Atomic and Molecular Physics
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Lecture - 58
Raman Spectroscopy (Contd.)

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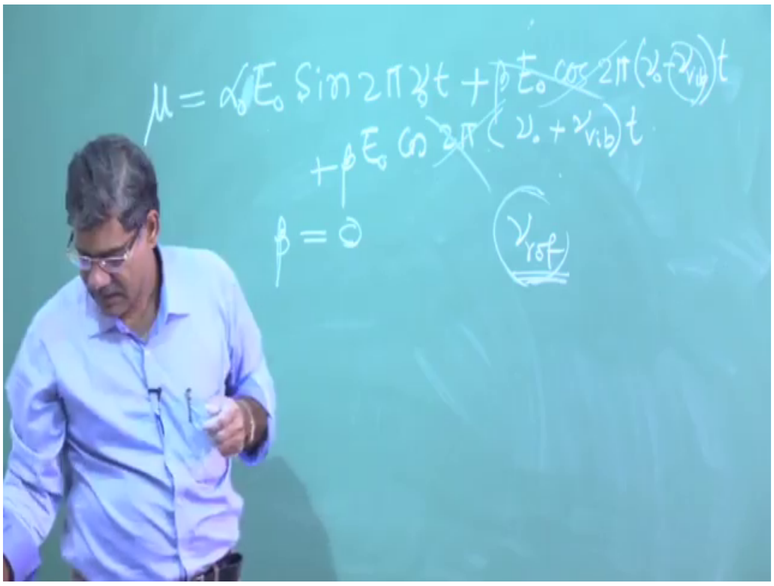

So, in last class we have discussed classical theory of Raman Effect. So, there we have seen that this dipole moment, it is a dipole moment of molecules under the external radiation of frequency mu 0. So, that was sin 2 pi nu 0 t plus, then it was I think alpha 0 then I think beta E 0 beta E 0 cos a minus v means 2 pi 2 pi nu 0 minus nu vibrational rotation, whatever t and beta E 0 cos 2 pi nu 0 plus nu vibration t.

So, this dipole will oscillate with 3 frequency. So, it will emit radiation of 3 frequency then we are telling the incident radiation of nu 0 falls on the on the molecules. And now it this it scattered by these molecules and this scattering radiation we are getting. So, that we are getting of 3 wavelength 3 frequency.

So, these are the frequency these are the frequency one is original frequency, that we are generally tells the valleys scattering and addition of these elastic scattering of course, and additional 2 frequency we are getting that is that is just exactly the same by same amount it is the higher and lower than the incident frequency.

So, that is the reason origin of the Stokes and anti-Stokes lines and that is the in q p null in rustic scattering and there is the basically Raman Effect. So, Raman scattering Raman Effect it is basically due to elastic inelastic scattering from the molecules.

Now, here one things is important that what is beta I told beta I told this rate of change of polarizability beta is rate of change of alright. Now, see if beta equal to 0 then what we will get there will not be this 2 table there will not be any Raman Effect ok. So, this t 2 term will not be there 0 beta equal to 0.

So, if there is no change of polarizability, when incident radiation is falling on the molecules, then you will not get a Raman Effect ok. So, it will be Raman in a tip molecule. So, it is compulsory to see the Raman Effect ok. So, the molecule has to be.

So, Raman active Raman active means it is there should be change of polarizability of the molecules. So, this change of polarizability so, whether it will change or not ok. So, that is the, if it is isotropic if it is isotropic the polarizability that I told you if it is isotropic so, spherical distribution of polarizability of the molecules ok.

So, this is Raman in acting ok. So, in that case only this molecule will from molecule we will get the scattering this the Rayleigh scattering elastic scattering ok. So, but the polarizability the distribution if it is ellipsoid ok; that means, that there is a change of polarizability ok. So, beta is not equal to 0. So, then it is Raman active and you will get the this Raman scattering ok. So, this star these two term will exist. So, so that is that is. So, we define this Raman active molecules and Raman inactive molecules.

So, the same rule here just I have taken these vibrations, but the same rule is valid for the rotation. So, only this nu vibration will just replace by nu rotation and this so, then you will see the effect of rotation ok. So, this you will get strokes and anti-stokes lines there. So, then there that basically we tell ramen shipped, what is the dimension what is the original incident wavelength or frequency.

Now, the Stokes lines and anti-Stokes lines it is coming just higher and lower side by this by same amount of this it is the it is the yeah I think that will discuss. So, this separation will defend this it is separation it will it is it will depend it is just and depend by this frequency either here so, rotational vibration.

So, that I will how the spectra looks like that I will discuss. So, this whatever this here we have considered only vibration. Now, if we the same things is varied fall also rotation. And also both can be seen in both can be seen. So, then we tell this it is vibrational and then we say this fine structure of the vibrational 1 so, that because of the rotation.

So, either only you can see this rotation one only you can see the vibration 1 and you can see both one in Raman spectroscopy and in that case vibration rotation 1. So, vibration 1 will be modulated with the rotation 1 and that is the there is the fine structure of the Raman spectra, vibrational spectra ok

So, now, let us discuss the quantum theory. So, now, now it is it is very easy, because already whatever we have discussed the vibration and rotation, the theory we have discussed from highway sanitation that is only quantum theory we have discussed.

So, already what already we know the what is the what is the vibrational structure of the molecules, what is the rotation of structure of the molecules? So, molecules have the rotational energy levels, molecules have the vibrational energy level, what are the quantum states of the of the molecules ok. Due to vibration due to rotation that already is known to us, but in that time it was not known it was not clear picture at that time ok.

Now, since we are quite familiar with this. So, quantum theory we tell is very easy you want to understand the Raman Effect it is very easy to understand the Raman Effect.

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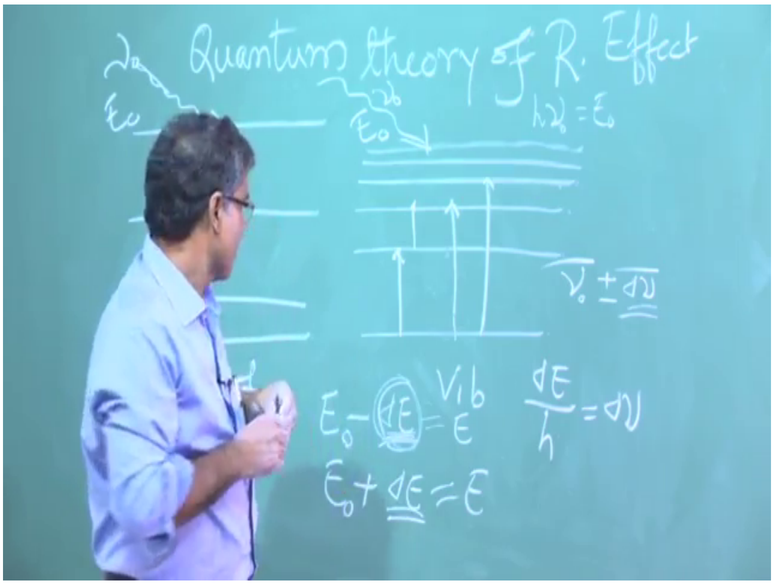

So, quantum theory of this quantum theory of Raman Effect quantum theory of Raman Effect, Raman Effect. So, so you have molecules, now molecules have these vibrational energy levels that is already known to us or molecules have the rotational energy levels rotational energy levels ok, rotational energy levels it is it is there in molecules ok. Now, incident radiation falls on it incident radiation falls on it and this radiation falls on the molecules ok.

Now, this radiation is frequencies nu 0 or energy is E 0 E 0. So, when radiation falls on it; Now, What is Radiation? Radiation is basically the it is a beam of photons ok. So, particle nature of the radiation is photon is falling on it. So, this photons energy is h nu 0 h nu 0 let us say E 0. Now, when h nu 0 equal to E 0 so these photons will fall on it these photons.

So, what will happen? So, these photons will be absorbed by the may be absorbed by the molecules, if it matches with this particular transition ok, if it matches with the particular transition ok. So, it may happen that this photo it may happen that these this incident radiation falls on it ok. So, it is not incident radiation is not just it is now you are consist considering that it consists of many it consists of many photons ok.

Now, these some photons here this it is a this molecules ok. Due to this photon it will absorb and it will go from it will be excited, it will go from one state to another state ok, it will go from one state to another state ok. So, so whatever the energy E now part of that is absorbed part of that is absorbed del E ok. So, E 0 part of it is absorbed, due to this it is it takes the molecules from higher state to lower state to higher state and then so, what that some energy is was absorbed ok.

Now, the radiation rest of the radiation will have the energy say E ok. Now, this rest of the radiation is coming out. So, that V tilde it is scattered from the it is scattered from the by the molecules and it is energy is now lower than the incident energy. And other case may happen other case may happen. So, when radiation falls on it, but now it is these molecules are in excited state, excited state. So, when radiation falls on it radiation falls on it.

So, now, because this molecule service it does not stay in accepts is longer time. So, it come back to the down state after, I think in a fraction of micro second it come back to the down state ok.

So, now it will emit some additional energy right. Now, you would incident 1 t 0 and now from excited state to down state these molecules have come from except is to down steps. So, you release some energy ok. So, so that is release of energy that is del E; So, now, scattered one radiation coming out. So, that one is now this energy of that one is higher than the incident 1 ok.

Now, del E and here we have whatever retained. So, this we are telling this is because of it is going from one state to another state; either from lower energy state to high energy state or from higher energy state to lower energy state. So, how much what will be the energy of this one del E. So, del E is basically energy is this energies is this or this or this or this ok.

So, as I told this vibration similar for rotation also. So, what will be the this del E what will be the del E. So, that is related with the electronic that is related with the rotational structure or vibrational structure of the molecules; and that information basically carrying is carried by the by the scattered radiation ok.

So, this del E is basically if that one has to find out; So, that frequency whatever nu 0. So, del E by h, h mean that the energy del E you. So, that will be our del E del E.

So, in terms of nu 0 plus minus del nu ok. So, del nu is nothing, but this or in terms of wave number if you want to write you can write this so, v number. So, whatever they say ok. So, that is the quantum theory to explain the stokes lines and anti-stokes lines in them.

Now, see this Raman scattering this Raman Effect this scattering is very very weak that is why as I told earlier. So, that is why it was difficult to see. So, radiation is falling most of the radiation 99 percent radiation is scattered it is elastically scattered ok.

Only maybe one percent or less than one percents are scattered elastically, because this probability to have this transition ok. Molecular this rotational or vibrational transition is very very poor small, but it is there ok. And that sort this inelastic scattered light or radiation is very small compared to the Rayleigh scattering ok.

So, these the explanation of this quantum theory from the quantum theory and let us see using this quantum theory and already is. Now, let us see this using quantum theory what will be the spectral lines Raman spectra lines for say due to the pure due to the rotation.

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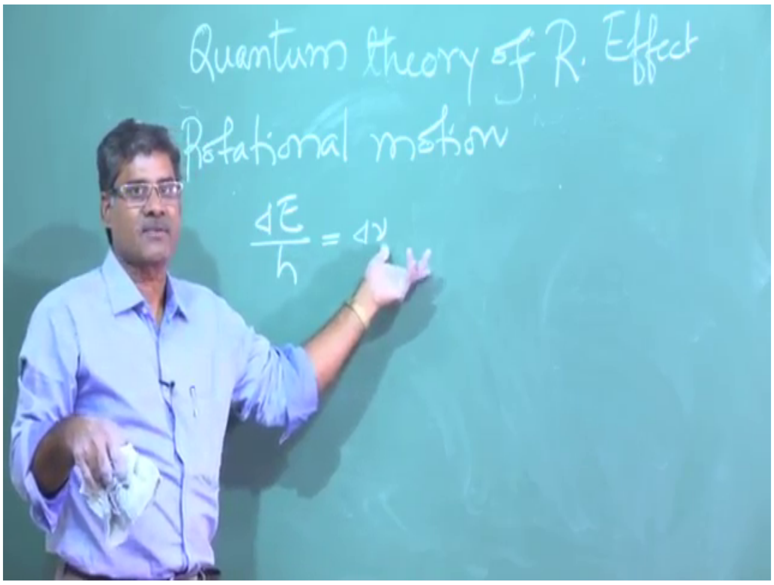

So, due to the rotational motion; due to the rotational motion; So, as I told this del E right del E by h that is basically del E ok. So, this already since we know we are familiar with the with the notations energy levels etcetera in terms of wave number. So, the same thing we are writing in wave number. So, in case of rotation we know this epsilon j equal to B J J plus 1 J J plus 1.

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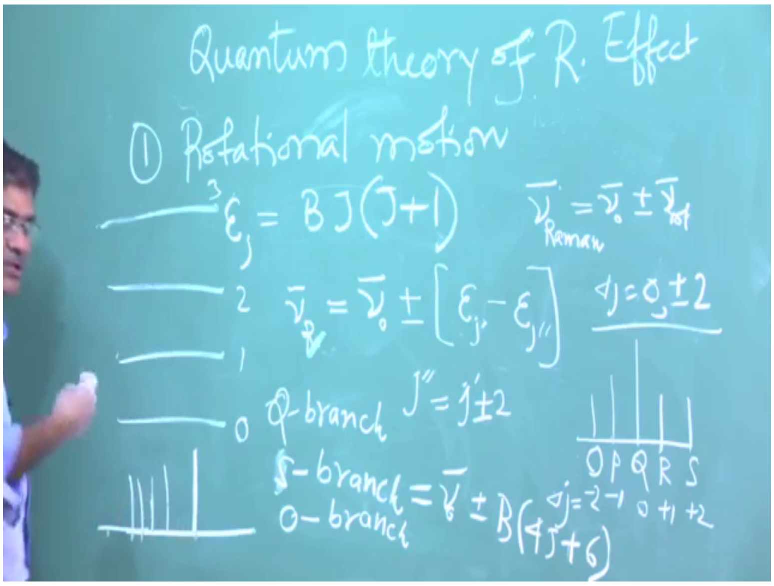

So, now this these are nothing, but this rotational energy level rotational energy level rotational energy level J equal to 0 1 2 3 etcetera right. Now, this thing to rotational our things is the nu bar of this Raman spectra, Raman spectra lines nu bar Raman spectra lines that will be nu 0 bar incident one then plus minus plus minus I will write that say nu bar it is a rotational nu bar rotational ok.

So, nu bar Raman let us write just r this will be basically we can write nu 0 bar plus minus, now what we can write here. This will be here this will be basically it is this is coming, because of transition from one rotational energy level to the another rotational energy level. So, one energy level to so, so I can write E j E j dash minus E j double dash give this condition at the going to excited state or coming from excited state to the lower state lower energy state is comes.

So, now here to get it so, we have to use selection rule. Now, selection rule for this you know the del j now in microwave spectroscopy pure rotation there we have seen this del J equal to plus minus 1 ok. And this different branch of spectral lines we till depending on the different depending on this on this on this j value.

So, we remember that this is the is a I think this Q this P this R R branch you will see different branch and then as the O and this is the S ok. So, this is I think del j del j equal to I think this is 0 this is plus 1, this is plus 2, this is minus 1, this is the minus 2 ok. So, these are different branch we have discussed earlier.

So, here in this in this case here the selection rule one has to choose so, which once you will see that will depend on the selection rules. So, in Raman in case of Raman effect or Raman scattering there the selection rule is different than this one and that selection rule is basically it is a 0 and plus minus 2 selection rule 0 and plus minus 2 ok.

So, why it is so, that is again it depends it is it is because of the it is because of the it is because of the polarizibility ok. So, whether it is ellipsoid or it is spherical ok. In case of spherical and it depends. So, ionized scope is there. So, it did so, this a nice would be because of this you see that depends on the on the direction of the electric field with respect to the bond axis of the molecules.

So, if electric field is applied when it is applied in the direction of the of the direction of the bond axis parallel to the bond axis, then you see this there will be change of this easy to change of these bond axis; So, easy to change the polarization or this polarizability. And others if you if molecules are this I think it is a electric field is perpendicular to the bond axis ok, then this change of this polarization or polarizability it is it is it is difficult in this crossed cross direction.

So, there will not be much change of this polarizability ok, But, so it depends on the direction of the electric field and the and the rotation of the of the axis of rotation of the molecules. So, due to this polarizability and isotropy in polarizability so, it is different situation is different case of Raman scattering, than the original or in micro in microwave what is the pure rotation with we have seen ok.

So, here basically there is effect of incident light there incident light we have not put. In pure rotation, that is microwave spectroscopy ok. In that case we have not put external radiation, but in case of Raman. Now, molecule is under external radiation and because of that there is a change of polarizability. And this polarizability sensitive to the direction of the to the direction of the of the electric field with respect to the bond axis ok.

So, that is why here this selection rule is different than the original 1. So, that that is the reason why selection rule is different. So, selection rule is del j equal to 0 plus minus 2 ok. So, when del j equal to 0. So, that is basically you will get the Q branch and you will get the you will get the Q branch yes and it is a del j equal to plus 2 and del j equal to minus 2. So, del j equal to plus 2 means you will see this s branch del j equal to minus 2 you will see the O branch ok

So, you will not see P and R 1 chain in this case because plus minus 1 is not allowed in Raman scattering due to rotation so, that is why you will see. Now, one has to this here one has to consider this transition you know, this V dash equal to for plus minus 1 J dash you replace J double dash equal to J dash plus 2 ok. So, then you will you put here in one case B J dash J dash plus 1 minus B J double dash J double dash plus 1 ok.

Now, considering this del j equal to plus 2 or minus 2 whatever in one cases the other one is one case plus 2 another case minus 2 ok. So, I think this a 1 can write and if you put there. So, you will get you will get basically I can write. So, two things we will get one is one you will get plus another is minus of course, but here you will get basically you will get Q branch, you will get 7 branch and you will get Q is an o branch.

And what will be the frequency of this that one can I think I can just write yes and yes. So, basically you will get if I consider plus 2 plus 2 means for this branch plus 2 if I just consider this one. So, you will get basically this part. So, nu 0 bar plus minus you will get I think 4 b 4 B, if I think I have to write B, then 4 J plus 6 ok. If we consider this J del J equal to plus 2. So, then you will get this one and yes.

So, that is for S branch similarly one can consider for other ones like one branch and of course, these are Q it is the 0. So, you will get you will get this Raman you will get this basically this original one and different branch, you will get, you will get for S branch say intensity will not be same for all anyway we are not discussing.

So, you will get this branch is branch you will get O branch ok. So, as your whole you will get the Raman spectra and they are. So, original Q Q branch you will see and then you will see, S branch you will see this, R branch not R branch O branch, because P and R will not be allowed ok.

So, these the these are Raman spectra due to modified with due to the rotation. Similarly, one can see the Raman spectra for the vibration and that I will discuss in next class.

So, let me stop here.

Thank you.