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Molecular Spectroscopy

Introduction:

Spectroscopy is the branch of science dealing with the study of interaction of electromagnetic 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 electromagnetic radiation with atoms which are most commonly in their lowest energy state called the ground state. e.g. most of the monoatomic substances exist in gaseous state and are able to absorb electromagnetic radiation resulting in electronic transitions.

(b) Molecular spectroscopy:

This deals with the interaction of electromagnetic radiation with molecules. This results in transitions 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 molecules.

Properties of Electromagnetic radiation:

Electromagnetic radiation is a form of energy that is transmitted through space at an enormous velocity. Electromagnetic radiation has the properties of electrical and magnetic component both of which are oscillating in a plane perpendicular to each other. Electromagnetic radiation needs no supporting media. In fact it passes more readily in vacuum than in air.

Characterization of Electromagnetic radiation

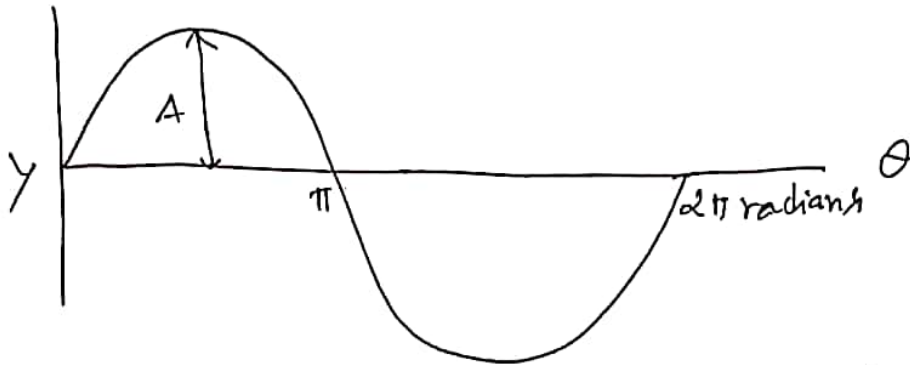
Electromagnetic radiation is a simple harmonic wave propagated from a source and travelling in a straight line except when refracted or reflected. This nature of electromagnetic radiation can be compared to vibration of stretched string.

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

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

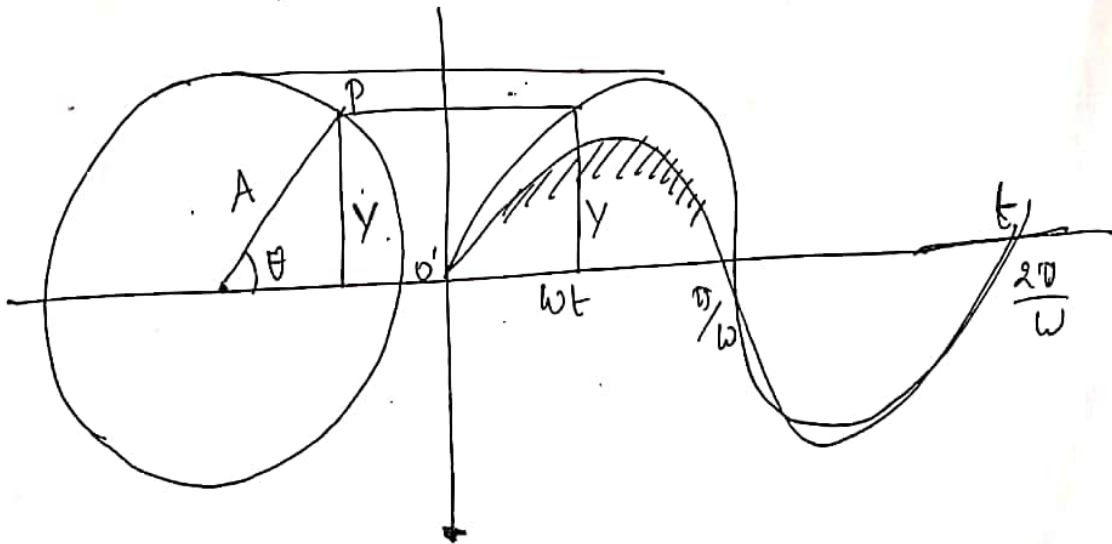
(3.)

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



Here y is the displacement having maximum value ' 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.



(4)

Consider the left hand side of the figure and consider the point P travels with uniform angular velocity $\omega \text{ rad s}^{-1}$ in a circular path of radius A . 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 $\theta = \omega t$ radians after time 't' seconds.

The vertical displacement can be given as
 $y = A \sin \theta$ (as $\sin \theta = \frac{y}{A}$)

$$\text{i.e. } y = A \sin \omega t \text{ (as } \theta = \omega t \text{)}$$

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

After a time of $\frac{2\pi}{\omega}$ seconds, P will return to O' and completing a cycle.

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

Frequency:

For a complete cycle the time taken is $\frac{2\pi}{\omega}$.
Therefore for one second the number of cycles can be given as $\frac{\omega}{2\pi}$ (i.e. $\frac{1}{2\pi/\omega}$).

(5)

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

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}).

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

$$1 \text{ MHz} = 10^3 \text{ kHz} = 10^6 \text{ Hz}$$

Now we can write the sine wave equation as

$$y = A \sin \omega t = A \sin 2\pi \nu t \quad (\text{since } \nu = \frac{\omega}{2\pi})$$

①

This is the basic equation of wave motion. So far we are concerned with displacement with time. Now we consider the displacement with distance where a term wave length arises.

As we know that

$$x = ct \quad (\because c = x/t) \quad \text{--- ②}$$

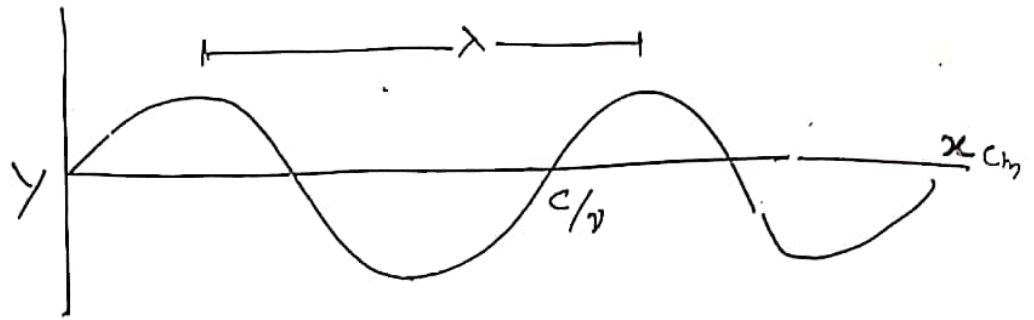
Where x is the distance covered in time t at a speed c .

On combining equation ① and ②

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

(6)

The wave is shown in fig.



Wave Length:

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

When the velocity is c metres per second and there are v cycles per second, there are evidently v waves in c metres. (or)

$$v\lambda = c \quad \text{or} \quad \lambda = \frac{c}{v} \text{ metres} \quad \text{--- (3)}$$

So we have

$$y = A \sin \frac{2\pi x}{\lambda} \quad \left(\because \frac{v}{c} = \frac{1}{\lambda} \right) \quad \text{--- (4)}$$

The wave length can be expressed in different

units

For microwave region \rightarrow cm (m.m)

I R Region \rightarrow micrometres
 $\mu\text{m}/\text{micron}$.

Visible and U.V. $\rightarrow 10^{-9} \text{ m}$ ($1 \text{ \AA} = 10^{-10} \text{ m}$)

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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:-

$$\bar{\nu} = \frac{1}{\lambda} \text{ cm}^{-1} \text{ --- (5)}$$

Hence $y = A \sin 2\pi \bar{\nu} x$ --- (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. $3 \times 10^{10} \text{ cm s}^{-1}$)

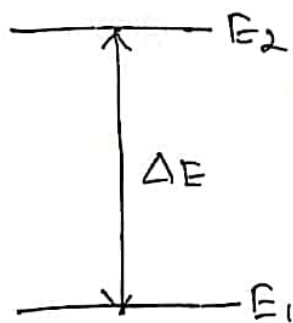
The Quantization of Energy

It was believed before 19th century that matters could take up energy continuously. In 1900 Max Planck gave a revolutionary idea that the energy of an oscillator is discontinuous and

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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 rotational, vibrational, electronic energy. The electron on an orbital has definite amount of energy and it will jump to next energy level only if full quanta 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 molecule example E_1 and E_2



Transition between these energy levels require a definite amount of energy. $\Delta E = E_2 - E_1$. It can either be absorbed or emitted.

Planck suggested that such energy can take the form of electromagnetic radiation and the frequency of the radiation can be

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given as $\nu = \Delta E/h$ #2 (5V) $\Delta E = h\nu$ Joules.

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

$$h = 6.63 \times 10^{-34} \text{ Joules} \cdot \text{second}^{-1} \cdot \text{mole}^{-1}$$

If a beam of radiation (monochromatic) is allowed to pass on a molecule which is in 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

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

Regions of the spectrum:-

The electromagnetic radiation has been divided 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 regions are as follows:

1. Radio frequency Region:-

Frequency = $3 \times 10^6 - 3 \times 10^{10}$ 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 = $3 \times 10^{10} - 3 \times 10^{12}$ Hz

Wave length = 1cm - 100 μ m.

Rotational Spectroscopy.

Energy between levels are in 100 Joules/mole.

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3. Infrared Region:-

$$\text{Frequency} = 3 \times 10^{12} \text{ — } 3 \times 10^{14} \text{ Hz.}$$

$$\text{Wavelength} = 100 \mu\text{m} - 1 \mu\text{m}.$$

Vibrational spectroscopy. Very useful to chemist

$$\text{Energy} = 10^4 \text{ Joules/mole.}$$

4. Visible and Ultraviolet Regions:-

$$\text{Frequency} = 3 \times 10^{14} \text{ — } 3 \times 10^{16} \text{ Hz}$$

$$\text{Wavelength} = 1 \mu\text{m} - 10 \text{ nm}.$$

Electronic spectroscopy.

$$\text{Energy} = 100 \text{ s of kJoules/mole.}$$

5. X-Ray Region:-

$$\text{Frequency} = 3 \times 10^{16} \text{ — } 3 \times 10^{18} \text{ Hz}$$

$$\text{Wavelength} = 10 \text{ nm} - 100 \text{ pm}.$$

Energy changes involving the inner electrons. ^h

$$\text{Energy} \approx 10,000 \text{ kilojoule/mole.}$$

6. γ-ray region:-

$$\text{Frequency} = 3 \times 10^{18} \text{ — } 3 \times 10^{20} \text{ Hz}$$

$$\text{Wavelength} = 100 \text{ pm} - 1 \text{ pm}.$$

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

(12)

Energy changes involve the rearranging of nuclear particles.

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

Mechanism of Interaction between Electromagnetic Radiation and nuclear, molecular or electronic changes :-

1. The Radio frequency Region:-

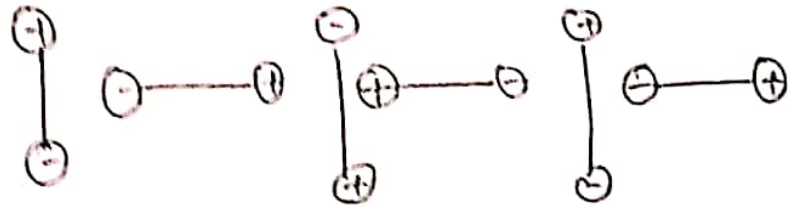
The nucleus and electron are tiny charged particles. As they spin they generate magnetic field. The result is magnetic dipole moment. It correspond with the electromagnetic radiation result in resonance. So it makes absorption & emission of radiation resulting in spectrum.

2. The Microwave Region:-

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

(1)

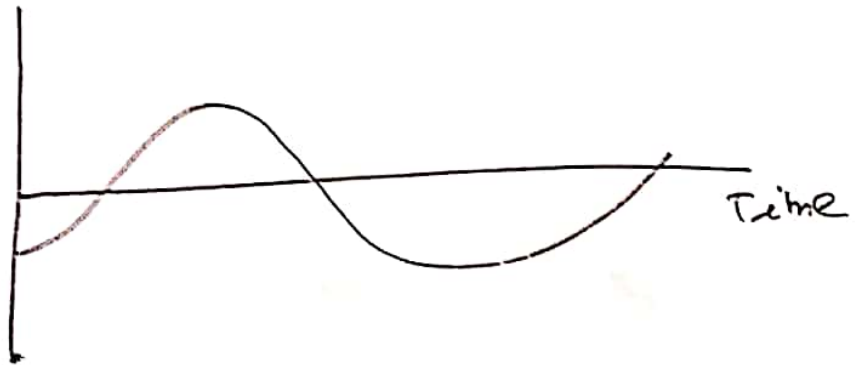
Direction of rotation



Direction of Dipole.



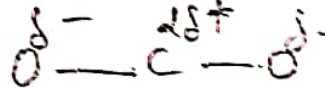
Vertical component of dipole



When we consider the molecules like H_2 or 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.

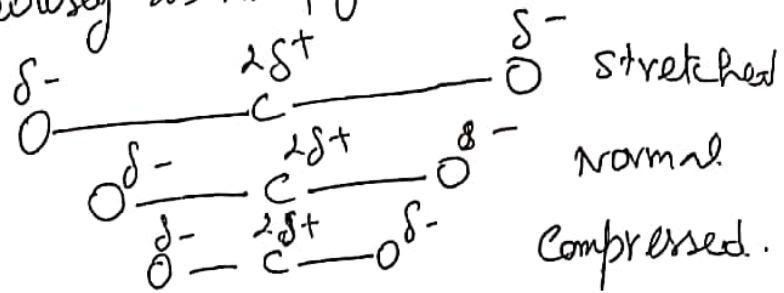
(3) The Infra Red Region:-

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.



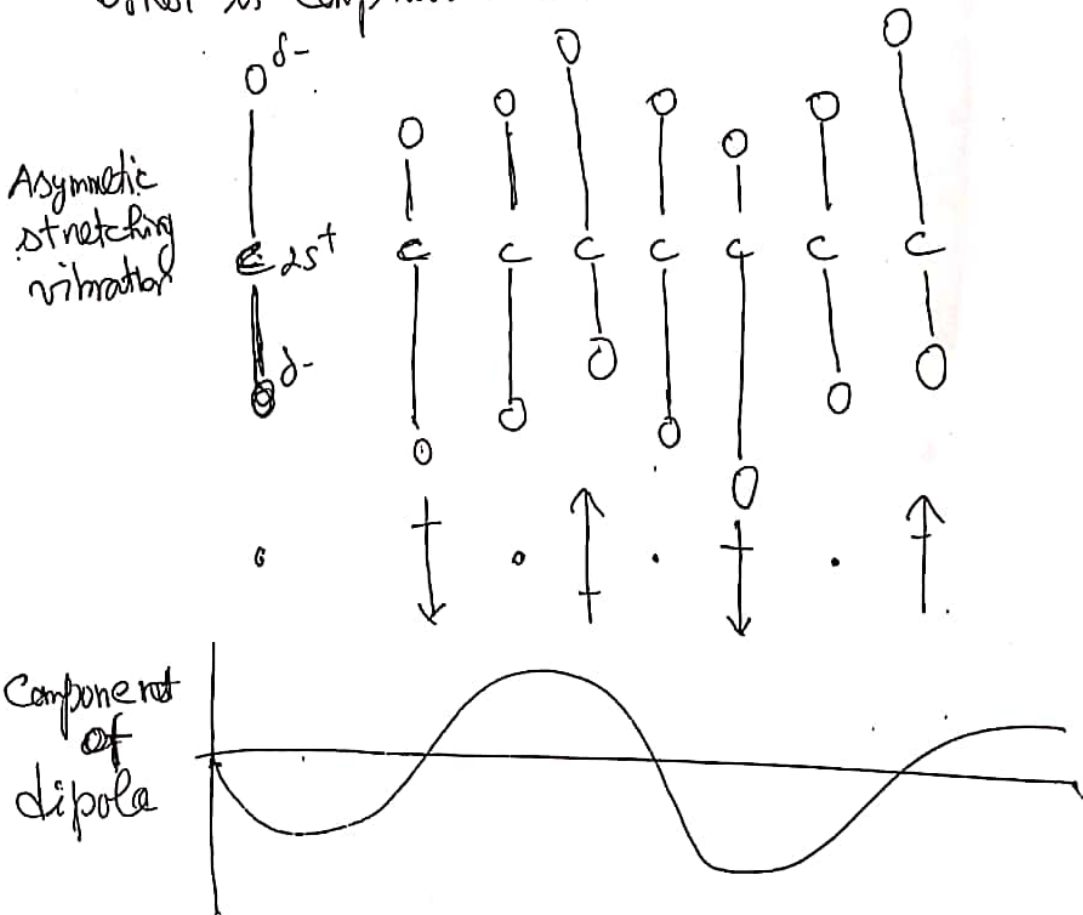
(14)

During symmetric stretching, the molecule is ~~not~~ stretched and compressed, both C-O bonds ~~are~~ simultaneously as in fig.



For CO₂ for symmetrical vibration, the dipole remains zero throughout the whole of this motion, and this particular vibration is infra-red inactive.

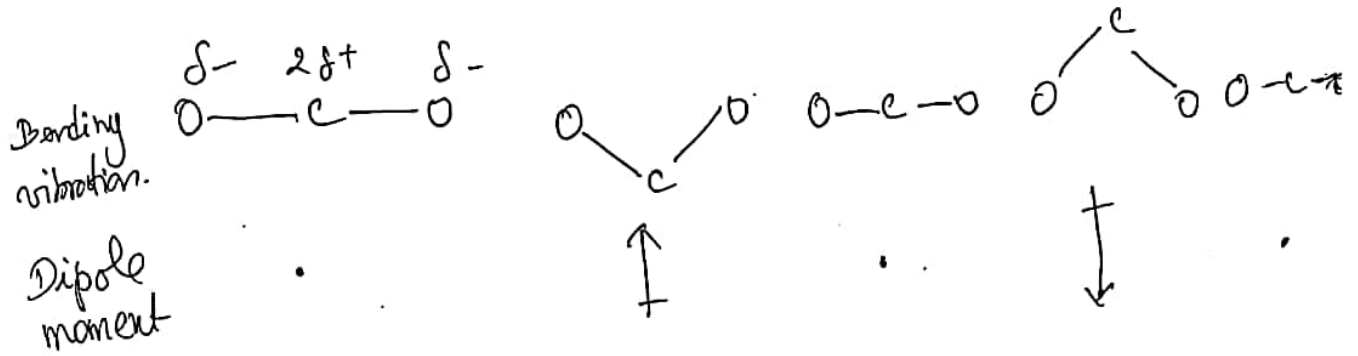
There is another stretching vibration known as asymmetric stretch. Here one bond stretches while the other is compressed and vice versa.



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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.



Vertical component of dipole

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 charges in the molecule. The consequent changes in electric dipole gives rise to a spectrum by its interaction with electric field of radiation.

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

Different types of molecular energies:

In addition to the translational motion, the molecule possesses rotational, vibrational and electronic energies.

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

(a) Rotational energy:

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

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

Where I is the moment of inertia, J is rotational quantum number. This equation is not applicable to liquid phase where molecular collisions are frequent. A molecule can rotate about any 3 axes. These rotations are known to be 3 rotational degrees of freedom.

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(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

$$E_{\text{vib}} = h\nu (v + 1/2)$$

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.

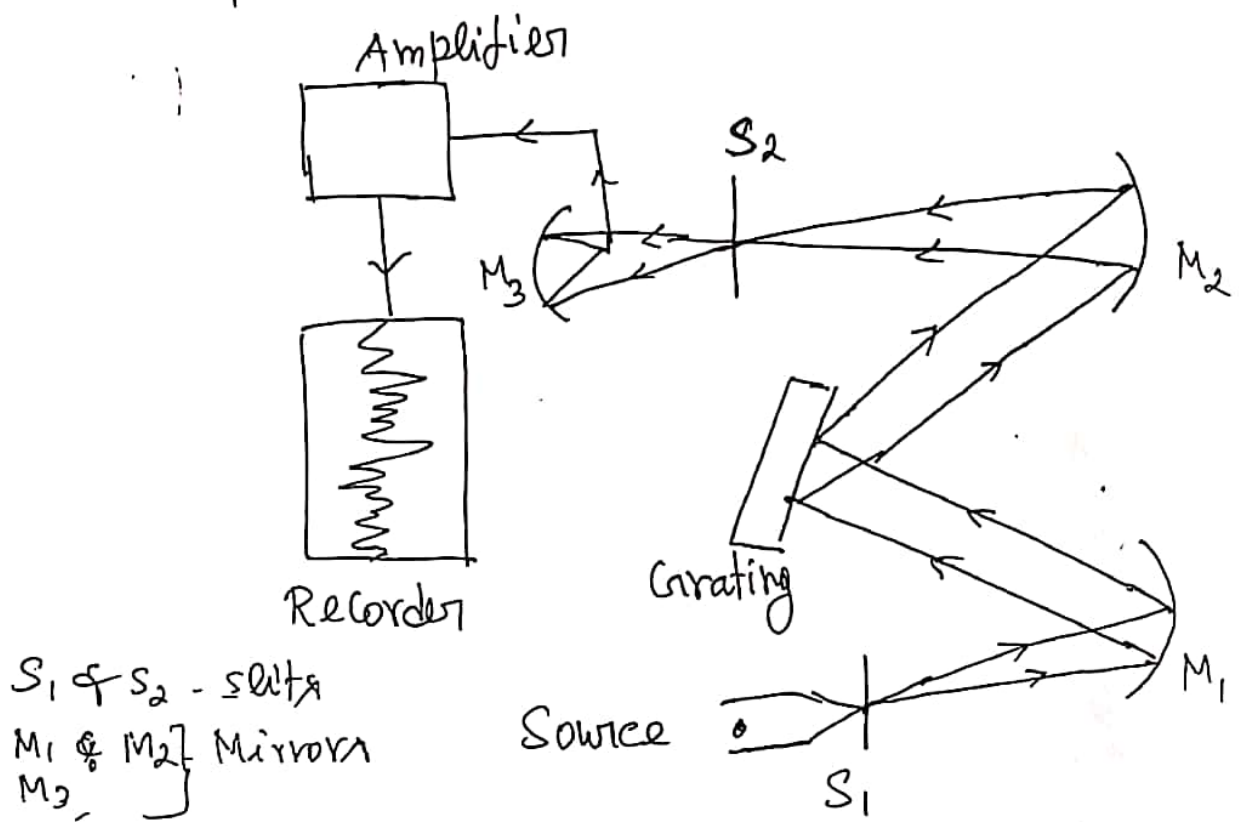
It involves the excitation of electron from ground state to excited state (higher energy state). The excitation varies with the type of molecular bond in which electron exist.

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 spectrometer consists of many components such as mirrors, slits, amplifiers, and recorder.

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The following diagram shows the operation of spectrometer.



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

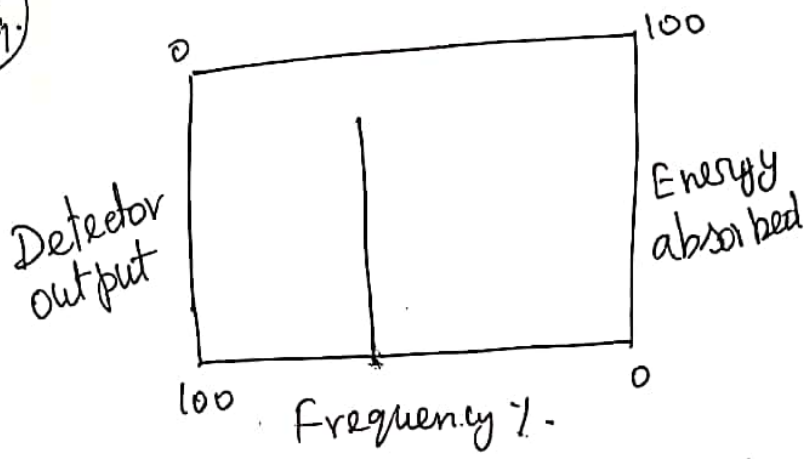
Recording of spectrum:-

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

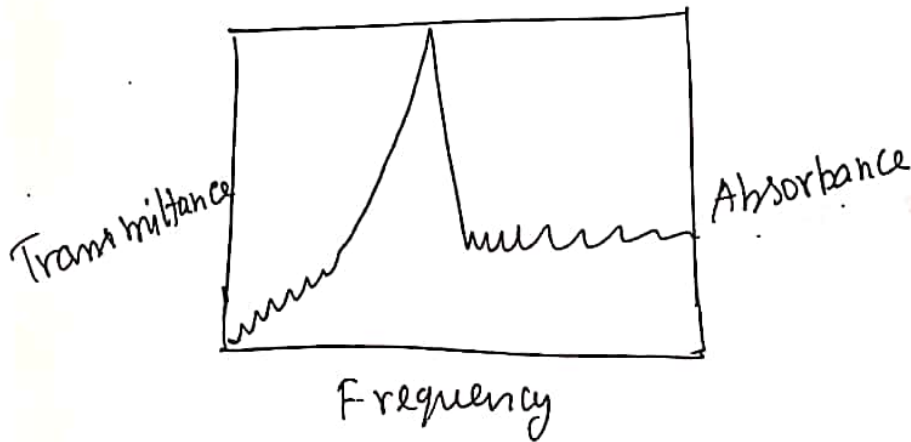
$$\nu = \frac{E_2 - E_1}{h}$$

The absorption versus frequency can be represented as follows:

(19.)



The above type of spectrum is seldom obtained practically. Actually 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 collectively referred to as noise on the spectrum.



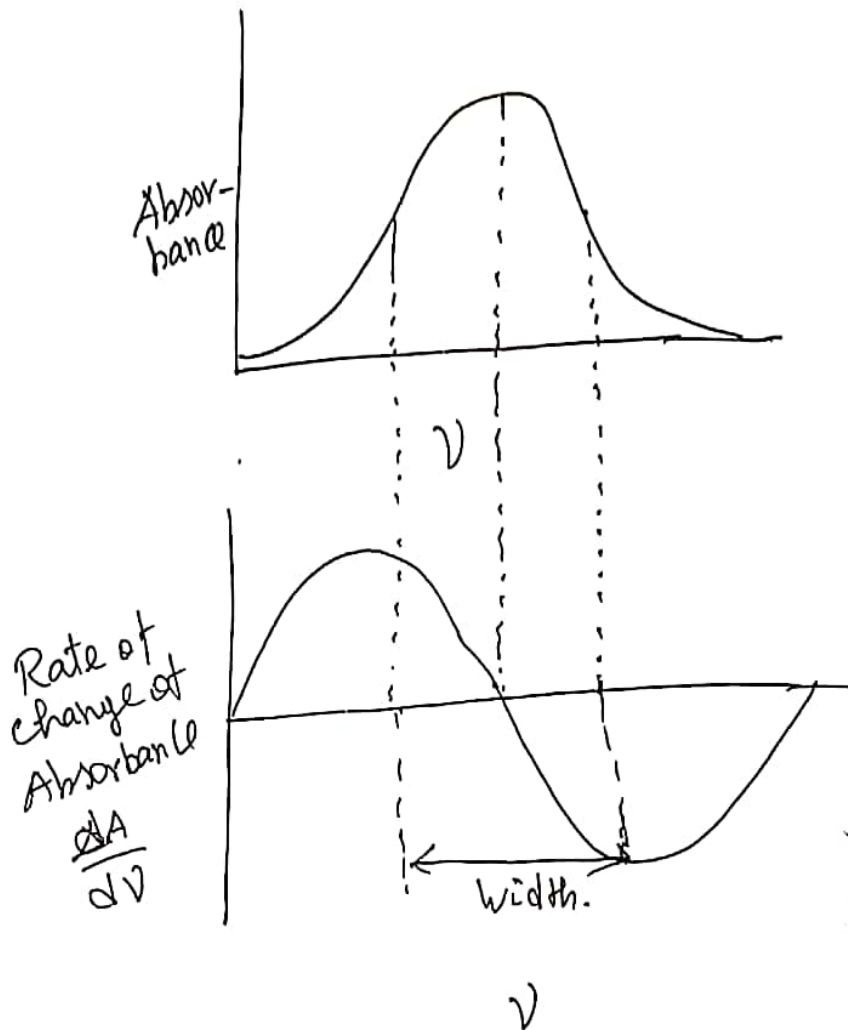
Derivative representation of spectra:-

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

$$\frac{dA}{d\nu} \quad \text{Where } A \text{ is the energy absorbed.}$$

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A derivative curve can be obtained by plotting $\frac{dA}{d\nu}$ versus ν



Advantages of derivative curves:-

- (1) It gives exact centre point of absorption
- (2) It gives exact measurement of width of ν
- (3) It shows clearly the frequency difference between the maximum and minimum of the
- (4) It gives accurate measurement of relative intensities.

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Signal to noise ratio :-

A signal may be defined as the output of a transducer 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). 20/11

Resolving power :-

The resolving power is a measure of performance of a spectrometer. It can be increased by using exit slit of narrower width. For a better resolution the width should be less than the separation between the lines. Here, complication arises as it allows total energy from the beam to reach the detector that makes the signal indistinguishable from noise.

The Intensity of spectral lines :-

The spectral intensities are concerned with the following factors - They are ① Transition probability ② The population ③ The concentration (or) path length of the sample.

① Transition probability :-

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

As the detailed calculation of transition probabilities involve the knowledge of quantum mechanics. By this, it is possible to decide whether a particular transition is forbidden or allowed.

By making use of selection rule, it is possible to decide which level transition give rise to spectral lines. Transitions which are possible

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according to selection rules are referred 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 $\Delta E = E_u - E_l$

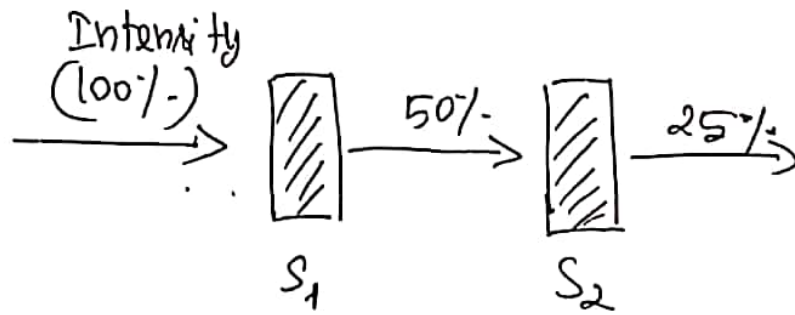
T = Temperature in Kelvin.

k = Boltzmann Constant = $1.38 \times 10^{-23} \text{ J K}^{-1}$

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

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

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$S_1 = S_2$ (same concentration).

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

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

In another form it can be written as

$$\log \frac{I_0}{I} = \epsilon cl$$

ϵ = molar absorption coef.

I_0 = Intensity of the incident light

I = Intensity of transmitted light

c = Concentration of the absorbing species g/mole

l = path length (cm)

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

$$\therefore A = \epsilon cl$$

25.

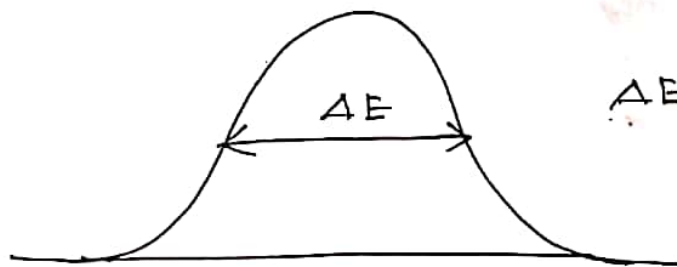
Width of spectral lines:-

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).



$\Delta E = \text{line width.}$

(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.

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(1) collision broadening:

Collision among atoms, molecules and ions can cause this effect. If the time of collision between two species X and Y is long compared with the time between collisions then the energy of an absorbing or emitting species, say X, will be perturbed by the electric and magnetic fields of Y. Consequently the spectral lines of X will be broadened by this disturbance.

(2) Doppler broadening: (Doppler shift)

Doppler shift is defined as when a moving body emits radiation a stationary observer sees shifted frequency.

Doppler effect arises when the molecule measured has a velocity v' relative to the observing instrument. If the molecule is moving 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

$$\text{by } \nu' = \nu \left(1 + \frac{v}{c}\right) \text{ or } \frac{\nu - \nu'}{\nu} = \frac{\Delta\nu}{\nu} = -\frac{v}{c}$$

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.

Doppler shift is important factor for gases.

(3) Heisenberg uncertainty 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

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

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

$$\Delta E \text{ of about } \frac{10^{-34}}{10^{-8}} = 10^{-26} \text{ J.}$$

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ΔE is the energy uncertainty for a transition. Then the corresponding uncertainty in the associated radiation frequency of $\Delta E/h$ is given as

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

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

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

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

This is apparently large uncertainty but small compared with the radiation (UV-visible) 10^{14} Hz and so the natural line width is small. So for electronic transition the line width is mostly due to collision and Doppler broadening.

But on the other hand an excited electron state has 10^{-7} s as lifetime. For this the frequency uncertainty is given as 10^7 Hz . This is comparable to the usual frequency of radiation $10^8 - 10^9 \text{ Hz}$. So for such transition, a Heisenberg uncertainty principle is by far the most important effect.

— x —

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Einstein Coefficients

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

Let us consider the interaction of light with a sample of N identical atoms. Let us assume that 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 population N_B).

$$\text{Therefore } N = N_A + N_B$$

As the energy difference $E_B - E_A$ is greater than the thermal energy kT , the atoms do not have sufficient 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 transition from A to B .

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

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

$$\text{(or)} \quad \text{rate} = - \frac{dN_A}{dt} = X_{AB} \rho_\nu N_A$$

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

In the absence of any decay mechanism, the rate of growth of the excited state population must be the negative of the rate of depletion of the ground state population because $N_A + N_B = \text{Constant} = 1$ any time. Therefore

$$- \frac{dN_A}{dt} = \frac{dN_B}{dt} = X_{AB} \rho_\nu N_A \quad \text{Absorption only}$$

N_A decreases and N_B increases with increasing

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

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The atoms relax back to the ground state by two pathways; spontaneous emission and stimulated 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 excitation with a ~~λ_{AB}~~ rate $-dN_B/dt$ depending on the excited state population N_B .

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

γ_{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.

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

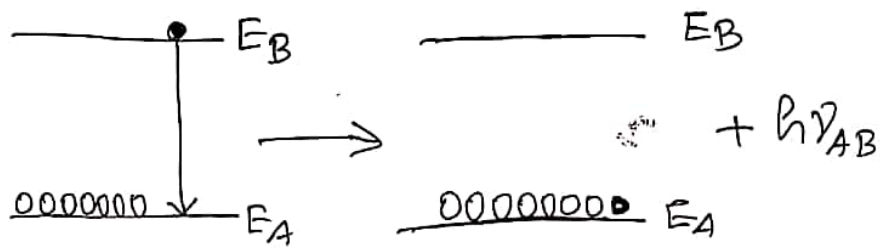
where X_{BA} is a third Einstein coefficient. Upon exposure to light, a sample of atoms simultaneously undergoes all three processes. Thus, the state of

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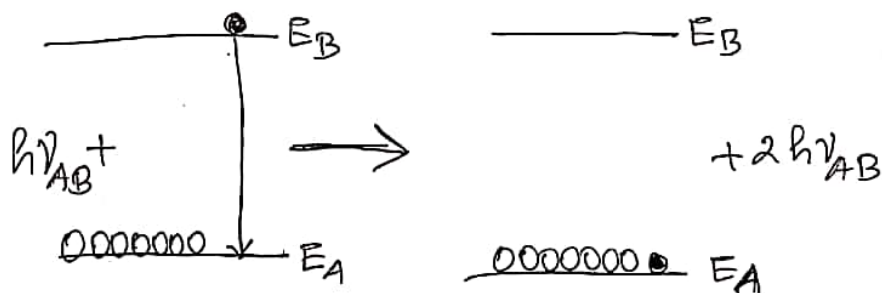
change in the population of either the ground state or the excited state must be the sum of the rates of these three processes.

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

Spontaneous emission



Stimulated emission



When the two energy states are in thermal contact

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

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

33

$$\chi_{BA} = \frac{8\pi^2 N_{AB}^2 V_{AB}^2}{c^3} \chi_{BA}$$

The net absorption intensity is given by

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

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.

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

(34)

of band values of f from 0.1 to 1 correspond to molar absorptivities in the range 10^4 to 10^5 depending on the width of the peak.

For a single symmetrical peak f can be approximated by the expression

$$f \approx (4.6 \times 10^{-9}) \epsilon_{\max} \Delta\nu_{1/2}$$

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

(35) (+)

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 constant 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 oscillator & 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 x

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

Case $f = -k(n - n_{eq})$ ($n - n_{eq} = x$)

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

~~$\frac{v}{c} = \frac{1}{2\pi} \frac{\sqrt{k}}{\sqrt{\mu}}$~~

~~$\sqrt{k} = \frac{v}{c} \sqrt{\mu} 2\pi$~~

~~$k = \frac{v^2}{c^2} \mu 4\pi^2$~~

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

~~where $\frac{v}{c} =$~~

~~$\Delta E = h \frac{v}{c} = \frac{h}{2\pi} \left(\frac{k}{\mu} \right)^{1/2}$~~

~~$\frac{v}{c} = \frac{1}{2\pi} \frac{\sqrt{k}}{\sqrt{\mu}}$~~

~~$\sqrt{k} = \frac{v}{c} 2\pi \sqrt{\mu}$~~

~~$k = \frac{v^2}{c^2} 4\pi^2 \mu$~~
 ~~$= 4\pi^2 \mu \omega^2$~~

Reference

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

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

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

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

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

$$\text{or } 4\pi^2 \omega^2 \mu$$

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

as $\bar{\nu} \cdot c = \nu$ wave
 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

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

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

$$= 2\pi^2 \omega^2 \mu A^2 \quad \text{--- (2)}$$

Since the classical mechanics does not restrict the magnitude of A , the amplitude, the vibrational 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 oscillator may be obtained by solving the Schrödinger equation (considering oscillations in one dimension only)

$$\frac{d^2 \psi}{dx^2} + \frac{8\pi^2 m}{h^2} (E_v - \frac{1}{2} kx^2) \psi = 0$$

The allowed energies under quantum mechanics are given by

$$E_v = \frac{h}{2\pi} \sqrt{\frac{k}{\mu}} (v + \frac{1}{2}) \quad \text{--- (4)}$$

$$E_v = (v + \frac{1}{2}) h \omega \quad \text{--- (5)}$$

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

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

$$\omega = \frac{2\pi \bar{\omega} c}{1}$$

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

$$E_v = h c \bar{\omega}$$

$$\bar{\omega} = (v + \frac{1}{2}) \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \quad \text{--- (6)}$$

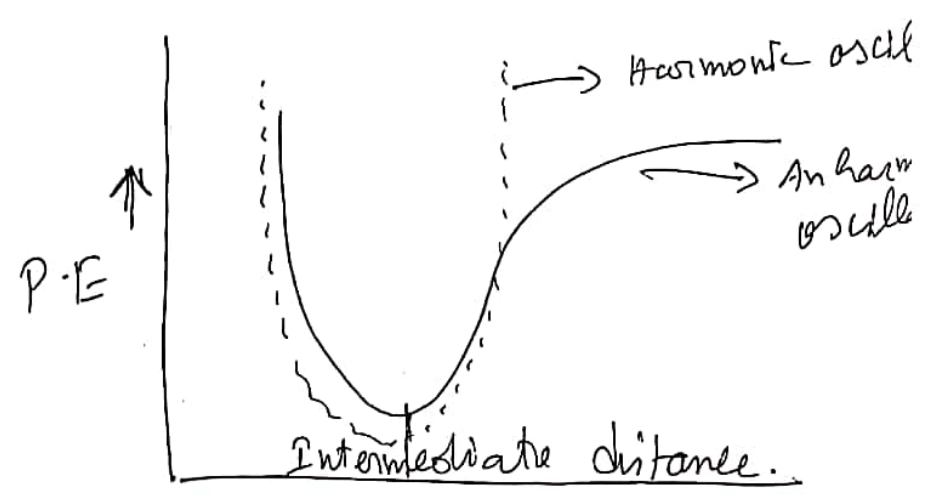
$$E_v = (v + \frac{1}{2}) \bar{\omega} \text{ cm}^{-1} \quad \text{--- (7)}$$

It is seen from (6) that when $v=0$, $E_0 = \frac{1}{2} h c \bar{\omega}$. 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~~ be at rest. It will be undergoing vibration.

✓ The Anharmonic oscillator.

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

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



(41) (27)

The allowed vibrational energy levels for anharmonic oscillators is

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

where $\bar{\omega}_e$ is an oscillator frequency (expressed in wave number) x_e is the corresponding ~~constant~~ anharmonicity constant.

The equation (1) can be written as

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

When compared with the energy levels of the harmonic oscillator

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

~~Multiply equation (2) by $\left(v + \frac{1}{2}\right)$~~

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

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

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

The zero point energy of the anharmonic oscillator can be obtained by putting $v=0$ in the eqn. (1)

$$\bar{\omega}_0 = \bar{\omega}_e \left\{ 1 - \frac{1}{2} x_e \right\} \text{ cm}^{-1} \rightarrow (4)$$

and substitute in eqn. in (2) as $v=0$

$$E_0 = \frac{1}{2} \bar{\omega}_e \left\{ 1 - \frac{1}{2} x_e \right\} \text{ cm}^{-1} \rightarrow (5)$$

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 -

$$\Delta v = \pm 1, \pm 2, \pm 3, \dots$$

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

(i) $v=0 \rightarrow v=1$ $\Delta v = \pm 1$ with constant Intensity

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

$$\Delta E = E_{v=1} - E_{v=0}$$

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

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

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

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

$$\Delta E = (2 + \frac{1}{2}) \bar{w}_e - \kappa_e (2 + \frac{1}{2})^2 \bar{w}_e - \left\{ \frac{1}{2} \bar{w}_e - (\frac{1}{2})^2 \kappa_e \bar{w}_e \right\}$$

$$= (\frac{5}{2}) \bar{w}_e - \kappa_e (\frac{5}{2})^2 \bar{w}_e - \frac{1}{2} \bar{w}_e + \frac{1}{4} \kappa_e \bar{w}_e$$

$$\bar{w}_e \left[\frac{5}{2} - \frac{1}{2} \right] - \kappa_e \bar{w}_e \left[(\frac{5}{2})^2 - \frac{1}{4} \right]$$

$$= \bar{w}_e (2) - \kappa_e \bar{w}_e \left[\frac{25}{4} - \frac{1}{4} \right]$$

$$= 2 \bar{w}_e - \kappa_e \bar{w}_e \left(\frac{24}{4} \right)$$

$$= 2 \bar{w}_e - \kappa_e \bar{w}_e (6)$$

$$= 2 \bar{w}_e (1 - 3 \kappa_e) \text{ cm}^{-1}$$

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.

$$\Delta E = (3 + \frac{1}{2}) \bar{w}_e - \kappa_e (3 + \frac{1}{2})^2 \bar{w}_e - \left\{ \frac{1}{2} \bar{w}_e - (\frac{1}{2})^2 \kappa_e \bar{w}_e \right\}$$

$$= 3 \bar{w}_e (1 - 4 \kappa_e) \text{ cm}^{-1}$$

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

(18)

To a good approximation, since $x_e = 0.01$, the 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 which 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 $1-10 \text{ cm}^{-1}$ (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.

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

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

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

$$\begin{aligned} E_{J,v} &= E_J + E_v \\ &= BJ(J+1) - DJ^2(J+1)^2 + HJ^3(J+1)^3 + \dots \\ &\quad + \left(v + \frac{1}{2}\right) \bar{\omega}_e - x_e \left(v + \frac{1}{2}\right) \bar{\omega}_e \text{ cm}^{-1} \quad (1) \end{aligned}$$

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

$$E_{\text{total}} = E_{J,v} = BJ(J+1) + \left(v + \frac{1}{2}\right) \bar{\omega}_e - x_e \left(v + \frac{1}{2}\right) \bar{\omega}_e \quad (2)$$

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

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

$$\Delta v = \pm 1, \pm 2 \text{ etc } \Delta J = \pm 1$$

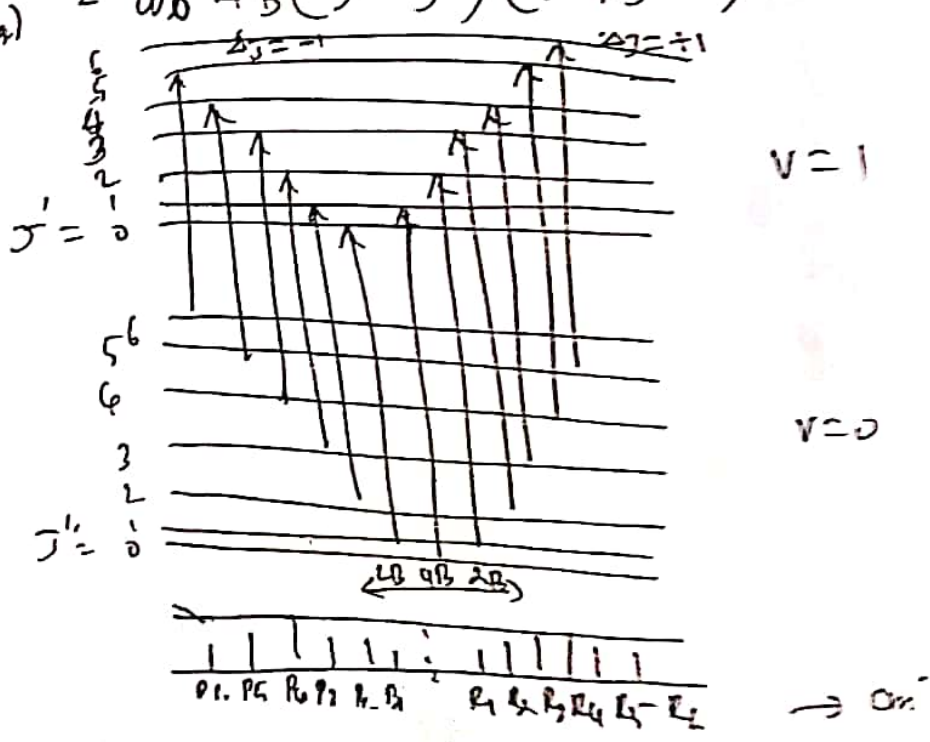
A spectrum may be obtained by applying selection rules to the energy levels, considering the $v=0 \rightarrow v=1$ transitions

$J' = \text{higher}$
 $J'' = \text{lower}$

$$\begin{aligned} \Delta E_{J',v} &= E_{J',v=1} - E_{J'',v=0} \\ &= B J'(J'+1) + \frac{1}{2} \bar{\omega}_e - 2 \frac{1}{4} x_e \bar{\omega}_e - \left\{ B J''(J''+1) \right. \\ &\quad \left. + \frac{1}{2} \bar{\omega}_e - \frac{1}{4} x_e \bar{\omega}_e \right\} \end{aligned}$$

$\frac{1}{4} x_e \bar{\omega}_e$
 $\frac{1}{2} \bar{\omega}_e - 2 \frac{1}{4} x_e \bar{\omega}_e$
 $= \frac{1}{4} \bar{\omega}_e$

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



Taking B is identical in the upper and lower vibrational states in 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

$$\Delta E_{J,V} = \bar{\omega}_0 + 2B(J'' + 1) \text{ cm}^{-1} \quad J'' = 0, 1, 2, \dots$$
(5)

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

$$\Delta E_{J,V} = \bar{\omega}_0 - 2B(J' + 1) \text{ cm}^{-1} \quad J' = 0, 1, 2, \dots$$
(6)

These two expressions may conveniently be combined in to

$$\Delta E_{J,V} = \bar{\nu}_{\text{spec}} = \bar{\omega}_0 + 2Bm \text{ cm}^{-1}$$

$m = \pm 1, \pm 2, \dots$

(7)

where 'm' ~~is~~ 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 referred 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 0 P R S branch

Rotation-vibration spectrum of carbon monoxide

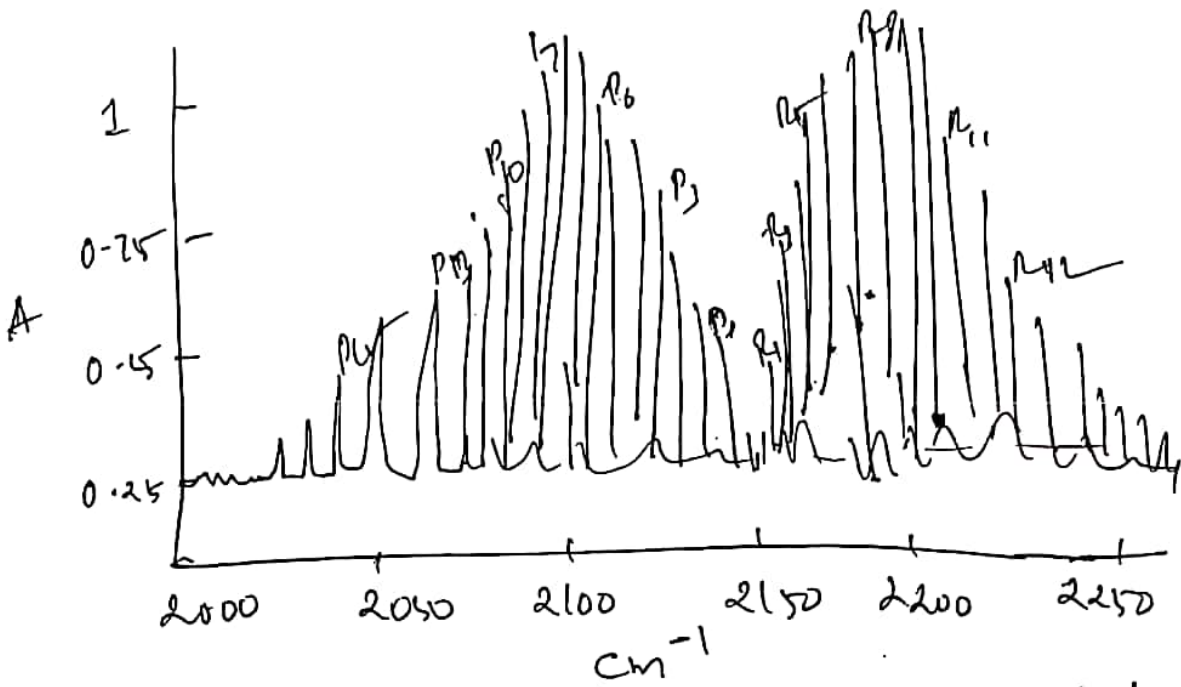
The fundamental vibration-rotation band of carbon monoxide under high resolution has been observed. The observed wave numbers for P and R branches are given in the table.

Line	$\bar{\nu}$	Separation $\Delta\bar{\nu}$	Line	$\bar{\nu}$	Separation $\Delta\bar{\nu}$
P(1)	2139.43	3.88	R(1)	2147.08	3.78
P(2)	2135.55	3.92	R(2)	2150.86	3.73
P(3)	2131.63	3.95	R(3)	2154.37	3.72
P(4)	2127.68	3.98	R(4)	2158.31	3.66
P(5)	2123.70		R(5)	2161.97	

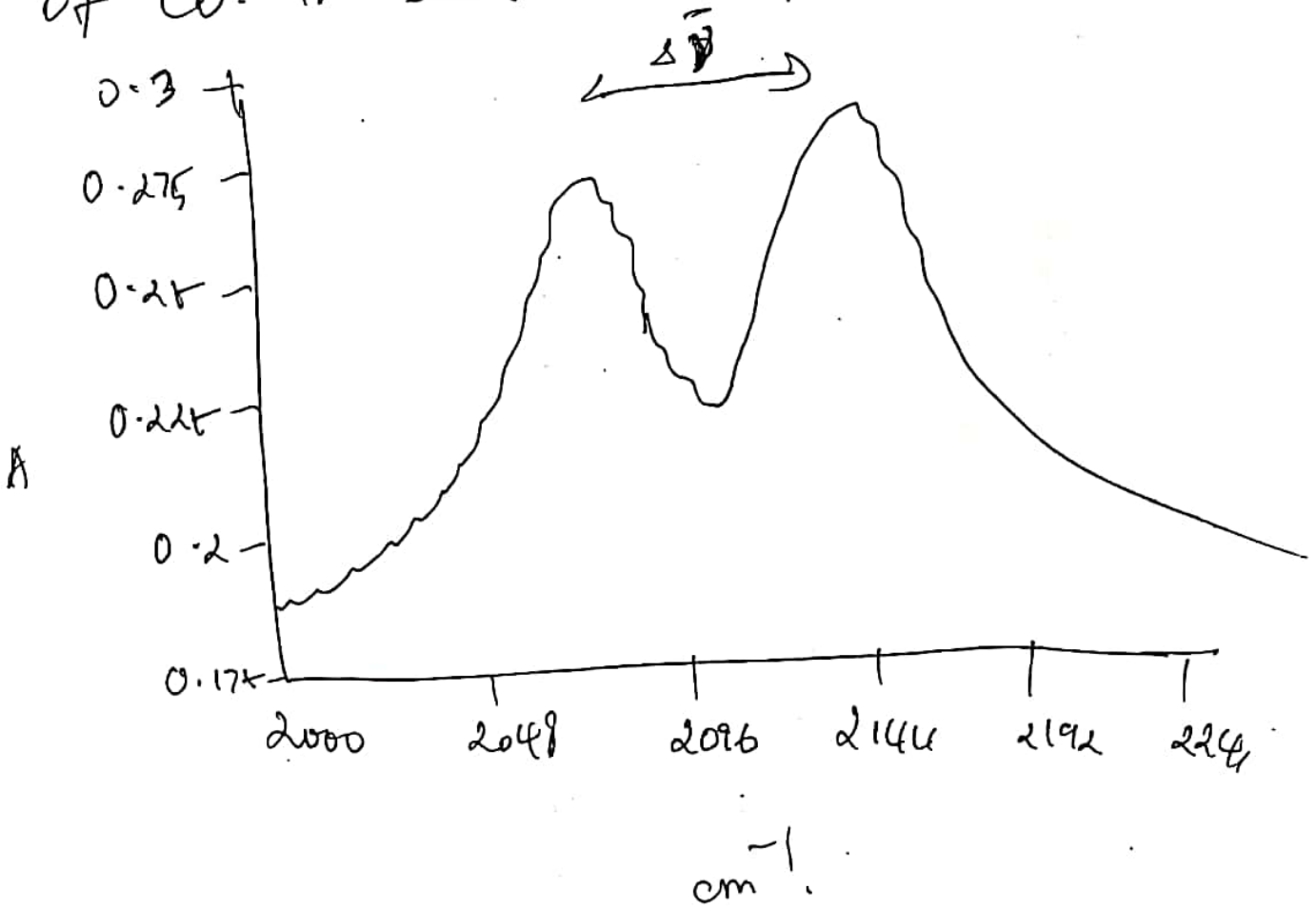
From the table we see that the band centre is at about 2143 cm^{-1} , while the average line separation near the centre is 3.83 cm^{-1} .

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

This is satisfactory agreement with the value $B = 1.92118 \text{ cm}^{-1}$ derived by microwave studies. It is useful to obtain good values of the rotational constant and the moment of inertia and hence 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 $\Delta \bar{\nu}$

given as

$$\Delta \bar{\nu} = 4B \sqrt{KT/2Bhc} + \frac{1}{2} = \sqrt{8KT B/hc}$$

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

we can write

$$\Delta \bar{\nu} = \sqrt{8KT B/hc} \quad B = hc(\Delta \bar{\nu})^2 / 8KT$$

where $\bar{\nu}$ is expressed in cm^{-1}

In the case of CO the separation is about 55 cm^{-1} at 300K.

— 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 change 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

$$B_v = B_e - \alpha (v + \frac{1}{2}) \quad \text{--- (1)}$$

B_v is the rotational constant in vibrational level v in terms of the equilibrium value B_e and α is a small positive constant for each molecule. Here we restrict our ~~dis~~ discussion to the fundamental vibrational change, i.e. the change $v=0 \rightarrow v=1$ and the respective B -values be B_0 and B_1 with

$$B_0 > B_1$$

$B = \frac{h^2}{8\pi^2 I c}$
 $I = m r^2$
moment of Inertia

For this transition

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

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

where as ~~before~~ $\bar{W}_0 = \bar{W}_e (1 - 2xe)$.

We have two cases

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

$$\Delta E = \bar{V}_R = \bar{W}_0 + (B_1 + B_0)(J''+1) + (B_1 - B_0)(J''+1)$$

and

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

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

$$\Delta E = \bar{V}_P = \bar{W}_0 - (B_1 + B_0)(J'+1) + (B_1 - B_0)(J'+1)$$

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

where \bar{V}_P and \bar{V}_R to represent the wave number of the P and R branch lines respectively. The two equations can be combined into the expression

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

where positive m values refer to R branch and negative to P branch. $(m = \pm 1, \pm 2, \dots)$

Ignoring vibration-rotation interaction involves

$B_1 = B_0$, The equation (7) simplifies to

$$\Delta E_{J,V} = \bar{\nu}_{\text{spec}} = \bar{\nu}_0 + 2Bm \text{ cm}^{-1} \quad (\text{Roth previous page})$$

But in this consideration

Since $B_1 < B_0$ the last term of equation (7) 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

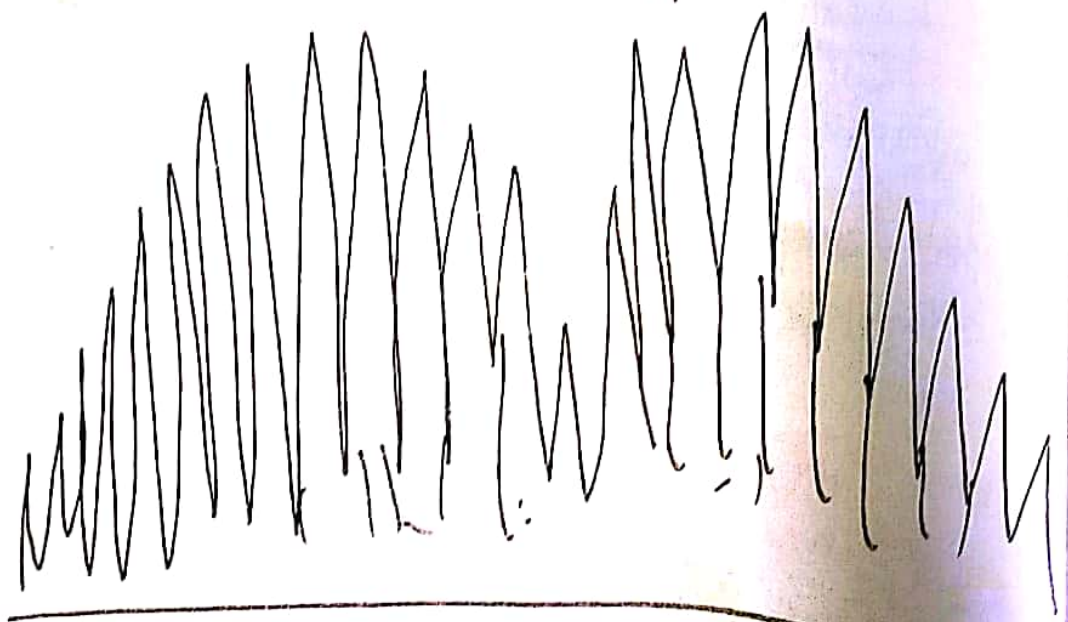
$\Delta J = \pm 1$ $\Delta V = \pm 1, \pm 2, \pm 3 \dots$ for anharmonic motion

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

Hence the spectra is similar in appearance, consisting

of P and R branches with lines about equally spaced on each side no line occurring at the band centre. The moment of Inertia may be considerably larger the B value correspondingly smaller and P and R spacing will be less. The figure shows part of spectrum of HCN, a linear molecule whose structure is $H - C \equiv N$. The band concerned is the stretching frequency at about 3310 cm^{-1} and spacing is observed to be about $2.8 - 3.0 \text{ cm}^{-1}$ near the band centre. This is to be compared 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 separate lines can no longer be resolved in the P and R branches. It is seen that a non-linear molecule can not give rise to this type of band shape.



Perpendicular Vibration:

The selection rule for this is found to be

$$\Delta V = \pm 1 \quad \Delta J = 0, \pm 1 \quad \text{for simple harmonic motion.}$$

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.

$$\Delta E = E_{J, V+1} - E_{J, V}$$

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

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

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

$$\Delta E = E_{J, V+1} - E_{J, V}$$

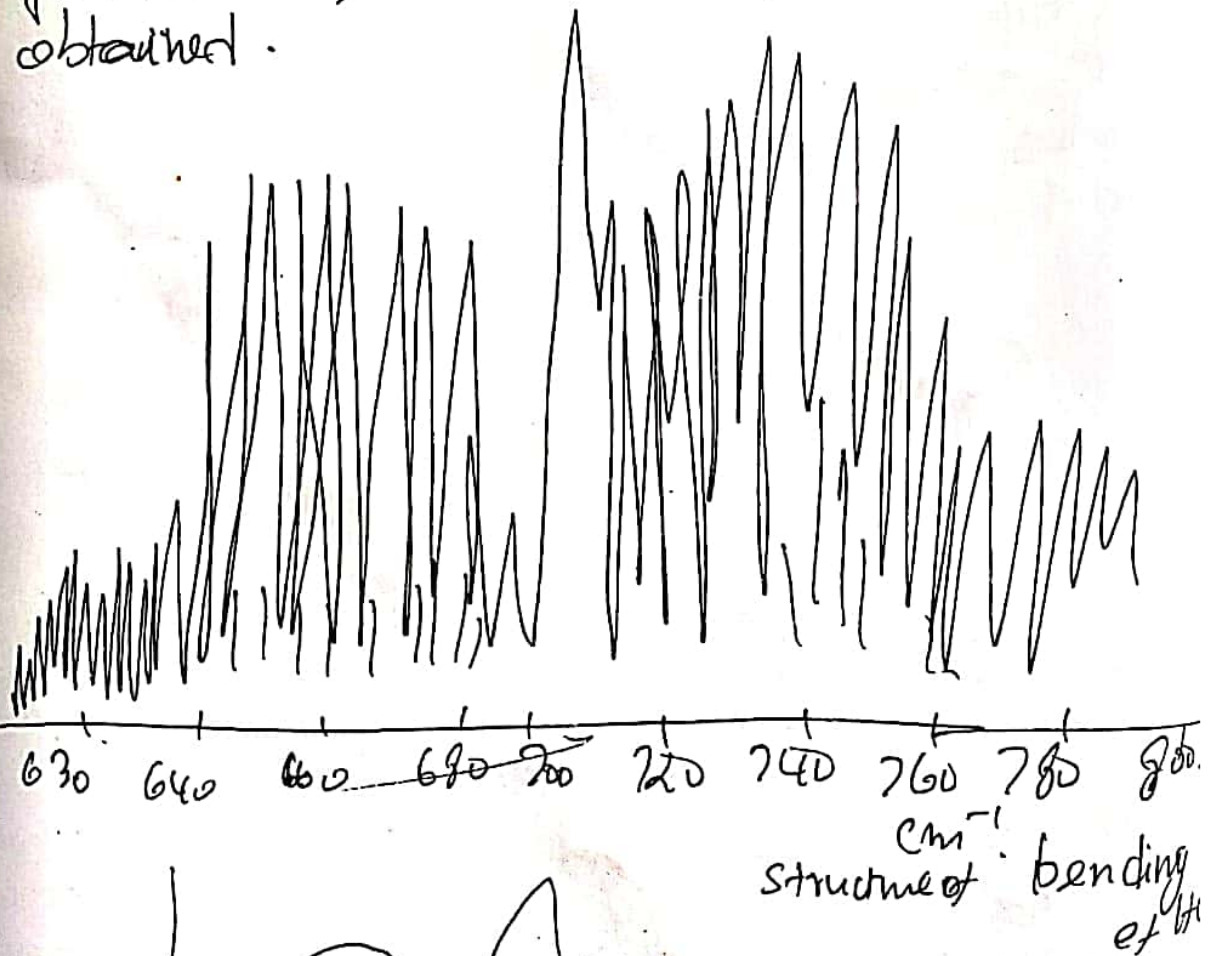
=

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

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

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 polyatomic molecules with zero dipole moment do not give rise to pure roto spectra in the microwave region (eg CO_2 , $\text{CH}_2\text{=CH}_2$). Such molecules show vibrational spectra in the IR red region (or Raman). If they exhibit resolved fine structure, the moment of inertia can be obtained.



Symmetric top molecules

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

$$E_{vib} = (v + \frac{1}{2}) \bar{h} \omega_e - (v + \frac{1}{2})^2 x_e \bar{h} \omega_e \text{ cm}^{-1}$$

and the rotational levels $(v = 0, 1, 2, 3, \dots)$

$$E_{rot} = B J(J+1) + (A-B) k^2 \text{ cm}^{-1}$$

$$[J = 0, 1, 2, \dots \quad k = J(J-1), (J-2), \dots, -J]$$

Thus

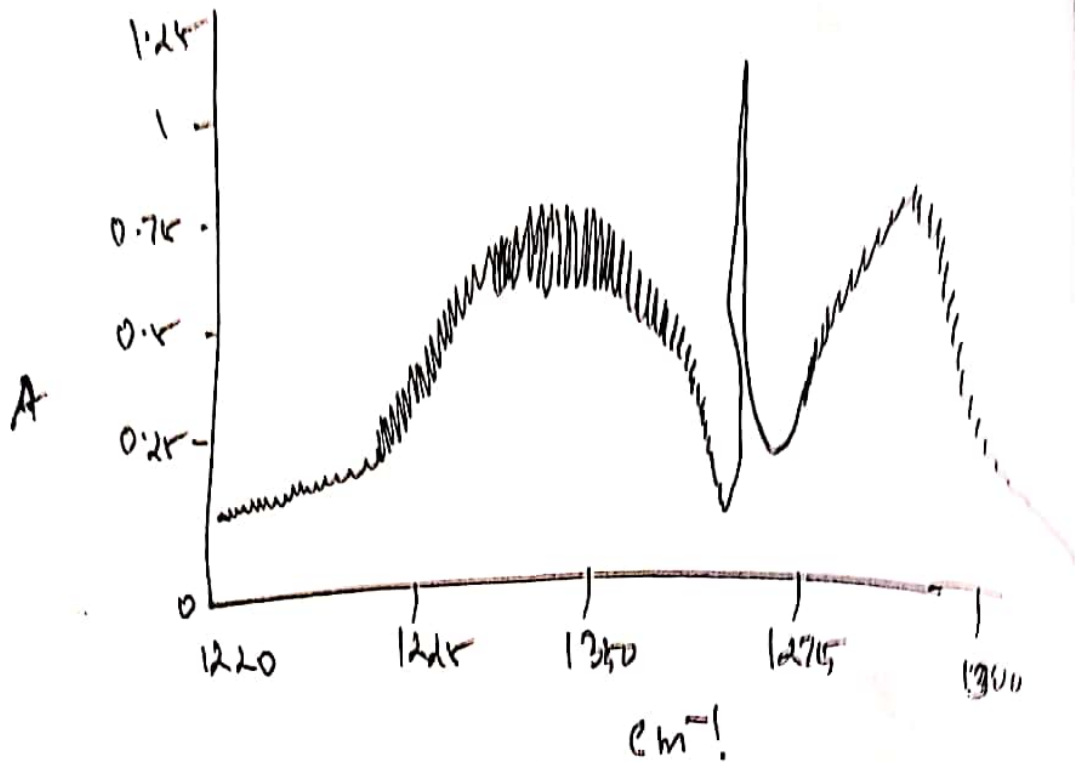
$$E_{Jv} = E_{vib} + E_{rot} = (v + \frac{1}{2}) \bar{h} \omega_e - (v + \frac{1}{2})^2 x_e \bar{h} \omega_e + B J(J+1) + (A-B) k^2 \text{ cm}^{-1}$$

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 with a P, R line spacing of $2B$ (which is unlikely to be resolved) and a strong central Q line. The spectrum of CH_3I is shown above. The intensity of the Q branch (relative to that in the P and R branches) varies with the ratio I_A/I_B in the limit, when $I_A \rightarrow 0$ the symmetric 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)

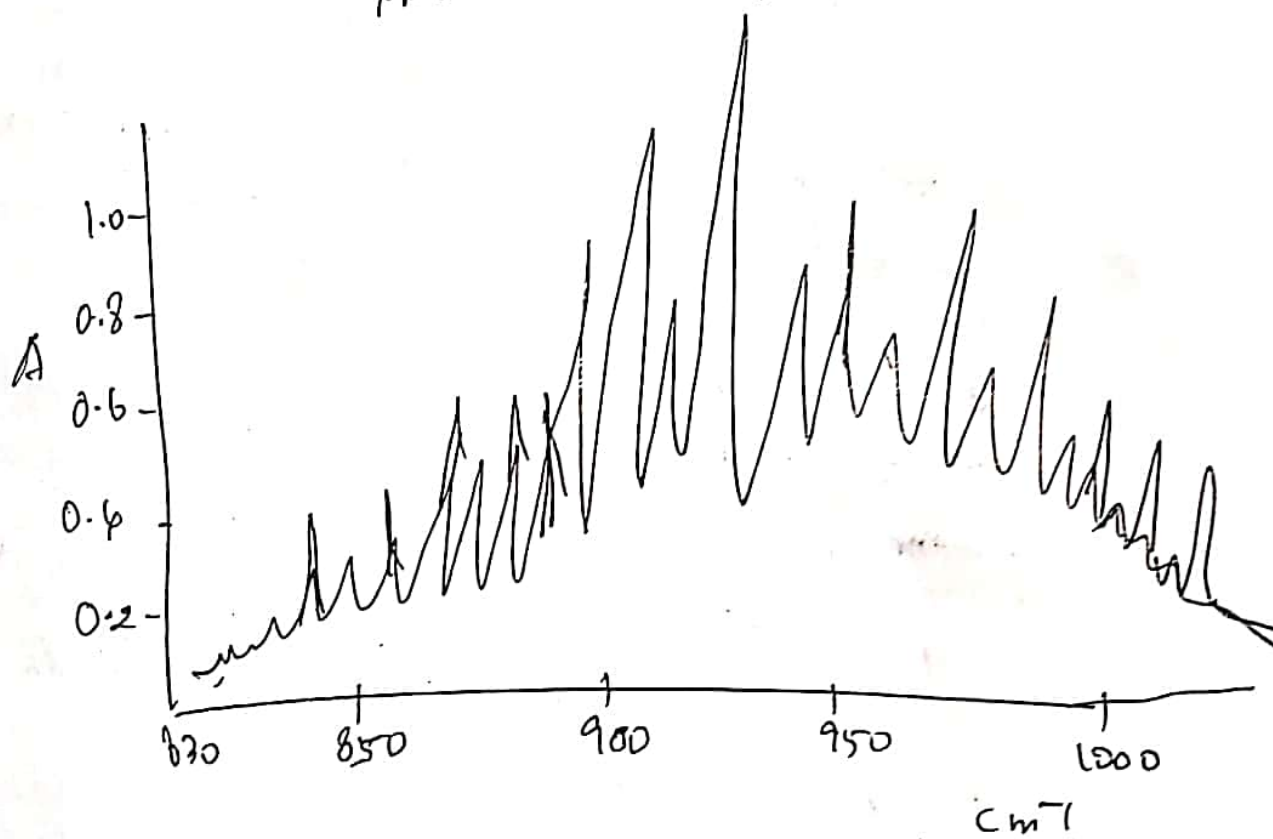
$$\Delta E = \bar{\nu}_{\text{prec}} = \bar{\omega}_e + 2B(J+1) + (A-B)(1 \pm 2k) \text{ cm}^{-1}$$

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

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

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

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



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 ($k = J, J-1, \dots, -J$). The wings of the spectrum being quite complicated as they have periodical variation as strong weak weak strong ... The Q branch ~~is~~ appears separated.

as a series of maxima above the P-R

The influence of Nuclear spin;

The centre of symmetry possessed by some like CO_2 , ethylene ($\text{O}=\text{C}=\text{O}$, $\text{H}-\text{C}=\text{C}-\text{H}$) has an effect on the intensity of alternate lines in the P and R branches. This effect is due to the existence of nuclear spin and is an additional factor determining the population of rotational levels. In the case of CO_2 every alternate rotational level is completely unpopulated and so alternate lines in the P and R branches ~~are~~ zero intensity. This leads to a line spacing of $4B$ instead of $2B$ (usual). This is explained by isotopic molecule $^{18}\text{O}-\text{C}-^{16}\text{O}$. Here there is no longer a centre of symmetry, nuclear 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 levels have population which differs by a factor of 2 so that the P and R branch lines show a strong, weak, strong, weak... alternation in intensity as shown in figure (Refer previous title)

Raman Spectra



✓ Rotational Raman spectra of Linear molecules:-

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

$$\Sigma_J = BJ(J+1) \text{ cm}^{-1} \quad (J=0, 1, 2, \dots)$$

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 the selection rule is $\Delta J = \pm 1$. Due to the symmetry of the polarizability ellipsoid the rotational 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
the ~~case~~ $\Delta J = +2$

$$\begin{aligned}\Delta J &= \sum_{J'=J+2} - \sum_{J''=J} \\ &= B(4J+6) \text{ cm}^{-1}\end{aligned}$$

Since $\Delta J = +2$, we may label these lines S₂ lines and write

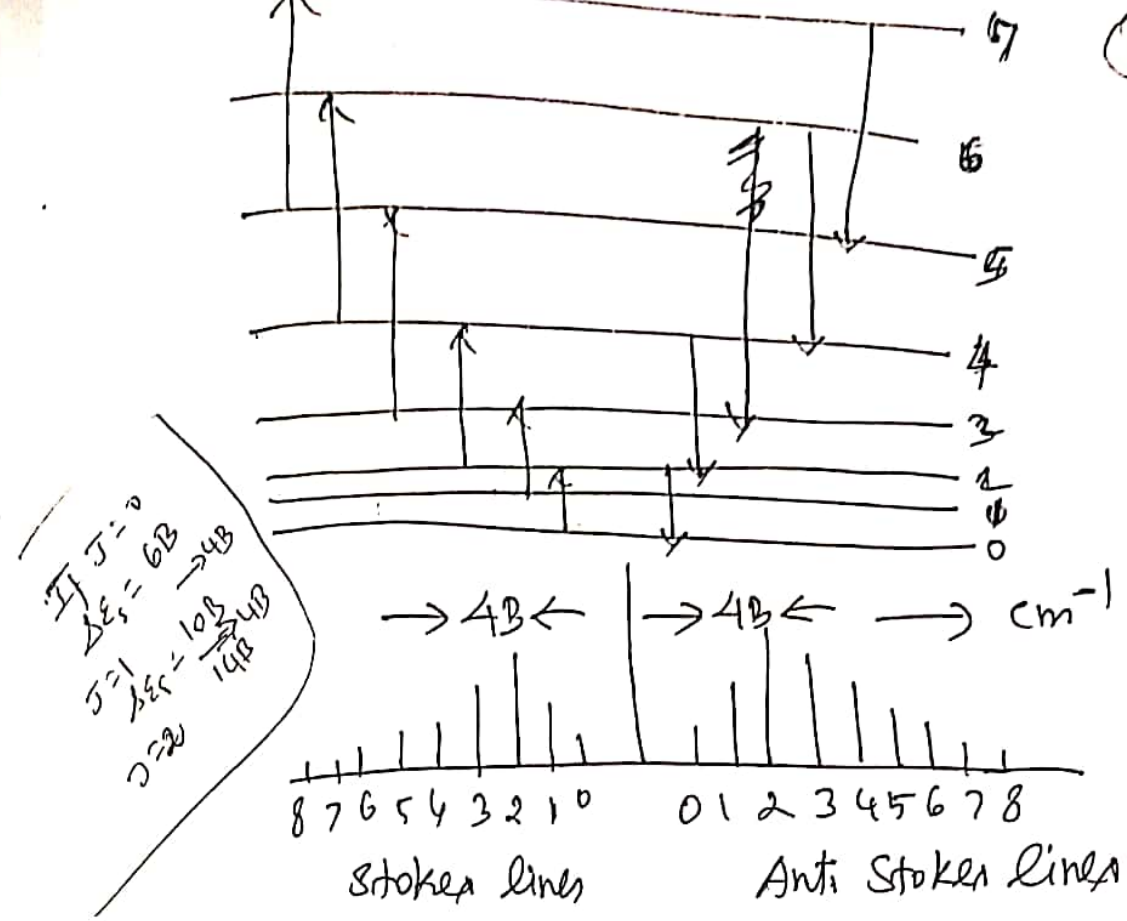
$$\Delta E_s = B(4J+6) \text{ cm}^{-1} \quad (J = 0, 1, 2, \dots)$$

The wave numbers of the corresponding spectral lines are given by

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

where the + line refers to anti-stokes lines, and minus to stokes lines. $\bar{\nu}_{ex}$ is the wave number of the exciting radiation.

The allowed transitions and the Raman effect are shown in the diagram. It should be noted that stokes and anti-stokes lines have comparable intensity because many rotational levels are populated.



$J=0$
 $\Delta E_s = 6B \rightarrow 4B$
 $J=1$
 $\Delta E_s = 10B \rightarrow 4B$
 $J=2$
 $\Delta E_s = 14B$

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.

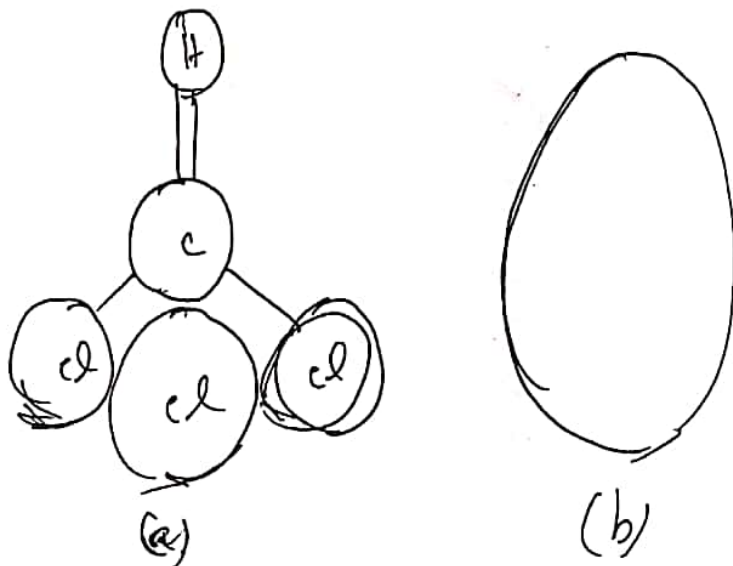
$\frac{h}{8\pi^2 I c}$
 $\frac{h}{8\pi^2 I c}$

$J = m, m+2, m+4, \dots$
 $\Delta E = 4B$

$\Delta E = \text{bond length}$

Symmetric top molecules:

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



In general, rotation about the top axis produces no change in the polarizability but end-on rotation will produce such change.

$$E_{J,k} = B J(J+1) + (A-B) k^2 \quad \text{cm}^{-1}$$

$$J = 0, 1, 2, \dots \quad k = \pm J, \dots$$

The selection rules for Raman spectra are

$$\Delta k = 0 \quad \Delta J = 0, \pm 1, \pm 2 \quad (\text{except for states where } \Delta J = \pm 2)$$

k is the rotational quantum number of a rotation, so the selection rule $\Delta k = 0$ implies that changes in the angular momentum about the top axis will not give rise to Raman spectra.

So it is Raman inactive.

Now we consider two cases

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

$$\Delta E_R = \epsilon_{J'=J+1} - \epsilon_{J''=J}$$

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

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

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

$$\Delta E_S = \epsilon_{J''=J+2} - \epsilon_{J'=J}$$

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

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

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

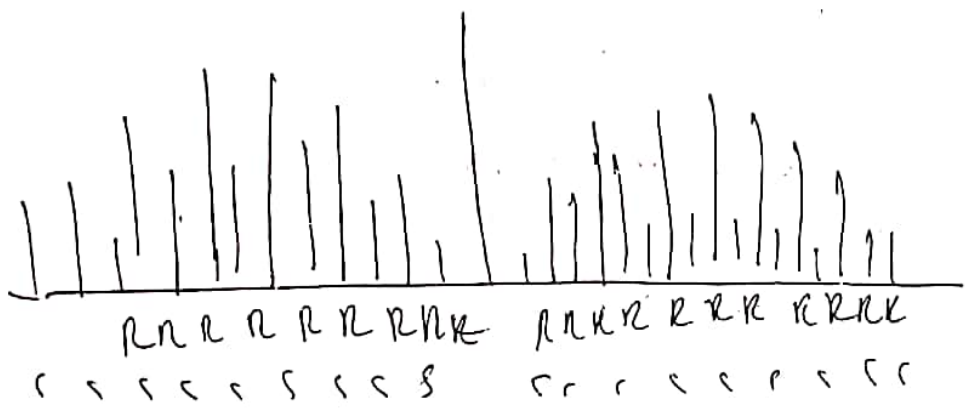
$$\bar{\nu}_R = \bar{\nu}_{0x} \pm \Delta E_R = \bar{\nu}_{0x} \pm 2B(J+1) \text{ cm}^{-1}$$

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

$$\bar{\nu}_S = \bar{\nu}_{0x} \pm \Delta E_S = \bar{\nu}_{0x} \pm B(4J+6) \text{ cm}^{-1}$$

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

The complete spectrum is given as



Vibrational Raman Spectra:

For energy vibrational mode, the expression can be written as

$$E = \bar{\omega}_e \left(v + \frac{1}{2} \right) - \bar{\omega}_e x_e \left(v + \frac{1}{2} \right)^2 \quad \text{etc.}$$

$(v = 0, 1, 2, \dots)$

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

x_e = Anharmonicity constant

The selection rule is $\Delta v = 0, \pm 1, \pm 2, \dots$

This is same for Raman as for IR spectra. The probability of $\Delta v = \pm 2, \pm 3, \dots$ decreases rapidly.

Particularly, we take into consideration to Raman active modes the selection rule is to be applied as follows:

$$v = 0 \rightarrow v = 1; \quad \Delta E_{\text{fundamental}} = \bar{\omega}_e \quad (1-2)$$

$$v = 0 \rightarrow v = 2; \quad \Delta E_{\text{overtone}} = 2\bar{\omega}_e \quad (1-3)$$

$$v = 0 \rightarrow v = 2; \quad \Delta E_{\text{hot}} = \bar{\omega}_e \quad (1-4)$$

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

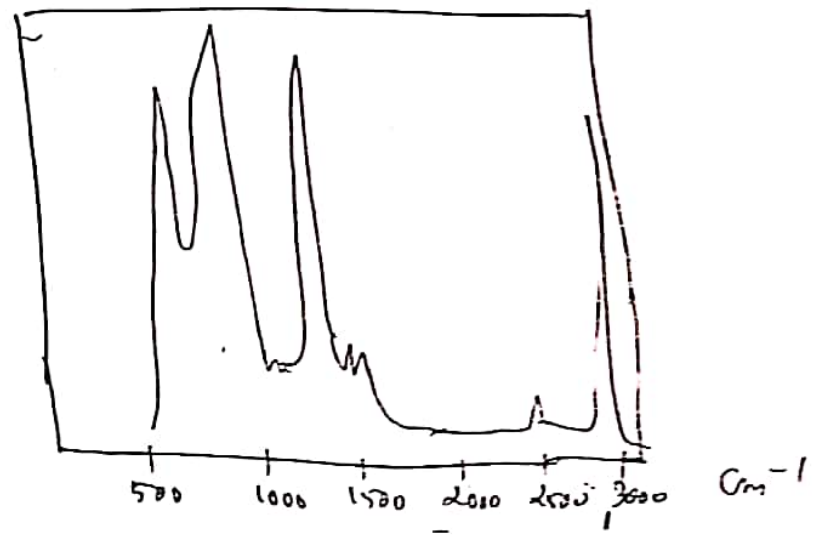
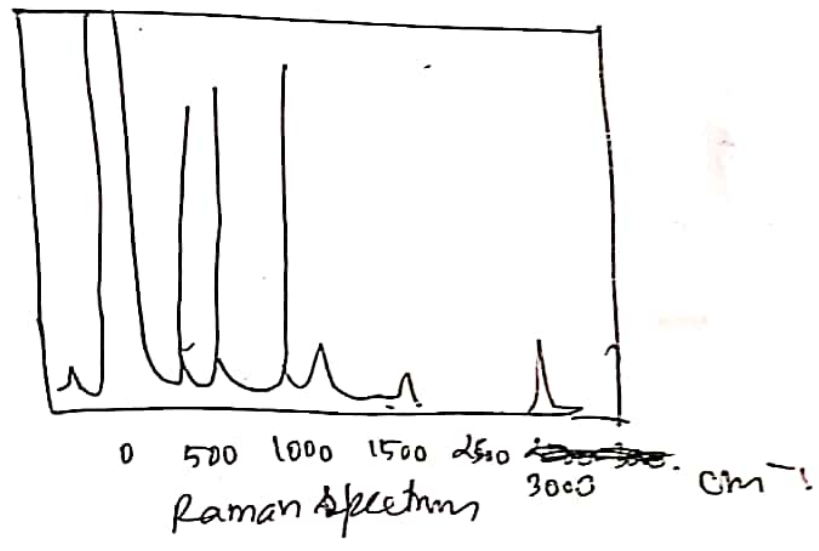
$$\bar{\nu}_{\text{fundamental}} = \bar{\nu}_{\text{nu}} \pm \Delta E_{\text{fundamental}} \text{ cm}^{-1}$$

How 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 anti-Stokes lines. The latter are ~~the~~ very weak. ~~to~~ (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 CHCl3 a symmetric top molecule is shown in the figure.



In the Raman spectrum the Raman lines appear at 262, 366, 668, 761, 1216 and 3019 cm^{-1} . on the low frequency (Stokes) side of the exciting line and at 262 cm^{-1} on the anti-Stokes - high frequency side.

For comparison the IR spectrum is also given. It shows lines appear at wave numbers corresponding very precisely with those of lines in the Raman spectrum but with very different relative intensities.

Rotational fine structure

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

$$E_{J,v} = \bar{\omega}_0 (v + \frac{1}{2}) - \bar{w}_e x_e (v + \frac{1}{2})^2 + B J(J+1) \text{ cm}^{-1}$$

$$(v = 0, 1, 2, \dots; J = 0, 1, 2, \dots)$$

As in the previous case, we ignore centrifugal distortion. For diatomic molecules the J selection rule $\Delta J = 0, \pm 2$ (refer previous titles) and combining this with the vibrational change $v=0 \rightarrow v=1$, we have

$$\Delta J = 0 \quad \Delta E_0 = \bar{\nu}_0 \text{ cm}^{-1} \quad (\text{for all } J)$$

$$\Delta J = +2; \quad \Delta E_2 = \bar{\nu}_0 + B(4J+6) \text{ cm}^{-1}$$

$$\Delta J = -2; \quad \Delta E_0 = \bar{\nu}_0 - B(4J+6) \text{ cm}^{-1} \quad J = 0, 1, 2$$

(89) (82)

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

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

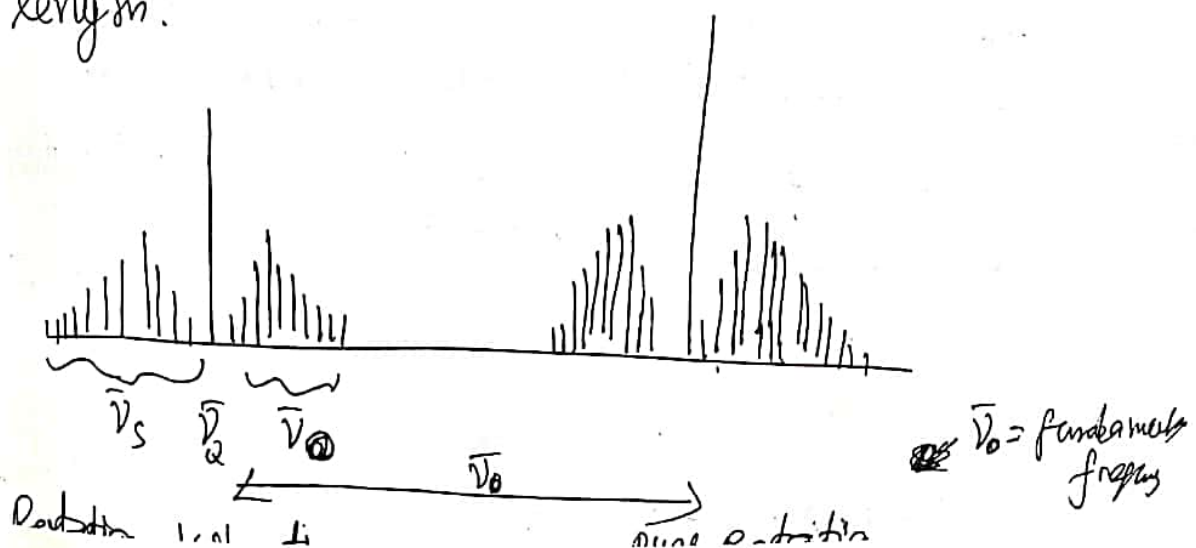
$$\bar{\nu}_O = \bar{\nu}_{ex} - \Delta \epsilon_O = \bar{\nu}_{ex} - \bar{\nu}_0 + B(4J+6) \text{ cm}^{-1}$$

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

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

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

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.



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: (X)

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

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

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

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

$$\Delta E_{\text{total}} = \Delta E_{\text{el}} + \Delta E_{\text{vib}} + \Delta E_{\text{rot}} \quad \text{em}^{-1}$$

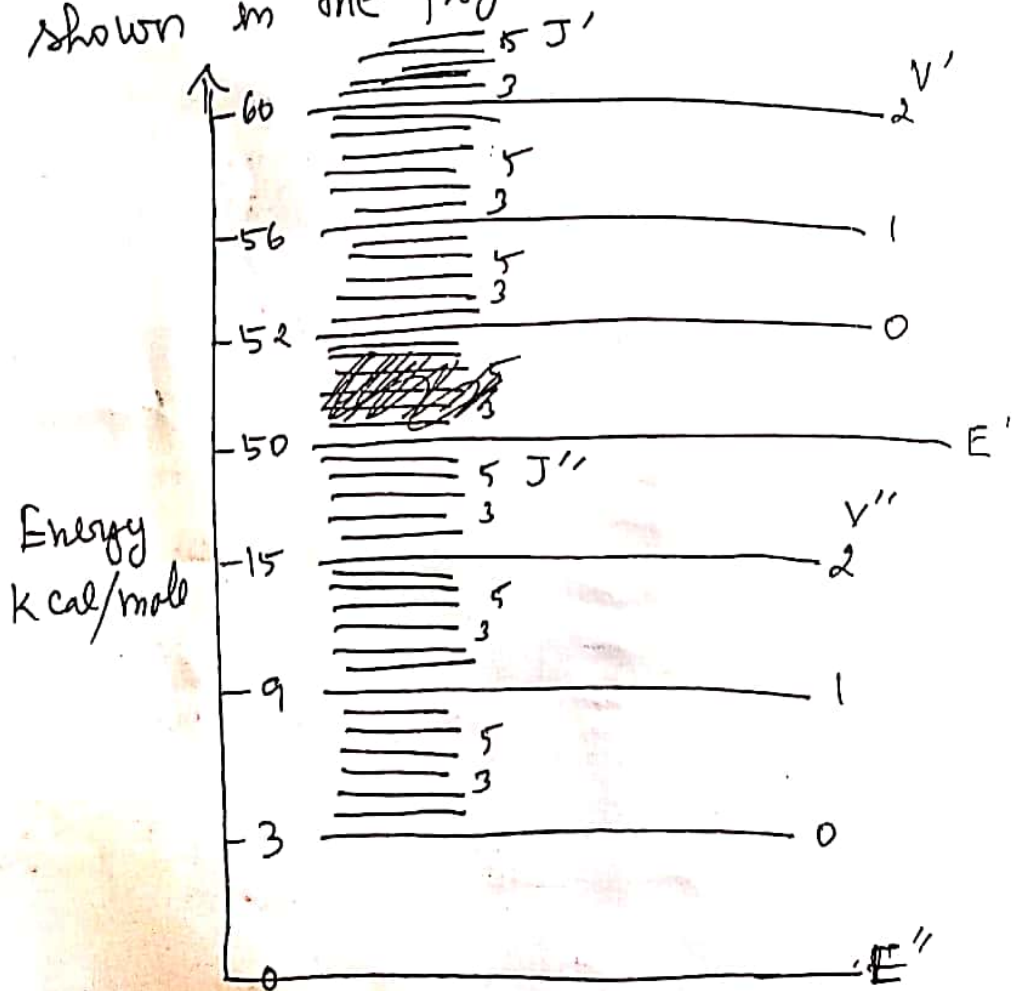
(2)

The approximate orders of magnitude of changes are

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

so we see that the vibrational changes with a coarse structure and rotational changes with fine structure on the spectra of electronic

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 kcal/mole that between vibrational energy levels is a few kcal/mole and that between rotational energy levels is only of the order of tens of cal/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.

(4)

Vibrational Coarse Structure

Progressions:-

If we consider the vibrational coarse structure of spectra and ignoring the rotational changes, the equation for E_{total} can be written as -

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

(or)

$$E_{total} = E_{el} + E_{vib} \text{ cm}^{-1} \quad \text{--- ①}$$

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

$$E_{vib} = (V + \frac{1}{2}) \bar{\omega}_e - (V + \frac{1}{2})^2 \bar{\omega}_e x_e \text{ cm}^{-1}$$

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

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

x_e = Anharmonicity Constant (It is always small and positive ($\approx +0.01$)).

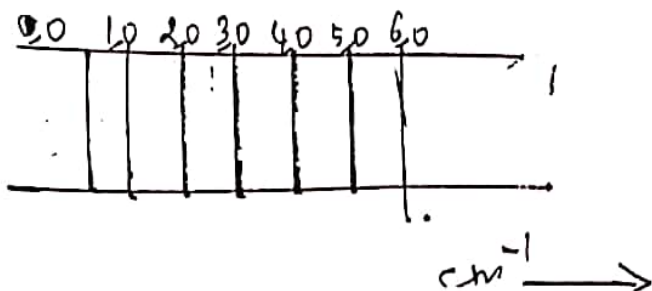
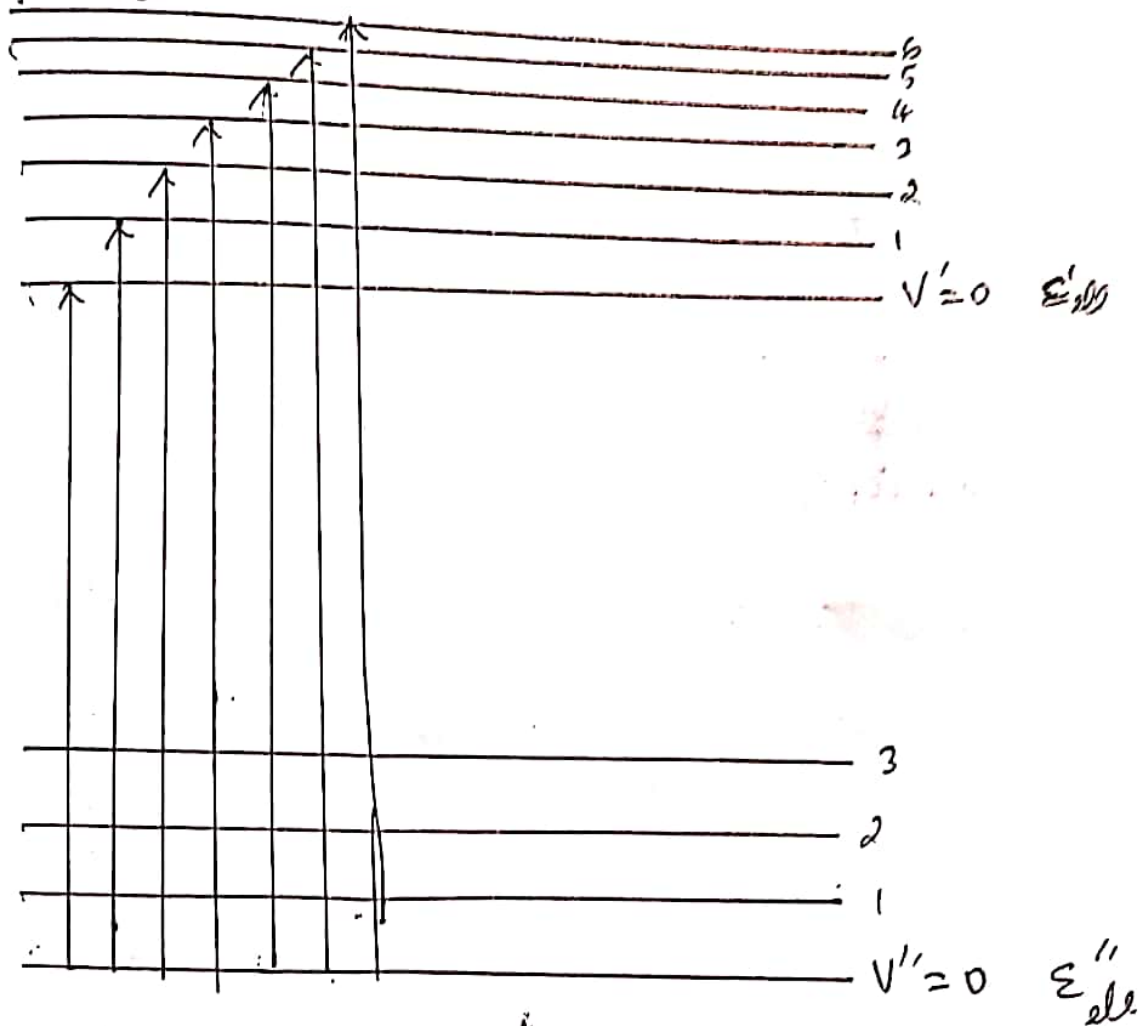
Substituting this value of E_{vib} in eqn. ① get

(5)

$$\epsilon_{total} = \epsilon_{elec} + (V + \frac{1}{2}) \bar{\omega}_0 - \alpha_0 (V + \frac{1}{2})^2 \bar{\omega}_0$$

cm^{-1}
— (5)

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



(6)

The lower states are denoted as V'' , E''_{ele} , where the upper states are V' , E'_{ele} .

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

There is no selection rule for V' when a molecule undergoes an electronic transition. i.e. every transition $V'' \rightarrow V'$ has some probability. Therefore spectral lines would be expected.

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

Such a set of transitions is called a band since, under low resolution, each line of the band appears somewhat broad and diffuse. This is more particularly called as V' progression, the value of V' increases by unity for each line in the set.

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

$$\Delta E_{\text{total}} = \Delta E_{\text{el}} + \Delta E_{\text{vib}}$$

$$\text{Therefore } \Delta E_{\text{total}} = (\epsilon' - \epsilon'') + \left\{ (v' + \frac{1}{2}) \bar{\omega}_2' - x_e' (v' + \frac{1}{2})^2 \bar{\omega}_2' \right\} - \left\{ (v'' + \frac{1}{2}) \bar{\omega}_2'' - x_e'' (v'' + \frac{1}{2})^2 \bar{\omega}_2'' \right\}$$

————— (3)

Thus the observation of a band spectrum leads not only to values of the vibrational frequency and anharmonicity constant in the ground state ($\bar{\omega}_2''$ and x_e'') but also to these parameters in the excited electronic state ($\bar{\omega}_2'$ 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 strengths 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

⑧ Intensity of vibrational-electronic spectra.

⊗ The Franck-Condon principle!

Although quantum mechanics imposes no restriction on the change in the vibrational quantum number during an electronic transition, the vibrational lines in a progression are not all observed to be of the same intensity.

In some spectra (00) transition is the strongest. In others, the intensity increases to a maximum at some value of v , while in yet others only a few vibrational lines with high v' are seen. This is explained by the Franck-Condon principle.

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

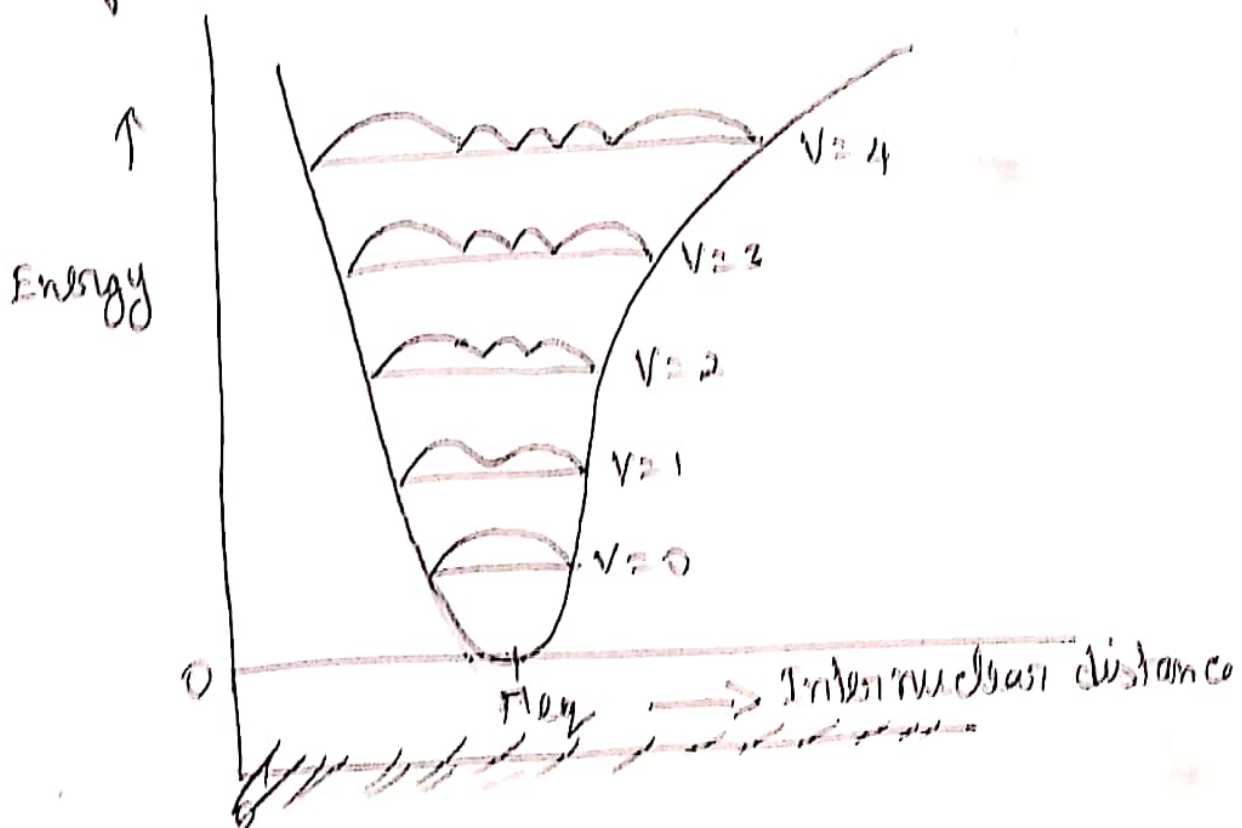
The energy of a diatomic molecule varies with internuclear distance is given by Morse curve. Here one atom is considered fixed on the $x=0$ axis and the other is allowed to oscillate between the limits of the curve. Classical theory says that the oscillating atom would spend

(7)

most of its time on the curve at the turning point of its motion since it is moving most slowly there.

Quantum theory agrees 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.

Fig. But for $v=1, 2, 3, \dots$ the most probable positions steadily approach the extremities until (for high v) both quantum and mechanical pictures merge. This behaviour is shown in figure.

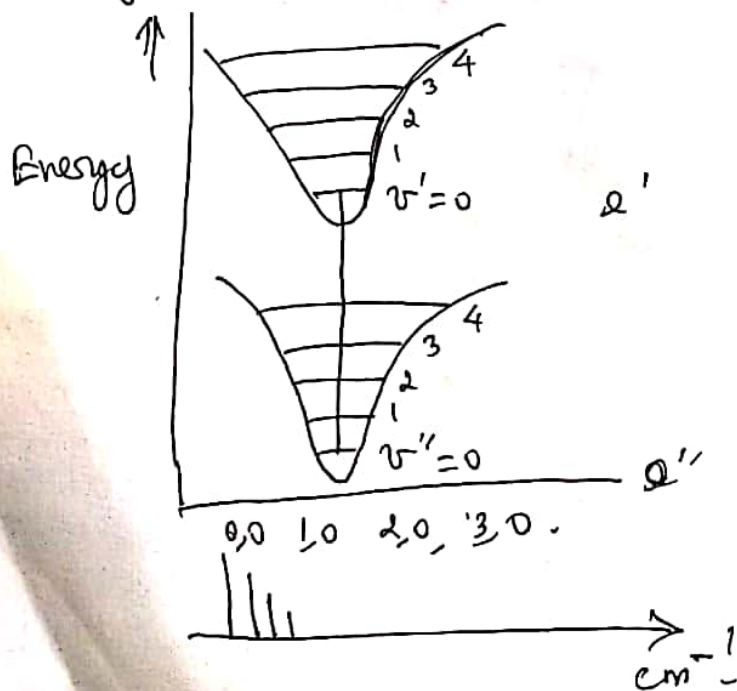


(10)

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

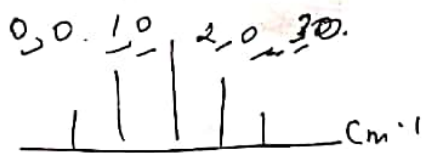
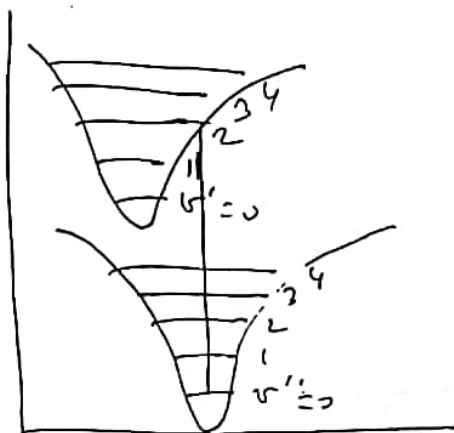
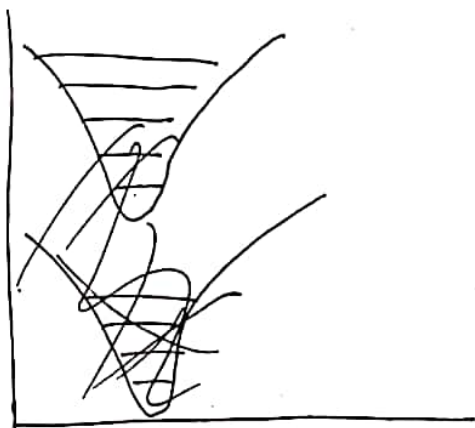
There are four possibilities for an electronic transition accompanying vibrational transitions.

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



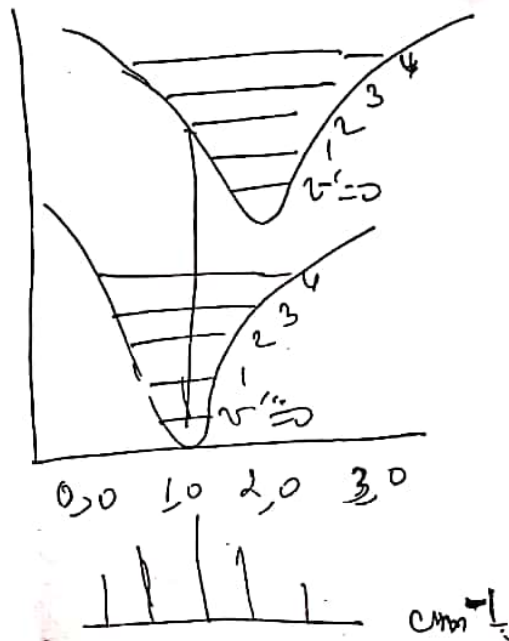
The strongest spectral line of the $v''=0$ progression will be the $(0,0)$. However, the quantum theory says that the probability of finding the oscillating atom, is greatest at the equilibrium distance in the $v=0$ state it allows some, although small chance of the atom being near the extremities of 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 diminish 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.



(12)

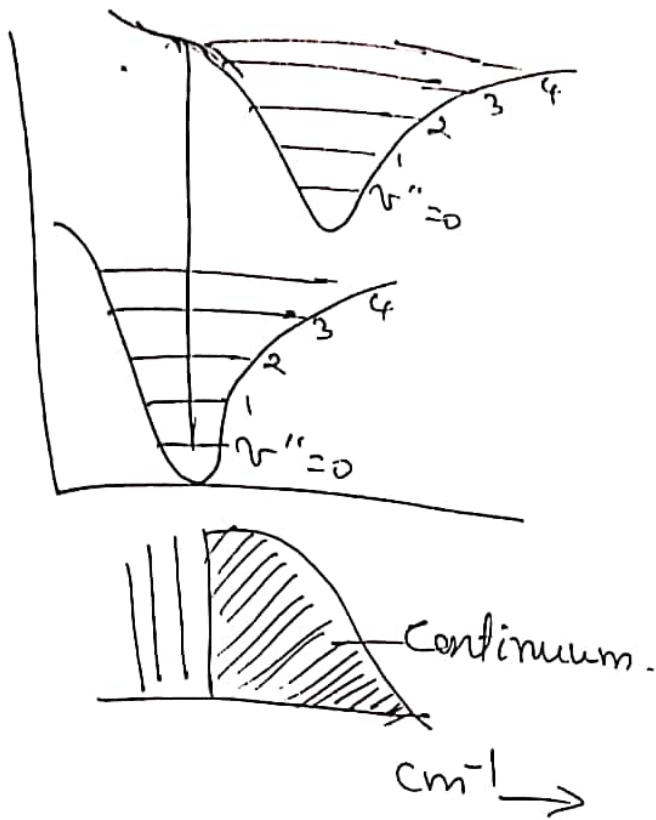
In the third possibility the excited electron state has a slightly larger internuclear separation than the ground state but the resulting transition and spectrum are similar as second.



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

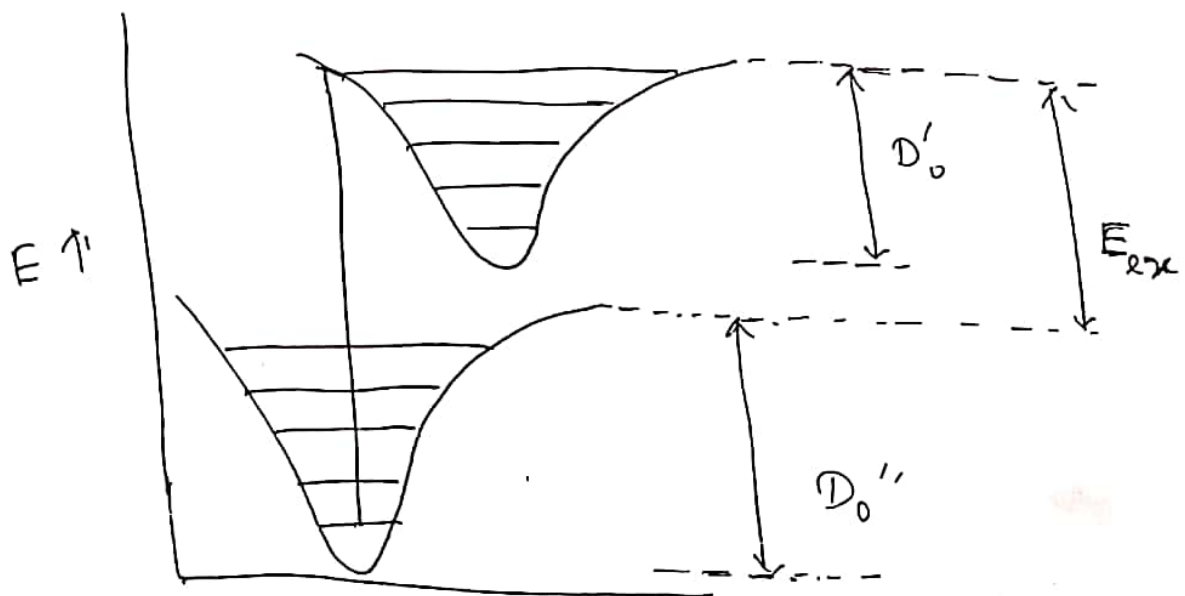
(13)

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



Exa 1

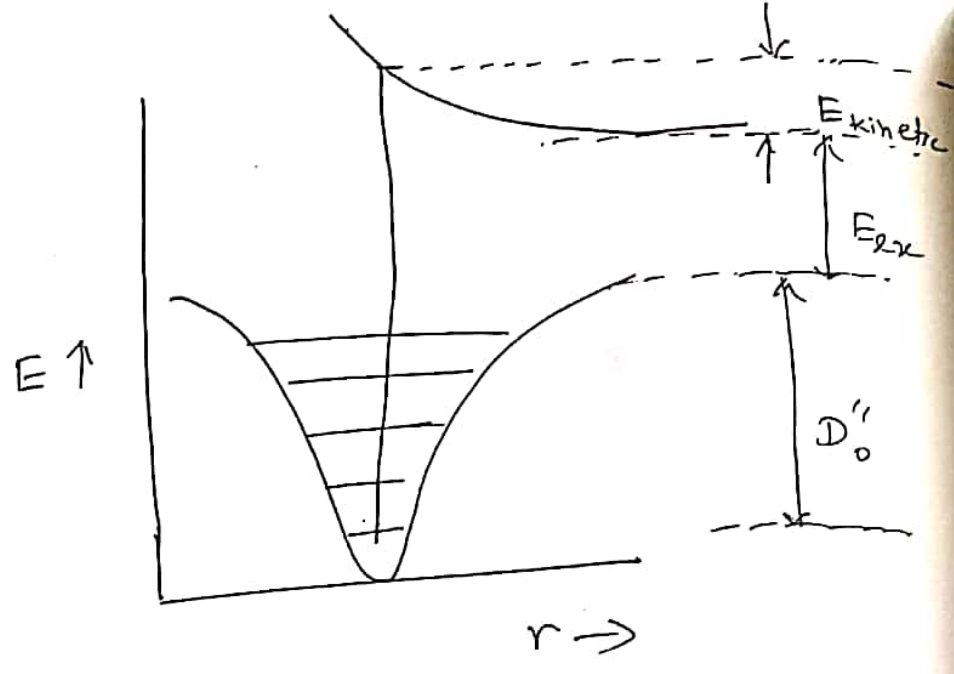


Fig. 2

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

The dissociation energies being D'_0 and D''_0 the $v=0$ state in each case. The total energy of the dissociation products (i.e atoms) from upper state is greater by an amount called E_{ex} than that of the dissociation products in the lower 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 transitions.

(15) followed by Continuum. The lowest wave number limit of this Continuum represent just the sufficient energy to cause dissociation and thus we have

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

\therefore 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 $D_0' + E_{\text{ex}}$. 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

(16) dissociation limit are of negligible probability. However it is possible to derive a value for dissociation energy by noting how the vibrational lines converge.

We know

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

and so the separation between neighbouring levels

ΔE is

$$\Delta E = E_{v+1} - E_v$$

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

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

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

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

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

$$\therefore v_{\max} = \frac{1}{2 \times 0.01} - 1 = \frac{1}{0.02} - 1 = 50$$

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

(17)

Generally two vibrational transitions are sufficient to determine $\bar{\nu}_2$ and χ_2 .

Illustration with examples:

For HCl molecule if the oscillation frequency $\bar{\nu}_2$ is 2990 cm^{-1} , and the anharmonicity constant χ_2 is 0.0174 . Find the maximum possible vibrational energy level V_{max} and the maximum value of the vibrational energy.

Solution:

$$V_{\text{max}} = \frac{1}{2\chi_2} - 1$$

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

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

$$E_V = (V + \frac{1}{2}) \bar{\nu}_2 - \chi_2 (V + \frac{1}{2})^2 \bar{\nu}_2 \text{ cm}^{-1}$$

$$V = 27$$

$$\bar{\nu}_2 = 2990 \text{ cm}^{-1}$$

$$\chi_2 = 0.0174$$

$$\therefore E_V = (27 + \frac{1}{2}) 2990 - 0.0174 (27 + \frac{1}{2})^2 2990 \text{ cm}^{-1}$$

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

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

$$\text{H.C. } 42880 \text{ cm}^{-1}$$

(18.)

$$\epsilon_v = 42850 \times 11.958 \text{ J mol}^{-1}$$

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

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

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

This value is comparable with more accurate value of $427.2 \text{ kJ mol}^{-1}$ evaluated thermodynamically despite discrepancy.

Discrepancy between calculated and experimental values:

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

Secondly we have assumed that equation (2) applies exactly even at high values of v . This is not true because cubic and quartic terms become important at this stage. Because of this $\Delta\epsilon$ decreases more rapidly than eqn (2) suggests. i.e. $\Delta\epsilon = \bar{\omega}_e \{ 1 - 2x_e (v+1) \} \bar{\omega}_e$

(19)

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 .

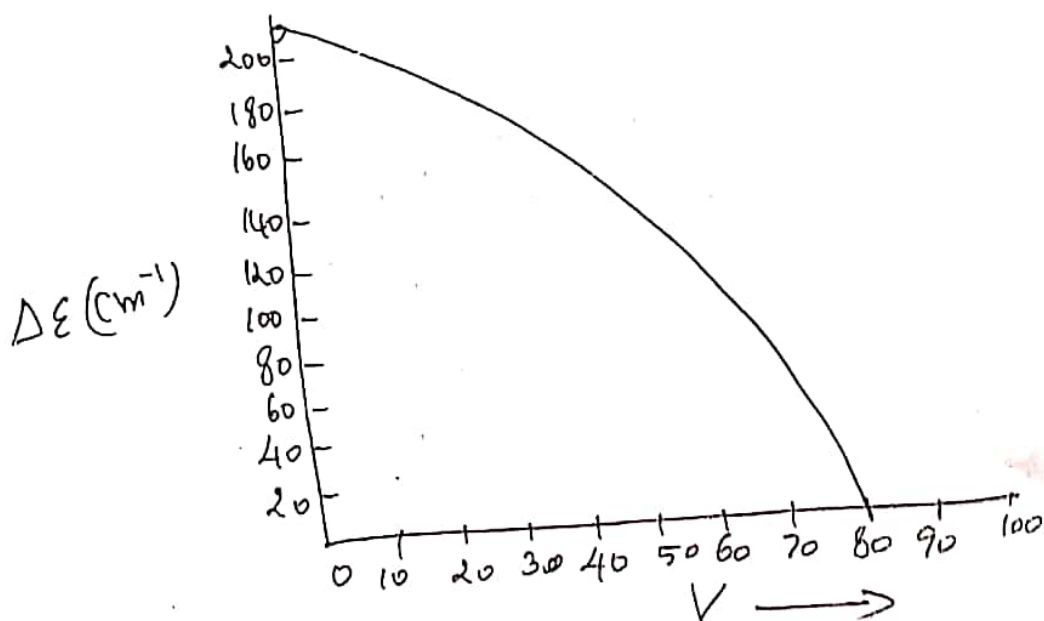
Initially equation (3) will apply quite accurately and the graph will be straight line which may be extrapolated to find V_{max} .

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.



(20)

On the other hand the graph of $\lambda \epsilon$ vs. V at high V begin to fall off more sharply as and quartic terms became significant. In case the most accurate determination of dissociation energy is obtained by extrapolating the smooth curve and finding the area beneath it.

In absorption spectra the series of lines originating from $v''=0$ state is observed. Molecules in excited states usually revert to ground state within fractions of a microsecond. The dissociation energy in the ground state can be found easily using the expression.

$$D'_0 = E_{(0,0)} + D'_0 - E_{\text{ex}} \text{ cm}^{-1}$$

Where E_{ex} can be obtained using atomic spectroscopy. D'_0 is obtained from Birge-Sponer extrapolation and we can measure $E_{(0,0)}$ the energy of the $(0,0)$ transition directly from observed energy levels.

— x —

21) Problem:

1. The absorption spectrum of O_2 shows vibrational structure which becomes a continuum at $56\,876\text{ cm}^{-1}$. 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 $15\,875\text{ cm}^{-1}$. Estimate the dissociation energy of ground state O_2 in kJ mol^{-1} .

Solution:

We know

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

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

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

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

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

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

$$= 41\,001 \times 11.958 \text{ J mol}^{-1}.$$

$$= 490\,289.96 \text{ J mol}^{-1}.$$

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

22.

∴ The dissociation energy of ground state
 $O_2 = 490.3 \text{ kJ mol}^{-1}$

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

	$\bar{W}_e \text{ cm}^{-1}$	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

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

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

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

$$= 70.32 - 1 = 69.32$$

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

(23)

(b) Excited state:-

$$\begin{aligned}V_{\max} &= \frac{1}{2 \times 9.19 \times 10^{-3}} - 1 \\&= \frac{1}{0.01838} - 1 \\&= 54.41 - 1 = 53.41 \\ \therefore V_{\max} &= 53\end{aligned}$$

II Dissociation energies

(a) Ground state

When $V = 69$

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

$$\bar{\omega}_e = 1641.4$$

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

$$v = 69$$

$$\therefore E_v = (69 + \frac{1}{2}) 1641.4 - 7.11 \times 10^{-3} (69 + \frac{1}{2})^2 1641.4 \text{ cm}^{-1}$$

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

$$= 11,4077.3 - 56,370.73 \text{ cm}^{-1}$$

$$= 57,706.57 \text{ cm}^{-1}$$

(24)

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

When $V=0$

$$\begin{aligned} E_V &= (0 + \frac{1}{2}) 1641.4 - 7.11 \times 10^{-3} (0 + \frac{1}{2})^2 1641.4 \\ &= 0.5 \times 1641.4 - 7.11 \times 10^{-3} \times 0.5 \times 0.5 \times 1641.4 \\ &= 820.7 - 2.92 \text{ cm}^{-1} \\ &= 817.78 \text{ cm}^{-1} \\ &= \frac{817.78 \times 11.958}{1000} = 9.78 \text{ kJ mol}^{-1} \end{aligned}$$

\therefore Dissociation energy in the ground state

$$\begin{aligned} D_0'' &= E_{V=69} - E_{V=0} \\ &= 690.05 - 9.78 = 680.27 \text{ kJ mol}^{-1} \end{aligned}$$

(b) Excited state

When $V=53$

$$\begin{aligned} E_V &= (53 + \frac{1}{2}) 1788.2 - 9.19 \times 10^{-3} (53 + \frac{1}{2})^2 1788.2 \\ &= 53.5 \times 1788.2 - 9.19 \times 10^{-3} \times 53.5 \times 53.5 \times 1788.2 \\ &= 95668.7 - 46597.35 \text{ cm}^{-1} \\ &= 49071.35 \text{ cm}^{-1} \end{aligned}$$

(25)

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

When $V=0$

$$\begin{aligned} E_v &= 0.5 \times 1788.2 - 9.19 \times 10^{-3} \times 0.5 \times 0.5 \times 1788.2 \\ &= 894.1 - 4.11 \text{ cm}^{-1} = 889.99 \text{ cm}^{-1} \end{aligned}$$

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

\therefore Dissociation energy in the excited state

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

$$= 586.8 - 10.64$$

$$= \underline{\underline{576.16 \text{ kJ mol}^{-1}}}$$

34

⊕ The Fortrat Diagram

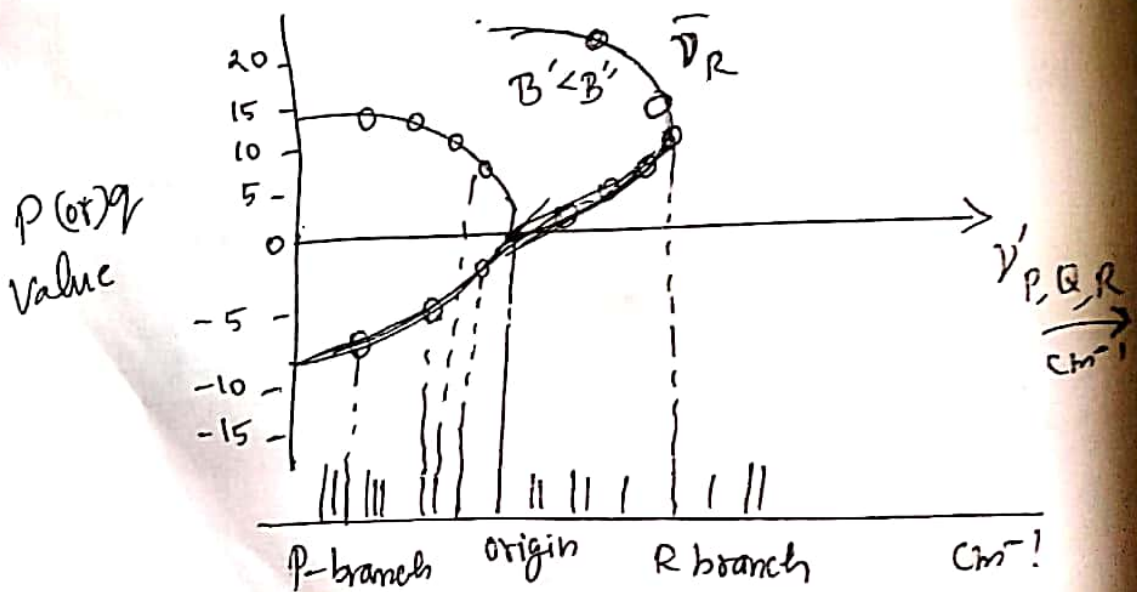
The expressions for the P, R and Q branch (lines) can be rewritten with continuously variable parameter.

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

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

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

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



As we know that p and q take only integral values (but not zero) we draw circles around the allowed points on the parabola. 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 line connects the spectrum of feet and fortat diagram at intervals.

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

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

$$(or) p = -\frac{B' + B''}{2(B' - B'')} \quad \leftarrow \text{Band head}$$

It is seen that if $B' < B''$ the band head occurs at positive p values, that is in the R-branch. The line of 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 $p \approx 10$ that is

$$p \approx 10 = J' + 1 = J'' + 1$$

(36)

If $P=10$

then

$$J'+1=10$$

$$J'=10-1=9$$

$$\text{or } J''=9$$

Ret:

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. $p \approx 10$.