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M.Sc II Sem
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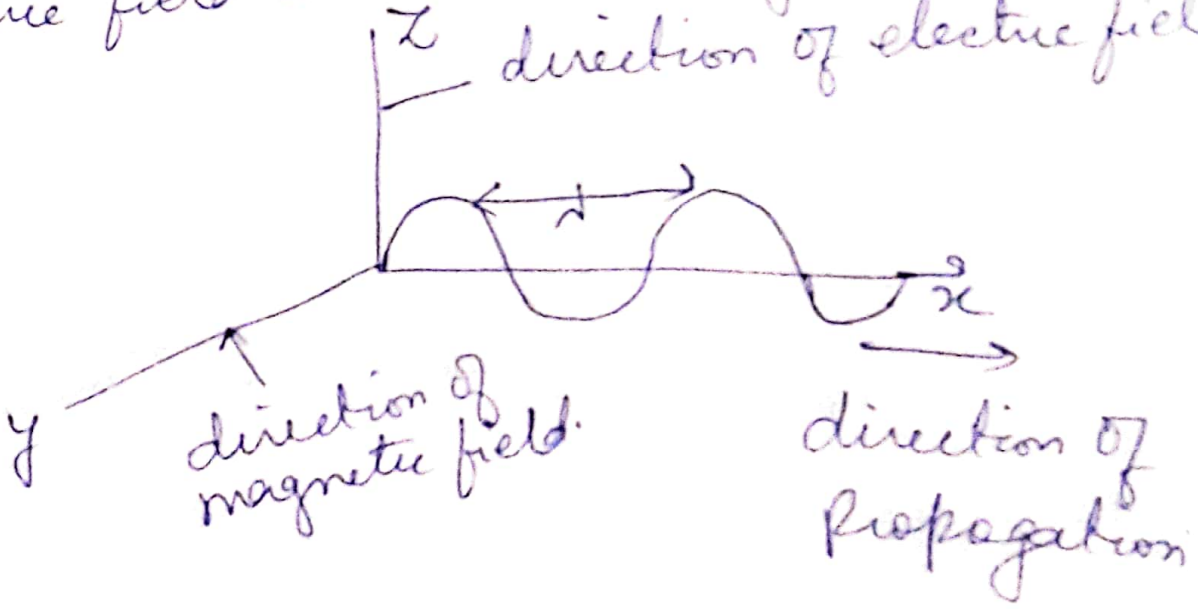
Unifying principles

- Spectro means radiation and scopy means measurements
- Spectroscopy is the branch of science which is associated with the interaction of radiations of different wavelengths with matter
- Electromagnetic radiations is the radiant energy emitted from any source in the form of heat or light or sound.
- Characteristics of electromagnetic radiations

* E.M.R possess the particle nature as well as the wave nature
* E.M.R travel with velocity of visible light $2,998 \times 10^8$ m/s
* E.M.R have electric and magnetic field associated with them at right angles
* If the radiation is moving along X-axis the magnetic field is oriented along Y-axis and electric field is oriented along Z-axis



10^{-8} (cm) 10^{-2} (cm)

Cosmic rays	γ rays	x rays	U.V	Visible	IR	Micro waves	Radio waves

10^{18} (H_3) 10^{10} (H_3)

Frequency decreases

← wave length decreases

← energy Increases

Terms used

wavelength (λ) - The distance between successive crest or trough λ is expressed in cm or nanometers

- Frequency (ν) - It is the number of successive crests which pass a stationary point in one second. The unit is Hertz
- wave number ($\bar{\nu}$) : It is reciprocal to wavelength unit is cm^{-1} $\bar{\nu} = \frac{1}{\lambda}$

Relation between frequency wavelength & wave number

$$\nu\lambda = c \quad , \nu = \frac{c}{\lambda}$$

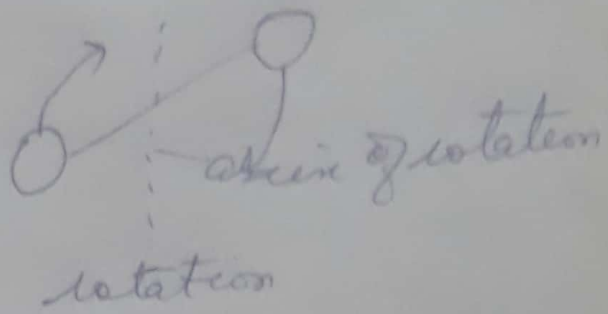
$$\bar{\nu} = \frac{1}{\lambda} cm^{-1}$$

$$\nu = c\bar{\nu}$$

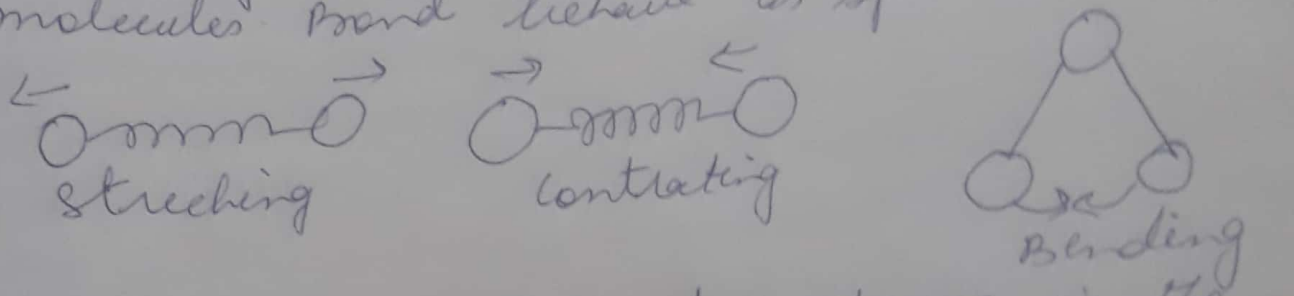
higher wavelength, lower frequency, lower is the energy

Rotational, Vibrational and Electronic energies of molecules:

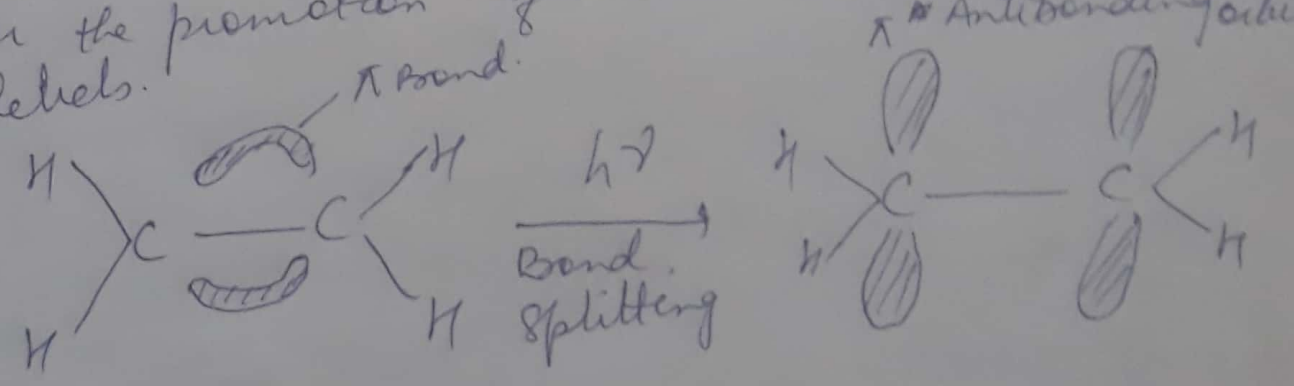
Rotational energy: It involves the rotation of molecules or of parts of molecules about the centre of gravity



Vibrational Energy: It is associated with stretching or bending of covalent bonds in molecules. Bond behave as springs made of wire



Electronic Energy: It involves change in the distribution of electrons by splitting of bonds or the promotion of electron into higher energy levels.



Signal to noise ratio: The signal produced in the analysis of a sample using spectrophotometer consist of two parts:

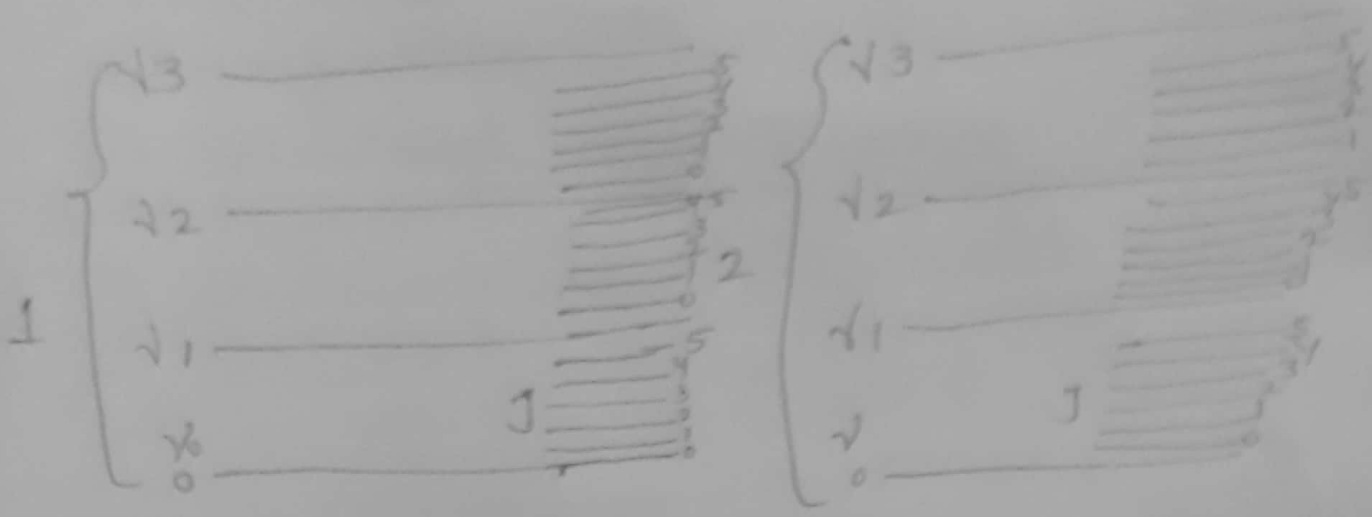
i) Signal produced due to the sample
ii) Signals produced due to other component and

the noise instrument used.
The signal produced by component and instrument is called noise. It is unwanted signal

Molecular spectroscopy versus atomic spectroscopy:

- When atom absorbs energy, electron jumps from lower orbit to higher orbit when they start coming back to lower orbit, emission of energy equal to difference in the energies of the two orbitals takes place in the form of atomic spectrum.
- Molecules when absorb energy then there may be rotation, vibration or electronic transition depending upon the amount of energy absorbed.
- The electronic energy is quantized, there are only discrete electronic energy level in an atom or a molecule, the rotational and vibrational energies are also quantized they are only discrete rotational and vibrational energy level in a molecule
- The rotational, vibrational and electronic energy can be called molecular energy levels
- The transition of energies take place between these levels. The result is a molecular spectra
- When the energy absorbed by molecule is so large that an electron can jump from one electronic energy level to another then energy required for transition from one vibrational energy level to another, the energy needed for rotational level to another level is very less.

Electronic energy level (n=1 to n=2)



Electronic energy levels n values
vibrational sub levels v values
rotational sub levels J values

- Each electronic level consists of a number of vibrational sub levels by v = 0, 1, 2, 3 etc
- Each vibrational level consists of a number of rotational sublevels J = 0, 1, 2, 3 etc

v and J are vibrational and rotational quantum numbers

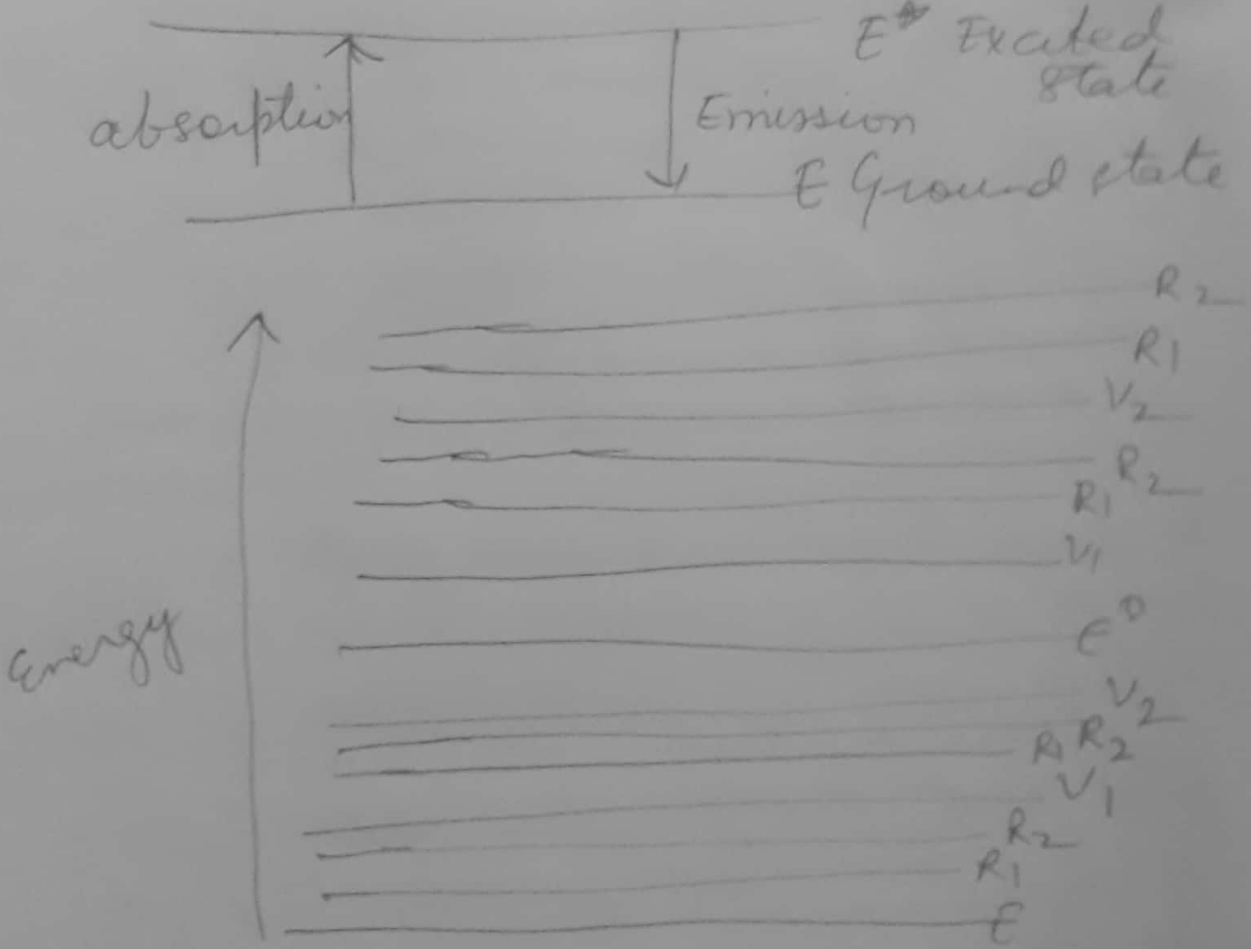
Born Oppenheimer Approximation

The total energy E of the molecule is the sum of translational energy, rotational energy, vibrational energy and electronic energy. Only translational energy is not quantised. Hence considered negligibale

$$E = E_{rotational} + E_{vibrational} + E_{electronic}$$

$$E_{electsonic} >> E_{vibrational} >> E_{rotational} >> E_{translational}$$

- The vibrational spectra of a molecule is observed in the infrared region of the electromagnetic spectrum
- The rotational spectra of molecule is observed in microwave region
- The electronic spectra of a molecule is observed in ultraviolet and visible region



Absorption spectra: When white light is passed through a coloured solution or vapour and the spectrum obtained is examined through a spectroscope black band appears, light is absorbed hence absorption spectrum is formed

Emission Spectra: When a solid is heated a light is emitted. Spectrum produced is emission spectra. The substance absorb engy and then emitt it

- Atoms produce line spectra,
- molecule produce band spectra It is continuous bands it is made up of closely spaced lines. It is called molecular spectra

Interference: Two wave of same wavelength are in phase with one another both of them attain maximum amplitude at same time and at same point in space.

- The wave superimposed on one another the intensity increases it is called constructive interference
- Two wave of same wavelength are out of phase one is at maximum other at minimum amplitude at same time, when they are superimposed the resultant is zero and called distructive interference