

Interpretative Spectroscopy
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Lecture 36

Numerical Problems related to IR Spectroscopy-1

Hello everyone. Once again it is my pleasure to welcome you all to MSB lecture series on interpretative spectroscopy. In my last lecture I was discussing about importance of IR spectroscopy in metal carbonyls and also when we have different type of mixed ligand complexes having one or more carbonyl groups, the stretching frequency of carbon monoxide gives vital information about the electron density surrounding the metal ion and also the donor and acceptor properties of other ligands as well. The donor and acceptor properties of other ligands present along with CO in a metal complex have remarkable influence on the stretching frequency of CO. So, let us continue with some more examples about IR spectra of metal complexes and also let us try to learn more about force constant and its relationship with the frequency. Here I have given a list of carbonyls: homoleptic carbonyl complexes, neutral complexes, anionic complexes and also cationic complexes and also, I have given the stretching frequency for CO in centimeter minus 1 (cm^{-1}) and some of those things I already discussed in my previous lecture.

If you see here nickel tetracarbonyl, it shows around 2060 centimeter minus 1 (cm^{-1}), whereas cobalt tetracarbonyl anion of course, when it is dimeric it is neutral because it is a 17-electron species and now with CoCO_4^- minus it is an 18 electron species. Here stretching frequency is 1890, drops considerably because of excess of negative charge on cobalt. So, if more and more electron density is there on metal, they will become better pi-donors. As a result, what happens, the stretching frequency of CO drops considerably because of population of electrons into pi star (π^*) or anti-bonding orbitals of carbon monoxide and similarly if you see here we have dianionic compound here, iron compound for example Na_2FeCO_4 , if you consider stretching frequency, it further drops to 1790 because two

negative charges are there and then when we look into positively charged metal ions such as MnCO_6 plus here metal is say reluctant pi-donor because of positive charge. As a result, not much significant change is there in the stretching frequency of carbon monoxide and it is towards higher side that means CO bond is more stable and MC bond is relatively longer and of course in CrCO_6 , we have substantial amount of back bonding because of d^6 electronic configuration and also metal in zero valence state. Again, vanadium hexacarbonyl anion is more or less comparable to that of CoCO_4 minus and free carbon monoxide is around 2143 and some books say 2130, but the to be precise it should be 2147 centimeter minus one and then the effect of binding can be clearly seen here in terminal binding of a carbon monoxide to metal. The range is around 1850 to 2120. When it acts as a bridging ligand holding two metal centers, it drops considerably to 1750 to 1850 and when it is bridging three or more metal centers, in such case stretching frequency further drops and here when it is bridging three metal centers it comes around 1620 to 1730 centimeter minus one (cm^{-1}). That means more and more bridging would leads to almost carbon monoxide behaving like ketonic carbon monoxide group we come across in organic chemistry. Influence of the trans ligand can be clearly seen in this series of complexes. I have shown here MoCO_3 , MoCO_3 might remain intact throughout and other three carbon monoxides are replaced by different type of phosphorus compounds and also nitrogen donors and also diene is there and also pyridine is there. When you see again, the same trends are observed. Here it is not about anionic or cationic charge present on the metal center, it is about the pi-acceptor ability of ligands, and if you see here, the pi acceptor ability of ligands are considerably dropping when you go from PF_3 to pyridine and of course PCl_3 and we have trimethyl phosphite, triphenylphosphine, about these things I have already analyzed in my previous lecture. Acetonitrile is only sigma donor, diene also partly it can take into pi star but it is a poor pi acceptor and pyridine and in all those things you can see how consistently the CO stretching frequency is dropping because when one or more carbon monoxide ligands are left and the others are only sigma donors, minimizing the interelectronic repulsion by back bonding falls only on three carbon monoxide groups. As a result, what happens, stretching frequency drops considerably here and also how immensely this data helps in arriving at different positions of these ligands in spectrochemical series, can be seen here, and of course, when we talk about the position of

ligands in a spectrochemical series, we are considering both sigma-donor ability, pi-donor ability as well as pi-acceptor abilities. Considering all those things we have made spectrochemical series. Similarly, for back bonding ligands also one can have spectrochemical series; follows this order here.

Now let us look into some problems here. This is related to stretching frequencies of different groups, for example, here thiocyanate complexes of mercury and iron with mercury in plus two state (Hg^{+2}) and iron in plus three state (Fe^{+3}), and corresponding stretching frequencies are given here, 2120 and 710 centimeter minus one (cm^{-1}) in case of mercury complex, and in case of iron complex, the values are 2055 and 1828. For assigning the linkage, whether S is connected to mercury or N is connected to mercury, and also iron, we have to have some information about free SCN. Free SCN stretching frequency is given here; the C triple bond N ($\text{C}\equiv\text{N}$) stretching frequency is 2053 and also for CS it is 748 centimeter minus one (cm^{-1}). Just for your information, I have also given isocyanate, in this one C triple bond N (cm^{-1}) resonates around 2060 centimeter minus one (cm^{-1}), and also it can have ranges depending upon what kind of R groups. It can have anywhere between 2060 to 2240 centimeter minus one (cm^{-1}).

Now the question is, in this complex which is the donor site and if you go back to linkage isomerism whether S is coordinated to mercury or N is coordinated to mercury and same thing is true in case of iron whether S or N. Now let us compare the data here with the data we obtained for this mercury and cyanide complexes. If you see, because the wave number of CN for the complex is higher, so this is higher compared to this one for SCN and the wave number for CS is lower in the complex compared to free CS. Because of this one, we can conclude that S is coordinating to mercury this is analogy and let us look into iron complex in case of iron complex if you compare the stretching frequency of CN with that of that one this is much lower here on the other hand CS stretching frequency is much larger compared to free ligand that indicates probably in case of iron N is coordinating to Fe^{+3} center from coordination chemistry point of view let us say I do not have data for comparison for the free ligands then how to assign simply by looking into it yes we can see here two things about looking to soft and hard interactions mercury 2 plus (Hg^{+2}) is a soft center so if since it is a soft center it would prefer to have a soft donor atom and hence

S is a soft donor atoms probably you can think that mercury is connected to sulfur on the other hand iron 3 plus (Fe^{+3}) is hard center it would prefer the hard side that means probably nitrogen is going from in this way also you can analyze and you can arrive at the right answer and also if you see mercury mercury ore is synapse or mercury sulfide so that also tells that mercury has more affinity towards S from that point of but here without any ambiguity simply by comparing the data with the data for free ligand the stretching frequencies we should be able to tell the correct linkage of such ligands which are capable of showing linkage isomerism whether S is coordinating S is binding or N is binding let us look into another example here this is a octahedral complex of cobalt penta cyano thiocyanate cobalt date it can appear of course because of linkage isomerism it can appear in two isomeric forms which give rise to the following IR absorption bands so here we have 2065 and 810 and another one is 2010 and 700 centimeter minus one (cm^{-1}) so by simply comparing to whatever the discussion I had with respect to mercury and iron complexes I showed in my previous slide you should be able to judge that yes in case of isomer one N is binding whereas in case of two S is binding you can say without any problem and of course you can also write the corresponding isomers having octahedral geometry without any problem i'm not going to go into write those things probably you can write and examine those things let us look into another example here the following infrared absorption bands are observed for the complex containing a bipyridine ligand and also thiocyanate ligands it is NCS not NSC in the region of NCS stretching modes that is we have a total of four stretching frequencies are there 2117, 2095, 842 and 700 now.

That means it's a probably a mixture of two isomers are there and we should be able to identify you know stretching frequencies corresponding to N coordination to palladium and also S coordination to palladium again with our previous experience of interpreting data in case of mercury 2 compound and iron 3 compound we can conclude here that when we have 2095 and 842 this can be assigned to palladium having NCS bond and similarly when we look into the data 2117 and 700 this can be assigned to palladium having SCN type of linkages so this how we can interpret and we can say without any ambiguity how the linkage of NCS takes place and then how we can interpret and elucidate the structures by giving the right kind of stretching frequencies to N as well as S bond complexes so now another problem is it's not a problem it's just for analysis you are already familiar I have

spoken many times about CO stretching frequencies CO stretching vibrations of CO can be found at 2155 centimeter minus one (cm^{-1}) that's the free carbon monoxide shows at 2150 again here it's at a different region that's what I am telling you is; from books to books, this value varies, 2130 to 2160 it goes up to that one but nevertheless the stretching frequency of free CO is always greater than what we see in case of metal carbonyls unless there is no back bonding at all. In those metal complexes, it lies in the range of 2100 to 1800 in metal carbonyl compounds that's very much true. The chemical bonds in metal carbonyl compounds is a superposition of a sigma metal to carbon bond and a metal to carbon back donation so that you are already familiar. I had showed you examples and also I showed you bonding modes through orbital interactions what information is obtained by the mean value of CO stretching modes according to the part of both contributions to the chemical bond in the following charged metal carbonyl ions that means whether we can look into the sigma donor component and pi acceptor component whether we can separate these two entities based on comparing the data for a series of compounds keeping the metal constant and changing the number of carbon monoxides are going for cationic anionic and neutral and also replace some of the carbon monoxide in a metal complex with sigma donor by acceptor sigma donor pi donor and also sigma donor and pi acceptor type of ligands and then we can analyze and probably we can but still the separation of sigma donor and pi acceptor abilities or components is very difficult because often we see they complement each other but nevertheless it gives some idea about the exact position of some of these ligands in the spectrochemical series so now let us look into the values given for a series of compounds here NiCO_4 (2094), $[\text{CO}(\text{CO})_4]^-$ (1946), $[\text{FeCO}_4]^{2-}$ so here we can conclude very nicely that when you go from early metals to late metals late metals despite having enormous electron richness they are reluctant by donors that can be seen in case of whether nickel tetracarbonyl or palladium or even silver complex having carbon monoxide whose stretching frequencies are much higher but on the other end early metals despite having electron deficiency and having less than six electrons they always they act as excellent pi donors and positive charge makes them reluctant by donors but negative charge on metal makes them better by donors and as a consequence of this one what happens the influence is on metal to carbon as well as carbon to oxygen bonds as more and more back bonding comes here not in this direction it comes in this way what would

happen is this bond become more and more elongated and stretching frequency drops considerably so this information already we have discussed in a number of times let us move on to other problems now a very interesting problem is there let me read it out an absorption at 3650 centimeter minus one (cm^{-1}) in the IR spectrum of a compound say x has been assigned to an OH stretching mode to what wave number is this band expected to shift upon deuteration that means where complex is there we have a OH stretching frequency is there and if we replace H with D what would happen to the stretching frequency that is the question and also during this one certain assumption has to be made what assumption one has to make while doing this calculation to find out approximate stretching frequency or absorption band for a compound having OD instead of OH group so now the from the standard expression that you already know $\bar{\nu}$ equals one over two pi c into square root of f over mu ($\bar{\nu} = \frac{1}{2\pi c} \sqrt{\frac{f}{\mu}}$) where f is a force constant stretching force constant and mu (μ) is the reduced mass and that means basically we can consider here this nu is inversely proportional to square root of mu reduced mass that means this is equal to we can say stretching frequency or the frequency absorption frequency for nu bar ($\bar{\nu}$) is inversely proportional to OH bond reduced mass so in that case what happens assuming both the OD and OH have very similar stretching force constant we can arrive at this equation here if you write for this one nu bar ($\bar{\nu}$) OD over nu bar OH ($\bar{\nu}$) equals to OH square root of mu OH (μ) over mu OD (μ) so now we know this relationship and now we know these entities we can calculate and we know this one now we have to calculate what is this so now what we do is reduce mass we have to find out in this fashion and this is one way of doing it or simply we can do this way also $m_1 m_2$ by $m_1 + m_2$ this would be rather easier but if you do with the first one what we have to do is here oxygen is there oxygen atomic weight is 16 and H is 1 and then D is 2 we should remember this one so 1×16 plus 1×1 this is equal to 1.0625 and then this is for $1 \times \mu$ of OH so μ OH equals what we get is 0.9412 atomic mass units we are getting and similarly we can also calculate now μ OD this is equal to 1×16 plus 1×2 so for this one we get 0.5625 if we go for μ OD it comes out 1.7778 this you can do calculation now we put here the values so this value is already given here 3650 and if you put here values this comes around 0.72757, so this gives approximately 2656 centimeter minus 1 so that means if you replace h with d then the stretching frequency of OD drops considerably from 3650 to

2656 centimeter minus 1 (cm^{-1}) so here the assumption is very important in most of such problems where we come across replacement of one isotope with another one probably we should assume that the stretching force constant would be very similar then only we can arrive at this kind of relationship here and hence we can calculate the values and solve the problem. So let's look into one more example here an absorption band at 3337 centimeter minus 1 (cm^{-1}) in the vibration spectrum of NH_3 shift to x value in ND_3 find out the value of x so again here we should come up with the same relationship whatever we saw we know now so this is inversely proportional to square root of μ (μ) if we use here so now let's calculate μ NH first of course, N we are considering 14, ^1H and ^2D per calculating reduced mass and here also we can do directly or something like this also we can do it it's 1 over 14 plus 1 by 1 so this is equal to 15 by 14 so this value will be 1.0714 and μ NH will be similarly so this value is going to be 0.933 and here the value will be 0.5714. So, N equal to 1.7500 so now we have to apply here this is given here so that means the value of x is this one so this how you can solve this very interesting problems let me come up with more examples in my next lecture until then enjoy this problem. Thank you.