Concepts of chemistry for engineering
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Lecture 43
Vibrational spectroscopy

We learnt about micro-spectroscopy and that has got to do with rotation of molecules. Now, we will try to see what information vibration of molecules can give us. And vibrations if you might remember, they are in infrared regime, energy of vibrations of molecules is typically in the infrared regime.

So, vibrational spectroscopy is also called IR spectroscopy. And again, this is a spoiler, IR spectroscopy gives us an idea of bond strength, rotational spectroscopy, micro spectroscopy gave us an idea of bond length, here we are going to get an idea of bond strength. So, again let us work with the same molecule the HCl.

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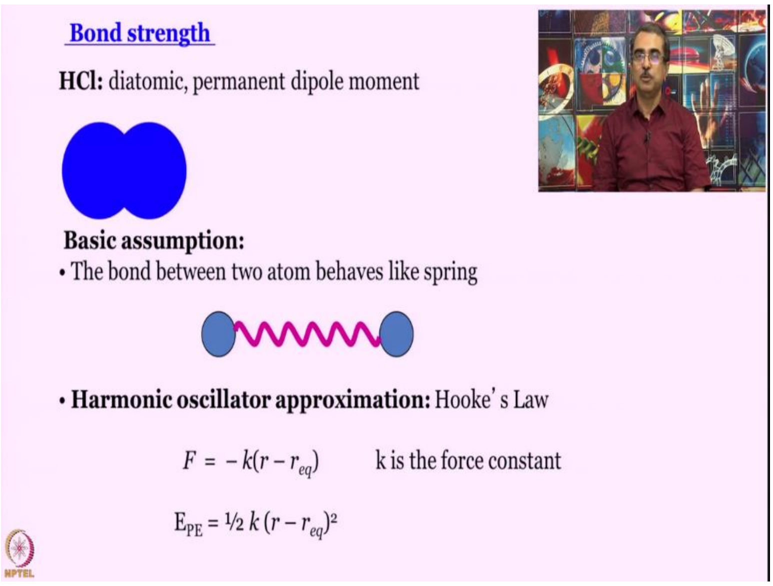

Bond strength

HCl: diatomic, permanent dipole moment

Basic assumption:

- The bond between two atom behaves like spring
- **Harmonic oscillator approximation:** Hooke's Law

$F = -k(r - r_{eq})$ k is the force constant

$E_{PE} = \frac{1}{2} k (r - r_{eq})^2$

HCl is a diatomic molecule with a permanent dipole moment. So, what happens when it vibrates, what happens? When it vibrates, essentially the dipole moment keeps changing. So, now, you can think, if you now plot the dipole moment along this direction, what will happen, it will go up then go down and then go up again.

Again, you get an oscillation kind of behaviour, oscillatory behaviour, but the graph will look a little different from what it did earlier because there is not going to be any minus sign. Because dipole moment will always point in one direction, the large dipole moment. Well, something like this keep on increasing become large, then keep on decreasing to that value, keep on increasing to that.

So, that kind of a variation, so maybe $\sin^2 \theta$ kind of, $\sin^2 x$ kind of variation will be there. So, the basic assumption in formulating the quantum mechanical treatment of HCl to start with at least is that the bond between two atoms behaves like a spring and not just any spring, a spring that is well behaved.

A spring that follows Hooke's law, Hooke's law you must have studied is such where the force, restoring force is proportional to the displacement and it is always towards the center that is why you get this minus sign and potential energy that comes here. Now, for the first time we are encountering potential energy after hydrogen atom, for hydrogen atom molecules we did have potential energy.

But here in rotations, there is no potential energy, for vibrations potential energy is there and that potential energy is a parabolic potential, $\frac{1}{2}\kappa(r - r_{eq})^2$, r_{eq} is the equilibrium distance or equilibrium bond length. So, deviation from that and square of that, that gives you the parabolic potential associated with harmonic oscillators. So, harmonic oscillator is the approximation we are going to use at least to start with.

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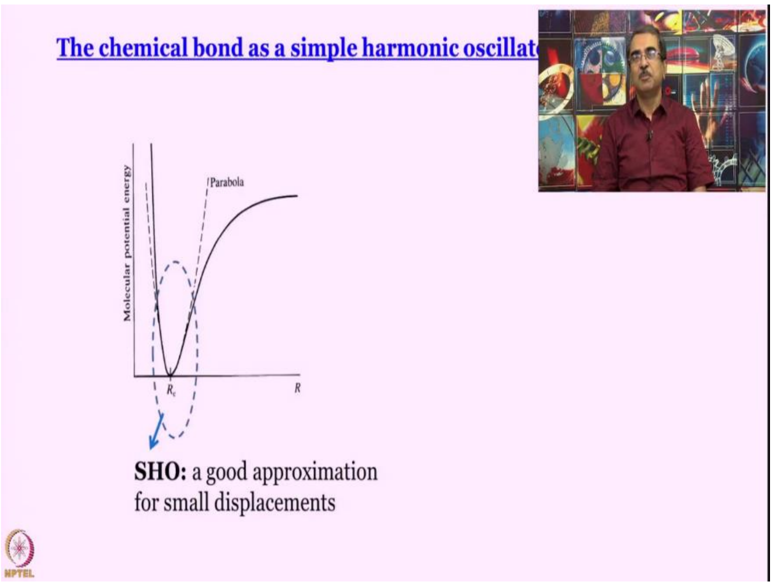

The chemical bond as a simple harmonic oscillat

SHO: a good approximation for small displacements

The question is, is this a valid approximation? To answer that, we have plotted this I hope you are familiar with this shape now, this is what we obtained when we talked about say di-hydrogen molecule and two atoms very far away from each other, energy of interaction is negligible, then they come close, close, close; energy keeps on decreasing, stability gives an increasing, goes to a minimum value at equilibrium bond length.

And then for further approach, there is a sharp increase in potential energy. So, this really is the potential energy surface, which is approximately can be modelled by something called a Morse potential. And this is definitely not parabolic. But if I draw a parabola on it, you can see that in this region, for small displacement, the parabola more or less holds up to here, then there is a deviation, here also then there is a deviation.

So, if you are content, working with small vibrational energies, small displacements, then the parabolic potential might work. So, we are starting with that kind of a hope. So, we are starting with the hope that good, it is a good approximation, simple harmonic oscillator for small displacements.

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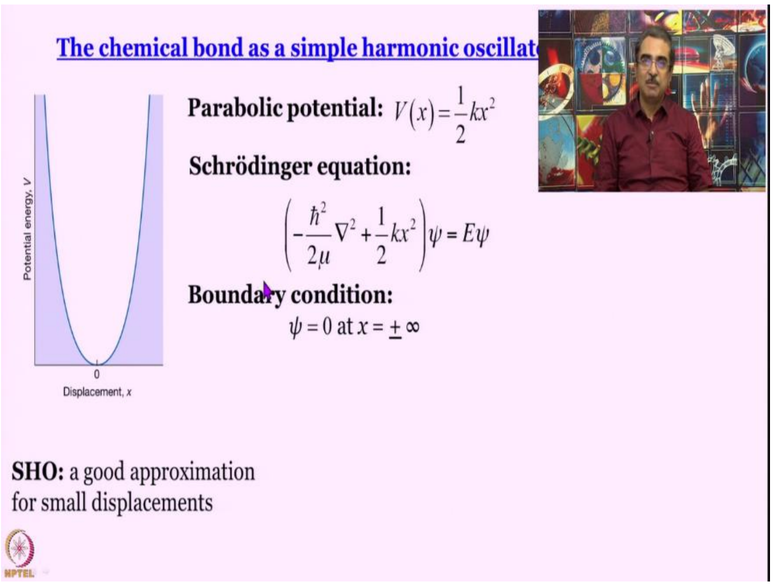


The chemical bond as a simple harmonic oscillat

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

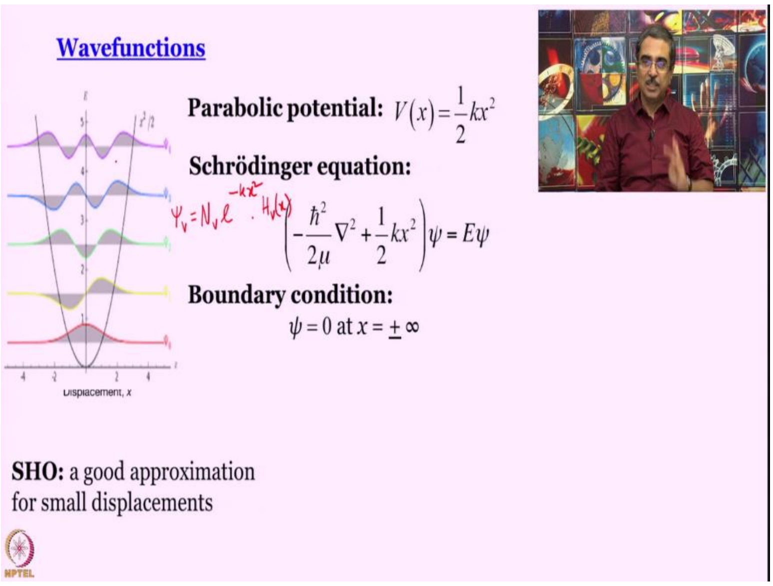
Schrödinger equation:

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

Boundary condition:

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

SHO: a good approximation
for small displacements



Wavefunctions

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

Schrödinger equation:

$\Psi_v = N_v e^{-kx^2} \cdot H_v(x)$

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

Boundary condition:

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

SHO: a good approximation for small displacements

So, this is our parabolic potential, and we can plot it like this. Now, we will write Schrodinger equation as usual. What is it? It is $(-\frac{\hbar^2}{2\mu}\nabla^2+\frac{1}{2}\kappa x^2)$. Remember, once again, we are using μ because it is a two-body problem, HCl, this is H, this is Cl. But we do not like two-body problems, more difficult to handle. So, we reduce it to a one body problem.

And when we do that, the mass that we need to consider is neither the mass of H nor the mass of Cl, rather the mass the reduced mass, $\frac{1}{\mu}=\frac{1}{m_H}+\frac{1}{m_{Cl}}$. So, $-\frac{\hbar^2}{2\mu}\nabla^2$, this gives you the kinetic energy, $\frac{1}{2}\kappa x^2$ as we have discussed already is the potential energy of the hamiltonian.

So, the Hamiltonian is there, we have done the equation, one can solve it. So, the boundary condition that we have to use here. Remember, it is boundary condition that produces your quantization. So, the boundary condition that we have to use here $\psi=0$ at $x=\pm\infty$, not at the surface, not at the surface.

What is the surface? You just plot it this parabolic potential for this value of x what is the value of V , there is no reason to think that at this point the wavefunction will become 0, it becomes 0 at $x=\pm\infty$,. So, using that boundary condition what you get is first of all you get quantization, you get different energy levels and you get this kind of wave function.

Do they look like particle in a box wave functions? Partially, yes, they do look like sin wave site and even particle wave function, particle in a box wave function, you had no node for the lowest energy, one node in the next one, two in the next and so on and so forth. But these are not sin waves. So, these are something like this, let me just write it here $\psi_v = N_v e^{-\kappa x^2}$for now just write k, and here I will just write k x^2 since we are just trying to give you an idea, this is a Gaussian function and this is multiplied by what is called a harmonic polynomial in x.

What is a harmonic polynomial? Please refer to our lecture series, we are not going to deal further here. Unfortunately, in this course, you have to believe me when I say that this is the form and when you plot this, this kind of a function is obtained it becomes 0 only at plus minus infinity. So, you can see some wave function outside the area, that where we have drawn the potential energy surface also. This is the quantum mechanical description of simple harmonic oscillator. Quantization is there, wave functions are there, the only thing that remains to be told at this point is what is the expression for the energies.

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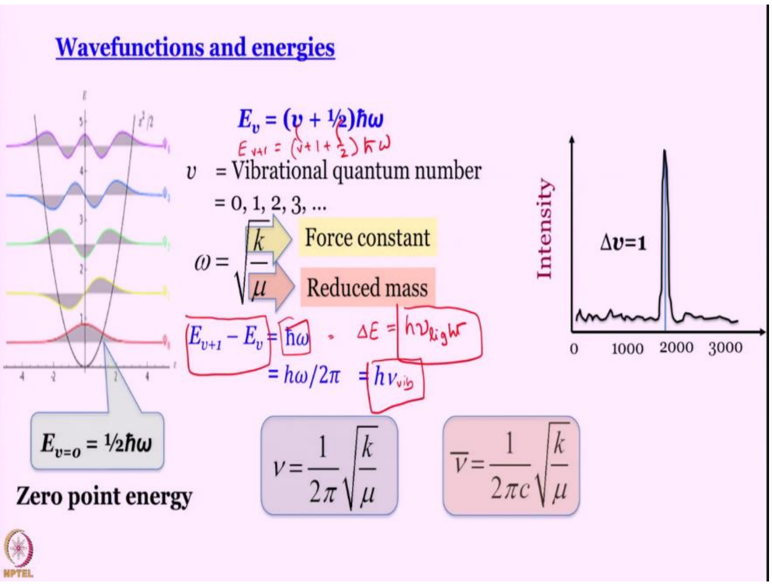

Wavefunctions and energies

$E_\upsilon = (\upsilon + ½)\hbar\omega$

$E_{\upsilon+1} = (\upsilon+1+\frac{1}{2})\hbar\omega$

υ = Vibrational quantum number = 0, 1, 2, 3, ...

$\omega = \sqrt{\frac{k}{\mu}}$

Force constant

Reduced mass

$\boxed{E_{\upsilon+1} - E_\upsilon} = \boxed{\hbar\omega}$. $\Delta E = \boxed{h\nu_{light}}$

$= h\omega/2\pi = \boxed{h\nu_{vib}}$

$E_{\upsilon=o} = ½\hbar\omega$

Zero point energy

$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$

$\overline{\nu} = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}}$

This is the expression for energies $E_\upsilon = (\upsilon + \frac{1}{2})\hbar\omega$, $\hbar$ you know h/ 2π, omega(ω) is the angular frequency of vibration, ν is the vibrational quantum number goes from 0, 1, 2, 3 so on and so forth. Now, we have an interesting situation, if you put ν = 0, what is Ev going to be? It will not be 0. It is going to be $\frac{1}{2}\hbar\omega$.

So, this energy is called zero-point energy, what it essentially says is if it was a classical simple harmonic oscillator, it would have gone down here to the bottom of the well and it could have had no energy at all, which means it would not vibrate. However, for a quantum harmonic oscillator, it is not possible to have zero energy, the oscillator is going to oscillate even at zero Kelvin, that is why it is called zero-point energy.

Why is it so? That is so, because otherwise you know uncertainty principle will be violated. So, we have a quantum harmonic oscillator, fine. So, it is vibrating, let us say I keep on decreasing temperature and it stops, it drops to the lowest possible level, vibration energy goes down, down, down and then it stops. Now, we know the separation r_0 that means, you know position, we know the momentum exactly it is 0.

So, position and momentum are both determined accurately that violates uncertainty principle. So, in order to ensure that it does not violate uncertainty principle, poor quantum harmonic oscillator has to oscillate even at 0 Kelvin with Zero-point energy. In fact, at room temperature only this level is populated because the separation is something like 1000 cm^{-1}.

If you use Boltzmann distribution, you will find that population of this, even your v = 1 state is going to be 0.008 or something, only 8 will be equal to 1 state and it will fall off rapidly. So, if ratio is 1000 to 8, what will the ratio 8 is to something v, it will be practically 0. So, only the v = 0 level is populated at ground state for all practical purposes, so all transitions originated from that. That is very important to understand. That being said, there is more interesting stuff coming up.

We know that angular frequency(ω) for a simple harmonic oscillator is $\omega = \sqrt{\frac{k}{\mu}}$, k is force constant, and μ is reduced mass. So, if we can somehow determine omega, then we should be able to determine force constant, provided I know which atoms I am working with, if I know which atoms I am working with, I know the masses. How do I find this? Let us see, what is the energy gap between two successive levels, $E_{v+1} – E_v$, then do the math very simply, write v +1 here, v and v will cancel, 1- ½ = ½ .

So, you are left with $\hbar\omega$. So, sorry, ½ will also cancel. Since I made a mistake, I will write it $E_{v+1} = (v + 1 + \frac{1}{2})\hbar\omega$ So, if $E_{v+1} – E_v$, is = $\hbar\omega$, well v and v cancel, half and half cancel, you are left with h cross omega. What is this omega? Remember, it is angular frequency of vibration. And if you think why I am saying this again you will see very soon why, angular frequency of vibration.

So, instead of writing $\hbar\omega$, I can write $h\omega/2\pi$. Fair enough? What is $\omega/2\pi$? $\omega/2\pi$ is ν. So, this becomes $E_{v+1} – E_v$ = hν. What is ν? ν is the frequency of vibration. I might as well write like this. But now, we are in an interesting situation. What is there on the left-hand side? $E_{v+1} – E_v$ that is ΔE.

You remember what ΔE is, we had written that it is called Bohr resonance condition, that is = $h\nu_{light}$. So, it turns out is that this $h\nu_{light} = h\nu_{vib}$, h and h cancel, we are left with $\nu_{light} = \nu_{vib}$, vibration. So, a simple harmonic oscillator would absorb only that light. Well, for Δv = 1 kind of transition, which is the only transition that is allowed is going to absorb that light whose frequency is exactly equal to the vibrational frequency, that is something that I find to be very amusing.

So, you can write like this vibrational frequency as $\frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$ we know that. So that is equal to frequency of light as well. And it is conventional in vibrational spectroscopy, like in rotational spectroscopy, to work with not frequency but wave number. So, $\bar{\nu} = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}}$. So, this here is an expression of light that would be absorbed for a v to v+1 transition. And that has k in the numerator, μ in the denominator.

If you know μ, you can easily find the force constant k. What would the force constant k tell us about? It tells us about how strong the bond is. So, it can determine bond strength. What would the spectrum look like? Actually, it would look like this one single line. Of course, there would be some width and all. But for Δv = 1, even if the transition is originated earlier, it does not matter.

It will always be just $h\nu_{vib}$. So, a single line is expected in the spectrum of simple harmonic oscillator more so because in any case, all transitions begin from v = 0 at room temperature. The selection rule is Δv = 1. How do we get it? Please refer to our spectroscopy lectures.

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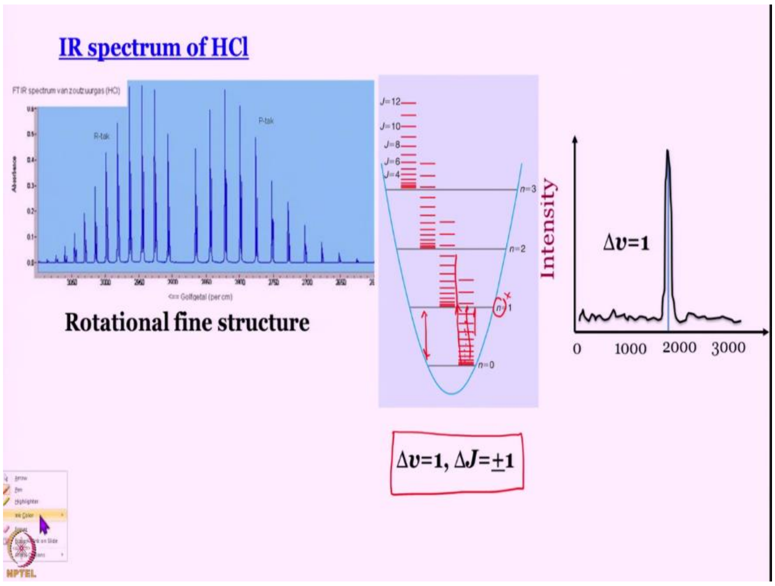
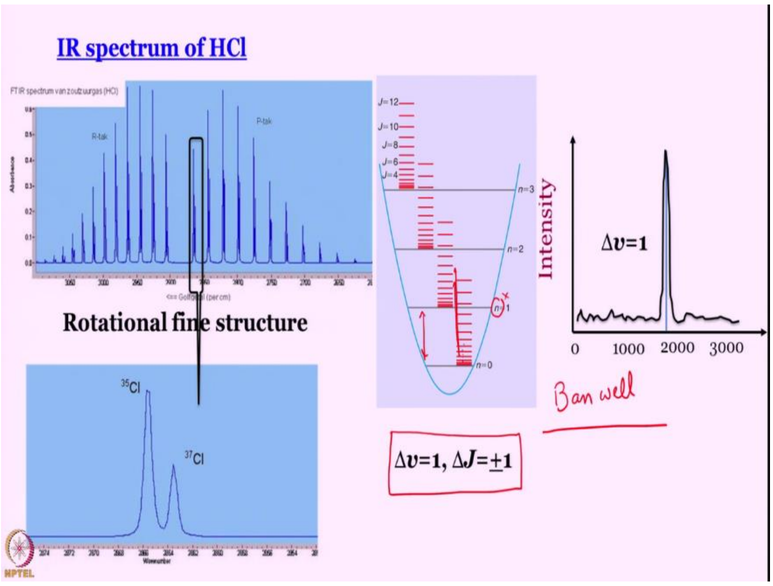


IR spectrum of HCl

Rotational fine structure

$\Delta\upsilon=1, \Delta J=\pm1$


IR spectrum of HCl

Rotational fine structure

Δυ=1, ΔJ=±1

Banwell

As usual, we will not close the discussion without showing you an actual spectrum. This is the expectation. One single line, this is the reality, if you use a good enough IR spectrometer, a high-resolution IR spectrometer, instead of one band you get well two branches of lines. Where do these branches arise from? These branches arise from the fact that every vibrational level is associated with rotational levels.

Now, you might remember here that we said that rotational levels are such that the higher levels are populated, why are they populated because the energy gap is so small, higher vibrational levels are not populated. Here, we have written n this is not populated much because the energy gap is too large, but for n = 0 all these levels will be populated in the same ratio as is predicted by Boltzmann distribution.

So, now upward transitions can begin from any of these levels. So, you get arrows of different length and without going into further detail, let us just believe this again that the selection rules are Δv = 1 and ΔJ = ±1. Meaning if you start from a J value, let us say J = 3. So, from here, you will be able to go to only particular J values associated with the v = 1 level.

Now, I recommend that you work out the expression of energies associated with this kind of transition from Banwell and McCash's book, I am not doing it here because it is very, very simple algebra. For those who are going to take this as an NPTEL course, if you want, we can do it in the interactive session. Others, if there is any problem, please write me an email or something and we will do it.

So, we get two lines, these are called the P branch and the R branch. And you might notice that there is nothing at the center where the line was expected to be. That is because you have Δv =

1 and $\Delta J = \pm 1$, ΔJ is = 0 is not there. That is why you get this kind of an expression, and this is kind of a line.

So, from one spectrum, if your spectrometer is good enough, you can get an idea of IR which gives you an idea of bond strength, as well as you can get an idea of separation of rotational levels, the separation is going to be 2B once again. So, you can get an idea of bond length and bond strength from the same experiment. If your IR spectrometer has high enough resolution.

There is one more thing, if you zoom into one of these lines, unfortunately, it is flipped here for whatever reason, you see that each line is actually a doublet, there are two lines associated with it. Why? Go back to class 8 level chemistry. Remember, chlorine occurs in nature as two isotopes chlorine 35 and chlorine 37, atomic rate of 35.5 is just an average. So, when you do the experiment, you actually sample individual molecules.

So, they are either HCl with chlorine 35 or HCl with chlorine 37. And here, you get two different lines for chlorine 37 and chlorine 35. The isotope effect shows up very, very nicely in this high resolution, what is called ro-vibrational spectrum as well.

So, we get an idea of isotope abundance, relative abundance of isotope, we get an idea of relative abundance of isotopes as well from high resolution IR spectra, which are often called ro-vibrational spectrum, rotation vibration, so ro-vibrational spectrum, so much for vibration and rotation. Next, we are going to go into electronic spectroscopy.