**MOLECULAR SPECTROSCOPY:
A PHYSICAL CHEMIST'S PERSPECTIVE**

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**Lecture No. – 29
Raman Spectroscopy and
Beyond Dipole Approximation**

So what we can say a little more easily than what a virtual state is we can say with a little more comfort what a virtual state is it. A virtual state is in the stationary state, okay, so anything that is there between two stationary states is a virtual state, it is not something for which sai star is constant, independent of time, it is not an eigenvalue of Hamiltonian is something in between so, you can even think that it is a construct that we require in quantum mechanics to explain Raman effect and something else that we are going to talk about shortly, okay, that is what a virtual state is, so it can be anywhere in between which takes us to an important consequence which will talk about in a few minutes.

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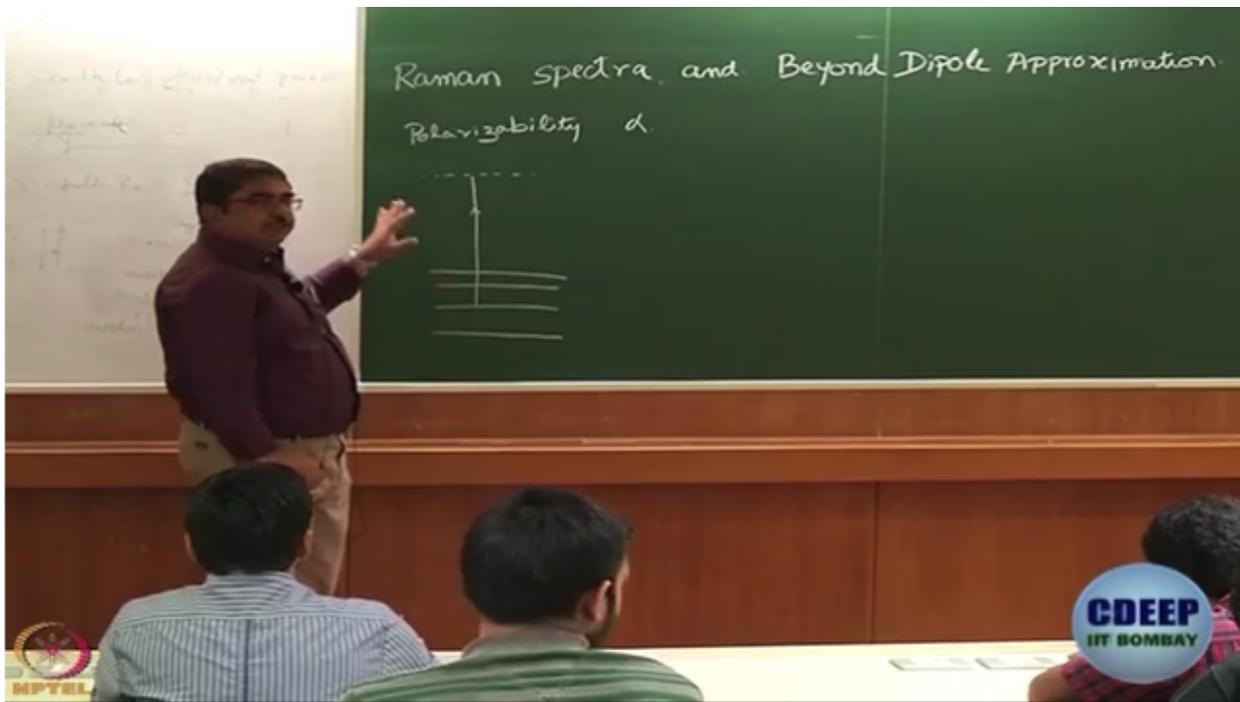
So what we said is that in Raman spectroscopy we have a transition to a virtual state and then when the system comes down if it comes down to the same state, first of all it is called scattering. Why is it called scattering? Because the second level that is involved is actually a virtual level, not a real level, okay, not a stationary state, so first of all it's a three state operation, out of which the initial and the absolutely final states are stationary states, but the intermediate one is the virtual state, so if it comes back to the same stationary state, what kind of a scattering is it? This is called Rayleigh scattering, you might think that it is the elastic scattering of photons in which no exchange of energy takes place between light and molecule, alright, but we discuss two other situations one in which you come down to a higher stationary state, one in which you come down to a lower stationary state, in this case the energy of this scattered light will be less than the energy of the incident light, so this is called a stokes shifted scattering.

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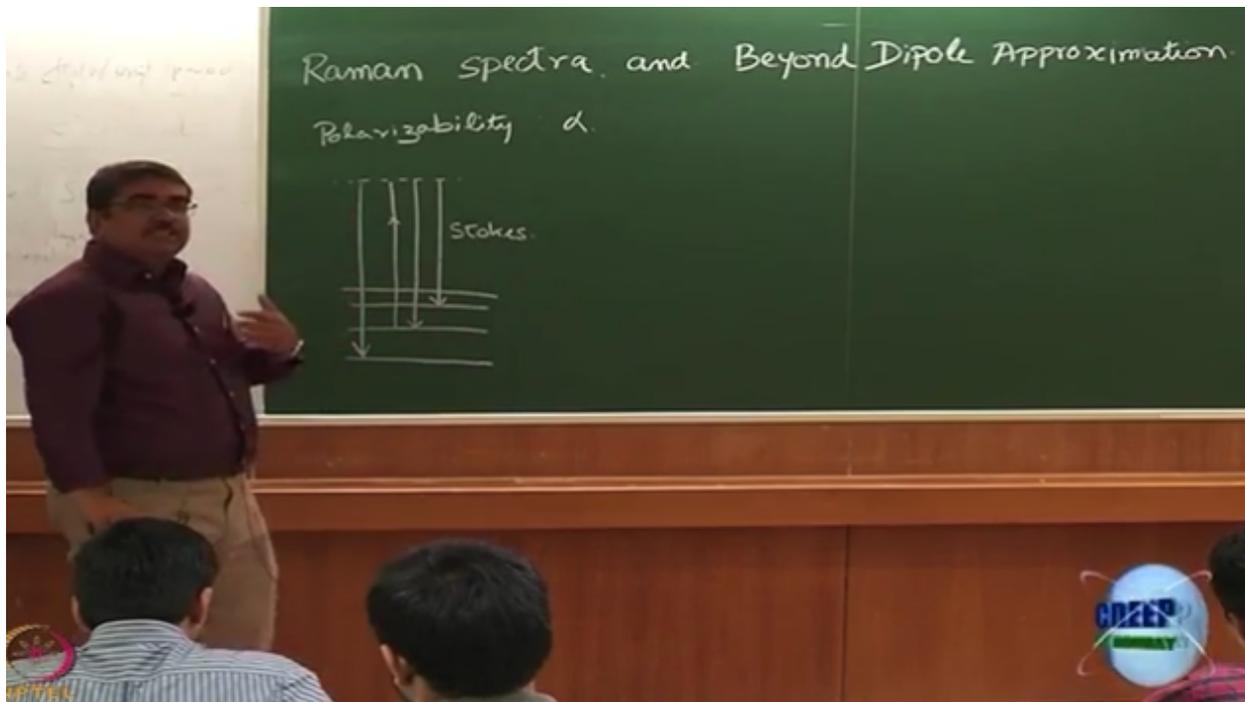
Stokes always means, a stoke shift always means a shift towards lower energy, great shift, and this is called anti-stokes scattering, and please remember the name of the scientist was Stokes, it was not stoke, so please don't write stokes shift with an apostrophe before S, you can write it with an apostrophe after S but that is not required, you just name after stokes that's all, okay, so this is what it is.

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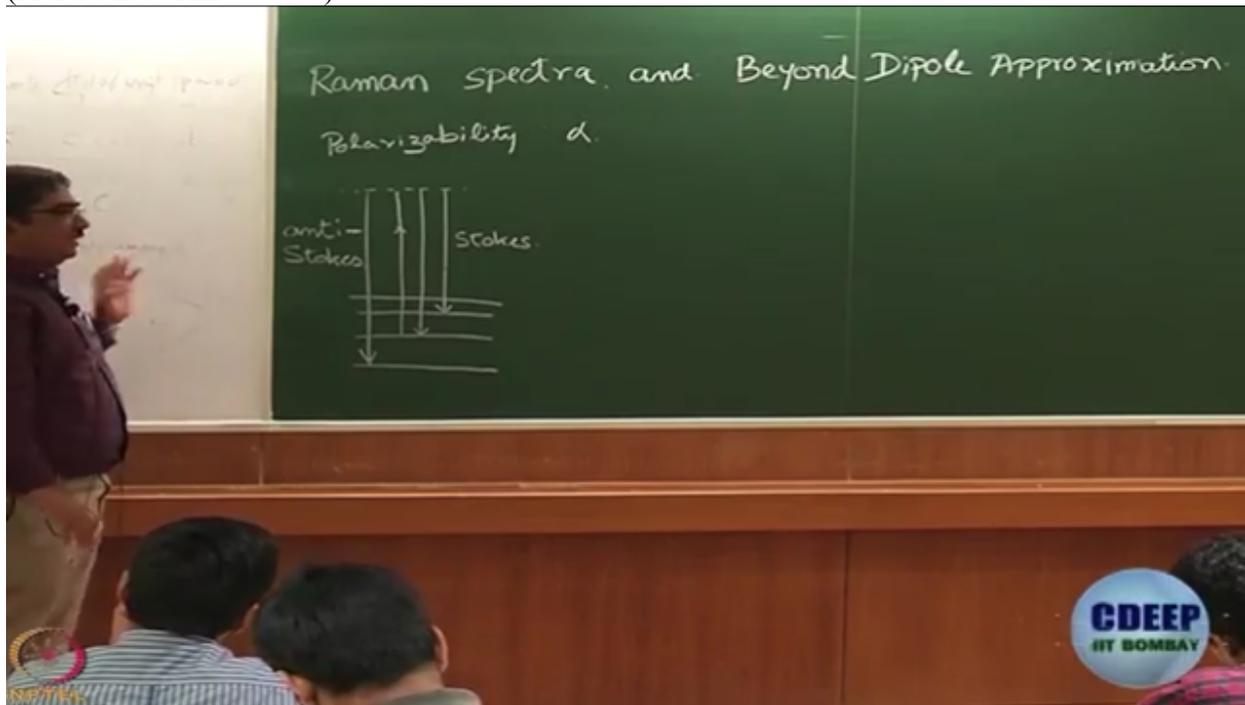
Now these levels could be vibrational levels, they could be rotational levels as well. In rotational Raman without derivation let me just tell you, and this is one of the few instances where we are going to actually have to take things extrasomatically we do not have the scope of deriving this selection rule unfortunately in this course, if you study a course in advanced spectroscopy in case it is offered next year, then perhaps you are going to study derivation of this selection rule, to do this you need to know matrix mechanics and you need to learn a few more tools of quantum mechanics without that there is no point in trying to derive it. If you read Banwell's book there is some hand waving argument, well let me write this selection rule first, for rotational Raman the selection rule is delta J = +-2,
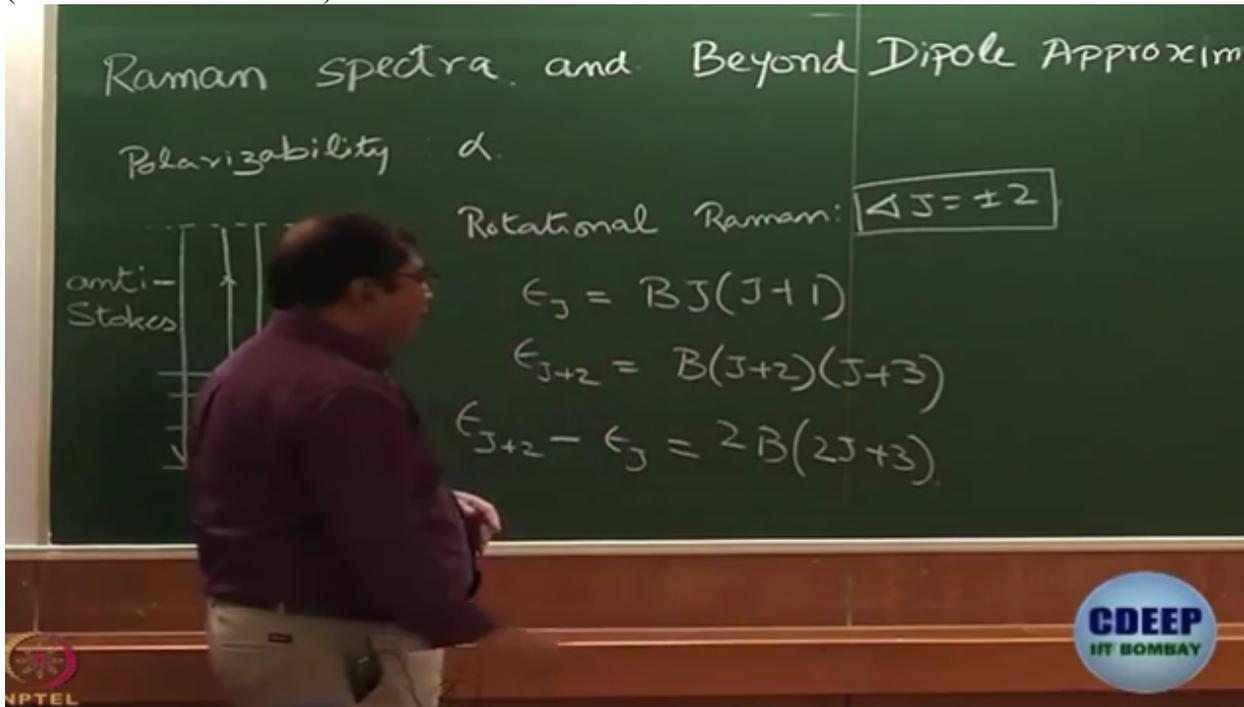(Refer Slide Time: 04:09)
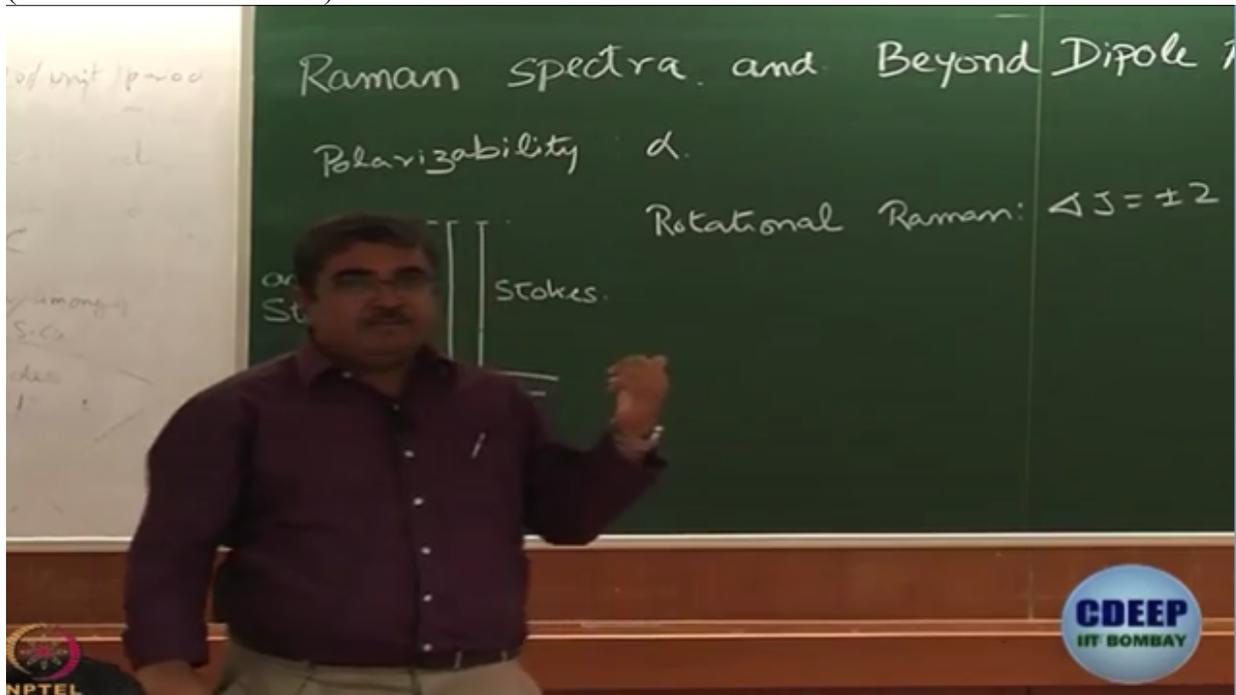


which of course you can see right away is different from the selection rule that we had in microwave spectroscopy.

Now why is it +-2? There is some hand waving argument that when the molecule rotates it presence the same polarizability ellipsoid twice to the field, but personally I do not like that argument, I mean if it makes sense to you, great, I don't understand that argument to be very honest, it comes from rigorous quantum mechanical treatment of the problem which you cannot do, so therefore let us just take extrasomatically for now, that for rotational Raman delta J = +-2 is the selection rule, okay.

What do the rotational spectra look like in that case? Of course you know what is the energy in centimeter inverse of the Jth level? BJ (J+1), energy in centimeter inverse of J+2 will be equal to B(J+2)(J+3), so what is your epsilon J+2 – epsilon J? Help me please. I know there will be a B, B multiplied by what? Yes, B square no, no, J square will cancel actually right, J square here and I'm subtracting this so J square goes.

What is the term in J? 3 + 2, 5, 5J – J here that will be 4J and what is the term independent of J? 6, so basically it is 4J + 6 I can take 2 out and write 2B into 2J right?
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2J+3 what is the range of J? 0, 1, 2 so on and so forth, and so this is the energy that you have for J to J+2 that kind of a transition,
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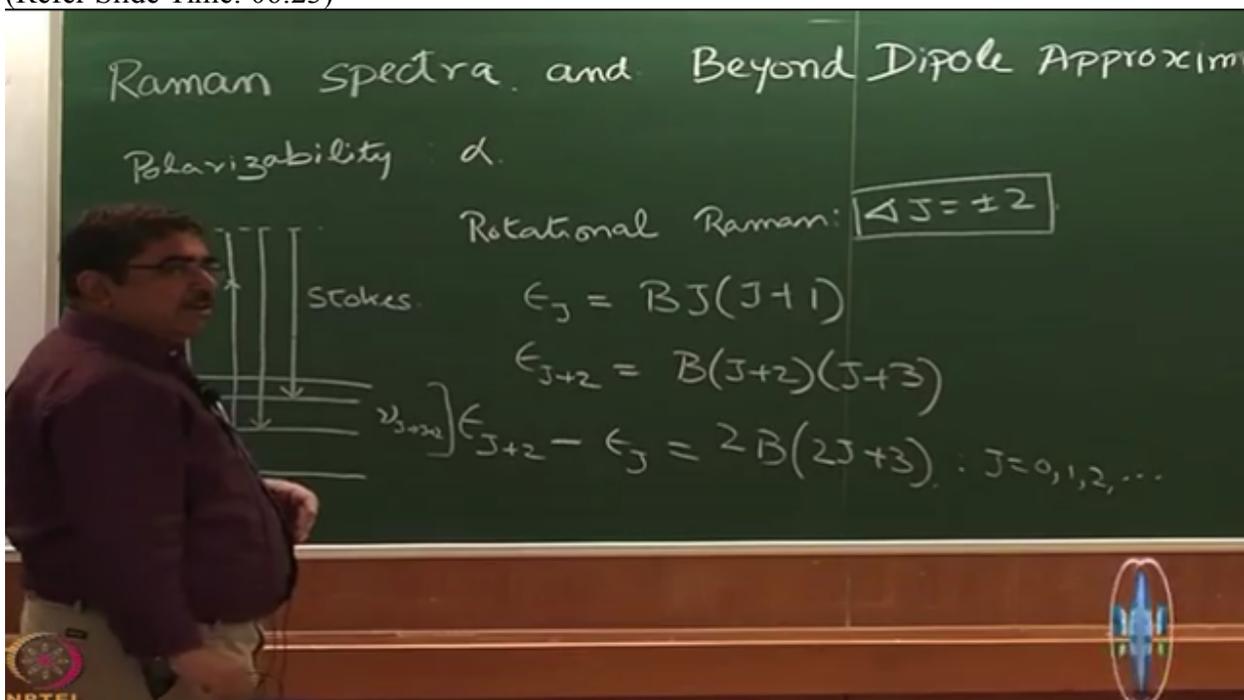


what about J to J-2? Well you get exactly the same kind of expression if you write something like this, nu J – 2 to J, why do I want to write it like this? If you remember what we did in

rovibrational spectroscopy, if you write it like this then once again J ranges from 0 to this whatever, infinity, okay, so then also you get exactly the same expression with a minus sign, right, with a minus sign, -2B into this, alright.

What do the spectra look like? Now when you plot Raman's spectra usually what you want to do is you want to have X axis as delta nu, because whatever you're measuring here, if nu X is the energy of excitation, and if nu S is the energy of scattered light you take the difference that is delta nu right? Actually it is this delta nu that gives you information about the spacing between the levels, of course this picture is not entirely correct for rotational levels because delta J is +-2, so this would have come down not here, but here, this is the delta nu that you would measure, okay.
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So delta nu 0, here do you have a line? Do you have a line at delta nu = 0? You do, and you have a very, very strong line that is due to Rayleigh scattered. Okay, for Raman when delta nu is positive, what is it? Is it stokes shift, is it anti-stoke shift? For delta nu positive, how many think it is stokes? Hand, stokes or anti-stokes? Everybody thinks its anti-stokes, right, of course you are right, so delta nu positive is anti-stokes, this side is anti-stokes Raman, and this side is stokes.
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Now here let me make another point, we are plotting delta nu right, do we agree that it does not matter what kind of excitation frequency I use, delta nu will be the same. See here the diagram I've drawn, in this diagram I have drawn, we have promoted the molecule from this stationary state to this virtual state that is there, so let us say I use a different frequency and cause the promotion to virtual state that is here,

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will that change delta nu? No right, it will change the frequency of this scattered photon that is right, but if you take the difference of frequencies of scattered and excitation photons they should

be the same, because delta nu is characteristic of the molecule that you have taken, right, this is an important aspect of Raman spectroscopy excitation wavelength does not matter, unless there is an unless will come to that later, but for regular Raman spectroscopy the good thing is remember when we talk about absorption spectrum in the beginning of the course or even when we talked about emission spectrum we said that you must have a tunable source, even for emission spectrum we had to excite a different wavelengths because we did not know which molecule would absorbed at which wavelength, that problem doesn't exist here, what you need is you need an intense source at any wavelength does not matter, there are many Raman setups that you can see with only one laser as excitation source, so why is one laser enough as excitation source? Because it doesn't matter to which virtual level you take it, delta nu would still be the same, point number 1.

Point number 2, why do we need a laser at all? We need a laser because you want this signal that you get from Raman is not very strong, it's a weak signals, weak scattering, okay, so you want to excite as many molecules as possible to get a good signal, so intensity of the laser that's an important parameter, second important parameter is the high degree of monochromaticity of the laser, because if there is an uncertainty in your excitation wavelength itself then the spectrum that we are going to draw now that will also have that inherent width of lines built into it, so your spectrum will not be very well dissolved, okay.

The third reason is that lasers usually give you polarized output, okay, but that will come to that when we talk about poly atomic molecules, okay. Now let us see where the first line will be, where will the first line be for this one $J = 0$? So if I put $J = 0$ here what do I get? 6B right, 6B and where will I get the first line in the stoke side? -6B, where do I get the next line? 18B 10B yeah.
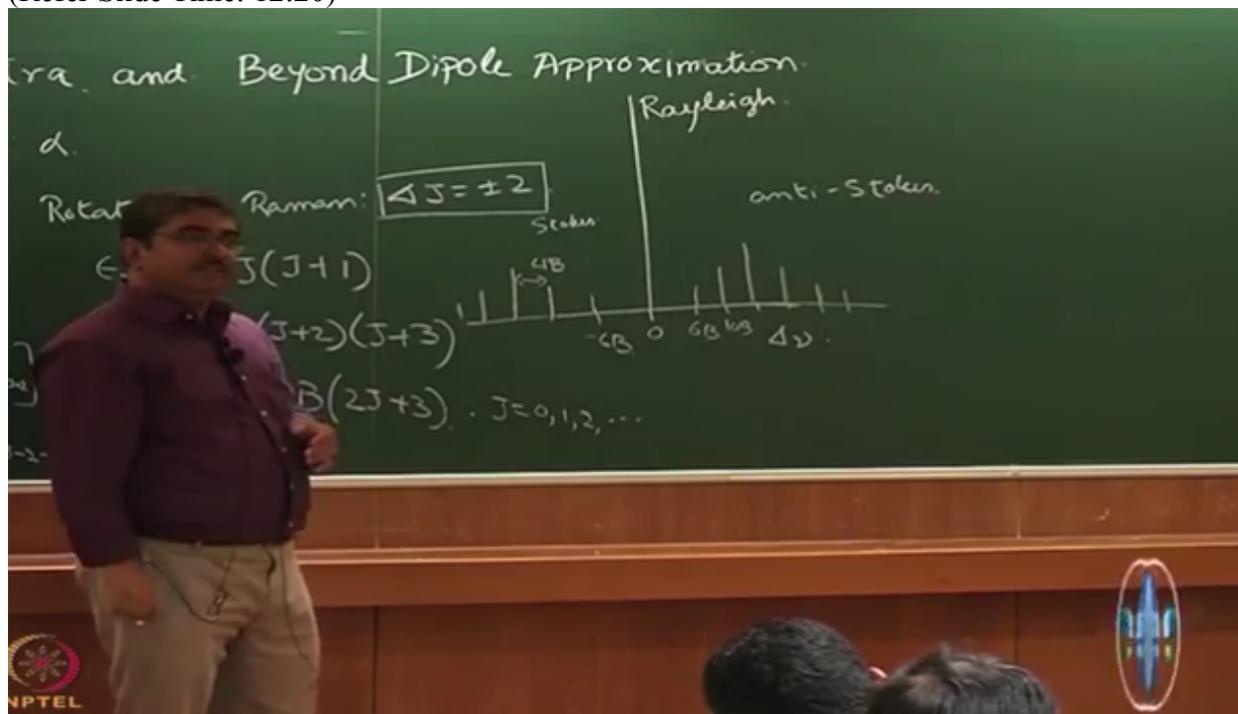(Refer Slide Time: 11:50)

Next line, 14B and so on and so forth, so what we get is this you get a spectrum that would look exactly like the rotational spectrum except for the fact that the separation of the lines is going to be 4B and not 2B,

okay, so for rotational Raman, what you get is you get what looks like a PQR structure, remember that PR structure here you also have a Q band, why do you have a Q band? Because Rayleigh's scattering is there, that is not Raman's scattering. If you want to be very conservative and say I'll talk only about Raman's scattering then it is PR structure, but if you look at this spectrum as a whole, it is PQR structure, Q is strong because that is Rayleigh's scattering, and P is the stokes shifted Raman, R is anti-stoke shifted Raman, they look like absorption spectra go through a maximum.

Why do the P and R branches go through a maximum? Same reason why your microwave spectra go through a maximum, I believe even in the statistical thermodynamic course you have learnt how to evaluate J max, right, so there is a J max which is more than 0 that is why it goes through a maximum, so this is what rotational Raman spectroscopy is all about, so what we learn is this, if you remember 2, 3 weeks ago we had stopped our discussion of rotational and vibrational spectroscopy with the question that is it impossible to get an idea about the bond length of something as simple as H2, because it is homonuclear diatomic does not have a permanent dipole moment and therefore is microwave inactive, but then we know very well that if he can determine B, we can determine bond length, can we not determine bond length of dihydrogen using spectroscopy, now you know the answer, we can, it's just that you cannot do microwave spectroscopy you have to do Raman spectroscopy, okay.

So that question that we had take a range icon at that time that is now answered, even though we have not really gone through the entire process of derivation of the selection rule, so what is the biggest difference? Difference is that the separation, there is another issue that comes in here, but

we are going to discuss that only after we have talked about electronic spectroscopy that issue is statistical weightage of different rotational levels, so once we have discussed, once we finished discussion of electronic spectroscopy we'll revisit this and you will see that the intensity that you have here is not entirely due to population, population itself not mentally due to your Boltzmann distribution, the population gets modulated significantly because of symmetry of the wave function.

Now this is rotational Raman, what about vibrational Raman? We'll do an even more sketchy job of discussing vibrational Raman at the moment for diatomics, because we are going to discuss it in much more detail from the point of view of symmetry when we talk about polyatomic molecules, but once, can you tell me what is going to be one significant difference between rotational Raman and vibrational Raman? Meaning what? Vibrational Raman we never band structure, meaning what? So what you're saying is that vibrational Raman will have fine structure due to rotation, is that what you meant? Okay fine, but there is something more fundamental, and even that has got to do with Boltzmann distribution, depending on temperature we'll be observing different population, okay.

So one thing at a time that is the right answer, but as usual it is more detailed than what I wanted, so what happens at room temperature? Which vibrational levels are populated? Only V = 0, right, so how does this diagram change in that case of vibration? For vibrational levels, these are not scaled, this is let us say the virtual state all upward transition will begin from V = 0, isn't it? V = 1, very few molecules are there in V = 1, so when it comes down it will either come down here to give you Rayleigh's scattering or it'll come down here or here somewhere to give you a stoke shifted Raman's scattering, so anti-stokes lines are not easy to observe when you look at vibrational Raman, so in rotational Raman you get stokes as well as anti-stokes band,
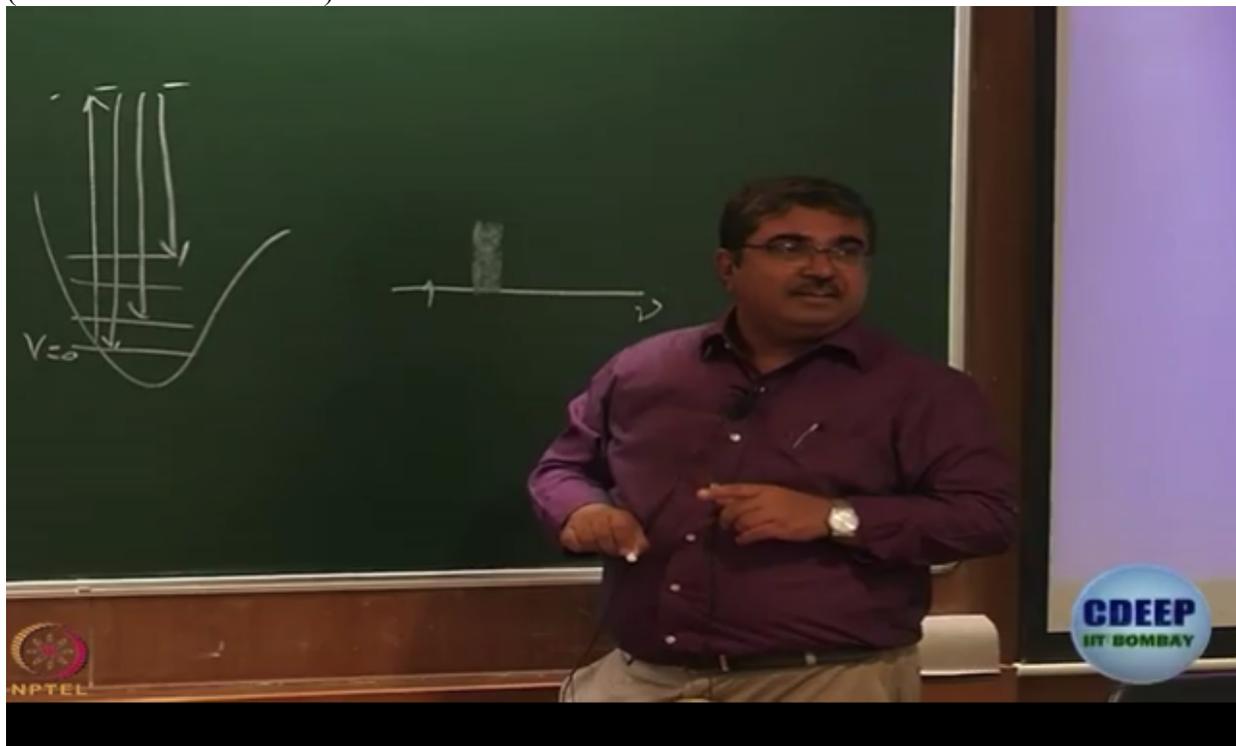(Refer Slide Time: 16:58)

in vibrational Raman at room temperature it is not so easy to observe the anti-stokes band, why because $V = 0$ is the practically only populated level.

But of course we don't stop there, Vijay don't stop saying that God has made it in this way that only $V = 0$ is populated therefore you cannot see anti-stokes Raman, in fact if you can see anti-stokes Raman in some way it is easier to interpret, you know why because the problem with stoke shifted Raman is this, you excite at this nu, now I'm plotting against nu, the band comes somewhere here, especially for vibrational Raman this is a part of an electronic manifold right, (Refer Slide Time: 17:52)



right? So you have some other electronic state here, it can be emissive, so very often what you have is this Raman over lacks with a much stronger fluorescent signal, (Refer Slide Time: 18:07)
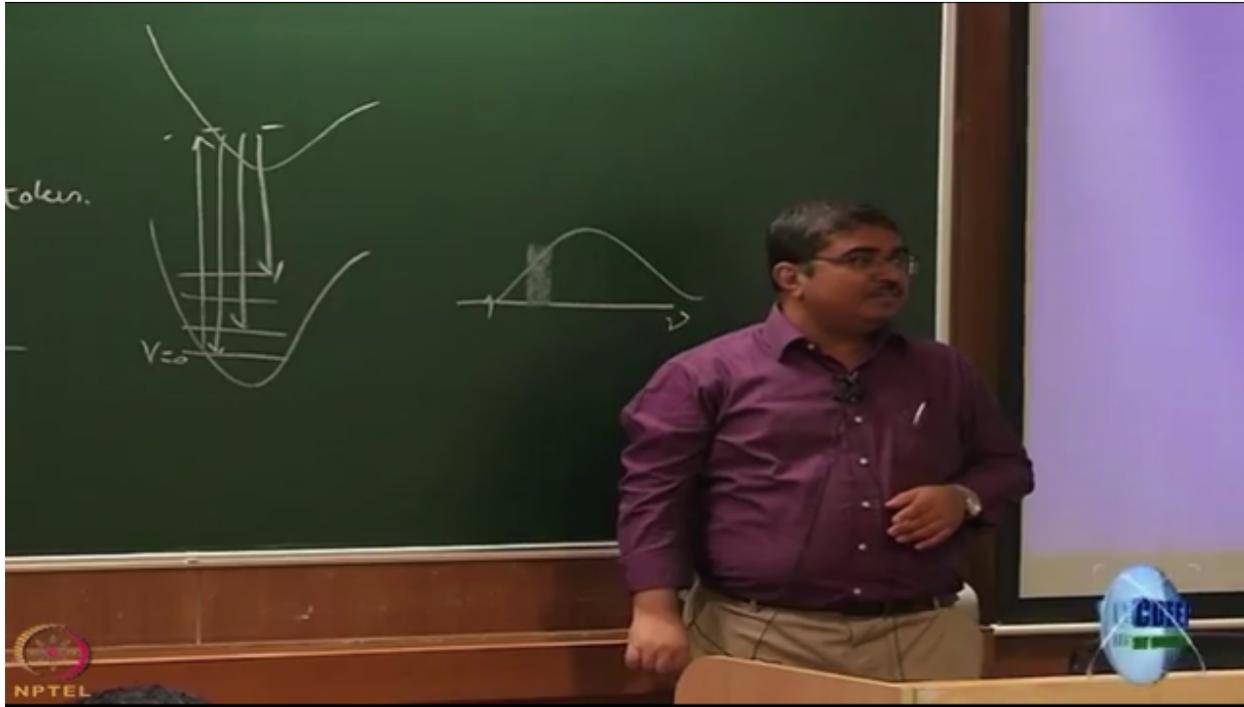
so that is why Raman spectroscopy and fluorescence spectroscopy don't like each other, for fluorescence spectroscopy is this Raman band that shows up in fluorescence spectra more often than not especially when you work with the weak therefore is a nuisance.

For Raman's spectroscopy is this broad and often strong background that you get from fluorescence is a nuisance, okay, so that is a problem with stoke shifted Raman's spectroscopy, there are ways to work around it of course, but one another way to do it is that instead of using one laser if you can use multiple lasers, remember a pumping, remember what we said about lasers, you had to pump and you can populate an excited state, if you can do that these are the vibrational levels, this virtual level is there, take it here somehow if you can make the system come down here and remain there until there is a significant population and then if you can somehow pump this level then you can see anti-stokes lines,
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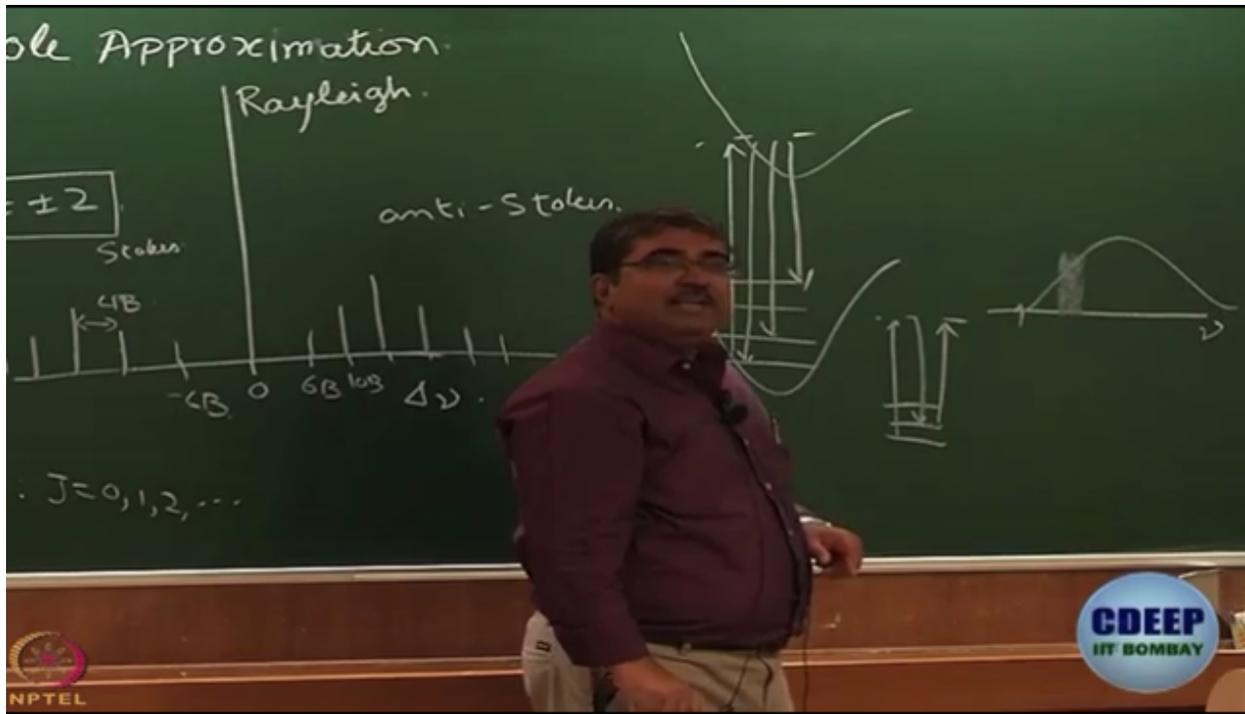
of course what it means is that you need one laser to do this, and another laser to do this, so it makes it a more complicated experiment, and the name of this experiment you might have heard is cars.

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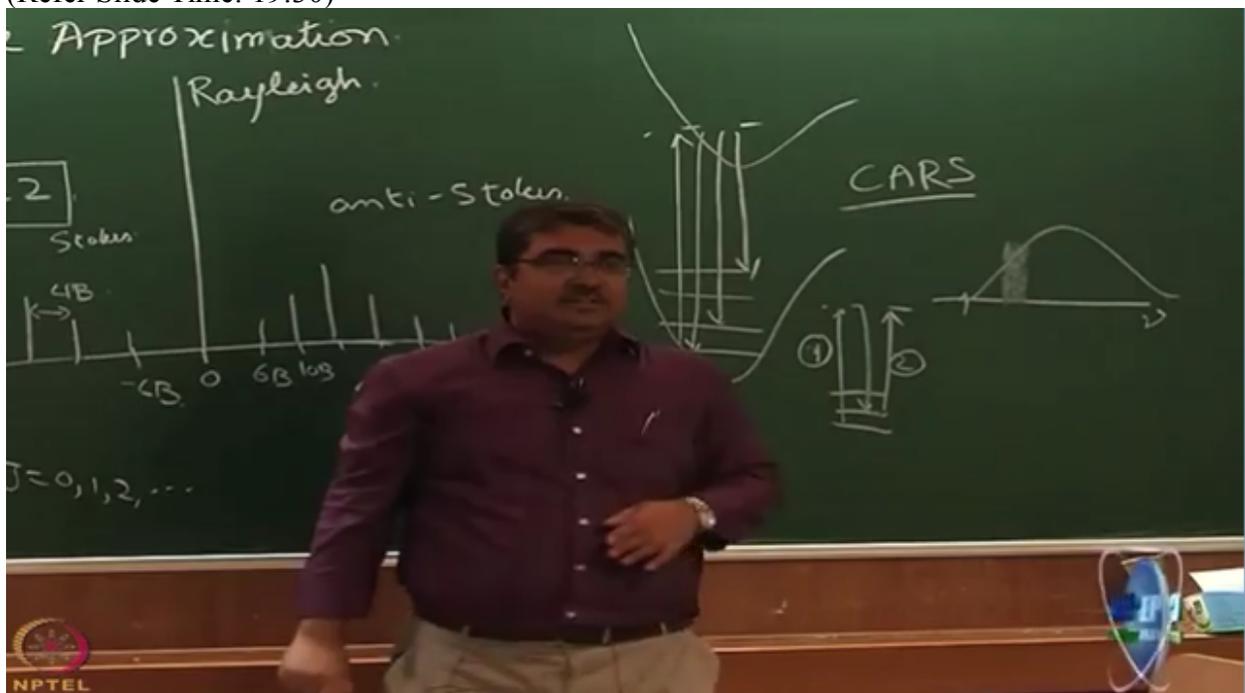


So you are not talking about Maruthi cars and Indica cars and all that here, cars means coherent anti-stokes Raman's spectroscopy, right these are more complicated technique once again we'll not discuss here, but you should be aware that something like this exists by which you can amplify the anti-stokes lines and you can actually see them, alright, that is one part of the story.
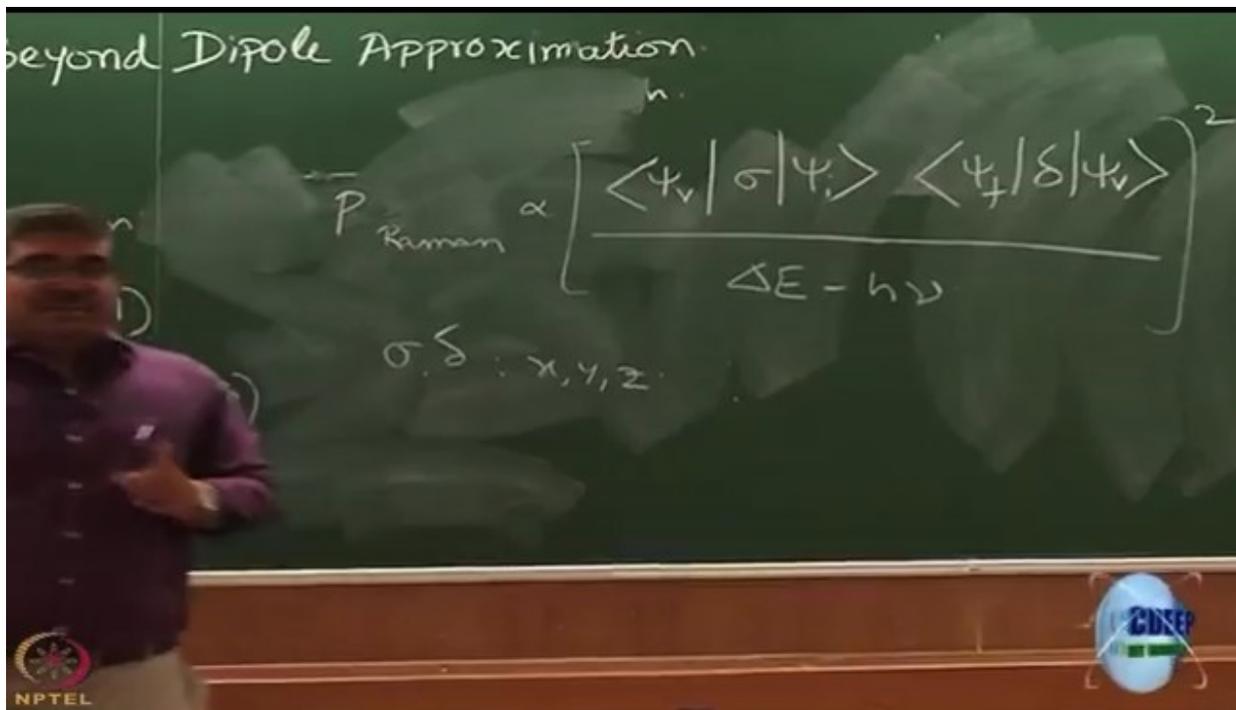
Another thing that I want to say is this, now once again without derivation since you have been very kind and polite and believing whatever I have said so far today, let me take advantage of that kindness and let me write little sketchy expression for what is called the Raman cross section, you can think it's performability of Raman transition, okay, I'll write it as sigma Raman, that is proportional to something like this sai V, where sai V is the, you can say the wave function for the virtual state which you can write as a linear combination of the wave functions of the stationary states, sigma this is sigma that is sigma we got a problem right, so I'll just write P.

Sai I, what is sai I? Sai I is the wave function of the initial state, and what is sigma? Sigma is either X or Y or Z, so it is sort of a transition moment integral, right, if you remember in transition moment integral mu you can write as mu X, mu Y, mu Z and in fact what is mu? Mu is your charge multiplied by separation, so you can actually write it as electronic charge multiplied by X, or Y, or Z, so you just doing that, we are writing either X or Y or Z, okay, but now that is not the entire story right, this stands for the promotion of the system from the initial state to the virtual state that is multiplied by another transition moment integral type of integral which is sai F you can understand that F stands for final.

Now I'll write delta, delta is also either X or Y or Z, sai V integrated over all space,
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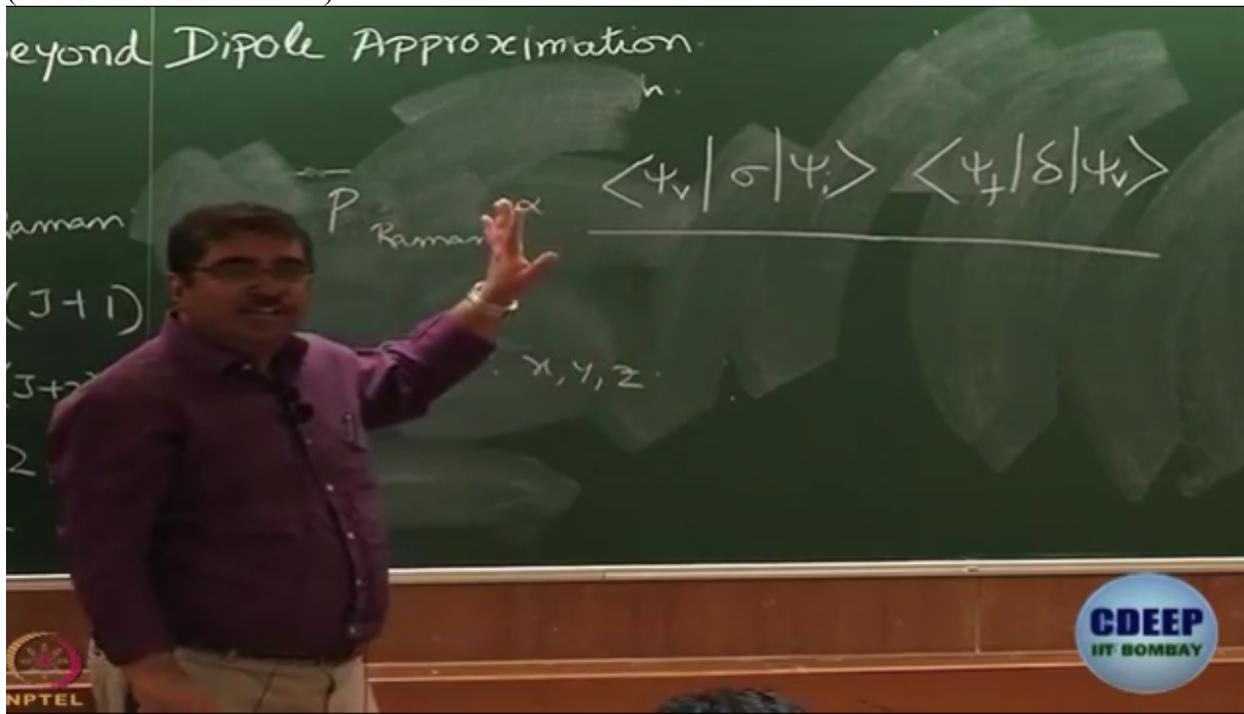


so even though we have not derived it perhaps you can kind of understand what this expression would mean, the first integrals stands for promotion from sai I to sai V, the second integral stands for the, should I call it demotion from sai V to sai F, alright, okay, please believe me on this. And the denominator is delta E – H nu, and well this is whole square,
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beyond Dipole Approximation

$$\bar{P}_{Raman} \propto \left[ \frac{\langle \psi_v | \sigma | \psi_i \rangle \langle \psi_f | \delta | \psi_v \rangle}{\Delta E - h\nu} \right]^2$$

$\sigma, \delta : x, y, z$

so this leads to two consequences, first of all what happens when delta E = H nu? Delta E = H nu, basically means that virtual state is actually a stationary state or energy of the virtual state is very, very close to another stationary state, in that case this term blows up, of course don't forget it's proportional so it will probability will never be more than 1, okay, it will actually much less than 1, but this term blows up that's a main point, so when it blows up what condition is that? Delta E = H nu, resonance condition right, this term you conveniently drop Boltz name, we have taken it 1, 2 many times, resonance condition.

So when this condition is satisfied the Raman spectroscopy that you do in this condition is called resonance Raman's spectroscopy, and the advantage of resonance Raman's spectroscopy is that since the term has blown up intensities are really very strong, okay, and this comes handy when you want to study really large molecules especially biomolecules, I'll discuss an example perhaps that will at least let us understand why resonance Raman is important.

I think we know the structure of hemoglobin is there a yes, is there a no? Okay, so hemoglobin consist of two parts, not very difficult, hem part and globin part, globin part is the protein part right, protein means its made up of a chain of amino acids, and hem part contains iron and something that looks like a prefoldin, okay.

Now what color is blood for human beings? Blue, for some of us maybe yes, but you actually cannot see that color, the color that you see is red, right, why is blood red? Which transition, which part? Yes hem part, hem part, the iron part, the iron part that is there that actually has a very strong absorption around 400 nanometer, so it absorbs all the blue light, what is left is red, okay, that's why blood is red. So 400 nanometer so you can think of it like this, I'll not draw the structure because first of all I don't remember it, secondly it is too complicated, so it's something like this,

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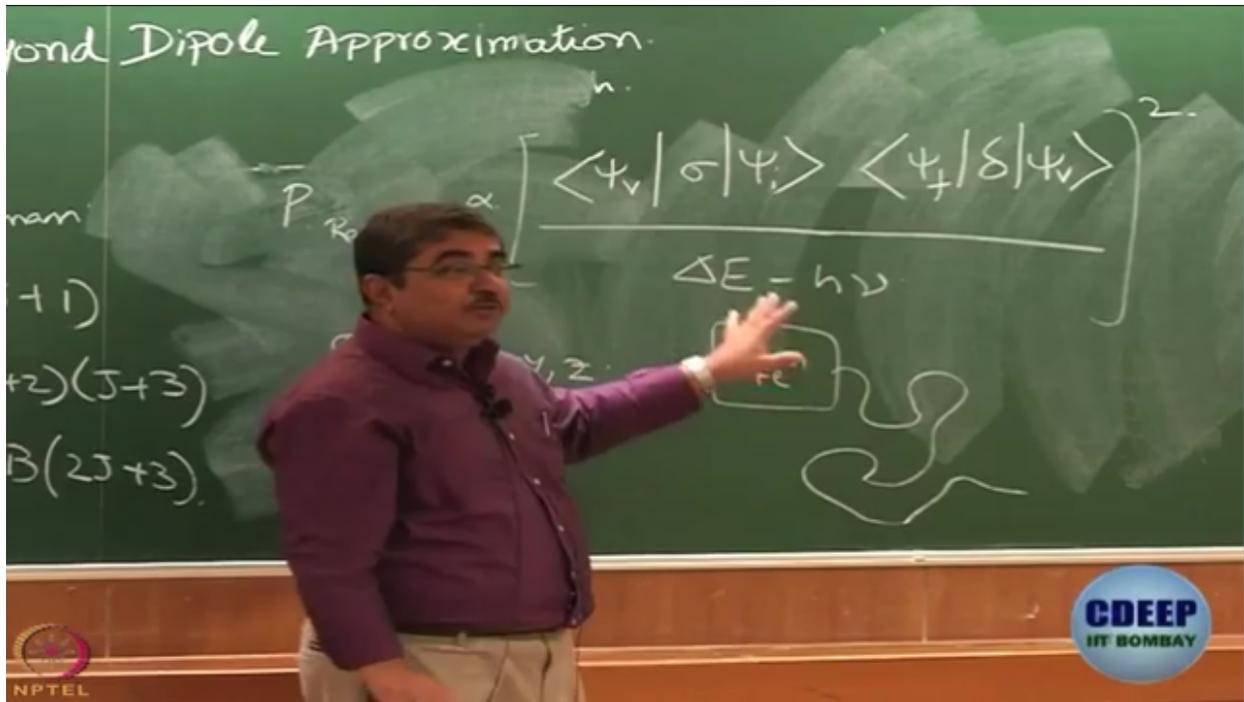
and of course hemoglobin for those of you who know it, hemoglobin is not just like this it is, how many mar is it? Is a tetramar actually right, 4 such units are joined together that leads to some interesting properties why hemoglobin can act as an oxygen transporter, so that let's not get into that.

So this part absorbs strongly at 400 nanometer, the protein part absorbs strongly at say 290 nanometer
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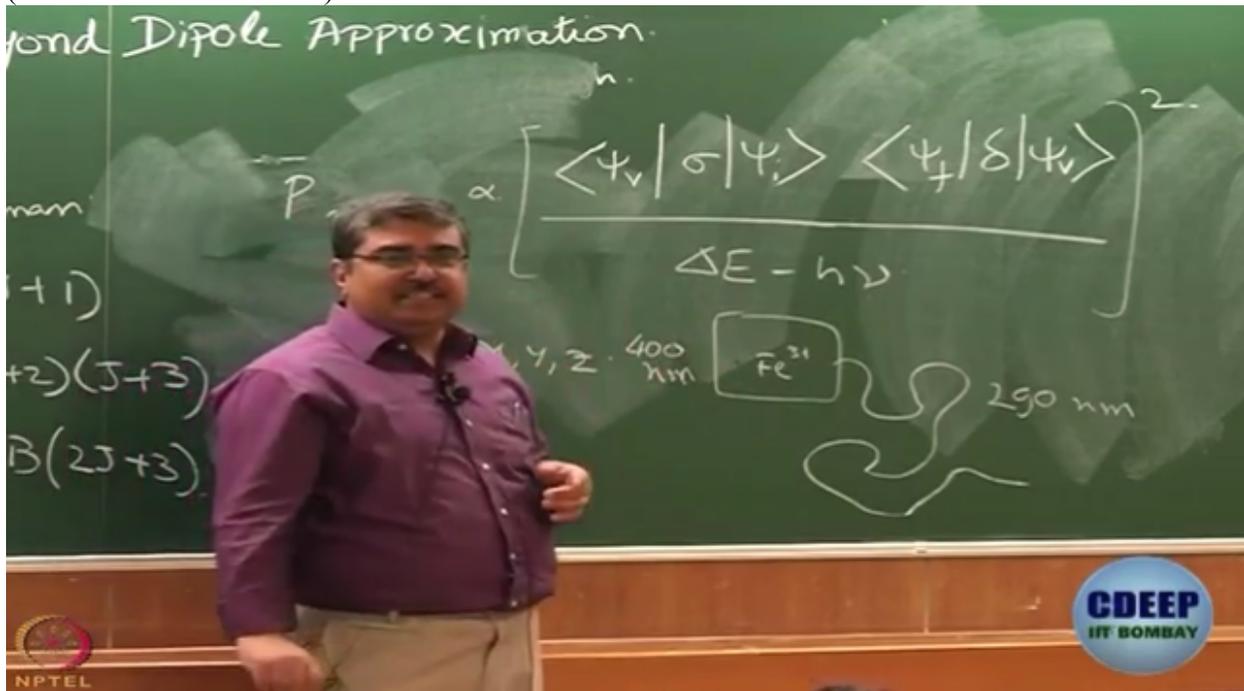
because there are some tryptophan residues which absorb that wavelength nicely, okay. Now problem with doing Raman spectroscopy of a molecule like this is that it's so big, that you will have a 100 of lines perhaps, so it's very difficult to understand which line is for which part, but then if you use a 400 nanometer laser then you selectively get Raman's signal from the hem part, okay, and it is a little easier to analyze. If you use a 290 nanometer laser of course it is not so easy to make a 290 nanometer laser as far as I know, no 290 nanometer laser exists so far, but we'll discuss in a few minutes how you can still get 290 nanometer laser light, so if you use that then the protein part comes into resonance, and so what happens is the Raman spectrum might be something like this whatever, okay, let us say for the sake of understanding this is for the hem part, this is for the globin part, so when you use 400 nanometer this part shoots up, this lines become really big compare to these, so you cannot even see the globin part spectrum compared to the hem part spectrum.

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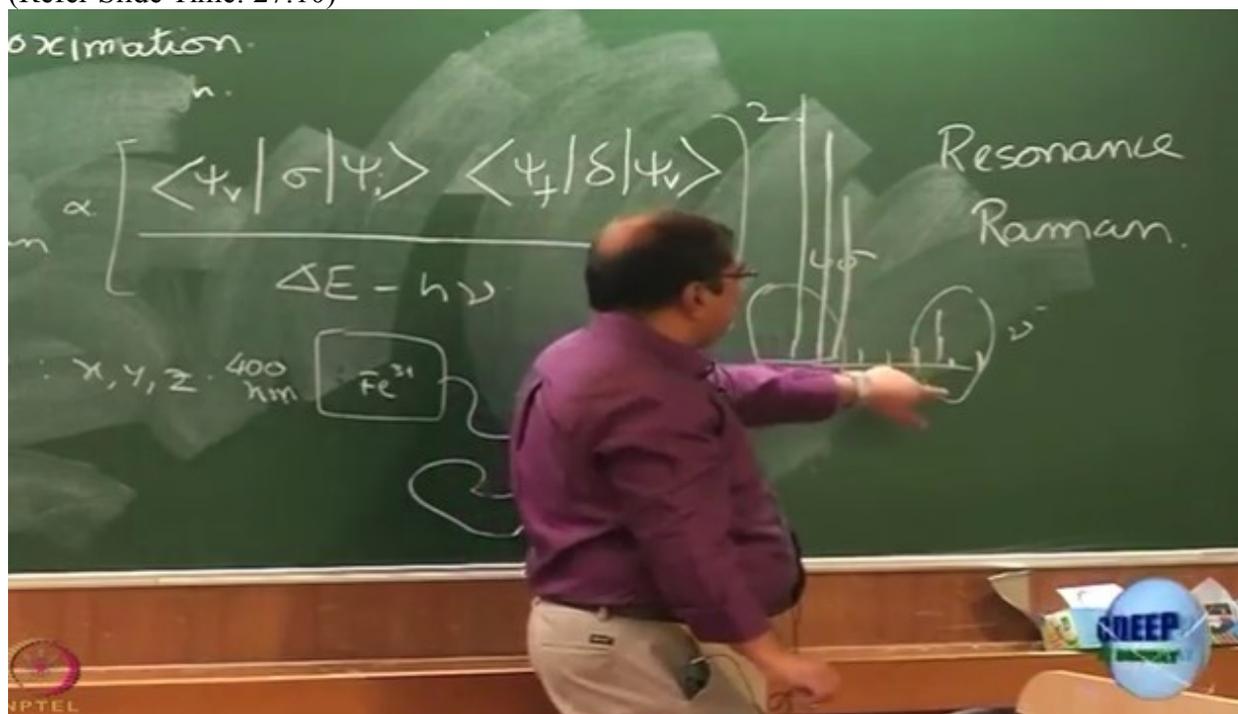


When you use 290 nanometer this part becomes huge, this part doesn't, okay, that is how resonance Raman works. Now any question so far? That is the advantage you can study complicated molecules or materials. What is the disadvantage? Disadvantage is that now that you have resonance, this problem of fluorescence becomes even more pronounced, okay, so when you do resonance Raman you need to do away with fluorescence, one way of doing it is to work using what we are discussed earlier Fourier transform of spectroscopy then you can very easily separate frequencies and you can get a nice resonance Raman's spectrum, okay.

Last question to be discussed in this part is this, I told you that there is, it is not so easy to remember the relationship between Einstein A and B coefficients, A coefficient becomes more and more predominant as you go higher up the energy ladder, 290 nanometer is in UV, so it is not so easy to get spontaneous emission there, okay, so how do I get 290 nanometer laser light? You get it by a process which is called second harmonic generation, but before that let me simplify this a little bit, so we have discussed the denominator, let us now focus on the numerator.

With a little bit of manipulation in the numerator what you can do is the part that matters is this,
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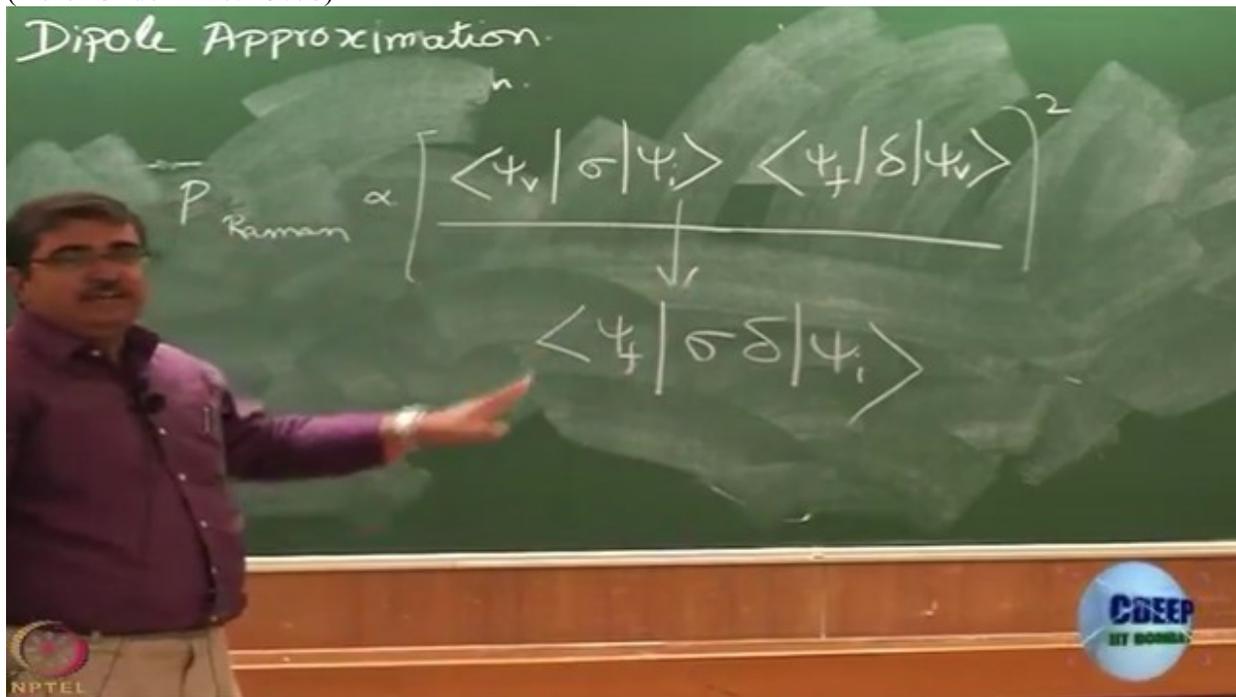


okay once again we are not doing the maths, we have to just believe me on this unfortunately but this is the final integral that tells us whether a Raman transition between sai I and sai F is going to take place or not, so you see the difference between this integral and the transition moment integral that we had use for resonance spectroscopy is that, well the wave functions are the same, but in the middle you don't have one coordinate, you have a product of two coordinates, okay, that is what we need to know, you have a product of two coordinates, okay.

Now let us discuss something else, as you will see this will have profound in implication when we discuss Raman activity and IR activity of poly atomic molecules, but before that let me discuss something very quickly this issue of second harmonic generation, and now I'll just draw like this, let us say these are two energy levels stationary states, this is the third stationary state, this is the virtual state somewhere in the middle, okay,
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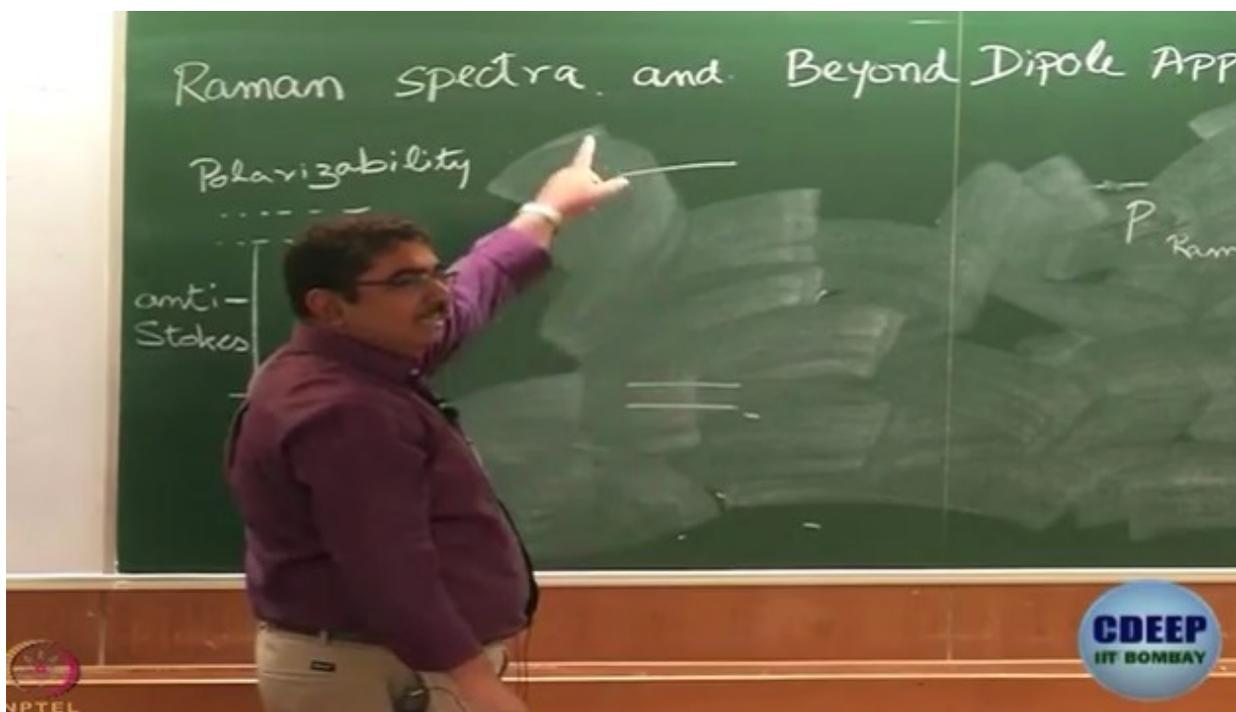
using laser you have done a promotion to this virtual level, what we have discussed so far is that now the molecule can come down to give you Rayleigh's scattering or Raman's scattering, okay.

Suppose I use very intense laser, okay, so intense laser that at the moment of excitation many other photons are available to interact with the molecule in the virtual state itself, don't forget life time of virtual state is 0, of course nothing is 0 0, but 0, very very small, so at the instant of excitation if you have a large number of photons then it is possible for another photon, it is possible for another photon to take the molecule from this virtual state to this stationary state, okay, so typically the wavelengths should be the same, so this virtue of state would be somewhere, exactly in the middle, so what we are saying is your one photon taking it from a stationary state to a virtual state, another photon taking it to this state, okay, this is called two photon absorption,
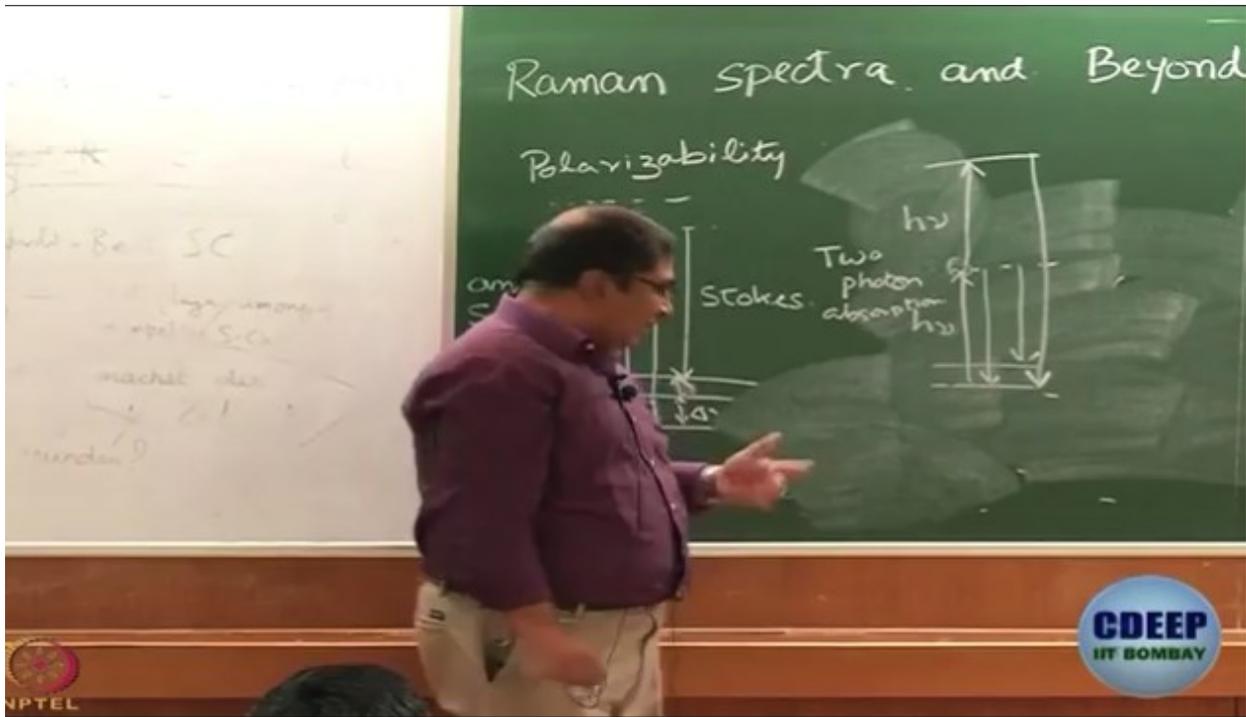
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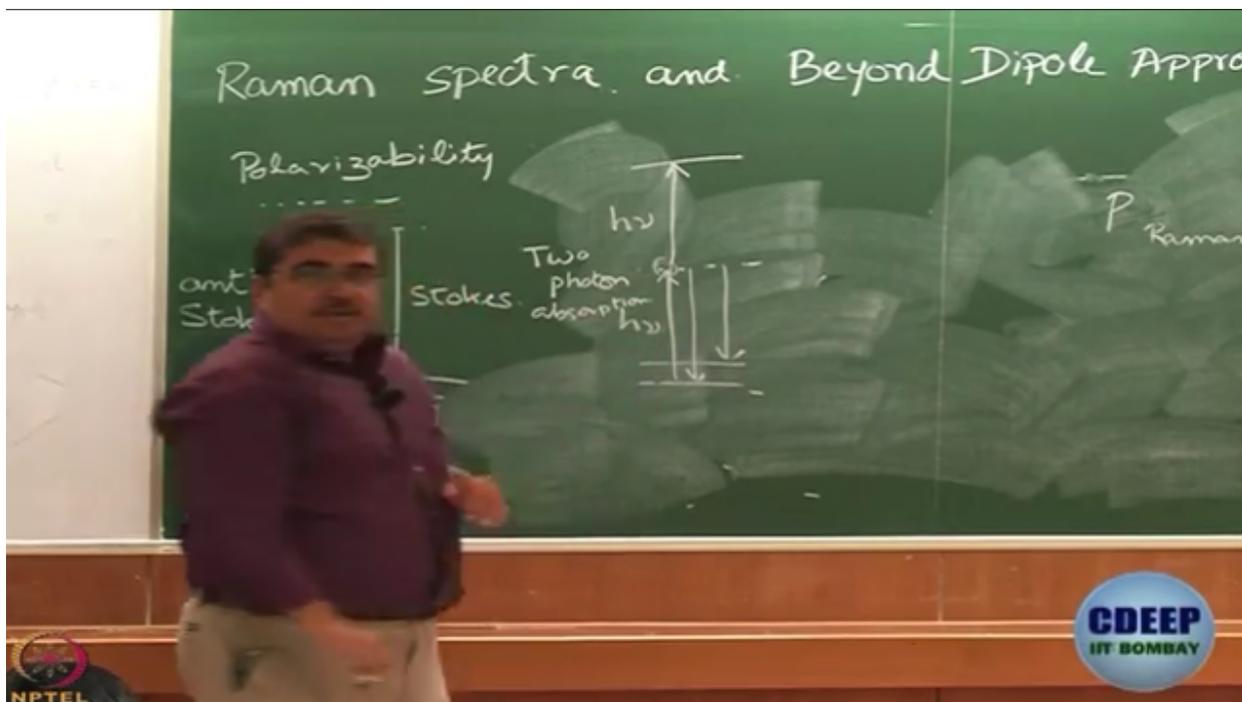
very crude analogy is you have two drops of water on a surface, okay, if you blow on the drops carefully what happens is, they can qualys, right or if two rain drops fall one on top of the other on the ground they join up to give you a bigger drop.

Here also what's happening is each photon is like a droplet of energy, right, two droplets of energy join up to give you a larger droplet that is the poetic rendition of two photon absorption, right, so this is what it happens.

Of course there is a lot of, lot of photon chemistry to do, quantum mechanics to do here, we are bypassing all that, in order to do this you need to have an idea of the density matrix, okay, so I have no option but to just tell you the story, alright.

Now if there is an emission from here, what will be the frequency of the photon?
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Or suppose this is not even a stationary state, let's say this is also a virtual state, that is possible, okay, if it comes down from virtual state then of course the frequency will be exactly 2 nu, okay,

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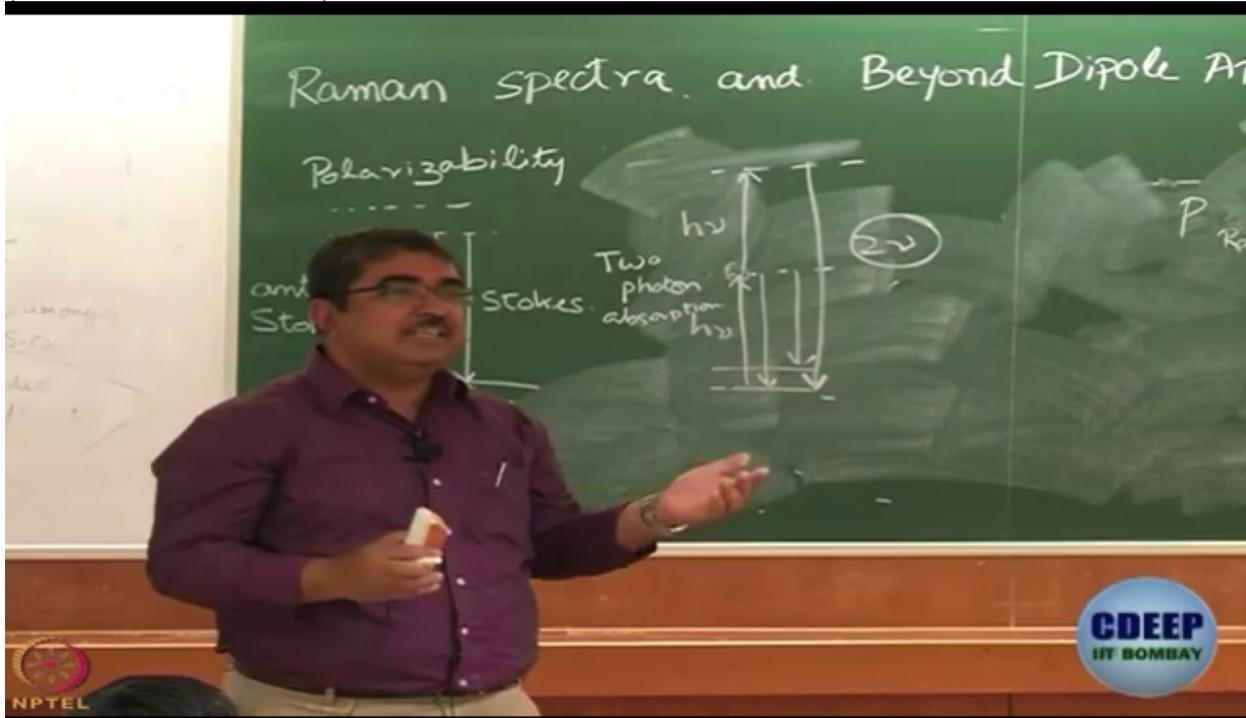


this is how you do second harmonic generation, this is how 2 droplets of energy join up to give you a bigger drop, so this is how suppose you have 290 x 2, how much is that? 580 nanometer right, see if you have a 580 x 2, how much is that? 580 x 2, 1160, 1160 is IR, not difficult to make a laser with emission at 1160. Now you make this go through a medium where it is

possible to add up the two photons that gives you 580 nanometer, do that once again you get 290 nanometer, so this is second harmonic generation, that is fourth harmonic generation. Third harmonic is mixing of this IR with the visible light that is also possible, okay, of course it is more difficult to do then the way I am putting it, but it is doable, so what we have done is that we have learnt that you can actually do something, if this is a stationary state, a stationary state for which one photon transition is not allowed, that transition might actually be allowed because of this kind of integral,

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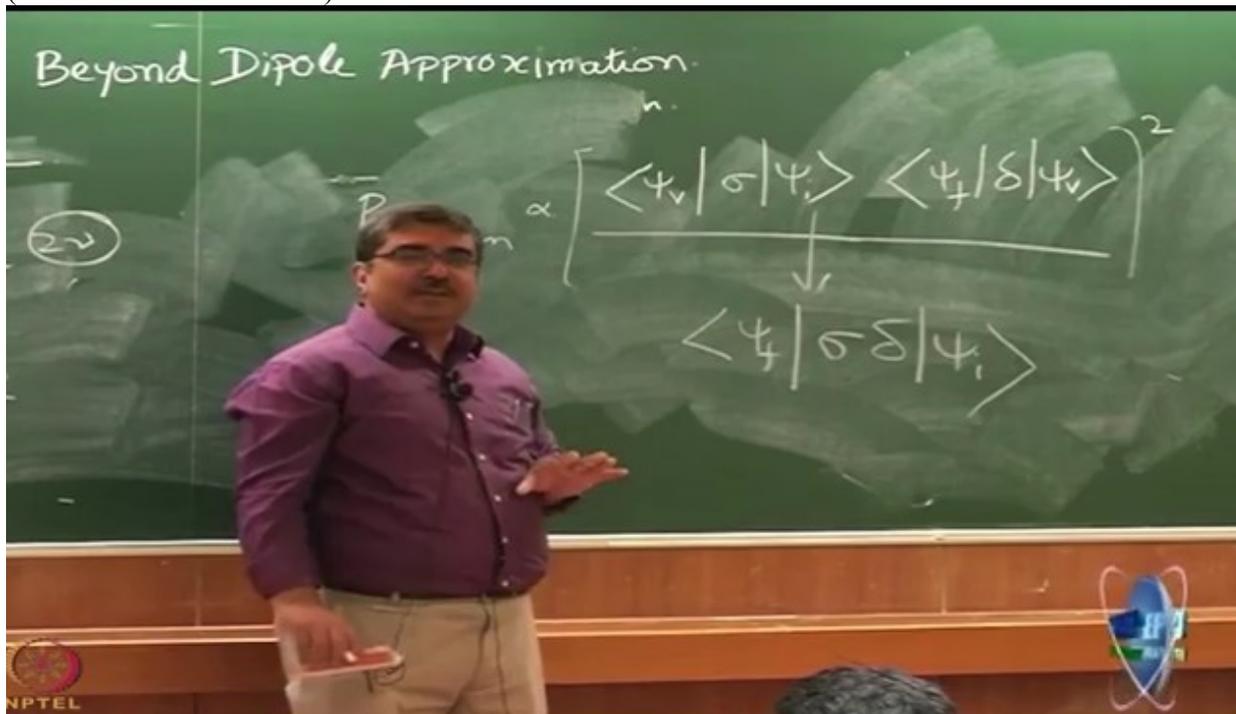


this is the integral that is important for two photon absorption, okay, that takes us beyond this one photon approximation, I have not written it actually. Two photons can also do a promotion, two photons together, but one photon cannot do two transitions.

The other thing is those of you who know what a quadrupole moment is, would perhaps recognize, there is alpha delta XY or X square or Z square or YZ, right, that is what you'd get if you use a quadrupole moment in place of a dipole moment, okay, quadrupole moment is something that we don't use so frequently as dipole moment, precisely because this dipole moment interactions are more, well are stronger than interactions with quadrupole, okay, but when dipole moment interaction is not there, when a transition is not allowed by the dipole mechanism then it might become allowed feebly by because of this integral which uses the quadrupole instead of the dipole that takes up beyond dipole approximation, okay.

If you remember when we began the discussion of this time dependent perturbation theory, we've said that it is not as if nothing else happens, we had modeled the interaction of radiation with matter to be the interaction of the electric field of radiation with the electric dipole of matter, at that time if you remember we had observe that that is not the only interaction, it is just that that is the most predominant, prominent interaction by far, that is why that is most important, but in cases where transition is not dipole allowed then you can see quadrupole allowed

transitions, very often you talk about transitions that are weekly allowed, right, what is the mechanism of this weekly allowed transition, this is one possible mechanism, okay, where you have to model the interaction using not the dipole but the quadrupole, okay, we have done a very sketchy job of presenting this to you, I'm not going to say, discussing this with you but the take home message is this, first of all in Raman's spectroscopy excitation wavelength does not matter, you still get the same spectrum.

Second you get predominantly stoke shifted Raman in case of vibration you get both, stokes and anti-stokes in case of rotation. Third expanding upon this concept of involvement of excited states you can think of the second transition instead of being the downward transition you can think of even upward transition, that is what gives you two photon absorption and that is what takes you in the hem of what is called nonlinear spectroscopy, we have not discussed why nonlinear let it be the story for another day.

Finally we said that as a consequence of two photon absorption you can have what is called second harmonic generation, what we have not told you so far is that the second harmonic generation can take place only in non-centrosymmetric media, if there is centrosymmetry then you cannot get second harmonic generation, and that is the first kind of observation that tells us that's, in spectroscopy symmetry place a very important role, in fact in the subsequent discussions that we have, what we are going to do is for a, say under dipole approximation for a diatomic molecule, what we attempted was we tried to work out the integral very vigorously and we tried to derive expressions which tells us which transitions is allowed and to what extent.

When you go to more complicated systems that is not going to be so easy, I'll not say it is impossible, but it's not going to be easy at all, so the approach will take is that we'll try to evaluate integrals like these or integrals that we have studied so far using the concept of symmetry, so this point onwards symmetry is going to be play a very, very major role in spectroscopy. We will start revising our concepts of symmetry, so this is the end of this module.

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