Fundamental of Spectroscopy

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Lecture – 01
Introduction to Spectroscopy

Hello everyone, I am Sayan Bagchi and I welcome you all to this first lecture on this course on the fundamentals of spectroscopy. In this course, I will introduce you to the general concepts and the common fundamental principles of spectroscopy. Over time, we will try to thoroughly understand these principles from the viewpoint of various forms of spectroscopy. I hope that everyone would enjoy this course, and it would be a good fun learning experience for all of you. So, because we are talking about spectroscopy, the first question we would ask is what is spectroscopy?

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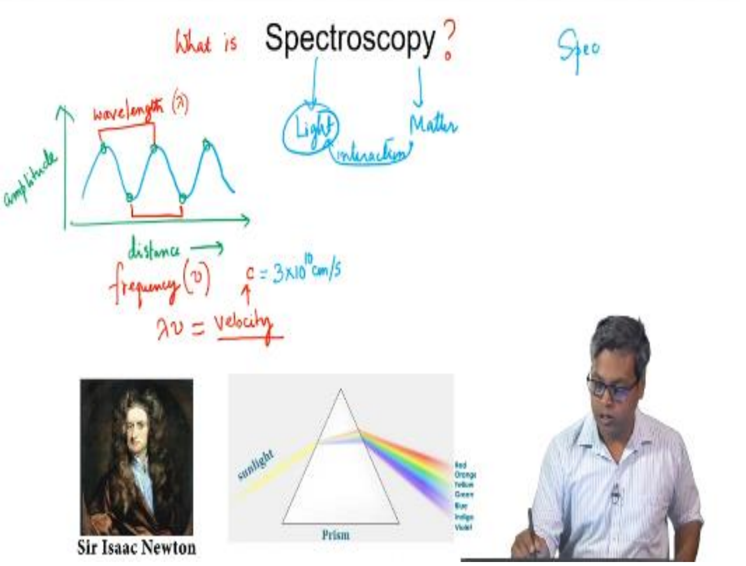

So, the question is what is spectroscopy? So spectroscopy is defined as the interaction between light and matter. In other words, we have 2 things in spectroscopy, we have light. And we have matter. And in addition to that, we have some interaction between light and matter. So first, let us focus on light. So because we have light and matter, we would ask what is light? Light is an electromagnetic wave which oscillates in space. So because we have talked about a wave, let us draw wave first.

So now we have drawn a wave and because this is a plot, let us try to label the axis. So on the y axis, we are showing the amplitude that means it tells us how large or small is the wave on the x axis, we are showing the distance traveled by the wave. So, if you look into the wave, we will see that there are several repeating points, where the wave has maximum amplitude and also there are several points where the wave has minimum amplitude.

So, now, if we join any 2 consecutive maxima or any 2 consecutive minimum of the wave, what we get that distance is called the wave length or is the length of the wave. So, for any wave there is a wavelength and wavelength is commonly represented by lambda. Similar, when we talk about a wave there is also a frequency associated with the wave. So, now the question is what is frequency? So, frequency refers to the number of full wavelengths per unit time frequency is commonly represented by nu thus if the length of the wave is large.

We have less number of waves per unit time of the frequency small, if the length is small, we have more number of waves per unit time of the frequency is large. Thus as we will see later, wave length and frequency are inversely proportional. That is shorter is the wavelength, the higher is the frequency and vice versa. Also for any wave, if you multiply the wavelength that is lambda with the frequency of the wave that is nu, what we get is the velocity with which the wave is traveling.

So, for a wave moving in a constant velocity, we can again see that wavelength and frequency are inversely proportional. Now, because light is a wave, there is a frequency and a wavelength associated with light. Now, if you multiply the wavelength and frequency of light, what we get is the velocity of light, which is represented by c, and the value of c is 3 times 10 to the power 10 centimeter per second in vacuum, however, the light that we normally see around us, for example, the sunlight is a composite light.

That means, this light is not composed of a particular frequency or a particular wavelength, but is composed of several wavelengths or several frequencies. In fact, in 1671 Newton showed that when sunlight is passed through a glass prism, we get a rainbow like band, where the components of the light are arranged in the order of the wavelengths, thus we can say that we can spread the electromagnetic wave into its different constituents in terms of wavelengths or frequencies, what we will get? We will get a spectrum and the process of getting the spectrum is called spectroscopy.

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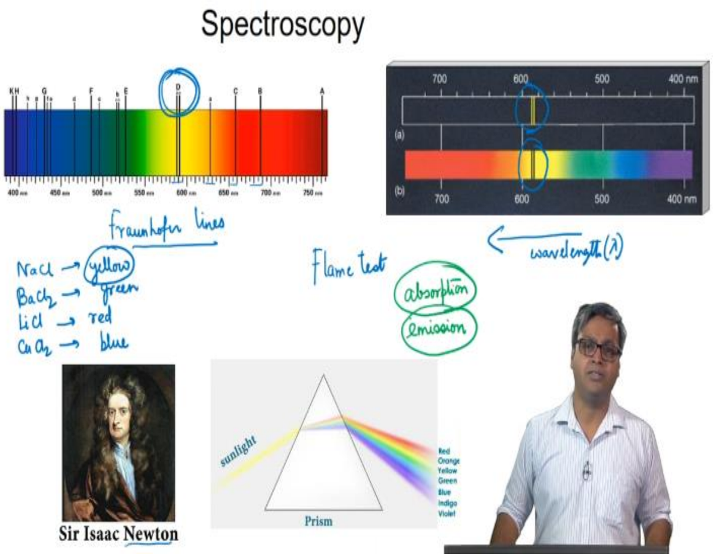

Spectroscopy

Before we go into the details of spectroscopy, first let us look a little bit into the history of spectroscopy. Spectroscopy began in the 17th century and Newton first applied the word spectrum to describe the solar spectrum or the rainbow of colors that we just talked about. Later on careful analysis showed that the solar spectrum consists of many dark lines. So, you see, these are the dark lines that the solar spectrum consists of.

So, these dark lines are also known as Fraunhofer lines and these lines can be used to find the existence of various elements in the solar atmosphere. So, to understand these dark lines, let us focus on another interesting experiment. This might be the first spectroscopy experiment that you have already performed, knowingly or unknowingly in the laboratory and that experiment is called the flame test.

So, for example, if you take sodium chloride and heat it in the flame of a Bunsen burner, you will see a bright yellow color. However, if you have a different matter instead of sodium say we have barium chloride or lithium chloride or copper chloride then we will see different colors. For example, barium chloride will show us green colored, lithium chloride will show us red color and copper chloride will show us blue color.

Now, if we pass this yellow light that we get from sodium chloride through a glass prism like Newton dead when he passed the sunlight through a glass prism. Now, if you do the same thing with the sodium chloride yellow light, we will get a sodium spectrum. And the sodium spectrum consists of 2 closely spaced lines of different wavelengths. So, here on the x axis, we are plotting wavelengths, actually the wavelength is increasing to the left side here. So, we are plotting wavelength or lambda on the x axis.

So, now, the origin of this yellow color lies in the fact that when sodium atom is heated, yellow light is emitted. And the 2 closely spaced lines obtained from sodium actually match 2 of these dark lines in the solar spectrum or the match these 2 of these Fraunhofer lines in the solar spectrum and these particular lines in the solar spectrum that match the sodium chloride spectrum are known as the D lines, you can see the label A to K all these black lines.

So, the 2 lines we get from sodium of the D lights in the solar spectrum. The result shows the sun's radiation is absorbed at selective wavelengths by various gas elements existing in the solar atmosphere. So, on one hand, sodium in the solar Casper absorbs the sunlight, we see 2 dark lines in the solar spectrum. On the other hand, in the flame test, the same 2 lines are being emitted. So spectroscopy can be of 2 types. So, one is absorption spectroscopy and the other is emission spectroscopy.

So what light is absorbs by matter, we get an absorption spectrum and when light is emitted by the matter, we get an emission spectrum. The wavelengths obtained from the flame test of sodium chloride are due to an emission process. That means, if have done this in the lab already, you have done emission spectroscopy or the flame test is an example of emission spectroscopy.

In general, it is observed that the spectrum obtained from atoms consists of discreet lines, whereas, molecules give us to bands, which are much broader than the lines obtained from that.

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Wave-Particle Duality of Light

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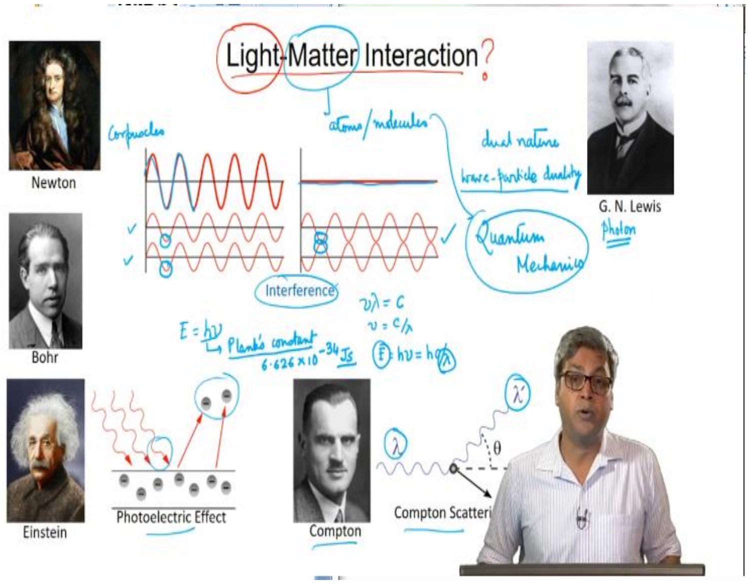

Light-Matter Interaction?

Because, we just talked about absorption and emission. We can understand that when light falls on matter, light interacts with matter the explanation of light matter interaction was first given by Niels Bohr in 1913. So, the obvious question is, what is the nature of light matter interaction but before we go into light matter interaction, let us spend some more time on light. So, I have mentioned light is an electromagnetic wave, or in other words, light should have wavelength properties.

However, in the 17th century, when Newton performed the first spectroscopy experiment of passing light through a glass prism, he believed that light is made up of tiny atoms like particles, which he called corpuscles. He could explain some properties of light using this concept. For example, reflection of light or how a beam of light bends when it travels from one medium to another. Later in the 19th century, scientists did a series of experiments that demonstrated that light cannot be made up of particles.

For example, when 2 beams of light cross paths that do not interact with one another, if light was made of a particles, then particles from one beam of light would crash into the particles of the other beam. And other thing, light makes interference patterns, which are undulations of 2 waves that occupy the same space. So here we have 2 waves, we can see the minima of wave one is coinciding with the minimum of 2. So when we add these 2 waves, we get a bigger wave.

On the other hand, in the second example, the minima of wave 1 is coinciding with a maximum of wave 2. So in other words, when we add these 2 waves, they cancel out one another. So, this interference pattern the second case is called the destructive interference and in the first case we have constructive interference. So, we can see waves only make interference patterns and particles do not. So, in the 19th century, light was thought of as a wave.

But in the 20th century, Einstein explained photoelectric effect; he showed that when you shine light onto a matter electron is emitted. These electrons are called photo electrons, as the light transfers his energy to the electrons. Now, let us ask whether this process is a physical or a chemical change. This is a chemical change because similar to a chemical reaction, here light is destroyed and a nu particle that is electron is formed.

Normally when we are studying bulk properties of matter, we can explain those properties using classical mechanics. When we think about chemical reactions, we have to think in terms of atomic nature of the matter. That is Einstein argued that when we are interested in the bulk properties of light, for example, reflection or interference, we can consider light as a wave. However, when we need to understand photoelectric effect, we need to consider the particle nature of light.

Einstein said that one quantum of light has the energy E equals h nu, where h is known as the Plank's constant. And this Plank's constant has the value or h has the value of 6.626 times 10 to the power -34 Joule second, Joule second is the unit of the Plank's constant or h, Compton later showed that when X ray hits electrons, the scattered wavelength of the X ray is different from the initial wavelength of the X ray. A changing the wavelength, refers to a change in energy, because we know E = h nu.

And we also know that we should multiply frequency with wavelength nu times lambda we get back of its speed of light. so we can write nu = c / lambda. In other words, E = h times nu, we can also write this as hc / lambda. That means, when there is a change in the wavelength, there is a corresponding change in energy, a change in energy can only happen when 2 particles collide. As electron is a particle, light also has to be a particle. In other words, in 1923 Compton showed that light is particle in nature.

Later, in 1926, G.N. Lewis introduced the term photon to describe the elementary particle of the quantum of light. So, G.N. Lewis coined the term photon to describe one quantum of light thus we can see that light has a dual nature. In other words, depending on the experiment, we have to invoke the wave or the particle nature of light to understand observations. For example, as we saw in experiments like photoelectric effect or Crompton effect, light behaves as made up of particles, whereas an interference or diffraction, light behaves as made up of waves.

This is known as the wave particle duality of light. And this wave particle duality let to the revolutionary nu concept called Quantum Mechanics. Generally in spectroscopy, light is considered as a classical electromagnetic wave. However, there is exceptions that is, there are cases where we need to consider light as photons. Now, after discussing the characteristics of light let us see what we mean by matter.

So, matter is composed of atoms and molecules. However, in case of matters, these atoms and molecules cannot be described using classical mechanics or we need quantum mechanics to describe matter. Using quantum mechanics it can be seen that the energy levels in matter are quantized does to appreciate spectroscopy. In other words to appreciate light matter interactions, a basic understanding of quantum mechanics is necessary. My co-instructor Anirban Hazra will introduce the basic concepts of quantum mechanics to you all in the next couple of lectures.

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Spectroscopic Transitions

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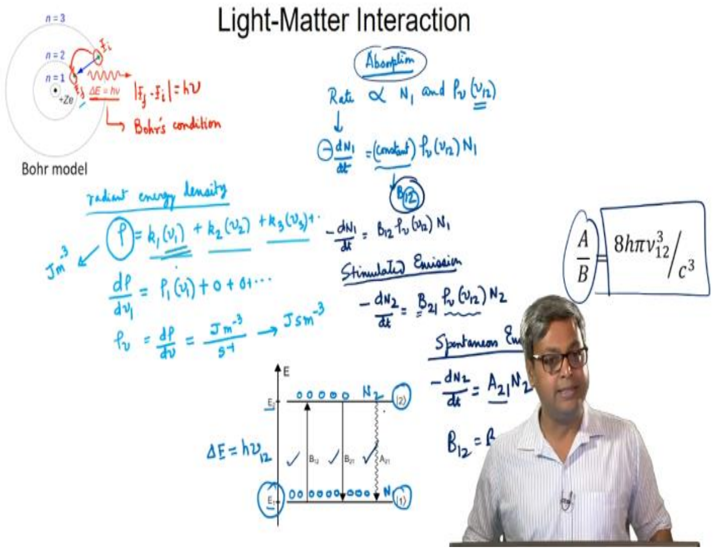

Light-Matter Interaction

$|E_j - E_i| = h\nu$

Bohr's condition

radiant energy density

$\rho = k_1(\nu_1) + k_2(\nu_2) + k_3(\nu_3) + \cdots$

$J m^{-3}$

$\frac{d\rho}{d\nu_1} = \rho_1(\nu_1) + 0 + 0 + \cdots$

$\rho_\nu = \frac{d\rho}{d\nu} = \frac{J m^{-3}}{s^{-1}} \rightarrow J s m^{-3}$

Absorption

Rate $\propto N_1$ and $\rho_\nu(\nu_{12})$

$-\frac{dN_1}{dt} = (\text{constant})\, \rho_\nu(\nu_{12}) N_1$

B_{12}

$-\frac{dN_1}{dt} = B_{12}\, \rho_\nu(\nu_{12}) N_1$

Stimulated Emission

$-\frac{dN_2}{dt} = B_{21}\, \rho_\nu(\nu_{12}) N_2$

Spontaneous Em

$-\frac{dN_2}{dt} = A_{21} N_2$

$B_{12} = B$

$\frac{A}{B} = 8h\pi\nu_{12}^3 / c^3$

$\Delta E = h\nu_{12}$

However, even before the advent of quantum mechanics Niels Bohr postulated that electrons in the hydrogen atom move in stationary states given by some quantum condition and electrons will remain in that stationary state forever, unless an external perturbation is applied. This postulate is consistent with the principles of quantum mechanics, which was formulated almost 12 years later, Bohr postulated that when light interacts with hydrogen atom, electron jumps from one stationary state to another stationary state.

If the energy of the initial stationary state is the E i, and the energy of the final stationary state is E f, then according to Bohr the difference in energy, that is E f - E i = h nu. In other words, if delta E is the difference in energy between the initial and final states of the matter, then delta E = h nu. This is known as Bohr's condition. However, although both postulated the existence of stationary states in hydrogen atom and the transitions between these states Bohr did not explain the mechanism of these transitions.

The mechanism was first given by Einstein when he was trying to derive Plank's blackbody radiation equation. Einstein postulated that the rate of absorption of light by matter is proportional to the radiant energy density of light with the right frequency. So as light can consist of more than one frequencies, we can write the total radiant energy density. So let us say this radiant energy density is rho. so we can write this as k 1 nu 1 + k 2 nu 2 + k3 nu 3.

This means this radiant energy density has multiple frequencies 1 with you 1, 1 with you 2, 1 with you 3. So this nu 1nu 2 nu 3 are the different frequencies of light and the unit of rho which is energy density. There is energy per unit volume is joules per meter cube. However, if we need to find the radiant energy density of a certain frequency, say nu one, then we have to compute d rho d nu one.

And if we compute d rho d nu one, we will get rho one, nu 1 and the all the other terms will be 0, because the other terms are not a function of the frequency nu , thus radiant energy density at a certain frequency. Let us say rho nu can be denoted by d rho d nu. And the unit of this radiant energy density at a particular frequency is the unit of rho that is Joules per meter cube divided by the unit of frequency that is the second inverse.

So, the unit becomes Joules second meter to the power - 3, we can think that there can be 2 kinds of transitions between 2 stationary states. For example, when E f is higher in energy than E i, the process is known as absorption. And when E f is lower in energy than E i, the process is known as a emission. But Einstein further divided the emission process into 2 types’ stimulated emission and spontaneous emission.

In stimulated emission light stimulates the emission process. That is we need light for this kind of emission to occur. On the other hand, for spontaneous emission, we do not need light That is atoms and molecules from a higher energy state can come down spontaneously to a lower energy state. Now, let us consider 2 states a ground state with energy E 1 and an excited state with energy E 2. And suppose initially there N1 molecules in the ground state and N2 molecules in the excited state.

So, if we consider the absorption process, Einstein proposed that the rate of excitation is proportional both 2 N1 and also rho nu, nu 12 but this nu 12 corresponds to the energy difference delta E between the 2 states the energy difference is given by h nu 12. The rate of transition from the ground to the excited state is given by minus dN 1 dt, or how the molecules in the ground state are changing over time.

The negative sign here indicates that N 1 is decreasing with time. So, we can write minus dN 1 dt equals some constant times rho nu nu 12 times N 1. Einstein name this constant, as B 12 the 12 subscript of the B coefficient refers to the transition from a state 1 to state 2. So, we can now write minus d N 1 dt equals B 12 rho nu nu 12 N 1. So, as this is an absorption process, B 12 is also known as Einstein's absorption coefficient. Now, let us consider the case of stimulated emission.

So, because there are N 2 number of molecules initial in the excited state and following the formalism of this absorption process, we can write minus d N 2 dt equals B 21rho nu nu 12 N 2 as both absorption and stimulated emission are stimulated by light. Einstein used a similar constant, which is B, but he wrote B 21 because now the transition is from 2 to 1. Now, if we look into spontaneous emission, for spontaneous emission light is not require, thus the rate of spontaneous emission should not depend on rho nu nu one.

Einstein proposed that first spontaneous emission, the rate equation can be written as minus d N 2 dt equals A 21 N 2, see now, he used a different constant A, as the spontaneous emission process is fundamentally different from the absorption and stimulated emission. So, while solving the Plank's blackbody radiation, Einstein argued that B 12 equals B 21 and thus this constant is generally known as Einsteins B coefficient. The other constant in the case of spontaneous emission is commonly known as Einsteins A coefficient.

The A and the B coefficients are related and it can be shown that A / B is given by this expression, which will come back later. Later on, it was seen that Einstein's assumptions of this absorption, stimulated emission and spontaneous emission processes can be justified using time dependent quantum mechanics. However, the elegance of Einstein's approaches that no quantum mechanics is required, except that the energy levels of the atoms are assumed to be quantized. So, now, we have come to the end of this lecture. So, we will end this lecture by solving a couple of problems.

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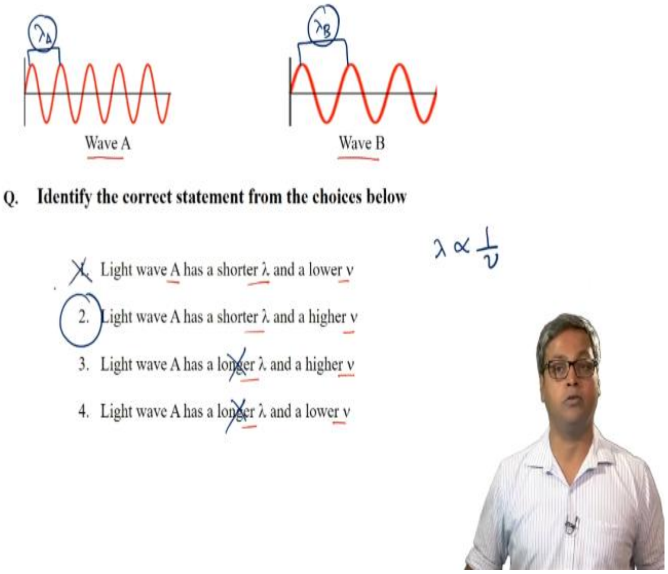

Q. **Identify the correct statement from the choices below**

$\lambda \propto \frac{1}{\nu}$

1. Light wave A has a shorter λ and a lower ν
2. Light wave A has a shorter λ and a higher ν
3. Light wave A has a longer λ and a higher ν
4. Light wave A has a longer λ and a lower ν

So, let us look into the first problem. So, we Have 2 waves, one is wave A and the other is wave B. And the question is, identify the correct statement from the choices below. What are the choices we have Light wave A has shorter lambda, lower frequency, shorter wavelength, higher frequency, longer wavelength, higher frequency, longer wavelength, lower frequency. So, one of these answers is correct. So, we can see that wavelength is defined if we can join the 2 maxima, constitutive maximum.

So, this is for lambda A, and for the wave B, this is lambda B. So, we can immediately see the wavelength of A is shorter than the wavelength of B. So, in that case, we can eliminate 3 and four. The second part is where the frequency is lower in case of A or higher in case of A. So, we know that wavelength is inversely proportional to frequency. So, if the wavelength is shorter than the frequency should be higher. In other words, the answer in this case will be option 2 and option 1 is not right.

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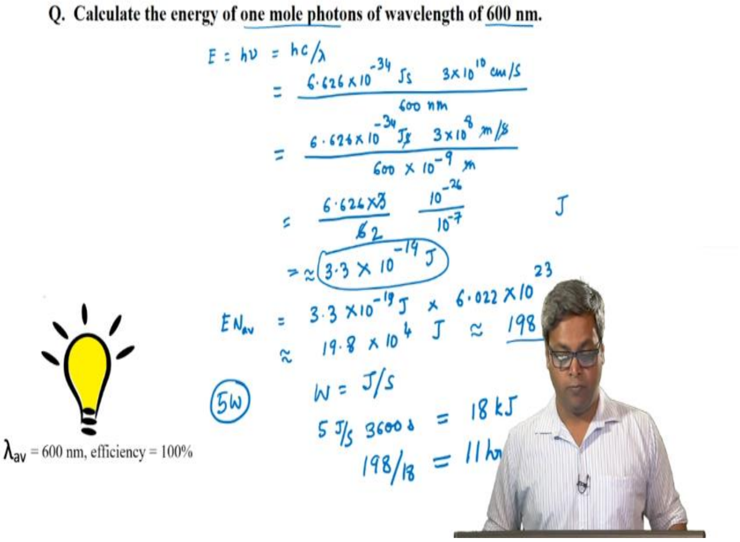

Q. Calculate the energy of one mole photons of wavelength of 600 nm.

$$E = h\nu = hc/\lambda$$

$$= \frac{6.626\times10^{-34}\ Js \quad 3\times10^{10}\ cm/s}{600\ nm}$$

$$= \frac{6.626\times10^{-34}\ J\cancel{s} \quad 3\times10^{8}\ \cancel{m}/\cancel{s}}{600\times10^{-9}\ \cancel{m}}$$

$$= \frac{6.626\times\cancel{3}}{\cancel{6}2} \quad \frac{10^{-26}}{10^{-7}} \quad J$$

$$\approx \boxed{3.3\times10^{-19}\ J}$$

$$EN_{av} = 3.3\times10^{-19}\ J \times 6.022\times10^{23}$$

$$\approx 19.8\times10^{4}\ J \approx 198$$

$$\boxed{5W}$$

$$W = J/s$$

$$5\ J/s\ 3600\ s = 18\ kJ$$

$$198/18 = 11\ h$$

λ_{av} = 600 nm, efficiency = 100%

So, the next question is calculate the energy of one mole of photons of wavelength 600 nanometer. So, how to solve this, we know E = h nu = hc / lambda. So, we can put in the values h is 6.626 times 10 to the power -34 Joules seconds, c is 3 times 10 to the power 10 centimeter per second and lambda is 600 nanometer, now if we put all the units to SI unit we still have 6.626 into 10 to the power -34 Joules seconds, but the speed of light in SI unit becomes 3 times 10 to the power 8 meter per second.

And the wavelength becomes 600 into 10 to the power - 9 meter. So we can see this meter and meter will cancel out this second part second cancels out, so the final unit will be in Joules. So, we 6.626 times 3 by 6 and on top we have 10 to the power - 26 below we have 10 to the power - 7. So what we get here, we get we can cancel 6 approximately what we get 3.3 into 10 to the power - 19 Joules, but this energy that we get is the energy of the one photon. Now, we have been asked to calculate the energy of one mole of photons.

So we have to multiply our answer with Avogadro number or for one mole of photons, the energy is E times N Avogadro that is 3.3 times 10 to the power -19 joules for one photon and we multiply with Avogadro number is 6.022 10 to the power 23. If we actually do this multiplication will end up with something around 19.8 times 10 to the power 4Joules, which we can write us 198 kilo Joules. So the energy of one mole of photon of wavelength 600 nanometers is around 198 kilo Joules.

So what does it mean? Let us say we have an LED bulb when the average wavelength of light emitted from the bulb is 600 nanometers. And let us say the efficiency of this bulb is 100 % that means, it is converting the electrical energy into light and that conversion is 100 %. Now if the energy of one mole of photon at 600 nanometer is 198 kilo Joule and if the power of the bulb let us say is 5 watts, then we can see how long does it take for this bulb to create one mole of photons? So watt is joules per second.

So let us say how much photons are created in 1 hour, in 1 hour, there are 3600 seconds, and the power of the bulb is 5 joules per second. So if we multiply that, what we get is we get 18 kilo Joules of energy is being created in 1 hour. So, it will take approximately 198 by 18. That is approximately 11 hours for the bulb to create one mole of photons when the output is at 600 nanometer