



Carbon dioxide capture by nitrogen containing organic materials – A density functional theory investigation

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ABSTRACT

The present work deals with study and analysis of density functional theory (DFT) methods for carbon dioxide capture using nitrogen containing organic polymer materials. Nitrogen containing organic materials as potential candidates for CO₂ capture is examined by using various density functional methods. The performance of a set range of several density functionals from the representative families of pure generalized gradient approximation (GGA), meta-GGA, hybrid, long range corrected (LRC) and dispersion corrected functionals were considered for their assessment in calculating binding energies associated with gas molecules (CO₂ and N₂) with the nitrogen containing model systems. The theory behind the different classes of density functionals was discussed and the functionals were assessed using statistical parameters such as mean average binding energy values, mean absolute errors and root mean square deviations in calculating the binding energies with the gas molecules. A total of 80 method/basis set combinations were examined through the analysis of binding energies of the gas molecules (CO₂ and N₂) with various nitrogen containing aromatic frameworks. Unlike previously reported DFT benchmarks, which calculate single point energies, in this work we have calculated binding energies for the geometries optimized at each theoretical methods. For comparison the complexes were evaluated using Møller–Plesset perturbation method of second order MP2/aug-cc-pVDZ level theory to yield a best estimate of binding energies. We found that conventional functionals are not suitable for N-containing model systems and tend to overestimate or underestimate the binding energies. Considering both accuracy and efficiency the functionals we recommend are ωB97X-D, CAM-B3LYP and M06-2X. Also the functionals ωB97, ωB97X, PBE0 and M06-HF show relatively less errors and give reliable binding energies for the complexes. We have also discussed the mechanism for carbon dioxide interaction with polymer fragment and functional groups in the model cluster systems. The conclusions obtained in the study would help in increasing awareness of the strengths and weaknesses of the DFT methods and assist the experimental researchers in efficient molecular engineering of porous covalent architectures for carbon dioxide capture.

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1. Introduction

Over the last few decades Molecular modeling techniques such as Density functional Theory (DFT) based methods and quantum calculations have developed to such an extent that they are considered as invaluable tool by researchers to predict molecular properties, thermochemistry, kinetics, spectroscopic properties for a broad range of systems and are able to compute even properties difficult or impossible to measure experimentally [1,2]. The numerous successful applications of DFT to investigate structure, bonding, spectroscopic properties, intermolecular interactions and their role in designing nanostructured future generation

materials can be found in literature available [3–5]. No doubt DFT has become an indispensable tool for experimental chemists, molecular engineers and material scientists in providing useful properties of the system and allowing them for establishing rational design of novel materials for future technological challenges. One such grave challenge that the world is facing is the global warming and climate change. The major cause of this global threat is due to rise in atmospheric CO₂ level. Carbon capture and storage (CCS) is considered one of the biggest problems of the twenty-first century and the role of molecular modeling and simulation is going to be pivotal to develop new materials of future. Novel carbon based nanomaterials and porous organic polymers have emerged as a new class of materials for carbon dioxide capture and considered as promising pillars of next-generation CCS

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technologies. Porous materials such as porous carbonaceous materials, zeolites, metal-organic frameworks (MOFs), covalent organic polymers (COPs) are excessively studied for carbon capture and storage [6–10]. Porous organic polymers are materials in which organic molecules are linked by strong covalent bonds which show better thermal and chemical stability compared to MOFs that are organized by coordination bond. Nitrogen containing organic porous polymers are of great interest due their increased selectivity without compromising CO₂ uptake capacity, higher thermal and chemical stability and structure tenability [11–14]. However, despite the advantages of nanoporous materials, there is still a great hurdle in designing of functional sorbent materials to work under specific thermodynamic conditions. An enormous variety of possible compositions and structures of porous polymers make the task of searching and screening of candidate carbon adsorbents through experiments quite cumbersome and unmanageable.

A key challenge in designing nanostructure carbon dioxide capture material is the requirement of highly precise molecular modeling, exact binding energies, orientation of functional groups, pore structure and accurate description of intermolecular interactions between the gas molecule and adsorbent system for selective gas adsorption [3]. Although, density functional theory (DFT) based methods are immensely popular tools in predicting and understanding of nanostructure materials, they are not perfect and suffer from faulty and erroneous results in the highly stringent accurate modeling of gas adsorbent materials. The design principles that govern materials for CO₂ capture with great selectivity and capacity require understanding of fundamentals of adsorption phenomena. It is thus vital to understand the physisorption strengths of CO₂ with many functional groups/molecules. Intermolecular interactions between the gas molecule and functional groups play an important role in defining selectivity for separation. It should be noted that the interaction of carbon dioxide gas molecules with nitrogen containing carbon materials is dominated by dispersion interactions and thus are a difficult challenge for ab initio computational chemistry methods, in particularly density functional theory (DFT) and wave function based methods [15–17]. The modus operandi followed by the most computational researchers is to develop new density functionals that can overcome the limitations of the previous generation density functionals, assess their ability to account for the interactions and evaluate the improved functional in terms of their accuracy in predicting the molecular properties of the system. The development of vast number of density functionals is one of the most popular and unambiguous way for electronic structure calculations and molecular properties of various diversely bonded systems [18,19]. In general, density functionals are classified into six major groups: local density approximation (LDA), generalized gradient approximation (GGA), meta-GGA, hybrid, long range corrected (LRC) and dispersion corrected functionals. The hierarchy of density functional approximations is popularly known as Jacob's ladder. However, with huge number of density functionals being developed within DFT framework, with various strengths and weaknesses, too many approximations and lots of electronic structure problems in a dazzling variety of material systems in the world, DFT still has lots of scope for improvement to overcome its inherent limitations. A beautiful account on perspective on density functional theory in relation to ever growing challenges and progress in materials and nanoscience could be found in literature [2]. Majority of the development of density functionals is aligned in the field of improvement of exchange correlation density functionals that has the ability to handle a large part of dynamic electron correlation in the calculation of electronic structure of molecular systems. Modern density functionals that are being developed have the capability to accurately predict the long range correlation and noncovalent interaction energies for different systems [20–22]. In practice, the exact

universal functional is unknown and the quest for the functional, which comes close to the 'true one', is still ongoing [23,24]. Since the quality of results depend on the choice of functional used, selecting a suitable form is a vital factor in quantum calculations. At the present time, there is no systematic way of choosing a density functional for a specific application and many times the best available functional for one application is often not the best for another purpose [18,25]. Often the best suitable density functional variants are selected on case-by-case basis of physical systems, through methodological assessment and careful benchmarking against wavefunction based methods [15].

For the interaction of CO₂ molecule with nitrogen containing organic molecules, the mechanism of CO₂ interaction with aromatic molecules, effect of heteroatom type and hybridization and binding energies associated with multi-N-containing superbases have been undertaken using MP2 and M06 Minnesota functionals [26,27]. Unfortunately studies on the systematic application of DFT to carbon dioxide capture using organic nitrogen containing polymer materials are scarce. It is therefore crucial to start filling this knowledge gap with our effort to describe the underlying physical phenomena of noncovalent weak interactions between the gas molecule and the functional group in the model system and assessment of density functionals in calculating binding energies between gas molecules (CO₂ and N₂) and nitrogen containing organic materials. In this work, we have adopted N-containing aromatic molecules as building blocks for porous polymeric framework material suitable for CO₂ capture applications and systematically explore the interaction of CO₂ onto various sites and orientations of the molecule using density functional theory and ab initio methods. At the molecular level, intermolecular interactions (CO₂-N-containing group, CO₂-aromatic group, CO₂-linker group) are the key parameters required for designing a better capture material. Several DFT methods from the classes of pure, hybrid, hybrid meta-GGA, long range dispersion corrected functionals, as well as Moller-Plesset perturbation theory second order (MP2) have been applied. The N-containing molecules (triazine, transazobenzene, triazine-benzene clusters) considered for the study were systematically evaluated for CO₂-BEs. Polymer framework materials having triazine groups as building blocks were evaluated for intermolecular interactions and understand carbon surface chemistry for gas molecule adsorption using dft methods. Different configurations of CO₂ molecule interacting with the polymer fragment are evaluated and their effect on the interactions and selectivity determination in presence of N₂ is studied using density functional theory (dft) methods. In order to study CO₂ and N₂ uptake capacity of the design molecule, the interactions of CO₂ and N₂ with nitrogen containing aromatic molecules were investigated using molecular simulations and their CO₂-BE and N₂-BE were calculated. A total of sixteen DFT functionals from five different classes were used in this study. The density functionals assessed in this work were PBE, PBELYP1W, BLYP, PBE0, PBE0-1/3, B3LYP, B3PW91, TPSS, TPSSLYP1W, M06, M06-2X, M06-HF, CAM-B3LYP, ωB97, ωB97X and ωB97XD. All the calculations for the selected functionals were done with a combination of six basis sets (6-31G, 6-31G(d,p), 6-31 + G(d,p), 6-311 + G(d,p), cc-pVDZ, cc-pVTZ) in order to assess the performance of the functionals.

2. Density functional methods

The density functional theory was introduced by the two Hohenberg-Kohn theorems [28,29] and Kohn Sham formalism [30]. The density functional theory (DFT) is presently the most successful approach to compute electronic structure of matter ranging from atoms, molecules and solids to nuclei and quantum fluids. The original DFT provides the ground state properties of the system

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