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Adsorption of methane on carbon models of coal surface studied by the density functional theory including dispersion correction (DFT-D3)

Nian-Xiang Qiu [a], Ying Xue [a,*], Yong Guo [a], Wen-Jing Sun [b], Wei Chu [b,*]

[a] College of Chemistry, Key Laboratory of Green Chemistry and Technology in Ministry of Education, Sichuan University, Chengdu 610064, PR China
[b] Department of Chemical Engineering, Sichuan University, Chengdu 610065, PR China

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ABSTRACT

The density functional theory including dispersion correction (DFT-D3) has been used to investigate the adsorption of methane on carbon models of coal surface, including C_6H_8, pyrene, and coronene. For the small model complex C_6H_8–CH_4, the interaction energies obtained using four kinds of the functionals, BLYP-D3, TPSS-D3, BP86-D3, and PBE-D3, were benchmarked against the best available result that was provided by the complete basis set (CBS) limit of CCSD(T) method, and the BLYP-D3 functional with the best performance was selected to treat the remained larger systems. Several adsorption positions and orientations of CH_4 on the hydrocarbon clusters were systematically considered. Our results indicated that the interaction energy in the complex increases as the size of the complex increases and the up configuration of CH_4 (with the hydrogen tripod directed to the surface) adsorbed on pyrene and coronene is greatly preferred when compared with both the down and bidentate configurations. The center adsorption site above the six-membered ring is preferred by the methane molecule adsorbed on coronene. It was shown that in coronene–methane model the interaction energies of −3.17 to −3.32 kcal/mol and the molecular distances of 3.36–3.39 Å obtained from the BLYP-D3 calculations are close to the values available in experiment for the binding of methane on graphite and can provide the accurate prediction to those in the coal surface–methane complex.

1. Introduction

Coalbed gas contains major CH_4 and a few amount of N_2, CO_2 and other gases. Currently, the co-mining research of coal and coalbed methane (CBM) has been important worldwide as CBM is becoming an available and effective clean energy source [1,2]. CBM in the coal can be presented as free gas within the macropores or as an adsorbed layer on the internal surfaces of the coal micropores, and evolving during the mining, result in rapid changes in rock mass strains and other phenomena. Therefore, understanding the interaction between adsorbed methane and coal surface may be a subject of interest in the optimum development of technologies of coal–gas co-mining and processing.

Coal is a kind of extremely complex matrix with across-linked molecular frameworks, which is comprised of microcrystalline graphite sheets or polycyclic aromatic structures with other functional groups acting as bridges. Many different structure models of coal have been presented on the basis of the results of physical and chemical analysis [3–5]. In spite of the heterogeneous and anisotropic characters of coal, these systems trend to be transformed into graphite structure under the high temperature condition [6]. So, some graphite materials, including graphite, graphene, carbon nanotubes, and polycyclic aromatic hydrocarbon clusters, are usually used as the local surface model of the coal for investigating the interactions of small gas molecule with coal surface [7–10].

On the other hand, the study of methane adsorptions on carbonaceous materials has the rich history for both its practical and theoretical importance in gas storage. In the past decades, there were some experimental investigations about heat capacity, adsorption isotherm, NMR, neutron scattering, and low energy electron diffraction to describe the adsorption behavior of CH_4 [11–16]. Numerous empirical potential simulations and quantum chemical calculations of methane on graphitic surfaces or in carbon nanotubes have appeared [17–26]. Based on the density-functional theory/coupled cluster method (DFT/CC), Rubeš et al. [25] investigated the physical adsorption of molecules C_2H_2, C_2H_4, C_2H_6, C_6H_6, CH_4, H_2, H_2O, N_2, NH_3, CO, CO_2, and Ar on a graphite substrate. Thierfelder et al. [26] used the density functional theory complemented with a semiempirical dispersion correction scheme (DFT-D) and the van der Waals density functional (vdW-DF) in conjunction with the PBE functional to study the methane–graphene interaction. Most of these electronic structure calculations have employed the single binding mode of the hydrogen tripod directed to the surface or to the vacuum.

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* Corresponding authors. Tel.: +86 28 85418330.
E-mail address: yxue@scu.edu.cn (Y. Xue).

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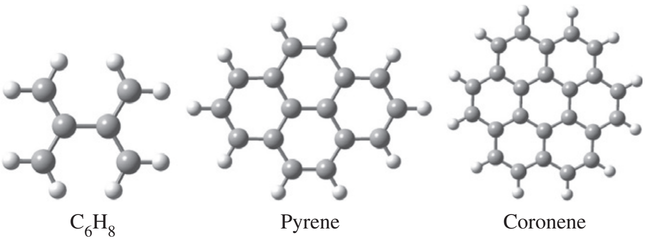

Fig. 1. The carbon models used to mimic carbon model of coal surface.

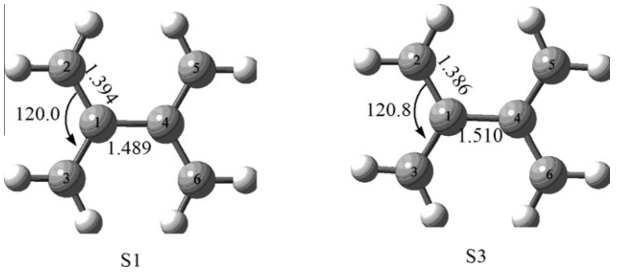

Fig. 2. The optimized geometries and atomic numbering of the singlet and triplet states of C_6H_8 model at the MP2/6-311++G(d,p) level (bond length in Å, bond angle in degree).

It is well known that the dominant part of interaction energy of small molecules with graphitic materials in many cases comes from the dispersion energy, which is more difficult to treat theoretically than traditional chemical bonds. The CCSD(T) method in the complete basis set (CBS) limit provides excellent result to take into account the dispersion energy, but it is impracticable for the large systems, since it is very expensive due to its unfavorable N^7 scaling with the size of the systems. Furthermore, the practicable method which is currently widely used, the density functional theory (DFT), cannot properly describe the dispersion interactions. Various approaches have been proposed to accurately model the very important dispersion interactions, including the nonlocal van der Waals density functional (vdW-DF) [27,28], the DFT-symmetry-adapted perturbation theory (SAPT) [29,30], the density functional theory/coupled cluster method (DFT/CC) based on the pairwise representability of the difference between the CCSD(T) and DFT energies [31], the density functional (DF) that takes account into dispersion interaction in a physical manner [32,33], and the DFT-D method [34–42,43] which describes the dispersion as the addition of a pairwise interaction energy correction term (C_6R^{-6}). Among the approaches above, the DFT-D method has been most widely employed because of its low numerical complexity, high accuracy, and easy analysis of its results. Recently, Grimme et al. [41,42] have reported the new DFT-D3 method providing higher accuracy, less empiricism and broader range of applicability than the previous versions (DFT-D1 [37] and DFT-D2 [38]). They have proposed for the first time a concept of geometry dependent information to solve the problem of system independency in the previous versions. The agreement between DFT-D3 and CCSD(T) methods was typically within about 10% [41,43].

In this study, we will adopt three hydrocarbon cluster models C_6H_8, pyrene, and coronene to mimic the local surface of coal and systematically investigate the adsorption of methane onto various adsorption sites and orientations on coal surface using the density functional theory with new dispersion correction scheme (DFT-D3). The predicted CCSD(T)/CBS interaction energies are used to benchmark the results of DFT-D3 method. The effect of the size of the model on the interaction energy between methane and polycyclic aromatic hydrocarbon cluster will be discussed.

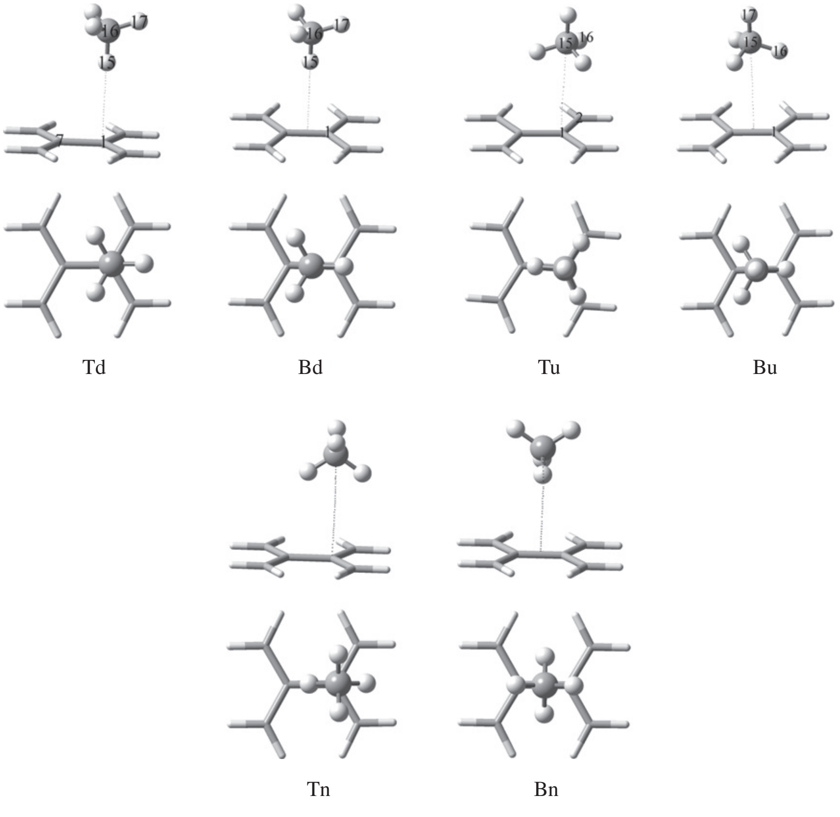

Fig. 3. The C_6H_8–CH_4 complex models. The side view and top view of six configurations (Td, Bd, Tu, Bu, Tn and Bn) are given.