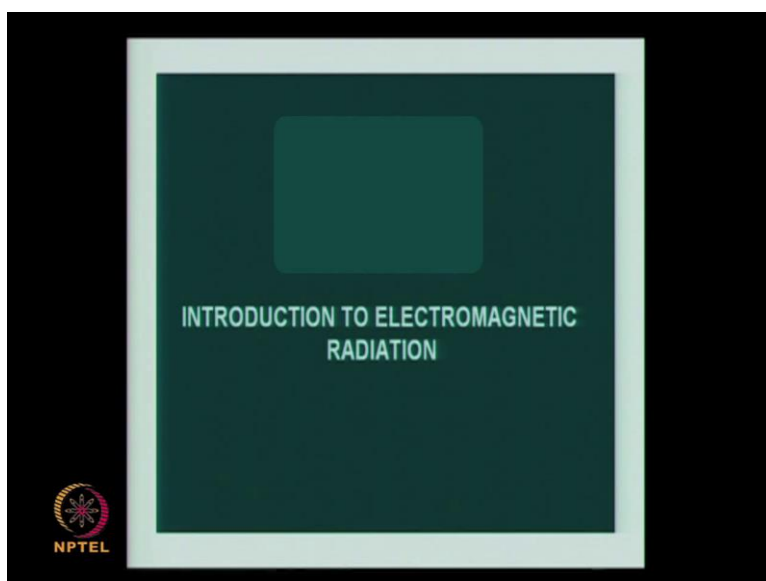


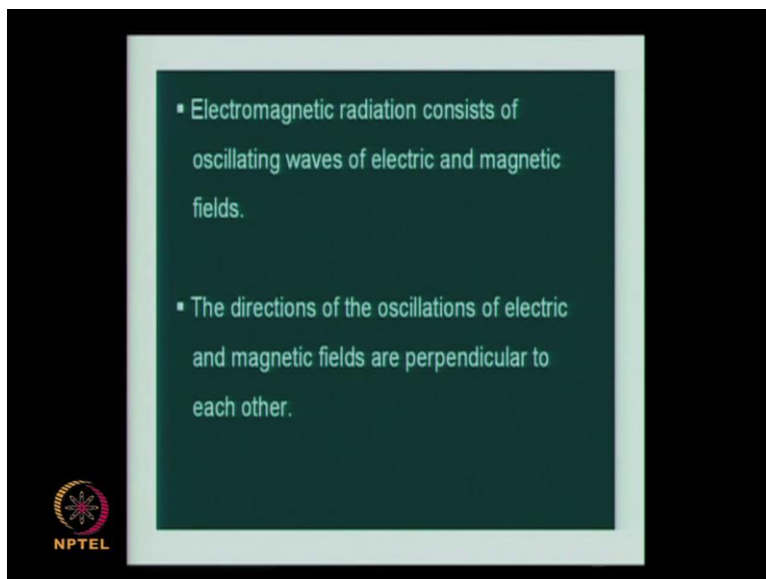
Introductory Quantum Mechanics and Spectroscopy
Prof. Mangala Sunder Krishnan
Department of Chemistry
Indian Institute of Technology, Madras

Lecture 8: Part 3
Introduction of Molecular Spectroscopy
Simple Relations & Spectra versus Properties

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Let me introduce the properties of electromagnetic radiation, very, very simple ones within few minutes, essentially to bring to your recollection that the electromagnetic radiation consists of oscillating waves of electric and magnetic fields. The electric and magnetic fields oscillate perpendicular to each other and are also perpendicular to the direction of propagation of the radiation. As you see here, the directions of the oscillations of the electric and magnetic fields are perpendicular to each other

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▪ The direction of propagation of the radiation is perpendicular to the direction of oscillations.

$$\vec{E}(z,t) = E_0 \cos(kz - \omega t + \delta) \hat{x}$$

Electric field oscillating in the \hat{x} direction

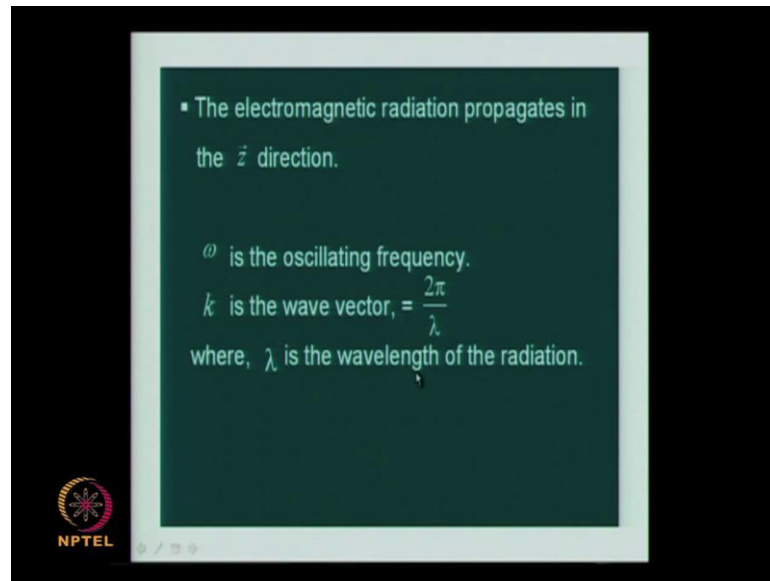
$$\vec{B}(z,t) = \frac{1}{c} B_0 \cos(kz - \omega t + \delta) \hat{y}$$

Magnetic field oscillating in the \hat{y} direction

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You see this in the animation, that it is also perpendicular to the direction of the propagation. The electric field is, in a very simple form is given by the cosine, the electric field oscillating in x-axis, as you see, it is cosine k z minus omega t wave vector angular frequency, we will see it in a few minutes. The magnetic field is oscillating in the y-direction again with the same oscillation frequency.

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▪ The electromagnetic radiation propagates in the z direction.

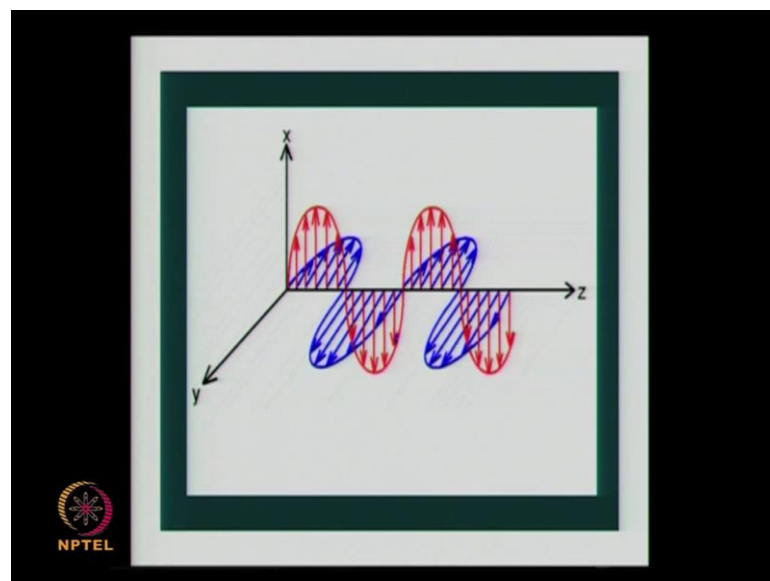
ω is the oscillating frequency.

k is the wave vector, $= \frac{2\pi}{\lambda}$

where, λ is the wavelength of the radiation.

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The diagram shows a 3D coordinate system with x, y, and z axes. The z-axis is the direction of propagation. Two perpendicular sinusoidal waves are shown: a red wave oscillating along the x-axis and a blue wave oscillating along the y-axis. Both waves are perpendicular to the z-axis and to each other.

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And the direction of the oscillation, the blue lines tell you one field, the red lines tell you the oscillations in the other, both of which are perpendicular to the direction of propagation, that is the z-axis. It is a very slow animation, but electromagnetic radiation travels at the speed of light, which obviously we cannot do here, but please understand, that the fields, the red lines, the oscillations and the blue lines are perpendicular to each other and are perpendicular to the direction of propagation.

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Units and definitions:

1. Wavelength : distance between two adjacent crests or troughs of a wave, λ has dimension of length.
2. Frequency : number of waves that pass a given point in unit time interval, ν has dimension of t^{-1}

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Let us define some units that we need to use in spectroscopy

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Amplitude

λ

$\psi(x) = A \sin \frac{2\pi}{\lambda} x$

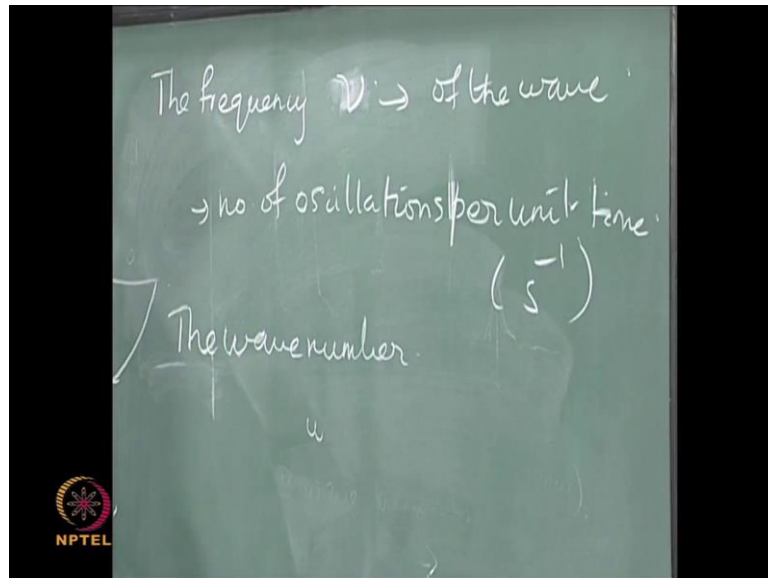
Wavelength $\lambda \Rightarrow$

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When we draw the amplitude of a wave, amplitude of a wave with against, say the precision. So, you can write the wave as a position as $A \sin 2\pi$ by λ x as a simple wave, which we can write in terms of a sine wave and so on, it keeps repeating. The maximum amplitude is A and the wavelength λ is basically, the distance between the two crests, this is λ or the two troughs, which I have drawn here.

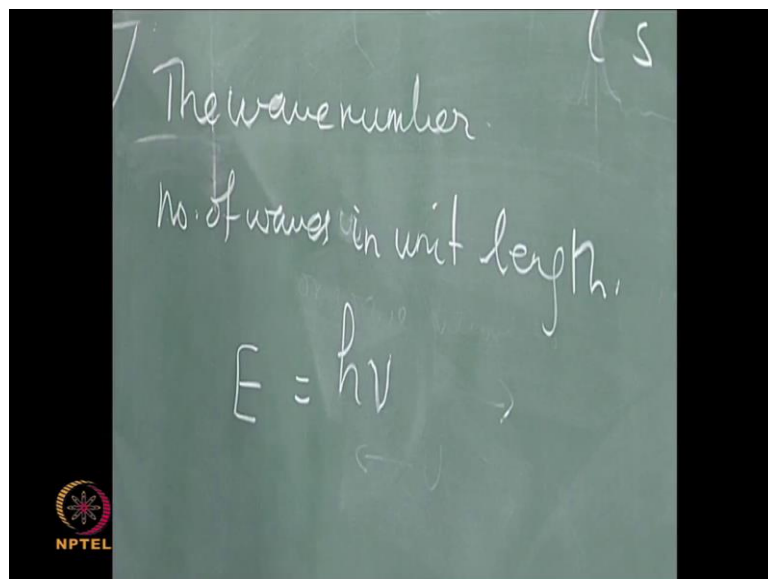
You can start from this point, this repeating point is typically, that is, when you put x is equal to λ . See, that this is one full oscillation. So, the wavelength λ is the distance between two successive repeating points. This, that this, if you draw this further and if you connect to this, between this and that the wave, that is, a periodic oscillation.

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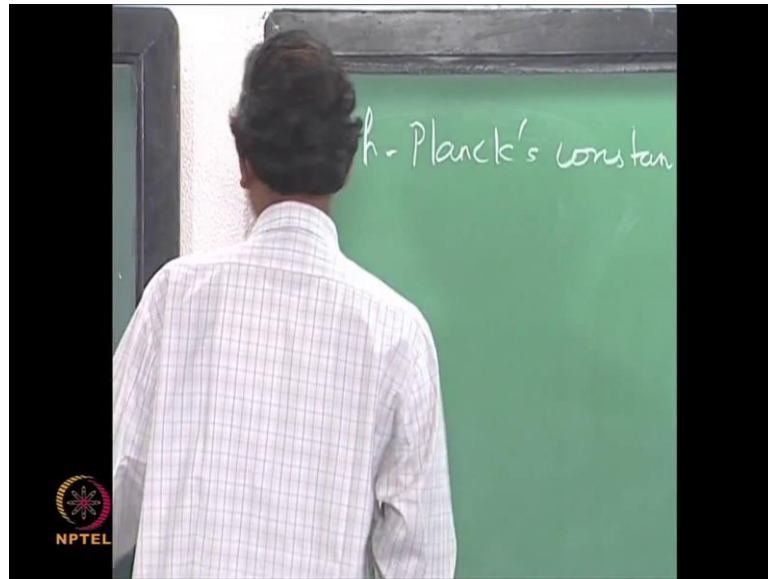


The frequency of ν usually is defined by the, denoted by ν . The frequency ν of a wave is the number of such oscillations in unit time, number of oscillations in the unit time, usually per second, number of oscillation per second.

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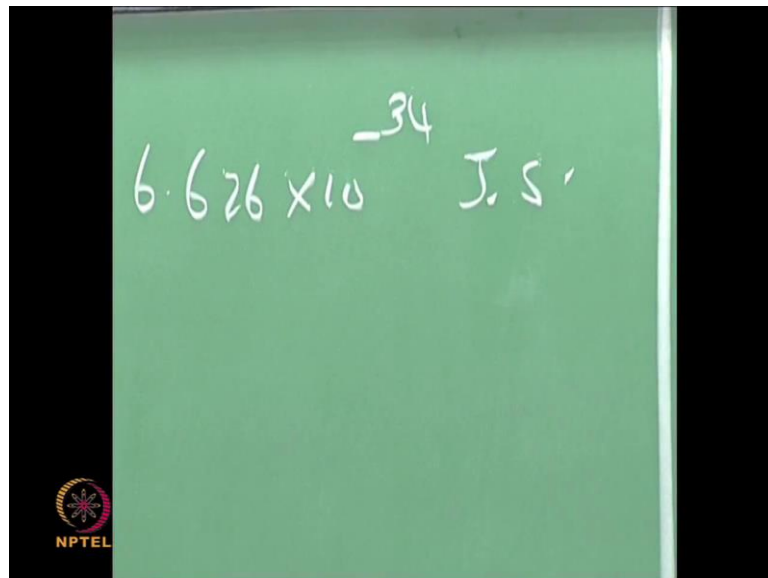


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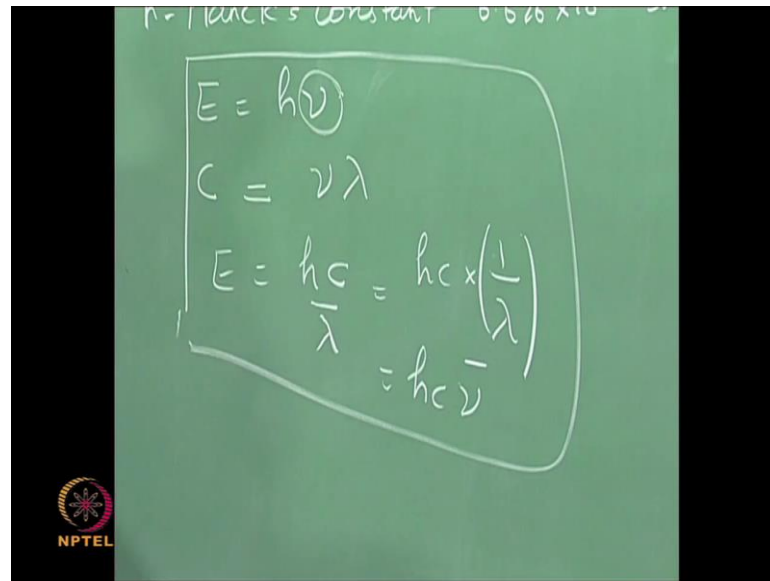
The wave number is defined as the number of waves in unit length, in unit length. Even though I said we will use the classical picture of the electromagnetic radiation as waves, please remember, that the Einstein relation for the electromagnetic radiation as a photon, if you recall, the energy is given by E is equal to $h \nu$ where h is Planck's constant.

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And its units in joules if I have to give is 6.626 into 10 times minus 34 joule second.

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$$E = h\nu$$
$$c = \nu\lambda$$
$$E = \frac{hc}{\lambda} = hc \times \left(\frac{1}{\lambda}\right) = hc\bar{\nu}$$

The E is equal to $h\nu$ tells you, that ν is the frequency. And if you write the relation between the frequency and the wavelength, the speed of light is $\nu\lambda$, which is a constant in vacuum and it is the maximum that you can think of as the speed of any information or object.

E is, therefore, given by hc/λ and if you write this as $hc \times 1/\lambda$, which tells you the number of waves for unit length. If λ is the wavelength, the inverse of λ tells you the number of waves per unit length and therefore, this is often denoted by its own unit called $hc\bar{\nu}$.

So, this is the basic, relation is the, relation, that one has to remember between the energy of the wave, the frequency of the wave, the wavelength of the wave and the wave number of the wave. This is a relation, which we will keep in mind and these are all defined with the appropriate units here in the transfer, in these transparencies.

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Units and definitions:

1. Wavelength : distance between two adjacent crests or troughs of a wave, λ has dimension of length.
2. Frequency : number of waves that pass a given point in unit time interval, ν has dimension of t^{-1}

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The wavelength is the distance between two adjacent crests or troughs of a wave and has the dimension of the length. The frequency is the number of waves that pass a given point in unit time interval and has a dimension number per unit time, and therefore you have t inverse.

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3. Wave number : number of waves in a unit length, $\bar{\nu}$ dimension of L^{-1} .

- Einstein's picture of electromagnetic radiation. It consists of photons of frequency, ν , and energy $E = h\nu$ where h is Planck's constant. Therefore, the energy is also given by

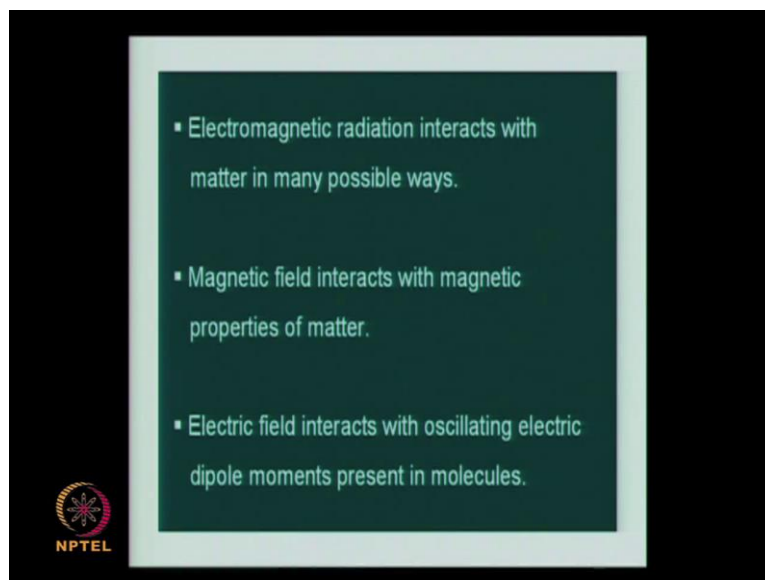
$$E = h\nu = \frac{hc}{\lambda} = hc\bar{\nu}$$

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And the wave number is the number of waves in a unit length of dimension unit, per unit length. And the relation is what I have written namely, the Plank's constant. h relates the energy of the wave to all these parameters.

Therefore, when you talk about the property of the wave, the property of the wave is ν or λ or ν/λ , one and the same, it is just different ways of expressing them. There is only one property, the extent to which it oscillates or the length.

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Let us talk about the interaction of radiation, how radiation interacts with matter qualitatively. Recall from the previous few minutes that the electromagnetic radiation consist of an oscillating electric field and an oscillating magnetic field. These are the two components that the radiation has. Therefore, these are the two quantities, which can interact with matter.

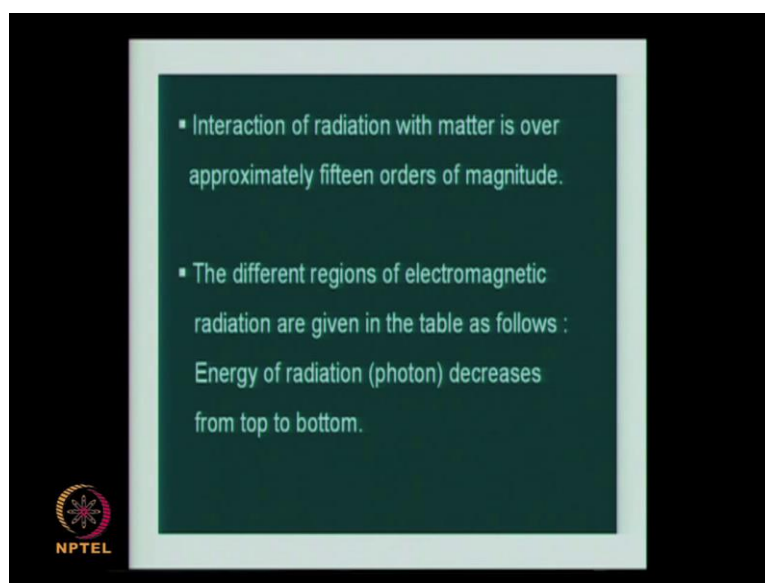
The electric component of the radiation may interact with an electrical oscillation that takes place in a molecule. For example, if a molecule rotates about an equilibrium axis, any temperature above 0 Kelvin, the molecule has the rotational degree of freedom, more than 1, often 2 or 3 degrees, rotational degree of freedom, that is, energy associated with that. The rotations may change the dipole moment in the, in the sense, dipole moment in the vector pointing in a certain direction may undergo rotation about the direction of the axis of rotation.

So, there is an oscillating, there is a property, which is changing an electrical property, which is changing in the molecule. If that change is synchronized with the frequency of the electromagnetic radiation, particularly the electrical property, you see the interaction of the electrical dipole moment of the molecule with the electric oscillations of the

electromagnetic radiation that is one possible interaction. The other is, of course, the magnetic component interacting with the magnetic moment of the molecule.

So, these are the two interaction at, what you call, at the linear level or at the, when the energy of radiation is not too high or when the intensity of the radiation is not too high, these are the two properties, and these both these interactions are directly responsible for the property aspect from that you see.

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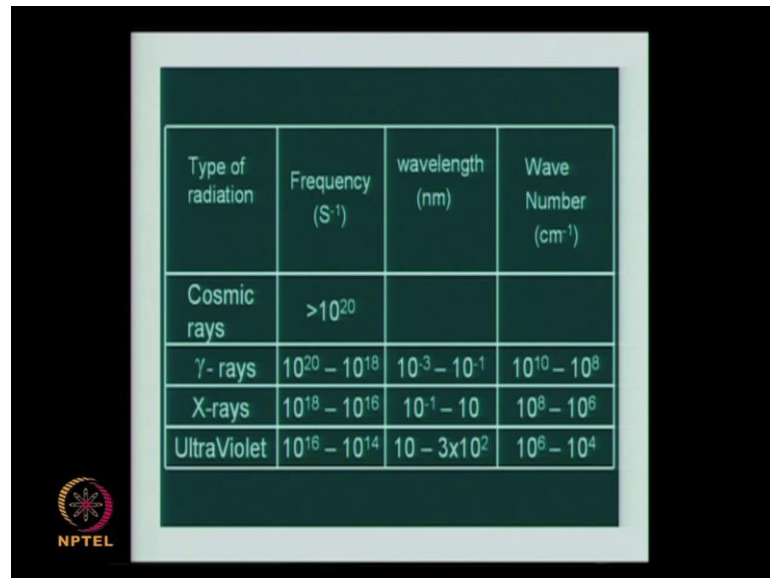
The ranges, of course, over 50 orders of magnitude, that is, from the radio frequency to the ((Refer Time: 10:33)). Now, microwave spectroscopy, infrared spectroscopy, electronic spectroscopy, all of which are usually called optical spectroscopy. The electric property of the radiation is important in the interaction with the electric property of the molecule.

The magnetic resonance spectroscopy, which is from the radio waves to microwaves often and when it, when we consider in the electrons, the magnetic interaction require sometimes the microwave power. So, if you look at that the magnetic resonance property concerns with the magnetic properties of the molecule.

So, there are two basic divisions to the electromag, to molecular spectroscopy, that is, the optical spectroscopy or what we conventionally call as molecular spectroscopy. And then there is the magnetic resonance spectroscopy, which is nuclear magnetic resonance or

nuclear or electron paramagnetic resonance or electron spin resonance and so on. There are, these are two divides. Now, when we say, that the range of the radiation is 15 orders of magnitude. Let us see what we mean. First, let us examine the electromagnetic radiation from the point of view of increasing energy of radiation. You recall that the energy of radiation is proportional to the frequency as given by the Einstein formula.

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Type of radiation	Frequency (S ⁻¹)	wavelength (nm)	Wave Number (cm ⁻¹)
Cosmic rays	>10 ²⁰		
γ-rays	10 ²⁰ – 10 ¹⁸	10 ⁻³ – 10 ⁻¹	10 ¹⁰ – 10 ⁸
X-rays	10 ¹⁸ – 10 ¹⁶	10 ⁻¹ – 10	10 ⁸ – 10 ⁶
UltraViolet	10 ¹⁶ – 10 ¹⁴	10 – 3x10 ²	10 ⁶ – 10 ⁴

So, here a table is given where approximate frequency ranges and wavelength, wave numbers are given. In fact, if I give you the frequency you should be able to write down immediately the corresponding wavelengths and also the wave numbers using the formula that I showed just a few minutes ago.

So, the type of radiation that you see here is organized from the highest energy radiation, namely, cosmic rays whose frequency seems to be greater than or about that 10 raise to 20 per second. You might recall, that per second in frequency units is called the Hertz and this is 10 raised to 20 Hertz or more.

The gamma rays, which are often produced from the nuclear decay, fall in the frequency range of 10 raise to 20 to 10 raise to 18. Around 3 orders of magnitude you have gamma rays and the corresponding wavelengths, if you look at nanometers, that is, 10 raise to minus 9 meters. What you see here is 10 raised to minus 3 nanometers to 10 to the minus 1 nanometer, or in terms of wave numbers, if you consider them as centimeter inverse.

These are the common units used in spectroscopy. The wave number is 10^8 to 10^{10} , 10^8 to 10^4 , this is the range.

X-rays are next lower in energy, 10^{18} to 10^{16} in frequency units and correspondingly for the wavelength, wave number. Ultra violet rays, we are told often, that ultra violet rays is what causes the skin cancer and the ozone layer surrounding the earth, when it is punctured, ultra violet rays enter. We also use ultra violet rays for various spectroscopic techniques. You see that the frequency range is approximately 10^{16} per second or 10^{16} hertz to 10^{14} hertz.

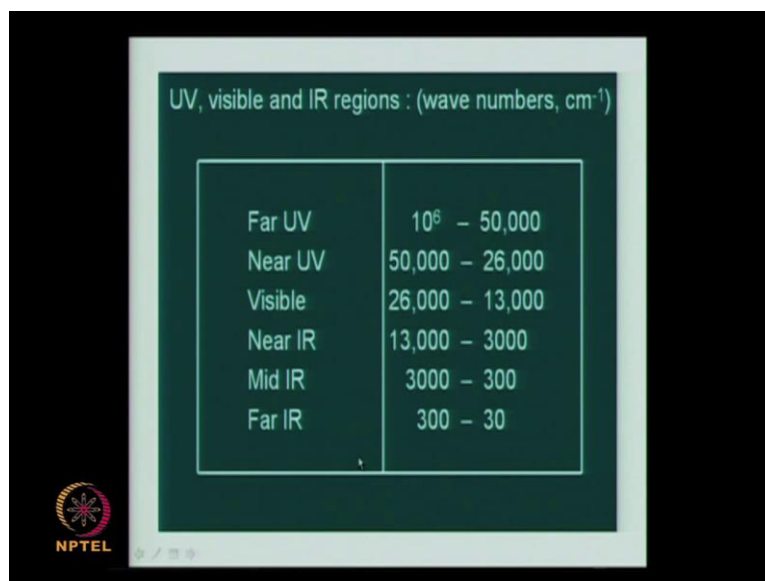
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Type of radiation	Frequency (S ⁻¹)	wavelength (nm)	Wave Number (cm ⁻¹)
Visible	8×10^{14} – 3×10^{14}	3×10^2 – 8×10^2	3×10^4 – 10^4
Infrared	10^{14} – 10^{12}	8×10^2 – 3×10^5	10^4 – 30
Microwave	10^{12} – 10^8	10^5 – 10^9	30 – 10^{-2}
Radiowave	$< 3 \times 10^8$	$> 10^9$	$< 10^{-2}$

Visible light is in the range, it is a very, very narrow range of the electromagnetic spectrum from the violet, which is at the ultra violet to the red, which is near the infra-red. Violet, indigo, blue, green, yellow, orange, red, which is our standard spectrum, is a very small range of frequencies and correspondingly in the wavelengths and in the wave numbers.

In the wave numbers, typically, they are from 30000 centimeter inverse, 10000 centimeter inverse to 30000 centimeter inverse. And infra-red light is lower in energy, again by this order 10^{14} hertz to 10^{12} hertz. Then, comes, of course, microwave, then the radio wave is the lowest in energy. In terms of frequencies, you see, that is the smallest number. So, this is the spectrum that you talk about between 10^{20} in terms of frequencies to 10^8 . So, 12 to, 12 to 14 orders of magnitude.

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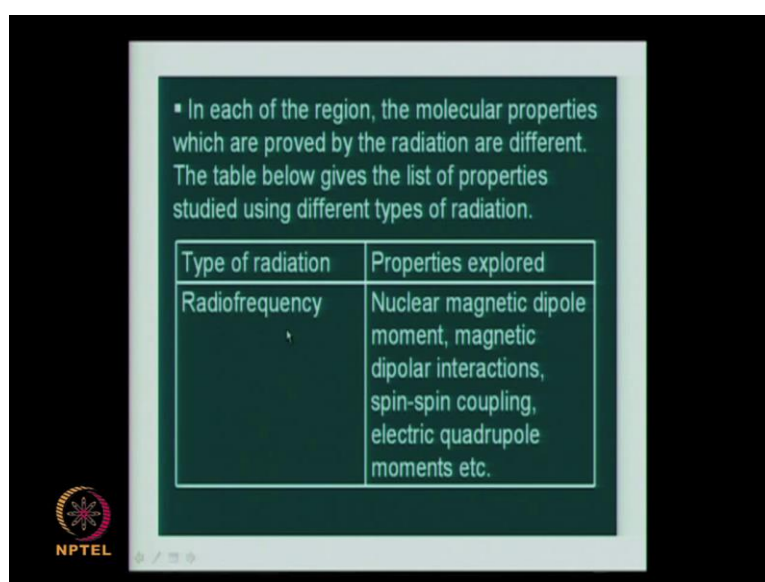
UV, visible and IR regions : (wave numbers, cm^{-1})

Far UV	$10^6 - 50,000$
Near UV	$50,000 - 26,000$
Visible	$26,000 - 13,000$
Near IR	$13,000 - 3000$
Mid IR	$3000 - 300$
Far IR	$300 - 30$

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UV, visible and IR regions in terms of wave numbers, I have given a small table here. These are all approximate numbers, I mean, there is no clear cut division between far UV and near UV. This is a temporary range, approximately accurate, I mean, correct range, 10^6 to $50,000$ centimeter inverse. Likewise, for near UV, visible, near IR, mid IR and far IR.

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▪ In each of the region, the molecular properties which are probed by the radiation are different. The table below gives the list of properties studied using different types of radiation.

Type of radiation	Properties explored
Radiofrequency	Nuclear magnetic dipole moment, magnetic dipolar interactions, spin-spin coupling, electric quadrupole moments etc.

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The reason for this tabulation is, that in each one of these ranges the molecular properties, that we will be able to study the molecular properties, which are responsible

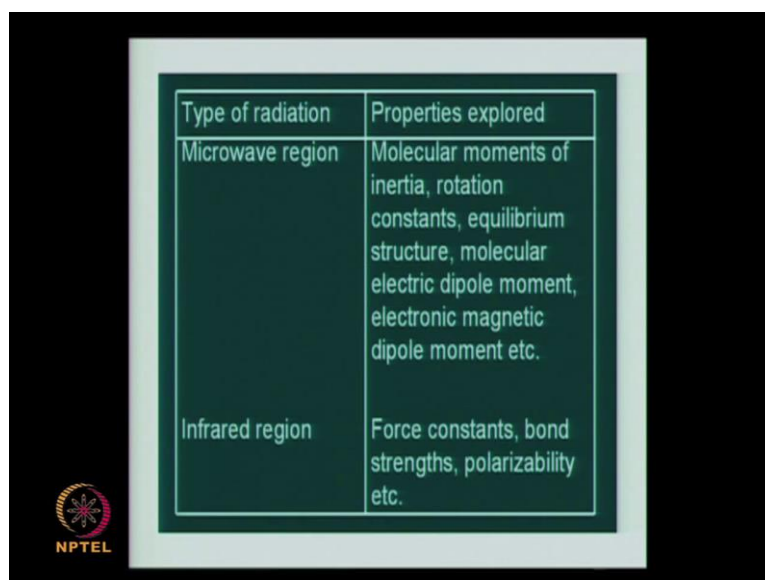
for the spectrum to appear in that region. They are different and therefore, we should also know when we are looking for a certain spect, where we are examining the certain spectrum, what type of interpretation that we should have in terms of the corresponding molecular properties.

So, in the table below I give you the radiation that is used to study the corresponding properties of the molecular. For example, when you talk about radio frequency range, which is the lowest in energy in the electromagnetic radiation in molecular spectrum. The properties, that one studies are nuclear magnetic dipole moments.

I talked about the magnetic resonance imaging that is one of the most well known applications of the medical field. In fact, nuclear magnetic resonance spectroscopy is perhaps the most important spectroscopy techniques that chemist use.

It is possible to interpret using the radio frequency spectroscopy, magnetic dipolar interactions in molecules in solids, the coupling between nuclear magnetic moments, call this spin-spin coupling, the nuclear quadrupole moments etcetera. All these things are the properties that one can study using radio frequency spectroscopy.

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Type of radiation	Properties explored
Microwave region	Molecular moments of inertia, rotation constants, equilibrium structure, molecular electric dipole moment, electronic magnetic dipole moment etc.
Infrared region	Force constants, bond strengths, polarizability etc.

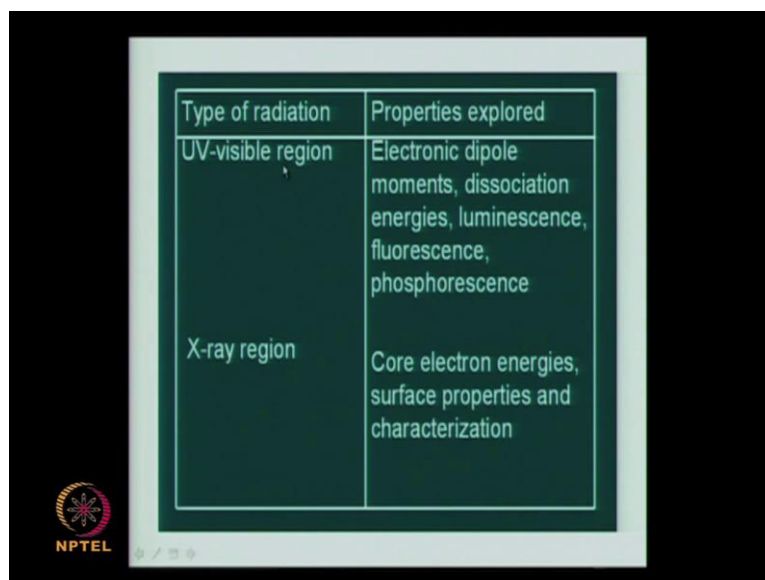
Using microwave spectroscopy one can obtain exact molecular geometries or very accurate molecular geometries by interpreting the spectrum and deriving molecular moments of inertia.

Properties called the rotation constants, which are related to the moments of inertia and through the rotation constants and inertia equilibrium structure of the molecule while for example, methane is tetrahedral, ethane is a tetrahedral, but there are 2 CH, 3 group structure as well as the shape of the molecule. The molecular electric dipole moment, if it has an electric dipole moment or it does not have an electric dipole moment, we can interpret from the spectrum.

The type of spectrum from the, in the microwave region, the electronic magnetic dipole moment, etc., all these things are derivable by the spectra using the microwave spectroscopy.

Using infrared spectroscopy one can understand what happens to the bond strength, what is the order of magnitude of the bond strength, the force constants, which are responsible for the bonds, which are responsible for the binding of the molecules, how strong they are, how weak they are, this is the quantitative value associated with that and the extent to which the molecule is polarizable or dipole moments can be induced when you put the molecule in the electric field. All these things can be study using infrared spectroscopy.

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Type of radiation	Properties explored
UV-visible region	Electronic dipole moments, dissociation energies, luminescence, fluorescence, phosphorescence
X-ray region	Core electron energies, surface properties and characterization

When you use UV-visible electromagnetic radiation, the properties of molecules that one can derive or electronic dipole moments, dissociation energies, luminescence property, fluorescence properties of molecules, phosphorescence properties. For example, the screen, that you are watching this perhaps is an example of phosphorescence properties

that you want to know. They are studied using the UV-visible region. And the X-ray region enables us to understand the surface properties of solids, various surfaces, interfaces and characterizing the interfaces and also the core electron energies of atoms and molecules.

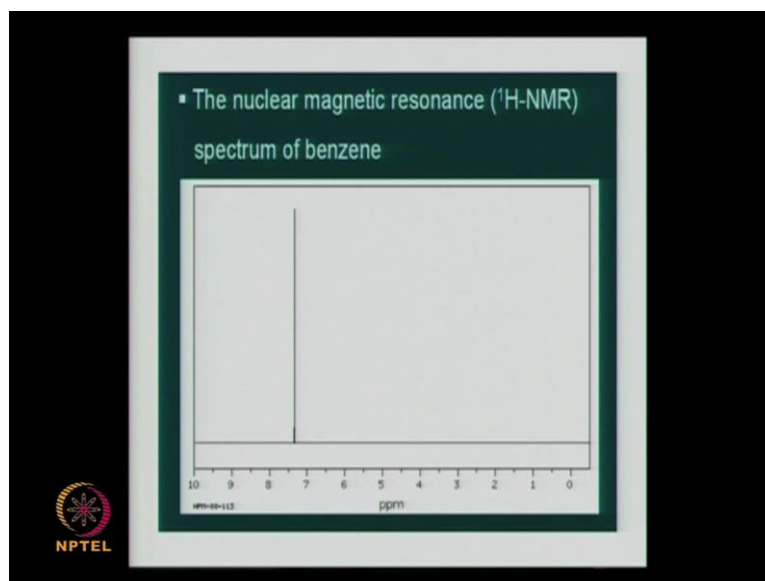
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Type of radiation	Properties explored
γ -ray region	Chemical shift or isomer shift, nuclear quadrupole moments etc.

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And gamma ray region is much higher in energy enables us to understand special properties like chemical shift or the isomer shift, nuclear quadrupole moment, etcetera. So, as you see that when you use different types of radiation, you study different properties of the same molecule.

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Let us me give you an example of what this, all of these things mean by just giving you two or three spectra of the same molecules for different spectroscopic methods. For example, the nuclear magnetic resonance spectrum, all this 1 H-NMR means, its proton, the atomic number, the nuclear magnetic resonance spectrum of benzene. Here, this is the atomic weight, the proton NMR spectrum benzene contains only one line.

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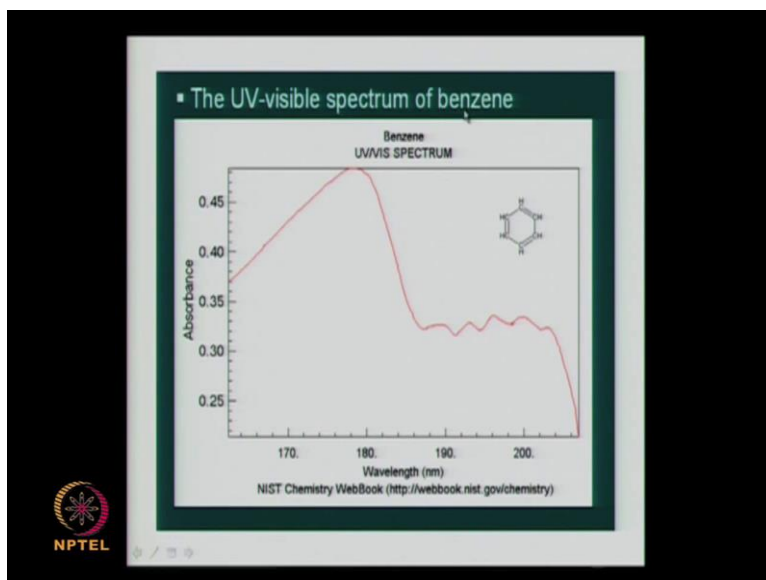


The infrared spectrum of the same molecule, now we use different radiation, different electromagnetic radiation and different concept. See that the infrared spectrum of

molecules, this is the intensity transmission, this is transmittance instead of absorbance, this is the light transmitted.

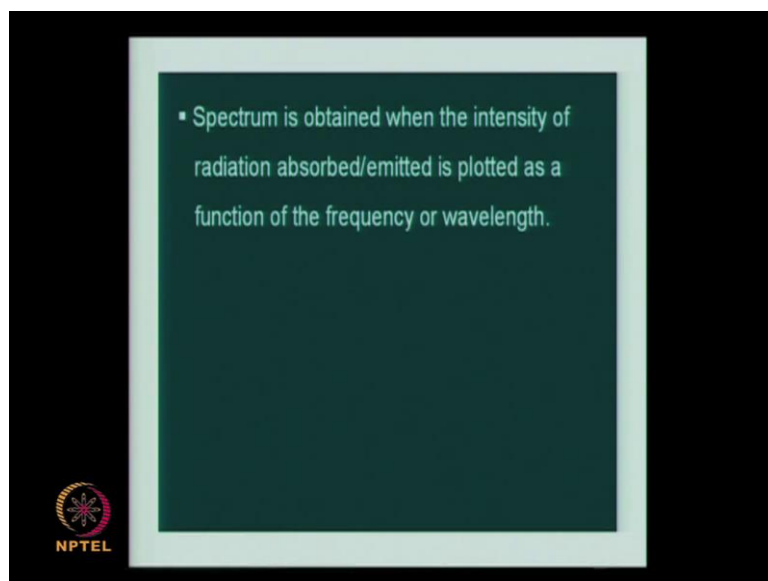
Then, you have the wave number here, the wave number decreases this way. And you have spectral patterns similar to what we drew namely, that there is a very characteristic spectrum, which is very different from the corresponding NMR spectrum of the same molecules.

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The UV-visible spectrum of benzene, for example, this is a very lower resolution. What you see is almost the absorbance here is plotted. You see that this is the pattern of the absorbance versus the wavelength. The absorbance is maximum at a particular point and then it sort of tapers off different wavelengths.

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So, this spectrum that we talked about is obtained when the intensity of the radiation observed or emitted is plotted as a function of the frequency of wavelength. And as I told you in the very beginning, that there are these three features: the line widths, the line position and the line intensities, these are the three characteristic quantities of any molecular proper, any molecular system, that we want to understand in each of these spectrum.