Chemistry II: Introduction to Molecular Spectroscopy
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Lecture - 11
Diatomic Vibration Morse Oscillator Model

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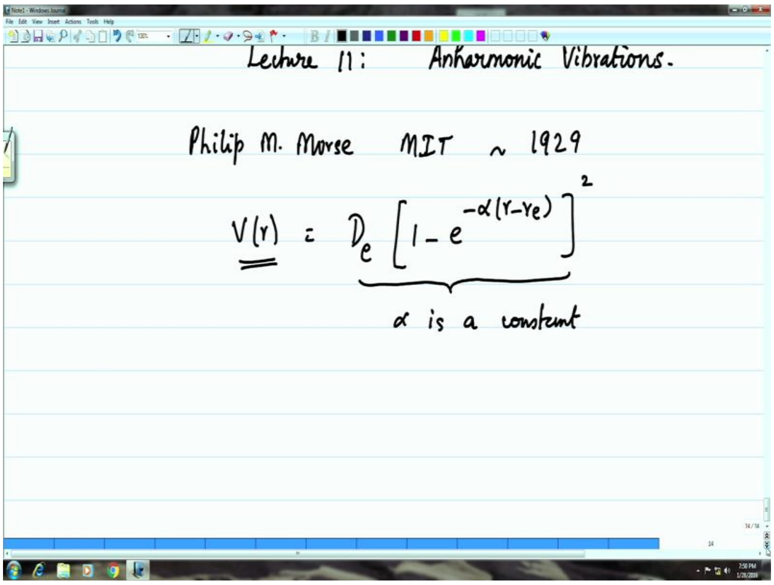

Lecture 11: Anharmonic Vibrations.

Philip M. Morse MIT ~ 1929

$$\underline{\underline{V(r)}} = D_e \underbrace{\left[1 - e^{-\alpha(r-r_e)}\right]^2}_{\alpha \text{ is a constant}}$$

Welcome back to the lectures on Chemistry and Introduction to Molecular Spectroscopy. We shall continue the lecture from the Harmonic Vibrational spectroscopy of a diatomic molecule to look at one model for the Anharmonic Vibration and this model is due to Professor Philip M Morse from M I T around 1929. He came up with the molecular motion being anharmonic and the Vibrational motion eventually leading to for very large frequencies of vibration or very large the energies of Vibrational quantum (Refer Time: 00:59) with very large quantum number the molecule eventually dissociate.

In the harmonic model dissociation does not exist because no matter how high the energy is; the parabolic nature of the harmonic potential energy curve tells you that the molecule eventually reaches back to it is equilibrium state and therefore, there is nothing called dissociation or a break way of a diatomic molecule accounted for in the harmonic model.

Therefore it is very important for vibrationally induced dissociation of chemical structures that the Vibrational motion is anharmonic and the model that was proposed by Philip Morse has the following form for the potential energy. As a function of the distance from the equilibrium the V r is given by the specific functional form a constant D e multiplied by this particular mathematical quantity alpha exponential of minus alpha r minus r e whole square. So, the potential energy has a very specific form due to exponential and alpha is a constant which we shall see in a minute how it is identified with the equilibrium or which is called the harmonic oscillated frequency. Now, it is important to visualize this potential energy first to understand why it is meaningful.

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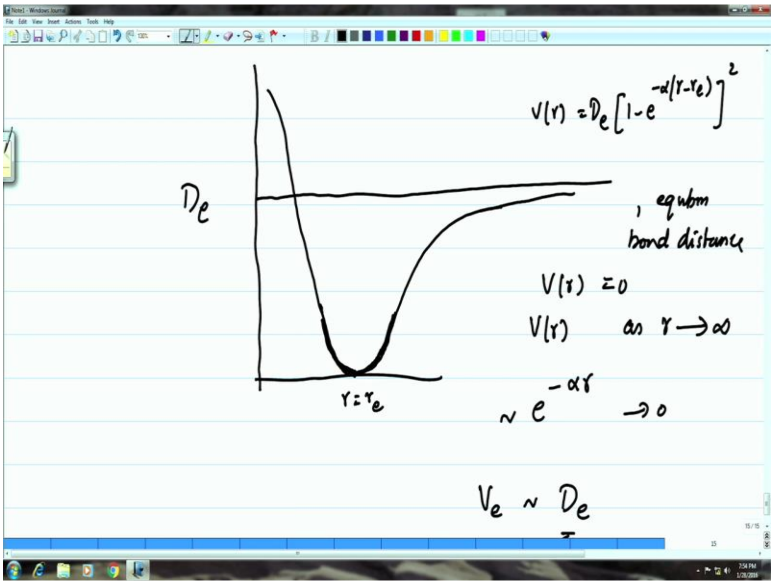

Now, if you plot V of r as a function of r it is D e times 1 minus exponential of minus alpha r minus r e whole square therefore, at r is equal to r e the equilibrium bond distance V of r is 0 because, this becomes 1 because, the exponent is 0 therefore, 1 minus 1 0 therefore, V of r is the minimum at r is equal to r e and for very large values r; V of r as r goes to very, very large values or say the element being the infinity you see that the exponential of minus alpha times r approximately r e is too small and as r goes to infinity this goes to 0 therefore, the potential energy V e becomes D e which is a positive constant therefore, for very large values of r if we go back to the graph and as r increases from the equilibrium value you see there is exponential of minus value for e therefore, the potential energy and this is a square therefore, as r is slightly different from r e this whole graph sort of grows up and eventually it reaches a plato and the value which does not change for very large values of r equals to r e is the asymptotic value which you can call this; this graph reaches the asymptotic value and that value is D e for r less than or r e this is negative and therefore, the exponent of the exponential becomes positive and if this becomes more negative then this increases forever and therefore, what you see here is that.

So, this is the form of the potential energy for a given value for alpha. If alpha is very large; then you see that this graph is narrower. If alpha is very small; this graph is more elongated therefore, the alpha gives the spread roughly between what is called the harmonic area. This area looks more like a parabola. So, therefore, you can see that for small values of r minus r e this function will actually become parabolic in the limit of r minus r e being very very small and at r equals r e this is the minimum. Therefore this is the parabolic potential which you have with the half k x square half k r square that you use for the harmonic oscillator model. It has that as the limit of small amplitude oscillations and for very large amplitude oscillations you see the active molecule is such that the atoms go far apart from each other they never come back and this is the dissociation limit.

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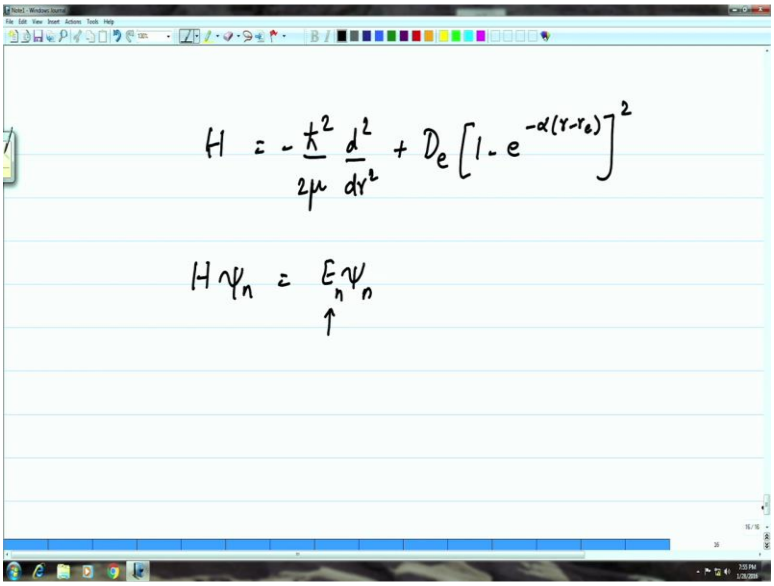

$$H = -\frac{\hbar^2}{2\mu}\frac{d^2}{dr^2} + D_e\left[1 - e^{-\alpha(r-r_e)}\right]^2$$

$$H\psi_n = \underset{\uparrow}{E_n}\psi_n$$

For this potential energy with is form if you write down the Hamiltonian as minus h bar square by 2 mu d square by d r square plus the dissociation energy D e times 1 minus e to the minus alpha r minus r e square.

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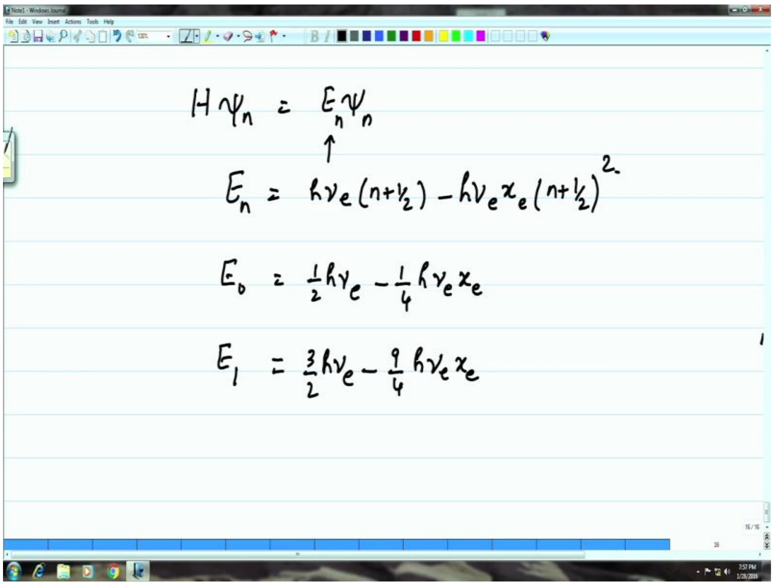

$$H\psi_n = E_n\psi_n$$

$$\uparrow$$

$$E_n = h\nu_e(n+1/2) - h\nu_e x_e(n+1/2)^2$$

$$E_0 = \frac{1}{2}h\nu_e - \frac{1}{4}h\nu_e x_e$$

$$E_1 = \frac{3}{2}h\nu_e - \frac{9}{4}h\nu_e x_e$$

The way functions h psi n is equal to E n psi n has actually close form solutions that is analytic solutions given by Philip Morse and later corrected by Professor Ter Haar that E n is h omega e times n plus half and there is another term which contains a small constant called anharmonic constant x e, but with n plus a half whole square. So, you can see that the energy level e 0 for example, is half h let me not write w e i think we have been using it for angular frequencies. So, let us write this as nu e and nu e. Then E n for E 0 where n is 0 is half h nu e minus number this is 1 by 4 h nu e x e. What is the next energy level for this problem is n is equal to 1; E 1 is 3 halves h nu e minus this is 3 half therefore, it is 9 by 4 h nu e x e.

Please remember for motion very near equilibrium; the x e is the small constant and it is called the anharmonic constant and therefore, the energy is not precisely a half h nu, but it is slightly lower than h half h nu x e is positive therefore, you see that the energy levels as you go from 0, 1, 2, 3 etcetera or more and more away from what is called the harmonic oscillator energy levels.

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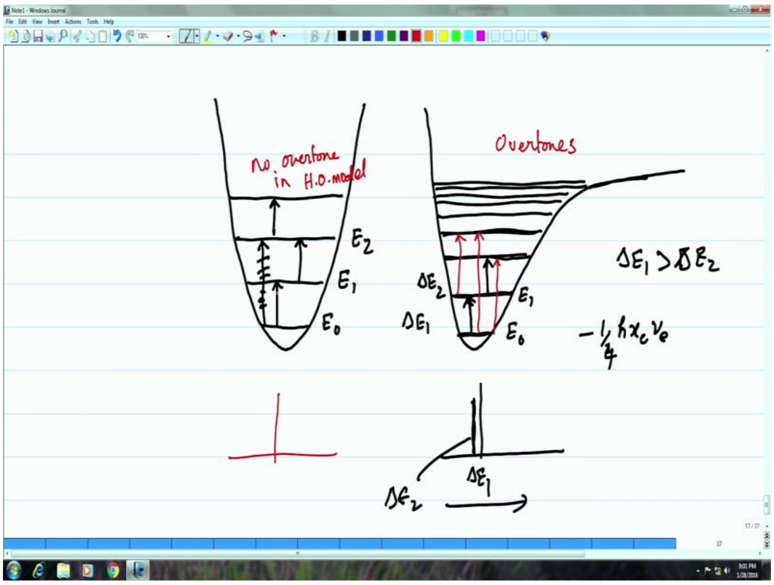

So, if you look at the harmonic oscillator energy levels if you write that it is suppose you call this is E 0 and then this is E 1 and this is as E 2 and compare that with the potential graph which goes something like that what you see is; the lower level is the lowest level is slightly lower than the original E naught this is E naught because it contains this minus half h x e nu e minus 1 by 4 sorry and then the E 1 is even lower than the harmonic value of E 1, E 2 is even closer and E 3 is closer and so on. And finally, you see that the energy level becomes very dense and so on. Now you can see that as you go further and further up if the hormone if the oscillation is sufficiently large, if the amplitude of the oscillation is fairly large and quantum energy levels are very high you see that the molecules eventually breaks down and dissociation takes place.

Therefore, the energy differences which in the harmonic oscillator model where identical between nearby levels or not so in the case of the Morse oscillator. This energy level is slightly more than this difference between the two energy levels E naught and E 1 is definitely more you call it as delta E 1 then this is more than delta E 2 therefore, the frequency at which the molecules absorbs if it is anharmonic molecule and if it satisfies (Refer Time: 11:03) anharmonic model this frequency of absorption is slightly more than this frequency of absorption and therefore, what you see here is of course, a spectra line corresponding to delta E 1, if this is the increasing E the next is the delta E 2 if you see it is slightly lower than lesser than the delta E 1. And of course, the intensities will also decrease because the higher the energy level is the fewer the molecules are at any given temperature subject to thermal equilibrium conditions and that is the Maxwell Boltzmann distribution law.

Therefore you see that delta E 2 if this is called delta E 2 and then delta E 3 is even smaller and so on. But something else also happens; in the harmonic oscillator model it is not possible for us to actually undergo a transition; actually force a molecule to undergo a transition from E 0 to E 2 this does not exist, it cannot be same the dipole moment operator does not connect to that; however, in the anharmonic oscillator model in the Morse oscillator model it is possible for you to see this transition, it is also possible for you to see let me put it on the point of medium point with some other color it is also possible for you to see this transition, it is possible for you to see this transition and even this and so on, and these are Vibrational overtones. There is no overtone in harmonic oscillator model. There is only one line what you see is only one line corresponding to this delta E and that is the same for every other transition as well.

Therefore, the Morse oscillator provides you a slightly more realistic what is called Vibrational spectroscopy and the Vibrational spectrum that you see in the case of diatomic molecules, but please remember we have kept the rotational motion completely out of these picture, we assume that the molecule is purely vibrating and we do not worry about the rotational energy is associated with that, but after we do the microwave spectroscopy we will see how to look at the Vibrational rotational spectrum together.

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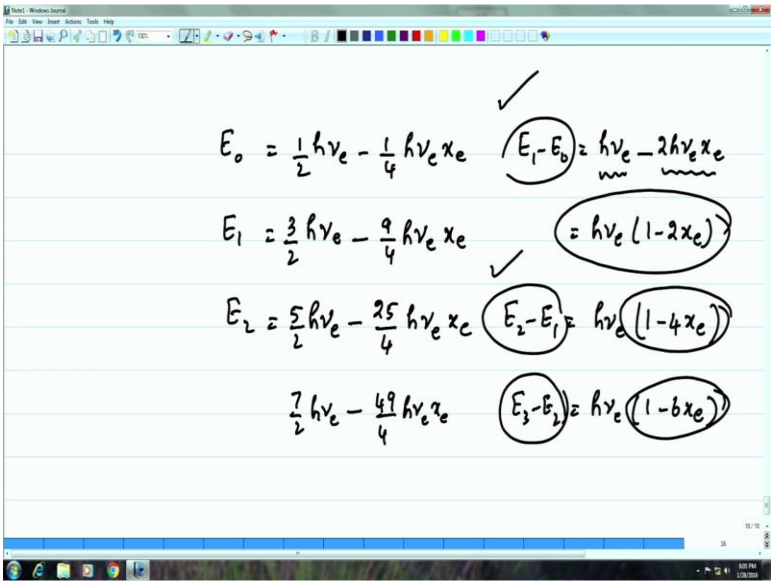

$E_0 = \frac{1}{2}h\nu_e - \frac{1}{4}h\nu_e x_e$ ✓ $\boxed{E_1 - E_0} = \underline{h\nu_e} - \underline{2h\nu_e x_e}$

$E_1 = \frac{3}{2}h\nu_e - \frac{9}{4}h\nu_e x_e$ $\boxed{= h\nu_e(1-2x_e)}$

$E_2 = \frac{5}{2}h\nu_e - \frac{25}{4}h\nu_e x_e$ ✓ $\boxed{E_2 - E_1} = h\nu_e\boxed{(1-4x_e)}$

$\frac{7}{2}h\nu_e - \frac{49}{4}h\nu_e x_e$ $\boxed{E_3 - E_2} = h\nu_e\boxed{(1-6x_e)}$

But for the time being the simple picture of the harmonic oscillator model gives you no transition other than one line; the anharmonic model due to Morse oscillator gives you several energy levels which are different from each other and therefore, the gap between them is also different. So, let us calculate the gap for a simple example say E naught was written as h nu e minus 1 by 4 h nu e x e, E 1 one was written as h nu e 3 by 2 sorry this is half h nu in this is 3 by 2 h nu e minus 9 by 4 h nu e x e and E 2 is written as 3 by 2 so then it is 5 by 2 h nu e minus 25 by 4 n plus the half whole square therefore, it is 5 by 2 whole square h nu e x e and so on. Therefore, if you calculate E 1 minus E naught the answer is h nu e minus 9 by 4 minus 1 by 4. So, you get 2 h nu e x e; x e is a very small number therefore, this is an extremely small number compared to h nu e. Essentially you can write this h nu e times 1 minus 2 x e; x e been very small this is close to x e, but what about E 2 minus E 1 if you look at that that again h nu e, but the difference is 25 by 4 minus 9 by 4 therefore, you get 1 minus 4 x e; the difference is 16 by 4. And the next one if you want to write is minus 7 by 2 h nu e and it is 49 by 4 h nu e x e and therefore, you see E 3 minus E 2 is h nu e times 49 minus 25 is 24. Therefore, you get 1 minus 6 x e.

See how the successive energy differences are becoming smaller and smaller due to the larger contribution of the x e this is minus 2 x e, here it is minus 4 x e and here it is minus 6 x e therefore, it is possible for us to actually obtain values for nu e and x e if we get two experimental spectral lines if we get a transition due to this and if we get a transition due to this then the two equations involving the nu e and the nu e x e can be solved and it is possible for us to obtain numerical values for the anharmonicity constant and therefore, use it for fitting experimental spectra of diatomic molecules where the motion is slightly unharmonic.

There are molecular problems where the motion is very very highly unharmonic and in the case of polyatomic molecule we will come to look at least for a brief moment what are called the non rigid molecular motions and so on. Therefore, it is easy to understand that Vibrational spectroscopy starts with the elementary model of a harmonic oscillator, but then the corrections to the harmonic oscillator and the real molecular spectrum are usually taken into account by correcting the potential energy in such a way that unharmonic corrections can be done.

The previous lecture in the previous lecture I mentioned the unharmonic corrections can be x cube like terms; the potential energy terms you have here that is r minus r e cube terms, r minus r e to the power four terms and so on; they are called cubic Anharmonisities and corpic and Anharmonisities and the r minus r e square is called the quadratic harmonic term. So, keep this in mind in solving some of the problem related to Anharmonic Vibrational motions of diatomic molecule.

In the next lecture we will continue this and look at polyatomic molecular motion and then in a similar way we will extend the harmonic oscillator model to molecules with many Vibrational degrees of freedom what are called the normal modes of the vibration they will also some picture pictorial representation of some of the normal modes of vibration through a calculation tool that is quite well known today called the Gaussian 0 9; the Gaussian program and the Gaussian program is a computational chemistry program which allows you to calculate molecular properties quite accurately we will see the harmonic oscillator model for a polyatomic molecule in the next lecture following this until then.

Thank you very much.