Atomic and Molecular Absorption Spectrometry for Pollution Monitoring

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Lecture – 05
Interaction of EM radiation with matter I

Greetings again, we meet once again to continue our discussion on the molecular absorption spectrometry for pollution control monitoring. In the last class we had discussed about the atomic structure and we had stop that the periodic table which I had shown you it is in front of you.

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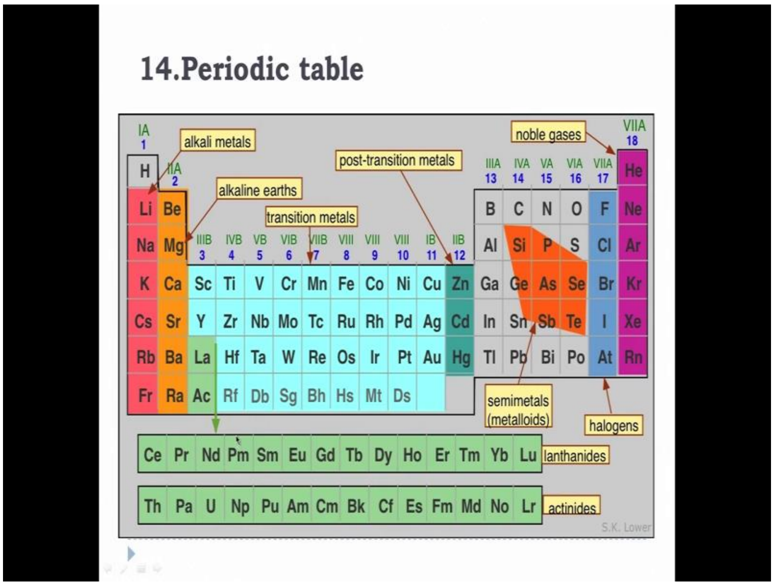

Now, depending upon the quantum numbers an periodic table atomic arrangement of electrons and nucleus around each other and then depending upon the atomic weight we had discussed that the periodic table has been constructed and the current periodic table that is invoke is essentially in front of you that is at the left side in the red, we have the lithium sodium potassium cesium rubidium francium these are the alkali metals.

In the next line beryllium magnesium etcetera strontium calcium etcetera these are the alkaline earth metals. Then we have transition metals in the green and then boron here on the right side on the corner we have the that is in the pink we have helium neon argon these are the inert gases and then fluoride chloride or bromide iodide and astatine these are the anions basically. And then halides known as generally known as halides, and here in the red on the right side you have the metalloids they behave partly as metals and partly as non metals, and then we have the lanthanides at the bottom here and here in the green colour the last bottom colour is actinides.

So, most of the elements what we know on this earth have been represented here in this periodic table and the spectroscopic techniques what we are going to discuss we will apply to most of these elements except the last line that is actinides because many of them are radioactive, but otherwise most of the spectrophotometric methods what we are going to discuss there are hundreds and thousands of methods for the determination of these metals using spectrophotometry which you are going to study in detail.

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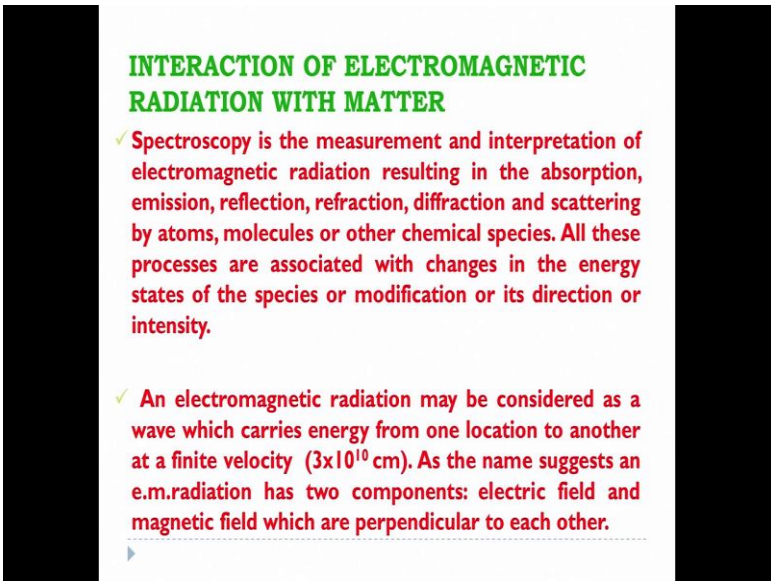

So, in the next this thing let us, next slide I am going to show you the interaction of electromagnetic radiation with matter, what we mean by matter? In this case is the material made up of atoms or elements, that we know in the periodic table.

So, how do we use the spectrophotometry or spectroscopy for the measurement of these elements? So, the science is known as spectroscopy that is the measurement and interpretation of electromagnetic radiation resulting in the absorption or emission or reflection or refraction, diffraction, scattering by atoms, molecules and other chemical species all these processes are associated with the changes in the energy states of the species or modifications or its direction or intensity. Therefore, basically what we may do measurement and spectroscopy is the measurement and interpretation of the change of properties of the electromagnetic radiation when it interacts with the matter.

So, what is an electromagnetic radiation? We can consider electromagnetic radiation as a simple wave which carries energy from one location to another at a finite velocity that is basically we are talking about something like visible light or a green light or a red light or a yellow light and all these things are bundles of energy whenever you see a light in any form, human eye sees any form it sees an electromagnetic radiation. And yellow colour, blue colour, red colour, violet colour, all these are basically electromagnetic radiation, part of the electromagnetic radiation and there are many other radiations which we do not see also. But the essentiality of the situation is that an electromagnetic radiation is a bundle of energy that is being transported from one point to another at a finite velocity of the light, the velocity of light is 3 into 10 raise to 10 centimeter per second.

So, as the name suggest electromagnetic radiation has two components to it one is electro part another is magnetic part. So, every electromagnetic radiation consist of two fields one is electric field another is magnetic fields which are perpendicular to each other. So, if I have a radiation coming in one direction like this I have a electrical field going off like this and then a magnetic field going of like this. So, it is very simple and direction of the light will be perpendicular to each other; that means, there are basically three access - one is the electrical field access another is a magnetic field access another is the a direction in which the light is proceeding.

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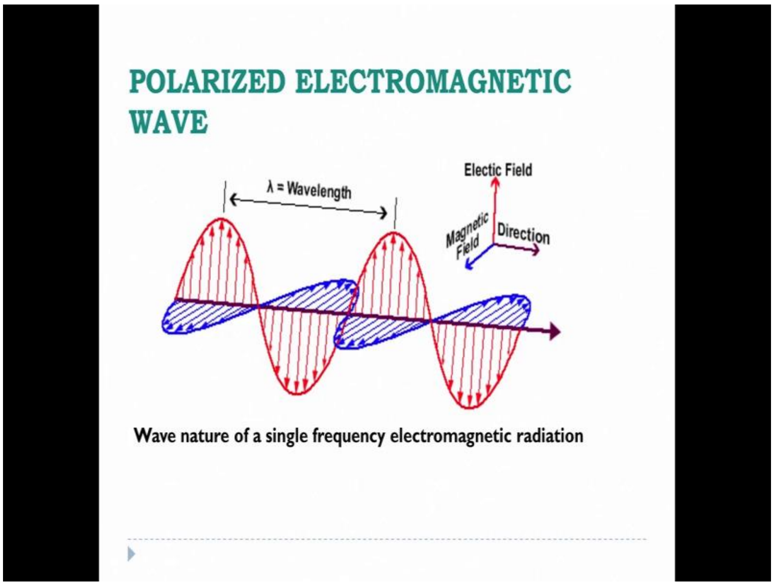

So, this is how we see and electromagnetic radiation you see the black line here is how the radiation is moving; that means, if a light is coming from a light bulb or something like that the direction of the light is represented by this and what is not represented is an simple, as a waveform associated with this black radiation this is the electrical area in which the electrical field is operating perpendicular to the moment of the this thing. This maybe next if the black radiation is in the x axis, this could be y axis and the blue one which is again perpendicular to both is the magnetic field.

So, here I have shown the direction of the light, light is proceeding like this, electric field is like this and then magnetic field will be like this. So, every electromagnetic radiation we associate with this kind of radiations.

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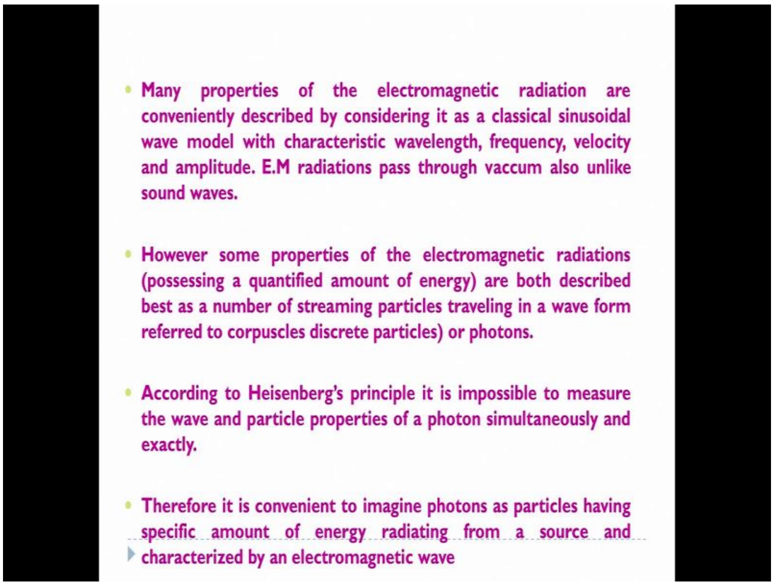

So, many properties of the electromagnetic radiations are conveniently described by, describing it as a classical sinusoidal wave model with characteristic, wavelength, frequency, velocity and amplitude. If you look at it like this, look at the red one go back to this here it is a waveform and associated with a minimum distance from here to here and then here to here, here to here like this and then it has an amplitude maximum amplitude is this and minimum is 0 and then we it goes to negative side and then again it comes on the positive side like that. So, EFM radiation passes through vacuum also unlike sound waves, sound waves you cannot hear them across a vacuum whereas, electromagnetic radiation pass through the vacuum also.

Some properties of electromagnetic radiations are both described best as a number of streaming particles travelling in a waveform referred to corpuscles are discrete particles or photons. Now go we go back to the previous one here I am assuming that the arrow represents a bundle of energy a particle. So, once this particle moves from one side to another particle will be coming in front of your vision. So, it is a number of streaming particles which will keep on passing in front of you when you see a radiation in front of you. So, these are known as corpuscles. But you can also see that the radiation is also in the form of waves here I have shown in the figure the blue and red one it is in the form of wave only. So, the arrow represents a particle that is a corpuscle and the waveform associated with each particle is the electric and magnetic field.

So, it is impossible to determine the wave side, wave particle and wave and particle properties of a photon simultaneously and exactly. At the same time that is we go back here is the particle size, but I can I can only determine its position, but not the velocity and vice versa this is known as Heisenberg principle, very well known principal and it represents the properties of a photon. Therefore, normally what happens is it is convenient to imagine photon as particles having specific amount of energy that is radiating from a source and characterized by an electromagnetic wave. So, this is how we should imagine a bundle of electromagnetic radiation.

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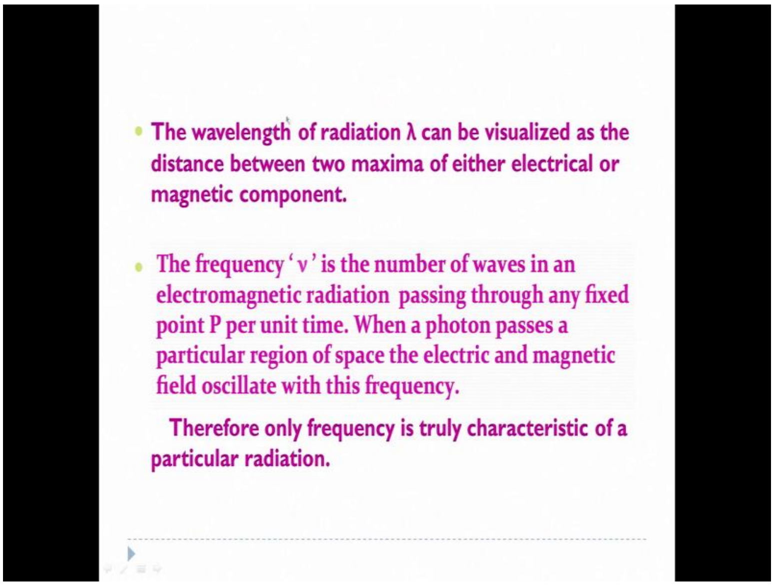

So, the wavelength of radiation lambda can be visualized as the distance between two maxima which I have shown you in the earlier figure - one is electrical component and another is magnetic component.

The frequency is the number of ways that pass any fixed point v per unit time. So, when a photon passes a particular region of space both the electronic and magnetic fields vibrate with each other just like this. So, only frequency therefore, only the frequency is truly characteristic of a particular radiation.

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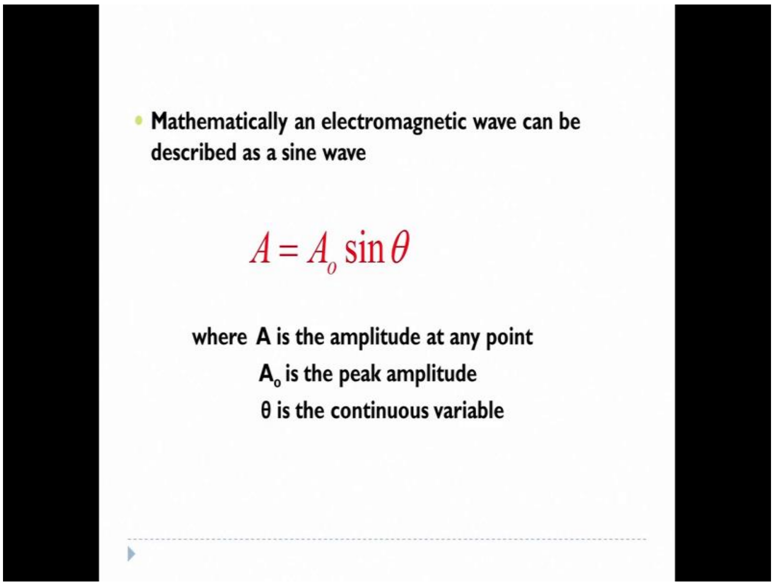

So, how do we normally represent a wave, it is the frequency. If I tell you the frequency of a substance; that means, a wave form is defined, now you should understand that mathematically what do you want to say is an electromagnetic wave I can describe it as a sin wave. You go back this is the red one which I have shown is the plot of a sine wave, similarly the blue one is also a plot of the sin wave.

So, any electromagnetic radiation would be represented by a is equal to a 0 into sin theta where a is the amplitude at any point and a 0 is peak amplitude and theta is the continuous variable. This equation represents an electromagnetic wave radiation completely and mathematically also.

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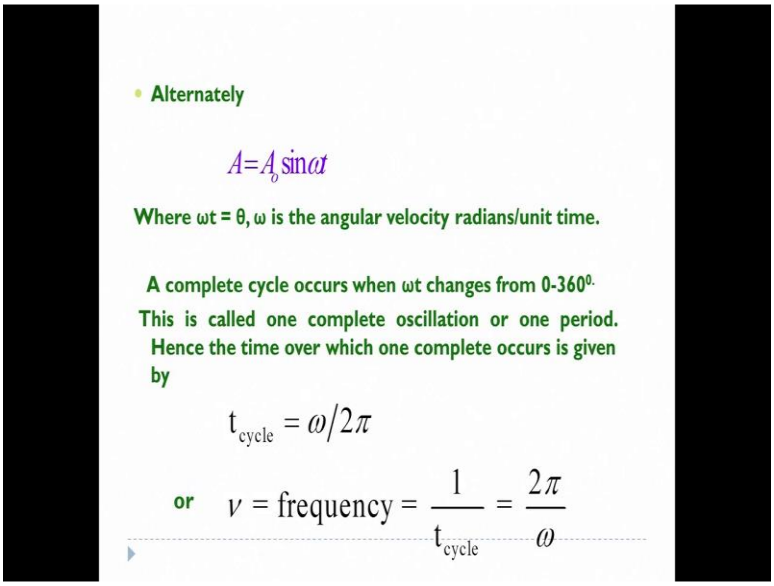

What it means is the amplitude a is equal to a 0 into sin omega t where omega t is essentially represent theta, that is the angular velocity measured in radians per unit time. What is a radium? Radium is the solid angle around a particular point. So, if you choose any point the solid angle around it would be exactly three 360 degrees. So, 360 radians make one full circle around you, sphere, and 1 by 360 is 1 degree have that is one radian.

So, a complete cycle wave, a wave completes a cycle that is from maximum going from 0 to maximum coming back to 0 and then going to negative and again coming up. So, one full crust and one full cleft both these represent a waveform. So, a complete cycle that is what we mean and that is known as frequency. So, that cycle is described by w by 2 pi, 1 pi is 360 radians and nu is the frequency, frequency is given by 1 over t by cycle that is 2 pi by w. What is w? w is the angular velocity radians per unit time. So, far any wave moving at a constant velocity v we can write where v is the frequency in milliseconds and that is hc by lambda and h is Planck’s constant 6.62 into 10 raise to minus 27 ergs and E is expressed as ergs and 6.63 into 10 raise to minus 34 Joules.

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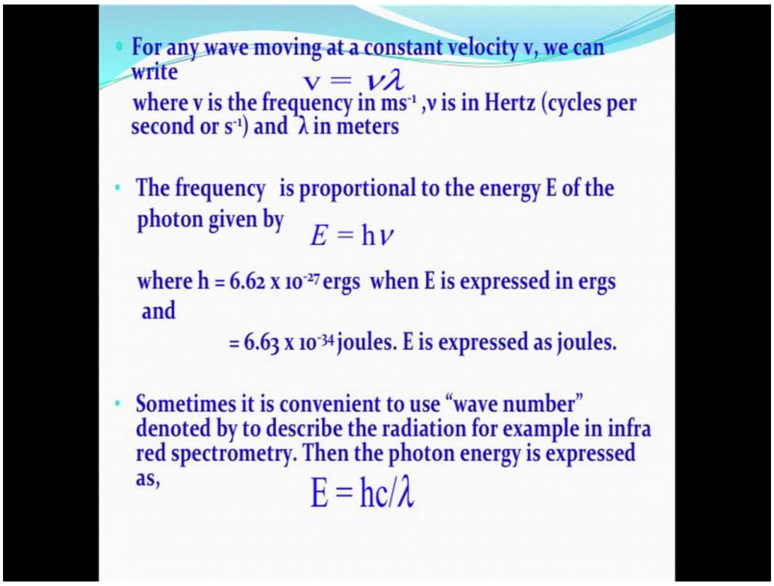

So, E is normally expressed as joules sometimes it is convenient to use wave number that is nu bar and all these symbols I am explaining to you in the form of a table now.

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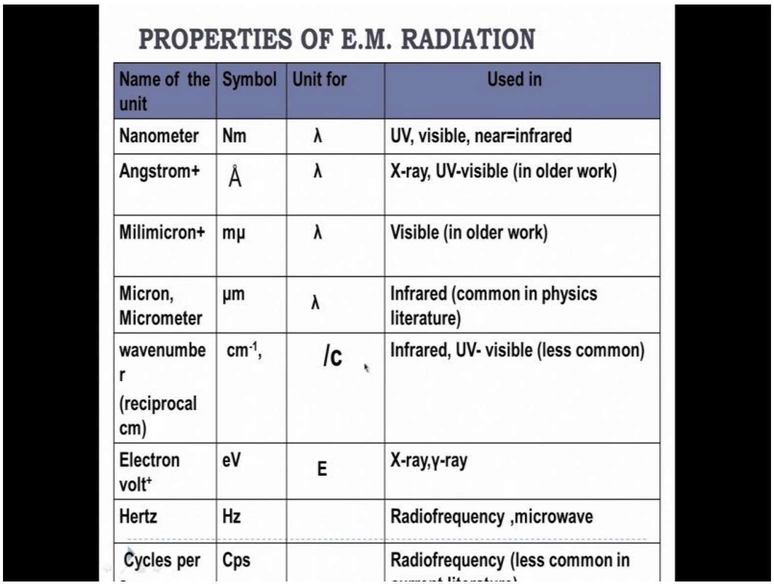

PROPERTIES OF E.M. RADIATION

Name of the unit	Symbol	Unit for	Used in
Nanometer	Nm	λ	UV, visible, near=infrared
Angstrom+	Å	λ	X-ray, UV-visible (in older work)
Milimicron+	mµ	λ	Visible (in older work)
Micron, Micrometer	µm	λ	Infrared (common in physics literature)
wavenumber (reciprocal cm)	cm^{-1},	/c	Infrared, UV- visible (less common)
Electron volt+	eV	E	X-ray,γ-ray
Hertz	Hz		Radiofrequency ,microwave
Cycles per	Cps		Radiofrequency (less common in

So, on the left side I have the distance and then units and symbols and where it is used, so here I have on the left side nanometer the symbol is nm, it is the unit is lambda, represented as lambda its used in UV visible near infrared, then I have angstrom units and it is also measure of wavelength then I have millimicron that is also wavelength. Micron and millimeter is again length of this thing, but it is more useful in infrared; that means, whenever we represent infrared radiation, we talk of infrared radiation we say the wavelength is in microns or micrometers.

So, similarly wave number we use in infrared also and UV visible, but in UV visible it is very less not so common. Then whenever we represent an electromagnetic radiation we see the say the energy of the radiation is in electron volts, but this will be very very weak in visible radiation, but in x-ray and gamma rays the energy of the electrons in a electrons and particles are described as electron volts. And then for radio frequency and micro wave frequencies we described the electromagnetic radiation in terms of hertz. If you listen to fm radio or something like that you would say you would hear quite often that you are listening to Mirchi wave, Radio Mirchi at 97.1 hertz kilo hertz etcetera they are the units which where the things are represented. And then cycles per second is also essentially the same, but that is in the radio frequency range nowadays its rarely used CPS.

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Interconversion of Energy and Wavelength

	nm	Å	cm^{-1}	eV	MHz	J*
nm		10	10^7	1.240×10^3	2.9979×10^{11}	1.986×10^{-16}
Å	.1		10^8	1.240×10^4	2.9979×10^{12}	1.986×10^{-15}
cm^{-1}	10^7	10^8		1.240×10^{-4}	2.9979×10^4	1.986×10^{-23}
eV	1.240×10^3	1.240×10^4	8.0655×10^3		2.418×10^8	1.602×10^{-19}
MHz	2.9979×10^{11}	2.9979×10^{12}	3.3356×10^{-5}	4.1355×10^{-9}		6.626×10^{-28}
J	1.986×10^{-16}	1.986×10^{-15}	5.034×10^{22}	6.241×10^{18}	1.509×10^{27}	
Spectrometric region	UV-vis	X-ray UV	Infrared	X-ray γ	Radiofrequency (NMR)	

*4.184 J = 1 cal

And this is essentially the interaction of the table the same table which I had described earlier and how they can be converted into each other units.

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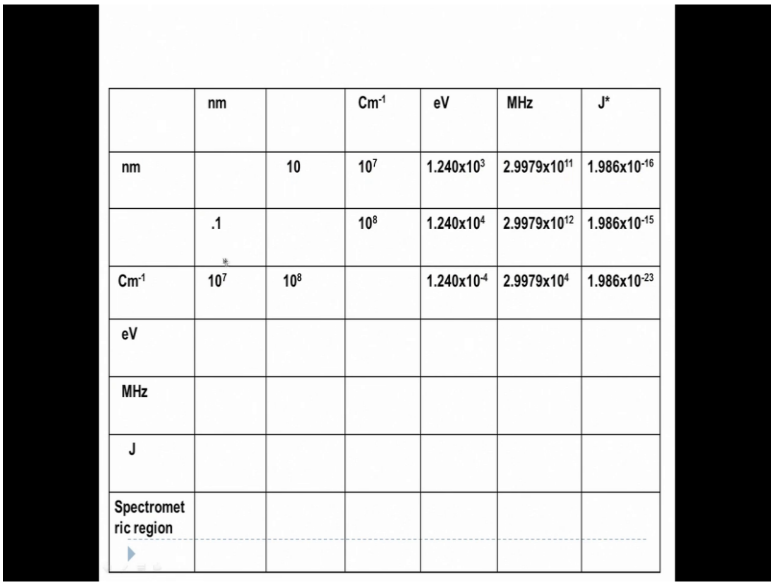

	nm		Cm^{-1}	eV	MHz	J*
nm		10	10^7	1.240×10^3	2.9979×10^{11}	1.986×10^{-16}
	.1		10^8	1.240×10^4	2.9979×10^{12}	1.986×10^{-15}
Cm^{-1}	10^7	10^8		1.240×10^{-4}	2.9979×10^4	1.986×10^{-23}
eV						
MHz						
J						
Spectrometric region						

So, it is essentially I have reproduce this here it is nanometer centimeter inverse and if you want to convert nanometers into centimeters inverse it will be 10 raise to 7 and then so many nanometers would also convert itself into 1.240 these are mainly used for inter conversion of radiation energy and vice versa. If I know the electron volt I can convert it into what is the wavelength etcetera and other units of energy.

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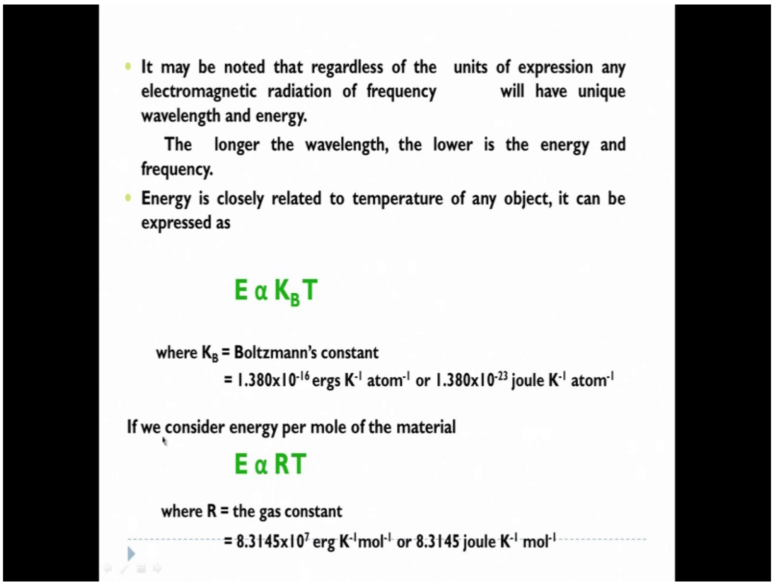

So, what we should do now is we note that regardless of the units of rate expression of any electromagnetic radiation of frequency it will have units of wavelength and energy.

So, the longer the wavelength lower is the energy and frequency. So, if the wavelength electromagnetic radiation is shorter the wavelength will be short frequency will be high energy also will be very high. So, the energy can be represented by this equation that is E is proportional to K B into T where T is the temperature, K B is the Boltzmann's constant and Boltzmann's constant is 1.380 into 10 raise to 16 minus 16 ergs per the degree Kelvin per atom or 1.380 into 10 raise to minus 23 joules per degree per atom.

So, if we consider energy per mole of the substance because nobody consider the energy of a material per atom it is rarely considered what we consider per mol that is what is a mole? A mole is a quantity containing 6.23 into 10 raise to 23 number of atoms. So, if I use that concept the energy per mole if we consider that aspect I can describe energy is proportional to R into T where R is the gas constant given by 8.3145 into 10 raise to 7 ergs per degree per mole or I can increase it to reduce it in terms of joules that is 8.3145 Joules per degree per mole. So, this is the relationship between the energy of an electromagnetic radiation when it interacts with one mole of the substance.

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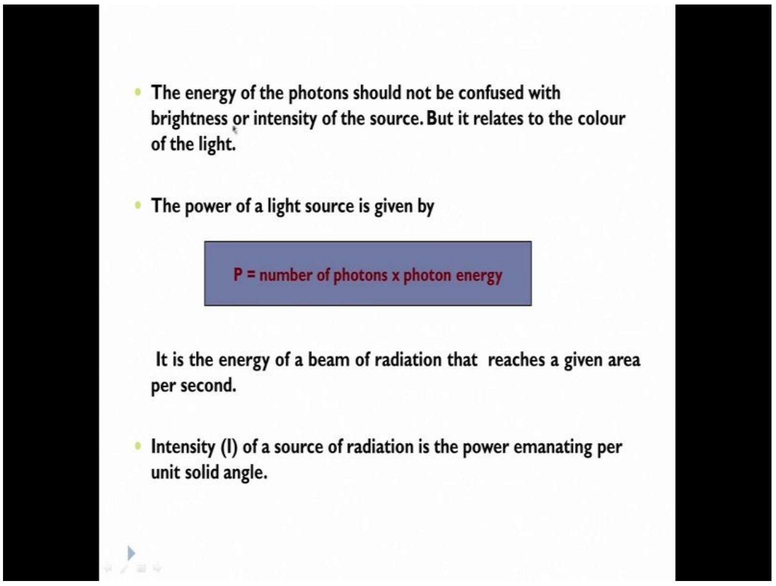

So, the energy of the photons should not be confused with the brightness or intensity of the source. So, this is very important for sometime quite often people confuse energy of the photons with the energy, if the energy is very high it is must be very bright energy, no, it is wrong and energy of the photon is very high means intensity of light should be very intense that is also wrong. So, what we mean is it has something to only to do with the frequency if the energy is very high frequency is very high, if the energy is very low frequency is very low. So, it has nothing to do with the intensity of the power and the power of a light source is given by the (Refer Time: 20:48). So, it is the energy of a beam of radiation that reaches a given area and this given area it has to reach per second. So, intensity I of a source of a radiation is the power emanating per solid angle, per unit solid angle that is the intensity.

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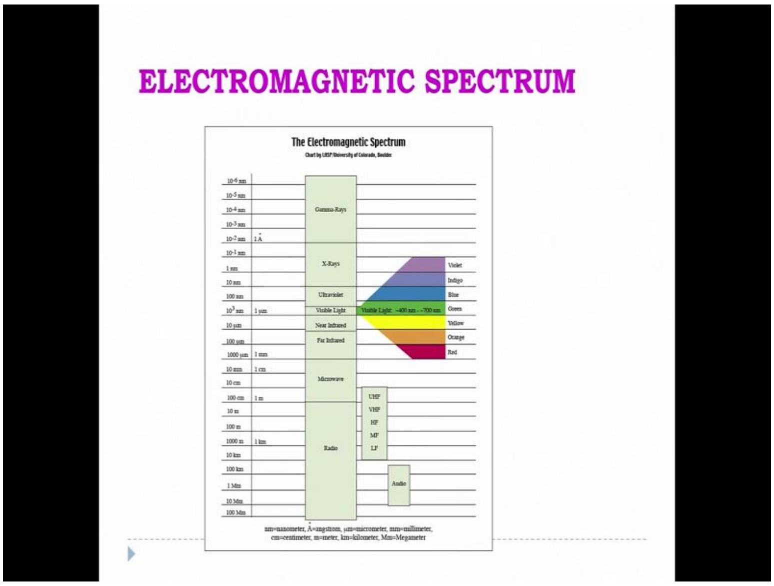

So, a visible light containing UV ultraviolet radiation may have may not be visible to at all, but if it is a blue radiation it will be visible. So, for example, now you are looking at the electromagnetic radiation this I have shown your earlier also this figure and it is the energy in terms of frequency here on the left side and then in terms of the same thing described here in terms of units and that is a length distance and these are the rays in which they are commonly known that is radiation up to 1 angstrom is known as gamma rays up to 10 angstrom is known as x-rays here. Then up to 100 nanometer is ultraviolet and then visible near infrared far infrared microwave radio waves at the bottom here. So, the radio waves at the bottom and here we can see that all these violet, indigo, blue, green, yellow, orange, red are small, a very small portion of the visible light which is at the center.

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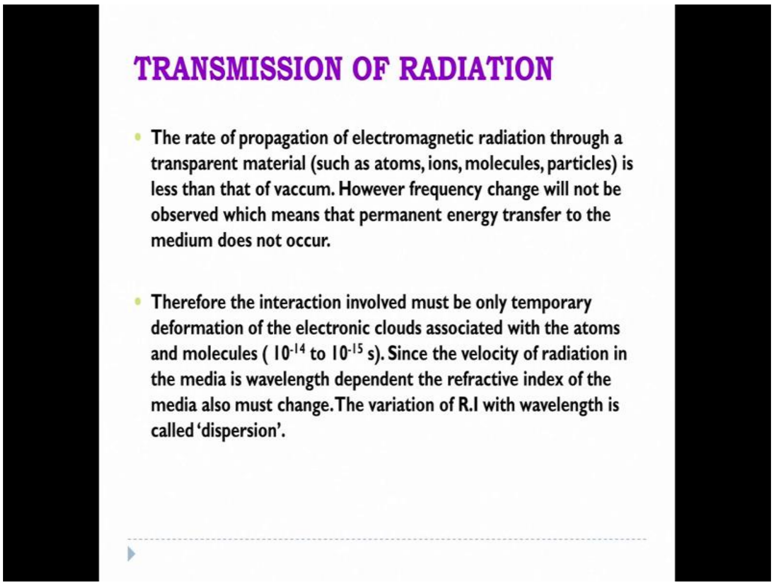

So, in an electromagnetic spectrum there is more to the eye than what eye sees and this electromagnetic radiation is what we are going to discuss now. So, what are the properties of the radiation? Because the whenever we talk of spectroscopy we always talk of interaction of matter with radiation. So, what does radiation do when it passes through, when it passes through a sort of through a given medium it may transmit, it may absorb, it may scatter, it may reflect, it may refract and it may diffract several other possibilities are always there whenever I take a an bundle of electromagnetic energy put it passes through a given material collect the radiation at the back.

So, the radiation what I collect will be entirely different from what is coming inside because of transmission, absorption, scattering, reflection, refraction, diffraction and many other possibilities. So, the rate of propagation of an electromagnetic radiation through a transparent material, the transparent material could be anything it can be atoms, it can be molecules, it can be particles, it can be a gas. So, in all these cases it may be a vacuum also sometimes so however, the frequency change the change in the characteristic of the radiation that is passing through that changed will not be observed which means that there is no permanent energy transfer; that means so long as you are radiation is passing through a given medium the moment will take out the medium the electromagnetic radiation reverse back to its original properties. So, there is absolutely no permanent energy transferred to the medium this does not happen. So, long as the material is there in the path it will undergo all these changes, but it will not be carried away or there will not be any memory effect once you remove the matter from the back, matter from the path of the electromagnetic radiation.

So, the interaction involved must be only basically temporary, what is temporary? It is the temporary deformation of the electronic cloud that is associated with the atoms and molecules, I have already explain to you that the electronic cloud around an atom or around a magnet around a molecule is a transient possibility of a position of the electron around the atom and this is a like a balloon. So, depending upon the pressure, depending upon the molecule the balloon maybe like this like this etcetera it may be deformed the moment and electromagnetic radiation it may expand or it may contract it may interact and then the moment you take out again it goes back to its original form.

So, the interaction involved is only a temporary the deformation of the electronic cloud associated with the atoms and molecules since the velocity of the radiation is dependent upon the refractive index of the media also that also must change. So, whenever the material is electromagnetic radiation is passing through a material, if the material is having some refractive index it will change.

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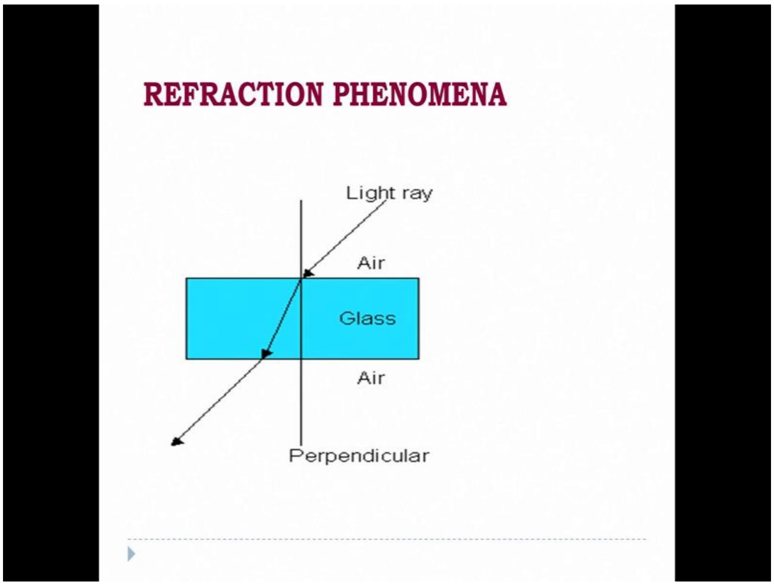

So, the variation of refractive index with wavelength is called as dispersion. You can see the next figure what I mean. Here this is known as refraction. So, what is happening the electromagnetic radiation is passing through light radiation, here I have a glass or something like that it passes through, it does not pass through the same way as if it is a straight line, but it changes its path and goes back.

So, this is only a temporary phenomena. As I have been explaining to the moment I remove this glass material this material it goes off, it cannot it will become straight line again as if there is nothing there. So, the transmission is always like this with radiation refractive index it affects the transmission and then dispersion is a complex phenomena.

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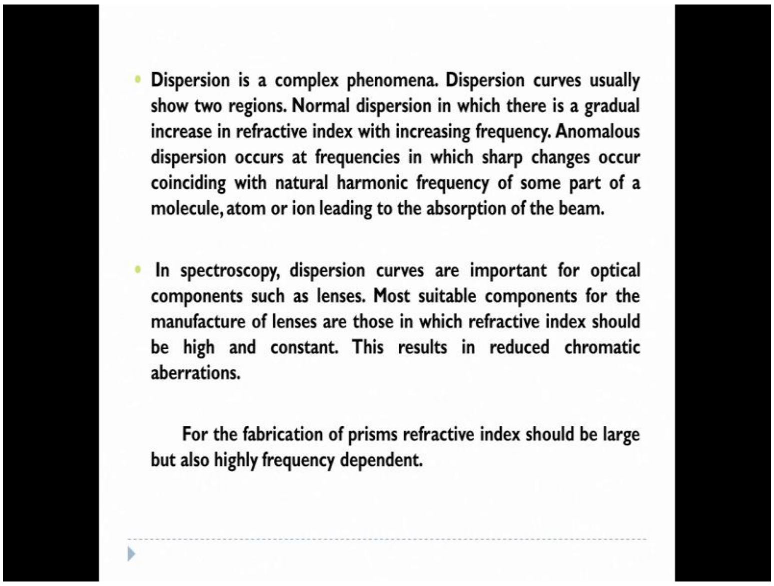

Normally the dispersion curves usually show two reasons one is normal dispersion in which there is a gradual increase in the refractive index with increasing frequency, anomalous dispersion occurs at frequencies in which sharp changes occur coinciding with the natural harmonic frequency of the some part of a molecule or an atom or an ion leading to the absorption of the beam.

So, in spectroscopy dispersion curves are more important because in spectroscopy what we use is we use glass we use prisms, we use concave mirror, we use air we use sample etcetera. So, the dispersion curves through a medium become assume importance and they are more so for lenses. So, what are lenses? Lenses or something which it in which a electromagnetic radiation if you pass it through a lens it will give a parallel beam or a concentrated been. So, whenever we want to measure atomic, molecular atomic molecular spectrum what we need is a parallel beam of radiation, it is not a jumble of radiation which are crust crossing each other, what I want is three parallel rays - 10 parallel rays, 100 parallel rays, they should not be interacting with each other. So, the lenses are most important part of all spectroscopic instruments.