Atomic and Molecular Physics
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Lecture - 55
Electronic structure of a molecule

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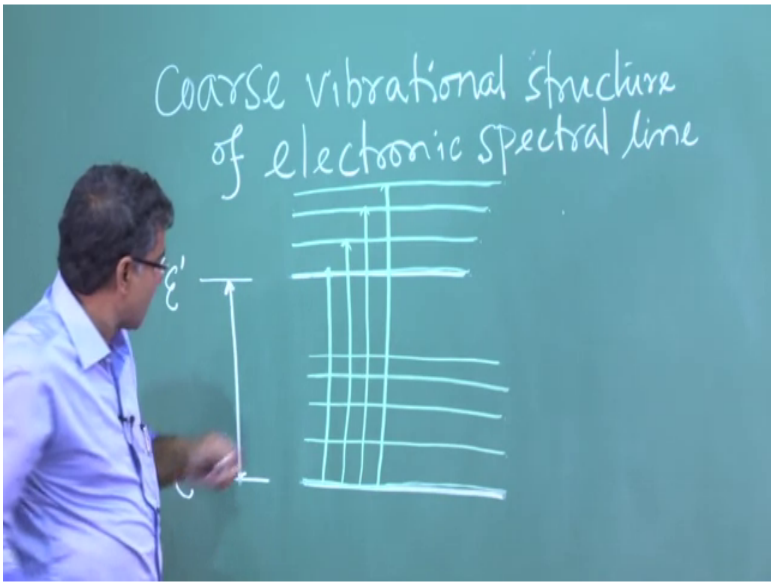

So, we are discussing about the Electric Transition in Diatomic Molecules. So, we have seen Coarse Electronic Vibrational Structure Coarse, I think I can write Coarse Vibrational Structure of Electronic Spectral line ok.

So, there we have seen that there is the electronic state say energy is the double dash in wave number of course, and this another electronic state E energy E dash. So, there will be transition between these two energy level electronic transition in molecule. So, you will get a spectral lines ok. So, transition among the other electronic energy levels. So, you will get you will get spectral lines electron spectral lines ok.

So, now for each for each electronic spectral lines. Now, these lines is not basically a one line. So, it form basically it forms basically a it has if forms a it consists of a group of group of spectral lines ok. So, that is that is called basically coarse vibrational structure of these spectral lines electron spectral lines.

So, what happens these each electronic spectral line yeah energy levels. So, it contains basically vibrational levels. So, this contains vibrational levels. So, this is itself is a then ok. So, these are the vibrational levels their separation is ten to the power minus ten to the power 3 centimetre inverse where this separation is 10 to the power 5 centimetre inverse.

So, now following the transition rule selection rule del V equal to 0 plus minus 1 plus minus 2 it is a etcetera; So, the single line. Now, it is basically it is a. So, in you will get a group of lines you will get a group of lines ok. So, these call the coarse structure it is because of vibrational vibration of the molecules. And now, this each vibrational energy level; Now, again it is a broad it is a no sharp line broad line. So, if you see in spectrometer of high resolution then one can see again it is not a single line it consists of a bunch of lines.

So, that basically because of the rotation of the molecule and so, if I consider just one anyone if you consider if you say if you consider these lines; So, these lines. So, this is not a single line basically; So, each vibrational energy level. Now, it consists of a of rotational energy level. So, basically this it has rotational energy level it has rotational energy level ok.

So, if I consider this one; So, here so, basically it again this vibrational level. Now, it has it has it consists of rotational energy level. So, separation of these energy levels is 10 to the power minus 1 centimetre inverse. So, this is really very small separation.

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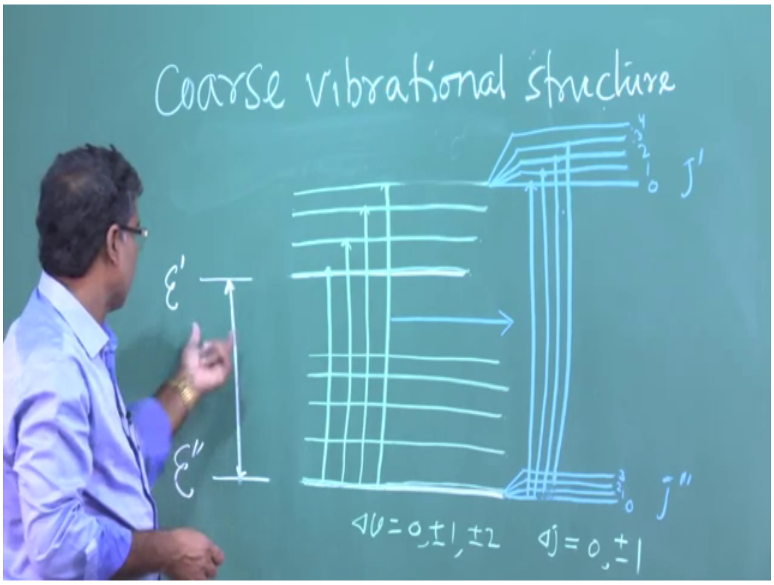

Now, this transition now these transition. So, this one vibrational lines; So, this due to this rotational transition. So, you will get ok. So, here I have shown this just following one del j equal to 0 plus 1 plus 2 plus 3 ok. So, that is not allowed.

So, depending on depending on here like del V equal to all transition possible, but following this way ok. But del j del j equal to 0 and plus minus 1 ok; only this one has to follow. So, del j equal to 0. So, from here to here it is possible from here to plus minus 1, the here to here it is possible. So, here to here it is not possible. So, basically it can be for from next level here to here; So, here 1 to 2 and here 1 to 2 and here 2 to 3. So, this is say this is J double dash double dash this is 0 1 2 3 and here J dash. So, this is 0 1 2 3 4 ok.

So, one has to follow this selection rule. So, we will discuss about this in details. So, basically each here just one have shown this consists of say they have been lines ok. So, similarly this one also consists of many lines, but their spacing a really very small it is a 10 to the minus 1 centimetre inverse in that range ok.

So, these this is basically electron one spectral lines, electronic spectral lines. Now, these electronic spectral lines is it has coarse structure due to vibration of the molecule. So, these are the spectral lines coarse. So, that we are telling coarse structure of the electronic spectra. Now, each line each line again has it consists of few lines. So, that is it is because of the rotation. So, this structure is called the fine structure; So, this fine structure due to rotation of the molecule ok.

So, ultimately; So, this one will is not a, it is not a single line it has coarse structure and then it has fine structure. Coarse structure is because of the vibration of the molecule and this fine structure is because of the rotation of the molecule ok.

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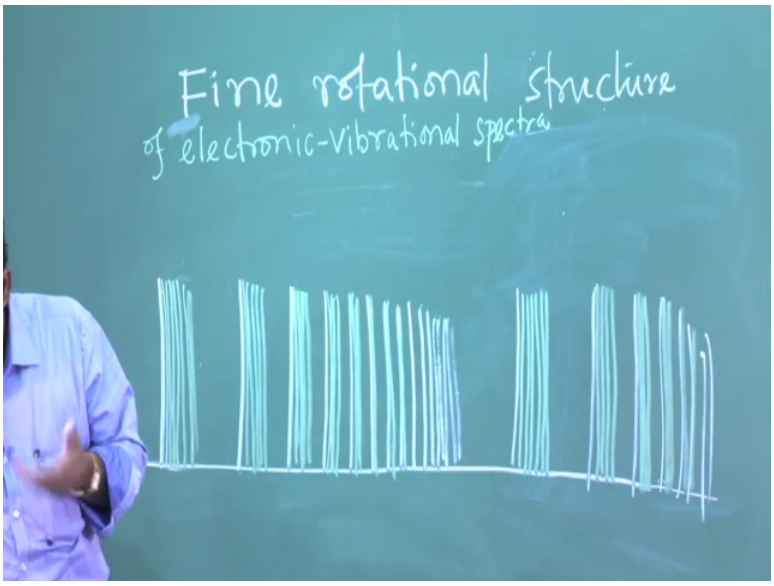

So, this we would like to just. So, fine rotational fine structure, fine rotational structure. Fine rotational structure of electronic vibration spectra; a of electronic structure of electronic of electric vibration electronic vibration vibrational we one can write electronic vibrational spectra or spectral lines ok.

So, ultimately what we will see basically. So, when you will see the spectra electronic spectra. So, we will get basically we will get we will get spectral lines ok. We will get different series of series of spectral line this is one series and then you will get another series. So, this say you will get another series ok.

So, you will get series of spectral lines. So, this is this is basically coarse structure and each spectral lines. So, here it is not a single line. So, it is a broad line ok. So, you will get this type of. So, these are the fine structure these are the fine structure; but as a whole overall. So, you will see this kind of electronic.

So, this kind of electronic spectra of a diatomic molecule of a molecule we will see and this is nothing but the electronic spectral lines electronic spectral lines of a molecule and in these electronic spectral lines of the molecules you have this kind of coarse structure and as well as fine structure, this coarse structure reduced due to vibration of the molecule and this fine structure is due to the rotation of the molecule. So, coarse structure we have discussed how intensity varies Franken Principle etcetera.

So, let us discuss slightly more about the this fine structure of the rotation of the due to the rotation of the molecule. So, what is the effect in electronic spectra.

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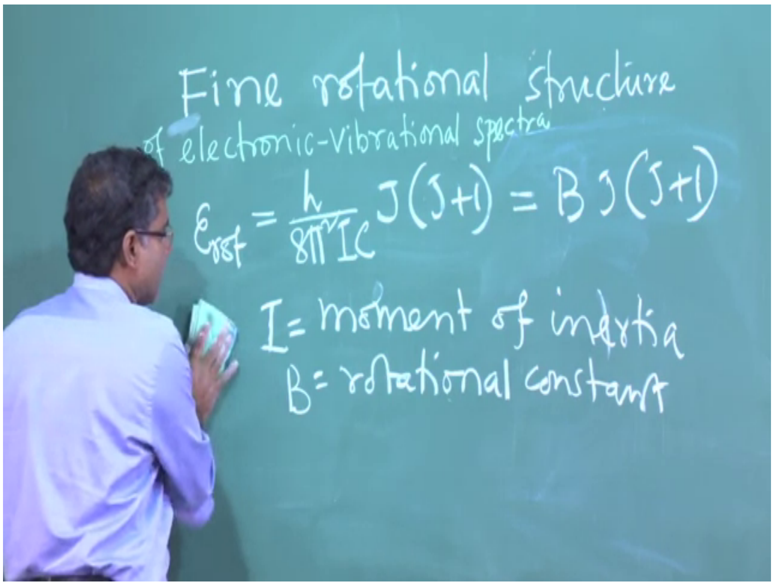

Fine rotational structure
of electronic-vibrational spectra

$$E_{rot} = \frac{h}{8\pi^2 IC} J(J+1) = BJ(J+1)$$

I = moment of inertia
B = rotational constant

So, rotational so energy due to rotation that is basically wave number centimetre inverse this is the in centimetre inverse, this is energy levels, rotational energy levels. So, this you know h by 8 pi square I C J J plus 1 J J plus 1 and if I neglect this distortion due to centrifugal force; centrifugal distortion this another term DE term was there. So, this is basically we are writing B J B J plus 1; or we remember I is a moment of inertia; and B is a rotational constant; B is a rotational constant right.

So, here we have, we have neglected this distortion term because D to distortion is very small term. So, here in this case in rotational in electronic spectra. So, that contribution is its very difficult to detect that contribution. So, that is why one can neglect that one.

So, now, fine; so, what happens? So, this is the rotational. And now, in electronic spectra in electric spectra what is the energy of the, what is the energy of the levels energy levels. So, that if we write E total E total. So, that will have contribution; that will have contribution E electronic plus E vibration plus plus this ok.

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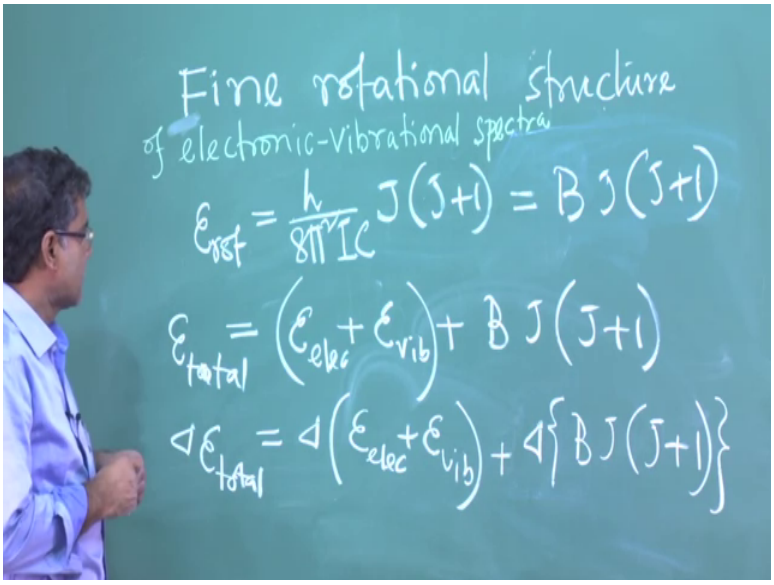

Fine rotational structure

of electronic-vibrational spectra

$$\varepsilon_{rot} = \frac{h}{8\pi^2 Ic} J(J+1) = BJ(J+1)$$

$$\varepsilon_{total} = (\varepsilon_{elec} + \varepsilon_{vib}) + BJ(J+1)$$

$$\Delta\varepsilon_{total} = \Delta(\varepsilon_{elec} + \varepsilon_{vib}) + \Delta\{BJ(J+1)\}$$

Now, so, due to transition; so, energy of the spectral lines energy of the spectral lines. So, that is basically del E del E total ok. This we can write del change of this electronic and vibrational energy; electronic and E vibrational ok.

Then change of this one, change of this rotational one B J J plus 1 ok. So, these we can write, this we can write. So, this is the energy of the spectral lines.

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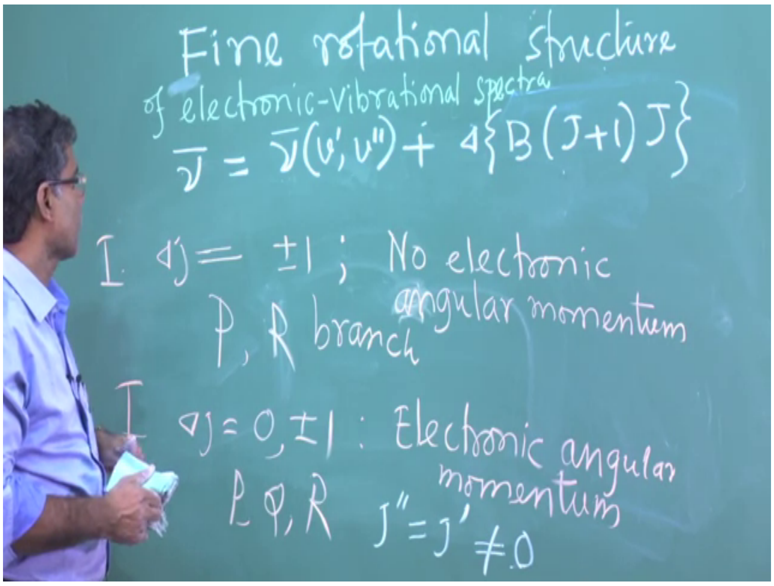

Fine rotational structure

of electronic-vibrational spectra

$$\bar{\nu} = \bar{\nu}(v', v'') + \Delta\{B(J+1)J\}$$

I $\Delta J = \pm 1$; No electronic angular momentum

P, R branch

II $\Delta J = 0, \pm 1$: Electronic angular momentum

P, Q, R $J'' = J' \neq 0$

So, now, this energy of the spectral lines this a if I write nu, nu bar. So, that will be equal to. So, here I can write nu bar due to transition between these two vibrational level V dash and V double dash ok. So, for that this is the. So, this term I am writing this plus. Now, here because of this rotational part; So, that. So, that transition one should actually write one should actually write that one has to think. So, this just I can write keep it keep it ok.

So, here we have to set selection rule, we have to set selection rules. So, it is slightly different than the then the rotation pure rotation spectra. So, that is. So, it is slightly different from that in electronic case; So, here. So, there we have seen del j equal to you remember. So, here selection rule del j equal to 0 plus minus 1. So, basically there are two kind of selection rule.

So, one in case of so, in case of one it is telling. So, del j equal to plus minus 1 del j equal to plus minus 1 del j is equal to 0 is not allowed. So, in this case; So, transition from so, plus minus 1. So, one can one can. So, when it is it is this transition is possible this transition this selection rule is valid it is telling that this that states; when this transition between states upper states and lower statements upper electronic state and lower electronic states ok.

So, states rotational states in lower electronic state, then from there transition to the upper rotational state our in upper electronic state ok. When these states two states involve these two states involve and if there is no if there is no electronic angular momentum of these states ok. So, transition between two states. Now, if these two states do not have do not have electronic angular momentum. Then in that case the selection rule del j equal to plus minus 1 ok.

So, in this case no electronic angular momentum of the states involved in this transition No electronic states. No electronic angular momentum. No electronic angular momentum of the states involved in this transition ok. So, in that case this del j equal to plus minus 1.

So, basically you will get P branch and Q branch only. So, that is same as we have seen in case of rotation rotational spectra. So, P and Q branch only we will see not Q P and R branch you will see ok, 1 P I think 1 for plus 1 and another for minus 1 ok.

And for other case second rule this one first second rule is del j equal to 0 and plus minus 1 this selection rule will be followed; In that case. So, this transition rule will follow when these that states involved in the transition. So, they will have electronic angular momentum. So, these will have electronic angular momentum, electronic angular momentum electronic angular momentum ok.

So, in this case you will get P Q and R branches ok. So, in this selectional here another things restriction is their del j equal to 0, but in this case J dash equal to J J double dash equal to J dash ok. But this is not equal to 0; that means, J double dash equal to 0.

So, from there this transition is not allowed to J dash equal to 0; although del j equal to 0, but this is not allowed ok; But other from 1 to 1 from 2 to 2. So, only those are allowed in that case, del j equal to 0; but del j double dash equal to J dash is not equal to 0. So, that restriction also one has to put ok.

So, following this selection rule; So, one I can write basically. So, now, only things is that whether you will get Q branch or not that will depend on whether states involving the transition have electronic angular momentum or not ok. So, just here we will write the condition for basically frequency or wave number of the spectral lines.

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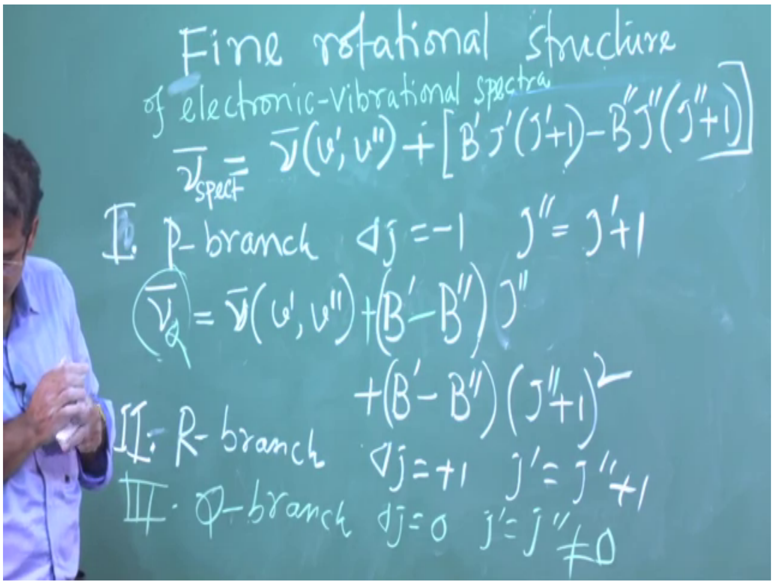

Fine rotational structure

of electronic-vibrational spectra

$\bar{\nu}_{spect} = \bar{\nu}(v', v'') + [B'J'(J'+1) - B''J''(J''+1)]$

I. P-branch $\Delta J = -1$ $J'' = J'+1$

$\bar{\nu}_Q = \bar{\nu}(v', v'') + (B' - B'')J''$

$+ (B' - B'')(J''+1)^2$

II. R-branch $\Delta J = +1$ $J' = J''+1$

III. Q-branch $\Delta J = 0$ $J' = J'' \neq 0$

So, there are three cases. One I can write one is I can write that what I will get, I think this. So, this is the spectral lines, this I can here. So, this I will get this I will get for I think yes I think I can right.

So, this will be the wavelength not wavelength wave number of the spectral lines and this is this will come for the electronic vibrational transition, this part and this part from rotational transition. So, here del of this I can write basically. So, basically I can write say B dash J dash J dash plus 1 minus B double dash J double dash J double dash plus 1 ok. So, that will be the basically wave number of the spectral lines ok.

So, for P branch for P branch del j equal to for P branch del j equal to minus 1 ok. So, that means, J double dash. So, J double dash the basically from lower electronic state there we have considered and the upper electronics are the J dash. So, J double dash equal to J dash plus 1 ok. So, this will be the condition for this spectral P for P branch.

So, the selection rule we have considered del j equal to minus 1. So, you will get P branch ok. And one can write this for P branch this is the wave number of spectral lines equal to this V dash V double dash plus if you if you replace J double dash equal to J dash plus 1 and then just simplify it.

So, you will get basically minus just I am writing minus I think B dash minus B double dash B dash minus B double dash not minus plus double dash J dash plus 1 J dash plus 1 and then plus B dash I think I should write here plus B dash minus B double dash J dash plus 1 I think whole square J dash minus 1 whole square yes. So, had J dash equal to 0 1 2 3 ok.

So, this is the P branch and similarly one can see this two R branch ok. So, in that case del j equal to plus 1. So, means J dash equal to J double dash plus 1 ok. So, just if you replace J dash equal to J double dash plus 1 here.

So, I think in that case, you will get here I can write. So, this I can write now just I am now writing here. So, just R and I think here it will be just there will be change of sign. I think this both are plus yes it will be just plus sign here and this will put double dash yeah just if you replace it you will get; This where J double dash equal to 0 1 2 3 ok. And this third one you will get Q branch where del j equal to 0 del j equal to 0 right, means J dash equal to J double dash ok. But J dash is, but is not equal to 0 ok.

So, if you put that one then it is the you will get this Q you will get Q this and for that I think yeah B minus I think here it will be just minus B dash minus B double dash J double dash J double dash J double dash. And then B dash minus B double dash J double dash yes yeah. I think this I think something I am doing mistake here just if you this I think this will be the same right. Because J equal to J double dash. So, it will be J double this I think this will be just B double dash it is B double dash you know just one can replace this J equal to J, if yeah ok.

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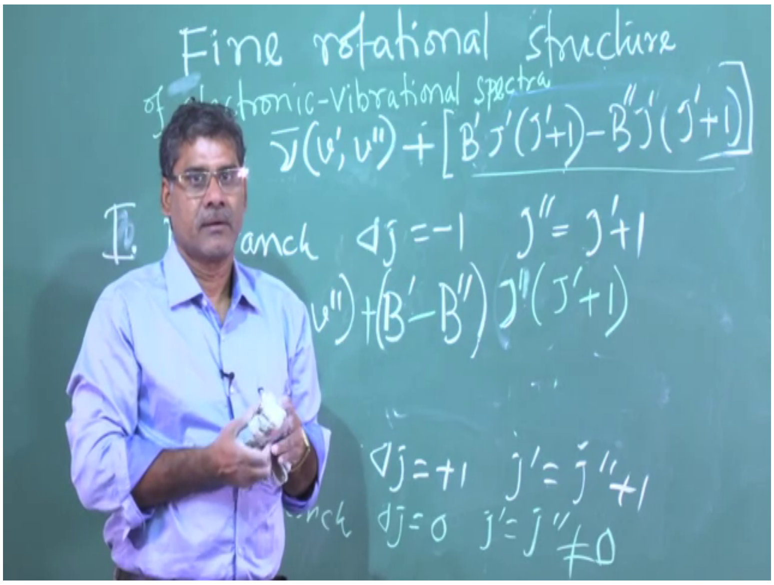

So, if you take commons of B dash minus B double dash into J dash J dash plus 1 ok. So, this part and then here is J yeah that I have to replace. So, I will get B dash minus B double dash and J dash J dash plus one yes. J dash J dash plus 1 just we have to take common J dash J J dash plus 1. So, it will be B minus B double dash ok. So, that will be nu Q ok.

So, in this case, basically in fine structures rotational structure you will get different branches (Refer Time: 35:30). So, it is similar to that pure rotational spectra we have we have seen. So, there, but there is some slightly difference on the condition on the selection rules ok; whether you will get the Q branch or not that will define on the on the situation.

And this is only in case of electron transition this restriction this kind of transition rule is valid; whereas, in case of pure rotation we have seen this only you will get P branch and R branch Q branch is not possible. But in this case, depending on the molecules you can get Q branch also and for that these states which are involved for transition should have the electronic angular momentum ok.

So, these are the fine structure, rotational structure of electric vibrational spectral lines ok. So, I think I will stop here.

Thank you.