CARBON CLUSTER FORMATION ENERGY

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A phenomenological model for calculation of formation energy of (CNC) carbon nano-clusters of definite shape was suggested.

The model uses three energetic parameters, E_c and W_5, being determined from comparison with experimental data and results of computer simulation for various CNC, and dangling bond energy.

We showed that there is a optimal opened tube having minimal energy keeping number of atoms N constant. Both tube length L and diameter D are determined uniquely by N and co-dependent as $L \propto D^2$ so $L \gg D$.

We calculate energies corresponded to spheroidal CNC and polyhedra-shape clusters of Y–symmetry, being topological equivalent to spheroids. First are energetically favorable for the bigger N but it was shown that under proper parameters chosen a such region of cluster size exists where fullerenes of polyhedral configuration have lower energy.

Introduction. Fullerenes and other carbon nanoscale clusters (CNC) have drew our attention due to, first, a regular geometrical shape, second, a variety of size and structure, third, certain stability of these products. It was attractive to search for some relation between geometrical and physical-chemical properties of such objects as ball-like fullerenes or their polyhedral-shape modifications, opened bucky-tubes of finite or infinite length, closed tubes or capsules. To begin with, now we present phenomenological model of formation of CNC. We try to calculate formation energy W_{CNC} for above-listed clusters in a common way. Within this model we need only three parameters those will be discussed below in detail.

Recent years a number of groups obtained some results concerned energetics of various CNC [1–7,9]. Despite of different computation approaches and certain difference in quantities to calculate we found these computer modeling data to be a good ground. We able to fit most of data and to explain some particular results of Refs. [1–7,9] using our model. Also we have made a number of predictions discussed below.

Energy of curved graphite-like surface. It stays unaccountable fact why only carbon in periodic system displays a great number of different structures. We have to stress that as concerning pure CNC each carbon atom has 3 chemical bonds like a graphite carbon atom. It was been noted previously [4] that degree of hybridization of carbon bonds in CNC vary from graphite to diamond depending on all 3 σ-bonds and last π-orbital co-orientation, but this change is directly connected with electron energy change. From other side, in conjunction three-coordinated carbon atoms make up geometrical net with regular polygon cells usually. Number of polygons in definite CNC is governed by Gauss-Bonnet theorem (considered also in [9]). Some CNC could be formed from only graphite hexagon net. Covering of other CNC consists of hexagons and pentagons. We believe that energy of any CNC is fully determined by all atom true positions through quantum chemical computation but hope that for cluster of high symmetry it could be empirically calculated depending on a few shape parameters.

We try to find energy dependence on radius for simplest case of infinite tube to start with. Gauss-Bonnet theorem allows us to cover with only hexagons a plane and equivalent body as cylinder and truncated cone. We suppose that all carbons of infinite tube are placed on surface of cylinder and arranged in regular hexagons. That means we neglect possible relaxation of bonds when atom displaced inside or outside of regular surface and for simplicity we not include change in bond length too, we will discuss this assumptions elsewhere.

To account additional energy of infinite tube in relation to graphite sheet of the same number of atoms we suppose energy of curved surface depends on squared curvature. We refer this additional curvature energy to one bond energy: $E_{bond}^{curv} = E^c \theta^2$, where E^c is first phenomenological parameter of model, in a stick-and-ball picture θ is angle between bond direction and its not curved planar original position. It is equal to zero in planar graphite structure and can be derived through bond length, b, and curvature radius, R, in limit of small angle $\theta \simeq b/R$. Throughout the paper we will use dimensionless length in units of bond length, $b \simeq 1.4$Å taken roughly about graphite value in order to evaluate energy. We suppose that there are quantum mechanical reasons for atom with 3 σ bonds displaced from planar position to have higher energy. Actually, direct computation of E^c is much beyond this consideration. Any

way if local geometry of bonds determines the curvature energy, it could be rewritten in terms of θ.

Note that dimensionless curvature of cylinder k simply coincides with θ determined above. Next point to stress is that curvature along the cylinder axis is zero and it is $1/R$ on perimeter. So we need substitute in equation for curvature energy effective k_σ along original planar σ-bond direction that makes angle φ with cylinder guide. It seems us very natural to suppose that in CNC of great radius angles between 3 σ-bonds of each carbon atom are equal to $\frac{2\pi}{3}$ original value for graphite. In that assumption curvature energy per CNC is calculated by simple integration over the CNC surface of energy per atom (we make use of continuous model of graphite-like slightly curved surface to change summation over all atoms positions with integration) as a sum over σ-bond directions – some kind of invariant in case of C_3 atomic symmetry

$$E_{atom}^c = \sum_{\sigma_{1,2,3}} k_\sigma^2 = \frac{9K^2}{2} - \frac{H}{2} = \frac{3(k_1 + k_2)^2}{4} + \frac{3(k_1 - k_2)^2}{8} \tag{1}$$

where we write usual two principal curvatures of surface k_1, k_2 and its combination Gauss curvature $H = k_1 k_2$ and mean curvature $K = (k_1 + k_2)/2$. All curvatures in general are functions of surface point but we will consider for clarity only surfaces with no dependence as cylinder, sphere, plane or some connected parts of these bodies. In this case integration gives us the CNC specific area producted by E_{atom}^c. Note that graphite unit cell has area $\frac{3\sqrt{3}}{2}$ in units of b^2 and possesses two carbon atoms. For cylinder of radius R it gives

$$W_{CNC} = \frac{2S}{\frac{3\sqrt{3}}{2}} E^c \frac{9}{8R^2} = \pi\sqrt{3} \, E^c \, \frac{L}{R} \tag{2}$$

where CNC area is $S = 2\pi LR$, L is tube length, and we obtain E^c parameter from specific energy per unit length of infinite tube computer simulation [5] to be about 0.9 eV. Within our model we get that any local orientation of σ-bond relatively to guides or axes of CNC is energetically equivalent, that depends only on assumption of C_3 symmetry of each carbon atom σ-orbitals with respect to neighborhood. We point that it demands not only local atomic symmetry but touches a few atoms in vicinity. When believing this model, we get energy per length of infinite tube to have no dependence on local geometry of regular hexagon net but only a tube radius or number of atoms per length. It was widely discussed that there are a number of tubes of same radius with different covering. It is self-evident if consider tube as folded and glued parallelogram which is cut from graphite sheet. An angle of parallelogram possesses discrete values in order to superimpose two glued sides of tube atom in atom. In our model energies of such different clusters are same. We conclude that this prediction fits to data from [5] quite well (see Fig. 1).

Size of optimal tube. On the base of model defined in last section we made optimization of tube formation energy. In the case of infinite tube specific energy diminishes as inverse radius squared. We define specific energy as W_{CNC}/N additional energy per atom comparing with planar graphite sheet. Number of atoms $N = 2S/S^{un.cell} = \frac{8\pi RL}{3\sqrt{3}}$ is specific CNC area. Minimum of specific energy of infinite tube is reached at infinitely large radius, $i.d.$ for graphite. First non-trivial optimization can be proceeded if one considers infinite tube with a number of dangling bonds. Energy of dangling bond is well known [5,6] for graphite $E^b = 1/3 \, E^{carb.at.} = 2.36$ eV and we mind that it is not so differ from actual value for CNC.

The dangling bond energy is proportional to number of atoms on a tube perimeter and depends on R only: $2\frac{2\pi R}{\sqrt{3}} \zeta E^b$, where geometrical multiplier ζ is included for different types of tube, $e.g.$ for tube of "zigzag" type (cf. [9]) it is equal 1, and $2/\sqrt{3}$ for "armchair" type depending on density of dangling bonds. Under larger R this energy grows compensating the decrease of curvature energy. So there is a minimum of energy for cluster of fixed number of atoms. Such cluster is called optimal and its energy is determined from minimization of function:

$$W_{CNC} + \lambda N = \pi\sqrt{3} \, E^c \, \frac{L}{R} + 2\frac{2\pi R\zeta}{\sqrt{3}} E^b + \lambda \frac{8\pi RL}{3\sqrt{3}} \tag{3}$$

where first term is curvature energy, the second is perimeter energy and λ is indefinite Lagrange multiplier to be found from condition of fixed number of atoms. Length and radius of optimal tube are co-dependent and can be uniquely written for definite number of atoms N_0:

$$L_0 = \left(\frac{9\zeta}{32\pi^2} \frac{E^b}{E^c}\right)^{\frac{1}{3}} N_0^{\frac{2}{3}} = \frac{2\zeta}{3} \frac{E^b}{E^c} R_0^2 \gg R_0 \tag{4}$$

$$R_0 = \left(\frac{9\sqrt{3}}{16\pi\zeta} \frac{E^c}{E^b}\right)^{\frac{1}{3}} N_0^{\frac{1}{3}} \tag{5}$$

Evidently when the radius of optimal tube grows the length increases rapidly so optimal tube is prolonged and it is more emphasized for bigger CNC. It is worth to note that for usual d dimensional (2D, or 3D) body a length is scaled as $N^{\frac{1}{d}}$, in this sense optimal cluster radius has 3D character but length behaves as 3D area. Energy of optimal tube grows as $3\left(\frac{3\pi^2}{2}\zeta^2 E^c E^{b2}\right)^{\frac{1}{3}} N^{\frac{1}{3}}$, and specific energy decreases as $N^{-\frac{2}{3}}$. Specific energy can be written depending on optimal radius:

$$\frac{E_o}{N_o} = \frac{27}{8\,R_o^2}\,E^c = 3E_o^c \tag{6}$$

that shows that optimal cluster curvature energy is two times less than its perimeter energy.

Sphere and polyhedra shape CNC comparison. We have used in our model only 3 phenomenological parameters. We need two above defined ones for description of cylindrical tubes. Now we will consider ball-like fullerenes and new term in formation energy appears. It originates from pentagon unit cells on spheroidal CNC surface. According Gauss-Bonnet theorem any closed spheroid does have 12 pentagons excepting arbitrary number of hexagons. We have no direct proof, but as a rule pentagons try to lie as far each from other as possible. It results from school geometry that 12 centers placed at maximal distance on sphere are located in vertexes of regular icosahedron. When a real CNC has Y_h symmetry of truncated icosahedron its geometry is simple. We calculated formation energy for such type of ball-like fullerenes within our model.

There are two principal ways to construct Y_h spheroid. The first developed in Ref. [6,7] is to make so-called Holdberg polyhedron that consists of 20 deltagonal faces as simple icosahedron but each face is combined from unit cell hexagons. In vertex pentagon is placed and can be arranged in two ways, depending on that number of CNC atoms is given by $20 \times n^2$ or $60 \times n^2$ where n is natural. We will use here only second type due to similarity in calculation. Number n determines number of hexagon rings between two pentagons, from other point of view it corresponds to CNC mean radius. We stress that pentagons slightly diminish mean radius, having less area than unit cell. Such polyhedron should be considered as 20 triangles cut from graphite sheet with sharp boundaries between. In other words, all surface curvature is concentrated in edges excepting a global topological curvature included in 12 pentagons according Gauss-Bonnet theorem. Note that this polyhedron geometry fixes the curvature degree both at vertexes and on edges. These quantities are expressed trough "golden section" $\tau = (1+\sqrt{5})/2$: for vertex $\xi_{vert}^2 = \frac{9}{16}(2\tau)^4\left(\frac{3}{4} - \frac{1}{4\tau^2}\right)\left(\frac{1}{3\tau^2} - \frac{1}{4}\right)$ and for edge $\xi_{edge}^2 = 1 - \frac{1}{4\left(1-\frac{1}{4\tau^2}\right)}$. The corresponding curvatures amount about 5 and 3 Å.

Closed spheroid has no dangling bonds but additional term in energy comes from pentagon formation. This is constant additive term for any ball-like CNC and is the third parameter of our model. We suppose energy of curved pentagonal bond to be the same as for hexagon E^c, it could be, generaly, treated as next fitting parameter. Due to number of "curved" bonds on edges scales as a length and other terms in polyhedron energy have no any dependence, total energy is linear on R of polyhedron. So specific energy decreases as inverse radius squared:

$$W_{CNC}/N = \left(60n^2\right)^{-1}\left(\mathcal{E}_{\triangledown} + 60\,E_c\xi_{vert}^2 + 60\,(n-1)\,E_c\xi_{edge}^2\right) \tag{7}$$

where $\mathcal{E}_{\triangledown}$ is constant formation energy term for spheroid. It was extracted through comparison with experimental data of C_{60} cluster formation energy [10]. Depending on polyhedron degree n, specific energy depends on R, mean radius of spheroid, determined as $N = 60 \times n^2 = \frac{16\pi R^2}{3\sqrt{3}}$.

Then let us consider "really" ball-like fullerenes such as C_{60}, those evolvements are identical to correspondent Holdberg polyhedra but curvatures are constant on the surface. Atom belonging to hexagon has 3 bonds with equal energy similar to infinite tube in first section, pentagon atom has two bonds with fixed energy (included in ball-like CNC constant term) and one bond with same energy as in hexagons. With radius or number of atoms grows total energy of sphere grows up to constant value that corresponds topological difference between sphere of infinite radius and sheet of plane:

$$W_{CNC} = \mathcal{E}_{\triangledown} + \left(\frac{16\pi R^2}{3\sqrt{3}}\right)\frac{3}{R^2}\,E_c + 60\frac{1}{R^2}\,E_c \tag{8}$$

First term is the constant pentagonal energy, second term comes from all atoms in hexagons, and third is connected with each pentagon atom bond shared between hexagons. In the case of sphere we also have only trivial specific

energy minimum at $R \to \infty$. It seems to be clear that infinite radius cluster prefers to be shaped uniformly as a sphere rather than to have sharp edge. We replot data from Ref. [5,7] on inverse number of CNC atoms in order to compare model calculation for spherical and polyhedral shape clusters (Fig. 3). For all data we find our results fit quite well except energy of very high mass cluster $N = 960$ that can be beyond the calculation accuracy.

We made a comparison of spherical and polyhedral shape cluster energy under equal number of atoms. In Figure 4 we plot the formation energy difference between sphere and polyhedron (Eq.(7), Eq.(8)). Surprisingly we found that energy difference changes sign. It means that there is a cluster mass region when formation of Holdberg polyhedron of order n is energetically favorable: $1 < n < 4$.

Conclusions. We suppose phenomenological model to calculate fullerene nanocluster formation energy. Within the model we made predictions about energetically preferable shapes of some CNC. Nevertheless we consider only a few types of clusters we hope that in general model is not false because of it fits well to independent different computation data. We will proceed elsewhere [11] some forward calculation within the model concerning some other types of CNC and will complicate model in order to analyze its stability on small shape or bond length deviations.

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