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UNIFYING PRINCIPLES

Introduction to Spectroscopy:

Spectroscopy is a branch of science which deals with the transitions induced in chemical species by its interaction with photons of electromagnetic radiation. Due to the interaction between chemical species and electromagnetic radiation, energy is either absorbed & emitted by the matter in descrete amounts called quanta. Generally spectroscopic methods are used to measure the energy difference between various molecular energy levels and to determine the atomic and molecular structures. The instruments used in such studies are called spectrophotometers

The study of spectroscopy can be carried out under the following types

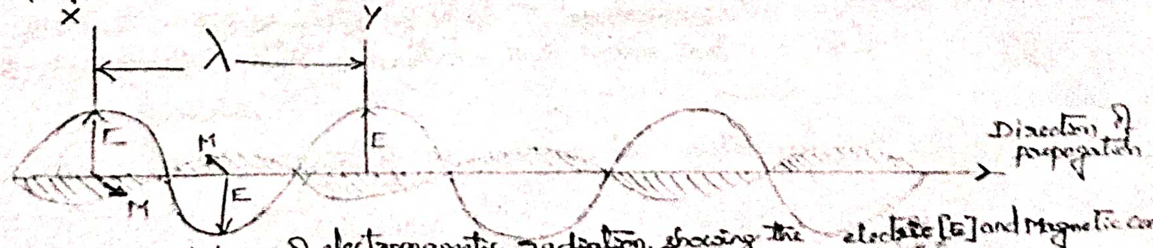
(a) Atomic Spectroscopy
(b) Molecular Spectroscopy

(a) Atomic spectroscopy: Atomic spectroscopy deals with the interaction of electromagnetic radiation with atoms.

(b) Molecular Spectroscopy: Molecular spectroscopy deals with the interaction of electro-magnetic radiation with molecules. Molecular spectra are much more complicated than atomic spectra.

Electromagnetic radiation:

Electromagnetic theory was developed by Maxwell. Light & Electromagnetic radiation is a form of energy that is transmitted through space at a constant velocity of 3×10^8 m/sec. Electromagnetic radiation can be considered as a simple harmonic wave propogated from a source and travelling in straight line. The electric and magnetic components oscillate in planes perpendicular to each other and perpendicular to the direction of propogation of the radiation.



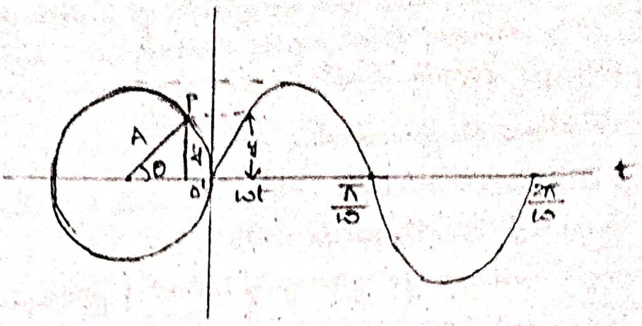
A beam of electromagnetic radiation, showing the electric [E] and Magnetic components

Light has dual nature i.e. wave nature and particle nature. This dual nature is very useful in understanding the interaction of radiations with matter.

WAVE THEORY:

Electromagnetic radiation travel in the form of waves, according to the wave theory Electromagnetic radiation has properties similar to that of Sine wave and hence Generally simple harmonic wave can be defined as $y = A\sin\theta$.

Where y is the displacement with a maximum value A and θ is an angle between 0 and 360° (or 0 and 2π radians). The above wave motion can also be represented as a circular motion.



Point P travels with uniform angular velocity ω rad/sec in a circular path of radius A. After a time t seconds point P crosses O' and describes an angle $\theta = \omega t$ radians. The vertical displacement of the wave can be given as follows.

$$y = A\sin\theta \Rightarrow y = A\sin\omega t.$$

After a time of $2\pi/\omega$ seconds, P will return to O', completing a cycle. Therefore the number of cycles formed in one second are $\omega/2\pi$ and this is referred as the frequency (ν) of wave. The SI unit of frequency is called the hertz and has the dimension of reciprocal seconds.

$$\therefore \nu = \frac{\omega}{2\pi} \Rightarrow \omega = 2\pi\nu$$

$$\therefore y = A\sin\omega t \Rightarrow y = A\sin 2\pi\nu t.$$

The fundamental relationship between distance - time is

$$x = ct \Rightarrow t = \frac{x}{c}$$

Where x is the distance covered in time t at a speed c

$$\therefore y = A\sin\left(\frac{2\pi\nu x}{c}\right)$$

There is another property by which the electromagnetic radiation can be characterised ~~by~~ i.e. wavelength λ. It is known that $c = \nu\lambda$

$$\therefore \lambda = \frac{c}{\nu} \text{ metres.}$$

Hence, the displacement of the wave can be written as

$$y = A\sin\frac{2\pi x}{\lambda}$$

There is yet another way by which the electromagnetic radiation can be characterised i.e. in terms of the wavenumber $\bar{\nu}$. Wavenumber is defined as the reciprocal of the wavelength.

$$\bar{\nu} = \frac{1}{\lambda}\ \text{cm}^{-1}$$

$$\therefore y = A\sin 2\pi\bar{\nu}x$$

Hence electromagnetic radiations can be characterised by either frequency (ν) or wavelength (λ) or wavenumber ($\bar{\nu}$).

Quantisation Of Energy:

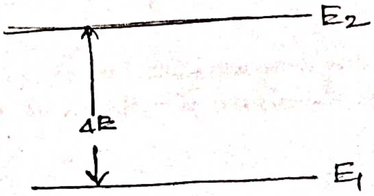
A molecule in space can have many sorts of energy i.e. it may possess rotational energy by virtue of bodily rotation about its centre of gravity; it may possess vibrational energy due to the periodic displacement of its atoms from their equilibrium positions; it may possess electronic energy by virtue of electronic transition.

According to quantum theory; electromagnetic radiation consists of a stream of energy packets called photons or Quanta. Emission or absorption of light by chemical species always occur as integral multiple of small units of energy i.e. photon. The energy E of the photon is proportional to the frequency of radiation and is given by the equation

$E = h\nu$ where 'h' is planck's constant (i.e. 6.625×10^{-27} ergs-sec or 6.625×10^{-34} Joule-sec)

As rotational, vibrational and electronic transitions are microscopic, quantum restriction can be imposed over such transitions and hence the corresponding energies (i.e. electronic, vibrational and rotation) are quantised.

Consider two possible energy states of a system – two rotational energy levels of a molecule labelled as E_1 and E_2. The suffixes 1 and 2 are infact quantum numbers. Transition between these two levels E_1 and E_2 occurs only when appropriate amount of energy i.e. $\Delta E = E_2 - E_1$ can be either absorbed or emitted by the system. The frequency of the radiation which is either absorbed or emitted can be given by the formula



$$\nu = \frac{\Delta E}{h} \text{ Hz}$$

The significance of this is that if a molecule in state 1 absorbs energy from the beam of incident radiation, the molecule jumps to state 2. The energy required for such transition is an integral multiple of a fixed quantity. Hence a molecule or an atom can either absorb or emit a fixed quantity of energy and cannot either absorb or emit any arbitrary amount of energy.

Electromagnetic Spectrum:

The spectrum of visible light has been long observed in nature in the form of a rainbow. The spectrum of visible light consists of seven colours. In addition to visible region, the electromagnetic radiation consists γ-rays, x-rays, uv radiations, IR, microwave and radiowave. The entire range which includes all the regions is known as electromagnetic spectrum. This electromagnetic spectrum includes an immense range of wavelengths. The visible region is relatively a small portion of the total electromagnetic spectrum.

The wavelength ranges of various regions can be given as follows.

Radiowaves: The radiofrequency region lies between 10^{3}cm - 1cm. This region is useful for Nuclear magnetic resonance (NMR) and Electron Spin resonance (ESR) spectroscopic studies. The energy changes involved in these spectroscopic studies arise from the reversal of spin of a nucleus or electron and are of the order of 0.001 - 10 joules/mole.

Microwave region: This region lies between 1cm - 10^{-2}cm (0.1mm). This region is useful for rotational spectroscopic studies. ~~&~~ Separation between rotational levels of molecules are of the order of hundreds of joules per mole.

Infra-red region: IR region lies between 10^{-2}cm - 10^{-4}cm. This region is further divided into three regions i.e. Far IR, Middle IR and near IR. Far IR region lies between 200μm - 15μm (2×10^{-2}cm - 15×10^{-4}cm); Middle IR region lies between 15μm - 2.5μm (15×10^{-4}cm - 2.5×10^{-4}cm); Near IR region lies between 2.5μm - 0.7μm (2.5×10^{-4}cm - 0.7×10^{-4}cm) This region is useful for vibrational spectroscopic studies. Separation between vibrational levels ~~are~~ is of the order of 10^{4} Joules/mole.

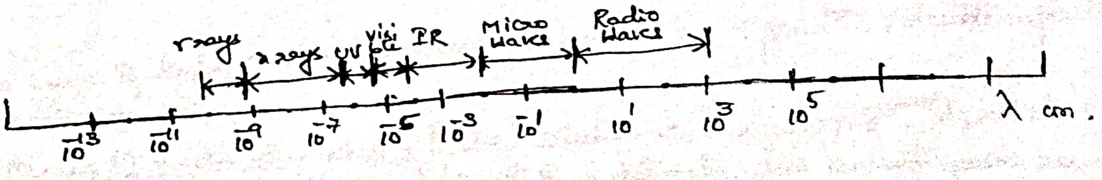
Visible region: Visible region lies between 7,800Å - 3800Å (0.78×10^{-4} - 3.8×10^{-5}cm)

UV region: UV region ranges from 380nm - 10nm (3.8×10^{-5}cm - 1×10^{-6}cm)

Both visible region as well as UV region are useful for electronic spectroscopic studies Energy separation electronic energy levels is of the order of some hundreds of ~~joules~~ kilo joules per mole.

X-ray region: This region lies between 10nm - 10pm (1×10^{-6}cm - 10^{-9}cm) This region is useful for studying the energy changes involving the inner electrons of an atom or a molecule. These energy changes are of the order of ten thousand kilojoules

γ-Rays: This region lies between 10pm to 10^{-10}cm (10^{-9}cm - 10^{-10}cm). This region is useful for studying the energy changes which involve in the rearrangement of nuclear particles. These energy changes are of the order of 10^{9} - 10^{11} joules per gram atom.



Interaction of Electromagnetic radiation with matter:

When a beam of light is incident on a matter then the light interacts with the matter. Because of interaction between light and matter, many changes may occur in both light and matter. These changes are of great importance to the chemists because they provide the basis for many important research tools eg spectrographs, refractometer, polarimeter, colorimeter etc. Thus it is very important to know what happens when light interacts with matter. Electromagnetic radiations are characterised by frequency (ν), wavelength (λ), intensity (I_o) and the direction. Some important changes that occur are.

(i) When light interacts with matter then it may undergo reflection and refraction by changing its direction.

Refraction of radiation: A change in the direction of the beam of radiation is observed, when it is allowed to pass from medium to another medium; having a different physical density than the first. The change in the direction of radiation is due to the differences in the velocity of radiation in two media. This phenomenon is called as refraction and the extent of refraction is given by

$$\frac{\sin\theta_1}{\sin\theta_2} = \frac{n_2}{n_1} = \frac{V_1}{V_2}$$

where n_1 and n_2 are refractive indices of the two media; V_1 and V_2 are the velocities of radiation in medium 1 and medium 2 respectively.

Reflection of radiation: Reflection takes place when a beam of radiation is allowed to cross an interface between media of different refractive indices. The fraction of the reflected beam increases with increasing difference in refractive index. If a beam is allowed to travel normal to the interface, the fraction reflected is given by

$$\frac{I_r}{I_o} = \frac{(n_2-n_1)^2}{(n_2+n_1)^2}$$

Where I_o is intensity of incident radiation.
I_r is intensity of reflected radiation.
n_1 and n_2 are refractive indices of two media.

(ii) The beam of light can be decomposed into another by diffraction, double refraction and scattering.

Scattering of radiation: When a turbid solution i.e., a suspension of solid particles in a ~~ligh~~ liquid is brought into the light path of a photometer, less radiant power reaches the photodetector in the light path. This reduction results from the scattering of light due to reflection and refraction by the suspended particles. The scattering of light by molecules can be explained by making use of electromagnetic theory. The study of Raman Spectroscopy is entirely based on the ~~study~~ study of scattered radiation.

Scattering by molecules & aggregates of molecules with dimensions smaller than the wavelength of the radiation is called Rayleigh scattering. Measurement of scattered radiation can be used to determine the size and shape of polymer molecules & colloidal particles. The phenomenon is also applied in Nephelometry and Turbidimetry.

Raman effect is the phenomenon due to which the scattering light has a slightly different frequency from that of the incident light and thus there is a change in the atomic oscillations within the molecule.

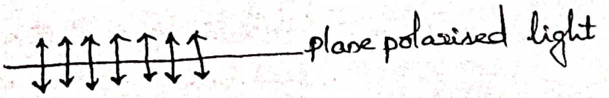
Dispersion: The refractive index of an optical medium may be defined as the ratio of velocity of radiation of a particular frequency in vacuum to that in the medium. The variation of refractive index of a substance with frequency & wavelength is called its dispersion. The dispersion of a substance throughout the electromagnetic spectrum is intimately related to the degree to which radiation is absorbed.

(iii) If the incident beam is plane polarised, the plane of polarisation may be rotated on passing through the substance, it is called the optical rotation and is measured by a polarimeter

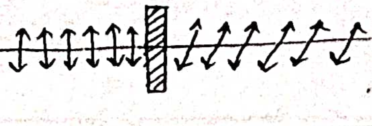
Polarisation and optical rotation:

Matter also has ability to polarise light. The ordinary light is also called as unpolarised light which consists of a very large number of vibrations in all planes with equal probability at right angles to the direction of propogation. unpolarised light can be represented as follows.

When an ordinary light is passed through certain substances like Tourmaline crystal the light is polarised and the vibrations are confined to a single direction. The light which has acquired the property of one-sideness is called polarised light. If a beam of polarised light proceeding in a straight line has all its vibrations in one plane i.e., at right angles to the propogation of light then the light is said to be linear and plane polarised.



Some other substances like quartz, sugar crystal (& sugar solution) etc., rotate the plane of vibration of plane polarised light passing through them. This property of rotating the plane of vibration of plane polarised light about its direction of travel by some crystal is known as optical activity. This phenomenon is known as optical rotation and the angle through which the plane of polarisation is rotated is known as angle of rotation.



There are two types of optically active substances, the substances which rotate the plane of polarisation in clockwise direction are called as dextro-rotatory (right handed), the substances which rotate the plane of polarisation in the anticlockwise direction are called laevorotatory (left handed).

Specific rotation(S) : The specific rotation at a particular temperature and for a given wavelength of light used may be defined as the rotation (of plane of vibration of polarised light) produced by one decimeter length of its solution when the concentration is 1gm per cc.

$$\therefore \text{Specific rotation } S = \frac{\theta}{l \times c}$$

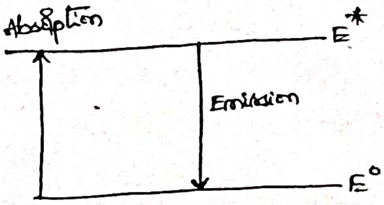
Where θ is angle of rotation in degrees, l the length of solution in decimeter and c is concentration of solution in gm per cc.

(IV) Absorption, Emission and Transmission :

When electromagnetic radiation is made to incident on the surface of matter, the electric component of the radiation interacts with atoms and molecules of the medium. As a consequence the radiation may be absorbed, transmitted, reflected or scattered.

Absorption is the process in which certain frequencies may be selectively removed when a beam of radiation is allowed to pass through a transparent layer of a solid, liquid or gas. When an atom or molecule absorbs energy, the atom or molecule will move to a higher energy state or excited state. In this manner, the electromagnetic energy is transferred to atoms or molecules

The two horizontal lines represent two energy levels with in the species. E^0 represents ground energy state E^* represents excited electronic state. An electron is capable of undergoing transition from E^0 to E^* state, if energy in the form of light or heat is absorbed. This absorption of radiation causes the molecule or atom to be in an excited state.



-A Simple energy level diagram

E^0 - lower energy level

E^* - Higher energy

Excited atoms or molecules are relatively short lived, and tend to return to their ground state after approximately 10^{-8} sec. Hence from the excited level the electron may return to its normal position either directly or in steps with the emission of certain amount of energy. When this emission of light is instantaneous, the phenomenon is known as fluorescence, but when after some time lag, it is known as phosphorescence. When the absorbed energy is stored by the atom or molecule and used in producing some chemical reaction, fluorescence and phosphorescence become absent and the resulting chemical reaction is photochemical reaction.

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Transmission of Radiation:

Transmission in particular may be regarded as a stepwise process involving oscillating atoms, ions or molecules as intermediates. The interaction which takes place in the process of Transmission, may be regarded as the alternating electrical field of the radiation, which causes oscillation of the bound electrons of the particles with respect to their heavy and fixed nuclei. As a consequence, periodic polarisation on the particles occur. Each polarised particle in a particular medium is expected to emit the radiation in all possible directions. This ultimately results in transmission of radiation.

Motion of Molecules - Energy associated with motion:

Generally molecules possess different types of energies. They are (a) Translational energy [E_t]; (b) Electronic energy [E_e]; (c) vibrational energy [E_v], (d) Rotational energy [E_r]

The translational energy is due to the translational motion of the molecule. The electronic energy of the molecule is due to the energy of its electrons. In addition, molecules also possess vibrational and rotational energies. Vibrational energy is due to the periodic displacement of its atom from their equilibrium point. Rotational energy is due to bodily rotation about its centre of gravity.

Except the translational energy, vibrational, rotational and electronic energies of molecule are quantised. For a gas kept in an ordinary sized container, the space available for the translational movement of each molecule is very large compared to the molecular dimensions. Thus it is not significant to expect quantum restrictions on translational energies. However for rotational motion of a molecule the space is confined to the volume of the molecule itself. Hence significant restrictions can be expected on rotational energies. In vibrational motion, the atoms of a molecule can displace upto an extent where the bond between them would not break. Hence quantum restrictions can be expected on vibrational energies. Similarly quantum restrictions can also be imposed on electronic energies because the electrons of a molecule are confined to be a part of the molecule.

The spacing between the electronic energy levels is larger than the spacing of the rotational energy levels. The energy difference between electronic energy levels is nearly 10 K.cal/mole, that between vibrational energy levels is only a few kilocal/mole and that between rotational energy levels is only of the order of tens of cal/mole.

Intensity of spectral lines:

The three main factors which are to be considered while discussing the intensity of spectral lines are

(a) Transition Probability.
(b) Population of states
(c) concentration & Path length of the sample:

(a) **Transition Probability**: The calculation of absolute transition probabilities can be precisely done from quantum mechanical approach. This calculation involve a knowledge of quantum mechanical wavefunctions of the two states between which the transition occurs. These quantum mechanical calculations are not simple. It is possible to explain the probable transitions qualitatively without attempting detailed calculations.

This qualitative approach decides whether a particular transition is forbidden or allowed. This essentially involves the deduction of selection rules. These selection rules are very much useful to predict, the transition between which levels give rise to spectral lines.

b. Population of states: If transitions from two levels to a third level are equally probable then the most intense spectral line will arise from the level which initially has the greater population. This is a simple statistical rule governing the population of a set of energy levels.

Suppose that N molecules are distributed between two different energy states, a lower and upper energy states (E_{lower} and E_{upper}) respectively. The distribution of N molecules between two states can be given by the formula

$$\frac{N_{upper}}{N_{lower}} = e^{\left(-\frac{\Delta E}{kT}\right)}$$

Where $\Delta E = E_{upper} - E_{lower}$, T is absolute temperature, k is Boltzmann constant $1 \cdot 36 \times 10^{-23}$ J/kelvin.

If ΔE is much greater than kT then the ratio of $\frac{N_{upper}}{N_{lower}}$ is very small. The ratio value smaller means, molecules in general will be in their lowest energy level.

(c) Concentration & Path length of sample: If a sample absorbs energy from a beam of radiation then more amount sample will absorb more energy from the beam of radiation. If double amount of sample is irradiated with a beam of radiation then we would expect twice the absorption, but this is not so.

Consider two identical sample of same material S_1 and S_2. Suppose S_1 & S_2 alone absorb 50% of energy falling on them, allowing remaining 50% to pass through. Let a beam of initial intensity I_0 is passed through S_1, 50% of I_0 will be absorbed and the intensity of the beam leaving S_1 will be $\frac{1}{2} I_0$. If this beam is passed through S_2, a further 50% will be absorbed and $\frac{1}{4} I_0$ will leave S_2. These two 50% absorptions in succession do not add upto 100%, but only to 75% absorption. Thus a similar relation exists between concentration of a sample and the amount of energy absorbed. From this we can say that a doubling of concentration produces something less than a doubling of the absorption.

The relationship between concentration (c), path length (l) and the incident and transmitted intensities of radiation (I_0 and I, respectively) be given by Beer-Lambert law

$$\frac{I}{I_0} = e^{(-kcl)}$$

Where k is a constant for a particular spectroscopic transition.

This equation can also be written as

$$\frac{I}{I_0} = 10^{-\epsilon c l} = T.$$

Where ϵ is molar absorption coefficient, T is transmittance.

or $\frac{I_0}{I} = 10^{\epsilon c l}$ or $\log\left(\frac{I_0}{I}\right) = \epsilon c l = A.$

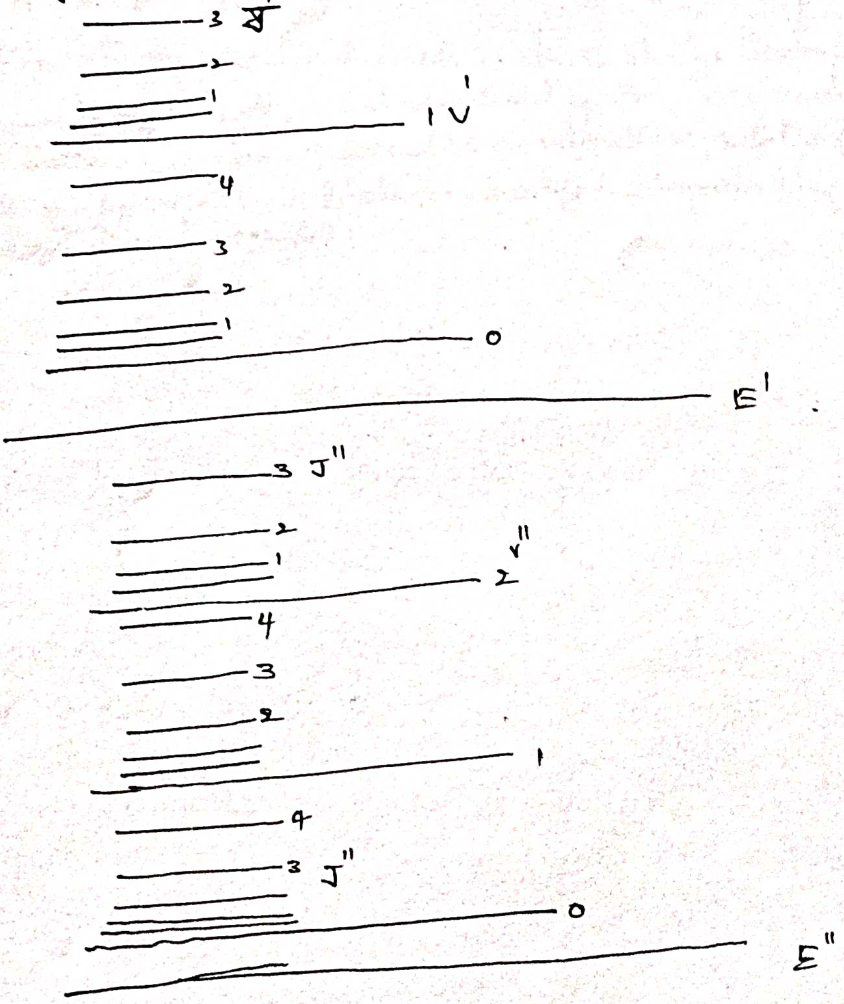
A is called absorbance or optical density.

Born-Oppenheimer approximation:

It is well known that electronic, vibrational and rotational energies are quantised. Hence these three types of molecular energies can be treated separately and the total energy can be written as

$$E_t = E_e + E_v + E_r$$

Where E_e, E_v and E_r are the electronic, vibrational and rotational energies per mole respectively. The quantised energy levels can be diagramatically represented as



In the above diagramatic representation, the spacing of the electronic energy levels is larger than the spacing of the rotational energy levels. We know that the atoms have different electronic energy levels which are determined by certain quantum numbers. By absorbing energy, the electron in an atom can be promoted to an excited state from the ground state. This transition gives rise to a line in the spectrum. If the electron is present in higher excited state, it emits energy and drops to ground state.

Similarly molecules also have energy levels and They can absorb & emit radiation. The energies that are either absorbed & emitted by a molecule can be measured by spectroscopic methods. The measured energies so obtained are quite useful to determine the structure and properties of the molecule.

The spectra that arise due to electronic transition between electronic energy levels is known as electronic spectra, Similarly transitions between vibrational levels with in the same electronic level will give rise to vibrational spectra, whereas transitions between rotational levels with in the same vibrational level will give rise to rotational spectra

A transition between vibrational levels is almost always accompained by sitions between rotational levels, so that vibrational spectra are really simultaneous brational and rotational spectra, referred to as vibration - rotation spectra. Similar a transition between two electronic levels is usually accompained by changes in vibrational and rotational energies.