Fundamentals of Spectroscopy

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Lecture – 8
Comparison between Chemical Reactions and Spectroscopic Transitions

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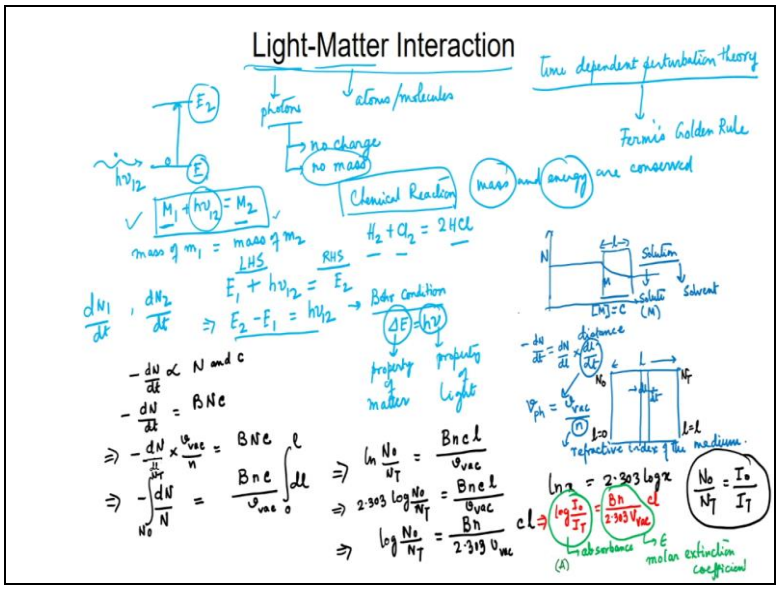

Hello everyone welcome to this lecture in the last lecture you learned about time-dependent perturbation theory and using time-dependent perturbation theory Fermi's golden rule was derived. In this lecture also we will derive a fundamental equation in spectroscopy which has important analytical applications. We have already discussed that matter is composed of atoms and molecules. When we consider the particle nature of light we saw light is composed of photons which are the elementary particles of light.

One important thing that we should remember about photons is photons have no charge also photons have no mass. When we were discussing the absorption process when one molecule interacts with one photon of energy nu 12 and goes from energy level E 1 to another energy level E 2 we saw we can write the spectroscopic transition as m 1 + h nu 12 equals m 2 this is similar to a chemical reaction chemical reaction where either some of the atoms and molecules are consumed during the reaction or new molecules are formed in the process.

For example let us write a simple chemical reaction hydrogen + chlorine gives hydrochloric acid here hydrogen and chlorine are being consumed during the reaction and hydrochloric acid is being formed. Now if we compare this chemical reaction with the spectroscopic transition we can see that here also a photon is being consumed the molecule changes from m1 to m2 that is it goes from one quantum state with energy E 1 to another quantum state with energy E 2 this analogy was first given by Einstein to derive Planck's radiation formula.

Now we know that in a chemical reaction mass and energy are conserved as we are comparing the chemical reaction with the spectroscopic transition let us look into the conservation of mass and energy for the spectroscopic transition. Mass conservation in the spectroscopic transition is obvious as the photon involved has no mass the molecule has just gone from one quantum state to another thus the mass of the molecule has not changed or we can write mass of m1 equals mass of m 2.

Now let us look into the energy conservation as E 1 is the energy of the initial state and h nu 12 is the energy of the photon we can see the energy of the left-hand side of m1 + h nu 12 equals m2 is E 1 + h nu 12. The energy of the right hand side is the energy of the final state that is E 2 now if energy has to be conserved we get E 1 + h nu 12 equals E 2 if we rearrange this equation we can write E 2 - E 1 equals H nu 12.

We can identify this equation with the Bohr condition, so the Bohr condition is for transition between 2 stationary states and is given by delta E equals h nu. Now if we see this equation carefully the left-hand side tells us about the property of matter because we are talking about the energy levels of the matter and the right-hand side corresponds to the property of light because we are talking about the frequency of light.

In other words this equation brings out the essence of spectroscopy which involves light matter interaction thus we can see that due to this light matter interaction we can investigate the properties of metal by using a light of suitable frequency. So, far we have used the concept of chemical reactions. Now when there is a chemical reaction there is a rate associated with the chemical reaction the study of this reaction rates is known as chemical kinetics.

We will now look into the rate of the spectroscopic transition which is analogous to the concept of study chemical kinetics. We have already used the concept when we were discussing

Einsteins A and B coefficient at that point we were looking at the transition rates from the mathers perspective. For example we wrote dN 1 dt or dN 2 dt or how the number density of molecules N 1 or N 2 change over time. However now we will look from the perspective of light this is the beauty of spectroscopy.

One can either look into the process from the perspective of light or can look into the process from the perspective matter. For example when we are doing a spectroscopy experiment we have to look from the point of view of light. On the other hand if we are doing some theoretical calculations using quantum mechanics where we estimate the energy levels of a molecule we have to look from the point of view of matter because the experiments and theory provide complimentary information.

We can also compare our theoretical results with those obtained from experiment we will discuss more on this later in the course. Let us consider light is passed through a solution containing light absorbing species M in other words because we are talking about a solution it has 2 components one is a solute the solute is the light absorbing species that is M there is another component that is the solvent here we are considering the solvent of the medium is transparent towards light that is the solvent cannot observe light.

Let N be the number of photons per unit volume at a particular wavelength passing through the solution. The concentration of the light absorbing species that is the concentration of M is C as light passes through the solution of length L the value of n changes continuously. In other words if we plot N on the y-axis and if we plot the distance travelled by light on the x-axis before the light enters a sample the value of N does not change.

But as light enters the sample the value of n changes continuously and again the value of M does not change when the light comes out of the sample. So, let us consider one molecule interacts with one photon at a time as we are evaluating from the photons point of view we will evaluate minus dN dt or at what rate the photons are being consumed. So, again we draw the sample the sample has length l and let us consider an infinitesimal length that is dl within the sample.

And the time taken by the light or photon to travel this length dl let it be dt so the value of dN dt can be written as dN dl times dl dt. Now this dl dt is the velocity of the photon in the medium

that is given by the velocity of the photon in vacuum divided by N where n is the refractive index of that medium. Considering one molecule interacts with one photon at a time we can understand that the rate at which the photons are being used up that is - dN dt is proportional to both N and C.

So, we can write -dN dt equals B N C where B is the proportionality constant this B is the Einsteins B coefficient we have already discussed this during Einsteins treatment of absorption. So, from this we can write minus dN dl times dl dt which is given by V vacuum by N equals B and C rearranging this equation we can write -dN by N equals B n C by V vacuum times dl integrating between the limits. So, now let us suppose that N0 is the number density of the photons when it was entering the sample.

And NT is the number density of the photons when the photons are exiting the sample or being transmitted from the sample and also at when the N is N0 l equals 0 when N equals NT else it was l. So, we can put these limits so we are integrating from N0 to NT and we are integrating from 0 to l. We have to keep in mind that B N and V vacuum are constants and C is the concentration of light that does not change due to absorption that is no photochemical reaction takes place.

So if we integrate this what we get is ln N0 by NT equals B n c l by V vacuum but we know that we can represent ln x as 2.303 log x so we can write from this 2.303 log N0 by NT equals B n c l by V vacuum. Now if I take 2.303 on the right hand side we can write log N0 by NT equals B n divided by 2.303 V vacuum times c times l and because N the number density of photon is proportional to I that is the intensity of light we can write N 0 by N t equals I 0 by I T.

So, if we use this expression N 0 by N T equals I 0 by I T so we can write log I 0 by I T equals B n 2.303 by V vacuum times c l. So, log I 0 by I T is known or defined as A and A is absorbents and this term B n divided by 2.303 times V vacuum is defined as epsilon where epsilon is molar extinction coefficient.

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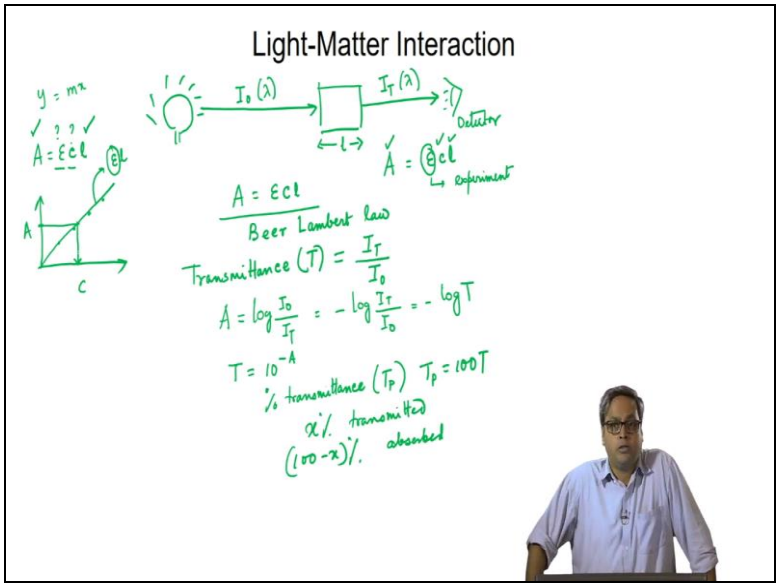

Now let us see how a spectroscopy experiment is done so in a spectroscopy experiment we have a light source. Let us say we have a lamp and the light from the lamp with intensity I 0 which is a function of wavelength passes through the sample and the intensity that comes out of the sample they say is I T which is also a function of lambda and this intensity I T is detected by a detector. So, when we do not have the sample the detector detects I 0 and when we have the sample the detector detects I T.

So when we are doing the experiments we are using a sample cell or a cuvette or in other words we know l which is the path length also because we made the solution we know the concentration of our sample. So, from experiment we can get a at a particular wavelength because A equals epsilon c l and we know c we know l we can get a from experiment we can get epsilon directly from the experiment, as epsilon is directly proportional to B epsilon is related to the transition probability that comes from theory.

If we have the knowledge of the wave function we can calculate B so this equation is a fundamental equation in spectroscopy where we can compare experiment and theory this equation A equals epsilon c l is known as the Beer-Lambert Law. Historically Lambert found out absorbance is proportional to l and much later they are discovered that absorbance is proportional to the concentration c. Later these two findings of Beer and Lambert were combined to obtain the Beer-Lambert Law.

So instead of absorbance we can also get transmittance from transmittance is denoted by T so we can get transmittance from the experiment transmittance is defined as I T by I 0, so we can

write absorbance equals log I 0 by I T equals - log I T by I 0 equals - log T or in terms of transmittance we can write T equals 10 to the power – A. So, we can also define something called percentage transmittance which is denoted by T P where T P equals 100 T we can think.

Let us say x% of the light is transmitted from the solution x% is transmitted then 100 - x% of the light is absorbed by the solution you will have a better understanding when we solve problems of this analytical application of spectroscopy depends on this Beer-Lambert law for example one can determine the concentration of the sample using this law. So, let us say we have a sample of unknown concentration.

So if we again write the Beer-Lambert Law we can write absorbance equals epsilon c l, so we know the path length if we do the spectroscopy experiment with the sample of unknown concentration we can get the corresponding absorbance but what we do not know is Epsilon as well as the concentration that is unknown. So, we can think that we can make a known concentration of the sample and that will give us the epsilon directly from the experiment. So, what normally is done is that we make different solutions of known concentrations and perform spectroscopic experiments on those solutions of known concentrations.

So, now if you plot absorbance of those known concentrations against the concentration we will get points and if we join these points we will get a line passing through the origin this is because absorbance equals epsilon c l is of the form y equals mx, so the slope of this line will be epsilon times l because we know l we can estimate Epsilon from this straight line and this straight line can act as a calibration line.

So, now if we do the experiment with the solution of unknown concentration and we can get an absorbance value we can directly estimate the unknown concentration. Now if we plot A versus wavelength for any molecule. So, we are plotting absorbance or A in the y-axis and wavelength on the x-axis we get a curve which is known as an absorption spectrum it appears from the spectrum that the value of A is a function of wavelength.

As A depends on wavelength comparing with Beer Lambert equation we can see the left hand side is wavelength dependent. In the right hand side we have c and l which are wavelength independent. So, we can easily understand that epsilon has to be wavelength dependent. So,

instead of plotting A versus lambda if we plot epsilon versus lambda then we get a spectrum with similar line shape. There are a few important things to note about a spectrum.

For a particular wavelength the value of A becomes maximum and this wavelength is known as lambda Max or this is also known as the peak position. The value of lambda Max and the corresponding epsilon is characteristic of the absorbing species. Also there is a width associated to the spectrum in contrast to a line which we would expect if transition from one energy level to another takes place. There are several mechanisms which lead to line broadening which we will study in the next lecture.

So, finally let us look into the limitations of Lambert law, the law is applicable only for dilute solutions at higher concentrations the solute may associate or aggregate such that the absorbing species will change and secondly at higher concentration the value of I T will be very small and as a result there will be appreciable error in the determination of I T by the detector and hence there will be an appreciable error in the determination of absorbance or A. So we will end this lecture by solving a couple of questions.

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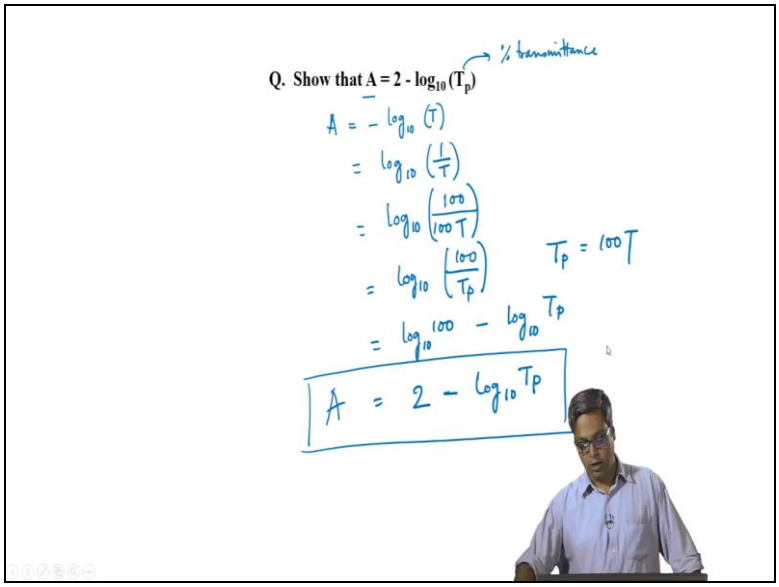

So the first question we have is shows that absorbance a equals to minus log T P where TP is percentage transmittance. So, we know that absorbance A equals - log base 10 T which we can write log 1 by T so now if I multiply both the numerator and denominator by 100 we get log base 10 100 by 100 T which we can write log 10 100 by T P because T P equals 100 T. So, that is log 10 100 - log 10 T P equals 2 - log 10 T P. So we have absorbance equals 2 - log 10 TP.

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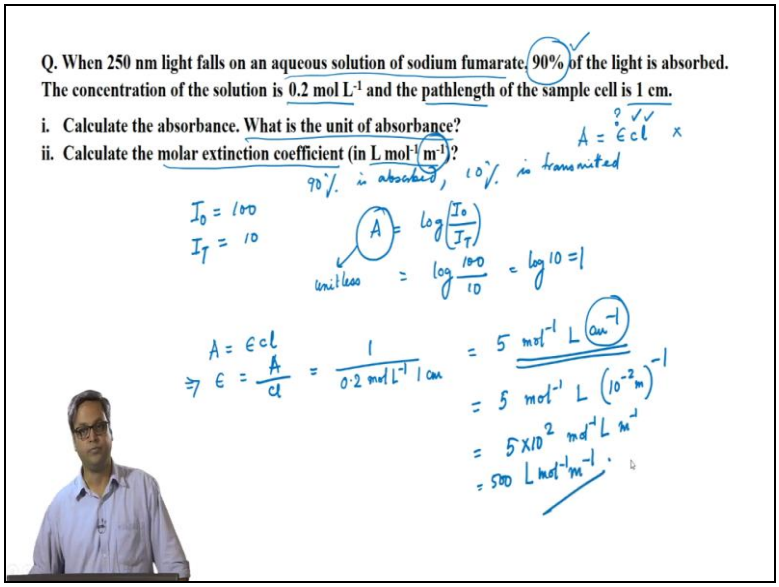

Now let us go to the next question the next question says when 250 nanometer light falls on an equal solution of sodium fumarate 90% of the light is absorbed. The concentration of the solution is 0.2 moles per litter and the path length of the sample cell is 1 centimetre. So, the first question we have is what is absorbance? We know from Beer-Lambert Law absorbance equals epsilon c l, here we know the path length we know the concentration but we have no information on the molar extinction coefficient.

So we cannot use this equation but we know from the question that the 90% of the light is absorbed. So, if 90% is absorbed we can say 10% is transmitted in other words let us say if we are 100 photons to start with or because N 0 is proportional to I 0 that size will equals 100 then I T is 10% of 100 that is 10 or in other words I can write absorbance equals log I 0 by I T that is log 100 by 10 which is log 10 equals 1.

So the first question has a second part what is the unit of absorbance. So, we should all remember absorbance is unit less. Now the second question we have is calculate the molar extinction coefficient in liter mole inverse meter inverse. So, now we will use the Beer-Lambert law equation absorbance equals epsilon c l. So, from here we can rearrange and write epsilon equals absorbance by c l equals 1 that is absorbance.

By concentration 0.2 moles per liter and path length is 1 centimetre, so this becomes 5 mol inverse liter centimetre inverse. So, this is the unit of epsilon or molar extinction coefficient but in the problem you have been asked to find in the unit of meter inverse instead centimetre

inverse. So, you have to do one more step that is 5 mole inverse liter centimeter we will write 10 to the power -2 meter whole inverse.

So that is 5 into 10 to the power 2 mole inverse liter meter inverse so that is 500 liter mole inverse meter inverse.