Atomic and Molecular Physics
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Lecture - 54
Electronic structure of molecules (Contd.)

So, we saw that the intensity of the vibrational core structure varies ok. The spectral lines that form the core structure of Electronic spectra. There is basically course vibrational structure and why the intensity varies that that we have seen from concord on principle.

Now, so, we have this; now vibrational spectra ok. Electronic spectra, but that core structure of these electronic spectra is basically vibrational core structure. And now what is the use of these of this core structure? What information we can get from this vibrational core structure? So, that I want to discuss.

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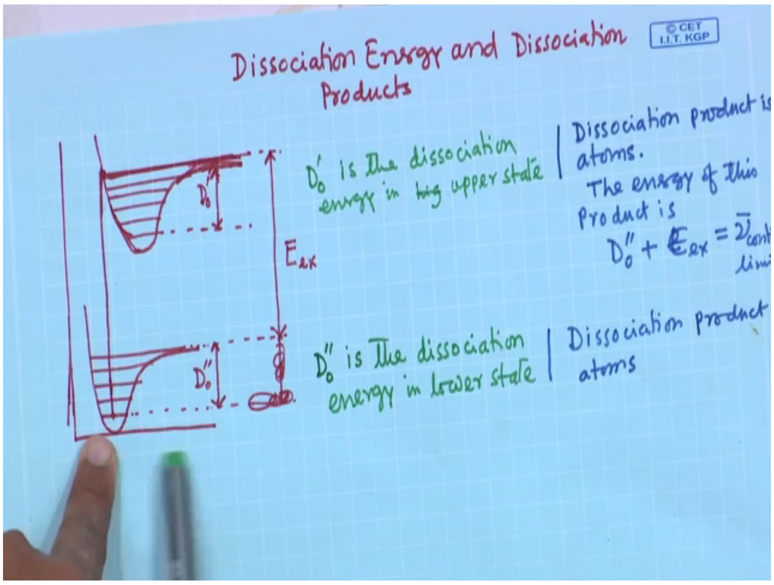

Dissociation Energy and Dissociation Products

D_0' is The dissociation energy in hig upper state | Dissociation product is atoms.
The energy of this Product is
$D_0'' + E_{ex} = \bar{\nu}_{cont}$ lim

D_0'' is The dissociation energy in lower state | Dissociation product atoms

So, we have seen that this here is you can see, basically Dissociation Energy and Dissociation Product. So, as you know that these molecules are vibrating. So, they have different vibrational energy levels, right.

Now, here and this vibration is basically asymmetric; which follows this nodes potential curve and here we see this separation when it is going higher states and if separation this inter nuclear distance are increasing ok. And ultimately at this level, it will this atoms will be dissociated this molecules will be dissociation and this it will basically this it will not be no longer molecules. So, this molecule will break and we will get this product is called Dissociation Product that basically the individual atom will get.

So, molecule diatomic molecule two atoms was there. Now, at higher vibrational state if it is higher vibrational level. So, at a particular value of vibrational quantum number higher value of vibrational quantum number; so, these molecules will shift and this will get the dissociation product that is nothing but the in form of atoms ok.

So, how much energy required to dissociate the molecules to breaks the molecules that is the basically Dissociation Energy. Dissociation energy and what will be the energy of the of the product Dissociation Product ok.

So, these here; so, here again this is the one electronic state and this is the another electronic state ok. And in each electronic state there are vibrational levels ok. So, when these molecules in this electronic state and it has depend vibrational level. So, in this level, in these electronic states itself if this molecules dissociate, then the amount of energy it is a D0 double dash is required to is required to dissociate to breaks the molecule. So, this energy is called the Dissociation Energy for this say ground state ok.

Now, when it is excited state, excited electronic state. And in excited electronic state there are vibrational states. Now, I will now, molecule is in a electronic excited state ok. Now, now, in this electronic excited state if molecules dissociate if molecule breaks ok. So, what is the dissociation energy for this yes for this exciting electronic state? So, this basically here D0 dash ok. So, this much energy required to breaks the molecules, when molecules is in the electronic excited state ok.

Now, molecule is in this ground state ground electronic state ok. Now, it is excited this molecule is excited in the higher electronic state and then and then it breaks also dissociate ok. So, that means, say that in this electronic state these molecules was in this vibrational level lowest energy vibrational level ok.

Now, in this condition if we dissociate; so, now, ultimately it is it will go to electronic state and then highest vibrational state where it will be x ok. So, then one need basically this much energy to dissociate the molecules ok.

So, here this D0 dash and D0 double dash, these are the dissociation energy. And this energy is only when it is already in that electronic state; either in this ground state or in this excited state.

Now, after that if you want to dissociate either in this state or in this state. So, these are the dissociate energy. But another case this electronic transition as well as this vibrational transition both together. So, from this state to it is coming here ok. So, that means, it is it will dissociate in the excited state, in the excited electronic state; coming from the, coming from the ground state ground electronic state as well as ground vibrational state. So, then this will be the total energy required to required to dissociate the molecules.

So, what will be the energy what will be the energy of the dissociation product? of the of the that dissociation products that that basically atoms. So, here basically here here in this case if D0 dash or double dash is the dissociation product is basically in both cases it is atoms, but the energy in this case as I mentioned that from this electronic energy state to the next higher electronic state as well as the vibrational change.

So, in that case the total energy basically it is the energy difference between the product energy difference between the dissociation product. So, that means, the energy dependence will be this one ok. So, if in this case if it is dissociate. So, the energy of the product will be D0 double dash and another case it is dissociate in this way ok. So, energy will be this ok so that it that is the energy of the of the dissociation product. So, what will be the energy difference between these two? So, that is basically one can write here. So, from here; so, this is called the Excited energy e x I have written. So, from here one can write that D0 double dash plus E excited. So, basically that is this. So, D0 double dash plus E excited.

So, that will be the energy of these spectral lines or wave number of the spectral lines ok. And there is there is the; it is called continuum limit because here from this transition you can see there is the basically at the continuous this continuum level of the of the spectral lines.

So, this one can tell this nu bar continuum limit equal to basically nothing but the dissociation energy D0 double dash plus this E excited ok. So, studying this; basically, this from the spectroscopy measurement one can measure this wave number of the spectral lines and determine the dissociation energy so that I will discuss. So, how spectroscopy is used to determine the dissociation energy of the molecules as well as the other parameters like anharmonicity constant as well as this say omega e bar; so, this natural frequency of the oscillator so that we will see.

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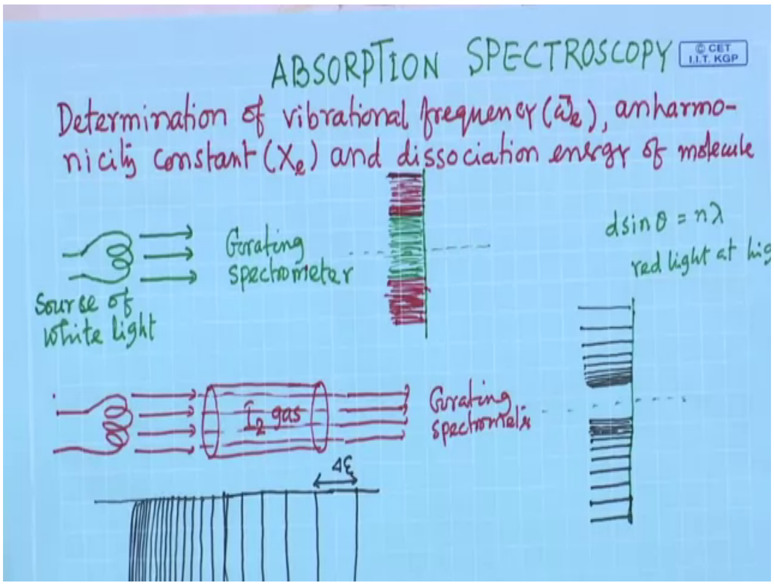

So, that is basically that people use the Absorption Spectroscopy; Absorption Spectroscopy ok. So, what is the absorption spectroscopy? So, spectrometer you know this spectrometer. So, it has collimator it has this table prism table or grating table and then we have the telescope ok. So, collimator is so, basically here generally people use the grating, because grating has higher resolution power ok. So, spectrometer basically contain the three component one is collimator, another is table, where we put the prism or the or the grating and you have option to rotate and measure the angle as well as we next component is the telescope.

So, basically this collimator in collimator there is a pre there is a lens convex lens. And this makes this basically this lens is used to make the parallel rays to full fill the condition of Fraunhofer Diffraction ok.

So, from source at a finite distance lighter coming; now, they are they are basically convert these lines are diverging line light diverging lines the rays. Now, if it falls on the on the lens means it is passing through the collimator following on the lens. Now, one can change the distance of the lens so that the source can be at the focal point of this of this lens. So, source is at the focal point of a lens, then other side you will get the parallel rays. As if the source is at infinite distance. So, source is that infinite distance then the rays comes then that we tell that it is a parallel rays.

So, in laboratory; so, this is the way we get the parallel rays as if light are coming from the infinity ok. Similarly collimators this side another side the telescope in telescope also there is a lens. So, that also in Fraunhofer Diffraction image also form at the infinity, but again using the using the lens. So, the slaves again we change the position in such a way that the screen here basically eyepiece, screen at the screen will be at the focal point of the lens ok.

So, we will we will basically the image will form on this on this eyepiece or screen which is which should be at the basically infinite distance because parallel rays will from the image. So, it is only possible parallel rays will meet and from the image at the infinity, but using the lens that in laboratory that we full fill the Fraunhofer condition and get the things at a finite distance ok. So, this is I think this is the spectroscope they have spectrometer that is the general configuration of any spectrometer.

Now, the spectrometer is used for this for the determination of the vibrational frequency anharmonicity constant as well as dissociation energy of molecules; so, these spectroscopy here different kind of spectroscopies there. So, here whatever I am discussing; now that is called absorption spectroscopy ok.

So, what is that? So, think that there is a source of light source of white light means all sorts of wavelengths are available in this light. So, now, if this light you if it if you put in the grating spectrometer if you use grating spectrometer. So, what will you will get you will see the diffraction; you know diffraction d sin theta equal to n lambda ok. So, wavelength is higher. So, it will be deviated; it will be deviated more from the direct light. So, it will be deviated more. So, this at higher angle you will get the red light and lower angle you will get the other (Refer Time: 17:22) light say ok.

So, since; so, you will get basically the here you will get the spectra of spectra of different colour and it is you will not get basically lines because all wavelengths are available. So, only you will get the distribution of colour means whole space will be illuminated, but only colours are separated ok. So, this type of things you will get ok.

So, now if I put say some gas in a cylinder cylindrical tube if we put gas and then this white light is coming now I if this light is passing through this gas say here I have taken iodine gas. Now, then through the gas this light is coming out. Now, again this light is analyzed using the grating spectrometer. Now, what we will see. So, without gas this type of distribution of the colour was observed. Now, if you put gas. So, you will get basically this type of distribution of the black lines ok.

So, that means, you are you will see the black lines in this in this in this bright distribution of the colours. So, there basically we will see the many black lines and black lines are arranged like this ok. So, this side one side this is the order ok. So, this is the basically n equal to so 0. Now, this side n equal to one this other side n equal to minus 1, etcetera, etcetera, ok.

So, basically here basically the black lines you are getting. So, that we are telling this particular these wavelengths are absorbed by this iodine gas. So, that is why this is called basically absorption spectroscopy ok. So, ah. So, absorption spectroscopy basically the we are we will see the lines black lines that corresponds to the absorption of that wavelength and in this absorption spectroscopy in case of iodine gas. So, this type of spectra absorption spectra is absorbed. This type of absorption spectra is absorbed. So, here you can see this ah. So, these are the lines. So, these lines are V equal to 0, V equal to 1, V equal to 3, 2, 3, 4, 5, etcetera.

Now, it is one can understand easily because this absorption spectral lines is basically correspond to the vibrational; it tells about the vibrational energy levels in this iodine molecule.

So, this type of spectra you will get. Now, measuring this wavelength measuring this wave number for different vibrational quantum number so that is possible in this using the spectrometer so that is the spectrometer one can find out the wave length of the spectral lines or wave number of the spectral lines ok. So, this type of spectral lines will be observed and this is nothing but the vibrational core structure ok; vibrational core structure. And now measuring the wavelength or wave number of the spectral lines one can determine this parameters whatever here I have shown that vibrational frequency, then anharmonicity constant and dissociation energy of the molecules ok.

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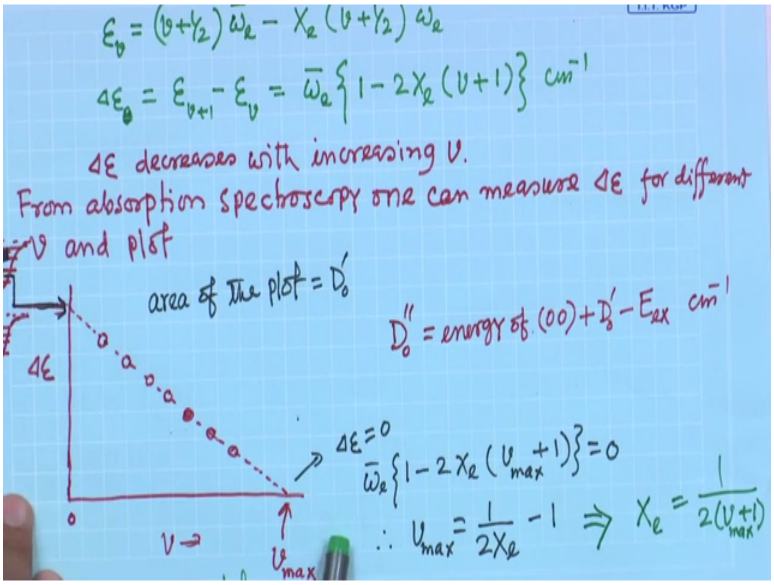

$$\varepsilon_v = (v+\tfrac{1}{2})\bar{\omega}_e - x_e(v+\tfrac{1}{2})\omega_e$$

$$\Delta\varepsilon_v = \varepsilon_{v+1} - \varepsilon_v = \bar{\omega}_e\{1-2x_e(v+1)\}\ \text{cm}^{-1}$$

$\Delta\varepsilon$ decreases with increasing v.

From absorption spectroscopy one can measure $\Delta\varepsilon$ for different v and plot

area of the plot $= D_0'$

$$D_0'' = \text{energy of } (00) + D_0' - E_{ex}\ \text{cm}^{-1}$$

$\Delta\varepsilon = 0$

$$\bar{\omega}_e\{1-2x_e(v_{max}+1)\} = 0$$

$$\therefore v_{max} = \frac{1}{2x_e} - 1 \Rightarrow x_e = \frac{1}{2(v_{max}+1)}$$

So, how it is done that I will I will discuss so, that also very interesting. So, there is a there is a if. So, that spectral lines we are getting that is basically it is the; yeah. So, this is the that is the energy of the spectral lines in centimeter inverse of course, right.

So, now what is the separation? What is the separation between the two spectral lines. So, if that is del E. So, this separation is the spectral lines is basically progression type. So, E V plus one minus E V ok; so, if you do that so, you will get this; so, separation of the successive spectral lines. So, that that separation that wave number is del E and that is this ok. So, from here one can see that separation will decrease because this is minus is there one minus these will decrease for increasing quantum vibrational quantum number. So, vibrational quantum number V will increase separation of the spectral lines will decrease. So, del E decrease with increasing v. Now, from vibration optional spectra that is what we have seen. Now, one can one can measure del E for different [vocalized-noise], right.

So, this spectral lines are there. So, one can measure the separation between two successive spectral lines and that is basically for different value of V. Now, if you plot this separation if you plot this del E versus this V. So, you will get you will see that with higher V. So, it will this separation is decreasing separation is decreasing ok.

Now, here I have I have connected them it is with straight line it is actually it is not exactly straight line, but here formula whatever we have taken it say here it is telling state line, but if you consider the higher terms that we have neglected. So, it is not exact straight line, but one can approximately consider it a straight line. So, I have connected them with dotted line and extrapolated in both side because, because it is very difficult to identify the spectral lines whether it is which one is V equal to one and what is the and at the continuum limit what is the value of V. So, that is difficult to difficult to identify. But using this plot if we extrapolate. So, one can find out the V max this continuum limit.

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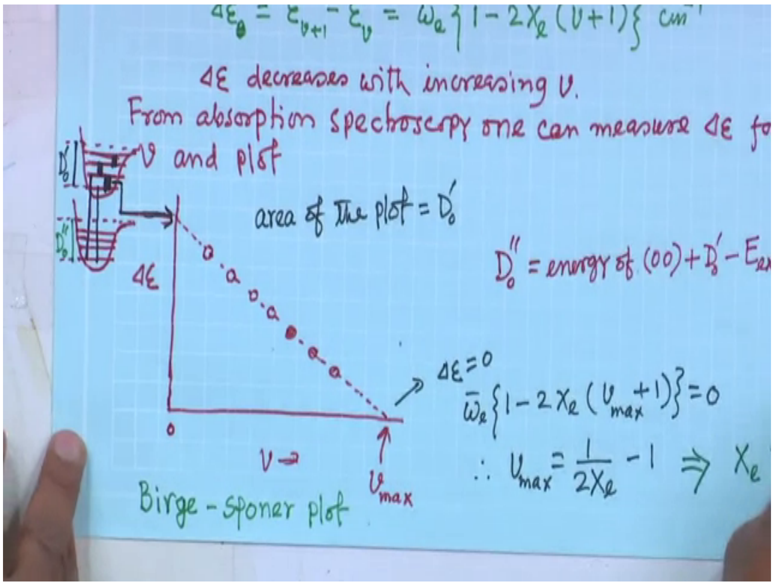

$\Delta\varepsilon_0 = \varepsilon_{v+1} - \varepsilon_v = \omega_e\{1 - 2x_e(v+1)\}$ cm^{-1}

$\Delta\varepsilon$ decreases with increasing v.

From absorption spectroscopy one can measure $\Delta\varepsilon$ fo

v and plot

area of the plot = D_0'

$D_0'' =$ energy of $(00) + D_0' - E_{ex}$

$\Delta\varepsilon = 0$

$\bar{\omega}_e\{1 - 2x_e(v_{max}+1)\} = 0$

$\therefore v_{max} = \frac{1}{2x_e} - 1 \Rightarrow x_e$

Birge - Sponer plot

So, how one can find out; so, here del E at this point del E equal to 0. So, del E equal to 0 means this parts this is equal to 0 ok. So, then you will get basically V max equal to 1 by 1 X e minus 1 ok.

So, from here basically one can get experimentally one can get the value of V max. Now, putting the using these V max using this V max here one can find out the anharmonicity constant of the molecule ok. So, this is very interesting. So, this way one can determine the anharmonicity constant. Similarly one can find out the dissociation energy dissociation energy. So, D0 dash or D0 double dash one can find out.

So, D0 dash; so, here I have written that area of the plot will be equal to D0 dash how? So, what we have plotted here, we have plotted here basically the separation of the separation of the spectral lines. So, so separation of the spectral lines is nothing but the separation of the vibration energy levels ok because we are considering just successive spectral lines. So, basically here whatever we have plotted. So, that is the differ energy difference between the two levels successive two levels. So, here we have plotted here basically this one is this? So, the next one is this. So, next one is this. So, their separation is decreasing. So, that is why it is decreasing goes to 0 ok.

Now, if I take the area means I am adding all the all the separation, I am adding all the separation basically right. I am adding all the separation. So, so add means is I am adding this one with the next one then next one. So, I am basically here after adding I am getting the energy from difference from here to here continue here continue. So, this is nothing but the D0 dash ok. So, that is why here I have written the area of the plot.

So, you plot it extrapolate it and then find out the area of this plot and then that is nothing but the D0 dash. A D0 double dash as I have shown there. So, that is basically energy of the 0 0 state energy of the 0 0 state; 0 0 state this one energy of these plus D0 dash D0 dash ok. So, from here to here and then D0 dash ok. So, plus D0 double dash that will be basically the E excited. No, I think this plus D0 dash. So, that is the that will be equal to the D0 double dash plus E excited. So, that is what I was showing you yeah I think this is the D0 double dash plus E excited that is equal to V continuum. So, V continuum comes from the basically that is these two this plus these D0 dash ok.

So, that is means this total is basically this 0 0 energy between that energy of this 0 0 spectral lines plus this D0 dash. So, that is that total that energy. So, that that will be equal to the D0 double dash plus this E excited. So, that is why I have written here. So, how to get D0 double dash. So, this is the energy of 0 0 plus D0 dash plus minus e x centimeter inverse.

Now, D0 dash I know energy of the 0 0 also you will know you know ok. So, because basically separation here and measuring means you know the wave number of each spectral lines. So, 0 0 lines you will you will get yes and only it is E excited that is not unknown that is unknown and this E excited with this nothing but it is related with the energy of the product you know because that separation is the here you can see this energy between. So, these this is basically this energy of the dissociation product in this state and this will be this D0 double dash plus this ok.

So, that will be the energy I think here that is what we have written. So, dissociation product in this case is ah. So, this here whatever the product I will get. So, here dissociation product atoms here dissociation product atoms. So, now, energy difference of these energy difference of the of the of the dissociation product in this case and this other case they are basically atoms and their energy difference will be this E excited one. So, basically this E excited one can one has to find out from the atomics spectroscopy that one has to know. So, that is I think from atomic spectroscopy this is the ex there is people generally find out this E excited.

So, now that E excited one has to use and then one can get this D0 double dash ok. So, absorbed spectroscopy is frequently used in the laboratory. In fact, in our laboratory we use also this for this experiment higher student generally plot this del E versus V and that is called basically Birge Sponer Plot Birge Sponer Plot this is very famous plot. And from this plot one can find out this anharmonicity constant one can find out; obviously, omega e one can find out because you are measuring you are measuring the wave the spectral lines wave number of the spectral line. So, one can find out this one also this what is called this; this frequency fundamental frequency one can find out as well as the dissociation energy one can find out ok. So, I think I will stop here.

Thank you.