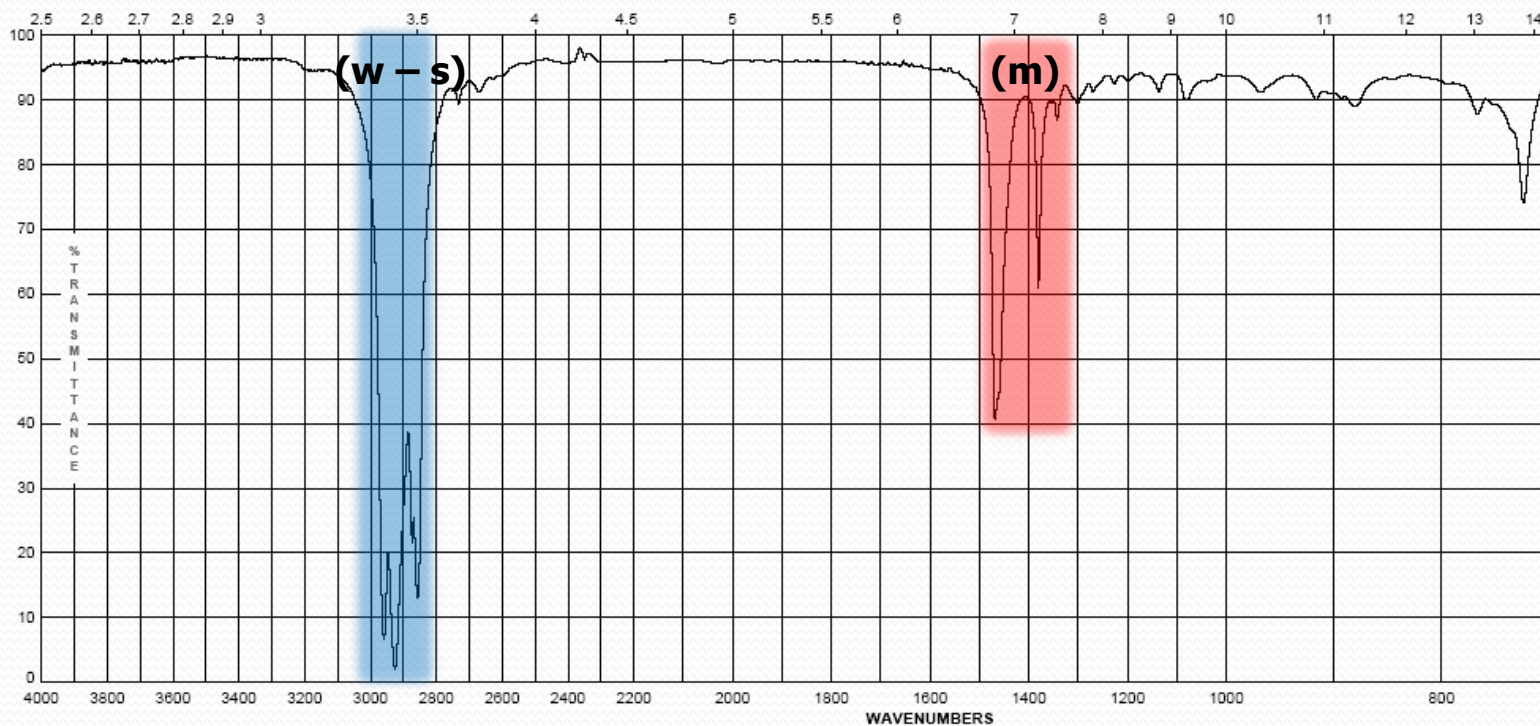
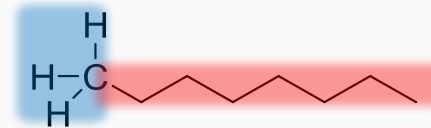
600 cm<sup>-1</sup>

# Infrared Spectroscopy

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

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

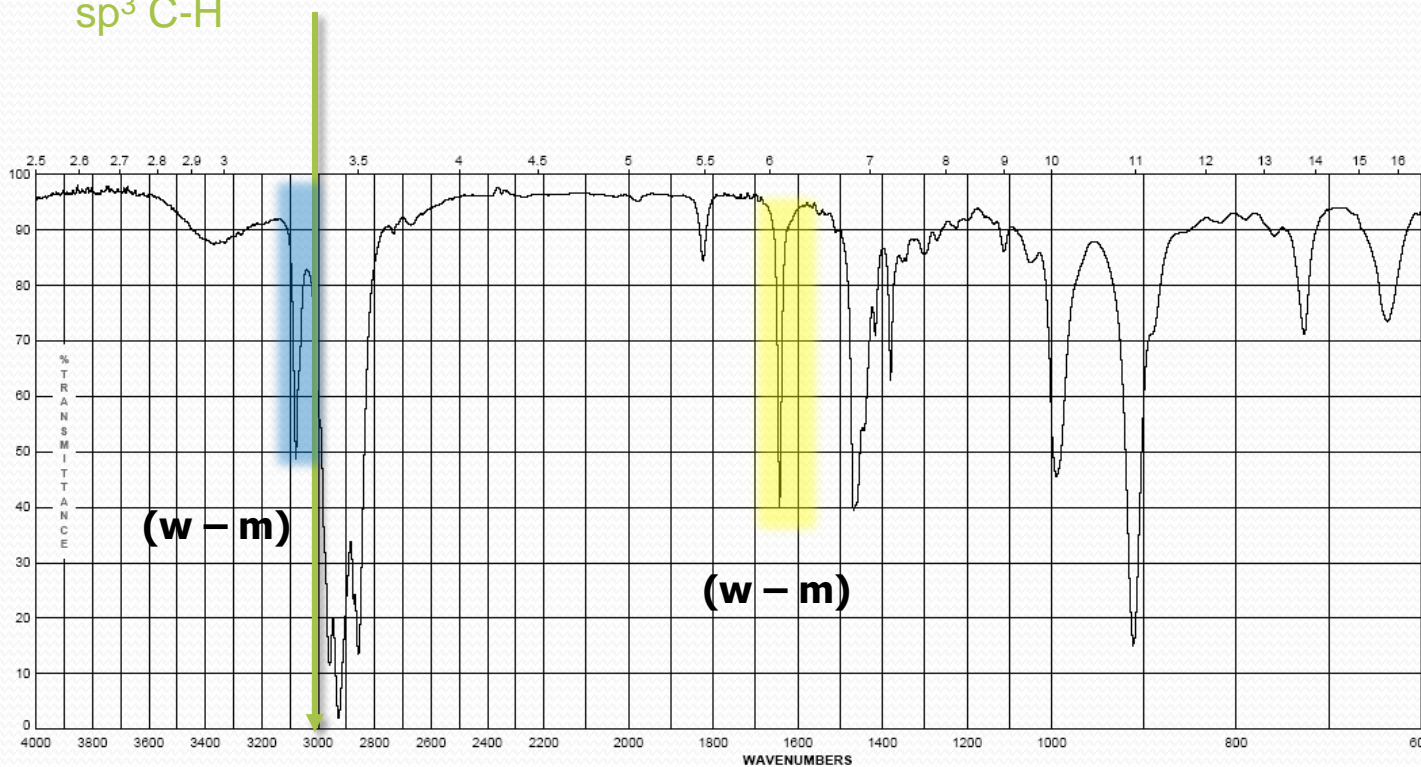
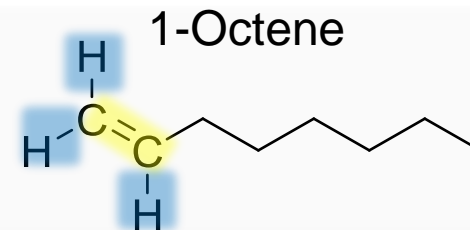
Octane



# Infrared Spectroscopy

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

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

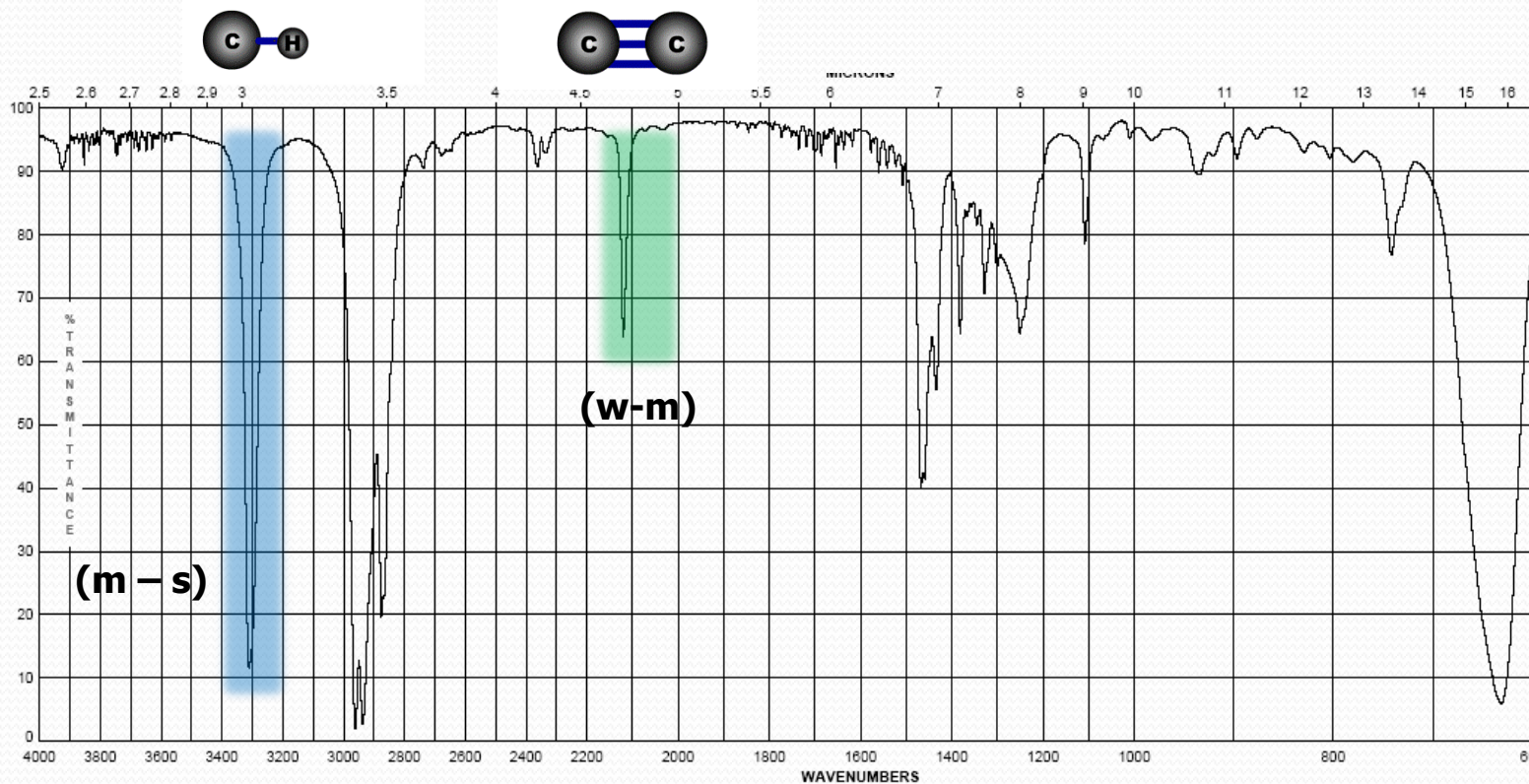
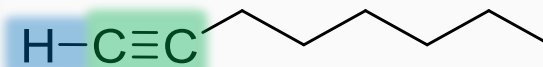


# Infrared Spectroscopy

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

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

1-Octyne

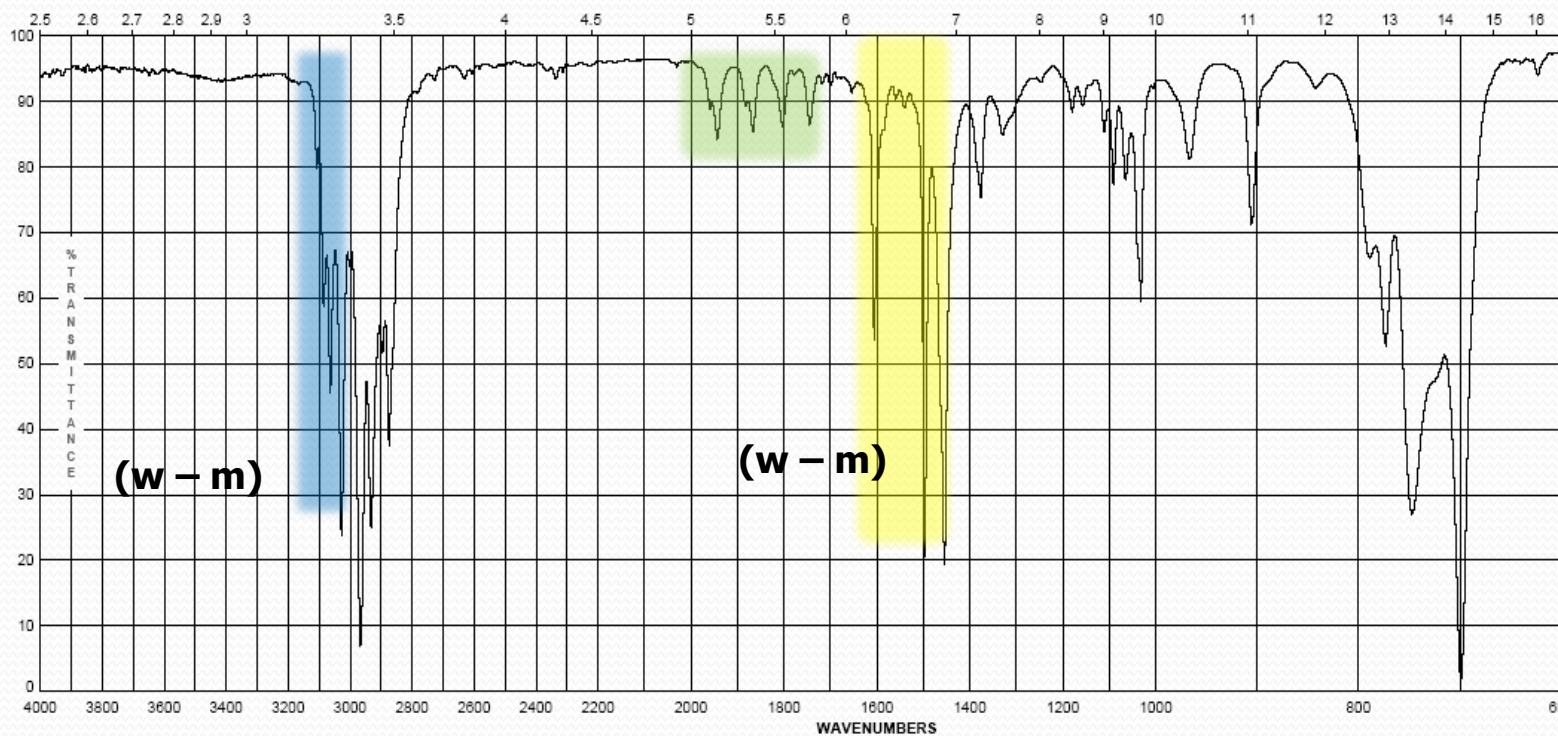
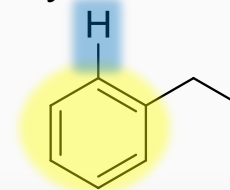


# Infrared Spectroscopy

## 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  $\text{cm}^{-1}$ , (lower frequency band is stronger)
- C-H bonds off the ring show up similar to vinyl C-H at 3000-3100  $\text{cm}^{-1}$

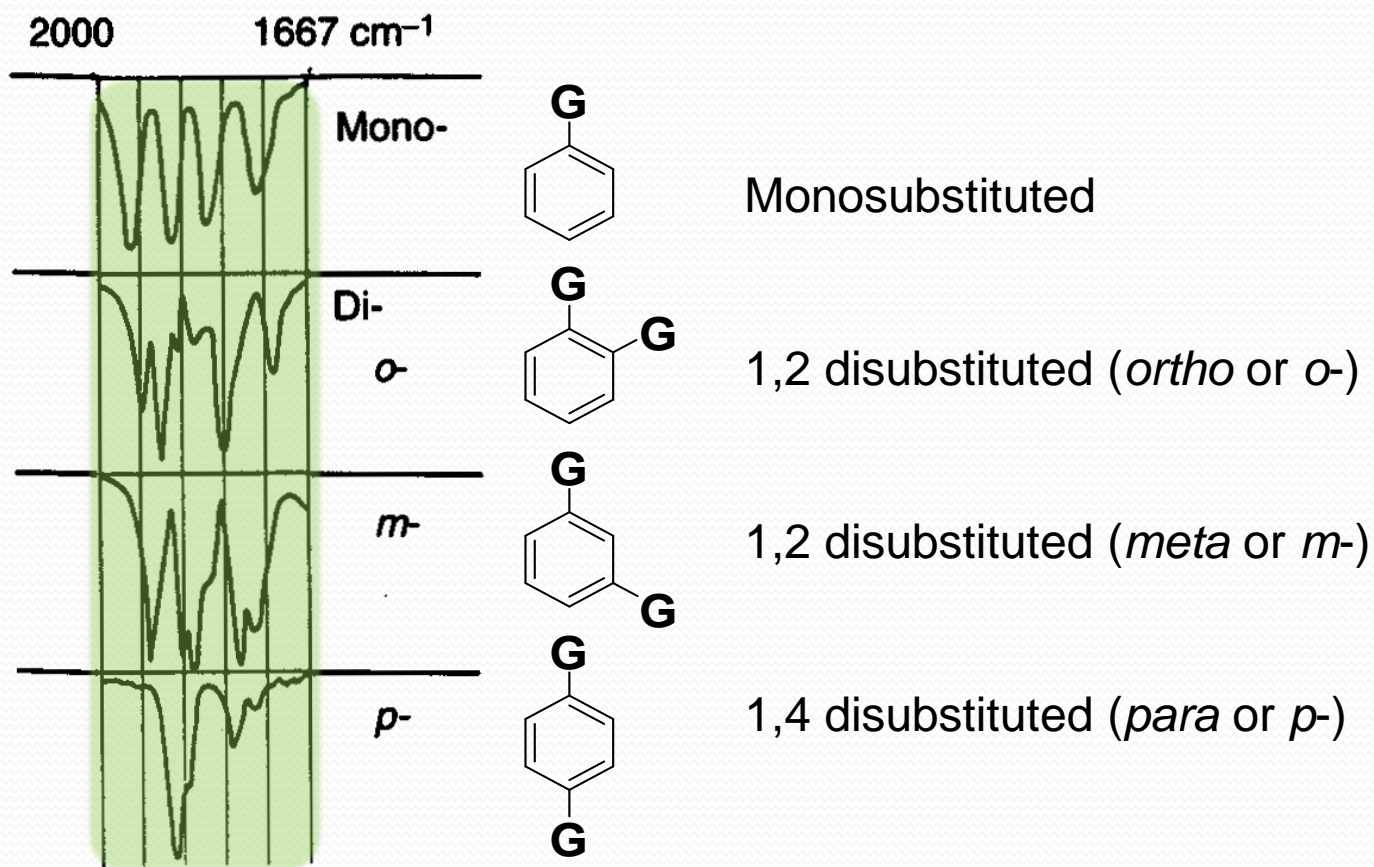
Ethyl benzene



# Infrared Spectroscopy

## 4. Aromatics

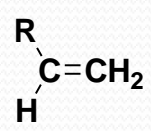
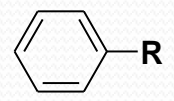
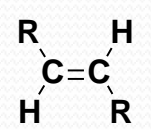
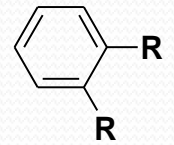
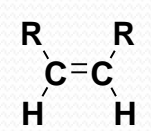
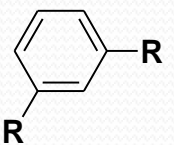
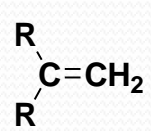
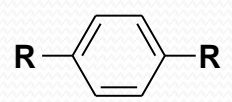
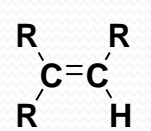
- If the region between  $1667\text{-}2000\text{ cm}^{-1}$  ( $w$ ) is free of interference (C=O stretching frequency is in this region) a weak grouping of peaks is observed for aromatic systems
- Analysis of this region, called the *overtone of bending* region, can lead to a determination of the substitution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

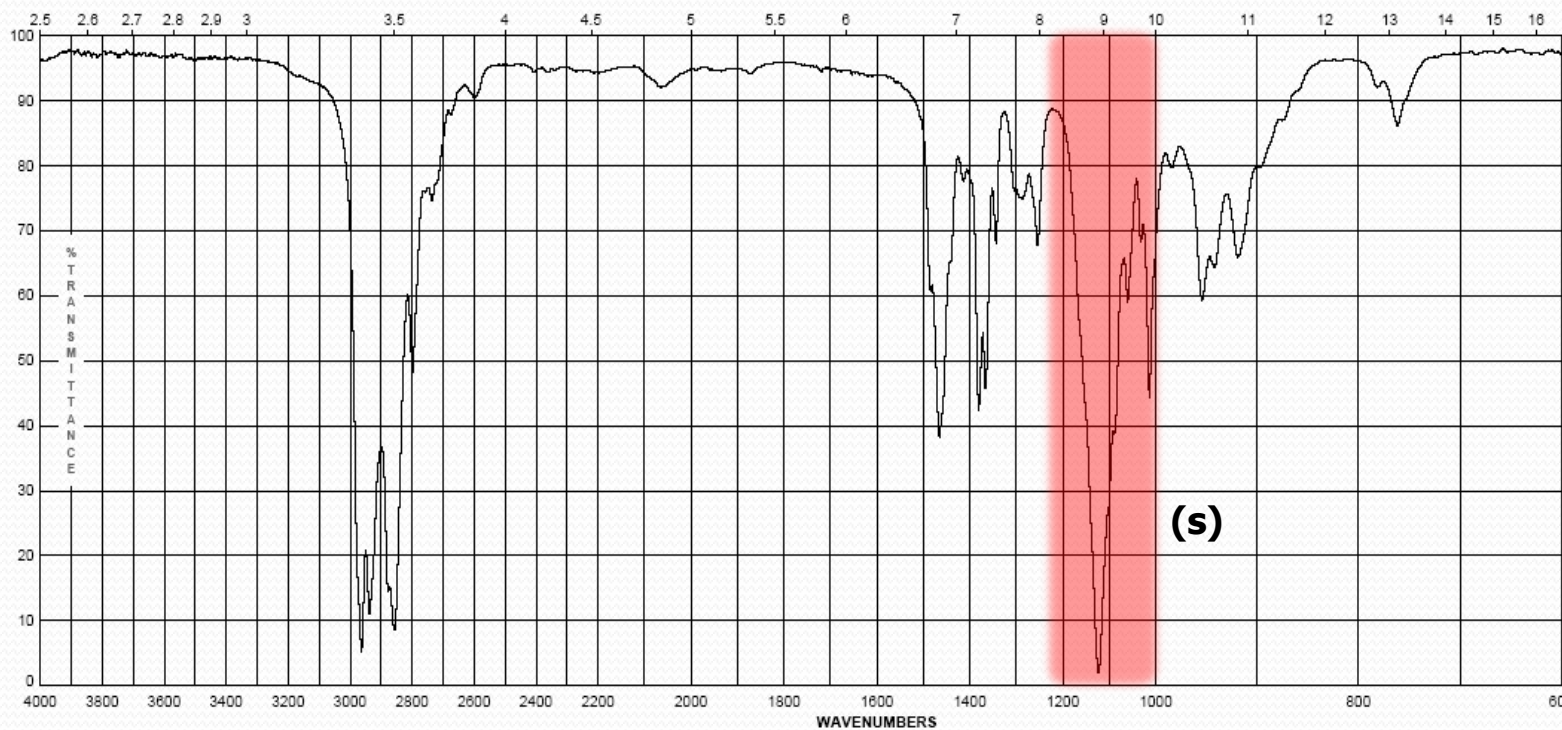
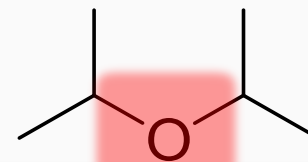
	<u>cm<sup>-1</sup></u>		<u>cm<sup>-1</sup></u>
	985-997 905-915		730-770 690-710
	960-980		735-770
	665-730		860-900 750-810 680-725
	885-895		800-860
	790-840		

# 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  $\text{cm}^{-1}$
- Otherwise, dominated by the hydrocarbon component of the rest of the molecule

Diisopropyl ether



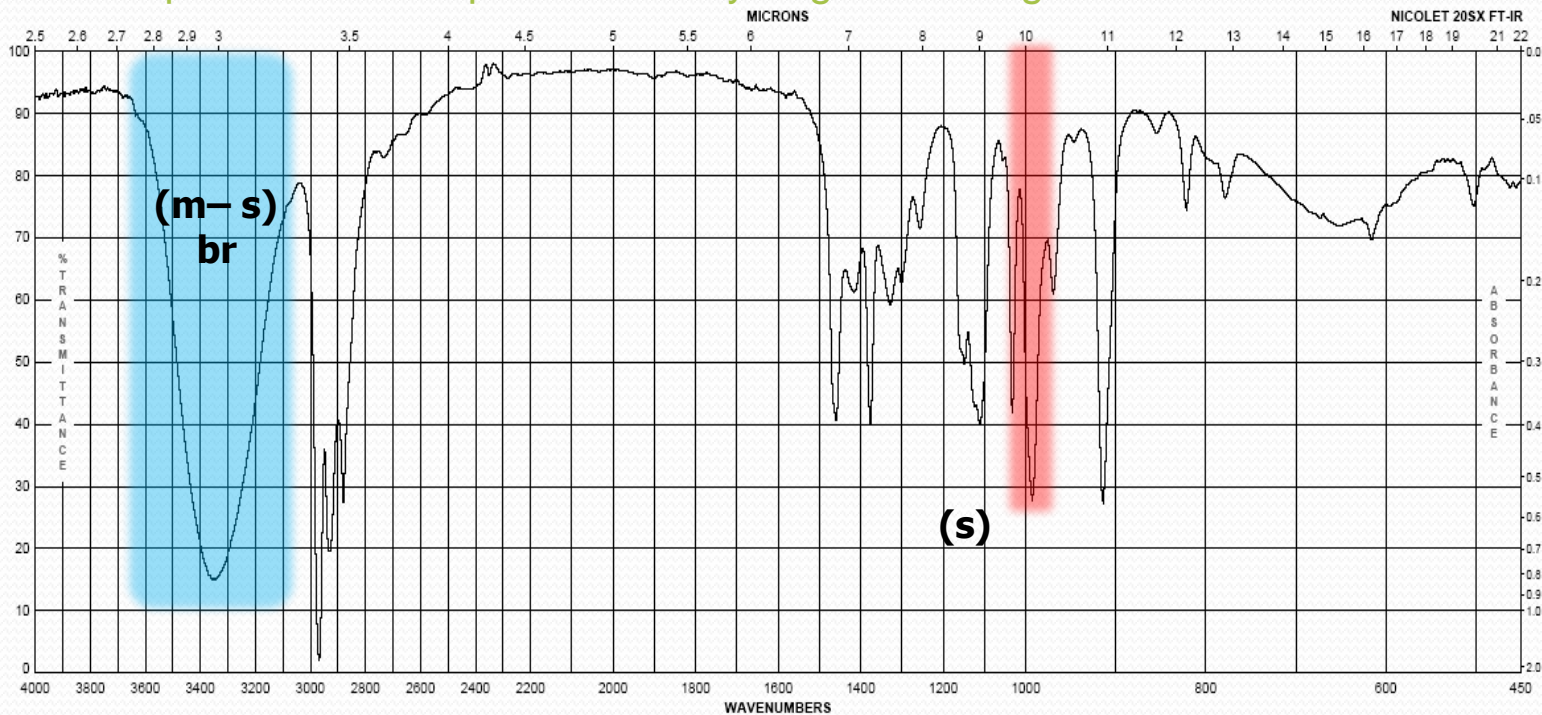
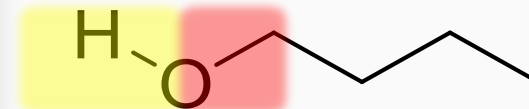


# Infrared Spectroscopy

## 7. Alcohols

- Strong, broad O-H stretch from 3200-3400  $\text{cm}^{-1}$
- Like ethers, C-O stretch from 1050-1260  $\text{cm}^{-1}$
- 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

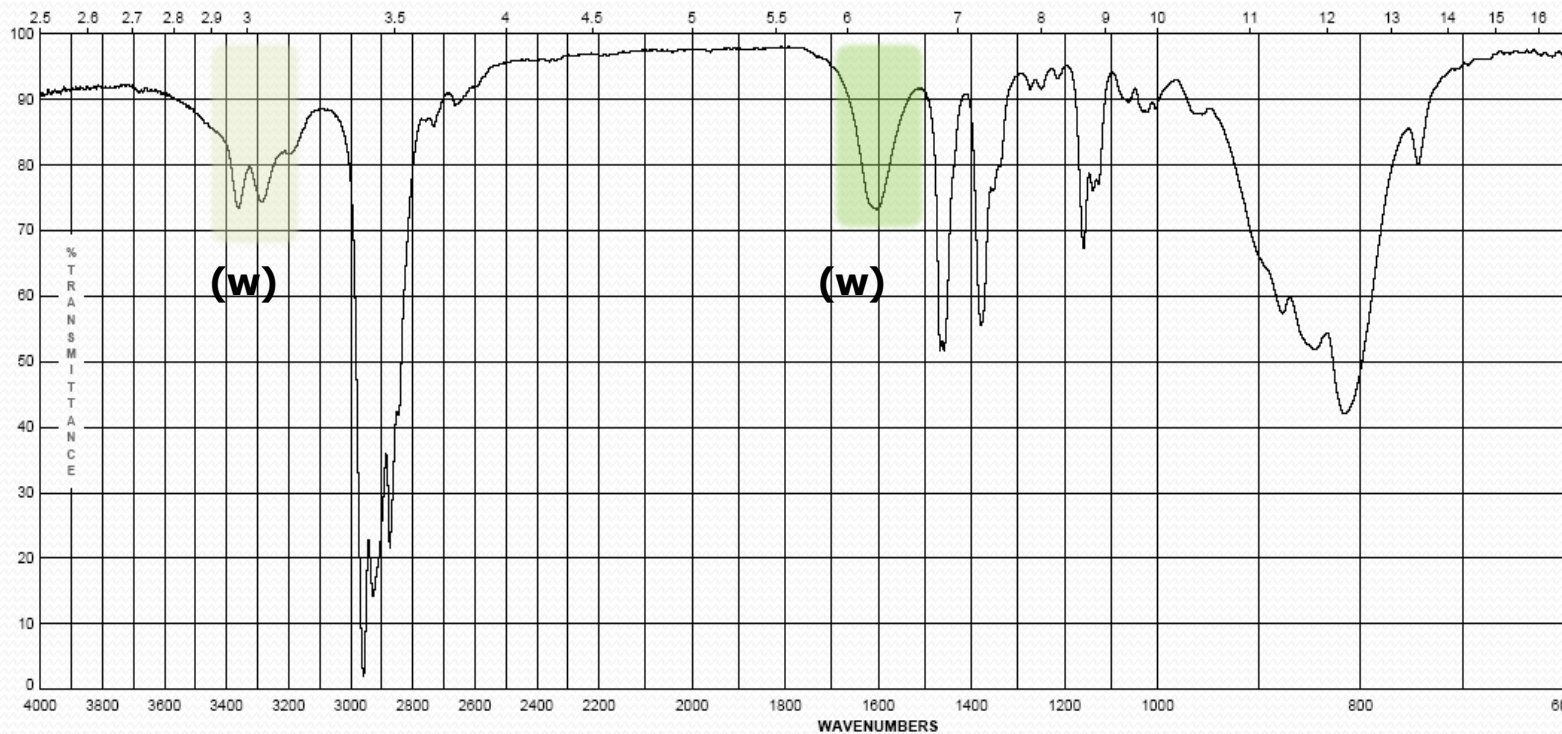
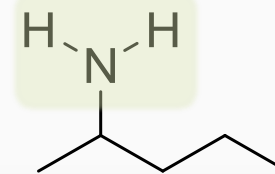


# Infrared Spectroscopy

## 8. Amines - Primary

- Shows the  $\text{-N-H}$  stretch for  $\text{NH}_2$  as a **doublet** between  $3200\text{-}3500\text{ cm}^{-1}$  (symmetric and anti-symmetric modes)
- $\text{-NH}_2$  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

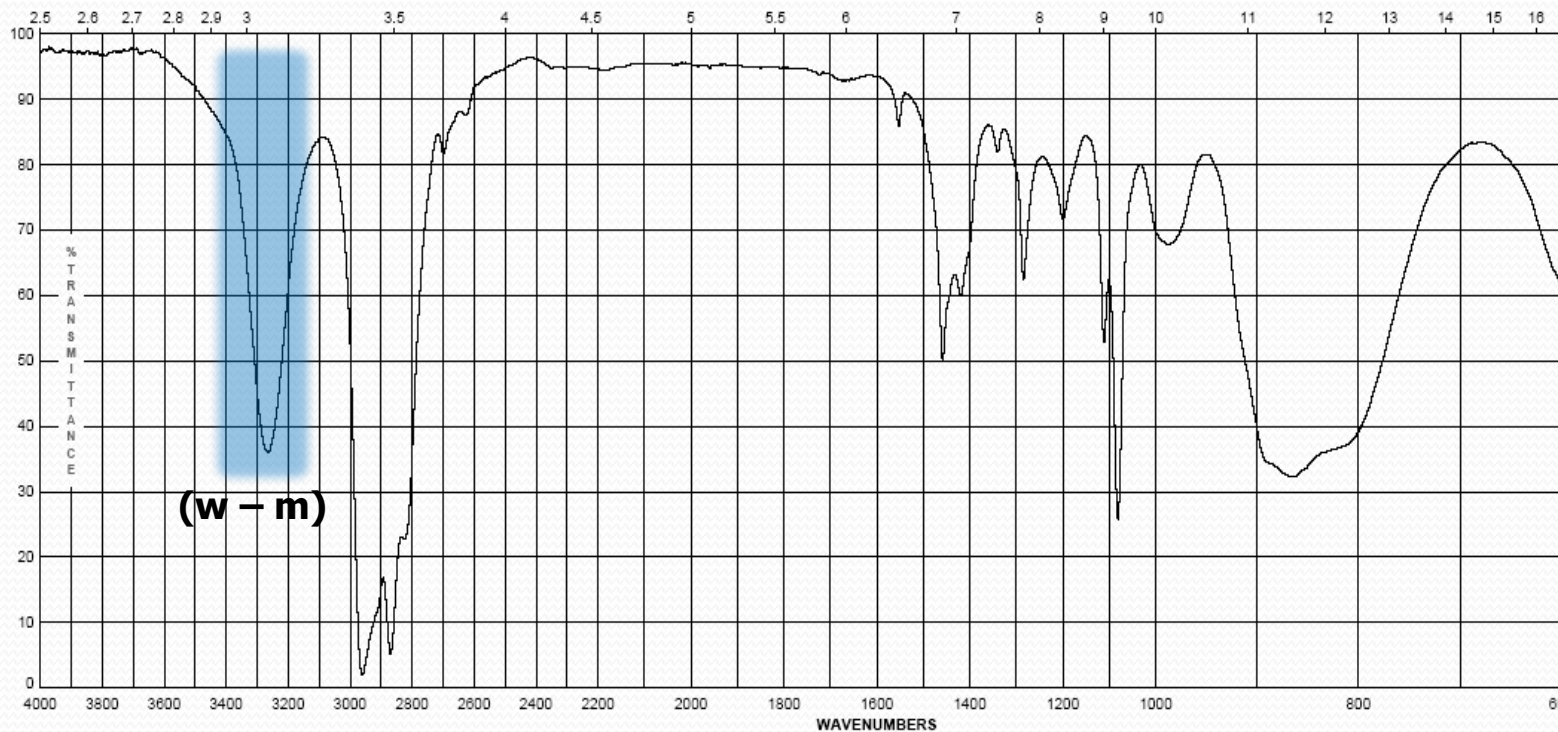
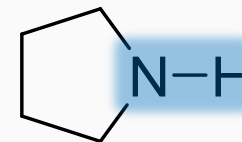


# Infrared Spectroscopy

## 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

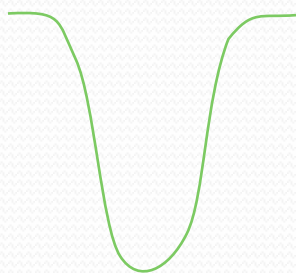
pyrrolidine



# Infrared Spectroscopy

## Pause and Review

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



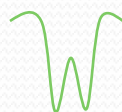
Broad U-shape peak  
**-O—H** bond



Sharp spike  
**-C≡C—H** bond

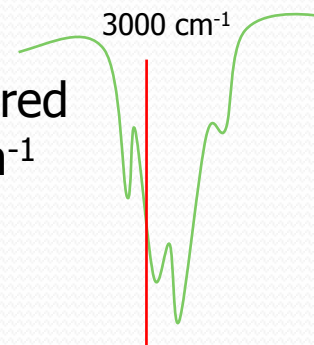


V-shape peak  
-N—H bond for  $2^\circ$   
amine ( **$\text{R}_2\text{N—H}$** )



W-shape peak  
-N—H bond for  $1^\circ$   
amine ( **$\text{RNH}_2$** )

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

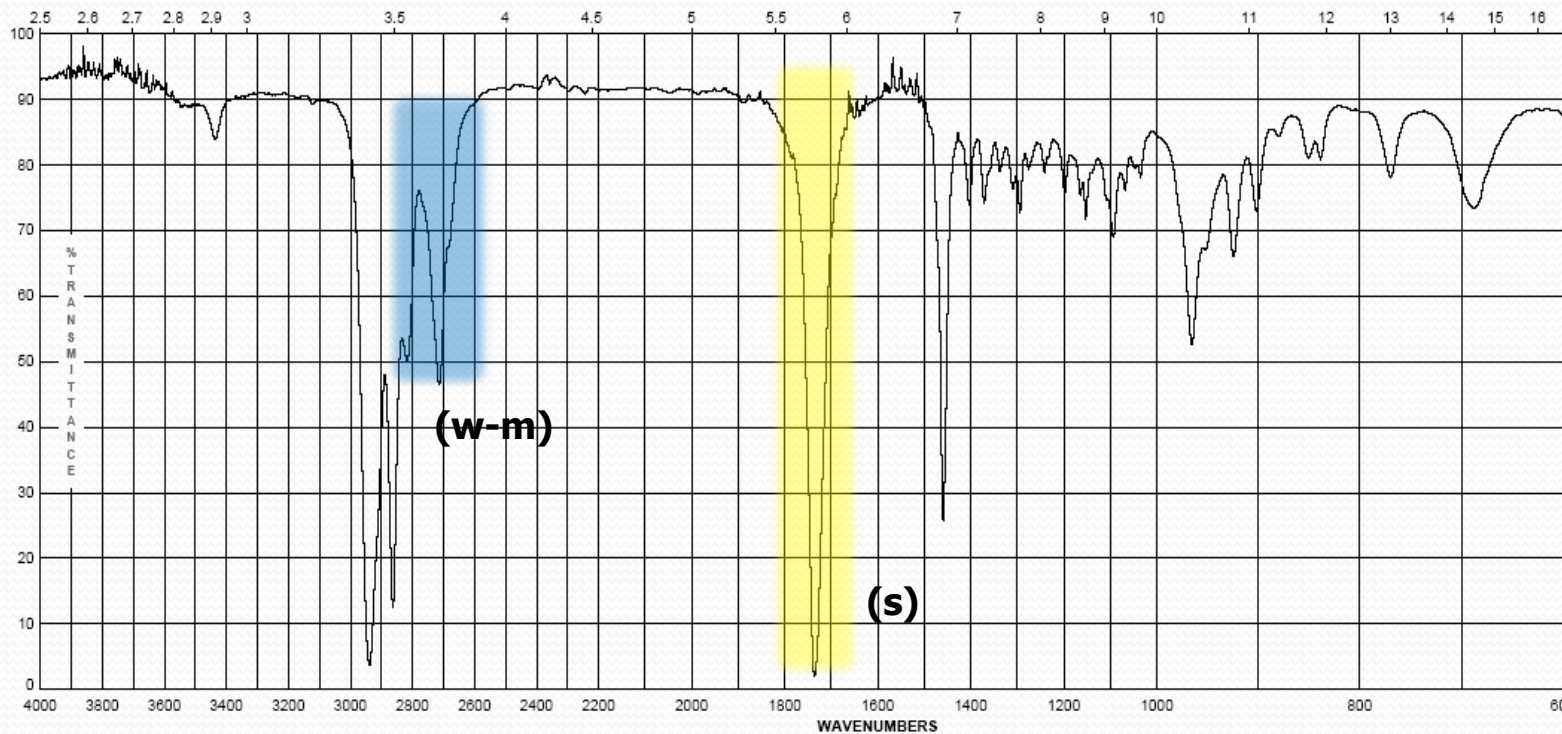
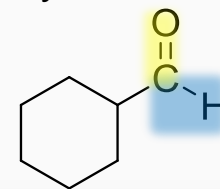


# Infrared Spectroscopy

## 10. Aldehydes

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

Cyclohexyl carboxaldehyde

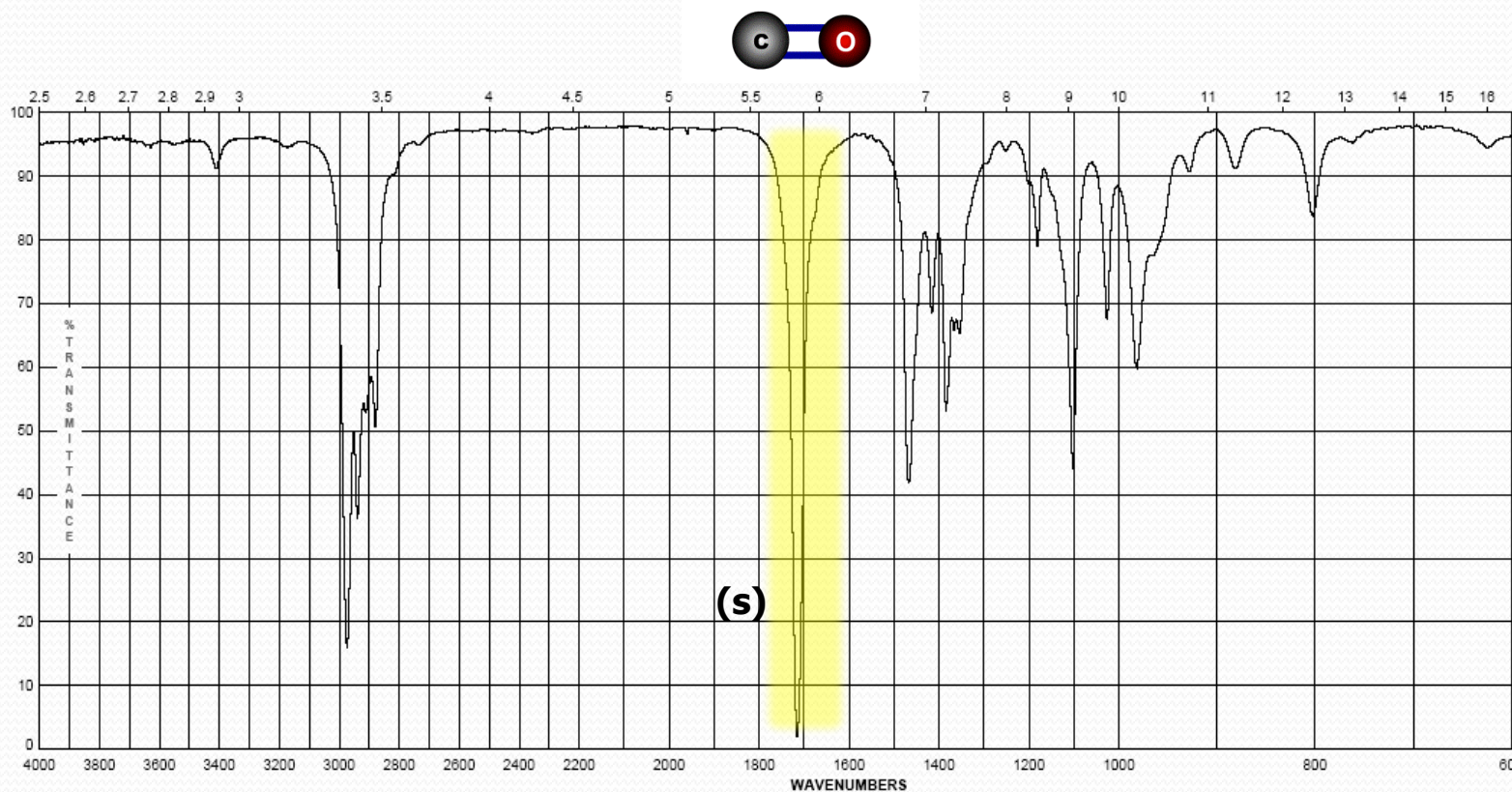
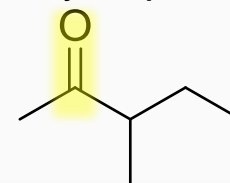


# Infrared Spectroscopy

## 11. Ketones

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

3-methyl-2-pentanone

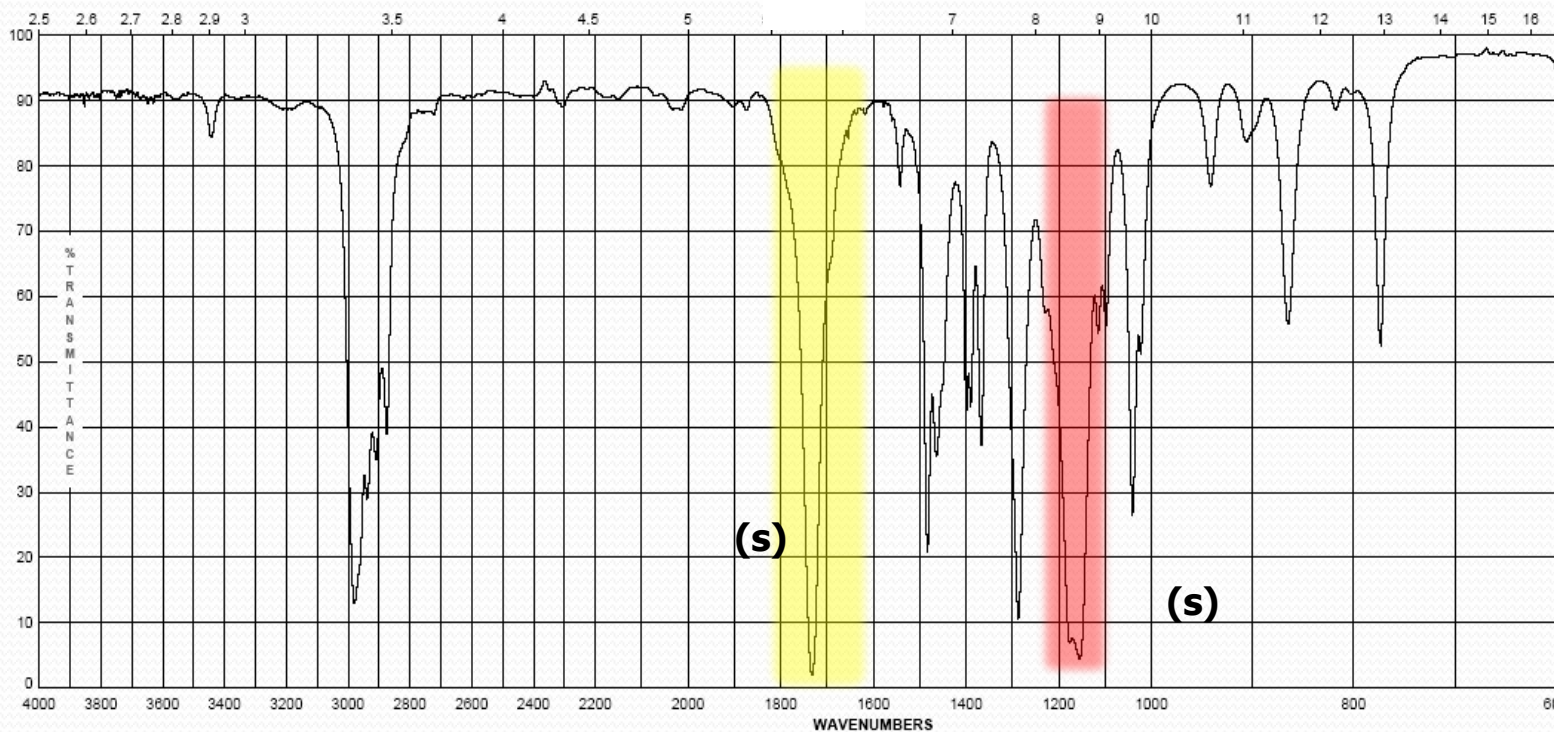
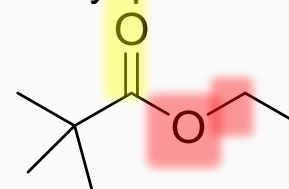


# Infrared Spectroscopy

## 12. Esters

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

Ethyl pivalate

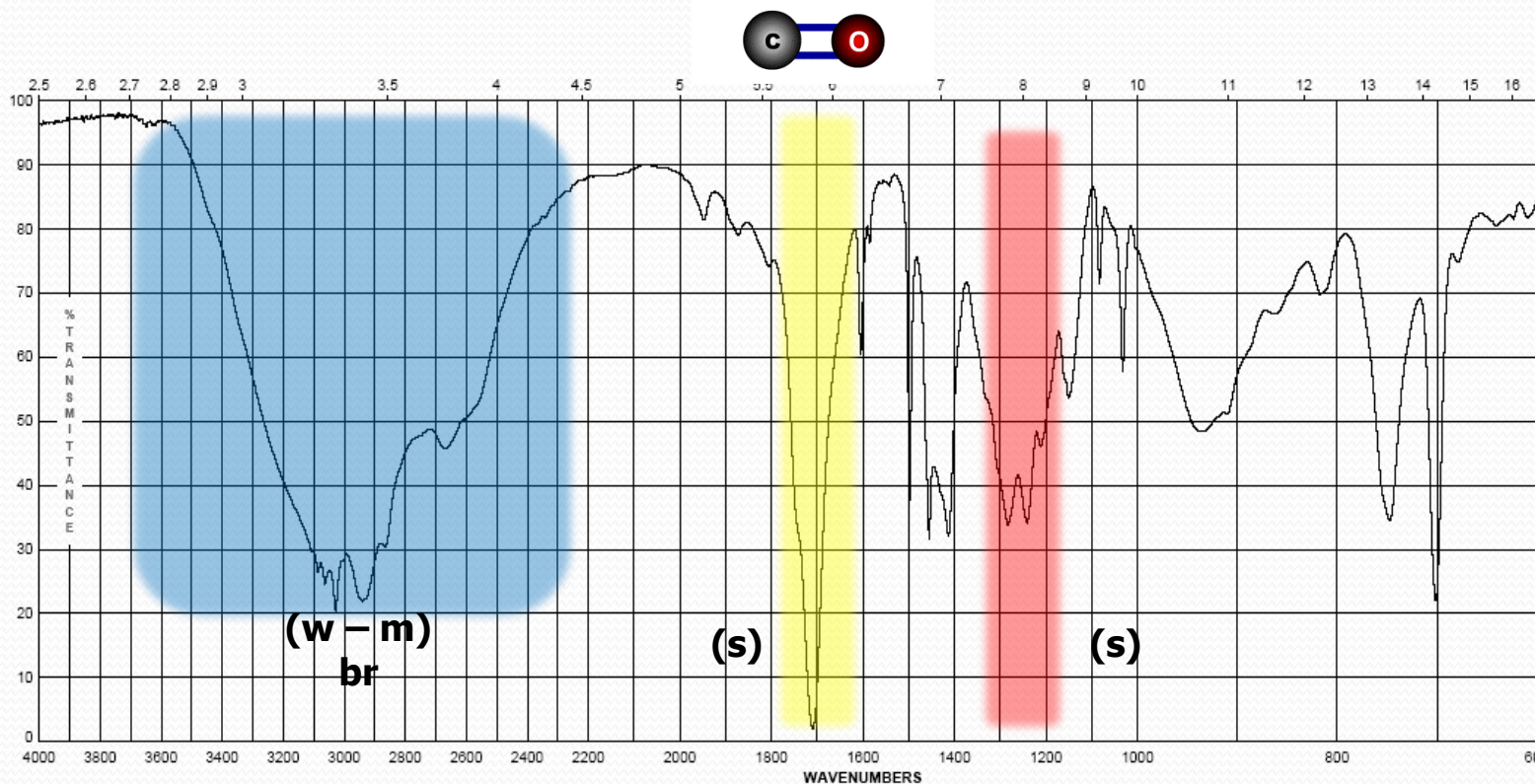
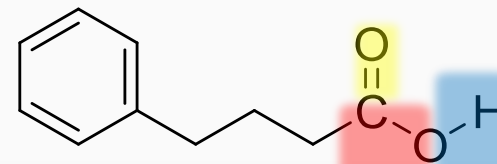


# Infrared Spectroscopy

## 13. Carboxylic Acids:

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

4-phenylbutyric acid



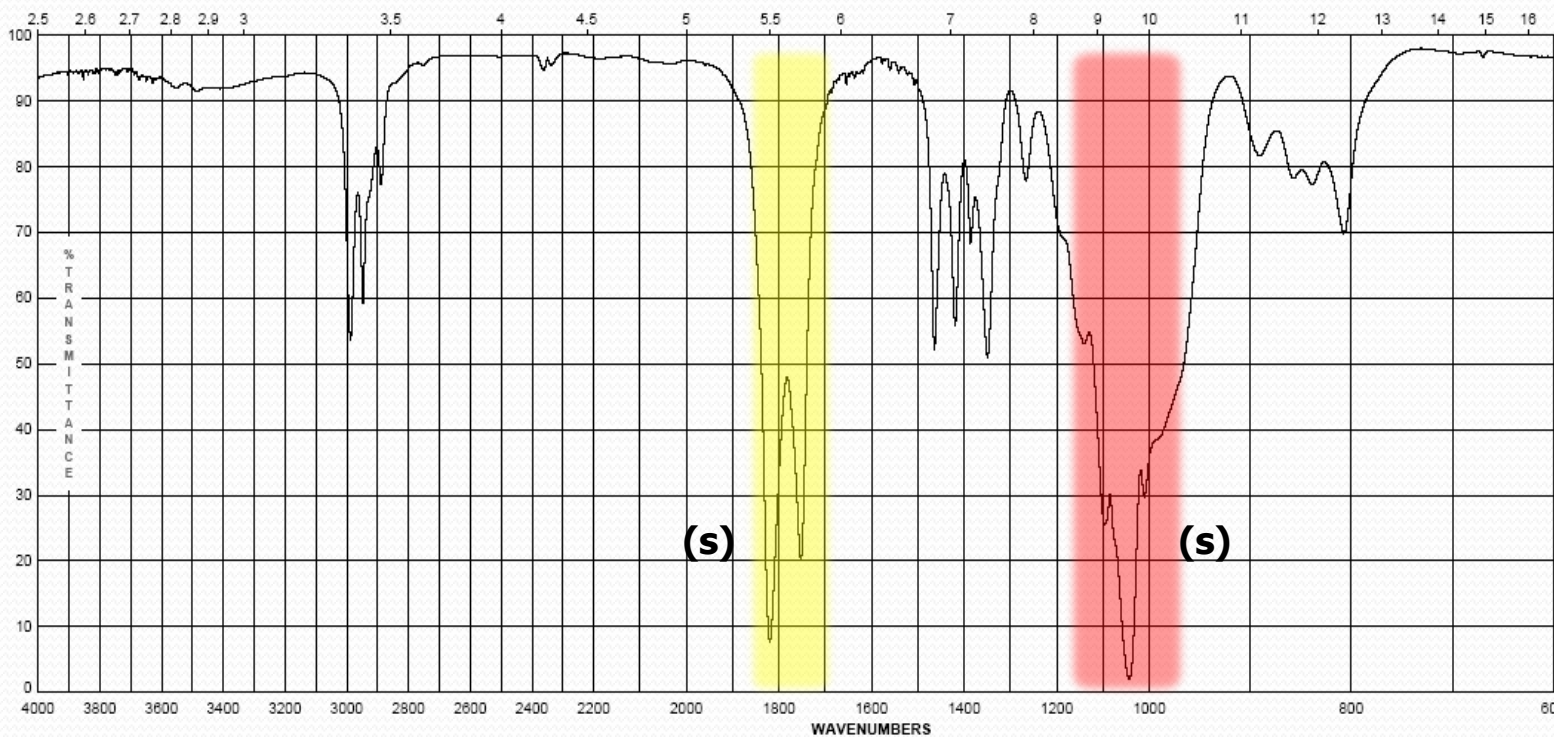
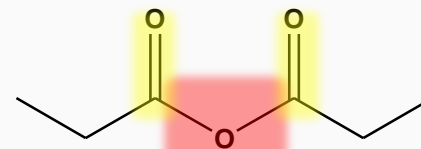


# Infrared Spectroscopy

## 14. Acid anhydrides

- Coupling of the anhydride through the ether oxygen splits the carbonyl band into two with a separation of  $70\text{ cm}^{-1}$
- 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

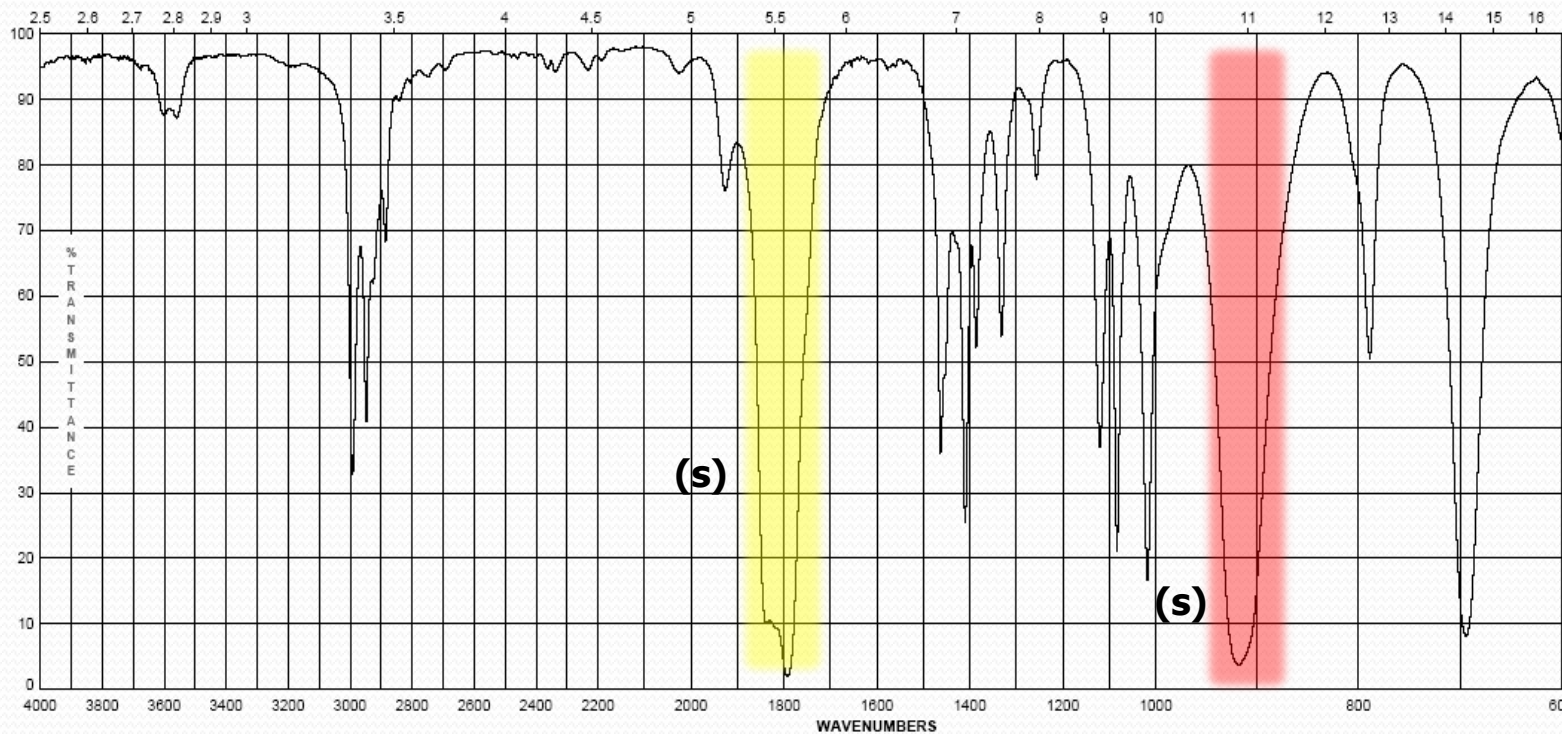
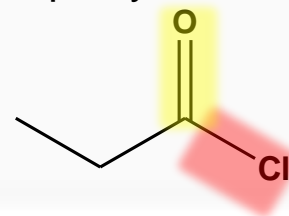


# Infrared Spectroscopy

## 15. Acid halides

- Clefited band at 1770-1820  $\text{cm}^{-1}$  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  $\text{cm}^{-1}$

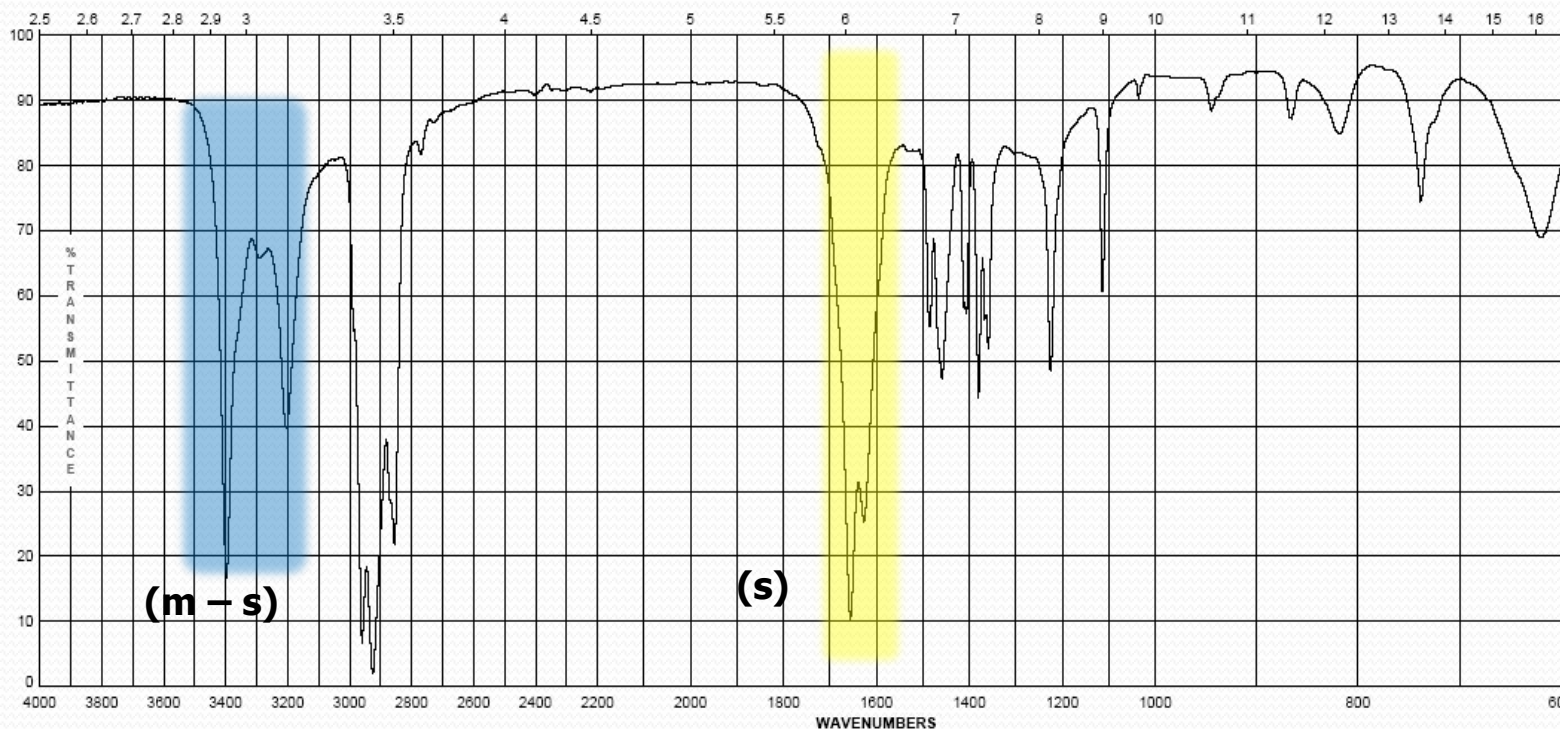
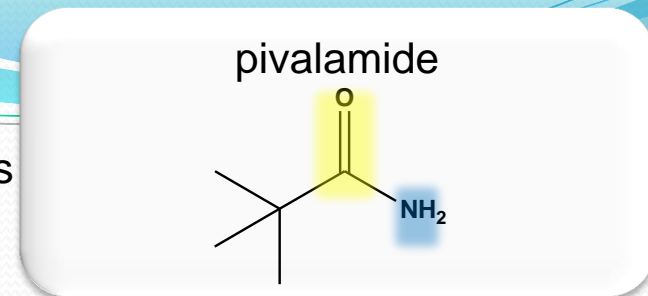
Propionyl chloride



# Infrared Spectroscopy

## 16. Amides

- Display features of amines and carbonyl compounds
- C=O stretch at 1640-1680  $\text{cm}^{-1}$
- If the amide is primary ( $-\text{NH}_2$ ) the N-H stretch occurs from 3200-3500  $\text{cm}^{-1}$  as a doublet
- If the amide is secondary ( $-\text{NHR}$ ) the N-H stretch occurs at 3200-3500  $\text{cm}^{-1}$  as a sharp singlet

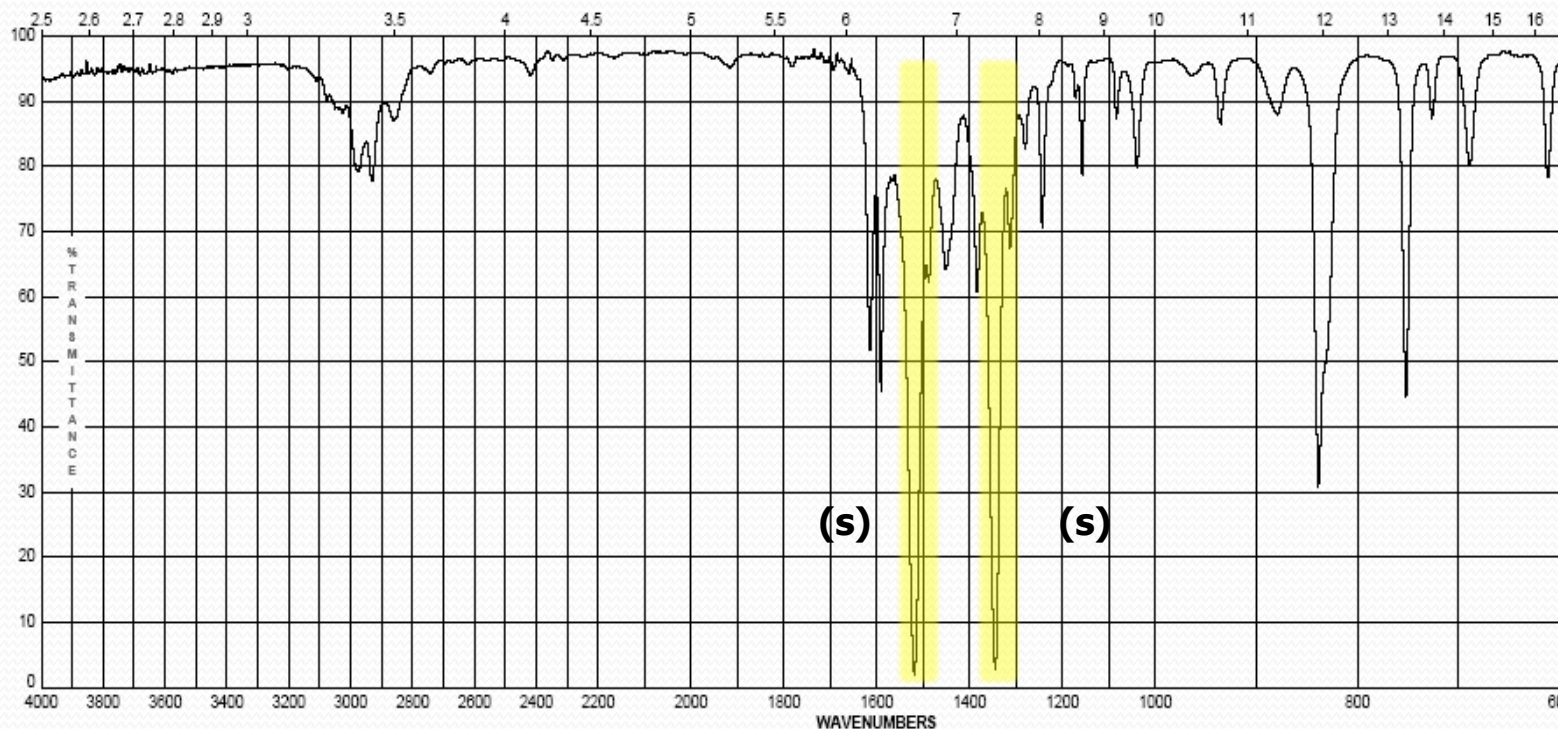
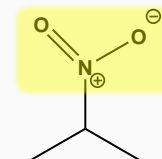


# Infrared Spectroscopy

## 17. Nitro group (-NO<sub>2</sub>)

- Proper Lewis structure gives a bond order of 1.5 from nitrogen to each oxygen
- Two bands are seen (symmetric and asymmetric) at 1300-1380 cm<sup>-1</sup> and 1500-1570 cm<sup>-1</sup>
- This group is a strong resonance withdrawing group and is itself vulnerable to resonance effects

2-nitropropane

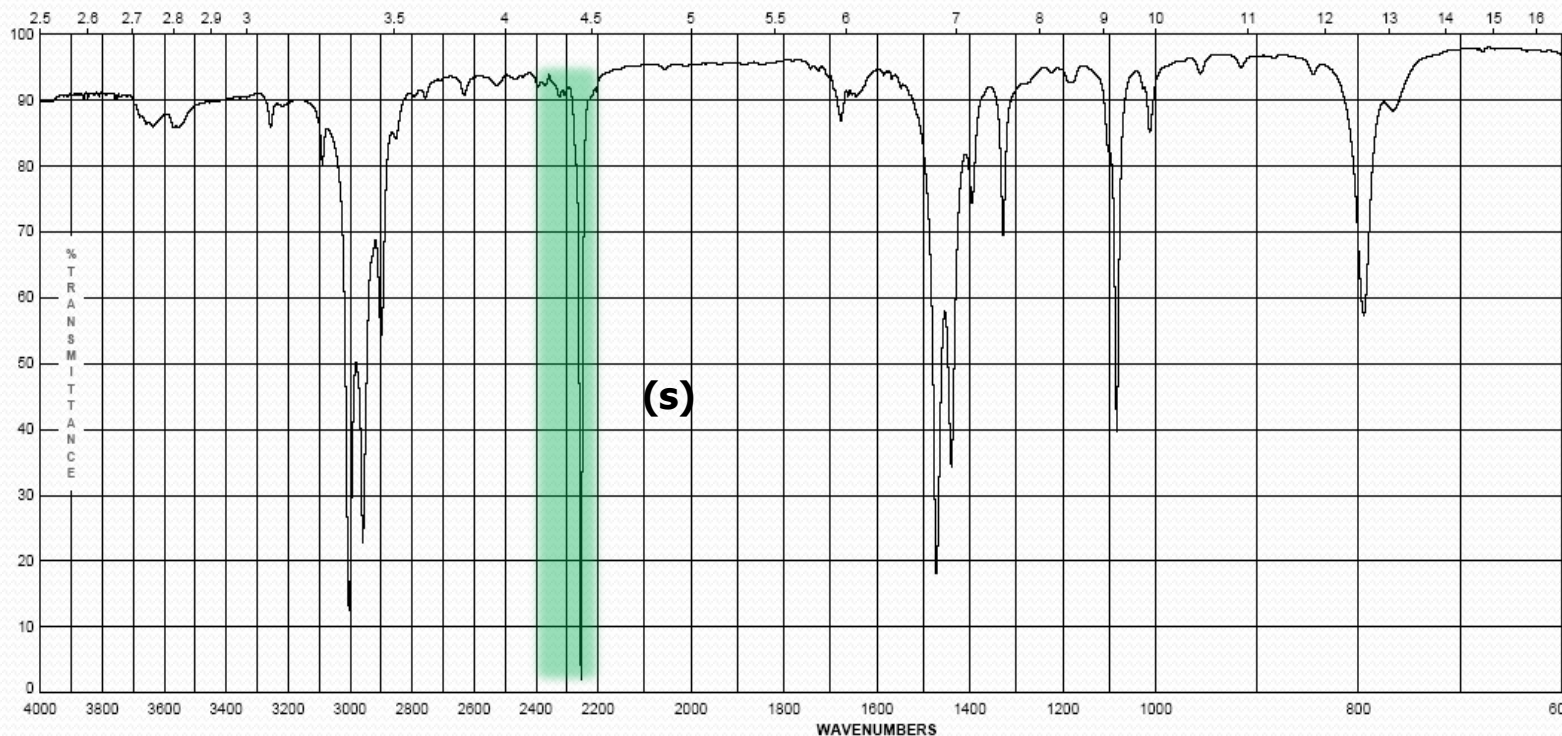
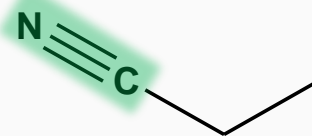


# Infrared Spectroscopy

## 18. Nitriles (the cyano- or $-\text{C}\equiv\text{N}$ group)

- Principle group is the carbon nitrogen triple bond at  $2100\text{-}2280\text{ cm}^{-1}$
- This peak is usually much more intense than that of the alkyne due to the electronegativity difference between carbon and nitrogen

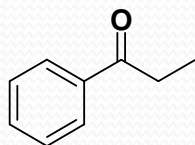
propionitrile



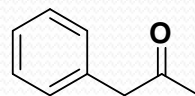
# Infrared Spectroscopy

## Effects on IR bands

- Conjugation** – by resonance, conjugation lowers the energy of a double or triple bond. The effect of this is readily observed in the IR spectrum:

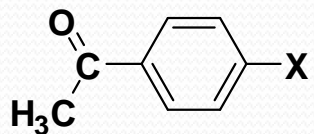


1684  $\text{cm}^{-1}$   
C=O

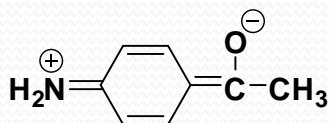


1715  $\text{cm}^{-1}$   
C=O

- Conjugation will lower the observed IR band for a carbonyl from 20-40  $\text{cm}^{-1}$  provided conjugation gives a strong resonance contributor

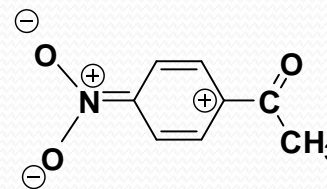


X =	NH <sub>2</sub>	CH <sub>3</sub>	Cl	NO <sub>2</sub>	
	1677	1687	1692	1700	$\text{cm}^{-1}$



**Strong resonance contributor**

vs.



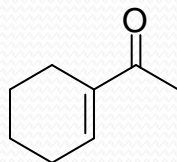
**Poor resonance contributor  
(cannot resonate with C=O)**

- Inductive effects are usually small, unless coupled with a resonance contributor (note  $-\text{CH}_3$  and  $-\text{Cl}$  above)

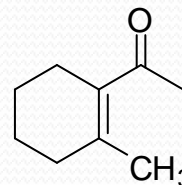
# Infrared Spectroscopy

## Effects on IR bands

2. **Steric effects** – usually not important in IR spectroscopy, unless they reduce the strength of a bond (usually  $\pi$ ) by interfering with proper orbital overlap:



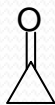
C=O:  $1686\text{ cm}^{-1}$



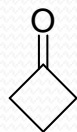
C=O:  $1693\text{ cm}^{-1}$

- Here the methyl group in the structure at the right causes the carbonyl group to be slightly out of plane, interfering with resonance

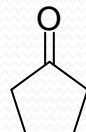
3. **Strain effects** – changes in bond angle forced by the constraints of a ring will cause a slight change in hybridization, and therefore, bond strength



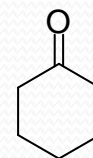
$1815\text{ cm}^{-1}$



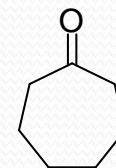
$1775\text{ cm}^{-1}$



$1750\text{ cm}^{-1}$



$1715\text{ cm}^{-1}$



$1705\text{ cm}^{-1}$

- As bond angle decreases, carbon becomes more electronegative, as well as less  $sp^2$  hybridized (bond angle  $< 120^\circ$ )

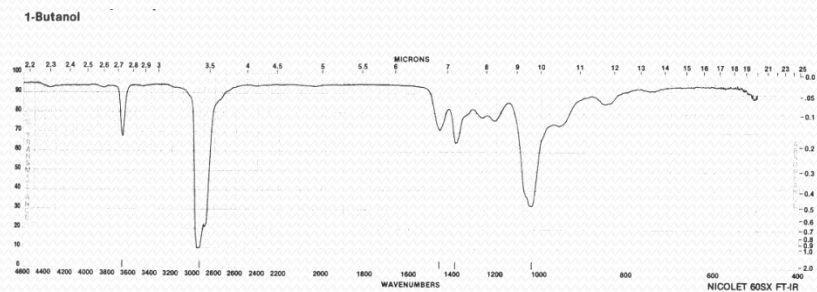
# Infrared Spectroscopy

## Effects on IR bands

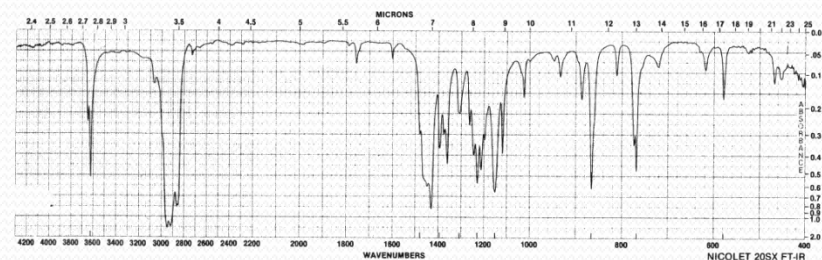
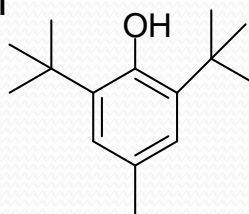
### 4. Hydrogen bonding

- Hydrogen bonding causes a broadening in the band due to the creation of a continuum of bond energies associated with it
- In the solution phase these effects are readily apparent; in the gas phase where these effects disappear or in lieu of steric effects, the band appears as sharp as all other IR bands:

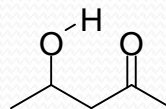
Gas phase spectrum of 1-butanol



Steric hindrance to H-bonding in a di-*tert*-butylphenol



- H-bonding can interact with other functional groups to lower frequencies



C=O; 1701 cm<sup>-1</sup>



# IR ABSORPTION FREQUENCY REGION

Major Functional Group	Absorption Frequency Region			
O-H	3650-3590			
N-H	3500-3300	1650-1590	900-650	
=CH-H	3100-3070	1420-1410	900-880	
=C-H	3100-3000	2000-1600		
C-H	2900-2700	1440-1320		
=-CH <sub>3</sub>	2880-2860	2970-2950	1380-1370	1470-1430
O-H	2700-2500	1320-1210	950-900	
C≡C	2140-2100			
C=O	1750-1700			
C=C	1600-1500			
C-N	1340-1250			
C-O-C	1200-1180			
-C-H	770-730			

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Gary M. Lampman, and  
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EM%202010%20IR%20Spectroscopy.pptx](http://chemistry.bd.psu.edu/justik/CHEM%202010/CH<br/>EM%202010%20IR%20Spectroscopy.pptx)**