Introductory Organic Chemistry - II
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Lecture 18
Essentials of IR Spectroscopy

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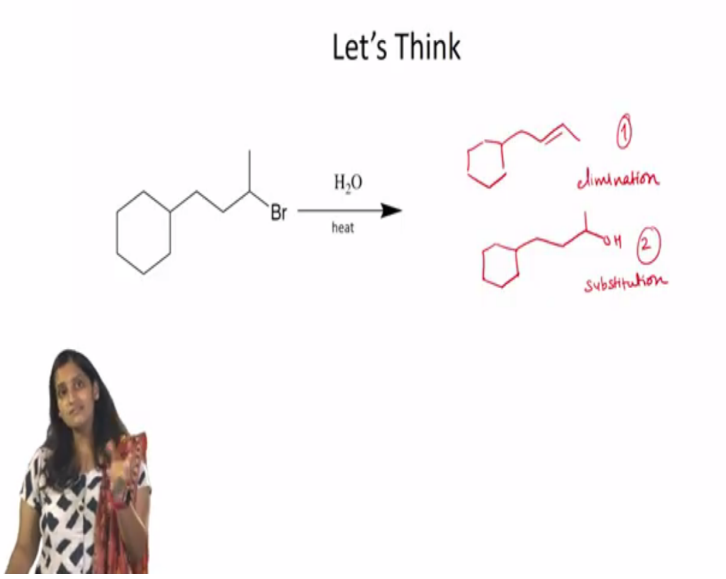

Hello, my name is Neeraja and today we will be going over some important techniques in Organic Chemistry. So, we are going to talk about Spectroscopy techniques. And today I will be introducing the Infrared Spectroscopy. But before we really start talking about spectroscopy, I want to go over why it is important to know these techniques and what real crucial role these techniques play in an organic chemists' life.

So, imagine that you are in a lab and you are trying to synthesize a particular compound. Now, the example I have taken here is that of an alkyl bromide, and when it reacts with water, let us say you heat it a little bit, what kind of products can this really form. So, can you help me with the answers. So, if you remember from the last course, we discussed the reactions of alkyl halides and alkyl halides can really undergoes substitution or elimination reaction.

So, either it can form this, which is an elimination product or it can form a substitution product. Now in the case of substitution product, it is going to result into an alcohol. And in the case of elimination, it is going to result into an alkene. Now, you want to really know so because you

have done the reaction in a flask, you have formed the product. Now you want to know which one of these two, whether it is the elimination, or whether it is the substitution, which one of these two reactions has really happened or occurred or is it a mixture of two, or have I formed a good mix of these two things.

And you could try this out. So, for example, you could try doing chemical testing, and go the chemical way of figuring out the structure of the compound. So, you could, for example, put your resulting product into bromine, and see if the bromine solution gets decolorized because if it gets decolorized, it is an alkene. Or you could do some tests for alcohols, the detection tests or the qualitative detection test for an alcohol and figure out if you have formed an alcohol.

But remember that nowadays, since we are synthesizing so many compounds, and literally everything around us is being synthesized. So, the food we eat to the drugs that we take, the medicines, as well as cosmetics, paints, polymers, everything around us is being manufactured artificially or chemically. I would not call it artificially but it is a chemical way of synthesizing things, we want to be sure that we have formed the product that we want.

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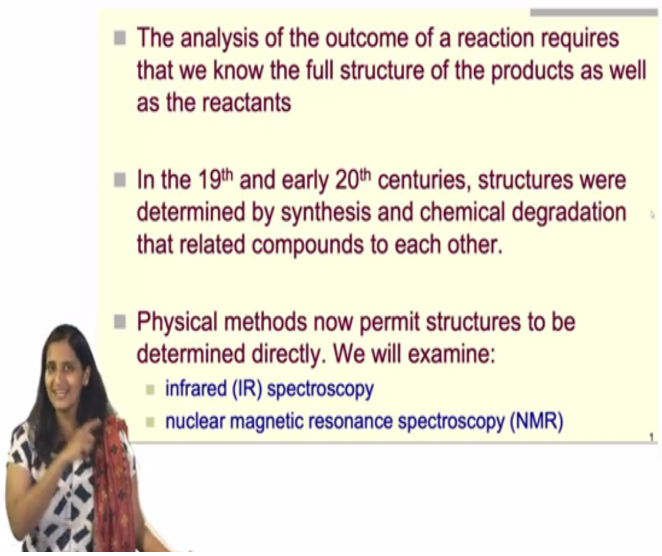

And that is where the role of spectroscopic technique comes in. So really, we want to know what is the product of our reaction. And earlier in the 19th and 20th centuries, people used to try

chemical degradation, people used to do a lot of synthesis and then do various chemical tests to figure out if they have really formed the compound. But nowadays, because of the advances of technology, we do not rely on those things, we instead have spectroscopic techniques. So, I am going to talk about infrared spectroscopy today and we are going to see how it helps us to figure out if we have formed an alcohol or if we have formed an alkene in the previous reaction.

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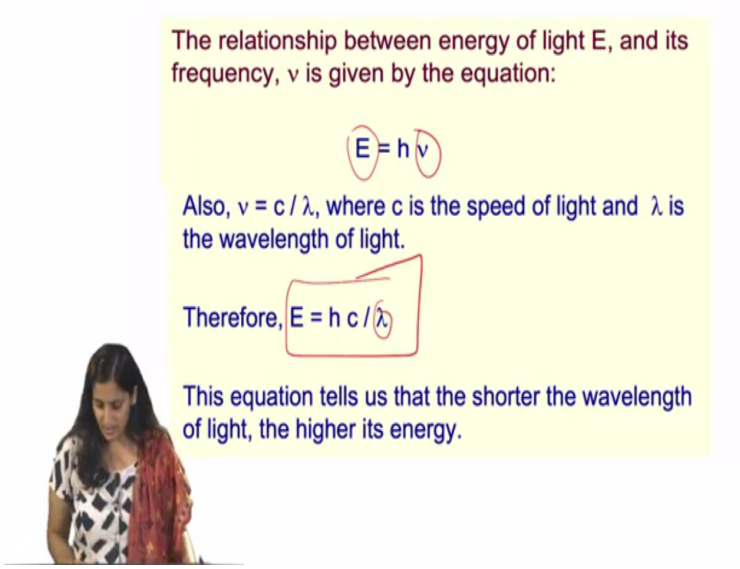

Now, before we go ahead and look at these techniques, I want to revise some fundamental principles and this has to do with the energy of light. So, we know that light is actually composed of various electromagnetic spectrum and then you also have very small part of it is actually the visible light that we see and the relationship between the energy of light that is E here with the frequency which is υ here is equal to

$$E = h \upsilon$$

And this tells us that the as the frequency increases, the energy also increases. And we also know that υ which is frequency, is

$$\upsilon = c/ \lambda$$

and c is the speed of light and lambda, λ will be the wavelength of that light. So, E is also equivalent to

$$E = h\,c/\lambda$$

So, these two equations are very important: $E = h\,\upsilon$ and $E = h\,c/\lambda$. Now, what it tells us is that the shorter the wavelength, so if you go on making this denominator smaller and smaller, the higher is the energy. So, it is going to increase the energy. So, the smaller the wavelength, the higher is the energy.

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And that is what we will see, in this particular spectrum here. The energy is going to increase in this particular direction. So, as we go from radio waves to gamma rays, all the way the energy is going to go on increasing, and the wavelength, so what will happen to the wavelength. So that is something you want to think about that as we go on increasing energy, the frequency is going to increase.

So, as you can see, from 10^{10} to 10^{20} it goes, whereas the wavelength goes on decreasing. So, from like, 10^{-2} meters, it goes to 10^{-12} meters. So, this is something very fundamental, I just thought of revising it before we actually go ahead and look at infrared.

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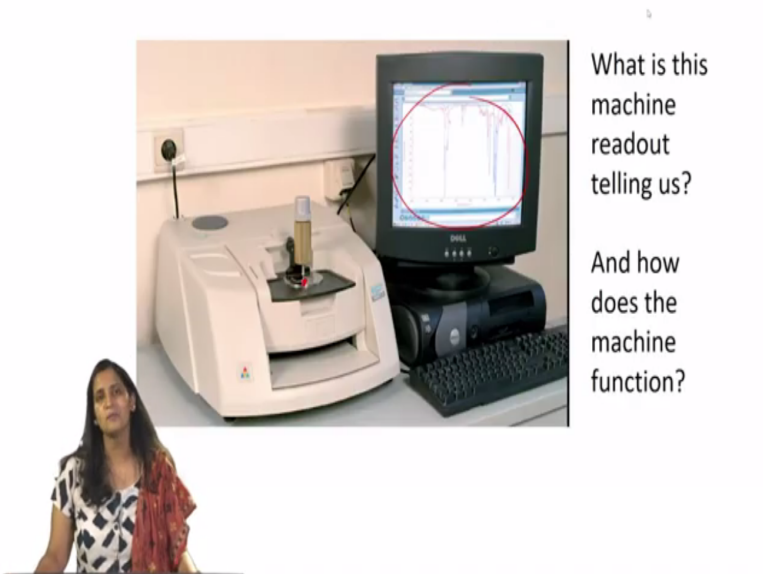

So, this is an Infrared Spectrometer. And what you do is, let us say you have performed that reaction that we were talking about, you take your product, and you put it down here, a little bit of a small, a crystal of it maybe, or if it is liquid, then there are other ways to or other chambers to analyze it. But you can even use some liquid here, wherein you can put it here, and then start the machine; the machine is going to give you a readout that looks like this.

So now we are trying to figure out what is this machine readout really telling us, how did it figure out that it is an alcohol or an alkene? And how does this machine really function. So that is what this talk about infrared spectroscopy is or IR spectroscopy.

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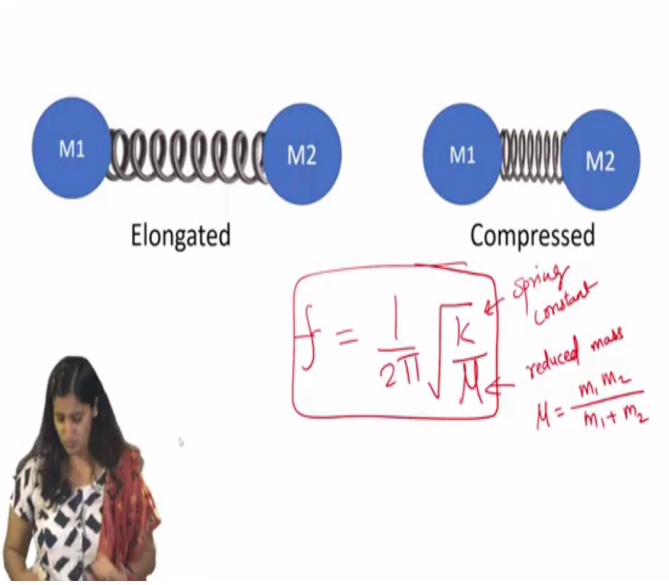

Before we go ahead to IR actually, I want to talk about Springs, and you might find it interesting, but I have a spring here. And remember that if I have two masses that are tied to this string, you can either have the springs such that it is kind of contracting together, so it is compressed, whereas you can stretch it also to make it elongated. So, I have also shown it in the slides, you can see two conformations- compressed and elongated.

So, this is going to vibrate. So, this is the kind of stretching that this particular string can do, or spring can do. And if we go back to again, the physics principles, the frequency with which this particular spring can vibrate is given by

$$\text{Frequency} = \frac{1}{2\pi}\sqrt{k/\mu}$$

, where k is the spring constant. And this really has to do with the construction of the spring. So, whether the spring is made up of metal or plastic, depending on how strong the spring is, it is going to change the spring constant, the stronger the spring, the tighter the spring, the higher is the spring constant and μ which is equivalent to the reduced mass.

And the reduced mass in this case, if we are talking about two masses, m1 and m2, mu is given by

$$\mu = \frac{m1 \times m2}{m1 + m2}$$

So, this is another important formula to remember $f = (1 / 2 \pi) \sqrt{k / \mu}$. You can even just remember the correlation that is f is proportional to $\sqrt{k / \mu}$ because we want to know if the spring constant increases, what will happen, the frequency will also increase, or if the reduced mass increases, the frequency is going to decrease.

So that is what we are going to now see, I was talking about springs, but really any bond for that matter, any bond between two atoms is actually like a spring. So, we typically represented with the ball and stick model, whenever we are talking about the representation, we say that this is one atom, let us say hydrogen, another hydrogen, they are bonded with a covalent bond. But remember, this bond is not solid, it is not rigid, as I am showing it here.

In fact, it is more like that spring that we were talking about. So, let us say that if these two were held together with a spring in between, these two could come together, or they could go out or they could kind of vibrate and that is what is happening because electrons in the bond are not rigid. They are not stationary or static in one place. They are in fact moving around and as a result of which, this particular bond or any bond for that matter can be imagined as a bond, that is equivalent to two masses being held by a spring.

Now in the case of hydrogen, hydrogen, I would say the mass of this one is 1, this one is 1, because of the mass number of hydrogen. For carbon, I would say one of them has a much higher mass than the other. So, that one would be 12 as compared to hydrogen on the other end. Now, remember, these are not the only kind of motion that these two can do,

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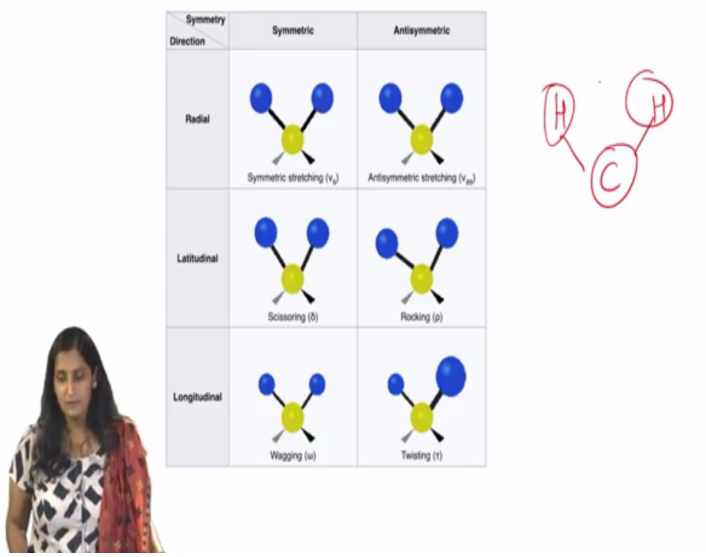

In fact, here and you can see a very nice animation, wherein you can have a symmetric stretching, meaning both, so imagine that there are three atoms of hydrogen, hydrogen and carbon, let us say there is a hydrogen, there is a hydrogen and there is a carbon in between. Now, with respect to these three atoms, the kind of stretching that can happen is that you can have a Symmetric stretching.

You can have an Asymmetric stretching such that one hydrogen is going away, the other hydrogen is coming together, or you can have something like Scissoring, or you can have Rocking or something like a Longitudinal. So, wagging or twisting various kinds of motion, the point I am trying to make here is that with respect to the bonds, you can have different degrees of freedom here, and they are going to move around in that degree of freedom.

In fact, you can have rotational motion as well. Between these two, these two can also do a rotational motion around each other. And all of these are happening so at room temperature, the bonds of a particular compound, so let us take hydrogen, for that matter, at room temperature, they are going to, let us say vibrate or stretch with the lowest energy, they do not want to spend a lot of energy in going back and forth. So, they will go with the lowest possible energy, they are going to be in that particular state.

But now, if I shine energy on this what is going to happen, this bond, or the electrons are going to get energy, and that is going to start vibrating much more faster and depending on the amount of energy that we are putting in, different kinds of transitions can be carried out in a particular molecule.

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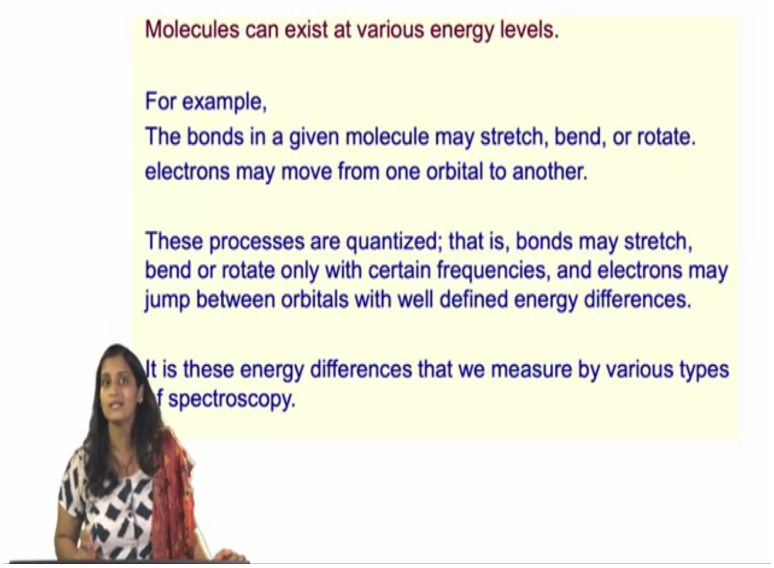

So, thing is that the molecules can exist at various energy levels. So, imagine that at room temperature, all the molecules are going to be at the lowest possible energy. But these bonds in that molecule, they can stretch, they can bend, they can rotate, electrons can jump from one orbital to another, all of these are transitions that can happen. And depending on the amount of energy given to that particular molecule, that is also going to determine the transition. But that is not the only thing.

These processes are quantized, meaning that the bonds will stretch, they will bend, they will rotate. But they will only do that in a certain frequency. And so, electrons also when they are jumping, we know that these are quantized transitions, meaning let us say you are starting from step 1, all the electrons are at step 1, they can either go to step 3, or step 5, but may not go to step 3 or 3.5, I mean it is a very quantized transition, it is a measured transition, they can go from one state to another state.

And depending on, let us say, you take a molecule, you shine light on it, you give it energy. How did the bonds in this particular molecule, or how did the electrons in this particular molecule, start vibrating, rotating, stretching, bending, all of these things, we can measure with the help of the energy difference, because remember, when we talked about E = h υ, the frequency is going to be proportional to that Energy. And depending on how much is the change, the energy difference, we can really understand what kind of bond is present.

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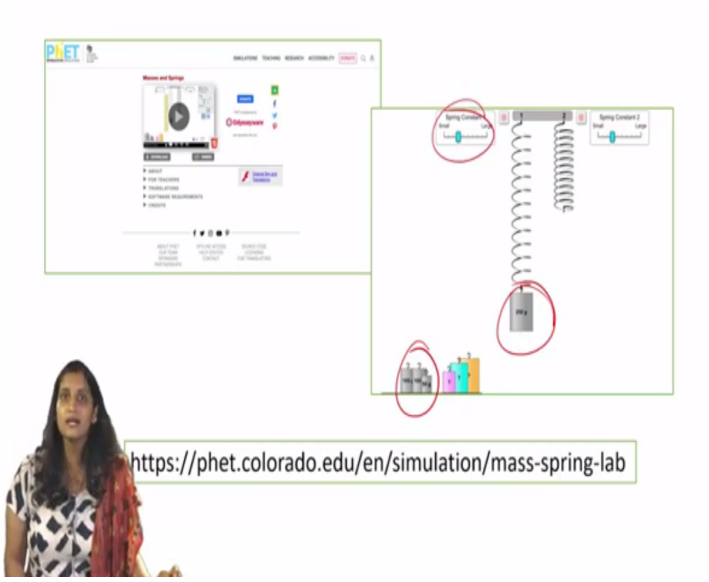

So, this is something interesting for you to do. If you want to just think about springs in general, this is a very nice simulation. If you go to phet.colorado.edu there are some really nice simulations here and try the simulation of the mass spring lab. Now in this particular simulation, you can actually change the kind of weights here on this spring, you can change the spring constant and then you can see how fast or how slow this particular spring is vibrating.

Why am I telling you to do this because the core principle of IR spectroscopy is very similar to the springs as we were talking about. So that is why I want to now start talking about bonds in general and go to actually applying that principle to the chemical bonds or the covalent bonds that we have talked about.

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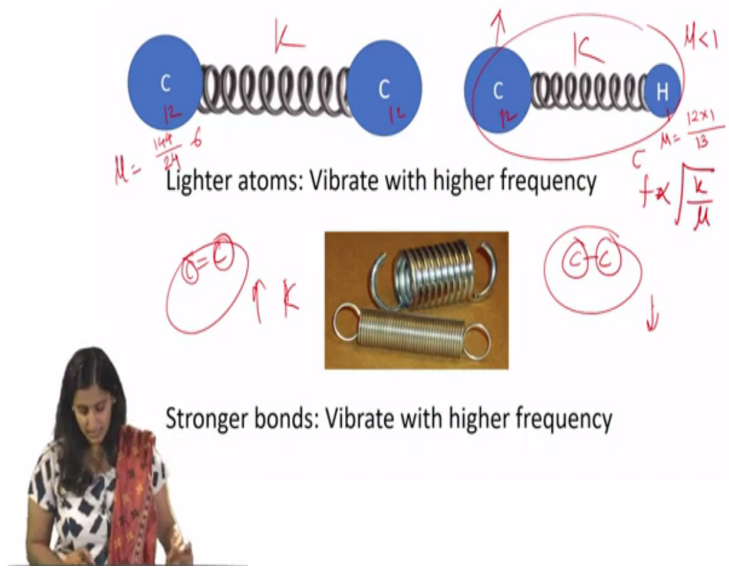

So now let us take two bonds, one is a carbon-carbon bond, and one is a carbon-hydrogen bond. Let us say that we shine light on both of these, and they have started vibrating. Now, we know that the frequency is proportional to $\sqrt{k/\mu}$, so which one will vibrate with the higher frequency? Now, to think about it, all single bonds, you can say have very similar spring constant.

So, the k here is very similar to the k here with a single covalent bond. It is probably having the same amount of or a similar spring constant. But remember, because now on one end, you have hydrogen, the reduced mass of this particular system has changed. So now if we take carbon as 12, this carbon is 12, this carbon is 12, this is 1. In this case, this is the reduced mass for the first system is

$$\mu = \frac{12 \times 12}{12 + 12}$$

$$\mu = 144/24 = 6$$

So that is 6.

Whereas, in this case, it is

$$\mu = \frac{12 \times 1}{12 + 1}$$

$$\mu = 12/13$$

So, the μ in this case is actually less than 1, so in the second system, your μ is less than 1. So, what can you tell me about the frequency, the frequency for this one is going to be much higher. So, the carbon-hydrogen bond is going to vibrate with a higher frequency than a carbon-carbon bond.

So that is something important to remember that lighter atoms typically vibrate with the higher frequency. Now you can think about two different bonds, so carbon-carbon double bond, versus carbon-carbon single bond. Now, I want you to tell me which one will vibrate with the higher frequency. If we go back to our formula, f is proportional to $\sqrt{k/\mu}$. What does that tell us that in this case, the μ is the same because in this case, all the atoms in both the bonds are carbon and carbon, so the μ is the same.

But now k has changed because now you have moved from a double bond, which means it is a much tighter bonding to a single bond, which is kind of a loose bonding. So, you can say a stronger bond versus a kind of weaker bond here, the stronger bond is going to vibrate with a higher frequency because it is going to have a higher k and whereas, this particular carbon-carbon single bond will vibrate with a lower frequency, and this is really what IR tells us.

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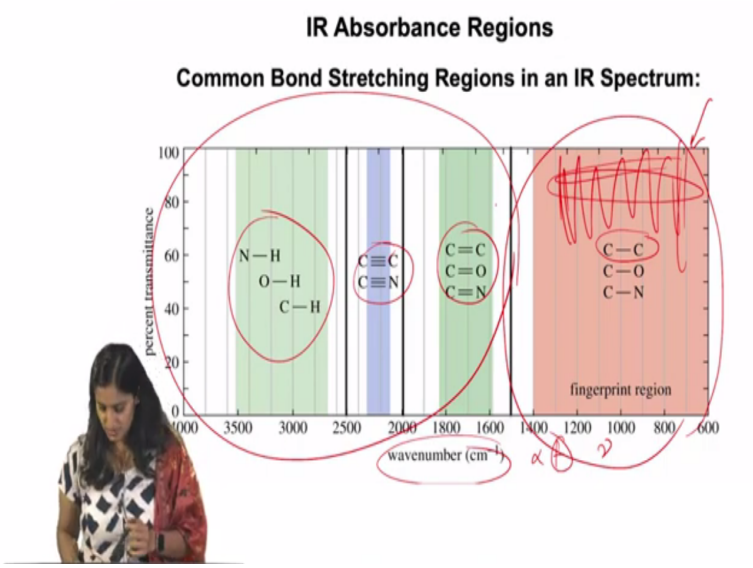

Like if we can now look at the IR absorbance regions here. First of all, let us look at this graph. What do we have here, we have here wave number, wave number is nothing but you can say it is basically telling us, frequency or υ. And what it is telling me is that depending on the wave number, where all different bonds will show up? So, you can see that carbon-carbon single bond as we talked about, can happen between 600 to around 1500 or 1400 region, you will see carbon-carbon single bond, carbon-oxygen single bond, carbon-nitrogen single bond, because these are single bonds, they are going to vibrate with a lower frequency.

Whereas, the moment you go to the double bonds for those corresponding things the frequency or the wave number here is increased. So, C=C, C=O and C=N is going to vibrate with a higher frequency. Similarly, C≡C and C≡N is going to be even higher.

So, triple bond much stronger, double bond little weaker than that, and single bond is much weaker than that. So, correspondingly you also see that in the IR spectrum, the machine readout that we were looking at. Also, here in from 2500 to 4000 you have your single bonds, but now they are not of the same atom, you have one very light atom, so as we were talking about that the springs with the lighter masses vibrate with the higher frequency.

So, you have N-H O-H C-H occurring between wave number 2500 to 4000. This particular region here from 600 to 1500, it is also called as a Fingerprint region, meaning it is unique, just like my fingerprint is unique for me, your fingerprint is unique for you, for almost all compounds, it is a very unique region. But because there are so many single bonds in compounds and because this particular region is very, very, very, very crowded, we typically do not try to interpret anything based on this.

Because this is, as we will see, in an actual spectrum, you will start seeing that so crowded that it becomes very difficult to read out. And that is why when people want to figure out if you have formed a particular functional group, they always rely on this side of the IR spectrum, they always rely from 1600, or rather 1400 onwards to 4000, and try to figure out the functional groups.

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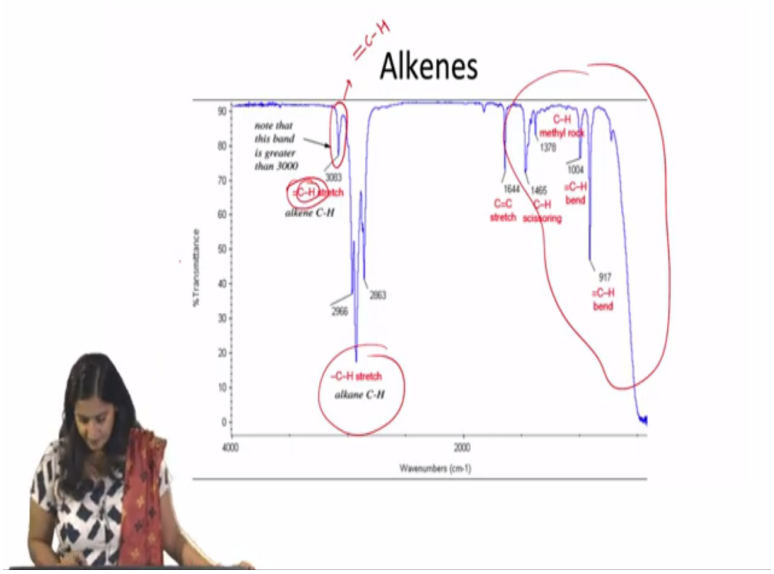

So, I have some functional groups here, and I thought of getting some spectras. Now, remember that this is the kind of an alkene spectra. And you can really see that in this particular region, below 1500, there are some peaks, but more importantly, for an alkene, we might pay attention to the peaks that are more than 1500. So, in this case, the =C-H stretch, this particular carbon hydrogen bond stretches at a frequency that is just about 3000.

And in fact, we have this small peak here, which indicates that I have a carbon-hydrogen single bond, or you can have various C-H stretches that happened close to 3000, which is because of the alkane part of it. The point I am trying to make is, whenever we look at this particular graph, which is percentage transmittance versus wave number, what people are trying to read is, what kind of bonds are present in the compound.

And I know this is not an extensive tutorial, so I will not be going into too much details, but I just want you to think of it this way that you take a molecule, you shine light on it, infrared light or the radiation belonging to the infrared wavelength or region and the molecule is going to start vibrating and stretching. We are going to measure how much it is vibrating, what are the energy differences between these transitions and we are going to figure out what kind of bonds are present in this particular molecule.

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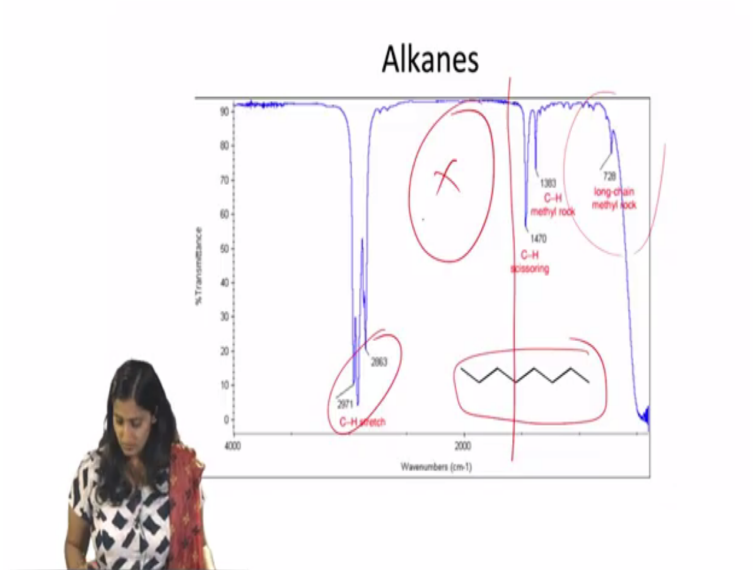

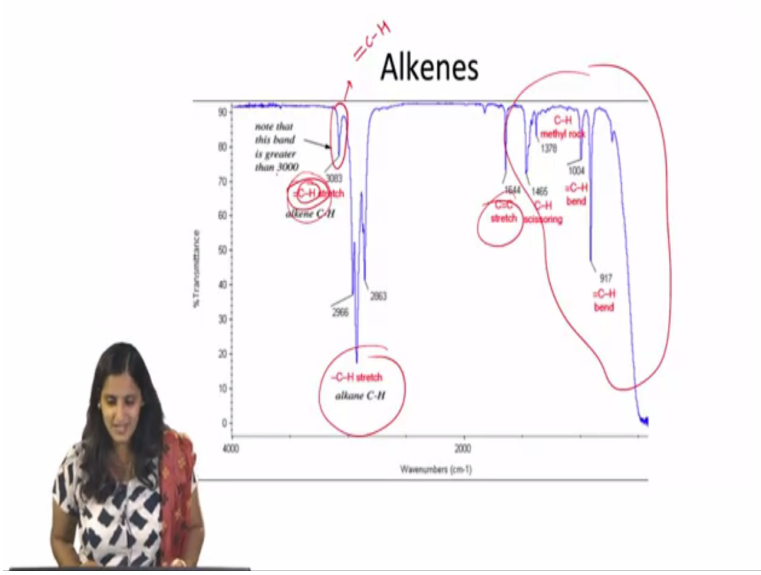

So, alkanes very simple kind of an IR, again, let us not look at below 1500. But in an alkane you pretty much how carbon-carbon and carbon-hydrogen bonds. Now, C-C bonds we know are somewhere below 1500. But C-H bonds, all of them will show up around 3000. So that is how I know that I do not have a C=C, for example, because if I had a C=C, I would see a peek here.

So, since it is missing, it does not have a C=C or a C=O, C=N. So, IR tells us about the functional groups that are present in the molecule. So, when we were doing the earlier example, if I had formed an alkene, I would not see a spectrum like this more likely, I would have seen a

spectrum like this, wherein I see some C=C stretch or I see a =C-H, or sp^2 hybridized carbon-hydrogen stretch.

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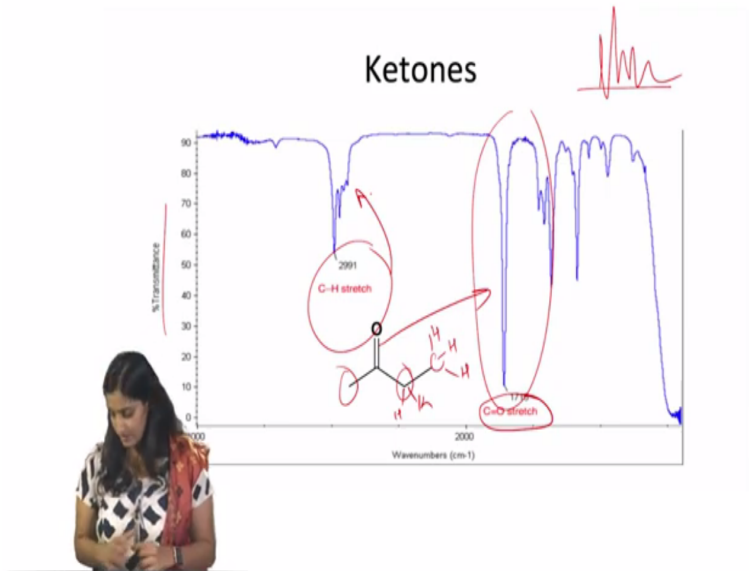

I have some Ketone here. So, this is 2-Butanone, and for a 2 Butanone, you can see that the C double bond O stretch, C=O is probably the kind of most distinctive IR peak that you can see, because it occurs between 1600 and 2000 and it is one of the peaks that has maximum percentage transmittance. And, you might be wondering that, why are we plotting transmittance something that is going down versus typically in most spectra as the peaks are going up like this.

Well, the story goes that the first time IR was recorded it was recorded in this particular fashion where it was recorded upside down and so henceforth chemists have just followed this tradition of recording it upside down. So, we record percentage transmittance, not absorption, although IR is an absorption spectroscopy. What do I have, in 2-butanone, I have a C=O, so I have that peak here. I also have a C-H, all of these C-H peaks. So, all of these peaks are going to result into a C-H stretch around 3000. I do not have an O-H, I do not have N-H, and all of that can be seen from this particular graph.

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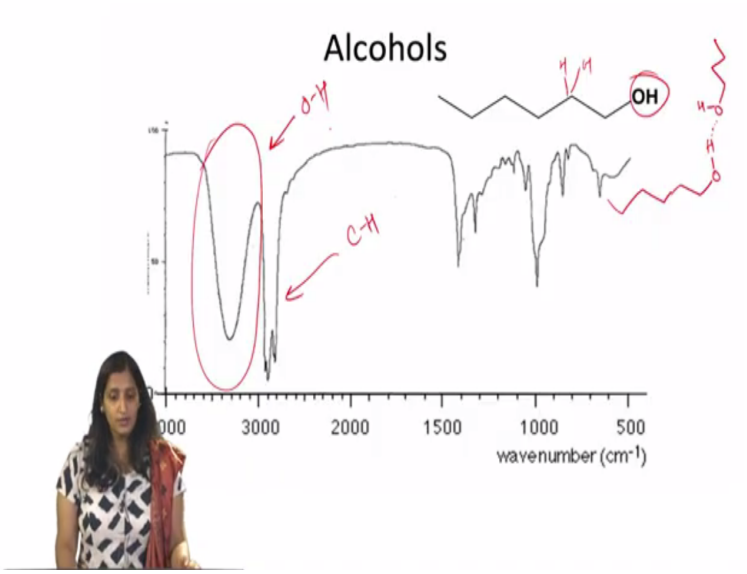

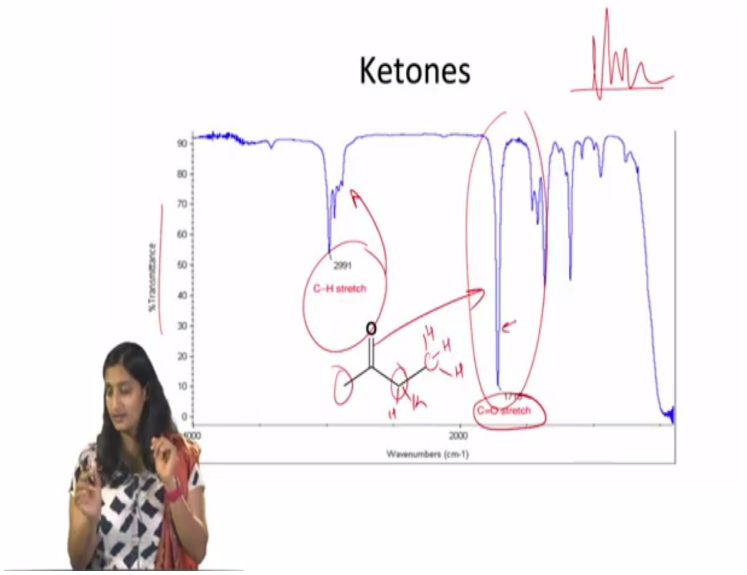

Let us go to alcohol. So, now, this is kind of a different compound because what you see is that you have a very nice and different peak, it looks kind of like a U-shaped peak, it is not thin and narrow. So, if you go back, remember this peak, how narrow and thin it was.

Now, in the case of alcohol, you have a very broad peak. And that results because this alcohol O-H is not such that it is very rigidly held. So, because of hydrogen bonding, this hydrogen is also going to hydrogen bond with another alcohol molecule, and so on and so forth. So, the

hydrogen is kind of held between 2 oxygens and that is why you are going to see that hydrogen bonding is going to result in a very broad peak for alcohols.

So again, you have C-H peaks here, all of these hydrogens, so that represents the C-H, whereas this one here represents the O-H peak. And for reference, you can refer to the IR table of various functional groups or other various bonds, and their corresponding stretching frequencies that are given. We have given it as a supplementary material, you can refer to that.

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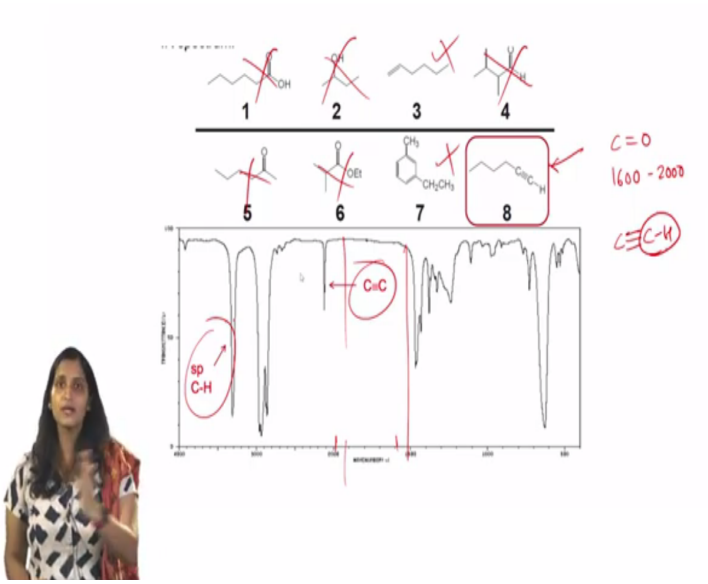

I am going to try solving this particular question here. And so, let us say that this is a compound that we have. And this is a spectrum that we have obtained. And we are trying to figure out which one amongst these compounds, 1 to 8, really the spectra belong to. So, I have actually given you the answer. But I want to go over why we chose compound number 8 as our answer.

First of all, remember that for C=O, there is a very distinctive peak between 1600 to 2000 wave number and that peak is very sharp, very long, narrow, nice peak, and around 1600 to 2000, I have nothing here in this particular region, there is nothing. So, all the molecules that have C=O in it, we can just simply scrap all of these are not our molecules, even C=C for that matter.

Now sp C-H, so when carbon is sp hybridized, and when you have a hydrogen, so terminal alkyne, for that matter, it is going to show you a peak, a very nice narrow peak around 3300. So

that is where this particular peak comes in and that is why between this particular molecule, this particular molecule, it is not an alcohol for sure, because alcohol would have given you that nice broad U; between these three, I would discard the alkenes or benzene for that matter and I would go for a terminal alkyne as my final answer.

So, IR does not give you all of the information. So, for example, it will not tell you what kind of terminal alkyne you have, it will not tell you whether it is a 5-carbon terminal alkyne or whether it is a 7-carbon terminal alkyne. It is very difficult to figure out. But IR definitely tells you that you have a terminal alkyne and you also have a C≡C. So, between 2000 and 2500 you have that nice sharp peak of C≡C. So that is how easy IR interpretation is. It is basically referring to a table figuring out what all peaks do you have in the spectra and then trying to narrow it down to the corresponding structure.

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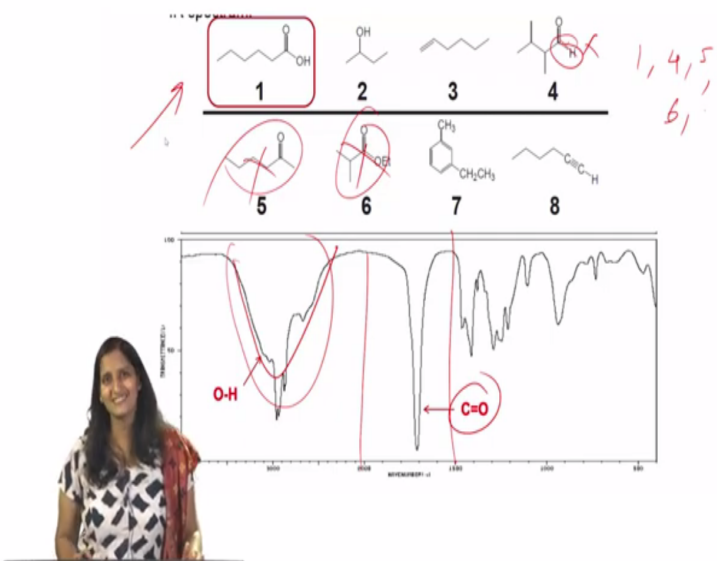

I have one more question here to be solved. So again, answer is given but we will try to rationalize why. Let us look at the peaks, between 1500 or 1600 and 2000. You have that one nice narrow sharp peak and which we know belongs to C=O. So now my molecule has to be having a C=O peak, wonderful. So, I can have options of 1, 4, 5, 6. So 1, 4, 5, and 6 these are the possible options because these molecules contain a C=O.

But I also have a very broad peak here and that broad peak is because of hydrogen bonding. So now out of 1, 4, 5, and 6 which are the molecules that allow for hydrogen bonding. In fact, carboxylic acids have this very characteristic stretch. Around it goes from 2700 to close to 3300, very nice, broad shape peak you get, because carboxylic acids always form dimers.

So, they have a hydrogen bonding between two carboxylic acid molecules. And thus, I will not select 4 because it does not allow for hydrogen bonding. Remember, this C-H cannot hydrogen bond, or it cannot be 5, because again, you do not have any hydrogen that is connected to an electronegative atom, or it cannot be 6. So, all of these are not my answer, but my answer is option number one, which is a carboxylic acid.

So, all of these are just for as a reference, I thought of solving some problems with you guys. We can solve a few more in the practice problems and tutorials. So, I hope that this gives you a basic understanding of what IR spectroscopy is. And as we go advanced in the course, of course, we can go dive deeper into various compounds and their corresponding IRs. Thank you so much.