Introductory Quantum Mechanics and Spectroscopy
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Lecture – 9
Molecular Spectroscopy – Part 2
Beer-Lambert Law

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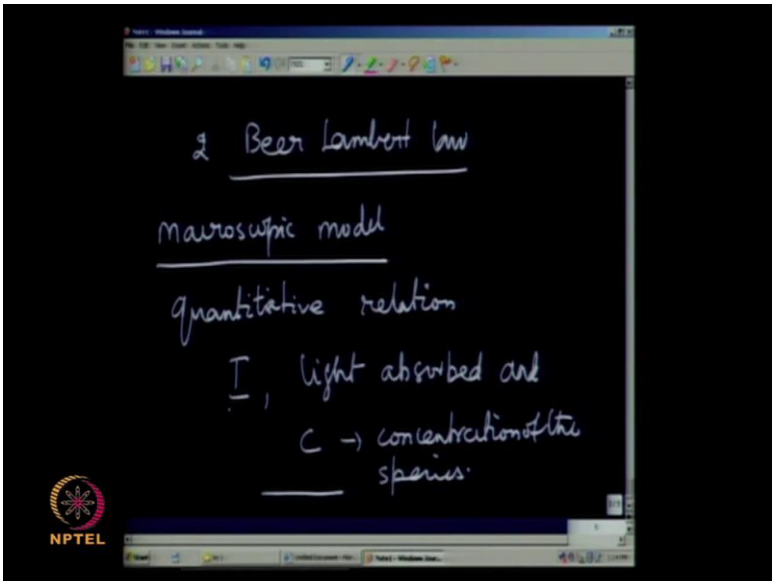

Let us go on to the next item in the lecture namely, the Beer-Lambert law. This is the second item. Again, this is for macroscopic model. And what is done here is to give a quantitative relation between amount of light absorbed, which I would call as light absorbed and the concentration of the species C – concentration of the species which absorbs. What you see here is a law which tells you that the amount of light absorbed is in some wave proportional to the concentration through an elementary process we will just derive that. And therefore, we can use this to determine the concentration of the species in some unknown samples and so on, which is done routinely in all the laboratories using spectrometric techniques. So, let us write down the basic relation or the process as follows.

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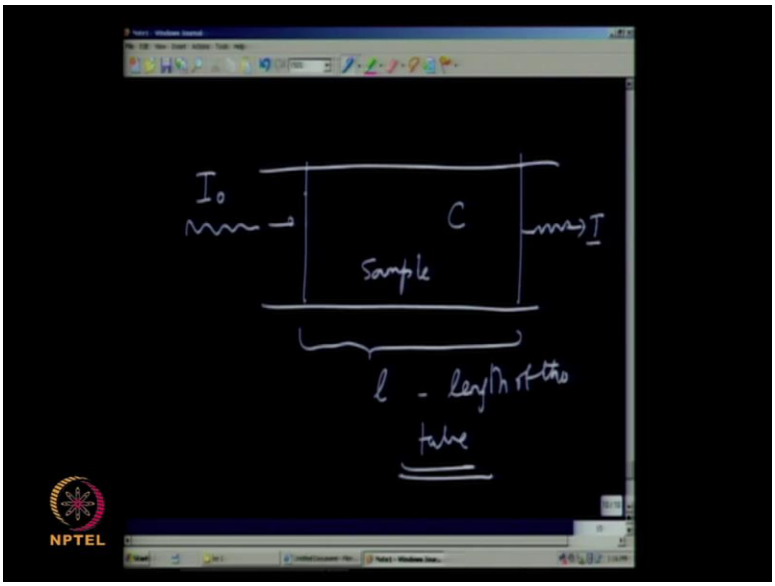

Let us assume that, light falls on a transparent tube that contains a sample. This window does not absorb any light. Let us assume that, this is a fully transparent window. And let the intensity initially be I naught – the light intensity. And the light that is emitted is proportional has the intensity I. And let the tube that is in has a sample, whose concentration is C. And let the length of the tube be l – length of the tube. Now, imagine qualitatively, what will happen. Assuming that we have a setup like this; if we shine light on a tube, which contains – a sample tube, which contains some sample in a solution for example; it is contained in that; and you have transparent windows.

Light falls on the sample and then of course, some light gets emitted. It is very easy to imagine that, if we shine more light; then more of it will get emitted. It is also easy to imagine that, if we have more sample here; if we shine light, more of it will be absorbed and less of it will be emitted. And also, if we increase the length of this solution window that light passes through; the cell – of a longer cell compared to a shorter cell. Supposing it has a same concentration; but if you increase the cell, all that you are doing is you are increasing the total number of the molecules, which are represent in that. Therefore, the amount of light that gets absorbed is also more. So, based on this qualitative expectations of what will happen to molecules, which absorbs light, Beer and Lambert arrived at the following proposition.

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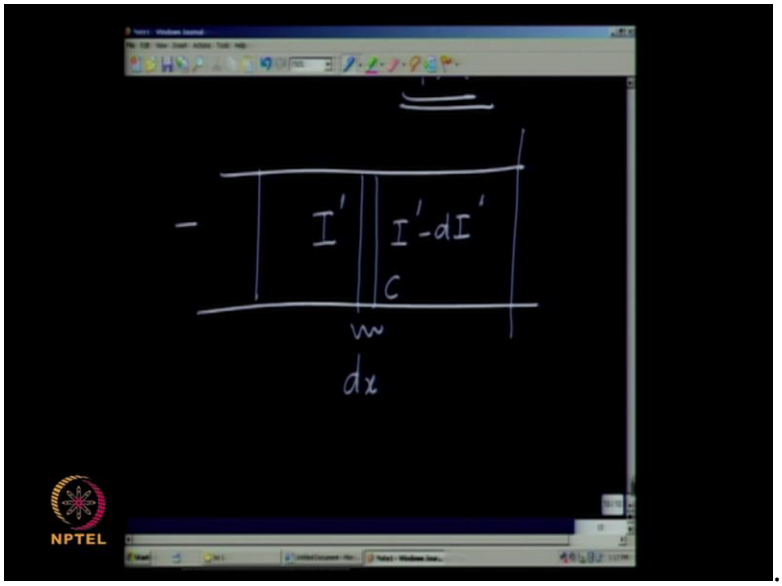

The change in the intensity… Let us take again the same sample; let us worry about a very small interval called dx. And let the intensity here be I prime; and let the intensity here be I prime minus d I prime, which is a very small change in the intensity. And the concentration of course of the cell is… The example is uniform. So, it is C. The propositions are the following.

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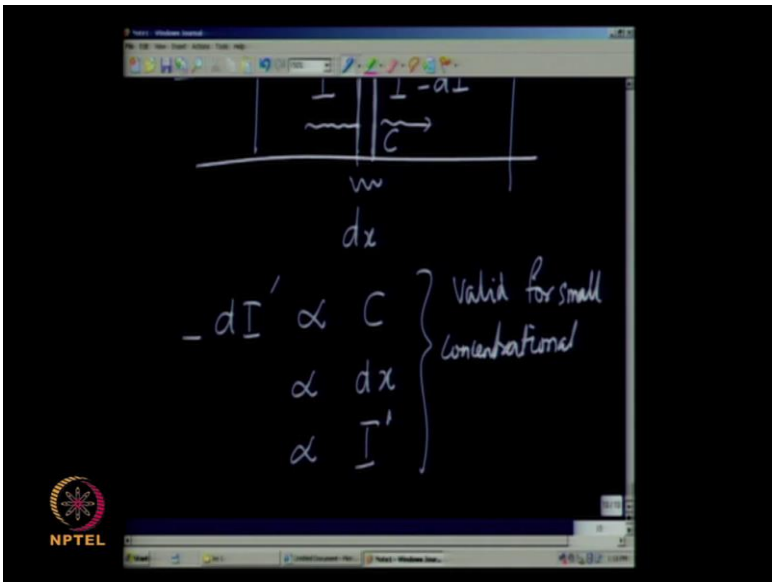

Minus d I prime, which is the change in the intensity as light goes from this end to this end in this small interval of space given by the length dx; the minus dI prime is proportional to the concentration of the sample that is present in the cell. These are all

qualitative observations; minus d I prime is proportional to the length dx present in the cell – the length dx of the cell ((Refer Time: 04:51)) this part. And the change in the intensity is also proportional to the actual intensity that falls on here. So, these were the three observations. And all of this is valid for small concentrations – less than something like 0.1 moles per liter or even less – even lower. The lower the concentration, the better the approximation that works. Again, this is based on a simple observation for many samples.

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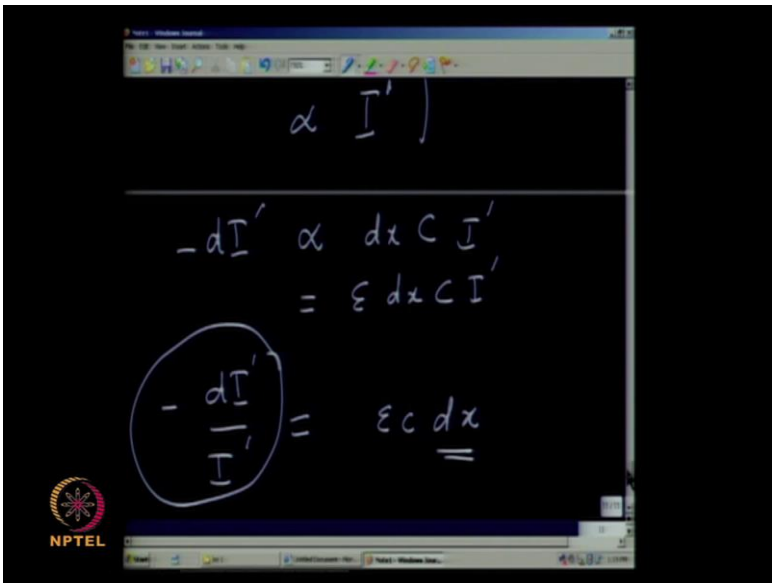

And this can be lumped together; this proportionality can be put together in the form of minus dI prime is therefore proportional to the product dx C and I prime; or a set equal to a proportionality constant epsilon multiplied by dx times C times I prime. Therefore, what you have is minus d I prime by I prime is equal to epsilon c and dx. You see that, the variable is the change in the intensity in the small interval dx. Now, this is what you considered for a very very small interval. And therefore, if you need the total change as light falls from this end of the cell to get emitted at this end of the cell here; the total change is nothing but the change that takes place in every little part. And therefore, add all these changes.

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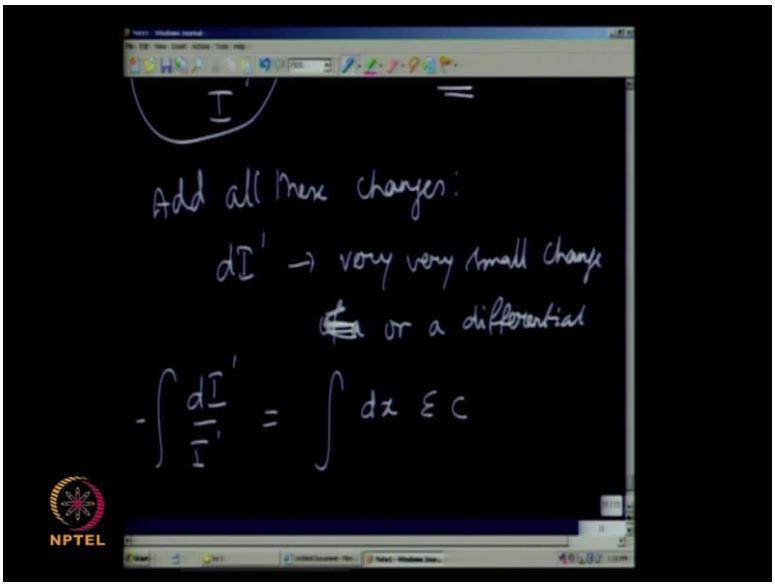

Add all these changes to ((Refer Time: 06:38)) And since dI is taken as a differential or a very very small change, dI prime is a very very small change or a differential or a differential of change. The addition is nothing but the integration minus dI prime by I prime is the same as the integration of dx times epsilon times C; C concentration is uniform throughout the cell is what we assume. And epsilon is proportionality constant is independent of the length of the cell or the intensity.

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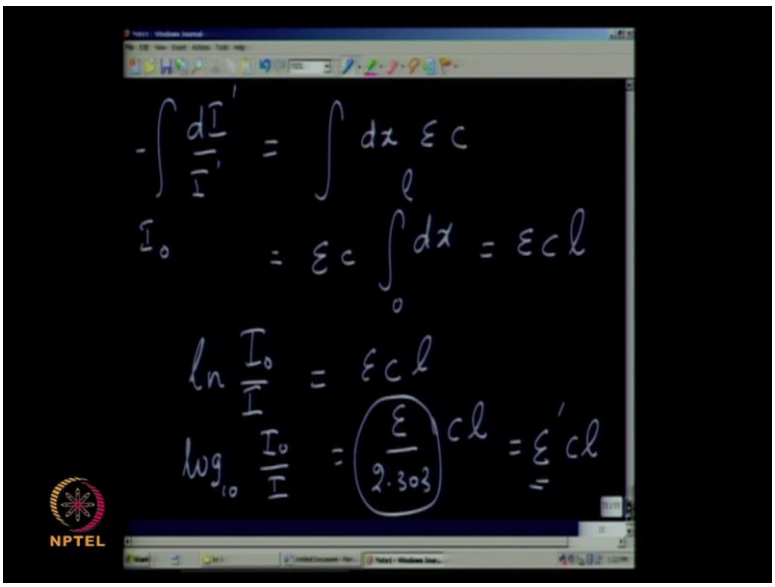

Therefore, what you have here is nothing but epsilon times C times dx from 0 to l, which is the length of the cell. So, what you have is epsilon C times l. And here if the initial intensity is I naught and the final intensity is I; so what you get out of this is nothing but

the log I naught by I; I would write it as ln – natural logarithm – ln I naught by I as epsilon times C times l. And therefore, if you have to do this log base 10, I naught by I what you have is – this is 2.303. So, it becomes epsilon by 2.303 Cl. And this is a constant, which we denote epsilon prime Cl is a constant, which relates the intensity of the radiation falling on the sample; the intensity of the radiation that is getting emitted from the sample is proportional to the concentration… The logarithm of the ratio is proportional to the concentration for very very small concentrations.

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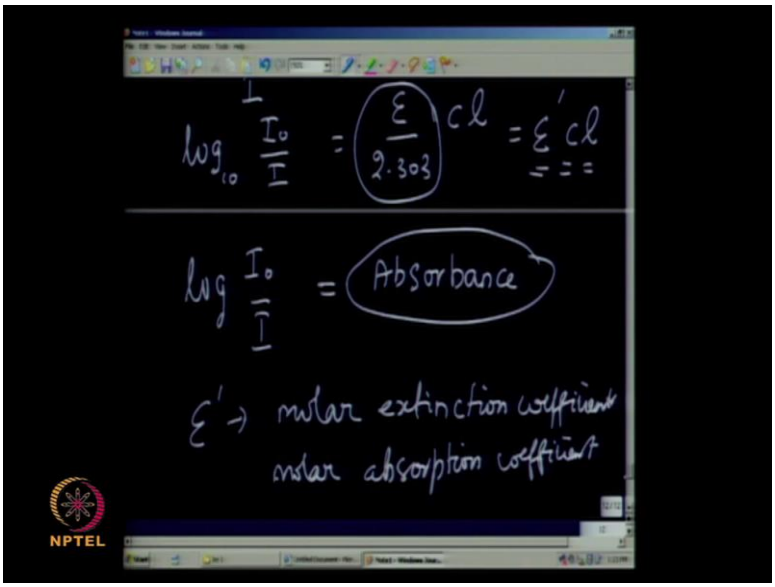

So, log I naught by I is called… In experimental measurements, it is called the absorbance. And this is what is usually plotted in the spectrum. And there is also transmission percentage of light transmitted and so on. But, this is the standard unit; it is a standard name given to log I naught by I. Absorbance is equal to the concentration times the length of the example times a constant. The constant epsilon prime is called molar extinction co-efficient. When you turn off light, somebody can say extinct the light, that is, turn it off. So, what you see as an extinction coefficient is the light that falls on, does not come up at the end, but a part of it is absorbed by this light is extinct and… So, that the word is an English word to say that, the amount of light absorbed per unit concentration per unit length. If you calculate that, the absorbance that is called the molar extinction coefficient; the other name given to that is molar – is called the absorption coefficient.

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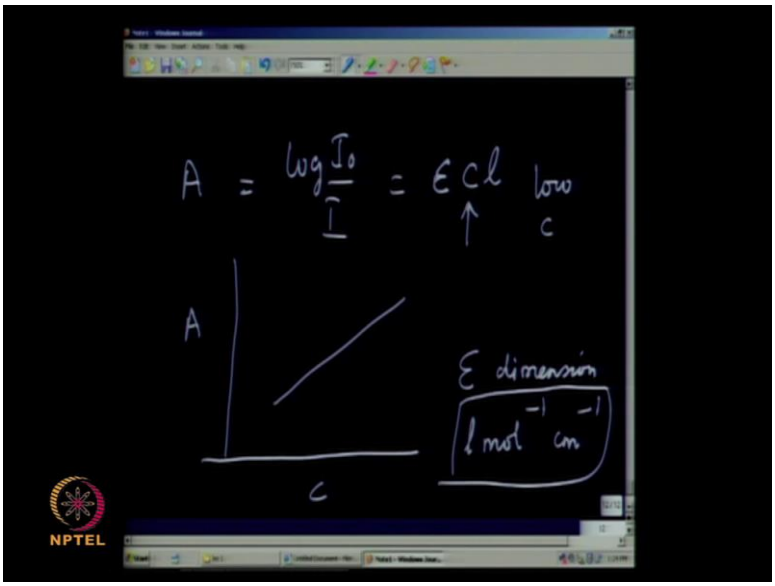

So, two things which are important; one – absorbance is proportional – A is defined as log I naught by I is epsilon C l proportional to the concentration for low values of concentration. Therefore, if you plot absorbance versus the concentration, you see a straight line. The dimension of the epsilon – you see absorbance is a ratio of the two same quantities logarithm. Therefore, this is dimensionless. And concentration is given in moles per liter. The length of the cell is given in centimeter or meter – whatever it is. Therefore, this right-hand side should also be dimensionless.

So, what you have is epsilon has the dimensions of… Epsilon dimension is length; this is length. So, you have liters per mole if you give concentration in moles per liter per centimeter, if you give the length of the cell in centimeters. So, this is usually the dimension, that is, a unit that is employed in determining the values of epsilon. And this linear law between absorbance and the concentrations of a substance absorbing light – this linear law is valid for small concentrations. And therefore, it is a very useful quantity to determine unknown concentrations of small amounts of substances in the laboratory in UV-visible spectrometer; very often experiments are designed in undergraduate laboratories to test and validate this law for students doing chemistry laboratory.

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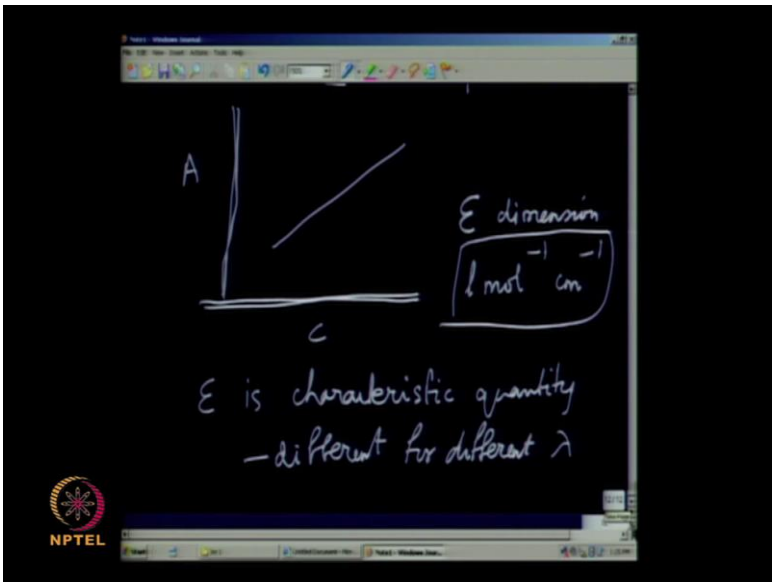

Now, what is important is the property epsilon is independent of the length of the cell is independent of the amount of light that is falling on the cell within this constraint that, small concentrations and so on. But, epsilon is characteristic of the frequency of light; epsilon is a characteristic quantity; and is different for different lambda – different wavelengths. So, what you see is that, if you plot the molar extinction coefficient of a substance by changing the lights with different frequencies; and if you plot the absorbance keeping all the other things constant; you will see that, substances absorb specific frequencies of lights more than the others. What I have here is a typical graph of the same thing.

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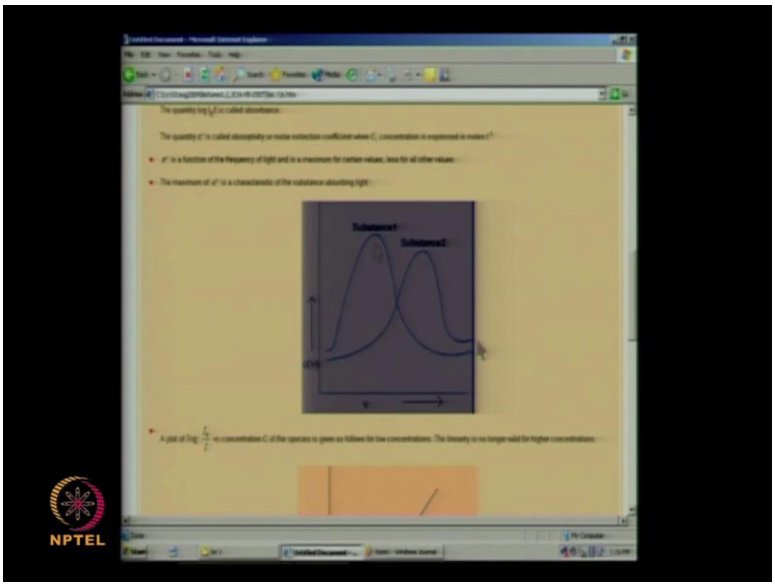

In this particular graph what you see here is a function of the absorption coefficient epsilon with respect to the frequency nu. And you see substance 1 has a maximum at a certain frequency; another substance has a maximum at another frequency. And therefore, in choosing which length that we should use for studying different substances, similar results are important.

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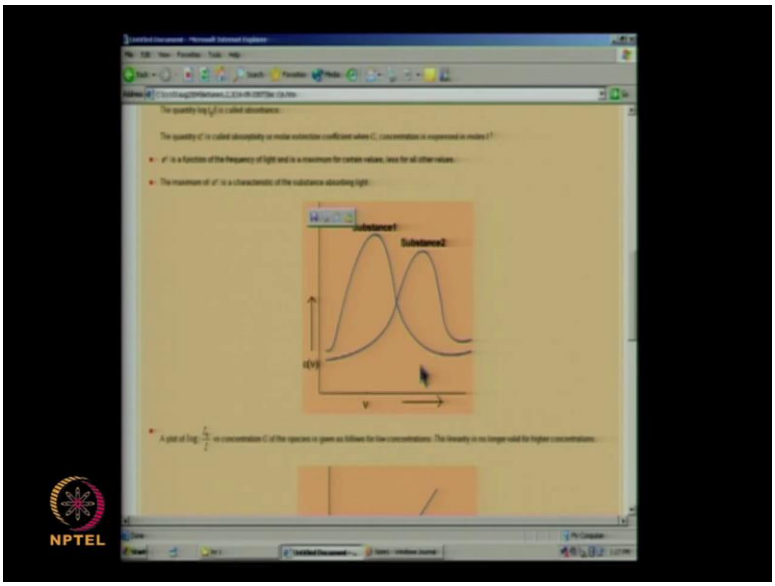

For substance 1, we will probably choose this substance 1 – this frequency as the appropriate frequency to do the experiment. And for substance 2, we choose this as the appropriate frequency. And therefore, you see that, this molar absorption coefficient is associated with a certain substance and with a certain frequency; and these two enable us to determine quantitatively small amounts of materials that we know. Therefore, a lot of tables can be prepared and lots of references can be made; and then one can refer to this; do a simple experiment; do a plotting linear calibration of concentration versus absorbance. And from the slope, one can determine unknown concentrations. Therefore, this is a quantitative law that is used in most spectroscopic laboratories for determining concentrations of species.