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NANOCLUSTERS OF A FULLERENE DERIVATIVE: COMPUTATION MODELING

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Abstract. In present paper we report results of computer simulation of crystalline and electronic structure of the molecular complexes: fullerene C_{60} and Leuco Crystal Violet (LCV). Quantum chemical calculations regard to 3D nanocluster which is built up of three layers comprising nine C_{60}·LCV molecules each. Electronic structure modeling results in the HOMO-LUMO gap width. It is shown that given modeling procedure produce the results corresponding to the AFM data. Thus, it can be successfully used for investigation of crystalline and electronic structures of fullerene-based nanomaterials.

1. INTRODUCTION

In recent years fullerene-based materials have brought up steadily increasing attention both in academic and industrial researches. It is of great interest to use fullerenes and fullerites not only by themselves but also as modified derivatives that enhance the properties of fullerenes and extend their application possibility. The development of new methods of fullerene derivative synthesis and study of their physical and chemical properties are of importance for making new functional materials. Recent developments suggest that fullerene-based materials could be successfully used in a wide range of areas such as IT devices, solar cells, clinical diagnostics, pharmaceuticals, environmental and energy industries. It seems interesting to study the electron-optical properties of photoactive fullerene C_{60}-based molecular complexes characterized by a high quantum efficiency of charge transfer and long-lived charge separation [1]. However, in the case of Van-der-Waals complexes the problem of rotational disorder of the C_{60} molecules arises. It makes diffraction researches of such compounds difficult reducing structure determination accuracy for materials. The modeling of material structure may be used in addition to or instead of direct study in such cases. In present paper we report results of computer modeling of crystalline and electronic structure of the nanocomplex: fullerene C_{60} with Leuco Crystal Violet (LCV). Quantum chemical calculations regard to 3D molecular cluster built of up to three layers comprising nine C_{60}–LCV molecules each. It is worth mentioning that the data on structure LCV·C_{60} are absent in Cambridge Crystallographic Data Centre [2].

2. MODEL AND METHODS

Hexagonal elementary cell was assumed as initial state for LCV·C_{60} crystal. Initial data preparation and intermediate transformations were carried out using original software. Equilibrium structure was calculated as follows. The structure of elementary cell LCV·C_{60} was determined in five ways; the first is the method of molecular mechanics Universal Force Field (UFF) [3], realized in software package ArgusLab [4]. It allows one to refine configuration quickly and, thus, to reduce total calculation time. The other approaches are two semi-empiri-

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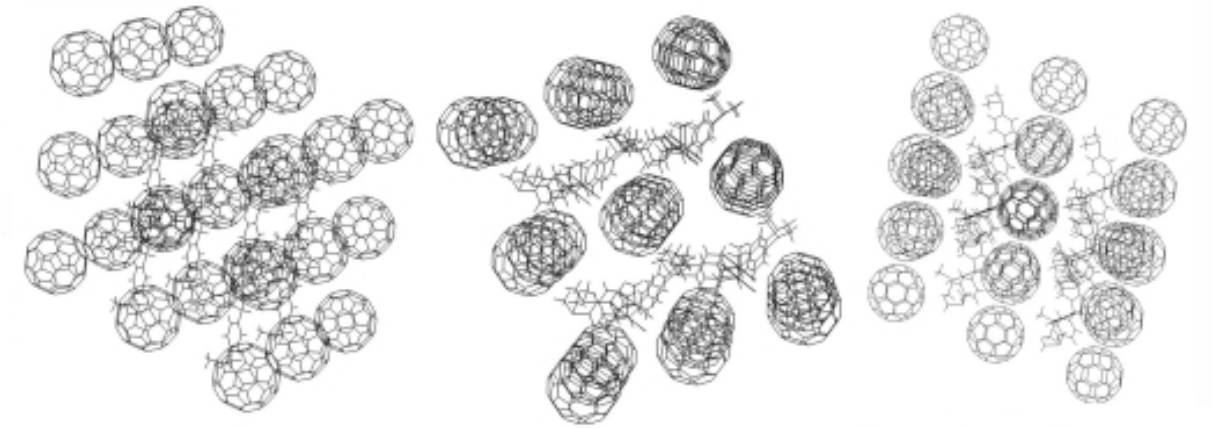

Fig. 1. Visualization of modeling results for nanocluster LCV·C_{60}.

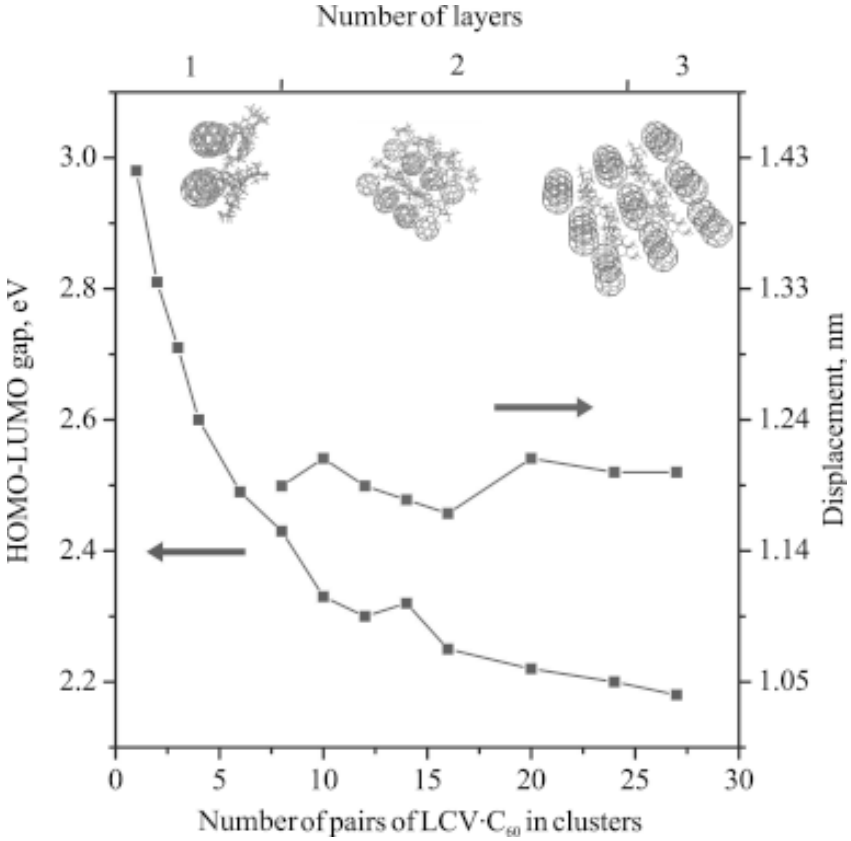

Fig. 2. General characteristics of LCV·C_{60} clusters.

cal methods (Parametric Method 3 (PM3) [5] and Austin Model 1 (AM1)) [6] in basis 6-31G in two quantum-chemical packages ArgusLab and PC-GAMESS [7]. For each number of particles in the cluster multiple runs of UFF method with various initial configurations and energy gradient step were executed. If the geometrical configuration and computing complexity allow it, each calculation was repeated using methods PM3 and AM1. In the latter case spacing parameters surpassed ones received by UFF method by 3-5% on the average that prove calculation result steadiness.

3. RESULTS

Fig. 1 shows the modeling results of Van-der-Waals LCV·C_{60} complex, consisting of three layers on nine pairs molecules of donor and acceptor. It is clear

that molecular complex has layered structure. The results of calculation of the cluster structure obtained by various methods do not contradict each other.

During calculations of a cluster consisting of three layers of nine elements each (Fig. 1), the steady state of the molecular complex LCV·C_{60} has been found with the following parameters: unit cell - *a=0.98* nm, *b=1.23* nm, *c=0.97* nm, α=*85°*, β=*79°*, γ=*89°; crystal system - triclinic; space group* – $P\bar{1}$. It is visible that the crystal cell has significant emptiness, in real conditions they are filled with molecules of a solvent.

The AFM image of a real crystal LCV·C_{60} was obtained to verify the modeling results. The AFM image shows real layered structure of LCV·C_{60} with a lot of point and extended defects of crystal structure. The determined center distances of the fullerene spheres in neighboring layers of the crystal are in the satisfactory agreement with the modeling results: L~1.2 nm (model) and L_{AFM}=1.07±0.09 nm (real).

Calculation of molecular structures has allowed construct dependence of width of HOMO-LUMO gap on the number of LCV-C_{60} pairs in cluster (see Fig. 2). The obtained results approximation for the cluster containing 30 layers on 30 pairs gives experimental (1.7 eV) HOMO-LUMO gap magnitude [8].

4. CONCLUSIONS

It is shown that given modeling procedure yields the results corresponding to the AFM data. Computation simulation can be successfully used for research and working out in detail crystalline and electronics structures of fullerene-based materials.

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