Fundamentals of Spectroscopy

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Lecture-23
Vibrational Spectroscopy: Energy Levels

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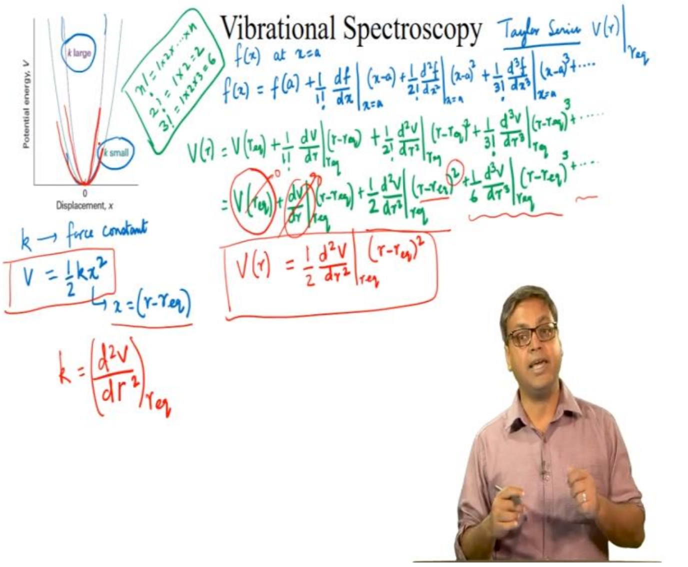

Vibrational Spectroscopy

Taylor Series $V(r)\Big|_{r_{eq}}$

$n! = 1\times2\times\ldots\times n$
$2! = 1\times2 = 2$
$3! = 1\times2\times3 = 6$

$f(x)$ at $x=a$

$$f(x) = f(a) + \frac{1}{1!}\frac{df}{dx}\Big|_{x=a}(x-a) + \frac{1}{2!}\frac{d^2f}{dx^2}\Big|_{x=a}(x-a)^2 + \frac{1}{3!}\frac{d^3f}{dx^3}\Big|_{x=a}(x-a)^3 + \ldots$$

$$V(r) = V(r_{eq}) + \frac{1}{1!}\frac{dV}{dr}\Big|_{r_{eq}}(r-r_{eq}) + \frac{1}{2!}\frac{d^2V}{dr^2}\Big|_{r_{eq}}(r-r_{eq})^2 + \frac{1}{3!}\frac{d^3V}{dr^3}\Big|_{r_{eq}}(r-r_{eq})^3 + \ldots$$

$$= \cancel{V(r_{eq})}^{0} + \cancel{\frac{dV}{dr}\Big|_{r_{eq}}}^{0}(r-r_{eq}) + \frac{1}{2}\frac{d^2V}{dr^2}\Big|_{r_{eq}}(r-r_{eq})^{2} + \frac{1}{6}\frac{d^3V}{dr^3}\Big|_{r_{eq}}(r-r_{eq})^3 + \ldots$$

$$\boxed{V(r) = \frac{1}{2}\frac{d^2V}{dr^2}\Big|_{r_{eq}}(r-r_{eq})^2}$$

$k \rightarrow$ force constant

$$\boxed{V = \frac{1}{2}kx^2}$$

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

$$k = \left(\frac{d^2V}{dr^2}\right)_{r_{eq}}$$

Hello everyone, welcome to the lecture. In the last lecture, we have started discussing vibrational spectroscopy. We saw that if k is the force constant of the bond, so we can write k. So this is the force, constant of the bond. The potential energy, which is presented by v can be written as half kx square. So, here x equal r - r equilibrium so, r is the bond length, at any point of time during the vibration and our equilibrium is the equilibrium bond length, the potential energy can be approximated by a parabola.

The steeper the walls of the parabola, that is, the stronger is the bond, the greater is the value of the force constant, as we see from the figure. So, the steeper is the wall, the value of k is large. And if the walls are not that steep, then the value k is small. So, in order to understand the connection between the shape of the molecule of potential and the value of k, we can expand the potential energy which is a function of r. So, we can expand v of r around the minimum by using something called Taylor series.

So, we have to expand using dealer series. So, in other words, as the minimum of the potential energy is found at the equilibrium bond length, we will be expanding this v of r around or equilibrium. So, Taylor series is a series expansion of a function about a point. So, the expansion of a function let us say, f of x at x = a is given by f of x = f of a + 1 / 1 factorial, df dx at x = a times x - a + 1 / 2 factorial, d 2 f, dx 2 at x = a times x - a whole square + 1 / 3 factorial, d 3 f, the dx 3 at x = a times x - a cubed.

And we can write also the higher terms 4 5 6, etc. So, we can expand v of r by writing v r = v at r equilibrium + 1 / 1 factorial dv, d r at r equilibrium r - r equilibrium + 1 / 2 factorial d 2 v dr 2, at r equilibrium times r - r equilibrium square + 1 / 3 factorial d 3 v dx 3 at r equilibrium times r - r equilibrium cubed plus dot dot. So we can further write this expression because we know that n factorial is 1 times 2 times dot dot dot times n. So 2 factorial = 1 times 2 = 2, and 3 factorial = 1 times 2 times 3 = 6.

So we can further write this as we are equilibrium, + dv, dr at r equilibrium r - r equilibrium plus half d 2 v dr 2 at r equilibrium, r - r equilibrium square + 1 / 6, d 3 v, dr. 3 r equilibrium r - r equilibrium cubed plus dot dot. The first time is a constant, which is the electronic energy at the equilibrium geometry or equilibrium bond length. So this term can be arbitrarily set to 0 in fact, in spectroscopy.

We are more interested in the difference between energy levels than the actual energy of the length the second term is 0 as the first derivative at r equilibrium is 0, this is because the v of r the potential is minimum at r equilibrium. And we know that the first derivative at the minimum is always 0. So the first surviving non 0 terms is the third time. This time, as we can see, is proportional to the square of the displacement from the equilibrium position.

For small displacements from the equilibrium bond length, r - r equilibrium is small the higher terms like the term I have written here and all the other higher terms can be ignored. As we have already discussed in the last lecture, for small displacements, the harmonic approximation holds good. For larger displacements from the equilibrium position, we have to consider the higher terms. So, we can write this v of r = half d 2 v dr 2 at r equilibrium times r - r equilibrium (())(08:50).

So, if we compare this equation with the question we have already written that is v = half kx square, where x = r - r equilibrium, we can identify that k = d 2 v = dr 2 at r equilibrium. In other words, if the potential energy is sharply carved at the minimum or close to the minimum, then k will be large. On the other hand, if the potential energy is wide and shallow, like the shown here for this carve around the minimum, that is close to the minimum.

When the k is small so we can calculate the potential energy of any particular bond length, then we could determine the curvature or we can determine what the curvature would be and therefore, calculate the force constant k and does we can calculate the vibrational frequency.

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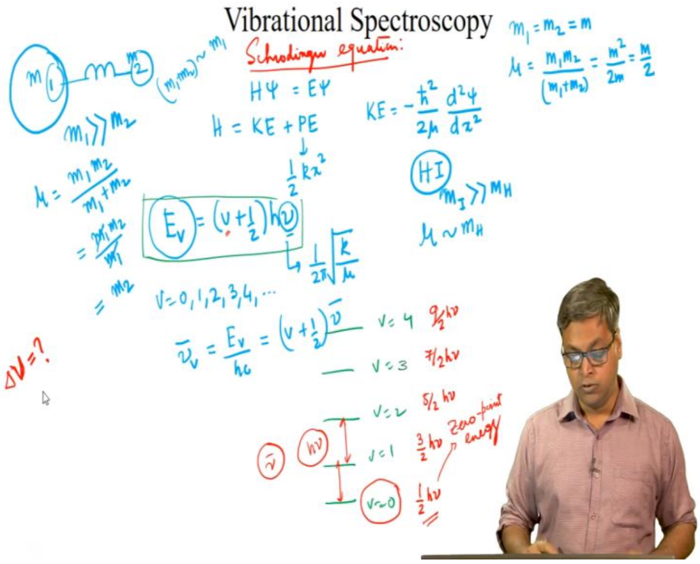

So, now, we have to focus on the energy levels of the simple harmonic oscillator. As we have discussed during rotational spectroscopy, one can obtain the energy by solving the Schrodinger equation for Schrodinger equation. So, we can write the Schrodinger equation as H psi = E psi the Hamiltonian that is the H is given by the kinetic energy operative plus the potential energy operator. We already know that the potential energy is half kx square where x = r - r equilibrium.

The kind of energy operator depends primarily on the coordinate system being used. So, we can write this kind of energy operative as minus h cross square / 2 mu d 2 psi dx 2. So the solution offered in your equation gives the energy we can write E v. So, E v = v plus half each nu. Here we are using or introducing a new quantum number v. so here v is the vibrational quantum number and nu is the vibrational frequency.

So nu is given by 1 / 2 pi root over k by mu, where k is the force constant of the bond. And mu is the reduce Morse of this data make simple harmonic oscillator. The vibrational quantum number can take integral values, like v can be 0 1 2 3 4 In other words, for every value of v, there is a corresponding wave function and a corresponding energy level. The vibrational energy that is E v that we have written here is induces.

So, if you want to express this vibrational energy in the unit of wave numbers, we can write nu bar v that is given by as we already know E v / hc. So, that is v plus half nu bar. As we can see, the vibrational energy depends on the reduced Morse of the molecule because it has dependency on the frequency the dependence of vibrational frequency and reduce Morse is physically reasonable. Let us say we have 2 atoms connected by a spring, we have item 1 and item 2.

And let us say the atom 1 is actually very heavy, then we can assume then the vibration will be of the lighter atom that is atom 2 relative to that of the heavier atom. So, if you look into the reduced Morse expression, we can write so, we have m 1 and m 2 these are the 2 Morse and if we have m 1 greater than greater than m 2, so, we know the reduce Morse mu is given by m 1, m 2 divided by m 1 + m 2. However, because m 1 is much greater than m 2, we can write m 1 + m 2 is approximately m 1.

So what we get is m 1 m 2 divided by m 1. So, m 1 m 1 cancels, we get empty. So the reduce Morse will be approximately m 2. Now, if we have a whole nuclear molecule, but the 2 Morse are the same, that is m 1 = m 2, then the reduce Morse becomes, so let us say this equals m. So, reduce Morse is m 1 m 2 divided by m 1 + m 2. So, it will be m square / 2 m = m / 2. But for a hetero nuclear molecule, they say we have a molecule like HI, but the atomic weight of iodine is much larger than hydrogen.

So, the Morse of iodine is much heavier in that case, we can write m I is much much greater than m H. So, in this case, the mu or the reduce Morse will be approximately = m of H. So, now, let us try to draw the vibrational limits. So, we know the energy expression is given by v plus half h nu. So, let us draw the energy levels. So, let us say v = 0, v = 1 v = 2 v = 3 v = 4. So the energies v = 0 is we have to put 0 in this expression. So what we get this half each nu, that is induce, if you had put in wave numbers would get nu bar / 2.

So for v = 1, we get 3 / 2 h nu 4 v = 2, we get 5 / 2 h nu. Then we have 7 / 2 h nu 4, v = 3, and we have 9 / 2 h nu 4, v = 4. So the first observation we made is that the energy levels are spaced. So, the equal spacing between the energy levels is given by each nu or in wave numbers is given by nu bar. This observation is different from what we saw in rotational spectroscopy. So, I want to mention it again that the spacing between the energy levels is given by each nu or nu bar.

And another interesting point to note is that, when the molecule is in the lowest vibrational energy state, that is, when the molecule is at v = 0, then the energy is half h nu. This energy is known as the 0 point energy. So for rotational spectroscopy, the lowest energy is 0. But in vibrational spectroscopy, the lowest energy is half h nu. That is the lowest energy is not 0 if the molecule is in its lowest energy state.

The physical significance of it is that even at the lowest vibrational level, the atom will still vibrate with the energy half nu bar. In other words, the molecule is never addressed. The prediction of the 0 point energy is the basic difference between classical and quantum approaches to molecule vibration. Classical mechanics could find no objection molecule possessing no vibrational energy, but quantum mechanics says that the molecule should always vibrate to some extent.

So in order to obtain a vibrational spectrum, because that is the reason we are discussing vibrational spectroscopy, so, because we need to obtain a spectrum, so in order to obtain the spectrum transitions should happen from 1 vibrational energy level to another. We have to ask the question between which levels can the transition take place? In other words, the question is what change in vibrational quantum number is allowed for a vibrational spectrum?

Or in other words, what is the allowed value for delta v so, in the next lecture, we will discuss the selection rules for vibrational transitions. And in the remaining part of this lecture will solve few questions on the topic that we have discussed today.

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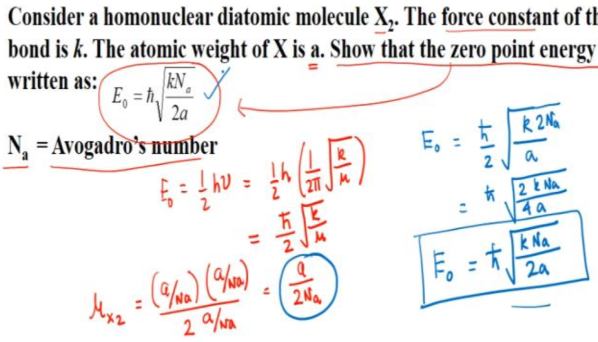

Consider a homonuclear diatomic molecule X_2. The force constant of the X-X bond is *k*. The atomic weight of X is a. Show that the zero point energy (E_0) can be written as: $E_0 = \hbar\sqrt{\frac{kN_a}{2a}}$

N_a = Avogadro's number

$$E_0 = \frac{1}{2}h\nu = \frac{1}{2}h\left(\frac{1}{2\pi}\sqrt{\frac{k}{\mu}}\right) = \frac{\hbar}{2}\sqrt{\frac{k}{\mu}}$$

$$\mu_{X_2} = \frac{(a/N_a)(a/N_a)}{2\,a/N_a} = \frac{a}{2N_a}$$

$$E_0 = \frac{\hbar}{2}\sqrt{\frac{k\,2N_a}{a}} = \hbar\sqrt{\frac{2\,kN_a}{4a}}$$

$$\boxed{E_0 = \hbar\sqrt{\frac{kN_a}{2a}}}$$

So, the first question we have is consider a homonuclear diatomic molecule X 2. The force constant of the X 2 or the X X bond is k, the atomic weight of X is given us a. So, what we have to do is to show that, the 0 point energy is 0 can be written as this expression has been given. So, we have to show that the 0 point energy can be return as this expression, and in this expression, in a is the Avogadro's number. So we know that the 0 point energy, this write by E 0 is given by half h nu.

So we can write this as half h, and nu, we can write 1 / 2 pi root over k / mu. So, this is, h / 2 pi becomes h cross, so h cross / 2 route over k / mu. So, we have to find that reduce Morse of x 2, so, the atomic rate is a, so we can write that the Morse of 1 atom is given by a / Avogadro number so, that reduced Morse is a / N a in a times a / N a in a divided by 2 times a / N a. So, that will be a / 2 times N a.

So, now we can see E 0 is we have h cross / 2 route over k and we will put the expression of the reduced Morse that is a times 2 times N a. So, we can write this as h cross root over 2 kN a divided by 4 a. So, this becomes each cross root over kN a divided by 2a. So, the 0 point energy is given by this expression. And this is the same expression that we have been asked to show in the question. So let us go to the second question.

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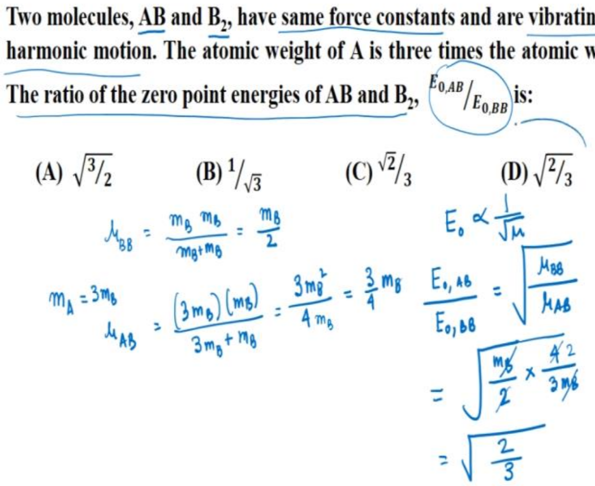

Two molecules, AB and B_2, have same force constants and are vibrating in simple harmonic motion. The atomic weight of A is three times the atomic weight of B. The ratio of the zero point energies of AB and B_2, $E_{0,AB}/E_{0,BB}$ is:

(A) $\sqrt{3/2}$ (B) $1/\sqrt{3}$ (C) $\sqrt{2}/3$ (D) $\sqrt{2/3}$

$$\mu_{BB} = \frac{m_B m_B}{m_B + m_B} = \frac{m_B}{2}$$

$$m_A = 3m_B$$

$$\mu_{AB} = \frac{(3m_B)(m_B)}{3m_B + m_B} = \frac{3m_B^2}{4m_B} = \frac{3}{4}m_B$$

$$E_0 \propto \frac{1}{\sqrt{\mu}}$$

$$\frac{E_{0,AB}}{E_{0,BB}} = \sqrt{\frac{\mu_{BB}}{\mu_{AB}}}$$

$$= \sqrt{\frac{\cancel{m_B}}{\cancel{2}} \times \frac{\cancel{4}\,2}{3\cancel{m_B}}}$$

$$= \sqrt{\frac{2}{3}}$$

So, we have 2 molecules, one is a homonuclear diatomic molecule that is AB and the other is a whole nuclear dyadic molecule that is B 2. And these 2 molecules have seen force constants and are vibrating in simple harmonic motion. That atomic weight of A is 3 times atomic weight of B and the ratio of the 0 point energies. So we have to find the ratio of the 0 point energies of AB and B 2 that is you have to find E 0, AB divided by E 0, BB or B 2. And this is a multiple choice question.

So we have to solve the question and see which answer is correct. So let us find the reduced Morse of BB or B2 to that we can write M B times M B divided by M B + M B. So that is given by M B / 2. So in the freshman it is given that the M A is 3 times of M B, so M A = 3 M B. So we can write mu of AB = 3 M B times M B divided by 3M B + M B. So this becomes 3M B square / 4M B. So that is, 3 / 4M B. So we know that the 0 point energy is given by, or inversely proportional to 1 / root over mu.

And the force constant cases the same for AB and B2. So we can write, easy through AB divided by E 0, BB. We can write this as route over mu BB B divided by mu AB. So that will be M B / 2. That is mu AB divided by 3 M B / 4 that is for view AB. So this is equals M B M B cancels. So we have route over 2 / 3. So now if you look into the choices, the right answer is choice D. So the issue is route over 2 / 3.

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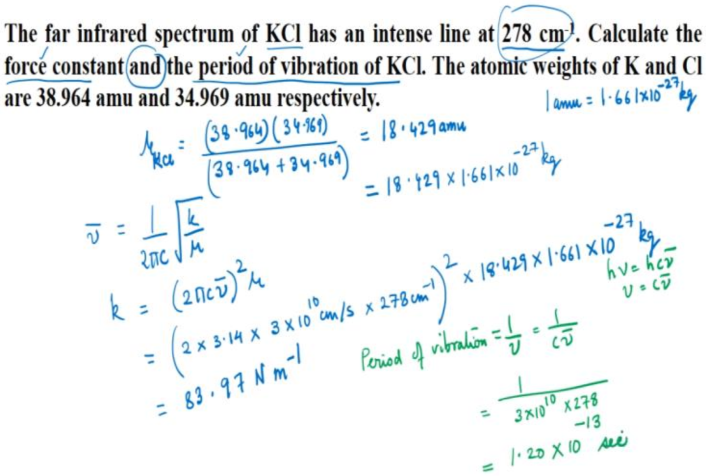

The far infrared spectrum of KCl has an intense line at 278 cm^{-1}. Calculate the force constant and the period of vibration of KCl. The atomic weights of K and Cl are 38.964 amu and 34.969 amu respectively.

$1\,\text{amu} = 1.661 \times 10^{-27}\,\text{kg}$

$$\mu_{KCl} = \frac{(38.964)(34.969)}{(38.964 + 34.969)} = 18.429\,\text{amu}$$

$$= 18.429 \times 1.661 \times 10^{-27}\,\text{kg}$$

$$\bar{\nu} = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}}$$

$$k = (2\pi c\bar{\nu})^2 \mu$$

$$= \left(2 \times 3.14 \times 3 \times 10^{10}\,\text{cm/s} \times 278\,\text{cm}^{-1}\right)^2 \times 18.429 \times 1.661 \times 10^{-27}\,\text{kg}$$

$$= 83.97\,\text{N m}^{-1}$$

$h\nu = hc\bar{\nu}$

$\nu = c\bar{\nu}$

$$\text{Period of vibration} = \frac{1}{\nu} = \frac{1}{c\bar{\nu}}$$

$$= \frac{1}{3 \times 10^{10} \times 278}$$

$$= 1.20 \times 10^{-13}\,\text{sec}$$

So we have another problem. The problem states that the far infrared spectrum of potassium chloride has an intense line at 278 wave numbers. Calculate the force constant. So we have to calculate the force constant and the period of vibration of KCL. So we have to calculate the force constant, and the period of vibration. And the atomic waves of K and CL are given. So let us first try to find the force constant. So let us evaluate the reduced Morse of KCL.

So this is given by 38.964 times 34.969 divided by 38.964 + 34.969. So this is equal to 18.4298 amu. so because 1 amu = 1.661 times 10 to the power - 27 kgs, so we can read this as 18.429 times 1.661 times 10 to the power - 27 kgs. So we know nu bar is given by 1 / 2 policy route over k / mu. Or in other words, because we have to find the force constant that is k, you can read k =2 pi c, nu bar whole square times nu.

Now, if you put in the values we have 2 times 3.14 then c 3 times 10 to the power 10 centimetres per second and nu bar here is given in the question that is 278 wave numbers. So, we have 278 wave numbers. So, we have to take the square of this entertaining times mu and mu is 18.429 times 1.661 times 10 to the power - 27 kg. So, if you do this math what we get is 83.97 Newton meter inverse.

So, we are also need to find the period of vibration. So, we can write period of vibration this equals 1 / nu. And because h nu = hc nu bar. So, we know nu = c nu bar. So, 1 / nu I can write as 1 / c nu bar. So, that is 1 / 3 times 10 to the power 10 centimetres per second times 278 centimetre inverse. So, what we get the final answer for the period of vibration is 1.20 times 10 to the bar - 13 second

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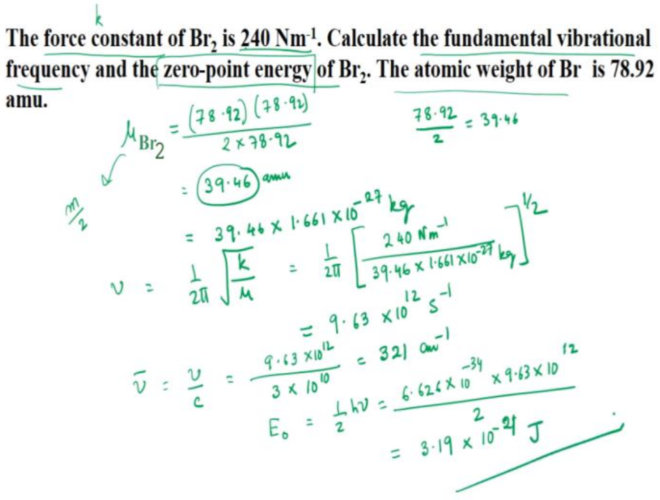

The force constant of Br_2 is 240 Nm^{-1}. Calculate the fundamental vibrational frequency and the zero-point energy of Br_2. The atomic weight of Br is 78.92 amu.

k

$$\mu_{Br_2} = \frac{(78.92)(78.92)}{2 \times 78.92} \qquad \frac{78.92}{2} = 39.46$$

$$= \boxed{39.46}\ \text{amu} \qquad \frac{m}{2}$$

$$= 39.46 \times 1.661 \times 10^{-27}\ \text{kg}$$

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} = \frac{1}{2\pi}\left[\frac{240\ \text{Nm}^{-1}}{39.46 \times 1.661 \times 10^{-27}\ \text{kg}}\right]^{1/2}$$

$$= 9.63 \times 10^{12}\ \text{s}^{-1}$$

$$\bar{\nu} = \frac{\nu}{c} = \frac{9.63 \times 10^{12}}{3 \times 10^{10}} = 321\ \text{cm}^{-1}$$

$$E_0 = \frac{1}{2}h\nu = \frac{6.626 \times 10^{-34} \times 9.63 \times 10^{12}}{2}$$

$$= 3.19 \times 10^{-21}\ \text{J}$$

So, the next question we have is the force constant so, now the k is given, so, the force constant of roaming is 240 Newton meter inverse. So, we have to calculate the fundamental vibrational frequency and the 0 point energy of roaming, that atomic weight of roaming has been given in the question. So, we will start by calculating that reduce Morse of roaming. So, reduce Morse of roaming is 78.92 times 78.92 divided by 2 times 78.92 that is 39.46 amu. But here you see this roaming is a homeowner nuclear diatomic molecule.

So the reduce Morse as I said is given by m / 2. So, we can also get this number 39.46 we just divide 78.92 divided by 2, this is also 39.46. So we have to convert into kg so we will write 39 times 46 times 1.661 times 10 to the power - 27 kg. So we have to find the frequency. So frequency is given by 1 / 2 Pi root over k / mu. So we can write this is 1 / 2 pi times k 240 Newton meter inverse, you had a mu that is 39.46 times 1.661 times 10 to the power - 27 kg.

So whole to the power half and if you do this calculation, what you get is 9.63 times 10 to the power 12 second inverse. So, the frequency in wave number is given by nu / c by sea or nu bar was nu / c. So we can write this as 9.63 times 10 to the power 12 divided by 3 times 10 to the power 10. So, that will be 321 wave numbers. So, we have found the vibrational frequency, both in second inverse and in wave numbers.

And now we have to find the 0 point energy. So, the 0 point energy that is E 0 is even by half h nu. So we can write this as 6.626 times 10 to the power - 34. That is a hell of h, then 9.63

times 10 to the power 12 divided by 2. So, if we do this what (())(35:25) we get is 3.19 times 10 to the power - 21 choose