Fundamentals of Spectroscopy

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Lecture-32
Ro-vibrational Spectrum-III

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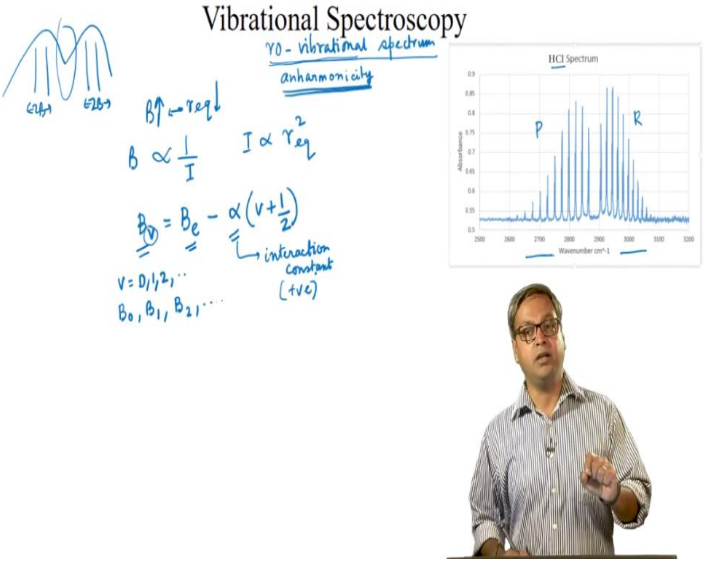

Vibrational Spectroscopy

ro- vibrational spectrum

anharmonicity

$B\uparrow \leftarrow r_{eq}\downarrow$

$B \propto \frac{1}{I}$ $\quad I \propto r_{eq}^2$

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

interaction constant (+ve)

$v = 0, 1, 2, \ldots$

$B_0, B_1, B_2, \ldots$

Hello everyone, welcome to the lecture. In today's lecture, we will continue our discussion on the ro vibrational spectrum of a diatomic vibrating rotor. So, we will talk about the ro vibrational spectrum. So, in our discussion so far in the previous lectures on ro vibrational spectrum, we said any 2 spectral lines in the P or R branches are equally spaced. So, if we have any to spectral line, either in the P branch or in the R branch.

They are equally spaced and the distance between any 2 spectral lines ignoring the gap at this band origin is given by 2B wave numbers. However, if we look into a real ro vibrational experimental spectrum, there is one spectral detail we need to resolve. So, let us look into the spectrum of gaseous HCl. If you notice carefully, we can see that at lower frequencies that is in the P branch, the lines are getting steadily farther and farther apart while at the higher frequencies that is in the R branch.

We can see that the lines are getting closer and closer together. So, we need to find out why the rotational fine structure is becoming crowded as we go to higher and higher frequencies. So, this does not agree with our previous discussion on ro vibrational spectrum. So, how can we resolve this contradiction? This reason behind this is anharmonicity. So, anharmonicity is responsible for this features in the spectral lines as we go to higher frequencies, the average bond length is getting longer.

The potential energy well is steeper at smaller bond lengths, but is shallower at larger bond lengths. This means that the average bond length is getting longer as we go to higher vibrational levels. So, going back to the lectures on rotational spectroscopy, we know that the bond length affects the rotational constant B. So, the rotational constant that is B increases as the average bond length or our equilibrium decreases.

So, this is because, this rotational constant B is inversely proportional to the moment of inertia, that is I and I in turn is proportional to the square of the average bond length. So, the rotational constant is inversely proportional to the square of the bond length. So we can see that the rotational constant for a molecule in v = 1 state is smaller than the rotational constant in the v = 0 state. In the previous analysis that we did in our previous lecture, we assumed that be the rotational constant will always be the same.

Now, let us see, what happens if we do not make that assumption. So, we can see that the rotational constant should be affected by the vibrational quantum number in a sense, we can say that the rotational energy is not independent of the vibrational state has the rotational energy is dependent on the vibrational state. They are coupled to one another. The expression that relates the rotational constant in different vibrational levels is given by B v = B e - alpha times v + half.

So in the left hand side, the subscript v denotes which vibrational level the rotational constant is associated with so, we can have values of 0 1 2 etc. In other words, we can have B 0, B 1, B 2 and so on. This B e on the right hand side is a hypothetical rotational constant that the molecule will have at the bottom of the potential energy well, that is, when there is no vibrational energy and the alpha is a constant, known as the interaction constant.

It is generally a small positive value for a particular molecule so, as alpha is positive, as we go to higher vibrational energy levels, the rotational constant gets smaller. So, let us rewrite the total ro vibrational energy as the sum of the vibrational energy and rotational energy, but this time, we will use the rotational constant that is dependent on the vibrational state.

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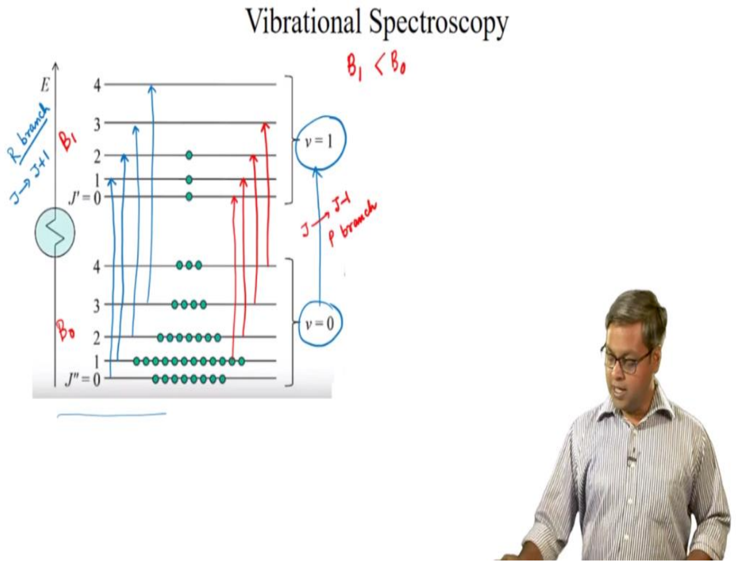

Vibrational Spectroscopy

So, let us look into the ro vibrational energy levels once again. So, these energy levels are associated with the fundamental band. That means, we are talking about a transition from v = 0 to v = 1. So, let us draw the answer branches so for the R branches, J increases / 1 so the transition is from J to J + 1. So this is for the R branch. So we can draw the transitions we can have from v = 0, J = 0 to v = 1, J = 1, from v = 0, J = 1 to v = 1, J = 2, from 2 to 3, and from 3 to 4.

And if we now draw the P branch transitions, where J decreases / 1 that means the transition is from J to J - 1. So this is for the B branch. So let us draw them. So we have from 1 is going to 0, then from v = 0, J = 2 to v = 1, J = 1 from v = 0 J = 3 to v = 1, J = 2 and from 4 to 3, so these are the P branches. So the rotational structure in the v = 0 state is associated with the v 0 rotational constant. But the rotational structure in the v = 1 state is associated with B 1 rotational constant. And as we know, B 1 is slightly smaller than B 0.

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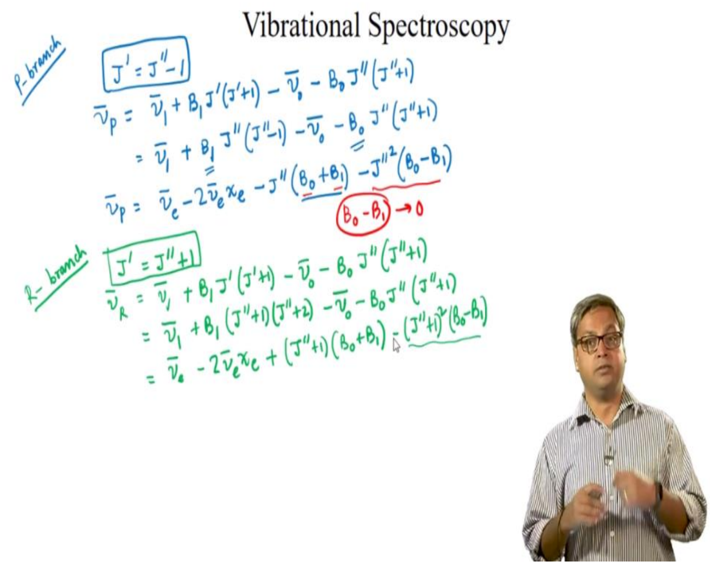

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P-branch

$$\boxed{J' = J'' - 1}$$

$$\bar{\nu}_P = \bar{\nu}_1 + B_1 J'(J'+1) - \bar{\nu}_0 - B_0 J''(J''+1)$$

$$= \bar{\nu}_1 + B_1 J''(J''-1) - \bar{\nu}_0 - B_0 J''(J''+1)$$

$$\bar{\nu}_P = \bar{\nu}_e - 2\bar{\nu}_e x_e - J''(B_0 + B_1) - J''^2 (B_0 - B_1)$$

$$\boxed{B_0 - B_1} \rightarrow 0$$

R-branch

$$\boxed{J' = J'' + 1}$$

$$\bar{\nu}_R = \bar{\nu}_1 + B_1 J'(J'+1) - \bar{\nu}_0 - B_0 J''(J''+1)$$

$$= \bar{\nu}_1 + B_1 (J''+1)(J''+2) - \bar{\nu}_0 - B_0 J''(J''+1)$$

$$= \bar{\nu}_0 - 2\bar{\nu}_e x_e + (J''+1)(B_0 + B_1) - (J''+1)^2 (B_0 - B_1)$$

So, let us again write the spectral line frequency for transition in the P branch. So, for the P branch, we know that J prime = J double prime - 1. So, this is for the P branch. So, we can write nu bar P equals so, the energy for the excited state that is nu bar 1 + B 1 J prime time's J prime + 1. So here, J double prime or the double prime denotes the initial state the single prime that is J prime denotes the final state.

So from here, we have to subtract the energy of the ground state or the initial state that is nu bar 0 - the 0, J double prime because we are talking about the initial state times J double prime + 1. So, because J prime = J double prime - 1, so we can write this as nu bar 1 + B 1, then J double prime time's J double prime - 1. And then I can subtract off nu bar 0, - B 0, J double prime time's J double prime + 1.

So this expression is almost the same as the expression we wrote in the earlier lecture, except for writing B as the rotational constant. Now we are writing B 1 for the rotational constant at B = 1 and B 0 for that at B = 0. So we can rearrange the above expression, as we can write, nu bar P = nu bar, e - 2 nu bar e chi e - J double prime, B 0 + B 1 - J double prime square, B 0 – B 1 this time,

We got this B 0 + B 1 instead of 2B as the rotational constants are different for V = 0 and V = 1. However, this B 0 and B 1 are almost the same. So B 0 + B 1 is almost = 2B, but maybe slightly different. But the major difference is in this last time. So before as B 1 was considered to be = B 0, that means B 0 – B 1 so this was 0. But now, as B 0 is slightly greater than B 1, this term appears this time is going to be small since B 0 is only slightly better than B 1. However, this term makes the energies lower as J double prime increases.

So, the lines in the P branch are farther and farther apart as the rotational level increases. So now let us look into the R branch. So we will now look into the R branch and for the R branch, we know that J prime = J double prime + 1. So, the energy expression for the R branch would look like we can write nu bar R = nu bar 1 + B 1 J prime time's J prime + 1 - nu bar 0 - B 0, J double prime time's J double prime + 1. What in this case, we will use this expression, that is J prime = J double prime + 1.

And if we do that, what we get, we can rewrite this as nu bar 1 + B 1 times J double prime + 1, J double prime + 2 - nu bar 0, - B 0 times J double prime time's J double prime + 1 and if you rearrange this expression, we can further write this as nu bar e - 2, nu bar e chi e, then I have + J double prime + 1, B 0 + B 1 ton, and then I have a J double prime + 1 whole square times B 0 - B 1.

So as B 1 is not = B 0 the last term that means this term does not cancel and the second time is also negative as B 0 - B 1 is positive and we have a negative sign here. So this entire time becomes negative. So, the energy decreases as J double prime increases and does the lines in the R branch are going to get steadily bunched together.

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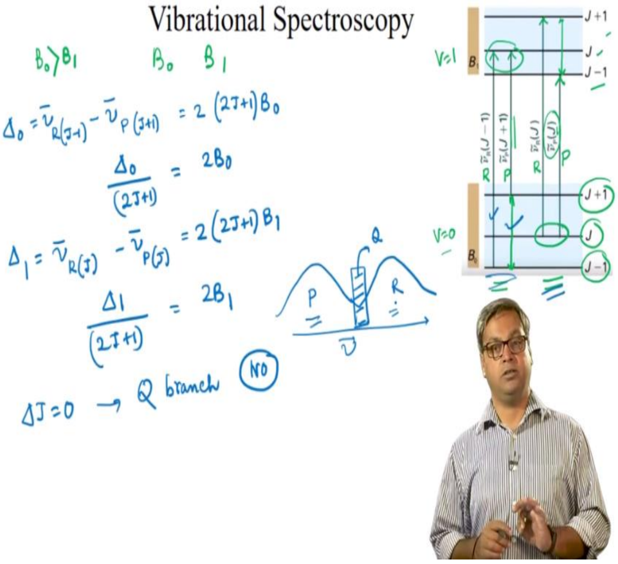

Vibrational Spectroscopy

$B_0 > B_1$ $\quad B_0 \quad B_1$

$\Delta_0 = \bar{\nu}_{R(J-1)} - \bar{\nu}_{P(J+1)} = 2(2J+1)B_0$

$\frac{\Delta_0}{(2J+1)} = 2B_0$

$\Delta_1 = \bar{\nu}_{R(J)} - \bar{\nu}_{P(J)} = 2(2J+1)B_1$

$\frac{\Delta_1}{(2J+1)} = 2B_1$

$\Delta J = 0 \rightarrow Q$ branch $\boxed{NO}$

So thus as B 0 is greater than B 1 the lines in the P branch are going to spread out as we go to higher initial J states. But for the R branch for the same reason that is B 0 greater than B 1, the lines are going to get closer together as we go to larger initial J states. So this is exactly what we saw in the gaseous HCl spectrum. The lines in the P branch are spreading out as we go to higher initial J states and the lines in the R branch are getting closer together as we go to initial or higher initial J states.

So can we find out what B 0 or B 1 are from the spectrum. To determine B 0 and B 1, we need to look closely at the ro vibrational spectrum. So here we see the J - 1, the J and the J + 1 levels for the v = 0 and the v = 1 states. So now let us look into the transitions on the left. So the first or the left most transition, it starts from v = 0 J - 1, and it goes to v = 1 J. And the second transition starts from v = 0 J + 1 level and it ends also in the J level in v = 1.

So, the first 1 is part of R branch, and the second one is part of P branch because in one case, the J increases / 1 in the final state, and in the other case, J decreases / 1 in the final state. So we can notice that both the transitions finish in the same vibration state we can see the difference in energy between these 2 lines depend only on the v = 0 state. So, now, let us focus on these 2 transitions on the right side.

So the first transition starts from J level of = 0 and goes to J + 1 level of = 1. So, as there is an increase of J / + 1 in the final state, this is an R branch. And the second transition on the right or the right most transition starts from the general of = 0 what goes to J - 1 level of v = 1. So as there is a decrease in the value of J in the final state. So this is a part of the P branch. And if you see this nomenclature, so this J in parentheses or bracket tells us the initial state.

Similarly here, the J + 1 for this P type transition tell us about the initial state. So, we can notice for the right side transitions, both of them start in the same initial rotational state, but end in different rotational states. So the energy difference between them only depends on the v = 1 level. So by taking the right combinations of the P and R lines, we can get information about B 0 and B 1.

So, for this left hand side transitions, we can write, let us say delta 0. This is nu bar R J - 1. That means this transition - nu bar P J + 1, that means this transition and what we get is 2 times 2 J + 1 times v 0 or we can write delta 0 / 2 J + 1 = 2B 0. So the expression has the same value for all values of J are similar analysis can be done for the transitions shown on the right side. So, let us denote the difference between these 2 transitions that is nu bar R J - nu bar P J as delta 1.

So, this will give us information about B 1. So this nu bar, R J - nu bar P J gives 2 times 2J + 1 times B 1 or we can write delta 1 divided by 2J + 1 = 2B 1 again the expression will have the same value for all values of J. In all these derivations, we have neglected the centrifugal distortion, but if we consider the centrifugal distortion, these expressions will be slightly different.

So, in diatomic molecules we normally get the P and the R branches. So, there is another branch consists of all the lines for delta J = 0 and this branch is known as the Q branch. So, this branch is allowed for a molecule like nitric oxide or no and appears at the vibrational transition number. In other words, we have the P branch. So, the frequency increases this side and we have the R branch.

So, this is R branch this is the P branch for in this fundamental gap that we talked about earlier in this place we will have the Q branch. So, in HCl or carbon monoxide, there is a gap between the P and R branch where the Q branch should appear. This is because the Q branch is forbidden for HCl or carbon monoxide. So, this brings us to the end of this lecture. We will end by solving one problem.

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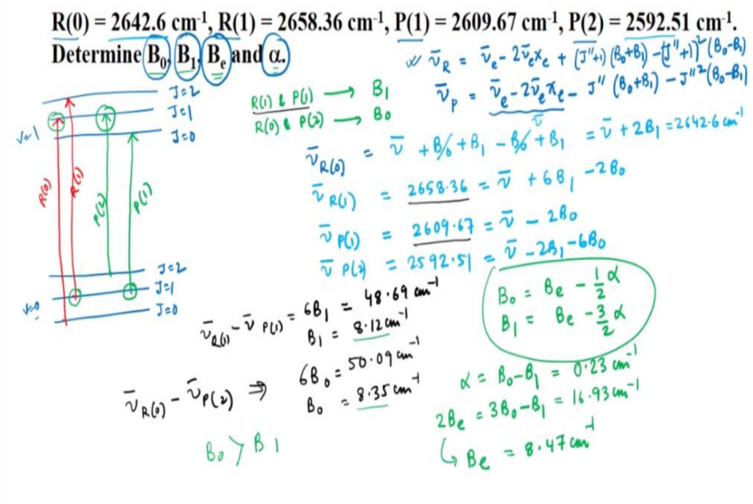

R(0) = 2642.6 cm^{-1}, R(1) = 2658.36 cm^{-1}, P(1) = 2609.67 cm^{-1}, P(2) = 2592.51 cm^{-1}.
Determine B_0, B_1, B_e and α.

$\bar{\nu}_R = \bar{\nu}_e - 2\bar{\nu}_e x_e + (J''+1)(B_0+B_1) - (J''+1)^2(B_0-B_1)$

$\bar{\nu}_P = \underbrace{\bar{\nu}_e - 2\bar{\nu}_e x_e}_{\bar{\nu}} - J''(B_0+B_1) - J''^2(B_0-B_1)$

R(1) & P(1) ⟶ B_1
R(0) & P(2) ⟶ B_0

$\bar{\nu}_{R(0)} = \bar{\nu} + \cancel{B_0} + B_1 - \cancel{B_0} + B_1 = \bar{\nu} + 2B_1 = 2642.6\ cm^{-1}$

$\bar{\nu}_{R(1)} = 2658.36 = \bar{\nu} + 6B_1 - 2B_0$

$\bar{\nu}_{P(1)} = 2609.67 = \bar{\nu} - 2B_0$

$\bar{\nu}_{P(2)} = 2592.51 = \bar{\nu} - 2B_1 - 6B_0$

$\bar{\nu}_{R(1)} - \bar{\nu}_{P(1)} = 6B_1 = 48.69\ cm^{-1}$

$B_1 = 8.12\ cm^{-1}$

$\bar{\nu}_{R(0)} - \bar{\nu}_{P(2)} \Rightarrow 6B_0 = 50.09\ cm^{-1}$

$B_0 = 8.35\ cm^{-1}$

$B_0 > B_1$

$$\boxed{\begin{aligned} B_0 &= B_e - \tfrac{1}{2}\alpha \\ B_1 &= B_e - \tfrac{3}{2}\alpha \end{aligned}}$$

$\alpha = B_0 - B_1 = 0.23\ cm^{-1}$

$2B_e = 3B_0 - B_1 = 16.93\ cm^{-1}$

$\hookrightarrow B_e = 8.47\ cm^{-1}$

So, we have a problem here so, the frequencies for R 0, R 1, P 1 and P 2 are given. And in this problem we have been asked to determine B 0. So this is the rotational constant associated with v = 0 level B 1, B e and alpha. So to understand properly, what are these R 0 R 1 P 1 and P 2, let us draw the energy levels. So, let us say this is v = 0, this is J = 0, J = 1, J = 2. And these energy levels are for v = 1.

So, we have J = 0, J = 1, J = 2 so now, let us draw the first transition, that is R 0. So R 0 starts from J = 0 v = 0 and ends at J = 1 v = 1. So this is my R 0. Now R 1 stars at J = 1, V = 0 and ends at J = 2 v = 1. So this is my R 1. Similarly, if we try to draw P 1, it starts from J = 1 v = 0, ends at J = 0 v = 1. So this is my P 1. And also P 2 starts from J = 2 v = 0 and ends at J = 1 v = 1. So this is my P 2.

So, we can see that R 1 and P 1 starts from J = 1 level of v = 0. So, as we have discussed in this lecture, a combination of R 1 and P 1 should give us information about v 1. Similarly, R 0 and P 2 the kind of end or the final state is a same level that is J = 1, v = 1. So, R 0 and P 2, a combination of these 2 transitions will give us information on B 0. So, let us write the general expressions, that is nu bar R = nu bar e - 2 nu bar e chi e + J double prime + 1, these 0 + B 1 - J double prime + 1 square B 0 – B 1.

And for the P branch transitions we can write nu bar P = nu bar e - 2 nu bar e chi e, then we have - J double prime, B 0 + B 1 - J double prime square B 0 – B 1. So let us try to find out what is the nu bar R 0. So we have to put J double prime = 0 in the expression of nu bar R. And if we do that, what we get, so let us write nu bar e - this 2 nu bar chi e as nu bar. So we can write this as nu bar + B 0 + B 1 - B 0 + B 1. So the B 0 B 0 cancels what we get this as nu bar + 2B 1 and R 0 is given us 2642.6. So this is 2642.6 wave numbers.

So, similarly, we can write nu bar R 1 that is = 2658.36 this = nu bar + 6B 1 - 2B 0. Similarly, nu bar P 1 is given by 2609.67 and this is nu bar - 2B 0 and nu bar P 2 which is 2592.51 is given by nu bar - 2B 1 - 6B 0. So now, if we combine R 1 and P 1, we can write nu bar R 1 - nu bar P 1, this = 6B 1. And if we do the math for 6B 1, because nu bar R 1 is 2658.36, and nu bar P 1 is 2609.67 so, the 6B 1 = 48.69 wave numbers, and so we can write B 1 = 8.12 wave numbers.

Similarly, if we take nu bar R 0 - nu bar P 2 so what we get from here, we get 6B 0 = 50.09 wave numbers that means B 0 = 8.35 wave numbers. So, we can see from here, these numbers 8.12 and 8.35 as you already know, and it should be that B 0 is greater than B 1. So, now, we have found out B 0 we have found out B 1. So now we need to find out B e and alpha. So, using the expression we discussed in this lecture, we can write B 0 = B e - half alpha and B 1 = B e - 3 / 2 alpha.

So if we solve these 2 equations, what we get is alpha = B 0 - B 1. So this is 0.23 wave numbers. So this is a small positive number. And what we get is 2B e = 3B 0 – B 1. So that is 16.93 wave numbers. So from here we can write B e = 8.47 wave numbers. So this B e as we discussed is the hypothetical rotational constant at the bottom of the potential energy well, and so the value of B e is larger than both B 0 and B 1.