Chemistry II: Introduction to Molecular Spectroscopy
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Lecture – 05
Radiation densities and Einstein’s Semiclassical model

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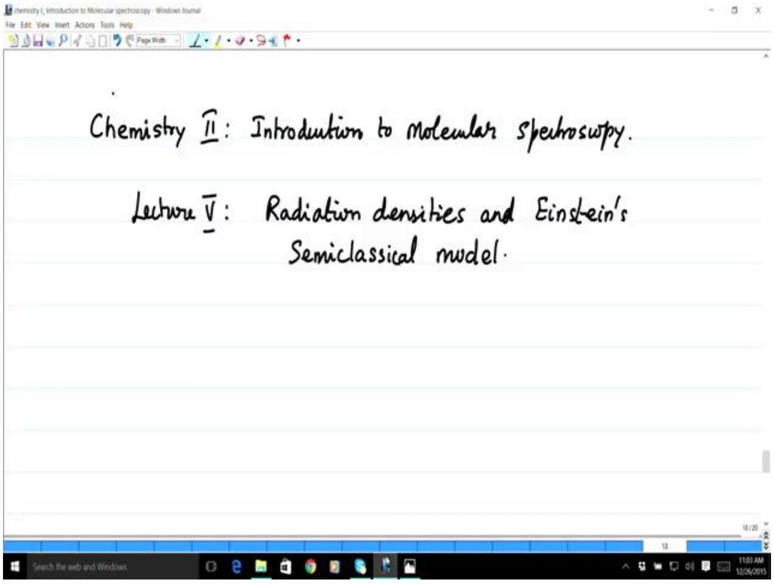

Chemistry II : Introduction to Molecular spectroscopy.

Lecture V : Radiation densities and Einstein's Semiclassical model.

Welcome back to the lecture on molecular spectroscopy as part of chemistry-2. In this which is a rather a long lecture, I shall describe a little bit about the radiation densities that we need use in the processes of spectroscopy, and also the Einstein’s semi classical model as an introductory concept for microscopic coefficients that can be measured.

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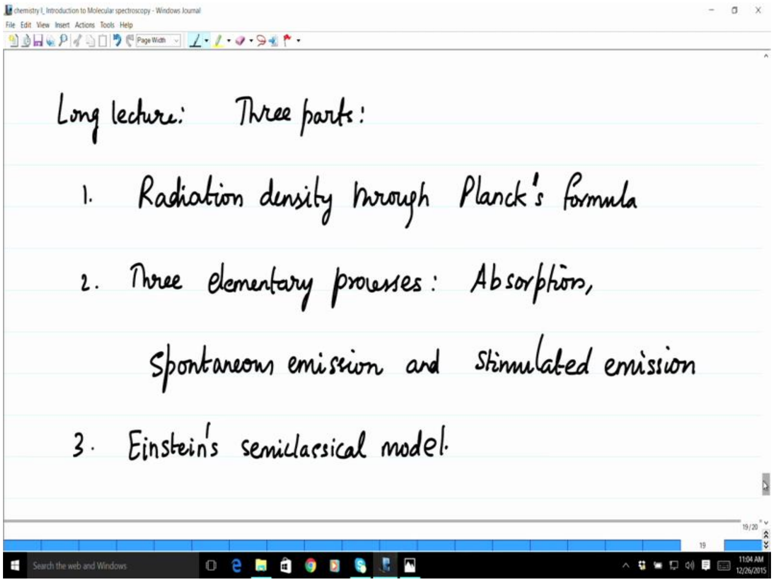

Long lecture: Three parts:

1. Radiation density through Planck's formula
2. Three elementary processes: Absorption, Spontaneous emission and Stimulated emission
3. Einstein's semiclassical model.

Now, the lecture has about three parts. The first part will contain a little bit on the radiation density and let me recall from your elementary atomic physics or chemistry, the Max Planck's formula, which revolutionized the whole of physics and lead to the discovery quantum mechanics later. Radiation interacts with matter and it was first conceived by Albert Einstein through a semi classical model by invoking three elementary processes; and these processes are known as absorption, spontaneous emission and stimulated emission. So, let me explain that a little bit, and also explain a bit on the Einstein's semi classical model.

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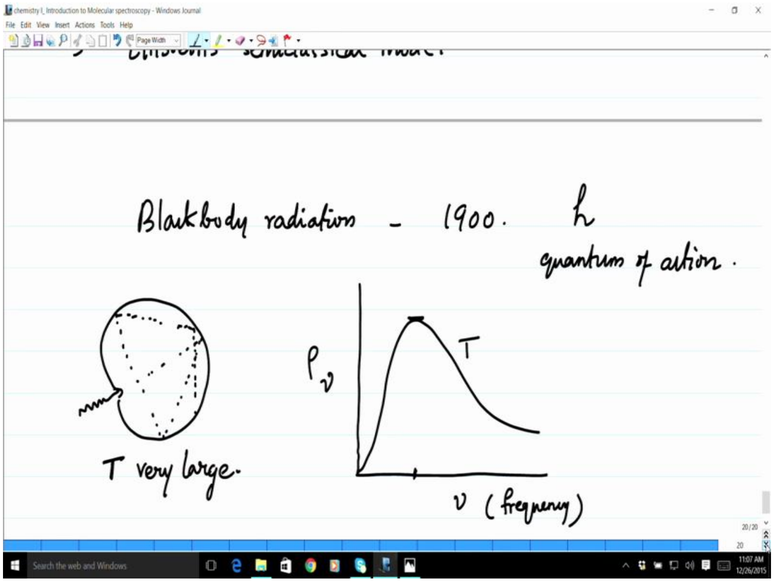

Blackbody radiation - 1900. h quantum of action.

First let us look at the Planck’s formula and the object of interest for radiation density in Planck’s formula is the idealized body known as the blackbody, which when it is heated to very high temperatures and is in thermally equilibrium with the radiation that gets emitted due to the heat, the blackbody emits all frequencies radiation of all frequencies. The thermally equilibrium essentially means a radiation is inside the cavity and it is an equilibrium with the black body, and one measures the radiation density as a function of frequencies, one gets a distribution like this for a given temperature. If you write the radiation density as rho nu as a function nu - the frequency, one typically gets a graph something like that for a given temperature T. Radiation density is distributed for various values of the frequency with different densities, but it also has a maximum frequency that is a densities maximum for a particular frequency at any given temperature.

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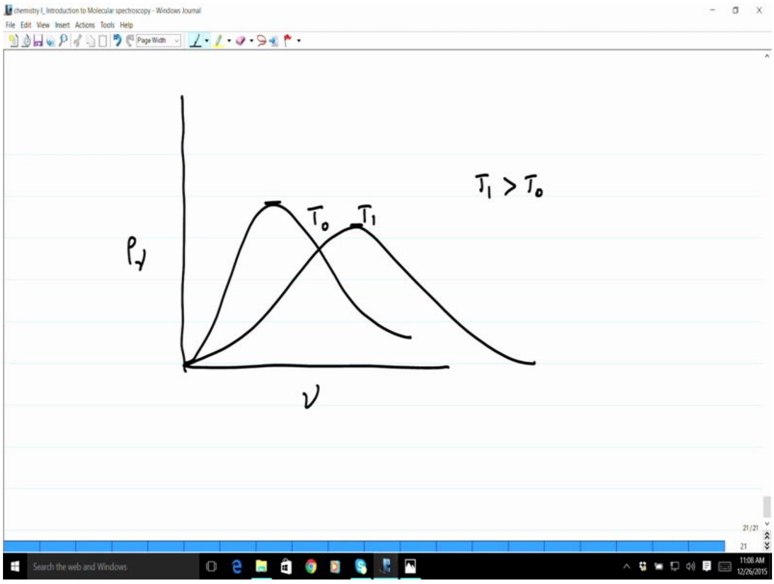

What one found was that if you plot this at various temperatures, for various temperatures of the black body rho nu 1 gets this for a T 1, say let us call it T 0. And another graph T 1, where the maximum radiation density that is a frequency for which the density is maximum is greater, if T 1 is greater than T naught; and likewise if the temperatures increased the maximum shifts towards higher and higher frequencies.

But please note that the radiation density is very low or it is almost 0 for very low frequencies, and also for very high frequencies, and therefore the blackbody emits radiation with frequencies which are in a rather limited range even though all frequencies are acceptable. What you see here is that low frequency radiation density approaches 0 and the high frequency radiation density also approach 0. And therefore, how do we obtain this graph.

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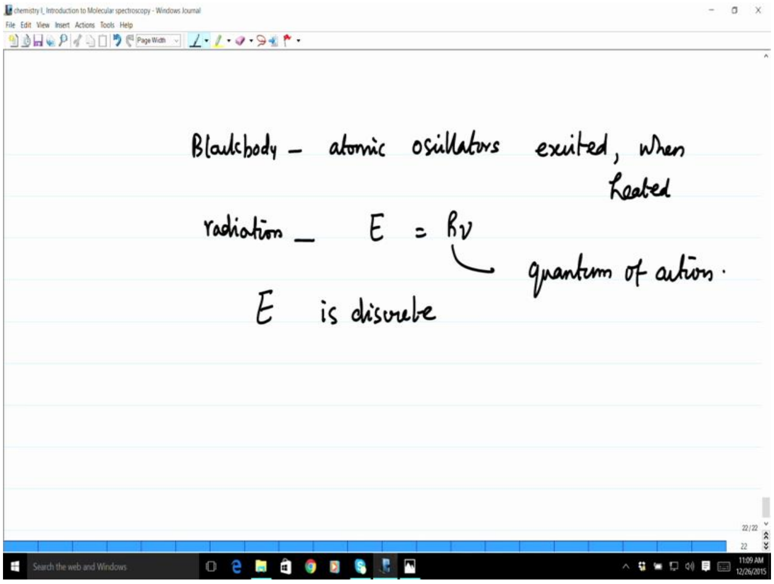

Blackbody – atomic oscillators excited, when
heated

radiation – $E = h\nu$

quantum of action.

E is discrete

Max Planck was the first one who solved this riddle with his own formula. And he came up with the idea that the blackbody has atomic oscillators which get excited when the temperatures are increased that is when it is heated. And the oscillators are in thermal equilibrium and they emit radiation; and the energy of the radiation that they emit is not arbitrary, the energy is proportional to the frequency, and a proportionality constants were introduced by Planck called the quantum of action. And these are very small number, but it is a finite number, therefore the energy emitted by the blackbody is discrete E is not all energies, but energy comes in the form of packets. This was the proposal that Planck came up with. And in this proposal of course, he introduced the constant of action which he called as the quantum of action it is an action constant in classical mechanics action means very, very specific things.

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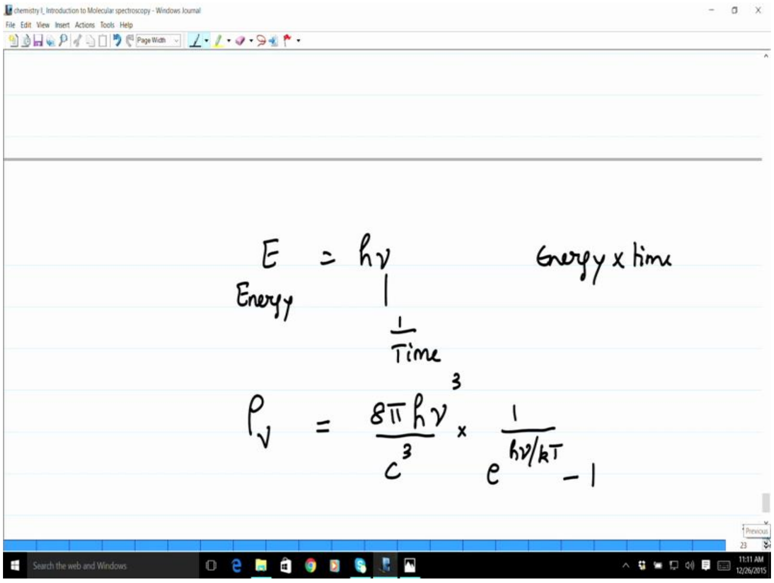

$E = h\nu$

Energy

$\frac{1}{\text{Time}}$

Energy x time

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

And Planck’s constant has the dimension E nu write h, this is 1 by time, and this is energy. Therefore, Planck introduced h ah energy into time. The radiation density rho nu for any given frequency nu, Planck’s proposal was to give this particular formula; he derived this formula with assumption that the energy is emitted in a discontinuous fashion. And it is h nu cube by c cube - the speed of light times 1 by e to the h nu by k t minus 1. Where nu is the frequencies, C is the speed of light, and k is the Boltzmann’s constant.

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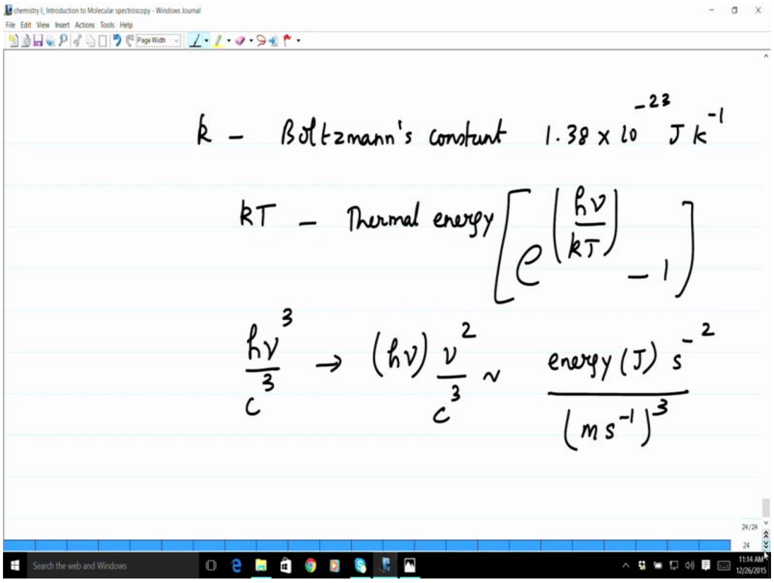

k – Boltzmann's constant $1.38 \times 10^{-23}\ J\,K^{-1}$

kT – Thermal energy $\left[e^{\left(\frac{h\nu}{kT}\right)} - 1\right]$

$$\frac{h\nu^3}{c^3} \rightarrow (h\nu)\frac{\nu^2}{c^3} \sim \frac{\text{energy}\ (J)\ s^{-2}}{(m\,s^{-1})^3}$$

K in honor of Ludwig Boltzmann, it is a Boltzmann's constant. And it is value is of course, very, very small and very precisely these days of course, these constants can be measured. And the value is approximately 1.38 into 10 to the minus 23 joules per Kelvin, and k T is thermal energy at any given temperature T. And h nu by k T is the factor which when exponentiation gives us the weight of the frequency nu to the radiation density rho nu.

Now, if you look at this formula carefully, rho nu as 8 pi h nu cube by c cube, of course, this factor is dimensionless, because it is energy divided by energy h nu by k t. Anyway, any exponential sign etcetera should have factors, which are dimensionless. But here if you look at the dimension of rho nu it is h nu cube by c cube. So, let me write that as h nu nu square by c cube dimensionally it is energy which you can write as joules per second square, because nu square and c cube is meter per second whole cube. Therefore, the dimension that you have for rho nu is energy time per volume; this is the radiation density formula.

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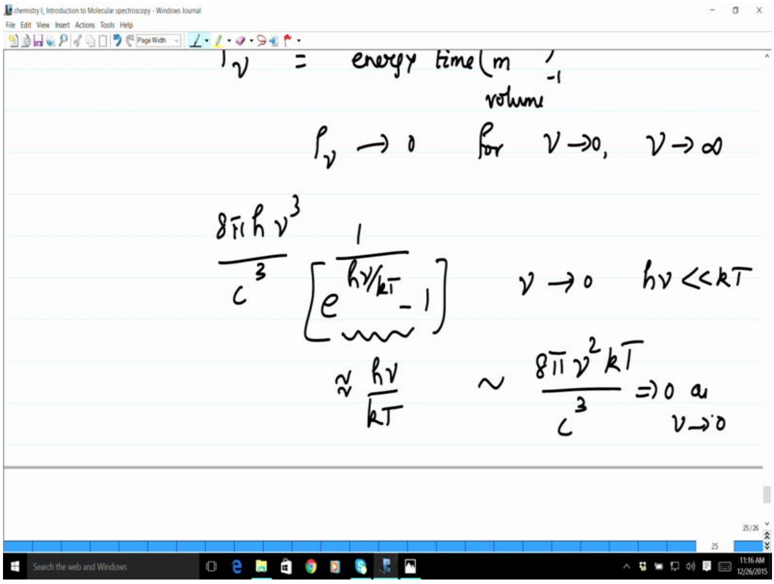

ν = energy time(m $^{-1}$ volume

$\rho_\nu \to 0$ for $\nu \to 0$, $\nu \to \infty$

$$\frac{8\pi h\nu^3}{c^3}\frac{1}{\left[\underbrace{e^{h\nu/kT}-1}_{\approx \frac{h\nu}{kT}}\right]} \qquad \nu \to 0 \quad h\nu \ll kT$$

$$\sim \frac{8\pi\nu^2 kT}{c^3} \Rightarrow 0 \text{ as } \nu \to 0$$

And it also is such that on both limit's when you take nu to be very large and nu to be very small, this formula leads to a value of rho nu going to 0; for nu going to 0, nu going to infinity that is very large values that is easy to check. Because if you write the formula as 8 pi h nu cube by c cube 1 by e to the h nu by k t minus 1, please remember this factor when nu is very small, h nu is much less than k T for any T and therefore, this is approximately h nu by k T because it is 1 plus x you know it is an exponential x. So, it is 1 plus x etcetera and this is the factor and this nu of course, cancels with that and. So, the formula for rho nu is 8 pi nu square k T by c cube which goes to 0 as nu goes to 0. Therefore, the lower end of the graph is reproduced by the max form max Planck's formula when nu goes to 0.

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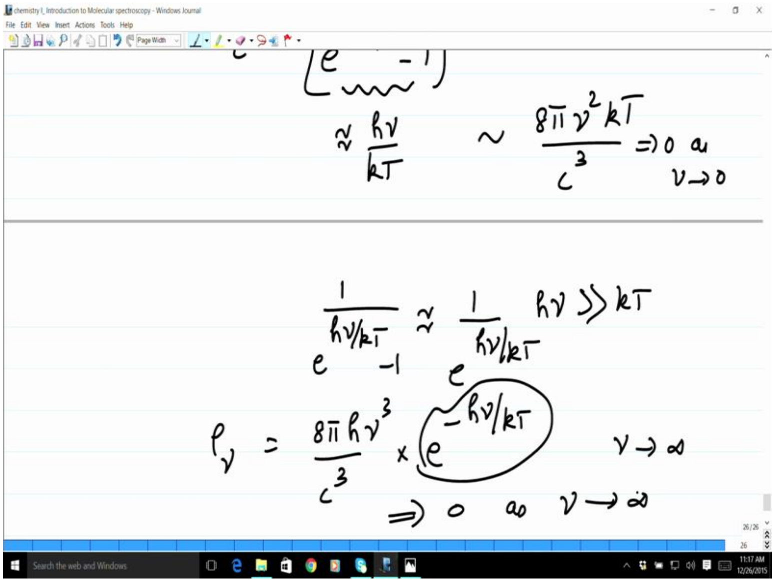

$$\approx \frac{h\nu}{kT} \quad \sim \quad \frac{8\pi\nu^2 kT}{c^3} \Rightarrow 0 \text{ as } \nu \to 0$$

$$\frac{1}{e^{h\nu/kT}-1} \approx \frac{1}{e^{h\nu/kT}} \quad h\nu \gg kT$$

$$\rho_\nu = \frac{8\pi h\nu^3}{c^3} \times e^{-h\nu/kT} \quad \nu \to \infty$$

$$\Rightarrow 0 \text{ as } \nu \to \infty$$

What about the higher value of nu that is also easy to see because when you write 1 by exponential h nu by k T minus 1, and if nu is very, very large, so that h nu is much larger than k T then this is approximately 1 by e to the h nu by k T and the rho nu therefore becomes 8 pi h nu cube by c cube times e to the minus h nu by k T. And you see that the exponential goes to 0 faster than the nu cube rising as nu goes to infinity, therefore rho nu also goes to 0 as nu goes to infinity. This is an extremely important formula that Max Planck's came up with for the blackbody radiation and we shall use that radiation density formula that Max Planck's use in the next item namely after we describe the three processes of the introduction of radiation with matter. First proposed in detail by Einstein and also worked out with some basic chemicals kinetics that we needed to look at.

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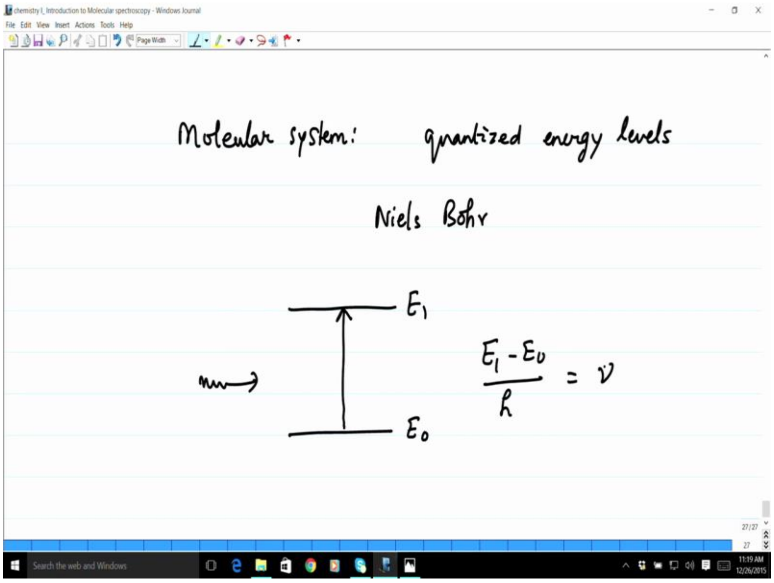

Molecular system: quantized energy levels

Niels Bohr

$$\frac{E_1 - E_0}{h} = \nu$$

So, let us look at those three processes. If you go back to the lecture, the three elementary processes that we want to look at or the absorption spontaneous emission and stimulated emission. Let us imagine molecular system that the energy levels of atoms or quantized was already known in 1617 when Einstein came up with this theory quantized energy levels because Niels Bohr had already studied the hydrogen atom spectra and came up with the quantization of the energies and so on. And therefore, let us assume for molecular system an isolated two energy levels E naught and E 1. We will only consider a two level system, I mean a three level and multilevel systems are the slightly more complex and to understand the basic physics it is possible for us to restrict ourselves to the two level system, radiation corresponding to the energy difference here E 1 minus E naught by h, if you put that as a frequency radiation of a frequency nu falling on the system.

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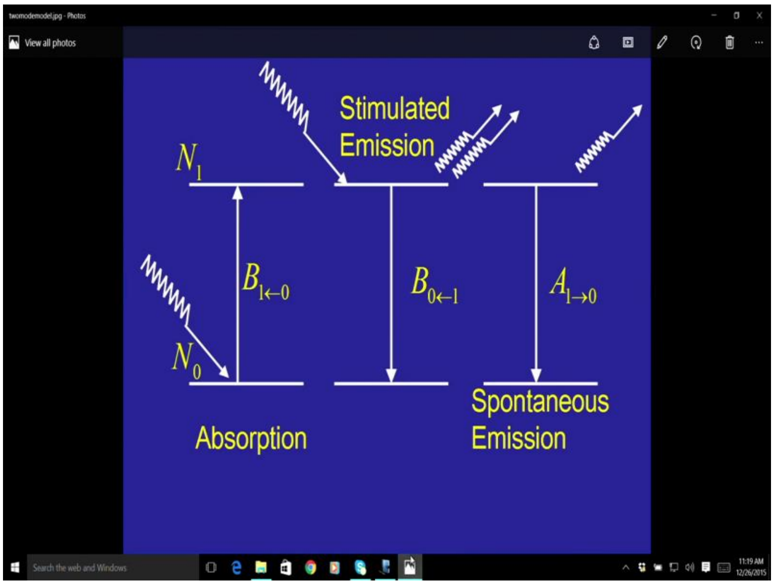

What are the three processes? So, here are the three processes that we need to consider. The absorption process is when the radiation falls on molecular system a large number of them N naught in the lower energy state. And N 1 in the higher energy state when radiation falls on molecular system in the lower energy state, the molecule rises to the higher energy it raises to the higher energy state through the process of radiation absorption. So, it is straight forward absorption process. The other process on the side is molecules which are already in the excited state by themselves spontaneously releasing the energy through radiation and coming down to the ground state, whether there is radiation or not this is a spontaneous emission for all the excited molecules. And you also know that when there are multiple energies for a molecular system at any given temperature and when we attain thermal equilibrium, we know that molecules are not all in the lower energies state or all in the higher state, but they are distributed and this distribution follows what is known as Maxwell Boltzmann distribution.

Therefore, we assume that there are more molecules in the lower energy states likely less in the higher energy state. But when equilibrium is attained the weight of energy absorption by the molecules due to radiation falling on it is equal to the rate of emission of the excited states of molecules reaching the ground state. The excited states can come down to the ground state by two processes; one is spontaneous emission, the other is the stimulated emission that is the radiation itself may stimulate the excited state to release it is energy and come down to the ground state if you call this as the lower energy state.

But in that process, conservation of the energy requires that two photons radiation photons or emitters, those are indicated by the two arrows here and the constant B 0 to 1, and B 1 to 0, and A 1 to 0, these are coefficients which connect the rates of change to the number of molecules and to the radiation density.

We will see that in the next step in the kinetics. The processes are absorption in the presence of radiation, stimulated emission in the presence of radiation, and spontaneous emission in the presence or in the absence it does not matter the emission happens spontaneously, radiation does not have their own.

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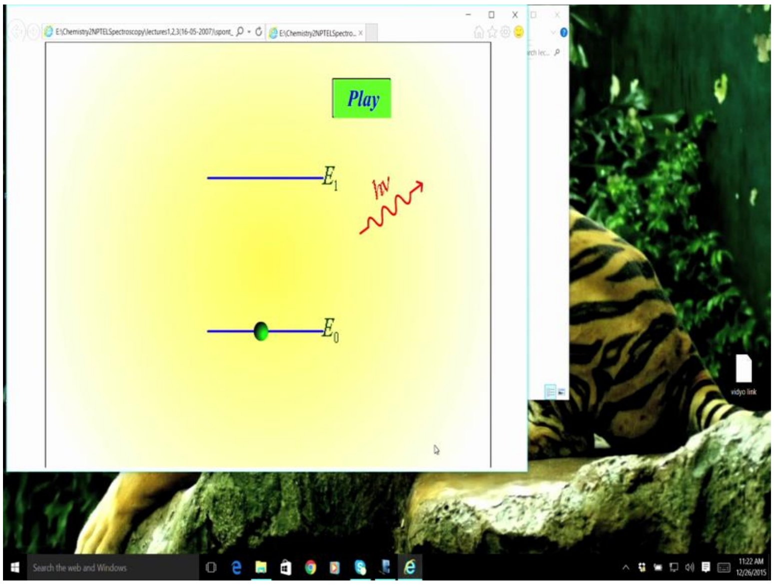

So, these three processes we can see and also there are very elementary animations for that, an absorption is essentially the molecule being raised to the higher energy state from the lower energy state due to absorption of energy from the radiation. And the spontaneous emission corresponds to molecule from the higher energy state by itself releasing the energy and reaching the ground state. And the stimulated emission is due to the presence of the radiation actually disturbing the excited state and the molecule releases it is energy, but in the process it releases two photons.

So, the idea of laser the stimulated emission light amplification through stimulated emission of radiation was conceived by Einstein almost 40 years before lasers were actually discovered and experimentally set up. So, these three processes can be used to study an elementary model for absorption versus emission. Let me pause for a break here, and then we will continue with the model for studying the thermal equilibrium in the presence of radiation through these three processes.

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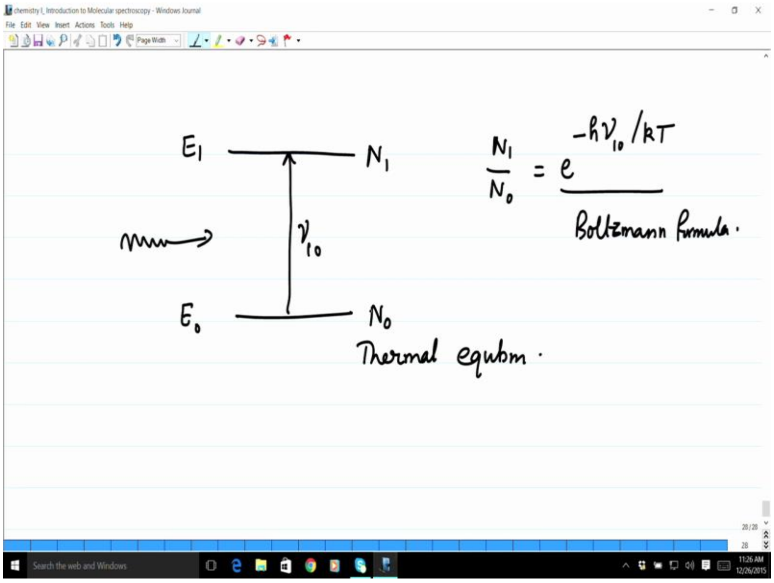

$$\frac{N_1}{N_0} = e^{-h\nu_{10}/kT}$$

Boltzmann formula.

Thermal equbm.

So, before we do this, we will again write the three processes. This is energy E 1, this is E naught and number of molecules in this state are is N naught and the number here is N 1. And the first thing that we know thermal distribution N naught by N 1 or let me write N 1 by N naught the higher energy state by n naught is given by the Boltzmann distribution namely E to the minus h nu 1 0 by k T. What is nu 1 0 that is this frequency nu 1 0. So, the ratio of the number of molecules in the excited state to the ground state is given by the Boltzmann formula. So, keep that in mind. Now, let us assume that this is all in equilibrium in the presence of radiation. So, there is thermal equilibrium. So, thermal equilibrium means that the rate of change of N naught due to absorption of radiation and it is excitement to reach the level N 1; E 1 is the same as the rate of change of N 1 to become N naught.

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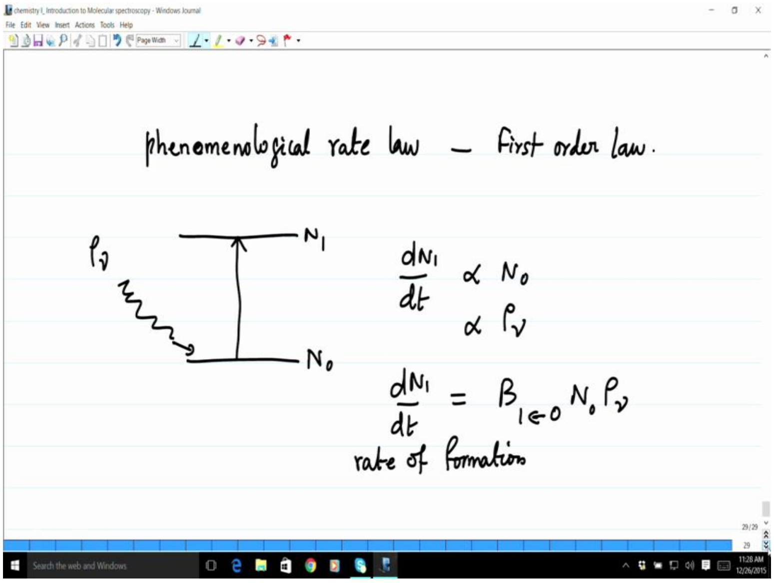

phenomenological rate law — First order law.

$$\frac{dN_1}{dt} \propto N_0$$
$$\propto \rho_\nu$$

$$\frac{dN_1}{dt} = B_{1\leftarrow 0} N_0 \rho_\nu$$

rate of formation

Therefore, let us calculate these two rates based on some phenomenological rate law. Usually we shall use the first order rate law; first order rate is also what is followed by most natural processes. And here in thermal equilibrium, suppose we talk about N 1 d N 1 by d t the rate of formation of N 1 from N naught then that dependence on N naught as well as on the radiation intensity or radiation density rho nu. Therefore, d N 1 by d t is proportional to N naught is proportional to the radiation density and the proportionality constant is the rate coefficient which we shall B 0 to 1 process from 0 to 1. This is N 1, N naught rho nu. Now, the rate of change of this is the rate of formation, it is positive.

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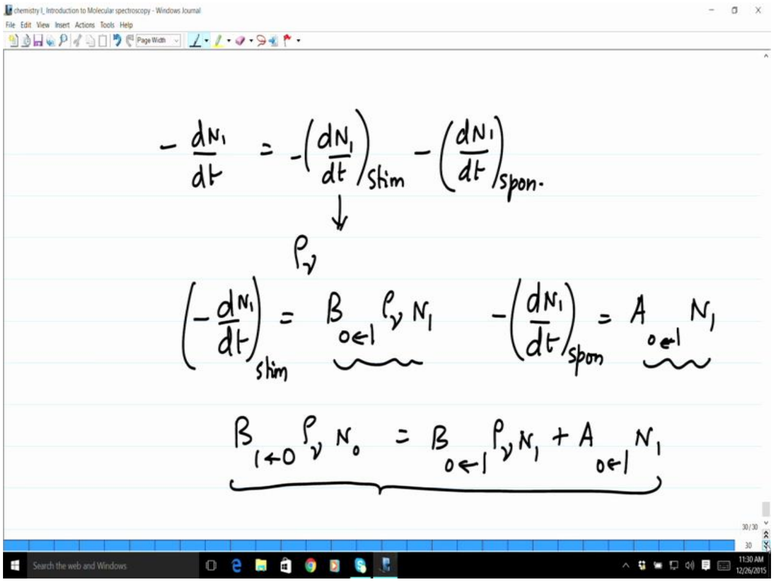

$$-\frac{dN_1}{dt} = -\left(\frac{dN_1}{dt}\right)_{stim} - \left(\frac{dN_1}{dt}\right)_{spon.}$$

$$\downarrow$$
$$\rho_\nu$$

$$\left(-\frac{dN_1}{dt}\right)_{stim} = \utilde{B_{0\leftarrow1}}\,\rho_\nu N_1 \qquad -\left(\frac{dN_1}{dt}\right)_{spon} = \utilde{A_{0\leftarrow1}}\,N_1$$

$$\underbrace{B_{1\leftarrow0}\,\rho_\nu N_0 = B_{0\leftarrow1}\,\rho_\nu N_1 + A_{0\leftarrow1} N_1}$$

The rate of decay d N 1 by d t minus is due to two processes namely the stimulated emission and spontaneous emission. These are two physical processes because in the stimulated emission, there is radiation density here there is no radiation density. Therefore, minus d N 1 by d t is that is the rate of decay is proportional to rho nu is proportional to the number N 1. And therefore, it has also the phenomenological coefficient B 1 to 0 rho nu N 1, this is stimulated. And the d N 1 by d t spontaneous minus, minus is to show that this is decay is simply another constant A 1 to 0, but it is simply proportional to the number N 1 because that is it is independent of the radiation density. So, the total rate is the sum of this and that and this is the rate of change of N 1 to N naught therefore; this is the same as the rate of formation of N 1. So, if you equate these two what you have is B 0 to 1 rho nu N 0 is B 1 to 0 rho nu N 1 plus A 1 to 0 that is the constant the rate coefficient times N 1. This is thermal equilibrium.

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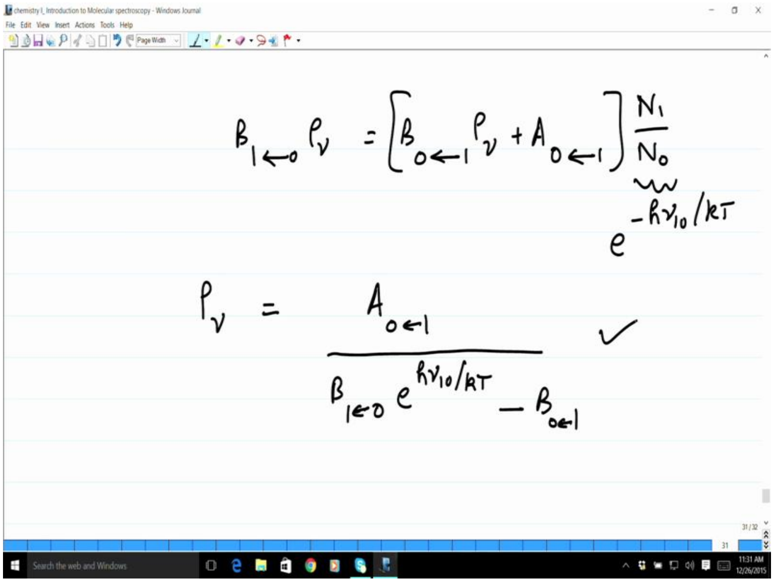

$$B_{1\leftarrow 0}\rho_\nu = \left[B_{0\leftarrow 1}\rho_\nu + A_{0\leftarrow 1}\right]\underbrace{\frac{N_1}{N_0}}_{e^{-h\nu_{10}/kT}}$$

$$\rho_\nu = \frac{A_{0\leftarrow 1}}{B_{1\leftarrow 0}\,e^{h\nu_{10}/kT} - B_{0\leftarrow 1}} \quad ✓$$

Now, just rearrange this a little bit and use the Maxwell Boltzmann formula namely we want to write N 1 by n naught. So, let us write B 1 to 0 rho nu this equal to B 1 to 0 rho nu plus A 1 to 0 times N 1 by n naught and this is given by e to the minus h nu 1 0 by k T. So, if you do you that then we can write a formula for the radiation density rho nu as A 1 to 0 divided by B 0 to 1 e to the h nu 1 0 y k T minus B, this is 0 to 1, this is 1 to 0. This is a just a rearrangement of this formula to give you this result. But remember Planck’s formula for thermal radiation in equilibrium with the hot body which is excited and that is actually 8 pi h nu cube in this case nu is the nu 1 0 by c cube times 1 by exponential h nu 1 0 by k T minus 1.

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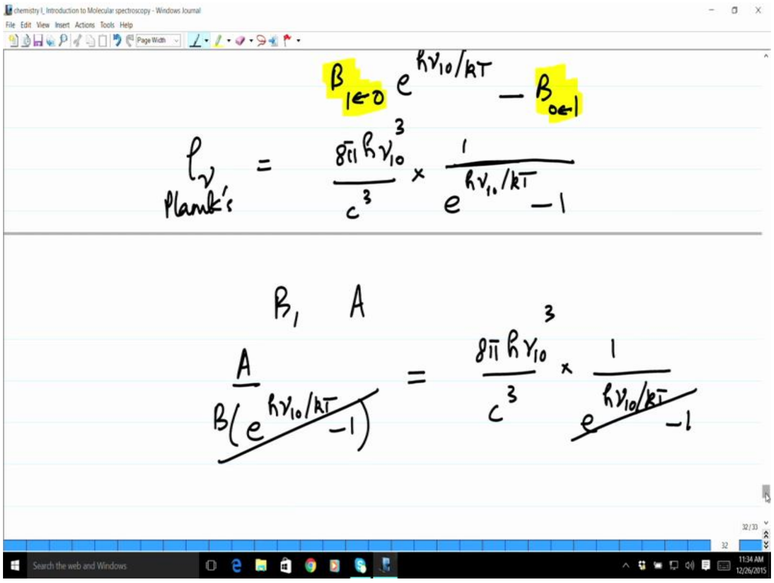

$$B_{1\leftarrow 0}\, e^{h\nu_{10}/kT} - B_{0\leftarrow 1}$$

$$\underset{\text{Plank's}}{\rho_\nu} = \frac{8\pi h\nu_{10}^3}{c^3} \times \frac{1}{e^{h\nu_{10}/kT} - 1}$$

$$B_1 \qquad A$$

$$\frac{A}{B\cancel{\left(e^{h\nu_{10}/kT} - 1\right)}} = \frac{8\pi h\nu_{10}^3}{c^3} \times \frac{1}{\cancel{e^{h\nu_{10}/kT} - 1}}$$

So, this is Planck’s formula and these two formulas make sense, and they are equal only if you notice that this one namely the B 1 to 0 is equal to B 0 to 1. It is also easy to visualize that the rate coefficient for the absorption of radiation and the rate coefficient for stimulated emission of radiation, which is that the state is in a higher energy and it is also being prompted by the radiation to reach the bottom. And it is possible to realize that microscopically these two processes will have the right coefficient, it is a principle of detailed balance one can verify one can argue that these coefficients are the same, but Planck’s formula also tells us that unless these two are equal, does not make sense.

Therefore, if we assume that the absorption coefficient and the stimulated coefficients - stimulated emission coefficients they are both equal then we an extremely simple formula. We have only one absorption coefficient namely one B and A, an A is physically different because it is spontaneous emission and you can see immediately the relation between A and B through this formula. First of all, what you see is that A, this is A by B times e to the h nu 1 0 by k T minus 1 is equal to 8 pi h nu 1 0 cube by c cube into 1 by e to the h nu 1 0 by k T minus 1. And this cancels out this goes away.

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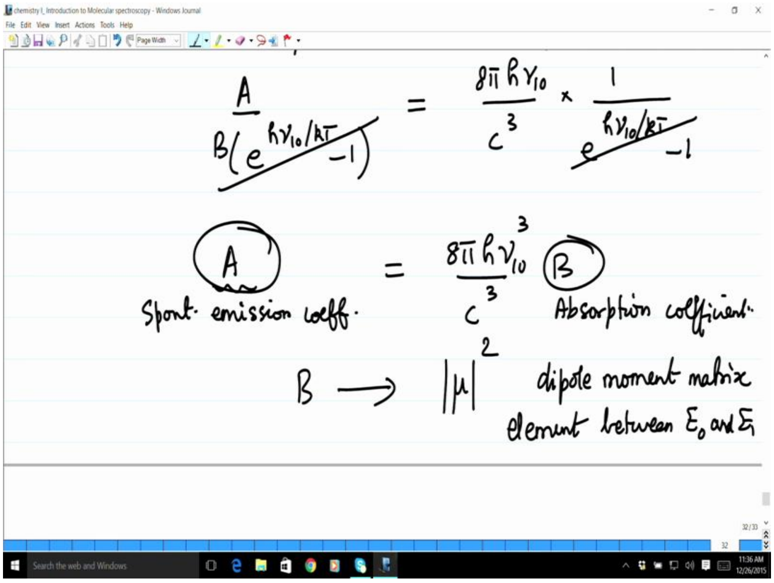

$$\frac{A}{\cancel{B\left(e^{h\nu_{10}/kT}-1\right)}} = \frac{8\pi h\nu_{10}}{c^3} \times \frac{1}{\cancel{e^{h\nu_{10}/kT}-1}}$$

$$\boxed{A} = \frac{8\pi h\nu_{10}^3}{c^3}\boxed{B}$$

Spont. emission coeff. Absorption coefficient.

$B \longrightarrow |\mu|^2$ dipole moment matrix element between E_0 and E_1

And therefore, what you have is A the spontaneous emission coefficient is equal to 8 pi h nu 1 0 cube by c cube times B, which is the absorption coefficient. Thus two microscopically measurable coefficients have been introduced to study the process. And there is also a relation between them based on what is called a phenomenological approach namely, assuming every elementary first order chemical kinetics, rate processes. And the more important one is that not only that A and B are related, but B will be later shown by more accurate quantum mechanical theories as leading to the square of the dipole moment matrix element.

We will see that later dipole moment matrix element between the two states E 0 and E 1, the absolute square of the dipole moment. And therefore, a microscopic coefficient will be directly proportional to a microscopic that is a molecule parameter the dipole moment and thus establishes the connection between molecular properties. And what you measure spectroscopically in an instrument using microscopic coefficient. This was a proposal and this was this was been verified at a linear level we have used the linear law namely the rate is proportional to the number, rate is proportional to the radiation density, these are linear relations. We have not used any concepts. Therefore, in the limit of what is called a low radiation densities and a reasonable degree of thermal equilibrium, these have been known and these are verified. We shall keep this in mind when we study the absorption coefficient using the dipole matrix moment element later, but this is a fundamentally important theoretical detail for understanding the first level the linear spectroscopy.

Let me stop at this point, and we shall see a little more about what is a dipole moment, what are polarizabilities, and what is the moment of inertia for a molecule in the next lecture and that is important because the moment of inertia is generally known as a second rank tensor and. So, is polarizability the dipole moment in a molecule is a vector, therefore we need to introduce these concepts before we start using the matrix elements, before we start using dipole moment square and so on in the measurement of microwave infrared and electronic spectroscopy. So, the next lecture, we will introduce these three properties, polarizability, dipole moment and moment of inertia.

Until then thank you very much.