Quantum Mechanics and Molecular Spectroscopy
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Lecture No -20
Einstein's Coefficients (Part-3)

Hello welcome to the lecture number 20 of the course quantum mechanics and molecular spectroscopy. We will go on with our lecture after a brief recap of the previous lecture. In the previous lecture we looked at two things one is the rate of absorption and as other is rate of emission based on this we can we got two equations.

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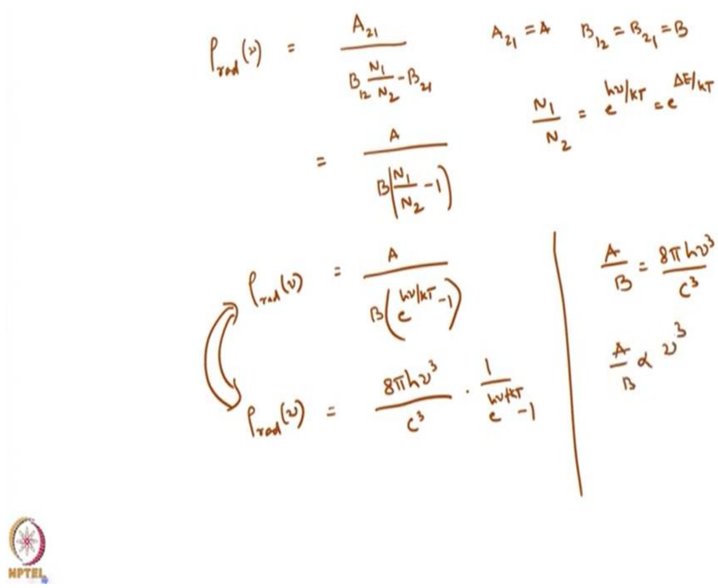

Rho radiation nu = A21 divided by B12 N1 by N2- B21 and this under the circumstances A21 is written as A and B12= B21=B we write A by B and N1 by N2 - 1. Now N1 by N2 is given by Boltzmann population. This is equal to e to the power of h nu by kt. This is same as e to the of delta e by kt, so this turns out to be A divided by B into e to the power of h nu by kt -1. Now rho radiation nu if I look at in terms of Planck's blackbody radiation that will give me 8 pi h nu cube by c cube into 1 over e to the power of h nu by by kt-1.

Now if I rho radiation nu and now if I equate these two equations then I can get A by B= 8 pi h nu cube by C cube and we also discussed that A by B is proportional to nu cube.

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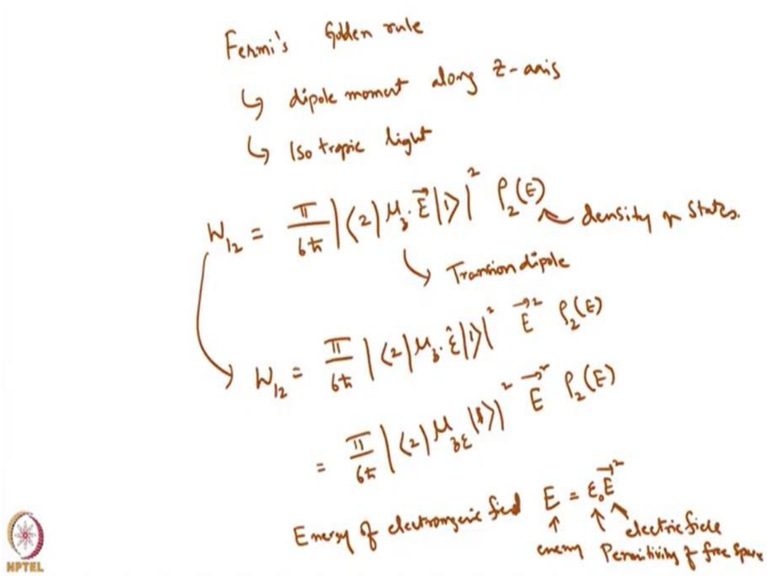

And another thing that we looked at if you starting from the Fermi Gold Fermi's Golden Rule and using dipole moment along z axis and also using isotropic light we said that W12 = pi by 6 h bar integral 2 mu z dot E 1 modulus square rho 2 and this is nothing your transition dipole moment and this is density of states. Now I want to make use this equation and get along. Now there is something that is there is that if I have this also can be written W12.

As can also be written as pi by 6 h bar 2 mu z to epsilon 1 modulus square and then I will get the electric field out square of it rho 2 E. So this is probably not the right way to write so this one can write as pi by 6 h bar 2 mu z, so only the component of mu z that is aligned with respect to the electric field i 1 square square rho 2. The reason why I want to bring the electric field out because the energy of electromagnetic field E = epsilon 0 E square.

So this is energy and this is nothing but electric field and epsilon 0 is permittivity of free space. So I can write rewrite this equation.

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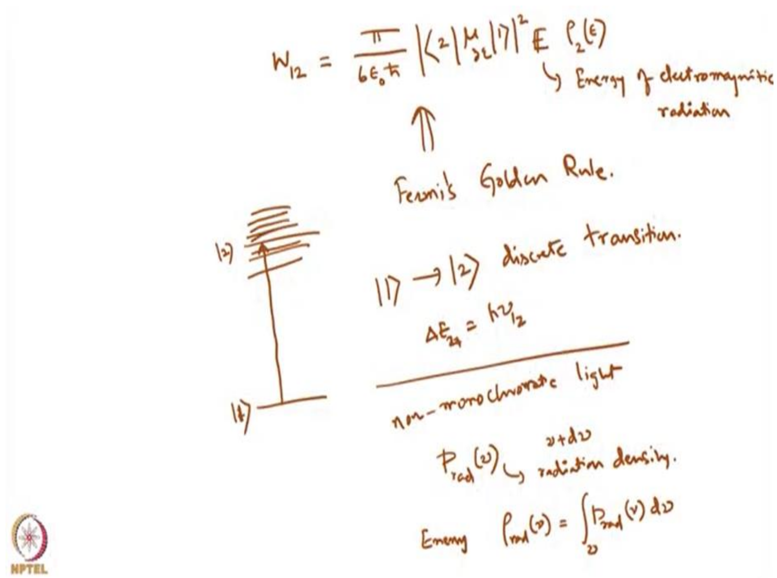

W12 = pi by 6 epsilon 0 h bar modulus of 2 integral 2 mu z epsilon 1 square E rho 2 of electromagnetic radiation. Now so this is what we have now what I want to do is I want to slightly now this is based on Fermi's Golden Rule and you know Fermi's Golden Rule happens because there is a density of states, it is going from a discrete initial state to state that is embedded in some density.

But now let us consider for example you have initial state 1 and your final state 2 which is embedded between in some density but I want to look at only this transition so I am looking for 1 to 2 discrete transition, no density it just the discrete transition. Now apart from that when you are looking at this discrete transition now all I want to do is I do not want to use so this will happen let us say it happens at delta E12 or 21 this is = h nu12.

It will happen at a very specific wavelength or a very specific frequency nu12. So if I want to make a discrete transition if I want to go from state 1 to state 2 I have to give the right frequency nu12 or the electromagnetic radiation with the right frequency nu12. But now if you look at we were talking about the candle or some kind of lamp so of course that is not going to give you a monochromatic energy or electromagnetic radiation.

So nu12 will not be very-very single very, very selective. You will get all sorts of nu and out of which only nu12 will cause the transition. Now if you use non monochromatic light so what I am trying to do is that I am going from state 1 to state 2 which has a energy difference of delta e and frequency of nu12 but using non monochromatic radiation, and when you have non monochromatic radiation you have let us say P radiation nu such that you have nu + d nu in the frequency nu + d nu.

Now that now this is the radiation density. So if I want to get the energy rho radiation nu I should get P radiation nu d nu if it is a small integral but if you have a large integral then this should be integrated over nu.

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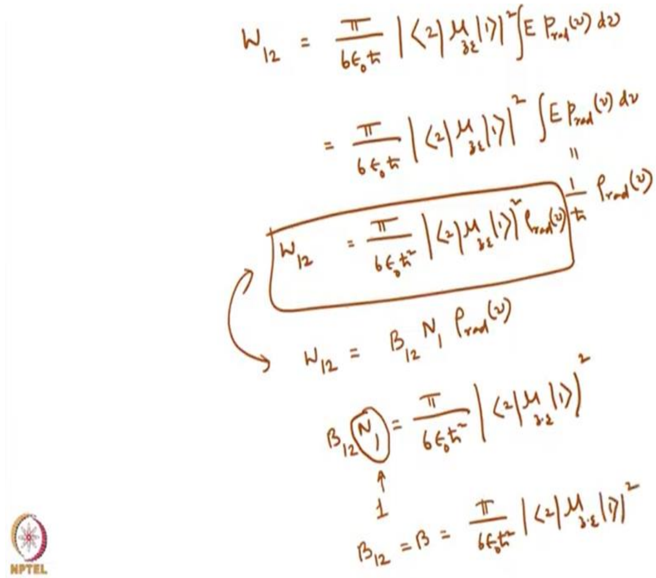

Now in such scenario your W12 will be equal to pi by 6 epsilon 0 h bar 2 mu z E 1 whole square energy E with radiation density P radiation e radiate it but we are looking at spreading the radiation so this must be integrated over d nu, so when I integrate over radiation d nu so what I will get is pi 6 epsilon 0 h bar 2 nu z epsilon 1 whole square integral by the E P irradiation nu d nu of course I am writing the same equation.

So when I integrate what I will get is this integral is given by 1 over h bar rho radiation, therefore your W12 is given by pi by 6 epsilon 0 h bar square integral to mu z along sum epsilon 1 square into rho radiation. So let me reiterate now according to Einstein's coefficients what was rho W12 rate for an absorption it was nothing but B12 N1 radiation. Now I can equate these two equations now so what you will get then B12 N1 =pi by 6 epsilon 0 h bar square 2 nu z 1 whole square whole square.

But there is a problem in this equation I do not know what this N1 is N1 we said is the population of the state but when you derive quantum mechanics rules we derive for one single molecule or one single quantum object so your N1 must be actually 1 because all this derivation of this the initial state to final state is based on one quantum object. So therefore N1 must be replaced by 1. So your B12 is nothing but your B= pi by 6 epsilon 0 h bar square + 2 nu z 1 whole square.

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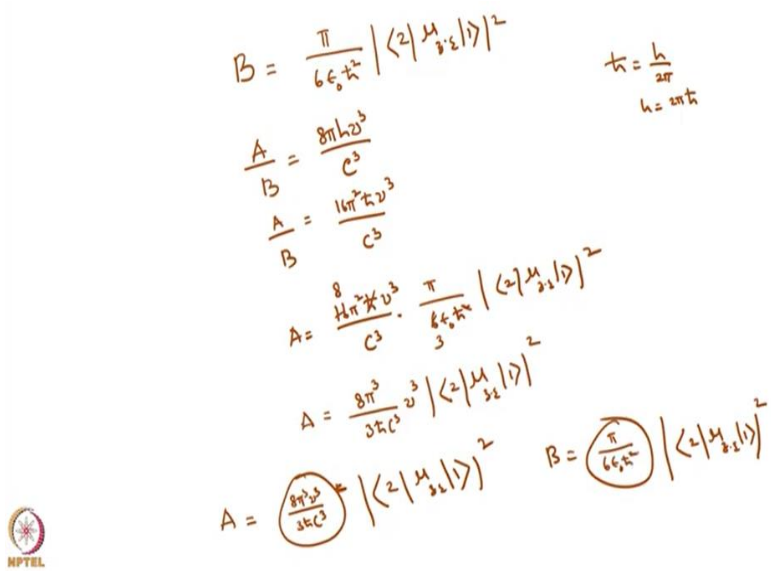

So let me look at so your B that is your Einstein's coefficient for absorption and stimulated emission is given by pi by 6 epsilon 0 h bar square and the integral 2 mu z modulus square, but we also know A by B = 8 pi h nu cube by C cube, now we know that h bar = h by 2 pi or h = 2 pi h bar so if I write in terms of h bar then I will get 2 pi so we will get 16 pi square h bar nu cube by C cube that is A by B.

But now we already know B so A =16 pi square h bar nu cube by C cube into B which is nothing but pi by 6 epsilon 0 h bar square to mu z 1 whole square. I can do some arrangement so this s square and this h bar will go away this pi becomes pi cube 6, 2 times 3 8 so this will become 8 pi cube by 3 h bar C cube nu cube 2 mu square so your A is given by this and B is given so what you have is A is some constant 2 mu z epsilon 1 whole square and B is some other set of constants 2 epsilon 1 whole square.

And these constants here will be 8 pi cube nu cube divided by 3 h bar c cube and this constant is pi by 6 epsilon naught h bar square. Now you can really see that the Einstein's coefficients A and B are proportional to the square of the transient dipole.

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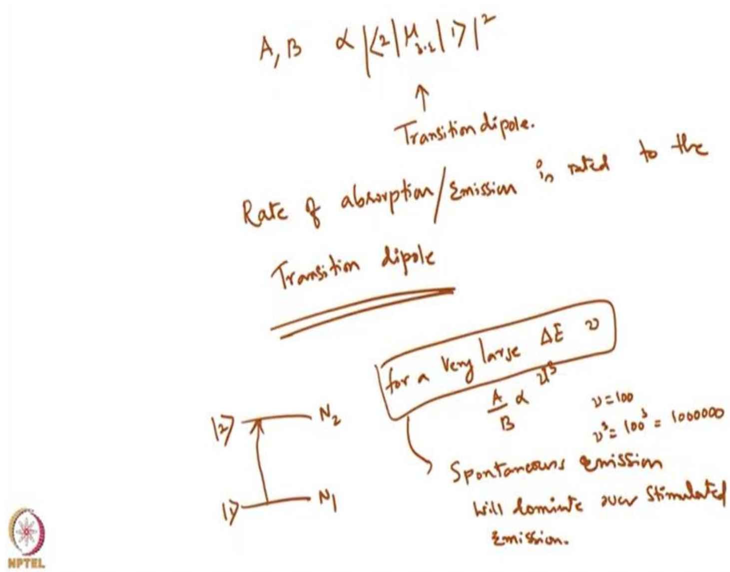

So both A, B are proportional to 2 mu z 1 square of this, so this is nothing but transition the proportionality constants are different but essentially it they are proportional to transient dipole 1. So if you know the transient dipole then you can get the Einstein's coefficients A and B and if you know the Einstein's coefficients A and B then you know the rate of absorption and rate of emission.

So essentially the rate of absorption slash emission is related to the transition dipole, let us suppose you have an excited state in ground state 1 and excite state 2 and you have N 1 and N 2. Now if you excite to from ground state to excite state for a very large delta E and we know as the large delta E increases nu also increases or very large nu which means your A by B is proportional to 1o proportional to nu cube that means if a very large nu the nu cube will be much more than the B.

So for example let us say nu is 100 so let us say nu = 100. So nu cube will be 100 cube so that will be 10,00,000. So you have nu of 100 the nu cube will be a million so generally nu cube is going to be is going to dominate over nu, that means A will dominate over B that means spontaneous emission will dominate over stimulated emission. So which means for a very large delta nu spontaneous emission will dominate over stimulated emission.

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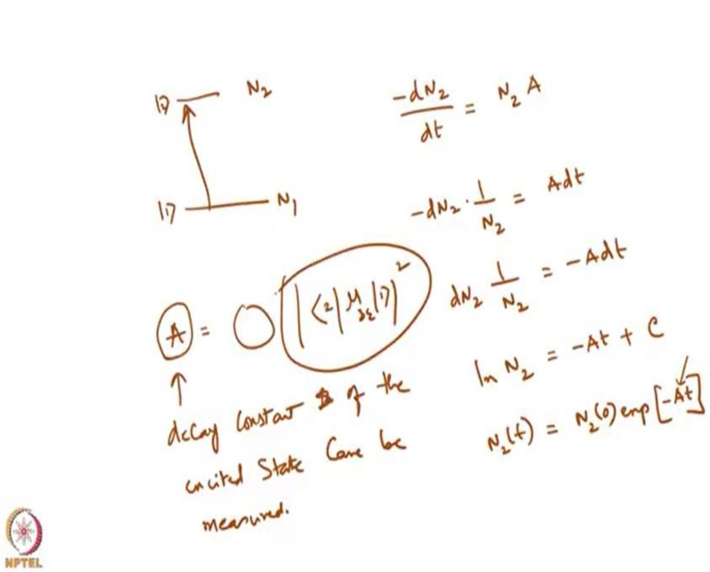

Now you can think of a scenario in which you are going from state 1 to state 2 your initial population is 1 and this is N2 at some point of time after you excite and then you switch off the light then what will happen everything will emit spontaneously so -d so dk of population from the excited state dN2 by dt should be proportional to the N2 times A the rate constant and the population. Now if I integrate this -d into or 1 over N2 = Adt.

So you can take the other side dN2 by N2 = -Adt so this will be nothing but ln N2 will be equal to -At. So if you take plus some constant of integration and when you rearrange it what you will get is N2 of t will be equal to N2 of 0 that is initial exponential -At. So this is so the decay will be given by a decay constant will be given by A. So what means the decay constant when you excite to molecule to the higher level the spontaneous emission will decay by rate constant of A.

Now this decay constant A is equal to some constants 2 mu epsilon 1 square this is nothing but your decay constant. So by measuring the decay constant and this can be experimentally measured I will come to this in the next lecture, decay constant in the excited of the excited state can be measured. So it is like a rate of reaction then you can measure the rate constant, that is a decay constant and that decay constant is proportional to the transition dipole.

So if you can somehow measure the decay constant experimentally then you can evaluate the transition dipole. We will stop here and continue in the next lecture.