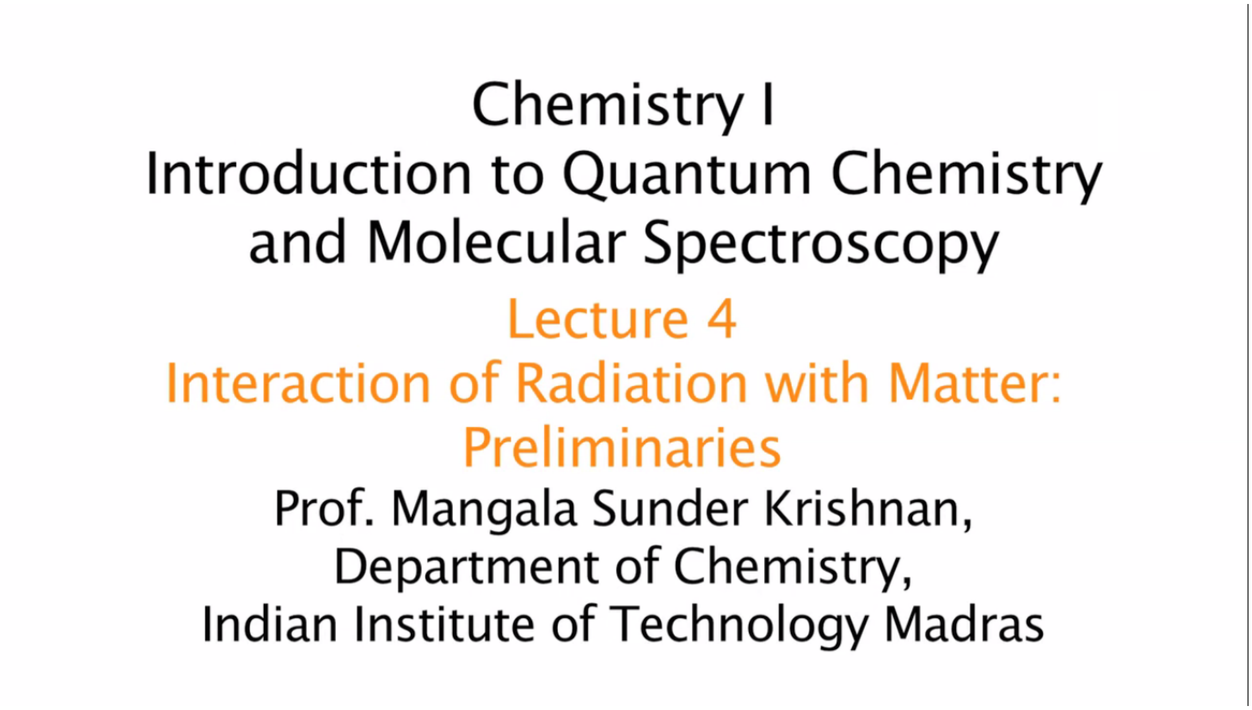
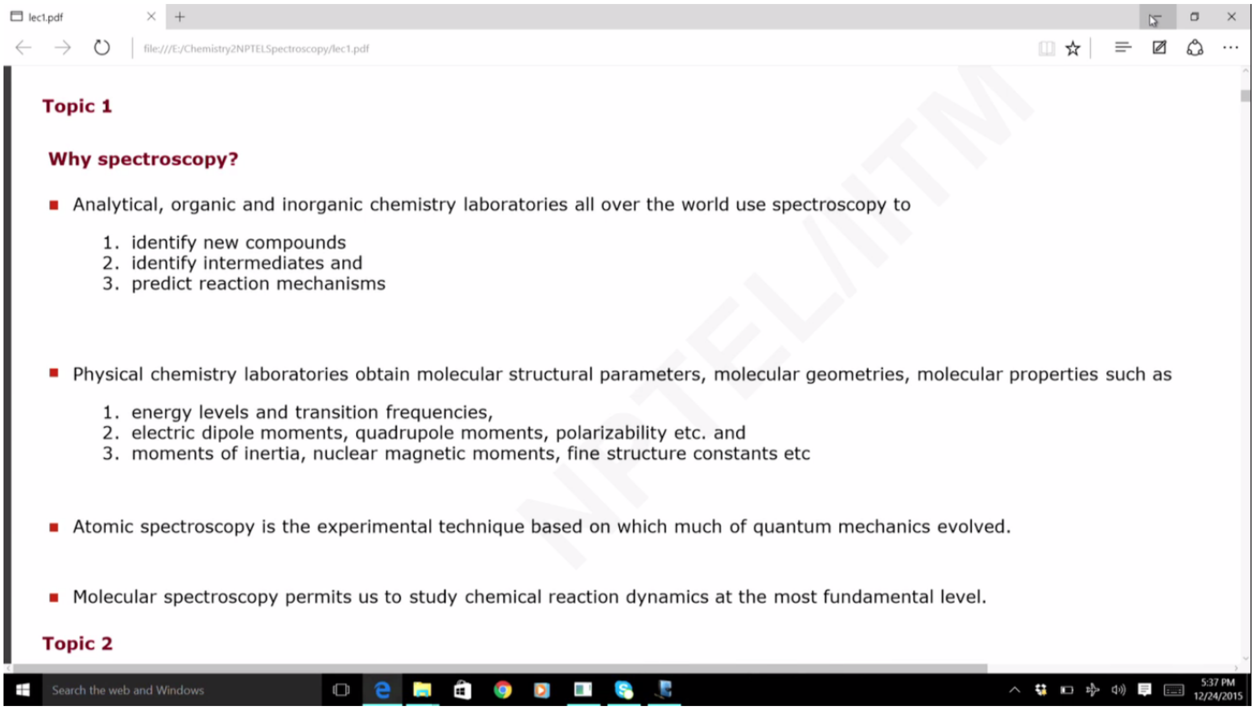


Chemistry I
Introduction to Quantum Chemistry and Molecular Spectroscopy
Lecture 4
Interaction of Radiation with Matter: Preliminaries

Prof. Mangala Sunder Krishnan,
Department of Chemistry,
Indian Institute of Technology Madras

Welcome back to the lecture. In this lecture on the introduction to molecular spectroscopy we shall look at the interaction of radiation with matter a little more in detail but first I would like to impress upon you why we need to study spectroscopy in such great detail. There are many reasons and I have listed some of these things since this is largely text. I have them already prepared as a text material. So why do we need to study spectroscopy. Many reasons.



Topic 1

Why spectroscopy?

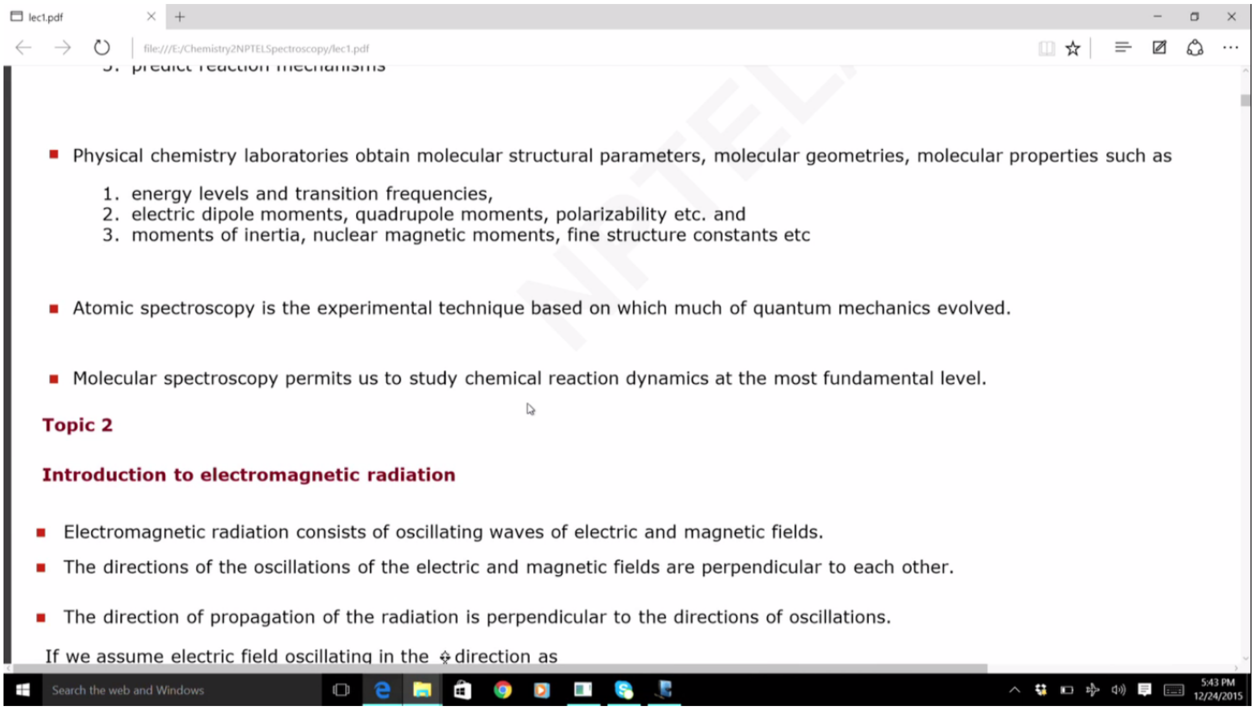
- Analytical, organic and inorganic chemistry laboratories all over the world use spectroscopy to
  1. identify new compounds
  2. identify intermediates and
  3. predict reaction mechanisms
- Physical chemistry laboratories obtain molecular structural parameters, molecular geometries, molecular properties such as
  1. energy levels and transition frequencies,
  2. electric dipole moments, quadrupole moments, polarizability etc. and
  3. moments of inertia, nuclear magnetic moments, fine structure constants etc
- Atomic spectroscopy is the experimental technique based on which much of quantum mechanics evolved.
- Molecular spectroscopy permits us to study chemical reaction dynamics at the most fundamental level.

Topic 2

First of all spectroscopy is the experimental science for understanding most of the developments of quantum mechanics, the theory, the prediction etc. at one level. But from the point of view of chemistry spectroscopy is the subject through which we are able to identify and analyze molecules and also new molecular compounds. So the entire branches of analytical organic and inorganic chemistry laboratories all over the world they use spectroscopy for several reasons obviously to identify new compounds, to identify intermediates in the chemical reaction because very often if the intermediates are slightly long-lived it's possible for us to actually detect them using several spectroscopic techniques depending on the lifetime. It's also important in our ability to understand how a chemical reaction takes place. Therefore predicting the reaction mechanisms is an extremely important objective and an activity of any chemist particularly organic and inorganic chemists.

In the physical chemistry laboratories of course we use molecular spectroscopy to obtain signatures of molecules. That is what is the molecule in terms of its size, shape, the bond length and bond angles between different elements in the molecule and therefore the entire range of molecular structural parameters, molecular geometries and molecular properties the electric and magnetic properties of the molecules can all be studied by using spectroscopic techniques as well as the quantum mechanical and physical chemical -- physical chemistry theories. So the energy levels of molecules of course we cannot measure the energy levels but we can measure the transition between the energy levels in the form of the light that is absorbed or by the light that is emitted. Therefore, transition frequencies can be experimentally observed which validate the calculation of the energy levels. We can study molecular electric properties such as the charge distribution in a molecule. If you think about carbon dioxide as an example carbon dioxide does not have an electrical charge distribution which is polarized. That is the carbon at the center with the two oxygens the positive and the negative charge centers coincide in terms of the electoral negativities and therefore carbon dioxide does not have any electric moment at the most elementary level it does not have a dipole moment. On the other hand if the carbon dioxide molecule during vibration is slightly bent you can see that the carbon oxygen bond may have an electric dipole because of the carbon being slightly positive and the oxygen being slightly negative there is a charge separation and there is a distance between them therefore the charge times the distance gives you the dipole moment and correspondingly on this side there is the other dipole moment and these two dipole moments being vectors actually add up to give you a net dipole moment. This is during the process of molecular vibration. Therefore it's possible for us to identify electric dipole moments which may not be there but which may appear. That's in the case a molecule such as carbon dioxide.

On the other hand if you think about say methyl chloride Ch3Cl you know that the carbon chlorine is one of the tetrahedral bonds and the carbon hydrogen is the other of the three tetrahedral bonds that you and therefore, there is a net dipole moment in the molecule and such molecular charge distributions due to the atoms in the molecule are measured in the form of electric dipole moments and they are measured in the form of quadrupole moments and also in the field of an external electric or magnetic field how these charge distributions rearrange themselves, they polarize themselves in the name of – in the form of what are known as the polarizability factors. So molecular electrical and magnetic properties are directly studied by associating the electric and the magnetic fields of the electromagnetic radiation with such properties and then determining them the changes that happen and so on. Molecular geometries are fully determined by calculating the moment of inertia, the center of mass in the molecule and then the moment of inertia about three mutually perpendicular axis and then the nuclear magnetic moments of the individual nuclei, the fine structure constants such as the chemical shift and the spin-spin coupling constants that you will eventually come to know of in a nuclear magnetic resonance and so on and there are many other fine structure constants. There fore, physical chemistry is very much concerned with determining the entire range of properties and distribution of electric and magnetic charges in a molecule. Therefore, spectroscopy is very important. Atomic spectroscopy of course is the experimental method is the experimental technique from which much of quantum mechanics evolve. Remember Niels Bohr trying to explain the spectrum of the hydrogen using the already known series of spectral lines known as the Lyman series the Balmer series, Paschen series and so on and Niels Bohr came up with the first idea of what is called the quantizing the energy of the electron in an atom and therefore atomic spectroscopy since then is one of the most important branches for understanding quantum mechanical concepts and also experimentally the behavior of atoms in magnetic and electric fields. Molecular spectroscopy of course permits us to study the chemical reaction dynamics of the most fundamental level and as the atoms move away from a molecule they either dissociate from a molecule and from other species and so on. If you want to follow that in detail molecular spectroscopy provides you much of the answers. So as a field spectroscopy has matured to give you many many answers.



predict reaction mechanisms

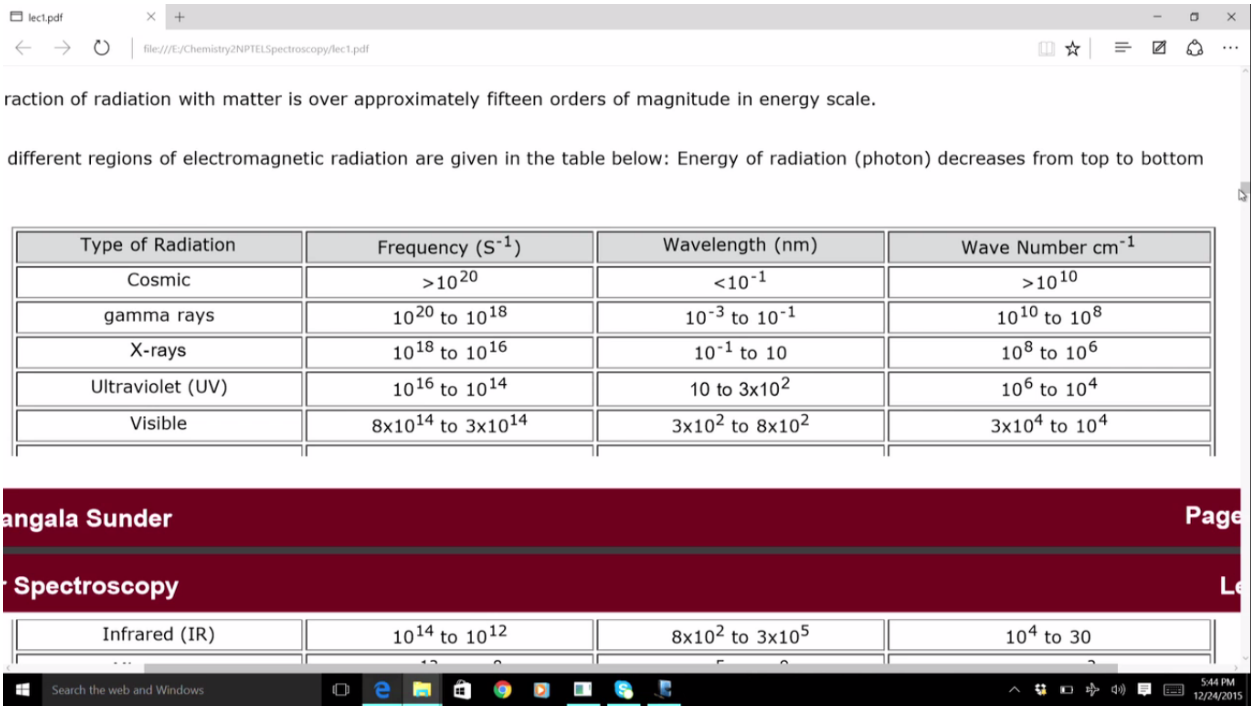
- Physical chemistry laboratories obtain molecular structural parameters, molecular geometries, molecular properties such as
  1. energy levels and transition frequencies,
  2. electric dipole moments, quadrupole moments, polarizability etc. and
  3. moments of inertia, nuclear magnetic moments, fine structure constants etc
- Atomic spectroscopy is the experimental technique based on which much of quantum mechanics evolved.
- Molecular spectroscopy permits us to study chemical reaction dynamics at the most fundamental level.

Topic 2

Introduction to electromagnetic radiation

- Electromagnetic radiation consists of oscillating waves of electric and magnetic fields.
- The directions of the oscillations of the electric and magnetic fields are perpendicular to each other.
- The direction of propagation of the radiation is perpendicular to the directions of oscillations.

If we assume electric field oscillating in the [illegible] direction as

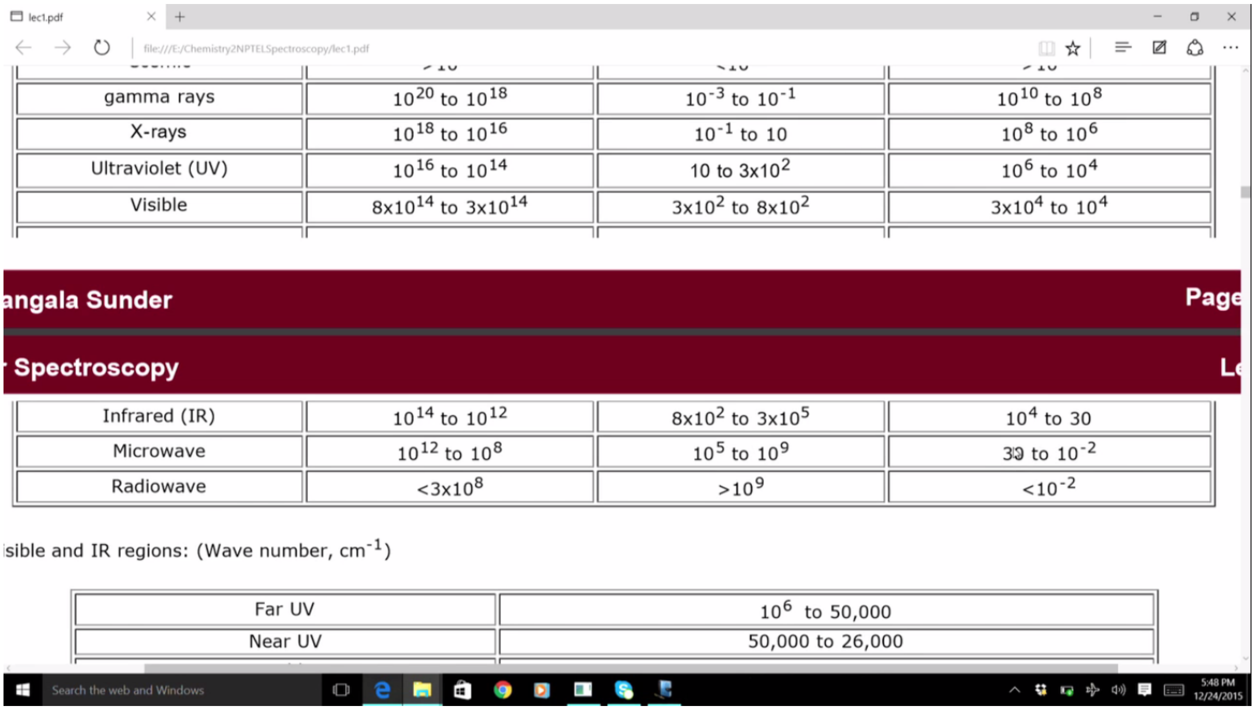


raction of radiation with matter is over approximately fifteen orders of magnitude in energy scale.

different regions of electromagnetic radiation are given in the table below: Energy of radiation (photon) decreases from top to bottom

Type of Radiation	Frequency (S^{-1})	Wavelength (nm)	Wave Number cm^{-1}
Cosmic	$>10^{20}$	$<10^{-1}$	$>10^{10}$
gamma rays	10^{20} to 10^{18}	10^{-3} to 10^{-1}	10^{10} to 10^{8}
X-rays	10^{18} to 10^{16}	10^{-1} to 10	10^{8} to 10^{6}
Ultraviolet (UV)	10^{16} to 10^{14}	10 to $3x10^{2}$	10^{6} to 10^{4}
Visible	$8x10^{14}$ to $3x10^{14}$	$3x10^{2}$ to $8x10^{2}$	$3x10^{4}$ to 10^{4}
Infrared (IR)	10^{14} to 10^{12}	$8x10^{2}$ to $3x10^{5}$	10^{4} to 30

Now it's not all happening through very simple processes. All of this does not happen by taking the electromagnetic radiation in any which way that we would like to but understanding the fact that different energies, different electromagnetic radiations of different energies have different impacts on the molecule. First of all how do we classify the electromagnetic radiation for spectroscopic studies. Here is one small table that you can see that gives you the type of radiation approximately in the corresponding frequency ranges and also the wavelengths corresponding to that frequency or the wave number corresponding to that. The most common unit of wave number is not a meter inverse but centimeter inverse. That's what you see in most textbooks. Of course wavelengths are often described in nanometers or even sometimes micrometers. Frequency is always in the form of second inverse and therefore it's – this unit is known as the Hertz. Cosmic radiation has a very very high frequency and therefore the individual photon has an extremely large energy. Gamma rays have frequencies in the range this is an approximate range in the range between 10 raised to 20 oscillations per second to 10 raise to 18 oscillations per second and the corresponding wavelength which is obtained from the relation I note down in the last lecture is approximately 10 to the minus 3 nanometers to that is this is like a Picometer and then 10 to the minus 1 nano meter and the wave number is about 10 to the 10 to 10 to the 8.



gamma rays	10^{20} to 10^{18}	10^{-3} to 10^{-1}	10^{10} to 10^{8}
X-rays	10^{18} to 10^{16}	10^{-1} to 10	10^{8} to 10^{6}
Ultraviolet (UV)	10^{16} to 10^{14}	10 to $3x10^{2}$	10^{6} to 10^{4}
Visible	$8x10^{14}$ to $3x10^{14}$	$3x10^{2}$ to $8x10^{2}$	$3x10^{4}$ to 10^{4}

angala Sunder Page

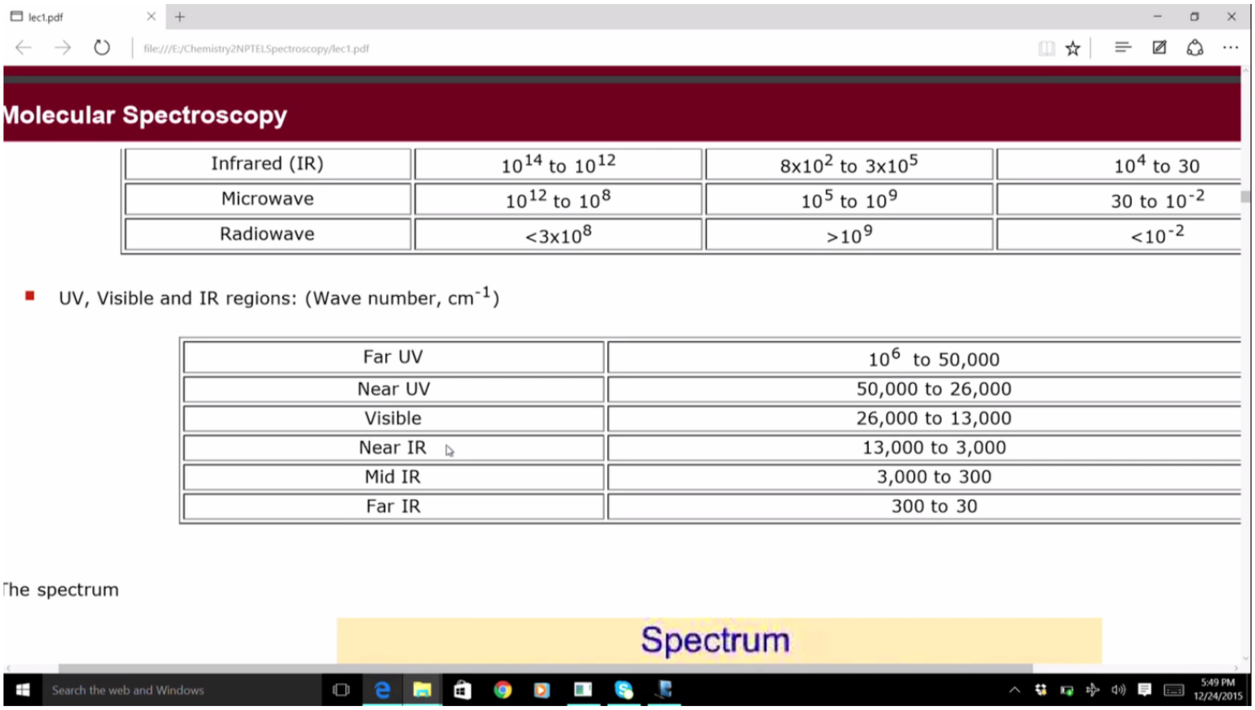
Spectroscopy Le

Infrared (IR)	10^{14} to 10^{12}	$8x10^{2}$ to $3x10^{5}$	10^{4} to 30
Microwave	10^{12} to 10^{8}	10^{5} to 10^{9}	30 to 10^{-2}
Radiowave	$<3x10^{8}$	$>10^{9}$	$<10^{-2}$

isible and IR regions: (Wave number, cm^{-1})

Far UV	10^{6} to 50,000
Near UV	50,000 to 26,000

X-rays are next lower in energy with a frequency between 10 to the 18 Hertz to 10 to the 16 Hertz and the wavelength is between a nanometer to one tenth of a nanometer. Ultraviolet rays are the lower in energy. The each photon if you write E equal to h nu the ultraviolet rays has lower energy than the X-ray Photon and you see that the frequency is 10 to the 16 Hertz to 10 to the 14 Hertz and the wavelength and wave numbers are accordingly the numbers that you see here. This is an approximate division for the energies and then visible light which all of us are very familiar with and all of us are impacted by so much is actually a very narrow range of electromagnetic radiation frequencies. It's 8 and 3 to 10 to the 14 Hertz. Therefore it's a very very narrow range in which you see all the seven colors and also the range of colors the visible light and the corresponding wavelength and the numbers are given here. These are important in understanding what properties that they allow us to investigate below with the light are the infrared radiation. Microwave radiation and radiowave. Both microwave and radiowave are extremely important in studying magnetic properties of the nuclei, magnetic properties of the molecules and therefore in the nuclear magnetic resonance and electron paramagnetic resonance the energies corresponding to microwave and radiowaves are typically used and you can see that the microwave frequency is roughly between this is one tenth of a gigahertz. A gigahertz is ten to the nine Hertz and this is about a thousand gigahertz. So you can see that this is the range of frequencies and the corresponding wavelength and the numbers are given here and the radiowave is of course among the lowest in energy with a frequency less than then a gigahertz. It's about 300 megahertz. That's what you have and the wave length is 10 to the 9 nanometer. That's almost a meter that's why it's called a radiowave. it's a meter wave okay. So these are the typical classifications of radio electromagnetic radiation but in the visible range and invisible and the UV visible and IR range there is further classification of radio electromagnetic radiation as far UV, near UV, visible, near infrared, mid infrared, and far infrared and these are approximately corresponding to the different types of interactions that the light will have with either the electronic motion or with the nuclear motion or with the overall rotation of the molecule and so on. Therefore this is important to remember. The approximate numbers of the wave numbers are given here.



olecular Spectroscopy

Infrared (IR)	10^{14} to 10^{12}	8×10^{2} to 3×10^{5}	10^{4} to 30
Microwave	10^{12} to 10^{8}	10^{5} to 10^{9}	30 to 10^{-2}
Radiowave	$<3\times10^{8}$	$>10^{9}$	$<10^{-2}$

- UV, Visible and IR regions: (Wave number, cm^{-1})

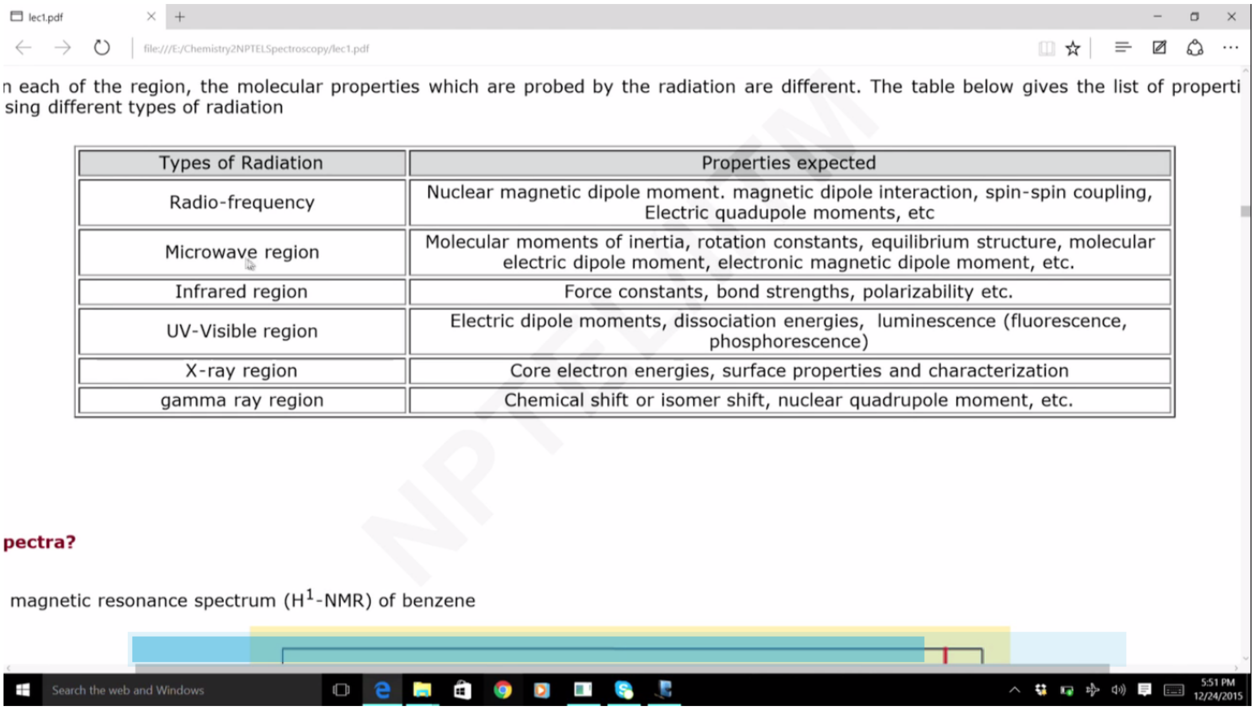
Far UV	10^{6} to 50,000
Near UV	50,000 to 26,000
Visible	26,000 to 13,000
Near IR	13,000 to 3,000
Mid IR	3,000 to 300
Far IR	300 to 30

he spectrum

Spectrum

The spectrum if you look at it the colorful spectrum that you have is actually only from far UV which is somewhere around here very high frequency to the far IR which is somewhere in here very low frequency. This is the visible spectrum roughly between 8 times 10 to the 14 Hertz to 3 times 10 to the 14 Hertz. Now why is it important because in each of these region as you see the radiation from cosmic rays to radio waves the molecular properties which are probed by the radiation are different. What are those properties you can see that list below.

So radio frequency, now we go the other way around radio frequency is the lowest in energy. Radio frequency enables us to measure what are called the nuclear magnetic dipole moments and therefore the magnetic dipole interactions between nuclei dipole-dipole interactions and also the nuclear spins how do they couple with each other through scalar and tensorial interactions and then the electric quadrupole moments which are basically charge distributions inside the nuclei which are non spherical charge distribution that is a nucleus is not a spherical nucleus but it's slightly distorted and how these non spherical charge distributions interact with non uniform charge distribution outside due to the electrons and those are called electric quadrupole moments. These are fundamental properties of many nuclei. All nuclei with the spin quantum number one or more. All of these are measured using radio frequency and microwave region and both these basically what we call as the magnetic. These are what we call as the magnetic resonance spectroscopy.



n each of the region, the molecular properties which are probed by the radiation are different. The table below gives the list of properti
sing different types of radiation

Types of Radiation	Properties expected
Radio-frequency	Nuclear magnetic dipole moment. magnetic dipole interaction, spin-spin coupling, Electric quadupole moments, etc
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.
UV-Visible region	Electric dipole moments, dissociation energies, luminescence (fluorescence, phosphorescence)
X-ray region	Core electron energies, surface properties and characterization
gamma ray region	Chemical shift or isomer shift, nuclear quadrupole moment, etc.

pectra?

magnetic resonance spectrum (H^1-NMR) of benzene

Microwave of course can also be used to measure the molecular moments of inertia and properties known as rotation constants from which it's possible for us to determine the equilibrium structure of the molecule and through the equilibrium structure we may also be able to calculate molecular electric dipole moment and the intensities of the radiation in microwave. Therefore, properties of the molecular structure and molecular electric charge distributions and the electronic magnetic dipole moment all those things are measured using microwave spectroscopy. Infrared region allows us to determine the bond strength of most molecules stable and lots of stable molecules. The extent to which the molecules can be polarized by external electric fields distorted and the force constants which are roughly proportional to the bond strengths. All these properties can be determined using infrared region.

The UV visible region allows us to understand electronic transitions in an atom in a molecule. Therefore, the electric dipole moments are due to the electronic motion and the dissociation energies of the molecule I mean what energy is required to break the molecules into individual components, etc. and also the optical properties, visible optical properties that we make use of in day to day life the luminescence properties of the light that you see here, the fluorescence property that you see here, the phosphorescence property the screen for example is phosphorescent and therefore that kind of electrical properties are studied; those kinds of electrical properties are studied using UV visible electromagnetic radiation.

X-ray region allows us to understand the core electron energies inside the molecule in an atom for example if you have say sodium atom you know from the element and the electronic structure that it has one valence electron and has ten core electrons which are in the 1s and 2s orbital transitions between them can be studied using X-ray region because these are very high energies and also X-ray is extremely important for surface properties and the surface analysis particularly in solids and in crystalline materials and so on. So surface properties and characterizations are very very usefully done using X-ray spectroscopy and Gamma-ray region which is due to the

Gamma ray which are extremely high in energy allow us to study the nuclear properties such as the nuclear quadrupole moment and the chemical shift or the isomer shift that we need to know.

So these are some of the properties which are scaled by different radiations of energies and therefore you can see that electromagnetic spectrum with 15 orders of magnitude in energies between say 10 to the 20 Hertz for the cosmic rays to about a megahertz 10 to the 6 Hertz in the case of MMR that is magnetic radiation magnetic resonance the nuclear magnetic resonance. The 15 orders of magnitude scan the entire and molecular properties and therefore it's very important for us to understand each and every one of them in detail. Of course this course will give you an overview of some of these in the case of microwave infrared and electronic spectroscopy. I will not be dealing with magnetic resonance in this particular course but in a separate course I will give you more details. We will continue this to understand a little bit more about what are the features that we look for in a spectrum in the next lecture. Until then thank.