INDIAN INSTITUTE OF TECHNOLOGY BOMBAY

NPTEL

NPTEL ONLINE CERTIFICATION COURSE

Molecular Spectroscopy – A Physical Chemist's perspective

Lecture-09

Conditions for Microwave Activity-II

With

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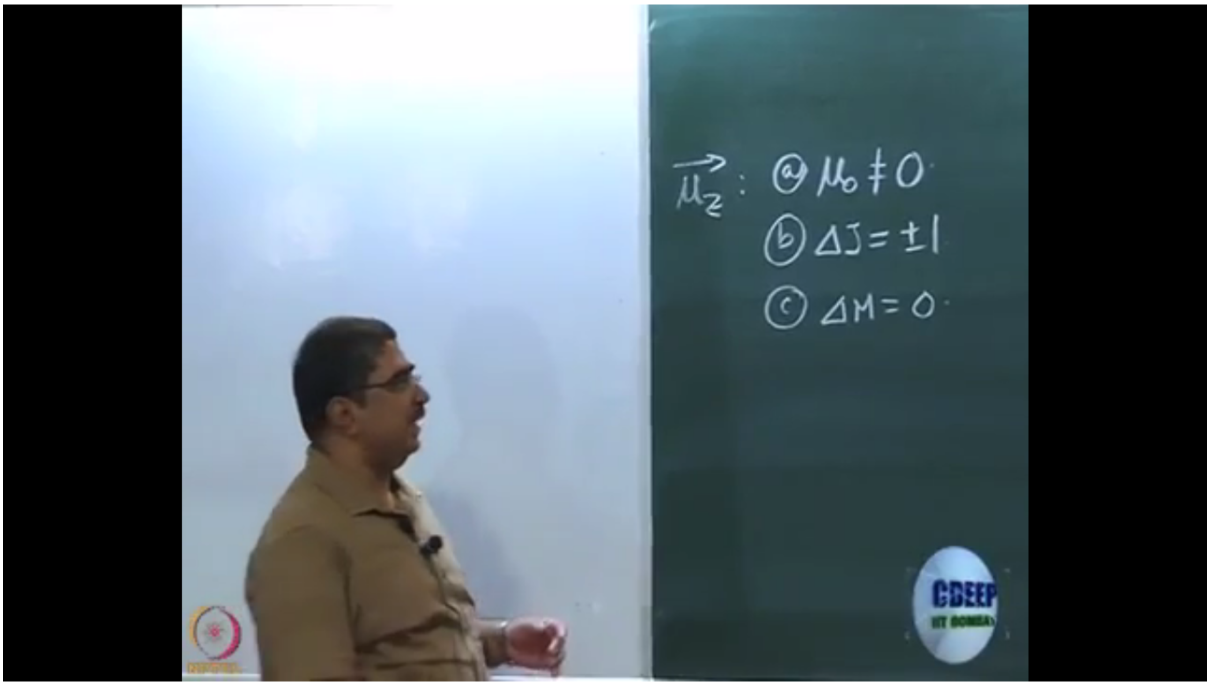
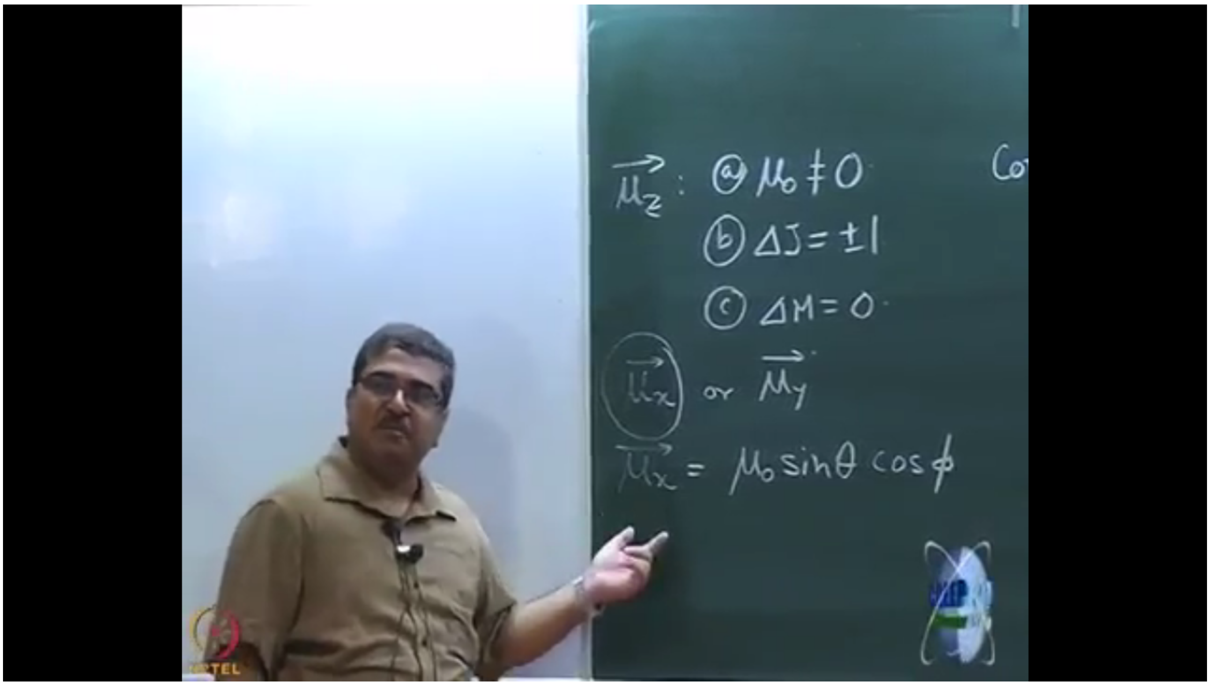
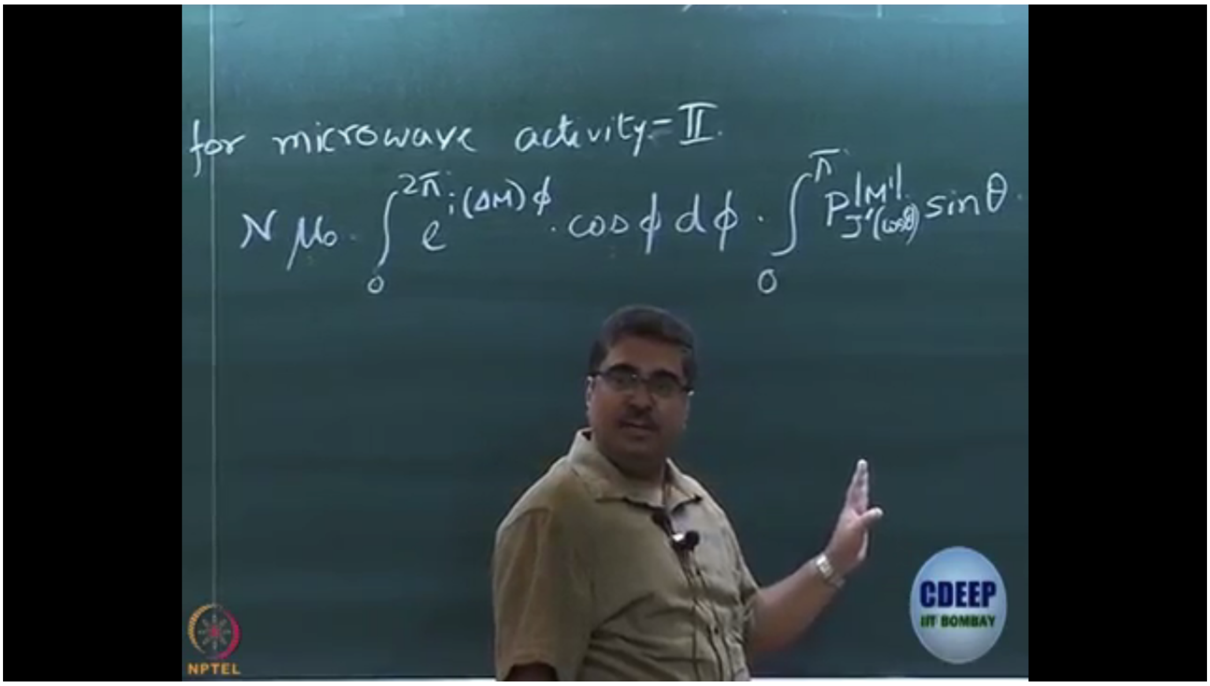


So far we have been able to establish the conditions for microwave activity involving the z component of the dipole moment, and the conditions we have established while utilizing the z component are first of all, the molecule must have a permanent dipole moment. μ_0 should be non-zero. Secondly, ΔJ must be ± 1 and thirdly, ΔM must be equal to 0.



Now we proceed to discuss what happens when you work with the x component or the y component of the dipole moment. Which of these conditions hold? Which of these conditions do not hold. So we are continuing with our condition for microwave activity, maybe I'll call it second part of our discussion. We start with the known premise. We start with the transition moment integral but suppose we are now interested in μ_x. I am only going to work to μ_x because μ_y follows exactly the same kind of discussion as μ_x.

What is μ_x you told me in the previous class, $\mu_0 \sin\theta \cos\varphi$. And right away you can see that our discussion is going to be a little more complicated than what it was for the z component. Okay, z component is the simplest. It will be complicated but not impossible and not so complicated also, let us see.



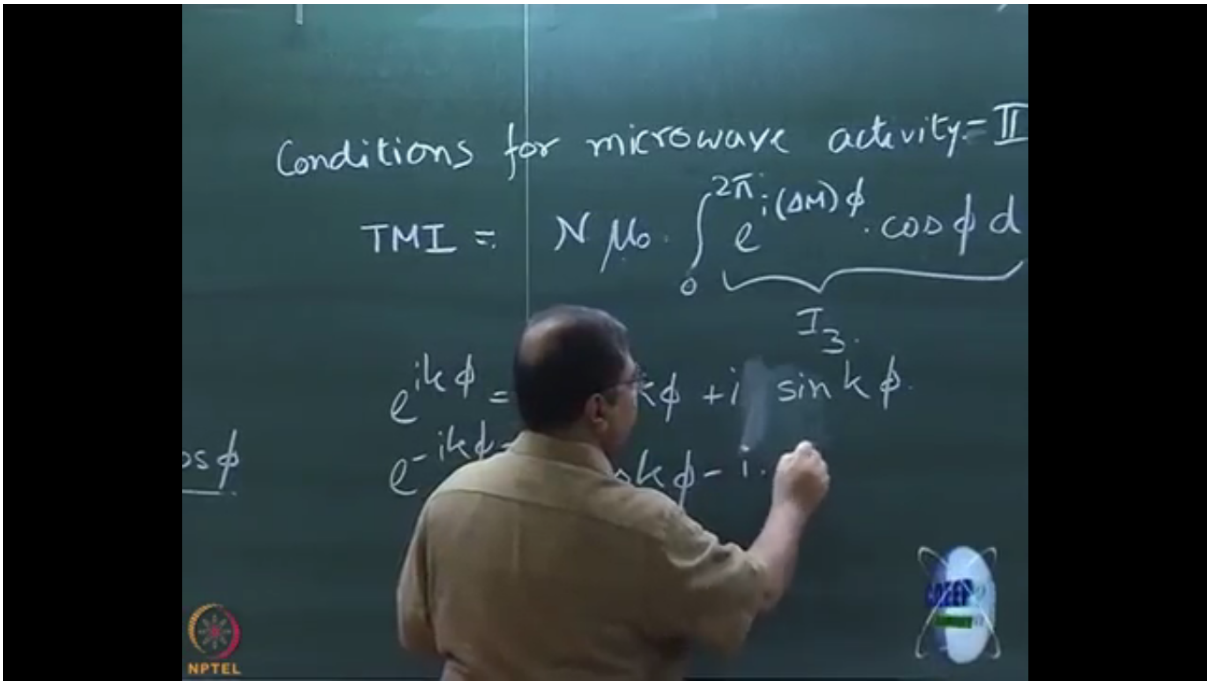
Transition moment integral when we talk about the x component is something like this and since we have done it once already, can I write the product right away? Can I step jump a little bit? So I'll write like this. Some normalization condition N, fine. I'll start writing the integrals, one will be for φ, for that limit be 0 to 2π and here you have $e^{i(\Delta M)\varphi}$ but that's not all. There's an additional φ part here. It comes from μ_x, isn't it, $\cos\varphi$. If you work with the y component it will be $\sin\varphi$. So this multiplied by $\cos\varphi d\varphi$.

So is this the complete φ that we have written? What comes out from here? μ_0 should come out once again, isn't it? This multiplied by integral limits 0 to π. M'. what do I get? This time I don't get $\cos\theta$; I get $\sin\theta$. $P_J^{|M|}$. Okay, I forgot to write what this is, $\cos\theta$. Then what do I write here? Is it $d\theta$ or is it something else? $\sin\theta d\theta$. So his is the transition moment integral, written as a product of the constituent trans.

Let us check once. What is x component of dipole moment? $\mu_0 \sin\theta \cos\varphi$, $\mu_0 \cos\varphi \sin\theta$. So I've written all the factors for dipole moment. What are the φ parts of the wave function? $e^{iM\varphi}$ out of which for the dashed away function, you need to take the complex conjugate. So I get $e^{i\Delta(M)\varphi}$ like what we got for your z component.

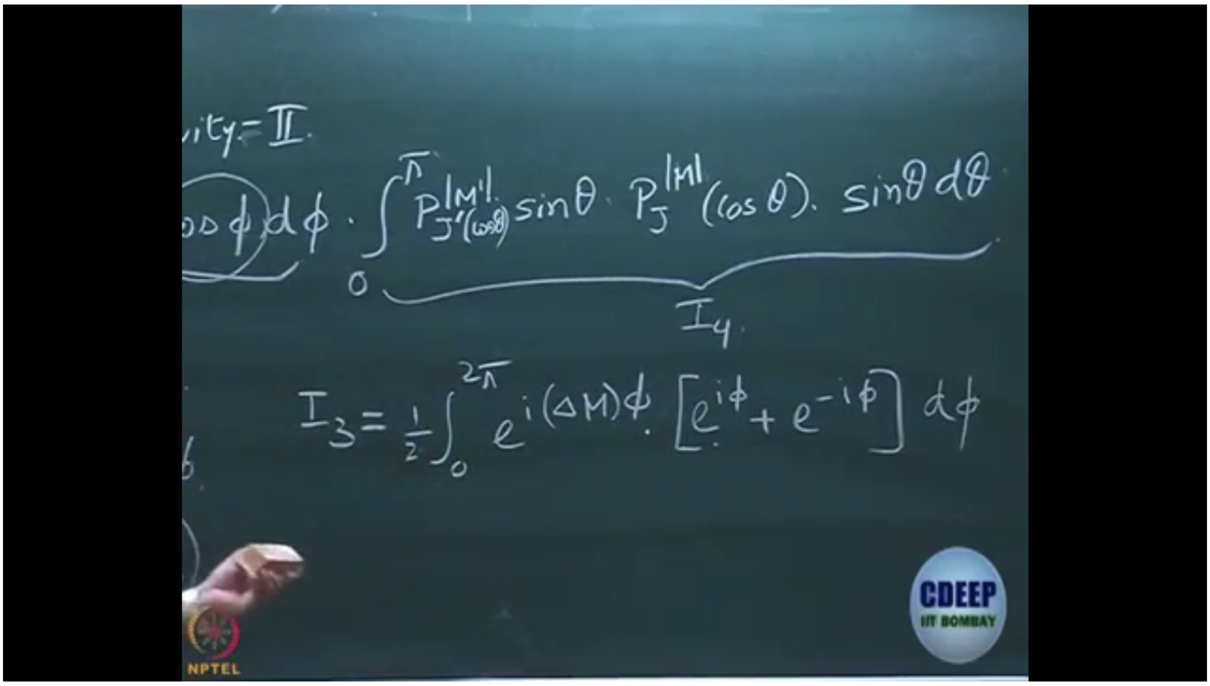
Additionally, you have this $\cos\varphi$ which comes in in the φ part of the integral. So first one is

$$\int_0^{2\pi} e^{i(\Delta M)\varphi} . \cos\varphi \, d\varphi . \int_0^{\pi} PJ'(\cos\theta)^{|M'|} \sin\theta \quad .$$



So far so good? Everything in place? Sure. Now we'll go ahead, we'll try to evaluate as usual the integrals separately. I had called the integrals I_1 and I_2 in the previous class. So here let us call them I_3 and I_4.

Okay to work to I_3 it will b easier if we write everything either in your trigonometric form or in the exponential form. In fact, I prefer the exponential form because we know already how to solve it. So remember we said $e^{ik\varphi} = \cos k\varphi + i\sin k\varphi$. Of course, $e^{-ik\varphi}$ is $\cos k\varphi - i.\sin k\varphi$.



So from here, it is not very difficult for us to work out this relationship; $\cos k\varphi = \frac{1}{2}(e^{-k\varphi}+e^{-ik\varphi})$

Is that right? I can substitute it here. In this case k=1. So what I really need is cosφ = ½($e^{i\varphi}+e^{-i\varphi}$). What does I_3 boiled down to then? I_3 becomes

$$e^{i\varphi}+e^{-i\varphi}$$
$$e^{i(\Delta M)\varphi}[¿]d\varphi$$
$$1/2\int_0^{2\pi} ¿$$

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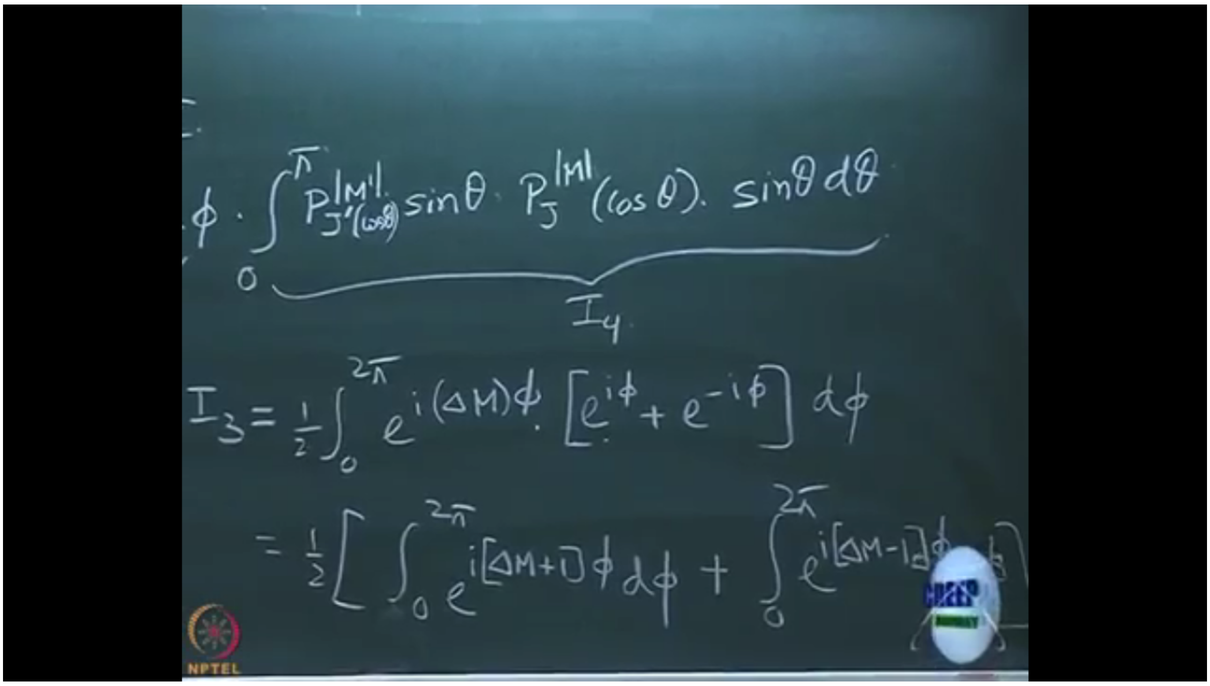


I think you have understood the solution already, haven't you? This boils down to

$$\Delta M+1$$
$$\Delta M-1$$
$$1/2[\int_0^{2\pi} e^{i[¿]\varphi d\varphi}+\int_0^{2\pi} e^{i[¿]\varphi d\varphi}]$$

and we already know the two conditions; one, when ΔM=0 and one when ΔM≠0. That's what we had used earlier. What is the condition we have to use here? One is when ΔM±1 = 0 and the other when ΔM±1≠0. If there is a doubt please ask. Understood? Sure?

So can I write something like this? I_3≠0. In fact, I_3=2π when ΔM±1=0 that is ΔM =±1. I will just write it $^-_+$ in order become it consistent. And I_3=2π when ΔM±1≠0 which brings us to a different condition from what we had using the z direction.

In this case ΔM=0 is not a favourable condition. ΔM must be equal to ±1. If there is any doubt about the math, this is the time to ask. Then we'll go on with the discussion. Do you have a question? Yeah, of course. Either ΔM+1 -- what she is asking is at any one point of time, either ΔM+1 will be 0 or ΔM-1 will be equal to 0, obviously yes. So I am writing the conditions together as ΔM =±1.

Vibha understood? Sure? Any question? Any doubt? Anyone? Are you all comfortable with this? We can go ahead. Yeah, yes.

Yes, not equal to, is that what I am reading? 2π ΔM±1=0. That is called Inertia of Motion. Of course, 0. I said 0 perhaps but I wrote 2π. Are we clear? Sure?

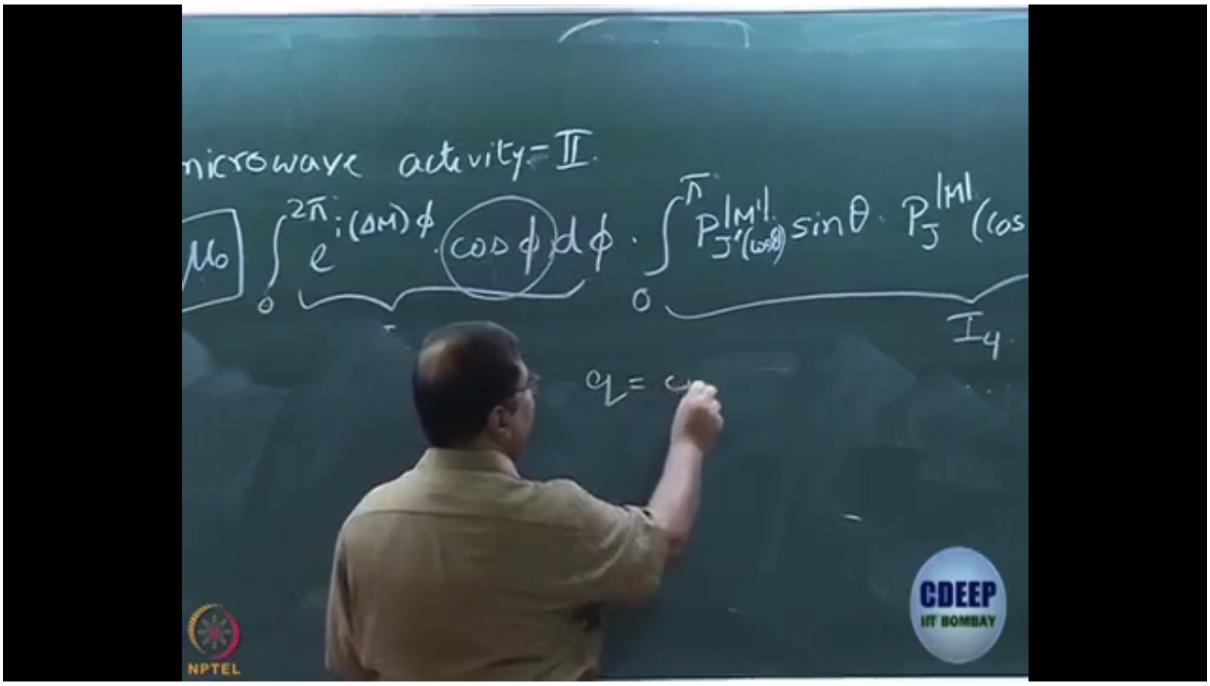
So now see, we have a different condition. This is the condition wherefore when you work with μ_z. but when you work with μ_x then ΔM has to be equal to ±1. What will happen if I work with μ_y? Same because instead of cosφ I am going to get sinφ. So if I get sinφ, how do I have to write this? Cosφ is

$1/2(e^{i\varphi}+e^{-i\varphi})$. Sinφ is simply one subtracted from the other. You have to divide by i. That is all. Yes, multiply by -i or divide by i, same thing.

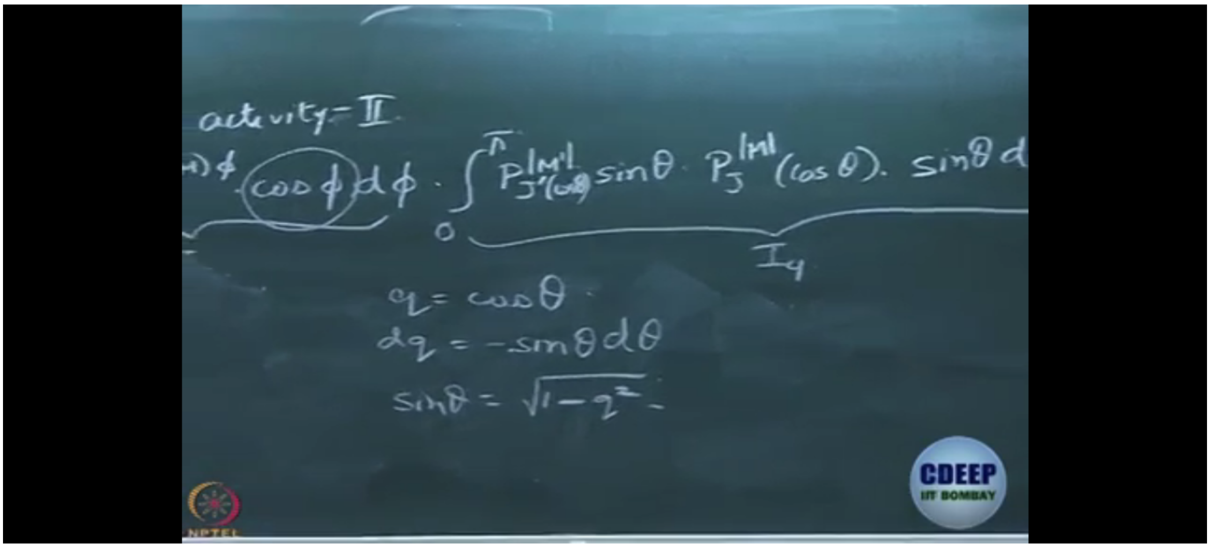
So are you all convinced that for μ_x as well as μ_y, the condition will be $\Delta M=\pm1$. I think we'll come back to this and discuss the physical significance of it after we have done our discussion of time dependent perturbation theory. I already did a little bit of it while talking about the z component but x and y, let's come back to it later.

Yes. What she is saying is it's complementary. Suppose we work with isotropic light, if I expand your question. Isotropic light, x, y, z all components are there and then $\Delta M=0$, $\Delta M=\pm1$, both will be allowed. $\Delta M=\pm2$ will not be allowed. See, $\Delta M=\pm1$ will be allowed if you work with x and y component. What happens when $\Delta M=\pm2$? So if you work with isotropic light, of course, z component of it can be absorbed with the condition $\Delta M=0$. x and y can be absorbed with $\Delta M=\pm1$. That is right, but what about ΔJ. That is what we have not discussed so far. We'll come back to it.

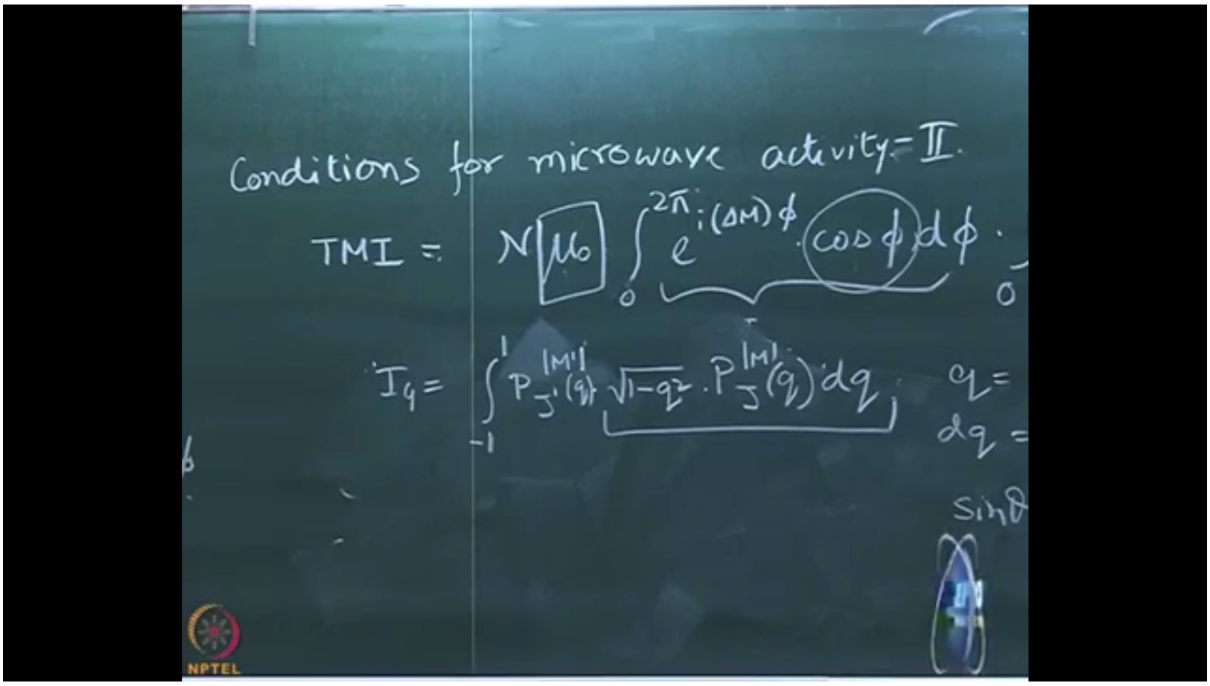
One more thing; μ_0 has come out of the integral here also. So no matter what direction you consider, x, y, or z, permanent dipole moment has to be there. That is an absolutely essential condition. Molecules that are not dipolar cannot absorb microwaves. H_2 cannot absorb microwave; HCl can absorb microwave.



Now let us come back and let us talk about I_3. No, let's talk about I_4 now, we have already discussed I_3. Discussion that we are doing today and what we did the previous class is available in [Gerald's] book.

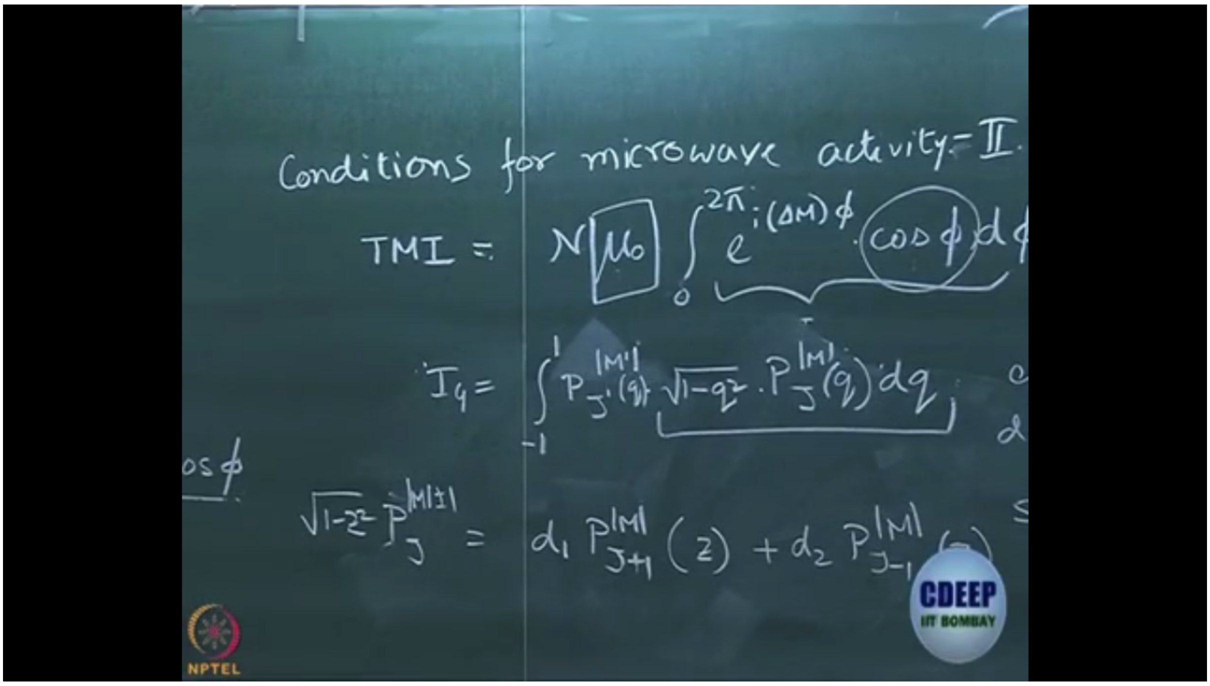


Again, instead of z let me write q this time. So let me say q is cosθ. As usual dq would be -sinθdθ. But I have two sinθs; one here and one there. One thing I can do is I can just multiply one by the other and write $\sin^2\theta$ but it actually makes more sense if I don't because I know very well that I have to convert this to dq. So let it be. How do I handle this sinθ?



Exactly. So sinθ will be $(1-q^2)^{1/2}$. Does that ring a bell? Do we see where we are going? Okay, so I_4 in that case becomes again I'll change the limits. I'll change the limits and make it -1 to 1 because I don't want to write that minus(–) explicitly. This becomes

$$\int_{-1}^{1} P J'^{|M'|} \frac{\left(1-q^2\right)^{1/2}}{\square} . P J^{|M|}(q)\, dq \quad .$$

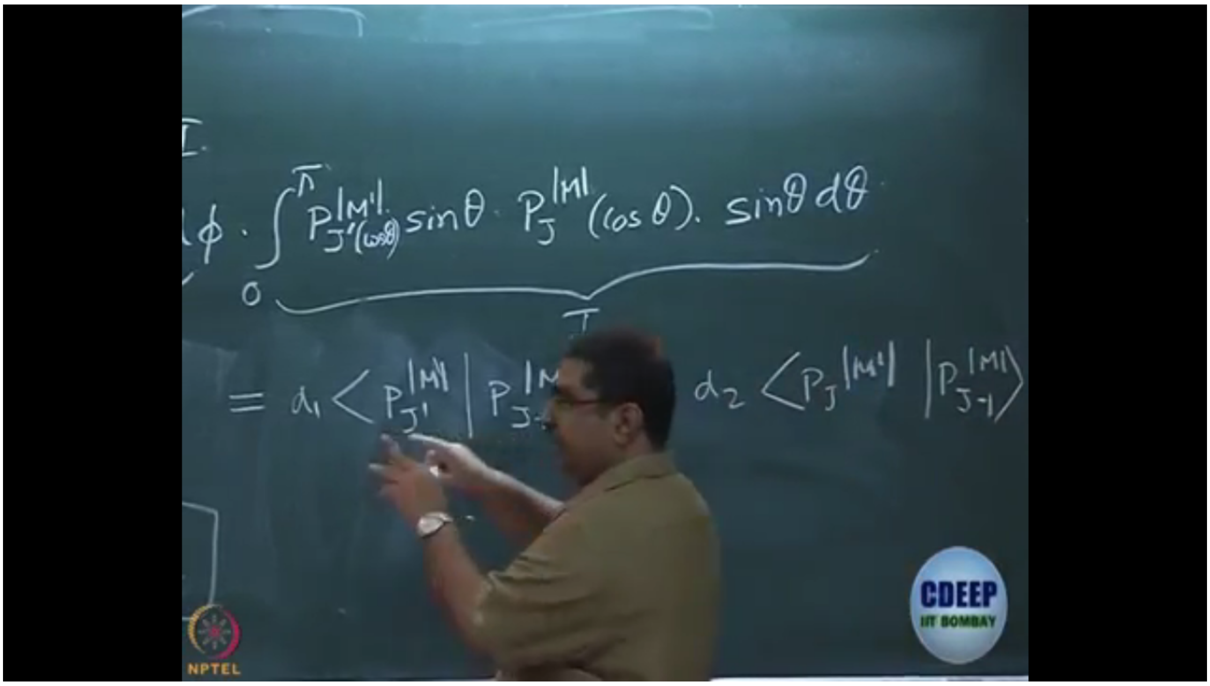


Now, look at this. If you remember, in the previous class, we had shown you three different recursion formulas. One was what happens when z is multiplied with this polynomial. The other two were something like this. Again, I write the right-hand side first, which status have we used already; a_1a_2, b_1b_2, c_1c_2. So let me write d_1d_2 now. $d_1P_{J+1}^{|M|}(z)+d_2P_{J-1}^{|M|}(z)$. On the left-hand side, if you remember, we had $(1-z^2)^{1/2}P_J^{|M|\pm1}$. What I have done is I have written the two recursion formulae that I have shown you in the previous class in one.

So now first of all, $|M|=|M|\pm1$. That fits in very nicely with the condition $\Delta M=\pm1$. Actually, the agreement is so good that I'll not blame you if you think that all this is just back calculation. I mean the agreement, I mean the things are falling into place beautifully but the thing is they fall into place beautifully because you can actually describe everything using mathematics.

If you are a Dan Brown fan or at least if you've read Dan Brown books, you'd have read in some of books of his where he has said that mathematics is the purest form of language. So that's what it is, everything. See, the Earth going around the Sun. You can write a mathematical equation for it. Even the cells dividing and all, disease, everything can be modelled using mathematics.

So this agreement is fascinating but it is not back calculation, let me just tell you that. Okay, so now I think our discussion is complete. All we have to do is use this recursion formula and expand this expression. If I use this recursion formula, what do you get?



Are you familiar with this bracket notation? So I'll write it in that way for a change. You get something like this. You get, of course, $d_1\langle P_{J'}^{|M|'}|P_{J+1}^{|M|}\rangle + d_2\langle P_{J'}^{|M|'}|P_{J-1}^{|M|}\rangle$. Here I have not written the q in bracket. I hope that's not a problem. So from these two, what is the selection rule that we get once again?

Again, $\Delta J=\pm1$ because as we discussed earlier, these polynomials also form orthonormal set. So this integral is going to survive only when the two polynomials are the same. So here also we get $\Delta J=\pm1$. So what is the only different between using the z component and using the x or y component? The only different is ΔM. Does it matter as far as the position of the lines is concerned? It doesn't because all the Ms are actually they are degenerated, they have the same energy. Energy B)(J)(J+1). M does not arise thee. So there is no problem there.

So with this we have completed our discussion of derivation of the conditions for microwave activity. Now that we know this, we are in a position to go on and discuss the spectra in a little more detail.