Infra Red Spectroscopy

FTIR

Infrared radiation was discovered in 1800 by astronomer Sir **Frederick William Herschel,** who was a German-born British astronomer and composer of music.

Infrared spectroscopy

Infrared Spectroscopy
IR Spectroscopy or
Vibrational Spectroscopy

is the measurement of the interaction of infrared radiation with absorption, emission or reflection.

It is used in characterization and identification of a chemical substances or functional groups in solid, liquid, or gaseous forms.

The method or technique of infrared spectroscopy is conducted with an instrument called an **infrared spectrometer** (or spectrophotometer) which produces an **infrared spectrum**.

The units of frequency used in IR spectra are reciprocal centimeters , sometimes called wave numbers, with the symbol cm^{-1}

A common laboratory instrument that uses this technique is a Fourier transform infrared (FTIR) spectrometer.

The infrared portion of the electromagnetic spectrum is usually divided into three regions;

1. Near IR: approximately 14,000–4,000 cm^{-1} (0.7–2.5 μm wavelength)
2. Mid IR: approximately 4,000–400 cm^{-1} (2.5–25 μm)

It is convenient to split the MID IR spectrum into two approximate regions:
4000-1000 cm^{-1} known as the ***functional group region***, and
< 1000 cm^{-1} known as the ***fingerprint region***

3. Far IR: approximately 400–10 cm^{-1} (25–1,000 μm)

The higher-energy near-IR, can excite a combination modes of molecular vibrations.

The mid-infrared is generally used to study the fundamental vibrations and associated rotational–vibrational structure.

The far-infrared has low energy and may be used for rotational spectroscopy and low frequency vibrations.

The energy levels can be rated in the following order:
Electronic (UV-Visible) > vibrational (Infrared)> rotational (IR).

Question:
The IR spectra of a molecule is sometimes called as Molecular Finger Print. Why?

Finger Print Region

The region between 400 cm^{-1} and 1400 cm^{-1} in an IR spectrum is known as the fingerprint region.

The IR spectra of a molecule in this region is unique just like Human Finger Print. Therefore, can be used to distinguish between compounds.

An IR spectra of a molecule is unique. Thus it is used in identification of a new compound.

No two different compounds can have IR spectra identical.

Therefore, It is called as the Molecular Finger Print.

A criterion for IR absorption is a net change in dipole moment in a molecule.

The dipole moment is determined by the magnitude of the charge difference and the distance between the two centers of charge. As the molecule vibrates, there is a fluctuation in its dipole moment; this causes a field that interacts with the electric field associated with radiation.

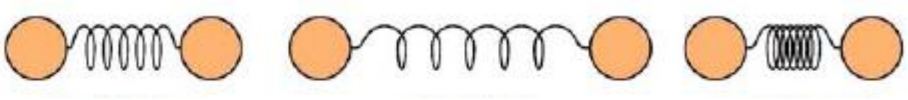
Molecules such as CO_2, HCl, HBr, H_2O have a changing dipole moment when they undergo rotational and vibrational motions, as a result, they can absorb IR radiation and produce IR spectra.

Molecules such as O_2, N_2, Br_2, do not have a changing dipole moment when they undergo rotational and vibrational motions, as a result, they cannot absorb IR radiation and do not produce IR signals.

Diatomic Molecular Vibration

The absorption of IR radiation by a molecule can be likened to two atoms attached to each other by a mass less spring.

Rigid rotor and **Harmonic oscillator** models.



Equilibrium **Stretched** **Compressed**

Polyatomic Molecular Vibration

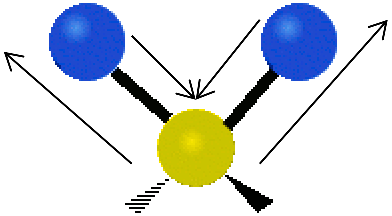
The bond of a molecule experiences various types of vibrations and rotations. This causes the atom not to be stationary and to fluctuate continuously.

Types of Vibrational Modes

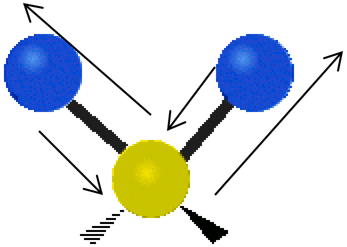
1. Stretching Mode and
2. Bending Modes.

Stretching Vibration: When there is a continuous change in the interatomic distance along the axis of the bond between two atoms, this process is known as a stretching vibration.

a. **Symmetrical Stretching:**
   Simultaneous elongation or compression in bond length.



b. **Asymmetrical Stretching:**
   Alternate elongation and compression in bond length.

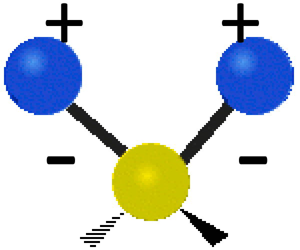


Bending Vibration: (AB_2) Triatomic molecule

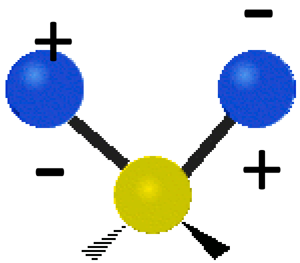
A change in the angle occurring between two bonds is known as a bending vibration.

Types of Bending Modes: Four bending vibrations exist.

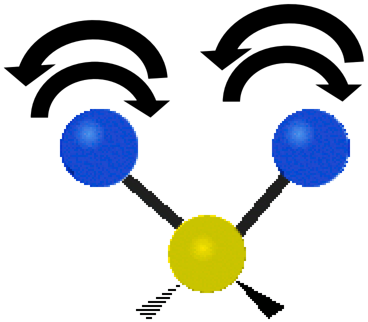
a. **Wagging** (simultaneous up and down) (Out of the Plane)



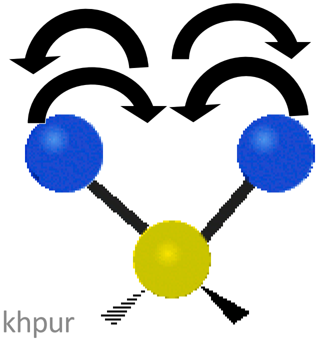
b. **Twisting** (Alternate up and down) (Out of the Plane)



c. **Rocking** (Simultaneously one side movement to & fro) (In the Plane)



d. **Scissoring** (Opposite side movement) (In the Plane)



Number of Vibrational Modes

1. Non Linear Molecules: Degrees of Freedom = 3N – 6
2. Linear Molecules: Degree of Freedom = 3N – 5

Question: Determine various vibrational modes in Water molecule.

Solution

H_2O molecule is a non-linear molecule due to the uneven distribution of the electron density.

The total degrees of freedom for H_2O = 3N-6 = (3×3)-6 = 9-6 = 3

The vibrational modes are illustrated below:

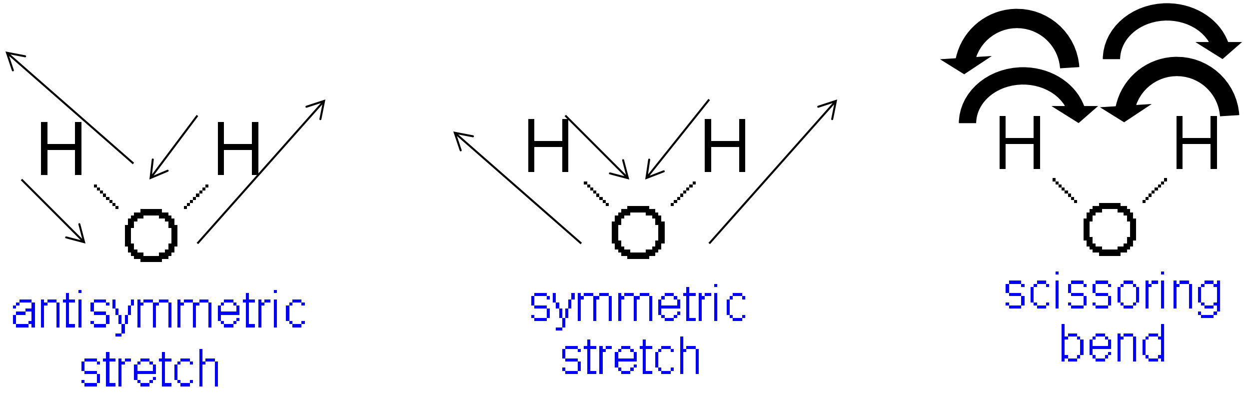


Diagram of Stretching and Bending Modes for H_2O.

Question: Determine the vibrational modes in CO_2 molecule.

Solution

CO_2 is a linear molecule and thus, Number of vibrational mode = (3N-5)

= 3(3)-5 = 9-5 = 4

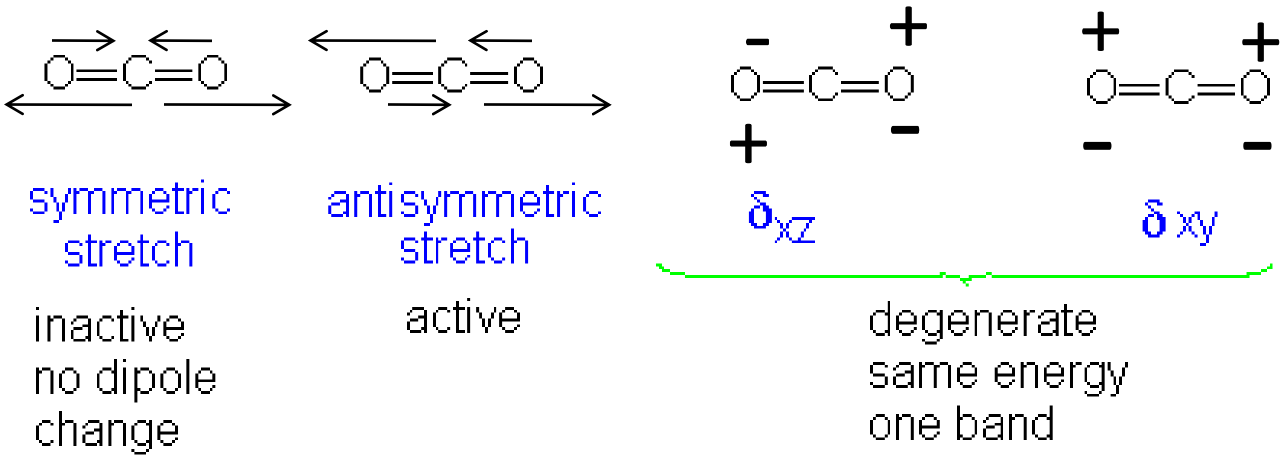
It has 4 modes of vibration.

a. CO_2 has 2 stretching modes, symmetric and asymmetric.

The CO_2 symmetric stretch is not IR active because there is no change in dipole moment because the net dipole moments are in opposite directions and as a result, they cancel each other.

In the asymmetric stretch, O atom moves away from the C atom and generates a net change in dipole moments and hence absorbs IR radiation at 2350 cm^{-1}.

b. And 2 bending modes with degenerate same energy.



Question

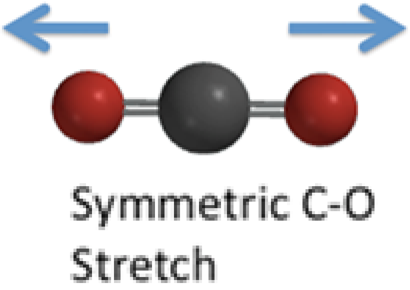
CO_2 is a linear molecule with resultant dipole moment zero but an IR active. Show how?

Explanation

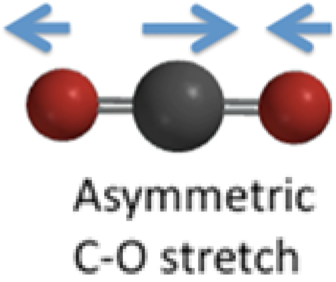
Since **carbon dioxide** is linear,

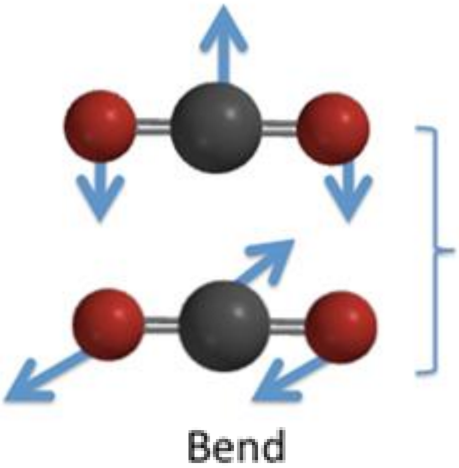
it has 3n−5= 3×3-5 = 4 vibrations.

a. The symmetric stretch **does** not result in a change (of the initially zero dipole moment), so it is **IR Inactive**
b. The asymmetric stretch **causes** a change in dipole moment so it is **IR Active**
c. The bend also results in a change in dipole moment so it is also **IR Active**



IR Inactive





IR Active

Selection Rules of IR

In order for vibrational transitions to occur, they are normally governed by some rules referred to as selection rules.

An interaction must occur between the oscillating field of the electromagnetic radiation and the vibrational molecule.
There must be some change in dipole moment.
This can be expressed mathematically as

$$\Delta\mu = +ve \quad \text{or} \quad \Delta\mu \neq 0$$

The selection rule for a rotational transition is, $\Delta J = \pm 1$
$\Delta J = +1$ Absorption
$\Delta J = -1$ Emission
J is rotational level.
Molecules such as HCl and H_2O will show vibrational-rotational spectra due to change in dipole moment while H_2, Cl_2 will not.

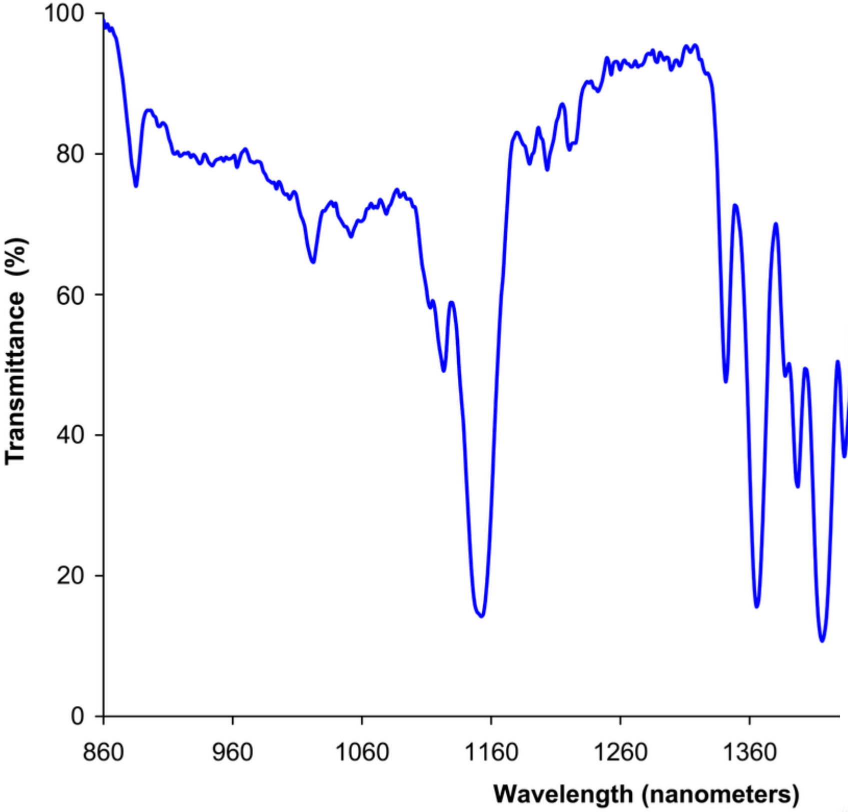
Advantages of IR

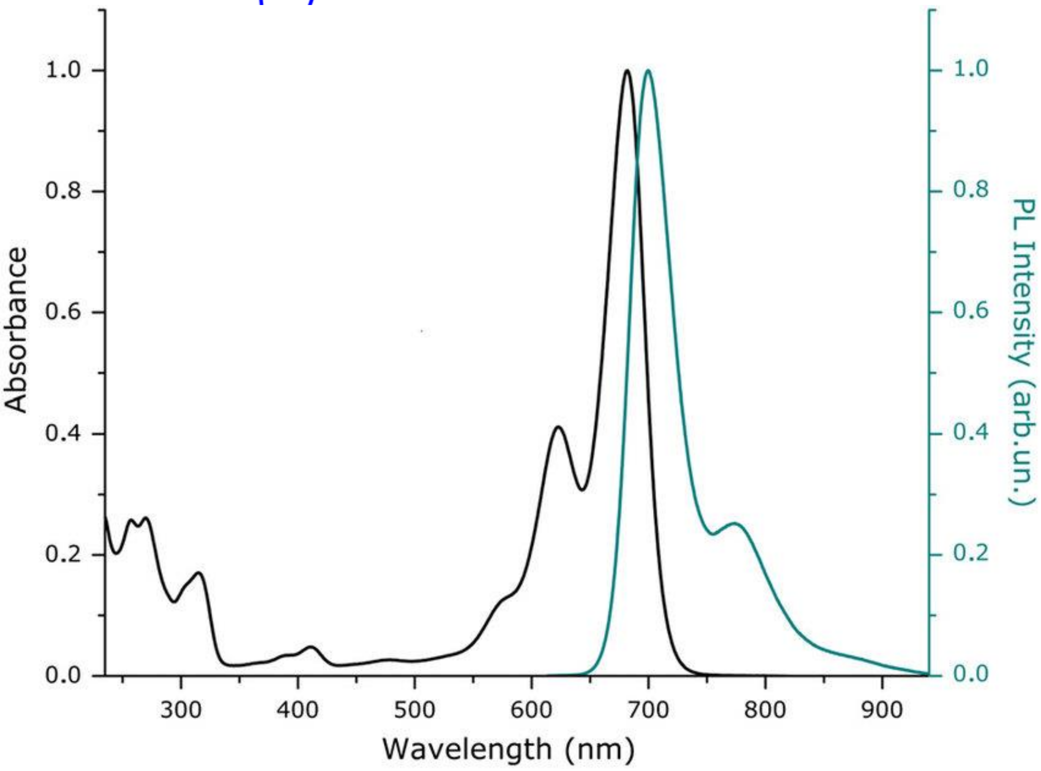
1. High Scan Speed
2. High Resolution
3. High Sensitivity
4. Wide Range of Application
5. Large Amount of Information
6. Non-Destructive

Disadvantages of IR

1. **Sample Constraint:** Infrared spectroscopy is not applicable to the sample that contains water since this solvent strongly absorb IR light.
2. **Spectrum Complication**: The IR spectrum is very complicated and the interpretation depends on lots of experience.
3. **Quantification**: Infrared spectroscopy works well for the qualitative analysis of a large variety of samples, but quantitative analysis may be limited under certain conditions such as very high and low concentrations.

Pattern of Spectra with respect to Transmittance and Absorbance of Radiation





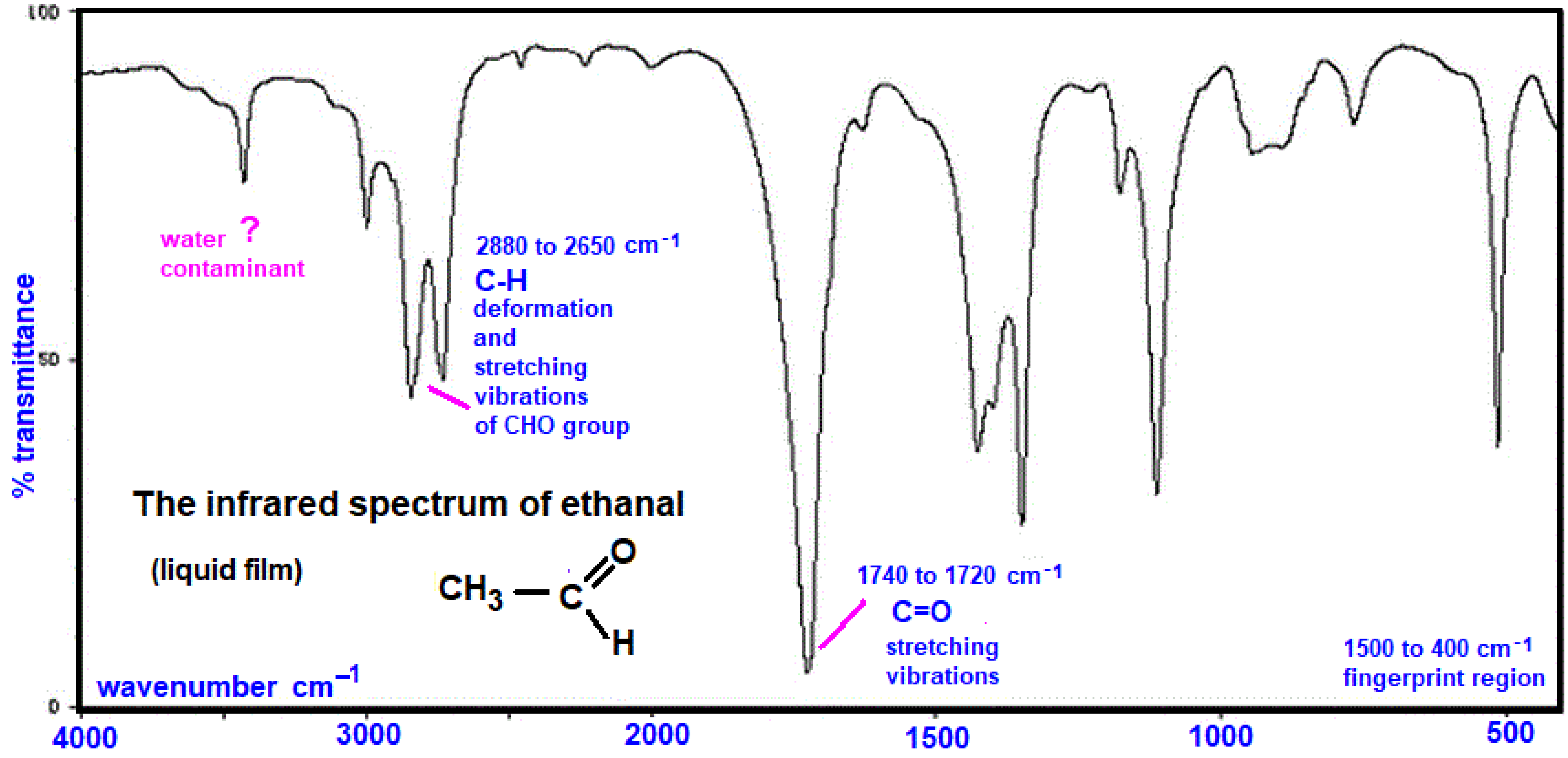
The IR spectra are generally expressed as Transmittance Vs wave number.

IR frequencies for various functional groups

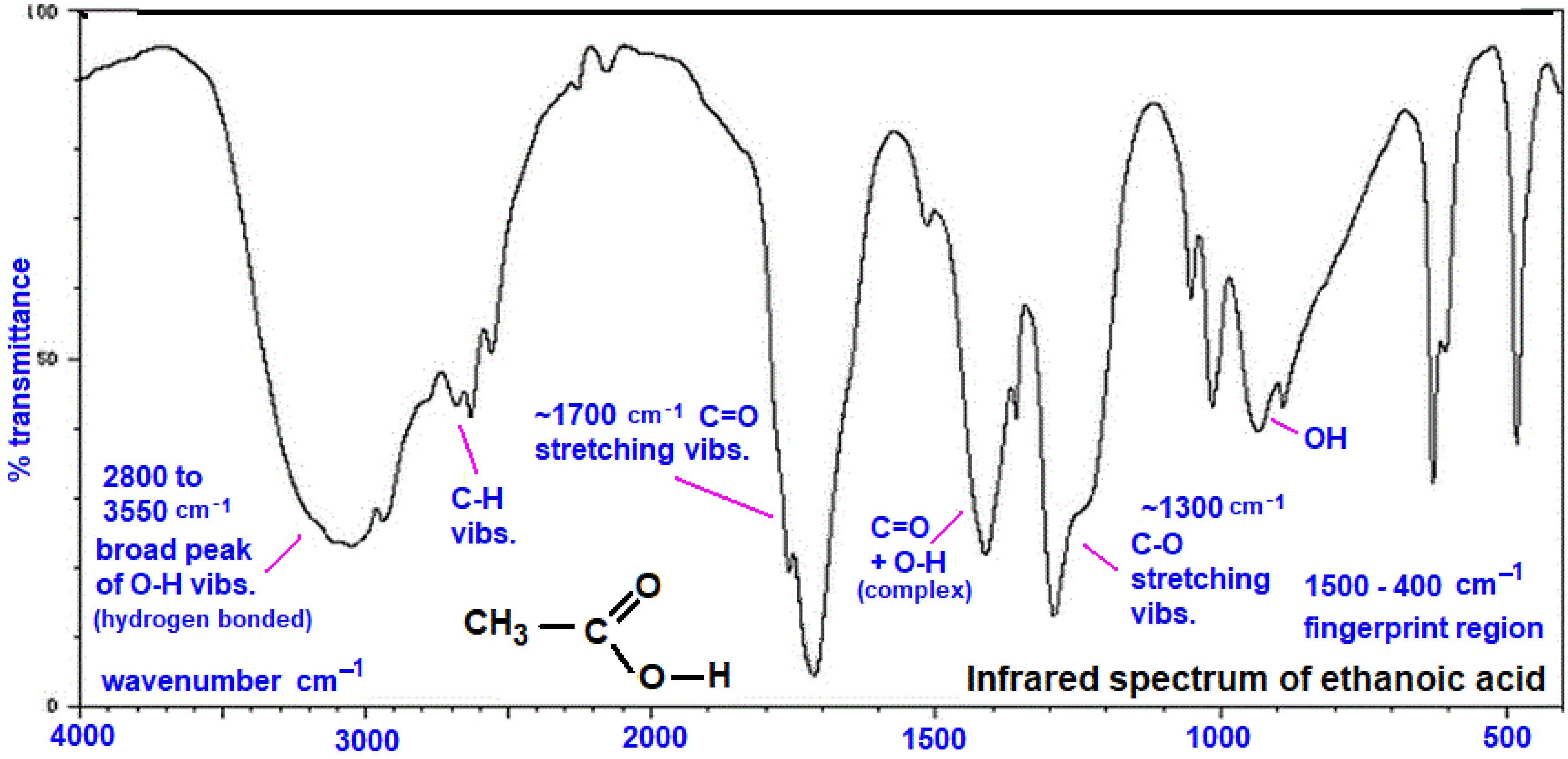
FunctionalGroup	Type	Frequencies cm-1
C-H	C-C-H	2850-3000
	C=C-H	3000-3250
	C≡C-H	3300
	aldehyde C-H	2750, 2850
N-H	Primary, secondary tertiary amine, amide	3500 - 3400
O-H	alcohols, phenols	3620-3580
	Hydrogen bond	3400-3200
	carboxylic acids	3500-2400
CN	nitriles	2280-2200
C≡C	acetylenes	2260-2100
C-O	Stretching	1300-1000
C=O	aldehydes	1740-1720
	ketones	1730-1710
	esters	1750-1735
	anhydrides	1820 -1750
	Carboxylic acid	1600 -1400
C=C	olefins	1680-1640

IR Spectra of Acetaldehyde CH_3CHO

1. The stretching vibrations of the C-H bond of the aldehyde group (CHO) occur at 2880 to 2650 cm^{-1}.
2. There is a very prominent C=O stretching vibration absorption at 1740 to 1720 cm^{-1}

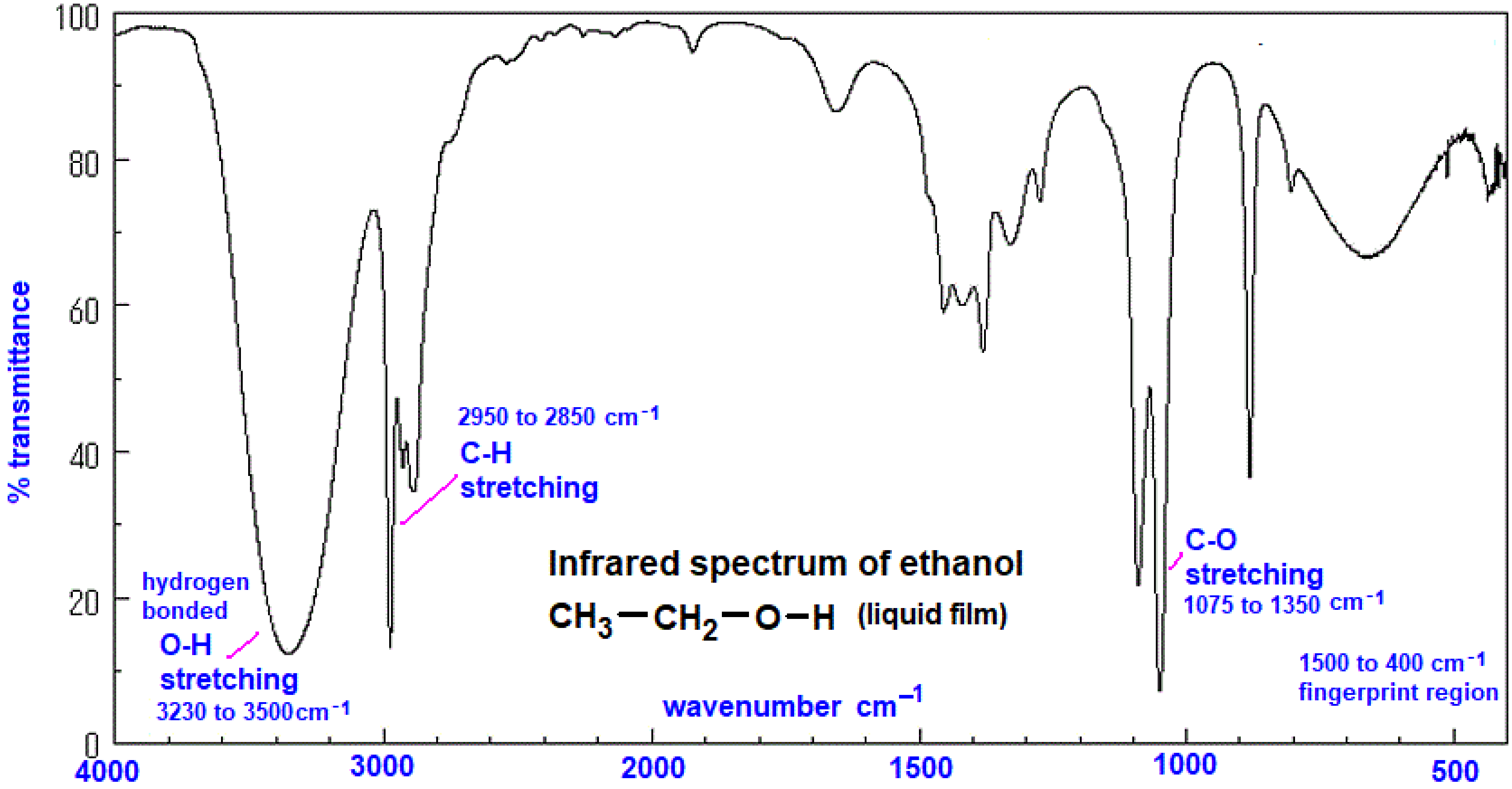


IR Spectra of Acetic Acid CH_3COOH

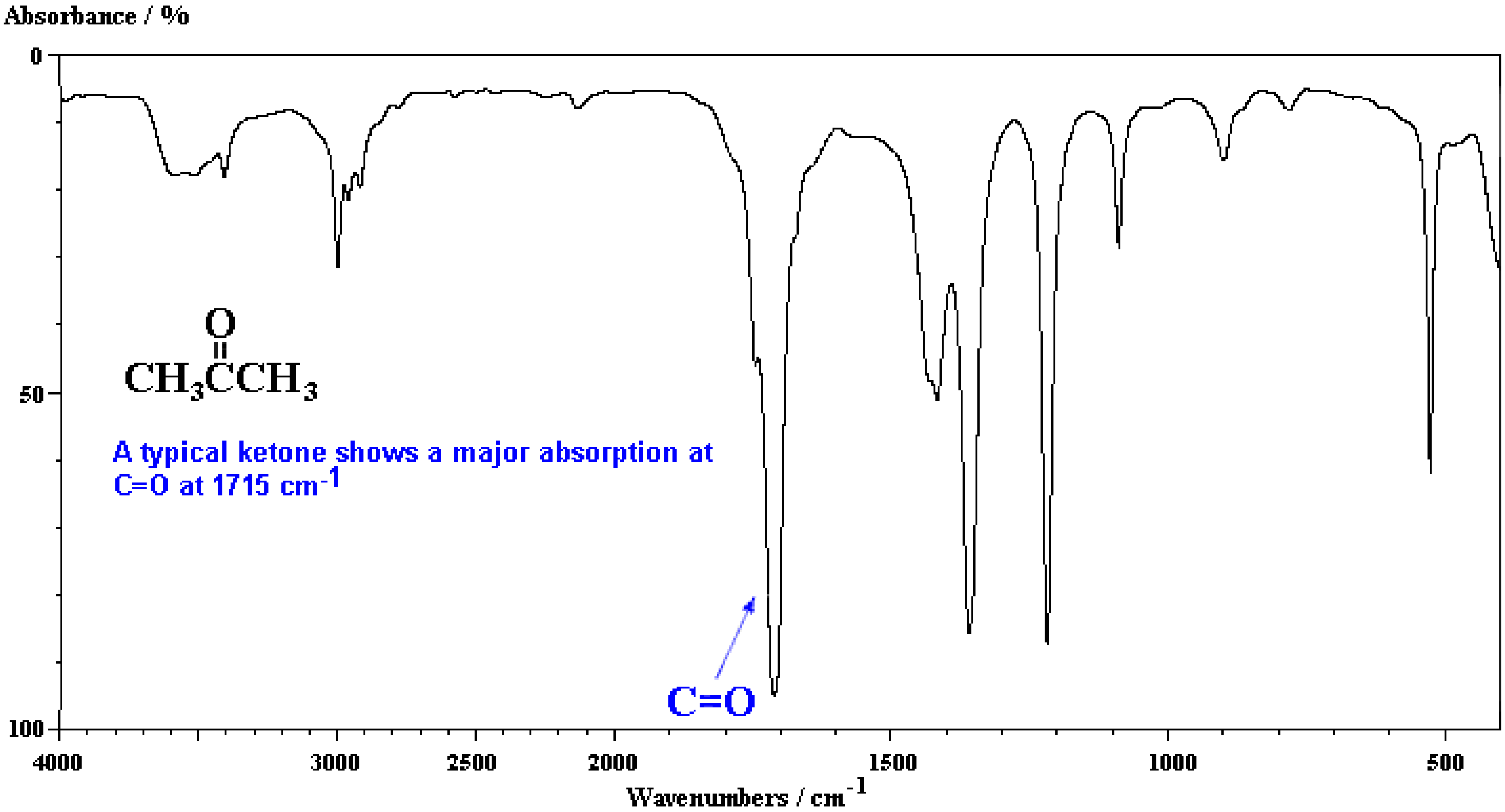


1. A very broad peak at 2800 to 3550 cm^{-1} for O-H stretching vibrations (H-Bond).
2. Typical C-H vibrations occur at ~2800 cm^{-1}.
3. A sharp and strong absorption ~1700 cm^{-1} is for C=O stretching.
4. Peaking at ~1300 cm-1 are the C-O stretching vibrations of the C-O bond.

IR Spectra of Ethyl Alcohol C_2H_5OH



IR spectra of Acetone CH_3COCH_3



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

A typical ketone shows a major absorption at C=O at 1715 cm^{-1}

Q. One of the isomers of the organic compound with molecular formula C_2H_6O produce IR spectra at 3500, 2900, 1200 cm^{-1} & forms ester with a carboxylic acid and other isomer gives IR spectra at 1200, 2900 cm^{-1}. Identify the compounds.

Solution

1. a. IR signal at 3500 cm^{-1} corresponds to OH group (3620-3580 cm^{-1})
   b. IR signal at 2900 cm^{-1} corresponds to C-H stretching (2850-3000 cm^{-1})
   c. IR signal at 1200 cm^{-1} corresponds to C-O stretching (1300-1000 cm^{-1})

   The compound may be CH_3CH_2OH, Ethyl Alcohol.

   $CH_3COOH + C_2H_5OH \rightarrow CH_3COOC_2H_5 + H_2O$

   Acetic Acid Ethyl Alcohol Ethyl Acetate (Ester)

   Thus the 1st Isomer is Ethyl Alcohol (CH_3-CH_2-O-H)

2. a. IR signal at 2900 cm^{-1} corresponds to C-H stretching (2850-3000 cm^{-1})
   b. IR signal at 1200 cm^{-1} corresponds to C-O stretching (1300-1000 cm^{-1})

   Thus the 2nd compound will be an ether i.e. Dimethyl Ether (CH_3-O-CH_3)

Application of IR Spectroscopy

a) Identification of different functional group.

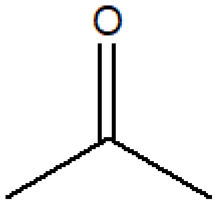
b) Distinction between intermolecular and intra-molecular hydrogen bonding.

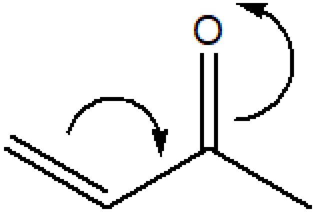
c) Identification of purity of the compound, if compound is impure then additional peaks are observed in the IR spectrum.

d) Study of chemical reaction:

Factor affecting vibrational frequency

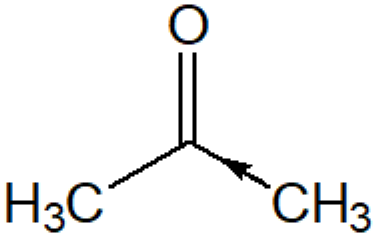
a) Conjugation: Conjugation decreases signal frequency.





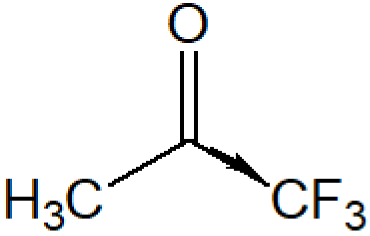
C=O (s) = 1720 cm^{-1} C=O (s) = 1680 cm^{-1}

b) Inductive effect: +I effect causes lowering in frequency and –I effect increases the IR frequency



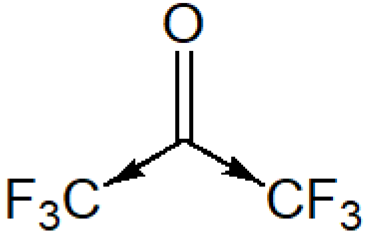
1720 cm^{-1}

+I effect



1760 cm^{-1}

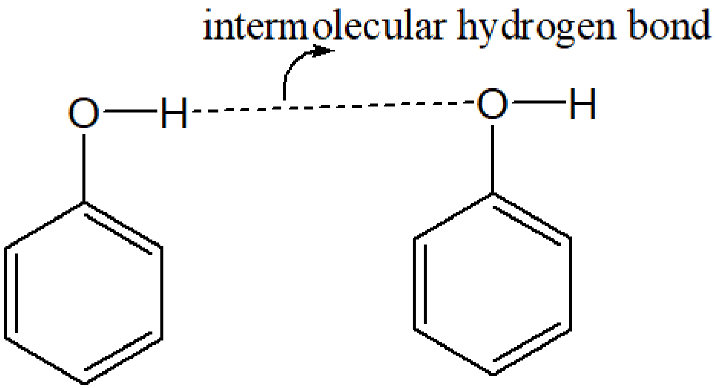
-I effect



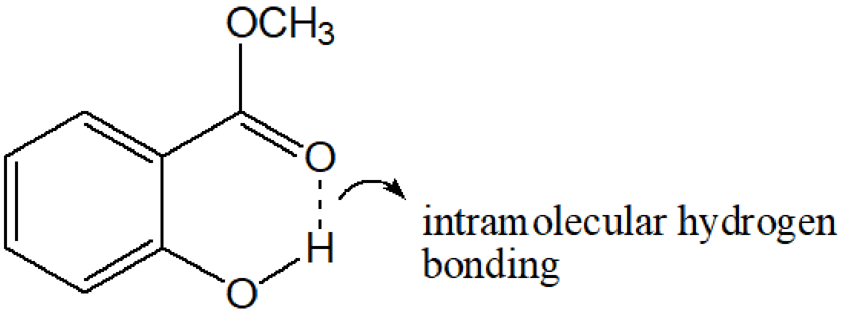
1790 cm^{-1}

-I effect

c) Hydrogen bonding: Intermolecular H-bond shows higher frequency



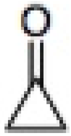
O-H frequency = 3400-3300cm^{-1}



O-H frequency centered at 3200 cm^{-1}

d) Ring strain: As the size of the ring increases, frequency of C=O decreases.

Ring Size of Ketone	**cm^{-1}**
Cyclopropanone	1800
Cyclobutanone	1775
Cyclopentanone	1751
Cyclohexanone	1715
Cycloheptanone	1702

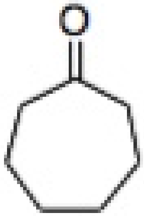


cyclopropanone

1800 cm^{-1}

cyclopentanone

1751 cm^{-1}



cycloheptanone

1702 cm^{-1}

Questions

Q.1. Explain the principle of IR spectroscopy. For XY_2 bent molecule show various types of stretching and bending Vibrations in IR spectroscopy.

Q.2. Discuss the significance of Finger print region.

Q.3. What is Beer-Lambert law in UV-Visible absorption spectroscopy?

Q.4. A compound having concentration 10^{-3} g/L resulted absorbance value 0.20 at λ_{max} 510 nm using 1.0 cm cell. Calculate its absorptivity and molar absorptivity values. Molecular weight of compound is 400.

Q.5. How can ultra-violet spectral data be useful to distinguish the following compounds? Give reasons.

(i) Ethyl benzene and styrene.

(ii) $CH_2=CH-CH_2-CH=CH_2$ and $CH_2=CH-CH=CH-CH_3$.

Q.6. State the selection rule for IR and Raman spectroscopy.

Q.7. Discuss the quantum theory of Raman spectroscopy and how the Stokes and anti Stokes lines appear in the Raman Spectroscopy?

Q.8. How does Raman differ from IR spectroscopy?

Thank You

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