Infrared Spectroscopy for Pollution Monitoring Prof. J. R. Mudakavi Department of Chemical Engineering Indian Institute of Science–Bangalore

Lecture-13 Interaction of electromagnetic radiation with matter-VI

Hello everyone, in the last class we had discussed about the different types of spectra's that we normally obtain in spectroscopy, those included line spectra, band spectra and continuous spectra we have been discussing. So line spectra are nothing but a series of well defined peaks and band spectrum consist of several groups of frequency closely spaced but not well resolved peaks.

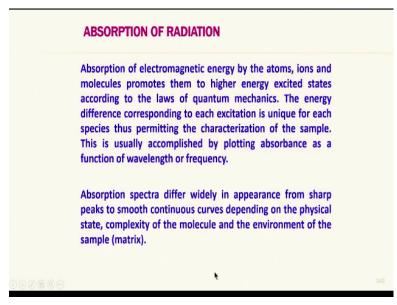
The continue spectrum of course as usual you can understand that there are no specific peaks to be identified in the region. So normally line spectra and band spectra are super imposed in the continual spectra okay and then we had discussed how the line spectra occur what are the typical weights of the peaks and other things like approximate peak it would be approximately about 10 raise to -5 nanometers.

And we have specifically stated that X-ray line spectra are produced by transitions of electrons to the inner most orbitals. And band spectra are essentially vibrational energy levels occurring around 10 raise to -15 seconds etc., therefore the transition occurs from the lowest transitional vibrational energy level of the excited state to any of the vibrational energy level of the ground state.

These are the typical transitions and then we have discussed about continued spectra, the energy peaks shift to shorter wavelength with increasing temperature heated solids or more important sources of UV, visible, infrared and all those things we had discussed. Now I want to continue our discussion with the absorption of radiation. So, absorption of radiation normally occurs in the electromagnetic energy by the atoms, ions and molecules that remove them to higher energy excited states.

According to the laws of quantum mechanics, there is no escaping quantum mechanics, laws anywhere in physics or spectroscopy. The energy difference corresponding to each excitation is unique for each species thus permitting the characterization of the sample. This is usually accomplished normally by plotting absorbance as a function of wavelength or frequency look at this slide now.

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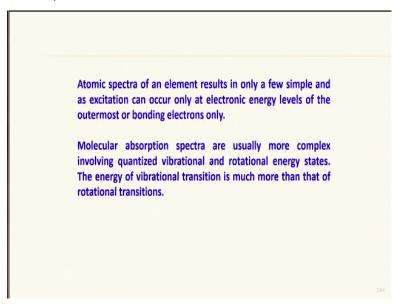
This is what exactly I have been trying to tell you, so the absorption spectra differ widely in appearance from sharp peaks small smooth continuous curves depending upon the physical state, complexity of the molecules and the environment of the sample which we call it as matrix. Sometimes the matrix maybe very simple pure compound, sometimes I want to find out what is a specific compound in a given sample.

Then the remaining all the other parts components of the sample is known as matrix except the analyte. So the matrix maybe in the form of a liquid or solid or it may be in the gaseous form but quite often it may not be possible to take this spectra directly as it is. We will have to do some pre-concentration or pre-treatment and then we should be able to take the spectra because quite often the requirements of a sample to be inserted in a spectrograph or spectrometer or spectrophotometer anything.

So they are very specific for example if you want to do the UV visible spectrum you need to take the sample in a cuvette about 1centimeter, 2 centimeter, 5 centimeter, 10 centimeter like that. And then if you want atomic absorption then you will have to aspire it the sample for that the sample must be in the dissolved form. Otherwise it is not possible like that there are different ways of preparing the sample for spectroscopic analysis.

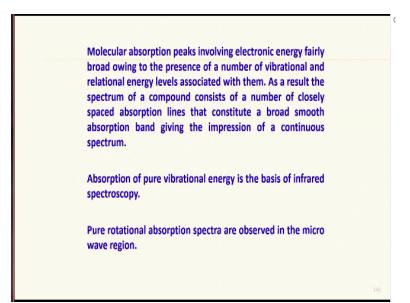
So, the quality of the spectrum also changes depending upon the suitability of the sample for the particular kind of spectroscopic analysis.

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So, atomic spectra of an element results in only a few simple and as excitation can occur only at electronic energy levels, the outermost or bonding electrons are involved. So, molecular absorption spectra are usually more complex because they involve quantized electronic vibrational and rotational energy levels. So, the energy of the vibrational transition is much more than that of rotational transitions and energy of the electronic transition is much more than the vibrational energy levels. So, that is it we will take a look at the molecular absorption peaks.

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That involve electronic energy what we had said earlier they are fairly broad going to the presence of number of vibrational and rotational energy levels associated with them. As a result the spectrum of a compound consist of number of closely spaced absorption lines that comes to it a broad smooth absorption band giving the impression of a continuous spectrum. So, absorption of pure vibrational energy is the basis of infrared spectroscopy.

That is what we are going to study in this course now, but pure rotational absorption spectra are also absorbed in the microwave region. This is also sort of useful for inorganic compounds characterization of inorganic compounds we do need rotational absorption spectra.

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Electronic spectral transitions in ions and molecules gives rise to spectrophotometry. The wavelength of the energy source does not change here. Only the change in the intensity of the incident beam and transmitted radiation are measured. Sometimes the absorbed energy of a molecule is reemitted as a radiation of lower frequency or longer wavelength. This results in fluorescence phenomenon. Energy changes occurring in the electrons and nuclei under a strong magnetic field are best studied by nuclear magnetic resonance or electron spin resonance.

So, electronic spectral transitions gives rise to spectrophotometry, wavelength of the energy source does not change here okay, only the change in the intensity of the incident beam and transmitted beam. Those 2 are the things which are measured, so we are going to plot the difference between the transmitted energy and the incident energy, so verses wavelength. So, I will get a small peak corresponding to the electronic transitions.

But every electronic transition is also associated with vibrational and rotational, so I get a broad peak in UV visible spectrometry. Sometimes they absorbed energy of the molecule is reemitted as a radiation of lower frequency and or lower wavelength. This results in fluorescence phenomena, this also I have taught earlier in my spectrometric course, sometimes energy changes occurring in the electrons and nuclei under the strong magnetic field are best studied by NMR.

That is nuclear magnetic resonance or electron spin resonance also are the suitable spectroscopic techniques for studying the changes occurring in the electrons and nuclear. So, now I will spend a little time on the spectrophotometer UV visible even though I had taught it earlier. Let us just have a quick look, so to absorbed radiation a molecule must interact with the radiation within a time frame of about 10 raise to -15 seconds.

To absorb radiation, a molecule	e must first interact
with the radiation within a time	frame of 10 ⁻¹⁵ sec.
Exchange of energy occurs only	by the interaction of
the potential energy component	of the molecules via
movement of the electrons which	can be represented
as a vertical line in the energy	diagram. Absorption
bands occur only at definite valu	es corresponding to
the energies required to promote	e electrons from one
level to another.	

So, exchange of energy occurs only by the interaction of the potential energy component of the molecules via movement of the electrons. These can be interpreted as a vertical line in the energy

diagram, this is how we draw these spectrum. So absorption bands occur only at specific wavelength values corresponding to the energy is required to promote the electrons from one level to another.

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Absorption terminates when the solute molecule in the excited state looses its energy to the ground state molecules of the solvent molecules. At this point the molecule returns to the ground state by means of radiationless processes. The excess energy is transferred to other molecules through collisions and/or by partitioning the excess energy to other vibrational and rotational modes within the excited molecule. Both these relaxation processes are accomplished by the loss of thermal energy.

So, absorption terminates when the solute molecule in the excited state loses it is energy see an excited electronic state cannot lost forever after sometime the electrons will revert back to the ground state. So, at that point the molecule must return to the ground state by means of radiation less processes, if it is accompanied by radiation then it will be of longer wavelength or lower energy than the incident radiation.

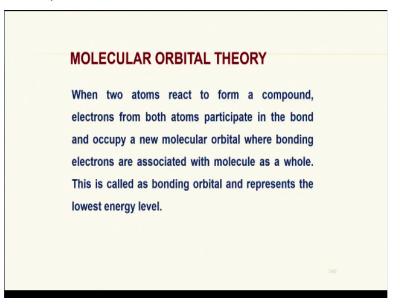
But it could be called as fluorescence but if there is no emission of radiation then we have absorption. So, only the absorption process is a radiation less process that means the incident radiation after absorption would have lost it is energy to the molecule and that energy cannot be recovered or something like that it is already lost, how it is lost, it is lost to maybe by increasing the temperature of the sample or it may be lost by transferring energy to the other molecules in the spectrum or the matrix.

Like that there are mechanisms we will also discuss a something and sometimes quite often the other molecules will colloid with the excited molecules all those things are possible. So, the excess energy is normally partition to other vibrational and rotational energy levels also. So, both

these relaxations these are called as relaxation processes. So what is the relaxation process, the relaxation process is 1 in which the excited the energy absorbed is lost into the matrix without appearing as electromagnetic radiation again.

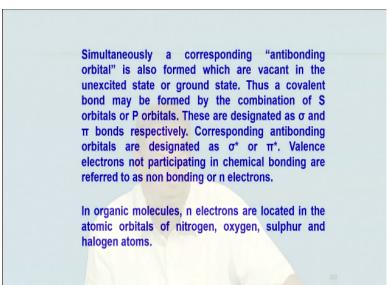
That is without appearing fluorescence, so the relaxation processes are accomplished by the laws of thermal energy only. So to explain all these we have the molecular orbital theory, so when 2 atoms react to form a compound electrons from both atoms participate that we have seen earlier and in the formation of the bond and they occupy a new energy level that is known as molecular orbital where bonding electrons are associated with the molecule as a whole this we know.

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So, this is called as bonding orbital and other is non-bonding orbital which is not populated at the lower level ground level or room temperature. So the bonding occupancy of the electrons in the bonding orbital represents a lowest energy level that is what I have written in this slide. So my first slide regarding the molecular orbital theory simply says that the electrons are there and they are in the bonding orbital.

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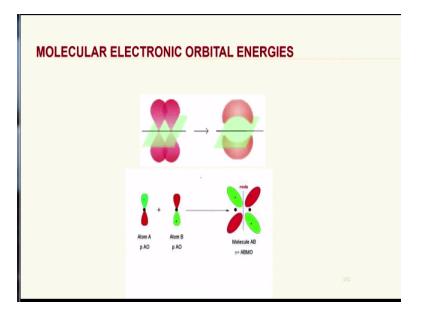


Now simultaneously a corresponding anti-bonding orbital is also formed in space okay or it is energy is higher than that than the bonding energy. But it is not a state which is visible to you for example even bonding energy level bonds are not visible to you in day today life you will see only a compound but you can visualize the structure of a bonded of a compound with the bonding, sigma bonding, Pi bonding etc.

And these have been taught to you if the high school level even college level etc., so there are ionic bonds, covalent bonds, coordinate bonds and several types of bonds are available. They form and these maybe formed by the combination of s, n, p orbitals sometimes d orbitals also and these are designated as sigma and pie bonds respectively. So corresponding anti bonding orbitals are sigma star and pie star.

This we were discussed a earlier little bit but this just to refresh your memory. So valance electrons not participating in chemical bonding are refer to as non bonding or n electrons. So, in organic molecules n electrons are located in the atomic orbitals of nitrogen, oxygen, sulphur and halogen.

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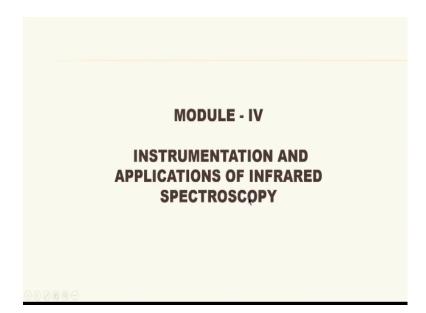


So, this is how the molecular orbital electronic orbital energies are represented here I am showing you the Pi bonds okay. The intersections represent 2 carbon atoms and there is a Pi bond and these Pi orbitals p orbitals or dumbbell shaped. But they are not rigid bonds, so there is certain amount of overlapping of each other. So in effect the before bonding but you can imagine that these could be in the same axis or perpendicular axis also.

So, if they are in the same axis it will look something like this 1 above and 1 below something like half-moon. And this also is possible the 1 which I am showing you at the bottom is again this is +, this is – so that means they are in 1 above the plane, 1 below the plane and atom A and atom B are there. So, the molecule AB maybe forming like this, so in this case the Pi bonds are oriented perpendicular to each other.

This is what happens when the anti bonding orbitals are present, so if the electrons are occupying anti bonding orbitals I have a shape something like this which I am showing you at the bottom and on the top it is bonding orbital. That means interactions of 2 p orbitals in bonding state is like this antibonding state would be like this.

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So, having understood that now let us move on to the infrared spectroscopy because now I feel that you have most of the request information regarding to learn the spectroscopy of infrared. So, now we will move on to that and before that I want you to appreciate that the infrared spectroscopy is only part of electromagnetic radiation it comes after visible region.

Before that there will be ultraviolet and vacuum ultraviolet, X-rays, gamma rays, cosmic rays and things like that. So please look at the slide now, so we are entering into module IVinstrumentation and application of infrared spectroscopy okay.

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In contrast to ultraviolet spectroscopy, the infrared spectrum provides a rich array of absorption bands which can provide a wealth of structural information about a molecule. It provides methods for studying materials in all three physical states i.e gas, liquid or solid. Analytically useful IR spectrum covers the following range of the electromagnetic range. NEAR IR 15000 CM-1 TO 3000 CM-1 0.67 MM-3.33 MM MID IR 4000 CM-1 TO 400 CM-1 2.5 MM-25 MM 200 CM-1 TO 10 CM-1 FAR IR 50 MM - 1000 MM MOST USED 4000 CM-1 TO 670 CM-1 2.5 MM - 15 MM

Now in contrast to ultraviolet spectroscopy which I have explain to you so far, the infrared spectrum provides a rich array of absorption bands which can provide a wealth of structural information about a molecule. Now you can imagine if you remember what I had taught you earlier you would always feel, you would always know that the ultraviolet and visible spectrum of a compound gives you hardly 2 or 3 peaks in the ultraviolet range and maybe 1 or 2 peaks in the visible range okay.

So, maximum you can see could be about 3 or 4 peaks corresponding to different electronic energy levels only in UV visible range. That is 400 to 750 or 800, 900 up to that is visible 180 to 350 is the 350 to 400 is the ultraviolet range. So in the ultraviolet range I will get about 2 or 3 peaks and in the visible region if it is colored if you can see the color perceive the color of a substance with your naked eye.

Then you will be able to see 1 or 2 peaks not more than that compare to that infrared spectrum will show you at least about 10 to 20 peaks maybe more. So, the every peak can provide you information about the compound, a functional group or presence of an element something like that. So, the wealth of a structural information about the molecule that is obtained is gives us a method for studying materials in all physical states.

That is I can take the infrared spectrum of a gaseous compound I can take the infrared spectrum of a liquid and also I can take the infrared spectrum of a solid. Now imagine if a substance is present in all the 3 forms I can get different spectra differing only slightly for the same compound in solid form, in liquid form and in the gaseous form. So again additional information can be obtained if I have to take the spectrum of infrared spectrum of a compound.

So whether it is gas or liquid or solid there are infrared spectrometers available which will be useful for the recording of an infrared spectrum. And analytically useful infrared spectrum range covers the following, so what are those ranges I have written here 1 is near infrared okay in the near infrared I have starting point is 15000 centimeters inverse to 3000 centimeters inverse.

This range of electromagnetic radiation is known as near infrared region okay. So, near infrared region quite often is available along with UV visible spectrophotometers. It is not part of regular routine organic chemist equipment where he uses all infrared regions no it is not. So, near infrared region is 1 part which is normally associated with a spectrophotometer.

That is UV, visible and near IR all 3 combined in 1 such spectrophotometers are available in the market and they are quite useful in characterizing a substance. They can be use for solid or liquid or gaseous either way which I have already explained, now let us go back to this infrared spectrum range. In this slide I have also given you the data in terms of micrometers actually this is micrometers we will correct this, so, it is not millimeter it is micrometer.

So, 0.67 to 3.33 micrometers is the range for near infrared and in the mid infrared range we have 4000 to it starts from 4000 centimeters inverse to 400 centimeters inverse okay. So, these are this is the area where lot of organic chemist use them and then corresponding range in micrometer is 2.5 to 25 micrometers okay. Now there is another part of infrared that is known as far IR that is 200 centimeters to 10 centimeters inverse.

Here it tends around 400 quite often normal infrared spectrum is spectrometers go up to 200 centimeters also. But from 200 to 10 centimeters if you want to cover infrared region then you should go for a far IR equipment. Now 50 micrometers to 1000 micrometer is the range for far IR, so among these the most used by all organic chemist is 4000 to 670 centimeters inverse.

But you cannot say it is just 670 centimeters inverse whatever instrument you have bought for your laboratory it maybe 400, it maybe 200 like that the centimeters inverse. And the used one is the range, so what I want you to appreciate is this 4000 to 3000 etc., it need not worry you because normally mid IR instruments range from 4000 to 400 or 200, near infrared regions may starts from 15000 centimeters inverse to 4000 or 3000 it does not matter whether 1000 centimeter this side or that side, you do not have to go to another IR.

If you want to cover 4000 here that may not be necessary same thing is true with respect to far IR okay. So, these are the ranges and people use the both centimeters inverse to describe the

availability of a peak or micrometers both of them continuous use depending upon the organic chemist preference. Some people are very good at remembering infrared spectrum at centimeters inverse, some people are very good at interpreting them in micrometers, both are quite useful and one can choose what 1 feels comfortable with.

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Microns or micrometers (μ or μm) were extensively used as the units of wavelength in the past but nowadays wave numbers (cm⁻¹) are the accepted units. A simple reciprocal relationship exists between wavelength (λ) and wave number i.e v (cm⁻¹) = 10000 / λ (μm). The wave number is directly proportional to the absorbed energy (K = E/hc) where as wavelength is inversely proportional to the absorbed energy.

So, the microns or micrometers where extensively used as the units of wavelength earlier but now a days wave numbers that is centimeters inverse are the accepted units. So, in most of the research papers you will be seeing the infrared spectrum of the such compound or a drug synthesize showed peaks at 4000 centimeters inverse, 16, 17 centimeters inverse, 4 or 625 centimeters inverse.

Like that different peaks can be described in the literature, so internationally accepted or centimeters inverse but it depends upon the personal use. So, a simple reciprocal relationship exist between wavelength and wave number this I have already taught to you when I was teaching you about the electromagnetic radiation. So, the wave number is nothing but 10000/lambda, you can look at this slide I have put it in the data for your convenience.

So, a simple reciprocal relationship exist between wavelength and wave number that is wave number is denoted by a frequency that is mu, centimeters inverse that is nothing but 10000/lambda, this lambda should be micrometers okay. So, the wave number is directly proportional to the absorbed energy that is K=E/hc whereas wavelength is inversely proportional to the absorbed energy.

This I need not you know emphasize again and again but suffice it to say that you can use wave number or wavelength both okay. So, if it is wavelength if it is wave number you use centimeters inverse and if it is the wavelength then you go for micrometers okay.

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The information contained in an IR spectrum originates from molecular vibrations. These are either fundamental modes that are associated with the vibrations of specific functional groups, complex modes of the total molecule, vibrational overtones or summational modes of fundamental vibrations. IR analysis may simply involve the characterization of a material with respect to the presence or absence of a specific group frequency associated with one or more fundamental modes of vibration or by a complex pattern recognition or by a computer search- match algorithm when an unknown spectrum is compared to an existing reference database. The spectral data is also used to measure one or more compounds in a simple or complex mixture.

Now the information contained in the infrared spectrum generally originates from the molecular vibrations. This I had explain to you earlier most of the IR spectrum are vibrational transitions occurring in the structure of a molecule when bombarded with electromagnetic radiation that is infrared okay, what is the infrared range, range is from 4000 to 200 and then 15000 to 3000 or 4000 or 25 micrometers to 10 micrometer, you can choose either of them any of them.

But there are dedicated instrument separate dedicated instruments for near IR there is 1 instrument that is normally comes with spectrophotometer UV visible near IR. And normal infrared starts from 4000 to 200 that is normal IR and another instrument is available which is much more costlier than the normal infrared. That is 25 microns to 10 microns see you can observe that I am saying so much centimeters inverse in the near IR.

And centimeters inverse in the mid IR and micrometers in the far IR, because it is 25 to 10 easy to remember. So the functional fundamental modes that are associated with the vibrations of specific functional groups that is what makes the infrared spectrometry a very special tool for us to identify a compound or follow a reaction. So, the functional groups like an acid group COOH attached to an organic moiety.

Or OH group alcoholic group attached to an organic moiety that alcohol, methyl alcohol, butyl alcohol all alcohols will have only OH group attached to an organic moiety. Then aldehydes methyl, formaldehyde, acetaldehyde, proponaldehyde etc., another class of compounds ketones like that amines, and many other compounds they are all having specific functional groups.

And the changes occurring in the molecular orbitals of these functional groups in the vibrational range are of these specific functional group can give rise to number of peaks. So, the total molecule infrared spectrum is a fairly complex structure or spectrum you will see. So sometimes you will see vibrational overtones that means another peak at double the wavelength but it refers to the same functional group.

So, they are known as overtones or summational modes, so the summational modes or vibrational overtones are available for fundamental vibration it they are not available for every transition no and sometimes they occur in the same region of mid IR or far IR or something like that sometimes if you are working in mid IR the overtone may occur in far IR also.

So, that time you will be not able to see the overtone or summational mode of the fundamental vibration. So, IR analysis simply involves the characterization of a material with respect to the presence or absence of a specific group of compounds frequency associated with 1 or 2 fundamental modes of vibration or by a complex. So, we need something like pattern recognition, so what we do we mean by pattern recognition.

It is pattern recognition can is to recognize a pattern if I know a compound if I prepare a pure compound I can record the spectrum of the compound and try to remember these general structure of the IR peaks all peaks. So, the next time I see a similar IR spectrum I will say yes this is ethyl alcohol spectrum something like that. So, that is pattern recognition but pattern recognition can happen in different modes.

For example a man who is very good at pattern recognition in particular component may not be good at the pattern recognition of some other compounds or a person maybe good in pattern recognition then other persons. So pattern recognition itself is a separate science where the computer algorithms are used to recognize particular patterns and say this is the compound.

So, pattern recognition by a computer search and match algorithm of an unknown compound can be compared to an existing compound. So using a reference database, reference database is of several infrared spectrometers, several infrared spectrum of thousands of compounds are available in databases. So, all you got to do is put them in the computer in the instrument itself and simply take the spectrum.

And ask it to do apply the algorithm to find out which compound the spectrum refers to. So, that is high end spectrophotometer that is infrared. So, the spectral data is also used to measure 1 or more compounds in a simple or complex mixture also. So, what we are saying essentially in this slide is the information available in infrared spectrum is complex it can be give us they are all associated with fundamental modes of the functional groups.

Like aldehyde acid, aldehyde alcohol and then acids, carboxylic acids, amines etc. and all these analysis can be identified or traced to the original compound by information process by the human eye looking at the complex spectrum or by the computer quite often you may not be interested in the whole compound as such but we are interested in a particular functional group.

So, the functional group also if I remember the wavelength I will be looking only at that wavelength whether a peak is there or not to just for pass fail test for such things. So the spectral data can be used to measure 1 or more compounds in a given mixture also. So, that becomes a little tricky especially if you want to do the unknown analysis okay. So a non linear molecule containing n atoms has 3n-6 possible vibrational modes through which infrared radiation maybe

absorbed. So you can imagine how many atoms are there in methyl CH4 one is carbon 4 hydrogen atoms.

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A nonlinear molecule containing n atoms has 3n - 6 possible vibrational modes through which infra red radiation may be absorbed. For example methane has 9 and benzene has 30 possible fundamental absorption bands respectively. In order that a particular vibration results in an absorption band, the vibration must cause a change in the dipole moment of the molecule. Thus molecules containing certain symmetry groups will display somewhat simplified spectra. The C=C stretching of ethylene and C-H stretching of methane do not result in an absorption band. Further if absorption occurs outside the IR region or too close for resolution or too weak in intensity, the observed number of absorption bands will be less than the predicted number .

So, look at the slide now what I am saying is there are n atoms in a given molecule and it has vibrational modes 3n-6. So, for 4 elements okay n for 4 atoms CH4 5 atoms, for 5 atoms like methane CH4 I have 3n-6 that is 3*5 -6 that is 9. So, simple compound like a methane has 9 peaks, 9 absorption vibrational modes and imagine the same for benzene C6H6 is the formula for benzene and that makes it 12, so 12*3 that is 36-6 that is 30.

So, 30 possible fundamental absorption bands can occur in benzene, so it almost humanly impossible to remember all the 30 possible fundamental vibrations and their wavelength etc. So, in order that a particular vibration is does not mean that all the each vibrational mode gives rise to an infrared peak no there are certain vibrational peak levels bands which are banned some are forbidden.

So, only a few vibrational modes appear in infrared spectrum but they are much more than UV visible. So that is what it means essentially we are looking at far more number of peaks compare to UV visible near infrared. But every vibrational mode does not lead to an IR peaks some are forbidden, so and every molecule does not give rise to IR peak in order that a particular vibration

results in a specific absorption band the vibration must cause a change in the dipole moment of the molecule.

This is a very important aspect we all asks this question in interviews, so what the question is what kind of molecule gives raise to infrared spectrum. The answer we expect is the only those compounds where there is a dipole moment change in the dipole moment occurs in a given molecule that compound can give rise to infrared spectrum all others are not. That means a symmetrical molecule cannot give raise to infrared spectrum.

So the molecules containing certain symmetry groups are automatically excluded right, so from the infrared or even if they give you some spectrum they are very simplified spectra. So if I have carbon-carbon double bond in ethylene, so what is the formula for ethylene it is CH2-CH2 you can imagine that it is a fairly symmetrical molecule okay. So, there are 2 carbon atoms, 2 hydrogen atoms like this in between a carbon atom.

And there is no change in the dipole moment, so a compound like ethylene may not give you an absorption spectrum in IR or carbon stretching CH stretching, carbon-hydrogen stretching of the methane may not result in an absorption band. Because there is 1 carbon, 1 hydrogen there is no change in the dipole moment, so if absorption occurs outside the IR region or too close for resolution or if it is too weak to appear as a distinct peak again I do not see an IR spectrum.

So, the observed number of actual absorption bands will be less than the predicted number always but they are much more. We will continue our discussion on the infrared spectrometer in the next session.