Advanced Transition Metal Chemistry_Spectroscopic Methods
Prof. M. S. Balakrishna
Department of Chemistry
Indian Institute of Technology - Bombay

Module - 11
Lecture - 53
Methods of Characterisation UV-Visible Spectroscopy

Hello everyone. Once again I welcome you all to MSB lecture series on Transition Metal Chemistry. Today let me begin my lecture that is fifty-third in the series on Methods of Characterisation with more emphasis for Spectroscopic Methods. So far we discussed in length about coordination compounds and to an extent about organometallic compounds.

In case if you make new organometallic compounds or coordination compounds, to ascertain its purity and to know in what quantity we got and what is the yield, how we can improve; to get all these things, to get an insight into the synthetic procedure that was used and also to improve the method, we should know what kind of compounds we got it. Of course, the mechanistic path and all those things, we already discussed in my last series of lectures.

Now, let us look into the characterisation of these compounds. For that one, we have to use analytical instruments as well as spectroscopic instruments. So, let us start with UV-visible spectroscopy. Before that, I shall give little bit introduction to the methods of characterisation or spectroscopic methods that we have at our disposal.

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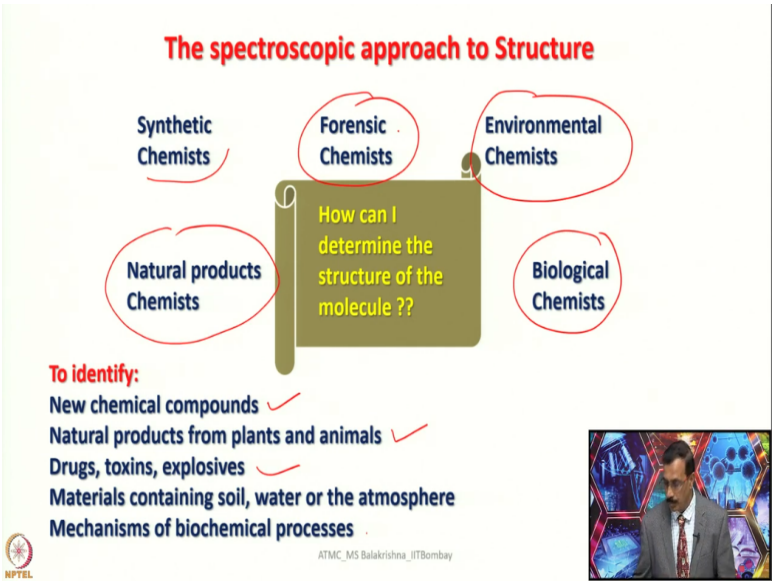

So, how to go with spectroscopic approach to understand the structure of a molecule and also its purity. Nowadays, these spectroscopic methods are widely used not only by inorganic chemists but also you can see synthetic chemists. Of course, synthetic chemists when we talk, it includes both organic chemists and inorganic chemists. And forensic chemists also, it is equally important to analyse the samples and also to ascertain toxicity and all those things.

And environmental chemists also, it is very vital. And of course, biological chemistry is inseparable with spectroscopic methods nowadays. And natural products chemists also, when they make new compounds or extract new chemicals from natural resources, to understand what kind of compounds they got, and what impurities are there and how to purify, so, spectroscopic methods come very handy.

That means to identify new chemical compounds that we make; and natural products from plants and animals that are made; and drugs, toxins and explosives; when it comes to forensic materials containing soil, water or the atmosphere, agricultural science; and mechanisms of biochemical process, to understand mechanisms of biochemical process. Not only biochemical process, in inorganic and organic process also the spectroscopy comes very handy and it is an important tool in the present scenario.

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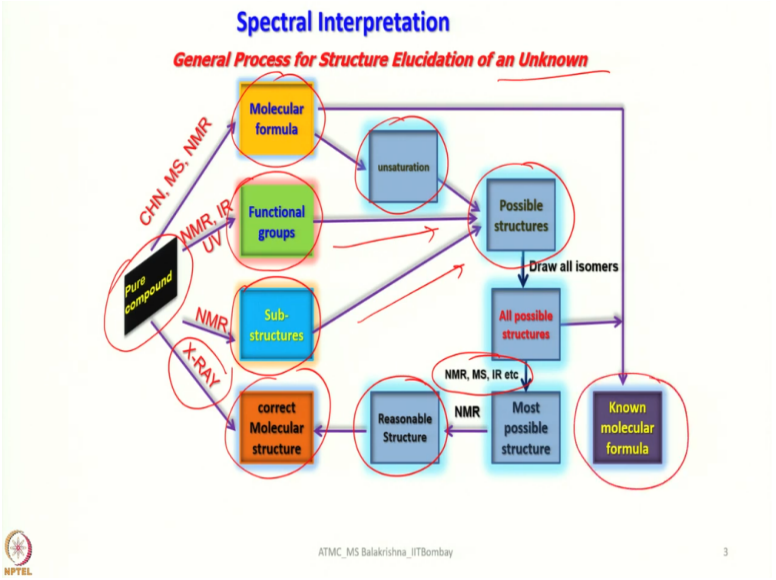

Let us look into spectral interpretation and general process we should follow for structure elucidation of an unknown sample. First what we should do is, let us begin about purification of the compound. Let us say we have pure compound. How to ascertain? We have to go for

CHN analysis or mass spectrometry data and NMR; that would give you information about molecular formula.

And then, NMR, IR, UV can also give you insight into the functional groups present in it. And NMR can also provide you information about sub-structures. For example, if we have, whether we have methyl group, aromatic group, and then carboxylic group; all this information comes. And of course, X-ray gives a complete; if it is a solid compound, if we can able to crystallise and get single-crystals suitable for analysing or performing X-ray crystallography, then we can get molecular structure.

Then, about unsaturation: We can get information from molecular formula. And then, possible structures come from all these avenues. And then we can draw all possible isomers. And then, once after writing all possible structures, we can again go back to NMR, mass and IR data to arrive at most appropriate structure. So, always we should have the habit of using more than one spectroscopic method or analytical method to ascertain the structure, to understand the purity of the compound, also to confirm that whatever the molecule we decide, that we have obtained in our synthetic method.

So, then, NMR would give you reasonable structure. And ultimately, single-crystal X-ray analysis would tell you what it is, provided it is a solid sample. So, that means known molecular formula. So, this is how we can go through various instruments and the data from those instruments to understand what kind of molecule we have made and also the details about that molecule.

So, to identify molecules that we prepare, we can use an array of structural information elucidated by spectroscopic methods. We want to get the information as rapidly as possible and we can deal with all phases of matter, mixtures and pure compounds. So, in that context, again spectroscopic methods are very vital in today's synthetic world.

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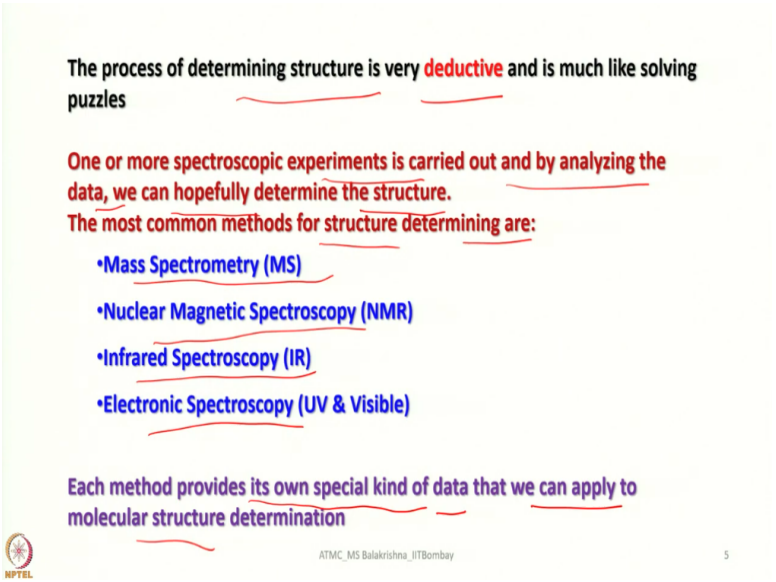

The process of determining structure is very deductive and is very much like solving puzzle. Often, if we make new compounds, certainly we can enjoy analysing and interpreting the data from spectroscopic and analytical methods, we get to understand what we have made. So, one or more spectroscopic experiments is carried out. And by analysing the data, we can hopefully determine the structure.

The most common methods for structure determination are mass spectrometry; and NMR, nuclear magnetic resonance spectroscopy; and infrared spectroscopy, IR; and electronic spectroscopy, UV and visible. Each method provides its own special kind of data that we can apply to molecular structure determination. And each spectroscopic information gives a very interesting and a special kind of data. And when you club together all this information without any ambiguity, we can understand the structure of a molecule.

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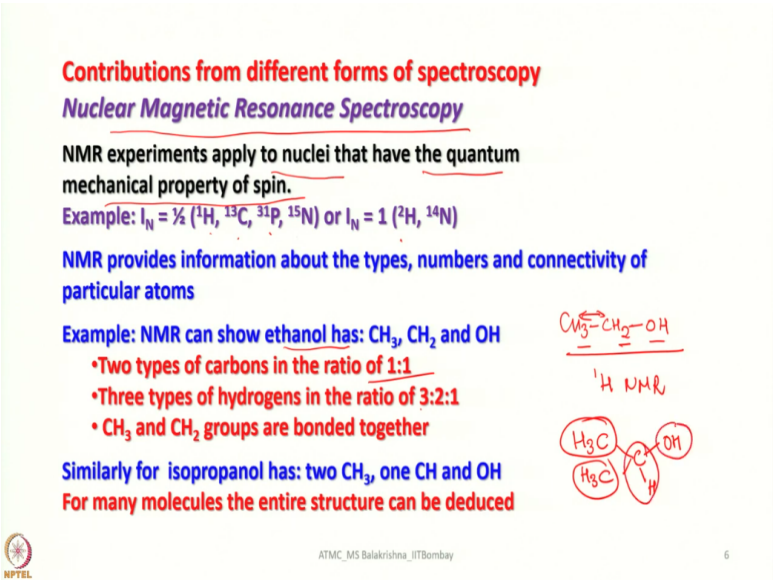

So, contributions from different form of spectroscopy comes towards understanding the purification of a sample. Among them, nuclear magnetic resonance spectroscopy plays an important role when we have NMR active nuclei in that molecule. So, NMR experiments apply to nuclei that have the quantum mechanical property of a spin. I shall elaborate more when I go to nuclear magnetic resonance spectroscopy after completing this UV-visible spectroscopy.

So, time being, let us know that all nuclear spin with I value half such as: ^{1}H, ^{13}C, ^{31}P, ^{15}N; or nuclear spin I = 1, for example, ^{2}H, ^{14}N, they provide information about the types, numbers and connectivity of particular atoms. For example, NMR can show ethanol has; if you take simple ethanol, if you record NMR spectrum, ^{1}H NMR spectrum for this one, so, it can tell you about the presence of 3 groups such as CH_3, CH_2 and OH. How?

2 types of carbons in the ratio of 1:1, that information comes. And then, 3 types of hydrogen in the ratio of 3:2:1, that information comes. And CH_3 and CH_2 groups are bonded together, this information also comes. So, that means that is good enough to understand, yes, if I have ethanol in my hand. Similarly, for isopropanol; if you take isopropanol, so, what we can get from ^{1}H NMR is, yes, it has 2 methyl groups, 1CH group and 1OH group. For many molecules, the entire structure can be reduced.

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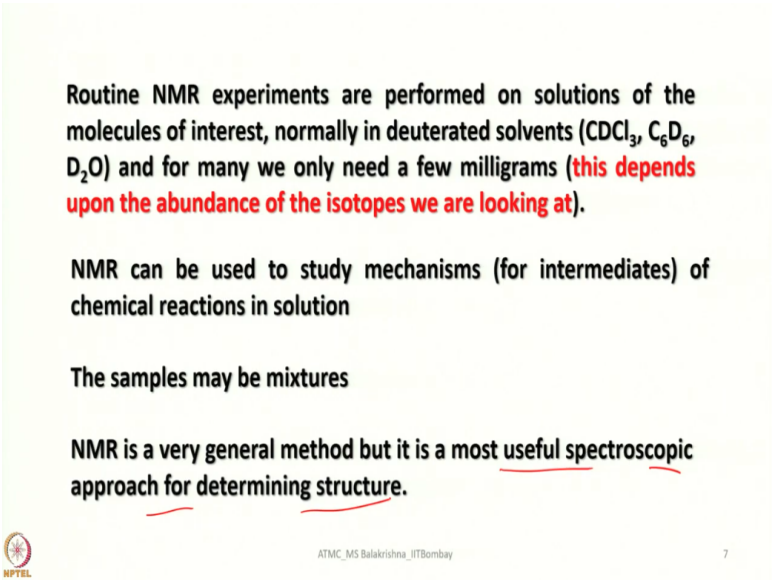

So, routine NMR experiments are performed on solutions of the molecules of interest, normally in deuterated solvents such as $CDCl_3$, C_6D_6, D_2O or even acetonitrile CD_3CN and for many, we only need a few milligrams. And in all these cases, when we perform NMR, we need very few milligrams of samples, about 10% of NMR active nuclei should be present in it. So, this depends upon the abundance of the isotopes we are looking at.

This is very important. If it is 100% abundant, very small quantity is sufficient; but the percentage of NMR active nuclei is small, then we need more samples. NMR can be used to study mechanisms and also, we can get an idea about presence of transient states or even intermediates of chemical reactions in solution. Especially, this holds good, it can provide more information when you perform a chemical reaction in solution medium.

The sample may be mixtures. So, NMR in general is a method, but it is most useful spectroscopic approach for determining the structure. So, NMR is a very general method, but it is a most useful spectroscopic approach for determining structure of molecules.

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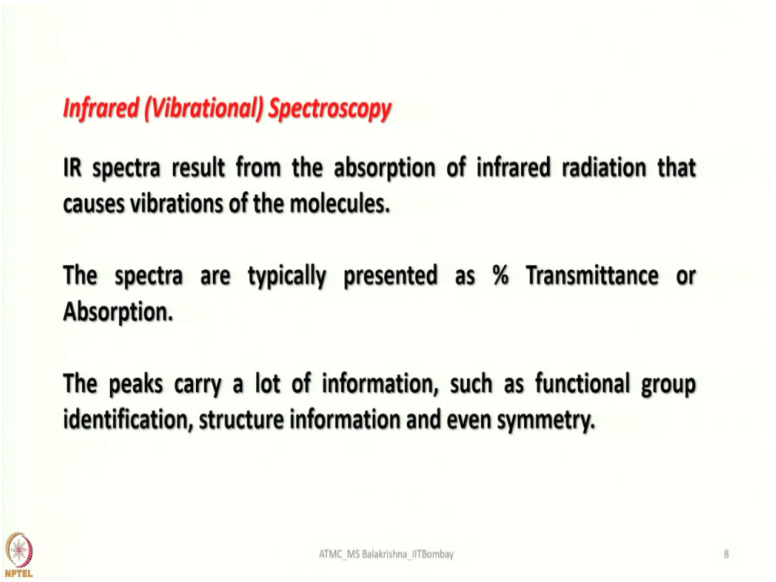

Infrared spectroscopy also called as vibrational spectroscopy. So, IR spectra results from the absorption of infrared radiation that causes vibrations of the molecules. The spectra are typically presented as percentage transmittance or absorption. The peaks carry a lot of information such as functional group identification, structure information and even symmetry.

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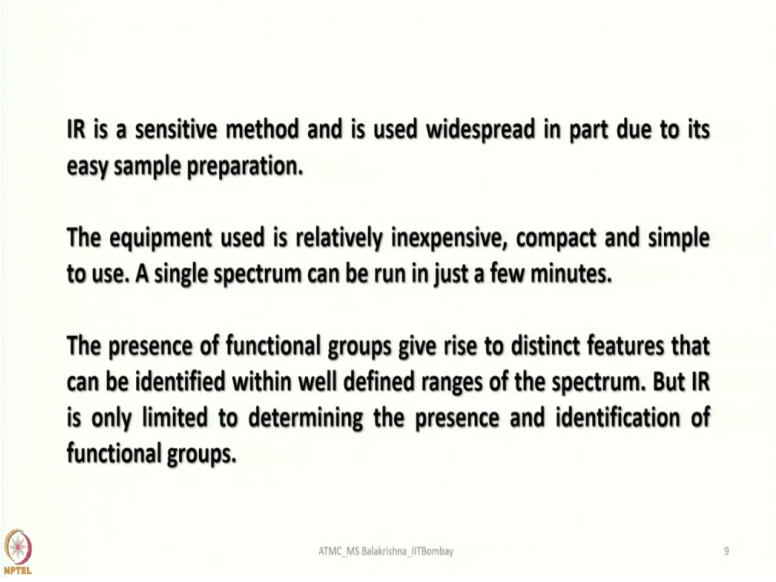

So, IR is a very sensitive method and is used widespread in part due to its easy sample preparation. Very easy to prepare sample. We can record sample in solid state, in solution and also for gaseous molecules we can still record IR spectrum. The equipment used is relatively inexpensive, very compact and simple to use. A single spectrum can be run in just a few minutes; it does not take very long duration of time for recording a spectrum or preparation of the sample.

Sample can be prepared in few minutes and also we can complete recording a spectrum within a few minutes. The presence of functional groups give rise to distinct features that can be identified within well-defined ranges of spectrum, but IR is only limited to determining the presence and identification of functional groups. It ends, it can give you some information about presence of those functional groups, that is it. It cannot go beyond and it is very difficult to understand the structure and composition of the entire molecule simply by using or recording IR spectrum.

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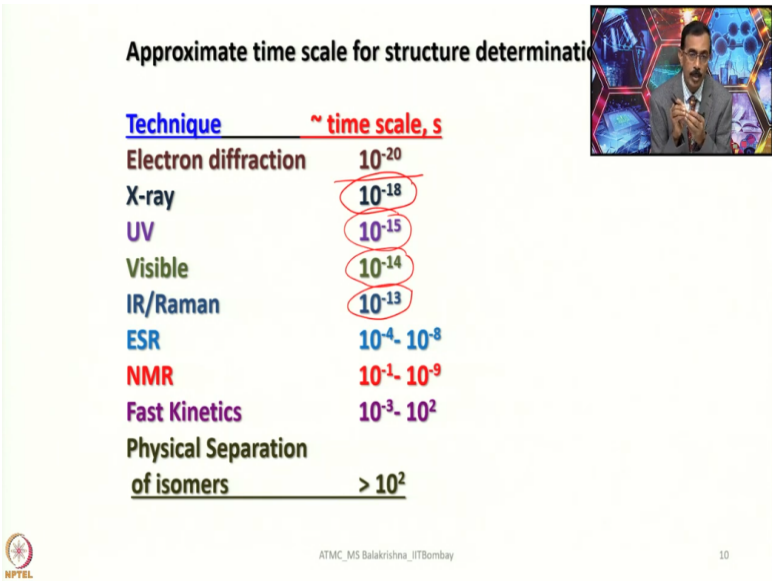

Now, let me give you approximate timescale for structure determination. You see, for example, here I have listed various techniques and also the timescale for that particular technique. So, electron diffraction, whatever the process that happens up to 10^{-20} seconds, one can record. That means, anything that is very fast, so, that can be recorded with electron diffraction.

And the X-ray, 10 to the power of -18 up to that; and UV-visible, up to 10 raised to -15; and visible, 10 raised to -14; and IR and Raman, 10 raised to -13; and ESR, 10 raised to -4 to 10 raised to -8; and NMR, 10 raised to -1 to 10 raised to -9. So, that means, whatever the dynamic process that happens in the timescale of 10 to the power of -1 to 10 to the power of -9 can be identified by NMR.

If the process is very slow, slower than 10 to the power of -1 or faster than 10 to the power of -9, then NMR fails to give any insight into those dynamics happening in solution. Fast kinetics, 10 raised to -3 to 10 to the power of 2. And physical separation, if any sample is

stable for more than 100 seconds, then one can visually look into it and pick them, hand-picking can be done too. And if they have different morphology, one can do hand-picking under a microscope. So, this is very important information as far as timescales are concerned for various techniques.

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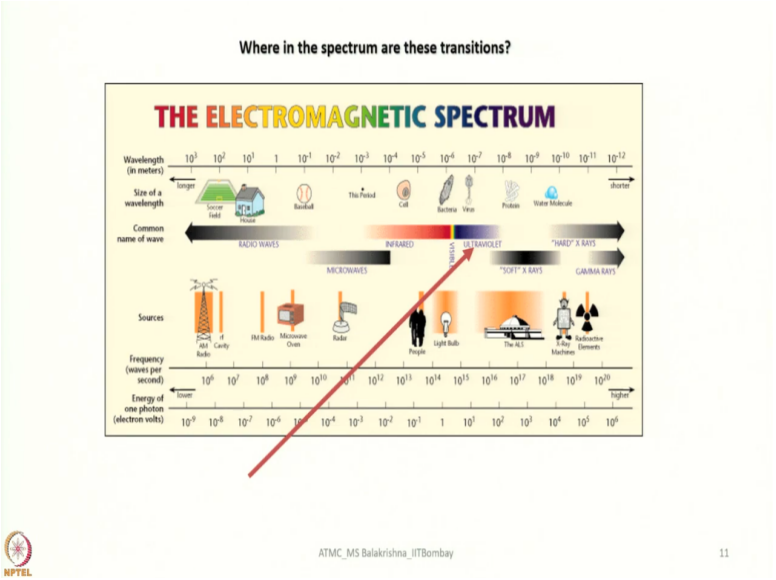

So, now, this gives electromagnetic radiation applied in different techniques here. So, our attention is ultraviolet. So, now let us try to look in more detail about UV-visible spectroscopy. Whenever we have to study something, the question pops up in our mind, why should we learn this stuff? And after all it makes sense here if I make this statement, because nobody solves structure with UV any longer, because just with UV you cannot solve the structure, but you need proof from many other instrumental data.

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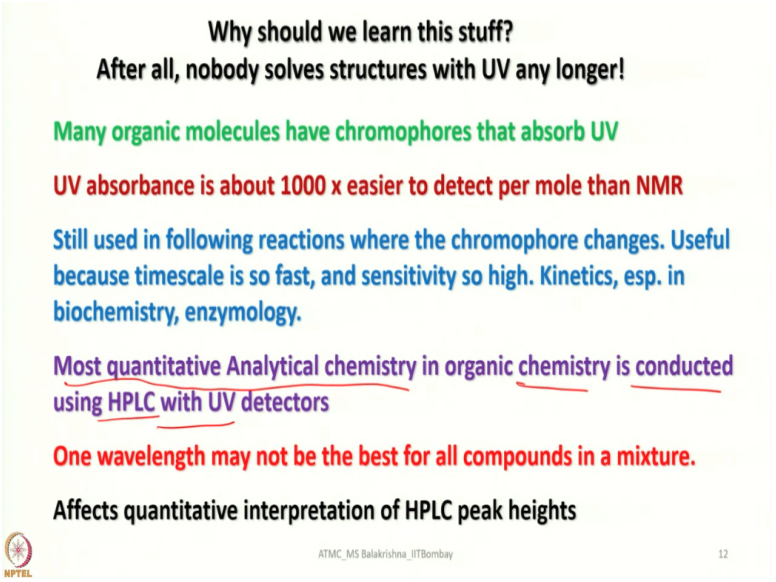

So, that means why we should learn this stuff? Because many organic molecules have chromophores that absorb UV light. And then, UV absorbance is about 1000 times easier to detect per mole than NMR. So, that means very easy. Still used in following reactions where the chromophore changes. Useful because timescale is so fast and sensitivity so high. And kinetics, especially in biochemistry and enzymology, use or depend heavily on UV-visible spectroscopy for the same reason.

Most quantitative analytic chemistry in organic chemistry still conducted using HPLC with UV detectors. One should remember about that one. If they asked why it is so important? Yes, it is very important because of this quantitative analytical chemistry involved in doing UV-visible measurements. So, in that case, what happens, one wavelength may not be the best for all compounds in a mixture. We have to use a range of wavelengths.

Instead of using monochromatic, we have to use a range of wavelengths so that it covers all absorption or transition that happens. So, affects quantitative interpretation of HPLC peak heights. This affects quantitative interpretation of HPLC peak heights.

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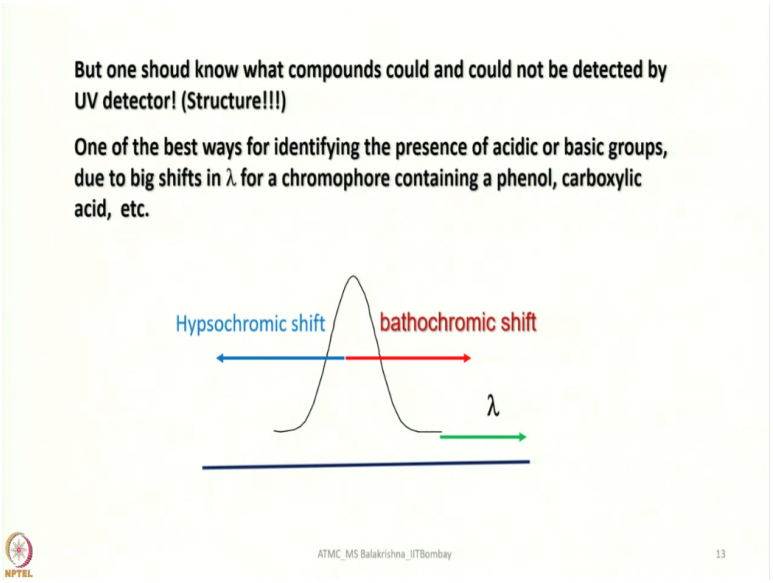

But one should know what compounds could and could not be detected by UV detector? One of the best ways for identifying the presence of acidic or basic groups due to big shifts in lambda wavelength for a chromophore containing a phenol, carboxylic acid, etcetera. So, what happens, if the peaks are shifted towards left, we call it as hypsochromic shift or we call it is blue shift. And if it is shifted other way around, it is called bathochromic shift or it is also called as red shift.

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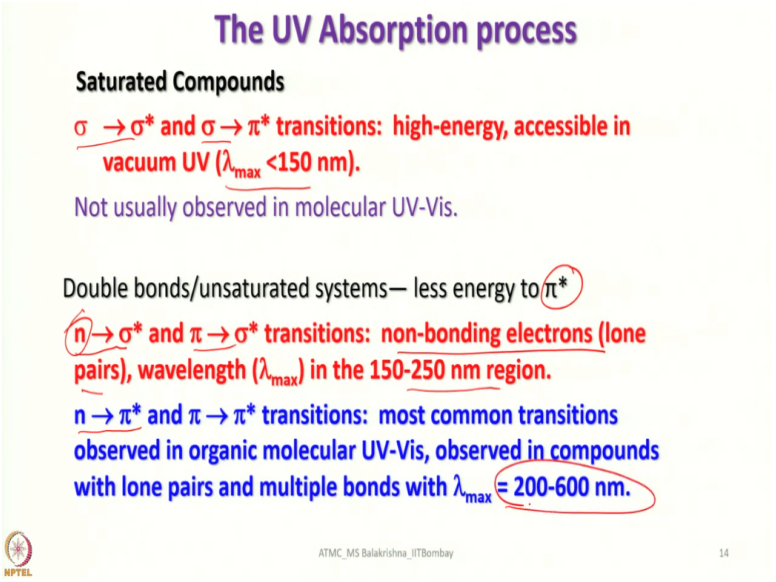

So, now, let us look into UV absorption process for saturated compounds. Saturated compounds anticipated electronic transitions are sigma to sigma star and sigma to pi star. They are high energy transitions accessible in vacuum; lambda maximum is around less than 150 nanometre. Not usually observed in molecular UV-visible. So, now, if we have double bonds and unsaturated systems, less energy for to pi star.

As a result, what happens, what we see is n to sigma star and pi to sigma star transitions. And non-bonding electrons or lone pairs are there. Wavelength will be in the range of 150 to 250 nanometre region. And these things are most common transitions among double bonded or unsaturated systems or n to pi star and pi to pi star observed in organic molecular UV-visible, observed in compounds with lone pairs and multiple bonds with lambda maximum will be in this range.

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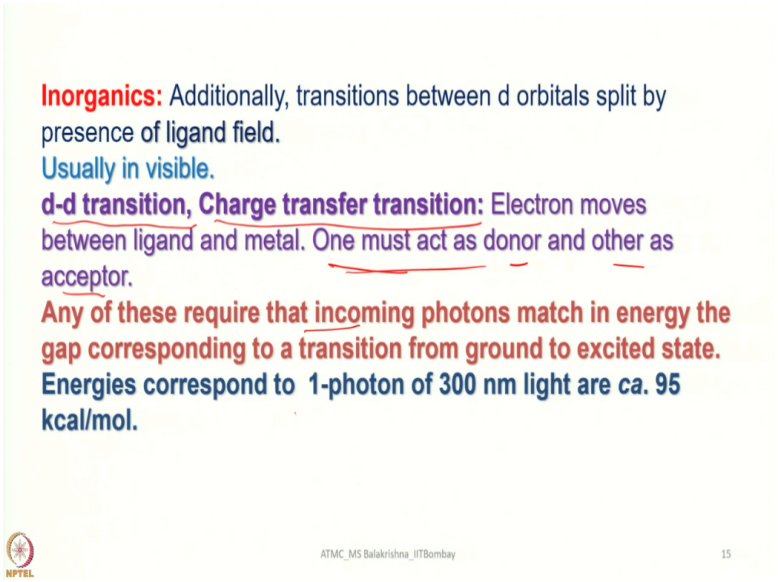

In inorganics, it is little different. Additionally, transition between d orbitals split by presence of ligand field. So, we have seen in ligand field theory how d-orbitals are split based on the influence of the ligand field. So, additionally, in getting different transitions; I showed you sigma, sigma star, pi to pi star and n to pi star. We also come across another one that is called d-d transitions. So, usually d-d transitions occur in visible region.

And besides d-d transition, in metal complexes we also come across charge transfer transitions. Of course, in case of charge transfer transitions, we come across 2 types of charge transfer transitions; metal to ligand charge transfer transitions and also ligand to metal charge transfer transitions. And there are instances where if you have a bimetallic system, metal to metal charge transfer transition also occurs.

Of course, in all these cases, one can also anticipate ligand to ligand transition as well. So, in those cases, whenever we talk about charge transfer transitions, one must act as a donor and the other act as an acceptor. Any of these require that incoming photons match in energy the gap corresponding to a transition from ground to excited state. That is obvious.

For example, if I consider highest occupied molecular orbital is here and lowest one is here, or any transition for that matter that has to occur between 2 energy levels, we have to supply the energy that matches the energy difference between those 2 levels. So, the energies correspond to 1 photon of 300 nanometre light are approximately 95 kilocalories per mole.

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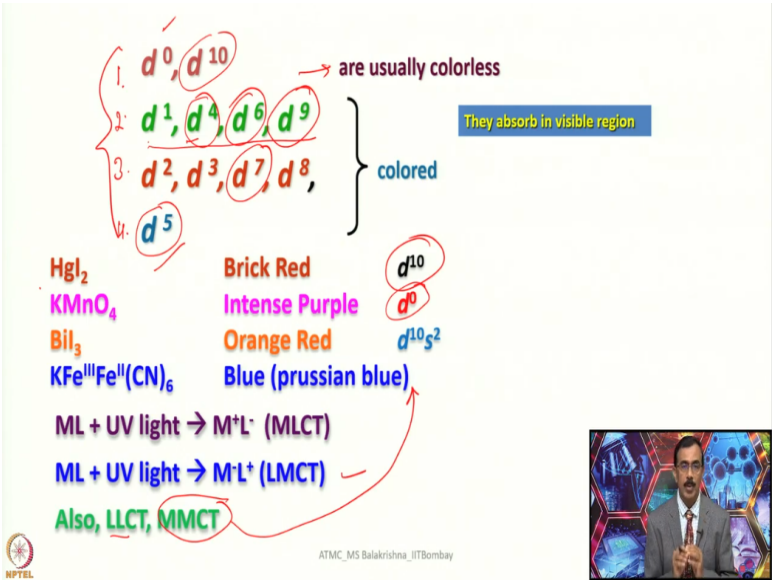

So, now, I have given little bit more information about metal complexes and also about d electronic configuration. Just I have segregated various d electronic configurations into 4 categories. And below that one; I will come back to this one later; so, let us look into mercuric iodide. This is brick red compound and it has a d^{10} electronic configuration. And then, let us look into $KMnO_4$, potassium permanganate, intense purple; you all have seen.

Here, metal is in +7 oxidation state. As a result, it has d^0 electronic configuration. And if you look into bismuth triiodide, orange red in colour; in this one what happens, d^{10}; of course, this s^2p^3 electronic configuration. In bismuth is in trivalent state, we have 2 electrons are left; so, now we have $d^{10}s^2$ electronic configuration, but this is very beautiful orange red in colour.

And then if you look into Prussian blue, we have intense blue colour, you can see. And that means here I am talking about metal to ligand charge transfer transition, ligand to metal charge transfer transition and also we can come across as I mentioned, ligand to ligand; but here, metal to metal charge transfer transition can be explained here for intense colour of Prussian blue molecule.

Now, look into the electronic configuration. Let us try to understand some similarities of groups segregated in 4 parts. d^0 ; d^{10}, yes, d^0 has no electrons; and d^{10} means all orbits are completely filled. They are usually colourless. And now, I have another group very interesting here. So, this group includes electronic configurations such as d^1, d^4, d^6 and d^9. Whereas, the third one in the series includes d^2, d^3, $d^7$and d^8.

And another one, fourth one is unique; it has d^5, half-filled electronic configuration. So, completely half-filled is fine, and no electrons is fine, and 10 electrons completely filled is also fine; then how these second and third categories were brought together? Yes, it is very interesting. You can see, 1 electron is there in d orbital. And then, if you look into this, 1 less than half-filled electronic configuration.

So, 1 electron is in d^1, and 1 electron less than half-filled electronic configuration, and 1 more than half-filled electronic configuration, and 1 less than completely filled electronic configuration. Is that clear? In this group, we have 1 electron system, and 1 less than half-filled electronic configuration, and 1 more than half-filled electronic configuration, and 1 less than completely filled electronic configuration.

So, now we can see some similarities among these electronic configurations of d^1, d^4, d^6 and d^9. Now, let us look d^2, d^3, $d^7$and d^8. Now, 2 electrons are there here. In the same way, 2 less than half-filled electronic configuration, and 2 more than half-filled electronic configuration, and 2 less than completely filled electronic configuration. So, now, it appears like later if I have spectra from all these electronic configurations, I should understand as probably in category 2, all these electronic configurations probably would show 1 type of spectrum or 1 type of absorption or 1 type of transition.

And similarly, category 3 where we have d^2, d^3, $d^7$and d^8 also probably show 1 type of; so, just remember the significance behind this kind of classification, you will understand as we progress with this course.

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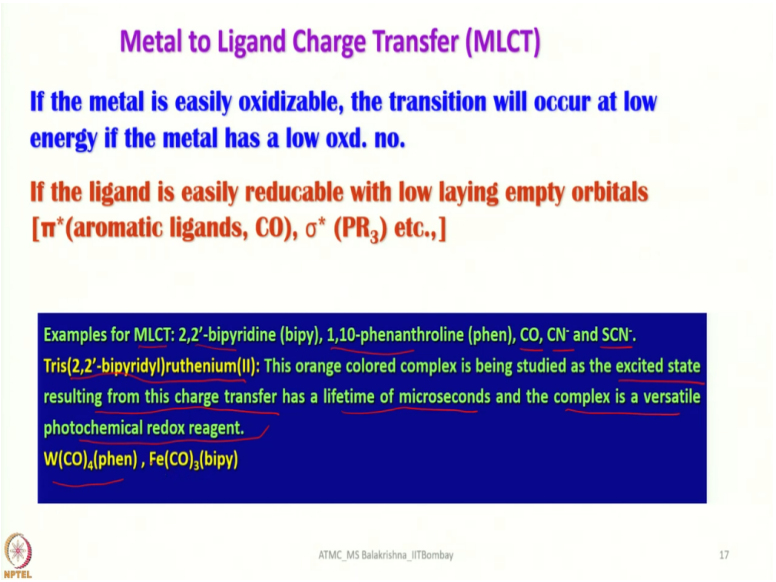

So, now, let us look into metal to ligand charge transfer, MLCT we call it as. If the metal is highly oxidizable, the transition will occur at low energy if the metal has a low oxidation number. So, that means, if the metal is easily oxidizable, the transition will occur at low energy if the metal has low oxidation state or oxidation number. If the ligand is easily reducible with low laying empty orbitals like pi star in a case of aromatic ligands or carbon monoxides, sigma star in PR_3, etcetera.

That means, basically, metal to ligand charge transfer occurs if the metal is in lower oxidation state. If it is in lower oxidation state, it is electron rich and also it is in lower oxidation state. And also when it is electron rich, because of repulsion, inter-electron repulsion, it is prone to oxidation. That we have already seen in our oxidative addition reaction, reductive elimination reaction scheme.

So, that is one criteria in order to see metal to ligand charge transfer transition. On the other hand, ligands should have empty orbitals to accept electrons given from the metal. So, that means metal to ligand charge transfer; that obviously, the name itself says that electrons are coming from metal to ligand. Usually, when we make a metal complex, ligands donate through sigma donation.

If the metal to ligand comes, it has to be in the form of pi electrons; you should remember. So, that means pi acceptor capable ligands can facilitate metal to ligand charge transfer. In that case, non-classical ligands such as carbon monoxide, phosphines, olefins, pyridines and

all those things play a major role. Examples for metal to ligand charge transfer includes 2,2'-bipyridine, 1,10-phenanthroline, carbon monoxide, cyanide and thiocyanate.

And if you just look into this compound here, this orange coloured complex is being studied as the excited state resulting from this charge transfer has a lifetime of microseconds and the complex is a versatile photochemical redox reagent. And then, we can also see, for example, tetracarbonyl phenanthroline tungsten complex or tricarbonyl bipyridine iron complex, etcetera.

So, let me stop here and come back in my next lecture discussing more about UV -visible spectroscopy. And then, we shall discuss about ligand to metal and then move on to understanding d-d transitions in more detail. Until then, have excellent time and also keep reading. Reading should not be stopped as far as we are learning something. Do well, take care. Thank you for your kind attention.