Structural, stability and electronic properties of Os_mC_n ($m+n\leq7$) clusters

M Luo[1], W L Guo[1]*, X R Zhang[2] & X G Meng[1]

[1]Department of Biology and Chemical Engineering, Jiangsu University of Science and Technology
Zhenjiang, Jiangsu, 212003, China

[2]Department of Mathematics and Physics, Jiangsu University of Science and Technology
Zhenjiang, Jiangsu, 212003, China

*E-mail: guowl1954@163.com

The structures, relative stabilities and electronic properties of Os_mC_n clusters for $m+n\leq7$ have been investigated by the density functional theory. The planar geometries have been preferred for small carbon mixed clusters up to $m+n=5$, for those with size of $m+n\geq6$, the C-rich clusters are still planar structures, while Os-rich clusters are three-dimensional structures, and the most energetic favourable structures tend to be capped pyramid or irregular prism. The stability analysis indicates that the mixed clusters are more stable than those of the corresponding pure Os_n clusters, among which OsC_2, Os_2C_2, Os_4C_2, Os_2C_4 exhibit higher stability than their neighbouring clusters. Os5d and C2p electrons play dominant roles in chemical reaction of mixed clusters.

Keywords: Os_mC_n ($m+n\leq7$) clusters, Structures, Stability, Density functional theory, Electronic properties

1 Introduction

The mixed clusters have rich diversities in composition, structure and properties which can greatly expand the properties of pure clusters and make them have more extensive and excellent performance[1-3]. Transition metals (TM) play important roles in the field of metallurgy and catalysis due to their d electrons, which make them exhibit special electronic structures and physical-chemical properties. Therefore, TM clusters and TM-mixed clusters have been extensively studied[4-10]. Os as one of the important TM especially Os-mixed clusters have been carried out in the past few years. Zheng *et al*[11]. calculated Os, OsC and OsN clusters by using first principle calculations, their results confirmed that Os, OsC, and OsN in the hexagonal structures are more stable than those under the structure of sodium chloride. Chen *et al*[12]. investigated the structures and electronic properties of OsB_2. Young *et al*[13,14]. found that mixing C, N, B, O and other light elements into transition metals may form a directed covalent bond. By the first principles plane-wave pseudopotential calculations based on the density functional theory, Liang *et al*[15]. studied the equations of states and structural properties of transition metal compounds OsB_2 and OsO_2, the possible high pressure phase transitions of OsO_2 and its rutile, pyrite and fluorite phases under high pressure, found that incorporating light elements (boron, oxygen, carbon or nitrogen) into osmium is possibly a new way to prepare super hard material. It would be a significant work to investigate lighter elements mixed osmium clusters.

Our research group[16-18] has studied the pure osmium clusters, Os-N and Os-B cluster system. However, the structural information of the mixed Os_mC_n clusters with $m+n\leq7$ has not been investigated so far. Therefore, the geometries, stabilities and electronic properties of Os_mC_n ($m+n\leq7$) clusters have been investigated in the present work. The density functional theory has been taken to study the lowest-energy optimized structures. However, it is a difficult task to experimentally determine the ground-state structures of small atomic clusters, so the density functional theory has been taken to find the lowest-energy optimized structures. As for each size cluster, hundreds of initial configurations are designed and the lowest energy structures are chosen from them.

The lowest energy structures of Os_mC_n ($m+n\leq7$) are reported. The average binding energies, the second-order differences of total energies, the energy gaps and the density of state are presented in the present study. The main goal of the work is to lay foundations for further studying the properties of carbon-osmium clusters and developing new materials with special functions.

2 Computational Methods

All the calculations were carried out with spin-polarized DFT at the level of generalized gradient approximation (GGA) via the Perdew-Wang exchange-correlation functional. In the calculation of the electronic structure, a double-numerical polarized basis set that includes d-polarization functions (DND) was chosen by us to describe the electronic wave functions. All of the possible spin multiplicities include singlet, triplet, quintet and seven spin states were calculated for each configuration to ensure that the obtained spin states are the lowest in energy. In order to accelerate the convergence of self-consistent field (SCF), the Pulay's direct inversion in an iterative subspace (DIIS) approach was designed with a convergence criterion of 10^{-5} Hartree. In the geometry optimization process, we chose the convergence criterion as follows: 2.0×10^{-5} Hartree for the total energy, 0.0040 Hartree/Å for gradient of force and 0.005 Å for atomic displacement. All our spin-unrestricted calculations were performed with the Accelrys DMOL package[3].

The reliability of the proposed computational method was checked by calculating the bond length of C_2 and Os_2 dimers, the value obtained for C_2 is 1.312 Å, which is in excellent agreement with the experimental value (1.312 Å) reported in the previous studies[19]. As for Os_2, the calculated bond length of 2.296 Å is consistent with the experimental data[20] of 2.28 Å. The above results indicate that our calculation method is reasonable and will provide reliable results for the Os_mC_n ($m+n \leq 7$) clusters.

3 Results and Discussion

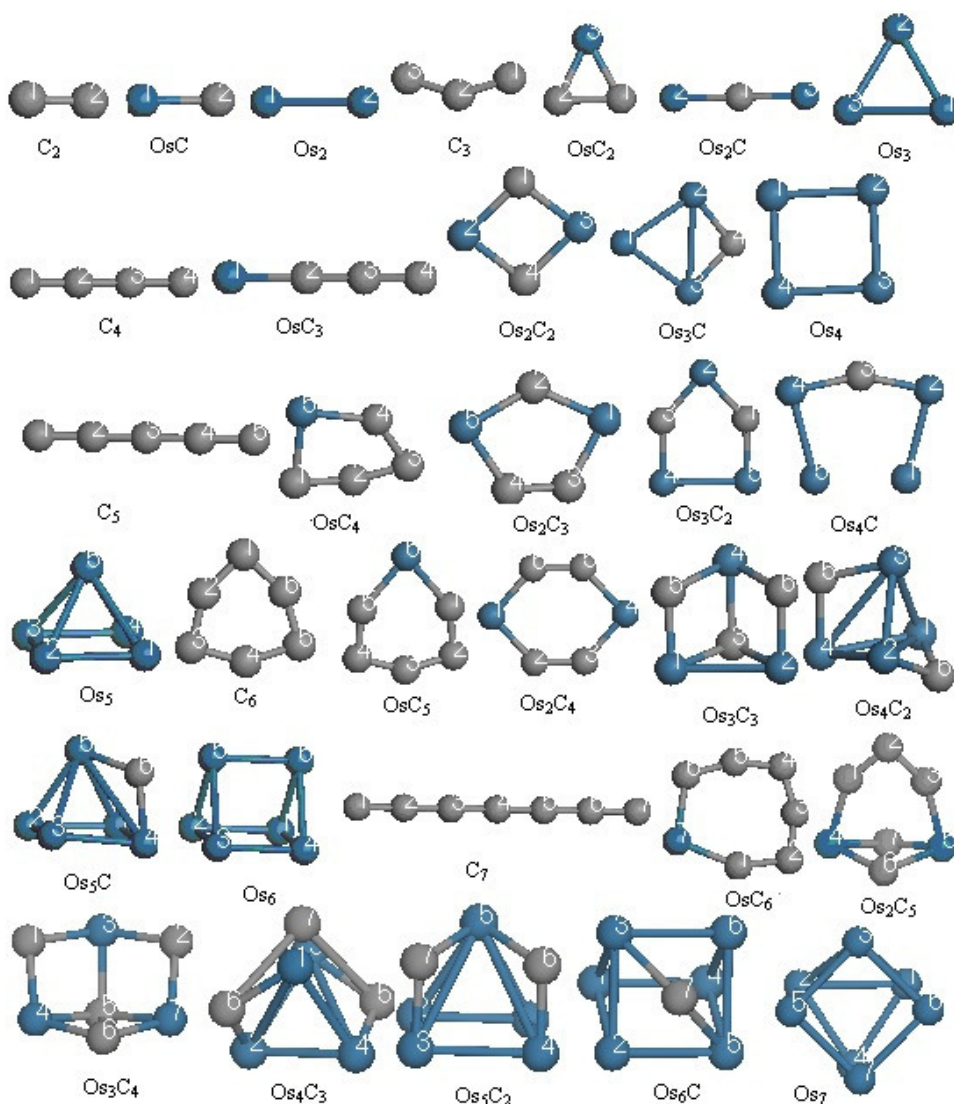### 3.1 Geometrical structures of Os_mC_n (m+n≤7) clusters

We have searched for a series of possible initial configurations for each size of the clusters on the basis of taking into full account the spin multiplicity to ensure the high accuracy of our determination for the ground-states of Os_mC_n ($m+n \leq 7$) clusters. The lowest-energy optimized structures are shown in Fig. 1. The spin multiplicity (S), structure symmetries and average bond lengths are listed in Table 1.

As can be seen from Fig. 1, for pure C_n ($n \leq 7$) clusters the most stable structures are linear with $D_{\infty h}$ symmetry except $n=3$ and 6. This is in good agreement with the results reported by Zhang $et\ al$[21]. The C-C bond lengths in pure C_n ($n \leq 7$) clusters are in the range 1.288-1.326 Å, which correspond to C-C double bond[22]. As for C_3, the 'V' shaped configuration

with an apex angle of 142.171° is the lowest-energy structure. While the lowest energy structure of C_6 is a regular hexagon (D_{3h}) with side length of 1.326 Å. That is in excellent agreement with the Binkley $et\ al$[23]. result. For the pure Os_n ($n \leq 7$) clusters, all the lowest energy structures obtained in our work are well consistent with the previous result[24] except the symmetry of Os_5 (C_{4v}).

For the binary clusters, the smallest one-OsC is in triplet state with $C_{\infty v}$ symmetry. The Os-C distance (1.690 Å) is shorter than the (1.981 Å) previous theoretical result[25]. In the isomers of OsC_2 cluster, equicrural triangle geometry with C_{2v} symmetry and singlet spin multiplicity has the lowest energy. The ground state of Os_2C is a linear structure (Os-C-Os) with $D_{\infty h}$ symmetry in quintet state which can be viewed as an Os atom located at the C atom of the OsC cluster rather than a C atom located at Os_2 cluster. This may be because the energy of C-C bond is higher than that of Os-Os bond. The Os_mC_n ($m+n=4$) clusters are the smallest ones that can display 3D structures, so we not only designed the linear and planar structures but also considered the tetrahedral structures. However, according to the optimized results, the planar configurations are found to be more stable than the tetrahedral structures in total energy. For the OsC_3, linear geometry with triplet multiplicity is found to be the ground state, which is similar to the GaC_3 cluster[27]. The ground state of Os_2C_2 is a planar rhombus (D_{2h}) with bond length of 1.837 Å. In the case of Os_3C, the planar quadrilateral with a C atom bridged over two Os atoms is the most preferred one, it can be seen to add a C atom to one side of Os_3. All the optimized geometries of Os_mC_n ($m+n=5$) binary clusters are also planar structures. The OsC_4 with C_s symmetry is an irregular pentagon, while the Os_2C_3 with C_{2v} symmetry is a regular pentagon, in this isomer the C-C bond length is 1.381 Å, which is obviously shorter than Os-C. This may be caused by the interaction between the C atoms. The ground state of Os_3C_2 (C_{2v}) is similar to OsC_4, in which the Os-Os bond length is 2.350 Å and Os-C bond length is 1.801 Å. The Os_4C can be viewed as adding two Os atoms to opposite ends of Os_2C.

For the hexamer, we attempted planar, octahedron, triple prisms and capped trigonal bipyramidal structures. As seen from Fig. 1, the structures of Os_mC_n ($m+n=6$) clusters transform from planar into three-dimensional structures with increasing number

Fig. 1 — Lowest energy structures of Os$_m$C$_n$ ($m+n \leq 7$) clusters

of Os atoms. The most stable structure of OsC$_5$ with C$_{2v}$ symmetry is found to be obtained by using one Os atom substituting for the C atom at the apex of C$_6$ cluster, C-C bond lengths are shortened due to the influence of Os. A regular hexagonal structure with D$_{2h}$ symmetry is obtained to be the ground state of Os$_2$C$_4$, the two Os atoms are at the opposite position. The Os$_3$C$_3$ cluster shows analogical triangular prism (C$_s$) as the ground-state geometry, in which there is no C-C bond. For Os$_4$C$_2$, the binary edge capped triangular pyramid geometry in singlet state with D$_{2d}$ symmetry is found to have the lowest energy. Influenced by the function of C atoms, the bond lengths of Os-Os that close to C atom are 2.927Å,

while the others away from C atom are 2.490 Å, all the bond lengths of Os-C are 1.837 Å. In the Os$_5$C, the C edge capped the square pyramid with C$_s$ symmetry is the most stable one.

While for Os$_m$C$_n$ ($m+n=7$), all the optimized geometries are three-dimensional structures except OsC$_6$, which is an irregular seven-membered ring with C$_s$ symmetry. For Os$_2$C$_5$, the ground-state geometry likes a basket with long handle (C$_{2v}$). In Os$_3$C$_4$, the most stable isomer in triplet state with C$_s$ symmetry can be viewed as adding a C atom to the bottom of Os$_3$C$_3$. Similarly, Os$_4$C$_3$ can be viewed as bridging the third C atom over the existed two C atoms in Os$_4$C$_2$, the average Os-Os bond length in it lies in the range

Table 1—Geometric parameters of lowest energy structures of Os_mC_n ($m+n\leq7$) clusters

Cluster	S	Sym	$\bar{R}(C-C)$ / Å	$\bar{R}(Os-C)$ / Å	$\bar{R}(Os-Os)$ / Å
C_2	3	$D_{\infty h}$	1.312	—	—
OsC	3	$C_{\infty v}$	—	1.690	—
Os_2	7	$D_{\infty h}$	—	—	2.296
C_3	1	C_{2v}	1.303	—	—
OsC_2	1	C_{2v}	1.585	1.758	—
Os_2C	5	$D_{\infty h}$	—	1.777	—
Os_3	5	D_{3h}	—	—	2.378
C_4	3	$D_{\infty h}$	1.311	—	—
OsC_3	3	$C_{\infty v}$	1.300	1.757	—
Os_2C_2	3	D_{2h}	—	1.837	—
Os_3C	7	C_{2v}	—	1.841	2.548
Os_4	5	D_{4h}	—	—	2.326
C_5	1	$D_{\infty h}$	1.292	—	—
OsC_4	1	C_s	1.397	1.829	—
Os_2C_3	1	C_{2v}	1.381	1.809	—
Os_3C_2	1	C_{2v}	—	1.801	2.358
Os_4C	5	C_{2v}	—	1.781	2.356
Os_5	1	C_{4v}	—	—	2.468
C_6	1	D_{3h}	1.326	—	—
OsC_5	1	C_{2v}	1.320	1.834	—
Os_2C_4	1	D_{2h}	1.392	1.774	—
Os_3C_3	3	C_s	—	1.908	2.555
Os_4C_2	1	D_{2d}	—	1.837	2.636
Os_5C	3	C_s	—	1.841	2.561
Os_6	5	D_{3h}	—	—	2.430
C_7	1	$D_{\infty h}$	1.288	—	—
OsC_6	1	C_s	1.328	1.805	—
Os_2C_5	1	C_{2v}	1.347	1.875	—
Os_3C_4	3	C_s	—	1.917	—
Os_4C_3	3	C_2	2.510	1.840	2.857
Os_5C_2	3	C_s	—	1.852	2.913
Os_6C	5	C_{2v}	—	2.039	2.472
Os_7	7	C_{3v}	—	—	2.464

2.437-3.325 Å. Os_5C_2 and Os_6C can be obtained by adding a C atom to Os_5C and Os_6, respectively.

3.2 Stabilities of Os_mC_n ($m+n\leq7$) clusters

For the purpose of analyzing the stabilities of the ground state Os_mC_n clusters, the average binding energies per atom (E_b/atom), the second-order differences of total energies (Δ_2E) and the energy gaps between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) have been calculated.

The average binding energies reflect the stability of the clusters. For the same size clusters, the higher the average binding energy is, the more stable the cluster will be.
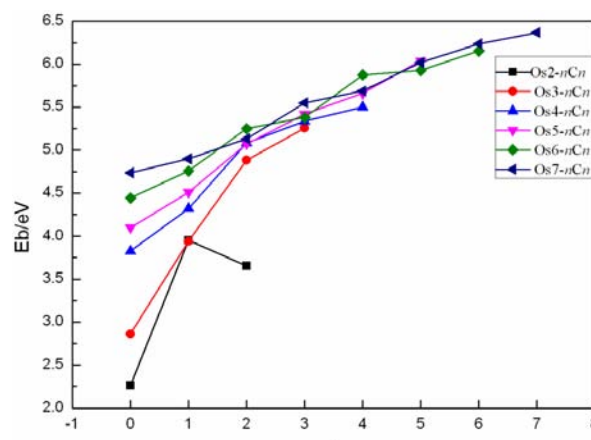

Fig. 2 — Average binding energies (E_b /atom) of Os_mC_n ($m+n\leq7$) clusters

The average binding energies of the mixed clusters can be described by the following formula:

$$E_b = [mE(Os) + nE(C) - E(Os_mC_n)] / (m+n) \qquad \dots(1)$$

where E (Os), E (C) represent the energy of isolated Os and C, respectively. E (Os_mC_n) represents the total energy of the Os_mC_n clusters, and E_b represents the average binding energy of system. These quantities of average binding energies are shown in Fig. 2 as a function of the number of C atoms. Both the average binding energies of pure Os_n and C_n clusters increase as the cluster sizes fill out, and all the average binding energies of pure C_n clusters are larger than those of Os_n clusters, this indicates that the stability of carbon clusters is better than that of osmium (Fig. 2). Whereas for mixed clusters, all the average binding energies increase with the number of carbon atoms and are between pure osmium clusters and pure carbon clusters except for C_2. Thus, from the above analysis, we conclude that the energy of C-C bond is stronger than that of Os-Os bond and the C-rich clusters are more stable than Os-rich clusters with the same number of total atoms. Though there is no obvious odd-even oscillation, five slight lifts corresponding to OsC_2, Os_2C_2, Os_2C_4, Os_4C_2, Os_3C_4, respectively. The emergence of these local magnitude maxima means that these clusters have stronger stabilities relative to their neighbours.

As the second-order differences of total energies (Δ_2E) can be used to measure the relative stability of clusters, so we calculated the Δ_2E of Os_mC_n ($m+n\leq7$). In order to investigate, the effect of the increasing number of C and Os atoms to the stabilities clearly,

both Δ_2E_n and Δ_2E_m have been calculated and the relationship between Δ_2E and n are shown in Figs 3 and 4, respectively. The Δ_2E is estimated in the following way:

$$\Delta_2E(n) = E(n+1) + E(n-1) - 2E(n) \qquad \ldots(2)$$

From Fig. 3, it is evident that the values of the second-order differences of total energies for C_3, C_5, OsC, OsC_2, Os_2C_2, Os_2C_4, Os_3C, Os_3C_2 and Os_4C_2 clusters are positive numbers, this shows that the stabilities of these clusters are relatively better. There exist clear even-odd oscillations in the curves of C_n and Os_2C_n clusters, C_3, C_5, Os_2C_2, Os_2C_4 and Os_3C_2 are more stable than their neighbouring ones. As well, we can easily find that the values of the second-order differences of total energies for Os_2, Os_4, OsC,
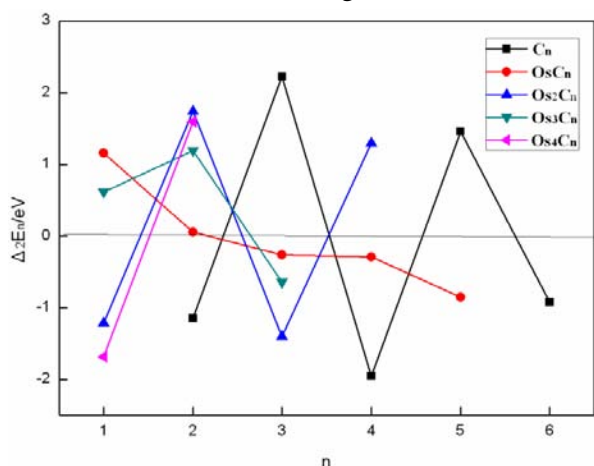

Fig. 3 — Second-order differences of total energies (Δ_2E_n) of Os_mC_n ($m+n\leq7$) clusters as a function of the number of C atoms
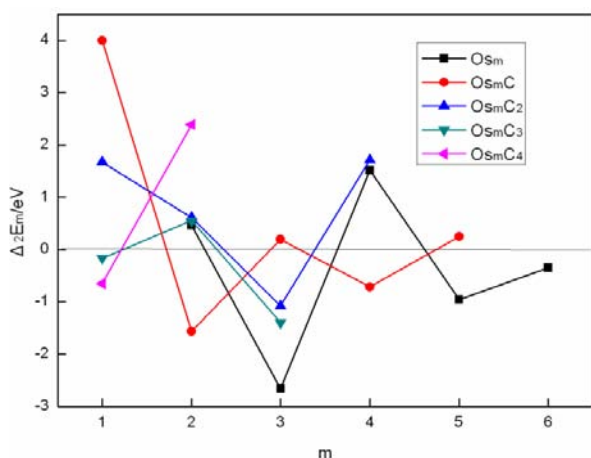

Fig. 4 — Second-order differences of total energies (Δ_2E_m) of Os_mC_n ($m+n\leq7$) clusters as a function of the number of Os atoms

Os_3C, Os_5C, OsC_2, Os_2C_2, Os_4C_2, Os_2C_3 and Os_2C_4 clusters are positive numbers from Fig. 4, indicating that these clusters possess stronger stabilities relative to their neighbours. The curves of Os_m and Os_mC clusters show the odd-even oscillation behaviour and two peaks can be found corresponding to Os_4 and Os_3C.

Combining the above analysis of both Δ_2E_n and Δ_2E_m, we can draw a conclusion that OsC, OsC_2, Os_2C_2, Os_2C_4 and Os_4C_2 are much more stable than other clusters in Os_mC_n ($m+n\leq7$).

The energy gaps E_g between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are able to used to reflect the stabilities of clusters from the chemical stability point of view, they are defined as:

$$E_g = E_{LUMO} - E_{HOMO} \qquad \ldots(3)$$

where E_{LUMO} is the energy of the lowest unoccupied molecular orbital, E_{HOMO} is the energy of the highest occupied molecular orbital.

The HOMO-LUMO energy gaps of the ground state geometries of Os_mC_n ($m+n\leq7$) clusters are plotted in Fig. 5. Compared with pure Os and C-mixed clusters, the pure C clusters (except C_4) have higher energy gaps, so pure C clusters have higher chemical stability than others, which coincides well with the result of the average binding energies and the second-order differences of total energies. It also can be found that most of the energy gaps of the C-mixed clusters are larger than those of the Os_n with the same cluster size; this result clearly indicates that the doping of C atom has lowered the chemical activity of
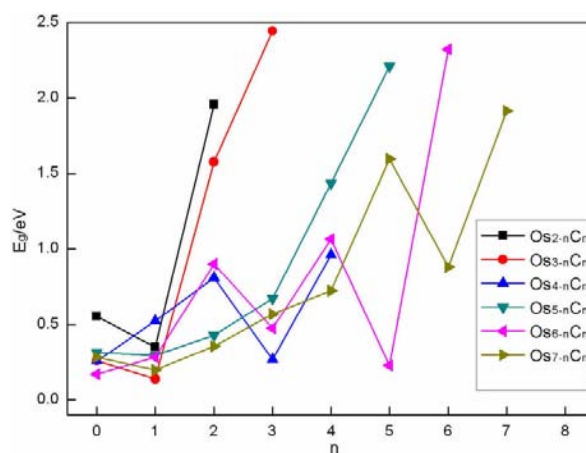

Fig. 5 — Energy gaps (E_g) of Os_mC_n ($m+n\leq7$) clusters as a function of the number of C atoms
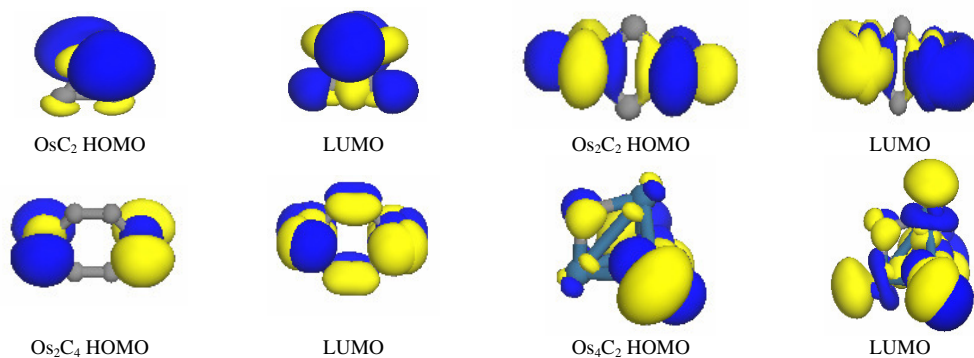
OsC₂ HOMO   LUMO   Os₂C₂ HOMO   LUMO

Os₂C₄ HOMO   LUMO   Os₄C₂ HOMO   LUMO

Fig. 6 — Corresponding HOMO and LUMO orbital isosurfaces of OsC$_2$, Os$_2$C$_2$, Os$_4$C$_2$ and Os$_2$C$_4$ clusters
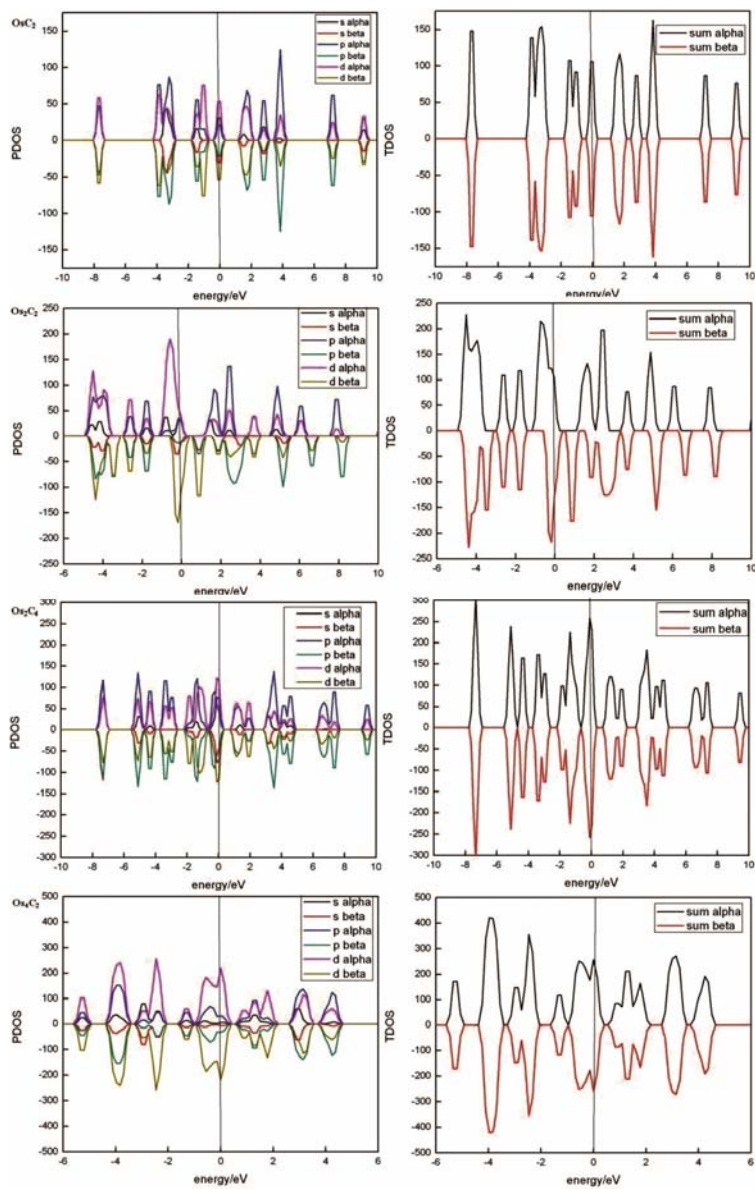

Fig. 7 — Partial density of states (PDOS) of s, p and d orbital and total density of states (TDOS) OsC$_2$, Os$_2$C$_2$, Os$_4$C$_2$, and Os$_2$C$_4$ clusters. The vertical line indicates the Fermi level

Os_n clusters. Among all the clusters, OsC_2, Os_2C_2, Os_4C_2, and Os_2C_4 display higher energy gaps as compared to their neighbours, which is coincident with the conclusions obtained from the average binding energy and the second-order differences of total energy.

3.3 Electronic properties of OsC_2, Os_2C_2, Os_4C_2, and Os_2C_4 clusters

In order to further explore the properties of Os_mC_n ($m+n \leq 7$) clusters, the HOMO and LUMO orbital isosurfaces of OsC_2, Os_2C_2, Os_4C_2 and Os_2C_4 clusters are shown in Fig. 6 (because they are thought to be the most stable clusters in the present paper), from which one can see that both HOMO and LUMO states are mainly contributed by Os5d orbital and C2p orbital. This indicates that there exists d-p hybridization between Os atoms and C atoms, which are the dominating factor for decrease of doping of C atoms the energy gaps of pure C_n cluster but increase the energy gaps of pure Os_n cluster. The corresponding total density of states (DOS) and partial density of states (PDOS) of these clusters are also calculated and shown in Fig. 7. The Fermi level is at zero energy presented as a vertical line, the upper side of the figure is related to DOS for electrons with upward spin, and the lower side is related to the electrons with downward spin. It is clear that in all the chosen clusters, all curves are discrete; this indicates that the energy levels for OsC_2, Os_2C_2, Os_4C_2 and Os_2C_4 clusters are discrete. It is also clearly seen from Fig. 7 that in the vicinity of the Fermi level, all the electronic states consist mainly of Os5d and C2p states, and the contribution of the s orbital electrons can be negligible as compared with p and d orbital electrons. There exist isolated peaks in the vicinity of the Fermi level of all the state density curves and in PDOS the peaks of all orbital are in one-to-one correspondents, this indicates that the d electrons of Os atoms and the s and p electrons of C atoms are relatively localized and there exist more or less spd hybridization in all of the selected clusters. For OsC_2, Os_4C_2 and Os_2C_4 clusters, both the PDOS and TDOS curves are symmetric, while for Os_2C_2 the situation is different. This indicates that there is a difference between the spin up electronic number and the spin down number in Os_2C_2, that is to say there exist unpaired electrons in this cluster. This result is consistent with the spin multiplicities of these clusters that previously mentioned.

4 Conclusions

Employed with PW91 functional within the generalized gradient approximation (GGA), the lowest energy structures of Os_mC_n ($m+n \leq 7$) clusters are obtained. The lowest energy geometries show that most of small pure carbon clusters are in single state while pure osmium clusters have higher spin multiplicity and symmetry. For binary clusters, the singlet and triplet state structures are more stable than others. The preferred Os_mC_n structures with size of m+n≤5 transform from chain-like geometries to ring-like structures except Os_5 which is a pyramid structure. As for those with size of $m+n \geq 6$, the C-rich clusters are still planar structures, while Os-rich clusters are three-dimensional structures and most of them tend to be capped pyramid or irregular prism. The relative stabilities are determined by analyzing the average binding energies, the second-order differences of total energies and the energy gaps. The OsC_2, Os_2C_2, Os_4C_2 and Os_2C_4 show stronger stabilities than their neighbouring ones. HOMO and LUMO orbital isosurfaces and DOS analysis of OsC_2, Os_2C_2, Os_4C_2 and Os_2C_4 indicate that Os5d and C2p electrons play dominant roles in chemical reaction of mixed clusters. As the partial DOS described, the d electrons of Os atoms and the s and p electrons of C atoms are relatively localized and there exist more or less spd hybridization in all of the selected clusters.

References

1. Zhai H J, Ni G Q, Zhou R F & Wang Y Z, *Prog Phys*, 17 (1997) 265.
2. Sheng Y, Tu M J & Mao H P, *Acta Phys Sin*, 57 (2008) 4153.
3. Wang Y L, *Henan university master's degree thesis*, (2012).
4. Lombardi J R & Davis B, *Chem Rev*, 102 (2002) 2431.
5. Kumar V & Kawazoe Y, *Phys Rev B*, 65 (2002) 125403.
6. Alonso J A, *Chem Rev*, 100 (2000) 637.
7. Hübner O, Himmel H J, Manceron L & Klopper W, *J Chem Phys*, 121 (2004) 7195.
8. Zhang L, Qi Y & Zhang C B, *Chin Phys*, 15 (2006) 2001.
9. Ma J, Chen Y H & Zhang C R, *Acta Phys Sin*, 55 (2006) 171.
10. Wang H Y, Chen X H, Zhu Z H, Li X B, Tang Y J & Wang C Y, *Acta Phys Sin*, 54 (2005) 3565.
11. Zheng J C, *Phys Rev B*, 72 (2005) 052105.
12. Chen Z Y, Xiang H J, Hou J G & Zhu Q S, *Phys Rev B*, 74 (2006) 012102.
13. Young T H & Chuang W Y, *J Membr Sci*, 210 (2002) 349.
14. Tian F Y, Wang Y X & Jing Q, *Acta Phys Sin*, 57 (2008) 1648.

15 Guo W L, Liang Y C & Fang Z, *Acta Phys Sin*, 56 (2007) 4847.
16 Zhang X R, Zhang F X, Chen C & Yuan A H, *Chin Phys B*, 22 (2013)123102.
17 Zhang X R, Wu L Q & Rao Q, *Acta Phys Sin*, 60 (2011) 083601.
18 Zhang X R, *Comput Appl Chem*, 27 (2010) 221.
19 Yadav P S, Yadav P K, Agrawal S & Agrawal B K, *J Phys Condens Matter*, 18 (2006) 7085.
20 Wu Z J, Han B, Dai Z W & Jin P C, *Chem Phys Lett*, 403 (2005) 367.
21 Zhang C J, Xu X, Wu H S & Zhang Q, *Chem Phys Lett*, 364 (2002) 213.
22 Zhang C J, Jiang Z Y, Wang Y L & Zhu H Y, *Comput Theor Chem*, 1004 (2013) 12.
23 Raghavachari K & Binkley J S, *J Chem Phys*, 87 (1987) 2191.
24 Takahashi K, Isobe S & Ohnuki S, *Chem Phys Lett*, 555 (2013) 26.
25 Zhao E J, Wang J P & Wu Z J, *J Comput Chem*, 31 (2010) 2883.