Interpretative Spectroscopy

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Lecture 32

IR stretching frequencies for various functional groups

Hello everyone, I once again welcome you all to MSB lecture series on interpretative spectroscopy. So, now we are discussing about IR spectroscopy, while it is not necessary to remember all of the peaks for each functional group, learning a few key characteristics will be enough to answer 99 percent of all IR related questions. I showed you a few IR spectra in my last lecture, if you just look into it you can identify certainly functional groups presence and also the fingerprint region. So, fingerprint region would not really tell you much information except for the fact that they can be compared with the known sample's pure spectrum. If you want to see whether you have performed some reaction and product have changed to something, that information would come only when you focus your attention to functional groups. Then that is good enough to answer 99 percent of all IR related questions. For example, if you have a formaldehyde spectrum, I will show you, it is not there, one can see that there are few different possible ways the bonds can behave which leads to many different peaks.

I would come back to that one again, before that let us look into the alkynes here, in case of alkynes we look into aliphatic hydrocarbons and also, we look into cyclohexane. Now, we shall look into alkynes here, here in this case the stretch would come around CH around 3310 centimeter minus 1(cm^{-1}) and alkyl CH stretch would come around 2857 to 2941 centimeter minus 1(cm^{-1}) and C triple bond C ($C\equiv C$) stretch would be around 2119 centimeter minus 1(cm^{-1}). Then when you look into CH bend which is attached to a triple bond, overtone will be around 1250 centimeter minus 1(cm^{-1}) and then CH bend fundamental vibration would appear at 630 centimeter minus 1(cm^{-1}). Strong and broad absorptions around 700 to 610 and overtones in the range of 1370 to 1220 centimeter minus 1 (cm^{-1}) are characteristic of alkynes.

If you have an alkyne group you should focus your attention to this range. In case of aromatic hydrocarbons, CH stretch appear around 3008 centimeter minus 1(cm^{-1}) and CH_3C-H stretch would be around 2850 to 2940 and then overtone or combination bands would be in the range of 2000 to 1667 centimeter minus 1(cm^{-1}) and C double bond C (C=C) present in the ring would be having stretching frequency around 1605 and also 1495 and 1466 centimeter minus 1(cm^{-1}). In plane C-H bend at 1052 and 1022 centimeter minus 1(cm^{-1}), and out of plane C-H aromatic bend would be around 741 centimeter minus 1(cm^{-1}), and out of plane C double bond C bend would be 438 centimeter minus 1 (cm^{-1}). So, these are the few things for your information. There is no need to remember all those things. What would happen if you have halogen bonds.

So, carbon to halogen bonds such as carbon to fluorine (C-F), carbon to chlorine (C-Cl), carbon to bromine (C-Br) in that case what happens C-F stretch would be in the range of 1110 to 1350 centimeter minus 1(cm^{-1}), whereas C-Cl bond should be 550 to 8500 centimeter minus 1(cm^{-1}). 850 centimeter minus 1(cm^{-1}), not 8500. C-Br stretch would be 550 to 690 centimeter minus 1(cm^{-1}). The strong CH_2 wagging bond for CH2X will be around 1150 to 1300 centimeter minus 1(cm^{-1}). So, these are important regions as far as C-X bonds, where X is a halogen, are concerned. The spectrum of propanamide is given here and you can identify NH stretching vibration is around 3500 to 3200 centimeter minus 1(cm^{-1}), and also, we have a carbonyl group. So, it comes around 1650 to 1690 centimeter minus 1(cm^{-1}). In the same region, N-H and C-N combined vibrations also come: 1590 to 1650 centimeter minus 1(cm^{-1}), and then C-H vibration one can identify here and then this 1500, if you take 1500 to 400, and this range this is called fingerprint region.

Let us look into the structure of anisole now.

So, anisole is methoxybenzene its molecular formula is C_7H_8O. Anisole has 5 sp^2 C-H links. So, here 1 2 3 4 5 sp^2 C-H links are there and they have between 2960 to 2838 centimeter minus 1(cm^{-1}), and 3 C double bond C (C=C) aromatic linkages are there between 1600 to 1500 centimeter minus 1(cm^{-1}), and 1 CO linkage is there here at 1249 centimeter minus 1(cm^{-1}), and 1 aliphatic CO bond at 1100 centimeter minus 1(cm^{-1}) and also 3 sp^3 CH linkages here. So, these are the bands you can anticipate in IR spectrum. Now we should look for the associated frequencies in its IR spectrum for its identification.

Now we have identified from the prior information, we have about the different stretching frequencies and other things we have identified whether we have sp, sp^2, sp^3 carbon and when we look into spectrum, we can see whether all these things are there or not. So, 2960 to 2988, we have here and then 3 C double bond C (C=C) around 1600 to 1500, we have here, and then C-O linkages at 1249. So, here 1249, it should come here and then 3sp^3 C-H linkages. C-O bonds have 2 pinnacles you can see here one because of the asymmetrical C-O-C at 1250. So, 1250 somewhere here this is and the other at 1040. This is the one this, 1040, because of symmetrical stretch asymmetric bending is stronger since the double bond character increases due to the resonance. The double bond feature gives increased bonding strength and improves the elongation frequency. So, this is the spectrum of anisole. Whatever the bands we identified from prior knowledge could be seen here with little or no difference.

So, now IR spectroscopy typically has a spectrum reading organized as shown below. We did not discuss about those things. For example, say transmittance versus the frequency in wave numbers. So, if you just consider this one, this spectrum is for formaldehyde and is typical of most infrared spectra. IR readings are inverted compared with UV visible spectra. Thus, the sample that did not observe at all would record a horizontal line at 100 percent transmittance, while one that observes a significant amount would be towards the bottom. This is in contrast to the spectrum, that is recorded and plotted in case of UV visible or NMR. The advantages as it is clearly mentioned, the horizontal line at 100 percent transmittance shows there is no absorption at all, but only wherever absorption is there that will be coming towards the bottom. Each peak dip on the graph represent various bond characteristics, because most functional groups have specific bonds, and hence they can be identified due to this reason. A typical IR spectrum will be plotted like transmittance versus frequency or you see one can look like this, then this will be absorbance.

This would look rather odd that is the reason the convenient way is to plot in the other way I showed something like this. The absorption spectrum, here the complexity of infrared spectra in the range 1450 to 600 centimeter minus 1(cm^{-1}), makes it difficult to assign all the absorption bands and because of the unique pattern, it is often called the fingerprint region. That is what I told you in my earlier lecture. It is not necessary to remember any peak in this region as they do not help you determine any significant functional groups. This one you have to identify, yes, this pattern is there or something is there, yes fingerprint region, there is no need to worry about interpreting all the bands, it is little bit more complex and it is unnecessary. Absorption bands in the region 4000 to 1450 region are usually due to stretching vibrations of diatomic units and this is sometimes called the group frequency region, this is also quite important.

Now in the IR spectrum shown below, focus on 3750 and 1750 areas. There is a sharp peak at 1700. This corresponds to a CO group, and it is most likely a ketone or an aldehyde.

That means you see here you should be able to think that this has to be due to a ketone or an aldehyde and that you see double bond O is there no broad or sharp groups above 3000 mark so that means there is no OH or NH why we decided ketone or aldehyde is because no OH group is there so carboxylic acid is ruled out. So, there is a sharp peak just below 3000 maybe due **to CH, CH_2 and/or CH_3 bonds,** but it could also be part of aldehyde CH bond. So, that means it gives you some idea about what type of molecule this IR is representing. If the choices are between 2 methyl cyclobutanol, 3 methyl butanol and 2 chloropentanoic acid certainly it should be clear to recognize that this is only due to 3 methyl 2 butanol has both necessary C=O bond and there is no OH bond at all. That means when you have option of identifying the spectrum with 3 or more choice, by simply analyzing we should be able to arrive at the right kind of molecule, this IR spectrum is representing.

Now I have given little bit elaborated and extensive table here for different groups and also the range in which absorption bands are seen and also what kind of assignments and comments can be given for those things. When you look into BOH the range is 3300 to 3200 it is sharp strong broadband due to OH stretch.

When we have BH or BH_2 it appears around 2650 to 2350 sharp, a doublet for BH_2 here and also, we can see 1200 to 1150 medium strong or 980 to 920 medium, and again 1430 medium and strong. So, they are respectively assigned to BH_2 deformation of BH, BH_2-wag and benzene ring vibration that means if there is a benzene ring, then if we look into B─N it shows a band in the region of 1460 to 1330 very strong stretch. Borazines and amino boranes, if you have borazines and amino boranes possibly you can identify using this range and BO 1380 to 1310 very very strong, this is a stretch for boronates and boronic acids and then if you have C─B─C 1280 to 1250 and antisymmetric stretch we can identify. Similarly, if you look into silicon compounds, if you have silicon hydroxide Si─OH bond we can see in the range 3700 to 3200 and O─H stretch, this is very similar to what we come across in case of alcohols or O─H, and then if you have SiH or SiH_2 or SiH_3 that means primary silane secondary silane or tertiary silane, primary silane, secondary silane or tertiary silane is not there here. We can see they all appear in the range of 900 to 820 centimeter minus 1(cm^{-1}) and Si─O stretch for the other one and then you see Si─H stretch here and then Si-H deformation or wag will appear in 950 to 800 and Si−Ar if it is connected to a phenyl group or aromatic group, it comes around 1430 as a medium and strong and 1100 very strong and this indicates, this ring mode here and then Si−O−C aliphatic 1100 to 1050 very very strong and this is due to antisymmetric stretch and then Si─O─Ar will show around 970 to 920 very strong it is again Si─O stretch and if you have Si−O−Si, we can see in the range of 1100 to 1000 very strong and it is again due to antisymmetric stretch. We have got phosphorus compounds, if you have a direct P─H bond phosphorus acids and esters and phosphines we come across 2425 to 2325 centimeter minus 1 (cm^{-1}). This is essentially due to new P−H and then we can also see bands in the region 2320 to 2240. This is again P−H stretch. This is very sharp and if you see 1090 to 1180 medium strong, P−H to deformation and then 990 to 910 medium it is for P−H wag. For P−OH in phosphoric acid or phosphorus acids and esters and salts they appear in the range 2700 to 2110. This is OH stretch, one or two broad and often they are weak and then if you see something around 1040 to 920 strong absorption band that is again due to P─OH stretch and P─O─C in aliphatic compounds will be in this range 1050 to 950 very strong it is. P−O─C anti symmetric and then 830 to 750 P−O─C symmetric stretch here OMe and OEt compounds of P only.

So, trimethyl phosphate or triethyl phosphates do show this kind of range for P−O−C symmetric stretch and then aromatic compounds, if you have PPh_3 or something like that or P─O, P─H thrice, triphenyl phosphate we come across 1250 to 1160 very strong aromatic C−O stretch, and then 1050 to 870 we have P−OH stretch. This should be C double bond C(C=C) not CO stretch, and then P−C aromatic compounds, we have 1450 to 1430, P directly on a ring, sharp band, then quaternary aromatic 1110 to 1090, P directly on a ring, sharp band is observed and many compounds are pentavalent tetra coordinated compounds, we come across P double bond O (P=O) and also we can identify whether the P double bond O is from the aliphatic compounds or aromatic compounds. They have distinct range again for aliphatic once P double bond O(P=O) appears in the range of 1260 to 1240. They are usually strong and sharp. If you see in the range of 1350 to 1300 indicates that we have aryl oxide groups on phosphorus. Aryl oxide phosphates, P double bond O (P=O) would appear around 1350 to 1300, a lower frequency P─H stretch and then 1250 to 1180 when OH is on P, and in phosphine oxides typically it will be in the range of 1140 to 1200 this is for nu-PO (ν_{PO}). Sometime we have phosphines and after performing catalysis or if they are converted into corresponding phosphine oxides, one can look into IR and get some idea, why catalytic activity has brought down, may be reduced, may be catalyst in which phosphine present is decomposed or it has come out of the metal in the form of a phosphine oxide. This information also comes from IR spectroscopy and then if you look into SH in thiols like mercaptans, you can see 2580 to 2500, this is due to S−H stretch strong in Raman and then C−S 720 to 600 weak C−S strong in Raman and then S−S in disulfides 550 to 450 very weak or absent again, S─S stretch yes active in Raman and then S double bond O (S=O), sulfoxides ,they have this characteristic region, 1060 to 1020 and dialkyl sulfides in the range 1220 to 1190 both are due to S double bond O (S=O) stretch and then SO_2, sulfones, sulfonamides, sulfonic acids, sulfonates sulfonyl chlorides, dialkyl sulfates, sulfonyl fluorides, all come in the range 1300 to 1290 and this is for SO_2 antisymmetric stretch and SO_2 for symmetric stretch and of course in case of 1420 to 1390 SO_2 anti symmetric, again 1220 to 1190 SO_2 symmetric stretch, and in case of S−O−C when we have S−O−C is from dialkyl we have 1050 to 850. This is S−O−C stretching; two bands are observed and for SOC sulfates, what we have is 1050 to 770. We can also anticipate here two or more bands. So, these are all just for information. In case, if you come across some compounds and if you have IR spectrum on hand you can readily analyze and look into it, whether such groups are present or not. So, few facts we should remember while analyzing. one such important factor is inductive effect, what it does? Increase in the inductive effect increases the bond order and hence the force constant in carbonyl compounds. Therefore, the wave number of C double bond O (C=O) stretching vibrations increases with the strength of the inductive effect of X, which is shown by the following examples.

For example, I have given here, if X is there, when X equal to H, 1740 when X equal to Cl it becomes 1800. It is considerably shifted by about 60 centimeter minus 1(cm^{-1}), and then the second one is mesomeric effect. So, first one is inductive effect. In mesomeric effect, mesomerism diminishes the bond order and hence the force constant, resulting in lower wave number of the stretching vibration.

That means it diminishes bond order and hence stretching frequency drops considerably. For example, if you take this compound here, X equal to H 1740, but when you replace X by aryl group it comes to 1685 and then when you take here X equal to H, 1645 to 1640. When you replace X with aryl, it drops to 1600 to 1145 centimeter minus 1(cm^{-1}). So, these effects one should know. Inductive effect and mesomeric effect: what influence they have on carbonyl carbon groups. If inductive effect is there stretching frequency increases, and if mesomeric effect is there, stretching frequency decreases.

Then if one were wishing to use IR to identify successful conversion of 3-ethylbutonic acid to 3-ethylbutanamide, which band change would prove the most useful. So, four options are given I read again. If one were wishing to use IR to identify successful conversion of 3-ethyl butonic acid to 3-ethyl butanamide which band change would prove the most useful or which band change is important in identifying this reaction. So, four options are there i) the gain of a broad band at 3200 and a narrow band at 1750, ii) the gain of a narrow band at 3400 and the loss of a broad band at 3200, iii) the loss of a narrow band at 3400 and the gain of narrow band at 1750, iv) the loss of a broad band at 3200 and the gain of a narrow band at 1750.

In all we have C=O, C=O is almost left unchanged and in that case what happens initially we had OH, that is disappearing and we are getting NH, that means basically the 3200 due to the OH is disappearing, probably option B is the correct one. Here you can also see, I have given a spectrum for both alcohol and amide you can see here. This is for amide and this is for alcohol; alcohol it comes around 12, OH is here and then it comes to 7 here you see NH1 otherwise this portion remains almost looks like unchanged here. So, that means here the catch is this one, but however one can also use NMR conveniently to see whether the reaction is completed or not in both of them products are very pure that means the OH group is converted into amide here that can also be confirmed from NMR spectroscopy.

So, we shall look into more examples, may be combined examples having both IR, NMR and UV data in my next lectures, until then have an excellent time. Thank you. Thank you.