Atomic and Molecular Absorption Spectrometry
for Pollution Monitoring

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Lecture- 08
Emission and absorption spectra

So, we are discussing emission and absorption processes. So, the difference in energy if it comes out as a form of radiation or a light or something like that it is emission, but if the there is no change no radiation change, but only the amount of energy is absorbed then it is absorption. So, on the process of monitoring the electric change in the electromagnetic radiation in the absorption is the amount of energy in one case, in the case of emission we have to measure the wavelength of the radiation that is coming out that is emitted.

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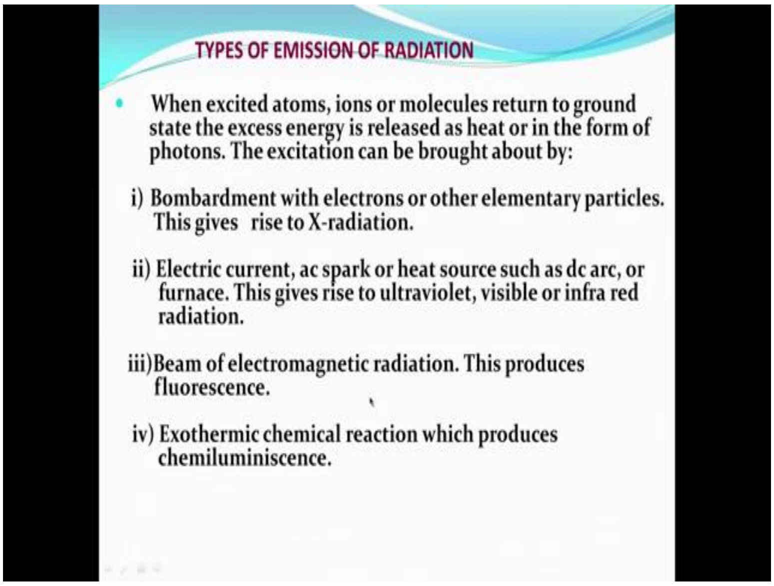

TYPES OF EMISSION OF RADIATION

- When excited atoms, ions or molecules return to ground state the excess energy is released as heat or in the form of photons. The excitation can be brought about by:

i) Bombardment with electrons or other elementary particles. This gives rise to X-radiation.

ii) Electric current, ac spark or heat source such as dc arc, or furnace. This gives rise to ultraviolet, visible or infra red radiation.

iii) Beam of electromagnetic radiation. This produces fluorescence.

iv) Exothermic chemical reaction which produces chemiluminiscence.

What are the different types of emission of radiation this we have already covered in the mean my last slide? So, when excited atoms ions or molecules they return to the ground state excess energy is released as heat or in the form of photons excitation can be brought about by bombardment supplying heat electrons etcetera. And we get ultraviolet visible infrared these are the absorption processes, UV absorption, visible absorption, infrared absorption. These are all very familiar to us in terms of absorption, because whenever you see a colored glass or something like that you will see only the color of the glass because like wearing a goggle. If you are wearing a blue goggle, you will see everything blue; that means, all other substance all other colors are absorbed. So, absorption is a phenomenon known to all of us. If you wear a green goggle you will be wearing you will be seeing everything in green color. So; that means, green color is emitted and all other colors are absorbed by the green colored goggle. So, goggle is the medium. So, ultra-same thing happens with whenever material goes to higher energy state using ultraviolet visible or infrared. So, these are all absorption processes. And a beam of electromagnetic radiation if it is emitted from, what you have supplied then it is known as florescence; that means, radiation entering is one wavelength radiation coming out is another wavelength. In the case of absorptions what goes in comes same thing comes out and exothermic chemical reaction means is here there is no energy supply as such, but from chemical reaction the outcome is in the form of radiation, that is known as chime luminescence.

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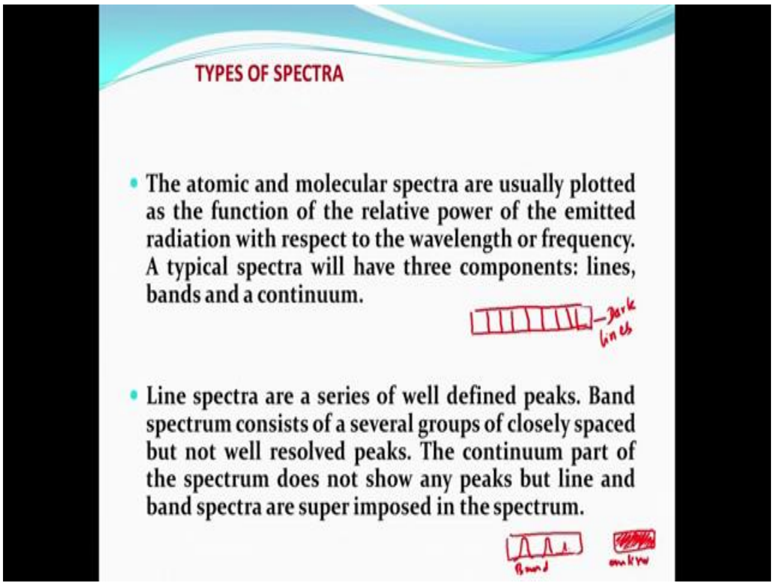

TYPES OF SPECTRA

- The atomic and molecular spectra are usually plotted as the function of the relative power of the emitted radiation with respect to the wavelength or frequency. A typical spectra will have three components: lines, bands and a continuum.
- Line spectra are a series of well defined peaks. Band spectrum consists of a several groups of closely spaced but not well resolved peaks. The continuum part of the spectrum does not show any peaks but line and band spectra are super imposed in the spectrum.

So, what are the different types of spectra we expect in molecular absorption. So, the here I have listed, one is they are usually line spectra and another is band spectra. So, basically what happens is the spectra what does it represent. It represents the function of the relative power of the emitted radiation, with respect to wavelength or frequency; that means, I will plot the interaction the result of interaction in the form of electromagnetic radiation as one axis and absorption or emission as another axis, percent absorption percent emission etcetera and these are in the different components. One is lines, one is bands and another is a continuum spectrum. So, there are 3 come types of absorption the type spectra, one is line spectra another is band spectra and another is the continuum spectra. So, what is the line spectra? Line spectra are a series of well-defined peaks; that means, they are. So, sharp that they look like dark lines on a photographic plate. So, band spectrum consists of several groups of closely related spaced but.

For example, I can draw it here. If I have a spectrum like this. I will see a peak like this different lines spectra on a photographic plate all these things will look dark lines. And in band spectra, what I see is a peak like this something like this. And in a continuum spectrum, what I see is a continuous color merging from one into another or it may be any other mixture that is slowly changing from one to another or it may be simply yellow color or brown color etcetera. This is a band spectrum this is continuum spectrum.

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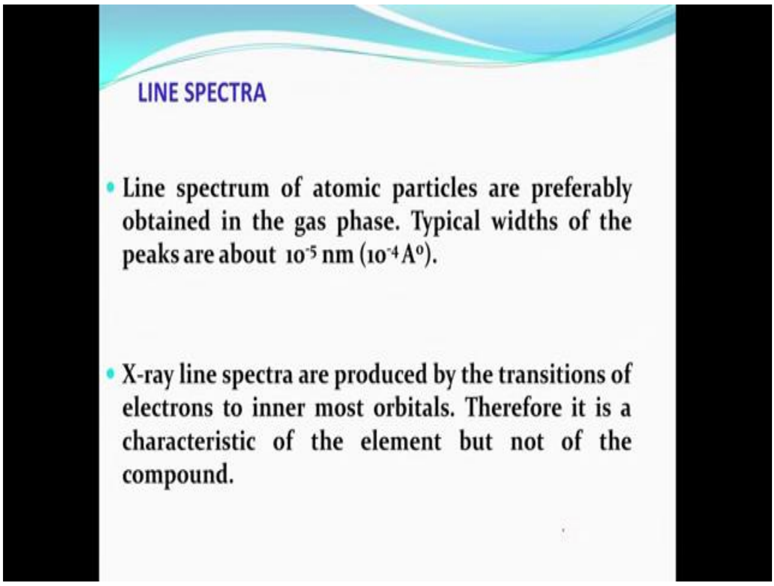

LINE SPECTRA

- Line spectrum of atomic particles are preferably obtained in the gas phase. Typical widths of the peaks are about 10^{-5} nm (10^{-4} A°).
- X-ray line spectra are produced by the transitions of electrons to inner most orbitals. Therefore it is a characteristic of the element but not of the compound.

So, in line spectra the atomic particles are preferably obtain in the gas ways; that means, if I take material in the form of a gas pass the radiation through the gas, I get line spectrum; that means, I put a photographic plate at the other end I get different line dark lines that is line spectrum. So, basically the typical widths of line spectra actually they are also peaks only. Because nothing is actually a simple line spectra. As I have explained to you any monochromatic slit will give you a group of frequencies and the width of the width if it is very small you will see it only as a line spectra. So, the typical width of a line spectra is of the order of about 10 raise to minus 5 9 nano meters for 10 raise to minus 4 angstrom units. That is why you will see them only as a single line whereas, because our eyes are not sensitive enough to see the full band. Now X-ray line spectra is another line spectra produced by the transition of the electrons and they are produced by the transitions of the electron to the inner most orbitals. Now imagine that we have an atom electron is there at the top and then it falls to the ground floor. Whenever then it falls to the lower energy level. So, atomic level at these stage of atomic level X-ray lines are produced. So, it is not a molecular spectrum, but it is atomic spectra. So, it is characteristic of the element, but not of the molecule or a compound, that is special about X-ray.

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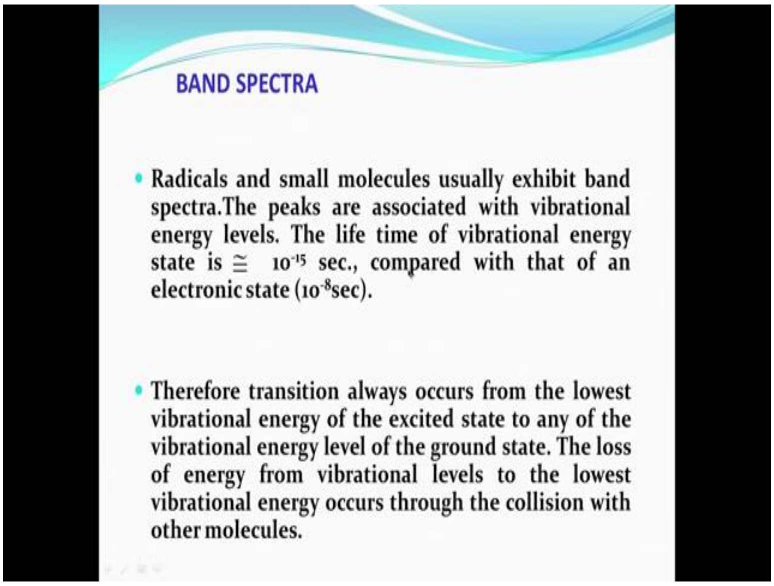

BAND SPECTRA

- Radicals and small molecules usually exhibit band spectra.The peaks are associated with vibrational energy levels. The life time of vibrational energy state is $\cong$ 10^{-15} sec., compared with that of an electronic state (10^{-8}sec).
- Therefore transition always occurs from the lowest vibrational energy of the excited state to any of the vibrational energy level of the ground state. The loss of energy from vibrational levels to the lowest vibrational energy occurs through the collision with other molecules.

Then the band spectra. Now we discuss about band spectra. So, what type of compound normally generate band spectra. So, if we look at it, as I have explained to you that if we have a group of molecule like O H C O O H aldehydes, ketones, etcetera. If I have the radiation falling on them, then I get radicals and small molecules usually exhibit band spectra, they do not exhibit line spectra. Because the band width is slightly more and our human eye is sensitive enough to see a Gaussian curve there. So, a Gaussian curve is typically characterized by a peak, which falls uniformly on the on both sides. So, there whenever I plot the energy and the excitation process, the band spectra will give me a Gaussian curve. Not necessarily Gaussian curve all the time, but 99 percent of the time you will be seeing a Gaussian curve in band spectra.

So, the life time and these are all associated with the vibrational energy levels. Not the electronic energy levels. The life time of vibrational energy state is approximately 10 raise to minus 15 seconds, within that time the whole excitation and emission occurs. Whereas, for an electronic transition it is only it is 10 raise to minus 8 seconds. You can imagine the difference almost 10 raise to minus 7 seconds is the difference; that means, the vibrational energy changes are 10 raise to 7 times faster than the electronic transitions. Therefore, transition always occurs from the lowest vibrational energy of the excited state to any of the vibrational energy of the ground state or the excited state. This I have already explained to you using the analogy of kicking a football from ground floor to higher floor with number of steps and each step is associated with number of smaller steps, that is they which represent floors represent, electronic energy level steps represent the vibrational energy level and small cuttings on the steps will represent rotational energy level. So, the loss of energy from vibrational energy levels to the vibrational, lowest vibrational energy the loss off energy. See generally what happens is whenever I have the energy levels are above the electronic level. So, the part of the energy slowly lost until it comes to the 0 level of the excited state. So, if it is higher than in the excited state if the vibrational energy is not 0. It may be 3 or 4 etcetera.

So, slowly they will lose a little bit of energy come to the ground state from there quantum jump to the lower energy state. So, but even the transition from one vibrational to low another vibrational level and one vibration rotational level to anther rotational level they also follow the quantum mechanical rules. So, it is nothing continuous from there. So, the lowest energy occurs through the how the energy loss occurs. The energy loss in vibration occurs by due to collision of the solvent molecules collision with other molecules. So, this energy loss is not usually represented as an absorption peak.

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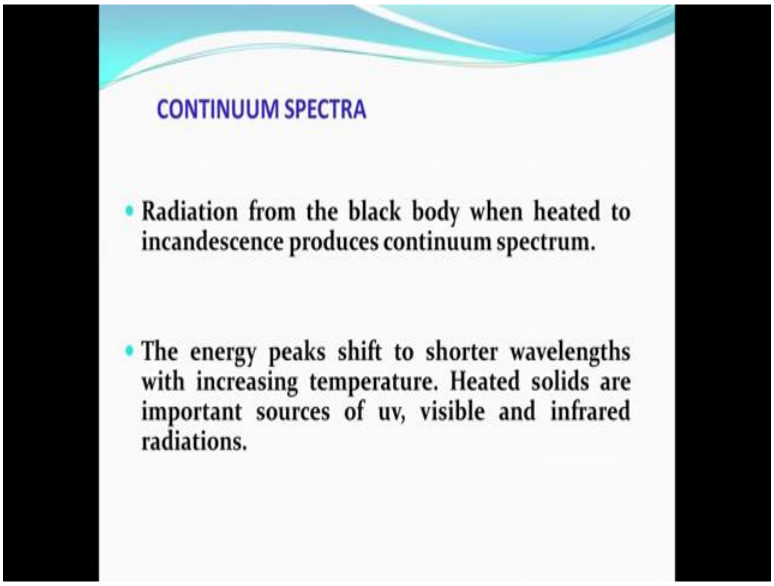

CONTINUUM SPECTRA

- Radiation from the black body when heated to incandescence produces continuum spectrum.
- The energy peaks shift to shorter wavelengths with increasing temperature. Heated solids are important sources of uv, visible and infrared radiations.

So, you now we talk about continuous spectra. In continuous spectra the radiation from the black body when heated to incandescence is what is the as a continuous spectrum. So, anything if you go to you are black smith and when he takes metal and keeps on heating it, and then before he beats it at that stage whatever radiation comes out when it is heated to red hot or white hot the we call it at still higher temperature, it becomes white. And that is a continuous spectrum. The radiation coming out from a black body around 3000 to 4000 degree centigrade, when it is heated whatever comes out is a continuous spectrum it is not a line spectrum it is not a band spectrum.

So, the energy peaks shift to shorter wavelength with increasing temperature. This is again a very well know phenomenon defined as wings law. And heated solids are important sources of ultra violet visible and infrared because it is a continuum spectrum. So, if I want to generate electromagnetic radiation, what I should do is suppose I want UV I want visible I want infrared or what I have to do is I just have to take a metal heated to the incandescence, I will get all the UV visible and infrared radiations from the metal.

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ABSORPTION OF SPECTRUM

- Absorption of electromagnetic energy by the atoms, ions and molecules promotes them to higher energy excited states according to the laws of quantum mechanics. The energy difference corresponding to each excitation is unique for each species thus permitting the characterization of the sample. This is usually accomplished by plotting absorbance as a function of wavelength or frequency.
- Absorption spectra differ widely in appearance from sharp peaks to smooth continuous curves depending on the physical state, complexity of the molecule and the environment of the sample (matrix).
- Atomic spectra of an element results in only a few simple lines as excitation can occur only at electronic energy levels of the outermost or bonding electrons only.
- Molecular absorption spectra are usually more complex involving quantized vibrational and rotational energy states. The energy of vibrational transition is much more than that of rotational transitions.

The 3 types of spectrum what we discussed are special. That is line spectra band spectra and continuum spectra. Now we talk about absorption of a spectra absorption spectra. So, atoms ions molecules, they as I have already explained to you they absorb electromagnetic radiation go to the excited state according to laws of quantum mechanics. The energy difference corresponding to each excitation is unique for each species or group of atoms this way also we have discussed number of times. So, how do you plot the energy difference. It is by plotting absorbance as the function of wavelength or frequency.

So, absorption spectra normally differ from the very sharp peaks to smooth continuous curve like a Gaussian curve depending on the physical state, complexity of the molecule and the environment of the sample. Suppose the I take the sample in a liquid state then the same absorption spectra will be in the liquid state will be different from the gaseous state or in the solid state. So, this is a very important aspect and it helps to know which state a substance is before we take the spectrum. So, the atomic spectra of an element results to only a few simple peaks. And excitation can occur only at electronic energy levels of the outer most or bonding electron you know you see it does not happen inner most electrons. Why because the inner most electrons are always you know satisfied with respect to quantum mechanical changes. Only the outer most electrons they are the once which undergo excitation emission absorption and all those things. So, the bonding electrons the are the outer most electrons only. So, the molecular absorption spectra are normally more complex involving quantized vibrational and rotational energy levels. The energy of vibrational transition is definitely much more than rotational and the energy of the excitation would be automatically higher than the vibrational energy levels.

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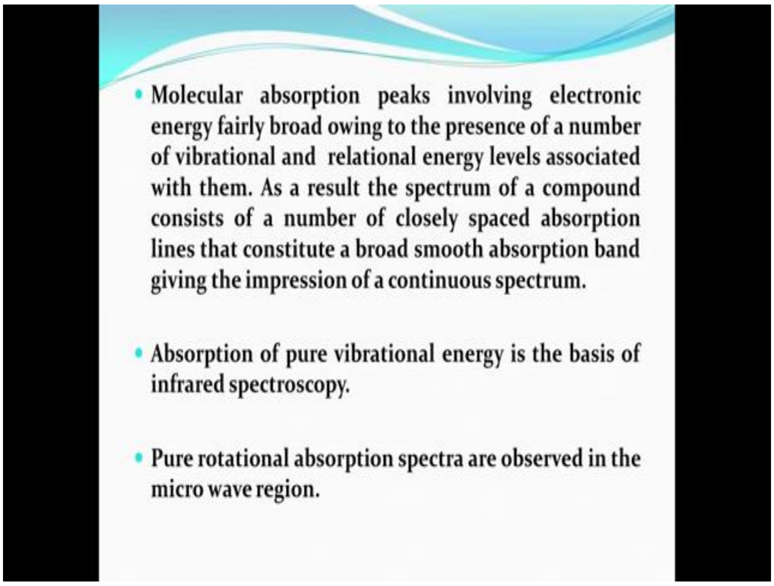

- Molecular absorption peaks involving electronic energy fairly broad owing to the presence of a number of vibrational and relational energy levels associated with them. As a result the spectrum of a compound consists of a number of closely spaced absorption lines that constitute a broad smooth absorption band giving the impression of a continuous spectrum.
- Absorption of pure vibrational energy is the basis of infrared spectroscopy.
- Pure rotational absorption spectra are observed in the micro wave region.

So, what we get actually is molecular absorptions peaks involving electronic energy transitions, they are fairly broad and owing to the presence of a number of vibrational and relational rotational energy levels, associated with them. As a result, what happens is the spectrum of a compound consist of a number of closely waste absorption lines that constitutes a broad smooth absorption band given the impression of a continuous spectrum. Basically it is not. So, for example, the molecular absorption what I was telling you is I wanted to show you a figure, how it will appear.

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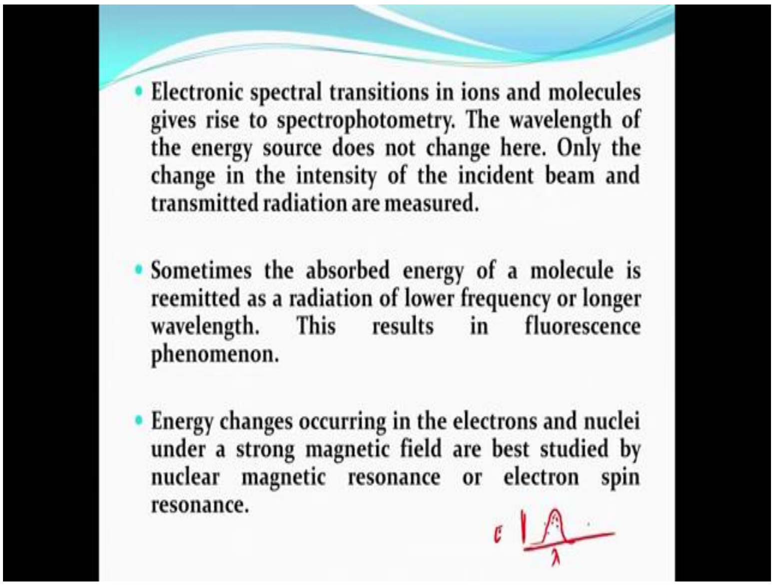

- Electronic spectral transitions in ions and molecules gives rise to spectrophotometry. The wavelength of the energy source does not change here. Only the change in the intensity of the incident beam and transmitted radiation are measured.
- Sometimes the absorbed energy of a molecule is reemitted as a radiation of lower frequency or longer wavelength. This results in fluorescence phenomenon.
- Energy changes occurring in the electrons and nuclei under a strong magnetic field are best studied by nuclear magnetic resonance or electron spin resonance.

As because the electrons, one electron may be here another electron may be here. So, there will be a group of electrons which are appearing as a peak e and wavelength. So, this you can keep it shows as a simple peak, but the transmitted radiations are always will always appear like this. Sometimes the absorbed energy is reemitted as a radiation of lower frequency. That is fluorescence and the energy changes occurring in the electrons and nuclear and the strong magnetic field are studied by nmr or esr, electron spin, but we are not going to study them this is only part of the continuation of our discussion on the molecular absorption spectra.

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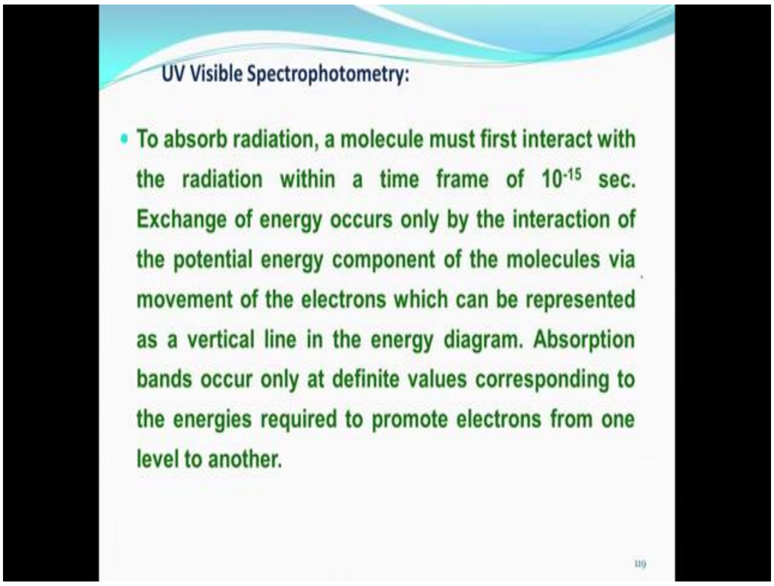

UV Visible Spectrophotometry:

- To absorb radiation, a molecule must first interact with the radiation within a time frame of 10^{-15} sec. Exchange of energy occurs only by the interaction of the potential energy component of the molecules via movement of the electrons which can be represented as a vertical line in the energy diagram. Absorption bands occur only at definite values corresponding to the energies required to promote electrons from one level to another.

So, this bring us that in spite of all the things that you have discussed earlier, we want to will be continuing our discussion mainly in UV visible spectrophotometry and related aspect that is turbidimetry and then fluorescence nefilometry etcetera. So, from now on our discussion will be mostly in UV visible spectrophotometry.

So, to absorb radiation, a molecule must interact with radiation within some time frame. This I have already explained to you that it could be it is of the order of about 10 raise to minus 15 seconds. So, the exchange of energy normally occurs only by the interaction of potential energy component of the molecules, because the molecules are at very high are in a state of agitation and the more electrons are also in a state of agitation, and they can be represented as a vertical line in the energy diagram. So, the absorption bands occur only at definite values corresponding to the energy changes required to promote the electrons from one level to another. This we have already discussed. And UV visible absorption spectrophotometry is no more different than other absorption spectrum.

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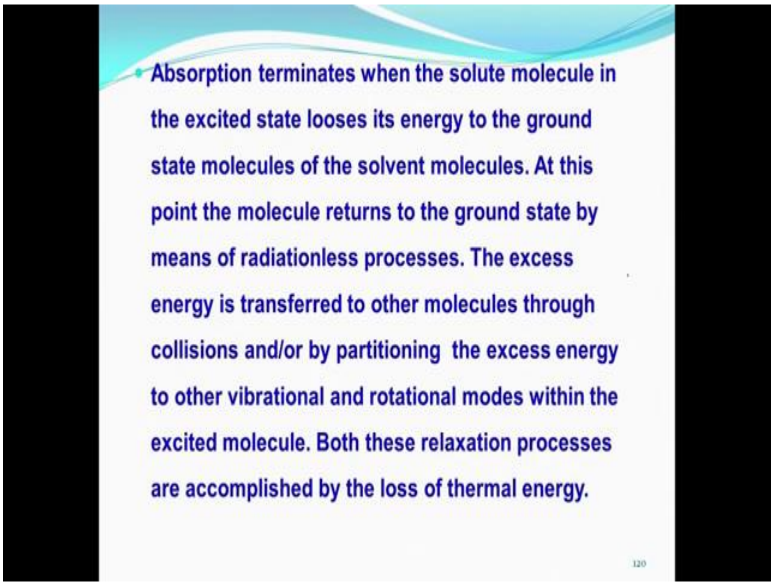

- Absorption terminates when the solute molecule in the excited state looses its energy to the ground state molecules of the solvent molecules. At this point the molecule returns to the ground state by means of radiationless processes. The excess energy is transferred to other molecules through collisions and/or by partitioning the excess energy to other vibrational and rotational modes within the excited molecule. Both these relaxation processes are accomplished by the loss of thermal energy.

So, when the solute molecule in the excited state loses it is energy, that is a solute molecule takes up the absorption and goes to higher energy state, but there is no emission the after sometime it loses it is energy, it falls back to the ground state and this solvent molecules absorb the additional energy that is released when it comes back to the ground state at this point the molecule returns to the ground state by means of radiation less processes; that means, no radiation, but only the release of heat; that means, the sample gets heated to certain extent.

So, the excess energy what happens to this heat energy. The excess energy is transferred to other molecules in the whenever in the medium. Suppose you are measuring a particular chemical and doing it in the aqueous medium. So, water molecules will be there. So, excess energy after absorption is transferred to water molecules. If you are doing it in a mivk methyl iso butyl ketone solvent the excess energy will be transferred to mivk solvent. If it is gaseous substances the other gas molecules will take up pick up the extra energy of absorption, when it driven the molecules comes back to the ground state. So, this happens by normal collision and kinetic theory takes care of it. And the excess energy to other vibrational and rotational all other modes will is within the excited molecule. So, both this relaxation processes are accomplished by the loss of thermal energy that is amount of amount of heat lost to the medium.

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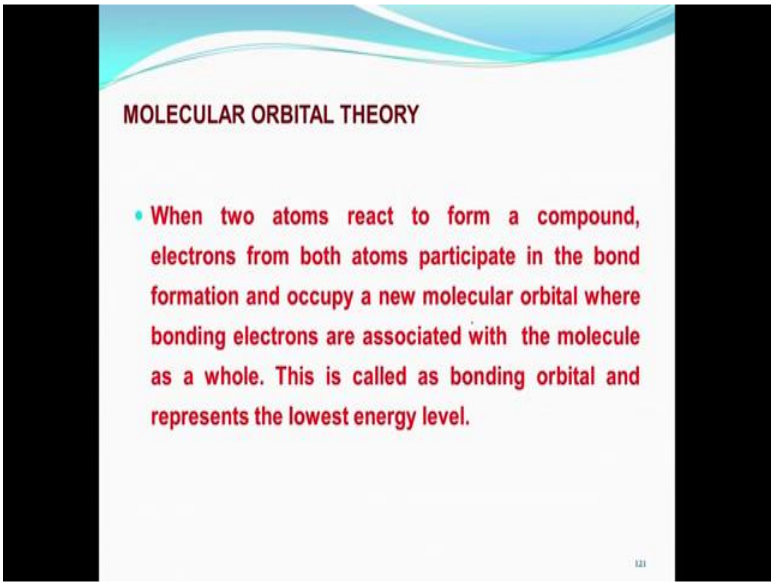

MOLECULAR ORBITAL THEORY

- When two atoms react to form a compound, electrons from both atoms participate in the bond formation and occupy a new molecular orbital where bonding electrons are associated with the molecule as a whole. This is called as bonding orbital and represents the lowest energy level.

So, now that bring us to the molecular orbital theory. Where to discuss this a little bit before we proceed in our discussion on the molecular absorption spectrum. So, what actually will be discussing is what happens when 2 molecules come and interact with each other. The 2 molecules whenever 2 atoms react to form a compound electron from both atoms participate that is understood. 2 atoms are there the come nearer and the electrons of one atom will react with the nucleus will be attracted by the nucleus of the other atom gets attracted and electrons from the nucleus will be at of one atom will be attracted by the electrons.

So, when 2 atoms interact to form a compound electron of both atoms participate in the bond formation. So, electron as I was explaining in to electrons of one atom will be attracted by the other nucleus and nucleus of one atom will be attracted by the electron of the other atom. So, whenever there is a chemical reaction there is bond formation from the outer most electrons. This is understood very simple. So, the when the molecule forms the electronic orbitals from molecular orbitals.

So, we do not call them no more electronic orbital, but we call them molecular orbitals. And in molecular orbitals bonding electrons are associated with the molecule as a whole. I think most of you are single bond double bond structures of several organic compounds and inorganic compounds and this is what we are talking about. Whenever there is a reaction of carbon atom there will be a sigma bond and then pi bond double bonds will be there triple bonds are also known and these are all molecular orbitals. So, there is a change in the molecular sigma bond a bond energy. This is called as bonding orbital, whenever a bond is formed the electrons occupy an orbital called as bond bonding orbital which represents the lowest energy state.

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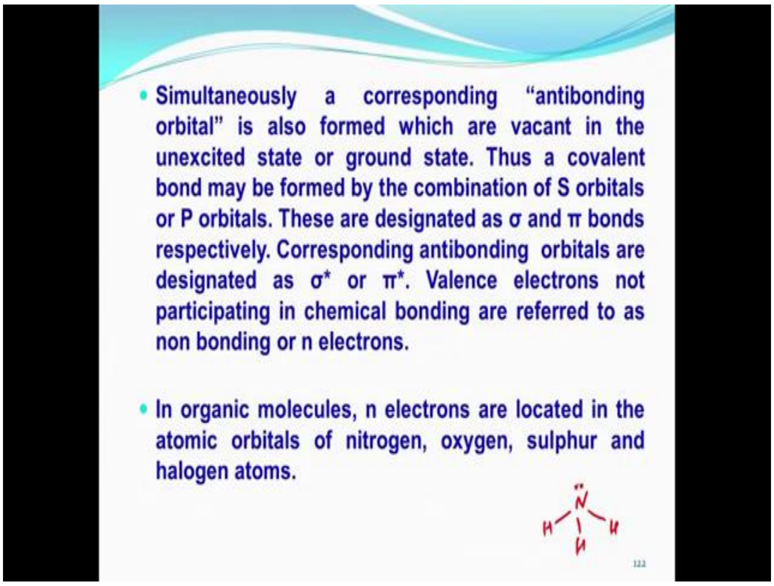

- Simultaneously a corresponding "antibonding orbital" is also formed which are vacant in the unexcited state or ground state. Thus a covalent bond may be formed by the combination of S orbitals or P orbitals. These are designated as σ and π bonds respectively. Corresponding antibonding orbitals are designated as σ* or π*. Valence electrons not participating in chemical bonding are referred to as non bonding or n electrons.
- In organic molecules, n electrons are located in the atomic orbitals of nitrogen, oxygen, sulphur and halogen atoms.

So, correspondingly an anti-bonding orbital also is formed, which are vacant in the ground state. Now imagine I have 2 hydrogen atoms and I bring them nearer. So, there will be attraction between the electrons and there will be a bond. And this bond is the lowest level. Now correspondingly there will be another level corresponding to this bonding orbital, there will be anti-bonding orbital at a higher state. So, at room temperature anti-bonding orbital are all vacant.

So, there is a possibility from the for the electron whenever I supply energy to the molecule the electron may be excited to be anti-bonding orbital still retain the molecular structure. So, this is what we normally expect whenever 2 molecules react with each other. There is a bonding orbital, but there is also a corresponding anti-bonding orbital which are normally vacant. So, a covalent bond all these things are known to you now because we know that a sigma bonds a covalent bond ionic bond we talk of all this thing a covalent bond is normally preferably present in most of the organic substances. So, we call them they are formed by the combination of the s orbitals or p orbitals of the carbon atoms and several other atoms also.

So, whenever there is a direct bond formation we call them as sigma bond, if it is a single bond we call it sigma bond, and if there is a double bond one of them would be pi bond. So, in an acetylene there is a one sigma bond and 2 pi bond triple bond. It is in ethylene there will be one sigma bond and one pi bond. So, it is a double bond in methane etcetera there are only sigma bonds. So, we have to imagine at this stage that every sigma bond is having an anti-bonding orbital known as sigma star. A pi bond will be having an anti-bonding orbital corresponding anti-bonding orbital that is pi star. So, normally valence electrons not participating in chemical bonding are referred to as nonbonding electrons or n electrons. Some times what happens is if you imagine a structure like ammonia. This is nitrogen this is hydrogen there is bond formation, but nitrogen is having 2 electrons, in the extra which are not involved in bond formation, but if I form an ammonium ion these 2 electron also will be these 2 electrons also will be involved in bonding.

So, these 2 electrons on the nitrogen are known as nonbonding electrons. So, what are the elements which have nonbonding electrons. These include nitrogen oxygen Sulphur a halogen atom and several other elements which are in in the periodic table, but in general in organic substances we normally come across nitrogen oxygen Sulphur and halogen atoms. So, all these atoms will be having nonbonding electron or n electrons in their functional groups; that means, we have 3 types of electrons in a molecule one is which is engaged in the formation of a sigma bond, engage in the formation of a pi bond thus there will be some extra electrons around the nitrogen or oxygen or Sulphur or phosphorus or many other things halogen atoms those electrons are not involved in bonding, but they can get excited to a anti-bonding orbital there is no guarantee that only the bonding electrons need to get excited to anti-bonding orbitals. Nonbonding electrons also can get excited to anti-bonding orbital and occupy them. So, whenever I take a substance which is having a compound like an element like nitrogen oxygen Sulphur the nonbonding electrons can also occupy the anti-bonding orbitals. So, that brings us to the shape of these orbitals.

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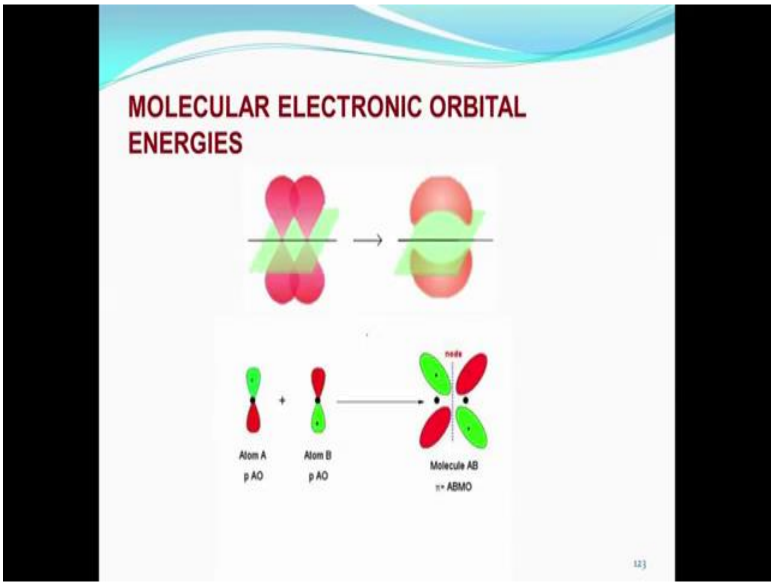

MOLECULAR ELECTRONIC ORBITAL ENERGIES

So, you can see here in this figure, I have molecular orbital here there is pi bonds and a molecular pi or bond pi bond will look something like this. And anti-bonding orbital would be looking the other way round. That is there it will be the space the electronic cloud will be occupied by at higher energy level these are the bonding orbitals.

So, here I have an atom A, and here I have p bond and then molecular orbital should be pi star. So, this would be the structure of the pi bond anti-bonding orbital at the bottom. On the top I have a bonding orbital.

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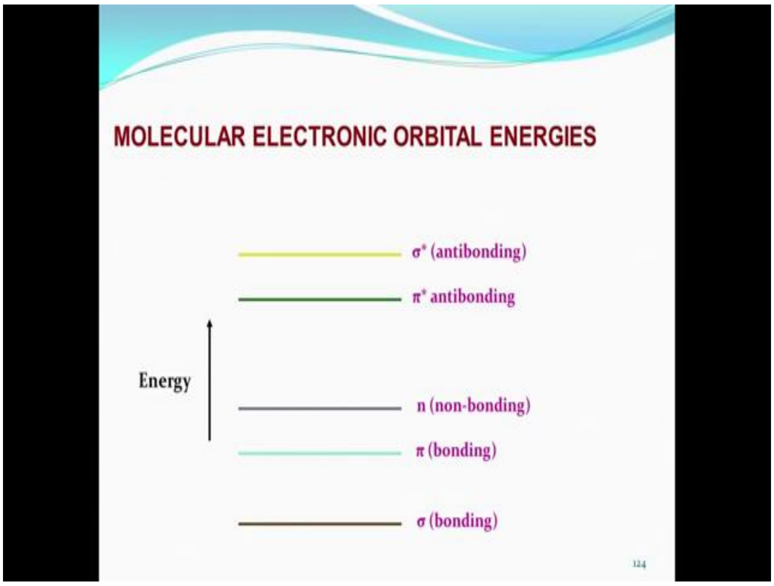

MOLECULAR ELECTRONIC ORBITAL ENERGIES

So, all it all I have 4 possibilities in a given molecule. One is sigma bond another is electrons occupy a sigma bond, electrons occupying a pi bond and electrons occupying nonbonding electrons. These 3 are at the lower level. So, these 3 are occupying at the lower level, that is sigma pi and n. Corresponding anti-bonding orbitals are pi star and sigma star; obviously, sigma star a sigma bonding is the lowest in energy levels. So, corresponding anti-bonding orbitals would be orbital would be highest sigma star. So, next is pi corresponding anti-bonding orbital would be lower than the sigma star pi sigma star. And then nonbonding electrons there is the corresponding nonbonding anti-orbital. The nonbonding anti-orbitals can only go to pi star or sigma star.

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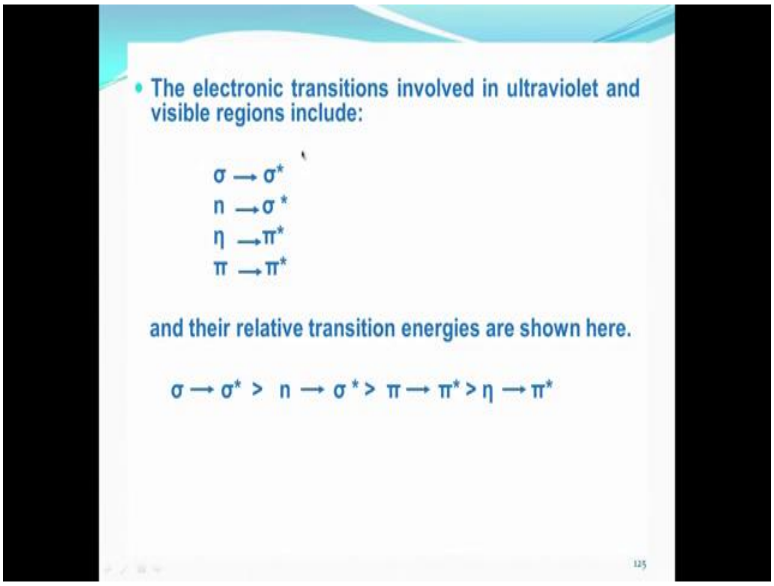

- The electronic transitions involved in ultraviolet and visible regions include:

$\sigma \rightarrow \sigma^*$

$n \rightarrow \sigma^*$

$\eta \rightarrow \pi^*$

$\pi \rightarrow \pi^*$

and their relative transition energies are shown here.

$\sigma \rightarrow \sigma^* > n \rightarrow \sigma^* > \pi \rightarrow \pi^* > \eta \rightarrow \pi^*$

So, in essence what we have is the electronic transition involved in ultra violet and visible regions, include sigma to sigma star n to sigma star, n to pi star and pi to pi star. And their relative transition energies are shown here. Which is sigma to sigma star is maximum energy n to sigma star is the next higher energy, and still lower would be pi to pi star and that would be greater than n to pi star. So, will come back to this basically regarding the atomic absorption the molecular absorption bonding and other things in the next class. And will be discussing more about the possible transitions of organic compounds that undergo these kind of changes, where the electrons are excited from bonding to no bonding orbital, how they can be used in our UV visible spectroscopy.

Thank you have a nice day.