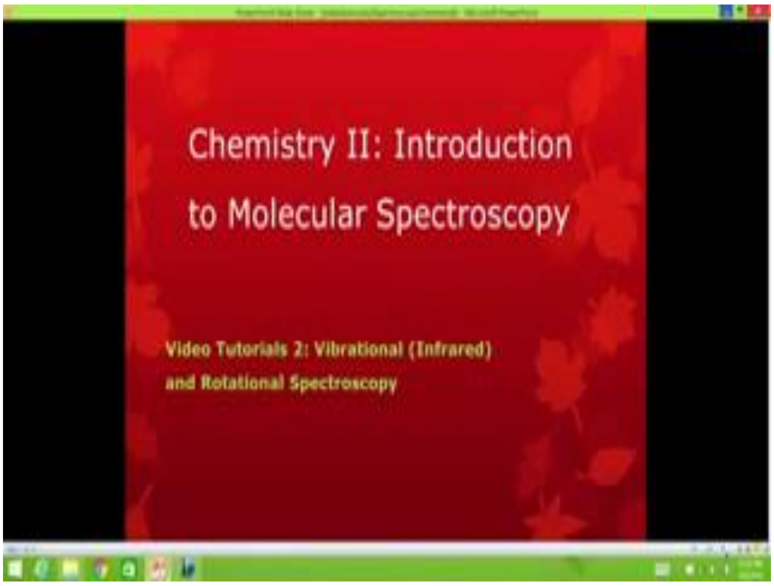
Chemistry II: Introduction to Molecular Spectroscopy

Prof. Mangala Sunder
Department of Chemistry and Biochemistry
Indian Institute of Technology, Madras

Lecture - 20
Video Tutorial 2: Part – I

Welcome back to the lectures on chemistry with introduction to molecular spectroscopy. This lecture section is to help you with problem solving ability and also to think about how to organize your thought process when a set of data are given and you are asked to find the solution. Problem solving is an important part of learning, but it is not the only part; it is important for you to listen to lectures, it is important for you to read and understand things discuss them with your friends and your teachers, but then use these problems has to give you confidence that you have understood the material understood within codes that material with (Refer Time: 01:13) degree of confidents.

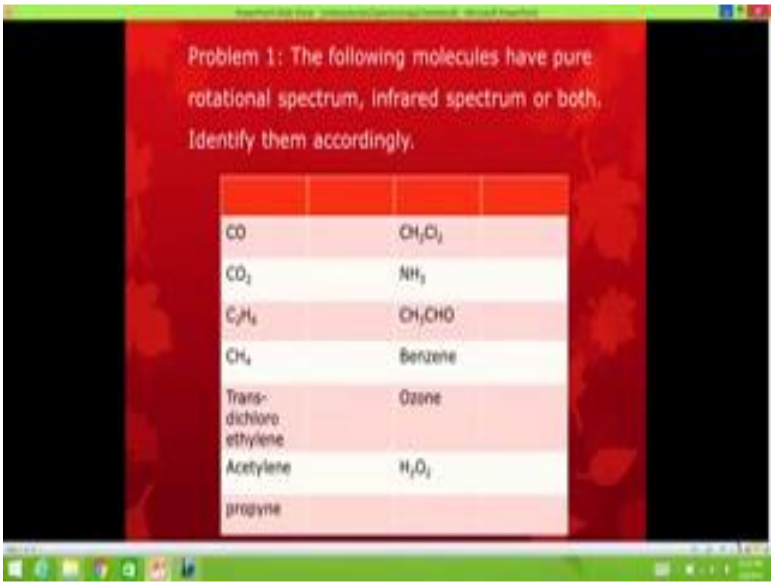
(Refer Slide Time: 01:19)



Chemistry II: Introduction to Molecular Spectroscopy

Video Tutorials 2: Vibrational (Infrared) and Rotational Spectroscopy

(Refer Slide Time: 01:21)



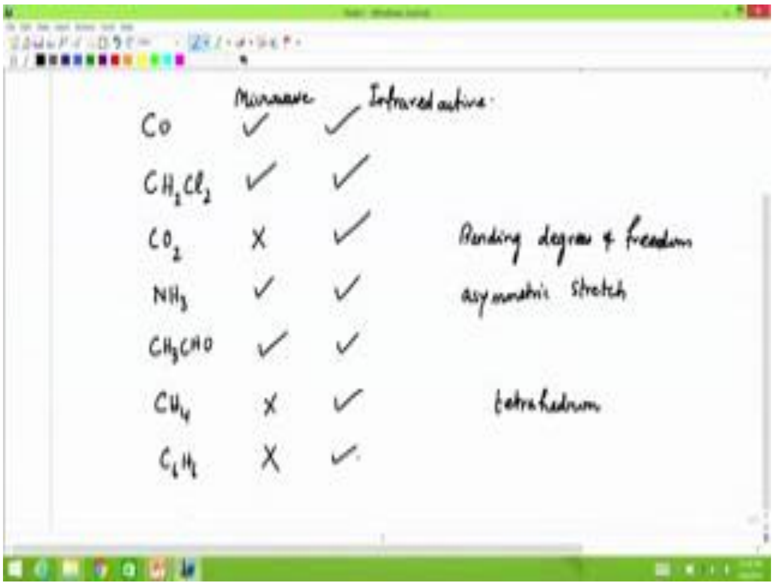
Problem 1: The following molecules have pure rotational spectrum, infrared spectrum or both. Identify them accordingly.

CO		CH_2Cl_2	
CO_2		NH_3	
C_2H_6		CH_3CHO	
CH_4		Benzene	
Trans-dichloro ethylene		Ozone	
Acetylene		H_2O_2	
propyne			

So, in this set of problems that we have ten problems, the first problem is requiring you to identify which molecules have pure rotational that is microwave spectrum and which molecules have infrared spectrum or the molecules which have both of them; and you are ask to identify them accordingly. The important point is; for a molecule to have a pure rotational or a microwave spectrum; the molecules should have a permanent dipole moment in it is equilibrium geometry or a disequilibrium configuration. For a molecule to have infrared spectrum during the vibrational motion the dipole moment must change. The dipole movement need not be there to start with, but if in the process of vibrational motion the dipoles are created and destroyed what you see is that that kind of a motion leads to an oscillation of the electric dipole moment and then such molecules will have infrared spectrum.

So, obviously molecules which have a permanent dipole moment will all have an infrared spectrum there is no question about that because during the molecular motion some of it is during at least some of this motion the dipole moment will change as the molecule vibrates and so on. So, let us take the first example carbon monoxide. Carbon monoxide has a strong dipole moment. Therefore, it has both microwave and IR spectrum.

(Refer Slide Time: 03:06)



	Microwave	Infrared active
CO	✓	✓
CH_2Cl_2	✓	✓
CO_2	X	✓
NH_3	✓	✓
CH_3CHO	✓	✓
CH_4	X	✓
C_2H_2	X	✓

Bending degrees of freedom

asymmetric stretch

tetrahedron

It has CO both microwave and IR spectrum. The next one is CH2 Cl2. This is a tetrahedral molecule and it has a permanent dipole moment due to the C Cl bond having electrical dipole differently from that of the C H2 and therefore, this molecule also has both microwave spectrum and infrared spectrum.

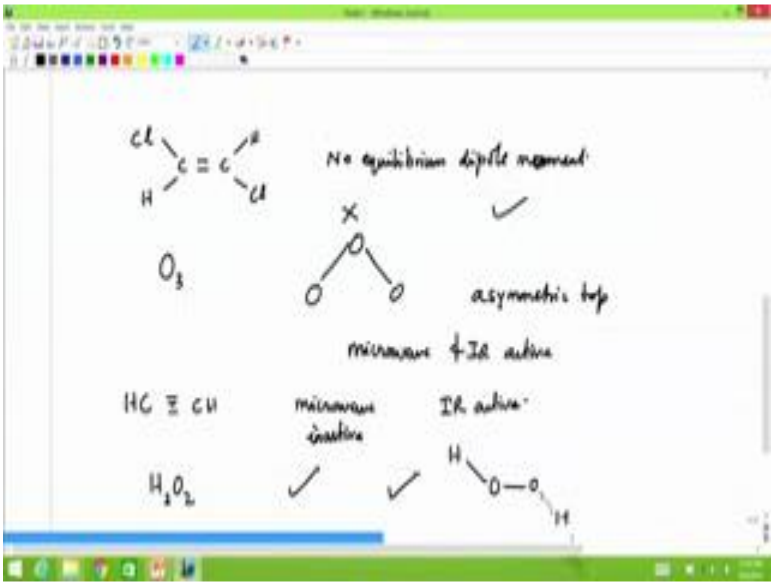
Carbon dioxide which is the third one; carbon dioxide does not have a permanent a dipole moment in it is equilibrium geometry or it is a zero point vibrations. Carbon dioxide does not have an electric dipole moment in it is equilibrium geometry therefore, it does not have a microwave spectrum, but it has two motions the bending degrees of freedom and the asymmetric stretch in both these normal modes of vibration; the molecule has a changing the dipole moment therefore, it has the infrared spectrum for these two degrees of freedom, the bending mode is doubly degenerate therefore, you have degeneracy involved.

But there two frequencies; one for the bending mode and the one for the asymmetry stretch. The molecule ammonium is pyramidal; it has the dipole moment therefore, it has both microwave spectrum and infrared spectrum. The molecule formaldehyde, acetaldehyde C H3 CHO not formaldehyde acetaldehyde; yes it has a dipole moment therefore, there are vibrational motions were the dipole will change during the vibration giving rise to both IR and microwave spectrum. Methane is a perfect tetrahedron and in it is tetrahedron geometry the electric dipole and cancel to each other and therefore, methane the does not have the microwave spectrum, but methane has vibrational motion. Please remember it is a five atom molecules therefore, it has 3 n minus 6 normal modes which is 9 normal modes some of these normal modes lead to change in the dipole moment therefore, it has infrared spectrum.

The symmetric stretch of CH4 will not have a dipole moment because all four hydrogen atoms vibrate away from equilibrium and also go into that. Such modes are not seen, but in general it has IR spectrum.

Benzene; the same thing in it is equilibrium structure does not have a dipole moment therefore, it is not microwave active. So, I will write microwave active here and this is infrared active here. So, when it benzene does not have a microwave spectrum, but it has many degrees of freedom which lead to IR spectrum.

(Refer Slide Time: 06:42)

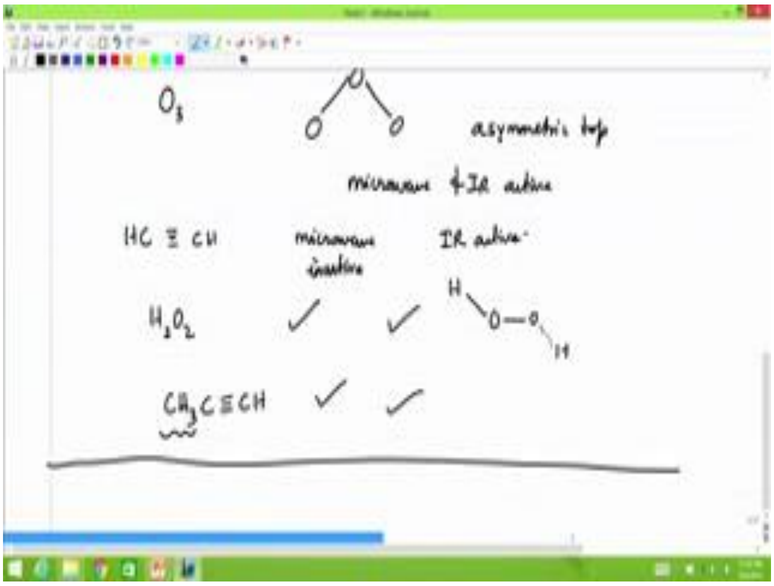


Trans dichloro ethane; ethylene so that is Cl C double bond CH Cl H this is given so that there is no equilibrium dipole moment. Therefore, this does not have a microwave spectrum, but it has IR spectrum. Ozone (Refer Time: 07:15) all the three oxygen's involved please remember ozone is an asymmetric top and this oxygen is differently bonded to the other two oxygen therefore, asymmetric top has and this molecule also has dipole moments therefore, it is microwave and IR active.

Acetylene it is quite clear that there is no dipole moment for those linier molecule this molecule has a center of asymmetry therefore, it is not microwave active that is microwave inactive, but it has vibrational motions therefore, it is IR active.

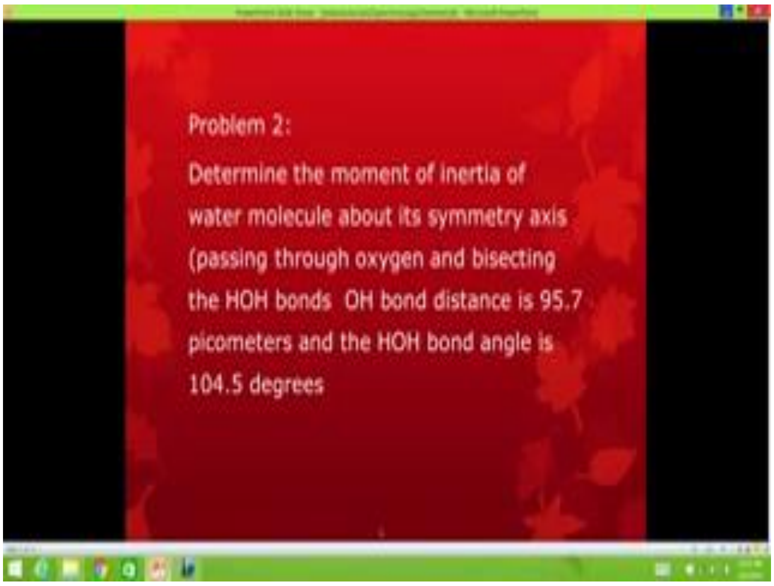
Hydrogen peroxide is a non planar structure bending structure and therefore, it is a non planar structure therefore, it has a dipole moment therefore, it is microwave active and IR active.

(Refer Slide Time: 08:33)



And the last is propine, C H3 C triple bond CH. So, this has the asymmetry groups C H3 here therefore, it is both microwave active and IR active. So, one has to look for the equilibrium geometry of the molecule and look for the all it is possible normal modes in determining, which of them or IR active and which of them are microwave active and so on.

(Refer Slide Time: 09:01)

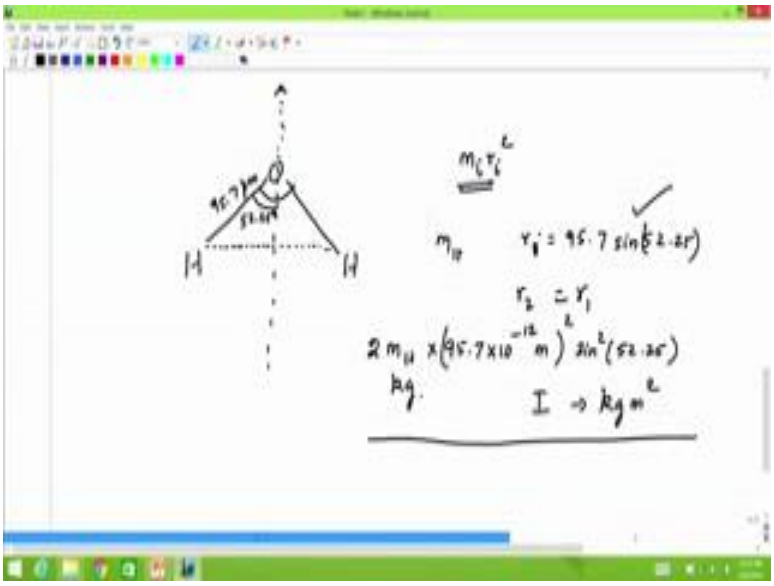


Problem 2:

Determine the moment of inertia of water molecule about its symmetry axis (passing through oxygen and bisecting the HOH bonds OH bond distance is 95.7 picometers and the HOH bond angle is 104.5 degrees

So, let us go to the second problem. This is an interesting elementary though problem on the determination of the moment of inertia of water molecule about it is symmetry axis. The symmetry axis of course, passes through oxygen and it bisects the HOH bonds. So, the OH bond distance is given to you as 95.7 picometers and the HOH bond angle is also given as 104.5 degrees.

(Refer Slide Time: 09:38)



$m_i r_i^2$ ✓

m_H $r_1 = 95.7 \sin(52.25)$

$r_2 = r_1$

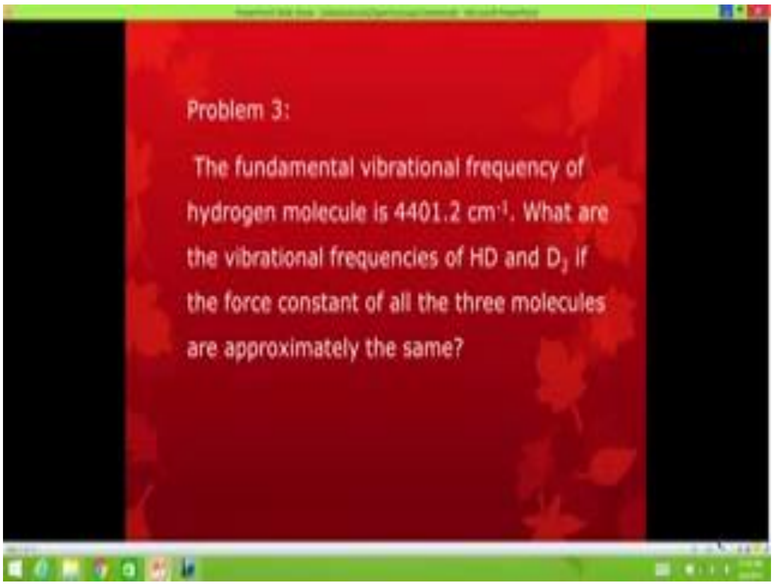
$2 m_H \times (95.7 \times 10^{-12} m)^2 \sin^2(52.25)$

kg. $I \to kg\,m^2$

So, the moment of the inertia if you recall for water molecule if you have to calculate about the symmetry axis this is the symmetry axis c2 symmetry axis and since on the c2 axis; the oxygen resides the oxygen does not contribute to the m i r i square term. r i is 0 for oxygen because it is on the axis. However, the hydrogens are at this distance which is perpendicular from the axis which the perpendicular distance that you have to take into account and therefore, you have a mass of hydrogen and since this angle is given has 104.5 degrees the half angle is 52.25 degrees and the bond length is give as 95.7 picometers.

Therefore it is easy for you to calculate this distance as r i as 95.7. So, this is sine 52.25 that is the r i. Therefore, two hydrogen atoms contribute to the overall moment of the inertia for this molecule therefore, this is; this value and since it is a symmetry axis that we are talking about hydrogen atom on this side is also r 1 and r 2 are both equal therefore, what you have is 2 m H times 95.7 into 10 raise to minus 12 meter square times sine square 52.25 and this is kilogram that you have to use therefore, you will have the moment of the inertia I in terms of kilogram meter square. I think the numbers can be calculated by you for let me not write that here.

(Refer Slide Time: 11:55)

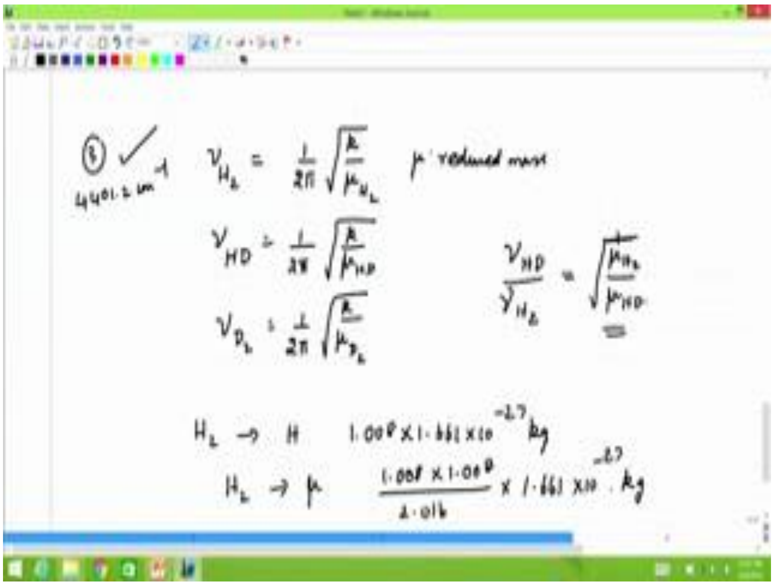


Problem 3:

The fundamental vibrational frequency of hydrogen molecule is 4401.2 cm^{-1}. What are the vibrational frequencies of HD and D_2 if the force constant of all the three molecules are approximately the same?

Let us go to the next problem. The next problem is about to the fundamental vibrational frequency of hydrogen molecule and how it is related to the vibrational frequency of it is isotopic substituent’s the HD in which one hydrogen item is substituted by the deuterium and D2 in which both the atoms are replaced by deuterium and one assumes that in these three species the chemical nature namely the force constant which contributes the bond strength of these three molecules do not change by much; it is in that limit how are these vibrational frequency is related to each other.

(Refer Slide Time: 12:42)



③ ✓ 4401.2 cm^{-1}

$$\nu_{H_2} = \frac{1}{2\pi}\sqrt{\frac{k}{\mu_{H_2}}}$$ μ reduced mass

$$\nu_{HD} = \frac{1}{2\pi}\sqrt{\frac{k}{\mu_{HD}}}$$

$$\frac{\nu_{HD}}{\nu_{H_2}} = \sqrt{\frac{\mu_{H_2}}{\mu_{HD}}}$$

$$\nu_{D_2} = \frac{1}{2\pi}\sqrt{\frac{k}{\mu_{D_2}}}$$

$H_2 \rightarrow H \quad 1.008 \times 1.661 \times 10^{-27}$ kg

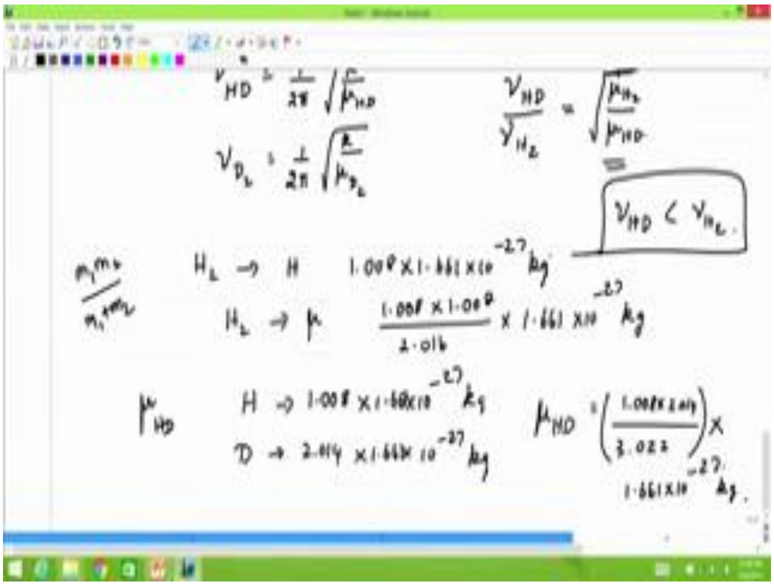
$H_2 \rightarrow \mu \quad \frac{1.008 \times 1.008}{2.016} \times 1.661 \times 10^{-27}$ kg

This is again it is very simple problem to look at because you know vibrational frequency for problem three; vibrational frequency is related to the force constant and the mass of the molecule that is the center of mass the sorry the reduced mass mu this is the expression. Therefore, if you are writing nu H2 is mu of H2 and k of H2 does not change from k of HD which is now; obviously related to the mu of HD by the same relation mu HD and nu of D2 is given by 1 by 2 pi square root of k mu D2.

Therefore, if you know this number as 4401.2 centimeter inverse; then you can calculate where should the nu HD should be by taking the ratio of this mainly nu HD divided by nu H2 will turn out to be 1 by because the case will cancel the two pi's will cancel; you will have 1 by square root or let me write the final form the square root of this HD therefore, it is mu of H2 divided by mu of HD; they are inversely proportional to the square therefore, the ratio is done.

And mu of H2 is easy to calculate; if you assume H2 to be the H atomic mass as 1.008 a mu; if you multiply that by 1.661 into 10 raise to minu27 kilograms that is the amount for one a mu; that is how that is the mass of a mu associated with that. Then H2 is the reduced mass is nothing, but 1.008, 1.008 divided by 2.016 times1.661 times 10 to the minus 27 kilograms. This is the mu of H2.

(Refer Slide Time: 15:00)



$$\nu_{HD} = \frac{1}{2\pi}\sqrt{\frac{k}{\mu_{HD}}} \qquad \frac{\nu_{HD}}{\nu_{H_2}} = \sqrt{\frac{\mu_{H_2}}{\mu_{HD}}}$$

$$\nu_{D_2} = \frac{1}{2\pi}\sqrt{\frac{k}{\mu_{D_2}}}$$

$$\boxed{\nu_{HD} < \nu_{H_2}.}$$

$$\frac{m_1 m_2}{m_1+m_2} \qquad H_2 \rightarrow H \quad 1.008 \times 1.661 \times 10^{-27}\ kg$$

$$H_2 \rightarrow \mu \quad \frac{1.008 \times 1.008}{2.016} \times 1.661 \times 10^{-27}\ kg$$

$$\mu_{HD} \quad H \rightarrow 1.008 \times 1.661 \times 10^{-27}\ kg$$

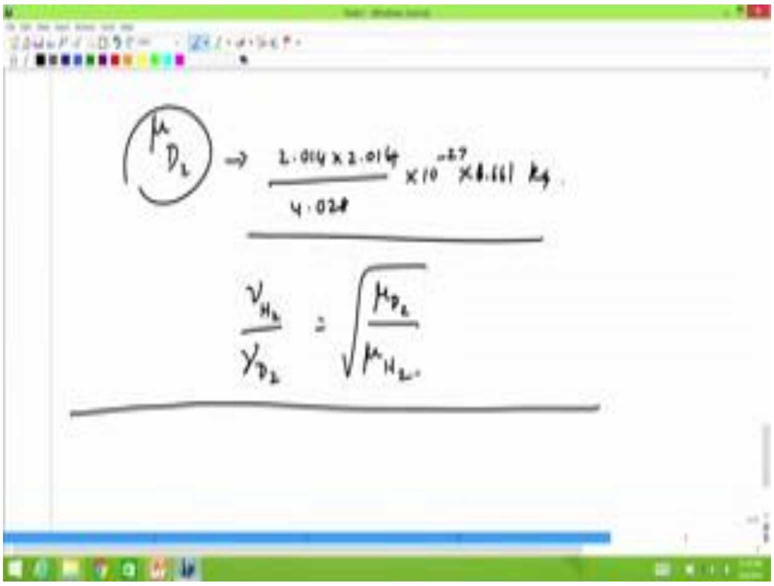
$$D \rightarrow 2.014 \times 1.661 \times 10^{-27}\ kg$$

$$\mu_{HD} = \left(\frac{1.008 \times 2.014}{3.022}\right) \times 1.661 \times 10^{-27}\ kg.$$

And likewise the mu of HD, if you want to do that please remember the relation m 1 m 2 by m 1 plus m 2. So, for mu of HD the D is I believe 2.014. So, H is 1.008 times 1.661 times 10 to the minus 27 kilograms and the D is 2.014 times 1.661 times 10 to the minus 27 kilograms. Therefore, the mu of HD can be calculated as 1.008 times 2.014 divided by 3.022 the sum of the 2 times 1.661 into 10 raise to minus 27.

So, this is the mu of HD. So, you can see that if you substitute mu of the HD the mu of HD is slightly more than the mu of the H2 and therefore, the square root of this number tells you that the nu of HD is a little less than the nu of H2.

(Refer Slide Time: 16:23)



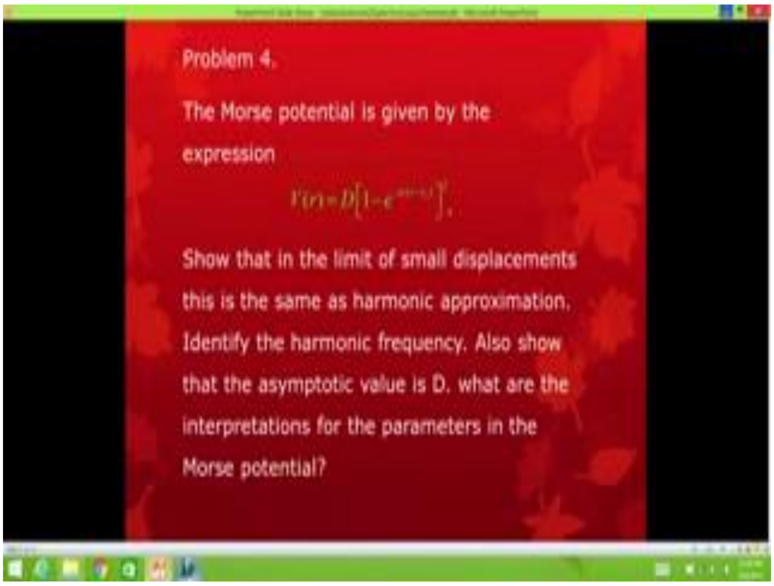
$$\boxed{\mu_{D_2}} \rightarrow \frac{2.014 \times 2.014}{4.028} \times 10^{-27} \times 1.661 \text{ kg}$$

$$\frac{\nu_{H_2}}{\nu_{D_2}} = \sqrt{\frac{\mu_{D_2}}{\mu_{H_2}}}$$

Now, it is a same thing that you have to do for D2; for D2 you would use 2.014 times 2.014 divided by 4.028 times 10 to the minus 27 into 1.661 kilograms; therefore, the mu of D2 is given by this number; then you can calculate nu of H2 the frequency H2 divided by the frequency of D2 is the square root of the mu of D2 divided by the mu of H2.

So, these are simple manipulations of the harmonic oscillator frequencies and also the isotopic concepts that vibrational and rotational frequencies do depend on the isotopic mass of the individual (Refer Time: 17:20)

(Refer Slide Time: 17:22)



Problem 4.

The Morse potential is given by the expression

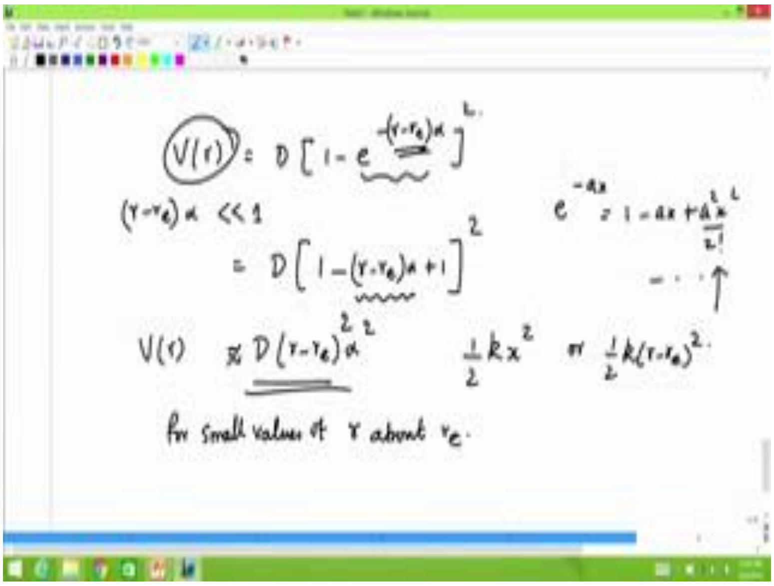
$$V(r) = D\left[1 - e^{\text{[illegible]}}\right]^2.$$

Show that in the limit of small displacements this is the same as harmonic approximation. Identify the harmonic frequency. Also show that the asymptotic value is D. what are the interpretations for the parameters in the Morse potential?

Then; the forth problem is on the Morse potential and you recall the Morse potential expression which is as V of r the potential energy and it is given by the factor D which is the dissociation constant times 1 minus e to the minus alpha r minus r e. r e is the equilibrium distance. r is the distance during the vibration therefore, this the potential term that would you use to solve for the Morse oscillator Hamiltonian. The kinetic energy of the Morse oscillator is already given by p square by 2 m and this is the V r and therefore, you use this to solve the potential energy.

Now, the question is; show that in the limit of small displacement that is an r minus r e is very, very small that this is the same as the harmonic oscillator approximation and identify the harmonic frequency. Also show that the asymptotic value is D. What are the interpretations for the parameter for the Morse potential?

(Refer Slide Time: 18:30)



$$\boxed{V(r)} = D\left[1 - \underbrace{e^{-(r-r_e)\alpha}}\right]^2$$

$$(r-r_e)\alpha << 1 \qquad e^{-ax} = 1 - ax + \frac{a^2x^2}{2!} - \cdots$$

$$= D\left[1 - \underbrace{(r-r_e)\alpha} + 1\right]^2$$

$$V(r) \approx \underline{\underline{D(r-r_e)^2\alpha^2}} \qquad \frac{1}{2}kx^2 \quad \text{or} \quad \frac{1}{2}k(r-r_e)^2.$$

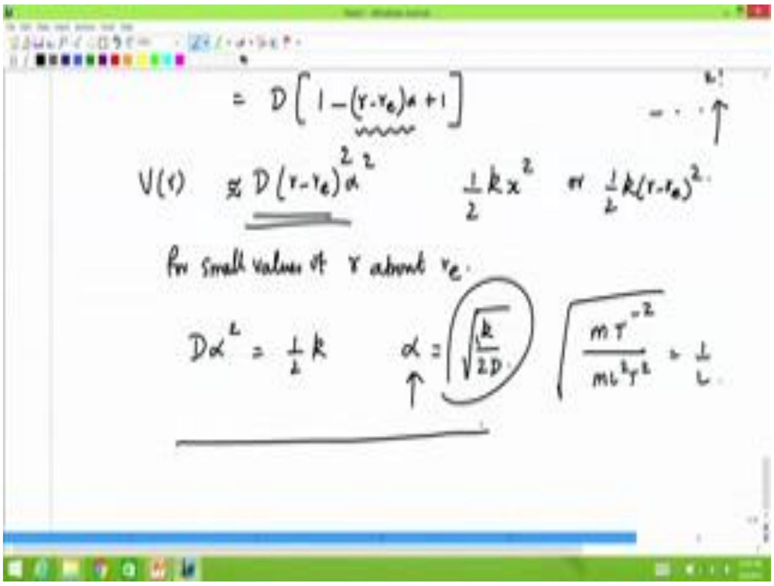
for small values of r about r_e.

So, first of all V of r is D times 1 minus e to the r minus r e times alpha whole square. So, suppose for r minus r e times alpha much less than 1; it is easy for us to expand this by writing D 1 minus please remember exponential of minus a x when a x is much less than 1 is 1 minus a x plus a square x square by 2 minus and so on. We are looking at small values this therefore, we stop with that. So, what we have is D is equal to 1 minus r minus r e alpha and also there is a 1 plus 1 because the exponential has 1 minus that. So, if we stop with that term just the first term and take the square of this term which is already a very small one we do not even go to the second term; then what you see is it is

D into r minus r e whole square and please remember this is the potential energy form and for the harmonic oscillator the potential energy form half k x square or in the notation of r minus r e it is half k r minus r e whole square.

Therefore you see that the alpha there is an alpha here therefore, this is an alpha square. So, D times r minus r e square times alpha square is approximately the potential V of r for small values of r about r e.

(Refer Slide Time: 20:33)



$$= D\left[1 - (r-r_e)\alpha + 1\right]$$

$$V(r) \approx D(r-r_e)^2\alpha^2 \qquad \frac{1}{2}kx^2 \quad \text{or} \quad \frac{1}{2}k(r-r_e)^2$$

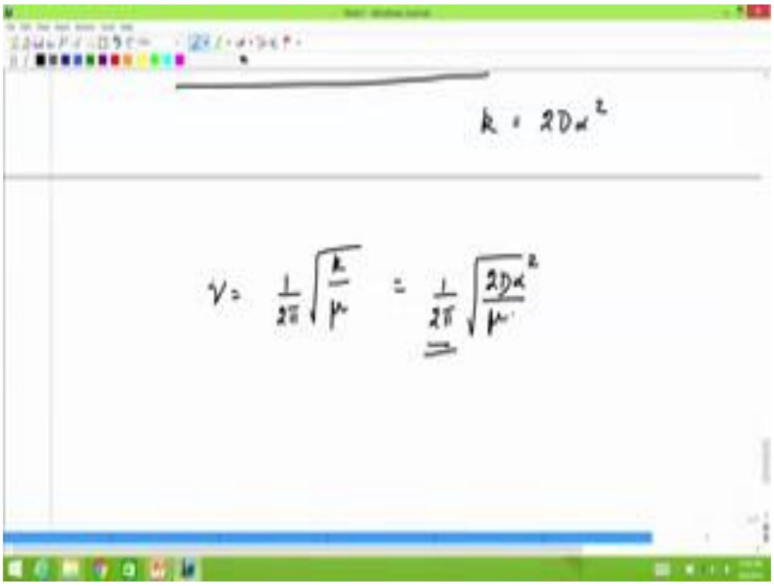
For small values of r about r_e.

$$D\alpha^2 = \frac{1}{2}k \qquad \alpha = \sqrt{\frac{k}{2D}} \qquad \sqrt{\frac{mT^{-2}}{mL^2T^2}} = \frac{1}{L}$$

So, what you have is D alpha square is equal to half k and therefore, alpha is given as square root of k by 2 D. So, this is the Morse oscillator parameter and please remember the Morse oscillator parameter has a dimension by 1 by the length and k has the dimensions mass into this is a force constant therefore, it is mass T to the minus 2 and this is energy which is mass into length square into T to the minus 2 therefore, the square root of this is 1 by length.

So, the interpretation of alpha is that if this k the force constant is basically 2 D alpha square. Now the next question is what is the harmonic frequency?

(Refer Slide Time: 21:43)

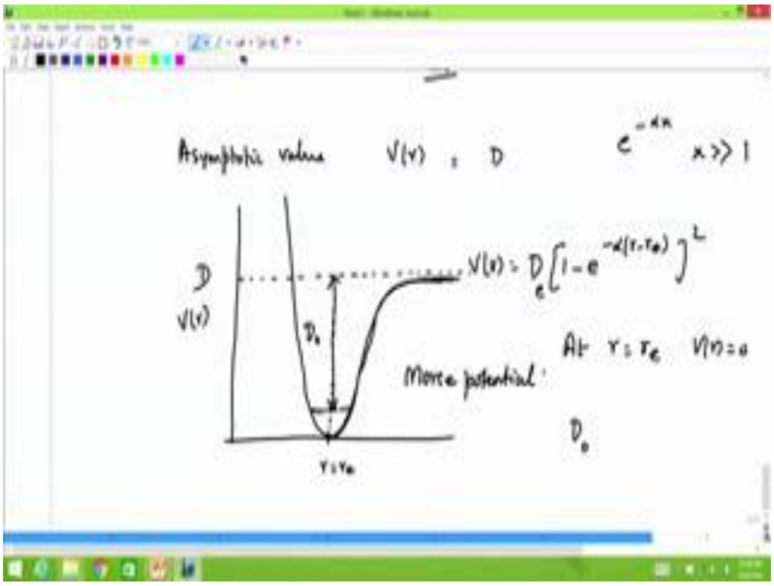


$k = 2D\alpha^2$

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} = \underline{\underline{\frac{1}{2\pi}}}\sqrt{\frac{2D\alpha^2}{\mu}}$$

Please remember the harmonic frequency is 1 by 2 pi into square root of k by mu and for the Morse oscillator we just now found that k is given by 2 D alpha squares. Therefore, the Morse oscillator frequency in harmonic limit will be 1 by 2 pi square root of 2 D sorry this is alpha square not subscript 2 D alpha square therefore, 2 D alpha square by mu. So, the Morse parameters D and alpha and the reduced mass of the molecule or you used to define the harmonic frequency in the limit of small approximation.

(Refer Slide Time: 22:50)



Asymptotic value $V(r) = D$ $\quad e^{-\alpha x}$ $\quad x >> 1$

$V(r) = D_e\left[1 - e^{-\alpha(r-r_e)}\right]^2$

At $r = r_e$ $\quad V(r) = 0$

D_0

And second question in that is show that the asymptotic value of V r is D. Now try to plot V r as a function of r minus r e. It is D 1 minus e to the minus alpha r minus r e whole square. At r is equal to r e the exponential has 0 exponent and therefore, it is 1 and therefore, 1 minus 1 is 0. So, the V of r is 0 this is V of r therefore, V r is 0 at r is equal to r e.

For all values of r greater than or e this number is smaller than 1 and therefore, this number is positive 1 minus e to the minus alpha r minus r e equal whole square is positive and since this keeps on becoming I mean this become smaller and smaller what happens is this keeps on increasing until it reaches the maximum value of a D. When r minus r e is so large that this exponent is almost 0 because (Refer Time: 24:11) exponential of minus alpha x and if x is very, very large then the exponential of minus alpha x goes 0 therefore, you see that the V r reaches an asymptotic values and this asymptote.

Therefore the D is the value for infinitely large r e or r compare to r e and when r is less than r e; please remembers this is negative and therefore, the exponential is a positive it has a positive exponent therefore, the exponential increases and this is the square. So, one minus this is negative, but this square of the that still increasing therefore, you see this increase very, very quick very, very steeply this is the shape of the Morse potentially in which the D is the dissociation energy from equilibrium.

You cannot measure D you can only measure the dissociation energy from the zero point energy; experimentally zero point energy will be the first V is equal 0 state and that will still have some energy namely half h nu if you remember that the nu being the harmonic frequency and therefore, this number in Morse oscillator called is D e dissociation energy from equilibrium, but the experimental values are D naught which is this number from zero point energy that is D naught. So, this is how interpretation for the Morse potentials are given for their parameters.

.So, let me stop here for a movement and we continue with the remaining five or six problems in the next part of this video.