



On the upper bound of the thermodynamic stability of fullerenes from small to giant



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ABSTRACT

From the large variety of C_{20} – C_{720} fullerenes, the energetically most stable isomers were chosen and studied within the PBE/3 ζ quantum-chemical approximation. A phenomenological model of the dependence of the standard enthalpy of formation and entropy of the selected isomers on the number of the carbon atoms is developed. From the analysis of the constants of the phenomenological model, it follows that the C_{60} , C_{70} , C_{180} , and C_{1500} molecules hold a prominent position among the hypothetical and/or experimentally discovered fullerenes. For the selected energy-stable isomers, the values of the singlet-triplet splitting were calculated. The ground state of the C_{260} – C_3 , C_{320} – D_{3d} and C_{500} – D_{3d} molecules were found to be of triplet multiplicity that may indicate their low kinetic stability and/or possibility of existence in the derivatized forms. In view of the lack of relevant experimental thermodynamic data on fullerenes, the obtained in this work approximation dependences, expressed in a simple analytical form, may provide useful tool for fast assessing the energetic characteristics of fullerenes, as well as for prediction of those undiscovered yet.

1. Introduction

Fullerenes constitute a class of polyhedral molecules composed of carbon atoms. The main features of fullerenes include (a) a rich spheroidal system of π -electrons; (b) an internal cavity readily filled by guest atoms and molecules; (c) the sizes of the order of 10^{-9} m (which is the lower limit of nanoparticle sizes); (d) a large number of reactive sites per one molecule and their high reactivity due to the nonplanar arrangement of sp^2 -hybridized carbon atoms; (e) a large number of vibrational and electronic degrees of freedom which gives rise to various statistical and collective phenomena; (f) strict geometry regularity of structure (fullerenes are made up of hexagons and pentagons only) and often high point symmetry groups of the molecules, up to I_h for C_{60} , the most famous representative of the fullerenes [1–13]. None of the other known classes of chemical compounds exhibit such a combination of the structural features above. All this provides the unique physicochemical properties of fullerenes, which have already been being studied for more than 30 years, and interest in them does not wane.

As for practical use, the most promising fullerene applications deal with organic solar cells [4], light-emitting devices [14],

endofullerene-based radiopharmaceuticals and quantum bits [5,15], fullerene switches [16], and molecular containers [17].

The first works in the field of fullerenes were devoted to the most abundant fullerenes C_{60} (I_h) and C_{70} (D_{5h}). Further, the advances in the modification of the arc-discharge fullerene synthesis and chromatographic separation techniques opened wide-range studies on the other fullerenes, which previously seemed exotic (up to C_{100}). At the same time, blind spots remain in the formation mechanism of fullerenes under plasma conditions [18] and synthesis by means of conventional chemical procedures [19]. Promising results in this field have been obtained from Irle and Morokuma's molecular dynamics simulations on the formation of fullerene structures from C_2 molecules [20] though this work did not reproduce the C_{60} formation in large amounts as observed experimentally. The interest in stability and formation of diverse fullerene structures is heated by the discovery of C_{60} (I_h) and C_{70} (D_{5h}) in very large amounts in outer space [18,21–23].

The list of experimentally identified fullerenes includes C_{20} [24], C_{60} [19,25–39], C_{62} [40], C_{70} [25,31,34,35,41–43], C_{72} [44], C_{74} [44,45], C_{76} [31,46–54], C_{78} [31,47,49,53,55–58], C_{80} [59–61], C_{82} [51,56,62–67], C_{84} [31,49,56,63,68–74], C_{86} , C_{90} , and C_{92} [31]. Current

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theoretical studies attempt to answer the question why some fullerene structures dominate while the other remain unachievable under laboratory and interstellar conditions. To address this problem, different approaches have been invoked. These are based on the estimation of structural and topological features of fullerenes [75–81], their thermodynamic and kinetic stability (see, e.g. [82–84], and molecular orbitals [85,86]).

Despite the progress in structural/topological and molecular orbital studies, the energetic parameters keep their significance for assessing the stability of diverse fullerene isomers. Therewith, depending on the context, the definition of “stable compound” is somewhat interpretative, e.g. experimentally obtained, isolated, or confirmed somehow. We pay special attention to the works of Kovalenko and Khamatgalimov [82,83,87,88], who introduced and adhered the following notion: “We relate to fullerenes as stable compounds that can be synthesized (the thermodynamic stability) and that remain unchanged for a long period of time under normal conditions, i.e., on air at room temperature (the kinetic stability)” [88].

Further, they have particularly focused on the plot of total energy per atom E_{total}/n versus n and pointed that stable fullerene isomers make up the “sector, or beam of stability” on this plot [82,83]. Thus, the border lines of the sector embound the reduced total energies (or standard enthalpies of formation) inherent to stable isomers of C_n fullerenes, partitioning off them from unstable ones. Herewith, it has been noticed that the increment of the energy E_{total}/n diminishes with n , so the extrapolation allows expecting the plateau on the E_{total}/n versus n plot. At the same time, this should be regarded as a conjecture since the works [82,83,87,88] cover only the C_n fullerenes barely ranging from $n = 60$ to $n = 90$.

In this context, a study of fullerenes from a wider range of the size is necessary for well-supported prognosis. In the present work, we have quantum-chemically studied the stabilities of the fullerenes from C_{20} to C_{720} to detail the abovementioned sector of stability and considered the criteria of fullerene stability in the augmented thermodynamic coordinates.

2. Computational details

All the calculations were performed following the density functional theory. Optimization of the fullerene structures, solving the corresponding vibrational tasks, and calculation of the thermal corrections to energy (necessary to obtain thermodynamic parameters of fullerenes) were carried out using PBE/3 ζ method (Perdew–Burke–Ernzerhof exchange-correlation functional in combination with the basis set of the triple-zeta quality) implemented in PRIRODA 16 program suit [89,90]. The preliminary screening of the objects for the present study was performed by the PBE/2 ζ method with smaller basis set. The PBE/3 ζ method was previously applied to fullerenes and revealed a reliable description of their geometry, electronic structure, thermodynamic parameters, polar characteristics, IR, and NMR spectra [9,12,76,91–97]. The original 3 ζ basis set describes the electronic configuration of carbon atoms by the contracted (11s,6p,2d)/[6s,3p, 2d] and density-fitting uncontracted Gaussian-type functions (10s,3p,3d, 1f). In the case of the 2 ζ basis set, these are (8s,4p,1d)/[4s,2p, 1d] and (7s,2p, 2d) functions, respectively.

Hereinafter, the calculated thermodynamic functions of fullerenes are referred to standard temperature ($T = 298$ K). In the case of the Gibbs energies and entropies, the calculations took into account the symmetry of the system via rotational symmetry number. The PBE/3 ζ method demonstrates reasonable accuracy with respect to such a hard-to-compute parameter as entropy. Indeed, the PBE/3 ζ values for entropy of C_{60} (I_h) and C_{70} (D_{5h}) fullerenes 131.09 and 147.27 cal mol⁻¹ K⁻¹ are in good agreement with the experimental gas-phase values 130.0 and 153.2 cal mol⁻¹ K⁻¹, respectively [98].

The quantum chemical description of bulky molecular systems is commonly known to be highly resource-consuming procedure and accompanied with computational and technical difficulties, which in this

work were overcome using the previously attained solutions [99].

Indeed, as the size of the molecular system grows, the convergence of the wave function (the solution of the self-consistent field equation is used to construct the electron density) worsens, and also the computational costs increase dramatically. Among the possible ways of eliminating the problem of convergence of the wave function is the increasing the number of iterations and microiterations (\$scf iterations = 50,50) when solving the self-consistent field equation (SCF). Another way is switching the default quadratically convergent Newton–Raphson algorithm (\$scf procedure = NR) to the Broyden–Fletcher–Goldfarb–Shanno algorithm (BFGS). One more useful expedient is saving the file of the wave-function eigenvectors (\$control save = “file.vec”) and using it during the subsequent calculations (\$guess read = 1). In extremely unfavorable cases, if the wave function did not converge even the recommendations above applied, the following artless procedure was used. The initial geometric structure of the spatially widespread molecular system was distorted by randomly varying the x, y and z coordinates of each atom in the tight range $-0.05 \dots +0.05$ Å, making the initial molecular geometry become farther away the equilibrium structure of the molecule. In all complicated cases, this procedure made the convergence of the SCF tasks possible without any fail, and allowed saving the wave-function vector files for further calculations. Among other things, with the aim of effective planning of the use of computing resources, the estimative dependences for the computational cost were obtained on the dimensions of electronic structure of the calculated molecules.

A correlation and statistic data processing was performed by means of Microsoft Excel 2010 and OriginLab Origin 9.0 program packages.

3. Results and discussion

3.1. Choice of objects

A part of the studied set of fullerenes has been taken from the Yoshida's fullerene library [100,101], in which the structures obtained via spiral algorithm [7] are collected. The isolated pentagon rule (IPR) is applicable to the C_n fullerenes starting from C_{60} [7]. To facilitate the computational task, we have excluded the non-IPR structures with $n \geq 60$. Additionally, we have considered the experimentally obtained C_{62} isomer with one isolated tetragon substructure [40]. Thus, the set contains in total 2486 fullerene structures (Table 1). All these structures were calculated by the PBE/2 ζ method, and for each number of atoms n among the multiple isomeric alternatives (if any) we have chosen the most stable isomers listed in Table 2 (all the designations are given in accordance with the notation accepted in Atlas [7]). Then these structures were further re-optimized with the PBE/3 ζ method and this level of theory was used for calculating the thermodynamic parameters of the fullerenes as well. The fact that the experimentally obtained isomers of higher fullerenes C_{76} (D_2) [46,49,53,54], C_{78-3} (C_{2v}) [49,55–58], C_{80-1} (D_{5d}) [59–61], C_{82-3} (C_2) [62,65–67] and C_{84-22} (D_2) [68,69,74] find themselves in the final set of the most stable structures is indicative of the reliability of our screening procedures. In the absence of isomeric alternatives, also included in Table 2 are the experimental isomers of C_{20} , C_{60} (I_h), C_{62} (C_{2v}), C_{70} (D_{5h}) and C_{74} (D_{3h}). The last one is presented only as endometallofullerene, exohedral derivative or dianionic form [82]. Pre-optimized geometry structures (Cartesian coordinates) for all the considered fullerenes are accessible at quantum chemical web-portal QChem.org; the re-optimized geometries for most stable fullerenes included in the final set (listed in Table 2) are gathered in Supporting Information.

3.2. Total energies per atom

To compare the fullerenes of different sizes, we use the energetic parameters (i) normalized to the number of carbon atoms n in the molecule and further (ii) reduced toward one of the objects of the set. In Table 2 and Fig. 1, for each fullerene, the calculated total energy E per

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