PHOTODETACHMENT SPECTROSCOPY AND UNDERSTANDING THE ELECTRONIC STRUCTURE OF METALLOCARBOHEDRENES

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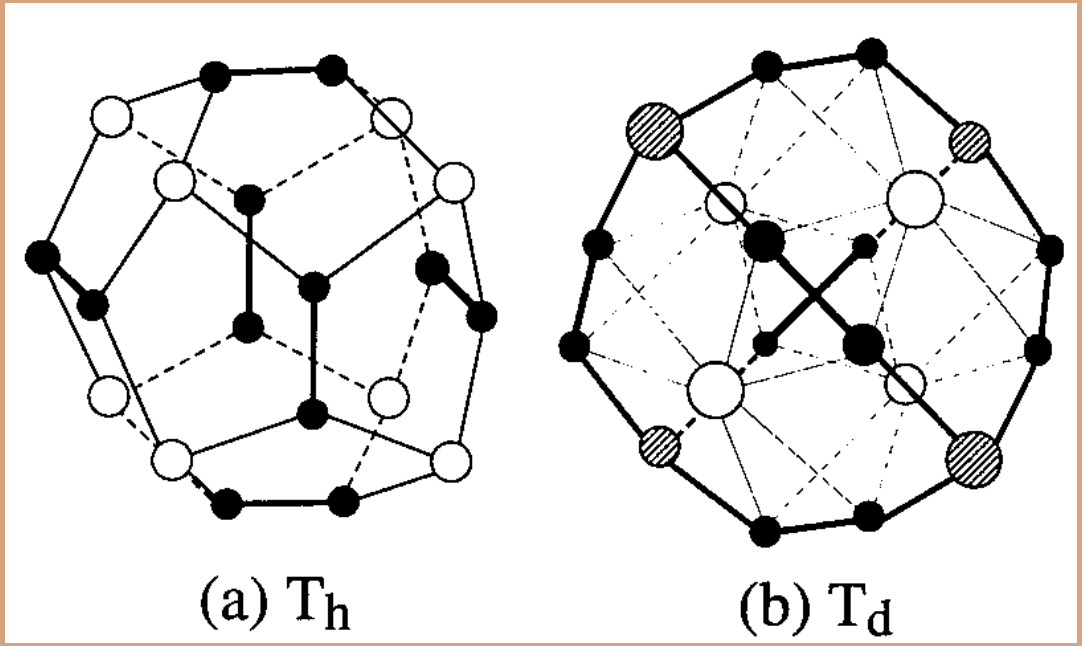
INTRODUCTION

=>Metallocarbohedrenes(met-cars) MnCy n=7,8 y=10-14

=>Castleman et al (1992),Ti_8C_{12},pentagonal dodecahedral

=>Theoretical calculations leads the different possible structures such as dodecahedral,tetrahedral,cubic and metal decorated C12 cage structure

=>Wang et al (1997) published experimental results in evidence for the tetrahedral structure



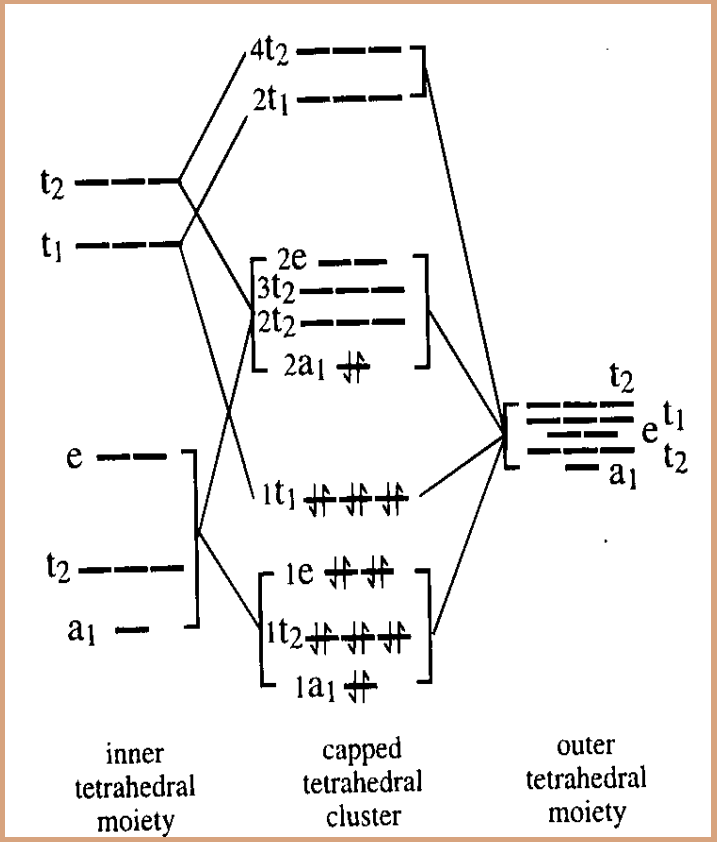
In T_d structure there are two subsets of metal atoms THN and thn

16 electrons of the Ti atom localize on one of the Tetrahedron site and the other 4 electrons localize on the remaining tetrahedran site

$Ti_4(0)_{THN}Ti_4(III)_{thn}$ -----> $Ti_4(III)_{THN}Ti_4(0)_{thn}$

Ground state Excited state

TETRACAPPED Ti_8C_{12} Met-Car ORBITAL DIAGRAME



=>The number of metal electrons in the cluster is 32

=>Contribution to C2 Dimer is 12 electrons

⇒So,that we have 20 remaining electrons for the metal-metal interaction that forms the valance orbital of the Met-Car.

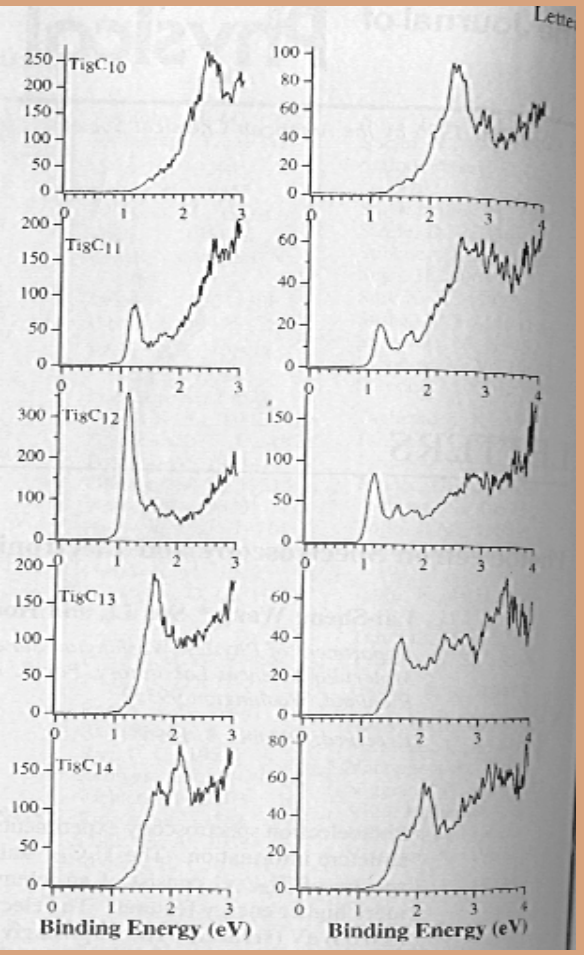
=>Four sets of four sets of orbitals available

=>Filling of the 9 bonding orbital is expected to make an especially stable Met-Car

=>The 2 extra electron fill the higher energy $2a_1$ orbital

=>This is consistent with the low Ionization potential measured for the Ti cluster

Photodetachment spectra of Ti_8C_y anion at two detachment laser



⇒Y can be 10-14

⇒Left panel at 3.49eV(355nm),right panel at 4.66 eV(266nm)

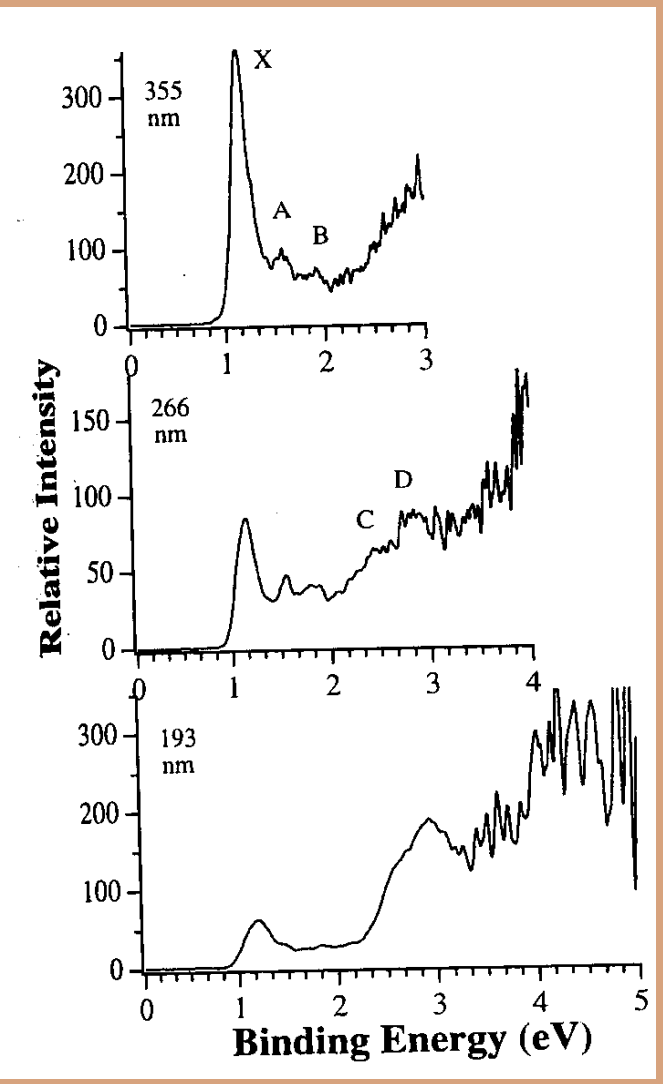
⇒Among the others Ti_8C_{12} anion spectrum has the special feathers

=>this cluster has the lowest Electron Affinity among the other cluster

=>The intense Threshold peak at Ti_8C_{12} anion indicates that the electron affinity of Ti_8C_{12} is 1.06(adiabatic,1.16(vertical)

=>the anomalously low EA for the Ti_8C_{12} is at least partially responsible for the low mass abundance of the Ti_8C_{12} cluster

Comparison of photoelectron spectra of Ti_8C_{12} anion at three photon energy



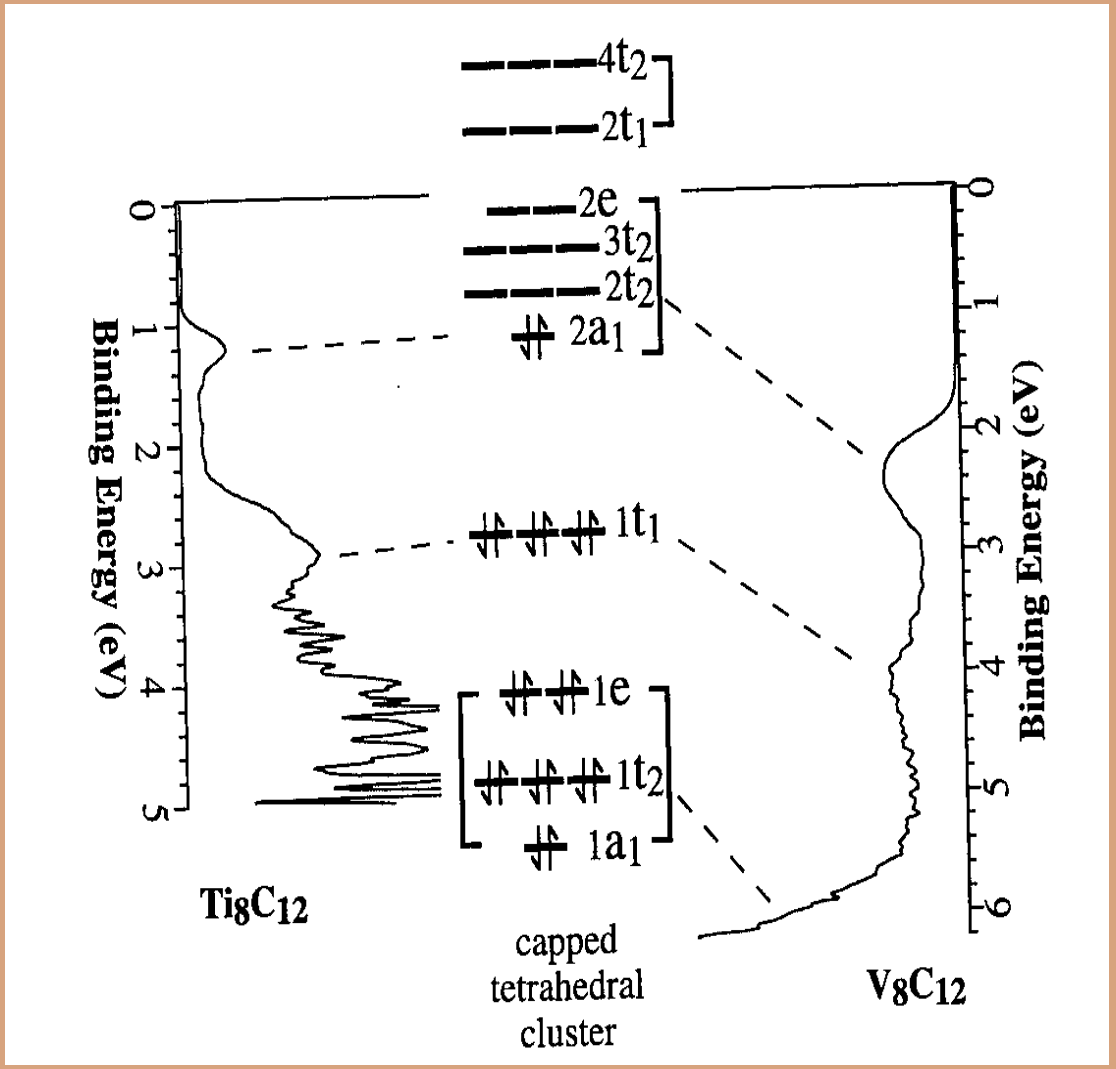
=>at 3.49 eV,three features were clearly observed(X(1.16eV) A(1.56) and B(1.81) and the signals at higher binding energies also observed

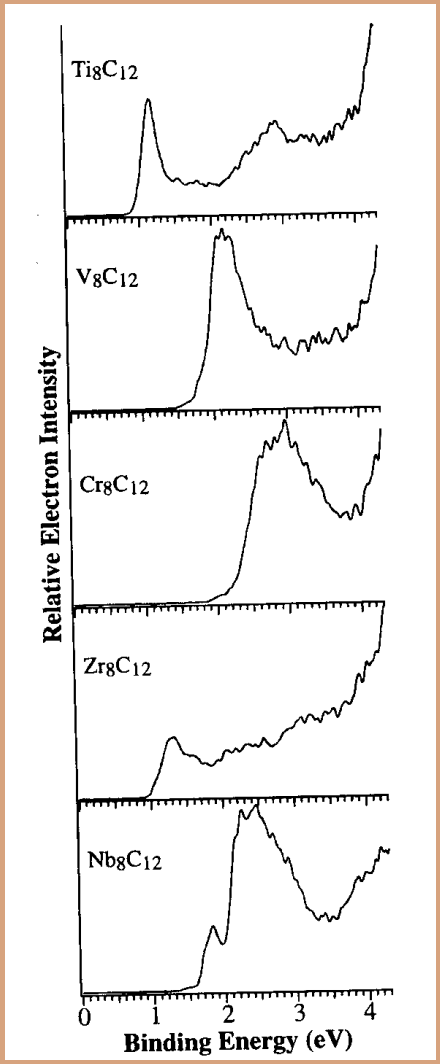
=>more transitions are shown at the 6.42 eV spectrum due to poor resolution and lower signal to noise ratio

=>features A and B are barely visible in the 6.42eV due to poor resolution and lower signals at this photon energy

=>In 6.42 eV spectrum the lower energy features(X,A,B) followed by a small energy gap(0.7 eV) and more transition at higher Binding Energy

The comparison for the photoelectron spectra of Ti_8C_{12} and V_8C_{12} anions and the valance molecular orbitals derived from the tetracapped tetrahedra M_8C_{12} metcar





CONCLUSION

[1] The electronic structure of Ti_8C_{12} discussed and the photodetachment spectra of that same kind cluster is compared with the corresponding Valance electron orbital

[2] Photodetachment spectra of various cluster has been interpreted

[3] The photoelectron spectra provide yet the most quantitative electronic structure and spectroscopic data that can be used to compare quantitatively with theoretical calculations

REFERENCES :-

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