Structures and bonding features of Al_nC_m (n=4, 6; m=1-4) clusters

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Synopsis The low-energy structures of Al_nC_m (n=4, 6; m=1-4) are determined by using the genetic algorithm combined with DFT and QCISD models and their electronic structures are investigated. Al atoms transfer their 3p electrons to C, and the 3s of Al and the 2s2p of C form bonding orbitals and antibonding orbitals. The former corresponds to the covalent C-Al bonds and the latter lone pair electrons at the outside of Al atoms. The C-Al bonds are both strongly covalent and strongly ionic.

Metal clusters have fascinating physical and chemical properties determined by their sizes and compositions. Doping with other metal or nonmetal atoms in the metal clusters can tune their properties for different purpose of applications. Aluminum is a kind of lightweight and cheap materials and the Al-based clusters have been extensively investigated. In recent years, aluminum-carbon clusters have attracted increasing attention as a new class of materials [1-5].

In the present work, the low-energy structures of Al_nC_m (n=4, 6; m=1-4) are determined by using the genetic algorithm combined with the hybrid density functional theory B3LYP and the QCISD models. The split basis set with polarization and diffuse function 6-311+G(d) is used. The electronic structures and bonding features are analyzed through the density of states (DOS), valence molecular orbitals (MOs) and electron localization function (ELF).

The results show that the carbon atoms tend to aggregate and sit at the center of the clusters. The C-C bond lengths in most cases accord with the double C=C bond pattern. Analyses on valence molecular orbitals confirm that the neighbor C atoms form double C=C bonds in the planar structures. The planar structures and tetrahedrally coordinated C atoms indicate the Al_nC_m clusters are combined together through covalent chemical bonds. The valence MOs and ELF show that the 3s orbitals of Al and the 2s2p orbitals of C form bonding and antibonding orbitals; the bonding orbitals correspond to the covalent C-Al bonds and the antibonding orbitals form lone pair electrons at the outside of Al atoms. Due to the large difference between the electronegativities of carbon and aluminum atoms, almost all the 3p electrons of Al transfer to C atoms. The positive charges on Al and the lone pair electrons residing at the outside of Al atoms form large local dipole moments and enhance the electrostatic interactions between C and Al atoms.

Planar geometry and multi-connection are prominent structural patterns in small Al_nC_m clusters. However, the multi-connection does not correspond to multi-center chemical bonding. There are multi-center bonds but they are much weaker than the σ C-Al bonds.

In the close-packed AlC clusters, the valence electrons form shell structures ($1s^21p^61d^{10}2s^21f^{14}2p^6$) similar to that in metal clusters based on the jellium model.

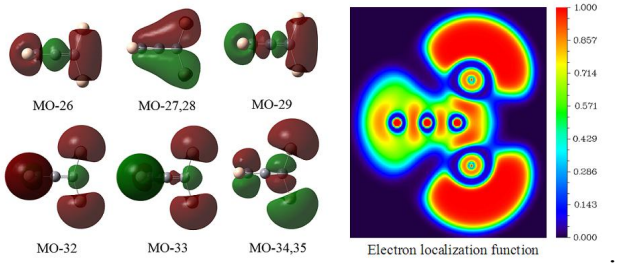

Figure 1. The 3s(Al) and 2s2p(C) form bonding and antibonding orbitals, corresponding to the covalent C-Al bonds and lone pair electrons respectively.

References

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