

$$\Delta \nu = (P-1) \omega$$

The shift increases as the order of band increases.

Molecule as Vibrating Rotator OR

Fine structure of Infra Red Bands

The near Infra Red spectra of molecules consist of band rather than lines. Each band is composed of close lines arranged in a particular manner. A line is missing at the centre of band in the series of lines that are not equidistant. The missing line is known as zero gap or null line. These lines show a poor tendency of convergence towards the higher wave number side and Band is said to be degraded toward the low wave number side i.e. towards the red.

The observed IR Band suggests that ^vvibrational transition the molecule

also changes its v rotational energy state and therefore it can be ~~also~~ treated as vibrating rotator.

Let any interaction between vibration and rotation of molecule is ignored so that term values of vibrating rotator are given by sum of term values of anharmonic oscillator and rigid rotator.

We know that term value of rigid rotator

$$F(J) = B J(J+1)$$

J - Rotational Quantum No.
Term value for Anharmonic oscillator is

$$G(V) = W_e(V + \frac{1}{2}) - W_e x_e (V + \frac{1}{2})^2$$

$V \rightarrow$ Vibrational Quantum number

Therefore term value for vibrating rotator is

$$F(J) + G(V)$$

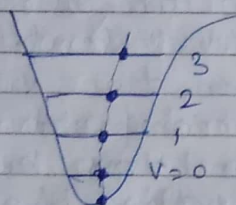
$$= B J(J+1) + W_e (V + \frac{1}{2}) - W_e x_e (V + \frac{1}{2})^2$$

Here B is rotational constant whose value is given by

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

In case of HCl 50 rotational levels are associated with each vibrational level. A transition between two vibrational level is accompanied by a number of transitions between two sets of rotational levels. This results in number of lines in a band. These lines form two branches of equidistant lines. These branches are named as **P and R Branch**. The spacing between lines of one branch slowly decreases and while other branch slowly increases as we move towards higher and higher lines of branch. This is attributed to vibration - rotation interaction. As seen from shape of potential curve, the

equilibrium inter nuclear distance r_e increases therefore moment of Inertia ($I \propto r^2$) also increases and hence Rotational Constant B ($B \propto \frac{1}{r^2}$) decreases.



r_e = Inter Nuclear Distance

The Rotational Constant B determines the spacing between rotational levels that is different for different vibrational state. Due to this rotational constant associated with vibrational state v is written as B_v

Due to change in inter nuclear distance, the rotational constant also changing during the vibration.

Hence mean value of Rotational Constant in a given vibrational state is used

$$B_v = \frac{h}{8\pi^2 \mu c} \overline{\left(\frac{1}{r^2}\right)}_v$$

Here $\overline{\left(\frac{1}{r^2}\right)}_v$ is mean value of $\frac{1}{r^2}$ in vibrational state v during vibration.

The rotational constant B_v in vibrational state v is given by

$$B_v = B_e - d_e \left(v + \frac{1}{2}\right) + \dots$$

d_e = constant depending upon shape of potential curve and $d_e \ll B_e$.

B_e is Rotational constant corresponding to separation r_e .

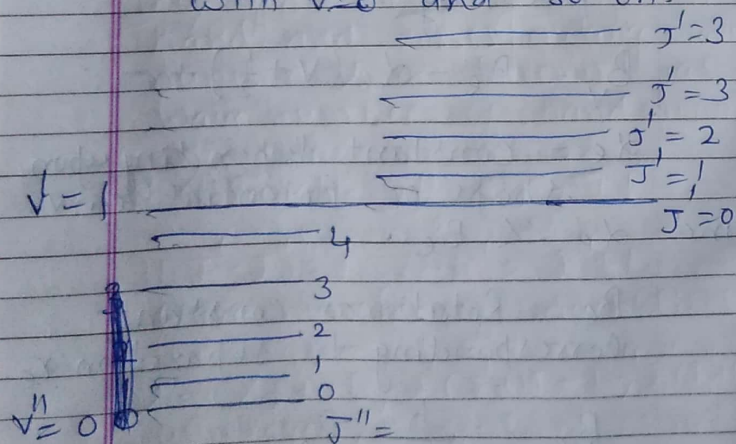
$$B_e = \frac{h}{8\pi^2 \mu r_e^2 c}$$

Now term value of vibrating Rotator becomes

$$G(V) + F(J) = W_e \left(V + \frac{1}{2} \right) - W_e x_e \left(V + \frac{1}{2} \right)^2 + B_v J(J+1)$$

The factor B_v decreases slightly with increasing v .

The spacing between rotational levels associated with $v=1$ are slightly smaller than those between levels associated with $v=0$ and so on.



Vibrating Rotator

The eigen functions of vibrating rotator are product of eigen functions of oscillator and rotational rotator. The selection rules are

$$\Delta J = \pm 1$$

$$\Delta V = +1, +2, \dots$$

Wave Number of Branches:

For a particular vibrational transition, the rotational transitions $\Delta J = +1$ give one set of lines referred to R-Branch while the transition $\Delta J = -1$ give other set of branches called as P Branch. All the lines of both branches form a Vibration Rotation Band. The wave number of branch lines of particular band

$$\nu = [G(V') + F(V', J')] - [G(V'' + F(V'', J''))]$$

$$\nu = G(v') - G(v'') + [B_v' J'(J'+1) - B_v'' J''(J''+1)]$$

$$= \nu_0 + B_v' J'(J'+1) - B_v'' J''(J''+1)$$

Here $\nu_0 = G(v') - G(v'')$ is

Wave number of pure vibrational transition for which $(J'=J''=0)$ that is not allowed due to selection rules ($\Delta J \neq 0$). This gives missing line in band and corresponding wave number ν_0 is known as wave number of band origin.

R Branch: If $\Delta J = +1$

$$J' - J'' = 1 \quad J' = J'' + 1$$

Wave number of such lines

$$\nu = \nu_0 + B_v' J'(J'+1) - B_v'' J''(J''+1)$$

Putting $J' = J'' + 1$

$$\nu_p = \nu_0 + B_v' (J''+1)(J''+2) - B_v'' J''(J''+1)$$

$$= \nu_0 + B_v' [J''^2 + 2 + 3J''] - B_v'' [J''^2 + J'']$$

$$= \nu_0 + J'' [3B_v' - B_v''] + J''^2 [B_v' - B_v''] + 2B_v' \quad \text{--- (A)}$$

Here J'' is lower rotational quantum number takes value 0, 1, 2, ... Hence R-Branch consists of series of lines named as R(0), R(1), R(2) corresponding to $J'' = 0, 1, 2, \dots$

Since $B_v' < B_v''$ therefore

$(B_v' - B_v'')$ is always negative and small.

$(3B_v' - B_v'')$ is always positive as B_v' is slightly smaller than B_v'' .

Therefore in eqⁿ (A) the linear and quadratic terms are in opposite sign.

Hence line spacing decrease very slowly as J'' increases.

P Branch: If $\Delta J = -1$ then

$$J' - J'' = -1$$

$$J' = J'' - 1$$

$$\nu_p = \nu_0 + B'_v J'(J'+1) - B''_v J''(J''+1)$$

Putting J' value

$$\nu_p = \nu_0 + B'_v J''(J''+1) - B''_v J''(J''+1)$$

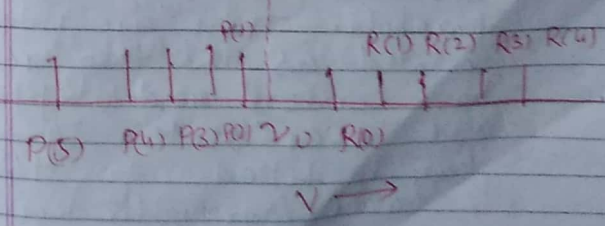
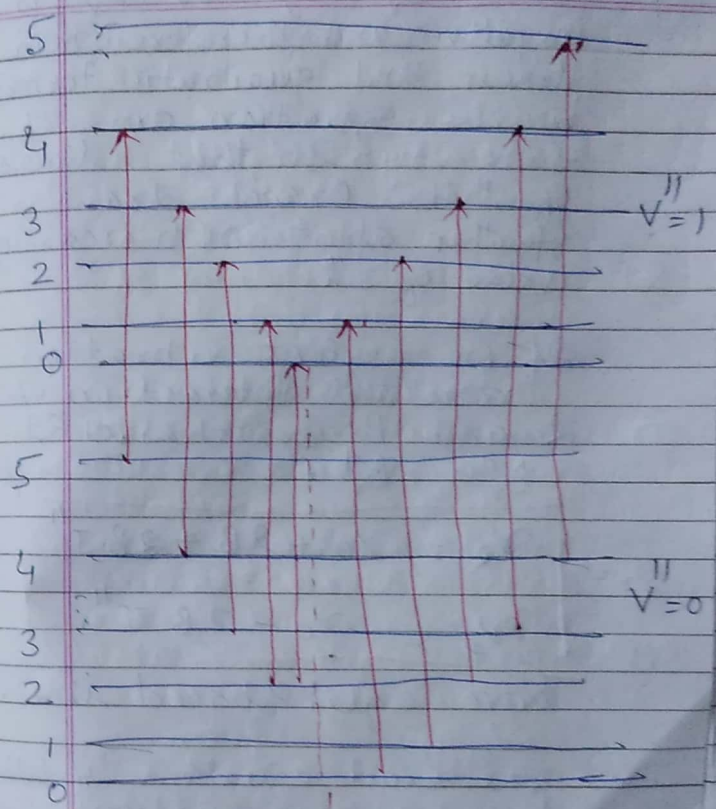
$$= \nu_0 + B'_v J''^2 - B''_v J''^2 - B''_v J''$$

$$= \nu_0 + (B'_v - B''_v) J''^2 - B''_v J''$$

$$= \nu_0 + (B'_v + B''_v) J'' + (B'_v - B''_v) J''^2$$

Here J'' is lower rotational quantum number takes the value 1, 2, 3, 4, ...

Here J'' can not be zero. as level $J' = -1$ does not exist. Therefore P branch are denoted as P(1) P(2) P(3) ... for $J'' = 1, 2, 3, \dots$



Further $B'_v < B''_v$ $B'_v - B''_v$ is negative and therefore both linear and quadratic terms in the equation are of same sign so that lines of this branch draw farther apart with increasing value of J'' .

If we neglect vibration rotation interaction of R and P branches, and $B''_v = B'_v$.

$$\nu_R = \nu_0 + 2B + 2BJ''$$

$$\nu_P = \nu_0 - 2BJ''$$

have equi spaced lines.

The exact equations of both branches are equations of parabolas. These are inter-related as the two branches have common ~~and~~ upper and lower state. They can be fitted to the same parabolic equation

$$\nu = \nu_0 + (B'_v + B''_v)m + (B'_v - B''_v)m^2$$

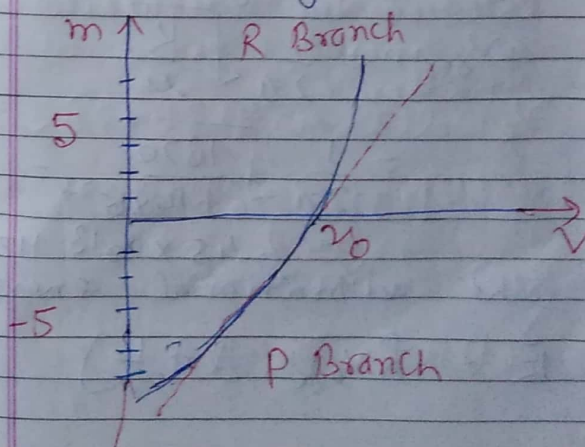
Here

$$m = J'' + 1 = 1, 2, 3 \dots \text{for lines } R(0), R(1), R(2) \dots$$

$$m = -J'' = -1, -2, -3 \dots \text{for lines } P(1), P(2), P(3) \dots$$

$m = 0$ for zero gap ν_0 .

A plot of the common parabolic equation is shown in figure where line indicates the corresponding plot for $B'_v = B''_v$



As the constant α_e is very small, the difference $(B_v' - B_v'')$ is very small. Hence curve is only very slightly deviated from the straight line because vibration rotation bands show a very poor tendency of band formation.

Numerical Problems

- ① The force constant of the bond in CO molecule is 1870 N/m . Find the energy of lowest vibrational level. The reduced mass is $1.14 \times 10^{-26} \text{ kg}$.

Solⁿ: The frequency of vibration is

$$\begin{aligned} \nu_{osc} &= \frac{1}{2\pi} \sqrt{\frac{K}{\mu}} \\ &= \frac{1}{2\pi} \sqrt{\frac{1870}{1.14 \times 10^{-26}}} \\ &= 6.45 \times 10^{13} \text{ Hz} \end{aligned}$$

The vibrational energy

$$E = h\nu_{osc} \left(V + \frac{1}{2} \right)$$

For lowest state $\nu = 0$

$$\begin{aligned} E &= \frac{1}{2} h\nu_{osc} = \frac{1}{2} \times 6.6 \times 10^{-34} \\ &\quad \times 6.45 \times 10^{13} \\ &= 21.4 \times 10^{-21} \text{ Joule} \end{aligned}$$

- ② If the fundamental band of $\text{H}^1\text{C}^{13}\text{O}$ lies at 3.46μ . Calculate wavelength of corresponding band of $\text{H}^2\text{C}^{13}\text{O}$.

Solⁿ

We know that

$$\frac{w^i}{w} = \sqrt{\frac{\mu}{\mu_i}} = f$$

$$w^i = f \cdot w$$

In terms of wavelength

$$\lambda^i = \frac{\lambda}{f} \quad f = \sqrt{\frac{1 \times 35/36}{2 \times 39/39}}$$

$$= 1.7158$$

$$\lambda^i = \frac{3.46}{1.7158} = 4.83 \mu (\text{micron})$$

③ The mean of internuclear distance for HCl^{35} in $v=0$ and $v=1$ level is 1.293 \AA . Calculate wave number difference between $R(0)$ and $P(1)$ lines of fundamental band. given $\mu = 1.61 \times 10^{-27} \text{ kg}$

Solⁿ Internuclear distance has been taken same for $v=0$ and $v=1$ means vibration rotation interaction has been ignored. The rotational constant

$$B = \frac{h}{8\pi^2 \mu r^2 c} = 1041 \text{ cm}^{-1}$$

The wavenumber of R and P branch when vibration rotation interaction is ignored, given

$$\nu_R = R(J) = \nu_0 + 2B + 2BJ$$

$$\nu_P = P(J) = \nu_0 - 2BJ$$

$$R(0) = \nu_0 + 2B$$

$$P(1) = \nu_0 - 2B$$

$$\begin{aligned} R(0) - P(1) &= 2B - (-2B) = 4B \\ &= 4 \times 1041 = 4164 \text{ cm}^{-1} \\ &= 4164 \text{ m}^{-1} \text{ or } 41.64 \text{ cm}^{-1} \end{aligned}$$

④ The 2806 cm^{-1} fundamental band of HCl can be shown to fit in equation

$$\nu = 2805.90 + 20.577m - 0.3034m^2$$

calculate value of B_0, B_1, B_2 , given $d_e = 0.3019 \text{ cm}^{-1}$

Solⁿ The general equation is

$$\nu = \nu_0 + (B'_v + B''_v)m + (B'_v - B''_v)m^2$$

Comparing it with equation for fundamental band $v' = 1, v'' = 0$

$$B_1 + B_0 = 20.577$$

$$B_1 - B_0 = -0.3034$$

$$B_1 = 10.1368$$

$$B_0 = 10.4402$$

We know

$$B_v = B_0 - de \left(v + \frac{1}{2} \right)$$

For $v=0$

$$B_0 = B_e - de \times \frac{1}{2}$$

$$B_e = B_0 + \frac{de}{2}$$

$$= 10.4402 + \frac{1.3019}{2}$$

$$B_e = 10.5909 \text{ cm}^{-1}$$

- ⑤ The values of w_e , $w_e x_e$ are 1500.36 and 12.073 cm^{-1} for ground state of molecular oxygen. Compute the zero point energy of O_2 molecule.

Soln. We know that

$$G(v) = w_e \left(v + \frac{1}{2} \right) - w_e x_e \left(v + \frac{1}{2} \right)^2$$

For ground state
 $v=0$

$$G(0) = w_e \frac{1}{2} - \frac{w_e x_e}{4}$$

$$= \frac{1500.036}{2} - \frac{12.073}{4}$$

$$= 790.018 - 3.01825$$

$$= 786.99 \text{ cm}^{-1}$$

As we know

$$1 \text{ cm}^{-1} = 1.24 \times 10^{-4} \text{ eV}$$

$$G(0) = 786.99 \times 1.24 \times 10^{-4} \text{ eV}$$

$$= .097586 \text{ eV}$$

- ⑥ Calculate the ratio of vibrational frequencies of Hydrogen iodide $H^1 I^{127}$ and Deuterated Hydrogen iodide $D^2 I^{127}$.

Soln. As we know

$$\frac{w^i}{w} = \sqrt{\frac{\mu}{\mu^i}}$$

$\mu^i \rightarrow$ Heavier Isotope

$$\mu^i = \frac{2 \times 127}{2 + 127} = \frac{254}{129}$$

$$\mu = \frac{1 \times 127}{1 + 127} \approx \frac{127}{128}$$

$$\frac{\omega^i}{\omega} = \sqrt{\frac{127 \times 129}{128 \times 254}}$$

$$\frac{\omega}{\omega^i} = \sqrt{\frac{128 \times 254}{127 \times 129}}$$

$$\frac{\omega}{\omega^i} = 1.98$$

Application of vibrational Spectroscopy [