

CHE 118A Discussion

Week 5: IR Spectroscopy

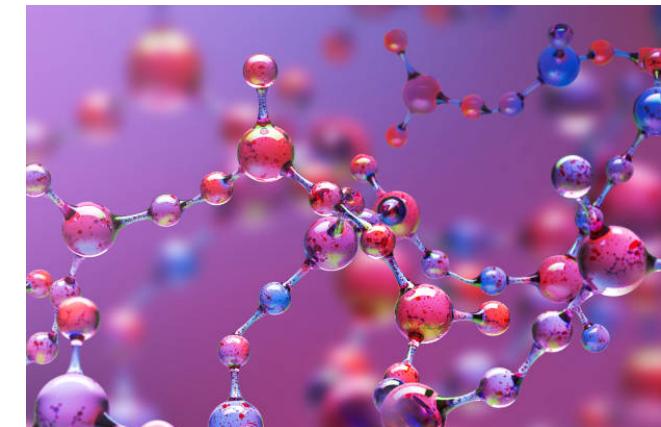
Course Professor: Dr. Wei

Section TA: Emma Morrow

Fall 2024

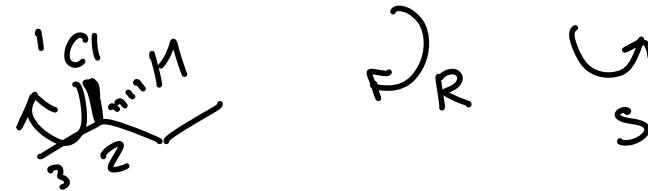
10/25/24

B03: Mondays, 10:30-11:50am Wellman 3
B05: Friday, 12:10-1:30 pm Wellman 207
B09: Friday, 3:10-4:30pm Olson 141
B14: Monday, 2:10-3:30 pm TLC 3213



Announcements

- Quiz 4 Today! 15 minutes at beginning of class
- Problem set 2 due 10/30
- Office Hours Tuesday, Thursday, 3-4pm in CHE 190D
 - Please come!!

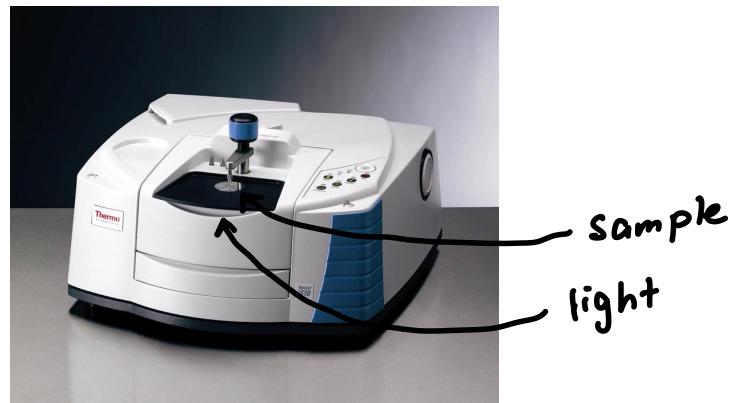


Discussion Schedule

	Oct-21	Oct-22	Oct-23	Oct-24	Oct-25	Oct-26
	Discussion 4	Discussion 4	Discussion 5	Discussion 5	Discussion 5	
Week 5	Quiz 3	Quiz 3	Quiz 4	Quiz 4	Quiz 4	Quiz 3 score release
	Oct-28	Oct-29	Oct-30	Oct-31	Nov-1	Nov-2
	Discussion 5	Discussion 5	Discussion 6	Discussion 6	Discussion 6	
Week 6	Quiz 4	Quiz 4	Quiz 5	Quiz 5	Quiz 5	Quiz 4 score release

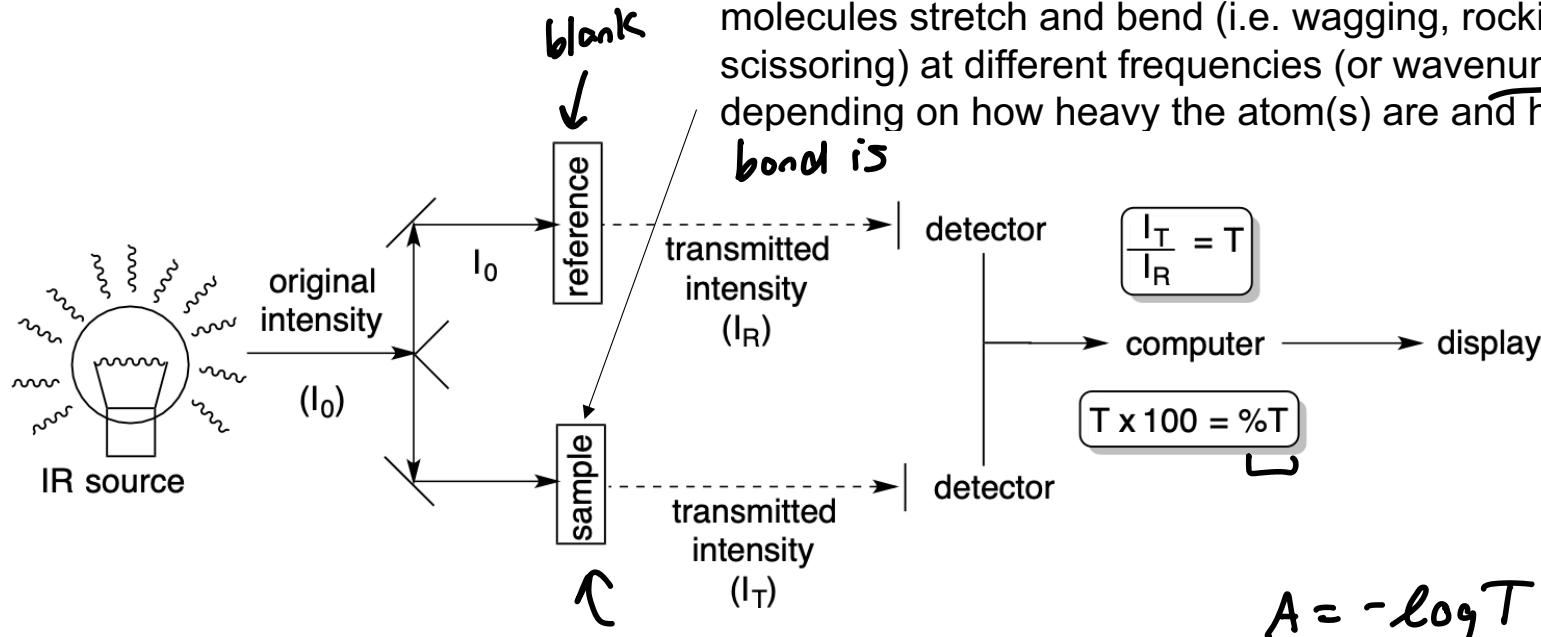
What is IR Spectroscopy?

- Stands for Infrared Spectroscopy
- This is really important after running a reaction
 - How do we know what we have made?
- IR is really helpful for finding functional groups in organic molecules!



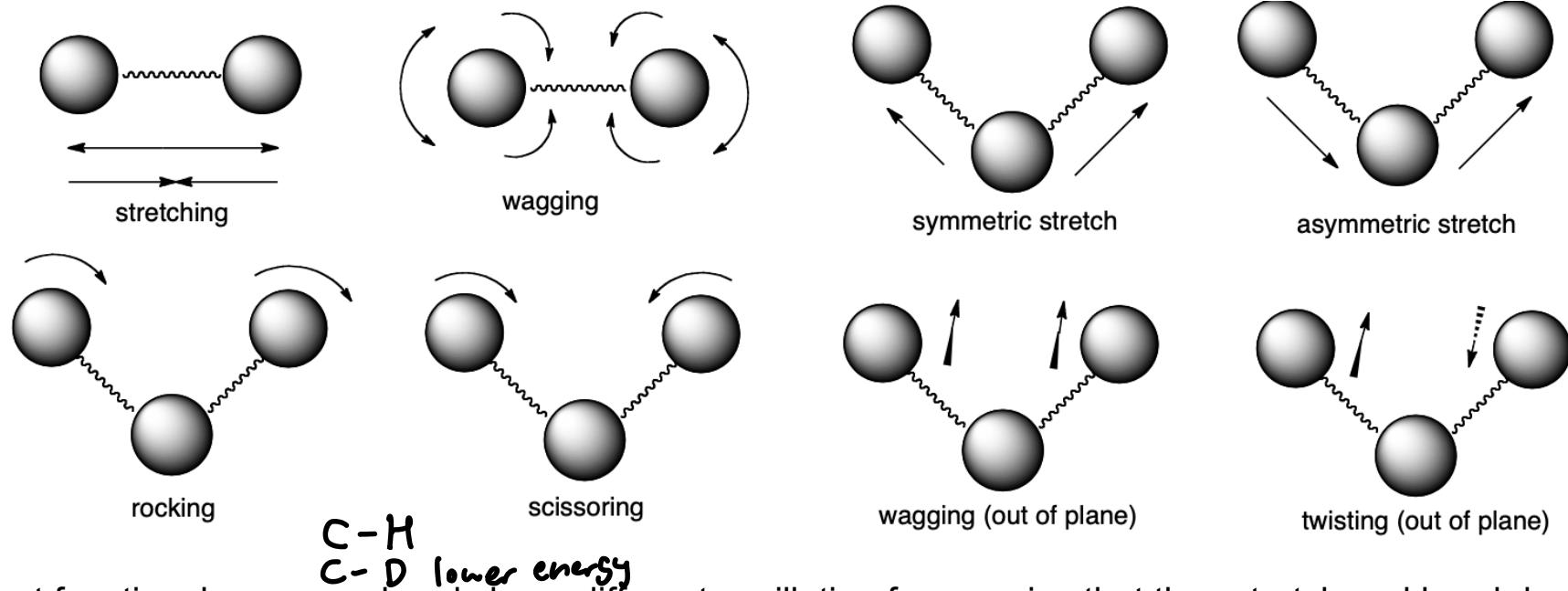
How does IR work?

When sample absorbs light, functional groups/bonds in molecules stretch and bend (i.e. wagging, rocking and scissoring) at different frequencies (or wavenumbers) depending on how heavy the atom(s) are and how strong the bond is



- Absorbance and transmittance are inversely related.
- The more polar a bond (i.e. C=O), the more light absorbed, and the less light transmitted (i.e. lower %T). This causes some peaks with more polar bonds to be more intense (i.e. lower %T or y-axis value).
- This is why some peaks are more intense in IR spectra than others).

Types of stretching and bending vibrations in IR:



Different functional groups or bonds have different oscillation frequencies that they stretch and bend depending on atom size and/or bond strength

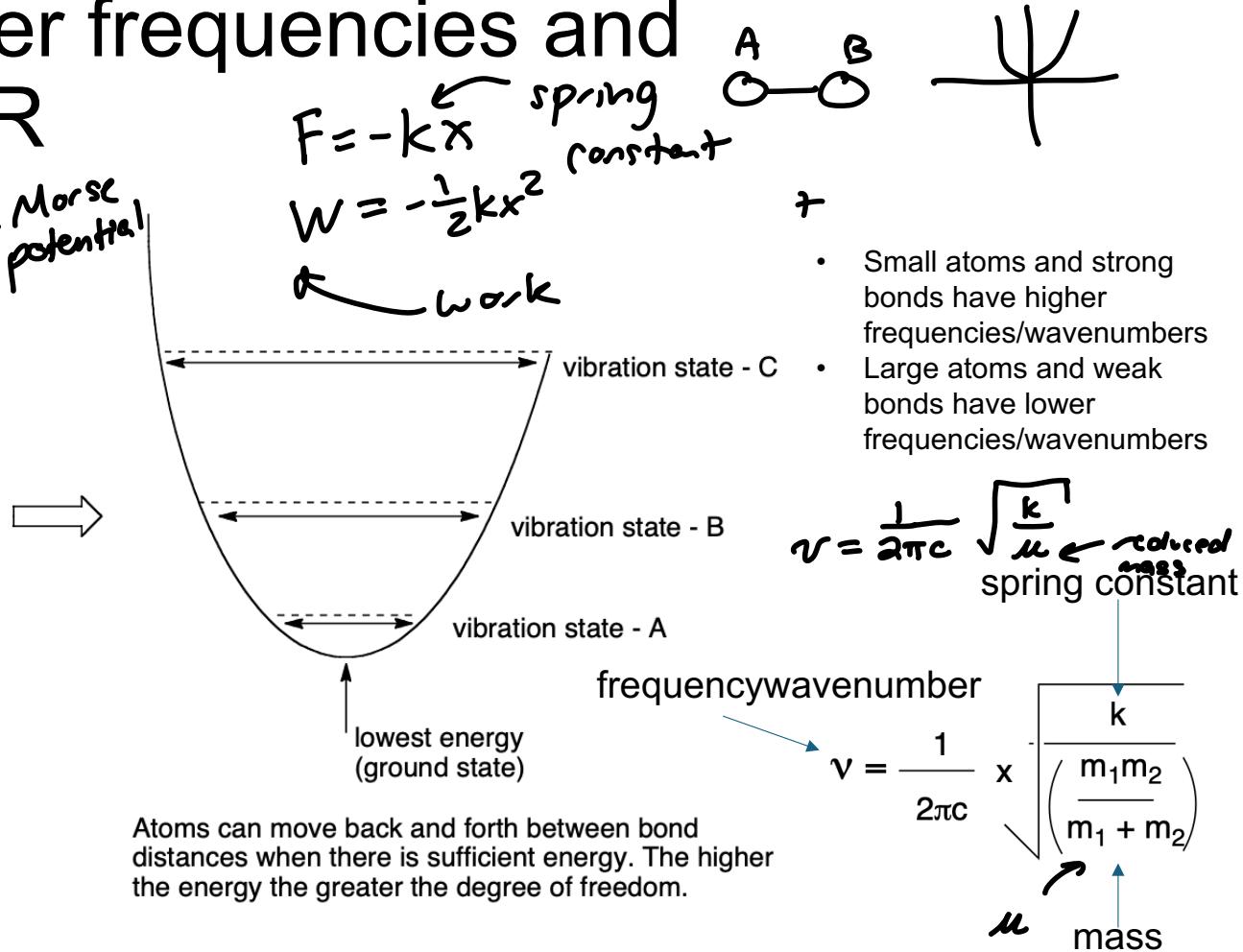
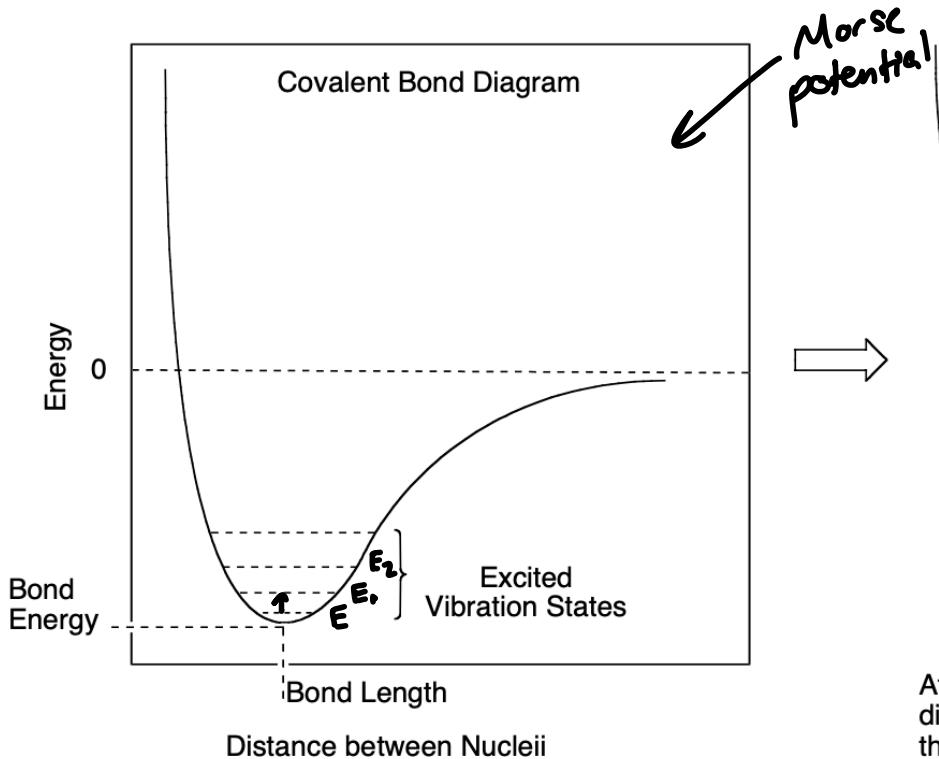
mass

- Lighter atoms (i.e. H) oscillate/stretch and bend at higher frequencies or wavenumbers due to being lighter so they will have a higher wavenumber
- Stronger bonds (i.e. sp C-H) stretch at higher frequencies or wavenumbers due to greater energy

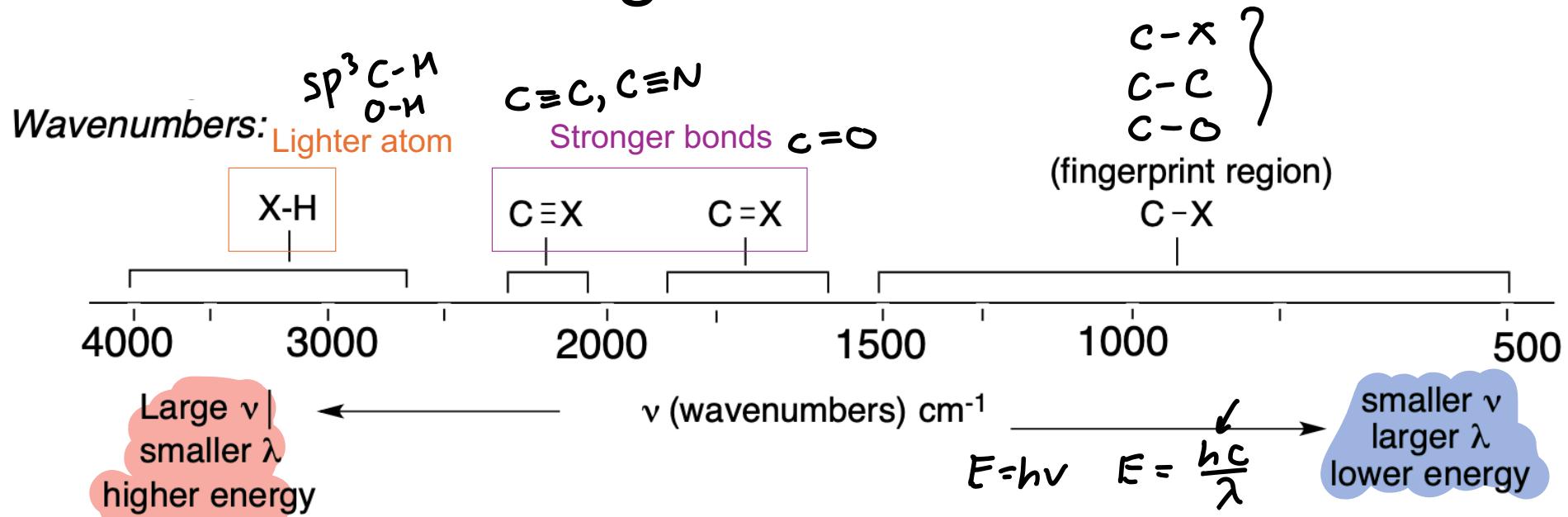
bond order

sp (triple bonds)

Hooke's Law: Why stronger bonds and lighter atoms having larger frequencies and wavenumbers in IR

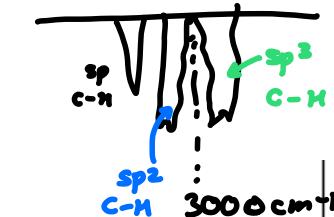
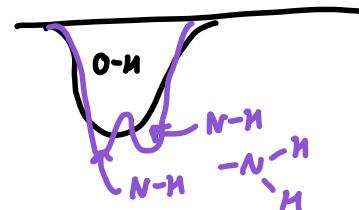
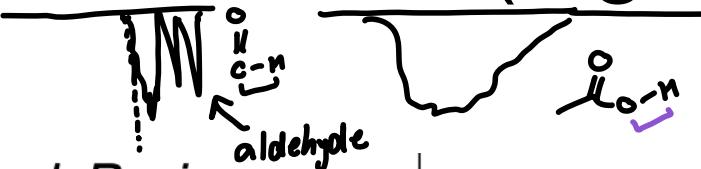


Wavenumber Regions in IR:



NOTE: The scale on a typical IR spectrum isn't a normal linear x-axis, a peak halfway between 2000 cm^{-1} and 1500 cm^{-1} isn't exactly 1750 cm^{-1} , but is closer to 1700 cm^{-1} .

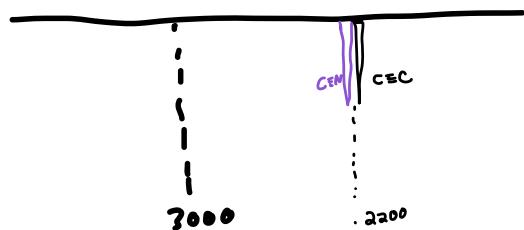
Zone 1: X-H Bonds (highest wavenumbers in IR)



Zone 1 - X-H bond Region		
Alcohols	O-H	3400-3650 cm⁻¹ (broad, strong)
Amines	N-H	3250-3500 cm⁻¹ (broad, strong) (NH_2 doubled)
Acids	COO-H	2500-3100 cm⁻¹ (broad, strong)
Alkynes	CC-H	3260-3330 cm⁻¹ (sharp)
Alkenes	=C-H	3050-3150 cm⁻¹
Aromatics	Benzene-H	~3030 cm⁻¹
Alkanes	C-H	2850-3000 cm⁻¹
Aldehydes	O=C-H	2850 and 2750 cm⁻¹

- H atoms are much lighter than other atoms – have higher frequencies of oscillation (i.e. bend and stretch faster) and thus have higher wavenumbers.

Zone 2: Triple Bonds (higher wavenumbers in IR)

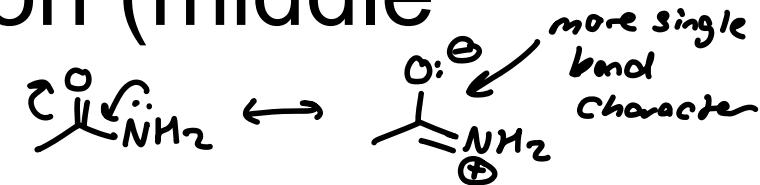


$C \equiv C \Rightarrow$ below 2200 cm^{-1}
 $C \equiv N \Rightarrow$ above 2200 cm^{-1}

Zone 2 – Triple bond Region ²			
Alkynes	$C \equiv C$	CC	$2100\text{-}2260\text{ cm}^{-1}$
Nitriles	$C \equiv N$	CN	$2220\text{-}2260\text{ cm}^{-1}$

- Triple bonds are stronger than double and single bonds, so they have larger spring constants (k) and thus oscillate at higher frequencies (i.e. bend and stretch faster) and have higher wavenumbers.

Zone 3: Double Bond Region (middle wavenumbers in IR)



Zone 3 – Double Bond Region			1700 cm^{-1}
Carbonyls (generic)		C=O	$1650-1850\text{ cm}^{-1}$ (strong)
Carboxylic acid		O=COH	$1710-1760\text{ cm}^{-1}$
Ester		O=COR	$1735-1750\text{ cm}^{-1}$
Aldehyde		O=CH	$1690-1750\text{ cm}^{-1}$
Ketone		O=CR	$1690-1750\text{ cm}^{-1}$
Amide		O=CNR ₂	$1650-1690\text{ cm}^{-1}$
Alkenes (generic)	$\text{C}=\text{C}$	C=C	$1620-1680\text{ cm}^{-1}$

Aromatic $\text{C}=\text{C}$

1600

- Double bonds are stronger than single and weaker than triple bonds, so have a k constant and thus wavenumber between triple and single bonds.

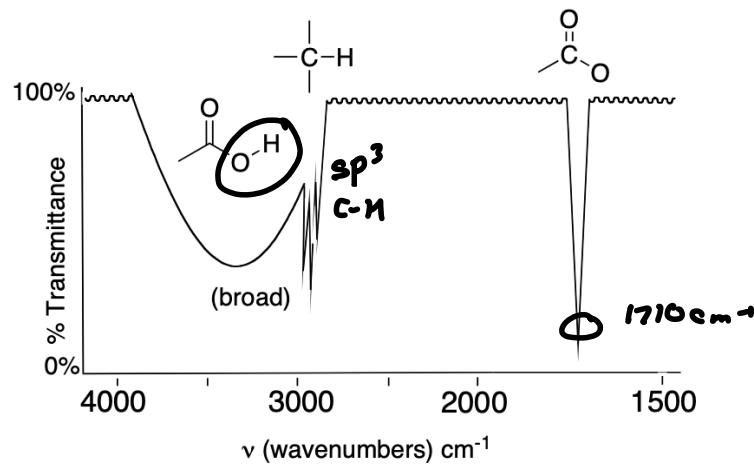
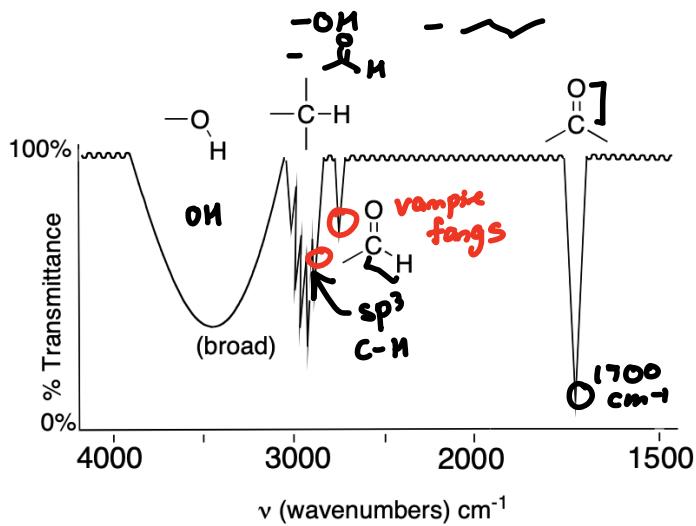
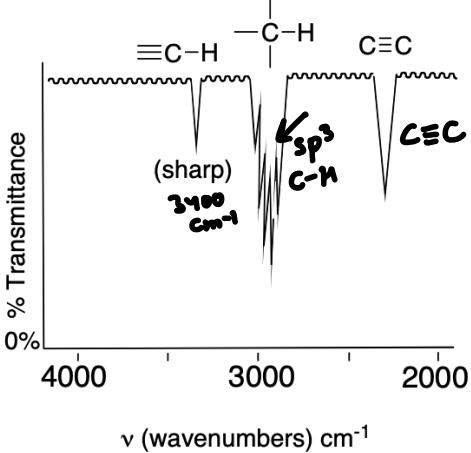


Zone 4: Single Bonds (lowest wavenumbers in IR)

<i>Zone 4 – Single bonds/Fingerprint region³</i>		
Oxygen	C-O	1000-1260 cm ⁻¹
Nitrogen	C-N	1030-1230 cm ⁻¹
Chlorine	C-Cl	600-800 cm ⁻¹
Bromine	C-Br	500-600 cm ⁻¹

- Single bonds are weaker than double and triple bonds, so have lowest k constant and thus lowest wavenumber
- C-C bond stretches are also in this region – since most organic molecules have many C-C bonds, this region is very busy.

Peak Shape and Intensity in IR:



- High peak intensity means a lower %Transmittance – this means that more light was absorbed by that functional group and therefore the sample has more of this functional group.
- O-H peaks are usually broad due to intramolecular and intermolecular hydrogen bonding in sample causing there to be many resonance frequencies.

Steps to Predict Structure/Functional Groups from IR Spectrum

- 1) Find the alkane C-H peak near 2950 cm^{-1} . Nearly all IR spectra will have some sp^3 C-H to show up here.
 - a. Look left. Is there a peak that is distinct from the mass of C-H?
 - i. Yes, and it's relatively sharp and narrow and near $3100\text{ cm}^{-1} \rightarrow \text{sp}^2$ C-H look for an alkene C=C near $1650\text{-}1600\text{ cm}^{-1}$
 - ii. Yes, and it's relatively broad and centered near $3300\text{ cm}^{-1} \rightarrow$ alcohol or secondary amine OH or NH
 - iii. Yes, and it's relatively broad and centered near 3100 cm^{-1} and overlapping the alkane C-H peak \rightarrow acid OH, look for a C=O near $1700\text{-}1750\text{ cm}^{-1}$.
 - iv. Yes, and it's a narrow peak well away from the alkane C-H near $3300\text{ cm}^{-1} \rightarrow$ terminal alkyne C-H, look for an alkyne CC near 2200 cm^{-1}
 - v. Yes, two that are both rather broad and connected centered near $3300\text{ cm}^{-1} \rightarrow$ primary amine $-\text{NH}_2$
 - vi. No. The molecule may have alkenes/alkynes, but they have no H attached.
 - b. Look right. Is there a peak that is distinct from the mass of C-H but closely associated?
 - i. Yes, aldehyde C-H. Look for an aldehyde C=O between $1700\text{-}1750\text{ cm}^{-1}$.

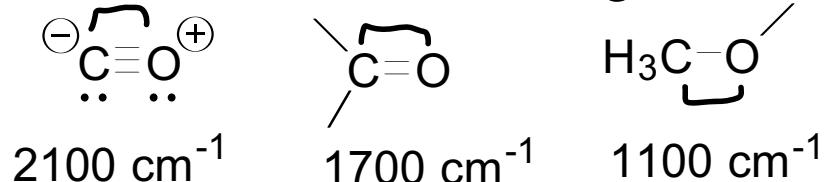
Steps to Predict Structure/Functional Groups from IR Spectrum

- 2) Look between $2100\text{-}2300\text{ cm}^{-1}$, is there a peak?
 - a. Yes, with alkyne C-H (above). \rightarrow Terminal alkyne
 - b. Yes, without alkyne C-H \rightarrow internal alkyne or nitrile. Check the formula for N.
 - c. No, then no triple bonds are present in the molecule.
- 3) Look between $1820\text{-}1600\text{ cm}^{-1}$, is there a peak?
 - a. Yes, between $1820\text{-}1680\text{ cm}^{-1}$ \rightarrow a carbonyl C=O
 - i. With acid OH \rightarrow carboxylic acid
 - ii. With aldehyde C-H \rightarrow aldehyde
 - iii. No other associated peaks \rightarrow ketone or ester.
 - b. Yes between $1650\text{-}1600\text{ cm}^{-1}$ \rightarrow an alkene C=C
 - i. Most alkenes will show sp^2 C-H, but some do not have C-H bonds
 - c. No, then no double bonds are present in the molecule.

NOTE: One of the most common difficulties is distinguishing C=O from C=C bonds. This is a problem even for experienced spectroscopists in cases where conjugation, ring strain, or other groups blurs the difference between them. Look for other clues aldehyde C-H, alkene C-H, acid OH, distance from fingerprint region etc.

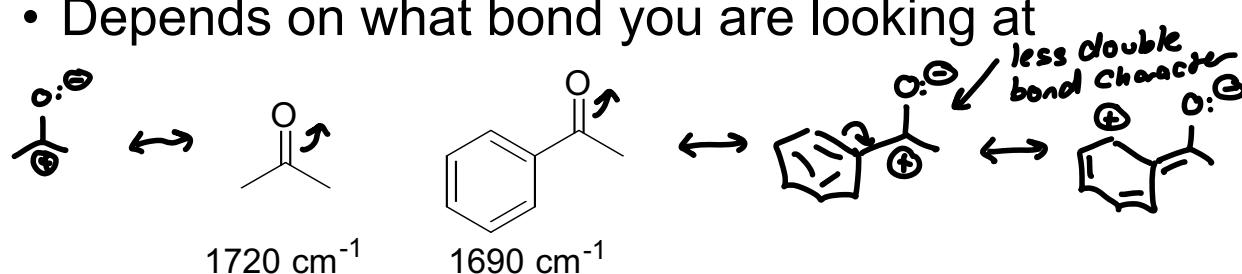
Summary of Trends in IR

- Heavier atoms vibrate slower because they are lower in energy
 - C-C has a lower wavenumber than C-H
- Higher bond order leads to higher wavenumber



- Resonance can effect bond order

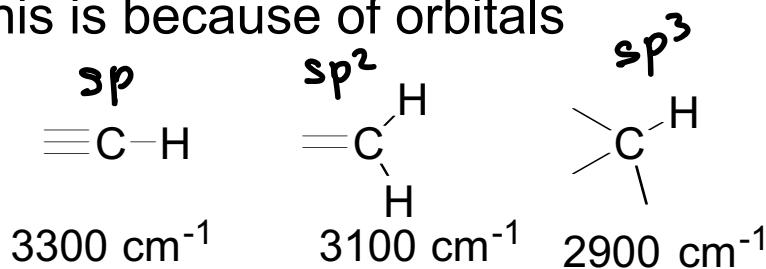
- Depends on what bond you are looking at



Summary of Trends in IR

- Hybridization affects bond strength

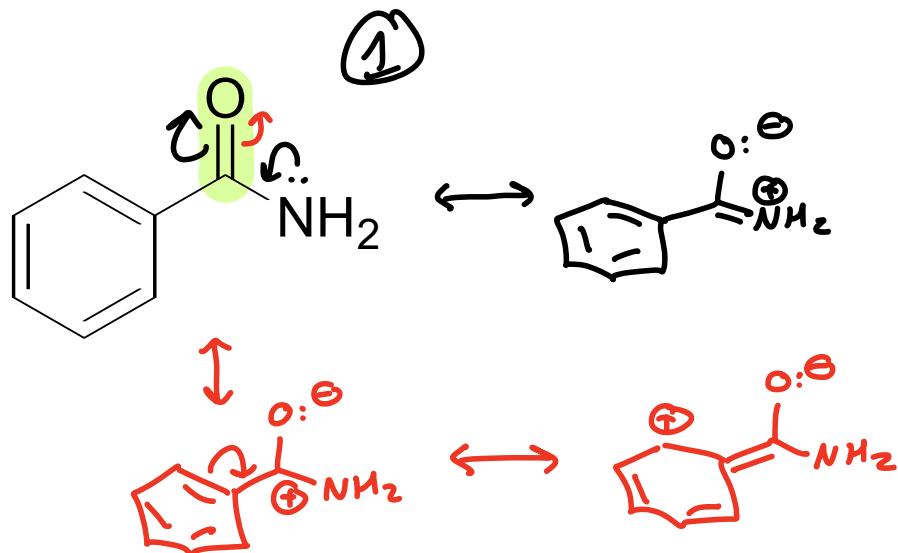
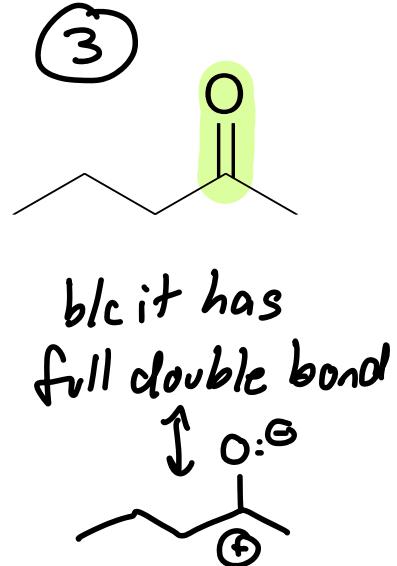
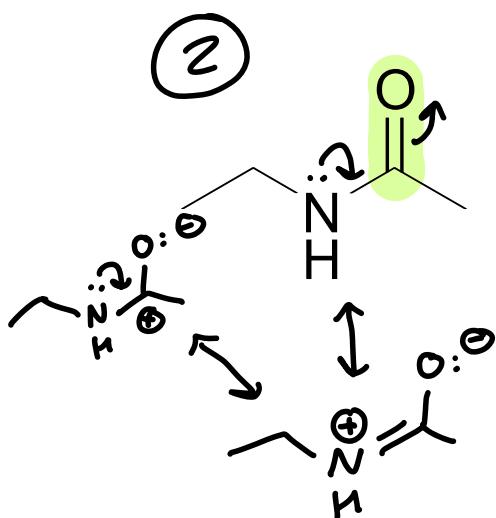
- This is because of orbitals



- sp hybridization has 50% more s character, sp^3 has only 25% s-character, which makes the bond longer and weaker bond, lower energy and lower wavenumber

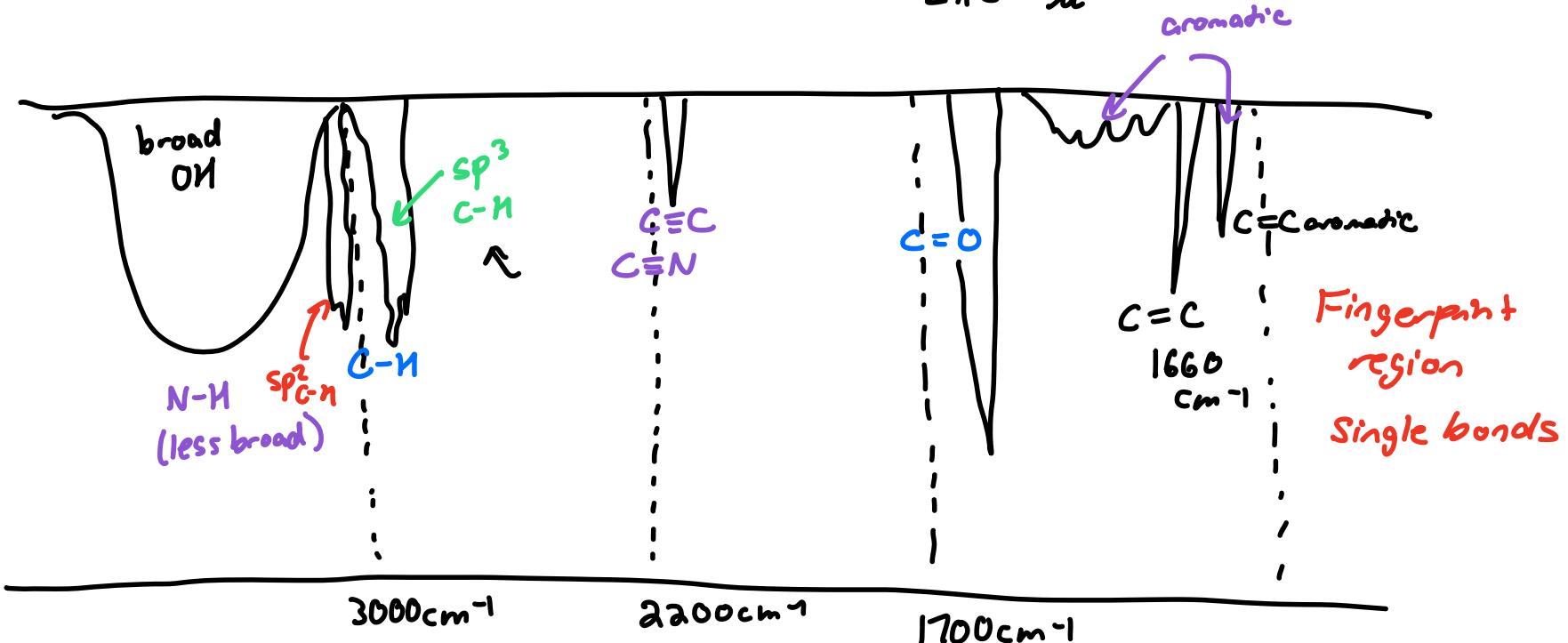
Practice

- Rank the C=O from lowest to highest wavenumber:



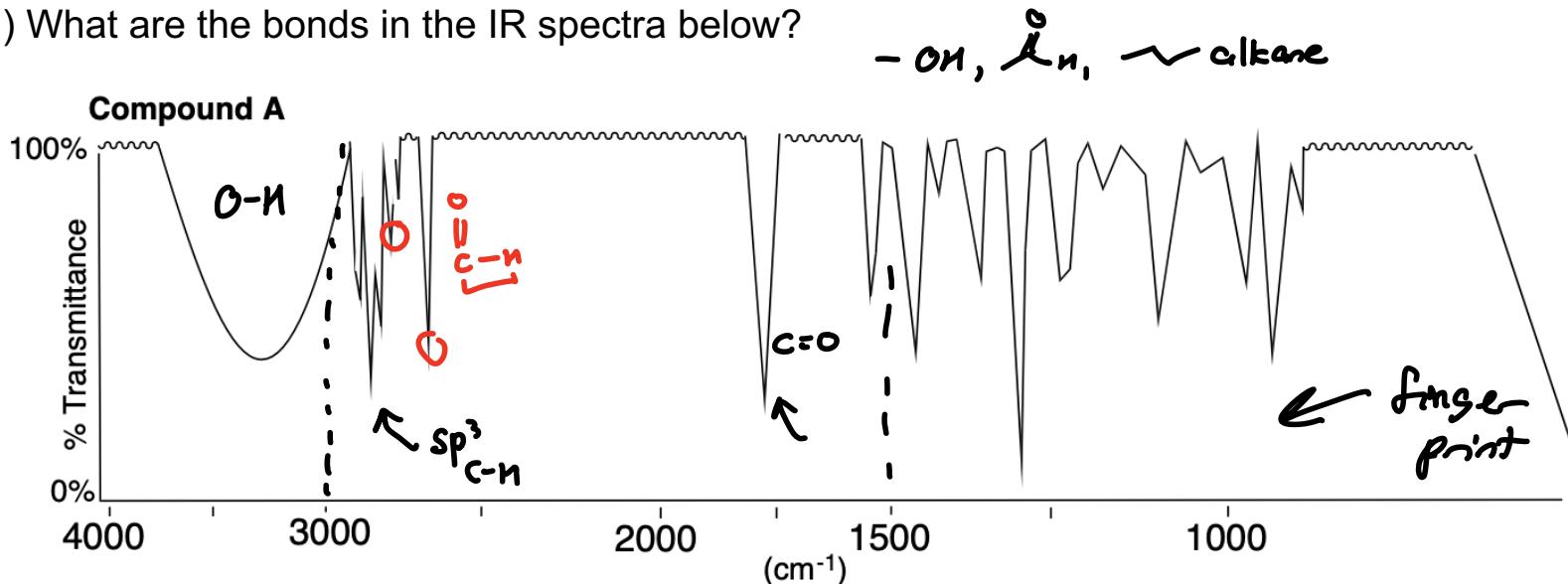
Range of Peaks in IR

$$\nu = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}}$$

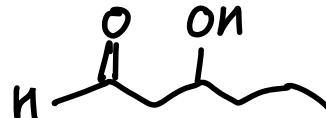
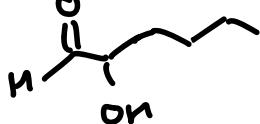


Practice-You try it!

1) What are the bonds in the IR spectra below?



2) What is a reasonable chemical structure with 6 carbons that could have produced the IR spectra above?

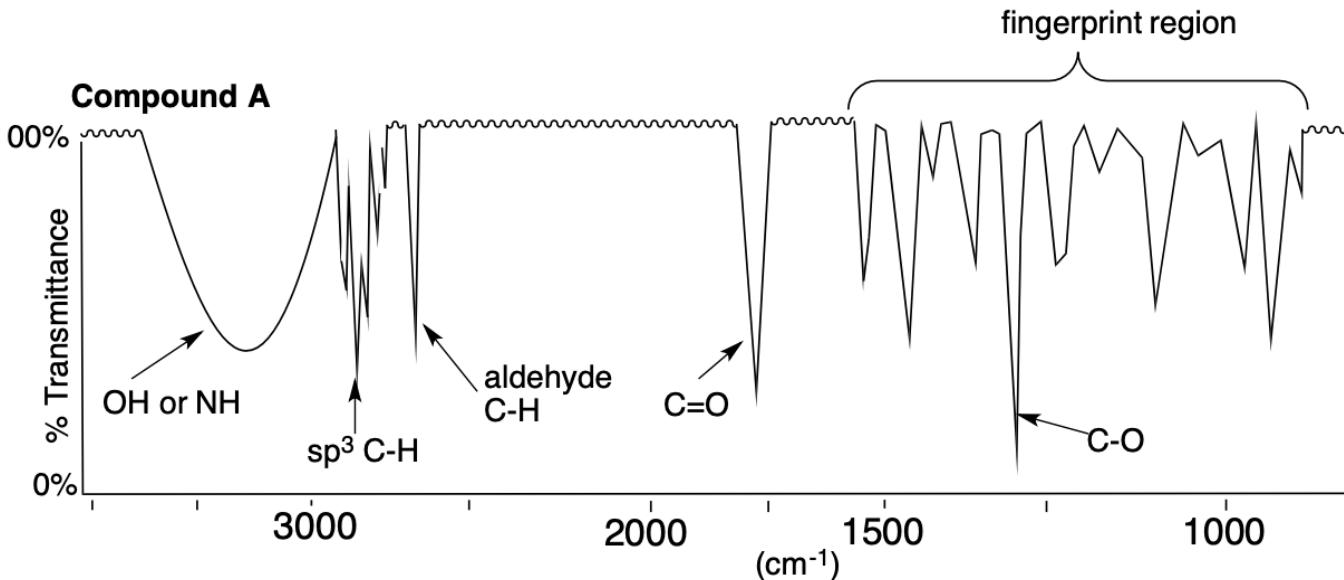


Next Week

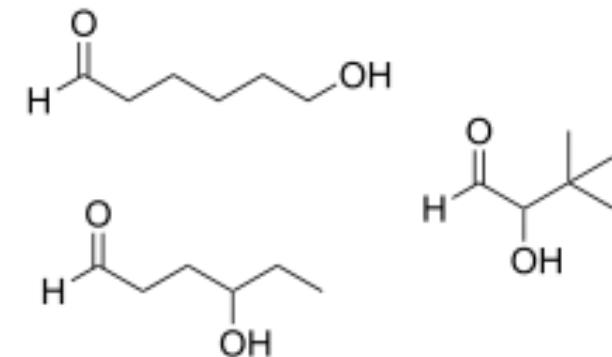
- Quiz 5
- Problem set 2 10/30
- Regrade requests for Midterm 1 due Monday!

Answer:

1) What are the bonds in the IR spectra below?



2) Reasonable chemicals structures:



This molecule contains an aldehyde as evidenced by the C=O and the aldehyde C-H. The presence of the aldehyde C-H ensures that the C=O is an aldehyde and not a ketone or ester. The broad OH/NH peak could be either an alcohol or a secondary amine, but the C-O single bond in the fingerprint region indicates an alcohol. The molecule most likely contains AN ALCOHOL and AN ALDEHYDE.