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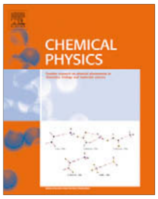

High multiplicity states in disordered carbon systems: *Ab initio* and semiempirical study

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ABSTRACT

Stability of non-zero spin projection states for disordered carbon clusters of low symmetry were examined using semiempirical and *ab initio* methods. The study proves previous results of V.D. Khavryuchenko, Y.A. Tarasenko, V.V. Strelko, O.V. Khavryuchenko, V.V. Lisnyak, Int. J. Mod. Phys. B 21 (2007) 4507, obtained for the large polyaromatic hydrocarbons clusters and shows that the phenomenon is intrinsic for carbon-rich systems and independent of their symmetries. The electronic properties of the carbon clusters may alter from insulating to semiconducting upon change of C/H ratio and stabilization of non-zero spin projection states. A partial collectivization of the electrons is observed in deeply carbonized carbon clusters in higher S_z states.

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1. Introduction

The carbon materials (CMs) are one of the bases of technologies from ancient times up to modern era. The CMs exhibit a huge number of structural polymorphs and composites with properties varying from insulating to metal-conducting, from mechanically hard to soft, from fragile to elastic [1–4]. However, the elementary points of the CMs structure and properties are sometimes obscure. Recently a series of works have been reported, showing a great impact of spin polarization on stability of the large polyconjugated carbon systems [5–8]. It has been demonstrated that upon growth in size after a certain threshold the polyaromatic hydrocarbons (PAHs) gain a stable biradical-like states and other broken symmetry (BS) states with $S_z \neq 0$, which should affect their physico-chemical properties greatly.

It is suggestive to explain the above-mentioned phenomenon by extremely high spatial and electronic symmetry of the PAHs. However, it is not yet proved or objected. Hence, in order to clarify the situation one should consider an opposite system, possessing no symmetry and being extremely disordered.

In the present paper we report an expansion of the "non-zero S_z as a basic electronic state" concept on disordered carbon systems. Spatial structures of carbonic clusters, previously reported in [9], have been used for a quantum chemical (QC) simulation. Those clusters refer to the different levels of carbonization of the polystyrene–divinylbenzene (PSDVB) copolymer [10,11], and give a good example of amorphous (spatially disordered) systems with different content of carbon (from 66 to 100 at.%).

2. Methodology

The QC calculations have been performed by semiempirical method PM3 [12,13] using a QuChem software [14,15] and by *ab initio* in the basis sets MINI and STO 6G-31 with GAMESS software [16,17].

The PM3 method is the modified neglect of diatomic overlap (MNDO) semiempirical method similar to the AM1 method. Similarly to all semiempirical methods of the MNDO "family", the PM3 method is based on the single-determinant Hartree–Fock theory. The core electrons are not included in the calculation; their effect is accounted effectively via the empirical core function. All three- and four-center two-electron integrals are neglected in accordance with the neglect of diatomic differential overlap (NDDO) approximation. The method is parameterized to reproduce the spatial structure and the heat of formation of "reference" molecules, experimentally measured at 298 K. Therefore, the QC derived data by the PM3 methods refer to the room temperature. The PM3 method is perfectly parameterised for reproducing spatial and electronic structure of the CH-containing compounds [18,19].

The complete space structure optimization, the evaluation of the wave function with properties derived from the wave function, namely the enthalpy of formation ($\Delta_f H$), the electron and spin densities and atomic orbitals (AO) contributions to HOMO, have been performed in a cluster (supermolecular) approach for each cluster

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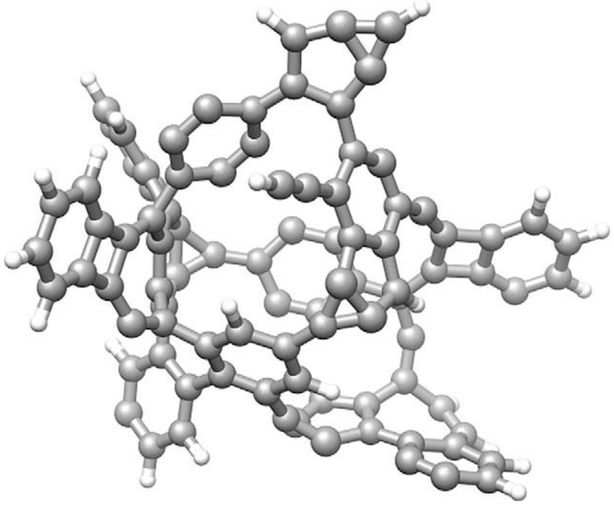

Fig. 1. QC optimized spatial structure of the PSDVB clusters #7 (*ab initio*, basis STO 6G-31).

considered for each spin projection from 1 to 7 (see Supplementary materials A). (Although Hartree–Fock (HF) methods tend to overestimate high-spin states if compared to the DFT calculations, the trends in alterations of properties still can be deduced.) The restricted Hartree–Fock (RHF) method has been applied in the present study for a close-shell singlet (^1S) state calculation. The unrestricted Hartree–Fock (UHF) method (implying different α and β orbitals) has been applied for the clusters in the states with spin projection $S_z = 0, 1, \ldots, 7$ (further referred to as multiplicities $1, 3, \ldots, 15$, respectively). The electronic structure of the optimized clusters appears to be dependent on the starting electron density matrix, which might be attributed to the Hartree–Fock instability of the solution [20]. Being aware of the problem's ambiguity (it is still neither proved nor objected whether this problem is a numerical calculation artifact or an intrinsic property of certain systems), we have performed the full optimization procedure for the UHF $S_z = 0$ state for all clusters simulated, starting from density matrices obtained for the corresponding clusters in higher S_z states (further referred to as "UHF $S_z = 0$ from higher multiplicities").

The *ab initio* level calculations have been performed for some key clusters in order to verify the data derived semiempirically. The binding energy of the cluster in the ^1S RHF state has been chosen as a zero point for the *ab initio* examined clusters.

3. Results and discussion

The spatial structures of 11 carbonized PSDVB clusters, optimized in ^1S state [9] (snapshot of cluster #7 is given on Fig. 1), have been used as starting geometries for the QC simulation in non-zero S_z states. The results of the QC simulations show that the connectivity (bonding order) of the clusters does not alter upon change of S_z state of the system, though structural parameters (namely, bond lengths, valent and torsion angles) sometimes altered significantly (refers to Supplementary materials A).

The EDOS function has been plotted for each cluster in ^1S state. The changes in the electronic structure of the QC simulated clusters upon decrease of the H/C ratio are shown on Fig. 2. The

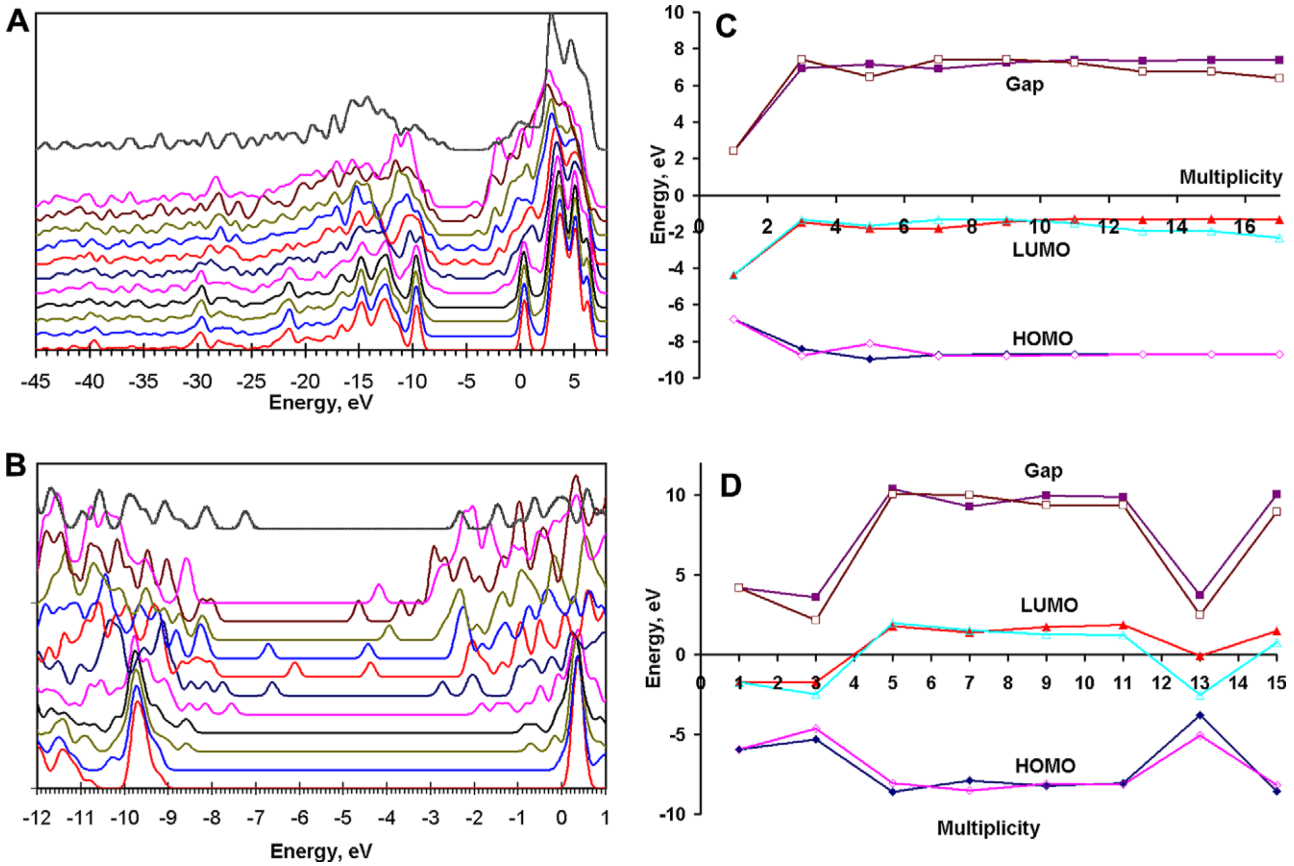

Fig. 2. QC evaluated EDOS function for carbonized PSDVB cluster in ^1S state (from bottom to top – clusters from #0 to #10, the topmost EDOS refers to the $C_{96}H_{24}$ PAH cluster [5]) (A), magnified – 12–1 eV region of EDOS in ^1S state (B), HOMO and LUMO energies and HOMO/LUMO gap of the PSDVB cluster #7 vs. multiplicity of the cluster, evaluated by PM3 (C) and *ab initio* in basis STO 6G-31 (D) (filled diamonds, triangles and squares refer to α-levels, empty diamonds, triangles and squares – to β-levels).

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