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Ab initio studies of carbon dioxide affinity to carbon compounds and minerals

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Abstract

We have performed quantum chemical computational studies to determine carbon dioxide affinity to carbon compounds and minerals, which could be present in shales. These studies shed light on the microscopic mechanisms of the possible carbon oxide sequestration processes. Our studies reveal that the carbon oxide can be adsorbed to various forms of carbon structures and also minerals such as periclase or illite. We find out that the strongest affinity of carbon oxide towards carbon structures occurs when the carbon structures exhibit sp^3 bonds.

1. Introduction

Carbon dioxide is one of the primary greenhouse gases implicated in global warming process. Alternative energy sources that make no contribution to CO_2 emission are still in the development phase and not likely to replace current carbon-based energy sources during the few next decades. Also carbon capture methods are intensively studied at present, however, it is difficult to foresee their effective employment in industry and everyday life. Carbon dioxide sequestration process seems to be an alternative, and therefore, is of critical importance to maintain or even reduce the CO_2 level in the atmosphere. Additionally, CO_2 sequestration process can be connected to the Enhanced Oil recovery in shale rocks. Therefore, accurate description of physicochemical mechanisms governing the CO_2 and CH_4 adsorption to various minerals and organic forms of carbon matter is an important step to understand mechanisms and to improve technologies of sequestration. The particular role of carbon in these processes is evident, since total

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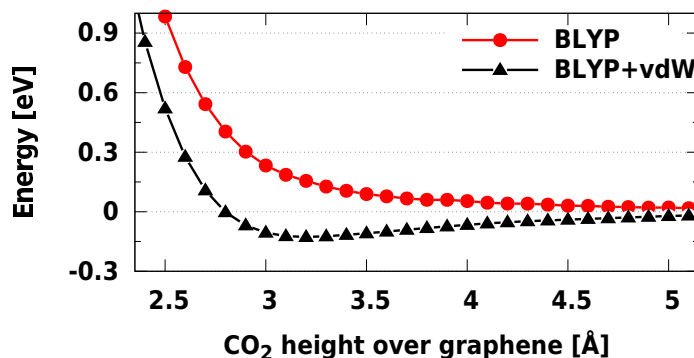 *E-mail address:* mateusz.wlazlo@fuw.edu.pl

Fig. 1. Adsorption energy vs. distance of CO_2 over ideal graphene obtained in calculations with (BLYP+vdW) and without (BLYP) the DFT-D2 correction. The presence of an energy minimum after including the correction indicates that CO_2 can be physisorbed on graphene and that it can only occur via van der Waals interaction. Reprinted from [1].

organic carbon (TOC) is an important parameter that characterizes the potency of a shale formation in hydrocarbon production, and a high TOC value ensures that a reservoir is useful in gas production.

In the present study, we employ quantum chemical computational techniques to study carbon dioxide adsorption processes on the atomistic level in organic and inorganic shale rock constituents and to gain understanding of these effects on the micro (atomic) scale. We have selected a few materials that mirror the heterogeneity of shales. In particular, we focus on the organic components, which are modeled by pure carbon allotropes such as graphene and spiral carbon nanoparticles (spiroids), however, we provide also some findings for magnesium oxide mineral, illite, and calcite rocks. We investigate the structural, energetic, and the thermodynamical aspects of CO_2 adsorption and desorption employing ab initio molecular dynamics (AIMD) within the canonical ensemble (i.e., keeping constant the following quantities: (i) number of atoms in the system, N, (ii) volume of the system, V, and (iii) the temperature, T, therefore indicated as NVT ensemble) and are able to determine the possible CO_2 capture reactions. In our studies, we consider generally the temperature range relevant for the shales deposits, typically 300-400 K. In particular, we would like to find out whether in these temperatures CO_2 makes chemical bonds to an adsorbent (i.e., the chemisorption occurs), or is it only weakly bound to the adsorbent through van der Waals forces (i.e., undergoes the physisorption process)

The present paper is organized as follows. In Section 2 we give a short and comprehensive description of the methodology employed in this study. The results of the study describing the mechanisms of the CO_2 adsorption to the carbon structures and minerals are presented in Section 3. Finally, the paper is concluded in Section 4.

2. Methods

The essential component of *ab initio* methods for predicting properties of a collection of atoms is a quantum mechanical scheme to calculate the ground state energy of the system studied. In our studies of the physicochemistry of the carbon dioxide adsorption to surfaces of various materials, we employ density functional theory (DFT) calculations that constitute nowadays the method of choice for the materials science. The Hohenberg-Kohn-Sham [2, 3] realization of DFT allows us to find not only the total energy of the system but also every observable of the system as a functional of the ground state electronic density. The total energy functional, often referred to as the Kohn-Sham functional (E_{KS}), is written in terms of the kinetic energy functional (T_s), the external potential acting on the electronic system (v_{ext}), the electron-electron interaction (Coulomb or Hartree interaction, E_H) and exchange-correlation interaction (E_{XC}):

$$E_{KS}[n] = T_s[n] + \int d^3r \, v_{ext}(\mathbf{r})n(\mathbf{r}) + U_H[n] + E_{XC}[n] \tag{1}$$