Atomic and Molecular Physics
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Lecture-57
Raman Spectroscopy

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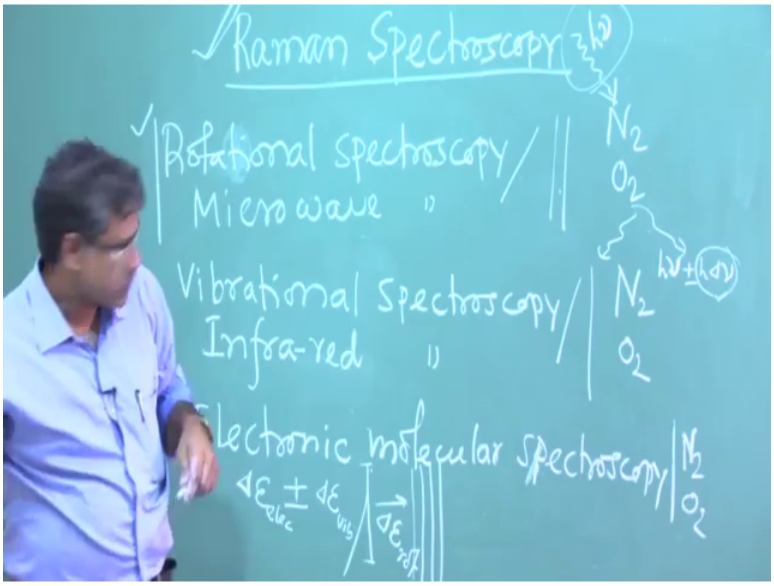

So, we are discussing about the Raman spectroscopy Raman Spectroscopy. So, basically Raman Effect based on Raman Effect the spectroscopy and this spectroscopy is very useful to study the molecular (Refer Time: 00:50) and rotation.

So, we have seen we have seen the infrared I think yeah. So, rotational spectroscopy or it is called also microwave spectroscopy. So, these for pure rotational motion or rotational structure of the molecules one can study using this rotational spectroscopy or microwave spectroscopy.

And, then we have seen these vibrational spectroscopy or infrared spectroscopy ok. So, this spectroscopy used to study the pure vibration or vibration rotation of molecule vibrational rotator or vibrational rotational motion of the molecules one can study using these infrared spectroscopy or the vibrational spectroscopy. And also we have seen that so, these can study the rotation and vibrational structure of the molecules ok and then third one this electronic spectroscopy, electronic molecular spectroscopy ok.

So, here basically electron transition and then it saturated with the rotation and vibration of the molecules. So, one can study the rotational and molecular structure of the of the of the molecules. So, here this we are telling that rotational structure of the molecule can be studied these we are telling vibrational or vibrational rotational structure of the molecule can be studied right.

And other one also we are telling that we can study the vibrational rotational structure of the molecule. So, everything all spectroscopy whatever we have discussed. So, far everything is telling that this spectroscopy used for studying the rotation and vibration of the molecules.

Now, third this fourth one whatever I am mentioning these also I am telling that Raman spectroscopy, it is also used for studying the studying the vibrational and rotational structure of the molecule. So, so what is the difference what is the difference among this all the spectroscopy and among them these Raman spectroscopy is very popular and very useful why it is. So, so to understand that one has to think that one things I have mentioned this rotational spectroscopy here this you cannot use for all molecules like say nitrogen oxygen if I take this to a example.

So, rotation of structure of this molecule cannot be studied because there is no permanent dipole moment. So, this spectroscopy is not useful to study rotational structure of these molecules which do not have dipole moment permanent dipole moment or induced dipole moment. And then also this vibrational spectroscopy or infrared spectroscopy also it is it cannot it cannot study this vibrational structure of these molecules; because same reason it has no dipole moment.

It is so; both are not infrared active and microbe active molecules. So, we cannot study them using this spectroscopy, but all these molecules can be studied they are molecular and vibration the molecular structure basically vibrational and rotational structure along with the electronic structure.

So, for all these molecules nitrogen oxygen and other molecules can be studied using this electronic molecular spectroscopy that, because when there is electronic transition then there will be dipole moment of these molecules and because of that it. It is, it will show it will show the yes it will show the it will show the rotational and vibrational effect on this electronic structure that we have discussed in details. So, core structure and this fine structure fine rotational structure.

And also and these this is slightly easier and popular than this other because here is this comes this wavelength or wave number of the spectral lines it comes it comes in the range of in the range of I think visible range end and ultraviolet range in that range. So, because here this it is not these spectral lines is basically it is mainly this electronic electronic this is the electronic spectral lines. So, it is wave number or wavelength or frequency it is in the range of ultra-value range or visible range.

Now, here these lines are basically these lines are basically modified with the rotation with the vibration. So, depending on this rotation and vibration just these lines are modified ok. So, this lines so, wavelength, wavelength is or wave number is this. Now, it is slightly it is it is these other lines whatever we are getting is differs by the by the amount of this amount of this corresponding energy level separation of vibrational energy level and rotational energy level ok.

So, here this you have you have basically mean this electronic electronic delta E del E I can write del E that is the electronic and then your I think maybe if I write this a plus minus, whatever your daily for vibration or daily for rotation etcetera.

So, so if it is just this originally this is the energy of the spectral lines. Now this energy is slightly modified with this or modulated with this the small energy of vibration or rotation ok. So, that is why it is in microwave range the infrared range and this is in ultraviolet range ok. So, that is why it is here this spectroscopy is slightly easier slightly easier to handle because it is in visible range or ultraviolet range ok. So, that is the advantage of the spectroscopy.

Now, Raman spectroscopy on soon it is in visible range or in ultraviolet range ok. So, in the same range now then again question is. So, whether these 2 are same or it is better. So, Raman spectroscopy is better than this one because here also what happens that from outside we have we have molecules, we have these molecules now this from externally incident radiation is falling on that ok. Now, these have some energy or whip or frequency or odd number ok. So, it is generally it is this wave them are. So, this I can choose this wave number, I can choose the incident light of particular frequency generally it is children in invisible range or ultraviolet range ok, as I told this it is easier to handle this range of frequency or wavelength.

So, now this one whatever the scattered one I am getting scattered one I am getting. So, that is wavelength also or frequency also this in this range ok, whatever incident radiation we are using it is in the same range only these are modified h nu h nu minus h delta nu h delta nu or plus minus delta h delta nu, now each delta nu that del nu change it is the it is the that is change is because of the rotation or vibration ok.

So, this change it is small, but we are observing this change in the range of the same range of this frequency or wavelength of incident light ok. So, so still although this rotational and vibrational that that that energy range that change it is in microwave range or this infrared range, but we are not detecting we are not detecting that that energy directly. So, basically indirectly we are we are proving this energy that spectroscopic whatever we using or this wavelength or frequency we are dealing in the spectroscopy that is actually it is in the range we have chosen clearly visible range or this ultraviolet range ok

So, that is why it is in the same as this one only difference is that here you will see so, many is this you will see it is a very difficult to resolve this vibrational ones core structure is also it is fine it is it one can resolve and study and major, but rotational one that is very difficult to resolve and you need really very high resolution spectroscopy.

So, one has to really to study the rotational effect from this spectroscopy one has to really use very high very high resolution of the spectrometer and that when you are going for higher and higher resolution then it will be for you have to be higher so, but so, in that way so, this Raman spectrometer. So, you are not dealing with that that speciation or you do not need to dissolve that one. So, here you are dealing in this range where just it is modified with this with the effect of rotation and molecules and that can be that can be easily resolved and detect in this spectroscopy ok. So, these the advantage of this Raman spectroscopy.

Now, question is this as I discussed earlier how it was discovered and now let us see the fury of this Raman spectroscopy or Raman effect as I mentioned last class that, that there are 2 lines stokes lines and anti-stokes lines. So, whatever the origin whatever the origin there is the incident wave length.

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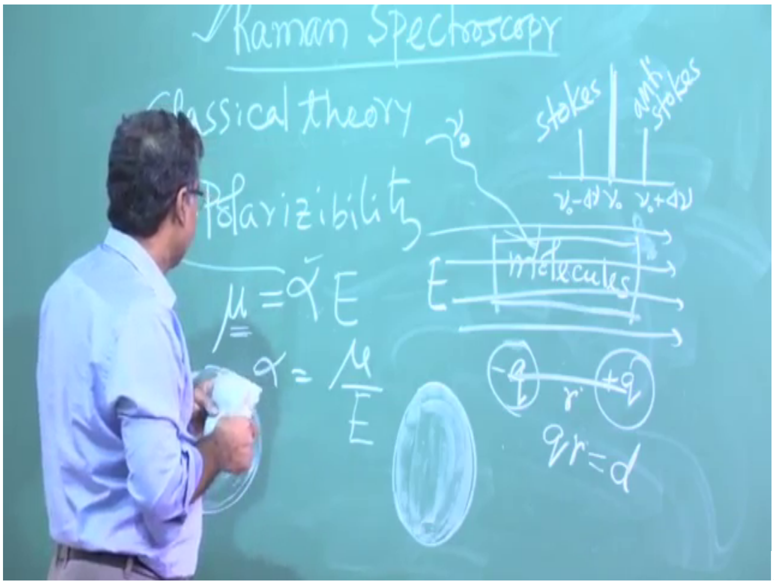

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So, this the origin one original incident original frequency of the incident one or wave number and then you are getting lower than this and higher than this lower wave number means lower energy means higher wavelength of course.

So, these are these called stokes lines and this is called anti stokes lines. So, it is if it is nu 0. So, it is nu 0 minus del nu we can say and this one nu 0 plus del nu you can say. So, these are stokes lines is the anti-stokes lines anti-stokes anti stokes lines and these the strokes lines ok.

So, what is the origin of the stokes lines and anti-stokes there is the theory successful theories there. So, now, this effect Raman effect it is easy to explain from quantum theory ok, but that time it was not easy to explain my Raman mainly I think he used this classical concept and that also it is interesting to discuss that one because it helps to understand physically of the system.

So, let us discuss the classical theory of this Raman Effect or classical theory of this Raman Effect. So, you know you one has to know this what is polarizibility? What is polara polari zi bility molecular polarizibility atomic olarizibility? So, both are similar polarizibility means if we apply electric field on molecule. So, you have molecules, now if you apply electric field E then what will happen these electric fields a static electric field.

So, it will polarize the molecules it will polarize the molecules and because you know this in so, it is same for atom also. So, atom or molecule have this molecule this is nothing, but the multinuclear atom ok. So, multi nuclear system so, it has positive charge center a positive charge also it has center of negative charge. So, in electric field means electric field have also positive pole and negative pole electric field can be considered that it generates from the from the source where positive pole and negative poles are there. So, in between you will get the electric field.

So, now we have we have a system higher positive charge and negative charge up there. So, positive charge of the system will be attracted towards the negative pole of the electric field and the other one negative charge will be attracted by the positive pole of the electric field ok. So, that means, there will be shift of the positive charge and negative charge in opposite direction.

So, molecule itself is a neutral. So, basically the center of positive charge and center of negative charge coincides ok, but in electric field now this center of positive charge and center of negative charge they are shifted in opposite direction. So, there will be induced dipole moment of the molecule ok. So, that means, when you will get when you will apply electric field. So, then there will be polarization it molecule will be polarized. So, it will have the, it will have the dipole moment induced dipole moment.

And if you and this dipole moment it is basically proportional to the electric field, if we apply higher and higher electric field this separation of the positive and negative charge will be higher and higher and this dipole electric dipole moment induced dipole moment will be higher and higher. Because dipole moment electric dipole moment you know this positive charge negative charges and positive charge ok. So, they are separated by distance r. So, q r q r will be the basically electric dipole moment ok.

So, this electric dipole moment it is it is basically proportional to the electric field. So, when it is in molecules. So, we tell this molecular dipole moment if it is atom atomic dipole moment or dipole moment for atom or dipole moment for molecule.

Now, this so, now, this dipole moment is proportional to electric field now it is proportional. So, there will be proportionality constant. So, this one can write equal to some proportionality constant is alpha. So, mu equal to alpha E ok. So, these alpha these alpha is basically called the polarizability this alpha is called the polarizability and so, it is it is basically it depends on the on the on the molecules it depends on the molecules, but for a particular molecules is maybe it is constant in a static electric field ok.

Now, for a now this polarizability for molecule basically, when these molecules are in electric field ok. So, it is polarized now this it is polarized now this polarizability basically one define alpha equal to mu by E mu by E so; that means, polarizability is defined as the is is nothing, but the induced dipole moment for unit electric field. So, for the unit electric field what is the, what will be the induced dipole moment. So, that is that is the polarizability ok. So, polarizability so, if you apply electric field different direction of the molecules or or molecules in electric field, if we molecule rotate the molecules so; that means, electric field is applied in different direction and if you study the polarizability.

So, then if you in 3 dimensional view if we see the polarizability. So, this basically most of the cases it is it is it is seen that there is a anisotropy in polarizability ok. So, depending on the basically axis of rotation of the molecules and the direction of the electric field. So, this polarized polarizability it we can see if it is spherical polarizability spherically distributed it is it is spherically distributed. So, then we tell it is isotropic ok, but it may be also it is found that it is elliptically distributed ok. So, then we tell it is the polarizability, it is the polarizability ellipsoid ellips the polarizability. So; that means, in this case we tell these polarizabilities of the molecule is an isotropic, but if so, this case. So, then we tell it is isotropic.

So, if it is an isotropic support; that means, polarizability changes it depends on the direction, it depends on the direction or it depends on the axis of rotation of the molecules in the electric field. So, this dipole moment then we can tell this dipole moment it does not depend only on this electric field also this polarizability it is it is not constant for a particular molecule it depends on the direction and axis of rotation of the molecules. So, so this value it is not only molecule dependence, it depends on also this direction of the electric field and axis of rotation of the molecules. So, or rotation or vibration both can affect.

So, this the polarizability now in case of Raman spectroscopy or Raman effect this radiation falls on the radiation falls on the atoms right radiation falls on the atoms not atoms radiations falls on the molecules. Now radiation electromagnetic radiation so, it is nothing, but it has electric component and magnetic component right.

So, so then we can consider basically this molecule is getting the electric field molecule is under electric field ok. So, that electric field is basically is coming from the from the radiation. So, radiation is there means electric it is this molecule is in electric field ok. So, here whatever we discuss in terms of electric field. So, basically radiation falling on it so, it is an electric field.

Now, this electric field now this electric field basically if it is frequency of this 1 is nu 0 ok. So, it is so, we can tell that.

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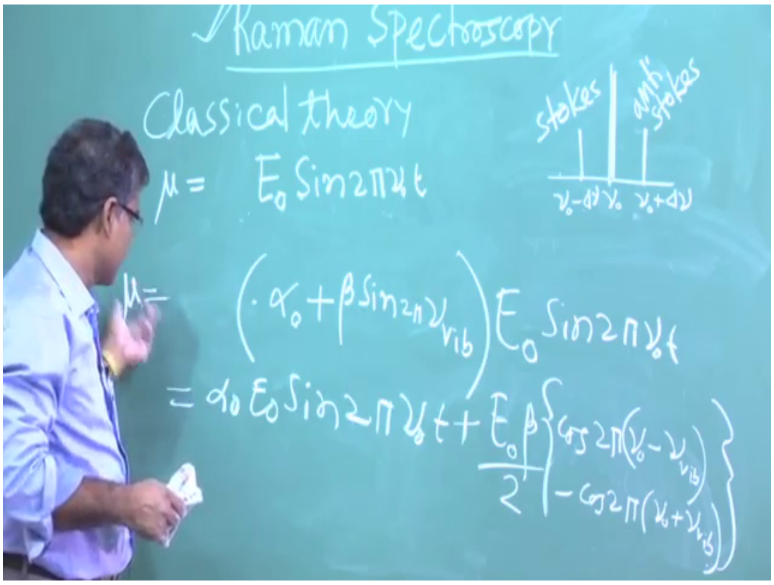

So, mu equal to mu equal to alpha now electric field here electric field is one can write E equal to E 0, because in this now not it is not static electric field, now it is a varying electric field there is electric component will value with this frequency of this radiation.

So, one can write E 0 sin 2 pi nu 0 t. So, this E it is now it is now static one it is alternating one ok. So, it is alternated alternating electric field with this frequency, now if you put mu equal to alpha. So, just E replaced by this one ok.

So, so; that means, this dipole moment of the molecules will change like this will change with the same frequency of the frequency of the of the incident radiation and and then what will happen? So, this dipole is oscillating then right.

Now, any oscillating dipole moment it emit radiation. So, if emit radiation that radiation will have the same frequency of the oscillating frequency. Now, this dipole is oscillating why it is oscillating that is because of this incident light incident radiation that is fine. So, after that with the same frequency it is radiation it is oscillating.

Now when it will oscillate dipole moment would oscillate with some frequency. So, it will emit radiation of the simplification ok. From electrodynamics one can tell that it will emit a pole radiates dipole radiates and the frequency of the radiation will be the same as it is it is it is frequency of it is oscillation ok. So, it will emit radiation ok.

So, that is the basically so; that means, that is the as if incident radiation thoughts and molecules. Now molecules is from molecules again that due to dipole oscillation it emits radiation; that means, it is radiation is coming out so, that is we tell the scattering of the of the incident radiation by the molecules and the scattering radiation, whatever we getting that the same frequency as this one. So, this is nothing, but the Rayleigh scattering ok.

So, that things will happen here is there and region of this is this as I explained. And now in addition to that in addition to that this molecule will undergo some internal motion such as rotation and vibration ok. And due to this rotation and vibration due to this rotation and vibration what will happen. So, molecules have some internal rotation and vibration and now external incident radiation falls on it ok. Now that due to this internal motion of the molecules so, that is basically due to vibration and rotation. Now these incident molecules will be affected or it will incident radiation will affect this motion ok. So, that effect one has to include.

So, what will happen? So, if you consider. So, this external in external or incident radiation it will affect the molecular motion, internal motion such as rotation and vibration and then there will be effect on this on this molecules, effect on the on the on the motion of the molecules; that means, it will affect the polarizability of the molecules ok. It will affect the polarizability of the molecules due to the due to the incident radiation. So, that alpha we have to so, that alpha is basically it is a alpha 0. And plus plus rate of change of this polarizability rate of change of the polarizability, if I write that is beta rate of change of the polarizability rate of change of the polarizability if I write beta.

So, this beta and that change will come that change it is come. So, sin say 2 pi sin 2 pi and sin 2 pi. So, so this as I told this it will affect the internal motion internal motion that is either vibration or rotation. So, just take any one. So, what is the what is the what is the motion of the vibration and the or frequency of the vibration or rotation.

So, let us consider just here vibration you can just replace with the frequency of the rotation. So, if I write nu that is for vibration. So, then polarizability will change like this alpha 0 plus this beta is the rate of change of the polarizability and that that is that is because of the internal motion of the molecules internal motion of the molecules here if it is if we consider vibration. So, what is the frequency of vibration new vibration or you can just consider the rotation also.

So, now you have to replace this alpha here by this one. So, you will get you will get basically mu equal to alpha is this one and then you have r 0 sin 2 pi nu 0 t ok. So, now, you know this if you just consider here what is there that is 2 parts 1 is alpha 0 E 0 sin 2 pi nu 0 t this is one part, another part you will have basically E 0 beta E 0 beta ok. And then sin a sin b sin a sin b equal to half cos A minus B minus cos A plus B hopefully I think just you apply this rule cos A minus B minus cos A plus B half of it ok.

So, if we consider so, this I can put half of it and then I will get cos cos a minus v means this is there 2 pi will be there 2 pi will be there. So, nu 0 minus nu vibration nu 0 minus nu vibration this is one part and then you will get minus minus cos E plus v so, nu 0 plus nu vibration ok.

So, here you are getting mu equal to this dipole moment that is equal to it context see the frequency one is nu 0 original one another is nu 0 minus nu vibration or nu rotation whatever and then another term nu 0 plus nu vibration ok.

So, now dipole is oscillating with 3 frequency ok. So, these you will get now whatever scattering incident one, now scattered light scattered radiation we are getting you will get this radiation of 3 wavelengths one is this original wavelength incident on other 2 is this ok. So, this is nothing, but this one is strokes lines we are telling and this other one we are telling this is anti-stokes line ok.

So, this way these are following the classical theory Raman or one can explain the this Raman effect what is the origin of stokes lines and anti-stokes line ok. So, I will discuss in next class this quantum theory. So, later on let us stop here.

Thank you.