Computational Design of Metallofullerene Production: X@C_{74}

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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 [1] while another concept of quantum computing aims at a usage of spin states of N@C_{60} [2] or fullerene-based molecular transistors [3]. The properties of metallofullerenes can further be tuned by external cage derivatizations. At present, however, a deeper knowledge of various molecular and production aspects of the endohedral compounds is needed before their tailoring to nanotechnology applications is possible.

The C_{74} fullerene endohedral family is rather extended as encapsulations 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} are known from previous experimental studies. The family is also interesting as there is just one C_{74} cage that obeys the isolated pentagon rule, namely of D_{3h} symmetry. The cage was experimentally confirmed in Ca@C_{74}, Ba@C_{74}, and La@C_{74}. However, the empty C_{74} (and also C_{72}) species could not be isolated yet, perhaps owing to solubility problems.

The experimental findings are thus of computational interest and calculations on several of the species will be reported based on the density functional methods in order to clarify structure, energy, stability as well as spectral aspects. As far as metallofullerene production is concerned, there is a general stability problem which members of a series, like X@C_{74}, are produced in high/low yields. Under equilibrium conditions we shall deal with the encapsulation equilibrium constants $K_{@,X,p}$. Temperature dependency of the encapsulation equilibrium constant $K_{@,X,p}$ is described by the van't Hoff equation controlled by the (negative) standard change of enthalpy upon encapsulation. In other words, $K_{@,X,p}$ must be decreasing with temperature. Let the metal pressure is close to its saturated pressure p_{sat}(X). We suggest a product, $p_{sat}(\mathrm{X})K_{@,X,p}$, as a pratical stability measure in a metallofullerene series. Interestingly enough, the product increases with temperature which is the basic scenario of the metallofullerene formation in, e.g., the electric-arc technique. The encapsulation equilibrium constants $K_{@,X,p}$ are computed using the potential-energy change evaluated at the B3LYP/6-31G* level and the partition functions at the B3LYP/3-21G level.

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