Statistical Thermodynamics for Engineers
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Lecture 45
Ro-vibrational spectroscopy (Complex model)

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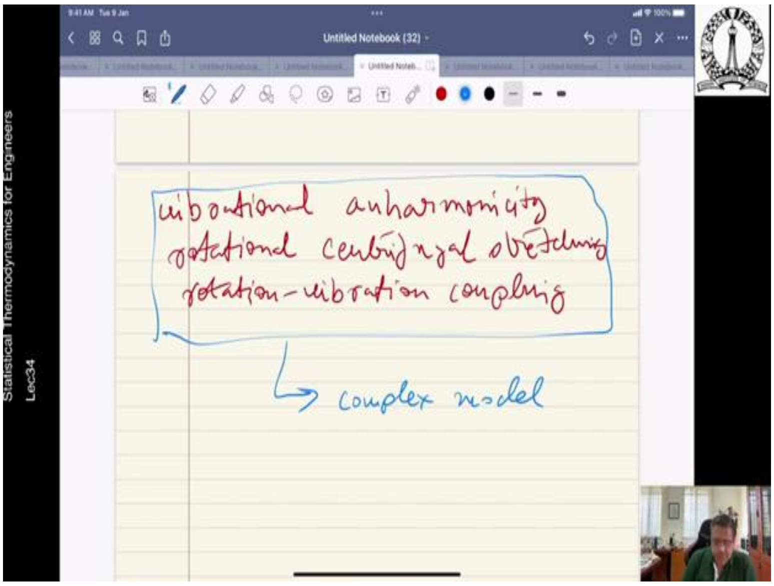
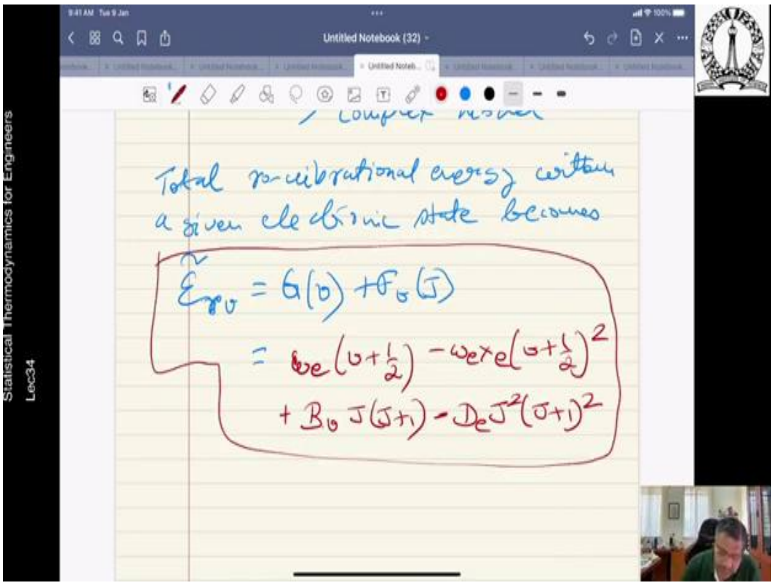


vibrational anharmonicity
rotational centrifugal stretching
rotation-vibration coupling

↳ complex model



Total ro-vibrational energy within a given electronic state becomes

$$\boxed{\tilde{\varepsilon}_{rv} = G(v) + F_v(J) = \omega_e\left(v+\frac{1}{2}\right) - \omega_e x_e\left(v+\frac{1}{2}\right)^2 + B_v J(J+1) - D_e J^2(J+1)^2}$$

Welcome to lecture number 34 of the statistical thermodynamics course, so previously we saw that how the complex model seems to address some of the combined effects of if you look at it here vibrational and anharmonicity, rotational centrifugal stretching and of course the rotation vibration coupling.

So, these were the three things that the complex model seems to incorporate, so this is what constitutes the complex model that we did in the previous lecture. In comparison to the

Simplex model which assumed that harmonic oscillator and rigid rotor. So, pursuing this avenue so the total ro-vibrational energy within given electronic state becomes Erv equal to Gv, Fv J this is the total ro-vibrational energy.

So, if we expand now this Gv and Fv J so it will be omega e plus half minus omega e xe b plus half whole square plus B these were the correction terms if you recall J into J plus 1 minus De J square into J plus 1 whole square. So, this is the total ro-vibrational energy for any given electronic state.

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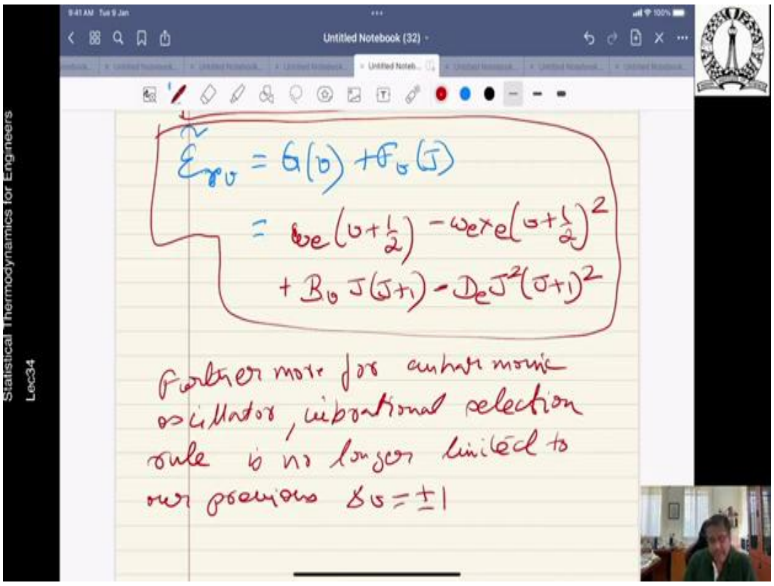
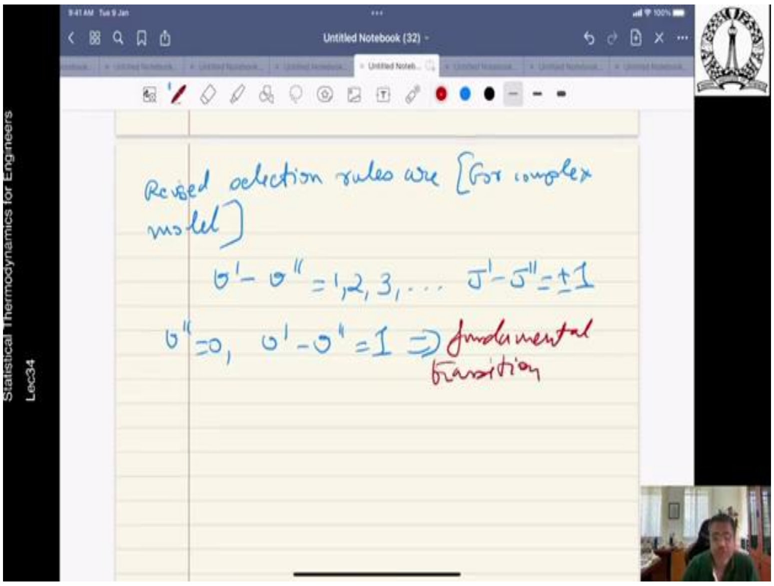


$$\boxed{\begin{aligned} \mathcal{E}_{rv} &= G(v) + F_v(J) \\ &= \omega_e\left(v+\tfrac{1}{2}\right) - \omega_e x_e\left(v+\tfrac{1}{2}\right)^2 \\ &\quad + B_v J(J+1) - D_e J^2(J+1)^2 \end{aligned}}$$

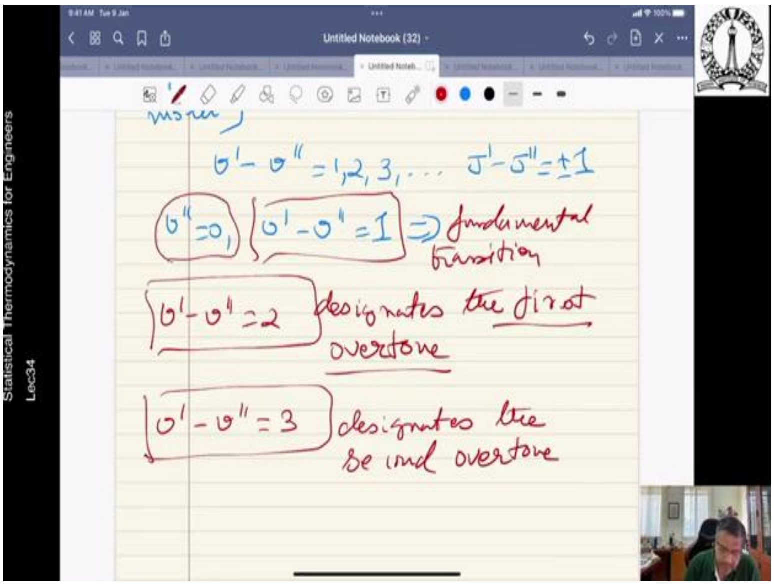
Further more for anharmonic oscillator, vibrational selection rule is no longer limited to our previous $\Delta v = \pm 1$



Revised selection rules are [for complex model]

$v' - v'' = 1, 2, 3, \ldots \qquad J' - J'' = \pm 1$

$v'' = 0, \quad v' - v'' = 1 \Rightarrow$ fundamental transition



$v' - v'' = 1, 2, 3, \ldots \quad J' - J'' = \pm 1$

$\boxed{v'' = 0,}\ \boxed{v' - v' = 1} \Rightarrow$ fundamental transition

$\boxed{v' - v' = 2}$ designates the first overtone

$\boxed{v' - v'' = 3}$ designates the second overtone

Now, furthermore for anharmonic oscillator the vibrational selection rule is no longer limited to our previous analysis which showed that V would be equal to delta V would be plus minus 1, in fact we should now have some revised selection rules. So, the revised selection rules are are for the complex model will be V Prime minus V double Prime equal to 1, 2, 3 dot, dot, dot(())(3:48) J prime J double Prime is equal to plus minus 1.

So that V double Prime equal to 0, then V Prime minus V double Prime equal to 1, this designates fundamental transition. On the other hand V Prime minus V double Prime is equal to 2 this designates the first overtone. And V Prime minus V double Prime equal to 3 designates the second overtone. So, now so you can see that these are so one is a fundamental transition these are what we call the first and the second overtones for V double Prime is equal to 0.

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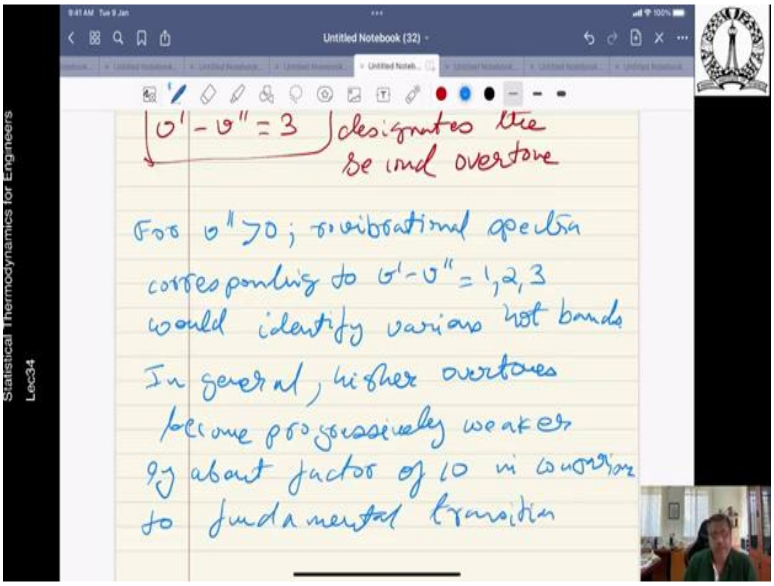
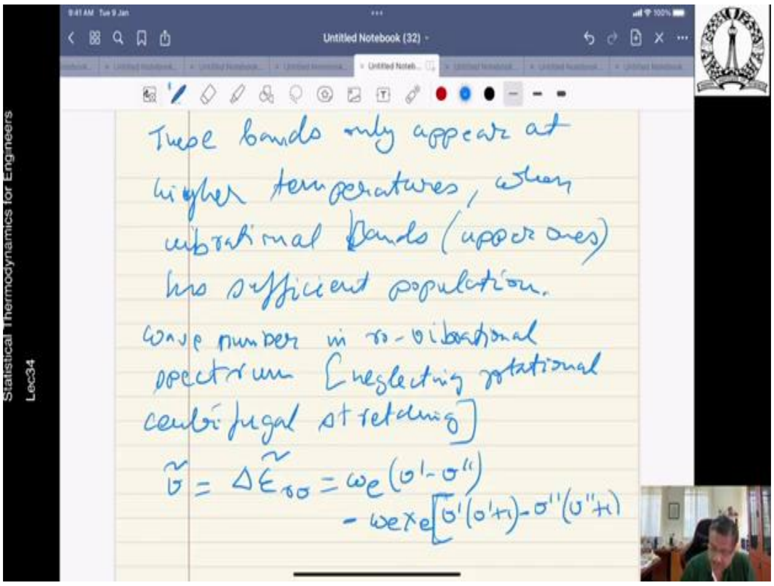


$\boxed{v' - v'' = 3}$ designates the second overtone

For $v'' > 0$; ro-vibrational spectra corresponding to $v' - v'' = 1, 2, 3$ would identify various hot bands

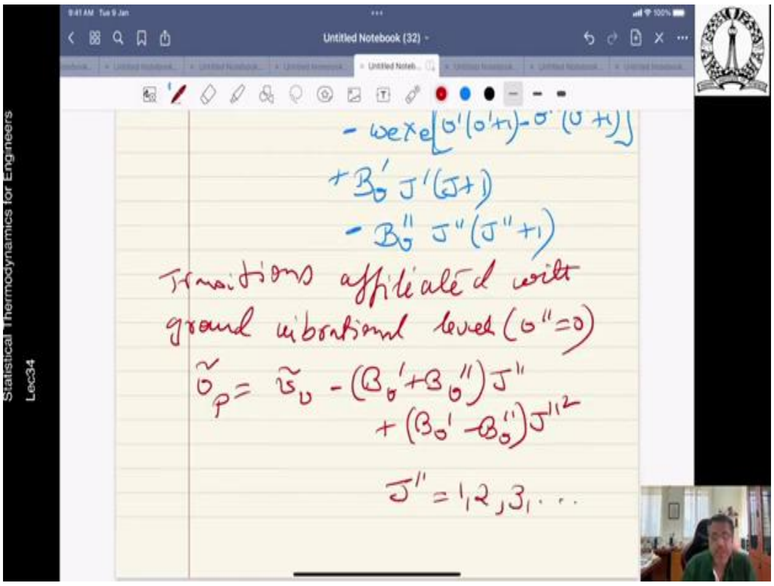
In general, higher overtones become progressively weaker by about factor of 10 in comparison to fundamental transition



These bands only appear at higher temperatures, when vibrational bands (upper ones) has sufficient population.

Wave number in ro-vibrational spectrum [neglecting rotational centrifugal stretching]

$$\tilde{v} = \Delta\tilde{E}_{rv} = \omega_e (v' - v'') - \omega_e x_e [v'(v'+1) - v''(v''+1)$$



$$-\omega_e x_e[v'(v'+1)-v''(v''+1)]$$

$$+B_v' J'(J'+1)$$

$$-B_v'' J''(J''+1)$$

Transitions affiliated with ground vibrational level ($v''=0$)

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

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

Now, for or V double Prime greater than 0 a ro-vibrational spectra corresponding to into V Prime minus V double Prime equal to 1, 2, 3 would identify by the various hot bands, it designate the various hot bands. In general so why they are called hot bands we will come a little later, in general higher overtones become progressively weaker by about factor of 10 one order factor of 10 in comparison to fundamental transition.

As the name implies these are called hot bands, because they only appear at high temperature, these bands only appear at higher temperatures when there is significant population is generated, then upper vibrational bands upper ones, upper vibrational bands has sufficient population. So, in for the Simplicity we can also neglect the rotational centrifugal stretching, because this complication is open minor in comparison to the remaining contributions.

So, therefore the wave numbers in any ro vibrational spectrum the wave numbers in ro vibrational spectrum this is assumed neglecting rotational centrifuging stretching is dealta e(())(8:35) Rv is equal to omega e, V Prime minus V double Prime minus omega e xe plus 1 minus V double Prime plus 1 plus Bv time J Prime J plus 1 minus Bv double Prime J double prime plus J double prime plus 1.

So, that transitions for those transitions which are associated with V Prime equal to 0 that means ground or at a slighted form of the transitions affiliated with ground vibrational level which is V double Prime is equal to 0 therefore becomes this is for the P branch ES two double prime plus 2 J double Prime equal to one two three similarly for the r branch minus Bv prime plus Bv J double Prime Plus J double Prime equal to 1, 2, 3.

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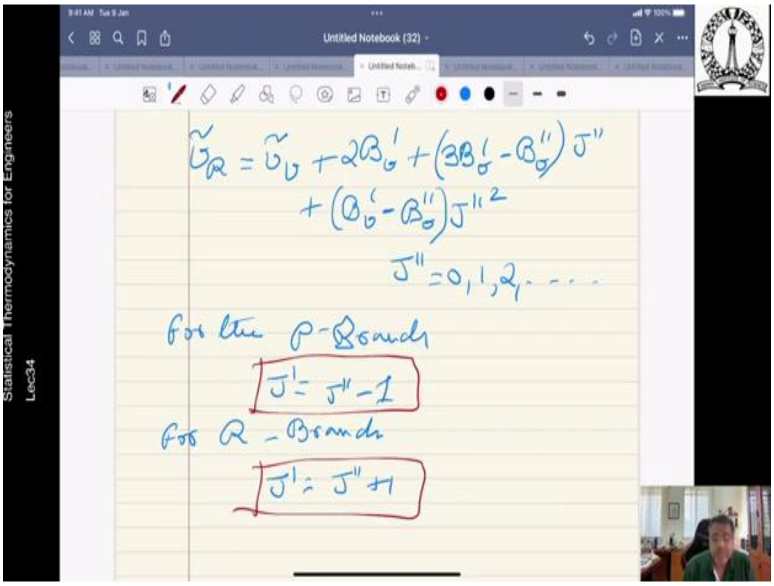


$$\tilde{\nu}_R = \tilde{\nu}_v + 2B_v' + (3B_v' - B_v'')J'' + (B_v' - B_v'')J''^2$$

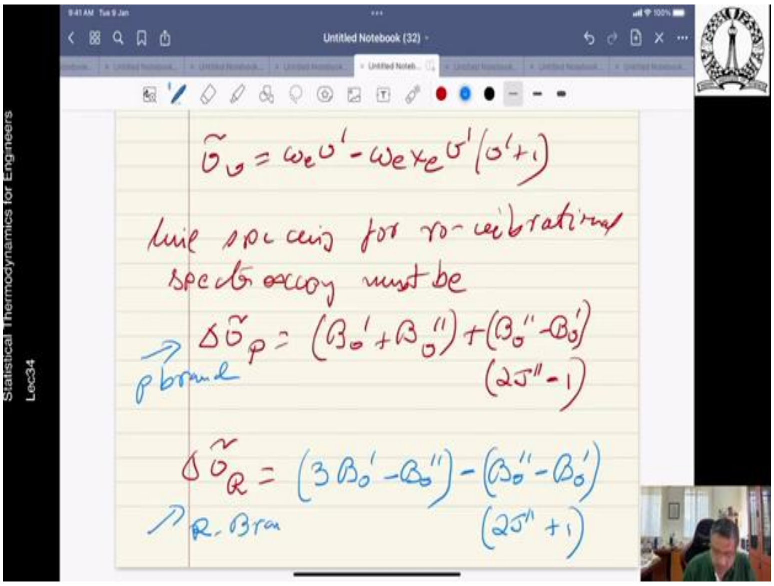
$$J'' = 0, 1, 2, \ldots$$

for the P-Branch

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

For R - Branch

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



$$\tilde{\nu}_v = \omega_e v' - \omega_e x_e v'(v'+1)$$

line spacing for ro-vibrational spectroscopy must be

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

↗ P branch

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

↗ R. Bra

Similarly, for the R branch, V R is equal to V plus 2 B v Prime plus 3 Bv prime minus B double Prime J double Prime plus B v Prime minus B v double Prime J double prime square and J double prime is equal to 0, 1, 2. So, for the P branch J prime is equal to J double prime minus 1. For R branch J prime is equal to J double prime plus 1 respectively.

So, you can see that if you compare it with the Simplex model the rotational energy is either added or subtracted from a pure vibrational contribution specified in this case. So, the basis of this the lines spacing for ro vibrational spectroscopy must be this is the line spacing for the P branch and for the R branch B and this is for the P branch, and this is for the R branch.

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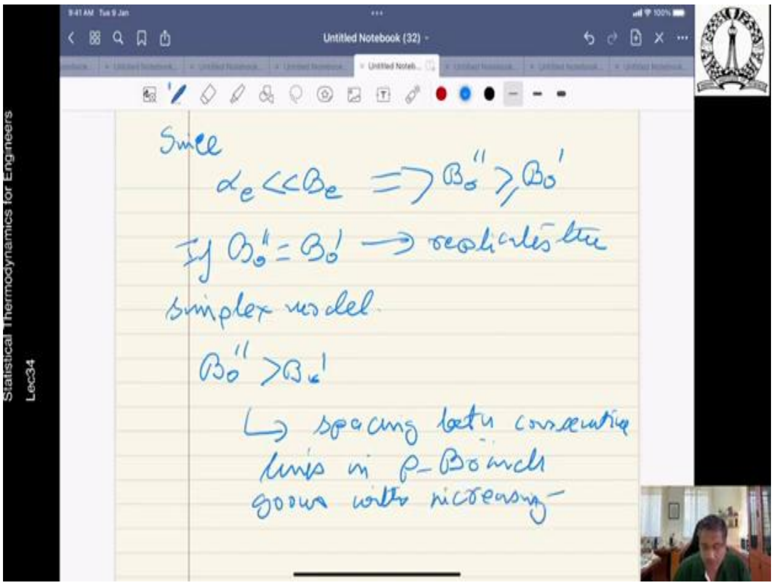


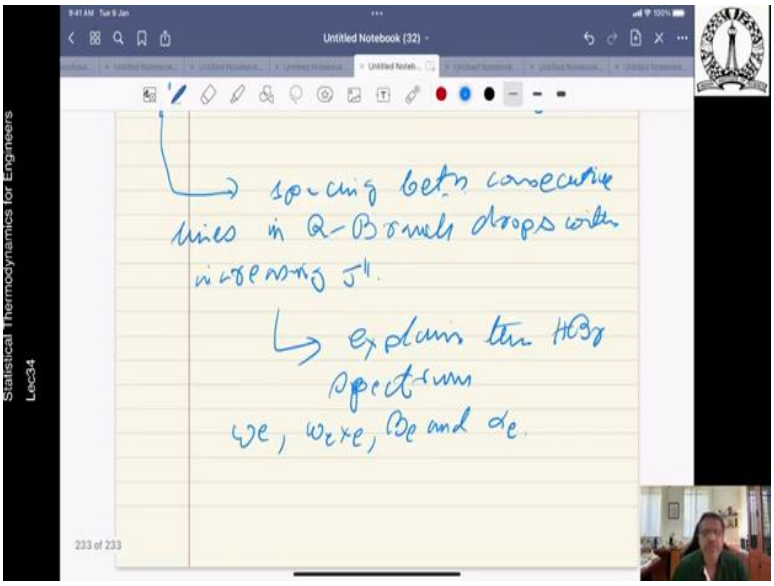
Since

$\alpha_e << B_e \Rightarrow B_0'' \geq B_0'$

If $B_0'' = B_0'$ → replicates the simpler model.

$B_0'' > B_0'$

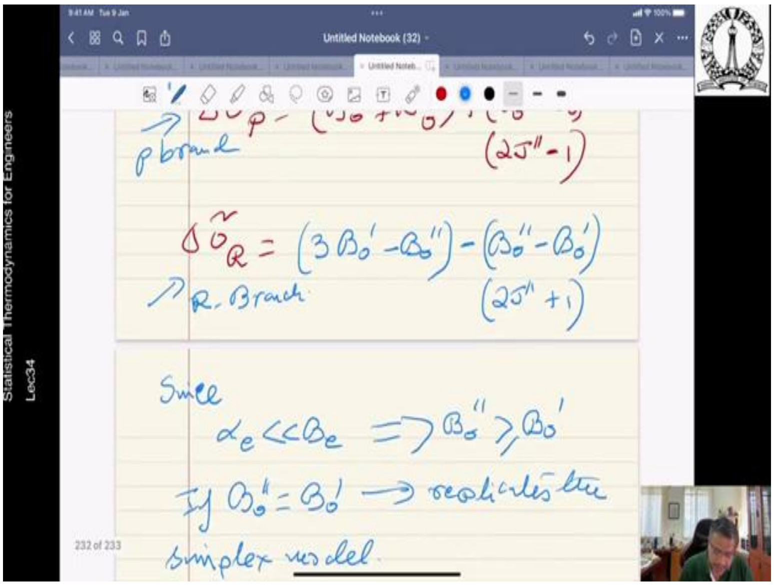
↳ spacing betn consecutive lines in P-Branch grows with increasing



↳ spacing betn consecutive lines in Q-Branch drops with increasing J''.

↳ explains the HBr spectrum

ω_e, $\omega_e x_e$, B_e and α_e.



P branch $(2J''-1)$

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

R. Branch

Since

$\alpha_e << B_e \Rightarrow B_0'' \geq B_0'$

If $B_0'' = B_0' \rightarrow$ replicates the simplex model

Now, since alpha e is much much less than B e we can conclude we can show that Bv double Prime is greater than equal to Bv Prime. If your Bv double Prime is equal to Bv Prime this basically replicates the Simplex model. If on the other hand Bv double Prime is greater than Bv Prime in the case then this actually says that the spacing between consecutive lines in P branch grows with increasing J double prime.

Also from the second expression if you look at this now this will imply that the spacing between consecutive lines in R branch in drops with increasing J double Prime. So, this is actually explains the HBR spectrum of Y-12, this explains the HBR Spectrum that we do earlier Spectrum by using all these square fits we can actually with the infrared Spectrum as we know that it is infrared dominant we can determine various structural parameters like omega e xe and alpha e. So, all this can be determined by just clicking on this square feet.

So, but this explains the Spectrum this is a model in which you can actually this model remember comes from the Morse potential by a power series expansion of the Morse potential we will skip the math, but these are the selection rules which now actually says that what advantages of the R branches of this particular series is all about. So, this takes us so now you can do sample problems which are also given in the book, so that we will cover in the tutorial part of this particular lecture.

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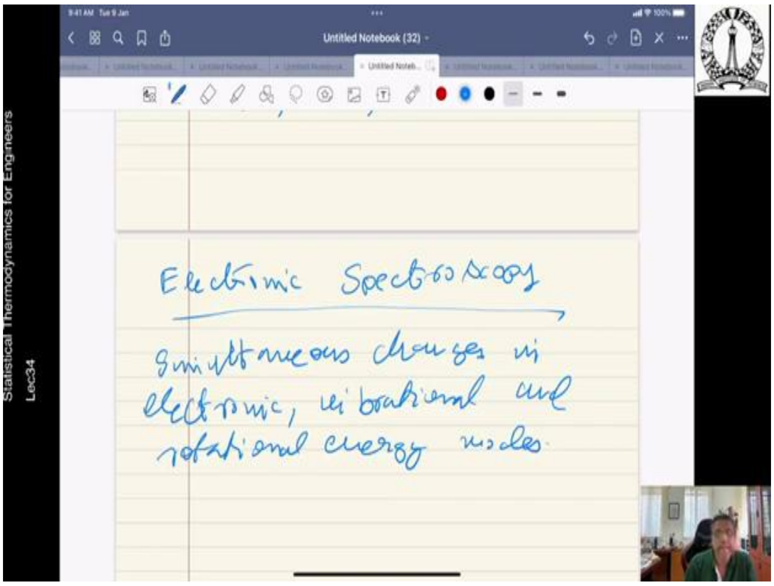
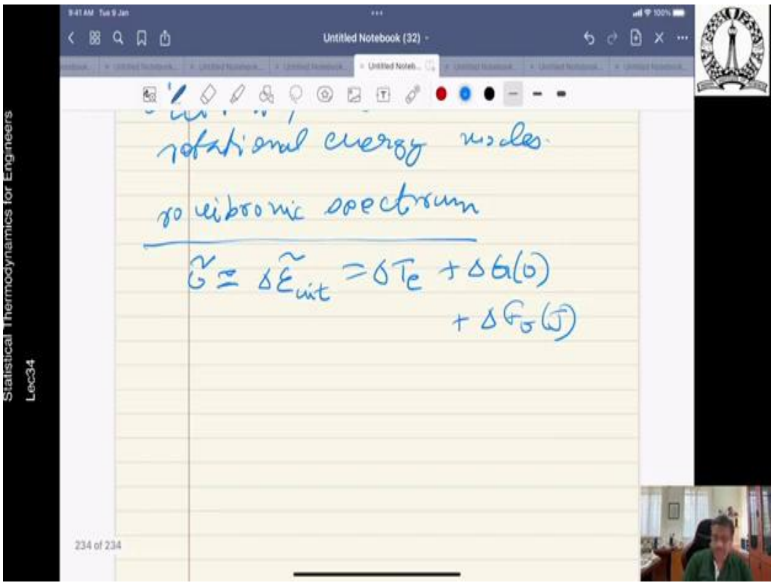


Electronic Spectroscopy

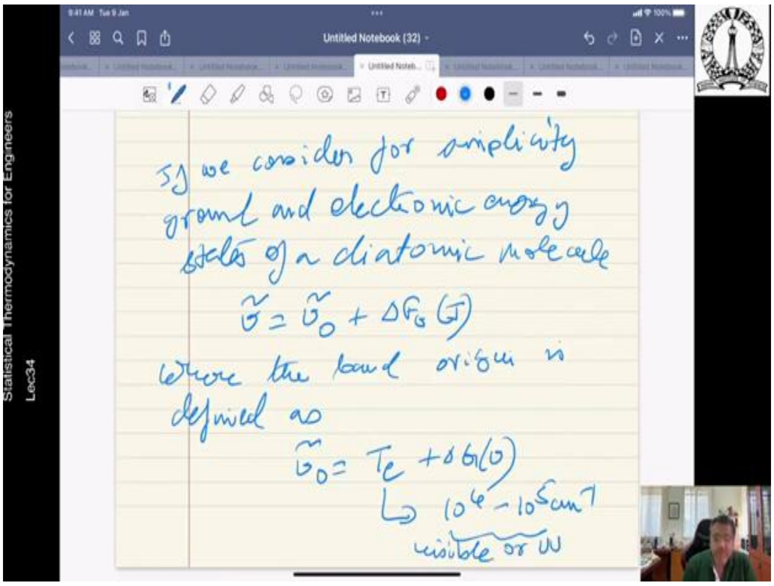
Simultaneous changes in electronic, vibrational and rotational energy modes.



rotational energy modes.

ro vibronic spectrum

$$\tilde{\nu} = \Delta\tilde{E}_{int} = \Delta T_e + \Delta G(v) + \Delta F_v(J)$$



If we consider for simplicity ground and electronic energy states of a diatomic molecule

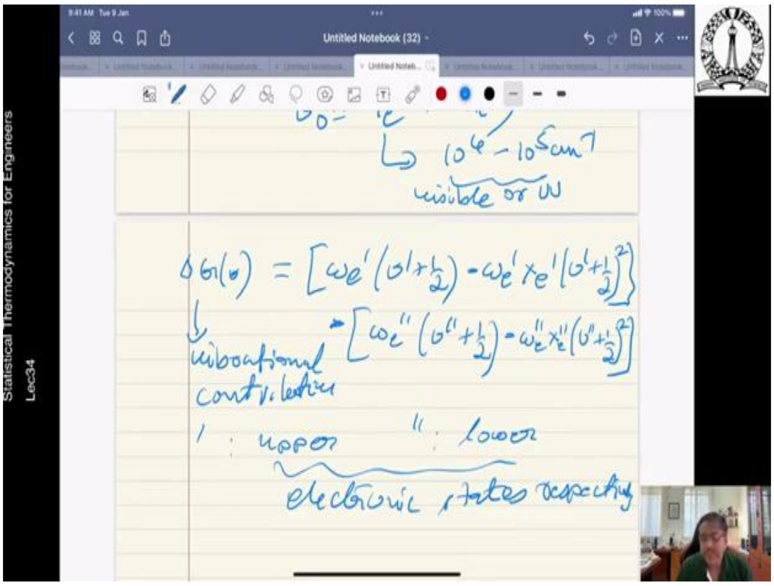
$$\tilde{\nu} = \tilde{\nu}_0 + \Delta F_v(J)$$

where the band origin is defined as

$$\tilde{\nu}_0 = T_e + \delta G(v)$$

$\hookrightarrow 10^4 - 10^5\ cm^{-1}$

$\underbrace{\text{visible or UV}}$



$\hookrightarrow 10^4 - 10^5\ cm^{-1}$

visible or UV

$$\Delta G(v) = \left[\omega_e'\left(v'+\frac{1}{2}\right) - \omega_e' x_e'\left(v'+\frac{1}{2}\right)^2\right] - \left[\omega_e''\left(v''+\frac{1}{2}\right) - \omega_e'' x_e''\left(v''+\frac{1}{2}\right)^2\right]$$

$\downarrow$ vibrational contribution

$'$: upper $''$: lower

$\underbrace{\qquad}$ electronic states respectively

We will move on to something which is called Electronics spectroscopy, now this is a little bit more complicated because now we have simultaneous changes in electronic, vibrational and rotational energy modes, we have simultaneous changes in electronic, vibrational and rotational energy modes.

So, now we will this ro vibronic spectrum, so for the ro vibronic spectrum, the change in internal energy is therefore given as delta Te Plus delta Gv delta F J, so the three terms represent the variation in the electronic vibrational and the rotational energies respectively.

Now, the shift in vibration and energy now depends both on the lower and the upper electronic energy levels, the same applies to the rotation of energy also, this depends moreover this change depends on both the lower and the upper vibration energy levels, in addition because you have this transition type of moment controlling the ro vibrational transitions even for symmetric molecules like oxygen and nitrogen you have electronic spectra.

So, now we consider for simplicity the ground and the excited electronic states of a diatomic molecule that can be written as J, so that is it ground and excited electronic states of a simple diatomic molecule where the band origin is defined as is defined as this, the band origin is dominated by about Te 10 to the power 4, 10 to the power 5 centimetre inverse, this corresponds to visible or UV, in the part of the spectrum.

So, therefore the vibrational contribution or delta Gv vibrational contribution can be written as omega e prime plus half square minus omega e double Prime plus half minus omega e double Prime xe double Prime v double Prime plus half square this(())(20:45) but the single and the double primes refers to the spectral parameters affiliated with the upper and the lower electronic states respectively, upper double Prime is a lower electronic states respectively. So, this refers to the upper and the lower electron states respectively.

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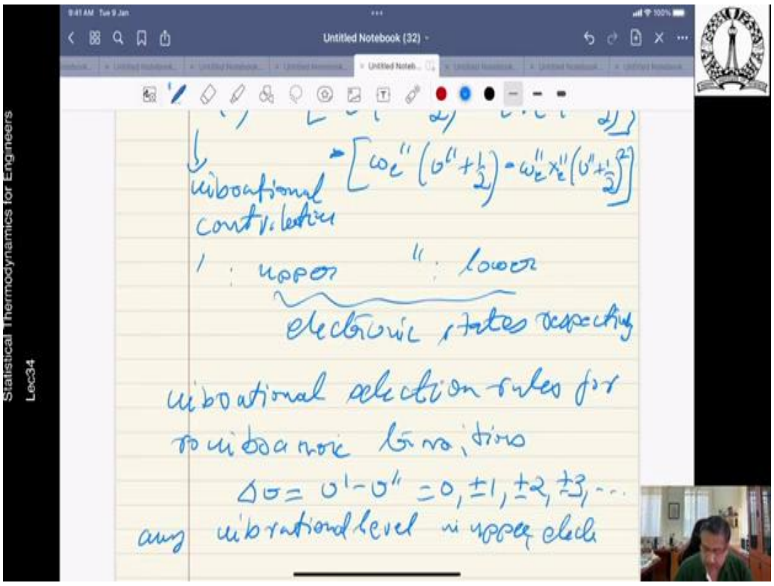


vibrational contribution

$$-\left[\omega_e''\left(v''+\frac{1}{2}\right)-\omega_e''x_e''\left(v''+\frac{1}{2}\right)^2\right]$$

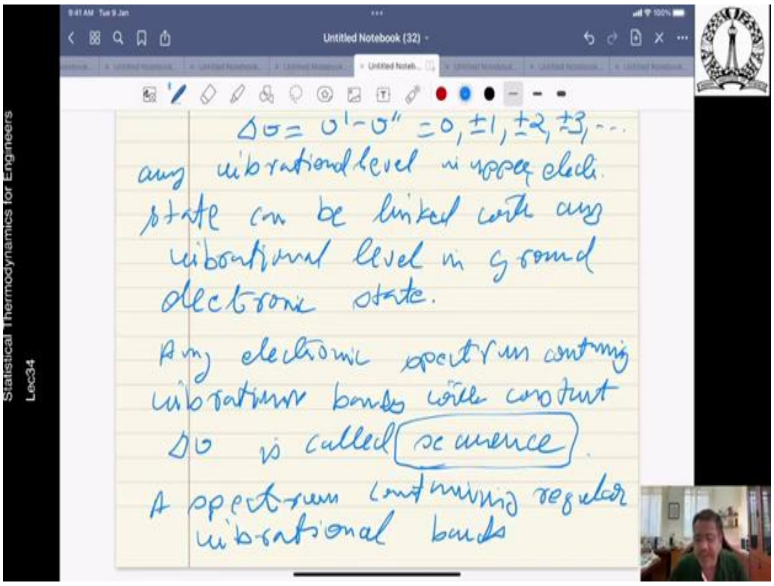
' : upper '' : lower

electronic states respectively

vibrational selection rules for rovibronic transitions

$$\Delta v = v'-v'' = 0, \pm 1, \pm 2, \pm 3, \ldots$$

any vibrational level in upper elec

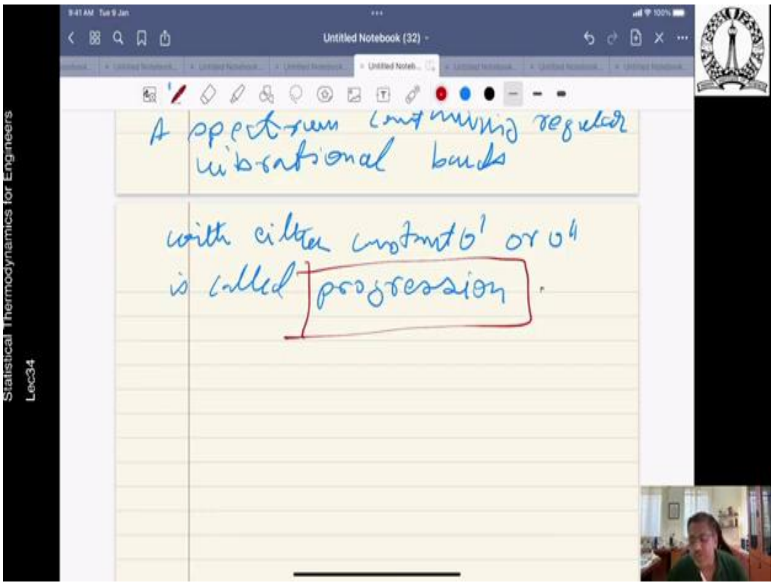


$$\Delta v = v' - v'' = 0, \pm 1, \pm 2, \pm 3, \ldots$$

any vibrational level in upper elec. state can be linked with any vibrational level in ground electronic state.

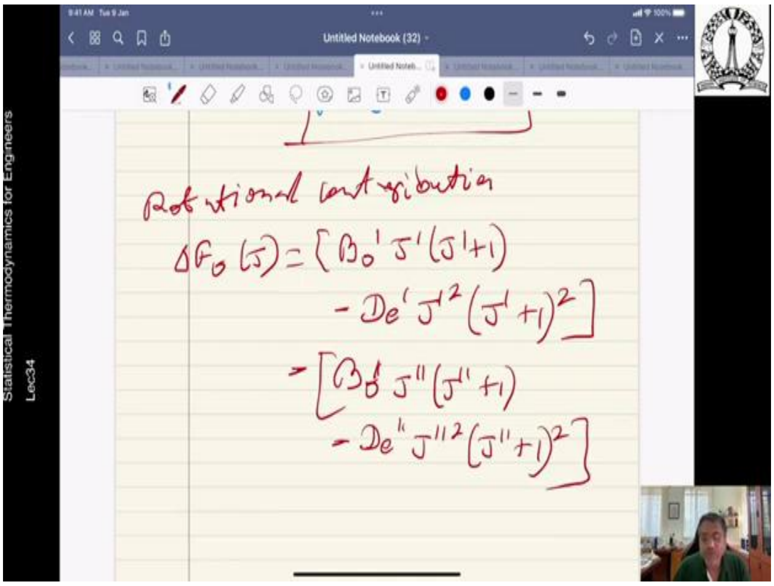
Any electronic spectrum containing vibrational bands with constant Δv is called $\boxed{\text{sequence}}$.

A spectrum containing regular vibrational bands



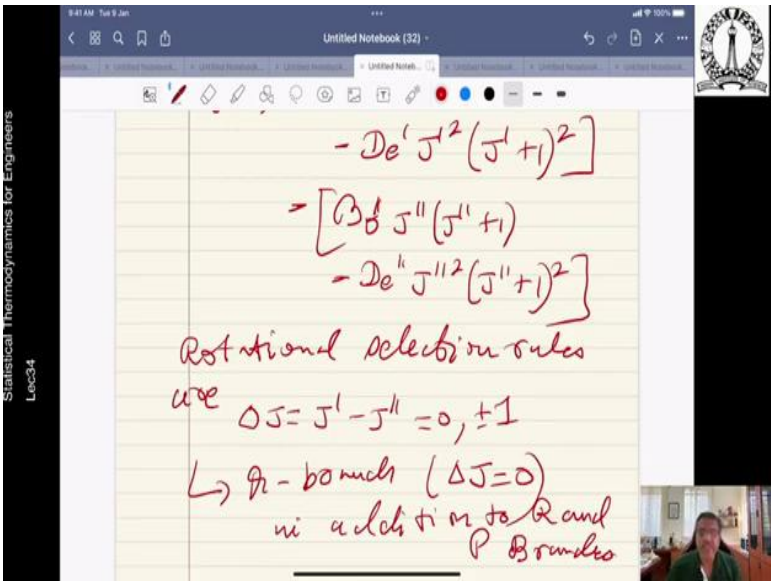
A spectrum containing regular vibrational bands

with either constant v' or v'' is called $\boxed{\text{progression}}$.



Rotational contribution

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



$$- D_e' J'^2 (J'+1)^2 \Big]$$

$$- \Big[B_0'' J''(J''+1) - D_e'' J''^2 (J''+1)^2 \Big]$$

Rotational selection rules are $\Delta J = J' - J'' = 0, \pm 1$

↳ Q - branch $(\Delta J = 0)$ in addition to R and P Branches

Analogous to the ro vibrational transitions now the selection rule the vibrational selection rules for ro vibronic transitions, delta v is 0 plus minus 1, plus minus 2, plus minus 3. So, any vibrational level in an upper electronic state can be linked with any vibrational level in the ground electronic state. So, any vibrational level in the upper and that is why you have the 0 plus minus 1 and plus minus 2 etc.

So, any vibrational level in upper electronic state can be linked with any vibrational level in ground electronic state, in particular an electronic spectrum containing vibrational bands with constant delta V is called a sequence and a spectrum containing regular vibrational bands with either constant V prime or V double Prime is called a progression, it is called a progression and the other one is called as.

So, just to make sure that what we call that any electronic spectrum containing vibrational bands with constant instant delta V is called sequence a spectrum containing regular vibrational bands and regular vibrational bands and spectrum containing regular vibrational bands with either constant V prime or V double Prime is called progression.

So, such sequences and progression are best understood if we use an energy level diagram which we will do in the next class. But so the ro vibrational we can write down to the rotational contribution is before we draw the diagram the rotational contribution as delta F b J is equal to Bv prime J Prime J plus 1 minus De Prime J prime square, again the double Prime and the single Prime refers to the upper and the lower electronic states respectively.

In comparison to the ro vibrational case the rotational selection rules are delta J 0 plus minus 1. So, we now entertain the possibility of a Q branch also, so there could be a possibility for a Q Branch which is basically delta J equal to 0 is possible, in addition to R and P branches. So, we will discuss more of this in the next class where we will also draw the energy level diagram also to explain sequence and progression in more details. So, let us stop here in the next class we will pick it up from here.