Atomic and Molecular Physics
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Lecture – 45
Rotation of a molecule (Contd.)

So, we have in last class we have discussed the model rigid rotator. And we have seen the this rotational spectra of linear diatomic molecule and that we have seen the spectral lines are equispaced ok. And this difference between 2 spectral lines is basically 2 B ok.

So now we will consider the non-rigid rotator ok. If this rotator is not rigid means the bond length will change during the rotation, then what will happens that we want to see that is basically non-rigid rotator ok. So, so, for diatomic molecule it is basically linear molecule and considering the non-rigid model.

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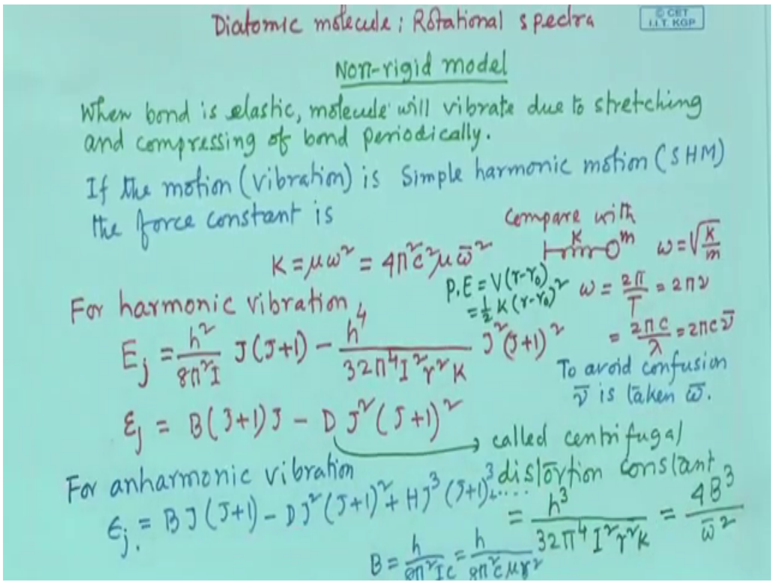

So, you want to we want to see this some correction will come. So, mean so what about rigid model the way we have solved the equation said this result now. If this some additional effect that will come from the that will come from the vibration of the molecule means, that will come from the stretching and compressing of the of the of the bond length ok.

So, some minor effect will come, but although it is minor effect, but I should not tell minor effect, but what will what effect will come that we want to see. So, so this non-rigid model as already I have discussed, when bond is elastic molecule will vibrate due to stretching and compressing of bond compressing of bond periodically so, this vibration will be basically periodically ok.

So, if the motion is simple harmonic. So now, it is it is basically changing the changing the bond length due to stretching and compressing periodically. So now, this vibration if it is again we are assuming if it is simple harmonic kind of motion, then this force constant K. So, this just compare with spring mass system one must be spring it is fixed at one end one end of the spring is fixed and other end is attached mass is attached with the other end.

Now, just if you if you just slightly stretch it this mass just pull it and leave it, so, it will oscillate so this the basically simple harmonic kind of motion it will oscillate and then it will oscillate with some frequency. So, that is natural frequency nearly it is omega equal to square root of K by m. So, K is spring constant force constant and m is mass so; that means, omega equal to yeah 2 pi by T and that is equal to 2 pi by nu 2 pi nu and nu equal to c by lambda. So, omega is basically 2 pi c nu bar ok.

So, here here I have written here this K K equal to then we can write K equal to omega square ok. So, in our system this mu omega square reduced mass mu omega square ok. So now, omega is replaced by this 2-pi c nu bar. So, then 4 pi square c square mu these are nu bar square, but I have written here omega bar square this wave number just to avoid confusion because nu bar we have already taken for the for expressing the energy of the spectral lines in terms of wave number.

So, that is to avoid confusion this I have written nu bar so. So now, you see this now when we are consi what is the difference that rigid model. So, there was no potential energy. Now for non-rigid model when this when this bond length it was it was r 0, but it is changing ok. So, changing bond length now it is a if it is just it is variable if we if we take it r. So, with respect to r 0 it is stretching and compressing. So, so from equilibrium length that is r 0. So, from r 0 it is basically it is change is r minus r 0. So, it is stretching and compressing. So, simple harmonic motion so for simple harmonic motion. So, what is the potential energy potential energy half K x square x here basically r minus r 0 square.

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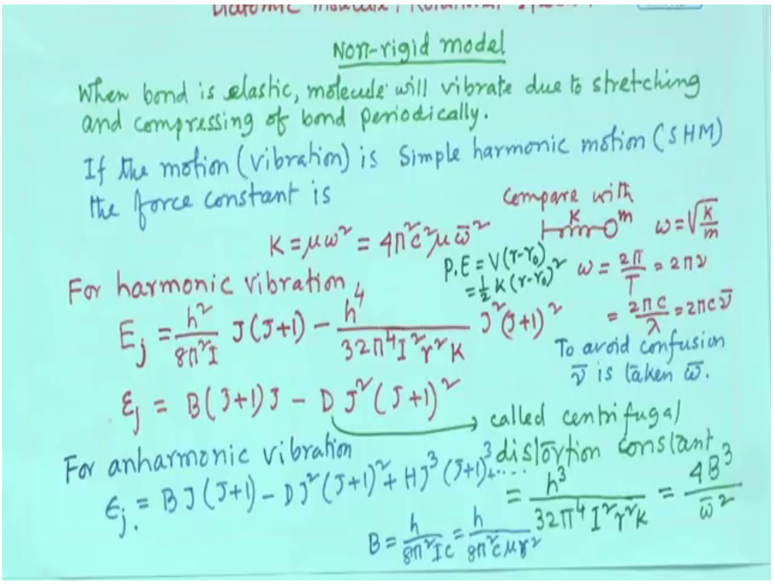

So now, in case of non-rigid model there will be potential energy for rigid model potential energy was 0. Now in this equation one has to include the include this potential term along with this kinetic energy. As we have consider kinetic energy for rigid model. So now, additional term one has to include, and then one has to calculate then basically for harmonic vibration as we have considered the motion is simple harmonic motion kind of things. So, for harmonic vibration so E j so this original term is there. So now, additional correction term will come.

So, it is like this it is like this. So, in this term you see the here your K term this K term is there. So, here just I have 2 2 2 2 2 I think yeah K is the force constant and how K depends on what? So that I have shown here. So, these term basically correction term due to this simple harmonic kind of motion; means stretching and compressing of the bond periodically. So, and that will that system will have some kinetic potential energy also and due to this this kind of situation.

So, your energy term it is corrected now this additional hired term additional term has come. So, there so this now epsilon this epsilon j or the energy noid number. So, this this is basically B J J plus 1 J J J plus 1 J, I have written later on anyway. So, minus so this correction term basically So, D J square J plus 1 square ok.

So, what what is D? D is basically from here so I have one can write this. So, in terms of one can show this ok. One can show these here whatever I have given data so if D is equal to this if this is the term correction term. So, D is is this so in terms of D and omega bar ok. So, 4 B cube by omega bar square, this D is called the centrifugal distortion constant.

Now, centrifugal distortion constant why it is called, because you know this when it is it is it is rotating right? It is rotating and during rotation now something is tracing ok. So, as if it is feeling some force to go outside. If it is rigid they are there is no scope to go out ok. Although it feels force centrifugal force, but they are there is no scope to go out. So, if scope so, if this bonding is weak. So, there will be stretching of this so, it will move towards centrifugal force. So, this correction term is basically it is due to the centrifugal force. And that is why there will be some distortion of this of this of this bond length ok. Although it is small, but it will be there. And so, that is why this constant D in correction term it is called distortion constant centrifugal distortion constant ok.

So, if it is un harmonic if it is unharmonic, harmonic and un harmonic. Harmonic means whatever the amount of stretching and the same amount of compressing ok. So, then it is harmonic motion, if it is not same stretching is not same as compressing ok. That spring mass system it is the compressed and this is the stretching, if this is not symmetric this stretching and compressing it is not symmetric, stretching is a more and compressing is less ok, when it is vibrating then it is called unharmonic motion unharmonic vibration. So, if it is unharmonic vibration and that I will tell when I will consider the vibration of the molecule later on I will tell why it will be unharmonic. So, harmonic it is not harmonic it is unharmonic. So, why it is unharmonic? So, that I will I will explain in other class.

So, if in case of if vibration is unharmonic so then basically E j equal to B J J plus 1. So, original term then D J square J plus 1 square so, this the higher term basic correction term, then other higher term J H J cube J plus 1 cube plus K J to the power 4 J plus 1 to the 4. So, there are higher terms will be there ok. So, so this so let us consider this the un harmonic motion. So, let us consider here concentrated on this only harmonic vibration. So, for harmonic vibration these will be the energy of the level rotational level. Now we can see this this whatever the energy for rigid rotator model whatever the energy level was there.

Now this energy levels will D value is very, very small compared to B value ok. So, this correction term it is it will be very small value for smaller J value, but if but for higher J value because it depends on J square J plus 1 so these value this term will be higher. So, so this is the original energy level. Now minus so, it will come down this energy level will come down so for lower J value it is very small for higher J value it will be higher value. So, there will be change in energy level. So, energy level will basically decrease from it is original level. So, so that is that is because of the harmonic vibration of the rotating molecule.

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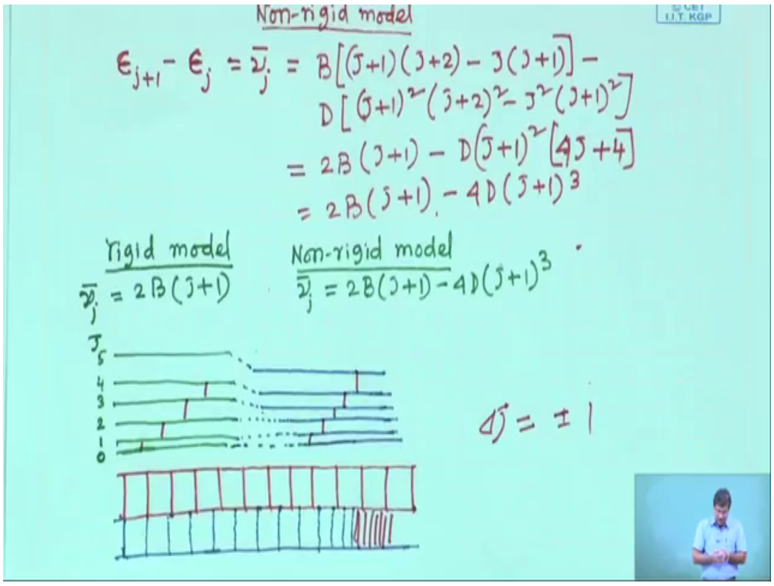

So, in case of non-rigid rotator if I take again nu J bars, this energy of the spectral lines in terms of wave number. So, one can show it will come 2 B J J plus 1 minus 4 D J plus 1 to the power cube ok. So, there you can see this was there now additional this is coming. So, so this see this, what about the energy of the spectral lines for rigid rotator. So now, it will decrease by this amount so, this will be higher for higher J value that is obvious because J plus 1 to the power cube ok. So, here just I have I have plotted to compare.

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So, this the from rigid model. So, these are the red these are the spectral lines equispaced spectral lines. And the energy level now energy level this is following this expression. So, energy level more or less same for J equal to 0 J equal to one, but above these 2 this just started to decrease higher and higher and higher ok. So, this is because of this now here important is that, now here this spectral lines was symmetric.

Now it is not symmetric it will not be symmetric, now you can see following these transition rule are same del J this del J equal to equal to plus minus 1 equal to plus minus 1. So, the same way I will get transition here here whatever transition in this case also we will get the same way transition.

Now, you can see when you are going higher and higher spectral lines then you will see this their spacing between the spectral lines will decrease will decrease which higher and higher ok. So, it become later on whatever. So, so seeing the spectral lines immediately one can tell that one can tell that whether this this molecule rotation of the molecule it is like rigid rotator molecules or it is like non-rigid non-rigid type of molecules ok. So, in reality, all molecules show this follows the rigid or non-rigid model mean when it is rotating it also change it is bond length ok. So, we get this spacing of the spacing of the spectral lines which is decreased with where with higher K value ok.

So, I think that is just I want to tell you that so these, the all for linear molecules, diatomic molecules not So, it is for basically whatever rigid model I discussed or non-rigid model discussed that is for the diatomic molecule and of course, it is linear molecule. Now polyatomic molecule also there ah, but having the polyatomic molecule, but it is linear molecule; as I gave example that carbon oxy fluoride not fluoride sulphide so that is the linear molecule, but it is polyatomic. So, this theory whatever we discussed it is valid for this any linear molecule ok. It can be diatomic molecule it can be polyatomic molecule, but this is valid for diatomic molecule only.

So, but only difference you will see this in case of polyatomic molecules this moment of inertia that value will be higher you know and then B value will be smaller, B value will be smaller because B equal to h by 8 pi square, this I is there right in denominator I is there. So, for polyatomic molecule moment of inertia will be higher because number of mass will be more so I will be higher and B will be smaller. So, spacing of the that spacing was 2 B, right? In case of rigid rotator non-rigid there is a correction term, but main is 2 B ok.

Now, B is very small will be very small. So, so for polyatomic molecule this spacing between the spectral lines will be will be very, very small so that is the difference on will see ah, but otherwise this it is it is valid for polyatomic molecule, but it has to be linear molecule ok.

And for other molecule that I will not so other molecule is slightly complicated because it will have this symmetric top molecules or this asymmetric top molecule's spherical symmetric spherical top molecules ok. They are not linear molecule and they will have more than one moment of inertia and then one has to. So, for each moment of inertia means you will get this.

So, we have seen that one rotational quantum number. So, if we have 2 moment of inertia 2 axis I x and I y both are there so you need you need 2 quantum number. So, that also one can solve it, but will not do that only you will get this to to describe this your system there only the 2 quantum number.

So, basically, I will not discuss this non-linear molecules polyatomic molecules. Now let me just finish telling you this application of the whatever we studied this rotational spectroscopy that is basically microwave spectroscopy microwave

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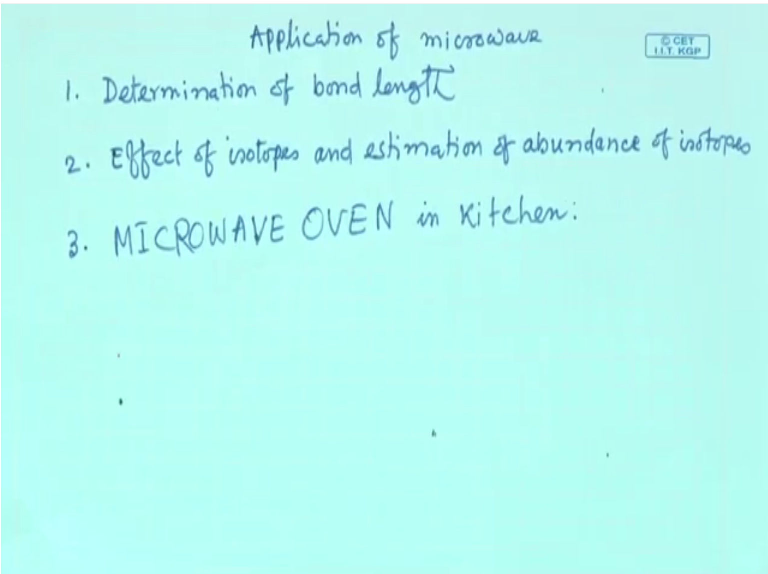

So, due to rotation of the molecules due to rotation of the molecules so, you will get the microwave or or that or the rotational due to the rotation of a molecule due to the rotation of a molecule we will get the will get the will gave will get the energy energy states and they are in they that they are difference in the range of micro wave ok.

So, application of this microwave spectroscopy is basically, one I have already discussed that is determination of bond length determination of bond length. So, studying these microwave spectroscopy of different molecules we can find out the bond length. So, this is very nice experiment and easy to find out the bond length of any molecules ok. So, second second application is one can see the effect of of isotopes.

You know effect of isotopes and estimate the abundance of isotope in the in the molecular system so; that means, say you have you have say I think I will write you have here I should write you have what say if I carbon say carbon monoxide ok.

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This is the molecule as I we have shown for carbon monoxide we have so, spectral lines you will see like this. So, this kind of spectral lines will see. Now this if carbon can be 13 carbon can be 12 right oxygen is 16 say in both cases ok. So, there is a difference in mass of carbon in these 2 molecules ok. So, this carbon 13 is basically isotope of carbon 12 or carbon 14 also isotope of isotopes of carbon 12 ok. So, in this spectral B is basically h by h by 8 pi square whatever. So, I is here so now, I is basically mu r 0 square right. So, mu mass. So, mu equal to mu equal to m one. So, m of carbon m of oxygen divide by m of carbon plus m of oxygen that I there right. So now, when mass of carbon for this case showing one case 12 and other case is 13. So, this reduced mass mu will be different for these 2 case although this carbon oxide that is the molecule so, but if there if there is any isotope then this I will different. So, I will be different for these 2 isotopes. So, B will be different B will be different.

So, for for 1 molecule C 12 O 16 if this is the spectral lines ok. Then C 13 and O 17. So, spectral lines will be so it will not coincide it will be shifted it will be shifted right, either this side or the other side does not matter it will be shifted ok. So, from the intensity of this spectral lines so seeing these types of spectral you want immediately you can tell that there is a isotope and from the intensity of the spectra one can tell one can tell about the abundance of the of the isotopes ok. So, this is another application and third application is very useful and every kitchen you will see the application of these of this whatever you study this rotation of a molecule that that effect you will see in each and every kitchen of of our country or in the world.

So, that is basically microwave that is basically microwave.

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Microwave not microwave oven microwave oven. So, I think most of the most of the kitchen in our country or in the world having this microwave oven, this is very useful to cook to warm the our food right. So, how this microwave works, this microwave this principle of this microwave is is because of the because of the rotational rotation of the molecules, right? Now imagine that we want to cook or we want to heat some our food so what we do? You take the heater of yeah, you take heater so you have you have food, you have some food you take heater yeah you take heater ok. So, there is a flame and yeah it is heating our our our food right. So, this is external heating of our food ok. So, when we heat.

So, this heat it is basically it will heat first surface of the food say one potato is there ok. So now, it will heat this surface of the potato and then heat will enter inside heat will enter inside and then it will reach center right. So, it takes time to cook our food because this gas oven or for heater oven we are using when we are using so that external heating we are supplying to our our food ok. And then first it will heat the surface of this of this food and that heat then slowly slowly it will enter towards the center of the of our container ok.

So, so, then it will cook this center food ok. So, so that is why here just I took example of potato. So, first potato surface will be heated and cooked and then slowly slowly inside so it takes time it takes time, but in microwave oven it is takes very short time ok. So, if here to boil to boil a egg or to boil a what is called it is potato, at least you need 10 minutes to boil it to just make it boiled one potato, but within I think it should not take 2 minutes more than 2 minutes to boil the potato in microwave oven ok. So, if this why it is faster in microwave oven? And what is the principle of microwave oven? And which principle it works? Now now you see microwave oven; obviously, that in that oven it radiate micro wave ok. I microwave oven there is a system there something is there which generates micro wave ok.

So, microwave radiation is coming inside the box. Now our food which ever we want to cook. So, we are we are keeping in the box at the center of the box and from the surrounding of the micro oven from inside of course, it is. So, this microwave are coming and hitting falling on the falling on the on the on the on the food whatever whatever we cook. So, just you imagine that one potato we have kept it inside one bigger potato we have kept inside ok. So now, this microwave will come and hit this potato.

So, microwave this is my potato say ok. So, microwave from surrounding inside the oven this microwave generator is there. So, it will come all sides and fall on tis potato. Now now what happens microwave falls on this what what will happen there should not be anything microwave it is not very good to heat, if I keep a if I keep a solid something so it will not heat microwave will not heat, if I keep some solid material say one glass one glass because have you seen or not I do not know if you use this glass pot ok.

And inside glass pot if you keep tea or milk and you are keeping this glass pot inside the microwave. So, when you are taking out you are seeing this no glass this pot it is not heated only this inside what we have milk or this water or this tea that is very hot ok.

So why that I will tell you see this microwave is coming. So, in food whatever we kept inside. So, that is. So, their something should be there which can absorb this microwave which can absorb this microwave. So, for all our food item wherever we are cooking it is not solid it always contain water, it always contain water and water molecule H2O as I told you it has it is this H H this is O it is polyatomic and asymmetric tough and it has So, this molecule hm.

So, it has rotational this molecule rotates it has rotational energy levels ok. So, in. So, rotational energy levels of course, it is in micro microwave range . So, water have this microwave range energy level. So, when this microwave is coming and potato of course, potato have this water component or tea or milk whatever ok. So now, when microwave will come. So, this this water molecules it will absorb this micro it will absorb this microwave and it will go higher state higher energy state it will go higher and higher and higher energy state ok.

So, when it is going higher and higher energy state absorbing this microwave. So, immediately it also emit there is the within 10 to the power minus 8 second it will come down ok. And it will emit again emit the radiation this water molecule again it is absorbing again it is emitting immediately it is emitting. So, this whatever it is emitting energy. So, that will act as a heat energy and it will basically cook or warm this these things ok.

So, as if in food component only if water molecules is not there. So, then it will not be hot you know. So, water molecule is there that is the absorber of this microwave because it water molecule have the have the microwave have the energy levels of microwave. So, it can absorb and from ground state it can go higher energy state and immediately it will emit this higher energy because it do not like to stay at higher energy immediately it will emit then again that energy.

So, that energy will supply will supply to the other component of the food right except water. So, that water whatever molecules whatever it is reemitting these energy So, that reemitted energy will act as a heat and that heat will cook the food ok.

Whatever other components rice etcetera whatever other there. So, so these so water molecule in your food whatever we have put it is (Refer Time: 34:52) inside. So, micro oven it is falling. So, all water it is not only on surface it is inside also inside of this of this potato also water is there. So, all water molecule from every point inside this potato or your food item. So, they will they will emit this reemit this energy ok.

So, as if these heat is coming from internal internally and it is coming from every point and that. So, that is why at a time all not only surface inside everywhere it will cook at a time ok. So, that is why within very for short time. So, it will be cooked and other externally fast it cooks surface and then it goes inside inside and then it is it is cooked centrally. So, then overall it will be cooked, but here at a time for each point water everywhere water is there water is giving heat reemitting these microwave again and giving heat everywhere at a time.

So, that is the within short time it is cooked ok. So, this is very nice application of whatever you learned from rotational spectroscopy or yeah or microwave spectroscopy so I will stop here.

Thank you for your attention.