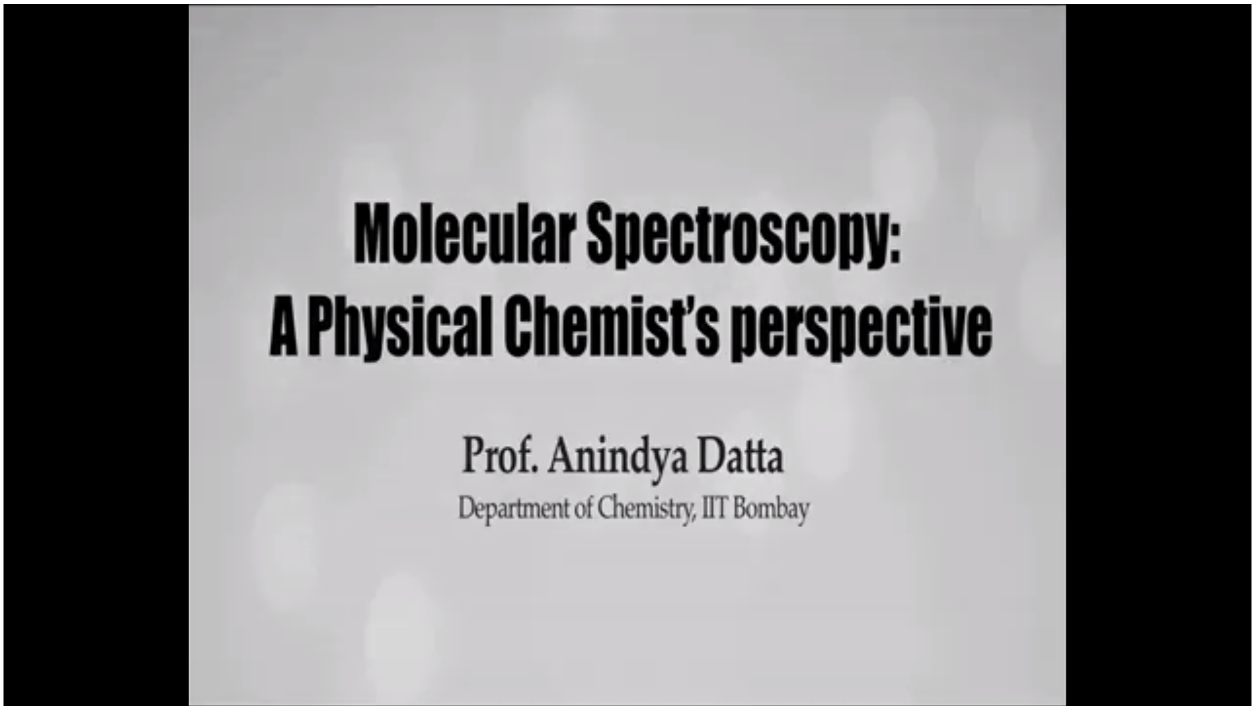
Male Speaker: Knowledge is Supreme



Molecular Spectroscopy:
A Physical Chemist's perspective

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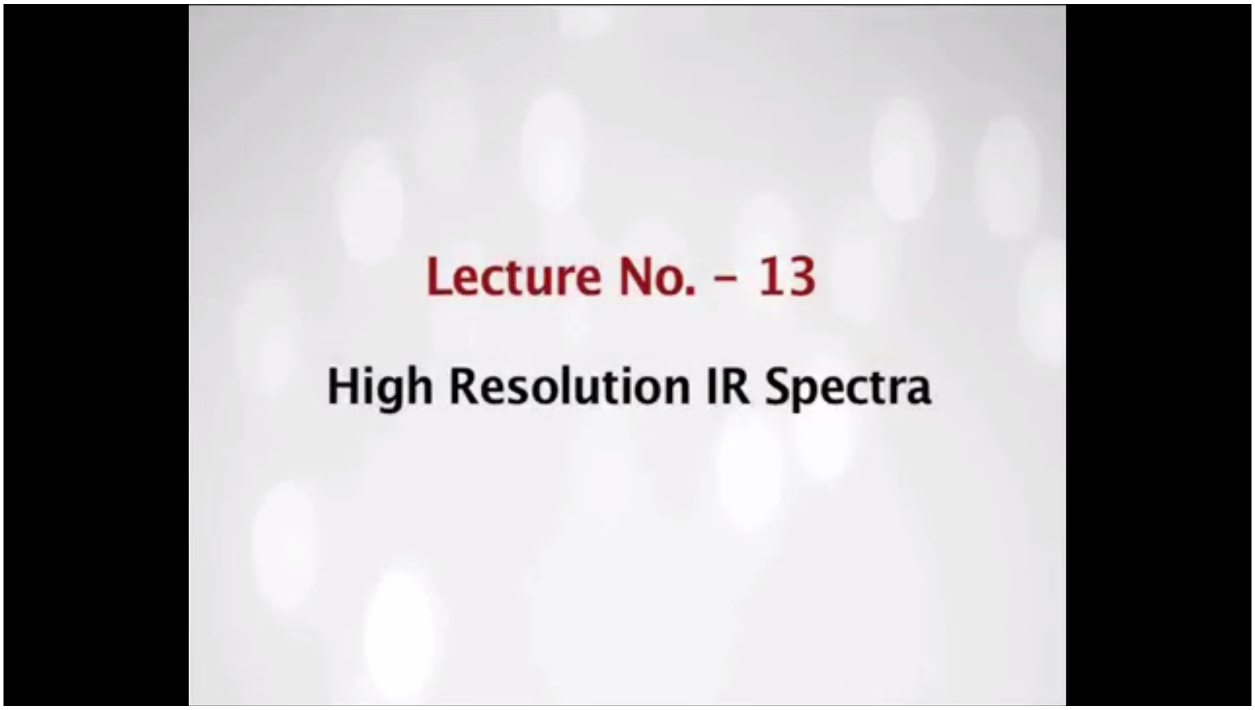


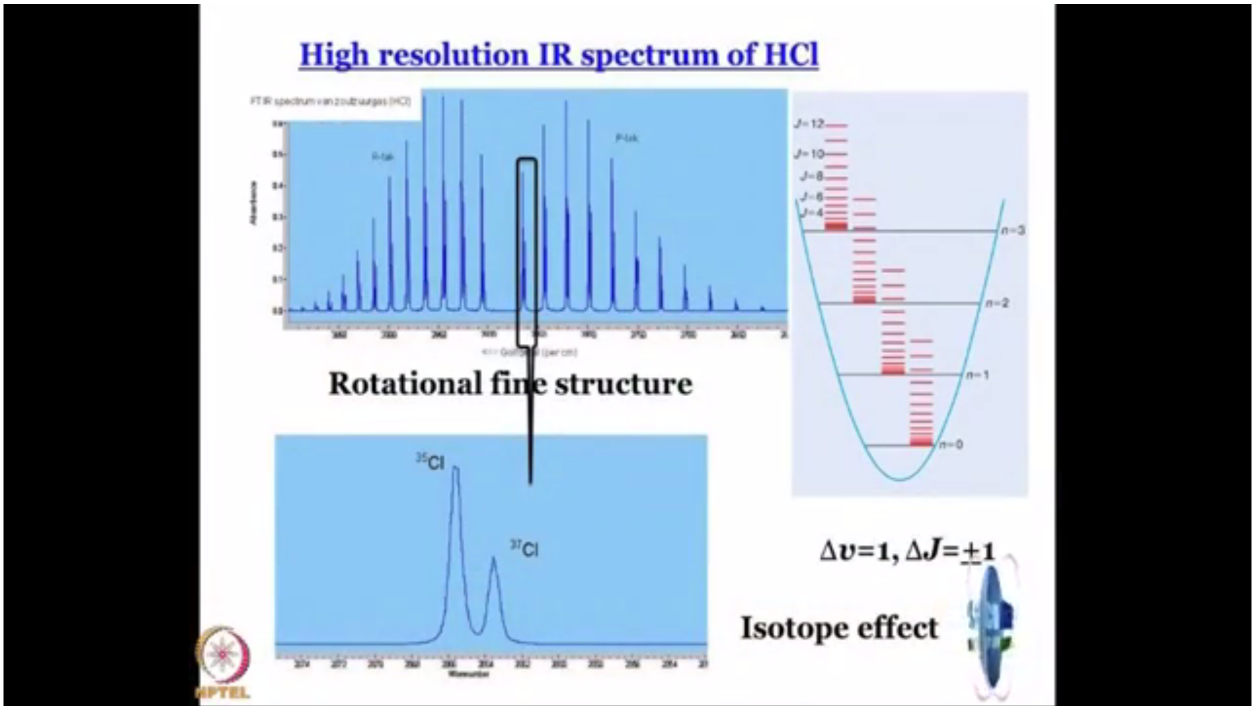
Lecture No. – 13

High Resolution IR Spectra

Prof. Anindya Datta: So, so far, we have talked about rotational spectra, microwave spectra and we've talked about vibrational spectra, that is IR spectra, right. Today, we are going to talk about what is called ro-vibrational spectra. Of course, anybody who has studied Hindi grammar would know that we’re very good at joining up two words and making one word out of two. So this is one such word, not in Hindi, but in English.

Ro-vibrational spectrum, obviously, it means a spectrum that has signatures from vibrational as well as rotational levels. So if you remember, in the last discussion, we had, we had said that for a harmonic oscillator, you expect your spectrum to look something like this, right, a single line, allowing for line broadening, which we are going to study a little more detailed later on, and allowing for some noise in the detector that we talked about very briefly in one of our earlier classes. You might look the spectrum to look something like this.

However, if you have a good enough spectrometer, then the spectrum actually look like this.



High resolution IR spectrum of HCl

Rotational fine structure

$\Delta v=1, \Delta J=\pm 1$

Isotope effect

This here is an experimentally recorded high resolution IR spectrum of HCl. HCl fits our bill, right, it has a permanent dipole moment, so if there’s a vibration, that dipole moment is going to change. If you remember, one condition for observing IR spectrum is that 02:01 at equilibrium position must be equal to zero that is of course satisfied by HCl. And when I say high resolution, how high resolution do I mean? Of course, unless your eyes have really very high resolution, I don expect you to be able to read what is written on the X axis. Let me see if I can. So the X axis reads something like 3000, this is 3000, this is 3050, and the small marks are like 10 cm inverse, separated by 10 cm inverse each, all right. So that is the kind of resolution you need in order to see this kind of a fine structure.

Why do we see this kind of fine structure? We see it because if I zoom in to your harmonic potential energy surface, let us say, I want to talk only about the V=0 and V=1, let us zoom into this part only. I understand that for each of the vibrational levels, the molecule can have as many rotational levels as there can be, right. So V=0 would be associated with, I can call this J’ = 0. What is the smallest value of J’, 0 or 1? Zero, right. Then J’ = 1, J’ = 2 and so on and so forth. So I’ll just -- of course this is a very -- this figure is not to scale. This separation may be about 1000 cm inverse; these separations would typically be about 10 cm inverse or so on.

Similarly, this one, I call this J”=0, J”=1, J”=2 and so on and so forth, right, and as you know, the energy spacing of rotational levels is such that it is not as if only J’=0 value is populated. See between V=0 and V=1 at room temperature for most case, we can say, without worrying too much that V=0 is populated, right, we discussed that earlier. For 1000 cm inverse energy gap, the population of V=1 is 8, if the population of V=0 is 1000. So practically, all molecules are V=0 not so for the J levels, right.

So in fact, as you know, all these J levels could be population, and the population distribution, if I can draw a 90-degree rotated curve would be something like this, right, where these are the different J levels. Remember this, we had discussed in light of Boltzmann distribution, $(2J+1)e^{-\Delta j}$/kt. 1 J max had the maximum value and I think you know the expression or you can work out the expression for that J max value, right. What is it? √kt/2HC - ½, right. So you don’t have to remember this. I will not remember this after maybe a month or so. I am sure.

So there’s a population distribution here. So now when you talk about say an upward transition, that upward transition can begin from any of the J levels, isn’t it? What about this level, is it populated at room temperature? No, because this J level is associated with a higher vibrational level, right. So because it’s associated with a higher vibrational level, there’s no population here. But then here, since all these are populated and it is not J’=0 that is maximum population, there’s a population distribution like this.

So now, you can understand transitions can begin from any of these levels, all right. The question is where do they terminate? Is this some selection rule for this or is there no selection rule, okay? And we’re going to do this in two kinds of scenarios, one in which Born-Oppenheimer approximation holds and the other in which Born-Oppenheimer approximation does not hold, all right.

To start with, we’re going to stick to our selection rules ΔV=1 and ΔJ=1. Of course, if Born-Oppenheimer approximation holds, then I is not very difficult that these selection rules are going to hold as well. What does Born-Oppenheimer approximation says, when you talk about one kind of transition, you do not have to worry about the other kind, right. That is Born-Oppenheimer approximation deconstructed and put in very simple language, okay, which means you can treat the vibrational problems separately and rotational problems separately. From there, this thing kind of follows, but we will derive it, we'll just go by this.

So first situation we say, when born-Oppenheimer approximation is valid. Do you have questions? Okay. So if Born-Oppenheimer approximation holds, what does that mean? That means the vibration does not affect the rotational parameter, right. What is the rotational parameter? B. So no matter whether you work with V=0 or V=1, B is the same, all right. So if that is the case, what is the energy, say, of V=0 and J=J'? It will be sum of the vibrational rotational energies, right. What would that be? If you remember, when I write ϵ, what do I mean, do I mean centimeter inverse or do I mean joule? I mean centimeter inverse. So what will be the expression for vibrational energy B? Nu bar, nu bar vibrational, let us say, multiplied V = ½, right.

Right now, we're working with harmonic oscillator. So for when V=0, it is going to be ½ ṽ and I'll write ṽ vib, but in our previous discussion, you might remember, we found out something interesting about this ṽ vib. What is that? frequency of vibration is equal to -- yeah, frequency of something else. Yes, frequency of radiation, right. So frequency of radiation is equal to frequency of vibration. So if I just wrote ṽ light that would also be valid, okay. Plus, B J'(J'=1).

Let us start with the ΔJ = +1. What would be the range of J' in this case if ΔJ = +1? J' is the level of origin, j" in my notation is level of destination. So if ΔJ = +1, what are the allowed values of J'? This might sound like a trivial question at this point.

Is that a question or is that an answer? Okay, but that might be a right answer to a different question. My question is if for ΔJ = +1, J' of course is the vibrational levels of V=0 and I am working with ΔJ = +1, so what is the range of allowed values of -- or I'll make it simpler. What is the minimum value of J' I can take? Zero, +1. If it was -1, now let me go to the next situation which we'll revisit in a while. For ΔJ = -1, what would be the minimum value of J' that I can use? Then it would be 1, right, because if it starts from 0, there's -1 level here, okay, but we'll come to that in a moment. Let's get done with this.

So range of J, let us not forget, J'=0, 1, 2 so on and so forth, okay. So far so good. Then what is ϵ1, J"? That would be ½ ṽ vib + B J" (J" + 1). But then I know already that ΔJ = +1, so J" can be replaced by J" + 1, isn't it? Yes, oh sorry, sorry, 3/2, my mistake. That's right, V = ½, right I forgot the V part. I was just so engrossed with J that I did not think about V. You're right. It is 3/2 ṽ vib + B (J”) (J” + 1), okay. Can I write, instead of J”, can I write J’ + 1? So this thing becomes, (J’+1) (J’+2). Is that right? Is there a question? No questions, sure, simple.

So in that case, what is your -- how do I write it? Let me write it as ṽ, right, ṽ for ΔJ = +1, what is that going to be? ϵ 1 J” - ϵ 0 J’, what does that turn out to be? That will be ṽ vib + B, I can take (J’+1) common and then I am left with (J’+2) - J’, that will be 2. So ṽ for ΔJ = +1 turns out to be ṽ of vibration + 2B (J’+1), clear, simple. Are we ready to go to the next one, ΔJ = -1? So I wrote Δj = ±1 earlier anyway. So, so far, we have discussed ΔJ = +1, now we’ll talk about ΔJ = -1.

Now if ΔJ = -1, what is the range of J’ you said? 1, 2, 3 so on and so forth, but then if I use that, I am going to get an expression that will look different from this. Also, I want to maintain the same range. So what I’ll do is, I’ll not work with J’; I’ll rather work with J”. Is it okay if I write J” = 0, 1, 2, so on and so forth? Okay. The minimum value of J’ is 1, but then from there, you can have a transition from here to J” = 0. So if I work with J” in this case instead of J’, then I can keep the same range as I did in the previous statement. That is why I work with J”. Are we clear 14:39, okay.

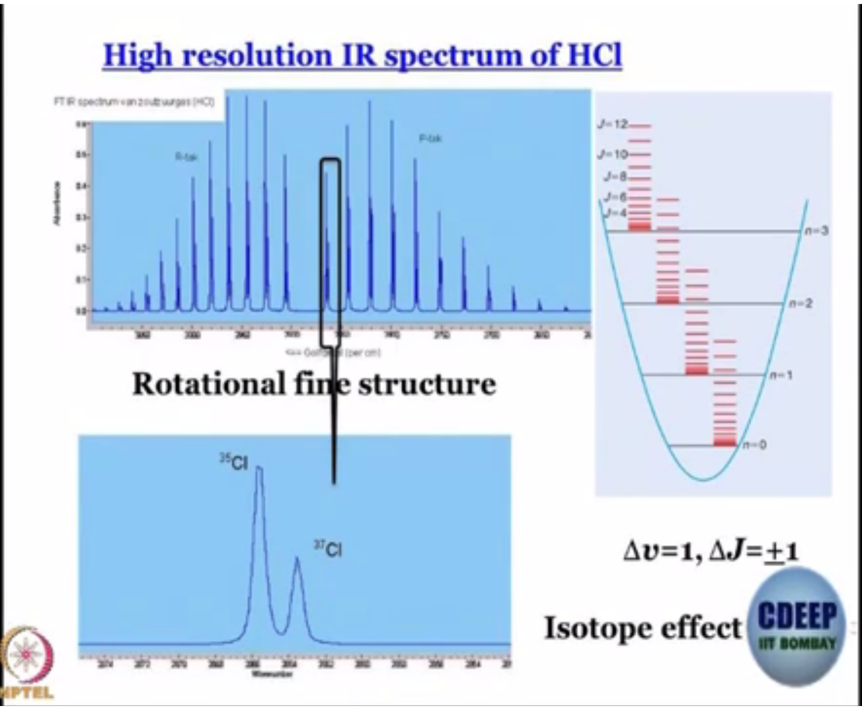
So now how do I write it? So we’re talking about this J’ -> J’-1 or in other words (J”+1) -> to J” kind of transition, isn’t it? Okay. So I am going to write this in terms of this, J’ now is J”-1. So -- sorry J”+1. How do I write it down? I can write it as J”+1 multiplied by, this become J”. Is that right? What about this? This becomes the simpler V J” (J” + 1), okay. What then is ṽ or ΔJ = -1? I think I’ve been able to confuse some of you at least. Yes, which should be +2? You are right, you’re right, J” + 2. What am I doing? This is okay; this is (J” + 2), you’re right.

Is this expression correct, or when I subtract one from the other what do I get? I get similar something. Here the only difference is, this becomes J”, this become minus and the range remains the same as what the range was for J’ zero onwards, okay. So I can write a general expression for ṽ to ṽ vib ±, to be into J + 1 where J = 0, 1, 2, so on and so forth. Is that correct? Is there a question? Okay.

So minimum value of J is 0, so when you put J = 0 here, where level of origin or level of destination is equal to 0, what do you get? You get ṽ vib ± 2B. What does that tell us? That tells us that there’ll no transition at ṽ vib. The wave number where you expect to see a transition, there will be none. Rather there will be transitions on the two sides, okay. So that is what you see there.

Let us say, this is your ṽ vib, there’ll be nothing there. Where will be the first transition on the higher energy side? J = 1. So J = 1 means what? Sorry, J =

0, J = 0 is +2. And what about the other side, lower energy side? -2B, right. So the first line is going to occur at +2B and here it will be -2B. So this separation is going to be 4B, all right. Where will the next line occur? 2B on that side -- no. So basically, this is 0, this is 2B. This is will occur at 4B, so 4B - 2B is 2B, right. So what you get essentially is you get two wings, each of which is exactly like the rotational spectrum of the molecule, one on the higher side, one on the lower side, of the frequency which represents the energy difference between B = 0 and B = 1, zero vibrational levels, okay. That is what you see experimented. Are we clear so far? Okay.



High resolution IR spectrum of HCl

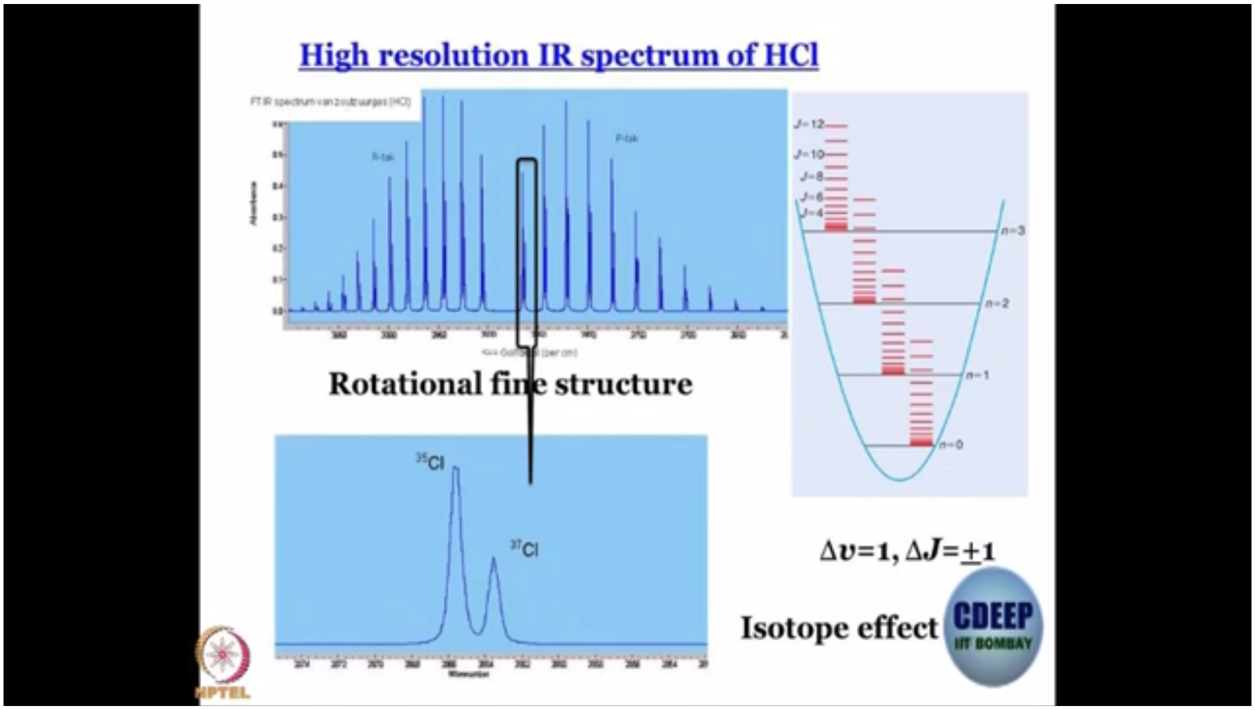
Rotational fine structure

$\Delta v=1, \Delta J=\pm 1$

Isotope effect

What do you expect to see? You expect to see equal space lines on both sides. Whether you see that or not, we'll come to that in a little while, but before that, I'd like to draw your attention to one thing. If you look at this closely. If you zoom -- this we have discussed. If you zoom into one of these lines, then what do you. Can you see from here that it doesn't look like one line, right? In fact, if you have a good enough resolution, this is what you'll see. Each line -- remember, this is HCl and we've discussed this already. Yeah, exactly, it's an effect of isotope, okay.

So you have two lines, one for Cl35 and one for Cl37. So if you have a good resolution in your IR spectrum, then not only you can tell what the bond strength is, you can also say what is the bond length and you can also get an idea of isotopic abundance, okay. Of course, we're saved by the fact that in case of hydrogen, deuterium, tritium, et cetera don't have so much of abundance. If they were also almost equally abundant, then what would happen? Each line would have had a more complicated structure, okay. It would not have been a doublet, it would have been multiplet, each line would have a multiplet consisting of smaller lines, but then you could get more information out of it as well, okay. Is there a question so far? No.



High resolution IR spectrum of HCl

Rotational fine structure

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Isotope effect

Then I want you to look at the spectrum a little more closely. What is the expectation? The expectation is that on both sides -- oh by the way, before I forget, the lower energy side, this is the lower energy side, this is called the P branch and the higher energy side, we call it not, Q, but R branch. If you run a line right here, then you'd call that a Q branch, okay. Please remember, this P is lower energy and R is higher energy, then what is expected if you don't have this rotation fine structure. Okay.

Now from the simplistic that we have developed so far, we expect that in this P branch and Q branch light should be equally spaced, right. Now I ask you to look at this a little more closely. Look at these and look at these. Are the spacings really equal? No, right, they are not equal. So the question is, why are they not. They are not equal because so far, we've worked under the ambit of Born-Oppenheimer approximation. We have assumed that Born-Oppenheimer approximation holds. That is not necessarily the case. It is possible that there is a breakdown of Born-Oppenheimer approximation and vibrations and rotations actually talk to each other, okay.

Then let's see what happens when vibrations and rotations talk to each other. Let us see what happens when Born-Oppenheimer approximation breaks down. So Born-Oppenheimer approximation breaks down. B is not going to the same for the two vibrational levels. So let us define like this, B =

B0 for v = 0, B1 for v=1, okay. And let us start with once again, ΔJ = +1. I’ll have to reset all this, B0 J’(J’ = 1). This one is, B J”(J” + 1), and we’re talking about ΔJ = +1, so the range of J” is 0, 1, 2 so on and so forth, all right. This I have to write B1.

Please remember this expression. When we considered that Born-Oppenheimer holds, we had something like ṽ vib ± 2B (J + 1), okay. So what is ṽ, this minus this, that will give you once again ṽ vib, plus this time we have a little more complicated scenario, right. I have B1 as well as B0, oaky. And of course, whoever has appeared in competitive exams involving math is master of manipulations, I mean mathematical manipulations, right. So it’s not very difficult for you to try and play around with this result and right it in a form that looks nice. And one of the techniques that you learn while doing mathematical manipulation is that we should try and collect all the terms in the same power of something, okay.

Here, you’re going to have, what, J'^2 J and J’ and so on and so forth, let us try and collect them, collect the same powers and let’s see what kind of results we get, but before that, once again, let us try the second on in terms of J’. Here again, J’ goes from 0 onwards, so this again becomes J’ + 1 (J’ + 2). This is correct. So let us first collect the terms in, say, J'^2. What do I have? B1 - B0 (J'^2), is that right? And now our remaining codes is kind of defined. We have try and find terms in B1 - B0, okay.

Now if I look at the terms in J’. What do I have from here? You have B0 J’, right. From here, what do you have? 3B1 J’, okay. So now the thing is since I have J'^2, X^2, whenever we have X^2, the first square that comes to our mind is $X^2 + 2XY = Y^2$, right. So let us see, if we can write it, since we already have 3AB term, let us write it as -- I am using XY and AB reversible, that is not good. Since we already have this XY term, let us see if we can write it in as, say, 2XY + XY, okay. So this is basically what, 3B1 J’, I’ll write it as 2 + 2J’ B1 + J’ B1. I hope nobody has an issue with that, okay. Now what else do I have? I have B0 J’. So I’ll write it like this. 2J’ (B1 - B0). Then what do I have to write here, J’ B1 + B0, right. What, is that so difficult?

What do I have here? I have B0 J’, okay. What do I have here? 2J’ - 2J’ B0 -- I am making a mistake somewhere, yeah. It is okay, right? Then what am I left with now? What is it that I have not written? 2B1, right. I’ll write it like this. + B1, +B1; here I’ll write -B0, here I’ll write +B0, done. What do I get then? I get ṽ vib + -- what was the expression I had for ΔJ = +1 earlier when Born-Oppenheimer approximation held? What was the expression there? Ṽ vib + 2B (J’ + 1). So what I can do is I can write it like this, B1 + B0 (J’ + 1) and + (J’ + 1)^2 multiplied by -- I have written it in the least changed manner, anyway -- +B1 - B0 (J’ + 1)^2. Does it make sense? Maybe I’ll write it here, ṽ = ṽ vib + (B1 + B0) (J’ + 1) + (b1 - B0) (J’ + 1)^2. What is the range of J’? Zero onwards, right. So this is the expression I have.

Now do we see -- is this expression, does it have any resemblance with the expression we had when Born-Oppenheimer approximation held or not? When Born-Oppenheimer approximation held, what was it? $\tilde{V}$ vib + 2B (J' + 1). This third term was not there. Now see, Born-Oppenheimer approximation holding means what? B1 should be equal to B0, then that would become 2B anyway. Now since Born-Oppenheimer approximation doesn't hold, that 2B has become B1 + B0 and we have another terms B1 - B0. Now do you expect B1 and B0 to be very, very different from each other or do you expect them to be close to each other? Not equal but close to each other, right, close to each other, that's what we expect.

So in that case, this term is actually small, isn't it? When does it become important? It becomes important for large values of J. Did I say all that a bit too quickly? What I am trying to say is this. B1 and B0 you told me are close to each other; B1 is B0 + some ΔB, okay. So this first term, if we consider B1 = B0, the first terms gives me exactly the same expression as what I would get if Born-Oppenheimer approximation held.

This one is the correction term. Well, there's already some correction here, instead of 2B, I've written B1 + B0, but this third term is really the correction term that comes in, in the energy and that is (B1 - B0) $(J' + 1)^2$, (B1 - B0) as you told me is small. So this term, well, not second, the third term that comes in as a correction, that is going to be important only for large values of J, okay.

If you look at the spectrum, in which part of the spectra, do you have contributions from large values of J, in the middle, on left hand side or right hand side? Yeah, left hand side means -- your left hand means this one, right. What about the right hand side? That also has contribution for high values of J. So if you look at the high end of the spectrum, high energy end of the spectrum and the low energy end of the spectrum, that is where you expect to see is deviation from what is expected when Born-Oppenheimer approximation holds. If you look at the center, say, look at these two lines and look at these two, they're more or less the same, right, the spacing is more or less the same. That is because J values involved are small, and since B1 - B0 is small anyway, you do not see so much of effect of Born-Oppenheimer breakdown in these features. In the high energy end and the low energy end, that is where the effect becomes prominent and you see that the lines are definitely equally spaces anymore, all right, understood. So this is what you see when Born-Oppenheimer breaks down. Is there any questions so far?

Yes. How can we determine how many rotational levels should be there for a vibrational level? In principle, there are infinite, but then, what matters is how many rotational levels have some sizeable population. That is determined by that (2J + 1) e-$^{\Delta e}$/Kt. If you remember, 2J + 1 of course is a line and the other one is an exponential decay. So wherever this becomes almost 0, it doesn't matter that 2J + 1 takes a large value, the product is still at 0, okay. So that will depend on B. What is the value of B? If the value of B is small, then what will happen, many higher levels will be populated. If value of B is large, then higher levels shall not be populated to that extent, this follow off of the exponential part is going to be very fast. So it depends what your B value is.

Good question. Any other question? All right, of course, we have done only half of the problem. I ask you to do the remaining half, and since today I have already made I think two or three mistakes in algebra, I'll ask you to do it yourself. What I am asking you to do, please work out the expression for ΔJ + -1. Same strategy, ΔJ = -1, so now you work not with J' but with J", because then you can keep the range the same. Work it out, you will see that this is what happens. Okay, the correction term does not change, it is still plus, it's not minus, okay.

Please work it out yourself, you'll see that the minus will come here like what it did in the earlier case, but in this (B1 - B0) term, it will still remain plus. That I'll leave to you as homework, and if you want to -- this is worked out in Banwell's book. Not in as many steps, but you can at least get the final results, okay. So you can study this part from Banwell's book.

Any other questions so far? If not, we conclude our discussion on ro-vibrational spectrum.