

## PERIODIC SYSTEM FOR BASIC PERFECT FULLERENES OBTAINED BY FUSION REACTIONS

A. Melker, M. Krupina, R. Zarafutdinov  
Peter the Great St. Petersburg Polytechnic University, Saint Petersburg, Russia

### I. INTRODUCTION

Fullerenes can grow by reacting with each other, similar to bubbles in a soap solution. This possibility was demonstrated by the example of such reaction as  $C_{24}+C_4 \rightarrow C_{28}$ ,  $C_{30}+C_{30} \rightarrow C_{60}$  through the use of a new molecular dynamics that takes into account simultaneously both atomic and electronic degrees of freedom [1, 2]. In spite of these encouraging results we came to conclusion that the problem of fullerene growth must be split into two: geometry and calculations. The reasons are as follows.

In 1984 it has been found that the time-of-flight mass spectrometry (TOF-MS) distribution of laser-evaporated graphite soot had a bimodal character [3], the low-mass distribution having peaks for  $C_{11}$ ,  $C_{15}$ ,  $C_{19}$  and  $C_{23}$  species with  $\Delta n = 4$  periodicity. Little later fullerenes  $C_{60}$  and  $C_{70}$  were synthesized and a set of simple, empirical chemical and geodesic rules was presented by H.W. Kroto to explain the remarkable stability observed for the  $C_{60}$  molecule [4]. The rules yield cluster magic numbers consistent with observation. The authors of the large review having 277 references [5] state: "Today we interpret the TOF-MS distribution as linear carbon chains in the region  $1 < n < 10$ , macrocyclic rings  $10 < n < 30$ , and fullerenes  $n > 36$  with a forbidden zone between  $n=30$  and  $36$ ".

We can't agree with this interpretation for many reasons, two of the most serious are:

The interpretation does not explain  $\Delta n = 4$  periodicity.

It was shown through the use of molecular dynamics [6] as well as analytically [7] that linear chains with free ends and with periodic boundary conditions (rings) are unstable with respect to vibrations; they transform at first into zigzag chains, helices, and then folds into compact structures. The reason is that small longitudinal vibrations transfer their energy to large transversal vibrations. This phenomenon was named as parametric resonance.

In Ref. [8, 9] using the analogy with polymer physics and radiation solid state physics we unexpectedly obtained the  $\Delta n = 4$  periodicity for caged carbon molecules  $C_{12}$ ,  $C_{16}$ ,  $C_{20}$ ,  $C_{24}$ . The structures have threefold, fourfold, fivefold and sixfold symmetry. Clearly the following reasoning was: if there exists the  $\Delta n = 4$  periodicity, provably there are other periodicities. Really, we have found the  $\Delta n=8$  periodicity [10] for the family of  $C_n$  fullerenes originating from the reactions of cupolas  $C_{10}+C_{10} \rightarrow C_{20}$ ,  $C_{12}+C_{12} \rightarrow C_{24}$ ,  $C_{16}+C_{16} \rightarrow C_{32}$ ,  $C_{20}+C_{20} \rightarrow C_{40}$ ,  $C_{24}+C_{24} \rightarrow C_{48}$ , where the structures had also the same symmetry. Since all these periodicities have one and the same main feature, namely, the transition from threefold symmetry to sixfold, it seems reasonable, to take this feature as a basis for fullerene classification and to search other periodicities. It should be noted that calculations performed for small fullerenes are unable to be such a basis on default of any other adequate explanation. For example, for  $C_{20}$  the most stable isomer can have a ring, a bowl or a fullerene structure, depending on the computational method employed [11].

In this contribution we consider the growth of fullerenes through a series of joining reactions of cupola half-fullerenes  $C_{16}$ ,  $C_{18}$ ,  $C_{24}$ ,  $C_{30}$ , and  $C_{36}$ . It will be shown that there appears the  $\Delta n = 12$  periodicity having the same symmetry transition.

### II. FUSION REACTIONS OF CUPOLA HALF FULLERENES

In 1889 Svante August Arrhenius postulated that a chemical reaction goes in the following way. At first there forms some intermediate compound and only afterwards a usual chemical reaction is going on. For fullerenes this postulate can be written as follows  $A + B \rightarrow (AB) \rightarrow C$ . In Ref. [10] we have developed an algorithm that has proved itself in predicting the growth of perfect fullerenes conserving an initial symmetry, so called the fusion reaction algorithm.

Reaction between two cupolas  $C_{16} + C_{16} \rightarrow (C_{16}C_{16}) \rightarrow C_{32}$  is shown in Figures 1 a, b, c.

Reaction between two cupolas  $C_{18} + C_{18} \rightarrow (C_{18}C_{18}) \rightarrow C_{36}$  is presented in Figures 1 d, e, f.

Reaction between two cupolas  $C_{24} + C_{24} \rightarrow (C_{24}C_{24}) \rightarrow C_{48}$  is displayed in Figures 1 g, h, i.

Reaction between two cupolas  $C_{30} + C_{30} \rightarrow (C_{30}C_{30}) \rightarrow C_{60}$  is exhibited in Figures 1 j, k, l.

Reaction between two cupolas  $C_{36} + C_{36} \rightarrow (C_{36}C_{36}) \rightarrow C_{72}$  is illustrated in Figures 1 m, n, o.

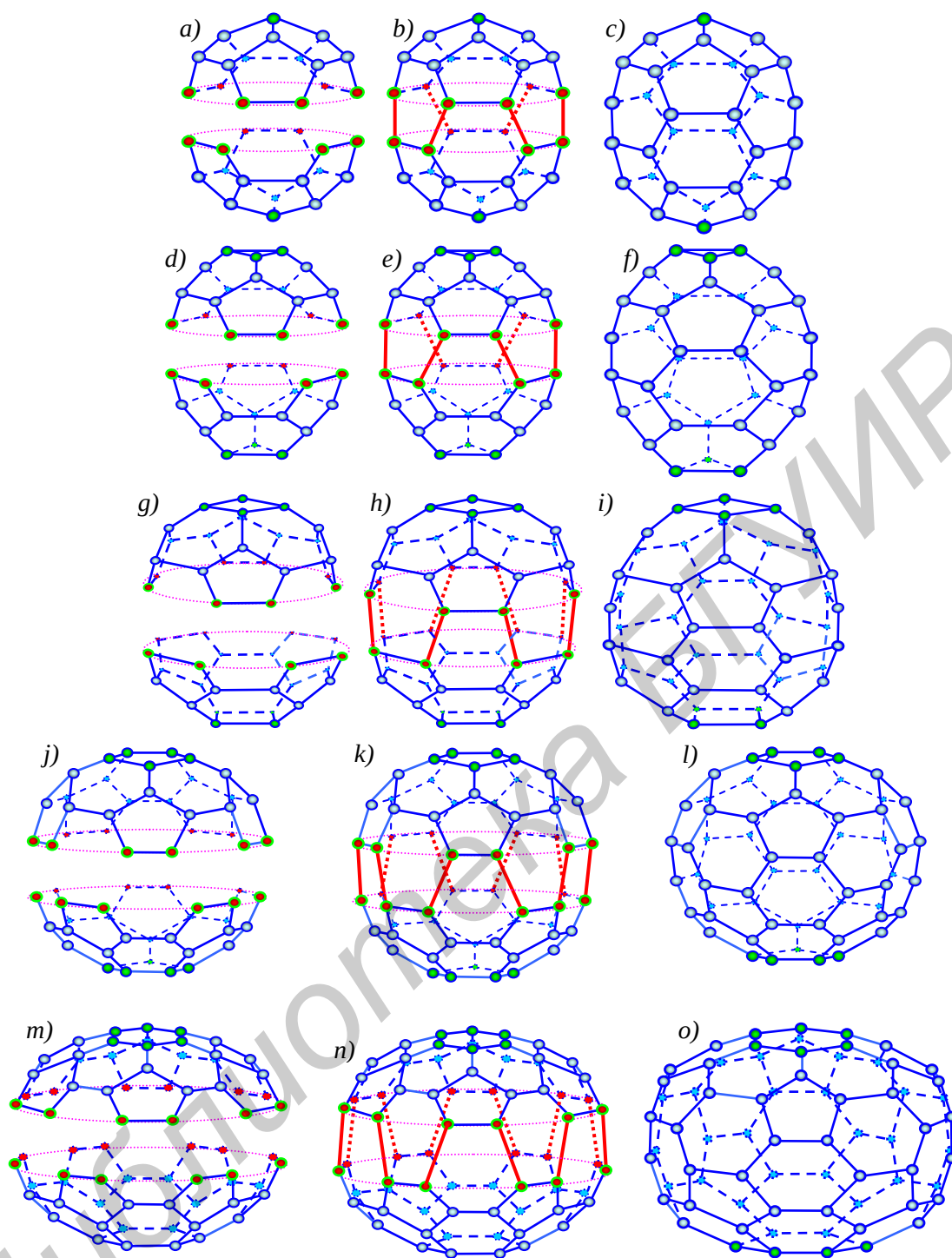
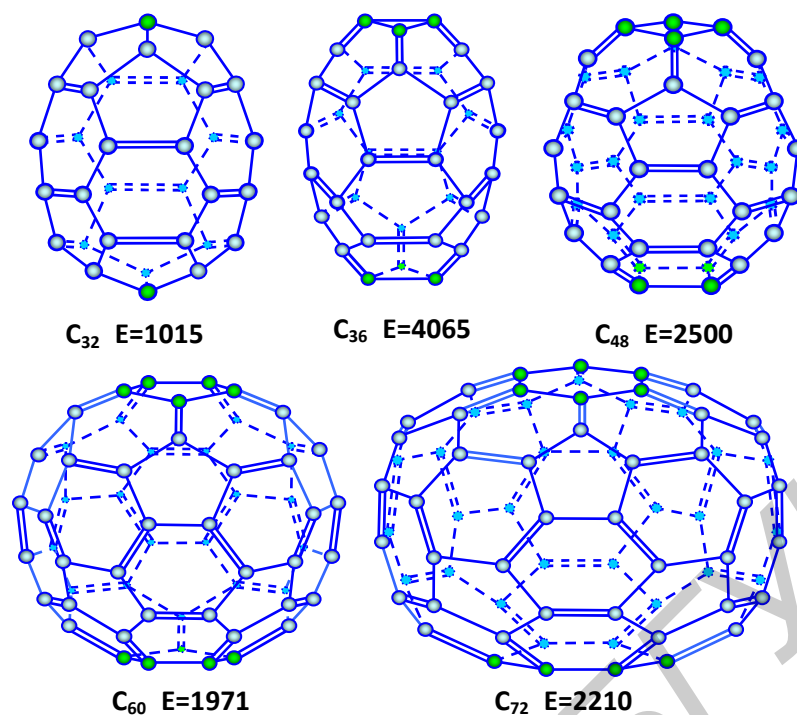


Figure 1 – Joining of two half-fullerenes  $C_{16}$ ,  $C_{18}$ ,  $C_{24}$ ,  $C_{30}$  and  $C_{36}$ . a, d, g, j, m) Separate carbon cupolas; b, e, h, k, n) Intermediate compound; c, f, i, l, o) Polyhedrons after relaxation. Dark-red and light-blue balls are reacting and neutral atoms, respectively; thin light-blue solid and dashed lines are covalent bonds; heavy dark-red solid and dashed lines are new covalent bonds.

### III. SINGLE AND DOUBLE BONDS

We assume that the symmetry of double bonds location about the major axis of cupolas and other fullerenes coincides with that of fullerene  $C_{60}$ . Using this postulate, we have all the necessary input data for the optimization of the fullerene and cupola structures designed by means of geometric modeling and for subsequent calculation of their properties. As it was described above, the cupolas having one and the symmetry can react with each other producing fullerenes  $C_{36}$ ,  $C_{48}$ ,  $C_{60}$ , and  $C_{72}$  with single and double covalent bonds and, in the case of fullerene  $C_{32}$ , with partially delocalized bonds too. The optimized structures of the fullerenes obtained through the use of Avogadro package [12] are shown in Figure 2.


 Figure 2 – Structure of the  $\Delta n=12$  series fullerenes with single and double bonds. Energy in kJ/mol

#### IV. SYMMETRY AND ENERGY OF PERFECT FULLERENES

Modeling the growth of fullerenes from  $C_{24}$  ( $D_{3h}$  symmetry) to  $C_{48}$ , we have obtained the perfect fullerenes  $C_{30}$  and  $C_{36}$  conserving three-fold symmetry [13]. Modeling the growth of fullerenes from  $C_{32}$  ( $D_{4h}$  symmetry) to  $C_{60}$ , we found perfect fullerenes  $C_{40}$  and  $C_{48}$  conserving four-fold symmetry [14]. The mass difference between successive fullerenes in the first case is  $\Delta m=6$ , in the second case  $\Delta m=8$ . It should be emphasized that in both cases the mass difference is equal to a double degree of symmetry.

It is intriguing to combine periodicities,  $\Delta m$  and  $\Delta n$ , in order to gain a better understanding of the energy results obtained. With this in mind, we designed the fullerenes of the neighbor periodicities  $\Delta n=8$ ,  $\Delta n=10$  and  $\Delta n=14$  using geometrical modeling, optimized their structures through the use of Avogadro package, and calculated their energies. The results are given in the table where all the fullerenes form five vertical columns (groups), having different symmetry. Two groups of three-fold symmetry differ by the structure of their apices. The 3-fold-symmetry group S has two sharp apices, the third-order axis going through them. The 3-fold-symmetry group T has two truncated apices, the third-order axis going through the centers of triangles.

The energy minimum for fullerenes  $C_{50}$  and  $C_{60}$  having fivefold symmetry can be explained in the context of strain-related instability [4, 13], however, the least energy obtained unexpectedly for fullerene  $C_{26}$  contradicts to this concept and needs more careful investigation. At this point we have a semi-quantitative explanation in the framework of electronic theory of molecule vibrations [15].

	3-fold S $\Delta m=6$	3-fold T $\Delta m=6$	4-fold $\Delta m=8$	5-fold $\Delta m=10$	6-fold $\Delta m=12$
$\Delta n=8$	$C_{20}$ 1647	$C_{24}$ 3667	$C_{32}$ 2291	$C_{40}$ 2007	$C_{48}$ 2562
$\Delta n=10$	$C_{26}$ 831	$C_{30}$ 3923	$C_{40}$ 2426	$C_{50}$ 1979	$C_{60}$ 2329
$\Delta n=12$	$C_{32}$ 1015	$C_{36}$ 4065	$C_{48}$ 2500	$C_{60}$ 1970	$C_{72}$ 2210
$\Delta n=14$	$C_{38}$ 1206	$C_{42}$ 4253	$C_{56}$ 2643	$C_{70}$ 2069	$C_{84}$ 2255

#### REFERENCES

- [1] A.I. Melker, S.N. Romanov, D.A. Kornilov, Computer simulation of formation of carbon fullerenes, Materials Physics and Mechanics, 2 (1) (2000) 42-50.

- [2] D.A. Kornilov, A.I. Melker, S.N. Romanov, Conformation transitions in fullerenes at non-zero temperatures, *Proceedings of SPIE*, 5127 (2003) 81-85.
- [3] E.A. Rohlfing, D.M. Cox, A. Kaldor, Production and characterization of supersonic carbon cluster beams, *J. Chem. Phys.* 81(7) (1984) 3322-3330.
- [4] H.W. Kroto, The stability of the fullerenes  $C_n$ , with  $n=24, 28, 32, 36, 60, 60$  and  $70$ , *Nature*, 329 (1987) 529-531.
- [5] S. Irle, A.J. Page, B. Saha, Y. Wang, K.R.S. Chandrakumar, Y. Nishimoto, H-J. Qian, K. Morokuma, Atomistic mechanisms of carbon nanostructure self-assembly as predicted by nonequilibrium QM/MD simulations. In: *Practical Aspects of Computational Chemistry II: An Overview of the Last Two Decades and Current Trends*, Eds. J. Leszczynski and M. K. Shukla, Springer-European Academy of Sciences, (2012) 59 p.
- [6] A.I. Melker, T.V. Vorobyeva, Polymer crystallization as the self-organization of chain macromolecules, *Zeitschrift für Naturforschung*, 49a (11) (1994) 1045-1052.
- [7] A.I. Melker, T.V. Vorobyeva, Parametric resonance of the transverse waves in polymer macro-molecules: a reason for folding, *Nanobiology*, 4 (1996) 71-82.
- [8] A.I. Melker, Possible ways of forming mini-fullerenes and their graphs, *Materials Physics and Mechanics*. 20 (1) (2014) 1-11.
- [9] A.I. Melker, S.A. Starovoitov, T.V. Vorobyeva, Classification of mini-fullerenes on graph basis, *Materials Physics and Mechanics*, 20 (1) (2014) 12-17.
- [10] A.I. Melker, T.V. Vorobyeva, Fusion reactions of cupola half-fullerenes, *St. Petersburg State Polytechnical University Journal. Phys. & Math.* 3 (248) (2016) 59-67.
- [11] Z. Chen, H. Jiao, M. Bühl, A. Hirsch, W. Thiel, Theoretical investigation into structures and magnetic properties of smaller fullerenes and their heteroanalogues, *Theoretical Chemistry Accounts*, 106 (2001) 352-363.
- [12] M.D. Hanwell, D.E. Curtis, D.C. Lonie, T. Vandermeersch, E. Zurek, G.R. Hutchison, Avogadro: an advanced semantic chemical editor, visualization, and analysis platform, *Journal of Cheminformatics* 4 (17) (2012); Avogadro: an open-source molecular builder and visualization tool. Version 1.XX. <http://avogadro.cc/>
- [13] A.I. Melker, M.A. Krupina, Geometric modeling of midi-fullerenes growth from  $C_{24}$  to  $C_{48}$ , *St. Petersburg State Polytech. University Journal. Phys. & Math.* 3(248) (2016) 52-58.
- [14] A.I. Melker, M.A. Krupina, Geometric modeling of midi-fullerenes growth from  $C_{32}$  to  $C_{60}$ , *St. Petersburg State Polytechnical University. Journal Phys. & Math.* 10 (1) (2017) 47-54.
- [15] A.I. Melker, M.A. Vorobyeva (now Krupina), Electronic theory of molecule vibrations, *Proceedings of SPIE*, 6253 (2006) 625305-1–62305-15.

## STRUCTURE AND ENERGY OF THE $\Delta n=6$ SERIES FULLERENES

A. Melker, T. Vorobyeva, R. Zarafutdinov

Peter the Great St. Petersburg Polytechnic University, Saint Petersburg, Russia

### I. INTRODUCTION

Earlier it was shown that fullerenes can grow by reacting with each other, similar to bubbles in a soap solution [1]. In this case fullerenes  $C_{24}$ ,  $C_{32}$ ,  $C_{40}$ , and  $C_{48}$  can be formed; the structure periodicity being  $\Delta n=8$ , where  $n$  is the number of carbon atoms. The periodicity has one and the same main characteristic feature; the fullerene structure changes from threefold symmetry to sixfold through four and fivefold ones. We suppose that this feature can be taken as a basis for rigorous fullerene classification in addition to the geometric classification developed for mini-fullerenes [2].

Now we want to increase the number of fullerenes fitted our classification by adding the fullerenes of the structure periodicity  $\Delta n=6$  designed in Ref. 3. In this contribution we present the structure and energy of such fullerenes. Knowing their structure allows one to activate the fullerenes, including unknown previously, for farther investigations and use of their properties.

### II. FUSION REACTIONS OF CUPOLA HALF FULLERENES

In Ref. [1] we have developed an algorithm that has proved itself in predicting the growth of perfect fullerenes conserving an initial symmetry, so called the fusion reaction algorithm. Consider reactions leading to mini-fullerenes  $C_{14}$ . In Fig. 1 the atomic configurations corresponding to reaction  $C_7 + C_7 \rightarrow (C_7C_7) \rightarrow C_{14}$  and  $C_4 + C_{10} \rightarrow (C_4C_{10}) \rightarrow C_{14}$  are shown. At first two molecules  $C_7$ , or  $C_4$  and  $C_{10}$ , are moving towards each other (Figs. 1, a and d). Then the boundary atoms (dark-red) interact with each other producing a compound (Figs. 1, b and e). During this process new covalent bonds (heavy red lines) are