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Molecular spectroscopy

Introduction :-

Spectroscopy is the branch of science dealing with the study of interaction of electro magnetic radiation with matter. Spectroscopy is one of the most powerful tools available for the study of atomic and molecular structure. The study of spectroscopy can be carried out in the following two ways.

(a) Atomic spectroscopy :-

This deals with the interaction of electro magnetic radiation with atoms which are most commonly in their lowest energy state called the ground state. e.g. Most of the monoatomic substance exist in gaseous state can able to absorb electro magnetic radiation resulting in electronic transition

(b) molecular spectroscopy :-

This deals with the interaction of electro magnetic radiation with molecules. This results in transition between rotational and vibrational levels in addition to electronic Transitions.

From the molecular spectra information may be obtained about molecular vibrations and rotations that reveal a great deal about structure of mol

Properties of Electromagnetic radiation :

Electromagnetic radiation is a form of energy that is transmitted through space at an enorm velocity. Electromagnetic radiation has the proper of electrical and magnetic component both of whic are oscilating in a plane perpendicular to each other. Electromagnetic radiation needs no supportin media. Infact it passes more readily in vaccum th in air.

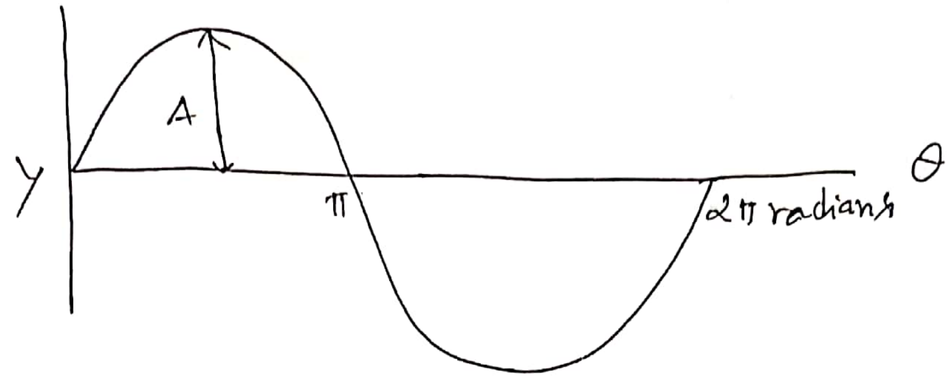
Characterization of Electromagnetic radia

Electromagnetic radiation is a simple harmoni wave propogated from a source and travelling in a straight line except when refracted or reflected. This nature of electromagnetic radiation can b compared to vibration of stretched string.

It is the fact that only the simple harmonic wave would have the properties of sine wave given as

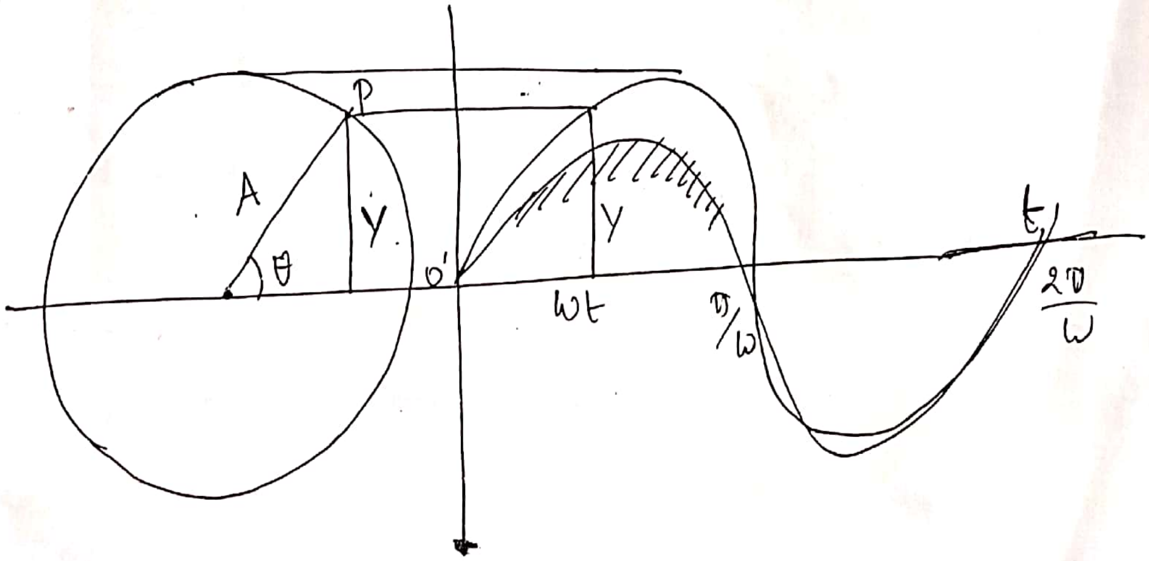
$$y = A \sin \theta .$$

A graph is obtained by plotting y versus θ radians as follows.



Here y is the displacement having maximum val 'A'. and θ is the angle varying between 0 and 360° (0 and 2π radians)

To prove the relevance of this representation, we may consider the following figure.



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Consider the left hand side of the figure and consider the point P travels with uniform angular velocity ω rad s^{-1} in a circular path of radius. If we measure the time from the instant when P passes O′ now we say that P have described an angle θ that is equal to θ = ωt radians aft time 't' seconds.

The vertical displacement can be given a

$$y = A \sin\theta \quad \left(\text{as } \sin\theta = \frac{y}{A}\right)$$

i.e. $y = A \sin \omega t$ (as θ = ωt).

By plotting this displacement against time we obtained the right hand side of the figure

After a time of $2\pi/\omega$ seconds P will return to O′ and completing a cycle.

Further cycles of P will be the repeatation of cycle with respect to time.

Frequency:-

For a complete cycle the time taken is $\frac{2}{\omega}$

Therefore for one second the number of cycles can be given as $\omega/2\pi$ (i.e. $1/(2\pi/\omega)$).

This is refered to as the frequency (ν) of the wave i.e. $\nu = \omega / 2\pi$

It is defined as the number of waves passing through a given point in a Unit time. The frequency is represented in hertz (Hz) and has the dimension of reciprocal seconds (s^{-1}).

$1\ Hz = 1\ cycle\ s^{-1}$

$1\ MHz = 10^3\ kHz = 10^6\ Hz$

Now we can write the sine wave equation as

$y = A \sin \omega t = A \sin 2\pi \nu t$ (since $\nu = \omega / 2\pi$) —— ①

This is the basic equation of w tion. So far we are concerned with displacement with time. Now we consider the displacement with distance where a term wavelength arises.

As we know that

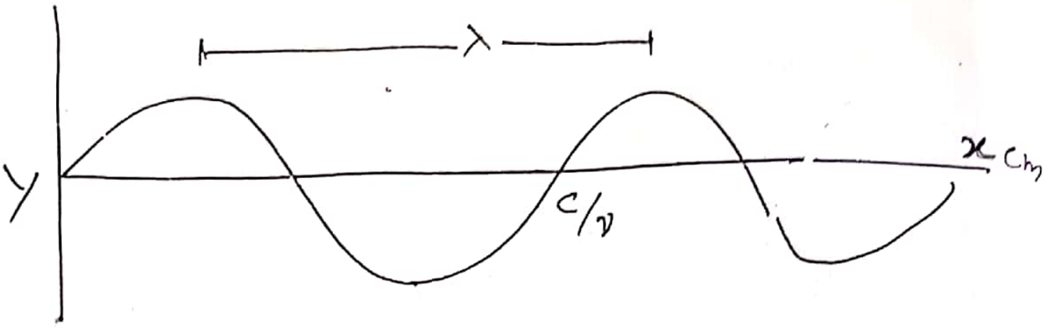
$x = ct$ ($\because c = x/t$) —— ②

Where x is the distance covered in time t at a speed 'c'.

On combining equation ① and ②

$$y = A \sin 2\pi \nu t = A \sin \frac{2\pi \nu x}{c}$$

The wave is shown in fig.



Wave length :- It is the distance travelled during a complete cycle. (or) It can be defined as the dista between two successive maxima.

When the velocity is 'c' metres per second and there are ν cycles per second, there are evidently ives in c metres. (or)

$$\nu\lambda = c \quad \text{or} \quad \lambda = c/\nu \text{ meters} \quad \text{———} ③$$

So we have

$$y = A\sin\frac{2\pi x}{\lambda} \quad (\because \nu/c = 1/\lambda) \text{ —} ④$$

The wave length can be expressed in different units

λ

For microwave region → cm / m.m

I R Region → micrometres μm/micron.

$1\,\mu m = 10^{-6}\,m.$

Visible and U.V. → $10^{-9}\,m$ ($1\,Å = 10^{-10}\,m$)

Wave number:-

The electromagnetic radiation can also be characterized in another way where the term wave number arises.

Wave number is the reciprocal of the wave length expressed in centimetres:-

$$\bar{\nu} = 1/\lambda \text{ cm}^{-1} \quad \text{———} \quad ⑤$$

Hence $$y = A \sin 2\pi \bar{\nu} x \quad \text{———} \quad ⑥$$

So we can define wave number as the number of complete waves (or) cycles in each centimetre length of radiation.

The frequency and wave number have been interrelated as

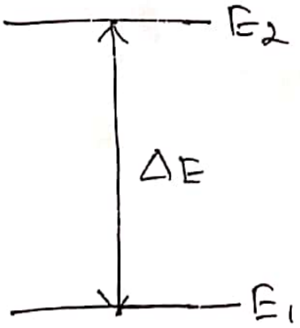
$$\nu = c\bar{\nu}$$

Where 'c' is the velocity of radiation expressed in centimetres per second (i.e 3×10^{10} cm s^{-1})

The Quantization of Energy

It was believed before 19th century that matters could take up energy continuously. In 1900 Max planck gave an revolutionary idea that the energy of an oscillator is discontinuous and any change in its energy content can occur by means of jump between two distinct energy states. The same is true for all energies of matter. A molecule in space can have rotati vibrational, electronic energy. The electron occ an orbital has definite amount of energy and it will jump to next energy level only if full quata of energy must be acquired by the electron. So the energy is quantised. In same way the rotational vibrational and other energies are also quantised.

Consider two possible energy states of a system two rotational energy levels of a molec example E_1 and E_2



Transition between these t energy levels require a defi amount of energy. $\Delta E = E_2 -$ It can either be absorbed o emitted.

Planck suggested that such energy can take the form of electromagnetic radiatio and the frequency of the radiation can be given as $\nu = \Delta E/h$ Hz (or) $\Delta E = h\nu$ Joules.

Where 'E' is the energy expressed in Joules. and 'h' is the planck constant.

$h = 6.63 \times 10^{-34}$ Joules ~~molecule~~ s molecule^{-1}

If a beam of radiation (monochromatic) is allowed to pass on a molecules which is on state 1 will jump to state 2 where the $\nu = \Delta E/h$ energy will be absorbed. The emitted radiation is tested by a detector and showed a decrease in intensity.

If the same molecule is otherwise subjected to a radiation consist of wide range of the frequencies only a particular frequency was ~~observed~~ absorbed by the molecule and resulting in change in intensity in that particular frequency of $(\nu = \Delta E/h)$. All other frequencies are left with undiminishing intensity. Thus we have the absorption spectrum. The emission spectrum would be produced in the reverse process.

The total energy involved when a gram-molecule of a substance changes its energy state

for this we multiply by Avogadro Number
$N = 6.02 \times 10^{23}$.

Regions of the spectrum:-

The electromagnetic radiation has been divi into various frequency regions. Although the boundary between the regions are not precise their interactions with molecules are different.

The increasing frequency order of the region are as follows:

1. Radio frequency Region:-

Frequency = $3\times10^{6} - 3\times10^{10}$ Hz
Wave length = 10m - 1cm.
Nuclear Magnetic Resonance (NMR) and Electron spin Resonance (ESR) spectroscopy
The energy order = 0.001 - 10 Joules/mole.

2. Microwave Region:-

Frequency = $3\times10^{10} - 3\times10^{12}$ Hz
Wave length = 1cm - 100 μm.
Rotational spectroscopy.
Energy between levels are in 100 Joules/mole.

3. Infra Red Region:-

Frequency = 3×10^{12} — 3×10^{14} Hz.
Wavelength = 100 μm – 1 μm.
Vibrational spectroscopy. Very useful to chemist
Energy = 10^4 Joules/mole.

4. Visible and Ultra violet Regions:-

Frequency = 3×10^{14} — 3×10^{16} Hz
Wavelength = 1 μm – 10 nm.
Electronic spectroscopy.
Energy = 100 s of kJoules/mole.

5. X-Ray Region:-

Frequency = 3×10^{16} — 3×10^{18} Hz
Wavelength = 10 nm – 100 pm.
Energy changes involving the inner electrons.
Energy $\approx$ 10,000 kiloJoule/mole.

6. γ- ray region:-

Frequency = 3×10^{18} — 3×10^{20} Hz
Wavelength = 100 pm – 1 pm.

(p = pico, 1 pm = 10^{-12} m)

(12)

Energy changes involve the rearrange

of nuclear particles.

Energy Range $10^9 - 10^{11}$ Joules per gram atom

Mechanism of Interaction between Elect magnetic Radiation and nuclear, molecular o electronic changes :-

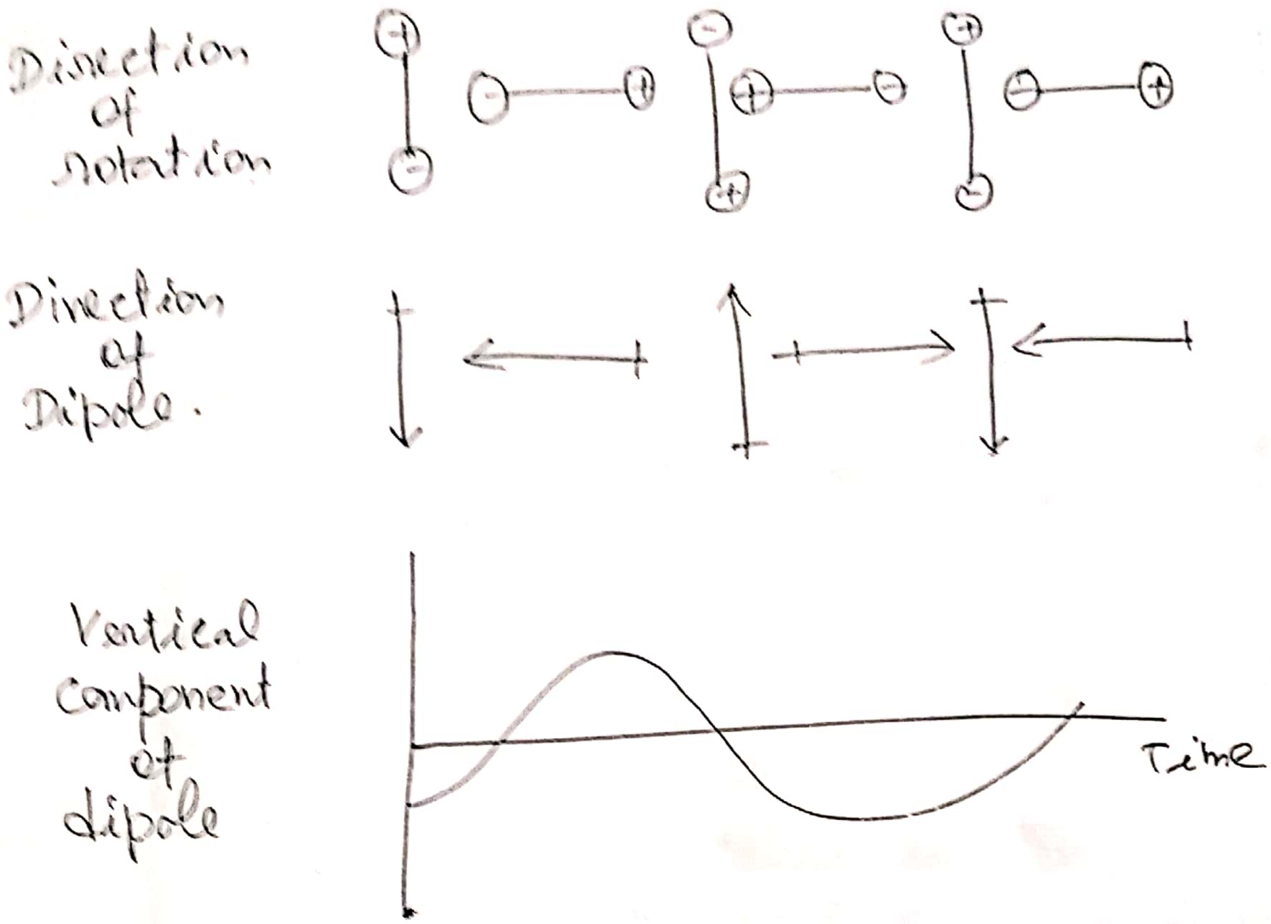
1. The Radio frequency Region :-

[illegible]

The nucleus and electron are tiny charges particles. As they spin they generate magneti field. The result is magnetic dipole moment. T correspond with the electromagnetic radiation result in resonance. So it makes absorption o emission of radiation resulting in spectrum

2. The microwave Region :-

Consider a molecule such as HCl. The o end of this molecule is +ve pole and other p is -ve. So totally it is a dipole. When this m rotating in its axis a dipole moment will b produced which will oscilate up and down plain paper that will resemble the electric fluctuation of ~~the~~ electromagnetic radia So, the interaction take place.

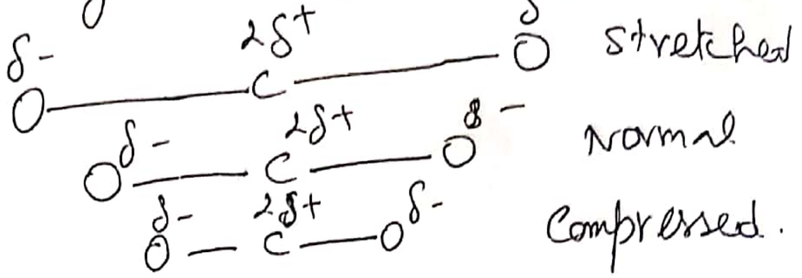


When we consider the moleculs like H_2 & Cl_2 there is no such charge separation have zero dipole. So they are microwave Inactive. So the active molecules like HCl, the interaction occur and result in emission or absorption to give rise to a spectrum.

(3) The Infra Red Region:-

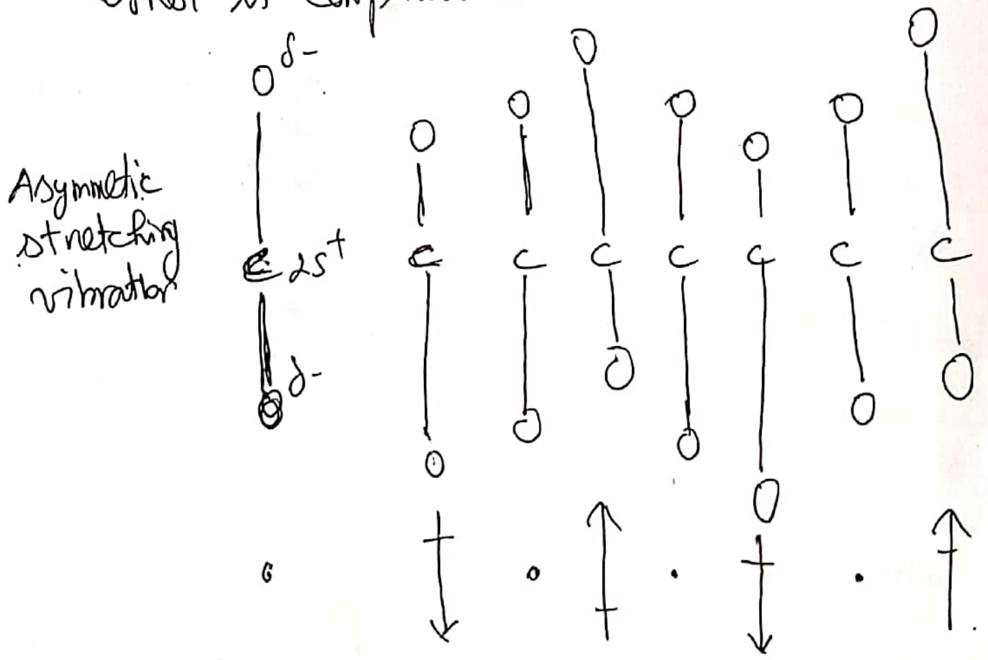
Consider the CO_2 molecule three atoms are arranged linearly with a small ~~amount of~~ net positive charge on the carbon and small negative charge on the oxygen. $\overset{\delta-}{O}—\overset{2\delta+}{C}—\overset{\delta-}{O}$

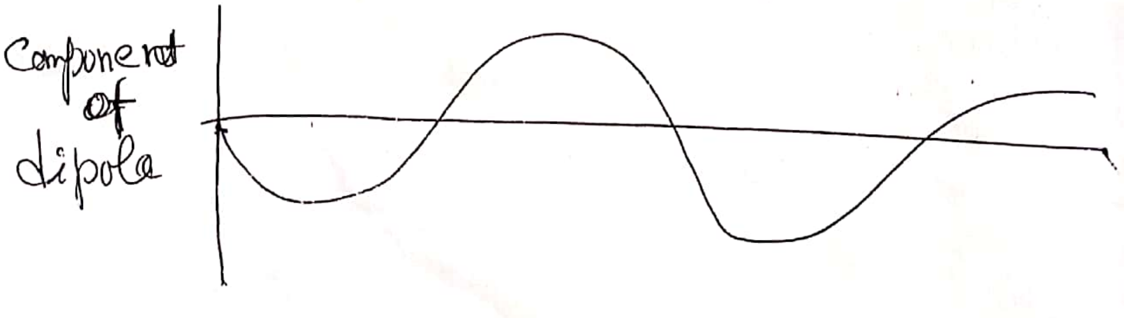
During symmetric streching, the molecule is al
stretched and compressed, both C—O bonds cha
simultaneously as in fig.



For CO_2 for symmetrical vibration, the dip
remains zero throughout the whole of this motion an
this particular vibration is infra-red inactive.

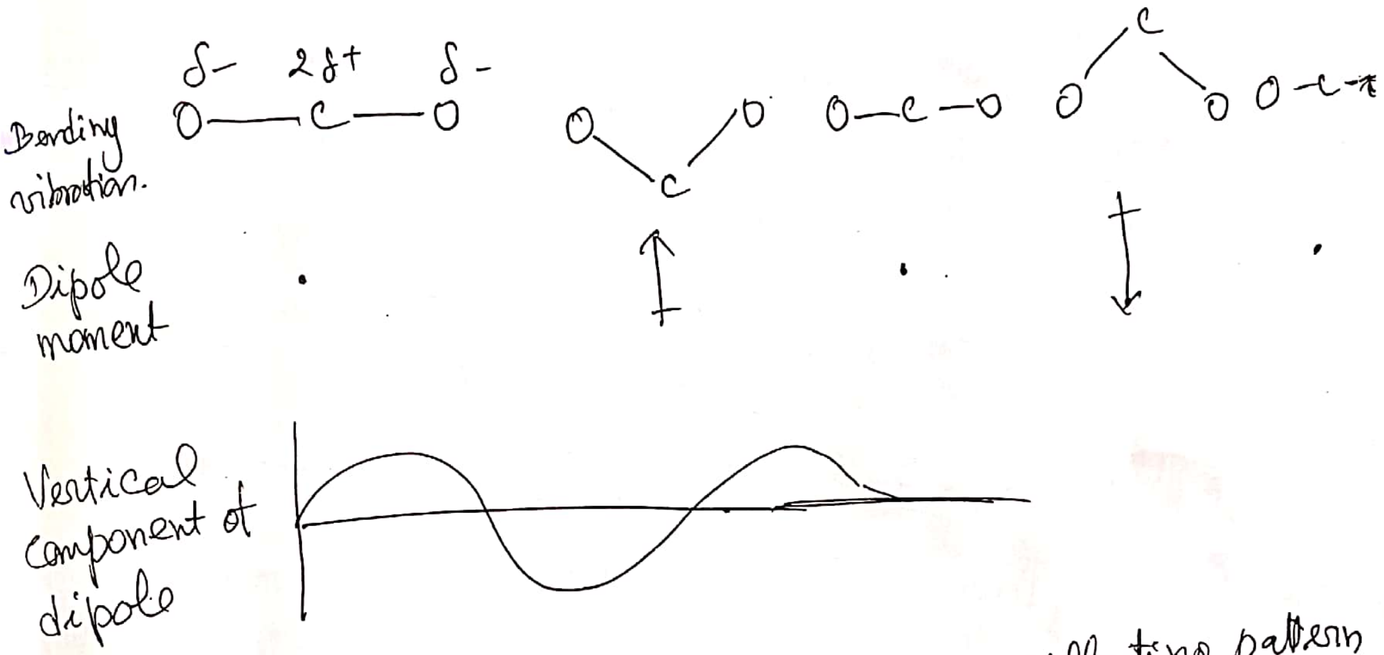
There is another streetching vibration known
asymmetric stretch. Here one band stretches while th
other is compressed and vice versa.





As the figure shows periodic alteration in the dipole moment the vibration is IR active.

One further vibration is bending mode. This is shown in figure.



This also IR active as the oscillating pattern of dipole moment resembles that of electromagnetic radiation.

④ The Visible and Ultra Violet region :

The excitation of valence electron involves the moving of electronic changes in the molecule. The consequent changes in electric dipole gives rise to a spectrum by its interaction with electric field of radiation.

⑤ For a molecule to be Raman active the electrical polarizability of the molecu must change during the motion.

Different types of molecular energies:

In addition to the translational motion, the molecules posses rotational, vibrational an electronic energies.

$$E_{internal} = E_{elec} + E_{vib} + E_{rot}.$$

(a) Rotational energy:

This energy corresponds to the rotation of molecule. It is given by the equation derived from quantum mechanics

$$E_{rot} = J(J+1)\frac{h^2}{8\pi^2 I}$$

Where I is the moment of inertia, J is rotatio quantum number. This equation is not applica to liquid phase where molecular collisions are frequent. A molecule can rotate about any coo axes. These rotations are known to be rotat degrees of freedom.

(b) Vibrational Energy :-

This energy is associated with the oscillation of atoms (or) the molecules about equilibrium position. The vibrational energy is given by the equation

$$E_{vib} = h\nu\,(V + 1/2)$$

Where ν is the vibrational frequency and V is vibrational quantum number. The increase in the vibrational motion of the molecule is also accompanied by increased rotation of the same molecule.

(c) Electronic spectroscopy.

It involves the excitation of electron from ground state to excited state (higher energy state). The excitation varies with the type of molecular bond in which electron exist.

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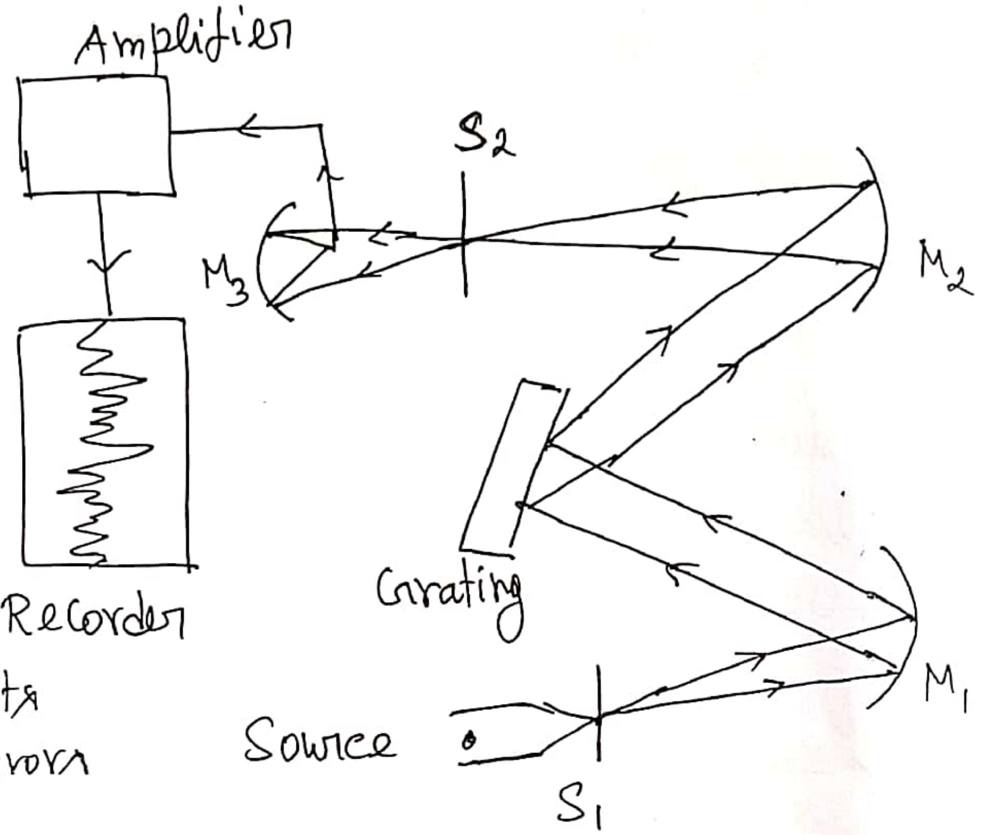
Representation of spectra

Spectrometer used for UV visible and IR regions uses a grating (a block of reflective material with a grid of parallel lines ruled on its surface) It is used to select the frequencies to pass through. Incandescent filament lamps are used as sources of radiation. The spectrometers consists of many components such as Mirrors, slits, Amplifiers, and Recorder.

The following diagram shows the operation o
spectrometer.



S_1 & S_2 - slits
M_1 & M_2, M_3 } Mirrors

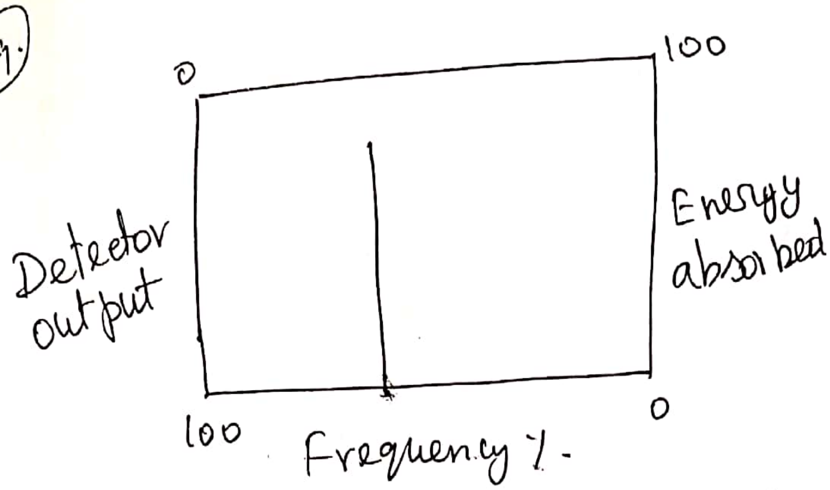
The sample may be placed anywhere in the p
Of the radiation. It is better to place near
slit S_2.

Recording of spectrum :-

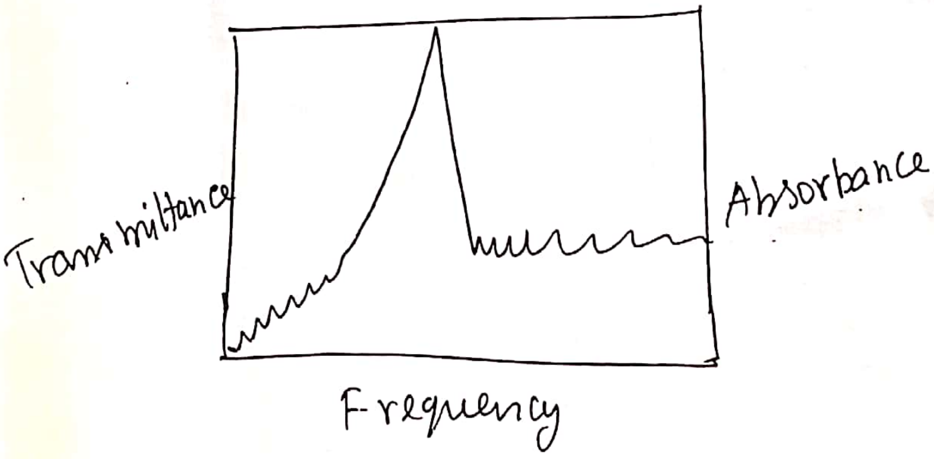
If the sample absorps energy, it would excite as $E_1 \rightarrow E_2$.

$$\nu = E_2 - E_1 / h$$

The absorption versus frequency can be re
as follows:



The above type of spectrum is seldom obtained practically. Actualy spectral lines are broadened due to many other factors. So the actual spectrum consists of small peaks and troughs due to randomly generated electrical signals in the detector, the amplifier or the pen recorder collectivily refered to as noise on the spectrum.



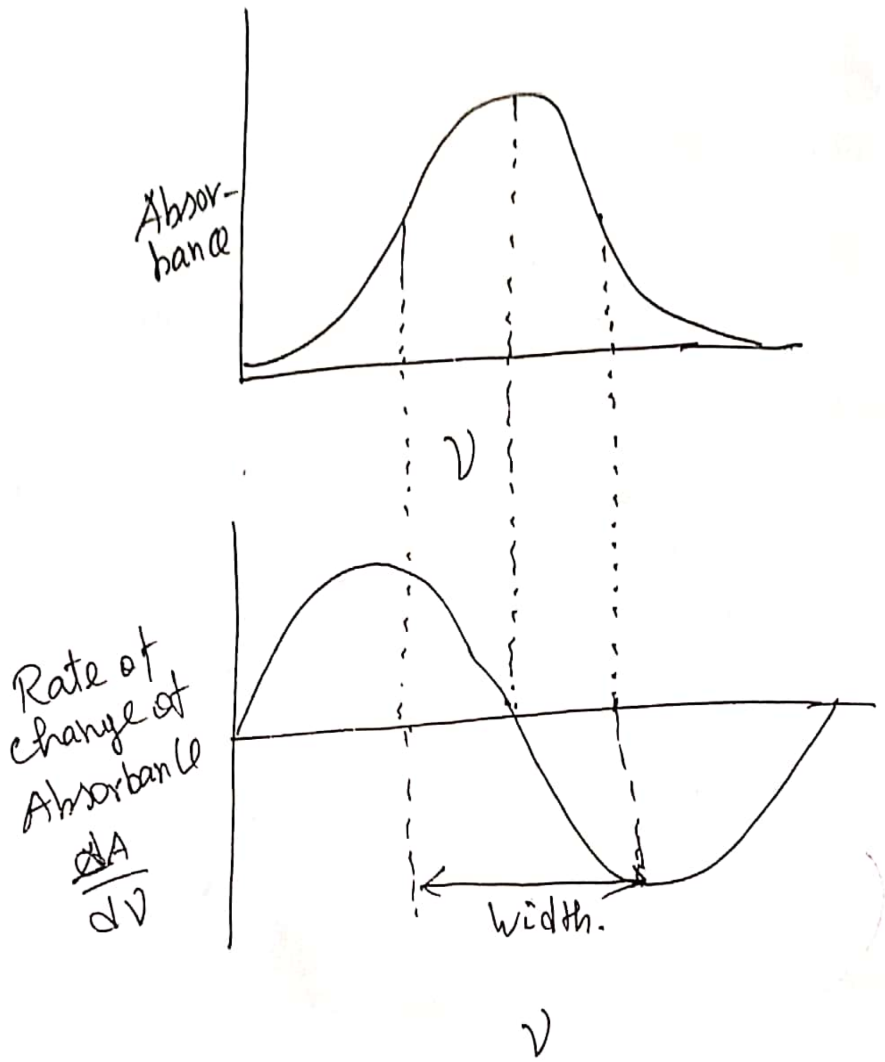
Derivative representation of spectra:-

Another form of presentation of spectra is derivative of the spectral trace. The derivative of a curve is actualy a slope given as

$\frac{dA}{d\nu}$ where A is the energy absorbed.

A derivative curve can be obtained by pl

$dA/d\nu$ versus ν



Advantages of derivative curves:-

(1) It gives exact centre point of absorption
(2) It gives exact measurement of width of p
(3.) It shows clearly the frequency differenc between the maximum and minimum of the
(4) It gives accurate measurement of relativ intensities.

Signal to Noise ratio :-

A signal may be defined as the output of a transdu that is responding to the chemical system of interest. The signal may be divided into two parts. One caused by the analyte and the other caused by other components of the sample and the instrumentation used in the measurement. The spurious electronic signals produced by the source or detector or generated in the amplifying unit causes random fluctuations in the background of the signal. These fluctuating backgrounds are referred to as noise. As concentrations decrease to trace levels or as signal source becomes weak the problem of distinguishing signals from noise becomes increasingly difficult resulting in decreased accuracy and precision measurements. The ability of an instrument system to discriminate between signals and noise is usually expressed as a signal-to-noise ratio (S/N)

$$\frac{S}{N} = \frac{\text{Average signal amplitude}}{\text{average noise amplitude.}}$$

An increase in the S/N ratio usually indicates a reduction in noise. For very weak signals, the noises are reduced using the Computer averaging Technique (CAT).

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Resolving power :-

The resolving power is a measure of perfo of a spectrometer. It can be increased by u exit slit of narrower width. For a better resolut the width should be less than the separation ~~lines~~ b the lines. Here, complication arises as it allows the total energy from the beam to reach the detecto that makes the signal inditinguishable from noi

The Intensity of spectral lines :-

The spectral intensities are concerned with ~~the~~ t factors. They are ① Transition probability ② The population ③ The concentration (or) path leng of the sample.

① Transition probability :-

It is the likelihood of a system in one stat changing to another state.

As the detailed calculation of transition p bilities involve the knowledge of quantum mechan By this, it is possible to decide whether a particula transition is forbidden or allowed.

By making use of selection rule, it is possi to decide which level transition give rise to spectral lines. Transitions which are possib according to selection rules are refered to as allowed transitions and those not possible are forbidden transitions.

The more probable transitions (allowed transitions) giving rise to more intense absorption, forbidden transitions (low probability) give absorption of very low intensity.

② Population of states:-

If there is a total of N molecules distributed between two different energy states, a lower and upper with energies E_l and E_u respectively, then the population distribution can be given by Boltzmann equation

$$\frac{N_u}{N_l} = e^{-\Delta E/kT}$$

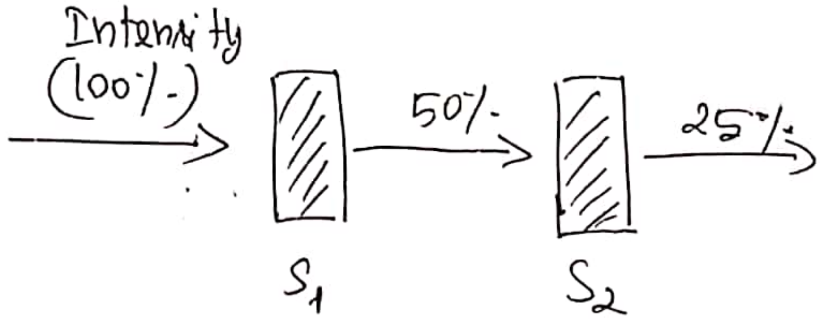
where $\Delta E = E_u - E_l$

T = Temperature in kelvin.

k = Boltzmann Constant. $= 1.38 \times 10^{-23}\ JK^{-1}$

③ Concentration (or) path length of the sample:-

When a beam of radiation is passing through a two samples S_1 and S_2 of same concentration, the absorption ~~Would be~~ by S_2 would be half that of S_1.



$S_1 = S_2$ (same concentration).

The relationship between concentration (c) pat (l) and the incident and transmitted intensitie radiation (I_0 and I respectively) can be giv by Beer-Lambert law,

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

In another form it can be written as

$$\log \frac{I_0}{I} = \varepsilon c l$$

ε = molal absorption Cof

I_0 = Intensity of the incident light

I = Intensity of transmitted light

c = Concentration of the absorbing specie g/mole

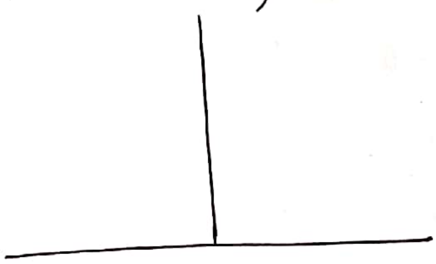
l = path length (cm)

$\log \frac{I_0}{I}$ = Absorbance 'A'.

$\therefore A = \varepsilon c l$

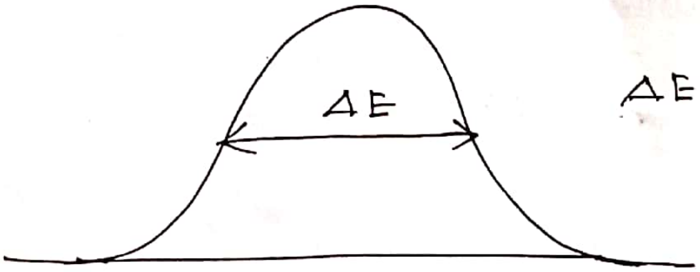
Width of spectral lines:-

Spectroscopic lines are not infinitely narrow. The figure (a) shows the spectral line of atomic (or) molecular system for which the energy levels are exactly defined. In such a case the spectral lines has no width.



(a)

But in reality the spectral lines have width because of the spontaneous emission and transition. The line width is defined to be the width at half height of the absorption line as shown below (b).



ΔE = line width.

(b)

Thus the width arises because of the energy levels of atomic and molecular systems are not precisely determined. Several factors contribute this line broadening. They are as follows.

(1) collision broadening :

Collision among atoms, molecules and ions Cau this effect. If the time of Collision between a two species X and y is long compared with m time between collisions then the energy of th absorbing or emitting species, say X, will be turbed by the electric and magnetic fields to y. consequently the spectral lines of X be broadened by this disturbance.

(2) Doppler broadening :- (Doppler shift)

Doppler shift is defined as " When a moving bod emitts radiation a stationary observer sees shifted frequency.

Doppler effect arises when the molecule measured has a Velocity 'v' relative to th Observing Instrument. If the molecule is movi away from the instrument with velocity −V, the observed frequency of radiation ν' is given by

$$\nu' = \nu\left(1 - \frac{V}{c}\right)$$

Where ν is the frequency of the radiation and 'c' velocity of light. Rearranging the equation we get

$$\frac{\nu - \nu'}{\nu} = \frac{\Delta\nu}{\nu} = \frac{V}{c}$$

$$\nu' = \nu - \frac{\nu V}{c}$$

$$\nu' - \nu = -\frac{\nu V}{c}$$

$$\nu - \nu' = \frac{\nu V}{c}$$

㉗

On the other hand if the molecule is moving toward the instrument with velocity V the observed frequency of radiation ν' (by the molecule) is given by $\nu' = \nu(1+\frac{V}{c})$ or $\frac{\nu-\nu'}{\nu} = \frac{\Delta\nu}{\nu} = -\frac{V}{c}$

Therefore depending on the direction of motion the observed frequency is shifted either toward the lower or higher frequency. that leads to spectral line broadening.

Dopplar shift is important factor for gases.

(3) Heisenberg uncertainity principle:

According to this principle if a system exists in an energy state for a limited time Δt seconds then the energy of that state will be uncertain to an extent ΔE where

$$\Delta E \times \Delta t = \frac{h}{2\pi} = 10^{-34}\ Js$$

Where 'h' is planck's Constant. Thus we see that the lowest energy ~~of a~~ state of a system is well defined since it will remain in that state for an infinite time, thus $\Delta t = \infty$ and $\Delta E = 0$. But for an example the life time of an electronic state is usually only about $10^{-8}s$ which gives a value for ΔE of about $\frac{10^{-34}}{10^{-8}} = 10^{-26}$ J.

ΔE is the energy uncertainity for a transiti
Then the Corresponding uncertainity in the assoc
radiation frequency of ΔE/h is given as

$$\Delta E \cdot \Delta t = \frac{h}{2\pi} \qquad (\because \Delta E = \Delta\nu \cdot h)$$

$$\Delta\nu = \frac{\Delta E}{h} \simeq \frac{h}{2\pi \Delta t\, h} \simeq \frac{1}{2\pi \Delta t}$$

For an example for electronic excitation, the life is given as 10^{-8}s.

$$\therefore \Delta\nu \simeq 10^{8}\ \text{Hz}$$

This is apparently large uncertainity but small Compared with the radiation (UV-visible) 10^{14} – 10 and so the natural line width is small. So fo electronic transition the line width is mostly d on Collision and Doppler broadening.

But On the other hand an excited electron state has 10^{-7}s as life time. For this the fre uncertainity is given as 10^{7} Hz. This is compar to the usual frequency of radiation 10^{8}–10^{9} Hz (R So for such transition a Heisenberg uncertaini principle is by far the most important effect.

— x —

Einstein Coefficients

Einstein Coefficients are the transition probabiliti and hence the intensities of the absorption and spontaneous processes that molecules undergo on interac with radiation.

Let us consider the interaction of light with a sample of N identical atoms. Let us assume tha each with two non-degenerate electronic states a ground state A (with energy E_A and population N_A and an excited state B (with energy E_B and populati N_B).

Therefore $N = N_A + N_B$

As the energy difference $E_B - E_A$ is greater than the thermal energy KT, the atoms do not have sufficie thermal energy to make a transition from A to B. Therefore essentially all the atoms in the sample will be in the ground state, so $N_A = N$. When the sample is exposed to electromagnetic radiation of frequency ν_{AB} where $h\nu_{AB} = E_B - E_A$. Some of the atoms will absorb light and make a Transiti from A to B.

Einstein proposed that the rate of excitati from A to B is proportional to the spectra radiant energy density ρ_ν and to N_A. The rat this excitation is given by

$$\text{rate} = -\frac{dN_A}{dt} \propto \rho_V N_A$$

(or)

$$\text{rate} = -\frac{dN_A}{dt} = \cancel{\propto}\ X_{AB}\rho_V N_A$$

Where X_{AB} is a proportionality constant call Einstein coefficient. The negative sign in the equation indicates that N_A decreases with incre time.

In the absence of any decay mechanism the of growth of the excited state population mus the negative of the rate of depletion of the g state population because $N_A + N_B$ = Constant = any time. Therefore

$$-\frac{dN_A}{dt} = \frac{dN_B}{dt} = X_{AB}\rho_V N_A \quad (\text{absorption only}$$

N_A decreases and N_B increases with increasi

Atoms do not remain in excited stat indefinitely. After a brief time, an atom em energy and returns to the ground state.

The atoms relax back to the ground state by two pathways; spontaneous emission and stimulate emission.

spontaneous emission accounts for the process by which atoms spontaneously emit a photon of energy $h\nu_{AB}$ (= $E_B - E_A$) at some time after excitati with a rate $-dN_B/dt$ depending on the excited state population N_B.

$$-\frac{dN_B}{dt} = Y_{BA} N_B \text{ (Spontaneous emission only)}$$

Y_{BA} is another Einstein Coefficient.

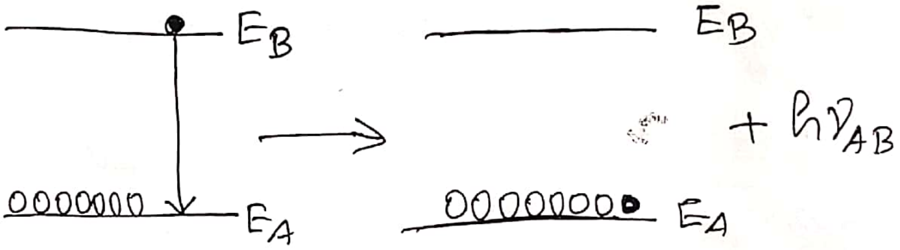
Exposure of an atom in an excited state to electromagnetic radiation energy $h\nu_{AB}$ stimulates the emission of a photon and thereby regenerates the ground state atom. The rate of this stimulated emission depends on both excited state population and spectral radiant energy density.

$$-\frac{dN_B}{dt} = X_{BA}\, \rho_\nu\, N_B \text{ (stimulated emission only)}$$

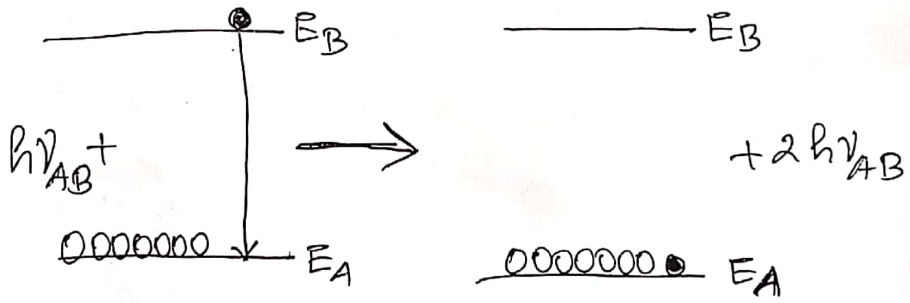
where X_{BA} is a third Einstein Coefficient. Upon exposure to light, a sample of atoms simultaneou undergoes all three processes. Thus the rate of change in the population of either the ground sta the excited state must be the sum of the slo of these three processes.

$$\frac{dN_A}{dt} = \frac{dN_B}{dt} = X_{AB}\rho_\nu N_A - Y_{BA} N_B - X_{BA}\rho_\nu$$

Spontaneous emission



Stimulated emission



When the two energy states are in thermal br

$$\frac{dN_B}{dt} = \frac{dN_A}{dt} = 0$$

From both Planck's black body distribution and Boltzmann distribution law, the value o Y_{BA} is given as follows.

$$Y_{BA} = \frac{8 h \pi V_{AB}^{3}}{c^{3}} X_{BA}$$

The net absorption intensity is given by

$$N_A X_{AB} P_V - N_B X_{BA} P_V = X_{AB} P_V (N_A - N_B)$$

Thus the intensity for a given absorption depends on the difference in the population in states A and B if P_V is kept constant.

— x —

Oscillator Strength.

A convenient parameter for expressing the intensity of an absorption band is the oscillator strength or f number.

$$f = 4.315 \times 10^{-9} \int \epsilon \, d\bar{\nu}$$

Where ϵ is the molar absorptivity and $\bar{\nu}$ is the frequency expressed in wave numbers.

The concept of oscillator strength is based on a simple classical model for an electronic transition. The expression indicates that $f = 1$ for an allowed transition.

The quantity f is evaluated graphically from the above equation by plotting ϵ versus the wave number $\bar{\nu}$ in cm^{-1} and calculating the area of band values of f from 0.1 to 1 Corresp to molar absorptivities in the range 10,00 100,000 depending on the width of the peak.

For a single symmetrical peak f can approximated by the expression

$$f \simeq (4.6\times10^{-9})\,\epsilon_{max}\,\Delta\nu_{1/2}$$

Where ϵ_{max} is the molar absorptivity of th peak maximum and $\Delta\nu_{1/2}$ is the half intens band width; i.e the width at $1/2\ \epsilon_{max}$.

Infrared spectroscopy

Energy of a diatomic molecule

The compression and extension of a bond may be likened to the behaviour of a spring and we may ~~extend the energy analogy~~ assume ~~that~~, it obeys Hooke's law. So we may write

$$f = -k(r - r_{eq})$$

where 'f' is the restoring force 'k' the force constants and 'r' the internuclear distance. In this case the energy curve is parabolic and has the form

$$E = \frac{1}{2} k (r - r_{eq})^2$$

This is the model of simple harmonic oscill It forms the starting point for the discussion of vibrational spectra.

* * *

✓ The Simple Harmonic oscillator.

The work done in stretching the spring (which represents a chemical bond) increases the potential energy of the system. The potential energy for the equilibrium length of ~~the~~ spring (or bond) is assumed to be zero.

The potential energy for any other length given by

$$P.E = \int_0^x (-F)\,dx = \int_0^x (kx)\,dx = \frac{1}{2} kx^2$$

(as $f = -k(r - r_{eq})$ $(r - r_{eq} = x)$)

where x is the displacement from the equilibrium length and k is the force constant $k = 4\pi^2 \mu \omega^2$. (Refer below).

Ref

$$\bar{\nu} = \frac{1}{2\pi c} \frac{\sqrt{k}}{\sqrt{\mu}}$$

✓

$$\sqrt{k} = \frac{\bar{\nu}\sqrt{\mu}\,2\pi}{c}$$

$$k = \frac{\bar{\nu}^2}{c^2}\mu\, 4\pi^2$$

$$k = ~~4\pi\omega^2\mu~~ \; 4\pi^2\omega^2\mu$$

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

$$\Delta E = h\bar{\nu}c = \frac{h}{2\pi}\sqrt{\frac{K}{\mu}}$$

$$\bar{\nu} = \frac{1}{2\pi \cdot c}\frac{\sqrt{k}}{\sqrt{\mu}}$$

$$\sqrt{k} = \bar{\nu}c\, 2\pi\sqrt{\mu}$$

$$k = \bar{\nu}^2 c^2 4\pi^2 \mu$$

$$= 4\pi\omega^2 \mu$$

Reference

$$\Delta E = h\bar{\nu}c = \frac{h}{2\pi}\sqrt{\frac{K}{\mu}}$$

$$\omega = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$

$$= \bar{\nu} = \frac{1}{2\pi \cdot c}\frac{\sqrt{K}}{\sqrt{\mu}}$$

$$\sqrt{K} = \bar{\nu}\cdot c\, 2\pi\sqrt{\mu}$$

$$k = \bar{\nu}^2 c^2 4\pi^2 \mu$$

$$\therefore k = \omega^2 4\pi^2 \mu$$

or

$$4\pi^2 \omega^2 \mu$$

as $\bar{\nu}.c = \nu$ ~~[illegible]~~
ω oscillato
frequ

---

contd....

At the extreme limit when $x = A$ the amplitude of vibration the kinetic energy is zero and the potential energy equals the total vibrational energy of the system. Hence for a harmonic oscillator the vibrational energy

$$E_v = P.E = \frac{1}{2}kx^2$$

$$= \frac{1}{\cancel{2}}\cancel{4}\pi^2 \mu\omega^2 A^2$$

$$= 2\pi^2\omega^2\mu A^2 \qquad ②$$

Since the classical mechanics does not restric the magnitude of A, the amplitude the vibra energy of a diatomic molecule can have any magnitude of continuously varying energy.

The quantum mechanical treatment however, only certain discrete energies for a vibrational The permissible energies of a harmonic oscilla may be obtained by solving the Schrodi equation (considering oscillations in one dim only)

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{8\pi m}{h^2}\left(E_v - \tfrac{1}{2}Kx^2\right)\psi = 0$$

The allowed energies under quantum re are given by

$$E_v = \frac{h}{2\pi}\sqrt{\frac{K}{\mu}}\left(V+\tfrac{1}{2}\right) \text{———} ④$$

$$E_v = \left(V+\tfrac{1}{2}\right)h\omega \text{———} ⑤$$

$$\text{since } \omega = \frac{1}{2\pi}\sqrt{\frac{K}{\mu}}$$

$$\text{or } \bar{\omega} = \frac{1}{2\pi c}\sqrt{\frac{K}{\mu}}$$

where V is the vibrational quantum number and can take up all positive integral values including zero $V = 0, 1, 2 \cdots$ ω is the oscillator frequency in Hz. The energy of an oscillator in the spectroscopic units cm^{-1} is

$$E_V = hc\bar{\omega}$$

$$\bar{\omega} = (V + 1/2)\frac{1}{2\pi}\sqrt{\frac{k}{\mu}} \qquad ⑥$$

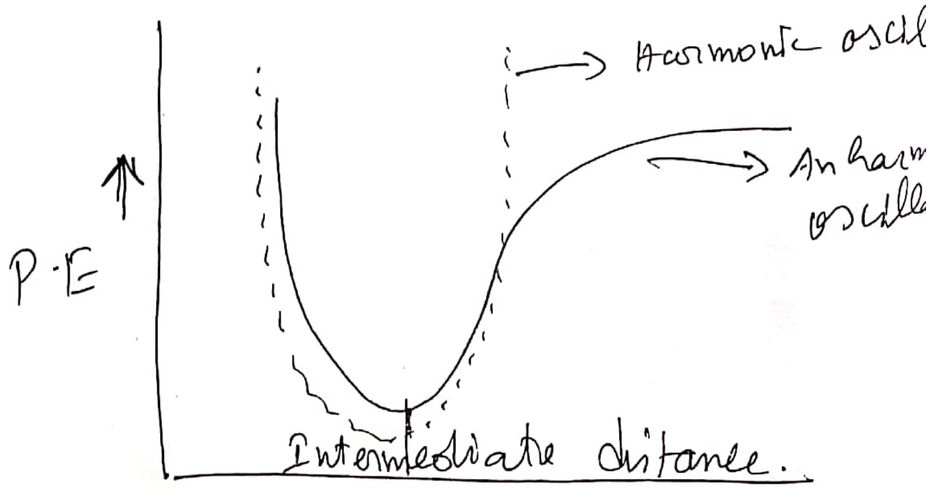
$$E_V = (V + 1/2)\bar{\omega} \text{ cm}^{-1} \qquad ⑦$$

It is seen from ⑤ that when $V = 0$, $E_0 = 1/2\, h\omega$. This energy is called zero point energy, in other words even in the lowest level $V = 0$, the molecule has some energy. So it can never be at rest. It will be undergoing vibration.

The Anharmonic oscillator.

Real molecules do not obey exactly the of simple harmonic motion. Real bonds elastic are not so homogeneous as to obey law.

If the bond between atoms is stretched instance there comes a point at which it will The molecules dissociates into atoms. For a compression and extension the bond may b as perfectly elastic. For larger amplitud greater than 10% of the bond length a more complicated behaviour must be as The following figure shows diagrammaticall shape of the energy curve for harmonic anharmonic oscillators.



The allowed vibrational energy levels for anharmonic oscillators is

$$E_v = \left(v+\frac{1}{2}\right)\bar{\omega}_e - \left(v+\frac{1}{2}\right)^2 \bar{\omega}_e x_e \quad cm^{-1} \quad \text{——} ①$$

where $\bar{\omega}_e$ is an oscillator frequency (expressed in wave number) x_e is the Corresponding ~~[illegible]~~ anharmonicity Constant.

The equation① can be written as

$$E_v = \bar{\omega}_e \left\{1 - x_e\left(v+\tfrac{1}{2}\right)\right\}\left(v+\frac{1}{2}\right) \ cm^{-1} \quad \text{——} ②$$

when compared with the energy levels of the harmonic oscillator

$$E_v = \left(v+\frac{1}{2}\right)\bar{\omega}_{osc}$$

~~multiply equation② by (v+½)~~

$$\bar{\omega}_e\left\{1 - x_e\left(v+\tfrac{1}{2}\right)\right\}\cancel{\left(v+\tfrac{1}{2}\right)} = \cancel{\left(v+\tfrac{1}{2}\right)}\bar{\omega}_{osc}$$

$$\therefore \bar{\omega}_{osc} = \bar{\omega}_e\left\{1 - x_e\left(v+\tfrac{1}{2}\right)\right\} \quad \text{——} ③$$

Thus the anharmonic oscillator behaves like the harmonic oscilator but with an oscillator frequency which decreases steadly with increasing v.

The zeropoint energy of the anharmonic oscillator can be obtained by putting $V=0$ in the eqn. ③

$$\bar{\omega}_{os} = \bar{\omega}_e \{1 - \tfrac{1}{2} x_e\} \text{ cm}^{-1} \rightarrow ④$$

~~and~~ and substitute in eqn. in ② as $V=0$

$$\mathcal{E}_{os} = \tfrac{1}{2} \bar{\omega}_e \{1 - \tfrac{1}{2} x_e\} \text{ cm}^{-1} \text{———} ⑤$$

The zero point energy for anharmonic oscillator differs slightly from that for the harmonic oscillator. The selection rules for the anharmonic oscillator are found to be.

$$\Delta V = \pm 1, \pm 2, \pm 3 \ldots$$

Most of the molecules are in the $V=0$ state. So we can restrict ourselves to the following transition.

(i) $V=0 \rightarrow V=1$ $\quad \Delta V \pm 1$ with considerable Intensity

$\Delta E = \bar{\omega}_0$ or cm^{-1}

$$\Delta E = \mathcal{E}_{V=1} - \mathcal{E}_{V=0}$$

$$= \left(1+\tfrac{1}{2}\right)\bar{\omega}_e - x_e\left(1+\tfrac{1}{2}\right)^2 \bar{\omega}_e - \left\{\tfrac{1}{2}\bar{\omega}_e\right.$$

$$\bar{\omega}_e\left(1+\tfrac{1}{2}-\tfrac{1}{2}\right) - x_e\bar{\omega}_e\left[\left(\tfrac{3}{2}\right)^2 - \left(\tfrac{1}{2}\right)^2\right]$$

$$= \bar{\omega}_e - x_e\bar{\omega}_e\left[\tfrac{9}{4} - \tfrac{1}{4}\right] = \bar{\omega}_e - x_e\bar{\omega}_e$$

$$= \bar{\omega}_e (1 - 2x_e) \text{ cm}^{-1}$$

(ii) $V=0 \rightarrow V=2$ $\Delta V = \pm 2$ With small Intensity

$$\Delta E = \left(2+\tfrac{1}{2}\right)\bar{\omega}_e - x_e\left(2+\tfrac{1}{2}\right)^2\bar{\omega}_e - \left\{\tfrac{1}{2}\bar{\omega}_e - \left(\tfrac{1}{2}\right)^2 x_e\bar{\omega}_e\right\}$$

$$= \left(\tfrac{5}{2}\right)\bar{\omega}_e - x_e\left(\tfrac{5}{2}\right)^2\bar{\omega}_e - \tfrac{1}{2}\bar{\omega}_e + \tfrac{1}{4}x_e\bar{\omega}_e$$

$$\bar{\omega}_e\left[\tfrac{5}{2}-\tfrac{1}{2}\right] - x_e\bar{\omega}_e\left[\left(\tfrac{5}{2}\right)^2-\tfrac{1}{4}\right]$$

$$= \bar{\omega}_e(2) - x_e\bar{\omega}_e\left[\tfrac{25}{4}-\tfrac{1}{4}\right]$$

$$= 2\bar{\omega}_e - x_e\bar{\omega}_e\left(\tfrac{24}{4}\right)$$

$$= 2\bar{\omega}_e - x_e\bar{\omega}_e(6)$$

$$= 2\bar{\omega}_e(1-3x_e)\ \text{cm}^{-1}.$$

Transition $V=0 \rightarrow V=2$ is called first overtone.

(iii) If $V=0 \rightarrow V=3$ $\Delta V = \pm 3$ with normally negligible intensity.

$$\Delta E = \left(3+\tfrac{1}{2}\right)\bar{\omega}_e - x_e\left(3+\tfrac{1}{2}\right)^2\bar{\omega}_e - \left\{\tfrac{1}{2}\bar{\omega}_e - \left(\tfrac{1}{2}\right)^2 x_e\bar{\omega}_e\right\}$$

$$= 3\bar{\omega}_e(1-4x_e)\ \text{cm}^{-1}.$$

Transition $V=0 \rightarrow V=3$ is called second overtone

To a good approximation, since $x_e = 0.01$ th spectral lines lie close to $\bar{\omega}_e$ $2\bar{\omega}_e$ $3\bar{\omega}_e$. The $\bar{\omega}_e$ is called the Fundamental Absorption whi those near $2\bar{\omega}_e$ and $3\bar{\omega}_e$ are called the ~~first~~ first and second overtones respectively.

Diatomic Vibrating Rotator:

For a diatomic molecule the rotational energy is in the order of 1 - 10 cm^{-1} (for HCl) while that of vibrational energy is nearly 3000 cm^{-1}. since the energies of the two motions are so different as a first approximation the molecule may be considered as to execute the rotations and vibrations independently. This is called as Born-Oppenheimer approximation which assumes that the combined rotational-vibrational energy is simply the sum of the separate energies.

$$E_{total} = E_{rot} + E_{vib} \quad \text{(Joules)}$$

$$\varepsilon_{total} = \varepsilon_{rot} + \varepsilon_{vib} \quad (\text{cm}^{-1})$$

Taking the separate expressions for ε_{rot} and ε_{vib} we have

$$\varepsilon_{J,v} = \varepsilon_J + \varepsilon_v$$

$$= BJ(J+1) - DJ^2(J+1)^2 + HJ^3(J+1)^3 + \cdots$$

$$+ \left(v+\tfrac{1}{2}\right)\bar{\omega}_e - x_e\left(v+\tfrac{1}{2}\right)^2\bar{\omega}_e \quad \text{cm}^{-1} \quad (1)$$

Initially, we shall ignore the small centrifugal distortion constants D, H etc., and hence write

$$\varepsilon_{total} = \varepsilon_{J,v} = BJ(J+1) + \left(v+\tfrac{1}{2}\right)\bar{\omega}_e - x_e\left(v+\tfrac{1}{2}\right)^2 \quad ②$$

For the two lowest vibrational levels v=0 v=1, the J values is only 1/1000 of that the separation between two levels of J in the sa in the v=0 and v=1 states.

It is shown that the selection rules for motions are same as those for each separately

$\Delta v = \pm 1, \pm 2$ etc $\Delta J = \pm 1$

A spectrum may be obtained by applying selection rules to the energy levels, considering the $v=0 \rightarrow v=1$ transitions

J' = higher
J'' = lower

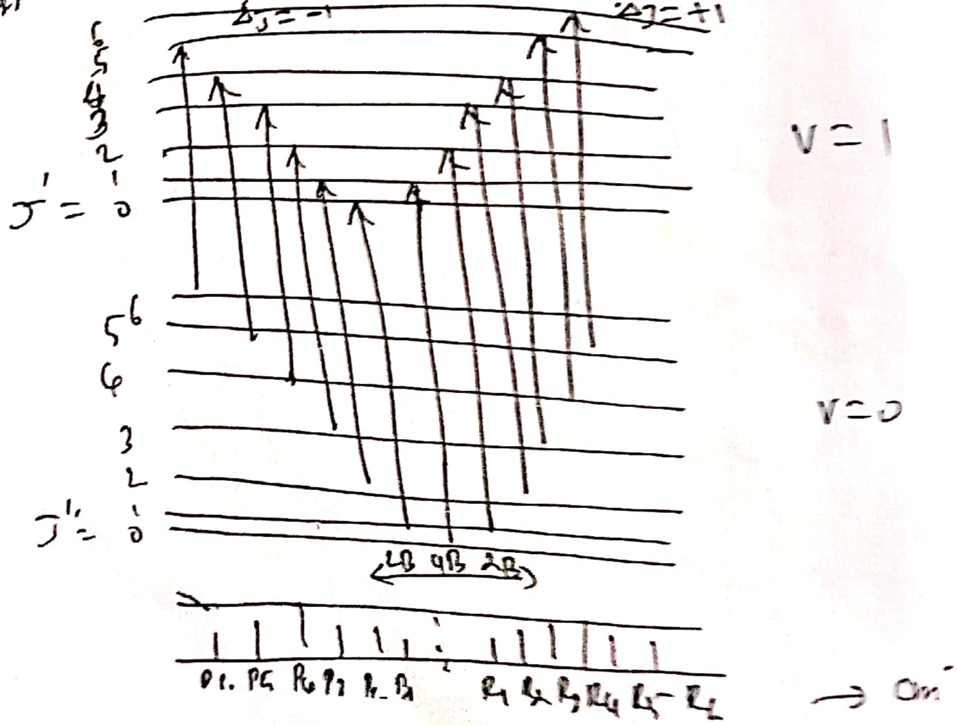
$$\Delta \varepsilon_{J,v} = \varepsilon_{J', v=1} - \varepsilon_{J'', v=0}$$

$$= BJ'(J'+1) + 1\tfrac{1}{2}\bar{\omega}_e - 2\tfrac{1}{4}x_e\bar{\omega}_e - \{BJ''(J''$$

$$+ \tfrac{1}{2}\bar{\omega}_e - \tfrac{1}{4}x_e\bar{\omega}_e\}$$

Put
$\bar{\omega}_e - 2x_e\bar{\omega}_e$
$\bar{\omega}_e(1 - 2x_e)$
$= \bar{\omega}_0$

$$= \bar{\omega}_0 + B(J' - J'')(J' + J'' + 1) \text{ cm}^{-1}$$



Taking B is identical in the upper and lower vibrational states is a direct consequence of Born-Oppenheimer approximation - rotation is unaffected by vibrational changes. So we have

(1) $\Delta J = +1$ that is $J' = J'' + 1$ (or) $J' - J'' = +1$

hence

$$\Delta \varepsilon_{J,v} = \bar{\omega}_0 + 2B(J''+1) \text{ cm}^{-1} \quad J'' = 0, 1, 2 \ldots \qquad (5)$$

(2) $\Delta J = -1$ that is $J'' = J' + 1$ or $J' - J'' = -1$ hence

$$\Delta \varepsilon_{J,v} = \bar{\omega}_0 - 2B(J'+1) \text{ cm}^{-1} \quad J' = 0, 1, 2 \ldots \qquad (6)$$

These two expressions may conveniently be combined in to

$$\Delta \varepsilon_{J,v} = \bar{\nu}_{spec} = \bar{\omega}_0 + 2Bm \text{ cm}^{-1} \quad m = \pm 1, \pm 2 \ldots \qquad (7)$$

where 'm' replacing $J''+1$ and $J'+1$ and has +ve value for $\Delta J = +1$ and -ve for $\Delta J = -1$. Note that m cannot be zero since this would imply that the values of J' or J'' to be -1. The frequency $\bar{\omega}_0$ is usually called the band origin or band centre. $\Delta J = -1$ corresponding to negative m is refered to as 'P' branch while those to the high frequency side (m positive, $\Delta J = +1$) is called R branch. ΔJ values of 0 and ± 2 also considered here.

Lines arising from $\Delta J = -2 \quad -1 \quad 0 \quad +1 \quad +2$
called O P Q R S branch

Rotation-Vibration spectrum of carbon mon

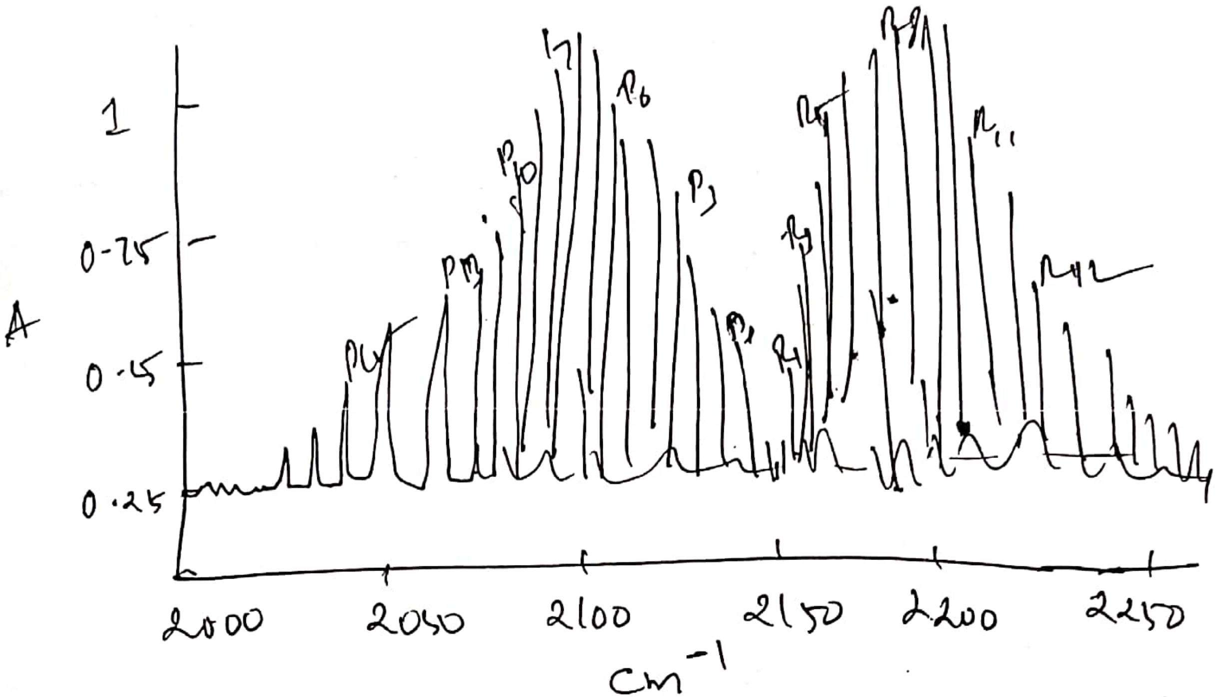
The fundamental vibration-rotation band of carbon monoxide under high resolution has been ob The oberserved wave numbers for P and R branch are given in the table.

Line	$\bar{\nu}$	Separation $\Delta\bar{\nu}$	Line	$\bar{\nu}$	Separation $\Delta\bar{\nu}$
$P_{(1)}$	2139.43		R(1)	2147.08	
		3.88			3.78
$P_{(2)}$	2135.55		R(2)	2150.86	
		3.92			3.73
$P_{(3)}$	2131.63		R(3)	2154.59	
		3.95			3.72
$P_{(4)}$	2127.68		R(4)	2158.31	
		3.98			3.66
$P_{(5)}$	2123.70		R(5)	2161.97	

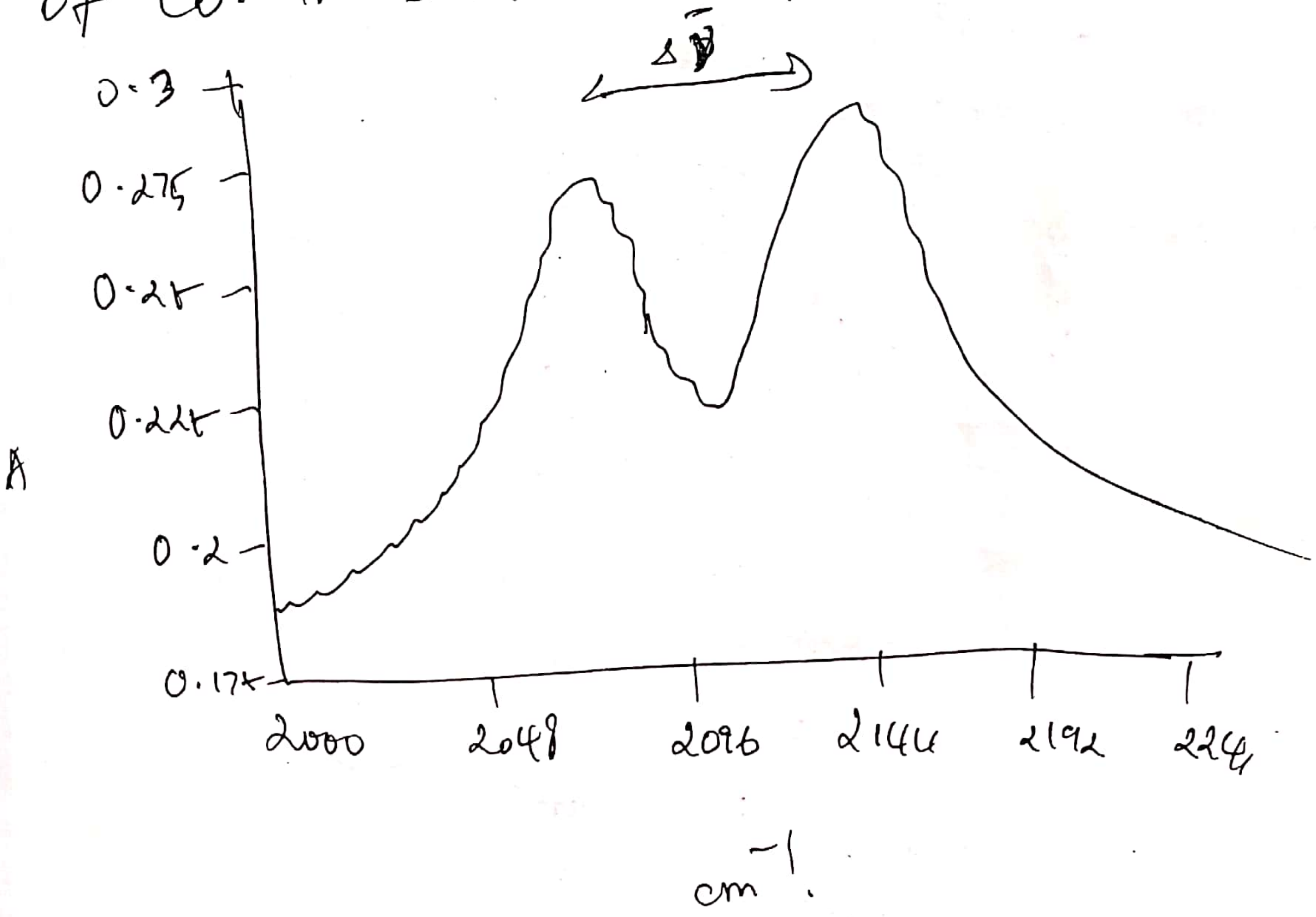
From the table we see that the band centre is at about 2143 cm^{-1}. while the average line separation near the centre is 3.83 cm^{-1}.

So $2B = 3.83\ cm^{-1}$ $\quad B = 1.915\ cm^{-1}$

This is satisfactory agreement with the value $B = 1.92118\ cm^{-1}$ derived by microwave studie It is useful to obtain good values of the rotation constant and the moment of Inertia and bond from IR spectra



The above figure is the high resolution spectrum of CO. The low resolution spectrum is given as



The separation between the two maximum Δ

given as

$$\Delta\bar{\nu} = 4B\sqrt{kT/2Bhc} + 1/2 = \sqrt{8kTB/h}$$

+

Since B is small compared with $\Delta\bar{\nu}$ we can write

$$\Delta\bar{\nu} = \sqrt{8kTB/hc} \qquad B = hc(\Delta\bar{\nu})^2/8kT$$

em

where 'c' is expressed in cms^{-1}

In the case of CO the separation is abou

55 cm^{-1} at 300 K.

— x —

Break down of the Born-Oppenheimer approximation. The interaction of Rotations and Vibrations:-

A molecule vibrates 10^3 times during a single rotation. So the bond length changes and also results in changes of moment of Inertia and 'B'. An increase in vibrational energy is thus accompanied by an increase in the vibrational amplitude and hence the value of B will depend upon the vibrational quantum number 'V'.

In the case of anharmonic vibration an increase in vibrational energy will lead to an increase in the average bond length. The rotational constant varies even more with vibrational energy.

It is evident that since r_{av} increases with vibrational energy, B is smaller in the upper vibrational state than in the lower. The equation is

$$B_v = B_e - \alpha (V + \tfrac{1}{2}) \quad \text{———} \quad ①$$

Bv is the rotational constant in vibrational level V in terms of the equilibrium value Be and α is a small positive constant for each molecule. Here we restrict our discussion to the fundamental vibrational change, i.e the change V=0 → V=1 and the respective B-values be Bo and B_1 with

$$B_0 > B_1 .$$

$B = \frac{h}{8\pi^2 I c}$

$I = mr^2$ moment of Inertia

For this transition

$$\Delta \varepsilon = \varepsilon_{J',V=1} - \varepsilon_{J'',V=0}$$

$$= \bar{\omega}_0 + B_1 J'(J'+1) - B_0 J''(J''+1) \text{ cm}$$

where as $\bar{\omega}_0 = \bar{\omega}_e(1-2x_e)$.

We have two cases

1. $\Delta J = +1$ $\quad J' = J''+1$

$$\Delta\varepsilon = \bar{\nu}_R = \bar{\omega}_0 + (B_1+B_0)(J''+1) + (B_1-B_0)($$

$(J''=0,1,2\ldots$

and

2. $\Delta J = -1$ $\quad J'' = J'+1$

$$\Delta\varepsilon = \bar{\nu}_P = \bar{\omega}_0 - (B_1+B_0)(J'+1) + (B_1-B_0)($$

$(J'=0,1,2\ldots)$

where $\bar{\nu}_P$ and $\bar{\nu}_R$ to represent the wave num of the P and R branch lines respectively. T two equations can be combined in to the exp

$$\bar{\nu}_{P,R} = \bar{\omega}_0 + (B_1+B_0)m + (B_1-B_0)m^2 \text{ cm}^{-1}$$

$(m = \pm 1, \pm 2 \ldots$

where positive m values refer to R branch a negative to P branch.

Ignoring Vibration-rotation interaction involves $B_1 = B_0$, The equation ④ simplifies to

$$\Delta \varepsilon_{J,v} = \bar{\nu}_{spec} = \bar{\omega}_0 + 2Bm \text{ cm}^{-1}$$ (Refer previous pages)

But in this consideration Since $B_1 < B_0$ the last term of equation ④ is always negative, irrespective of the sign of m and the effect on the spectrum of a diatomic molecule is to crowd the rotational lines more closely together with increasing 'm' on the R branch side, while the P branch lines become more widely spaced as (negative) m increases normally B_1 and B_0 differ only slightly and the effect is marked only for high 'm' values.

The Influence of Rotation on the spectra of poly-atomic Molecules :-

Linear molecules :-

Parallel Vibrations :- The selection rule for these is identical with that for diatomic molecules.

i.e. $\Delta J = \pm 1$ $\Delta v = \pm 1$ for single harmonic motion

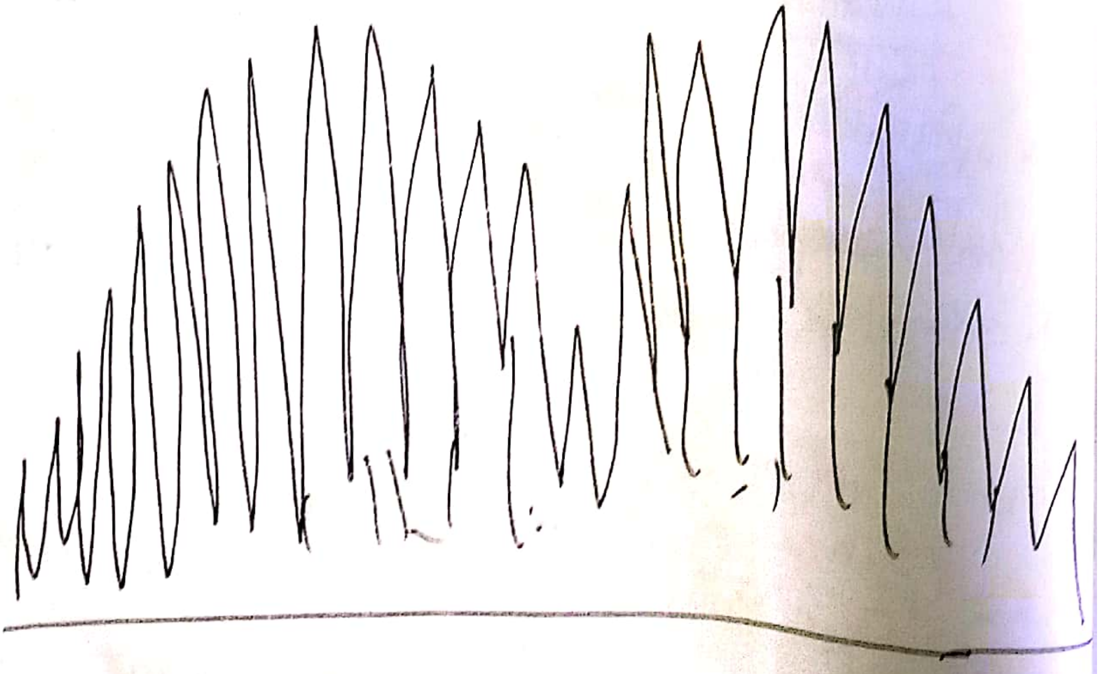
$\Delta J = \pm 1$ $\Delta v = \pm 1, \pm 2, \pm 3 \ldots$ for anharmonic motion

(since a diatomic molecule is linear and can undergo only parallel vibrations)

Here the spectra is similar in appearance, consisting

of P and R branches with lines about equally spa
on each side no line occuring at the band cen
The moment of Inertia may be considerably larger
the B value correspondingly smaller and P &
spacing will be less. The figure shows part o
spectrum of HCN, a linear molecule whose st
is H — C ≡ N. The band concerned is the symm
stretching frequency at about 3310 cm^{-1}. and
spacing is observed to be about 2.8 – 3.0 cm
near the band centre. This is to be compared
example with the spacing of about 4.0 cm^{-1} in
case of CO.

For larger molecules other than above example the value of B may be so small that sepa lines can no longer be resolved in the P and branches. It is seen that a non-linear mole cannot give rise to this type of band sha



Perpendicular Vibration :-

The selection rule for this is found to be

$\Delta v = \pm 1 \quad \Delta J = 0, \pm 1$ for simple harmonic motion.

Here it implies that a vibrational change can take place with no simultaneous rotational transition. The result is given in the figure. Transitions with $\Delta J = 0$, correspond to a Q branch whose lines may be derived from the equations.

$$\Delta \varepsilon = \varepsilon_{J,V+1} - \varepsilon_{J,V}$$

$$= 1\tfrac{1}{2}\bar{\omega}_e - 2\tfrac{1}{4}x_e\bar{\omega}_e + BJ(J+1)$$

$$- \left\{ \tfrac{1}{2}\bar{\omega}_e - \tfrac{1}{4}x_e\bar{\omega}_e + BJ(J+1) \right\}$$

$$= \bar{\omega}_e \text{ cm}^{-1}. \text{ for all } J.$$

Thus the Q branch consists of lines superimposed upon each other at the band centre $\bar{\omega}_e$, one contribution arising for each of the populated J values. The resultant line is usually very intense. (Figure next page)

If we take into account the fact that the B values differ slightly in the upper and lower vibrational states, we would write

$$\Delta \varepsilon = \varepsilon_{J,V+1} - \varepsilon_{J,V}$$

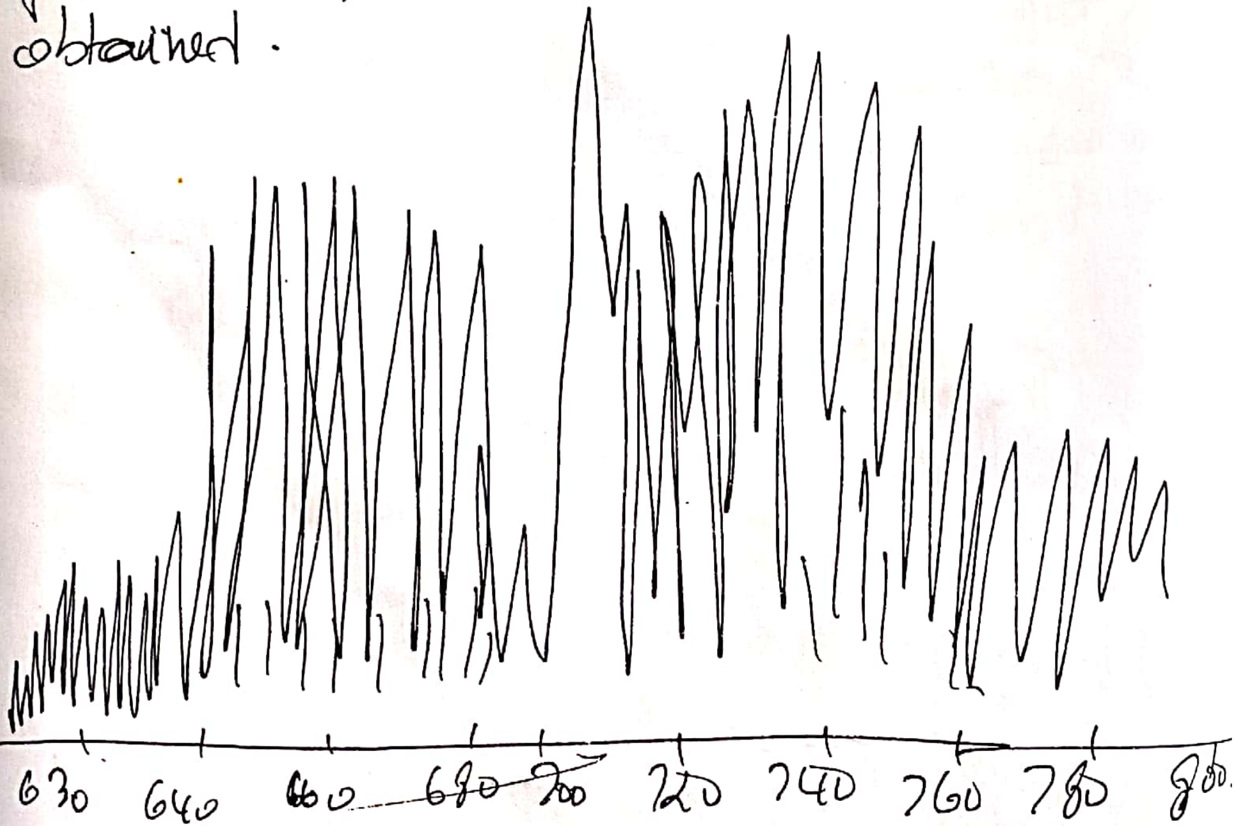
$$=$$

$$= 1\tfrac{1}{2}\bar{\omega}_e - 2\tfrac{1}{4}x_e\bar{\omega}_e + B'J(J+1) - \left\{\tfrac{1}{2}\bar{\omega}_e - \tfrac{1}{4}x_e\bar{\omega}_e + B''(J+1)\right\}$$

$$= \bar{\omega}_e + J(J+1)(B' - B'')$$

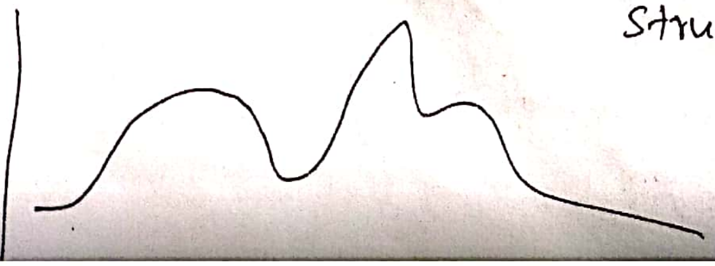
Further we see that if $B' < B''$ the Q branch line would split into a series of lines on the low frequency side of $\bar{\omega}_e$ (since $B' - B''$ is negative)

It is remembered that poly-atomic molecules with zero dipole moment do not give rise to pure rota spectra in the microwave region (eg CO_2, $CH \equiv CH$ such molecules show vibrational spectra in the Infra red region (or Raman). If they exhibit resolved fine structure, the moment of inertia can be obtained.



Structure of bending

of H



Symmetric top molecules

Applying the Born-Oppenheimer approximation as the total energy is sum of separate energies of Rotation and vibration.

$$\varepsilon_{vib} = (v+\tfrac{1}{2})\bar{\omega}_e - (v+\tfrac{1}{2})^2 x_e\bar{\omega}_e \ \text{cm}^{-1}$$

$(v=0,1,2,3\ldots)$

and the rotational levels

$$\varepsilon_{rot} = BJ(J+1) + (A-B)K^2 \ \text{cm}^{-1}$$

$$[J=0,1,2\ldots \quad K = J, (J-1), (J-2)\ldots -J]$$

Thus

$$\varepsilon_{Jv} = \varepsilon_{vib} + \varepsilon_{rot} = (v+\tfrac{1}{2})\bar{\omega}_e - (v+\tfrac{1}{2})^2 x_e\bar{\omega}_e$$

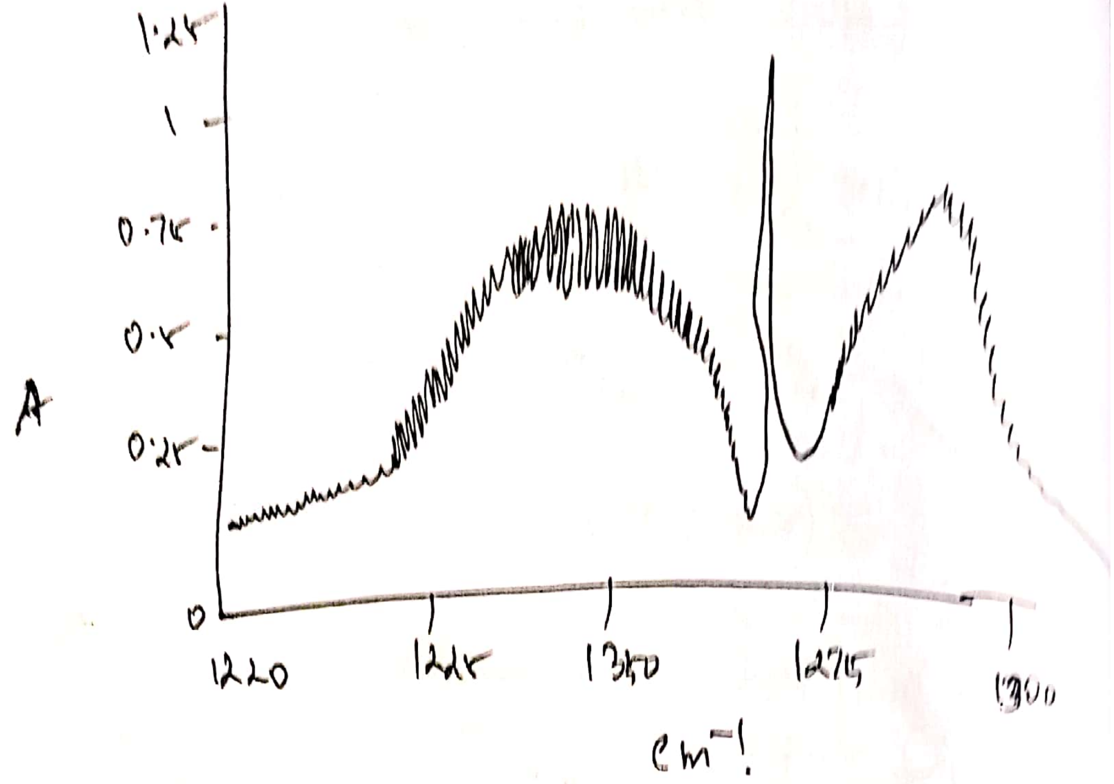
$$+ BJ(J+1) + (A-B)K^2 \ \text{cm}^{-1}.$$

Parallel vibrations:-

The selection rule is

$$\Delta v = \pm 1 \quad \Delta J = 0, \pm 1, \quad \Delta K = 0$$

Since $\Delta K = 0$ terms in K will be identical in the upper and lower state and the spectral frequencies will be independent of K. The situation is identical to the perpendicular vibrations of linear molecule



The spectrum will contain P, Q, and R b with a P,R line spacing of 2B (which is unli to be resolved) and a strong central Q br The spectrum of CH_3I is shown above. Th intensity of the Q branch (relative to li in the P and R branches) varies with the ra I_A/I_B in the limit, when $I_A \rightarrow 0$ the sy top becomes a linear molecule and the Q has zero intensity.

Perpendicular Vibrations:

For these the selection rule is

$\Delta V = \pm 1 \quad \Delta J = 0, \pm 1 \quad \Delta K = \pm 1$

(i) $\Delta J = \pm 1$ $\Delta k = \pm 1$ (R branch lines)

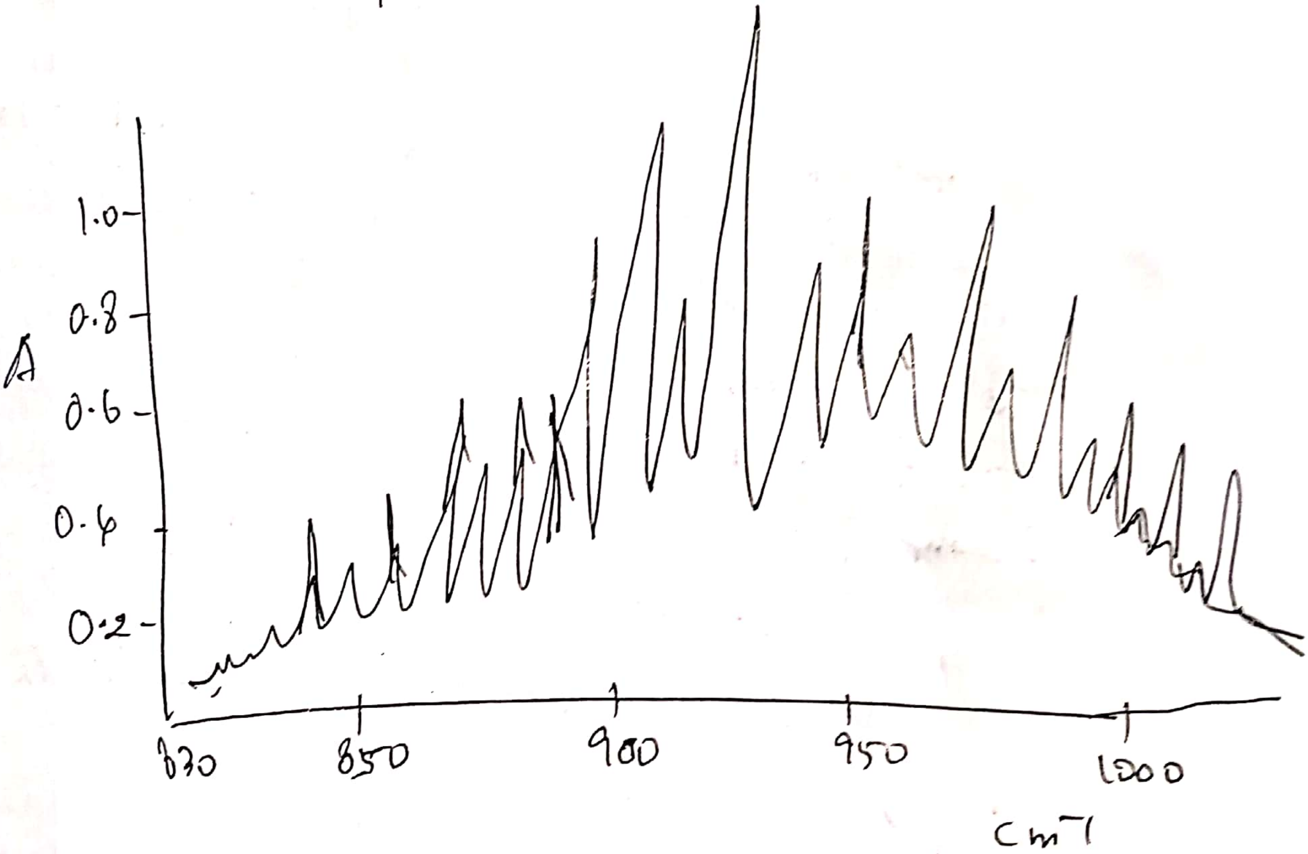
$$\Delta E = \bar{\nu}_{spec} = \bar{\omega}_e + 2B(J+1) + (A-B)(1 \pm 2k)\ \text{cm}^{-1}$$

(ii) $\Delta J = -1$ $\Delta k = \pm 1$ (p branch lines)

$$\bar{\nu}_{spec} = \bar{\omega}_e - 2B(J+1) + (A-B)(1 \pm 2k)\ \text{cm}^{-1}$$

(iii) $\Delta J = 0$ $\Delta k = \pm 1$ (Q branch lines)

$$\bar{\nu}_{spec} = \bar{\omega}_e + (A-B)(1 \pm 2k)\ \text{cm}^{-1}$$



Here we see that this type of vibration gives many sets of p and R branch lines since for each J value there are many allowed values of K (K = J, J−1 …. −J). The wings of the spectrum being quite complicated as they have periodical variation as strong weak, weak strong … The Q branch appears separated as a series of maxima above the P-R

—o—

The influence of Nuclear spin:-

The centre of symmetry possesed by some like CO_2, ethylene ($O=C=O$, $H-C\equiv C-H$) has an effect on the intensity of alternate in the P and R branches. This effect is due the existence of nuclear spin and is an additional factor determining the popula of rotational levels. In the case of CO_2 eve alternate rotational level is completely unoc and so alternate lines in the P and R branches zero intensity. This leads to a line spac of 4B instead of 2B (usual). This is expla by isotopic molecule $^{18}O—C—O^{16}$. Here there is no longer a centre of symmetry nucl spin does not now affect the spectrum and the line spacing is found to be just half that for normal CO_2.

In the case of acetylene, alternate leve have population which differ by a factor of so that the P and R branch lines show a strong, weak, strong, weak... alternation in intensity as shown in figure (Refer previous titl

Raman Spectra

Rotational Raman spectra of Linear molecules:-

In Raman spectroscopy, the precision of the measurements does not normally warrant the ~~rotation~~ retention of the term involving D, the centrifugal constant. So we take the simpler equation excluding D

$$\mathcal{E}_J = BJ(J+1)\ \text{cm}^{-1} \quad (J = 0, 1, 2 \cdots)$$

The selection rule for this is

$$\Delta J = 0 \text{ or } \pm 2 \text{ only.}$$

The selection rule for Rotational Raman spectroscopy is in contrast with that of microwave spectroscopy where in the selection rule is $\Delta J = \pm 1$. Due to the symmetry of the polarizability ellipsoid the rotation ~~chan~~ quantum number changes by 2 units not by 1 unit.

For the following consideration the selection rule $\Delta J = -2$ can be ignored since, for pure rotational change, the upper state quantum number must necessarily be greater than that in the lower state. Further $\Delta J = 0$ is trivial since it represents no change in the molecular energy and hence Rayleigh scattering only.

Now we consider only

$\Delta J = +2$

$$\Delta J = \varepsilon_{J'=J+2} - \varepsilon_{J''=J}$$

$$= B(4J+6)\ \text{cm}^{-1}$$

Since $\Delta J = +2$, we may label these lines S br lines and write

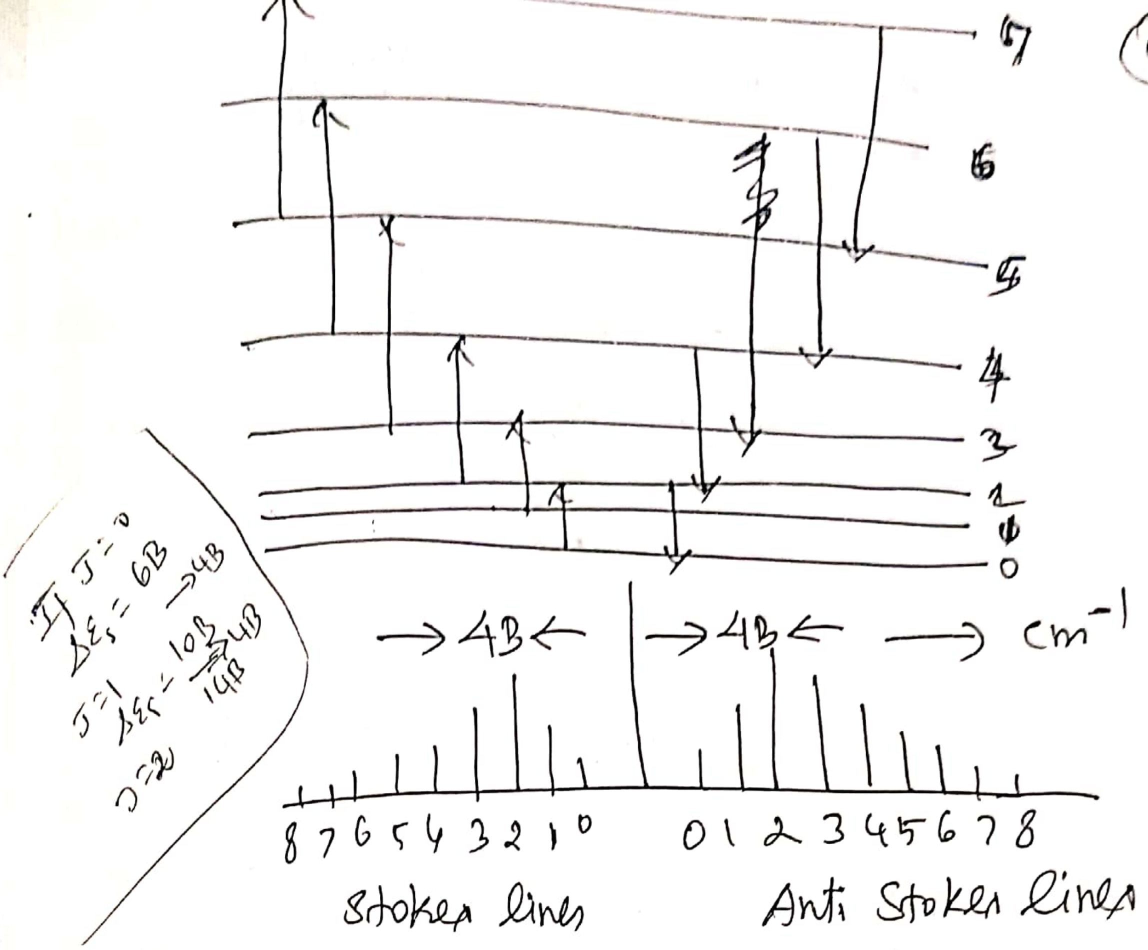
$$\Delta\varepsilon_S = B(4J+6)\ \text{cm}^{-1} \quad (J = 0, 1, 2 \ldots)$$

The wave numbers of the corresponding spectral are given by

$$\bar{\nu}_S = \bar{\nu}_{ex} \pm \Delta\varepsilon_S = \bar{\nu}_{ex} \pm B(4J+6)\ \text{cm}^{-1}$$

where the + line refers to antistokes lines, th minus to stokes lines. $\bar{\nu}_{ex}$ is the wave numb of the exciting radiations.

The allowed transitions and the Raman sp are shown in the diagram. It should be not that Stokes and anti stokes lines have compar intensity because many rotational levels a populated.



For diatomic and light triatomic molecules the rotational Raman spectrum will normally be resolved and 'B' value can be obtained. Hence the moment of Inertia and bond lengths can be obtained.

It is noted that the homonuclear diatomic molecules give no infrared or microwave spectra since they possess no dipole moment. But they give a rotational Raman spectrum. So the Raman spectrum is useful to obtain the data unavailable in previous techniques.

$B = \frac{h}{8\pi^2 Ic}$

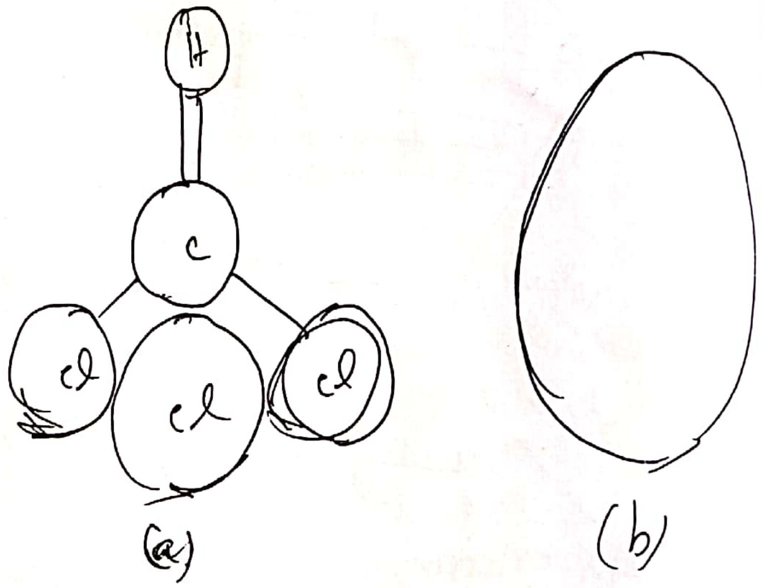
$I = m_1 r_1^2 + m_2 r_2^2$

$= \mu r^2$

r = bond length

Symmetric top molecules:-

The polarizability ellipsoid for a symmetric top molecules, for example $CHCl_3$, is given as follows.



(a) (b)

In general rotation about the top axis produ no change in the polarizability but end-ove rotation will produce such change.

$$\mathcal{E}_{J,K} = BJ(J+1) + (A-B)K^2 \quad cm^{-1}$$

$J = 0, 1, 2 \ldots \quad K = \pm J,$

The selection rules for Raman spectra are

$\Delta K = 0 \qquad \Delta J = 0, \pm 1, \pm 2$ (Except for states wher $\Delta J = \pm 2$

K is the rotational quantum number of a rotation so the selection rule $\Delta K = 0$ impl that changes in the angular momentum about the t axis will not give rise to Raman

So it is Raman inactive.

Now we consider two cases

(1) $\Delta J = +1$ (R branch lines)

$$\Delta \mathcal{E}_R = \mathcal{E}_{J'=J+1} - \mathcal{E}_{J''=J}.$$

$$= 2B(J+1)\ cm^{-1}$$

$(J = 1, 2, 3 \ldots$ but $J \neq 0)$

(2) $\Delta J = +2$ (S branch lines)

$$\Delta \mathcal{E}_S = \mathcal{E}_{J'=J+2} - \mathcal{E}_{J''=1}$$

$$= B(4J+6)\ cm^{-1}$$

$(J = 0, 1, 2 \ldots)$

Thus we have two series of lines in the Raman spectrum.

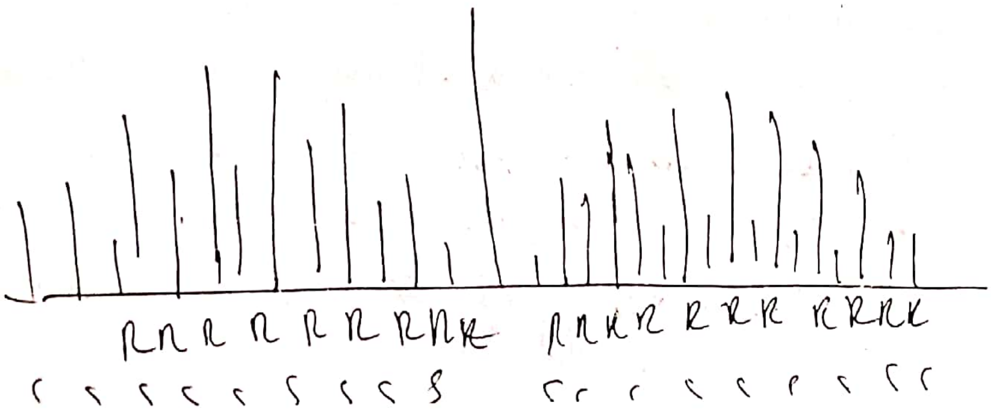
$$\bar{\nu}_R = \bar{\nu}_{ex} \pm \Delta\mathcal{E}_R = \bar{\nu}_{ex} \pm 2B(J+1)\ cm^{-1}$$

$(J = 1, 2, 3 \ldots)$

$$\bar{\nu}_S = \bar{\nu}_{ex} \pm \Delta\mathcal{E}_S = \bar{\nu}_{ex} \pm B(4J+6)\ cm^{-1}$$

$(J = 0, 1, 2 \ldots)$

The complete spectrum is given as



✓ Vibrational Raman Spectra :-

For every vibrational mode, the expression can written as

$$\varepsilon = \bar{\omega}_e (v+1/2) - \bar{\omega}_e x_e (v+1/2)^2 \quad cm^{-1}$$

$$(v = 0, 1, 2 ..$$

where $\bar{\omega}_e$ = vibrational frequency.

x_e = Anharmonicity Constant

The selection rule is $\Delta V = 0, \pm 1, \pm 2 ...$

This is same for Raman as for IR spectra the probability of $\Delta V = \pm 2, \pm 3 ...$ decreas rapidly.

Particularly we take into consideration to Ra active modes the selection rule is to be ap as follows:-

$V = 0 \longrightarrow V = 1$; $\Delta E_{fundamental} = \bar{\omega}_e (1-$

$V = 0 \longrightarrow V = 2$; $\Delta E_{overtone} = 2\bar{\omega}_e (1-$

$V = 0 \longrightarrow V = 2$; $\Delta E_{hot} = \bar{\omega}_e (1-4$

Since the Raman scattered light is very weak intensity, the overtones and hot b can be ignored completely. Now we ~~ea~~ ex Raman lines corresponding to fundamental vibrations only.

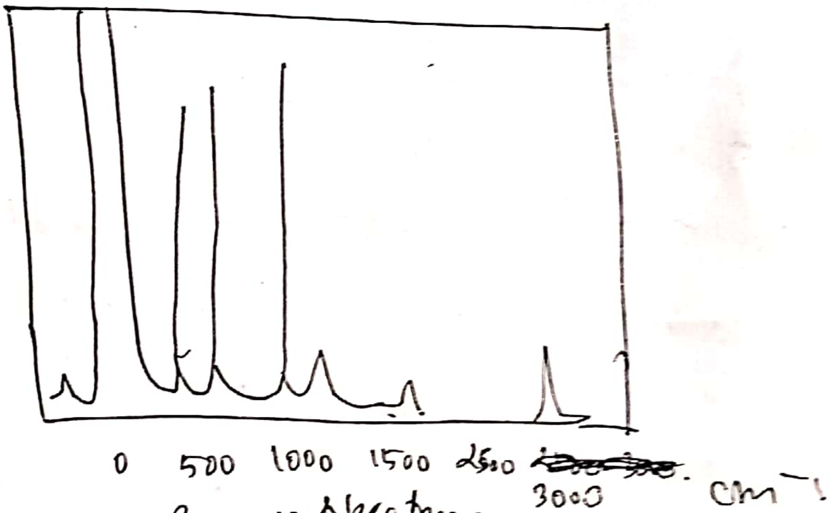
$$\bar{\nu}_{fundamental} = \bar{\nu}_{ex} \pm \Delta\varepsilon_{fundamental} \ cm^{-1}.$$

Also the Raman lines appear at distances from the exciting line corresponding to each active fundamental vibration.

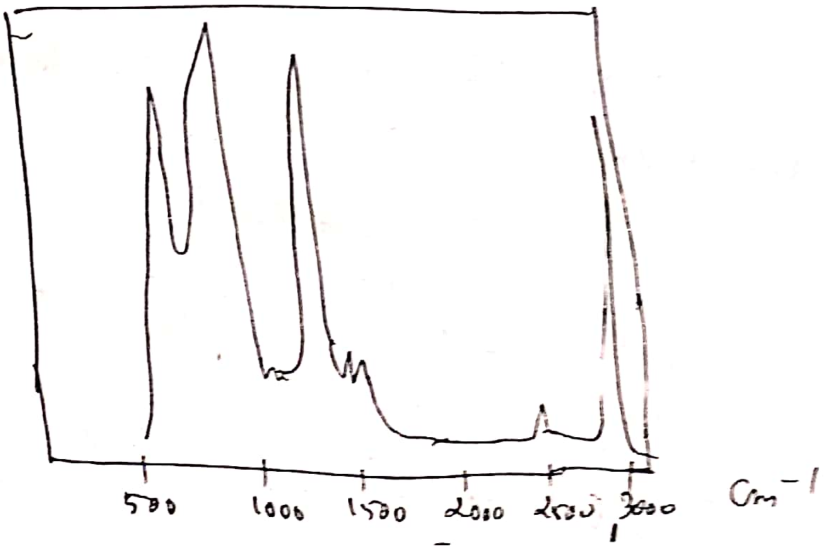
In the above expression the − sign represents the stokes lines and + sign represents antistokes lines. The latter are very weak. (not observed)

The vibrational Raman spectrum is simple and show a series of intense lines to the low-frequency side of the exciting line with a much weaker, mirror image series on the high frequency side.

As an example the Raman spectrum of chloroform $CHCl_3$ a symmetric top molecule is shown in the figure.



Raman spectrum



In the Raman spectrum the Raman lines appea at 262, 366, 668, 761 1216 and 3019 cm⁻¹. on the low frequency (stokes) side of the exciting line and a at 262 cm⁻¹ on the antistokes - high frequency side For comparison the IR spectrum is also given. It shows lines appear at wave numbers correspondi very precisely with those of lines in the Raman spectrum but with very different relative inten

— × —

Rotational fine Structure

~~Raman spectra~~ The Rotational fine structur of Raman spectra is very rarely resolved excep in the case of diatomic molecules. For the dia molecules we can write

$$\varepsilon_{J,V} = \bar{\omega}_e (v+1/2) - \bar{\omega}_e x_e (v+1/2)^2 + BJ(J$$

cm

(v = 0, 1, 2 ... ; J = 0, 1,

As in the previous case, we ignore centrifugal stortion. For diatomic molecules the J selec ule $\Delta J = 0, \pm 2$ (Refer previous titles) and ombining this with the vibrational change $v = 0 \rightarrow v = 1$, we have

$\Delta J = 0$ $\quad \Delta\varepsilon_Q = \bar{\nu}_0$ cm⁻¹ (for all J)

$\Delta J = +2$; $\quad \Delta\varepsilon_S = \bar{\nu}_0 + B(4J+6)$ cm⁻¹

$\Delta J = -2$. $\quad \Delta\varepsilon_O = \bar{\nu}_0 - B(4J+6)$ cm⁻¹ $\quad J = 0, 1, 2$

where $\bar{\nu}_0 = \bar{\omega}_e(1-2x_e)$ and O, Q, S in the subscripts represents O, Q and S branches respectively.

$$\bar{\nu}_Q = \bar{\nu}_{ex} - \Delta\varepsilon_Q = \bar{\nu}_{ex} - \bar{\nu}_0 \ \text{cm}^{-1} \quad (\text{for all } J)$$

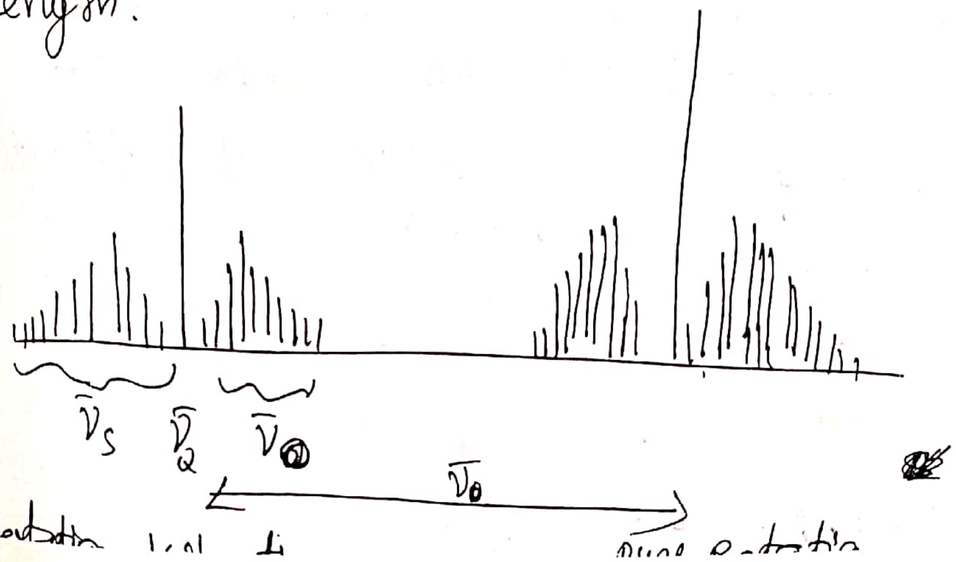
$$\bar{\nu}_O = \bar{\nu}_{ex} - \Delta\varepsilon_O = \bar{\nu}_{ex} - \bar{\nu}_0 + B(4J+6) \ \text{cm}^{-1}$$

$$(J = 2, 3, 4 \ldots)$$

$$\bar{\nu}_S = \bar{\nu}_{ex} - \Delta\varepsilon_S = \bar{\nu}_{ex} - \bar{\nu}_0 - B(4J+6) \ \text{cm}^{-1}$$

$$(J = 0, 1, 2 \ldots)$$

The Raman spectrum containing rotational fine structure is given in the figure. The presence of the strong Q branch in the Raman spectrum is to be noted and compared with the P and R branches only which occur for a diatomic molecule in the Infra-red. The analysis of the O and S branches in the Raman spectrum to give a value for 'B' and hence for the moment of Inertia and bond length.



$\bar{\nu}_0$ = fundamental frequency

Electronic Spectra

Electronic spectra of Diatomic molecules:-

The total energy of an individual gas-phase molecule is made up of four different types. They are Translational, rotational, vibrational and electronic. Of the four types of molecular energies rotational, vibrational and electronic energies are quantised. i.e. They have quantum restrictions.

Born-Oppenheimer approximation:- ⓧ

According to this approximation ~~By this~~ the three types of quantised molecular energies can be treated separately. We can write as

$$E_{total} = E_{electronic} + E_{vibrational} + E_{rotation}$$

which implies that the electronic, vibrational and rotational energies of a molecule are completely independent of each other.

A change in the total energy of a molecule may then be written as

$$\Delta E_{total} = \Delta E_{ele} + \Delta E_{vib} + \Delta E_{rot} \quad J$$

(or)

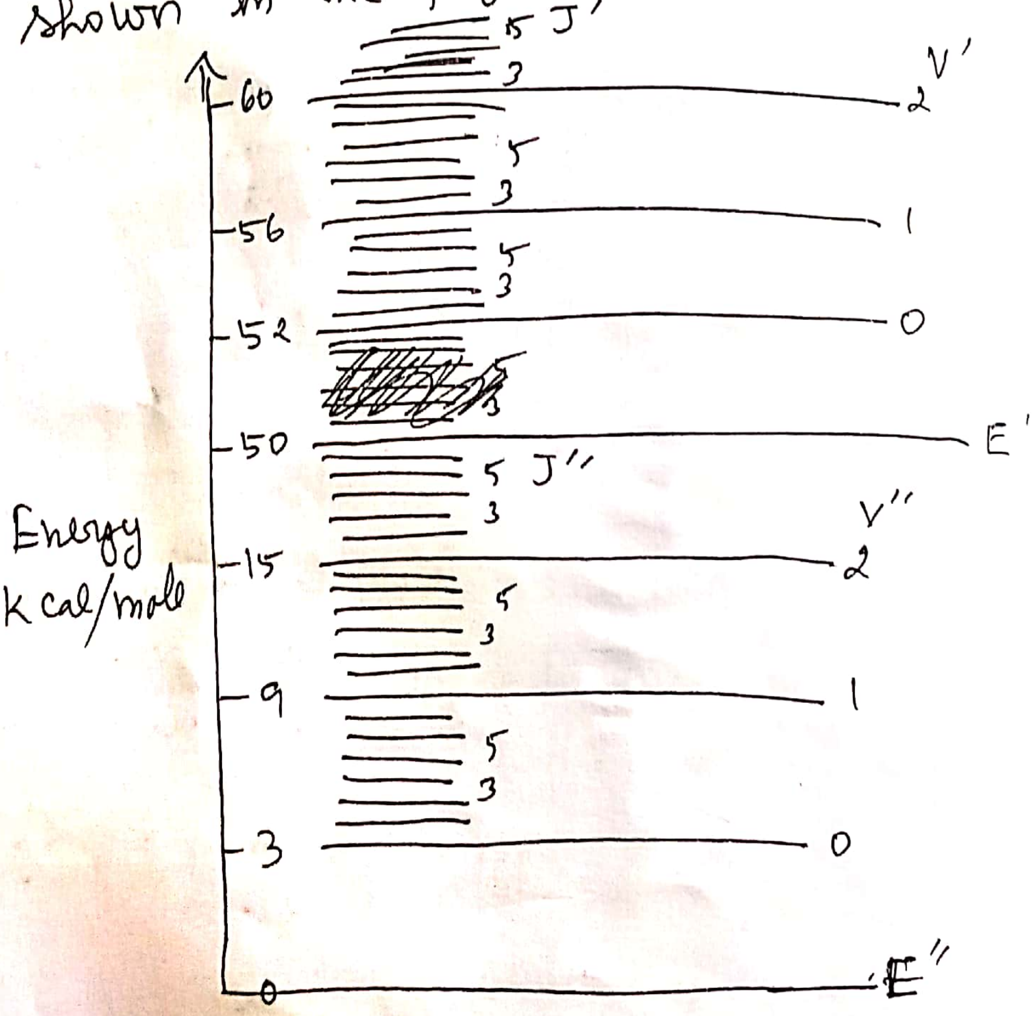
$$\Delta E_{total} = \Delta E_{ele} + \Delta E_{vib} + \Delta E_{rot} \quad cm^{-1}.$$

The approximate orders of magnitude of changes are

$$\Delta E_{elec} \simeq \Delta E_{vib} \times 10^3 \simeq \Delta E_{rot} \times 10^6$$

so we see that the vibrational changes wil a Coarse structure and rotational changes fine structure on the spectra of electronic t

The quantised levels of these energies shown in the figure.



It is seen that the spacing between electronic energy level is larger than that of vibrational energy levels and in turn latter is larger than rotational energy levels.

Thus the difference between the electronic energy levels is usually some tens of K cal/mole that between vibrational energy levels is a few K cal/mole and that between rotational energy levels is only of the order of Tens of cals/mole.

It should be noted from the figure that a transition between two vibrational levels is almost always accompanied by Transitions between rotational levels, so that vibrational spectra are really simultaneous vibrational and rotational spectra.

In the same way a transition between two electronic levels is usually accompanied by changes in vibrational and rotational energies.

Initially we ignore rotational fine structure and discuss the appearance of the vibrational Coarse structure of spectra.

⊗ Vibrational Coarse structure

Progressions:-

If we Consider the vibrational coarse stru of spectra and ignoring the rotational changes, the equation for Etotal can be written as

$$E_{total} = E_{elle} + E_{vib} \quad J.$$

(or)

$$E_{total} = \varepsilon_{ele} + \varepsilon_{vib} \quad cm^{-1} \text{ ———— } ①$$

As real molecules do not obey exactly the la of simple harmonic motion, using quantum mechan derivations, the equation is given as

$$\varepsilon_{vib} = \left(V+\tfrac{1}{2}\right)\bar{\omega}_e - \left(V+\tfrac{1}{2}\right)^2 \bar{\omega}_e x_e \quad cm^{-1}.$$

where V = Vibrational quantum number = 0, 1, 2.

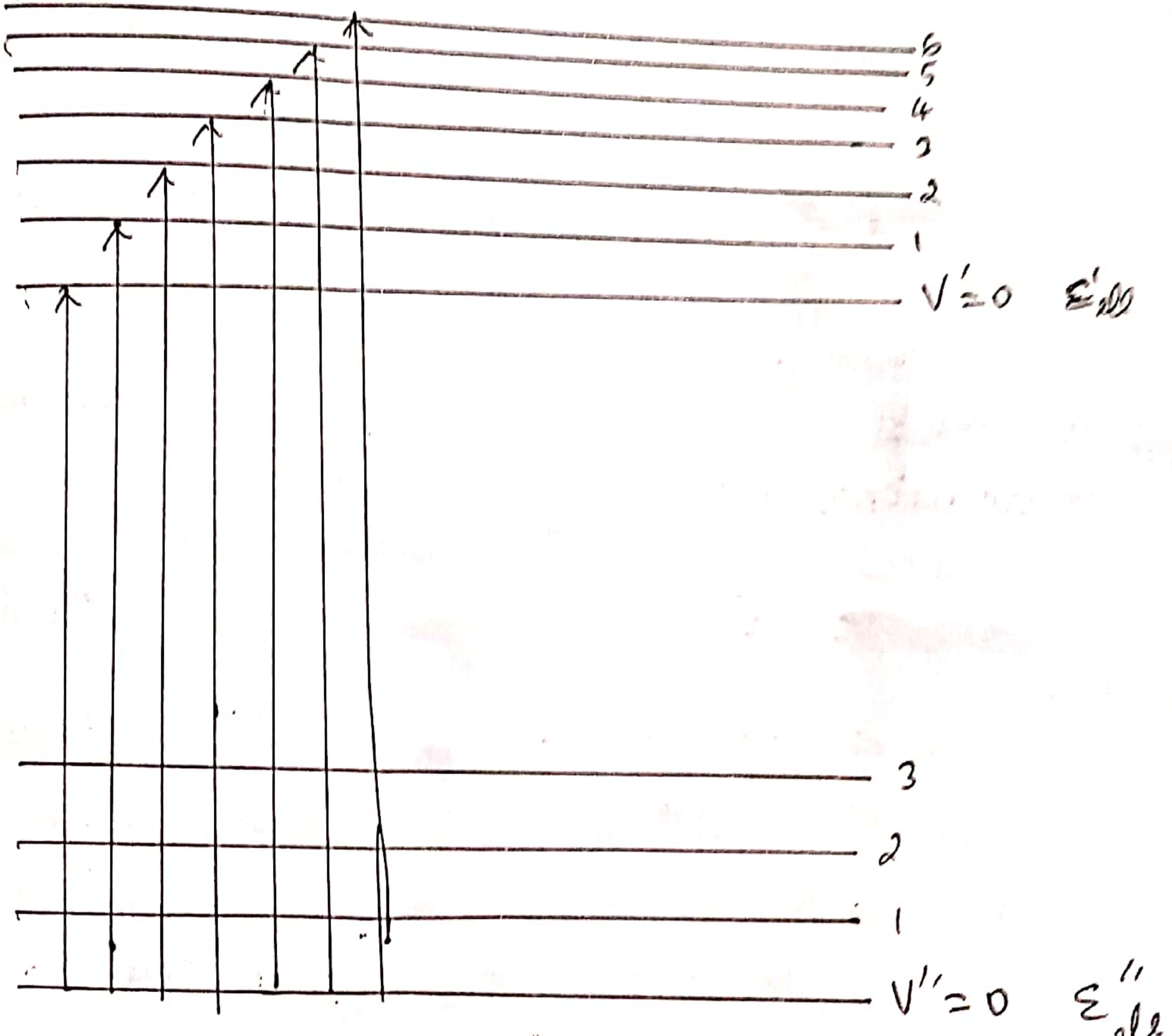
$\bar{\omega}_e$ = Oscillation frequency (expressed in wave nu

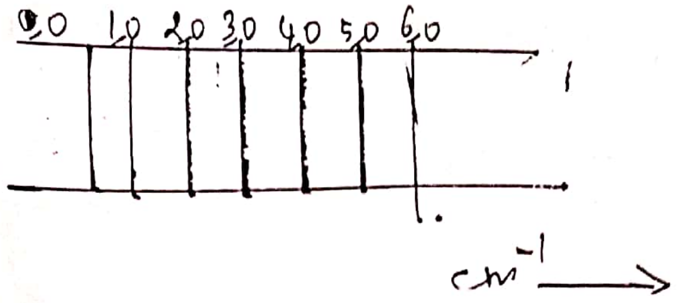
x_e = Anharmonicity Constant (It is al small and positive (≈ +0.01).

Substituting this value of ε_{vib} in eqn. ① get

$$\varepsilon_{total} = \varepsilon_{elec} + \left(v + \tfrac{1}{2}\right)\bar{\omega}_e - x_e\left(v + \tfrac{1}{2}\right)^2 \bar{\omega}_e \ \text{cm}^{-1} \quad \text{—②}$$

The energy levels of this equation are shown in the following figure for two arbitrary values of ε_{ele}.





The lower states are denoted as V'' – ε''_{ele}, whe
the upper states are V', ε'_{ele}.

The spacing between the upper vibrational
is shown to be rather smaller than that betwe
lower, since an excited electronic state usual
corresponds to a weaker bond in the molecule
and hence a smaller vibrational wave number ω

There is no selection rule for V' when a molecul
undergoes an electronic transition. i.e. every tra
tion, $V'' - V'$ has some probability. Therefore m
spectral lines would be expected.

Here all the molecules exist in the lowest vib
state, i.e $V''=0$ state. So the only transition
to be observed with appreciable intensity are
indicated in the figure. These transitions are la
according to their vibrational energy level numb
(V', V'') i.e. (0,0) (1,0) (2,0) (3,0) etc.

such a set of transitions is called a <u>band</u>
since, under low resolution, each line of the se
appears some what broad and diffuse. This is
more particularly called as V' <u>progression</u>; si
the value of V' increases by unity for each li
in the set.

So an expression relating both states can be given as follows:-

$$\Delta \varepsilon_{total} = \Delta \varepsilon_{ele} + \Delta \varepsilon_{vib}.$$

Therefore $\Delta \varepsilon_{total} = (\varepsilon' - \varepsilon'') + \{(v'+\tfrac{1}{2})\bar{\omega}_e' - x_e'(v'+\tfrac{1}{2})^2\bar{\omega}_e'\} - \{(v''+\tfrac{1}{2})\bar{\omega}_e'' - x_e''(v''+\tfrac{1}{2})^2\bar{\omega}_e''\}$ —— ③

Thus the observation of a band spectrum leads not only to values of the vibrational frequency and anharmonicity constant in the ground state ($\bar{\omega}_e''$ and x_e'') but also to these parameters in the excited electronic state ($\bar{\omega}_e'$ and x_e').

This information is valuable since such excited states may be extremely unstable and the molecule may exist in them for very short time. Hence the band spectrum can tell us a great deal about the bond strength of such species.

Normally, the molecules may have many excited electronic states and the ground states can undergo a transition to several excited states. Hence each transition will be accompanied by a band spectrum similar to that one shown in the figure

Intensity of vibrational-electronic spectra.

The Franck-Condon principle:-

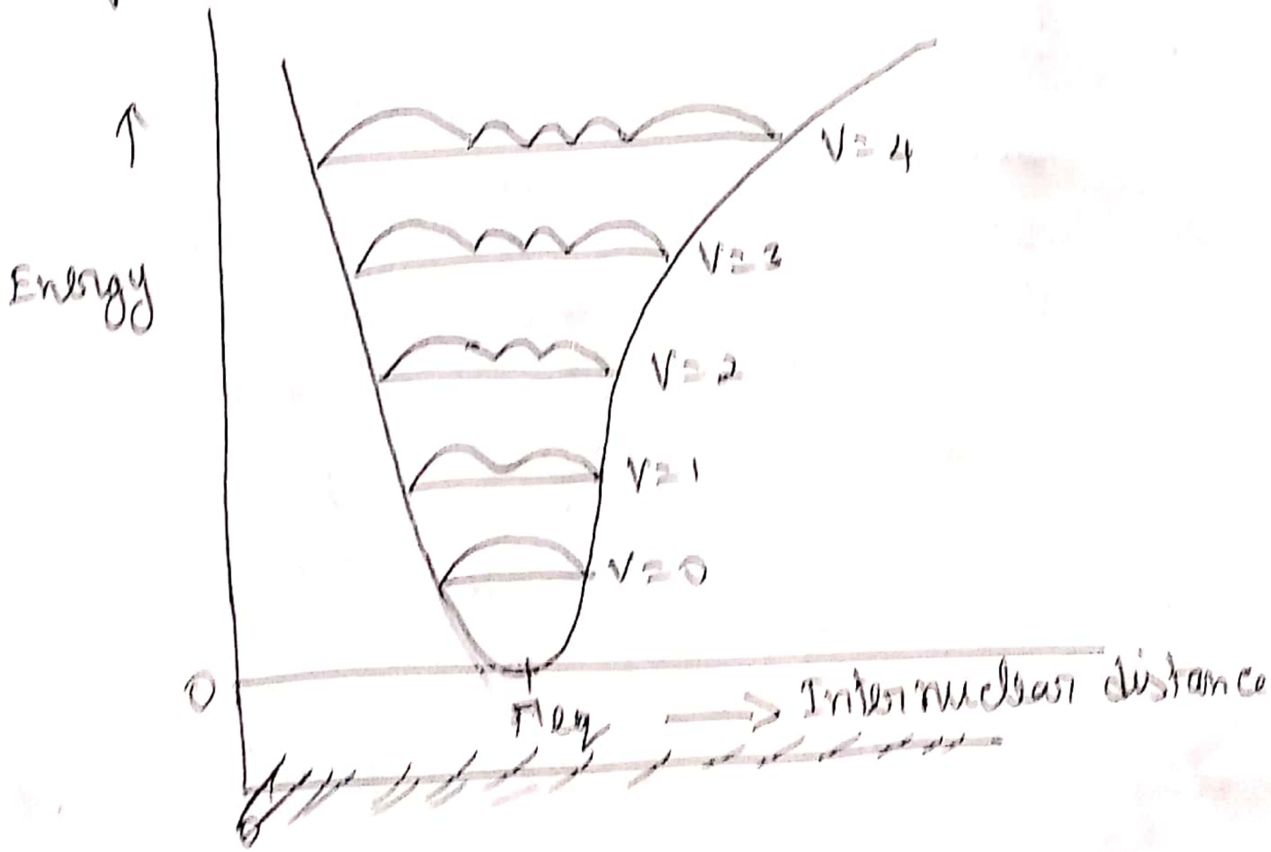
Although quantum mechanics imposes no restrict on the change in the vibrational quantum numbe during an electronic transition, the vibrational li in a progression are not all observed to be of th same intensity.

In some spectra (0,0) transition is the stro in others, the intensity increases to a maximu at some value of v, while in yet others only a vibrational lines with high v' are seen fo by continuum. Frank-Condon principle explai the above observations.

It states that an electronic transition takespla so rapidly that a vibrating molecule does not ch its internuclear distance appreciably during the transition.

The energy of a diatomic molecule varies w internuclear distance is given by Morse Curve Here one atom is considered fixed on the $r=0$ axis and the other is allowed to oscillate between the limits of the curve. classical theo says that the oscillating atom would spen most of its time on the curve at the turning point of its motion since it is moving most slowly there.

Quantum theory agree this view for high values of the vibrational quantum number. But it says that for v=0 the atom is most likely to be found at the centre of its motion i.e, at the equilibrium internuclear distance. r_{eq} ∴ But for v= 1,2,3... the most probable positions steadily approach the extremities until (for high v) both quantal and mechanical pictures merge. This behaviour is shown in figure.

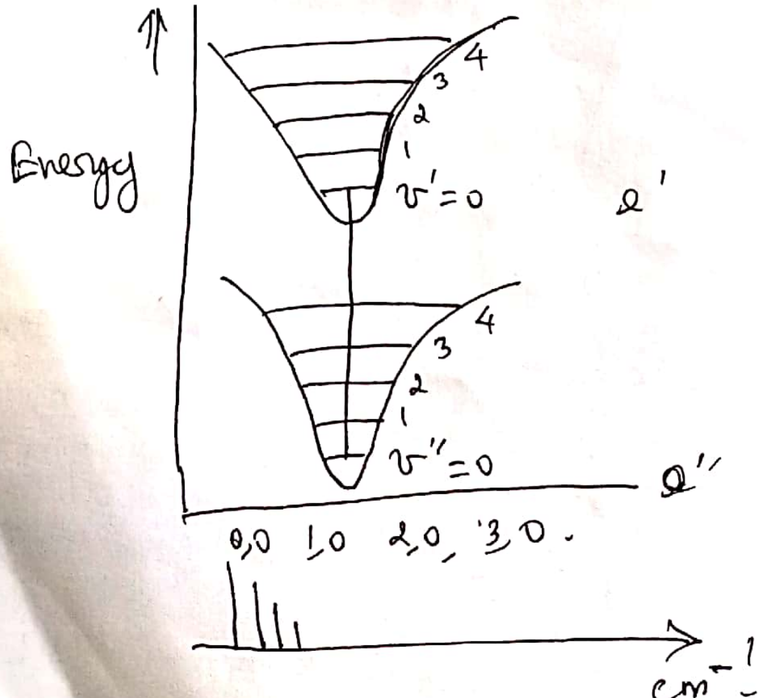


⑩

If a diatomic molecule undergoes a transi
into an upper electronic state in which the exci
molecule is stable with respect to dissociation into
atoms, then we can represent the upper state by
Morse curve similar to that of ground electroni
state.

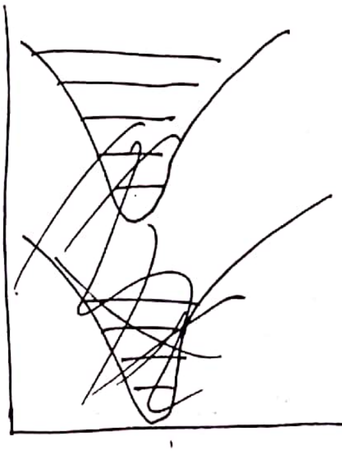
There are four possibilities for an electroni
transition accompanying vibrational transit

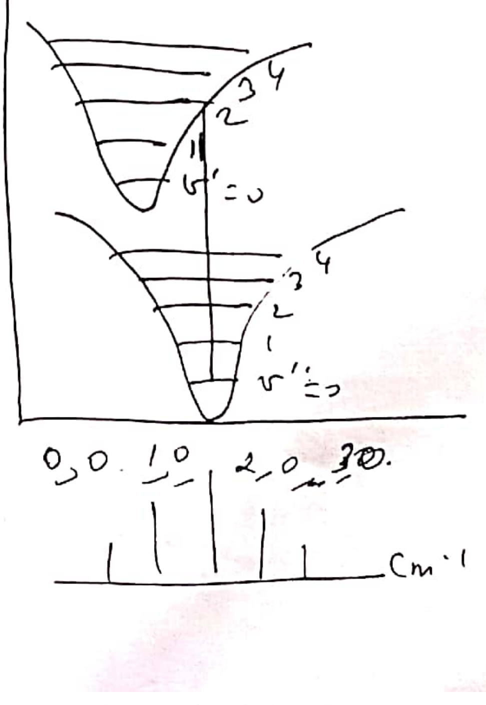
① In the first possibility, the upper electronic
having the same equilibrium internuclear dista
as the lower. Now the Frank-Condon principle
suggests that a transition occurs vertically on th
diagram, since the internuclear distance does not
If we consider the molecule to be initially in
ground state both electronically (ε'') and vibrat
($v''=0$), then the most probable transitio
indicated by vertical line.



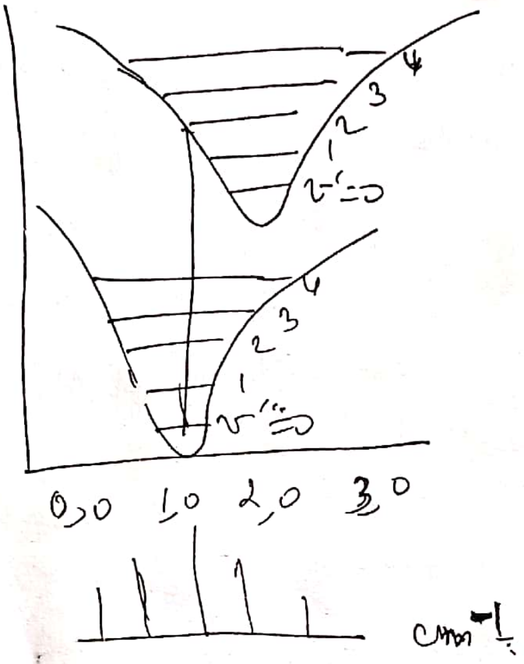
The strongest spectral line of the $v''=0$ progression will be the (0,0). However the quantum theory says that the probability of finding the oscillating atom, is greatest at the equilibrium distance in the $v=0$ state it allows some, although small chance of the atom being near the extremities of its vibrational motion. Hence there is some chance of the transition starting from the ends of the $v''=0$ state and finishing in the $v'=1,2$ etc states. The (1,0), (2,0) etc lines dimish rapidly in intensity as shown at the foot of fig.

In the second possibility the excited electronic state has a slightly smaller internuclear separation than the ground state. A vertical transition from the $v''=0$ level into the upper vibrational state $v'=2$ is most likely to occur. Other transitions i.e to lower and higher v' states are less likely.



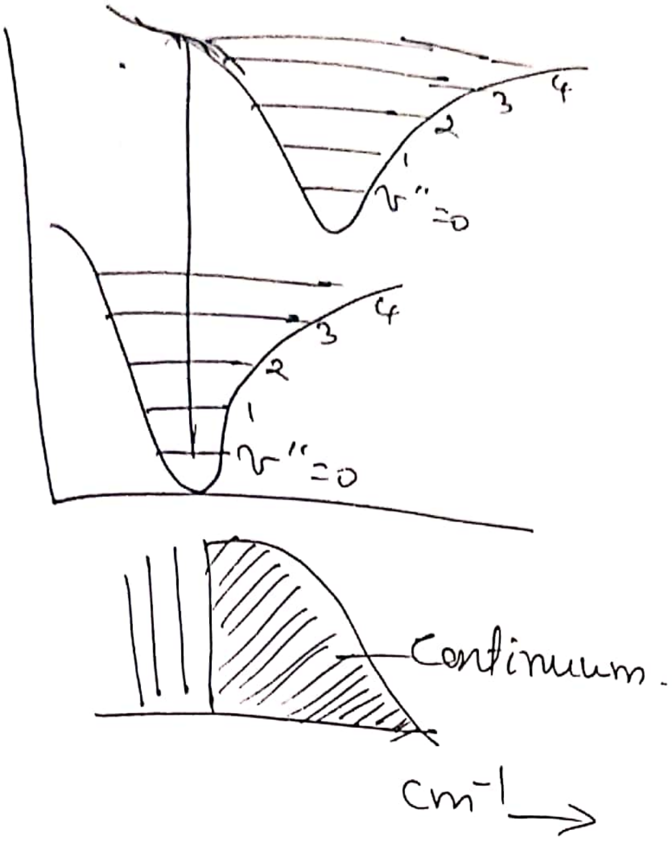


In the third possibility the excited electroni state has a slightly larger inter nuclear separat than the ground state but the resulting transi and spectrum are similar as second.



In the fourth possibility the upper state (excited state) is considerably greater with to internuclear distance than that in the lower sta Here transition takes place with high v' value. Further transitions can occur to a state where excited molecule has energy in excess of its o dissociation energy. From such states the mo will dissociate without any vibrations and a stage the molecule can take up any value kinetic energy (transitions are not quantise and a Continuum will result.

This is shown at the foot of the figure.



Dissociation Energy and Dissociation products

There are two ways in which the electronic excitation can lead to dissociation

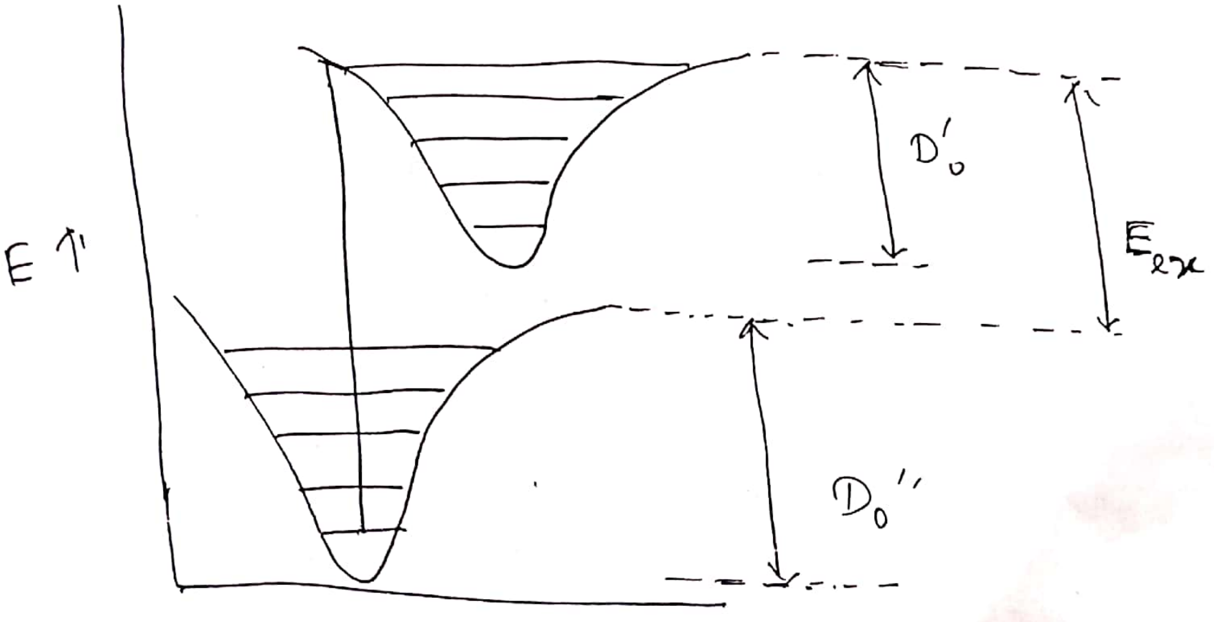


Fig 1

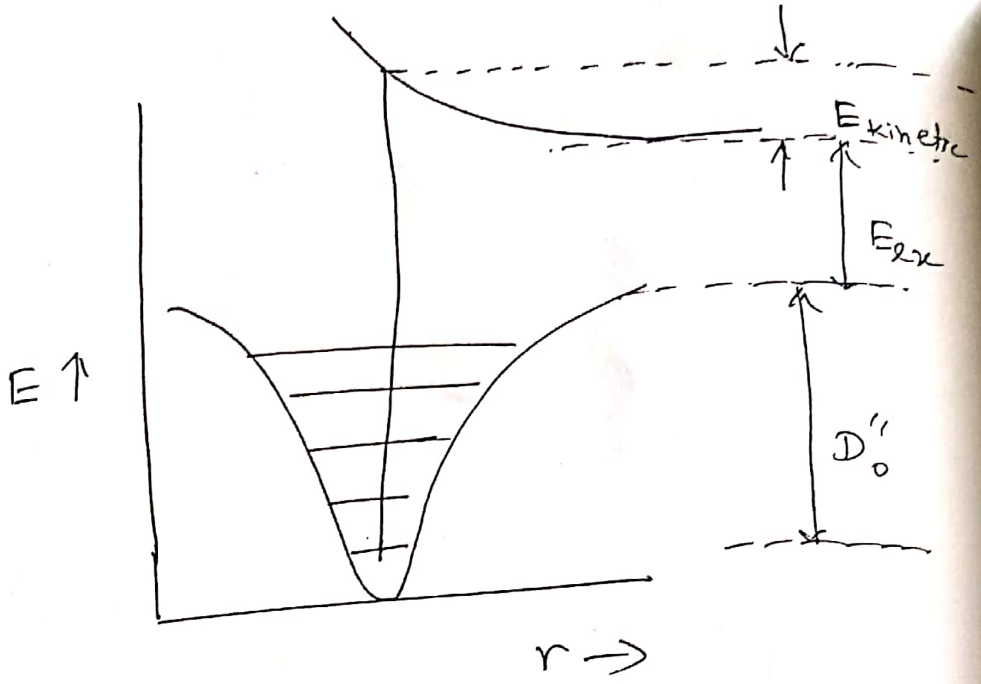


Fig. 2

Fig 1 represents the case where the equilib
inter nuclear separation in the upper state is considerably greater than that in the lower state. The dashed line limits of the Morse curve represe the dissociation of the normal and the excited molecule into atoms.

The dissociation energies being D'_o and D''_o the $v = 0$ state in each case. The total ener of the dissociation products (i.e atoms) from upper state is greater by an amount called E than that of the dissociation products in the l state. This energy is the excitation energy one of the atoms produced on dissociation

For this case the spectrum consists of lines correspond to vibrational transiti followed by Continuum. The ~~wave~~ lower wave number limit of this Continuum represent just the sufficient energy to cause dissociation and thus we have

$$\bar{\nu}_{\text{continuum limit}} = D_0'' + E_{ex} \ \text{cm}^{-1} \text{ ——— } (1)$$

∴ We can measure the dissociation energy, D_0''. if we know the excitation energy of the products which can be readily measurable by atomic absorption spectroscopy.

Fig ② illustrate the case in which the upper electronic state is highly unstable. There is no minimum in the energy curve. As soon as the molecule is raised to this state by excitation, the molecule dissociates into products with total excitation energy E_{ex}. Then the product fly apart with kinetic energy $E_{kinetic}$. The kinetic energy is the excess energy in the final state above the energy sufficient to cause dissociation of the molecule. Since $E_{kinetic}$ is not quantized the whole spectrum for this system will exhibit a Continuum and the lower limit of this will be the energy $D_0'' + E_{ex}$. D_0'' can be measured if E_{ex} is known.

In many spectra no Continua appear at all. Because the internuclear distances in the upper and lower states are such that transitions near to the

dissociation limit are of negligible probabilit
However it is possible to derive a value for the dissociation energy by noting how the vibrat lines converge.

We know

$$\varepsilon_v = (v+\tfrac{1}{2})\bar{\omega}_e - x_e(v+\tfrac{1}{2})^2\bar{\omega}_e \text{ cm}^{-1} \quad \text{—— ②}$$

and so the separation between neighbouring leve $\Delta\varepsilon$ is

$$\Delta\varepsilon = \varepsilon_{v+1} - \varepsilon_v$$

$$\Delta\varepsilon = \bar{\omega}_e\{1-2x_e(v+1)\} \text{ cm}^{-1} \quad \text{—— ③}$$

This separation decreases linearly with increa v and the dissociation limit is reached when $\Delta\varepsilon \rightarrow 0$. Thus the maximum value of v is give by v_{max} where

$$\bar{\omega}_e\{1-2x_e(v_{max}+1)\} = 0$$

$$\text{i.e. } v_{max} = \frac{1}{2x_e} - 1 \quad \text{—— ④}$$

As we know that the anharmonicity consta x_e is of the order of 10^{-2}.

$$\therefore v_{max} = \frac{1}{2\times 0.01} - 1 = \frac{1}{0.02} - 1 = 5$$

Hence we can have $v_{max} \simeq 50$.

Generally two vibrational transitions are sufficient to determine x_e and $\bar{\omega}_e$.

Illustration with example:

For HCl molecule if the oscillation frequency ω_e is 2990 cm^{-1}, and the anharmonicity constant x_e is 0.0174. Find the maximum possible vibrational energy level V_{max} and the maximum value of the vibrational energy.

Solution:

$$V_{max} = \frac{1}{2x_e} - 1$$

$$V_{max} = \frac{1}{2 \times 0.0174} - 1 = \frac{1}{0.0348} - 1 = 28.74 - $$
$$= 27.74$$

$\therefore V_{max} = 27$ (the next lowest integer)

$$\varepsilon_V = (V + 1/2)\,\bar{\omega}_e - x_e (V + 1/2)^2\, \bar{\omega}_e \ cm^{-1}.$$

$V = 27$

$\bar{\omega}_e = 2990\ cm^{-1}$.

$x_e = 0.0174$

$$\therefore \varepsilon_V = (27 + 1/2)\,2990 - 0.0174\,(27 + 1/2)^2\, 2990 \ cm^{-1}$$

$$= 27.5 \times 2990 - 0.0174 \times 27.5 \times 27.5 \times 2990$$

$$= 82225 - 39344.66\ cm^{-1}$$

$42880\ cm^{-1}$.

$$\mathcal{E}_V = 42880 \times 11.958 \text{ J mol}^{-1}$$

$$\left[\because 1\text{ cm}^{-1} = 11.958 \text{ J mol}^{-1}\right]$$

$$= 512759 \text{ J mol}^{-1}$$

$$= 512.759 \text{ kJ mol}^{-1}$$

This value is comparable with more accurat value of 427.2 kJ mol^{-1} evaluated thermody mically despite discrepancy.

Discrepancy ~~between~~ between calculated and exp -mental values:

Firstly the IR spectra consists of only two o three vibrational transitions (The fundamental plus the first and second overtones). But the electronic spectrum shows many more vibrat transitions.

Secondly we have assumed that equation ② applies exactly even at high values of V. Th is not true because cubic and quatric ter became important at this stage. Because of this $\Delta\mathcal{E}$ decreases more rapidly than eq suggests. i.e $\Delta\mathcal{E} = \bar{\omega}_e \{1 - 2x_e(v+1)\}$ cm

Both these points may be met if we plot the separation between vibrational transitions ΔE, as observed in the electronic spectrum against the vibrational quantum number V.

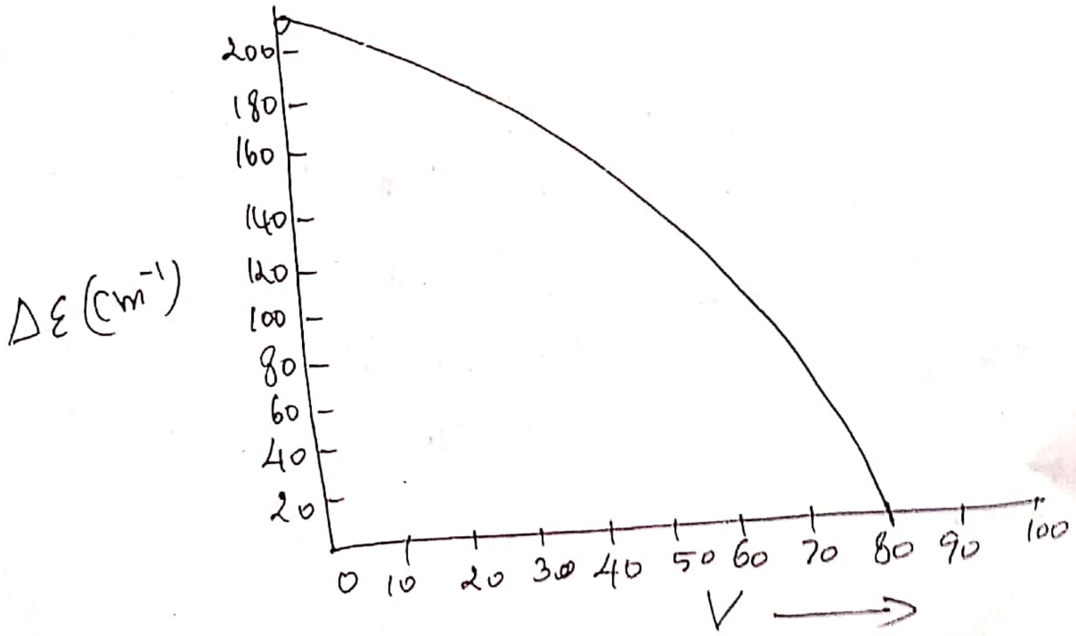
Initially equation ③ will apply quite accurately and the graph will be straight line which may be extrapolated to find V_{max}.

Birge and Sponer Extrapolation :-

since the dissociation energy is simply the sum of all the increments.

ΔE from $V=0$ to $V=V_{max}$.

The plot of separation between vibrational transitions ΔE Vs vibrational quantum number V will give a line enclosing the area which gives the direct value of ΔE. Such a linear extrapolation was suggested by Birge and Sponer.



On the other hand the graph of ΔE vs V wil at high V begin to fall off more sharply as cub and quartic terms became significant. In thi case the most accurate determination of dissoci energy is obtained by extrapolating the smooth curve and finding the area beneath it.

In absorption spectra the series of line originating from $V'' = 0$ state is observed. Th molecules in excited states usually revert to ground state within fractions of a microsec the dissociation energy in the ground state ca be found easily using the expression.

$$D_0'' = E_{(0,0)} + D_0' - E_{ex} \text{ cm}^{-1}$$

Where E_{ex} can be obtained using atomic spectroscopy. D_0' is obtained from Birge-Spone extrapolation and we can measure $E_{(0,0)}$ the energy of the (0,0) transition directly from th observed energy levels.

— x —

21)

Problem:

1. The absorption spectrum of O_2 shows vibrational structure which becomes a continuum at 56 876 cm⁻¹ The upper electronic state dissociates into one ground state atom and one excited atom. The excitation energy of which measured from the atomic ~~absorption~~ spectrum is 15875 cm⁻¹. Estimate the dissociation energy of ground state O_2 in kJ mol⁻¹.

Solution:

We know

$$\bar{\nu}_{continuum} = D_0'' + E_{ex} \text{ cm}^{-1}$$

$$\bar{\nu}_{continuum} = 56\,876 \text{ cm}^{-1}$$

$$E_{ex} = 15,875 \text{ cm}^{-1}$$

$$\therefore D_0'' = \bar{\nu}_{continuum} - E_{ex} \text{ cm}^{-1}$$

$$= 56\,876 - 15\,875 \text{ cm}^{-1}$$

$$= 41,001 \text{ cm}^{-1}$$

$$= 41,001 \times 11,958 \text{ J mol}^{-1}$$

$$= 490289.96 \text{ J mol}^{-1}$$

$$= 490.29 \text{ kJ mol}^{-1}$$

(22.)

∴ The dissociation energy of ground state

$O_2 = 490.3$ kJ mol^{-1}!

(2.) The values of $\bar{\omega}_e$ and x_e in the ground and a particular excited state of a molecule

	$\bar{\omega}_e$ cm^{-1}	x_e
Ground state	1641.4	7.11×10^{-3}
Excited state	1788.2	9.19×10^{-3}

Find the number of vibrational energy level below the dissociation limit and hence the dissociation energy of that molecule in both states.

Solution:

I Vibrational energy levels

(a) ground state

$$V_{max} = \frac{1}{2x_e} - 1$$

$$= \frac{1}{2 \times 7.11 \times 10^{-3}} - 1$$

$$= \frac{1}{0.01422} - 1$$

$$= 70.32 - 1 = 69.32$$

$$\therefore V_{max} = 69$$

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(b) Excited state:-

$$V_{max} = \frac{1}{2 \times 9.19 \times 10^{-3}} - 1$$

$$= \frac{1}{0.01838} - 1$$

$$= 54.41 - 1 = 53.41$$

$$\therefore V_{max} = 53$$

II Dissociation energies

(a) Ground state

When $V = 69$

$$\mathcal{E}_V = (V + \tfrac{1}{2})\bar{\omega}_e - x_e (V + \tfrac{1}{2})^2 \omega_e \ cm^{-1}$$

$\bar{\omega}_e = 1641.4$

$x_e = 7.11 \times 10^{-3}$

$V = 69$

$$\therefore \mathcal{E}_V = (69 + \tfrac{1}{2}) 1641.4 - 7.11 \times 10^{-3} (69 + \tfrac{1}{2})^2 1641.4 \ cm^{-1}$$

$$= 69.5 \times 1641.4 - 7.11 \times 10^{-3} \times 69.5 \times 69.5 \times 1641.4 \ cm^{-1}$$

$$= 1{,}14{,}077.3 - 56{,}370.73 \ cm^{-1}$$

$$= 57706.57 \ cm^{-1}$$

$$\frac{57706.57 \times 11.958}{1000} = 690.05 \text{ KJ mol}^{-1}$$

When $V = 0$

$$\mathcal{E}_V = (0+\tfrac{1}{2})\,1641.4 - 7.11\times10^{-3}(0+\tfrac{1}{2})^2\,1641.4 \text{ cm}^{-1}$$

$$= 0.5\times1641.4 - 7.11\times10^{-3}\times0.5\times0.5\times1641.4 \text{ cm}^{-1}$$

$$= 820.7 - 2.92 \text{ cm}^{-1}$$

$$= 817.78 \text{ cm}^{-1}$$

$$= \frac{817.78\times11.958}{1000} = 9.78 \text{ KJ mol}^{-1}$$

∴ Dissociation energy in the ground state

$$D_0'' = \mathcal{E}_{V=69} - \mathcal{E}_{V=0}$$

$$= 690.05 - 9.78 = 680.27 \text{ KJ mol}^{-1}$$

(b) Excited state

When $V = 53$

$$\mathcal{E}_V = (53+\tfrac{1}{2})\,1788.2 - 9.19\times10^{-3}(53+\tfrac{1}{2})^2\,1788 \text{ cm}$$

$$= 53.5\times1788.2 - 9.19\times10^{-3}\times53.5\times53.5\times 1788.2 \text{ cm}^{-1}$$

$$= 95668.7 - 46597.35 \text{ cm}^{-1}$$

$$= 49071.35 \text{ cm}^{-1}$$

(25)

$$= \frac{49071.35 \times 11.958}{1000} = 586.8 \text{ KJmol}^{-1}$$

When $V=0$

$$\varepsilon_V = 0.5 \times 1788.2 - 9.19 \times 10^{-3} \times 0.5 \times 0.5 \times 1788.2 \text{ cm}^{-1}$$

$$= 894.1 - 4.11 \text{ cm}^{-1} = 889.99 \text{ cm}^{-1}$$

$$= \frac{889.99 \times 11.958}{1000} = 10.64 \text{ kJmol}^{-1}$$

∴ Dissociation energy in the excited state

$$D_0' = \varepsilon_{V=53} - \varepsilon_{V=0}$$

$$= 586.8 - 10.64$$

$$= 576.16 \text{ KJ mol}^{-1}$$

⊕ The Fortrat Diagram

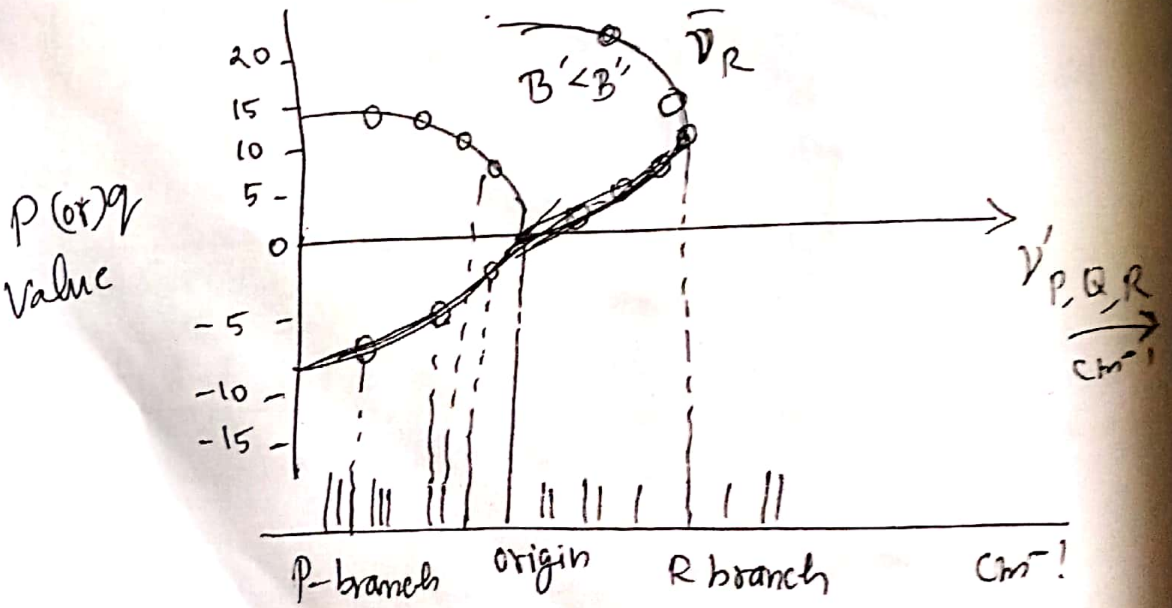
The expressions for the P, R and Q branche (lines) can be rewritten with continuously variable parameter.

$$\bar{\nu}_{P,R} = \bar{\nu}_{(v',v'')} + (B'+B'')p + (B'-B'')p^2$$

$$\bar{\nu}_{Q} = \bar{\nu}_{(v',v'')} + (B'-B'')q + (B'-B'')q^2$$

These equation represent a parabola where p takes both positive and negative values and q takes only positive value.

A parabola can be sketched by choosing th same condition $B' < B''$. Label the regions positive p with $\bar{\nu}_R$ and negative p with $\bar{\nu}_P$. Th parabolae are referred to as the Fortrat's parab (or) diagram.



As we know that p and q take only integral values (but not zero) we draw circles round the allowed points on the parabolae. This is useful for us to read directly the $\bar{\nu}$ values of the spectral lines from the graph.

It is seen from the figure that the dotted lines are connecting the spectrum at foot and fortrat diagram at intervals.

An important use of the Fortrat diagram is to calculate the position of the band head which positioned at the vertex of the parabola. For this the equation can be differentiated.

$$\frac{d\bar{\nu}_{PR}}{dp} = B'+B''+2(B'-B'')p = 0$$

$$(or)\quad p = -\frac{B'+B''}{2(B'-B'')} \longrightarrow (3)$$

It is clear that if $B' < B''$ the band head occurs at positive p values, that is in the R-branch.

The line at maximum wave number being given by the nearest integer to p.

Conversely if $B' > B''$ the band head occurs in the region of p negative i.e. in the p-branch.

If there is 10% difference between B' and B'' then Band head occurs at $p \simeq 10$ that is

$p = m = J'+1 = J''+1$

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If $P=10$

then $J'+1=10$

$J'=10-1=9$

or $J''=9$

Ref:

For B' and B'' 10% difference.

$$p = \frac{-(9+10)}{2(9-10)} = -\frac{19}{2\times -1} = -\frac{19}{-2} = 9.5$$

i.e $p \simeq 10$.