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Tuning the interaction strength and the adsorption of CO_2 in metal organic frameworks by functionalization of the organic linkers

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ABSTRACT

The interaction strength of CO_2 with a set of fourteen, strategically selected, functional groups was investigated by performing MP2 calculations. These functional groups potentially can be incorporated in MOF linkers. Initially, the energetically most favorable intermolecular structures for each of the CO_2–functional group complexes were found, starting from several different initial configurations of CO_2 over the functional groups. Among the functional groups that were considered, the highest interaction energy (−5.4 kcal/mol) with CO_2 was found for phenyl hydrogen sulfate (OSO_3H), which is almost 2 times larger than the corresponding binding energy for benzene (−2.9 kcal/mol). Electrostatic potential maps of the functionalized benzenes and electron redistribution density plots of the corresponding complexes with CO_2 were generated to understand the nature of the interaction of CO_2 with the functionalized benzenes. Additionally, we tried to find any correlations between the obtained binding energies and the geometrical parameters of the CO_2–functional group complexes. The best functional groups were tested for their ability to capture CO_2 at 298 K for a wide pressure range by performing GCMC simulations.

1. Introduction

The emission of greenhouse gases has been recognized as one of the main issues that has to be controlled in order to avoid further undesirable changes in the climate. The capture of these gases has been a major challenge for the scientific community in the past years, especially the amounts of them which are produced from the human activities. More specifically, CO_2 capture and storage has attracted a lot of attention, since it is believed that the large CO_2 emissions play a critical role in the increment of the global temperature [1]. Carbon Capture and Storage (CCS) [2] technologies have been developed with the aim to decrease the CO_2 emissions in the atmosphere. Three major techniques have been proposed for carbon capture, namely pre-combustion, oxy-fuel and post-combustion. Among them, post-combustion presents some more advantages, such if the carbon capture system fail to work properly it will not prohibit the normal operation of power plant. The most widely used technique for carbon capture is based on the post combustion technique by using aqueous amine absorbents. This technique require large amounts of energy during absorption and regeneration procedure, which can be approximately 30% of the amount of energy produced by a power plant. In order to reduce the amount of energy consumed, porous solid adsorbents such as zeolites, aluminosilicates and mesoporous silicas, have been proposed alternatively. These materials must fulfill several requirements, such as selective adsorption of CO_2 over the other gases in the flue gas mixture, large CO_2 adsorption capacity, large surface area and pore volume, increased stability, low cost of regeneration etc. The properties of many candidate materials for carbon capture were recently described in the review article by Sneddon et al. [3].

Metal-Organic Frameworks (MOF) have been proposed as suitable porous materials for capturing CO_2 from a mixture of gases and to store CO_2 in their pore networks [4]. They are composed by inorganic building units interconnected with properly functionalized organic linkers, in order to form a framework material with a pore network. A lot of families of this type of materials has been synthesized such as IRMOFs, ZIFs, MILs and UiO [4–7]. These materials present extremely high physicochemical properties such as high surface area and pore volume, high thermal and chemical stability, which make them candidate materials for carbon capture applications. Moreover, the properties of these materials can be tuned by changing the inorganic building unit or the organic linker. Introduction of unsaturated metal sites in the former or functional

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groups in the latter further tune their properties and play essential role in the design of novel MOF materials with excellent performance in gas storage and separation, catalysis, energy conversion etc.

One of the key parameters to increase CO_2 selectivity in a MOF is to enhance the adsorption strength of CO_2 over that of the other gases in the mixture. Depending on the other important components of the gas mixture, H_2 and N_2 in pre-combustion and post-combustion procedure respectively, MOF can be specifically designed to maximize the selectivity by tailoring its structural characteristics. This is also valid for the case of the natural gas upgrading, where a gas mixture of CO_2 and CH_4 must be treated. Enhancement of the CO_2 adsorption strength in MOF can happen by introducing unsaturated metal sites in the inorganic building units or by creating new binding sites due to the existence of functional groups in the organic linkers. Quantum chemistry calculations have been widely used to study the interaction of CO_2 and other gases with MOFs [8]. Such calculations are essential in understanding the CO_2 adsorption in MOFs, since they can provide us with CO_2 binding strengths and also reveal the nature of the interaction.

MOF that contain unsaturated metal sites has been proven as very efficient materials for CO_2 capture. This has been attributed to the enhanced interaction of CO_2 with the unsaturated metal atoms of the inorganic building unit. Some of the most known MOF with unsaturated metal sites are HKUST-1, M-MOF-74 [9,10], MIL-101 [11] and ZJU-26 [12], which can accommodate one CO_2 molecule per unsaturated metal site. It has been found that the interaction energy for this type of MOF range from 5 kcal/mol to 15 kcal/mol [13,14], depending on the metal and the structure of the inorganic building unit. Mg containing MOF have found to exhibit the largest interaction strength among other metals studied, including first row transition metal MOF.

The interaction of the CO_2 with organic linkers is also very important, because linkers play a dominant role in the adsorption of CO_2 in a MOF. Furthermore, functional groups can be added on them in order to tune the interaction with CO_2. A few studies have been published on the interaction of CO_2 with organic molecules by means of quantum chemical calculations [15–22]. Some of them [19–21] were devoted to give insight in the solubility of some organic molecules in supercritical CO_2. The rest of these studies examined the nature of CO_2 interaction with already existing or proposed linkers for MOF or ZIF. In a previous study [15] we performed high quality quantum mechanical calculations, including CCSD (T) methods, to investigate the interaction of CO_2 with nitrogen containing organic molecules which could act as linkers in ZIFs. We also performed a benchmark of various methods on the accuracy of the prediction of the binding energies with respect to CCSD (T)/CBS method. Vitillo et al. [18] performed MP2 calculations to study the interaction of CO_2 with aliphatic and aromatic amines. Torrisi [16,17], used Density Functional Theory (DFT) to study the interaction of CO_2 with a range of substituted aromatic molecules, including substitution with single or multiple atoms or functional groups. The highest binding energy was found for the interaction of CO_2 with $C_6H_5{-}SO_3H$ (−3.8 kcal/mol), which has been verified for each excellent performance towards CO_2 in a recent MP2 study of us [22].

As has been mentioned in previous studies [15,18], electrostatics and dispersion forces mainly contribute to the binding energy of CO_2. It has been shown [13] that dispersion forces contribute almost equally in many cases depending on the system. The electrostatic contributions are based on the permanent quadrupole moment of CO_2 and its ability to act as weak Lewis acid (through the C deficient atom) or as weak Lewis base (through the electron rich O atoms).

Results from accurate quantum calculations can be further used to tune the parameters of classical force-fields that describe the interaction between these groups and the CO_2 molecule. The parameters can be used to classical simulations like Grand Canonical Monte Carlo (GCMC) calculations in order to calculate the adsorption capacity of CO_2 from the modified frameworks. Using accurate set of partial charges for the framework atoms and correct set of parameters for the classical potential is of crucial importance for determining the amount that can be adsorbed from the structures. The parameter sets available from the various forcefields existing in literature can work fine in general cases. Nevertheless, when incorporating non trivial atom types, their performance is poorer than expected. Both charges and potential parameters can be extracted from the outcome of the QM calculations, linking in this way the QM calculations with the GCMC ones. The multi-technique method of combining quantum mechanics calculations with Monte Carlo simulations has been successfully used in many previous studies from us [23] and others [24] for the prediction of the adsorption properties in porous framework materials with respect to corresponding experimental data.

In the present study, we performed accurate quantum chemistry calculations to investigate the nature of the interaction of CO_2 with a set of fourteen, strategically selected, functionalized benzenes (shown in Fig. 1) which potentially can be incorporated in MOF linkers. The selection was mainly based in chemical intuition. An investigation for physical correlations between the binding energy and the geometrical parameters was performed in order to find any existing trends between them. In addition, we attempted to understand and explain the nature of the optimized complexes by creating plots of the electrostatic potential of the functionalized benzenes and by constructing electron density redistribution plots. Since many of the organic linkers used in MOF are based on aromatic rings, the simplest model that we could take was that of a functionalized benzene. It is expected that the binding energy and the geometrical parameters of the calculated complexes will be only slightly different when they are placed in a MOF framework, especially when there are no narrow cavities in the MOF structure. On the other hand, our calculations can serve as a general strategy that can be applied in any kind of framework materials. The best two groups among the ones studied in this work, were further used to determine the enhancement of the CO_2 uptake from the modified structures compared to the parent materials. This was done by employing GCMC simulations to the unmodified framework IRMOF-8 and the corresponding derivatives that contain the specific functional groups. The improvement of the uptake was determined in terms of gravimetric and volumetric uptake.

2. Methods

Second-order Moller–Plesset (MP2) perturbation theory in the resolution of identity (RI) approximation [25] was applied for the geometry optimization of the complexes, along with the def2-TZVPP [26] basis set and the corresponding MP2 optimized auxiliary basis set for the RI approximation [27]. The SCF (Self-consistent field Hartree–Fock (HF)) convergence criterion was set at 10^{-8} au. All geometry optimizations were performed without any symmetry constraints and the optimized structures were verified as minima by applying numerical frequency calculations. In order to locate the most stable complex geometry between the two interacting monomers, many different initial geometries were generated around each functional group. The different possible approaching orientations of CO_2 were also included in the generation of the initial geometries. For all calculations, the binding energies of the complexes were calculated by using the