Interpretative Spectroscopy

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Lecture 37

Numerical Problems related to IR Spectroscopy-2

Hello everyone, I once again welcome you all to MSB lecture series on Interpretative Spectroscopy. This is going to be the last lecture on IR spectroscopy. At the end as I mentioned I would come up with more examples in each case, but in this lecture let me conclude IR with few more problems. What you should remember when we are looking into stretching force constant and its relationship with stretching frequency? The stretching frequency is inversely proportional to the reduced mass and it is directly proportional to stretching force constant, that you should remember. Also, when we are replacing one with other isotope say H with deuterium or ^{12}C with ^{13}C or ^{17}O with ^{18}O what you should remember is we should assume that the stretching force constant is more or less same in case of both the bonds.

With that one nu bar is inversely proportional to the square root of mu of that bond. So, we should use reduced mass. That we should remember, with that let me try to make you familiar with this kind of problems by giving another 2 or 3 problems. Let me continue with such problems again.

So, now I have another problem here: An absorption at 3161 centimeter minus 1 (cm^{-1}) in an IR spectrum is assigned to CH stretching mode, at what wave number will this band appear upon deuteration.

If I replace CH with CD what would happen to the stretching frequency, presently it is 3161. So, again we have to go for the same relationship as I had mentioned. We know that

this one equal to 2 pi C square root of F over mu($\bar{\nu} = \frac{1}{2\pi C}\sqrt{\frac{f}{\mu}}$). F is force constant, mu is reduced mass and then if you are considering now CH. So, this is inversely proportional to CH.

Now, let us calculate the value. In previous problems I took like this one or we can directly calculate also by considering m1m2 over m1 plus m2. So, this is for CH. So, for this one, what we will do is we can calculate here this is ^{12}C, ^{1}H and ^{2}D. So, here it is 12 into 1 over 12 plus 1 similarly CD equal to 12. So, now we know that the relationship value is given here for mu CH.

So, this is the stretching frequency value for CD in place of CH. That means the band after deuterating the H would appear at 2320 centimeter minus 1(cm^{-1}). So, this how you should do. I think you have understood. Now you should be able to solve any such problems without any problem.

So, now let us look into one more example here, it is quite interesting. An absorption in the IR spectrum of a compound containing an XH bond shifts from 3657 to 2661 upon deuteration. Find out whether X is C or O. So, that means we have a XH bond for which shift is 57 to 2661 then we have to find out whether X is C or O.

So, what we should do for this one? we have to consider in both the cases and have to calculate. For example, let us take nu OH equal to this. is the one and then if you consider nu OH this will be 16 by 17 this will be equal to 0.94417. Well I am giving whatever the value I get when I do calculation from the calculator. So, do not worry about it. Up to two decimals is good enough. Similarly, I can calculate muOD this is 32 by 18. So, this will give you 1.7777. Similarly, I would also like to calculate and keep it, CD for example, here it is 12 by 13 this is 9.92370 and here it is 24 by 14. So, this will be 1.71. So, now we have to calculate and we use the same analogy here nuCD over nu CH equal to square root of CH over CD.

So, if you put here nu C H into this value put here 3657 and if you this value if you put it here C H 0.92307 or 1.71 this will be 3657 into 0.7347. So, this comes around 2687 centimeter minus 1(cm^{-1}).

So, now let us do the same calculation for nuOD. Similarly, if I do for nuOD which will be nuOH into OD and here the value is again same because we do not know which is the value into if you put here the value I am just taking up to three here and then 1.7777. So, this equal to 3657 into 0.7277. So, this will come around 2661 centimeter minus 1(cm^{-1}).

So, this is the value given here. So, we got this one. We can say now X equal to O and also simply by looking into the data also you can see if the stretching frequency comes around 3657 centimeter minus 1(cm^{-1}). Certainly, it is not for CH it is for OH. OH usually shows around 3600, but on the other hand CH shows around 3000.

That information also you can see. However, to rationalize our understanding, we have to go through this process. Even let us say, we get it in the first place itself, it is always advisable to check for other option to conclude without any ambiguity that this bond we are referring to is OH. OH initially shows 3657 centimeter minus 1(cm^{-1}) after deuteration we are getting OD that comes to 2661 centimeter minus 1(cm^{-1}). So, this is how of course, we can take the hint from the chemistry knowledge we have and also from spectral bands. But on the other hand, when such problems are there, we learn more and get some confidence over solving the problems. Now, it matches perfectly to this value here.

So, you can say without any hesitation, X is O and we are talking about OH bond and it is shifted to lower frequency upon deuteration. Now, let me come to some understanding of CO stretching frequencies here. Which of the two isoelectronic compounds $CrCO_6$ and VCO_6 minus. Both are 18 electron complexes, it is a d^6 12 electrons from carbon monoxide and 6 electrons from the metal 18 electron. And here vanadium $3d^3 4s^2$ plus 1 electron become 6 and again 12 electrons, both are isoelectronic will have the highest CO stretching

frequency. So, which one will have the highest stretching frequency, which of the two compounds? Again this first question is among isoelectronic species such as chromium hexacarbonyl and vanadium hexacarbonyl anion which one would be having higher stretching frequency and the next question is if we have two chromium compounds having $CrCO_4$ moiety and two different phosphines, one is triethylphosphine one is triphenylphosphine; which one will be having lower stretching frequency and which will have the shorter M-C bond. The one which has higher stretching frequency will be having longer M-C bond and the one having lowest will be having shorter MC bond because as more and more CO bond is weakened metal to carbon bond will be strengthened.

This is again about metal to carbon back bonding ability and the negative charge on vanadium complex results in greater metal dpi-pi* here t_{2g} (d_{xy} d_{yz} or d_{zx}) giving the electrons to pi star of CO compared to the chromium complex. That means compared to chromium, vanadium is a good pi-donor, as a result stretching frequency of CO drops considerably in case of vanadium complex compared to chromium complex. So, job is done. This results in weakening of CO bond with a corresponding decrease in stretching frequency. So, thus chromium complex has higher stretching frequency and its chromium to carbon bond length will be little longer.

In case of two phosphines, we have triethylphosphine and triphenylphosphine. So, ethyl groups are electron donating, whereas phenyl group is electron withdrawing. So, that means when we have electron withdrawing groups on phosphorus, makes it poor sigma donor, but excellent pi acceptors. On the other hand, electron donating groups on phosphorus makes it very good sigma donor, but poor pi acceptor. That means here triethylphosphine complex will have greater electron density because triethylphosphine is a good sigma donor and also relatively it is a weak pi acceptor compared to carbon monoxide. As a result, more and more electron density goes to carbon monoxide rather than going to phosphine.

So, here stretching frequency drops considerably and metal to carbon bond strengthens, whereas in case of triphenylphosphine what happen it is also a good π acceptor as a result

back bonding will be little less as we see in case of chromium. This how we can analyze. Which of the two iron compounds $FeCO_5$ and $FeCO_4(PEt_3)$ will have the higher ν_{CO}, which one will have the longer MC bond. So, same analogy you can use here. In case of iron pentacarbonyl, we have 5 carbon monoxides and equally electrons are distributed. As a result, stretching frequency is less because 5 are there and CO stretching frequency is little bit higher here, whereas in this case what happens one carbon monoxide is replaced by another electron pumping group. As a result, more electron density is there on iron and also it has to be taken care by only 4 carbon monoxide. So, here the stretching frequency will be less and iron to carbon bond is stronger.

So, this how simply by looking into the nature of the ligands present, we can analyze and we can conclude about the stretching frequency trends among these complexes. So, let me look into one more example before I conclude on IR spectroscopy in this lecture.

This is again about isotopic labeling or exchanging: The IR spectrum of free carbon monoxide shows an absorption band at 2170 centimeter minus 1(cm^{-1}) assigned to vibrational mode of the molecule. If the sample is enriched in ^{13}C, what change do you expect to see in its IR spectrum?

So, this is again about exchange. Earlier we are talking about exchanging H with deuterium, here we are talking about ^{12}C with ^{13}C and O remains same.

That means, basically we have to look into again this relationship is inversely proportional to. Now let us try to find out the reduced mass. Here we have to find out ^{13}CO versus ^{12}CO this relationship. If we write is ^{12}CO. We have to calculate now mu ^{12}CO. This equal to m_1m_2 by m_1 plus m_2. So, this is 12 into 16 over 12 plus 16 is 28.

So, this comes around 6.8571 and similarly if we calculate for ^{13}CO reduced mass, this will be 13 into 17 by 29 this comes around 7.1724. Now, if you apply the same here. So, value is given here 2170. If you apply the same here. Value is given here 2170. So, this is the answer. So, that means, this answer is this one. What change we expect to see in its IR spectrum. In IR spectrum, stretching frequency due to ^{13}CO drops considerably from 2170 to 2122 centimeter minus 1(cm^{-1}). Again here the assumption what we made is the

stretching force constant in case of both ^{12}CO and ^{13}CO would remain more or less unchanged then only we can arrive at this relationship here.

With this, one let me stop today's lecture and conclude about IR spectroscopy and then probably in my next lecture I am going to start about mass spectrometry and at the end, about 10 to 12 lectures, I devote completely to solving all kinds of very interesting problems having one or more spectroscopic components in it. So, until then have an excellent time. Thank you.