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$_8$C$_{12}$, pentagonal dodecahedral
=> Theoretical calculations leads the different possible structures such as dodecahedral, tetrahedral, cubic and metal decorated C$_{12}$ 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.

\[
\text{Ti}_4(0)_{\text{THN}} \text{Ti}_4(\text{III})_{\text{thn}} \quad \longrightarrow \quad \text{Ti}_4(\text{III})_{\text{THN}} \text{Ti}_4(0)_{\text{thn}}
\]

Ground state  Excited state

\[
\text{TETRACAPPED Ti}_8\text{C}_{12} \text{ Met-Car ORBITAL DIAGRAME}
\]

\[
\Rightarrow \text{The number of metal electrons in the cluster is 32}
\]

\[
\Rightarrow \text{Contribution to C2 Dimer is 12 electrons}
\]

\[
\Rightarrow \text{So, that we have 20 remaining electrons for the metal-metal interaction that forms the valance orbital of the Met-Car.}
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\[
\Rightarrow \text{Four sets of four sets of orbitals available}
\]

\[
\Rightarrow \text{Filling of the 9 bonding orbital is expected to make an especially stable Met-Car}
\]

\[
\Rightarrow \text{The 2 extra electron fill the higher energy } 2\text{a}_1 \text{ orbital}
\]

\[
\Rightarrow \text{This is consistent with the low Ionization potential measured for the Ti cluster}
\]
Photodetachment spectra of Ti$_8$C$_y$ anion at two detachment laser

⇒ Y can be 10-14
⇒ Left panel at 3.49 eV (355 nm), right panel at 4.66 eV (266 nm)
⇒ Among the others Ti$_8$C$_{12}$ anion spectrum has the special feathers
⇒ this cluster has the lowest Electron Affinity among the other cluster
⇒ The intense Threshold peak at Ti$_8$C$_{12}$ anion indicates that the electron affinity of Ti$_8$C$_{12}$ is 1.06 (adiabatic), 1.16 (vertical)
⇒ the anomalously low EA for the Ti$_8$C$_{12}$ is at least partially responsible for the low mass abundance of the Ti$_8$C$_{12}$ cluster
Comparison of photoelectron spectra of Ti$_8$C$_{12}$ anion at three photon energy

=> at 3.49 eV, three features were clearly observed (X (1.16 eV), 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 6.42 eV 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$_8$C$_{12}$ and V$_8$C$_{12}$ anions and the valance molecular orbitals derived from the tetracapped tetrahedra M$_8$C$_{12}$ metcar
CONCLUSION

[1] The electronic structure of Ti$_8$C$_{12}$ 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 :-

=> R. Selvan, T. Pradeep, Curr. Sci. 74(vol), 1998(year) 666(page)