

UNIT II

MOLECULAR SPECTROSCOPY

Molecular absorption spectrometry – Measurement of Transmittance and Absorbance – Beer's law – Instrumentation - Applications -Theory of fluorescence and Phosphorescence –Instrumentation – Applications – Theory of Infrared absorption spectrometry – IR instrumentation - Applications – Theory of Raman spectroscopy – Instrumentation – applications.

INTRODUCTION

Spectroscopy is one of the most powerful tool used to derive information about atomic and molecular structure. Spectroscopy is the study of the interaction between matter and electromagnetic radiation. It involves the study of radiation emitted, absorbed or scattered by the matter under study. It provides valuable information regarding chemical structure such as functional groups, unsaturation, bond strength, molecular structure such as molecular symmetry, bond distances, bond angles etc.

ORIGIN OF SPECTRA

Spectrum can originate from atoms or molecules due to absorption or emission of radiation.

(a) Atomic spectra

Atomic spectrum is obtained when atoms interact with electromagnetic radiation. During the interaction, the atoms absorb radiation and get excited from ground state electronic energy to higher energy level. Some salient features of atomic spectra are

1. Atomic spectra are generally very sharp. Hence it is also known as **line spectrum**.
2. Spectral lines are regularly spaced.
3. The wavelengths of light emitted are the characteristic of the element, so unique that it can be considered as "atomic fingerprint".

Typical example of atomic spectra is hydrogen spectra. Hydrogen spectrum consists of number of lines.

(b) Molecular spectra

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Molecular spectrum is obtained when molecules interact with electromagnetic radiations. Unlike atoms, molecules have additional energy levels. So molecular spectra is quite complex when compared to atomic spectra. Absorption of radiation will result in change in rotational, vibrational and electronic levels. These three transitions occur simultaneously which produces a band spectrum and not a line spectrum.

Infrared spectra, uv-visible spectra are some examples of molecular spectra.

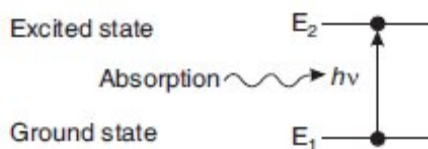
Atomic spectra and Molecular spectra

S.No.	Atomic spectra	Molecular spectra
1.	Atoms interact with electromagnetic radiation.	Molecules interact with electromagnetic radiation.
2.	Line spectra are observed (simple).	Broad (band) spectra are observed (complex).
3.	Due to electronic transition only.	Due to vibrational, rotational and electronic transitions.
4.	Tells about the nature (characteristic) of element.	Tells about the nature of bonds, functional groups etc.
5.	Example: Spectra of hydrogen.	Example: uv-visible spectra of compounds.

Absorption spectra

When electromagnetic radiation is passed through a medium, certain frequencies are *absorbed*. Due to this an atom or a molecule from a lower energy level is promoted to a higher energy level. The spectrum, thus obtained due to absorption of radiation is known as **absorption spectra**. The measurement of decrease in intensity (based on Lambert-Beer's law) of the incident radiation is the basis for absorption spectroscopy.

Since the energy levels are quantized the energy of the photon absorbed should be exactly equal to $E_2 - E_1$.

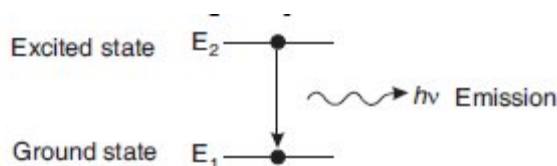


Example: uv-visible spectra

An absorption spectrum is usually a plot of absorbance versus wavelength. Absorption spectra can be of two types: atomic absorption spectra and molecular absorption spectra.

Emission spectra

When a beam of radiation is allowed to pass through a molecule in ground state, the molecule absorbs energy and undergoes a transition from ground state to excited state. Molecule in the excited state is highly unstable and it returns back to ground state with emission of photon of energy " $h\nu$ ". This emitted radiation is plotted as a function of frequency or wavelength, and it is then called an **emission spectra**. Energy of the photon emitted will be exactly equal to $E_2 - E_1$.



Example: LASER, fluorescence, phosphorescence.

Each element emits specific radiation depending on the energy gap between the ground state and the excited state. Therefore, emission spectra can be used to identify the chemical species.

ENERGY LEVELS IN A MOLECULE

In atoms, energy levels are determined by motion of electrons. Molecules are formed when atoms combine chemically. Sum of the energy levels of involved atoms in molecules are lower than unbound atoms.

Molecules have different energy levels. They are

- (a) Translational energy (E_{trans}):** This energy is concerned with the translational motion of molecules along three axes. It is significant only in gases and to a lesser extent in liquids. In solids, molecules have fixed position, so generally solids are not associated with translational energy.
- (b) Rotational energy (E_{rot}):** This energy involves the spinning of molecules about the axes passing through centre of gravity.
- (c) Vibrational energy (E_{vib}):** This energy is associated with to and fro motion (vibrations) of the molecule. Examples of such vibrations are stretching and bending.

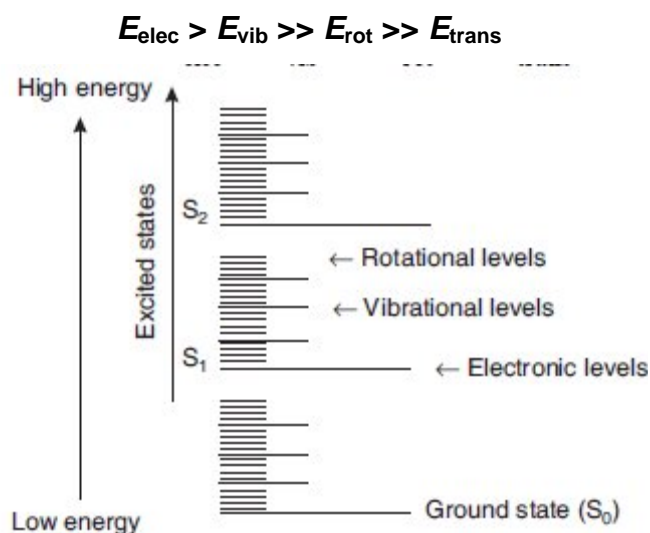
(d) Electronic energy (E_{elec}): Electronic energy deals with the transition of an electron from ground state to an excited state due to the absorption of energy.

Total energy (E_{tot}) of a molecule can be expressed as the sum of all these energies.

$$E_{\text{tot}} = E_{\text{elec}} + E_{\text{vib}} + E_{\text{rot}} + E_{\text{trans}}$$

Translational energy levels are so close together that they are essentially continuous (not quantized) and can be ignored.

Moreover,



The energies associated with electronic (E_{elec}), rotational (E_{rot}) and vibrational (E_{vib}) motions of a molecule are quantized. Therefore, the total (quantized) energy level of a molecule is

$$E_{\text{tot}} = E_{\text{elec}} + E_{\text{vib}} + E_{\text{rot}}$$

This equation is known as **Born Oppenheimer approximation**.

The energy requirements for various energy level changes and radiations which cause these transitions are given below.

<i>Transitions</i>	<i>Energy requirement</i>	<i>Radiation causing transition</i>
Rotational transitions	$\sim 0.01\text{--}1 \text{ KJmol}^{-1}$	Microwave
Vibrational transitions	$\sim 1\text{--}100 \text{ KJmol}^{-1}$	Infrared
Electronic transitions	$\sim 100\text{--}10,000 \text{ KJmol}^{-1}$	Ultraviolet-visible

LAMBERT'S LAW

Lambert's law explains the relationship between absorption of light by molecules and thickness of the medium. Lambert's law can be stated as "When a beam of monochromatic radiation is allowed to pass through a homogeneous absorbing medium, the rate of decrease of intensity of radiation dI , with the thickness of absorbing medium dx is proportional to intensity of incident radiation, I ".

Mathematically,

Lambert's Law

$$\frac{-dI}{dx} = kI$$

(Where k = proportionality constant or absorption coefficient)

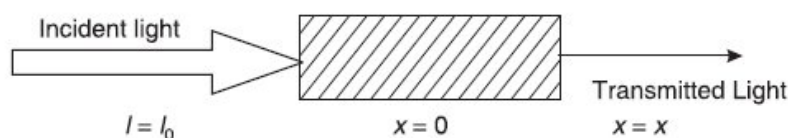


Fig. 3.3.

On integrating between limits, as shown below.

$$\int_{I=I_0}^I \frac{dI}{I} = - \int_{x=0}^{x=x} k dx$$

$$\ln \frac{I}{I_0} = -kx \quad \text{[or } I = I_0 e^{-kx}]$$

Where, k is a constant depending upon the wavelength and absorbing medium used.

$$2.303 \log \frac{I}{I_0} = kx \quad \text{[or } I = I_0 10^{-kx}]$$

$$\log \frac{I}{I_0} = \frac{k}{2.303} x$$

$$\frac{k}{2.303} = K, \text{ absorption coefficient. i.e., } I = I_0 10^{-Kx}$$

Absorption coefficient, K is defined as "the reciprocal of the thickness which is required to reduce the light to 1/10 th of its initial intensity".

Beer's Law or Lambert-Beer's Law

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Lambert-Beer's law gives the relationship between intensity of light with concentration and path length.

Lambert-Beer's law state that "When a beam of monochromatic radiation passes through a homogeneous solution of an absorbing substance, the rate of decrease of intensity of radiation dI , with the thickness of absorbing solution dx is proportional to the intensity of the incident radiation, I , as well as the concentration of the solution c ".

Mathematically,

$$-\frac{dI}{dx} = kcI \quad \text{where } k \text{ is a constant}$$

i.e.,
$$\frac{dI}{I} = -kc \, dx$$

Integrating between limits as shown below.

$$\int_{I_0}^I \frac{dI}{I} = -\int_0^x kc \, dx$$

$$\ln \frac{I}{I_0} = -kc x$$

$$2.303 \log \frac{I}{I_0} = -kc x$$

Or

$$\log \frac{I}{I_0} = -\frac{k}{2.303} c x$$

$$\log \frac{I_0}{I} = \frac{k}{2.303} c x$$

$$\log \frac{I_0}{I} = \epsilon c x \quad \text{or } A = \epsilon c x$$

Where ϵ is a new constant called molar absorptivity or molar extinction coefficient. Its value depends upon the units of concentration. The concentration is expressed in mol dm^{-3} and x in centimetres.

Where 'A' = $\log I_0 / I$, absorbance or optical density (O.D).

ϵ = molar absorptivity or molar extinction coefficient. ($\epsilon = k/2.303$).

c = Concentration of absorbing species.

x = length of absorbing medium (path length).

$$A = \epsilon c x$$

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When $c = 1 \text{ mole dm}^{-3}$ and $x = 1 \text{ cm}$, then, $\epsilon = A$.

Molar absorption coefficient is the absorbance of the solution when concentration is 1 mole dm^{-3} and path length is 1 cm .

Ratio I/I_0 is known as transmittance (T). $A = -\log T$.

S. No.	Absorbance (A)	Molar absorption coefficient (ϵ)
1.	It is an extensive property of the substance.	It is an intensive property of the substance.
2.	It varies with the change in concentration and thickness of the container.	It remains constant, i.e., independent of the concentration and thickness of the vessel.
3.	It is dimensionless quantity	It has unit $\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$.

Applications of Lambert-Beer's law

1. Determination of unknown concentration

By knowing the absorbance of a standard solution, the unknown concentration of another solution can be found out,

$$A_s = \epsilon C_s x \text{ (for standard)}$$

$$A_u = \epsilon C_u x \text{ (for unknown solution)}$$

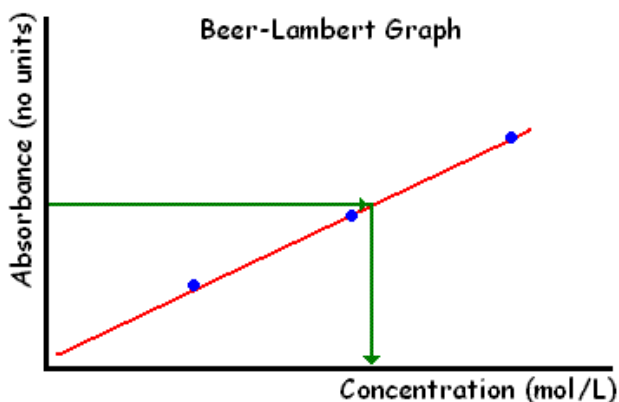
Where, A_s and A_u are the absorbance of standard and unknown solution respectively. C_s and C_u are the concentrations of the standard and unknown respectively. ϵ is the molar absorptivity of the solution.

$$\frac{A_s}{A_u} = \frac{\epsilon C_s x}{\epsilon C_u x}$$
$$C_u = \frac{A_u}{A_s} \times C_s$$

Experimental procedure:

A series of concentrations of standard solution (10, 20, 30, 40, 50 ppm) are prepared. Corresponding absorbance is measured using colorimeter or spectrophotometer. A blank solution with reagents alone is also prepared and the absorbance of this blank is set as zero. Absorbance increases linearly with concentration. After measuring absorbance of standard solutions, the absorbance of the unknown sample is measured. Concentration corresponding to that particular absorbance is the concentration of unknown sample.

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2. Identification of sample

ϵ , the molar extinction coefficient is a physical constant. Therefore, by knowing or comparing values, chemical identity of a sample can be found out.

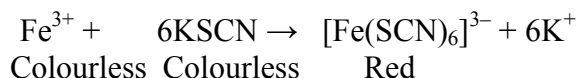
3. Determining rate of a reaction

The change in concentration can be followed by measuring absorbance (A) as a function of time. This is useful in chemical kinetics for determining rate of chemical reactions.

4. Colorimetric estimation of metal ions

Lambert-Beer's law is the principle of colorimetric estimation. Metals like Fe, Co, Ni, Cu etc. can be estimated even in low concentrations using colorimetry. Basic principle of colorimetry is that absorbance of a solution varies with concentration. Colour of the solution is measured using a spectrophotometer.

Ferric ion reacts with thiocyanate ion, forming a deep blood red coloured complex which can be estimated by colorimetry.



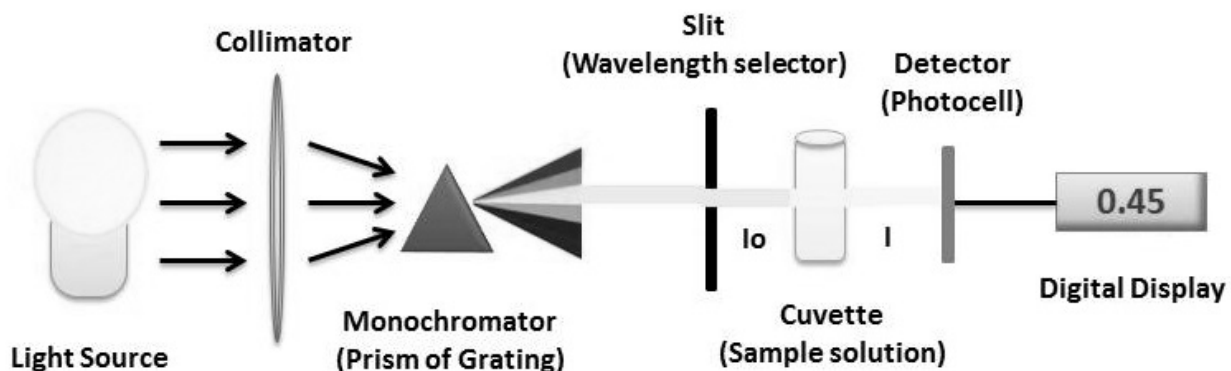
Limitations of Lambert-Beer's law

1. The law is obeyed when radiation is monochromatic.
2. It is applicable only for dilute solutions.
3. The temperature of the system should not vary significantly.
4. It is applicable only for true solutions (non colloidal solution)
5. Impurities present in solution can cause deviation.

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6. The law is not obeyed, if there is association or dissociation of sample in solution.

INSTRUMENTATION- BEERS LAW



Basic Instrumentation of a Spectrophotometer

FOR EXPLANATION OF PARTS (REFER UNIT I, REPETITIVE)

LUMINESCENCE

A molecule after absorbing a photon gets promoted to a higher energy level. Life time of a species in the higher energy excited level is less, so it comes back to the ground state by losing excess energy. One method of losing such energy is by luminescence.

Luminescence is defined as the emission of radiation by a molecule, or an atom, due to some cause other than temperature. Luminescence is of the following types.

1. **Photoluminescence:** Luminescence caused by light is known as photoluminescence. **Example:** fluorescence and phosphorescence.
2. **Chemiluminescence:** Luminescence resulting from chemical reactions is known as chemiluminescence.
3. **Cathodoluminescence:** Luminescence caused due to bombardment of electrons is known as cathodoluminescence.
4. **Electroluminescence:** Luminescence resulting from the application of electric field to matter is known as electroluminescence.

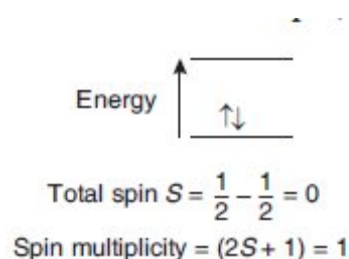
ELECTRONIC STATES

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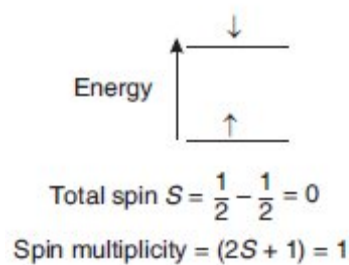
Before going into the details of the theory of luminescence, a brief knowledge about electronic states is essential. Electronic states of molecules can be grouped into two broad categories, **singlet states and triplet states**.

An electron present in orbital can have two spins (s_i) $+1/2$ or $-1/2$. The quantity $2S + 1$ is known as spin multiplicity of the state, where S is the total electronic spin, $S = \sum s_i$.

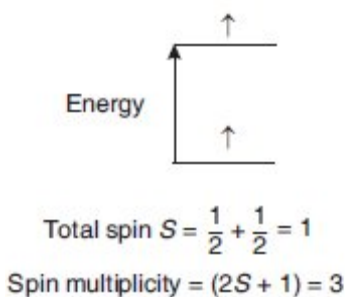
Pair of electrons occupying the same electronic ground state have opposite spins and is said to be in a **singlet spin state** ($S = 0$, $2S + 1 = 1$). In ground state, most of the molecules having even number of electrons have paired spin. Ground-state singlet and is designated by **S_0** .



Absorption of an ultraviolet or visible photon promotes electron from its lower energy state to an excited state. This phenomenon is called “excitation”. Electron can absorb energy can move to higher **singlet excited state** ($S = 0$, $2S + 1 = 1$). Singlet excited states are designated by **S_1 , S_2 and S_3** etc.



Electron can be promoted to the higher excited state by flipping (inversion) of spin. Such a species is referred to be in **excited triplet state** ($S = 1$, $2S + 1 = 3$). Triplet states are those in which one set of electron spin have become unpaired. Triplet excited states are designated by **T_1 , T_2 and T_3** etc.



A triplet state will always lie lower in energy than its corresponding singlet state according to Pauli's exclusion principle.

$$E_{S_1} > E_{T_1}, E_{S_2} > E_{T_2}, E_{S_3} > E_{T_3}$$

ORIGIN OF FLUORESCENCE AND PHOSPHORESCENCE

The excited states formed by the absorption of energy are not stable and electrons will not stay indefinitely in higher energy states. A molecule in the excited state, at some random moment will spontaneously return to the ground state by losing the excess

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energy. This process is called **decay, deactivation or relaxation**. Under some special conditions, the energy absorbed during the excitation process is released during the relaxation in the form of a photon (light). This type of relaxation is called **emission**.

Ways of relaxation

A molecule in the excited state can lose energy in several ways. The most common methods of relaxation are the following.

(a) By emission (radiative transition)

Excited molecule can lose the excess energy by emitting radiation. This is known as **radiative transition**. Most often, the energy of the radiation emitted will be slightly lower than the absorbed energy. **Example:** Fluorescence and phosphorescence.

(b) Radiationless transition

A molecule in the excited state can lose its energy without emitting radiations. This is termed as radiationless transition. Some examples are

(i) Vibrational relaxation: In this case, a molecule in an excited vibrational energy level loses energy as it moves to a lowest vibrational energy level in the same electronic state. Vibrational relaxation is very rapid ($\sim 10^{-12}$ s or less). Usually, loss of energy happens due to collisions with other molecules. **Example:** $\nu = 3$ to $\nu = 0$ transition within an electronic state.

(ii) Internal conversion (IC): In this case, a molecule in the ground vibrational level of an excited electronic state passes directly into a high vibrational energy level of a lower energy electronic state of the same spin state (**Example:** $S_2; \nu = 0$ to $S_1; \nu = 3$). By a combination of internal conversions and vibrational relaxations, a molecule in an excited electronic state may return to the ground electronic state without emitting a photon. **Example:** Transition between a singlet excited state, S_2 and a singlet excited state, S_1 .

(iii) Intersystem crossing: This is a radiationless relaxation in which a molecule in the ground vibrational energy level of an excited electronic state passes into a high vibrational energy level of a lower energy electronic energy state with a different spin state. **Example:** Transition between a singlet excited state, $S_1(\nu = 0)$, and a triplet excited state, $T_1(\nu = 3)$.

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The **Jablonski diagram** is used to explain the electronic states of the molecule and their relative energies. In Jablonski diagram,

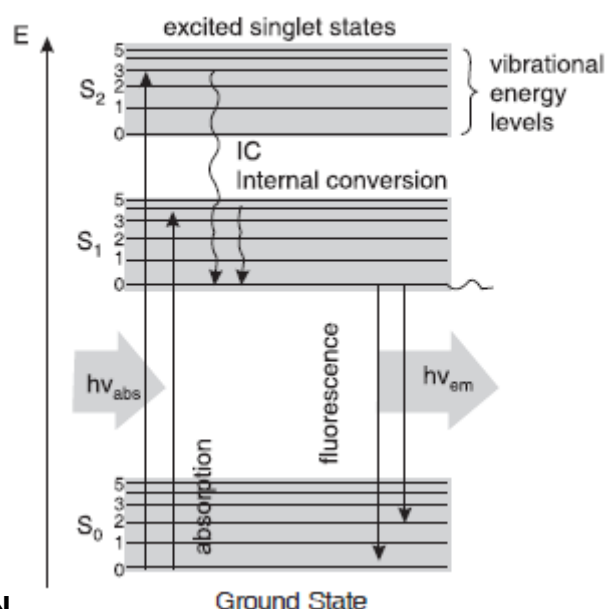
- Singlet electronic states are denoted by S_0 , S_1 , S_2 etc. and triplet electronic states as T_1 , T_2 , etc. A triplet state will always lie lower in energy than its corresponding singlet state.
- Vibrational levels associated with each state are denoted as $\nu = 0$, $\nu = 1$, $\nu = 2$ etc. in order of increasing energy.
- Radiative transitions are drawn as straight arrows (fluorescence and phosphorescence) and radiation-less transitions as wavy arrows (internal conversion and inter system crossing).

3.12.1 Fluorescence

Emission of a photon from a singlet excited state to a singlet ground state, or between any two energy levels with the same spin, is called **fluorescence**. Light re-emitted immediately stops as soon as the source is removed. Life time of fluorescence is 10^{-8} s or less. Substances which start re-emitting radiations under stimulating light are fluorescent substances.

Mechanism

An electron in the ground singlet state (S_0) absorbs energy and gets promoted to higher energy (excited) singlet states like S_1 , S_2 , S_3 etc. These excited states are of higher vibrational energy level. The electron then loses energy and comes to the lowest vibrational energy level (vibrational relaxation) in the lowest excited singlet state (S_1 , $\nu = 0$). Usually the energy is lost by “radiation less” mechanism. **Example:** collisions with other excited molecules or with solvents. This is known as **internal conversion**. Internal conversion is an intermolecular process of



molecule that passes to a lower electronic state without the emission of radiation. This is easily explained by **Jablonski diagram**.

The electron after reaching the lowest singlet excited level can lose the energy in the form of radiation and come to ground state. This process is called **fluorescence**.

To summarize, the process of fluorescence consist of

Absorption of photon → Excited singlet state (higher vibration level) → Excited singlet state (lowest vibration level) → Electronic ground state (higher vibration level) → Electronic ground state (lowest vibration level).

Characteristics of fluorescence

1. Re-emitted fluorescent light stops as soon as the incident radiation stops. Life time of fluorescence is 10^{-8} s or less.
2. Absorption of radiation happens at one wavelength followed by nearly immediate re-radiation usually at a different wavelength. Emitted radiation will be of higher wavelength or lower energy.
3. Fluorescence is a property shown by solids, liquids and gases. Gases show fluorescence only at low pressures.
4. Different substances show the phenomenon of fluorescence at different wavelengths of light. Thus, fluorspar shows fluorescence with blue light, chlorophyll with red light, uranium glass with green light etc.
5. Fluorescent light from solutions is usually polarized and degree of polarization depends on the concentration of the solution.

Types of fluorescence

(a) Resonance fluorescence

In some cases, the fluorescent light has the same frequency of the incident light. This phenomenon is known as resonance fluorescence.

When mercury vapour at low pressure is exposed to radiation of wavelength 253.7 nm, it gets excited. Later it returns to ground state emitting the radiation of same frequency it absorbed.

(b) Sensitized fluorescence

A substance which is non fluorescent may become fluorescent in presence other fluorescent substances. This phenomenon is known as sensitized fluorescence.

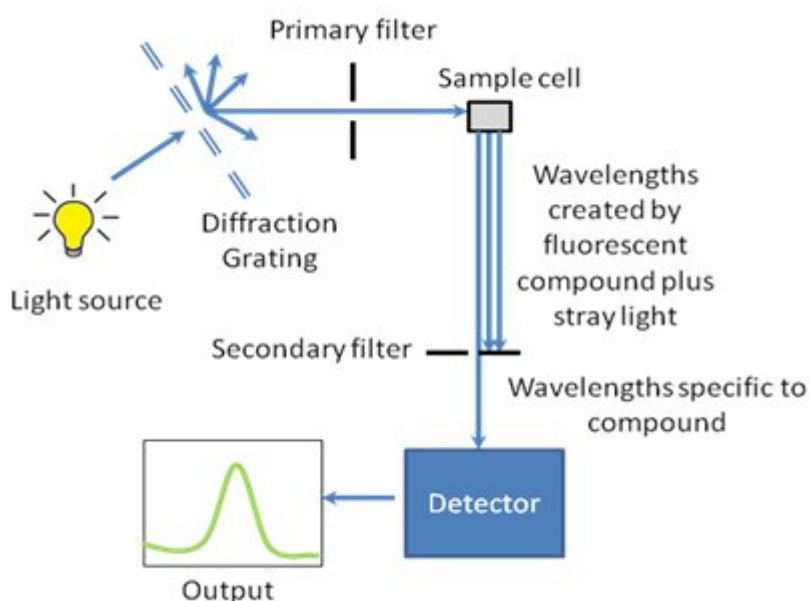
Thalium vapour do not absorb radiation at 2537 Å. In the presence of mercury vapours, a part of excitation energy is transferred to these atoms and they get excited and undergo fluorescence. Here mercury vapour absorbs energy from the incident light and its atom gets excited to higher energy levels. Thalium atoms undergo collisions with these mercury atoms and gets excited to higher energy levels. These atoms then return to ground state by emitting its own characteristic fluorescence.

Examples of fluorescent substances

1. Chlorophyll, the naturally green pigment in plants shows fluorescence.
2. Aniline is fluorescent while benzoic acid is not. Electron with drawing groups like -COOH can reduce/destroy fluorescence.

INSTRUMENTATION OF FLUORESCENCE SPECTROSCOPY

The block diagram of spectrofluorometer is given below



Source: Most widely used light source for a spectrofluorometer is a xenon (Xe) arc lamp. These lamps provide a relatively continuous light output from 250 to 700 nm. Deuterium lamps can also be used.

Excitation monochromator: Monochromators are used to disperse polychromatic or white light into the various colors or wavelengths. This dispersion can be accomplished using prisms or diffraction gratings. The monochromators in most spectrofluorometers use diffraction gratings rather than prisms.

Sample cell and sample preparation:

A proportion of the light from the primary filter is absorbed by the sample. After the sample gets excited, the fluorescent substance returns to the ground state, by emitting a longer wavelength of light in all directions. A part of this light passes through a secondary filter. Cuvettes made of quartz is usually used as sample cell.

Secondary filter

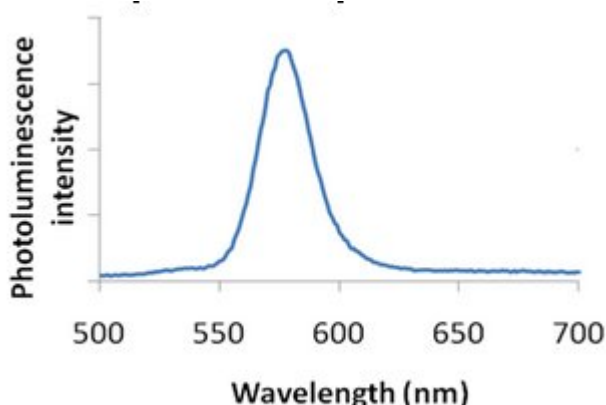
The secondary filter is placed at a 90° angle to the original light path to minimize the risk of transmitted or reflected incident light reaching the detector. Also this minimizes the amount of stray light, and results in a better signal-to-noise ratio. From the secondary filter, wavelengths specific to the sample are passed onto the detector.

Detector

Almost all fluorometers use photomultiplier tubes (PMTs) as detectors.

Output

The output is the form of a plot of intensity of emitted light as a function of wavelength as shown below.



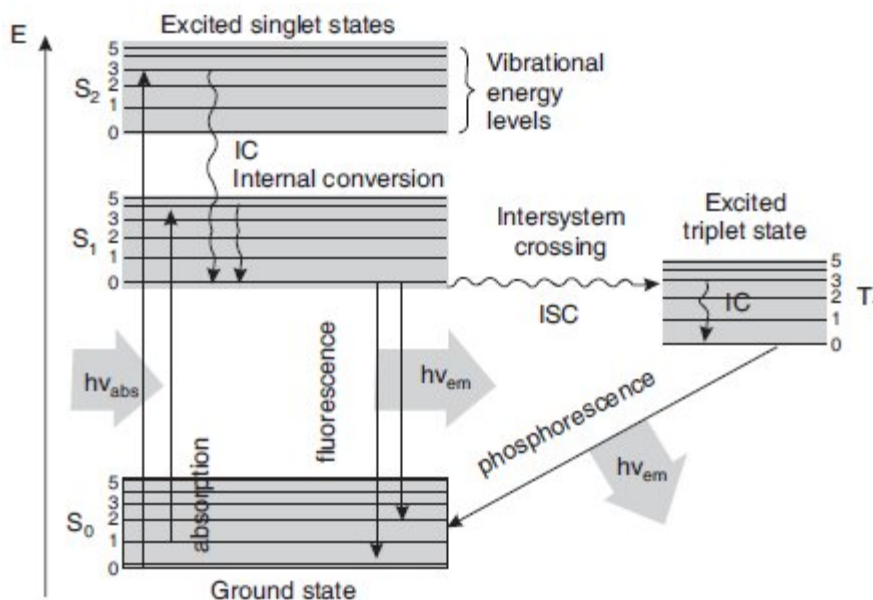
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PHOSPHORESCENCE

Emission between a triplet excited state and a singlet ground state, or between any two energy levels that differ in their respective spin states is called **phosphorescence**. As the average lifetime for phosphorescence ranges from 10^{-4} to 10^2 s, phosphorescence continues for some time after removing the excitation source.

Mechanism

An electron in the ground singlet state (S_0) absorbs energy and gets promoted to higher energy (excited) singlet states like S_1 , S_2 , S_3 etc. This electron may move to an excited triplet state which is slightly lower in energy. This is known as **intersystem crossing**. Intersystem crossing is a process where there is a crossover between electronic states of different multiplicity, *i.e.*, the spin of the excited electron is reversed. After crossing to the triplet state, deactivation occurs by internal conversion. On reaching the lowest triplet state, electron emits radiation and returns to the ground state. This is known as **phosphorescence**. The decay from excited triplet to ground singlet state is “**spin forbidden**” and hence is very slow (10^{-8} to 10^{-3} s).



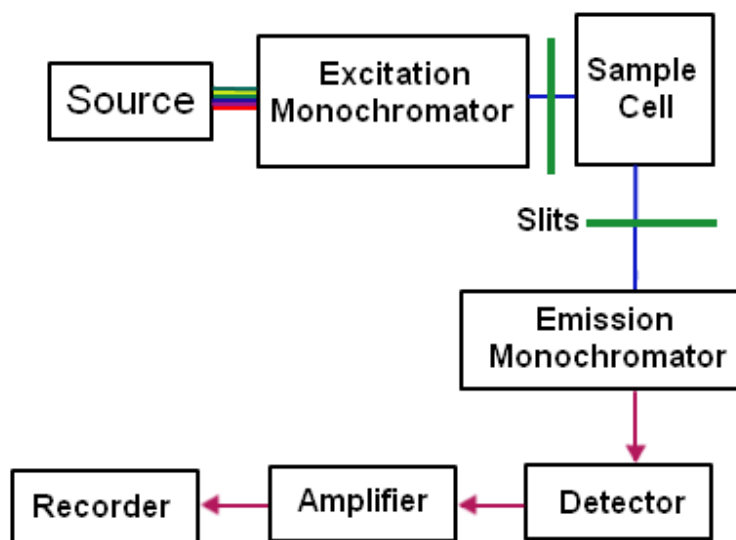
Characteristics of phosphorescence

1. Materials exhibiting phosphorescence emit radiation in 10^{-4} s or longer. It can be as long as few seconds. This is because the lifetime of the molecule in the triplet state is longer. Thus, the life time of phosphorescence is much longer than fluorescence.
2. Phosphorescence is usually caused by ultraviolet and violet parts of the spectrum.
3. Re-emitted light will be having longer wavelength than the incident light.
4. Phosphorescence is primarily shown by solids.
5. The magnetic and dielectric properties of the phosphorescent substances are different before and after emission.

Examples of phosphorescent substances

1. Zinc sulphide (ZnS), Sulphides of Calcium, Barium and Strontium (CaS, BaS, SrS).
2. Minerals ruby and emerald.

INSTRUMENTATION OF PHOSOPHORESCENCE SPECTROSCOPY



Instrumentation of phosphorescence spectroscopy is very similar to fluorescence spectroscopy with functions of components remaining the same which was mentioned in the previous chapter.

Factors influencing fluorescence and phosphorescence

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1. All molecules do not show the phenomenon fluorescence and phosphorescence. Only those molecule which **absorbs uv or visible radiation** will show these. In general, greater the absorbance of the molecule, greater will be its luminescence. So the molecules having conjugate double bonds show luminescence.
2. Substituents have a marked effect in fluorescence and phosphorescence. Generally, electron donating substituents like -NH_2 , -OH enhances fluorescence. On the other hand, electron withdrawing substituents like -COOH , -NO_2 decreases, or even destroy fluorescence.
3. pH of the solution also have an remarkable effect on fluorescence and phosphorescence. For example, aniline shows fluorescence while aniline in acid solution (anilinium ion) does not.
4. Temperature of the sample has a considerable effect on fluorescence. At higher temperature, molecules gets deactivated by collisions. Lower temperature gives a better fluorescence signal.
5. Dissolved oxygen causes destruction of phosphorescence. Oxygen is triplet in ground state. A molecule in excited state transfers energy to oxygen, rather than flipping and inverting spin. So we observe oxygen emission rather than phosphorescence. Oxygen should be totally excluded to be able to detect phosphorescence.

Applications of fluorescence and phosphorescence

Fluorescence

1. Uranium salts can be determined quantitatively by fluorescence. This is widely used in nuclear research.
2. The intensity and colour of fluorescence of many substances depend upon the pH of the solution, hence it is used as indicators. Fluorescent indicators can be used for different volumetric titrations. **Example** : Eosin, Fluorescein.
3. Fluorescence is used for analysis of
 - (i) Drug and dyes.
 - (ii) Medicine
 - (iii) Textile
 - (iv) Fuel and chemicals

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Phosphorescence

1. Phosphorescence is used to analyze water, air, drugs and chemical pollutants.
2. Phosphorescent materials are used in luminous clock dials.

Comparison of fluorescence and phosphorescence

S.No.	Fluorescence	Phosphorescence
1.	Fluorescence stops immediately as soon as the incident light is stopped.	Phosphorescence continues for longer time even if the incident light is stopped.
2.	Fluorescence has much shorter decay period (10^{-6} to 10^{-9} s).	Phosphorescence has much longer decay period (10^{-4} to 100 s).
3.	Fluorescence is the radiation emitted in a transition between states of same multiplicity (singlet to singlet).	Phosphorescence is the radiation emitted in a transition between states of different multiplicity (triplet to singlet)
4.	Fluorescence spectrum is a mirror image of absorption spectrum.	Phosphorescence spectrum is not a mirror image of absorption spectrum.
5.	Fluorescence is shown by solids, liquids and gases. Gases show fluorescence at low pressures.	Phosphorescence is shown mainly by solids.
6	Examples of fluorescent substances Aniline, Luminol etc.	Examples of phosphorescent substances: ZnS, CaS, BaS, etc.

INFRARED SPECTROSCOPY

Absorption of radiant energy in the infrared region by a molecule causes transitions between vibrational energy levels. Therefore this spectroscopy is also known as **vibrational spectroscopy**. Vibrational energy level change is accompanied by a large number of rotational energy changes. So it is also known as **vibrational-rotational spectroscopy**. The energy change between vibrational levels is of the order of 1 to 100 KJ mol⁻¹.

Infrared portion of electromagnetic spectrum is divided into three regions: the near-, mid- and far- infrared.

Far infrared	400–10 cm ⁻¹
Infrared (mid)	4000–400 cm ⁻¹
Near infrared	14000–4000 cm ⁻¹

Condition for a molecule to absorb infrared radiation

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All types of molecules cannot interact with infrared radiation. The essential condition for a molecule to absorb infrared radiation is given below.

“For a vibration to be IR active there should be a change in dipole moment of the molecule or the molecule should have permanent dipole moment”.

Molecule	Dipole moment	Infrared absorption
H_2, N_2, O_2	No dipole moment	No infrared absorption
CH_4, CO_2^*, H_2O	Have dipole moment	Absorb infrared

* CO_2 does not have a permanent dipole moment but its dipole moment changes during asymmetric stretching and bending.

Modes of Molecular Vibrations

A molecule is not rigid. Atoms in a molecule can be considered as balls of different masses connected by tiny weightless springs.



When a molecule absorbs infrared radiation, it results in vibrations. The two modes fundamental molecular vibrations known are

1. Stretching vibrations: In stretching vibrations, bond distance between two atoms increases or decreases but the bond angle remains constant. There are two types of stretching vibrations.

(a) Symmetric stretching: Atoms of the molecule move symmetrically with respect to the central atom.

(b) Asymmetric stretching: Atoms of the molecule move in the opposite direction with respect to central atom.

Stretching:



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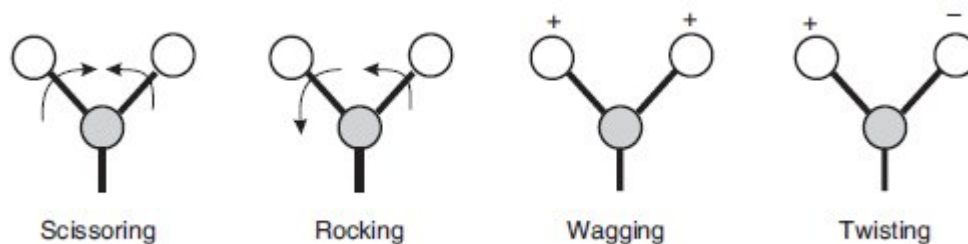
2. Bending vibrations: In bending vibrations, the bond length remains constant, but the bond angle varies. Energy required for bending is less than energy required for stretching vibration. Four types of bending vibration are known.

(a) Scissoring: The atoms move away and closer like the movement of scissors. This happens in a plane.

(b) Rocking: In this vibration, movement of atoms takes place in the same direction within a plane.

(c) Wagging: In this vibration, two atoms simultaneously move up and down the plane with respect to the central atom.

(d) Twisting: In this vibration, one atom moves up the plane and the other atom moves down the plane with respect to the central atom.

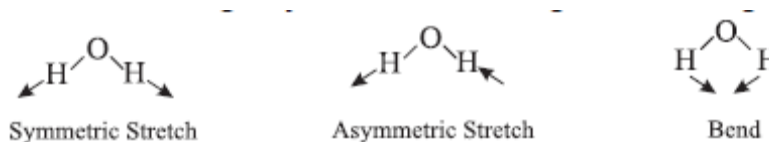


The number of fundamentals vibrational modes for a polyatomic molecule can be calculated as follows.

(a) For a **non-linear molecule** containing N atoms has **$(3N - 6)$** fundamental vibration modes.

H_2O triatomic, non linear. Therefore $(3N - 6) = (3 \times 3 - 6) = 3$ fundamental modes of vibration.

They are symmetric stretching, asymmetric stretching, and bending vibration.



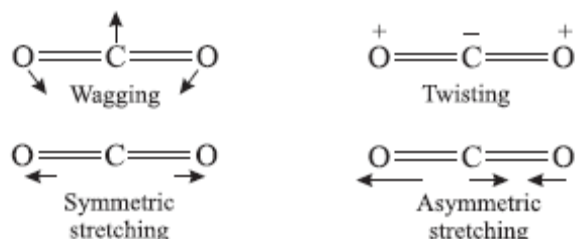
$\text{CH}_4 \rightarrow (3 \times 5 - 6) = 9$ fundamental vibration modes.

$\text{C}_6\text{H}_6 \rightarrow (3 \times 12 - 6) = 30$ fundamental vibration modes

(b) For a **linear molecule** containing N atoms has $(3N - 5)$ fundamental vibration modes.

CO₂ triatomic linear, Therefore $(3N - 5) = (3 \times 3 - 5) = 4$ fundamental modes of vibration.

They are symmetric stretching, asymmetric stretching, and in plane bending and out of plane bending.



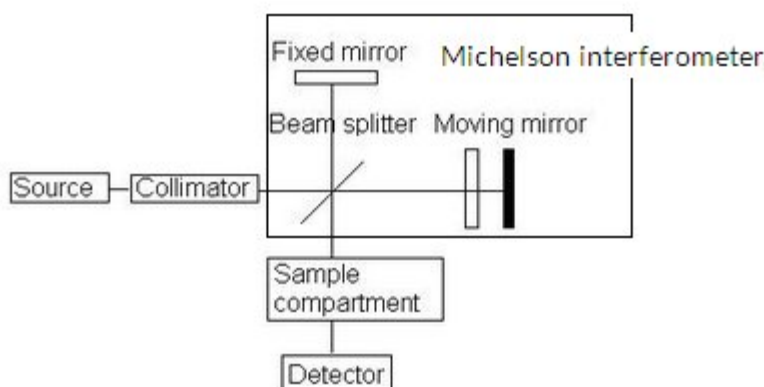
Of four normal modes of vibration of CO₂, only the symmetric stretching is not infrared active as there is no net change in dipole moment during stretching. The other three vibrations (asymmetric stretching, twisting and wagging) are all infrared active.

INSTRUMENTATION AND WORKING OF INFRARED SPECTROPHOTOMETER

Earlier, dispersive instrument with grating monochromator was widely used but now Fourier Transform (FT) infrared spectrophotometers are widely used. FT-IR is a method of obtaining infrared spectra by first collecting an interferogram of a sample signal using an interferometer, and then performing a Fourier Transform (FT) on the interferogram to obtain the spectrum. An FT-IR Spectrometer collects and digitizes the interferogram, performs the FT function, and displays the spectrum. The major difference between an FTIR spectrometer and a dispersive IR spectrometer is the Michelson interferometer.

A common FTIR spectrometer consists of a

1. Radiation Source
2. Interferometer
3. Sample cell (compartment)
4. Detector
5. Read out device.



1. Radiation Source: The common radiation sources for infrared spectrometer is an inert solid heated electrically to 1000 to 1800° C. Three popular sources of radiation are

- (a) Nichrome wire.
- (b) Nernst Glower (a rod of made from mixture of oxides of Zr, Th and Ce).
- (c) Globar (silicon carbide rod).

They all produce continuous radiations, but with different energy profiles.

Ideal source must be a) intense enough for detection b) steady c) extend over the desired wavelength.

2. Interferometer: It consists of three active components

- A moving mirror
- A fixed mirror
- A beam splitter

Principle and Working:

- Radiation from the broadband IR source is collimated and directed to fall on the beam- splitter.
- At the beam-splitter half of the IR beam is transmitted to the fixed mirror and the remaining half is reflected to the moving mirror. After the divided beams are reflected from the two mirrors, they are recombined at the beam-splitter.
- Then by changing the position of the moving mirror, a different optical path difference is modified and the detector can measure another intensity of the total

beam as the second data point. If the beam is modified for each new data point by scanning the moving mirror along the axis of the moving arm, a series of intensity versus each optical path length difference are collected. So instead of obtaining a scan spectrum directly, raw data recorded by the detector.

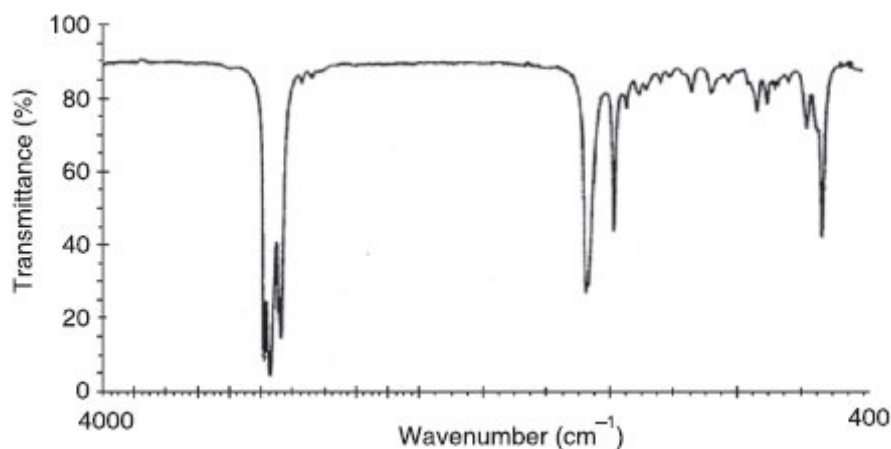
- The raw data is actually the intensity of the interfering wave versus the optical path difference (also called Interferogram). The spectrum of the sample is actually encoded into this interferogram. Because the analyst requires a frequency spectrum (a plot of the intensity at each individual frequency) in order to make identification, the measured interferogram signal cannot be interpreted directly. Hence Fourier transformation is performed by the computer which then presents the user with the desired spectral information for analysis.

3. Sample cell: Solid samples are usually mixed with dry KBr and made into transparent disk at high pressure. Liquid samples can be either recorded neat or as solutions in CCl_4 , CHCl_3 or CS_2 . These samples are kept between transparent NaCl plates.

4. Detector: Various photon detectors and thermal detectors can be used. (**For details refer Unit I**)

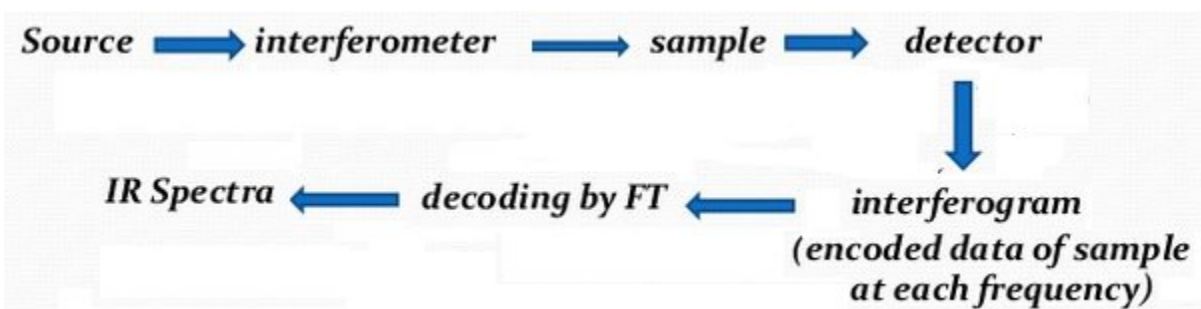
5. Read out: Final spectra is observed in a computer monitor and taken print out.

Representative IR Spectrum of a sample



Entire process of FT IR can be summarized as below

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Analysis of the Spectra

Entire infrared spectrum is divided into group frequency region and fingerprint region.

Group frequency region: (4000–1400 cm^{-1})

In group frequency region, the peaks corresponding to different functional groups can be observed. Functional groups can be determined as different functional groups absorb at different frequencies. Organic chemists use the information in group frequency region to identify and characterize organic compounds. For example, C = O stretch occurs around 1700 cm^{-1} while O–H stretching occurs around 3200 cm^{-1} . This region is also known as functional group region.

Representative stretching frequencies of some common functional groups are given below.

<i>Functional group</i>	<i>Stretching frequencies (in cm^{-1})</i>
C – H	2900–3100
C = C	1600–1700
O – H	3100–3500
C = O	1700–1800
N – H	3300–3400

Fingerprint region: (1400–700 cm^{-1})

In this region molecules give very rich and intense absorption bands which are unique and characteristic of the molecule. This is true for even simple molecules. Every compound has unique absorption peaks in this region, just as every person has unique fingerprints. No two organic compounds (except enantiomers) will have an identical absorption bands in the fingerprint region. Hence this region can be considered as a

fingerprint of a molecule. Therefore the sample can be qualitatively found out by carefully studying the fingerprint region.

Applications of Infrared Spectroscopy

(i) Detection of functional groups

Various functional groups can be detected from the functional group region from the infrared spectrum. Each functional group absorbs at different wavenumbers. For example, C=O stretch occurs around 1700 cm^{-1} while O–H stretching occurs around 3200 cm^{-1} .

Bond	Frequency (Wavenumber Range, cm^{-1})	Intensity
C=O	1735-1680	strong
C=C	1680-1620	variable
C\equivC	2260-2100	variable
C\equivN	2260-2220	variable
C-H	3300-2700	variable
N-H	3150-2500	moderate
O-H	3650-3200	broad

(ii) Identification and characterization of compounds

Fingerprint region can be used for the identification of compounds. No two compounds (except enantiomers) can have same set of peaks in the fingerprint region.

(iii) Studying the progress of the reaction

Progress of chemical reaction can be determined by examining the small portion of the reaction mixture withdrawn from time to time. The rate of disappearance of a characteristic absorption band of the reactant group and/or the rate of appearance of the characteristic absorption band of the product group due to formation of product is observed. For example, when an alcohol is oxidized to corresponding aldehyde or ketone, the absorption band $\sim 3300\text{ cm}^{-1}$ due to O–H stretching diminishes and a new absorption band appear $\sim 1700\text{ cm}^{-1}$ due to C=O stretching.

(iv) Detection of impurities

Infrared spectrum of the test sample to be determined is compared with the standard compound. If any additional peaks are observed in the infrared spectrum, then it is due

to impurities present in the compound. Impure sample generally give broad and poorly resolved bands.

(v) To find out intermolecular and intramolecular H-bonding in molecules.

Free O-H and hydrogen bonded O-H absorbs at different frequencies. Infrared spectra can be used to identify between intermolecular and intramolecular hydrogen bonding. Intramolecular hydrogen bonding is independent of concentration, peaks shows no much change on dilution. On the other hand intermolecular hydrogen bonding peaks diminishes on dilution.

(vi) Moisture content in samples

If a sample contains moisture it shows absorption bands around 3300 cm^{-1} due to O-H stretching. If moisture is absent, no such peak will be present. This can be used to ensure the dryness of the samples.

RAMAN SPECTROSCOPY

INTRODUCTION

Raman spectroscopy is a spectroscopic technique (vibrational spectroscopy similar to infrared (IR) spectroscopy) based on **inelastic scattering** of monochromatic light, usually from a laser source. Unlike other spectroscopy, Raman spectroscopy deals with the **scattering of light** and not absorption or emission. Inelastic scattering means that the frequency of photons in monochromatic light changes upon interaction with a sample. Photons of the laser light are absorbed by the sample and then reemitted. Frequency of the reemitted photons is shifted up or down in comparison with original monochromatic frequency, which is called the Raman effect. This shift provides information about vibrational, rotational and other low frequency transitions in molecules. Raman spectroscopy can be used to study solid, liquid and gaseous samples.

While IR bands arise from a change in the dipole moment of a molecule due to an interaction of light with the molecule, Raman bands arise from a change in the polarizability of the molecule due to the same interaction. That is, Raman bands arise from specific molecular vibrations. Certain vibrations that are allowed in Raman are forbidden in IR and vice versa and can be thought of as complementary.

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PRINCIPLE

SCATTERING OF LIGHT

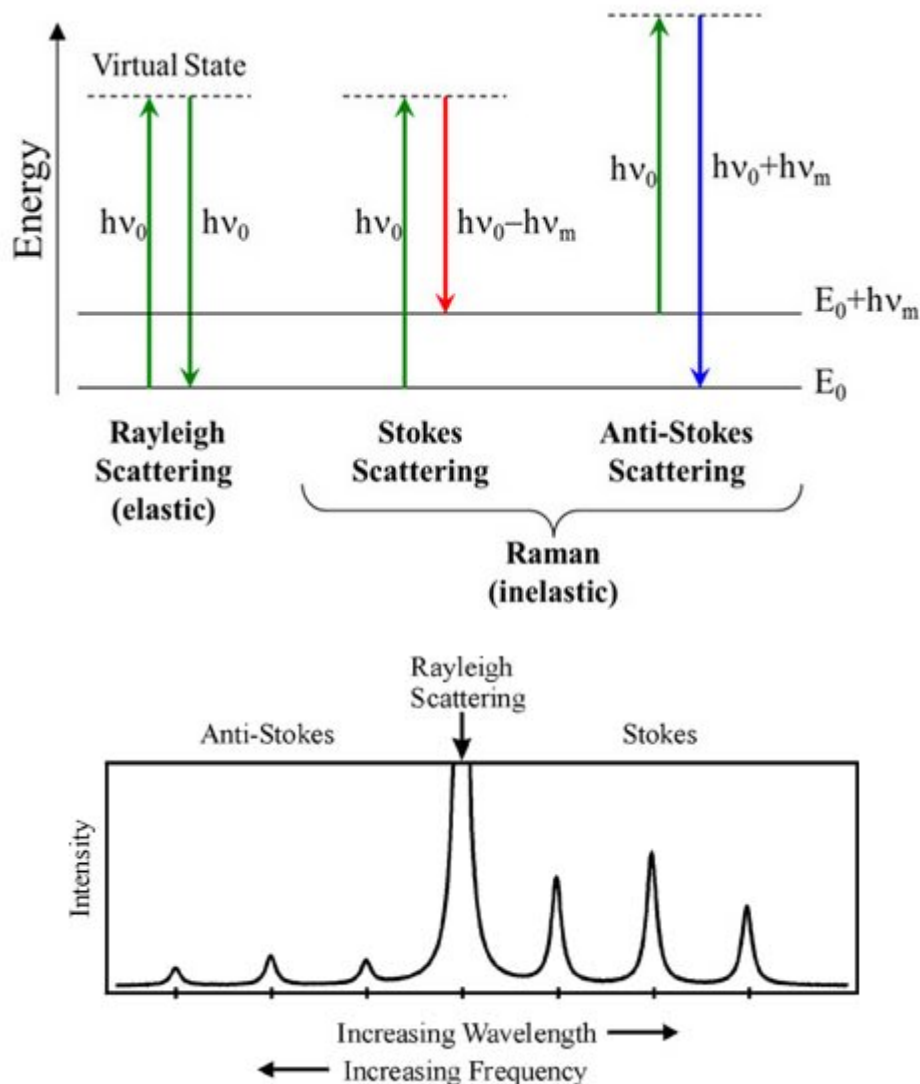
Rayleigh scattering

When a beam of strong radiation of definite frequency is passed through a transparent substance, the radiation is scattered at right angles to the direction of the beam and its frequency of the scattered radiation is same as the original frequency. This type of scattering is known as **Rayleigh scattering**. Most light passing through a transparent substance undergoes Rayleigh scattering. This is an elastic scattering, which means that the light does not gain or lose energy during the scattering. Therefore it stays at the same wavelength. The amount of scattering is strongly dependent on the wavelength, being proportional to λ^{-4} .

Raman scattering

The phenomenon of Raman scattering was discovered in 1928 by Indian physicist **C.V. Raman**, who received the Nobel Prize in physics in 1930 for his work. He discovered that “when a beam of strong radiation of definite frequency is passed through a transparent substance (gas, liquid or solid), the radiation scattered at right angles has not only the original frequency but also some other frequency generally lower and occasionally higher than that of the incident radiation”. This is termed **Raman scattering**. **Raman scattering** is different in that it is inelastic. The light photons lose or gain energy during the scattering process, and therefore increase or decrease in wavelength respectively. If the scattered photon has less energy (longer wavelength) than the incident photon, it is called **Stokes scattering**. If the scattered photon has more energy (shorter wavelength) than the incident photon, it is called **anti-Stokes scattering**.

The difference in energy between the incident photon and the Raman scattered photon is equal to the energy of **a vibration of the scattering molecule**. A plot of intensity of scattered light versus energy difference is a Raman spectrum.



Only about 1 in 10^7 photons undergo Stokes Raman scattering and so this is usually swamped by the far more prominent Rayleigh scattering. The amount of anti-Stokes scattering is even less than this.

Raman Scattering explanation based on quantum theory

According to quantum theory, Raman effect is considered to be the outcome of the collisions between the light photons and molecules. Thus, applying the principle of conservation of energy, we can write

$$E_p + \frac{1}{2}mv^2 + h\nu_i = E_q + \frac{1}{2}mv^2 + h\nu_s \quad (1)$$

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Where E_p and E_q are the intrinsic energies of the molecules before and after collision, respectively, m is the mass of the molecule and v and v' are the velocities of the molecule before and after collision respectively, and ν_i and ν_s are the frequencies of the incident and scattered photon respectively.

As the collision does not cause any appreciable change of temperature, it may be assumed that the kinetic energy of the molecule remains practically unchanged in the process. Hence equation (1) becomes

$$\begin{aligned}
 E_p + h\nu_i &= E_q + h\nu_s \\
 \text{Therefore } h(\nu_s - \nu_i) &= E_p - E_q \\
 \text{or } \nu_s &= \nu_i + \frac{E_p - E_q}{h} \quad (2)
 \end{aligned}$$

The three possibilities which arise from equation 2 are:

- (i) If $E_p = E_q$ then $\nu_s = \nu_i$ which represents unmodified lines, ie Rayleigh scattering.
- (ii) If $E_p > E_q$ then $\nu_s > \nu_i$ which refers to anti-Stokes lines. In this case, the molecule transfers some of its energy to the incident photon and thus the scattered photon has higher energy than the incident photon.
- (iii) If $E_p < E_q$ then $\nu_s < \nu_i$ which refers to Stokes lines. In this case, the molecule absorbs some of its energy to the incident photon and thus the scattered photon has lower energy than the incident photon.

RAMAN SPECTRA- CONDITIONS FOR A MOLECULE TO BE RAMAN ACTIVE

It is the polarizability of the molecule which determines whether the Raman effect will be observed or not. A molecule subjected to electromagnetic radiation will be polarized because the electric component of radiation force field will subject the electrons and protons to forces in opposite directions. The induced dipole moment, μ , is proportional to the strength of the electric field, ϵ

$$\mu \propto \epsilon$$

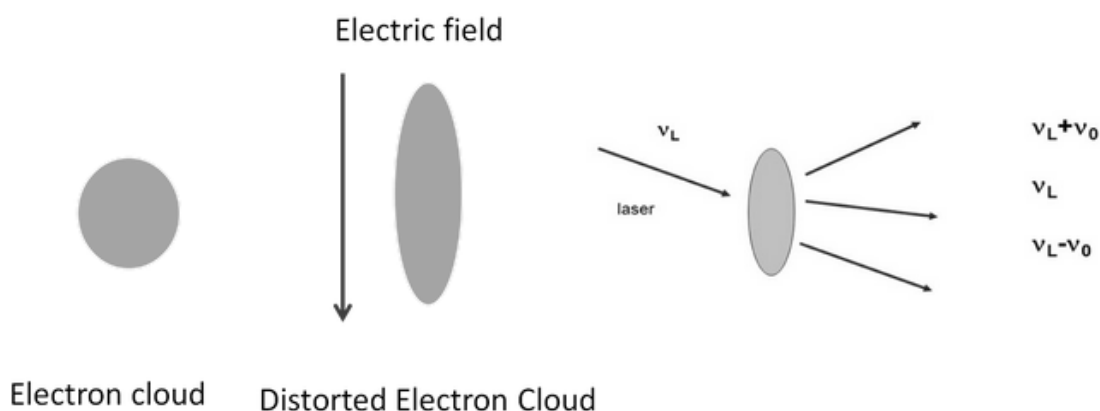
$$\mu = \alpha \epsilon$$

$$\alpha = \frac{\mu}{\epsilon}$$

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The constant of proportionality is called polarizability, α . Thus, the polarizability is obtained by dividing induced dipole moment with the strength of the electric field causing induced dipole. Polarizability, is thus a measure of elastic deformation of the vibrational configuration of the molecule and in Raman effect it is the measure of the deformability of the electron cloud by electric field.

The molecule will be Raman active only when the polarizability of the molecule changes with the vibrational mode. The intensity of a Raman band is proportional to the square of the change in polarizability caused by the vibration giving rise to the band.



Summary:

Electron cloud → No distortion (Absence of electric field)

Electron cloud → Distortion (Presence of electric field from EMR)

Distorted electron cloud → Electromagnetic radiation → Elastic scattering (Rayleigh scattering) and inelastic scattering (Raman effect)

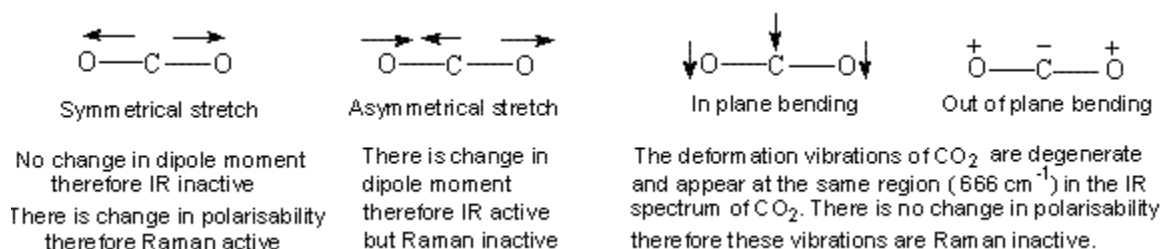
Rule of mutual exclusion

This rule states that “if a molecule has a center of symmetry, then Raman active vibrations are IR inactive. If there is no center of symmetry, then some (but not necessarily all) vibrations may be both Raman and IR active.

Consider O_2 molecule (A molecule with centre of symmetry). O_2 molecule **does** create a change polarization while stretching, so Raman vibrations are seen. On the other hand there is no change in dipole moment during stretch, so it is IR inactive.

Raman and IR vibrations of CO₂

Mode of vibration of CO ₂	Raman	Infra-red
ν_1 : symmetric stretch	Active	Inactive
ν_2 : bend	Inactive	Active
ν_3 : asymmetric stretch	Inactive	Active



For a complex molecule that has no symmetry except identity element, all of the normal modes are active in both IR and Raman. This does not; however mean that they can be observed. In both types the neighbouring strong bands may obscure weak bands, while others may be intrinsically too weak to be observed even if they are theoretically “allowed”. In general the strong bands in the IR spectrum of a compound correspond to weak bands in the Raman and vice versa.

RAMAN INSTRUMENTATION

In Raman spectrometer the sample is irradiated with monochromatic light and the scattered light is observed at right angles to the incident radiation.

A Raman system typically consists of four major components:

1. Excitation source (Laser)
2. Sample holder
3. Wavelength selector (Filter)
4. Detector and Recorder

1. **Raman Source:** Since the intensities of the scattered radiation are roughly 0.01 % of that of the incident radiation, extremely intense source of has to be used. Helium-Neon laser which emits highly monochromatic light at 632.8 nm is commonly used in many modern spectrometers. Argon ion lasers are also used. Filters need not be used when highly monochromatic radiations are used.

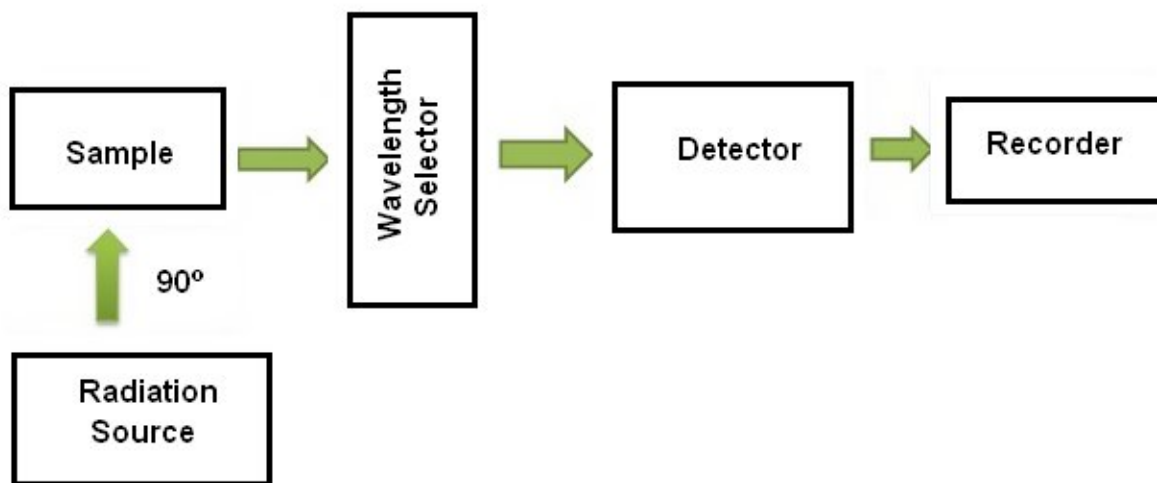
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2. Sample Raman tube: Sample usually liquid is taken in the sample tube provided with optical window at the end. Variety of sample tubes of different size and shapes are used. Water is an excellent solvent for Raman spectroscopy as it has only few interference bands and dissolves many inorganic substances.

For study of Raman spectra of gases, the gas sample can be placed inside the laser cavity. In case of solid samples, the laser beam is focused into a capillary tube containing a powdered solid. Only few milligrams of the powdered solid samples are adequate to give good spectra.

3. Filters: In order to obtain high signal-to-noise in Raman measurements, it is necessary to block Rayleigh scattering from reaching the detector while transmitting the Raman signal. Notch filters transmit both Stokes and anti-Stokes Raman signals while blocking the laser line. Edge filters (also known as barrier filters) transmit either Stokes (longpass) or anti-Stokes (shortpass).

4. Detectors and recorder: Modern Raman instruments have photomultiplier tubes for direct measurement and automatic scanning of the spectrum. Photomultiplier tube detects the signal, then amplified and recorded.



Block diagram - Instrumentation of Raman spectroscopy

Advantages of Raman Spectroscopy

Raman spectroscopy is useful for chemical analysis for several reasons:

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Specificity: Raman spectrum can be used for everything from “fingerprinting” of samples.

Analysis of aqueous systems: The IR spectrum of water is strong so aqueous solutions cannot be used.

Analysis of organic and inorganic compounds: If a covalent chemical bond exists between chemical species then a unique Raman signature may be produced.

Wide Concentration Range: The measured intensity of a Raman species is directly proportional to the concentration. This allows a Raman analysis to measure a species concentration from a fraction of 1% to 100% without sample dilution.

No sample preparation: Unlike most other chemical analysis techniques, Raman requires no special preparation of the sample. In fact, no contact with the sample is needed at all because Raman involves only illuminating a sample with a laser and collecting the scattered photons.

Non-destructive Analysis: Because Raman involves only illuminating a sample, often through a window, with a laser and collecting the scattered photons this makes Raman spectroscopy *non-destructive*, ie sample is not lost during analyses.

Compatible with Common Windows: Can utilize standard sampling containers and windows manufactured of glass, sapphire, transparent polymers, and diamond to measure samples in situ.

Quantitative Raman: Because the intensity of a Raman band is directly proportional to the number of molecules giving rise to the band, then the Raman band can be used to provide a measure of the concentration of a molecule.

Short measurement times: A good Raman spectrum can be obtained in few seconds.

APPLICATIONS OF RAMAN SPECTROSCOPY

- **Informations obtained from Raman Spectra**

Observation	Inference	Examples
Characteristic Raman frequencies	Composition of the material	Eg: MoS ₂ , MoO ₃
Changes in the frequency of Raman peak	Stress/strain state	Eg: Si 10cm ⁻¹ shift is observed for every percentage of strain
Polarization of Raman peaks	Crystal symmetry and orientation	Orientation of CVD diamond grains
Width of Raman peaks	Quality of crystal	Amount of plastic deformation
Intensity of Raman peak	Amount of material	Thickness of transparent coating

- **Determination of Structure of inorganic compounds**
- **Structure of centro-symmetric molecules:** CO₂ is a centro-symmetric molecule with linear *structure* (O = C = O). One expects two fundamental modes in IR and one in Raman which was observed experimentally.
- **Structure of N₂O:** Structure of N₂O could be N-O-N (symmetric) or N-N-O (unsymmetric). If it were to symmetric vibrations similar to CO₂ were to be expected. If it were to be unsymmetric, vibrations were expected to be seen both in Raman and in IR. Infact, it was found to be unsymmetric with both IR and Raman vibrations.
- **Structure of water:** For water to have bent structure then all vibrations should be both Raman and IR active. It is true experimentally.

Determination of Structure of organic compounds

- **Identification of molecules:** Raman spectra are similar to infrared spectra in that they have regions that are useful for functional group detection and fingerprint regions that permit the identification of specific compounds.
- **Presence of absence of specific linkages in molecules:** Raman spectroscopy can be used to measure bands of symmetric linkages which are weak in an infrared spectrum (e.g. -S-S-, -C-S-, -C=C-).

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- **Determination of cis and trans isomers:** Consider, planar dichloroethylene, CH_2Cl_2 , which can be either cis or trans. Trans alone has a centre of symmetry. Cis isomer will give coincident frequencies in both IR and Raman. While Trans will give peaks exclusively in Raman or IR.
- **Presence of Tautomers:** Raman spectrum can be used to show the presence of tautomers. For example, keto and enol tautomers can be detected using Raman spectra.

Differences between IR and Raman methods

Raman	Infrared
It is due to the scattering of light by the vibrating molecules	It is the result of absorption of light by vibrating molecules.
The vibration is Raman active if it causes a change in polarisability.	Vibration is IR active if there is change in dipole moment.
The molecule need not possess a permanent dipole moment.	The vibration concerned should have a change in dipole moment due to that vibration.
Water can be used as a solvent.	Water cannot be used due to its intense absorption of IR.
Sample preparation is easy, it can be in any state.	Sample preparation is elaborate Gaseous samples can rarely be used.
Gives an indication of covalent character in the molecule.	Gives an indication of ionic character in the molecule.
Cost of instrumentation is very high	Comparatively inexpensive.
Standard sample holders can be used- glass, plastic, etc.	IR transparent materials (salts) are generally used for sample holders in many cases.
Requires a laser source	Requires a broadband IR source
Symmetric stretches are strong. Asymmetric stretches and bends are weak.	Asymmetric stretches and bends are strong. Symmetric stretches are not seen.