Chemistry II: Introduction to Molecular Spectroscopy
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Lecture – 14
Vibrational Polyatomic Infrared Spectroscopy Local Modes and Group Frequencies

Welcome to the lectures on chemistry this is a series of lectures brought to the benefit of engineering and the science under graduate students under the program called the national program on technology enhanced learning the program is funded by the ministry of human resource development to all the Indian Institute of Technology.

And Indian institute of science and in the first phase we have been creating a large number of web and videos based courses for the benefit of teachers and students outside of the IITs to many private institutions and government colleges.

In this series of lectures on chemistry I have been examining the basic principles of chemistry particularly physical chemistry and this is a series of modules. The current module in which I have been lecturing for the past 7 hour 8 lectures is known as the molecular spectroscopy module.

Today we will continue with the vibrational or polyatomic infrared spectroscopy with the emphasis not on the normal mode as we did in the previous lecture, but on what are called local modes and group frequencies and will give you a little bit about how infrared spectroscopy is employed in the laboratories in actual practice.

Today on the lectures on molecular spectroscopy today's lecture is on polyatomic vibrational we are looking at infrared radiation therefore; infrared spectroscopy and we shall look at what are called group frequencies or local vibrational modes.

Is an extremely important subject in vibrational spectroscopy the fact that we talk about local vibrational modes as opposed to normal vibrational modes means a fundamental distinction to begin with the local vibrational modes can be anharmonic they can be very large amplitude vibrational motions as in the case of a ring torsion that you saw in benzene in the last example.

Or in Trinitro Telvin where you saw the methyl groups are rotate fairly with large amplitude fairly significantly it is a low frequency mode, but it is a large amplitude vibration. A large amplitude vibration essentially means that the forces associated with them restoring the vibration back to the equilibrium the forces are not necessarily linear in the displacements.

Forces being linear in the displacement are how you understand the harmonic motion leads to a harmonic potential in the form of a parabolic curve and then we are able to solve this as a beautiful oscillations pertaining to very standard amplitude periodicity all those things.

Now, if a molecule vibrates in a single vibration when it goes to very large amplitudes simply decides to rupture because there is sufficient amount of energy then there is no harmonicity of oscillations backwards the molecule has dissociated the carbon, hydrogen bond.

For example, associated with methane in the presence of chlorine in sunlight elementary organic chemistry tells you gives you if the CH bond breaks it is abstracted by a free radical and then what you have id the CH3CL being formed and that is a bond rupture.

The bond breakage can happen through electronic excitation energy transferred to the local bond which stretches and eventually the atoms get pulled out such motions which are very large amplitude vibrational motion if you talk about it in a single vibrational mode the molecule can break away those are anharmonic vibrations.

There are vibrations associated with bonds and all also energies associated with groups of atoms like very familiar example for you is the functional group that you take about in organic chemistry phenolic group, carboxylic group, the carbonyl group.

The acetyl group different groups have you can identify them as species oscillating with respect to the rest of the molecule and contributing to a local absorption resonance of the absorption and these resonance absorptions on this different groups will show a characteristic spectrum which is what we call as the local mode spectrum or group frequency spectrum.

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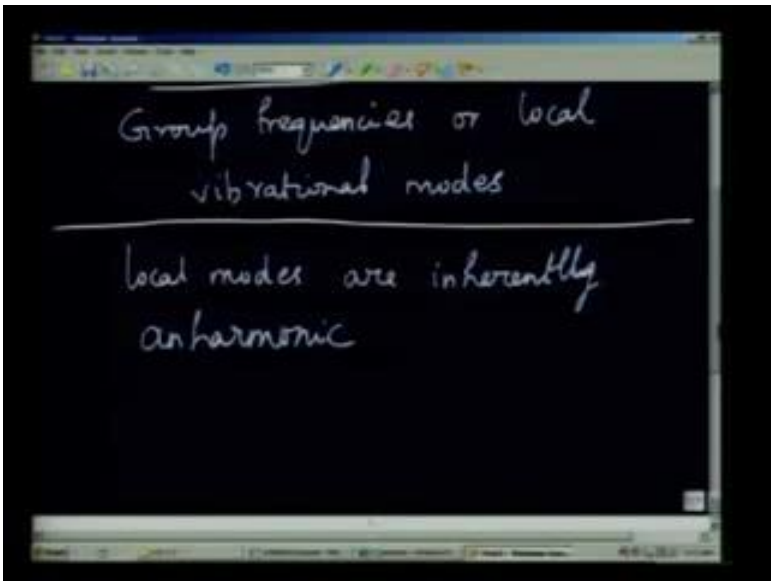

Group frequencies or local vibrational modes

local modes are inherently anharmonic

So, local modes when we discuss are inherently an harmonic now let me give you a typical example of a spectrum before we start looking at these specifics ok.

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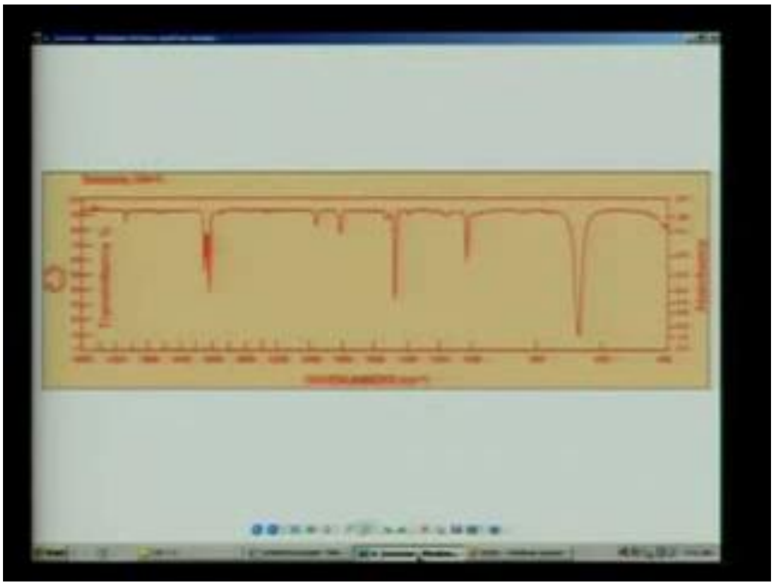

One I have here is the structure of benzene this is the transmittance me the absorption one by the absorption is the transmittance here percent the transmittance percentage is given from hundred percent transmission which means no absorption to less and less transmission therefore, this is can be converted into absorbance is nothing, but quantifying the intensities absorption intensities and on this axes what you have is the wave numbers here wave numbers decrease this is the smallest 400 centimeter inverse you will not be able to read this numbers.

Let me give you the numbers this end is 400 centimeter inverse vibrational and this end is 4,600 centimeter inverse and in between you see the scales 400, 800, 1200 1600 and so on.

This is the axes of increasing wave numbers from right to left. And what you see is a typical absorption line at about 3000, 3,200 between 3000 and 3100 there is a significance absorption then there is a very large absorption near about 900 this is sorry 650, 680, 700 centimeter inverse this is about 700. So, you are looking at an absorption frequency corresponding about 670 centimeter inverse.

There is another major absorption peak at about 1500 centimeter inverse. So, let us list them down to see what we mean by group frequencies. Benzene there are 3 vibrational frequencies.

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Benzene absorption frequencies

~ 3000 – 3100 cm^{-1}

~ 1500 - cm^{-1}

~ 660 - 670 cm

Toluene

Large absorption frequencies what are the values there is 1 at about 3,100 between 3000 and 3100 centimeters. Centimeter inverse then there is 1 around 1600 no around 1500 centimeters.

Approximately, 1500 centimeter inverse and then there is 1 at about 670 centimeter inverse this is 800, this is 600, roughly 670, 660, 670 centimeter inverse 3 frequencies.

Now, let me a molecule which is close in structure to benzene me take the structure of toluene this is the sorry it goes outside the range this is the IR spectrum of toluene ok.

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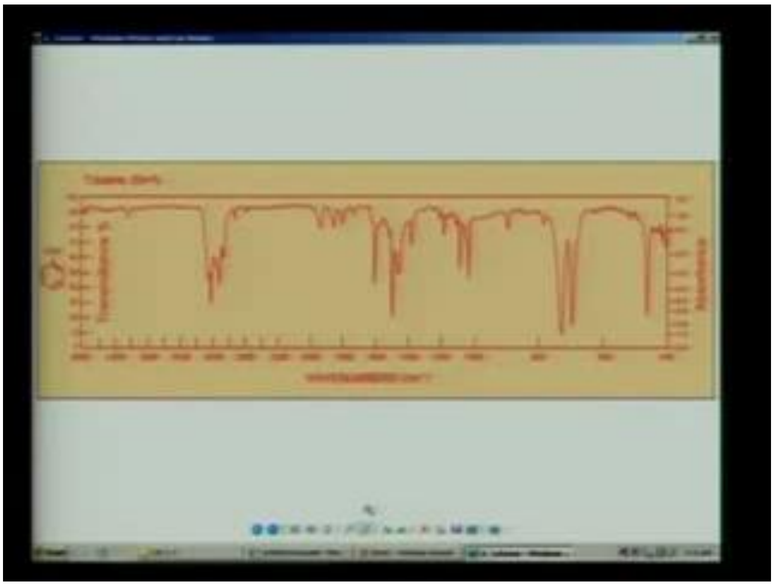

Toluene which is C6, H5, CH3 1 extra methyl group, now let us look at the spectrum of this and see what features are similar to what we have near the benzene 1 again we have an absorption near 3000 to 3,100 around that centimeter inverse IR, but except that now it is a multiplied.

We have again absorption near about 1500 centimeter inverse you remember this near 1500 centimeter. We have one around 3000 centimeter inverse, but with a much more let us look at it with a much broader absorption or there are overlapping absorption's here.

And then we also have 1 near 670 that 680 centimeter inverse and again at about 750 you see additional lines. So, what you see is for toluene you see lines similar to what you will see in benzene, but in addition you see extra lines due to possibly the oscillation are CH3.

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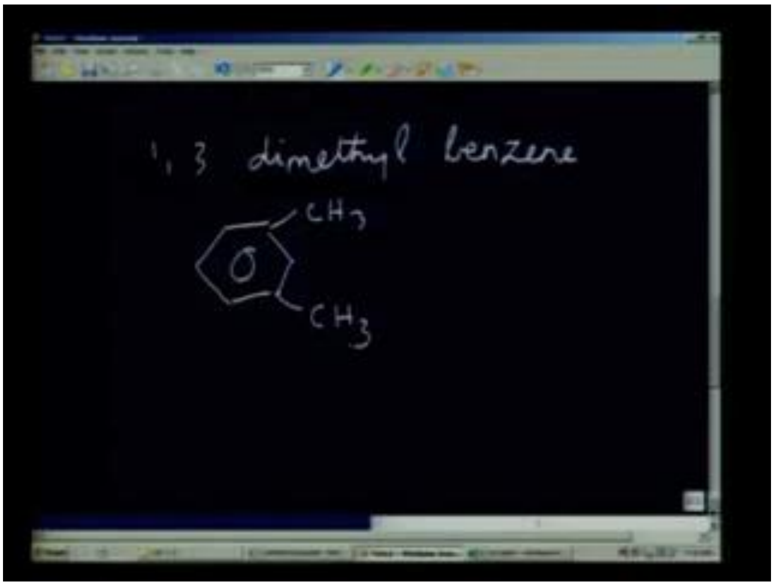

Now if we have some doubts about this if we look at the structure of the infrared spectrum of the next compound para not para sorry this should be that we find out this is mesitylene.

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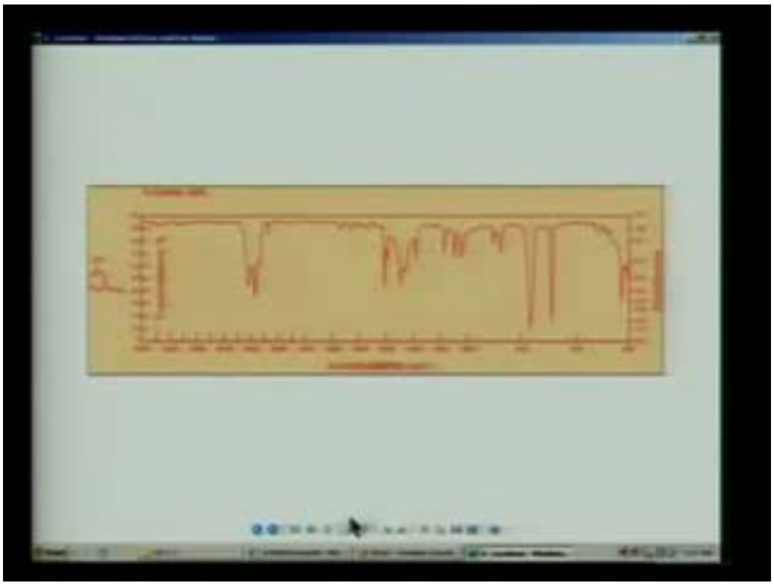

This is meta this is basically 1 3 dimethylbenzene. So, what we have is we have one more group CH3 and this CH3 and let us look at the spectrum of the compound again what you see is near 3000, 3,100 centimeter around this area there is a large absorption.

And you see this pattern is pretty close to the pattern of the previous compound namely toluene with one methyl group instead of 2 methyl group here there are 2 methyl groups there is one at position 1 and position 3 benzene you see a pattern similar to that and again you see the absorption frequency near 600 and 700 and something 670, 680 and also a large significant absorption around this area, but there are additional frequencies which appear which are not there in benzene, which are not there in toluene, but which are there in metasyle.

Now, what is a point of all of this is that pattern reorganization if you think about it is how the majority of chemists would approach spectroscopic techniques particularly with respect to identifying compounds.

So, now, you have a series of similar compounds benzene, toluene, and then metasylene of course, you can extend this to other compounds I am only picking up the idea you identify pattern which are common to that of the benzene ring you identify patterns which are common to the benzene with respect to ACH3 stretching this is a local CH3 group oscillation with respect to the benzene and then when there are 2 such groups that they are interfere with each other or they interact with each other and then the patterns likely changes and so on.

Therefore what you have is a series of compounds giving you similar spectra which can be identified as spectra or components frequencies due to specific groups present in the molecule. Now let us go back to the basic picture of what is meant by local modes.

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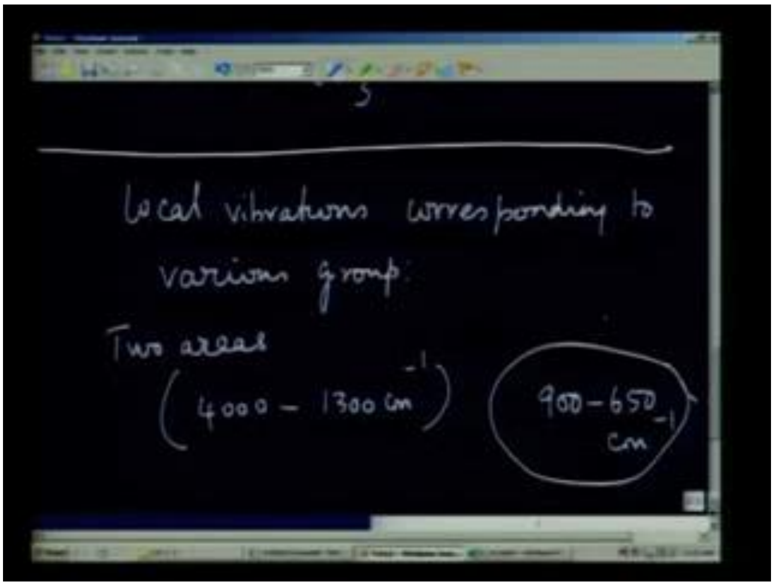

Local vibrations corresponding to various group:

Two areas

(4000 – 1300 cm^{-1}) (900–650 cm^{-1})

Local vibrations corresponding to various groups for example, the for 2 areas that the can concentrate or around 4000 to 1300 centimeter inverse this is one section and the other where we can look for vibrations which are characteristic of the compound are between 900 and 650 centimeter inverse.

Now, remember from the previous pictures the last lecture remember the progression that we had torsional vibrations the plane of the ring or the plane of the atoms in a ring gently getting distorted is a very small frequency then we have the bending vibrations atoms or a bond angle getting shortened and lengthened a bending vibrations of slightly higher resonance frequencies infrared frequencies and then of course, then these stretching vibrations which correspond to the actual stretching of a very strong bond therefore, the force constant is very large if you remember the old picture of normal modes. So, we had grouped them in that order.

Now obviously, when you look at this 900 to 650 centimeter inverse we are going to look at the frequencies or absorption, which distort the equilibrium structure by distorting the planer or distorting the, what is called the torsional modes.

Torsional modes are basically modes in which a group of 3 atoms in one plane versus group of 3 atoms in another plane and how they basically rotate with respect to each other.

So, that is our lower frequency which you will see pretty much in this then the high frequency N 3,100 here 4000 this is corresponding to stretching of the carbon hydrogen bond CH bond is one of the strongest bonds in organic chemistry. 90 kilo calories 94 kilo calories huge amount of energy therefore, stretching that bond is going to require a large amount of energy and what you see at the high end is the stretching frequency and in between you will see stretching various groups.

Groups which are not highly non polar bonds or the, what is called the highly covalent bonds versus ionic bonds if you look at or semi ionic bonds you see that a whole range of frequencies fall in this region ok. Yes list some of these numbers for your convenience.

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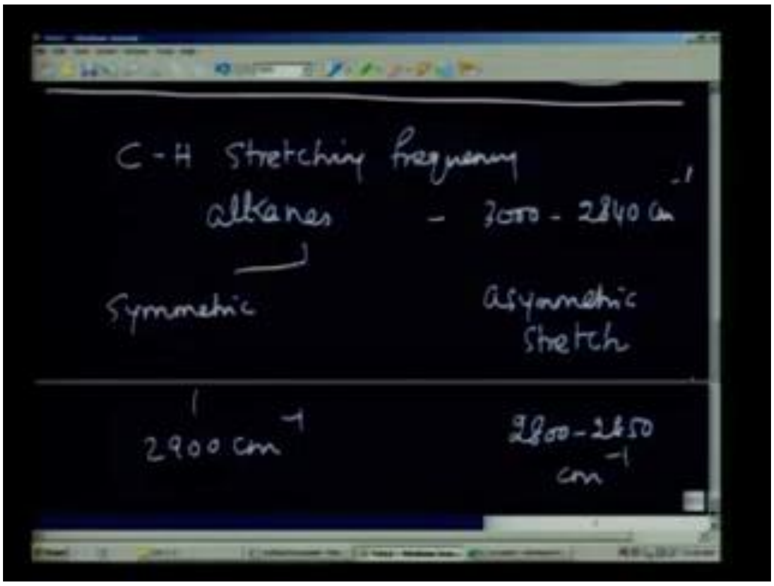

C - H Stretching frequency

alkanes – 3000 - 2840 cm^{-1}

Symmetric

asymmetric Stretch

2900 cm^{-1}

2800 - 2850 cm^{-1}

You will have a group frequencies these are experimentally absorbed carbon h stretching frequency typically in all Alkanes that is saturated hydrocarbons you will see approximately absorptions in the range of 3000 to 28, 40 centimeters inverse.

These are observations are based on many many molecules millions and millions of molecules and over a period of time spectra have been tabulated and such tabulations are available for libraries and for the organic for the chemistry laboratories.

So, here is the stretching frequency Alkanes in that range then the asymmetric again in the stretching there are symmetric and then a symmetric stretch. Symmetric stretch approximately 2900 centimeters inverse and the asymmetric stretches between 2800 to 2850 centimeter inverse.

This is the usual stretching frequency that you find for the Methylene groups and for the carbon hydrogen groups then there are, what are called the scissoring motions scissors.

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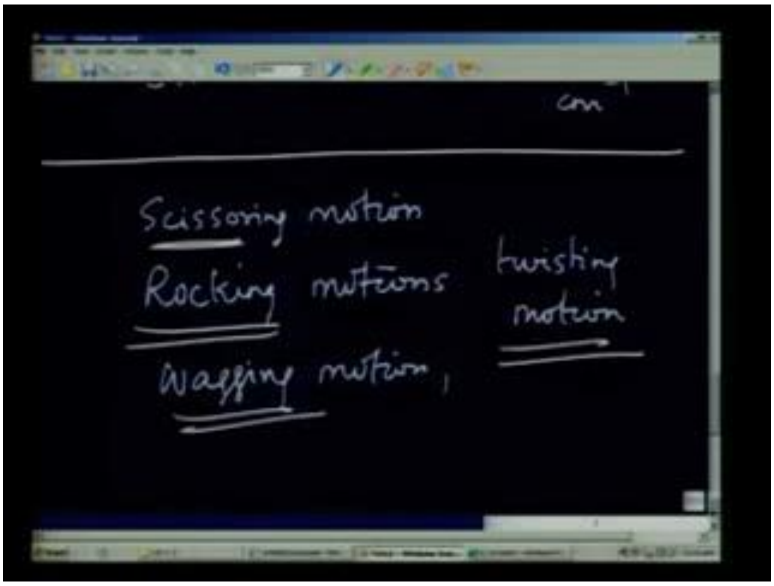

cm

Scissoring motion

Rocking motions

Wagging motion,

twisting motion

Scissoring motion then there are rocking motions what is meant by rocking keep taking the base rocking motion then there is wagging motions for group frequencies dogs tails wags with respect to the rest of the body.

So, there is a small group of atoms which sort of oscillates with respect to the other the other bulk of the molecule remains pretty stationary whereas of course, the molecule never remains stationary in a genuine vibration in the sense the center of mass remains constant.

But every part has to compensate for the motion, but bulk of the group which is very small reduced mass oscillating a large and a large reduced mass of the rest of the group not showing up much. So, it looks like a part of the body is oscillating like a tail wagging dogs tail wags ok.

Then what are the there is also twisting motion these are all various types of molecular motions the twisting motion is you remember what you do for a twist most of you who wash clothes will have to twist it sometimes in the absence of the dryer and the modern day gadgets many of us twisted the clothes to take the water out.

So, basically twisting it like this. So, parts of the molecule which rotates with respect to the other part which rotates in the anti direction that is a twist this is a twist. So, there are different types of molecular motion that one can observe in what is called this general infrared spectroscopy is very hard to classify them as only normal modes or only local modes, but whenever they are referred to a group frequency I would like to put them as a local mode because that refers to a local group.

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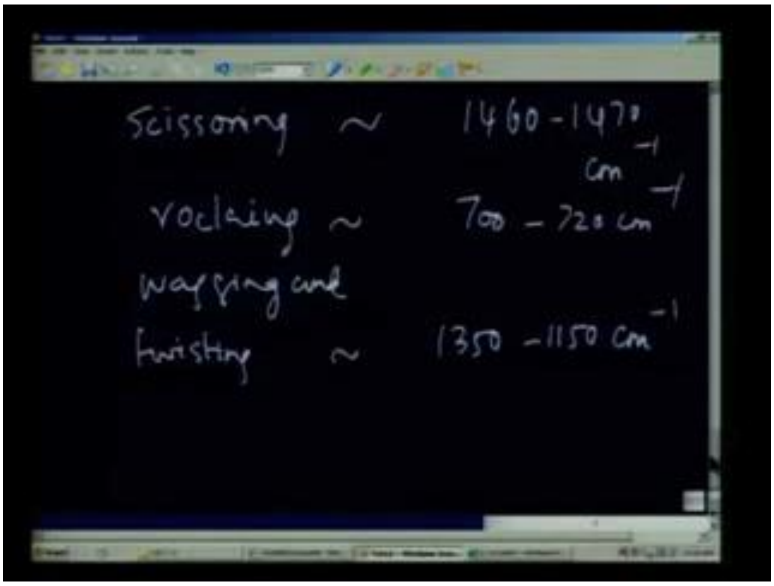

Scissoring ~ 1460 - 1470 cm^{-1}

rocking ~ 700 - 720 cm^{-1}

wagging and twisting ~ 1350 - 1150 cm^{-1}

So, typically where do these frequency various frequencies come in scissoring motions the range is between 1460, 1470 centimeter inverse rocking very low frequency about 700 to 720 centimeter inverse wagging and twisting fairly somewhere between 1350 to 1150 centimeter inverse you have seen some of these examples in the previous case, but let me try and see if I can find one of those examples here.

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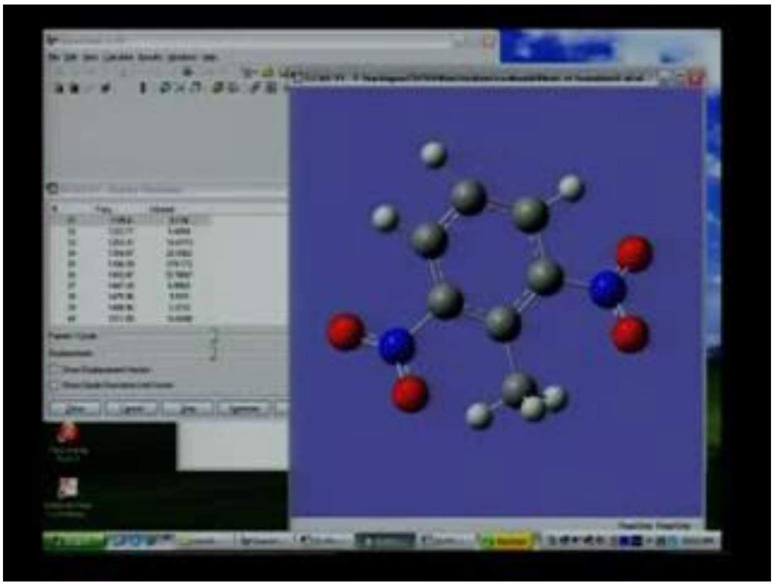

Now, the spectrum the I R vibrational mode that I have here in this screen corresponds to this is the methyl group. So, this is toluene with 2 nitrogen’s groups here this is a hydrogen nitrogen nitro NO2 groups here NO2. So, it is 2, 6 dinitrotoluene is a low frequency vibrational mode what you see here is 1195 even though these are normal mode frequencies you can see significantly that this is 3 hydrogen atoms moving relative to rest of the body looks like this is if you call this as the end of the tail or I do not know whether it should be called tail wagging, but it falls in the frequency range of about 1150 to 1350 that we talked about. So, that is a small part of the molecule moving relative to the rest this is one example.

And the other group vibrations that you see here even this is normal mode what you see is largely one group vibrating relative to the other let us see if we have the a torsional motion of the benzene the toluene group somewhere here ok.

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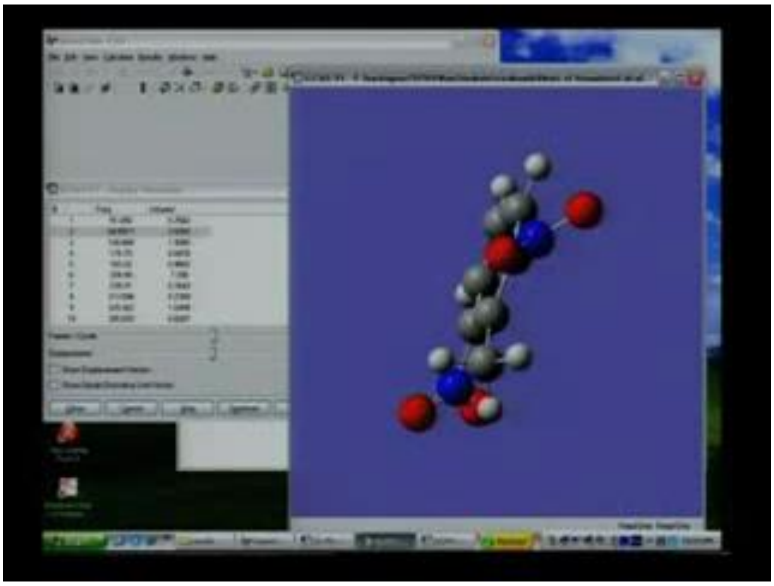

Now, what you see is this is the in plane and out of plane motion of the nitro groups 178 now what we are looking for is here is a torsional motion of the methyl group relative to the rest of the ring. So, this is a torsional vibration.

So, likewise we can identify groups and groups of frequencies now let us continue with the classification of some of these frequencies in order to complete this lecture there are many molecules for which we can it down and look at the vibrational modes one after the other normal mode picture is one thing, but now let us group the frequencies for what are called group frequencies,

Now I talked about the alkanes and the methyl group vibrational frequencies earlier and we got side track into scissoring rocking wagging and twisting and all those things please remember that molecular analogy’s are very interesting anyway.

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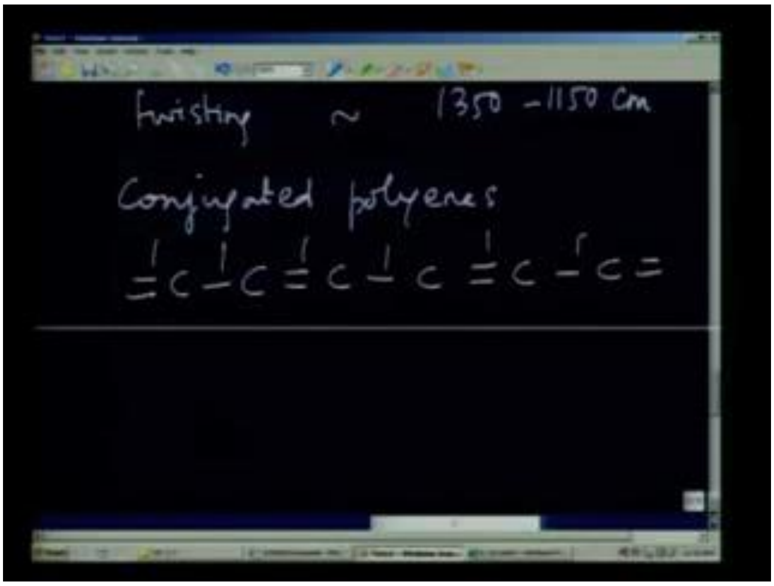

twisting ~ 1350 - 1150 cm

Conjugated polyenes

$=\overset{|}{C}-\overset{|}{C}=\overset{|}{C}-\overset{|}{C}=\overset{|}{C}-\overset{|}{C}=$

Let us look at the conjugated poleyenes you know what this means what this means is double bond alternating single bond and so on double bond single bond double bond alternating a double single double single such alternating bonds are called conjugated structures aromatic hydrocarbon sorry the hydrocarbon structure.

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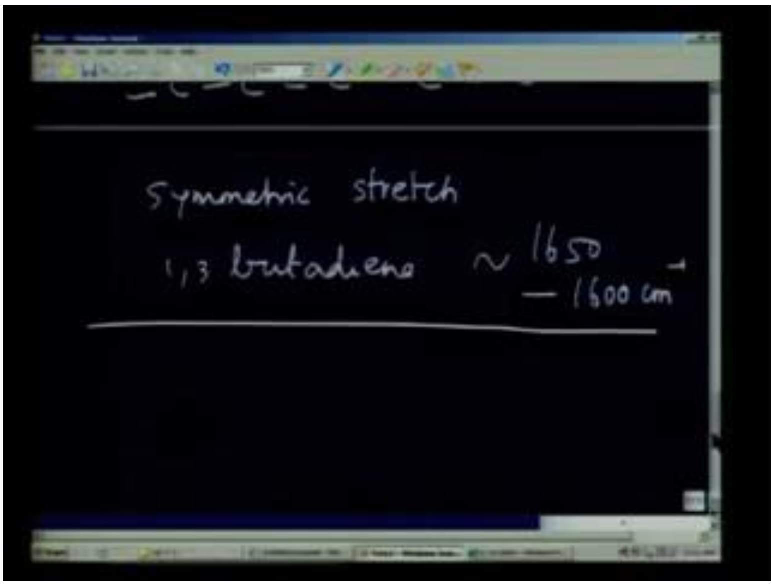

Symmetric stretch

1,3 butadiene ~ 1650 — 1600 cm^{-1}

And conjugated alkanes have symmetric stretch for one 3 butadiene for example, approximately 1650 to 1600 centimeter inverse these are patterns characteristic of symmetric conjugated dying structure then you have for alkanes.

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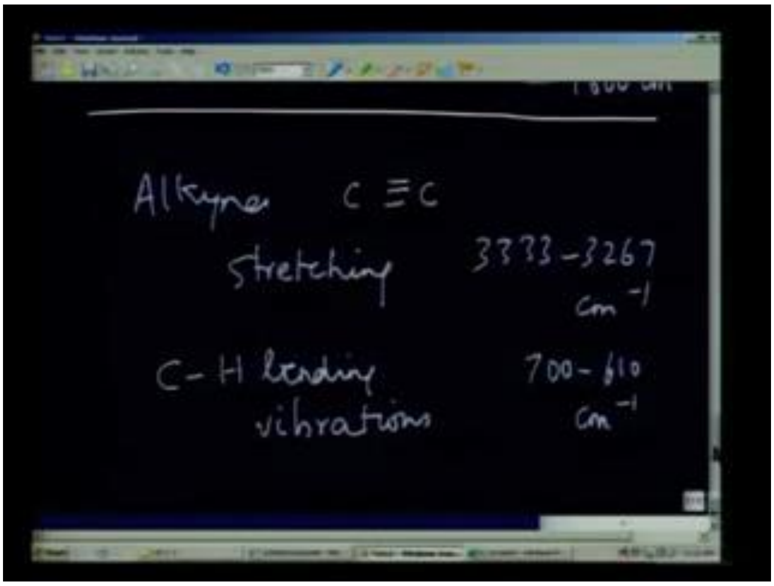

Alkyne $C \equiv C$

stretching 3333-3267 cm^{-1}

C-H bending vibrations 700-610 cm^{-1}

The C triple bond C the vibrations or stretching vibrations are approximately 33, 32, 67, centimeter inverse and the CH butadiene vibrations around 700, 610 centimeter inverse ok.

Now, let us just look at some of the groups functional groups for a change and let us list the functional group frequencies which are important in IR spectra the functional group when.

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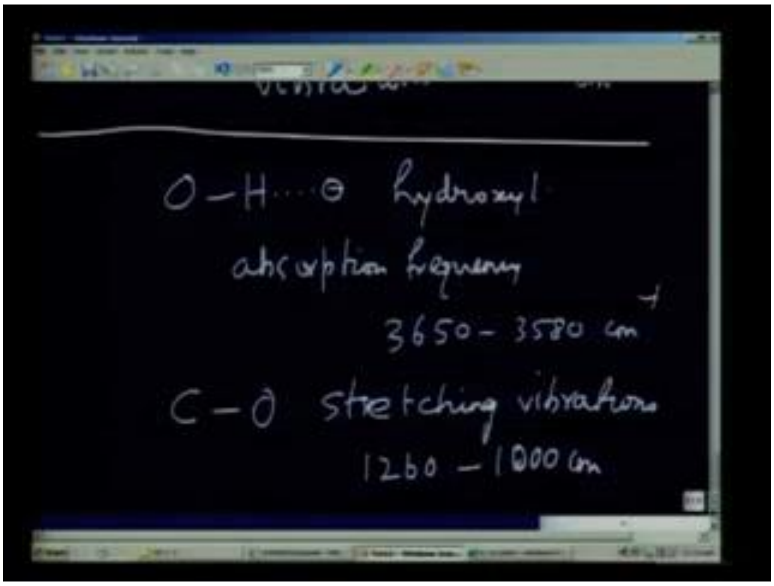

$O-H \cdots O$ hydroxyl

absorption frequency

3650- 3580 cm^{-1}

C-O stretching vibrations

1260 - 1000 cm

You look at the phenolic group or alcoholic group OH for hydroxyl the absorption frequency is between 36, 50 and 35, 80 centimeter inverse then molecules with hydrogen bonding of course, will have a slightly reduced frequency because the OH is stretched by the presence of another O here slightly weaker bond and therefore, what you have is the vibrational frequency for this OH group gets reduced a little bit the CO stretching vibrations are between 12 60 and 16 about 1000 centimeter inverse.

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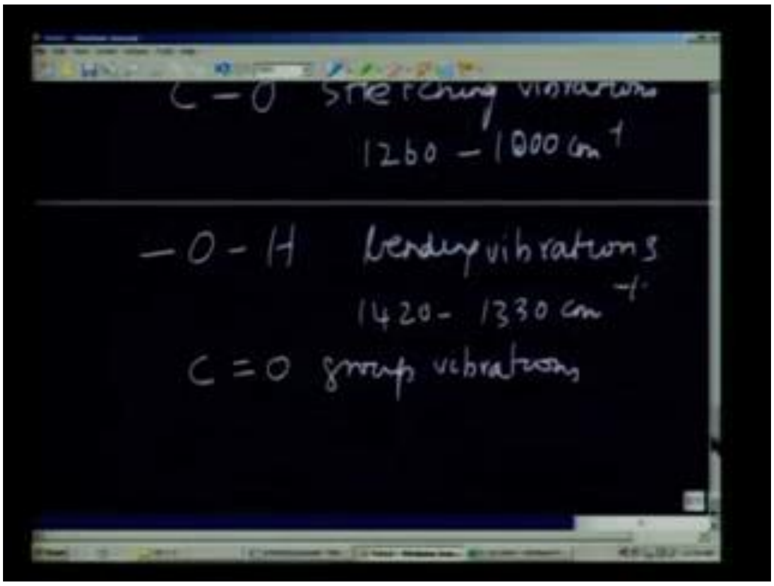

C – O stretching vibrations

1260 – 1000 cm^{-1}

–O–H bending vibrations

1420 – 1330 cm^{-1}

C = O group vibrations

And the OH bending vibrations as you had seen earlier for water molecule with the other hydrogen here, but in general the bending vibrations for OH fall in the range between 14 20 and 13 30 centimeter inverse and likewise you have this C double bond O the carbonyl group vibrations.

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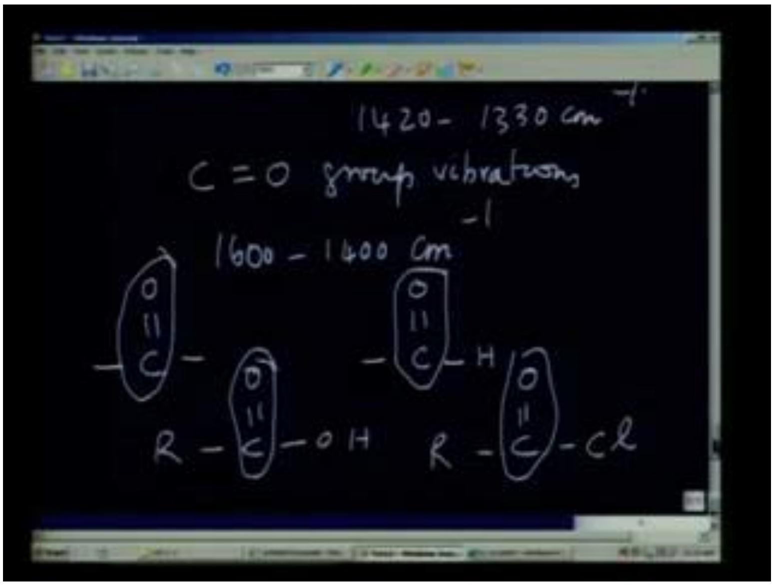

$1420 - 1330\ cm^{-1}$

C=O group vibrations

$1600 - 1400\ cm^{-1}$

The carbonyl group vibrations fall in the range between 1600 to 1400 centimeter inverse for the variety of components the carbonyl group can be a ketone it can be from an aldehyde or the CO group frequency may be in the environment of a carboxylic group.

Or it can be in the acyl chloride the typical each CO depending on the environment in which it is in shows up a slightly different frequency and therefore, one can obtain a series of these spectra take the finger print and then pattern the pattern identify the patterns in them and using these patterns from unknown components we can try and identify what kind of functional groups are present in the molecule this is what we do with respect to the infrared spectroscopy of some of the organic compounds as we see in liquid state.

Now, what is important is in the solution state when we do this spectra liquid meaning that these are these are all been some solvents and you take the spectrum of these compounds.

The infrared spectrum of these compounds and solutions states give raise to these kind of frequencies that you have seen which are quite different from the infrared frequency of these compounds in the gas waves where the interactions between the different molecules is minimized and also in the gas waves a large part of the spectra are cluttered by the rotational the coupling of these molecular motion with the rotational motion of the molecule.

Because in solution phase the rotational motion averages how we do not see them in the and also the infrared spectra meters that we have for solution phase have a very poor resolution that is they are of the order one centimeter inverse is 1 to 2 centimeter inverse is what you see as a normal laboratory IR spectra meter gas wave spectra are much much more highly resolved depending on the spectra meter that we use and also they give raise to additional features of the vibrational lines in the form of rotational structure sub structure to this.