Research Article

Molecular Dynamics Simulations of CO₂ Molecules in ZIF-11 Using Refined AMBER Force Field

W. Wongsinlatam¹ and T. Remsungnen^{1,2}

¹ The Applied Mathematics Research Group (AMRG), Department of Mathematics, Faculty of Science, Khon Kaen University, Khon Kaen 40002, Thailand

² Faculty of Applied Science and Engineering, Nong Khai Campus, Khon Kaen University, Nong Khai 43000, Thailand

Correspondence should be addressed to T. Remsungnen; rtawun@kku.ac.th

Received 1 August 2013; Accepted 8 September 2013

Academic Editor: Hakan Arslan

Copyright © 2013 W. Wongsinlatam and T. Remsungnen. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Nonbonding parameters of AMBER force field have been refined based on *ab initio* binding energies of CO₂–[C₇H₅N₂][–] complexes. The energy and geometry scaling factors are obtained to be 1.2 and 0.9 for ϵ and σ parameters, respectively. Molecular dynamics simulations of CO₂ molecules in rigid framework ZIF-11, have then been performed using original AMBER parameters (SIM I) and refined parameters (SIM II), respectively. The site-site radial distribution functions and the molecular distribution plots simulations indicate that all hydrogen atoms are favored binding site of CO₂ molecules. One slight but notable difference is that CO₂ molecules are mostly located around and closer to hydrogen atom of imidazolate ring in SIM II than those found in SIM I. The Zn–Zn and Zn–N RDFs in free flexible framework simulation (SIM III) show validity of adapting AMBER bonding parameters. Due to the limitations of computing resources and times in this study, the results of flexible framework simulation using refined nonbonding AMBER parameters (SIM IV) are not much different from those obtained in SIM II.

1. Introduction

The increase in carbon dioxide (CO₂) in Earth's atmosphere is a subject of worldwide attention as being the cause of global warming. Human activities such as combustion of fossil fuels (coal, oil, and natural gas) in power plants, automobiles, and industrial facilities are main sources of CO₂ emission. The cost-effective and scalable technologies to capture and store CO₂ are now of great interest [1–7]. The low energy requirement technologies based on adsorption processes are highlighted as promising methods, stimulating recent works to investigate suitable adsorbent materials. Metal-organic frameworks (MOFs) are a class of nanoporous materials that are promising candidates for CO₂ capture, due to their potential applications in separation processes, catalysis, and gas storage [8–14]. Zeolitic imidazolate frameworks (ZIFs) are subclass of MOFs, in which positive metal ions such as Zn, Co, and Cu are linked by diprotic imidazolate ligands [15, 16]. Some ZIFs are attracted as materials which are used to keep

the emissions of CO₂ out of the atmosphere in hot energy-producing environments like power plants due to their exceptional chemical and thermal stabilities and nontoxic crystals [17–19]. The ZIF-11 is one of ZIFs which exhibits the RHO topology. It is composed of Zn²⁺ ion clusters linked by diprotic benzimidazolate ([C₇H₅N₂][–]) ligands with chemical formula Zn[C₇H₅N₂]₂ [15] (see Figure 1).

The high-throughput methods can be successfully applied to the development a robust synthesis protocol for several ZIFs in short time [20]. Computer models and simulations can be used to rapidly screen and develop promising ZIFs with large savings in experimental time and cost [9]. There are some computer simulations where bonding and non-bonding parameters of general force fields such as AMBER are applied [21]. This is one of well-known force fields that supplies reliable intramolecular force constants within the organic linker; however it is not developed directly for the system of MOFs or ZIFs as in this study.

FIGURE 1: The topologies of ZIF-11, $[\text{C}_7\text{H}_5\text{N}_2]^-$, and CO_2 .

In this study, the protocol to refine and validate molecular interactions was obtained from general force fields in order to meet both accuracy and time saving for using in specific system like adsorption of CO_2 in ZIF-11. Since some investigations show that the imidazolate organic linker is most favored adsorption site of guest molecules [17–19], by assumption the interactions between CO_2 and ZIF-11 frameworks are almost contributed by interactions between CO_2 molecule and $[\text{C}_7\text{H}_5\text{N}_2]^-$ groups. Nonbonding parameters obtained from AMBER force field are refined using *ab initio* data corresponding to the calculated partial atomic charge. The bonding parameters of AMBER force field are also adapted to represent the flexible framework of ZIF-11. Molecular dynamics simulations of rigid and flexible frameworks are done in order to validate the parameters.

2. Material and Methods

2.1. Models of CO_2 and ZIF-11 Framework. In this study, a geometrical structure of $[\text{C}_7\text{H}_5\text{N}_2]^-$ is cut directly from ZIF-11 framework [15] and is not theoretical optimized (see Figure 1). The linear rigid model of CO_2 molecule is taken from [22] with C–O bond length of 1.16 Å and O–C–O bond angle of 180° . The partial atomic charges of $[\text{C}_7\text{H}_5\text{N}_2]^-$ were computed according to the Merz-Singh-Kollman scheme [23, 24] and then further refined these ESP charges to so-called RESP charges using an Antechamber package [21, 25] with a total charge of -1 , while the partial charge of the Zn^{2+} was fixed to be $+2$. The force fields and simulations atom types and their corresponding atomic partial charges are shown in Table 1.

2.2. Single Point Energies of CO_2 - $[\text{C}_7\text{H}_5\text{N}_2]^-$ Complexes. The binding energy, ΔE , of a CO_2 - $[\text{C}_7\text{H}_5\text{N}_2]^-$ complex is defined on the basis of the supermolecular approach according to

$$\Delta E(AB) = E(AB) - E(A) - E(B), \quad (1)$$

where $E(AB)$, $E(A)$, and $E(B)$ are the total energy of complex, the energy of CO_2 molecule, and the energy of $[\text{C}_7\text{H}_5\text{N}_2]^-$, respectively. The binding energy without basis set superposition error (BSSE) correction of a complex AB is defined as

$$\Delta E_{\text{UN}}(AB) = E_{\text{AB}}(AB) - E_A(A) - E_B(B), \quad (2)$$

TABLE 1: The simulation and AMBER force field atom types and their corresponding partial charges of $[\text{C}_7\text{H}_5\text{N}_2]^-$ and CO_2 molecules.

Simulation atoms	AMBER model	RESP charges (e)
C1	CR	0.582
N	NA	-0.901
C2	CC	0.400
C3	CA	-0.367
C4	CA	-0.279
H1	HC	0.001
H3	HA	0.200
H4	HA	0.155
Zn^{2+}	Zn^{2+}	2.000
C	C	0.596
O	O	-0.298

where $E_{\text{AB}}(AB)$ denotes the total energy of the complex AB calculated with the full basis set AB of the complex. The $E_A(A)$ and $E_B(B)$ denote the total energies of the monomers A and B , each calculated with its basis sets, respectively. The counterpoise BSSE corrected binding energy [26] is represented by

$$\Delta E_{\text{CC}}(AB) = E_{\text{AB}}(AB) - E_{\text{AB}}(A) - E_{\text{AB}}(B), \quad (3)$$

where $E_{\text{AB}}(AB)$, $E_{\text{AB}}(A)$, and $E_{\text{AB}}(B)$ denote the total energy of complex, the energy of monomer A , and the energy of monomer B which are computed using the union of the two basis sets of monomer A and B , respectively.

Several structures of CO_2 - $[\text{C}_7\text{H}_5\text{N}_2]^-$ complexes are generated by varying positions and orientations of CO_2 molecule around $[\text{C}_7\text{H}_5\text{N}_2]^-$ (see Figure 2). Then their corresponding binding energies without and with BSSE correction were calculated at level of HF/6-31G* using Gaussian 09 package [27]. These energies are used as data for refinement nonbonding parameters of AMBER force field.

2.3. The Parameters of the Intramolecular and Intermolecular Interactions. In this study, the functions in the AMBER force field which is known to be reliable for biomolecules and organic species are adopted to represent CO_2 molecules in ZIF-11 framework system as follows:

$$U_{\text{total}} = U_{\text{bonded}} + U_{\text{nonbonded}}. \quad (4)$$

The intramolecular energy, U_{bonded} , includes bond stretching and bending and proper and improper torsional potentials:

$$U_{\text{bonded}} = U_{\text{bond}} + U_{\text{bend}} + U_{\text{proper}} + U_{\text{improper}}. \quad (5)$$

The parameters used to describe the flexibility of ZIF-11 framework from previous studies [28–30] are adopted for ZIF-11 framework in this study and are summarized in Table 2.

The AMBER force field describes the nonbonding interaction of two atom sites, i and j with Lennard-Jones parameters and the following formula

$$U(r_{ij}) = 4\epsilon \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^6 \right] + \frac{q_i q_j}{r_{ij}}. \quad (6)$$

FIGURE 2: The possible configurations of $\text{CO}_2\text{--}[\text{C}_7\text{H}_5\text{N}_2]^-$ complexes used to determine the *ab initio* binding energies.

FIGURE 3: The ZIF-11 framework used as the simulations cell; (a) and (b) are both side views that represent the full cages (big grey balls) within the framework.

The Lorentz-Berthelot mixing rules were applied to obtain the cross-interactions parameters ϵ and σ (see Table 3) between different atom types, i and j [31–33], with $\epsilon_{ij} = (\epsilon_i \epsilon_j)^{1/2}$ and $\sigma_{ij} = (\sigma_i + \sigma_j)/2$. Formula (6) can be transformed into

$$U(r_{ij}) = \frac{A}{r_{ij}^{12}} - \frac{B}{r_{ij}^6} + \frac{q_i q_j}{r_{ij}}, \quad (7)$$

where $A = 4\epsilon_{ij}\sigma_{ij}^{12}$ and $B = 4\epsilon_{ij}\sigma_{ij}^6$, respectively.

2.4. Molecular Dynamics Simulations of CO_2 Molecules in ZIF-11. All MD simulations are performed using DL.POLY (version 2.20) package [34] in canonical ensemble (NVT) for 9 CO_2 molecules in the ZIF-11 frameworks (see Figure 3).

The simulations box with a cubic length of 57.52 Å, subject to periodic boundary conditions, consists of $2 \times 2 \times 2$ unit

cells of ZIF-11, which contains at least 9 full cages (see Figure 3). This corresponds to a loading of about one CO_2 molecule per unit cell. The precision of Ewald summation for long length dispersion force had been set to 0.0001. In order to maintain a constant temperature of 300 K, the Nosé-Hoover thermostat with a relaxation time and time step of 0.001 ps was applied along the whole simulations. The simulations were equilibrated for 1,000,000 time steps (1 ns), and then further simulations of 1 ns were carried out in order to provide data for structural and dynamical properties evaluation. There are four simulations in this study and denote as SIM I, SIM II, SIM III, and SIM IV for the rigid framework simulations using original AMBER force field, the rigid framework simulations using sAMBER force field, the flexible framework simulations for free ZIF-11, and the flexible framework simulations for CO_2 in the ZIF-11 using sAMBER force field, respectively.

TABLE 2: The AMBER force field parameters for ZIF-11 flexible framework.

Bond potential: $U_{\text{bond}} = K_r (r - r_{\text{eq}})^2$			
Bond type	K_r (kcal·mol ⁻¹ ·Å ⁻²)	r_{eq} (Å)	
Zn-N	157.0	2.011	
Cl-H1	734.0	1.080	
Cl-N	954.0	1.343	
C2-C2	1,024.0	1.375	
C2-N	844.0	1.385	
C2-C3	1,036.0	1.371	
C3-C4	938.0	1.400	
C3-H3	734.0	1.080	
C4-H4	734.0	1.080	
C4-C4	938.0	1.400	
Bending potential: $U_{\text{bend}} = K_{\theta} (\theta - \theta_0)^2$			
Angle type	K_{θ} (kcal·mol ⁻¹ ·rad ⁻²)	θ_0 (degree)	
C2-C3-C4	126.00	120.00	
C3-C4-C4	126.00	120.00	
N-Cl-N	140.00	120.00	
N-Cl-H	70.00	120.00	
Cl-N-C2	140.00	120.00	
N-C2-C3	140.00	132.80	
C2-C3-H3	70.00	120.00	
H3-C3-C4	70.00	120.00	
C3-C4-H4	70.00	120.00	
H4-C4-C4	70.00	120.00	
N-C2-C2	140.00	120.00	
N-Zn-N	70.48	109.48	
Zn-N-Cl	97.36	128.33	
Zn-N-C2	64.95	126.40	
C2-C3-C4	126.00	120.00	
C3-C4-C4	126.00	120.00	
Dihedral: $U_{\text{proper}} = A (1 + \cos(n\varphi - \varphi_0))$			
Dihedral type	A (kcal·mol ⁻¹)	n	φ_0 (degree)
Cl-N-C2-C2	5.40	2.0	180.0
C3-C2-C2-C3	0.00	2.0	0.0
N-C2-C2-C3	21.50	2.0	180.0
Zn-N-Cl-H1	9.30	2.0	180.0
C2-N-Cl-H1	9.30	2.0	180.0
Zn-N-C2-C2	5.60	2.0	180.0
N-C2-C2-N	21.50	2.0	180.0
N-C2-C3-H3	21.50	2.0	180.0
N-C2-C3-C4	21.50	2.0	180.0
C2-C2-C3-C4	0.00	2.0	180.0
C2-C2-C3-H3	21.50	2.0	180.0
C2-C3-C4-H4	14.50	2.0	180.0
C2-C3-C4-C4	14.50	2.0	0.0
H3-C3-C4-H4	14.50	2.0	180.0
H3-C3-C4-C4	14.50	2.0	180.0
C3-C4-C4-H4	14.50	2.0	180.0
H4-C4-C4-H4	14.50	2.0	180.0

TABLE 2: Continued.

Improper: $U_{\text{improper}} = A [1 - \cos(\phi)]$		
Improper type	A (kcal·mol ⁻¹ ·rad ⁻²)	θ_0 (degree)
C4-C4-C3-H4	2.2	180
C3-C4-C2-H3	2.2	180
C2-C2-C3-N	2.2	180
Cl-N-N-H1	2.2	180
N-Zn-Cl-C2	2.2	180

TABLE 3: The parameters ϵ_{ij} and σ_{ij} of AMBER force field.

AMBER		
Types	σ_{ij}	ϵ_{ij}
CR	1.9080	0.0860
NA	1.8240	0.1700
CC	1.9080	0.0860
CA	1.9080	0.0860
HC	1.4870	0.0157
HA	1.4590	0.0150
Zn	1.9600	0.0125
C	1.9080	0.0860
O	1.6612	0.2100

3. Results and Discussion

3.1. Obtained Refined Parameters. By using the BSSE corrected *ab initio* binding energies as data to refine the AMBER parameters, the energy and geometry scaling factors are obtained to be 1.2 and 0.9 for ϵ and σ , respectively. The consequence A and B parameters for original and scaled parameters are summarized in Table 4 while Figure 4 shows the comparison between ΔE_{CC} , ΔE_{AMBER} , and ΔE_{sAMBER} energies of CO_2 - $[\text{C}_7\text{H}_5\text{N}_2]^-$ complexes. The results show that all A and B parameters of scaled AMBER are less than those obtained from original AMBER but the total binding energy is more close to the *ab initio* data. Then only the sAMBER parameters are used in the flexible framework simulation.

3.2. Molecular Dynamics Simulations of CO_2 Molecules in Rigid ZIF-11 Framework. The radial distribution functions (RDFs) are used to measure the distribution of intermolecular distances between CO_2 molecules and the framework of ZIF-11. All RDFs for rigid simulations (see Figures 5 and 6) show notable difference between both simulations, that is, in SIM II, the CO_2 molecules lie closer to the $[\text{C}_7\text{H}_5\text{N}_2]^-$ groups than those obtained from SIM I. The smallest distance is found of about 2.5 Å with a first peak of about 3.0 Å in H1-O RDF (see Figure 5(d)) of SIM II, while these distances are increased by about 0.9 Å in H1-O RDF of SIM I. This makes sense, since the energies and the geometrical parameters of sAMBER are stronger and shorter than those of original AMBER. The favorite adsorption sites of CO_2 molecules are found at H3 and H4 positions in SIM I, while all hydrogen atoms (H1, H3, and H4) are equally favored in SIM II. One can say that CO_2 molecules are found more located around H1 in

FIGURE 4: The comparison between ΔE_{CC} (—), ΔE_{AMBER} (---), and ΔE_{SAMBER} (-o-) energies of some CO_2 -[$\text{C}_7\text{H}_5\text{N}_2$] $^-$ complexes.

FIGURE 5: The obtained (a) Cl-CO_2 , (b) C3-CO_2 , (c) C4-CO_2 , and (d) HI-CO_2 RDFs of SIM I (—X-C, ---X-O) and SIM II (- -X-C, •••X-O) when X=Cl, C3, C4, and HI, respectively.

TABLE 4: The parameters A_{ij} and B_{ij} (kcal/mol) that are obtained from the AMBER and sAMBER force fields.

i	Atom	Force field			
		AMBER		sAMBER	
	j	A_{ij}	B_{ij}	A_{ij}	B_{ij}
C	C1	3279886	1062	1941479	855
	N2, N3	3530476	1306	2060296	1044
	C4, C5	3279886	1062	1941479	855
	C6, C7, C8, C9	3279886	1062	1941479	855
	H10	344616	225	188575	174
	H11, H12, H13, H14	304980	209	165897	161
	Zn	1470963	439	498532	280
O	C1	2297573	1111	1420611	914
	N2, N3	2427317	1354	1479780	1106
	C4, C5	2297573	1111	1420611	914
	C6, C7, C8, C9	2297573	1111	1420611	914
	H10	217704	223	124434	176
	H11, H12, H13, H14	191163	207	108610	163
	Zn	1470963	462	498532	269

FIGURE 6: The obtained (a) H3-CO₂, (b) H4-CO₂, (c) N-CO₂, and (d) Zn-CO₂ RDFs of SIM I (—X-C, ---X-O) and SIM II (····X-C, ·····X-O) when X=H3, H4, N, and Zn, respectively.

FIGURE 7: The position distributions of CO_2 molecules in ZIF-11 framework from (a) SIM I, (b) SIM II, and (c) SIM IV simulations, respectively.

FIGURE 8: The Zn-Zn and Zn-N RDFs of ZIF-11 frameworks obtained from SIM I (---), SIM III (-.-), and SIM IV (-.-), respectively.

SIM II than those found in SIM I. The distribution plots in Figure 7 indicate that in both simulations, all CO_2 molecules are located only in one pore along the whole simulation times. In addition, CO_2 molecules in SIM II obtained a bit wider distribution than those in SIM I. The self-diffusion coefficients of CO_2 molecules are obtained as $1.1 \times 10^{-12} \text{ m}^2/\text{s}$ and $3.5 \times 10^{-11} \text{ m}^2/\text{s}$ in SIM I and SIM II, respectively, being less than those obtained in ZIF-8 [18, 35], ZIF-68, and ZIF-69 [19].

3.3. Molecular Dynamics Simulations of CO_2 Molecules in Flexible ZIF-11 Framework. The flexibility of the framework is modeled by AMBER force field with the RESP partial atomic charges. The free framework simulation (SIM III) had been done first. The RDFs of Zn-Zn and Zn-N of ZIF-11 frameworks (see Figure 8) are plotted in comparison to

those obtained from XRD data (SIM I). The results show that the flexible model can remain the main structure of the frameworks without collapsing during the whole simulations. This indicates the validity of the flexible model at least for NVT ensembles that used in this study. Moreover the CO_2 -framework interactions models in SIM IV simulation have no significant effect on the main flexible structure of the framework.

The RDFs of ZIF-11 framework and CO_2 molecules are shown in Figures 9 and 10. The oriented structure of CO_2 molecules in ZIF-11 obtained from flexible framework simulation is similar to those obtained from rigid framework simulations (SIM II). Slight difference can be obtained in the distribution plot (see Figure 7) which indicates that H1 is more favorable binding site than H3 and H4. The distributed areas which obtained from the flexible simulation

FIGURE 9: The obtained (a) Cl-CO₂, (b) C3-CO₂, (c) C4-CO₂, and (d) H1-CO₂ RDFs of SIM IV (—X-C, - -X-O) when X=Cl, C3, C4, and H1, respectively.

FIGURE 10: The obtained (a) H3-CO₂, (b) H4-CO₂, (c) N-CO₂, and (d) Zn-CO₂ RDFs of SIM IV (—X-C, - -X-O) when X=H3, H4, N, and Zn, respectively.

(Figure 7(c)) are smaller than those obtained from the rigid simulations (Figures 7(a) and 7(b)). This corresponding to almost zero value (less than 10^{-14} m²/s) of obtained self-diffusion coefficient of CO₂ in flexible framework. It is difficult to point here that this value is realizable or not. However some previous work [18] convinces that ZIF-11 framework is promising to use for separate CO₂ from natural gases.

4. Conclusion

Several single point interaction energies of CO₂-[C₇H₅N₂]⁻ complexes are calculated and this data was used in the processes of modifying the general AMBER force field. The method of calculations at HF/6-31G* gives large BSSE which needs to be corrected in order to have accurate binding energies. The rigid framework simulations, SIM I and SIM II, give similar results; that is, all hydrogen sites are favored binding site but CO₂ molecules are found more located around H1 in SIM II than those found in SIM I. Due to the limited time and computer resources, we success only a flexible simulations for testing parameters both intramolecular and intermolecular interactions. However the results which obtained from flexible simulations are not much different from those obtained from rigid framework simulations. The distribution plots are slightly different which indicates that H1 is more favorable binding site than H3 and H4. Until now this study is one of the successful works on flexible ZIF-11.

In further works, one should focus to try some other both rigid and flexible models of CO₂ molecules and also other flexible force fields of ZIF-11. Several simulations such as varying number of CO₂ molecules in the framework and mixing CO₂ molecules with other natural gases molecules are of great interest.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgments

The authors would like to thank the Higher Education Research Promotion and National Research University Project of Thailand, Office of Higher Education Commission, through the Advanced Functional Materials Cluster of Khon Kaen University.

References

- [1] G. I. Panov, A. K. Uriarte, M. A. Rodkin, and V. I. Sobolev, "Generation of active oxygen species on solid surfaces. Opportunity for novel oxidation technologies over zeolites," *Catalysis Today*, vol. 41, no. 4, pp. 365–385, 1998.
- [2] J. A. Z. Pieterse, G. Mul, I. Melian-Cabrera, and R. W. van den Brink, "Synergy between metals in bimetallic zeolite supported catalyst for NO-promoted N₂O decomposition," *Catalysis Letters*, vol. 99, no. 1-2, pp. 41–44, 2005.
- [3] W. F. Hoelderich, "Environmentally benign manufacturing of fine and intermediate chemicals," *Catalysis Today*, vol. 62, no. 1, pp. 115–130, 2000.
- [4] Q. M. Wang, D. Shen, M. Bülow et al., "Metallo-organic molecular sieve for gas separation and purification," *Microporous and Mesoporous Materials*, vol. 55, no. 2, pp. 217–230, 2002.
- [5] H. Rodhe, "A comparison of the contribution of various gases to the greenhouse effect," *Science*, vol. 248, no. 4960, pp. 1217–1219, 1990.
- [6] G. Centi, S. Perathoner, and F. Vazzana, "Catalytic control of non-CO₂ greenhouse gases: methane, fluorocarbons, and especially nitrous oxide can be decomposed and even reused by implementing new catalytic techniques," *ChemTech*, vol. 29, no. 12, pp. 48–55, 1999.
- [7] H. K. Song, K. W. Cho, and K. H. Lee, "Adsorption of carbon dioxide on the chemically modified silica adsorbents," *Journal of Non-Crystalline Solids*, vol. 242, no. 2-3, pp. 69–80, 1998.
- [8] J. R. Li, Y. Ma, M. C. McCarthy et al., "Carbon dioxide capture-related gas adsorption and separation in metal-organic frameworks," *Coordination Chemistry Reviews*, vol. 255, no. 15-16, pp. 1791–1823, 2011.
- [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," *Journal of the American Chemical Society*, vol. 131, no. 51, pp. 18198–18199, 2009.
- [10] D. Saha, Z. Bao, F. Jia, and S. Deng, "Adsorption of CO₂, CH₄, N₂O, and N₂ on MOF-5, MOF-177, and zeolite 5A," *Environmental Science and Technology*, vol. 44, no. 5, pp. 1820–1826, 2010.
- [11] C. M. Lu, J. Liu, K. Xiao, and A. T. Harris, "Microwave enhanced synthesis of MOF-5 and its CO₂ capture ability at moderate temperatures across multiple capture and release cycles," *Chemical Engineering Journal*, vol. 156, no. 2, pp. 465–470, 2010.
- [12] Q. Yang, C. Zhong, and J. F. Chen, "Computational study of CO₂ storage in metal-organic frameworks," *Journal of Physical Chemistry C*, vol. 112, no. 5, pp. 1562–1569, 2008.
- [13] A. G. Wong-Foy, A. J. Matzger, and O. M. Yaghi, "Exceptional H₂ saturation uptake in microporous metal-organic frameworks," *Journal of the American Chemical Society*, vol. 128, no. 11, pp. 3494–3495, 2006.
- [14] Y. Li and R. T. Yang, "Gas adsorption and storage in metal-organic framework MOF-177," *Langmuir*, vol. 23, no. 26, pp. 12937–12944, 2007.
- [15] K. S. Park, Z. Ni, A. P. Côté et al., "Exceptional chemical and thermal stability of zeolitic imidazolate frameworks," *Proceedings of the National Academy of Sciences of the United States of America*, vol. 103, no. 27, pp. 10186–10191, 2006.
- [16] J. C. Tan, T. D. Bennett, and A. K. Cheetham, "Chemical structure, network topology, and porosity effects on the mechanical properties of zeolitic imidazolate frameworks," *Proceedings of the National Academy of Sciences of the United States of America*, vol. 107, no. 22, pp. 9938–9943, 2010.
- [17] B. Wang, A. P. Côté, H. Furukawa, M. O'Keeffe, and O. M. Yaghi, "Colossal cages in zeolitic imidazolate frameworks as selective carbon dioxide reservoirs," *Nature*, vol. 453, no. 7192, pp. 207–211, 2008.
- [18] M. William, H. Ning, G. Keith et al., "A combined experimental-computational study on the effect of topology on carbon dioxide adsorption in zeolitic imidazolate frameworks," *Journal of Physical Chemistry C*, vol. 116, no. 45, pp. 24084–24090, 2012.

- [19] D. Liu, C. Zheng, Q. Yang, and C. Zhong, "Understanding the adsorption and diffusion of carbon dioxide in zeolitic imidazolate frameworks: a molecular simulation study," *Journal of Physical Chemistry C*, vol. 113, no. 12, pp. 5004–5009, 2009.
- [20] R. Banerjee, A. Phan, B. Wang et al., "High-throughput synthesis of zeolitic imidazolate frameworks and application to CO₂ capture," *Science*, vol. 319, no. 5865, pp. 939–943, 2008.
- [21] J. M. Wang, R. M. Wolf, J. W. Caldwell, P. A. Kollman, and D. A. Case, "Development and testing of a general amber force field," *Journal of Computational Chemistry*, vol. 25, no. 9, pp. 1157–1174, 2004.
- [22] C. S. Murthy, K. Singer, and I. R. McDonald, "Interaction site models for carbon dioxide," *Molecular Physics*, vol. 44, no. 1, pp. 135–143, 1981.
- [23] U. C. Singh and P. A. Kollman, "An approach to computing electrostatic charges for molecules," *Journal of Computational Chemistry*, vol. 5, no. 2, pp. 129–145, 1984.
- [24] B. H. Besler, K. M. Merz Jr., and P. A. Kollman, "Atomic charges derived from semiempirical methods," *Journal of Computational Chemistry*, vol. 11, no. 4, pp. 431–439, 1990.
- [25] J. Wang, W. Wang, P. A. Kollman, and D. A. Case, "Automatic atom type and bond type perception in molecular mechanical calculations," *Journal of Molecular Graphics and Modelling*, vol. 25, no. 2, pp. 247–260, 2006.
- [26] S. F. Boys and F. Bernardi, "The calculation of small molecular interactions by the differences of separate total energies," *Molecular Physics*, vol. 19, no. 4, pp. 553–566, 1970.
- [27] M. J. Frisch, H. B. Schlegel, G. E. Scuseria et al., *Gaussian 09 Revision A1*, Gaussian Inc., Wallingford, Conn, USA, 2009.
- [28] L. Hertäg, H. Bux, J. Caro et al., "Diffusion of CH₄ and H₂ in ZIF-8," *Journal of Membrane Science*, vol. 377, no. 1-2, pp. 36–41, 2011.
- [29] H. Zhongqiao, Z. Liling, and J. Jianwen, "Development of a force field for zeolitic imidazolate framework-8 with structural flexibility," *Journal of Chemical Physics*, vol. 136, no. 3, pp. 244–703, 2012.
- [30] B. Zheng, M. Sant, P. Demontis, and G. B. Suffritti, "Force field for molecular dynamics computations in flexible ZIF-8 framework," *Journal of Physical Chemistry C*, vol. 116, no. 1, pp. 933–938, 2012.
- [31] H. A. Lorentz, "Ueber die Anwendung des Satzes vom Virial in der kinetischen Theorie der Gase," *Annalen der Physik*, vol. 248, no. 1, pp. 127–136, 1881.
- [32] D. Berthelot, "Sur le mélange des gaz," *Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences*, vol. 126, pp. 1703–1855, 1898.
- [33] J. Delhommelle and P. Millié, "Inadequacy of the Lorentz-Berthelot combining rules for accurate predictions of equilibrium properties by molecular simulation," *Molecular Physics*, vol. 99, no. 8, pp. 619–625, 2001.
- [34] W. Smith and T. R. Forester, "DL-POLY-2.0: a general-purpose parallel molecular dynamics simulation package," *Journal of Molecular Graphics*, vol. 14, no. 3, pp. 136–141, 1996.
- [35] P. Puphasuk and T. Remsungnen, "Structures and dynamics of CO₂ molecules in zeolitic imidazolate frameworks-8: molecular dynamics simulations using *ab initio* fitted interaction and generic force fields," *Journal of Computational and Theoretical Nanoscience*, vol. 10, no. 1, pp. 227–231, 2013.