

Lecture 29 Title: The rotational-vibrational spectra

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In this lecture, we will find out the rotational-vibrational spectrum of a diatomic molecule.

The analysis of the rotational spectrum will be carried out using non rigid rotor approximation.

The rotational structure of the vibrational band will be understood.

The temperature effect of the rotational-vibrational spectrum will also be discussed.

In the last lecture we have considered the vibration and rotation separately. We now consider the actual case in which a diatomic molecule is simultaneously executing both vibrational and rotational motion.

Classically, the calculated periods of vibration and rotation are of the order of 10^{-14} and 10^{-12} sec, respectively. Therefore, a molecule can vibrate one hundred times during one rotation.

As a first approximation, we separate the two types of motion and calculate the rotational energy using a mean value of B_v for the rotational constant that is averaged over the change in the bond length that occur during much more rapid vibrational motions of the nuclei.

$$B_v = \frac{\hbar^2}{2\mu hc} \left(\frac{1}{R^2} \right)_v \text{ in cm}^{-1}. \dots\dots\dots(29.1)$$

Where $\left(\frac{1}{R^2} \right)_v$ is the mean value for the v the vibrational state.

So rotational energy $F_v(J) = B_v J(J+1)$ in cm^{-1} .

Now the radial equation becomes

$$-\frac{\hbar^2}{2\mu R^2} \frac{d}{dR} \left(R^2 \frac{d\Re}{dR} \right) + E_{ROT} \Re(R) + E(R) \Re(R) = E \Re(R) \dots\dots\dots(29.2)$$

We already

$$-\frac{\hbar^2}{2\mu R^2} \frac{d}{dR} \left(R^2 \frac{d\Re}{dR} \right) + E(R) \Re(R) = E_{vib} \Re(R) \dots\dots\dots(29.3)$$

So $E = E_{vib} + E_{ROT}$

And the term value $T_{v,J} = G_0(v) + F(J)$ in cm^{-1} .

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The energies for the rotational levels are derived by assuming that there is a rigid fixed bond between the nuclei. This is known as RIGID ROTOR approximation.

This is not true for an actual molecule undergoing anharmonic oscillations and the following two modifications must be introduced.

Modification-1:

Average internuclear distance increases slightly with ν for an anharmonic oscillator.

Therefore the mean value of $\left(\frac{1}{R^2}\right)_\nu$ correspondingly decreases.

So in this case $B_\nu = B_e - \alpha_e \left(\nu + \frac{1}{2}\right)$ where B_e is the rotational constant at the equilibrium internuclear distance R_e and α_e is the small constant and depends on the shape of the vibrational potential curve.

Modification-2:

In any given vibrational state ν the expression for the rotational terms $F(J)$ must include a correction for the centrifugal distortion of the elastic bond between the nuclei.

Therefore a better model representing as shown in figure-29.1 the rotation is given by “NON RIGID ROTOR”.



Figure-29.1

Non rigid rotor model can be visualize as two spheres are connected by a spring.

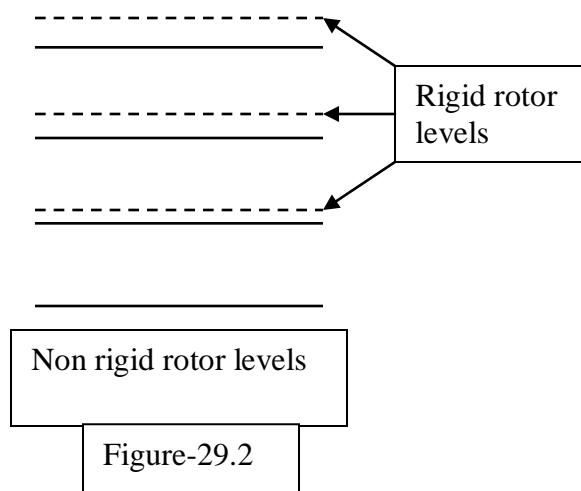
Classically, increased rotational energy corresponds to an increased rate of rotation of the molecule. The centrifugal force which is proportional to the square of the angular momentum $F_c = \mu R_e \omega^2$ expands the bond against its restoring force, and the work consumed in this process must be subtracted from the energy calculated in the rigid rotor approximation.

$$F(J) = B_v J(J+1) - D_v J^2(J+1)^2 + \dots \quad \dots\dots\dots(29.4)$$

The constant D_v is usually smaller than B_v by a factor of 10^{-4} or more.

The infra red rotational spectrum

$$\begin{aligned} \bar{\nu} &= F(J+1) - F(J) \\ &= 2B_v(J+1) - 4D_v(J+1)^3 \end{aligned}$$



Vibrating Rotor term value

$$T_{\nu,J} = G_0(\nu) + F(J)$$

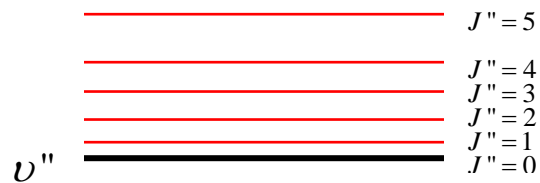
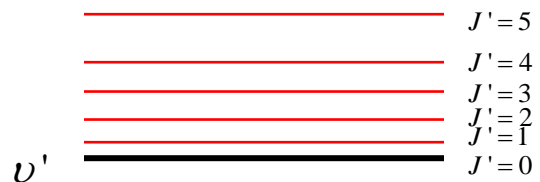
$$= \omega_0 \nu - \omega_0 x_0 \nu^2 + \omega_0 y_0 \nu^3 + B_\nu J(J+1)$$

The energy level diagram of these two vibrational levels are shown in figure-29.3

Now let us look at the transitions of rotational lines between the two vibrational levels ν' and ν'' . This is known as rotational structure of vibrational transition or rotation-vibration spectrum.

$$T_{\nu'',J''} = G_0(\nu'') + B_{\nu''} J''(J''+1)$$

$$T_{\nu',J'} = G_0(\nu') + B_{\nu'} J'(J'+1)$$



Vibration-rotation levels

Figure-29.3

The transition selection rule is $\Delta v = \pm 1, \pm 2, \pm 3, \dots$
 $\Delta J = \pm 1$

$$\begin{aligned}\bar{\nu} &= T_{v', J'} - T_{v'', J''} = G_0(v') - G_0(v'') + B_{v'} J'(J'+1) - B_{v''} J''(J''+1) \\ &= \nu_{v'v''} + B_{v'} J'(J'+1) - B_{v''} J''(J''+1)\end{aligned}$$

Let,

$$\left. \begin{aligned} J' &= J''+1 \\ J' &= J''-1 \end{aligned} \right\} \Delta J = \pm 1$$

When $J' = J''+1$, this is known as R branch

For $J' = J''+1$,

$$\begin{aligned}\bar{\nu}_R &= \nu_{v'v''} + B_{v'}(J''+1)(J''+2) - B_{v''} J''(J''+1) \\ &= \nu_{v'v''} + B_{v'}(J''^2 + 3J'' + 2) - B_{v''}(J''^2 + J'') \\ &= \nu_{v'v''} + 2B_{v'} + J''(3B_{v'} - B_{v''}) + J''^2(B_{v'} - B_{v''}) \\ &\quad \text{where } J'' = 0, 1, 2, 3, \dots\end{aligned} \dots\dots\dots(29.5)$$

When $J' = J''-1$, this is known as P branch

For $J' = J''-1$,

$$\begin{aligned}\bar{\nu}_P &= \nu_{v'v''} + B_{v'}(J''-1)J'' - B_{v''} J''(J''+1) \\ &= \nu_{v'v''} + B_{v'}(J''^2 - J'') - B_{v''}(J''^2 + J'') \dots\dots\dots(29.6) \\ &= \nu_{v'v''} + J''(B_{v'} - B_{v''}) + J''^2(B_{v'} - B_{v''}) \\ &\quad \text{where } J'' = 0, 1, 2, 3, \dots\end{aligned}$$

In some cases $J' = J''$ is allowed and it is known as Q-branch.

Take rotationally resolved IR spectrum. Fitting it we get

$$\left. \begin{aligned} B_{v'} \text{ \& } B_{v''} & \quad ; \quad B_{v'} = B_e - \alpha_e \left(v' + \frac{1}{2} \right) \\ B_{v'} &= \frac{\hbar^2}{2\mu R^2 hc} \quad B_{v''} = B_e - \alpha_e \left(v'' + \frac{1}{2} \right) \end{aligned} \right\} B_e = \frac{\hbar^2}{2\mu R^2 hc}$$

If $B_{v'} = B_{v''} = B$ then

$$\bar{\nu}_R = \nu_0 + 2B + 2BJ$$

$$\bar{\nu}_P = \nu_0 - 2BJ$$

Where ν_0 is $v' \leftarrow v''$ transition and is known as vibrational origin transition.

The rotational structure of the vibrational transition is shown in figure-29.4

If $B_{v'} \neq B_{v''}$

Then we can write a single formula for the R and P branch transitions.

$$\bar{\nu}_m = \nu_0 + (B_{v'} + B_{v''})m + (B_{v'} - B_{v''})m^2 \quad \dots\dots\dots(29.7)$$

Where $m = 1, 2, 3, \dots$ give the R branch and

$m = -1, -2, -3, \dots$ give P branch

$m = 0$ is the missing line

Generally, $B_{v'}$ & $B_{v''}$ do not differ much, so the rotational vibrational spectrum consists of equally spaced lines.

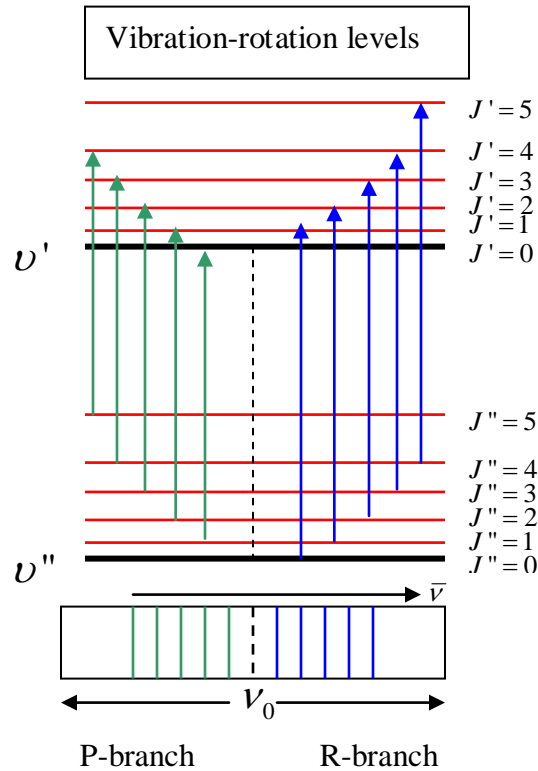


Figure-29.4

Intensities of rotation-vibration spectra:

The intensity of spectral lines depends not only on the transition probability and frequency of the light but also on the number of the molecules in the initial state.

For the prediction of the intensity, knowledge of the numbers of molecules in the initial state is necessary, in addition to the transition probabilities.

Since almost all infrared spectra are observed under conditions of thermal equilibrium we need to consider the distribution of the molecules over the different quantum states in thermal equilibrium.

Vibration:

Thermal distribution of quantum states.

According to the Maxwell Boltzman Distribution law, the number of molecules dN_E

between E & $E + dE$ is proportional to $e^{-E/kT} dE$

The quantities $e^{-G_0(v)hc/kT}$ give the relative number of molecules in the different vibrational levels referred to the number of molecules in the lowest vibrational level. If the total number of molecule is N then state sum (Boltzman factors over all states) partition function is given by,

$$Q_v = 1 + e^{-G_0(1)hc/kT} + e^{-G_0(2)hc/kT} + \dots$$

Therefore, no. of molecules in state v ,

$$N_v = \frac{N}{Q_v} e^{-G_0(v)hc/kT}$$

Since

$$N \propto Q_v \Rightarrow N = KQ_v \Rightarrow K = \frac{N}{Q}$$

if $G_0(1)$ is very large,

$$\text{then } e^{-G_0(1)hc/kT} \approx 0$$

and for $Q_v = 1$,

$$N_v = N e^{-G_0(v)hc/kT}$$

The figure-29.5 gives the relative distribution of the no. of molecules in a given vibrational state.

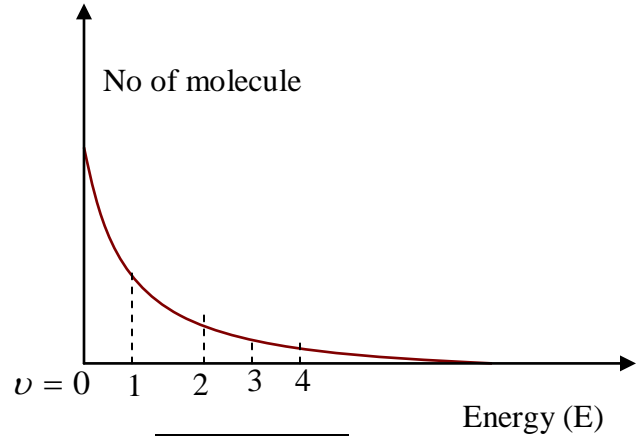


Figure-29.5

Rotation:

The thermal distribution of the rotational level is not only given by the Boltzman factor

$e^{-E/kT} dE$, we have to consider the degeneracy of the rotational levels. Each rotational level J is consisting of $(2J+1)$ of m degenerate levels.

And thus the no. of molecules of a J level is given by

$$N_J \propto (2J+1) e^{-F(J)hc/kT}$$

Substituting the value of $F(J)$, we get

$$N_J = K (2J+1) e^{-BJ(J+1)hc/kT} \dots\dots\dots(29.8)$$

To get the rotational quantum number for which the no. of molecule will be maximum, we have to differentiate equation 29.8 with respect to J, and we get

$$\left. \frac{d N_J}{d J} \right|_{J_{\max}} = 0$$

$$\left. \frac{d N_J}{d J} \right|_{J_{\max}} = K 2 e^{-B J(J+1)hc/kT} + K(2J+1)[-2BJ-B] \frac{hc}{kT} e^{-B J(J+1)hc/kT} = 0$$

Solving this equation,

$$\Rightarrow 0 = 2K e^{-B J(J+1)hc/kT} - K(2J+1)^2 \frac{Bhc}{kT} e^{-B J_{\max}(J_{\max}+1)hc/kT}$$

$$\Rightarrow (2J_{\max}+1)^2 \frac{Bhc}{kT} = 2 \quad \Rightarrow (2J_{\max}+1)^2 = \frac{2kT}{Bhc}$$

$$\Rightarrow 2J_{\max}+1 = \sqrt{\frac{2kT}{Bhc}} \quad \Rightarrow 2J_{\max} = \sqrt{\frac{2kT}{Bhc}} - 1$$

$$\Rightarrow J_{\max} = \sqrt{\frac{kT}{2Bhc}} - \frac{1}{2} = 0.5896 \sqrt{\frac{T}{B}} - \frac{1}{2}$$

The rotational state sum

$$Q_r = 1 + 3e^{-2Bhc/kT} + 5e^{-6Bhc/kT} + \dots$$

$$N_J = \frac{N}{Q_r} (2J+1) e^{-B J(J+1)hc/kT}$$

For large T & small B,

$$Q_r \approx \int_0^{\infty} (2J+1) e^{-Bhc J(J+1)/kT} dJ$$

$$N_J = N \frac{hcB}{kT} (2J+1) e^{-B J(J+1)hc/kT} = \frac{kT}{hcB}$$

$$I_{abs} = \frac{C_{abs} \nu}{Q_r} (2J''+1) e^{-B'' J''(J''+1)hc/kT}$$

where, $C_{abs} \Rightarrow \text{Constant}$

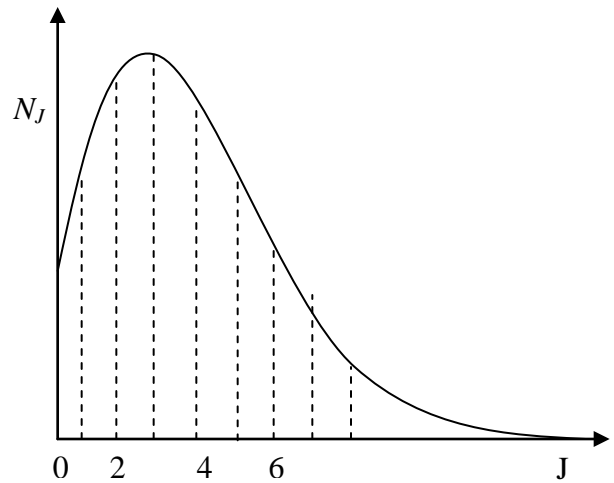


Figure-29.6

Intensity of the P and R branch

Let us consider $B_{v'} \approx B_{v''} = B$. Then,

$$\begin{aligned}\nu_R &= \nu_{v',v''} + 2B_{v'} + J''(3B_{v'} - B_{v''}) + J'^2(B_{v'} - B_{v''}) \\ \Rightarrow \nu_R &= \nu_{v',v''} + 2B + 2BJ''\end{aligned}$$

And,

$$\begin{aligned}\nu_P &= \nu_{v',v''} + J''(B_{v'} + B_{v''}) + J'^2(B_{v'} - B_{v''}) \\ \Rightarrow \nu_P &= \nu_{v',v''} - 2BJ''\end{aligned}$$

Putting the J_{\max} ,

$$\nu_R|_{J_{\max}} = \nu_{v',v''} + 2B + 2BJ_{\max}$$

$$\nu_P|_{J_{\max}} = \nu_{v',v''} - 2BJ_{\max}$$

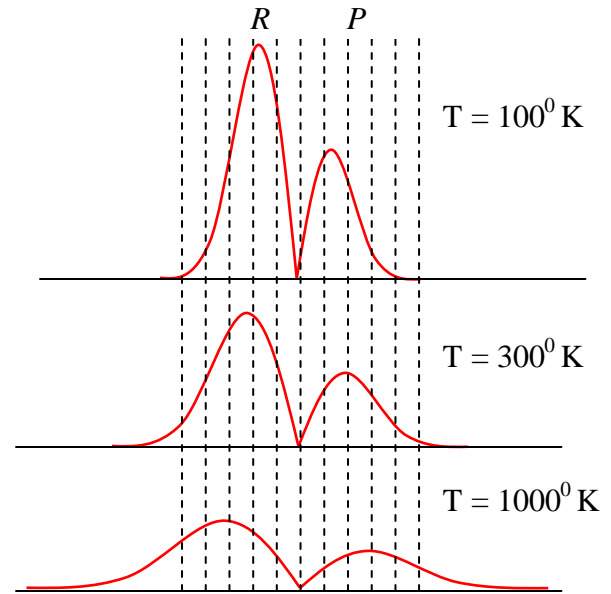


Figure 29.7

$$\begin{aligned}\nu_R - \nu_P|_{J_{\max}} &= 2B + 4BJ_{\max} = 4B \left[\frac{1}{2} + J_{\max} \right] \\ &= 4B \left[\frac{1}{2} + \sqrt{\frac{kT}{2Bhc}} - \frac{1}{2} \right] = \sqrt{\frac{8BkT}{hc}} = 2.3583\sqrt{BT}\end{aligned}$$

So the separation of the P branch and R branch maximum will depend on the value of T and B. For a given molecule, if T increases then the separation of P and R branch maxima will increase. The figure shows the intensity pattern of the rotation-vibration spectrum for different temperatures.

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Recap

In this lecture we have learnt the non rigid approximation of the rotational energy levels.

Due to the different vibrational frequency the rotational levels get modified.

The intensity of the rotational structure of the vibrational bands depend on the temperature of the system

A close look at the P and R brach maximum in the rotational structure of the vibrational bands provide information about the temperature of the system