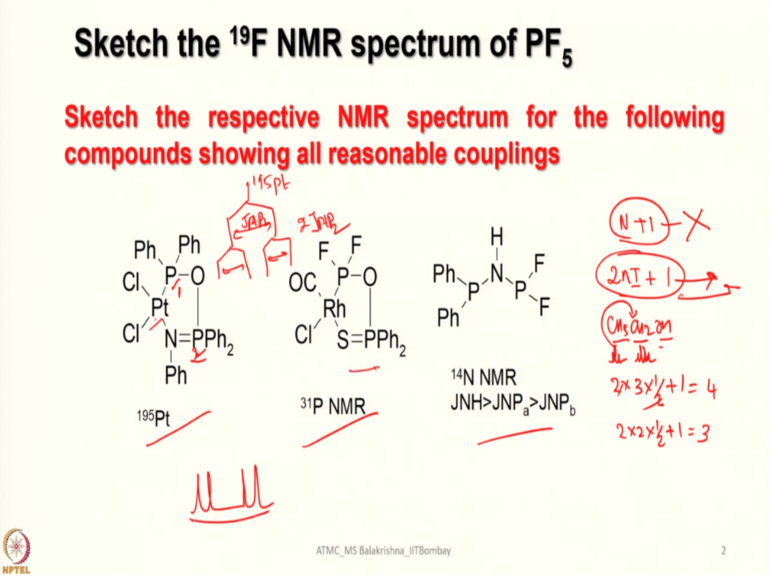
Advanced Transition Metal Chemistry_Spectroscopic Methods
Prof. M. S. Balakrishna
Department of Chemistry
Indian Institute of Technology - Bombay

Module - 12
Lecture - 59
NMR and IR Spectroscopy

Hello everyone. It is a pleasure to welcome you all to the MSB lecture series on Transition Metal Chemistry. This is the last but one lecture. So, in this lecture, let me give a little bit information about a few multinuclear NMR spectra and how to interpret the spectra, and also brief information about IR spectroscopy. So, in my next lecture, I shall try to conclude and summarise whatever the 59 lectures I gave, covering most of the aspects revolving around coordination compounds and to an extent organometallic compounds.

(Refer Slide Time: 00:51)



Sketch the ^{19}F NMR spectrum of PF_5

Sketch the respective NMR spectrum for the following compounds showing all reasonable couplings

So, now, I have given a few molecules here, sketch the ^{19}F NMR spectrum of PF_5. If a question like this is asked, one thing you should know, if the information is not given about the dynamic process or it is not given information or it does not have any information whether the molecule is static or dynamic with functionality; and of course, PF_5 is known for switching their equatorial and axial PF bonds via Berry pseudorotation.

But however, if the question does not explicitly say about the molecule, we should understand that functionality is there in it. In that case what happens, all 5 will look almost identical with respect to NMR timescale. As a result, what happens, if you look into ^{19}F NMR spectrum, it should show simply a doublet, all 5 will be equivalent, they will be coupled with phosphorous.

In my previous lecture, I was telling about remembering n + 1 rule to identify number of lines in a splitting pattern, but I would say, instead of this one, it is better if you use 2nI + 1 rule; I is the nuclear spin of the interacting nucleus and also n is number of equivalent nuclei. For example, if CH_3CH_2OH is there, and if you want to know; of course, you just leave this one; if you consider CH_3, how it is splitting this one, so here, 2 x 3 x ½ + 1, it gives 4 lines.

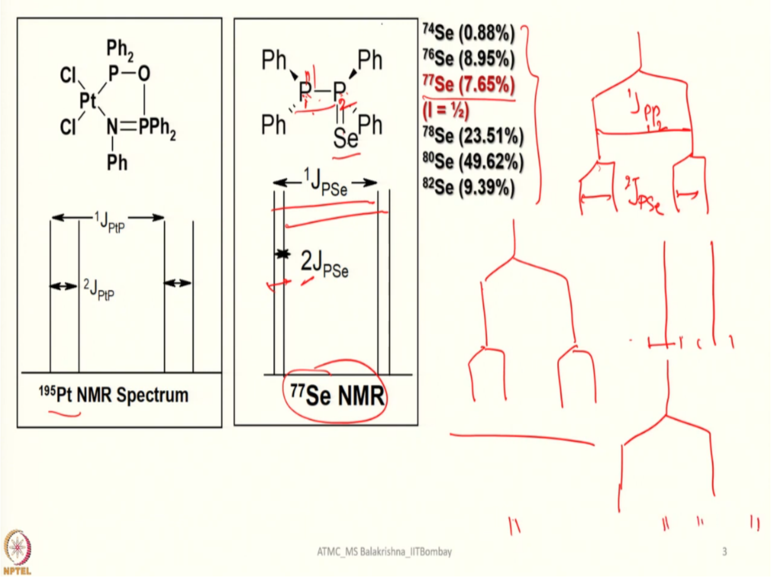
So, this will give 4 lines for this one. So, it looks like this. And then for this one, it is 2 x 2 x ½ + 1 = 3. So, this will give 3. So, I think this is better; go with this one, this one would tell you the number of lines, the splitting pattern irrespective of number of equivalent nuclei and also the type of nucleus we are using, whether I =1/2 or 3/2, it is applicable for all type of nuclei and also better to use this one rather than using this one; do not use this one.

Now, let us look into; so, ^{19}F NMR would show a doublet. But on the other hand, you should remember, if they are assuming it is a static molecule, in that case what happens, 2 axial are different from 3 in the plane. So, that means first axial will split by PF coupling to give a doublet; and then doublet each line will be split into a quartet because of 3F in the plane.

On the other hand, 3 in the plane would first split by phosphorous to a doublet and each line in the doublet will be split into a triplet because of this 2F. So, if time permits, I shall tell you about that one, but you should be able to work out. So, now, we have this molecule here. And of course, this is NMR active; this is NMR active. Now, the question is asked about this one, so, ^{195}Pt.

^{195}Pt, when the question is asked, you should not worry about abundance because we are looking into the NMR nuclei, that itself. So, in this case, now we have to see, this platinum is 1 bond apart from P1 and 2 bond apart from P 2. Now, first it will be split into a doublet and then each line will be further split into a doublet. So, this coupling would say this is for ^{195}Pt, platinum. So, this would say 1 J Pt P 1. And then, this one or this one would say $^2J_{PtP}$. So, that means spectrum would look like something like this. For this one, I have given in the next slide.

(Refer Slide Time: 04:41)



So, you can see here, and of course, this is how it looks ^{195}Pt NMR. And if you just look into this molecule here, we have 2 phosphorous; one is trivalent, one is pentavalent. So, they are magnetically and chemically non-equivalent. So, they couple each other with a large coupling constant. And now, we have selenium is there. And this selenium will couple to this one as well in this one, but if the selenium NMR is asked here, then you can see here, these are the possible isotopes out of which only one is NMR active, 77-selenium, I = ½ .

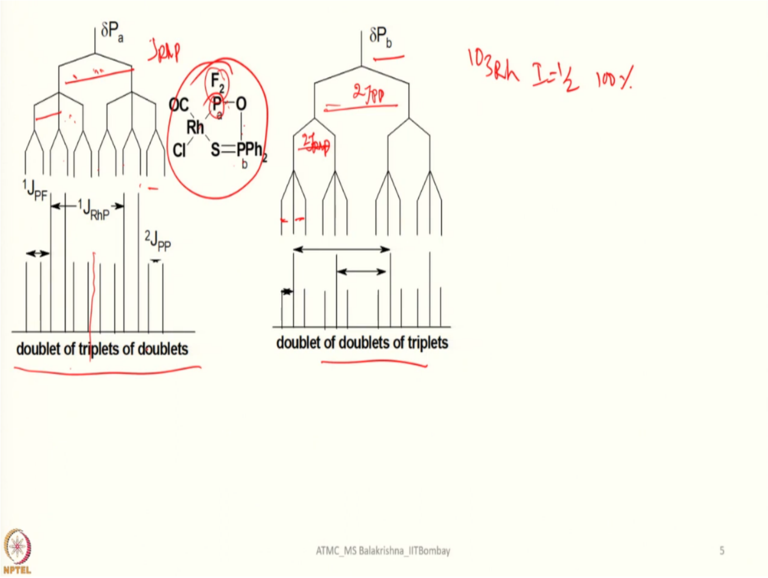
That means, out of 100 molecules if you consider, out of that one, 77.65; let us say 7 molecules are NMR active, remaining to 63 are NMR inactive, that means basically. But when we look into ^{77}Se NMR, you have to consider very similar to here. So, now, first this one will be coupled with this one. This is something like this. And then, each will be split by this second; this due to $^2J_{SeP}$.

And this is how the spectrum would look like. This coupling is this one and this coupling or this coupling is $^1J_{PSe}$. So, this is how you should be able to write for other nucleus. But only thing is, when I am looking into ^{31}P NMR; if I look into ^{31}P NMR of this one, we have 2 signals in this case. First let us say this one is coupled with this one, gives a doublet; this is due to $^1J_{PP}$ coupling if I put P_1 and P_2.

And now, P_1 will be coupled with this; small coupling will be there. So, this is your $^2J_{PSe}$ coupling; this one also. So, it looks like; and other one, now this one also will show very similar to that one, but it may show larger coupling. So, now, how it looks like? The first, this is coupled with; so, now, it is not 100%. As a result, what would happen is, first you get something like this, a doublet, and each doublet will be further split into small.

This one will be something like this and this will be something like this. So, this is PSe coupling. But when you take this one, it will also show a doublet, but here it will show a larger coupling. So, larger coupling how it shows? Something like this, depending upon how much selenium-selenium coupling, it would be splitting like this. So, you should see that one. I will show you few more examples.

(Refer Slide Time: 07:12)



Now, let us look into this molecule here. See here, we have 2 phosphorus, one is bonded directly to rhodium, other one is two bonds apart. Now, let us look into first here. First this one will be coupled with rhodium. This rhodium coupling is larger, ^{103}Rh; ^{103}Rh is I = ½ and 100% abundant. So, first we get a line like this. And then, this is your $^1J_{RhP}$.

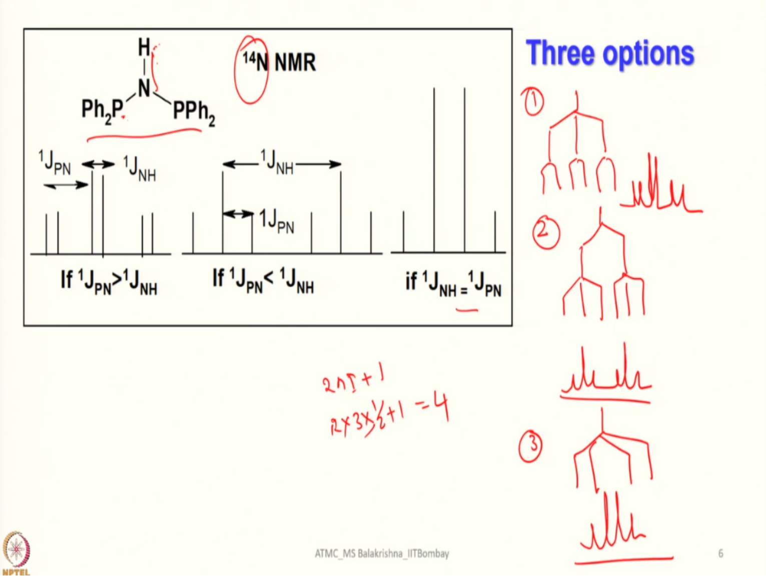
And now, this will be further split by this one to triplet. This should be triplet because PF coupling; so, this is PF coupling triplet. And now, each line will be split into a doublet because of $^2J_{PP}$ coupling. So, now it looks like that. So, basically, a doublet, a triplet and a triplet each line will be a doublet. So, that means doublet of triplets of doublet.

So, this how it is, doublet of triplets of doublets; this is how you mention the spectra. In the same way if you go for P_b here, first this would be coupled with say ^2J, rhodium-phosphorus coupling will be there; or if PP coupling is more, that would be there. Here PP coupling would be more here; so, $^2J_{PP}$ coupling. This one will be little less, and this is $^2J_{RhP}$.

And then, this will be further split by fluorine on this one; so, this smaller coupling. Then this is called doublet of doublets of triplets. You should be able to distinguish and interpret properly. So, first phosphorus, if you consider this one, this is coupled with rhodium because the coupling is larger, about 250 hertz. And then, each line of this one, a doublet will be split by triplet because of PF coupling.

PF coupling will be less in magnitude compared to rhodium phosphorus 1 J coupling. And then, each line will be further split into PP coupling. So, this is how you can see the coupling tree. You can write like this. Then one can write a spectrum like this. So, two are there, doublet of triplets of doublets.

(Refer Slide Time: 09:24)



^{14}N NMR

Three options

If $^1J_{PN} > {}^1J_{NH}$

If $^1J_{PN} < {}^1J_{NH}$

if $^1J_{NH} = {}^1J_{PN}$

$2nI+1$

$2 \times 3 \times \frac{1}{2} + 1 = 4$

ATMC_MS Balakrishna_IITBombay

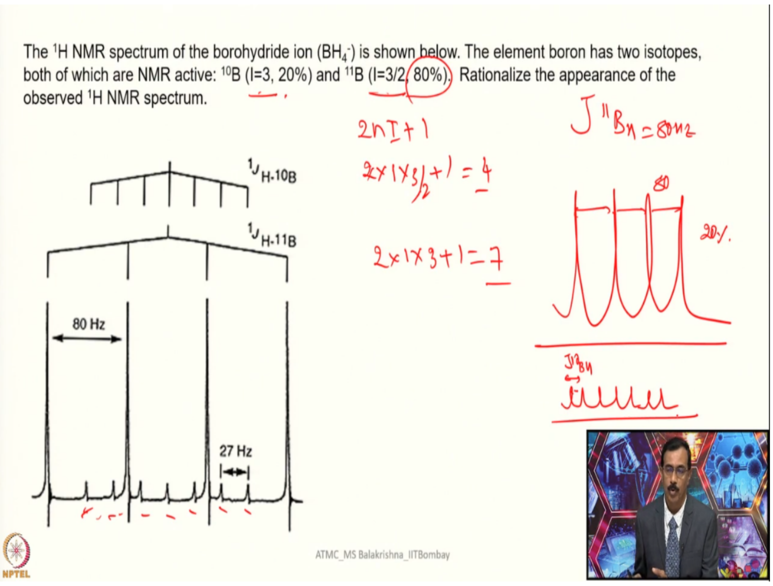
6

So, now, when you consider this molecule here, if somebody asks you to sketch ^{14}N NMR for this one, we have 3 options; 3 options are there. What are those? If you see, this hydrogen is 1 bond apart; these 2 phosphors are 1 bond apart. You do not know the magnitude of NP coupling and NH coupling. So, in this case, we have to see whether PN coupling can be larger than NH coupling, 1 case, or PN coupling will be smaller than NH coupling or both of them can be identical.

In that case, first let us look into PN coupling is larger. First in that case what happens, it will first split into a triplet because PN coupling is a larger triplet. And then, each one will be split into a doublet like this. So, this is one. Second option is, a PN coupling is smaller than NH coupling. NH will first give a doublet due to NH coupling. And then, each one will be split into a triplet, 1:2:1.

So, the spectrum will be something like this. And in this case, in the third case, both are identical; this is interacting with 3 identical nuclei, although they are of different elements. So, now, how to say? Again, use 2nI + 1 rule. I = half here; so, 2 into; so, 3 are there; 3 into half, 4 lines. So, what do you get is 4 lines in third case. So, first it will split into something like this; then it will be 1:3:3:1. So, these 3 conditions are there and you should see what condition matches which one, you should know.

(Refer Slide Time: 11:19)



The ^1H NMR spectrum of the borohydride ion (BH_4^-) is shown below. The element boron has two isotopes, both of which are NMR active: ^{10}B (I=3, 20%) and ^{11}B (I=3/2, 80%). Rationalize the appearance of the observed ^1H NMR spectrum.

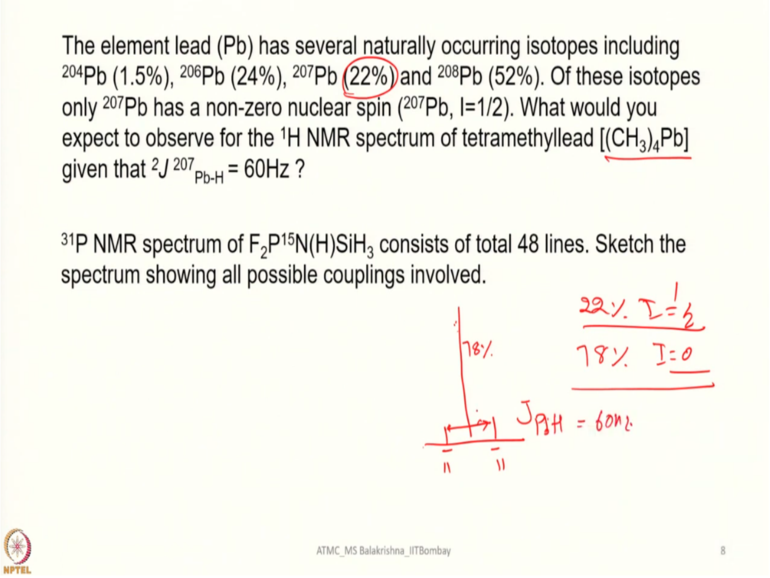
Now, let us look into the most common question we come across about boron hydride, sodium borohydride if you take, anion here BH_4 anion. So, the spectrum is shown here. This is ^1H NMR spectrum. Now we have to explain why these lines are 4 lines are equivalent and also we have some lines here. Now, we should remember, boron consists of 2 isotopes, 10-boron with I = 3, and then 11-boron, I = 3/2.

So, now, you should see, if 2nI + 1 rule you should apply for this one, this is the 80%. That means, out of 100 molecules, 80 molecules have 11-boron and 20 molecules have 10-boron. So, first we should write for 80. Now, 2 x 1 x 3/2 + 1. So, you should give 4 lines of equal intensity, something like this. So, this is for 10-boron H coupling, 4 lines. And this separation is identical.

This is approximately 80%. Now, you should remember, now we have 20%; if this is 80%, then 20% intensity will be for this one, 20 molecules. They have 10 boron. If 10-boron I = 3, so, 2 x 1 x 3 + 1. So, here it is 7. So, there should be 7 lines. These 7 lines you can see here, 1, 2, 3, ..., 7. They will be essentially 1, 2, 3, ..., 7, something like this. And then each separation is identical.

This separation is 10-boron and H coupling. So, this is how you can interpret and you can also explain why these smaller lines are there; it is overlapping of both. Because, when you look into boron NMR, it will account for 10 boron as well as 11 boron. Molecules with ^{11}B are 80 and ^{10}B are 20. So, if you look into intensity of this one, if it is 80, say each one is 20 intensity. And then here, 10 means 10 by 6 you can see how much it will be, about 1.5 intensity or something. At the end, both of them should match 100%. So, this is how one can interpret.

(Refer Slide Time: 13:32)



The element lead (Pb) has several naturally occurring isotopes including ^{204}Pb (1.5%), ^{206}Pb (24%), ^{207}Pb (22%) and ^{208}Pb (52%). Of these isotopes only ^{207}Pb has a non-zero nuclear spin (^{207}Pb, I=1/2). What would you expect to observe for the ^{1}H NMR spectrum of tetramethyllead [$(CH_3)_4Pb$] given that $^2J\ ^{207}{}_{Pb\text{-}H}$ = 60Hz ?

^{31}P NMR spectrum of $F_2P^{15}N(H)SiH_3$ consists of total 48 lines. Sketch the spectrum showing all possible couplings involved.

22% I = ½

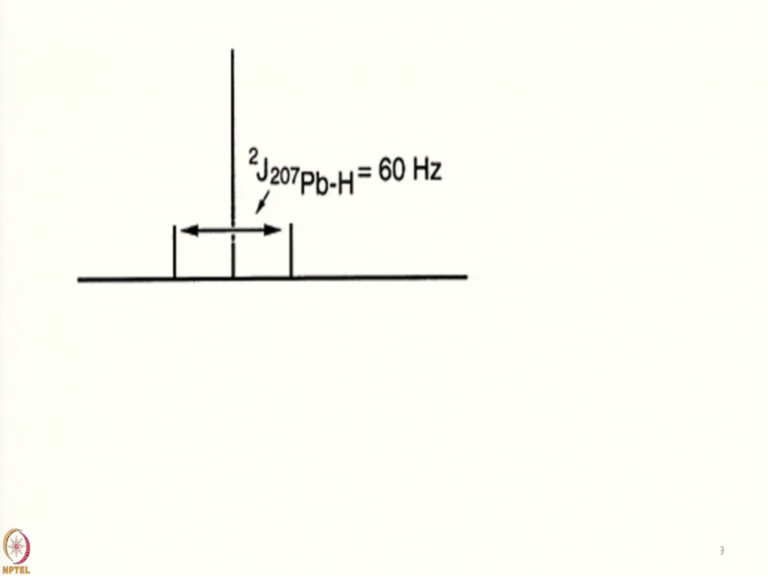
78% I = 0

Now, one more question, the element lead has several naturally occurring isotopes including all these things. Of these isotopes, only 207 has a non-zero nuclear spin I equals half. What would you expect to observe for ^{1}H NMR spectrum of tetramethyllead given the 2 J coupling is 60 hertz. So, then, how do we explain this one? The question is very simple; we have given here. So, now it is ^{1}H NMR spectrum.

So, that means, if you just look into all isotopes except for 22%; 22% is NMR active, I = ½. Other you can consider 78% NMR, I = 0, you can ignore. So, that means basically we have 100 molecules; 22 molecules have I = ½. ^{207}Pb, others are, we should not worry. That means those 78% will first show a singlet. And then, these 22% what happens, this will be split into doublet, and then like equidistance from this one.

These are called satellite peaks. And now it is, this is 11%; this is 11%; this will be 78% if you look into the intensity. And now, this separation is called $^1J_{PbH}$ coupling. This is equal to 60 hertz. So, this is what is given.

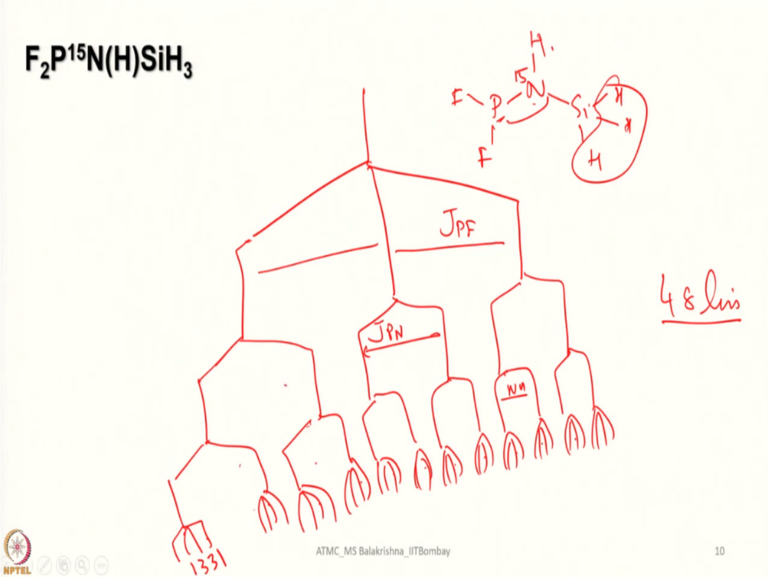
(Refer Slide Time: 14:49)



to

Something like this; this is how the spectrum looks like.

(Refer Slide Time: 14:52)

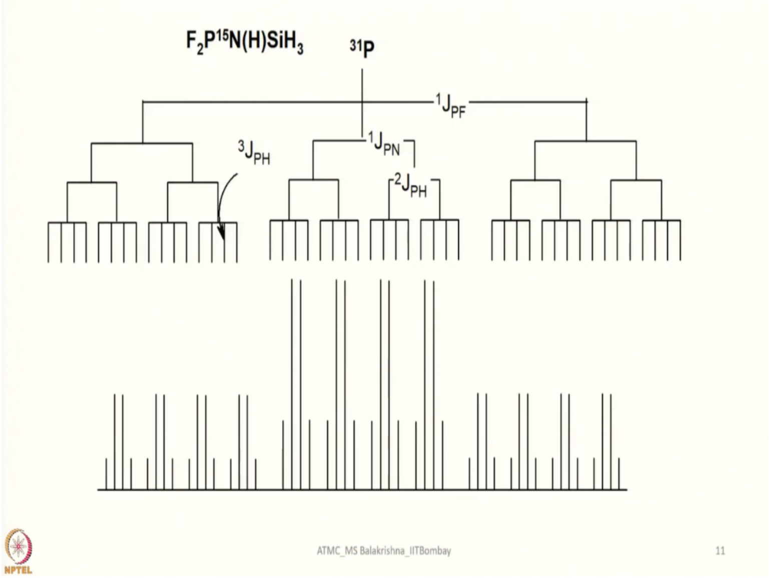

$F_2P^{15}N(H)SiH_3$

So, now let us look into this one. This is very interesting. First, let me write ^{31}P NMR and let me write the structure of the molecule quickly, N; and remember this is ^{15}N is 100%, it is ^{15}N. So, now SiH; this something like this. All are NMR active, so, something like this. This one is strongly coupled with 2 fluorine atoms. First it should give a triplet. So, let me write little bigger because lot of couplings will be there.

So, triplet; this is PF coupling, same triplet. And now, this is coupled with N, a doublet. So, doublet, each one is a doublet. This is done; this is your PN coupling. Now, this H coupling; so, H coupling will come another doublet, doublet; this is your NH coupling. And now, these 3 are there; these 3 will also couple; each one will be split into a quartet. And intensity will be 1:3:3:1.

So, you should be able to sketch this spectrum beautifully. So, 1, 2, 3, ..., 12; 12 into 2, 48 lines will be there totally. So, then you can say triplet of doublets of doublets of quartets. This is how the NMR would look like.

(Refer Slide Time: 16:38)



You can see here, this is how it looks like, and this is how you can interpret and do it. Try for ^{15}N, also ^1H NMR also you should try.

(Refer Slide Time: 16:46)

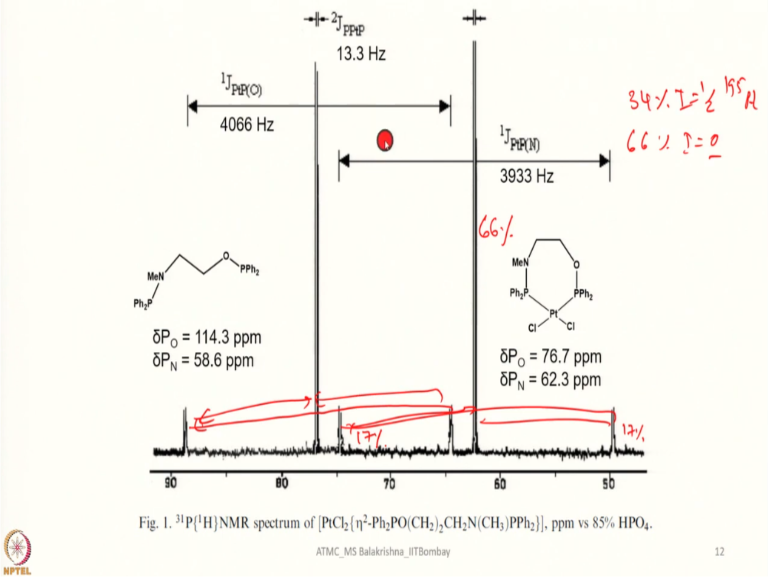


Fig. 1. $^{31}P\{^{1}H\}$NMR spectrum of $[PtCl_2\{\eta^2\text{-}Ph_2PO(CH_2)_2CH_2N(CH_3)PPh_2\}]$, ppm vs 85% HPO_4.

ATMC_MS Balakrishna_IITBombay 12

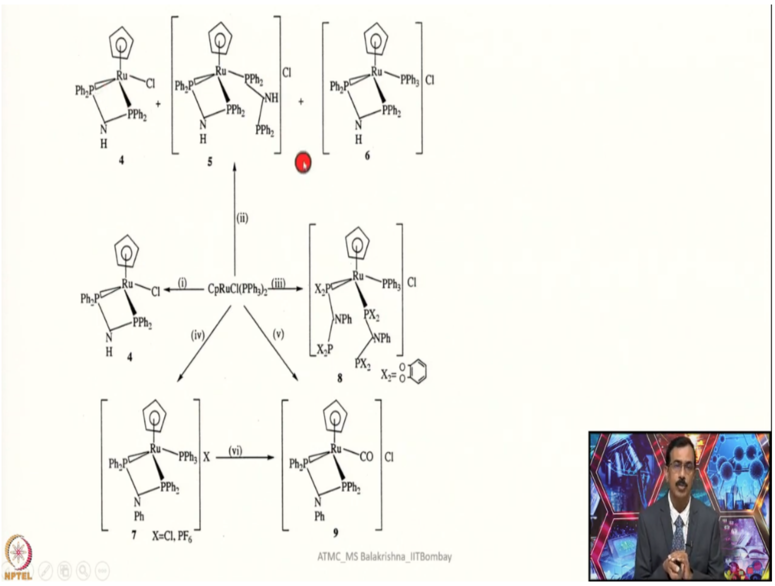
This is very interesting, just look into this molecule here, these P, P are far away. And then if you see here, it will show single peak for both the phosphorus atom; 1 is a nitrogen, 1 is an oxygen; they do not have any coupling because they are far away from each other. But in the complex, now they are 2 bonds apart because of platinum chelation. Now they can show PP coupling. Now, this small separation is PP coupling.

And now, platinum again; if you consider platinum, 34% of platinum is NMR active I = half, that is 195-platinum; rest is, 66 is, we should not worry, I = 0, for 196-platinum. So, that means, basically if I have 100 molecules, so, each one would show a doublet; PP coupling, this also shows a doublet. Now, they will show satellite peaks due to this one; each intensity will be 17%. So, this one, you can see, this is one and this is one.

So, here this is separation. This separation or this separation is identical. This is for this Pt coupling and this one and this one for this Pt coupling. So, this is satellite peaks. And if you just look into this one, this is 17% and then this is 17% and then this is 66%. So, this is how you can write satellite peaks, equidistance from the central one, that is for I = 0 Pt-196 isotope. So, this is how you can see.

And magnitude I have given, the $^{1}J_{PtP}$ coupling is very large. When they are cis, 4000 to it can go even up to 6000 to 7000. And usually when 2 phosphorus are trans to each other, PtP coupling will be less than 2000 hertz or it may be 2400. That means, if any isomerisation is there or if you have a cis compound or trans compound, you should be able to tell immediately, simply by looking into phosphorus-platinum coupling.

(Refer Slide Time: 18:38)

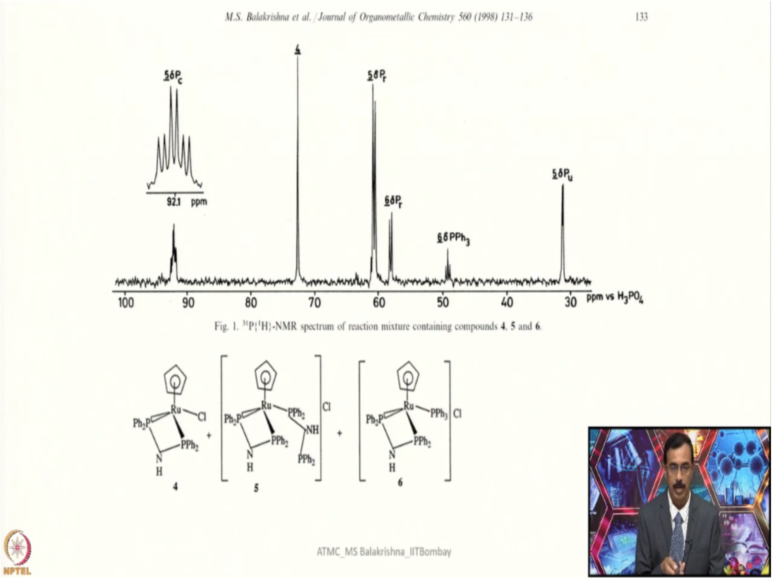


So, now, here for example, this compound is taken, bis(triphenylphosphine)rutheniumCpCl. This compound was prepared using, I showed you the method. And when it is reacted with a bis phosphene, all possible; we got all the products as a mixture. And how to assign this one, here simply ^{31}P NMR can tell you what are the products you have in the mixture. For example, this will show a singlet, whereas this one show a doublet for these 2 and a triplet for this one.

And then, this would show a doublet for this one. And these 2 will couple with this one; it shows a triplet. And then this would show a triplet and each triplet line will be split into a doublet. And then, if you look into the intensity, you can also get the information in what ratios these compounds were made. And also, if you know the reaction condition, whether in case if there is a problem in separating these 3, we should think of separate reaction method for isolation of these compounds by looking into the stoichiometry and reaction condition.

For example, here RuCl bond is broken; that means the yields of this compound can be enhanced by using a polar solvent, whereas, if you use nonpolar solvent, you can retain RuCl bond and simply you can replace 2 triphenylphosphine with a chelate ligand. Here what happens, entropy is the driving force for this one so that you can analyse using spectrum and also you can understand the reaction condition and accordingly you can change the reaction condition to make the desired compounds. I will show you the spectrum here.

(Refer Slide Time: 20:06)



M.S. Balakrishna et al. / Journal of Organometallic Chemistry 560 (1998) 131–136 133

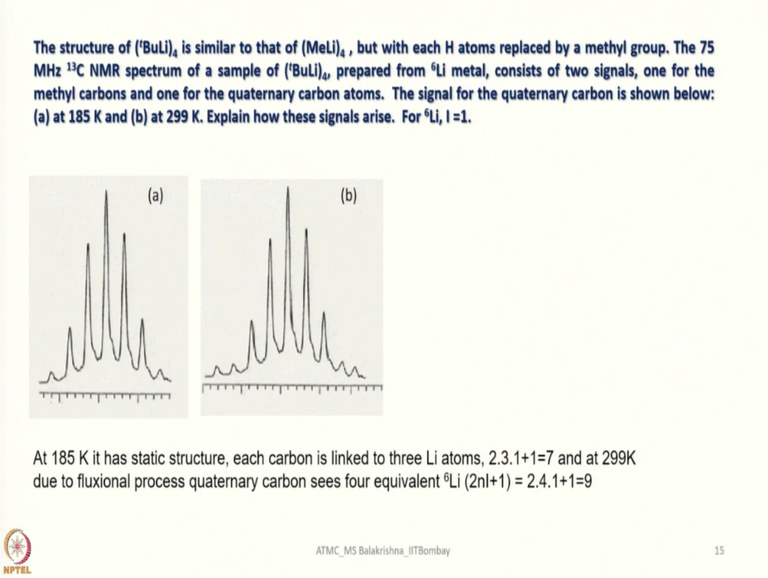
Fig. 1. ^{31}P{^{1}H}-NMR spectrum of reaction mixture containing compounds 4, 5 and 6.

ATMC_MS Balakrishna_IITBombay

This is how the mixture looks like, compound 1, where we have simple chelation, all are identical, one you are getting as I mentioned here. Very nicely you can interpret the data for 3 types of compounds we have. This one will show a singlet and this will show you a complicated 3 lines. And then, this will show a doublet and a triplet, these 2, whereas this one is a doublet for this one.

And then, this is a doublet of doublet here. And then this one shows a triplet and each triplet line is split into doublet. So, one can very nicely interpret and understand what kind of products you got in your reaction.

(Refer Slide Time: 20:41)



The structure of (^{t}BuLi)$_4$ is similar to that of (MeLi)$_4$, but with each H atoms replaced by a methyl group. The 75 MHz ^{13}C NMR spectrum of a sample of (^{t}BuLi)$_4$, prepared from ^{6}Li metal, consists of two signals, one for the methyl carbons and one for the quaternary carbon atoms. The signal for the quaternary carbon is shown below: (a) at 185 K and (b) at 299 K. Explain how these signals arise. For ^{6}Li, I =1.

At 185 K it has static structure, each carbon is linked to three Li atoms, 2.3.1+1=7 and at 299K due to fluxional process quaternary carbon sees four equivalent ^{6}Li (2nI+1) = 2.4.1+1=9

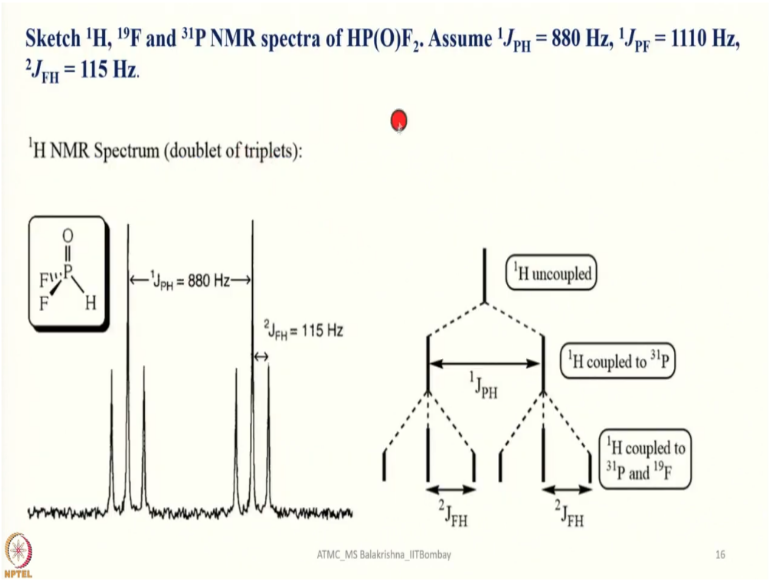
ATMC_MS Balakrishna_IITBombay 15

And now, if you just look into n-butyllithium, it has a cubane structure. For example, 2 spectra are given at 195 K, it is static structure. Here 3 lithiums are connected to each carbon;

a cubane structure is there. Just recall my teaching in my main group chemistry lecture. If you have looked into or you can just go to my lectures and look into it the structure. So, 3 lithiums are connected to tertiary carbon here.

So, this one will show 7 lines here, because lithium has I = 1, so, if you use 3nI + 1, 3 into 2 plus 1, 7 lines it shows. But on the other hand, when the fluxional process is there, we have 4 equivalent lithiums are there. In cubane, 4 alternate carbons are occupied by lithium and methyl group. So, we have totally 4 lithium atoms are there. Are all are interacting with carbon because of fluxional process. In that case, we get 9 lines. So, very nicely you can interpret the data.

(Refer Slide Time: 21:37)

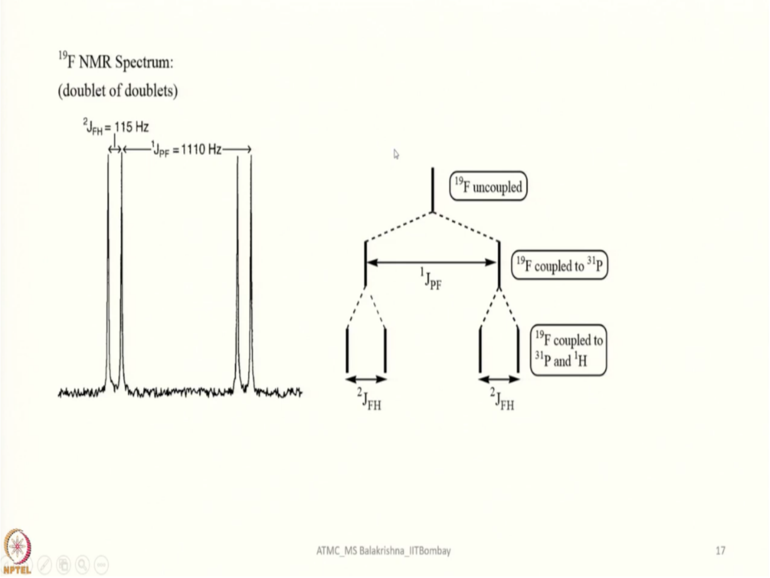


Sketch ^{1}H, ^{19}F and ^{31}P NMR spectra of $HP(O)F_2$. Assume $^{1}J_{PH}$ = 880 Hz, $^{1}J_{PF}$ = 1110 Hz, $^{2}J_{FH}$ = 115 Hz.

^{1}H NMR Spectrum (doublet of triplets):

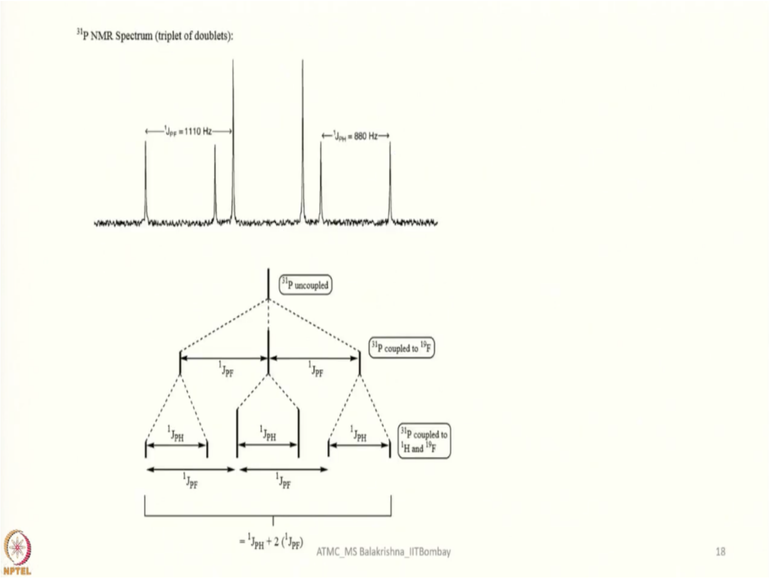
So, this is about, similarly you can look into this one. And you can just see I will stop now, I shall proceed for IR spectroscopy for few minutes.

(Refer Slide Time: 21:40)



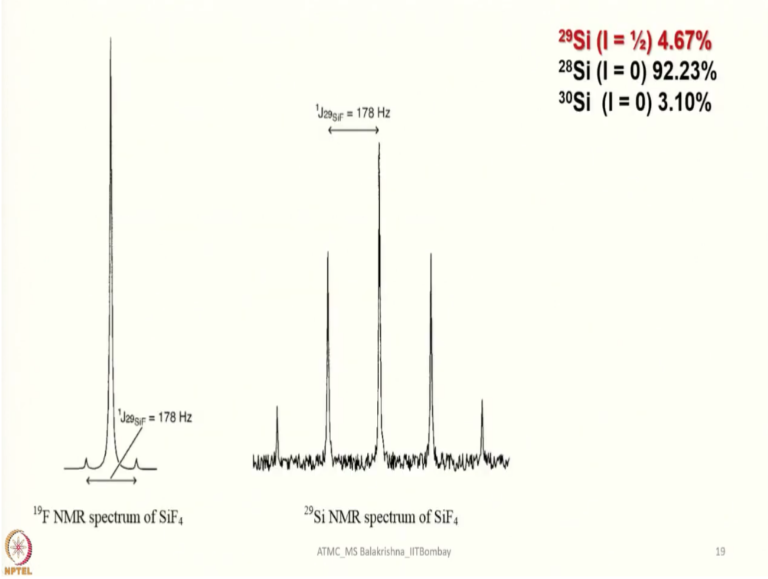
^{19}F NMR Spectrum:
(doublet of doublets)

(Refer Slide Time: 21:42)



^{31}P NMR Spectrum (triplet of doublets):

(Refer Slide Time: 21:43)

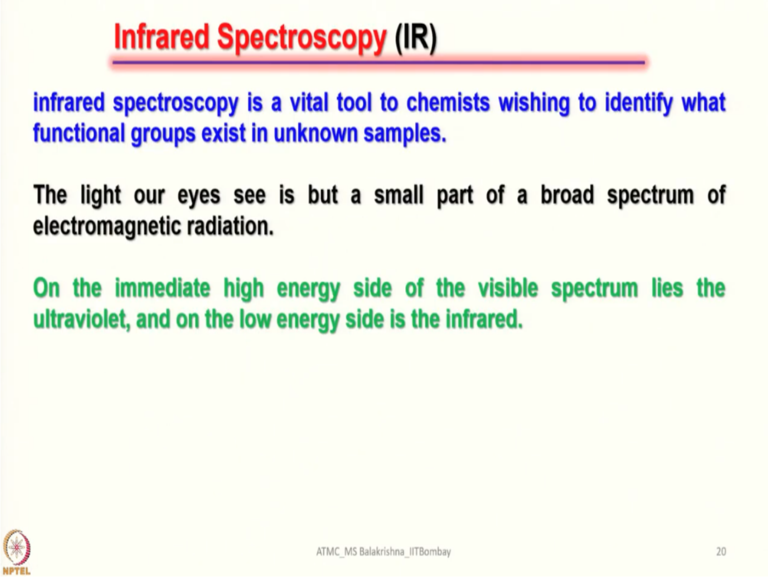


^{29}Si (I = ½) 4.67%
^{28}Si (I = 0) 92.23%
^{30}Si (I = 0) 3.10%

^{19}F NMR spectrum of SiF_4

^{29}Si NMR spectrum of SiF_4

(Refer Slide Time: 21:44)



Infrared Spectroscopy (IR)

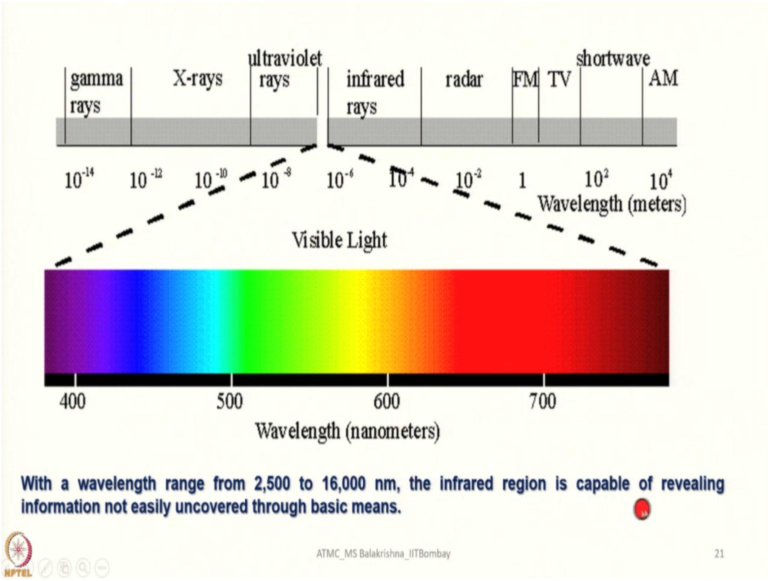
infrared spectroscopy is a vital tool to chemists wishing to identify what functional groups exist in unknown samples.

The light our eyes see is but a small part of a broad spectrum of electromagnetic radiation.

On the immediate high energy side of the visible spectrum lies the ultraviolet, and on the low energy side is the infrared.

So, infrared spectroscopy is a vital tool to chemists wishing to identify what functional groups exist in unknown samples. The light our eyes see is but a small part of a broad spectrum of electromagnetic radiation in the visible region. And in the immediate high energy side of the visible spectrum lies the ultraviolet and on the low energy side is the infrared one.

(Refer Slide Time: 22:10)



With a wavelength range from 2,500 to 16,000 nm, the infrared region is capable of revealing information not easily uncovered through basic means.

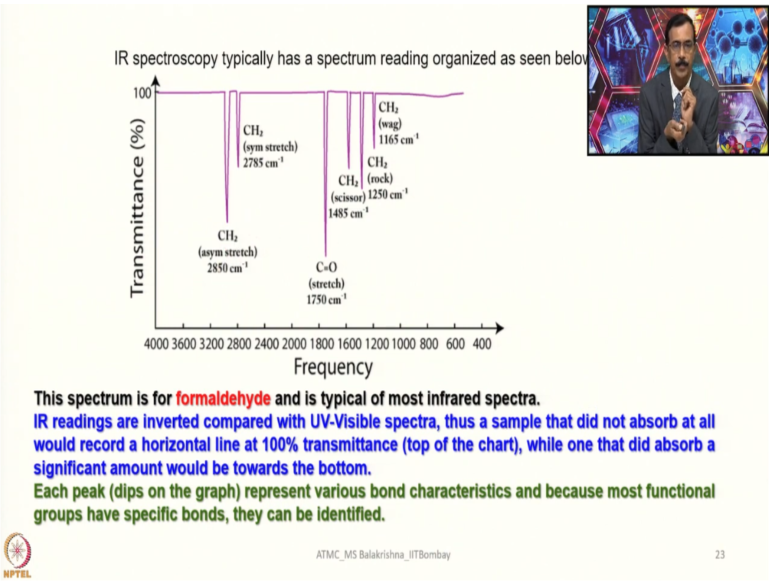
ATMC_MS Balakrishna_IITBombay 21

So, you can see here, this is the range. So, with a wavelength range of 2500 to 16,000 nanometre, the infrared region is capable of revealing information not easily uncovered through basic means. And what are those things? So, proton energies associated with the infrared region are not large enough to excite electrons but they are still strong enough to induce vibrational excitation of covalently bonded atoms and groups.

So, when you look into a bond, **(Video Starts: 22:43)** so, covalent bonds are not rigid sticks or rods but are like spring that can be rotated, if the single bond is there, or they can be stretched like this or they can be bent. This is how by simply absorbing energy in the infrared region, this will be stretching, bending or rotation. **(Video Ends: 23:03)**

So, this wide variety of vibrational motions is characteristic to a molecule's component atoms. All organic and inorganic compounds will absorb infrared radiation that corresponds in energy to these vibrations. And infrared spectrometers permit chemists to obtain absorption spectra of compounds that are unique reflections of their molecular structure.

(Refer Slide Time: 23:28)



IR spectroscopy typically has a spectrum reading organized as seen below,

This spectrum is for formaldehyde and is typical of most infrared spectra.

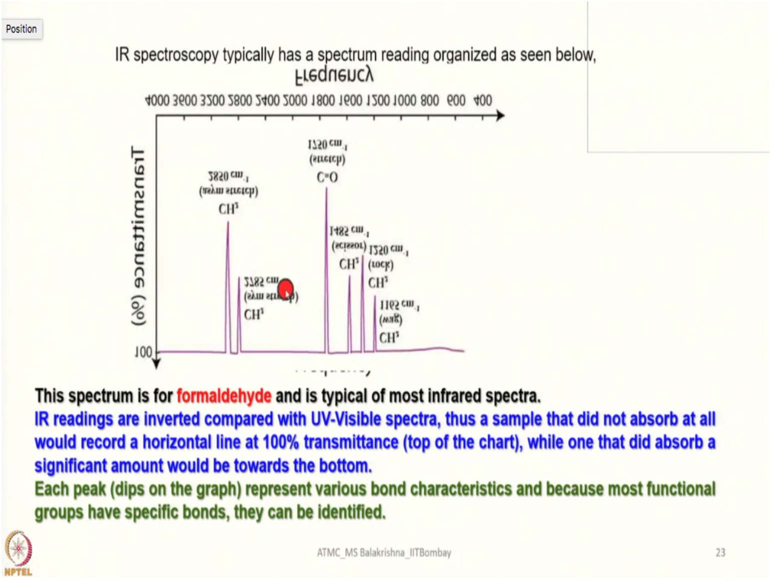
IR readings are inverted compared with UV-Visible spectra, thus a sample that did not absorb at all would record a horizontal line at 100% transmittance (top of the chart), while one that did absorb a significant amount would be towards the bottom.

Each peak (dips on the graph) represent various bond characteristics and because most functional groups have specific bonds, they can be identified.

So, now, let us look into a typical spectrum I have given here, and this is for formaldehyde. So, IR readings are inverted compared with UV-visible spectra. UV-visible spectra you can see like, it is coming, but it looks like inverted one with sharp peaks; while that one did not absorb, a significant amount would be towards the bottom. If they are absorbing, they will be falling down; those do not absorb will go flat like that.

Each peak dips on the graph represents various bond characteristics and because most functional groups have specific bonds, they can be readily identified. I have given the groups and also corresponding stretching frequency here. Formaldehyde, what is important is ketone carbonyl group is there and shows around 1750 centimetre minus.

(Refer Slide Time: 24:16)



IR spectroscopy typically has a spectrum reading organized as seen below,

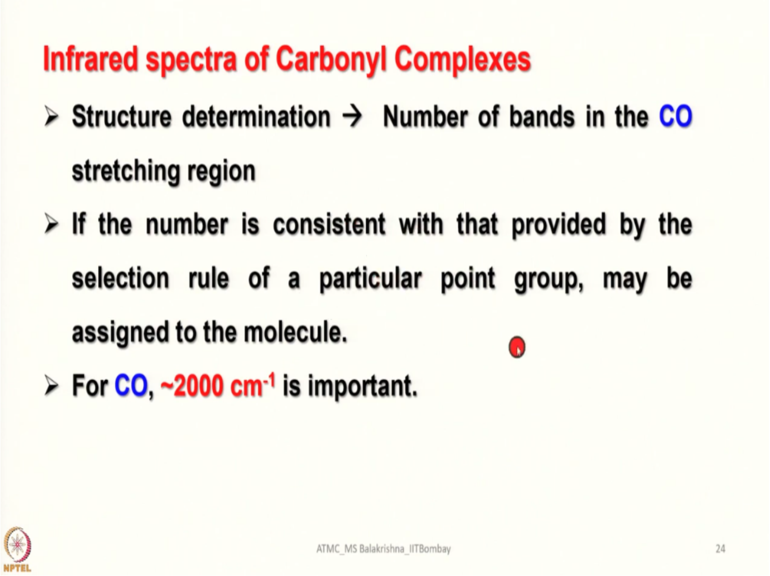
This spectrum is for formaldehyde and is typical of most infrared spectra.

IR readings are inverted compared with UV-Visible spectra, thus a sample that did not absorb at all would record a horizontal line at 100% transmittance (top of the chart), while one that did absorb a significant amount would be towards the bottom.

Each peak (dips on the graph) represent various bond characteristics and because most functional groups have specific bonds, they can be identified.

So, this is how, this is the inverse one. We are not considering this one; so, this how it looks like.

(Refer Slide Time: 24:22)

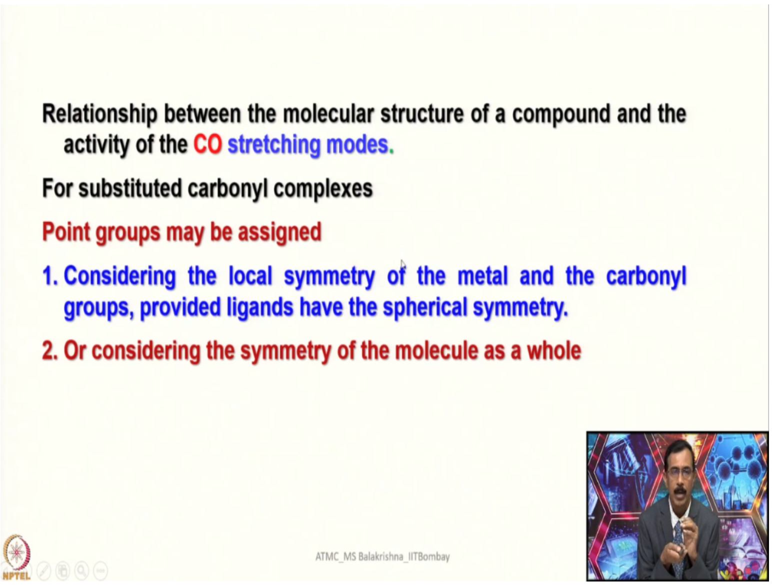


Infrared spectra of Carbonyl Complexes

- Structure determination → Number of bands in the CO stretching region
- If the number is consistent with that provided by the selection rule of a particular point group, may be assigned to the molecule.
- For CO, ~2000 cm^{-1} is important.

So, now, how it helps? It is very important in carbonyl complexes, infrared; and it is very vital in structure determination, also by simply looking into the number of bands in the CO stretching region. If the number is consistent with that provided by the selection rule of a particular point group, may be assigned to that molecule. Also, for CO, around 2000 centimetre inverse is very important.

(Refer Slide Time: 24:45)



Relationship between the molecular structure of a compound and the activity of the CO stretching modes.

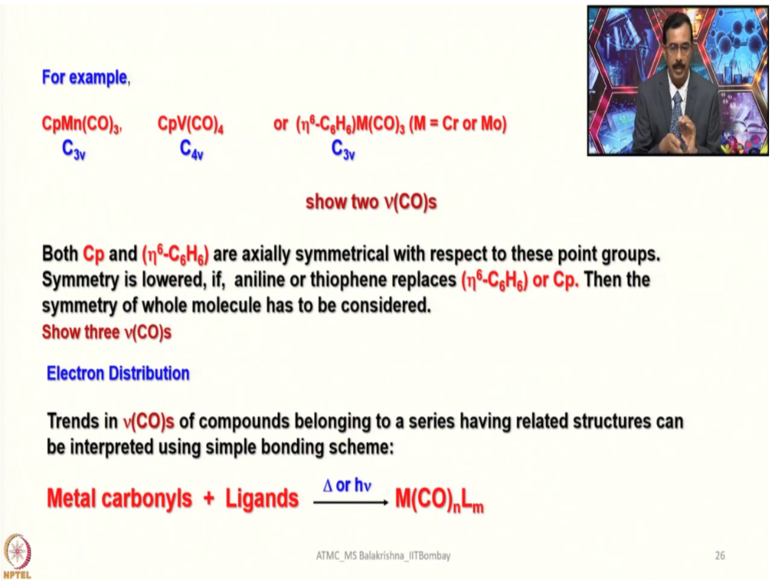
For substituted carbonyl complexes

Point groups may be assigned

1. Considering the local symmetry of the metal and the carbonyl groups, provided ligands have the spherical symmetry.
2. Or considering the symmetry of the molecule as a whole

Relationship between the molecular structure of a compound and the activity of stretching modes can also be understood and analysed to arrive at the structure of a molecule. For substituted carbonyl complexes, we can think of assigning point groups. Considering the local symmetry of the metal and the carbonyl groups, provided ligands are spherical symmetry, or by considering the symmetry of the molecule as a whole. So, we have 2 options before we assign, look into stretching frequencies.

(Refer Slide Time: 25:12)



For example,

$CpMn(CO)_3$, C_{3v} $CpV(CO)_4$ C_{4v} or $(\eta^6\text{-}C_6H_6)M(CO)_3$ (M = Cr or Mo) C_{3v}

show two ν(CO)s

Both Cp and $(\eta^6\text{-}C_6H_6)$ are axially symmetrical with respect to these point groups. Symmetry is lowered, if, aniline or thiophene replaces $(\eta^6\text{-}C_6H_6)$ or Cp. Then the symmetry of whole molecule has to be considered.

Show three ν(CO)s

Electron Distribution

Trends in ν(CO)s of compounds belonging to a series having related structures can be interpreted using simple bonding scheme:

$$\text{Metal carbonyls} + \text{Ligands} \xrightarrow{\Delta \text{ or } h\nu} M(CO)_nL_m$$

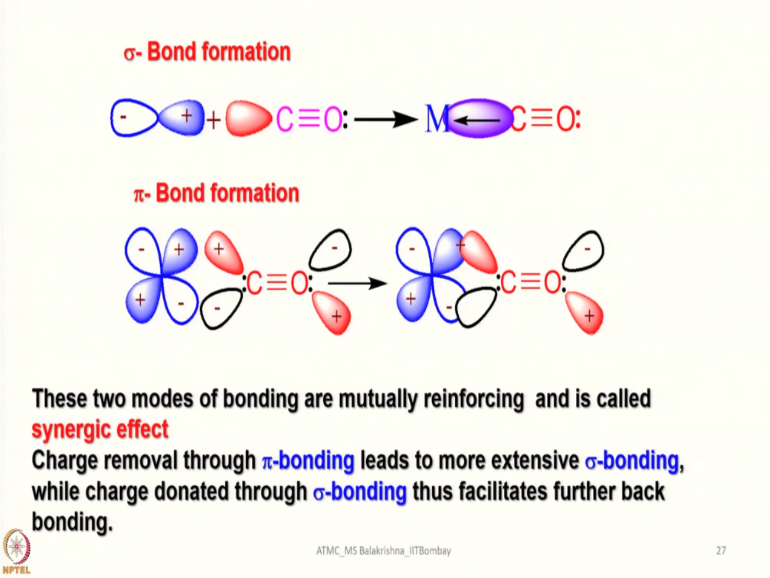
ATMC_MS Balakrishna_IITBombay

For example, let us look into example shown here. $CpMn(CO)_3$, it has C_{3v} symmetry; and $CpV(CO)_4$, it has C_{4v} symmetry; and if you just look into this one, arene $M(CO)_3$, it has again C_{3v} symmetry. So, all of them show 2 stretching frequencies for carbon monoxide. And both Cp and C_6H_6, arene are axially symmetrical with respect to these point groups. That means you can rotate through that one, passing through the middle of your Cp group or benzene, you can do the rotation.

And in case if we replace arene group with say aniline or thiophene, what happens, symmetry will be lowered, then the symmetry of whole molecule has to be considered. So, you should not consider local symmetry of metal, you have to consider the whole symmetry. In that case what happens, we will see 3 stretching frequencies. Electron distribution of course, electron distribution, I have discussed in length, how a pair of electrons on carbon will go to metal through sigma bonding and metal t_{2g} electrons will be transferred to pi star through back-bonding.

So, depending upon to what extent electrons are moving from metal to ligand, stretching frequency will vary accordingly.

(Refer Slide Time: 26:25)



These two modes of bonding are mutually reinforcing and is called **synergic effect**

Charge removal through π-bonding leads to more extensive σ-bonding, while charge donated through σ-bonding thus facilitates further back bonding.

ATMC_MS Balakrishna_IITBombay

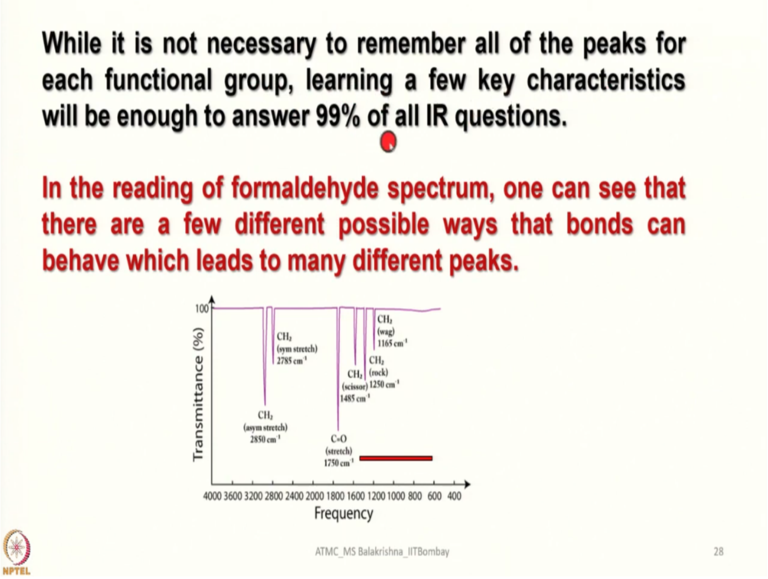
27

So, this is the typical bond explanation. So, this is sigma bonding and this is pi bonding. These 2 modes of bonding are mutually reinforcing and strengthening metal to carbon bond. This is called synergy effect or synergistic effect. Charge removal through pi bonding leads to more extensive sigma bonding, while charge donated through sigma bonding thus facilitates further back-bonding.

So, that means it is give and take. Because of sigma donation, now see carbonyl become electron deficient and metal become rich; it gives through back-bonding. With back-bonding what happens, metal become poor and carbon monoxide become rich, so, sigma bonding will be stronger. So, both of these opposite direction bonding strengthens each other. As a result, what happens, we call it as synergistic effect.

So, eventually, metal to carbon bond is strengthened and carbon to oxygen bond is weakened. So, to what extent this is weakened or strengthened depending upon how much electrons are coming from metal to pi star of carbon monoxide. So, that is a measure of the overall electron density at the metal centre. And if you are looking into the combined or mixed ligand complexes, what is the share of other back-bonding ligands and how they compare in terms of their back-bonding capabilities.

(Refer Slide Time: 27:39)



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% of all IR questions.

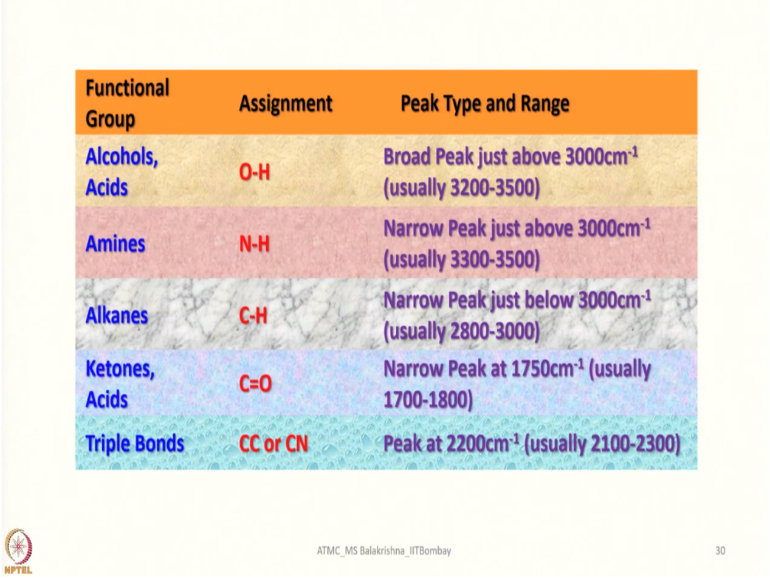
In the reading of formaldehyde spectrum, one can see that there are a few different possible ways that bonds can behave which leads to many different peaks.

For example, 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% of all IR questions. In the reading of formaldehyde spectrum, we have lots of peaks here. We should not focus on those things, we have to focus on only few things like CO stretching where it is, and also whether we have CH_3 stretching or any other.

So, these are very important while characterising. This we call it as fingerprint region. So, the complexity of infrared spectra in the 1450 and to 600 cm^{-1} region makes it very difficult. We get lot of peaks in this reason. It is difficult to assign all the absorption bands and because of unique pattern found there, it is often called the fingerprint region. It is not necessary to remember any peaks in this region as they will not help you determine any significant functional groups and not any significant functional groups come in that region either.

So, absorption bands in the 4000 to 1450 cm^{-1} are important; are usually due to stretching vibrations of diatomic units, and this is sometimes called the group frequency region. It is this region which is most practical to identifying groups. Some notable frequencies that should be remembered, I have shown here.

(Refer Slide Time: 29:00)



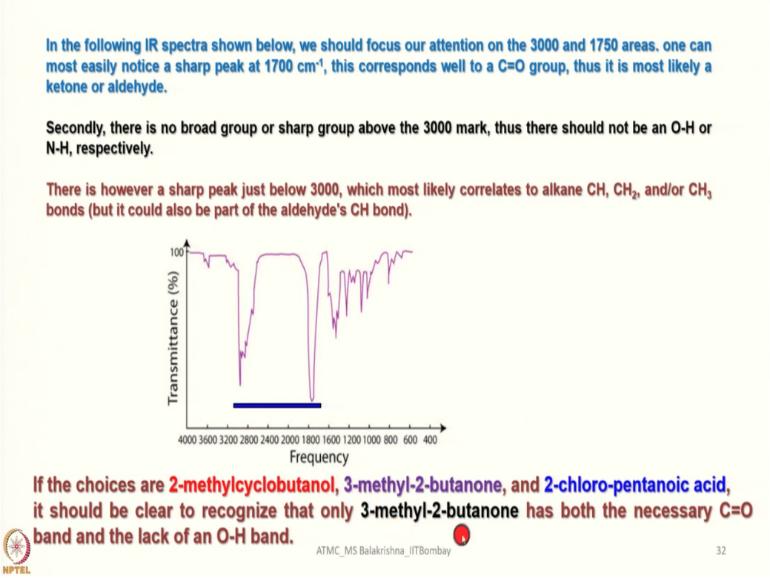
Functional Group	Assignment	Peak Type and Range
Alcohols, Acids	O-H	Broad Peak just above 3000cm^{-1} (usually 3200-3500)
Amines	N-H	Narrow Peak just above 3000cm^{-1} (usually 3300-3500)
Alkanes	C-H	Narrow Peak just below 3000cm^{-1} (usually 2800-3000)
Ketones, Acids	C=O	Narrow Peak at 1750cm^{-1} (usually 1700-1800)
Triple Bonds	CC or CN	Peak at 2200cm^{-1} (usually 2100-2300)

You can see, alcohols and acids O-H group is there; in this range it is there. For amines, N-H, this will be in this range. And for alkanes, C-H they come here, narrow peak. And ketones, acids, CO group will be here. And for triple bonds, CC or CN, it will be important; acetonitrile binding is there or acetylene binding is there; these are very important. So, one thing to keep in mind about IR spectra is that it can only tell you whether a group is present or not; it will not tell you how many groups or how large the molecule is.

One should remember, it is just qualitative, not quantitative. For example, if you see a sharp peak at 1750 cm^{-1}, it will tell us that there is some sort of a carbonyl group, it can be ketone, ester or part of an acid, etcetera or sometime it can be metal carbon monoxide with extensive backbonding or it may be bridging 2 metal centres, but it will not tell us perhaps there are 2 or 3 ketone groups present.

So, it would not tell you how many such groups are present. As I mentioned, it is qualitative, not quantitative. With this in mind and using only the selected few important peaks, we have to remember. So, we can say easily or we can guess what functional groups are present and thus identify the molecules from a few selections.

(Refer Slide Time: 30:20)



In the following IR spectra shown below, we should focus our attention on the 3000 and 1750 areas. one can most easily notice a sharp peak at 1700 cm^{-1}, this corresponds well to a C=O group, thus it is most likely a ketone or aldehyde.

Secondly, there is no broad group or sharp group above the 3000 mark, thus there should not be an O-H or N-H, respectively.

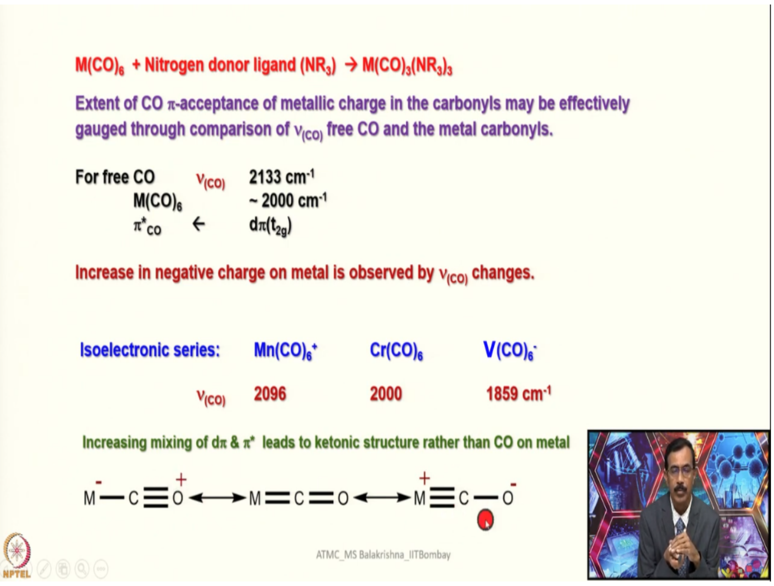
There is however a sharp peak just below 3000, which most likely correlates to alkane CH, CH_2, and/or CH_3 bonds (but it could also be part of the aldehyde's CH bond).

If the choices are 2-methylcyclobutanol, 3-methyl-2-butanone, and 2-chloro-pentanoic acid, it should be clear to recognize that only **3-methyl-2-butanone** has both the necessary C=O band and the lack of an O-H band.

In the following spectrum if you see, we should focus our attention on 3000 and 1750 cm^{-1}. One can most easily notice a sharp peak around 1700 cm^{-1} easily. So, that means you can conclude that there is a CO group. Thus, it is most likely a ketone or an aldehyde; this range also tell you. Secondly, there is no broad group or a sharp group around 3000 cm^{-1}, so, that means there is no O-H or N-H.

So, there is however a sharp peak just below 3000 cm^{-1}, which most likely corresponds to alkane, CH, CH2 and or CH3 bonds; it could be part of the aldehydic CH bond as well. So, that means, if the choices are there, like 2-methylcyclobutanol or 3-methyl-2-butanol and 2-chloropentanoic acid; if the options are these, it should be very clear that we will recognise this as 3-methyl-2-butanol which has both necessary CO bond and it lacks a O-H bond as well. So, immediately we can pick the right one among these 3 to say that this spectrum belongs to this molecule here. It is that easy.

(Refer Slide Time: 31:25)



$M(CO)_6$ + Nitrogen donor ligand (NR_3) → $M(CO)_3(NR_3)_3$

Extent of CO π-acceptance of metallic charge in the carbonyls may be effectively gauged through comparison of $\nu_{(CO)}$ free CO and the metal carbonyls.

For free CO $\nu_{(CO)}$ 2133 cm^{-1}
$M(CO)_6$ ~ 2000 cm^{-1}
$\pi^*_{CO} \leftarrow d\pi(t_{2g})$

Increase in negative charge on metal is observed by $\nu_{(CO)}$ changes.

Isoelectronic series:	$Mn(CO)_6^+$	$Cr(CO)_6$	$V(CO)_6^-$
$\nu_{(CO)}$	2096	2000	1859 cm^{-1}

Increasing mixing of dπ & π* leads to ketonic structure rather than CO on metal

$$\overset{-}{M}-C\equiv\overset{+}{O} \longleftrightarrow M=C=O \longleftrightarrow \overset{+}{M}\equiv C-\overset{-}{O}$$

ATMC_MS Balakrishna_IITBombay

So, now let us look into metal carbonyls. Metal carbonyls with nitrogen donors, you can make a maximum, you can replace a maximum of 3 carbonyls I mentioned. So, now if you see here, a free carbon monoxide is around 2133 cm^{-1} and metal hexacarbonyls will show around 2000 cm^{-1}. And increase in negative charge on metal is absorbed by νCO changes. For example, you can see here; so, it is positive charge and it is here neutral, and it is negative charge here.

So, when negative charge is there, more electron density is there; as a result, stretching frequency will drop, more electron density goes to the pi star, and it is midway, 2000 cm^{-1}, whereas here it is positively charged. So, less electron density goes from the metal. As a result, stretching frequency is more. So, we should be able to analyse the electron density that resides on metal very easily by looking into the stretching frequencies.

And of course, the 2 extreme cases of metal carbonyls are shown here, very strengthened and very weak and very strong here, CO group. And here of course, metal to carbon strength increases in this order. This information very nicely comes from IR spectroscopy.

(Refer Slide Time: 32:29)

π-acceptor ability of CO in $M(CO)_6$ place it at ~ 0.1-1.2 electron pairs per CO

1. $\nu_{(CO)}$ decreases as more and more CO groups are substituted
2. Complete substitution of COs from $M(CO)_6$ has been achieved only by polydentate ligands or ligands with electronegative substituents on donor atoms.

The best competitors for CO are phosphines.

Advantages with phosphines is coordination properties can be readily altered.

Among no π-acceptors ligands: diglyme, NH_3, H_2O etc.,

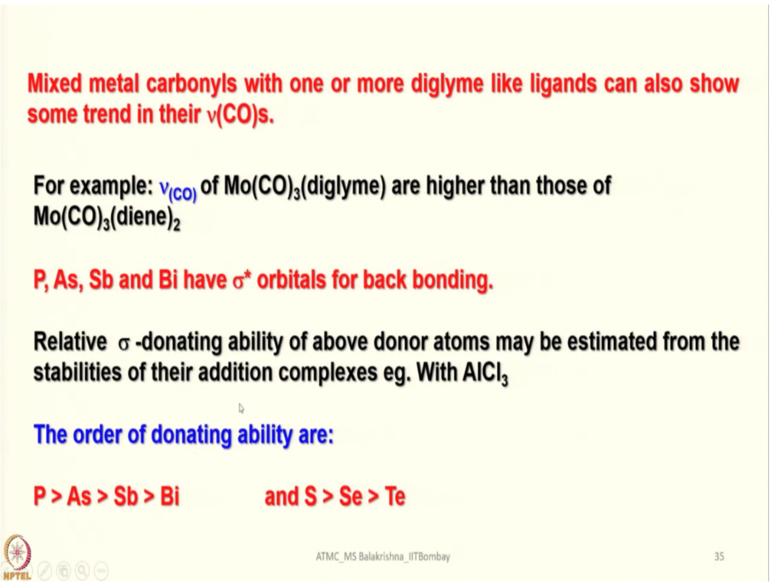
Diethylene glycol dimethyl ether

So, pi acceptor ability of CO in metal hexacarbonyls will tell you that it can take anywhere between, 0.1 to 1.2 electron pairs to its pi star orbitals. So, νCO decreases as more and more groups are substituted. That means more and more groups are substituted with non-back-bonding ligands. In that case what happens, the responsibility falls on few carbon monoxide left on the metal.

As a result, the stretching frequency decreases. So, complete substitution of CO from $M(CO)_6$ has been achieved only with strong pi acceptor ligands such as PF_3. The best competence for CO are phosphines, especially having strong electron withdrawing groups or electronegative groups on phosphorous. So, advantage with phosphines is, coordination properties can be readily altered, but you cannot do with carbon monoxide.

So, among more pi acceptor ligands; example, diglyme, ammonia and all those things; if you want to know what is a diglyme, it is an ether, something like this. And how to spell it, you can say diethylene glycol dimethyl ether. Many reactions you come across diglyme; you should be able to write the structure and you can tell it is diethylene glycol dimethyl ether.

(Refer Slide Time: 33:43)



Mixed metal carbonyls with one or more diglyme like ligands can also show some trend in their ν(CO)s.

For example: $\nu_{(CO)}$ of $Mo(CO)_3$(diglyme) are higher than those of $Mo(CO)_3(diene)_2$

P, As, Sb and Bi have σ* orbitals for back bonding.

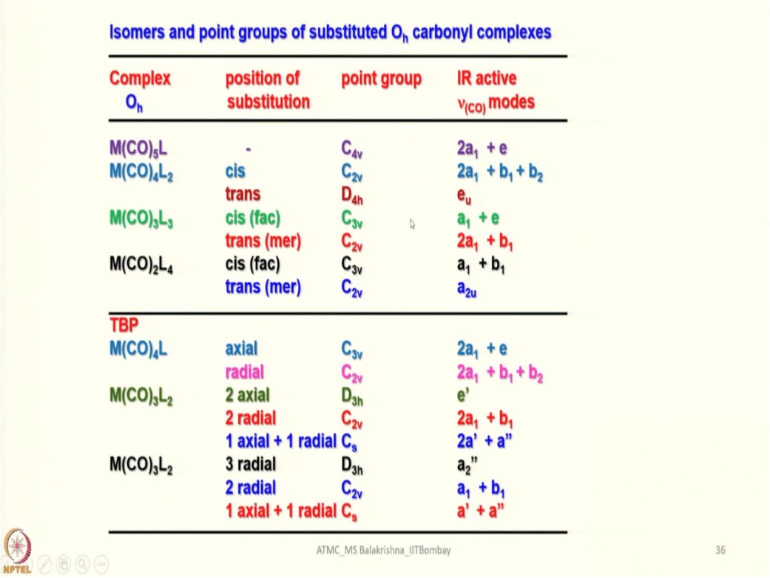
Relative σ-donating ability of above donor atoms may be estimated from the stabilities of their addition complexes eg. With $AlCl_3$

The order of donating ability are:

P > As > Sb > Bi and S > Se > Te

So, mixed metal carbonyls with one or more diglyme like ligands can also show some trends in their stretching frequencies. For example, if diglyme is there, that shows higher stretching frequency than having simple diene here. Also, when we have these things, sigma orbitals for back bonding decreases. And then, relative sigma donor ability of above donor atoms may be estimated from the stabilities of their addition complexes, especially with aluminium trichloride as a Lewis acid. The order of donating ability also follows this order. This is about only back bonding, this has to do nothing with stretching frequencies.

(Refer Slide Time: 34:19)

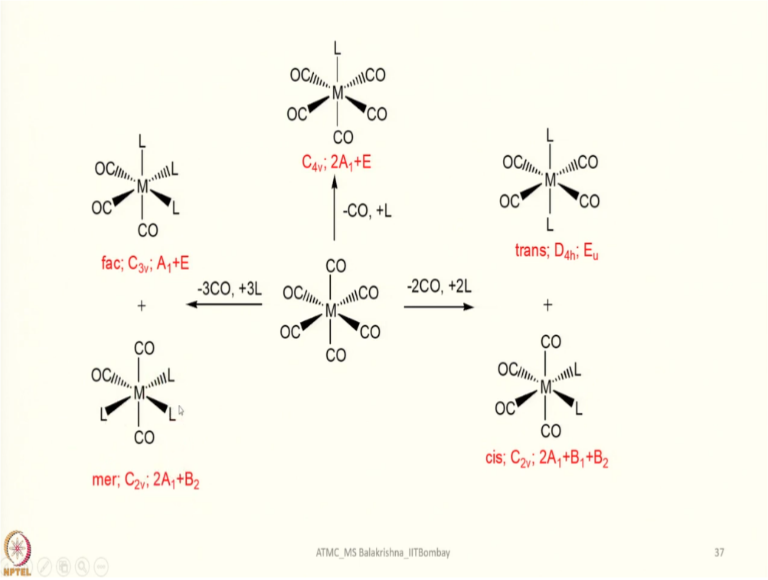


Isomers and point groups of substituted O_h carbonyl complexes

Complex O_h	position of substitution	point group	IR active $\nu_{(CO)}$ modes
$M(CO)_5L$	-	C_{4v}	$2a_1 + e$
$M(CO)_4L_2$	cis	C_{2v}	$2a_1 + b_1 + b_2$
	trans	D_{4h}	e_u
$M(CO)_3L_3$	cis (fac)	C_{3v}	$a_1 + e$
	trans (mer)	C_{2v}	$2a_1 + b_1$
$M(CO)_2L_4$	cis (fac)	C_{3v}	$a_1 + b_1$
	trans (mer)	C_{2v}	a_{2u}
TBP			
$M(CO)_4L$	axial	C_{3v}	$2a_1 + e$
	radial	C_{2v}	$2a_1 + b_1 + b_2$
$M(CO)_3L_2$	2 axial	D_{3h}	e’
	2 radial	C_{2v}	$2a_1 + b_1$
	1 axial + 1 radial	C_s	2a’ + a”
$M(CO)_3L_2$	3 radial	D_{3h}	a_2”
	2 radial	C_{2v}	$a_1 + b_1$
	1 axial + 1 radial	C_s	a’ + a”

So, now I have given depending upon the type of point group possessed by these molecules and how many IR active modes are there. For example, $M(CO)_4L$ is there, you can see 3 CO bands. And if you have something like this cis, you can see 4. And if you have trans, you can see 1. And you can just go through this one, I have given for octahedral geometry and I have given for trigonal bipyramidal geometry as well. Also, I have mentioned position of carbon monoxide and also the point group here; just you can look into it.

(Refer Slide Time: 34:50)



C_{4v}; $2A_1$+E

-CO, +L

fac; C_{3v}; A_1+E

-3CO, +3L

-2CO, +2L

trans; D_{4h}; E_u

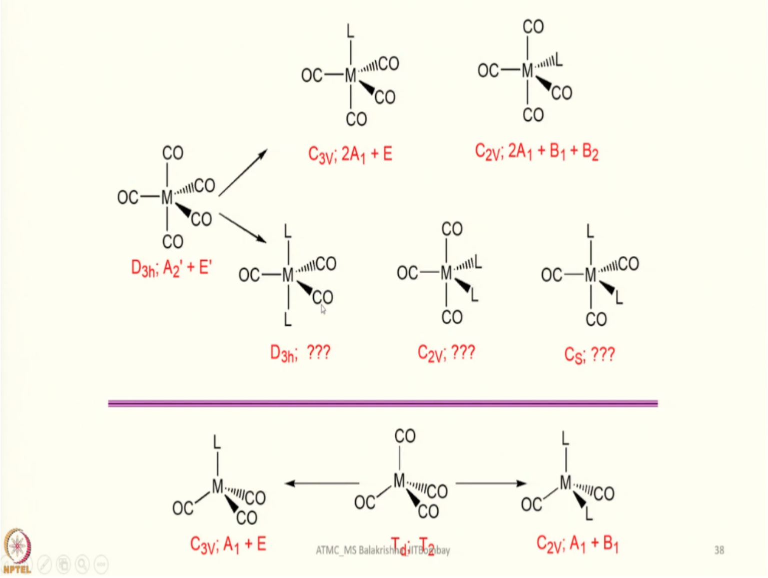
+

mer; C_{2v}; $2A_1$+B_2

cis; C_{2v}; $2A_1$+B_1+B_2

And now for example, you take hexacarbonyl and if you replace 1, 3 and you get a facial; in that case, we get only 2 provided all ligands are identical. And then, in case what happens, if you have $M(CO)_5L$, you get 3 stretching frequencies. And if you have trans, we get only one stretching frequency. Similarly, if we have cis here, we can get 4 stretching frequencies. And if we have something like this here, we can get 3 stretching frequencies, meridional.

(Refer Slide Time: 34:50)



C_{3V}; $2A_1$ + E

C_{2V}; $2A_1$ + B_1 + B_2

D_{3h}; A_2' + E'

D_{3h}; ???

C_{2V}; ???

C_S; ???

C_{3V}; A_1 + E

T_d; T_2

C_{2V}; A_1 + B_1

So, in the same way, when we go for pentacarbonyl and if you start replacing carbon monoxide with L, the number of stretching frequencies would be shown in this figure here. So, 3 active; here 4 active are there; and in this case, CS, so, all of them are unique, you can see 3 different and same thing here and same thing here. With this, so, let me conclude about IR spectroscopy and NMR spectroscopy.

And overall whatever I wanted to tell as a part of this course, probably in my last lecture, I shall try to consolidate and sum-up. Also if anything is left, little bit I will highlight about that one and conclude my lecture. So, that would be the 60th lecture. So, thank you for your kind attention. And I have to go through quickly in case of IR and NMR because of lack of time.

Of course, but everything is there in the slides and also I have spoken already. Please listen to what I say and also try to look into all the slides in detail and try to understand the chemistry behind these things. Thank you so much.