Advance Analytical Course

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Lecture No. # 26

Introduction to spectroscopy – spectroscopy is a very vast area, but proper understanding of the electromagnetic radiation and the spectrum of race belonging to the electromagnetic radiation is very important. Why, because each area of electromagnetic radiation has to contribute something to molecular structural determination. And, that is the advantage of using various regions of UV region, visible region, IR region, radio frequency region for different types molecular structural detailing. And, it is the beauty that each one contributes only a part of information about the molecule. So, let us try to understand what spectroscopy has to offer.

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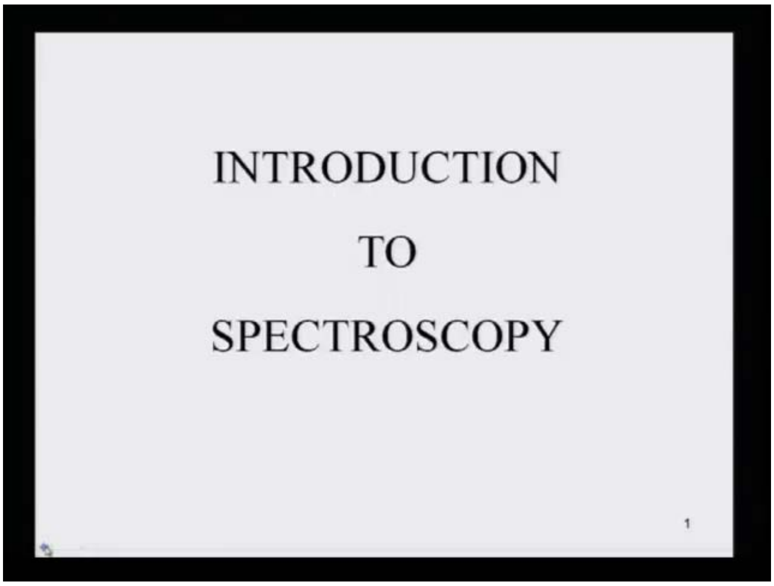

INTRODUCTION
TO
SPECTROSCOPY

We have been referring to very important two techniques in analytical chemistry: one is the chromatographic technique and the other one is the spectroscopic technique. The chromatographic technique is responsible for the separation of complex mixtures, so that individual compounds can then be analyzed on spectroscopic methods.

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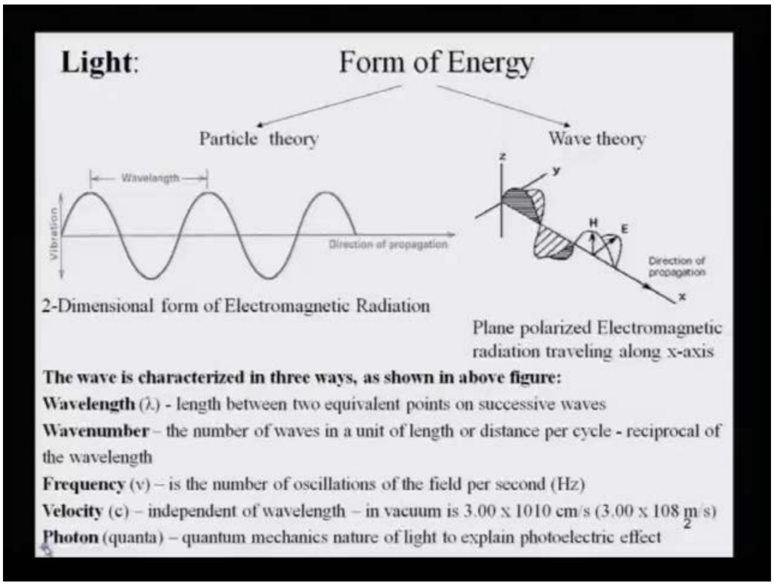

Light: Form of Energy

Particle theory

Wave theory

2-Dimensional form of Electromagnetic Radiation

Plane polarized Electromagnetic radiation traveling along x-axis

The wave is characterized in three ways, as shown in above figure:

Wavelength (λ) - length between two equivalent points on successive waves

Wavenumber – the number of waves in a unit of length or distance per cycle - reciprocal of the wavelength

Frequency (ν) – is the number of oscillations of the field per second (Hz)

Velocity (c) – independent of wavelength – in vacuum is 3.00 x 1010 cm/s (3.00 x 108 m/s)

Photon (quanta) – quantum mechanics nature of light to explain photoelectric effect

If we try to look at the various forms of energy and particularly with respect to light, it can be explained by wave theory or by particle theory – 2-dimensional form of electromagnetic radiation; plane polar electromagnetic radiation travelling along an x-axis. So, it is debatable whether the energy or the light is in form of a particle or a wave. Nevertheless, we still consider it as a wave. The wave is characterized in three ways as shown in the above figure. It can be described as a wavelength, that is, the difference between the two humps; or, it is described as wave number, that is, the number of waves in unit length or distance for cycle – reciprocal of wavelength. So, if we say wavelength, then it is the reciprocal of wave number; or, it can be expressed in terms of frequency nu – is the number of collisions of the field per second; that is expressed in hertz. It can also be expressed in terms of velocity, c – independent of wavelength – in vacuum, the velocity of light is considered as 3 into 10 to the power of 10 centimeters per second; or, it can again be called as photon or quanta. Quantum mechanics nature of light to explain the photoelectric effect is where the photon term is used. Most popularly, we talk about the wavelength or the frequency. The wave number, the velocities are not so frequently used when we are referring to different radiations of electromagnetic radiation.

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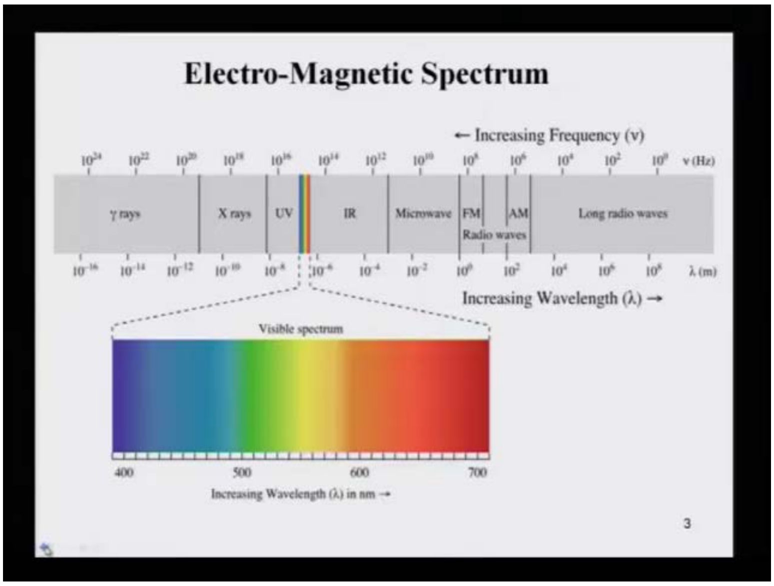

Electro-Magnetic Spectrum

Now, if you try to look at this particular slide, you will see that the areas are very clearly demand – the X ray area, the gamma ray area, the UV area. And, you will see a very small visible region, which has been expanded at the bottom. And then, next to the visible region is the IR region. Then, comes the microwave region; then, comes the FM radio waves and the AM radio waves. And furthermore, are long radio waves, which are responsible for the NMR analysis. So, you see that the entire spectrum, as I mentioned a little while ago, different regions and their energy or their wavelength are having certain properties, which can excite only some part of a molecular structure, and therefore, imparts information only about that part. So, X rays will give inner bonding and crystal lattice structures information; UV will give information related to unsaturation in the molecule; IR will give information related to the functional groups that are present in a molecule, and so on and so forth.

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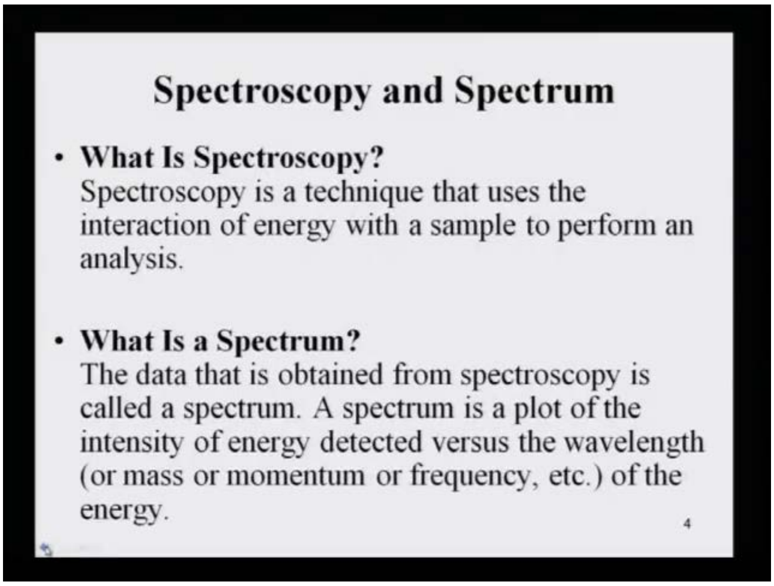

Spectroscopy and Spectrum

- **What Is Spectroscopy?**
  Spectroscopy is a technique that uses the interaction of energy with a sample to perform an analysis.

- **What Is a Spectrum?**
  The data that is obtained from spectroscopy is called a spectrum. A spectrum is a plot of the intensity of energy detected versus the wavelength (or mass or momentum or frequency, etc.) of the energy.

Now, what is meant by term spectroscopy and what is a spectrum? It should be clearly understood. Spectroscopy is a technique that uses the interaction of energy with a sample to perform an analysis. So, the technique is called spectroscopy. And, the data that is obtained from the spectroscopy is called a spectrum. A spectrum is a plot of intensity of energy detected versus the wavelength or mass or momentum or frequency of the energy. So, spectrum is the graph that it is obtained out of this spectroscopic analysis.

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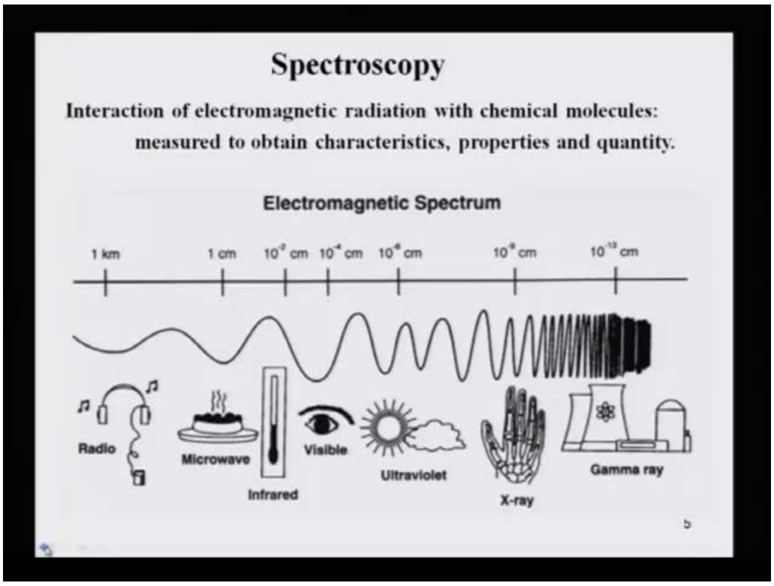

Spectroscopy

Interaction of electromagnetic radiation with chemical molecules: measured to obtain characteristics, properties and quantity.

Electromagnetic Spectrum

Now, this is a very interesting slide, where I want to draw your attention to see how the interaction of electromagnetic radiation can really affect our day-to-day life and our molecular structures, and the molecules that we deal within day-to-day life. And, it is measured by the characteristics, and the properties, and the quantity. Radio waves are responsible for FM; radio waves are also responsible for NMR. Microwaves are responsible for different types of digestion processes that I had covered a while ago; and, they are also used in domestic purposes for baking cakes. Infrared is a region, where we get functional, the thermometers; and, different types of infrared heating devices are made out of it. Visible region is what we can see. Ultraviolet is related to sunlight. X rays are related to the X rays that are taken for broken bones or even intact bones. And, gamma rays of course, we know, are used in different other purposes. So, this was just to give you an overall idea – how spectroscopy even plays a very important role in our domestic life.

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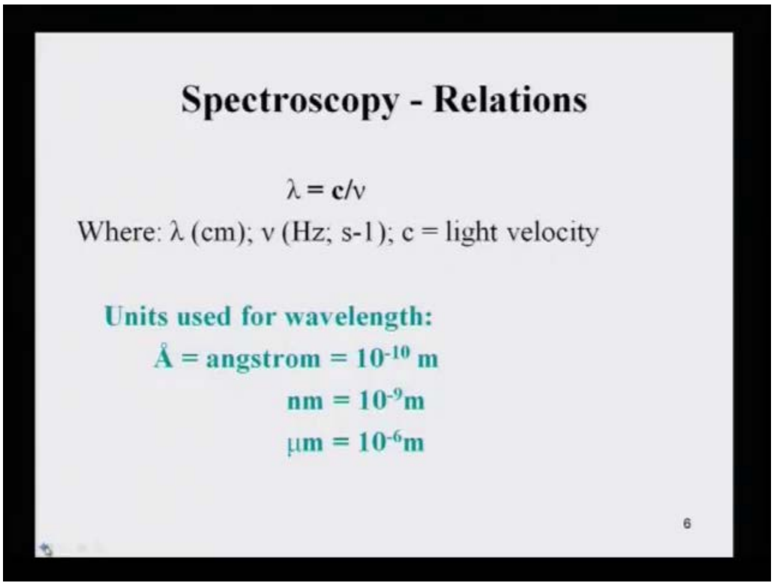

Spectroscopy - Relations

$\lambda = c/v$

Where: λ (cm); v (Hz; s-1); c = light velocity

Units used for wavelength:

Å = angstrom = 10^{-10} m

nm = 10^{-9}m

μm = 10^{-6}m

Now, when we try to look at the spectroscopy and the relationship between them, the wavelength is directly proportional to the frequency. And, when we try to find out the sign of proportionality, it is always replaced by a constant. And, here c is the velocity of light. So, lambda, which is the wavelength, is equal to c by v. And, the units of wavelength are normally angstrom, which is 10 to the power of minus 10 meters; or, 10 to the power of minus 9 if it is nanometer; if it is micrometer, it is 10 to the power of minus 6 meters. So, these are certain relationships, which I wanted to make it very clear to you, because time and again, we will be referring to angstrom or nanometers, and one should know where does it stand in a meter scale.

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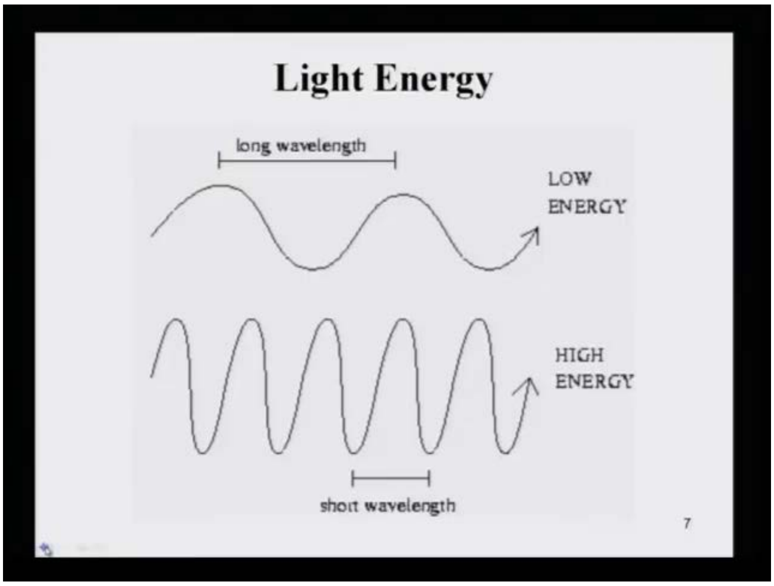

Light Energy

Now, light energy could have a longer wavelength, but that longer wavelength light will have lower energy; or, it may have shorter wavelength and light will have higher energy.

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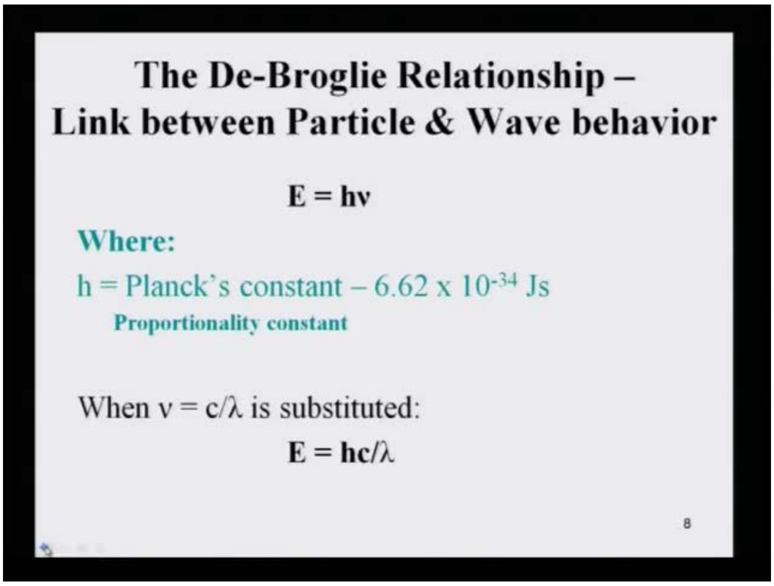

The De-Broglie Relationship – Link between Particle & Wave behavior

$$E = h\nu$$

Where:

h = Planck’s constant – 6.62 x 10^{-34} Js

Proportionality constant

When $\nu = c/\lambda$ is substituted:

$$E = hc/\lambda$$

The De-Broglie relationship link between particle and wave behavior should also be understood, because whether it is a particle or a wave, it must be understood very clearly. E is equal to h nu; where, h is Planck’s constant and it also a sign of proportionality; or, when we can say that nu is c by lambda. So, it can be substituted that E is equal to h c by lambda. So, these are different relationships of energy with Planck's constant with velocity of light and wavelength and frequency. So, how they are interrelated must be understood.

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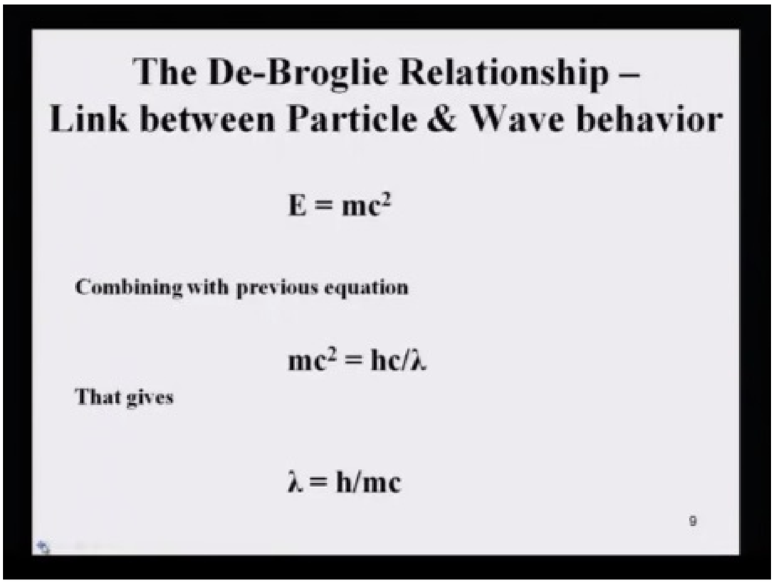

The De-Broglie Relationship –
Link between Particle & Wave behavior

$$E = mc^2$$

Combining with previous equation

$$mc^2 = hc/\lambda$$

That gives

$$\lambda = h/mc$$

The De-Broglie relation with E is equal to m c square is also very well-known. Combining with the previous equation, that is, c is equal to m c square, that will be equal to h c by lambda; or, that gives that lambda is equal to h by m c. So, these are different types of energy, mass, and wavelength, and velocity of light, Planck's constant. How they are connected to each other – De-Broglie relationship gives this equation very clearly.

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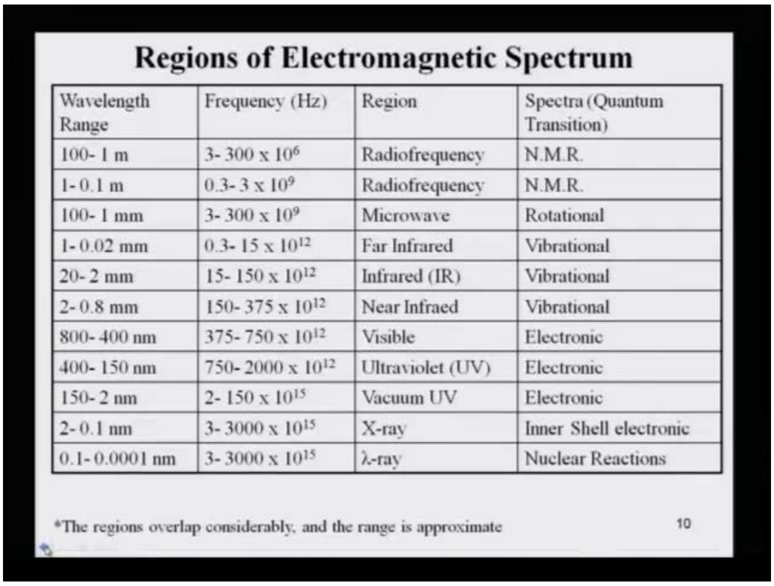

Regions of Electromagnetic Spectrum

Wavelength Range	Frequency (Hz)	Region	Spectra (Quantum Transition)
100- 1 m	3- 300 x 10^6	Radiofrequency	N.M.R.
1- 0.1 m	0.3- 3 x 10^9	Radiofrequency	N.M.R.
100- 1 mm	3- 300 x 10^9	Microwave	Rotational
1- 0.02 mm	0.3- 15 x 10^{12}	Far Infrared	Vibrational
20- 2 mm	15- 150 x 10^{12}	Infrared (IR)	Vibrational
2- 0.8 mm	150- 375 x 10^{12}	Near Infraed	Vibrational
800- 400 nm	375- 750 x 10^{12}	Visible	Electronic
400- 150 nm	750- 2000 x 10^{12}	Ultraviolet (UV)	Electronic
150- 2 nm	2- 150 x 10^{15}	Vacuum UV	Electronic
2- 0.1 nm	3- 3000 x 10^{15}	X-ray	Inner Shell electronic
0.1- 0.0001 nm	3- 3000 x 10^{15}	λ-ray	Nuclear Reactions

*The regions overlap considerably, and the range is approximate

Now, when we look at the different regions of electromagnetic spectrum, we see that radio frequencies are responsible for the NMRs. Similarly, the microwave is responsible for the rotational power of a bond. Then, comes the far infrared, infrared and near infrared. They are responsible for causing vibration in a bond. And similarly, the visible, and the ultraviolet, and the vacuum ultraviolet are responsible for the electronic excitation; that is, pi to pi star or n to pi star excitation of electrons are brought about by these particular electromagnetic radiation areas. Then, comes the X ray, which excites the inner shell electrons. And then, comes the gamma rays, which cause nuclear reaction and give out alpha, beta, gamma rays. So, that is how the regions of electromagnetic spectrum are divided and each area contributes to its particular functioning.

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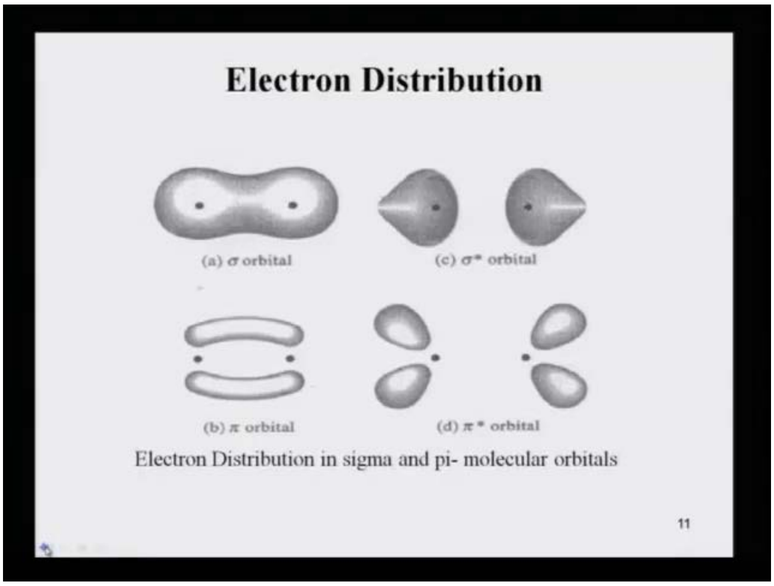

Electron Distribution

(a) σ orbital

(c) σ* orbital

(b) π orbital

(d) π* orbital

Electron Distribution in sigma and pi- molecular orbitals

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Now, when we try to look an electron distribution in an orbital, the sigma and the sigma star, and the pi and the pi star orbitals look like this.

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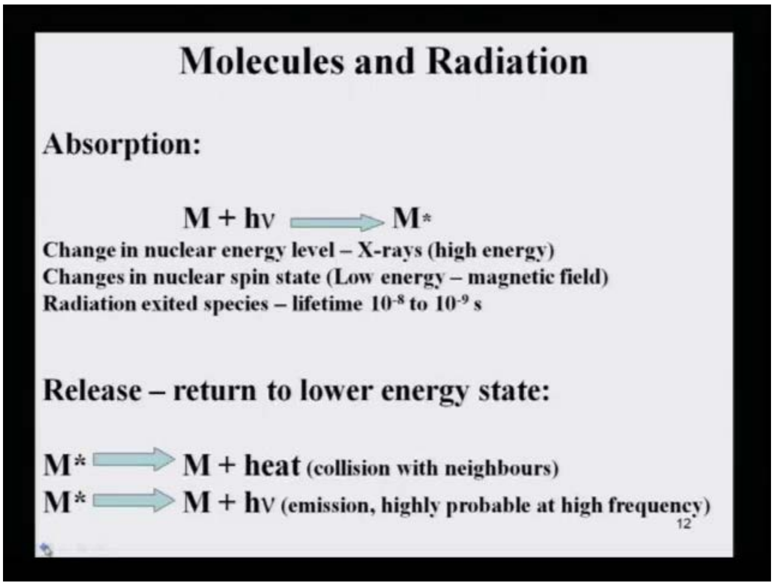

Molecules and Radiation

Absorption:

$$M + h\nu \rightarrow M^*$$

Change in nuclear energy level – X-rays (high energy)
Changes in nuclear spin state (Low energy – magnetic field)
Radiation exited species – lifetime 10^{-8} to 10^{-9} s

Release – return to lower energy state:

$M^* \rightarrow M$ + heat **(collision with neighbours)**

$M^* \rightarrow M + h\nu$ **(emission, highly probable at high frequency)**

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Molecules – when they are radiated, what exactly happens? When molecule is excited with h nu – h nu is an energy source, what exactly happens to that? It forms M dot. That means it is in an excited state; the mass has now become excited. Change in nuclear energy level X rays is very high. Change in nuclear spin state lower energy and causes magnetic field. Radiation excited species have a life time of 10 to the power of minus 8 to the 10 to the power of minus 9 seconds. So, what it happens that this excited molecule either gives then the normal molecule and heat by collision with the neighbors or it may give h nu by emission, highly probable at high frequency. So, either it can give some heat and come back to its normal state or the excited molecule, that is, the M star will emit some energy.

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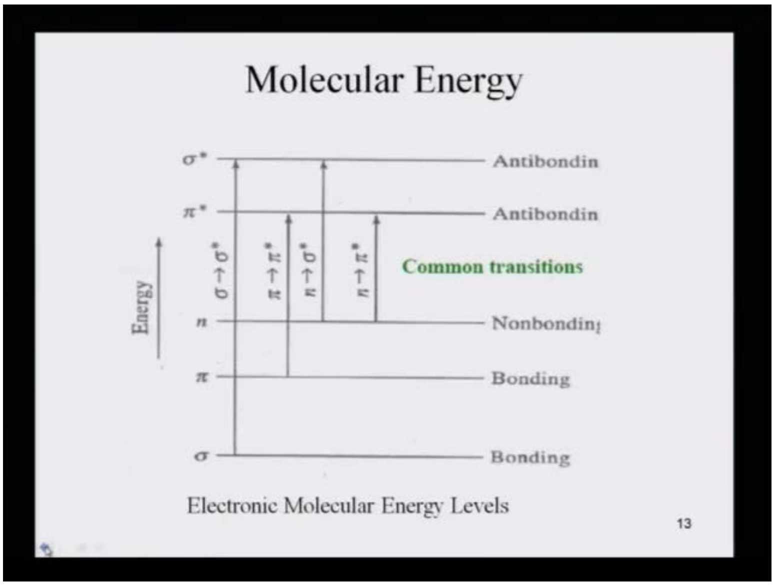

Molecular Energy

Electronic Molecular Energy Levels

Now, these are certain molecular electronic transitions that are permitted. You will see that from the transition of pi to pi star, it is the most fissile energy exchange that can occur; or, n to pi star. But, n to sigma star or sigma to sigma star requires the highest energy. So, depending on what kind of UV light is shown on the molecule, the most fissile exchange or the most fissile excitation would be pi to pi star; whereas, the next fissile exchange would be n to pi star. However, n to sigma star or sigma to sigma star requires still higher energy.

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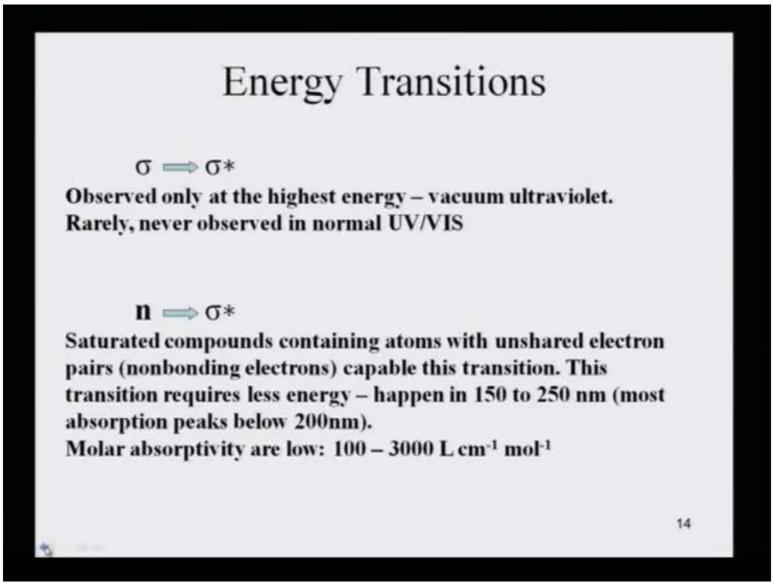

Energy Transitions

$\sigma \Rightarrow \sigma^*$

Observed only at the highest energy – vacuum ultraviolet. Rarely, never observed in normal UV/VIS

$n \Rightarrow \sigma^*$

Saturated compounds containing atoms with unshared electron pairs (nonbonding electrons) capable this transition. This transition requires less energy – happen in 150 to 250 nm (most absorption peaks below 200nm).

Molar absorptivity are low: 100 – 3000 L cm^{-1} mol^{-1}

Now, energy transitions, that is, sigma to sigma star – observed only in highest energy, that is, vacuum ultraviolet. Rarely, never observed in the normal UV and visible range. Whereas, n to sigma star – saturated compounds containing atoms with unshared electron pairs, that is, nonbonding electrons capable of this transition. This transition requires less energy – happens in 150 to 250 nanometer range and the absorption below – mostly 200 nanometer is what is observed. The molar absorptivity are fairly low; that is, 100 to 3000 liters per centimeter for mole. So, this is why these two transitions – energy transitions are not so popular, when we are talking about electronic excitations.

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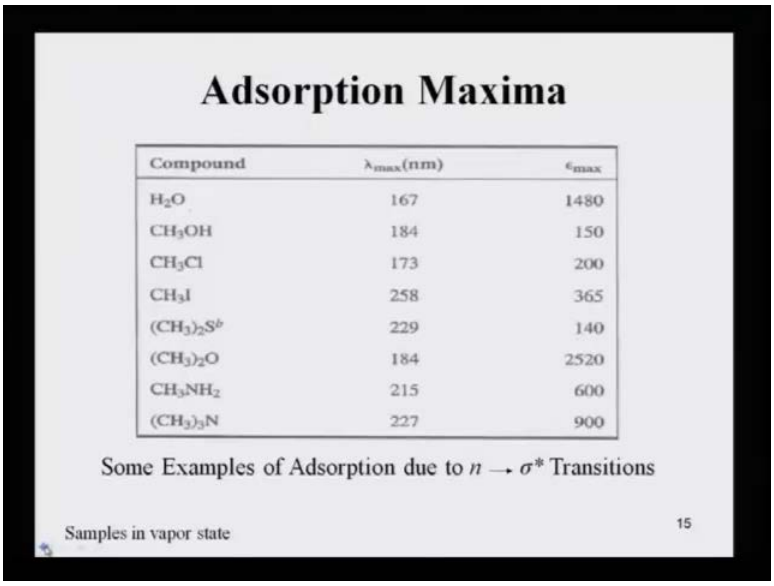

Adsorption Maxima

Compound	λ_{max}(nm)	ϵ_{max}
H_2O	167	1480
CH_3OH	184	150
CH_3Cl	173	200
CH_3I	258	365
$(CH_3)_2S^b$	229	140
$(CH_3)_2O$	184	2520
CH_3NH_2	215	600
$(CH_3)_3N$	227	900

Some Examples of Adsorption due to $n \rightarrow \sigma^*$ Transitions

Samples in vapor state

Adsorption maxima of certain solvents are given here. You will see some examples adsorption due to n to sigma star transition, has been shown here. And, water particularly, which adsorbs at 167 nanometers having lambda max of 167, shows a molar adsorptivity – 1480; whereas, methanol shows lambda max at 184 and molar adsorptivity at 150. Similarly, methylene chloride shows lambda max at 173 and has a molar adsorptivity at 200. Iodomethane shows lambda max at 258 and has a molar adsorptivity at 365, and so on. One can go on looking at the list and see that the lambda maxs are much lower and the molar adsorptivity of diethyl ether is very high; otherwise, most of these compounds have very low molar adsorptivity. And, these are typical examples of n to sigma star transitions and the samples are all taken in vapor state.

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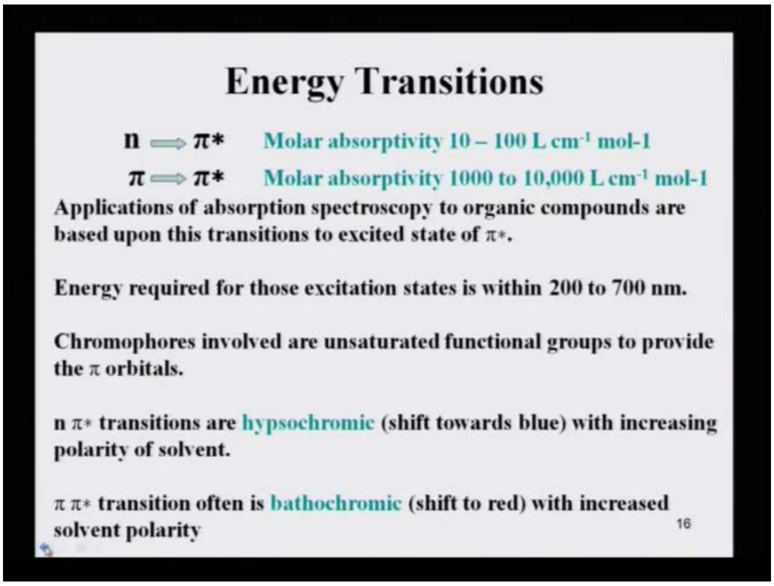

Energy Transitions

$n \Longrightarrow \pi^*$ Molar absorptivity 10 – 100 L cm^{-1} mol-1

$\pi \Longrightarrow \pi^*$ Molar absorptivity 1000 to 10,000 L cm^{-1} mol-1

Applications of absorption spectroscopy to organic compounds are based upon this transitions to excited state of π^*.

Energy required for those excitation states is within 200 to 700 nm.

Chromophores involved are unsaturated functional groups to provide the π orbitals.

$n\ \pi^*$ transitions are hypsochromic (shift towards blue) with increasing polarity of solvent.

$\pi\ \pi^*$ transition often is bathochromic (shift to red) with increased solvent polarity

Energy transitions, which are more popular are the n to pi star and pi to pi star. And, they have molar adsorptivity, which are in the range of 10 to 100 liters per centimeter per mole, and therefore, pi to pi star is still more popular, which has a molar adsorptivity between 1000 to 10,000 liters per centimeter per mole. Applications of these two particular energy transitions are what we are going to study in adsorption spectroscopy to understand the chemistry of organic compounds, and it is based on this transition to excited state of pi star. Energy required for those exited states is within 200 to 700 nanometers. So, it is well within the UV region. Chromophores involved are unsaturated functional groups to provide the pi orbitals. n to pi star transitions are hypsochromic; that means, they shift towards blue light with increasing polarity of the solvent. And, pi to pi star transition is bathochromic, which shifts to red with increasing solvent polarity.

Now, let me explain you a little bit about these things, because it is now getting a bit more complicated. What is a chromophore? A chromophore is a part of a molecule, which has the pi and the n bonds, and is in conjugation with single bond. When the double bond, single bond, double bond are in line with each other, one after the other, we say that the system is conjugated. And, the more the number of pi bonds, the more will be the excitation of these pi electrons to pi star; or, n electrons from the hetero atoms like nitrogen, oxygen, chlorine, sulfur, phosphorous and so on to the pi star. Now, these cause increasing of wavelength or decreasing of wavelength, and that is what is known as the hypsochromic and bathochromic changes in polarity.

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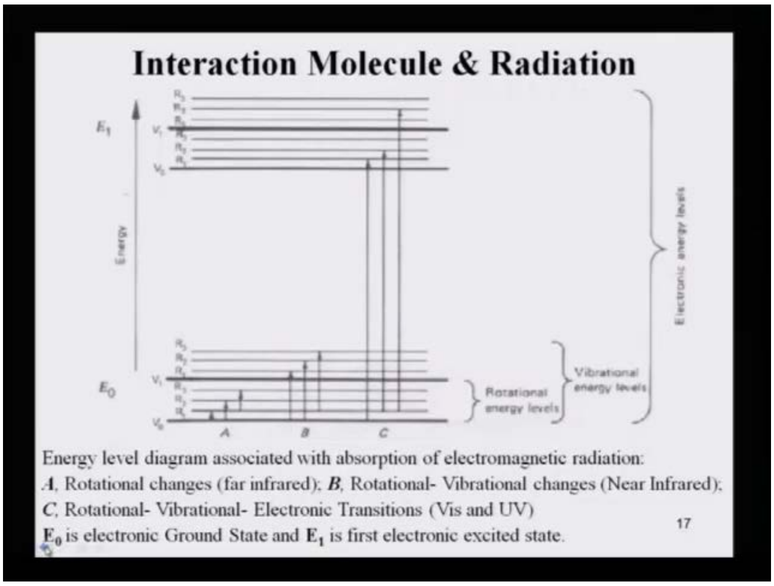

Interaction Molecule & Radiation

Energy level diagram associated with absorption of electromagnetic radiation:
A, Rotational changes (far infrared); ***B***, Rotational- Vibrational changes (Near Infrared);
C, Rotational- Vibrational- Electronic Transitions (Vis and UV)
$\mathbf{E_0}$ is electronic Ground State and $\mathbf{E_1}$ is first electronic excited state.

When try to look at the interactions of molecules with this radiation, it is very interesting to see that the energy levels can create different types of interaction. It can either cause rotational energy levels or it can create vibrational energy levels or it can finally, cause electronic energy. Now, the rotational and the vibrational are brought about by the IR energy or IR lights; whereas, the electronic energy transitions, which are much higher in magnitude are brought about by the UV light or the visible light.

Energy level diagram associated with absorption of electromagnetic radiation; that is, the rotational changes are shown by the far infrared region; the rotational-vibrational changes are shown by near infrared region; the rotational-vibrational-electronic transitions are given by the visible and UV regions, and therefore, from the electronic ground state to the electronic first excited state are depicted by E 0 and E 1. So, you can get a relative idea – what are the energy contents, whether the IR energy is stronger than the UV energy? The immediate answer will be that IR energies are causing rotation or vibration. So, they are smaller in their energy content; whereas, the UV lights excite the electron from one level to another orbital, and therefore, they have larger energy content.

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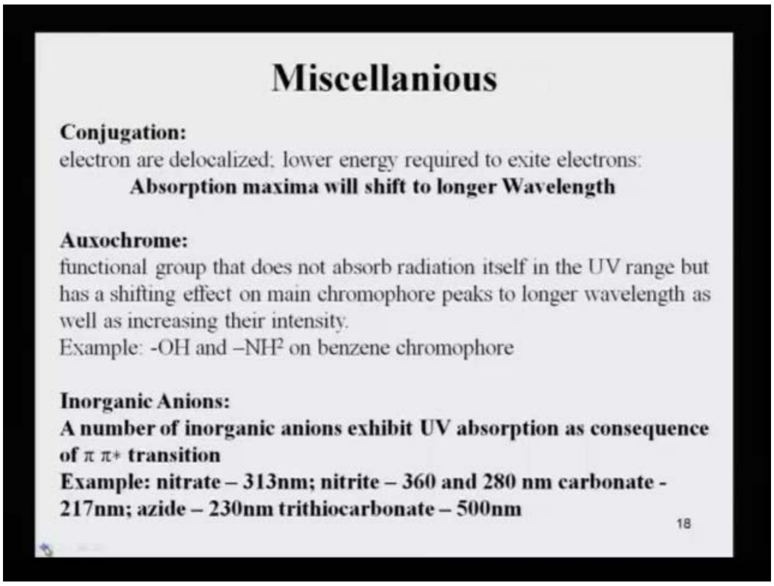

Miscellanious

Conjugation:
electron are delocalized; lower energy required to exite electrons:
Absorption maxima will shift to longer Wavelength

Auxochrome:
functional group that does not absorb radiation itself in the UV range but has a shifting effect on main chromophore peaks to longer wavelength as well as increasing their intensity.
Example: -OH and $-NH^2$ on benzene chromophore

Inorganic Anions:
A number of inorganic anions exhibit UV absorption as consequence of π $\pi*$ transition
Example: nitrate – 313nm; nitrite – 360 and 280 nm carbonate - 217nm; azide – 230nm trithiocarbonate – 500nm

Miscellaneous information that is related to conjugation – little while ago, I was talking about single bond, double bond, single bond being in reputation. Now, when such a system exists in a molecule, then we call it that the molecule is conjugated or the system has conjugation. Electrons in that are delocalized; lower energy is required to excite electrons. Absorption maxima will shift to longer wavelength; that means, because I just told you a while ago, longer wavelength, shorter energy; shorter wavelength, higher energy. So, that should be kept in mind. If you keep one in mind, the other one will be automatically remembered, but if you try to remember both of them together, there is a possibility of mixing it up.

Now, you have already understood what are chromophores. But, what about understanding another additive, which is called oxochrome? Oxochrome on their own do not impart any color contribution. However, they help in the conjugation process. If a functional group that does not absorb radiation by itself in the UV range, but has a shifting effect on the main chromophore peak to longer wavelength as well as increasing their intensities; for example, like hydroxy group – it is not absorbing by itself, but when it is in conjugation with a double bond or other such conjugated system or NH2 or benzene chromophore, then on the benzene chromophore, they will act as oxochrome.

Inorganic ions – a number of inorganic ions exhibit UV absorption as a consequence of pi to pi star transition. For example, nitrate will absorb at 313 nanometers; whereas, nitrite absorbs at 360 and 280 nanometers. Carbonate absorbs at 217 nanometers; whereas, azide absorbs at 230 nanometers; whereas, trithiocarbonate absorbs at 500 nanometers. So, you see that different types of inorganic ions have different wavelengths, because they absorb differently, and because they have different types of oxochromes attached to the main chromophore.

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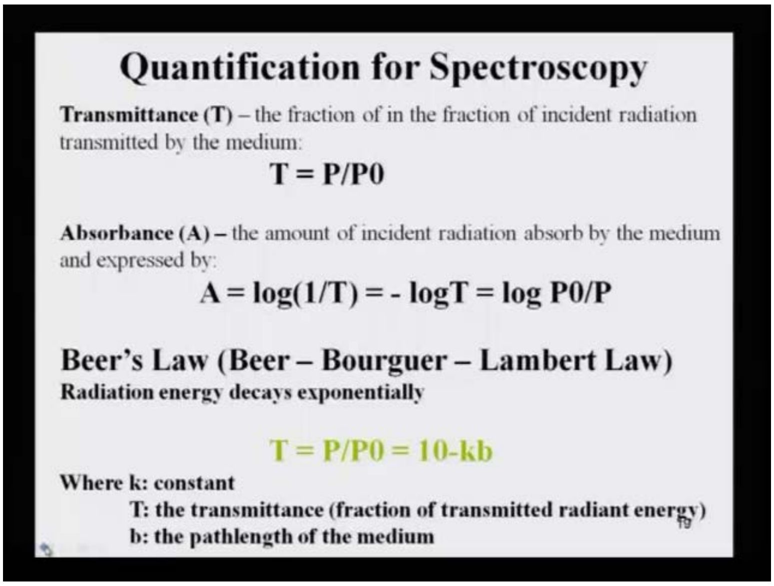

Quantification for Spectroscopy

Transmittance (T) – the fraction of in the fraction of incident radiation transmitted by the medium:

$$T = P/P0$$

Absorbance (A) – the amount of incident radiation absorb by the medium and expressed by:

$$A = \log(1/T) = - \log T = \log P0/P$$

Beer's Law (Beer – Bourguer – Lambert Law)

Radiation energy decays exponentially

$$T = P/P0 = 10-kb$$

Where k: constant

T: the transmittance (fraction of transmitted radiant energy)

b: the pathlength of the medium

Quantification for spectroscopy – now, this is the most important part of the spectroscopy. Why, because this is the crux. What happens in a spectroscopic transformation or data collection? Either we consider transmittance; that means, the fraction of light that is incident and the fraction of light that is transmitted are compared; that is called transmittance. Or, it can be a light as incident; it absorbs and then it transmits the light, which is slightly less in its energy. Now, a part that the amount of incident radiation, which has been absorbed by the medium is expressed as log 1 by T; or, is equal to minus log T; or, is equal to log P 0 by P.

Beer's law (Beer-Bourguer-Lambert's law) – radiation energy decays exponentially and T, that is, the transmittance is always proportional to P over P 0. And therefore, it is to be understood that it is proportional means, whatever be the molecular species concentration, only that much will absorb, and therefore, it is a method of quantifying these substances, because the number of species, the concentration is related directly to its absorption energy.

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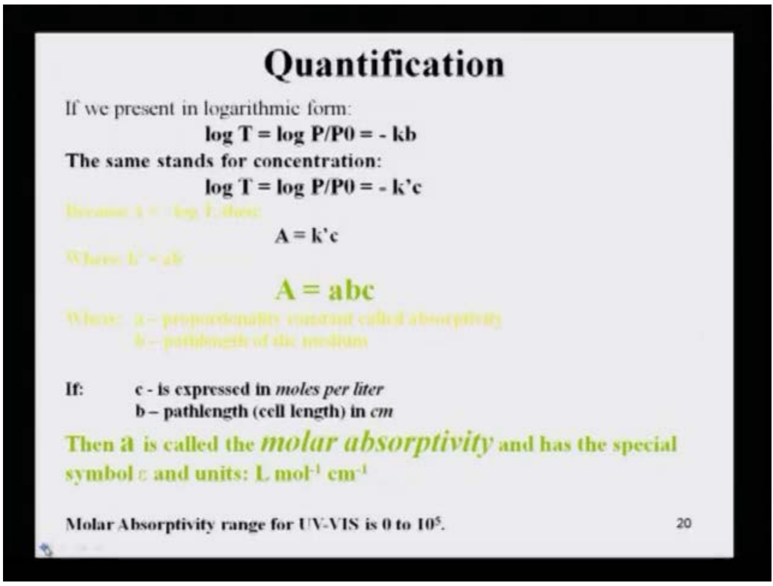

Quantification

If we present in logarithmic form:

$$\log T = \log P/P0 = -\,kb$$

The same stands for concentration:

$$\log T = \log P/P0 = -\,k'c$$

Because A = - log T, then:

$$A = k'c$$

Where: k' = ab

$$A = abc$$

Where: a – proportionality constant called absorptivity
b – pathlength of the medium

If: c - is expressed in *moles per liter*
b – pathlength (cell length) in *cm*

Then a is called the *molar absorptivity* and has the special symbol ε and units: L mol^{-1} cm^{-1}

Molar Absorptivity range for UV-VIS is 0 to 10^5.

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Quantification – if we present in logarithm form, log T is equal to log P by P 0 is equal to minus k b. The same stands for concentration, that is, log T is equal to log P by P 0 is equal to minus k prime c; or, A is equal to k prime c; or, A is equal to abc. Now, what are these a and b and c? The small a is the proportionality constant of absorption; and, b is the path length of the method or the medium. Now, path length – that means how much light is being shown, is also very important. And therefore, it is expressed in moles per liter; C is expressed in moles per liter. And, path length or cell length is expressed in centimeter. Then, the small a are the molar absorptivity has the special symbol, and the units are liters per mole per centimeter. The molar absorptivity range for UV visible is 0 to 10 to the power of 5. So, it is as low as 0 and it can be as high as 10 to the power of 5.

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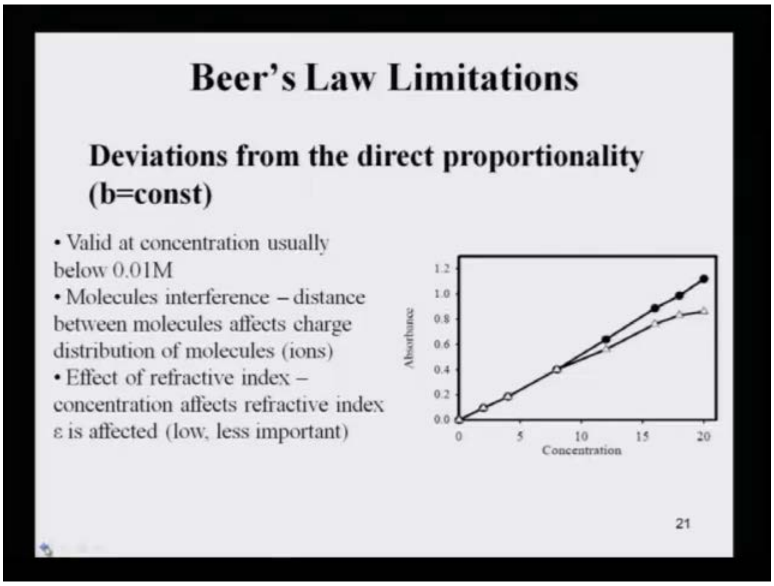

Beer’s Law Limitations

Deviations from the direct proportionality (b=const)

- Valid at concentration usually below 0.01M
- Molecules interference – distance between molecules affects charge distribution of molecules (ions)
- Effect of refractive index – concentration affects refractive index ε is affected (low, less important)

When we try to see, understand Beer’s-Lambert’s law, we also have to remember that these molecular species are not interactive among each other. Each species is an individual, and that individual species absorbing light and the absorption directly proportional to the concentration of the material. But, sometimes, when these molecules are in aggregates, the Beer’s-Lambert’s law will not hold good. There is deviation from its direct proportionality, because it is only valid at concentrations usually below 0.01 molar. If the solution is very concentrated, it may not have that complete effect of its reaction and each entity will not be just one entity, but will be an aggregation of more than one entity.

Molecules interference – distance between molecules affects charge distribution of molecules particularly in the case of ions. Effect of relative index – concentrations effect relative index, and therefore, molar absorptivity is affected. So, either it will be low or too less; or, linear graph is no more linear. It then takes a turn and that is not considered as one of the best methods of analysis, because for any law to be valid, it is important that the calibration graph should be a straight line passing through the axis; and, the axis is the point where the y-axis and the z-axis actually collide. So, this 0 should be passing through the 0. And, one axis gives the absorbance, the other axis gives the concentration, and that is what shows the proportionality between the two. But, if the solution is very concentrated, if there are molecular aggregates, then this proportionality will not hold good.

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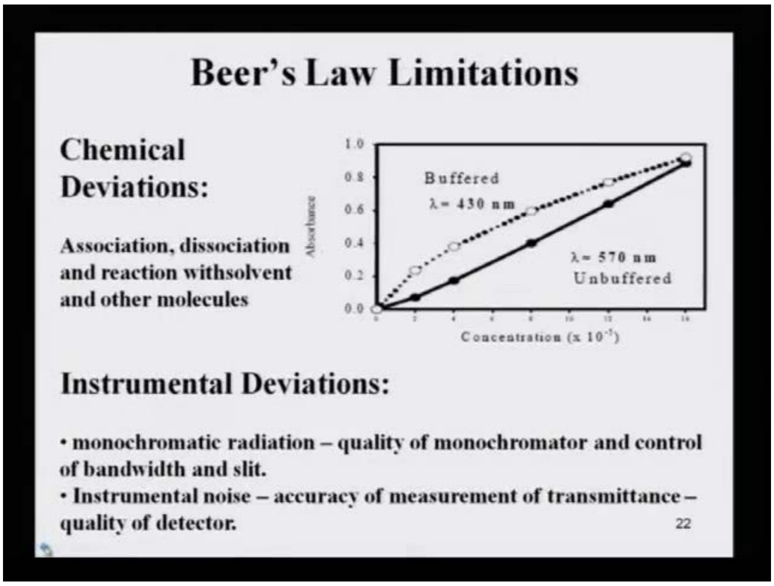

Beer’s Law Limitations

Chemical Deviations:

Association, dissociation and reaction withsolvent and other molecules

Instrumental Deviations:

- **monochromatic radiation – quality of monochromator and control of bandwidth and slit.**
- **Instrumental noise – accuracy of measurement of transmittance – quality of detector.**

Beer-Lambert’s law also faces challenges when there are chemical deviations – either the molecule is associated or dissociated, and the reaction takes place with the solvent and other molecules like in buffered solution or unbuffered solution. Then, the instrument will not show correct data; why, because the Beer’-Lambert’s law is not holding good. So, one has to keep in mind, first thing, solutions should be very dilute, so they are fairly apart. There should be no association, no dissociation or reaction with any kind of solvents or other molecules when the analysis is being carried out.

Instrumented deviation – monochromatic radiation – quality of monochromator and control of bandwidth and slit are other parameters that need to be considered. Instrumental noise – accuracy of measurement of transmittance – quality of detector also should be very good. If these have little bit of discrepancies, or if the instruments shows any kind of deviation, or if the instrument is not regularly calibrated, or if the quality of monochromatic light is not good, and the bandwidth and the split are not maintained at the right parameters, then also, the Beer’s-Lambert’s law will not hold good.

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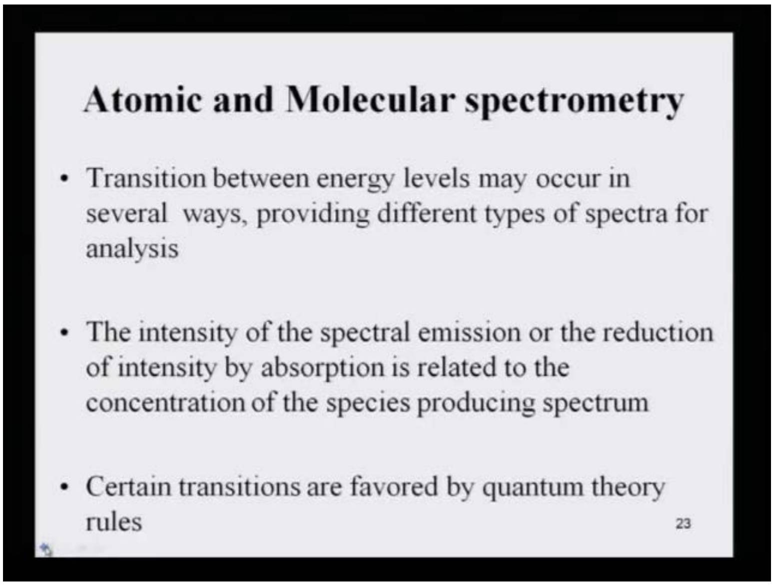

Atomic and Molecular spectrometry

- Transition between energy levels may occur in several ways, providing different types of spectra for analysis
- The intensity of the spectral emission or the reduction of intensity by absorption is related to the concentration of the species producing spectrum
- Certain transitions are favored by quantum theory rules

Atomic and molecular spectrometry – this is what we are going to study in this whole chapter of spectroscopy. What happens to a molecule when it is subjected to electromagnetic radiation or what happens to molecules when they are subjected to electromagnetic radiation? Atoms behave slightly different way – we just saw when we were doing atomic absorption spectroscopy that came under the category of atomic spectroscopy; whereas, molecular spectroscopy is where we are looking at the entire picture of the molecule. Transitions between energy levels may occur in several ways providing different types of spectra for analysis. So, molecular spectrometry is much complicated as compared to atomic.

The intensity of the spectral emission or the reduction of intensity by absorption is related to the concentration of the species producing the spectrum. So, when we try to look at the intensities of the spectrum emission or reduction of intensity by absorption, it will be either emitted or absorbed. These are the two things that happened when electromagnetic radiation is shown. And, that will produce a different type of spectrum. Certain transitions are favored by quantum theory rules; why, because energies are quantized. It is not that by putting some energy, some excitation will take place. The energies when they are matching with the molecular part or chromophore, will only show excitation, not otherwise.

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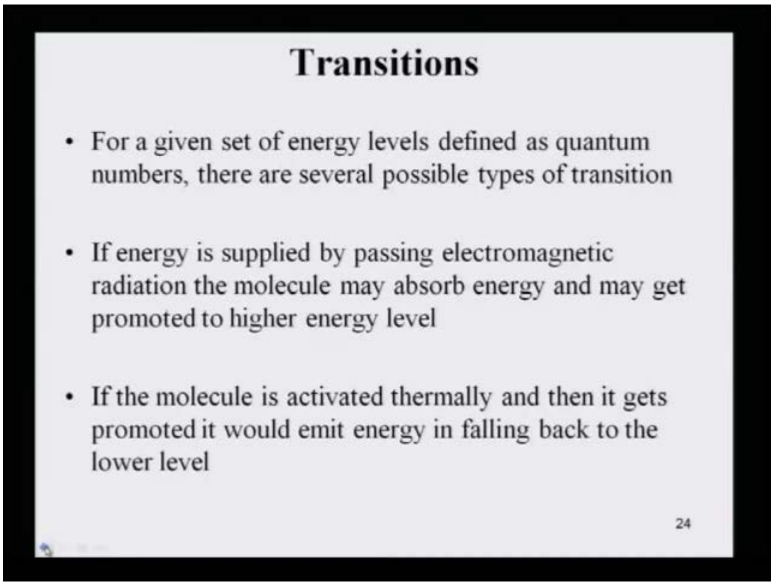

Transitions

- For a given set of energy levels defined as quantum numbers, there are several possible types of transition
- If energy is supplied by passing electromagnetic radiation the molecule may absorb energy and may get promoted to higher energy level
- If the molecule is activated thermally and then it gets promoted it would emit energy in falling back to the lower level

Transitions – for a given set of energy levels defined as quantum numbers, there are several possible types of transition, but only several possible types. If energy is supplied by passing electromagnetic radiation, the molecule may absorb energy and may get promoted to higher energy level. So, it is possible that if the energy levels are matching, then only these absorptions will take place. And therefore, if energy supplied by passing electromagnetic radiation, the molecule may absorb only when it is compatible and may be promoted to higher level, because it is rightly matching with the kind of energy that is required for pi to pi star transition. If the molecule is activated thermally and then it gets promoted, it would emit energy in falling back to the lower level. So, obviously, if a molecule is heated and then it is thermally excited, then it will give out that heat by emitting that energy and comes back to its natural position.

Let me tell you one thing that molecules always want to be at a peaceful situation. So, whenever they are excited, either they have to emit or they have to absorb. And so, they cannot keep this energy within themselves. So, this absorption has to be emitted in some form or the other; they may revert back to their original space by emitting or they may show that they are excited, and that absorption will be studied.

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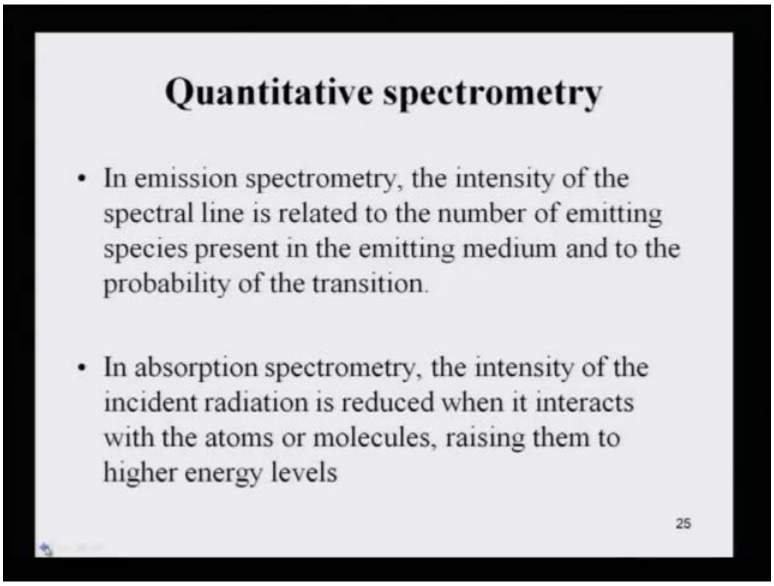

Quantitative spectrometry

- In emission spectrometry, the intensity of the spectral line is related to the number of emitting species present in the emitting medium and to the probability of the transition.
- In absorption spectrometry, the intensity of the incident radiation is reduced when it interacts with the atoms or molecules, raising them to higher energy levels

Quantitative spectrometry – the word quantitative means it is an absolute value; a quantity it decided. In emission spectrometry, the intensity of the spectral line is related to the number of emitting species present in the emitting medium and to probability of the transition. So, in emission spectroscopy, it is the intensity of spectral line, which shows that it is going to emit species that have been absorbed or excited or elevated to a higher energy level.

In absorption spectrometry, the intensity of the incident radiation is reduced, which is because it has interacted with the atoms or the molecules, raising them to higher energy. So, here what happens that incident light has some energy and the light which is coming out has some other energy. This is at a higher energy; this is at a lower energy. So, it is assumed that this loss of energy is what has been taken up by the atom. So, it is very quantitative; as much it will absorb as the concentration of these molecules or atoms are present in the medium. It cannot get lost; it cannot get added up; it has to be in sign of proportionality. And, that is what helps us to understand the spectroscopic method.

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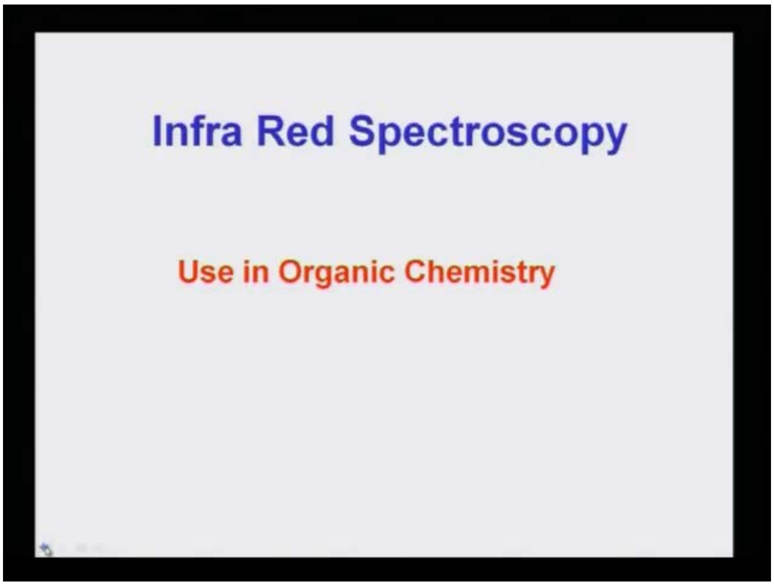

Infra Red Spectroscopy

Use in Organic Chemistry

Coming to infrared spectroscopy – particularly, which is used in organic chemistry.

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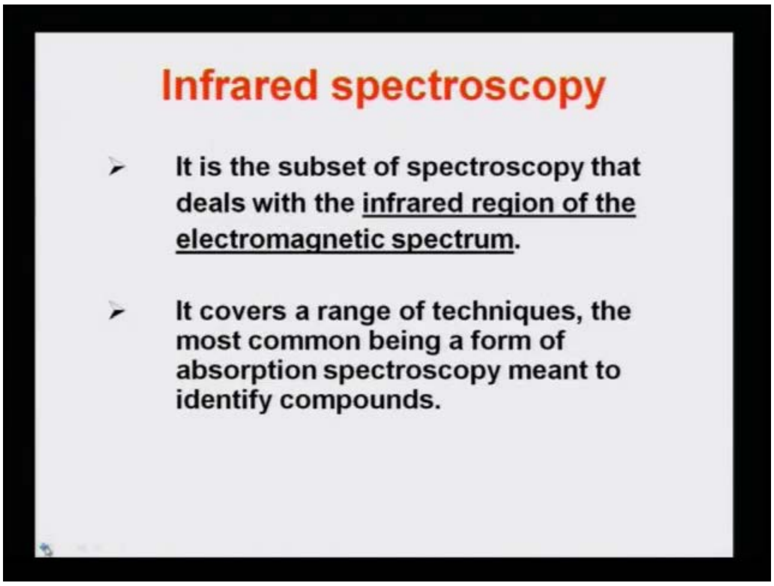

Infrared spectroscopy

- It is the subset of spectroscopy that deals with the infrared region of the electromagnetic spectrum.
- It covers a range of techniques, the most common being a form of absorption spectroscopy meant to identify compounds.

Infrared spectroscopy – because here the light source will be infrared – it is the subset of spectroscopy that deals with the infrared region of the electromagnetic radiation or electromagnetic spectrum. It covers a range of techniques, the most common being a form of absorption spectroscopy meant to identify compounds. So, it should be understood, that part of electromagnetic radiation or spectrum, which deals with infrared region is what the study of the present lecture is. It covers a range of techniques, the most common being the form of absorption spectroscopy meant to identify the compounds only from the point of view of their functional group – whether an OH moiety is present or not; whether NH 2 is present or not; whether carbonyl is present or not; if the carbonyl present, then whether it is aldehyde or ketone; or, does it belong to acyl carbonil; or, does it belong to anhydride carbonyl – is the study that will be understood through the use of infrared radiation.

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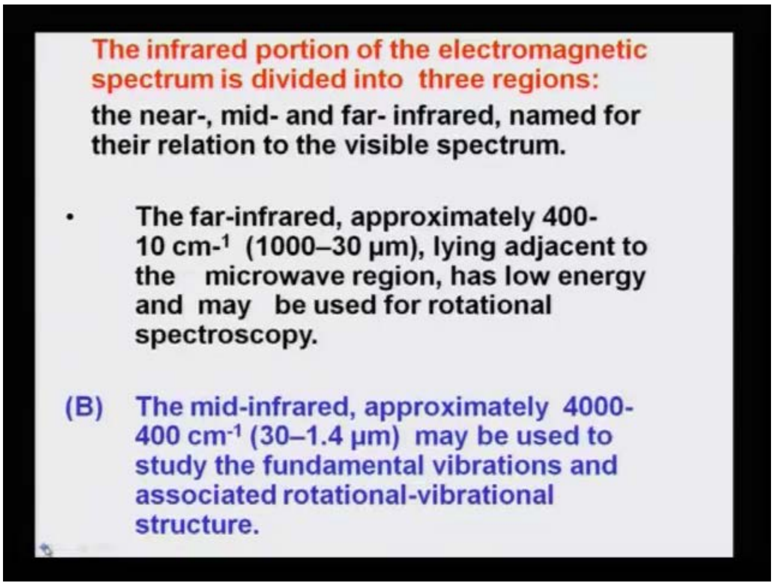

The infrared portion of the electromagnetic spectrum is divided into three regions:
the near-, mid- and far- infrared, named for their relation to the visible spectrum.

- **The far-infrared, approximately 400-10 cm^{-1} (1000–30 μm), lying adjacent to the microwave region, has low energy and may be used for rotational spectroscopy.**

(B) **The mid-infrared, approximately 4000-400 cm^{-1} (30–1.4 μm) may be used to study the fundamental vibrations and associated rotational-vibrational structure.**

The infrared portion of the electromagnetic spectrum is divided into three regions; as what we saw also in one of the earlier slides, the near-, the mid- and the far-infrared, named for their relation to the visible spectrum. The far-infrared, approximately in the region of 400 to 10 centimeter inverse, lying adjacent to the microwave region, has low energy and may be used for rotational spectroscopy. Second, the mid-infrared, approximately ranging from 4000 to 400 centimeter inverse – this is the one which is most properly used – may be used to study the fundamental vibrations and associated rotational and vibrational structure. And therefore, these are regions, which are of very great importance for knowing the functional group and its presence.

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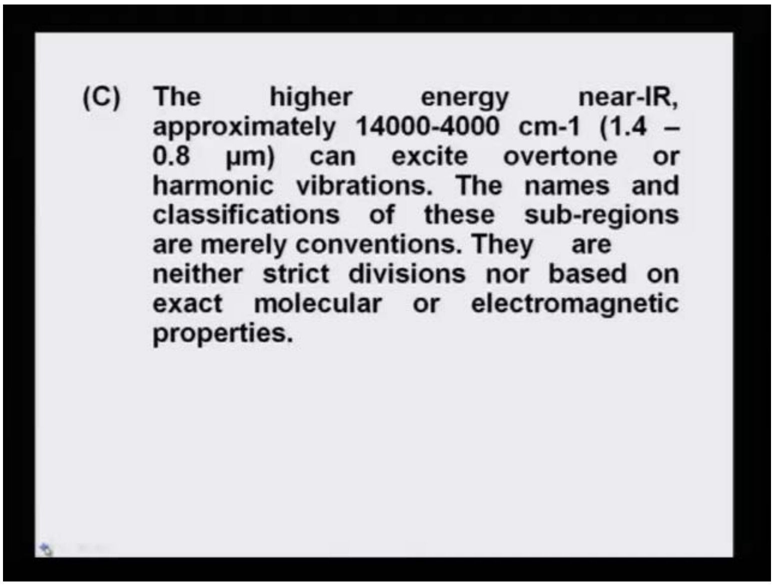

(C) The higher energy near-IR, approximately 14000-4000 cm-1 (1.4 – 0.8 μm) can excite overtone or harmonic vibrations. The names and classifications of these sub-regions are merely conventions. They are neither strict divisions nor based on exact molecular or electromagnetic properties.

And, the third region that is important is the higher energy near-IR, approximately ranging from 14000 to 400 centimeter inverse, can excite overtone or harmonic vibrations. The names and the classifications of these sub-regions are merely for conventions, because they belong to different regions and they do different things in a molecule. That is why the information imparted by these groups is also very clear. They are neither strict divisions nor based on exact molecular or electromagnetic properties.

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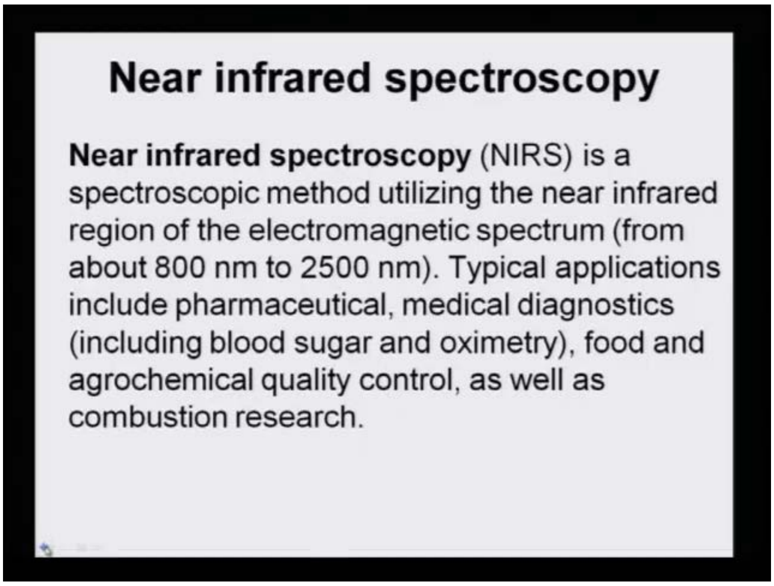

Near infrared spectroscopy

Near infrared spectroscopy (NIRS) is a spectroscopic method utilizing the near infrared region of the electromagnetic spectrum (from about 800 nm to 2500 nm). Typical applications include pharmaceutical, medical diagnostics (including blood sugar and oximetry), food and agrochemical quality control, as well as combustion research.

Near infrared spectroscopy – near infrared spectroscopy, which we will refer as NIRS is a spectroscopic method utilizing the near infrared region of the electromagnetic spectrum from about 800 nanometers to 2500 nanometers. Typical applications include pharmaceutical, medical diagnostics including blood sugar and oximetry, food and agrochemical quality control, as well as combustion research. So, you see, it has a versatile area in which it can be used. And, the information imparted by the near infrared spectroscopy can be so important that it can serve in the areas of pharmaceutical, medical diagnostics including blood sugar, in the area of food and food chemistry, in the area of agrochemical quality control, and in the area of combustion research.