Infrared Spectroscopy for Pollution Monitoring

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Lecture- 08

Interaction of electromagnetic radiation with matter-I

So, we were discussing about the electromagnetic radiation and a pictorial representation of that I am going to show you now okay. So, this is the pictorial representation here I have in this slide here I have the red one.

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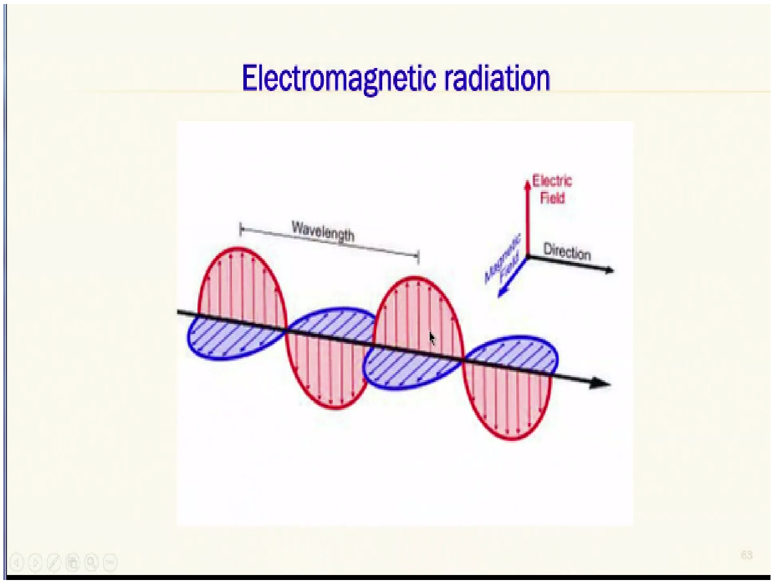

Electromagnetic radiation

That is you can imagine a waves along this line along this black line a wave going like this and then coming down cutting it again going up like this that is 1 wave. And imagine another wave perpendicular to that going like this. And then again coming here and going out like this etc., so this is sort of how an electromagnetic radiation will move along this direction. So, it has got a direction, it has the electric field is aligned perpendicular to that.

And it is aligned magnetic field is also aligned perpendicular to that in the x, y inside direction. The distance between the 2 peaks is known as wavelength, so I think most of you are familiar with the wave forms.

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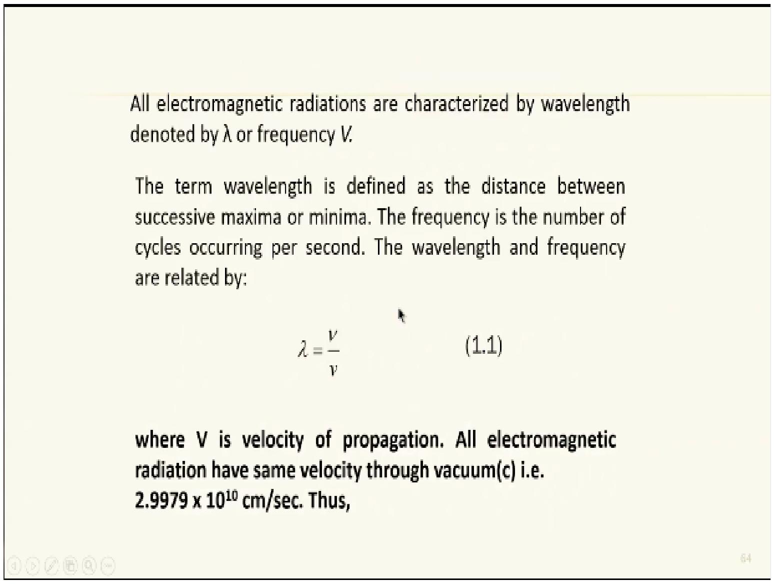

All electromagnetic radiations are characterized by wavelength denoted by λ or frequency V.

The term wavelength is defined as the distance between successive maxima or minima. The frequency is the number of cycles occurring per second. The wavelength and frequency are related by:

$$\lambda = \frac{v}{\nu} \qquad (1.1)$$

where V is velocity of propagation. All electromagnetic radiation have same velocity through vacuum(c) i.e. 2.9979 x 10^{10} cm/sec. Thus,

We will simply say that all the electromagnetic radiations are characterized by the wavelength denoted by lambda or frequency mu. The term wavelength is defined as the distance between successive maxima or minima okay. So, like I was showing you now here the every wave has got which is a peak point and then it reaches 0 and then it reaches another peak point in the opposite direction that is negative.

So, I have 1 maxima here, 1 minima here okay, 1 minimum actual maxima and minima are the plural terms. So, 1 maxima, 1 minima and again maxima again minima like that the waves will move on. So, the frequency is the number of cycles occurring per second. So, if I start from this end now look at the red one I am marking it here, if I start from here reach 0 and then reach -1 and then again reach 0 here.

So, this is known as 1 frequency, so the number of frequencies per second how much it moves is the frequency per second. So, the number of cycles occurring per second is the frequency, so how do these 2 are related to each other a very simple relation lambda mu/v, v/mu and where v is the velocity of the propagation and all electromagnetic radiation you should remember that they all travel in the space with or without matter at the same rate.

That is same velocity that is 2.9979*10 raise to 10 centimeter per second for simplicity we call it 3, 3*10 raise to 10 centimeters per second. So, that is the velocity of the light speed of light that is visible to us sun’s rays etc., that is also the same velocity that is 3*10 raise to 10 centimeters per second or 3*10 raise to 8 kilometers per second. So, you can measure the distance between the sun and the earth by the time the sun’s radiation reaches the earth and dividing it by the time by the speed okay.

So, it is possible for us to determine the exact distance of all planets or all astronomical bodies by the time the light from the astronomical body reaches the earth. So, it is a very separate signs by itself okay.

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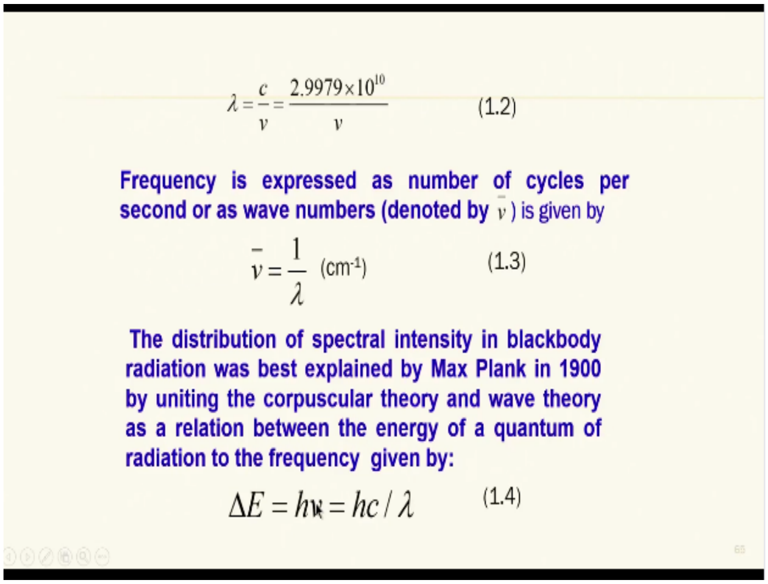

$$\lambda = \frac{c}{\nu} = \frac{2.9979\times10^{10}}{\nu} \qquad (1.2)$$

Frequency is expressed as number of cycles per second or as wave numbers (denoted by $\bar{\nu}$) is given by

$$\bar{\nu} = \frac{1}{\lambda}\ (\mathrm{cm}^{-1}) \qquad (1.3)$$

The distribution of spectral intensity in blackbody radiation was best explained by Max Plank in 1900 by uniting the corpuscular theory and wave theory as a relation between the energy of a quantum of radiation to the frequency given by:

$$\Delta E = h\nu = hc/\lambda \qquad (1.4)$$

So, we also known that lambda is nothing but wavelength is nothing but frequency speed of light divided by frequency. Now frequency is expressed as number of cycles per second or as wave numbers okay, this wave number is important as far as IR is also concerned and wave number is given by mu bar=1/lambda. So, this also is the parameter we are suppose to remember.

So, the distribution of spectral intensity in blackbody radiation was best explained Max Plank in 1900 by uniting the corpuscular theory that is assuming that the electromagnetic radiations are also the radiations containing particles. So, that is a corpuscular theory and just because it moves in the wave form it is also called as wave theory. So, it was considered that is the relation between the energy of a quantum of radiation to the frequency that is given by delta e=h ~~mew~~ mu or hc/lambda.

That means the energy of the radiation can be determined if I know the wavelength only hc/lamda c is the velocity of light, h is plank's constant that is also known, c is known 3*10 raise to 10 only lambda if I know lambda I can find out what is the corresponding energy of the electromagnetic radiation that is very simple.

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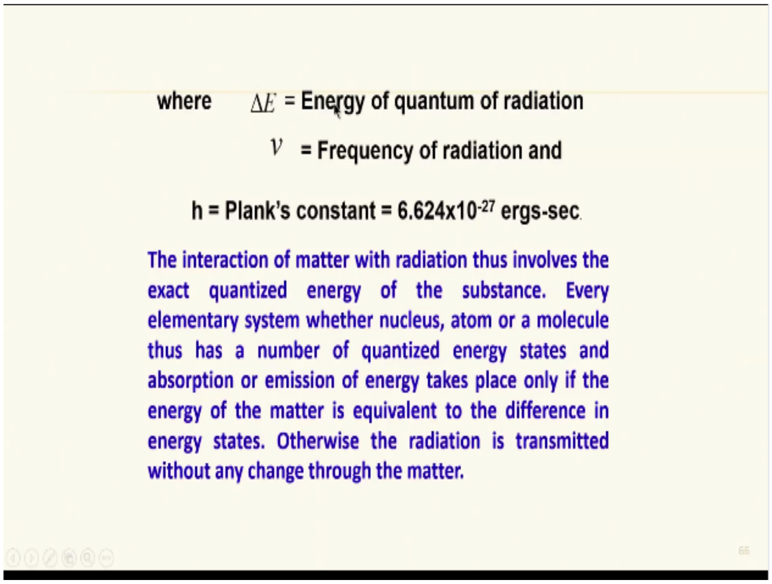

where ΔE = Energy of quantum of radiation

v = Frequency of radiation and

h = Plank's constant = $6.624\text{x}10^{-27}$ ergs-sec.

The interaction of matter with radiation thus involves the exact quantized energy of the substance. Every elementary system whether nucleus, atom or a molecule thus has a number of quantized energy states and absorption or emission of energy takes place only if the energy of the matter is equivalent to the difference in energy states. Otherwise the radiation is transmitted without any change through the matter.

So, here in that equation delta E is the energy of the quantum of radiation and v mu is the frequency of radiation, h is in ergs seconds that is 6.624*10 raise to -27 ergs second. So, the interaction of matter with radiation thus involves the exact quantized energy of the substance why because all the energy of the wave length electromagnetic radiation is also quantized. So, every elementary system whether nucleus or an atom or a molecule thus has a number of quantized energy levels which we have seen earlier that in the form of n, l, s and m.

And absorption are emission of energy takes place only if the energy of the matter is equivalent to the difference in and the energy states this is another quantum mechanical theory that changes in the absorption or emission of energy takes place if the energy of the matter is also equivalent to the difference between the energy states. Otherwise the radiation is transmitted without any change through the matter, so this is an important concept we should remember.

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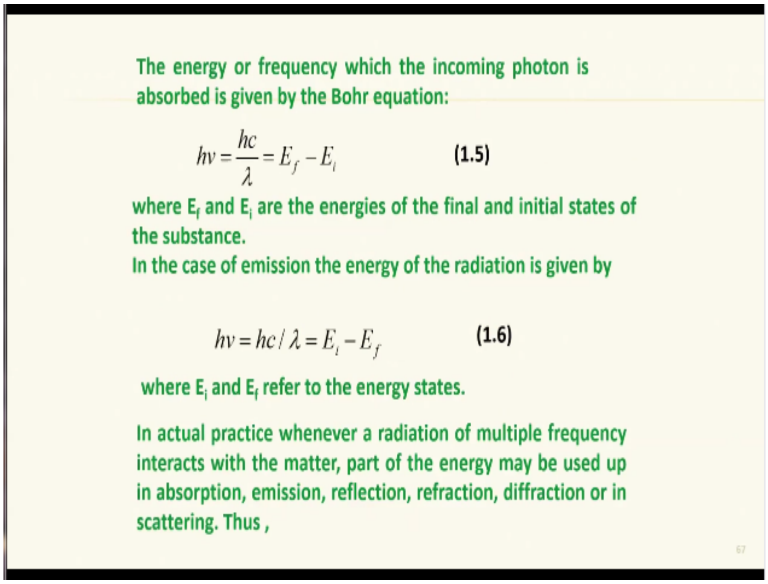

The energy or frequency which the incoming photon is absorbed is given by the Bohr equation:

$$h\nu = \frac{hc}{\lambda} = E_f - E_i \qquad \textbf{(1.5)}$$

where E_f and E_i are the energies of the final and initial states of the substance.

In the case of emission the energy of the radiation is given by

$$h\nu = hc/\lambda = E_i - E_f \qquad \textbf{(1.6)}$$

where E_i and E_f refer to the energy states.

In actual practice whenever a radiation of multiple frequency interacts with the matter, part of the energy may be used up in absorption, emission, reflection, refraction, diffraction or in scattering. Thus ,

So, the energy of the frequency the same equation which same expression which I earlier told that if the energy has to match the energy of the electromagnetic radiation and of the particles. I can write an equation something like this h mu that is hc/lambda that is the energy of the final state-energy of the initial state. So, this delta E this is the energy that is to be matched by the electromagnetic radiation as well as the particulates.

That are interacting with the electromagnetic radiation, this equation is known as Bohr radiation, Bohr's equation. So, in this equation Ef and Ei are the energies of the final and initial states of the substance. So, in case of emission the energy of the radiation is given by h mu==hc/lambda that is Ei-Ef, here I am defining 2 aspects, 1 is emission another is absorption. So, emission is E final state- absorption is E final state-E energy of the initial state.

And emission is the energy difference between the energy of the initial state and energy of the final state that is the difference. But the quantum maybe same not maybe quantum is always same, so the again in emission Ei and Ef refer to the energy states of the particulates. So, in actual practice what happens, so whenever a radiation of multiple frequencies interacts okay, so with the matter multiple frequencies I cannot choose a radiation with only one single wavelength.

That is a little difficult not that it cannot be done but I think those of you who are familiar with scientific advances and who are familiar with the science know that we do have laser rays etc with single wavelength. But in general if I am dealing with an electromagnetic radiation coming from a particular body black body or any other body I get a set of waves having different energies and set of having different wavelengths, different frequencies, it is a bundle of energy.

So, the part of whenever I using I am getting bundle of energy I call it something like multiple frequency radiation. If I am getting only one single wavelength then it is a single wavelength radiation. So, when I get multiple energy radiations passing through a given space containing empty space, electrons, neutrons and whatever it is, air molecules etc., lot of things can happen what can happen.

The energy maybe used up in absorption part of the energy maybe absorbs by the matter or it may be reflected by hitting on the particulate and then going in some other direction. And then another possibility is it may enter a glass like material go through the glass bend a little bit and come out on the other side okay. So, part of some of it if it is a black color glass or something all of it will be absorbed.

And it can be emitted, it can be reflected as if hitting something some hard surface coming here and going of like this okay it is reflection like a mirror. And then refraction it passes through the matter but with a change in the direction and then it can get diffracted, it can get scattered in all directions, so many other possibilities. So, if we have to consider the interaction of electromagnetic radiation we should consider all these things absorption, emission, reflection, refraction, diffraction, scattering and all these things.

So, the sum total of the energy when it is interacting is given by the next equation on the next slide that is E=E absorption is look at the slide now.

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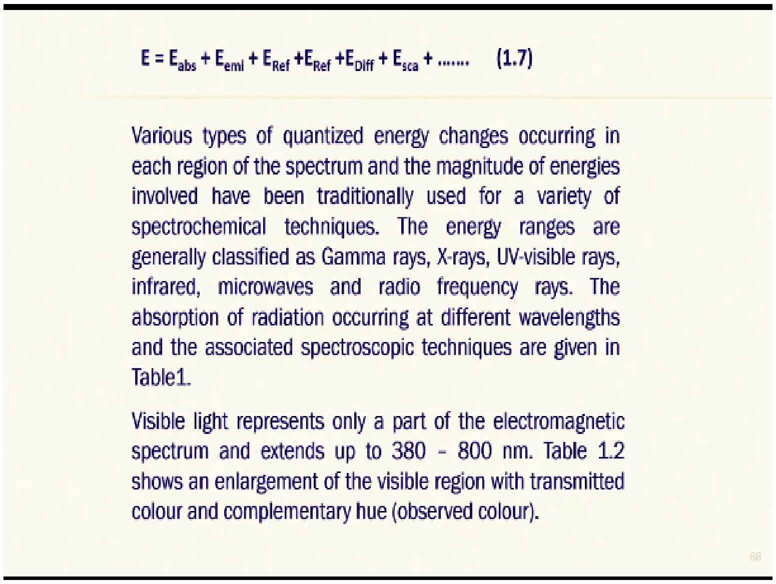

$$E = E_{abs} + E_{emi} + E_{Ref} + E_{Ref} + E_{Diff} + E_{sca} + \ldots\ldots \quad (1.7)$$

Various types of quantized energy changes occurring in each region of the spectrum and the magnitude of energies involved have been traditionally used for a variety of spectrochemical techniques. The energy ranges are generally classified as Gamma rays, X-rays, UV-visible rays, infrared, microwaves and radio frequency rays. The absorption of radiation occurring at different wavelengths and the associated spectroscopic techniques are given in Table1.

Visible light represents only a part of the electromagnetic spectrum and extends up to 380 – 800 nm. Table 1.2 shows an enlargement of the visible region with transmitted colour and complementary hue (observed colour).

E=E absorbed energy emitted, energy reflected, energy refracted, energy diffracted, energy scattered and so many other forms of energy dispersion. So, that but the sum total of the energy should be same because that is the law of conservation of energy. I think most of you are familiar with the law of conversation of energy that is energy can be neither created nor destroyed.

The total energy available on the surface of the earth or anywhere else in the whole universe is essentially same. So, it can get converted from 1 form and another but you cannot create energy it is a sort of human restriction maybe god can do it but we do not know all right. But as far as humans are concerned the last very firm you cannot create energy nor you can destroy energy you can only altercate to some extent.

So, various types of quantized energy changes occurring in each region of the spectrum and the magnitude of energies involved have been traditionally used for a variety of spectrochemical techniques. And these energy changes are generally classified into different waves and these energy changes also had different wavelengths and different frequencies. So, what are the different kinds of energies we talk about or electromagnetic radiation we talk about yesterday I had mentioned.

During my introduction that electromagnetic radiation will have gamma rays, X-rays, ultraviolet and vacuum ultraviolet, ultraviolet, visible rays, infrared, microwaves, near infrared I had mentioned and then far infrared, microwaves and radio frequency. So, the absorption of radiation occurring at different wavelengths and the associated spectroscopic techniques I have listed in table 1 that is coming in the next slide. So, I am going a little bit I had and coming back again okay.

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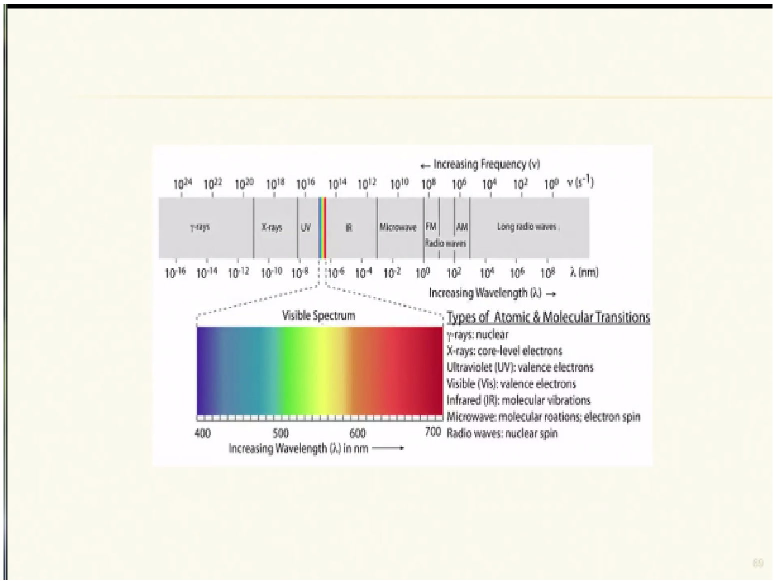

Types of Atomic & Molecular Transitions

γ-rays: nuclear

X-rays: core-level electrons

Ultraviolet (UV): valence electrons

Visible (Vis): valence electrons

Infrared (IR): molecular vibrations

Microwave: molecular roations; electron spin

Radio waves: nuclear spin

So, this is the electromagnetic radiation and you can see here I have plotted this is a Google picture I have not plotted okay. So, the whole electromagnetic radiation contains gamma rays, X-rays, ultraviolet rays, visible rays and then infrared, microwaves and the FM radio waves and then AM radio waves and then long radio waves okay. Here on the top I have listed the frequencies.

So, if the gamma rays high energetic highly energetic electromagnetic radiations are in the gamma rays okay, they are slightly more than that also will be there in the cosmic rays but I am not showing you that okay. So, our experiences most of the gamma rays range from 10 raise the frequency ranges from 10 raise to 24 to 10 raise to 19 or something like that. And then comes X-rays having 10 raise to 18 frequency.

Then ultraviolet rays are around 16 and visible range are around 15 and frequencies for IR are 10 raise to 14, 12 etc., so the frequency keeps on decreasing as we go through the electromagnetic radiation from left to right. Let me use the frequency is decreasing wavelength keeps on increasing I think you are familiar with that relation now okay, so lambda =1/frequency okay.

So, I have put the wavelength also at the bottom of this strip here, so the wavelength of gamma rays if it is 10 raise to 24, per second 24 waves should pass through a given space and the wavelength should be approximately 10 raise to -16. So, it keeps on decreasing again that means waves the wavelength keeps on increasing and then it reaches somewhere in here it is all Armstrong's up to 10 raise to -8 centimeter is Armstrong.

And then it comes here when it comes to IR etc., they keep on increasing they are slightly longer than visible rays. And then still longer than UV rays and then it keeps on increasing 10 raise to 0, 10 raise to 2 radio waves and then long radio waves are all 10 raise to 4, 10 raise to 6, 10 raise to 8 centimeters okay. So, that is the increasing wavelength, so as the frequency increases wavelength also as the frequency decreases wavelength increases.

That is the inverse relationship we keep on talking you should also see that the radiation here I am showing you a small portion with blue, red and green that I have expanded below. And when I expand that below I get colors like this that is one side it is dark gray or blue and another side it is somewhat red and violet. So, the visible range as we experience them covers from 400 to approximately 700 by the 800 a little bit, slightly more this side that side it depends upon the individual okay.

So, the wavelength range corresponding to this is I am describing as in nanometers not in centimeters or 10 raise to -6 centimeter not in 10 raise to Armstrong's units are something like that. So, this is where the visible range is there as part of the electromagnetic radiation, so the types of molecular transitions that occur in the when the electromagnetic interact they are all I have listed here on the side.

That is gamma rays whenever you take a gamma rays and make them bombard on the element or on a metal changes in the nuclear structure take place that is what I have written gamma rays nuclear. And if you take X-rays and make them impinge on the metals I get core level electron changes that is X-rays, soft X-rays etc., so the energy of the matter that comes out would be in the form of about 20 raise to -10 centimeters.

Then comes ultraviolet and in ultraviolet region it is the valance electron that is electrons moving around their nucleus those electrons get affected and they may get excited to next higher energy level or lower energy level. And I have listed those interactions as valance electron interaction with electromagnetic radiation. So, these are all atomic and molecular transitions happening in s-orbital, p-orbital, d-orbital and f-orbitals.

So, microwave also that is the region where molecular rotations take place and electrons pin changes if you take electromagnetic radiation in microwave impinge them on the metal elements. Then what happens the electrons will change their spin from positive half to negative half. So, as usual it is like that still lower energy radio waves they result in nucleus itself may be moving like this. So, that kind of changes also will be taking place in the electromagnetic radiation, so this is how then electromagnetic radiation you should visualize.

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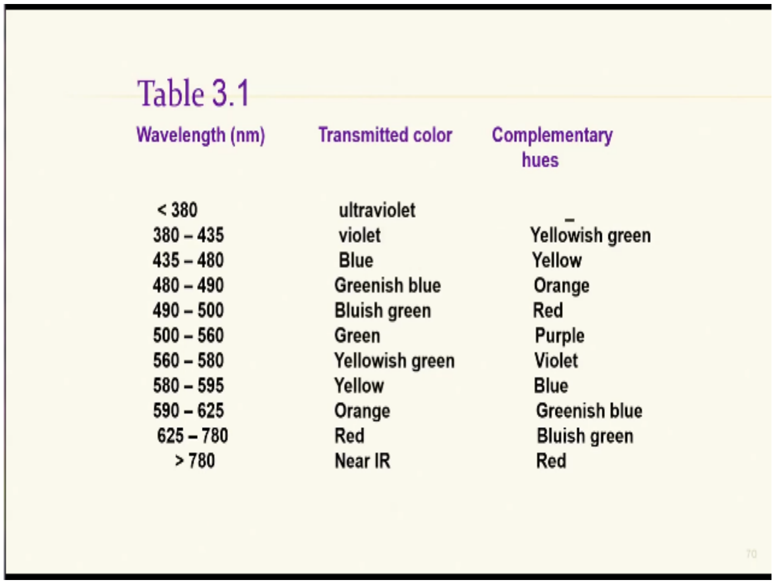

Table 3.1

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

And I hope you are talking you are fairly comfortable now what we are talking about. Now in this table 3.1 I am taking the visible radiation okay, so if you remember here it is 400 to 700 that is the visible range. And that visible range I am cutting into different ranges again and that is less than 380 most of it is ultraviolet range and 380 to 435 nanometers is what color of the radiation is transmitted.

That means if the radiation in this range if I pass the violet radiation it will pass through the matter, it is just like taking a violet glass and what comes out is violet glass whatever is the light on the other side okay. So, that is known as transmitted light what comes out on the other side is transmitted what is held in the glass is the complementary hue okay that is how the glass will look like okay.

So, whenever electromagnetic radiation passes through a matter there is there are 2 components, 1 is part of it is absorbed, part of it is transmitted, what is transmitted is not absorbed and whatever is not transmitted is all absorbed. So, suppose I take violet color, violet is absorbed and the remaining 6 colors from the VIBGOR they all constitute another color which is known as complementary view.

That is how it looks to us, the radiation coming out will look violet but the actual material will look the combination of all other colors that are retained in the material that is known as complementary view. So, now look at the slide now from 380 to 435 I have violet color and the complementary view is yellowish green the material will look like yellowish green. So, 435 that means if a material looks yellowish green to you as an observer you should say that it transmits violet color.

So, if the material is yellow then what is transmitting is blue color if it is orange it is greenish blue or bluish green and green if it is transmitting green color it will look purple to you and similarly other colors like yellowish green, violet, yellow, blue, orange, red. So, you can see that most of these transmitted color and complementary hues are approximately you know inversely related.

So, yellow is here and yellow is at the top of the complementary view and orange is transmitted around between 590 to 625 but it looks like greenish blue where is greenish blue, greenish blue corresponds to 480 to 590. So like that any visible range the transmitted color and complementary hues are different. So, the same thing is true in other radiations also interactions of the matter with radiations.

But we may not be able to see them unless they are in the visible range. So, infrared and many other things they generally predominantly look like infrared means it will look like red only okay. Microwaves you may not be able to see them at all and near infrared you can see sometimes color or not and near ultraviolet you will see them light yellow or colorless okay that is all human eye is capable of seeing the colors okay.

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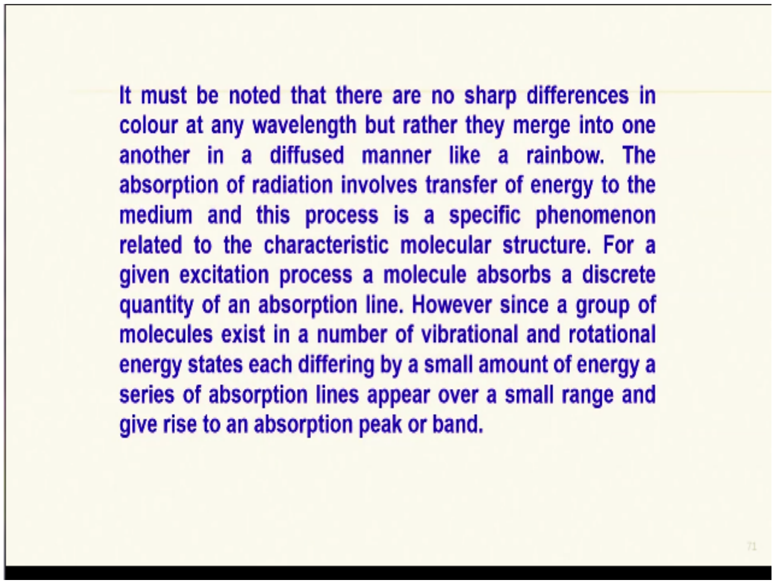

It must be noted that there are no sharp differences in colour at any wavelength but rather they merge into one another in a diffused manner like a rainbow. The absorption of radiation involves transfer of energy to the medium and this process is a specific phenomenon related to the characteristic molecular 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.

Now it must be noted here that there are no sharp differences in color or wavelength for example in the previous slide now I was showing you this is 480 to 435 and this is 435 to 480. Now what about 440, 380 to 435 it is violet how would 440 look like I have no way of telling exactly. Because it all depends upon the observer your eye, your capability of how good your eyes are, how sharp your eyes are etc.

So, the merging of the colors is sort of you know in general to lot of people it may look the same but actually lot of people have colorblind also it looks different to them many times it happens. So, the remaining colors merge into one another in a diffused manner like a rainbow. So, the absorption of radiation involves transfer of energy to the medium and this process is a specific phenomena related to the characteristic molecular structure alright.

So, for a given excitation process a molecule absorbs, a discrete quantity of an absorption line however since a group of molecules exits in a number of vibrational and rotational energy states each differing by a very small amount of energy. A series of absorption lines appear over a small range and thus it gives rise to an absorption peak or an absorption bank.

So, you should look at this slide a little more carefully, so try to understand what is written here, what I am saying is the absorption of radiation involves transfer of energy and this process is a specific phenomena. That means if I had to have a specific phenomena when the absorption line should correspond to only one wavelength. But actually when you see a spectrum you see that it is a peak like thing, now why do I get a peak.

The answer is for a given excitation process molecule definitely absorbs discrete of an absorption line. But a group of molecules exist in a slightly different differing energy levels even this. Therefore even though the exact quantity of energy is absorbed the molecule with higher energy it absorbs the same amount of it, it goes to it appears like a slightly higher, the molecule at lower will appear a little lower.

So, with the result that we have a figure like a peak and that is the reason why we see instead of a single absorption line I see a peak over here over a small range that gives rise to an absorption band okay.

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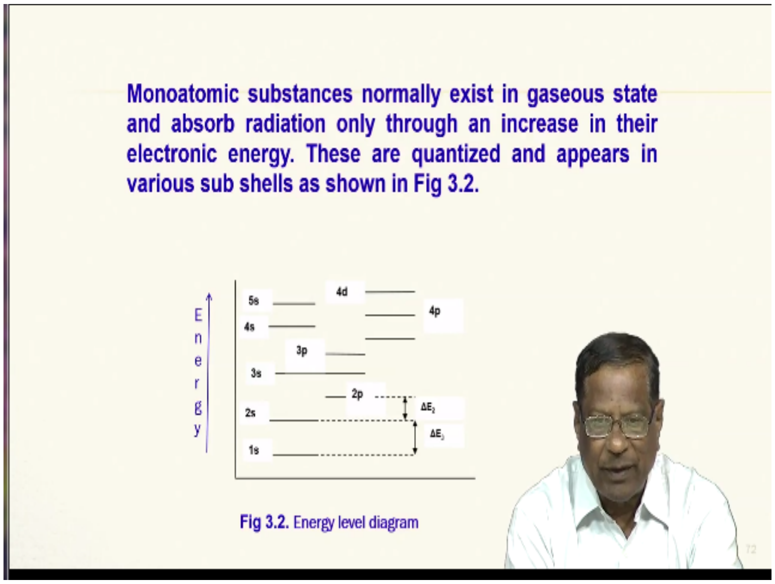

Monoatomic substances normally exist in gaseous state and absorb radiation only through an increase in their electronic energy. These are quantized and appears in various sub shells as shown in Fig 3.2.

Fig 3.2. Energy level diagram

Now here I am showing you the energy level diagram of different shells different orbitals. Here it is 1s, 2s, 2p, 3s, 3p, 3d and then this is 4s, 4p, 4d etc., and the transition should I am showing you here by arrow marks and you can see that these energies are quantized that means if I supply energy somewhere here it does not take place the transition does not take place. Only when I supply the energy corresponding to 2s-1s then transition delta E3 will take place. Similarly between 2s and 2p delta E2 will take place only when it matches okay.

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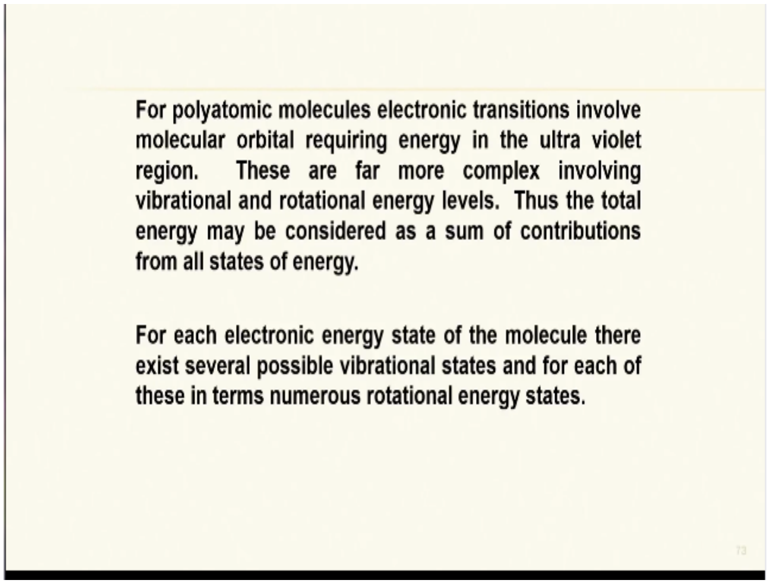

For polyatomic molecules electronic transitions involve molecular orbital requiring energy in the ultra violet region. These are far more complex involving vibrational and rotational energy levels. Thus the total energy may be considered as a sum of contributions from all states of energy.

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.

So, for monoatomic substances that means atoms with single elements with single element that is hydrogen for example. It has got single element nitrogen single element, so such substances normally exist in gaseous state very low atomic weight atomic number etc., they all staying gaseous state. And they absorb radiation only through an increase in their electronic energy that is the energy level between 1s, 2s, 3s etc., okay.

Their transition between 2s and 2p, 3s and 3d like that it does not happen. So, for polyatomic transitions that is not the case because they involve molecular orbitals requiring energy in the ultraviolet region and these are for more complex involving vibrational and rotational energy levels. So, the total energy maybe considered as the sum of the contributions from all states of energy.

So, for all each electronic energy state of the molecule there exist several possible vibrational states and for each of these vibrational states there are numerous rotational energy states. So, this is what I was trying to explain to you many molecules maybe in different vibrational energy levels and different rotational energy levels. You can imagine them to be like steps in a multistory building.

So, in a multistory building if you want to climb the stairs you will have to go from ground floor to first floor to second floor, third floor like that and then there will be landing and if you stand at the bottom of a ground floor, you kick a ball to the first floor it may land on the first floor or it may land 1 or 2 steps before that or 1 or 2 steps above that also. So, imagine a molecule is absorbing energy corresponding to 1 step below 1 step exactly same step and exactly 1 step above that.

So, all these 3 molecules if they represent I get a peak okay in terms of energy that is plotting in terms of energy. So, these energy states are represented as vibrational states for each of these in terms of rotational energy states also okay.

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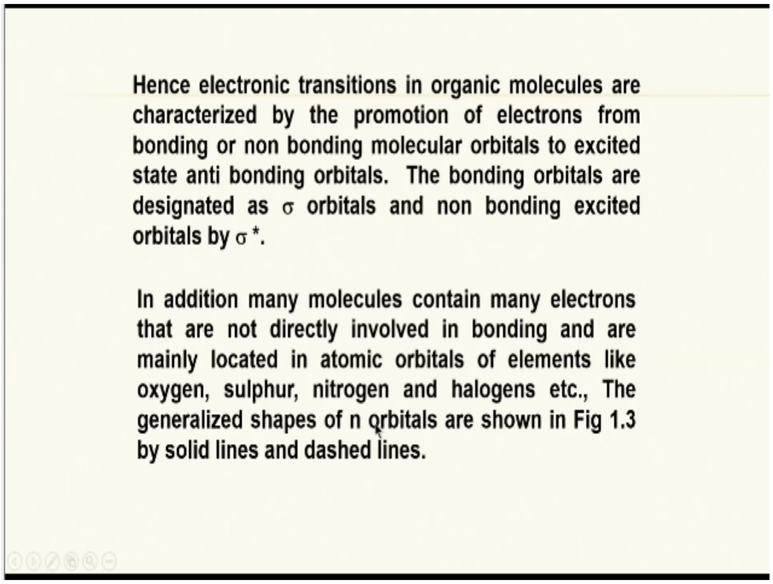

Hence electronic transitions in organic molecules are characterized by the promotion of electrons from bonding or non bonding molecular orbitals to excited state anti bonding orbitals. The bonding orbitals are designated as σ orbitals and non bonding excited orbitals by σ *.

In addition many molecules contain many electrons that are not directly involved in bonding and are mainly located in atomic orbitals of elements like oxygen, sulphur, nitrogen and halogens etc., The generalized shapes of n orbitals are shown in Fig 1.3 by solid lines and dashed lines.

So, electronic transitions in organic molecules are characterized by the promotion of electrons from bonding or nonbonding orbitals to the excited state anti bonding orbitals okay. So, the bonding orbitals are designated as sigma orbital and nonbonding orbitals transitions are designated as sigma star. Now you should have a figure like this I will show you in the next class but try to understand what I am writing here.

The electronic transitions are all characterized by the promotion of electrons from ground state to higher energy state that means all electrons bonded in a single bond, double bond etc. They are all bonding electrons those electrons are getting excited by interaction with the molecular interaction with the electromagnetic radiation those electrons go to a state defined as non bonding orbital.

So, or anti bonding orbital either of them, so the bonding orbitals are designated as sigma orbitals and nonbonding excited orbitals are called as sigma star okay. These are virtual energy levels not exactly defined you cannot visualize them in actual practice. But we can picturize them pictorially we can represent that I will show you in the next class. So, in addition from sigma to sigma star transitions I have many molecules with may contain many electrons that are not directly involved in bonding.

And these are mainly located in atomic orbitals of elements like oxygen, sulphur, nitrogen and halogens. For those of you who are familiar with the chemistry we know that there are 2 lone pair of electrons in what oxygen which are usually in present in water etc., 2 hydrogen, 1 oxygen. But on the oxygen there are 2 lone pair of electrons, similarly there are unpaired unshared pair of electrons an elements like sulphur, nitrogen and halogens and when they are combined with other elements. We have the generalized shapes of n orbitals can be shown in lines, solid line, dash line etc., we will study them in detail in our next class, thank you very much.