SCIENTIFIC BULLETIN OF THE LODZ UNIVERSITY OF TECHNOLOGY
No. 1224 Physics, Vol. 39 2018

SYLWESTER KANIA[1,2], BARBARA KOŚCIELNIAK-MUCHA[2], JANUSZ KULIŃSKI[2], PIOTR SŁOMA[2], KRZYSZTOF WOJCIECHOWSKI[2]

[1] Institute of Physics, Lodz University of Technology, ul. Wólczańska 219, 90-924 Łódź, Poland
[2] Centre of Mathematics and Physics, Lodz University of Technology,
Al. Politechniki 11, 90-924 Łódź, Poland, e-mail: janusz.kulinski@p.lodz.pl

AB INITIO INVESTIGATION OF ETHANOL-TETRACENE INTERACTIONS DURING ADSORPTION

Ab initio calculations presented in this work are performed to investigate the geometry, interaction energy and bonding properties of binary complexes formed between neutral ethanol and tetracene molecules. Two different geometries were applied for the study. The interaction energies between molecules in the complex posses minimum at the distance of about 3.6 Å among oxygen atom in ethanol and the neighbouring carbon atom of tetracene skeleton.

Keywords: noncovalent interactions, adsorption energy, quantum chemistry calculations.

1. INTRODUCTION

Is well known that the interactions between molecules during adsorption are mainly an effect of a delicate balance between several weak noncovalent interactions [1]. Such interactions have been investigated extensively, both theoretically and experimentally in our previous works [2, 3, 4]. Kinetics of the change of the conductivity of the tetracene layer when exposed to ethanol vapour was considered as a phenomenon leading to an injection of the charge carriers. The thermodynamic force of this process was described as a consequence of the existence of two processes, the first being the two body interactions between the ethanol molecules in gas phase [4] and the second being two body interaction between ethanol molecule from the adsorption layer and tetracene molecule belonging to the solid film [3]. Our previous article [2] was devoted to the problem of the entanglement of the quantum states. Such a problem appears during creation of the the dimer made of the ethanol and the tetracene molecules. The magnitude of the energy of the basis set superposition error (BSSE) was studied as a function of the distance *d* between ethanol and tetracene molecules calculated as the distance of the oxygen atom from ethanol molecule to the corner carbon atom at the side benzene ring of tetracene skeleton.

In this article, we review our previous results and report on new ones concerned with energy of interaction between ethanol and tetracene molecules. DFT (density funcional theory) calculations with use Gaussian 09 package for interactions between neutral ethanol – tetracene molecules are presented. This is carried out to perform a comparative analysis of interactions between molecules of tetracene and ethanol for two similar geometries created by these molecules that form complex.

The dependence of the energy of the interaction of molecules with each other on the distance *d* is presented in this work.

2. EXPERIMENTAL APPROACHES

The basic technique for our adsorption studies of the ethanol – tetracene system is measurement of the dark current induced in the tetracene during activation by vaporization with ethanol molecules. The measuring cell of the "sandwich" type was a thin film made of tetracene supplied with Au-Al electrodes. Thin film of polycrystalline tetracene ($C_{18}H_{12}$) was prepared by evaporation in vacuum under a pressure of the order of 10^{-5} Torr on a glass substrate plate covered with Au electrode. The temperature of the substrate was about 300 K and the evaporation rate was varied within the range 20-30 Å/s. The thickness of the tetracene films were from 15 µm to 20 µm. The measuring cells were fixed in a vacuum chamber in a vacuum of approximately 10^{-5} Torr and were then subjected to the action of the activator vapour. The activator, C_2H_5OH, is characterized by high polarity with permanent dipole moment 1.7 D depending on the presence of OH group. This makes the sorption process possible. The measurements were performed at room temperature. The time dependence of the current flowing through the layer under an increasing concentration of active ethanol molecules in the vacuum chamber was recorded (see Fig. 1). The measurement device (Fig. 1) consists of a current source and an electronic *I-t* recorder. The ethanol vapour pressure was 0.2 Torr. A single recording cycle of measuring data with multiple changing of the concentration of active ethanol molecules was of 1800 s. During a single cycle of recording of measurement data, the chamber was repeatedly supplied with new portion of active ethanol molecules. It was done when the current signal was saturated.

The measurements ended after rapid evacuation of the measuring system to high vacuum of 10^{-5} Torr. The electrical response measured in ethanol vapour showed a decrease of the resistance of the examined tetracene films. When the ethanol vapour flow was cut off and the measuring chamber was pumped to a high vacuum of 10^{-5} Torr, a rapid decrease in the current value to the level by one order greater than the initial value registered before ethanol was for the first time put into contact with a measured film.

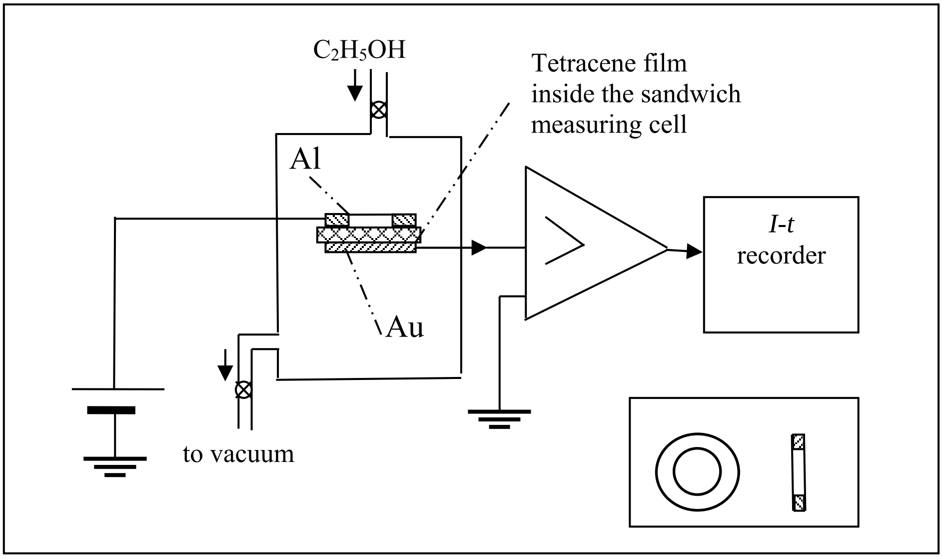


Fig. 1. Experimental set-up for activating the tetracene films and for recording the *I-t* characteristics of the dark current induced by the activation process. Insert shows the construction of the upper aluminium electrode of the measuring cell.

3. COMPUTATIONAL DETAILS

The scan methodology allowed in the Gaussian 09 package was applied to illustrate the intermolecular interactions. The DFT calculations were made for neutral fragments. The B3LYP functional was chosen from a literature [5] as an effective tool for calculations of basic states of aromatic hydrocarbons. Ethanol-tetracen complex can be treated as a supermolecular system whose energy is obtained as an result of adding up the energy of the each individual molecular component. We have proved in our previous work [2] that basis set superposition error (BSSE) energy is of the order of magnitude of the ethanol-tetracene interactions. We must also bear in mind the fact that the magnitude of van der Waals dispersive interactions are of the order of millielectronvolts. The BSSE arises because the orbitals of the neighbouring molecules will decrease the energy of the subject molecule even without transfering of the charge. Correction for the problem is supplied by the counterpoise method of Boys and Bernardi [6]. Such reasons and the complexity of calculations related to presence of heavy atoms as well as hydrogen make us to use B3LYP/6-311++G(d,p) with counterpoise correction. This *ab initio* technique gives a good agreement between the experiment and the calculated energies of orbitals for polycyclic hydrocarbons [7]. Employing calculations at such level of theory enabled us to realize the theoretical studies on the variability of the interaction caused when the ethanol molecule comes nearer in distance to the tetracene molecule.

The calculations were carried out for two cases: first, when the oxygen atom belonging to the ethanol molecule is moving in the distant plane parrallel to the benzene of the tetracene skeleton and second one when the oxygen belonging to ethanol molecule is moving in the plane of tetracene skeleton.

3.1. Accuracy of the model

In order to model chemical systems accurately, one must account for their inherent quantum nature. The problem of exact energy decomposition of intermolecular interaction between two molecules is multifactorial. The total interaction energy E_T between two molecules can be described by an equation [8, 9]:

$$E_T = E_C + E_{excl} + E_p + E_{disp} \tag{1}$$

where E_C corresponds to the direct Coulomb interaction between two unperturbed charge distributions, E_{excl} denotes Pauli exclusion principle (exchange repulsion), E_p denotes the induction factor always attractive for electron pairs bonding, polarization and charge transfer, E_{disp} denotes always attractive intermolecular van der Waals interactions. For neutral fragments, the sum of E_C and E_{excl} is named as steric interactions [10, 11].

The complexity of the problem of quantum interactions between ethanol and tetracene molecules has been explored in an earlier works [2, 3]. It was shown that the problem of adsorption layer of ethanol at the solid layer of tetracene may be solved in the limits of the theory of an area law for entanglement from exponential decay of correlations [12] as a two body interaction problem. In practical quantum-chemical calculations we have studied such a two body interaction problem [2] with use DFT calculations with bases with a finite dimentions. Such calculations lead to a base superposition error (BSSE). This error of calculations was minimalized [2] thanks to the counterpoise correction (CP) proposed by Boys and Bernardi [6].

The evaluation of the magnitude of the error appears during DFT calculations made at temperature of 300 K was applied to confirm the validity of our numerical results.

The oxygen atom 31O of ethanol was placed initially at the distance $d = 3.43636$ Å from carbon atom 20C of tetracene skeleton (Fig. 2). Optimization of the system was made with MP2/6-21g conterpoise calculation method. In Fig. 3 the dispersion of the calculations is presented. The uncertainty of the distance *d* we can estimate as $3 \cdot 10^{-5}$ Å, of the bond length (20C-21C) as $4 \cdot 10^{-6}$ Å, but the uncertainty of the total energy is of $6 \cdot 10^{-7}$ eV.

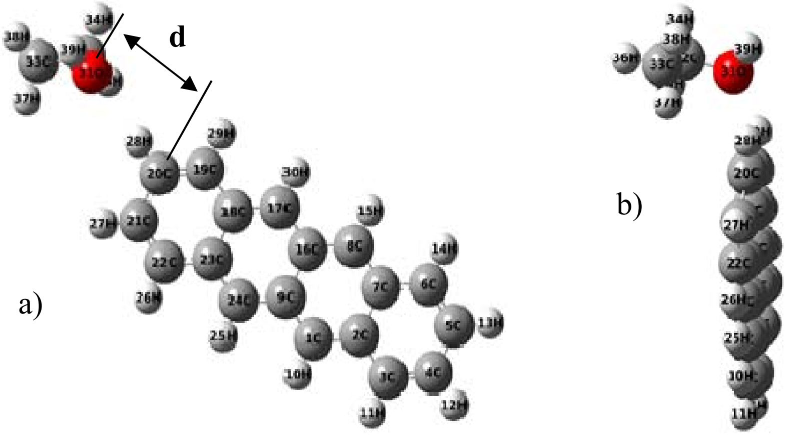


Fig. 2. Schematic images of the position of the ethanol and tetracene molecules determined in calculations by the distance *d* between oxygen atom 31O of ethanol with respect to the carbon atom 20C of tetracene skeleton: view of the entire complex, a) view of the position of the ethanol molecule in respect to the plane of tetracene skeleton b).

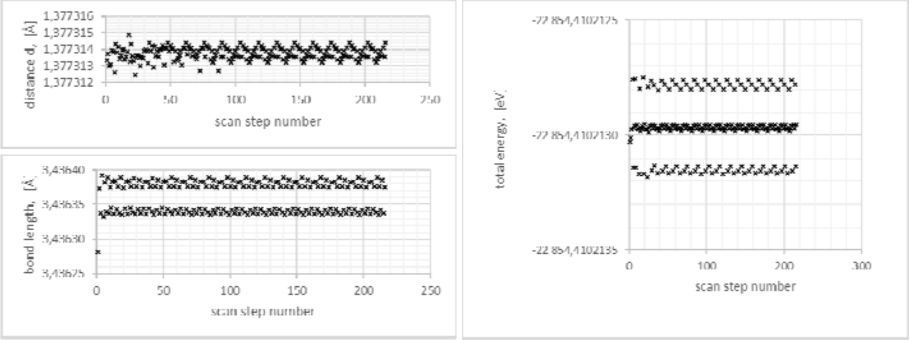


Fig. 3. Results of the DFT calculations of the equilibrium distance *d* of oxygen atom 31O of ethanol with respect to the carbon atom 20C in the plane of tetracene skeleton, bond length 20C-21C and total energy of a system.

4. RESULTS AND DISCUSSIONS

The quantum-chemical calculations with use of Gaussian 09 package were made with counterpoise correction of BSSE error with use of B3LYP/6-311++G(d,p) functional. In addition, the scan of the equilibrium structures along the distance *d* between 31O and 21C was performed. The transition states were calculated. Such transition states are difficult to observe experimentally because they are short-lived. They are not populated at equilibrium. Knowledge of such transition states allows understanding the mechanism of the possible path of charge transfer.

4.1. Simulation results

Proces of adsorption of ethanol on the tetracene surface is connected with decomposition of ethanol molecule at the tetracene and with transfer of electron from ethanol to tetracene during this process. The simulation results we want to present here can partially explain this phenomenon.

Fact that the tetracene molecule is more stable than ethanol is connected with the fact that the second excited level of ethanol molecule LUMO+1 is positive (see Table 1). It means that only one stable excitation level of –0.339 eV exists for electron in ethanol molecule, that is the LUMO orbital. Tetracene molecule in excited state LUMO+1 does not transmit electron easily because of the negative energy of orbital in the range of –0.812 eV. Such a set of orbital energy values prefers transmission of electron from ethanol to tetracene when ethanol molecule approaches teracene molecule while adsorption process is in progress.

Table 1

Frontier orbitals energies for ethanol and tetracene calculated by (DFT B3LYP/6-311++G(d,p)

	Ethanol	Tetracene
Orbital	Energy[eV]	Energy [eV]
LUMO+1	+0.201	–0.812
LUMO	–0.339	–2.401
HOMO	–7.635	–5.141
HOMO-1	–9.228	–6.759

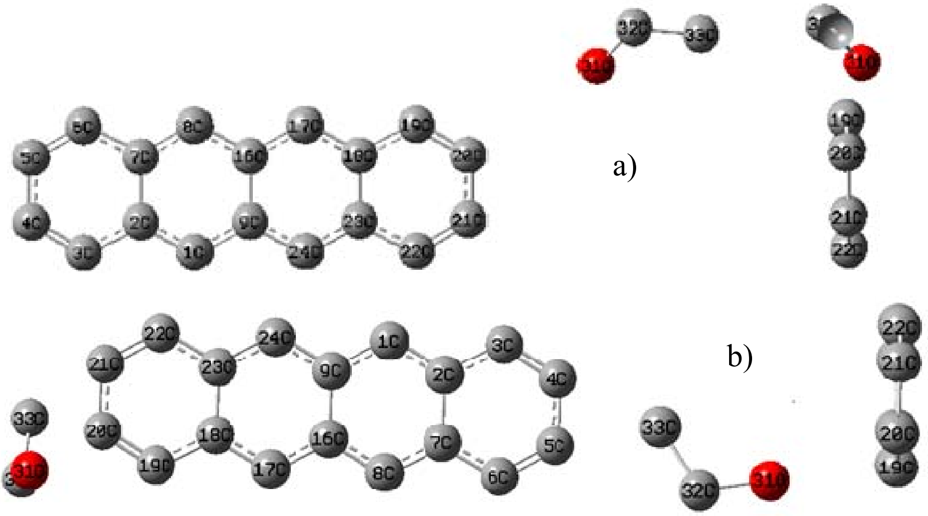


Fig. 4 The positions of two different orientations used to plot the HOMO LUMO levels in the Tables 2 and 3 (two views): ethanol in the tetracene plane a), ethanol distant from tetracene plane b).

The differencies of the magnitude of energy of the same frontier orbitals for ethanol and tetracene (see Table 1) are responsible for observed shapes of HOMO and LUMO orbitals of the complex composed of interacting molecules as presented in figures placed in Table 2 and Table 3.

The geometry of two equilibrium ethanol positions relative to tetracene used for B3LYP/6-311++G(d,p) scan calculations with counterpoise correction is shown in the Fig 4.

The calculations of total energy also confirmed the existence of an adsorption layer built from ethanol molecules distant of about 3,6 Å from tetracene molecule. The observed minimum of total energy of the complex when ethanol is in tetracene plane at the distance of *d* = 3,54 Å (Fig. 5a.), and when ethanol is distant from tetracene plane at the distance *d* = 3,58 Å (Fig. 5b.).

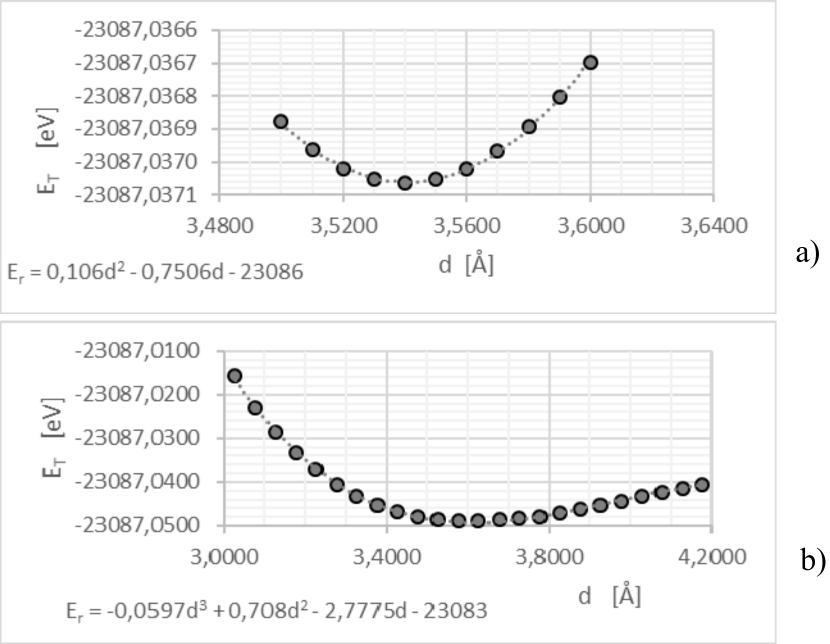


Fig. 5 Total energy of ethanol-tetracene complex of two different orientations used in DFT calculations: ethanol in the tetracene plane a), ethanol distant from tetracene plane b).

Table 2

Calculated energy and shapes of van der Waals LUMO orbitals (iso-value of 0.020) for both gemetries of molecular complexes.

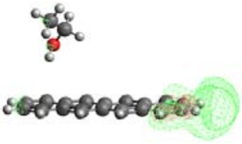
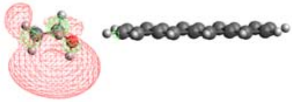
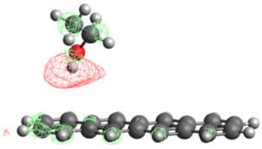
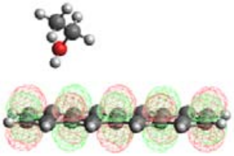
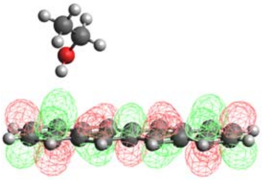
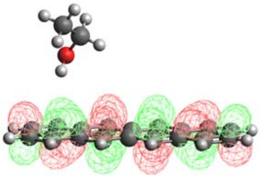
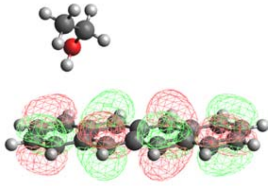
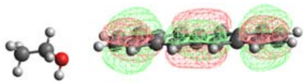
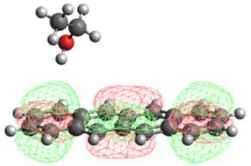
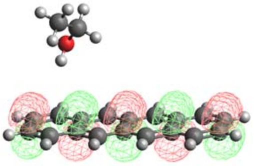
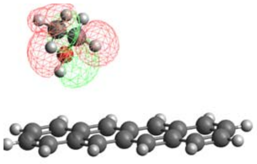
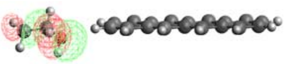
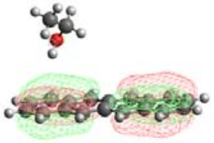
	Ethanol in tetracene plane		Ethanol distant from tetracene plane	
Orbital	Energy [eV]	complex	Energy [eV]	complex
LUMO+4	–0.101		–0,154	
LUMO+3	–0.473		–0.307	
LUMO+2	–0.669		–0.918	
LUMO+1	–0.707		–0.966	
LUMO	–2.305		–2.547	

Table 3

Calculated energy and shapes of van der Waals HOMO orbitals (iso-value of 0,020) for both geometries of molecular complexes.

	Ethanol in tetracene plane		Ethanol distant from tetracene plane	
orbital	Energy [eV]	complex	Energy [eV]	complex
HOMO	−5.054		−5.297	
HOMO-1	−6.518		−6.772	
HOMO-2	−6.594		−6.846	
HOMO-3	−7.074		−7.455	
HOMO-4	−7.877		−7.927	

5. CONCLUSIONS

The energy dependence seen in Fig. 5 of the scan of total energy as the function of the distance *d* proved that a simplified van der Waals (vdW) dimer can be rather fluxional (without a well-defined geometric structure or equilibrium constant between the two molecules which form the complex) even at low temperatures, due to the very flat potential energies. The depth of the potential well ΔE_T does not exceed the value of kT at the calculated range of the variation of the distance *d*, i.e. in the order of 1 Å. The Boltzmann factor *f* determines the increase of the density of molecules in the potential well in comparison to the density in the outer space is determined as

$$f(\Delta E_T) = \frac{1}{\exp(-\Delta E_T / kT)} \tag{2}$$

where *k* is the Boltzmann constant $1.38 \cdot 10^{-23}$ JK^{-1}, *T* – Kelvin temperature used for calculations, $T = 300$ K. Its value equal to $1/\exp(-1) = 2.73$ confirms the possibility of existence of the adsorption layer and tendency for ethanol to form clusters [13]. This adsorption layer appears as a result of interactions between neutral molecules. Such a process can explain only physiosorption, i.e. the process without the exchange of electons between interacting molecules. But our experiments have shown that conductivity of the tetracene layer increases in several orders of magnitude during vaporization of this tetracene layer with ethanol vapour. When analyzing this phenomenon it must be taken into account that the physical dimensions of ethanol molecule are so great that the diffusion of this molecule inside the tetracene layer is nearly impossible. Therefore, the only way for increase of the conduction of the teracene layer, in that situation, is transfer of electrons in the contact interaction in the chemisorption layer or the desintegration of the ethanol molecule into smaller fragments.

The dynamic processes with exchange of electrons between ethanol and tetracene molecule, are different in two paths of movement described in this article. When ethanol moves in the tetracene plane (see Table 2) then the exchange of electrons is most probably when the transition LUMO+3 – LUMO+4 takes part. But when ethanol moves in the distant from tetracene plane but over the centre of the benzene ring of the tetracene skeleton than the exchange of electrons is most probably when the transition LUMO+2 – LUMO+3 takes part. The problem of how the molecule can be excited to the energy leading to above mentioned transitions needs further confirmation.

Acknowledgements

The results of quantum-mechanical calculations presented in this paper applied Gaussian-09 package implemented in the PLATON project infrastructure in the Computer Centre of the Lodz University of Technology.

REFERENCES

[1] Karlický F., Otyepková E., Lo R., Pitonák M., Jurecka P., Pykal M., Hobza P., Otyepka M. 2017. Adsorption of organic molecules to van der Waals materials: comparison of fluorographene and fluorographite with graphene. J. Chem. Theory Comput. 13: 1328-1340.

[2] Kania S., Kościelniak-Mucha B., Kuliński J., Słoma P., Wojciechowski K. 2017. Sensitivity of tetracene layer. Sci. Bull. Techn, Univ.Lodz, Physics, 38: 45-51.

[3] Kania S., Kuliński J. 2013. Adsorption of ethanol to thin layer of acenes as a process of interconnected networks. Sci. Bull. Techn, Univ.Lodz, Physics, 34: 27-34.

[4] Kania S., Kuliński J. 2011. Absorbtion enhanced currents in thin layers of low dimension organics. Sci. Bull. Techn. Univ. Lodz, Physics, 32: 23-30.

[5] Mallocci G., Cappellini G., Mulas G., Mattoni A. 2011. Electronic and optical properties of families of polycyclic aromatic hydrocarbons: a systematic (time-dependent) density functional theory study, Chem. Physics 384: 19-27.

[6] Boys S.F., Bernardi F. 1970. The calculation of small molecular interactions by the differences of separate total energies. Some procedures with reduced errors. Mol. Phys. 19: 553-566.

[7] Coropceanu V., Cornil J., da Silva Filho D.A., Olivier Y., Silbey R., Bredas J-L. 2007. Charge Transport in Organic Semiconductors, Chem. Rev. 107: 926-952.

[8] Morokuma K., Kitaura K. 1981. Energy decomposition analysis of molecular interactions. [in:] Chemical Applications of Atomic and Molecular Electrostatic Potentials, ed. Politzer P., 215-242. New York: Springer Science and Business Media.

[9] Chen W., Gordon M.S. 1996. Energy decomposition analyses for many-body interaction and applications to water complexes. J. Phys. Chem. 100:14316-14328.

[10] Grimme S., Anthony J., Ehrlich S., Krieg H. 2010. A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu. J. Chem. Phys. 132: 154104-01-154104-19.

[11] Grimme S., Ehrlich S., Goerigk L. 2011. Effect of the damping function in dispersion corrected density functional theory. J. Comp. Chem. 32: 1456-1465.

[12] Brandão F.G.S.L., Horodecki M. 2015. Exponential decay of correlations implies area law. Commun. Math. Phys. 333: 761-798.

[13] Karlický F., Otyepková E., Banás P., Lazar P., Kocman M., Otyepka M. 2015. Interplay between ethanol adsorption to high-energysites and clustering on graphene and graphite alters the measured isosteric adsorption enthalpies. J. Phys. Chem. C 119: 20535-20543.

BADANIE AB INITIO ODDZIAŁYWANIA ETANOL-TETRACEN PODCZAS ADSORPCJI

Streszczenie

Obliczenia kwantowo chemiczne potwierdziły istnienie warstwy adsorpcyjnej etanolu w odległości *d* ok. 3,6 Å od narożnego węgla w bocznym pierścieniu szkieletu tetracenu. Warstwa ta zapewnia jedynie zachodzenie procesu fizykosorpcji. Ponieważ badania doświadczalne wykazały wzrost skrośnego prądu płynącego przez warstwę tetracenu podczas procesu aktywacji tej warstwy w wyniku oddziaływania z parami etanolu, to musi tu jeszcze zachodzić proces związany z transferem elektronów. Proces taki jest procesem chemisorpcji. Uzyskane wartości energii orbitali LUMO dla kompleksu złożonego z cząsteczki tetracenu i etanolu wskazują że w przypadku, gdy wymiana elektronów zachodzi pomiędzy cząsteczką etanolu leżącą w płaszczyźnie szkieletu tetracenu a cząsteczką tetracenu to związane jest to z przejściem pomiędzy poziomami LUMO+3 i LUMO+4 kompleksu. Jeżeli jednak wymiana elektronu zachodzi podczas przemieszczanie się etanolu w płaszczyźnie odległej o ok. 3,3 Å od płaszczyzny szkieletu tetracenowego ponad środkiem bocznego pierścienia benzenowego szkieletu tetracenu to wówczas wymiana elektronu pomiędzy cząsteczką etanolu a cząsteczką tetracenu zachodzi przy przejściu pomiędzy poziomami LUMO+2 i LUMO+3 kompleksu.