Statistical Thermodynamics for Engineers
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Lecture 46
Ro-vibronic spectroscopy

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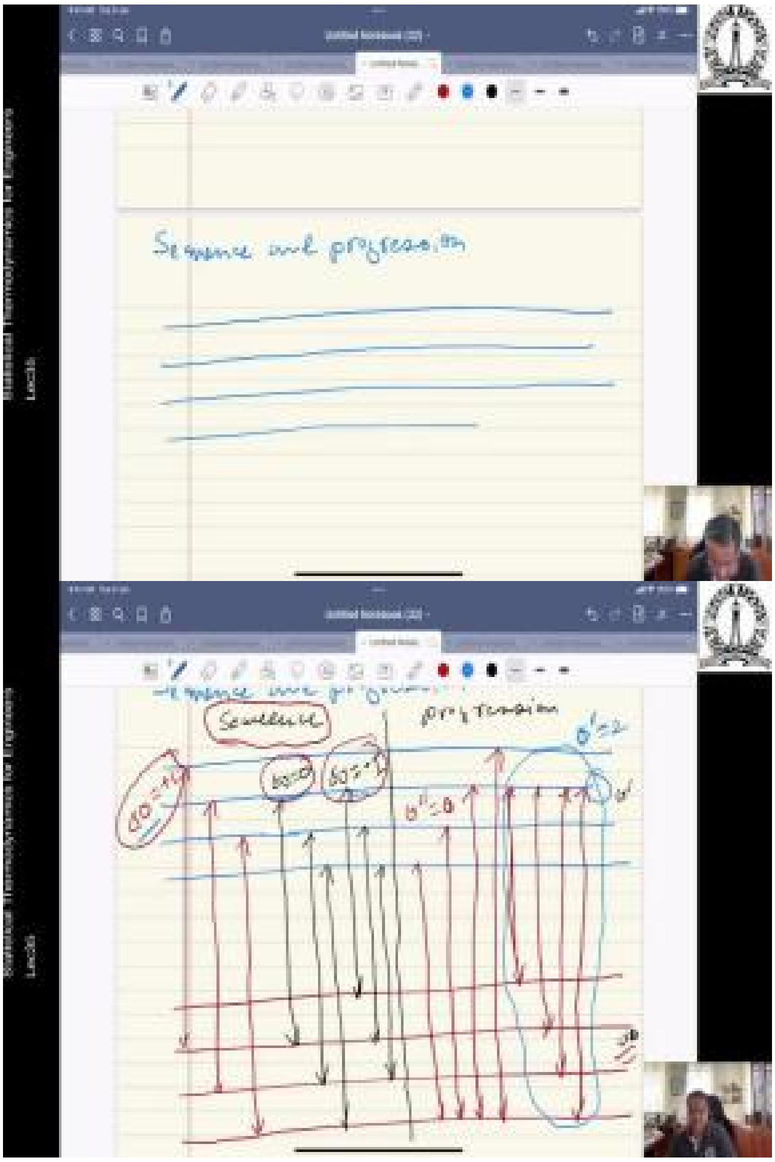

Welcome to lecture number 35 of the statistical thermodynamics course. So, let us draw now, if you remember that we brought in the concept of sequence and progression. So, sequence was when the electronic spectrum containing the vibrational bands with a constant delta v is called a sequence whereas, with spectrum which contains regular vibrational bands with a constant v prime or v double prime is called a progression.

So, let us draw that to how this can be best represented this progression and the sequence. We already talked about sequence and progression. So, let us look at it in a little bit more details.

So, let us look at some transitions which would be relevant to. So let us draw this, is the sample example though this one. So, let us put a marker in between so, this part we are going to sequence, this is for the progression alright.

So, and this is of course v prime v double prime. So, let us look at some of the transitions now let us mark it as red (())(1:58). So, this is like delta v is equal to this one plus one always it is going from a second to a third vibration that is the kind of transitions that we are looking at. Now, if we so this is one family that we can look into another family now where (())(2:52) let us look at the thin from 2 to 2, this is of delta v is equal to 0 into del type of transitions this is still del v equal to minus 1.

So, this is plus 1, this is 0, and this is minus 1. So, this is sequence so, you see that this is a constant if you look at it, it is a constant delta v so that is why it is called sequence, it is a constant delta v that you see. We will look at the transitions from here to here this is plus and or from here to there is plus and a plus and then this is the same way so you can see there is a plus one vibrational level this is 0 it is migrating from a v 1 prime to v 1 double prime which is equal to 0.

And so this is the way of the sequence part actually works. And this side we call it the progression. So the progression will be like it is easy to draw this is for a constant v prime or a v double prime as you can see here, where v double prime is equal to 0, this is the v double prime part. Similarly, you can have so you are not bothered about the delta v percent, you are only concerned about where the transition is taking place.

So, this part is for v prime is equal to 2 that is where the transitions have started from. So, this is a progression, because it has a constant v prime or v double prime. Here of course, it is a for sequence because it maintains a constant delta v. So, these are the two types of electronic spectrum which containing the vibrational bands with a constant delta v or with a constant delta v prime or v double prime. So, this is what is represented in this particular diagram, which we said that we are going to cover in the next in the previous class.

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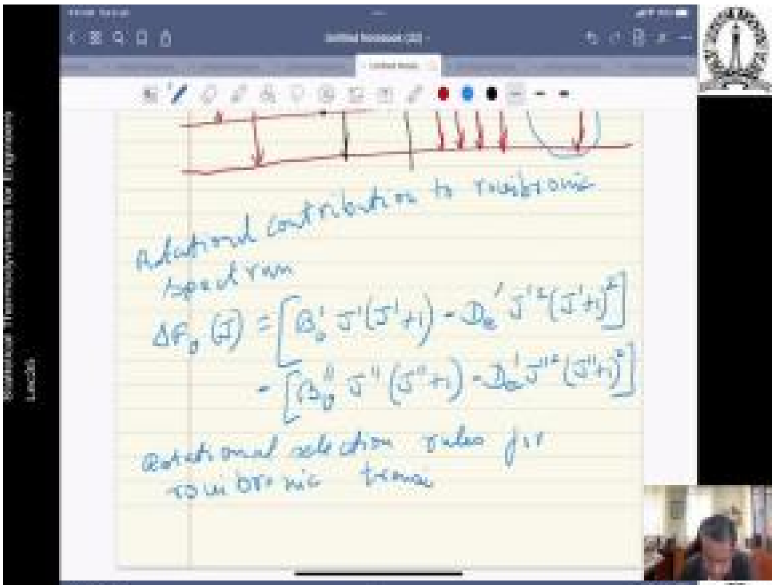
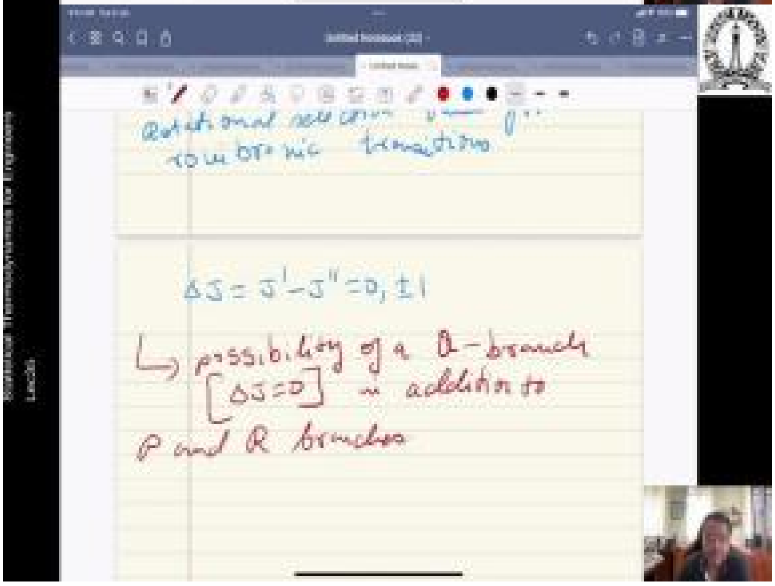


Rotational contribution to rovibronic spectrum

$$\Delta F_v(J) = \left[B_v' J'(J'+1) - D_e' J'^2(J'+1)^2\right] - \left[B_v'' J''(J''+1) - D_e' J''^2(J''+1)^2\right]$$

Rotational selection rules for rovibronic trans



Rotational selection rules for rovibronic transitions

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

$\hookrightarrow$ possibility of a Q-branch $[\Delta J = 0]$ in addition to P and R branches

Now, let us rewrite the rotational contribution to the ro-vibronic spectrum. Where this delta F v J B v prime J prime J prime plus 1 minus D e prime J prime square J prime plus 1 square minus B v double prime J double prime J double prime plus 1 D e prime J double prime square J double prime plus 1 square. So, again the single and the double as we said refer to the upper and the lower electronic states.

So, in comparison to the rovibrational case the rotational selection rule or ro-vibronic transitions this turns out to be delta J equal to J prime minus J double prime equal to 0 plus minus 1. So, there is a possibility now possibility of a Q branch which corresponds to delta J is equal to 0, in addition to P and R branches.

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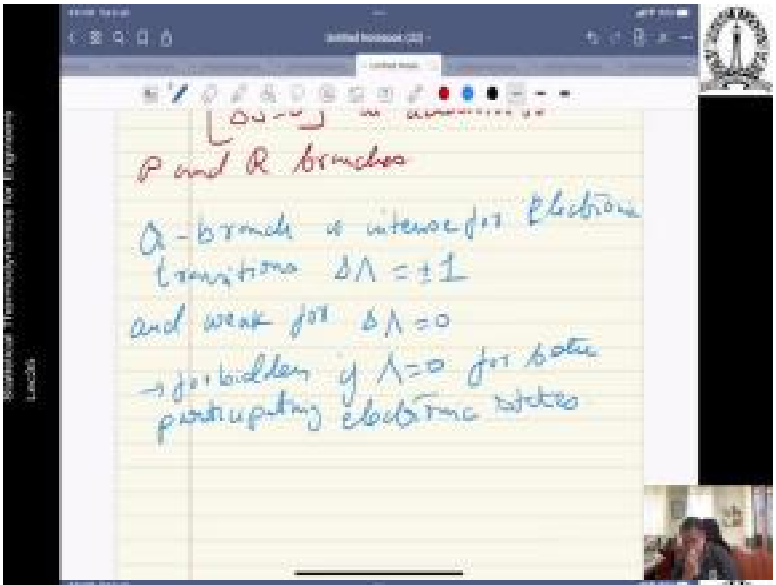
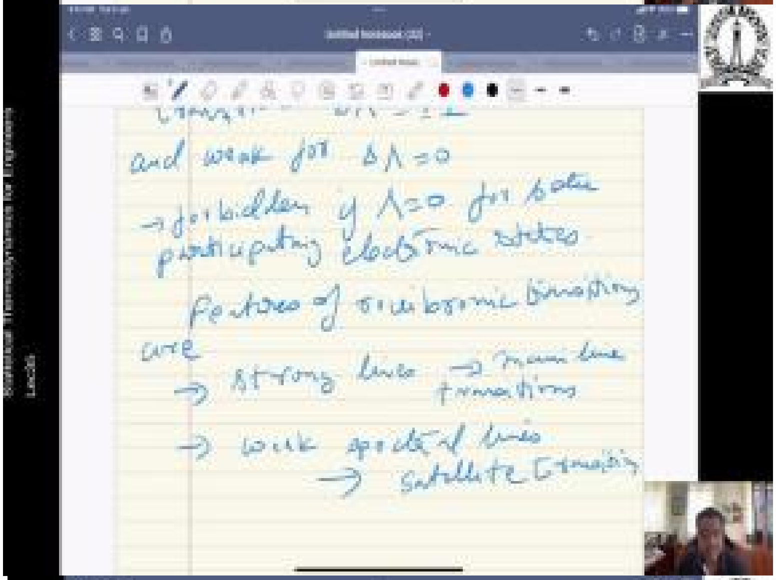


P and R branches

Q-branch is intense for electronic transitions $\Delta\Lambda = \pm 1$

and weak for $\Delta\Lambda = 0$

→ forbidden if $\Lambda = 0$ for both participating electronic states



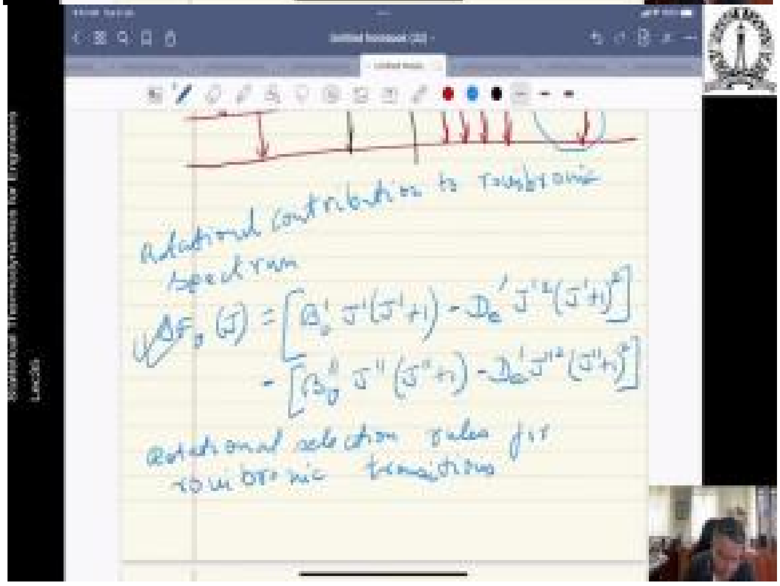
and weak for $\Delta\Lambda = 0$

→ forbidden if $\Lambda = 0$ for both participating electronic states

Features of vibronic transitions are

→ strong lines → main line transitions

→ weak spectral lines → satellite transitions



Rotational contribution to vibronic spectrum

$$\Delta F_v(J) = \left[B_v' J'(J'+1) - D_e' J'^2(J'+1)^2\right] - \left[B_v'' J''(J''+1) - D_e' J''^2(J''+1)^2\right]$$

Rotational selection rules for vibronic transitions

So, Q branch let us look at the features of Q branch, Q branch is intense for electronic transitions this is given by this is equal to plus minus 1 and weak for same electronic transition of 0. And lastly it is forbidden, when it will be forbidden? Forbidden if this is equal to 0 for both participating electronic states.

So, some of the features therefore of the ro-vibronic transitions are, features of ro-vibronic transitions, number one strong lines correspond to the main line transitions and weak spectral lines., these corresponds to satellite transitions. So, you can see it so, these are the features of the rovibrational transition.

Now, if you study the situation over here this particular equation this represents a rotational structure within the vibronic bands which is already we have we know that if you remember what we call the band origin, so it is a rotational structure within a vibronic band, so it is a it is a rotational structure within the vibronic band.

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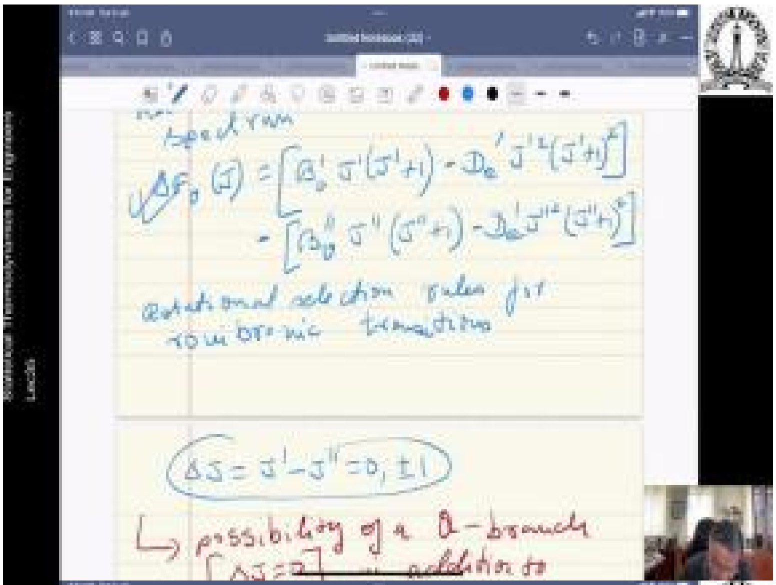


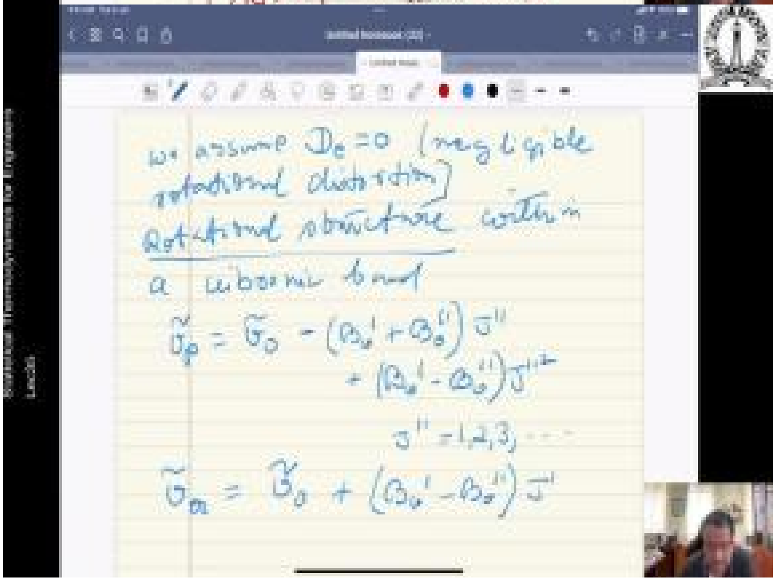
spectrum

$$\Delta F_0(J) = \left[B_0' J'(J'+1) - D_e' J'^2(J'+1)^2\right] - \left[B_0'' J''(J''+1) - D_e'' J''^2(J''+1)^2\right]$$

Rotational selection rules for rovibronic transitions

$$\boxed{\Delta J = J' - J'' = 0, \pm 1}$$

↳ possibility of a Q-branch [$\Delta J = 0$] in addition to



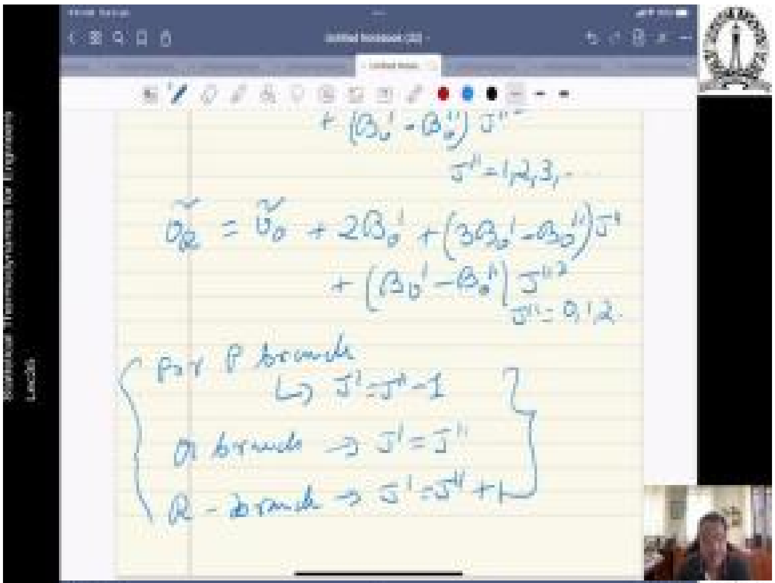
we assume $D_e = 0$ (negligible rotational distortion)

Rotational structure within a vibronic band

$$\tilde{\nu}_P = \tilde{\nu}_0 - (B_0' + B_0'')J'' + (B_0' - B_0'')J''^2$$

$J'' = 1, 2, 3, \ldots$

$$\tilde{\nu}_Q = \tilde{\nu}_0 + (B_0' - B_0'')J'$$



$+ (B_v' - B_v'')J''^2$

$J'' = 1,2,3,\ldots$

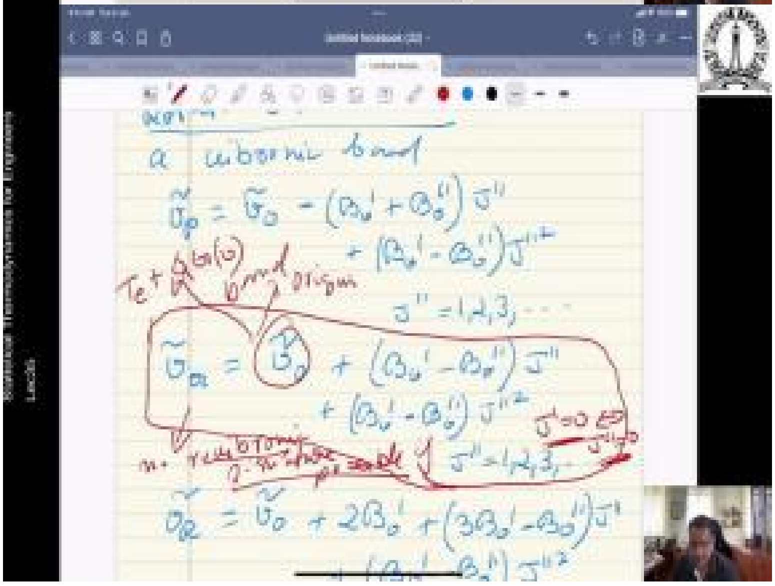
$\tilde{\nu}_R = \tilde{\nu}_0 + 2B_v' + (3B_v' - B_v'')J'' + (B_v' - B_v'')J''^2$

$J'' = 0,1,2$

For P branch
↳ $J' = J'' - 1$

Q branch → $J' = J''$

R - branch → $J' = J'' + 1$



a vibronic band

$\tilde{\nu}_P = \tilde{\nu}_0 - (B_v' + B_v'')J'' + (B_v' - B_v'')J''^2$

$J'' = 1,2,3,\ldots$

$T_e + G(v)$ band origin

$\tilde{\nu}_Q = \tilde{\nu}_0 + (B_v' - B_v'')J'' + (B_v' - B_v'')J''^2$

$J' = 0 \nrightarrow J'' = 0$

rotational [illegible] $J'' = 1,2,3,\ldots$

$\tilde{\nu}_R = \tilde{\nu}_0 + 2B_v' + (3B_v' - B_v'')J'' + (B_v' - B_v'')J''^2$

Now the rotational structure now, if we apply this equation and port it there we will just see what happens, let us use a new page and we assume it D e is equal to 0 that is negligible rotational distortion rotational distortion we can now represent the three branches the rotational structure. So, the rotational structure within vibronic band is given by this equation, so this is the rotational structure.

So, once again we can find out that what is rotational structure is going to be. So, let us write these are all covered previously we just consult back the notes what we did in the last class plus square where J double prime is equal to 1, 2, 3, dot dot. Similar, the Q branch and this has given as B v prime plus B v double prime J prime J double prime plus J double prime square, J double prime equal to 1, 2, 3, dot dot.

Then off course we have R which is (())(14:25) this 2 B v this were all not very difficult to understand plus prime double prime J double prime square, J double prime is equal to 0, 1. So, for the P is now of the P branch for P branch, J prime is equal to J double prime minus 1. Q branch, J double prime equal to J, and then R branch J prime is equal to J double prime plus 1. These are the three branches and we observe from this particular equation if you look at this particular equation, what do you see in this equation?

If you see this equation there is no ro-vibronic signature is possible for J double prime 0 to J prime 0 to J double prime 0. So, here this equation suggests no ro-vibronic signature is possible because these will cancel if you look at this, this will cancel no ro-vibronic signature is possible if J prime is equal to J double prime (())(16:29) to frame this exactly this.

This is actually when J prime equal to zero to J double prime equal to 0. So, there is no ro-vibronic signature possible if you substitute this this will just cancel out and you will be left with only the v 0 delta, where v 0 is basically the band origin, v 0 was the band origin this was called the band origin and this was written as T e plus delta G.

So, no ro-vibronic signature is possible if J prime is equal to 0 and J double prime is equal to 0. For others we have transition possible. So, in other words there will be a gap now that will appear in the ro-vibronic spectrum corresponding to the band origin at (())(17:37) the analogy with a similar gap with the infrared part of the spectrum.

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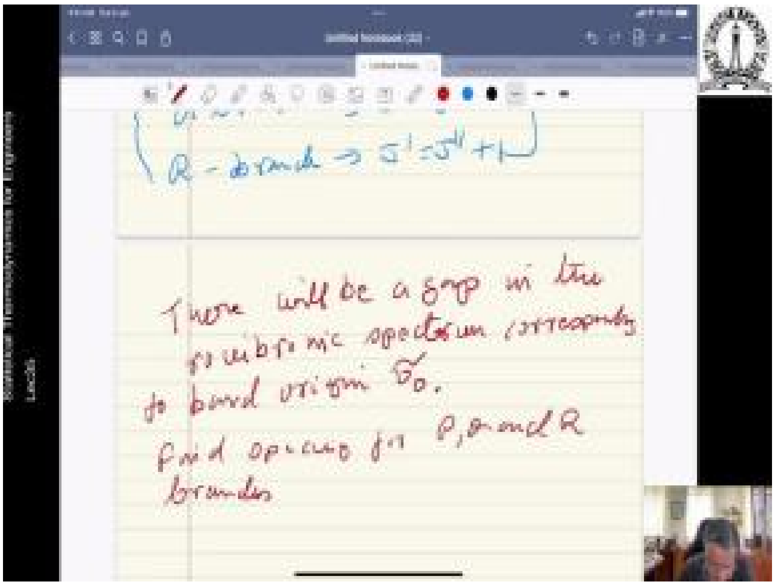
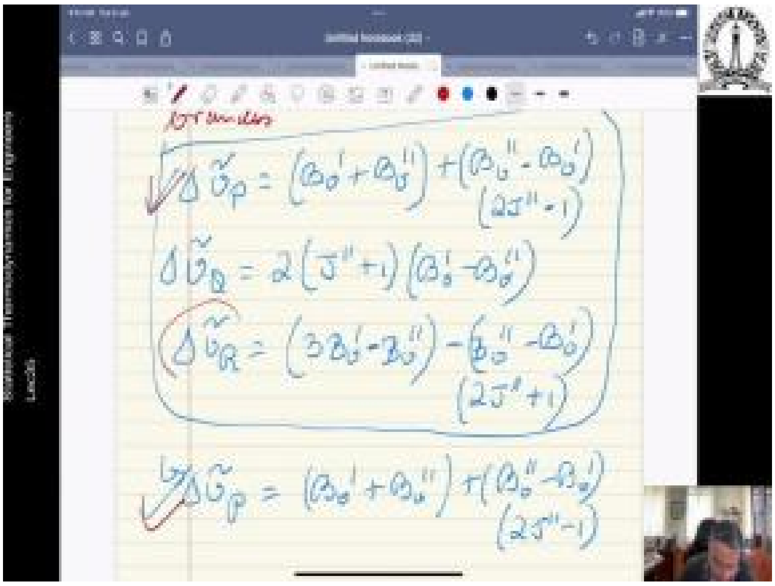


R - branch → $J' = J'' + 1$

There will be a gap in the rovibronic spectrum corresponding to band origin $\tilde{\nu}_0$.

Find spacing for P, Q and R branches



$$\Delta\tilde{\nu}_P = (B_0' + B_0'') + (B_0'' - B_0')(2J''-1)$$

$$\Delta\tilde{\nu}_Q = 2(J''+1)(B_0' - B_0'')$$

$$\Delta\tilde{\nu}_R = (3B_0' - B_0'') - (B_0'' - B_0')(2J'+1)$$

$$\Delta\tilde{\nu}_P = (B_0' + B_0'') + (B_0'' - B_0')(2J''-1)$$

So, there will be a gap so, this suggests there will be a gap in the ro-vibronic spectrum corresponding to band origin which is at v o, this is similar to the infrared spectrum as well. Now, if we utilize all these equations now we find the spacing for the P, Q and R branches. So the spacing would be equal to B prime (())(18:55) B double prime, 2 J double prime therefore (())(19:08) delta v Q equal to 2 J double prime plus 1, B v prime B double prime that of course where is R is 3 B v prime, B double prime 2.

So, these are the spacing's between the consecutive ro-vibronic lines within the P, Q and the R branches. So, despite that we have a similarity if we now look at the (())(20:01) a long time back. So, if you look at for non-electronic transmissions or non-electronic spectroscopy, which is just IR spectroscopy in that particular case. Remember we wrote v P as B v prime plus B v double prime plus B v double prime minus B v prime J double prime minus 1, remember that we wrote this for the P branch for the rovibrational spectroscopy.

Now, for the electronic spectroscopy, if we now look at the electronic spectroscopy now, you will find that the sequence that we wrote this was the electronics spectroscopy function, this came from the rovibrational spectroscopy. So, there is an equivalence as we can see from this situation and what you see here they look kind of very similar, similarly, you will have the same equation for the R branch as well, but, there is a catch here.

So, it looks very similar, this one and this one, similarly, you will have similarity with this one and the corresponding one in the rovibrational counterpart that we should recognize.

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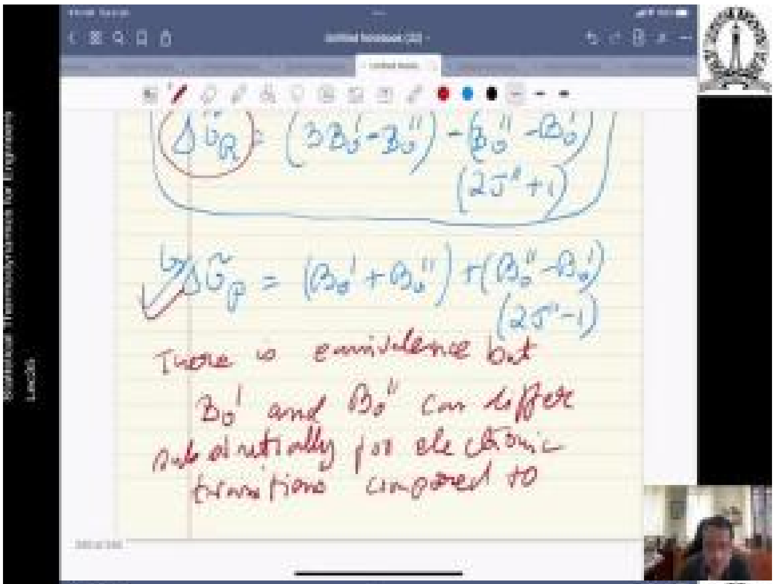
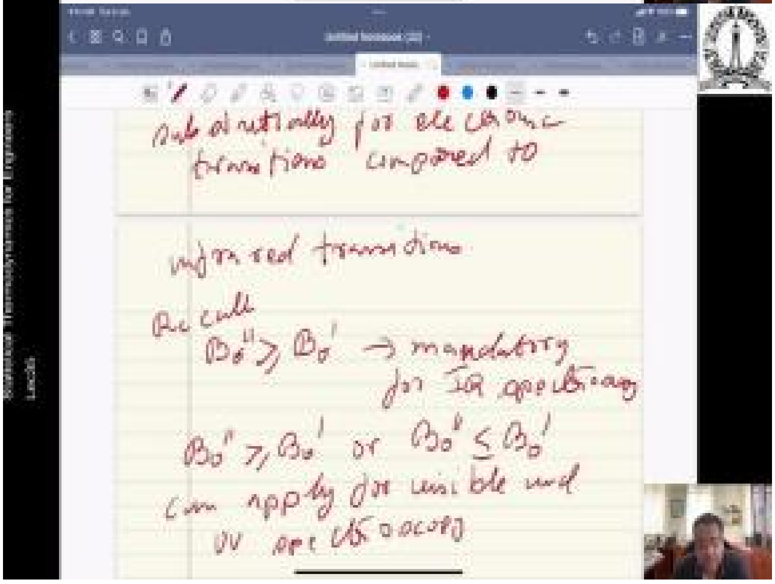


$$\Delta\tilde{G}_R = (3B_0' - B_0'') - (B_0'' - B_0')(2J''+1)$$

$$\Delta\tilde{G}_P = (B_0' + B_0'') + (B_0'' - B_0')(2J''-1)$$

There is equivalence but B_0' and B_0'' can differ substantially for electronic transitions compared to



substantially for electronic transitions compared to

infrared transitions

Recall

$B_0'' \geq B_0'$ → mandatory for IR spectroscopy

$B_0'' \geq B_0'$ or $B_0'' \leq B_0'$ can apply for visible and UV spectroscopy

Now there is equivalence but there is a catch. So, we must recognize that B v prime and B v double prime can differ and differ substantially for electronic transitions compared to infrared transitions. Now, recall B v double prime has to be greater than or equal to B v prime this is mandatory for IR spectroscopy.

Now, this is mandatory but however B v prime greater than equal to B v double prime greater than equal to B v prime or B v double prime less than or equal to B v single prime can apply for visible and u V spectroscopy that is a rotational constant depends on the Morse potential but each specific electronic state, rotational constant depends on the Morse potential for each specific electronic state.

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So, what happens with the as a result of this is that these all these features that we talked about, enforce this ro-vibronic lines lie within a band to crowd together and may eventually reverse their spectral directions also, what we call a well-defined band head. In fact, so, just putting a few points over here, these ro-vibronic lines within a band crowd together and then eventually reverse their spectral directions creating band head.

The band heads can lie within the P and the R branch, so what we can do is that, we can set we can set this to be equal to zero, this P and R if we set P is equal to 0, so we can get what we call the band head. So, for each band head, so if we set delta v P, delta v R is equal to 0 you can calculate what we call a band head and that band head is given as half multiply B double prime divided by, J R double prime, double prime.

So, now, if we recall that if B v double prime is less than equal to B v prime then the band head which is reversal band head appears in P branch and if B v double prime is greater than equal to B v prime the band head appears in R branch. So, the sectoral analysis between the ro-vibronic lines of mandate use of R branch for this and P branch for other one, we just reverse it. On the other hand the band heads are inevitably the most easily observable feature in any ro-vibronic spectrum because of spectral crowding and reversal.

So, it just is very easy to identify in a particular spectrum. So, we will also show an example in the next class that how one sub spectrum actually looks like the u V spectrum, nitrogen actually. So, you can understand that why the band heads should appear in the two bands. So, in the next class we are going to look at it in a little bit more details and look at the figure for the nitrogen spectrum and see how that actually goes. So, till the next class.