Modelling of Coal Solid Phase Based on Average Structural Unit of Coal Organic Mass

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Abstract. Structural analysis of the average structural unit of C29H28O2 coal organic mass within electronic density functional theory using B3LYP functional in the localized orbitals basis has been performed. With account of intermolecular Van der Waals interactions, it has been demonstrated that it is possible to form a dimer and a trimer of this molecule and, therefore, it is possible in principle to form coal solid phase. The obtained structures are analyzed using theoretical and experimental IR spectra.

1. Introduction
A significant part of the world's coal resources is concentrated in the Siberian region. The unique resource potential and high prospects for the growth of coal mining require a scientifically based approach to its further exploration. Petrographic composition of coal is characterized by containing several groups of macerals, lithotypes and mineral inclusions. Macerals have a different elemental composition. Vitrinite contains relatively more oxygen, liptinite - hydrogen, while inertinite - carbon. To study coal structure, first one needs to examine the average structural unit of coal organic mass.

The elemental composition of coal organic mass, the structure of macromolecules, and the nature of supramolecular structuring determine basic physico-chemical properties of coals. The structure of coal organic mass can be presented by molecular models of corresponding structural and chemical formulae. A large number of coal molecular models are currently known (~150), their review can be found in the following works [1-6]. Most models are those for common black coal, but there are also examples for brown coal, sub-bituminous coal and anthracite.

It should be noted that the existing models are largely presented by two-dimensional (2D) structures, which are commonly used in organic chemistry. However, with the introduction of computer methods in coal chemistry, three-dimensional (3D) models [7-9] have started to be developed that take into account molecular interactions of close and distant atomic groups. Possible conformations of molecular systems are established on the basis of the minimum total potential energy principle. However, despite the appearance of appropriate tools, there are still no models that describe the bulk structure of coal in the most complete and consistent manner.

The objective of this work is to prove the possibility of existence of the coal solid phase on the basis of the average structural unit of coal organic mass. To do this, it is necessary to develop a relatively simple model of the average structural unit of coal organic mass and, taking into account the dispersion forces, to show the possibility of dimer and trimer formation on its basis. The obtained structures are analyzed with the help of the calculated and experimental IR spectra, which are to a
considerable degree a manifestation of the physical properties of coals.

2. Computational details
To sturdy coal structure and to determine its physical and chemical characteristics, X-ray diffraction analysis, electron microscopy, IR spectroscopy, mass spectrometry, electron paramagnetic resonance, nuclear magnetic resonance and a wide range of classical chemical and physico-chemical methods are used. The combination of IR spectroscopy and elemental analysis is used more often than the others. Computer simulation methods are used to analyze the structures and physico-chemical properties of macromolecules of coal organic mass and have significant advantages, which are not so much in economic expenditures as in fundamental understanding of the nature of interactions of different nature (covalent bond, donor-acceptor, hydrogen, van der-Waals, etc.).

In the present work the authors used the density functional theory (DFT), one of the most common methods in computational physics and chemistry. The density functional theory is a strict many-electron theory, where the system is described by the electron density \( \rho(r) \), including the contribution of all the electrons, and not by the wave function. Different functionals are used in this theory to calculate many-electron systems. There are local functionals (if the only dependency is that on \( \rho \)) and non-local (gradient, if there also is a dependency on \( \nabla \rho \)) exchange-correlation functionals. Thus, BLYP exchange-correlation functional is obtained by combining LYP exchange functional (Lee, Yang, Parr, 1988) and B88 correlation functional (Becke 1988). By combining exchange and correlation functionals with account of the Hartree-Fock functional, it is possible to obtain the so-called "hybrid" functional, a good example of which is the most commonly used B3LYP hybrid functional. This functional and the MINI basis set of Firefly software package [10] were used to calculate the geometry of molecular structures. The package has the standard procedures of geometry optimization, total energy calculation, electron subsystem energy, vibration frequencies, thermodynamic potentials and functions.

It is necessary to take into account intermolecular interaction to obtain dimer and trimer structures of coal organic mass. As conventional DFT approaches poorly model weak dispersion interactions, one of the promising technique was used, the so-called S. Grimme technique, that is DFT-D method. Behind this method, there is the additive scheme of energy calculation: addition of the dispersion correction term to the energy obtained in the DFT approximation (\( E_{\text{DFT-D}} \)):

\[
E_{\text{DFT-D3}} = E_{\text{KS-DFT}} - E_{\text{disp}}
\]

So far there are several variants of this method that differ in the form of dispersion. To account for intermolecular interaction, it was decided to use one of the latest models, which is considered more accurate, that is DFT-D3(BJ). In this case, the energy dispersion component is calculated using the following formula:

\[
E_{\text{disp}}^{\text{D3(BJ)}} = \frac{1}{2} \sum_{A \neq B} s_6 R_{AB}^6 \left( \frac{C_6^{AB}}{R_{AB}^6} + [f(R_{AB}^0)]^6 + s_8 R_{AB}^8 \left( \frac{C_8^{AB}}{R_{AB}^8} + [f(R_{AB}^0)]^8 \right) \right)
\]

where \( s_6 = 0.418, a_1 = s_6 = 0.0, s_8 = 0.25, a_2 = 5.65 \). \( S_6 \) establishes correlation for GGA and hybrid functionals, and \( S_8 \) is used to improve correction of repulsive behavior at short and medium distances of the exchange functional, \( a_1 \) and \( a_2 \) are free parameters of the system for BJ (Becke and Johnson). \( C_n^{AB} \) is an average coefficient of the n-th order dispersion for the atom of AB pair and \( R_{AB} \) is their interatomic distance, while \( R_{AB}^0 \) is a cutoff radius for the corresponding atoms.

3. Results and discussion
Macromolecule (C_{29}H_{28}O_2) modelling the average structural unit of coal from [12] was used as a basis for dimer and trimer of coal organic mass. The methyl group (-CH_3), the hydroxyl group (-OH) were used as bridge bond, and -CH_3 was used as an alkyl substituent R. The search of 3D model of this
molecular structure was carried out in several stages. At the first stage in the naphthalene molecule one hydrogen was replaced by –OH hydroxy group, then in the similar way the functional group (-CH$_3$) and four methyl groups (-CH$_2$) were consistently attached. One of the methyl groups (-CH$_2$) in the obtained structure plays the role of bridge bond. On the final stage this bridge bond is attached by the same structure without bridge bond. As a result a 3D model of the average structural unit of coal, organic mass was obtained (Fig.1). Among all known structures, describing coal organic mass [13], this structure contains the minimum possible number of atoms. This fact basically allows constructing dimer and trimer on its basis. The percentage of various chemical elements in the structure is as follows: C – 86.4%, H – 7.2%, O – 6.4%. According to the structural analysis the content of structural fragments characteristic of real coal was as follows: CH$_3$ – 7.4%, CH$_2$ – 24%, Ar-H – 1.48%, Ar-C – 58.8%, Ar-O – 7.83%. A number of typical structural parameters were determined for the obtained average structural unit of coal organic mass: angle $\alpha$=113.34°, bond length $a$=1.518 Å and $b$=1.516 Å. It should be noted that in comparison to naphthalene a slight deformation of internal angles (0.1%-1.2%) and bond lengths C-C (0.4%-2.2%) is observed [8]. The obtained model of the average structural unit of coal organic mass is a three dimensional one, the calculated Van der Waals volume is 630.34 Å$^3$.

![Figure 1. A model of the average structural unit of coal organic mass.](image)

Based on the 3D model of the average structural unit of coal organic mass, 3D models of dimer and trimer were later constructed. In the obtained dimer and trimer structures (Fig.2) the characteristic angles and bond lengths, marked in the average structural unit of coal organic mass, changed slightly. For the dimer in the first molecule, they are as follows: 112.76°, 1.502 Å and 1.505 Å; in the second molecule: 103.45°, 1.526 Å and 1.526 Å. And for the trimer, respectively: 114.81°, 1.511 Å, 1.505 Å; 116.97°, 1.501 Å, 1.502 Å; 104.70°, 1.529 Å and 1.528 Å. The important structural characteristic for the dimer and trimer of the average structural unit of coal organic mass is the distance between molecules, which is $d$=4.356 Å in the dimer, while it is $d_1$=4.571 Å and $d_2$=4.263 Å in the trimer. The Van der Waals volume for the obtained structure of the trimer of the average structural unit of coal organic mass is 1876.74 Å$^3$, which corresponds to 622.58 Å$^3$ for one formula unit.
Figure 2. The trimer structure of the average structural unit of coal organic mass.

Figure 3. a) Trimer IR spectrum; b) \( \text{C}_{29}\text{H}_{38}\text{O}_2 \) IR spectrum; c) Long-flame gas coal IR spectrum.
It is energy characteristics of a particular structure that usually define its stability. The total energy per molecule for all the structures obtained was such characteristic. Due to this parameter, the structure of trimer is the most energetically attractive. The binding energy, calculated using $\Delta E = E_n - n \cdot E_m$, where $E_n$ is the total energy of the dimer or trimer, $E_m$ is the total energy of the average structural unit of coal organic mass and $n$ is the number of macromolecules, which is -111.61 kcal/mol and -214.76 kcal/mol, respectively. The contribution of intermolecular interaction to binding energy for the dimer and trimer is -75.26 kcal/mol and -125.40 kcal/mol, respectively.

Due to the presence of IR spectrometers, relative simplicity of spectral interpretation and significant information content, infrared (IR) spectroscopy is one of the most common methods for studying coal and coal products [14-15]. Therefore, the IR spectra were theoretically obtained for the calculated structures allowing the most complete analysis of compounds and their comparison. It is possible to distinguish the ranges of characteristic frequencies on the obtained IR spectra (Fig. 3): from 3300 cm$^{-1}$ to 4000 cm$^{-1}$ corresponding to the vibrations of O-H bond, from 3100 cm$^{-1}$ to 3200 cm$^{-1}$ corresponding to the vibrations of C-H bond, from 1400 cm$^{-1}$ to 1700 cm$^{-1}$ corresponding to the vibrations of C-O, C-C bond, from 1100 cm$^{-1}$ to 1200 cm$^{-1}$ of C-O, O-H bond and from 600 cm$^{-1}$ to 800 cm$^{-1}$ for the vibrations of C-H bond. Intermolecular vibrations are of interest to us. When comparing the trimer IR spectrum to the spectrum of the average structural unit of coal organic mass, it is possible to distinguish a specific peak at 3608 cm$^{-1}$ frequency. This peak indicates the existence of intermolecular hydrogen bonds between oxygen-containing groups in the trimer. The remaining peaks in the trimer IR spectrum are displaced with respect to the corresponding ones in the IR spectrum of the average structural unit of coal organic mass, while the intensity of the vibrations is increased. A relatively small peak at 3200 cm$^{-1}$ frequency is due to valence vibrations of the saturated C-H bond. It indicates the existence of -CH$_2$-, -CH$_3$- fragments. These fragments can be from an alkyl side chain, bridge bond or saturated carbon rings in coal. The peak at 3456 cm$^{-1}$ frequency is caused by the vibrations of hydrogen-containing hydroxyl groups and indicates the existence of intramolecular hydrogen bonds between oxygen-containing groups in the structure. This peak overlaps valence vibrations peak of C-H aromatic bond at 3442 cm$^{-1}$. The peak at 1518 cm$^{-1}$ corresponds to bending vibrations of the saturated or unsaturated C-H bond. The peak at 1190 cm$^{-1}$ contributes to O-H bending vibrations and C-O valence vibrations. Having compared the calculated IR spectrum and the experimental IR spectrum, obtained for long-flame gas coal, it can be stated that the obtained structure of coal organic mass can be included in coal composition as there is coincidence across a number of peaks.

4. Conclusion
The conducted research reveals that dimer and trimer are energetically more efficient structures than the individual molecule of the structural unit of coal organic mass. It is obvious that further addition of the coal organic mass molecules will also be an energetically more advantageous process with the formation of the polymer structure. Thus, it is possible to form the coal solid phase based on the average structural unit of coal organic mass under consideration.

The analysis of the obtained 3D model of the structural unit of coal organic mass makes it possible to use it in the future when modeling coal, as the minimum permissible structural element. The analysis of the characteristic geometric parameters and the total energy for the models allows us to state that these important physical and chemical characteristics are weakly dependent on the density and basis functionals used.

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References
[1] Gagarin S G 2012 Molecular Models of Coal’s Organic Matter and the Reflectance of the
Materials: A Review. Coke and Chemistry. 55 409

[2] Heredy L A and Wender I 1980 The molecular representations of coal – A review. ACS Division of Fuel Chemistry Preprints 25 38

[3] Jonathan P Mathews and Chaffee L Alan 2012 The molecular representations of coal – A review. Fuel. 96 1

[4] Barsky V, Vlasov G and Rudnitsky A 2009 Composition and structure of coal organic mass. Analytical review. Chemistry and Chemical technology. 3 315

[5] Gyulmaliev A M, Gagarin S G and Golovin G S 2004 Structure and Properties of the Organic Mass of Coal. Khim. Tverd. Topl. 1(6) 10

[6] Jie-Ping Wang, Guang-Yue Li, Rui Guo, An-Qi Li, and Ying-Hua Liang 2017 Theoretical and Experimental Insight into Coal Structure: Establishing a Chemical Model for Yuzhou Lignite. Energy Fuels 31(1) 124

[7] Kairbekov Zh K, Gyulmaliev A M, Yarkova T A, Smagulova N T and Kairbekov A Zh 2015 Structure and Properties of Heavy Organic Residue from Coal Hydrogenation. Coke and Chemistry. 58(10) 367

[8] Zhuravlev Yu N, Fedorov I A and Kiyamov M Yu 2012 First-principles study of the crystal structure and equation of state of naphthaline and anthracene. Journal of Structural Chemistry. 53(3) 417

[9] Nie Baisheng, Wang Longkang, Li Xiangchun, Wang Chao and Li Li 2013 Simulation of the interaction of methane, carbon dioxide and coal. International Journal of Mining Science and Technology. 23 919

[10] Alex A. Granovsky, Firefly version 8, www.http://classic.chem.msu.su/gran/firefly/index.html

[11] Grimme S, Ehrlich S and Goerick L. 2011 Density Functional Theory Journal of Computational Chemistry. 32 1456

[12] Gyulmaliev A M, Golovin G S and Gladun T G 2003 Theoretical grounds of chemistry coal (Moscow: Publishing house of Moscow state mining university) p 556

[13] Porohnov A N and Zhuravlev Y N 2014 Computer simulation of structural fragments of coal organic mass. Bulletin of Kemerovo state university 2(60) 133

[14] GUO Juan-Juan, ZHU Chuna, HE Qiong-Qiong, WANG Xin-Hua, FENG Li, WU Jian-Jun, LIU Jiong-Tian and CAO Ze-Xing 2013 Infrared Spectra and Pyrolysis of Selected Molecular Models of Coal: Insight from Density Functional Calculations. Chinese J. Struct. Chem. 32(6) 863

[15] Gagarin S G and Gyulmaliev A M 2007 Simulation of the IR Spectra of the Organic Mass of Coal and Coal Products. Coke and Chemistry 50(10) 275