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## Relative Stability of Different Fullerenes Formed in Plasma

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*A method explaining the relative yield of nanostructures during the plasma chemical synthesis is proposed. The method is based on calculation of probability of molecule destruction. This probability is considered as the maximal probability among all chemical bonds in the molecule to stretch upon the critical distance due to molecule thermal vibrations. By calculations of vibration eigenfrequencies and eigenvectors and suppose that all vibrations are independent and their phases are random, it is possible to calculate the probability of every bond destruction. Choosing the maximal one, corresponding the weakest bond destroying, it is possible to calculate probability of the molecule destroying. Using this method for yield of some fullerenes and single wall carbon nanotubes, it is shown that it can qualitatively explain the data of experimental yield. Because of general treatment of the method, one can expect that this method can provide an explanation of other nanostructures yield.*

*Keywords: fullerene, plasma-chemical synthesis, DFT, ab-initio calculations, nanostructure, stability, vibrations.*

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## Introduction

Although fullerenes have been known for over two decades, surprisingly, their formation mechanisms are still unclear. A lot of models were proposed to explain it, but all of them suffered from some drawbacks. In the models [1, 2, 3] a fullerene molecule was formed from small cluster by atoms insertion like a snail is growing, in the "snow ball" model [4], "pentagon path" [5] and [6] models basket-kind structures were grown and transformed to spheroid clusters

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by atoms or atom pairs insertion and formation of new pentagons. Unfortunately, these models can only explain the formation of the first stable fullerene  $C_{60}$  but not higher fullerenes, whose formation from most stable  $C_{60}$  molecule is obscure. Nevertheless there is experimental evidence [7] that often giant fullerenes (GF) are formed which shrink to subsequently smaller fullerenes by removal of carbon atom pairs, see Fig.1.

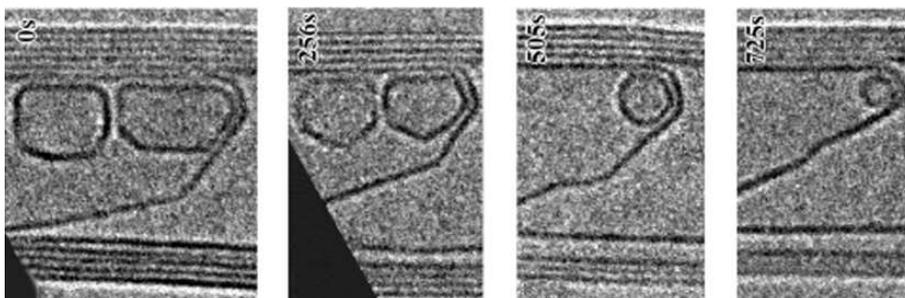


Fig. 1. Shrinking of the giant fullerene inside multiwall carbon nanotube to the small fullerene under electron beam influence, see [7]

In the present work the authors provide the first direct confirmation to the proposed "shrink-wrap" [5], [8] mechanism and its generalization and to a recent "hot-giant" [12, 13, 14] mechanism. "Shrink wrap" mechanism refers to the creation of subsequently smaller fullerenes by removal of carbon atoms from a giant fullerenes, while "hot giant" refers to the concept that all fullerenes are initially formed as GFs that then are reduced via shrink wrapping to sizes as small as a  $C_{60}$  molecule. This concept can be indirectly proved in [11] by wide carbon cluster mass distribution distribution, see Fig. 2.

In the figure one can see that in products of the fullerene synthesis, that is carbon black soot, there is a lot of carbon clusters which are larger than  $C_{60}$  fullerenes, which could be precursors of  $C_{60}$  molecule. At that the role of dimer  $C_2$  evaporation during shrinking of vibrationally excited, floppy giant fullerenes resembles Smalley's shrink wrap mechanism of laser-excited  $C_{60}$ , where  $C_2$  fragmentation was observed very early in the history of the fullerenes [5]. The important role of  $C_2$  cluster evaporation during carbon nanocluster transformation was also demonstrated in [9].

To summarize, all known data says that in the carbon contained plasma during the fullerene synthesis large carbon clusters exist and fullerenes can be produced from them by shrink process when dimers  $C_2$  are evaporated from the clusters. At that one can expect that life time of these clusters is essentially smaller than that for fullerenes due to relative stability of fullerenes. So it is possible to suppose that relative yield of different fullerenes would be proportional to the life time of them. Assuming that the life time of fullerene molecules is proportional to the probability of the molecule destruction, one can expect that relative proportional to the probability of the destruction. At that one should remember that it is often used proportionality between yield of different nanostructures and  $\exp\left(-\frac{E_{\text{bind}}}{kT}\right)$  value, where  $E_{\text{bind}}$  is the binding energy per atom of the nanostructure and  $T$  is the synthesis temperature is wrong for the fullerene synthesis description.

With regard to binding energy dependence on the number of atoms in the fullerene molecule, see Fig. 3, one can expect that the yield of heavier fullerenes should be larger than  $C_{60}$  yield

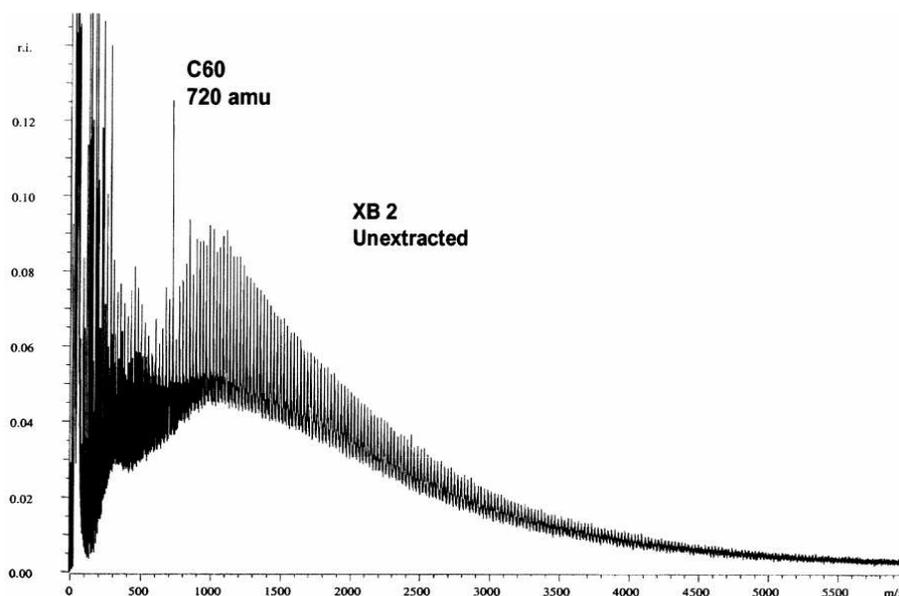


Fig. 2. MALDI mass spectrum showing  $C_{60}$  and higher fullerenes in carbon black soot, see [11]

that is contradictory to experiments, see Table 1. It means that fullerene synthesis process is not equilibrium and it is necessary to create the method explaining yield of different nanostructures.

Table 1. Relative yield of some fullerenes in the arc discharge method (Krötschmer method)

$C_{60}$ /soot	10%
$C_{70\_D5H}/C_{60\_IH}$	10%
$C_n$ ( $n=74, 76, 78, 80, 82, 84$ , etc)/ $C_{60}$	<1%
$C_{36\_D6H}/C_{60}$ (*)	small quantity

(\*)C.Piskoti, J.Yargen, A.Zettl, *Nature*, **393**(1998), 771

So, the aim of this work is to propose the method based on probability of destruction computations and to check this method on experimental data concerning the yield of some fullerenes and SWCNT.

## 1. Details of Calculations

First of all, total electronic structure for some fullerenes and single wall carbon nanotubes(SWCNT) have been calculated. For that VASP 4.6 package [9-10] was used. This package allows one to make ab-initio calculations on the base of density functional [11, 12] theory with the generalized gradient approximations of PBE [13] for the exchange-correlation potential and plane wave basis set. At that electron-ion interaction is taken into account via ultrasoft Vanderbilt-kind pseudopotential formalism [14]. For SWCNT calculations the integration over the first Brillouin zone (BZ) was made with help of 4  $k$ -points inside BZ. These  $k$ -points were chosen along the

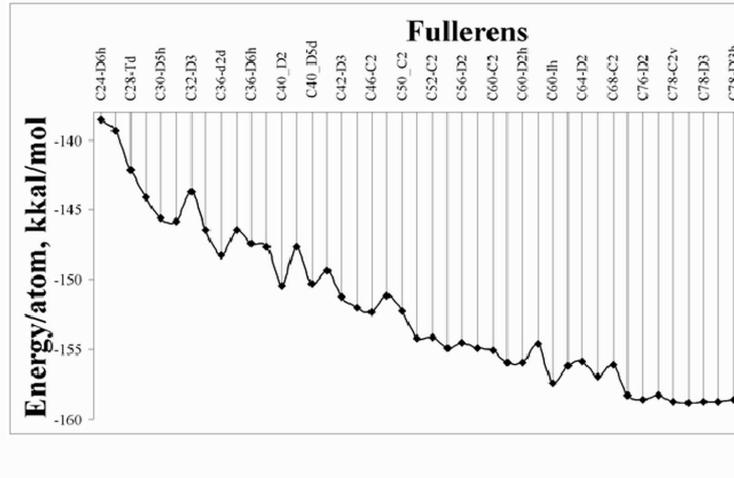


Fig. 3. Binding energy per atom of different fullerenes, see [10]

CNT axis by Monkhorst-Pack  $k$ -point sampling [15]). In all cases the geometry optimization was carried out using preconditioned conjugate gradient procedures [16, 17] until the forces acting on each atom become less than  $0.05 \text{ eV}/\text{\AA}$ . The kinetic-energy cutoff used for all the plane-wave expansions of electronic wave functions were 287 eV. Then, total vibration spectra and corresponding eigenvectors for all investigated nanostructures have been calculated with help of the ab initio frozen phonon method [18]. Because of large computational difficulty the only  $k$ -vectors  $(0,0,0)$  and  $(0,0, \pi/a)$  for the phonon curves have been used.

Let's coordinates vector of atom  $n$  is

$$\vec{R}(n) = \vec{R}_0(n) + \sum_{i=1}^{3(N-1)} \vec{X}_i(n) \exp(i(\omega_i t + \delta_i)) \quad (1)$$

where  $\vec{R}_0(n)$  — coordinates of atom  $n$  in equilibrium,  $\vec{X}_i(n)$  is vibration eigenvector of vibration  $i$  for atom  $n$ ,  $\omega_i$  is eigenvalue(frequency) of the vibration and  $\delta_i$  is the value of the vibration initial phase. Remember that for harmonic vibration  $i$  the average kinetic and potential energies are equal, one can find:

$$E_{pot} = E_{kin} = \frac{m}{2} \sum_{n=1}^N \left| \vec{X}_i(n) \right|^2 = \frac{m}{2} \omega_i^2 \vec{X}_i^2 \quad (2)$$

where  $\vec{X}_i^2$  is square of norm for vibration  $i$  eigenvector  $\vec{X}_i(n)$  and  $\omega_i$  is corresponding vibration frequency.

Using well known formulas for the total energy and the magnitude of harmonic vibrations, we obtain:

$$\begin{aligned}
E_{\text{total}} &= E_{\text{kin}} + E_{\text{pot}} = kT; \\
|\vec{X}_i| &= \sqrt{\frac{kT}{m\omega_i^2}};
\end{aligned}
\tag{3}$$

Relative displacement of  $n$  and  $m$  atoms is equal to

$$\Delta\vec{R}(n, m) = \vec{R}(n) - \vec{R}(m) = \sum_{i=1}^{3(N-1)} \left( \vec{X}_i(n) - \vec{X}_i(m) \right) \exp(i\omega_i t + \delta_i)
\tag{4}$$

Further it is convenient to introduce projected to the bond direction displacement  $\Delta R(n, m)$ :

$$\Delta R(n, m) = \left| \Delta\vec{R}(n, m) \right| \cos(\Delta\vec{R}(n, m), (\vec{R}_0(n) - \vec{R}_0(m)))
\tag{5}$$

Remember that  $\Delta R(n, m)$  is the sum of contributions of large number of vibrations, equal to  $3(N-2)$ , where  $N$  is the number of atoms in isolated molecule, and suppose that the contributions from different vibrations are independent due to random values of vibration initial phases  $\delta_i$ , it is natural to use the central limit theorem of probability theory. This theorem asserts that the sum  $X$  of independent values  $X = \sum_{i=1}^n X_i$  having equal variance  $\sigma^2 = \frac{1}{n} \sum_{i=1}^n (X_i - \bar{X})^2$  and the average  $\bar{X} = \sum_{i=1}^n X_i$  converges to the following normal distribution:

$$f_{\mu\nu}(X) = \frac{1}{\sqrt{2\pi\sigma}} \exp\left(-\frac{(X - \bar{X})^2}{2\sigma^2}\right)
\tag{6}$$

as  $n$  tends to infinity. Now we can use the Lindeberg's condition implementation of the central limit theorem, which does not require that all independent random variables  $X_i$  should be identically distributed, so they can have different variance  $\sigma_i^2$ . Under that condition the total variance and the distribution of the sum converges to the normal distribution (5) as  $n$  approaches infinity. So, using central limit theorem and the formulas (2-5), it is possible to calculate the distributions of projected displacement between all pairs of nearest atoms  $(n, m)$ . Assuming that chemical bonding between  $n$  and  $m$  atoms would be broken if the distance between  $n$  and  $m$  atoms exceeds some critical distance  $X_{\text{max}}$ , it is possible to calculate the probability of that:

$$P\left(\frac{\sum_{i=1}^{3(N-2)} X_i}{\sigma_n} > X_{\text{max}}\right) = \frac{1}{\sqrt{2\pi}} \int_{X_{\text{max}}}^{\infty} \exp\left(-\frac{u^2}{2}\right) du,
\tag{7}$$

where

$$\frac{1}{\sqrt{2\pi}} \int_{X_{\text{max}}}^{\infty} \exp\left(-\frac{u^2}{2}\right) du$$

is the normal cumulative distribution function. In calculations of the rate of chemical bonding destroying the critical distance  $X_{\text{max}}$  was defined as follows. Using  $C_{60}$  as the base for the first step destroying calculation, the distance between pair of nearest atoms was increased from the equilibrium value 1.45Å(initial state) to 2.66Å(final state), see Fig. 4.

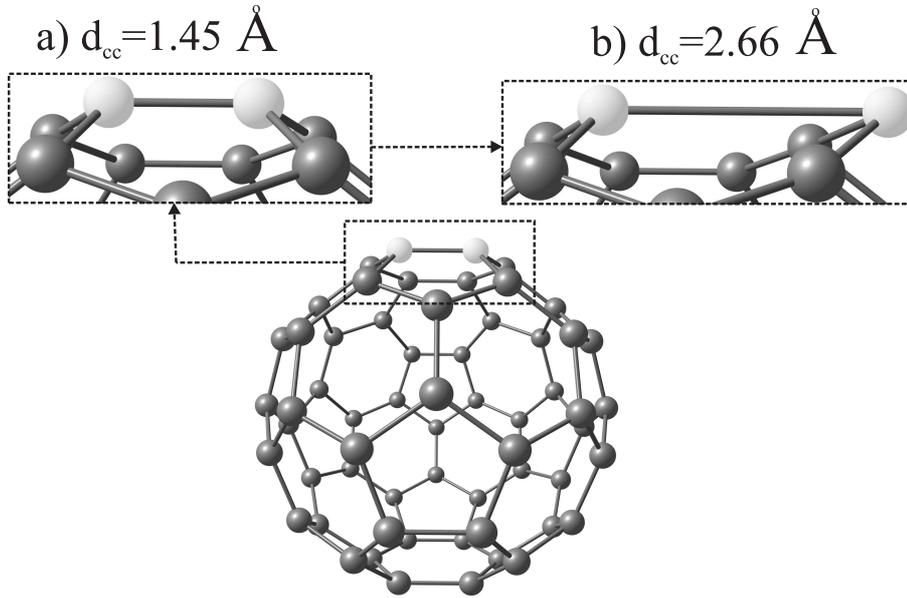


Fig. 4. Initial a) and final b) states of  $C_{60}$  molecule for calculations of the total energy dependence upon the C-C distance

At that all other interatomic distances were fixed. The atom pair was chosen as separating pentagon and hexagon because of weaker bonding between them as compared with bonding between two adjacent hexagons, where C-C equilibrium distance is  $1.391\text{\AA}$ . Using the both distances as the initial and the final geometries, the transition state theory was used to calculate energy barrier value. With help of the nudged elastic band method (NEB) [25] the total energy dependence upon generalized coordinates variable from the initial to the final states was calculated, see Fig. 5.

From the Fig. 5 one can see that the total energy of  $C_{60}$  molecule begin to increase rapidly when distance between the atom pair exceed some critical distance  $X_{\max}$  in the range  $1.9\text{-}2.0\text{\AA}$ . Therefore for the estimation of the critical distance when the chemical bonding begin to destroy, the value  $X_{\max} = 1.95\text{\AA}$  was chosen. After  $X_{\max}$  definition and calculation of the vibration eigenvalues and corresponding eigenvectors the destruction rate  $P_{\text{destr}}$  was calculated by oversight of destruction rate for all connected atom pairs and choosing the maximal rate. The destruction rate  $P_{\text{destr}}$  for set included some fullerenes and SWCNT are shown in the Table 2, column 2-3. As vibration amplitude dependent for the temperature, see (2), the temperature value  $T=3000\text{K}$  was used in all calculations. This value was chosen because it is estimation of the temperature of fullerenes formation. For comparison, the relative concentration  $\frac{C_{\text{equil}}^1}{C_{\text{equil}}^2}$  calculated with help of thermodynamic equilibrium

$$\frac{C_{\text{equil}}^1}{C_{\text{equil}}^2} = \frac{\exp(-E_{\text{bind}}^1/kT)}{\exp(-E_{\text{bind}}^2/kT)}$$

distribution is shown in the Table 2, last column. From this it is obvious that fullerene  $C_{70}$  should be the most stable and its yield should be higher than that for  $C_{60}$  molecule what is

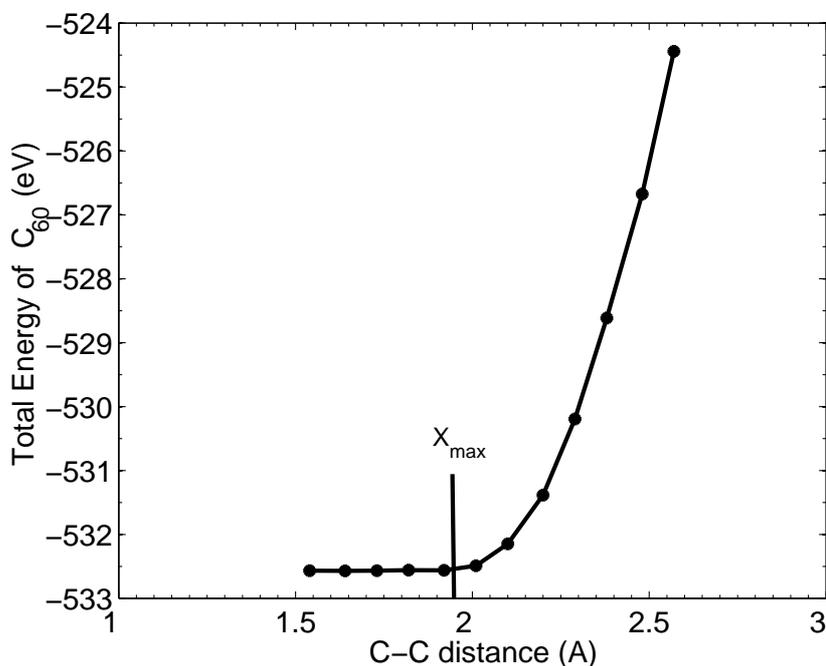


Fig. 5. Dependence of the  $C_{60}$  molecule total energy from the C-C distance between adjacent hexagon and pentagon

contradict to experimental facts, see Table 1.

By the Table 2 analysis one can see that the calculated inverse rate of destruction for different fullerenes qualitatively agrees with the experimental yield of the fullerenes. The  $C_{60\_IH}$ ,  $C_{70\_D5H}$  and  $C_{36\_D6H}$  fullerenes have minimal rate of chemical bonding destruction and they have maximal yield during the plasma-chemical synthesis. The analysis of SWCNT rate of destruction also qualitatively agrees with the experiments. One can see that carbon nanotube (CNT) yield, which is proportional to the inverse rate of destruction, increased with CNT diameter increasing, compare (6,0) and (8,0) CNT. At that zigzag SWCNT (8,0) is more stable than armchair NT (5,5) even at last diameter is larger. This fact is experimentally explained by larger deformation of hexagons in armchair CNT in comparison with zigzag CNT, where 1/3 of all bonds directed along the tube axis and they are not deformed. After the destruction rate analysis the role of atoms surrounding the adjacent atoms constrained by weakest vibrating bond was investigated. For that vibrations and the rate of the destruction of the cluster consist from this atom pair plus surrounding 4 atoms were calculated, see Table 2, column 3. At that all other atoms in the cluster were fixed. One can see that freezing of all atoms except six can change the rate of destruction cardinally for some investigated fullerenes, especially for  $C_{30\_D5H}$  fullerene. Recall that the influence of number of atoms involved in the vibrations on the rate of the destruction for this fullerene was investigated, see Table 3. By observing Tables 2, 3, the important conclusion about importance of all atoms involved in the calculation of the rate of nanostructure destruction can be made.

Table 2. Comparison of chemical bond destruction probability  $P_{\text{destr}}$  for different carbon nanostructures

Structure	$P_{\text{destr}}$	$\frac{P_{\text{destr}C_{60}}}{P_{\text{destr}}}$	$P_{\text{destr}}^*$	$E_{\text{bind/atom}}(\text{eV})$	$\frac{C_{\text{equil}}^1}{C_{\text{equil}}^2}$
$C_{70\_D5H}$	7.57E-14	0.112814	3.12E-14	-5.912	1,096
$C_{60\_IH}$	8.54E-15	1	2.99E-15	-5.887	1
$C_{52\_C3V}$	1.50E-10	5.69E-05	1.50E-12	-5.736	0.574
$C_{40\_TD}$	8.05E-12	0.001061	2.07E-12	-5.7	0.502
$C_{36\_D6H}$	2.76E-12	0.003094	6.39E-13	-5.685	0.476
$C_{36\_C1}$	1.88E-10	4.54E-05	4.14E-11	-5.654	0.425
$C_{30\_D5H}$	2.62E-08	3.26E-07	9.09E-13	-5.548	0.287
$C_{30\_C2v}$	1.92E-11	4.44E-04			
$C_{28\_D2}$	1.02E-09	8.37E-06	1.61E-10	-5.529	0.268
$C_{20\_IH}$	1.92E-06	4.45E-09	2.92E-10	-5.379	0.154
CNT(5,0) (D=3.91Å)	1.66E-13	0.051	3.43E-14	-5.794	0.711
CNT(6,0) (D=4.69Å)	4.99E-15	1.711	1.77E-15	-5.89	1.0351
CNT(8,0) (D=6.26Å)	3.33E-16	25.64	3.33E-16	-6.00	1.516
CNT(5,5) (D=6.77Å)	1.11e-016	1.3	1.11E-16	-6.022	1.642

\*(6 vibrating atoms only)

## 2. Conclusions

In the present work a method explaining the relative yield of some fullerenes and SWCNT is proposed. This method is based on calculation of the probability (rate) of the molecule destruction. This rate is considered as the possibility for the weakest bond to stretch upon the critical distance  $X_{\text{max}}$  due to molecule thermal vibrations. By calculations for the molecule of all vibration eigenfrequencies and eigenvectors and suppose that all vibrations are independent it is possible to calculate the probability of every bond destruction at a given temperature  $T$ . Considering all bond probabilities of destruction and choosing the maximal probability corresponding the weakest bond destroying, it is possible to calculate the rate of the molecule destroying. By comparison of experimental and calculated data of some fullerenes and SWCNT yield, it is shown that this method can qualitatively explain the relative yield of fullerenes and SWCNT. At that one can expect that this method can provide an explanation of other nanostructures yield.

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Table 3. Dependence of chemical bond destruction probability  $P_{\text{destr}}$  on the number  $NN$  of free vibrating atoms for fullerene  $C_{30\_D5H}$ 

Number of neighbour layers	Number of vibrating atoms	$P_{\text{destr}}$
1	2	5.47E-13
2	6	9.09E-13
3	12-14	3.15E-12
4	18-19	5.89E-12
5	24-25	1.05E-10
6	29	2.55E-8
7	30	2.67E-8

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## Относительная стабильность различных фуллеренов, образующихся в плазме

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*Предложен метод, объясняющий относительную стабильность наноструктур, образующихся при плазменно-химическом синтезе. Метод основан на вычислении вероятности развала молекулы. Данная вероятность определялась по вероятностям разрыва среди всех химических связей молекулы при растяжении их до критической величины благодаря тепловым колебаниям. Для этого, путем вычисления собственных частот и векторов всех колебаний и предполагая некоррелированность фаз всех колебаний, определялась вероятность развала каждой химической связи. Выбор максимальной вероятности, соответствующей разрыву самой слабой связи, определял вероятность разрушения молекулы при данной температуре. Применяя данный метод для некоторых фуллеренов и углеродных нанотрубок, показано, что он дает качественное согласие с экспериментальными данными. Благодаря общей формулировке метода, можно ожидать, что он может использоваться и для объяснения образования других наноструктур.*

*Ключевые слова: фуллерены, плазменно-химический синтез, метод функционала плотности, первопринципные вычисления, наноструктуры, стабильность, колебания.*