INFRARED SPECTROSCOPY

SEM-4, CC-8
PART-3, PPT-9

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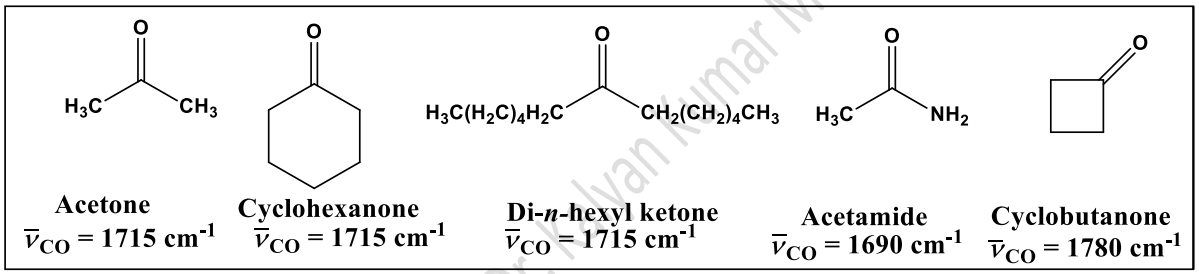
INFRARED SPECTROSCOPY (PART-3, PPT-9)

Application of IR Spectroscopy

1. To determine the functional group present in the compound
2. To investigate the progress of the reaction
3. To establish the identity of two samples/compounds

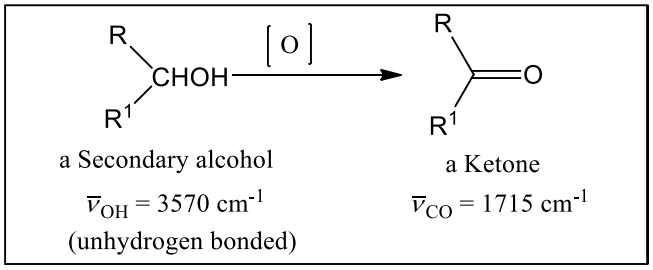
Determination of the Functional Group

In the absence of any electrical or steric effects that would affect the vibrational frequency of a given group, that particular functional group will absorb IR energy of very nearly the same wavelength in all molecules. So, wave number will be fixed for a particular functional group. For example, the absorption owing to the carbonyl stretching vibration of acetone is at the same place as that for cyclohexanone and di-*n*-hexyl ketone. On the other hand, it is different for acetamide (an electrical effect) and for cyclobutanone (a steric effect).



Investigation of the Progress of the Reaction

The progress of most organic reactions can be followed readily by examining spectra of aliquots withdrawn. For example, in the oxidation of a secondary alcohol to a ketone, one learns to expect the disappearance of hydroxyl (O-H) stretching at ~3570 cm^{-1}, and the appearance of carbonyl (C=O) stretching at ~1715 cm^{-1}.



Establishment of the Identity of Two Samples/Compounds

One of the most important functions of IR spectroscopy is to establish conclusively the identity of two samples/compounds. Two identical compounds have exactly the same spectra

when run in the same medium under similar conditions. The identity of two samples/compounds can be ascertained by obtaining superimposable IR spectra. This is because no two molecules, *except the enantiomers*, in the universe have the same IR spectrum.

Absorptions of Aliphatic Hydrocarbons

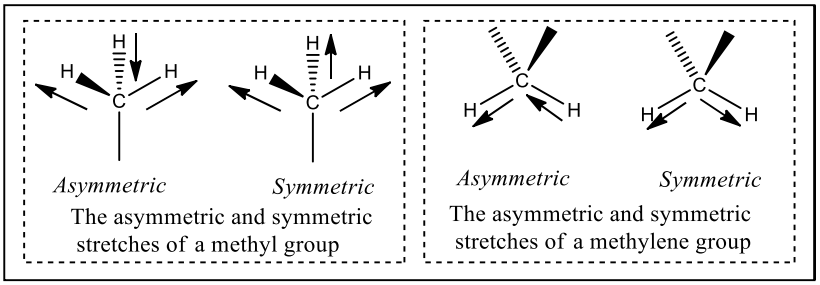
Absorptions of Normal Alkanes [$CH_3CH_2(CH_2)_nCH_3$]

Alkanes consist strictly of carbon-carbon, and carbon-hydrogen single bonds. The spectra of normal alkanes can be interpretated in term of four vibrations, the stretching and bending of C-H and C-C bonds.

1. **C-H Stretching Vibrations**: Absorption arising from C-H stretching in the alkanes occurs in the general region of 3000-2840 cm^{-1}.
2. **C-H Bending Vibrations**: The various C-H bending vibrations appear in the region 1485-1340 cm^{-1}.
3. **C-C Stretching Vibrations**: The bands assigned to C-C stretching vibrations are weak and appear in the broad region of 1200-800 cm^{-1}. Generally, they overlap and difficult to identify.
4. **C-C Bending Vibrations**: The C-C bending vibrations occur at very low frequencies (below 500 cm^{-1}) and therefore do not occur in IR spectra.

C-H stretching Vibration of a Methyl Group

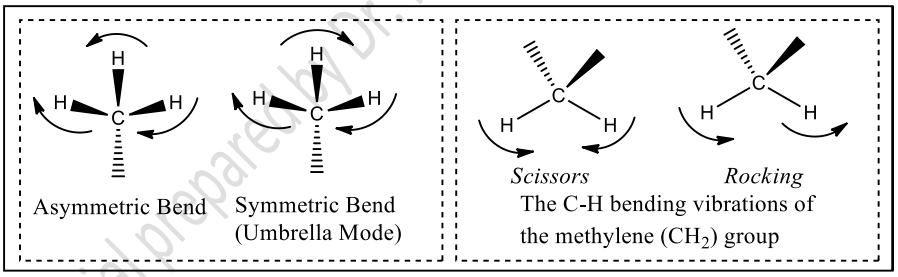
- The methyl (CH_3) group gives rise to two distinct C-H stretching bands occurring at ~2962 cm^{-1} and ~2872 cm^{-1}, for the asymmetric and symmetric C-H stretches, respectively.
- The methyl asymmetric stretch is more intense than the symmetric stretch. This is because the dipole moment change for the asymmetric stretch is larger than for the symmetric stretch.
- The asymmetric C-H stretching motion involves one C-H bond contracting while the other two bonds are lengthening, or two bonds contracting and one lengthening.
- The symmetric C-H stretching motion of a methyl group involves all three C-H bonds lengthening or contracting at the same time.



C-H Stretching Vibration of a Methylene Group

- The methylene (CH_2) structural unit also has symmetric and asymmetric vibrations. The asymmetric C-H stretching vibration for CH_2 involves one C-H bond contracting while the other bond is lengthening. This vibration appears at ~2926 cm^{-1}.
- The symmetric methylene stretch involves both the C-H bonds lengthening or contracting at the same time. This band typically appears at ~2855 cm^{-1}.
- The methylene asymmetric stretch is more intense than the symmetric stretch. This is because the dipole moment change for the asymmetric stretch is larger than for the symmetric stretch.

C-H Bending Vibrations in Methyl Group

- Like C-H stretching vibrations, bending modes are also categorized as symmetric and asymmetric.
- The symmetrical bending vibration involves the in-plane bending of the C-H bonds and the asymmetrical bending vibration involves out-of-plane bending of the C-H bonds.
- 

- The bending vibrations of the C-H bonds of a methyl group appear at ~1460 cm^{-1}.
- The methyl symmetric bends (umbrella modes) show up at ~1375 cm^{-1}.

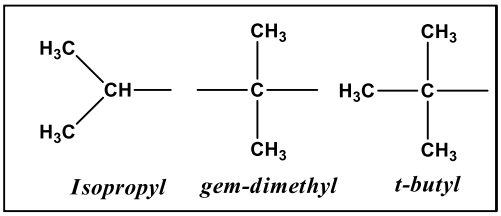
C-H Bending Vibrations in a Methylene Group

- The four bending vibrations are referred to as scissoring, *rocking, wagging, and twisting*. Scissoring vibration involves the H-C-H bond angle getting bigger and smaller, and appears in alkanes at ~1465 cm^{-1}.
- The methylene rocking vibration in alkanes occurs at ~720 cm^{-1}. This band only occurs in molecules with 4 or more CH_2 groups in a row. Molecules with short hydrocarbon chains do not have a band at ~720 cm^{-1}.

- Absorption due to methylene wagging and twisting vibrations is observed in the 1350-1150 cm^{-1}. These bands are generally weak.

Absorptions of Branched Chain Alkanes

- The simplest branch points that can be observed via IR spectroscopy are the gem-dimethyl and isopropyl groups.



- The methyl C-H stretching vibrations for the asymmetric and symmetric CH_3 stretches appear at ~2955 cm^{-1} and ~2870 cm^{-1}.
- The isopropyl and *gem*-dimethyl groups show a strong doublet with two peaks of about equal intensity in the region 1385-1380 cm^{-1} and 1370-1365 cm^{-1} as the C-H bending vibrations.
- The *t*-butyl and isobutyl groups give rise to two C-H bending bands (with 1:2 intensity ratio), one in the 1395-1385 cm^{-1} region and one near 1370 cm^{-1}.
- The splitting is caused by vibrational interaction between the umbrella modes of the two methyl groups.

C-H stretching and bending vibrations in Alkanes

The Wavenumber Ranges for the C-H Stretches of Alkanes (in cm^{-1})	
Vibration	**Wavenumber Range**
CH_3 Asymmetric	~2962
CH_3 Symmetric	~2872
CH_2 Asymmetric	~2926
CH_2 Symmetric	~2855

The C-H Bending Vibrations of Alkanes (all numbers in cm^{-1})	
Vibration	**Wavenumber Range**
C-CH_3 Asymmetric bend	**~1460**

C-CH_3 Symmetric bend (umbrella mode)	**~1375**
C-CH_2 Scissors	**~1465**
C-CH_2 Rock	**~720**

C-H Stretching and Bending Bands for Branched Alkanes (all numbers in cm^{-1})	
Vibration	**Wavenumber Range**
Methine C-H Stretch	~ 2900 (weak)
Isopropyl and *gem*-dimethyl groups	2 bands; 1385 – 1380 and 1370 – 1365; Intensity ratio ~1:1
Isobutyl and *t*-butyl groups	2 bands; 1395 – 1385 and 1370 Intensity ratio ~1:2
Methine C-H bend	~ 1350 (weak)

Cyclic Alkanes

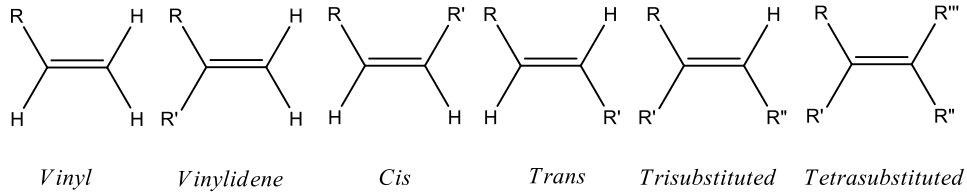
- C-H Stretching Vibrations: The methylene stretching vibrations of unstrained cycloalkanes are much the same as those observed for acyclic alkanes. Increasing ring strain moves the C-H stretching bands progressively to high frequencies.
- Cyclopropanes have high C-H stretching frequencies, and appears in the region 3070-3040 cm^{-1}. The C-C-C bond angle is substantially contracted below the normal 109.5°, leading to increased *s*-character in the C-H bonds, and thus to high frequencies.
- C-H Bending Vibrations: Cyclization decreases the frequency of the CH_2 scissoring vibration. Cyclohexane absorbs at 1452 cm^{-1}, whereas *n*-hexane absorbs at 1468 cm^{-1}. Cyclopentane absorbs at 1455cm^{-1}, cyclopropane absorbs at 1442 cm^{-1}.

Absorptions of Olefinic Hydrocarbons

Infrared Spectra of Alkenes

- An alkene (olefins) is any molecule that contains a carbon-carbon double bond (C=C). It introduces several new modes of vibration into a hydrocarbon molecule. These are:

1. C=C Stretching Vibration
2. =C-H Stretching Vibration
3. =C-H Bending (in-plane) Vibration
4. 4. =C-H Bending (‘oop’) Vibration



The substitution pattern around vinyl, vinylidene, *cis*, *trans*, trisubstituted, and tetrasubstituted double bonds

- Note: Tetratsubstituted double bonds have no hydrogens attached to the C=C and do not exhibit C-H stretching or bending bands.
- 'oop' stands for 'Out-of-Plane'

C=C Stretching

Unconjugated Linear Alkenes

- The C=C stretching mode of unconjugated alkenes usually shows moderate to weak absorption at 1670-1640 cm^{-1}.

1. Monosubstituted alkenes, that is, vinyl groups absorb near 1640 cm^{-1} with moderate intensity.
2. Disubstituted *trans*-alkenes, tri-, and tetra-alkyl substituted alkenes absorb near 1670 cm^{-1}.
3. Disubstituted cis-alkenes and vinylidene alkenes absorb near 1650 cm^{-1}.

Intensity of Absorptions

As more alkyl groups are added, the intensity of absorption decreases since the vibrations now results in a smaller change of dipole moment. In the case of tetrasubstituted-, trisubstituted- and relatively symmetrical disubstituted *trans*-alkenes, C=C stretching band is often of very low intensity and is absent in the IR spectrum. Since, this vibration in these molecules results in no change or any appreciable change in dipole moment.

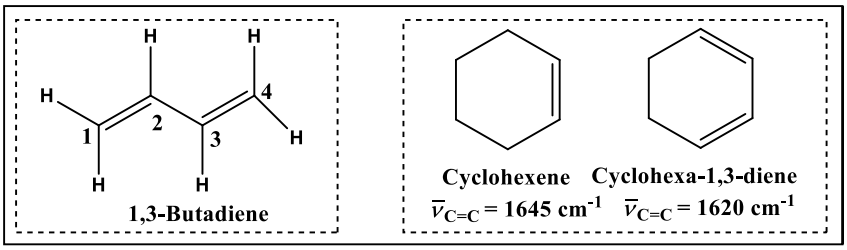
The *cis*-alkenes, which lack the symmetry of the *trans* structure, absorb more strongly than *trans*-alkenes. Internal double bonds generally absorb more weakly than terminal double bonds because of pseudosymmetry.

C=C Stretching

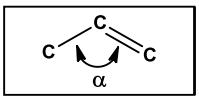
Conjugated Systems

The alkene bond stretching vibrations in conjugated dienes without a centre of symmetry interact to produce two C=C stretching bands. The spectrum of an unsymmetrical conjugated diene, such as 1,3-pentadiene, shows absorption near 1650 and 1600 cm^{-1}. The symmetrical

molecule 1,3-butadiene shows only one band near 1600 cm^{-1}, resulting from asymmetrical stretching; the symmetrical stretching band is inactive in the IR.



Reonance results in a partial π-bond character between the two double bonds, with decreased density and decreased stiffness in the double bonds themselves. Conjugated double bonds, therefore, vibrate at lower frequencies than do similar isolated double bonds.

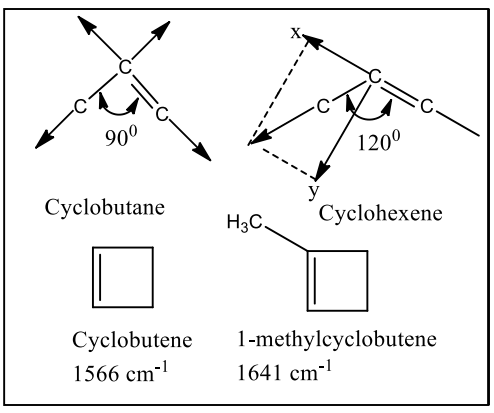


Cycloalkenes with Internal Double bonds

Absorption of the internal double bond in the unstrained cyclohexane system is essentially the same as that of a *cis*-isomer in an acyclic system. The C=C stretching vibration is coupled with the C-C stretching of the adjacent bonds. As the angle α becomes smaller the interaction becomes less until it is at a minimum at 90° in cyclobutene (1566 cm^{-1}). In the cyclopropene structure, interaction again becomes appreciable, and the absorption frequency increases (1641 cm^{-1}).

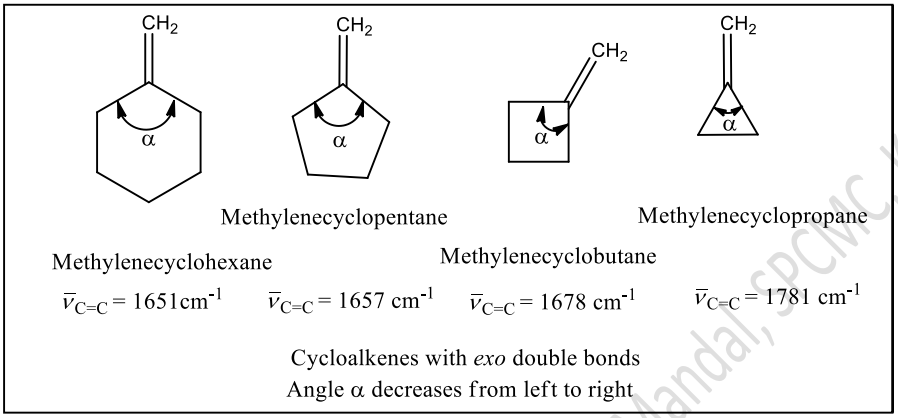
The substitution of alkyl groups for an α-hydrogen atom in strained ring systems serves to increase the frequency of C=C absorption. Cyclobutene absorbs at 1566 cm^{-1}, 1-methylcyclobutene at 1641 cm^{-1}. The unexpected increase in frequency in cyclopropene is due to the fact that C=C vibration is strongly coupled to the attached C-C single-bond vibration. When the attached C-C bonds are perpendicular to the C=C axis, as in cyclobutene, their vibrational mode is orthogonal to that of the C=C bond and does not couple. When the angle is greater than 90°, the C-C single-bond stretching vibration can be resolved into two components, one of which is coincident with the direction of the C=C stretch.

In the diagram, components ***x*** and ***y*** of the C-C stretching vector are shown. Since component ***x*** is in line with the C=C stretching vector, the C-C and C=C bonds are coupled, leading to a higher frequency of absorption. A similar pattern exists for cyclopropene, which has an angle less than 90°.



Cycloalkenes with External Double bonds

External (*exo*) double bonds give an increase in absorption frequency with decreasing ring size. Smaller rings require the use of more *p*-character to make the C-C bonds from the requisite small angles. This removes *p*-character from the sigma bond of the double bond and gives it more *s*-character, thus strengthening and stiffening of the double bond. The force constant *k* is then increased, and the absorption frequency increases.



C-H Stretching

- Like the C-H bonds of alkanes, the =C-H bonds of alkenes can also stretch and bend. The C-H stretches for almost all unsaturated groups (H-C=C, H-C≡C, and aromatic rings) fall above 3000 cm^{-1}.
- In alkenes, C-H stretching absorption band appears in the region 3100-3000 cm^{-1}. The =C-H stretch of 1-octene appears at 3077 cm^{-1}. The intensity of alkene C-H stretching absorption are influenced by the pattern of substitution.
- The vinyl group produces three closely spaced =C-H stretching bands. Two of these result from symmetrical and asymmetrical stretching of the terminal $=CH_2$ groups, and the third from the stretching of the remaining single =C-H.

Positions of C-H Stretches versus Saturated and Unsaturated Groups	
C-H Stretch Position	**Sample contains**
Below 3000 cm^{-1}	saturated carbon atoms (C_{sp3}-H) only
Above 3000 cm^{-1}	unsaturated carbon atoms ($C_{sp/sp2}$-H) only
Above and below 3000 cm^{-1}	both saturated and unsaturated carbon atoms

C-H Stretching (C_{sp2}-H)

- The band at 3077 cm^{-1} of 1-octene is due to the asymmetric C-H stretch of the $=CH_2$ part of the vinyl group. The vinylidene group, since it also contains a $=CH_2$, also exhibits this stretching vibration. The $=CH_2$ asymmetric stretch of vinyl and

vinylidene groups generally occurs between 3090 and 3075 cm^{-1}. These groups also show a $=CH_2$ symmetric stretch between 3050 and 3000 cm^{-1}.

- The other substituted double bond types (*cis*, *trans*, and trisubstituted) also exhibit a =C-H stretching vibration between 3050 and 3000 cm^{-1}.

Positions of C-H Stretches for Saturated and Unsaturated Functional Groups	
Functional Groups	**C-H Stretch Position**
Saturated (CH_3, CH_2, CH), (C_{sp3}-H)	< 3000 cm^{-1}
Unsaturated (C=C, C=C, Aromatic Rings), (C_{sp2}-H)	> 3000 cm^{-1}
Vinyl/vinylidene CH_2 asymmetric stretch, (C_{sp2}-H)	3090-3075 cm^{-1}

C-H Bending (C_{sp2}-H)

- Alkene C-H bonds can undergo bending either in the same plane as the C=C bond or perpendicular to it; the bending vibrations can be either in-plane or out-of-plane with respect to each other. The most useful group wavenumbers for alkenes are the out-of-plane C-H bends of the hydrogens attached to the double bond. These vibrations appear from 1000 to 650 cm^{-1}. Out-of-plane =C-H bending vibrations are typically the most intense bands of an alkene.

- The vinyl group absorbs near 1416 cm^{-1} due to a scissoring vibration of the terminal methylene. For vinyl groups in general, out-of-plane =C-H bending vibrations occur at ~990 cm^{-1} and ~910 cm^{-1}.

- The disubstituted types of double bonds, vinylidene, *cis*, and *trans*, exhibit an out-of-plane C-H bending band at ~890, ~690, and 965±5 cm^{-1}, respectively. Out-of-plane C-H bending bands distinguish between *cis* and *trans* isomers easily.

- Trisubstituted double bonds exhibit an out-of-plane C-H bending band in the region 840-790 cm^{-1}.

Summary of Group Wavenumbers for Alkenes (all numbers in cm^{-1})

The C=C Stretching, C-H Stretching, and C-H Bending Bands of Alkenes			
Alkene	**=C-H Stretch**	**C=C Stretch**	**=C-H Bend**
Vinyl	3090-3075	1660-1630	990 ± 5, 910 ± 5
Vinylidene	3090-3075	1660-1630	890 ± 5
Cis	3050-3000	1660-1630	690 ± 5
Trans	3050-3000	1680-1665	965 ± 5
Trisubstituted	3050-3000	1680-1665	815 ± 25
Tetrasubstituted	Absent	1680-1665	Absent

Absorptions of Alkynic Hydrocarbons

- **The two stretching vibrations in alkynes involve C≡C and C_{sp}-H stretching.**
- **C≡C Stretching:** The most characteristic group wavenumber for alkynes is the C≡C stretch. This band is found in the region 2140-2100 cm^{-1} for monosubstituted alkynes. For disubstituted alkynes, the C≡C stretch appears in the region 2260-2190 cm^{-1}. This band appears in a unique position and, when present, is a strong indication that there is a triple bond in a sample. This band is relatively weak.
- For reason of symmetry, a terminal C≡C produces a stronger band than an internal C≡C (pseudosymmetry). The intensity of the C≡C stretching band is increased by conjugation with a carbonyl group. However, if an alkyne is symmetrically substituted, the dipole moment change for the C≡C stretch is zero, and there will be no C≡C stretching band. If an alkyne is almost symmetrically substituted, the C≡C stretch will be weak and may be difficult to see.

Infrared Spectra of Alkynes

- **≡C-H Stretching:** The spectra of monosubstituted alkynes are marked by an intense, high wavenumber C-H stretching vibration in the region 3350-3250 cm^{-1}. This C-H stretching band can be distinguished from O-H and N-H stretching bands that also occur in the same region because the alkyne C-H stretch is sharper than O-H or N-H bands.
- ≡C-H Bending: The ≡C-H bending vibration of a monosubstituted alkyne is called a "wag." The wag band is typically strong, broad, and found in the region 700-600 cm^{-1}. The first overtone of the C-H bending vibration appears as a weak, broad-band in the 1320-1220 cm^{-1} region.
- A disubstituted alkyne does not have any hydrogen attached to the C≡C, and so does not exhibit C-H stretching or bending vibrations.

Summary of Group Wavenumbers for Alkynes (all numbers in cm^{-1})			
Alkene	**=C-H Stretch**	**C=C Stretch**	**=C-H Bend**
Substitution	C≡C Stretch	≡C-H Stretch	≡C-H wag
Monosubstituted	2140-2100	3350-3250	700-600
Disubstituted	2260-2190	Absent	absent

Absorption of Aromatic Compounds

Benzene is the prototype aromatic hydrocarbon. Since it contains 12 atoms, it has 30 (3x12-6) normal modes of vibration. Of these, only a handful is infrared active because of the high

symmetry of the molecule. However, substituted benzenes have lower symmetry and can exhibit quite a number of IR bands. The characteristic vibrations are:

- **=C-H Stretching Vibrations:** Since aromatic rings are unsaturated with respect to hydrogen substitution, the C-H stretches of an aromatic ring fall above 3000 cm^{-1}. In general, the C-H stretches of aromatic rings are found in the region 3100-3000 cm^{-1}.
- **Overtone/Combination Bands:** Aromatic rings have a series of weak bands in the 2000-1650 cm^{-1} region that arise from overtones and combinations of lower wavenumber vibrations. These weak absorptions can be used to assign the ring substitution pattern.
- **C=C Stretching Vibrations:** In the 1620-1400 cm^{-1} region of aromatic spectra there are bands called Ring modes/Skeletal vibrations. These bands are due to the stretching and contracting of the carbon-carbon bonds in the benzene ring. Bands appear near 1600 (strong), 1580 (medium), 1500 (medium), and 1450 cm^{-1} (medium) for C=C vibrations.
- Ring modes are lower in wavenumber than C=C stretches because the bond order of aromatic carbon-carbon bonds is lower than in alkenes. The concomitant lowering of the force constant causes the difference between the spectra of the two functional groups.

C-H Bending Vibrations

- **In-Plane Vibrations:** The region 1300-1000 cm^{-1} in an aromatic spectrum is usually populated by bands due to the C-H bond bending in the plane of the benzene ring. However, these bands are rarely useful because they overlap other, stronger absorptions that occur in this region.
- **Out-of-Plane Vibrations:** The best bands for determining the presence of an aromatic ring in a sample are the out-of-plane C-H bending vibrations. These bands usually show up between 900 and 675 cm^{-1} and involve the C-H bond bending above and below the plane of the benzene ring. These extremely intense absorptions, resulting from strong coupling with adjacent hydrogen atoms, can be used to assign the positions of substituents on the aromatic ring.

1. ***Monosubstituted Rings***: Two strong absorption bands appear in the region 750-690 cm^{-1}. One appears at ~ 750 cm^{-1} and the other at ~700 cm^{-1}.
2. ***ortho-Disubstituted Rings***: One strong absorption band near 750 cm^{-1} is obtained.
3. ***meta-Disubstituted Rings***: Three absorption bands appear in the spectra. 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}.
4. ***para-Disubstituted Rings***: One strong band appears in the region 850-800 cm^{-1}.

Summary of Vibrations in aromatic Compounds

IR Spectrum of Aromatic Hydrocarbons		
	Region (cm^{-1})	**Assignments**
1	3100-3000	C-H Stretching
2	2000-1650	Overtone/Combination Bands
3	1620-1400	Ring Modes/Skeletal Vibrations
4	1300-1000	In-plane C-H Bends
5	900-675	Out-of-plane C-H Bends

Bands for Mono- and Disubstituted Benzene Rings			
Substitution Pattern	**Out-of-plane C-H bending**	**Ring Bend* ($690 \pm 10\ cm^{-1}$)**	* This bending band appears as intense band at ~ 694 cm^{-1}. This band is due to the bending of the C-C bonds in the aromatic ring, and is called the "ring-bending" band. This band is very much symmetry dependent.
Mono	750-690	Yes	
ortho	770-735	No	
meta	880-690	Yes	
para	850-800	No	