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QUANTUM-CHEMICAL MODELLING OF ORNIDAZOLE SOLVATION AND ADSORPTION ON THE SILICA SURFACE

The ability of water and aqueous solutions to washout ornidazole adsorbed on the surface of fine silica, which ability was found experimentally, was investigated by theoretical modelling with the semiempirical quantum chemical method PM3 in a cluster approximation. Ornidazole is proven to bind to the silanol groups of the surface by hydrogen bonds through the nitro group and through other polar groups of the ornidazole molecule. It was found out that water molecules destroy the adsorption complex of ornidazole on the surface of silica by embedding between hydroxyl groups of the surface and active centers of the drug molecule. The hydrated complex formed in such a way is more stable than a complex in which direct interaction of the adsorbed molecule with the surface is present, and water molecules form weak links with this molecule and are displaced further away from the surface. Thus, solvated ornidazole is transferred from the surface of silica to a solution where it can realize antimicrobial action inherent thereof.

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INFLUENCE OF ADSORBED POTASSIUM ATOMS ON THE ENERGY SPECTRUM OF GRAPHENE

The paper studies the influence of adsorbed impurities, namely potassium atoms, on the energy spectrum of electrons in graphene. The electron states of the system are described in the frame of the self-consistent multiband strong-coupling model. It is shown that, at the ordered arrangement of potassium atoms corresponding to a minimum of the free energy, the gap arises in the energy spectrum of graphene. It is established that, at the potassium concentration such that the unit cell includes two carbon atoms and one potassium atom, the latter being placed on the graphene surface above a carbon atom at a distance of 0.286 nm, the energy gap is equal to ~0.25 eV. Such situation is realized if graphene is placed on a potassium support.

Introduction

One of the ways of the targeted change in the properties of graphene with the purpose to apply it in nanoelectronics is the introduction of impurities of different elements. The presence of impurities can cause a change in the symmetry of a crystal lattice and the appearance of additional energy gaps, whose widths depend on the types of impurities and their concentrations. The studies showed that substitutional impurities and adsorbed atoms differently affect the energy spectrum of electrons in graphene [1–3]. In work [1] the electron structures of an isolated graphene monolayer, a double layer of graphene, three-layer graphene, and graphene grown on ultrathin layers of hexagonal boron nitride (h-BN)

were investigated in the frame of density functional theory with the use of the method of pseudopotential. It was shown that the energy gap 57 meV in width appears in graphene grown on an h-BN monolayer.

Graphene with impurities of aluminum, silicon, phosphorus, and sulfur was studied in work [2] within the method analogous to the above-mentioned one. It was shown that graphene with a 3-% phosphorus impurity has a gap 0.67 eV in width.

In work [3], the electron structure of graphene was studied in the frame of density functional theory with the use of a generalized gradient approximation for the exchange-correlation potential. Software QUANTUM-ESPRESSO showed a possibility for a gap in the energy spectrum of graphene to be opened at the introduction of the impurities of boron and nitrogen atoms (gap width is 0.49 eV) and the impurity of boron atoms and lithium atoms adsorbed on the surface (gap width is 0.166 eV).

In work [4], in the Lifshits one-band one-electron model, it was established that the gap 0.45 eV in width in the electron energy spectrum arises in graphene deposited on the potassium support. It was assumed [4] that its appearance is related to a change in the crystal symmetry. This assumption is corroborated by the results of the earlier work [5], where the influence of the atomic order on the energy spectrum and the electrical conductivity of the alloy were analytically considered in the Lifshits one-band model. It was established [5] that, at the long-range order of the alloy, the gap in the electron energy spectrum appears. Its width is equal to the difference of the scattering potentials of the alloy

components. It was found that, in the case where the Fermi level enters the gap, the metal-dielectric transition happens at a long-range order in the alloy. However, no clear comprehension of the nature of the influence of impurities and a support on the energy gap appearance is available.

In the present work, we study the influence of adsorbed impurities, namely potassium atoms, on the electron energy spectrum of graphene. The electron states of the system are described in the frame of the self-consistent multiband strong-coupling model.

Strong-coupling model in the theory of energy spectrum of graphene with impurities

The dependence of the energy of an electron on the wave vector for graphene is calculated from the equation for Green's function poles for the electron subsystem [6; 7]:

$$det\left\|\varepsilon\delta_{\gamma\gamma'}\delta_{ii'} - h_{i\gamma,i'\gamma'}(\boldsymbol{k}) - \Sigma_{i\gamma,i'\gamma'}(\boldsymbol{k},\varepsilon)\right\| = 0. \quad (1)$$

In formula (1), $h_{i\gamma,i'\gamma'}(\boldsymbol{k})$ is the Fourier transform of the hopping integral, $\Sigma_{i\gamma,i'\gamma'}(\boldsymbol{k},\varepsilon)$ is the mass operator of electron-electron interaction, and i is the number of a node of the sublattice in the unit cell. Here, γ is a superindex which incorporates the quantum numbers for the principal energy eigenvalue $\tilde{\varepsilon}$, the standard quantum numbers of angular momentum l and m, and the z-component of spin σ.

The mass operator of electron-electron interaction $\Sigma_{i\gamma,i'\gamma'}(\boldsymbol{k},\varepsilon)$ is determined from the system of equations

$$G(\boldsymbol{k},\varepsilon) = \left\|\varepsilon\delta_{\gamma\gamma'}\delta_{ii'} - h_{i\gamma,i'\gamma'}(\boldsymbol{k}) - \Sigma_{i\gamma,i'\gamma'}(\boldsymbol{k},\varepsilon)\right\|^{-1}, \quad (2)$$

$$\Sigma_{i\gamma,i'\gamma'}(\boldsymbol{k},\varepsilon) = \Sigma^{(1)}_{i\gamma,i'\gamma'}(\boldsymbol{k},\varepsilon) + \Sigma^{(2)}_{i\gamma,i'\gamma'}(\boldsymbol{k},\varepsilon), \quad (3)$$

$$\Sigma^{(1)}_{i\gamma,i'\gamma'}(\boldsymbol{k},\varepsilon) =$$
$$-\frac{1}{4\pi iN}\int_{-\infty}^{\infty}d\varepsilon_1\sum_{\boldsymbol{k}_1}f(\varepsilon_1)\Gamma^{(0)i_2\gamma_2,i_1\gamma_1}_{i\gamma,i'\gamma'}(\boldsymbol{k};\boldsymbol{k}_1;\boldsymbol{k}_1)\left[G_{i_1\gamma_1,i_2\gamma_2}(\boldsymbol{k}_1,\varepsilon_1) - \right. \quad (4)$$
$$\left. G^*_{i_1\gamma_1,i_2\gamma_2}(-\boldsymbol{k}_1,\varepsilon_1)\right],$$

$$\Sigma^{(2)}_{i\gamma,i'\gamma'}(\boldsymbol{k},\varepsilon) = -\left(\frac{1}{2\pi iN}\right)^2\iint_{-\infty}^{\infty}d\varepsilon_1 d\varepsilon_2\sum_{\boldsymbol{k}_1,\boldsymbol{k}_2}f(\varepsilon_1)f(\varepsilon_2)\Gamma^{(0)i_2\gamma_2,i_1\gamma_1}_{i\gamma,i'\gamma'}(\boldsymbol{k};\boldsymbol{k}_1 +$$
$$\boldsymbol{k}_2 - \boldsymbol{k};\boldsymbol{k}_1)\left\{\left[G^*_{i_2\gamma_2,i_5\gamma_5}(-\boldsymbol{k}+\boldsymbol{k}_1+\boldsymbol{k}_2,\varepsilon-\varepsilon_1-\varepsilon_2)G_{i_1\gamma_1,i_4\gamma_4}(\boldsymbol{k}_1,\varepsilon_1) - \right.\right.$$
$$G_{i_2\gamma_2,i_5\gamma_5}(\boldsymbol{k}-\boldsymbol{k}_1-\boldsymbol{k}_2,\varepsilon-\varepsilon_1-\varepsilon_2)G^*_{i_1\gamma_1,i_4\gamma_4}(-\boldsymbol{k}_1,\varepsilon_1)\right]\left[G_{i_6\gamma_6,i_3\gamma_3}(\boldsymbol{k}_2,\varepsilon_2) - \right.$$
$$\left. G^*_{i_6\gamma_6,i_3\gamma_3}(-\boldsymbol{k}_2,\varepsilon_2)\right] + \left[G_{i_2\gamma_2,i_5\gamma_5}(\boldsymbol{k}-\boldsymbol{k}_1-\boldsymbol{k}_2,\varepsilon-\varepsilon_1-\varepsilon_2) - G^*_{i_2\gamma_2,i_5\gamma_5}(-\boldsymbol{k}+\right. \quad (5)$$
$$\boldsymbol{k}_1+\boldsymbol{k}_2,\varepsilon-\varepsilon_1-\varepsilon_2)]\left[G_{i_1\gamma_1,i_4\gamma_4}(\boldsymbol{k}_1,\varepsilon_1)G_{i_6\gamma_6,i_3\gamma_3}(\boldsymbol{k}_2,\varepsilon_2) - \right.$$
$$\left.\left. G^*_{i_1\gamma_1,i_4\gamma_4}(-\boldsymbol{k}_1,\varepsilon_1)G^*_{i_6\gamma_6,i_3\gamma_3}(-\boldsymbol{k}_2,\varepsilon_2)\right]\right\}\Gamma^{i_5\gamma_5,i_6\gamma_6}_{i_4\gamma_4,i'\gamma'}(\boldsymbol{k}-\boldsymbol{k}_1-\boldsymbol{k}_2,\varepsilon-\varepsilon_1 - $$
$$\varepsilon_2;\boldsymbol{k}_2,\varepsilon_2;\boldsymbol{k}_1,\varepsilon_1).$$

In formula (5), $\Gamma_{i_1\gamma_1,i\gamma}^{i_2\gamma_2,i_3\gamma_3}\left(\boldsymbol{k}_1,\varepsilon_1;\boldsymbol{k}_2,\varepsilon_2;\boldsymbol{k}_3,\varepsilon_3\right)$ is the vertex part of the mass operator of electron-electron interaction given by the expression

$$\Gamma_{i_1\gamma_1,i\gamma}^{i_2\gamma_2,i_3\gamma_3}(\boldsymbol{k}_1,\varepsilon_1;\boldsymbol{k}_2,\varepsilon_2;\boldsymbol{k}_3,\varepsilon_3) =$$

$$\sum_{n_1,n_2,n_3}\Gamma_{n_1i_1\gamma_1,ni\gamma}^{n_2i_2\gamma_2,n_3i_3\gamma_3}(\varepsilon_1;\varepsilon_2;\varepsilon_3)exp\left[-i\boldsymbol{k}_1\left(\boldsymbol{r}_{n_1,i_1}-\boldsymbol{r}_{ni}\right)-i\boldsymbol{k}_2\left(\boldsymbol{r}_{n_2,i_2}-\boldsymbol{r}_{ni}\right)+\right.\quad(6)$$

$$\left.i\boldsymbol{k}_3\left(\boldsymbol{r}_{n_3,i_3}-\boldsymbol{r}_{ni}\right)\right],$$

$$\boldsymbol{r}_{ni}=\boldsymbol{r}_n+\boldsymbol{\rho}_i,\qquad(7)$$

$$\Gamma_{n_1i_1\gamma_1,ni\gamma}^{(0)n_2i_2\gamma_2,n_3i_3\gamma_3}(\varepsilon_1;\varepsilon_2;\varepsilon_3)=\tilde{v}_{n_3i_3\gamma_3,ni\gamma}^{(2)n_1i_1\gamma_1,n_2i_2\gamma_2},\qquad(8)$$

$$\tilde{v}_{n_3i_3\gamma_3,ni\gamma}^{(2)n_1i_1\gamma_1,n_2i_2\gamma_2}=v_{n_3i_3\gamma_3,ni\gamma}^{(2)n_1i_1\gamma_1,n_2i_2\gamma_2}-v_{ni\gamma,n_3i_3\gamma_3}^{(2)n_1i_1\gamma_1,n_2i_2\gamma_2}.\qquad(9)$$

In relation (7), r_n is the radius-vector of a node of the crystal lattice, $\tilde{\boldsymbol{n}}_i$ is the radius-vector of a node of the sublattice i. In formula (9), $v_{n_3i_3\gamma_3,ni\gamma}^{(2)n_1i_1\gamma_1,n_2i_2\gamma_2}$ is a matrix element of the Hamiltonian of binary electron-electron interaction [7]. In formulas (4) and (5), $f(\varepsilon)$ is the Fermi function. Over the index $i\gamma$, which is present twice in formulas (4) and (5), the summation should be made.

To calculate the electron spectrum of graphene with adsorbed potassium atoms, we chose the wave functions of the *2s* and *2p* states of neutral noninteracting carbon atoms as the basis. In the calculation of matrix elements of the Hamiltonian, we took three first coordination spheres. The energy spectrum of graphene was calculated for the temperature $T = 0$ K. In calculations, we neglect the renormalization of vertices of the mass operator of electron-electron interaction. In other words, we set

$$\Gamma_{n_1i_1\gamma_1,ni\gamma}^{n_2i_2\gamma_2,n_3i_3\gamma_3}(\varepsilon_1;\varepsilon_2;\varepsilon_3)=\tilde{v}_{n_3i_3\gamma_3,ni\gamma}^{(2)n_1i_1\gamma_1,n_2i_2\gamma_2}\quad(10)$$

in relation (5).

Energy spectrum of graphene with adsorbed potassium atoms

In Fig. 1, we show the dependence of the electron energy ε in graphene with adsorbed potassium atoms on the wave vector **k**. The vector **k** is directed from the Brillouin zone center (point Γ) to the Dirac point (point K).

In Fig. 1, the structural periodic distance from a potassium atom to a carbon atom is 0.28 nm. It is seen from Fig. 1 that, at the ordered arrangement of potassium atoms, a gap in the energy spectrum of graphene arises. Its value depends on the concentration of adsorbed potassium atoms, their location in the unit cell, and the distance to carbon atoms. We established that, at the potassium concentration such that the unit cell includes two

carbon atoms and one potassium atom, the latter being placed on the graphene surface above a carbon atom at a distance of 0.286 nm, the energy gap is ~0.25 eV. The location of the Fermi level in the energy spectrum depends on the potassium concentration and is in the energy interval -0.36 Ryd $\leq \varepsilon_F \leq$ -0.23 Ryd. Such situation is realized, if graphene is placed on a potassium support.
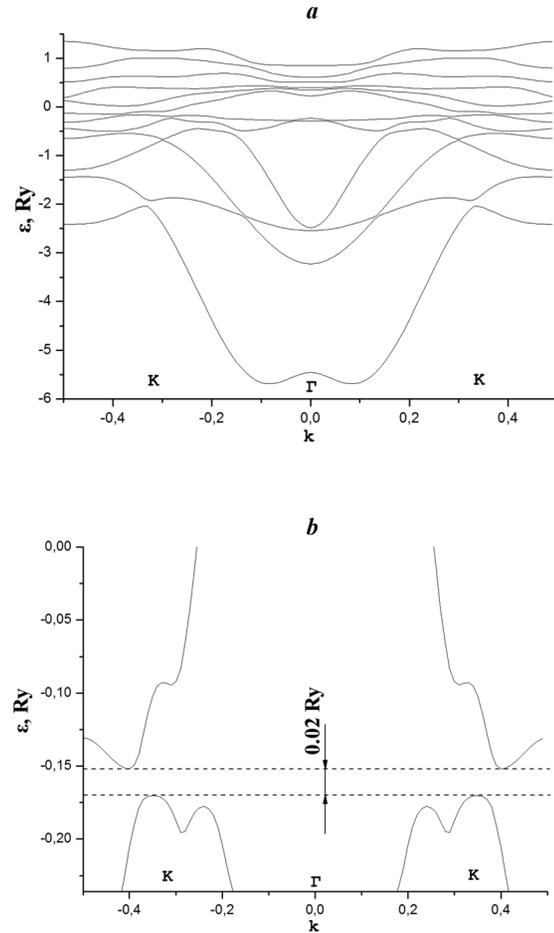
Fig. 1. Dependence of the electron energy ε on the wave vector k in graphene with potassium impurity; *a* – for all energy bend, *b* – for Fermi area

Conclusions

We have established that, at the potassium concentration such that the unit cell includes two carbon atoms and one potassium atom, the latter being placed on the graphene surface above a carbon atom at a distance of 0.286 nm, the energy gap is ~0.25 eV. Such situation is realized, if graphene is placed on a potassium support.

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ВПЛИВ АДСОРБОВАНИХ ДОМІШОК АТОМІВ КАЛІЮ НА ЕЛЕКТРОННИЙ СПЕКТР ГРАФЕНУ

У роботі досліджено вплив адсорбованих домішок атомів калію на електронний спектр графену. Електронні стани системи описано в рамках самоузгодженої багатозонної моделі сильного зв'язку. Показано, що при упорядкованому розташуванні атомів калію, яке відповідає мінімуму вільної енергії, в енергетичному спектрі графену виникає щілина. Встановлено, що при концентрації калію, коли на елементарну комірку припадає два атоми вуглецю і один атом калію, який розташований на поверхні графену над атомом вуглецю на відстані 0,286 нм, величина енергетичної щілини становить ~0.25 еВ. Така ситуація реалізується, коли графен розташований на калієвій підкладці.

Ключові слова: функція Гріна, масовий оператор, вершинна частина масового оператора, електрон-електронна взаємодія, енергетична щілина.