

Structure Determination

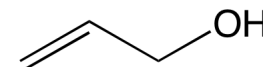
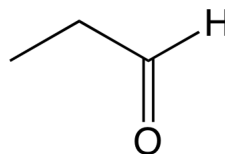
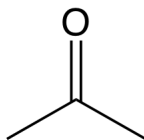
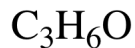
How to determine what compound that you have?

One way to determine compound is to get an elemental analysis

-basically burn the compound to determine %C, %H, %O, etc.
from these percentages can determine the molecular formula

Still need to determine structure from molecular formula

We have learned various isomers can result from a given molecular formula

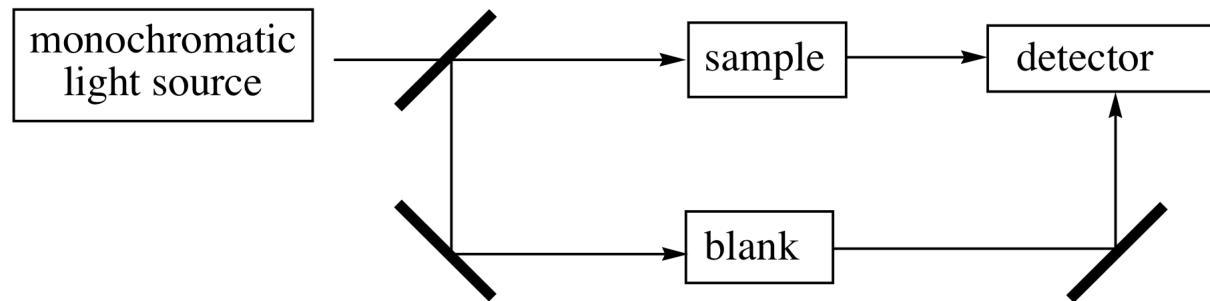


Structure Determination

Need methods to distinguish between possible structures

A nondestructive way is to use absorption spectroscopy

In a simplified picture:



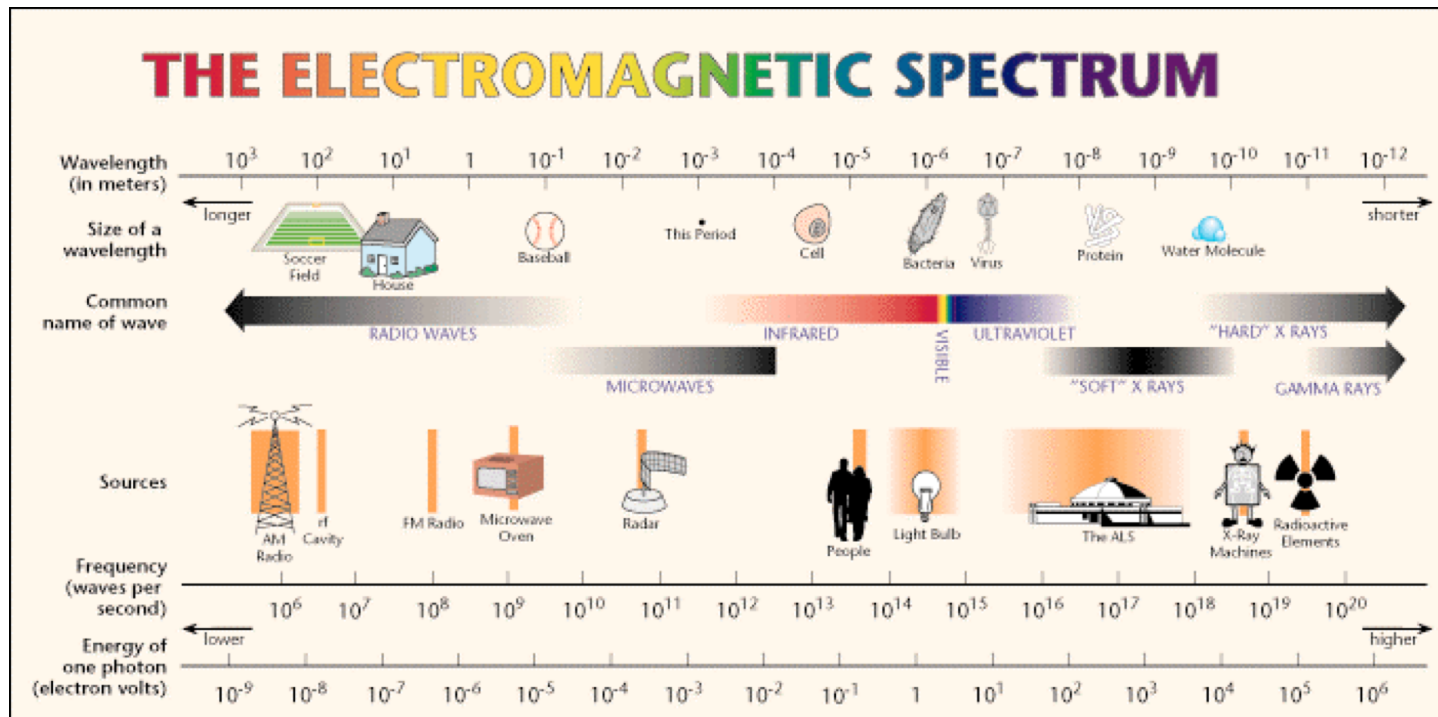
The ability of the sample to absorb incident radiation is measured by the difference in absorbance at the detector versus the blank

Electromagnetic Spectrum

All light travels at a constant speed

The difference is the wavelength of the light
(which also determines the energy of the light)

$$E = h\nu = (hc) / \lambda$$



Infrared Region

Wavelength of infrared radiation is $\sim 800 \text{ cm}^{-1}$ to 4000 cm^{-1} wavenumbers
(wavenumbers correspond to number of wavelengths of light in 1 cm)
-common descriptor for IR frequencies by organic chemists

As the wavenumber becomes larger the energy increases

The energy level of infrared light corresponds to the energy required
to cause molecular vibrations

Depending upon what type of bond is present determines
the exact energy required to cause the vibration

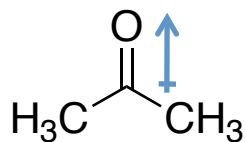
The energy of light absorbed therefore indicates what functional group is present

Bond Vibration

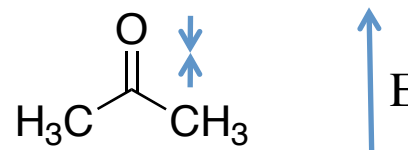
The energy of the infrared light can interact with the resonant vibrational frequency of the bond

Since different bonds have different energies, they require different energy to cause vibration

consider acetone



The carbonyl has a strong dipole



When electric field aligns with dipole, bond shortens

The absorption of the infrared light thus changes the dipole for this bond as it vibrates

Active versus Inactive

IR only causes a vibration if there is a change in dipole during vibration

Therefore symmetric bonds are inactive

$\text{CH}_3\text{-CH}_3$ the carbon-carbon bond of ethane will not observe an IR stretch

Or any other symmetric bond

An IR “active” bond is therefore a bond that changes dipole during vibration,
While an IR “inactive” bond is a symmetric bond that doesn’t change dipole during vibration

Number of Vibrations

The number of possible vibrations for a given molecule is determined by the number of atoms present

For nonlinear molecules obtain $3N-6$ vibrations
(N equals number of atoms present)
 $3N-5$ vibrations for linear molecule

For example consider acetone again ($C_3H_6O_1$)
Acetone has 10 atoms and is nonlinear
Therefore expect $3(10)-6 = 24$ vibrations

Intensity of Absorbance

Intensity of light absorbed by a molecule is related to the dipole of the bond

The greater the dipole, the greater the absorbance intensity

C-O bond stretches are therefore more intense than C-C stretches

Realize the intensity of absorbance is not related to the wavenumber
The wavenumber is related to the force constant for the bond vibrating
(the stiffness of the bond)

Factors to be considered in an IR spectrum

1) Position of absorbance (wavenumber)
Energy required for absorbance

2) Intensity of absorbance
Related to the dipole of the bond

3) Shape of absorbance
(broad or sharp peaks)
Tells information about the type of bond

Specific Functional Groups

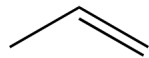
As mentioned specific functional groups have characteristic absorbance frequencies

Consider carbon-carbon bonds

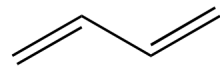
	wavenumber
C—C	~1200 cm ⁻¹
C=C	~1660 cm ⁻¹
C≡C	~2200 cm ⁻¹

As the number of bonds increases between two atoms, the stiffness of the bond increases which results in a harder bond to stretch

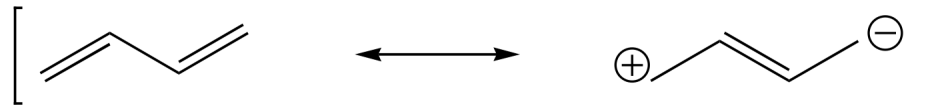
Conjugation lowers the stretching frequency
(RESONANCE!!!)



1640 - 1680 cm⁻¹



1620 - 1640 cm⁻¹



C-H Bond Stretching

As the %s character increases in a bond, the bond becomes stiffer
(already saw that sp hybridized C-C bonds are stiffer than sp³ hybridized C-C bonds)

Same is true for carbon-hydrogen bonds

sp ³ hybridized	2800-3000 cm ⁻¹
sp ² hybridized	3000-3100 cm ⁻¹
sp hybridized	~3300 cm ⁻¹

Key point: only sp³ hybridized C-H bond stretches are below 3000 cm⁻¹

Alcohols and Amines

Both O-H and N-H bonds are “stiff” bonds

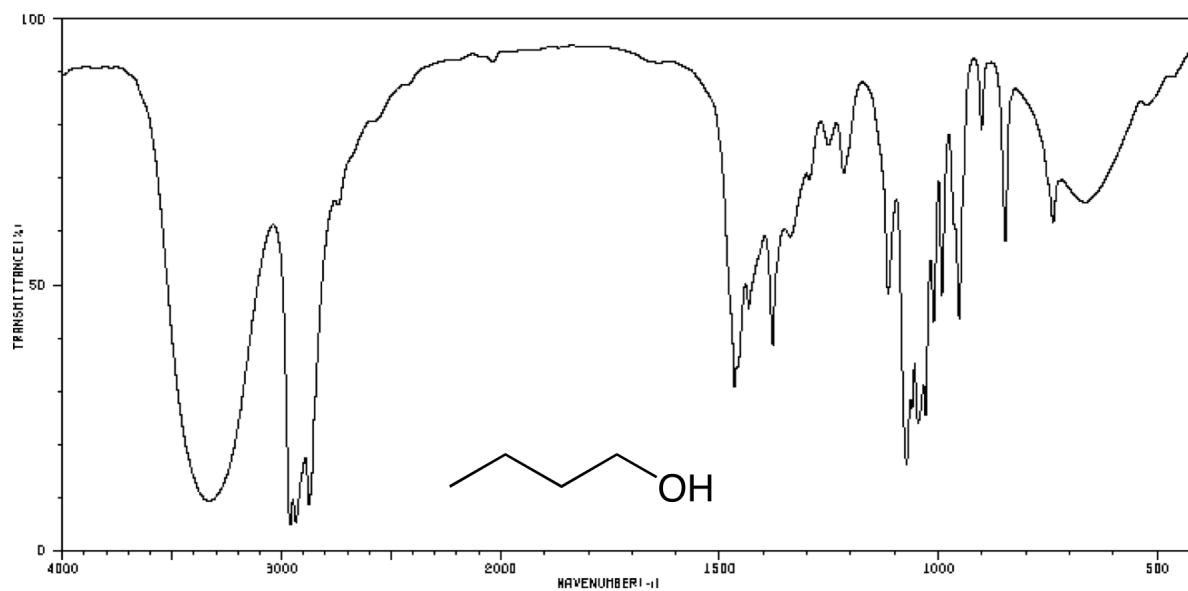
Therefore they have a higher vibrational frequencies

Alcohol	RO-H	$\sim 3300 \text{ cm}^{-1}$
Acid	RCO ₂ -H	$\sim 3000 \text{ cm}^{-1}$
Amine	RN-H	$\sim 3300 \text{ cm}^{-1}$

Both N-H and O-H bonds are involved in hydrogen bonding

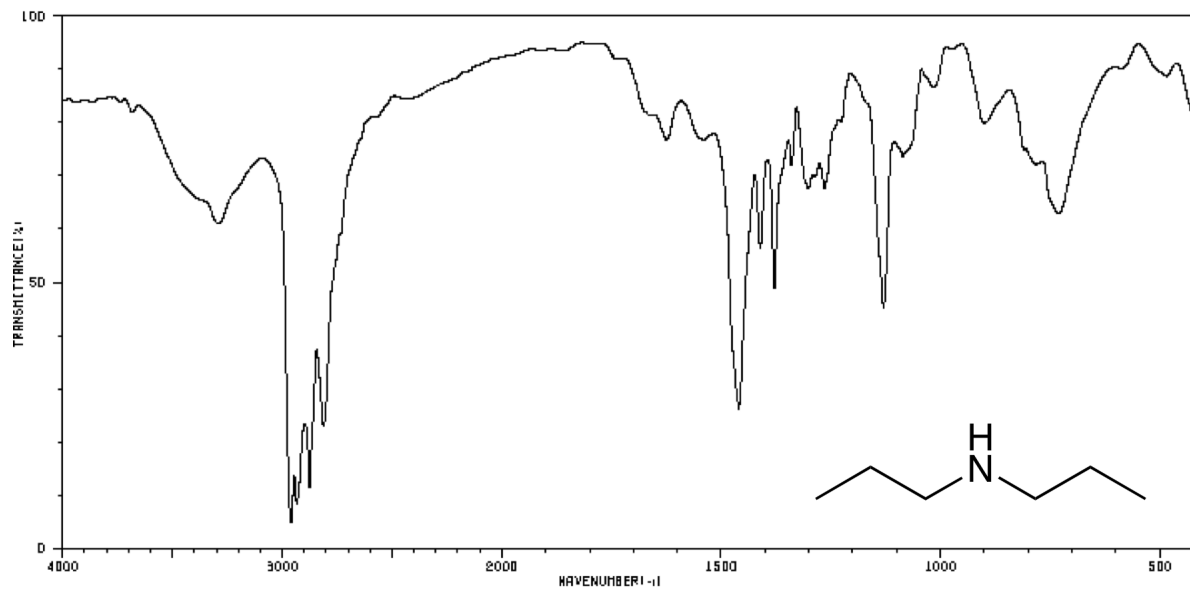
Due to this hydrogen bonding, each individual O-H bond will have a slightly different vibrational frequency

Therefore this causes the appearance of a broad peak



Amine peaks show the same broad features
(N-H bonds are also involved in hydrogen bonding)

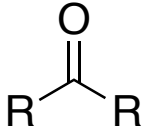
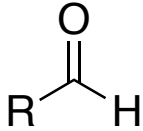
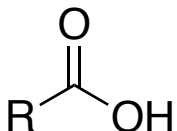
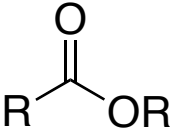
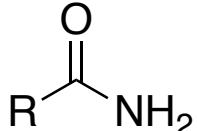
Difference is that often observe a sharp peak in the midst of the broad peak
(due to one conformation of hydrogen bonding having a preferential formation)



Carbonyl Compounds

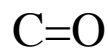
One of the best diagnostic features of IR is for carbonyl compounds

Remember there are many types of carbonyl groups
(each can be differentiated only with an IR spectrum)

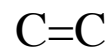
					
	ketone	aldehyde	acid	ester	amide
ν (cm ⁻¹)	1715	1720	1715	1735	1660

Carbonyl Compounds

Due to the large dipole of carbonyl bonds, all carbonyl groups display strong, relatively sharp peaks



large dipole



small dipole

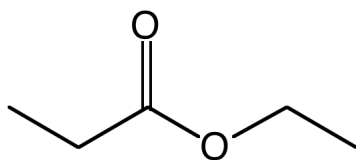
Most carbonyl stretching frequencies are centered around 1710-1720 cm^{-1} and can be distinguished easily from alkene stretches (\sim low 1600's cm^{-1}) due to both the higher frequency and the more intense absorbance

Carbonyl Compounds

Some carbonyl stretching frequencies are noticeably different than 1710-1720 cm^{-1}

Esters are one type

Esters have an appreciably higher stretching frequency



1738 cm^{-1}

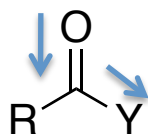
Higher frequency means a “stiffer” bond

Carbonyl Compounds

What causes a “stiffer” carbonyl bond?

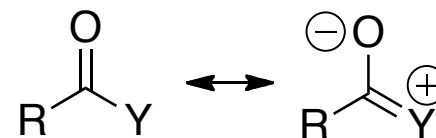
Substituents on the carbonyl carbon can affect the C=O bond stretch in two ways:

Inductive effect



More electronegative Y pulls electron density from carbon, which then pulls electrons from oxygen to create a stiffer bond

Resonance effect



Lone pair of electrons on Y atom can resonate to create a C=Y double bond and thus a C-O single bond – therefore a weaker C-O bond

The question is which effect is larger

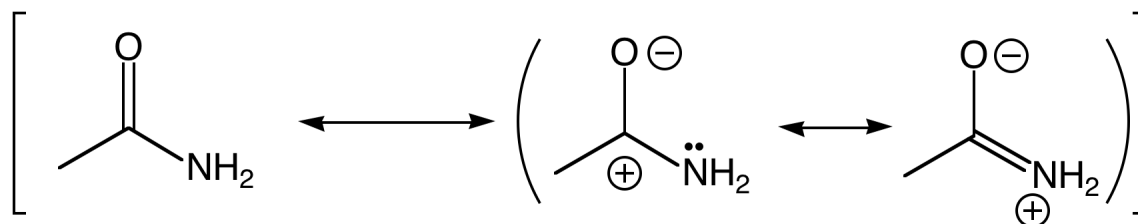
Generally the greater difference in electronegativity between C and Y causes inductive effect to become dominant

Y	ν (cm ⁻¹)	Stronger effect
Cl	1810	inductive
OR	1735	inductive
NH ₂	1660	resonance

Carbonyl Compounds

Amide group lowers the frequency due to the resonance effect

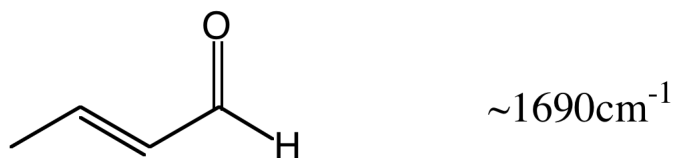
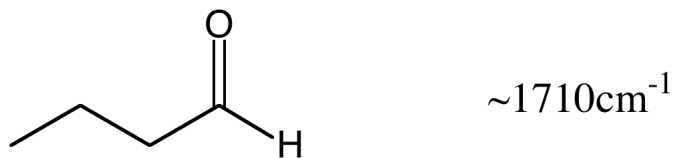
If a nitrogen is attached to the carbonyl carbon then the lone pair of electrons on nitrogen can stabilize the resonance form



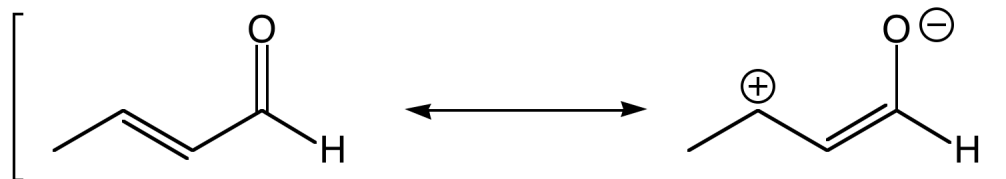
Due to this lower energy resonance form the carbonyl carbon-oxygen bond is less “stiff”, therefore the stretching frequency is LOWER

Carbonyl Compounds

Resonance with extra conjugation will also lower the stretching frequency for a carbonyl



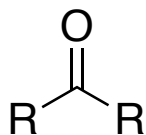
Resonance allows delocalization of π electrons,
therefore carbonyl is less “stiff”



Other Diagnostic Peaks for Carbonyl Compounds

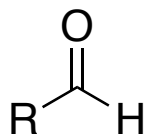
As already observed many carbonyl groups are $\sim 1710\text{-}1720\text{ cm}^{-1}$

How to distinguish?



Ketone

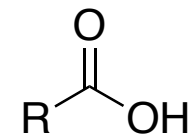
$\sim 1715\text{ cm}^{-1}$ for carbonyl



Aldehyde

observe aldehyde C-H stretch

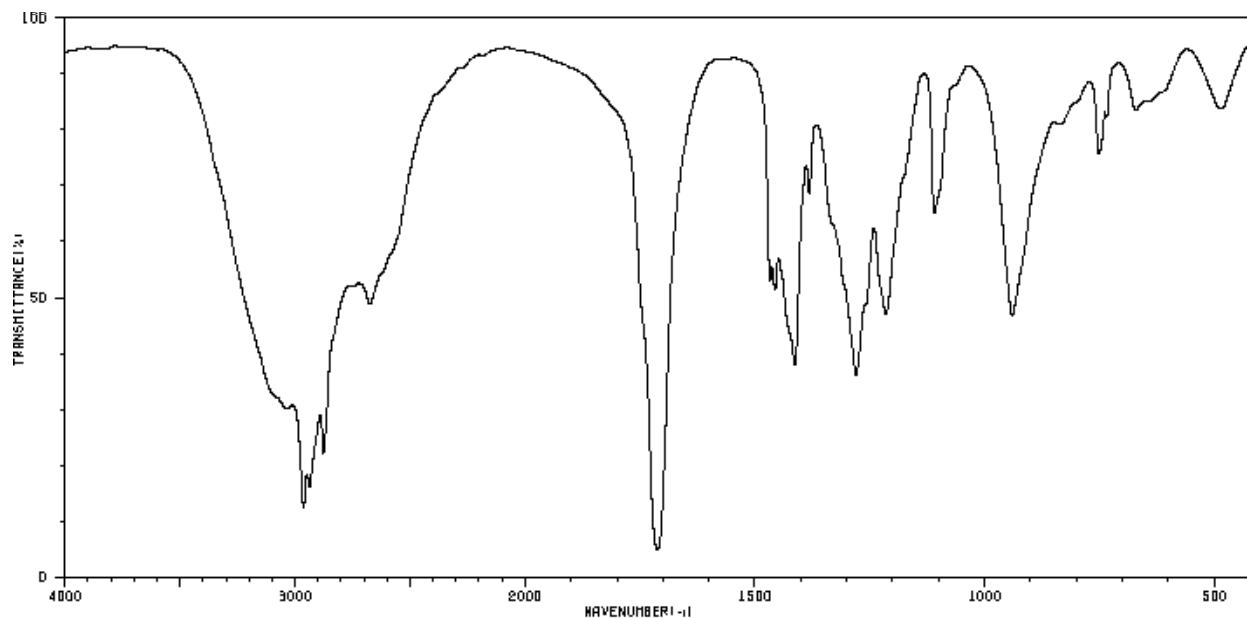
Two peaks at ~ 2700 and $\sim 2800\text{ cm}^{-1}$



Acid

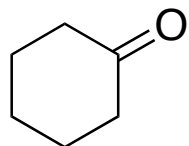
observe broad O-H stretch

$\sim 3000\text{ cm}^{-1}$

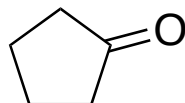


Small Rings

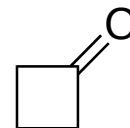
Small rings also have a shift in vibrational frequency to higher energy,
Therefore 5,4, or 3 membered rings have the carbonyl stretching frequency shifted



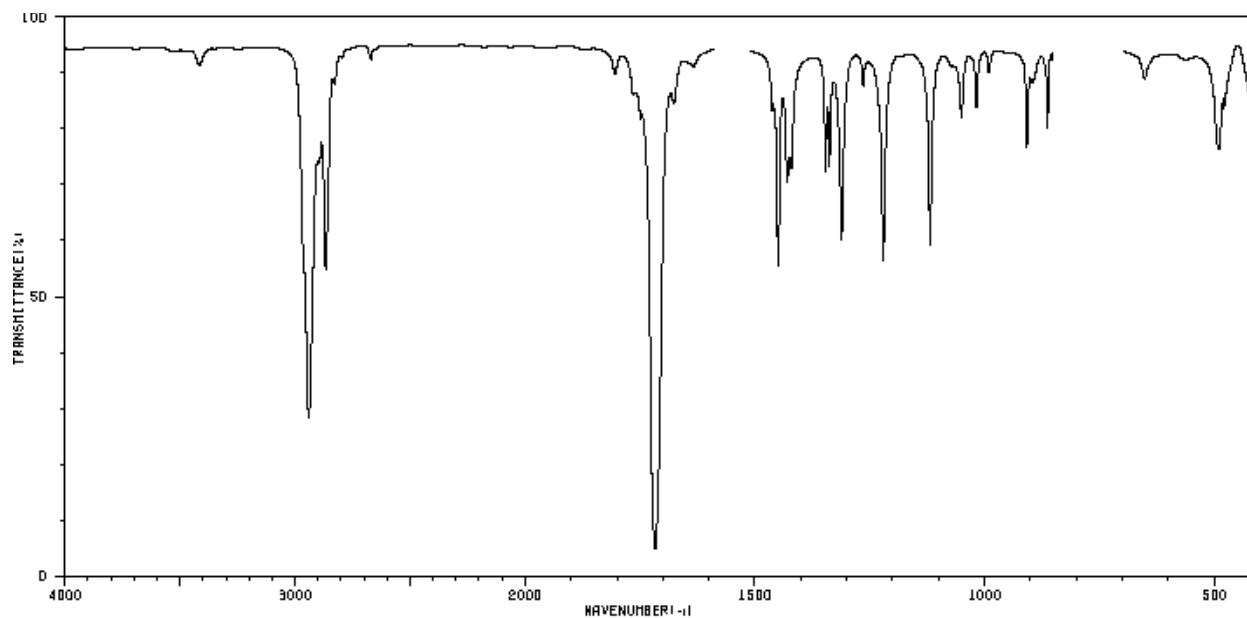
1715 cm^{-1}



1745 cm^{-1}



1785 cm^{-1}



Angle strain in these rings causes the carbonyl group to have more electron density,
Therefore a “stiffer” bond

C-N Bonds

C-N bonds are in similar regions to C-C bonds

	wavenumber
C—N	1200
C=N	1600
C≡N	>2200

The intensity of absorbance, however is higher due to greater dipole of C-N bond compared to C-C

Fingerprint Region

The so-called “fingerprint” region is below $\sim 1500\text{ cm}^{-1}$

Vibrations in this region are often complex and hard to assign to a specific functional group of the molecule

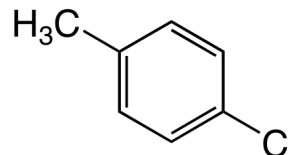
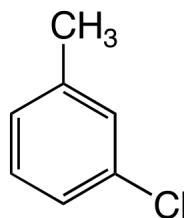
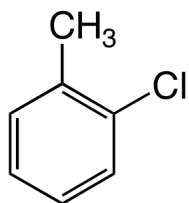
-a given molecule, though, has a **DISTINCT** pattern in this region (reason for this region being called the “fingerprint” region)

One common pattern – differentiating substitution isomers

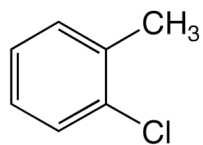
One example:

Aromatic isomers

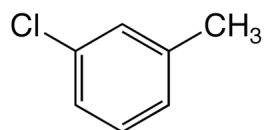
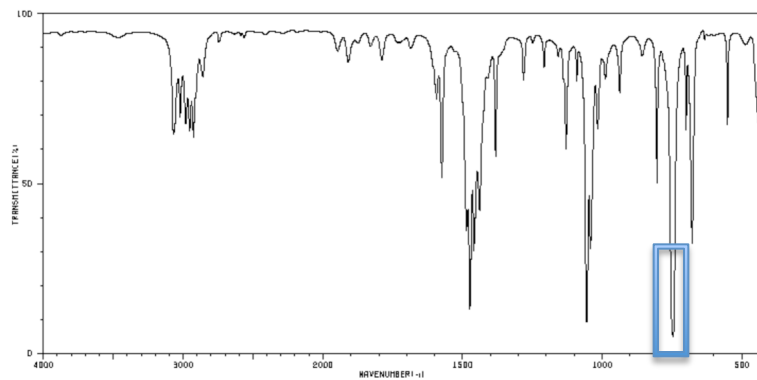
Ortho	one peak	$770\text{-}735\text{ cm}^{-1}$
Meta	three peaks	$900\text{-}860, 810\text{-}750, 725\text{-}680\text{ cm}^{-1}$
Para	one peak	$860\text{-}800\text{ cm}^{-1}$



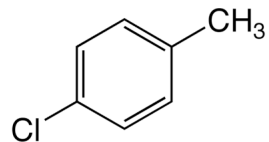
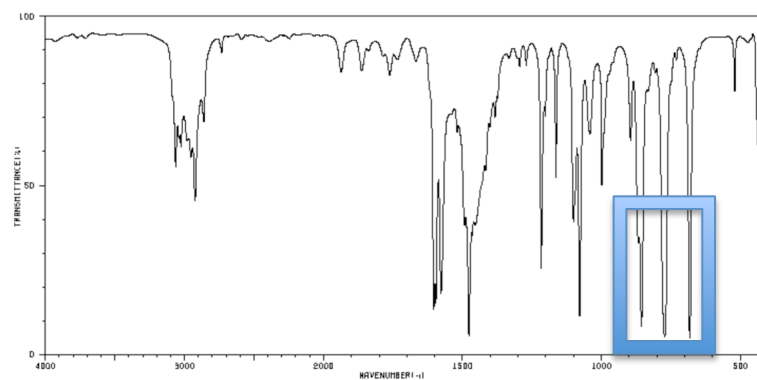
Fingerprint Region



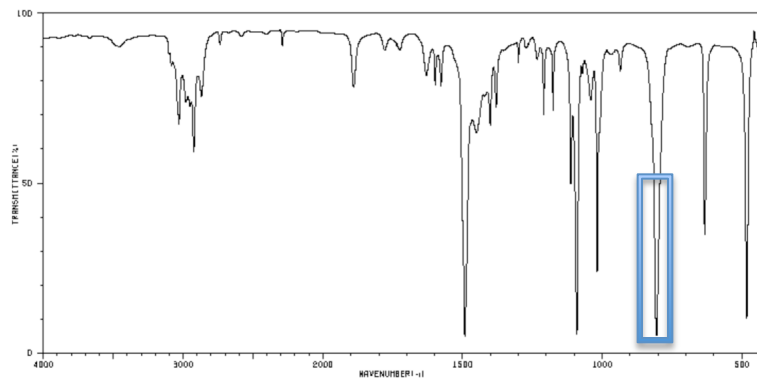
strong peak 747 cm⁻¹



strong peaks 866, 773, 682 cm⁻¹



strong peak 806 cm⁻¹



Overtone and Combination Bands

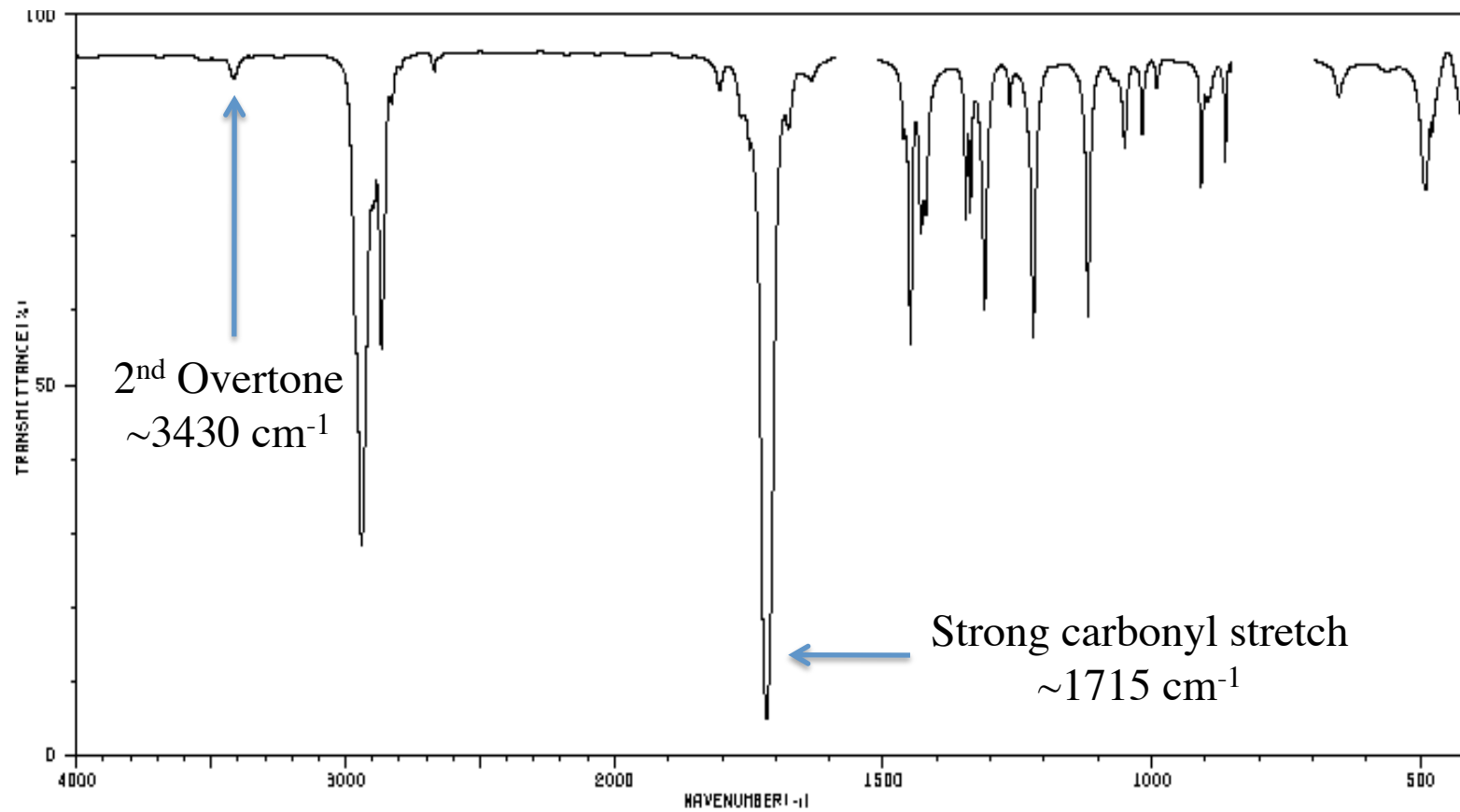
Overtone

-when assigning IR spectra be careful to note overtone bands
(an intense peak will display a smaller peak at a multiple [2x, 3x, etc.] of that peak)

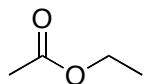
Combination Bands

Two or more vibrations can couple to cause a vibration at a different position
(vibrations must be “coupled” to observe these combination bands)

Overtone Bands

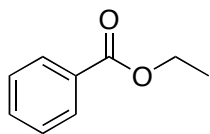
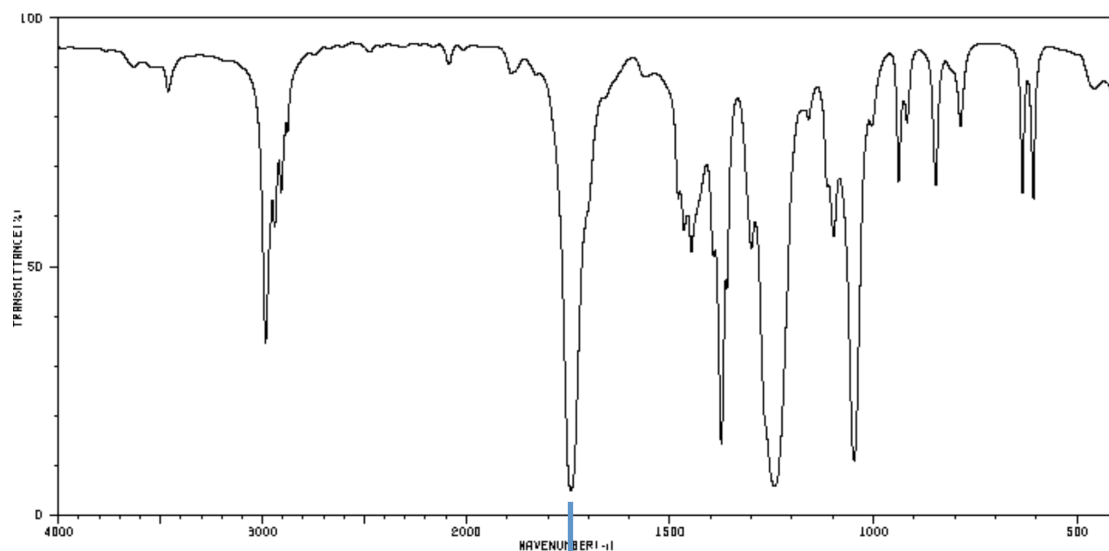


Predicted IR Differences



ester carbonyl

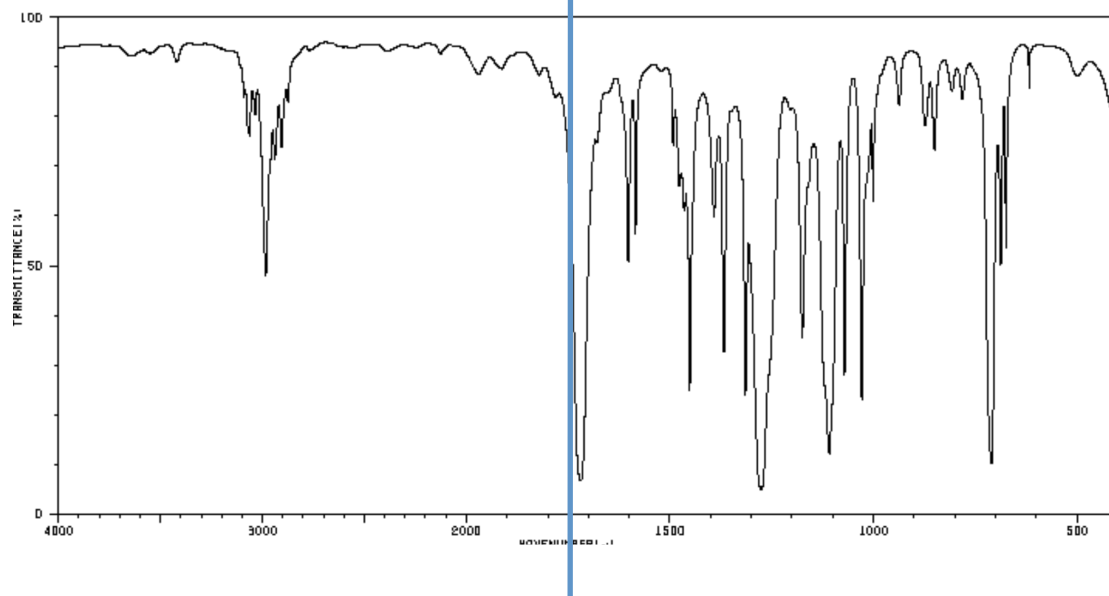
sp^3 C-H bonds

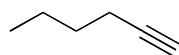


conjugated ester carbonyl

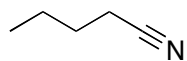
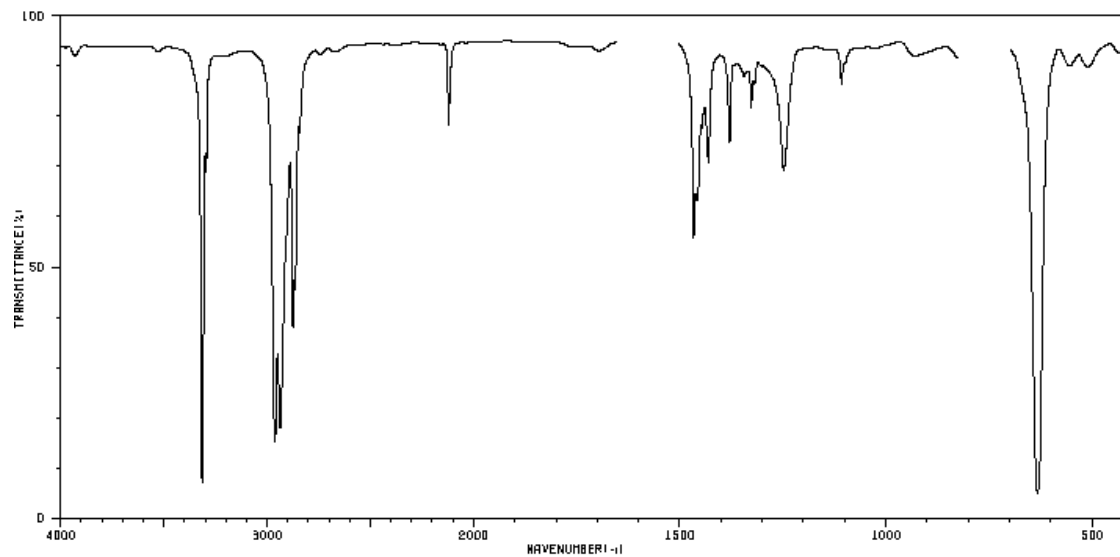
sp^3 and sp^2 C-H bonds

sp^2 carbons

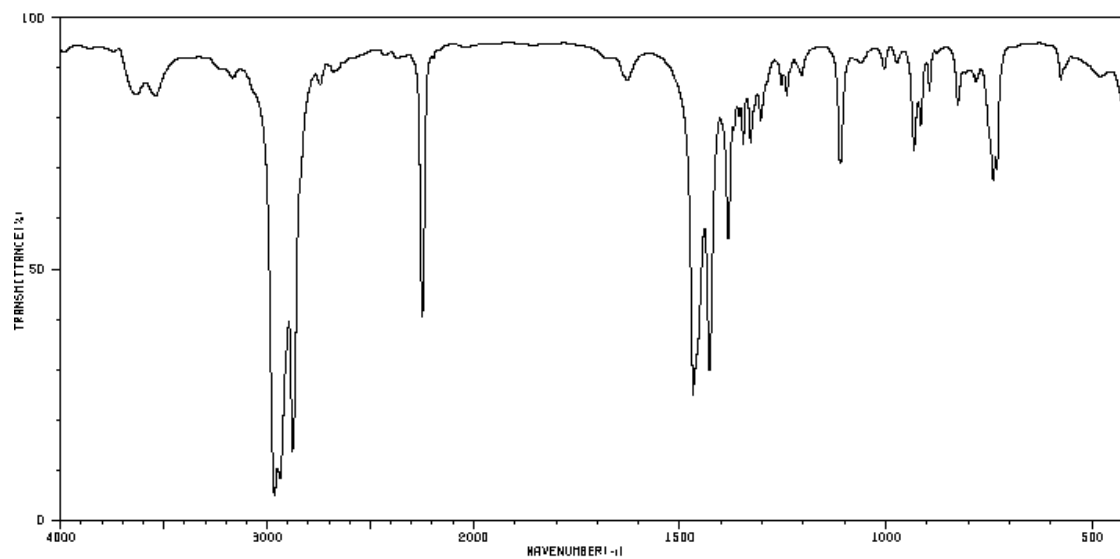




weak C-C triple bond
sp and sp³ C-H bonds



strong C-N triple bond
only sp³ C-H bonds



Isomers of $C_4H_8O_1$

