# Fundamentals of Spectroscopy

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## Lecture-24
## Vibrational Spectroscopy: Selection Rules

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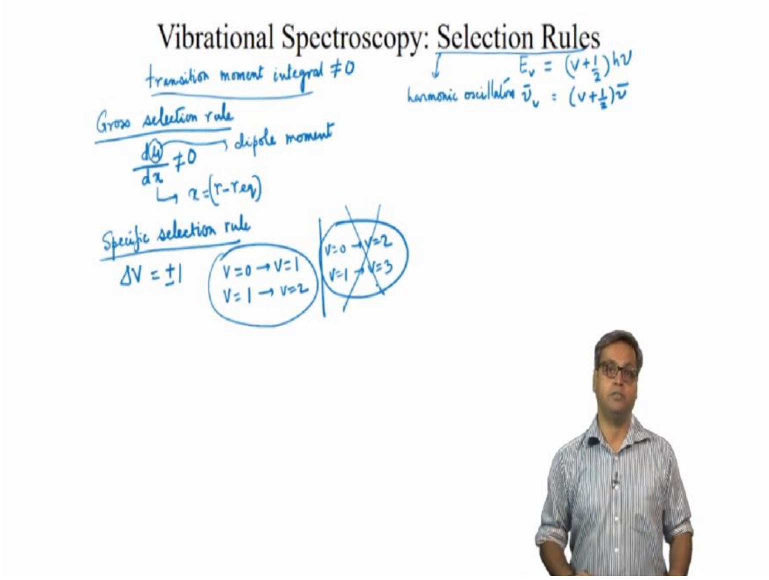

Vibrational Spectroscopy: Selection Rules

transition moment integral $\neq 0$

harmonic oscillator $E_v = (v+\frac{1}{2})h\nu$

$\bar{\nu}_v = (v+\frac{1}{2})\bar{\nu}$

Gross selection rule

$\frac{d\mu}{dx} \neq 0$ dipole moment

$x = (r - r_{eq})$

Specific selection rule

$\Delta v = \pm 1$

$v=0 \rightarrow v=1$

$v=1 \rightarrow v=2$

$\cancel{v=0 \rightarrow v=2}$

$\cancel{v=1 \rightarrow v=3}$

Hello everyone welcome to the third lecture on vibrational spectroscopy. In the last lecture we learned about the energies of different vibrational levels. So we saw the energy E v can be written as v plus half h nu where v is the vibrational quantum number. So in terms of wave numbers we can write nu bar v = v plus half nu bar. So in order to obtain a vibrational spectrum transitions should happen from one vibrational energy level to another.

The vibrational transitions depend on the selection rules. In today's lecture we will discuss the vibrational selection rules of harmonic oscillators and the effect these selection rules have on the vibrational spectrum. To determine the vibrational selection rules we have to follow the same approach as we had for the rotational system. Our vibrational transition will happen if the transition moment integral is nonzero. So the transition moment integral should not be equal to 0.

In other words we have to evaluate this transition moment integral to identify the selection rules before looking into the integral let us first state the selection rules. So we have our gross selection rule. So the gross selection rule states that the gradient of the dipole moment with respect to the equilibrium position must be nonzero or we can say d mu d x not equal to 0. So here mu is the dipole moment. So we can write mu as the dipole moment.

And x is the displacement from the equilibrium position that is x = r - r equilibrium. This means that the dipole must change with displacement at the equilibrium position. As the vibration goes through the equilibrium position the dipole moment of the molecule must be changing. But as we will see later this does not mean that the molecule has to have a permanent dipole moment as we saw in the case of rotational spectroscopy. The Second selection rule we can write this as the specific selection rule.

So the specific selection rule says that the change in the vibrational quantum number that is delta v must be plus or minus 1. Thus transitions can happen from v = 0 to v = 1. Also a transition can happen from v = 1 to v = 2. So these are the allowed transitions. On the other hand transitions cannot happen from v = 0 to v = 2 or let us say v = 1 to v = 3. So these are the transitions that are not allowed. In other words we can only have transitions between adjacent vibrational levels.

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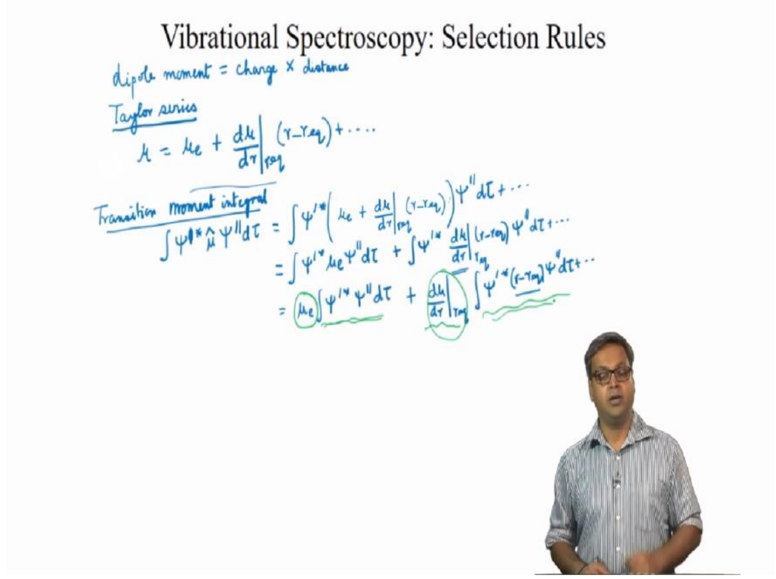

Vibrational Spectroscopy: Selection Rules

dipole moment = charge × distance

Taylor series

$$\mu = \mu_e + \left.\frac{d\mu}{dr}\right|_{r_{eq}} (r - r_{eq}) + \cdots$$

Transition moment integral

$$\int \psi'^* \hat{\mu} \psi'' d\tau = \int \psi'^* \left( \mu_e + \left.\frac{d\mu}{dr}\right|_{r_{eq}} (r - r_{eq}) \right) \psi'' d\tau + \cdots$$

$$= \int \psi'^* \mu_e \psi'' d\tau + \int \psi'^* \left.\frac{d\mu}{dr}\right|_{r_{eq}} (r - r_{eq}) \psi'' d\tau + \cdots$$

$$= \mu_e \int \psi'^* \psi'' d\tau + \left.\frac{d\mu}{dr}\right|_{r_{eq}} \int \psi'^* (r - r_{eq}) \psi'' d\tau + \cdots$$

So now let us try to find out where these 2 selection rules come from. We know that the dipole moment changes with one length we know that dipole moment is charge times distance. So we can write this as charge times distance. So if the bond length changes during the vibration that means there is a change in the distance. So the dipole moment will change we can expand the dipole moment that is mu around the equilibrium position as a function of the displacement r - r equilibrium or x. In other words we can expand the dipole moment as a Taylor series.

So we did the Taylor series expansion for the potential in the last lecture. So now we will do the Taylor series expansion for the dipole moment. So we can write mu the dipole moment is given by mu e. So the dipole moment at the equilibrium position is the permanent dipole moment of the molecule which is represented by mu e then we have the second term that is d mu dr at r equilibrium r - r equilibrium and we have the other higher terms.

So we will ignore all the higher order terms and will only consider the first 2 times in the expansion as shown here. So now if you substitute this expression for dipole moment in the transition moment integral so we can write the transition moment integral we can write this as integration psi double prime star then we have the dipole moment operator then we have psi prime d tau.

So this becomes or let us makes this as double prime to go with the convention and let us make this as the single prime. So this transition moment integral. If we put the expression of this expanded dipole moment here we can write psi prime star then we will put the expression for mu that is mu e + d mu dr r equilibrium r - r equilibrium. Then we have psi double prime d tau and we have plus dot dot dot the high terms.

So here we can expand this and write as psi prime star mu e psi double prime d tau + psi prime star d mu dr at r equilibrium r - r equilibrium psi double prime d tau plus the hydrometers. So the mu e is the dipole moment at the equilibrium position. And so this mu e is a constant so we can take it out of the first integral and we can write this as mu e times psi prime star psi double prime d tau.

So because we can take out the mu e this is because it does not affect the wave function in the second term the gradient of the dipole moment that is this term d mu dr at r equilibrium with respect to the displacement is also a constant. So you can take this time out of the second integral. So this becomes d mu dr r equilibrium integration psi prime star r - r equilibrium psi double prime d tau so the displacement term that is r - r equilibrium however cannot be taken out of the integral as wave functions themselves are function of the displacement.

So the integral is also a function of the displacement. So we know that for a vibrational transition to happen the transition moment integral has to be nonzero. So the first time is 0 the mu equilibrium is that dipole moment at the equilibrium position or is the permanent dipole moment of the molecule. So mu equilibrium can either be 0 or nonzero depending on the molecule but the permanent dipole moment being 0 or nonzero does not make any difference.

This is because the integral associated with the permanent dipole moment in the first term of the right hand side is 0 without going to the details vibrational wave functions are the solutions to the harmonic oscillator Schrodinger equation these way functions are orthogonal to one another. So integrals like these what we have here that is psi prime and psi double prime we have 2 different states.

So the integrals like these are always 0 as there is a change in the vibrational state from let us say psi prime to psi double prime. So let us focus on the second term in the right hand side. If a vibrational transition needs to happen the second term has to be nonzero. In other words both the parts of the second term has to be nonzero. So we have 2 parts we have this radiant term and then we have the integral.

So the gradient of the dipole moment with respect to displacement has to be nonzero and the integral has to be nonzero. Now you can see the first part being nonzero is the gross selection thus we can understand that solving this integral should provide us with the specific selection rule. That is this should give us delta v equals plus minus 1.

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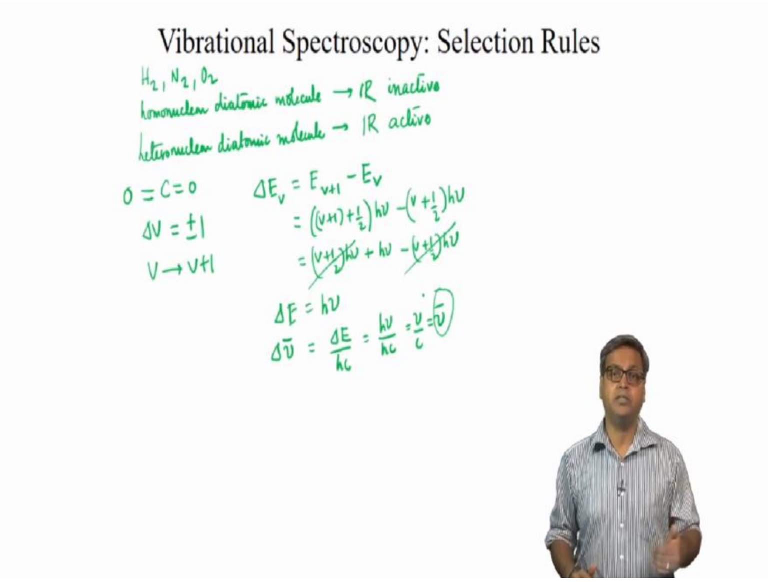

Vibrational Spectroscopy: Selection Rules

$H_2, N_2, O_2$

homonuclear diatomic molecule → IR inactive

heteronuclear diatomic molecule → IR active

$O=C=O$

$\Delta v = \pm 1$

$v \rightarrow v+1$

$$\begin{aligned} \Delta E_v &= E_{v+1} - E_v \\ &= \left((v+1)+\tfrac{1}{2}\right)h\nu - \left(v+\tfrac{1}{2}\right)h\nu \\ &= \cancel{\left(v+\tfrac{1}{2}\right)h\nu} + h\nu - \cancel{\left(v+\tfrac{1}{2}\right)h\nu} \end{aligned}$$

$$\Delta E = h\nu$$

$$\Delta\bar{\nu} = \frac{\Delta E}{hc} = \frac{h\nu}{hc} = \frac{\nu}{c} = \boxed{\bar{\nu}}$$

So let us revisit the first selection rule that the dipole moment has to change as a function of the displacement from the equilibrium position. So for homo nuclear diatomic molecules like we have is the hydrogen nitrogen or oxygen this cannot occur the dipole moment of the homo nuclear diatomic molecule is 0 no matter what the bond length is that is during vibration both is dipole moment and the gradient of the dipole moment remain 0.

Thus homo nuclear diatomic molecules cannot exhibit an infrared spectrum or we can say homo nuclear diatomic molecules they are IR inactive. So this does not mean that the homo nuclear diatomic do not have the vibrational levels it just means it cannot use these vibrational levels for electromagnetic radiation or to interact with electromagnetic radiation we excite a molecule from one vibrational state to another.

This is similar to the case where a homo nuclear diatomic molecule cannot be excited from one rotational level to another using microwave radiation but those vibrational or rotational levels exists and their energies can be obtained by solving the Schrodinger equation for hetero nuclear diatomic molecules. So hetero nuclear diatomic molecules the dipole moment changes during vibration as dipole moment is just charged time distance as the bond length changes the dipole moment changes.

So hetero nuclear diatomic molecules have infrared spectra and thus these molecules are IR active in other words carbon monoxide or co which is a hetero nuclear diatomic molecule when dissolved in a solvent shows are banned in the internet. So now let us considered a molecule like co2 or carbon dioxide co2 as we know does not have a permanent dipole moment but is IR active we might expect that this molecule will not have a dipole moment while vibrating.

But as we will see later more than one kind of vibration can occur in this molecule carbon dioxide. The symmetric stretching mode where both the co bonds are either expanding or contracting during the vibration at the same time is IR inactive as the dipole moment is 0 at every point during vibration. In other words we can say there is no change in the dipole moment with respect to the displacement from the equilibrium position.

But during the asymmetric stretch that is once your bond gets smaller while the other co bond gets larger the dipole moment changes during the vibration making the mode IR active. There is another mode that is the bending mode of co2 which we will discuss later this mode is also an IR active mode. So now we know from the specific selection rule that delta v equals plus minus 1. So let us look into a vibrational transition let us say from v to v + 1.

So if we calculate the change in energy so we can write delta E v that is the change in energy during the transition from v to v + 1. This is E of v + 1 - E of v. So this is v + 1 plus half h nu - v plus half h nu. So we can write this as v plus half h nu + h nu - v plus half h nu. So these 2 will cancel what we have is delta E = h nu in wave number units we can write delta nu bar is delta E / hc that is h nu / hc. So this is nu / C = nu bar.

So in other words the change in energy gives the energy associated in the spectral line. So for harmonic oscillators as the energy levels are equally spaced all transitions will exhibit a spectral feature at the same frequency that is nu bar as the spectral lines associated with every transition will occur at the same frequency. In other words we can say that they will lie on top of one another in the IR spectrum.

So we should expect a single spectral line you think this situation to be much simpler than the rotational spectrum where we had many equally spaced lines. So now we have stated that transitions from v to v + 1 will require the same energy. That means it can be any value of v to v + 1 it will require the same energy. The Associated frequency or wavelength for transition falls in the infrared region of the electromagnetic spectrum.

This frequency when matches with the frequency or wavelength of light during the light matter interaction. The transition takes place from one vibrational level to another thus we can consider IR spectroscopy as a form of resonance spectroscopy at room temperature.

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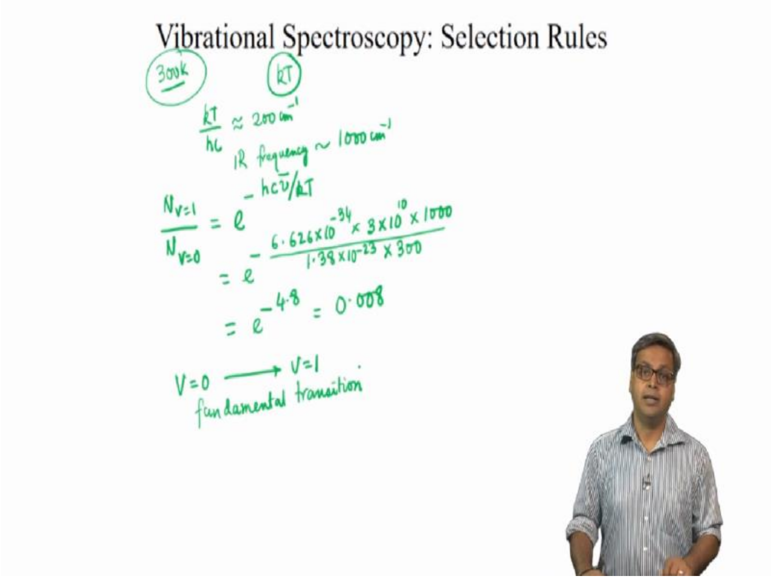

Vibrational Spectroscopy: Selection Rules

$\boxed{300K}$ $\boxed{kT}$

$\frac{kT}{hc} \approx 200\ cm^{-1}$

IR frequency $\sim 1000\ cm^{-1}$

$$\frac{N_{v=1}}{N_{v=0}} = e^{-hc\bar{\nu}/kT}$$

$$= e^{-\frac{6.626\times10^{-34}\times3\times10^{10}\times1000}{1.38\times10^{-23}\times300}}$$

$$= e^{-4.8} = 0.008$$

$V=0 \longrightarrow V=1$

fundamental transition

Let us say 300 Kelvin the thermal energy at room temperature is given by kT. As IR spectral transition is commonly reported in wave numbers the thermal energy is approximately kT / hc. And if you put the values here then what we will get is approximately this is 200 wave numbers but most vibrational wave numbers are significantly greater than 200 wave numbers or in other words this IR frequency in wave numbers we can say there in the order of thousand wave numbers.

Thus from Boltzmann distribution we can write N v = 1 / N v = 0 this ratio as we know is given by e to the power - hc nu bar / kT. So if you put the values we can write e to the power minus the value of h is 6.626 times 10 to the power - 34. Then we have the speed of light that is 3 times 10 to the power 10 times nu bar will put 1000 wave numbers divided by k that is 1.38 times 10 to the power - 23 times the temperature this is 300 Kelvin.

And if you do this the value that you get is e to the power - 4.8. so this becomes 0.008. In other words the population of equals one is approximately 1% of the ground state equals 0. So almost all the molecules will be in their vibrational ground state initially. Hence the dominant spectral transition is v = 0 to v = 1. So the dominant spectral transition is v = 0 to v = 1. And this transition is known as the fundamental transition. With the increase in temperature the population of equals one will increase.

But in harmonia approximation all these lines have the same frequency that is if the transition starts from v = 0 or = 1 and thus the spectrum is also a single line. So now the question is do we get a single line from the experimental IR spectrum? We will discuss this in the next lecture. So now let us look into some problems.

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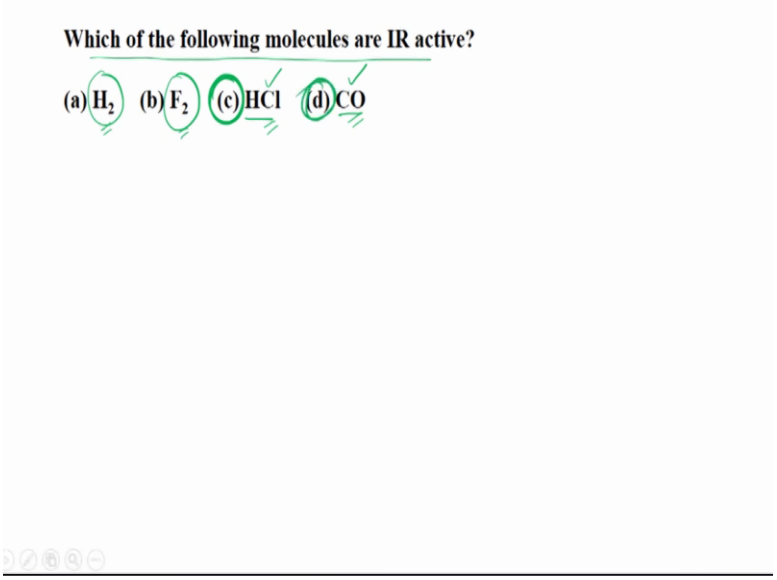

**Which of the following molecules are IR active?**

(a) $H_2$ (b) $F_2$ [✓ (c) HCl] [✓ (d) CO]

The first question we have is which of the following molecules IR active. So we have 4 choices H 2, F 2, HCL and CO or carbon monoxide. So, as we can see H 2 and F 2 they are homonuclear diatomic molecules on the other hand, HCL and carbon monoxide hetero nuclear diatomic molecules. So, we know so, HCL and CO they will be IR active. So, the right answers are c and d.

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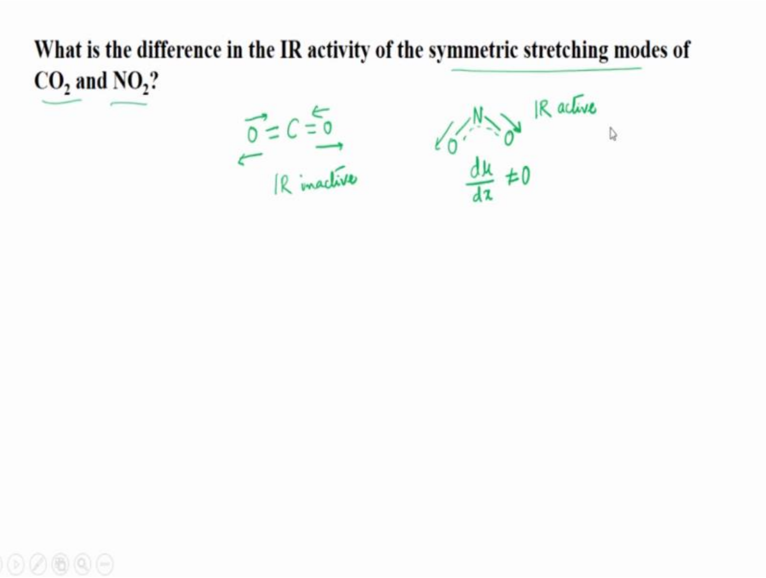

**What is the difference in the IR activity of the symmetric stretching modes of $CO_2$ and $NO_2$?**

So let us look into the next question, what is the difference in the IR activity of the symmetric stretching modes of CO 2 and NO 2. So we discuss in the class this carbon dioxide the symmetric stretching mode is both the CO bonds are either lengthening or their contracting at the same time. So because this is a linear molecule there is no change in dipole moment with respect to the displacement from the equilibrium bond length.

So, this is IR inactive on the other hand when we have NO 2 so this is like a bent molecule and as this molecule is bent, even though the stretching happens in a symmetric fashion that means both the NO bonds are stretching at the same time there is a change in the dipole moment with respect to displacement. So here we can write del mu del x is not equal to 0. So NO 2 symmetric stretching mode will be IR active.

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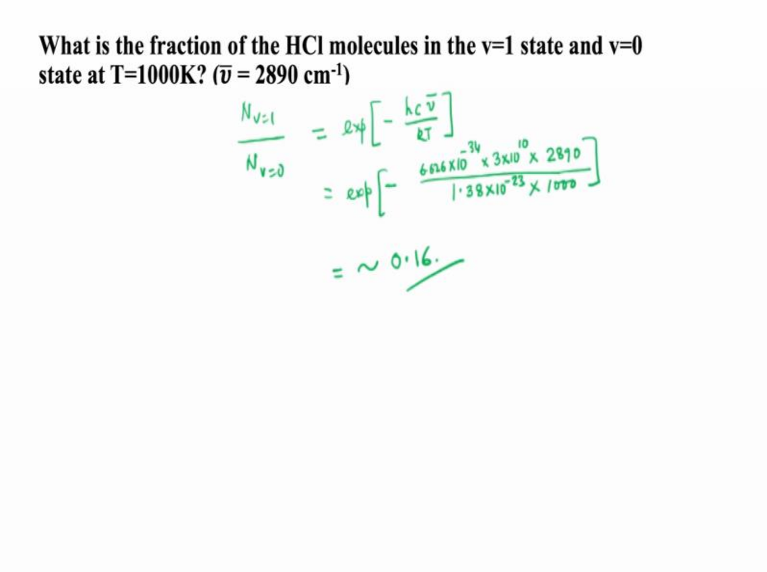

**What is the fraction of the HCl molecules in the v=1 state and v=0 state at T=1000K? ($\bar{\upsilon}$ = 2890 cm$^{-1}$)**

$$\frac{N_{v=1}}{N_{v=0}} = \exp\left[-\frac{hc\bar{\nu}}{kT}\right]$$

$$= \exp\left[-\frac{6.626\times10^{-34}\times3\times10^{10}\times2890}{1.38\times10^{-23}\times1000}\right]$$

$$= \sim 0.16.$$

So, we have the last question here for today. So, what is the fraction of the HCl molecules in the v = 1 state and v = 0 state? So, we have to find N v = 1 divided by N v = 0. The temperature we have to find this fraction is 1000 Kelvin. So we know that N v = 1 / N v = 0 is given by exponential, we can write - hc nu bar / kT. So this is we can write exponential will put the values. So this is 6.626 times 10 to the power - 34 times.

The speed of light that is 3 times 10 to the power 10 and times the frequency, which is 2890. So we will divide this by k that is 1.38 times 10 to the power - 23. And temperature that is 1000 Kelvin. So if you do this math answer we get is approximately 0.16.