

Applications of infra-red spectroscopy

1: Identification of an Organic Compound. The identity of an organic compound can be established from its finger print region ($1400\text{--}900\text{ cm}^{-1}$).

2: Structure determination. This technique helps to establish the structure of an unknown compound.

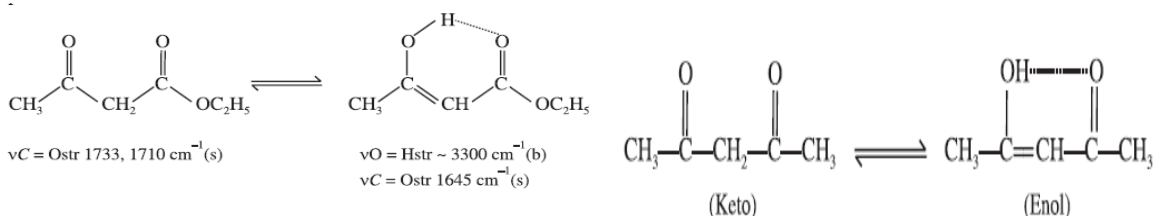
3: Qualitative analysis of functional groups. The presence or the absence of absorption bands help in predicting the presence of certain functional groups in the compound.

4: Distinction between two types of hydrogen bonding.

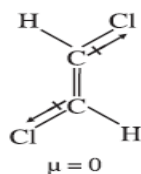
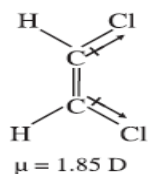
5: Quantitative analysis. It helps to make a quantitative estimation of an organic mixture.

6: Study of a Chemical reaction. This technique is quite useful for studying chemical reactions. Consider the reduction of a saturated aliphatic ketone to form secondary alcohol. Ketone forms a strong band at about 1710 cm^{-1} . When it is subjected to reduction, it forms Butan-2-ol which absorbs at 3300 cm^{-1} due to O-H str. The progress of reaction can be studied from time to time and the reduction will be complete when a strong band due to C = O str will be missing and only a band due to O-H str. is present.

7: Study of Keto-enol tautomerism. Diketones and ketoesters exhibit keto-enol tautomerism provided they have α -H atom in them. The infra-red spectrum of such a compound contain bands due to C=O, O-H and C=C bonds. Consider ethyl acetoacetic ester. It exists in keto-enol isomers in equilibrium. The lowering of C=O str. absorption in the enolic form is due to intra-molecular hydrogen bonding which is stabilized by Resonance. The appearance of the above bands clearly confirm keto-enol tautomerism in acetoacetic ester. Similar absorption bands are also noted in case of β -diketones.



8: Geometrical Isomerism. It is known that a vibration is infra-red active only if it causes a change in dipole-moment of the molecule. Also the intensity of absorption depends upon the change in the dipole moment. This technique clearly makes a distinction between cis and trans isomers. Consider 1, 2-dichloro ethene. Its geometrical isomers are:



9: Detection of Impurity in a compound. Infra-red spectroscopy is also useful in the detection of impurity in a compound by comparing its spectrum with the spectrum of the authentic sample of the compound. Moreover, a pure sample always consists of sharp peaks and bands while impure sample will consist of poor bands and also some additional bands.

***THE INFRARED SPECTROMETER**

Two types of infrared spectrometers are in common use in the organic laboratory: **dispersive** and Fourier transform (**FT**) instruments. Both of these types of instruments provide spectra of compounds in the common range of 4000 to 400 cm^{-1} . Although the two provide nearly identical spectra for a given compound, FT infrared spectrometers provide the infrared spectrum much more rapidly than the dispersive instruments.

Fourier Transform Infrared (FT-IR) spectrometry was developed in order to overcome the limitations encountered with dispersive instruments. The main difficulty was the slow scanning process. Thus, the time element per sample is reduced to a matter of a few seconds rather than several minutes.

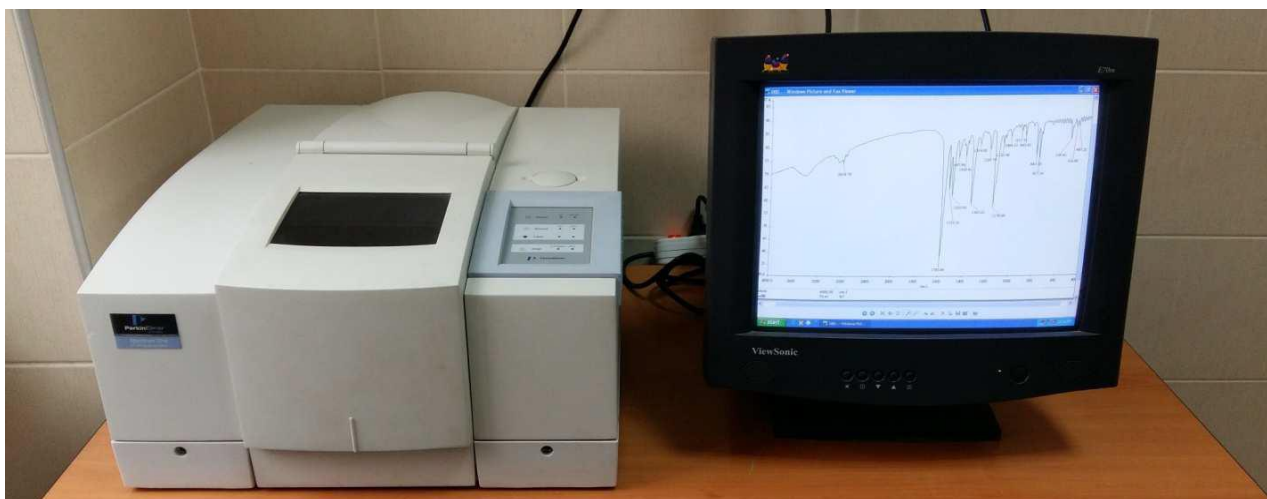
Advantages of FT-IR

Some of the major advantages of FT-IR over the dispersive technique include:

- **Speed:**
- **Sensitivity:**
- **Simplicity:**
- **Internally Calibrated**

PREPARATION OF SAMPLES FOR INFRARED SPECTROSCOPY

To determine the infrared spectrum of a compound, one must place the compound in a sample holder, or cell. Cells must be constructed of ionic substances typically sodium chloride or potassium bromide, (Because glass and plastics absorb strongly). Potassium bromide plates are more expensive than sodium chloride plates but have the advantage of usefulness in the range of 4000 to 400 cm^{-1} . Sodium chloride plates are used widely because of their relatively low cost. The practical range for their use in spectroscopy extends from 4000 to 650 cm^{-1} . NaCl begin to absorb at 650 cm^{-1} , and any bands with frequencies less than this value will not be observed. Since few important bands appear below 650 cm^{-1} , sodium chloride plates are in most common use for routine infrared spectroscopy.



Liquid samples: A drop of a liquid organic compound is placed between a pair of polished sodium chloride or potassium bromide plates, referred to as salt plates.



Solid samples: there are at least three common methods for preparing solid samples such as: **KBr pellet**, **Nujol mull** and **use of organic solvents** such as (CCl_4 , CHCl_3).

Gases: The gaseous sample is introduced into a 'gas cell'. The walls of the cell are made of sodium chloride. Sodium chloride windows allow the cell to be placed directly in the path of the sample beam. The gas cell is usually 10 cm long. Very few organic compounds can be examined as gases. The low frequency rotational changes in the gaseous phase often split the high frequency vibrational bands.



Spectra examples of most functional groups and their interpretations:

1: HYDROCARBONS: ALKANES, ALKENES, ALKYNES and ARAMATIC

A: Alkanes

Alkanes show very few absorption bands in the infrared spectrum. They yield four or more **C-H** stretching peaks near 3000 cm^{-1} plus CH_2 and CH_3 bending peaks in the range $1475\text{--}1365\text{ cm}^{-1}$.

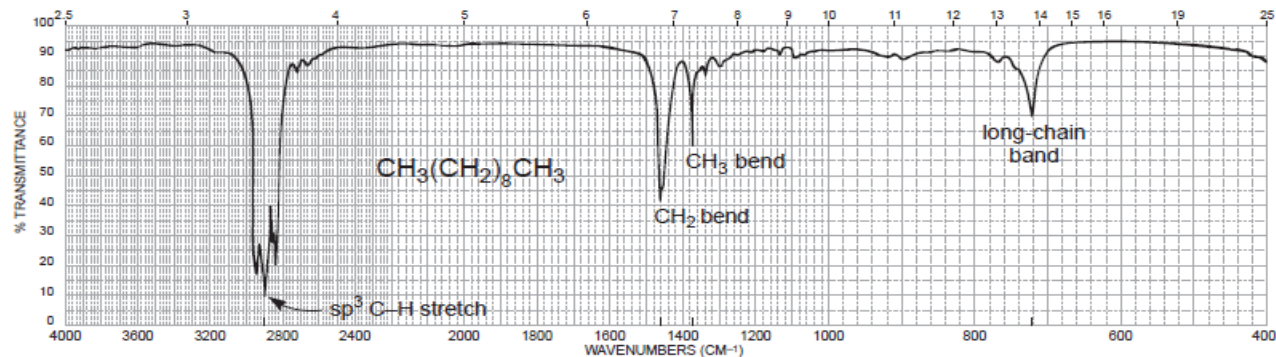


Fig (1): The infrared spectrum of decane (neat liquid, KBr plates).

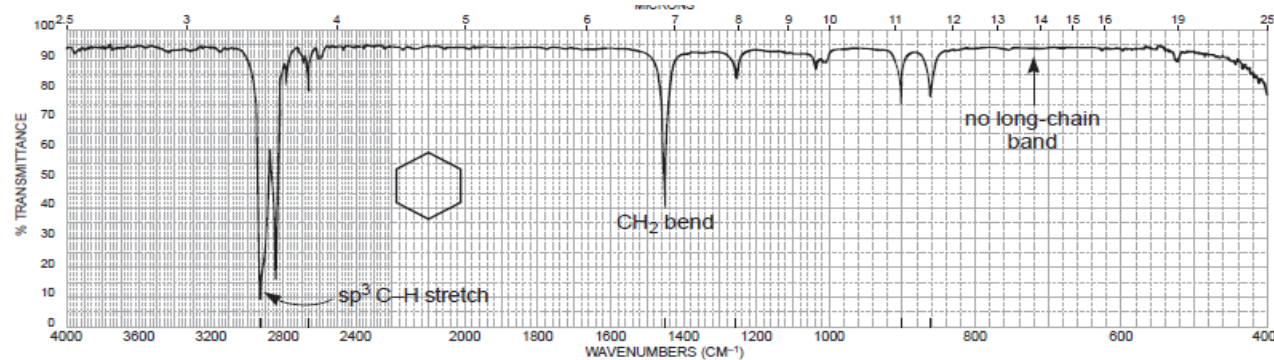


Fig (2): The infrared spectrum of cyclohexane (neat liquid, KBr plates).

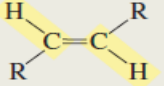
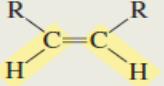
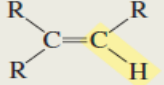
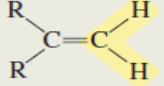
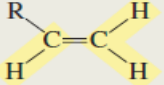
STRETCHING VIBRATIONS FOR VARIOUS sp^3 -HYBRIDIZED C-H BONDS

Group		Stretching Vibration (cm^{-1})	
		Asymmetric	Symmetric
Methyl	$\text{CH}_3\text{--}$	2962	2872
Methylene	$\text{--CH}_2\text{--}$	2926	2853
Methine	$\begin{array}{c} \\ \text{--C--} \\ \\ \text{H} \end{array}$	2890	Very weak

B: Alkenes

=C-H Stretch for sp^2 occurs at values greater than 3000 cm^{-1} ($3095\text{--}3010\text{ cm}^{-1}$).

=C-H Out-of-plane (oop) bending occurs in the range $1000\text{--}650\text{ cm}^{-1}$.

	trans	980–960
	cis	730–675
	trisubstituted	840–800
	terminal alkene	890
	terminal alkene	990 and 910

C=C Stretch occurs at $1660\text{--}1600\text{ cm}^{-1}$; conjugation moves C=C stretch to lower frequencies and increases the intensity.

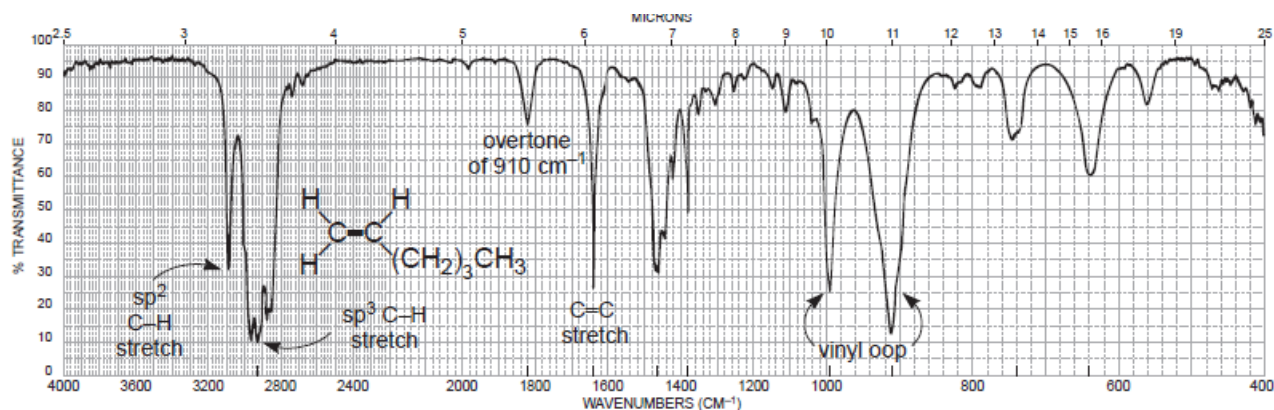


Fig (3): The infrared spectrum of 1-hexene (neat liquid, KBr plates).

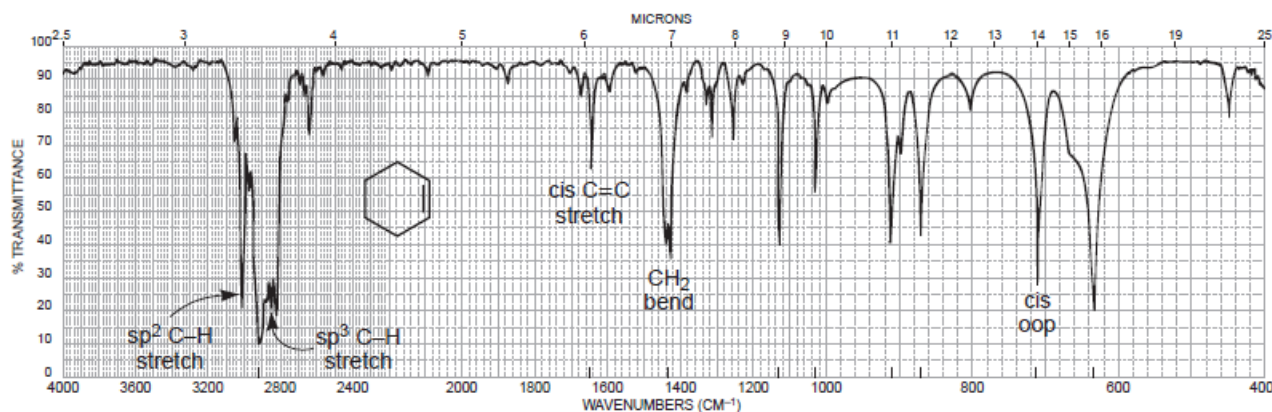


Fig (4): The infrared spectrum of cyclohexene (neat liquid, KBr plates).

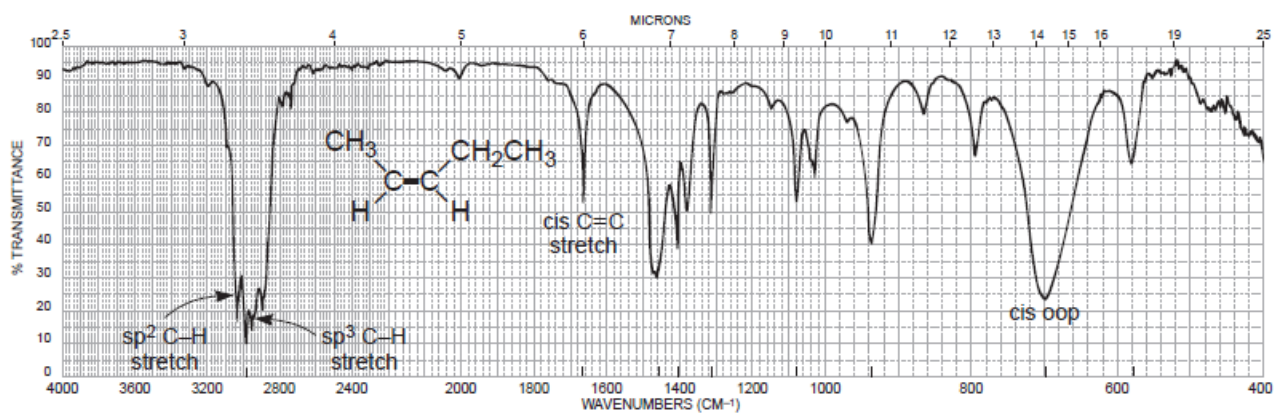


Fig (5): The infrared spectrum of cis-2-pentene (neat liquid, KBr plates).

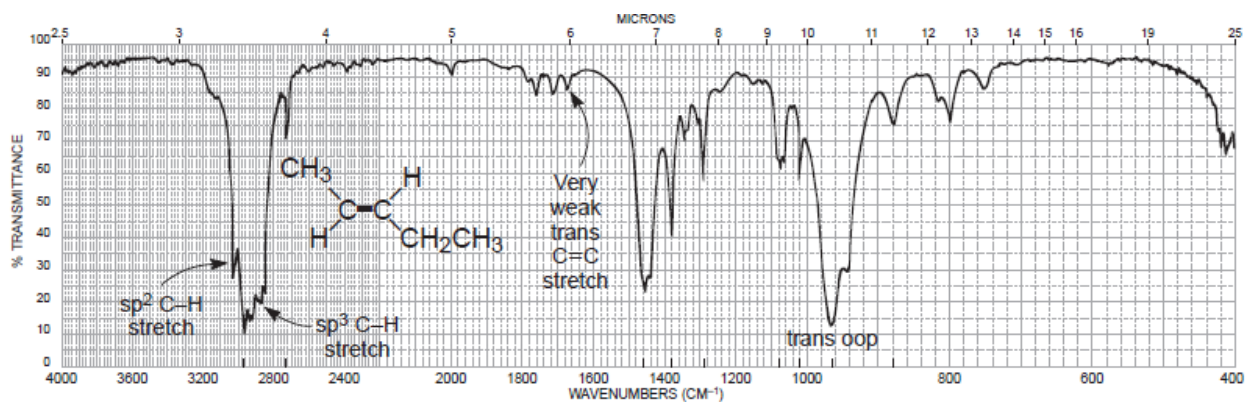


Fig (6): The infrared spectrum of trans-2-pentene (neat liquid, KBr plates).

C: ALKYNES

$\equiv\text{C-H}$ Stretch for sp C-H usually occurs near 3300 cm^{-1} . $\text{C}\equiv\text{C}$ Stretch occurs near 2150 cm^{-1} ; conjugation moves stretch to lower frequency.

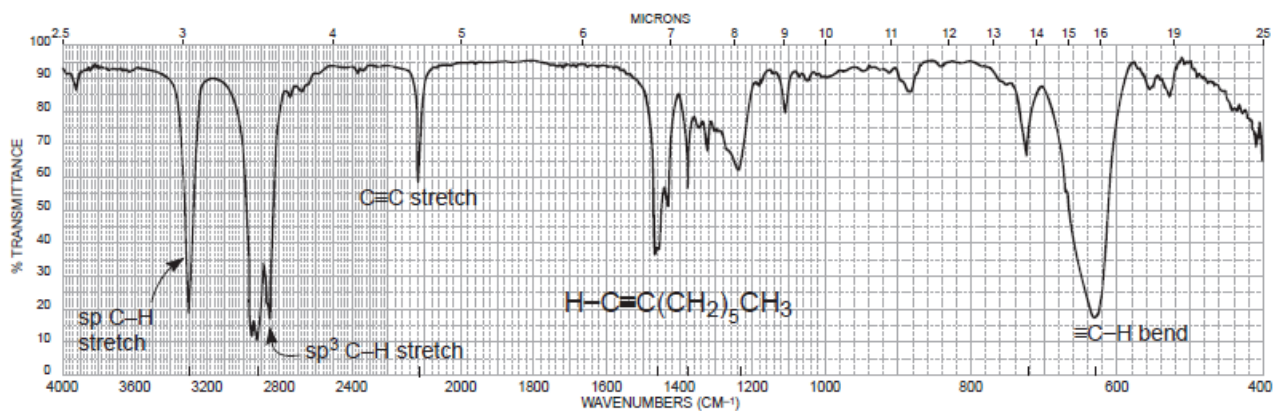


Fig (7): The infrared spectrum of 1-octyne (neat liquid, KBr plates).

D: Aromatic Compounds

C=C Ring stretch absorptions often occur in pairs at 1600 cm^{-1} and 1475 cm^{-1} . Overtone/combination bands appear between 2000 and 1667 cm^{-1} .

=C-H Stretch for sp^2 C-H occurs at values greater than 3000 cm^{-1} ($3050\text{--}3010\text{ cm}^{-1}$).

=C-H Out-of-plane (oop) bending occurs at $900\text{--}690\text{ cm}^{-1}$. The out-of-plane C-H are extremely intense absorptions, resulting from strong coupling with adjacent hydrogen atoms, can be used to assign the positions of substituents on the aromatic ring.

Monosubstituted Rings. This substitution pattern always gives a strong absorption near 690 cm^{-1} . If this band is absent, no monosubstituted ring is present. A second strong band usually appears near 750 cm^{-1} .

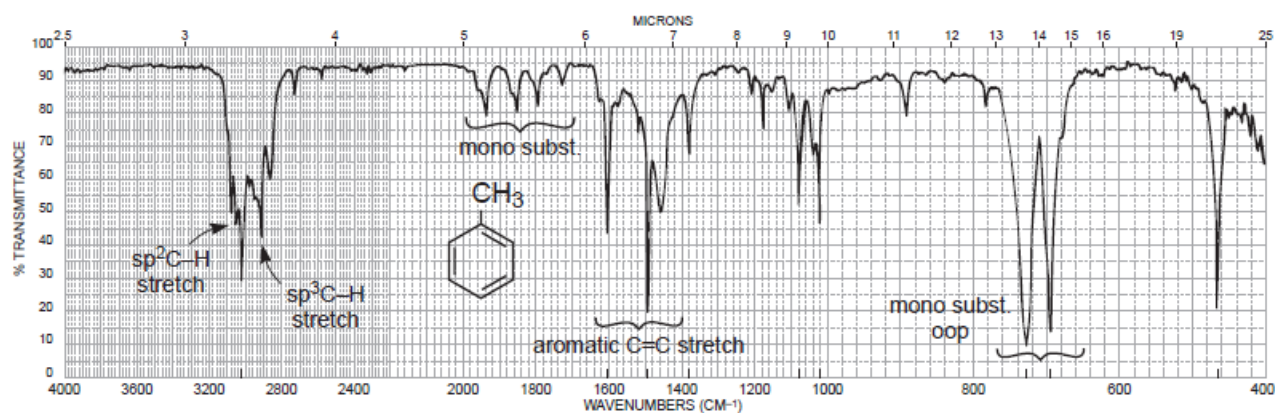


Fig (8): The infrared spectrum of toluene (neat liquid, KBr plates).

ortho-Disubstituted Rings (1,2-Disubstituted Rings). One strong band near 750 cm^{-1} is obtained.

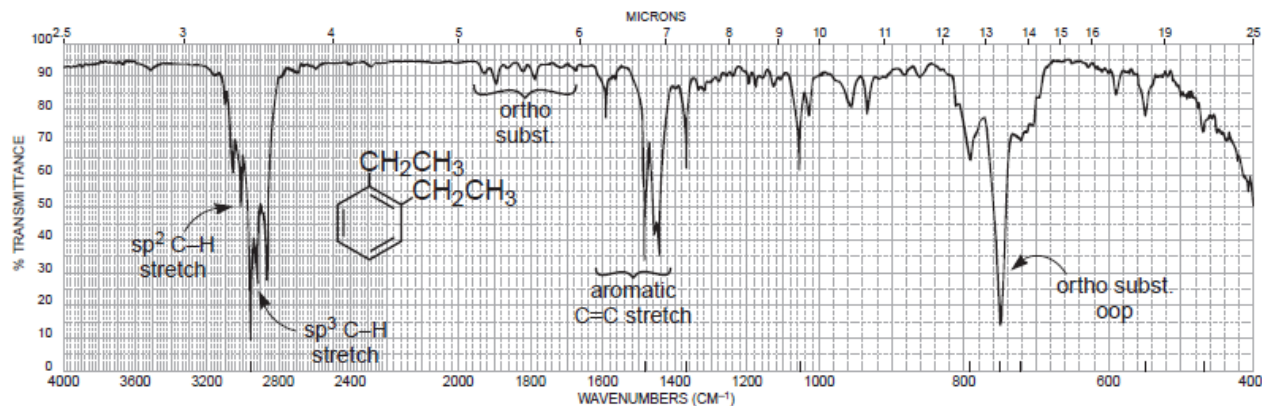


Fig (9): The infrared spectrum of *ortho*-diethylbenzene (neat liquid, KBr plates).

meta-Disubstituted Rings (1,3-Disubstituted Rings). This substitution pattern gives the 690-cm^{-1} band plus one near 780 cm^{-1} . A third band of medium intensity is often found near 880 cm^{-1} .

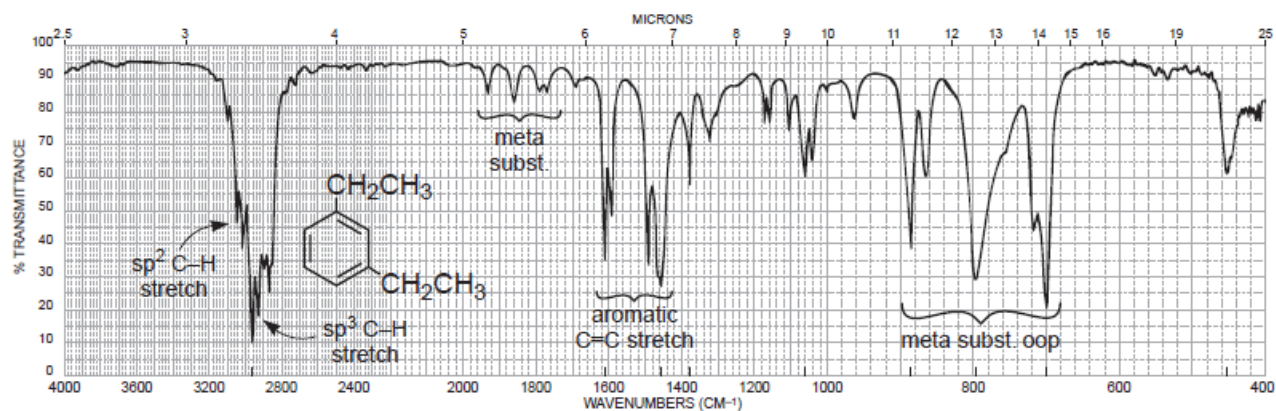


Fig (10): The infrared spectrum of *meta*-diethylbenzene (neat liquid, KBr plates).

para-Disubstituted Rings (1,4-Disubstituted Rings). One strong band appears in the region from 800 to 850 cm^{-1} .

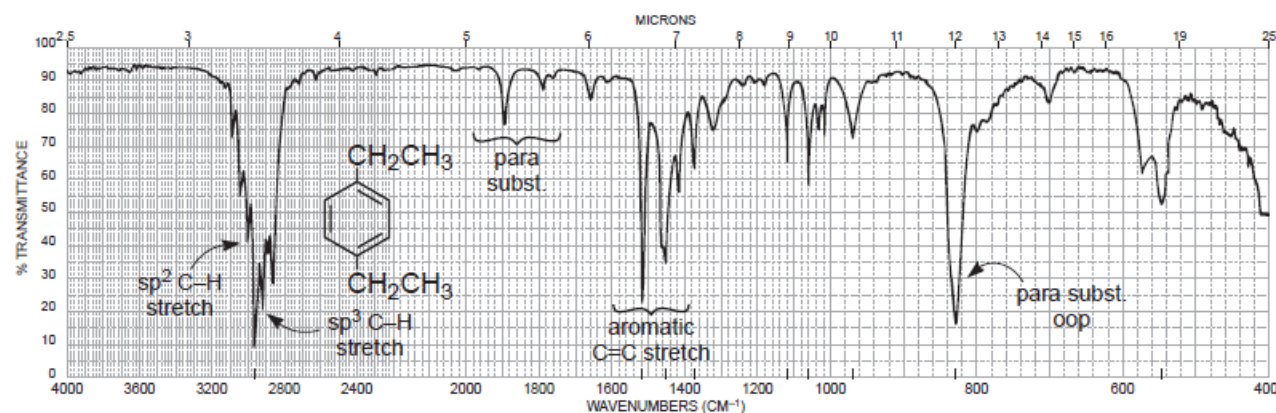


Fig (11): The infrared spectrum of *para*-diethylbenzene (neat liquid, KBr plates).

2- ALCOHOLS AND PHENOLS

Alcohols and phenols will show strong and broad hydrogen-bonded O-H stretching bands centered between 3400 and 3300 cm^{-1} . In solution, it will also be possible to observe a “free” O-H (non-H-bonded) stretching band at about 3600 cm^{-1} (sharp and weaker) to the left of the hydrogen-bonded O-H peak. In addition, a C-O stretching band will appear in the spectrum at $1260\text{--}1000\text{ cm}^{-1}$.

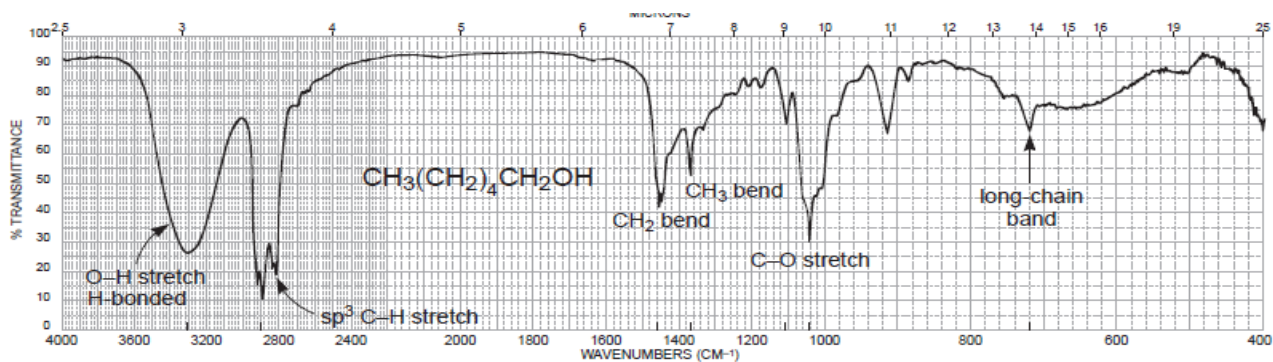


Fig (12): The infrared spectrum of *1-hexanol* (neat liquid, KBr plates).

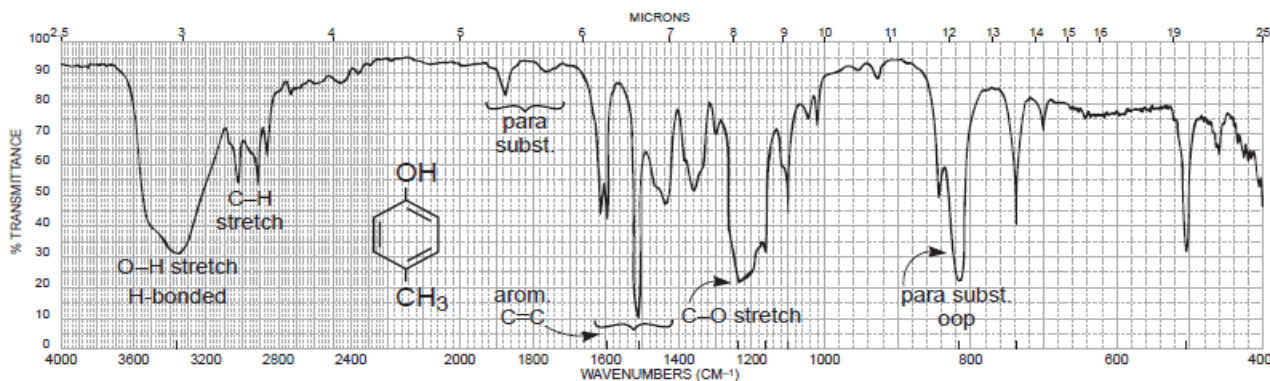


Fig (13): The infrared spectrum of *p-cresol* (neat liquid, KBr plates).

3- CARBONYL COMPOUNDS

The carbonyl group is present in aldehydes, ketones, acids, esters, amides, acid chlorides, and anhydrides. This group absorbs strongly in the range from 1850 to 1650 cm^{-1} because of its large change in dipole moment.

3a- Aldehydes

Aldehydes show a very strong band for the carbonyl group ($\text{C}=\text{O}$) that appears in the range of 1740–1725 cm^{-1} for simple aliphatic aldehydes. This band is shifted to lower frequencies with conjugation to a $\text{C}=\text{C}$ or phenyl group.

Conjugation of $\text{C}=\text{O}$ with $\alpha, \beta\text{-C}=\text{C}$; 1700–1680 cm^{-1} for $\text{C}=\text{O}$ and 1640 cm^{-1} for $\text{C}=\text{C}$.

Conjugation of $\text{C}=\text{O}$ with phenyl; 1700–1660 cm^{-1} for $\text{C}=\text{O}$ and 1600–1450 cm^{-1} for ring.

A very important doublet can be observed in the C-H stretch region for the aldehyde C-H near 2850 and 2750 cm^{-1} .

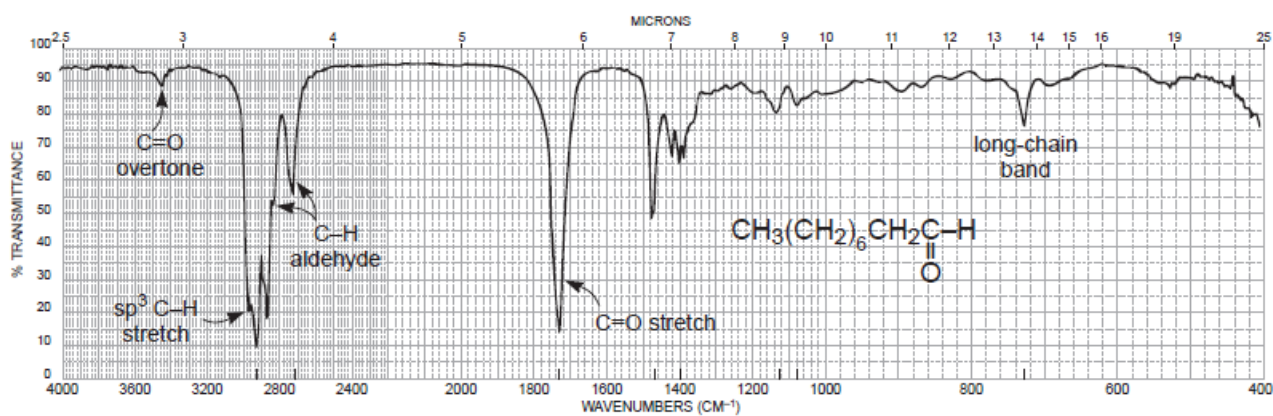


Fig (14): The infrared spectrum of *nonanal* (neat liquid, KBr plates).

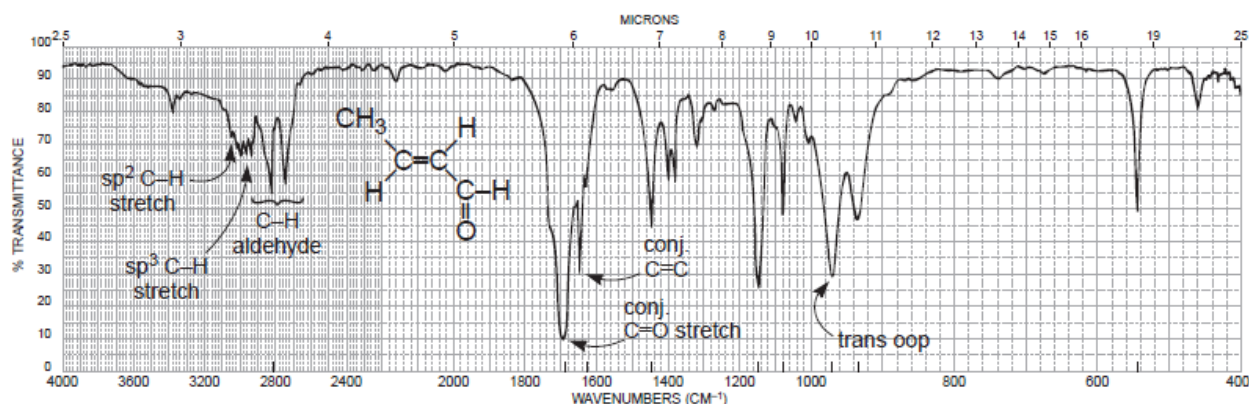


Fig (15): The infrared spectrum of *crotonaldehyde* (neat liquid, KBr plates).

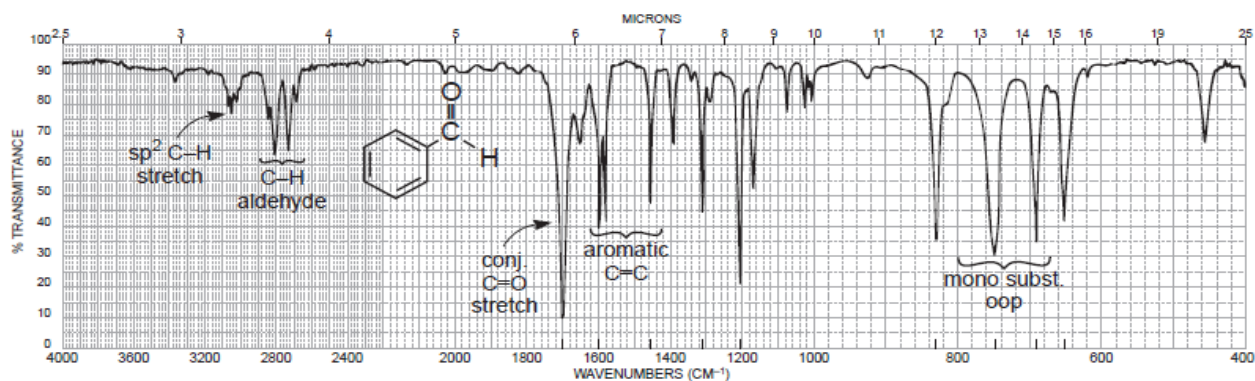


Fig (16): The infrared spectrum of *benzaldehyde* (neat liquid, KBr plates).

3b- Ketones

Ketones show a very strong band for the C=O group that appears in the range of 1720–1708 cm^{-1} for simple aliphatic ketones. This band is shifted to lower frequencies with conjugation to a C=C or phenyl group. Conjugation of C=O with $\alpha, \beta\text{-C=C}$; 1700–1675 cm^{-1} for C=O and 1644-1617 cm^{-1} for C=C. Conjugation of C=O with phenyl; 1700–1680 cm^{-1} for C=O and 1600–1450 cm^{-1} for ring

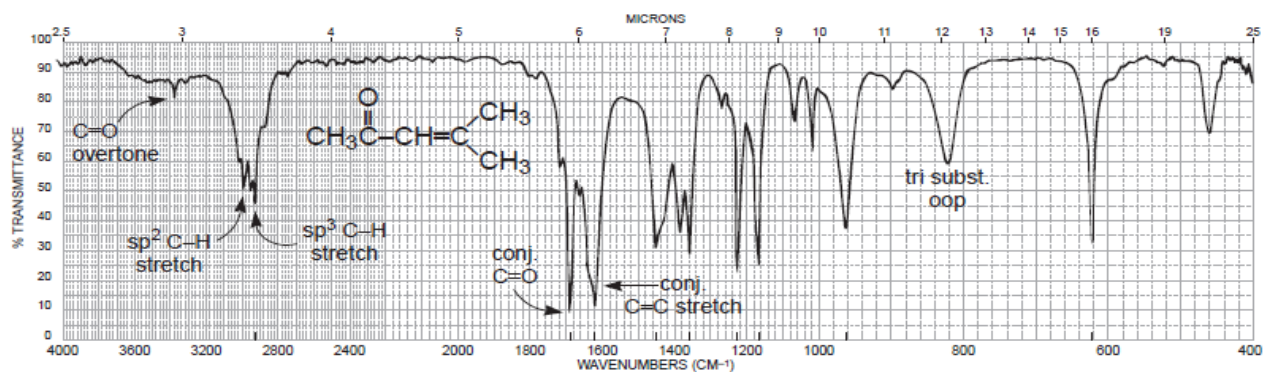


Fig (17): The infrared spectrum of *mesityloxide* (neat liquid, KBr plates).

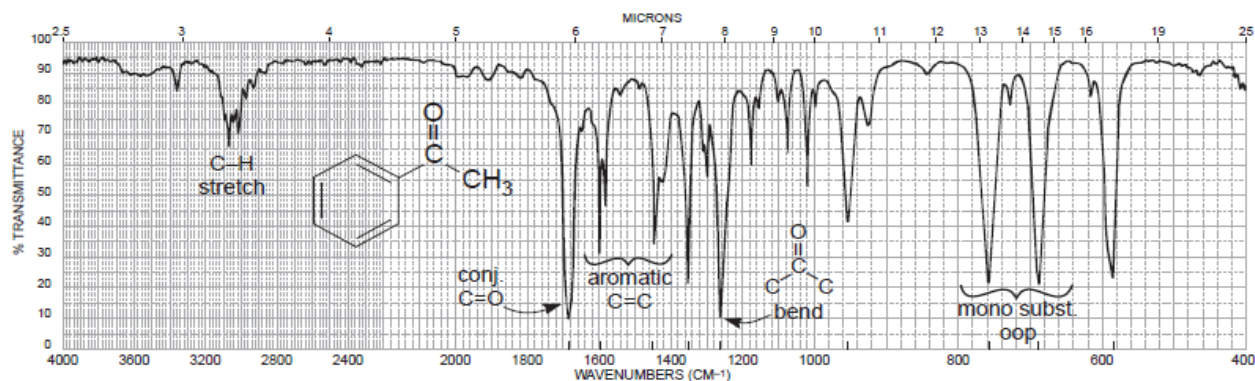


Fig (18): The infrared spectrum of *acetophenone* (neat liquid, KBr plates).

3c- Carboxylic Acids

O-H Stretch, usually *very broad* (strongly H-bonded), occurs at $3400\text{--}2400\text{ cm}^{-1}$ and often overlaps the C-H absorptions.

C=O Stretch, broad, occurs at $1730\text{--}1700\text{ cm}^{-1}$. Conjugation moves the absorption to a lower frequency. C-O Stretch occurs in the range $1320\text{--}1210\text{ cm}^{-1}$, medium intensity.

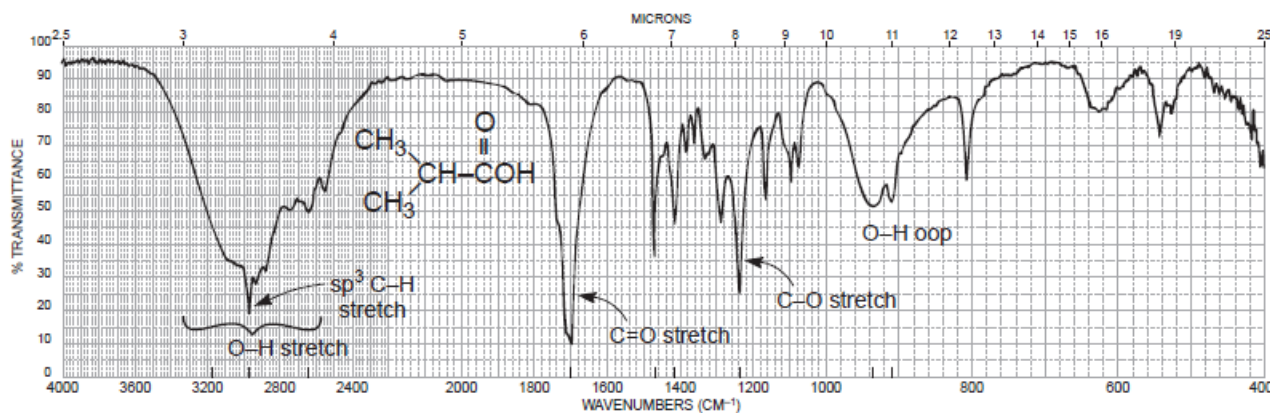


Fig (19): The infrared spectrum of *isobutyric acid* (neat liquid, KBr plates).

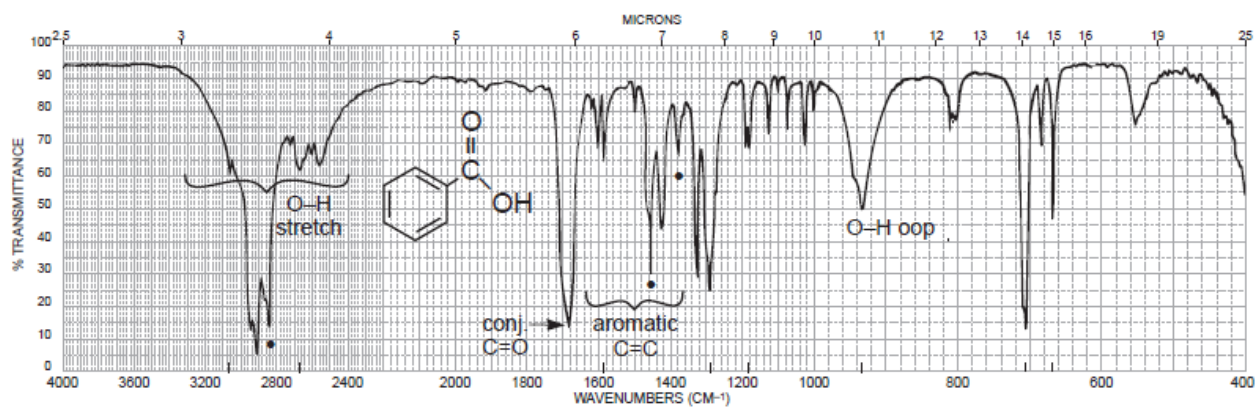


Fig (20): The infrared spectrum of *benzoic acid* (neat liquid, KBr plates).

3d- Esters

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

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

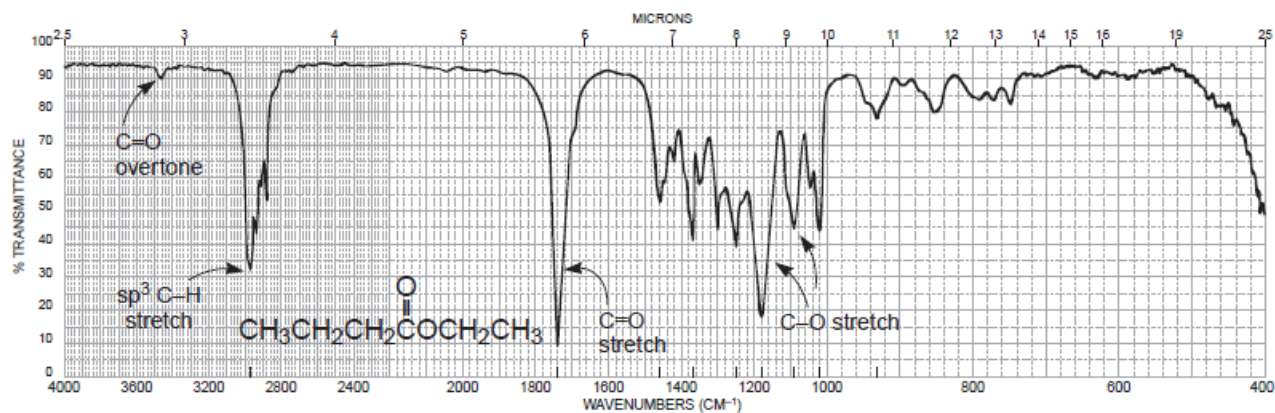


Fig (21): The infrared spectrum of *ethylbutyrate* (neat liquid, KBr plates).

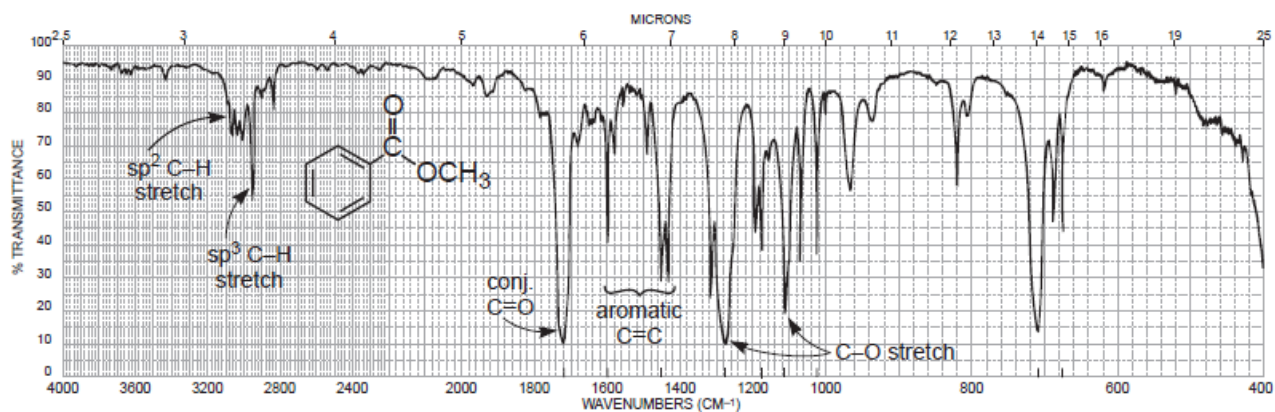


Fig (22): The infrared spectrum of *methylbenzoate* (neat liquid, KBr plates).

3e- Amides

C=O Stretch occurs at approximately $1680 - 1630 \text{ cm}^{-1}$. N-H Stretch in primary amides ($-\text{NH}_2$) gives two bands near 3350 and 3180 cm^{-1} . Secondary amides have one band ($-\text{NH}$) at about 3300 cm^{-1} . N-H Bending occur around $1640 - 1550 \text{ cm}^{-1}$ for primary and secondary amides.

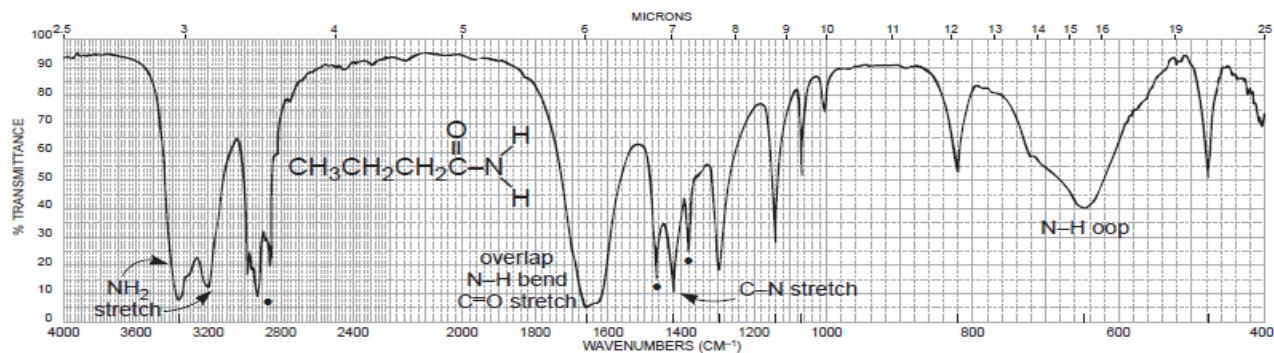


Fig (23): The infrared spectrum of *butanamide* (neat liquid, KBr plates).

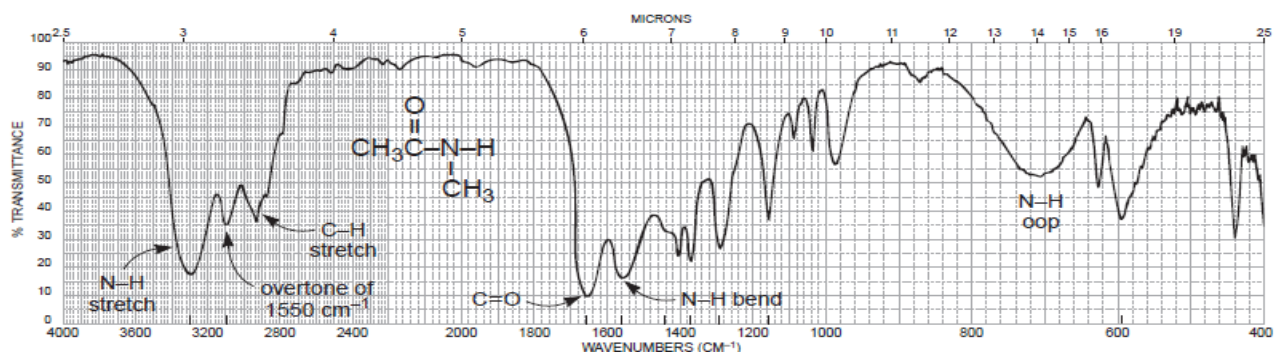


Fig (24): The infrared spectrum of *N-methylethanamide* (neat liquid, KBr plates).

3f- Acid halides C=O Stretch occurs in the range $1810 - 1775 \text{ cm}^{-1}$ in unconjugated chlorides. Conjugation lowers the frequency to $1780 - 1760 \text{ cm}^{-1}$.

C-Cl Stretch occurs in the range $730 - 550 \text{ cm}^{-1}$.

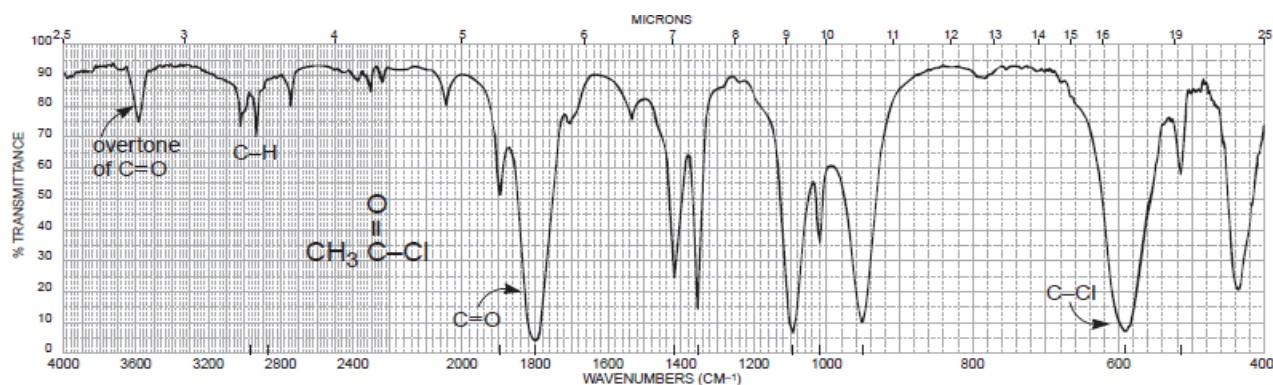


Fig (25): The infrared spectrum of *acetylchloride* (neat liquid, KBr plates).

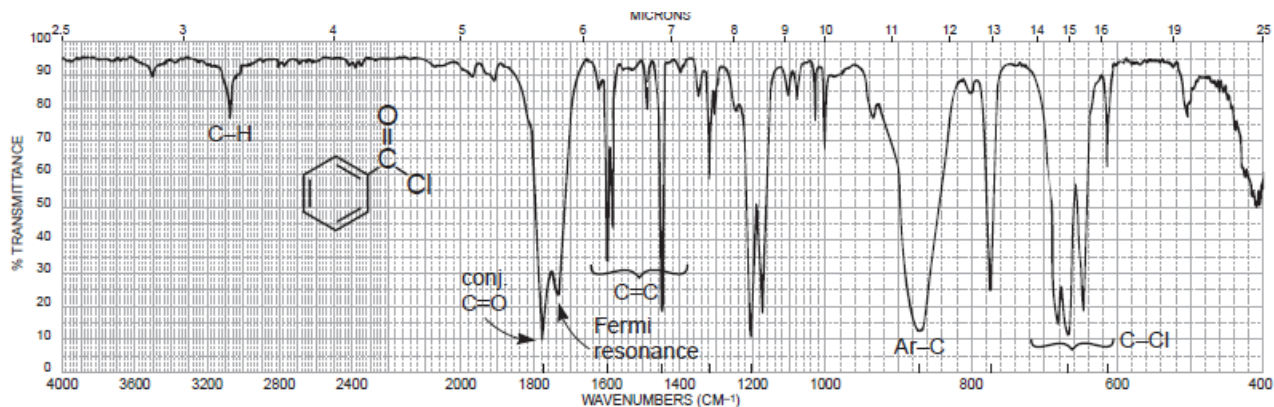


Fig (26): The infrared spectrum of *benzoylchloride* (neat liquid, KBr plates).

3g- Anhydrides

C=O Stretch always has two bands, $1830\text{--}1800\text{ cm}^{-1}$ and $1775\text{--}1740\text{ cm}^{-1}$, with variable relative intensity. Conjugation moves the absorption to a lower frequency. Ring strain (cyclic anhydrides) moves the absorptions to a higher frequency.

C-O Stretch (multiple bands) occurs in the range $1300\text{--}900\text{ cm}^{-1}$.

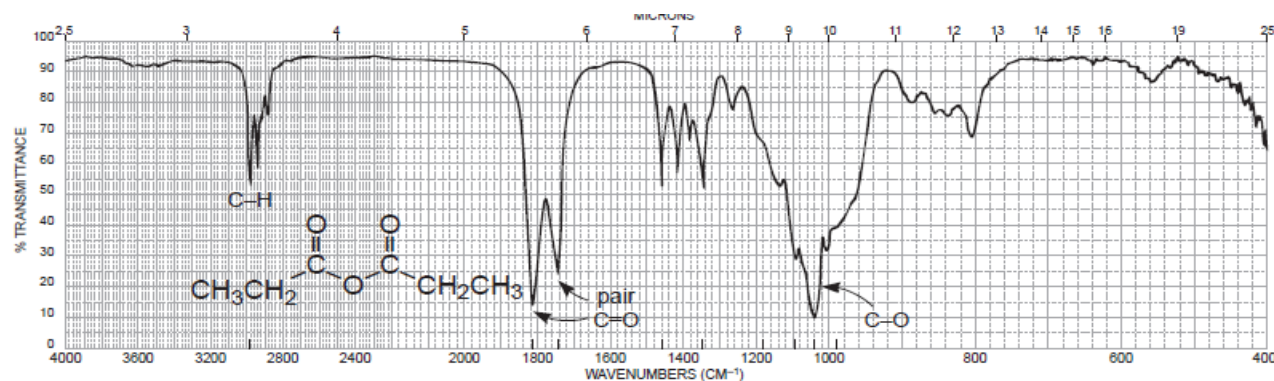


Fig (27): The infrared spectrum of *propanoicanhydride* (neat liquid, KBr plates).

4- Amines

N-H Stretch occurs in the range $3500\text{--}3300\text{ cm}^{-1}$. Primary amines have two bands.

Secondary amines have one band: a vanishingly weak one for aliphatic compounds and a stronger one for aromatic secondary amines. Tertiary amines have no N-H stretch.

N-H Bend in primary amines results in a broad band in the range $1640\text{--}1560\text{ cm}^{-1}$.

Secondary amines absorb near 1500 cm^{-1} .

N-H Out-of-plane bending absorption can sometimes be observed near 800 cm^{-1} .

C-N Stretch occurs in the range $1350\text{--}1000\text{ cm}^{-1}$.

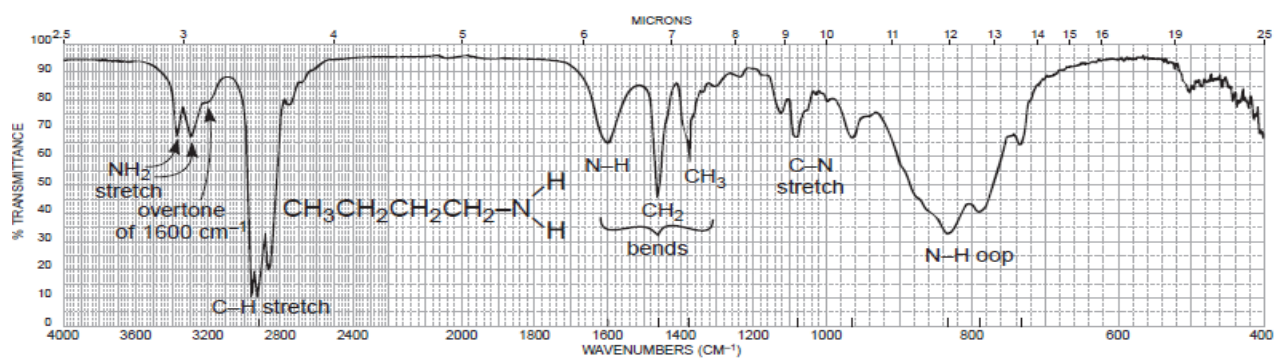


Fig (28): The infrared spectrum of *butylamine* (neat liquid, KBr plates).

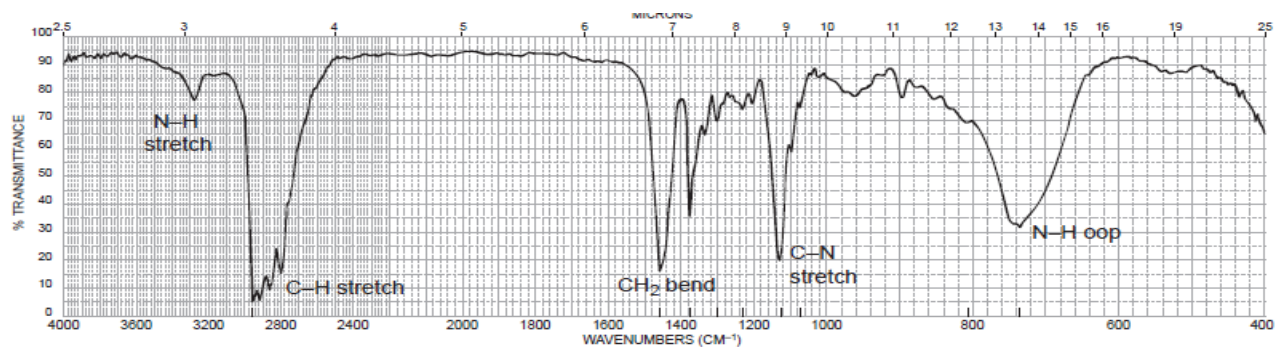


Fig (29): The infrared spectrum of *dibutylamine* (neat liquid, KBr plates).

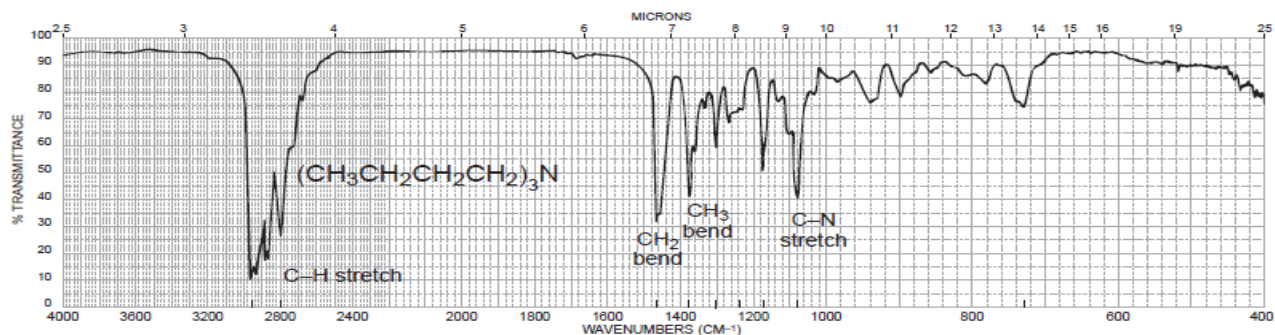


Fig (30): The infrared spectrum of *tributylamine* (neat liquid, KBr plates).

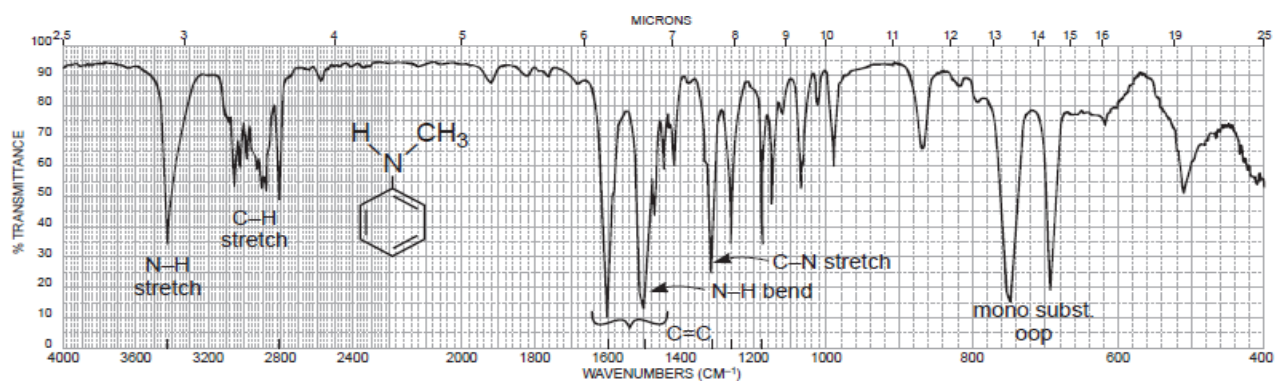


Fig (31): The infrared spectrum of *N-methylanilines* (neat liquid, KBr plates).

5: NITRILES, ISOCYANATES, ISOTHIOCYANATES, AND IMINES NITRILES

R-C≡N

-C≡N Stretch is a medium-intensity, sharp absorption near 2250 cm^{-1} . Conjugation with double bonds or aromatic rings moves the absorption to a lower frequency.

ISOCYANATES R-N=C=O

-N=C=O Stretch in an isocyanate gives a broad, intense absorption near 2270 cm^{-1} .

ISOTHIOCYANATES R-N=C=S

-N=C=S Stretch in an isothiocyanate gives one or two broad, intense absorptions centering near 2125 cm^{-1} .

IMINES R₂C=N-R

R₂C=N- Stretch in an imine, oxime, and so on gives a variable-intensity absorption in the range $1690\text{--}1640\text{ cm}^{-1}$.

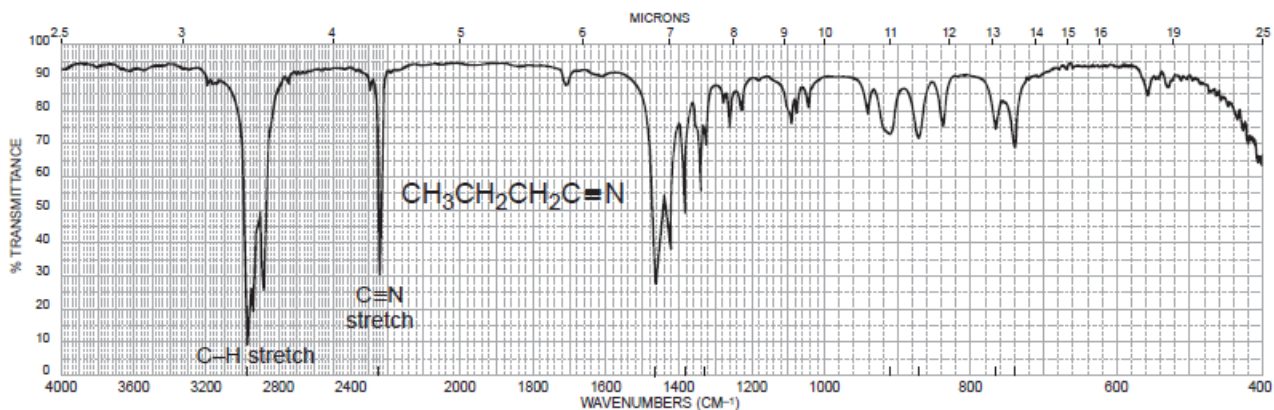


Fig (32): The infrared spectrum of *butyronitrile* (neat liquid, KBr plates).

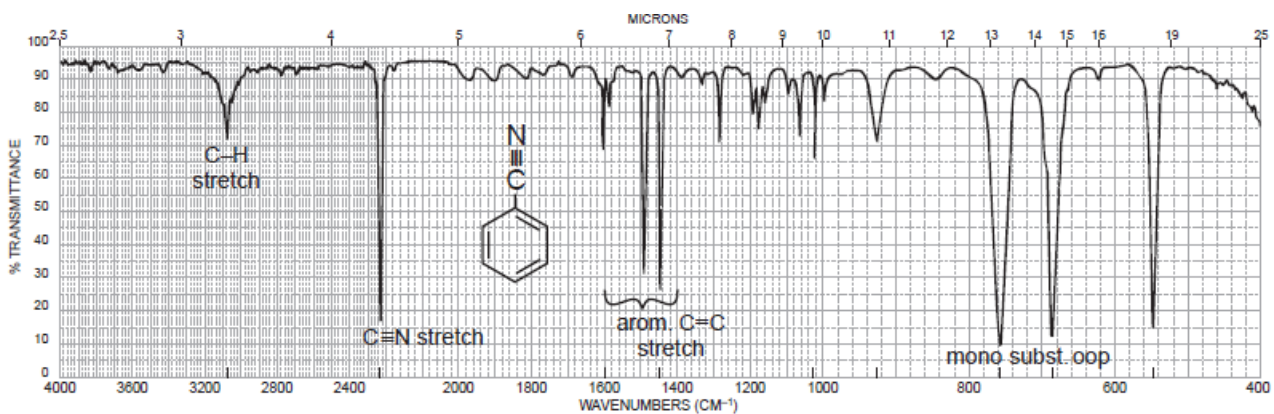


Fig (33): The infrared spectrum of *benzonitrile* (neat liquid, KBr plates).

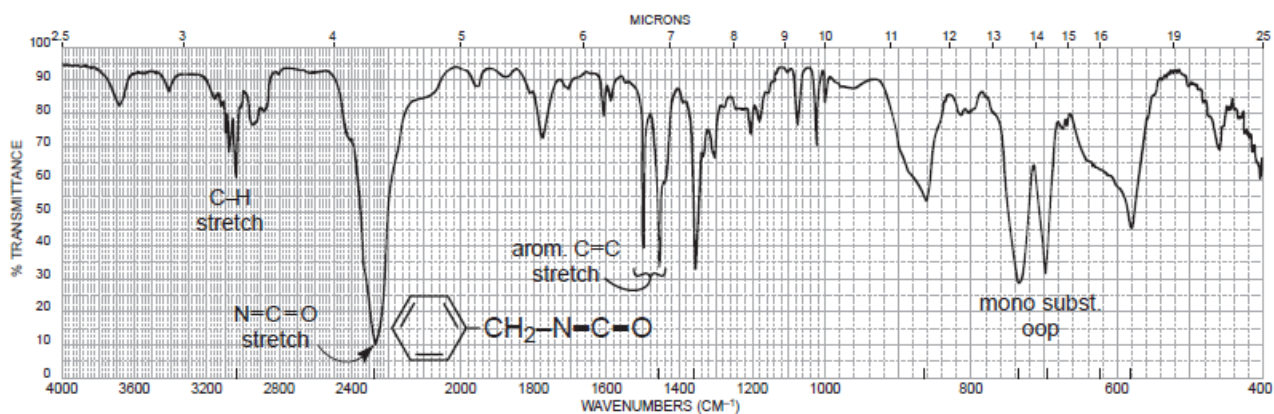


Fig (34): The infrared spectrum of benzyl isocyanate (neat liquid, KBr plates).

6: Nitro Compounds

Aliphatic nitro compounds: asymmetric stretch (strong), $1600\text{--}1530\text{ cm}^{-1}$; symmetric stretch (medium), $1390\text{--}1300\text{ cm}^{-1}$.

Aromatic nitro compounds (conjugated): asymmetric stretch (strong), $1550\text{--}1490\text{ cm}^{-1}$; symmetric stretch (strong), $1355\text{--}1315\text{ cm}^{-1}$.

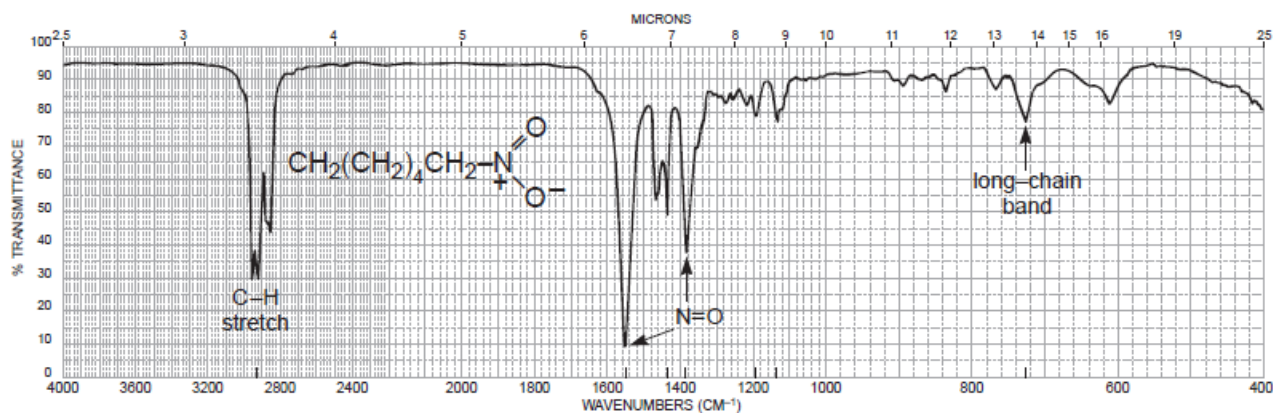


Fig (35): The infrared spectrum of 1-nitrohexane (neat liquid, KBr plates).

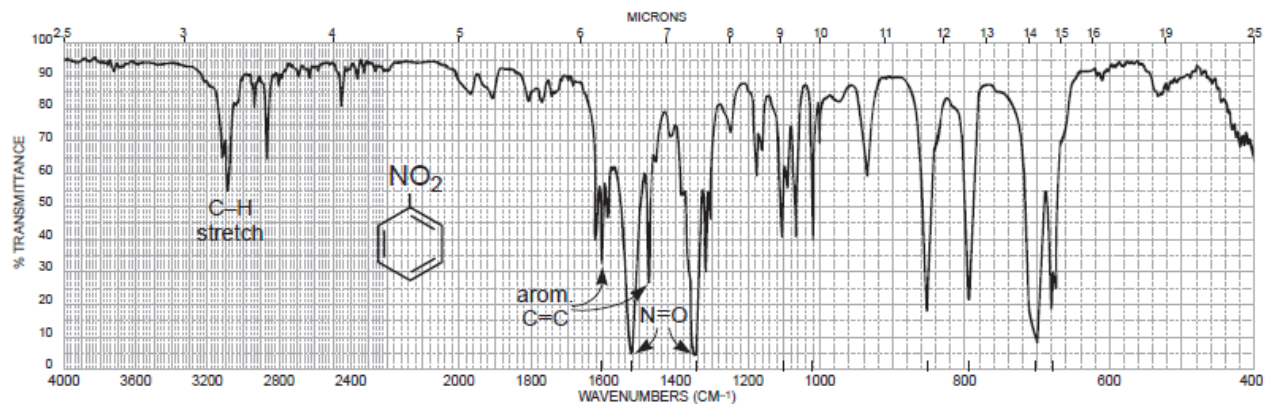


Fig (36): The infrared spectrum of nitrobenzene (neat liquid, KBr plates).

7: CARBOXYLATE SALTS, AMINE SALTS, AND AMINO ACIDS

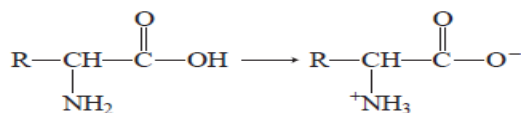
CARBOXYLATE SALTS $R-\overset{\overset{\text{O}}{\parallel}}{\text{C}}-\text{O}^- \text{Na}^+$; $-\overset{\overset{\text{O}}{\parallel}}{\text{C}}-\text{O}^-$ Asymmetric stretch (strong) occurs near 1600 cm^{-1} ; symmetric stretch (strong) occurs near 1400 cm^{-1} .

Frequency of C=O absorption is lowered from the value found for the parent carboxylic acid because of resonance (more single-bond character).

AMINE SALTS NH_4^+ RNH_3^+ R_2NH_2^+ R_3NH^+

N-H Stretch (broad) occurs at $3300\text{--}2600 \text{ cm}^{-1}$. The ammonium ion absorbs to the left in this range, while the tertiary amine salt absorbs to the right. Primary and secondary amine salts absorb in the middle of the range, $3100\text{--}2700 \text{ cm}^{-1}$. A broad band often appears near 2100 cm^{-1} . N-H Bend (strong) occurs at $1610\text{--}1500 \text{ cm}^{-1}$. Primary (two bands) is asymmetric at 1610 cm^{-1} , symmetric at 1500 cm^{-1} . Secondary absorbs in the range $1610\text{--}1550 \text{ cm}^{-1}$. Tertiary absorbs only weakly.

AMINO ACIDS



These compounds exist as zwitterions (internal salts) and exhibit spectra that are combinations of carboxylate and primary amine salts. Amino acids show NH_3^+ stretch (very broad), N-H bend (asymmetric/symmetric), and COO^- stretch (asymmetric/symmetric).

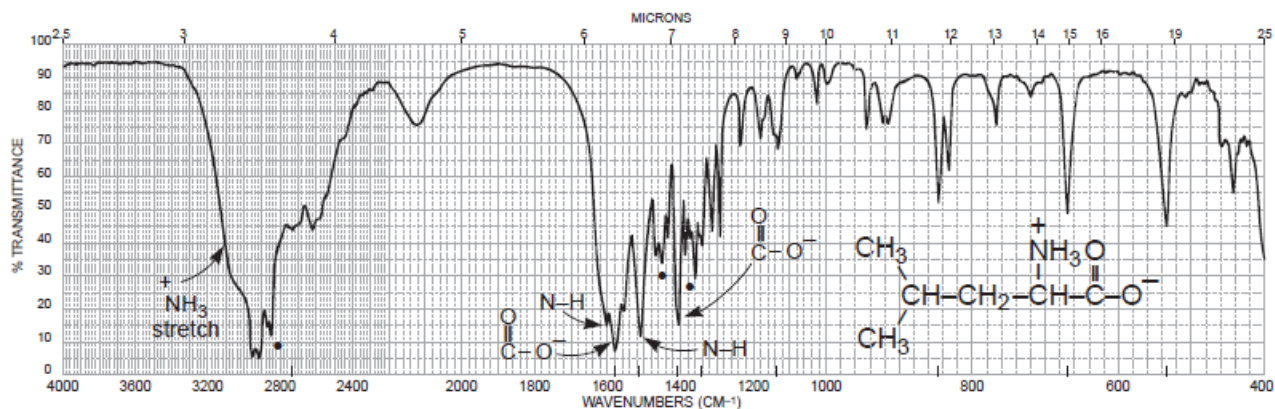


Fig (37): The infrared spectrum of (Leucine) 2-amino-5-methylhexanoic acid (2-ammonio-5-methylhexanoate) (neat liquid, KBr plates).

Simple Problems and short questions on infra-red Spectroscopy

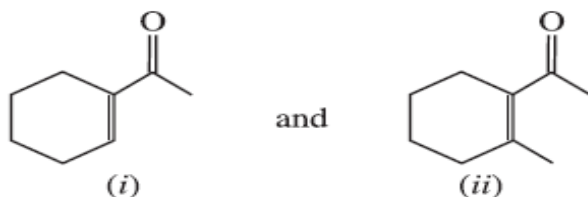
1. An organic compound with molecular mass C_8H_{18} shows the following characteristic absorption bands :

(i) 2925 cm^{-1} (st), (ii) 1465 cm^{-1} , (iii) 1380 cm^{-1} and (iv) 720 cm^{-1} .

Determine the structure of the compound.

2: The analytical data and the molecular mass determination gave C_8H_8O as the molecular formula of the compound. The compound burns with a sooty flame and gave an oxime with hydroxylamine hydrochloride. Following absorption bands appear in its Infra-red spectrum : (i) 2825 cm^{-1} , (ii) 2717 cm^{-1} , (iii) 3060 cm^{-1} and (iv) 1700 cm^{-1} (s) and 830 cm^{-1} . Deduce the structure of the compound.

3: Which of the following two compounds will show $C=O$ stretching absorption band at a higher wave number? Give suitable reason for your answer.



4: An aromatic organic compound decolourises bromine in carbon tetra-chloride and exhibits the following absorption position.

(i) 3090 cm^{-1} (ii) 3040 and 3000 cm^{-1} (iii) 2820 and 2750 cm^{-1} (iv) 1685 cm^{-1} (s)
(v) 1630 cm^{-1} (vi) 1580 and 1450 cm^{-1} (vii) 750 cm^{-1} .

5: Can you distinguish a pair of enantiomers by infra-red spectroscopy?

6: What happens to O-H str position when 10 ml of carbon tetrachloride is added to 2 ml of ethyl alcohol?

7: In acetylene, $\text{—C}\equiv\text{C—H}$ str. appears at about 3300 cm^{-1} . How will you distinguish it from an O-H str. in alcohol?

8: What is the effect of hybridization of carbon on the stretching frequency of C-H bonds?

9: How will you distinguish between *cis* and *trans*-cinnamic acid?

Ans. *cis*-Cinnamic acid absorbs at a higher wave number as compared to its *trans*-isomer. It is partially explained due to the steric effect caused by the bulky groups on the same side of the double bond. Due to repulsive interactions, the C = O part of —COOH group goes out of the plane of the double bond. Thus, conjugation diminishes and hence C = O absorption occurs at a higher wave number.

10: An organic compound (A) with molecular formula C₃H₇NO gives absorption peaks in the regions 3413 (*m*), 3236 (*m*), 3030–2899 (*m*), 1667 (*s*), 1634 (*s*) and 1460 cm⁻¹ (*s*). Give its probable structure.