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MODELS AND SIMULATIONS OF CO_2 MOVING IN NANOPOROUS

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Abstract

The mathematical models are used to develop molecular interactions between CO_2 molecule and zeolitic imidazolate framwork-8. These interactions are applied in molecular simulations of CO_2 in ZIF-8 nanoporous in order to understand the behaviors of diffusion process. The molecular moving part to the pore windows is explored by statistical geometry analysis and some graphical snapshots.

1 Introduction

In order to reduce carbon dioxide (CO_2) which is a major greenhouse gas, the cost-effective and scalable methods for purification and recovery of CO_2 from flue or natural gases are of great interest nowadays. The metal organic frameworks (MOFs) is a class of porous materials which has attracted as a potential CO_2 adsorbent and storage material [1, 2, 3, 4]. ZIF-8 is one of ZIFs that are subclass of MOFs that is composed of Zn^{2+} ion clusters linked by dipotic 2-Methylimidazolate, $[C_4N_2H_5]^-$, ligands as a chemical formula of $Zn[C_4N_2H_5]_2$ which has highly porous open framework structure, large accessible pore volume and a sodalite topology network. Since it has been demonstrated that ZIF-8 has high CO_2 adsorption capacity [5, 6, 7], it is highly attractive for the separation of CO_2 from natural gas.

Key words: molecular dynamics, interactions, diffusion, molecular moving, nanoporous, statistical geometry analysis.

The understanding at molecular level of guest-framework binding behavior is key to improve potential uses of the material. Mathematical models and simulations are widely used to enhance this understanding since not only the experiment costs can be reduced or replaced but also some information contents can be better explored. Molecular dynamics simulations are important tools for understanding the physical basis of the structural and dynamical behaviors of movement particles under force models. In MD simulations, the successive configurations of the system can be obtained from the integration of Newton's equation of motion, as the result, the trajectory collects the variations of the positions and velocities of the particles moving in the system. The statistical geometry analysis and some graphical snapshots obtained from simulation trajectory can be used to explore the dynamics of molecular processes.

2 Models and Simulations

Since there are some investigations which show that imidazolate organic linker ($[C_4N_2H_5]^-$, mIM) is favorite site for adsorption, the modification of the linkers rather than metal types in ZIFs is more interesting [8, 9]. Then the CO_2-framework interaction is modeled by CO_2-mIM interaction. This interaction, so-called binding energy is defined on the basis of the supermolecular approach according to equation 1,

$$\Delta E_{AB} = E_{AB} - E_A - E_B, \tag{1}$$

where E_{AB}, E_A, and E_B are the total energy of complex, the energy of CO_2 molecule and the energy of mIM, respectively. The geometrical structure of mIM is cut directly from the framework of single XRD data [10]. The geometry model of CO_2 molecule is taken from the interaction site model [11] with the bond length of 1.16 Å and bond angle of 180^o (see Figure 1). Several single point binding energies are calculated by quantum mechanics (QM) at HF/6-31G(d) level for stuctures that generated by placing of CO_2 molecule around the plan of 5-membered mIM ring. These energies are used to obtain site-site parameters A_{ij} and B_{ij} which coresponding to equation 2 using Levenberg-Marquardt algorithm, where $U(r_{ij})$ is binding energy, r_{ij} is distance between atom i of CO_2 molecule and atom j of mIM molecule, respectively. The partial atom charges q_i and q_j are used from previous work [12, 13].

$$U(r_{ij}) = A_{ij}/r_{ij}^{12} - B_{ij}/r_{ij}^{6} + q_i q_j / r_{ij}, \tag{2}$$

The obtained fitted parameters, then are used in MD simulations of 120 CO_2 molecules in $2\times2\times2$ unit cells of ZIF-8 both rigid and flexible frameworks. The NVT ensemble is applied at temperature of 300 K and time step of 1.0 fs [13].

The simulations were equilibrated for 1.0 ns (1 000 000 steps) , then further 1.0 ns were carried out under the same conditions to provide trajectories data at every 50 time steps for structural and dynamical analyses.
The site-site radial distribution functions (RDFs) is a statistical analysis which gives the probability, $g_{\alpha\beta}(r)$ of finding a particle β in the distance r from a given α particle and can be numerated as equation 3,

$$g_{\alpha\beta}(r) = \frac{n(r)V}{4\pi r^2 N_\beta dr}, \tag{3}$$

where $n(r)$ is the number of β particles at distance between r and $r + dr$ from α particles.

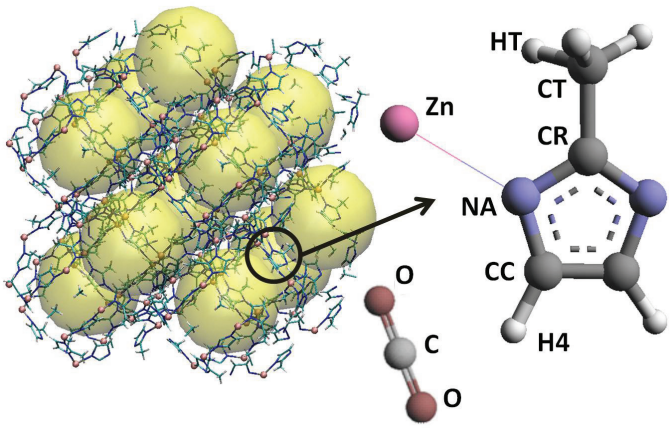

Figure 1: Topologies of ZIF-8 framework and CO_2 molecule.

3 Results and Discussions

The QM fitted parameters are reported in previous publications [12]. Figure 2 shown the comparison between obtained fitted parameters and general AMBER forcefield parameters to their some coresponding QM data. It is obtained clear that the fitted parameters give a better esimated binding energies coresponding to QM data than those obtained from general AMBER forcefield. Since the models of interactions between gas and the material frameworks are very important and should be well validated for the interested system, the directly used non-bonding general AMBER forcefiled should be concerned about the validity and reliability of its parameters. The RDFs as shown in Figure 3, can be used to represent 2D binding structures of CO_2 molecule on mIM.

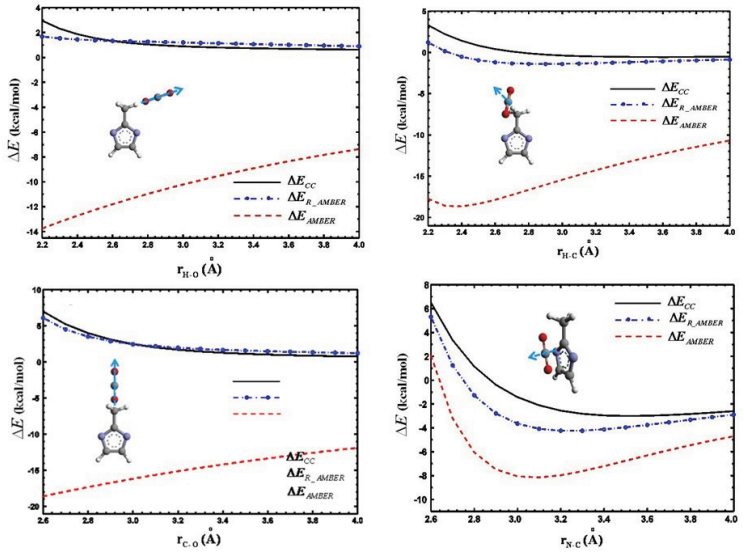

Figure 2: Comparison between corrected (solid), fitted (dash-dot) and general AMBER (dash) parameters.

First there are not significant difference between the binding structures derived from both rigid and flexible frameworks simulations. The H4 sites of framework are more favorable than HT sites for binding. The first peak of O-H4 rdfs appears at distance which a little bit shorter than those obtained in C-H4 rdfs. This indicates the orientation of CO_2 molecules which turn O toward to H4 of mIM. The distribution plot of CO_2 molecules on the same defined plane (see Figure 4a) shows the 3D locations of CO_2 around mIM ring. The H4 and HT sites observed to be favoured sites for binding. However, some CO_2 molecules are found lie above the ring. In addition, Figure 4b shows the location of cage-to-cage migrating CO_2 molecules, which are at about center and have perpendicular orientation with respect to six-Zn-membered windows.

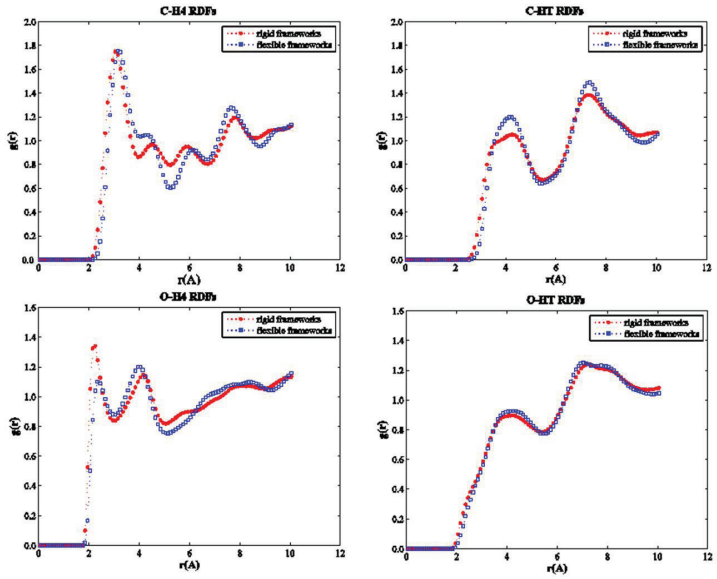

Figure 3: Some RDFs that can be used to explore 2D binding structures between CO_2 and ZIF-8 framework.

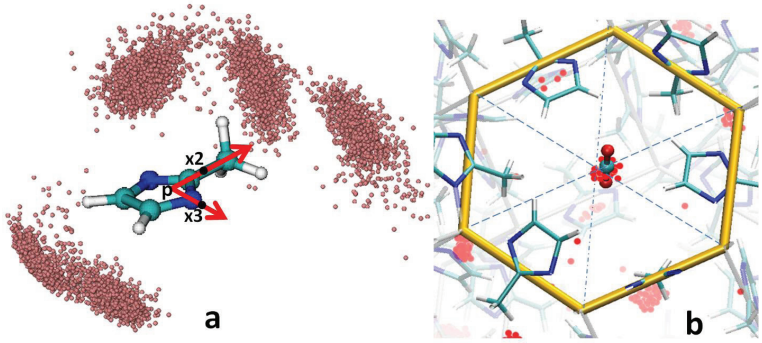

Figure 4: a) Projection of CO_2 molecules on the plane of mIM ring defined by $p\vec{x}_2$ and $p\vec{x}_3$ vectors, and b) the distribution plot of CO_2 molecules when are at times of cage-to-cage migrations.

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References

[1] A. Sayari, Y. Belmabkhout, R. Serna-Guerrero, *Flue gas treatment via CO_2 adsorption* Chem. Eng. J. 171 (2011), 760-774.

[2] B. Arstad, H. Fjellvg, K. O. Kongshaug, O. Swang, R. Blom, *Amine functionalised metal organic frameworks (MOFs) as adsorbents for carbon dioxide* Adsorption 14 (2008), 755-762.

[3] H. Yang, Z. Xu, M. Fan, R. Gupta et al., *Progress in carbon dioxide separation and capture: A review* J. Envi. Sci. 20 (2008), 14-27.

[4] J. R. Li, Y. Ma, M. C. McCarthy et al., *Carbon dioxide capture-related gas adsorption and separation in metal-organic frameworks* Coord. Chem. Rev. 255 (2011), 1791-1823

[5] A. R. Millward, O. M. Yaghi,*Metal-organic frameworks with exceptionally high capacity for storage of carbon dioxide at room temperature* J. Am. Chem. Soc. 127 (2005), 17998-17999.

[6] C. M. Lu, J. Liu, K. Xiao, A. T. Harri, *Microwave enhanced synthesis of MOF-5 and its CO2 capture ability at moderate temperatures across multiple capture and release cycles* Chem. Eng. J. 156 (2010), 465-470.

[7] Q. Yang, C. Zhong, J. F. Chen, *Computational study of CO2 storage in metal-organic frameworks* J. Phys. Chem. C 112 (2008), 1562-1569.

[8] J. R. Li, Y. Ma, M. C. McCarthy et al., *Carbon dioxide capture-related gas adsorption and separation in metal-organic frameworks* Coord. Chem. Rev. 255 (2011), 17911823.

[9] A. O. Yazaydin, R. Q. Snurr, T. Park et al., *Screening of metal-organic frameworks for carbon dioxide capture from flue gas using a combined experimental and modeling approach* JACS, 131 (2009), 18198-18199.

[10] K. S. Park, Z. Ni, A. P. Ct et al., *xceptional chemical and thermal stability of zeolitic imidazolate frameworks* Proc. Natl. Acad. Sci. U.S.A. 103 (2006), 10186-10191.

[11] C. S. Murthy, K. Singer, I. R. Mcdonald, *Interaction site models for carbon dioxide* Mol. Phys. 44 (1981), 135-1943.

[12] P. Puphasuk, T. Remsungnen, *Refinement of Molecular Interaction Parameters of AMBER Force Field for CO_2 and 2-Methylimidazolate Complexes* J. Comput. Theor. Nanosci. 9 (2012), 889-893.

[13] P. Puphasuk, T. Remsungnen, *Structures and Dynamics of CO_2 Molecules in Zeolitic Imidazolate Frameworks-8: Molecular Dynamics Simulations Using Ab Initio Fitted Interactions and Generic Force Fields* J. Comput. Theor. Nanosci. 10 (2013), 227-231.