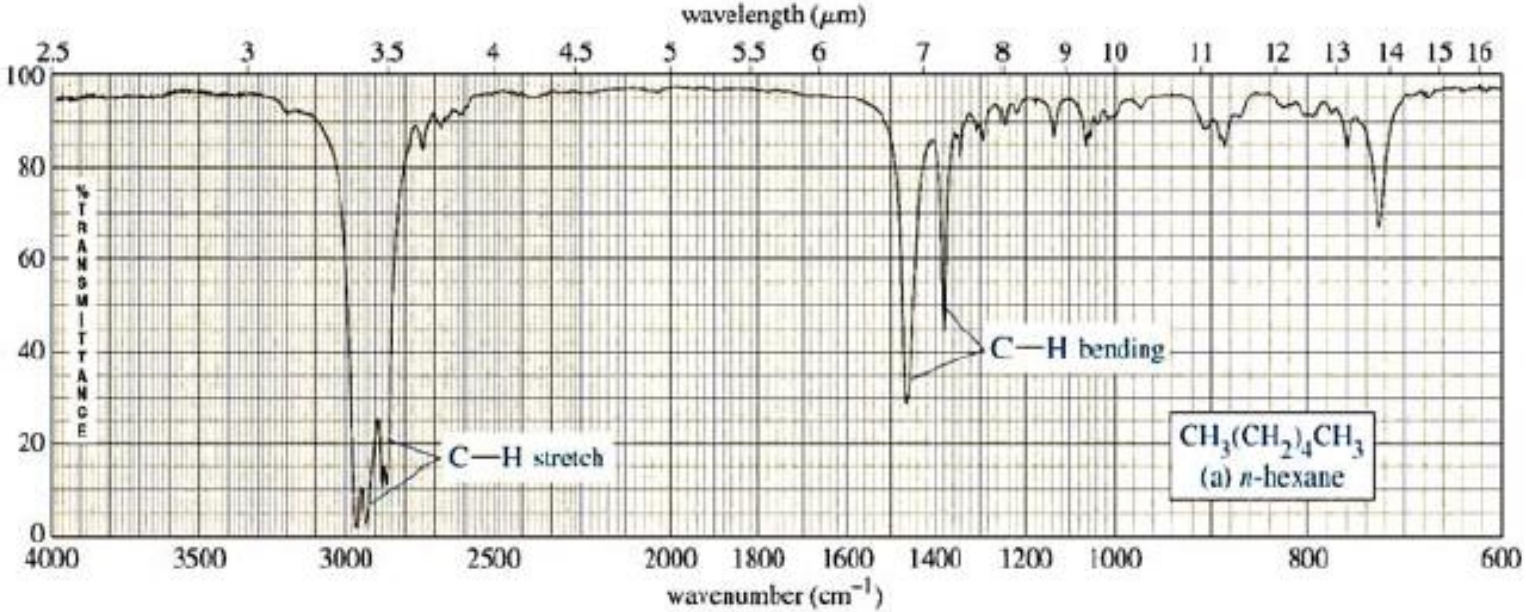
IR SPECTRUM OF ALKANES

Alkanes have no functional groups. Their IR spectrum displays only C-C and C-H bond vibrations. Of these the most useful are the **C-H bands**, which appear around **3000 cm^{-1}**. Since most organic molecules have such bonds, most organic molecules will display those bands in their spectrum.



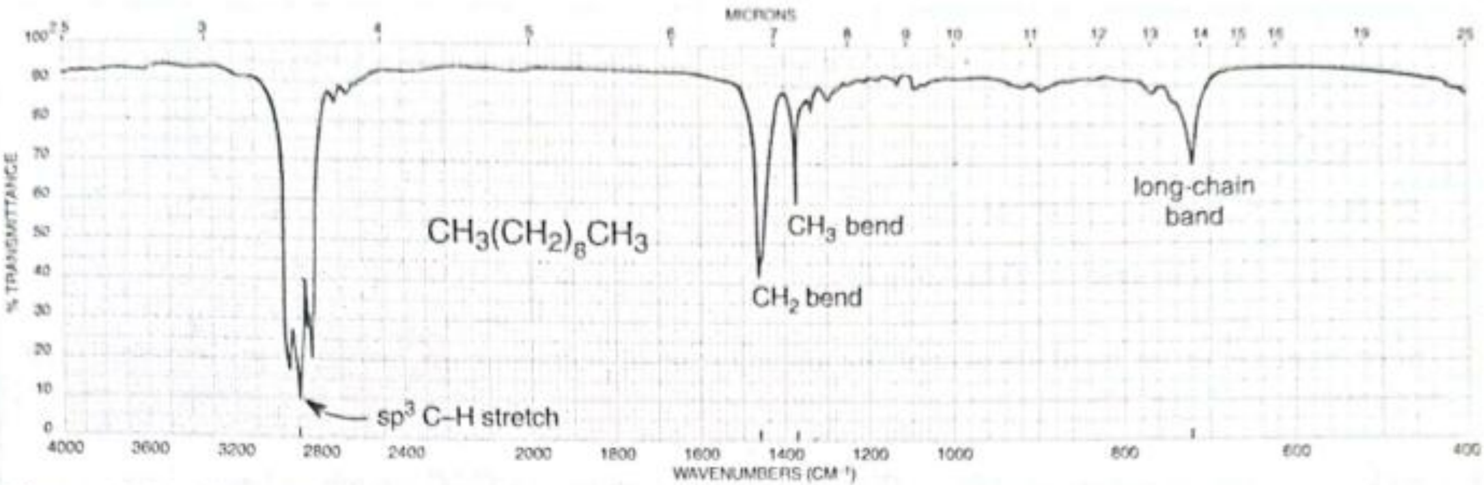


Figure 2.6 *The infrared spectrum of decane (neat liquid, KBr plates).*

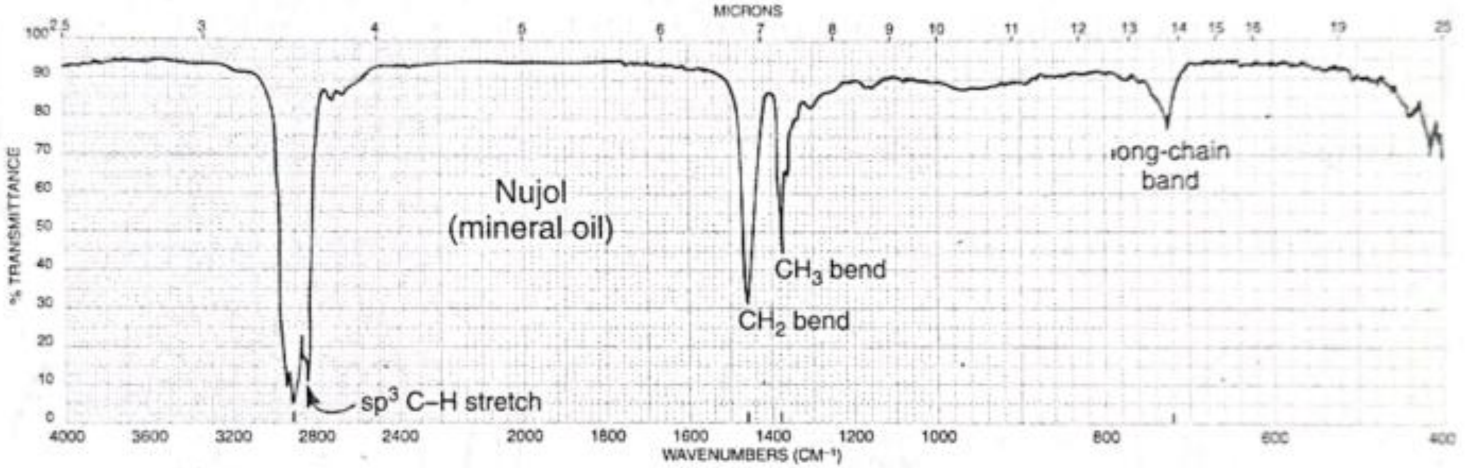
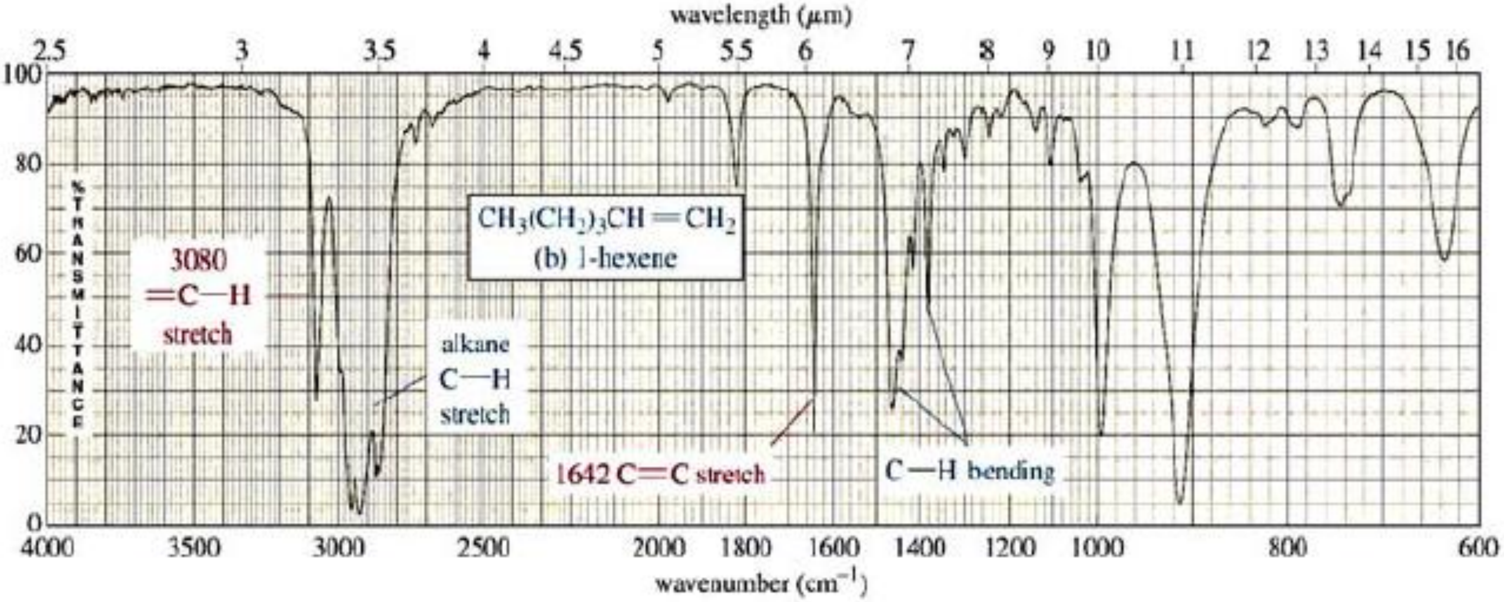


Figure 2.7 *The infrared spectrum of mineral oil (neat liquid, KBr plates).*

IR SPECTRUM OF ALKENES

Besides the presence of C-H bonds, alkenes also show sharp, medium bands corresponding to the **C=C bond stretching vibration** at about **1600-1700 cm^{-1}**. Some alkenes might also show a band for the =C-H bond stretch, appearing around **3080 cm^{-1}** as shown below. However, this band could be obscured by the broader bands appearing around 3000 cm^{-1} (see next slide)



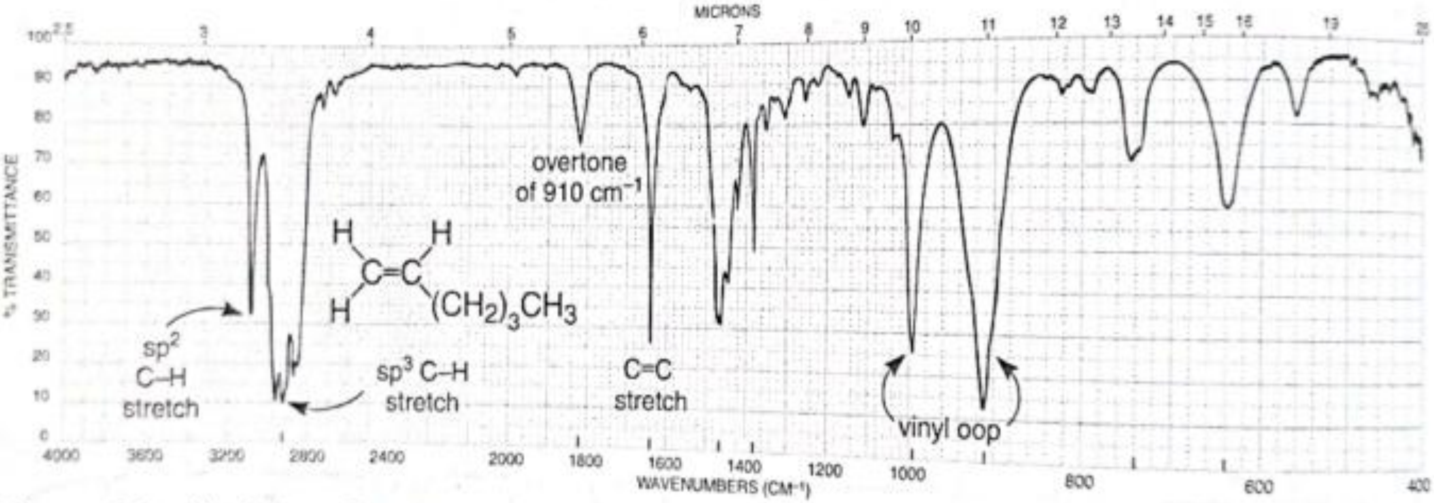


Figure 2.9 *The infrared spectrum of 1-hexene (neat liquid, KBr plates).*

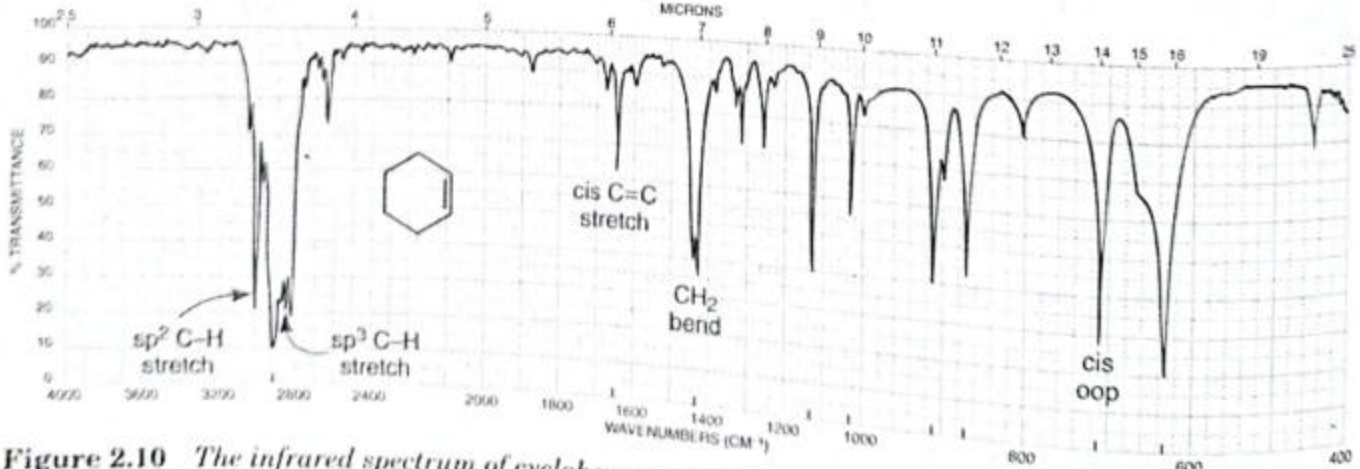
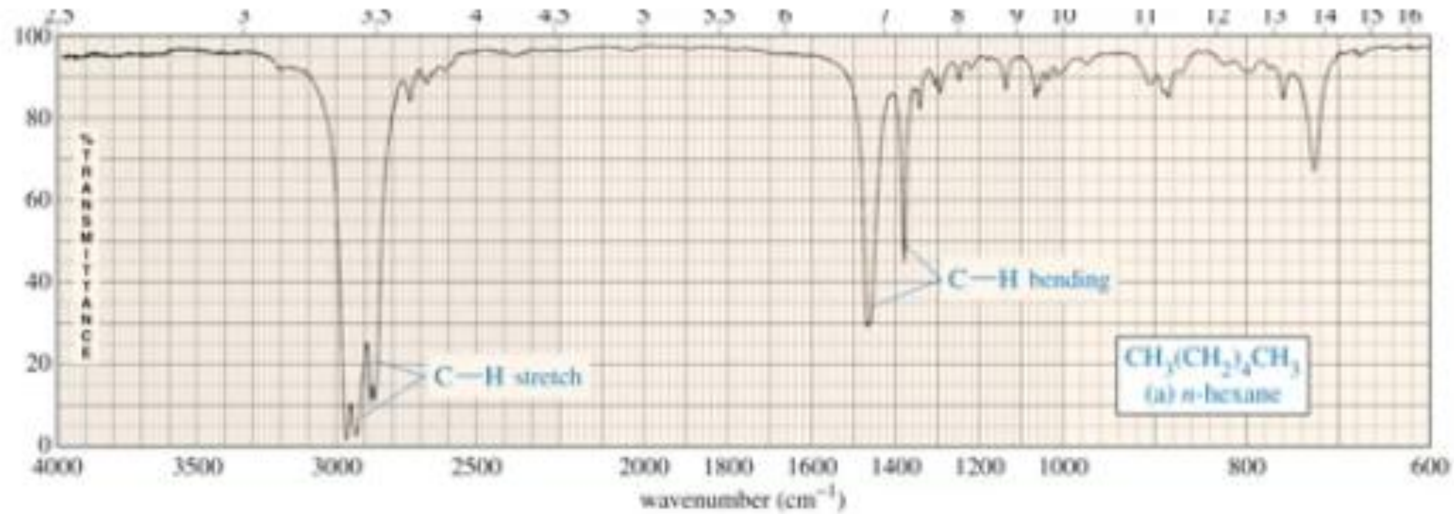
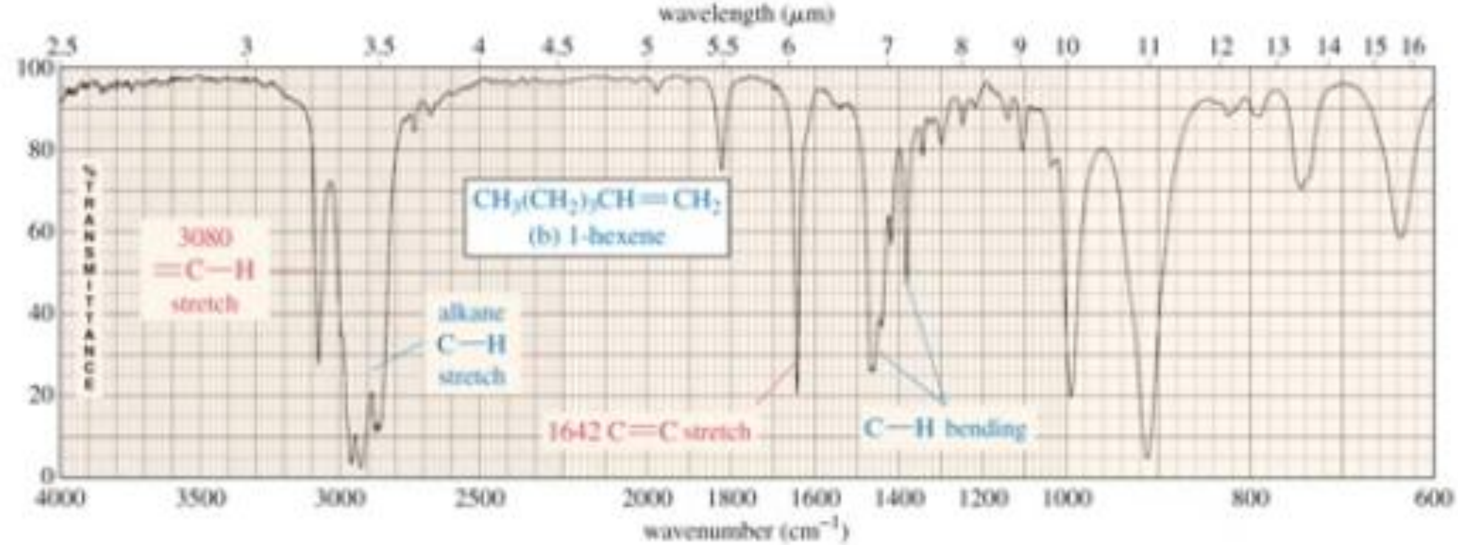


Figure 2.10 *The infrared spectrum of cyclohexene (neat liquid, KBr plates).*



2.5
3
3.5
4
4.5
5
5.5
6
7
8
9
10
11
12
13
14
15
16
100
80
60
40
20
0
% TRANSMITTANCE
C—H bending
C—H stretch
$CH_3(CH_2)_4CH_3$
(a) n-hexane
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
wavenumber (cm^{-1})



wavelength (μm)
2.5
3
3.5
4
4.5
5
5.5
6
7
8
9
10
11
12
13
14
15
16
100
80
60
40
20
0
% TRANSMITTANCE
$CH_3(CH_2)_3CH{=}CH_2$
(b) 1-hexene
3080
$=C-H$
stretch
alkane
C—H
stretch
1642 C=C stretch
C—H bending
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
wavenumber (cm^{-1})

IR SPECTRUM OF ALKYNES

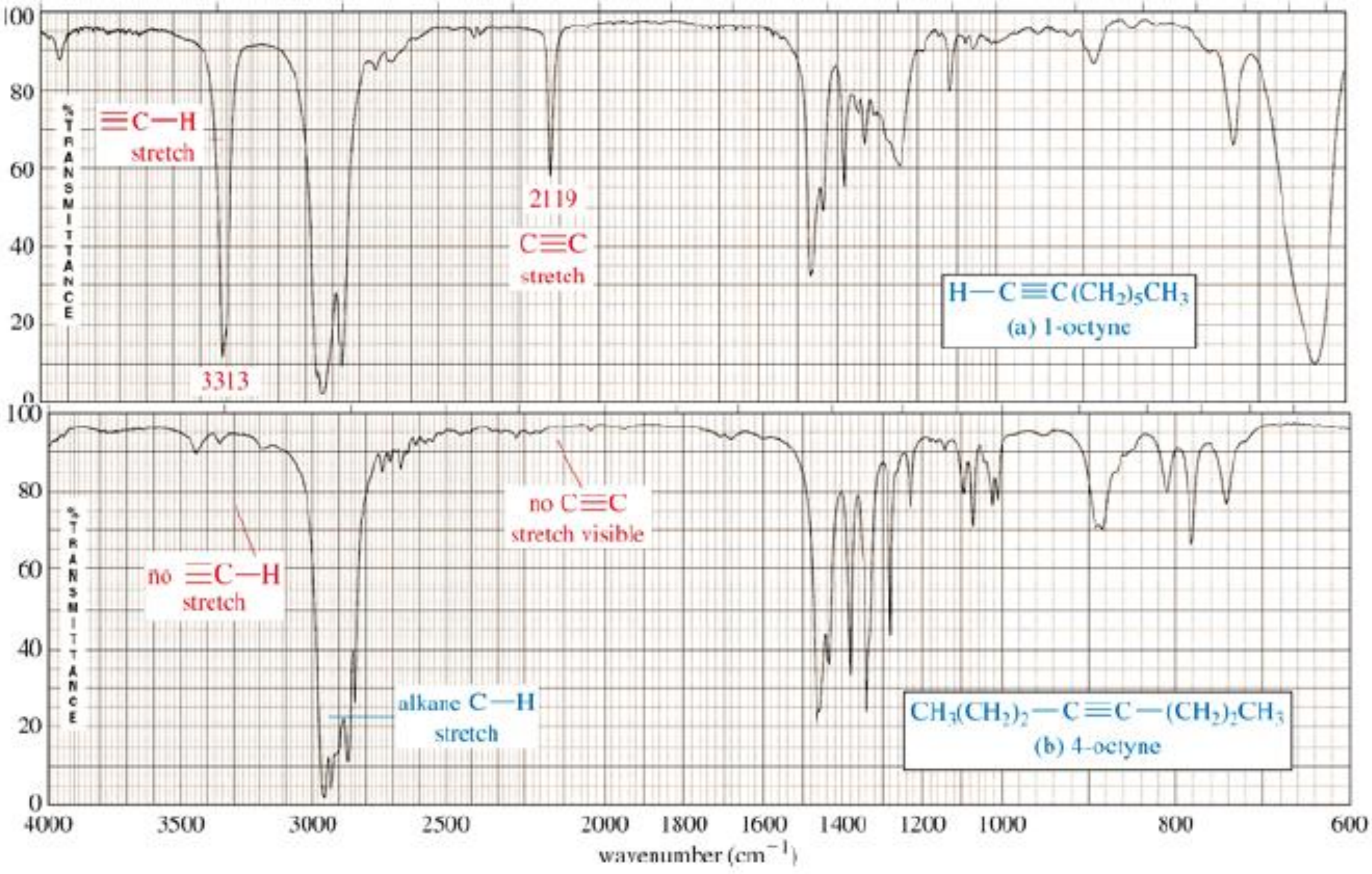
The most prominent band in alkynes corresponds to the **carbon-carbon triple bond**. It shows as a sharp, weak band at about **2100 cm^{-1}**. The reason it's weak is because the triple bond is not very polar. In some cases, such as in highly symmetrical alkynes, it may not show at all due to the low polarity of the triple bond associated with those alkynes.

Terminal alkynes, that is to say those where the triple bond is at the end of a carbon chain, have C-H bonds involving the *sp* carbon (the carbon that forms part of the triple bond). Therefore they may also show a sharp, weak band at about **3300 cm^{-1}** corresponding to the C-H stretch.

Internal alkynes, that is those where the triple bond is in the middle of a carbon chain, do not have C-H bonds to the *sp* carbon and therefore lack the aforementioned band.

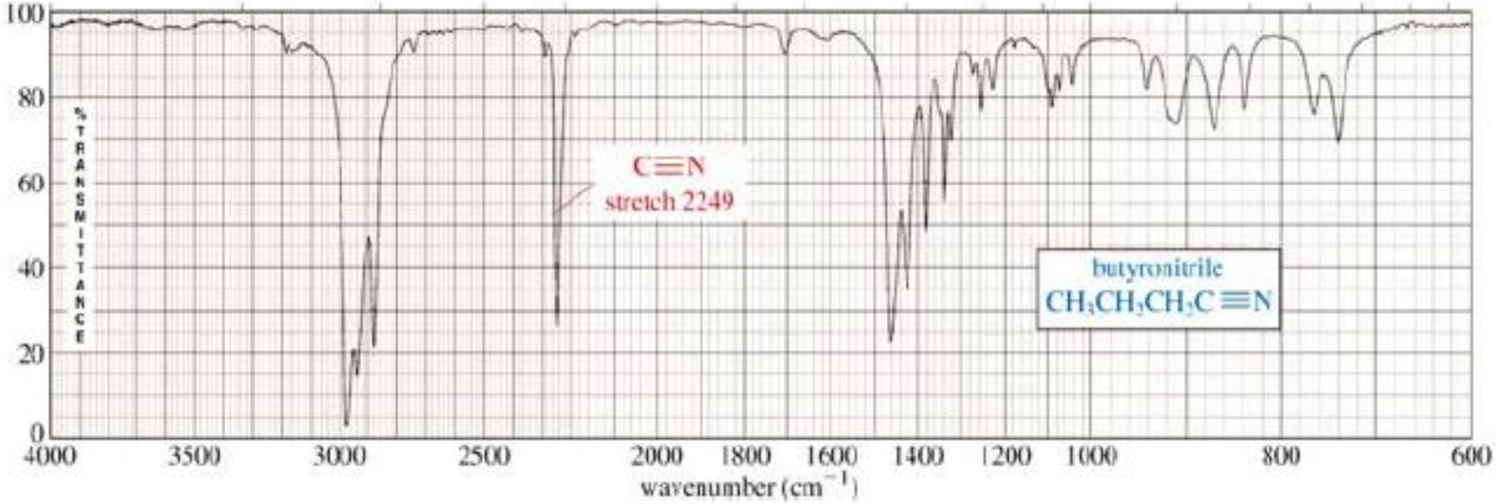
The following slide shows a comparison between an unsymmetrical terminal alkyne (1-octyne) and a symmetrical internal alkyne (4-octyne).

IR SPECTRUM OF ALKYNES



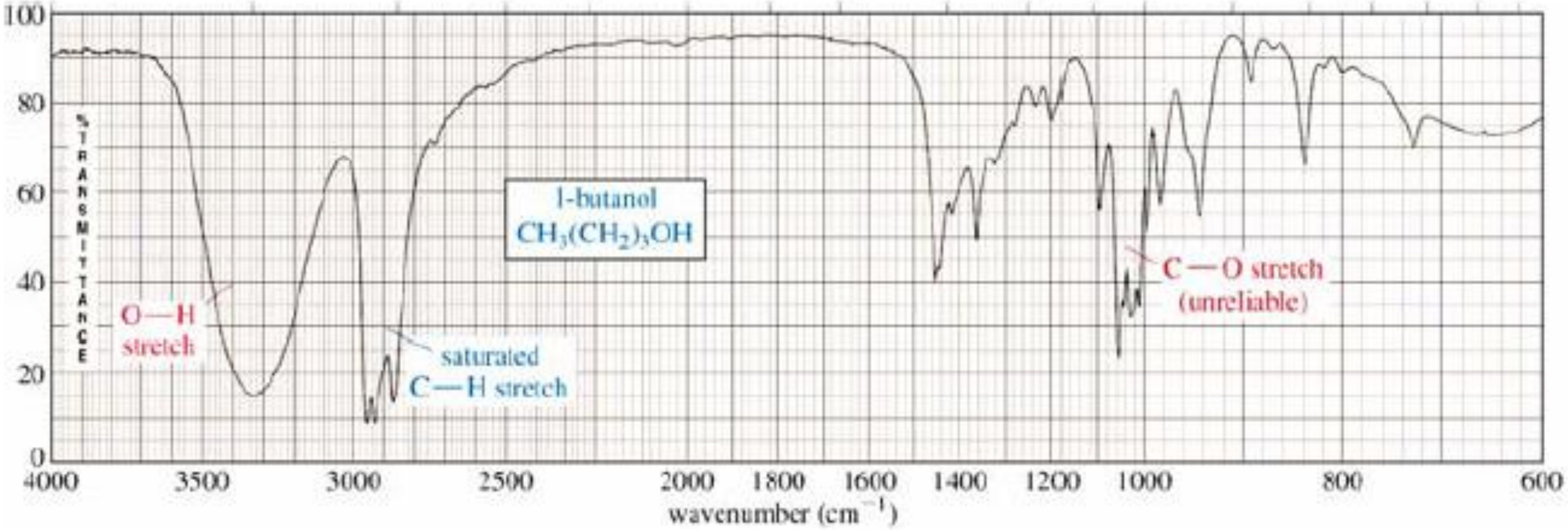
IR SPECTRUM OF A NITRILE

In a manner very similar to alkynes, nitriles show a prominent band around **2250 cm^{-1}** caused by the **CN triple bond**. This band has a sharp, pointed shape just like the alkyne C-C triple bond, but because the CN triple bond is more polar, this band is stronger than in alkynes.



IR SPECTRUM OF AN ALCOHOL

The most prominent band in alcohols is due to the **O-H bond**, and it appears as a strong, broad band covering the range of about **3000 - 3700 cm^{-1}**. The sheer size and broad shape of the band dominate the IR spectrum and make it hard to miss.



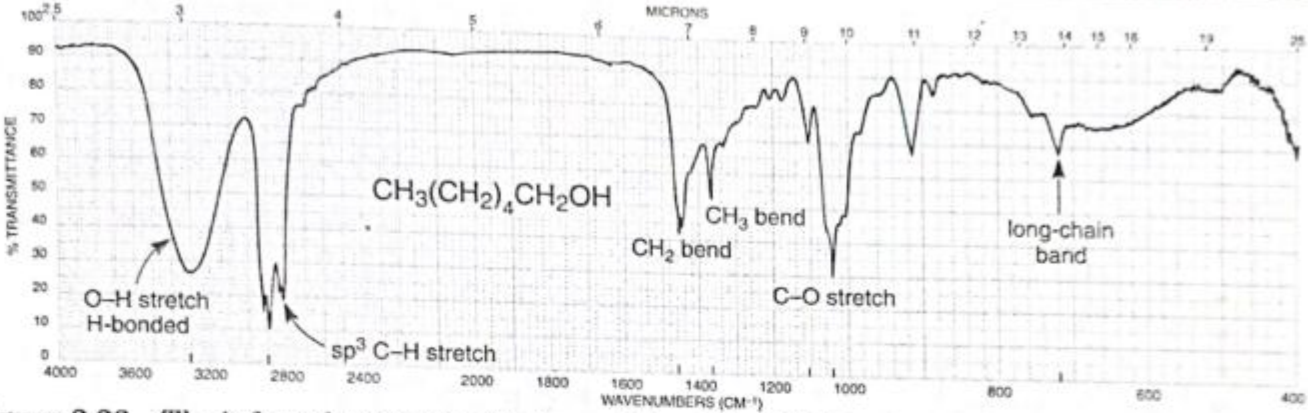


Figure 2.28 *The infrared spectrum of 1-hexanol (neat liquid, KBr plates).*

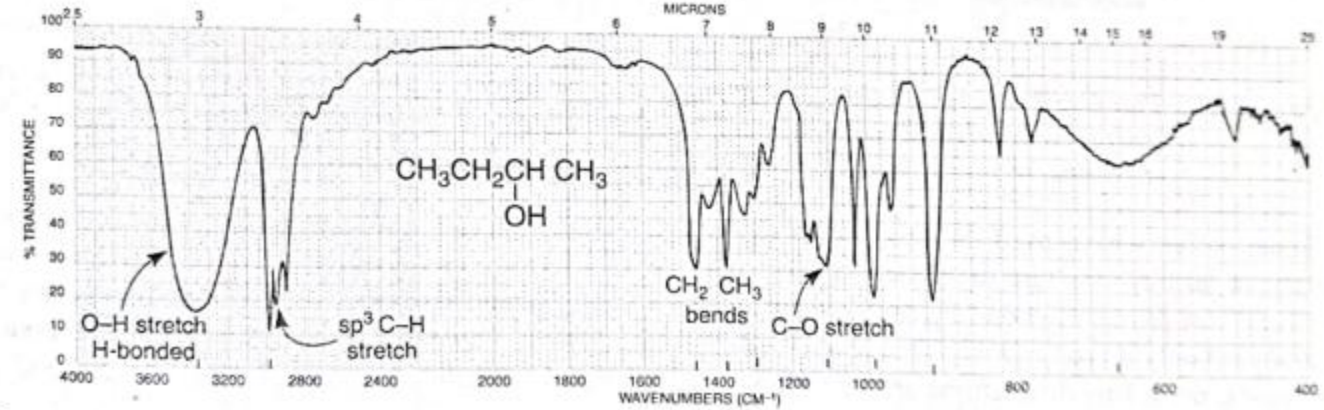


Figure 2.29 *The infrared spectrum of 2-butanol (neat liquid, KBr plates).*

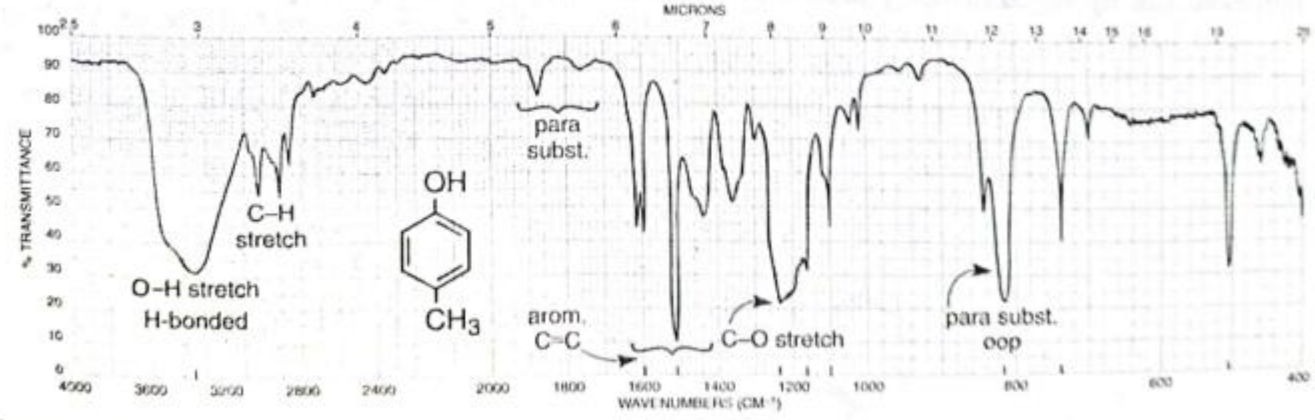


Figure 2.30 *The infrared spectrum of para-cresol (neat liquid, KBr plates).*

IR SPECTRUM OF ALDEHYDES AND KETONES

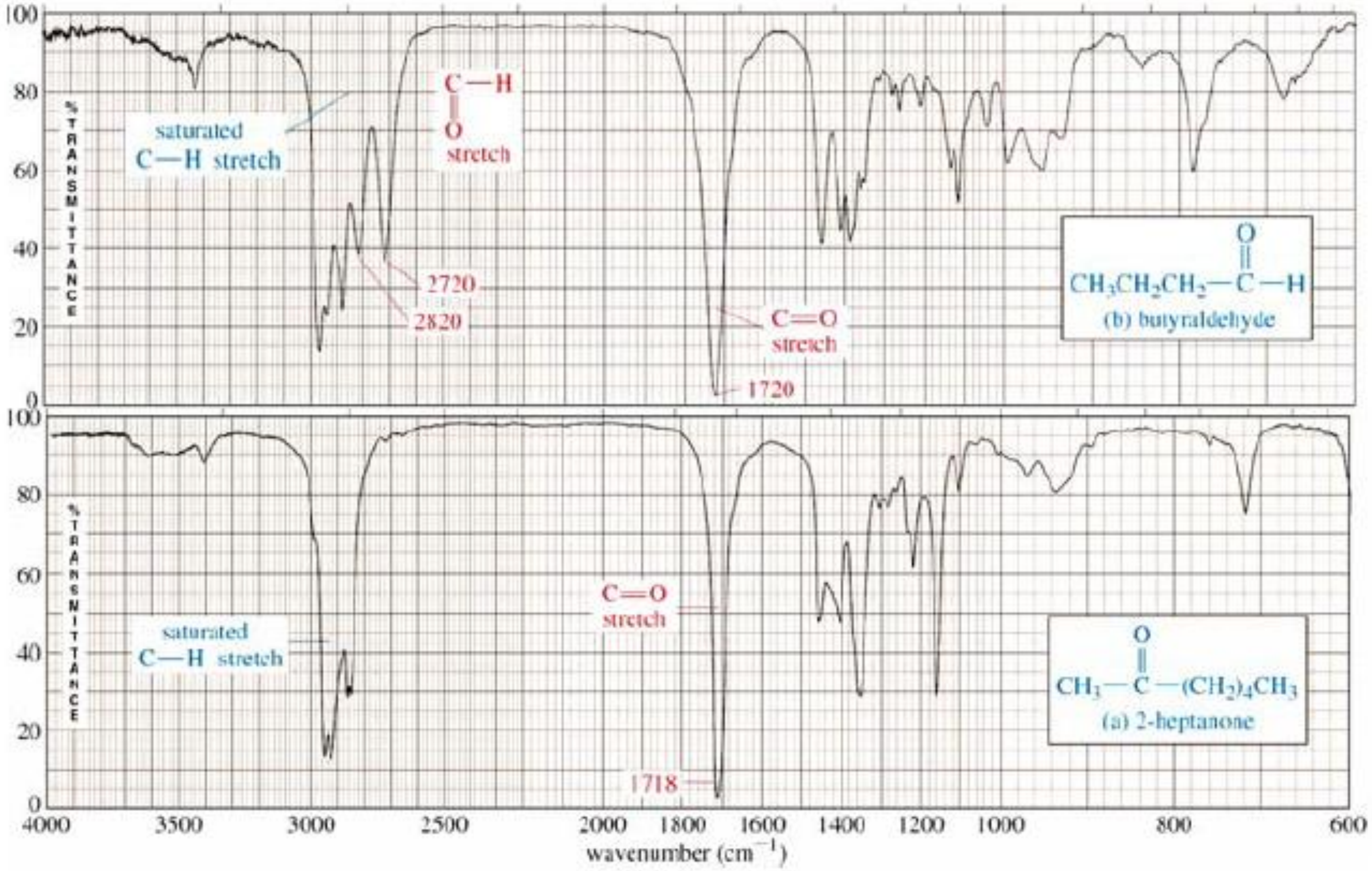
Carbonyl compounds are those that **contain the C=O functional group**. In aldehydes, this group is at the end of a carbon chain, whereas in ketones it's in the middle of the chain. As a result, the carbon in the C=O bond of aldehydes is also bonded to another carbon and a hydrogen, whereas the same carbon in a ketone is bonded to two other carbons.

Aldehydes and ketones show a strong, prominent, stake-shaped band around **1710 - 1720 cm^{-1}** (right in the middle of the spectrum). This band is due to the **highly polar C=O bond**. Because of its position, shape, and size, it is hard to miss.

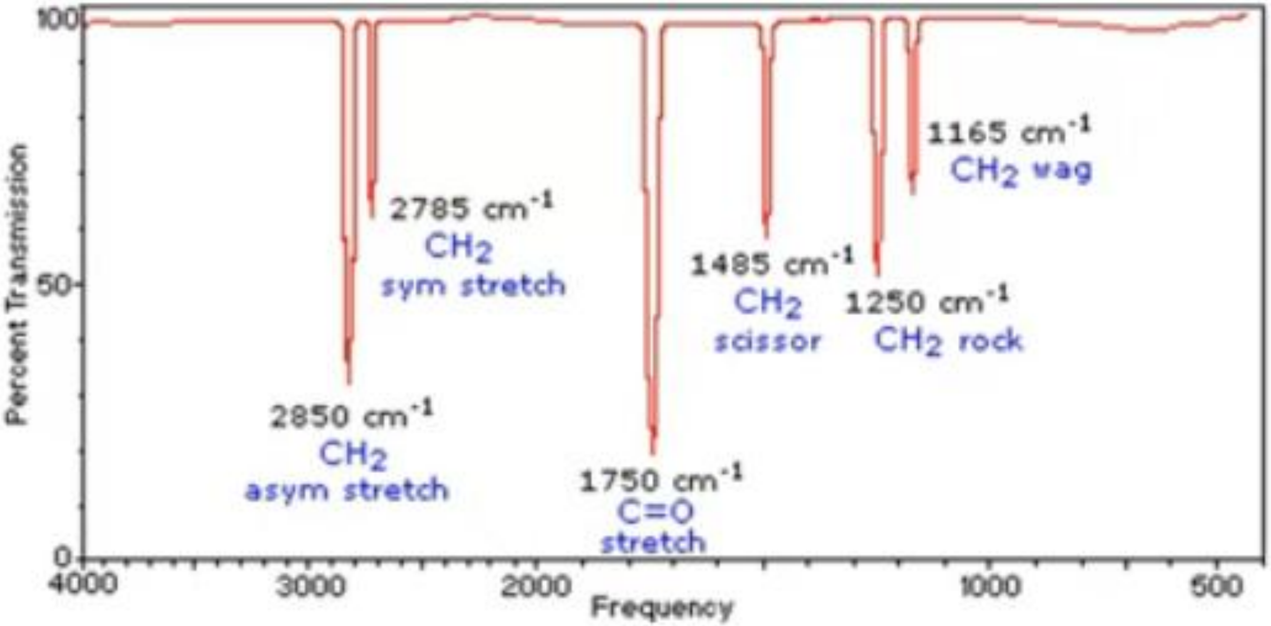
Because aldehydes also contain a C-H bond to the sp^2 carbon of the C=O bond, they also show a pair of medium strength bands positioned about **2700** and **2800 cm^{-1}**. These bands are missing in the spectrum of a ketone because the sp^2 carbon of the ketone lacks the C-H bond.

The following slide shows a spectrum of an aldehyde and a ketone. Study the similarities and the differences so that you can distinguish between the two.

IR SPECTRUM OF ALDEHYDES AND KETONES

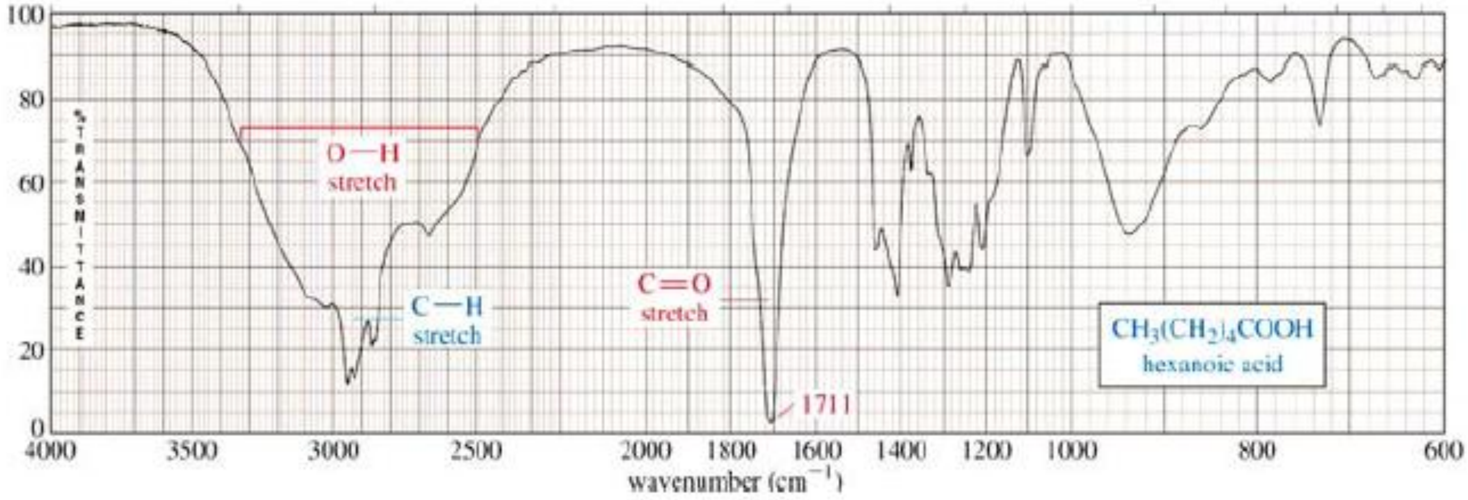


IR Spectrum of formaldehyde



IR SPECTRUM OF A CARBOXYLIC ACID

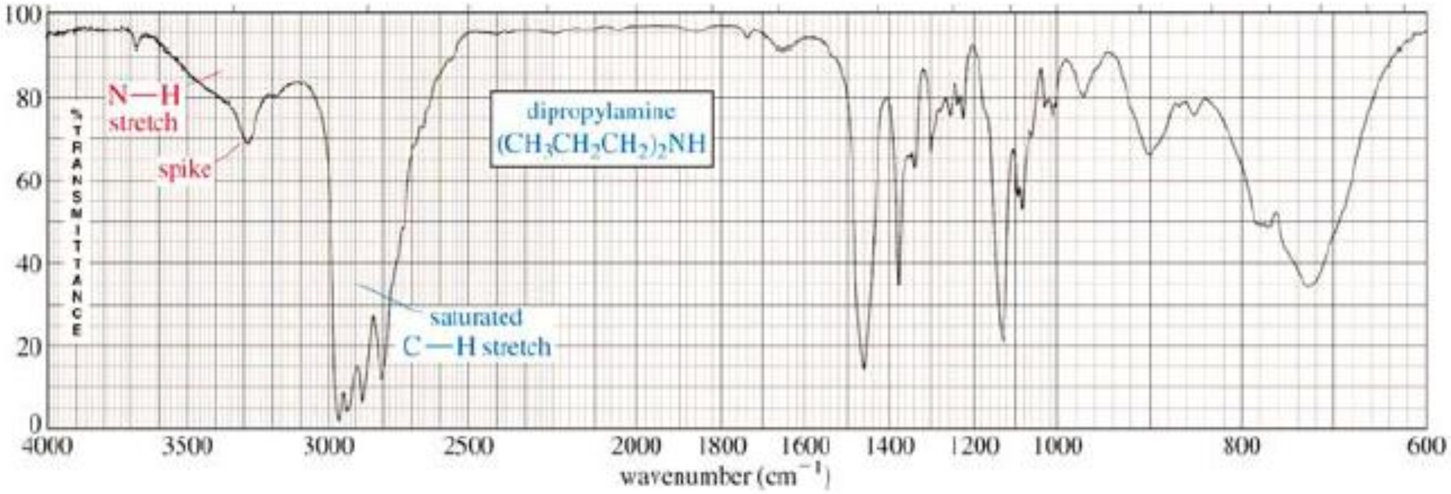
A carboxylic acid functional group combines the features of alcohols and ketones because it has both the **O-H bond** and the **C=O bond**. Therefore carboxylic acids show a very strong and broad band covering a wide range between **2800** and **3500 cm^{-1}** for the O-H stretch. At the same time they also show the stake-shaped band in the middle of the spectrum around **1710 cm^{-1}** corresponding to the C=O stretch.



IR SPECTRA OF AMINES

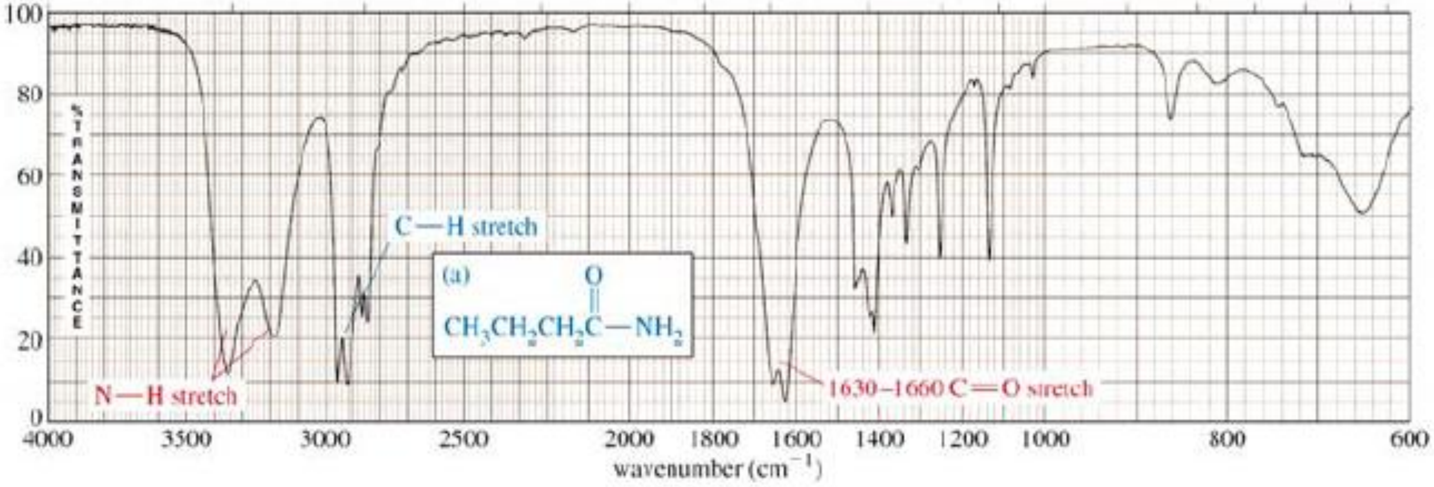
The most characteristic band in amines is due to the **N-H bond stretch**, and it appears as a weak to medium, somewhat broad band (but not as broad as the O-H band of alcohols). This band is positioned at the left end of the spectrum, in the range of about **3200 - 3600 cm^{-1}**.

Primary amines have two N-H bonds, therefore they typically show two spikes that make this band resemble a molar tooth. Secondary amines have only one N-H bond, which makes them show only one spike, resembling a canine tooth. Finally, tertiary amines have no N-H bonds, and therefore this band is absent from the IR spectrum altogether. The spectrum below shows a secondary amine.



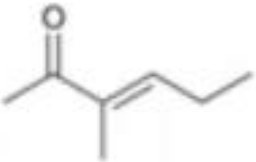
IR SPECTRUM OF AMIDES

The amide functional group combines the features of amines and ketones because it has both the **N-H bond** and the **C=O bond**. Therefore amides show a very strong, somewhat broad band at the left end of the spectrum, in the range between **3100** and **3500 cm^{-1}** for the N-H stretch. At the same time they also show the stake-shaped band in the middle of the spectrum around **1710 cm^{-1}** for the C=O stretch. As with amines, primary amides show two spikes, whereas secondary amides show only one spike.

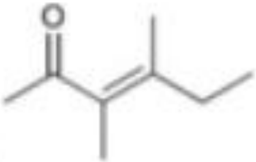


س/ اي من المركبات التالية تعطي اشارة اعلى من 3000 سم$^{-1}$ في مطيافية تحت الحمراء

(a)

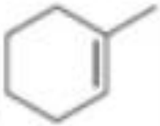


(b)

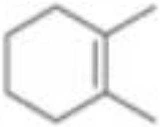


(c)

(d)

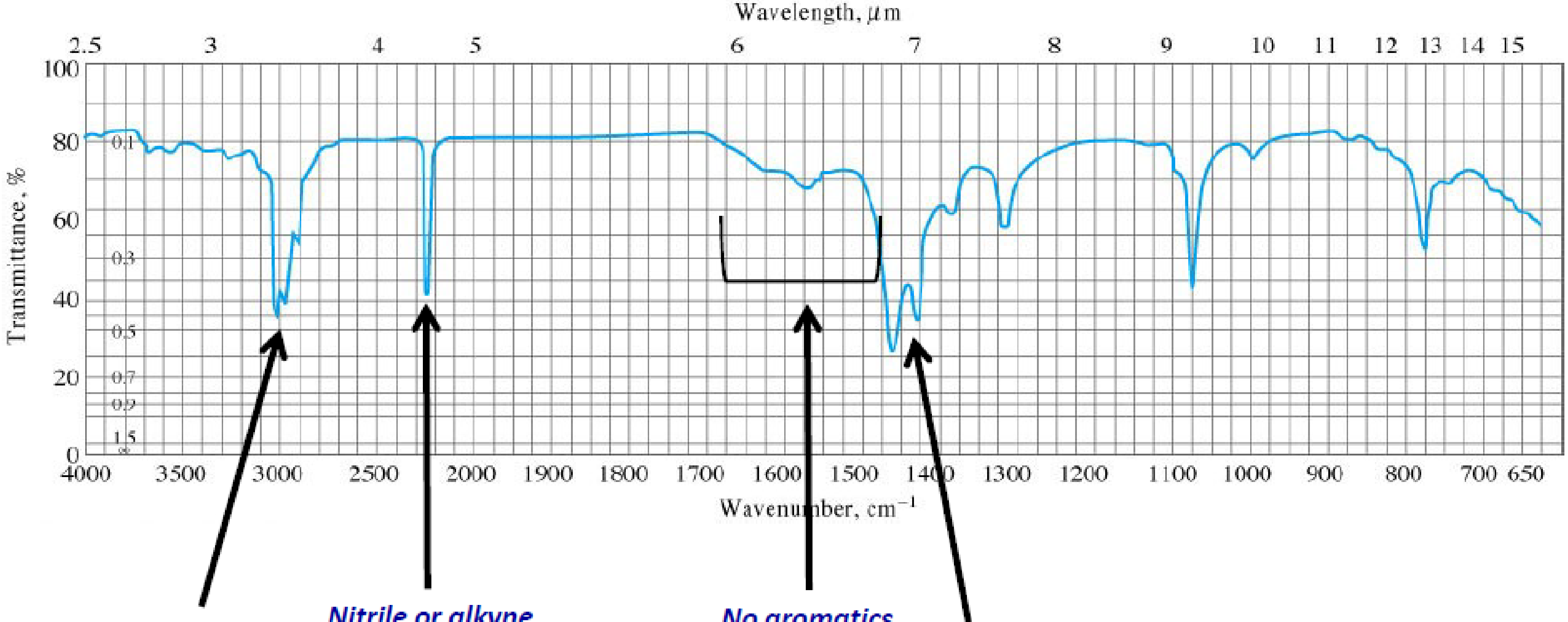


(e)



(f)

Example : The spectrum is for a substance with an empirical formula of C_3H_5N. What is the compound?

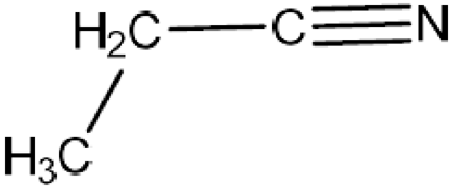


Aliphatic hydrogens

Nitrile or alkyne group

No aromatics

One or more alkane groups



SPECTRAL ANALYSIS BOX

ETHERS

C—O The most prominent band is that due to C—O stretch, 1300–1000 cm^{-1}. Absence of C=O and O—H is required to ensure that C—O stretch is not due to an ester or an alcohol. Phenyl alkyl ethers give two strong bands at about 1250 and 1040 cm^{-1}, while aliphatic ethers give one strong band at about 1120 cm^{-1}.

Examples: dibutyl ether (Fig. 2.33) and anisole (Fig. 2.34).

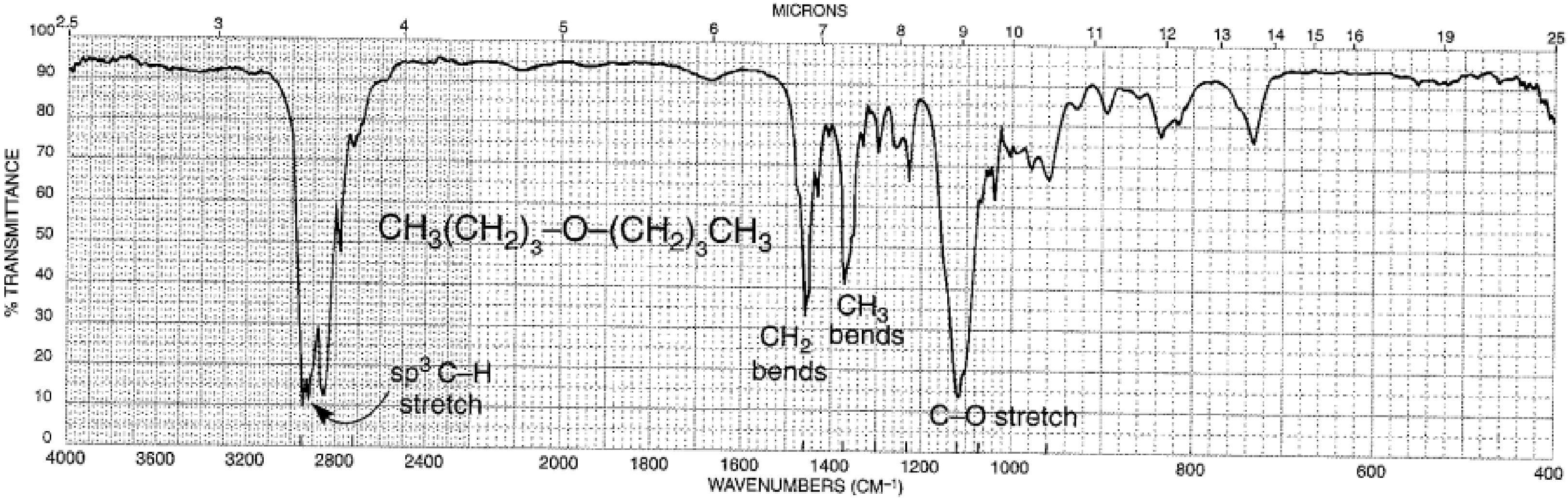


FIGURE 2.33 The infrared spectrum of dibutyl ether (neat liquid, KBr plates).

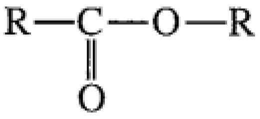
E. Esters

Esters show a very strong band for the C=O group that appears in the range of 1750–1735 cm^{-1} for simple aliphatic esters. The C=O band is shifted to lower frequencies when it is conjugated to a C=C or phenyl group. On the other hand, conjugation of a C=C or phenyl group with the *single-bonded oxygen* of an ester leads to an increased frequency from the range given above. Ring strain moves the C=O absorption to a higher frequency in cyclic esters (lactones).

SPECTRAL ANALYSIS BOX

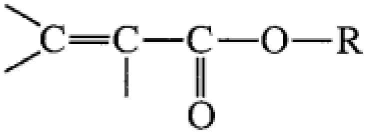
ESTERS

C=O

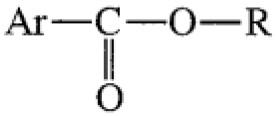


$R-\underset{\underset{O}{\|}}{C}-O-R$

C=O stretch appears in range 1750–1735 cm^{-1} for normal aliphatic esters.



Conjugation of C=O with α,β C=C; 1740–1715 cm^{-1} for C=O and 1640–1625 cm^{-1} for C=C (two bands for some C=C, *cis and trans,* p. 52.)



$Ar-\underset{\underset{O}{\|}}{C}-O-R$

Conjugation of C=O with phenyl; 1740–1715 cm^{-1} for C=O and 1600–1450 cm^{-1} for ring.

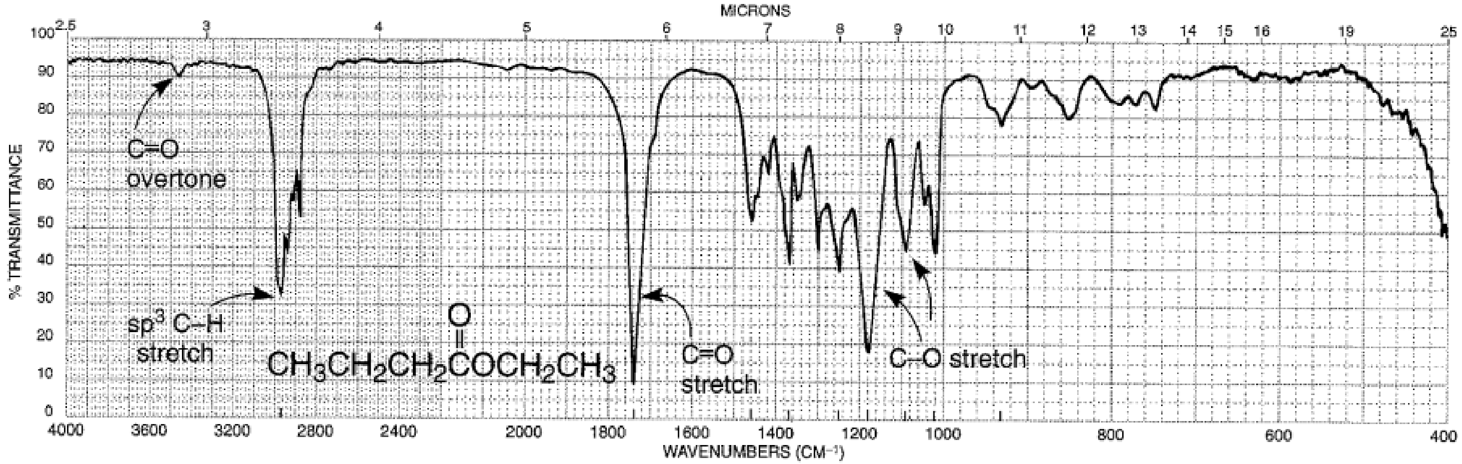


FIGURE 2.47 The infrared spectrum of ethyl butyrate (neat liquid, KBr plates).

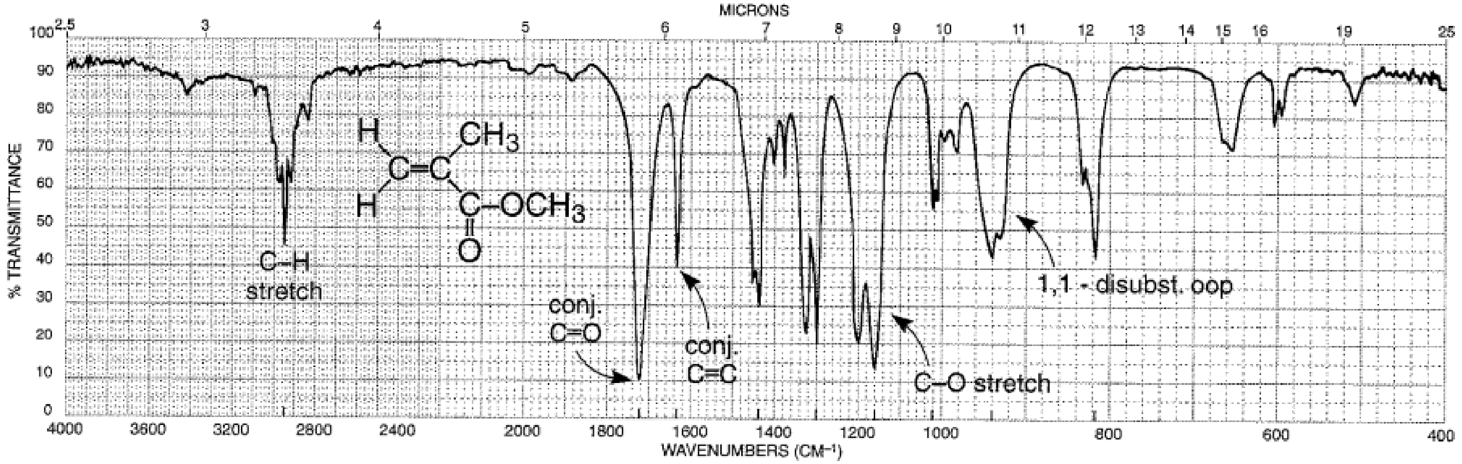


FIGURE 2.48 The infrared spectrum of methyl methacrylate (neat liquid, KBr plates).