Atomic and Molecular Physics

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Lecture - 47
Vibration of a molecule (Contd.)

So, we are discussing about the Vibration of the molecule. And we have seen that this vibration of a molecule it is a it is a similar problem of simple harmonic motion or simple harmonic oscillator ok. And we have seen this solution of simple harmonic oscillators is the is known to us, because this is the standard problem in quantum mechanics. So, what we have seen this basically simple harmonic vibration of a molecule.

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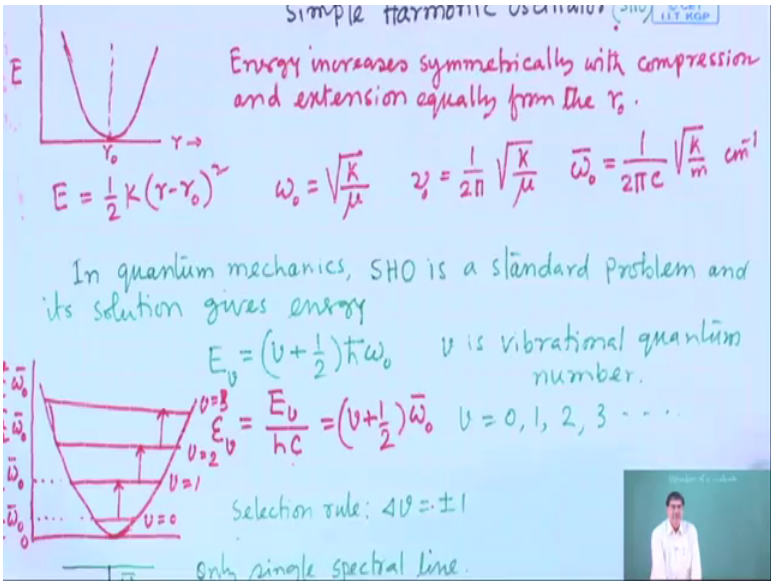

This if we take model, this basically model if you take model that fits a it is a model of simple harmonic motion simple harmonic oscillator. So, you can see this when we tell this simple harmonic motion. So, this is potential energy basically it changes like this ok.

So, this is the energy and this is the distance between two molecules two atoms of the molecule. So, r 0 is the equilibrium distance or bond length. So, it is then it is potential energy is half k r minus r theta square, or if you take this change distance from this equilibrium position.

So, then r minus r 0 1 can take it is x ok. So, the just displacement from the equilibrium position, if you take as x. So, x is nothing, but r minus r 0, so, half k x square ok. So, then this potential is symmetric basically and this kind of potential of any particle it is it is it is nothing, but the is the simple harmonic motion simple harmonic oscillation.

So, in this case so, when it is oscillating it has natural frequency that frequency omega 0 equal to square root of k by m; k is this bond strength basically and mu is the reduced mass. And so, corresponding mu 0 frequency this is the angular frequency angular yes.

So, corresponding frequency mu 0 1 by 2 pi omega 0; so, square root of k by mu and then and then in wave number in wave number so, just you have to. So, mu equal mu 0 equal to c by lambda. So, 1 by lambda is mu bar. So, mu bar will be so, divided by c ok. So, 1 by 2 pi c square root of k by m that will be in centimetre inverse in wave number ok.

So, here I have used this in place of omega in place of this mu bar I have used this omega 0 bar. So, just generally mu bar we use for the, for to represent the spectrum that wave number of spectral lines. So, that is why just to differentiate it. So, this omega 0 bar I have written, but it is nothing but the mu bar ok.

So, as I mentioned this in quantum mechanics simple harmonic motion is a standard problem and solution keeps energy; that is E v equal to v plus half h cross omega 0 ok. And v is the vibrational quantum number, v can take value 0 1 2 3 ok. So, in wave number energy levels energy in wave number in wave number so, mu bar this mu v ok. So, in different notation I have written that equal to this hc E v by hc ok. So, that v plus half omega 0 bar ok.

So, these just this is in joule energy joule or electron volt whatever ok and here this energy is in centimetre inverse wave number ok. So, if this is the energy expression so, in wave number if I plot, so, this will be the energy levels for v equal to 0 1 2 3. So, just one can one can draw lines from the energy for different value of v. So, this will be the and you can see this v equal to 0.

So, it is a half omega naught bar. Then v equal to 1 3 by 2 omega naught bar pi by 2 omega naught bar 7 by 2 omega naught bar. So, these are increasing with so, separation between these energy levels are basically same for all cases and that is nothing but omega 0 ok omega 0 bar.

So, here the spectral lines you will get only 1 because these all are same energy ok, if selection rule is del v equal to plus minus 1 and in this case it is in this selection rule is del v equal to plus minus 1; as the similar case we have seen for rotational spectra where selection rule was thus del j equal to plus minus 1.

So, in this case also this the selection rule is del v equal to plus minus 1. So, only single spectral line you will get from the vibration of the molecule under the simple harmonic oscillator model. Means, if we consider that the vibration of molecule is nothing but the it is like a simple harmonic oscillator.

Then this from the spectra means microwave spectroscopy from microwave spectroscopy sorry from infrared spectroscopy or vibrational spectroscopy, yield we can see this spectra and we should see or we will see only one spectra, which will have the frequency omega 0 bar in centimetre inverse ok, means in wave number.

So, that is the case for a for a vibration of molecule, when we are considering the single when we are considering the simple harmonic motion ok. So, but it is it is seen that this it is not the case you know, it is not the only one spectral lines we are seeing in case of vibrational spectra of a of a molecule. But only one line is very strong and there are some other lines although they are they are comparatively very very weak, but other lines are also there.

And what are the source of this lines? So, then it is realized that this considering the simple harmonic motion simple harmonic oscillation model. So, it is it is a it is an ideal case ok. So, real molecule actually deviates from this model, simple harmonic oscillation model and it is vibration is deviated or distorted from this simple harmonic oscillation ok. So, that is basically called anharmonicity or enharmonic oscillator ok.

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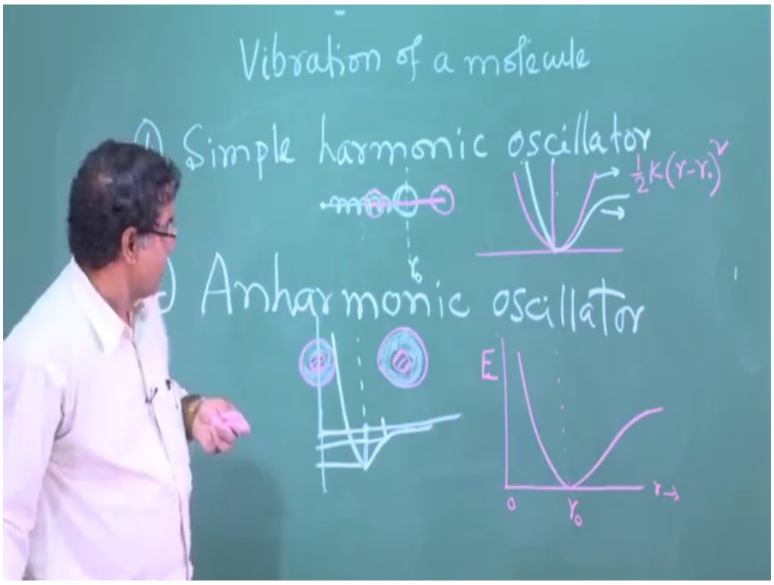

So, simple harmonic, so, one model was basically simple harmonic oscillation ok. So, simple harmonic oscillation what does it mean? So, in case of say if we have reduced this we have reduced this problem to one body problem. So, that is it is it is like a spring it is like a spring ok.

So, it is oscillating it is oscillating. So, these are these the this distance these the say r 0 position equilibrium distance, now it is oscillating. So, it is it is simple harmonic oscillation, when will consider that is displacement is displacement in this side. And it is displacement from here this other side, it is symmetric other side it is other side it is symmetry ok.

So, from here it is going. So, it is oscillating like this it is oscillating like this. So, this expansion and compression these are symmetric ok. The amount is expanded ok, that it is compressed with the same amount ok. If so, then we tell it is simple harmonic oscillator.

But in reality in case of in case of molecule, in case of molecule this model is really it is not suitable, it is slightly deviated from this model and that is called basically anharmonic oscillators, harmonic oscillators simple harmonic oscillator, if I write oscillator then another case is anharmonic oscillator.

So, what is that? It is when this oscillation in both side from the equilibrium position, if it is not symmetric, if it is asymmetry. Means the amount it expanded ok for same energy it is compression is not same ok, for same energy it is compression is not same or other way; for same expansion whatever the energy of the system for same compression same amount of compression the energy of the system is not same, it is different.

And, it is seen that due to the compression, same amount of compression, it is energy is higher than the same amount of expansion ok. So, from where this asymmetry comes? From where this asymmetry comes? So, that is basically because of real molecules. So, in real molecules what we have seen? You have a, you have a nucleus and this electronic charge surrounding it electronic charge surrounding it and another molecule another atom.

So, it has electronic charge ok and I have shown you I have shown you this it is a it is a energy changes when you are changing the distance between these two, you are changing the distance between these two. So, it is energy changes it is energy changes as I as I showed that it is it is energy changes like this ok.

So, what does it mean? What does it mean? Its meaning is that when; that means, these the equilibrium distance equilibrium distance. Now when it is expanded, when it is expanded; say by this amount so, its energy changes. So, energy changes from here to here ok. When, it expanded fine, now if it is compressed if it is compressed by same amount ok, if it is compressed by same amount. So, like this. So, it is energy will be like this energy is like this ok.

So, now, it is energy is higher, for same compression and same expansion for compression this energy is higher ok. So, if you so, energy change is not symmetric due to compression and due to the expansion. Reason is that this side this side as I told that change of energy is very rate of change of energy is very high, it is sharp change when slide distance when slightly it is compressed, but when it is expanded ok, this molecule bond length is slightly extended ok. It is you know change of energy is like this, it is rate of change is change of energy is very slow ok.

So, that is why the change of energy due to compression and expansion is not symmetric. So, that is why in real molecule this we see the we see the change of. So, in this case whatever we have considered whatever we have considered that this change of energy is symmetric is symmetric, but in real molecule in real molecule the change is basically, it is sharp change is sharp and here change is slow and then it goes to the it is just like this, it is goes to the saturation value ok.

So, this is the potential this is the energy this for this energy, when it is harmonic oscillator, when molecular behave like harmonic oscillator. So, this will be the change of energy due to compression and expansion and this will be the change of energy, this curve will be followed when this oscillation is anharmonic ok.

And in reality in real atoms so, it is it is not harmonic oscillator, it deviate from this harmonic behaviour and some asymmetry introduced in this behaviour and thus it is called basically anharmonic oscillator.

So, for anharmonic oscillator some are potential energy curve is basically it will change like this ok. So, this is the equilibrium distance r 0 and here it is 0, here the change of r ok and this side is change of energy ok. So, this anharmonicity basically so, for this harmonic oscillator the potential energy, we have seen the potential energy it is half k r minus r 0 square ok. So, that is why it is symmetric. So, that is the potential energy. Now for these enharmonic oscillators, so, what is the potential energy ok? What is the potential energy?

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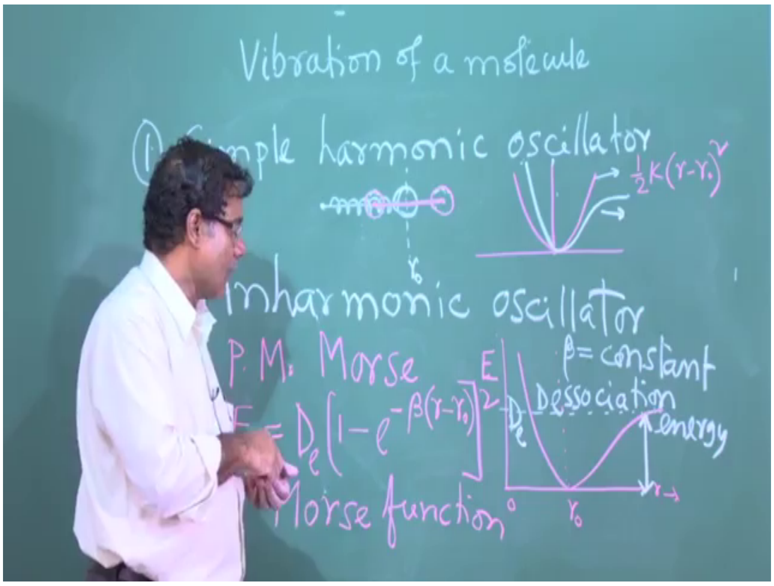

So, that just purely empirical formula was given by P. M. Morse, P. M. Morse one empirical formula was given by given by P. M. Morse, fitting the experimental curve fitting the experimental curve; this P. M. Morse he deduced a empirical formula and he gave this potential energy for this anharmonic oscillators or which follows this curve.

So, this E is equal to basically D e, it is D e 1 minus e to the power minus beta r minus r 0 then square ok, then square. So, this kind of potential energy this is a purely empirical formula, but it fits this experimental observation ok. And this potential energy curve it is a this follows this function and is called Morse function, Morse function it is called Morse function ok.

So, one has to use this potential energy in place of in place of in place of this potential energy, which is for harmonic oscillator and this is for anharmonic oscillator. So, using this potential energy one has to again repeat this calculation Schrodinger's one has to solve the Schrodinger equation considering this potential energy and one can find out the energy expression. So, I will write just that energy expression.

So, here unknown is D e and beta. So, beta is basically a constant for a particular molecule; beta is a constant for a particular molecule. So, here I can write beta is a constant for a particular molecule ok. So, for different molecule beta will be different, it is just constant and D e is called D e is called basically D e is called this value is basically D e; this value is basically D e, it is called dissociation energy, D is called dissociation energy; this D is called dissociation energy dissociation energy ok, it is called dissociation energy.

Means the atom will the molecule will breaks at this energy. So, this energy value is basically this energy this is the value of this energy, when energy of this energy D energy will be supplied to the molecule ok. So, this molecule will go in this state and then basically it is that is why it is the constant saturated energy ok, at that energy this molecule will breaks.

So, molecule basically it is a it is vibrating, it is asymmetric vibration it is asymmetric vibration ok, it is basically a symmetric vibration ok, or the compressed, but it is elongated more ok. So, energy is higher and higher. So, it will be elongated more and more. So, after some time what will happen? They will be separated. So, that is the that is called dissociation.

So, to dissociate the molecules, to separate the atoms how much energy is required? So, that is basically dissociation energy, say that is D ok. So, now, considering this Morse potential one has to one has to solve the Schrodinger equation and that solution is also and that solution will be one can write E, it is v, E v equal to or at a time I can write I think this with the so, in terms of wave number E v.

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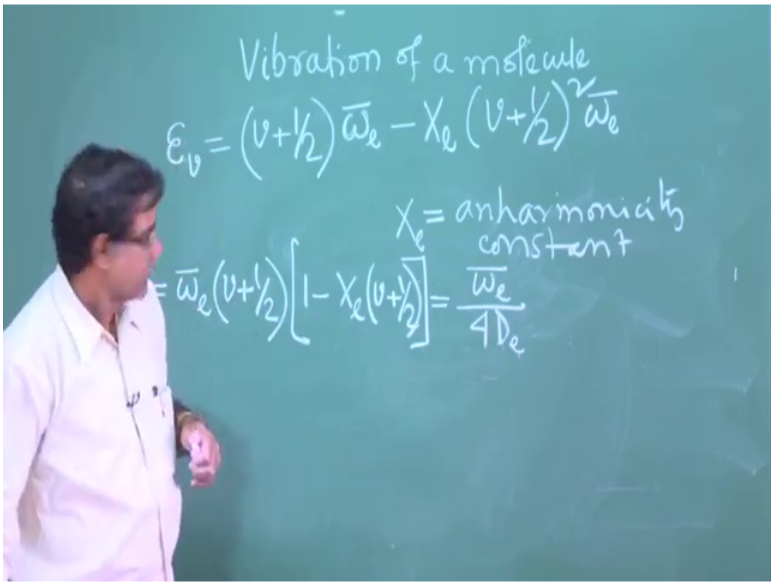

So, that so, what is happening you see this at lower energy it is up to this you can see symmetric ok. So, when it is vibrating oscillating with the smaller energy. So, it is it is it is like a simple harmonic oscillator ok. But when it is going to the higher energy, so then it is becoming asymmetric, then it is becoming asymmetric ok. So, this so, this solution itself will tell us that this whatever the energy for simple harmonic oscillator, so, that was v plus half omega 0 I wrote omega 0 bar ok.

Here, I am writing omega e bar or just for anharmonic case, it is here also D e I am using this symbol in case of anharmonic oscillator ok. So, here I have used D e. So, here I am writing omega e. So, this natural frequency omega 0 and corresponding wave them are omega 0 bar, so, for harmonic oscillator.

So, in this case this wave number omega e bar is not same as the omega 0 bar ok, it is different. So, different symbol I have used. So, this v plus half omega e bar. Now this correction term will come this due to this anharmonicity. So, that is basically minus another term will come. So, that is X e, what is X e I will tell you; X e v plus half square ok, omega e bar omega e bar ok.

So, here X e is called X e is called this anharmonicity constant an anharmonicity constant anharmonicity constant, it is called anharmonicity constant ok. And it is I think it is related with the yeah omega e and dissociation energy. So, this equal to omega e bar by 4 D ok, 4 D ok. So, these the anharmonicity constant. So, it is related with the dissociation energy.

And so, this I can. So, this I can write that basically if E v for the enharmonic oscillator. So, I can write omega e bar v plus half ok. So, then 1 minus X e X e v plus half ok. So, this I will just remove it, I will just remove it ok. So, this will be the energy for anharmonic oscillators in wave number in centimetre inverse of course.

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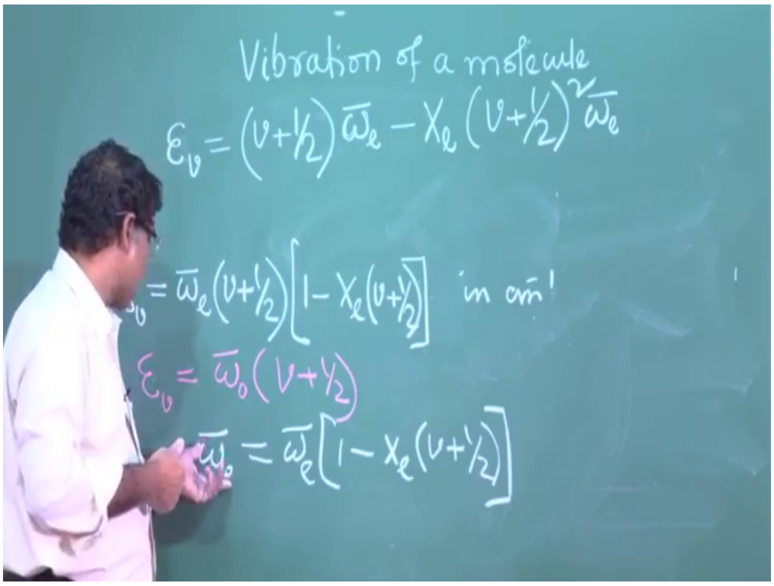

So, this just to show that it is a in terms of wave number and for harmonic oscillator what we saw harmonic oscillator, what we saw that energy expression was omega 0 bar v plus half ok. So, now if you compare these two if you compare these two you can write this omega 0 bar ok. This natural frequency of this harmonic oscillator omega 0 bar that equal to. So, omega e omega e bar, 1 minus X e v plus half ok. So, one can tell that this enharmonic oscillator it is basically it is what does it mean? What does it mean of this expression?

It is meaning of this is that this anharmonic oscillator as if it will oscillate harmonically, it will it will be it will oscillate like harmonic oscillator with different frequency with this frequency and that frequency, that frequency is not same for all energy level all v ok. For different vibrational level, for different energy states, this frequency will not be same this frequency will change with v and it will decrease, this frequency will defuse with higher energy level with higher v ok.

So, that is the meaning. So, anharmonic oscillator also it is it will it is it is one can consider that it will it will oscillate like a harmonic oscillator, but it frequency it is not omega 0 bar ok. In that case omega 0 bar will be this which will vary which will vary with v for higher v for higher vibration energy level. So, this frequency will be lower and it will change with v ok.

So, yes yeah. So, I next class I will I will discuss about the spectral lines of this harmonic anharmonic oscillator. So, let me stop here.

Thank you.