Atomic and Molecular Physics
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Lecture - 48
Vibration of a molecule (Contd.)

So, for anharmonic oscillator will see the Vibrational Spectra ok. So, you can so, what we have seen that, this in case of anharmonic oscillator.

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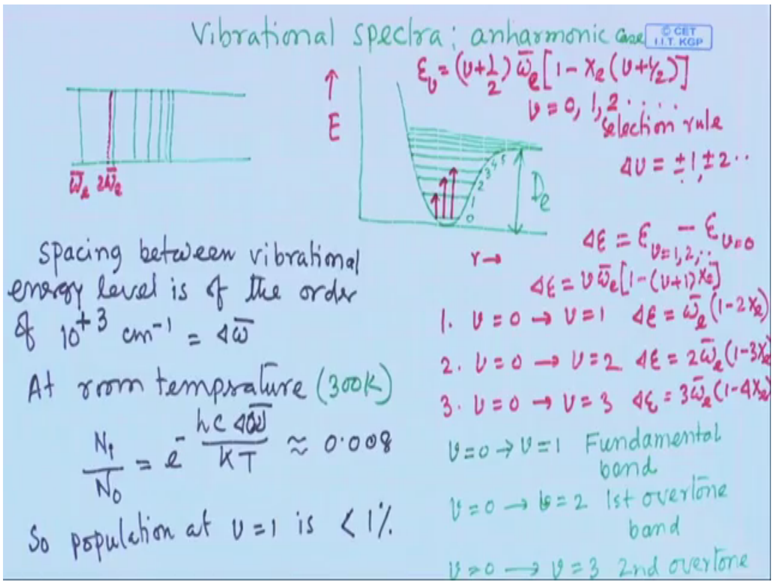

Vibrational spectra: anharmonic case

$\varepsilon_v = (v+\frac{1}{2})\bar{\omega}_e[1 - x_e(v+\frac{1}{2})]$

$v = 0, 1, 2 \ldots$

selection rule

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

Spacing between vibrational energy level is of the order of 10^{+3} cm^{-1} $= \Delta\bar{\omega}$

At room temprature (300K)

$\frac{N_1}{N_0} = e^{-\frac{hc\Delta\bar{\omega}}{kT}} \approx 0.008$

So population at $v = 1$ is $< 1\%$

$\Delta\varepsilon = \varepsilon_{v=1,2,\ldots} - \varepsilon_{v=0}$

$\Delta\varepsilon = v\bar{\omega}_e[1-(v+1)x_e]$

1. $v = 0 \rightarrow v = 1$ $\Delta\varepsilon = \bar{\omega}_e(1-2x_e)$

2. $v = 0 \rightarrow v = 2$ $\Delta\varepsilon = 2\bar{\omega}_e(1-3x_e$

3. $v = 0 \rightarrow v = 3$ $\Delta\varepsilon = 3\bar{\omega}_e(1-4x_e$

$v = 0 \rightarrow v = 1$ Fundamental band

$v = 0 \rightarrow v = 2$ 1st overtone band

$v = 0 \rightarrow v = 3$ 2nd overtone

So, this energy in wave number of course, so, this energy is v plus half omega e bar here I will write omega e I think it is written 0 omega e bar 1 pass x e v plus half. So, x is the enharmonic constant and v is vibrational quantum number. So, v can take value v can take value 0 1 2 etceteraetera right. And in this case selection rule so, for harmonic oscillator selection rule was del v equal to plus minus 1, but in this case and the selection rule is del v equal to plus minus 1, plus minus 2, plus minus 3 etcetera ok.

So, now, from this energy expression if you draw the energy levels so, these are the energy levels ok, different energy levels and you can see you when for higher vibrational levels the separation of energy levels will decrease from this expression one can see just I have I have shown here. So, if this energy change due to the transition from e v v equal to 1 2 3 minus e v equal to 0 ok, means from 0 v equal to 0 to v equal to 1, v equal to 2, v equal to 3 ok.

If this transition occurs so, then what will be the energy of this a spectral lines. So, that is del e. So, del e if you if you if you put v equal to 0 here and for v equal to v. So, e v minus e v equal to0. So, you will get this expression del e equal to v omega e bar 1 minus v plus 1 omega e bar ok. So, this energy of this transition lines. So, 3 cases I have calculated v equal to 0 to v equal to 1. So, del e equal to omega e bar 1 minus 2 x e just here, you put v equal to 0 yes no v equal to 0 I have already put. So, here because v equal to 0 you have put. So, now, v equal to this v equal to 1 2 3 4 ok.

So, if you put 1. So, 1; that means, omega e here 1 minus 1 plus 1 to the 1 minus 2 x e similarly for v equal to 2 1 minus 3 x e and v equal to 2. So, v equal to 3 del e equal to 3 omega e bar 1 minus 2 plus 3 plus 1 4 x e ok. So, from here you can you can see that that energy levels energy levels here I have shown that separation will decrease with higher v. So, when transition from same level v equal to 0. So, the spectral lines energy spectral lines energy their separation will decrease, because it will follow the separation and that is what it is happening? So, this is the first transition line for v equal to 0 to v equal to 1 if it is for simplicity, if you neglect this part you know effect of x e. So, what you will see these spectral lines it is energy is omega e bar this 1 2 omega e bar this 1 3 omega e bar 4 omega e bar etcetera right.

But, now these are the from this 2 omega e 3 omega e omega e bar 4 omega e bar. So, basically this will be slightly smaller than that because of this term because of this 1 minus 2 x u 2 minus 1 minus 3 x e ok. So,. So, because of this anharmonistic otherwise what we could get? So, it could be equally spaced spectral lines right and separation would be omega e bar ok, because it is the omega y bar. So, this could be omega e bar omega e bar this omega e 2 omega e bar etcetera.

So, this separation would be omega e bar. So, all would be the equally spaced, but this is not the case because of this anharmonicity ok. So, this it is it is slightly less than these 2 omega e bar. So, actual level will be here actual level will be here it is slightly less than 2 omega e bar. So, that is why this space between the omega e bar spectral lines in this vibrational spectra ok.

So, that will be a gap will be smaller than the omega e bar. And it will increase for higher vibrational level transition to the higher vibrational level ok. So, so in case of harmonic oscillator we have seen just only 1 spectral lines and it has energy is omega 0 bar omega

0 bar ok. Now, in case of enharmonic case we are getting this multiple number of spectral lines.

So, these spectral lines their separation is decreasing when we are going to the higher order of spectral lines means for higher value of vibrational quantum number ok. So, so basically here since the selection rule is del v equal to plus minus 1 plus minus 2 plus minus 3. So, that means, transition from v equal to 0 to 1 to 3 so; that means, it is v equal to the change of this del v equal to plus 1, plus 2, plus 3 ok. So, so, due to the selection rules we are getting this multiple spectral lines and this transition from the same energy levels v equal to 0 to the higher energy levels for v equal to 1 2 3 ok.

So, these spectral lines will see and there is a [vocalized-nosie] I think this there are some names of this spectral lines. So, first vector lines for v equal to 0 to v equal to 1, it is called fundamental lines or fundamental bands. So, why it is called band that I will you I will tell you later on band means it is not single line it is a it is a branch of line ok. So, why it is called band so, that I will I will tell you later on and you will understand when will go ahead. So, this is the fundamental band and then this other 1 v equal to 0 to v equal to 2. So, that spectral line this say v equal to 0 to v equal to this 1 ok. So, that 1 is called this past overtone band. Next one v equal to 0 to v equal to 3 this called second overtone band ok. So, these are the name of the spectral lines.

Now, here just suddenly why I have I have shown the spectral lines or I have shown the transition only from v equal to 0 to other levels, why not v equal to 1 to v equal 2 v equal to 3 v equal to 4?

So, there should be another sets of spectral lines similarly another set we could get this starting from v equal to 2 to v equal to 3 v equal to 4 v equal to 5, because there is no problem because the selection rules rule will allow for all these transitions. So, why I have not drawn that one suddenly I have done these 3 lines here all 3 lines that is transition starting from the v equal to 0 the reason is that this, it depends on the population of the population of the of the energy level ok.

So, how many population means if you consider a if consider quite large number of of molecules same molecules, but quite a large number of molecules in the system now how many are the there? So, they are in different energy states they can be in different energy states ok. So, if you check that how many are in the down state means v equal to 0 state and how many are in the in the first excited state that is v equal to 1 second excited state etcetera right.

So, one can show one can see that this at room temperature almost all molecules will be at at the ground state, all molecules will be at the v equal to 0 state ok. So, that is that is what here this here we have I try to explain that spacing between vibrational energy levels is of the order of 10 to the power plus 3 centimetre inverse.

So, there is the basically spacing between the energy levels in case of vibrational energy levels. So, that is if it is delta if I write delta e so, then at room temperature. So, this as in case of in case of rotation of a molecule there we have seen this, this, this Boltzmann factor is used for this type of calculation with this factor tells this basically the population at different levels.

So, v equal to 1. So, they are in 1 number of particles or molecules and v equal to 0 N 0 number of. So, this N 1 by N 0 equals e to the power minus. So, this e by K T e here hc del new bar. So, it is in centimetre inverse. So, that is why 1 has to multiply with hc for converting to energy divided by K T. So, if you calculate taking this value 10 to the power plus 3 centimetre inverse and other are constant and it is a room temperature k equal to t equal to 300 Kelvin see if we calculate it is a 0.0 0 8 means it is a 0.0 1.

So, it is just it is the 1 percent of n 0 you know. So, what about the number of total number of molecules out of them only 1 percent molecule can be at the first excited state means at v equal to 1 and 99 percent molecule will be at the at the down state v equal to 0 ok. So, this is the reason here I have shown this type of transition starting from v equal to 0. And at room temperature generally you will see this type of only this kind of spectra other spectra means from first excited state to the other excited state. If it transition from other excited states corresponding the spectral lines that generally we do not see at room temperature ok, reason is that if there is no molecular at v equal to 1.

So, if it is, it is just less than 1 percent. So, this transition this transition probability for v equal to 0 to other excited states excited levels that is 99 percent higher than the than the transition from the v equal to 1 to the other excited states ok.

So, even So, this transition 1 percent transition will be there ok. So, compared to 99 percent so, intensity of that spectral lines which will come from v equal to 1 to the higher excited state. So, that intensity of the spectral lines will be very very weak or you can tell it is it is just interesting 1 percent of the spectral lines, which is coming from v equal to 0 to v equal to 1 ok.

So, that is why these other states will not see in spectrometer. So, only this type of spectral lines will see which are that is why this, this particular names was given. And also this here why we have given these names, because we will not see many spectral lines we will see only few spectral lines ok.

So, because this is probability from v equal to 0 to v equal to 1 and probability from v equal to 0 to v equal to this probability will decrease ok. So, the intensity will decrease, when it is going from v equal to 0 to 3 4 5 6 and higher energy levels. So, this intensity also will decrease ok. So, we will see effectively very few lines and those lines are called as I mentioned this fundamental band first overtone second overtone third overtone etcetera.

So, since they are few. So, the name are given to them.

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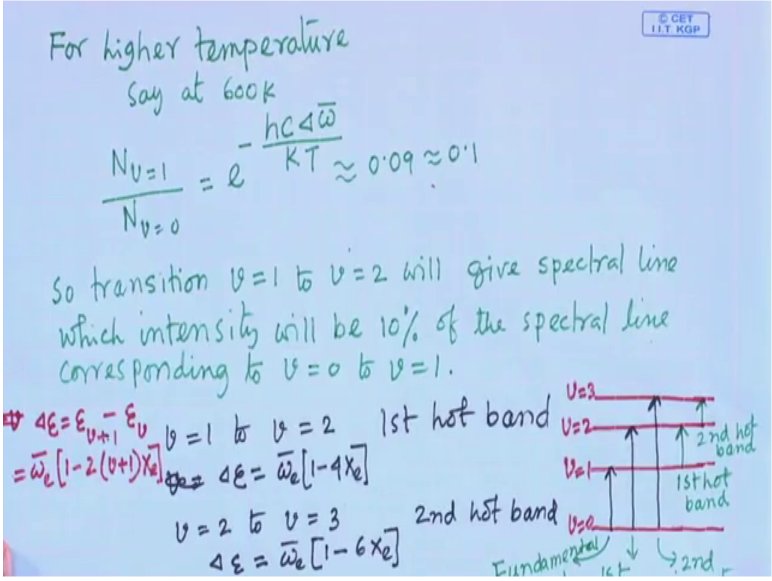

For higher temperature

say at 600K

$$\frac{N_{v=1}}{N_{v=0}} = e^{-\frac{hc\Delta\bar{\omega}}{KT}} \approx 0.09 \approx 0.1$$

So transition $v=1$ to $v=2$ will give spectral line which intensity will be 10% of the spectral line corresponding to $v=0$ to $v=1$.

$\Delta\varepsilon = \varepsilon_{v+1} - \varepsilon_v$

$= \bar{\omega}_e[1-2(v+1)x_e]$

$v=1$ to $v=2$ 1st hot band

$\Delta\varepsilon = \bar{\omega}_e[1-4x_e]$

$v=2$ to $v=3$ 2nd hot band

$\Delta\varepsilon = \bar{\omega}_e[1-6x_e]$

So, next I will I will discuss that, whether those transition from v equal to 1 to v equal to 3, v equal to 2, v equal to 3, or v equal to 2 to v equal to 3, v equal to 4 this higher transition between the different excited state whether it is possible or not yes it is possible.

So, one has to one has to increase the temperature of the system. So, you have you have you have a system of many molecules. So, if you increase the temperature. So, then we see these some other spectral lines. So, what is the probability to have these other spectral lines? So, that is I have shown here just calculation this say higher temperature it is 600 Kelvin. So, for 600 Kelvin if you just calculate, this it is shown 0.1 ok.

So, 0.1 means it is 10 percent. Now, it is say see this when the system is at temperature 600 Kelvin, then the population of the states having quantum number v equal to 1. So, there the 10 percent molecules will be there. So, now, there will be transition means there will be transition of course, now there will be more transition from v equal to 1 2 v equal 2 v equal to 3 and we will see the we will see the spectral lines all those that spectral lines will not be very strong it will be weak, but it is intensity will be reasonable ok. So, one can detect that intensity.

So, increasing the temperature of the system we can see these higher spectral lines transition among the among the excited levels. And those spectral lines, since it is because of the heating of the system molecular system we get this type of spectral lines. So, that is why these spectral lines or band spectral band it is called hot band ok.

So, transition v equal to 1 to v equal 2 will give spectral lines ok, which whose intensity will be 10 percent of the spectral line corresponding to v equal to 0 to v equal to 1 ok. Because, now population in v equal to 1 it is higher than the population was at temperature 300 Kelvin ok, it was only 1 percent now it is 10 percent.

So, we will get intensity. So, intensity will be basically proportional to the population. So, that is why will get reasonable intensity at least it will be 10 percent of this fundamental band. So, this, these bands is called hot bands. So, so this here I have shown you that these are energy level v equal to 0 1 2 3. Now this transition this already we have shown v equal to 0 to 1 v equal to 0 to 2 v equal to 0 to 3 ok. So, these spectral lines as per the selection rule these are allowed and this one is called fundamental then this one is called first overtone band and basically this one is called second overtone band.

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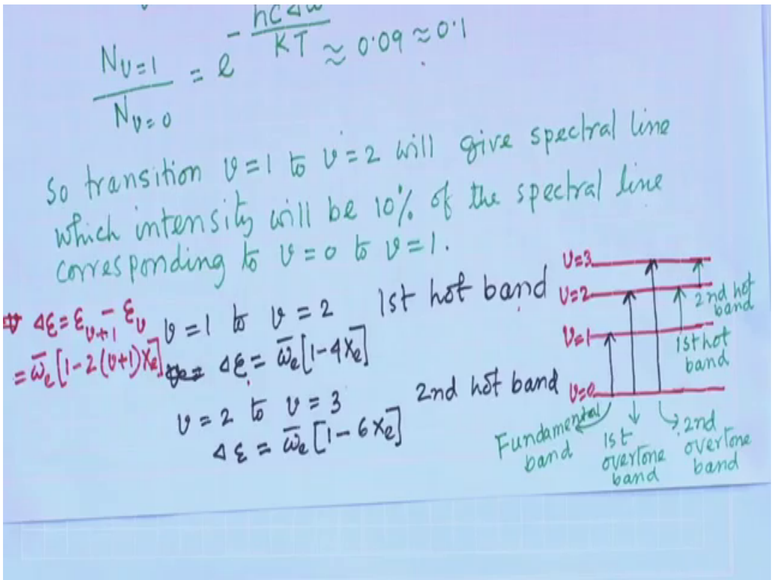

$$\frac{N_{v=1}}{N_{v=0}} = e^{-\frac{hc\Delta\omega}{KT}} \approx 0.09 \approx 0.1$$

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$v=2$ to $v=3$ 2nd hot band

$\Delta\varepsilon = \bar{\omega}_e[1-6x_e]$

And, now v equal to 1 to v equal to as this intense will be 10 percent of this one, but now it is it will be visible. So, this will see only at higher temperature and so, that is why it is called v equal to 1 2 v equal to it is called fast hot band v equal to 2 to v equal to 3 it is called second hot band.

So, we will see these spectral lines and depending on their transition, whether it is from v equal to 0 or it is from v equal to 1 or v equal to so, they are given some name ok. So, this basically here this for fast hot band so, this v equal to 1 to v equal to 2 so, this will be the energy or wave number of the spectral lines so, this hot bend. So, that is omega e 1 minus 4 x e ok.

So, this one was omega e 1 minus 2 x e this 1 omega e 1 minus 3 x e that we have seen earlier ok. So, in this case also one can calculate what will be the frequency, what will be the frequency of these spectral lines? So, this for first band first hot band. So, omega e bar 1 minus 4 x e omega e bar 1 minus 6 x that will be for second hot band.

So, one can calculate this ah. So, these are the basically band we will see these are the band we will see for the molecules, which have anharmonic in their oscillation. So, basically that is that is that is the anharmonic oscillator model. And for that we have we have seen that this, what will be the energy and spectral lines for this diatomic vibrating molecule this basically anharmonic diatomic molecule.

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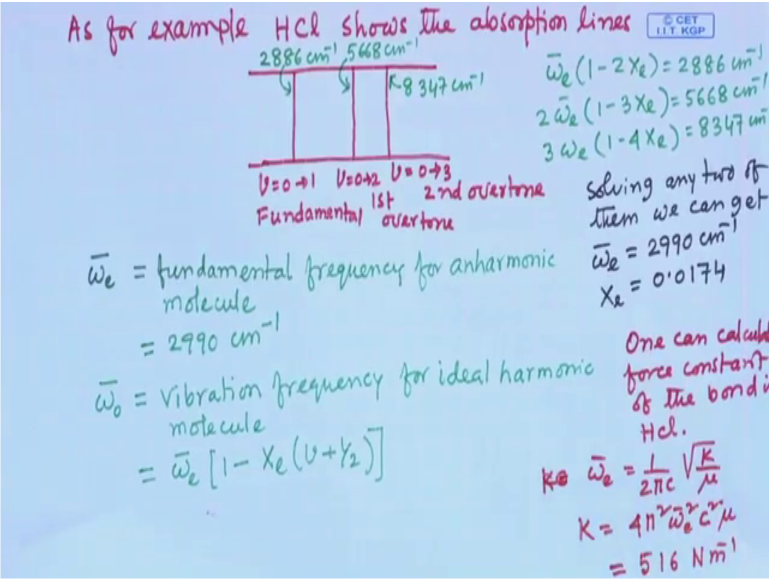

As for example HCl shows the absorption lines

$\bar{\omega}_e(1-2x_e) = 2886\ \text{cm}^{-1}$

$2\bar{\omega}_e(1-3x_e) = 5668\ \text{cm}^{-1}$

$3\omega_e(1-4x_e) = 8347\ \text{cm}$

solving any two of them we can get

$\bar{\omega}_e = 2990\ \text{cm}^{-1}$

$x_e = 0{\cdot}0174$

$\bar{\omega}_e$ = fundamental frequency for anharmonic molecule

$= 2990\ \text{cm}^{-1}$

$\bar{\omega}_0$ = Vibration frequency for ideal harmonic molecule

$= \bar{\omega}_e[1 - x_e(v + 1/2)]$

One can calcul force constant of the bond i HCl.

$\bar{\omega}_e = \frac{1}{2\pi c}\sqrt{\frac{K}{\mu}}$

$K = 4\pi^2\bar{\omega}_e^2 c^2 \mu$

$= 516\ \text{Nm}^{-1}$

So, now, from this study you can, if I take one example. So, from basically infrared spectrometer using infrared spectrometer so, one has to take the molecules ok. So, if I take H C l molecule, if I take H C l molecule and then this molecule will keep at a particular temperature.

So, if it is it is room tempertaure that is also fine. Now, we use spectrometer we use spectrometer to see the spectra ok. Because, all the time this transition is happening all the time this transition is happening. Now due to this transition there are some radiation infrared radiation, now we have few spectrometer ok.

Spectrometer you know prism spectrometer, grating spectrometer right for visible light I think you will use you have used in lab or you will use in lab. So, spectrometer basically you have qualimeter right. So, it qualimates the it qualimates the light from the source. So, you have source now this from the source light is falling on this on this qualimeter.

Now from through these qualimeter this light will fall on the on the spectrometer table on table either we have kept prism or say grating ok. So, when this light will fall on the prism or grating. So, now, there will be special there will be special separation there will be special separation of this of the radiation of the light depending on their wavelength ok.

So, if you use white light. So, white light have all sorts of colour wavelength colour. So, you will see the separation of all colours after passing through the prism or after passing through the grating ok. And that we see so, after so, that is basically diffraction from grating when we will tell grating. So, there will be diffraction. So, diffraction phenomena is used to separate the separate the light as far there as a function of their of their wavelength ok.

So, these the spectrometer is used to separate the spectral lines depending on their wavelength or energy or wave number. And that we see so, we use telescope to see the spectra either prism spectra or the grating spectra we use the telescope. So, this as a whole this is called spectrometer spectrometer is having the having the qualimeters and then table prism table or getting table and then this you have telescope ok. And so, these are these the spectrometer and spectrometer is used to measure the wavelength of the spectral lines energy of the spectral lines ok.

So, in case of infrared so, you need this. So, you have to you have to so, you have to use infrared sensitive detector ok. To sense the intensity to sense the intensity at in spatial resolution so, in what is called to sense the intensity in space ok.

And in space you will get intensity means different spectral lines at different at different space, because their wavelengths or energy are different and that is why spectrometer does ok. As for according to their wavelength or energy it is faded over a over a space ok. And so, this special separation is basically it is it depends on the on the energy of the spectral lines. So, infrared detector will be used to detect the intensity ok. As a function of this special distance and one can measure, one can measure the energy or spectra wavelength of the spectral line.

So, just I want to just describe the spectrometer this is the standard spectrometer. Now here I will use this one term absorption. So, jelly infrared etcetera we use the in this case with the absorption spectra ok, the absorption spectra this term we I use for that I explain the spectrometer. So, what will do? So, white light ok. So, instead of putting to the qualimeter directly so, white light will pass through the to the system of molecules.

So, if H C l molecules so, assembly of H C l molecules in a in a glass tube ok, now this white light means having all sorts of wavelength. Now, it will pass through this molecule gas and then the then the light through this molecular gas it will fall on the qualimeter ok. Now from qualimeter to yours it will come to your spectrometer ok.

So, so at the in spectrometer additionally I am putting a I am putting if a if a glass tube having the H C l molecules or other molecules ok. Now, white light was coming now if any absorption happen in this in this gas tube H C l gas tube then that line will be missing in spectrometer, because there is when there is no gas. So, I will I will see this all sorts of wavelength, now I have put gas in the in the in the path of this white light.

Now, there will be if any transition in this H C l level. So, there will be some absorption of this some radiation of wavelength ok. So, that wavelength will not reach and that wavelength will be missing. So, that spectral lines will be missing and then that will be so, in a white spectra of different colours. So, there will see dark line dark line means that radiation has not come it is absorbed. So, that is the absorbed by this H C l molecule

So, so, basically this way we in infrared spectroscopy, or microwave spectroscopy, we generally study the this absorption spectra, really we study the absorption spectra and absorption spectra this emission spectra as per this both are same in one case it is emitting that we are seeing other case.

So, other case this from white light. So, some lines are missing some lines are observed. So, that absorbed by the gas molecular molecule gas and that should that that the that missing of the spectral lines, which will see a dark line that (Refer Time: 33:59) attain this absorption line

So, here this term I have used this H C l shows the absorption lines ok. So, from infrared spectrometer one can measure the spectral lines. So, fundamental lines first overtone second overtone and it is major for H C l it is major and this is the, these are the values and yes. So, I think I will stop here I will continue this class these discuss in next class.

Thank you.