

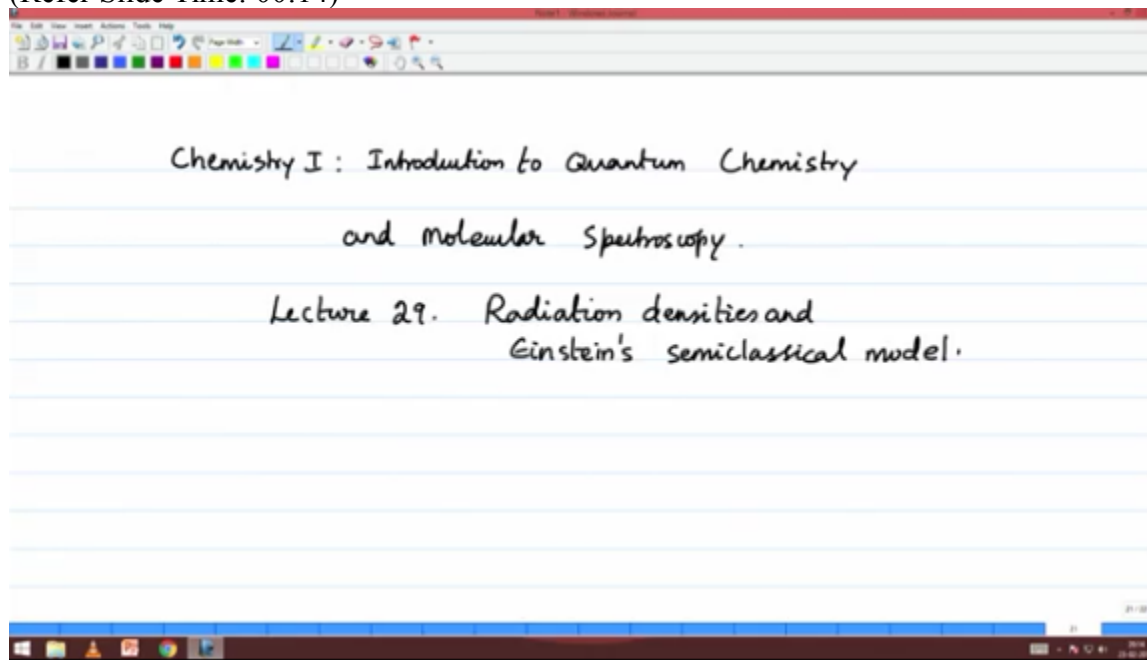
**NPTEL
NPTEL ONLINE CERTIFICATION COURSE**

**Chemistry 1
Introduction to Quantum Chemistry and
Molecular Spectroscopy**

**Lecture 29
Radiation Densities and
Einstein's Semi-classical model**

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

Now the lecture has about 3 parts,
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Long lecture: Three parts:

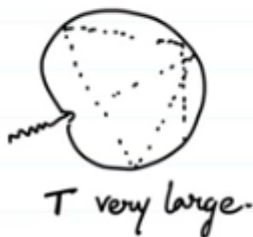
1. Radiation density through Planck's formula
2. Three elementary processes: Absorption, Spontaneous emission and Stimulated emission
3. Einstein's semiclassical model.

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 led to the discovery of quantum mechanics later.

Radiation interacts with matter and it was first conceived by Albert Einstein through a semi-classical model by knocking 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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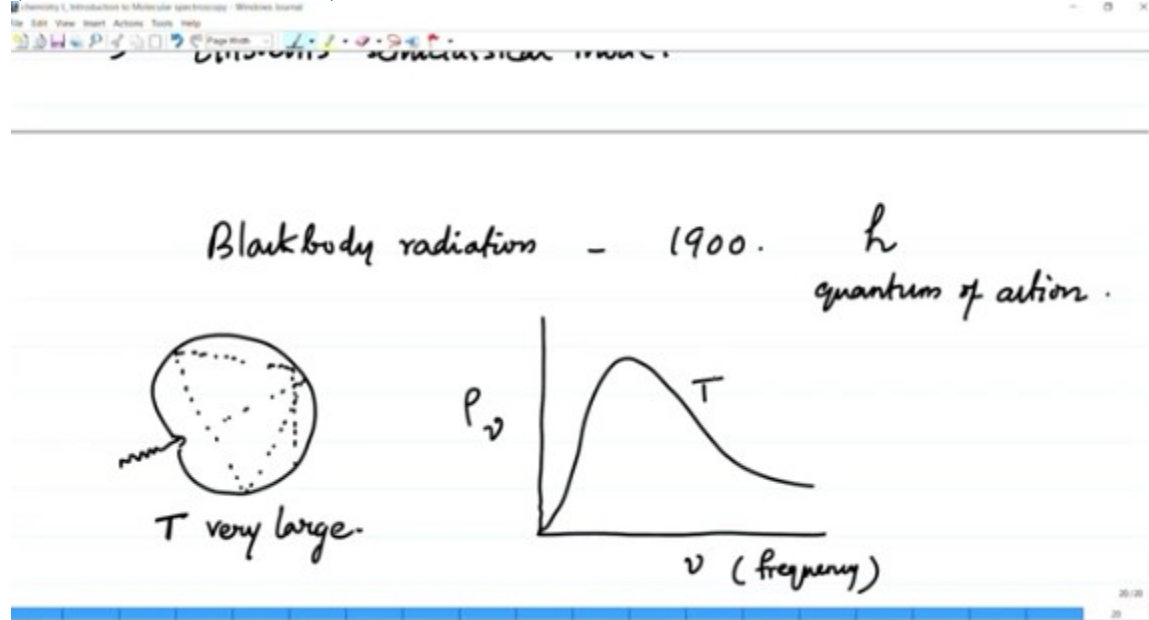
Blackbody radiation - 1900. h
quantum of action.



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 a black body which, when it is heated to very high temperatures and this in thermal equilibrium with the radiation that get emitted due to the heat, the black body emits all frequencies radiation of all frequencies, the thermal equilibrium

essentially means the radiation is inside the cavity and it's 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 a radiation density as ρ_ν , as a function of ν the frequency, one typically gets a graph something like that for a given temperature T .

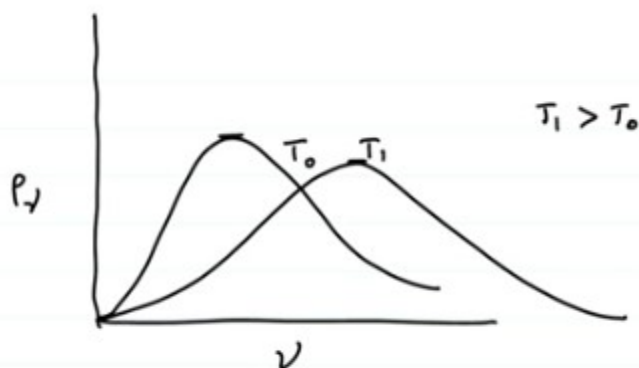
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Radiation density is distributed for various values of the frequency with different densities but it also has a maximum frequency that is the density is maximum for a particular frequency at any given temperature.

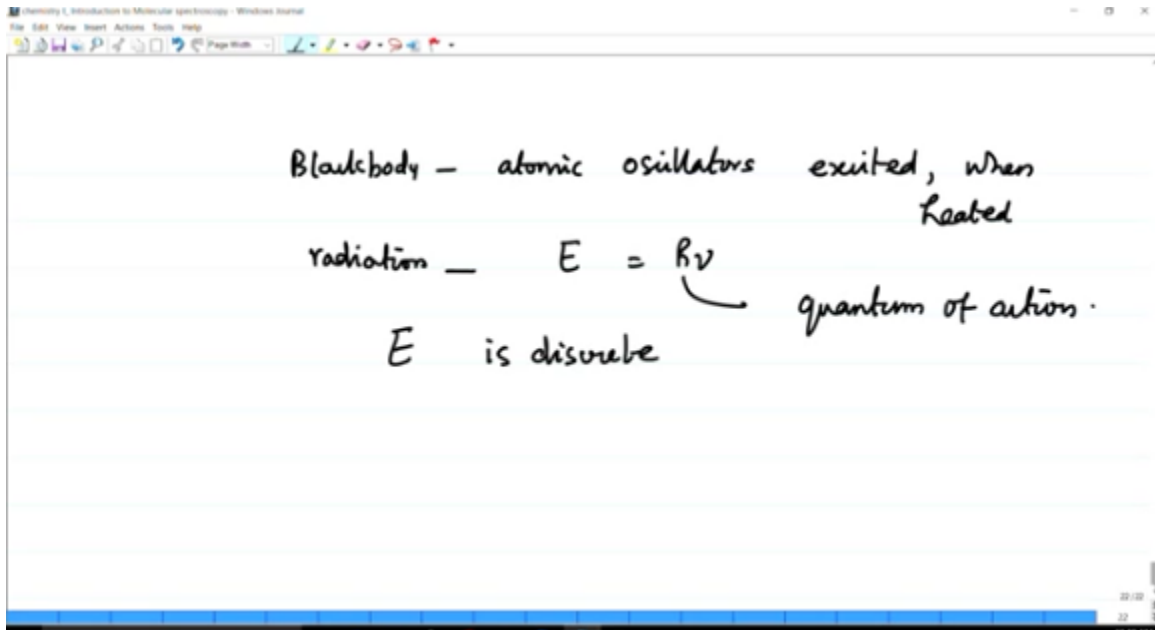
What one found was that if you plot this at various temperatures, for various temperatures of the black body ρ_ν one gets this for a T_1 , say let's call it T_0 and another graph T_1 where the maximum radiation density that is the frequency for which the density is maximum is greater if T_1 is greater than T_0 .

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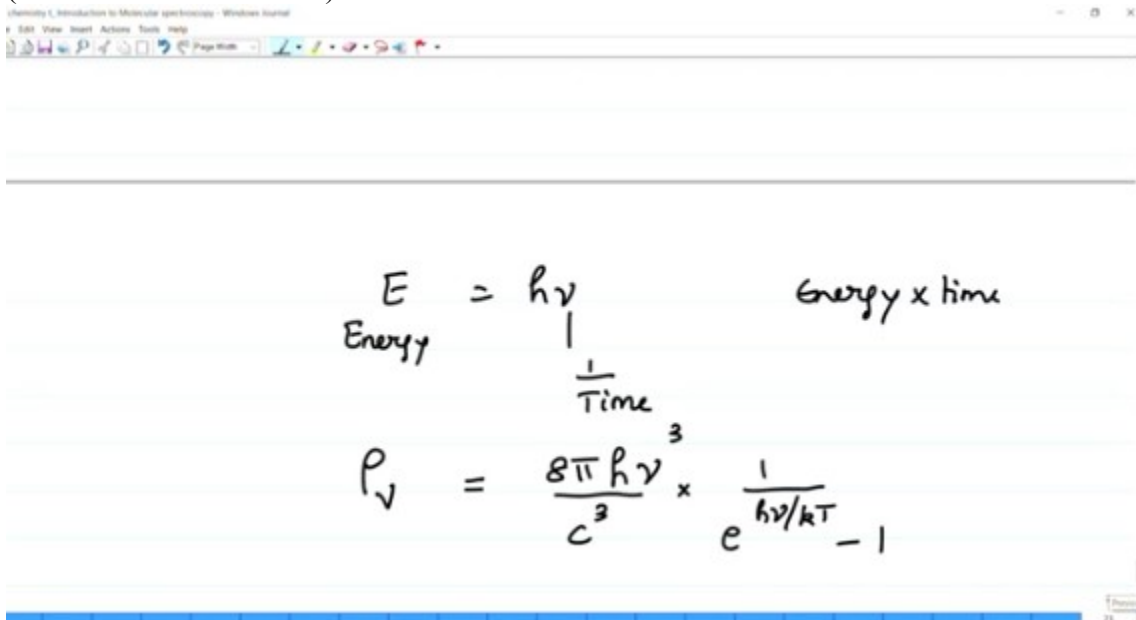
and likewise if the temperatures increased the maximum shift towards higher and higher frequencies, but please note that the radiation density is very low or its almost 0 for very low frequencies and also for very high frequencies, and therefore the black body emits radiation with frequencies which are 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 a 0 and therefore how do we obtained this graph? Max Planck was the first one who solved this riddle with his own formula and he came up with the idea that the black body has atomic oscillators which get excited when the temperatures are increased, that is when it is heated, when 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 constant was introduced by Planck called the quantum of action, and it's a very small number but it's a finite number therefore the energy emitted by the black body is discrete.

E is not all energies but energy comes in the form of packets, this was the proposal that Planck came up with,
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and in this proposal of course he introduced the constant of action which he call as the quantum of action, it's an action constant in classical mechanics, action means very very specific things and Planck's constant has the dimension E, you write h this is 1/time, and this is energy therefore Planck introduced h as energy into time, okay.

The radiation density ρ_ν for any given frequency ν , Planck's proposal was to give this particular formula, he derived to this formula with that assumption that the energy is emitted in a discontinuous fashion and it's $h\nu^3/C^3$, the speed of light times $1/E$ to the $h\nu/KT - 1$, okay, where ν is the frequency,
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C is the speed of light and K is the Boltzmann constant, K in honor of Ludwig Boltzmann, so Boltzmann constant.

And its value is of course very very small and very precisely these days of course its constant can be measured and the value is approximately 1.38×10^{-23} joules per kelvin, and kT is thermal energy at any given temperature T , and $h\nu/kT$ is the factor which when exponentiated gives us the weight of the frequency ν to the radiation density ρ_ν , okay.
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Handwritten notes on a digital whiteboard:

- k - Boltzmann's constant $1.38 \times 10^{-23} \text{ J K}^{-1}$
- kT - Thermal energy $\left[e^{\left(\frac{h\nu}{kT} \right)} - 1 \right]$

Now if you look at those formula carefully ρ_ν as $\frac{8\pi h\nu^3}{c^3}$, of course this factor is dimensionless because its energy divided by energy $h\nu/kT$ anyway, any exponential sign etcetera should have factors which are dimensionless, but here if you look at the dimension of ρ_ν it is $\frac{h\nu^3}{c^3}$, so let me write that as $\frac{h\nu^3}{c^3}$ dimensionally it is energy which you can write as joules and the per second square, because ν^2 and c^3 is meter per second whole cube,
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Handwritten notes on a digital whiteboard:

- k - Boltzmann's constant $1.38 \times 10^{-23} \text{ J K}^{-1}$
- kT - Thermal energy $\left[e^{\left(\frac{h\nu}{kT} \right)} - 1 \right]$
- $\frac{h\nu^3}{c^3} \rightarrow (h\nu) \frac{\nu^2}{c^3} \sim \frac{\text{energy (J)} \text{ s}^{-2}}{(\text{m s}^{-1})^3}$

therefore the dimension that you have for rho nu is energy time per volume, per volume, this is the radiation density formula and it also is such that on both limits 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, then it's very large values, that's easy to check because if you write the formula as $8 \pi h \nu^3 / C^3 [e^{h\nu/KT} - 1]$, please remember this factor when nu is very small, $h \nu$ is much less than KT , for any T and therefore this is approximately $h \nu / KT$ because it's $1+X$ anyway it's an exponential X so it is $1+X$ etcetera, and this is the factor. And this nu of course cancels with that and so the formula for rho nu is $8 \pi \nu^2 KT / C^3$ which goes to 0 as nu goes to 0, okay,

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$\rho_\nu = \frac{\text{energy} \times \text{time}}{\text{volume}}$
 $\rho_\nu \rightarrow 0$ for $\nu \rightarrow 0, \nu \rightarrow \infty$
 $\frac{8\pi h \nu^3}{c^3} \left[\frac{1}{e^{\frac{h\nu}{kT}} - 1} \right]$ for $\nu \rightarrow 0, h\nu \ll kT$
 $\approx \frac{h\nu}{kT} \sim \frac{8\pi \nu^2 kT}{c^3} \Rightarrow 0$ as $\nu \rightarrow 0$

therefore the lower end of the graph is reproduced by the Max Planck's formula when nu goes to 0.

What about the higher value of nu? That's also easy to see because when you write $1 / [e^{h\nu/KT} - 1]$ and if nu is very, very large so that $h \nu$ is much larger than KT then this is approximately $1 / e^{h\nu/KT}$ and the rho nu therefore becomes $8 \pi h \nu^3 / C^3$ times $1 / e^{h\nu/KT}$, and you see that the exponential goes to 0, first or then the nu cube rising as nu goes to infinity therefore rho nu also goes to 0 as nu goes to infinity.

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

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

$$p_\nu = \frac{8\pi h\nu^3}{c^3} \times e^{-\frac{h\nu}{kT}} \quad \nu \rightarrow \infty$$

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

This is an extremely important formula that Max Planck came up with for the black body radiation, and we shall use that radiation density formula that Max Planck used in the next item namely after we described the 3 processes of the introduction of radiation with matter first proposed in detail by Einstein and also with some basic chemical kinetics that we need to look at.

So let's look at those three processes,
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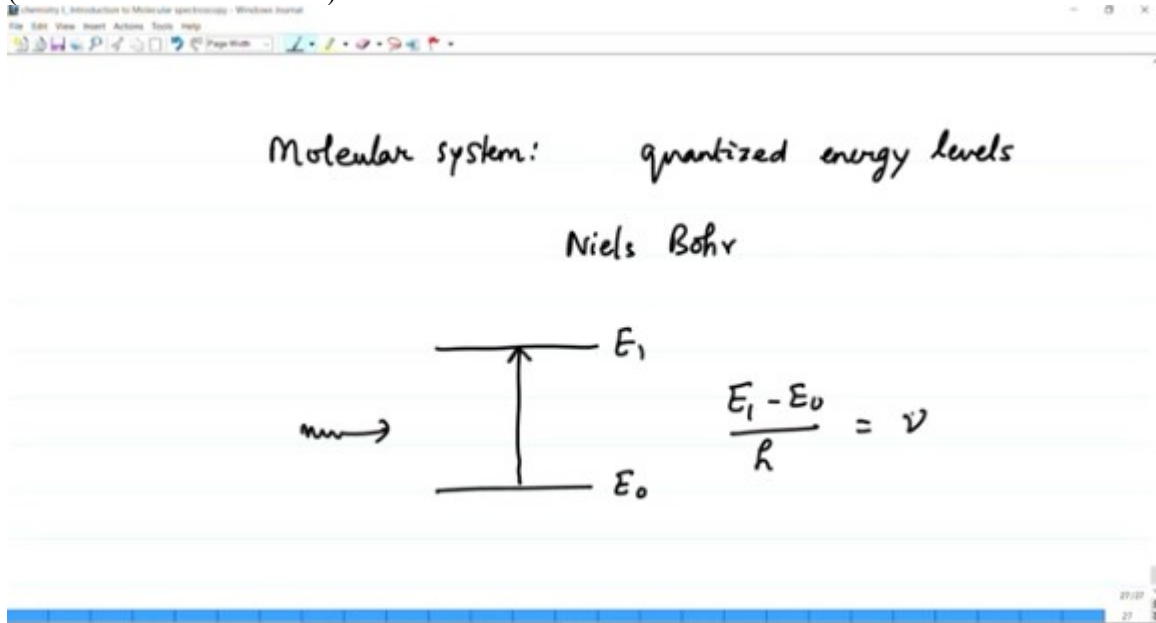
Long lecture: Three parts:

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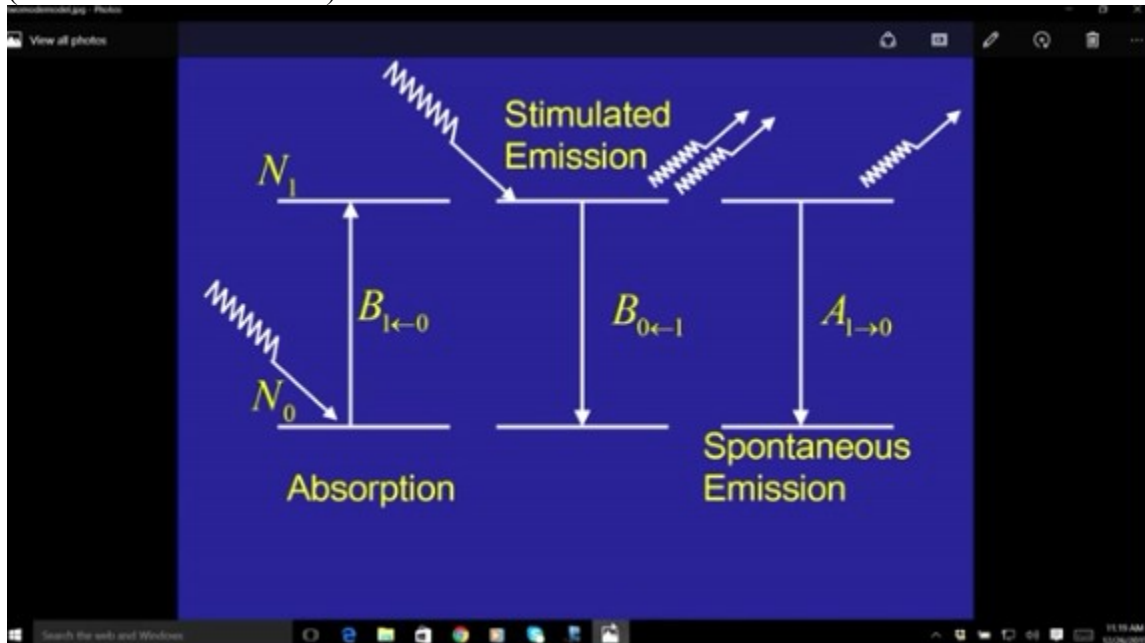
if you go back to the lecture the elementary processes that we want to look at or the absorption spontaneous emission and stimulated emission.

Let's imagine molecular system that the energy levels of atoms or quantized was already known in 1916-17 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, so therefore let's assume for molecular system an isolated two energy levels E_0 and E_1 . We'll only consider a two level system, I mean a three level and multi-level systems are the slightly more complex and to understand the basic physics it's possible for us to restrict ourselves to the two level system and radiation corresponding to the energy difference here $E_1 - E_0/h$, if you put that as a frequency so radiation of a frequency ν falling on the system. (Refer Slide Time: 13:42)



What are the three processes?
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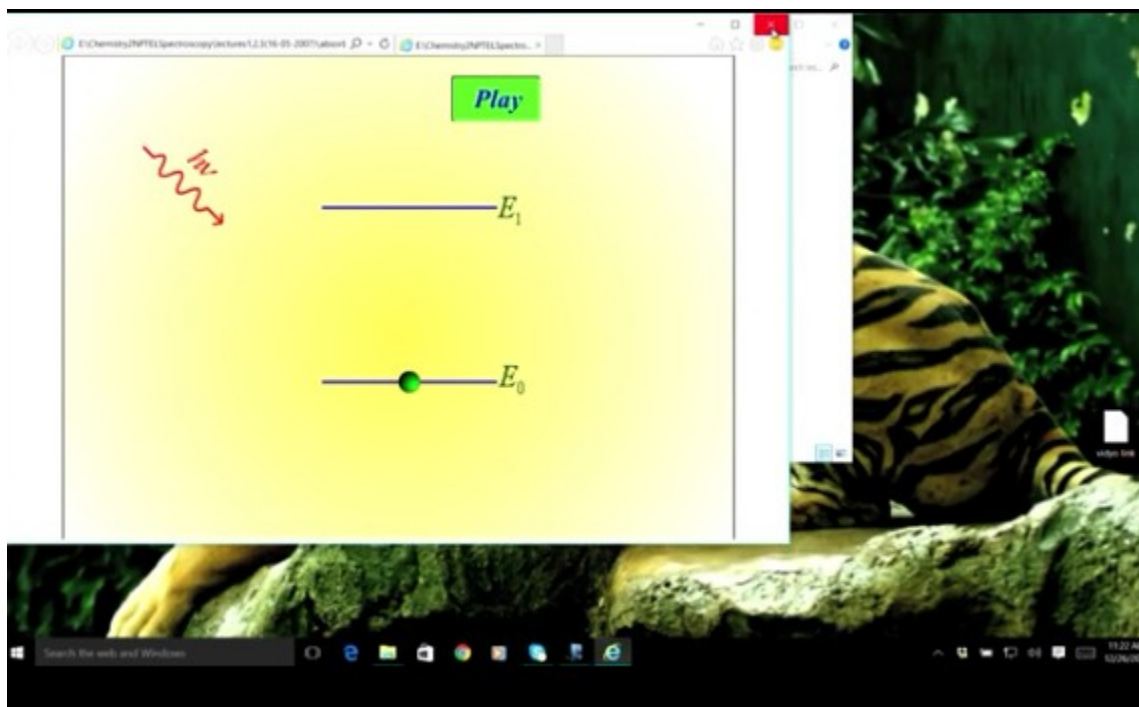
So here are the three processes that we need to consider, the absorption process is when the radiation falls on molecular system, a larger number of them N_0 in the lower energy state, and N_1 in the higher energy state when radiation falls on molecular system in the lower energy

state the molecule rises to the higher energy, it raises to the higher energy state through the process of radiation absorption, so it is a straight forward absorption process.

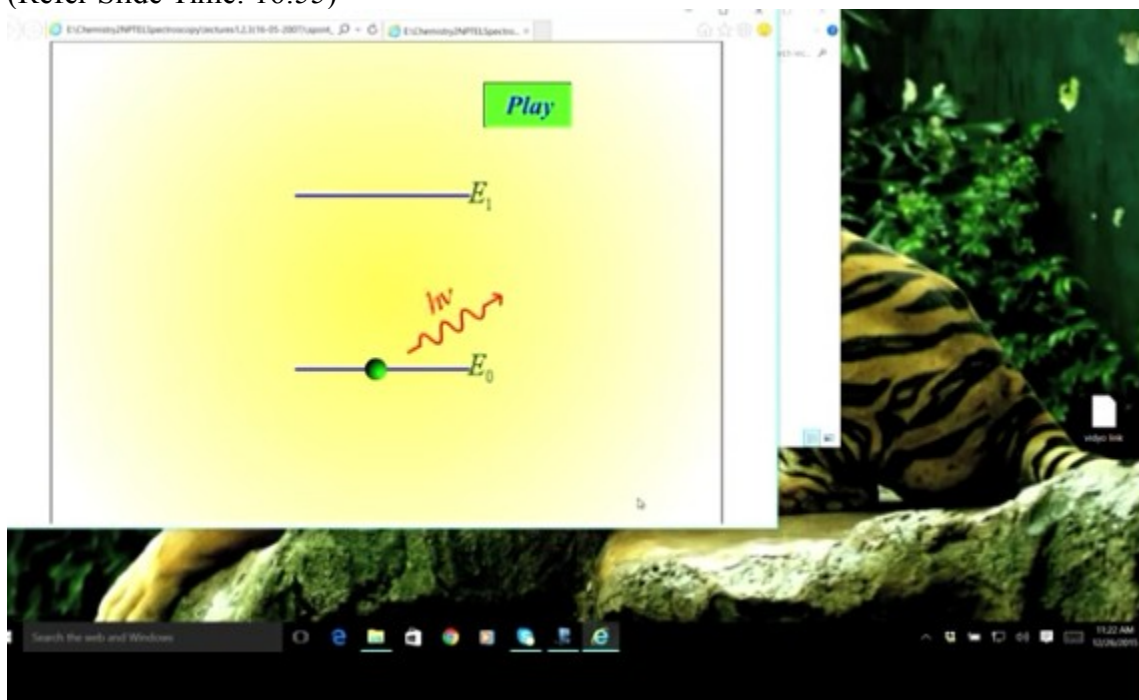
The other process on this side is molecules which are already in the excited state by themselves spontaneously releasing the energy through radiation and coming down to the ground state, whether there is radiation or not this is a spontaneous emission for all the excited molecules, and you also know 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 energy state or all in the higher energy state, but they are distributed, and this distribution follows what is known as the Maxwell Boltzmann distribution, therefore we assume that there are more molecules in the lower energy state slightly less and the higher energy state, but when equilibrium is attained the rate 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 just stimulated emission that is the radiation itself means stimulate the excited state to release its energy and come down to the ground state if you call this as the lower energy state, but in that process conservation of energy requires that two photons, radiation photons are emitted so those are indicated by the two arrows here, and the constants $B_{0 \rightarrow 1}$ and $B_{1 \rightarrow 0}$ and $A_{1 \rightarrow 0}$ 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 of 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 or spontaneously radiation doesn't have a role, so these three processes we can see and also there are the re-elementary animations for that.

So 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
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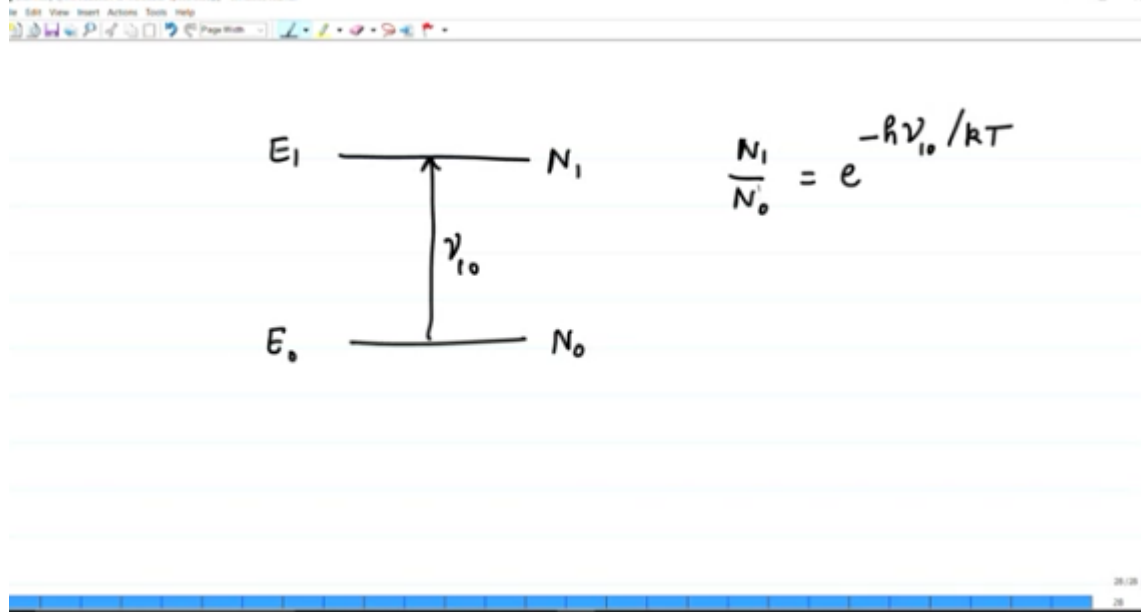


and the spontaneous emission corresponds to molecule from the higher energy state by itself, (Refer Slide Time: 16:55)



releasing the energy and reaching the ground state, and stimulated emission is due to the presence of the radiation, actually disturbing the excited state and the molecule releases its 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 this process can be used to study, and the 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, okay. So before we do this we will again write the three processes, this is energy E_1 , this is E_0 and number of molecules in this state or is N_1 , and the number here is N_0 , and the first thing that we know thermal distribution N_1/N_0 or let me write N_1/N_0 , the higher energy state by N_0 is given by the Boltzmann distribution namely $E_1 - E_0$ to the, namely $E_1 - E_0$ to the $-h\nu_{10}/kT$, what is ν_{10} ? That's the frequency, give me one second, (Refer Slide Time: 18:49)



so the ratio of the number of molecules in the excited state to the ground state is given by the Boltzmann formula, we'll keep that in mind.

Now let's 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_0 due to absorption of radiation and its excitement to reach the level N_1 , E_1 is the same as the rate of change of N_1 to become N_0 , 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 law is also what is followed by most natural processes and here in thermal equilibrium, suppose we talk about N_1 , dN_1/dt the rate of formation of N_1 from N_0 then that depends on N_0 as well as on the radiation intensity or radiation density ρ_{ν} , therefore dN_1/dt is proportional to N_0 is proportional to the radiation density and to the proportionality constant is the rate coefficient which we shall write $B_{0 \rightarrow 1}$ process from 0 to 1, this is N_1 , $N_0 \rho_{\nu}$.

Now the rate of change of, this is the rate of formation,
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phenomenological rate law — First order law.



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

$$\propto \rho \nu$$

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

its positive, the rate of DK $\frac{dN_1}{dt}$ — is due to two processes namely the stimulated emission and the spontaneous emission, spontaneous, these are two different physical processes because in the stimulated emission that is radiation density, here there is no radiation density therefore — $\frac{dN_1}{dt}$ is that is the rate of DK is proportional to $\rho \nu$ is proportional to the number N_1 and therefore it has also the phenomenological coefficient $B_{1 \leftarrow 0} \rho \nu N_1$ this is stimulated. And the $\frac{dN_1}{dt}$ spontaneous minus, minus is to show that this is DK is simply another constant $A_{1 \leftarrow 0}$ to 0, but it's simply proportional to the number N_1 , but that is, it's 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} , so therefore this is the same as the rate of formation of N_1 ,
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$$-\frac{dN_1}{dt} = -\left(\frac{dN_1}{dt}\right)_{\text{stim}} - \left(\frac{dN_1}{dt}\right)_{\text{spon}}$$

$$\left(\frac{dN_1}{dt}\right)_{\text{stim}} = \underbrace{B_{0 \leftarrow 1}}_{\rho \nu} N_1 \quad -\left(\frac{dN_1}{dt}\right)_{\text{spon}} = \underbrace{A_{0 \leftarrow 1}}_{\rho \nu} N_1$$

so if you equate these two what you have is $B_{0 \leftarrow 1} \rho_{\nu} N_0 = B_{1 \leftarrow 0} \rho_{\nu} N_1 + A_{1 \leftarrow 0} N_1$ that's the constant, the rate coefficient times N_1 .
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$$-\frac{dN_1}{dt} = -\left(\frac{dN_1}{dt}\right)_{stim} - \left(\frac{dN_1}{dt}\right)_{spont.}$$

$$\left(\frac{dN_1}{dt}\right)_{stim} = B_{0 \leftarrow 1} \rho_{\nu} N_1 \quad \left(\frac{dN_1}{dt}\right)_{spont.} = A_{0 \leftarrow 1} N_1$$

$$B_{1 \leftarrow 0} \rho_{\nu} N_0 = B_{0 \leftarrow 1} \rho_{\nu} N_1 + A_{0 \leftarrow 1} N_1$$

This is thermal equilibrium.

Now just rearrange this a little bit and use the Maxwell Boltzmann formula namely we want to write N_1/N_0 so let's write $B_{1 \leftarrow 0} \rho_{\nu} = B_{1 \leftarrow 0} \rho_{\nu} + A_{1 \leftarrow 0} N_1/N_0$ and this is given by E_{10}/kT ,
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$$B_{1 \leftarrow 0} \rho_{\nu} = \left[B_{0 \leftarrow 1} \rho_{\nu} + A_{0 \leftarrow 1} \right] \frac{N_1}{N_0}$$

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

so if you do that then we can write a formula for the radiation density ρ_{ν} as $A_{1 \leftarrow 0} / [B_{0 \leftarrow 1} E_{10}/kT - B_{1 \leftarrow 0}]$, this is 0 to 1, this is 1 to 0, this is just the rearrangement of this formula to give you this result,
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$$B_{1 \leftarrow 0} P_\nu = \left[B_{0 \leftarrow 1} P_\nu + A_{0 \leftarrow 1} \right] \frac{N_1}{N_0} e^{-h\nu_{10}/kT}$$

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

but remember Planck's formula for thermal radiation in equilibrium with the hot body which is excited and that's actually $8\pi h \nu^3$, in this case the ν is the ν_{10}/c cube times $1/\text{exponential } h \nu_{10}/kT - 1$, 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 $B_{1 \leftarrow 0}$ is equal to $B_{0 \leftarrow 1}$. (Refer Slide Time: 25:00)

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

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

It's also easy to visualize that the rate coefficient for the absorption of radiation and the rate coefficient for stimulator emission of radiation which is not the state is in fire energy and it's also being prompted by the radiation to reach the bottom, and it's possible to realize that microscopically these two processes will have the rate coefficient, it's a principal of detailed balance what can verify, one can argue that these coefficients are the same, but the Planck's formula also tells us that unless these two were equal it doesn't make sense, therefore if you assume that the absorption coefficient and the stimulated coefficients, stimulated emission

coefficients they are both equal then we have an extremely simple formula, we have only one absorption coefficient namely $1B$, a B and then A , when 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/B times E to the $h\nu_{10}/kT - 1$ is equal to $8\pi h\nu_{10}^3/c^3 \times 1/e^{h\nu_{10}/kT} - 1$ and this cancels out, this goes away and therefore what you have is A spontaneous emission coefficient is equal to $8\pi h\nu_{10}^3/c^3$ times B which is the absorption coefficient. Thus two microscopically measurable coefficients have been introduced to study the process and

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

$$\text{Spont. emission coeff. } \textcircled{A} = \frac{8\pi h\nu_{10}^3}{c^3} \textcircled{B} \text{ Absorption coefficient}$$

there is also a relation between them based on what is called the 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, I mean we will see that later on, 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 numerator spectroscopically in (Refer Slide Time: 28:41)

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

$$\text{Spont. emission coeff. } \textcircled{A} = \frac{8\pi h\nu_{10}^3}{c^3} \textcircled{B} \text{ Absorption coefficient.}$$

$$B \rightarrow |\mu|^2 \text{ dipole moment matrix element between } E_0 \text{ and } E_1$$

an instrument using spectroscopy coefficient, this was a proposal and this was been very fried at a linear level, we have used the linear law namely the latest proportional to the number, latest proportional to the radiation density, this are linear relations we have not used any other concepts, therefore in the limit of what is called the 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 moment matrix 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's 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 the dipole moment squares and so on in the measurement of microwave, infrared and electronic spectroscopy, so the next lecture will introduce these three properties polarizability dipole moment and moment of inertia, until then thank you very much.

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