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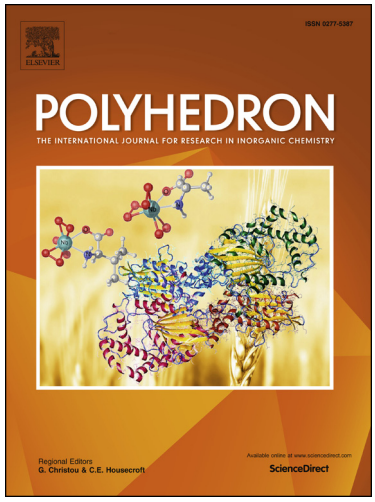

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ELECTRONIC STRUCTURES OF ENDOHEDRAL FULLERENES WITH SCANDIUM, TITANIUM AND IRON ATOMS AND METAL-CARBON CLUSTERS

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Abstract

The electronic structures of the endohedral forms of the C_{28}, C_{40}, C_{60} and C_{80} fullerenes encapsulating the 3d-atoms Sc, Ti and Fe, and in the case of C_{80} with M_2C_2 clusters (M = Sc, Ti, Fe) were investigated using the ab initio Dmol^3 method. For the C_{60} and C_{80} cages, we found preferable positions of the metal atoms and their carbon clusters near the internal surface of the fullerene shell. The analysis of the formation energy variation and the role of the magnetic state of 3d-atoms is presented.

Keywords: Fullerenes; Metallocarbohedrenes; Ab initio methods; Stability; Magnetic ordering.

Introduction

The discovery of fullerenes in 1985 [1] initiated the synthesis of many useful materials based on carbon cages of various sizes. Nowadays, there is an opinion that the most prospective modifications are based on the so-called endohedral fullerenes (EFs), formed by the encapsulation of various micro-objects inside the fullerene cages [2]. According to the results of experimental studies [2-7], the EFs interior can contain individual atoms, molecules, metal clusters, binary clusters of M_xC_y or M_xN_y types and more complex objects as well. Such species are interesting because of the possibility of their applications in biology and medicine; on the other hand, electron transfer from the internal species to the carbon cage makes these systems an ideal object for investigations into the properties and behavior of entrapped atoms or clusters [8,9].

Analysis of the experimental works showed that the probabilities for the encapsulation of various atoms inside the fullerene cages are considerably different using both the arc discharge and laser ablation methods for their generation. Additionally, the majority of the elements in the periodic table were never detected inside the fullerene shells, and the production yield of EFs with metals is higher than that with non-metals. However, the probabilities of EF formation with various metals are considerably different, e.g. the elements Sc and Y (as well as their clusters with carbon and nitrogen) give rise to endohedral particles in higher yields than Ti and Zr [7]. It is interesting that most transition metals could not form EFs, but the presence of Cu, Ni and Fe can increase the yield of other metal endohedral species [7,10]. The nature of these catalytic processes is not yet clear.

The aim of the present work was quantum-chemical modelling of EFs containing atoms and metal-carbon clusters of the 3d-metals Sc, Ti and Fe; a comparison of the peculiarities of the electronic structures of these objects, which can be responsible for the different probabilities of their formation.