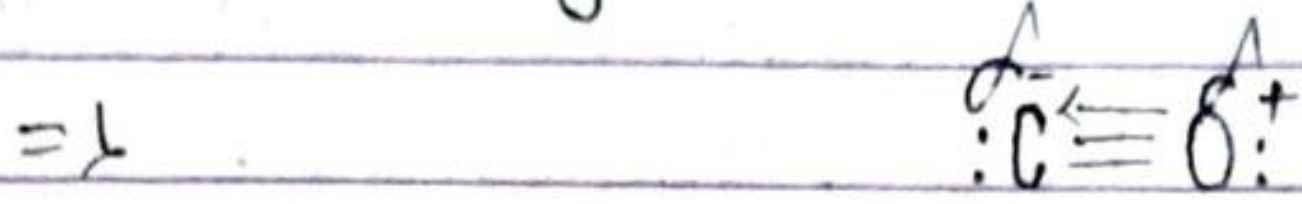
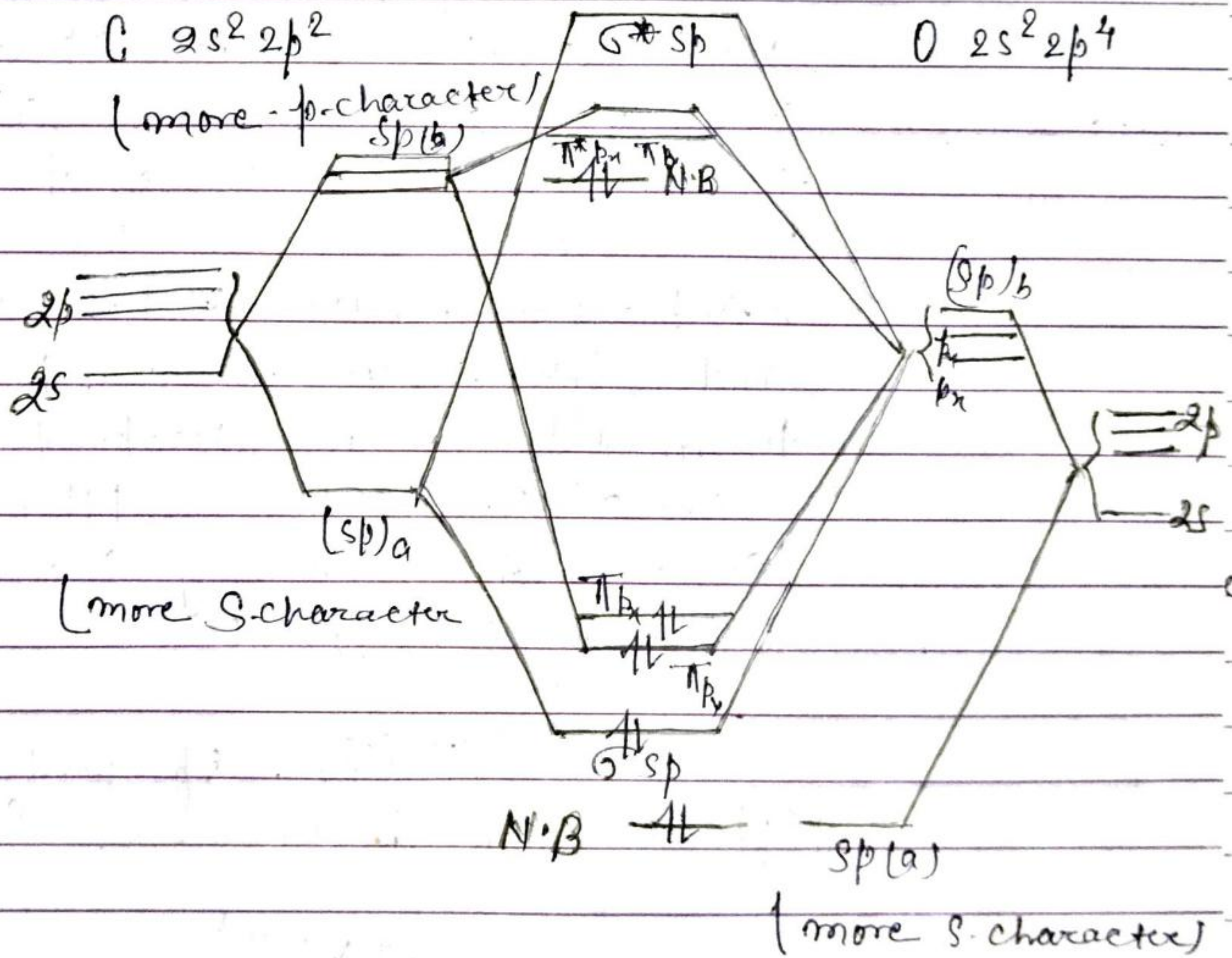


Q: Why bonding in metal carbonyls occur through carbon (C) and not through O?



As there is \ominus charge on C while on oxygen (O), there is \oplus charge. Hence there is greater electron density on C than O. And that is why bonding in metal carbonyl take place through C & not through O.

On the basis of M.O diagram of CO.

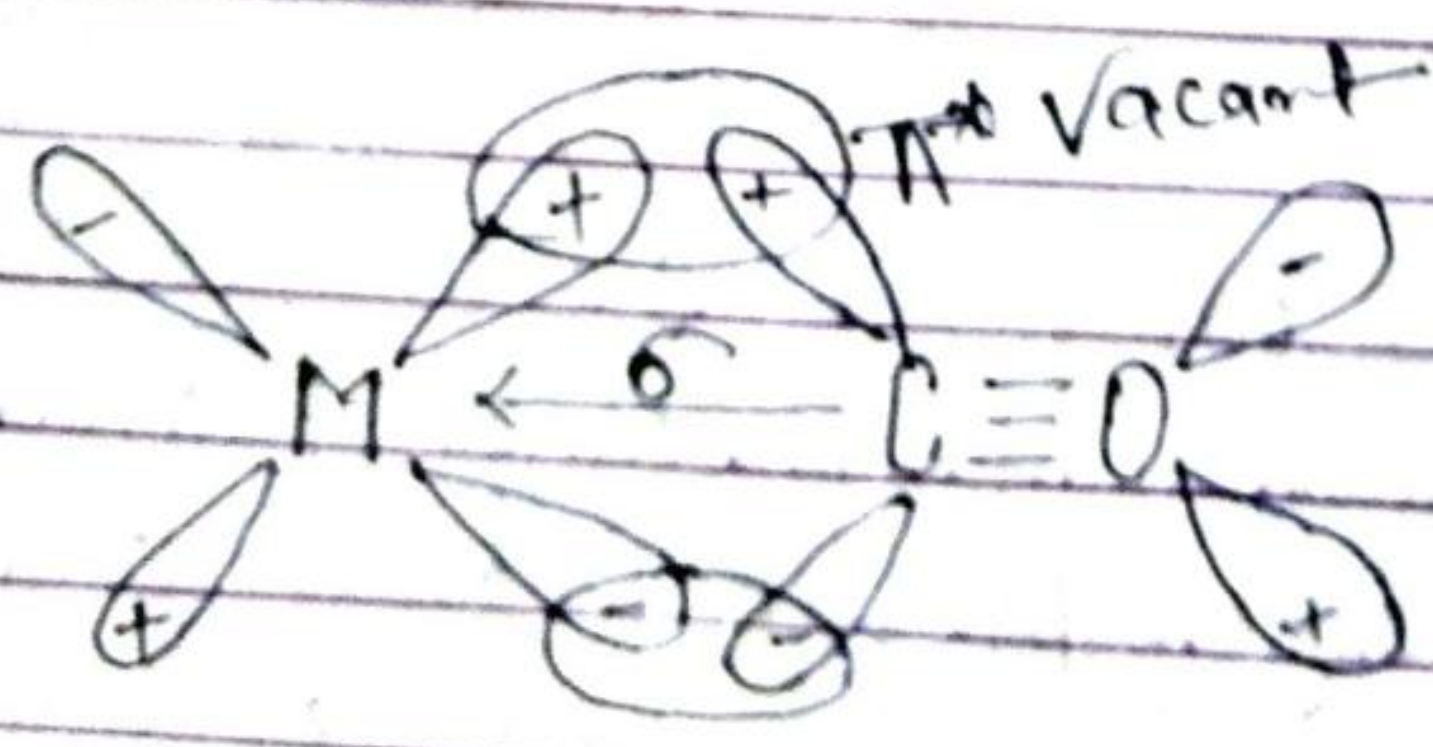
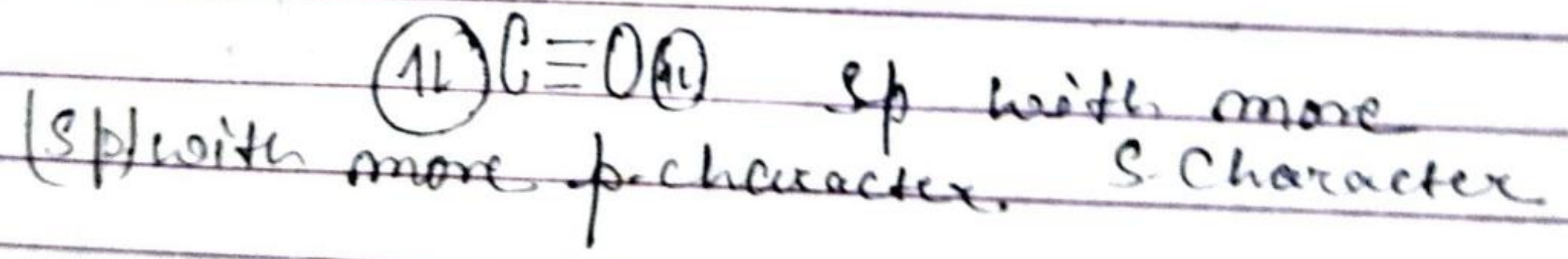


Here, on both C & O sp hybridisation occurs producing two non-equivalent sp hybrids on each C & O ($sp(a)$ has more s-character & hence, lower in energy while $sp(b)$ has more p-character & hence higher in energy $sp(a)$ of O.

& $(sp)_5$ of C remain as NiB orbitals
 It is obvious from M.O
 diagram of CO that both C & O have
 a lone pair on each. The lone pair
 on O resides in $(sp)_5$ hybrid which
 has more s-character. Hence, it is
 much closer to the oxygen nucleus
 and thus under the complete control
 of oxygen nucleus. Secondly due to
 more s-character, the electron cloud
 doesn't spread away from the nucleus

The lone pair on C also resides
 in sp hybrid but with more p-character
 and hence the electron cloud spreads
 away from the nucleus. At the same
 times it is not under the control of
 the nucleus as on O.

Subsequently, the lone pair on C is better
 and appropriate position to be donated
 to metal ion in respect of lone
 pair on O. That is why in metal
 carbonyl the bonding occurs through
 C & not through O.

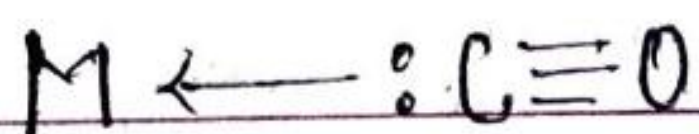


$$\nu = \frac{1}{2\pi} \sqrt{k/\mu}$$

So, where k = force constant
and μ = reduced mass.

Since for CO molecule will be the same whether it is free complex with the metal and hence vibration frequency of CO will depend on the force constant of $C \equiv O$

Since the CO bond order and hence force constant in free CO bond order is three which on co-ordination to a metal ion gets decreased,



Secondly, in metal complex of CO metal back donates electron density towards the π^* molecular orbital of CO and this also causes decrease in bond order of CO in metal complexes. Thus, the bond order of CO and hence, the bond force constant in CO changes from free CO to metal complex.

As the force constant decreases of CO in metal complexes, the vibrational frequency of ligated CO is expected to decrease from free CO to ligated CO.

The free CO has vibrational freq^y 2250 cm⁻¹. While for ligated the vibration frequency is observed at 2220 to 1700 cm⁻¹.

The extent of decrease in vibration absorption frequency of free CO in metal complex depends on the extent of decrease in three bond character and hence force constant of CO after complexes.

CO molecule in a metal complex may remain into two different forms.

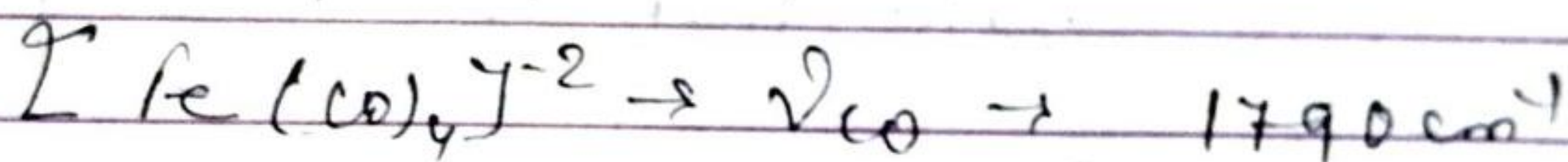
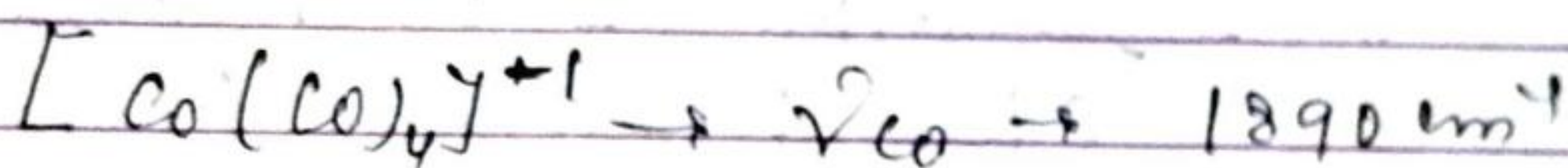
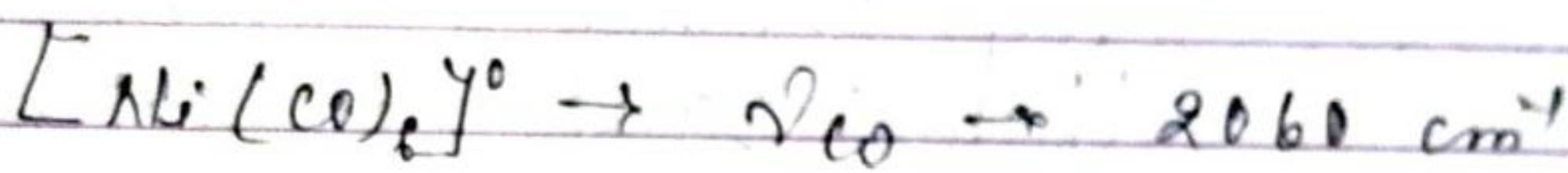
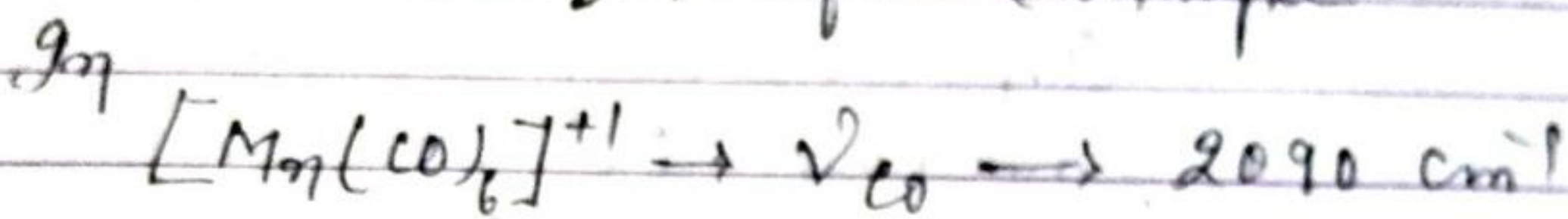
- (i) As terminal CO complexed or co-ordinated to only one metal ion. While in second cases it may remain as bridged CO molecule simultaneously co-ordinating to same and different metal ion.

In terminal carbonyl, the bond order of CO decreases mainly by back donation of electron density of a metal to antibonding π^* of CO molecule. The back donation capacity of metal depend on the charge on in metal carbonyl.

The greater is -ve charge on metal ion, the greater back donation of electron density toward the π^* MO of CO. Hence, greater is decreased in triple bond character of CO and that's why the greater is decreased in vibrational frequency of CO.

Quite Contrary to this. If there is opposite charge on metal and metal carbonyl, there is only a little back donation of electron density from metal to π^* of CO and this cause only a slight decrease in triple bond character of CO and there is only a slight decrease in vibration absorption frequency of CO.

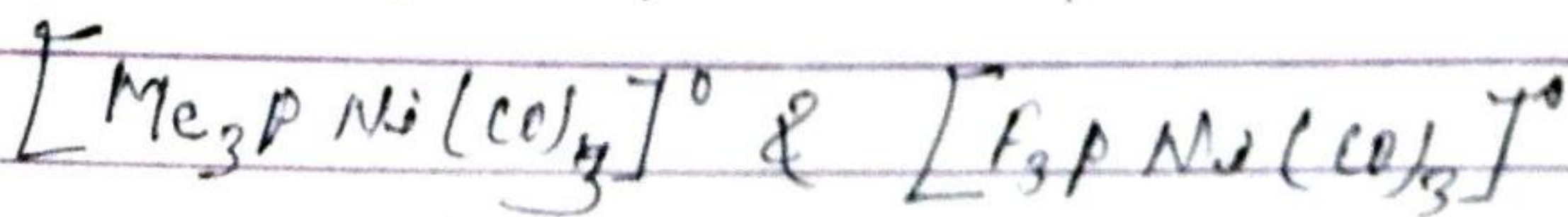
As for example



Thus, A terminal CO generally absorbs near 2000 cm^{-1}

The wave number of terminal CO in metal complex also depend on π -acceptor character of any other ligand. If there is a ligand with very strong π -acceptor character there will be only a little back donation to CO molecule and hence, there is only a little decrease in vibrational absorption frequency of terminal CO.

As for example



Due to greater electronegativity of fluorine, Pt is greater π -acceptor than $(C_6H_5)_3P$, so back donation to CO molecule in $(Me)_3P$ is less than in $[Ni(CO)_2Pt_2]$

that's why ν_{CO} 1790 cm^{-1} in $[Pt_2Ni(CO)_3]$ is greater than that in $[Me_3P Ni(CO)_3]$

In bridging carbonyl complexes the bridging CO resembles a CO group in organic complex compound like (ketone) and hence the bridging CO absorbs at vibrational frequency very close to carbonyl (CO) of ketone of like that i.e. nearly 1700 cm^{-1} .

Thus, A bridging carbonyl absorbed at 1700 cm^{-1}

Generally, A bridging CO usually shows two vibrational frequency that is at 1850 cm^{-1} and 1700 cm^{-1} . This also differs from a bridging CO terminal CO in metal carbonyl.