INFRARED SPECTROSCOPY

Absorptions in infrared region of the electromagnetic spectrum (hence the name)

Absorptions due to stretching and bending of covalent bonds in molecules

Visible region – 400 to 800 nm

Visible wavelengths typically expressed in *nanometers*
(1 nm = 1 x 10^{-9} m)

Infrared region – wavelengths longer than visible

Infrared wavelengths typically expressed in *micrometers*
(1 μm = 1 x 10^{-6} m)

Typical infrared spectrum covers between 2.5 μm to 25 μm (2500 nm to 25000 nm)

Energy is inversely related to wavelength, so infrared light has less energy than visible light

Typical units in infrared spectroscopy are *wavenumbers* (ν) - the reciprocal of the wavelength (in centimeters)

$$2.5\ \mu m = 2.5 \times 10^{-4}\ cm = 4000\ cm^{-1}$$

$$25\ \mu m = 2.5 \times 10^{-3}\ cm = 400\ cm^{-1}$$

Thus your typical IR spectrum runs from 4000 to 400 cm^{-1}

Wavenumber is directly related to energy; the higher the energy of the absorption

Types of IR Absorptions

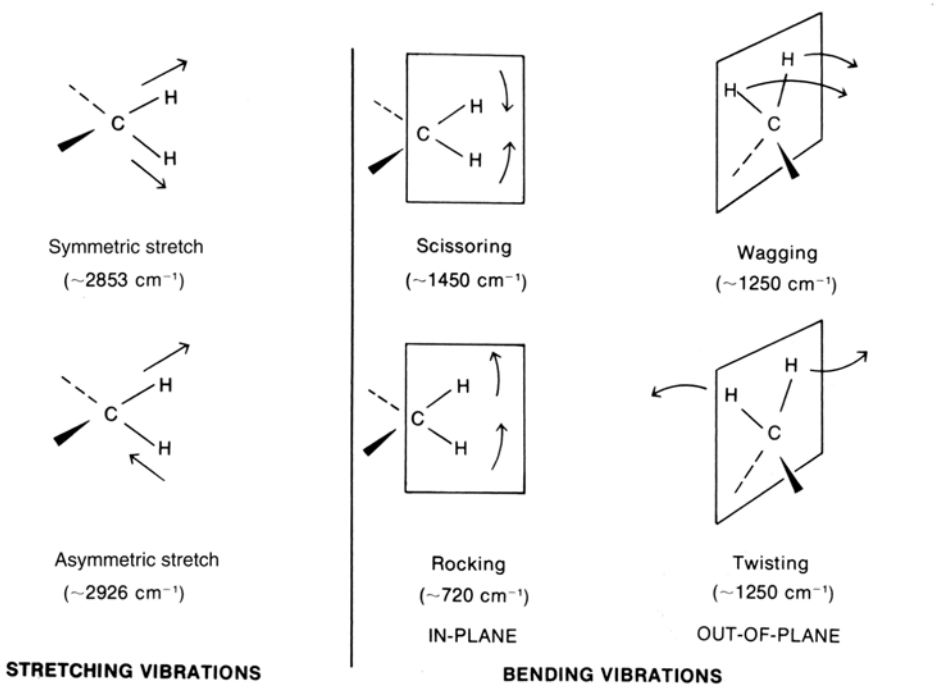
IR absorption occurs from the stretching and bending of the covalent bonds in molecules

To be accompanied by IR absorption a stretch or bend must change the dipole moment of the molecule

> Molecules with symmetric bonds such as N_2, O_2, or F_2 do not absorb in the infrared since bond stretching does not change the dipole moment of the molecule

The two primary modes of vibration are *stretching* and *bending*

> Stretching modes are typically of higher energy than bending modes
>
> Stretching modes are often divided into two a symmetric and asymmetric stretch; the asymmetric stretch is usually of higher energy



The energy of the stretch decreases as the mass of the atoms is increased

C-H	3000 cm^{-1}
C-C	1200 cm^{-1}
C-O	1100 cm^{-1}
C-Cl	750 cm^{-1}
C-I	500 cm^{-1}

The energy of the stretch is related to the hybridization in the order sp > sp^2 > sp^3

C-H sp	3300 cm^{-1}
C-H sp^2	3100 cm^{-1}
C-H sp^3	2900 cm^{-1}

Dispersive IR Spectrometers

Beam from an IR source is split into two halves using a mirror

One beam is passed through a reference cell; the other is passed through a sample cell

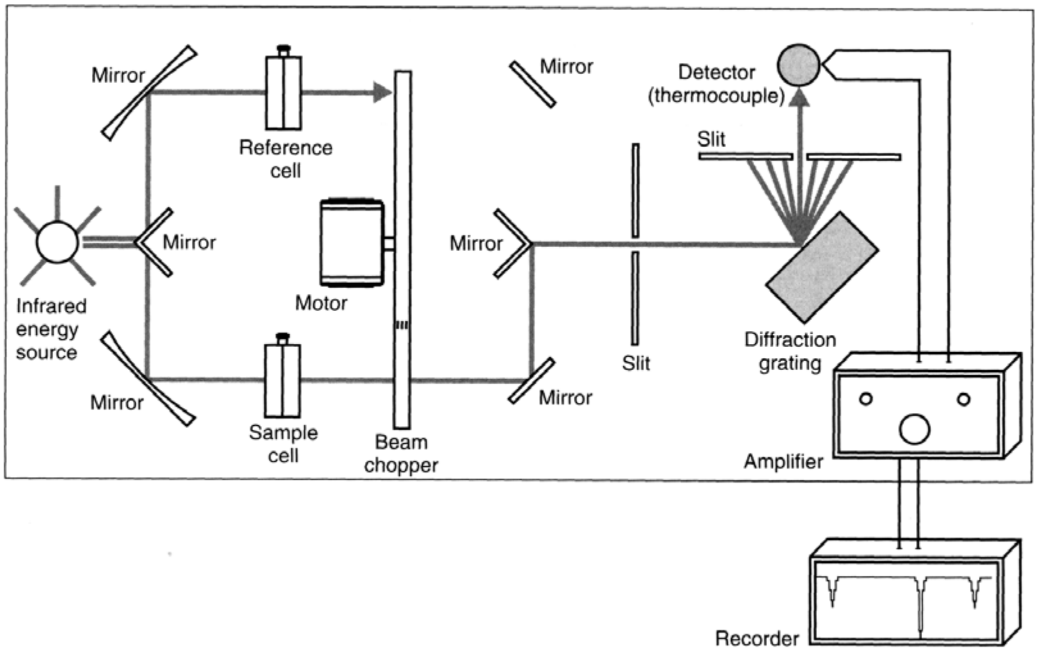
The two beams are alternately passed to the diffraction grating using a *beam chopper*

Absorption of radiation is detected by comparing the two signals

Light is dispersed (spread into constituent wavelengths) by a grating much as it would by be by a prism

The grating is slowly rotated, which changes the angle if diffraction and which wavelengths are passed to the detector

Spectrum recorded in the frequency domain



FTIR Spectrometers

Most modern IR spectrometers are of this type

Spectrum obtained as a function of time rather than frequency; a Fourier transform is used to convert from time domain to frequency domain

Most are single-beam spectrometers

> A background scan is first performed, then scan of the sample, and the background scan is detected from the sample scan by computer

Sample Preparation for IR Work

Three major methods of sample preparation

1. Sample is mixed with a mulling agent such mineral oil and pressed between plates made of sodium chloride

   Sodium chloride is used because it has no IR absorptions; glass or plastic plates would have IR absorptions of their own

   Sodium chloride plates are good from 4000 to 650 cm^{-1}; below 650 cm^{-1} they begin to absorb

   Potassium bromide plates can be used in place of sodium chloride and are transparent to 400 cm^{-1}, but they are more expensive.

   Downside of this method is absorptions due to the mineral oil

2. Sample is mixed with solid potassium bromide and pressed into a pellet under high pressure

   No absorptions from mulling agent

   Only works for solids

3. Sample is dissolved in carbon tetrachloride and pressed between salt plates

   Downside of this method is absorptions due to the CCl_4

Absorptions of Alkanes

C-H stretch occurs at 3000 – 2840 cm^{-1}

CH_2 bending modes at 1465 cm^{-1}

CH_3 bending absorption at 1375 cm^{-1}

CH_2 (four or more CH_2 groups) rocking at 720 cm^{-1}

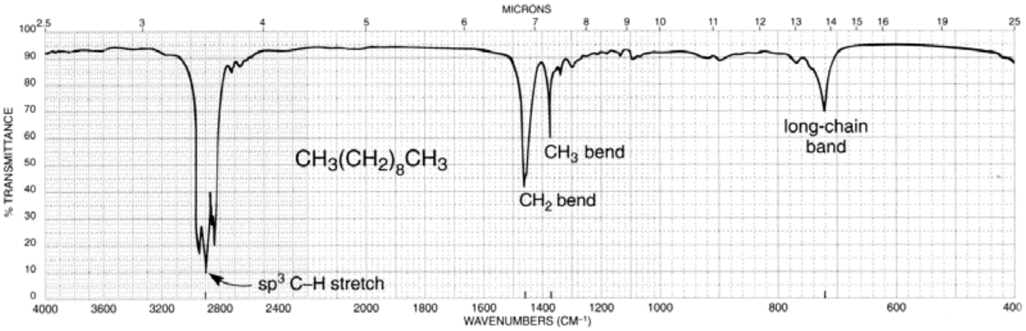


FIGURE 2.7 The infrared spectrum of decane (neat liquid, KBr plates).

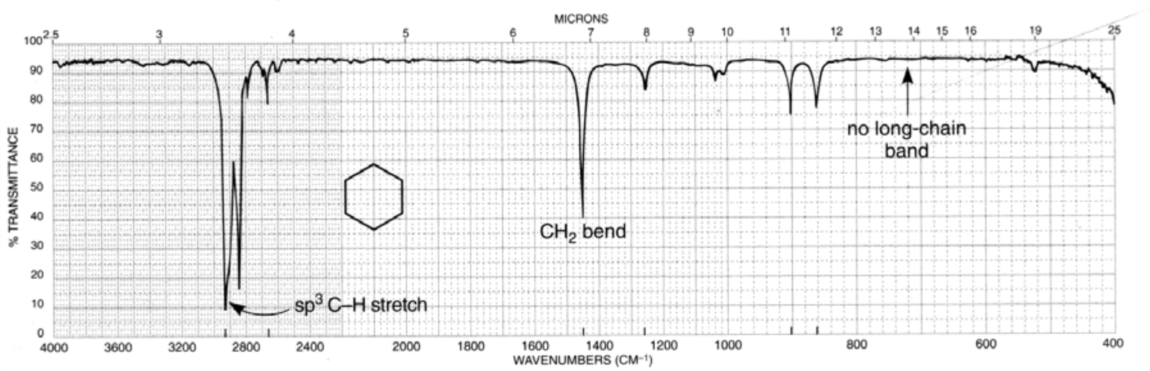


FIGURE 2.9 The infrared spectrum of cyclohexane (neat liquid, KBr plates).

Note lack of long-chain bend and CH_3 bend in above spectrum

Absorptions in Alkenes

C-H stretch occurs in region of 3095 – 3010 cm^{-1}
(note higher wavenumber relative to alkanes)

C=C stretch occurs in region of 1670 – 1640 cm^{-1}

Can be used to determine type of substitution:

Symmetrically substituted does not absorb at all

A *cis* isomer absorbs more strongly than a *trans* isomer
(*cis* is less symmetrical than *trans*)

Simple monosubstituted absorbs at 1640 cm^{-1}

Simple 1,1-disubstituted absorbs at 1650 cm^{-1}

C-H out of plane bending (oop) absorbs at 1000 – 650 cm^{-1}

Often very strong absorptions

Can be used to determine type of substitution:

Monosubstituted gives two peaks near 990 and 910 cm^{-1}

1,2-disubstituted (*cis*) gives one strong band near 700 cm^{-1}

1,2-disubstitued (*trans*) gives on band near 970 cm^{-1}

1,1-disubstituted gives one strong band near 890 cm^{-1}

A trisubstituted double bond absorbs near 815 cm^{-1}

A tetrasubstituted double bond does not absorb at all

A monosubstituted alkene gives two strong peaks near 990 and 910 cm^{-1}

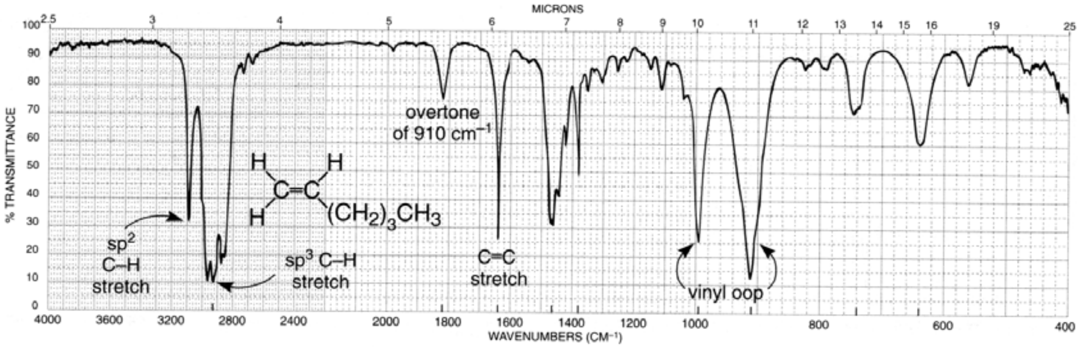


FIGURE 2.10 The infrared spectrum of 1-hexene (neat liquid, KBr plates).

A *cis* 1,2-disibstiuted alkene gives one strong band near 700 cm^{-1}

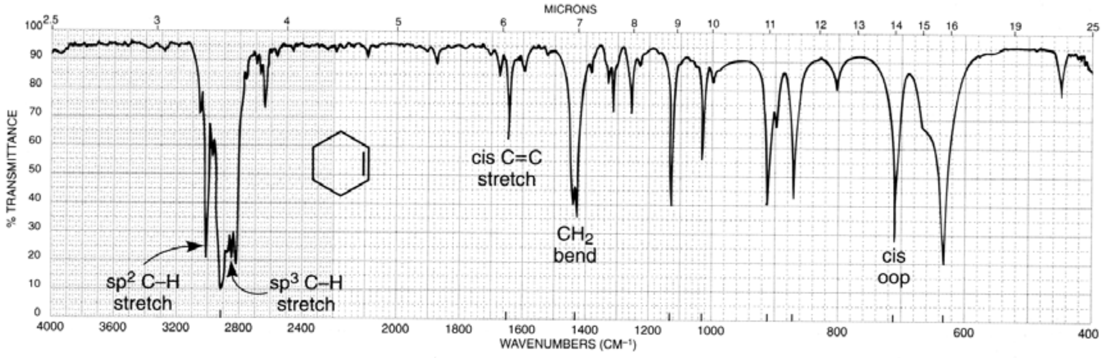


FIGURE 2.11 The infrared spectrum of cyclohexene (neat liquid, KBr plates).

Note that the C=C stretch is much less intense than for the monosubstituted example

The strength of the C=C stretch can serve to differentiate between *cis* and *trans* isomers

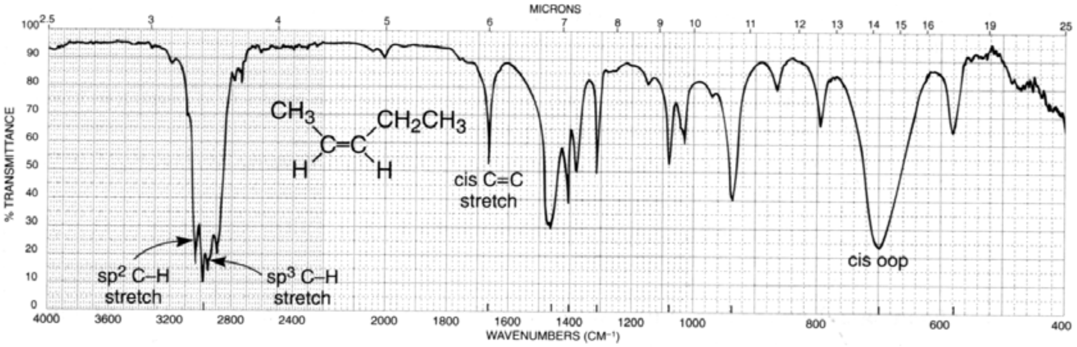


FIGURE 2.12 The infrared spectrum of *cis*-2-pentene (neat liquid, KBr plates).

The *cis* isomer – more intense C=C stretch

Note the single large peak at 700 cm^{-1} (indicates *cis* isomer)

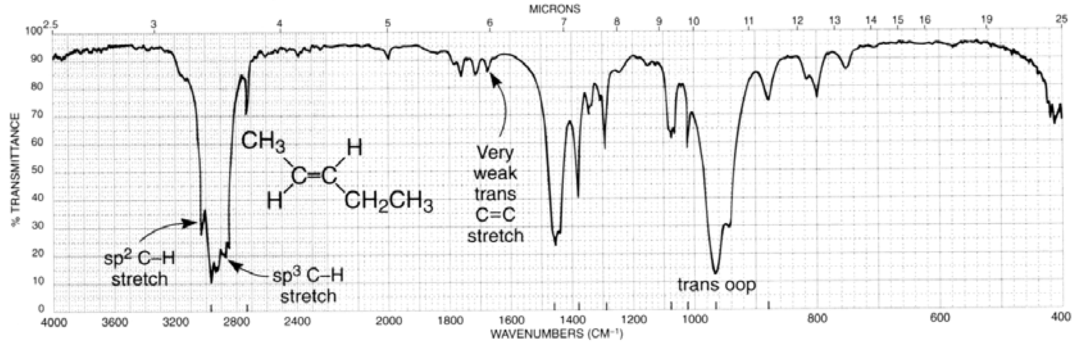


FIGURE 2.13 The infrared spectrum of *trans*-2-pentene (neat liquid, KBr plates).

The *trans* isomer – less intense C=C stretch

Note the band near 970 cm^{-1} (indicates *trans* isomer)

Absorptions in Alkynes

C-H stretching frequency is approximately 3300 cm^{-1}
(still higher than for alkanes or alkenes)

C-C stretch occurs at approximately 2150 cm^{-1}
(but not observed if alkyne is symmetric)

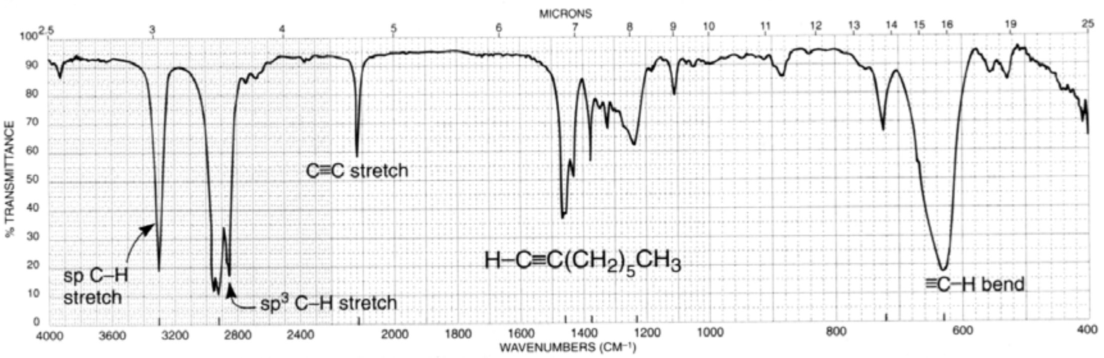


FIGURE 2.14 The infrared spectrum of 1-octyne (neat liquid, KBr plates).

An asymmetric alkyne

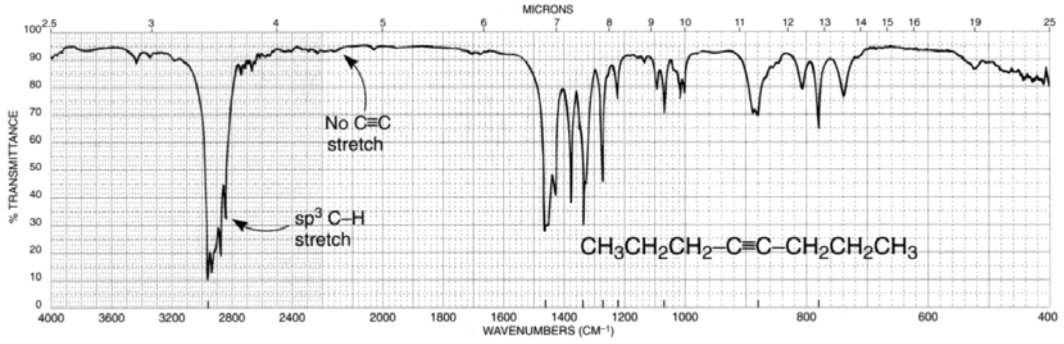
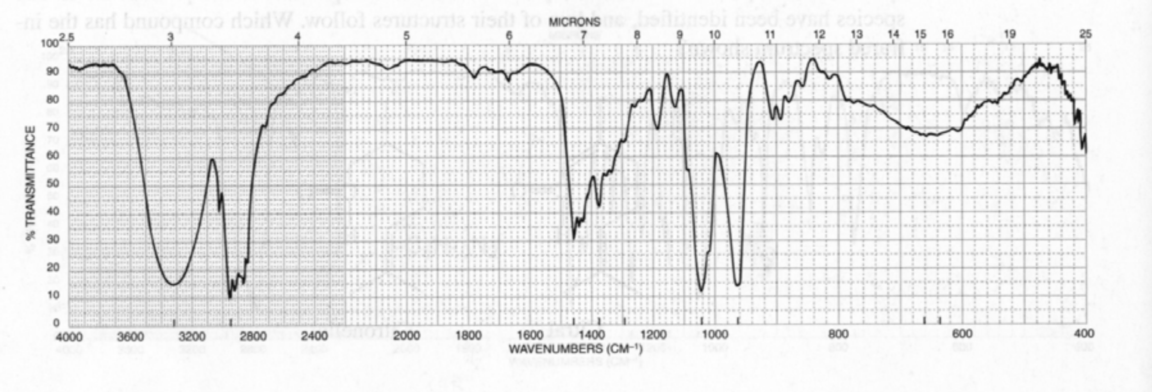


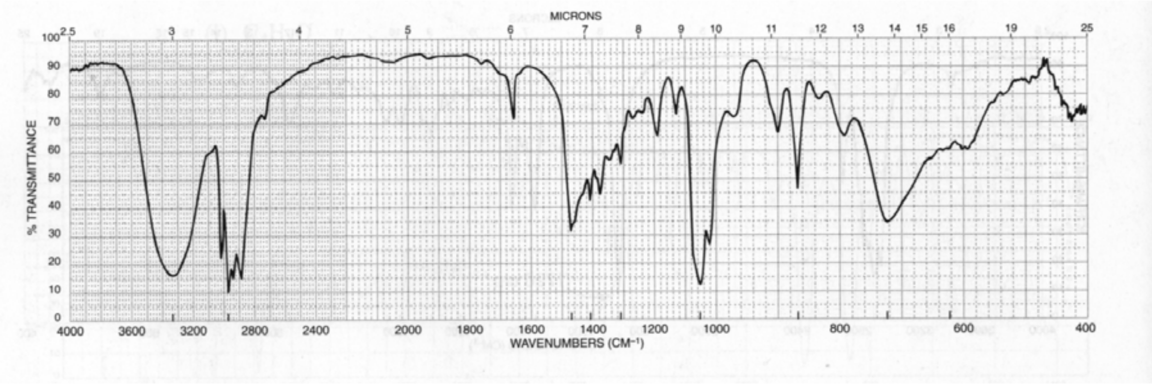
FIGURE 2.15 The infrared spectrum of 4-octyne (neat liquid, KBr plates).

A asymmetric alkyne (no C-C stretch)

Example Problem 1

Shown below are spectra for *cis* and *trans* 3-hexen-1-ol. Assign a structure to each.

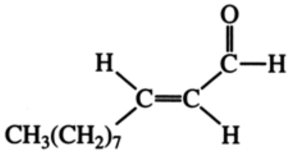




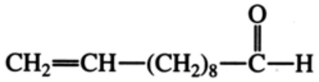
Solution

Example Problem 2

Which of the following structures matches the spectrum shown below?

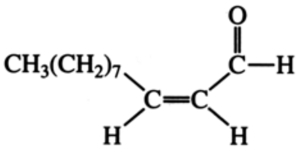


A

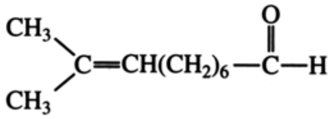


$CH_2{=}CH{-}(CH_2)_8{-}\overset{O}{\overset{\|}{C}}{-}H$

B

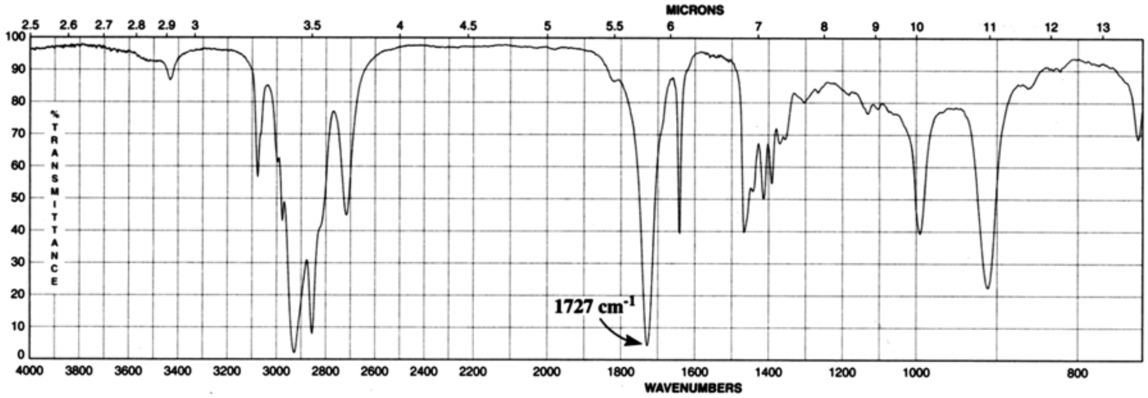


C



$(CH_3)_2C{=}CH(CH_2)_6{-}\overset{O}{\overset{\|}{C}}{-}H$

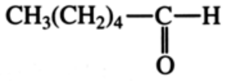
D



Solution

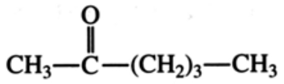
Example Problem 3

Which of the following structures matches the spectrum shown below?



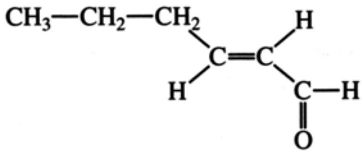
$\mathrm{CH_3(CH_2)_4{-}\underset{\underset{\displaystyle O}{\|}}{C}{-}H}$

A

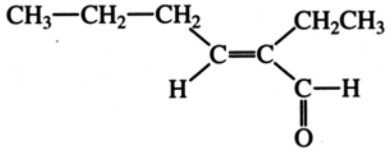


$\mathrm{CH_3{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}(CH_2)_3{-}CH_3}$

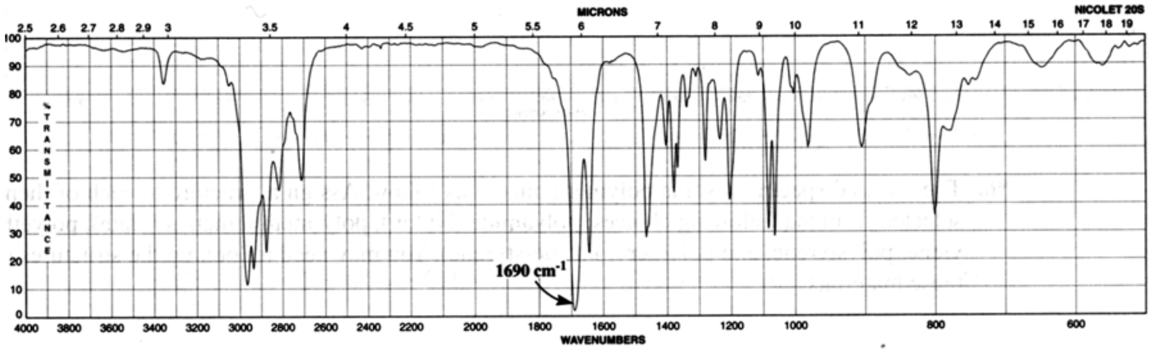
B



C



D



Absorptions in Aromatic Compounds

C-H stretch occurs between 3050 and 3010 cm^{-1}

C-H out-of-plane bending occurs at 900 – 690 cm^{-1}
(useful for determining type of ring substitution)

C=C stretching often occurs in pairs at 1600 cm-1 and 1475 cm^{-1}

Overtone and combination bands occur between 2000 and 1667 cm-1

Monosubstituted rings give strong absorptions at 690 cm^{-1} and 750 cm^{-1} (second may be masked by hydrocarbon solvent)

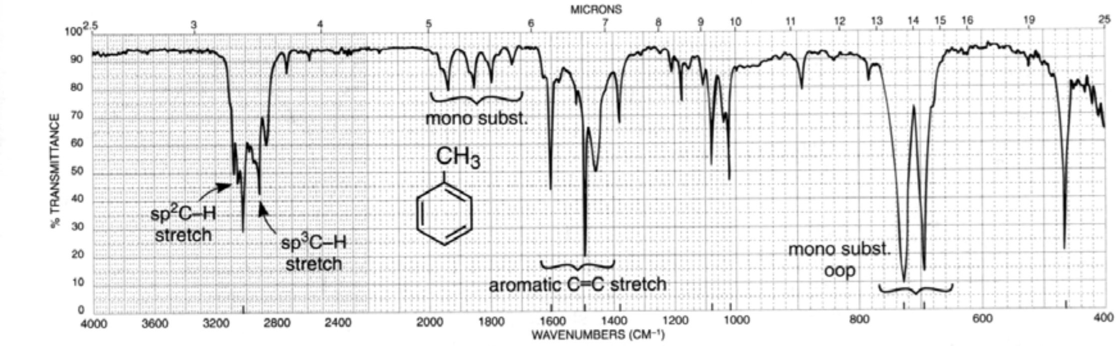


FIGURE 2.23 The infrared spectrum of toluene (neat liquid, KBr plates).

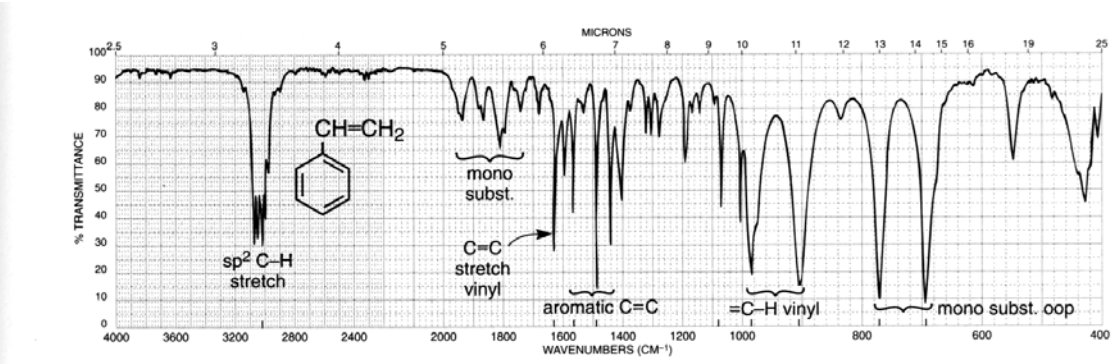


FIGURE 2.27 The infrared spectrum of styrene (neat liquid, KBr plates).

Ortho substituted rings give one strong band at 750 cm^{-1}

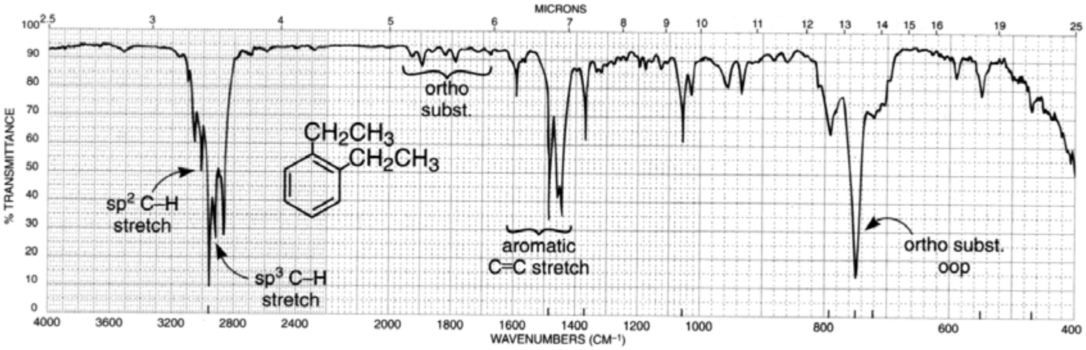


FIGURE 2.24 The infrared spectrum of *ortho*-diethylbenzene (neat liquid, KBr plates).

Meta substituted rings gives bands at 690 cm^{-1}, 780 cm^{-1}, and sometimes a third band of medium intensity at 880 cm^{-1}

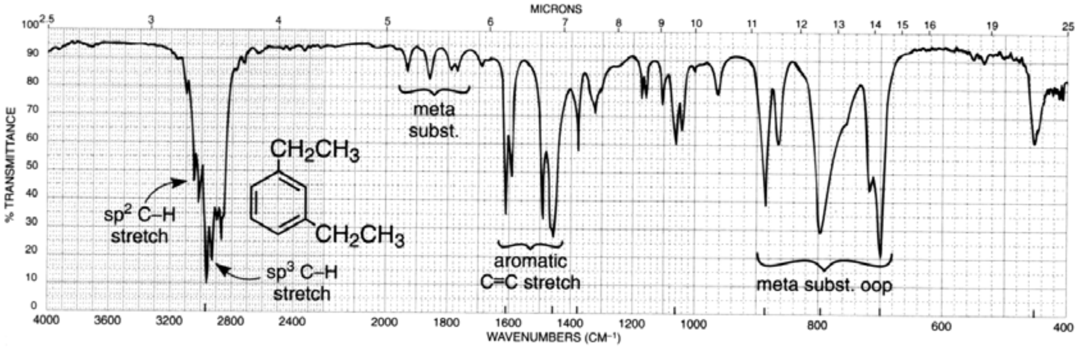


FIGURE 2.25 The infrared spectrum of *meta*-diethylbenzene (neat liquid, KBr plates).

Para substituted rings give one band from 800 to 850 cm^{-1}

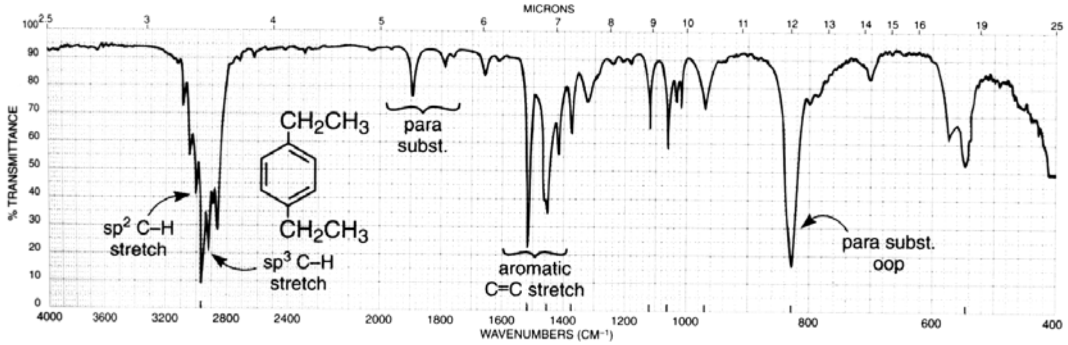


FIGURE 2.26 The infrared spectrum of *para*-diethylbenzene (neat liquid, KBr plates).

Alcohols and Phenols

Hydrogen-bonded O-H stretching occurs as a very broad and intense peak at 3400-3300 cm-1

Free O-H stretching (only observed when dilute) occurs at
3600 – 3650 cm^{-1}

C-O-H bending - a broad and weak peak at 1550-1220 cm^{-1}

C-O stretching occurs in range 1260 – 1000 cm^{-1}

The position of the C-O stretch can be used to determine the type of alcohol

Phenols – 1220 cm^{-1}

Tertiary alcohols – 1150 cm^{-1}

Secondary alcohols – 1100 cm^{-1}

Primary alcohols – 1050 cm^{-1}

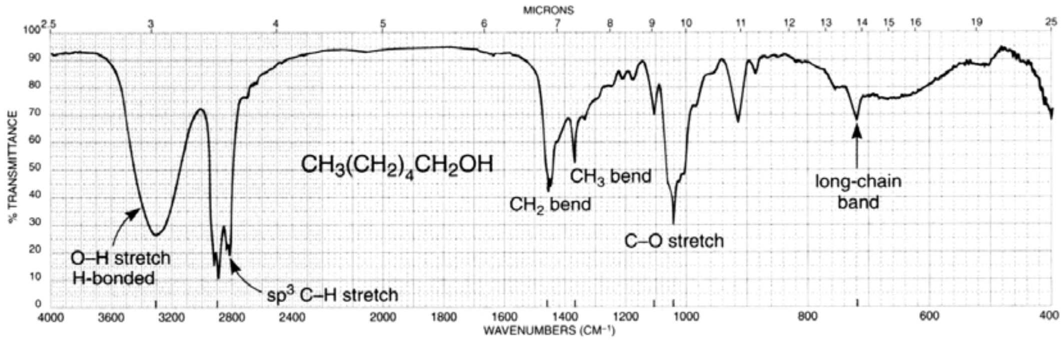


FIGURE 2.29 The infrared spectrum of 1-hexanol (neat liquid, KBr plates).

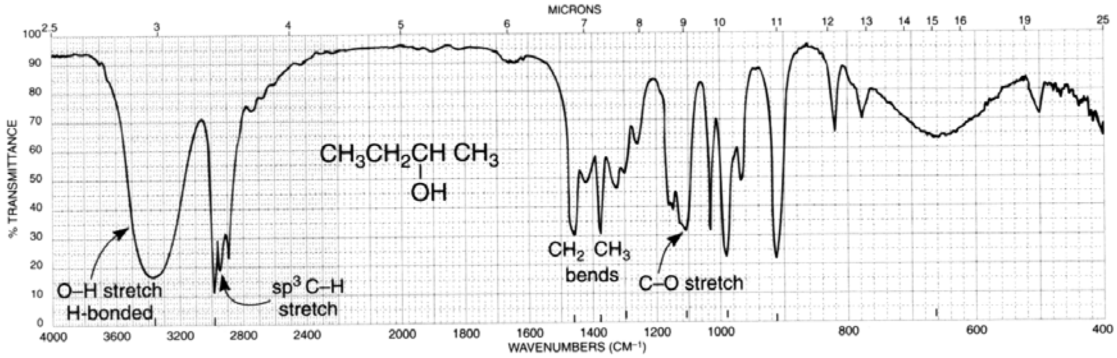


FIGURE 2.30 The infrared spectrum of 2-butanol (neat liquid, KBr plates).

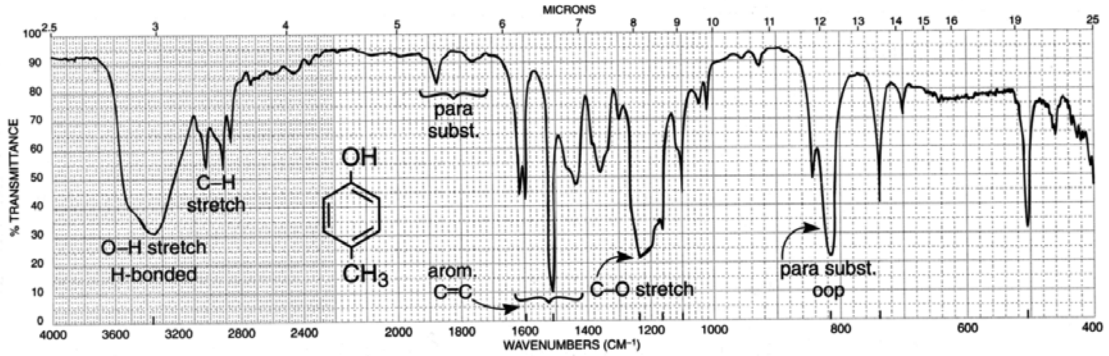


FIGURE 2.31 The infrared spectrum of *para*-cresol (neat liquid, KBr plates).

Ethers

C-O stretch most important, occurs at 1300-1000 cm^{-1}

In dialkyl ethers occurs as a strong band at 1120 cm^{-1}

Aryl alkyl ethers give two peaks; asymmetric C-O-C stretch near 1250 cm-1 and a symmetric stretch near 1040 cm^{-1}

Vinyl alkyl ethers give two peaks, a strong asymmetric stretch at 1220 cm-1 and a weak symmetric stretch near 850 cm^{-1}

C-O stretches also occur in alcohols and esters, so look for O-H or C=O stretches before concluding a compound is an ether

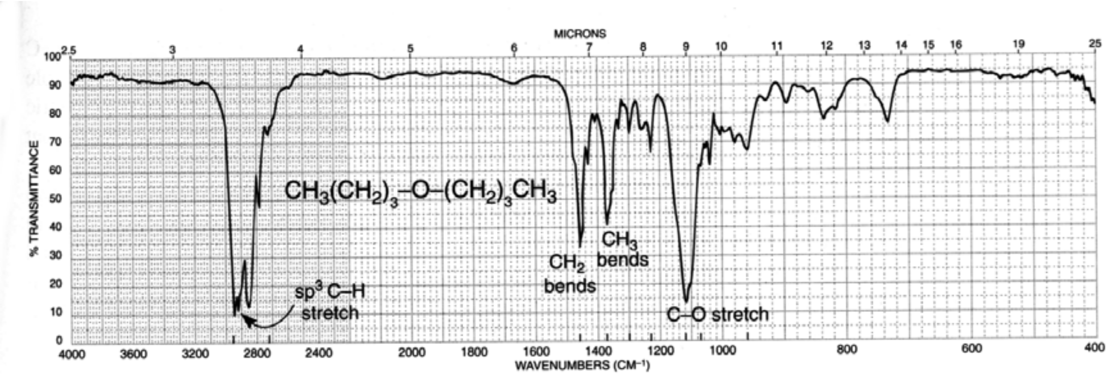


FIGURE 2.33 The infrared spectrum of dibutyl ether (neat liquid, KBr plates).

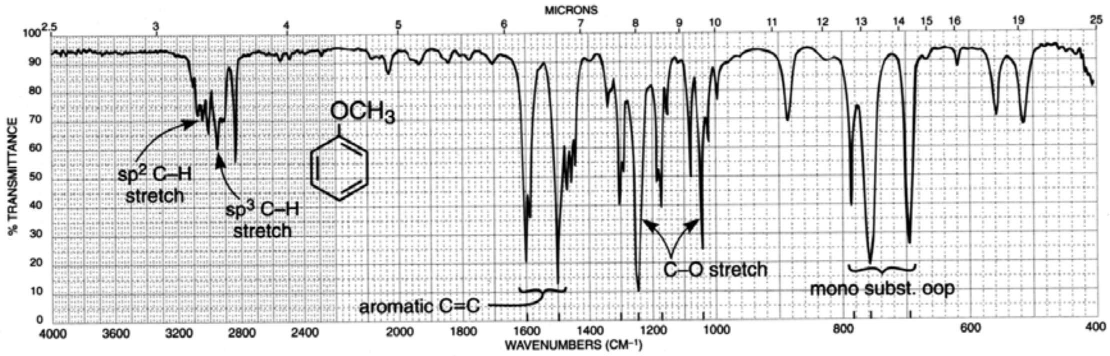


FIGURE 2.34 The infrared spectrum of anisole (neat liquid, KBr plates).

Aldehydes

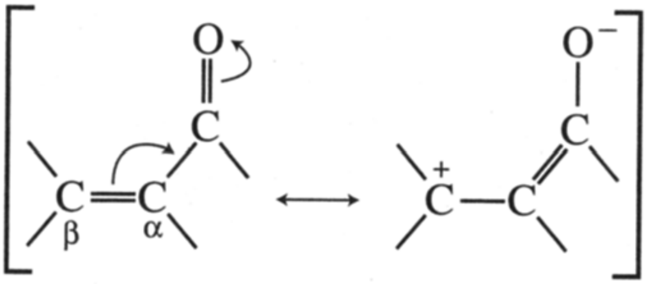
Contains a C=O stretch at:

1740 – 1725 cm^{-1} for normal aliphatic aldehyde

1700 – 1680 cm^{-1} for conjugation with double bond

1700 – 1660 cm^{-1} for conjugation with phenyl group

Conjugation decreases the C-O bond order and therefore decreases the stretching frequency



The (CO)-H stretch occurs as a pair of weak bands at 2860 – 2800 cm^{-1} and 2760 – 2700 cm^{-1}; the higher-frequency bands are often masked by alkane C-H absorptions

Above band can help to differentiate between aldehydes and ketones as these both have a carbonyl group

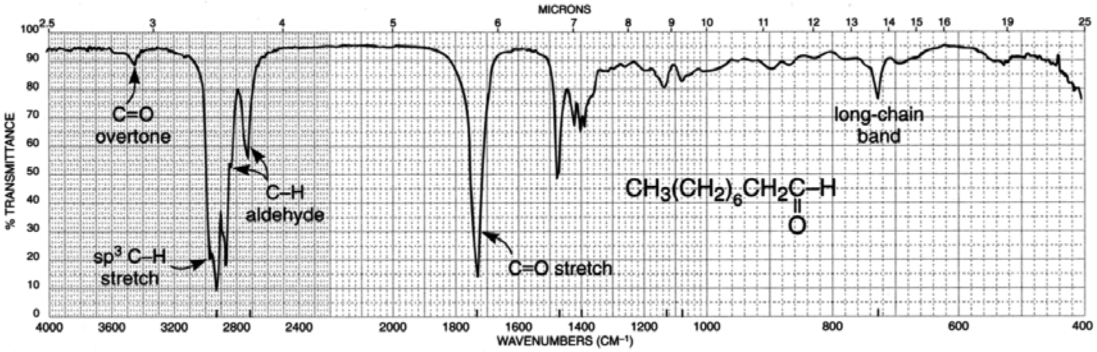


FIGURE 2.36 The infrared spectrum of nonanal (neat liquid, KBr plates).

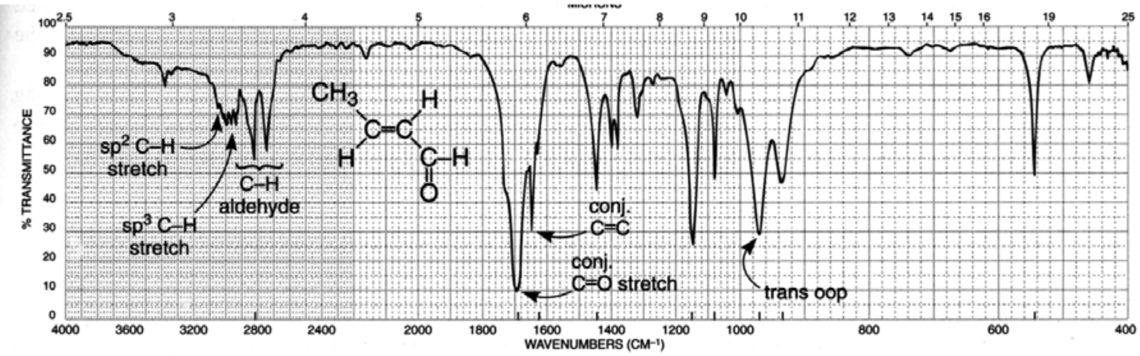


FIGURE 2.37 The infrared spectrum of crotonaldehyde (neat liquid, KBr plates).

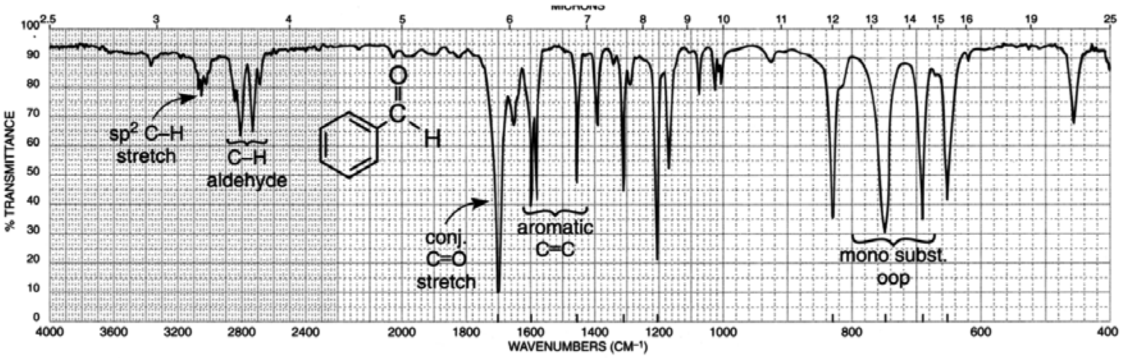


FIGURE 2.38 The infrared spectrum of benzaldehyde (neat liquid, KBr plates).

Ketones

Contains a C=O stretch at:

1720 – 1708 cm^{-1} for normal aliphatic aldehyde
(slightly lower frequency than for aldehydes)

1700 – 1675 cm^{-1} for conjugation with double bond

1700 – 1680 cm^{-1} for conjugation with one phenyl group

1670 – 1600 cm^{-1} for conjugation with two phenyl groups

~ 1716 cm^{-1} for 1,2 diketones (not conjugated)

~ 1680 cm^{-1} for 1,2 diketones (conjugated)

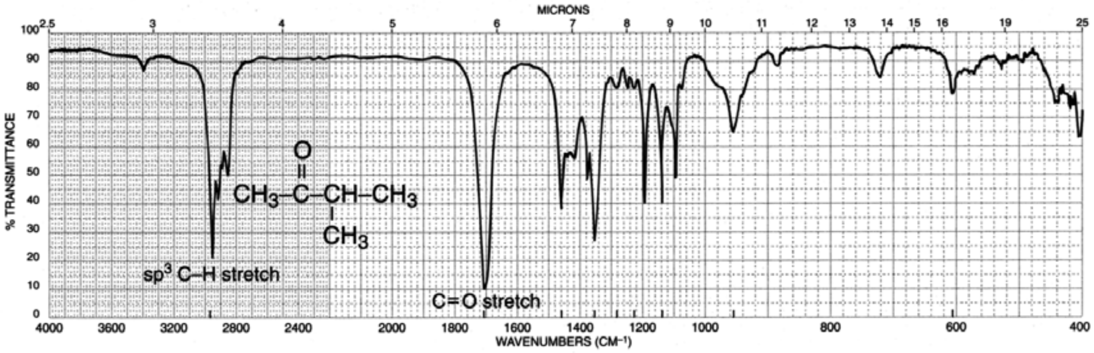


FIGURE 2.4 The infrared spectrum of 3-methyl-2-butanone (neat liquid, KBr plates).

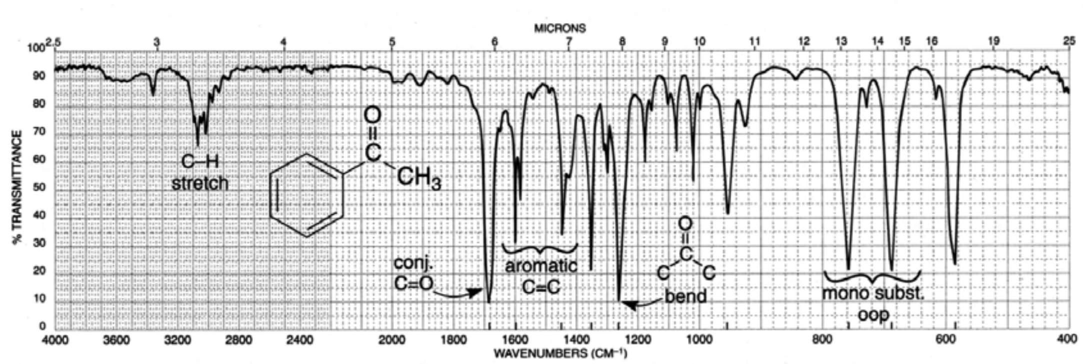
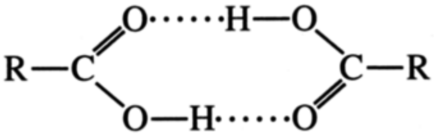


FIGURE 2.40 The infrared spectrum of acetophenone (neat liquid, KBr plates).

Carboxylic Acids

Carboxylic acids occur as hydrogen-bonded dimers unless in dilute solution



C=0 stretch occurs in the following regions:

1730 – 1700 cm^{-1} for simple aliphatic acids in dimeric form

Occurs at lower frequencies if conjugated with an alkene or aromatic

O-H stretch occurs as a very broad peak at 3400 to 2400 cm^{-1}, may partially obscure C-H stretching bands

C-O stretch of medium intensity observed at 1320 –1210 cm^{-1}

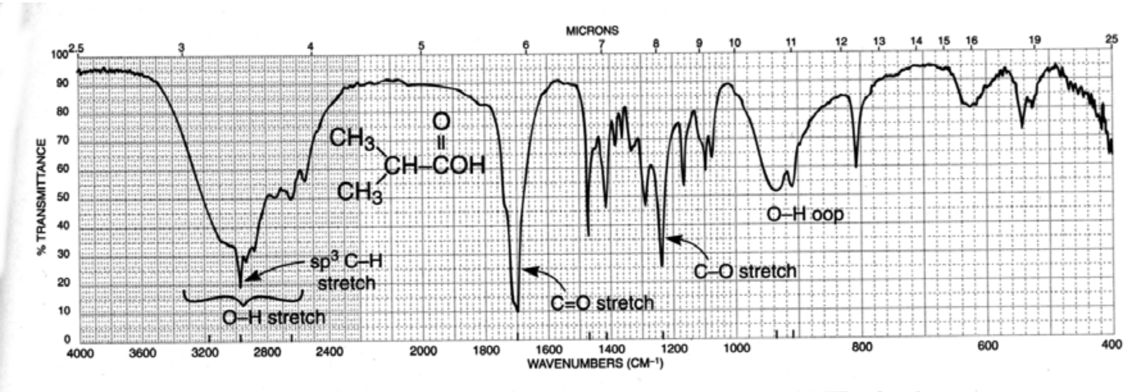


FIGURE 2.45 The infrared spectrum of isobutyric acid (neat liquid, KBr plates).

Esters

C=O stretch occurs at:

1750 – 1735 cm^{-1} for normal aliphatic esters
(example – ethyl butyrate, 1738 cm^{-1})

1740 – 1750 cm^{-1} if carbonyl carbon conjugated with an alkene
(example – methyl methacrylate, 1725 cm^{-1})

1740 – 1715 cm^{-1} if carbonyl carbon conjugated with aromatic
(example – methyl benzoate, 1724 cm^{-1})

1765 – 1762 cm^{-1} if oxygen atom conjugated with alkene or aromatic (note that this is a shift to higher frequency)
(example – phenyl acetate, 1765 cm^{-1})
(example – vinyl acetate, 1762 cm$^{-1)}$

The C-O stretch occurs as two bands, one stronger and broader than the other, at 1300 – 1000 cm^{-1}

Ethyl butryate – simple aliphatic ester

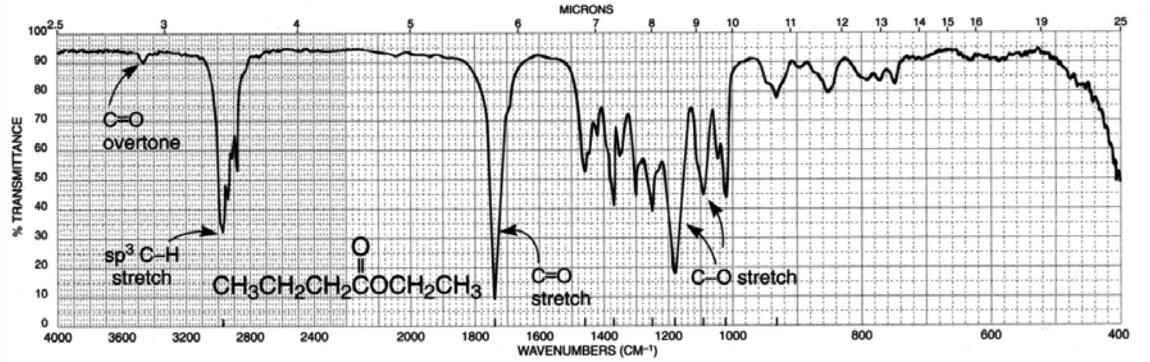


FIGURE 2.47 The infrared spectrum of ethyl butyrate (neat liquid, KBr plates).

Vinyl acetate – alkene group adjacent to C=O group

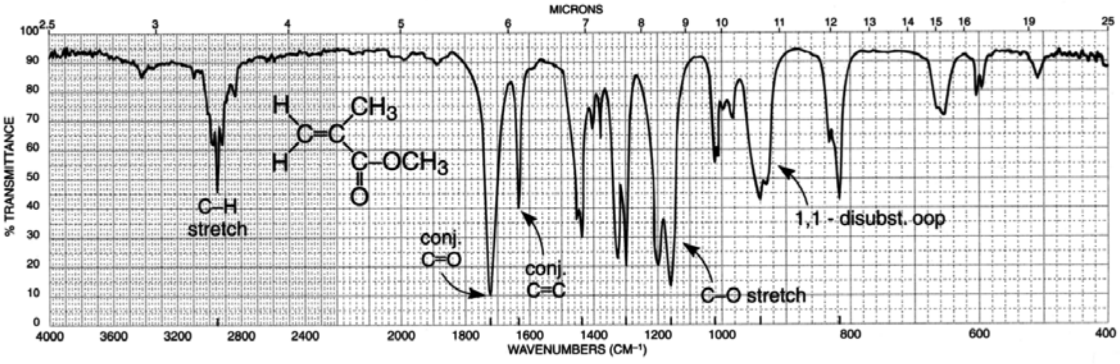


FIGURE 2.48 The infrared spectrum of methyl methacrylate (neat liquid, KBr plates).

Vinyl acetate – oxygen atom conjugated with alkene

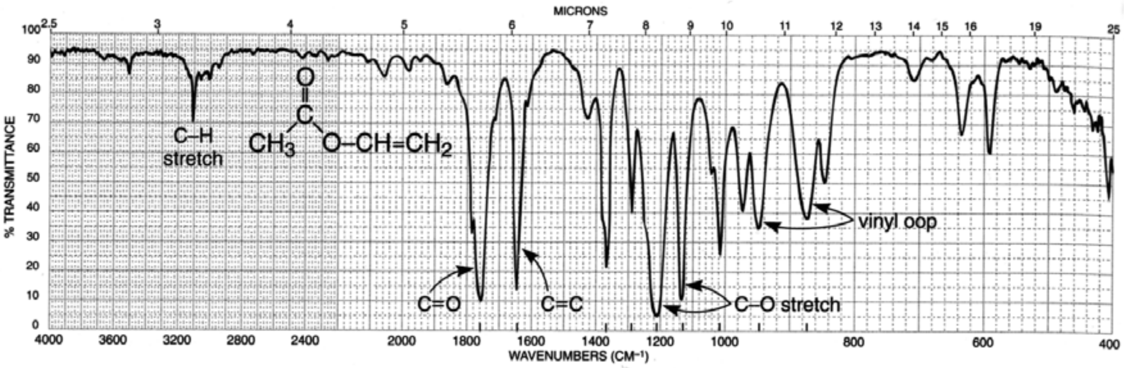


FIGURE 2.49 The infrared spectrum of vinyl acetate (neat liquid, KBr plates).

Methyl benzoate – aromatic group adjacent to C=O group

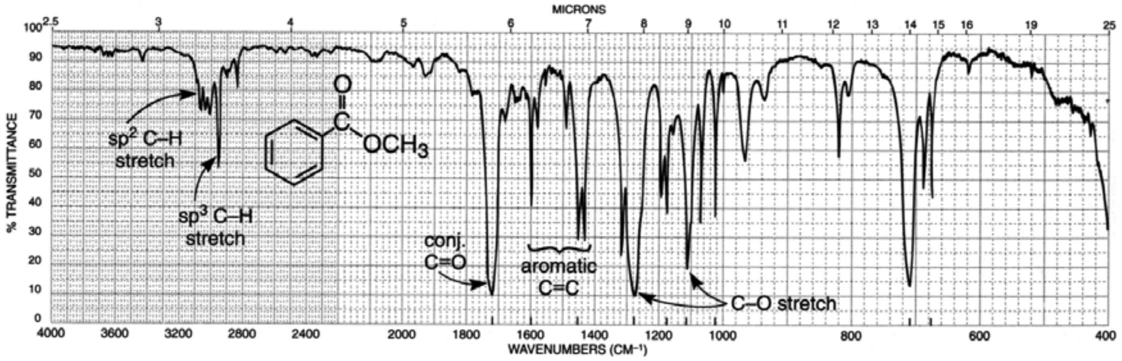


FIGURE 2.50 The infrared spectrum of methyl benzoate (neat liquid, KBr plates).

Amines

N-H stretch occurs at 3500 –3300 cm^{-1}

Primary amines – two bands

Secondary amines – one band; weak for aliphatic amines but stronger for aromatic

Tertiary amines have no absorption in this region (no N-H bonds)

N-H bending

Broad band at 1640 – 1560 cm^{-1} for primary amine

Secondary amines absorb at 1500 cm^{-1}

N-H out of plane bending occurs at 800 cm^{-1}

C-N stretching occurs at 1350 – 1000 cm^{-1}

Butylamine – primary amine

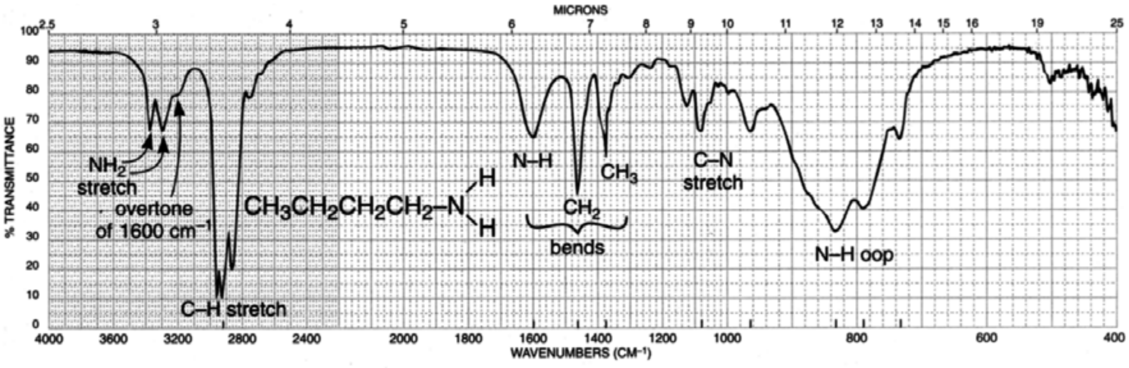


FIGURE 2.58 The infrared spectrum of butylamine (neat liquid, KBr plates).

Dibutyl amine – secondary amine

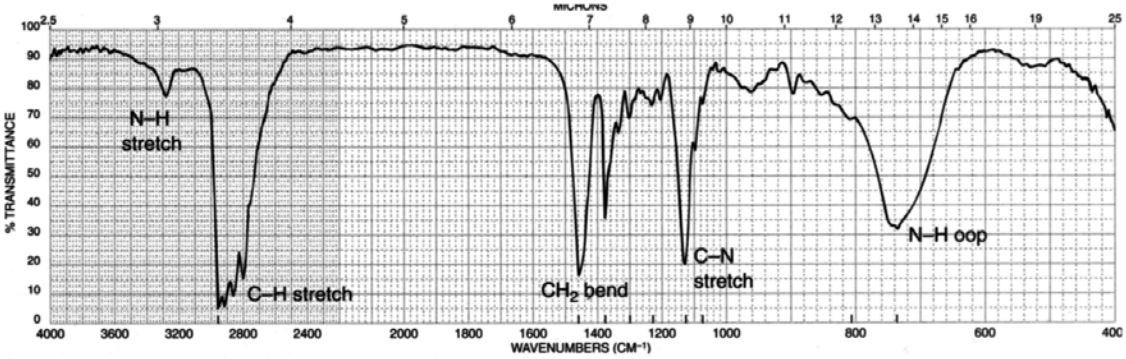


FIGURE 2.59 The infrared spectrum of dibutylamine (neat liquid, KBr plates).

N-methyl aniline – secondary aromatic amine

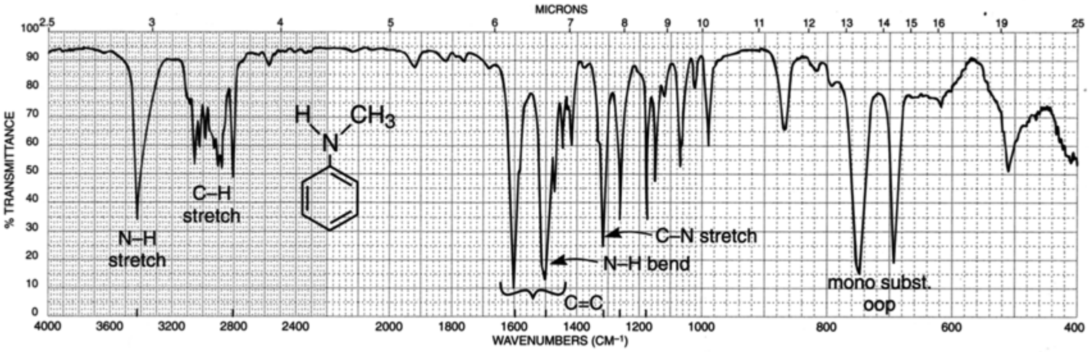
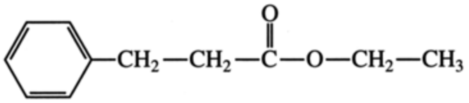


FIGURE 2.61 The infrared spectrum of *N*-methylaniline (neat liquid, KBr plates).

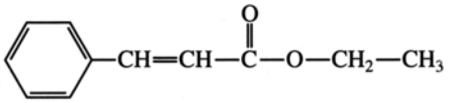
Example 4

5. In each part, choose the structure that best fits the infrared spectrum shown.

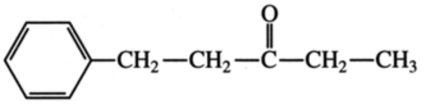
*(a)



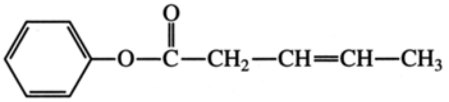
A



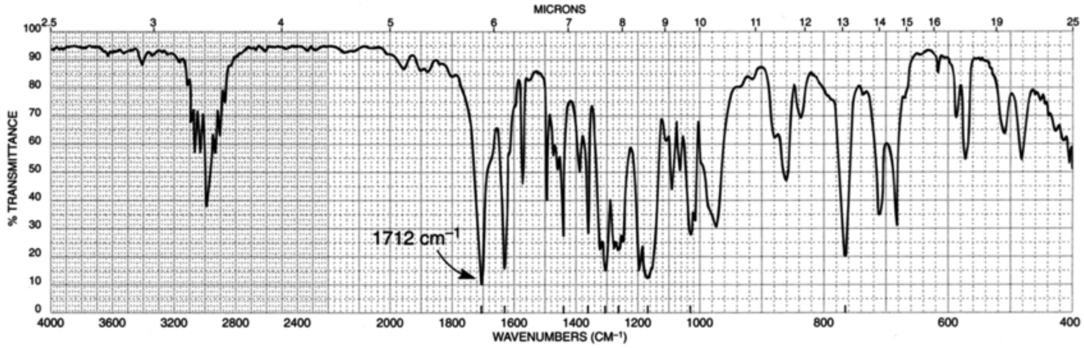
B



C



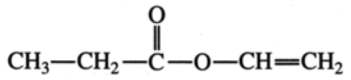
D



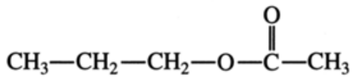
Example 5

Match each spectrum to the appropriate structure (try on your own before jumping to solution)

A



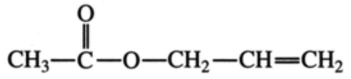
$CH_3-CH_2-\overset{O}{\overset{\|}{C}}-O-CH=CH_2$



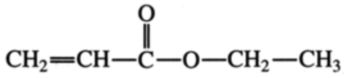
$CH_3-CH_2-CH_2-O-\overset{O}{\overset{\|}{C}}-CH_3$

C

B

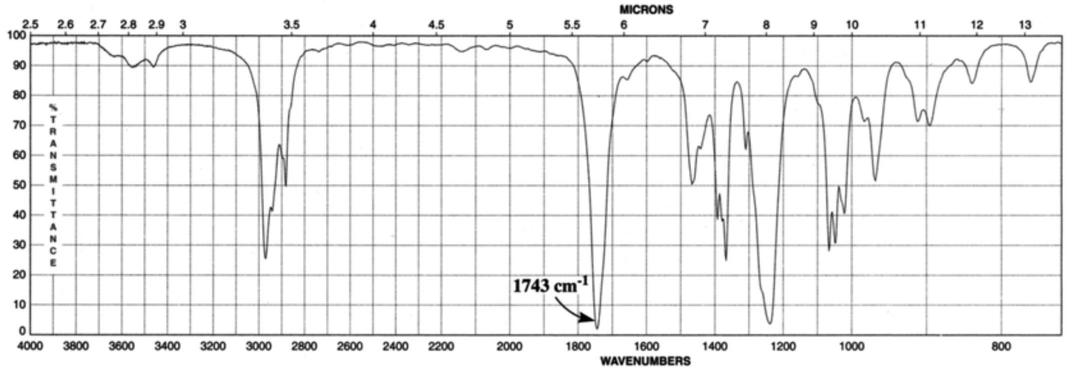


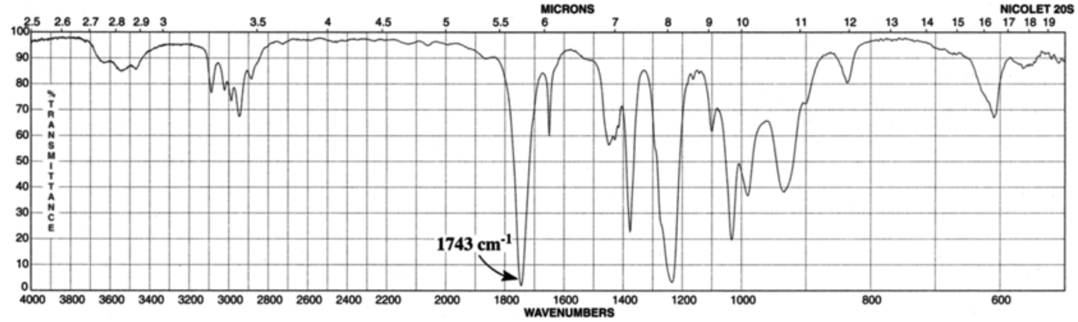
$CH_3-\overset{O}{\overset{\|}{C}}-O-CH_2-CH=CH_2$

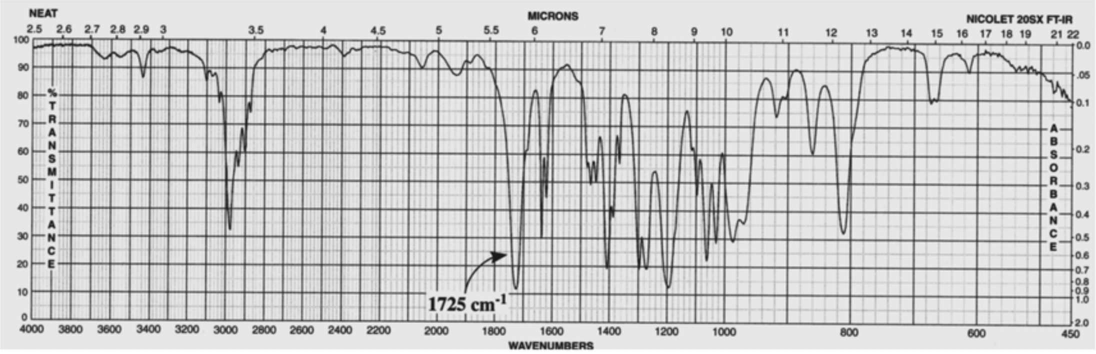


$CH_2=CH-\overset{O}{\overset{\|}{C}}-O-CH_2-CH_3$

D







Solution