Computed Enthalpy-Entropy Interplay for Isomeric Fullerenes

Zdeněk Slanina,[1] Xiang Zhao[2] and Filip Uhlík[3]

[1]Institute of Chemistry
Academia Sinica
128 Yen-Chiu-Yuan Rd., Sec.2
Nankang
Taipei, ROC 11529
Taiwan - R. O. C.

[2]Department of Knowledge-Based Information
Engineering
Toyohashi University of Technology
1-1 Hibarigaoka
Tempaku-cho
Toyohashi, J 441-8580
Japan

[3]Department of Physical and Macromolecular Chemistry
School of Science
Charles University
Albertov 6
Prague 2, CZ 12843
Czech Republic

Isomeric fullerenes already represent an extended family of species and several such isomeric sets are well characterized experimentally. Such observed sets naturally also attract interest from computations. At present, C_{96} is the highest set of isomeric fullerenes that has been studied by ^{13}C NMR spectra (T. Minami, Y. Miyake, K. Kikuchi and Y. Achiba, in The 18th Fullerene General Symposium, The Fullerene Research Association of Japan, Okazaki, 2000, p. 42). In the experiment, ten species have been recognized. We have been performing corresponding quantum-chemical computations on the C_{96} system (the complete set of the isolated-pentagon-rule (IPR) isomers of C_{96} consists of 187 cages).

Our general approach to the sets of isomeric fullerenes has been based on simultaneous calculations of enthalpy and entropy terms. This more advanced treatment is required by the fact that the potential energy term alone cannot always produce reliable relative stabilities at high temperatures. Thus, the entropy terms are also computed and the relative-stability problem is entirely treated in terms of the Gibbs function. These computational studies have supplied ample support for the key presumption of a kind of inter-isomeric thermodynamic equilibrium in experiments. However, there may also be other interpretation, namely that the inter-isomeric equilibrium is not yet reached, but the relative non-equilibrium and equilibrium isomeric concentrations do not differ significantly. The computational treatment of isomeric mixtures has several interesting features: The results depend on temperature but not on pressure, only the relative and not the absolute values of the heats of formation are needed, the form of the master equation allows for an ample cancellation of terms in the partition functions (in particular, the cluster mass is cancelled out exactly). There are however some still open questions like inclusion of anharmonicity effects, contribution from electronic partition function, or even interactions between individual, yet separated motions.