Introductory Quantum Mechanics and Spectroscopy
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Lecture - 9
Molecular Spectroscopy - Part 1
Semiclassical theory

Welcome to the lectures on chemistry. In this module, we have been looking at molecular spectroscopy. This is the second lecture in molecular spectroscopy. If you recall from the previous lecture, we discussed why we are interested in molecular spectroscopy, why as engineering or science students you must learn the basic methods in spectroscopy, basic techniques in spectroscopy, what are the various types of molecular spectroscopy and so on.

I also discussed the three most important aspects that one should pay attention to in any branch of molecular spectroscopy namely, the line positions in spectrum, the line intensities in the spectrum, also the line widths. Exploring these three aspects of any spectrum gives you the details about the molecule that we are trying to understand or trying to explore.

In this lecture, in today's lecture we will take it further to give you two quantitative relations, which are very common in all of spectroscopy. One relation is called Beer-Lambert’s law, the other relation involves molecular dipole moments with the molecular processes. These two will be followed by a preliminary discussion on molecular electronic spectroscopy.

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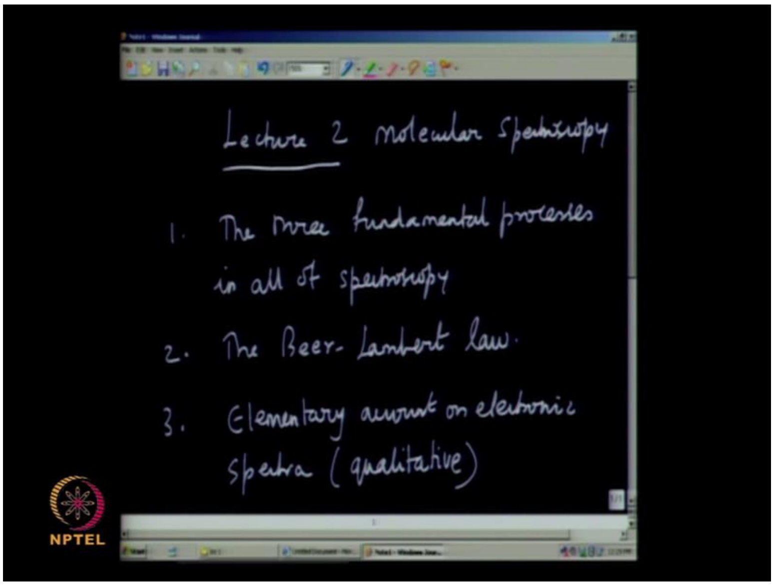

Lecture 2 molecular Spectroscopy

1. The three fundamental processes in all of spectroscopy
2. The Beer-Lambert law.
3. Elementary account on electronic spectra (qualitative)

So, let us start with lecture 2 on molecular spectroscopy. The aspects we will study are, one, the three fundamental processes in all of spectroscopy, a quantitative relation called the Beer-Lambert law and this we will follow by elementary account of electronic spectra. I would call this, in addition to elementary, I would say qualitative aspects instead of quantitative relations and energy levels, transitions, etc., which are much more difficult to understand in the first instance. What we shall do with the electronic spectroscopy is, that let us bring out some of the qualitative ideas. So, let us start with the processes which are fundamental to the molecular spectrum.

So, when we talk about spectrum, recall, that it is nothing but the outcome of the interaction, the radiation with matter. And radiation, as you know consist of the electric and magnetic fields oscillating in mutually perpendicular directions and also in the direction perpendicular to the direction of propagation, that is, a wave picture.

Now, if you recall the corresponding photoelectric effect and the picture, that was proposed by Einstein, electromagnetic radiation consist of, what are called, the photons. The name photons was not given by him, he called the mass, wave packets. The name photon was given to the Einstein's packets later by a chemist, Gilbert Newton Lewis, but that is irrelevant, what is important is that it consists of photons.

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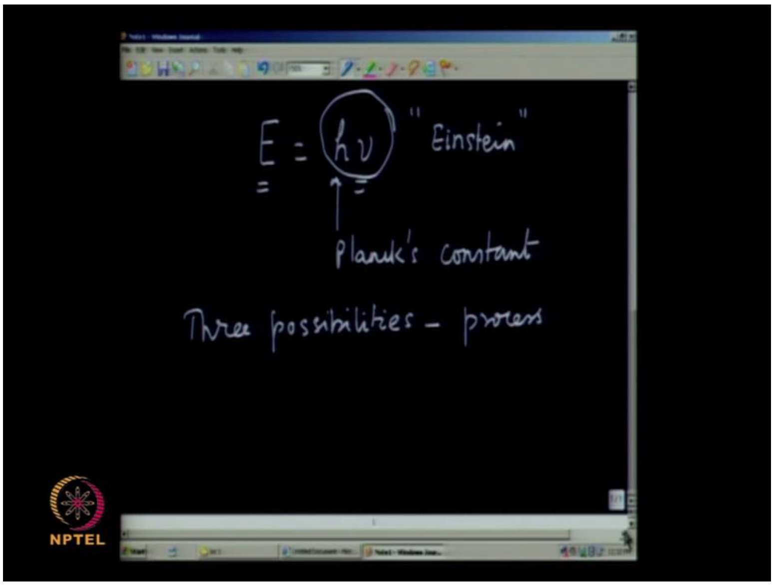

And the radiation energy of the photon is given by this Einstein law, a proposition that Einstein made in 1905 for photoelectric effect, that the energy of the photon is proportional to the frequency of the radiation and the proportionality constant is Plank's constants. This you are familiar for quite some time.

Now, when we discuss the three processes, let us make use of this idea, that energy of the photon is what gets transferred and the molecule goes into an exited state or when the molecule comes from an excited state to a lower energy state, that it emits photons, then it is possible to visualize three possibilities and each one of these possibilities is called the process.

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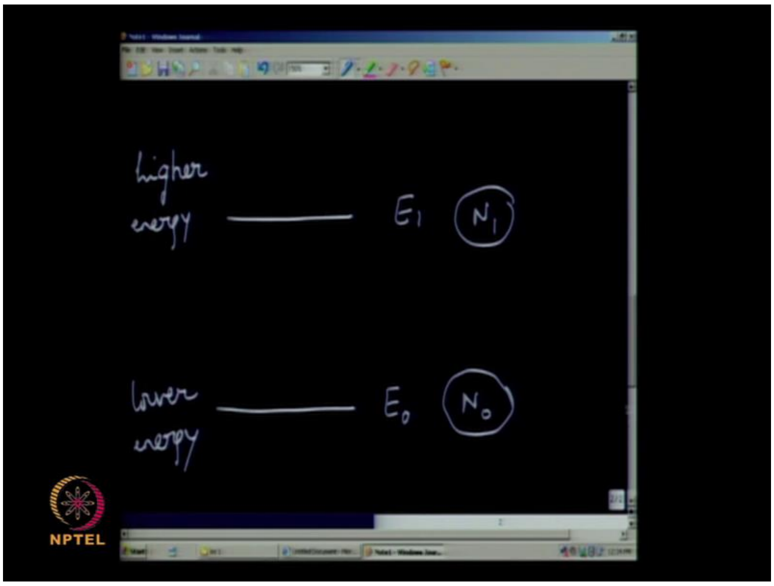

The first process, let us think about a very elementary situation in which there are, there is a molecule with only two energy levels, a lower energy level called E naught and an excited energy state called E 1. Let us assume, instead of one molecule, maybe N naught molecules in the lower energy state and M 1 molecules in the higher energy state. So, let we write this as the higher energy and this as the lower energy.

Now, recall from your elementary kinetic theory, that molecules at any temperature about 0 Kelvin distribute themselves into various possible energies and therefore, even in the absence of radiations it is possible for some molecules to be in the excited state E 1 and others to be in the ground state E naught. The numbers N naught and N 1 being statistically distributed and the distribution is given by the Boltzmann law, the Maxwell Boltzmann distribution law for the kinetic energies and for the average velocities of the molecules is very much applicable here for a system in equilibrium, in thermal equilibrium.

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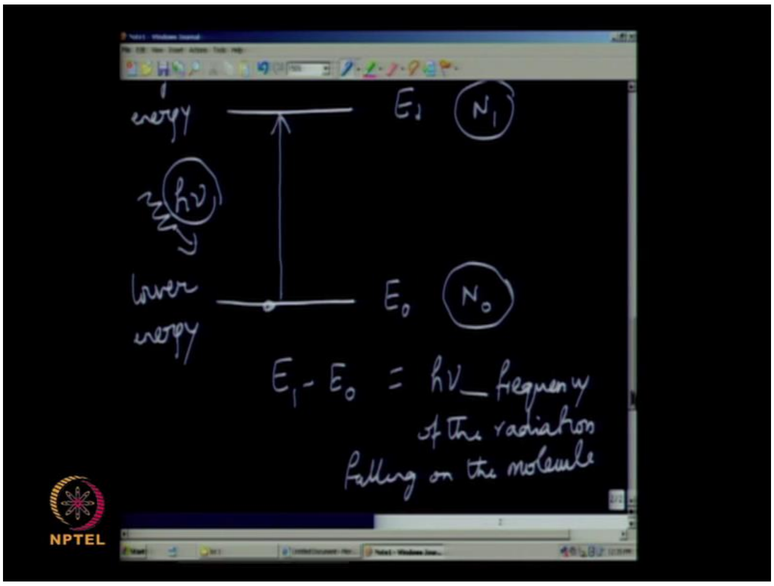

So, if we assume that there are already a certain number of molecules in the excited state and hopefully, a much larger number of molecules in the ground state, what we have is in the absence of radiation. This is the scenario in the presence of radiation. Let us light shine on the molecules, let the electromagnetic radiations interact with the matter for brief amount of time.

Supposing the molecule is in the ground state and if the energy of this radiation h nu corresponds to exactly the gap between these two energies, namely if E 1 minus E naught is equal to h nu where nu is the frequency of the radiation falling on the system, falling on the molecule, then what you see is, what you are familiar from the Bohr picture like the electron jumping from one energy level or one orbital, one orbit of the hydrogen atom to another orbit.

Similar things can happen here, that when the energy falls on a molecule with the lower energy state E naught, it gets excited to the higher state E 1 because the difference in energy that is required for the molecule to go from E naught to E 1 is equal to the energy that is being supplied. Such a process is called absorption. This is one of the three processes.

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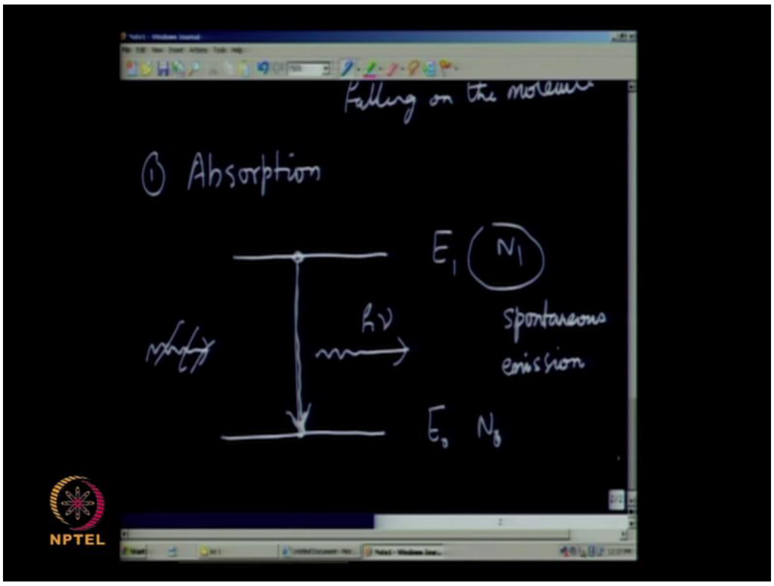

The second process is, let us assume, that there are some molecules in the excited state and since you talk about thermal equilibrium E 1, N 1, E naught, N naught, it does not mean, that the molecules, which are excited and which are in the energy state E 1 stay there. It does not mean, that the molecules, which are in the ground state stay there. No, there is a constant equilibrium of change between the two states meaning, that some of the molecules in the excited state come back on their own, lose the energy and in the process, of course, they emit radiation whose frequency is exactly the same as the energy difference between the two states. So, they come back to the ground state.

Now, this can happen in the presence of the radiation or in the absence of the radiation, both ways, depending on the process. If it happens in the absence of radiation by itself, then it is called spontaneous emission.

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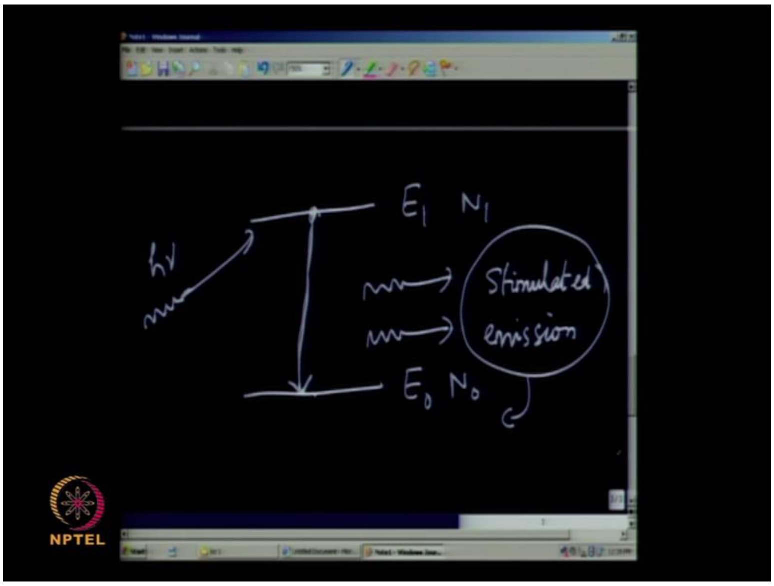

Now, if this happens because for some reason the molecule is trapped in the excited state and is unable to come down to the ground state, but the radiation, for example, kicks the molecule that is in the excited state, it, it sort of starts a process by which the molecule is now able to come down to the ground state.

Due to the presence of the radiation h mu, you see the energy conservation requirement clearly tells you, that this radiation energy plus the energy, that is released in the process of coming down from here to here, both should appear here as radiation, and therefore what you get is for one photon, which sort of interacts with the molecule in the excited state. The output will be two photons coming out and this process being stimulated, being enabled by the presence of the radiation is called stimulated emission.

So, if you go back, you look at it, there are three processes, that is, absorption molecules getting into the excited state, due to the presence of the radiation exciting the molecule from E naught to E 1 molecules, which are in the excited state jumping down to the lower energy state by themselves, call this spontaneous emission. And then there are those who are trapped, who need to be pushed from the top to the bottom due to the presence of the radiation called the stimulated emission.

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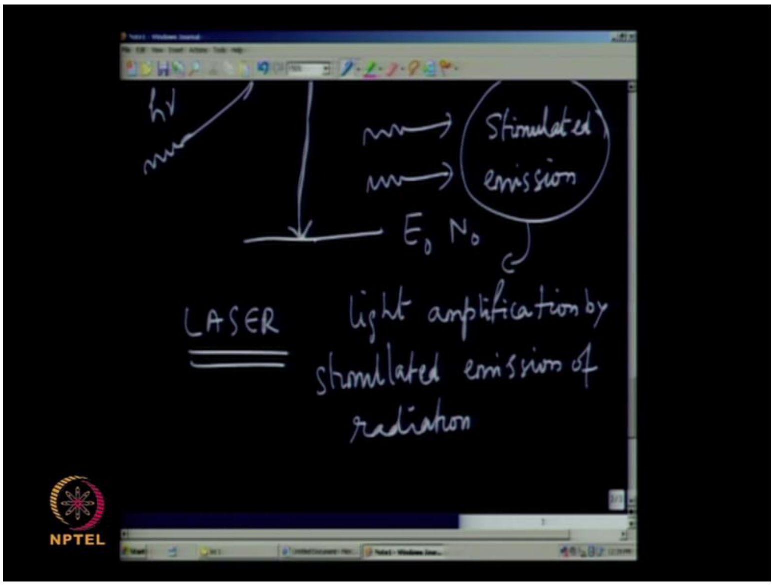

LASER light amplification by stimulated emission of radiation

Stimulated emission is what we today make use of in what is called the laser light and lasers are common everywhere, the light amplification by a stimulated emission of radiation, by stimulated emission of radiation, which was discovered around the 1950s or 1960s was conceived, this, this process was conceived by Albert Einstein in the early 1917s, 1920s, around that period. So, almost 30, 35 years before the experiments determined laser light and discovered laser light, the process was conceived and the spectroscopy was developed with what is called the semi classical approach of the interaction of radiation with matter.

It is partly, it is called the semi classical because the radiation is treated classically here as photons and doing nothing but exciting the molecules or bringing them to the down state without directly change in any other way, molecular state, you retain the properties of the radiation as a classical electromagnetic radiation. You treat the molecule as quantum mechanical because they have the energy levels and you discuss that, you determine the energy levels of the molecule, describe the molecular states quantum mechanically. Therefore, it is a mix of both classical and a quantum mechanical picture and such an approach is called semi classical.

The semi classical theories of radiation for the study of spectroscopy is by and large sufficient for chemistry for there are, there are many cases where we cannot read the radiation as a classical electromagnetic way. We might have to involve the radiation as taking an active part in changing the molecular Eigen function, changing the molecular Hamiltonian completely. Such treatments are not needed in this particular series of lecture.

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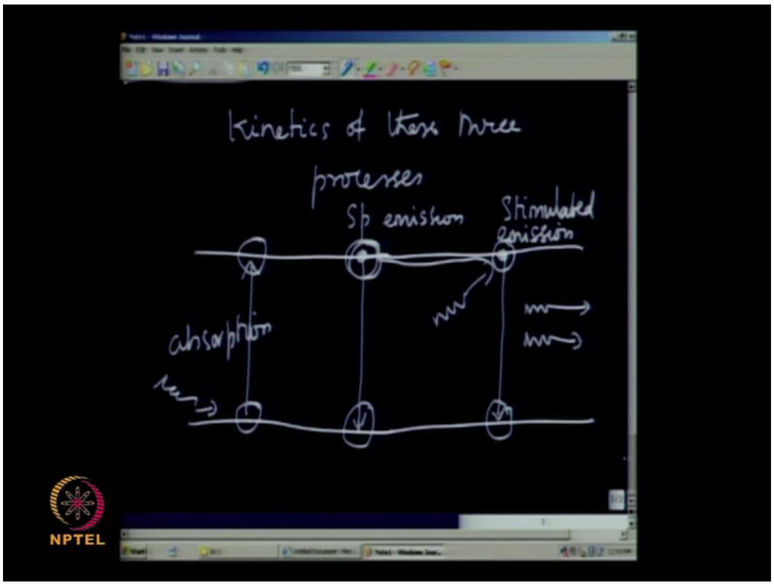

These are the three processes that I would like you to remember. Let us try and quantify these three processes by a simple rate process that you are familiar with from the kinetics. So, let us look at what is meant by the kinetics of these three processes.

Let us look at absorption. Let us write all the three in one and the same process. This is absorption, which takes place in the presence of radiation. Then, there is emission, spontaneous emission, which is independent of the radiation and then there is stimulated emission, which takes place when radiation falls on the excited state. And then you have two radiation, two photons appearing as a result of the molecular transition.

Now, if radiation is in equilibrium, if the whole process is an equilibrium process, if radiation is in thermal equilibrium with the system, then you see the number of molecules, which are changing from one level. For example, from the lower level to the upper level, as it is in the case of absorption and the number of molecules, which are coming down from the upper to the lower level, these numbers should be the, this the rate with this is happening, the rate should be the same, that is rate of absorption, which is responsible for changing the distribution from lower to the upper, should be equal to the total rates of the two processes, namely, the process of spontaneous emission, the process of stimulated emission, because both these process change the total number from whatever, N 1, N naught to a different number. If the process is in equilibrium, then the rate of absorption should be equal to the rate of emission.

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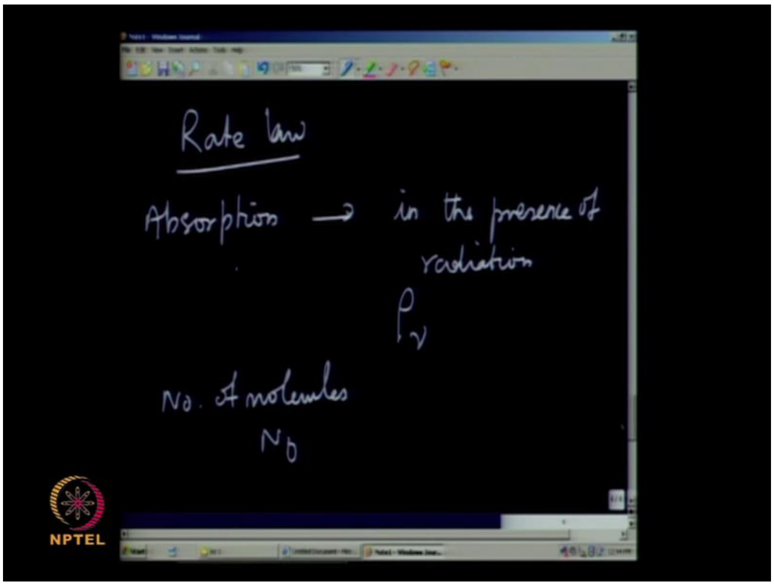

Rate law

Absorption → in the presence of radiation

ρ_ν

No. of molecules

N_0

Then, let us use a simple first order kinetics law and second order kinetics law to determine the rate law. Here, absorption takes place in the presence of, in the presence of radiation. Therefore, if the radiation density volume is given by rho v and if the number of molecules in the ground state N 0, then the rate of change dN naught by dt is proportional to the radiation density because this process does not happen in the absence of radiation. If you assume a first order rate law, the number is proportional to the radiation density and it is also proportional to the number of molecules in the ground state. dN naught by dt is called, is propositional to the product of rho v times N naught.

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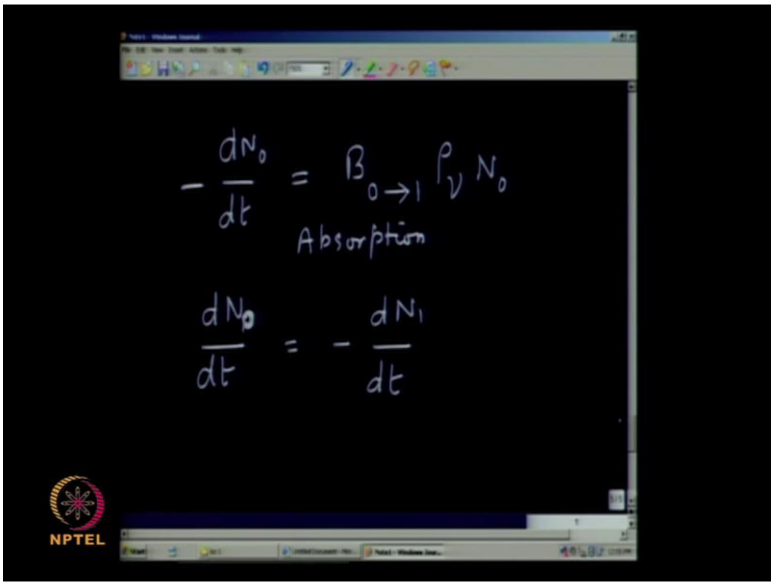

$$-\frac{dN_0}{dt} = B_{0\to1}\,\rho_\nu\,N_0$$

Absorption

$$\frac{dN_0}{dt} = -\frac{dN_1}{dt}$$

The proportionality constant, if we write it dN naught by dT as B constant and since the process is from the lower state to the higher energy state, this is an absorption process. And since the number N naught is changing, is reducing, let us put a minus sign to be careful about what is called the rate. This is the rate at which N naught is decreasing. B 0 to 1 times rho v times N naught, this is the process of absorption. Of course, this should be equal to the process with which the N naught is created, which is the same as the rate are, which N 1 is getting converted into N naught.

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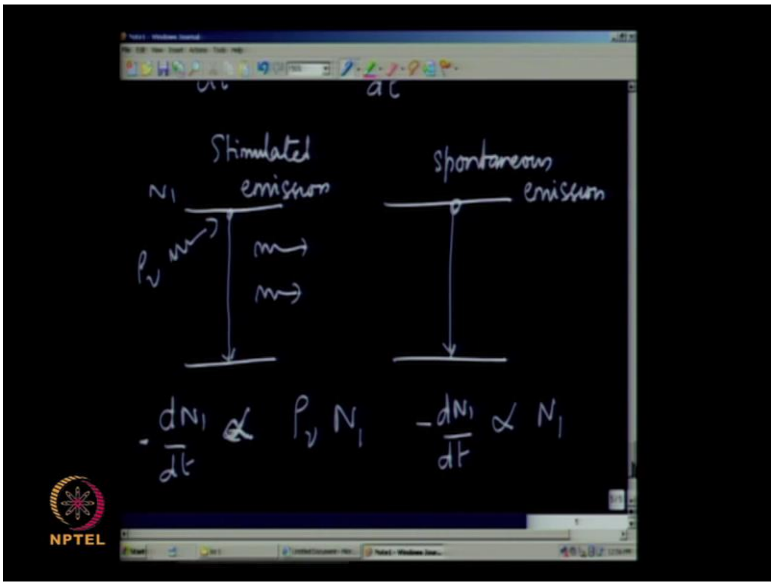

$$-\frac{dN_1}{dt} \propto \rho_\nu N_1 \qquad -\frac{dN_1}{dt} \propto N_1$$

So, if we look at the process by which N naught is obtained, go back and see, that there are two processes, namely the stimulated emission, stimulated emission and the spontaneous emission. And the kinetics of these two processes are different, because the stimulated emission is possible in the presence of rho v, in the presence of radiation rho v. When radiation falls on the excited state, you get two radiations, two photons coming out, whereas the spontaneous emission does not depend on the radiation, the presence of the radiation. Therefore, if you think about the rate at which d N 1 by dt is getting changed in minus is the sum of two processes.

If we consider only the stimulated emission, let us it is proportional to rho v and proportional to the number N 1, that is present in the excited state N 1. The other spontaneous emission process minus d N 1 by dt, that is the rate of change of N 1 due to spontaneous emission is proportional only to the number N 1.

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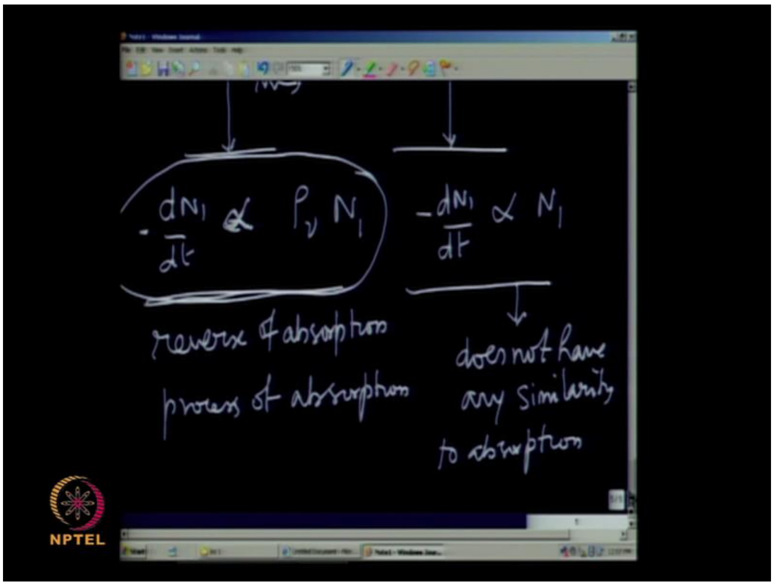

$$-\frac{dN_1}{dt} \propto \rho_\nu N_1 \qquad -\frac{dN_1}{dt} \propto N_1$$

reverse of absorption
process of absorption

does not have any similarity to absorption

Now, please understand, that the physics of these two processes are different. The stimulated emission process requires the radiation, the spontaneous emission process does require radiation and the stimulated emission process is essentially, the reverse of absorption. In the presence of radiation what happens and the presence of radiation what happens to the excited state, therefore there is a certain physical similarity. The process here is similar to the process of absorption, whereas process of absorption, whereas, the spontaneous emission process does not have any similarity to absorption, to absorption.

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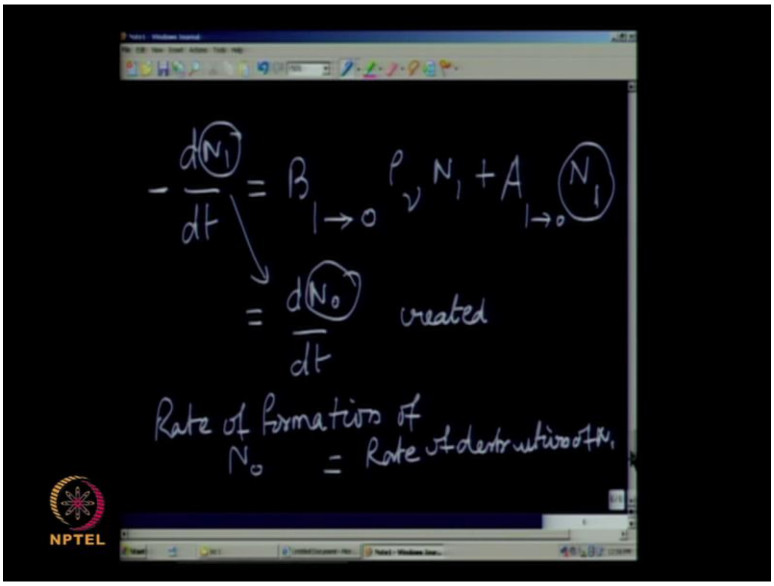

$$-\frac{dN_1}{dt} = B_{1\to 0}\,\rho_\nu N_1 + A_{1\to 0}\,N_1$$

$$= \frac{dN_0}{dt}$$ created

Rate of formation of N_0 = Rate of destruction of N_1

Therefore, when we worry about the kinetics, when we write the two processes, d N 1 by dt, we use the constant, another constant B, where the molecule goes from the excited state to the ground state B 1 0. So, minus d N 1 by dt is proportional to rho v propositional to N 1. However, let us use for the stimulated emission, for the spontaneous emission let us use a different constant, A 1 to 0 and you remember, that it is proportional only to the number present in the excited state.

Now, if this were equal to d N naught by dt, the rate at which N naught is created because anything that is changing from N 1 is landing over in N naught. Therefore, what you have is the rate of formation of N naught is equal to the rate of change of N naught into N 1, rate of formation of N naught and is equal to the rate of destruction of N naught to N 1.

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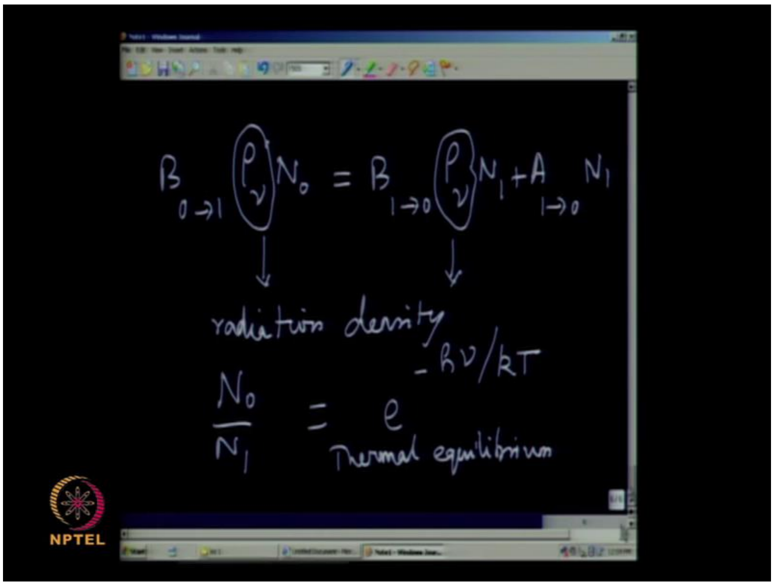

$$B_{0\to1}\,\rho_\nu N_0 = B_{1\to0}\,\rho_\nu N_1 + A_{1\to0}\,N_1$$

radiation density

$$\frac{N_0}{N_1} = e^{-h\nu/kT}$$

Thermal equilibrium

When you do that the two rates are now set equal by B 0 to 1 rho v N 0. This is a rate at which N naught is changed, is equal to B 1 to 0 rho v times N 1 plus A 1 to 0 times N 1. So, this is radiation density, radiation density, radiation density and the ratio N naught by N 1 in thermal equilibrium is e to the minus h nu by kT, which is a Maxwell Boltzmann distribution for the energies in thermal equilibrium.

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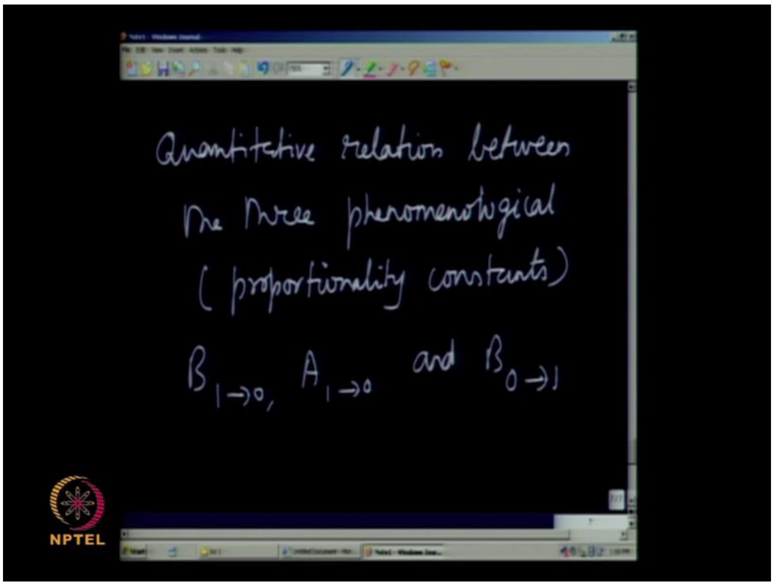

Quantitative relation between the three phenomenological (proportionality constants)

$B_{1 \to 0}$, $A_{1 \to 0}$ and $B_{0 \to 1}$

Therefore, now you see that there is a quantitative relation between absorption, relation between the three phenomenal logical constants, phenomenal logical constant, that is, the proportionality constants. What are they? They are the B 1 to 0, A 1 to 0 and B 0 to 1.

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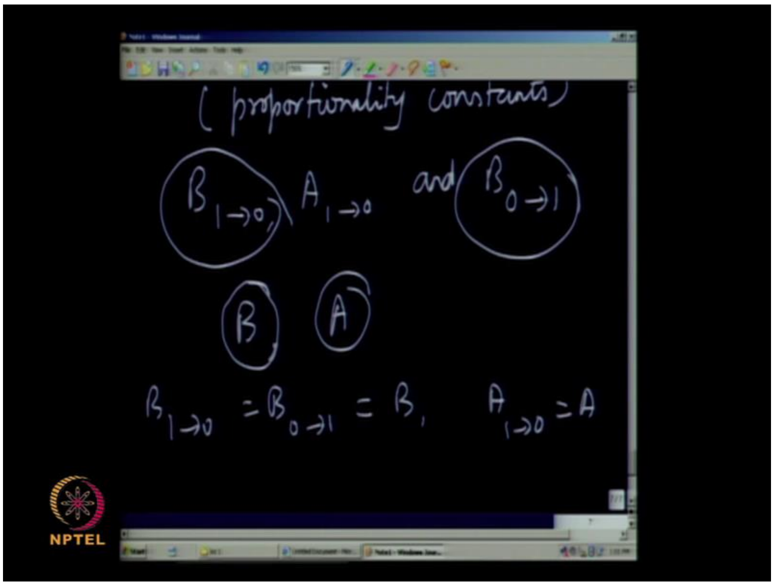

(proportionality constants)

$B_{1 \to 0}$, $A_{1 \to 0}$ and $B_{0 \to 1}$

B A

$B_{1 \to 0} = B_{0 \to 1} = B$, $A_{1 \to 0} = A$

Now, the principle of microscopic reversibility is one of the most fundamental principles in chemical kinetics. If you are not familiar with it please believe, that it is a very basic principle on which much of the chemical kinetics rests on. The principle of microscopic reversibility states, that the two coefficients B 1 to 0 and B 0 to 1 are equal, that is, the rate at which the molecules are excited in presence of radiation and the rate at which the molecules are de-excited again in the presence of radiation, those two constants are equal.

And therefore, what you have is a B coefficient and an A coefficient, which is in summary B 1 to 0 is equal to B 0 to 1 is what I call as B. And if we write, if A 1 to 0 as a coefficient, then one is the stimulated emission, emission absorption coefficient as given by B.

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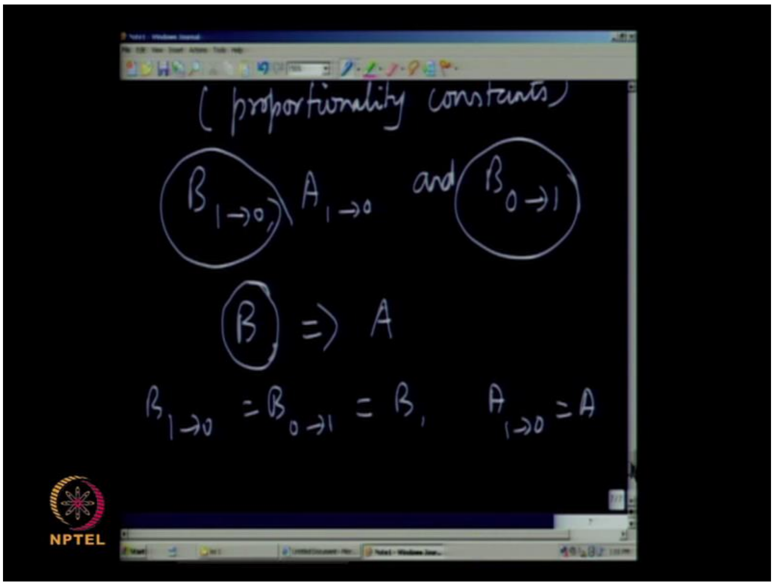

(proportionality constants)

$\boxed{B_{1\to 0}}\; A_{1\to 0}$ and $\boxed{B_{0\to 1}}$

$\boxed{B} \Rightarrow A$

$B_{1\to 0} = B_{0\to 1} = B, \quad A_{1\to 0} = A$

And the other, which is in the spontaneous emission coefficient A, as you have here, there is a relation between the two, which can be worked out from this equation that I have written, namely the coefficient. Now, we can replace B 0 to 1 by B, B 1 to 0 by B and A 1 to 0 by A and you have the ratios of N naught versus N 1.

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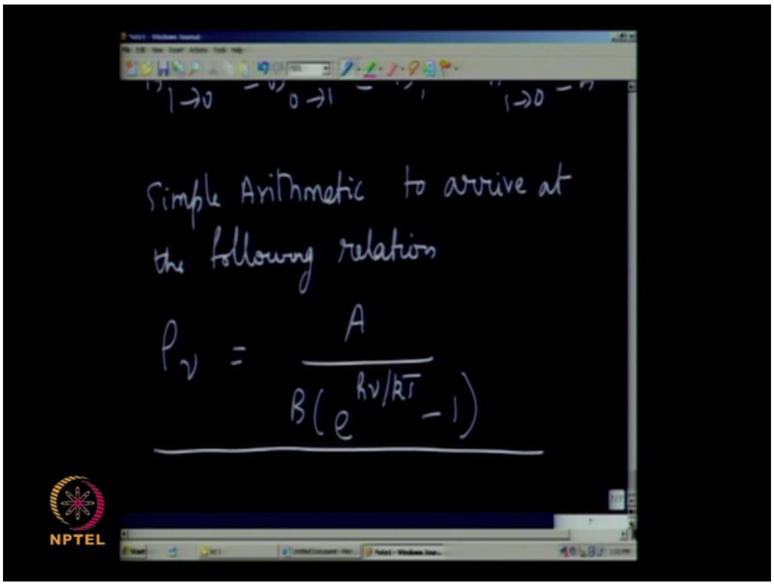

Simple Arithmetic to arrive at the following relation

$$\rho_\nu = \frac{A}{B\left(e^{h\nu/kT} - 1\right)}$$

So, it is a very simple arithmetic to arrive at this relation, which I will leave it to you as an exercise, arithmetic to arrive at the following relations, following relation, namely rho v is given in terms of the coefficients A and B as B into e into the h nu by kT minus 1.

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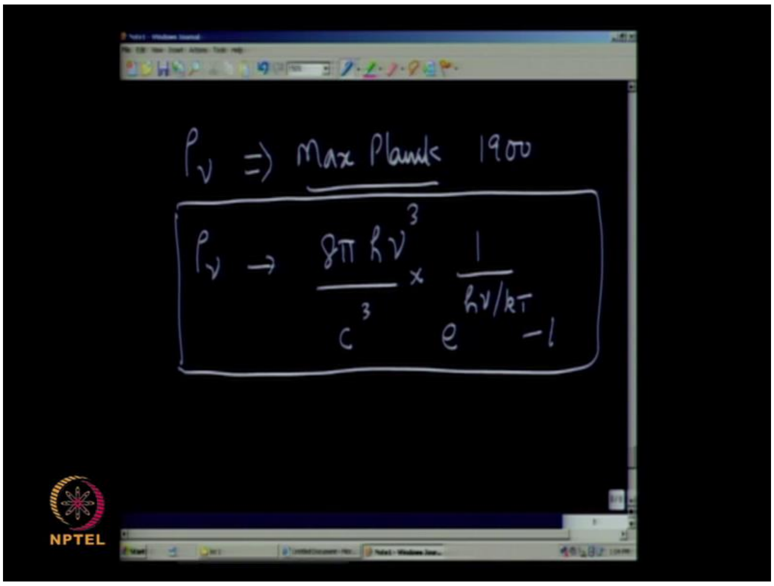

$\rho_\nu \Rightarrow$ Max Plank 1900

$$\boxed{\rho_\nu \rightarrow \frac{8\pi h\nu^3}{c^3} \times \frac{1}{e^{h\nu/kT} - 1}}$$

There is one relation regarding the Planks distribution that you might be familiar with. Rho v was given by Max Plank in 1900, Plank 1900, which changed the physics from classical to quantum mechanics. The Max Plank’s relations for the radiation density rho v is given by this formula, 8 pi h nu cube divided by C cube into 1 by e to the h nu by kT minus 1.

So, this is the formula that Max Plank used for black body radiation assuming, that all the conditions are ideal, that we are talking about the thermal equilibrium. We are talking about absorption and emission processes under ideal conditions.

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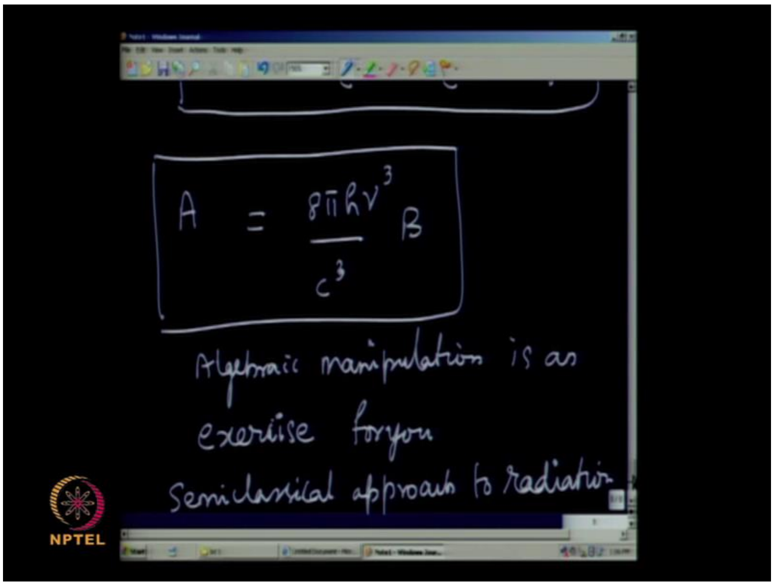

$$\boxed{A = \frac{8\pi h \nu^3}{c^3} B}$$

Algebraic manipulation is an exercise for you

Semiclassical approach to radiation

If we use the relation for the thermal radiation density rho v in terms of the Plank's formula and also the relation between rho v and the coefficients A and B, the stimulated, the spontaneous emission coefficient A and the stimulated emission or the absorption coefficient B, then you see, that there is the relation between A and B.

And again, algebraically, it is very easy to write down the relation. The relation between A and B, is given by, A is equal to 8 pi h nu cube by C cube into B. After you do a simple algebraic manipulation, this is given as an exercise for you, is an exercise for you. The algebra is nothing but substituting for rho v. This expression in this equation rho v is equal to, you put this exponential, h nu by kT. So, you right away, that the exponential h nu by kT sort of goes away, therefore A by B is given by this coefficient. There is nothing hidden, there is no hidden algebra here. This is called the phenomenal logical or semi classical theory, semi classical approach to radiation.

What is the relevance of this process? The relevance of this process is the following. We have defined two macroscopic coefficients called A and B. One coefficient refers to the rate at which, for example, A, if you talk about it as a spontaneous emission coefficient, it talks about a process by which the molecules come down from its excited state to the ground state spontaneously. Therefore, it is associated with that, it is the macroscopic coefficient. As of now we have not identified any other means, said it is a constant.

And also, there is another constant in which it is referring to a different phenomenal, namely the absorption of energy by radiation and we are relating these two coefficients based on an elementary kinetic law, first order rate law, second order rate law in the presence of the radiation, wherever that is necessary.

So, the whole approach is to quantitatively visualize two different phenomena and associate with it two measurable coefficients and then determine how these coefficient are related to the molecular properties, which are responsible for the emission and the absorption in the first place. If you remember the molecular property, that is responsible for emission or absorption of radiation, electrical radiation is, of course, the dipole moment of the molecule or the change in the dipole moment of the molecule, but in some way or the other connected to the molecular electric properties.

Therefore, if we can identify A and B, the two rate constants, which are arbitrarily introduced assuming ideal conditions and thermal equilibrium, radiation equilibrium and if we can identify these constants with the molecular properties, then we have a way of understanding how molecular properties influence the process of spectrum, of obtaining the spectrum.

Therefore, this was all done very, very early, even before the discovery of quantum mechanics in the form of Schrodinger’s wave equation and it is very much applicable in spectroscopy today, that the relation between the As and Bs on the one hand and the identification of a relation between A and B with a molecular property like the dipole moment. I will just give you the final relation, that the coefficient A and B have with the dipole moment and will not elaborate, but this can be derived using more rigorous theories.

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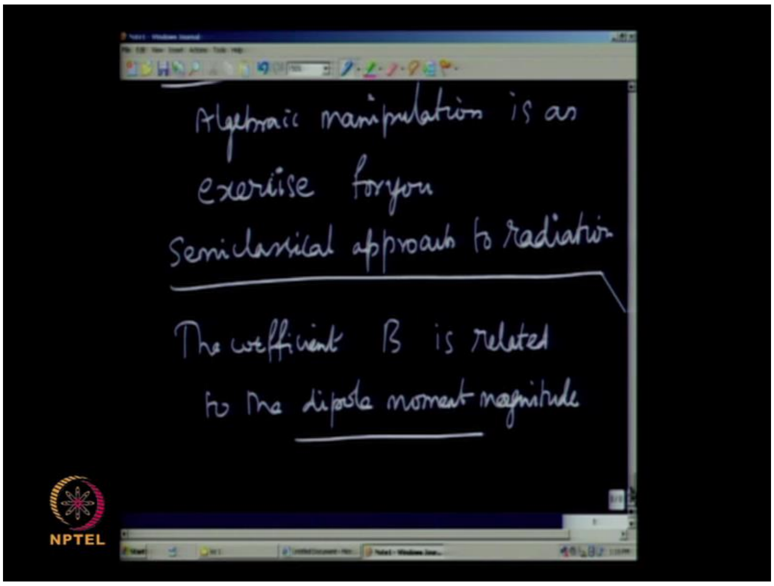
Algebraic manipulation is an exercise for you

Semiclassical approach to radiation

The coefficient B is related to the dipole moment magnitude

The coefficient B is related to molecular property, is related to the dipole moment of the molecule, dipole moment magnitude.

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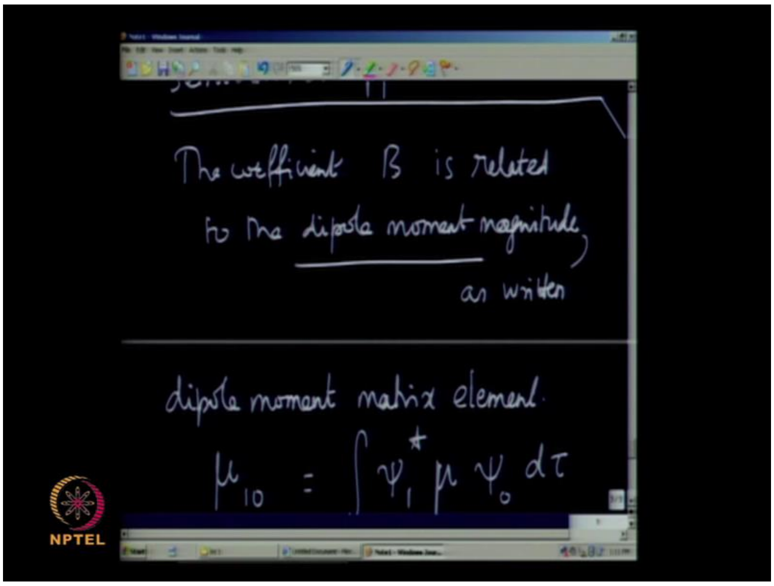
The coefficient B is related to the dipole moment magnitude, as written

dipole moment matrix element

$$\mu_{10} = \int \psi_1^* \mu \psi_0 \, d\tau$$

But there is a very special quantity, as we go further in spectroscopy we will try and understand is not the magnitude as I have written, but as written, but what is called the dipole moment matrix elements, dipole moment matrix elements.

Since you already have had a description of quantum mechanics, the dipole moment matrix elements mu 1 0 is written as the molecular Eigen function corresponding to the excited state psi 1 star the operator dipole moment and the molecular Eigen function corresponding to the ground stage d tau. This is called the matrix element, dipole moment matrix element and the coefficient B is related to this dipole moment by this formula.

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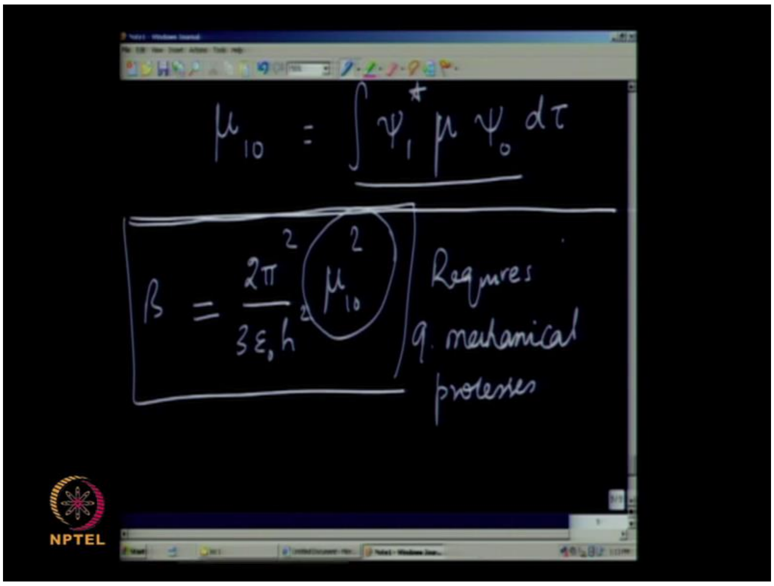

$$\mu_{10} = \underline{\int \psi_1^* \mu \psi_0 \, d\tau}$$

$$\boxed{B = \frac{2\pi^2}{3\varepsilon_0 h^2} \mu_{10}^2}$$

Requires q. mechanical processes

B is given by 2 pi square by 3 epsilon naught h square mu 1 0 square. Therefore, you see that the arbitrary coefficient that we introduced as a constant for the rate process, let me rewrite it again, and the molecular property called the dipole moment matrix element.

Now, you see, how quantum mechanics and once model are determined and the relations are determined by these, the wave function are obtained by quantum mechanics by the solution of the Schrodinger equation. The dipole moment is determined in equilibrium for a molecule using microwave spectroscopy and then we have what is called the absorption coefficient related to the dipole moment matrix element through a theory, which of course, I have not given this. I have not derived this, please this requires a little bit of advanced mathematics, let us not do that, requires quantum mechanical theory processes.

But let us try and simply write the fundamental relation here in terms of the absorption coefficient and the molecular property to show, that a semi classical method with a little bit of ingenuity can take you for an understanding a spectrum in terms of a coefficient, that can be measured experimentally and a molecular property, which can be interpreted. This is what is the first part of the lecture namely, the three processes and the relations between them.