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SENSITIVITY OF TETRACENE LAYER AS AN EFFECT OF ENTANGLEMENT

Application of the method of quantum-mechanical calculations allowed for studies of variability of interactions between molecules of ethanol and tetracene. Entanglement of quantum states is seen during calculations in two ways: as a change of electric dipole moment and as an increase of the basis set superposition error (BSSE) with decreasing distance between molecules under study. There are observed the dependences of the total energy of the system due to the mutual arrangement of the long axes of the molecules and due to the orientation of the bond of the oxygen atom to the carbon atom with respect to the plane of benzene skeleton of tetracene molecule.

Keywords: quantum-mechanical-calculations, tetracene, ethanol, basis set superposition error.

1. INTRODUCTION

The demand for reusable gas sensors stimulates the development of existing and new technologies for the production of such type of sensors. The basic types of chemical sensors include the active layer of the transducer. Multiple phenomena occur as a result of interaction with the ambient gas. Final effects of them are transformed into an electrical signal. A useful electronic signal shows frequency variation, current change or voltage change. Gas detection technologies use semiconductor type: catalytic, electrochemical and acoustic gas sensors [1]. For economic reasons, the desirable property of sensors is the possibility of their multiple use. The possibility of obtaining such sensors is available when the adsorption process taking place in the adsorbent layer is

reversible. Such properties are exhibited *e.g.* by pentacene layers for the adsorption of water molecules [2]. A similar phenomenon was observed for tetracene layers [3] where enhancement in the conductivity of thin films was caused by ethanol adsorption. Kania and Kuliński [4] proposed that the adsorption and charge transfer process was related to mutual collisions of ethanol molecules in the adsorption layer, and to the dissociation of the ethanol molecule on the surface of tetracene. They showed that the increase in the conductivity of the tetracene layer depends on the concentration of active activator molecules (ethanol). The time constant for the adsorption at the starting point was 30.8 s at the ethanol vapour pressure of 0.2 Tr at room temperature, whereas the desorption time constant was only 11.3 s when the pressure obtained a value of 10^{-5} Tr. The low value of the time constant for desorption is puzzling due to the presence of a significant activation energy for adsorption of $\Delta H = 84$ kJ/mol, demonstrating the presence of weak chemisorption. The problem needs to be explained on the basis of quantum-mechanical calculations.

The problem of the adsorption mechanism is complex and requires considering the adsorbent particles forming the solid surface and the adsorbed molecules in the form of gas molecules as a quantum system. This type of problem can be solved only by quantum-mechanical calculations. A convenient tool for solving such a problem is the density functional theory method (DFT) [5-7].

In the presented article, we have taken up the problem of the emergence and increase of interactions between the upcoming ethanol molecule and the tetracene molecule. Both of the approaching particles are not pointwise. Each molecule has an internal structure and occupies a specific volume in space. The approaching of molecules is related to the energy cost associated with the overlap of electron clouds of both these molecules, electrostatic interactions and the appearance of dispersion forces. The problem of this type (encountered in the arenes) was investigated by various researchers [8-10] and is related to the steric effect observed in the theory of reactive collisions used to describe the activation parameters of chemical reactions [11].

2. COMPUTATIONAL PROCEDURES

2.1. Theoretical model

For the complex ethanol-tetracene (E-T) consisting of two subsystems: the molecule of ethanol (E) and the molecule of tetracene (T), the energy of interaction ΔE_{ET} , can be described as a relation:

$$\Delta E_{ET} = E_{ET} - (E_E + E_T) \quad (1)$$

where E_{ET} , E_E and E_T means energy of the complex, energy of subsystem E and energy of subsystem T , respectively. In practical calculations, we use bases with a finite dimension, which leads to a base superposition error (BSSE). Minimizing this error is possible thanks to the counterpoise correction (CP) proposed by Boys and Bernardi [12]. This method requires all calculations to be performed in the same functional basis. The dimer-centred functional basis set (DCBS) of the whole complex is used here, in which both the energy of the complex and its components are taken into account. Therefore, when energy for ethanol is calculated, the functions of the tetracene sub-system, called ghosts functions, are added to its monomer-centred basis set (MCBS). The level of BSSE can be treated as the measure of quantum entanglement of the states of the separate subsystems, *i.e.* the molecule of ethanol and of tetracene.

2.2. Quantum-mechanical calculations

The quantum-mechanical calculations were carried out with use of Gaussian-09 package. The density functional theory (DFT) with use of the B3LYP functional was chosen for calculations. The B3LYP functional was chosen from a literature [13] as an effective tool for calculations of basic states of aromatic hydrocarbons. Due to the complexity of calculations the functional B3LYP/6-31++G(d,p) was used, with diffusion functions for heavy atoms as well as hydrogen atoms. This approach gives a good agreement between the experiment and the calculated energies of orbitals for polycyclic hydrocarbons [14]. The calculations at this level of theory were made to study the variability of the interaction caused when the ethanol molecule come closer to the tetracene molecule. The calculations were carried out for two cases, when the bond of the oxygen atom to the carbon atom in the ethanol molecule is perpendicular to the plane determined by the benzene skeleton of tetracene and when the bond lies in the plane of this skeleton.

3. RESULTS AND DISCUSSION

The quantum mechanical calculations were carried out for the case when the ethanol molecule approaches the tetracene molecule along the line lying in the tetracene skeleton plane. Total energy of the system was corrected by a counterpoise correction (CP), determination of the BSSE energy. The whole energy of the system and the total dipole moment μ were calculated applying the

above mentioned procedure. The results shown in Table 1 apply to the calculation when the oxygen-carbon bond of the ethanol molecule is perpendicular to the tetracene plane, and the results presented in Table 2 concern the case when this bond lies in the tetracene plane. Both of these situations are presented in Fig. 1.

Table 1

The results of approaching the ethanol molecule along the line lying in the plane of tetracene molecule, when the ethanol bond C-O is perpendicular to the tetracene plane

distance d O(ethanol) – C(tetracene) (Å)	4.069	3.873	3.322	2.784
CP corrected energy [eV]	-23081.813	-23081.808	-23081.720	-23081.097
BSSE energy [eV]	$8.19 \cdot 10^{-3}$	$9.81 \cdot 10^{-3}$	$1.65 \cdot 10^{-2}$	$2.76 \cdot 10^{-3}$
Dipole moment μ [D]	2.099	2.120	2.214	2.437

Table 2

The results of approaching the ethanol molecule along the line lying in the plane of tetracene molecule, when the ethanol bond C-O lies in the tetracene plane

distance d O(ethanol) – C(tetracene) [Å]	3.812	3.578	2.952	2.446
CP corrected energy [eV]	-23081,837	-23081,835	-23081,657	-23080,420
BSSE energy [eV]	$8.87 \cdot 10^{-3}$	$1.24 \cdot 10^{-2}$	$2.84 \cdot 10^{-2}$	$4.62 \cdot 10^{-2}$
Dipole moment μ [D]	2.221	2.294	2.725	3.889

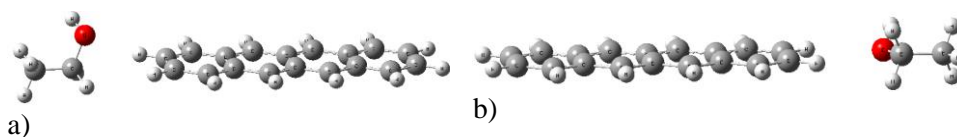


Fig. 1. Schematic images of the two different positions of the C-O bond of ethanol with respect to the plane of tetracene skeleton used in calculations: a) perpendicular, b) in the plane

The BSSE energy as a function of the distance of oxygen of ethanol relative to the corner carbon atom belonging to tetracene for both cases presented in Tables 1 and 2 is shown in Fig. 2. The nature of the relationship indicates that at

the distance less than 3 Å the both dependencies strongly differ. This kind of difference is seen also when we analyse the dependence of BSSE energy in function of the total dipole moment, μ , as shown in Fig. 3.

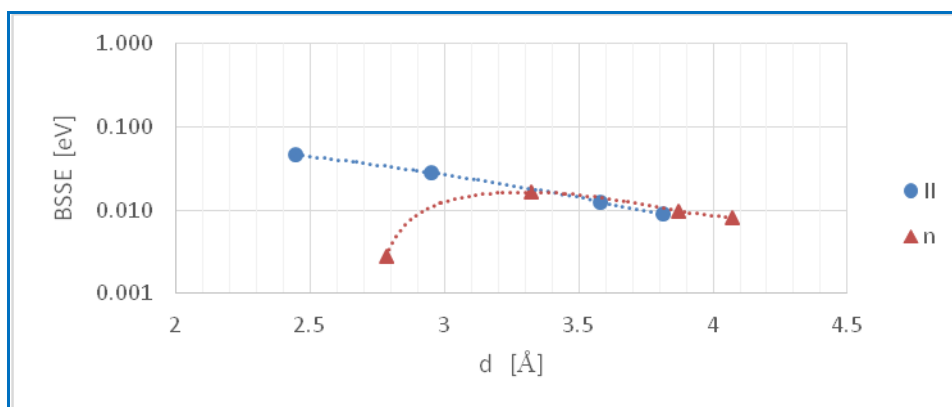


Fig. 2. The BSSE energy as the function of the distance d from the oxygen atom in ethanol molecule to the corner carbon atom in the side benzene ring of tetracene skeleton (n – from Table 1, || – from Table 2). Trend lines are obtained by the least squares method with use of the fourth order polynomial

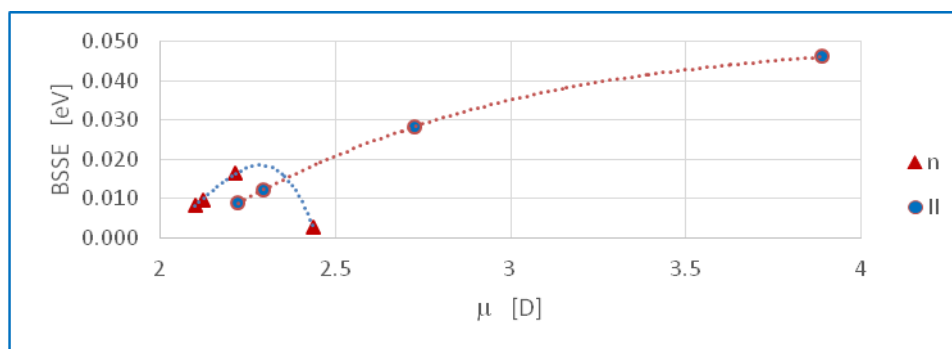


Fig. 3. The BSSE energy as the function of the dipole moment μ of the oxygen atom of the ethanol in respect to the corner carbon atom in the side benzene ring of tetracene skeleton (n – from Table 1, || – from Table 2). Trend lines are obtained by the least squares method with use of the third order polynomial

4. CONCLUSIONS

It is clearly visible that at the distance d less than 3 Å, the BSSE corrections are strongly dependent on the orientation of oxygen carbon bond in ethanol with respect to the tetracene plane (see results in Table 1 and 2, and Fig. 1). The BSSE energy, treated as a measure of quantum entanglement, is 20 times higher for C-O bond of ethanol molecule lying in the tetracene plane than for C-O bond of ethanol molecule perpendicular to the tetracene plane (Fig. 2). This is a circumstantial evidence that the quantum interaction of the ethanol molecule with the tetracene molecule is in the first case about 20 times greater. The dependence between electrostatic interactions, seen as an induced total dipole moment and quantum entanglement seen as BSSE energy, presented in Fig. 3, is different in two studied cases. The above suggests that we are dealing with a steric effect applied in the theory of active collisions in the adsorption reactions [11]. This also means that the nature of the collisions of the ethanol molecule with tetracene molecule is different for the above mentioned cases of orientation of the C-O bond belonging to methanol with respect to the tetracene plane (see Fig. 1). We can assess that the translational component of the ethanol molecule conserves to a large extent during active collisions in the case of setting the C-O bond of ethanol perpendicular to the tetracene plane (Fig. 1a). If that bond lies in the tetracene plane (Fig. 1b), the interaction should favour the oscillation of the ethanol molecule. Thus, the problem of an organic sensor based on tetracene requires further studies applying quantum mechanical calculations.

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SENSORYCZNOŚĆ WARSTW TETRACENU JAKO WYNIK SPLĄTANIA KWANTOWEGO

Streszczenie

Zastosowanie metod obliczeń kwantowo-mechanicznych umożliwiło badanie zmienności oddziaływań pomiędzy cząsteczkami etanolu i tetracenu. Obecność splątania kwantowego stanów kwantowych widziana jest podczas obliczeń na dwa sposoby – jako zmiana momentu dipolowego i jako narastanie błędu superpozycji bazy (BSSE), gdy odległość między badanymi cząsteczkami maleje. Obserwowane są zależności całkowitej energii układu zależnie od chwilowego wzajemnego ustawienia długich osi cząsteczek, jak też i orientacji wiązania atomu tlenu z węglem w etanolu względem płaszczyzny szkieletu benzenowego cząsteczki tetracenu.