Evolution of properties of metal cluster cages via encapsulation of molecular dopants

B. Irving, F. Y. Naumkin[1]

[1] *Faculty of Science, UOIT, Canada*

Fedor.Naumkin@uoit.ca

Cluster shape and other properties can be altered by inserting an atomic or molecular species inside. Novel $C_n@Al_m$ core-shell nanoclusters have been investigated at a DFT level. The systems of C_n cores (n = 1-4) encapsulated by Al_{12} shells have been characterized in terms of geometries and stabilities, ionization energies and electron affinities. Other isomers, with the C_n moiety attached to the Al_{12} surface, have also been studied and found to be less stable. For both series, the stability peaks for n=2, which can be related to the relaxation energies of the carbon and aluminum fragments upon dissociation, and to their interaction in the system. The effect of the core on the vertical ionization energies and electron affinities is most pronounced for n=1, even though the shell geometry alters increasingly with n, up to a considerable reshaping for n=4. Another peculiarity of the n=2 system is manifested in the relative VIE and VEA values of the core-shell and surface-attached isomers. Analysis of trends for these properties includes evaluation of contributions from the carbon and aluminum components, demonstrating the effects of shape and composition. Also considered is a structural extension to a $C_4@Al_{14}$ system featuring a surprising invariability of the above properties as compared to those of Al_{14} in spite of a major shape alteration upon doping, as well as reversible shape-variations controlled by charge and spin states.
In general, comprehensive (involving composition, size, shape) structure-property relationships can be employed for cluster design and parameter manipulation. Applications of such and similar core-shell nanoparticles include new nanocomposite materials, tunable nanocatalysts, building blocks, molecular/cluster switches, etc.

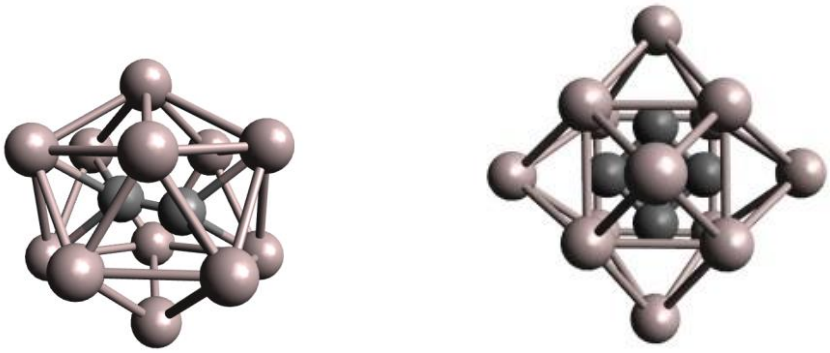

Figure 1: $C_2@Al_{12}$ and $C_4@Al_{14}$ core-shell systems.

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[2] J. Chem. Phys. 141 (2014) 131102.