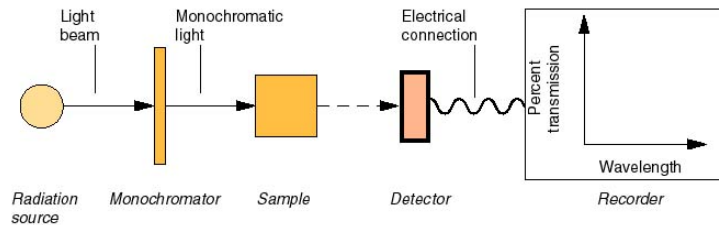
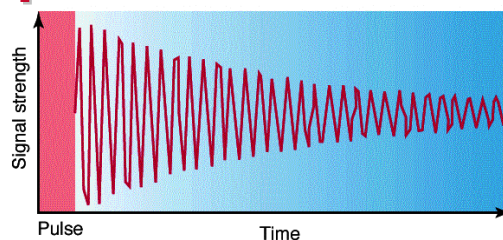


## Continuous-Wave (CW) Spectrometers



- ◆ The spectrometer scans through a range of frequencies
- ◆ The sample is interrogated with one frequency at a time.
- ◆ As the frequency range is scanned, a plot of signal intensity vs. frequency is generated.

## Fourier Transform (FT) Spectrometers



A typical FID

- ◆ The sample is interrogated with a range of frequencies, “all frequencies at once.”
- ◆ The decay of the signal over time is observed as a **F**ree **I**nduction **D**ecay (FID)
- ◆ A Fourier transform changes the signal vs. time plot into a signal vs. frequency plot.

## FT Spectrometers

- ◆ **A Fourier-transform instrument**
  - Irradiates the sample with a specified range of frequencies (**sweep width**) for a specified period of time (**pulse width**).
  - Observes the FID (**observation time**) and waits for sample to “relax” to its ground state before irradiating again (**relaxation delay**).
  - Transforms the FID into a signal/frequency plot.
- ◆ **Relaxation times: needed to make sure signal is reproducible**
  - Short for IR spectroscopy (several microseconds)
  - Long for NMR (several seconds)

## Advantages of FT over CW Spectrometers

- ◆ **If a signal is weak, many scans must be averaged to enhance the signal/noise ratio.**
  - Signal/noise ratio rises as the **square root** of number of scans
  - Only FT instruments can obtain a large number of scans in a reasonable time.
- ◆ **A scan can be performed much more quickly.**
  - CW-IR: 7 minutes; FT-IR: 1-3 seconds.
  - CW-NMR: 5 minutes; FT-NMR: 5 seconds.

## Infrared Spectroscopy

- ◆ The IR region covers
  - $7.8 \times 10^{-7}$  m (just above the visible region) to
  - $2.0 \times 10^{-3}$  m (just below the microwave region)
- ◆ Organic chemistry uses mainly the vibrational IR, which covers
  - $2.5 \times 10^{-6}$  m ( $2.5 \mu\text{m}$ ) to  $2.5 \times 10^{-5}$  m ( $25 \mu\text{m}$ )
- ◆ Absorption of IR radiation in this region causes molecules to transition from a lower vibrational energy level to a higher one

## Infrared Spectroscopy

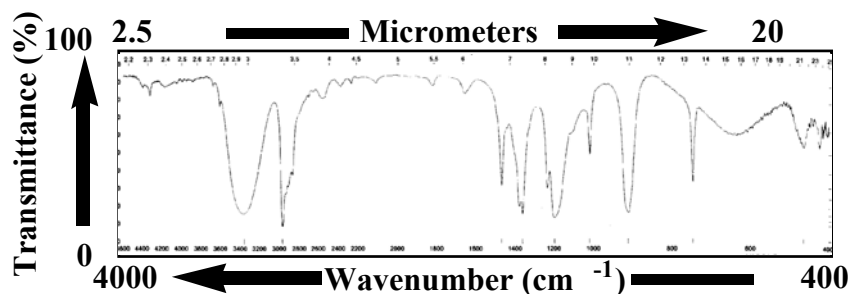
- ◆ The frequency of IR radiation is commonly expressed in wavenumbers ( $\bar{\nu}$ )
- ◆ **Wavenumber:** the number of waves per centimeter,  $\text{cm}^{-1}$  (“reciprocal centimeters”)
- ◆ Expressed in wavenumbers, the vibrational IR extends from  $4000 \text{ cm}^{-1}$  to  $400 \text{ cm}^{-1}$

$$\frac{10,000 \mu\text{m} \cdot \text{cm}^{-1}}{2.50 \mu\text{m}} = 4000 \text{ cm}^{-1}$$

$$\frac{10,000 \mu\text{m} \cdot \text{cm}^{-1}}{25.0 \mu\text{m}} = 400 \text{ cm}^{-1}$$

## Infrared Spectroscopy

- ◆ Standard IR spectra are recorded on the following scale:



## Molecular Vibrations

- ◆ Atoms joined by covalent bonds undergo continual vibrations relative to each other
- ◆ The energies associated with these vibrations are **quantized**; within a molecule, only specific vibrational energy levels are allowed
- ◆ The energies associated with transitions between vibrational energy levels for most covalent bonds are from 2 to 10 kcal/mol (8.4 to 42 kJ/mol)

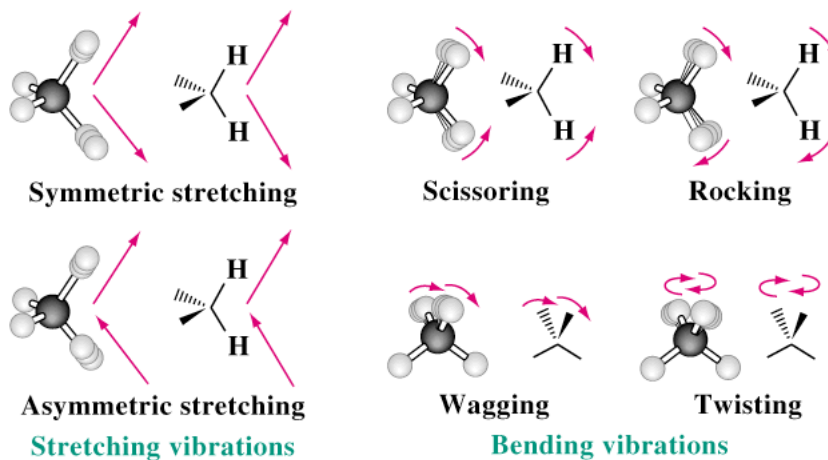
## Molecular Vibrations

- ◆ For a molecule to absorb IR radiation, the bond undergoing vibration
  - must be polar and
  - its vibration must cause a periodic change in the bond moment
- ◆ Covalent bonds which do not meet these criteria are said to be IR inactive
  - the C-C double and triple bonds of symmetrically substituted alkenes and alkynes, for example, do not absorb IR radiation because they are not polar bonds

## Molecular Vibrations

- ◆ For a nonlinear molecule containing  $n$  atoms, there are  $3n - 6$  allowed fundamental vibrations
- ◆ For even a relatively small molecule, a large number of vibrational energy levels exist and patterns of IR absorption can be very complex
- ◆ The simplest vibrational motions are bending and stretching

## Fundamental modes of vibration for a methylene group



## Molecular Vibrations

- ◆ Consider two covalently bonded atoms as two vibrating masses connected by a spring
- ◆ As the bond vibrates, its energy continually changes from kinetic to potential and vice versa
- ◆ The total energy (KE + PE) is proportional to the frequency of vibration

## Molecular Vibrations

- ◆ For a simple harmonic oscillator, the frequency of a stretching vibration is given by an equation derived from Hooke's law for a vibrating spring

inverse frequency  $\rightarrow \bar{\nu} = \frac{1}{2\pi c} \sqrt{\frac{NK}{\mu}}$   
(wavenumbers)

N = Avogadro's number

c = velocity of light

K = a force constant, which is a measure of the

bonds' strength

$\mu$  = the reduced mass

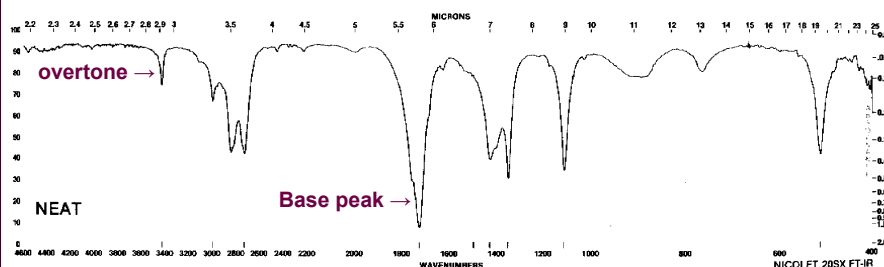
$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

## Molecular Vibrations

- ◆ From this equation, we see that the **position** of absorption of a stretching vibration depends on
  - the strength of the vibrating bond and
  - the masses of the atoms connected by the bond
- ◆ The stronger the bond and the lighter the atoms connected by the bond, the higher the wavenumber of the vibration
- ◆ The **intensity** of absorption depends primarily on the polarity of the vibrating bond

## Overtone

- ◆ Especially strong peaks will show “overtone”
- ◆ These appear at twice the base frequency
- ◆ Inexperienced interpreters often interpret overtones as separate peaks!!



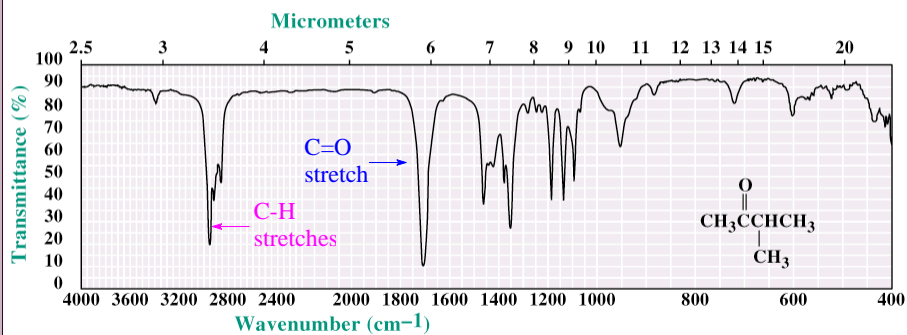
## Correlation Tables

- ◆ Characteristic IR absorptions for the types of bonds and functional groups we deal with most often

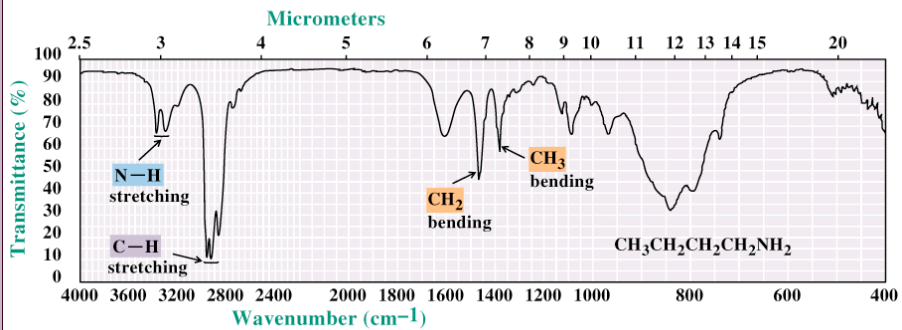
Bond	Frequency (cm <sup>-1</sup> )	Intensity
O-H	3200-3650	strong and broad
N-H	3100-3500	medium
C-H	2850-3300	medium to strong
C=O	1630-1810	strong
C=C	1600-1680	weak
C-O	1050-1250	strong



### Infrared spectrum of 3-methyl-2-butanone



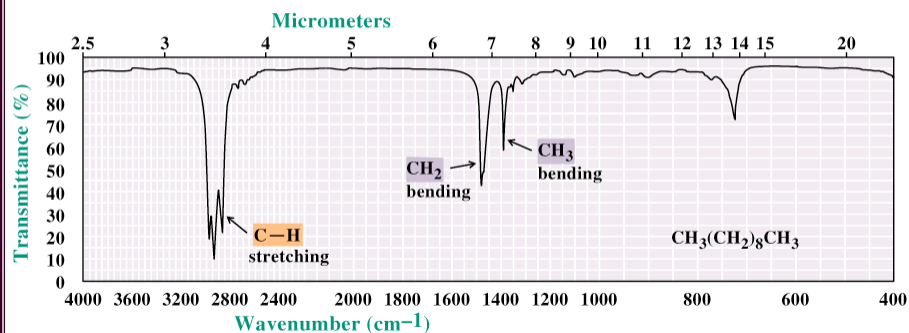
### IR spectrum of 1-butanamine



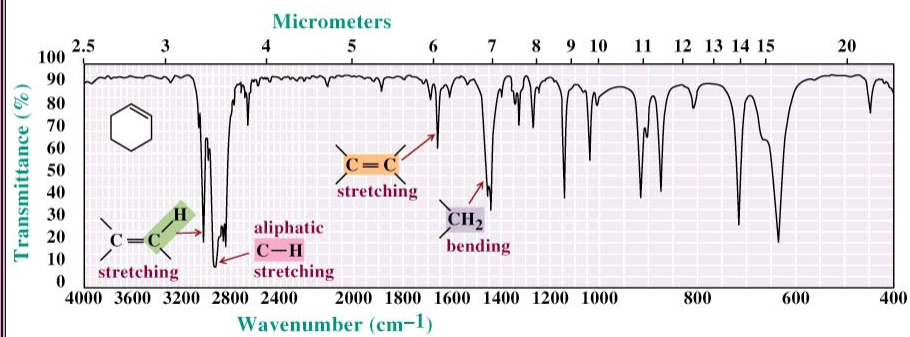
# Hydrocarbons

Hydro-carbon	Vibration	Frequency (cm <sup>-1</sup> )	Intensity
<b><u>Alkane</u></b>			
C-H	stretching	2850 - 3000	strong
CH <sub>2</sub>	bending	1450	medium
CH <sub>3</sub>	bending	1375 and 1450	weak to medium
<b><u>Alkene</u></b>			
C-H	stretching	3000 - 3100	weak to medium
C=C	stretching	1600 - 1680	weak to medium
<b><u>Alkyne</u></b>			
C-H	stretching	3300	medium to strong
C≡C	stretching	2100-2250	weak

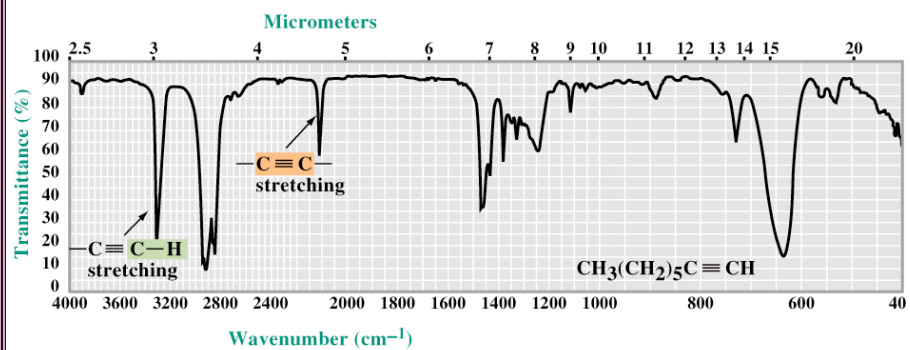
IR spectrum of decane



### IR spectrum of cyclohexene



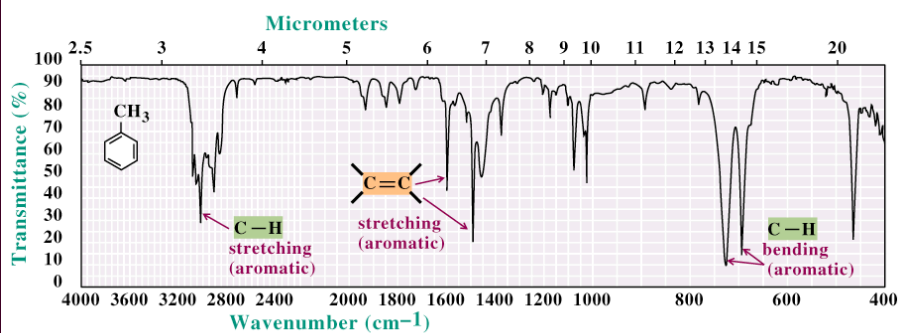
### Infrared spectrum of 1-octyne



## Conjugated Hydrocarbons

- ◆ Conjugation lowers a double-bond stretch by about  $40\text{ cm}^{-1}$ .
  - Conjugated carbonyls also show a strong  $\text{C}=\text{C}$  stretch at about  $1650\text{ cm}^{-1}$ .
- ◆ Aromatic rings have two or three peaks in the range  $1600\text{-}1500\text{ cm}^{-1}$ .

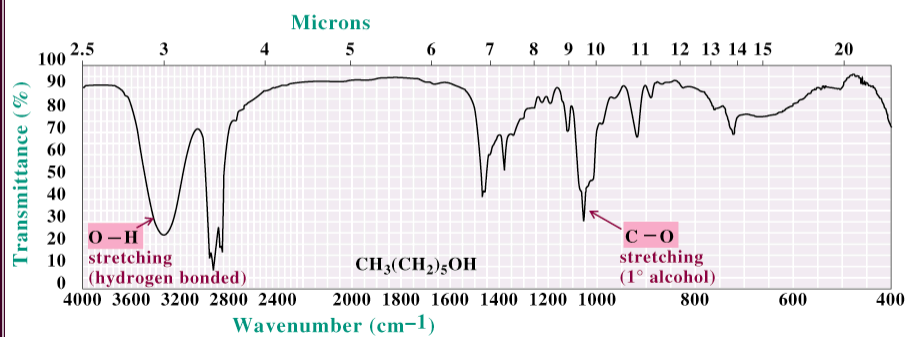
IR spectrum of toluene



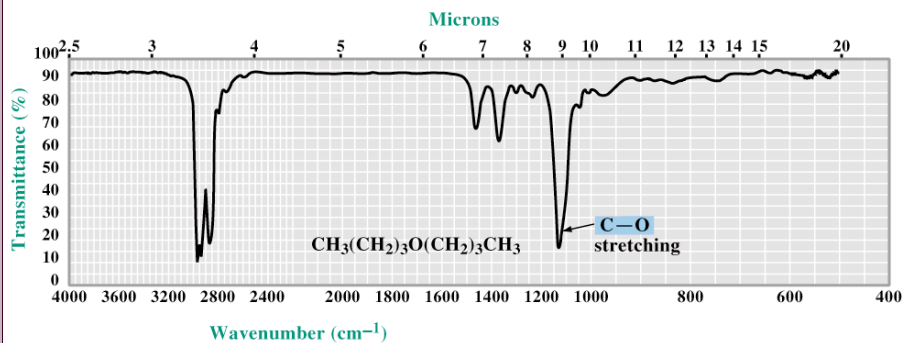
# Alcohols & Ethers

Bond	Frequency, $\text{cm}^{-1}$	Intensity
O-H (free)	3600-3650	weak
O-H (hydrogen bonded)	3200 - 3500	medium, broad
C-O	1050 - 1250	medium

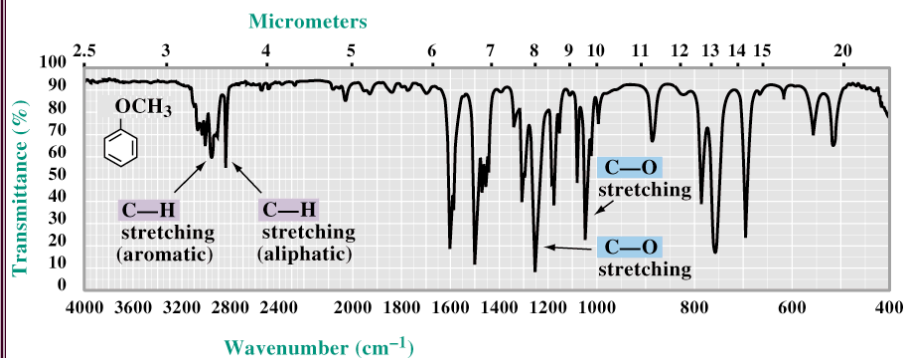
IR spectrum of 1-hexanol



### Infrared spectrum of dibutyl ether



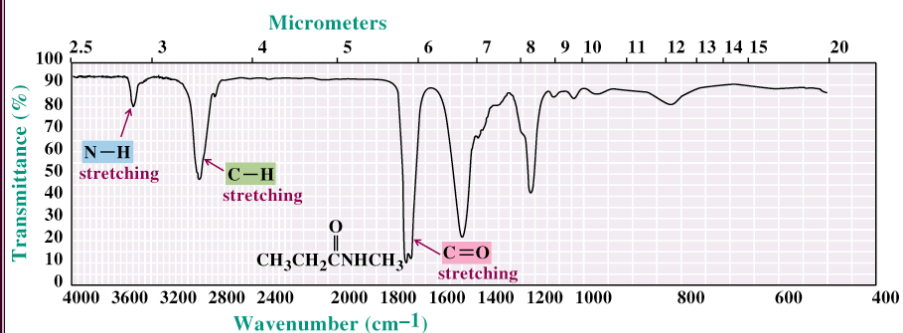
### Infrared spectrum of anisole



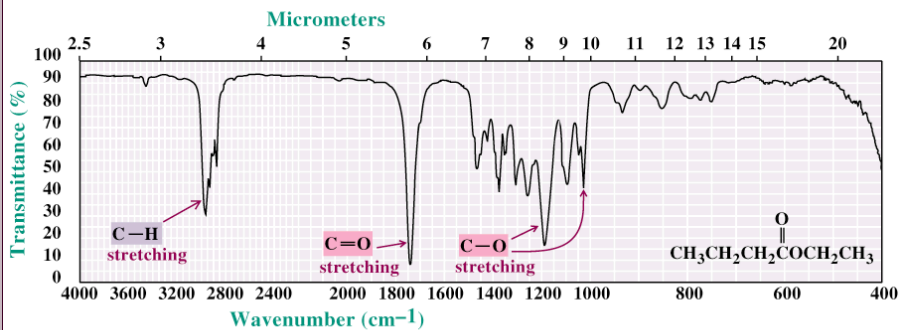
## Infrared absorptions for carboxyl derivatives

Compound	Stretching Absorption (cm <sup>-1</sup> )	Additional Absorptions (cm <sup>-1</sup> )
$\begin{array}{c} \text{O} \\    \\ \text{RCCl} \end{array}$	1790–1800	
$\begin{array}{c} \text{O} \quad \text{O} \\    \quad    \\ \text{RCOCR} \end{array}$	1740–1760 and 1800–1850	C—O stretching at 900–1300
$\begin{array}{c} \text{O} \\    \\ \text{RCOR} \end{array}$	1735–1800	C—O stretching at 1000–1100 and 1200–1250
$\begin{array}{c} \text{O} \\    \\ \text{RCOH} \end{array}$	1700–1725	O—H stretching at 2400 – 3400 C—O stretching at 1210 – 1320 N—H stretching at 3200 and 3400 (1° amides have two N—H peaks) (2° amides have one N—H peak)
$\begin{array}{c} \text{O} \\    \\ \text{RCNH}_2 \end{array}$	1630–1680	
$\text{RC}\equiv\text{N}$	2200–2250	

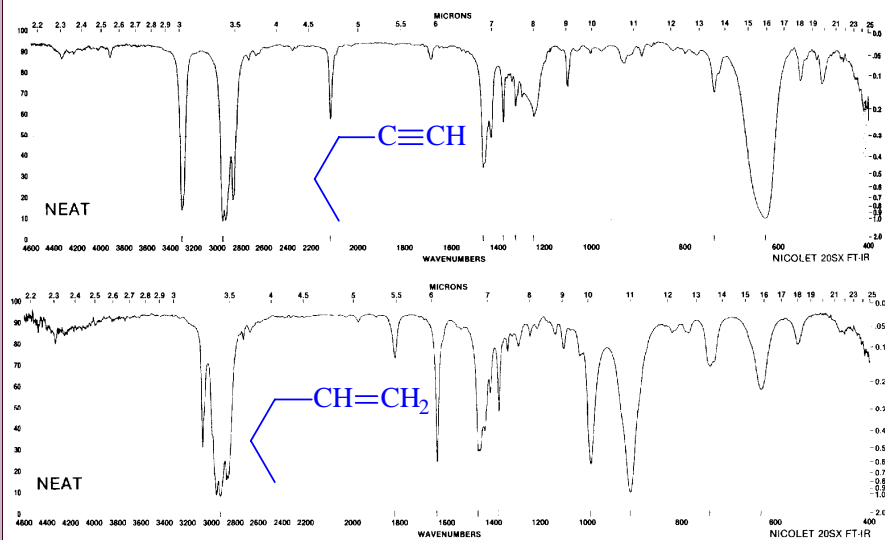
### IR spectrum of N-methylpropanamide



### IR spectrum of ethyl butanoate

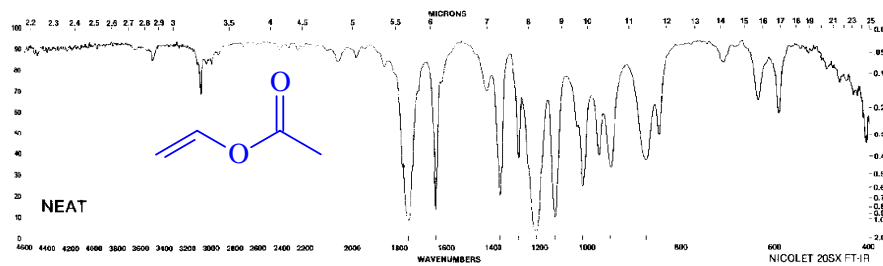
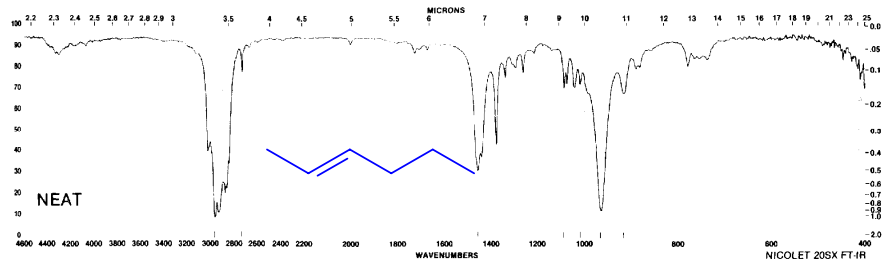


### 1-Hexyne, 1-Hexene

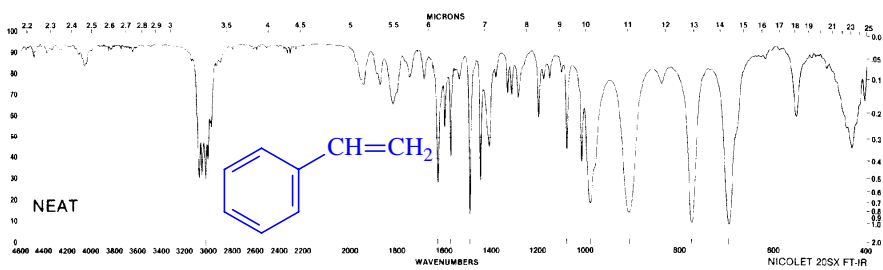
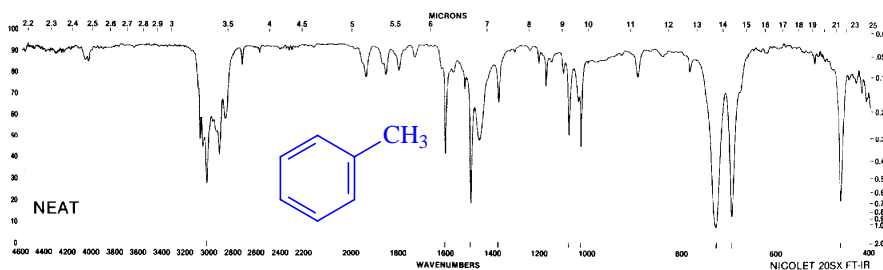




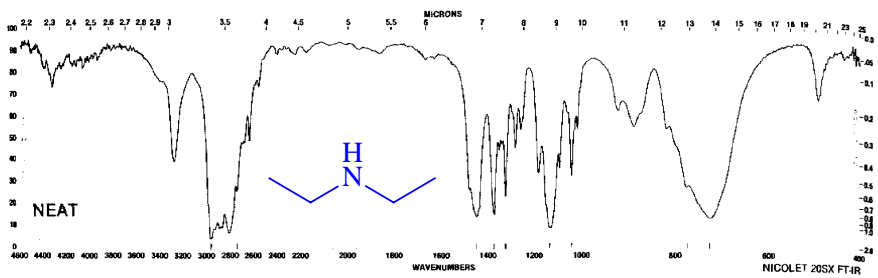
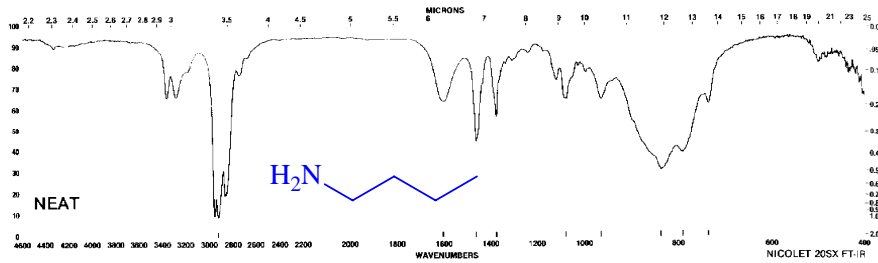
# 2-Hexene, Vinyl Acetate



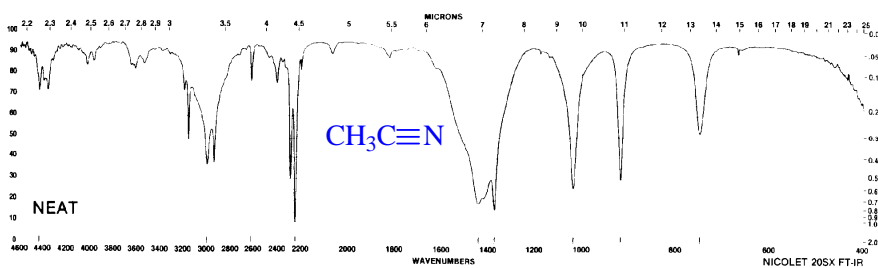
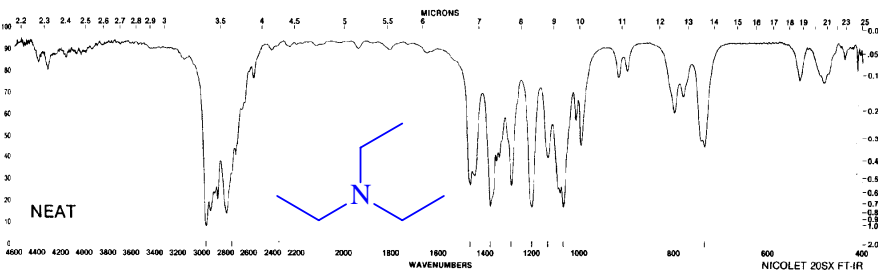
# Toluene, Styrene



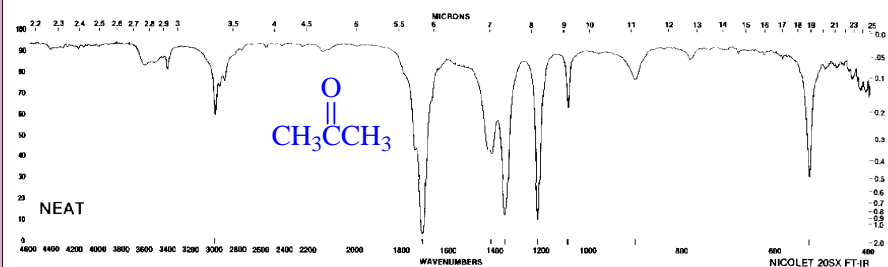
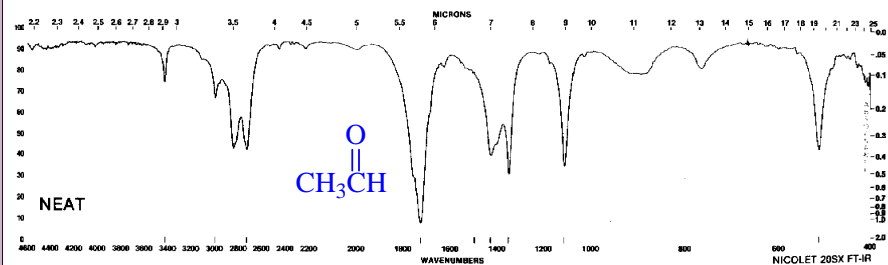
# Butanamine, Diethylamine



# Triethylamine, Acetonitrile



# Acetaldehyde, Acetone



# Ethyl Acetate, Acetic Acid

