Fundamentals of Spectroscopy

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Lecture-28
Ro – Vibrational Spectrum – II

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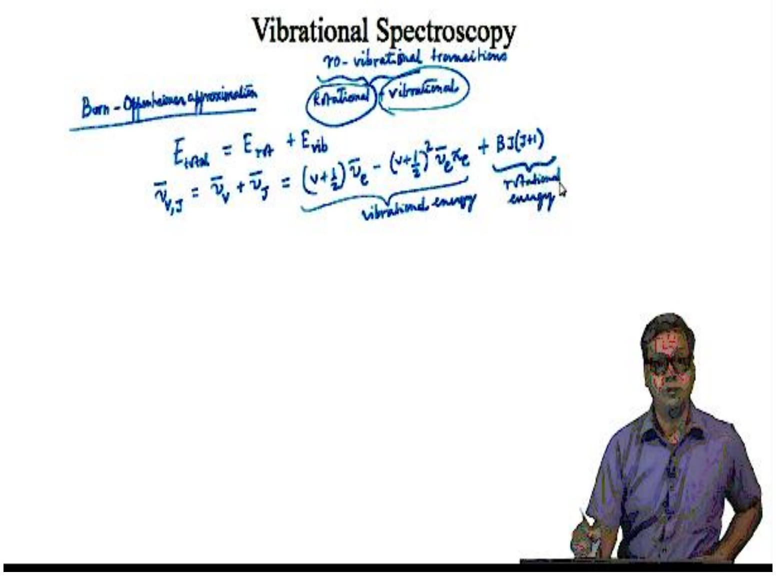

Vibrational Spectroscopy

ro- vibrational transitions

Rotational + vibrational

Born - Oppenheimer approximation

$$E_{total} = E_{rot} + E_{vib}$$

$$\bar{\nu}_{v,J} = \bar{\nu}_v + \bar{\nu}_J = \underbrace{\left(v+\frac{1}{2}\right)\bar{\nu}_e - \left(v+\frac{1}{2}\right)^2 \bar{\nu}_e x_e}_{\text{vibrational energy}} + \underbrace{BJ(J+1)}_{\text{rotational energy}}$$

Hello everyone, in the last lecture, we were discussing about ro vibrational transitions. ro vibrational transitions. Ro vibrational stands for rotational + vibrational. So this is rotational + vibrational. In other words, if you vibrational excited molecule, it is also rotational excited or de excited in today's lecture, first we will revisit the Born Oppenheimer approximation. So, first we will talk about Born Oppenheimer approximation, this approximation separates electronic motions from nuclear motions.

Or in other words, this is a way of separating electronic energy from the rotational and the vibrational energies. Let us try to imagine what happens to the electron when we stretch a bond in a molecule. Do this stay where they originally were? Or do they move because of the difference in the energies and the difference in the masses of the electrons and the nuclei, what happens is that the electrons change instantaneously compared to the speed with which the nuclei are moving.

It enables us to discuss vibration and rotation independently of the electrons themselves. So, we can just consider the molecule rotating and vibrating in the potential energy well, we can assume that the potential energy or the potential energy well does not adjust because of the vibrations and the rotations. So, this is an incredibly good approximation. Moreover, due to the differences in energies, we can largely separate the vibrational energy from the rotational energy and just consider the total ro vibrational energy that is, we will write E total.

So, this total ro vibrational energy is the sum of the vibrational energy and the rotational energy. So, we can write E total = e rotation + e vibration. So, let us now consider vibration and rotation to be independent. We will also ignore the centrifugal distortion for now, the energy of a molecule that is in the V vibrational state and the J rotational state is just the vibrational energy plus the rotation of energy. So, we can write nu bar in wave numbers.

when the vibrational state is V and the rotational state is J = nu bar v + nu bar J. So, nu bar V, we can write v + half nu bar e - v + half whole squared, nu bar e chi e and the rotational energy we can write B times J times J + 1. So we are considering anharmonic rigid rotor or anharmonic diatomic molecule, which behaves like a rigid rotor. So the first 2 terms here comes from the vibrational energy and the last term comes from the rotational energy

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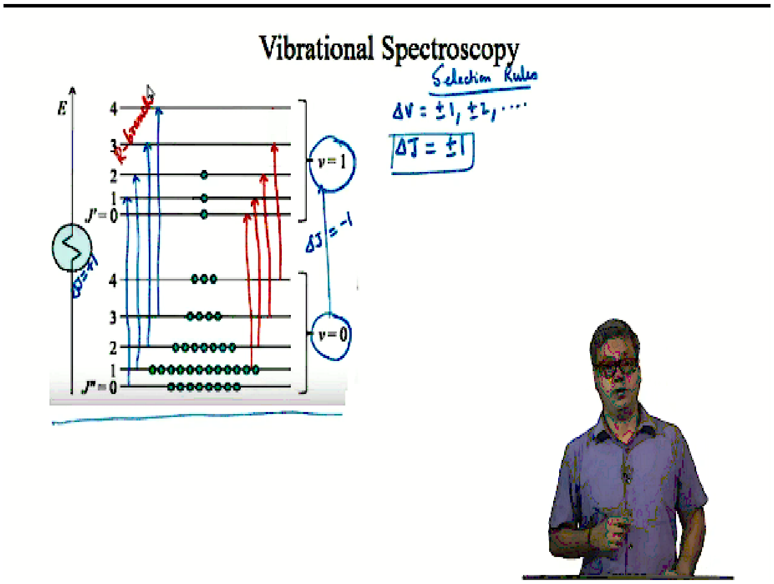

Vibrational Spectroscopy

Selection Rules

$\Delta V = \pm 1, \pm 2, \cdots$

$\boxed{\Delta J = \pm 1}$

To predict the spectrum that will result from the ro vibrational transition, we need to take into account of the selection rules. So, the selection rule for anharmonic oscillator is given by delta V = plus minus 1 plus minus 2 and so on. And for a rotational transition for a rigid rotor, the selection rule is given by delta J = plus minus 1. So, delta nu greater than plus minus 1 will exhibit much weaker intensities. So, let us see how these selection rules affect the spectrum. Let us look into the ro vibrational energy levels again.

So these are the expanded form of the ro vibrational energy levels. And we will focus only on the fundamental band in which we excite molecules from V = 0 to V = 1. So, the delta J has to be equal to plus or minus 1. So, what does this mean? This means I can get transitions where delta J = + 1 that means I can get transitions from V = 0, J = 0 to V = 1, J = 1, I can get transitions from J = 1 to J = 2, also from J = 2 to J = 3, and from J = 3 to J = 4. Similarly, I can also have transitions where delta J = - 1.

So, in this case, we will have transitions from J = 1 to J = 0, then J = 2 to J = 1 J = 3 to J = 2 and from J = 4 to J = 3. So, in the blue transitions, J is increased by 1 and in the rate transitions as shown in the figure J is decreased by 1. So, when J is increased by 1, we identify these transitions as the R branch all these R branch transitions will be greater than the fundamental frequency, the fundamental frequency can be identified in a hypothetical transition in which delta

J = 0 or in other words in which J does not change, when J is decreased by 1, we identify these transitions as P branch transitions.

These transitions where J has decreased will be at a frequency smaller than the fundamental frequency. So, we use our knowledge of the vibrational and rotational energies and the selection rules to predict transitions in the P branch where J decreases by 1 and in the branch where J increases by 1.

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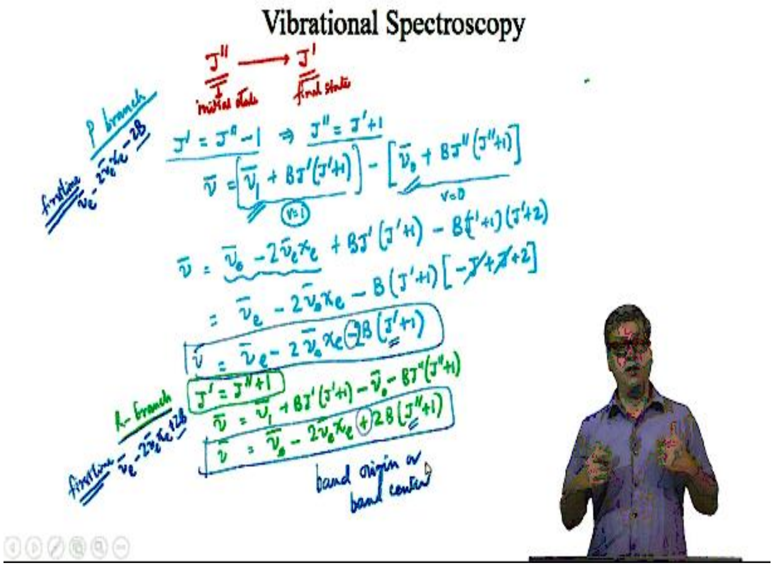

Vibrational Spectroscopy

$J'' \longrightarrow J'$
initial state
final state

P branch
first line $\bar{\nu}_e - 2\bar{\nu}_e x_e - 2B$

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

$\bar{\nu} = \underbrace{[\bar{\nu}_1 + BJ'(J'+1)]}_{v=1} - \underbrace{[\bar{\nu}_0 + BJ''(J''+1)]}_{v=0}$

$\bar{\nu} = \bar{\nu}_e - 2\bar{\nu}_e x_e + BJ'(J'+1) - B(J'+1)(J'+2)$

$= \bar{\nu}_e - 2\bar{\nu}_e x_e - B(J'+1)[-\cancel{J'}+\cancel{J'}+2]$

$\boxed{\bar{\nu} = \bar{\nu}_e - 2\bar{\nu}_e x_e - 2B(J'+1)}$

R-branch
first line $\bar{\nu}_e - 2\bar{\nu}_e x_e + 2B$

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

$\bar{\nu} = \bar{\nu}_1 + BJ'(J'+1) - \bar{\nu}_0 - BJ''(J''+1)$

$\boxed{\bar{\nu} = \bar{\nu}_0 - 2\bar{\nu}_e x_e + 2B(J''+1)}$

band origin or band centre

So, for the P branch, the J value changes from J double prime to J prime. So, this double prime indicates the initial state and the J single prime or this J prime indicates the final state. So, this is purely a convention and we have discussed it before when we were discussing rotational spectroscopy. So for the P branch, we can write J prime, there is the final state = J double prime, there is the initial state minus 1. So this is for the P branch. Or from here we can write J double prime = J prime + 1. So we can write this nu bar = nu bar 1 + B times J prime times J prime + 1.

So this is the energy of the V = 1 state and where to subtract nu bar 0 + BJ double prime time's J double prime + 1. So this is for v = 0. So now, if we put this J prime = J double prime - 1, or in other words, if we put J double prime = J prime + 1, what we get is nu bar = nu bar e - 2 nu bar e chi e + BJ prime time's J prime + 1 then we have minus BJ prime + 1 time's J prime + 2. So, this part nu bar e - 2 nu bar e chi e comes from this nu bar 1 - nu bar 0 considering and anharmonic oscillator.

So, if you further simplify this, what we get is nu bar e - 2 nu bar e chi e minus, if I take B and J prime + 1 common then we have minus J + J + 2. So, this j j cancels out. So, we have nu bar e - 2 nu bar e chi e - B or 2B J prime + 1. So, this is for the P branch. So we will consider R branch now. So for R branch, I can write J prime = J double prime + 1. So, similarly, we can write nu bar = nu 1 bar + BJ prime time's J prime + 1, then minus nu bar 0 - BJ double prime time's J double prime + 1.

So now, if we put this condition that is J prime = J double prime + 1, and we simplify this expression, what we get is nu bar = nu bar e - 2 nu bar e chi e + 2B J double prime + 1. So, there are 2 differences between P and R branches. Number 1, in the P branch, the difference between the rotational energies is negative. In other words, we have a negative sign here. However, in the R branch, it is positive, because we have a positive sign here and number 2 the P branch, we define the energy difference in terms of J prime the final J value, but in the R branch, we define the energy difference in terms of J double prime.

So, this is solely done to show the similarity between the expressions. Note that we never get a transition at exactly the fundamental frequency. So, these 2 equations, one is this one and the other is this one. So, these 2 equations define all the spectral lines in the P branch and in the R branch there are no other branches for diatomic molecule. For the P branch, the minimum value of J prime is 0, the first line of the P branch will be at nu bar e - 2 nu bar e chi e – 2B, the minimum value of J double prime is 0 as well. So, the first line of this R branch will be at.

So, the first line will be at nu bar e - 2 nu bar e chi e + 2B. So there will be a gap of 2B and 2B there is a gap of 4B between the first line of the P branch and the first line of the R branch and in the middle of that 2 lines will be the gap for the fundamental frequency. So, this enables us to identify what the first line in the P branch is and what the first line in the R branches because all we need to do is to find that gap. Once the gap is found, the lines at smaller frequencies are P branch lines and the lines at higher frequencies are R branch lines.

The centre of this gap associated to the fundamental frequency is known as the band origin or the band centre. So, there will be 2 sets of rotational fine structures on either side of this band origin and this is exactly what we saw in the last lecture for the carbon monoxide spectrum.

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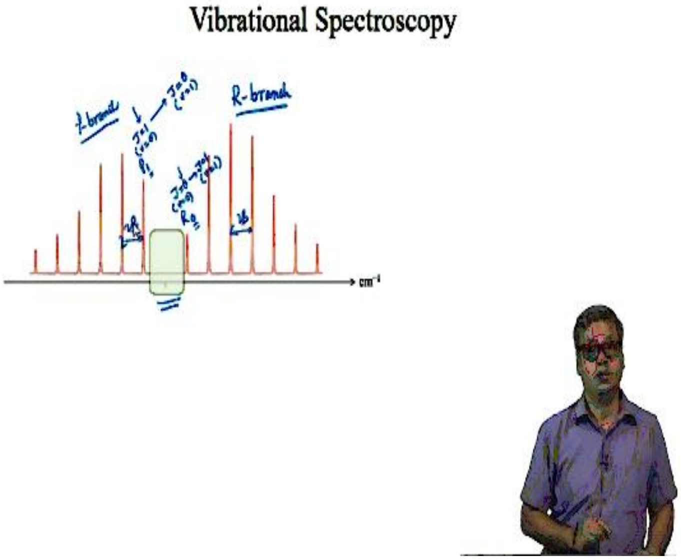

Vibrational Spectroscopy

This is a ro vibrational spectrum provided by our expression for the spectral line frequencies for transitions in the P branch and the R branch. So, this is the P branch and this is the R branch. The shaded part shown here shows the gap at the fundamental frequency. The R 0 is the first line in the R branch, as it is associated with J = 0 to J = 1 transition. So, J = 0 to J = 1, so J = 0 is for V = 0, and J = 1 is for V = 1. The first line in the P branch can be labeled as P1, because it is associated with J = 1 to J = 0 transition. Again, here J = 1 corresponds to V = 0, and J = 0 corresponds to V = 1.

So the number these are 0, or P1, this number refers to the initial level, because in this case, the initial level is 0. And in the other case, the initial level is 1. This is just a convention. The numbers that we generally use, when we label as spectrum line refers to the initial state in this analysis, where we have ignored the centrifugal distortion, the spectral lines are evenly spaced the distance between any 2 spectral line ignoring the gap at the band origin is 2B.

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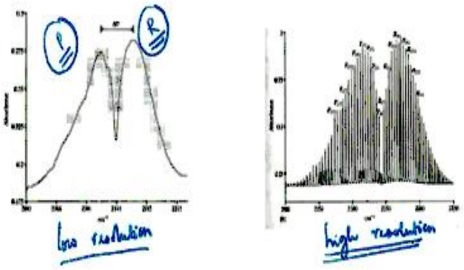
Vibrational Spectroscopy



So we can write this as 2B. So this explains the carbon monoxide spectra in the low resolution spectra. The low resolution of the spectrometer averages out the fine rotational structures. And so, we have 2 broad bands. We have the P band and the R band and we have 2 broadband's associated with this Result P and R spectral lines, but at high resolution we have a different spectra. So, at high resolution, we can see the rotational fine structure and that these are evenly space lines. So, in the next lecture, we will continue our discussion on the vibrating diatomic rotor. So, we will end this lecture by solving a problem.

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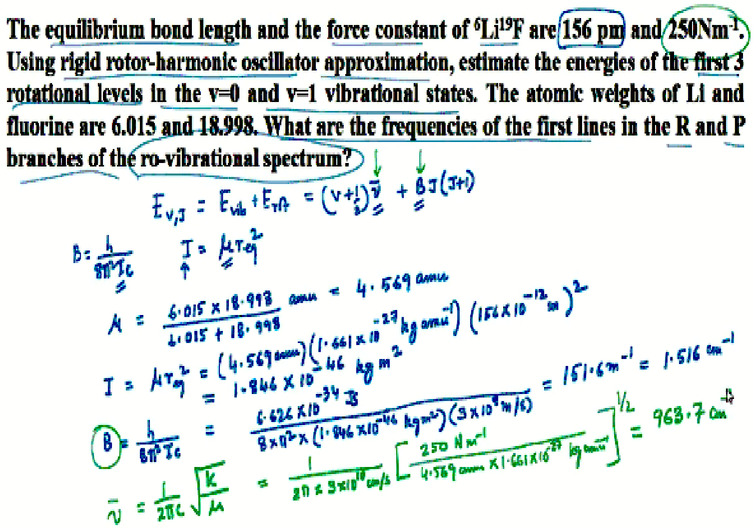

The equilibrium bond length and the force constant of $^6Li^{19}F$ are 156 pm and 250Nm^{-1}. Using rigid rotor-harmonic oscillator approximation, estimate the energies of the first 3 rotational levels in the v=0 and v=1 vibrational states. The atomic weights of Li and fluorine are 6.015 and 18.998. What are the frequencies of the first lines in the R and P branches of the ro-vibrational spectrum?

$$E_{v,J} = E_{vib} + E_{rot} = \left(v+\tfrac{1}{2}\right)\bar{\nu} + BJ(J+1)$$

$$B = \frac{h}{8\pi^2 Ic} \qquad I = \mu r_{eq}^2$$

$$\mu = \frac{6.015 \times 18.998}{6.015 + 18.998}\ \text{amu} = 4.569\ \text{amu}$$

$$I = \mu r_{eq}^2 = (4.569\ \text{amu})(1.661\times10^{-27}\ \text{kg amu}^{-1})(156\times10^{-12}\ \text{m})^2 = 1.846\times10^{-46}\ \text{kg m}^2$$

$$\boxed{B} = \frac{h}{8\pi^2 Ic} = \frac{6.626\times10^{-34}\ \text{Js}}{8\times\pi^2\times(1.846\times10^{-46}\ \text{kg m}^2)(3\times10^{8}\ \text{m/s})} = 151.6\ \text{m}^{-1} = 1.516\ \text{cm}^{-1}$$

$$\bar{\nu} = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}} = \frac{1}{2\pi\times3\times10^{10}\ \text{cm/s}}\left[\frac{250\ \text{N m}^{-1}}{4.569\ \text{amu}\times1.661\times10^{-27}\ \text{kg amu}^{-1}}\right]^{1/2} = 963.7\ \text{cm}^{-1}$$

So, we have the problem here the equilibrium bond length and the force constant of Li F are given. So, the question is using rigid rotor harmonic oscillator approximation, estimate the energies of the first 3 rotational levels in the V = 0 and V = 1 vibrational states. The atomic weights of lithium and fluorine are given also there is a question what are the frequencies of the first lines in the R and P branches of the ro vibrational spectrum. So, because we are only considering rigid rotor harmonic oscillator, so, then the energy E as a function of v and J can be written as e vibrational + e rotational.

So, we can write this as v + half nu bar because we are only considering the harmonic oscillator + B times J times J + 1, because we are considering rigid rotor. So, in order to find the energies, we have to find nu bar also, we need to find B. So first, let us find B, so we know B = h / 8 pi square IC. That means, we need to know the value of I and also we know I = mu that is reduced mass times r equilibrium square. So, in order to know I that is the moment of inertia, we need to know the reduced mass.

So, let us start from the beginning. Let us try to find the reduced mass. So, the reduced mass is given by the atomic weights are given. So, 6.015 times 18.998 divided by 6.015 + 18.998. So this is in amu. So the answer is 4.569 amu. Now once we have found out that reduce mass, let us look into the moment of inertia I. So I = mu times r equilibrium square. So that is the value of mu is 4.569. emu and we convert that into kg, so to multiply with 1.661 times 10 to the power - 27 kilo gram amu inverse, and then we have to multiply this with the r equilibrium square, so r equilibrium is 156 Pico meter.

So we can write 156 times 10 to the power - 12 meters whole square. And once we do this calculation, what we get is 1.846 times 10 to the power - 46 kilogram meter squared. So now, we can find the value of B. so the value of B is given by h / 8 pi square IC. So, let us put the values, the value of h is 6.626 times 10 to the power - 34 joules second, then I have 8 times pi squared. Then I have moment of inertia that is 1.846 times 10 to the power - 46 kilogram meter squared. And then I have the speed of light see, that is 3 times 10 to the power 8 meter per second.

So if we do this, the answer we get is 151.6 meter inverse. So we can write this as 1.516 centimeter inverse. So, now we have found out the value of B which was need for this energy expression. So, now, we need to find the value of nu bar. So, nu bar is given by 1 / 2 pi C root over K / mu. So let us put in the values. So 1 / 2 pi times 3 times 10 to the power 10 centimeter per second. And then we have K that is 250 Newton meter inverse. So, this is given here divided by mu that is 4.569 amu times 1.661 times 10 to the power - 27 kilogram amu inverse. So, this whole thing is a bracket to the power half and this gives answer as 963.7 centimeter inverse or wave numbers.

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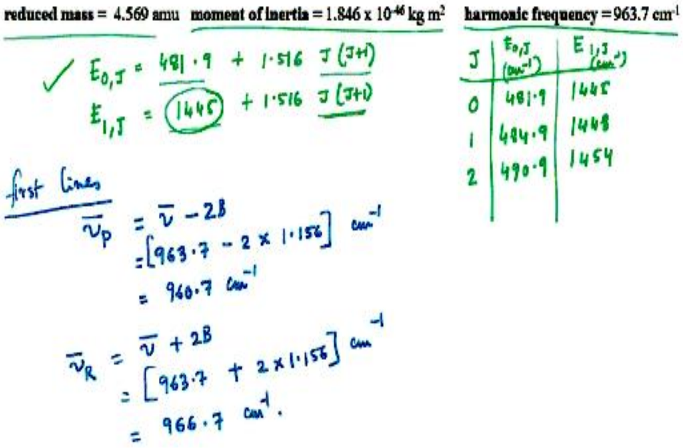

reduced mass = 4.569 amu moment of inertia = 1.846×10^{-46} kg m^2 harmonic frequency = 963.7 cm^{-1}

$$✓\ E_{0,J} = \underline{481.9} + 1.516\ \underline{J(J+1)}$$

$$E_{1,J} = \boxed{1445} + 1.516\ \underline{J(J+1)}$$

J	$E_{0,J}$ (cm^{-1})	$E_{1,J}$ (cm^{-1})
0	481.9	1445
1	484.9	1448
2	490.9	1454

first lines

$$\bar{\nu}_P = \bar{\nu} - 2B$$
$$= [963.7 - 2 \times 1.156]\ \text{cm}^{-1}$$
$$= 960.7\ \text{cm}^{-1}$$

$$\bar{\nu}_R = \bar{\nu} + 2B$$
$$= [963.7 + 2 \times 1.156]\ \text{cm}^{-1}$$
$$= 966.7\ \text{cm}^{-1}.$$

So, now we have found that the reduced mass, we have found the moment of inertia and we have also calculated the harmonic frequency. So, the energy for the rotational levels for vibrational level = 0 is given by E 0, J that can be written as 481.9 because v = 0 So, we have found out nu bar. So, all we are putting here, this is nu bar / 2 + 1.516 that is the value of v J times J + 1. So, this is a general expression for any J level and E 1 J is given by 1445. So, this is equivalent to V = 1 + half nu bar + 1.516 J times J + 1.

So, we have to find the energies of the first 3 rotational levels for V = 0 and V = 1. So, I will not do the entire calculation, but I will just try to make a table so that you can do the calculation and check it yourself. So we will put J here. So J is 012 these are the first 3 J levels. So, here we will put a 0 J in centimeter inverse. That means, this is for V = 0 and I will put in another column E 1 J in centimeter inverse, that is for V = 1. So, if you do the calculation with this expression, this energy expression you get the energy is 481.9 because here J = 0.

If you put J = 1, you get 484.9. So, you see the energy increases and for J = 2 v = 0 the energy is 490.9 similarly, for the V = 1 state J = 0, the energy is 1445. That is this number because J = 0 for J = 1 is 1448 and for J = 2, it is 1454. So, now, we also need to find the first lines in the B and the R branches. So, for the first lines, let say I want to find the first line in the P branch. As we have discussed in the lecture, this is given by nu bar - 2B.

So this is 963.7 - 2 times 1.156 everything is in wave numbers. So, the answer is 960.7 with numbers. Now for the R branch that is nu bar R is given by nu bar + 2 B. So now the answer will be 963.7 + 2 times 1.156 wave numbers and so this will be 966.7 wave numbers. So here we have solved the entire problem. And in the next couple of lectures, my co instructor Anirban Hazra will talk about the selection rules and the wave functions related to vibrational spectroscopy.