Quantum Mechanics and Molecular Spectroscopy
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Lecture – 22
Relationship Between Transition Dipole and Extinction Coefficient

Hello, welcome to the lecture number 22 of the course quantum mechanics and molecular spectroscopy. In the last lecture, we looked at the relationship between the transition moment integral or the transition dipole with the Einstein's coefficients A and B.

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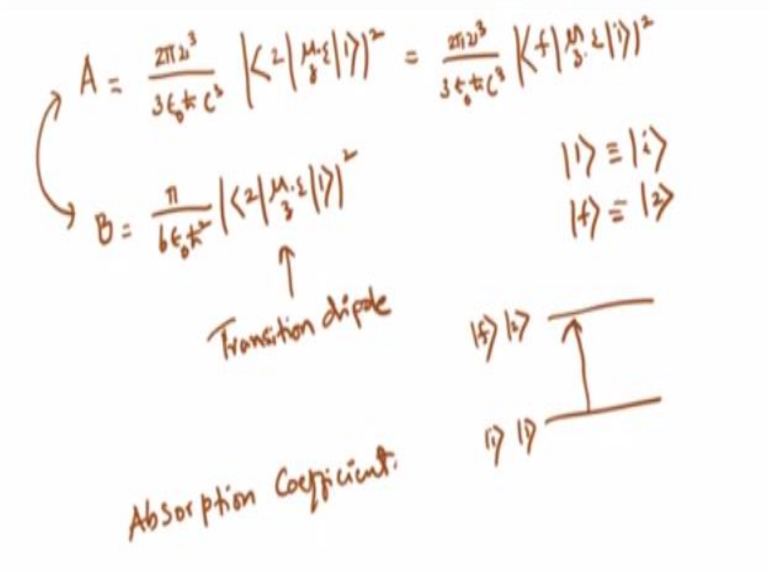

We ended up with A = 2 pi nu cube divided by 3 Epsilon 0 h bar C cube into 2 mu z epsilon 1 whole squared. This could also be written as 2 pi nu cube by 3 epsilon 0 h bar C cube f mu z along epsilon direction 1 or i whole squared okay. Here, I assume that the state 1 is identically equal to state i and state f is identically equal to state 2, so which is nothing but looking at transition between state 1 or i to state 2 state or f okay.

Similarly, we have the absorption coefficient or the standard emission coefficient to B pi by 6 epsilon 0 h bar square 2 mu z 1 whole square because this is along the dot product. Now it turns out that these 2 coefficients okay are related to the transition moment, this is called transition dipole, and square of the transition dipole moment okay. Now there are experimental quantities the one you can easily measure and one should equate to A and B.

So one such experimental quantity is the absorption coefficient okay. So, we will try to derive the relationship between the Einstein’s coefficients A and B and absorption coefficient.

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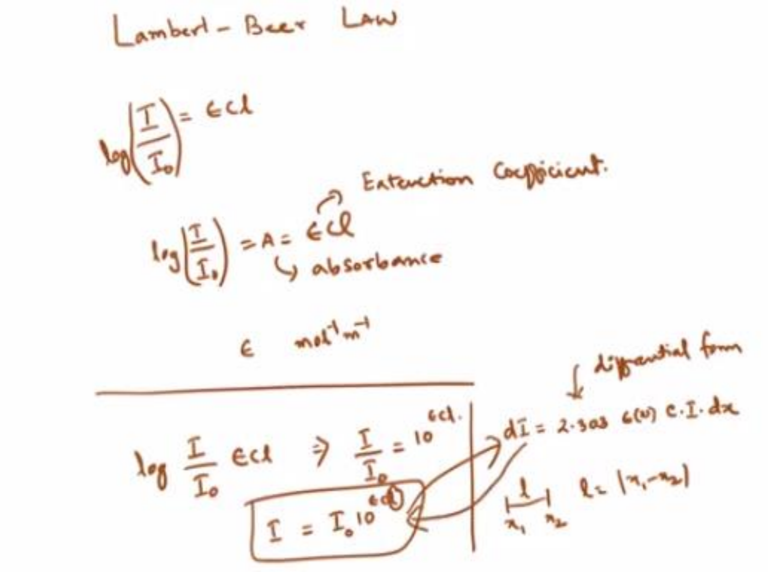

Lambert - Beer LAW

$$\log\left(\frac{I}{I_0}\right) = \epsilon c l$$

Extinction Coefficient.

$$\log\left(\frac{I}{I_0}\right) = A = \epsilon c l$$

absorbance

ϵ $mol^{-1} m^{-1}$

$$\log \frac{I}{I_0}\ \epsilon c l \Rightarrow \frac{I}{I_0} = 10^{\epsilon c l}$$

$$\boxed{I = I_0 10^{\epsilon c l}}$$

differential form

$$dI = 2.303\ \epsilon(\nu)\ c \cdot I \cdot dx$$

l x_1 x_2 $l = |x_1 - x_2|$

Now, when we think of absorption, one thing that comes to our mind is the Lambert-Beer law okay. What does Lambert-Beer law says? Lambert-Beer law simply says that the I equals to or I by I0 log of this is equal to epsilon cl okay and log of I by I0 is also called absorption A, this is equal to epsilon c absorbent. So this is absorbent and this is the extinction coefficient okay.

So extinction coefficient epsilon will have the units of mol inverse meter inverse okay because absorbance by itself does not have any units. Slightly differently if I can write this relationship, so if I write log of I by I0 epsilon cl. So if I take you know exponential on both sides okay, so this will be equal to I by I0 will be equal to 10 to power of epsilon cl. We can always write I equals I0 okay 10 to the power of epsilon cl okay.

Now, this is the form, so one can write a differential form. So dI = 2.303 epsilon, which is a function of nu c times I times dx okay. What is your length? Length is nothing but l is the length, so if you have gone from say x1 to x2, this is going to be l, l is equal to modulus of x1 – x2 okay. So if you look at the differential form, so this is nothing but differential form okay. So essentially it comes from this equation or in fact if you integrate, you will get back this equation okay.

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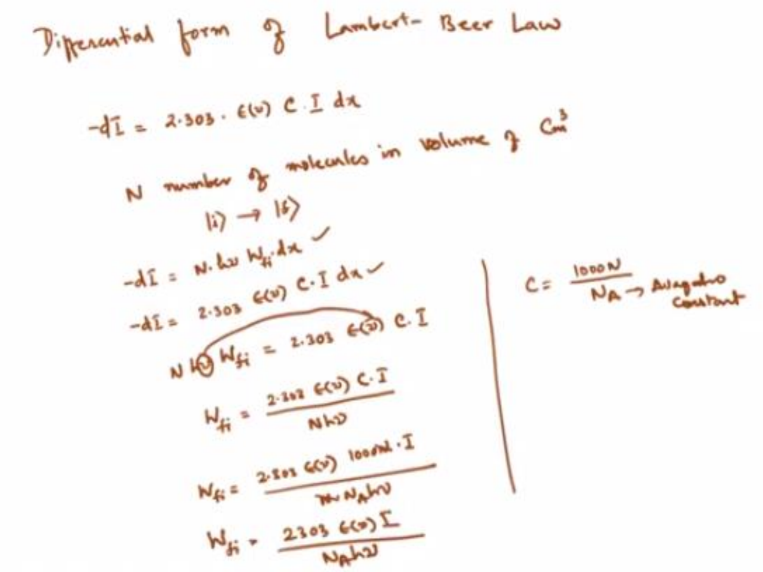

Differential form of Lambert-Beer Law

$-dI = 2.303 \cdot \epsilon(\nu)\, C \cdot I\, dx$

N number of molecules in volume of cm^3

$|i\rangle \rightarrow |f\rangle$

$-dI = N \cdot h\nu\, W_{fi} \cdot dx$ ✓

$-dI = 2.303\, \epsilon(\nu)\, C \cdot I\, dx$ ✓

$N\, h\nu\, W_{fi} = 2.303\, \epsilon(\nu)\, C \cdot I$

$W_{fi} = \frac{2.303\, \epsilon(\nu)\, C \cdot I}{N h\nu}$

$W_{fi} = \frac{2.303\, \epsilon(\nu)\, 1000\cancel{N} \cdot I}{\cancel{N}\, N_A h\nu}$

$W_{fi} = \frac{2303\, \epsilon(\nu)\, I}{N_A h\nu}$

$C = \frac{1000N}{N_A}$ → Avogadro constant

So the differential form of Lambert-Beer law okay will be nothing but -dI I = 2.303 into epsilon of nu C is the concentration I is the intensity dx okay. Now, let us assume that there are N number of molecules in volume of centimeter cube okay and that is going from initial state I to final state f under the light condition okay. So your -dI will be equal to N times h nu, h nu is nothing but your energy, Wfi that is the rate coefficient into dx okay.

So the absorption, the incremental absorption that will happen will depend on number of molecules, the energy and it is the rate of absorption into multiplied by this okay. Now, -dI according to Lambert-Beer law will also be equal to 2.303 epsilon of nu c times I dx okay. Now, you can see these two are equal, so this is written in terms of molecule and this is in terms of Lambert-Beer law, so we can equate them.

So N h nu W that is a rate constant between f and i, rate of fi okay, dx is written right now because it is an incremental change, you can remove that. Now this will be equal to 2.303 epsilon of nu, this nu and this nu are the same C times I. So, I can write rate of absorption is equal to 2.303 epsilon nu C dot I divided by N h nu okay. Now, you can see that concentration is nothing but 1000 times N divided by NA, N by NA is number of moles is not it?

N by NA, NA is Avogadro constant and concentration is thousand times because it is written in decimeter okay. So when I plug in that, so what do you get is Wfi = 2.303 epsilon nu this is thousand times N okay into I divided by N into NA h nu, and this NA and this NA will cancel, so what we will get, 1000 into 2.303 will give 2303 epsilon of nu I divided by NA h nu okay that is your rate of absorption.

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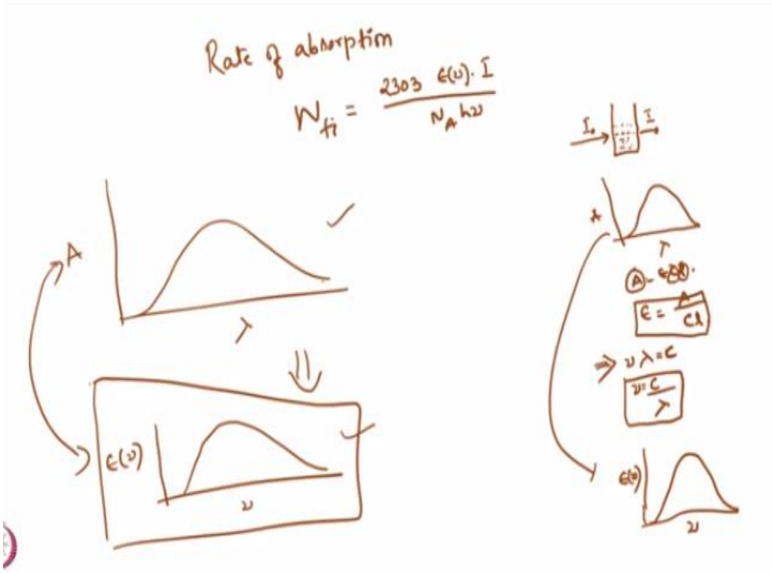

So now the rate of absorption is given by Wfi going from state i to state f, so this will be equal to 2303 epsilon of nu times intensity of light divided by Avogadro numbers h nu, h nu is where the energy is happening. Now, this is a very simple equation except that we need to now slightly rearrange this equation. Before I go, I want to look at something. So let us suppose that you have a solution okay of some molecules okay and then you shine light.

So you will get I0 and you get back I okay. Now what happens is that if you generally look out this the solution, what to get, you get a band. So what you plot is absorbance A versus lambda okay. Now we know that absorption is nothing but epsilon cl. So if you know absorption, if you know the concentration, if you know the length, so epsilon will be A divided by cl okay and we know nu lambda = c, so nu = c by lambda.

So we know these 2 equations. So I can convert this plot as plot of epsilon of nu versus nu okay. So what I am trying to tell you here is that if I have an absorption band, some molecule getting absorbed in solution and which is generally plotted absorbance verses wavelength, one can transform this using appropriate conversion factors is that one can plot the same thing as nu versus epsilon of nu. This is just a different representation okay.

So what you can get is that you can get the absorption coefficient or the extinction coefficient as a function of the wavelength or the frequency. Of course, wavelength and frequency are related with respect to the multiplication of that you see here okay. So one can always plot, generally we plot it like this okay, but one could also plot like this okay. Now, why I want to use it, I will come to this little, but just remember that one can also plot an absorption spectrum as a function of nu and the epsilon nu okay.

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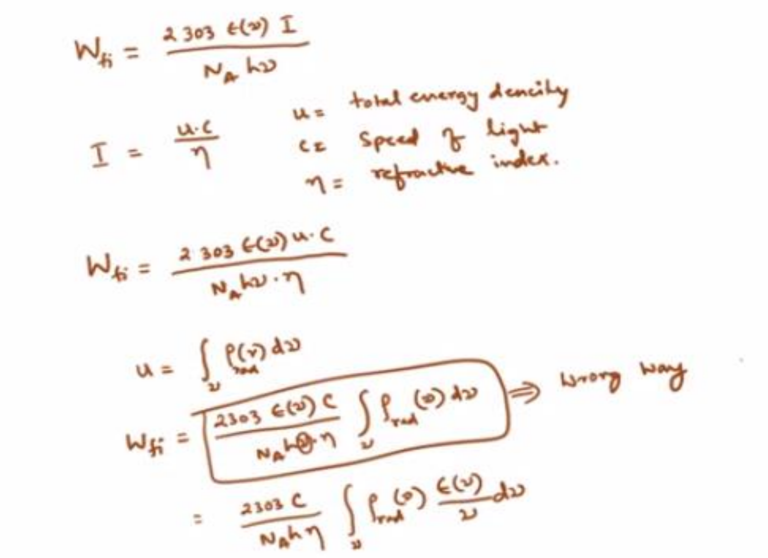

$$W_{fi} = \frac{2.303\, \epsilon(\nu)\, I}{N_A h\nu}$$

$$I = \frac{u \cdot c}{\eta}$$

$u =$ total energy dencity

$c =$ Speed of light

$\eta =$ refractive index.

$$W_{fi} = \frac{2.303\, \epsilon(\nu)\, u \cdot c}{N_A h\nu \cdot \eta}$$

$$u = \int_\nu \rho_{rad}(\nu)\, d\nu$$

$$W_{fi} = \boxed{\frac{2303\, \epsilon(\nu)\, c}{N_A h\nu \cdot \eta} \int_\nu \rho_{rad}(\nu)\, d\nu} \Rightarrow \text{wrong way}$$

$$= \frac{2303\, c}{N_A h \eta} \int_\nu \rho_{rad}(\nu) \frac{\epsilon(\nu)}{\nu}\, d\nu$$

Now, let us look at the equation that we had. We had the equation of rate equals to 2.303 epsilon of nu times I divided by NA h nu okay. Now, the intensity of light I in any medium is given by u dot c by eta okay where u is the total energy density and c is speed of light and eta is refractive index okay. Now if I plug in that, then I will get Wfi = 2.303 epsilon of nu u dot c divided by Na h nu into eta.

But the energy density u is given by integral over nu okay rho radiation nu d nu that is the total and so if you want the total energy density okay, what you need is the energy density at each frequency and you integrate over all the density okay. So when I use this is you have Wfi = 2.3, sorry this is not 2.3 but it is, I am sorry about this so erase, it should be 2303, so that this does not exist okay.

This is 2302 epsilon of nu u, instead of u I write, okay I will write it later, into c divided by NA h nu into eta integral over nu rho radiation of nu d nu. Of course, this is not the right way to because you see there is a nu here as well okay. So in pencil one should write it as 2303 c because this also depends on u, so this is actually wrong way of writing okay. Now, because this is integral over nu, any quantity that has nu must be inside that integral.

So 2.303 c divided by NA h eta integral over nu rho radiation nu epsilon nu by nu d nu so that is the right way to write okay because you are integrating over all the value nu, so any variable that has nu dependence must be integrated okay.

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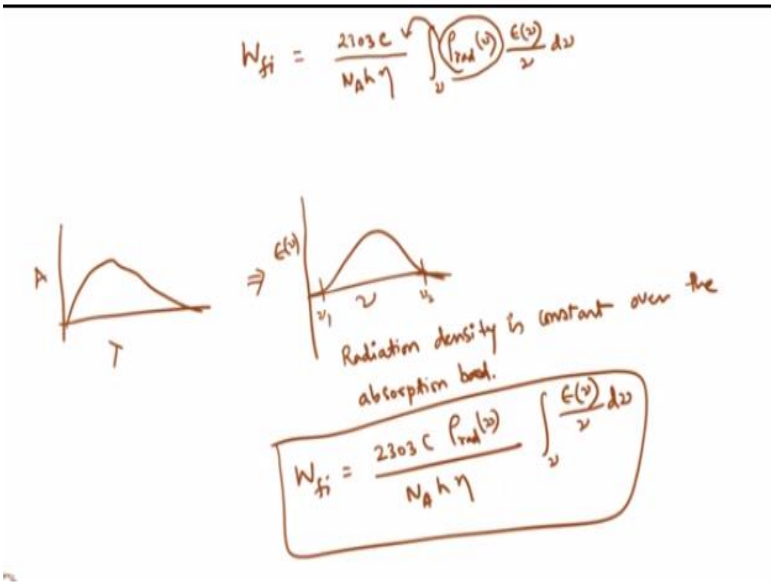

So the rate of absorption = 2303 c divided by NA h eta integral over nu rho radiation of nu epsilon of ny by nu d nu okay. Now what I am going to do is the following. Now think of it like this, you have an absorption spectrum, absorption as a function of lambda, we will get some peak okay. Now this, I told you I can transform in a way that I can plot epsilon of nu versus nu thing like that okay.

So that is what I have done. Now, when I record from say nu1 to nu2 which are the two ends of the spectrum okay, then what I would assume is that the rho radiation or radiation density is constant. So radiation density is constant over the absorption band okay. If that is a constant then which means this one I can bring it outside because when you integrate constants just get multiplied.

So what you get is Wfi = 2303 c rho radiation of nu divided by NA h eta integral over nu epsilon of nu by nu d nu okay. Now, what you are doing is that you get this, you get the rate constant okay.

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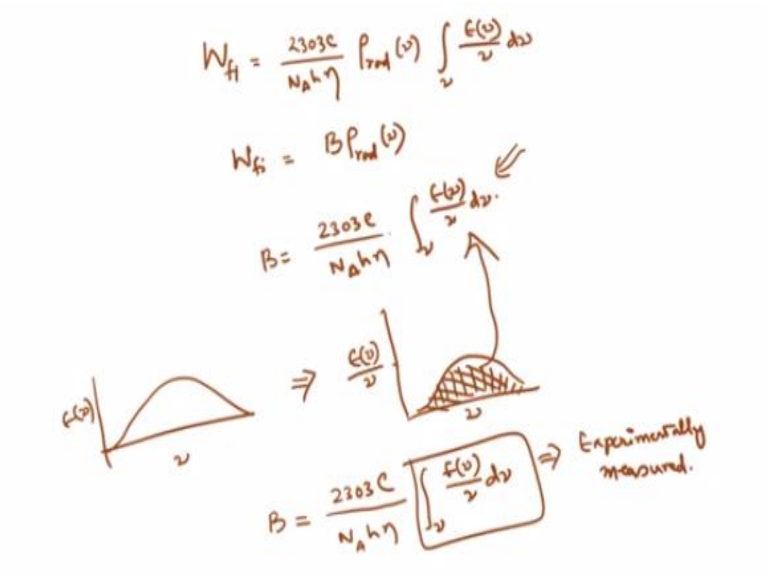

Now we have 2 equations okay. One is the radiation density, sorry one is the rate constant Wfi = 2303 c divided by NA h eta rho radiation of nu integral nu epsilon nu by nu d nu okay, but we know our rate of absorption Wfi per molecule is just given by B times rho radiation nu. Now when I equate these 2 constants, I will get B = 2303 c divided by NA h eta integral nu epsilon nu by nu d nu okay.

So I need to just get this integral. Now what is this integral? I told you that you could also have an absorption spectrum as a function of nu epsilon nu. So for each value of nu, there is a different epsilon. So what you do is you divide epsilon nu by nu. So what you do is you transform this plot as epsilon nu by nu into nu. So if you plot that plot and this area under this integral okay. So this area is this integral.

So your rate B is 2303 times c that is speed of light NA Avogadro constant h eta and this integral whatever is that you measure epsilon nu by nu d nu and this integral can be experimentally measured okay.

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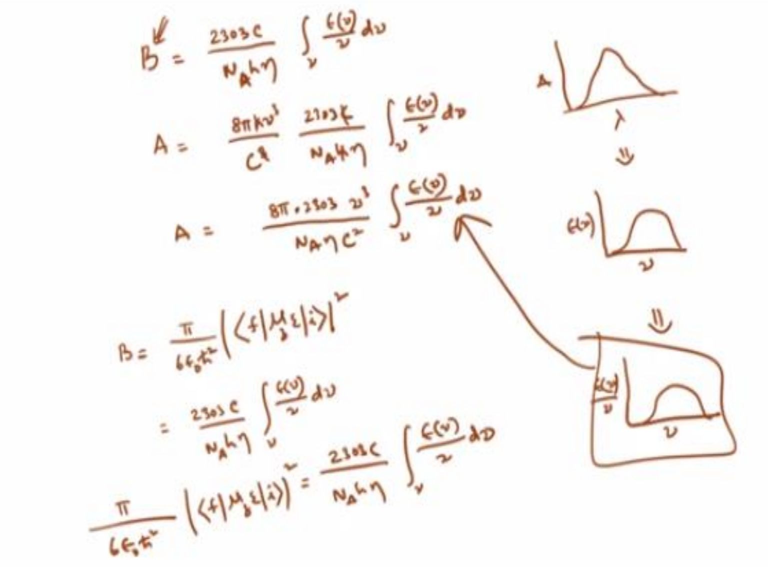

$$B = \frac{2303c}{N_A h \eta} \int_\nu \frac{\epsilon(\nu)}{\nu} d\nu$$

$$A = \frac{8\pi h\nu^3}{c^3} \frac{2303c}{N_A h \eta} \int_\nu \frac{\epsilon(\nu)}{\nu} d\nu$$

$$A = \frac{8\pi \cdot 2303\, \nu^3}{N_A \eta c^2} \int_\nu \frac{\epsilon(\nu)}{\nu} d\nu$$

$$B = \frac{\pi}{6\epsilon_0 \hbar^2} \left(\langle f | \mu_z | i \rangle \right)^2$$

$$= \frac{2303c}{N_A h \eta} \int_\nu \frac{\epsilon(\nu)}{\nu} d\nu$$

$$\frac{\pi}{6\epsilon_0 \hbar^2} \left| \langle f | \mu_z | i \rangle \right|^2 = \frac{2303c}{N_A h \eta} \int_\nu \frac{\epsilon(\nu)}{\nu} d\nu$$

So by measuring the extinction coefficient, epsilon nu by nu or other way around, so what we get is the following okay. Your Einstein's coefficient B is given by 2303 c by NA h eta integral over nu epsilon nu by nu d nu okay. Now you see B that is Einstein's coefficient of absorption is now proportional to the extinction coefficient. So there is a relationship between the extinction coefficient and the absorption coefficient okay.

Similarly, one can write A is equal to, now A was nothing but 8 pi h nu cube by c cube okay B so 2303 c by NA h eta integral nu epsilon nu by nu d nu. So this c and c square this and this h would get cancel, so what you get is 8 pi into 2303 divided by NA eta c square nu cube integral nu epsilon of nu by nu d nu that is A.

So you can by measuring the absorption spectrum and plotting, So when you measure the absorption spectrum A versus lambda, you can transform it as epsilon of nu versus nu which can again be transformed as epsilon of nu by nu by nu. So one can do this transformation and when you have this spectrum, and this is nothing but this okay, then you can actually calculate the Einstein's A efficient and B coefficient.

So Einstein's A coefficient and B coefficient can be related to the absorption spectrum okay. Now, it turns out we also know that Einstein's A coefficient, B coefficient also is related to transition moment integral. So we know B is nothing but equal to pi by 6 epsilon 0 h bar square f mu z i whole square, but this is same as 2303 c by NA h eta integral over nu epsilon over nu by nu d nu. Now, when you equate these two, so let us do that.

So, pi by 6 epsilon 0 h bar square f mu z i whole square = 2303 c by NA h eta integral over nu epsilon nu by nu d nu.

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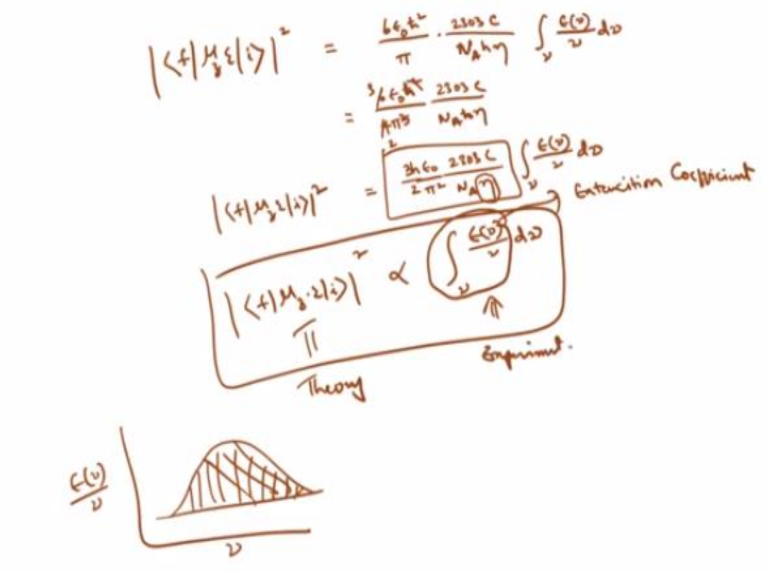

So, which means your transition dipole f mu z epsilon i whole square = 6 epsilon 0 h bar square by pi into 2303 c NA h eta integral over nu epsilon nu by nu d nu okay. So this is equal to 6 epsilon 0 h bar square is h square by 4 pi square, there is already pi so 4 pi cube 2303 c by NA h eta, so this h and this square gets canceled, this 4 two times and three times 2 pi epsilon 0 2303.

So one can write it as 3 by 2 epsilon 0 pi square 2303 c by NA eta there is h on above into h integral over nu epsilon nu by nu d nu. So one can think of the transition dipole moment square is proportional to integral over nu epsilon over nu by nu d nu okay. This is the relationship that I wanted to bring. So epsilon nu is nothing but extinction coefficient okay. So the transition dipole of a transition between state i and state f or state 1 and state 2 is proportional to this integral which is made of extinction coefficient.

So once we know extinction coefficient or rather we know, so if you have a band okay and we know the integral underneath it, so the entire band integral, the way you plot it is epsilon of nu by nu versus nu. If you know this integral, then this integral is proportional to you transition dipole. So if you have it, by the way all of these are constants okay, except to know if you change the solvent e refractive index will change, other than that everything else is a constant okay.

So once you change the transition from say molecule A to molecule B, if the area under the curve changes, then you know the transition moment or transition dipole is changing or not. So this is a theoretical quantity and this is an experimental quantity. So this is theory and this is experimental okay. So one can always relate that transition dipole to the extinction coefficient, not in a straight way, but you know in the kind of integral.

So there is an integral here, but it is basically that entire transition or extension coefficient of a band, not exactly at one position, not at the peak or lambda max, it is the extinction coefficient over the entire band okay. So which can be experimentally measured using an absorption spectrum and theoretically one can also get the transition dipole. So these two are related to each other. So we will stop here and continue in the next lecture. Thank you.