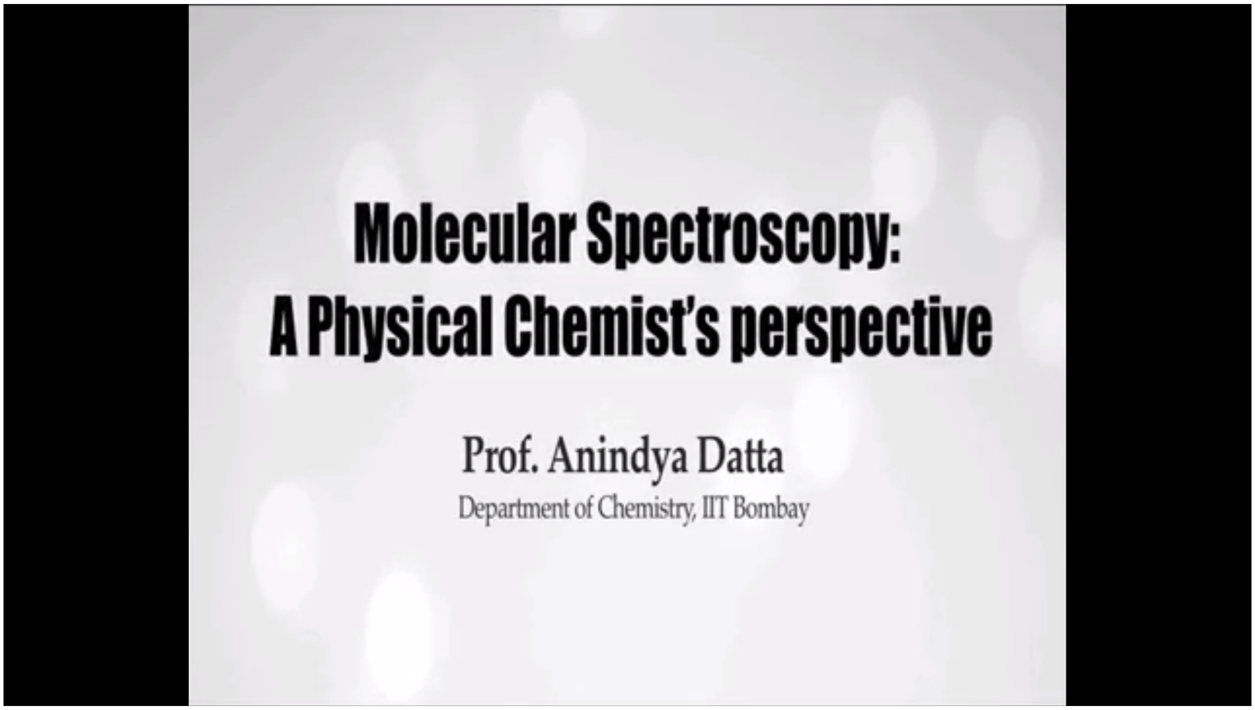

# Molecular Spectroscopy: A Physical Chemist's perspective

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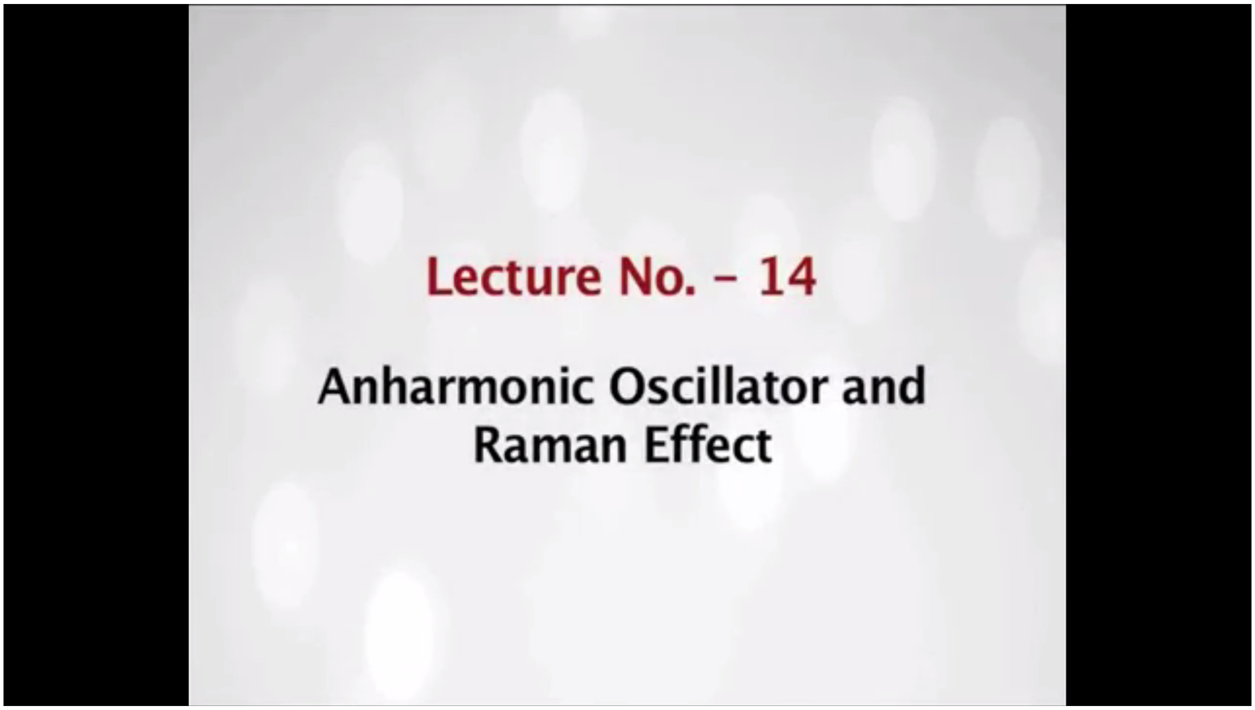
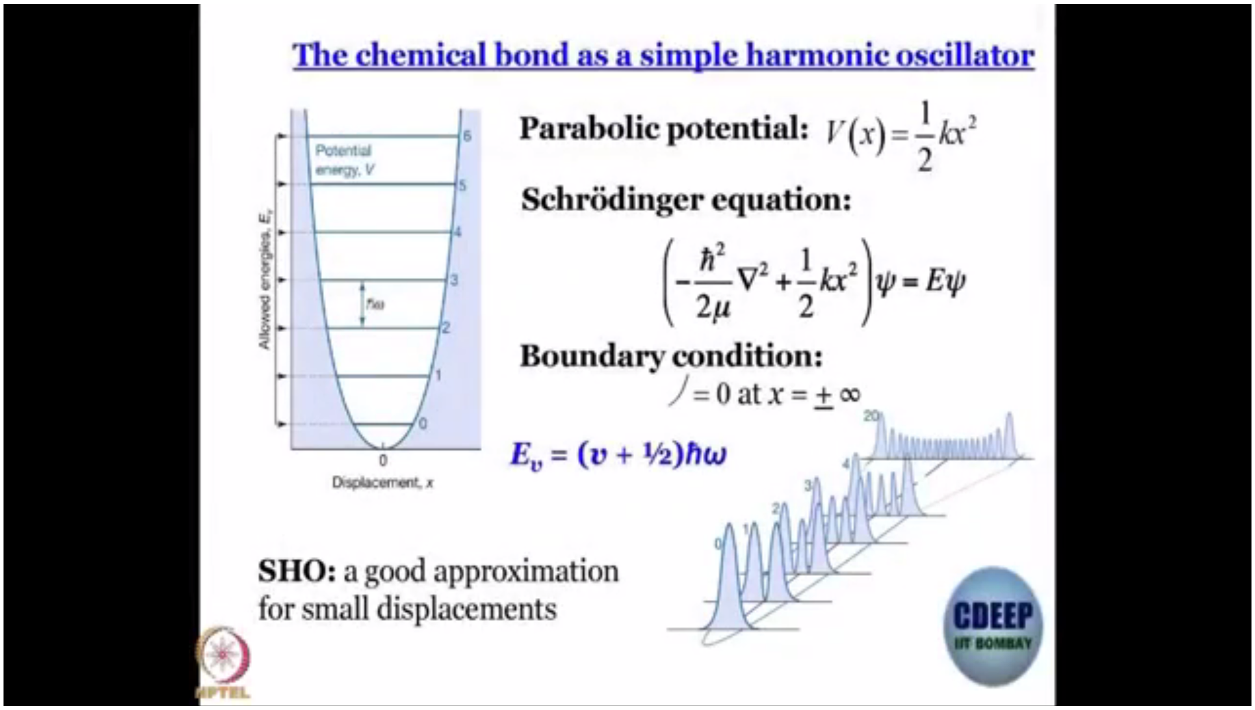


## Lecture No. - 14

## Anharmonic Oscillator and Raman Effect



## The chemical bond as a simple harmonic oscillator

**Parabolic potential:** $V(x)=\frac{1}{2}kx^2$

**Schrödinger equation:**

$$\left(-\frac{\hbar^2}{2\mu}\nabla^2+\frac{1}{2}kx^2\right)\psi=E\psi$$

**Boundary condition:**

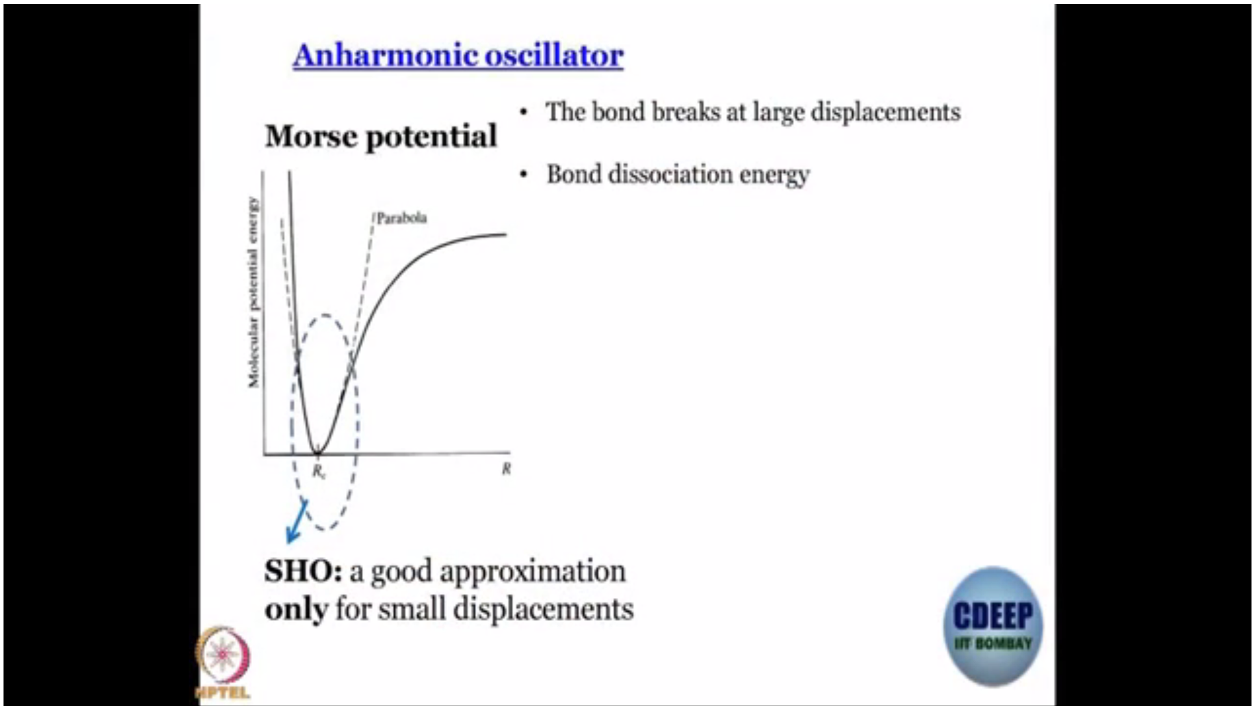
$\psi=0$ at $x=\pm\infty$

$E_v=(v+½)\hbar\omega$

**SHO:** a good approximation for small displacements

Prof. Anindya Datta: Now we move on to the next part of our discussion of vibrational spectroscopy. So far, we had worked with the assumption that the potential is ½ $kx^2$, the bond behaves like harmonic oscillator, but as you understand, especially for the atomic molecules, the bond cannot behave like a harmonic oscillator, because if that is the case, then even when x is infinity, the bond will not break, isn't it? It's a parabola, it just keeps going up, but then, as you know, HCl does break. If you make it vibrate took much, then it's going to break. That is impossible that in a real molecule, in a real atomic molecule at least, you can have these harmonic potentials.

As we'll see later on, in case of polyatomic molecules, you can have what are called normal modes of vibration, which are harmonic, okay, but for the atomic molecules at least, this cannot be the right potential. This is we've studied so far.



Anharmonic oscillator

**Morse potential**

- The bond breaks at large displacements
- Bond dissociation energy

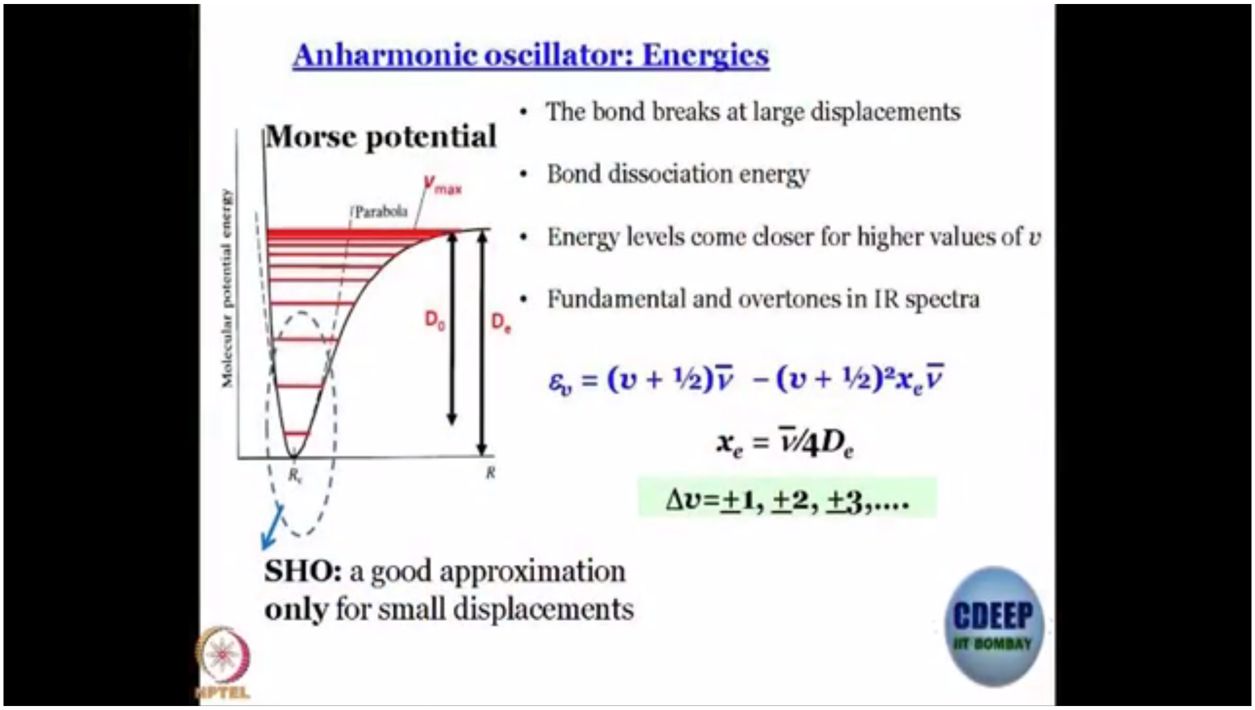
**SHO:** a good approximation **only** for small displacements

So the correct potential for the atomic molecule has to be something like this, for large values of x, it has to turn and reach a saturation, okay. This kind of oscillator is called an anharmonic oscillator.

The potential that is used most commonly to describe anharmonic oscillator is called Morse potential. You do not have to remember it, but you can think in which ways, we can try to arrive at this potential. In the discussion we had about ro-vibration spectrum. If you remember the last expression we had for the energy of the spectral lines, what was the correction term? The correction term was (B1 - B0) $(J +1)^2$, right. So if you now look at the entire expression, what is it? You have a term, which is 0th order in (J = 1), then you have a term that is first order, right, and then you have a term that is second order.

Similarly, what you can do is you can expand this potential. You have ½ $kx^2$, right. That is the potential energy for harmonic oscillator. Now you can take something which is $x^4$ and this way, you can try and get the correct potential. There is actually an ongoing problem. People, even now, try to use different kinds of potentials to see where they get the basic result, but he globally accepted potential that we use at least at this level is Morse potential, which gives you a nice curve like this.

And then if you look at this region, you see the deviation from harmonicity is not much. Anharmonicity causes a small deviation from harmonicity, and when that happens, as you all know by now, we can use what is called perturbation theory. When the deviation from the ideal situation is no too much, then we can get away using perturbation theory. That is what is done, anharmonicity is dealt with as small perturbation, and that is how the problem is solved, and when it is solved, this is the result. We are not going to solve he actual quantum mechanics of anharmonic oscillator, but the results look like this.



**Anharmonic oscillator: Energies**

- The bond breaks at large displacements
- Bond dissociation energy
- Energy levels come closer for higher values of $v$
- Fundamental and overtones in IR spectra

$$\varepsilon_v = (v + \tfrac{1}{2})\bar{\nu} \; - (v + \tfrac{1}{2})^2 x_e \bar{\nu}$$

$$x_e = \bar{\nu}/4D_e$$

$$\Delta v = \pm 1, \pm 2, \pm 3, \ldots.$$

**SHO:** a good approximation **only** for small displacements

What is the major difference from harmonic oscillator? In harmonic oscillator we had energy levels that were equally spaced, right. Now we have energy levels that keep coming closer and closer and closer as you go higher up the ladder. Why does that happen? That happens because of anharmonicity. Eventually, there cannot be any energy level beyond this, isn’t it? This is where all the energy levels should come together and that is where you should reach what is called the classical limit. And this energy difference is called the dissociation energy, okay.

So what is the expression for the energy? If you remember perturbation theory, you know, in perturbation theory, we write the Hamiltonian S, 0th order Hamiltonian plus first order correction to Hamiltonian. Energy once again is the uncorrected energy first, plus the first order correction term. Here also the first order correction that comes and as you can now guess, what the first order correction term would be. If you remember our experience with ro-vibrational spectrum. This uncorrected energy is v + ½, the first order correction term comes as a second order term in v + ½, okay. -v + ½, why minus, because as you can see, the energies actually go down as you go higher up the ladder, and this is multiplied by Xc multiplied by ṽ. What is Xc? It is called the anharmonicity constant.

Now what should it be related to? What is the major difference between harmonic oscillator and anharmonic oscillator? Exactly. A simple harmonic oscillator can oscillate without breaking and anharmonic oscillator -- so the main difference between harmonic and anharmonic oscillator is dissociation energy, okay. So you understand that this Xc has to be related to dissociation energy. What is the dissociation energy for a harmonic oscillator? Infinite. What should Xc be for a harmonic oscillator? Zero, right, you're right. And when you have some value of B, Xc also shows up. So of course, you understand that it is inversely proportional, the actual relationship is something like this. Xc is ṽ divided by 4De. So if you can determine Xc, the anharmonicity constant, you can find out what the dissociation energy is, all right. Yeah.

What shows up after solving? Yeah, yes, it comes from a perturbation theoretical treatment of the anharmonic oscillator problem. It's not curve rating. Now for this, the selection rules looks amusing. The selection rules, as you can see, in front of you are ΔV = ±1, ±2, ±3, and that should actually make you wonder, why we call this selection rule? The ±1, ±2, ±3 so on and so forth essentially means all transitions are possible. So where is the selection? You understand what I am saying? Where is the selection, why do we call it selection rule? We call it selection rule because this ΔV = ±1 is by far the most probable transition. ΔV = ±2 has significantly lower probability, ΔV = ±3 has significantly lower probability than even ΔV = ±2 and we'll show you the evidence for that, okay.

So what you're trying to say is ΔV = ±1, ±2, ±3 fine, but this is the order in which decreased improbability also takes place, probability of transition. Question? How to determine probability of transition? Well, again, we'll take a raincheck on that question. Just believe me now when I say, probability of transition is proportional to square of transition movement integral, okay. We're going to prove that maybe in couple of weeks. Probability of transition is proportional to this square of transition moment integral.

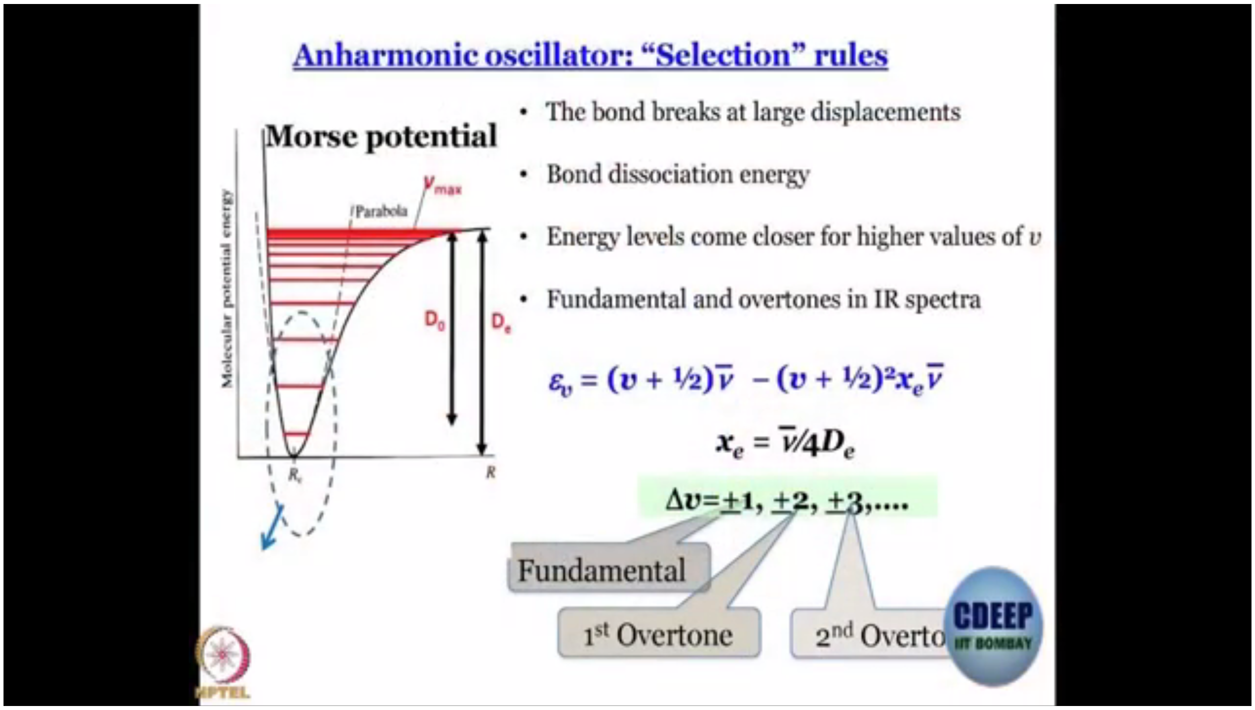
Now why is I that all transitions are allowed? Because what is transition moment integral, you remember, <Ψf / µ / Ψi. We're working under the ambit of perturbation theory. We've already discussed how you describe the Hamiltonian, how you describe the energy, how to describe wave function of a perturb system in terms of the wave function of unperturb system. Again, it will be Ψ0 plus some first order correction. Now, I don't know if you've studied this, but more often than not, what you want to do is you want to represent this first order correction as a linear combination of the unperturb wave function. Do you know this? You know this, right. Why do we do it? And we could have done anything, right. Why do we do it and is the statement valid? Can somebody answer that question?

Is it valid to write the perturb wave function as a linear combination of unperturb wave functions? Why is it valid? Because we have a complete set of wave functions for the harmonic oscillators. So anything -- so when you have a complete set, what you can do is, the coefficient is in your hand, right, so you can change the coefficient in such a way that -- again, somebody talked about 11:22, now it boils down to _______. You have a set of functions, some polynomial set, I can always combine them in many different ways to reach what I want to fit, okay. So of course, if I write it like this, let us say, I want to talk about the Vth level of the perturb system, okay. Actually what I should write it as is the unperturb wave function plus some correction term, right. So this correction term is the linear combination, but then I might as well include this in the linear combination, isn't it. This one particular V, these are many different Vs, Vi, so I might as well include everything and write something like this, ∑i, ai, Ψi(0).

Can you comment on what these ais will look like? If I plot ai versus i and I am trying to reach some particular Ψv, like I am trying to get the expression of some particular Ψv perturb system, let's say, that Ψv is somewhere here. This is a V. Can I draw a plot that will kind of tell me at least qualitatively what the distribution of the amplitudes are? Just look at this expression, Ψv is this and don't forget where we started from, we started from Ψv(0) + Ψv'. Don't forget Ψv' is a small term with respect to Ψv(0). Yes. So it will be something like this. Is it right? Have you understood? Sure.

The coefficient of Ψv(0) is going to be maximum of course. So that has by and large -- not by and large -- largely it is actually unperturb wave function, and then we follow up on the two sides. So Ψv = 1 and Ψv = -1, the unperturb wave functions, they will have significant contribution, right. Ψv + 1 and Ψv + 2 and Ψv - 2 is a little less and so on and so forth. So when you expand his transition moment integral, then you essentially get something like that. the probability also falls off on the two sides. So v + 1, v + 2, everything is allowed, but the probability falls off as you move farther and father away from V. Understood, okay.

I'll share a couple of pages from 14:32 books where this is discussed with a particular example, but don't forget that example is an arbitrator -- I am not done. I am not done, all right.



## Anharmonic oscillator: "Selection" rules

- The bond breaks at large displacements
- Bond dissociation energy
- Energy levels come closer for higher values of $v$
- Fundamental and overtones in IR spectra

$$\varepsilon_v = (v + ½)\bar{\nu} \;\; - (v + ½)^2 x_e \bar{\nu}$$

$$x_e = \bar{\nu}/4D_e$$

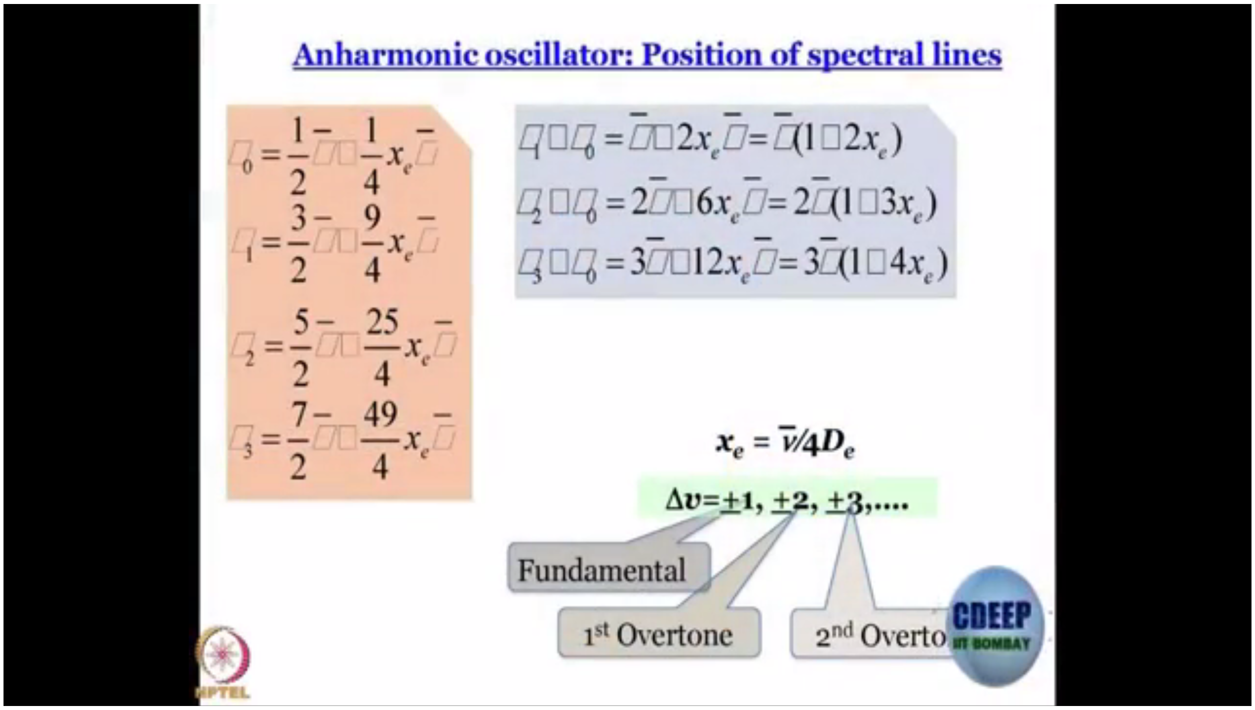
$\Delta v = \pm 1, \pm 2, \pm 3, \ldots.$

Fundamental

1st Overtone

2nd Overto

Let's finish this discussion. This is what it is. So I think you already know the remaining part, but we'll just go through for the sake of completeness. For Δv = ±1, that is called the fundamental transition. ±2 is the first overtone and ±3 is a second overtone, ±3 is a second overtone, ±3 is a second overtone. Where have you encountered these terms earlier, fundamental and overtones? Soundwaves, right, in physics chapter of sound.



## Anharmonic oscillator: Position of spectral lines

$$\varepsilon_0 = \frac{1}{2}\bar{\nu} - \frac{1}{4}x_e\bar{\nu}$$

$$\varepsilon_1 = \frac{3}{2}\bar{\nu} - \frac{9}{4}x_e\bar{\nu}$$

$$\varepsilon_2 = \frac{5}{2}\bar{\nu} - \frac{25}{4}x_e\bar{\nu}$$

$$\varepsilon_3 = \frac{7}{2}\bar{\nu} - \frac{49}{4}x_e\bar{\nu}$$

$$\varepsilon_1 - \varepsilon_0 = \bar{\nu} - 2x_e\bar{\nu} = \bar{\nu}(1 - 2x_e)$$

$$\varepsilon_2 - \varepsilon_0 = 2\bar{\nu} - 6x_e\bar{\nu} = 2\bar{\nu}(1 - 3x_e)$$

$$\varepsilon_3 - \varepsilon_0 = 3\bar{\nu} - 12x_e\bar{\nu} = 3\bar{\nu}(1 - 4x_e)$$

$$x_e = \bar{\nu}/4D_e$$

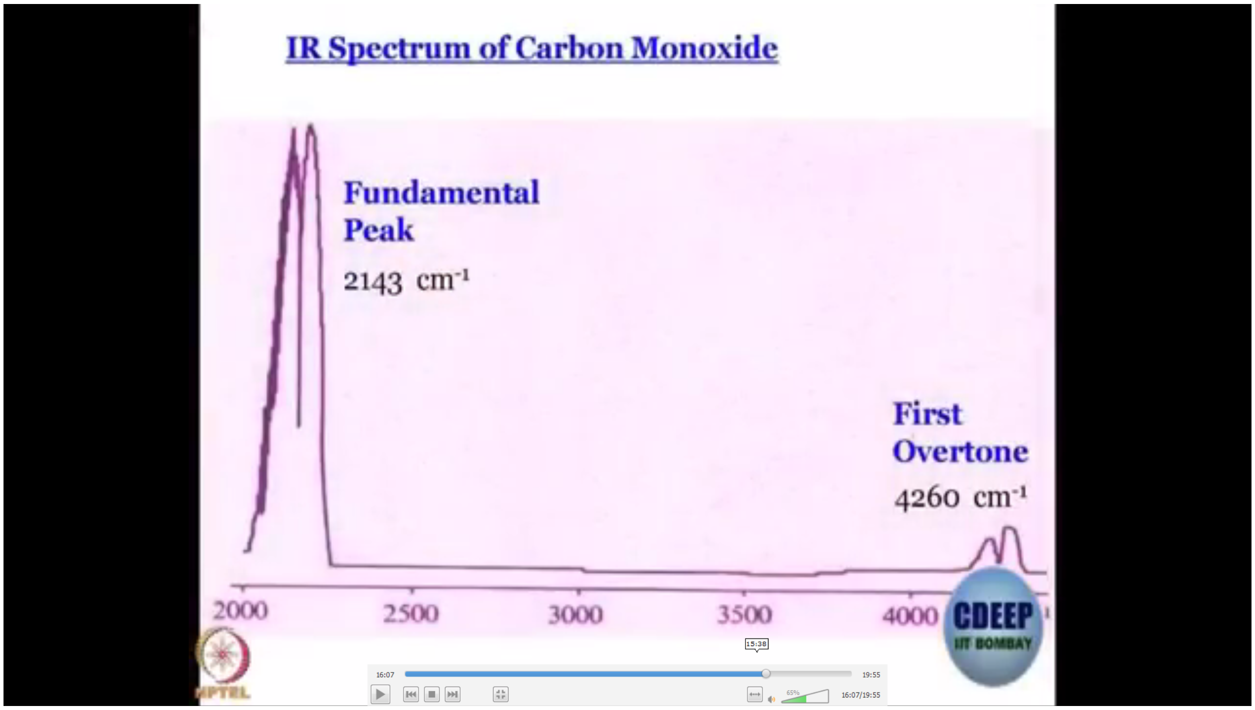
$\Delta v = \pm 1, \pm 2, \pm 3, \ldots.$

Fundamental

1st Overtone

2nd Overto

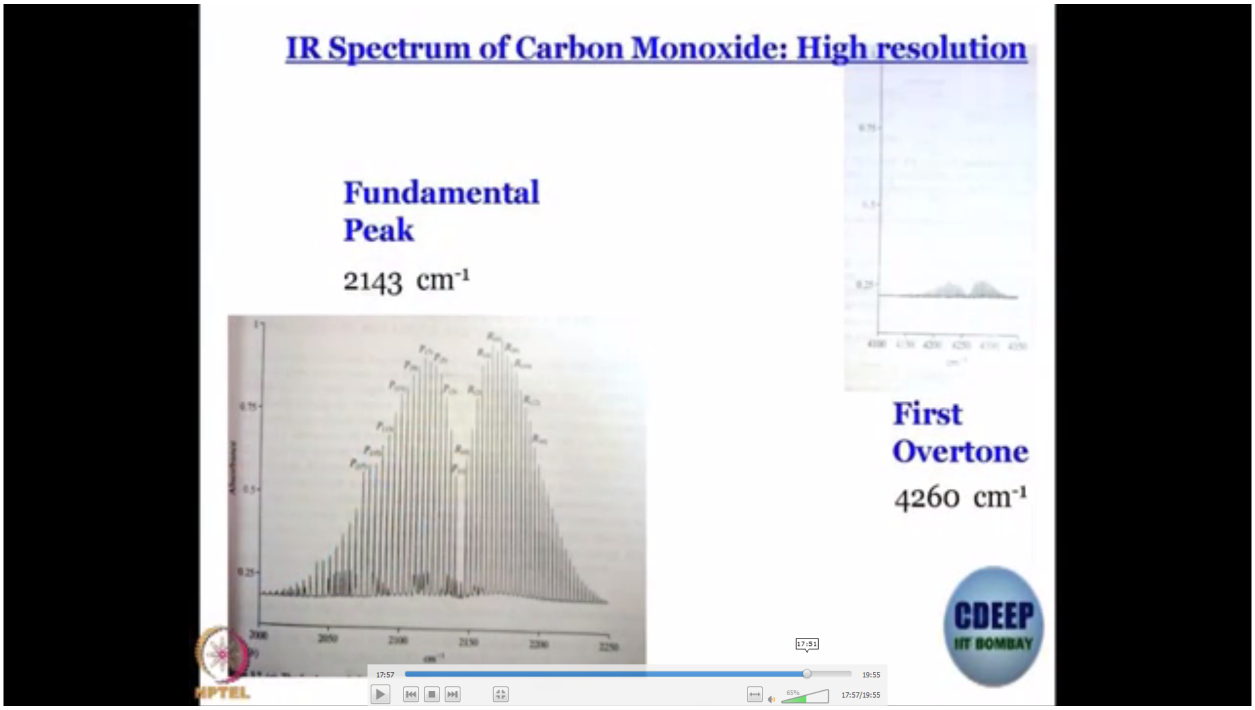
Now one thing that we need to remember, and this is very simple algebra so you could do it yourself, this is what we get, the energy gaps. The energy of the fundamental is ṽ 1-2x, it is not just ṽ. First overtone is 2ṽ (1 -3Xc). Second overtone in this case is 3ṽ (1 - 4Xc). So it is not ṽ, 2ṽ, 3ṽ, please remember that. That’s a little childish animation, but well, this is what it looks like, okay. So as you go higher up, the energy is more and more smaller than what is expected.


IR Spectrum of Carbon Monoxide

To conclude this discussion, let me show you a real spectrum, this time of carbon monoxide. This is a fundamental peak at 2143. This is the first overtone at 4260, and if I give you these tow values, what can you figure out, what can you figure out? I don’t know the names of these guys. What can you work out if I tell you that the fundamental occurs at 2163 cm inwards and the first overtone occurs at 4260 cm inwards. Yeah please tell me, louder. Repeat the questions.

I am telling you that the fundamental occurs at 2143 cm inwards, the first overtone occurs at 4260 cm inwards. If I give you these values, what are the molecular parameters that you can work out? So if I go back to the energy expression, you can figure out what is ṽ, and that tells you how strong the bond is. You can also figure out what is Xc, right, two variables, two unknowns -- two variables and two equations. So you can determine both and from Xc you can say, what is the dissociation in it?

Last question, why do these look like this, why don't I have one line in fundamental -- so I hope you have noted, how small the first overtone is compared to the fundamental. Now my question is, why do I have such a funny structure, why do I not have one line here and one line there? Because who has said the ro-vibrational will not be observed if it is anharmonic oscillator, of course, it will be observed. So whatever algebra we did in the discussion of ro-vibrational spectrum holds here as well, okay.


IR Spectrum of Carbon Monoxide: High resolution

Fundamental Peak

2143 $cm^{-1}$

First Overtone

4260 $cm^{-1}$

And in fact, if you have a good enough spectrum, what I am showing you here is a low resolution IR spectrum. If I actually show you a high resolution, this is what it looks like. This here is a fundamental. That is the first overtone, you see clear PR structure, and do you see this another PR branch here, smaller PR branch there. Why? Again, isotopic rate, right. Isotope of what, carbon or oxygen? Carbon, C13 is there in small amount, right, that's why you can do with C13 in MR and all. So that is what shows up in the spectrum as well. So see, nu has changed, nu has itself changed and also spacing has change, okay.

That completes our discussion or IR spectroscopy, but we still have one more question to ask, which is very important in meteorology. The question is, suppose -- we know very well how to do microwave spectroscopy and IR spectroscopy. Now let us think of the simple non-metal H2. Is it impossible for us to determine the rotational levels energies and vibration energies of H2. From the discussion so far, it's impossible, right, because H2 does not have a dipole moment. No matter how much it vibrates, it will never develop a dipole moment. So the way out is using the perhaps most important Indian contribution to modern science, that is Raman Effect, if you do Raman spectroscopy, then you can actually get an idea of rotational and vibrational levels of non-polar molecules as well. That is what we discuss tomorrow.