

Title: Rotational structure of particular electronic transition

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In the previous lecture, we have learnt the vibrational structure of the electronic transition. We have neglected the rotational structure while discussing the vibrational structure.

In fact, the resolution of the observed spectrum determines what to consider in theory. For example, if the resolution of the spectrum is such that it can not resolve the rotational structure since the rotational bands are very closely spaced, we do not consider the rotational term in calculation.

However, if the resolution of the observed spectrum is higher than the separation of rotational bands, we observe the rotational structure. In that case, it is necessary to consider the rotational term and important to analyze the rotational structure.

In this lecture, we will learn how to analyze the rotational structure and how to derive the important information about the molecule such as bond length from this structure.

In the previous lecture, we have already derived the wavenumbers of the spectral lines between two electronic states given in equation-31.7,

$$\bar{\nu} = T'_{final} - T''_{initial} = (T'_e - T''_e) + (G(v') - G(v'')) + (F_{v'}(J') - F_{v''}(J'')) \dots\dots\dots(32.1)$$

Here, $T''_{initial}$ and T'_{final} are the term values of the initial and final states respectively.

Second part is the vibrational term and the third part is the rotational term.

If the final state is the excited electronic state and initial state is the ground state, then this is known as electronic absorption. If the transition is from excited electronic state to ground or other lower electronic state then it is known as emission. If the transition is from ground electronic state to excited electronic state then it is known as absorption. Here the single prime refers to the excited state and double prime is used for the ground state.

For a particular vibrational transition between the two electronic states from equation-32.1 can be written as

$$\bar{\nu}_{v',v''}(J', J'') = \bar{\nu}(v', v'') + (F_{v'}(J') - F_{v''}(J'')) \dots\dots\dots(32.2)$$

Where the rotational part considering non-rigid rotor can be written as

$$F_v(J) = B_v J(J+1) - D_v J^2(J+1)^2 + \dots\dots\dots(32.3)$$

In equation-32.3 the first term is the usual rigid rotor term where

$$B_v = \frac{h}{8\pi^2 \mu R_e^2 c} \dots\dots\dots(32.4)$$

(discussed in lecture-28, equation 28.8). The second term is the correction term due to non rigid rotor.

Substituting equation 32.3 in equation 32.2, we get

$$\bar{\nu}_{v',v''}(J', J'') = \bar{\nu}(v', v'') + [\{B_{v'} J'(J'+1) - D_{v'} J'^2(J'+1)^2\} - \{B_{v''} J''(J''+1) - D_{v''} J''^2(J''+1)^2\}] \dots\dots\dots(32.5)$$

Now the selection rules for the rotational transitions are

$$\Delta J = J' - J'' = 0, \pm 1$$

For $J' = J'' + 1$, we have the *R*-branch transitions.

For $J' = J''$, we have the *Q*-branch transitions.

For $J' = J'' - 1$, we have the *P*-branch transitions.

In figure-32.1, these branches are shown. Here, the transitions are from the ν'' vibrational state of the lower electronic state to ν' of the upper electronic state.

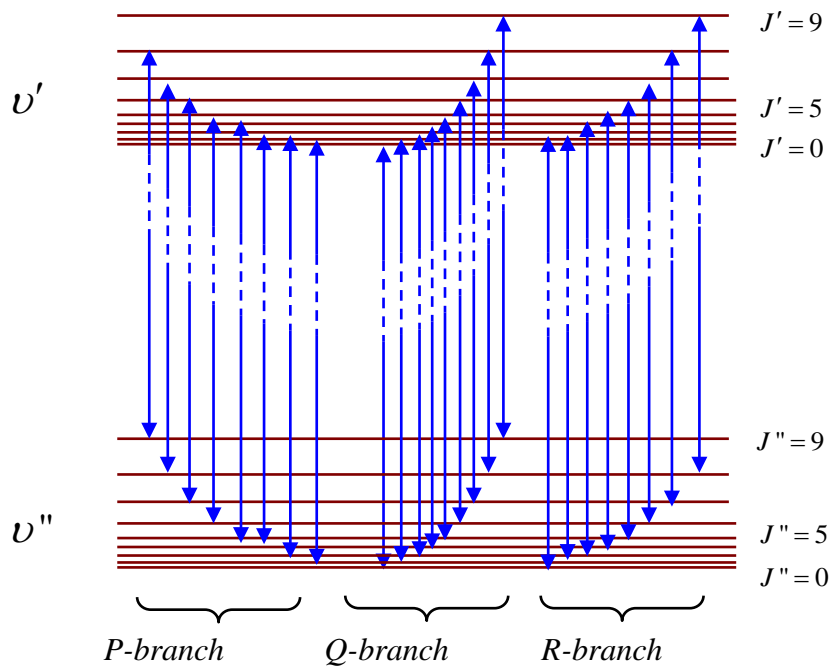


Figure-32.1

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For $J' = J'' + 1$, we have the R -branch transitions

$$\bar{\nu}_{v',v''}^R(J',J'') = \bar{\nu}(v',v'') + [F_{v'}(J''+1) - F_{v''}(J'')]$$

Writing only for the ground state quantum number J , we get

$$\bar{\nu}_{v',v''}^R(J) = \bar{\nu}(v',v'') + [F_{v'}(J+1) - F_{v''}(J)] = R(J)$$

So,

$$\begin{aligned}\bar{\nu}_{v',v''}^R(J) &= \bar{\nu}(v',v'') + [B_{v'}(J+1)(J+2) - B_{v''}J(J+1)] \\ &= \bar{\nu}(v',v'') + 2B_{v'} + (3B_{v'} - B_{v''})J + (B_{v'} - B_{v''})J^2 \quad \dots\dots\dots(32.6) \\ &= R(J)\end{aligned}$$

For $J' = J''$, we have the Q -branch transitions

$$\bar{\nu}_{v',v''}^Q(J',J'') = \bar{\nu}(v',v'') + [F_{v'}(J'') - F_{v''}(J'')]$$

Writing only for the ground state quantum number J , we get

$$\bar{\nu}_{v',v''}^Q(J) = \bar{\nu}(v',v'') + [F_{v'}(J) - F_{v''}(J)] = Q(J)$$

So,

$$\begin{aligned}\bar{\nu}_{v',v''}^Q(J) &= \bar{\nu}(v',v'') + [B_{v'}J(J+1) - B_{v''}J(J+1)] \\ &= \bar{\nu}(v',v'') + (B_{v'} - B_{v''})J + (B_{v'} - B_{v''})J^2 \quad \dots\dots\dots(32.7) \\ &= Q(J)\end{aligned}$$

For $J' = J'' - 1$, we have the P -branch transitions

$$\bar{\nu}_{v',v''}^P(J',J'') = \bar{\nu}(v',v'') + [F_{v'}(J''-1) - F_{v''}(J'')]$$

Writing only for the ground state quantum number J , we get

$$\bar{\nu}_{v',v''}^P(J) = \bar{\nu}(v',v'') + [F_{v'}(J-1) - F_{v''}(J)] = P(J)$$

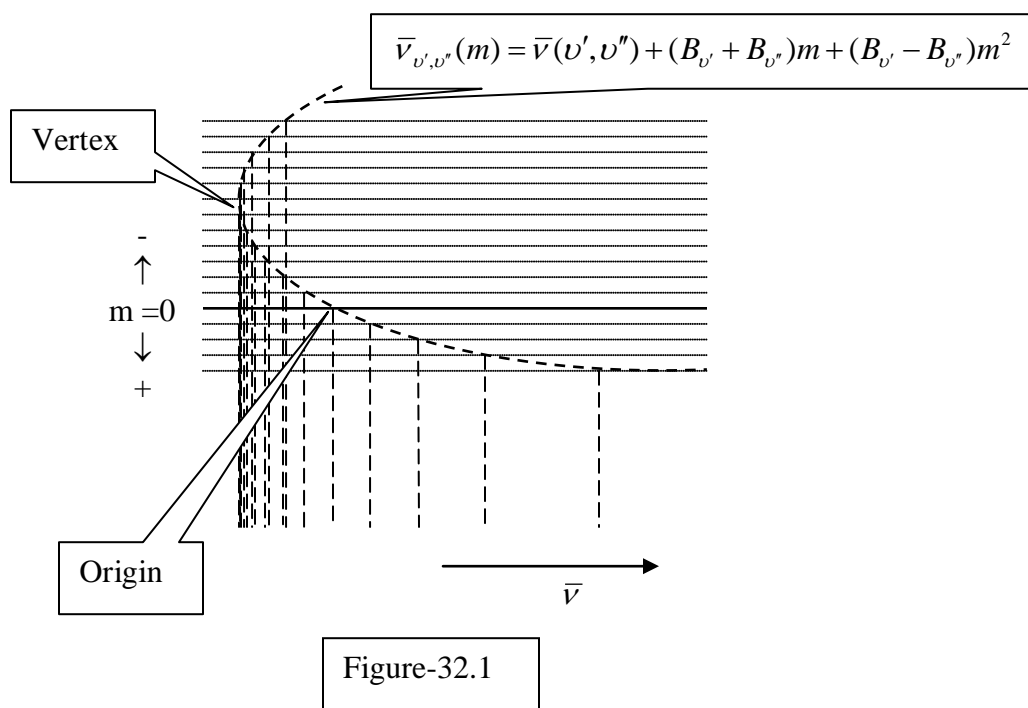
$$\begin{aligned}\bar{\nu}_{v',v''}^P(J) &= \bar{\nu}(v',v'') + [B_{v'}(J-1)J - B_{v''}J(J+1)] \\ &= \bar{\nu}(v',v'') - (B_{v'} + B_{v''})J + (B_{v'} - B_{v''})J^2 \quad \dots\dots\dots(32.8) \\ &= P(J)\end{aligned}$$

For the r-branch equation-32.6 and for the P-branch equation-32.8, we can combine to get a single equation such as

$$\bar{\nu}_{\nu',\nu''}(m) = \bar{\nu}(\nu',\nu'') + (B_{\nu'} + B_{\nu''})m + (B_{\nu'} - B_{\nu''})m^2 \dots\dots\dots(32.9)$$

Where, $m = -J$ for the *P-branch*, $m = -1, -2, -3, \dots\dots$
 $= J + 1$ for the *R-branch*, $m = 1, 2, 3, \dots\dots$

This equation-32.9 is a parabolic equation. This equation is very interesting in the sense that depending on the values of $B_{\nu'}$ and $B_{\nu''}$, the rotational constants between the two electronic states, we get different nature of the parabola. In figure-31.1, this parabola is plotted.



The position of the vertex at m_{vertex} is defined as when the change of the separation is zero. So,

$$\frac{\delta}{\delta m}[\bar{\nu}_{\nu',\nu''}(m_{vertex})] = (B_{\nu'} + B_{\nu''}) + 2(B_{\nu'} - B_{\nu''})m_{vertex} = 0$$

From this we get,

$$m_{vertex} = -\frac{(B_{\nu'} + B_{\nu''})}{2(B_{\nu'} - B_{\nu''})} \dots\dots\dots(32.10)$$

Substituting equation 32.10 to equation-32.9, the position in terms of wavenumber we get,

$$\begin{aligned} \bar{\nu}_{\nu',\nu''}(m_{vertex}) &= \bar{\nu}(\nu', \nu'') + (B_{\nu'} + B_{\nu''})m_{vertex} + (B_{\nu'} - B_{\nu''})m_{vertex}^2 \\ &= \bar{\nu}(\nu', \nu'') + (B_{\nu'} + B_{\nu''})\left[-\frac{(B_{\nu'} + B_{\nu''})}{2(B_{\nu'} - B_{\nu''})}\right] + (B_{\nu'} - B_{\nu''})\left[-\frac{(B_{\nu'} + B_{\nu''})}{2(B_{\nu'} - B_{\nu''})}\right]^2 \\ \bar{\nu}_{\nu',\nu''}(m_{vertex}) &= \bar{\nu}(\nu', \nu'') - \frac{(B_{\nu'} + B_{\nu''})^2}{4(B_{\nu'} - B_{\nu''})} \dots\dots\dots(32.11) \end{aligned}$$

This is also known as band head.

Now the position of the origin of the vibrational transition $\bar{\nu}(\nu', \nu'')$ in terms of $B_{\nu'}$ and $B_{\nu''}$, from equation 32.11 we get

$$\bar{\nu}(\nu', \nu'') = \bar{\nu}_{\nu',\nu''}(m_{vertex}) + \frac{(B_{\nu'} + B_{\nu''})^2}{4(B_{\nu'} - B_{\nu''})} \dots\dots\dots(32.12)$$

Next, let us discuss the transition pattern depending on the relative magnitude of $B_{\nu'}$ and $B_{\nu''}$.

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Case-I

Let us first consider the case where $B_{v'} = B_{v''} = B_v$

In this case, equation-32.9 reduces to

$$\bar{\nu}_{v',v''}(m) = \bar{\nu}(v',v'') + 2B_v m \dots\dots\dots(32.13)$$

So the separation between the two transitions will be $2B_v$ and the transition pattern will look as shown in figure-32.2.

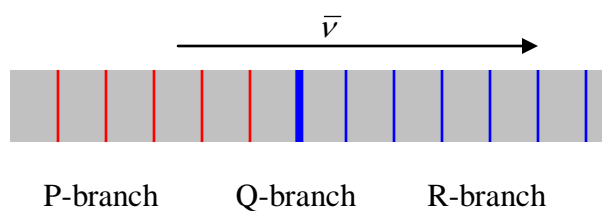


Figure -32.2

If we see this kind of pattern it means that the equilibrium internuclear distances for the upper state and the lower electronic state are same. The diatomic molecule does not change the molecular conformation going from lower electronic state to higher electronic state.

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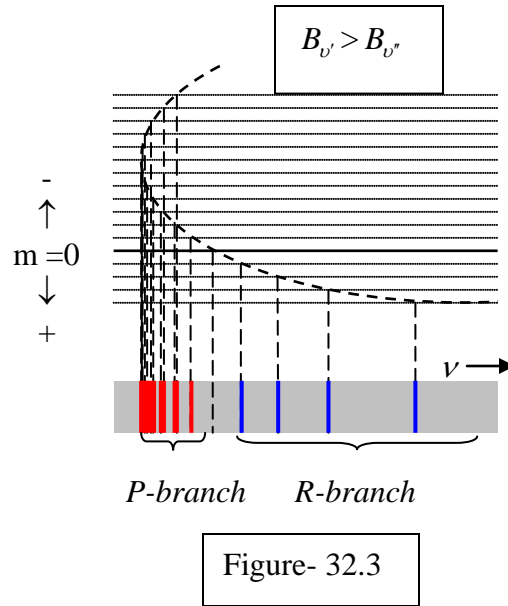
Case-II

Let us first consider the case where $B_{v'} > B_{v''}$

In this case, from equation-32.9

$$\bar{\nu}_{v',v''}(m) = \bar{\nu}(v',v'') + (B_{v'} + B_{v''})m + (B_{v'} - B_{v''})m^2$$

it can be seen that $(B_{v'} - B_{v''})$ is positive quantity. So for m positive i.e *R-branch*, the separation will go on increasing. On the other hand, for m negative, the sign of the second and the third term will be opposite. Hence for *P-branch* the spacing between the lines will decrease and slowly the lines will merge. This forms the band head in the *P-branch* which is the vertex of the parabola as shown in figure-32.3.



If we see this kind of pattern it means that the equilibrium internuclear distances for the upper state is smaller than that of the lower electronic state. The diatomic molecule does change the molecular conformation going from lower electronic state to higher electronic state.

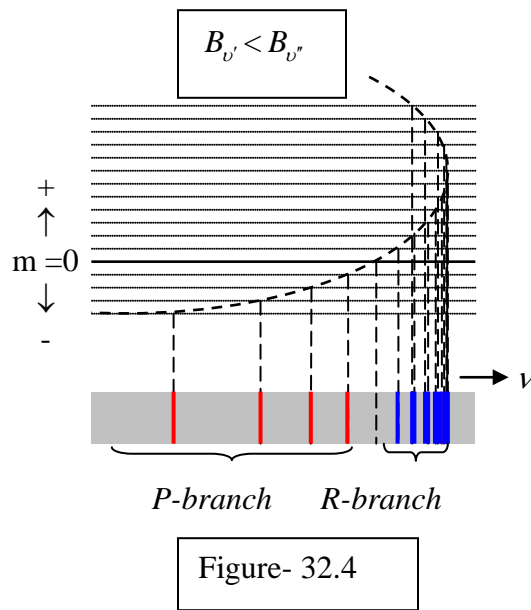
Case-III

Let us first consider the case where $B_{v'} < B_{v''}$

In this case, from equation-32.9

$$\bar{\nu}_{v',v''}(m) = \bar{\nu}(v',v'') + (B_{v'} + B_{v''})m + (B_{v'} - B_{v''})m^2$$

it can be seen that $(B_{v'} - B_{v''})$ is negative quantity. So for m negative i.e *P-branch*, the separation will go on increasing. On the other hand, for m positive, the sign of the second and the third term will be opposite. Hence for *R-branch* the spacing between the lines will decrease and slowly the lines will merge. This forms the band head *R-branch* which is the vertex of the parabola as shown in figure-32.4.



If we see this kind of pattern it means that the equilibrium internuclear distances for the upper state is larger than that of the lower electronic state. The diatomic molecule does change the molecular conformation going from lower electronic state to higher electronic state.

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Now let us discuss the experiment of rotational structure of CN diatomic molecule. This molecule is produced by the two carbon rod discharge as shown in figure-32.5. The emission from this CN molecule is collected by a spectrometer.

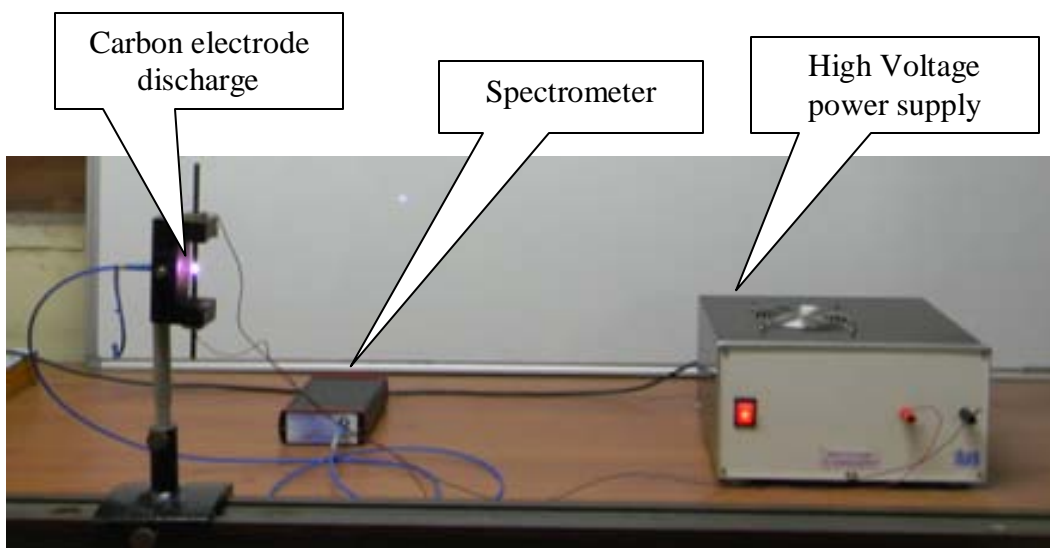


Figure-32.5

The observed spectrum is shown in figure-32.6. The first band is at 388.35nm is $\nu' = 0 \rightarrow \nu'' = 0$ with the rotational structure. The second band is the sequence band $\nu' = 1 \rightarrow \nu'' = 1$. We will

focus only the rotational structure of $\nu' = 0 \rightarrow \nu'' = 0$ band i.e. the *P-branch* and the *R-branch*. The numbers 5, 4, 3, 2, 1 are the running number m .

The selection rule is $\Delta J = \pm 1$. So we were not suppose to see $m = 0$ band. But here this is coming from the higher value of *P-branch*.

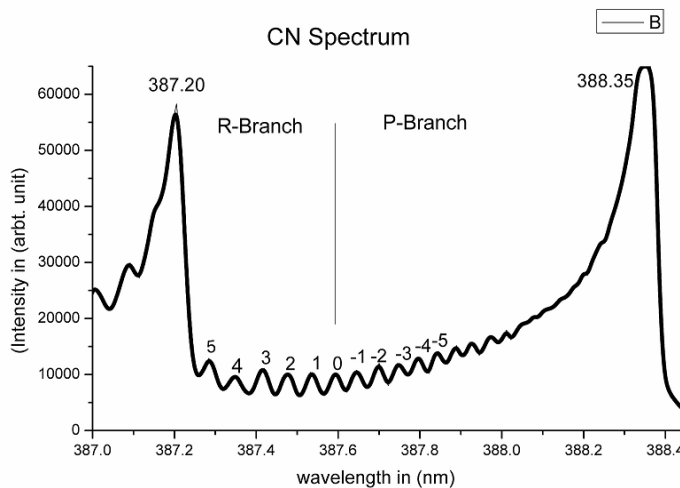


Figure-32.6

Since the band head is in the *P-branch*, so here obviously according to case-II, $B_{v'} > B_v$.

The observed wavelengths are listed in the following table.

m	Observed wavelength (nm)	Observed wavelength (Å)	Observed energy (cm ⁻¹)	$\Delta\bar{\nu}(m)$ (cm ⁻¹)
-9	388.011	3880.11	25772.46	
-8	387.978	3879.78	25774.65	2.19
-7	387.923	3879.23	25778.31	3.65
-6	387.889	3878.89	25780.57	2.25
-5	387.845	3878.45	25783.49	2.92
-4	387.801	3878.01	25786.42	2.92
-3	387.756	3877.56	25789.41	2.99
-2	387.7	3877	25793.13	3.72
-1	387.644	3876.44	25796.86	3.72
0	387.6	3876	25799.79	2.92
1	387.532	3875.32	25804.32	4.52
2	387.476	3874.76	25808.05	3.72937
3	387.42	3874.2	25811.78	3.73
4	387.352	3873.52	25816.31	4.53
5	387.284	3872.84	25820.84	4.53

The first difference between the two observed lines

$$\Delta \bar{\nu}(m) = \bar{\nu}(m+1) - \bar{\nu}(m) = 2B_{\nu'} + 2(B_{\nu'} - B_{\nu''})m \quad \dots\dots\dots(32.14)$$

Since this is linear expression we can evaluate from the plotting of $\Delta \bar{\nu}(m)$ with respect to m .

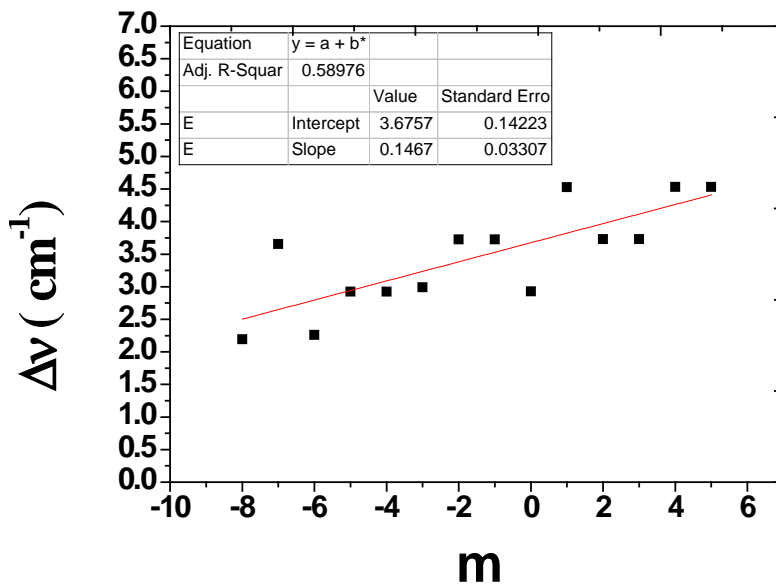


Figure-32.7

From the figure-32.7, it is found that

$$2B_{\nu'} = 3.6757 \text{ cm}^{-1} \text{ and } 2(B_{\nu'} - B_{\nu''}) = 0.1467 \text{ cm}^{-1}$$

$$\text{Thus, } B_{\nu'} = 1.8375 \text{ cm}^{-1} \text{ and } B_{\nu'} - B_{\nu''} = 0.07335 \text{ cm}^{-1} \quad \dots\dots\dots(32.15)$$

$$\text{From these, we calculate } B_{\nu''} = 1.7645 \text{ cm}^{-1} \quad \dots\dots\dots(32.16)$$

$$\text{So } B_{\nu'} + B_{\nu''} = 3.60235 \text{ cm}^{-1} \quad \dots\dots\dots(32.17)$$

Now we calculate the internuclear distances for the upper and lower electronic states.

Since, from equation-32.4

$$B_v = \frac{h}{8\pi^2 \mu R_e^2 c}$$

Substituting the values :

$$h = 6.626 \times 10^{-27} \text{ erg-sec}; \quad c = 3 \times 10^{10} \text{ cm/sec}$$

$$\mu_{CN} = 10.726 \times 10^{-24} \text{ gm}$$

We get

$$R^2 = \frac{28.001}{10.726 B}$$

So, using $B_{v'} = 1.8375 \text{ cm}^{-1}$ the internuclear distance for the upper state is

$$\begin{aligned} R'_e &= \sqrt{\frac{28.001}{10.726 \times 1.8375}} \times 10^{-8} \text{ cm} \\ &= 1.192 \text{ \AA} \end{aligned}$$

And using $B_{v''} = 1.7645 \text{ cm}^{-1}$, we get

$$\begin{aligned} R''_e &= \sqrt{\frac{28.001}{10.726 \times 1.7645}} \times 10^{-8} \text{ cm} \\ &= 1.216 \text{ \AA} \end{aligned}$$

$$\text{From equation-32.10, we get } m_{\text{vertex}} = -\frac{(B_{v'} + B_{v''})}{2(B_{v'} - B_{v''})} = -\frac{3.60235}{2 \times 0.07335} = -24.5$$

Thus the band head is in the p-branch and at $m_{\text{vertex}} = 24$

Since $m = -5$ is on the fitting line on the graph in figure-32.7, we take this to calculate the origin band.

From equation 32.9

$$\bar{\nu}(\nu' = 0, \nu'' = 0) = \bar{\nu}_{v', v''}(-5) - (B_{v'} + B_{v''})(-5) + (B_{v'} - B_{v''})(-5)^2 = 25799.67 \text{ cm}^{-1}$$

This is very close to the observed value 25799.79 cm^{-1} in the table.

The band head calculated from equation-32.11 is 25755.44 cm^{-1} .

Recap

In this lecture, we have understood the rotational structure of the electronic vibrational transition

If the rotational constant does not change going from ground state to excited state then we get the equidistant bands in the rotational structure. It means that the equilibrium internuclear distances for the upper state is larger than that of the lower electronic state.

If we see the band head is in the P-branch, then the equilibrium internuclear distances for the upper state is lower than that of the lower electronic state.

If we see the band head is in the R-branch, then the equilibrium internuclear distances for the upper state is larger than that of the lower electronic state.

In both the cases where the rotational constants change, the diatomic molecule does change the molecular conformation going from lower electronic state to higher electronic state.

The analysis of the rotational structure provides the average internuclear distance or bond length of the diatomic molecule.