

Electronic structure and stability of the non-IPR isomers 6140 (D_3) and 6275 (D_3) of fullerene C_{68}

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The analysis of energy and geometrical parameters (bonds lengths, valence angles and their sums at the given atom, dihedral angles between two hexagons, between hexagon and pentagon, in hexagon and in pentagons) for molecules of two non-IPR isomers of fullerene \tilde{N}_{68} (isomer 6140 (D_3) and 6275 (D_3)) has been carried out on the basis of results of quantum-chemical DFT calculations and earlier developed criteria [1, 2].

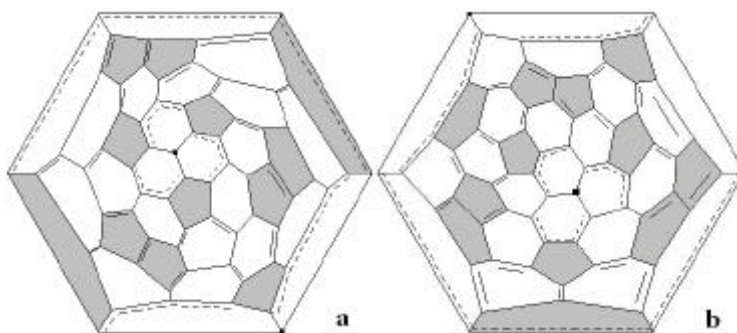


Figure 1. Schlegel diagrams of isomers 6140 (a) and 6275 (b) of fullerene \tilde{N}_{68}

The data about distribution of single, double and delocalized pi-bonds in both molecules of non-IPR isomers of fullerene C_{68} are obtained for the first time (see Fig.). It is necessary to note that in structure of both isomers occurs the partial delocalization of pi-bonds. It is shown that the reason of instability of "empty" isomers 6140 and 6275 are presence of pentalene and phenalenyl-radical substructures and also local sterical strains in these molecules.

Comparison of geometrical parameters of isomers 6140 (D_3) and 6275 (D_3) of fullerene \tilde{N}_{68} has shown that isomer 6275 is characterized by greater local sterical strains. In both isomers of fullerene \tilde{N}_{68} essential distortion of hexagons and pentagons is noted. However in isomer 6275 it is much more, that, obviously, is the reason of instability of isomer 6275 even in the form of endohedral metallofullerene.

This work was supported by the Department of chemistry and materials science of the RAS and CRDF.

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Catalytic properties of Pd₇₀Co₂₀Mo₁₀ and a comparison of its experimental and theoretical structure

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Results obtained by computer modeling and simulation using ab-initio and molecular dynamics techniques for the structural and catalytic properties of the PdCoMo trimetallic compound are reported; a comparison of these results with those obtained by sputtering deposition onto a nafion membrane to be used as catalyst for a 1KW PEM fuel cell is made. The use of computational ab-initio and molecular dynamics techniques have been widely accepted as one way to have prior information about specific properties of the compounds before study, giving very valuable information about thermodynamics, reactivity, structure, optical properties, etc. Structure was calculated by ab-initio methods and experimentally determined by XRD, TEM, and AFM techniques. Catalytic properties were calculated by ab-initio and molecular dynamics techniques, and experimentally determined directly on a 1 KW PEM fuel cell.

The dependence of the clusters and atoms collision cross-section from collision energy

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The processes of clusters formation in gas and plasma are of importance for up-to-date nanotechnology. Methods of direct simulation, for example the Direct Simulation Monte-Carlo (DSMC) method [1], rank as main methods of these processes modeling. One of the central parameters of the particles collision description is the collision cross-section. At the simulation of processes in gas and plasma the collision cross-sections averaged over energy and often temperature are used usually. As well as the average collision cross-sections are resulted in the experiments, for example at the mobility measurement. However, the principal feature of cluster formation in gas is the very wide range of vapor temperature change (300-7000K). Therefore using the average collision cross-sections can lead to the low accuracy.

The computation of the collision cross-sections dependent on particle collision energy is possible by the direct calculation of the scattering function. The scheme described in the work [2] allows computing the collision cross-section using solely the particles interaction potential. The interaction potential was computed by the density functional theory (DFT) method. The dependence of the collision cross-sections of silicon, carbon and helium from particle collision energy was obtained in the context of the common model of the clusters formation processes [3].

This work was supported by the INTAS grant (N 03-51-5208).

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Models of clusters collisions at direct Monte-Carlo simulation of nanoclusters formation in expanding vapor

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The details of cluster formation from vapor are of fundamental interest to the study of gas–condensed phase transitions laying in the basis of many modern technologies of nanoclusters and nanocluster materials production. One of the main methods modeling these processes is the Direct Simulation Monte-Carlo (DSMC) method [1]. The realization DSMC method requires the description of particles collision at a microscopic level. However in many cases the needed information is missing even for ordinary transition metals and semi-conductors (as silicon).

In this work the problem of the particles collision model selection was considered by the example of DSMC modeling of condensation of silicon vapor expanding into vacuum or inert gas. The important feature of this problem is the wide range of vapor temperature change (300-7000K) at expansion. In these conditions using the simple collision models (as hard sphere) leads to the low accuracy. The more complete model of atoms and clusters collisions was created in the context of the common model of clusters formation processes [2] in the mixture of silicon vapor and helium. The model takes into consideration the dependence of the collision cross section from the collision energy. The model is based on the calculations executed partially by the scheme described in the work [3] using the potential obtained by the density functional theory (DFT) calculations.

This work was supported by the INTAS grant (N 03-51-5208).

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Calculations of crystalline structure of the fullerene C₆₀ complex with Leuco Crystal Violet (LCV)

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In the case of Van der Waals complexes the problem of rotational disorder of the C₆₀ molecules takes place. It makes difficulties for diffraction researches of such compounds and reduces their structure determination accuracy. The aim of the present work is modelling of crystalline structure of the molecular complex LCV·C₆₀.

Equilibrium structure was calculated in three stages. I – Initial arrangement of molecules was carried out by means of the original software. II – Geometry optimization by UFF method realized in program package ArgusLab [1,2].

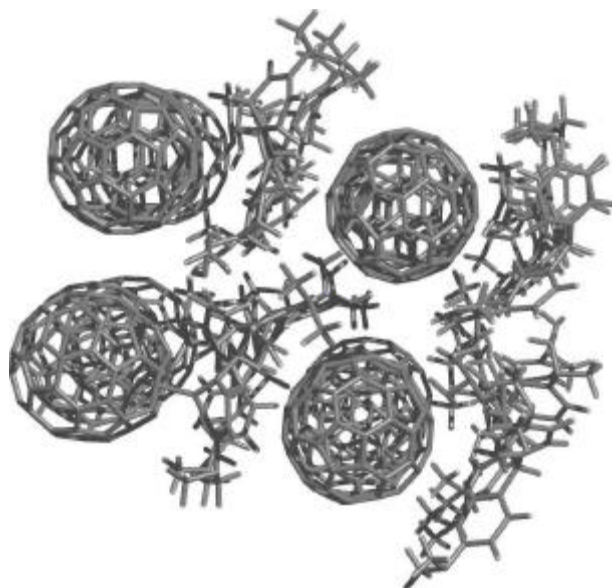


Figure 1. Visualization of molecular structure of cluster LCV·C₆₀

It allows to receive quickly refined configuration, in comparison with initial, and to reduce general time of calculations. III – The received results were used as the input data for quantum-mechanical calculations by semi-empirical PM3 method in GAMESS program [3]. The AFM image of the crystal LCV·C₆₀ was obtained to check up the modeling results. The determined center distances of the fullerene spheres in neighbouring layers of the crystal are in the satisfactory agreement with the modeling results: $L=1.096$ nm (model) and $L_{AFM}=1.07\pm 0.09$ nm (real).

It is shown, that given modelling procedure yields the results corresponding to the AFM data. Thus, it can be successfully used for research and working out in detail of crystalline and molecular structures of fullerene-based materials.

The work was supported by the RFBR grant 06-02-96323 r_center_a.

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Kinetics of the carbon nanotube formation from catalyst melt

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The modeling of the nanotube formation by the both CVD- and arc methods is necessary for the development of these methods.

The first step of such modeling, described in [1], was a simple thermodynamics model of the nanotube nucleation on the vapor-liquid-solid (VLS) mechanism. The nucleus of the nanotube in this model was a fullerene-like surface fragment (island) on the surface of a metallic melt nanodrop, supersaturated with carbon. The central part of the island is connected with the nanodrop by Van-der-Waalse interactions. The atoms at the verge of the island (radicals), which have only two carbon neighbors in the islands, are bonded chemically with the atoms of the melt. In the course of both the nucleation and the growth of the island, regarded as the sequence of chemical reactions, the bonds between radicals and metallic atoms of the melt are broken to be replaced by bonds between radicals and the carbon atoms of the melt. Herewith, these carbon atoms leave the melt to be included to the island.

Two parameters were chosen for the characterization of the nucleation process (apart from its size): the difference ΔE_{Me-C} of the total bonding energy between a radical and a carbon atom in graphite, and the surface tensions on the carbon-metal $\sigma_{Met-graph}$ and metal-vacuum $\sigma_{Met-Vac}$ interfaces. These parameters and the supersaturation quantity determine the maximum of the Gibbs energy for the critical island formation.

The kinetic problem of the nucleation of the island was researched in two model situations: a long catalyst nanodrop in a deep pore of the substrate (herewith the carbon atom diffusion from the carbon feeder decomposition site can be a partially limiting stage) and a nanodrop in a shallow pore. The parameters to be calculated were the maximal supersaturation, evolving the nucleus formation, and typical time for this maximal supersaturation to be reached. Besides the earlier described parameters, the result was also dependent on the $\dot{I}/\ddot{I}^{(1)}$ quantity – the ratio of the carbon feeder decomposition rate to the direct reaction rate of carbon extraction from supersaturated melt (the ratio depends on temperature only).

For these two situations the behavior of both the island critical size and maximal supersaturation turned out to be similar and merely dependent of the model for the island expansion along the nanodrop surface. The model predicts the growth of the SWNT size with the temperature increase, which tendency is correspondent with the experiment. Typical supersaturation did not exceed several units, as a rule.

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***Ab initio* study of relative energy, charge distribution, and NICS for fullerenes C₂₄~C₃₄ and its cationic, and its anionic forms**

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Fullerenes are characterized with presence of 12 five-membered rings and varying number of six-membered rings in their structures.

Fullerenes (C_n) with sizes n=58, 56...etc., have been observed in C₆₀ collisions with fast highly charged atomic ions, electrons and laser pulses. The knowledge of the structured properties and binding energies, and charge distribution and aromatic properties of these fullerenes are essential to understand the fragmentation trends and, in particular, why fullerenes with a certain number of carbon atoms appear more frequently than others. In present study C₂₄~C₃₄ and its C₂₄⁺~C₃₄⁺, C₂₄²⁺~C₃₄²⁺, C₂₄³⁺~C₃₄³⁺, C₂₄²⁻~C₃₄²⁻ charged forms have been considered for ab initio calculations. The geometries of all neutral species considered in this work were fully optimized at HF/6-31G*. Then geometries were reoptimized in the frame work of the density functional theory (DFT).

For the charged species, geometry optimizations were preformed at the B3LYP/6-31G* basis sets. Two different spin multiplicities were considered in the case of charged species.

NICS values were taken form GIAO-SCF/3-21G and GIAO-B3LYP/6-31G* levels using optimized B3LYP/6-31G* geometries. In these calculations only closed-shell singlet states considered.

The results and discussions for each structure with figures and tables are shown later.

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