

## 4. IR spectroscopy

In contrast to ultraviolet spectroscopy IR spectrum provides a rich array of absorption bands which can provide accurate structural information about a molecule. It provides the methods for studying materials in all three physical states i.e. solid, liquid and gas. Analytically useful IR spectrum covers the following range of electromagnetic spectrum.

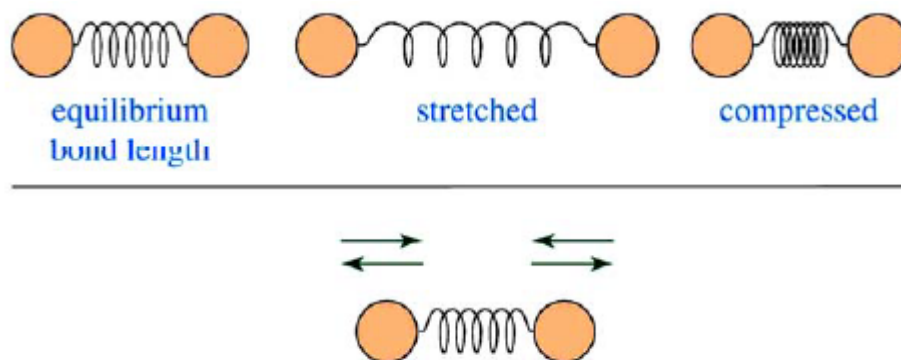
Near IR  $15000\text{ cm}^{-1}$  to  $3000\text{ cm}^{-1}$

Mid IR  $4000\text{ cm}^{-1}$  to  $400\text{ cm}^{-1}$

Far IR  $200\text{ cm}^{-1}$  to  $10\text{ cm}^{-1}$

Most used  $4000\text{ cm}^{-1}$  to  $670\text{ cm}^{-1}$

Infrared radiation is largely thermal energy. It induces stronger molecular vibrations in covalent bonds, which can be viewed as springs holding together two masses, or atoms. Specific bonds respond to (absorb) specific frequencies.

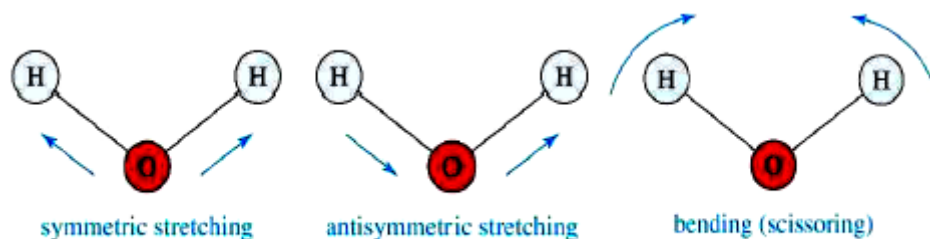


### VIBRATIONAL MODES:

The information contained in IR spectrum originates from molecular vibrations. These are either fundamental vibrational modes that are associated with the vibrations of specific functional group, or molecule, vibrational overtones or summational modes of fundamental vibrations.

A molecule resembles a system of balls of varying masses corresponding to atoms of a molecule and spring of varying lengths corresponding to various chemical bonds. There are two fundamental vibrational modes.

1. **Stretching**: in which the distance between the two atoms increases or decreases but the atoms remain in the same bond axis.
2. **Bending**: in which the position of the atom changes relative to the bond axis. Covalent bonds can vibrate in several modes, including stretching, rocking, and scissoring.



The various stretching and bending vibrations occur at certain frequencies. When an IR radiation of same frequency is incident on the molecule, the energy is absorbed and the amplitude of that vibration increases correspondingly. When the molecule returns to ground state the absorbed energy is released as heat.

A nonlinear molecule containing  $n$  atoms has  $3n-6$  possible vibrational modes through which IR radiation may be absorbed. For example, methane has 9 and benzene has 30 possible fundamental absorption bands respectively. In order that a particular vibration results in an absorption band, the vibration must cause a change in the dipole moment of the molecule.

### Which substances give a signal in IR spectrum?

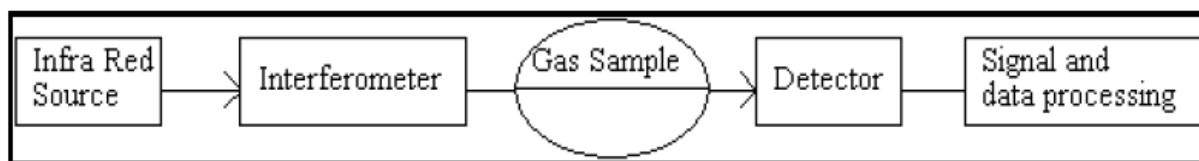
**Ans:** The molecules that contain polar bonds i.e. molecules composed of atoms of different elements, organic compounds and inorganic compounds ( $\text{H}_2\text{O}$ ,  $\text{CO}_2$ ,  $\text{NO}_2$ ,  $\text{HCl}$ , salts...) can give a signal in IR spectrum. Whereas pure chemical elements in molecular or crystal state e.g. Ar,  $\text{O}_2$ ,  $\text{O}_3$ ,  $\text{N}_2$ ,  $\text{Cl}_2$ ,  $\text{S}_8$ , silicon, graphite, Diamond etc cannot give a signal in IR spectrum.

### Basic Principle:

When a sample is placed in a beam of infrared radiation, the sample will absorb radiation at frequencies corresponding to molecular vibrational frequencies, but will transmit all other frequencies. The frequencies of radiation absorbed are measured by an infrared spectrometer, and the resulting plot of absorbed energy vs. frequency is called the infrared spectrum of the material. Identification of a substance is possible because different materials have different vibrations and yield different infrared spectra. Furthermore, from the frequencies of the absorption it is possible to determine whether various chemical groups are present or absent in a chemical structure.

### Instrumentation of FTIR:

The basic components of an FTIR are shown schematically in fig.



1. **The Source:-** Infrared energy is emitted from a glowing black body source. This beam passes through an aperture which controls the amount of energy presented to the sample (and, ultimately, to the detector).

2. **The Interferometer:-** The beam enters the interferometer where the “spectral encoding” takes place. The resulting interferogram signal then exits the interferometer.

3. **The Sample:-** The gaseous sample can be directly analysed. Liquid can also be used directly but in diluted form in NaCl plates. Solid compound can be mixed with KBr and formed a pallet and used.

The beam enters the sample compartment where it is transmitted through or reflected off of the surface of the sample, depending on the type of analysis being accomplished. This is where specific frequencies of energy, which are uniquely characteristic of the sample, are absorbed.

4. **The Detector:-** The beam finally passes to the detector for final measurement. The detectors used are specially designed to measure the special interferogram signal.

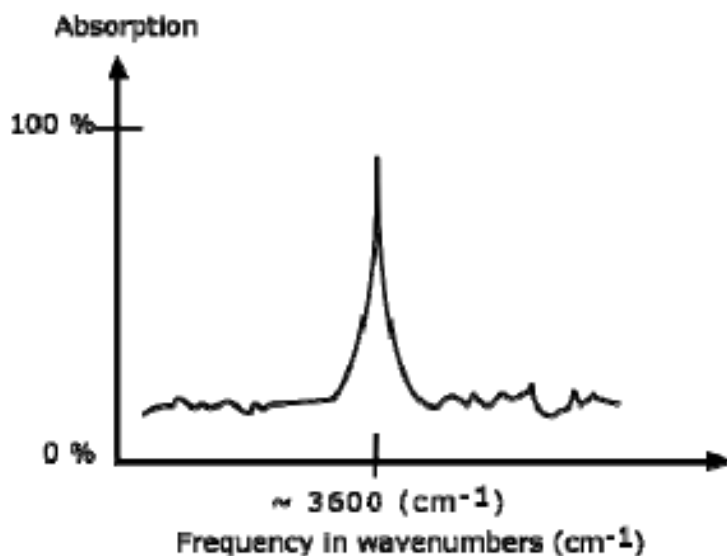
5. **The Computer:-** The measured signal is digitized and sent to the computer where the Fourier transformation takes place. The final infrared spectrum is then presented to the user for interpretation and any further manipulation.

### Working:

The infrared source emits a broad band of different wavelength of infrared radiation. The IR source used is a SiC ceramic at a temperature of 1550 K. The IR radiation goes through an interferometer that modulates the infrared radiation. The interferometer performs an optical inverse Fourier transform on entering IR radiation. The modulated IR beam passes through the gas sample where it is absorbed to various extents at different wavelengths by the various molecules present. Finally, the intensity of the IR beam is detected by a detector, which is a liquid nitrogen cooled MCT (Mercury–Cadmium–Telluride) detector. The detected signal is digitised and Fourier transformed by the computer to get the IR spectrum of the sample gas.

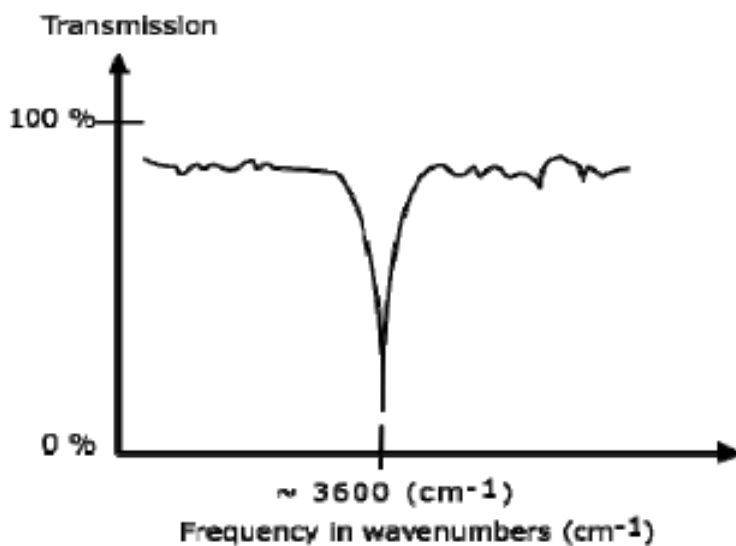
### AN IR SPECTRUM IN ABSORPTION MODE:

The IR spectrum is basically a plot of transmitted (or absorbed) frequencies vs intensity of the transmission (or absorption). Frequencies appear in the x-axis in units of inverse centimeters (wavenumbers), and intensities are plotted on the y-axis in percentage units.



The graph above shows a spectrum in **absorption** mode.

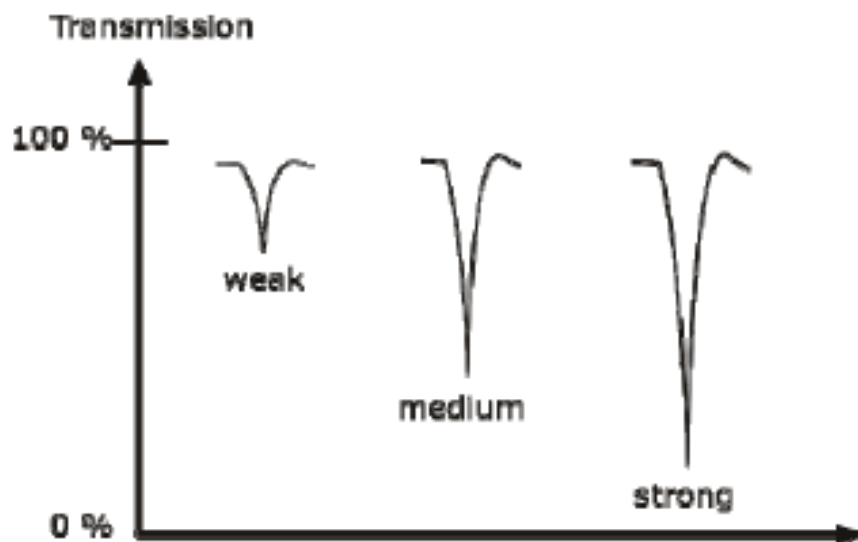
#### AN IR SPECTRUM IN TRANSMISSION MODE:



The graph above shows a spectrum in transmission mode. This is the most commonly used representation and the one found in most chemistry and spectroscopy books.

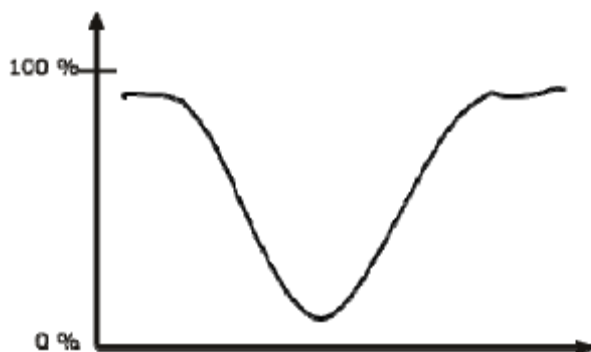
#### CLASSIFICATION OF IR BANDS

IR bands can be classified as strong (s), medium (m), or weak (w), depending on their relative intensities in the infrared spectrum. A strong band covers most of the y-axis. A medium band falls to about half of the y-axis, and a weak band falls to about one third or less of the y-axis.



Infrared band shapes come in various forms. Two of the most common are narrow and broad. Narrow bands are thin and pointed, like a dagger. Broad bands are wide and smoother.

A typical example of a broad band is that displayed by O-H bonds, such as those found in alcohols and carboxylic acids, as shown below.



### INFORMATION OBTAINED FROM IR SPECTRA

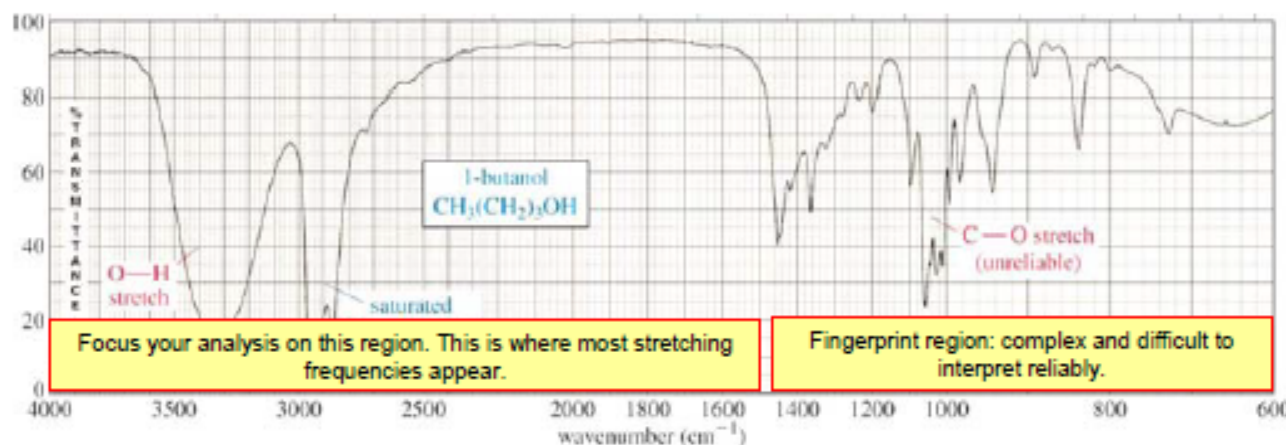
- IR is most useful in providing information about the presence or absence of specific functional groups.
- IR can provide a molecular fingerprint that can be used when comparing samples. If two pure samples display the same IR spectrum it can be argued that they are the same compound.
- IR does not provide detailed information or proof of molecular formula or structure. It provides information on molecular fragments, specifically functional groups.
- Therefore it is very limited in scope, and must be used in conjunction with other techniques to provide a more complete picture of the molecular structure.

## THE FINGERPRINT REGION

Although the entire IR spectrum can be used as a fingerprint for the purposes of comparing molecules, the 600 - 1400  $\text{cm}^{-1}$  range is called the fingerprint region.

This is normally a complex area showing many bands, frequently overlapping each other.

It is much more difficult to pick out individual bonds in this region than it is in the "cleaner" region at higher wavenumbers. The importance of the fingerprint region is that each different compound produces a different pattern of troughs in this part of the spectrum.



## FUNCTIONAL GROUPS AND IR TABLES:

### Characteristic IR Absorption Frequencies of Organic Functional Groups

Functional Group	Type of Vibration	Characteristic Absorptions ( $\text{cm}^{-1}$ )	Intensity
<b>Alcohol</b>			
O-H	(stretch, H-bonded)	3200-3600	strong, broad
O-H	(stretch, free)	3500-3700	strong, sharp
C-O	(stretch)	1050-1150	strong
<b>Alkane</b>			
C-H	stretch	2850-3000	strong
-C-H	bending	1350-1480	variable
<b>Alkene</b>			
=C-H	stretch	3010-3100	medium
=C-H	bending	675-1000	strong
C=C	stretch	1620-1680	variable
<b>Alkyl Halide</b>			
C-F	stretch	1000-1400	strong

C-Cl	stretch	600-800	strong
C-Br	stretch	500-600	strong
C-I	stretch	500	strong
<b>Alkyne</b>			
C-H	stretch	3300	strong, sharp
$\text{—C}\equiv\text{C—}$	stretch	2100-2260	variable, not present in symmetrical alkynes
<b>Amine</b>			
N-H	stretch	3300-3500	medium (primary amines have two bands; secondary have one band, often very weak)
C-N	stretch	1080-1360	medium-weak
N-H	bending	1600	medium
<b>Aromatic</b>			
C-H	stretch	3000-3100	medium
C=C	stretch	1400-1600	medium-weak, multiple bands
Analysis of C-H out-of-plane bending can often distinguish substitution patterns			
<b>Carbonyl</b>	<a href="#">Detailed Information on Carbonyl IR</a>		
C=O	stretch	1670-1820	strong
(conjugation moves absorptions to lower wave numbers)			
<b>Ether</b>			
C-O	stretch	1000-1300 (1070-1150)	strong
<b>Nitrile</b>			
CN	stretch	2210-2260	medium
<b>Nitro</b>			
N-O	stretch	1515-1560 & 1345-1385	strong, two bands

IR Absorption Frequencies of Functional Groups Containing a Carbonyl (C=O)				
Functional Group	Type of Vibration	Characteristic (cm-1)	Absorptions	Intensity

<b>Carbonyl</b>			
C=O	stretch	1670-1820	strong
(conjugation moves absorptions to lower wave numbers)			
<b>Acid</b>			
C=O	stretch	1700-1725	strong
O-H	stretch	2500-3300	strong, very broad
C-O	stretch	1210-1320	strong
<b>Aldehyde</b>			
C=O	stretch	1740-1720	strong
=C-H	stretch	2820-2850 & 2720-2750	medium, two peaks
<b>Amide</b>			
C=O	stretch	1640-1690	strong
N-H	stretch	3100-3500	unsubstituted have two bands
N-H	bending	1550-1640	
<b>Anhydride</b>			
C=O	stretch	1800-1830 & 1740-1775	two bands
<b>Ester</b>			
C=O	stretch	1735-1750	strong
C-O	stretch	1000-1300	two bands or more
<b>Ketone</b>			
acyclic	stretch	1705-1725	strong
cyclic	Stretch	3-membered - 1850 4-membered - 1780 5-membered - 1745 6-membered - 1715 7-membered - 1705	strong
, -unsaturated	Stretch	1665-1685	strong
aryl ketone	Stretch	1680-1700	strong

**How to analyse the IR spectrum?**



When analysing the IR spectrum of an unknown molecule, first efforts on determining the presence or absence of a few major functional groups. The C=O, O-H, N-H, C-O, C=C,  $\text{—C}\equiv\text{C—}$ , -CN, and NO<sub>2</sub> peaks. These peaks are most conspicuous and give immediate structural information if they are present. Do not try to make a detailed analysis of the C-H absorption near 3000cm<sup>-1</sup>, almost all the compounds have these absorptions.

Follow the steps

- 1. Is carbonyl group is present?** The -C=O group give rise to a strong absorption in the region 1820-1660 cm<sup>-1</sup>. The peak is often stongest in the spectrum and of medium width.
- 2. If C=O is present**, then check the following types
- 3.

<b>Acids</b>	Is O-H also present? Broad absorption near 3400-2400cm <sup>-1</sup> usually overlaps with C-H
<b>Amides</b>	Is N-H also present? Medium absorption near 3400cm <sup>-1</sup> , sometimes double peaks with same size.
<b>Esters</b>	Is C-O present? Strong intensity absorption near 1300-1000cm <sup>-1</sup>
<b>Anhydrides</b>	Two C=O absorption near 1810 and 1760cm <sup>-1</sup>
<b>Aldehydes</b>	Is aldehyde C-H present? Two weak absorption near 2850 and 2750 cm <sup>-1</sup>
<b>Ketones</b>	The preceding five choices have been eliminated

4. **If C=O absent**, then check the following options

<b>Alcohols, Phenols</b>	Check for O-H, broad absorption near 3400-3300cm <sup>-1</sup> , confirm this by finding C-O near 1300-1000cm <sup>-1</sup>
<b>Amines</b>	Check for N-H, Medium absorptions near 3400cm <sup>-1</sup>
<b>Ethers</b>	Check for C-O near 1300-1000cm <sup>-1</sup> and absence of O-H near 3400cm <sup>-1</sup>

5. **Double bonds and/or aromatic rings**

1. C=C is weak absorption near 1650cm <sup>-1</sup>
2. Medium strong absorption in the region 1600-1450cm <sup>-1</sup> , these often imply on aromatic ring
3. Confirm the double bond or aromatic ring by consulting the C-H region; aromatic and vinyl C-H occurs to left of 3000cm <sup>-1</sup> , aliphatic C-H occurs to right of this value.

4. **Triple bonds**

1) $\text{C}\equiv\text{N}$ is medium sharp absorption near 2250cm <sup>-1</sup>
2) $\text{C}\equiv\text{C}$ is e weak, sharp absorption near 2150cm <sup>-1</sup>
3) Check also for acetylenic C-H near 3300cm <sup>-1</sup>

5. **Nitro groups**

Two strong absorption at  $1600\text{-}1530\text{cm}^{-1}$  and  $1390\text{-}1300\text{cm}^{-1}$

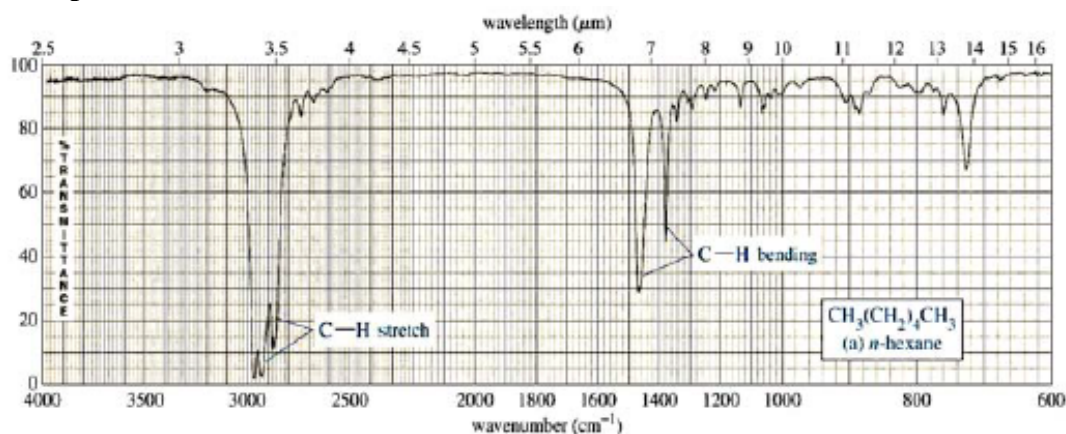
## 6. Hydrocarbons

None of the preceding found.

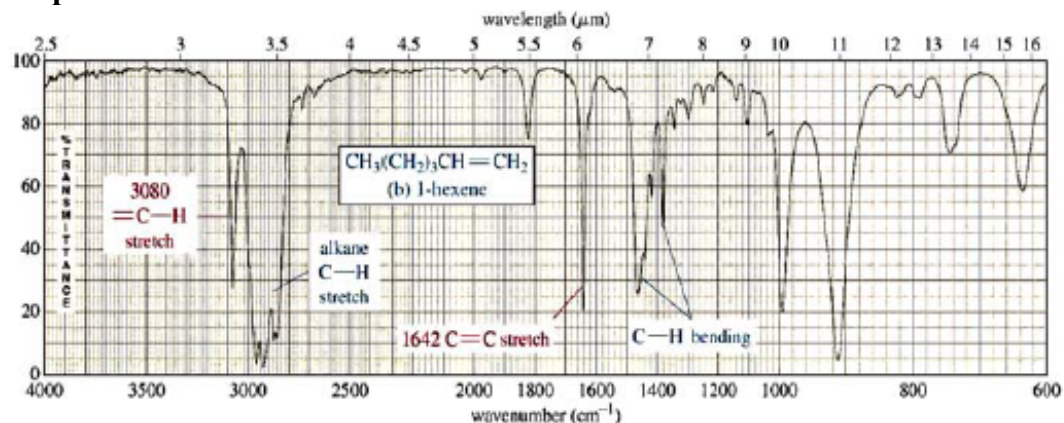
Major absorptions are in C-H region near  $3000\text{cm}^{-1}$

Very simple structure the only another absorption appear near  $1460$  and  $1375\text{cm}^{-1}$

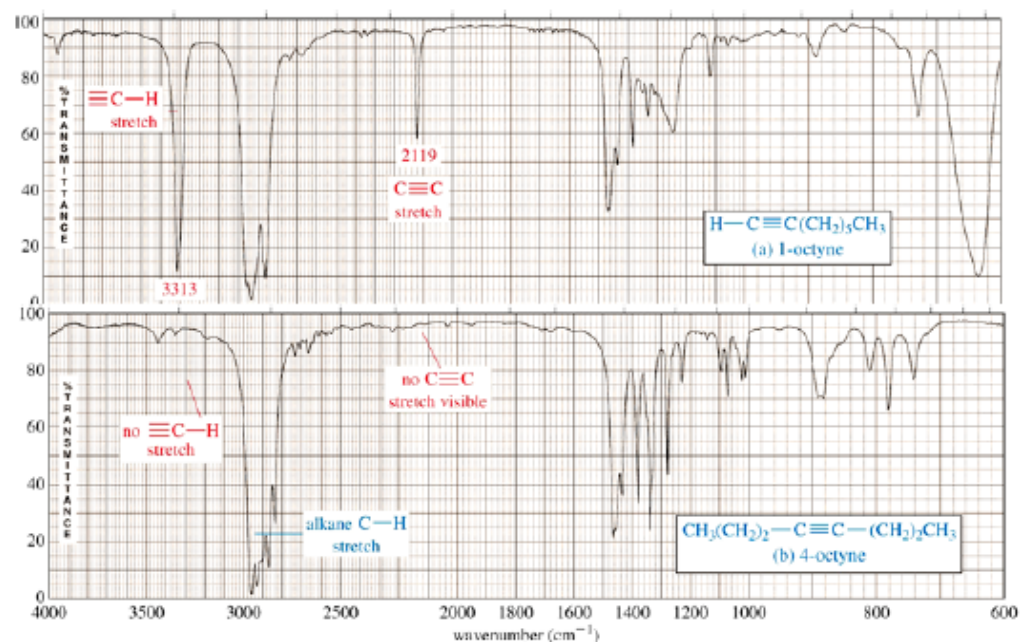
### IR spectrum of n-Hexane



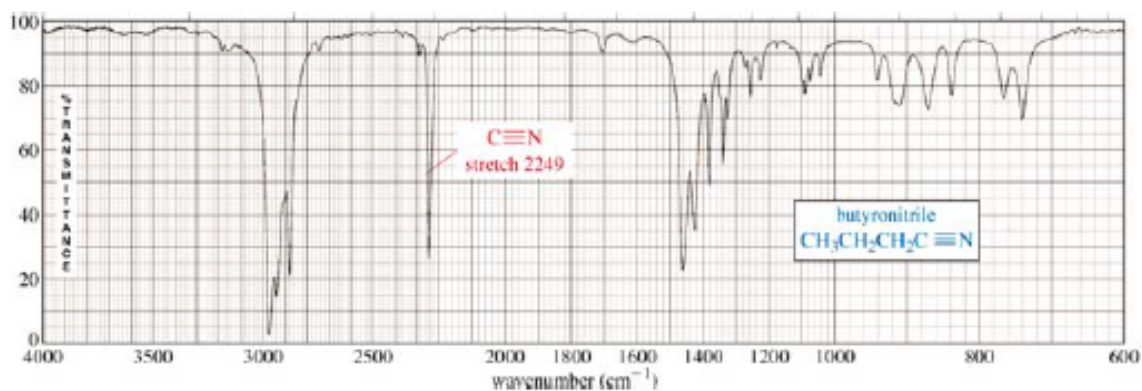
### IR spectrum of 1-Hexene



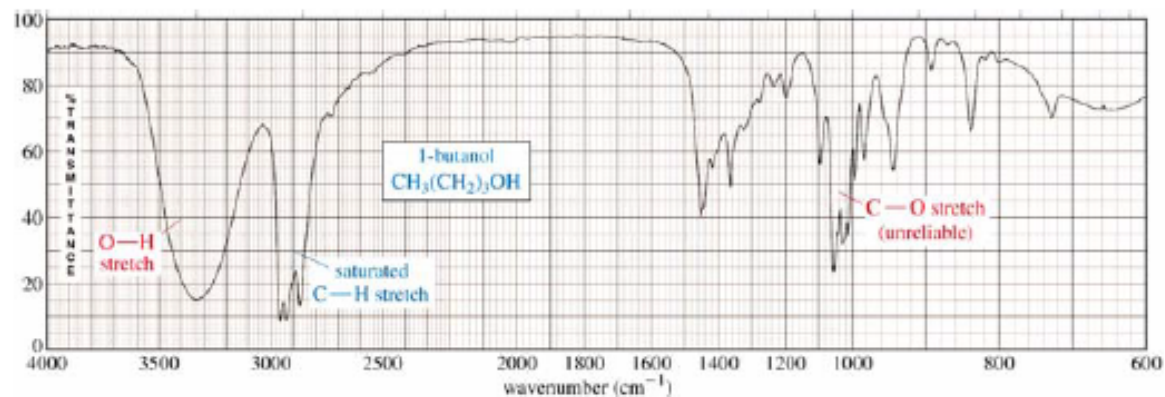
## IR spectrum of 1-Octyne and 4-Octyne



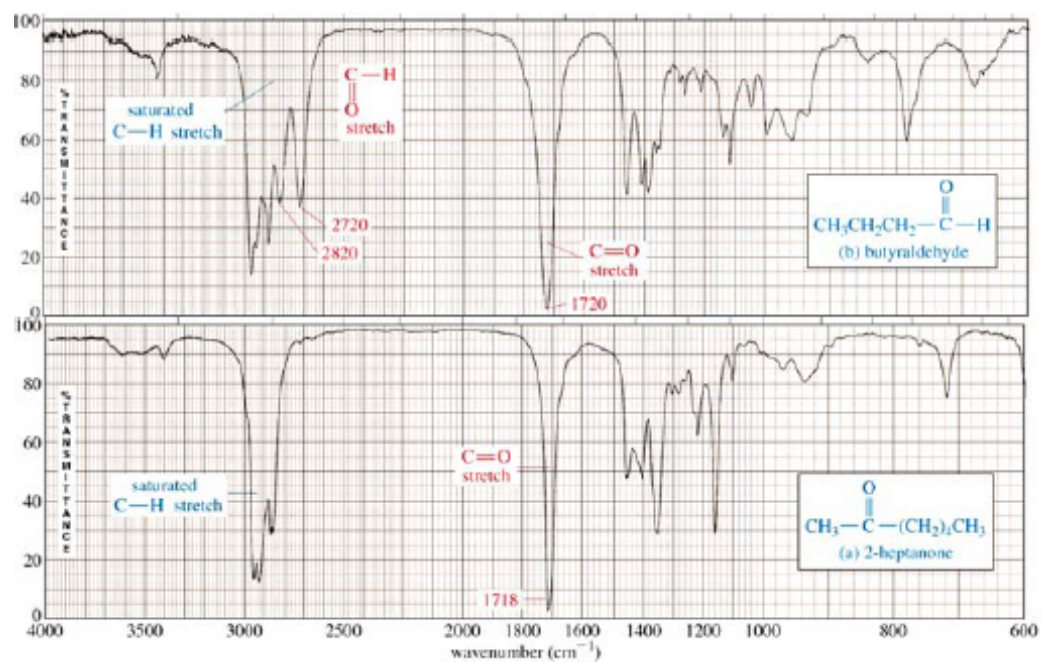
## IR spectrum of Butyronitrile



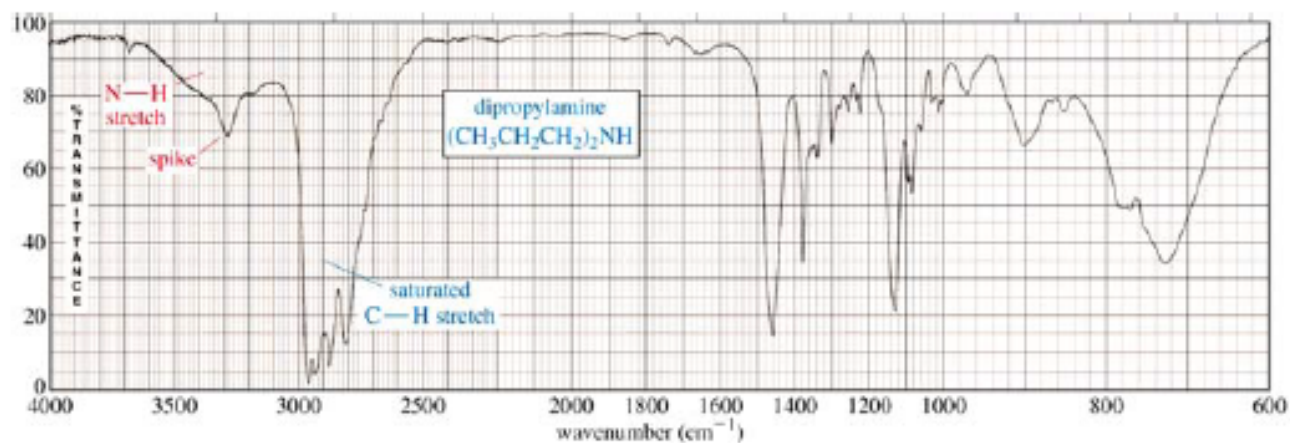
## IR spectrum of 1-Butanol



## IR spectrum of 1-Butanal and 2-Heptanone

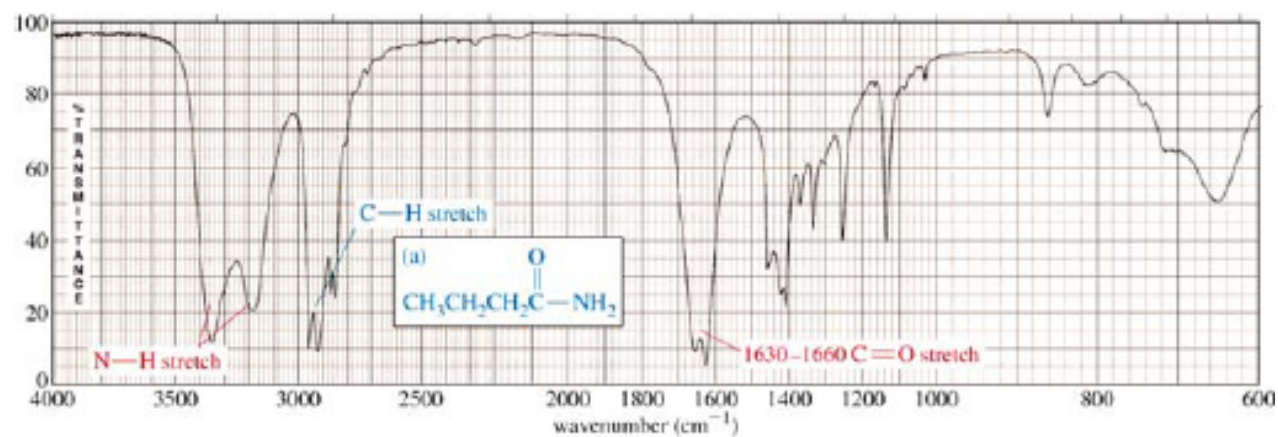


### IR spectrum of n-Hexanoic acid





### IR spectrum of 1-Butanamide



### IR spectrum of 3-Bromoaniline

