Pharmacy 570

Infrared (IR) Spectroscopy - Part III

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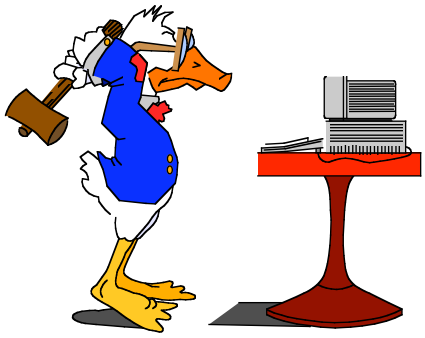
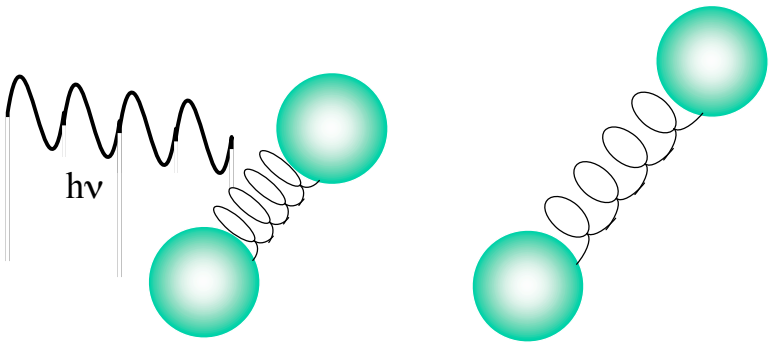
Hours: anytime after 4 pm

Lecture Notes Available At:

- http://redpoll.pharmacy.ualberta.ca

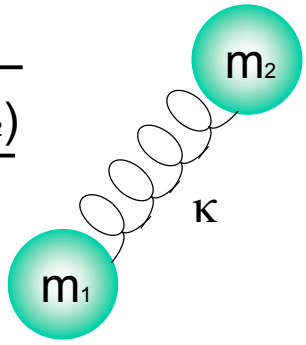


Principles of IR



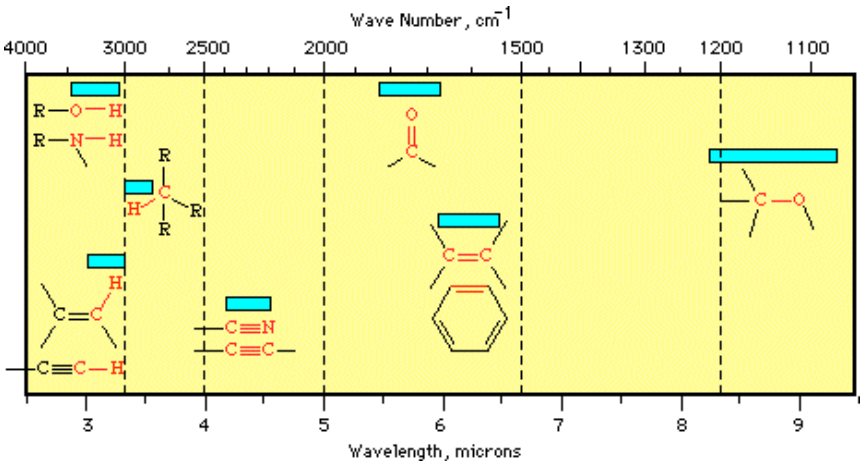
The IR Equation

$$k = \frac{1}{2\pi c}\sqrt{\frac{\kappa(m_1 + m_2)}{m_1\, m_2}}$$



$$\nu = c/\lambda \text{ or } \nu = ck$$

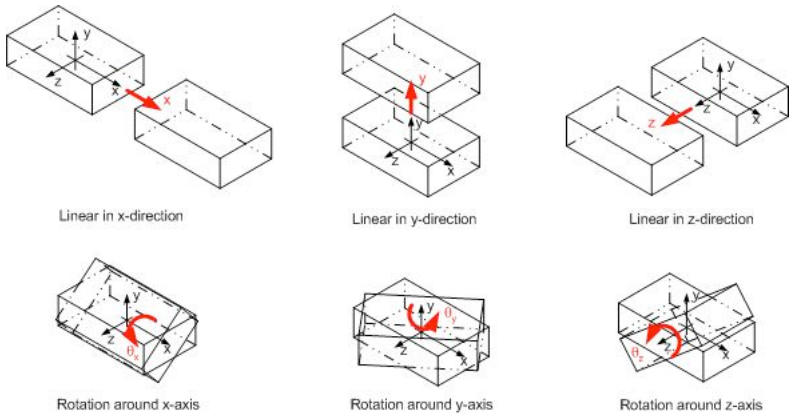
IR Characteristic Vibrations



Other IR Influences

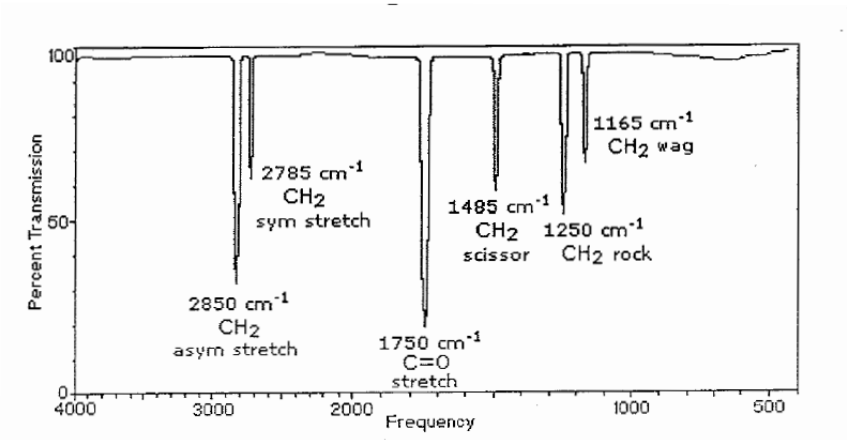
- **Hydrogen Bonding**
  - Shift IR absorption bands
- **Electronic Effects**
  - Seen in conjugation/delocalization effects
- **Bond Angles**
  - Strained bonds change spring constants
- **Field Effects**
  - Interactions between halides & carbonyls

Degrees of Freedom



6 degrees of freedom for a rigid, nonlinear object

Formaldehyde IR Bands

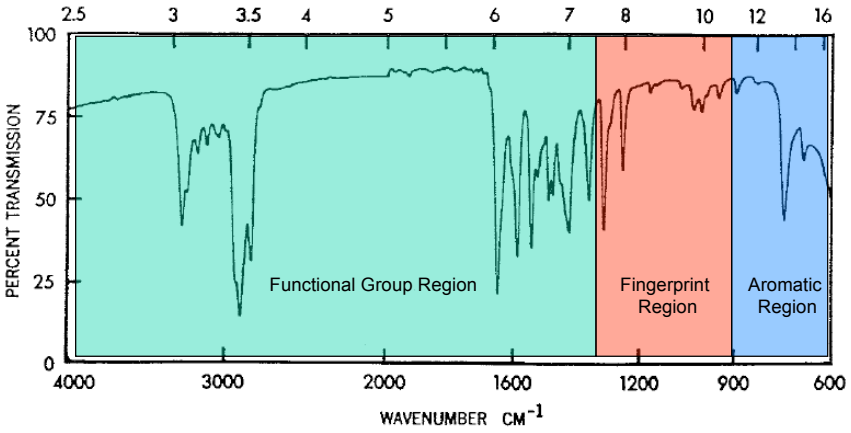


3n-6 = 3*4-6 = 6 bands predicted: 6 bands observed

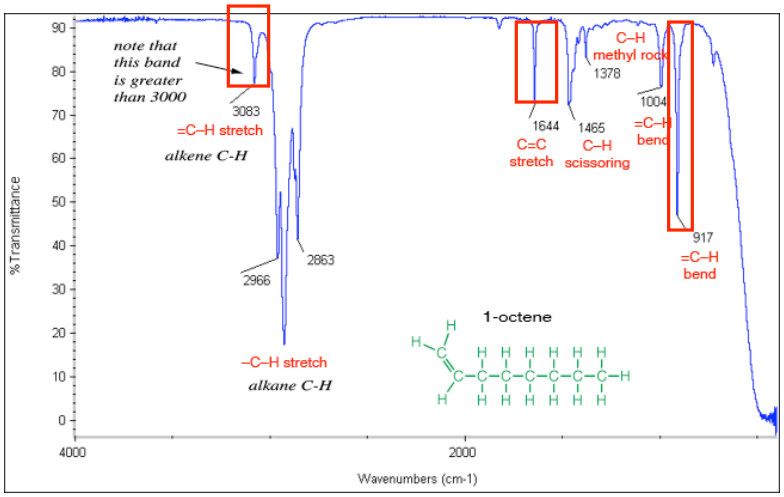
Effects on IR Band Numbers

- Other contributions can lead to an increase or decrease in # of IR bands
- Overtone bands
  - Forbidden transitions
- Combination tones or bands
  - Forbidden transitions too
- Coupled bands
  - Closely spaced band effects
- Fermi resonances/doublets

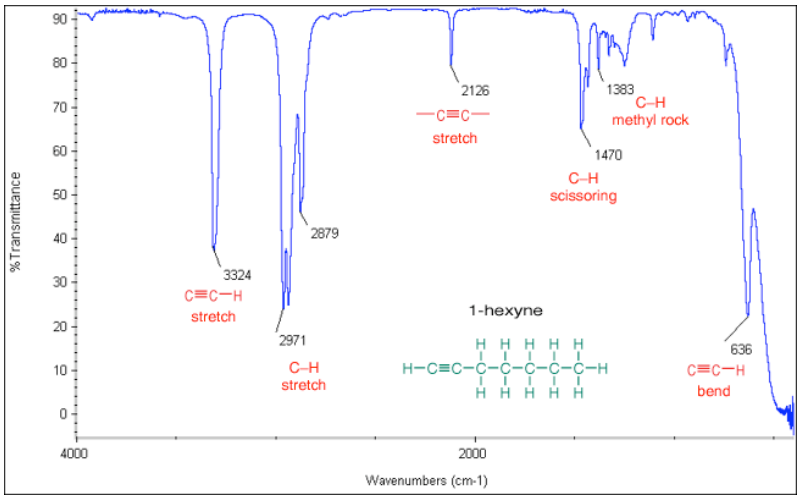
Presentation of IR Spectra



Alkene IR Spectra



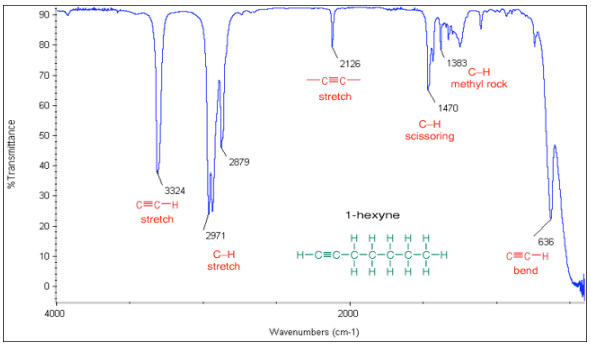
Alkyne IR Spectra



Alkyne IR

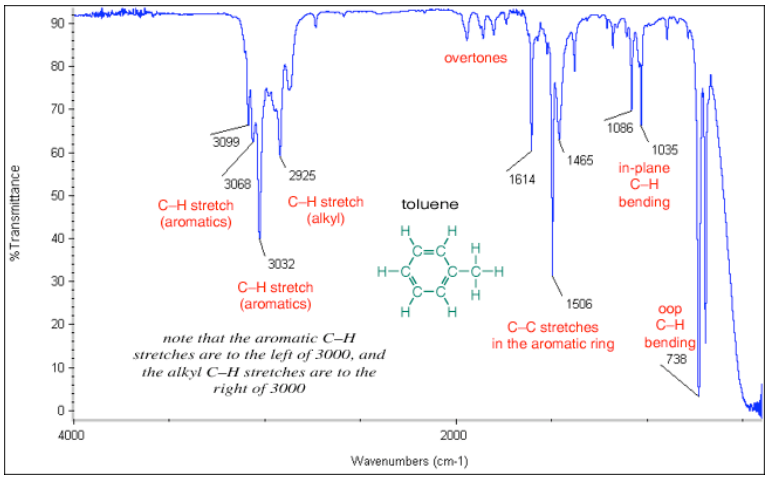
- Triple bonded molecules exhibit stronger bonds to C-H groups which lead to absorptions at 3300 cm^{-1} vs. 2900 cm^{-1} (alkanes) or 3000 cm^{-1} (alkenes)
- C-H alkyne bands can be mistaken for O-H bands but are much narrower
- C≡C stretching is also much higher than C=C stretching (2200 cm^{-1} vs. 1600 cm^{-1})

Alkyne IR Spectra



Group	Character/Type	Frequency
≡C-H	stretch	3267-3333 (m-s)
≡C-H	bend	610-700 (s) broad
C≡C (terminal)	stretch	2100-2140
C≡C (internal)	stretch	2210-2260

Aromatic IR Spectra



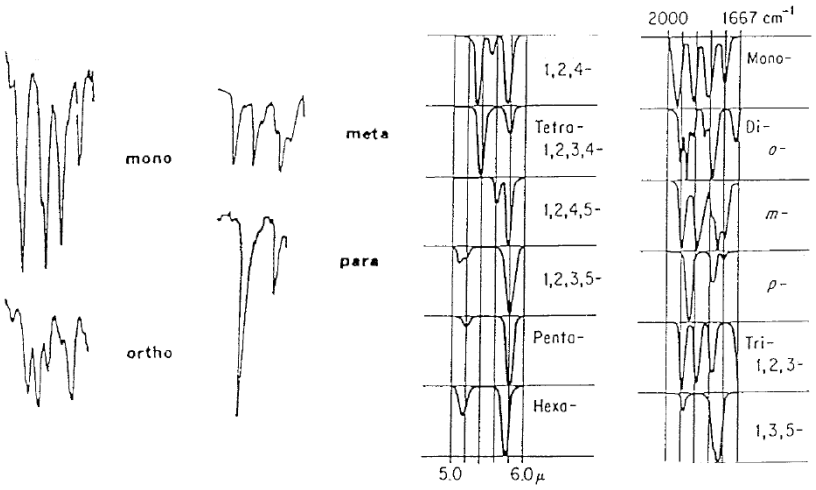
Aromatic IR Spectra

- **These spectra are characterized by:**
  - **An aromatic C-H band above 3000 cm^{-1}**
  - **An overtone from C-H bending between 1700-2000 cm^{-1}**
  - **An aromatic C=C "breathing" band at 1600 cm^{-1}**
  - **A band at 1000-1100 cm^{-1} from in-plane deformations**
  - **A series of bands in the aromatic region (650-900 cm^{-1})**

Overtone Aromatic Bands

- Often the overtone aromatic bands at 1700-2000 cm^{-1} are weak but do provide diagnostic patterns for substituted aromatics
  - Monosubstituted have 4 “fingers”
  - Ortho-substituted have 2 triplets
  - Meta-substituted have 2 lines & a triplet
  - Para-substituted have 2 lines (1 big, 1 small)

Overtone Aromatic Bands



Other Aromatic Bands

- C=C ring "breathing" bands from 1500 - 1600 cm^{-1} are very diagnostic for aromatics - especially these 4 bands:
- 1600 cm^{-1} (w-s), 1580 cm^{-1} (s), 1500 cm^{-1} (w-s), 1450 cm^{-1} (s)
- Most aromatics show 3 of the 4 C=C bands with the 1450 band often absent, sometimes 1580 & 1600 will coalesce to form a single band

Other Aromatic Bands

- Most important band(s) for aromatics are the out-of-plane bending bands from 675-900 cm^{-1}
- ***At least one strong band in this region is required for aromaticity***
- If substitutent is electron donating bands shift to lower frequency
- If substituent is electron withdrawing bands shift to higher frequency

Electron Donating vs. Electron Withdrawing

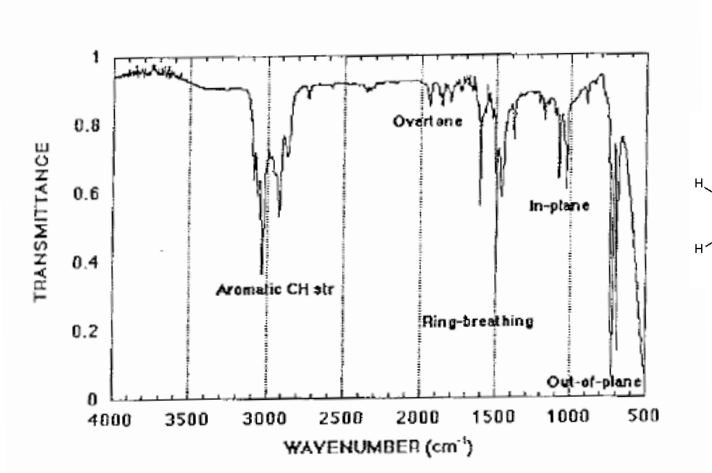
- Electron donating groups have N, O, S or X or unbonded n-orbitals
  - e.g. OH, OCH_3, NR_2, SR, Cl, Br, I
- Electron withdrawing groups have double bonds or filled n-orbitals
  - e.g. NO_2, COR, CONH, N^+R_3

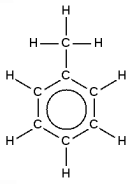
Out-of-plane Aromatic Bands

- Number and position of these bands helps to ID substitution patterns
- Rules are given below:

Substitution Pattern	Absorption Band
Mono-substituted	730-770 cm^{-1} and 690-710 cm^{-1}
Ortho-disubstituted	735-770 cm^{-1}
Meta-disubstituted	690-710 cm^{-1} and 750-810 cm^{-1}
Para-disubstituted	800-860 cm^{-1}

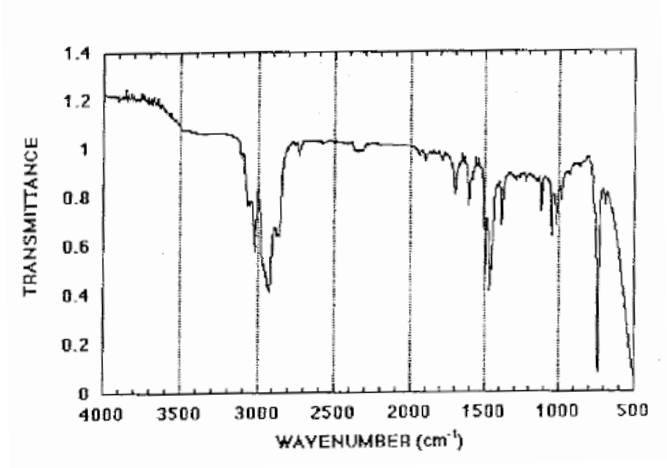
Example #1 - Toluene

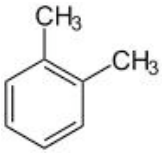




Monosubstituted aromatic with two out of plane bands at 690 and 750 cm^{-1}

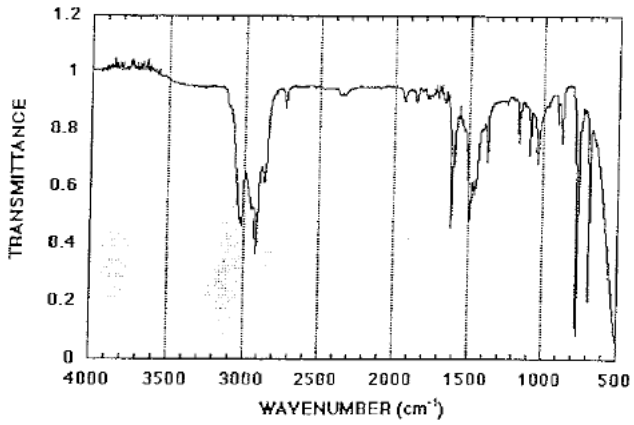
Example #2 ortho-Xylene

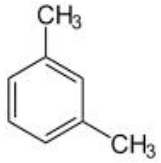




Disubstituted aromatic with one out-of-plane band at 750 cm^{-1}

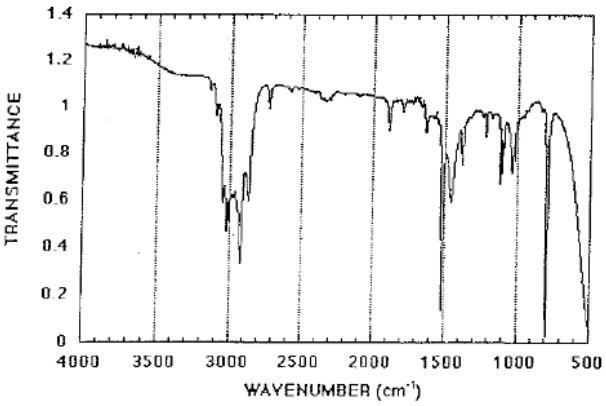
Example #3 meta-Xylene





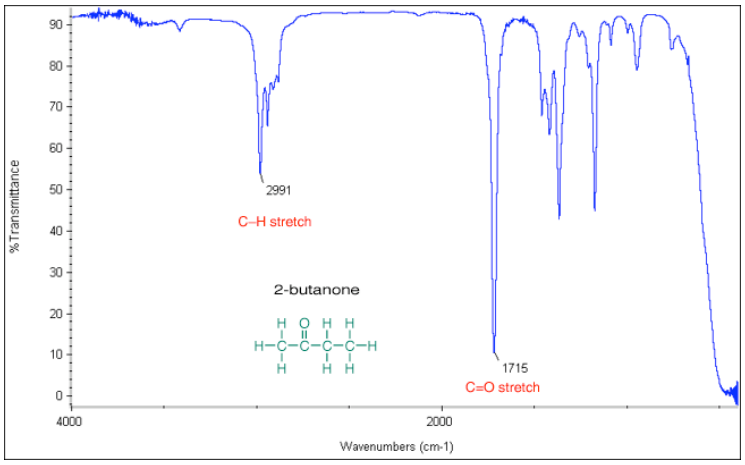
Disubstituted aromatic with two out-of-plane bands at 690 cm^{-1} and 780 cm^{-1}

Example #4 - para-Xylene



Disubstituted aromatic with one out-of-plane band at 800 cm^{-1}

Ketone & Aldehyde IR



Ketone & Aldehyde IR

- Ketones, aldehydes, carboxylic acids, esters, lactones, amides, acid halides and anhydrides all show a strong C=O band around 1550-1850 cm^{-1}
- Carbonyl band is one of the most useful in all of IR spectroscopy
- Position of this band depends on electronic interactions, H-bonding and ring strain

Ketone & Aldehyde IR

- Presence of oxygen, halides or other electron donating groups or increased ring strain reduces C=O bond length and increases the frequency of C=O vibrations
- Presence of electron withdrawing groups decreases double bond character, lengthens the bond and lowers frequency
- Strong C=O bonds resonate at high ν
- Weak C=O bonds resonate at low ν

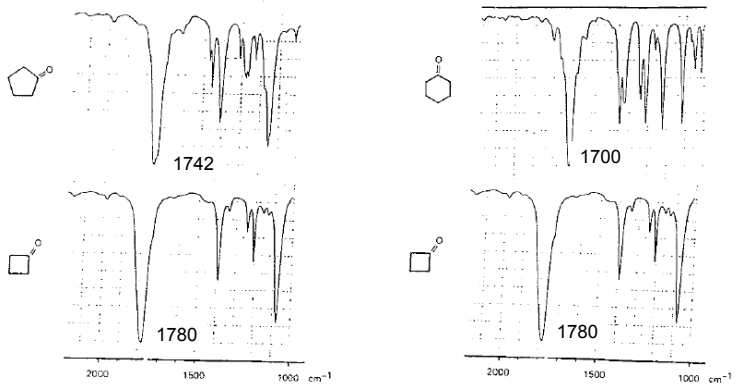
Ketone & Aldehyde IR

- Line of unsaturation for C=O bonds is 1700 cm^{-1}
- Presence of aromatic groups, double bonds, triple bonds, etc. is signaled by a C=O band below 1700 cm^{-1}

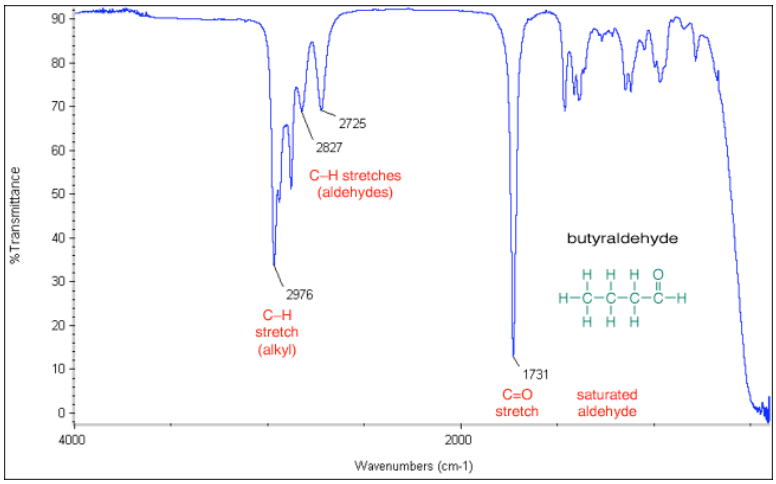
Ketone	Frequency
Acyl chlorides (Cl, Br, F)	~1800 cm^{-1}
Unsubstituted ketone	1700-1720 cm^{-1}
α,β unsaturated ketone	1685 cm^{-1}
Aromatic ketone	Below 1700 cm^{-1}
β-diketone	1625, 1720 cm^{-1}
Nitrile substituted	1700-1615 cm^{-1}

Cyclic Ketone IR

- **Bond angle of the C-CO-C group changes position of C=O band**



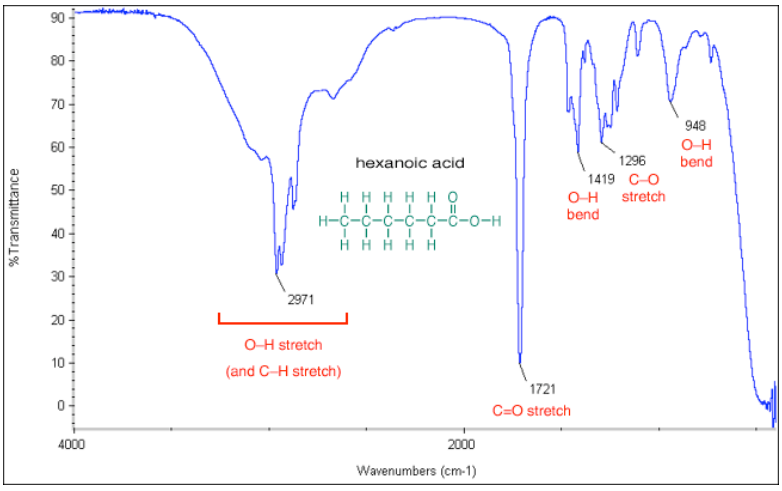
Aldehyde IR Spectra



Aldehyde IR Spectra

- Very similar to ketone IR spectra
- C=O stretch is slightly higher (around 1720-1740 cm^{-1})
- This is because the H group is more electron withdrawing than the CH_3 group, this increases the strength of the C=O bond
- Also characterized by a Fermi doublet C-H band at 2720 and 2820 cm^{-1}

Carboxylic Acid IR



Carboxylic Acid IR

- Carboxylic acids tend to exist as dimers in non-polar solutions due to strong H-bonding
- Dimerization is characterized by:
  - Broad intense OH band at 3300-2500 cm^{-1}
  - Strong C=O stretch at 1760-1690 cm^{-1}
  - A C-O-H out-of-plane bend at 940-920 cm^{-1}

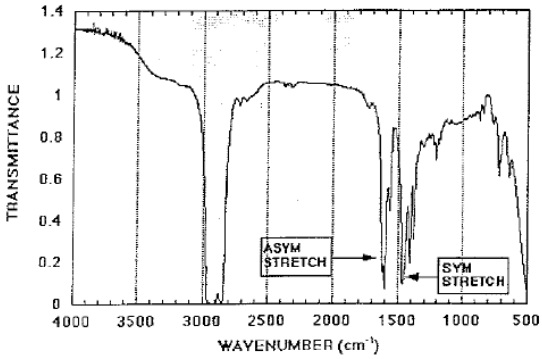
Carboxylic Acid IR

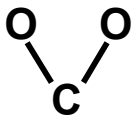
- Characteristic IR absorption bands in carboxylic acids (monomer/dimer)

Band	Description	Frequency
C=O	Stretch (dimer) Stretch (monomer)	1710 cm^{-1} 1750 cm^{-1}
O-H	Stretch (dimer) Stretch (monomer) Bend (out-of-plane)	2500 cm^{-1} 3520 cm^{-1} 935 cm^{-1}
C-O/O-H	Coupled O-H bend Coupled C-O stretch	1300 cm^{-1} 1420 cm^{-1}

IR of Carboxylate Salts

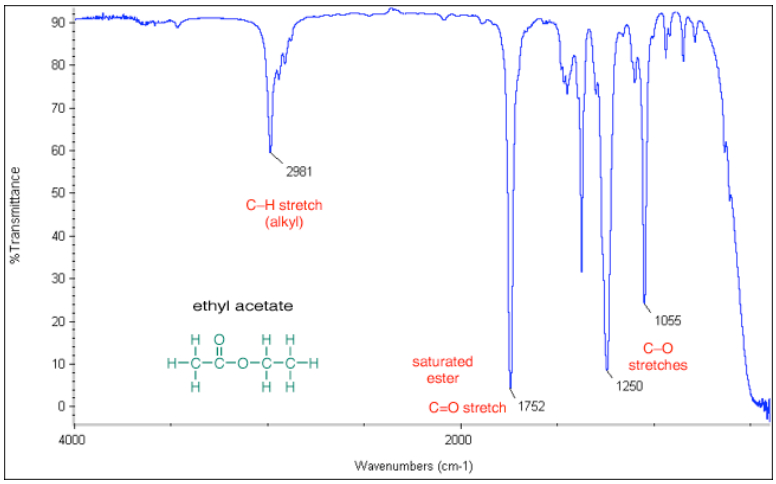
- **Carboxylates (RCOO-) have both asymmetric & symmetric stretches**





Similar to CH_2 stretches

IR of Esters



IR of Esters

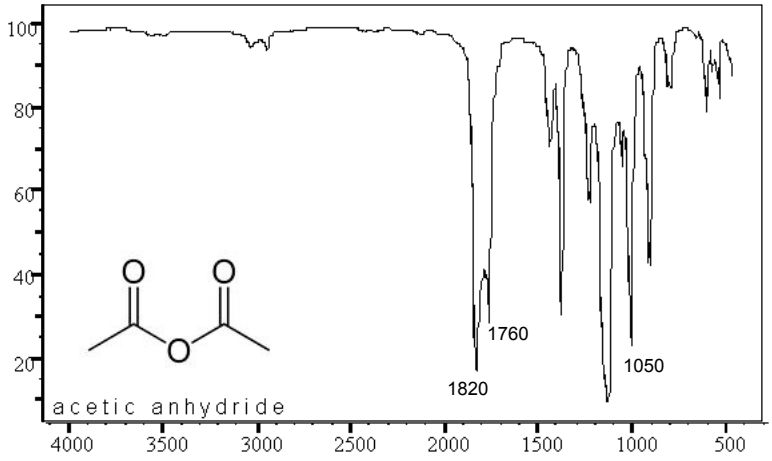
- Spectra characterized by a C=O band at 1760-1780 cm^{-1}
- Also characterized by an intense C-O stretching band at 1200-1250 cm^{-1}
- C=O stretch of esters is at a higher frequency than ketones because of e^- withdrawing nature of the adjacent O
- Addition of conjugations and/or H-bonds leads to reduction in C=O ν

IR of Esters

- The characteristic ester absorption bands are summarized below:

Group	Character/Type	Frequency
C=O	Linear unconjugated	1740-1750
C=O	conjugated	1720
C=O	Conjugated + H bond	1680
C-O	stretch	1100-1280

IR of Anhydrides



IR of Anhydrides

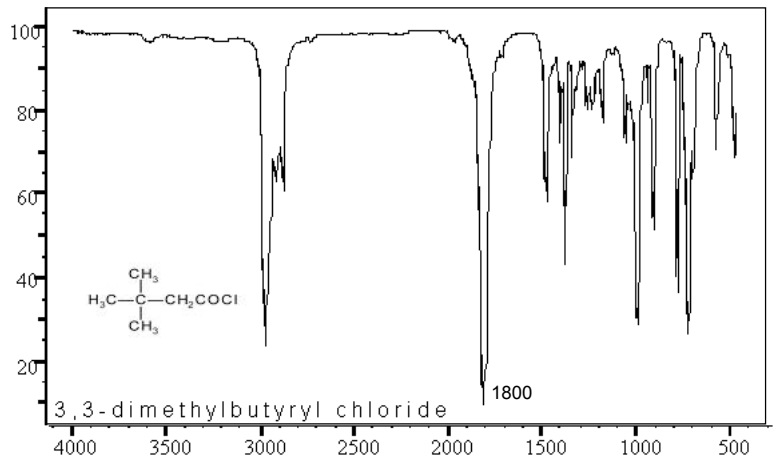
- Have 2 C=O stretching bands from asymmetric and symmetric stretches
- Saturated acyclic anhydrides absorb at 1820-1750 cm^{-1}
- Conjugated acyclic anhydrides absorb at 1775-1720 cm^{-1}
- Cyclic anhydrides absorb at 1865-1780 cm^{-1} (ring strain)

IR of Anhydrides

- C-O-C stretch for linear unconjugated anhydrides is ~1050 cm^{-1}
- C-O-C stretch for cyclic anhydrides is ~1300-1180 cm^{-1}
- Main anhydride bands summarized below:

Group	Vibration Mode	Frequency
C=O	Asymmetric stretch	1820
C=O	Symmetric stretch	1760
C-O-C	Stretch	1050-1300

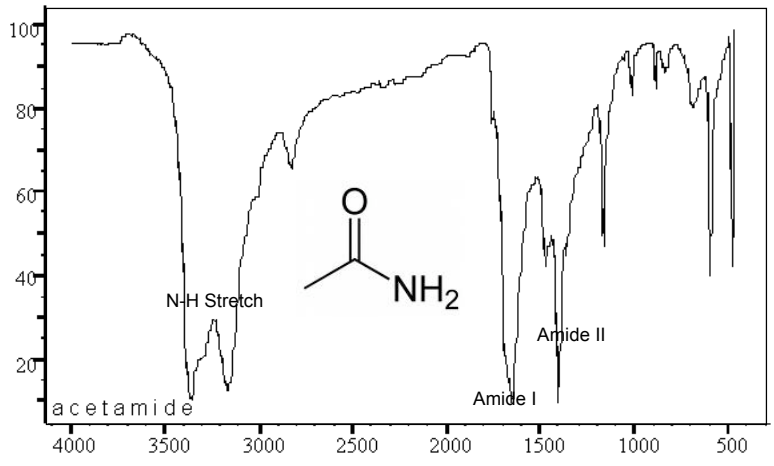
IR of Acid Halides



IR of Acid Halides

- Strong C=O band around 1815-1785 cm^{-1}
- Higher frequency due to electronegative nature of halides leading to shortening or strengthening of C=O bond
- Conjugated acid halides have lower absorption frequencies (1780-1750 cm^{-1}) because resonance effects reduce C=O force constants

IR of Amides



IR of Amides

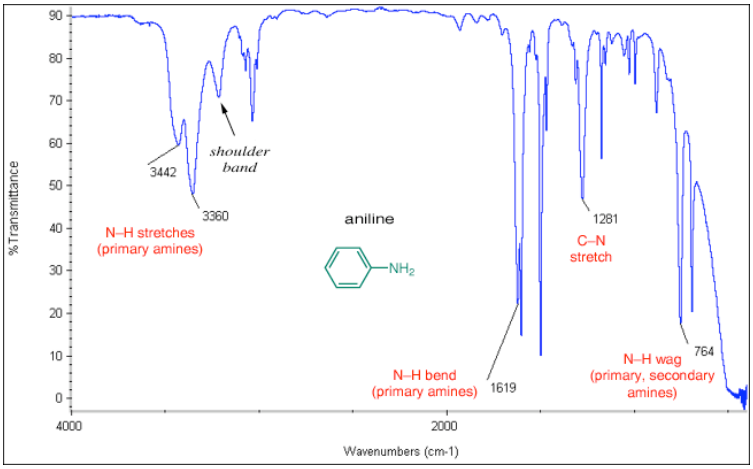
- Primary amides characterized by 2 NH stretching bands around 3500 and 3400 cm^{-1} (in solid samples the ν is lower due to extensive H-bonding)
- Secondary amides characterized by only 1 NH stretching band
- C=O band (Amide I band) is lower (~1650 cm^{-1}) than most C=O bands because of electron donating nature of NH_2 group

IR of Amides

- Following are the characteristic or main amide absorption bands

Group	Character/Type	Frequency
C=O	Amide I stretch	1650 (s)
N-H	Amide II bend	1500-1640 (s)
C-N	Amide III stretch	1300-1400 (s)
N-H	stretch	3100-3500

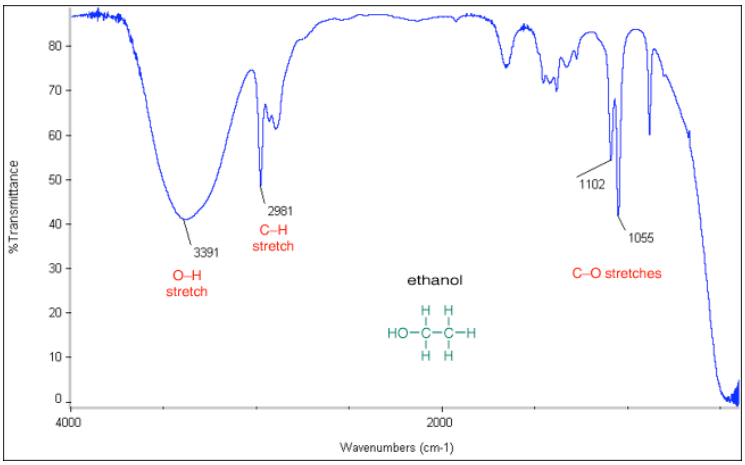
IR of Amines



IR of Amines

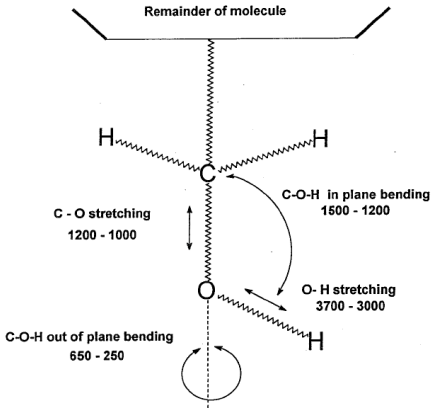
- Primary amines show 2 (weak) NH stretch bands at 3500 and 3400 cm^{-1}
- Secondary amines show only 1 band
- N-H bending in primary amines is seen at 1650-1580 cm^{-1}
- N-H bending in secondary amines is seen at 1620-1560 cm^{-1}
- N-H bending in aromatic amines is seen at ~1515 cm^{-1}

IR of Alcohols



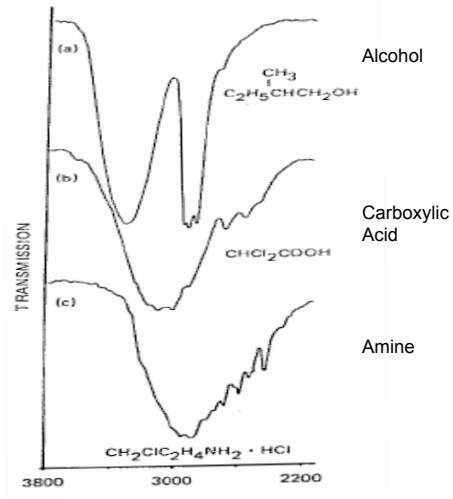
IR of Alcohols

- Alcohols are characterized by 3 characteristic bands:
- An O-H stretching band (3700-3000 cm^{-1})
- An O-H bend band (1500-1200 cm^{-1})
- A C-O stretching band (1200-1000 cm^{-1})



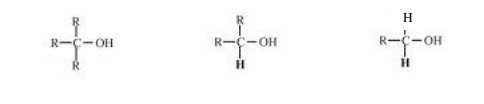
IR of Alcohols

- OH stretch at 3500 cm^{-1} can be confused with NH stretching bands (although NH is sharper)
- Compare between alcohol, carboxylic acid and amine

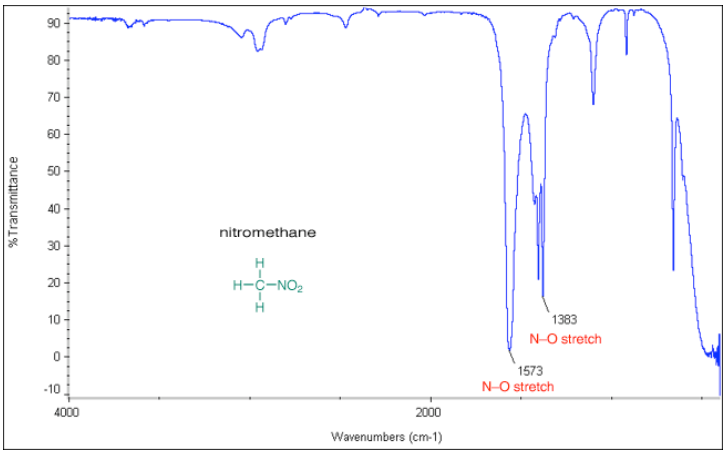


IR of Alcohols

- The C-O stretching band (more correctly the C-C-O asymmetric band) is quite diagnostic for certain alcohol classes
- ~1200 cm^{-1} for saturated tertiary alcohols
- 1120-1080 cm^{-1} for saturated secondary alcohols
- 1080-1050 cm^{-1} for saturated primary alcohols



IR of Nitro Groups



IR of Nitro Groups

NITRO

NO_2	asym stretch	1500 - 1570
	sym stretch	1300 - 1370

conjugation lowers frequency

C - N	stretch	860 - 930

IR of Misc. Groups

CN	alkyl	2240 - 2260 (m - s)
	aryl	2220 - 2240 (s)
	α,β-unsaturated	2215 - 2235 (s)
SO_2	asym stretch	1310 - 1350
	sym stretch	1120 - 1160
OCH_3	C - O - C stretch	1190 (s)
	C - H stretch	2815 - 2830 (s)

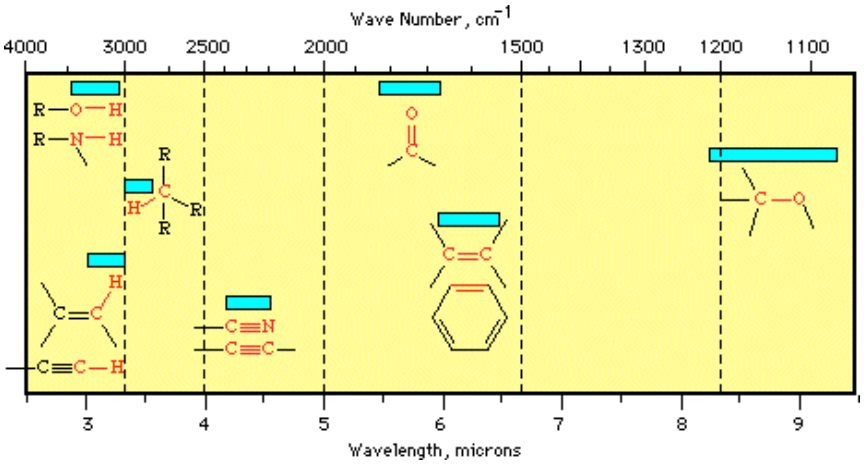
Analyzing IR Spectra

- Look for C=O peak (1820-1660 cm^{-1})
- If C=O check for OH (3400-2400 cm^{-1})
  - indicates carboxylic acid
- If C=O check for NH (3500 cm^{-1})
  - indicates amide
- If C=O check for C-O (1300-1000 cm^{-1})
  - indicates ester
- If 2 C=O absorptions (1810 & 1760 cm^{-1})
  - indicates anhydride
- If no OH, NH or C-O then ketone

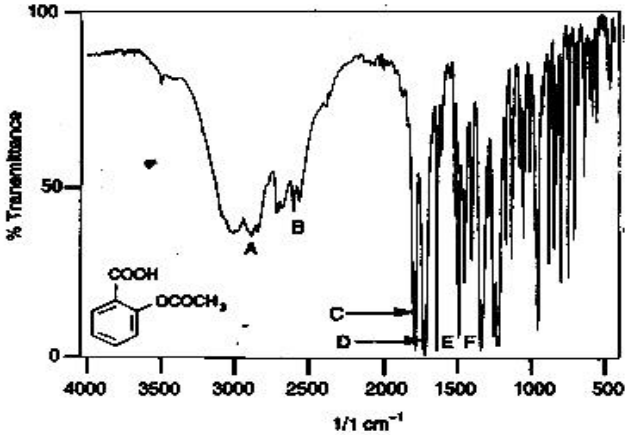
Analyzing IR Spectra

- If no C=O check for OH (3600-3300 cm^{-1})
  - indicates alcohol
- If no C=O check for NH (3500 cm^{-1})
  - indicates amine
- If no C=O & no OH check C-O (1300 cm^{-1})
  - indicates ether
- Look for C=C (1650-1450 cm^{-1}) then aromatic

IR Characteristic Vibrations



Sample IR Spectrum #1



A - CO-OH stretch (3000)

B - CH stretch (2800)

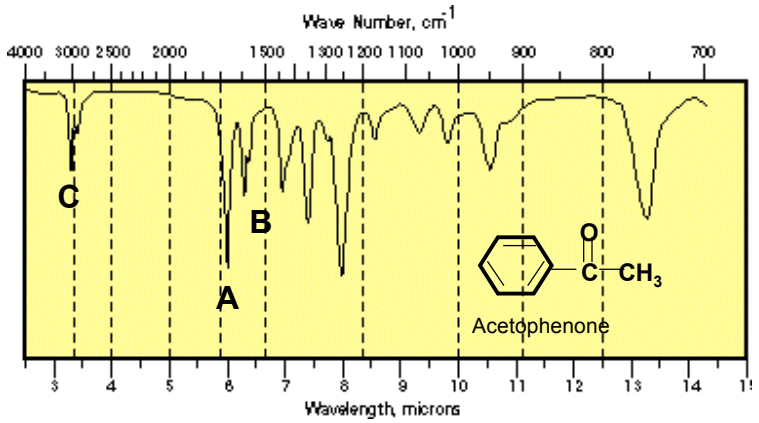
C - C=O ester (1757)

D - C=O carboxy (1690)

E - C=C aromatic (1608)

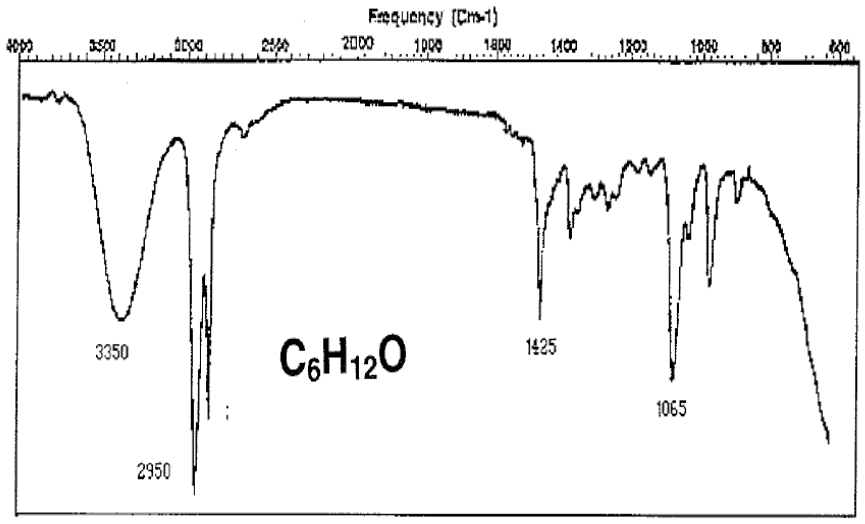
F - C=C aromatic (1460)

Sample IR Spectrum #2

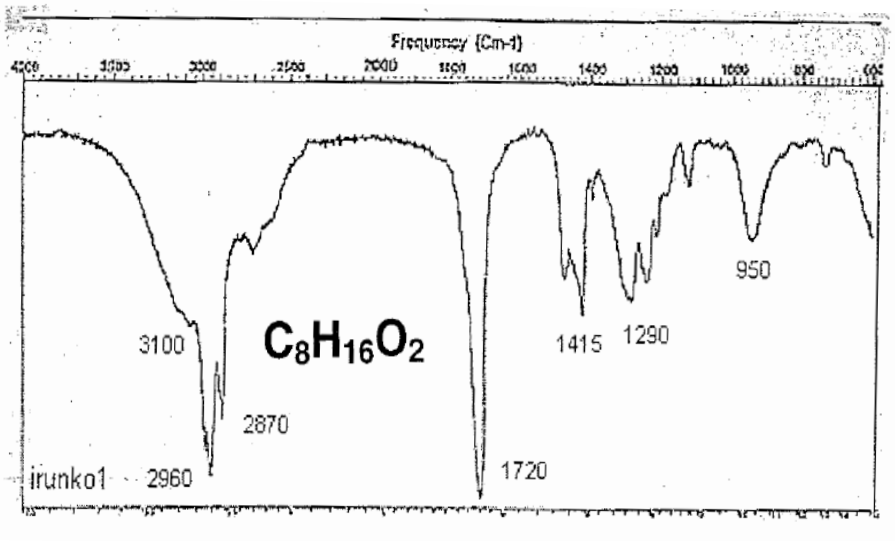


A) C=O (1730) B) C=C aromatic (1590) C) C-H aromatic (3050)

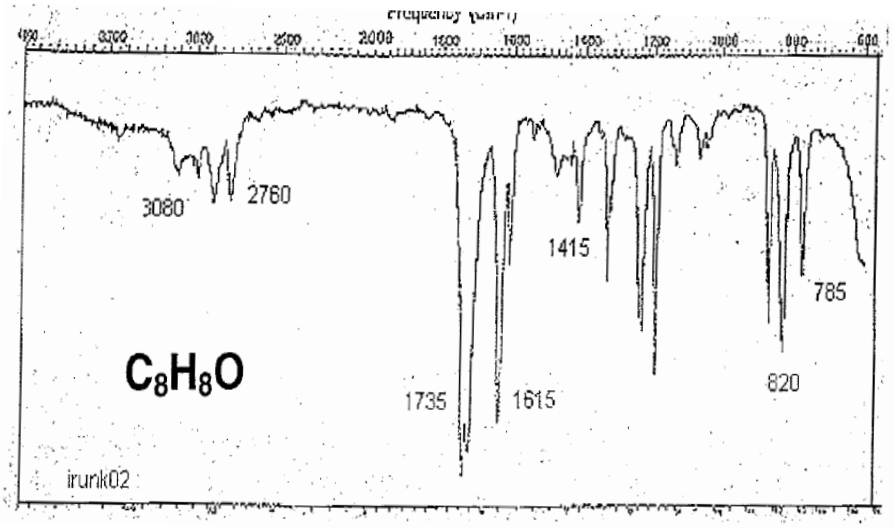
Unknown #1



Unknown #2



Unknown #3



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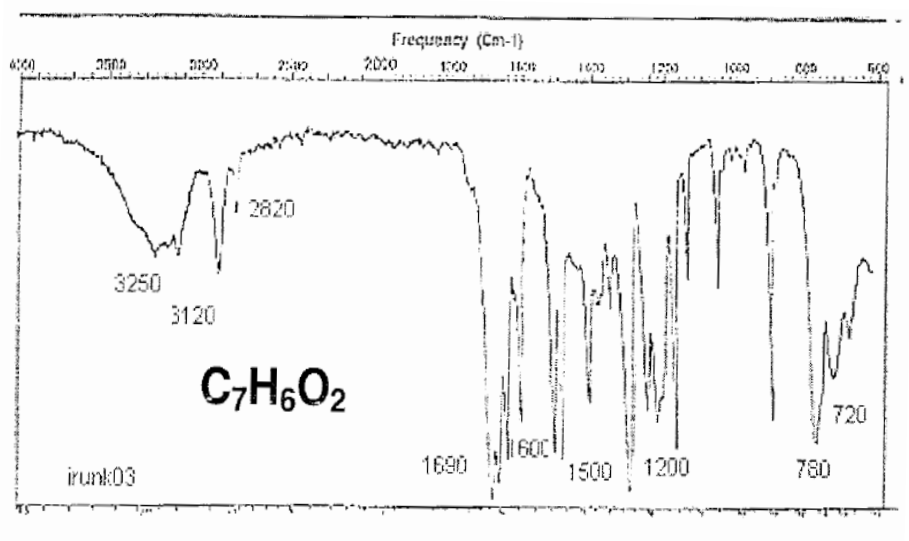
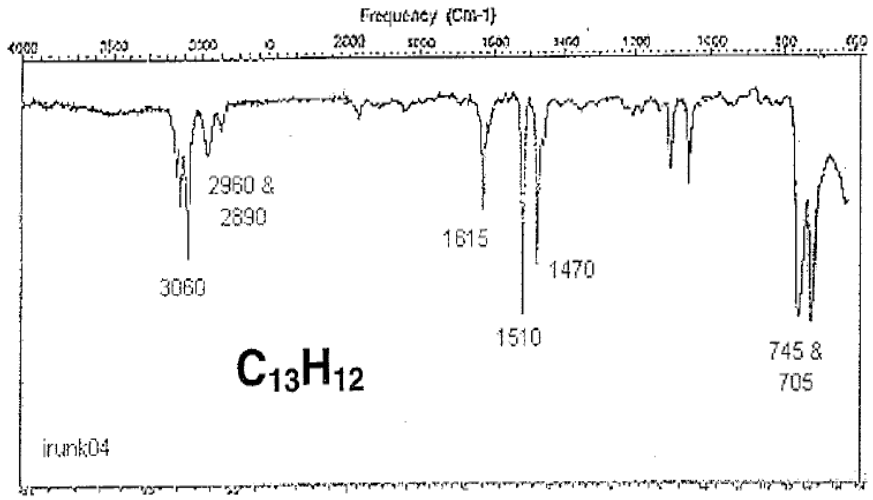
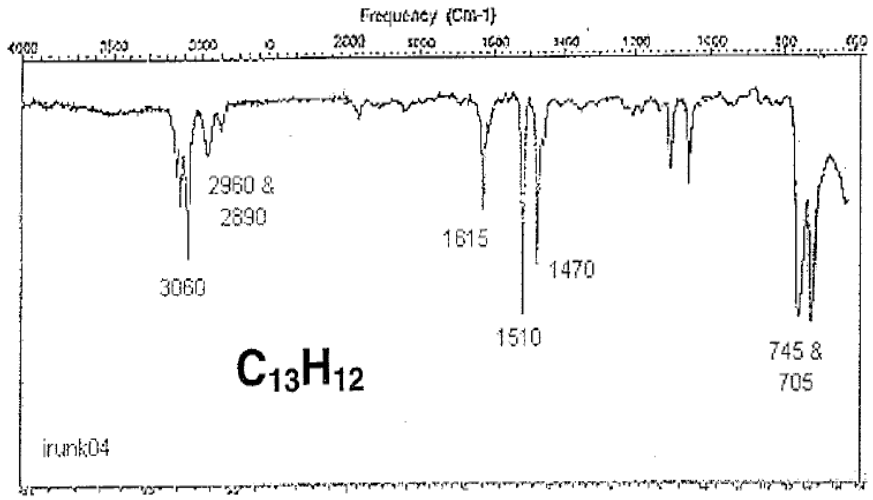


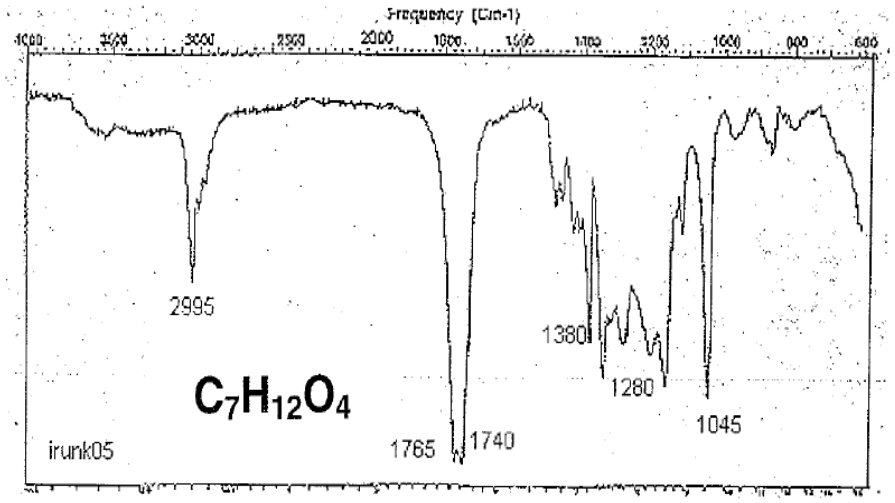
Unknown #5



Unknown #5



Unknown #6


Frequency (Cm-1)
2995
1380
1280
1045
$C_7H_{12}O_4$
irunk05
1765
1740