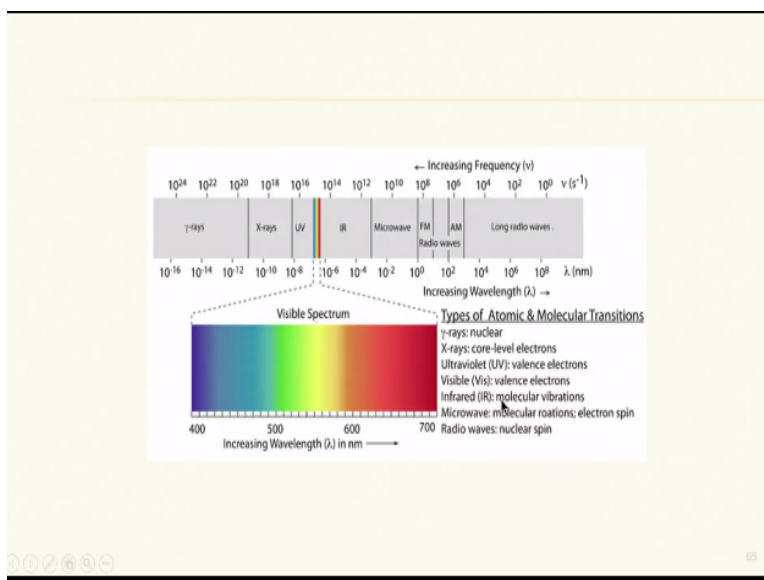


Infrared Spectroscopy for Pollution Monitoring
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Lecture-09
Interaction of electromagnetic radiation with matter–II

Greetings to you, we are going to continue our discussion on the infrared spectroscopy and we were discussing the electromagnetic radiation that is the interaction of electromagnetic radiation with matter. I had shown you the spectrum of the electromagnetic radiation that it contained gamma rays, cosmic rays, X-rays, ultraviolet rays and then soft X-rays, UV visible IR, near infrared, infrared, microwave, far infrared and all those things I had shown you this slide in my last class.

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Look at this slide now, so what I had told you was this is the whole spectrum it has frequency range from 10^{24} to several kilo 10^0 several frequencies 10^0 and then it has a wavelength that is range from 10^{-16} to several kilometers of the amplitude. And I had shown you that the visible spectrum is a very small portion of the total spectrum which we perceive personally as human beings and I had explain to you about this earlier okay.

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Table 3.1

Wavelength (nm)	Transmitted color	Complementary hues
< 380	ultraviolet	—
380 – 435	violet	Yellowish green
435 – 480	Blue	Yellow
480 – 490	Greenish blue	Orange
490 – 500	Bluish green	Red
500 – 560	Green	Purple
560 – 580	Yellowish green	Violet
580 – 595	Yellow	Blue
590 – 625	Orange	Greenish blue
625 – 780	Red	Bluish green
> 780	Near IR	Red

Then I had explained to you that the visible range can further be divided into several areas and the transmitted color and complementary views I had explained that transmitted color is what comes out and complementary hue is what the material looks to you as an observer. That is it retains all the other reds or to colors okay.

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It must be noted that there are no sharp differences in colour at any wavelength but rather they merge into one another in a diffused manner like a rainbow. The absorption of radiation involves transfer of energy to the medium and this process is a specific phenomenon related to the characteristic molecular structure. For a given excitation process a molecule absorbs a discrete quantity of an absorption line. However since a group of molecules exist in a number of vibrational and rotational energy states each differing by a small amount of energy a series of absorption lines appear over a small range and give rise to an absorption peak or band.

So, we noted that there are no sharp differences in the color at any wavelength etc. etc., and then we I had explain to you how we get an absorption peak if we use a molecule for the interaction of electromagnetic radiation which will end up interaction transitions of the electrons from electronic vibrational and rotational energy levels. And I had also explained to you how we get a peak instead of a single sharp line especially in the UV visible and IR regions okay.

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Monoatomic substances normally exist in gaseous state and absorb radiation only through an increase in their electronic energy. These are quantized and appear in various sub shells as shown in Fig 3.2.

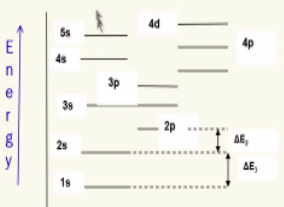


Fig 3.2. Energy level diagram

And then I had explain to you that monoatomic substances normally exist and gaseous state and absorbed radiation only through an increase in the electronic energy. There are no vibrational or rotational energy levels in monoatomic substances. These electronic energy levels are also quantized and appear in various sub shells I had shown you this figure and these figures are arranged according to their increasing energy that is 1s, 2s, 2p, 3s, 3p and then 4s, 3d, 4s etc., etc., and these are the electronic energy levels.

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For polyatomic molecules electronic transitions involve molecular orbital requiring energy in the ultra violet region. These are far more complex involving vibrational and rotational energy levels. Thus the total energy may be considered as a sum of contributions from all states of energy.

For each electronic energy state of the molecule there exist several possible vibrational states and for each of these in terms numerous rotational energy states.

Subsequently we had discussed about the polyatomic molecules where electronic transitions involve molecular orbital changes. The requiring energy in the ultraviolet region and visible

region etc. and these are far more complex because they involve vibrational and rotational energy levels also. So, the total energy maybe considered as a sum of the contributions of all the energy all the states of energy of a molecule whenever it is exposed to electromagnetic radiations.

So, for each electronic state of the molecule there exist several possible vibrational state and for each vibrational state there exist several rotational energy levels, I had explain to you giving you a analogy of kicking a football on the staircase to land on the first floor, second floor etc. and that is the best analogy available as of now. So, the electronic transitions in organic molecules are also characterized by the promotion of the electrons from the bonding and non bonding molecular orbitals to excited energy state.

That is the excitation is always into anti bonding orbitals okay from the bonding orbitals, so the bonding orbitals are designated as sigma and Pi orbitals. Then there are other electrons in a molecule where the electrons are not bound but they are free. They are known as non bonding it is electrons and they occupy certain energy level in the molecular bounding hierarchy. So, these non bonding electrons are quite often found in compounds containing oxygen, nitrogen fluorine , sulphur etc.

So, many molecules contain these compounds these elements and you can see that aldehydes, ketones you know they all contain oxygen water contains oxygen, ammonia contains nitrogen amongst contain nitrogen. All these every element oxygen, nitrogen, sulphur or halogens are other anions would be having these non bonding electrons. So, especially when such molecules are subjected to electronic excitation.

These electrons also get affected. They absorb energy and go to the higher energy states described by anti bonding orbitals. So, the generalized shapes of the orbitals also I had shown you in my last class.

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In the excited state some if not all the electrons occupy antibonding orbitals. Even in the antibonding orbitals the molecule retains sufficient bonding character to ensure the stability otherwise dissociation would occur. The electronic transitions possible in ultraviolet and visible spectrum are $\sigma \rightarrow \sigma^*$, $\sigma \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$. The energy required for these transitions decreases in the same order as shown below

Saturated hydrocarbons
Alcohols, Chlorides and iodides
Saturated aldehydes & ketones

And then I had shown you that the stability or dissociation occurs stability gets affected dissociation occurs. If I submit the electrons to very high energy levels that would require crossing the anti-bonding energy levels also. So, the electronic transitions possible in ultraviolet regions we had defined a sigma to sigma*, sigma to Pi* and Pi to Pi*. So, for every bonding there is sigma* and Pi star that for n electrons that is compounds containing oxygen, nitrogen, sulphur etc.

There are no anti bonding n orbitals only sigma* and Pi*, so n to if the excite the electrons in the nonbonded electrons like oxygen, nitrogen etc., those electrons where they will they end up. They end up either from n to sigma* same existing levels or n to Pi*, so both these possibilities are there but there are no n to n* anti bonding orbitals. So, what happens basically we are talking about sigma to sigma* and then Pi to Pi*, n to sigma* and n to Pi*.

So, 4 excitations especially in the bonding and anti bonding orbitals, so suppose I have only sigma bonds all compounds are saturated hydrocarbons. There are no Pi bonds okay, so only single bonds between each atom it whether it is carbon-carbon or carbon nitrogen, carbon that is it basically hydrocarbons means compounds containing only carbon and hydrogen, so there are only single bonds in a set of series.

Then I can expect only sigma to sigma* transitions because there are no pi electrons and Pi* energy maybe there. But it is not defined because they are all containing only sigma bonding similarly alcohols contain oxygen and sometimes they if you look at the structure of aldehydes or ketones I have Pi bonds acetic acid or any carboxylic acids I have got a functional group of C double bond O and OH, that is the functional group.

So, COOH is a compound having a Pi bond and non bonding electrons also, similarly CHO aldehyde, ketones and many other compounds. So, that the transitions energy required for the transitions from sigma to sigma* would be much more than they are in the from Pi to Pi* or n to Pi*, n to sigma* also the energy will be require. So, the highest energy level would be for sigma to sigma*.

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The electronic excited energy levels involve large amounts of energy ranging from 35.71 k cal in the visible to regions several hundreds in the far UV. Each electronic levels associated with several vibrational modes but maximum population is at $v=0$ level. Consequently the absorption arising out of this transition will be most intense. This tendency is enhanced in the liquid state where the vibrations are further dampened by intermolecular inter actions. Thus a broad absorption band results.

The σ to σ^* transitions are very energetic and are found only below 200nm i.e in the vacuum ultraviolet region.

So, the electronic excitation energy levels involve large amount of energy ranging from 35.71 kilo calories in the visible region to several 100 kilo calories in the far ultraviolet region. So, each electronic level associated with vibrational modes but maximum population would be at $\mu=0$ that is vibrational energy level 0 and consequently absorption arising out of $v=0$ would be having maximum population of the electrons okay.

So, whenever I have a molecule a group of molecules present in the ground state level maximum population of the electrons would be at $v=0$. And such energy transitions starting from $v=0$ to

$v=1$ next to etc. energy levels. They would be maximum also, so the intensity of the absorption peak would be maximum starting from $v=0$ to next higher energy level. But it does not mean that there are no other vibrational energy levels where electrons are not populated.

They also occur to some extent, so what happens is in the end we see a sort of broad absorption instead of a sharp absorption peak. So, I had explain to you look at the slide now, the sigma to sigma* transitions are basically very energetic this I had explain to you because you need several kilo calories from 35 kilo calories to several 100 kilo calories for excitation from sigma to sigma star, so they are called as very energetic excitation states.

They are found only below 200 nano if more energy id required then the absorption peak would be appearing only at very low wavelength. That means that is how the whole system of electromagnetic radiation works higher the wavelength, low is the energy, lower the wavelength high is the energy. So, because sigma to sigma star transitions are very high energy levels, the excitation absorption peaks should appear at low wavelength range okay.

And higher frequency range also, both mean the same, so spectroscopy is basically the measurement and interpretation of electromagnetic radiation passing through the system containing molecules etc. molecules water, solvents whatever are the other things that contain in the and that are contain in the matrix. So absorption, emission, reflection, refraction everything will occur when electromagnetic radiation is interacting with the molecules or chemical species. So, all these processes are associated with energy changes.

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Spectroscopy is the measurement and interpretation of electromagnetic radiation resulting in the absorption, emission, reflection, refraction, diffraction and scattering by atoms, molecules or other chemical species. All these processes are associated with changes in the energy states of the species or modification of its direction or intensity.

An electromagnetic radiation may be considered as a wave which carries energy from one location to another at a finite velocity (3×10^{10} cm). As the name suggests an e. m. radiation has two components: electric field and magnetic field which are perpendicular to each other.

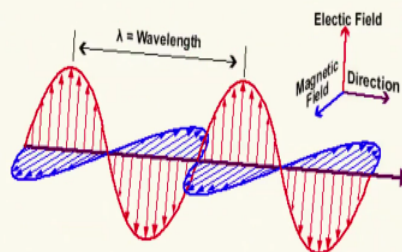
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And the energy states of the species or modification of it is direction or intensity, so every electronic transition is associated with the changes in the electronic state, electronic energy and the direction also. So, what is electromagnetic radiation that is considered as a wave which carries energy from 1 location to another at a finite velocity that we have already seen it is velocity of light.

That is 3×10^{10} irrespective of the wavelength or frequency, so as the name suggest electromagnetic radiation has 2 components okay, 1 is electric field and another is magnetic field which are perpendicular to each other.

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POLARIZED ELECTROMAGNETIC WAVE



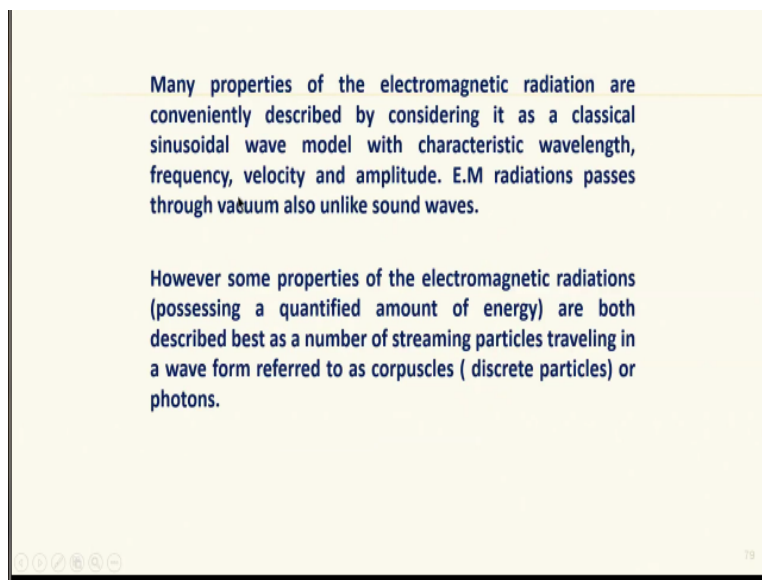
Wave nature of a single frequency electromagnetic radiation

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I had shown you this figure also earlier and 1 is perpendicular to another that is the red one appears should appear to you as an observer if you are looking at an electromagnetic radiation it appears as a peak like this whereas the magnetic field will appear as perpendicular wave. So, the direction is very important as far as electromagnetic variation that is what I had shown you in this figure.

It has got x-axis, it has got y-axis and the direction of propagation of the electromagnetic radiation I have shown here it is in this direction. But electric field is like this and then it goes like this, it goes like this etc., whereas magnetic field will go perpendicular to that.

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So, many properties of the electromagnetic radiations are considered as discrete classical discrete energy levels, particle energy discrete energy particles is one thing another thing is we can also consider it has a wave. So, conveniently we can describe the properties of both that means any electromagnetic radiation as a classical sinusoidal wave which I shown you earlier.

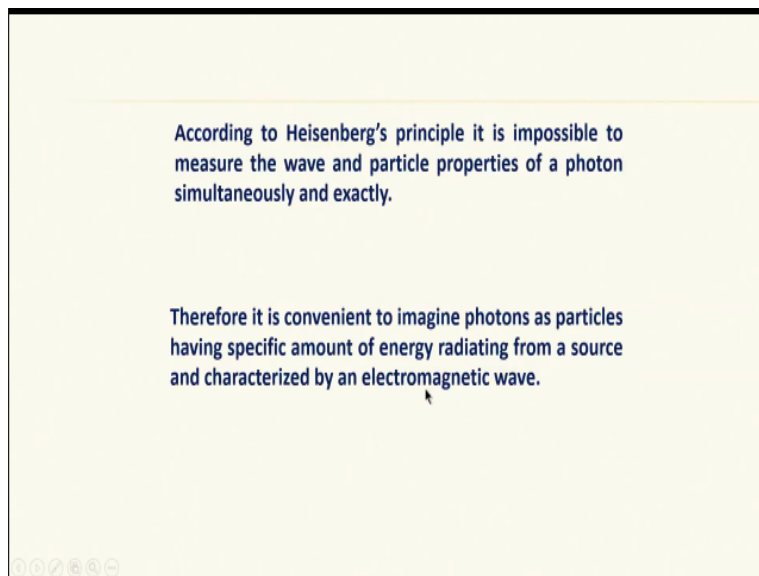
So, it has got characteristic wavelength, frequency, velocity and amplitude, so electromagnetic radiation passing through vacuum also will contain all these components even if it is in vacuum unlike sound waves. Sound waves cannot travel through the vacuum. So, some properties of the electromagnetic radiation they are both described best as a number of streaming particles instead of waves that means if a light is.

If you are seeing a light coming from a bulb through a battery you will see a straight line a shining light penetrating the space quite often you will see that just put on a torch and see how you can see the light coming in a straight line. So, that means if you assume that the photons or the electromagnetic radiation contains number of particles, those particles are moving in a straight line.

Actually it is not a straight line but the particles which are called as photons it appears to you as if it is passing through a straight line path. And then you can consider it as a streaming particles that move from 1 place to another. So, because electron has got velocity and electromagnetic radiation also has got velocity it can travel. So, we can consider it as a bundle of energy travelling through the space from 1 point to another.

So, these properties are best described as a number of streaming particles travelling in a wave form that they are known as corpuscles that is discrete particles or photons. More popularly they are known as photons but corpuscular theory is a typical word used in several physics text books etc. which does not which means it is particulate theory.

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So, according to Heisenberg's principle here we will invoke that it is impossible to measure the wave and particle properties of a photon. Simultaneously you cannot measure assume that a

wave is moving like this at a given point you cannot determine the particle where it is and at the same time you cannot determine how is the wave moving. There will be certain amount of uncertainty or error if you want to measure both.

This is a very important concept quantum mechanical concept what it says is you cannot measure them simultaneously or if you measure simultaneously you cannot measure them exactly. So, it is convenient for us to imagine photons as particles having specific amount of energy radiating from a source just like I was explaining to you that if you consider a battery torch cell.

You can see that it is everyday battery you must have seen so many torches, LED batteries, keychain or most of them appear as if bright light is going through a straight line cutting the darkness. So, from a source the specific amount of energy radiating from a source can be characterized by the electromagnetic wave okay.

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The wavelength of radiation λ can be visualized as the distance between two maxima of either electrical or magnetic component.

The frequency ' ν ' is the number of waves in an electromagnetic radiation passing through any fixed point P per unit time. When a photon passes a particular region of space the electric and magnetic field oscillate with frequency.

Therefore only frequency is truly characteristic of particular radiation.

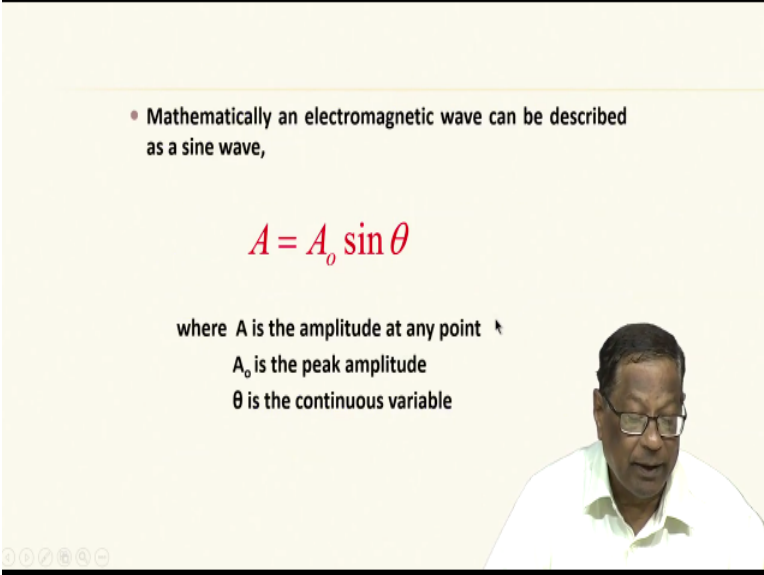
So, the how do we characterize them that is again from the properties only we have to do it only from the properties. So, the properties what we are trying to describe they would be something like wavelength of the radiation I can measure that is very simple λ can be visualized as a distance between 2 maxima which I have shown you earlier. And you can use them either electrical you can measure the amplitude or the wavelength.

Either through the electrical field or magnetic field either way both will be same, so you can measure the distance between the 2 maxima either of either electrical or magnetic component. So, obviously now when you measure the distance that is amplitude between the 2 maxima it is also characterized by the frequency you can say I you can measure the frequency also know it for measuring both.

Because when you measure the frequency automatically wavelength is fixed, so the frequency we define as the number of waves in an electromagnetic radiation passing through a fixed point. Now comes the Heisenberg's principle, if the radiation is passing through a fixed point we can measure it is position but not the velocity there will be certain amount of error.

So, the when a photon passes a particular region of space the electric and magnetic fields oscillate with the frequency, they get disturbed a little bit. So, only when they get disturbed it is difficult to measure the wavelength amplitude. So, the only measure of electromagnetic radiation is the frequency, frequency it does not alter much. So, it is the truly the characteristic of a particular radiation okay.

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• Mathematically an electromagnetic wave can be described as a sine wave,

$$A = A_0 \sin \theta$$

where A is the amplitude at any point
 A_0 is the peak amplitude
 θ is the continuous variable

Now how do we define it mathematical very simple I define it as $A=A_0*\sin$ theta any electromagnetic radiation whether it is cosmic, whether cosmic high whether it is gamma rays or ultraviolet rays or X-rays, visible rays, infrared anything all waves can be characterized and

defined mathematically as a simple expression that is $A=A_0*\sin \theta$. Here we call A is the amplitude at any point A_0 is the peak amplitude.

And $\sin \theta$ is the θ is the continuous variable that is the degree in which the photon is moving. So, $\sin \theta$ when it is maximum value that is 90, so A would be $=A_0$ that is the maxima and any other degree its value will be less than 1. So the wave function can be described something like this go up and come back, go up come back. So, it has to be sinusoidal wave because $\sin 0$ is 0, $\sin 90$ is 1, $\sin 180$ is 0, $\sin 270$ is -1 and $\sin 360$ is 0 again the value of that.

So, after 360 again you will be repeating the same cycle because θ will be where θ can vary only from 0 to 360. So, this is almost a complete description of the electromagnetic wave, I can also write $A=A_0*\cos \theta$. Because the $\cos \theta$ also is essentially same except the magnitude \cos when θ is 0 when $\sin \theta$ is 0 the whole thing when θ is 0 $\sin \theta$ is 0.

So, A_0*0 would be 0 that means when θ is 0 the amplitude of wave is 0 but in when I described $\cos \theta$ when θ is 0 $\cos \theta$ is 1. So, A_0*1 would be A_0 that means the whole electromagnetic radiation when I am describing either a $\sin \theta$ or $\cos \theta$ they are differing only by a it is appearance of maxima and minima rather than it is true character okay.

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• Alternately

$$A = A_0 \sin \omega t$$

Where $\omega t = \theta$ and ω is the angular velocity in radians/unit time.

A complete cycle occurs when ωt changes from 0-360°. This is called one oscillation or one period. Hence the time over which one complete occurs is given by,

$$t_{\text{cycle}} = \omega / 2\pi$$

or

$$\nu = \text{frequency} = \frac{1}{t_{\text{cycle}}} = \frac{2\pi}{\omega}$$

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So, I can also say ωt instead of $\sin \theta$, so $\omega t = \theta$ but ω is the angular velocity in radians per unit time, this is how he define normally.

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• For any wave moving at a constant velocity v , we can write

$$v = \nu \lambda$$

where v is the frequency in ms^{-1} , ν is in Hertz (cycles per second or s^{-1}) and λ in meters

• The frequency is proportional to the energy E of the photon given by

$$E = h \nu$$

where $h = 6.62 \times 10^{-27}$ ergs when E is expressed in ergs and $= 6.63 \times 10^{-34}$ joules. E is expressed as joules.

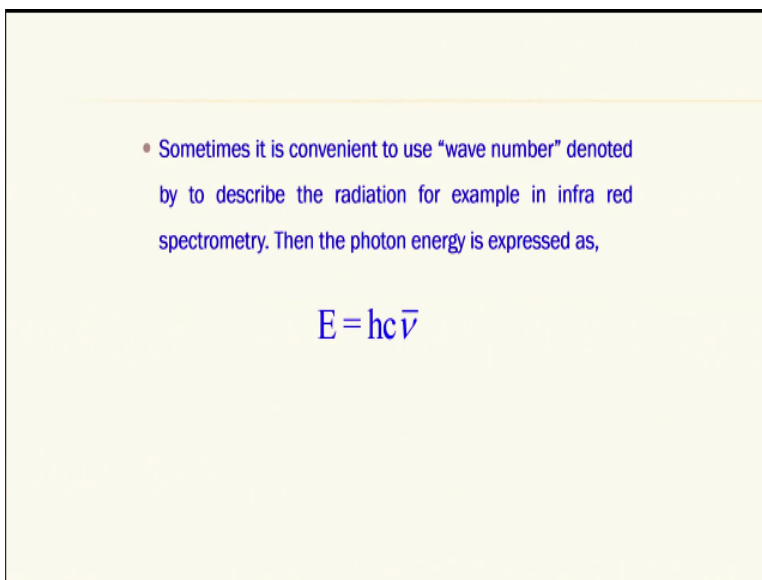
So, a complete cycle occurs when a ωt changes from 0 to 2π this already explain to you 0 to 360 degrees this is called 1 oscillation or 1 period 0 to 360 whether it is \sin or \cos . Hence the time over which 1 complete period occurs is given by the frequency that is t cycle I have written here 1 cycle is nothing but $2\pi/\omega$, what is 2π , 2π is 360 degrees or I can say frequency = $1/t$ cycle how many maxima or minima occur.

That so is given by $2\pi/\omega$ okay. So, for any wave moving at a constant velocity V we can write $V = \nu \lambda$ frequency okay velocity, velocity = $\nu \lambda$ where ν is the frequency in microseconds, ν is the velocity. And in hertz that is cycles per second or seconds inverse and λ is in meters, normally we go for meters even though we use centimeters etc.

But the usually the variation depends upon the convenience of the expression depends upon the convenience of the waves. Generally if the wave is long the amplitude is long we can say in centimeters or even in meters like that or even kilometers if it comes to that. But when it comes to the other side you cannot say 10^{-9} centimeters it looks awkward even though not wrong.

So, we say centimeter, nanometer, picometer like that or Armstrong units that also we can say many things. So, the frequency is proportional to the energy of the photon and that is given by this equation that is $E=h\nu$, look at the slide now, now I have written here $E=h\nu$ again the numbers h means it is 6.62×10^{-27} ergs when e is expressed in ergs or it express in joules. Then it is 6.63×10^{-34} , 10^{-7} ergs is 1 joule, so E is expressed as 1 joule okay.

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• Sometimes it is convenient to use "wave number" denoted by $\bar{\nu}$ to describe the radiation for example in infra red spectrometry. Then the photon energy is expressed as,

$$E = hc\bar{\nu}$$

Now sometimes we can define it is convenient to use wave number instead of the frequency or wave length or anything. And wave number is denoted here by this expression $E=h\nu$ instead of writing hc/λ we have write $hc \cdot \bar{\nu}$ that means $\bar{\nu} = 1/\lambda$ that is 1/wave length. Wave number is nothing but 1/wave length and this is especially true if I am going to measure in infrared spectrum of the compounds which we are going to studying now.

The point is you can use wave number also or wave length or frequency now to describe the electromagnetic transitions occurring in infrared okay.

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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	\AA	λ	X-ray, UV-visible (in older work)
Millimicron	m μ	λ	Visible (in older work)
Micron, Micrometer	μm	λ	Infrared (common in physics literature)
wavenumber (reciprocal cm)	cm^{-1}	$\bar{\nu}$	Infrared, UV- visible (less common)
Electron volt*	eV	E	X ray, γ ray
Hertz	Hz		Radiofrequency, microwave
Cycles per s	Cps		Radiofrequency (less common in current literature)

Each system measurement or energy measurement of the wavelength or energy normally is associated with a specific spectroscopic technique which I was explain into you just now that is you are using wave number, it is for infrared. Like that now I have made this table and here I am putting properties of the electromagnetic radiation as nanometer and unit is nanometer is a unit for wavelength.

And where nanometers are typically used they are all used in ultraviolet, visible and near infrared typically used. So, nanometer Armstrong and 1 Armstrong is 10^{-8} centimeter, so this is the symbol for Armstrongs, it λ for wavelength and Armstrong units are usually used for X-ray and UV visible region. Earlier people use to refer to the wavelength in Armstrongs 4000 Armstrongs, 4030 Armstrongs, 4300 Armstrongs like that.

But now a days we are replace that with nanometer, so millimicron is another one again it is measure the unit of wavelength that is visible. That is in again a millimicron is an older unit, older unit means people use to refer to it as millimicron a few years back. That means when you study they would write like this but what you essential to understand is millimicron or essentially nanometers okay.

Then there are units like microns and micrometers these are defined like this and then I have again it is a wavelength, infrared it is used in infrared spectroscopy. That is common in physics

literature that means technical books in physics will refer to the infrared radiation in terms of micrometers. This is also popular among chemist, so wave number we use them centimeters inverse I have already told you denoted by $\bar{\nu}$.

That is infrared as well as UV visible but in UV visible it is less sometimes in near infrared okay. Then you can use electron volts instead of wavelength. Because in electron volts the notation is UV but they are mostly used in X-ray and gamma rays. Then I can use simply frequency that is radio frequency and microwave all of you must have heard that whenever you listen to FM radio or all India radio.

This is such station giving you at 91.7 hertz something like that you would have heard they are all in frequency. Similarly cycles per second is also unit for radio frequency that is rarely used now a days.

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Spectro metric region	UV-Visible	X-Ray UV	Infrared	X-Ray γ Ray	Radiofreq uency (NMR)	ESR
	nm	Å	cm^{-1}	eV	MHz	J^*
nm	1	10	10^7	1.240×10^3	2.9979×10^1	1.986×10^{-16}
Å	0.1	1	10^8	1.240×10^4	2.9979×10^1	1.986×10^{-15}
cm^{-1}	10^7	10^8	1	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	1	2.418×10^8	1.02×10^{-19}
MHz	2.9979×10^{11}	2.9979×10^{12}	3.3356×10^{-5}	4.1355×10^{-9}	1	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}	1

So, the inter-conversion of units I have try to attempt here, so it is only for you to remember okay. And you can see nanometer can be converted into X-ray, infrared X-ray, radiofrequency anything all are interchangeable okay. So, I will not go more into detail but this serves you as a guide for you to convert 1 energy level, 1 unit of 1 lenergy into another unit that is it.

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It may be noted that regardless of the units of expression any electromagnetic radiation of frequency will have unique wavelength and energy.

The longer the wavelength, the lower is the energy and frequency.

Energy is closely related to temperature of any object, it can be expressed as,

$$E \propto K_b T$$

where K_b = Boltzmann's constant

$$= 1.380 \times 10^{-16} \text{ ergs K}^{-1} \text{ atom}^{-1} \text{ OR}$$

$$1.380 \times 10^{-23} \text{ joule K}^{-1} \text{ atom}^{-1}$$

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So, it may be noted that regardless of the units of expression any electromagnetic radiation of frequency will have unit wavelength and unique wavelength any frequency will have unique wavelength and energy okay. So, the longer the wavelength as I have explain to earlier lower is the energy and lower is the frequency and energy is closely related to the temperature also.

That is very important for us to remember and that is expressed as E is proportional to $K_b \cdot T$ where K_b is the Boltzmann constant given by $1.380 \cdot 10$ raise to 16 ergs per degree per atom or $1.380 \cdot 10$ raise to -23 joules per kilo per atom. We will continue our discussion regarding the electromagnetic radiation a little more before we go on to interact, thank you.