Factor effecting vibrational frequency

1. Coupling interaction.
2. Fermi resonance.
3. Hydrogen bonding.
4. Electronic displacement effects.

1- Coupling interaction

- It is expected that there is a stretching absorption frequency for an isolated C-H bond. But in case of Methylene(-CH2-) group, two absorption occurs which corresponds to symmetric & asymmetric vibrations.
- Asymmetric vibration always takes place at high wave number compared with symmetric vibration.
- These are knows as coupled vibrations because vibration occurs at different frequencies than that required for an isolated C-H stretching.

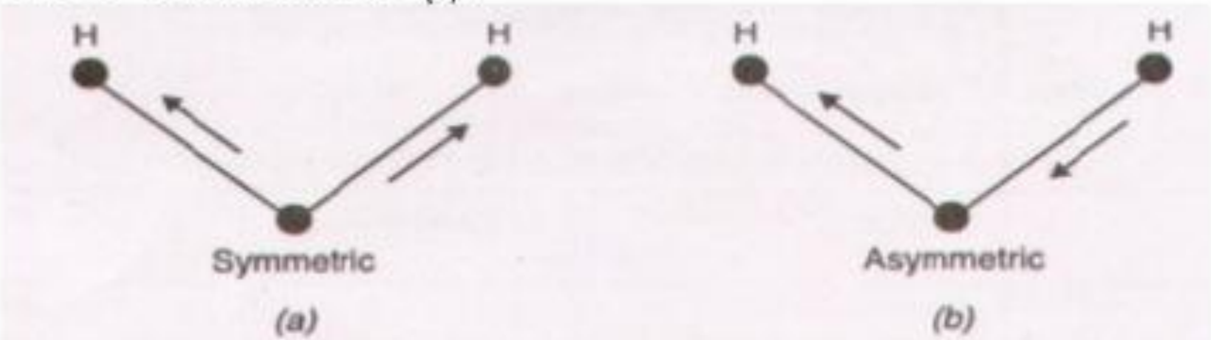
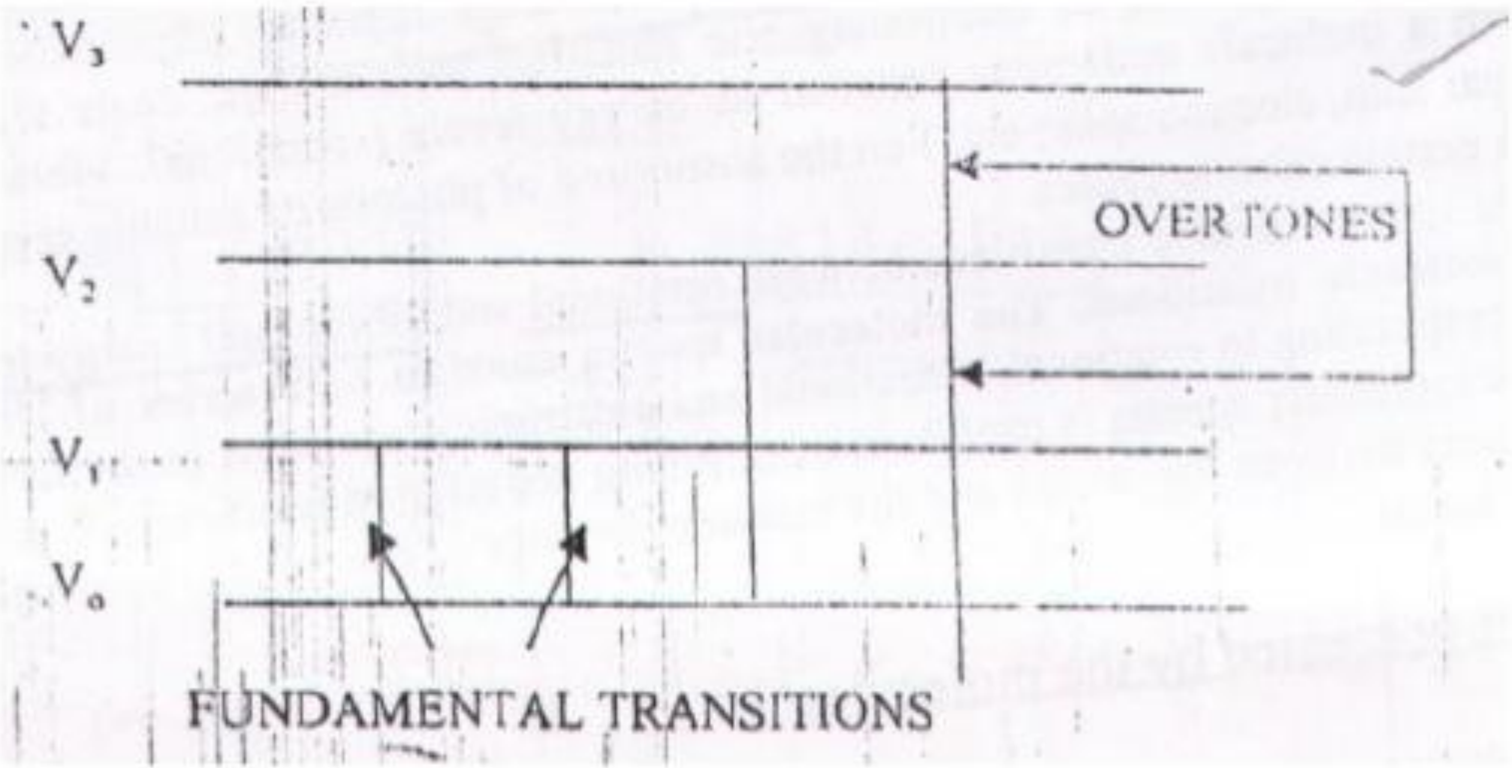


Fig. 3.25 : Stretching vibrations in methylene group.

2- Fermi resonance

- It occurs when a fundamental vibration couples with an overtone or combination band.
- When an overtone or a combination of band has the same frequency to a fundamental, two bands appear close together.



2- Fermi resonance

- The effect is greatest when the frequencies match, and the two bands are referred to as a *Fermi doublet*.
- When two bonds share a common atom as in the case of a linear tri-atomic molecule CO2, consisting of two CO bonds (O=C=O), two fundamental stretching vibrations: symmetric and asymmetric takes place.
- As the symmetric stretching vibration produces no change in the dipole movement of the molecules, it is inactive in the IR spectra.
- In the asymmetric vibration, one oxygen approach the carbon atom as other may be away. Asymmetric stretching vibration appears in the IR region 2330 cm-1

3- Hydrogen bonding

- Hydrogen bonding gives rise to downward frequency shifts.
- Stronger the bonding, greater the absorption shift towards lower wave number from normal value.
- Generally, intermolecular hydrogen bonds are sharp and well defined.
- Intermolecular hydrogen bonds are concentration dependent. On dilution, intensities of such bands decreases and finally disappears.

4- Electronic Displacement Effect

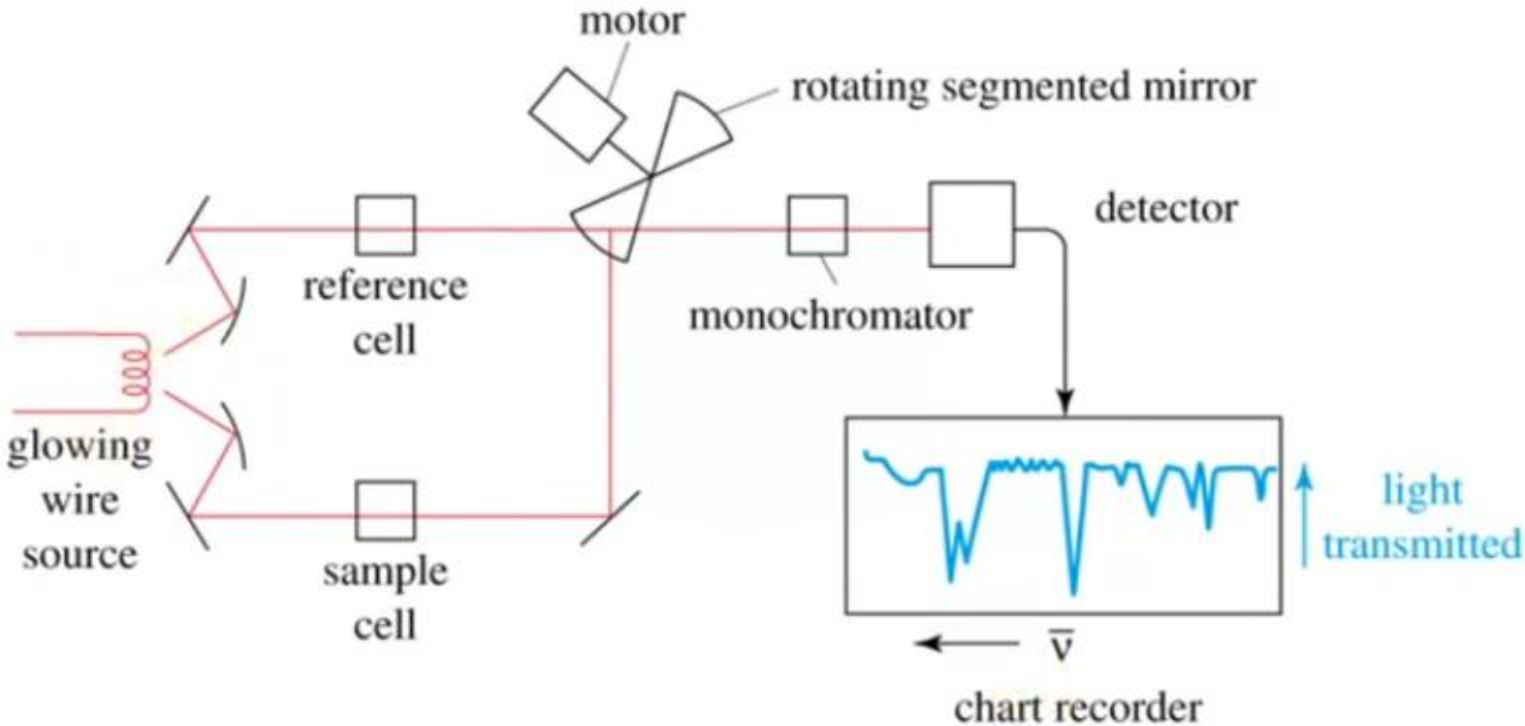
- The frequency shifts from normal position of absorption occur because of electronic effects which include: Inductive effect, mesomeric effect, configuration effect or field effect .
- Under the influence of these effects, the force constant (K) or the bond strength changes and its absorption frequency shifts from the normal value.

INFRARED ABSORPTION SPECTROSCOPY

- An IR spectrum is used to identify functional groups that are present.
  - Not enough information is present to conclusively identify a structure unless an IR spectrum of an authentic (known) sample of the compound is available.

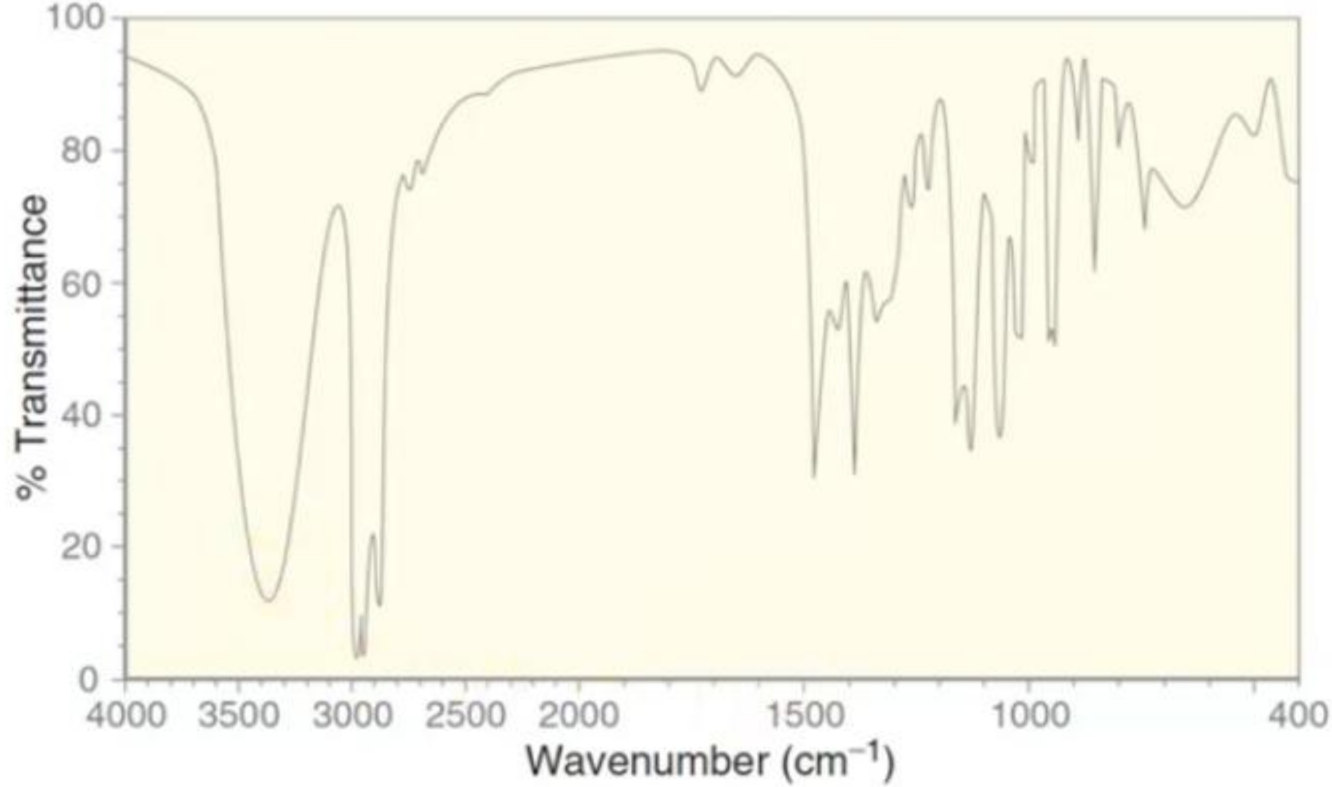
- Absorptions from specific functional groups are found in certain regions of the IR spectrum.

INFRARED ABSORPTION SPECTROSCOPY



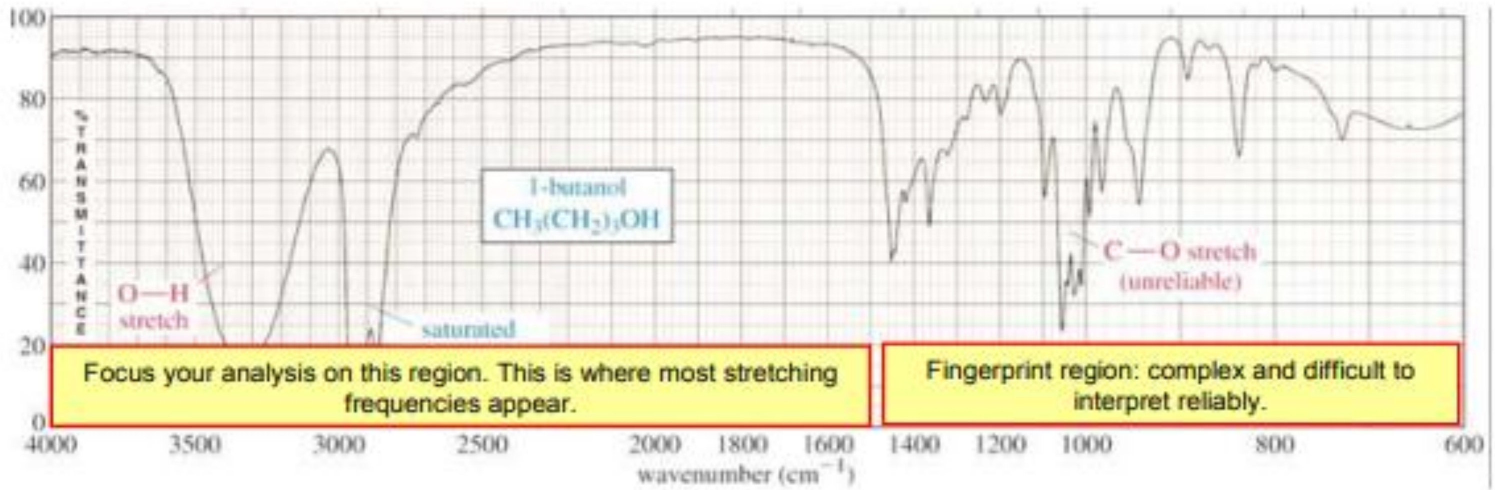
INFRARED ABSORPTION SPECTROSCOPY

The General Shape of an IR Absorbance Spectrum



THE FINGERPRINT REGION

Although the entire IR spectrum can be used as a fingerprint for the purposes of comparing molecules, the **600 - 1400 cm^{-1}** range is called the **fingerprint region**. This is normally a complex area showing many bands, frequently overlapping each other. This complexity limits its use to that of a fingerprint, and should be ignored by beginners when analyzing the spectrum. As a student, you should focus your analysis on the rest of the spectrum, that is the region to the left of 1400 cm^{-1}.

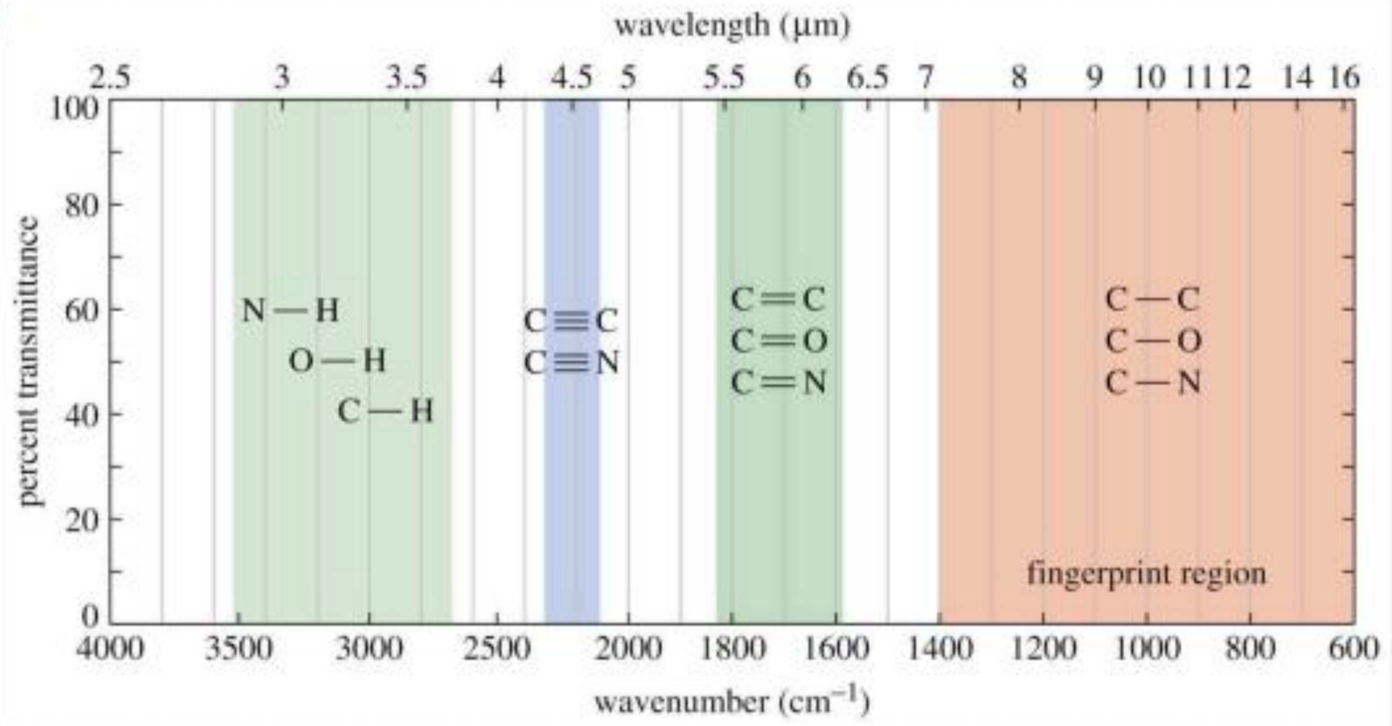


Graphics source: Wade, Jr., L.G. *Organic Chemistry*, 6th ed. Pearson Prentice Hall Inc., 2006

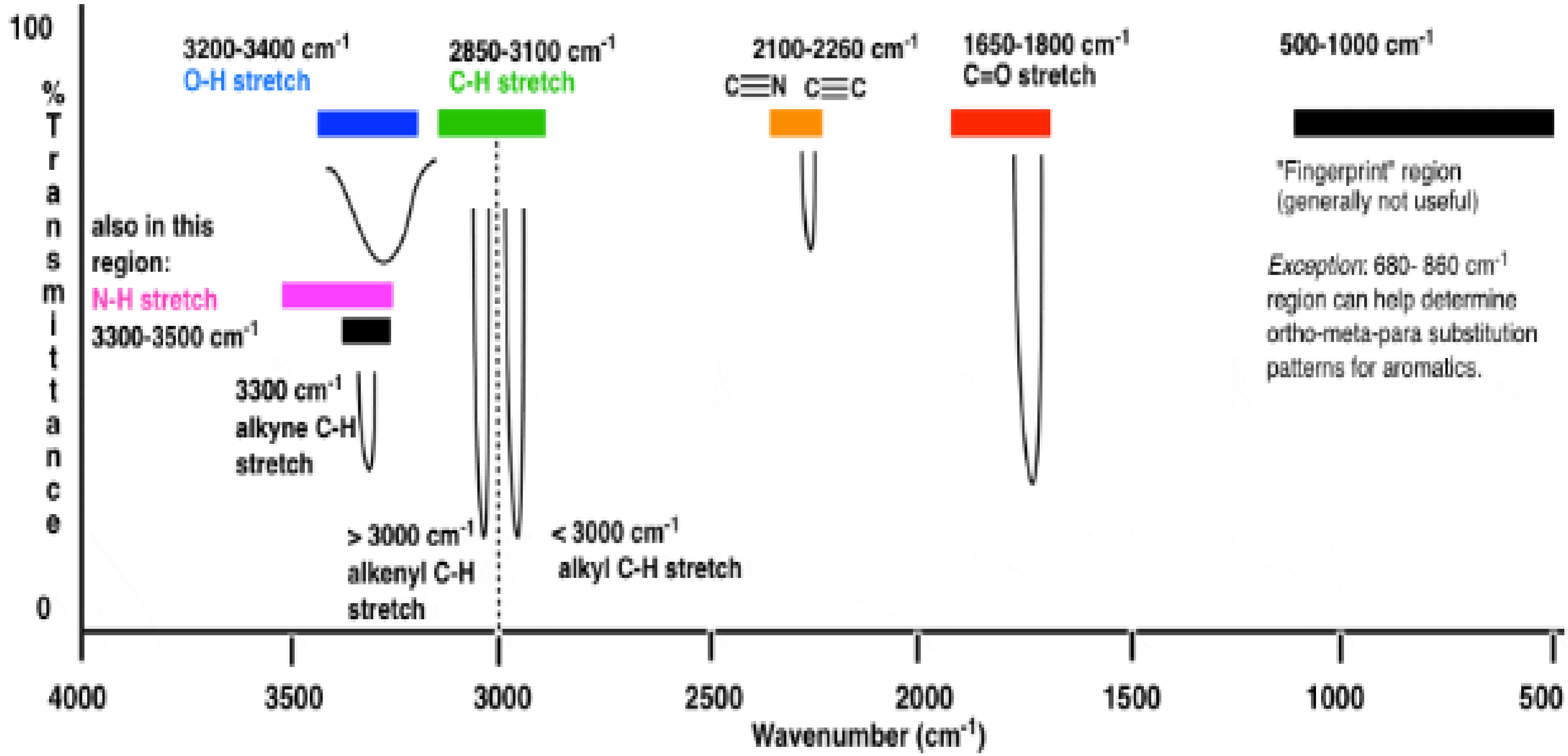
C-H Alkanes (stretch)	stretch	3000 – 2850	s
$-CH_3$	Bend	1450 - 1375	m
$-CH_2-$	Bend	1465	m
Alkenes	Stretch	3100 - 3000	m
	bend	1000-1700	s
Aromatics	Stretch	3150-3050	S
	Out of plane bend	1000-700	S
Alkyne	Stretch	3300	s
Aldehyde		2900 – 2800 2800 - 2700	W w
C=C Alkene		1600-1680	
C=C Aromatic		1400 – 1600	
CC Alkyne		2100- 2250	
C=O Aldehyde		1740 - 1720	
C=O Ketone		1725 - 1705	
C=O Carboxylic acid		1725 - 1700	

C=O Ester		1750 – 1730	
C=O Amide		1700 - 1640	
C=O Anhydride		1810 1760	
C-O Alcohols, ethers, esters, Carboxylic acid		1300 – 1000	
O-H alcohols, Phenols			
Free		3650-3600	
H-Bonded		3400 - 3200	
Carboxylic acid		3300- 2500	
N-H primary and secondary amines		3500	
CN Nitriles		2260- 2240	
N=O Nitro		1600-1500 1400 – 1300	
C-X Floride		1400 - 1000	
Chloride		800 - 600	
Bromide , Iodide		<600	

Summary of IR Absorptions

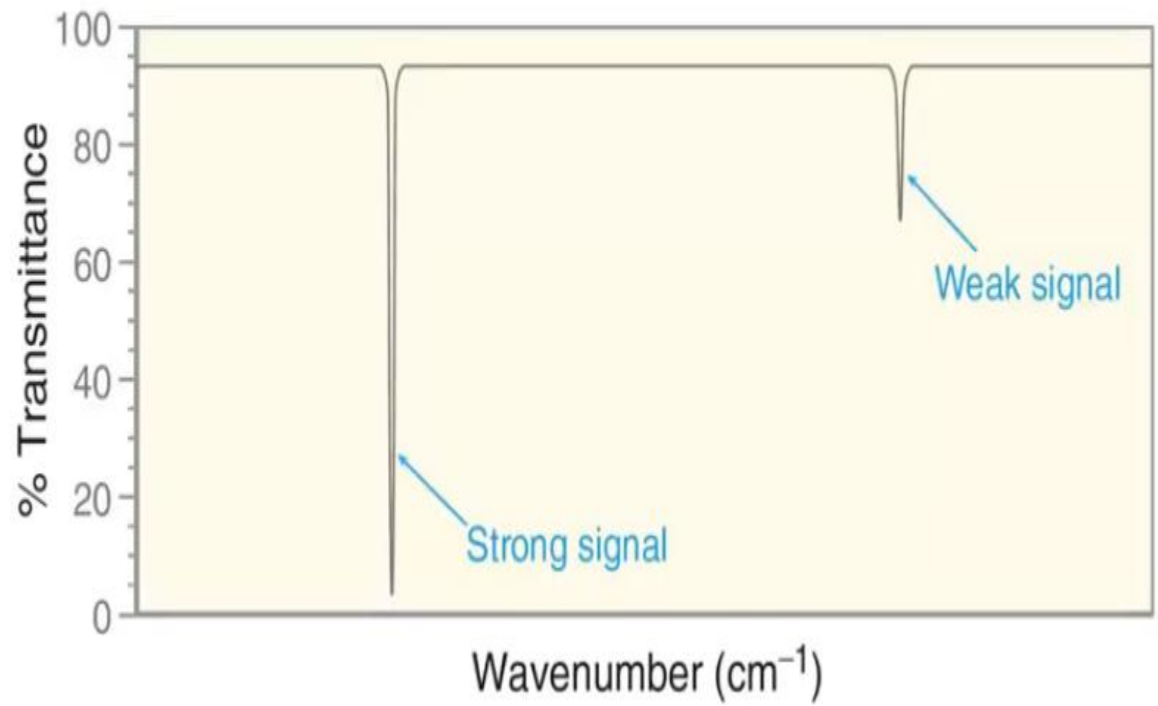


Typical Infrared Absorption Values For Various Types of Bonds



Signal Characteristics: Intensity

The most important factor that influences the intensity of an IR absorption band is the change in dipole moment that occurs during a vibration.



Signal Characteristics: Intensity

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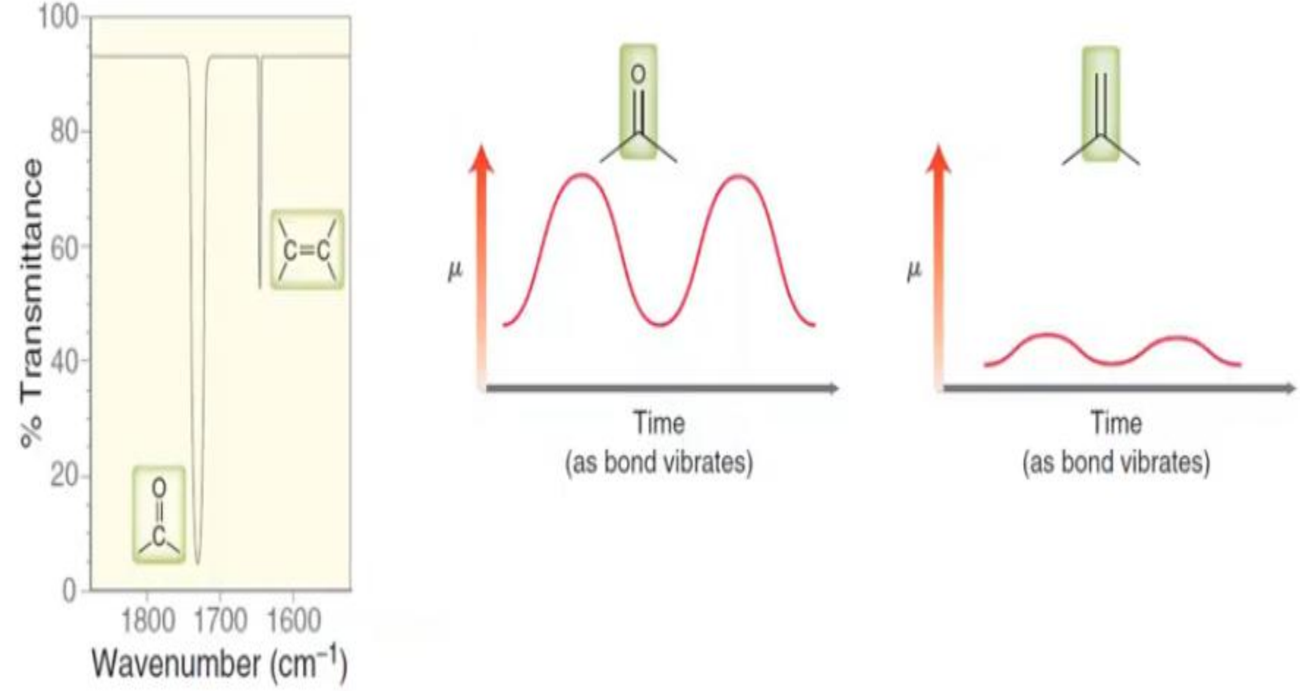
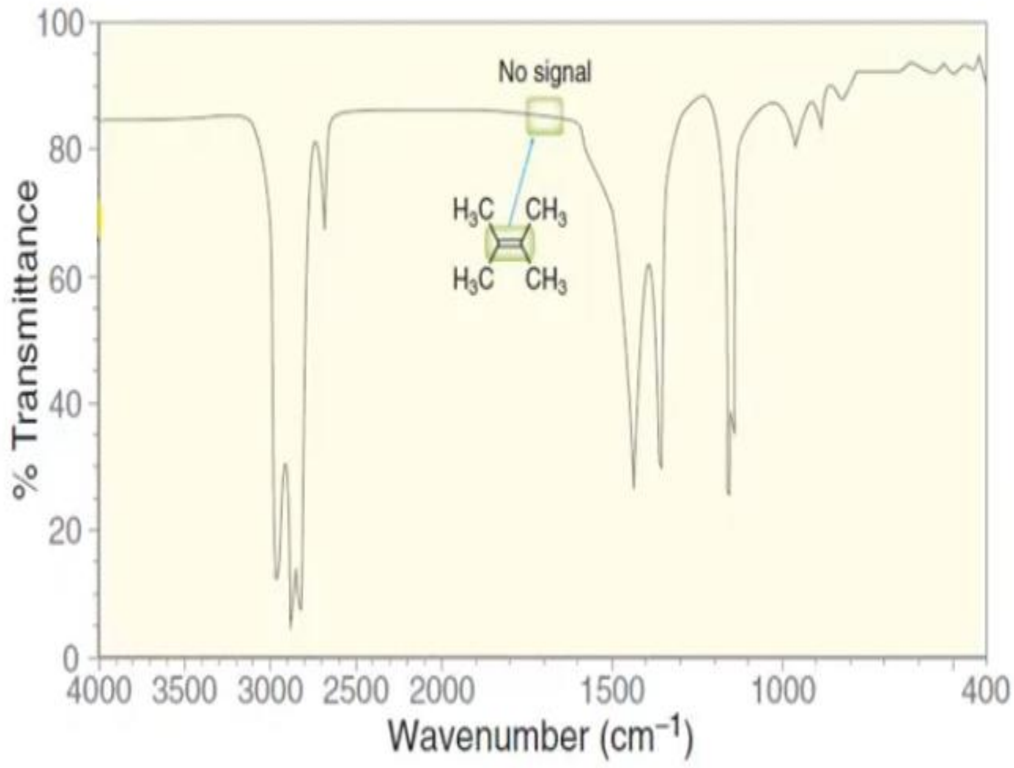


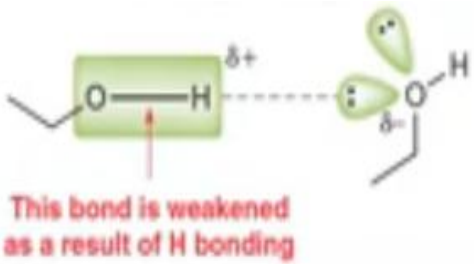
Signal Characteristics: Intensity

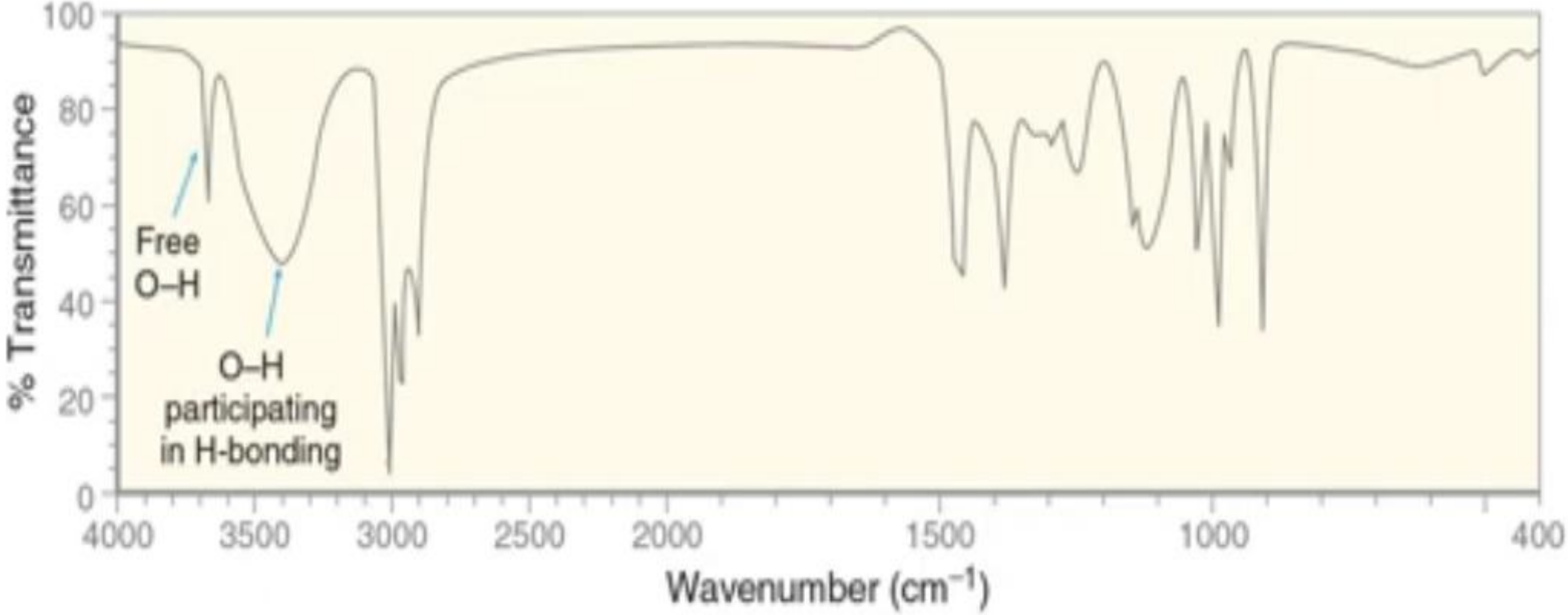
In fact, some alkenes do not even produce any C=C signal at all. For example, consider the IR spectrum of 2,3-dimethyl-2-butene. This alkene is symmetrical. That is, both vinylic positions are electronically identical, and the bond has no dipole moment at all.



Effects of Hydrogen bond

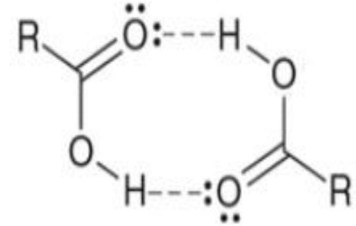
Alcohols

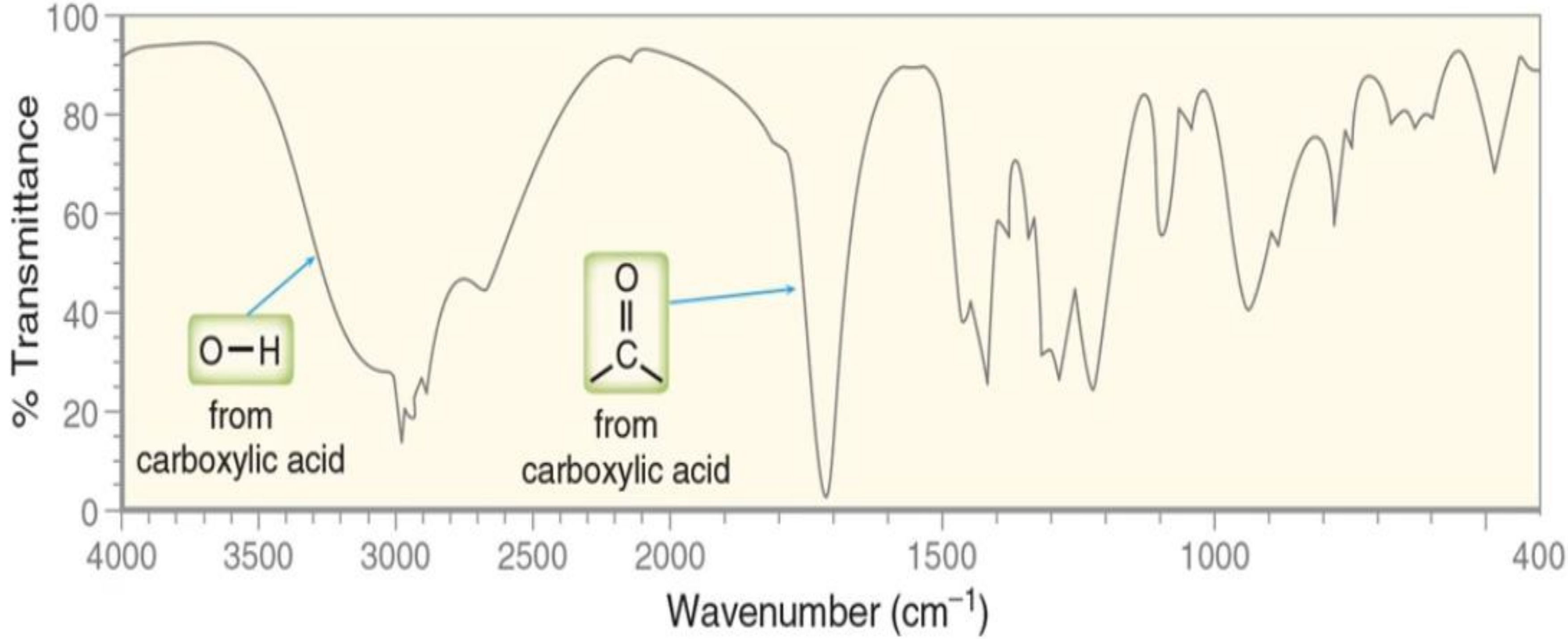




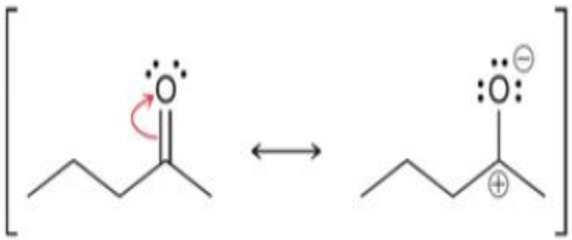
Effects of Hydrogen bond

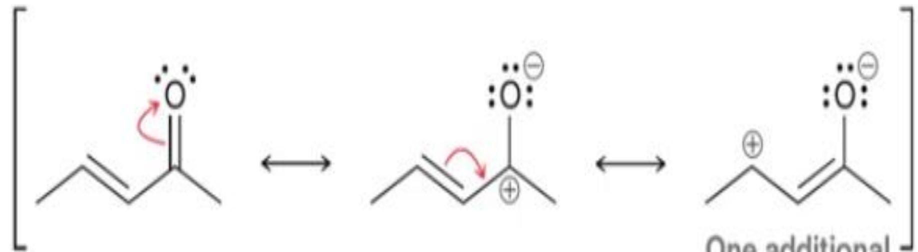
Carboxylic acid



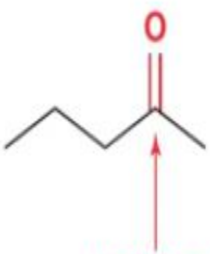


Effect of Resonance



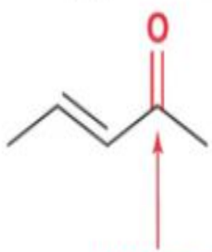


A ketone



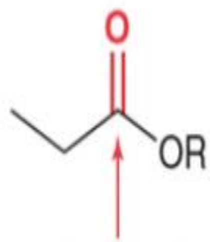
$1720\ cm^{-1}$

A conjugated ketone



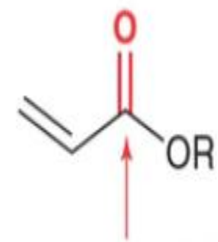
$1680\ cm^{-1}$

An ester



$1740\ cm^{-1}$

A conjugated, unsaturated ester



$1710\ cm^{-1}$

Carbon-Hydrogen Bonds

- Bonds with more *s* character absorb at a higher frequency.
  - *sp^3* (alkane) C-H
    - just below 3000 cm^{-1} (to the right
  - *sp^2* (alkene or aromatic hydrocarbon) C-H
    - just above 3000 cm^{-1} (to the left)
  - *sp* (alkyne) C-H
    - at 3300 cm^{-1}

Bond Lengths and Bond Strengths for (sp^3, sp^2, sp) C-H Bonds

Hybridization	*sp^3* C(H$_2$)–H	*sp^2* C(H)–H	*sp* —C≡C–H
s Character	25 % s	33 % s	50 % s
Length	1.10 Å	1.09 Å	1.06 Å
Strength	98 kcal/mol 410 kJ/mol	104 kcal/mol 435 kJ/mol	125 kcal/mol 523 kJ/mol

Higher s character, stroger bond.