Interpretative Spectroscopy

Prof. Maravanji S. Balakrishna

Department of Chemistry

Indian Institute of Technology Bombay

Lecture 31

Interpretation of IR Spectra

Hello everyone, I once again welcome you all to MSB lecture series on interpretative spectroscopy. We are now discussing about IR spectroscopy and I am sure you are having good time learning about spectroscopy, especially interpretation part. Let me continue from where I had stopped. I was discussing about hydrogen bonding. As I mentioned, when the hydrogen bonding occurs between hydrogen atom bonded to an electronegative element such as oxygen or nitrogen, to another atom via its bonding or non-bonding electrons or the lone pairs of another electronegative atom interacting with 1s orbital which is already shared with the other electronegative atom. For example, if a OH bond is there, OH bond has the H, H would interact with lone pair or electrons of pi bonds. Hydrogen bonding will be stronger when the bond formed are linear with bond angles nearing 180 degree. If it is anywhere from approximately 170 to 180, it is stronger, and if it is less than 170, then you can say it is weak hydrogen bonding.

Then how to assess the presence of hydrogen bonding using IR spectroscopy. First of all, you will see a broadening of the band associated with the one that is involved in hydrogen bonding. For example, OH stretching frequency will also increase in the intensity and also it shifts to lower wave numbers. It can shift up to even 50 or 80 centimeter minus 1.

Hydrogen bond involved OH and NH bond show stretching bands between 2500 to 3500 centimeter one (cm^{-1}), nuOH (ν_{OH}) or nu NH (ν_{NH}) lower than those without hydrogen bonding. The change in the stretching frequency is a measure of the strength of the hydrogen bonding which is in the order of 4 to 6 kilo calories per mole (kcal/mol). It can give precise information about the strength of hydrogen bonding that we see in such

molecules where there is a possibility of hydrogen bonding. Now let us look into, how to prepare the samples for recording IR spectra.

Dissolve the sample in a volatile solvent, say dichloromethane or heptane or something provide in which it is soluble. Take a drop of it between the two KBr plates or put a drop of it on a KBR plate and evaporate the solvent and place the second KBr plate on that one like sandwich. A clear solution can be taken in a solution. If we do not want to have a solvent, a neat sample recording can also be done. In that case a clear solution can be taken in a solution cell with a thickness of 0.1 to 1 millimeter (mm), that is volume of about 0.1 or a drop. To obtain IR in solution, one has to subtract solvent spectrum from the sample spectrum or one has to use IR invisible solvent. Dry solid samples may be grinded with a tiny drop of mull, Nujol mull and a small amount of mixture is pressed between two KBr discs.

Invariably if you are taking a volatile solvent in which a sample is dissolved, take a drop of it, put on a KBr plate and evaporate bulk of it and then squeeze the drop with another KBr plate on that one or put a drop of it on a KBr plate and evaporate the solvent and place the second KBr plate or one can also take a clear solution in a solution cell. Solution cell will be different with a thickness of 0.1 to 1 millimeter (mm) and volume will be about 0.1 to 0.2 ml. To obtain IR in solution one has to subtract solvent spectrum from the sample spectrum or one has to use IR invisible solvent. So that we can take out the absorption bands due to solvent. Dry samples may be grinded with a tiny drop of mull and a sample is pressed between two KBr discs. Take a tiny amount of solid material and add a drop of Nujol mull, it is a hydrocarbon and then grind it well to make a homogeneous paste and then take a small quantity of that one and press between two KBr discs and then take IR. You should never put a small quantity of powder on KBr cell and rub two KBr cells. Sample has to be made in a separate device and then that should be used. Very dry sample can be mixed with dry KBr and grind to form a fine powder using a mortar and subjected to high pressure to make a pellet or a thin disc and then IR can be taken.

Very dry KBr has to be taken to avoid water and hence OH bands. Whatever the KBr we are using is highly hygroscopic in nature, one has to ensure that it is always anhydrous KBr and also while preparing, we have to ensure that moisture from atmosphere is not getting into it. In that case what happens, we will see IR band broadening due to the OH absorbed by KBr. So KBr pellets or discs should not be touched with fingers. One should remember you can press and make a homogeneous powder of KBr with the sample (solid sample) grind it well then in a press we have to make a very thin disc tablet type very thin and then we have to measure it and we have to ensure that we are not touching that disc with fingers

Directly, solid sample can also be considered which requires special attachment to the spectrometer. There will be probe that you can dip directly into the powder and you can measure. This is only for quality control. Certainly, this is not used, as resolution is not very good. That is not used for analyzing the research samples.

Then a typical IR instrument would look like this. I have put lot of effort in generating this picture here. A beam of infrared light is passed through the interferometer and then splits into two separate beams, because we are considering the sample and reference; two separate beams. One is passed through sample, the other passed through a reference. The beams are both reflected back towards a detector, after passing through a splitter, which quickly alternates which of the two beams enter the detector.

The two signals are then compared and a spectrum is obtained. The two-beam-setup gives accurate spectra even if the intensity of the light source drifts over time. This is the advantage of having two beam-setup. This is a typical setup we come across in an IR instrument. Of course, at the end, you can see the plot would come here on display.

So, the interferometer consists of a beam splitter, a fixed mirror and a mirror that translates back and forth very precisely. The beam splitter is made of a special material that transmits

half of the radiation striking it and reflects the other half. You can see here beam splitter, this is the one. The beam splitter is made of a special material that transmits half of the radiation striking it and reflects the other half. Then how to interpret a data obtained from IR spectra.

So, the interpretation of IR spectra is very easy compared to any other spectra we come across like UV spectra or NMR spectra. First, one has to see whether bands are present or not. One has to write down the structure of the molecule and identify the functional groups that are present and looking for their presence in IR spectrum. From IR easily one can find out the presence of various E-H bonds E can be any other atom in the molecule and the presence or absence of C-double bond C (C=C) and C-triple bond C (C≡C), carbonyl groups (CO), aromatic rings, NH, OH and other functional groups. That means most of these functional groups can be certainly identified from recording an IR spectrum for a given molecule.

The information obtained from IR must be combined with the data from NMR and mass spectra for precise understanding the structure and elucidation of the structure eventually for an unknown sample. We can get vital information from IR. It is always better to record NMR, at least NMR and mass spectra to elucidate the structure without any ambiguity. One thing to keep in mind about IR spectra is that it can only tell you whether a group is present or not, that means it is qualitative. It will not tell you how many groups or how large the molecule is, even in tiny amount if it is present, it can show you. So that means one has to be careful about that one.

A sharp peak say at 1750 centimeter minus one will tell us that there is some sort of a carbonyl group (CO), but it does not say whether it is a ketone, it is an ester or it is an acid. It will not tell us if there are two or three ketone groups present as well. So, with this in mind using only selected few important peaks we have to remember. We can easily guess what functional groups are present and thus identify the molecule from a new selection. That means, one should not depend heavily on IR spectroscopy to understand and confirm the structure of the molecule, that is on our hand. I have given here various functional

groups and also the finger print region where it exactly comes and also if you have different type of functional groups, what is the expected stretching frequency, all this information is given here and as I said in IR spectra 400 to 4000 centimeter inverse (cm^{-1}) is very prominent range. If you see any peaks or bands in the region of 3700 to 3100 possibly we can think of presence of OH group or NH group or an alkyne CH group and then if you see any band in the region 3100 to 3000 centimeter minus 1 (cm^{-1}), then we can think of possibility of presence of a CH or a C double bond C bond (C=C) attached to CH or another CH attached to triple bond (≡). We can see here, and then if you see any band in the region 2800 to 2400 that may be due to either the presence of a PH bond or a SH bond or a SiH bond or we can have C triple bond C (C≡C) or C triple bond N (C≡N) -C triple bond N (C≡N) sometime can even stretch up to 2300 as well. For acetonitrile, it can come between 2300 to 2400 and then if you have bands in the region 2000 to 1870 it can be benzene derivatives or due to vinyl group and then if you have 1870 to 1650 it will identify carbonyl group, it can be due to ketone, aldehyde or carboxylic acid or an amide. Then 1650 to 1550 can tell you about possibility of a presence of a C double bond C (C≡C) or again OH or NH and 1550 to 1300 can tell you about presence of a methyl group or a methylene group and then 1300 to 1100 can tell you possibility of a C-O-C or C-O-H or S double bond O (S=O). Similarly, from 1000 to 650 one can think of CH attached to double bond and aromatic NH_2 and NH also and 600 to 400 possibly, we can see C-Cl or C-Br bond, beyond that also one can go to identify whether we have transition metal bonded halogens; they come around 300 and below 270, 220 all those things. For that one, we have to go for special IR instrument where we can scan up to 200 centimeter minus 1 (cm^{-1}). So some more information is given here functional groups, if we consider alcohols and acids have OH so broad peak just about 3000 centimeter minus 1(cm^{-1}), usually it is around 3200 to 3500 that would tell you that this OH group is present and the compound may have alcoholic hydroxy group or an acid group and then amines a narrow peak just about 3000 centimeter minus 1 usually this comes in the range of 3300 to 3500 centimeter minus 1(cm^{-1}). For alkanes we are talking about CH narrow peak just below 3000 or it is usually around 2800 to 3000. Ketones and acids are there we are looking for carbonyl group (C=O), narrow peak at 1750 and usually it comes around 1700 to 1800 so that can tell you the presence of a CO group and then triple bond yes C≡C triple bond come around 2200 centimeter minus

1((cm^{-1}) or usually they are in the range of 2100 to 2300 or sometime little above 2300 they can go up to 2350 also in some cases. So, this information is adequate to identify functional groups and making the assignments in the corresponding IR spectrum. So here little bit more information is given.

Alkanes one can see medium in the region I have shown here and also you can say medium and weak can be seen here and then another medium can be seen here and strong and weak band can also be seen here. So these are the possible different type of vibrational modes you can see for alkanes and in case of alkanes the range I have shown here it can be here or it can be here or it can be here and then intensity also one should focus towards the intensity and you should remember this is strong, weak, and strong and then aromatic again weak and then they will be strong around 1600 C double bond C (C=C) and in case of OH we can see it around 3500 to 3200 it can be the medium and sharp or strong and broad and then you can also see in this region 1400 a sharp one a strong one and then for CO we will see anywhere between 1600 range 17 to 1600 or 1800 and then NH to NH you can see in this range and CN this range is very important C triple bond N (C≡N) and then NO_2 is here around 1600 to 1200 and for SH we will see around 2600 and then S double bond O (S=O) will see a strong one around 1200 and same thing, around 1200 we also see for P double bond O (P=O) and then in the sulphur dioxide we will see in this range here. So, this is little bit elaborated one and to identify all possible modes of vibrations at various frequencies as wave numbers. So, knowing the molecules through IR spectra, alkanes possess stretching and bending vibrations of CH bonds.

Now let us consider a simple molecule such as n-heptane and n-octane. If you consider the N octane, CH stretch can be anywhere from 3000 to 2850 centimeter minus one (cm^{-1}) and CH bend or scissoring will be in the range of 1470 to 1450 centimeter minus one (cm^{-1}). CH rock, methyl from 1370 to 1350 centimeter minus one (cm^{-1}) or to be precise, it comes around 1383 and CH rock, methyl seen only in long chain alkanes that comes around 725 to 720 centimeter minus one (cm^{-1}). Since most organic compounds have these features these CH vibrations are usually not noted when interpreting a routine IR spectrum.

That means one should not heavily depend on looking into these CH vibrations because most of the organic molecules invariably show this one. As a result, really you cannot use this one to identify the products that have been made or of unknown samples.

A typical spectrum is shown here. If you see here, n-octane is there here for n-octane CH stretch is shown in this one and CH scissoring is shown here. CH rock for methyl group is shown here and then long chain methyl rock is shown here. The region between 1300 to 900 is called fingerprint region. So, 1300, if you start from here, this region whatever I have highlighted here. This is called fingerprint region. The bands in this region originate in interacting vibration modes resulting in a complex absorption pattern usually this region is quite complex and it is not easy to interpret we should not worry about interpreting the data obtained in the fingerprint region, but only we have to identify whether we have unique pattern here that is unique pattern for a given molecule. Each organic compound has its own unique absorption pattern that we call it as fingerprint region and fingerprint region is less helpful in illustrating the structure nevertheless one can identify that in a particular given range. So, in this and thus IR spectrum can be used to identify compound by matching it with a sample of known compound for this one what you should do is you should go for the known compound spectrum recorded for the pure one and you can match it and you can confirm that yes this function group this part of the is fingerprint region is present in the given molecule, but characterizing one should not heavily depend on we have to look for functional groups that is where IR comes very handy in its elucidation.

I have given for another one here for heptane. This is the characteristic one, and this is the characteristic one, and this region is called fingerprint region. When you look into branched chain alkanes like we have branched chain here, CH stretch is shown here. This is CH stretch and CH bent is shown here, all characteristic the pattern, is more complex due to greater number of C-C bonds and corresponding overlapping bands are there and then this is called the fingerprint region. If we just compare this one with other branched chain molecules, we come across this one and that confirm that yes, we have this group in this given molecule. Now, let us look into some cyclic alkanes, the simple one being

cyclohexane. In cyclohexane CH stretching would appear in the range 2950 to 2845 centimeter minus 1(cm^{-1}) and CH deformation vibrations of CH_2 groups will appear at 1480 to 1440 centimeter minus 1 (cm^{-1}). Multiple peaks amounting to strong absorption due to CH stretching vibrations will be in CH_2 or CH_3 groups in octane. That means, the multiple peaks amounting to strong absorption due to CH stretching vibrations in this range, CH_2 middle where we have CH_2 groups or CH_3 group in octane, CH the other CH absorptions due to CH deformation vibrations of the CH_2 groups at 1480 to 1440 centimeter minus 1 and skeletal C-C vibrations will be appearing at 950 centimeter minus 1(cm^{-1}) for $(CH_2)n$ where n is greater than 3 and then which is obviously the case of cyclohexane. CC and CH vibrations are common in organic molecules and alkanes like cyclohexane have no functional groups that gives a characteristic vibration. So, this is about the cyclic alkanes, the most common one is cyclohexane. If it is simply cyclohexane, we do not have anything else other than CH_2.

So, probably one also should look for NMR as well as mass if such groups are present in the molecule. This is the cyclohexane spectrum here you can see stretching vibrations of CH_2 is shown here and CH vibrations are shown here and long chain C-C and CH_2 vibrations are shown here. In this one, and also this also constitute the fingerprint region 1500 to 400 centimeter minus 1(cm^{-1}). So, you can see CH stretching, you can see CH vibrations, and the long chain C-C and CH vibrations also can be seen and also, we have a fingerprint region from 1500 to 400 characteristic of cyclohexane.

So, let me stop here and continue discussing more on infrared spectroscopy in my next lecture. Until then have an excellent time. Thank you.