SIMULATION OF THE ELECTRONIC VALENCE BAND STRUCTURE OF 1D-CARBYNOID SYSTEMS WITH HYDROGEN

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Introduction

The aim of a detailed study of electronic structure of 1D- carbon with attached hydrogen atoms [1] is very important owing to hydrogen is contained in a main backbone in carbon containing polymers. The general pattern of electron dispersion in valence band corresponds qualitatively to the one in carbyne [2] that is the third quasi-one-dimensional form of carbon. The study of peculiarities of band structure of 1D-carbon system caused by attaching hydrogen atoms to the backbone is included.

1D polymeric carbon containing systems are applied practically e.g. in fuel cells as membranes. Studies in this tendency can lead to produce a more efficiency device for separation chemically bounding hydrogen. Perspectives of molecular electronics based on quasi-one-dimensional chains are known.

Semi-empirical method of quasi-molecular extended unit cell (QEUC) [3] is used to band calculations. The density of electron states in valence band of 1D carbon-hydrogen system has been also calculated. The results of this calculation are discussed.

Results and discussion

Electronic structure of linear and zig-zag chains are simulated. Each QEUC contains 4 carbon atoms at a distance of 0.128 nm. 8 and 4 hydrogen atoms are attached to the linear and zig-zag backbones step-by-step, correspondingly. Valence angles are 90 ° to the linear and 120 ° to the zig-zag chains. Distances between carbon and hydrogen atoms along the chain axis are 0.109 nm in both cases. The translation periods of QEUC are d=0.512 nm for linear chains and d=0.443 nm for zig-zag chains. The translation periods along two other directions in Cartesian's scale are equal infinity.

The dependence of band energy *E (k)* on quasi-momentum *k* for valence electrons in adduced Brillouin's band for the zig-zag chain is shown in Fig. 1 (on the left) and the same chain with one hydrogen atom is on the right. Zero of the binding energy corresponds to the valence band edge. The symmetry of wave functions on valence sub-bands is marked by s, p_x, π_1 and π_2, correspondingly. The width of valence band (19-21 eV) and electron distribution near its bottom (s- and p_x- sub-bands in Fig. 1) are identical in all allotropic forms of condensed carbon [4]. Two inferior s-, p_x–sub-bands have σ-symmetry of wave functions (σ- sub-band). π_2- sub-band is determined by the yield of p_z- component of wave function. The other π_1- sub-band is a superposition of two wave p- functions: p_x and p_y. It is due to interaction with hydrogen atoms. The upperest H– sub-band has hybrid wave functions s, p_x and p_y. This sub-band is a result of attaching hydrogen to a chain. The energy gap E_g between valence and conductive bands divides H– sub-band into two parts. The value of energy gap E_g depends on the quantity of hydrogen atoms and places of their attachment to the chain.

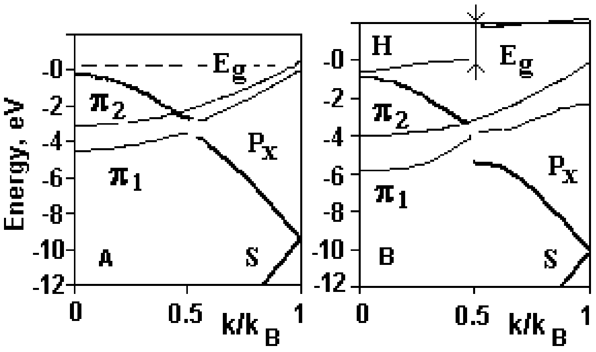

Fig. 1. Energy dispersion in the near by upper edge of valence band of one-dimensional carbon zig-zag chain (on the left, A) and of the same chain with one hydrogen atom (on the right, B). k_B corresponds to the edge of Brillouin's band for the diatomic chain.

Presumably, the bottom part of H– sub-band is filled by electrons adopted from hydrogen. Hydrogen with respect to carbon displays donor properties.

The results of the simulation of density of states N (E) in valence band are presented in Fig. 2 (linear) and Fig. 3 (zig-zag) chains contained hydrogen. Zero of the binding energy corresponds to the valence band edge (see Fig. 1). Curves N (E) are normalized on the total number of valence electrons.

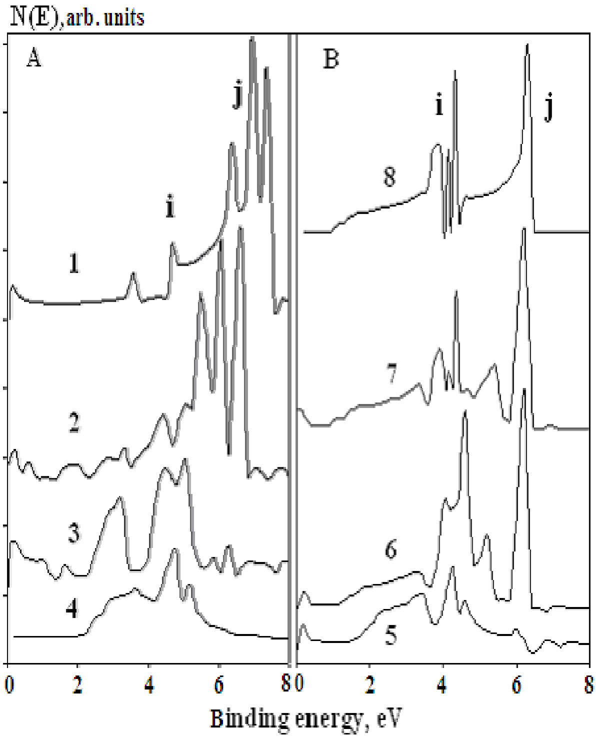

Fig. 2. Density of states N (E) in the near by upper edge of valence band (binding energy < 8 eV) of the linear chain with attached hydrogen atoms. Integers 1 – 8 correspond to the quantity of hydrogen atoms attached to the chain step-by-step on the one side of the chain (A) then on the opposite side of the chain (B). Letters *i* and *j* define the regions of higher density of states at binding energies ≈ 4 eV (*i*) and ≈ 6 eV (*j*), correspondingly.

The binding energy range 0 ÷ 8 eV includes all main properties peculiar to the bottom π_1, π_2, H– sub-bands and to the upper edge of p_x- sub-band (or σ- sub-band). The edge of H-sub-band at binding energy near ≈ 4 eV (region *i* in Fig. 2) is localized. Locale maxima in the density of states N(E) at binding energy 6 eV (region *j*) are peculiar to the π_1-, π_2 – sub-bands and p_x- sub-band. The relative contribution of these peculiarities (*i* and *j*) in N (E) varies on the dependence of the quantity of hydrogen atoms attached to the chain.

Similarity picture is observed in the case of simulation the zig-zag chain (see Fig. 3) when valence angles are 120 °.

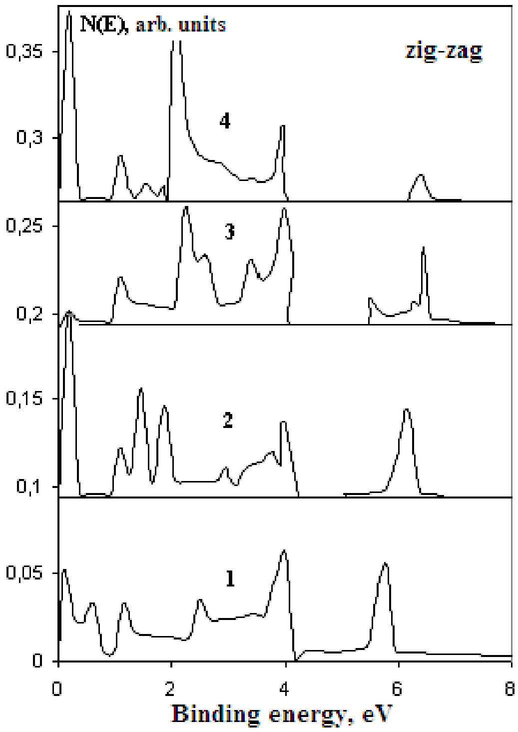

Fig. 3. Density of states N (E) in the near by upper edge of valence band of the zig-zag chain with attached hydrogen. Integers 1- 4 correspond to the quantity of hydrogen atoms attached to the chain.

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