INDIAN INSTITUTE OF TECHNOLOGY ROORKEE
NPTEL
NPTEL ONLINE CERTIFICATION COURSE
Structural Analysis of Nanomaterials
Lecture – 19
Microscopic Structural Analysis
Of Nanomaterial-11
With
Dr. Kaushik Pal
Department of Mechanical & Industrial Engineering
Indian Institute of Technology Roorkee

Hello, in this lecture we are going to discuss about the microscopic structural analysis of Nanomaterials part2. So first what are the types already in, if you remember that in our last lecture we have already discussed about the,

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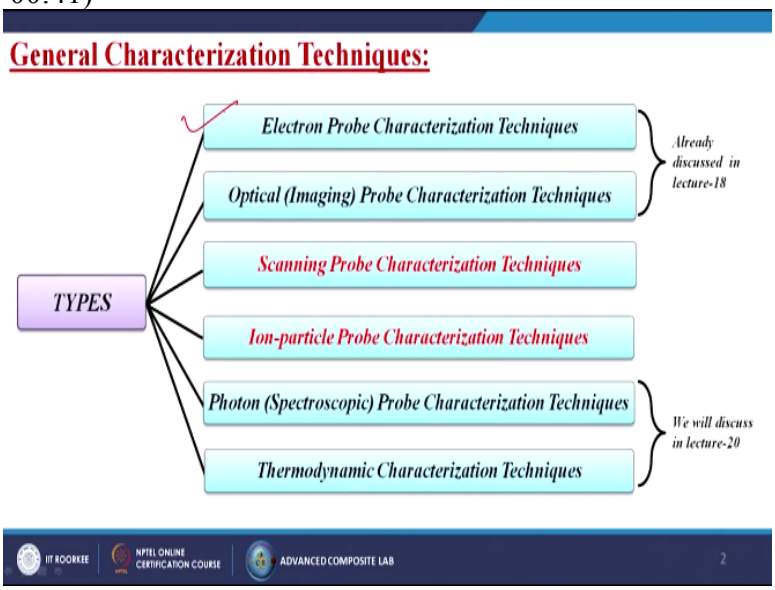

Electron probe characterization techniques and the optical imaging probe characterization techniques. In this particular lecture we are going to discuss about the scanning probe characterization techniques and the ion particle probe characterization techniques. And another two will be left, which we are going to discuss in our next lecture. So first what is scanning probe characterization techniques? So generally the STM scanning tunneling microscopy,

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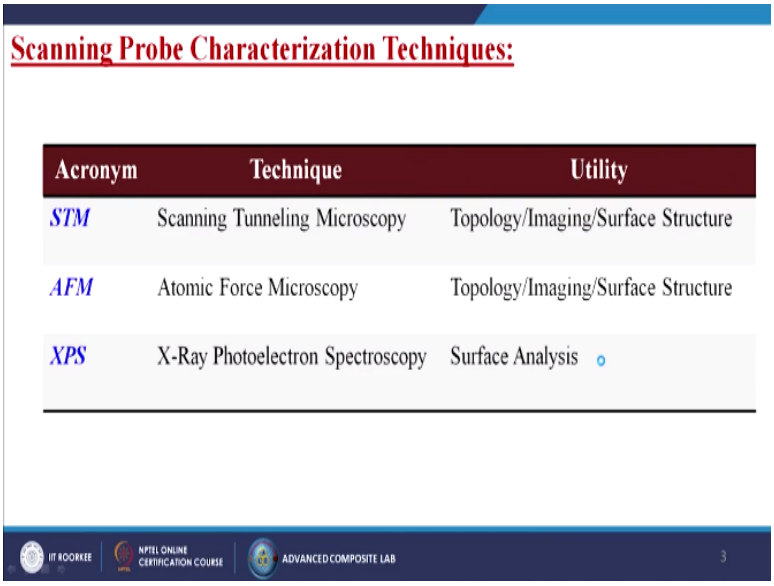

Which will give you the information about the topology, imaging or maybe surface structure, AFM atomic force microscopy, topology or maybe imaging or maybe the surface structure, then the last one is XPS, this is the latest technology or may be the latest characterization. So x-ray photoelectron spectroscopy which will give you the surface analysis of that particular material.

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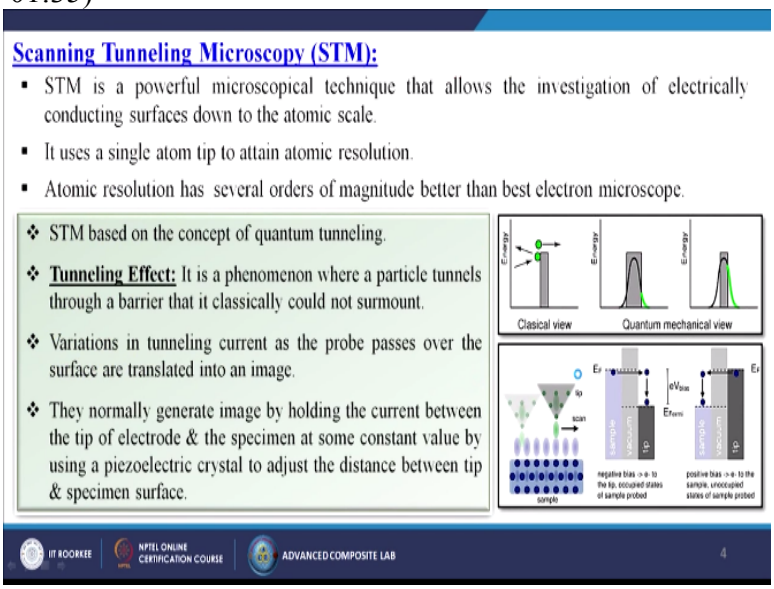

First we are going to discuss about the scanning tunneling microscopy (STM). So STM is a powerful microscopical technique that allows the investigation of electrically conducting surfaces down to the atomic scale. It uses the single atom tip to attain atomic resolution. Atomic resolution has several orders of magnitude better than best electron microscope. STM based on the concept of quantum tunneling, how it is taking place? What is tunneling effects?

It is a phenomenon of where a particle tunnels through a barrier that it classically could not surmount. Variation in tunneling current as the probe passes over the surface are translated into an image. They normally generate image by holding the current between the tip of electrode and

the specimen at some constant value by using a piezoelectric crystal to adjust the distance between tip and specimen surface. So automatically it will maintain a constant gap over there.
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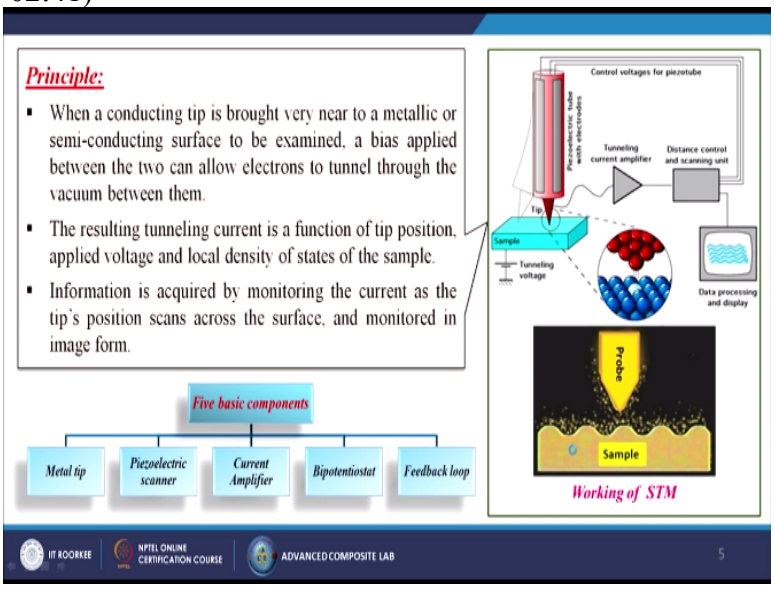

What is the working principle? When a conducting tip is brought very near to a metallic or semi-conducting surface to be examined, a bias applied between the two can allow electrons to tunnel through the vacuum between them so this is talking place. The resulting tunneling current is the function of tip position, applied voltage and local density of state of the sample itself.
Information is acquired by monitoring the current as the tip's position scans across the surface, and monitored in image form, so this is the sample and this is the probe. So generally it moves like this, so five basic components metal tip, piezoelectric scanner, current amplifier, bipotentiostat, and the feedback loop.
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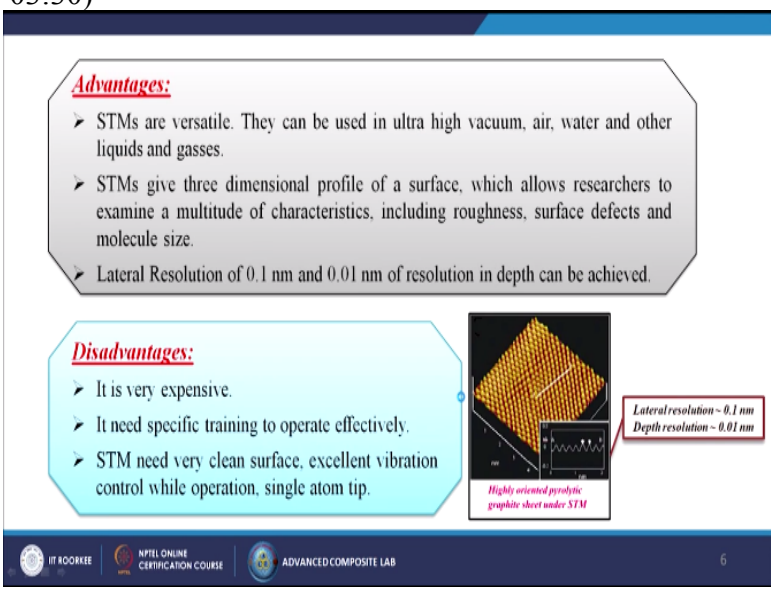

What are the advantages? STMs are versatile. They can be used in ultra high vacuum, air, water and other liquids and gasses. STMs give three dimensional profile of a surface, which allows

researchers to examine a multitude of characteristics, including roughness, surface defects and molecule size. Lateral resolution of 0.1 nm and 0.01 nm of resolution in depth can be achieved. Of course there are certain disadvantages; it is very expensive, it needs specific training to operate effectively.

STM need very clean surface, excellent vibration control while operation, single atom tip. So here, this is highly oriented paralytic graphite seat under the STM. So lateral resolution is here 0.1 nm and the depth resolution is 0.01 nm. Next is called the atomic force microscopy or short it is known as AFM.

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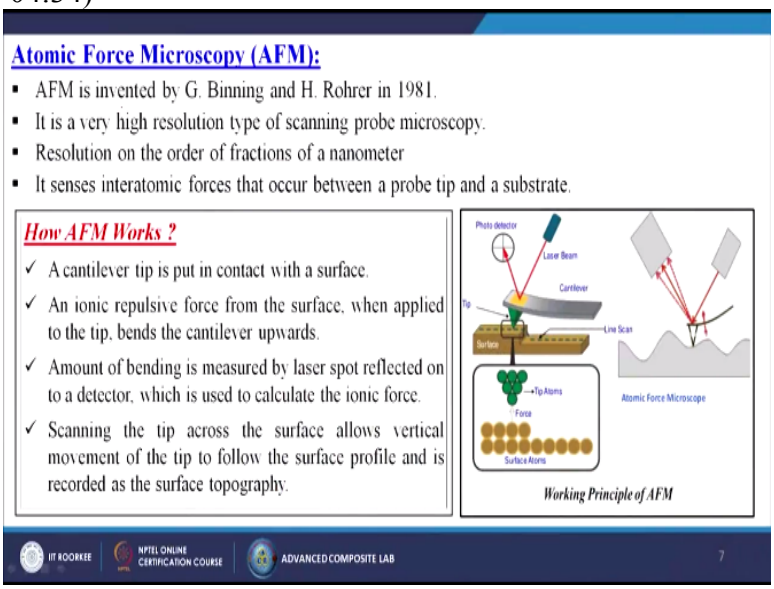

AFM is invented by G. Binning and H. Rohrer in the year of 1981. It is a very high resolution type scanning probe microscopy, resolution on the order of fractions of a nanometer. It senses interatomic forces that occur between a probe tip and a substrate. How AFM works? A cantililever tip is put in contact with a surface itself, a cantilever tip here it is touching the surface.

An ionic repulsive force from the surface, when applied to the tip, bends the cantilever upwards yes of course. When it is touching so due to its reach pattern it is going up and down. Amount of bending is measured by laser spot reflected on to a detector, which is used to calculate the ionic force. Scanning the tip across the surface allows vertical movement of the tip to follow the surface follow the surface profile and is recorded as the surface topography.

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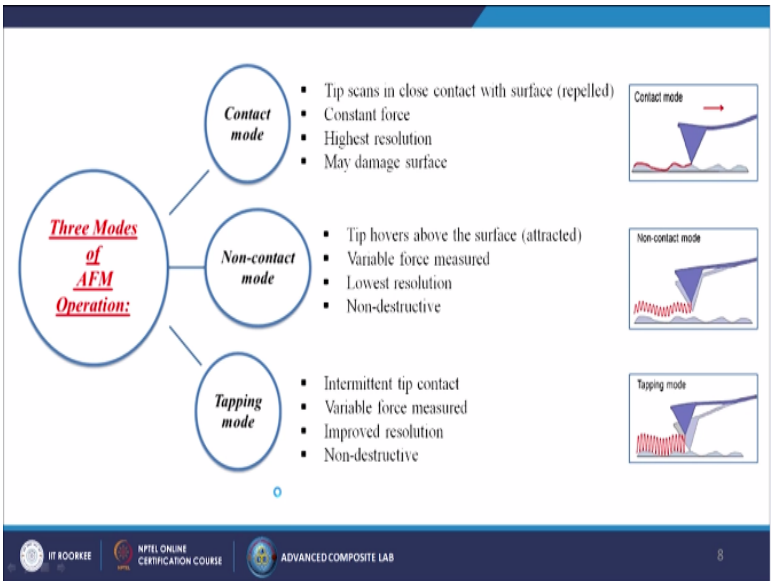

Generally there are three modes of AFM operations. First one is called contact mode in which the probe is touching the surface of the materials. Tips scans can close contact with surface repelled. Constant force, highest resolution, may damage the surface. Second one is called the non contact mode, tip hovers above the surface attracted, variable force measured, lowest resolution, non destructive.

And the last one is called tapping mode or maybe semi contact mode. Intermittent tip contact, variable force measured, improved resolution, non destructive in nature.

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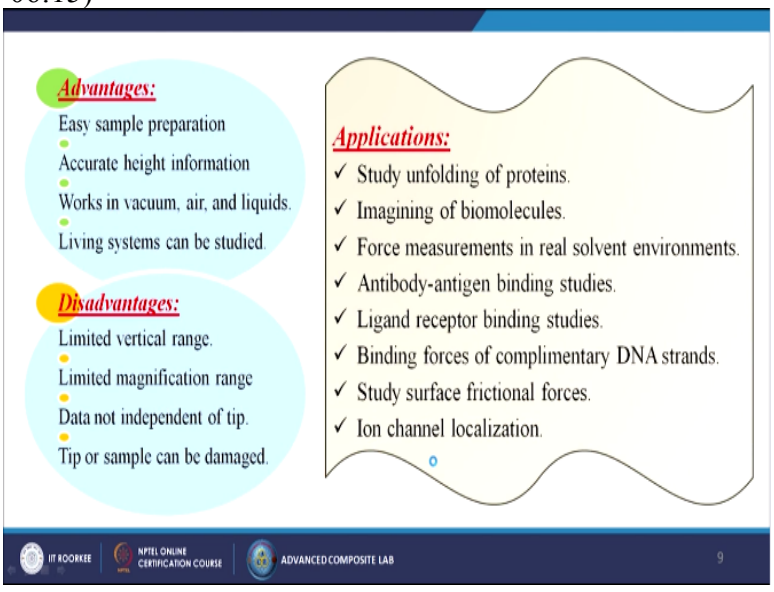

What are the advantages? Easy sample preparations, accurate height information, works in vacuum, air, and liquids, living systems can be studied. What are the disadvantages? Limited vertical range, limited magnification range, data not independent of tip, and tip or sample can be damaged. Of course there are certain applications, what are those?

Study unfolding of proteins, imaging of biomolecules, force measurement in real solvent environments, antibody-antigen binding studies. Ligand receptor binding studies, binding forces

of complimentary DNA strands, study surface frictional forces, ion channel localizations. Then next one is called the x-ray photons spectroscopy or maybe XPS. So XPS is a,
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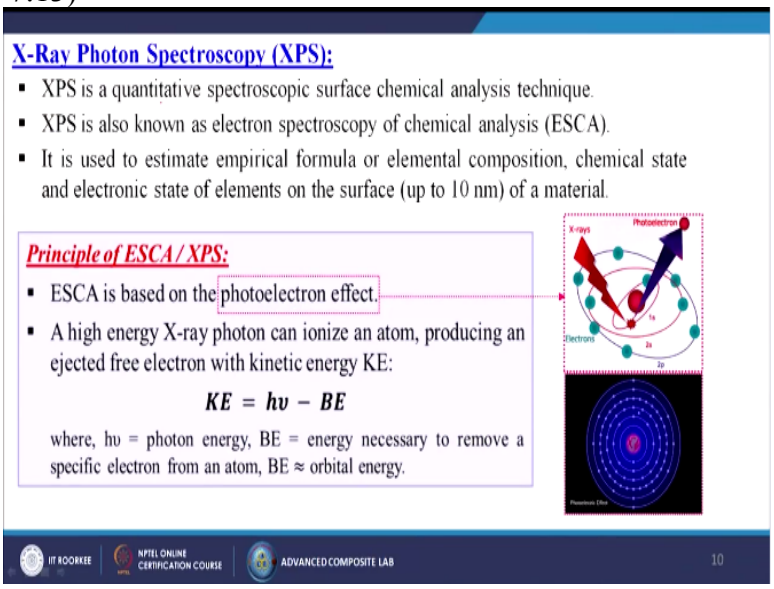

Quantitative spectroscopic surface chemical analysis techniques, XPS is also known as electron spectroscopy of chemical analysis or in short form it is called the (ESCA). It is used to estimate the empirical formula or element composition, chemical state and electronic state of elements on the surface up to 10 nm of a material.
So simple x-ray is falling on the orbitals and the photo electron is roving so in this particular case it is removing. So ESCA is based on the photoelectron effect. So these effects are called the photoelectron effect. High energy x-ray photon can ionize an atom, producing an ejected free electron with kinetic energy KE: generally kinetic energy you are calling it as a KE, so KE is equal to hv minus BE. Where h mu is the photon energy, BE is the energy necessary to remove a specific electron from an atom, or BE is equivalent to the orbital energy.
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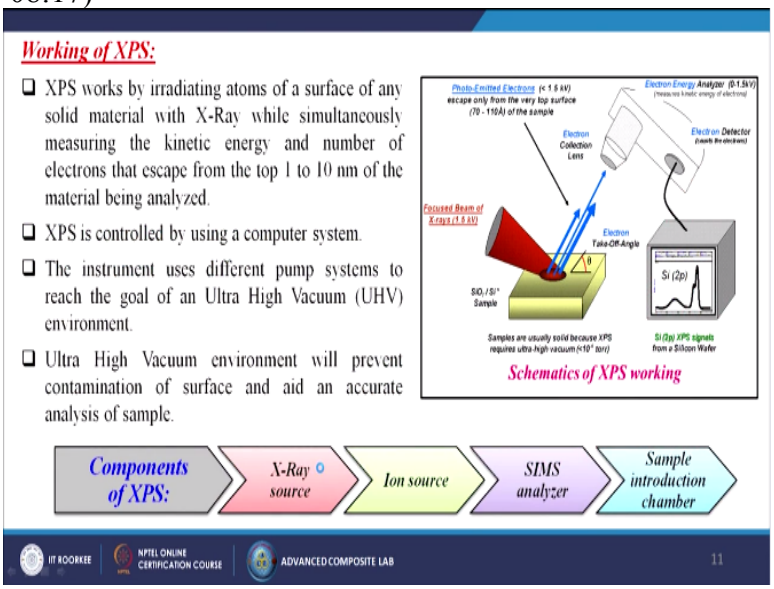

Now working of XPS: XPS works by irradiating atoms of a surface of any solid material with x-ray while simultaneously measuring the kinetic energy and number of electrons that escape from the top 1 to 10 nm of the material being analyzed, XPS is controlled by using a computer system; the instrument uses different pumps systems to reach the goal of an ultra high vacuum (UHV) environment, ultra high vacuum environment will prevent contamination of surface and aid an accurate analysis of the sample itself.

So generally component of XPS first is the x-ray source, ion source, SIMS analyzer, sample introduction chamber.

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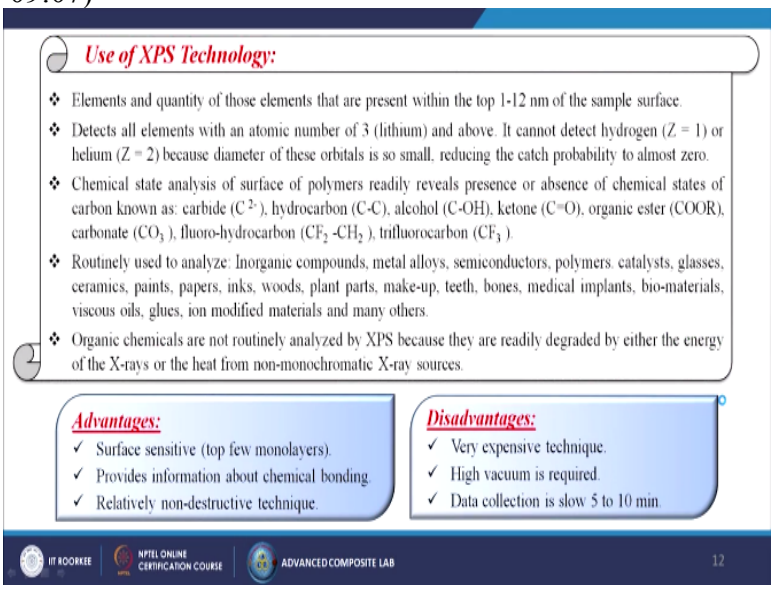

What are the use of XPS technology: elements and quantity of those elements that are present within the top 1-12 nm of the sample surface, detects all element with an atomic number of 3 lithium and above hydrogen and helium cannot be detected. It cannot be detecting hydrogen, z is equal to one or helium z is equal to two. Because diameter of these orbital's is so small, reducing the catch probability to almost zero. Chemical state analysis of the surface of polymer readily reveals presence or absence of the chemical states of carbon known as carbide, hydrocarbon, alcohol, ketone, organic ester, carbonate, fluoro-hydrocarbon or maybe trifluorocarbon. Routinely used to analyze inorganic compounds, metal alloys, semiconductors, polymers catalysts, glasses, ceramics, paints, paper, inks, woods, plant parts, makeup, teeth, bones, medical implants, bio-materials, viscous oils, glues, ion modified materials and many others.

Organic chemicals are not routinely analyzed by XPS because they are readily degraded by either the energy of the x-rays or the heat from non-monochromatic x-rays sources. What are the advantages? Surface sensitive top few monolayer's, provides information about chemical bonding, relatively non destructive techniques. What are the disadvantages?

Very expensive techniques, high vacuum is required, data collection is slow it's almost 5 to 10 minute. Then the next one is the ion particle probe characterization techniques. So in this particular case we are having four types, one is called the NMR nuclear magnetic resonance spectroscopy, it is generally using for analysis off odd number of nuclear species, XRD x-ray diffractions, crystal structure.

We have already discussed XRD in our previous lecture for these particular courses. RS Raman spectroscopy, it is generally for the vibration analysis and another one is called the SAXS, small angle x-ray scattering surface analysis and the particles sizing generally 1 to 100 nm.
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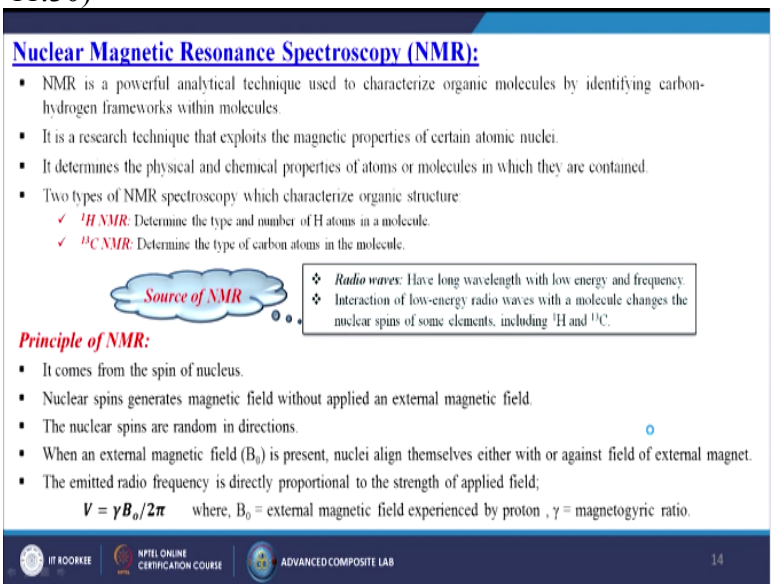

So first is called the nuclear magnetic resonance spectroscopy or maybe (NMR). NMR is a powerful analytical technique used to characterize organic molecules by identifying carbon-hydrogen frame work within molecules. It is a research technique that exploits the magnetic properties of certain atomic nuclei.
It determines the physical and chemical properties of atom molecules in which they are contained. Two types of NMR generally spectroscopy which characterize organic structure, one is called the 1H NMR, determine the type and number of hydrogen atom in a molecule and another one is called the terteincy NMR which determine the type of carbon atoms in the molecule. What is the source of NMR? Radio waves have a long wavelength with low energy and frequency, interaction of low energy radio waves with molecule changes the nuclear spin of some elements, including 1H and the 13c. Principle of NMR: it comes from the spin of nucleus. Nuclear spin generates magnetic field without applied an external magnetic field.
The nuclear spins random in directions, when am external magnetic field B0 is present; nuclei align themselves either with or against field of external magnet. The emitted radio frequency is directly proportional to the strength of applied field. That is new equal to gamma B0 by 2 π, where B0 is equal to external magnetic field experienced by proton, gamma is the magnetogyric ratio. So now what are the components of NMR? First one is called the sample holder,
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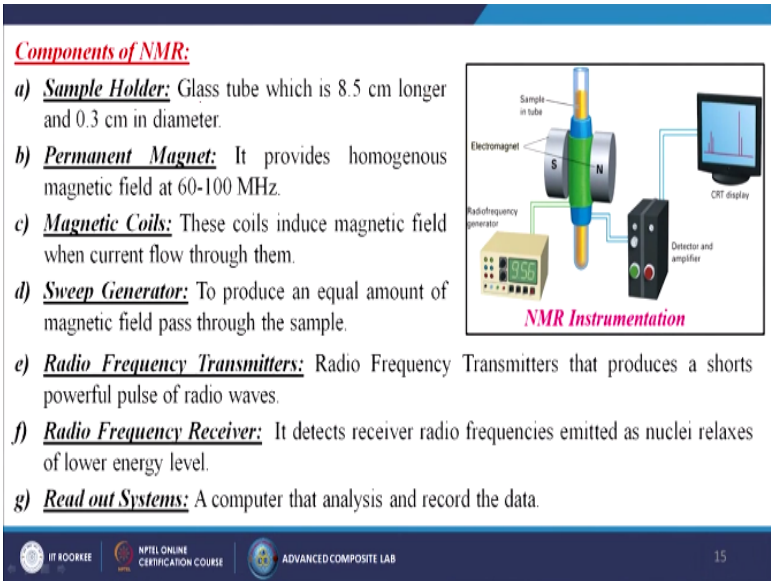

That means glass tube which is 8.5 cm longer and 0.3 cm in diameter. Next is the permanent magnet, it provides the homogeneous magnetic field at 60-100 MHz, so in this particular case you can see this is the sample tube which is number one, then we are having that magnet that is number two. Then magnetic coils, these coils induce magnetic field when current flow through them. Sweet generators, to produce an equal amount of magnetic field pass through the sample itself, so we are having that radio frequency generator over there.

Then we are having that radio frequency transmitter, a radio frequency transmitter that produces a shorts powerful pulse of radio waves. Then radio frequency receiver, it detects receiver radio frequencies emitted as nuclei relax of the lower energy level. And the last one is the read out systems, a computer that analysis and records the data. What are the applications?

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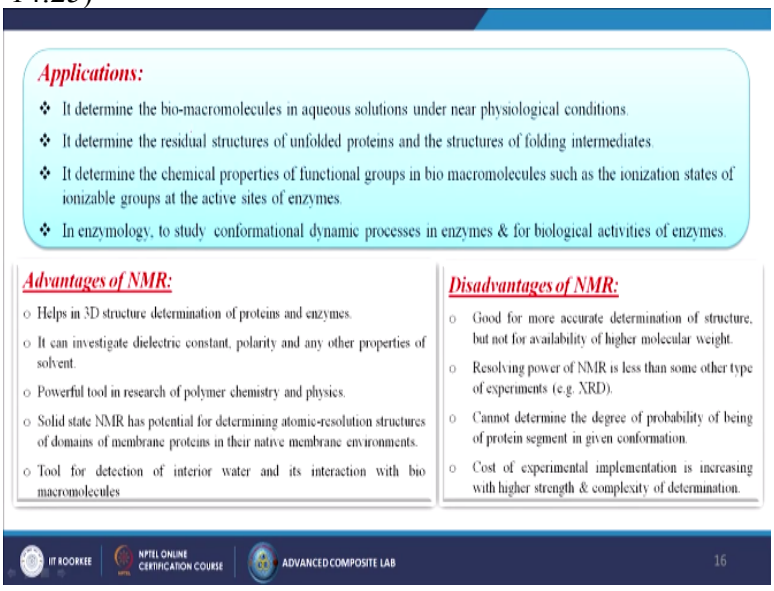

It determines the bio-macromolecules in aqueous solution under near physiological conditions. It determines the residual structure of unfolded proteins and the structure of folding intermediates. It determines the chemical properties of functional group in bio macromolecules such as the

ionization state of ionizable groups at the active sites of enzymes, in enzymology, to study the conformational dynamic process in enzymes and for the biological activities of enzymes. What are the advantages of NMR?

Helps in 3d structure determination of proteins and enzymes; it can investigate dielectric constant, polarity and any other property of solvent. It is a powerful tool in research of polymer chemistry and physics. Solid state NMR has potential for determining atomic resolution structures of domains of membranes, proteins in their native membrane environments. Tool for detection of interior water and its interaction with bio macromolecules, there are certain disadvantages also, good for more accurate determination of structure, but not for availability of higher molecular weight.

Resolving power of NMR is less than some other type of experiments like XRD. Cannot determine the ° of probability of being of protein segment in given confirmation, cost of experiment implementation is increasing with higher strength and complexity of determination.

Now the next one is called the Raman's spectroscopy, Raman spectroscopy was,

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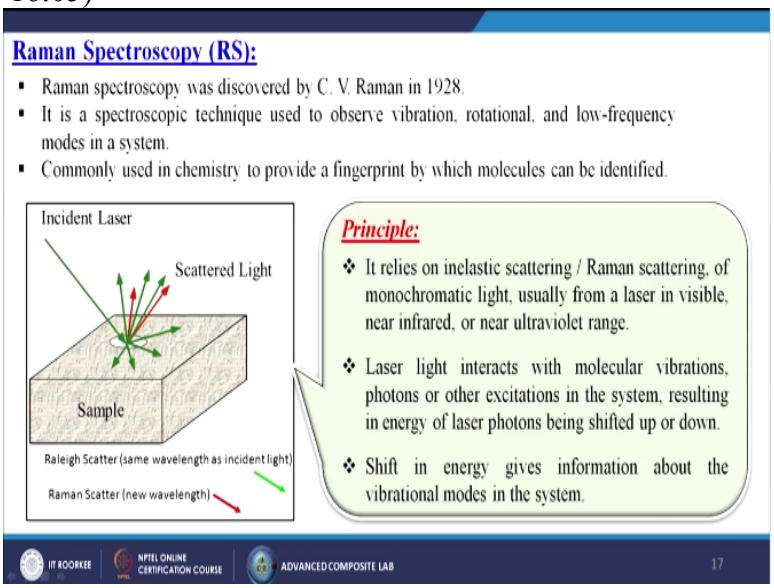

Discovered by C.V. Raman in 1928, it is a spectroscopy technique used to observe vibration, rotational, and low frequency modes in a system, commonly used in chemistry to provide a finger print by which molecules can be identified. So what are the principles? It relies on inelastic scattering or maybe Raman scattering of monochromatic light, usually from a laser in visible, near infrared, or near ultraviolet range.

So incident beam are coming and it is falling on to the sample itself. Then the lights are scattering. Laser light interacts with molecular vibrations, photons or other excitation in the system, resulting in energy of laser photons being shifted up or bottom. Shift in energy gives information about the vibrational modes in the system itself. So in this particular case we are having the Raleigh scatter same wave length as incident light and the red color is the Raman's scatter that is the new wavelength form. Components of Raman spectroscopy, first one is called the laser source.

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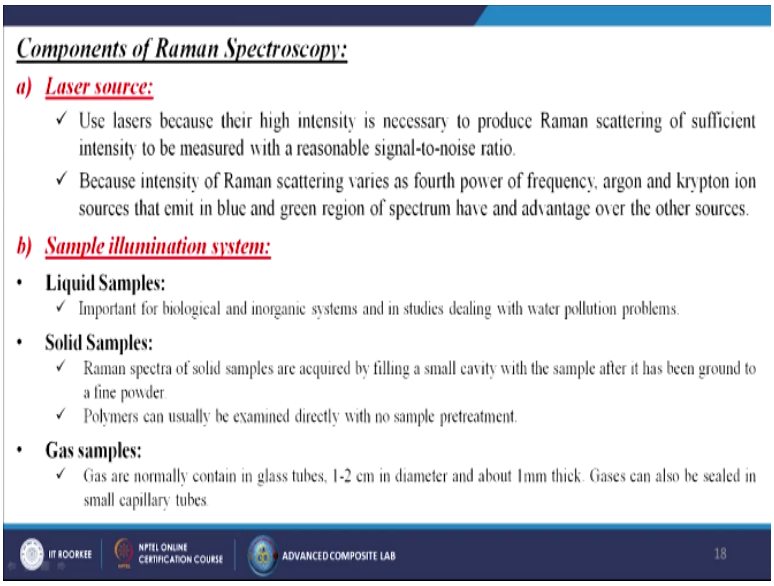

Use lasers because their high intensity is necessary to produce Raman scattering of sufficient intensity to be measured with a reasonable signal-to-noise ratio. Because intensity of Raman scattering varies as fourth power of frequency, argon and krypton ion source that emit in blue and green region of spectrum have an advantage over the other sources.

Next is the sample illumination system, liquid samples, important for biological and inorganic systems and in studies dealing with water pollution problems? Solid samples, Raman spectra of solid samples are acquired by filling a small cavity with the sample after it has been ground to a fine powder. Polymers can usually be examined directly with no sample pretreatment. Gas samples, gas are normally contain in glass tubes, 1-2 cm in diameter and about 1mm thick gases can also be scaled in small capillary tubes.

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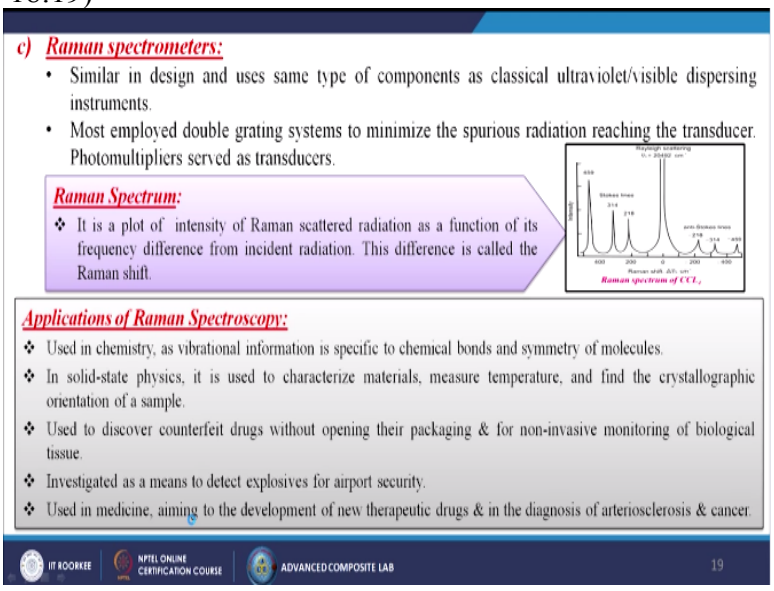

Then Raman spectrometers: similar in design and use same type of components as classical ultraviolet or maybe visible dispersing instruments. Most employed double grating systems to minimize the spurious radiation reaching the transducer photomultipliers served as transducers,

photomultipliers served as transducers. Raman spectrum: it is a plot of intensity of Raman scattered radiations as a function of its frequency difference from incident radiations. This difference is called the Raman shift. Application of Raman spectroscopy: used in chemistry, as vibrational information is specific to chemical bonds and symmetry of molecules.

In solid state physics, it is used to characterize materials, measure temperature, and find the crystallographic orientation of a sample, used to discover counterfeit drugs without opening their packaging and for non-invasive monitoring of biological tissue, investigated as a mean to detect explosive for airport security, used in medicine, aiming to the development of new therapeutic drugs and in the diagnosis of arteriosclerosis and cancer. Next one is called the small angle x-ray scattering or maybe the SAXS.

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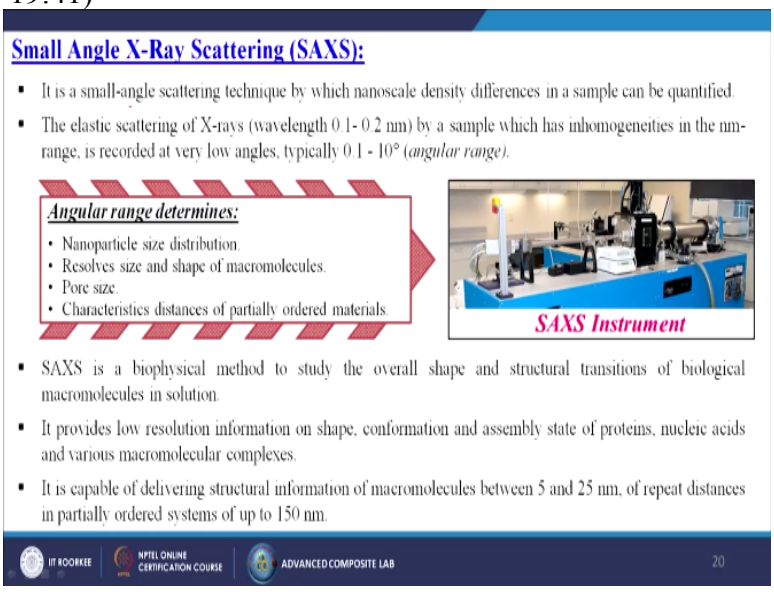

It is a small angle scattering technique by which nanoscale density difference in a sample can be quantified, the elastic scattering of x-ray wavelength generally 0.1 to 0.2 nm by a sample which has inhomogeneities in the nm range, is recorded at very low angles, typically 0.1 to 10 ° angular range. How to determine the angular range? Nanoparticle size distribution, resolves size and shape of macromolecules, pore size, characteristic distance of partially ordered Nanomaterials.

So generally the SAXS instrument is looking like this. SAXS is a biophysical method to study the overall shape and structural transitions of biological macromolecules in solution. It provides low resolution information on shape, conformation and assembly state of proteins, nucleic acids and various macromolecular complexes. It is capable of delivering information of macromolecules between 5 and 25 nm, of the repeat distances in partially ordered systems of up to 150 nm. Constituently SAXS experiment is simple,

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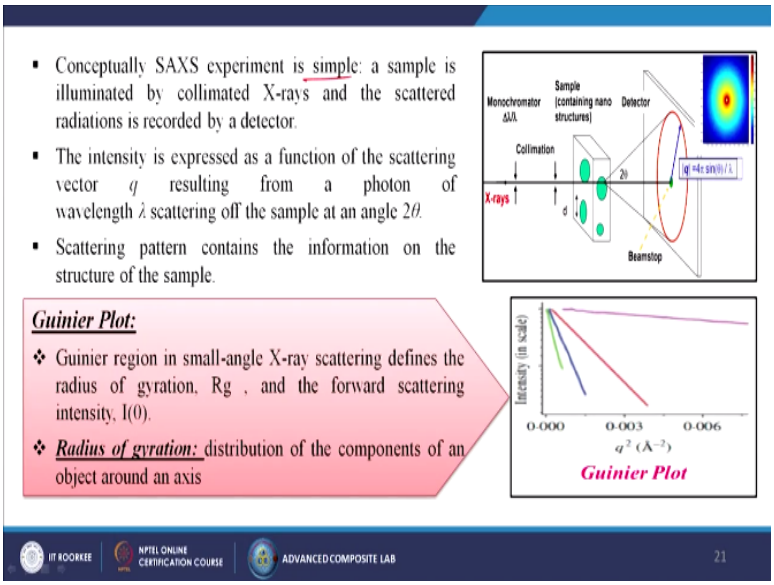

A sample is illuminated by collimated x-rays and the scattered radiation is recorded by a detector itself. so the collimations, so monochromated x-rays is going, this is the sample containing nano structures and then we are having the detectors and it looks like this, the intensity is expressed as a function of the scattering vector q resulting from a photon of wavelength lambda scattering of the sample at an angle 2 theta.

Scattering pattern contains the information on the structure of the sample itself. Guinier plot: Guinier region is small angle x-ray scattering defines the radius of gyration Rg, and the forward scattering intensity I0. Radius of gyration: distribution of the components of an object around an axis.

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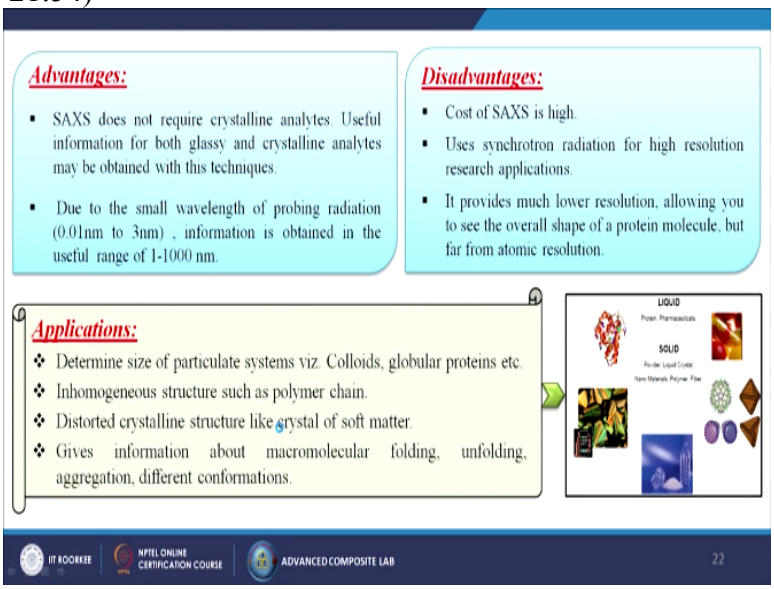

What are the advantages? SAXS does not require crystalline analytes; useful information for both glassy and crystalline analytes may be obtained with the techniques. Due to the small wavelength of probing radiation 0.01 nm to 3nm information is obtained in the useful range of 1-1000 nm. Of course there are certain disadvantages also. Cost of SAXS is high, uses synchrotron

radiation for high resolution research applications. It provides must lower resolution, allowing you to see the overall shape of a protein molecule, but far from the atomic resolution. What are the applications? Determine size of particulate systems like colloids, globular proteins etc, inhomogeneous structure such as polymer chain, and distorted crystalline structure like crystal of soft matter, gives information about macromolecular folding, unfolding, and aggregation, different conformations.

So now we have come to the last part of this particular lecture, now we have to summarize the whole lectures. So in this particular lecture we are discussed about the nano technology, which is nothing but the assents of molecular synthesis,

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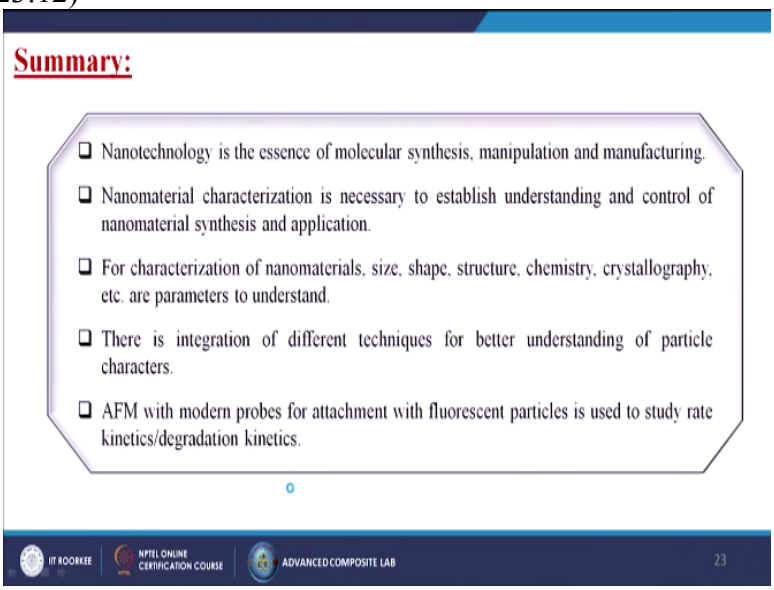

Manipulation and manufacturing, Nanomaterials characterization is necessary to establish understanding and control of nanomaterial synthesis and application, for characterization of nanomaterial, size, shape, structure, chemistry, crystallography, etc are parameters to understand, there is integration of different techniques for better understanding of particle characters. AFM with the modern probes for attachment with fluorescent particles is used to study rate kinetics and the degradation kinetics. Thank you.

For Further Details Contact
Coordinator, Educational Technology Cell
Indian Institute of Technology Roorkee
Roorkee-247667
Email: etcell@iitr.ernet.in,etcell.iitrke@gmail.com
Website: www.nptel.iitm.ac.in

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Prof. Ajit Kumar Chaturvedi
Director, IIT Roorkee
NPTEL Coordinator
Prof. B.K.Gandhi
Subject Expert
Dr. Kaushik Pal

Department of Mechanical & Industrial Engineering
IIT Roorkee
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