(Foreign language) Knowledge is supreme.

So now let us try to think what, let us try to get into a little more detail, no too much of detail of Raman spectroscopy, okay. What have we learned so far? What have we learned so far about spectroscopy in general? Why do transitions take place according to the discussion we have had, according to, well of time dependent perturbation theory? What is the mechanism of interaction of molecule with radiation. It is an interaction between a dipole and an electric field, right. And remember, when we had that discussion we had concluded that in order to get a vibrational transition, the dipole moment must change as a consequence of a vibration. In order to have a rotation transition, the permanent dipole must be there, okay, in order to see it, and we had ended that discussion with a question, is it then impossible to get an idea about rotational level and vibrational levels of say dihydrogen, H2. Can we not get an idea about their bond length and bond strength that comes from a discussion of rotational spectroscopy and vibrational spectroscopy. And then we had said, if you remember, that you can do it using Raman spectroscopy, okay.

So now in these molecules homonuclear diatomics, dipole is not there, right, but it is possible to have even in these systems, induced dipole, right. I believe you have studied things like London dispersion forces and all that. You know that you can have dipole-dipole interaction, you can also have transitory induced dipole, induced by the field and that can also interact. So now that hydrogen, so dihydrogen and other whole homonuclear diatomics, do not have a permanent dipole. It is possible for us to have an interaction of their induced dipole with the field, okay, that is the mechanism that is useful in Raman spectroscopy. So Raman spectroscopy is all about interaction of induced dipoles with the electric field of light, okay. An induced dipole as you know, if I write is as Mu I, Mu for dipole, I for induced, that would be equal to the electric field multiplied by some constant alpha, what is this alpha called, yes, polarizability, alpha is polarizability, you are right. But actually this is not all. You can have higher terms in E as well. So you can write something, like there are different ways to write it, I will just write beta x E square plus gama x E to the power cube and so on and so forth. Where beta gama, these are coefficients for higher powers of E. Now when you go from alpha to beta, there is a huge decrease in value. Beta is usually much-much smaller than alpha, if it is non 0, even if it is non 0. Gama is usually much-much less than beta, and so on and so forth. So these are called, okay, what is beta and gama, what are they called in general? Yes, I heard an answer, so what is that answer? Higher, higher coefficients, actually that’s right, but then the thing is, if you give a name, you have to give it a name that sounds, virial coefficient, okay virial coefficient, yeah, but then virial coefficients are generic, there is specific name to it, oh I thought you said higher, and I was going to building my story on that. So it's like this, alpha is what polarizability, right, these beta gama, these are called the hyperpolarizabilities of second order, third order, and so on and so forth. I think some of you know it, right. And they are also denoted as something like the sky 2 and so on and so forth, okay. So if we have to consider these, you understand that since these numbers are small, or I should not say numbers, since these quantities are small, this E has to have a very large value for the higher order terms to be important, okay, that takes us to the regime of what is called non-linear spectroscopy. Non linear spectroscopy, we will not discuss that in this course, but for our purpose, what we can do is, we can restrict ourselves to what you know already, Mu I = alpha E, but alpha is not a straight forward number, it is important that we understand this. It is going to come handy in a few weeks time. So what you can do is, what is the meaning of this alpha, polarizability. That means how easily you can distort your electron cloud, let us say, right. Now electron cloud is not a one dimensional thing, right or electron cloud is not a point, it is somewhat like a three dimensional object. So let us think of it in simple terms as say a balloon. Will you agree with me that a balloon could be a reasonable model for an electron cloud, the air that is there inside. Now what is the meaning of this, I apply a field. So if I take a balloon, what I do is I hold this balloon in my hand and press from two sides, that is applying a field. What happens, the balloon gets distorted, agreed. Now my question is this, when you press the balloon this way, does it get distorted only in this direction? It does get distorted in the other directions as well, isn't it. You compress, the balloon becomes smaller along the axis, along which you put the pressure, but even along perpendicular axis, the balloon tries to expand. Exactly the same thing happens, if I put in a very-very qualitative fashion, exactly the same thing happens, when you apply an electric filed to an electron cloud, okay. So it is not very difficult to understand that this Mu I being a vector, I can write it as Mu I X, Mu I Y, Mu I Z. X ray, Y and Z denote the three directions. Of course that should bring us to the question of lab fixed coordinate and molecule fixed coordinate. So what I am trying to say is this, this will not be a function of just EX. It will be a linear combination of terms in EX EY and EZ, okay. So I can write like this, EX, EY, EZ, since I am writing alpha, first term I will write alpha XX, first X for this, second X for this, first X for the direction of the component of the induced dipole movement, second X for the direction of the field, component of the field. Plus I will write alpha XY into EY, X because I am talking about Mu IX, Y because the field, direction of field I am considering is along Y. The third constant will of course be alpha XZ, okay. So far so good. If I have a balloon and I press it, so let us say this is a direction, this is it. So now I have applied the field in one particular direction, but then I have distortion, not only along this direction, but also along X and Y. So if I just have to write this equation what will it be, then actually it will not be this kind of an equation, it will be the other way round. You will write total Mu induced will be vector sum of Mu IX + Mu IY + Mu IZ. Mu IX will be alpha XX into EX. Okay, what about the Z distortion you have, sorry… I am applying, I am applying the field in Z direction, so that will be Mu IX is alpha XZ into EZ, then Y distortion, what will it be alpha YZ into EZ. So for the balloon, I will get something like this. Mu I will be alpha XZ plus alpha YZ, plus alpha ZZ, multiplied by EZ, because I have applied the field in only one particular direction. Now if I apply the field in any random direction, I can take XYZ components of that, understood. So for that, induced… so now I am writing the other… writing it the other way. I am writing for Mu IX, I will have contributions from EZ, EX, as well as EY, is that clear. So what will this be alpha YX EX + alpha YY EY + alpha YZ EZ. What about this alpha, well this will be EX, EY, EZ of course. Here distortion is along Z, field is along X, so it will be alpha ZX, actually alpha ZX and alpha XZ are one and the same plus alpha YZ, no ZY right, but then ZY and YZ are actually the same, we are not going to prove it, just believe me. Mu + alpha ZZ. Of course this can be written very conveniently in matrix form, isn't it. What I will do is, I will write it like this. So this equation that we have written is really… it should be written like this, what is called a matrix Eigenvalue equation, well no no… let's just say, it should be written as matrix equation, okay. So what we see is instead of alpha we have to use this matrix. So alpha is really, what is called a tenser, what is a tenser, what is a tenser? There is no reason to be tensed about tenser, tenser is just an array of numbers. You are okay with matrix, right. So that is all we will need for our case. Now what I do is, I write a matrix like this then I write a matrix in front, then I write another matrix in front, so that gives me a tenser, basically it's an array of number. It’s a useful mathematical tool. For our case, it is enough, if we think that alpha is a matrix, a tenser of rank 2, okay. So now you have to actually deal with all these components and you see that for, if I think of the components of the field, field is a vector, right. What are the three components of field, EX, EY, EZ. Dipole moment is a vector. So I have to deal with three components, Mu IX, Mu IY, Mu IZ. However, when we talk about polarizability, one direction is not enough, okay. You have to talk about alpha XX, that means polarizability produced in X direction by a field in X direction, alpha X, XY is polarizability in X direction produced by a filed in Y direction. Alpha XZ, well dipole moment induced in X direction by a field in Z direction and so on and so forth. Of course these are going to be largest. XX, XY, XZ, so if you go back to the balloon example, distortion will be most in the direction in which you apply pressure, right. So in fact you… what you could do is you can do a transformation of coordinates and diagonalize this matrix, which is a very-very common tool in quantum mechanics, right, but we will not try to do all that, what we need to understand is that, when we want to talk about components of polarizability, one direction is not enough. It is always two directions that are required, product of 2X. So this is going to come handy for us later on when we try to determine the selection rules for Raman transitions for polyatomic vibrations and something like that, yes. For a polarizability, we need to reference this, yes. So that is why if you want to perform a complete discussion of Raman spectroscopy from quantum mechanics, you need to invoke what are called direction cosines. Direction cosines are essentially cosines of angles between the axis in a space fixed coordinate and a molecule fixed coordinate, okay. In fact if we discuss direction cosines, you will understand, it is not difficult at all. What is problematic is the next part. When you use direction cosines as operators, then we have to learn a few things more before we can use it to actually do the quantum mechanics, that’s why you are not getting into that. But it is right that there are two frames of reference. In any problem like this, there are always two frames of reference, one is space fixed and the other is molecule fixed. Let us proceed, remember this, this is going to come handy later on. In order to develop a simplistic idea pertaining to Raman effect, what we can think is this. We know how to write E, don’t we. How did we write E earlier. 2E0 sign 2 Pi Nu T, what is this Nu, Nu is the frequency of light, okay. What we can do is we can write alpha as alpha 0 plus A sin 2 Pi Nu M T. What is the meaning of 2 Pi Nu M T. Let us say there is a molecular motion that causes a change in polarizability. Let us think of dihydrogen. Well there are two things that we need to understand here. Let us discuss this first then we will come to the other one. So we have dihydrogen. At equilibrium, when it's an equilibrium bond length, there is some kind of polarizability, right. What happens when I stretch the molecule. Does the polarizability remains same or does the polarizability change. Without getting into the discussion about whether it increases or decreases. Whether it increases or decreases, might be a little more difficult to understand. But I hope it is not difficult to understand that if I change the bond length, if I increase it or if I decrease it, then my… not my… polarizability of dihydrogen molecule is going to change, agree with that. Now think of what vibration is, it’s a periodic motion, right. So what vibration would do is that it would change the polarizability periodically, okay. So for something like that, am I allowed to write polarizability like this. Alpha 0 is the polarizability at equilibrium bond distance and the modulation is brought in by the sin 2 Pi Nu M Tau. So what would this Nu M be, Nu M in this case would be the vibrational frequency of the molecule, right. Okay let us think about rotation. Does polarizability change when dihydrogen molecule doesn’t vibrate, but rotate. To do that, we need to invoke the concept of what is called polarizability ellipsoid. Anyone who has studied Banwell's book would, I mean anyone who has studied Raman's spectroscopy for Banwell's book would be familiar with this term, polarizability ellipsoid. Polarizabiilty Ellipsoid is defined as the plot of 1 by root over alpha I. Actually Y 1 by root over alpha I all of a sudden, that is because it comes from something called, when you discuss angular momentum, that is why this ellipsoid was first used, this is an extrapolation of that. So let us just take it axiomatically, okay 1 by root over alpha I. Now think of hydrogen molecule. Polarizability of ellipsoid if you look at from this direction is something like this. What am I trying to say here, I am trying to say that it is easier to distort the electron cloud this way than this way. Of course the length is inversely proportional to square root, don’t forget. So wherever this ellipsoid is longish, there the polarizability is actually small. Wherever the ellipsoid is narrower, there the polarizability is actually more. Do you agree with me when I say that it's easier to distort the bond this way than this way? Because when you actually distort this way, then you are working with the nucleus. When you try to distort this way, then you have to overcome the attraction of the electron that it has with both the nuclear. So it is easier to polarize the electron cloud along the bond then perpendicular. But then if you look from this direction, then what do you see what kind of Ellipsoid do you see, is the perspective clear. This is hydrogen molecule, first is this, and now I am saying you look at it in… from this direction. What kind of shape will you see, what will the cross-section be, this direction and this direction let us say, there is no difference, same. so this cross section is actually is circular. So now what you do is you mentally superpose these two, what is the shape that you get. You get the shape of a well behaved egg, right. Eggs are not really symmetric, right there is a small curvature on one side and a larger curvature on one side. If you have an egg that is perfect, okay, completely symmetric, then that is the shape that you would get. In books I think it says the shape is of tangerine. I don't know how many of you know, what a tangerine is. I don't know if I have ever seen a tangerine in my life, so egg is easier to understand, everybody has seen an egg, right, but an idealized egg, that is completely symmetric on both sides, okay. So that is what the polarizability of ellipsoid looks like. Now think of it, even forget this, think that the molecule is rotating. Let us say I apply the field in this way and the molecule rotates. What will happen, in this position, what is the kind of polarizability that will be seen by the field, then when the molecule has gone like this, then the field will interact with a polarizability that is like this, okay so do you agree with me that when dihydrogen molecule rotates then it presents different polarizabilities at different time to the field and since rotation is a period motion, this change in polarizability is also periodic. So for rotation also, it is okay if I write my polarizability in this fashion. Alpha 0 + A into sin 2 Pi Nu M T, Nu M is the frequency of the molecular motion, vibration, or rotation. You can read this part from Banwell's book, you can read it from Ramil's book as well, but Banwell's book is good enough, so it's okay. Can I proceed with this, alright. So now if I expand this, I get Mu I = alpha 0 + A sin 2 Pi Nu M T multiplied by 2 E 0 Sin 2 Pi Nu… Let me write it Nu LT, just to emphasize that it is the frequency of light. So this gives me 2 alpha 0 E0 Sin 2 Pi Nu LT + 2 alpha 0, nowhere did alpha 0 come again, 2A E0 sin 2 Pi Nu M T sin 2 Pi Nu LT. This is what you get 2 alpha 0 E0 sin 2 Pi Nu LT +, there is a two and there is a half, so that will cancel, A E0 sin, no not sin, sorry, cos 2 Pi Nu M minus Nu L x T, then +/- minus A E0 cross 2 pi Nu M + Nu L x T is that right. Now as you know, how do we decide, which transitions will take place and which transitions will not, transition moment integral, right. What do you use in the transition moment integral, we use wave functions and we use this dipole moment. Here instead of dipole moment we want to use the induced dipole moment. So from here since I have three terms in induced dipole moment, I will get three terms in the transition moment integral as well. The first term is corresponding to a frequency of light that is unchanged, okay, that is what gives us Rayleigh scattering. The second term corresponds, this is, we have to use this in pre… pre-transition moment integral, right. We have to use this in the perturbation theoretical treatment itself, because T is still there. So this one, gives you what, what kind of frequency will it be, Nu M sorry… usually this is what you write, Nu L – Nu M, Nu L + Nu M. No harm if you write the other way round, but this is conventional. So this is what, what is this frequency. It's a different frequency then Nu L, right and what is the difference. The difference is the frequency of molecular motion. What is this, Nu L + Nu M. So once again a different frequency and the difference of frequency is equal to the frequency of molecular motion. So these two terms would give you the term for Raman effect. Alright, and as you see Raman effect can be of two kinds, one in which frequency is decreased, frequency of the scattered light is less than frequency of the incident light and other one in which frequency of scattered light is more than frequency of incident light. So if you think classically, what does this mean, it means that in the first case, what did you say frequency is, a frequency of scattered light is less than the frequency of incident light, that means the photon has given up some energy to the molecule, right. and in the second case it is more, Nu L + Nu M, so in that case the photon has taken up some energy from the molecule, you can think this way. That's a classical way of thinking.

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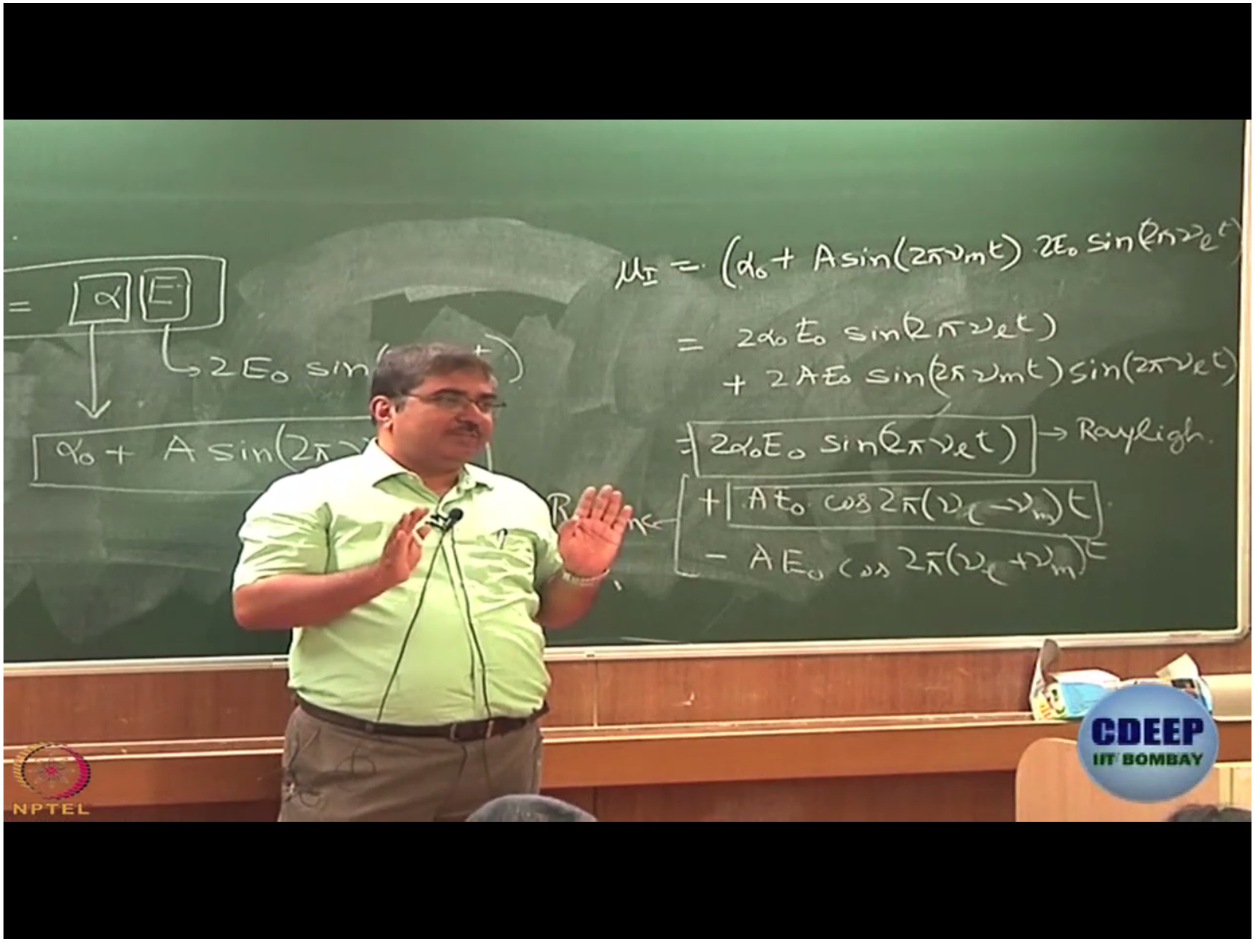

The quantum way of thinking is something that we can denote using a diagram, something like this. Suppose these are the energy level of the molecule, can be rotational, can be vibrational. What you do is typically you use a frequency that is much more than the kind of frequency you are trying to study. So if you want to study vibrational levels, you use visible light. If you want to study rotational levels, then you use IR light. So what this light does is, suppose you are here initially, it takes the system out of the manifold to what is called a virtual level. Now that brings us to the un-resolvable, at this level question of what a virtual level is, what is a virtual level? I do not have a good answer without going into detailed time dependent perturbation theoretical treatment of the problem. All I have is a couple of analogies to try and give you the impression that you have understood what virtual level is, but analogies always have to be taken with a pinch of salt. There are… they are very crude ways of understanding things. So before saying what a virtual level is, what's is a real level, or what we generally call, are stationary states. What's the definition of a stationary state? A stationary state is one in which Psi Psi Star is independent of time, right, and they are always associated with specific values of energy, right. So they are good Eigenfunction of Hamiltonian. Virtual states are not good Eigenfunctions of Hamiltonian. For them Psi Psi Star is not time independent. So if you can promote the molecule to a virtual state, then what happens is life time of this virtual state is very small, it has to come down immediately, okay. What are the analogies, analogy is this, I cannot even recall one of them, the other one is this. What are you doing here, you have some kind of an electron distribution, right. When there is a resonant excitation, what you do essentially is that light comes in and then takes the state to another kind of electron distribution, right. You need to watch my hands. Let us say, this is electron distribution in ground state, this is the electron distribution in the excited state, stationary state, okay. So what we are saying essentially from Raman effect is that when light comes and falls on it, your electron cloud has not studied quantum mechanics, right, so it doesn’t really know that it is not supposed to get distorted from here to here. What happens is the distortion starts okay, but then after a while you run out of gas, you run out of petrol. Energy is not enough, energy of the incident light is not enough to take the electron cloud from this shape to this shape, which is stationary, so it takes it to whatever state it does with that energy and then since the light is gone, it just comes back, that is analogy number 1. I remember the analogy number 2, that is perhaps even more crude, that analogy is got to do… has got to do with basketball. Think of a basketball, you hold it in your hand, that is ground state, okay. If you don’t tire, and of course we are all dealing with ideal systems, so we will say that we are also an ideal system, our hands don’t tire, if you don’t tire, then you can hold the ball for an eternity, okay. Lifetime of the ground state is infinity. Then you throw it towards the basketball ring, if you throw it with the right direction and right energy, then what will happen, the ball enters the basket, and then it stays there for a few seconds, it falls, right. So that basket is analogous to an excited state of the molecule, it has a finite lifetime, are we clear. Of course if you tie the ends of that basket, then lifetime can be infinity, but fortunately its note. Now think what happens, if you throw the ball towards the basket, but with insufficient energy, let's say same... right... direction is right, in sufficient energy, what happens, the ball rises to some height and then falls, okay. Whatever, height it reaches is analogous to the virtual state of the molecule. How... what is the height that will be achieved by the ball? That depends on how hard you throw it. If I throw it like this, it will go up to this, if I throw it a little harder, it will go up to this, okay. So virtual state can be anywhere between the two stationary states, anything between these two can be virtual state. Quantum mechanically you write the wave function of that as a linear sum of all possible wave functions, there of course is not a Eigenfunction anymore. Now we come to Rayleigh and Raman. You have thrown the basketball it reaches whatever, height it reaches, it has not reached the basket, it comes down, and you catch it again, okay. Suppose you threw it from this side and catch it at this site as well, what is the total energy transfer? 0, right. However, you can hold it here, when it falls, you can catch it a little higher or you can catch it a little lower, right. Coming back to the molecule, what that would mean is that your basketball has reached this height, it comes down, and let us say you catch it here, that means it has come down to a level that is higher than the level of origin or it can come down lower, okay. Think of the energies of the photons that will be emitted in these two cases, in this case the energy is smaller than the energy that you have provided initially, so frequency is going to be Nu, how do you write it, Nu L minus Nu M. In this case frequency will be Nu L + Nu M. This is called a stoke shifted Raman scattering, this is called anti-stokes shifted Raman scattering. So we will stop here today, next day we will perhaps invest 10 15 minutes to complete this discussion and then move on to the next topic.

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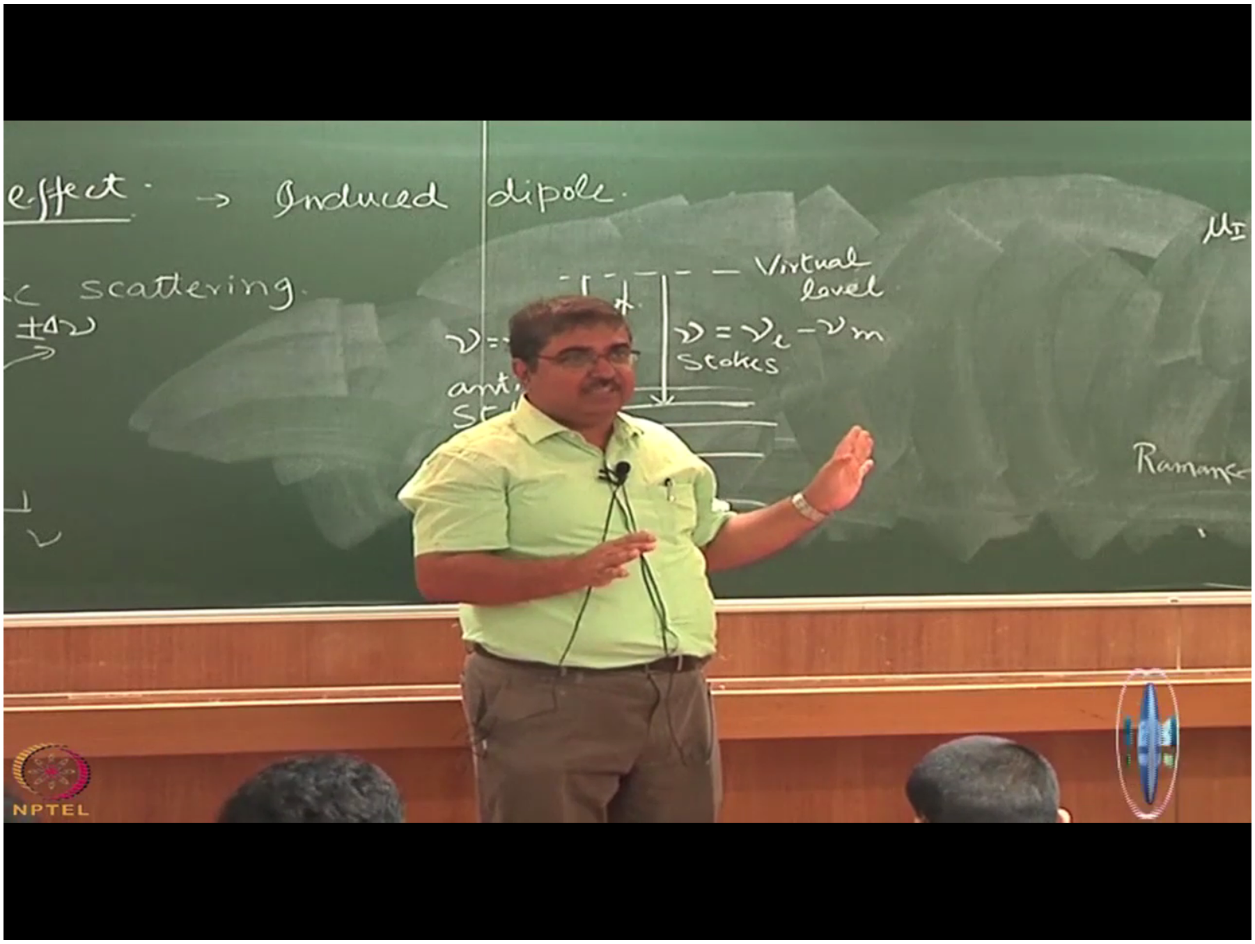
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