Fundamentals of Spectroscopy

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Lecture-25
Vibrational Spectroscopy: Anharmonicity

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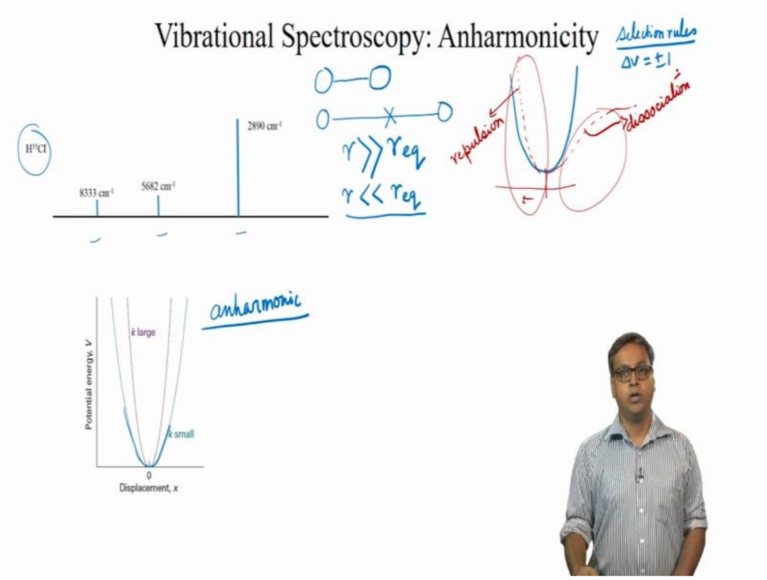

Vibrational Spectroscopy: Anharmonicity

Hello everyone welcome to the lecture. In the last lecture we learned about the selection rules of a harmonic oscillator. So we learned about the selection rules of harmonic oscillator we saw that the specific selection rule is delta v = + - 1 as all the energy levels in a harmonic oscillator are equally spaced. This means that the IR spectrum should have a single line but when we see the experimental spectrum of HCL we do not see a single peak.

But what is observed is a series of peaks with diminishing intensity. This is because real molecules do not exactly follow simple harmonic motion or we can say they do not obey Hooke’s law. If you look into the potential function of the harmonic oscillator when the bond length is increased, the molecule oscillates more vigorously. This is because with increase in the bond length that is with increase in the displacement from the equilibrium position the energy increases and ideally if we stretch a real bond too much it will get to a stage where it breaks.

So if you draw a molecule and this is a bond connecting these 2 atoms, if you stretch this molecule too much at some point this bond will break or in other words the molecule should dissociate. This bond breaking is the basis of chemical reactions or we can say this bond breaking is the basis of chemistry. But in the harmonic oscillator model the potential energy curve as we can see is a parabola.

A parabola does not allow the bond to dissociate thus we can see that harmonic approximation fails in real molecules. So we can say that vibrational motion for large displacement is anharmonic that means that is not a harmonic. So this is anharmonic in the sense that the restoring force is no longer proportional to the displacement as we saw in case of harmonic oscillator does we need to introduce a more realistic potential function to reflect that the bond dissociates if we have r is greater than or much greater than r equilibrium.

Moreover the nuclei repel each other when the bond gets much smaller than the equilibrium bond length or in other words the nuclear repel each other and r is less than r equilibrium. So, the potential is much steeper than what predicted from the harmonic oscillator model. So, let us say we have this is our harmonic potential at r less than r equilibrium the potential will be much steeper.

So the harmonic oscillator also implies that the nucleus goes through each other, which does not make any sense. So the potential energy surface that we really want is that which becomes steeper at smaller inter nuclear distances that is in this region and which becomes shallower means, it should become shallower at larger inter nuclear distances that is in these regions and these properties in the potential energy surface reflect repulsion and dissociation. So this part reflects repulsion and this part reflects dissociation.

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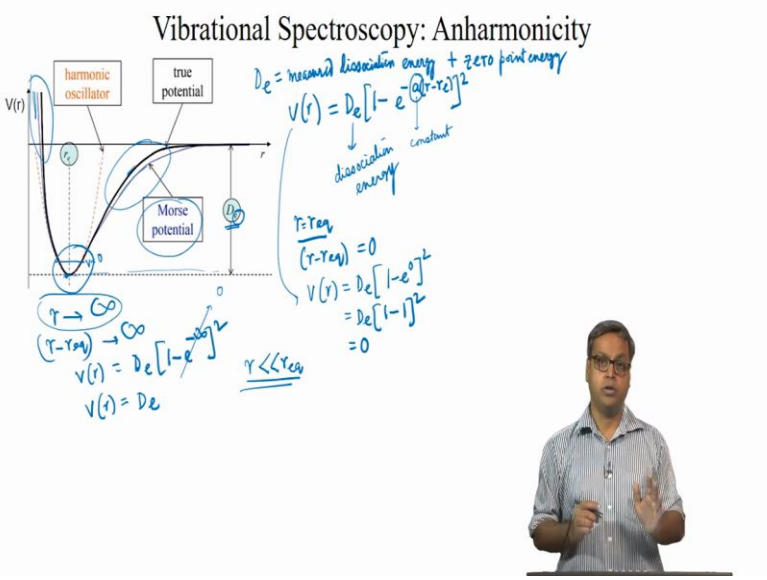
Vibrational Spectroscopy: Anharmonicity

D_e = measured dissociation energy + zero point energy

$V(r) = D_e[1 - e^{-a(r-r_e)}]^2$

dissociation energy

constant

$r = r_{eq}$

$(r - r_{eq}) = 0$

$V(r) = D_e[1 - e^0]^2$

$= D_e[1-1]^2$

$= 0$

$r \to \infty$

$(r - r_{eq}) \to \infty$

$V(r) = D_e[1 - \cancel{e^{-\infty}}]^2$

$V(r) = D_e$

$r << r_{eq}$

So one of the simplest functions that has been introduced to represent these properties is known as the Morse potential. So it is known as the Morse potential. Let us look at this figure the black line here. So this black line is meant to illustrate the true potential we can see the equilibrium bond length is the minimum of the potential function and we have something called De. This De is the dissociation energy, the subscript e in De means it is the dissociation energy from the equilibrium position.

The peculiarity of this dissociation energy is that it cannot be directly measured from experiments. This is because the molecules are never at the bottom of the energy where the lowest energy they can possibly have is the 0 point energy or the energy at V = 0 which in the harmonic oscillator was given by half h nu or nu bar / 2 the 0 point energy as we can see is slightly above the bottom of the energy well.

So we never really measured De what we measure the dissociation energy from the 0 point energy level or the V = 0 level thus De is the sum of the measured dissociation energy. So this is the sum of the measured dissociation energy plus the 0 point energy. So if you focus on the harmonic potential curve that is given by this orange dotted curve we can see that the harmonic potential represent nicely.

The true and harmonic potential that is the black curve at the bottom part of the potential energy well that is why the harmonic potential works well for the low vibrational states. That is the vibrational quantum number. That is when the vibrational quantum number V is small. In other words as long as the displacement is small the harmonic oscillator will work. The Morse potential has the right kind of shape. So the Morse potential is this blue curve.

So this has the right kind of shape but does not perfectly match the true and harmonic potential. In general it is not quite as deep as the true potential as the nuclide gets closer and closer we see the difference here. Moreover there is slight mismatch, as seen from this finger at larger inter nuclear separation. In other words the Morse potential is purely an empirical expression that fits the curve corresponding to the true potential to a good approximation.

The expression for the Morse potential is given by V of r is De times 1 - e to the power - ar - r equilibrium whole square. So here a is a constant. So a is a constant and De is the dissociation energy. So at the equilibrium position that means at r = r equilibrium we have r - r equilibrium = 0. So we can write V of r = de times 1 - e to the power 0 square and as we know that the exponential term that is e to the power 0 is 1.

So we have De times 1 - 1 square so this becomes 0. So the potential becomes 0 and thus it is a minimum. Now if we have the condition that r terms to infinity so when r terms to infinity r - r equilibrium is also infinity. So the exponential time that we have what we can write V of r = De 1 - e to the power -infinity square and as we know e to the power by minus infinity is 0. So what we have that is V of r is De.

So the potential equals the dissociation energy from the equilibrium position. Now if we actually consider the case where r is less than less than r equilibrium so for r less than less than r equilibrium the potential increases exponentially which is an improvement over the harmonic oscillator. So the Morse potential has the properties we are looking for it does have a dissociation energy associated with it and it does have a minimum at r = r equilibrium.

We have another parameter that is a we have this parameter e in this Morse potential. So this a is a property of the molecule and changes from molecule to molecule as a gets bigger the potential gets steeper at both large and small inter nuclear distances in essence a is a fitting parameter. So, there is no significant theory which underpins what it should be. It is an empirical value obtained from observation.

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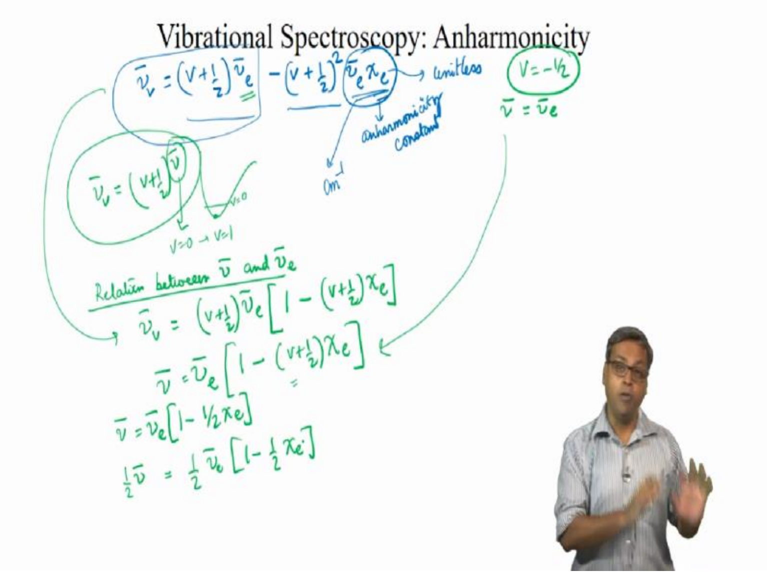

Vibrational Spectroscopy: Anharmonicity

$$\bar{\nu}_v = \left(v+\frac{1}{2}\right)\bar{\nu}_e - \left(v+\frac{1}{2}\right)^2 \bar{\nu}_e x_e$$

$x_e \rightarrow$ unitless

anharmonicity constant

cm^{-1}

$v = -\frac{1}{2}$

$\bar{\nu} = \bar{\nu}_e$

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

$v=0 \rightarrow v=1$

Relation between $\bar{\nu}$ and $\bar{\nu}_e$

$$\bar{\nu}_v = \left(v+\frac{1}{2}\right)\bar{\nu}_e\left[1-\left(v+\frac{1}{2}\right)x_e\right]$$

$$\bar{\nu} = \bar{\nu}_e\left[1-\left(v+\frac{1}{2}\right)x_e\right]$$

$$\bar{\nu} = \bar{\nu}_e\left[1-\frac{1}{2}x_e\right]$$

$$\frac{1}{2}\bar{\nu} = \frac{1}{2}\bar{\nu}_e\left[1-\frac{1}{2}x_e\right]$$

If the potential energy form of the Morse potential is used in the Schrodinger equation instead of half kx square and analytical solution can be obtained. The solution to the Schrodinger equation reveals that the vibrational levels are quantized. So the solution can be written as we can write nu bar v that = v plus half nu bar e - v plus half whole square nu bar e chi e. So the solution is very similar to the one we had before and this chi e is known as the anharmonicity constant.

So the first term is the harmonic oscillator term and additional term is obtained from the Morse potential. So which has v plus half square dependence thus for very large values of v where the harmonic oscillator does not work very well the second term becomes more and more important the value of the second term becomes larger as compared to the first term because of the v plus half square dependence rather than v plus half dependence.

And this nu bar e chi e factor is a small number the anharmonicity constant is essentially the point of vision we are applying to the harmonic problem to take into account of the anharmonicity. And this chi e is unit less but this nu bar e has the unit of wave numbers. So nu bar e chi e together they have the unit of wave numbers. So the second term in general is a small perturbation to the vibrational energy for small values of v.

We can ignore this part and just have the harmonic oscillator part these corroborate with the fact that for small values of v it should tend to the harmonic solution. In case of harmonic oscillator we used nu bar. So we wrote nu bar v for harmonic oscillator we wrote v plus half nu bar but for anharmonic oscillator we have used nu bar e instead so nu bar e is not something we can measure from the spectrum. It is something we have to derive by fitting this equation to the spectral data.

So we can say this is a hypothetical frequency it is the frequency the molecule will be vibrating if the molecule was at the bottom of the potential energy well when the molecule is in v = 0 that is not at the bottom of the potential energy well but at v = 0 it will not be vibrating quite at that frequency. So nu bar in the harmonic oscillator model what we have used this nu bar is the frequency in wave number of the photon absorbed when the molecule goes from v = 0 to v = 1.

So let us try to see the relation between nu bar and nu bar e. So what we want to see is a relation between nu bar and nu bar e. So we can write this expression as nu bar v equals and if we take v plus half nu bar e common what we have is 1 - 3 plus half chi e. So now if you compare with the energy level of the harmonic oscillator or let us say compared with this expression we can see that nu bar = nu bar e times 1 - 3 plus half chi e.

Thus the anharmonic oscillator behaves like the harmonic oscillator but the oscillation frequency decreases steadily with increasing v. In fact when we have a let us say we have a hypothetical energy state that is v = - half. So at v = - half the nu bar becomes equal to nu bar e. So because nu bar = nu bar e the molecule will be at equilibrium at 0 vibrational energy. Thus nu bar e can be defined as the hypothetical equilibrium oscillation frequency of the anharmonic system. That is the frequency for infinitely small vibrations about the equilibrium point.

But for any real vibrational state where v is positive the energy is given by this expression. So thus in the ground state we have nu bar = nu bar e times 1 - half chi e and the 0 point energy which is given by half nu bar is half nu bar e 1 - half chi e. So we can see that the 0 point energy differ slightly in the anharmonic oscillator from the 0 point energy of the harmonic oscillator.

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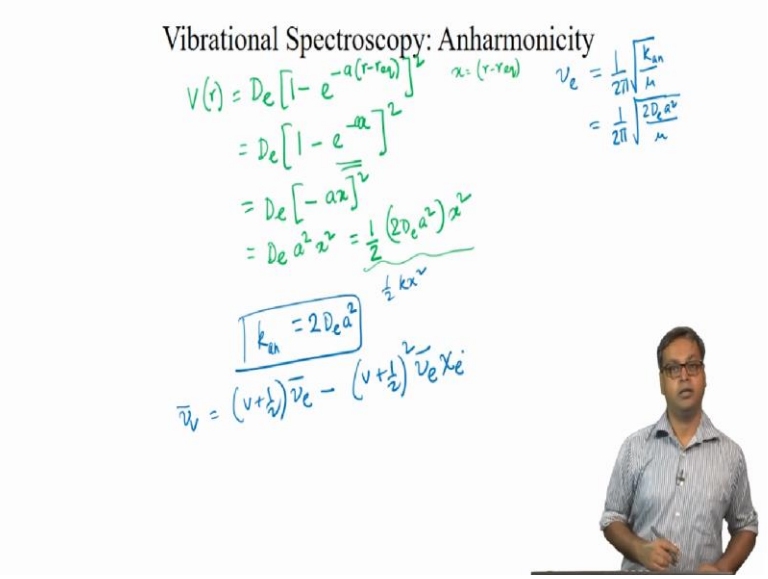

Vibrational Spectroscopy: Anharmonicity

$$V(r) = D_e\left[1 - e^{-a(r-r_{eq})}\right]^2 \qquad x = (r - r_{eq})$$

$$= D_e\left[1 - e^{-ax}\right]^2$$

$$= D_e\left[-ax\right]^2$$

$$= D_e a^2 x^2 = \underbrace{\frac{1}{2}\left(2D_e a^2\right)x^2}_{\frac{1}{2}kx^2}$$

$$\boxed{k_{an} = 2D_e a^2}$$

$$\bar{\nu}_v = \left(v + \frac{1}{2}\right)\bar{\nu}_e - \left(v + \frac{1}{2}\right)^2 \bar{\nu}_e x_e$$

$$\nu_e = \frac{1}{2\pi}\sqrt{\frac{k_{an}}{\mu}} = \frac{1}{2\pi}\sqrt{\frac{2D_e a^2}{\mu}}$$

So let us look at the expression for the Morse potential again. So we know the expression is given by v of r equals the dissociation energy De times 1 - e to the power - a r - r equilibrium whole square. So we can write this if we take x = r - r equilibrium we can write De 1 - e to the power - x or kx whole square. And now we expand e to the power - x and put the expansion here.

Then we can simplify this as De times - ax whole square. So this becomes De a square x square. Or we can write this as half 2 De a square times x square. So comparing this expression if I compare this expression with let us say half kx square we get that the force constant that is k for anharmonic oscillators is given by 2 De times a square. So is if we substitute this in our vibrational frequency we get nu e.

If you go back to this expression 1 / 2pi root over k / mu so we can write k anharmonious here. So what we can write is 1 / 2pi root over 2De a square divided by mu. So the question is how has this changed the energy levels? The energy expression by taking into account of anharmonicity it is given by we know this is nu bar v is v plus half nu bar e - v plus half whole square nu bar e chi e.

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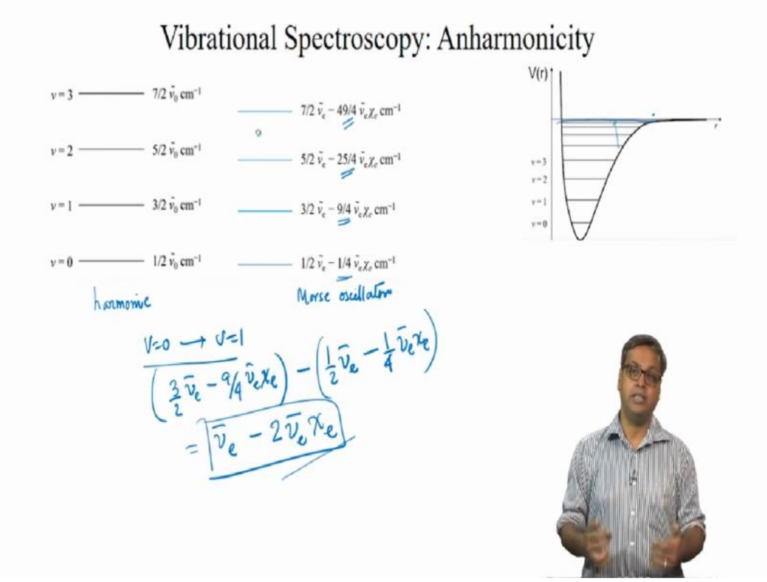

Vibrational Spectroscopy: Anharmonicity

$v = 3$ — $7/2\ \tilde{\nu}_0\ \text{cm}^{-1}$ — $7/2\ \tilde{\nu}_e - 49/4\ \tilde{\nu}_e\chi_e\ \text{cm}^{-1}$

$v = 2$ — $5/2\ \tilde{\nu}_0\ \text{cm}^{-1}$ — $5/2\ \tilde{\nu}_e - 25/4\ \tilde{\nu}_e\chi_e\ \text{cm}^{-1}$

$v = 1$ — $3/2\ \tilde{\nu}_0\ \text{cm}^{-1}$ — $3/2\ \tilde{\nu}_e - 9/4\ \tilde{\nu}_e\chi_e\ \text{cm}^{-1}$

$v = 0$ — $1/2\ \tilde{\nu}_0\ \text{cm}^{-1}$ — $1/2\ \tilde{\nu}_e - 1/4\ \tilde{\nu}_e\chi_e\ \text{cm}^{-1}$

harmonic

Morse oscillator

$v=0 \rightarrow v=1$

$$\left(\frac{3}{2}\bar{\nu}_e - \frac{9}{4}\bar{\nu}_e x_e\right) - \left(\frac{1}{2}\bar{\nu}_e - \frac{1}{4}\bar{\nu}_e x_e\right)$$

$$= \boxed{\bar{\nu}_e - 2\bar{\nu}_e x_e}$$

So this is a perturbation to the harmonic solution. So let us compare the harmonic and the anharmonic solution. So, on the left we have the harmonic solution and on the right we have the anharmonic solution that is coming from the Morse oscillator. So then harmonicity constant is a positive number. So, we are subtracting a positive number from the harmonic energies. So the lines of the energy levels on the right hand side are steadily getting closer and closer together.

As the value of the vibrational quantum number increases due to the v plus half square dependence of the anharmonic term. So we can see that for v = 0 we have this term that is 1 / 4. Now it increases to 9 / 4 for v = 1 to 25 / 4 to 49 / 4 so the energy levels are coming closer and closer. Thus as we are going to higher and higher vibrational energies the energy levels are getting closer and closer together as we approach the dissociation limit in terms of spectroscopy.

Now that we know the energies of any level we can calculate the frequencies of any transition. So the fundamental frequency that is for V = 0 to V = 1 transition for the anharmonic case what we have we have 3 / 2 nu bar e - 9 / 4 nu bar e chi e. So this is for V = 1 - half nu bar e - 1 / 4 nu bar e chi e. So this is the frequency of the transition. And if we simplify this what we get is nu bar e - 2 nu bar e chi e.

So this differs from the harmonic solution in the second term. So the fundamental thing is that the energy levels are not equally spaced. As we approach the dissociative limit, the levels get closer and closer. So we can imagine that there is a maximum vibrational quantum number beyond which it will dissociate. Finally I would like to say that the molecule is vibrating very nearly at the same frequency independent of which vibrational state it is in. The reason the molecule has more vibration and energy in higher vibrational states is because it is stretching and compressing over a wider range and this requires more energy.