ఓం నమః శివాయ ఓం శ్రీ వేంకటేశ్వరాయ నమః ఓం నమో నారాయణాయ ④

complet : ~~February~~ January 16th

Infrared Spectroscopy - IV

The technique of infrared spectroscopy is based on the fact ~~at~~ a chemical substance shows marked absorption in infrared region. The molecules of chemical substance after absorbing IR radiations vibrate at many rates, giving rise to close packed absorption bands called IR absorption spectrum. Especially, the functional groups and bonds present in a chemical substance will have characteristic absorption bands in IR region. Thus an IR spectrum of a chemical substance is fingerprint for its identification.

In IR spectroscopy the band positions are expressed conveniently by the wavenumber $\bar{\nu}$, whose unit is cm^{-1}. The relation between wavenumber $\bar{\nu}$, wavelength λ and frequency ν is as follows

$$\nu = \frac{c}{\lambda} \quad \& \quad \bar{\nu} = \frac{\nu}{c} = \frac{1}{\lambda}$$

Where c is velocity of light. Wave number can be defined as the reciprocal of wave length.

In IR spectroscopy, the intensities are usually expressed either in terms of transmittance (T) or absorbance (A). Transmittance is defined as the ratio of radiant power transmitted by a sample to the radiant power incident on the sample. Whereas absorbance is defined as the logarithm, to the base 10, of the reciprocal of the transmittance i.e.

$$A = \log_{10}\left(\frac{1}{T}\right)$$

The infrared region constitutes three parts

(a) Near IR region
(b) Middle IR region
(c) Far IR region.

The near IR region corresponds to energies in the range 37-10 K.cal/mole. The middle IR region corresponds to energies in the range 10 - 1.0 K.cal/mole and far IR region corresponds to energies in the range 1.0 - 0.1 K.cal/mole. The near IR and far IR regions are of little use for spectroscopic purposes because absorptions of organic molecules in these regions are very few. Spectroscopy in the middle IR region (usually 4000-666 cm^{-1}) is extremely useful for the study of organic compounds. Wave length of middle IR region is 2.5μ - 15 μm

For a molecule to absorb IR radiations the following requirements are to be fulfilled.

(a) correct wavelength of radiation

(b) Electric dipole

(a) Correct wavelength of radiation: The radiation will be absorbed by the molecule only when the natural frequency of vibration of some part of a molecule is same as the frequency of the incident radiation

To understand this let us consider an example. The natural frequency of vibration of HCl molecule is 8.7×10^{13} sec^{-1}. When IR radiations are passed through the sample, only a part of the incident radiation which has a frequency of 8.7×10^{13} sec^{-1} is absorbed by the HCl molecule and the remaining radiations are transmitted. Thus, the frequency 8.7×10^{13} sec^{-1} is characteristic of HCl molecule.

(b) Electric dipole: Another important condition for a molecule to absorb IR radiation is that by absorbing IR radiation a dipole should be created. A molecule is said to have electric dipole when there is a slight positive charge and a slight negative charge on its component atoms.

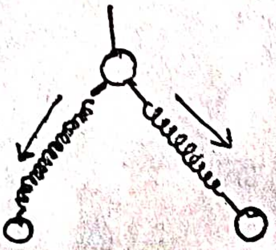
When a molecule having electric dipole is kept in the electric ~~field~~ field (i.e. IR radiation beam), this electric field will exert forces on the charges in the molecule. Opposite charges will experience forces in opposite direction. This tends to decrease & increase separation.

Types of vibrations:

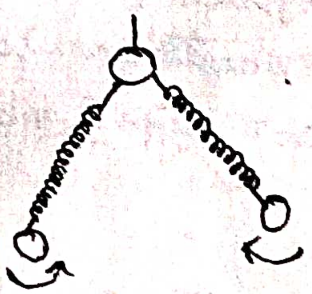
The atoms in a molecule are not held rigidly. When IR light is passed through the sample, the vibrational and rotational energies of the molecule are increased. There are two types of fundamental vibrations

(a) Stretching vibrations
(b) Bending vibrations

(a) **Stretching vibrations:** These are the vibrations in which the distance between the two atoms increases & decreases but the atoms remain in the same bond axis



(a)



(b)

(b) **Bending vibration:** These are the vibrations in which the position of the atoms change with respect to the original bond axis

It is well known that more energy is required to stretch a spring than that required to bend it. Hence, we can say that stretching absorptions of bond appear at high frequencies as compared to the bending absorptions of the same bond. These bending vibrations can also be termed as deformation modes of vibration.

Types of stretching vibrations

Stretching vibrations can be broadly divided into two types (i) Symmetric stretching and (ii) asymmetric stretching

(i) Symmetric stretching

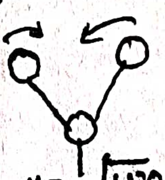
In this type of stretching vibration, the movement of the atoms with respect to a particular atom in a molecule is in the same direction

(ii) Asymmetric stretching: In these vibrations, one atom approaches the central atom while the other departs from it.

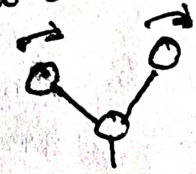
Types of bending vibrations:

Bending vibrations are four types

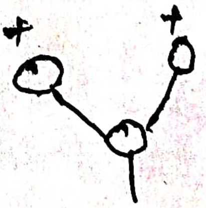
(i) Scissoring: In this type of vibration, the two atoms approach each other.



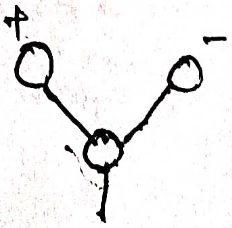
(ii) Rocking: In this type of bending vibration, the two atoms move in the same direction.



(iii) Wagging: In this type, the two atoms move up and below the plane with respect to the central atom.



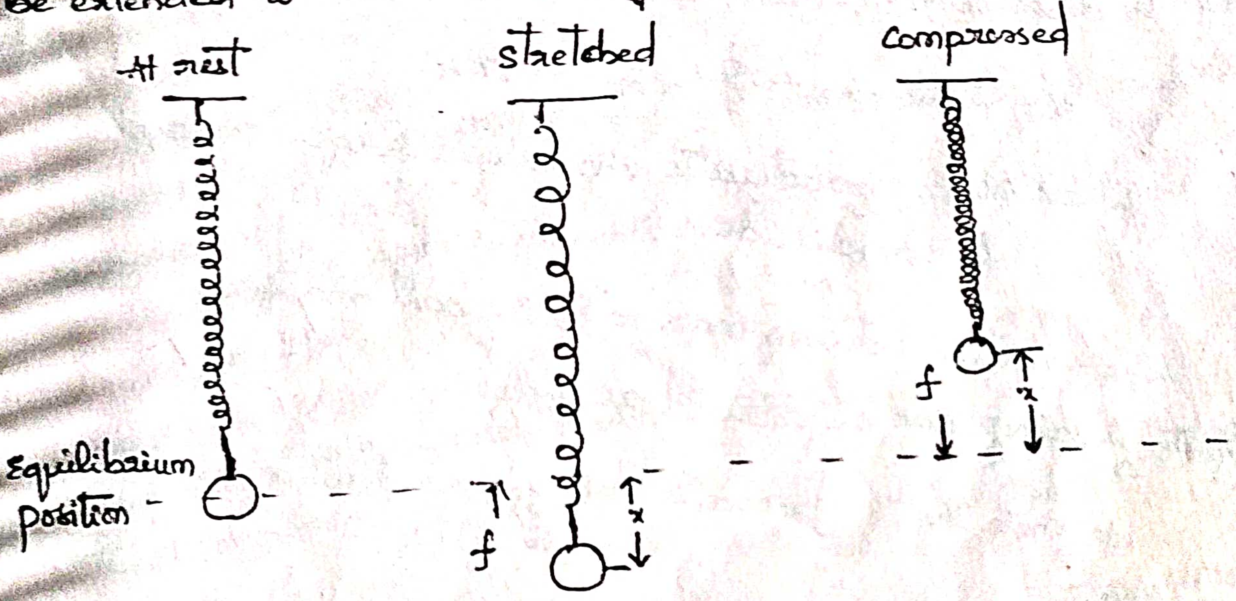
(iv) Twisting: In this type of bending vibration, one of the atoms move up the plane while the other moves down the plane with respect to the central atom



- The scissoring and rocking vibrations are known as in-plane deformations, while twisting and wagging vibrations are termed as out-of-plane deformations.

✓ Vibrational motion of systems that behave classically:

The vibrational motion of a diatomic molecule can be approached by considering the vibrations of two balls connected by a spring. We can better understand these vibrations, at first, by considering a simpler system of that of a ball and spring and latter it can be extended to two ball arrangement



Vibration of a ball and spring system.

From the above figure, it is clear that the restoring force of the spring that acts on the ball when the ball is displaced by a distance 'x' is in the opposite direction to the direction of displacement of the ball.

If the above system behaves as a harmonic oscillator then it obeys Hooke's law and this law states that the restoring force is proportional to the amount of displacement of the mass from the equilibrium position. Mathematically, the Hooke's law can be written as

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$f = -kx$ ——— ①

Where k is proportionality constant, called the force constant of the spring. The negative sign indicates that the restoring force acts in opposite direction to the displacement of the ball. From the above equation, we can say that k is the value of restoring force per unit displacement and is a measure of the stiffness of the spring.

As the spring moves up and down periodically, the ball attached to the spring also undergoes a periodic motion. The variation in displacement (x) with time 't' can be given as

$x = A \sin 2\pi\nu_0 t$ or $x = A \cos 2\pi\nu_0 t$

where ν_0 is characteristic vibrational frequency and A is amplitude.

The relation between mass 'm' of the ball and force constant k of the spring can be derived as follows.

We know that $f = ma$, where a is acceleration which is equal to d^2x/dt^2

$$\therefore f = m\frac{d^2x}{dt^2} \quad ——— ②$$

From ① and ② we can write

$$-kx = m\frac{d^2x}{dt^2}$$

As $x = A \sin 2\pi\nu_0 t$

$$\Rightarrow \frac{dx}{dt} = A\, 2\pi\nu_0 \cos(2\pi\nu_0 t)$$

$$\Rightarrow \frac{d^2x}{dt^2} = -4\pi^2\nu_0^2 A \sin 2\pi\nu_0 t$$

$$\Rightarrow -k(A\sin 2\pi\nu_0 t) = m(-4\pi^2\nu_0^2 A\sin 2\pi\nu_0 t)$$

$$\Rightarrow k = m\,4\pi^2\nu_0^2$$

$$\Rightarrow \nu_0^2 = \frac{1}{4\pi^2}\,\frac{k}{m}$$

$$\Rightarrow \nu_0 = \frac{1}{2\pi}\sqrt{\frac{k}{m}} \quad \text{———} ③$$

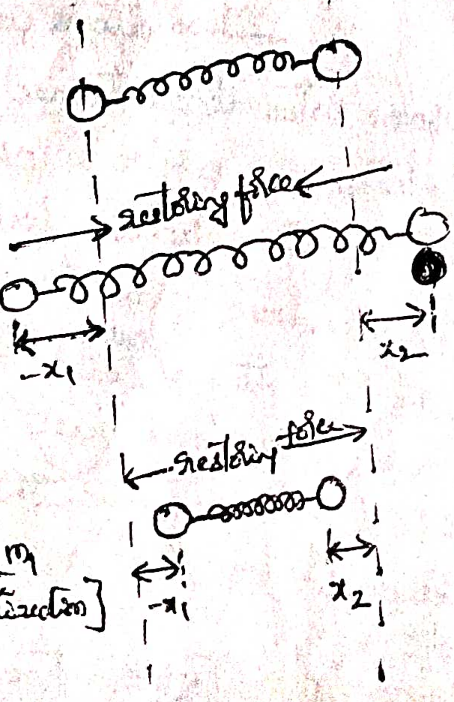
From the above equation, it is clear that the system has a characteristic or fundamental frequency of vibration. This frequency is related to the force constant and mass of the system and is independent of the amplitude.

This treatment can be extended to a system of two balls connected by a spring.

The net displacement can be written as $(x_2 - x_1)$

$$\therefore f = -k(x_2 - x_1)$$

We can express the acceleration of the first and second particles as $\frac{d^2x_1}{dt^2}$ and $\frac{d^2x_2}{dt^2}$



The relationship between mass 'm' and force constant can be given as

$$+k(x_2 - x_1) = m_1\frac{d^2x_1}{dt^2} \quad \text{———} ④$$

$$-k(x_2 - x_1) = m_2\frac{d^2x_2}{dt^2} \quad \text{———} ⑤$$

[∵ Restoring forces at m_2 and m_1 are in opposite direction]

The displacements can be written as

$$x_1 = A_1\sin 2\pi\nu_0 t$$

$$x_2 = A_2\sin 2\pi\nu_0 t$$

By substituting the values of x_1, x_2 and $\frac{d^2x_1}{dt^2}$ and $\frac{d^2x_2}{dt^2}$ in ④ and ⑤ we can obtain two equations in terms of amplitude.

$kA_2 + (4\pi^2\nu_0^2 m_1 - k)A_1 = 0$ and $(4\pi^2\nu_0^2 m_2 - k)A_2 + kA_1 = 0$.

Eliminating the amplitudes A_1 and A_2 in the above equations,

$$\frac{4\pi^2\nu_0^2}{k} = \frac{m_1+m_2}{m_1m_2} = \frac{1}{\mu}$$

$$\Rightarrow \nu_0 = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} \quad \text{———} ⑥$$

where μ is the reduced mass of the two-particle system, ν_0 is the fundamental frequency of the system.

* VIBRATIONAL SPECTRA OF DIATOMIC MOLECULES ✓

Energy of a diatomic molecule:

Two atoms combine to form a stable covalent molecule with some internal electronic rearrangement. Because of the repulsions between the positively charged nuclei of both the atoms and between the negative electron clouds and because of the attractions between the nucleus of one atom and electron cloud of the other and vice versa, the two atoms settle at a mean internuclear distance such that the two forces are just balanced and the energy of the whole system is at a minimum. This distance is known as equilibrium inter nuclear distance (r_{eq}) & it can be called as bond length.

If the two atoms are brought closer, the repulsive force rises rapidly and if the two atoms are moved apart, the attractive forces restrict it. In either case an attempt to distort the bond requires an input of energy and hence energy can be plotted against internuclear distance.

- The compression or expansion of a bond may be just like the behaviour of a stretched string which obeys Hooke's law. Mathematically Hooke's law can be written as

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

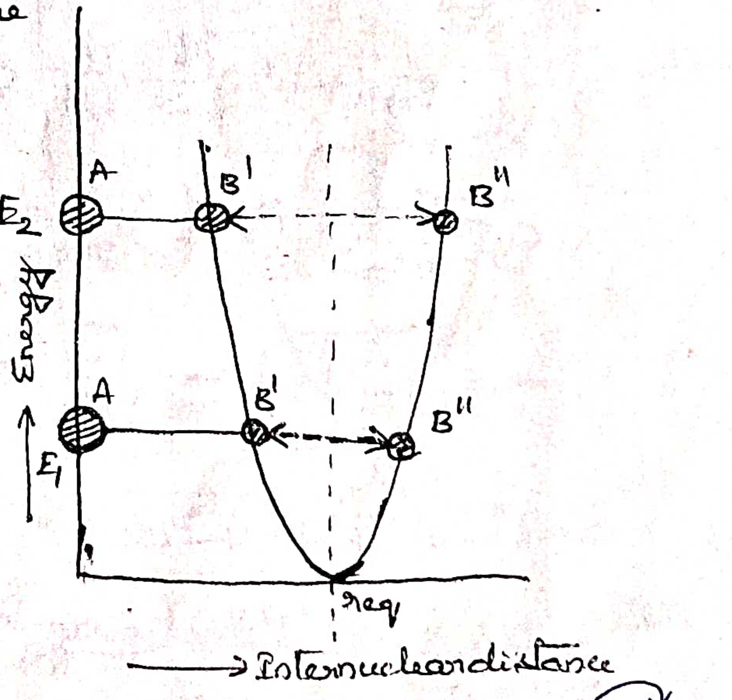
where f is restoring force, k is force constant, r is internuclear distance, r_{eq} is equilibrium internuclear distance.

The energy of a vibrating diatomic molecule which is in simple harmonic motion can be given as

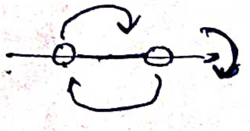
$$E = \frac{1}{2}k(r - r_{eq})^2$$

Simple Harmonic oscillator:

A vibrating diatomic molecule can be assumed as a simple harmonic oscillator and the simple harmonic motion can be diagramatically represented as follows. In the figure energy E is plotted against internuclear distance. The zero of the curve is found at $r = r_{eq}$ and any energy excess of this for example E_1 arises because of extension or compression of the bond.



In the above figure atom A is considered stationary on the r=0 axis and the other atom B will be oscillating between B' and B''. At higher energies the oscillations will be more vigorous, that is the degree of compression or extension will be more.

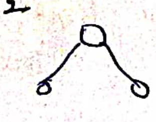


The vibrational frequency is given by

$$\nu_{osc} = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}\ \text{Hz} \quad ①$$

Internuclear (r=0)

3n-3-2
3n-5



3n-3-3
3n-6

Where μ is the reduced mass of the system. This is converted to wavenumbers by dividing with velocity of light.

i.e. $$\frac{\nu_{osc}}{c} = \frac{1}{\lambda} = \bar{\nu}_{osc} = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}}\ \text{cm}^{-1} \quad \text{———} ②$$

Because of the vibrations of atoms in a molecule vibrational energies are created. Like all other molecular energies, vibrational energies are also quantised. Vibrational energies for any particular system may be calculated from Schrodinger equation. The schrodinger equation for the harmonic oscillator is

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2\mu}{h^2}\left(E - \frac{kx^2}{2}\right)\psi = 0.$$

Solving the above equation, the allowed energy levels are given by

$$E_v = (V + 1/2)h\nu_{osc}\ \text{joules} \quad (V = 0, 1, 2, \cdots)$$

where V is called vibrational quantum number

$$E_v = \left(V + \frac{1}{2}\right)\frac{h}{2\pi}\sqrt{\frac{k}{\mu}}\ \text{joules}.$$

$$\epsilon_v = \frac{E_v}{hc} = \left(V + \frac{1}{2}\right)\frac{h}{2\pi hc}\sqrt{\frac{k}{\mu}}\ \text{cm}^{-1}$$

$$\rightarrow \epsilon_v = \left(V + \frac{1}{2}\right)\frac{1}{2\pi c}\sqrt{\frac{k}{\mu}}\ \text{cm}^{-1}$$

$$\Rightarrow \epsilon_v = \left(V + \frac{1}{2}\right)\bar{\nu}_{ose}\ \text{cm}^{-1} \quad \text{———} ③$$

The lowest vibrational energy can be obtained by putting V=0

$$\epsilon_v = \frac{1}{2}\bar{\nu}_{ose}\ \text{cm}^{-1}$$

This quantity $\frac{1}{2}\bar{\nu}_{ose}$ is known as 'zeropoint energy' which means that a molecule must always vibrate and can never be at rest.

The existence of zeropoint energy has been predicted by wave mechanics. Wave mechanics insists that a molecule should vibrate to some extent.

The selection rule for simple harmonic oscillator is given by

$$\Delta V = \pm 1$$

The vibrational energy changes will only give rise to an observable spectrum if the vibration can interact with radiation. i.e. if the vibration involves a change in the dipolemoment of the molecule.

Applying selection rule we have

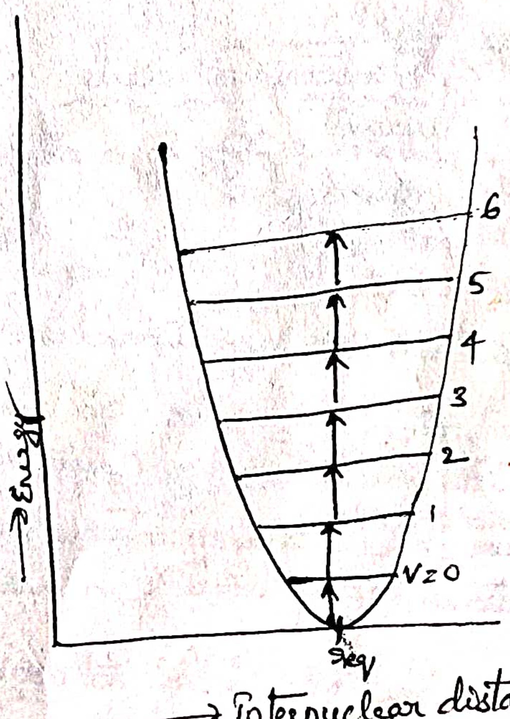
$$\epsilon_{V+1\to V} = \left(V+1+\tfrac{1}{2}\right)\bar{\nu}_{osc} - \left(V+\tfrac{1}{2}\right)\bar{\nu}_{osc}$$

$$= \bar{\nu}_{osc}$$

Putting V=0, 1, 2, 3, ... etc in ③ we get

$\epsilon_0 = \frac{1}{2}\bar{\nu}_{osc}$, $\epsilon_1 = \frac{3}{2}\bar{\nu}_{osc}$, $\epsilon_2 = \frac{5}{2}\bar{\nu}_{osc}$, $\epsilon_3 = \frac{7}{2}\bar{\nu}_{osc}$, $\epsilon_4 = \frac{9}{2}\bar{\nu}_{osc}$ cm^{-1}

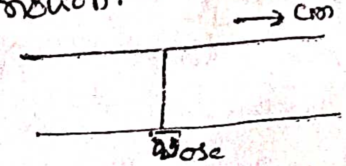
If the energy is plotted against equilibrium internuclear distance, then the resulting curve is as shown.



The vibrational energy levels and allowed transitions between them for a diatomic molecule undergoing simple harmonic motion.

Since vibrational energy levels are equally spaced difference between any two neighbouring states will give rise to the same energy change. The energy difference between two neighbouring energy levels gives directly the wave number of the spectral line emitted or absorbed.

$$\Delta \epsilon_V = \bar{\nu}_{osc} \text{ cm}^{-1}$$



Draw backs for considering a diatomic molecule as harmonic oscillator.

(1) Considering a diatomic molecule as a harmonic oscillator, it is possible, to describe the lowest vibrational states and fails for higher vibrational state ~~by considering the diatomic molecule to be harmonic oscillator~~.

(2) Experimentally it was found that vibrational energy levels are less separated as V increases, but whereas the harmonic oscillator results in even spacing.

(3) ~~He~~ Harmonic oscillator consideration does not explain the existence of overtones and combinations which were actually observed.

Vibrating diatomic molecule as Anharmonic oscillator:

The potential energy of a molecule which behaves as harmonic oscillator is given by

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

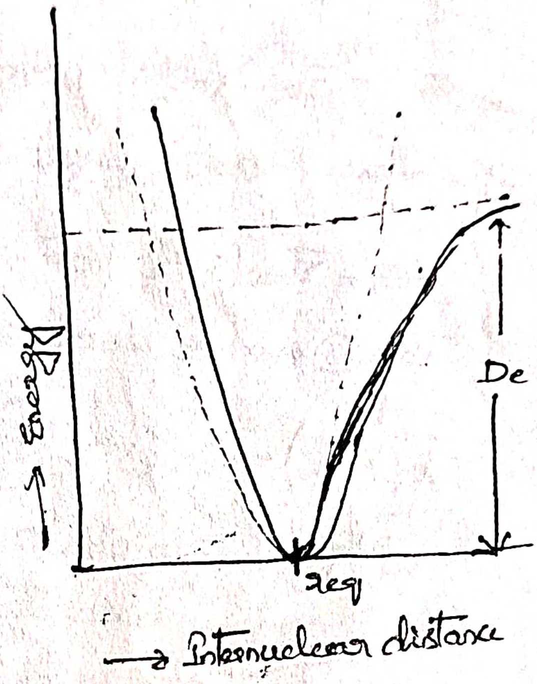
The allowed vibrational energies are given by

$$\epsilon_v = \left(V+\frac{1}{2}\right)\bar{\nu}_{osc}\ \text{cm}^{-1}$$

The potential energy curve rises ~~rapidly~~ parabolically from a minimum i.e. equilibrium internuclear position as shown in figure. The vibrational energy levels of a harmonic oscillator are equally spaced.

Real molecules do not obey exactly the laws of simple harmonic oscillator. For small compressions and extensions, real bonds may be taken as perfectly elastic obeying Hooke's law. But for large distortions the real molecules deviate from Hooke's law behaviour. Thus, for larger extensions, the restoring force will no longer increase in proportion to the extension. For small extensions, where Hooke's law is obeyed, the potential energy will increase parabolically. For larger extensions, the increase in potential energy is not predominant but for very large extensions, the potential energy ceases to increase

- On the other hand if the bond is compressed, the atoms are brought very close to each other and as a result repulsive forces increase and hence potential energy will rise very steeply.



Morse curve: The energy of a diatomic molecule undergoing anharmonic extensions and compressions.

Hence real molecules behave as anharmonic oscillators and the extensions and compressions will have the shape as shown by thick line. The dotted parabola in figure represents an ideal diatomic molecule which is in simple harmonic motion. The energy curve of real molecules can be explained by an emperical formula given by P.M. Morse and is known as Morse function. The Morse function is

$$E = D_e\left(1-e^{-\beta x}\right)^2$$

Where De is dissociation energy for a particular molecule, β is a constant for a particular diatomic molecule, x is displacement which is equal to $(r-r_{eq})$.

When the above emperical formula is used instead of $E = \frac{1}{2}k(r-r_{eq})^2$ in the Schrodinger equation, the allowed vibrational energies are found to be

$$E_v = h\nu'_{osc}\left(v+\tfrac{1}{2}\right)\left[1-a\left(v+\tfrac{1}{2}\right)\right] \text{ joules.}$$

$$= h\nu'_{osc}\left(v+\tfrac{1}{2}\right) - h\nu'_{osc}\left(v+\tfrac{1}{2}\right)^2 a \qquad \text{——— ①}$$

Where ν'_{osc} is vibrational frequency of anharmonic oscillator, V is vibrational quantum number and a is the corresponding anharmonicity constant.

In terms of wave number it can be written as

$$E_v = \bar{\nu}'_{osc}\left(v+\tfrac{1}{2}\right) - \bar{\nu}'_{osc}\left(v+\tfrac{1}{2}\right)^2 a \ \text{cm}^{-1} \text{ ——— } ②$$

$$\Rightarrow E_v = \bar{\nu}'_{osc}\left(v+\tfrac{1}{2}\right)\left[1-a\left(v+\tfrac{1}{2}\right)\right] \ \text{cm}^{-1} \text{ ——— } ③$$

The allowed energy levels of a simple harmonic oscillator are

$$E_v = \bar{\nu}_{osc}\left(v+\tfrac{1}{2}\right) \ \text{cm}^{-1} \text{ ——— } ④$$

From ③ and ④ we can write

$$\bar{\nu}_{osc}\left(v+\tfrac{1}{2}\right) = \bar{\nu}'_{osc}\left(v+\tfrac{1}{2}\right)\left[1-a\left(v+\tfrac{1}{2}\right)\right] \text{ ——— } ⑤$$

Where $\bar{\nu}_{osc}$ is vibrational frequency of harmonic oscillator
$\bar{\nu}'_{osc}$ is vibrational frequency of anharmonic oscillator.

From equation ⑤ it is clear that, the oscillation frequency of anharmonic oscillator is less than the oscillation frequency of harmonic oscillator and the oscillation frequency decreases with increase in the vibrational quantum number (v) value.

Let us consider the hypothetical energy state obtained by putting $v = -\tfrac{1}{2}$. In this energy state the molecule would be at the equilibrium point with zero vibrational energy

$$\Rightarrow \bar{\nu}_{osc} = \bar{\nu}'_{osc}\left[1-a\left(-\tfrac{1}{2}+\tfrac{1}{2}\right)\right]$$

$$\Rightarrow \bar{\nu}_{osc} = \bar{\nu}'_{osc} \text{ ——— } ⑥.$$

Thus $\bar{\nu}'_{osc}$ may be regarded as the (hypothetical) equilibrium oscillation frequency of the anharmonic oscillator.

The energy of the lowest vibrational state, i.e. $v=0$ is given by

$$E_v = \bar{\nu}'_{osc}\left(v+\tfrac{1}{2}\right)\left[1-a\left(v+\tfrac{1}{2}\right)\right] \quad \because (3)$$

$$\Rightarrow E_v = \bar{\nu}'_{osc}\left(\tfrac{1}{2}\right)\left[1-a\left(0+\tfrac{1}{2}\right)\right]$$

$$\Rightarrow E_v = \frac{\bar{\nu}'_{osc}}{2}\left(1-\tfrac{1}{2}a\right) \text{ ——— } ⑦$$

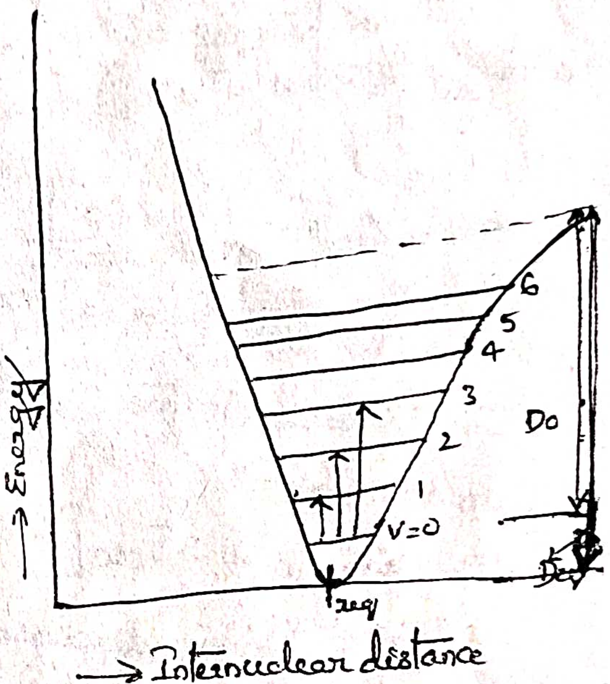
The zero point energy for the anharmonic oscillator differs slightly from that of the harmonic oscillator.

The vibrational energy levels of harmonic oscillator are equally spaced but for anharmonic oscillator the vibrational energy levels are not equally spaced.

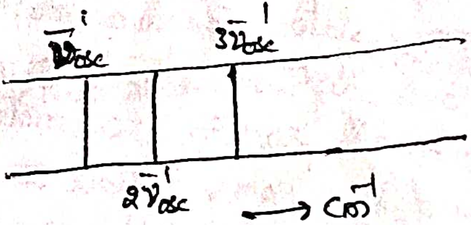
The selection rules for the anharmonic oscillator are

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

The selection rule for anharmonic oscillator are same as that for harmonic oscillator with additional possibility of longer jumps. These longer jumps were predicted theoretically and were observed practically. But these transitions were found to be diminishing rapidly and normally only the lines of $\Delta v = \pm 1, \pm 2, \pm 3$ at the most have observable intensity.



The transitions from V=0 state such as $V=0$ to $V=1$, $V=0 \rightarrow V=2$, $V=0 \rightarrow V=3$ etc. are known as fundamental, first overtone, second overtone etc.



The energy of the fundamental transition from $v=0 \rightarrow v=1$ is

$$\Delta\epsilon_v = \epsilon_{v=1} - \epsilon_{v=0}.$$

$$= \bar{\nu}'_{osc}\left(1+\tfrac{1}{2}\right)\left[1-a\left(1+\tfrac{1}{2}\right)\right] - \bar{\nu}'_{osc}\left(0+\tfrac{1}{2}\right)\left[1-a\left(0+\tfrac{1}{2}\right)\right]$$

$$= \bar{\nu}'_{osc}\left(\tfrac{3}{2}\right)\left[1-a\left(\tfrac{3}{2}\right)\right] - \bar{\nu}'_{osc}\left(\tfrac{1}{2}\right)\left[1-a\left(\tfrac{1}{2}\right)\right]$$

$$= \bar{\nu}'_{osc}\left[\frac{3}{2} - \frac{9}{4}a - \frac{1}{2} + \frac{1}{4}a\right]$$

$$= \bar{\nu}'_{osc}\left[1 - \frac{8a}{4}\right]$$

$$\Rightarrow \Delta\epsilon_v = \bar{\nu}'_{osc}\left[1-2a\right] \longleftarrow ⑧$$

The energy of the first overtone of small intensity is obtained by the transition from v=0 → v=2

$$\Delta\epsilon_v = \epsilon_{v=2} - \epsilon_{v=0}$$

$$= \bar{\nu}'_{osc}\left(2+\tfrac{1}{2}\right)\left[1-a\left(2+\tfrac{1}{2}\right)\right] - \bar{\nu}'_{osc}\left(0+\tfrac{1}{2}\right)\left[1-a\left(0+\tfrac{1}{2}\right)\right]$$

$$= \bar{\nu}'_{osc}\left(\tfrac{5}{2}\right)\left[1-a\left(\tfrac{5}{2}\right)\right] - \bar{\nu}'_{osc}\left(\tfrac{1}{2}\right)\left[1-a\left(\tfrac{1}{2}\right)\right]$$

$$\Delta\epsilon_v = \bar{\nu}'_{osc}\left[\tfrac{5}{2} - \tfrac{25}{4}a - \tfrac{1}{2} + \tfrac{1}{4}a\right]$$

$$= \bar{\nu}'_{osc}\left[2-6a\right]$$

$$= 2\bar{\nu}'_{osc}\left[1-3a\right]\ cm^{-1}$$

The second overtone of negligible intensity is obtained by the transition from v=0 → v=3.

$$\Delta\epsilon_v = \epsilon_3 - \epsilon_0 = 3\bar{\nu}'_{osc}\left[1-4a\right]\ cm^{-1}$$

The transitions discussed till now are from v=0 state to higher energy states. Because most of the molecules initially exist in this state at ordinary temperature. But at very high temperatures (say above 200C), a small fraction of the molecular population may be in the v=1 state. The transitions from v=1 state to higher states are very weak and are referred as hot bands.

Let us consider the transition from v=1 → v=2.

$$\Delta\epsilon_v = \epsilon_{v=2} - \epsilon_{v=1}$$

$$= \bar{\nu}'_{osc}\left(2+\tfrac{1}{2}\right)\left[1-a\left(2+\tfrac{1}{2}\right)\right] - \bar{\nu}'_{osc}\left(1+\tfrac{1}{2}\right)\left[1-a\left(1+\tfrac{1}{2}\right)\right]$$

$$= \bar{\nu}'_{osc}\left[\tfrac{5}{2} - \tfrac{25}{4}a - \tfrac{3}{2} + \tfrac{9}{4}a\right]$$

$$= \bar{\nu}'_{osc}\left[1-4a\right]\ cm^{-1}$$

This weak absorption is found to be close to and slightly lower wavenumbers than the fundamental

The diatomic Vibrating Rotator

When molecule in gaseous phase absorbs IR radiations, in addition to the vibrational energy change of the molecule, rotational energy changes also occur. Each absorption due to transition between vibrational energy levels found to consist of a number of relatively closely spaced absorption lines. These absorption lines are the rotational components of the band and can be related to the rotational energy changes that occur simultaneously with the vibrational energy change.

Since the energies of the two motions are so different we may assume that a diatomic molecule can execute rotations and vibrations quite independently. When there is no interaction between vibrational energy and rotational energy, the total energy can be written as

$$E_{total} = E_{rot} + E_{vib}$$

Now two conditions arise, they are

(1) the diatomic molecule may behave as a harmonic oscillator and rigid rotator

(2) the diatomic molecule may behave as anharmonic oscillator and non rigid rotator.

(1) Diatomic molecule as a harmonic oscillator and a rigid rotator

The total energy due to vibration and rotational changes can be given as

$$E_{V,J} = E_{tot} = E_{vib} + E_{rot}.$$

$$= (V+1/2)\nu_{osc} h + \frac{h^2}{8\pi^2 I} J(J+1) \quad \text{———} \quad ①$$

The selection rules for the combined motions are

$$\Delta V = \pm 1, \quad \text{and} \quad \Delta J = \pm 1$$

The change in energy for the transition from the vibrational level V' to V'' and from rotational level J' to J'' can be given as

$$E'_{v,J} - E''_{v,J} = (v'-v'')h\nu_{osc} + \frac{h^2}{8\pi^2 I}\left[J'(J'+1) - J''(J''+1)\right] \quad \text{——— ②.}$$

In terms of wave number the above equation can be written as

$$\epsilon_{v',J} - \epsilon_{v'',J} = (v'-v'')\bar{\nu}_{osc} + \frac{h}{8\pi^2 I c}\left[J'(J'+1) - J''(J''+1)\right]$$

$$= (v'-v'')\bar{\nu}_{osc} + B\left[J'(J'+1) - J''(J''+1)\right] \quad \text{——— ③}$$

$$= (v'-v'')\bar{\nu}_{osc} + B\left[J'^2 + J' - J''^2 - J''\right]$$

$$= (v'-v'')\bar{\nu}_{osc} + B\left[(J'+J'')(J'-J'') + (J'-J'')\right]$$

$$= (v'-v'')\bar{\nu}_{osc} + B\left[(J'-J'')(J'+J''+1)\right] \quad \text{——— ④.}$$

As diatomic molecule is assumed as harmonic oscillator, the possible vibrational transitions are $v'-v''=1$. Thus equation ④ becomes

$$\Delta\epsilon = \bar{\nu}_{osc} + B(J'-J'')(J'+J''+1) \quad \text{——— ⑤}$$

From the above equation it is evident that the frequency of the lines vary with the values of J' and J''. Thus.

(i) If $\Delta J = +1$ i.e. $J'-J''=1 \Rightarrow J' = 1+J''$, then equation ⑤ becomes.

$$\Delta\epsilon_R = \bar{\nu}_{osc} + 2B(J''+1)\ \text{cm}^{-1} \quad \text{where } J'' = 0,1,2,\ldots \text{ etc.} \quad \text{——— ⑥}$$

(ii) If $\Delta J = -1$ i.e. $J'-J''=-1 \rightarrow J'+1 = J''$, then the equation ⑤ becomes

$$\Delta\epsilon_P = \bar{\nu}_{osc} - 2B(J'+1)\ \text{cm}^{-1} \quad \text{where } J' = 0,1,2,3\ldots \text{ etc.} \quad \text{——— ⑦}$$

From equations ⑥ and ⑦ we can write.

$$\Delta\epsilon = \bar{\nu}_{osc} \pm 2Bm\ \text{cm}^{-1} \quad \text{——— ⑧}$$

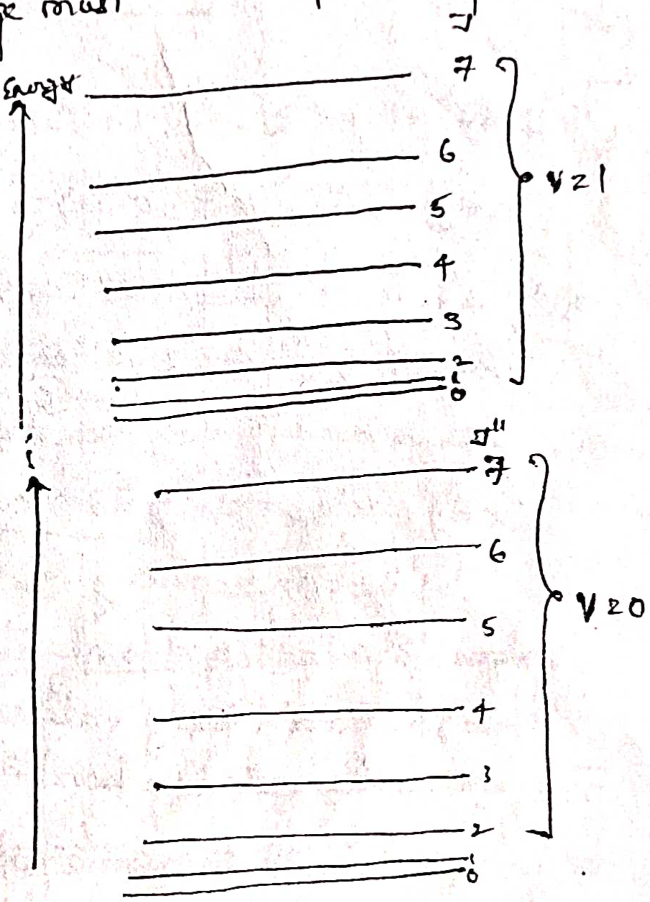
where $m = \pm 1, \pm 2, \pm 3, \ldots$ etc. The value of m cannot be zero because the value of J' & J'' should be -1 which is not possible.

From equation ⑧ it is clear that the spectrum consists of equally spaced lines with a spacing of $2B$ on each side of band origin.

If $v'-v''=1$ and $J'-J''=0$, then ⑭ becomes

$$\Delta E = \bar{\nu}_{osc}$$

$J'-J''=0$ i.e. $\Delta J=0$, which is not possible under normal circumstances, because a vibrational change must be accompanied by simultaneous rotational change.



Some of the rotational energy levels for the first two vibrational states of a diatomic molecule.

(2) Diatomic molecule as anharmonic oscillator and a non-rigid rotator:

$$E_{tot} = E_{vib} + E_{rot}$$

$$E_{v,J} = hc\left\{\left[BJ(J+1) - DJ^2(J+1)^2 + \cdots\right]\right\} + \left\{h\nu'_{osc}\left(v+\tfrac{1}{2}\right)\left[1-a\left(v+\tfrac{1}{2}\right)\right]\right\} \quad ①$$

Where D is centrifugal distortion constant and $D = \dfrac{h^3}{32\pi^4 I^2 r^2 kc}$

The selection rules are

$\Delta V = \pm1, \pm2, \pm3, \ldots, \Delta J = \pm1$

For a good IR spectrometer having high resolving power, the value of D can be neglected. Hence equation ① can be written as

$$E_{v,J} = hc\,BJ(J+1) + h\nu'_{osc}\left(v+\tfrac{1}{2}\right)\left[1-a\left(v+\tfrac{1}{2}\right)\right] \quad ②$$

$$\Rightarrow \epsilon_{v,J} = BJ(J+1) + \bar{\nu}'_{osc}\left(v+\tfrac{1}{2}\right)\left[1-a\left(v+\tfrac{1}{2}\right)\right] \quad ③$$

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Consider the transitions from $V=0$ to $V=1$ and from J' to J''.

$$\Rightarrow \Delta\epsilon = B\left[J'(J'+1) - J''(J''+1)\right] + \bar{\nu}'_{osc}\left\{\left(1+\frac{1}{2}\right)\left[1-a\left(1+\frac{1}{2}\right)\right] - \left(0+\frac{1}{2}\right)\left[1-a\left(0+\frac{1}{2}\right)\right]\right\}$$

$$\Rightarrow \Delta\epsilon = \bar{\nu}_{osc} + B(J'-J'')(J'+J''+1) \qquad \left[\because \bar{\nu}_{osc} = \bar{\nu}'_{osc}(1-2a)\right]$$

——— ④

(i) If $\Delta J = +1$ i.e. $J'-J'' = 1 \Rightarrow J''+1 = J'$ then ④ becomes.

$$\Delta\epsilon_{J,V} = \bar{\nu}_{osc} + 2B(J''+1)\ \text{cm}^{-1} \text{ where } J'' = 0, 1, 2, \ldots \text{ etc.}$$

——— ⑤

(ii) If $\Delta J = -1$ i.e. $J'-J'' = -1 \Rightarrow J'+1 = J''$ then ④ becomes

$$\Delta\epsilon_{J,V} = \bar{\nu}_{osc} - 2B(J'+1)\ \text{cm}^{-1} \quad \text{where } J' = 0, 1, 2, \ldots$$

——— ⑥

The above two expressions may be conveniently be combined into

$$\Delta\epsilon_{J,V} = \bar{\nu}_{spe} = \bar{\nu}_{osc} \pm 2Bm\ \text{cm}^{-1} \quad m = \pm1, \pm2, \ldots$$

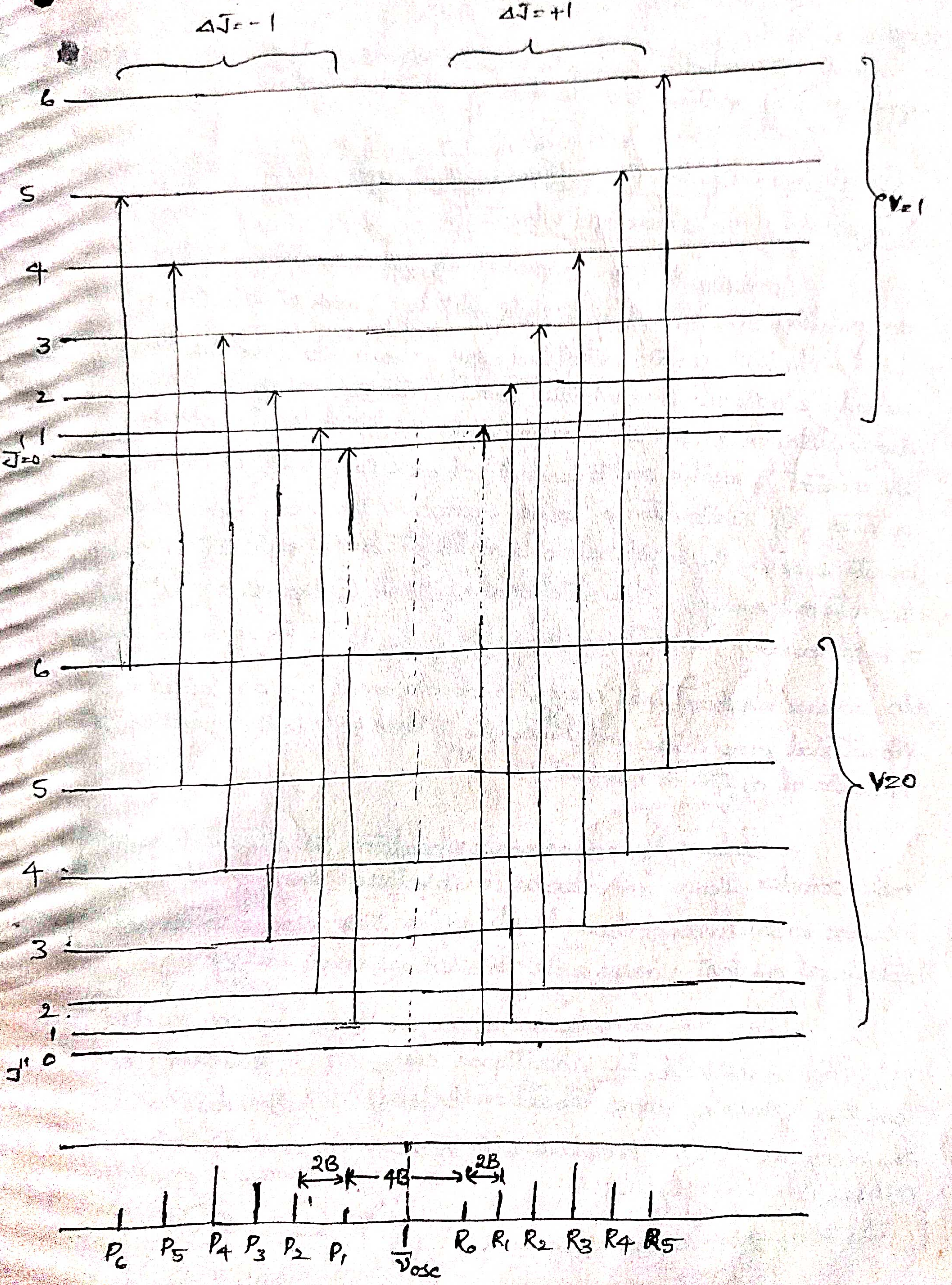
——— ⑦

Where m, replacing $J''+1$ in ⑤ and $J'+1$ in ⑥. m ~~has~~ is positive ~~values~~ for $\Delta J = +1$ and is negative for $\Delta J = -1$. m cannot be zero since this would imply values of J' & J'' to be -1. The frequency $\bar{\nu}_{osc}$ is usually called the band origin or band centre

Equation ⑦ represents the combined vibration-rotation spectrum. From ⑦ it is clear that rotational lines are equally spaced ($2B$) on each side of the band origin $\bar{\nu}_{osc}$, but since $m \neq 0$, the line at $\bar{\nu}_{osc}$ itself will not appear.

Lines to the low frequency side of $\bar{\nu}_{osc}$, corresponding to negative m [i.e. $\Delta J = -1$] are referred to as the P branch, while those to the high frequency side (m positive, $\Delta J = +1$) are called the R branch.

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


ΔJ=-1
ΔJ=+1
6
5
4
3
2
1
J=0
v=1
6
5
4
3
2
1
J'' 0
v=0
2B
4B
2B
P6
P5
P4
P3
P2
P1
ν_osc
R0
R1
R2
R3
R4
R5

extending the selection rules to include $\Delta V = \pm 2, \pm 3$ etc, also allows the appearance of overtone bands having identical rotational structures

Breakdown of the Born-Oppenheimer approximations: The interaction of rotations and vibrations.

According to Born-Oppenheimer approximation, the vibrations and rotations can proceed quite independently of each other. But, every bond is elastic to certain extent and every molecule has some vibrational energy. usually a molecule ~~ano~~ vibrates some 10^3 times during the course of a single rotation. Due to these vibrations, the bond length (and hence the moment of inertia and B constant) changes continually during the rotation. If the vibration is simple harmonic the mean bond length will be the same as the equilibrium bond length and it will not vary with vibrational energy. The rotational constant B depends on $1/r^2$ [where r is the average value] and the value of $\frac{1}{r^2}$ is not the same as $\frac{1}{r_{eq}^2}$. An increase in vibrational energy is accompanied by an increase in the vibrational amplitude and hence the value of B will depend on the vibrational quantum number (V).

Incase of anharmonic vibrations the situation is much more complex. Hence, an increase in vibrational energy will lead to an increase in the average bond length. under these circumstances, the rotational constant varies more with vibrational energy.

From the above consequences, we it can be concluded that r_{av} increases with the vibrational energy [i.e. $r_{av} > r_{eq}$] and B is smaller. Thus in upper vibrational levels, the B value is smaller. The decrease in the B value with increase in vibrational quantum number can be given as

$$B_V = B_e - \alpha\left(V + \frac{1}{2}\right) \quad \text{——} \quad ①$$

Where B_v is rotational constant in vibrational level v, B_e is equilibrium rotational constant and x is ~~cont~~ a constant for a molecule.

$B_e > B_v$

– For the fundamental vibrational change i.e. $v=0 \rightarrow v=1$, the rotational constants can be taken as B_0 and B_1 with $B_0 > B_1$

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

$$= \bar{\nu}_{osc} + B_1 J'(J'+1) - B_0 J''(J''+1) \quad cm^{-1}$$

Where $\bar{\nu}_{osc} = \bar{\nu}'_{osc}[1-2x]$

Now two cases will arise

i.e. $\Delta J = +1$ and $\Delta J = -1$

First case (i): $\Delta J = +1$, $J' = J''+1$

$$\Delta E = \bar{\nu}_R = \bar{\nu}_{osc} + B_1(J''+1)(J''+2) - B_0 J''(J''+1)$$

$$= \bar{\nu}_{osc} + (J''+1)\left[B_1(J''+2) - B_0 J''\right]$$

$$= \bar{\nu}_{osc} + (B_1+B_0)(J''+1) + (B_1-B_0)(J''+1)^2 \quad cm^{-1}$$

$$(J'' = 0, 1, 2, \dots) \quad ②$$

Second case (ii) $\Delta J = -1$, $J'' = J'+1$

$$\Delta E = \bar{\nu}_P = \bar{\nu}_{osc} - (B_1+B_0)(J'+1) + (B_1-B_0)(J'+1)^2 \quad cm^{-1}$$

$$(J' = 0, 1, 2, \dots) \quad ③$$

Where $\bar{\nu}_P$ and $\bar{\nu}_R$ represent the wavenumbers of P and R branch lines respectively.

Equation ② and ③ can be combinedly written as

$$\Delta E = \bar{\nu}_{P,R} = \bar{\nu}_{osc} + (B_1+B_0)m + (B_1-B_0)m^2 \quad cm^{-1} \quad [m = \pm 1, \pm 2, \dots] \quad ④$$

where positive m values refer to the R branch and negative to P.

- When there is no vibration–rotation interaction [i.e. $B_1 = B_0$] then the equation transforms as

$$\Delta\varepsilon_{J,v} = \bar{\nu}_{spe} = \bar{\nu}_{osc} + 2Bm \ \text{cm}^{-1} \quad [m = \pm 1, \pm 2, \ldots] \quad ⑤$$

As $B_1 < B_0$, the last term in equation ④ is always negative, irrespective of the sign of m, the rotational lines are more closely observed with increasing m on the R ~~branch~~ branch side. Whereas the P branch lines are more widely spaced as negative m increases.

Applications:

Generally molecules possess two types of vibrations, they are parallel vibrations and perpendicular vibrations. The selection rules for various rotational transitions depends upon the type of vibration i.e. parallel vibration & perpendicular vibration. The selection rules and energies also depend upon the shape of the molecule.

Linear Polyatomic molecules:

Parallel vibration: The selection rule for these molecules is identical with that of diatomic molecules i.e.

$\Delta J = \pm 1$ $\Delta V = \pm 1$ for simple harmonic motion.

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

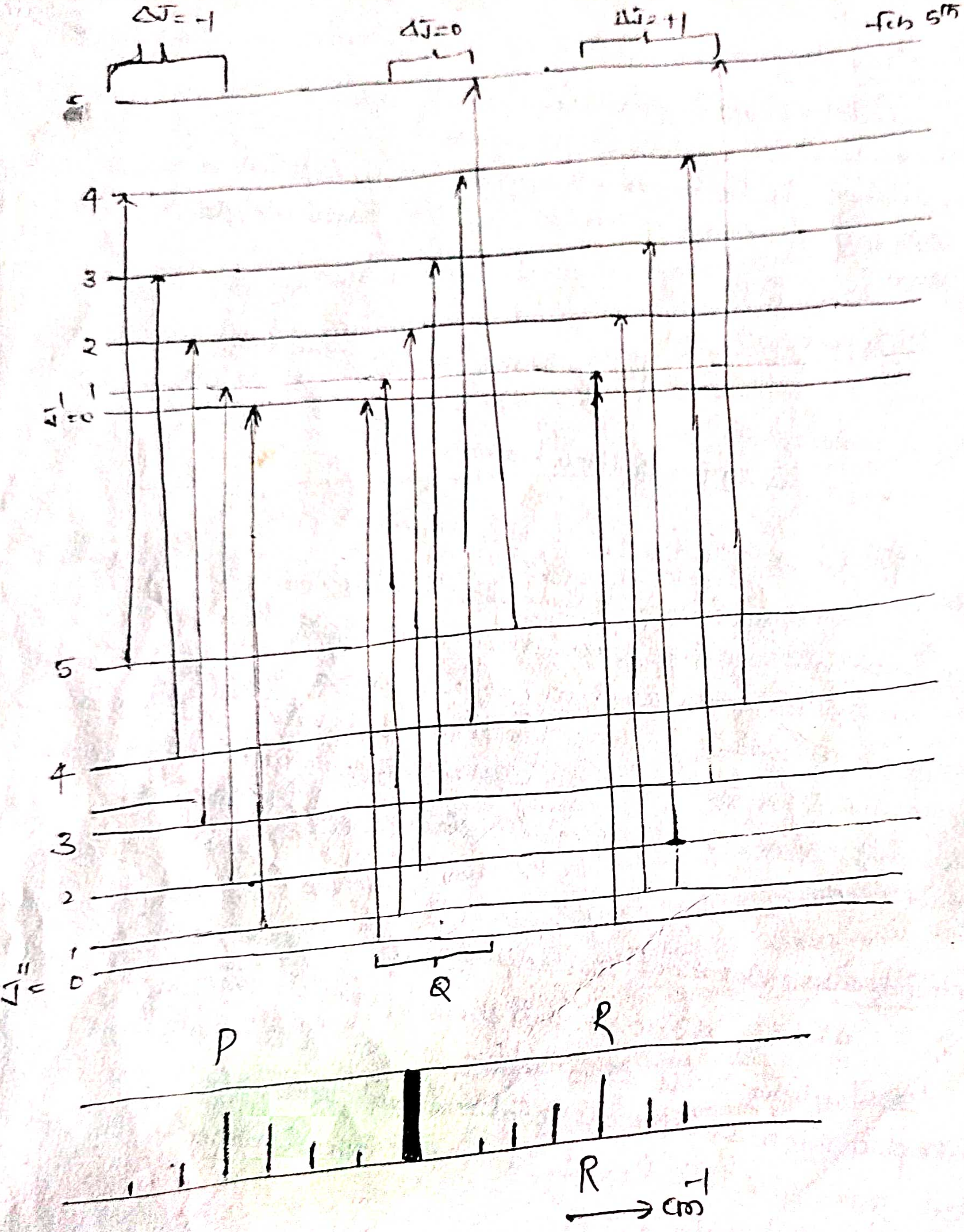
The IR spectra of these vibrations consists of P and R branches with lines about equally spaced on each side of the band centre. The spacing between the lines in P and R branches decreases with decrease in B value. For larger molecules the value of B may be so small that separate lines can longer be resolved in the P and R branches. Non-linear molecules cannot give rise to this type of band shapes.

Perpendicular vibrations: The selection rule is found to be for simple harmonic motion.

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

The selection rule $\Delta J = 0$ implies that a vibrational change can take place with no simultaneous rotational transitions. Now this selection rule gives rise to Q branch along with P and R branches corresponding to the selection rule $\Delta J = \pm 1$.

The Q branch consists of lines superimposed upon each other at the band centre ν_0. The resultant line is usually very intense.



If the B value differs slightly in the upper and lower vibrational states Then we can write

$$\Delta E = \epsilon_{J,v+1} - \epsilon_{J,v}$$
$$= \bar{\nu}_{osc} + (B' - B'') J(J+1)$$

Where $B' < B''$. As $B' < B''$ the Q branch line would become split into a series of lines on the low frequency side

It is well known that polyatomic molecules with zero dipole moment do not give rise to pure rotation spectra in the microwave region. However such molecules show vibrational spectra in the IR region.

Eg: CO_2, $HC\equiv CH$, CH_4 etc.

Symmetric top molecules:

Following the Born-Oppenheimer approximation, the vibrational-rotational energy levels of this type of molecules can be written as

$$\epsilon_{vib} = \bar{\nu}_e \left(V+\tfrac{1}{2}\right)\left[1-a\left(V+\tfrac{1}{2}\right)\right] \ cm^{-1} \quad (V=0,1,2,3,\dots)$$

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

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

$$\therefore \epsilon_{J,V} = \epsilon_{vib}+\epsilon_{rot}$$

$$= \bar{\nu}_e\left(V+\tfrac{1}{2}\right)\left[1-a\left(V+\tfrac{1}{2}\right)\right]+BJ(J+1)+(A-B)K^2 \ cm^{-1}$$

(a) Parallel vibrations:

The selection rule for parallel vibrations is

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

$\because \Delta K = 0$, K will be identical in the upper and lower levels and the spectral frequencies are independent of K. Thus the situation will be identical to that discussed for the perpendicular vibrations of a linear molecule. The spectrum will contain P, Q and R branches with a P, R line spacing of 2B and a strong central Q branch.

(b) Perpendicular vibrations:

For these the selection rule is

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

Each of the following expressions is readily derivable for the spectral lines,

(i) [illegible] $= \pm 1$, $\Delta K = \pm 1$ (R branch lines)

$$\Delta E = \bar{\nu}_{spec} = \bar{\nu}_0 + 2B(J+1) + (A-B)(1 \pm 2k)\ cm^{-1}$$

(ii) $\Delta J = -1$; $\Delta K = \pm 1$ (P branch lines)

$$\bar{\nu}_{spe} = \bar{\nu}_0 - 2B(J+1) + (A-B)(1 \pm 2K)\ cm^{-1}$$

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

$$\bar{\nu}_{spe} = \bar{\nu}_0 + (A-B)(1 \pm 2K)\ cm^{-1}$$

This type of vibration gives rise to 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 will thus be quite complicated and will not normally resolvable into separate lines. Similarly the Q branch is also complex because it will consist of a series of lines on both sides of $\bar{\nu}_0$ separated by $2(A-B)$. For $A \gg B$, Q branch lines will be well separated and will appear as a series of maxima above the P, R envelope.

Overtone and combination frequencies:

The selection rule for a simple Harmonic oscillator is $\Delta v = \pm 1$ and the
selection rule for anharmonic oscillator is $\Delta v = \pm 1, \pm 2, \pm 3, \ldots$ i.e. in addition
to ± 1, longer jumps pertaining $\pm 2, \pm 3, \ldots$ are also allowed in case of
anharmonic oscillator. These longer jumps results in the first, second etc
overtones occurring at frequencies near $2\nu_1, 3\nu_1, \ldots, 2\nu_2, 3\nu_2, \ldots 2\nu_3, \ldots$ etc,
where each ν_i is a fundamental mode. In addition to the overtones, the selection
rules now permit combination bands and difference bands. The former arise
simply from the addition two or more fundamental frequencies or overtones.
Such combinations as $\nu_1 + \nu_2$, $2\nu_1 + \nu_2$, $\nu_1 + \nu_2 + \nu_3$ etc become allowed. The
intensities are normally very small for these combination bands. Similarly the
difference bands, for example $\nu_1 - \nu_2$, $2\nu_1 - \nu_2$, $\nu_1 + \nu_2 - \nu_3$ etc, have small intensities
but are often to found in the complex spectrum.

Skeletal and Group frequencies:

For a molecule with N atoms either 3N-6 (if non linear) or 3N-5 (if linear)
modes of vibrations are possible. usually complex molecules exhibit complex IR
spectrum as large no of vibrations are possible for complex molecules. Each normal
mode involves some displacement of all, or nearly all, the atoms in the molecule.
In some other modes all atoms may undergo approximately the same displa-
-cement, ~~[illegible]~~ while in some other modes the displacement of a small group of atoms may
be much more vigorous than those of the remainder. Thus the normal modes
of vibrations may be divided into two classes skeletal vibrations and
Group vibrations. In skeletal vibrations, the displacement of many of the
atoms occur to the same extent. Group vibrations, involve only the vibration of a small portion
of the molecule, the remainder being more or less stationary. Skeletal vibrations
usually fall in the range 1400–700 cm^{-1}.

Group frequencies:

Group frequencies fall in the regions well above and well below
that of the skeletal modes. In certain molecules, a particular group like
$-CH_3$, $-OH$, $-C \equiv N$, $>C=O$ vibrate quite independent of the structure of the
molecule as a whole. The group vibrations of light atoms in terminal groups

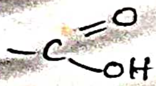
(for example $-CH_3$, $-OH$, $-C\equiv N$, $>C=O$ etc) are of high frequency, while those of heavy atoms ($-C-Cl$, $-C-Br$, metal-metal etc) are low in frequency. These frequencies are highly characteristic of the group and can be used for analysis. For example, $-CH_3$, group gives rise to a symmetric C-H stretching absorption invariably falling between 2850 and 2890 cm^{-1}, an asymmetric stretching frequency at 2940 – 2980 cm^{-1}, a symmetric deformation at about 1375 cm^{-1}, and an asymmetric deformation at about 1470 cm^{-1}. Similarly $>C=O$ group shows a very sharp and intense absorption between 1600 and 1750 cm^{-1}.

The significance of group frequencies data can be ~~understood~~ identified from the following discussion.

In acetic acid, if one of the oxygen atom has been replaced by sulphur then immediate question which arises in the mind is that the thioacetic acid is either CH_3COSH or CH_3CSOH. The IR spectrum gives a very clear answer. The molecule shows a very sharp absorption at about 1730 cm^{-1}, and one at about 2600 cm^{-1}, and these are in accordance with the presence of $>C=O$ and $-SH$ groups respectively. Also the spectrum does not exhibit strong absorption at 1100 cm^{-1}, thus indicating the absence of $>C=S$.

Some important group frequencies

Group	Approximate frequency (cm^{-1})	Assignment
$-OH$	3550 – 3650	ν_{OH} (free)
$-CH_3$	2940 – 2980	ν_{as}
	2850 – 2890	ν_s
	1445 – 1475	δ_{as}
	1365 – 1385	δ_s

Group	Approximate frequency (cm^{-1})	Assignment
$-CH_2-$	2910 – 2945 2835 – 2865 1455 – 1485	ν_{as} ν_s δ
$=CH_2$	3065 – 3095 2960 – 2990	ν_{as} ν_s
CH (aromatic)	3020 – 3050	ν
 $-C(=O)OH$	2800 – 3000 1600 – 1750 1220 – 1300	ν_{-OH} $\nu_{C=O}$ ν_{C-O} etc.