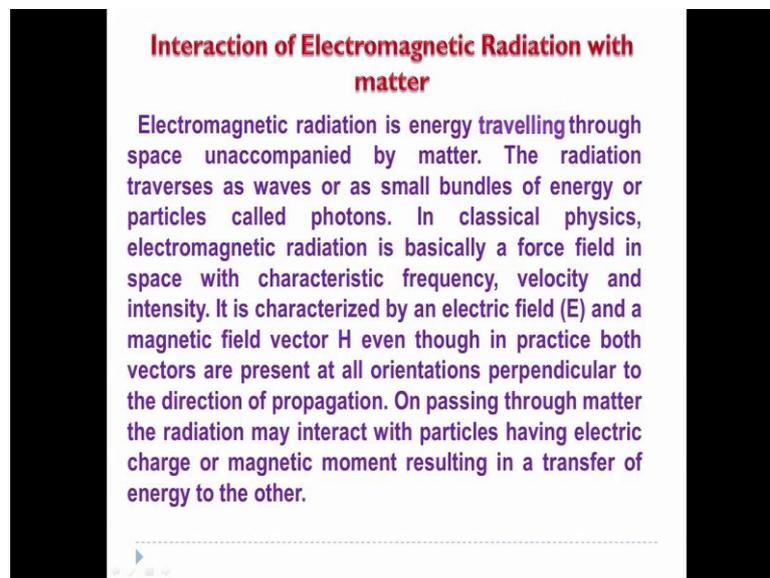


**Atomic and Molecular Absorption Spectrometry
for Pollution Monitoring
Dr. J R Mudakavi
Department of Chemical Engineering
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**Lecture – 03
Interaction of EM radiation with matter**

Greetings to you, this is a second class, we are having regarding the pollution monitoring and spectroscopic methods now. Yesterday, we have seen the interrelationship between the spectroscopic techniques and the pollution monitoring we also saw the; a little bit about the structure of the atoms which in which we elaborate and that the basic fundamental particle with are electrons protons and neutrons and even though there are other matters per sub atomic particles which may or may not have independent existence for this spectroscopic purpose is I think the basic structure of atom has containing electrons protons and neutrons are more than enough for the for our purpose.

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Now, , we will continue our discussion on the interaction of electromagnetic radiation with matter the slide that has come up in front of you is which states that electromagnetic radiation is basically an energy wave travelling through the space and accompanied by the matter that is radiation for example, if you wish to see light travelling it does not have a mass. So, it is just a form of energy and that is traveling through the space and

accompanied by the matter. So, how does this energy travel through a through the space basically almost all the electromagnetic radiations traverses either as waves or a small bundles of energy or particles bundles of energy particles called as photons you can contain both of the both waves Newton had proposed that light moves has waves and subsequently it was also provide that light also can be considered as a small bundle of particle contained called as photons.

So, in classical physics electromagnetic radiation is basically a force field in which the radiation is characterized by the frequency velocity and intensity for example, if we say that I have a wave electromagnetic wave corresponding to 490 frequency and its velocity is 3×10^{10} centimeter and its intensity is how many lumens. So, lumen the length is the unit for frequency and distance is the unit of velocity distance covered by per unit time or something like that and intensity is the amount of energy that the bundle of energy what we have been discussing.

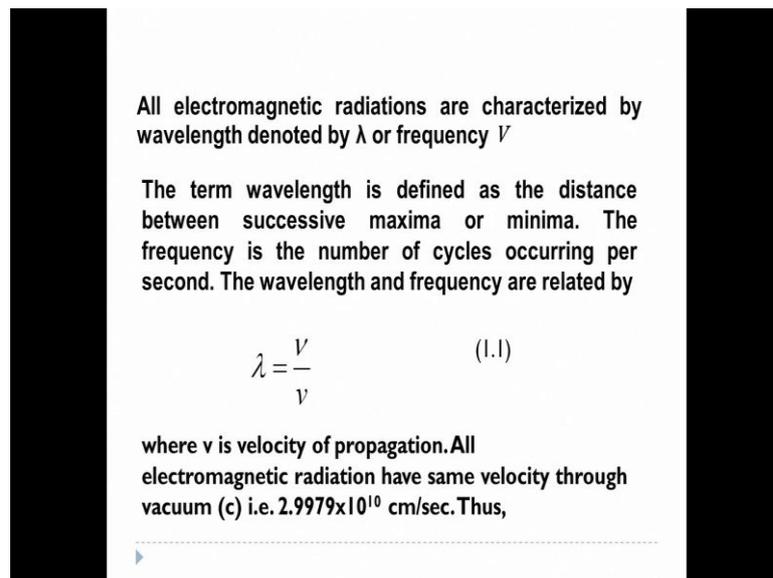
So, basically it is characterized by an electric field and a magnetic field, electric field is denoted by E and magnetic field is denoted by h both any electromagnetic wave whether it is cosmic ray or gamma rays or x rays or ultra violet rays or visible rays infrared rays microwave any of the radiation that we consider must be accompanied by an electric field and magnetic field these fields are in perpendicular direction to each other. In general, I will show your photograph of the this field vector and in practice both vectors are present at all orientations perpendicular to the direction of propagation; that means, if the light is traveling like this as a bundle of energy the force field will be all around it the light field will be passing through the centre and force field will be on the left side, right side, up above and below the field of propagation; that means, if the light is traveling the force field also be travelling along with that if we consider light has a photon on passing through the matter the radiation may interact with the particles of the matter having electric or magnetic moment resulting in a transfer of energy from one to the other.

What do we mean basically we are talking about light energy passing through light can pass through either in vacuum or in a air field or in an in air it can also pass through solid materials like glass and other things. So, if we are talking about a light travelling in a particular medium the medium may not contain anything that is vacuum the medium may contain air particle, sulphur dioxide, gas particles, gas molecules, etcetera sulphur

dioxide carbon monoxide nitrogen dioxide ozone and all these gases are present in our air atmosphere.

So, if the light was passing through an earth atmosphere it has to pass through all these medium containing different gases now these gas molecules are made up of atoms which are again made up of protons neutrons and electrons and the gas particles dust particles also will be there they also will have certain amount of mass and then electronic structure containing electron proton neutron etcetera and the electromagnetic radiation that passing through any of the medium will interact with these particles unless it is vacuum. So, if there is a matter present in the path of the light electromagnetic radiation there will be transfer of energy either from the electromagnetic radiation to the particles or from the particles to the electromagnetic radiation either read can happen. So, that is what we have been trying to say here.

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All electromagnetic radiations are characterized by wavelength denoted by λ or frequency ν

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

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

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

So, all electromagnetic radiations are therefore, characterized by wavelength denoted by lambda or frequency that is ν the term wavelength is defined as the distance between successive maxima or minima now you remember that I discussed that the light particles will be going like this waves and the successive waves or distance between 2 adulations or crust or the troughs when the wave goes like this there will be a trough as well as a crust. So, in between the distance between the 2 successive maxima or minima is determined is termed as wavelength that is the distance the frequency is number of

cycles how many how many how crusts appear or how many troughs appear in a per unit time that is per second.

So, the wavelengths and frequency are related by lambda is equal to velocity divided by the frequency here nu is the frequency and V is the velocity. So, velocity of propagation all electromagnetic radiations in general have the same velocity through the vacuum that is 2.9979 into 10 raise to 10 centimeters per second.

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$$\lambda = \frac{c}{\nu} = \frac{2.9979 \times 10^{10}}{\nu} \quad (1.2)$$

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

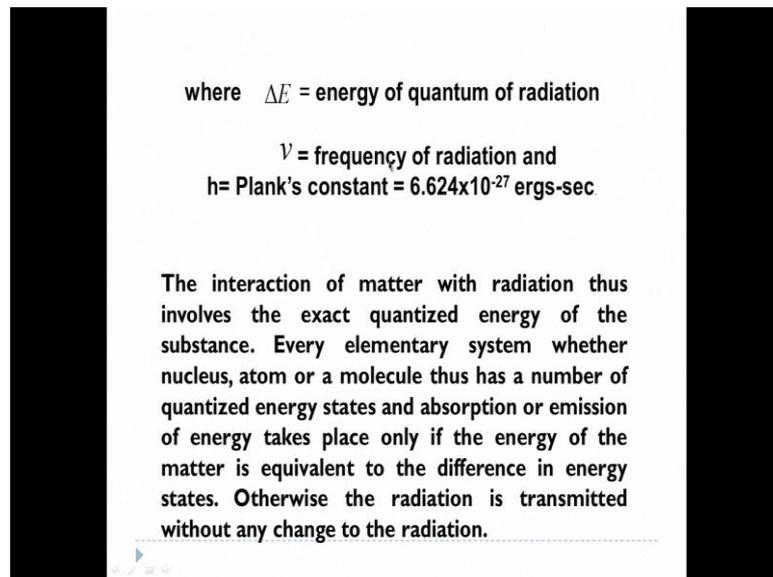
$$\bar{\nu} = \frac{1}{\lambda} \quad (\text{cm}^{-1}) \quad (1.3)$$

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

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

So, that we calculate the approximate this thing frequency is expressed as number of cycles per second or where it is also denoted by wave number that is denoted by nu bar and it is written here and the nu bar wave number is given by one over lambda that is wavelength the distribution of the spectral density intensity in a black body radiation was explained by Max Planck in 1900 by uniting the corpuscular theory that is light made up of photons as bundle of energy particles and wave theory is a relation between the energy of a quantum radiation to the frequency as given by this expression that is delta E is equal to that is energy is equal to h nu h is Planck's constant nu is frequency nu is also given by velocity of light divided by the wavelength.

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where ΔE = energy of quantum of radiation

ν = frequency of radiation and
 h = Planck's constant = 6.624×10^{-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 to the radiation.

So, this is a very famous equation and the interaction of matter with radiation therefore, it involves the exact quantized energy because it is not a continuous energy as of now every elementary system whether nucleus or atom or a molecule thus has a number of quantized energy states and absorption emission of energy must take place only if the energy of the matter is equivalent to the distance between the energy states. So, the if it is not matching if the energy of the 2 states does not match with the energy of the radiation then there is no interaction it will just pass through the matter without showing any change either in the velocity or in the energy or something like that.

But if there is a matching between the energy states as described by Planck's theory that is energy is quantized in discrete energy levels. So, in between there is a gap of energy and that gap is not occupied that space is not occupied by any particle or any transition during interaction. So, the radiation is transmitted without any change if there is if it does not match the quantum requirements.

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

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

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

$$h\nu = hc / \lambda = E_i - E_f \quad (1.6)$$

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 it may be used up in absorption, emission, reflection, refraction, diffraction or in scattering. Thus

So, the energy or frequency which the incoming photon is absorbed is given by this energy is given by the Bohr equation that is $h\nu$ is equal to hc/λ that also should be equal to energy of the final state and minus the energy of the initial state of the substance; that means, we assume that the electrons occupy particular energy levels one energy is E_i higher energy is E_f and the difference between the energy difference between E_f and E_i is given by $h\nu$ that is hc/λ .

In the case of emission of energy the; this much amount of energy is released. So, the again whether it is absorption or emission between 2 states of energy levels the energy absorbed is same as the difference between the 2 states as well as if it is emitted again the energy difference is exactly the same that is again given by $h\nu = hc/\lambda$ in this case it is energy of the initial state minus energy of the final state in the now when we refer to E_i and E_f that is energy of the final and initial states we if it is emission the final energy state will be at a lower energy and if it is absorption the final energy state would be at a higher energy level.

The only difference between the 2 between emission and absorption in practice therefore, what we say in practice whenever a radiation of multiple frequency; that means, we are not talking of the single energy of a single wavelength I am talking of a bundle of energy coming like this bundle of energy going like this containing energies of different

frequencies different wavelength for example, the sunlight what you see is a bundle of energy containing multiple frequency.

Similarly, if you see only a blue light it means it has got only single frequency white light in general we know from Newton's theory that its contains about seven different colors of the light apart from that there will be different energy electromagnetic radiations which are not visible to us there may be cosmic rays there may be gamma rays there may be u V rays, but they are not visible. So, if I am looking at a source of energy a electromagnetic radiation coming from the sun it will be a bundle of energy. So, this bundle of energy will have multiple frequency if such a radiation interacts with the matter part of it may be absorbed part of it may be used for emission part of it may be reflected again part of it may be refracted part of it may be diffracted or part of it could be scattered away.

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$$E = E_{\text{abs}} + E_{\text{emi}} + E_{\text{Ref}} + E_{\text{Ref}} + E_{\text{Diff}} + E_{\text{sca}} + \dots$$

(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 Table I.

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

So, there are different kinds of interaction will take place when a multiple energy radiation reacts with a with the matter therefore, we can write as very simple expression like this total energy E refers to energy of absorption energy of emission and that is energy of emission part of it is reflected refracted and then diffracted scattered and their maybe so many other interactions which we may not be going into details. Now, therefore, various types of quantized energy changes occurring in each region of the spectrum and the magnitude of energy involved have been traditionally used for a variety

of spectrochemical techniques; that means, what we are saying is the quantized energy levels because they occur at particular energy difference and the energy difference between 2 states are different for different kinds of molecules the any transition that can be occurring could be the characteristic of the substance therefore, such transitions have been used for as a spectrochemical technique.

The energy ranges normally we always say it is gamma rays it could be x rays it could be u v visible, it could be infrared it could be microwaves radio frequency rays etcetera etcetera the absorption of radiation occurring at different wavelengths and associated spectroscopic techniques I have given them in the next table. So, you can see that I am going to the table right now.

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Wavelength	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

This is the table of u visible range here you can say I put wavelength on the light transmitted color and complementary hue. So, this is 3 hundred and eighty nanometers that is less than 380 nanometer that is considered as ultraviolet this I am talking only about the sunlight basically.

What colors we see and experience in our day to day life for example, from 380 to 435 wavelength if an energy of radiation contains wavelengths between 380 to 435, what you will see it will transmit violet light and what you will be actually seeing would be yellowish green there; that means, what is transmitted remaining is absorbed. So, what it absorbs is a color, what we say that is what we write it as complementary hues it is H U

E S hues. So, from suppose it contains 435 to 435 nanometers, it will transmit all blue colors and the remaining colors that are not transmitted are absorbed and it will look yellowish yellow color.

Similarly, if we go down the visible range that is 4 eighty to 4 ninety we have greenish blue transmitted color and it looks somewhat orangish. So, if a substance is looking orange to you it only means that it is transmitting greenish blue color and absorbing all other color the combined effect of all other colors that is a substance is showing is orange it is not the transmitted color similarly if we go down for ninety to five hundred we will look bluish green, but we will transmit bluish green, but we will transmit bluish green, but it will look dark red to you and 500 to 560 range nanometer it will transmit green and it will show you purple color and five sixty to five eighty yellowish green and it will look violet to you we are all very familiar with all these colors which all I am showing you has a complimentary hues these are all colors of the rainbow if you have ever seen a rainbow in your in the sky you would see that yellowish green yellow orange red purple violet blue green etcetera all these colors are visible in the rainbow.

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It must be noted that there is 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.

Mono atomic 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 4.4

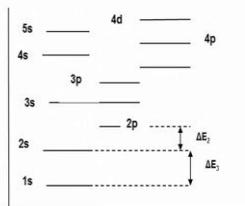
Similarly, the remaining ranges yellow, orange, red near infrared, all these colors are visible to you all these colors are visible to you. So, it must be noted that when I go back to this the range is not exactly sharp it is 380 to 435 does not mean it is exactly 435, but it could be 444, 445 like that the range is not sharp at any wavelength, but rather they

merge into one another in a diffused manner like a rainbow and the absorption of radiation normally involves transfer of energy to the medium and this process is a specific phenomena 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 are existing in the number of vibrational energy levels I cannot pin point that the energy is only corresponding will go only through that process.

Therefore if a number of atoms are present in number of vibrational energy levels what I normally see in is vibrational energy level is also associated with number of rotational energy level I will show you a diagram regarding that. So, any energy level is associate is called as electronic energy level and then each electronic energy level is associated with number of vibrational energy levels and then each vibrational energy levels is associated with number of rotational energy levels. So, when I am talking of electronic energy level is it me I am also it means I am talking of a number of vibrational and rotational energy levels associated with each of these and every molecule can be in any of the electronic energy level maybe same, but it can be in any of the associated vibrational and rotational energy.

So, the each of these molecules will differ by a small amount of energy. So, it therefore, if I draw a absorption of a substance it it will appear like a band a big curve Gaussian curve instead of a sharp peak single line peak. So, many atomic substances normally exist in gaseous state and absorb radiation only through the; and increasing their electronic energy. So, all these things and there is no need to emphasize again that they are all quantized and appear in various sub shells.

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For poly atomic 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 poly atomic molecules; that means, a substance which is a single mono atomic means the existing gas molecules existing as single molecule or it may be a group of they are known as poly atomic molecules.

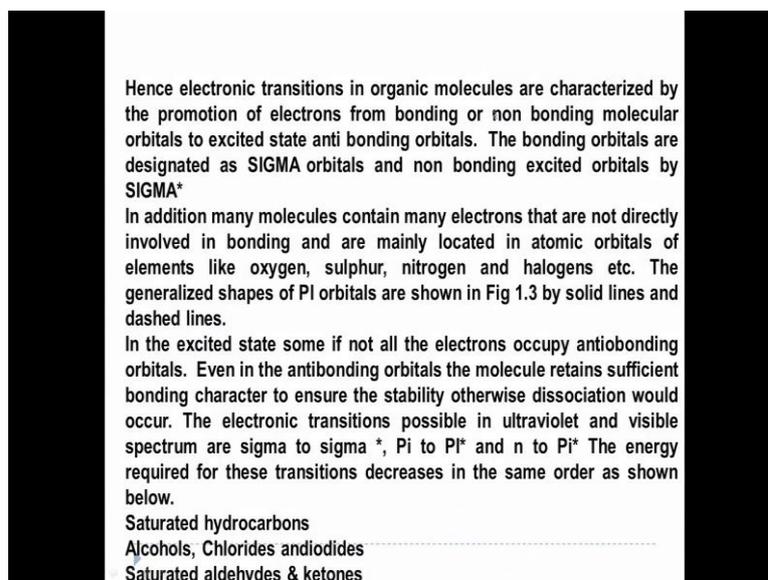
So, for example, if it is hydrogen then it is a mono atomic if it is oxygen it is a mono atomic substance, but if it is carbon dioxide it contains carbon and 2 oxygen atoms. So, it is a poly atomic molecule. So, functional groups aldehydes, ketones and several other substances occupy they are all known as poly atomic molecules. So, poly atomic molecules electro for them the electronic transitions involve not atomic orbitals, but molecular orbitals because the orbital energy level for poly atomic molecules they contain number of molecules associated with each other therefore, these atomic orbitals merge into each other to form molecular orbitals. So, for single atoms we call them atomic orbitals and for number of molecules if they are there the resulting energy levels are called as molecular orbital.

So, for poly atomic molecules whenever we talk of transition from one energy state to another state we call it has molecular orbitals reveals and these are more complex than the atomic orbital because we know that in atomic orbitals s orbitals is round shaped P orbital is dumbbell shaped like that we know very simple structures, but for polyatomic molecules there will be several SS orbitals may be merging with each other several P orbitals may be merging with each other therefore, the structure actually if we imagine in

a 3D structure there will be much more complex therefore, the total energy maybe considered as a some of the contributions from all states of energy for each energy electronic energy state of the molecule there exist several possible vibrational state this I have already told you know and for each of these intern they contain numerous rotational energy levels.

Now, here in this figure I have shown you number of energy levels this is one s this is 1S, this is 2S, this is 2 P and then 3 S, 3 P and then 3 D, 4 S 3 D like that there are different energy levels associated with a an atom as well as a molecule only difference is for single atom mono atomic substances we call them orbitals and if there are number of atoms we call them poly atomic orbitals.

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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 SIGMA orbitals and non bonding excited orbitals by SIGMA*

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 PI orbitals are shown in Fig 1.3 by solid lines and dashed lines.

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 to sigma *, Pi to Pi* and n to Pi* The energy required for these transitions decreases in the same order as shown below.

Saturated hydrocarbons
Alcohols, Chlorides and iodides
Saturated aldehydes & ketones

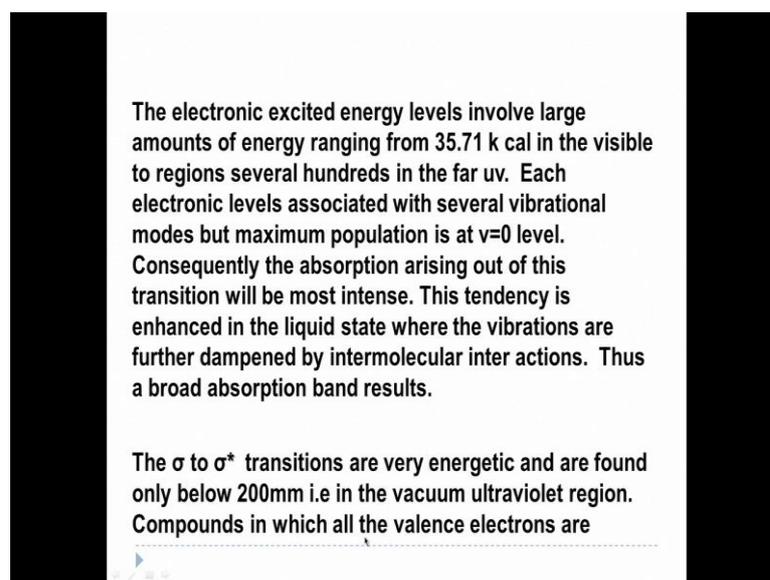
So, electronic transitions in organic molecules are characterized by the promotion of electrons from either bonding or non bonding electrons what are bonding electrons bonding electrons are the substances in which there is a chemical bond as we see in many chemical structure they will be associated with sigma bond pi bond like that the electrons are bound in a particular energy level pi bonds they are also bound in this thing, but there are a number of a atoms number of electrons where the electrons are free to move around the atom. So, we will see some of these structures after about some after about 5-10 minutes for the time being what I want you to do is to remember is the

bonding orbitals are designated as sigma bonds and the nonbonding orbitals are designated as pi, pi star etcetera.

If an electron situated in a sigma bond that is bond between 2 atoms gets excited to higher energy level then I have a transition from sigma to sigma star now there if suppose there is a pi bond just like an ethylene. So, there is one sigma bond and one pi bond in which the electrons are shared now a pi bond is also bound to the atom, but in a different fashion at a slightly lower energy level that also I can excite the it to the next higher energy level that is known as pi to pi star the lower energy level is pi and higher energy level is pi star designated as pi star. So, if not all the electrons are bound they may be there may be a chemical bonding as you remember ionic bond covalent length bond coordination bond etcetera and then there could also be the electrons which are free around the nucleus for example, in they are called as loan pair of electrons.

So, in the excited state if not all the electrons occupy anti bonding orbitals even in anti bonding orbitals the molecule retain sufficient bonding character to ensure the stability of the system otherwise dissociation would occur. So, whenever we talk of a substance which is having higher energy level; that means, the molecule is at a higher energy state excited, but it is not completely dissociated. So, this means that energy is excited; that means, I have used part of the energy of the electromagnetic radiation to increase the energy level to higher state, but still the molecule is impact the moment I take off my energy that is electromagnetic radiation it will revert to the ground state and be stable. So, the electronic transitions possible in uv and visible spectrum are basically designated as sigma to sigma star pi to pi star and n to pi star these are n means non bonding electrons the energy required for these transitions it decreases in the same order as shown below.

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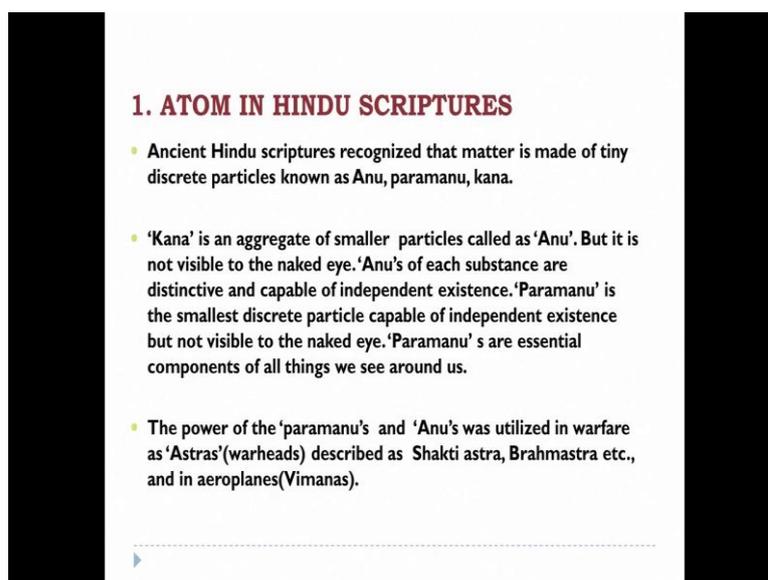
The electronic excited energy levels involve large amounts of energy ranging from 35.71 kcal in the visible to regions several hundreds in the far uv. Each electronic levels associated with several vibrational modes but maximum population is at $v=0$ level. Consequently the absorption arising out of this transition will be most intense. This tendency is enhanced in the liquid state where the vibrations are further dampened by intermolecular interactions. 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. Compounds in which all the valence electrons are

Now, saturated hydrocarbons alcohols chlorides all these are different organic compounds that we come across in our day to day life. So, the electronic energy excited energy levels involve large amount of energy this you must understand whenever we talk of ultraviolet or visible absorptions spectrometry we are talking of electronics excited energy levels excitation only in the electronic range that is the range from 35.71 kilo calories in the visible range, but it can extend up to several 100 kilo calories in the far ultraviolet range. So, each electronic level associated is associated with several vibrational energy levels that I have already told you and each vibrational energy level is associated with number of rotational energy levels. So, consequently the absorption arising out of this transition would be most intense, but 0 to one. So, that will be most intense and this tendency is enhanced in the liquid state where vibrational energy levels are dampened by the electronic molecular and interactions and abroad absorption band results.

So, sigma to sigma star transitions are very energetic and are found only below 200 millimeter that is 200 nanometer that is in the vacuum ultra violet range. So, in general you do not see sigma to sigma star transitions in which all the valence electrons are present.

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1. ATOM IN HINDU SCRIPTURES

- Ancient Hindu scriptures recognized that matter is made of tiny discrete particles known as Anu, paramanu, kana.
- 'Kana' is an aggregate of smaller particles called as 'Anu'. But it is not visible to the naked eye. 'Anu's of each substance are distinctive and capable of independent existence. 'Paramanu' is the smallest discrete particle capable of independent existence but not visible to the naked eye. 'Paramanu' s are essential components of all things we see around us.
- The power of the 'paramanu's and 'Anu's was utilized in warfare as 'Astras'(warheads) described as Shakti astra, Brahmastra etc., and in aeroplanes(Vimanas).

So, pi to pi star transitions you will see them in the visible range ultraviolet range etcetera in addition you will see non bonding transitions that is electrons not involved in bonding, but they also get excited to higher energy level that is pi star n to pi star is a very well known example many of these reactions are also known as the charge transfer reactions. So, such things are also visible in ultraviolet and molecular spectroscopic which we will be dealing with in our next session.

Thank you.