Optical Spectroscopy and Microscopy

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Lecture – 14

Fundamentals of Optical Measurements and Instrumentation

Welcome to the course on optical spectroscopy and microscopy. In the last lecture, what we have seen is that how Fermi's golden rule relates the rate of transition that you observe to the properties of the system, properties of the chromophore that you have taken in terms of the matrix element, the perturbation, and so on and so forth.

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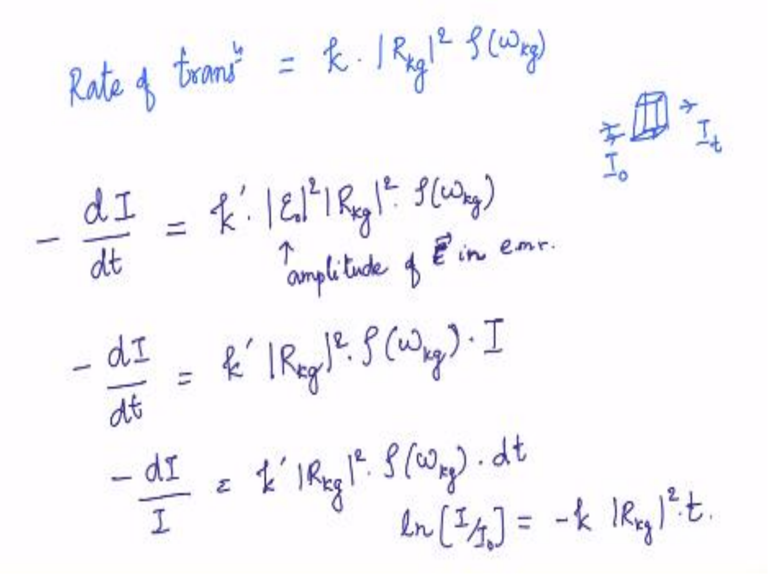

Rate of trans^n $= k \cdot |R_{kg}|^2 \, \rho(\omega_{kg})$

$$-\frac{dI}{dt} = k' \cdot |E_0|^2 |R_{kg}|^2 \cdot \rho(\omega_{kg})$$

$\uparrow$ amplitude of $\vec{E}$ in e.m.r.

$$-\frac{dI}{dt} = k' |R_{kg}|^2 \cdot \rho(\omega_{kg}) \cdot I$$

$$-\frac{dI}{I} = k' |R_{kg}|^2 \cdot \rho(\omega_{kg}) \cdot dt$$

$$\ln[I/I_0] = -k \, |R_{kg}|^2 \cdot t.$$

So briefly, the Fermi's golden rule is given by the rate of transition, we will start from there, is equal to a bunch of constants let us call that as some k and we introduced the term Rkg, modulus Rkg square and then density of the state rho kg. Now in the k, so far what we are going to do now is to say that okay this is what I know in terms of how the system is going to respond for me introducing a perturbation. Now, let us see I take a sample okay, a cuvette and then shine some light and then ask, so let us call that I0 and I can measure how much of the light is actually coming out, so It.

So I am interested in knowing how much of this incident light will be absorbed by this molecule or for that matter if the molecule even will absorb and if it absorbing how much of the light is going to absorb. Now how do we approach this? We know the rate of transition.

So given an incident light of a frequency and intensity, what is the rate of transition that we expect?

Now the frequency is clearly coming in here in through omega term, however where is the intensity. Now if you look back at the rate of transition, what we have done is that we made a dipolar approximation and then we introduced this, please remember we introduced the electric field right. Now all of that is being inside that constant k. So I am going to specifically write it out. So rate of transition here would correspond to my experimentally absorbed change in the light intensity, right.

So I can write it as the rate at which the light intensity is changing dI by dt that corresponds to my rate of transition which is some k prime times modulo E0 square modulus Rkg times rho kg and so forth. So now, this epsilon0 square is proportional to the intensity. So we can explicitly put that because this is light intensity, its amplitude E0 is the amplitude of the E field in our electromagnetic radiation right, in our perturbation. So in such a case, what we can actually do is we can rearrange this whole term in terms of dI by dy is k Rkg omega kg times the intensity.

So now, only the intensity is time dependent and the rest everything is constant with respect to time. So you can rearrange this into a differential form that we know of which is dI by I = k prime Rkg square rho omega kg into dt. Now if we solve for it, we will see that and then use the initial conditions as we have seen, to start with at t = 0, the intensity of the light is represented by I0. So we can say it is lon of I by I0 = -K + modulus Rkg square t okay.

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$$\ln\left(\frac{I_0}{I}\right) = \text{Absorbance} = k\,|R_{kg}|^2 \cdot \underline{\underline{t}} \cdot [\text{Con.}]$$

$$t \rightarrow \frac{l}{c}$$

$$\text{Absorbance} = \overbrace{\frac{k}{c}\,|R_{kg}|^2}^{\epsilon} \cdot l \cdot [\text{Con}]$$

$$(\text{Beer-Lambert's law})$$

$$= \epsilon \underset{\hookrightarrow [\text{con}]}{C}\, l$$

In other words k Rkg modulus square t the concentration of the substance, the concentration comes into picture here because if you actually look at the experiment what we need to know is this is the molecular transition rate, so we need to know how many number of molecules the light encounters in its path and actually for us to do that the intensity is the number of photons per unit area. So if you take away the area, then I mean if you multiply that by the concentration what you have is this and then this also a molar absorption cross section.

So we have to also express it in molar concentrations so that we relate them to the number of molecules in the system. If you do that, then what we have is this expression. Now here, the t is basically the time the light spends interacting with the sample so that is given by the, let us l be the path length of the cuvette okay. Then what we are going to do here is to obtain t, t is the interaction time right. So interaction time we are going to calculate, this t then is given by the time taken by the light to traverse the distance l, right.

So this will be l divided by c gives you the t. So that we can actually plug it in the above expression, so we have absorbance as given by k Rkg times l the path length times the molar concentration by c the velocity of light on collecting them with the constants. Now this is nothing but your Beer-Lambert's law, Lambert-Beer’s law or Beer-Lambert's law. I repeat so what we have done here is that we said I am going to write down the expression for the rate of transitions. I took this rate, then recognized that this is a molecular rate constant so.

So order for me to actually represent the true absorbance, I need to do few things, one is to introduce the absorbance is for a molar substance, one mole of a substance. We multiplied this by the molar concentration, molar concentration is defined as the number of moles of a substance per unit volume. The volume here is important because we need to know the number of molecules that the light is interacting with so that is really given by this molar concentration and then we replaced the time of interaction by the path length using the relationship that the light gets to interact with the molecule as long as it is traveling inside the cuvette.

Given that l is the path length of the cuvette, c is the velocity with which the light is traveling, so we can say t is l by c. now put that in, you have k by c the familiar expression right. So k by c Rkg modulus square l times the concentration. I claim this to be the Beer-Lambert's law wherein you have the path length dependence in terms of the l, concentration dependence in terms of direct concentration itself and the epsilon it is a molar extinction coefficient that is the probability that the molecule will absorb a given wavelength of light is given by this, right, because this is totally determined by the molecule, Rkg is a molecular property.

Given a molecule, you define what is eg and ek. As a result, modulus Rkg is a molecular property and then you can think of this as epsilon and hence your familiar thing of epsilon cl where c here should not be confused, let us put this, the capital C here is really the molar concentration, not the velocity c. So now in going through this elaborate process of describing the light matter interaction using a framework of quantum mechanics.

What we have done is that we have arrived at few important conclusions or few import important findings which to start with we would not have been able to, we will not have know, one is to say that rate of transition of a process, rate of transition between two energy states because of a perturbation is directly proportional to the matrix element defined by this modulus square of the matrix element, the matrix element here itself is defined by the initial and the final energy kets and the operator corresponding to the perturbation okay, that is our modulus Rkg square okay.

So that determines the rate of the transition. Since it goes as modulus square, we also said the same perturbation can take or can mediate the transition from the lower energy state to the higher energy state or the higher energy state to the lower energy state with equal probability because if you flip the things it does not matter because it is modulus square. It is exactly the same in magnitude, you are only looking at the magnitude, the magnitude is exactly the same.

As a result, we predicted that the same light that can cause the absorption and the resultant transition of the molecule from the ground state to the excited state can also take the molecule if it were to be to start within the excited state to the ground state with equal probability. After that we said hey if this were to represent the rate process, rate of a transition experimentally in a laboratory, we measure something called as an absorbance in a spectrometer that is I take cuvette, shine the light, and then ask how much of the light is actually being absorbed by the molecule.

This is really of my interest as a spectroscopist right. I want to know if I shine a particular light what is the probability of that transition happening, now that I should be able to predict. The way we did that is to recognize the fact the rate of the transition is for a particular wavelength omega and if since we are taking a broadband excitation, you could actually use, you could integrate this rate over this entire spectrum accounting for the fact that there could be different states, states with slightly different energy levels present around the ek state the final state.

So let us account for that and if you do this, then what we have is an expression we termed as the Fermi's golden rule that tells you that the probability of occurrence of the transition in such situations and we said now let us equate it to the difference in the intensity that we would see because the rate of transition should correspond to to the amount of light that get absorbed by the molecule. If that is true, let us write down the expression and the differential expression that describes this process we wrote down and solved for it.

Then what we have gotten is reminiscent of the Beer-Lambert's law, I mean it is really the Beer-Lambert's law and then what I would like to say is what has been derived empirically by these 2 scientists we were able to relate it to an expression that we derived for the rate of transition from the fundamental principles of quantum mechanics. Now this is good, nice.

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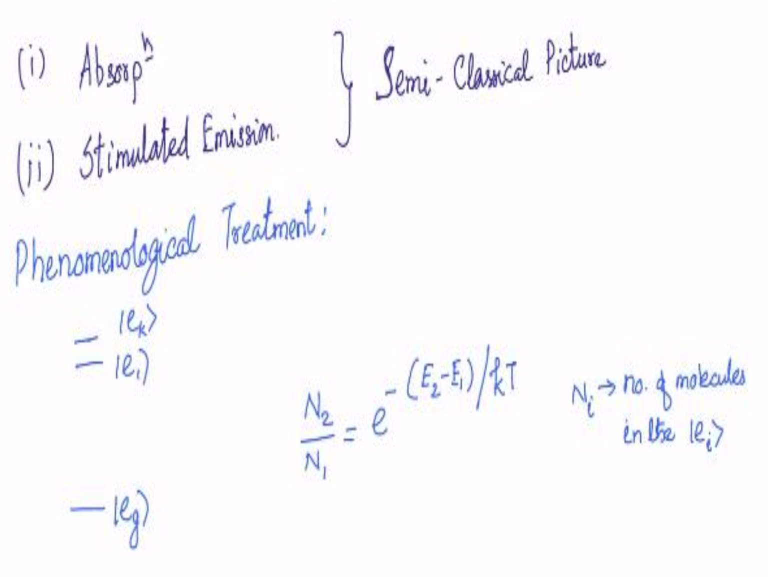

(i) Absorp^n } Semi-Classical Picture

(ii) Stimulated Emission.

Phenomenological Treatment:

$$\frac{N_2}{N_1} = e^{-(E_2-E_1)/kT}$$

$N_i \rightarrow$ no. of molecules in the $|e_i\rangle$

We have a way of understanding the process of absorption, our framework really allows us to understand this. In the process, it also predicted that there will be stimulated emission. This is what we have obtained using what is called as a semi-classical picture. We still treated the light, the perturbation until the perturbation it is fully quantum mechanics, no problem at all, but the moment we put the perturbation as E0 a sinusoidal electromagnetic wave, then that is a classical treatment of the light with the quantum mechanical treatment of that.

So that is why we call it as semi-classical treatment or semi-classical picture. Albert Einstein was equally interested in understanding these transitions, but he approached it in a totally phenomenological manner. In fact, he argued that there is something more intrinsic that has to be understood beyond this absorption and stimulated emission and he did that through totally phenomenological means, what do I mean by this? Let us take a look at his approach and his description of this whole process and then see what he predicted okay.

He argued hey look we know, thanks to Boltzmann, that if you take a system, a system of chromophores and then let us say if we let it equilibrate with a black body that is kept close to it. Meaning if you keep them close to each other, then you can think of thermal equilibrium that has been set in between the system that we are probing and the black body itself and in such a case Boltzmann predicted the population of the molecules in different energy states okay, so what we are doing now here is the phenomenological approach.

So I am going to call it as phenomenological treatment of this process wherein we still have these energy states right, we have the molecules and they have this different energy states and you can call it as eg being the lower energy, e1 so on in generally k. What Boltzmann tells us is that if you were to actually write down an expression for the number of molecules that are present in each of these levels, then they should be following a distribution and this distribution would be given by N2 by N1 = e –E2 – E1 whole divided by k absolute temperature okay.

Where Ni is the number of molecules or in otherwise you can think of that as the occupancy of the state, number of molecules in the energy state ei okay. So now if you just let us start to make it make things easier for us to understand but you can easily generalize.

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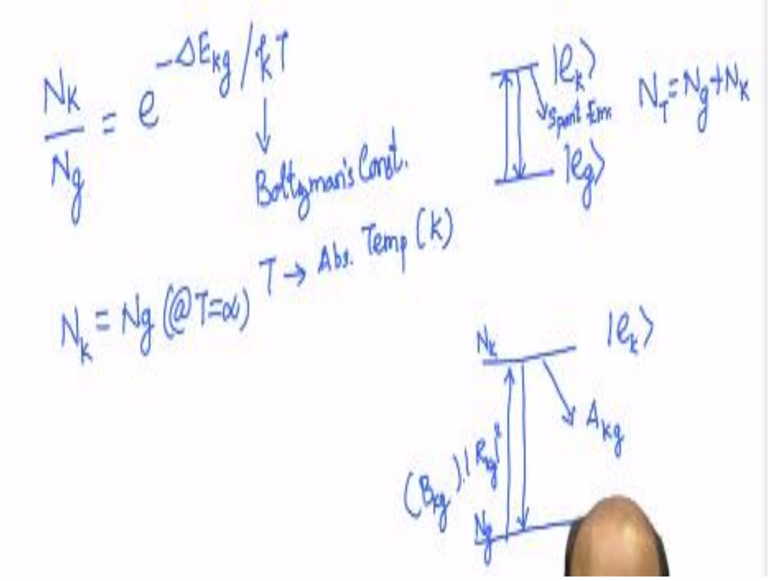

You can think of a 2-level system just like our k and g, then this whole expression can be written as e Nk by Ng = e to the power - delta Ekg divided by k capital T, k this is Boltzmann's constant. This being the case, you can see even if the temperature T, right the capital T, so T is the absolute temperature in Kelvin scale right okay. So even if the capital T goes to infinity making this whole term = 0 Nk can at the most become equal to Ng in all other at T = infinity. As you keep increasing the temperature, the Nk keeps going up.

You have to understand, I have to tell you that the since it is a 2-level system, the N total, right that is a fixed number of molecules that we are sticking with is given by Ng + Nk, so which means to start with right, to start with you have a certain number of ground state molecules and Nk and certain number of excited state molecules, depending on the energy gap between them it can be very small to almost negligible, nothing is there at all.

However, irrespective of wherever you start with as the temperature goes up, the population, I mean this fraction is slowly going to increase but it will increase towards reaching 1, this fraction will inch towards reaching 1, that means the Nk starting any way lower from g can approach as close to Ng as possible when the temperature is at infinity which practically means that you are not going to be there at all, whether you will see that or not very much depends on how big is the delta E right, infinity here of temperature is in comparison with delta E okay.

So if capital T is sufficiently large with respect to E, then only you will see that is the meaning of the statement that immediately told Einstein that hey I know that the molecular transition rate given by Fermi's golden rule going from g to k or k to g is exactly the same okay, so that corresponds to the rate constant being exactly the same at a given intensity of the perturbation right, intensity of the light, electromagnetic light, but still here have a system which is at thermal equilibrium because basically meaning whatever the population that is present here are not changing as a function of time.

I am looking at the number of molecules present in the ground state and then number of molecules that are present in the excited state, when there is a thermal equilibrium that is all it means that the numbers are steady, they reached the steady state, they are not changing, they may fluctuate here and there but they on an average remain the same and yet this being lower, the excited state number is still lower.

The only way that is possible is that that should be another path or another way that the molecule can come down from the excited state to the ground state early in the system that needs to exist such that this can remain lower, otherwise see that if the molecular rates are equal, then the steady state would be at steady state you would expect the numbers to be equal to. The fact that we know that it is not equal means that there is a leak and he called this leak as spontaneous emission.

That is, an emission process that is not dependent on the presence of light. If the light were to modulate right, so if the light intensity were to modulate this ray it depends on that, then we know that already that that rate, a stimulated emission rate is exactly equivalent to the absorption rate, so that is not sufficient, we need to have another term, that is a leak term that's not dependent on the light. So that is the key here. That term he called it a spontaneous emission.

Now this whole thing can be nicely set in terms of the chemical, you can think of this as a chemical reaction and then we can write down the rates of these processes. The idea being we are interested in this spontaneous emission, if it were to be spontaneous emission, I would like to know what determines it? How is it related to the absorption and the emission process that is caused by the light itself. To obtain this, it is very easy. So what we are going to do is that we are going to do the number balancing.

So let us expand this rate, the energy state diagram, so ek so where I can actually mark down my rate processes. So we will see the number of molecules in the ground state is Ng and the number in the excited state is Nk. Now this is the absorption process okay. Now we know this is proportional to Rkg modulus square and same thing also happening here, sorry not leave in but the crossed one, the spontaneous rate constant let us call it as, he called it as Akg. He called these ones, the stimulated ones as Bkg.

So they are famously called as Einstein’s A and B coefficients. In the next class, what we will see is that how using this simple diagram and the balancing of the rates, he obtained an expression for Akg the spontaneous emission rate constant in terms of the stimulated emission which we know can be expressed in terms of the molecular properties, okay. I will see you in the next class.