

Statistical Thermodynamics for Engineers
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Lecture 43
Ro-vibrational Spectroscopy (Simplex model)

So, welcome to lecture number 32 of the Statistical Thermodynamics for Engineers. In this particular class now we are going to look at, we started looking at the vibrational spectrum and we know the fundamental vibrational frequency that is associated. Now, we are going to look at what happens to the, and we also saw that this fundamental vibrational wave that leads to the knowledge of the bond strength for a diatomic molecule.

So, but however we also know that if you are dealing with a homonuclear diatomics because the oscillations, the vibrational transition leads to radial gradients in that electric dipole moment during the harmonic oscillations. So, generation of such moments or such gradients and impossible but symmetric molecules which is in this case homonuclear diatomics because they are symmetric and they offer no spectral signatures owing to the molecular vibration.

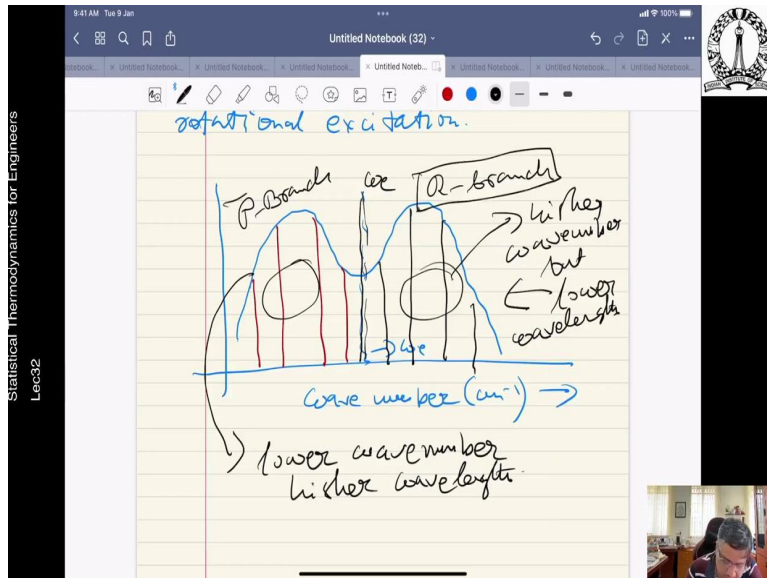
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Now we also note that
 $\omega_e \gg B_e$
↳ excessive energy accompanying vibrational motion would automatically lead to rotational excitation.

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Now, we, now, we also note also note that w_e is much, much greater than B_e . So, we might expect that the excessive energy, energy accompanying vibrational motion would automatically lead to the rotational excitation. So, if we now actually employ a spectrometer at a very high resolution we see actually not one single line but a multitude of lines when you are under, when we are doing the spectroscopy.

So, let us look at one such spectrum. So, let us see this, and if we look at it, it will resemble something like that. So, this is in the wave number or centimeter inverse, this way. This is the central, which is basically ω_e . Now, here you will see a kindred of lines. Here, we will see another set of lines. So, this is called the P-Branch. We will come to that what they are, this is called the R-branch, and this is ω_e .

So, if you employ a spectrometer with a very high resolution, high grading, you will find that there is no one single fundamental line like the one here but you see a kindred of lines, as indicated by this particular figure, rather two groups of lines. This is one group, this is the other group, on the both sides of a fundamental wave number.

The group of lines at lower wave numbers, so these are group of lines lower wave number which means higher wavelength, they are called the P-Branch while this which happens at higher wave number, higher wave number but lower wavelengths, lower wavelengths, so this is called the R-branch. This is called the P-branch and this is called the R-branch.

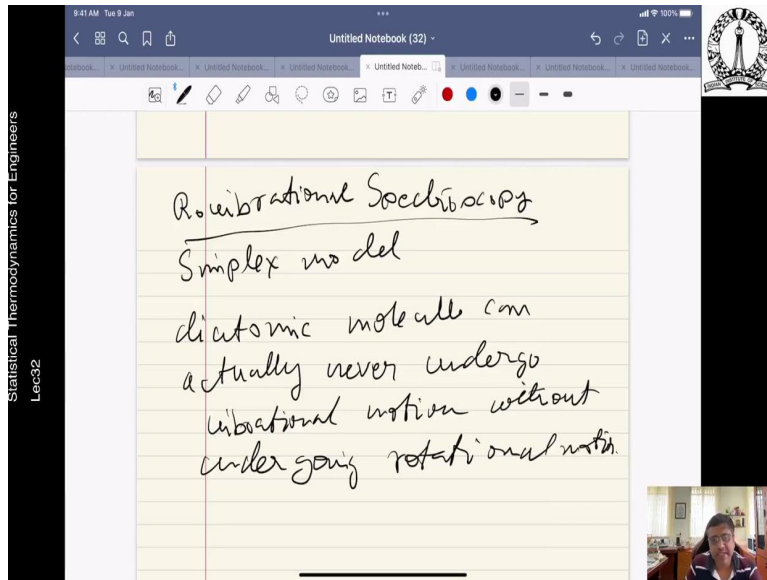
The tip between the two branches is still centered around the vibrational wavelength. However, simultaneous excitation of rotational motion eliminates this anticipated vibrational frequency in favor of the replacement signatures on both sides. So simultaneous excitation of the rotational motion eliminates this fundamental frequency, that is what we mean.

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Ro-vibrational Spectroscopy
Simplex model

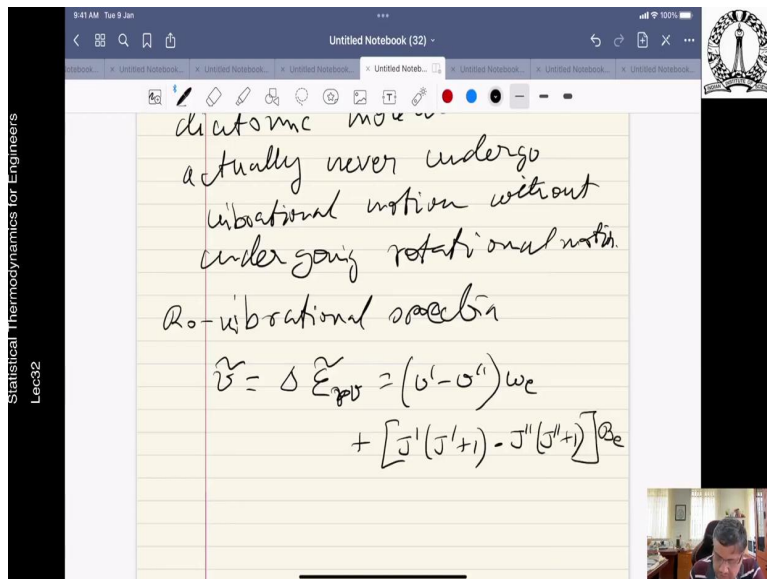
diatomic molecule can actually never undergo vibrational motion without undergoing rotational motion.



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diatomic molecule can actually never undergo vibrational motion without undergoing rotational motion.

Ro-vibrational spectra

$$\tilde{\nu} = \Delta \tilde{E}_{rov} = (\nu' - \nu'') \omega_e + [J'(J'+1) - J''(J''+1)] B_e$$


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$$\tilde{\nu} = \Delta \tilde{E}_{rov} = (\nu' - \nu'')\omega_e + [J'(J'+1) - J''(J''+1)]B_e$$

conjoined rigid rotor - harmonic oscillator model.

for the simplex model

$$\nu' - \nu'' = 1$$

$$J' - J'' = \pm 1$$

So, let us do something called Ro-vibrational spectroscopy, which is also called the Simplex model. So, in the Simplex model, the vibrational and the rotational energies must be additive. So, a diatomic molecule can actually never undergo vibrational motion without also undergoing rotational motion. So, a diatomic molecule, diatomic molecule can actually, actually never undergo vibrational motion, vibrational motion without undergoing rotational motion. And the rotational and the vibrational energies must be additive, therefore producing the Ro-vibrational spectrum.

So, the Ro-vibrational spectrum is given as this, ν' , this ν' , you have ν' prime ν' double prime ω_e plus J' prime into J' prime plus 1 minus J'' double prime J'' double prime plus 1 into B_e . So, this is like a conjoined, conjoined rigid rotor, rigid rotor slash harmonic oscillator model. Again, the signal prime and the double prime refers to the upper and lower vibrational levels, respectively. And it is used, even when used to identify the rotational quantum numbers within each vibrational band. So, for this Simplex model, the rules are, the selection rules are still the same, still the same. So, we obtain two separate cases corresponding to ΔJ plus minus 1 whether for absorption or for emission. So, for clarity, we can draw a diagram like this.

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$J' - J'' = \pm 1$

ψ'

ψ''

$J' = 3$

$J' = 2$

$J' = 0$

$J'' = 3$

$J'' = 2$

$J'' = 0$

P -branch

R -branch

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$J'' = 3$

$J'' = 2$

$J'' = 0$

ψ''

P -branch

R -branch

$J' = J'' - 1$

$J' = J'' + 1$

$\tilde{\nu}_P = \omega_e - 2B_e J'' \quad J'' = 1, 2, 3, \dots$

$\tilde{\nu}_R = \omega_e + 2B_e (J'' + 1) \quad J'' = 0, 1, 2, \dots$

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$\tilde{\nu}_P = \omega_e - 2B_e J''$ $J'' = 1, 2, 3, \dots$
 $\tilde{\nu}_R = \omega_e + 2B_e (J'' + 1)$ $J'' = 0, 1, 2, \dots$

Spectral line spacing for both branches

$$\Delta \tilde{\nu}_P = \Delta \tilde{\nu}_R = 2B_e$$

So, let us put the vibration, let me write, so J' double prime equal to 0, J' double prime equal to 2, J' double prime 3, and then of course, so this is J' prime equal to 3, J' prime equal to 2, J' prime equal to 0. And this is one G 1. So, this is a typical, typical thing that you have. So, the allowable things, if I put it properly $J' = 2$ to $J' = 3$, $J' = 1$ to $J' = 2$ is allowed, $J' = 0$ to $J' = 1$ is also allowed. So, then if we put it in location. So, this is actually the P-Branch. We will see, sub shells.

J' double prime equal to 0, 2, 1. There is one possibility, then other possibility of course. This is the third possibility. So, this is how a typical Ro-vibrational spectrum would actually look like. So, P-Branch refers to the case where J' prime is equal to J' double prime minus 1, where R-branch refers to the case where J' prime equal to J' double prime plus 1, plus 1. So, these are the two corresponding spectral lines.

So, using this particular situation, so the wave number for the P-Branch is $\omega_e - 2B_e J'$ double prime, J' double prime equal to 1, 2, 3, dot, dot, dot. And of course, you have the R-Branch which is $\omega_e + 2B_e (J' + 1)$. This is utilizing that the substitutions. And J' double prime is equal to 0, 1, 2, dot, dot, dot. So, the spectral line spacing, so the spectral line spacing, spacing for both branches, both branches is $\Delta \tilde{\nu}_P = \Delta \tilde{\nu}_R = 2B_e$.

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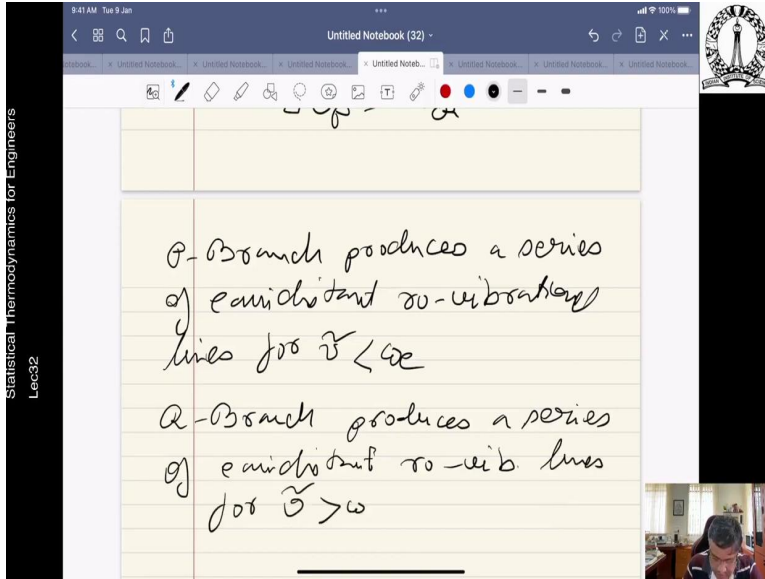
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Q-Branck produces a series of equidistant ω -vibrational lines for $\tilde{\nu} < \omega_e$

Q-Branck produces a series of equidistant ω -vib lines for $\tilde{\nu} > \omega_e$



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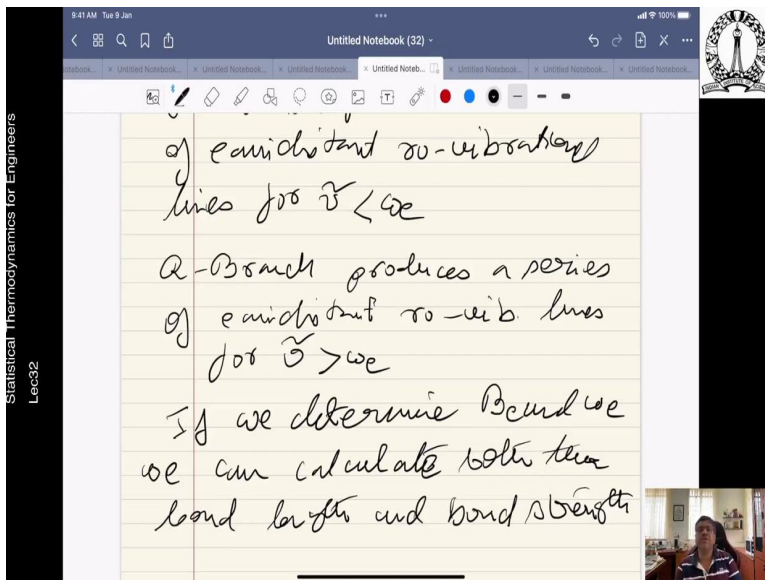
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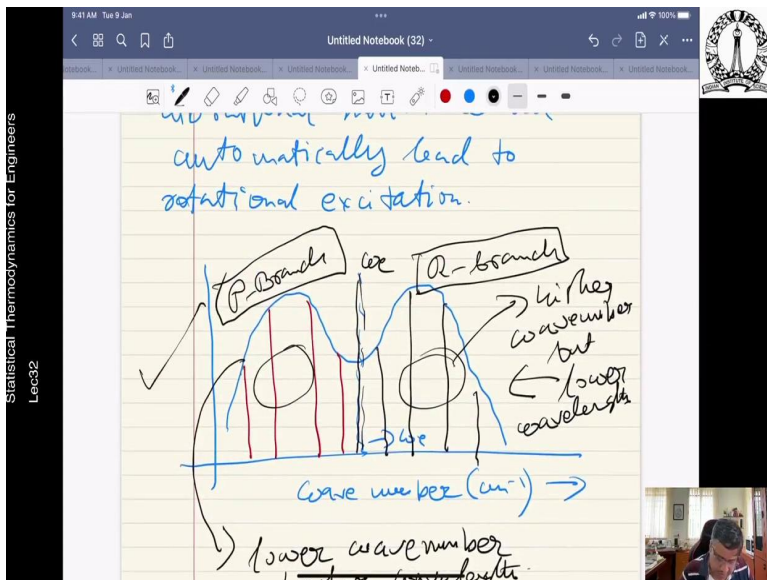
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Q-Branck produces a series of equidistant ω -vibrational lines for $\tilde{\nu} < \omega_e$

Q-Branck produces a series of equidistant ω -vib lines for $\tilde{\nu} > \omega_e$

If we determine B and ω_e we can calculate both the bond length and bond strength.





P-branches R-branches

$$J' = J'' - 1 \qquad J' = J'' + 1$$

$$\tilde{\nu}_P = \omega_e - 2B_e J'' \qquad J'' = 1, 2, 3, \dots$$

$$\tilde{\nu}_R = \omega_e + 2B_e J'' \qquad J'' = 0, 1, 2, \dots$$

Spectral line spacing for both branches

$$\Delta \nu_P = \Delta \nu_R = 2B_e$$

So, we can see that therefore the P-Branch, P-Branch produces, produces a series, series of equidistant, equidistant Ro-vibrational bands, Ro-vibrational lines or frequency less than omega e where R-Branch, R-Branch produces, produces a series of equidistant, equidistant, Ro-vibration, again, Ro-vibrational lines for greater than omega e. This is what we suggested in the figure. If you look at this particular figure, this is what was suggested there.

So, we also note that the, again, the fundamental pure vibrational frequency was missing because of the addition and subtraction of the rotational energy with respect to omega e. We have subtraction for addition of rotational energy, energy. So, so you can see that the second, so there is a subtractive and then there is an additive for the, for the two lines.

So, we can see right here therefore that the R-Branch and the P-Branch that produces lines which are of the two sides of the fundamental frequency. Furthermore, because rotational vibrational, Ro-vibrational spectroscopy encompasses both vibrational and rotational motion, if we just do a least square fit of the spectrum which we saw in figure 7.2 in the book or the spectrum that we showed over here, the P-Branch and the R-Branch of the spectrum. So, they would actually give us both the bond strength and bond length.

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for $\omega > \omega_e$

If we determine B_e and ω_e
we can calculate both the
bond length and bond strength

Rigorous notation

$$B_0(J'')$$

$B = P, R$

$B = P$ for a line in P Branch
 $B = R$ for a line in R Branch

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Rigorous notation

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$B = P, R$

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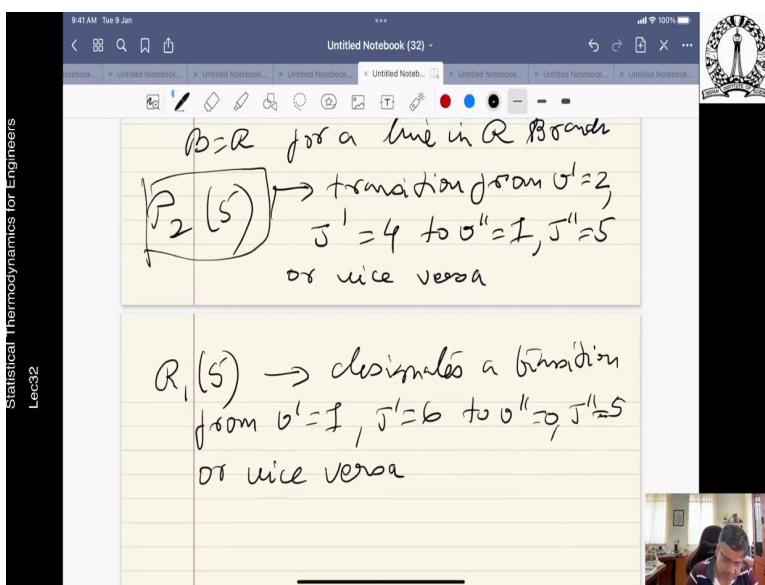
$P_2(5) \rightarrow$ transition from $v' = 2$
 $J' = 4$ to $v'' = 1, J'' = 5$
or vice versa

So, if we, if we determine B_e and ω_e , we can calculate, calculate both the bond length and bond strength. We can calculate both the bond length and the bond strength. From a more practical

perspective, when discussing a particular Ro-vibrational line, we must be able to describe it in an unequivocal fashion.

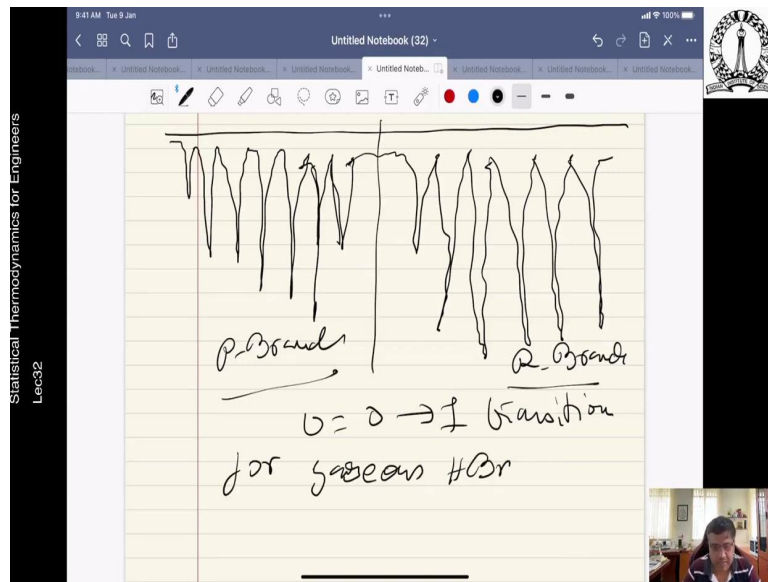
As a result of that we have developed this rigorous notation to rigorous notation to, rigorous notation, rigorous notation is $B' v' J'' = B v J$ or a line in P-Branch, where $B' = B$ in R-Branch. So, if we say it is $P_2 5$ let us say for example, it designates, what does it do? It designates a transition, transition from $v' = 2, J' = 4$ to $v'' = 1, J'' = 5$ or vice versa.

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Similarly, if we write $R_1 5$, this designates a transition, from $v' = 1, J' = 6, v'' = 0, J'' = 5$, or vice versa. So, this is what a P-line should look like, a sample, this is what an R-line should look like. So, this is more for a rigorous rotation of the Ro-vibrational spectroscopy that we see over here.

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So, let us look at a simple spectrum like this. So, also there in the book something like this. It is crudely drawn. It is also given in the book. These are very sharp lines actually. With a little bit of a width of the lines, we will state later why they are so. This is the P-Branch, R-Branch, designates v equal to 0 to 1 transition for gaseous HBr. So, this is the P-Branch, this is R-Branch, and this is where the fundamental kind of lies. So, it is on the both sides of the spectrum.

So, the only (17:16) here is that the Simplex model understates the inherent complexity of combined rotational and vibrational motion. So, if you look at that the, at this particular infrared spectrum which is figure 7.4 in the book, you will find that there is no, consistent with the Simplex model there is no pure vibrational line. The variations in line intensity again reflects analogous differences in rotational population.

However, in comparison, if you look at the results, the spacing between the lines drops as we move within the P-Branch closer to the fundamental frequency or fundamental wave number. And this spacing rises in the R-Branch as of the frequency approaches fundamental frequency. So, in Simplex model cannot really reproduce, because the lines are supposed to be equidistant.

So, it cannot really reproduce the actual positions for the various transitions in the rovibrational spectrum. So, this general result underscores the limitation of this combined rigid rotor and harmonic oscillator model. So, given this outlook, we need a more realistic model for the combined vibration or rotational motions of a diatomic molecule.

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P-Branch | R-Branch

$\nu = \nu_0 \rightarrow$ transition
for gaseous HBr

HBr spectrum indicates that
spacing betⁿ consecutive
spectral lines within P-Branch
drops as $\nu \rightarrow \omega_e$

So, for if the HBr spectrum, so just to form on the right, spectrum indicates, indicates that the spacing, and this is also Figure 7.4 in the book, spacing between consecutive spectral lines, spectral lines within P-Branch, P-Branch drops, drops as the as we approach, the frequency approaches are fundamental.

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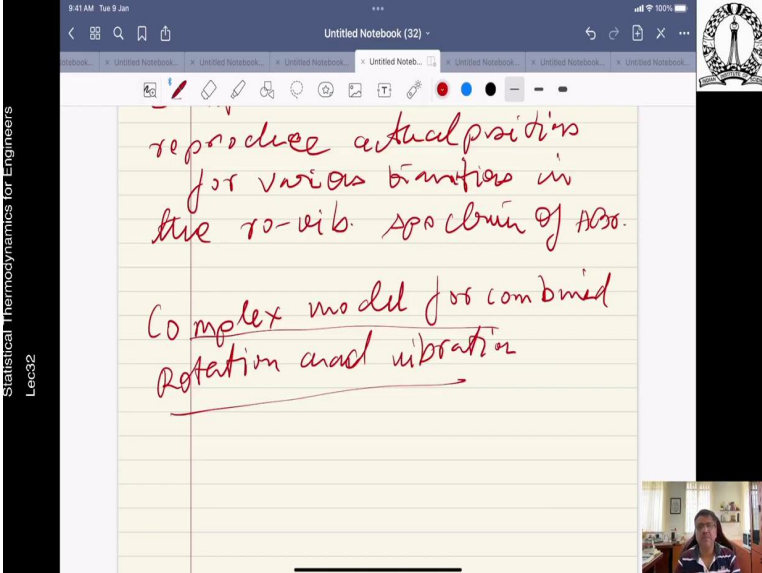
Similarly with in R-Branch
this spacing rises as $\nu \rightarrow \omega_e$

Simplex model cannot
reproduce actual positions
for various transitions in
the ro-vib spectrum of HBr.

Similarly, within R-Branch, this spacing rises as these approaches. So, the Simplex model, Simplex model cannot, cannot reproduce the spectrum, the actual positions for various transitions, in the Ro-vibrational spectrum of HBr. So, these results therefore states that the

combined rigid rotor and harmonic oscillator model is not a good example given this outlook. We need a more realistic model. Essentially, that is what it is. So, that is what that is what is needed over here.

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reproduce actual positions for various transitions in the ro-vib spectrum of ABO .

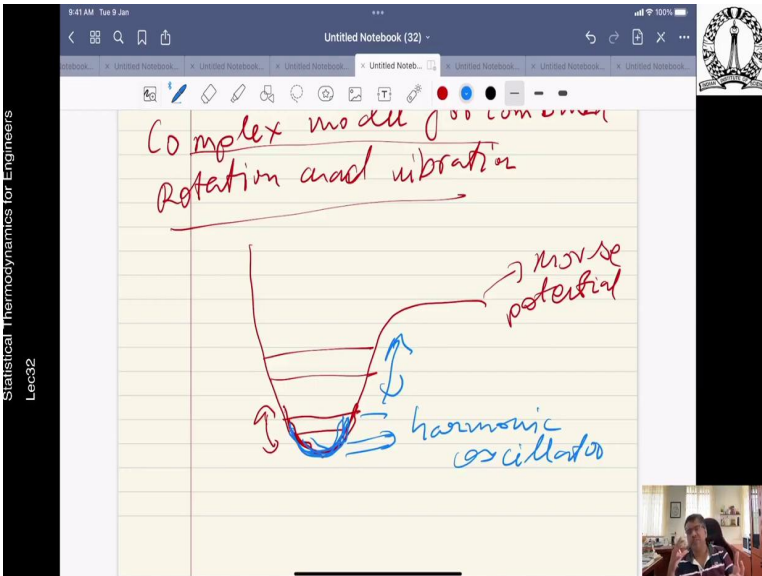
Complex model for combined rotation and vibration

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Complex model for combined rotation and vibration

Morse potential

harmonic oscillator

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So, we need what we call a complex model, complex model for combined rotation and vibration. We need a more complex model. But before doing that, you can work out, you can see the example in the book that where it says the Raman spectrum of a diatomic molecule can be investigated by excitation with a laser beam.

So, the spectrum results from Ro-vibration and modulation of the scattered laser intensity to produce the sidebands which is basically the salt around the laser frequency. And the Stokes component, we will see what the Stokes component is, but you can look at this example and you can apply the selection rules and you can work out. So, this will give us a good idea. So, we are not covering this in this particular lecture but you can take a look at it which is example number 7.1 in the book, Chapter 7.

So, but let us just do a little bit of a discussion on the Complex model, the Simplex model assumes complete separation of vibrational and rotational energy, complete separation. So, the vibration is modeled as a harmonic oscillator, rotation is modeled as a rigid rotor. But we recognize of course through the HBr spectrum that the line spacing which was supposed to be equidistant or not. So, their distance actually changes closer to R, closer to the fundamental wave number.

So, this model is therefore too simplistic. We also saw that the harmonic oscillator was a good approximation of the Morse potential only at lower vibrational energies, lower value. So, as we go on to higher vibration of energies, because this value is for a particular electronic level, so within that well as we go higher and higher, so you can look at it. So, it is only valid for this lower part, this part.

But the higher parts, it is not a good approximate, this is the Morse potential, if you recall. And this is where the harmonic oscillator did a good job, supposedly good job. So, this was the harmonic oscillator. So, the harmonic oscillator in itself did a good job only in the lower parts of the spectrum. It did not do, it did a very poor job at the upper part for the higher vibrational energies.

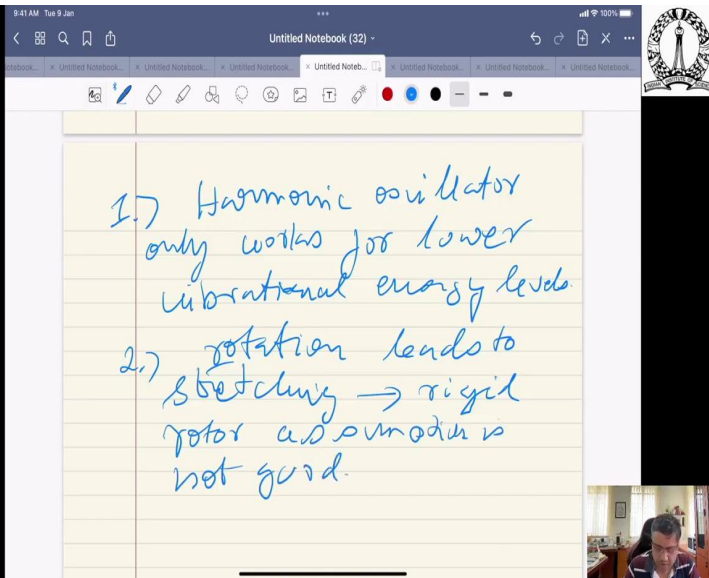
So, secondly by imagining the diatomic molecule as two masses linked with a string we also realize that a rotation will also lead to the stretching of this string. So, you will stretch the string also. So, this therefore makes a rigid rotor model virtually impossible. Thirdly, carrying this further, that enhanced vibration will also expand the mean bond length, thus affecting the movement of inertia that is required for rotation. So, in other words there is a coupling between the vibration and the rotational energy levels.

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1.) Harmonic oscillator only works for lower vibrational energy levels

2.) rotation leads to stretching \rightarrow rigid rotor approximation is not good.

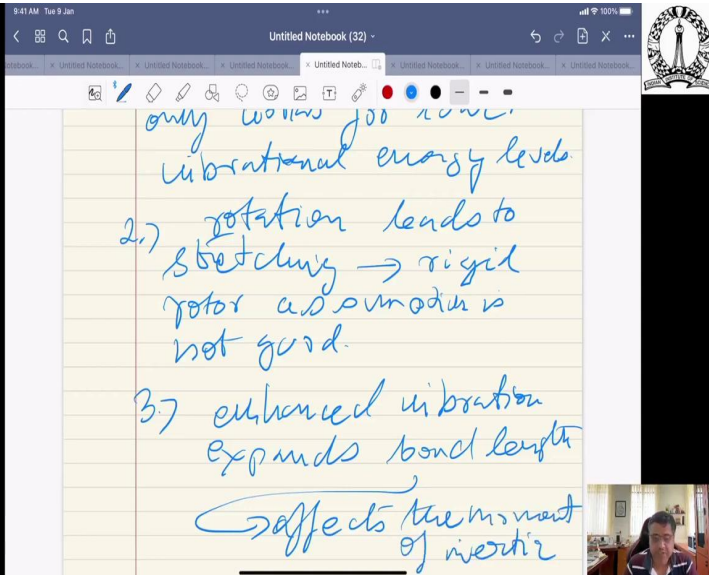


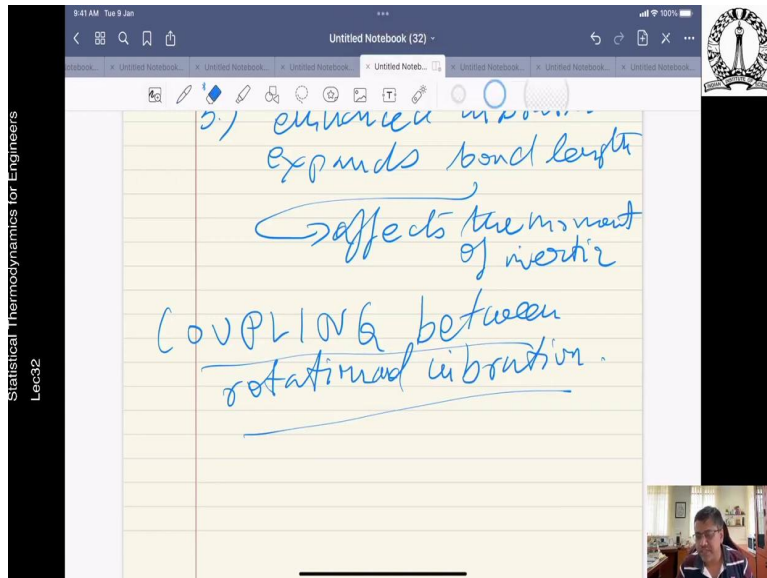
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only works for lower vibrational energy levels

2.) rotation leads to stretching \rightarrow rigid rotor approximation is not good.

3.) enhanced vibration expands bond length \rightarrow affects the moment of inertia





So, what are the three things? Let us write it down quickly. One is basically the harmonic oscillator, harmonic oscillator. Only works the works for lower vibrational energies, vibrational energy levels, energy levels. Second is rotation leads to stretching, leads to stretching, stretching. So, rigid rotor assumption is not good. And third point which is one of the biggest point is that enhanced vibration, vibration leads, expands the bond length, which further, which further affects the moment of inertia, affects the moment of inertia. So, there is coupling between, between rotation and vibration, which means what we need to address. There is inevitable coupling between rotation and vibration which is exactly what we need to clarify in the next lecture. Thank you.