Computational treatments of endohedral fullerenes for nanoscience applications: alkaline earth series X@C_{74}

F. Uhlik[1], Z. Slanina[1,2], and S. Nagase[2]

[1] *School of Science, Charles University, 128 43 Prague 2, Czech Republic*
[2] *Institute for Molecular Science, Okazaki, Aichi 444-8585, Japan*
[3] *Institute of Chemistry, Academia Sinica, Taipei 11529, Taiwan-ROC*

Various endohedral cage compounds have been suggested as possible candidate species for molecular memories and other future nanotechnological applications. One approach is built on endohedral species with two possible location sites of the encapsulated atom while another concept of quantum computing aims at a usage of spin states of N@C_{60}.

Although empty C_{74} fullerene is not yet available in solid form, several related endohedral species have been known like Ca@C_{74}, Sr@C_{74}, Ba@C_{74}, La@C_{74}, Eu@C_{74}, Yb@C_{74}, Sc_2@C_{74} or Er_3@C_{74}. In the Yb@C_{74} case, two isomers were in fact isolated. This isomerism finding is particularly interesting as there is just one C_{74} cage that obeys the isolated pentagon rule (IPR), namely of D_{3h} symmetry. The cage was experimentally confirmed in Ca@C_{74}, Ba@C_{74} and La@C_{74}. Obviously, with Yb@C_{74} a non-IPR cage should be involved.

The C_{74} metallofullerene family is naturally of computational interest. The present paper deals with Be@C_{74}, Mg@C_{74}, Ca@C_{74}, Sr@C_{74}, and Ba@C_{74}. The computations treat a set of up to six metallofullerene isomers, using the carbon cages investigated previously with Ca@C_{74}, namely the three structures selected from dianion energetics, and three additional cages with non-negligible populations as empty C_{74} cages (IPR, three non-IPR cages with a pair of connected pentagons, two cages with a pentagon/pentagon pair and one heptagon).

In order to respect high temperatures in metallofullerene preparations, the Gibbs energies are to be used for relative stability considerations rather than the mere potential energy terms. Moreover, to get production abundancies for different metallofullerenes, saturated metal pressures are to be also included. Under equilibrium conditions, we explicitly deal with the encapsulation equilibrium constants for encapsulation of a metal X into a carbon cage C_n. Moreover, it is supposed that the metal pressure is close to the respective saturated pressure. The computed equilibrium constants exhibit a temperature decrease. However, if we consider the combined products of the encapsulation equilibrium constants and the metal saturated pressures, we get a different picture. The combined products can increase, stagnate, or decrease with temperature, which represents possible situations for the metallofullerene formation in the electric-arc technique. With the combined treatment, the relative populations in a series of encapsulates can be predicted, and illustration is presented with the alkaline earth series X@C_{74}.