INDIAN INSTITUTE OF TECHNOLOGY BOMBAY

IIT BOMBAY

NATIONAL PROGRAMME ON TECHNOLOGY ENHANCED LEARNING (NPTEL)

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MOLECULAR SPECTROSCOPY: A PHYSICAL CHEMIST'S PERSPECTIVE

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Lecture No. – 49
Rotational Fine Structure

So let us continue with the discussion we had yesterday, what we have been talking about is electronic spectroscopy. When we talk about transitions like what we did in rovibrational transitions, you are going to have fine structure because of sublevels that are there, every electronic level is associated with vibrational and rotational sublevels, so when a transition takes place, it's not as if it takes place from level.

So when you talk about vibrational levels only then the saving grace is that the, or level of origin can only be V = 0, that is what it gives us a vibrational structure, but then when you consider the involvement of rotational levels as well, the level of origin is not necessarily J = 0, right, as you know at room temperature higher J levels are populated, in fact one of the higher J levels has maximum population and you know the expression for it J max, okay, so all these rotational levels are going to contribute and the selection rule as we discussed yesterday is delta J = +-1 for all transitions except for singlet sigma to singlet sigma transition, will learn today hopefully what singlet sigma is, and for singlet sigma to singlet sigma transitions the selection rules are delta J = 0 and +-1, with the condition that J =0 to JI = 0 that kind of transition is not allowed, okay, how we get these selection rules maybe we'll do it later or I'll ask you to read it up, it's not very difficult.

But let us today see what kind of rotational fine structure we get, it's a little different from what we get for rovibrational transition, it is actually more complicated, more complex, so let us see what happens when you have, no but even before that, what is the energy we said? Energy of, well delta epsilon energy for transition between two levels that of course will be if you write it in centimeter inverse the wave number of this spectra line that is going to be nu bar EV, nu bar EV is the line that we talk about for transition from one electronic level to another electronic level

between V = 0 and some V dash, right, so what we have talked about so far is this kind of spectrum, right. This can be 0-0 dash, 0-1 dash, 0-2 dash and so on and so forth, okay.
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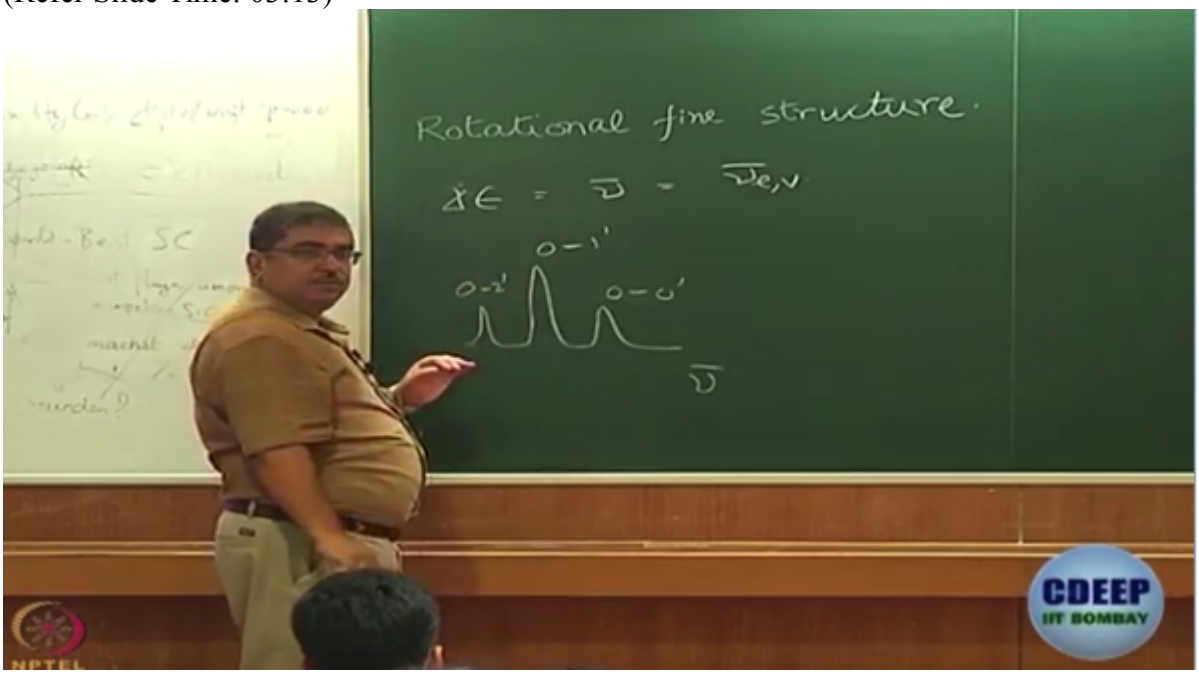

Now what we are trying to do is take one of these and see whether this can have multiple structure, actually it will have, this is the rotational fine structure, okay, this is what we want to study, right.
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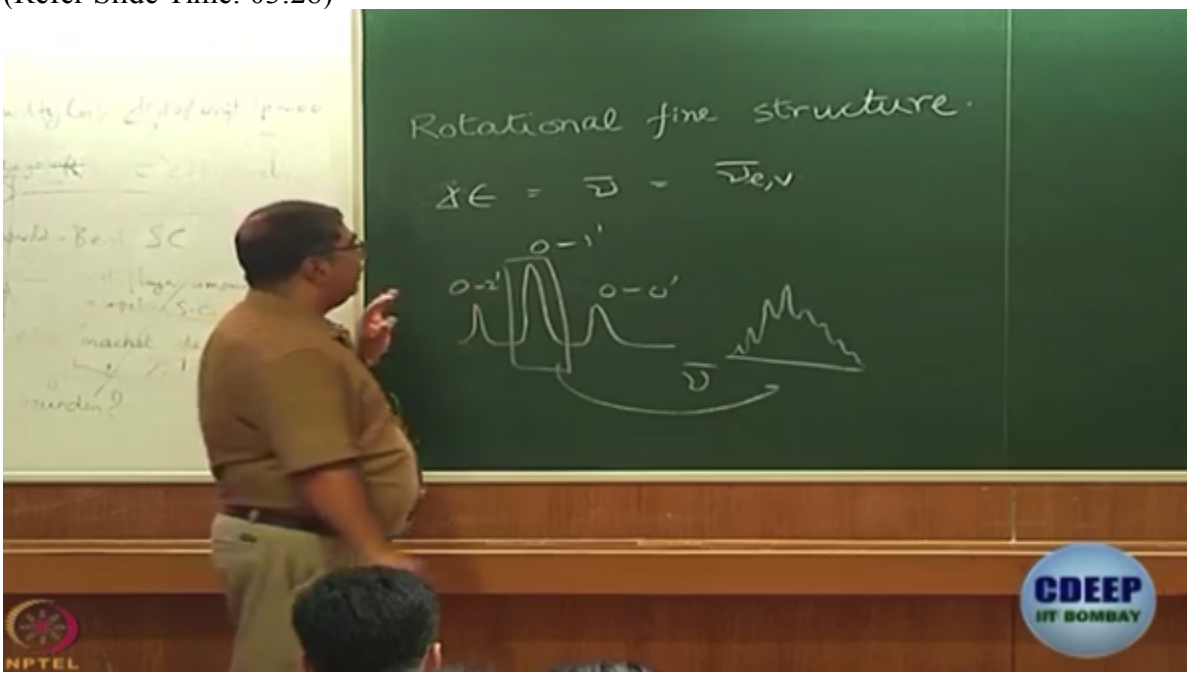

So what will it be? In addition to this there will be a term because of the rotational levels and that is going to be delta BJ(J+1), and what we discussed yesterday is that the reason why we write B inside delta,
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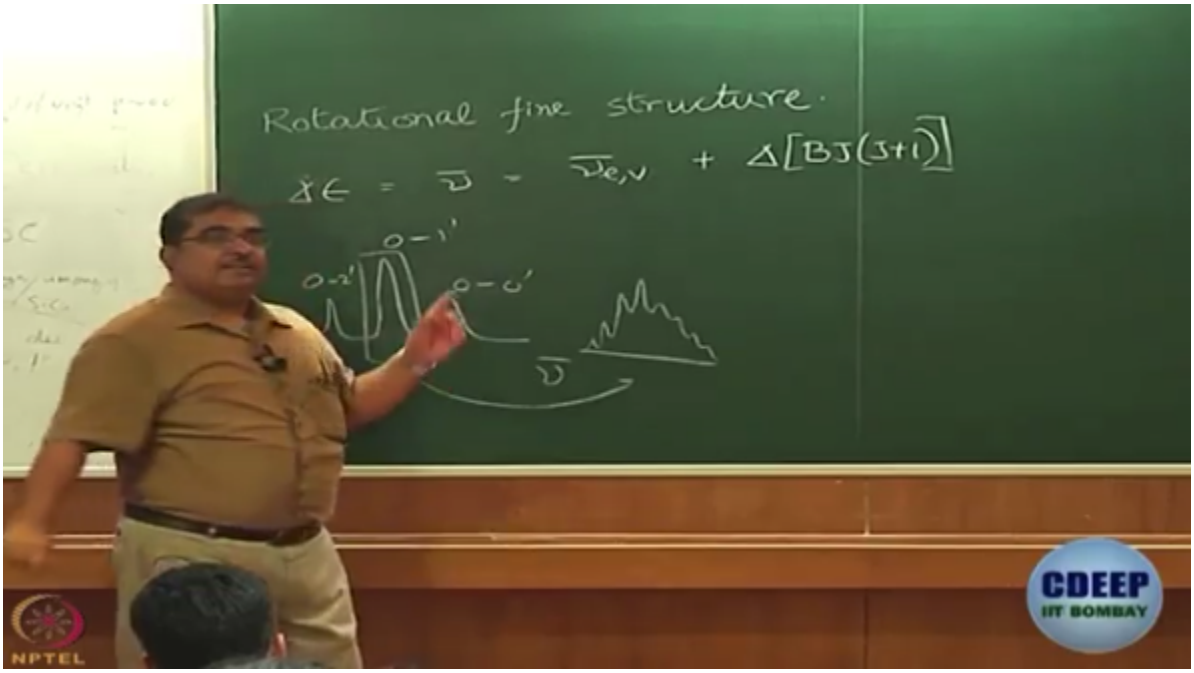

B inside the bracket after delta is that rotational constants B are not usually the same, can be same, but not necessarily the same between two different electronic levels, because as we discussed the equilibrium bond length did not necessarily be the same in the excited state as what it is in the electronic ground state, so if the equilibrium bond length is different of course you know that B is proportional to 1/R0 square, so B is also going to change, and what we discussed was if the transition is such that it weakens bond then R0 square is going to become bigger so B is going to become smaller in the excited state, however there can be a transition where the equilibrium bond length become shorter also then it will be the other one, but what we do now is that we expand this, and we expand this this way nu bar EV + we can write B dashed, J dashed(J dash + 1) where dash indicates the excited state, excited electronic level – I can just write B into J(J+1) or maybe I'll write B double dash into J double dash(J double dash + 1) so what I mean is this double dash indicates the level of origin, lower electronic state.

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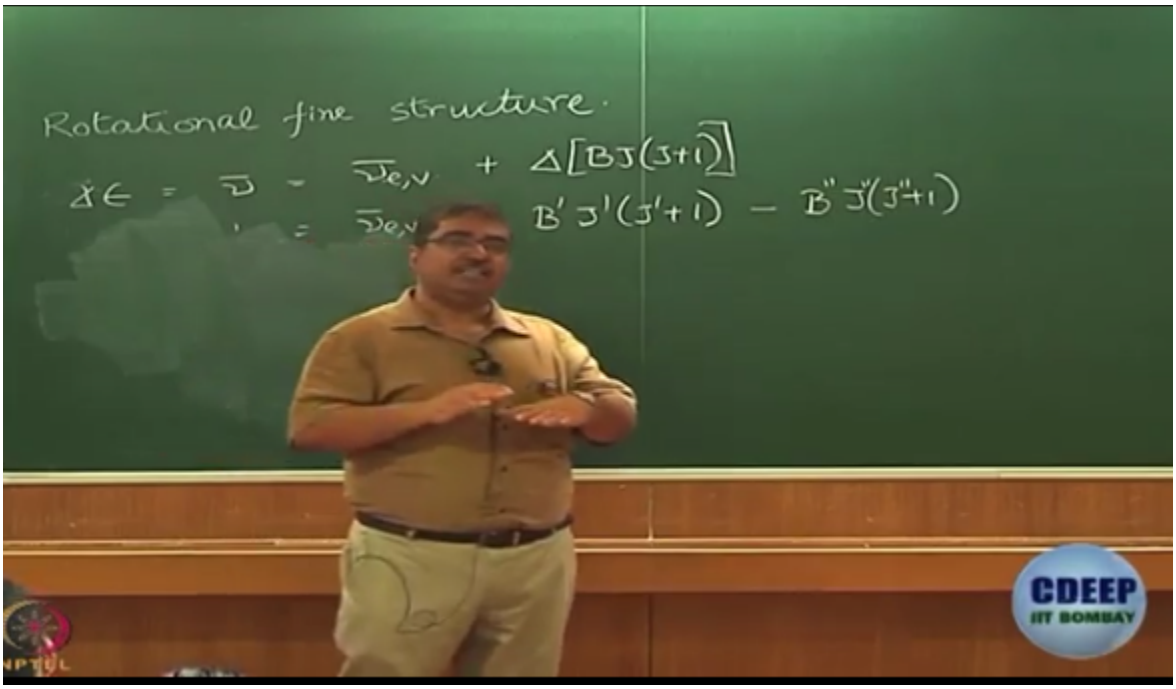

J dashed means the destination rotational levels those associated with the excited electronic state, so let us do it for three different cases, first when delta J = 0.

For delta J = 0 what will it be? Nu bar will be nu bar EV + B dashed – B double dashed, and I can simply write your J(J+1) because J dashed = J double dash anyway in this case, right. Now when delta J = 0 what is the range of J's?

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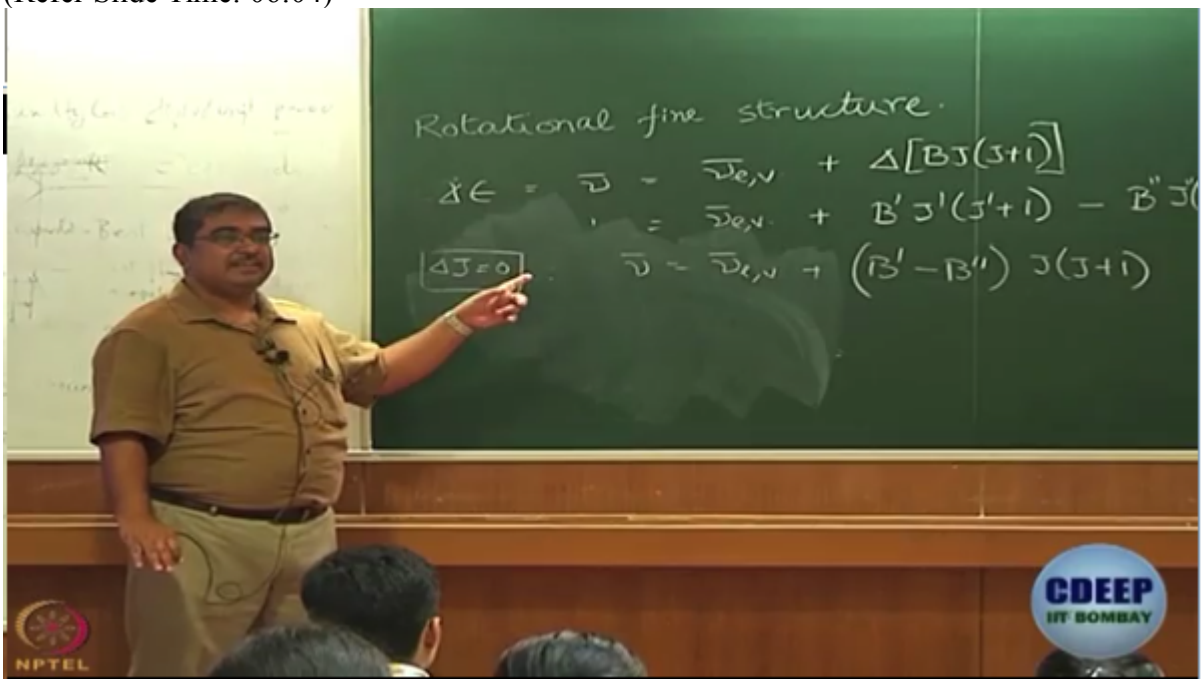

What are the possible values of J? -1, then 0 is not there, this is one thing we have to remember, and if you remember we said that J = 0 to J = transition is not allowed, okay, so range of J is 1, 2, 3 and so on and so forth, so what kind of an equation is this? Yeah, so what shape is it? Parabola

right, this is the equation of a parabola, right, full parabola, half parabola? Half, because you cannot have negative values of J, and not only that the parabola doesn't go all the way up to 0, okay,
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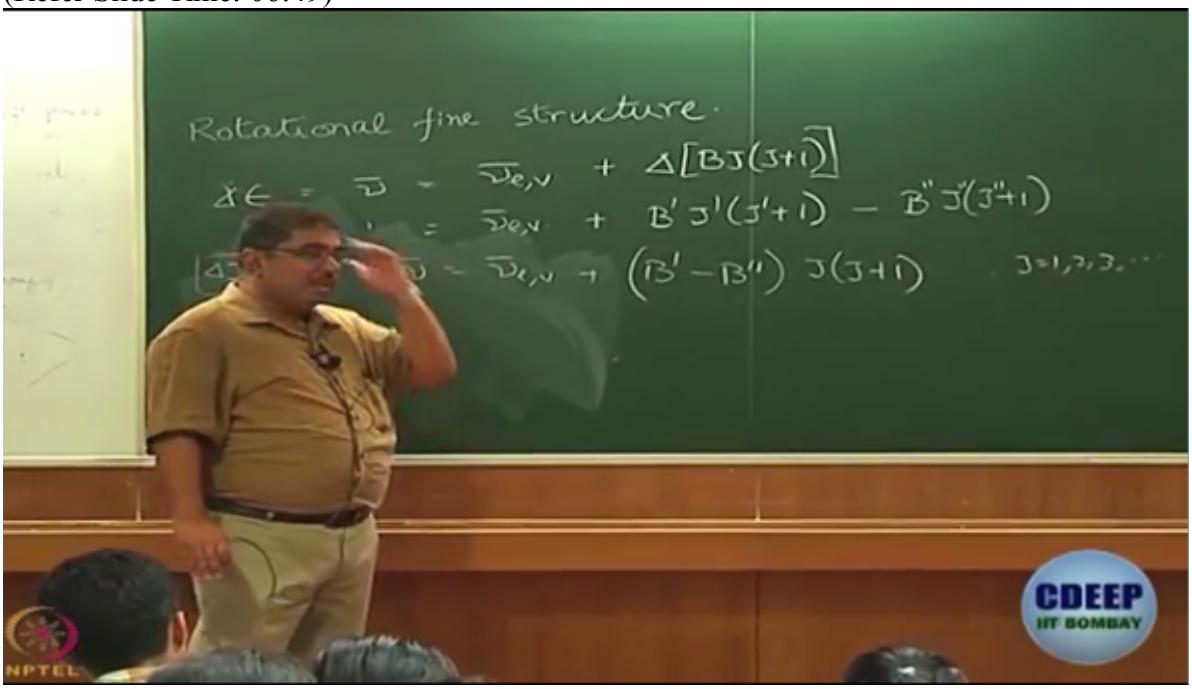

it is conventional to draw a parabola that is drawn by 90 degrees, since I have no idea why it was drawn that way, but maybe I have an idea we'll talk about that, so that kind of a diagram is called a fortrat diagram, so what will do is instead of trying to draw the spectrum, when spectrum is going to get complicated as you will see, we'll draw this what is called fortrat diagram, to understand what kind of rotational fine structure comes in these electronic spectra.

So J = 1, two letters go up to 20, and the reason why I'm writing J in the second column is that we'll draw a parabola that is turn by 90 degrees, okay, so I want this column to be the Y axis, I want the other column to be X axis, so what will it be? Accha,
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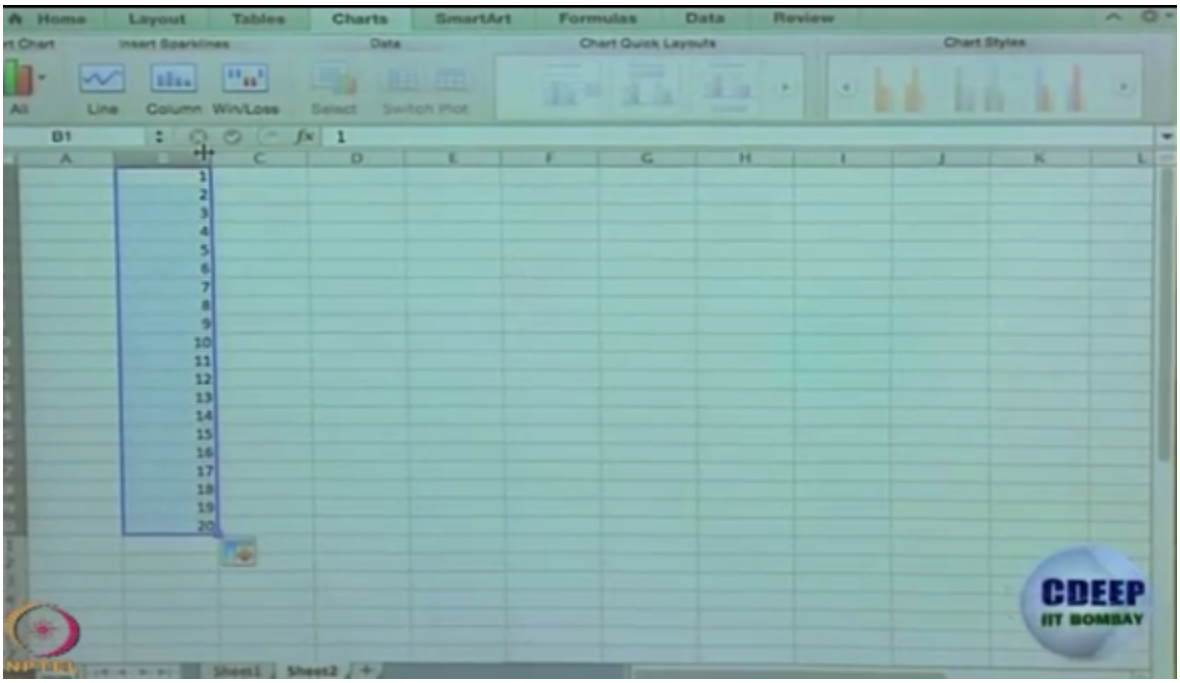

what are the values of B dash and B double dash? What is the typical value of B? 8, okay, so let us say there is a 10% change, so 10% change means how much? And let us say there is a decrease, so B double dash you are saying is 8 centimeter inverse, B dashed is 7.2, right, so what will it be? I'm not going to plot this, I'll only plot this delta BJ(J+1) kind of thing, so it will be what?

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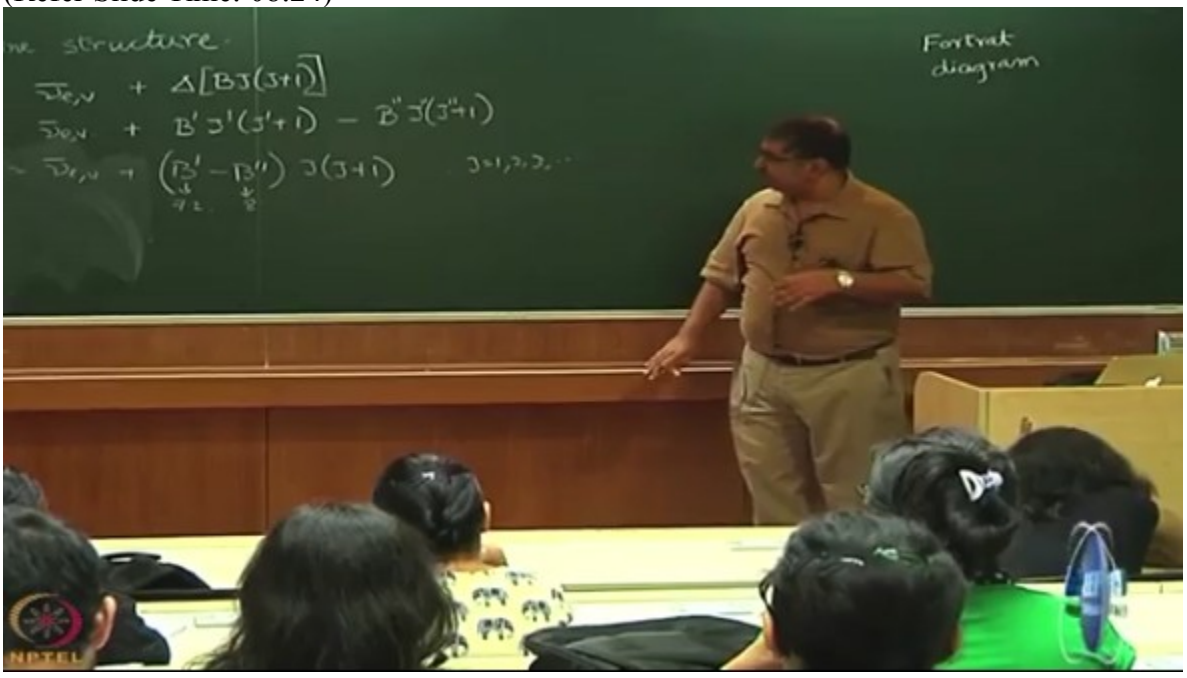

-0.8 into J(J+1), -0.8 into B1(B1+1), right J(J+1), and here we go, these are the values, so see what's happening, -1.6, -4.8, so it goes all the way up to -336,

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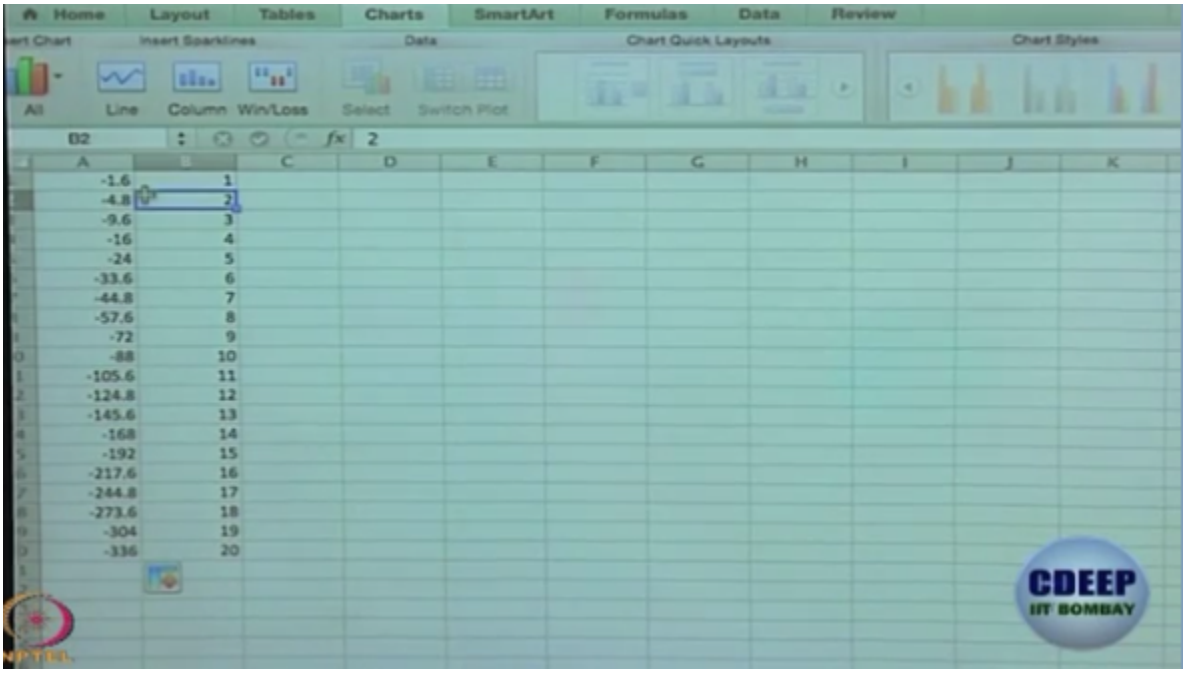

okay, and we are using centimeter inverse, so if you go up to J = 20, then given the parameters we see a total shift of -336 centimeter inverse, so the reason why it is called fine structure is what is a typical value for electronic transition, you told me the other day 10,000, 20,000 something like that or even more, so in 10,000 or 20,000 centimeter inverse the total contribution, so that is the position of the maximum, right, and this one is 336 centimeter inverse, so if I plot this what do I get? I get the half parabola, this is what you get, alright, so this is the fortrat diagram for which one? P or Q or R?

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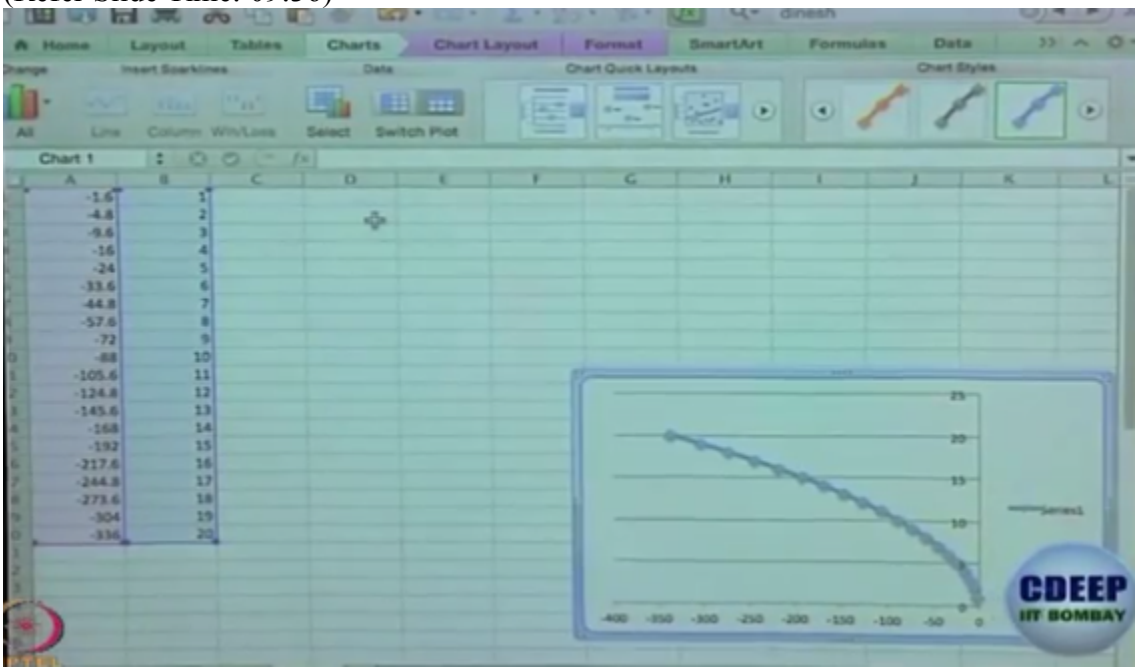

Which branch is this? Do you call this P or Q or R? Q, right, let us now see what happens for P and Q.

So for P what is it? Delta G = -1, so J dashed = J double dash -1, so in this case what we can do is we can write it in terms of, I want to maintain the same range of J's right, so I'll write it in terms of J double dashed, what is the range of J double dash? 1, 2, 3 so on and so forth, J double dash cannot have a value of 0, so what will it be? Nu bar = nu bar EV + B dash, instead of J dash what will I write? I will write J double dash – 1 multiplied by J double dash – B double dash J double dash multiplied by J double dash +1, is this okay? This is correct,

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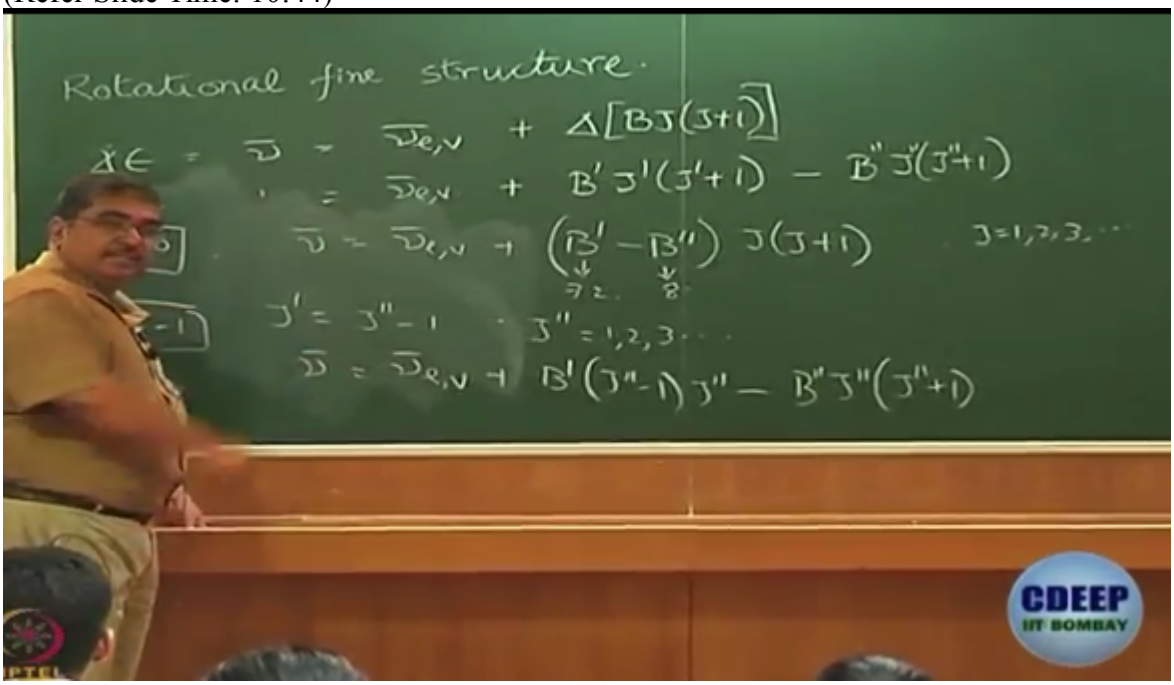

so that's going to be nu bar is nu bar EV + what do I do? Collect the terms in J dash square so it will be V dash – B double dash multiplied by J double dash square, and what else do I have? –J double dash into B dash – J double dash into B double dash, is that right? So –B dash + B double dash multiplied by J double dash, is that correct? Correct.

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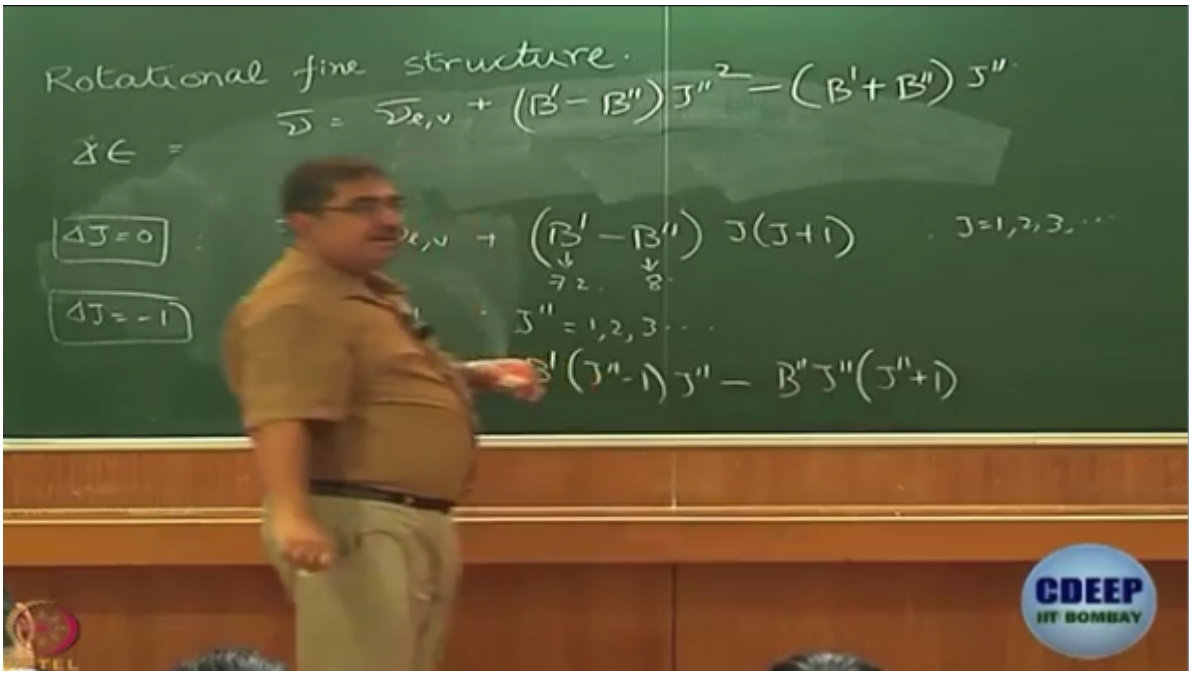

Well, let us do the other one as well for delta this is what it is for delta J = -1, what is it for delta J = +1?

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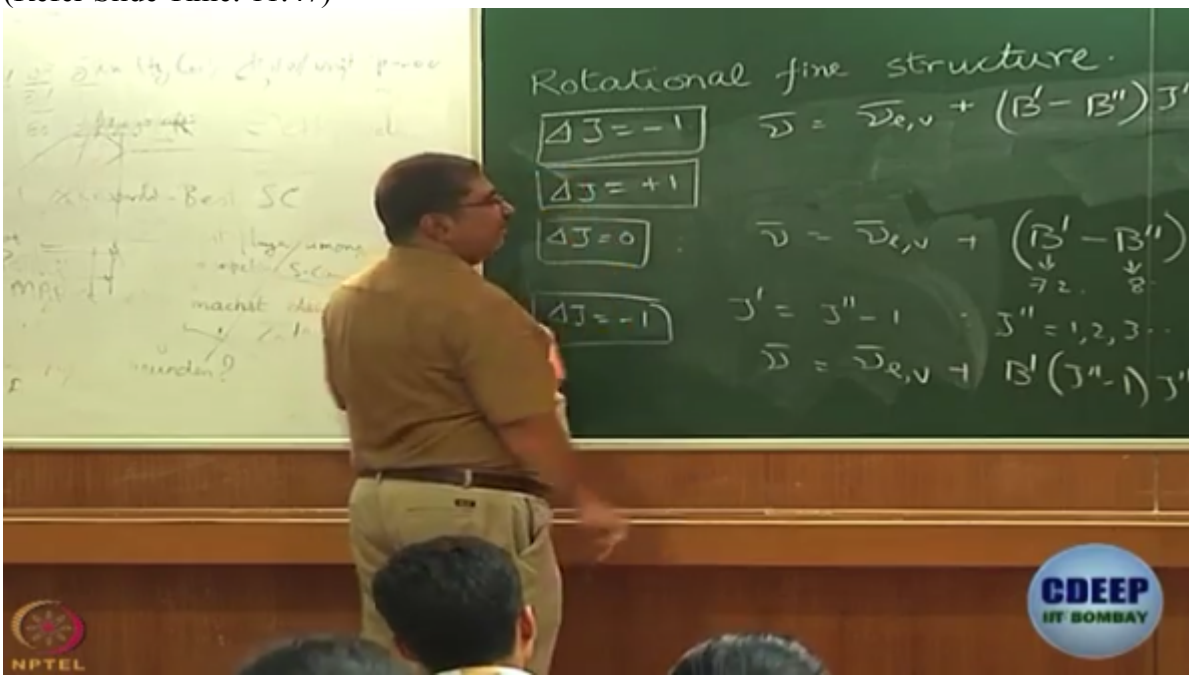

What will it be for delta J = +1? Will get a similar expression, what will be the only difference? Minus which one? Which one will be minus? Nu bar = nu bar EV, then here I have a minus, minus, what do I have it here? –B dash – B double dash, J double dash square then, plus or minus? Plus or minus? Minus, B dash + B double dash J double dash, so if I write them together, what will it be? I can write it generically, isn't it? So these speech you together I can write as nu

bar PR, and this I can write nu bar Q, that will be equal to nu bar EV + - B dash – B double dash J dashed square – B dashed + B double dash(J double dash) that's easy right,
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I hope you have not made any mistake in the second one, because second one I did not calculate, you did.

Okay, with that so let's plot one by one. Yes sir, sorry, plus minus should be for which one? So what I have done? Where is the, which one is not correct? This or this? That's what I am asking, what should it be? This is plus, and this is minus, this is also plus? Yes, yeah, okay, actually I thought something is going wrong, so this will be what? This will be plus, J dash square this will be +-, is that right now? Now I'll get the correct parabola,
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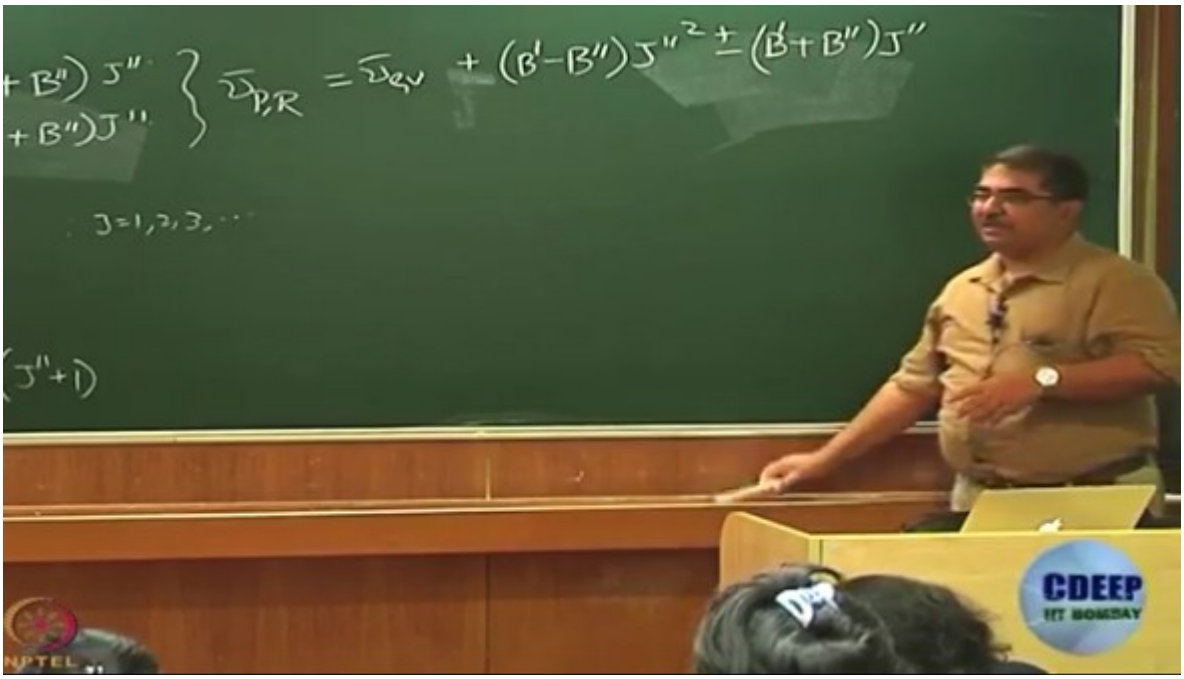

so which one is P, which one is Q? Which one is P, which one is R? Sorry, is this P or is this R? Delta J = -1 that is P, right, let us do that first.

So maybe what I will do is I'll just copy paste this, B dash – B double dash how much is that? -0.8 multiplied by J dash square, so this this minus, what is B dash + B double dash? 15.8, 15.2 multiplied by J dash, this is P and what is Q? For Q, not Q why am I saying Q again and again? For R, for R which sign should I change? The sign of J dash square, right, so this becomes,

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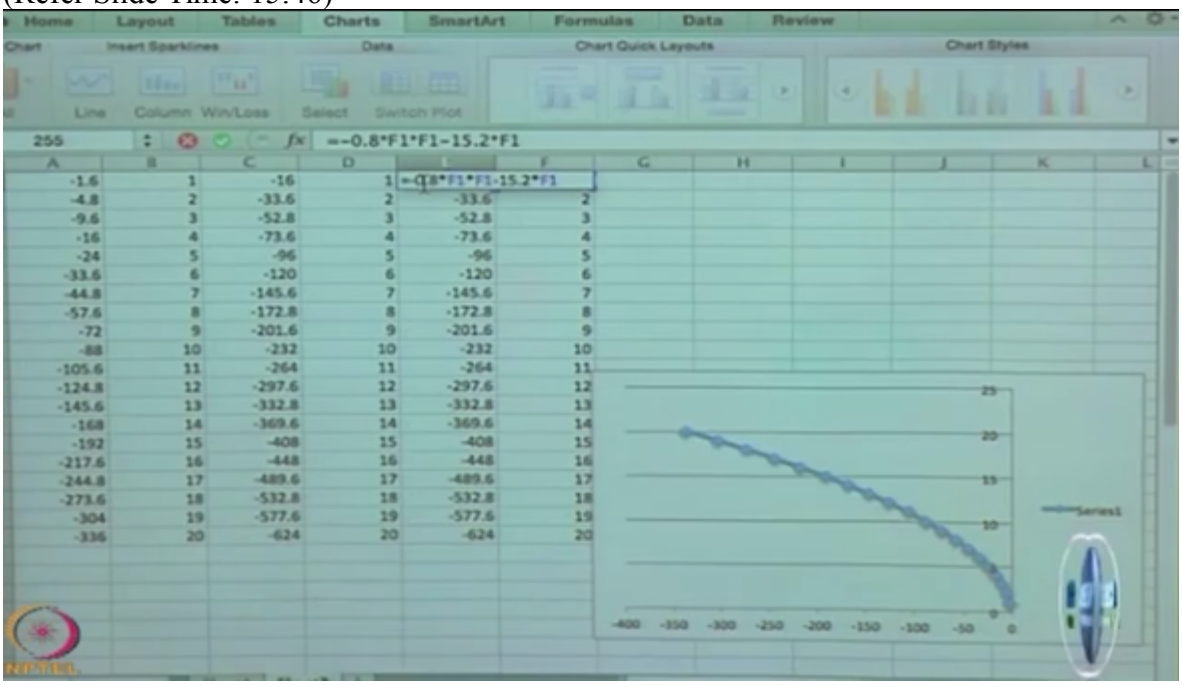

yeah, +15, okay.

So let me just plot, then we'll see, yeah where you are?
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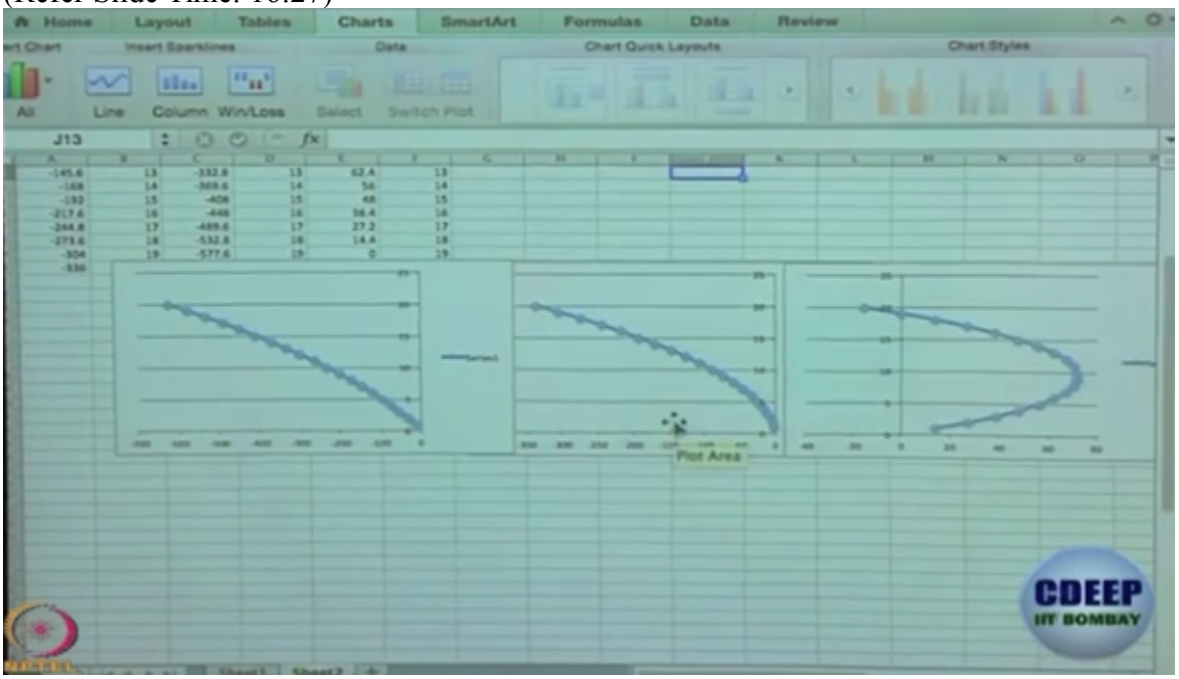

So this is the fortrat diagram for P branch, this is what it is for Q, and this is what it is for R, so you see for R we get a complete parabola, not complete we get both sides of the parabola it turns, and this point where it turns is called the bandhead, so you can now imagine that if you only, the PQR structure that we are familiar with vibrational transition is one branch here, one branch in the middle, one branch on the other side, right, nicely well separated, this is not nicely separated that is a point I was trying to make, right, so for both P and Q you see half parabola and for R you actually see greater portion of the parabola that it turns, so what is the difference between P and Q? Can you read these values? Or is that asking for too much?

Now we don't have to see everything together, this is P right, see how far it has gone, remember we have used the same values for J, 1 to 20, okay, for that we have gone out to -700, for R we had already discussed -350, so for P what you get is you get lines that are more closer together or far apart, naturally far apart right, because the rains that you get for V = 20 is more, for than what it is for Q, and for R this is what you get, smaller range so tighter packing and not only that you don't get a monotonic increase or decrease it turns, so this point where it turns this is called your bandhead.

What is band origin? The position that would have, you have got, that you would have got without any rotational fine structure okay, this is band origin for this discussion, and what is this? It is the bandhead, bandhead means the higher energy up to which the band is there, right, so much for your rotational fine structure.

I'll share it there so, share it with you this is something I had done for practice, the only difference is the B values nothing else, so I'll share this with you not an issue. Now so that is the end of this part of our discussion.

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