Fundamentals of Spectroscopy

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Lecture-22
Vibrational Spectroscopy: Simple Harmonic Oscillator

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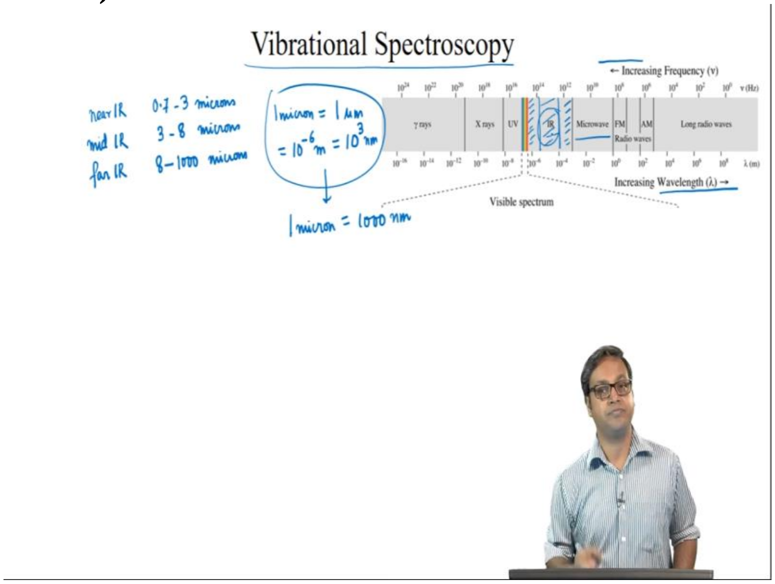

Vibrational Spectroscopy

near IR 0.7 - 3 microns
mid IR 3 - 8 micron
far IR 8 – 1000 micron

1 micron = 1 μm
= 10^{-6} m = 10^{3} nm

1 micron = 1000 nm

Hello everyone, in this lecture, we will start a new module where we look into vibrational spectroscopy. So in this module we will look into vibrational spectroscopy. We already know that the electromagnetic spectrum can be divided into 2 different regions like gamma rays, X rays, UV, IR, microwave, etc. So in the last module, we have discussed in details about microwave spectroscopy, where the frequency of the light corresponds to the microwave region of the electromagnetic spectrum.

In this module, we will discuss about a different region of the electromagnetic spectrum that is the infrared region. So, as we mentioned before, the form of spectroscopy associated with this frequency region of the electromagnetic spectrum is vibrational spectroscopy. The form of spectroscopy or this form of spectroscopy is related to the vibration of the bonds of a molecule.

So, we can divide the infrared region of the electromagnetic spectrum into 3 parts, namely near IR mid IR and far IR.

So, the wavelength range corresponding to these regions are approximately. We can write 0.7 to 3 microns for near IR then we have 3 to 8 microns for mid IR and we can have 8 to much larger microns for the far IR. So, here, 1 micron, that is 1 micron = 1 micro meter. That means 1 micro meter = 10 to the power - 6 meter or we can write this as 10 to the power 3 nanometer. So, from here, what we get is 1 micron = 1000 nanometers.

So, as wavelength is inversely proportional to frequency, we can see here the wavelength is increasing at the right hand side and frequency is increasing to the left. So, because wavelength is inversely proportional to frequency, the near IR which has lower wavelength has higher frequency. So, near IR is close to the visible range. On the other hand, the far IR has lower frequency and this is near the microwave range and the middle part of this IR frequency range is the mid IR.

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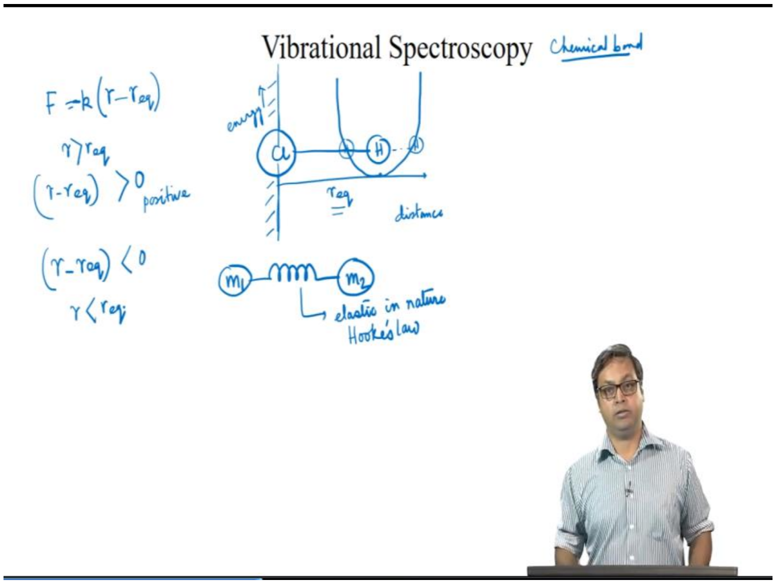

Vibrational Spectroscopy

So, the first question one may have is that how the bond vibration is related to infinite spectrum. To explain this, let us revisit the concept of up chemical bond. So, in a chemical bond, so let us say we have 2 atoms, we have one hydrogen atom and we have another chlorine atom. So, these 2 atoms come together to form HCL, such that the atoms settle to a particular distance between them, maintaining the minimum energy of the system. On one hand, there is repulsion between the positively charged nuclei of both atoms moreover.

There is repulsion between the negatively charged electron clouds of both atoms. On the other hand, there is attraction between the nucleus of this atom and the electron cloud of this atom and also the nucleus of this atom and the electron cloud of the other atom. So, the 2 atoms settle in a mean inter nuclear distance. So, there is a mean internuclear distance which is given by r equilibrium such that these attractive and repulsive forces are balanced and the total energy of the whole system is a minimum.

So, we can think that, pushing the 2 atoms will cause the repulsive forces to rise rapidly, while pulling them apart will be resisted by the attractive force thus any attempt to distort this equilibrium bond length will need an input of energy. So, if you plot the energy versus the internuclear distance, so let us plot the energy versus the internuclear distance. So, we are plotting distance on the x axis and energy on the y axis. So what we will get? Will get a curve like so here it will be minimum and we will get a curve like this.

That means that if we push this chlorine and hydrogen atoms closer to one another, that means if you put the hydrogen atom here there will be an increase in energy. And if you pull these 2 atoms that is we put the hydrogen atom here, there will also be increase in energy. So, in other words, we can say that either pushing or pulling that mean changing the internuclear distance will change the energy of the system.

And here what we have done, we have put the chlorine atom, let us say it is embedded in a wall and we are kind of pushing and pulling only the hydrogen atom. So, we can think of a model where the 2 atoms are connected by a spring. So, let us say I have 2 atoms will take a general case I have 2 atoms m 1 and m 2 and they are connected by a spring. That means, we can think that the bond is elastic in nature.

So the bond is elastic in nature and we can stretch the bond according to Hooke’s law. So according to Hooke’s law, that applied force is proportional to the cause displacement in the spring does the restoring force is proportional to the distance away from the equilibrium position, or the equilibrium bond length given by r equilibrium. So, we can write the force or the restoring force equals k times r – r equilibrium.

So here r is the bond length at any point of time. And r equilibrium is the equilibrium bond length, and k is the force constant. So let us see, if r is greater than r equilibrium, then r – r equilibrium is greater than 0. So this is positive. But due to the negative sign, we have a negative sign here. So the negative sign makes the restoring force in the opposite direction to r. So if r - r equilibrium is positive, that is, we have a bond length longer than the equilibrium bond length, then there is a force trying to compress the bond.

But if r - r equilibrium is negative, that means r is less than r equilibrium, then the force will be positive because of the negative sign and will try to stretch the bond back towards the equilibrium bond length.

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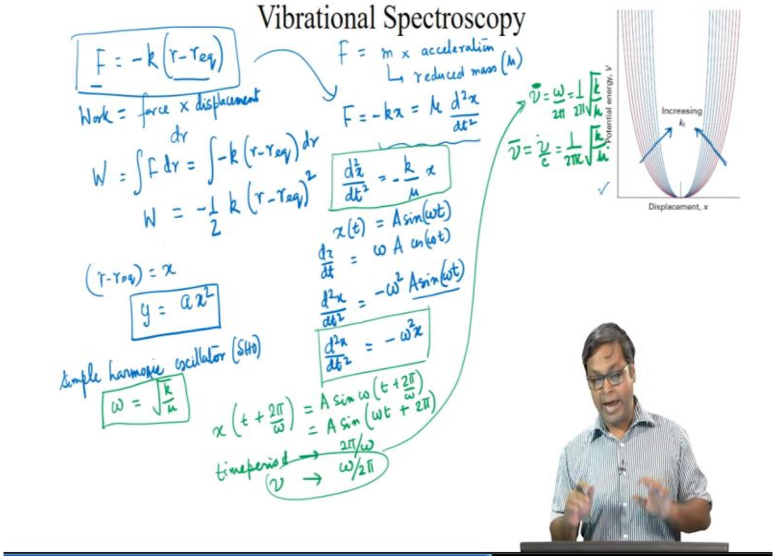

Vibrational Spectroscopy

$\boxed{F = -k(r - r_{eq})}$

Work = force × displacement

$W = \int F\,dr = \int -k(r - r_{eq})\,dr$

$W = -\frac{1}{2}k(r - r_{eq})^2$

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

$\boxed{y = ax^2}$

Simple harmonic oscillator (SHO)

$\boxed{\omega = \sqrt{\frac{k}{\mu}}}$

F = m × acceleration
↳ reduced mass (μ)

$F = -kx = \mu\frac{d^2x}{dt^2}$

$\boxed{\frac{d^2x}{dt^2} = -\frac{k}{\mu}x}$

$x(t) = A\sin(\omega t)$

$\frac{dx}{dt} = \omega A\cos(\omega t)$

$\frac{d^2x}{dt^2} = -\omega^2 A\sin(\omega t)$

$\boxed{\frac{d^2x}{dt^2} = -\omega^2 x}$

$x\left(t + \frac{2\pi}{\omega}\right) = A\sin\omega\left(t + \frac{2\pi}{\omega}\right) = A\sin(\omega t + 2\pi)$

timeperiod → $2\pi/\omega$

$\nu \rightarrow \omega/2\pi$

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

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

So a plot of this restoring force forces the displacement from equilibrium bond length results in a straight line, because we have force = - k r - r equilibrium. So if you plot force versus displacement from equilibrium position that is r - r equilibrium will have a straight line and the slope of the straight line will give us k the force constant. Now, let us focus on the work done in the system, we know work is force times displacement.

So, that is force times displacement over the entire displacement range. So, the amount of work is actually the area under the curve that can be obtained from the plot of force versus r - r equilibrium. And we can find this area by integrating the force over in finite similarly, small distances let say dr. So we can write work done equals integration of f dr. And now we put f as - k r - r equilibrium dr. So if we integrate this, we find the work done is given by minus half k, r - r equilibrium, whole square.

So the potential or the potential energy is half k r - r equilibrium whole square. In other words, we have r parabolic potential curve, because if we think r - r equilibrium = x, then we have something as y = a x square where a = k / 2. So, we have a parabolic potential and a parabolic potential leads to harmonic oscillation. And hence, this type of system is known as simple harmonic oscillator or in short we can write SHO.

So, we will see later that the simplified model is valid for energy levels having relatively lower energy for higher energy levels, this approximation would not work. In other words, we can say that the parabolic potential can only be applied to the bottom of the well and not at the top. So the value of k or the force constant is extremely important as it is used to define the stiffness of the well.

So a strong force constant means a sharp well, so as you can see from this figure and a stronger bond, so the force constant is increasing in this direction. So, as this parabola becomes narrower and narrower, the value of k increases or the force constant increases. So, we know f = - k times r - r equilibrium, and we have already assumed r - r equilibrium = x. We also know force is given by mass times acceleration.

So because we have 2 atoms here, we have a diatomic molecule. So the mass will consider is the reduced mass that is, mu. So we can write force = - k x that we get from this expression equals mass that is mu times acceleration, there is d 2 x, dt 2. Or, if we rearrange this part, we get d 2 x dt 2 = k / mu there is a minus sign times x. So, let us write x at any point of time t = A sin omega t. So we can see dx dt is given by omega times A cos omega t and d 2 x dt 2 is given by minus omega square A sin omega t. What is A sin omega t part is nothing but x.

So we can write this as d 2 x dt 2 = - omega square x. So, now if we compare this expression, that is d 2 x dt 2 = - k / mu x and d 2 x dt 2 = - omega square x, we can write omega equals root over k / mu. So now if we evaluate the value of x at x = t + 2 pi / omega, what we have this equals A sin omega times t + 2 pi / omega. So this becomes A sin omega t + 2 pi but we know that sin omega t + 2 pi = sin omega t.

So that means it is like an oscillation or a repetitive pattern. And the time period of this repetition is given by, so the time period is given by 2 pi / omega. And the frequency of this oscillation is given by the inverse of the time period. So the frequency we can write which is mu is given by omega / 2 pi. So, when we have an oscillation, the frequencies omega / 2 pi. So, from here we can write that nu = omega / 2pi = omega / 2pi root over k / mu because we already knew from previous that omega equals root over k / mu.

And so this is frequency and now if I express it in nu bar that in wave number units, I know nu bar = nu / c. So, nu bar will be 1 / 2 pi c root over k / mu. So, from this equation, it is obvious that vibrational frequency will be proportional to the force constant that is the strength of the bond. And the vibrational frequency has an inverse relation to the reduced mass. In other words, the vibrational frequency will increase if either the bond becomes stronger or the reduced mass decreases and vice versa.

So the frequency of oscillation when it matches with the frequency of light during the light matter interaction, we have transition from one vibrational level to another. So we can think that vibrational spectroscopy is also form of resonance spectroscopy. So this brings us to the end of this lecture. So we will end this lecture by solving a few problems.

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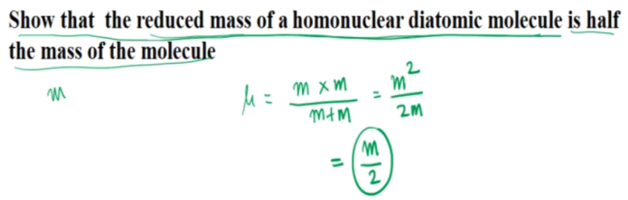

Show that the reduced mass of a homonuclear diatomic molecule is half the mass of the molecule

m

$$\mu = \frac{m \times m}{m+m} = \frac{m^2}{2m} = \boxed{\frac{m}{2}}$$

So we have the first problem. The first problem is show that the reduced mass of a hormone nuclear diatomic molecule is half the mass of the molecule. So the mass of the molecule is, let us say, m for homonuclear diatomic molecule. What we have the reduced mass is m times m divided by m + m. So, this is given by m square / 2m.That is, if you can say m and m, what do we get is m / 2. So, this is easy to show that the reduce mass of a homonuclear diatomic molecule is half the mass. So, let us go to the next question.

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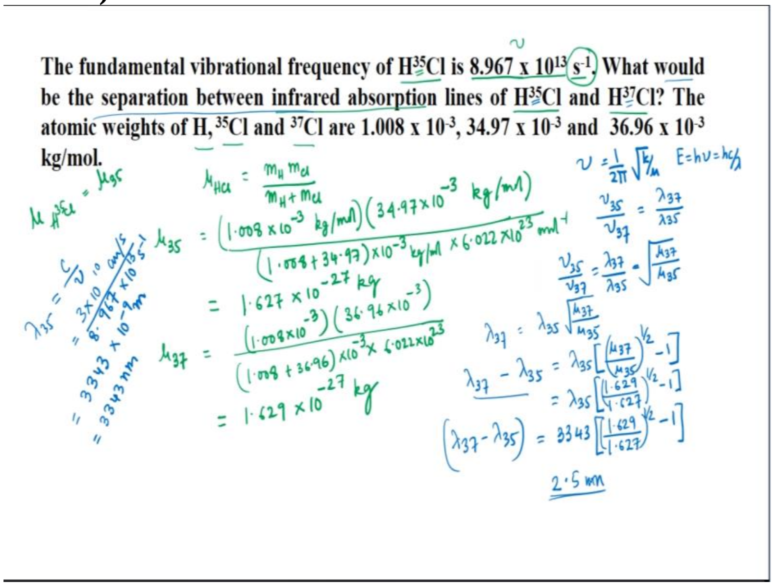

The fundamental vibrational frequency of $H^{35}Cl$ is 8.967×10^{13} s^{-1}. What would be the separation between infrared absorption lines of $H^{35}Cl$ and $H^{37}Cl$? The atomic weights of H, ^{35}Cl and ^{37}Cl are 1.008×10^{-3}, 34.97×10^{-3} and 36.96×10^{-3} kg/mol.

$\tilde{\nu}$

$\mu_{H^{35}Cl} = \mu_{35}$

$$\mu_{HCl} = \frac{m_H m_{Cl}}{m_H + m_{Cl}}$$

$$\mu_{35} = \frac{(1.008 \times 10^{-3}\ kg/mol)(34.97 \times 10^{-3}\ kg/mol)}{(1.008 + 34.97) \times 10^{-3}\ kg/mol \times 6.022 \times 10^{23}\ mol^{-1}}$$

$$= 1.627 \times 10^{-27}\ kg$$

$$\mu_{37} = \frac{(1.008 \times 10^{-3})(36.96 \times 10^{-3})}{(1.008 + 36.96) \times 10^{-3} \times 6.022 \times 10^{23}}$$

$$= 1.629 \times 10^{-27}\ kg$$

$$\lambda_{35} = c/\tilde{\nu} = \frac{3 \times 10^{10}\ cm/s}{8.967 \times 10^{13}\ s^{-1}} = 3343 \times 10^{-9}\ m = 3343\ nm$$

$\nu = \frac{1}{2\pi}\sqrt{k/\mu}$ $E = h\nu = hc/\lambda$

$$\frac{\nu_{35}}{\nu_{37}} = \frac{\lambda_{37}}{\lambda_{35}}$$

$$\frac{\nu_{35}}{\nu_{37}} = \frac{\lambda_{37}}{\lambda_{35}} = \sqrt{\frac{\mu_{37}}{\mu_{35}}}$$

$$\lambda_{37} = \lambda_{35}\sqrt{\frac{\mu_{37}}{\mu_{35}}}$$

$$\lambda_{37} - \lambda_{35} = \lambda_{35}\left[\left(\frac{\mu_{37}}{\mu_{35}}\right)^{1/2} - 1\right]$$

$$= \lambda_{35}\left[\left(\frac{1.629}{1.627}\right)^{1/2} - 1\right]$$

$$(\lambda_{37} - \lambda_{35}) = 3343\left[\left(\frac{1.629}{1.627}\right)^{1/2} - 1\right]$$

$\underline{2.5\ nm}$

So, the next question states that the fundamental vibrational frequency of HCl, when we have that 35 isotope of chlorine is 8.969 times 10 to power 13 second inverse here, it is given this a nu because the unit is second inverse. So, what would be the separation between the infinite lines of

H 35 Cl and H 37 Cl the atomic weights of hydrogen 35 Cl and 37 Cl are also given. So, we know that the reduced mass of HCl is given by mass of hydrogen mass of chlorine divided by the mass of hydrogen plus mass of chlorine.

So, for H 35 Cl for reduced mass of this molecule in sort we will write, mu 35, so we can write mu 35 = 1.008 times 10 to the power - 3.That is in kilogram per mole. Then we have 34.97 times 10 to the power - 3, we have kilogram per mole divided by we have 1.008 + 34.97 times 10 to the power - 3.So, that is kilo gram per mole and we have time 6.022 times 10 to the 23 mole inverse. So if you do this calculation, what we get is 1.627 times 10 to the power – 27 kilograms.

So if we find the mu of H 37 Cl between H 37 what we get here is 1.008 times 10 to the power - 3, that is the first term the second term changes to 36.96 times 10 to the - 3, we have 1.008 + 36.96 times 10 to the power - 3 times avogadro number 6.022 10 to the power 23.So this is 1.629 times 10 to the power - 27 kilogram. So, we know that nu = 1 / 2 pi root over k / mu. We also know that E = h nu = hc / lambda.

In other words we can write nu 35 divided by nu 37 = lambda 37 / lambda 35.So, we can write nu 35 divided by nu 37 = lambda 37 divided by lambda 35 = root over mu 37 divided by mu 35 or lambda 37 = lambda 35 root over mu 37 divided by mu 35 or lambda 37 - lambda 35. We will evaluate this, because in the question, it has been asked, what would be the separation between the infrared absorption lines of this 35 and 37.

So, lambda 37 - lambda 35 is given by lambda 35 times mu 37 divided by mu 35 to the power half – 1. So, we can write this as lambda 35 times 1.629 divided by 1.627 to the power half - 1. So, we need to find lambda 35. So, we know that the frequency is 8.967 times 10 to the power 13 second inverse. So lambda 35 is given by c / nu. This is equal to 3 times 10 to the power 10 centimeter per second divided by 8.967 times 10 to the power 13 second inverse, so, that will be 3343 times 10 to the power - 9 meter that means 3343 nanometers.

So, if you put the value here, so lambda 37 - lambda 35 = 3343 times 1.629 divided by 1.627 to the power half - 1. So, if we do this calculation, what we will get is 2.5 nanometer so, that is the separation between the 2 lines.

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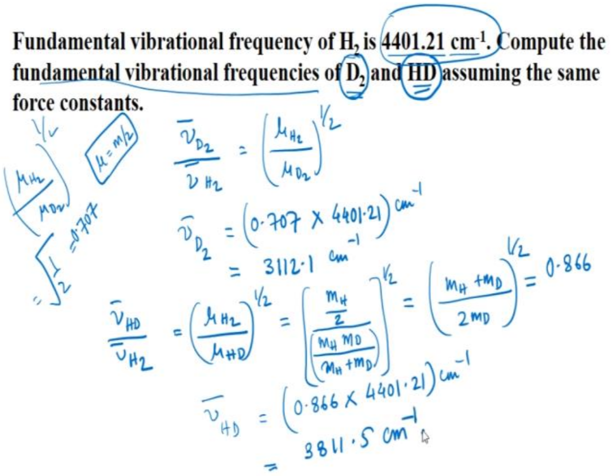

Fundamental vibrational frequency of H_2 is 4401.21 cm^{-1}. Compute the fundamental vibrational frequencies of D_2 and HD assuming the same force constants.

$$\left(\frac{\mu_{H_2}}{\mu_{D_2}}\right)^{1/2} = \sqrt{\frac{1}{2}} = 0.707 \qquad \boxed{\mu = m/2}$$

$$\frac{\bar{\nu}_{D_2}}{\bar{\nu}_{H_2}} = \left(\frac{\mu_{H_2}}{\mu_{D_2}}\right)^{1/2}$$

$$\bar{\nu}_{D_2} = (0.707 \times 4401.21)\ cm^{-1} = 3112.1\ cm^{-1}$$

$$\frac{\bar{\nu}_{HD}}{\bar{\nu}_{H_2}} = \left(\frac{\mu_{H_2}}{\mu_{HD}}\right)^{1/2} = \left[\frac{\frac{m_H}{2}}{\left(\frac{m_H m_D}{m_H + m_D}\right)}\right]^{1/2} = \left(\frac{m_H + m_D}{2 m_D}\right)^{1/2} = 0.866$$

$$\bar{\nu}_{HD} = (0.866 \times 4401.21)\ cm^{-1} = 3811.5\ cm^{-1}$$

Now, let us look into the other problem here, the fundamental frequency of hydrogen is given to be 4401.21 centimeter inverse. So, we have to compute the fundamental vibrational frequency of D 2 which is an isotope of H 2 and a mixed isotope HD assuming the same force constants for all these molecules. So, we know we can write nu bar D 2 divided by nu bar H 2 = mu H 2 divide by mu D 2 to the power half.

So mu H 2 / mu D 2 to the power half equals half root over half that is 0.707.So, we can write nu bar D 2 = 0.707 times the nu bar H 2 which is given us 4401.21 wave numbers that is 4401.21. This is a wave numbers. So this will be 3112.1 wave numbers. So we have found the fundamental vibrational frequency of D 2. Now we have to find the fundamental vibrational frequency of HD.

So we can write nu bar HD divided by nu bar H 2 = mu H 2 / mu HD to the power half. So, we could directly write that mu H 2 / mu HD is half to the power half, because we know for a homonuclear diatomic molecule, the reduced mass is given by m / 2 but for HD, it is not a homonuclear diatomic molecule. So, we have to write here as m hydrogen / 2 because that is a homonuclear diatomic molecule not for HD we have write m H times m D divided by m H + m D the entire thing to the power half.

So, if we simplify this it becomes m H + m D divided by 2 mD to the power half. And if you put the values, this expression will be 0.866. So nu bar HD will be 0.866 times 4401.21 wave numbers. So that will be 3811.5 wave numbers.