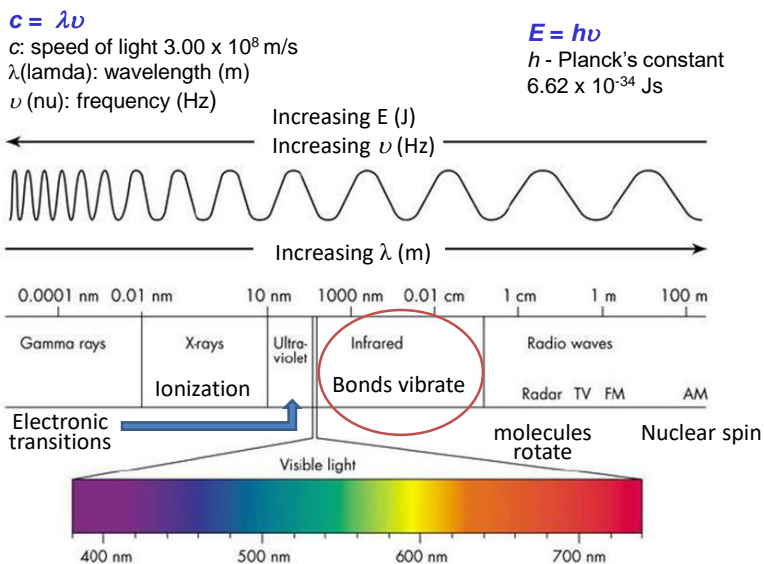



SPECTROSCOPY MEASURES THE INTERACTION BETWEEN LIGHT AND MATTER



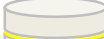
<http://www.scienceline.ucsb.edu/images/wavelength1>

Sample Preparation


- in solution
 - must subtract the "background" (peaks arising from the solvent)
 - need matching "sample" (sample + solvent) and "standard" (solvent) cells
- a thin film on NaCl plates



Evaporate a drop of solution to give a solid film

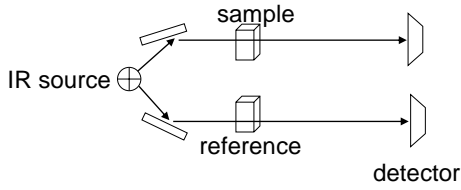


Liquid between two plates
- in a "mull" – a mixture of a solid in an oil
 must ignore the peaks of the oil (e.g., Nujol = a hydrocarbon)
- in a KBr pellet


- ATR ("Attenuated Total Reflection") – solid sample



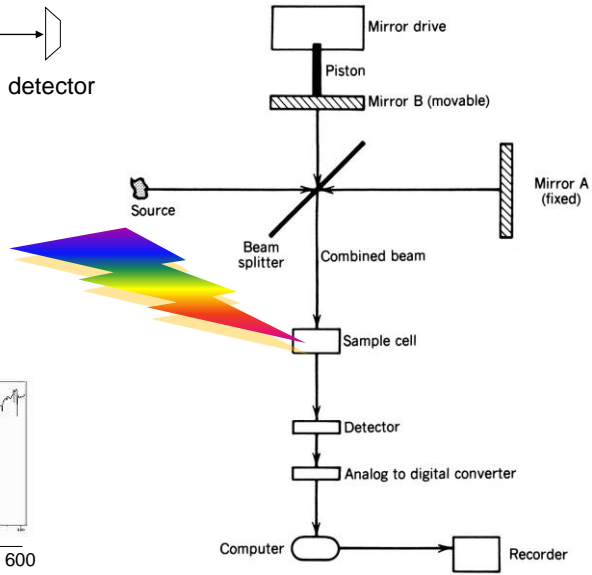
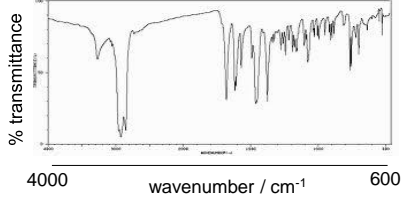
Fourier transform IR



Free induction decay (FID)

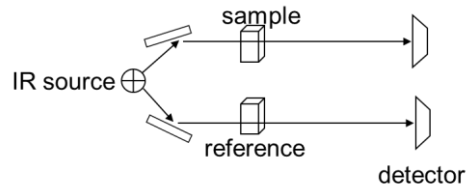


Spectrum

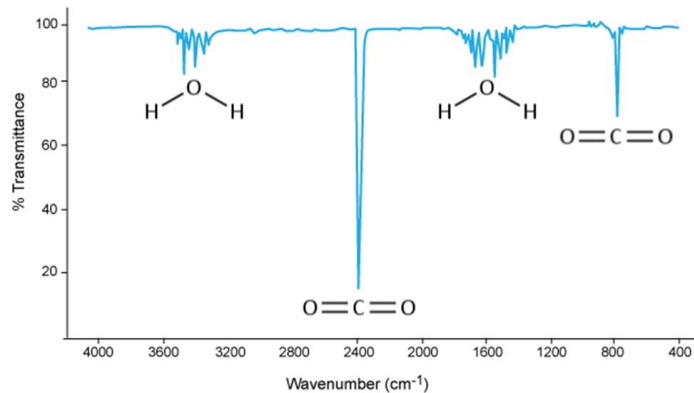


Reference beam

Wet sample: H-O str. of H₂O



CO₂ and H₂O in atmosphere not cancelled out by reference beam:



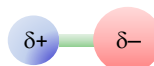
TO OBSERVE A BOND VIBRATION BY IR SPECTROSCOPY THERE MUST BE A CHANGE IN DIPOLE MOMENT UPON VIBRATION

Nonpolar Bonds



Nonpolar bonds in a symmetrical molecule absorb weakly or not at all
e.g., $R-C\equiv C-R$

Polar Bonds



Polar bonds are usually IR-active and show stronger peaks
e.g., $C=O$

Frequency of Fundamental Vibrations

Hooke's Law:

K: force constant $\nu = 4.12 \sqrt{\frac{k}{\mu}}$

U: reduced mass

$$\mu = \frac{m_A m_B}{m_A + m_B}$$

Units for IR

Electromagnetic Radiation for molecular vibrations

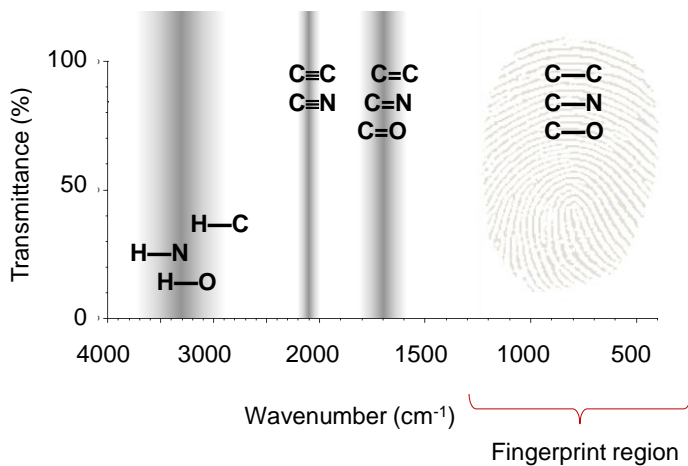
Frequency, $\nu = 1.25 \times 10^{13}$ to 1.25×10^{14} Hz

Wavelength, $\lambda = 25$ to $2.5 \mu\text{m}$

In order to correlate the wavelength with energy

Define wavenumber, $\bar{\nu} = 1/\lambda$ (in cm)

$\bar{\nu} = 400$ to 4000 cm^{-1} where high numbers are a high energy and low numbers are low energy



Other vibrations

Spectra include a number of other peaks. In addition to *fundamental stretching and bending absorptions*....

Overtone: lower intensity vibration at an integral times the fundamental frequency

$$\nu_{\text{overtone}} = n \times \nu_{\text{fundamental}}$$

Combination bands: the sum of two interacting vibrational frequencies, but only certain combinations are allowed

$$\nu_{\text{combination}} = \nu_1 + \nu_2$$

Difference bands: similar to combination bands, but the difference of two interacting vibrations

$$\nu_{\text{difference}} = \nu_1 - \nu_2$$

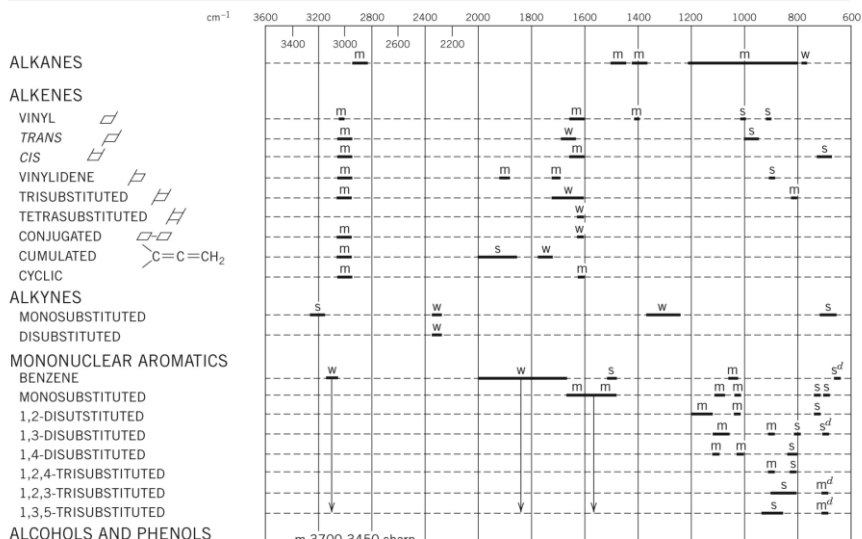
Fermi resonance: when a fundamental absorption couples with an overtone or combination band, most often observed for C=O

Selected infrared absorptions for bond *stretches*

Functional Group	Range cm^{-1}	Intensity and shape	Pavia 2.7-2.9
$sp^3\text{C-H}$	2850-2960	medium to strong; sharp	
$sp^2\text{C-H}$	3010-3190	medium to strong; sharp	
$sp\text{C-H}$	about 3300	medium to strong; sharp	
C=C	1620-1660	weak to medium; sharp	
$\text{C}\equiv\text{C}$	2100-2260	weak to medium; sharp	
N-H	3300-3500	medium; broad	
O-H (very dilute)	about 3600	medium; sharp	
O-H (H-bonded)	3200-3550	strong; broad	
O-H (carboxylic acid)	2500-3000	medium; very broad	
C-O	1050-1150	medium to strong; sharp	
C=O	~1700	very strong; sharp (see later)	
$\text{C}\equiv\text{N}$	2200-2260	medium; sharp	

Pavia Appendix I

APPENDIX B CHARACTERISTIC GROUP ABSORPTIONS^a

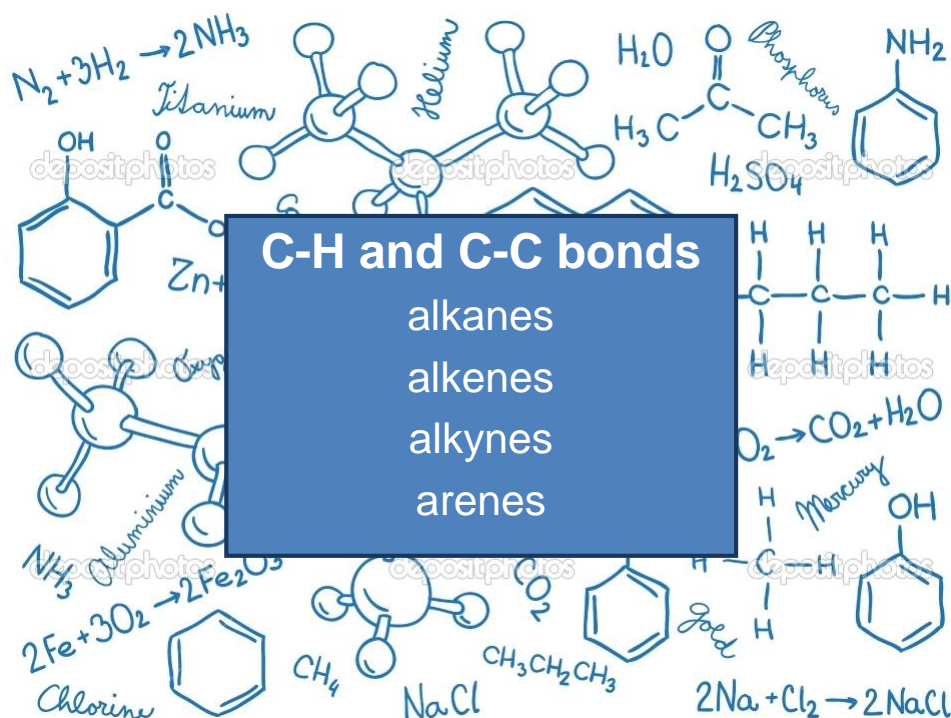


Lecture organization

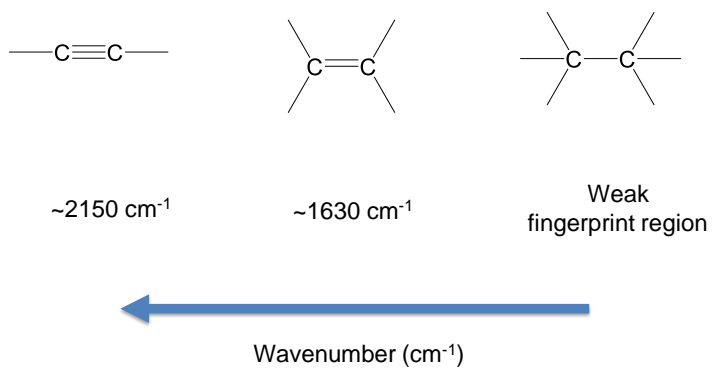
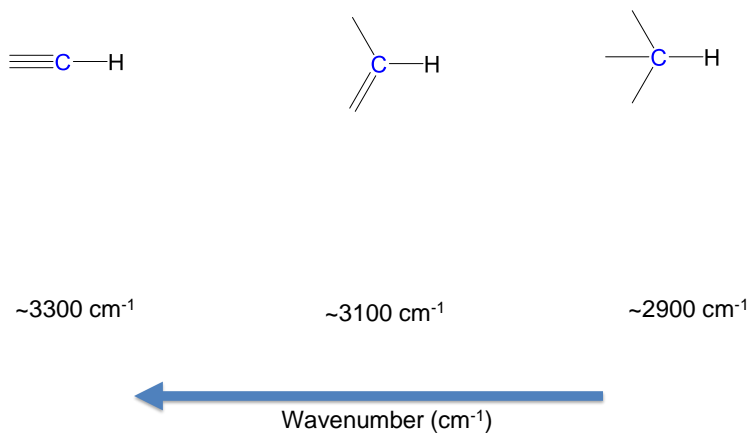
C-H and C-C bonds
O-H and N-H bonds
C-O bonds
C=O bonds
C-N, C=N, C≡N bonds

Textbook organization

Hydrocarbons **Pavia 2.10**
Arenes **Pavia 2.11**
Alcohols and Phenols **Pavia 2.12**
Ethers **Pavia 2.13**
Carbonyl compounds **Pavia 2.14**
Amines **Pavia 2.15**
Nitriles **Pavia 2.16**
more.... **Pavia 2.17-21**

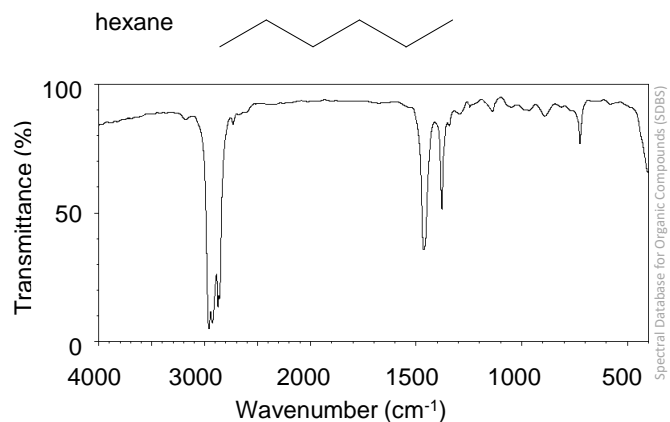


Pavia 2.10, pg 36



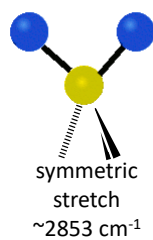
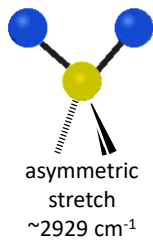
Alkanes

Pavia 2.10

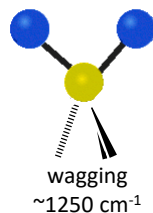
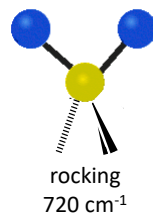
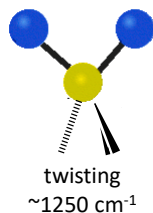
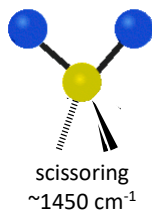


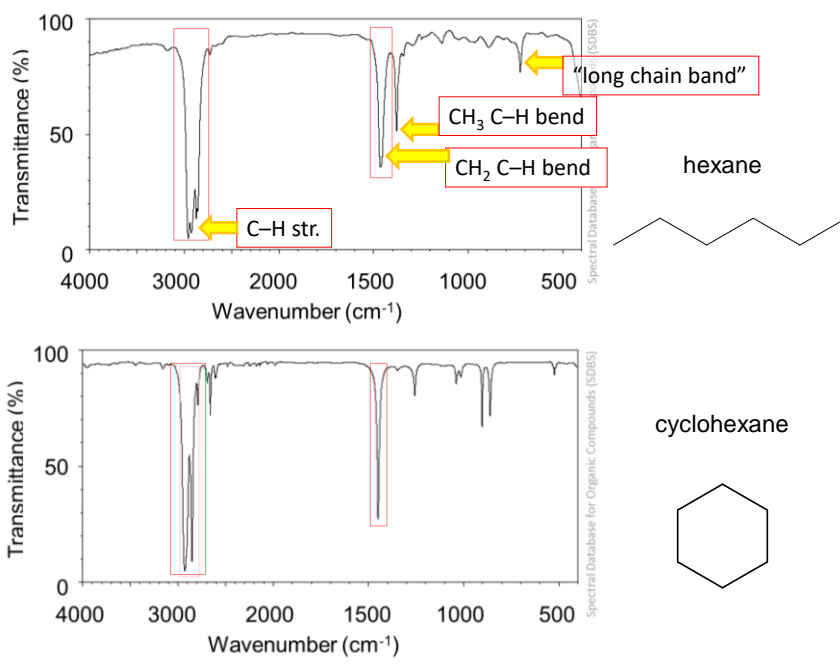
Polyatomic bond vibrations

CH_2 Stretches



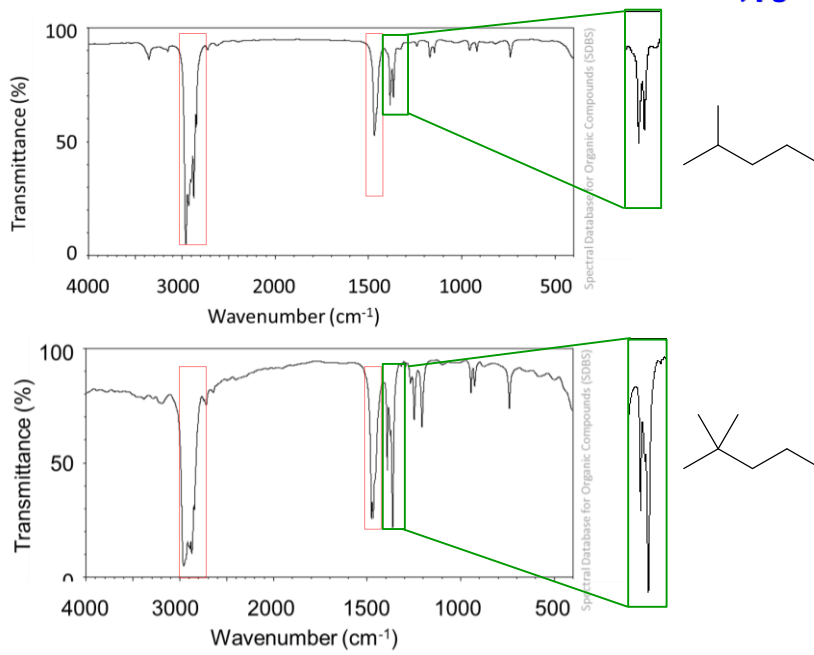
CH_2 Bends

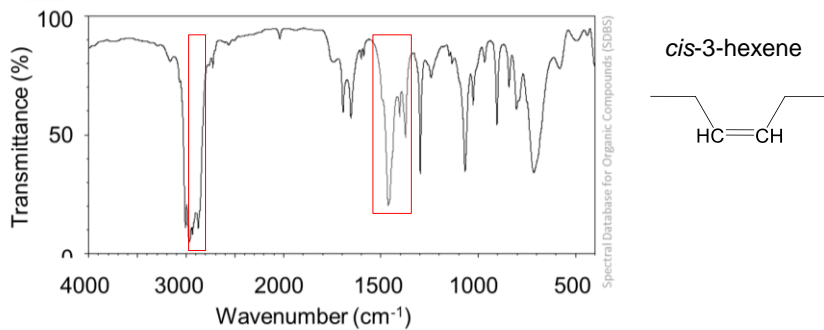
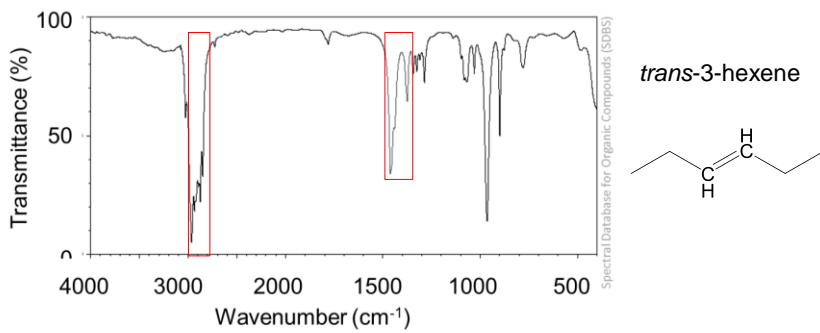
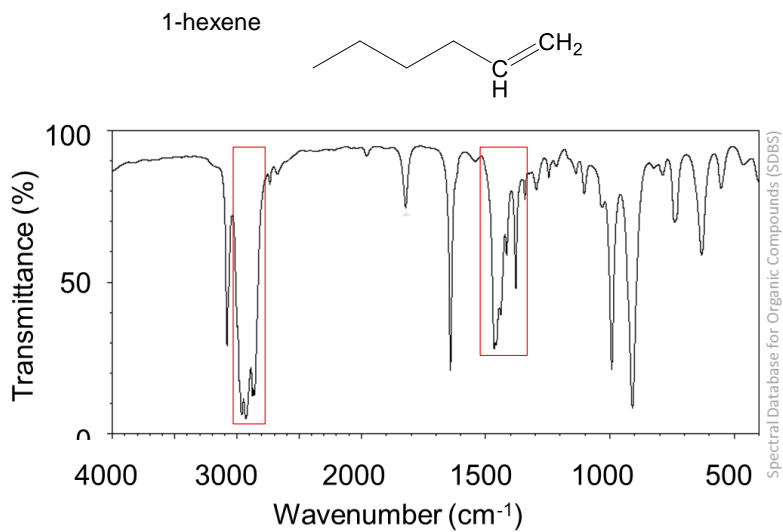




Branched alkanes

Pavia 2.10, pg. 38





Characteristic C-H oop bending peaks for alkenes

Pavia Table 2.22

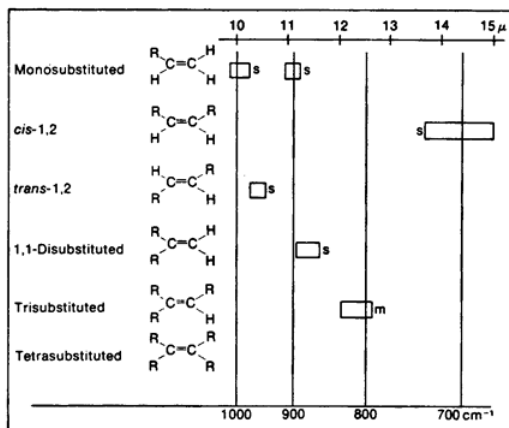
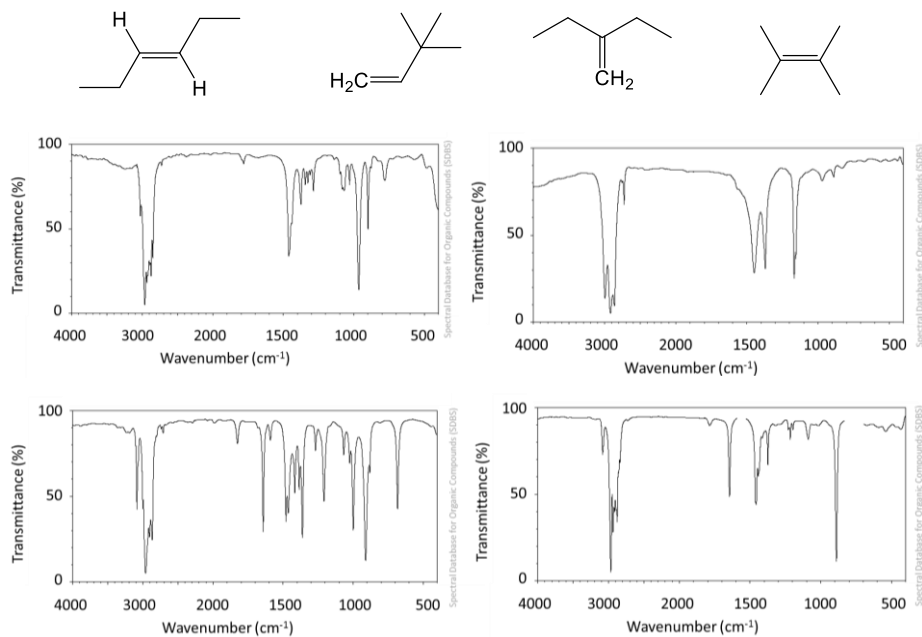
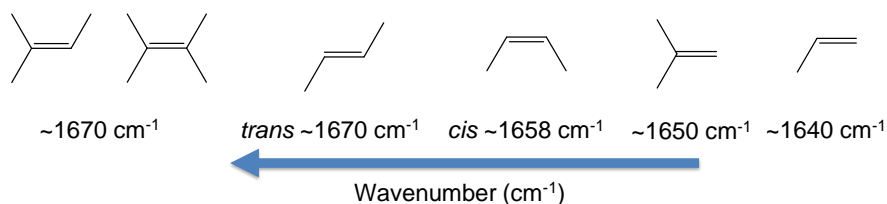


FIGURE 2.22 The C—H out-of-plane bending vibrations for substituted alkenes.

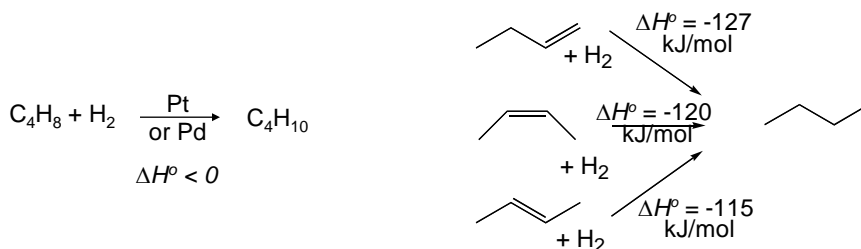


Increasing the number of substituents, increases $\bar{\nu}$

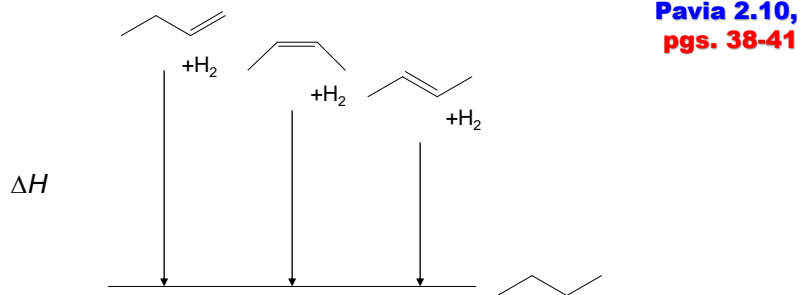


What does this imply about bond strength?

Relating this effect to something you have seen before... heats of hydrogenation

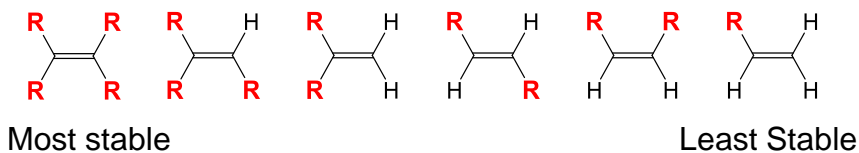


Increasing the number of substituents, increases C=C bond strength, and therefore increases ν

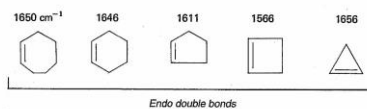
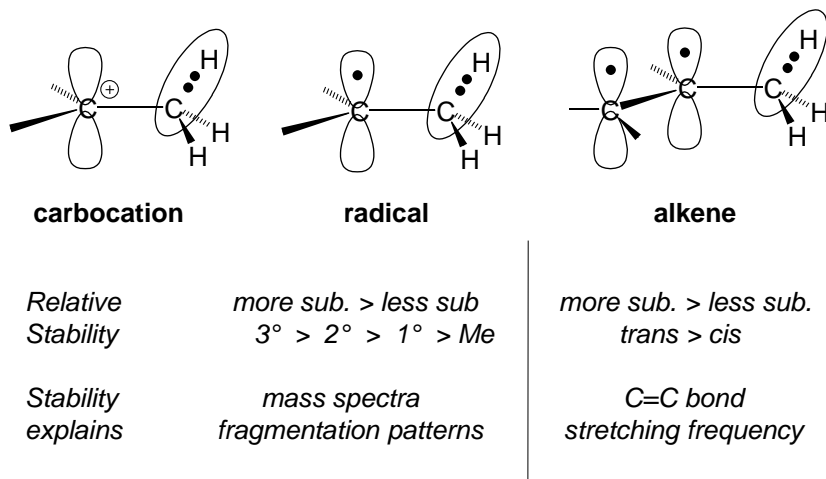


**Pavia 2.10,
pgs. 38-41**

Relative Stability



Hyperconjugation accounts for the enhanced stability of cations, radicals and alkenes with higher degrees of substitution.




(a) Strain moves the peak to the right.
Anomaly: Cyclopropene
(b) If an endo double bond is at a ring fusion, the absorption moves to the right an amount equivalent to the change that would occur if one carbon were removed from the ring.
e.g.:  $\sim 1611 \text{ cm}^{-1}$

FIGURE 2.19 C=C stretching vibrations in endocyclic systems.

Significant increases in the frequency of the absorption of a double bond contained in a ring are observed when one or two alkyl groups are attached directly to the double bond. The increases are most dramatic for small rings, especially cyclopropenes. For example, Figure 2.20 shows that the base value of 1656 cm^{-1} for cyclopropene increases to about 1788 cm^{-1} when one alkyl group is attached to the double bond; with two alkyl groups the value increases to about 1883 cm^{-1} .

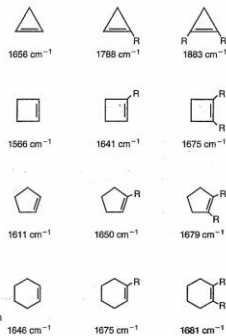
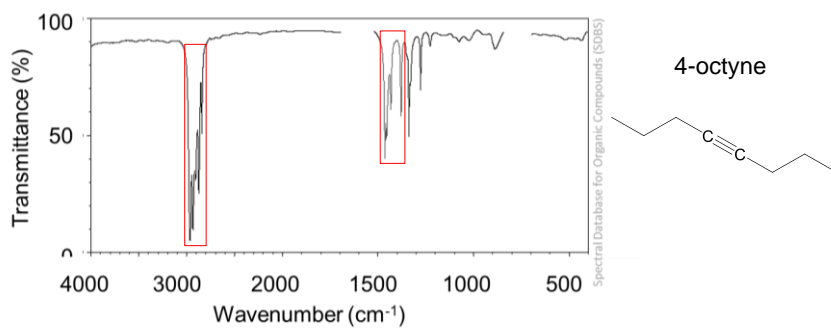
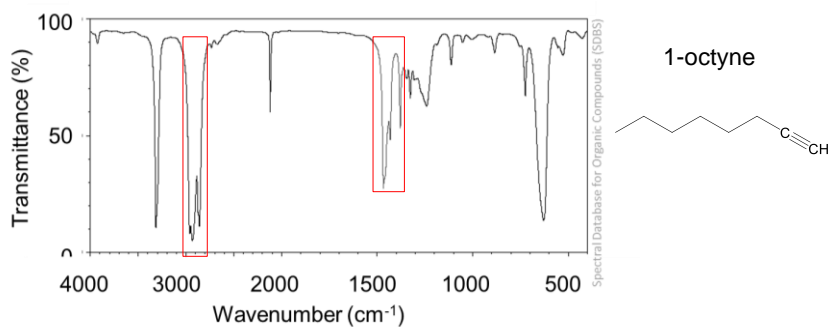
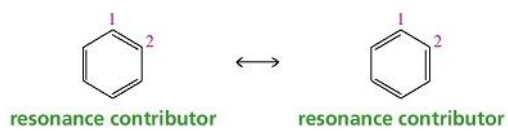
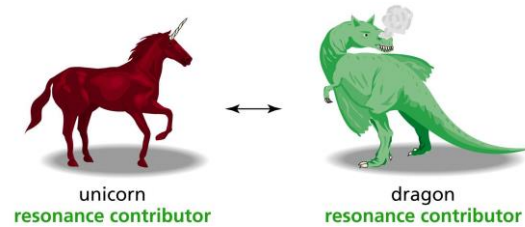


FIGURE 2.20 The effect of alkyl substitution on the frequency of a C=C bond in a ring.



Resonance hybrids



Effect of Resonance on C=C stretching of alkenes

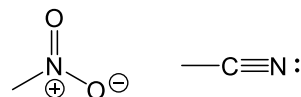
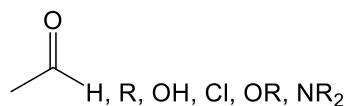
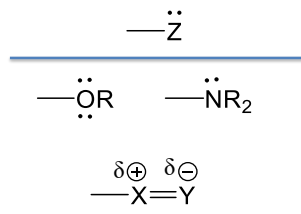
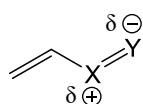


~1640 cm⁻¹ ~1600 cm⁻¹

- Electron donating groups

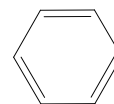
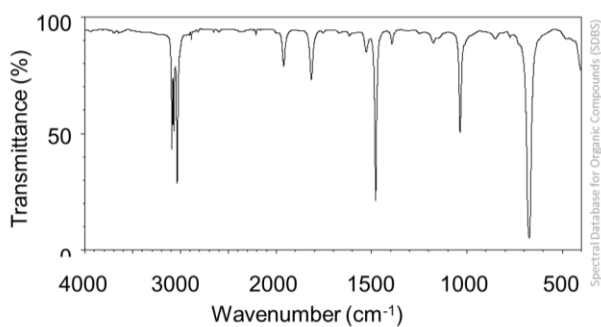


- Electron withdrawing groups

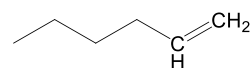
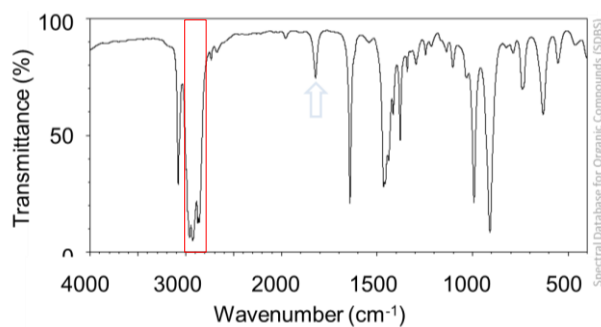


Aromatic Molecules

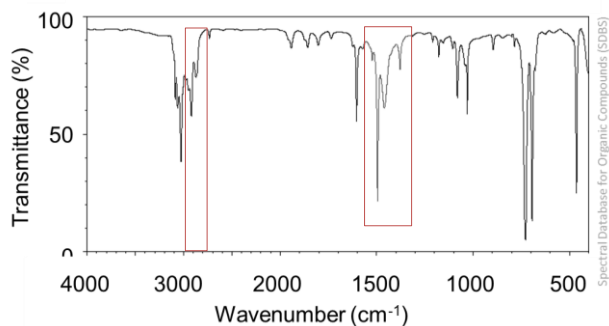
Pavia 2.11



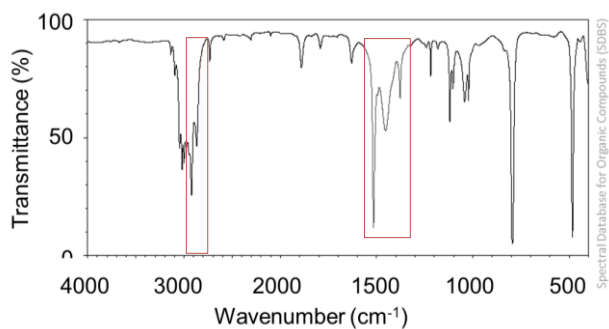
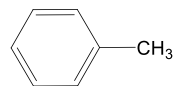
benzene



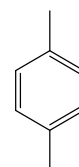
1-hexene



toluene

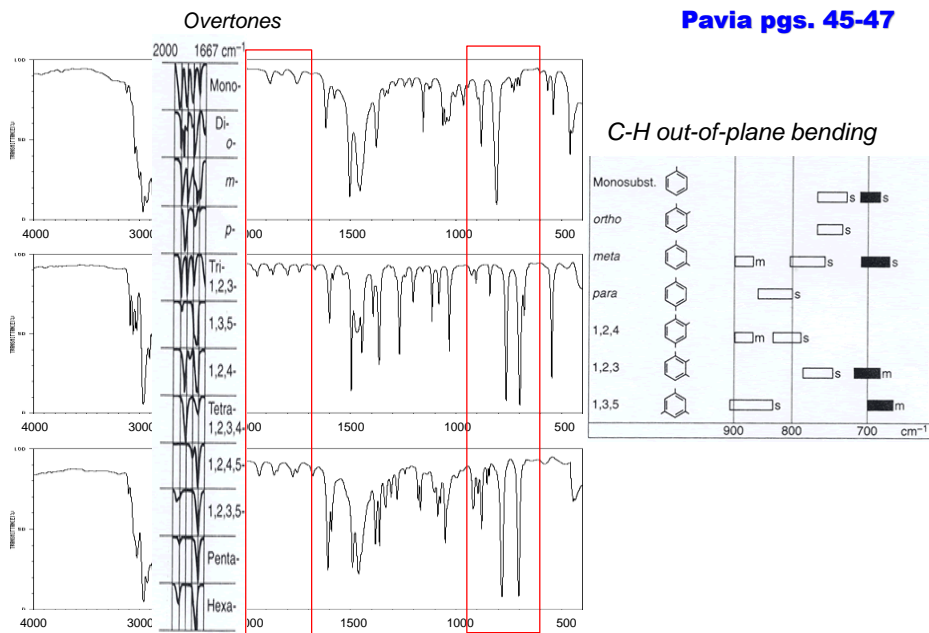


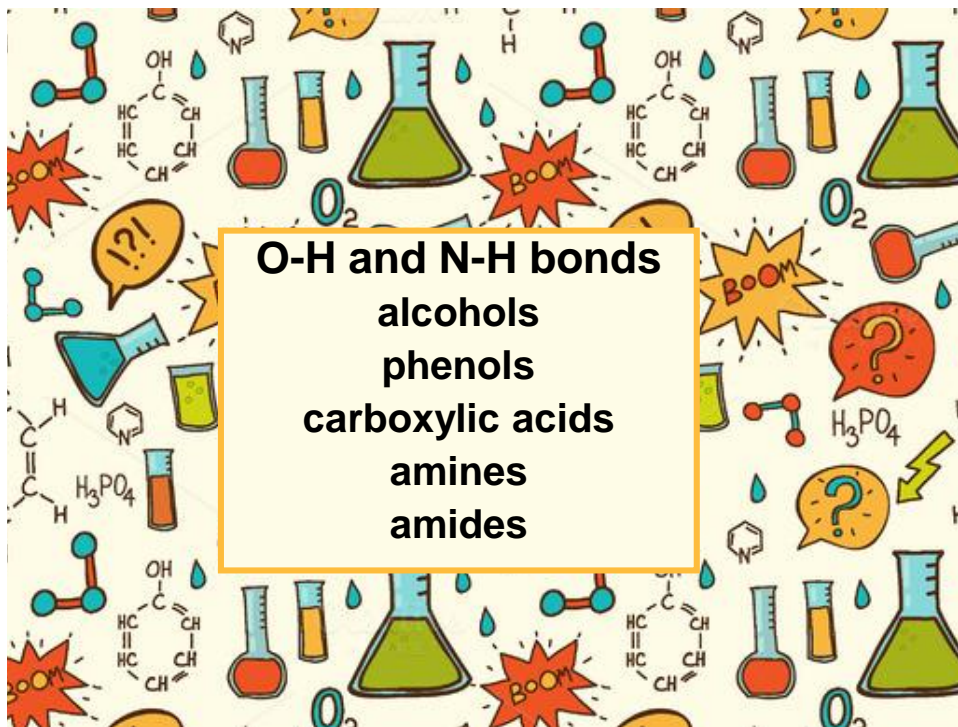
p-xylene



Identify the substitution pattern for three isomers of $C_{10}H_{14}$

Pavia pgs. 45-47

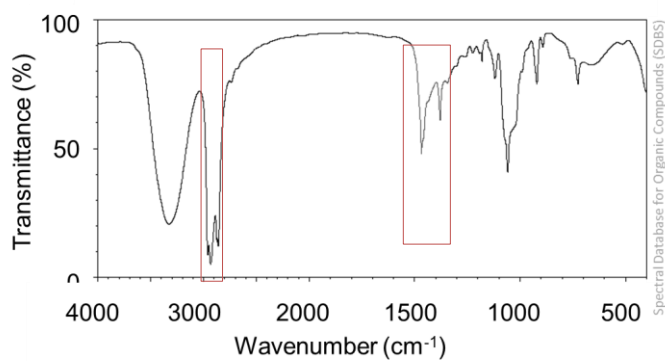
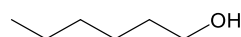




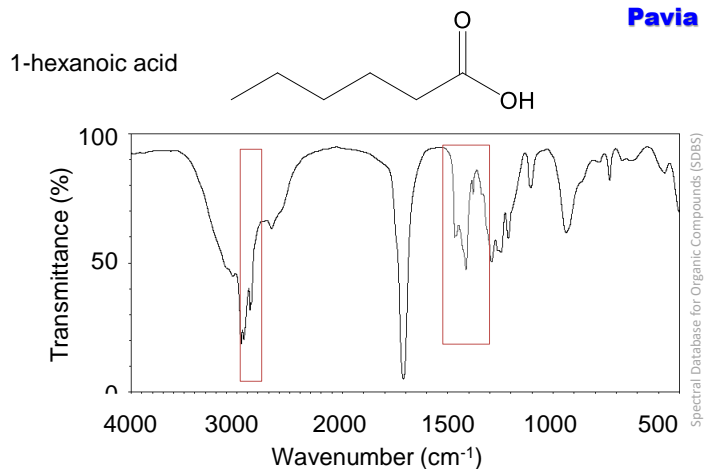
O-H and N-H bonds: Alcohols, Carboxylic Acids, Amines and Amides

Pavia 2.12

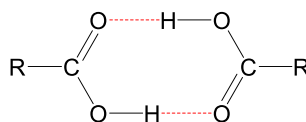
1-hexanol



Pavia 2.14D

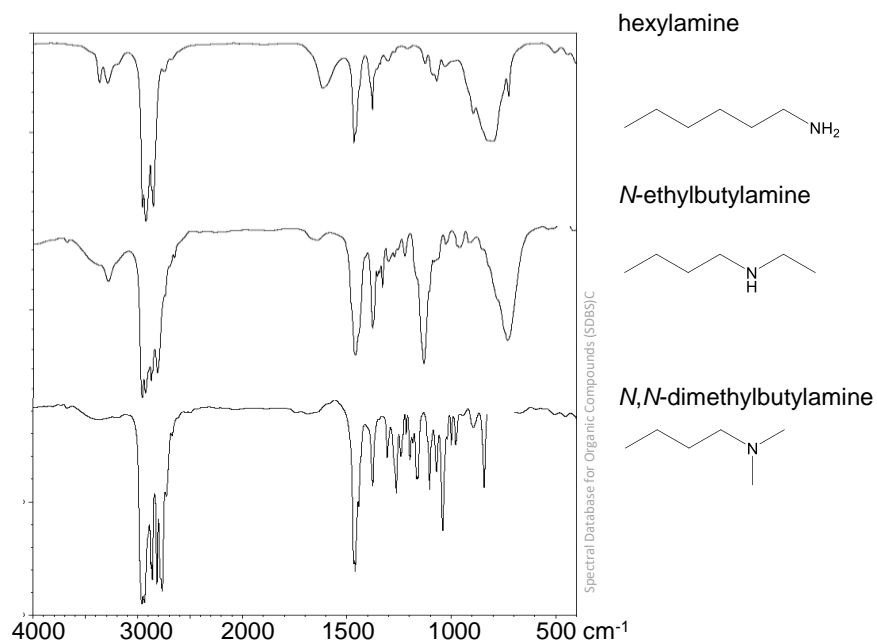


Carboxylic acid are present as H-bonded dimers when neat or in concentrated solution

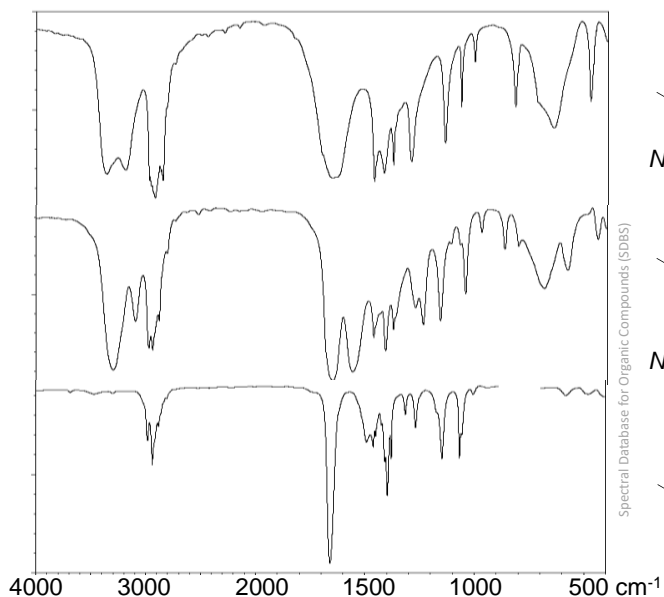


Primary and Secondary Amines

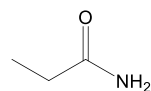
Pavia 2.15



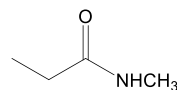
Primary, Secondary and Tertiary Amides



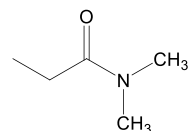
propionamide



N-methylpropionamide



N,N-dimethylpropionamide

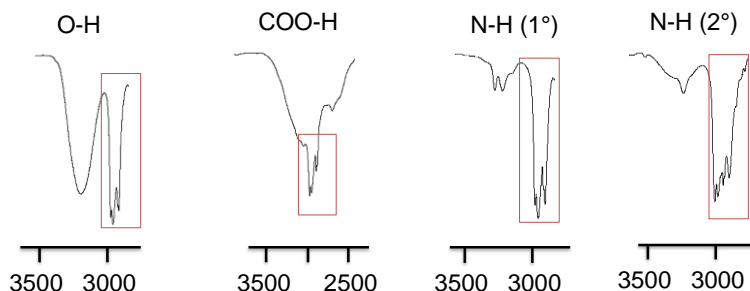


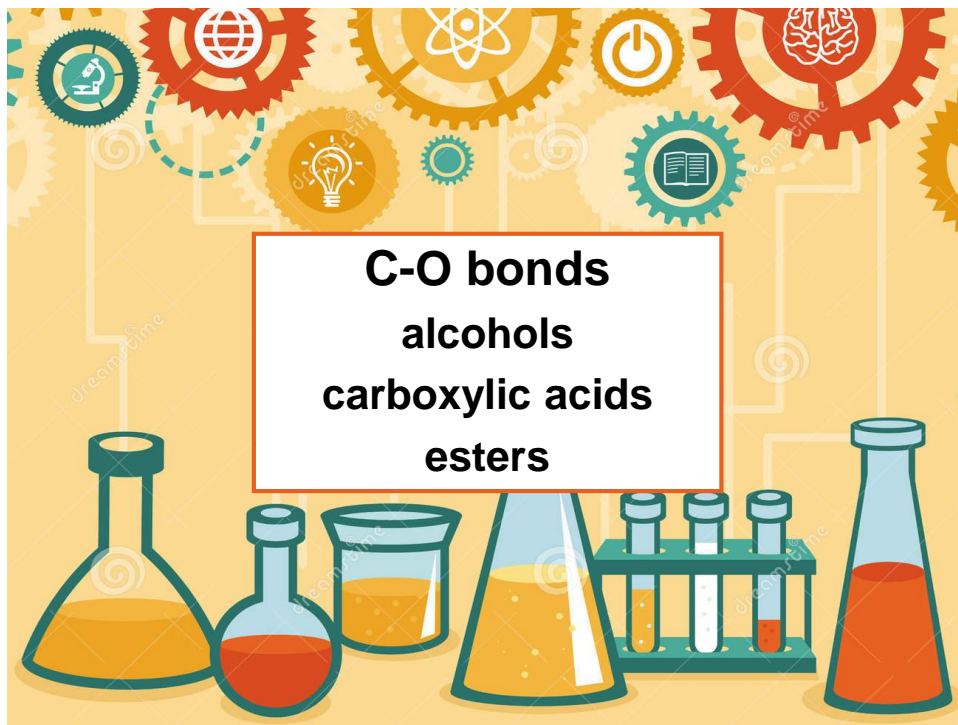
Summary: O-H, N-H stretches

O-H of alcohols and N-H of amine both have stretching vibrations at $\sim 3300 \text{ cm}^{-1}$.

- Alcohol O-H stretching peaks are broad with rounded tip
- Secondary amines (R_2NH) are often broad with a sharp spike.
- Primary amine (RNH_2) are broad with two sharp spikes
- H-bonding important to appearance

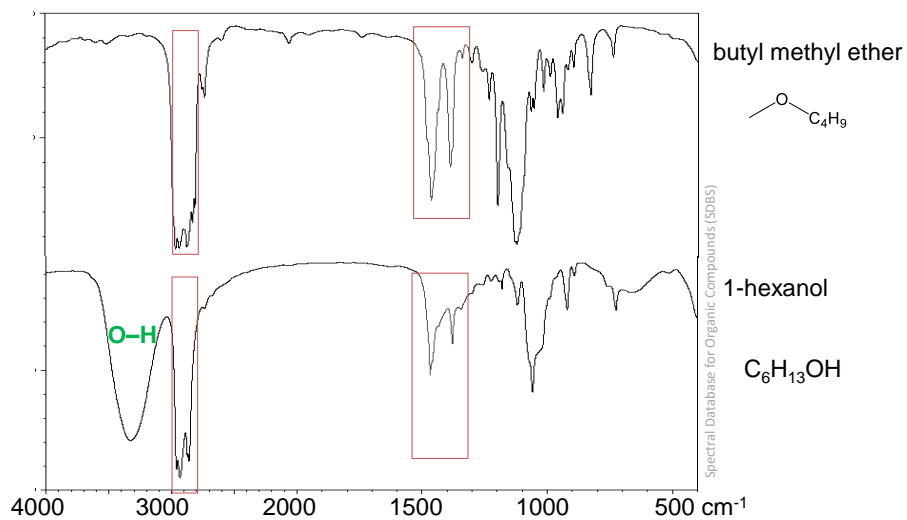
The O-H of carboxylic acids appears as a very broad peak, between 3800 and 2600 cm^{-1} , often with a W-shape.



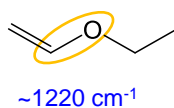
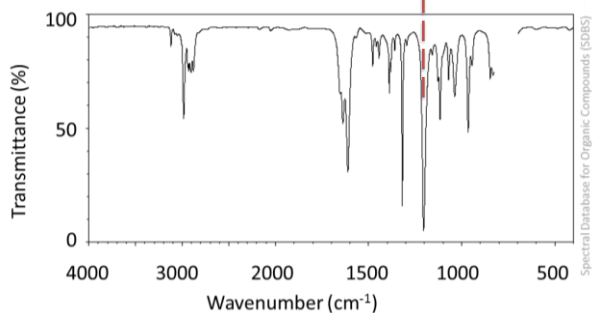
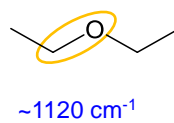
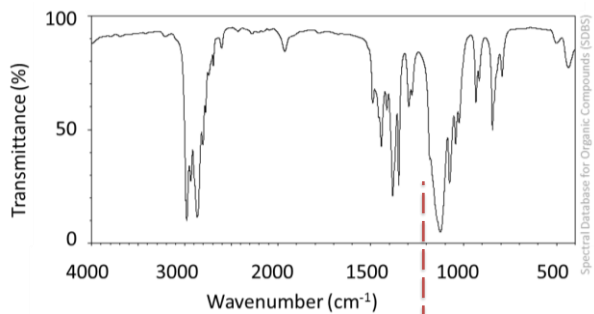


C-O bonds: Alcohols and Ethers

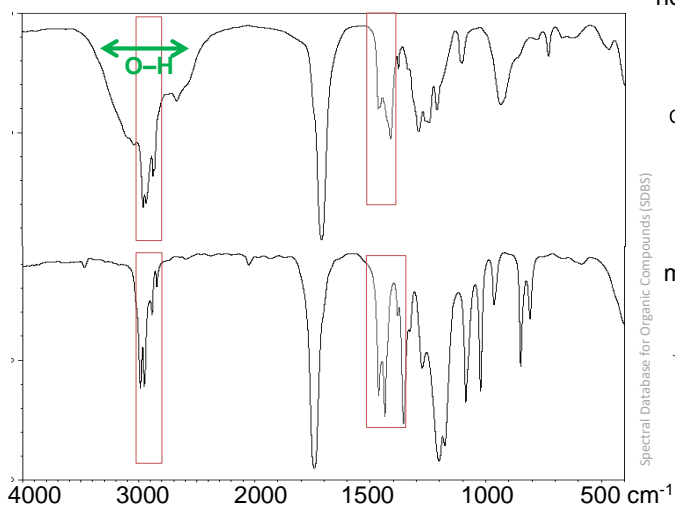
Pavia 2.12 -2.13
Pg. 50



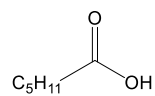
Effect of Resonance on C–O str.



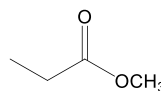
C–O bonds: Esters and Carboxylic Acids

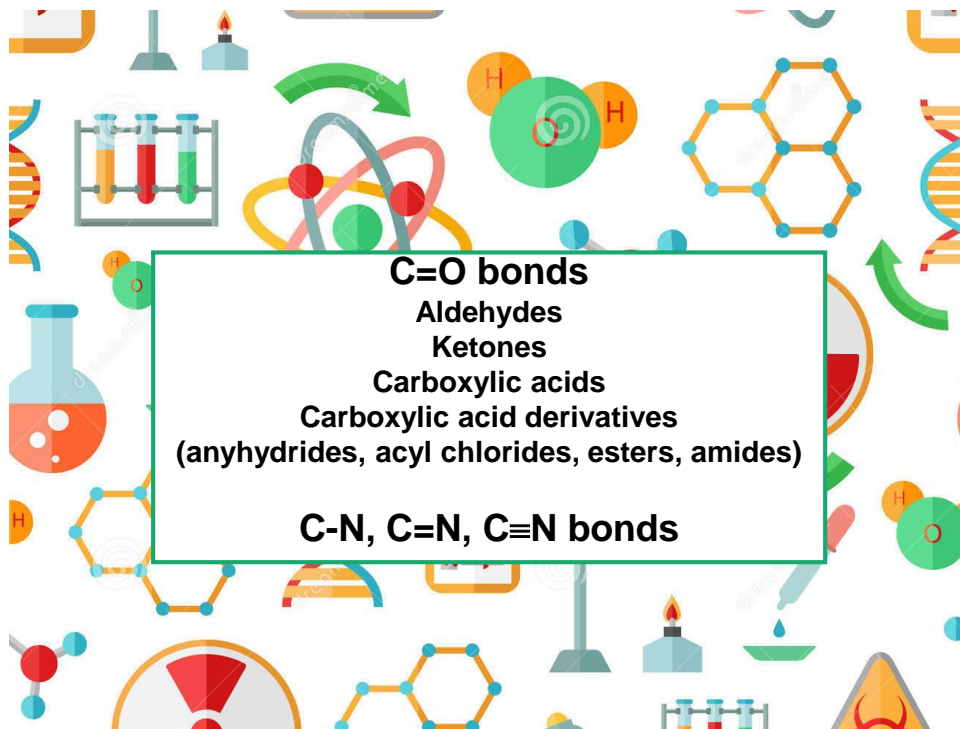


hexanoic acid



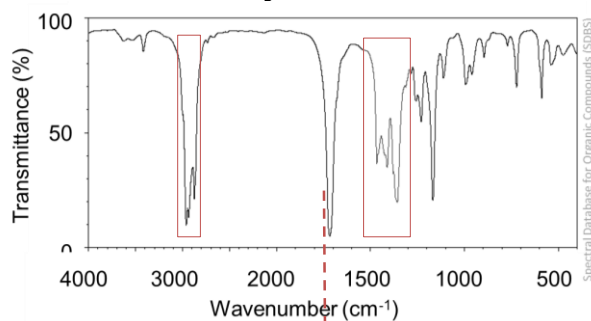
methyl propionate



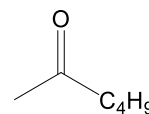


C=O Bonds: Aldehydes and Ketones

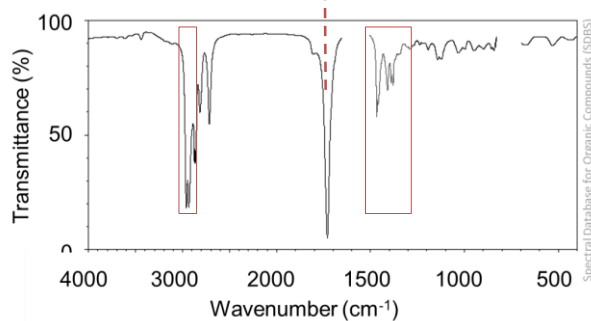
Pavia 2.14B-C



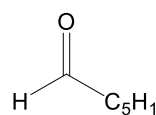
2-hexanone



C=O ~1715 cm⁻¹

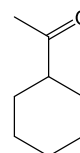
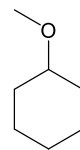
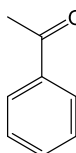
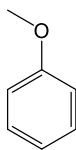
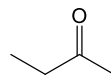
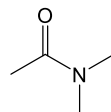
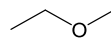
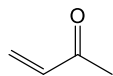
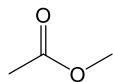
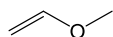
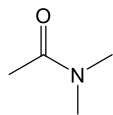


hexanal



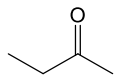
C=O ~1725 cm⁻¹

Resonance Review

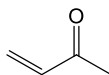


Pavia 2.14A

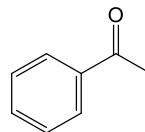
Effect of conjugation in aldehydes and ketones



1718 cm^{-1}



1707 cm^{-1}

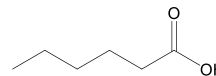


1686 cm^{-1}

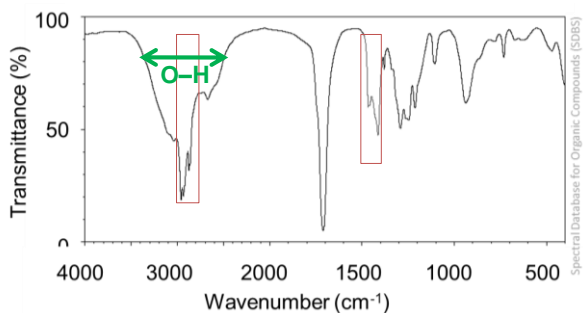
C=O Bonds: Carboxylic Acids and Derivatives

Pavia 2.14D-H

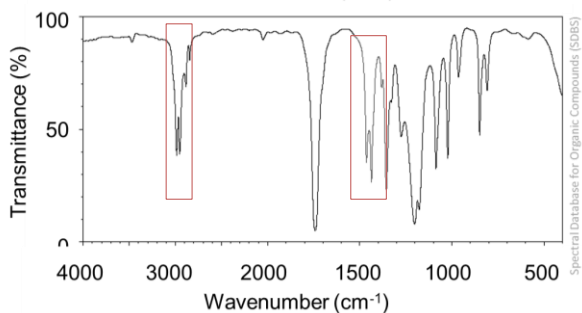
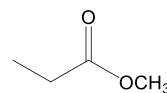
hexanoic acid



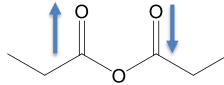
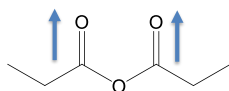
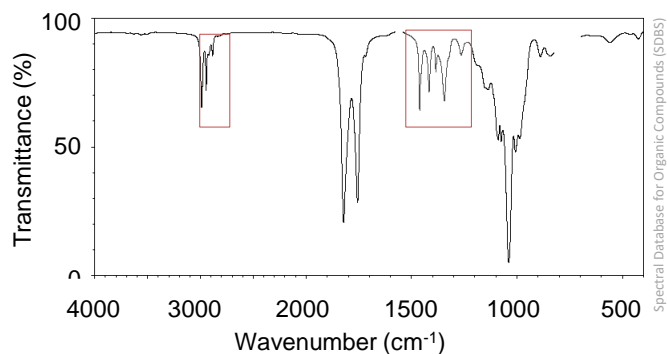
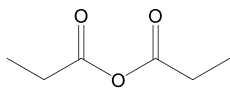
Carboxylic acid are present as H-bonded dimers when neat or in concentrated solution



methyl propionate



propionic anhydride



C=O str. frequencies of acid derivatives

Based on these frequencies, which of the following has the strongest bond?

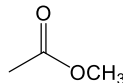
Why?

Pavia 2.14G

1810-1775 cm⁻¹

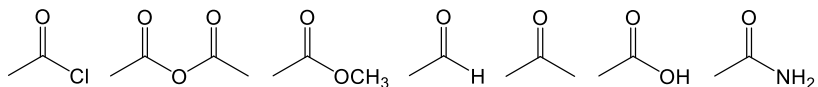
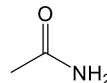


1750-1735 cm⁻¹



Pavia 2.14F

1695-1690 cm⁻¹



1810-1760

1735

1725

1715

1710

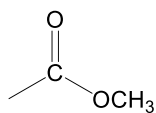
1690

← cm⁻¹ →

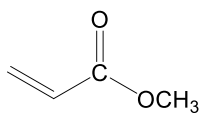
C=O str.: Effect of resonance of C=O of esters...

...conjugation with C=O

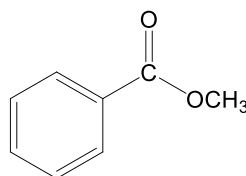
Pavia 2.14E



1748 cm^{-1}

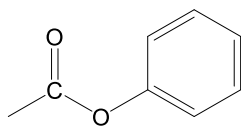


1732 cm^{-1}

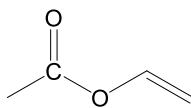


1724 cm^{-1}

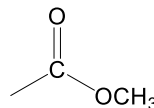
...conjugation with -O-



1765 cm^{-1}

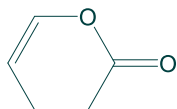


1762 cm^{-1}

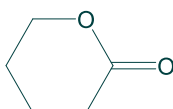


1748 cm^{-1}

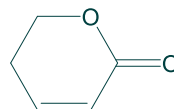
C=O str.: Effect of resonance and ring size on C=O str. frequency of lactones



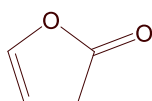
1760 cm^{-1}



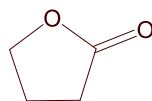
1720 cm^{-1}



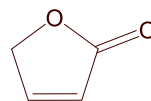
1735 cm^{-1}



1800 cm^{-1}



1770 cm^{-1}



1750 cm^{-1}

Summary of C=O str.

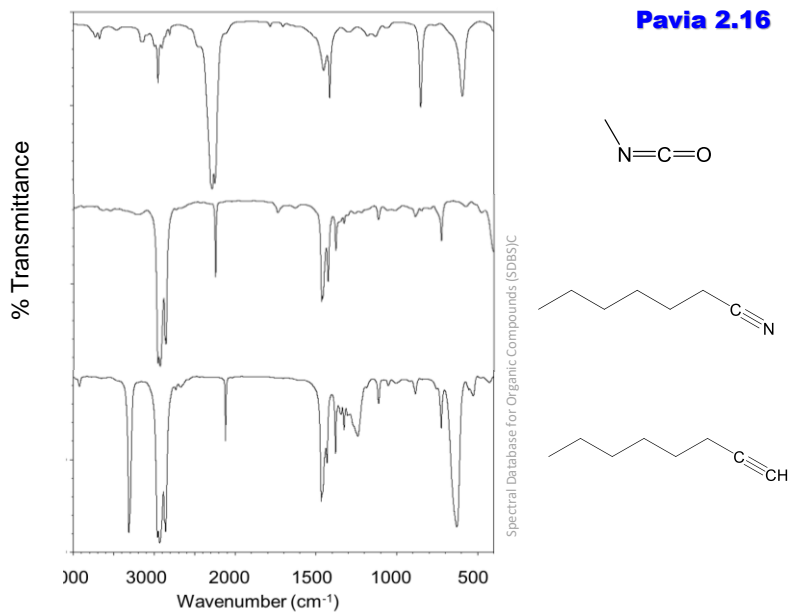
The C=O str. is often the strongest peak in the IR spectrum.

Aldehydes and ketones can be distinguished by the presence of a C(=O)-H str. (aldehydes) and a R-C(=O)-R bend (ketones).

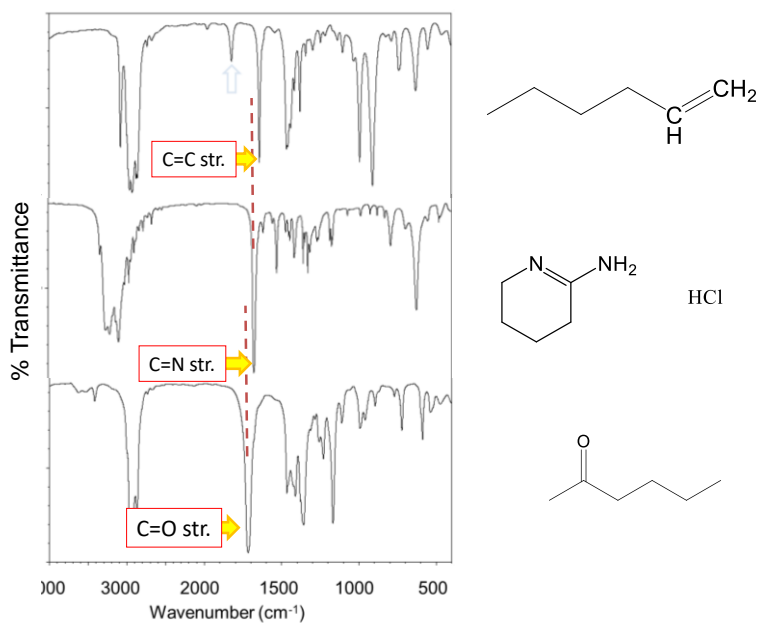
Conjugation of C=O lowers the stretching frequency (corresponding to a weaker bond.)

C=O str. frequencies of carboxylic acid derivatives can be rationalized in terms of the electronic effects of the substituent.

Isocyanates and Nitriles

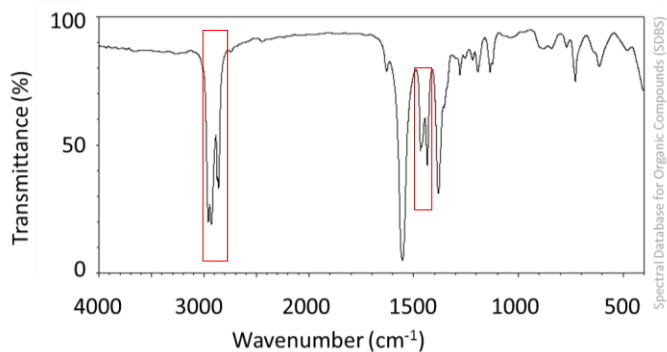
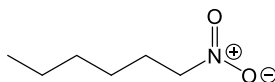


Imines



Pavia 2.17

Nitro compounds



Pavia 2.24F, 15, 16

Carbon – Nitrogen Stretching Vibrations

C–N absorbs around 1200 cm⁻¹.

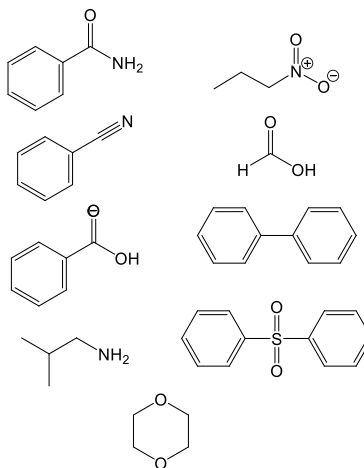
C=N absorbs around 1660 cm⁻¹ and is much stronger than the C=C absorption in the same region.

C≡N absorbs strongly just *above* 2200 cm⁻¹. The alkyne C ≡ C signal is much weaker and is just *below* 2200 cm⁻¹.

Select a compound that best fits each of the following sets of IR bands (in cm^{-1}). Each set corresponds to a list of just a few important bands for each compound.

Benzamide	Diphenyl sulfone
Benzoic acid	Formic acid
Benzonitrile	Isobutylamine
Biphenyl	1-Nitropropane
	dioxane

- a. 3080 (w), nothing 3000–2800, 2230 (s), 1450 (s), 760 (s), 688 (s)
- b. 3380 (m), 3300 (m), nothing 3200–3000, 2980 (s), 2870 (m), 1610 (m), ~900–700 (b)
- c. 3080 (w), nothing 3000–2800, 1315 (s), 1300 (s), 1155 (s)
- d. 2955 (s), 2850 (s), 1120 (s)
- e. 2946 (s), 2930 (m), 1550 (s), 1386 (m)
- f. 2900 (b, s), 1720 (b, s)
- g. 3030 (m), 730 (s), 690 (s)
- h. 3200–2400 (s), 1685 (b, s), 705 (s)
- i. 3350 (s), 3060 (m), 1635 (s)
- s = strong, m = medium, w = weak, b = broad



Reporting IR Spectra in Papers and Progress Reports

A

B

C

D

IR (neat): 3100 (aromatic C–H str.), 2218 (C≡C str.), 1725 (C=O str.) cm^{-1} .

- A** Form of the sample (e.g., neat, nujol mull, CCl_4 solution) or method used (e.g., ATIR).
- B** Only list peaks that can be assigned to bonds in the structure you are describing. You do not need to list all the other peaks that might be present in the compound
- C** Assign the peaks to specific bonds, and mode of vibration.
- D** Units!

