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# Molecular dynamical modelling of endohedral fullerenes formation in plasma

A S Fedorov<sup>1,2</sup>, E A Kovaleva<sup>2</sup>, T A Lubkova<sup>2</sup>, Z I Popov<sup>1,3</sup>, A A Kuzubov<sup>2</sup>,  
M A Visotin<sup>2</sup> and S Irle<sup>4</sup>

<sup>1</sup> Kirensky Institute of Physics, 50/38 Akademgorodok, Krasnoyarsk, 660036 Russia

<sup>2</sup> Siberian Federal University, 79 Svobodny pr., Krasnoyarsk, 660041 Russia

<sup>3</sup> National University of Science and Technology MISiS, Moscow, 119049 Russia

<sup>4</sup> Department of Chemistry, Graduate School of Science, Nagoya University,  
Furo-cho, Chikusa-ku, Nagoya, 464-8601 Japan

E-mail: visotin.maxim@gmail.com

**Abstract.** The initial stages of fullerene and endohedral metallofullerene (EMF) synthesis in carbon-helium plasma at 1500 K and 2500 K have been simulated with quantum chemical molecular dynamics (MD) based on density-functional tight-binding (DFTB). The cases of formation of large (>100 atoms) sp<sup>2</sup>-carbon clusters with scandium atoms inside were observed. These clusters are considered as precursors of fullerenes or EMFs, and thus it is shown that formation of EMFs can be explained within the framework of "shrinking hot giant" mechanism. Also, the dependence of formation rates on plasma parameters, including temperature, buffer gas and metal atoms concentrations, has been studied.

## 1. Introduction

Since the discovery of buckminsterfullerene C<sub>60</sub> [1], the family of fullerenes has attracted much attention due to their unusual electronic and optoelectronic properties, such as high electron affinities as well as novel chemical reactions [2]. It's well-known that encapsulations of metal atoms or small molecules into fullerene's cage lead to significant change of its chemical and physical properties [3,4]. The chemistry of these complexes is considerably different from that of bare fullerenes, in particular, their reduction-oxidation properties. The most promising and well investigated are endohedral metallofullerenes (EMFs, fullerenes with metal atoms inside) and endohedral metal carbide fullerenes (EMCFs, fullerenes containing metal atoms and a carbon molecule) [5-7].

These promising compounds have a lot of various applications due to their unusual electronic and magnetic properties, which strongly depend on their structure. Moreover, being very inert, carbon EMF cage can be used for medical purposes [8, 9]. Such structures may be used as carriers of radioactive isotopes [10], radiotracers or MRI contrast media [11]. The possibility of their using in anticancer therapy is also intensively investigated.

However, the yield of EMFs via plasma chemical synthesis is very low at the present moment. There are still many questions about endohedral metallofullerenes' formation mechanisms, as well as thermodynamic and kinetic stability. For example it can be mentioned that large fullerenes (C<sub>n</sub>, n>70) are thermodynamically more favorable, whereas the fullerene mixture consists essentially of C<sub>60</sub>. Thereby, two opposed mechanisms can be realized: growth of the fullerene and its shrinking via C<sub>2</sub> evaporation (so-called "fullerene road" and "shrinking hot giant" mechanisms, respectively) [12-14].



According to the recently developed "shrinking hot giant" mechanism, large fullerenes are formed first during carbon cluster aggregation process. Being the result of differently sized carbon clusters' coagulation and due to high thermodynamic stability, these giant fullerenes include large number of atoms as well as structural defects. Subsequently, these giant fullerene clusters shrink in size by the loss of the  $C_2$  clusters [14] during the further process of plasma cooling, because the larger clusters have less kinetic stability [12].

This mechanism of fullerene formation was supported by a number of investigations, including quantum-chemical molecular dynamical simulations [12, 15]. One possible confirmation of this model is the fact that yields of  $C_{70}$  and higher fullerenes in fullerene mixture are much higher at high helium pressure (more than 0.10 MPa) [16] than at reduced pressure (0.013 MPa) [12].

In this work, plasma chemical synthesis of fullerenes and EMFs is simulated by quantum-chemical molecular dynamics. It is shown that formation of endohedral fullerenes can be explained within the framework of "shrinking hot giant" mechanism. Also, the dependence of formation rates on plasma parameters (including temperature, buffer gas and metal atoms concentrations) is studied.

## 2. Methods

All MD simulations were performed within the framework of non-consistent charge density-functional tight-binding (NCC DFTB) method [17, 18]. This method is often used for conducting MD for large systems (thousands of atoms) and for long run times (up to several nanoseconds), while having results comparable with conventional DFT [13].

In order to model large systems, we used boxes sized  $100 \times 100 \times 100 \text{ \AA}$ . Each MD box contained 120  $C_2$  dimers and different numbers of He and Sc atoms (0, 120 or 240 helium atoms and 12 or 24 Sc, respectively). The spatial distribution of atoms and molecules as well as  $C_2$  dimers orientations were uniformly random. Each box was simulated at two finite temperatures (1500 and 2500 K) by Berendsen thermostat [19] with coupling parameter of 100 fs. Taking into account that the system under consideration is large, only  $\Gamma$  point was used for the reciprocal space sampling. MD runs were conducted up to 0.6 ns with a time step of 1 fs. At least 5 different trajectories for each combination of parameters (i.e. temperature, number of He and Sc atoms) were simulated to get statistics for averaging the formation rates values.

In order to measure the dynamics of cluster aggregation and transformation, changes in orbital hybridization type of carbon atoms were tracked with time. Atoms having four, three and two carbon neighbors within a coordination sphere with radius equal to  $1.9 \text{ \AA}$  were considered to be in  $sp^3$ ,  $sp^2$  and  $sp$  hybridization states respectively. Some atoms had only one neighboring C atom, for example atoms on the ends of chains or atoms in  $C_2$  dimers. This state is further referred as 1b. The time evolution of number of atoms in certain hybridization states was averaged among 5 calculated trajectories for every parameters set.

## 3. Results and discussion

### 3.1. Fullerene formation mechanism

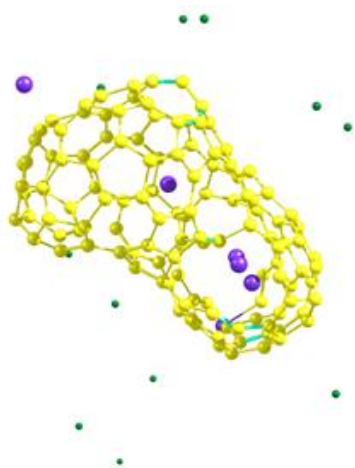
Qualitatively, almost the same picture is observed for all the trajectories with all the parameter sets:

At the beginning of MD run, constant collisions of  $C_2$  dimers lead to formation of  $C_n$  chains. This initial chain building process is rapid and almost irreversible, as the driving force for their formation is the creation of carbon-carbon  $\sigma$ -bond between two carbon atoms with energy of nearly 3.4 eV. As a consequence, these long chains grow longer and longer, until almost no free  $C_2$  molecules are present in the system. This stage is reached in a very short time in the order of tens of picoseconds.

After that, chains gradually begin to connect and form so-called "Y-junctions" containing a single  $sp^2$ -type carbon atom, and subsequently forming cyclic structures, containing pentagons, hexagons, and heptagons, as a result of thermal vibrations and bending. Formation of energetically favorable hexagons and heptagons from the interaction between two long carbon chains are also frequently observed. This can be considered as the initial stage of the growth of a carbon sheet fragments.

After formation of a cycle-containing nucleus, the cluster begins a transformation into a network of  $sp^2$ -type carbon atoms. The transformation is mainly due to bond formation between linear carbon chains attached to the nucleus in close proximity to each other. The driving force for this process is growing  $\pi$ -conjugation and stabilization, so the most kinetically stable pentagons and hexagons are formed. The pentagons, introducing a uniform curvature to the growing cluster, give it a bowl shape.

Concerning Sc atoms, we observe frequently that ends of carbon chains are terminated by Sc atoms, connected to the carbon chain by Sc-C  $\sigma$ -bond. The Sc atoms participate actively in the carbon sheet growth process too. We observed that Sc become di- and sometimes even trivalent, effectively replacing  $sp^2$  carbon. Some of the carbon sheets formed also contain Sc at the ends of carbon side chains or on top of the  $sp^2$ -type carbon networks, with the position inside a carbon cage bowl being more stable.



**Figure 1.** One of EMF cages after 0.4 ns simulation. Yellow balls represent carbon atoms, purple – scandium, cyan – helium.

Similar to nanotube to fullerene conversion, long carbon chains attached to the opening of the bowl reach over the opening and thereby form additional large macrocyclic rings, which in turn can collapse in a “zipper”-type cycloaddition reaction mechanism. As a result, clusters of more than 100 carbon atoms are likely to evolve into a form, which resembles a giant defect-rich fullerene. Figure 1 shows an example of such a structure, consisting of 125 C atoms and 3 Sc atoms inside the almost closed carbon cage.

### 3.2. Effect of plasma parameters

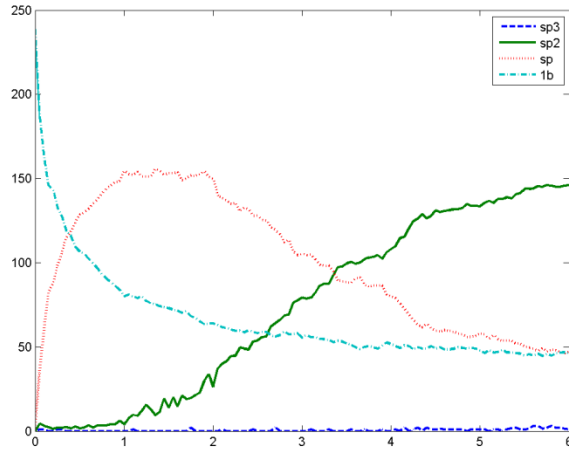
The rates of fullerene formation are proportional to the rates of  $sp^2$ -carbon network growth. Thus, we can compare the rates of  $sp^2$ -carbon network growth in order to estimate, how different plasma parameters affect fullerene and endohedral fullerene production in plasma chemical synthesis. The dynamics of carbon atom transformation from 1b state to  $sp^2$  are shown in figure 2. It should be noted, that there are almost no atoms in the  $sp^3$  state.

**3.2.1. Effect of buffer gas concentration.** Buffer gas atoms are known to play crucial role in fullerene growth. Comparing the rates of changes in the number of  $sp^2$  carbon atoms (in figure 2 He concentration rises from top row to bottom), we can conclude that presence of helium atoms nearly doubles the speed of carbon cages growth. This fact can be explained by the heat transfer from the growing  $sp^2$  nucleus to the buffer gas, which results in stabilization of the nucleus. However, the effect comes to saturation at high helium concentrations. The results for equal carbon and buffer gas concentrations (120  $C_2$  dimers and 120 He atoms) are almost the same as for 1:2 proportion.

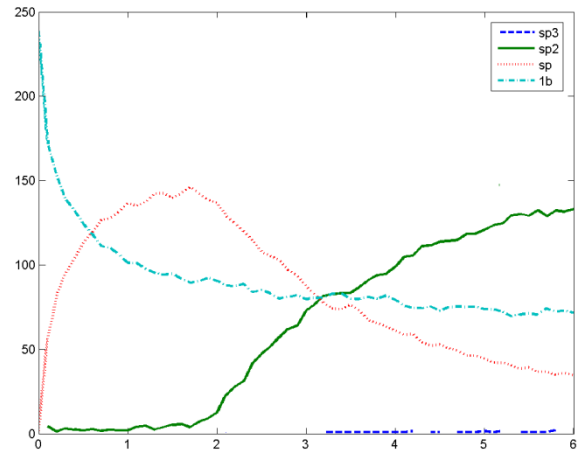
**3.2.2. Effect of plasma temperature.** MD simulations at 1500K and 2500K reveal unusually weak temperature dependence of  $sp^2$ -carbon cluster formation rates. We speculate that the rates of cluster transformation to  $sp^2$  sheet depend on internal vibrational energy of the cluster, which can be higher than the plasma temperature, because of the energy released during new bonds creation [20].

**3.2.3. Effect of metal atoms concentration.** Comparing the results for the He-free systems with different Sc atom numbers (see figure 2 (a) and (d)) we can see that increase in Sc concentration rises amounts of carbon atoms in 1b state. Analysis of the trajectories showed that this is due to Sc atoms hanging on the ends of carbon chains and thus not allowing them to connect to each other. As a result, the growth rates of unbranched chains and cycles are significantly reduced. In the cases with the buffer gas, however, the effect doesn't take place, because collisions with He atoms tear Sc from chain ends.

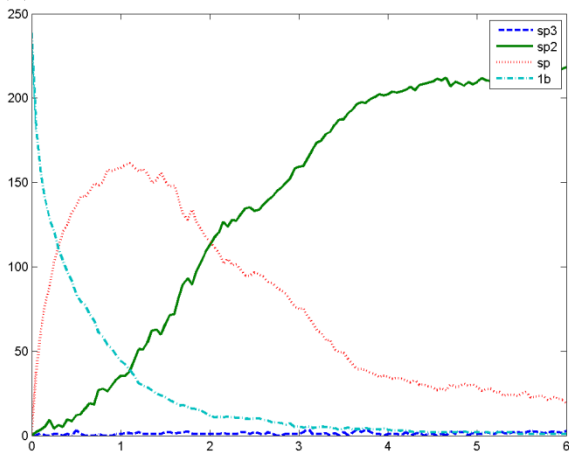
(a) 240 C, 0 He, 12 Sc; T= 2500 K



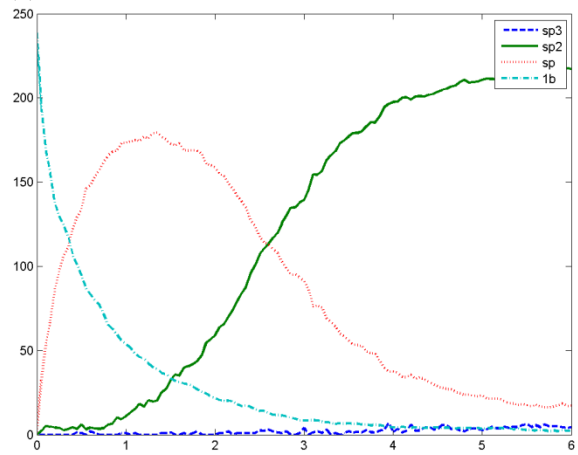
(d) 240 C, 0 He, 24 Sc; T= 2500 K



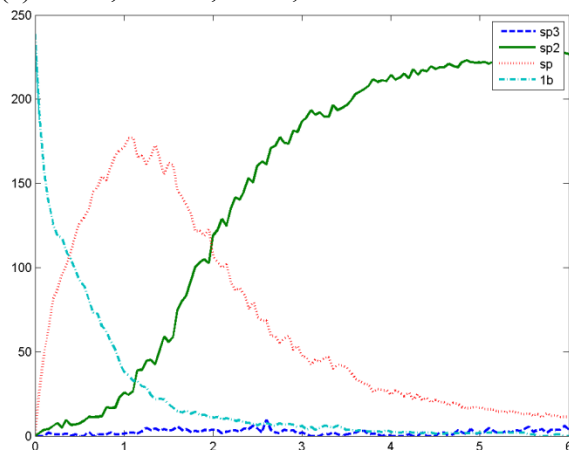
(b) 240 C, 120 He, 12 Sc; T= 2500 K



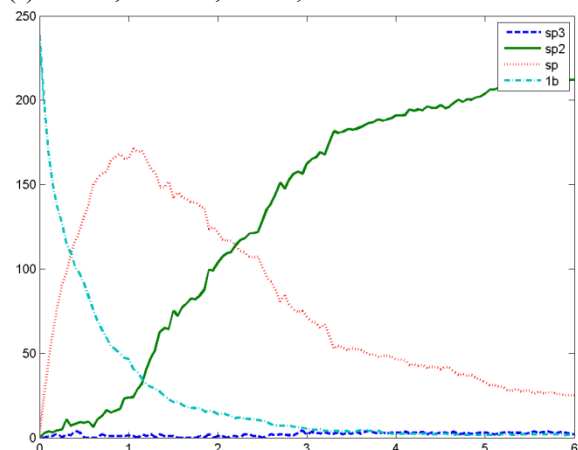
(e) 240 C, 120 He, 12 Sc; T= 1500 K



(c) 240 C, 240 He, 12 Sc; T= 2500 K



(f) 240 C, 240 He, 12 Sc; T= 1500 K



**Figure 2.** (a) – (f) Time evolution of the number of atoms in different hybridizations states. The numbers of carbon and helium atoms as well as the temperature used in the simulations are given above each plot. Horizontal time axes are in  $10^5$  fs.

#### 4. Conclusions

In the present work we have performed DFTB MD simulations of the initial stages of fullerenes and scandium EMFs' synthesis in carbon-helium plasma at temperatures of 1500K and 2500K. During the simulations, which have started from uniformly distributed separate C<sub>2</sub> dimers, He and Sc atoms, most of the carbon have coagulated with formation of large (>100 atoms) sp<sup>2</sup>-carbon shell-like clusters. It also should be noted, that there was almost no sp<sup>3</sup>-associated clusters. The observed closed sp<sup>2</sup>-carbon cage structures, some of which had several scandium atoms inside, can be considered as precursors of fullerenes or EMFs, which will obtain their stable structure after further annealing. These observations confirm the "shrinking hot giant" mechanism of fullerenes or EMFs formation in plasma.

Also the dependences of sp<sup>2</sup>-carbon cage growth rates from the plasma parameters were investigated. It was shown that sp<sup>2</sup>-carbon cage growth rates are almost 2 times bigger at 1:1 He and C<sub>2</sub> concentrations than without helium at all, although the further increase of He concentration has no visible effect. Also, an unusually weak dependence of sp<sup>2</sup>-carbon cage growth rate on the temperature was found. Finally, it was shown that increase in Sc concentration lowers the growth rates of unbranched chains and cycles in the cases without helium, but has no effect in cases with buffer gas.

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