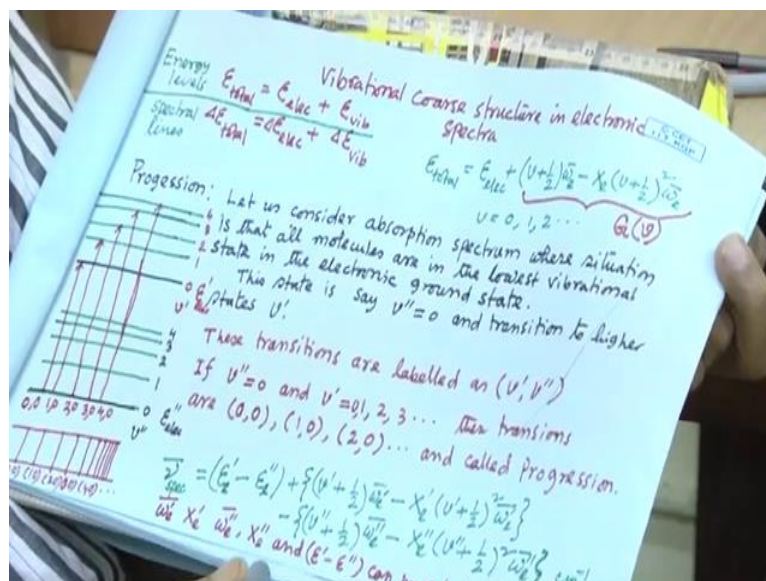


Experimental Physics - III
Prof. Amal Kumar Das
Department of Physics
Indian Institute of Technology, Kharagpur

Lecture - 45
Study of Absorption Spectrum of Iodine Vapour (Continued)

Let me slightly, let me discuss slightly more about the about the theory.

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Whatever I told that is vibrational is called vibrational course structure in electronic spectra. Whatever their spectra I showed that is electronic spectra. Now it is a band, it is a band because there you will see vibrational course structure; vibrational course structure in electronic spectra ok. Total energy of that spectral line is E electronic plus E vibration as I told I have neglected the rotational one ok, because this energy separation of rotational one is very small.

The spectroscopy here we will use. It is difficult to get that that much regulation. We will we will only, we will only the; we will only the concentrate on the vibrational part. This is the energy levels or this is the spectral lines in centimeter inverse this energy of the spectral lines ok. Here if you this is the energy level.

Now if you take the difference between the two energy levels then you will see spectral lines. E_{total} is an electronic energy plus this vibrational energy. This vibrational energy I represent by either e electronic or another notation generally people use G_v ok. For this notation also one can use.

here you can see these two black lines, these two black lines are the electronic energy levels $E_{\text{electronic}}$ and this is the $E_{\text{electronic}}$, $E_{\text{electronic}}$ double dash electronic two energy levels. Now with each electronic energy level, there are vibrational energy levels. One electronic one this if we take that is ground one. That is $v=0$ equal to 0 here v double dash and here v dash ok. 0, 1, 2, 3 vibrational energy level.

here 0, 1, 2, 3 that is a v dash vibrational energy level in this two electronic energy levels ok. Here in this case this selection rule for vibrational quantum number is $\Delta v = \pm 1$ ok. It can be 0, 1, 2, 3 ok. All sorts of all sorts of transition is possible. Now at room temperature; generally, molecules are at the ground state level ok. it is expected that all molecules, the population of the molecules will be at the v double dash equal to 0 at this population maximum will be at this vibrational energy level ok.

Now, if you exposed, if you exposed these molecules to the light of continuous wavelength white light. What will happen? These molecules will absorb energy; absorb light appropriate light to go for the transition. It will go from this v double dash equal to 0 to v dash equal to 0, 1, 2, 3, 4. This type of series is called progression series; there can be other type of series also. You will get spectral lines this 0, 0 means this is the; this is 0, 0 means this v double dash is 0 and v dash is 0.

this called 1, 0; v dash v double dash that way we can designate this spectral line 0, 0 1 0, 2 0, 3 0, 4 0 ok. there here this kind of spectral lines you will see and; obviously, this spectral lines you can see that this energy, electronic energy is there this is the say electronic energy vibrational level 0 to 0 and then next one is coming this plus this ok. This is having the energy of this one plus this one ok.

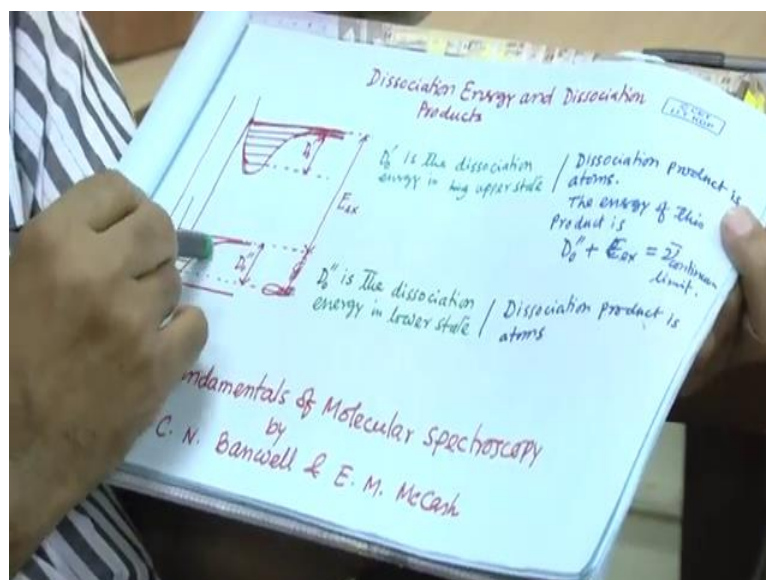
This one is if I subtract this two, if I subtract this two I will get the energy of this energy difference of this vibrational energy level ok. If I subtract this and this, this and this I will get the vibrational energy difference between these two energy levels. Here what about the vibrational energy levels we are seeing. After measuring their energy; if you take

successive difference of this spectral lines, then you will get the energy separation of the energy separation of the vibrational energy levels.

This is very important, this is very important to study the vibrational spectra of molecules ok. So here if these lines is. Here you can see if I take difference. If I take difference of these two energy levels this is the energy. Now if I take difference this is difference up to this v dash and v double dash, v double dash ok. E dash and E double dash. This this is the difference and that difference is giving these spectral lines.

This will be the wave number this will be the wave number of this spectral lines ok. And these wave number will have the information of here you can see information of the anharmonicity constant as well as this frequency ok, fundamental frequency also you will have I will show you later on information of dissociation energy ok. Here this expression is giving the spectral lines. Now will analyze the spectral lines taking the difference of successive spectral line there it will give us the information of the vibrational energy levels.

(Refer Slide Time: 08:42)



If I want to tell you about the dissociation energy. This is the potential energy, this is the potential energy of the anharmonic oscillator and these are the vibrational energy levels. When it is one state, one electronic and vibrational state and this is another electronic and vibrational energy state ok. Therefore, dissociation energy when electrons transition

from one energy level to another energy level in the molecule happens. There this there this there a vibrational state or separation of the molecules atoms in the molecule may not remain same ok.

Before transition and after transition of electron their separation may not be same it can be different ok. In addition, their dissociation energy means; from that molecule to get to get the individual atoms ok, to dissociate it the required energy may not be same for this before transition of electrons and after transition of the electrons it may not be same. That is why we have written D_0 dissociation energy D_0 dash and D_0 double dash ok. This is for say ground state and this is for excited state ok.

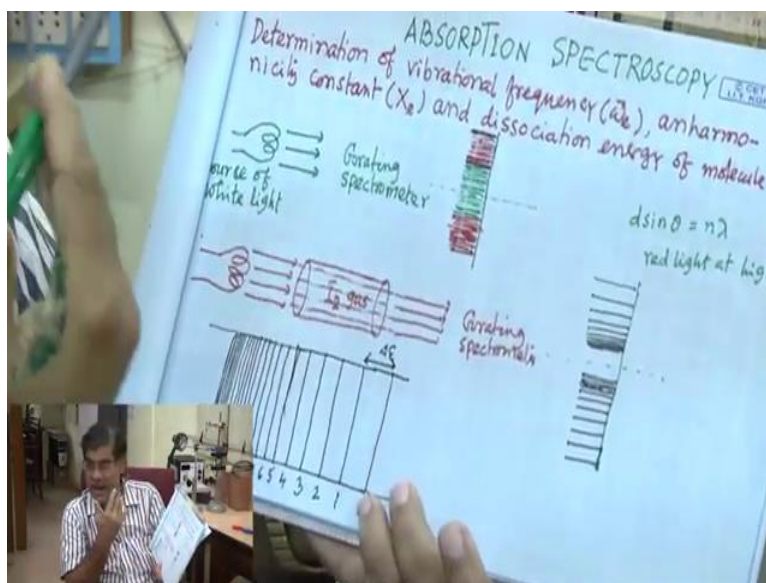
So dissociation energy for this state from lower energy to the lower vibrational energy level to the highest vibrational energy level where it is this line. Here this separation of the lines is almost 0. There is a continuous energy levels will be continuous at this position. That means; they are a vibration is so asymmetric, it will break and it will form atom it will not they no longer the molecule ok.

How much energy required dissociating it. This is the energy, so that is the called dissociative energy this energy can be different from a one this is called this is also dissociative energy, but it is in another state of the molecules ok. And these called the excited energy these called the excited energy. What is that excited energy? It is the energy it is the energy difference, energy difference between the atomic state of the molecular ground state and the atomic state of the molecule in the excited state ok. When in this state it will be atom, this molecule will be dissociative atom. Whatever the energy?

In this state, in an excited state ok, when this molecule will be dissociated and become atom. Energy difference between these two is called excited energy. This apart from the fundamental frequency, apart from the anharmonic anharmonicity constant one can find out the dissociation energy as well as one can find out the excited energy also ok. Whatever I have discussed about the molecular spectroscopy molecular spectra. For that, this reference one can follow fundamentals of molecular spectroscopy by C N Banwell and E M Mccash or I have one NPTEL video on atomic and molecular physics or physics of atomics and molecules.

From YouTube we can you can get it. There also I have I have discussed molecular spectroscopy. That also I have discussed from this book. Either you can follow a boor you can follow this video NPTEL video it is recorded by me. It is available in YouTube. That can be also helpful for you.

(Refer Slide Time: 14:26)



if I want to go to demonstrate the experiment what type of this this experiment what we are going to demonstrate that is it is called absorption spectra or absorption spectroscopy ok, absorption spectroscopy as well as another spectroscopy is their emission spectroscopy. Difference as I mentioned earlier and when I will do with this experiment, it will be clearer to you; absorption spectroscopy.

There we want to determine the vibrational frequency new this is ω_e , anharmonicity constant X_e and dissociation energy of the molecule D_0 ok. actually we will we will measure the dissociation energy of D_0 double dash will not be able to measure. If you want to measure the D_0 double dash. You have to do emission spectroscopy of the same molecule, but you have to study emission spectroscopy.

Why that probably will be clear through the discussion. In this set of what; what will be there? We will use grating spectrometer; we will use grating spectrometer, now if you use grating spectrometer and light source if you use the white light source of white light ok. All sources of light having all wavelength, all colours ok. That will fall on the will

fall on the grating. Now if you see through the telescope then, what you will see? You will see this type of, this type of pattern. It is a grating spectra this is the central position and left side you will see the different order of the different order of the of the diffraction pattern.

Here a white light all sorts of wavelengths are there although I have shown here this two to show this is the red light will have the highest deviation ok, then the green violet light. It is just opposite to the prism. In case of prism, the deviation is minimum for the red and maximum for violet, but in case of grating, it is just opposite ok. you will see this type of this is a first order, this is a first order; in first order, you will get as if this continuous you will get a you will get band white light all wave lengths are there. All lines are available ok.

For different colour, this is the first order of different colours ok. Now, now if I put if I put something here this is the light this is the light white light. Now here I have put iodine gas, now here I have put iodine gas ok. Now this light is passing through the iodine gas and thereafter, then it is falling on the grating and then we have we will see the spectra ok. If we see this spectra just if, we insert the iodine gas and then, now we will see the spectra like this ok. It is a here I have drawn the black line. Here actually all colours will be there, but some colours are missing. That I have drawn with this black line.

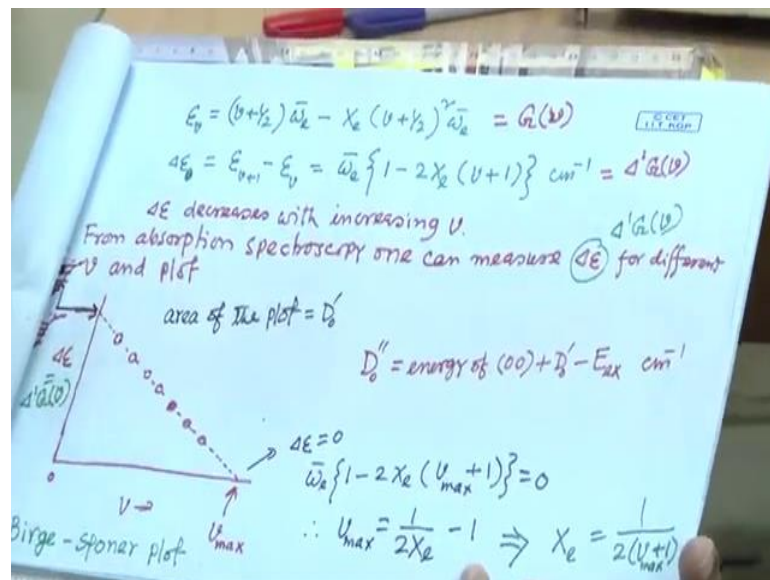
This some colours are missing, why these colours are missing. Here it is present, but here it is not present. That colour is absorbed by the iodine ok. This line will tell me the absorption of the iodine molecule ok. that absorption of the molecule those lines are absorbed which will be equal to the energy difference between the energy levels energy levels of the iodine molecules ok.

Actually here, this I can just show once more. Iodine atom, iodine not atom molecule will absorb will absorb those energy which will be equal to either this or this or this or this ok. That it can go from one level to the level absorbing this energy. Absorption spectra the missing of the light of particular wavelength that missing line is nothing but, the line. These missing lines are nothing, but the line. Whatever the emission spectra here we are getting that we will be, absorb in the absorption spectra.

That is happening, that will happen in our case whichever I will demonstrate. This kind of spectra black line you will see, black line you will see, other colours will be there, but particular line will be missing. That will be black line ok. In addition, these black lines as I told that you would not see the only line you will see band you will see band. It is not that one line for the corresponding to the vibration transition, vibration vibrational transition you will see, but corresponding rotational transition also will be there.

This lines you will see broad lines ok. You will see broad lines and those broad lines will have the information of the rotational energy levels with the vibrational energy level as well as the electronic that is there all the time that is there with each one ok.

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I think after grating what we will what we will do using the spectrometer? We will measure the wavelength; we will measure the wavelength of the black lines ok. Then that so what will be the energy of that energy of that vibrational for? As I told, the spectral lines have the spectral lines have the electronic part as well as vibrational part ok.

If you take, difference of two successive spectral line electronic part will go because this remains same and only you will see the difference of two vibrational energy levels. Difference of two vibration energy level. you will get this and that that we are writing that difference say here $\Delta G(v)$ I have written there are another may be requirement for this we use 2 symbol 2 instead of 1, but I think that I will not use here.

Anyway, so this is difference of two vibrational, these spectra whatever we got if you take difference of successive two. That will be this ok. Now if I plot this one as a function of v ; if I plot that this difference successive difference of energy vibrational energies as a function of v . we will get this type of points for different vibrational quantum number and if you if you fit them you will get a straight line and if you extrapolate the straight line towards these and towards other side. It will intersect the x-axis and y-axis.

Look at this equation. this Y equal to here X is X is v . here you can see that minus two X e ω_e \bar{v} is there means X . y equal to mx plus c ; if you think then your slope your slope will be your slope will be minus 2 ω_e \bar{v} X e here if you can find out slope, if you can find out slope; that slope will give you this this slope will be equal to slope will be equal to this. Now again for here you can see that energy separation energy separation, this is your plotting this is for different. You are going higher and higher value of v the energy separation of these two energy levels will decrease then it will be continuous.

This ΔG_v that will be 0 for higher energy higher vibrational levels ok. If we extrapolate this one. At this point this is 0, that ΔG_v is 0 ΔG_v is 0. For which value of vibration number it is 0. This is 0, this is 0 this equal to 0 if we put this equal to 0 that is for maximum v max. From here, you can find out v max, v max equal to 1 by $2 X e$ minus 1 ok. From here $X e$ equal to from here if you simplify $X e$ equal to 1 by $2 v$ max plus 1 ok.

This plot is very important and it is called the birge sponer plot. this from this plot if we extrapolate you will get v max, if you get v max you can calculate the anharmonicity constant anharmonicity constant if you can calculate the anharmonicity constant and their slope the slope whatever I am telling the slope will give you as I told this $2 \omega_e \bar{v} X e$ this slope. Now, $X e$ you will get from here this equal to slope and then you can find out ω_e . that is the fundamental frequency ω_e ok.

That also you can find out and dissociation energy, dissociation energy you can calculate from this graph itself. Now here what is this point? What is this point? This point is the energy difference, this point is this ΔG is a function of v . here you can see is the energy difference of this two successive vibrational energy level; v equal to 0 v equal to

1, 2,3. Your plotting initially may not be able to get this initial 1, 2, 3, 4 you are taking reading from somewhere say 5, 6 7 ok.

So, this is telling you this is telling you if I go this if I go here that $\Delta v G$ that $\Delta v G$ is nothing but, nothing but this $\Delta v G$ is nothing but this because v equal to 0 and v equal to 1, v equal to 1 and v equal to 2 this if I add them if I add them this plus this plus this plus this plus this plus up to continuum position, up to continuum position where this $\Delta v G$ $v = 0$ ok. then if you add them, you are getting you are getting energy of from v equal to 0 to v equal to maximum v_{max} ok.

You are getting this total energy from here to here and that is nothing but, the dissociation energy as I showed you. That is nothing but, the dissociation energy as I showed you that is nothing but the dissociation energy D_0 ; from this curve from this curve. If you add if you add all of them if you add all of them, this is nothing but the area of this triangle area of this triangle if you find out the area of this triangle area of this triangle. This is nothing but the dissociation level ok. So this as I told this curve is very important birge spencer plot, what we are plotting here?

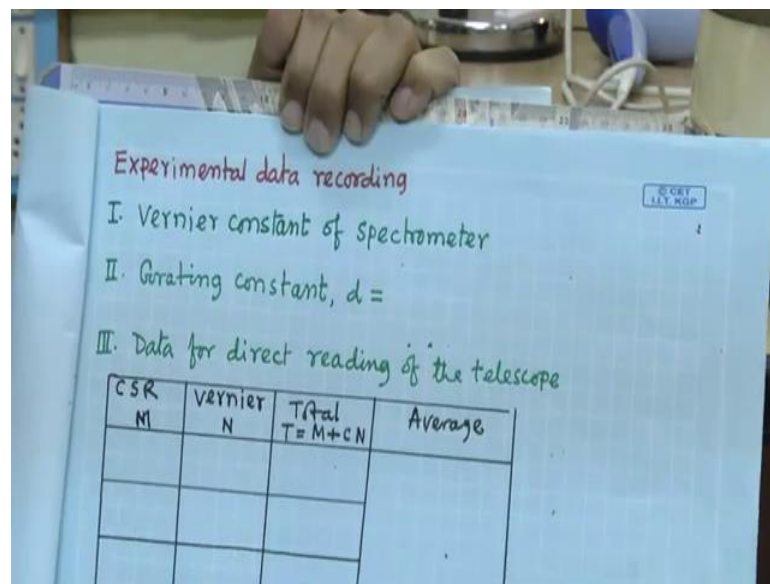
That is spectral lines whatever we are getting, whatever we are noting down the wavelength of a spectral line or energy of the spectral lines. Here we are plotting just taking successive difference of the two spectral lines and that is giving the energy separation of successive two energy levels. In addition, when I am going to the next point that is the energy separation of the higher to energy level vibration energy level higher then it is a continuous position ok.

here is continuum position from there v_{max} anharmonicity constant you can find out then from their slope we can find out this ω_e and then find out the area you can find out the dissociation energy ok. This fantastic experiment, but slightly difficult to understand, but I try to tell you in simple way.

Let me let me tell you what you have to do the do in experiment. As I told is the very simple experiment it is the just prism spectrometer we will use, light source will be there; that is white light source. Now this the white source and the spectrometer collimator ok.

In between, we will put the iodine molecule. Iodine molecule absorb some energy, some wavelength of the white light ok. That will be missing those spectra. That that spectra we will analyze using the prism spectrometer and we will measure the measure them. that is the diffraction phenomena $d \sin \theta = n \lambda$ we will measure the angle of different spectral line adjacent spectral lines and then from that data we will find out the difference of successive spectral lines that will plot as a function of wave number, vibrational quantum number and from that plot; we can find out different parameters ok.

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experiment data recording; Vernier constant of the spectrometers; you have to note down, then grating constant d , you have to note down. In our case 16, I think 600 per millimeter lines of these grating lines. That 600 for in 1 millimeter there are 600 grating element. Then what will be d ? 1 millimeter divided by 600 that will give, you would ok. Then data for direct reading in the telescope, in telescope you have to take direct reading because grating spectrometer already you have used. Direct reading I will take and then deviation of the different orders that we have to note down.

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IV. Calculation of $\Delta^1 G(\nu)$ for the first order band of the absorption spectra of Iodine molecules.

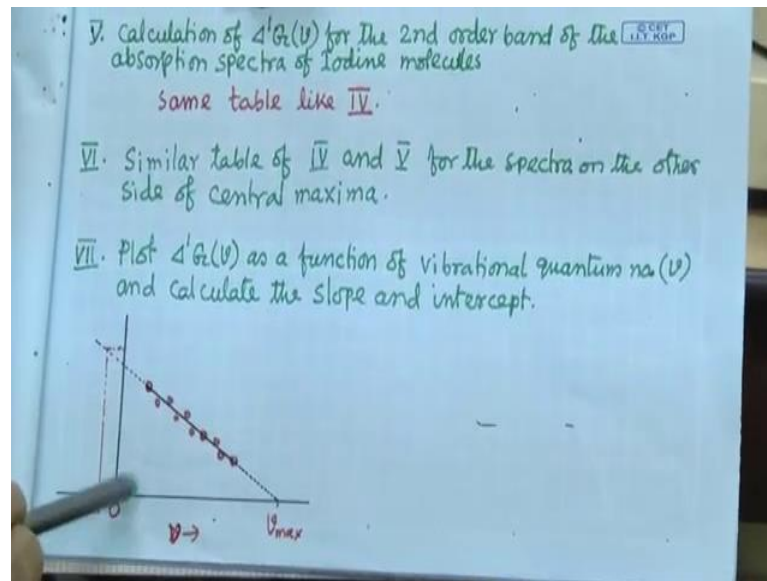
Spectral line number	CSR	VSR	Total reading	Angle of deviation	$\sin \theta$	$G(\nu) = \frac{1}{\lambda} = \frac{1}{d \sin \theta}$	$\Delta^1 G(\nu)$ cm^{-1}

direct reading we have to note down then, then we will see the spectra from that spectra will give calculate $\Delta^1 G(\nu)$, you can forget, but you can keep it also $\Delta^1 G(\nu)$ why you have written? For finding out slope again, you have to take difference of this $\Delta^1 G(\nu)$ ok. That generally you note down you note it as $\Delta^2 G(\nu)$ ok. That is why here $\Delta^1 G(\nu)$, difference $\Delta^1 G(\nu)$ we have written and second one is difference $\Delta^2 G(\nu)$ ok.

calculation of $\Delta^1 G(\nu)$ as a function of ν for the first order band of the absorption spectra of iodine molecule ok. We will see spectra and we have to measure the as usual the way one can measure the atomic spectra. Same way you have to take reading circular scale reading, Vernier scale reading, total then angle of deviation just find out angle of deviation then that $\sin \theta$ it is θ . $\sin \theta$ from there you can find out G as a function of ν $\frac{1}{\lambda} = \frac{1}{d \sin \theta}$.

From there you will get reading; taking the difference of successive to it will give you $\Delta^1 G(\nu)$ in centimeter inverse ok. Now, you can continue the same thing for second order ok.

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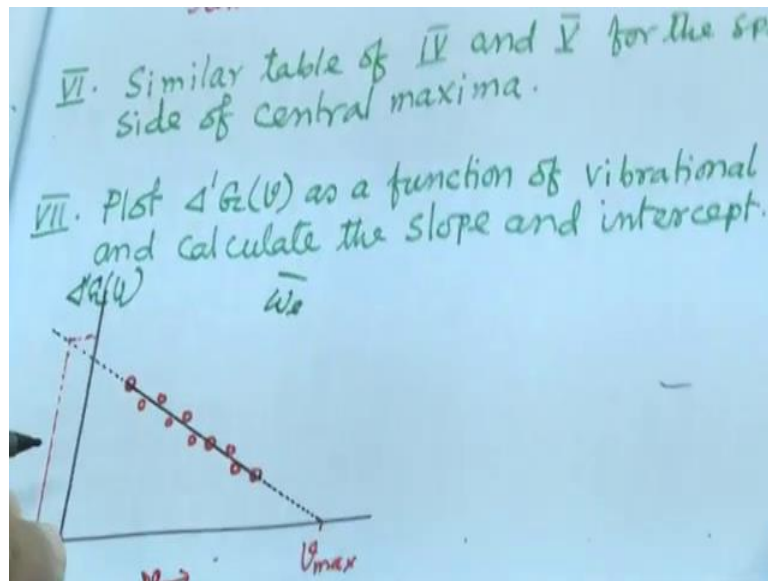


Calculation of this for the second order band of the absorption spectra of iodine molecule ok; same table like four you should do it and do the measurement. Similarly, this if it is from left side you are taking from for side other side; also, there are first order and second order. Similar table of 4 and 5 for the spectra on the other side of the central maxima ok.

You will get 4 sets of data; 2 from the left side for first order and then second order and 2 from the for the side ok. First order and second order. This type of 4 graph you may you will get and from each graph, you will find out this parameter and then take average of them ok. That that is what this plot; this as a function of vibrational quantum number v and calculate the slope and the intercept calculate the slope and intercept ok; here the why I have extended this side.

in this formula in this formula; if you see if you if you see if you v equal to minus 1, if you put v equal to minus 1, I think here you see if you put v equal to minus 1 then this part is 0 ok. Then then whatever you are getting. This del whatever you will get del G that will be equal to the $w e$ ok. From their directly itself we can find out ωe , not del e , ωe ok. From slope, you can find out as well as from taking the value of del g at v equal to 0 del g at v equal to 0, sorry v equal to minus 1.

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You have to extrapolate and what is the value of $\Delta'G_e$. This is the $\Delta'G_e$ I think I should write it this is the $\Delta'G_e$ ok. Whatever the value at v equal to minus 1. That is will be equal to the ω_e that will be equal to the ω_e ok. That way also you can find out ω_e . Yes and I think you can calculate. There are table for calculation of anharmonicity constant dissociation energy.

(Refer Slide Time: 41:03)

VIII. Calculation of anharmonicity constant and dissociation energy. ($1 \text{ eV} = 8065 \text{ cm}^{-1}$)

Graph no.	Value of ω_e	Anhar. const. $X_e = \frac{1}{2} \frac{\omega_e^2}{\omega_e^2}$	Average X_e	Base of the triangle	Height of the triangle	Area of the triangle cm^{-1}	Average dissociation energy in $\text{cm}^{-1} = \text{Area of triangle}$	Dissociation energy in eV

Graph from I told this there will be 4 graph 2, 3, 4 graph ok. Then from each graph v_{max} , you can find out v_{max} vibrational this maximum where intersecting the v ok. From

and if you know this one, this anharmonicity constant equal to $\frac{1}{2} (1 + \nu_m)$. you can find out the anharmonicity constant then average anharmonicity constant you find out then base of the triangle; this as I told this find out the area that will be the dissociation energy. Base of the triangle you note down the base of the triangle in ν number height of the triangle ΔG ok.

Then this half of this into this will give the area of this triangle. for each cases, you find out and then take average of that in centimeter inverse, you will get average dissociation energy in centimeter inverse will be equal to the area of the triangle. Now, you can convert it the dissociation energy in electron volt, where a relation I have given one electron volt equal to 8065 centimeter inverse ok. I think I will stop here and next I will show you demonstrate the experiment.

Thank you.